Spirocyclic Anion Exchange Membranes for improved Performance and Durability

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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

Project ID: FC178

Overview

Timeline and Budget

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

- Total project budget: $300k
  - Total recipient share: $0K
  - Total federal share: $300K
  - Total DOE funds spent*: $170K

* As of 3/31/19

Barriers

- Cost
- Performance
- Durability

Partners

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

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 $\leq$ 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

Synthesize novel spirocyclic ionomers to membranes and ionomers in Alkaline Membrane Fuel Cells (AMFCs).

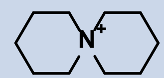
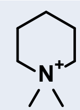
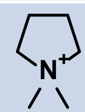
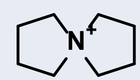
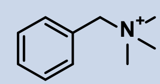
Optimize performance to meet DOE AMFC targets

*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

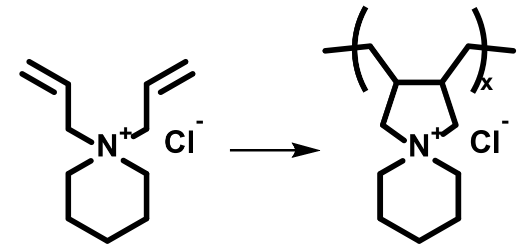
- State of the art trimethyl ammonium cations exhibit limited durability under fuel cell operating condition
- Research has indicated that cations with a spirocyclic structure have improved durability
    - Higher activation energy for both Hoffman elimination and substitution degradation mechanisms
- 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 repeat units that of an ASU/ASN hybrid structure



