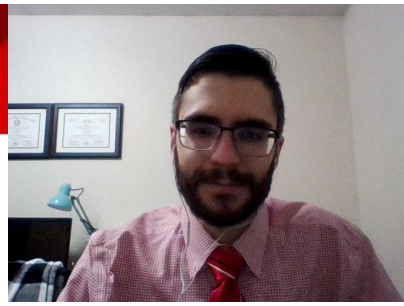


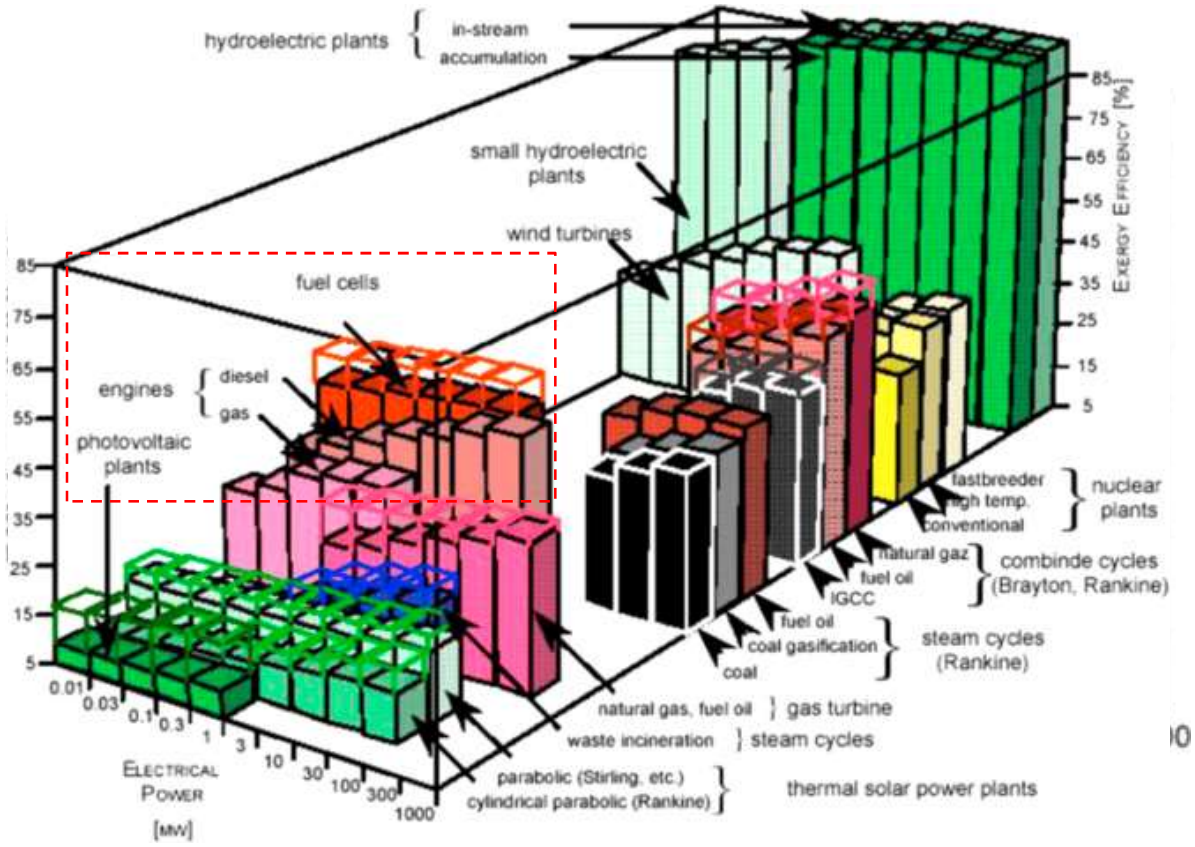
Anionic Exchange Membrane (AEM) Stability:

Synthesis Optimization of Multication Side Chains

Michael Lee
PI: Dr. Christopher Cornelius

Background

- Applications:
  - Fuel Cell Development:
    - Alternative means of energy production
  - Electrodialysis
- Current energy scale:
  - Transportation
  - Portable Energy
- Fuel Cell Type:
  - Anionic Exchange Membrane Fuel Cells (AEMFCs)



Carrette L, Friedrich KA, Stimming U. Fuel Cells - Fundamentals and Applications. *Fuel Cells*. 2001;1(1):5-39. doi:10.1002/1615-6854(200105)1:1<5::aid-fuce5>3.0.co;2-g

