Spirocyclic Anion Exchange Membranes for Improved Performance and Durability

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Project ID: FC178

Overview

Timeline and Budget

- Project start date: 01/01/18
- Project end date: 09/30/19

- Total project budget: $150k with additional $150K possible
  - Total recipient share: $0K
  - Total federal share: $150K
  - Total DOE funds spent*: $20K

Barriers

- Cost
- Performance
- Durability

Partners

- NREL only project
- Multiple interactions across AEM space, leverage significant effort at NREL on related projects

* As of 3/31/18

Relevance/Impact
DOE (Preliminary) Milestones for AMFCs*

- **Q2, 2017:** Develop anion-exchange membranes with an area specific resistance ≤ 0.1 ohm cm^2, maintained for 500 hours during testing at 600 mA/cm^2 at T > 60 ^{o}C.
- **Q4, 2017:** Demonstrate alkaline membrane fuel cell peak power performance > 600 mW/cm^2 on H_2/O_2 (maximum pressure of 1.5 atma) in MEA with a total loading of ≤ 0.125 mg$_{PGM}$/cm^2.
- **Q2, 2019:** Demonstrate alkaline membrane fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atma) in MEA a total loading of < 0.1 mg$_{PGM}$/cm^2 , and less than 10% voltage degradation over 2,000 hour hold test at 600 mA/cm^2 at T > 60 ^{o}C. Cell may be reconditioned during test to remove recoverable performance losses.
- **Q2, 2020:** Develop non-PGM catalysts demonstrating alkaline membrane fuel cell peak power performance > 600 mW/cm^2 under hydrogen/air (maximum pressure of 1.5 atma) in PGM-free MEA.

Impact/Team Project Goals

Novel Synthesis - Improve novel perfluoro (PF) anion exchange membrane (AEM) properties and stability.

Fuel Cell Optimization - Employ high performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells (AMFCs).

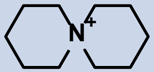
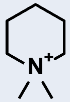
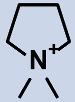
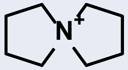
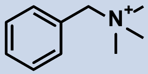
Model Development - Apply models to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate related).

*taken from D. Papageorgopoulos presentation AMFC Workshop, Phoenix, AZ, April 1, 2016

Relevance/Objectives

Alkaline exchange membranes continue to be challenged with cation degradation at high temperature and pH conditions

- State of the art trimethyl ammonium cations exhibit limited durability under fuel cell operating condition
- Research has indicated that cations with a spirocyclic structure have improved durability
    - Higher activation energy for both Hoffman elimination and substitution degradation mechanisms
- Incorporation of spirocyclic ammonium cations into alkaline exchange membranes to improve durability

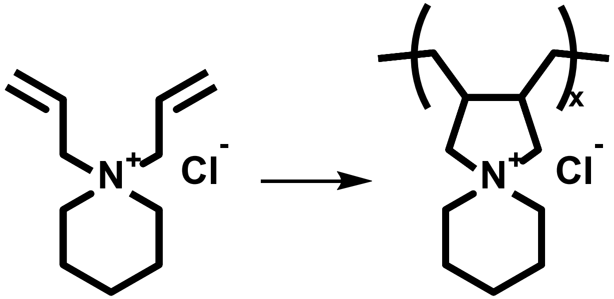
Quaternary Ammonium	Abbreviation	Half-life [hr]
	ASU	110
	DMP	87.3
	DMPy	37.1
	ASN	28.4
	BTMA	4.18

Marino, M. G.; Kreuer, K. D., Alkaline Stability of Quaternary Ammonium Cations for Alkaline Fuel Cell Membranes and Ionic Liquids. *ChemSusChem* **2015,** *8* (3), 513-523.

Approach

Synthesis

- Diallyl monomers undergo ring closing radical polymerization
- Polymerization of diallypiperidinium chloride produces polymer of ASU/ASN hybrid structures



Polymer & copolymer characterization

- Structure
- IEC
- Conductivity

Accelerated aging

- Polymer & AEM durability
- Degradation pathways and rates

Leverage NRELs in-house expertise and MEA testing equipment

MEA fabrication and characterization

- Fuel cell performance
- Long term durability

- Previous work generated multiblock copolymers of polydiallylpiperidinium segments in a high performance polysulfone backbone
- Current synthesis focuses on scaling synthetic procedure for production of larger (>20 g) batches
  - Provide ample material for complete MEA characterization and durability studies