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

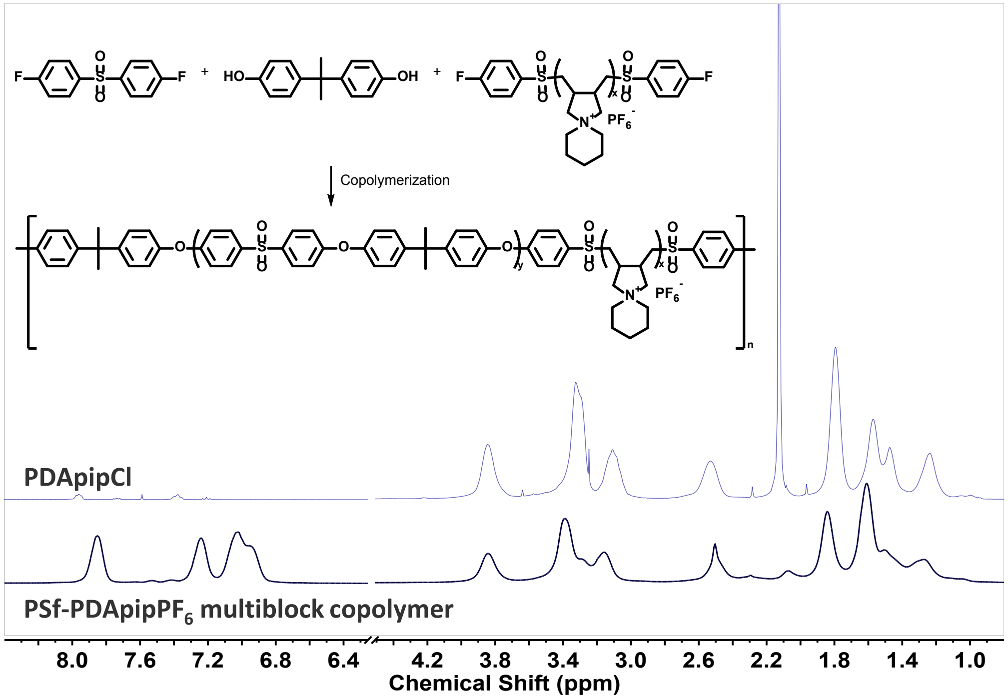
Approach - Milestones

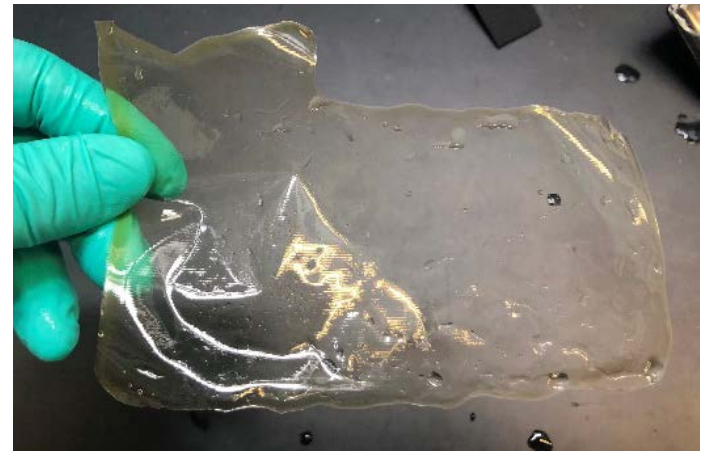
	Milestone Name/Description	End Date	Type
Q1	In alignment with DOE 2019, Q2 AEM target, Demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm2 on H2/air (maximum pressure of 1.5 atma) in MEA, and less than 10% voltage degradation over 1,000 hour hold test at 600 mA/cm2 at T>60 oC.	12/31/2018	Milestone - Met at 500 hours
Q2	Develop ionomer solutions based on spirocyclic AEM polymers.	3/31/2019	Progress Measure - Met
Q3	Quantify fuel cell performance of at least 3 different MEAs using spirocyclic ionomers and compare to baseline AMFC performance.	6/30/2019	Progress Measure – On track
Q4	Optimize fuel cell performance based on a fully spirocyclic system where cathode and anode ionomer and membrane are spirocyclic based.	9/30/2019	Progress Measure – On track

AEM FC 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.	12/31/2018 – conditionally met

Accomplishments and Progress

Synthesis/Characterization





Polymer	IEC (measured) [mmol/g]	Cl^- Conductivity @RT in Water [mS/cm]	Water Uptake (%)	Peak Power Density (W/cm^2)
SpiroCyclic AEM	1.3	14.0	22	0.85
SpiroCyclic AEM	1.5	13.8	42	1.22
SpiroCyclic AEM	1.7	16.1	80	1.48
Gen 2 PF AEM	0.9	13.4	18	1.10

Accomplishments and Progress

Durability

Before and (where possible) after Degradation

- Teflon-lined Parr reactors (20 mL)
- Dry samples of ~100 mg in Cl^- form
- 1 M KOH (10 mL)
- 80 °C in oven for 1000 h
- Room Temperature, Liquid H_2O, Cl^- Conductivity and IEC tested before/after

Gen 2

- More opaque color
- Still soft/flexible
- Broken/tears easily
- IEC ↓ 2.8%
- Conductivity ↓ 21%

PSF-1.7

- Darker orange color
- Hard/inflexible
- Breaks easily
- IEC ↓ 50%
- Conductivity ↓ 4%