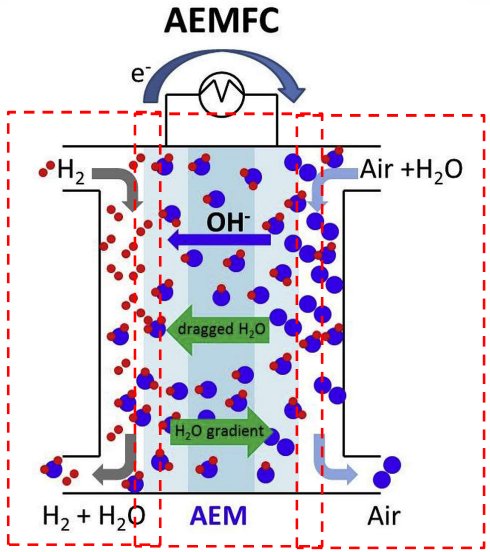
Sharaf OZ, Orhan MF. An overview of fuel cell technology: Fundamentals and applications. Renew Sustain Energy Rev. 2014;32:810-853. doi:10.1016/j.rser.2014.01.012

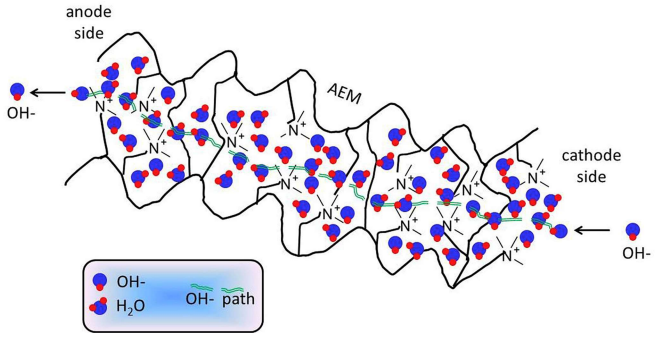
Introduction

- Basic Ionomer Operation
  - Polymer electrolyte transports ions
  - Donnan exclusion repels electrons

- AEMFC high pH advantages:
  1. Catalyst cost
  2. Avoiding incomplete oxidation
  3. Multiple fuel type compatibility
  4. Favorable cathode reduction kinetics

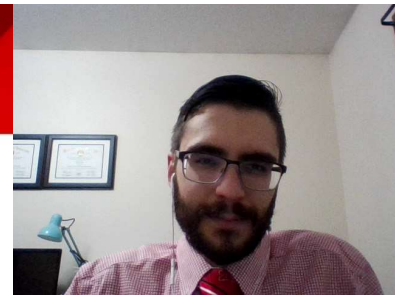
- Major problem: Alkaline Stability
  1. E1 and E2 type eliminations
  2. Direct nucleophilic substitution
  3. Nitrogen Y lide formation



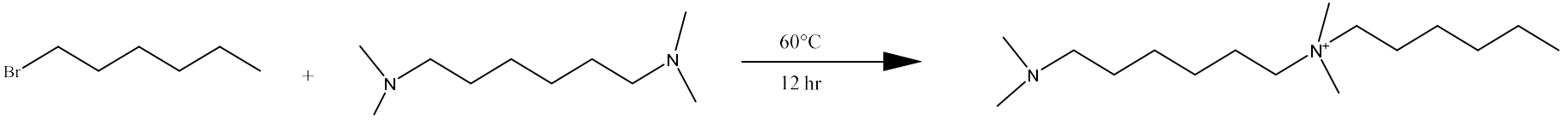


Dekel D r. - Review of cell performance in anion exchange membrane fuel cells. J Power Sources. 2018;375(31):158-169. doi:10.1016/j.jpowsour.2017.07.117.

Previous Work



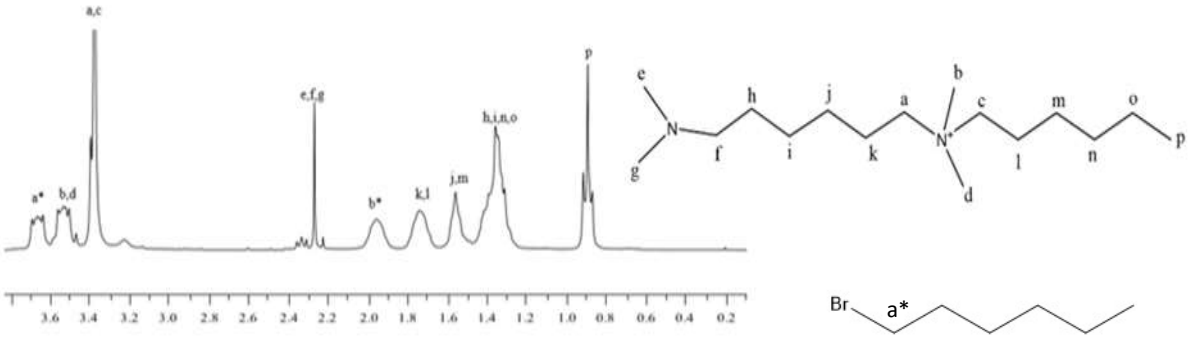
- Optimizing Liung et al. proposed synthesis:

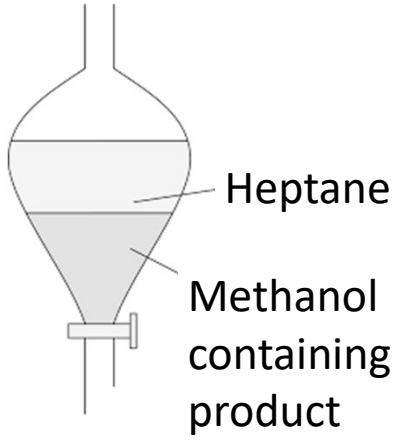


1-bromohexane

N,N,N',N' - tetramethyl-1,6- hexanediamine

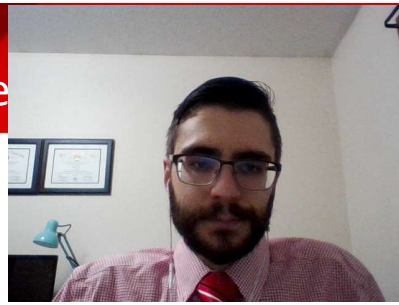
1-(N' ,N' -dimethylamino)-6-(N,N,N-trimethylammonium) dodecane bromide





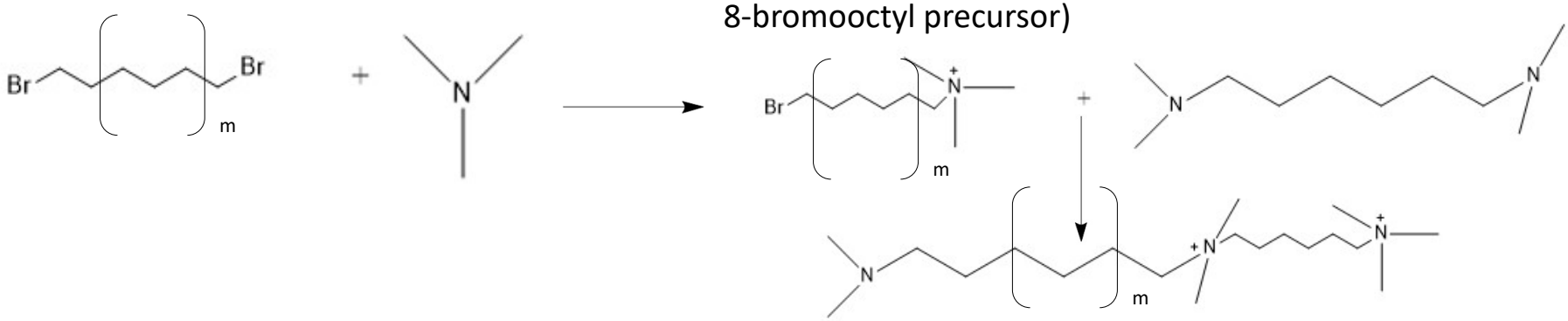
Li J, Wang L, Shi F, et al. Quaternary ammonium ionic liquids as Bi-functional catalysts for one-step synthesis of dimethyl carbonate from ethylene oxide, carbon dioxide and methanol. Catal Letters. 2011;141:339-346. doi:10.1007/s10562-010-0498-6

Zhu L, Yu X, Hickner MA. Exploring backbone-cation alkyl spacers for multi-cation side chain anion exchange membranes. J Power Sources. 2018;375:433-441. doi:10.1016/j.jpowsour.2017.06.020



- Triple cation side chains:

8-bromooctyl precursor)