D. Strasser, PhD Thesis, Colorado School of Mines

Approach - Milestones

Milestone Name/Description	End Date	Type
Produce sufficient materials (> 20 g) to accomplish degradation evaluation of both the homopolymer and mulitblock copolymer membrane.	12/31/2017	Progress Measure
Quantify poly(polydiallylpiperidinium hydroxide) degradation rates using temperature as an accelerating factor up to 160 °C.	3/31/2018	Progress Measure
Demonstrate membrane ASR ≤0.02 Ω in fuel cell tests.	6/30/2018	Progress Measure
Demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atma) in MEA, and less than 10% voltage degradation over 1,000 hour hold test at 600 mA/cm^2 at T>60 ºC.	9/30/2018	Annual Milestone

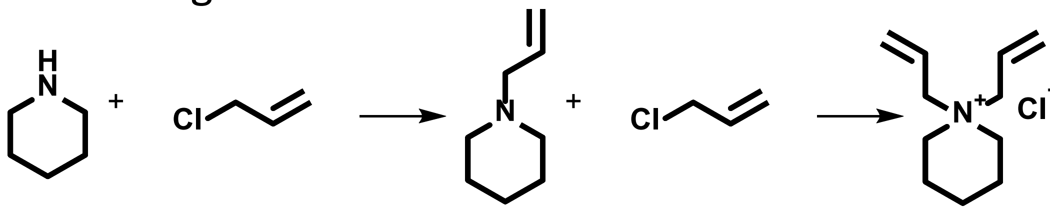
Go/No-Go Description	Criteria	End Date
AEMFC Durability	In alignment with DOE 2019, Q2 AEM target, demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atma) in MEA, and less than 10% voltage degradation over 1,000 hour hold test at 600 mA/cm^2 at T>60 ºC.	9/30/2018

Accomplishments and Progress

Synthesis

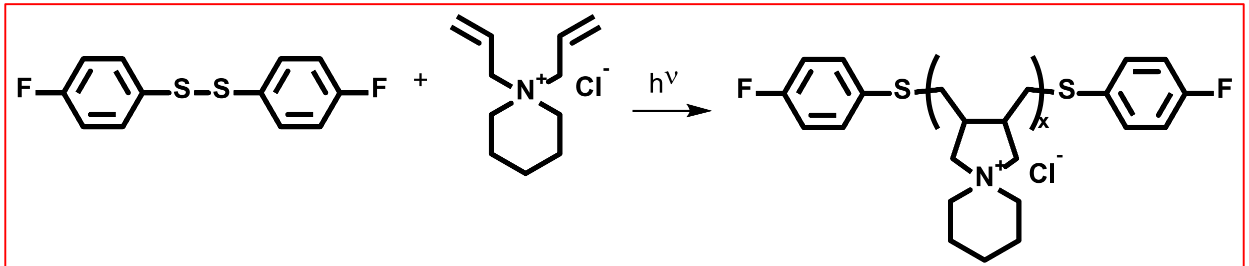
Monomer

- Two step process completed in 4-5 days
- Easily produce > 100 g batches



Poly(diallylpiperidinium chloride) (PDApip)

- 24 hr. photopolymerization
- Small batch (≈ 5 g) 50 % recovery
- Larger batch (30-40 g) 15 % recovery
- **bottleneck for larger scale copolymerization**