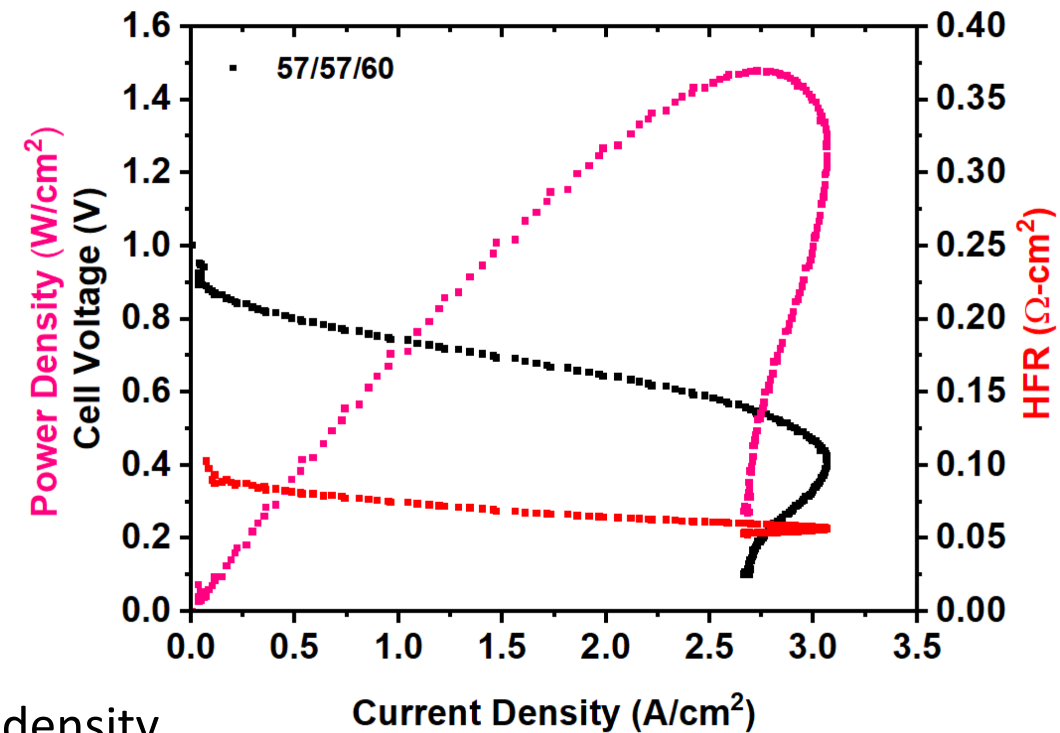
PSF-1.5

- Orange/brown color
- Hard/inflexible
- Broken/tears easily
- IEC ↓ 66%
- Conductivity ↓ 60%

Accomplishments and Progress

Spirocyclic AEM in-situ Fuel Cell Performance

Membrane: Spirocyclic IEC 1.7 mmol/g (55 µm)



<u>Membrane Electrode Assembly</u>

- Cell Temp: 60°C
- Active Area: 5 cm^2
- Pressure: 121 kPa_{abs}
- Ionomer: Varcoe ETFE AEI ionomer
- GDL: Toray H-060
- Gases: H_2 var°C, O_2 var°C, 1.0 slpm
- Anode: 0.8 mg/cm^2 PtRu/Vu
- Cathode: 0.5 mg/cm^2 Pt/Vu

➢ ~ 1.48 W/cm^2 in peak power density

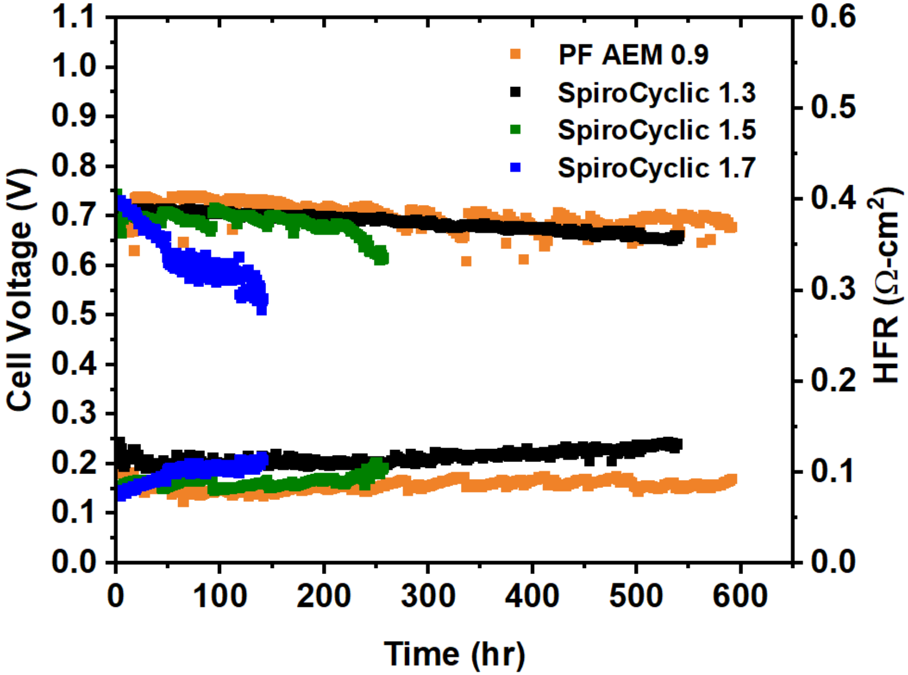
➢ ASR ~ 0.007 Ω (0.036 Ω-cm^2)