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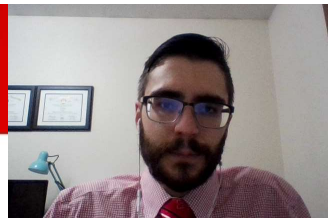
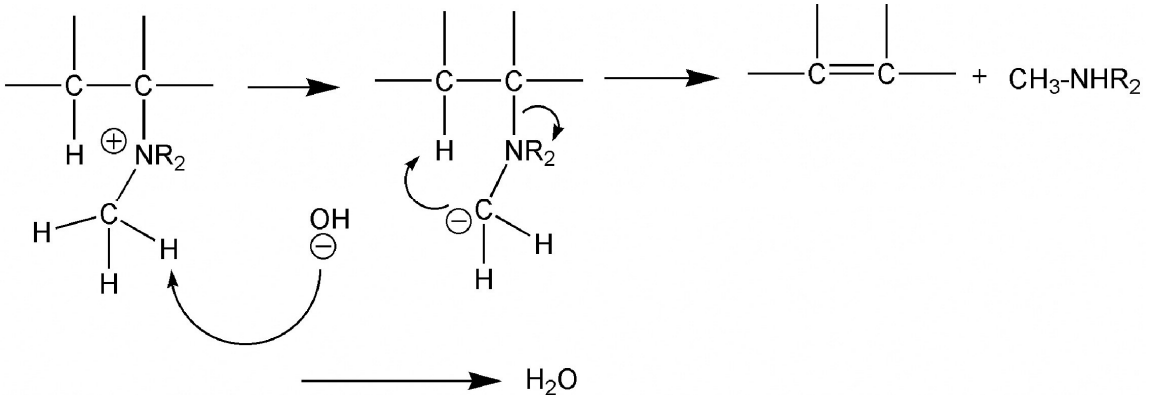
Zhu L, Yu X, Hickner MA. Exploring backbone-cation alkyl spacers for multi-cation side chain anion exchange membranes. J Power Sources. 2018;375:433-441. doi:10.1016/j.jpowsour.2017.06.020