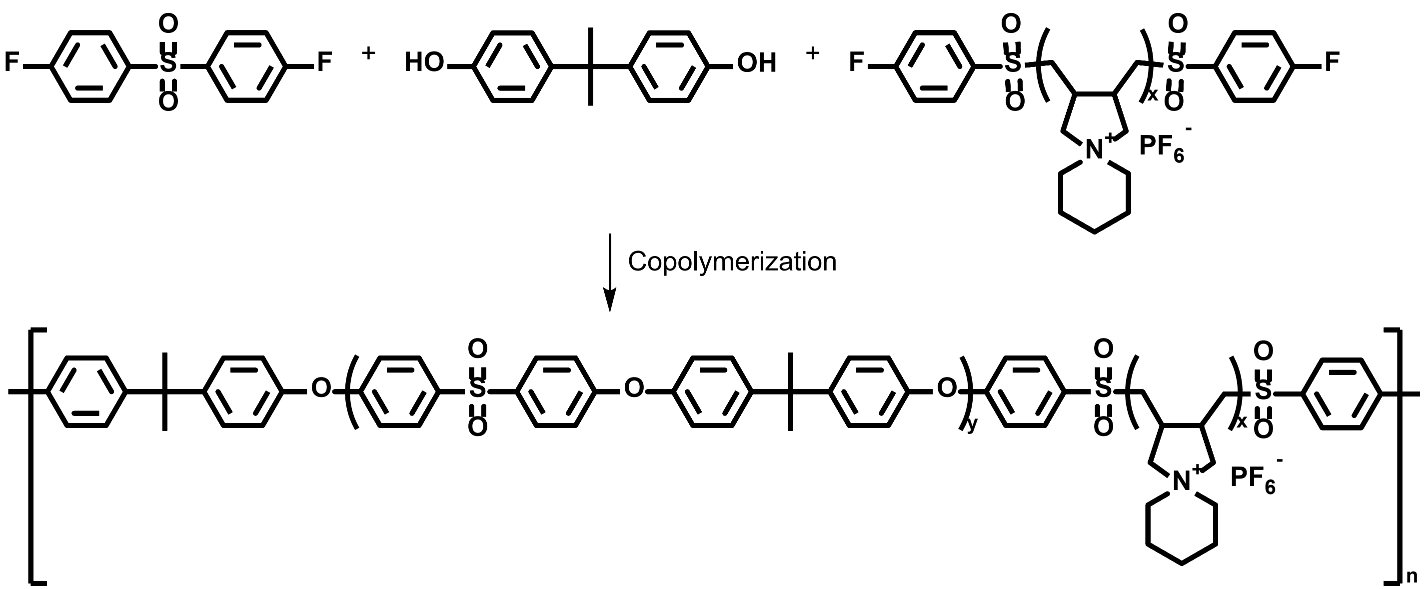


Accomplishments and Progress

Synthesis

Polysulfone-PDApip multiblock copolymers

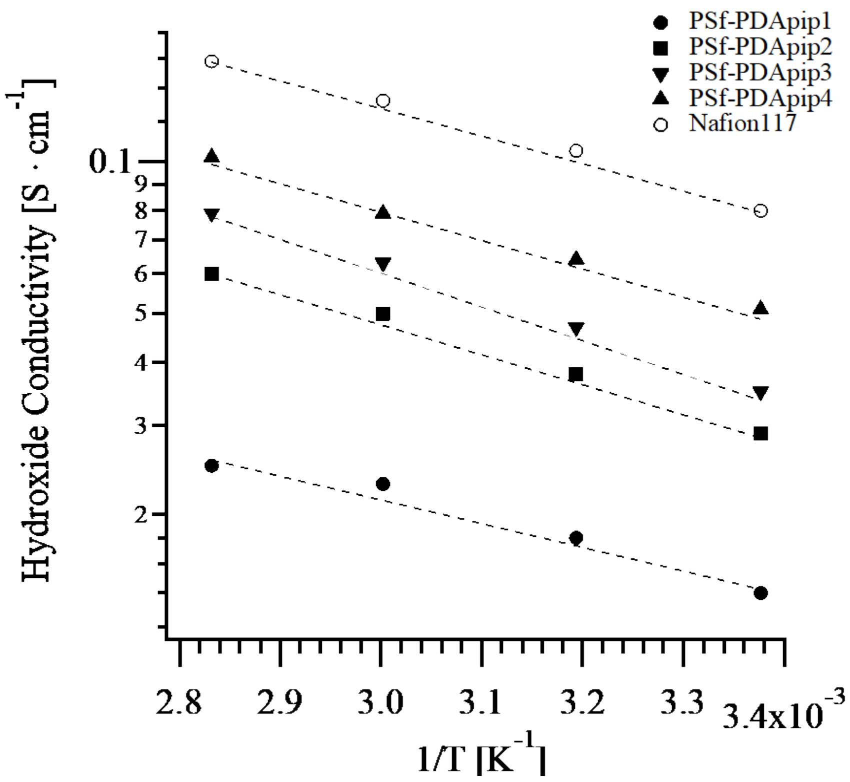
- A single 16 g batch has been copolymerization completed
- Copolymerization had low viscosity – indicating low molecular weight
- ^{1}H NMR estimation of PDApip end group concentration was insufficient
  - Indicates the presence of non-functional end groups



Accomplishments and Progress

Polymer & Copolymer characterization

- Previous work has shown the Polysulfone-PDApip multiblock copolymer membranes to efficiently conduct hydroxide
- The activation energy for hydroxide conduction was very similar to Nafion117
- Hydroxide conductivity was able to reach 102 mS/cm^2 at 80 °C