➢ Close to state-of-the-art performance

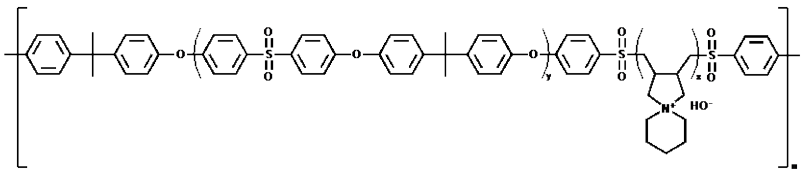
Accomplishments and Progress

In-situ Fuel Cell Durability: Spirocyclic VS PF AEM

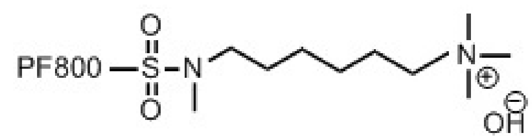
Durability 600mA/cm^2 hold, H_2/Air, 122 kPa$_{abs}$



Spirocyclic



Gen 2 PF AEM



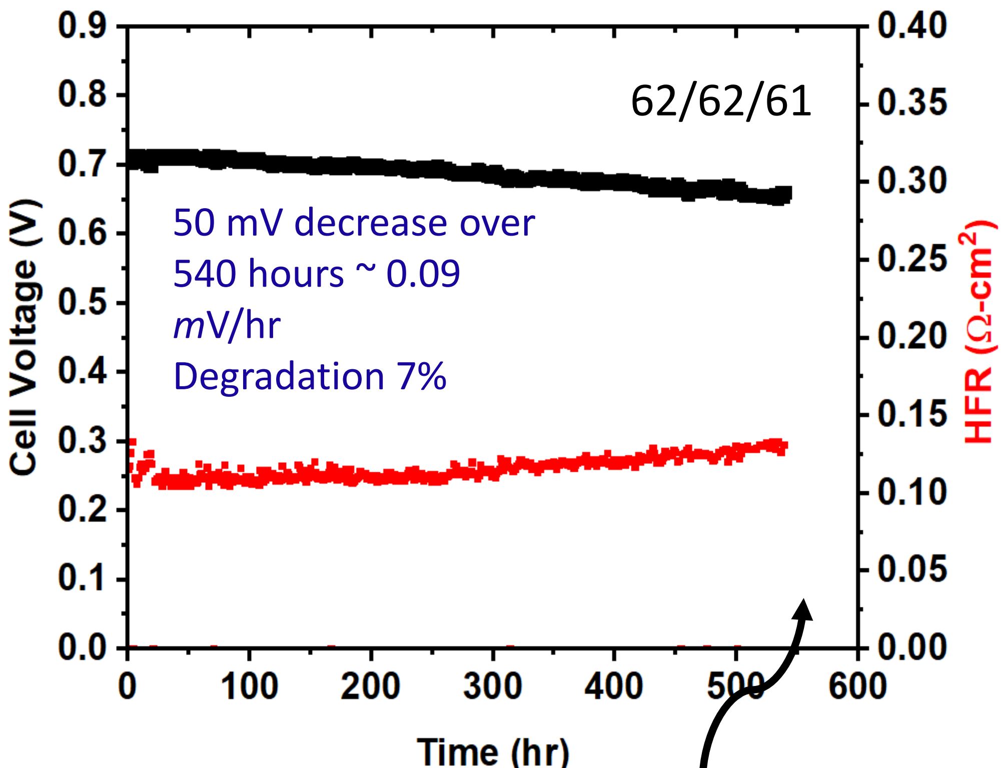
AEM	IEC (measured) [mmol/g]	Cl^- Conductivity @RT in Water [mS/cm]	Water Uptake (%)	Peak Power Density (W/cm^2)
SpiroCyclic AEM	1.3	14.0	22	0.85
SpiroCyclic AEM	1.5	13.8	42	1.22
SpiroCyclic AEM	1.7	16.1	80	1.48
Gen 2 PF AEM	0.9	13.4	18	1.40