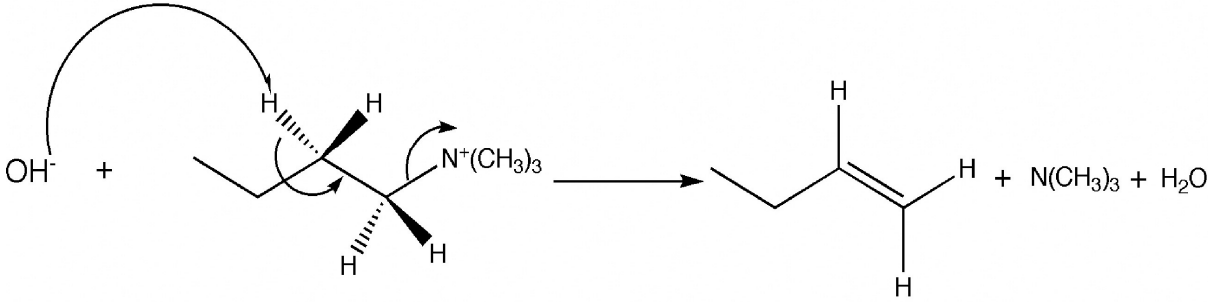
Problematic Reactions



- α and β hydrogen elimination- Hofmann reaction
- E1

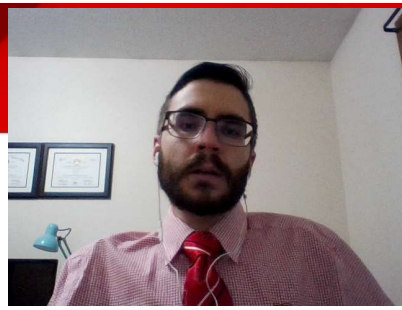


- E2

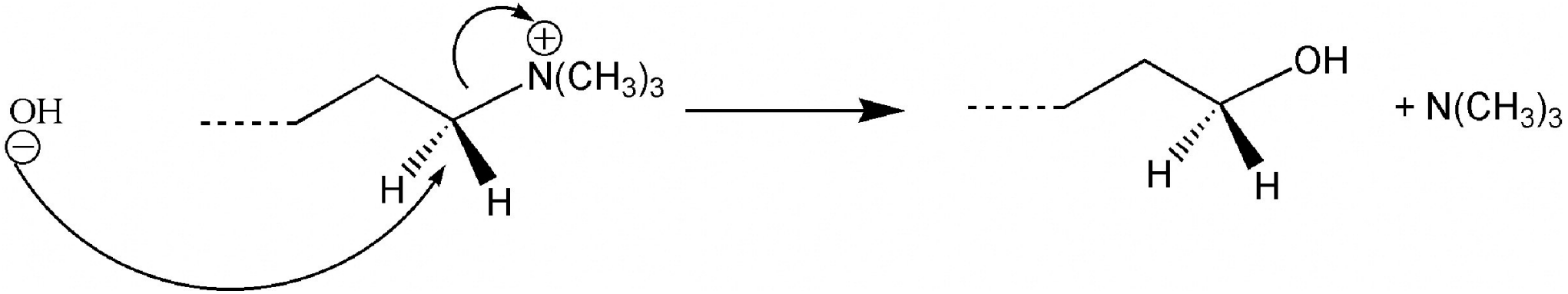


Merle G, Wessling M, Nijmeijer K. Anion exchange membranes for alkaline fuel cells: A review. *J Memb Sci*. 2011;377(1-2):1-35. doi:10.1016/j.memsci.2011.04.043

Problematic Reactions



- Direct nucleophilic substitution



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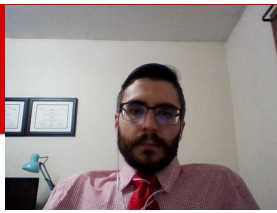
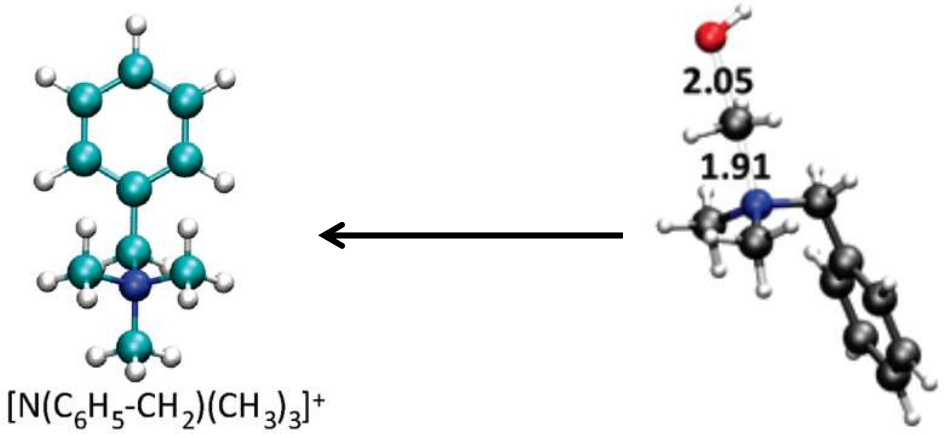


- Nitrogen Ylide formation: Benzyltrimethylammonium

Attack Location	Equation	ΔE*	ΔE, transition*	ΔG^0*
Benzyl hydrogen	$N(CH_3)_2(CH_2-C_6H_5)+OH^- \rightarrow (CH3)_3N^+-(C_6H_5-CH)^- + H_2O$	7.260	7.337	11.1
Methyl hydrogen	$N(CH_3)_2(CH_2-C_6H_5)+OH^- \rightarrow (CH3)_2(C_6H_5-CH_2)N^+-(CH_2)^- + H_2O$	8.357	8.365	10.9

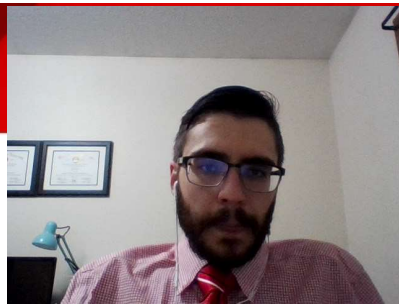
* Units are kcal/mol



Chempath S, Einsla BR, Pratt LR, et al. Mechanism of tetraalkylammonium headgroup degradation in alkaline fuel cell membranes. J Phys Chem C. 2008;112(9):3179-3182. doi:10.1021/jp7115577

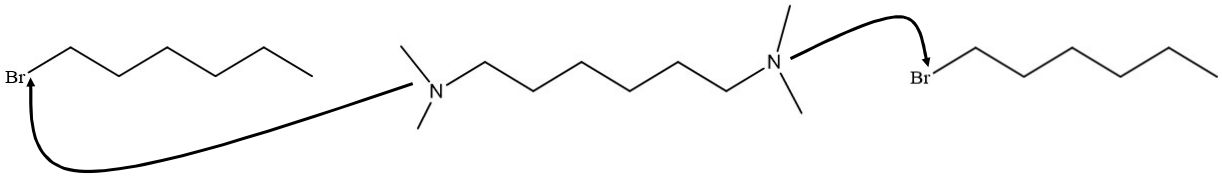
Chempath S, Boncella JM, Pratt LR, Henson N, Pivovar BS. Density functional theory study of degradation of tetraalkylammonium hydroxides. J Phys Chem C. 2010;114(27):11977-11983. doi:10.1021/jp9122198