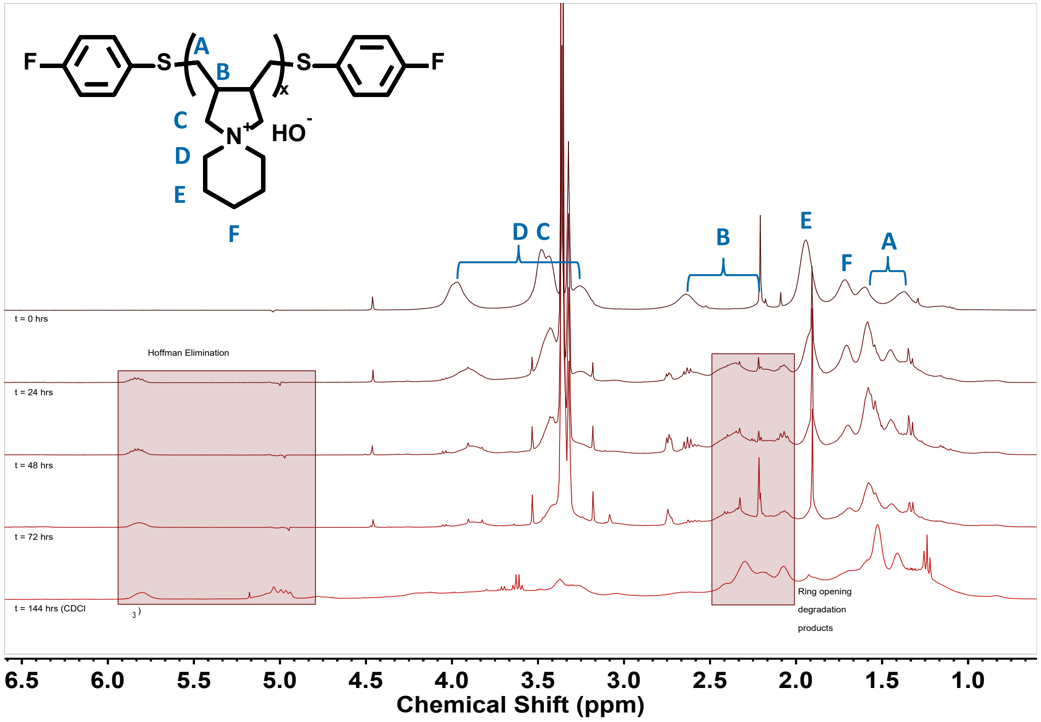
Strasser, D. J.; Graziano, B. J.; Knauss, D. M., Base stable poly(diallylpiperidinium hydroxide) multiblock copolymers for anion exchange membranes. *Journal of Materials Chemistry A* **2017,** *5* (20), 9627-9640.

Accomplishments and Progress

Polymer Durability

- Previous investigation of the PDApip durability indicated negligible degradation, by ^1H NMR, over 1000 hours at 80 °C in a 1M KOH/Methanol-d_4 solution

- Current durability studies adapt NRELs established accelerated aging conditions
- PDApip aged at 140 °C for 144 hours in 2:1 MeOH/2M KOH
- Hoffman elimination and ring opening degradation was observed over 144 hours