Accomplishments and Progress

Spirocyclic AEM in-situ Fuel Cell Durability

Durability 600mA/cm^2 hold

Membrane: Spirocyclic IEC 1.3 mmol/g (10 µm)

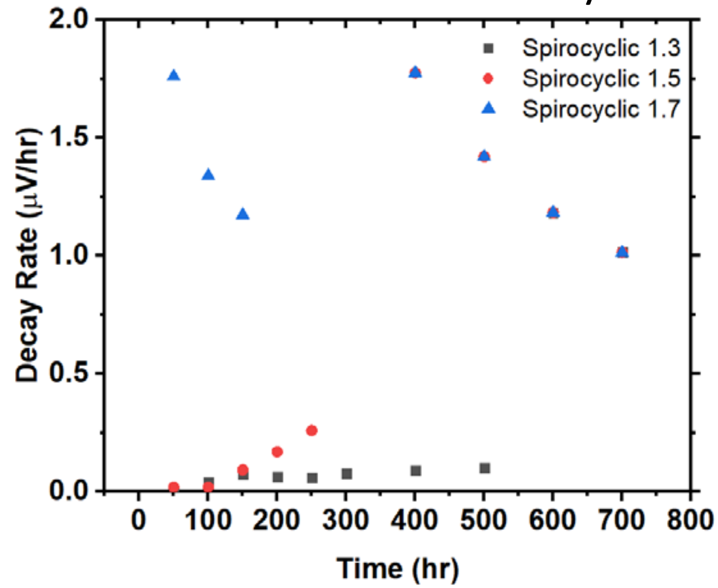


Cell shut down due to house H_2 outage @ 540th hour

Membrane Electrode Assembly

- Cell Temp: 61°C
- Active Area: 5 cm^2
- Pressure: 122 kPa$_{abs}$
- Ionomer: Varcoe ETFE AEI ionomer
- GDL: Toray H-060
- Durability: H_2 var°C, Air var°C, 1.0 slpm
- Anode: 0.8 mg/cm^2 PtRu/Vu
- Cathode: 0.5 mg/cm^2 Pt/Vu

Performance Stability



Accomplishments and Progress

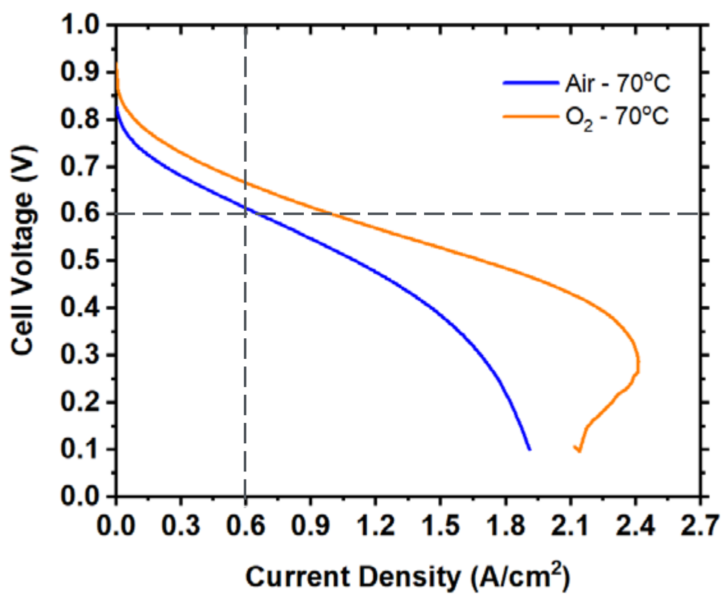
PGM-free Cathode, Low loading Spirocyclic AEM MEA

Go/No-Go Decisions: Completed.