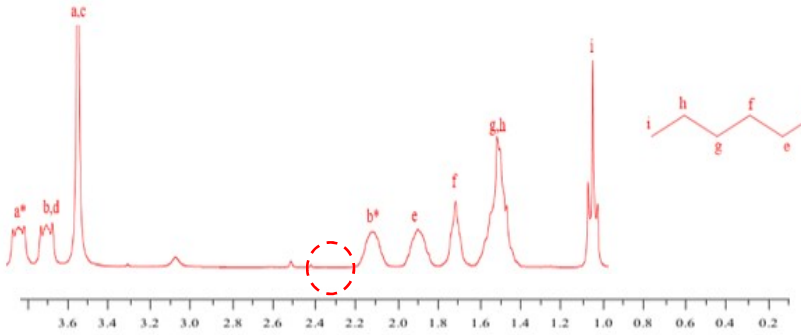
Research Objective

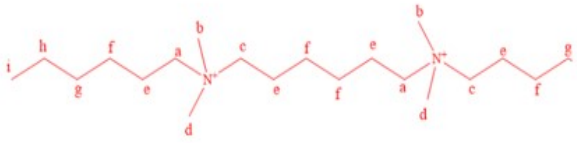


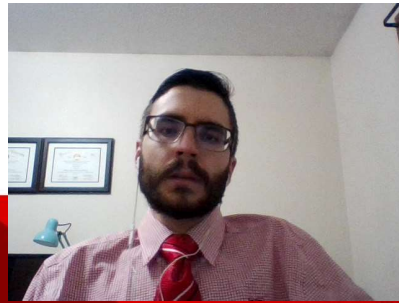
Development of durable, high performance, low cost membrane via side chain addition.

- Undesired bismethonium:
  - Molar ratio
  - Addition sequence of reagents
  - Recovery techniques