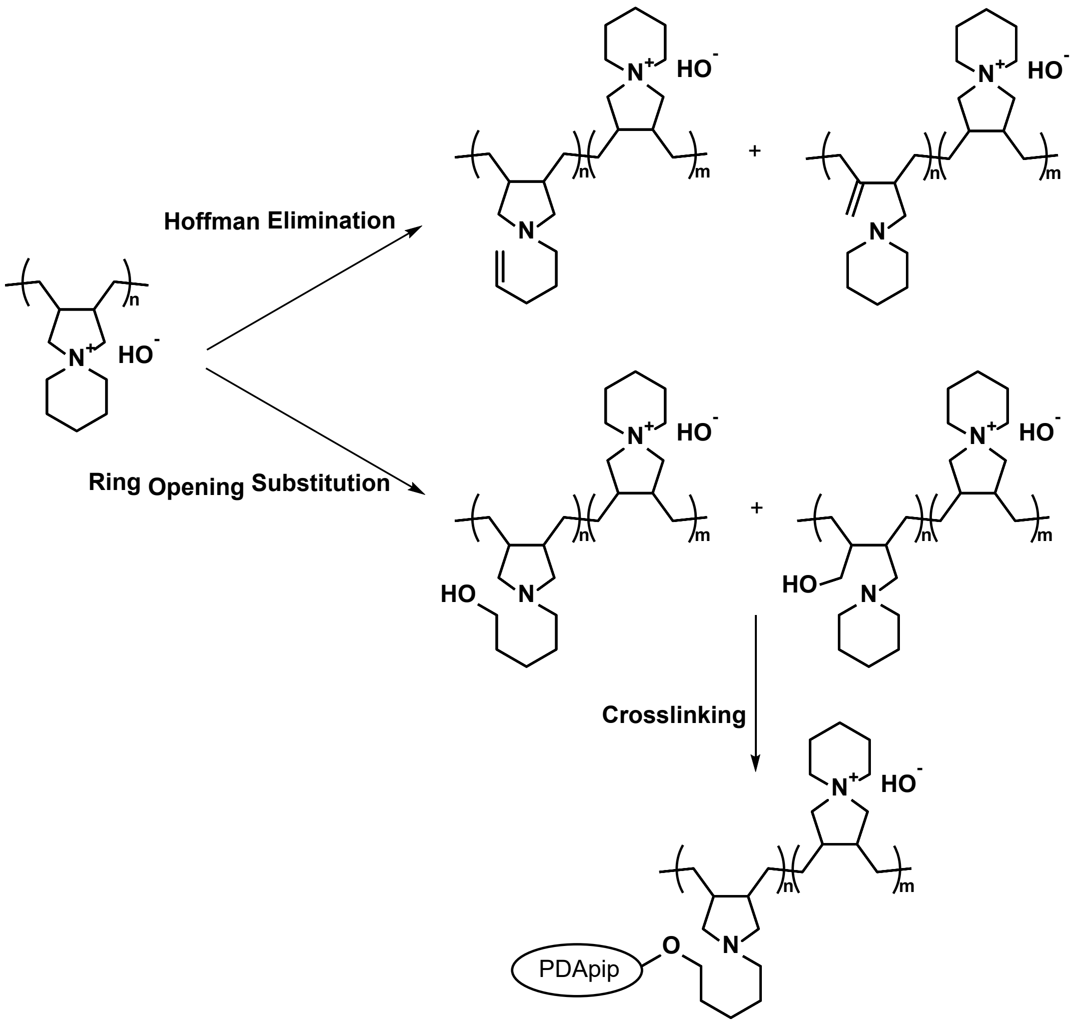


Accomplishments and Progress

Degradation Pathways

- After 144 hours some insoluble material was left behind in the reactor

- Insolubility indicates crosslinking resulting from ring opening attack of hydroxyl degradation products



Remaining Challenges and Barriers

Synthesis

- Large scale PDApip synthesis has poor yield
  - Limits the copolymerization scale

Accelerated aging characterization

- ^{1}H NMR unable to quantitatively assess the amount of degradation in PDApip polymers
  - Developing titration analytical method

Proposed Future Work

Synthesis

- Continue to work on the scale up of the PDApip polymerization
  – improve conversion
- Generate ~ 10 – 15 g batches of PDApip
- Produce ~ 20 g batches of Polysulfone-PDApip copolymer

Polymer and copolymer characterization

- Molecular weight analysis of produced PDApip polymers
- UV characterization of end groups – improve copolymerization
- Confirm IEC and measure ionic conductivity of Polysulfone-PDApip membranes

Accelerated aging

- Continue accelerated aging experiments to further elucidate the rate of degradation and major degradation pathways

MEA fabrication and characterization

- Fabricate MEAs and optimize fuel cell test conditions
- Conduct long term durability study with Polysulfone-PDApip materials

Any proposed future work is subject to change based on funding levels

Summary

Milestone Name/Description	End Date	Type	Progress
Produce sufficient materials (> 20 g) to accomplish degradation evaluation of both the homopolymer and mulitblock copolymer membrane.	12/31/2017	Progress Measure	Can produce > 15 g batches of multiblock membrane material
Quantify poly(polydiallylpiperidinium hydroxide) degradation rates using temperature as an accelerating factor up to 160 °C.	3/31/2018	Progress Measure	Shown accelerated degradation and pathways • Need rates of degradation • Further elucidation of pathways
Demonstrate membrane ASR ≤0.02 Ω in fuel cell tests.	6/30/2018	Progress Measure	Not started
Demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (maximum pressure of 1.5 atma) in MEA, and less than 10% voltage degradation over 1,000 hour hold test at 600 mA/cm^2 at T>60 ^{o}C.	9/30/2018	Annual Milestone	Not started

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