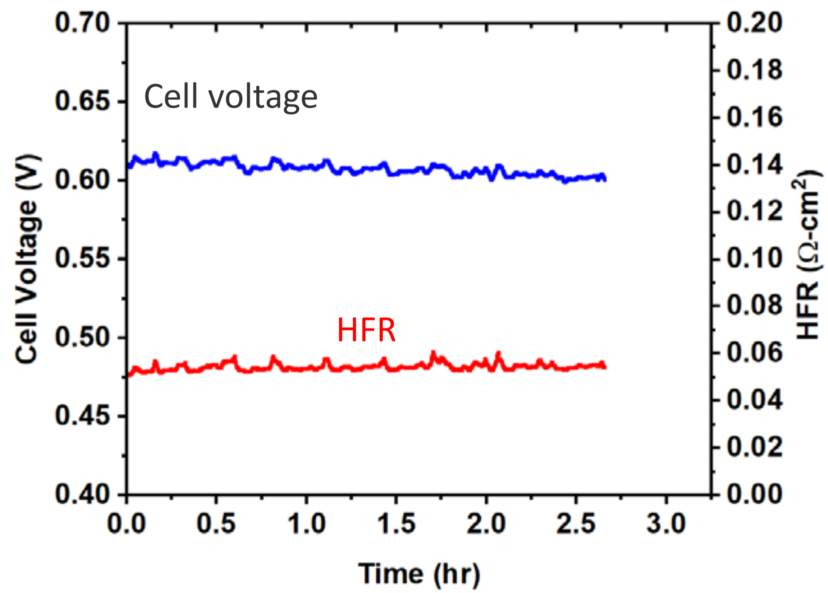
Demonstrate AEM fuel cell initial performance of 0.6 V at 600 mA/cm^2 on H_2/air (max. 1.5 atma) in MEA at T > 60°C with loading < 0.1 mg PGM/cm^2.

Membrane Electrode Assembly

- Cell Temp: 70°C
- Active Area: 5 cm^2
- Pressure: 132 kPa_{abs}
- GDL: Toray H-060
- Anode: 0.1 mg/cm^2 PtRu/Vu
- Cathode: 2.2 mg/cm^2 Ag/Vu
- Membrane: Spirocyclic, 1.7mmol/g, (42µm)