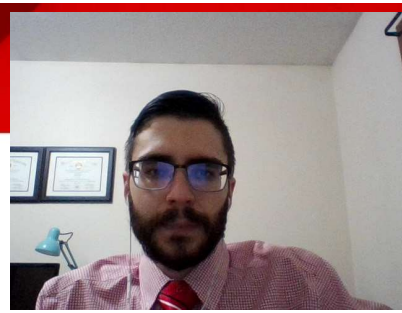




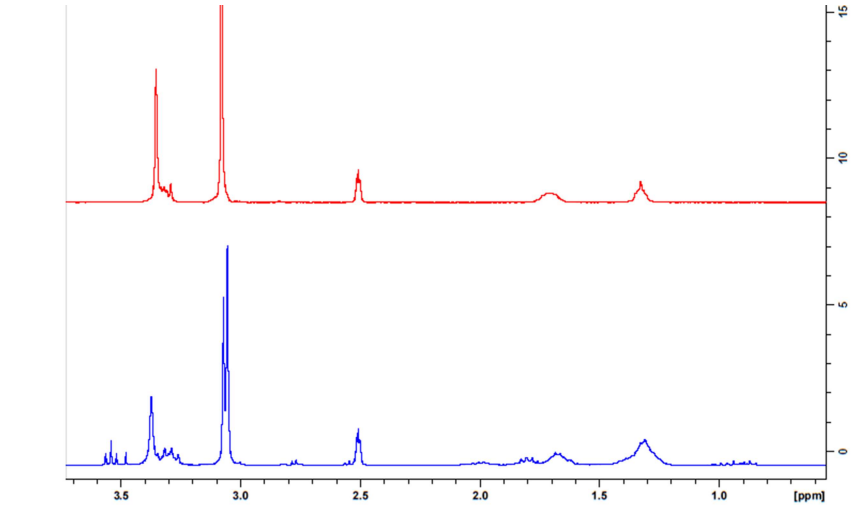


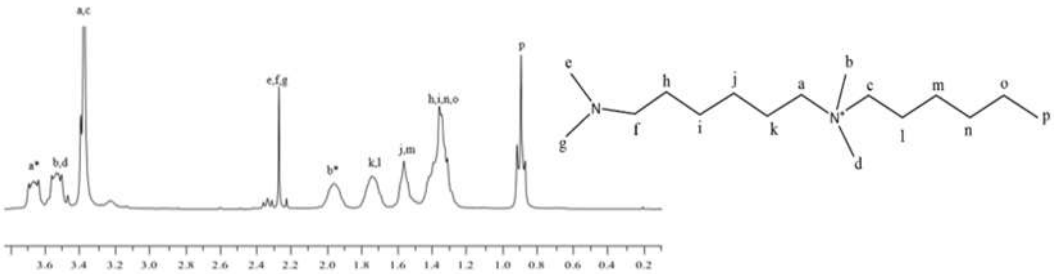


Results



- Undesired bismethonium:
- Desired-bromooctyl:





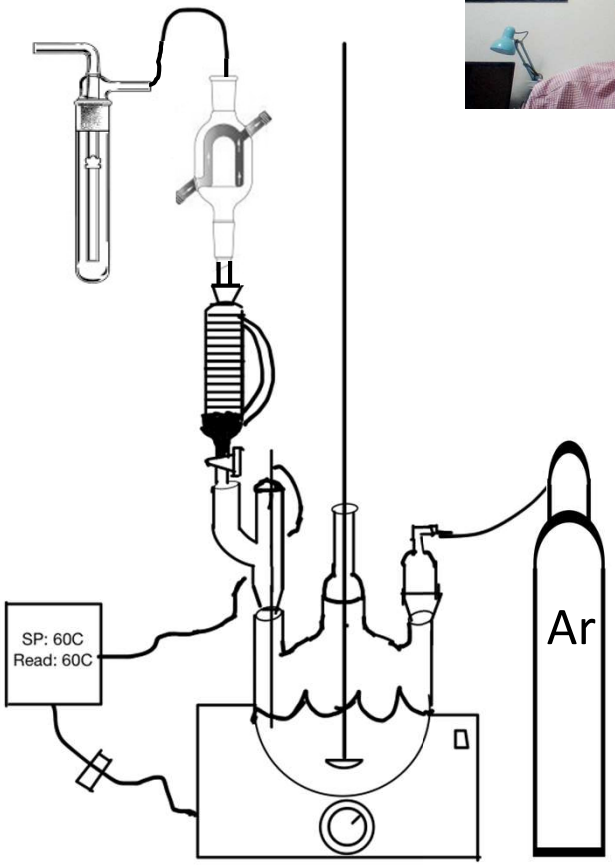
PRECURSOR: H NMR ($(CD_3)_2SO$), 300MHz): 1.26-1.29 (m, 8H), 1.71 (t, 2H), 1.82 (t, 2H), 3.22 (t, 2H), 3.3 (s, 9H), 3.5-3.6 ppm (t, 2H)
DODECANE BROMIDE: H NMR (CDCl3), 300MHz): 0.88-0.9(t, 3), 1.34-1.54(m, 12), 1.6-1.8(s, 4), 2.25-2.28 (s, 2), 3.41 (s, 6), 3.5-3.6 (m, 4)

Li J, Wang L, Shi F, et al. Quaternary ammonium ionic liquids as Bi-functional catalysts for one-step synthesis of dimethyl carbonate from ethylene oxide, carbon dioxide and methanol. Catal Letters. 2011;141:339-346. doi:10.1007/s10562-010-0498-6

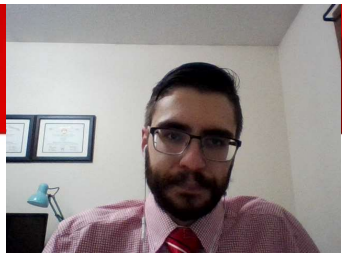
Zhu L, Yu X, Hickner MA. Exploring backbone-cation alkyl spacers for multi-cation side chain anion exchange membranes. J Power Sources. 2018;375:433-441. doi:10.1016/j.jpowsour.2017.06.020

Experimental

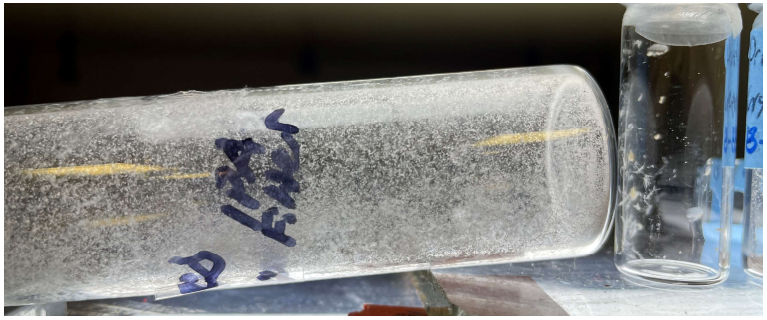
- Synthesis Components:
  - Bubbler Mineral Oil
  - Reflux Condenser
  - Graduated Addition Funnel
  - Heating Mantel
  - Stir Bar with blade
  - Argon Gas

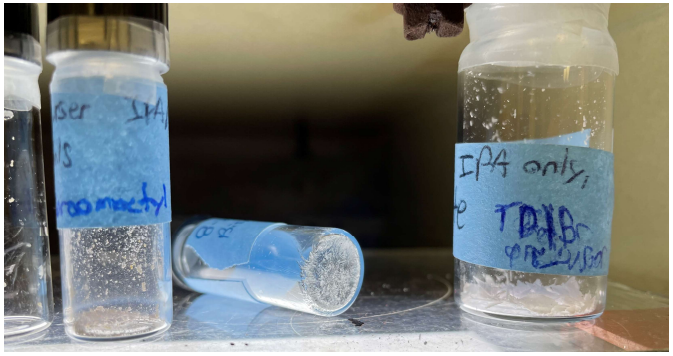


Conclusion

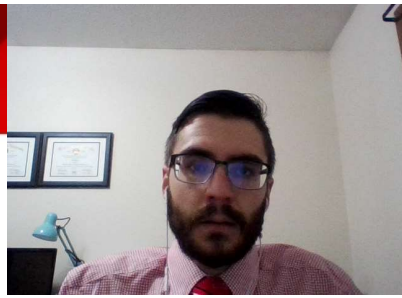


- Key parameters:
  - Solvent
  - Atmosphere control
  - Temperature
  - Reagent molar ratio
  - Addition sequence

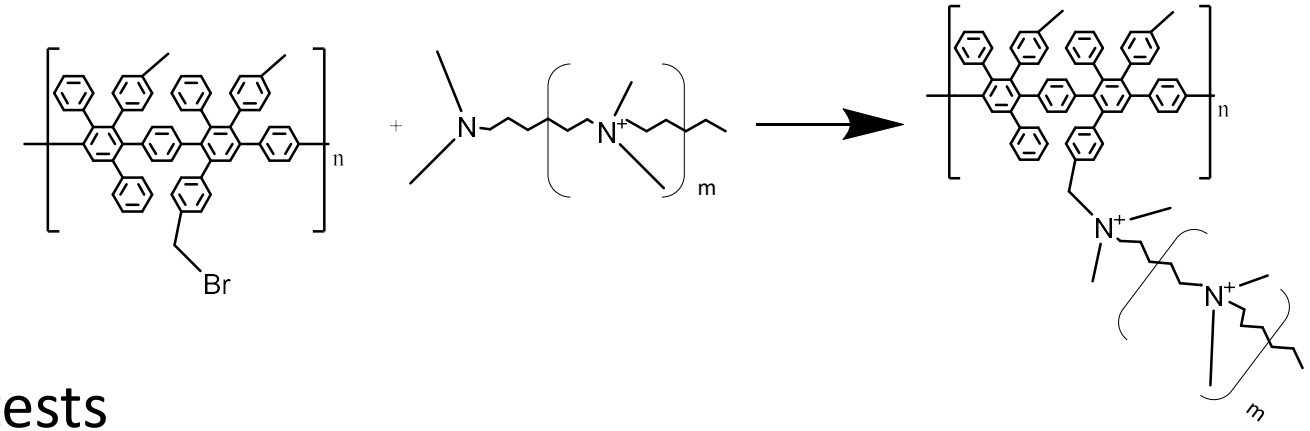




Future Studies



- Attachment to a poly (phenylene) membrane



- Degradation tests
  - 80°C Baths over 30 days
  - Conductivity measurements via electrical impedance spectroscopy

Largier TD, Cornelius CJ. Random quaternary ammonium Diels-Alder poly(phenylene) copolymers for improved vanadium redox flow batteries. *J Power Sources*. 2017;352:149-155. doi:10.1016/j.jpowsour.2017.03.130

Acknowledgements

- Cornelius Lab Group
  - Dr. Chris Cornelius- PI
  - Thivani Senathiraja- Graduate student
  - Casey Holte- Undergraduate assistant
  - Aidan Larsen- Undergraduate assistant

- Funding Source: NCESR

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