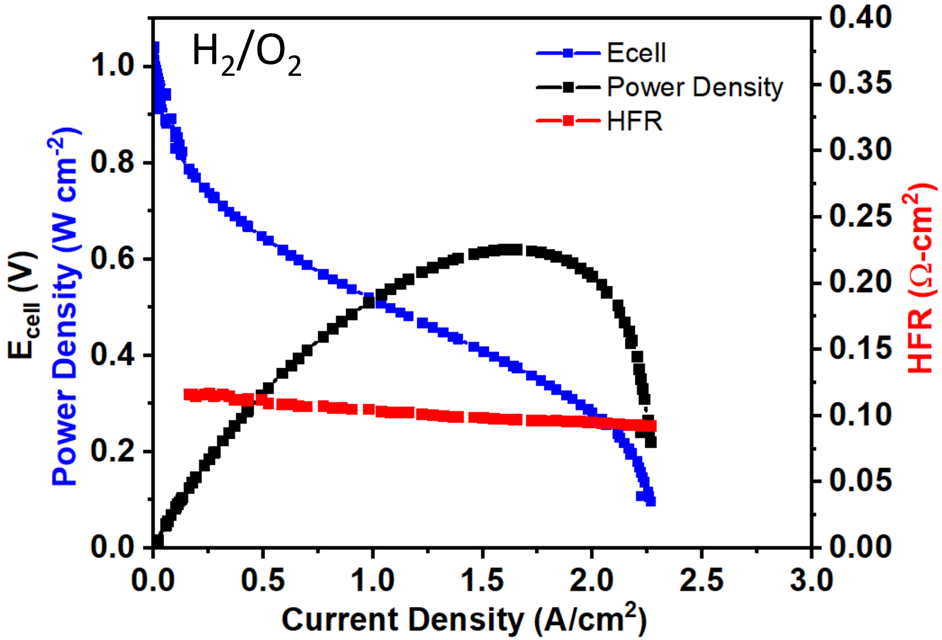
600 mA/cm^2, H_2/air, 70°C

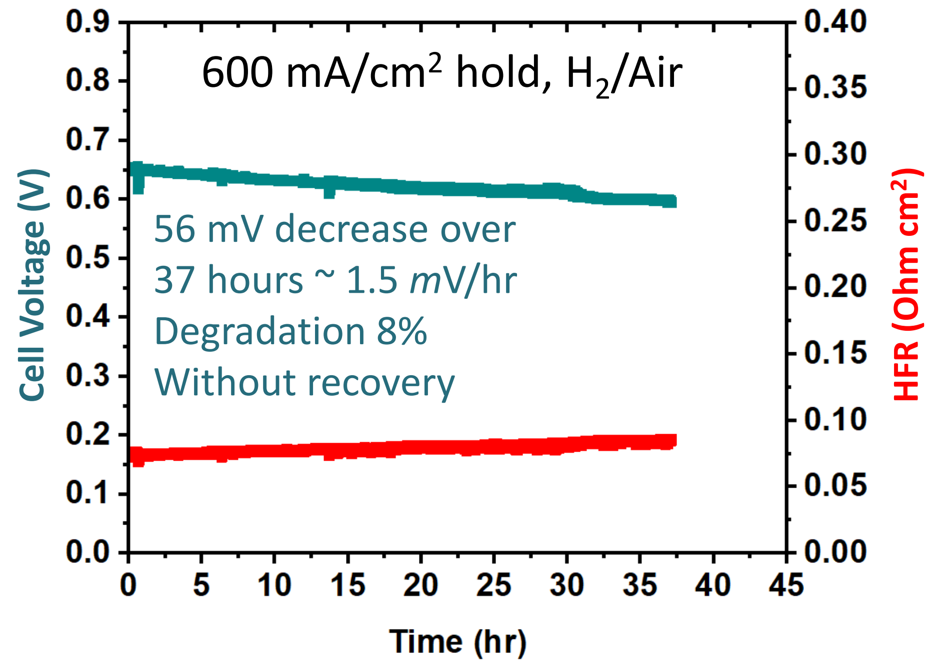


Accomplishments and Progress

Spirocyclic as Ionomer Incorporated into Electrodes

PF AEM Gen2 AEM, Spirocyclic ionomer





- ➢ Spirocyclic serves as a good ionomer with high performance and durability.
- ➢ At 37 hours of durability test, cell shut down occurred due to H_2 outage.

Membrane Electrode Assembly

- Cell Temp: 60°C
- Active Area: 5 cm^2
- Pressure: 121 kPa$_{abs}$
- GDL: Toray H-060
- Anode: 0.5 mg/cm^2 Pt/Vu
- Cathode: 0.5 mg/cm^2 Pt/Vu
- Membrane: Gen 2 PF AEM (40µm)
- Dew points: 60/60/60

Collaborations and Coordinations

- NREL only (limited-funds) project that highly leverages significant effort at NREL on related projects including
  - PF AEM project (FC 142)
  - Membrane Working Group (FC 301)
  - ARPA-E efforts
  - FCTO HydroGEN AWSM (EMN) efforts

Summary

- We synthesized spirocyclic polymers of multiple ion exchange capacity (IEC)
- Lower IEC polymers were synthesized due to trends witnessed for increased durability with decreasing IEC.
- Thinner membranes were employed to limit the impact of lower IEC membranes in fuel cell tests.
- With optimized membranes greater than 500 hours of durability above 0.6V at 600 mA/cm2 was demonstrated.
- High performance with low total PGM loading was shown using spirocyclic membranes.
- Initial performance and durability of spirocyclic ionomer based electrodes showed promise.

Response to Reviewers comments: Project presented last year but not reviewed.

Remaining Challenges and Barriers/Future Work

Remaining Challenges and Barriers

- Polymer stability remains an issue as IEC and conductivity losses in ex-situ testing were high, but fuel cell durability was reasonable when used as a membrane and in initial studies as an ionomer
- Further optimization as an electrode ionomer
  - Ink composition and processing
  - Specific IEC of ionomer material

Future Work

- Focus on ionomer implementation of spirocyclic polymer with a focus on probing cation-catalyst interactions
- Further investigation of low PGM-loaded MEAs

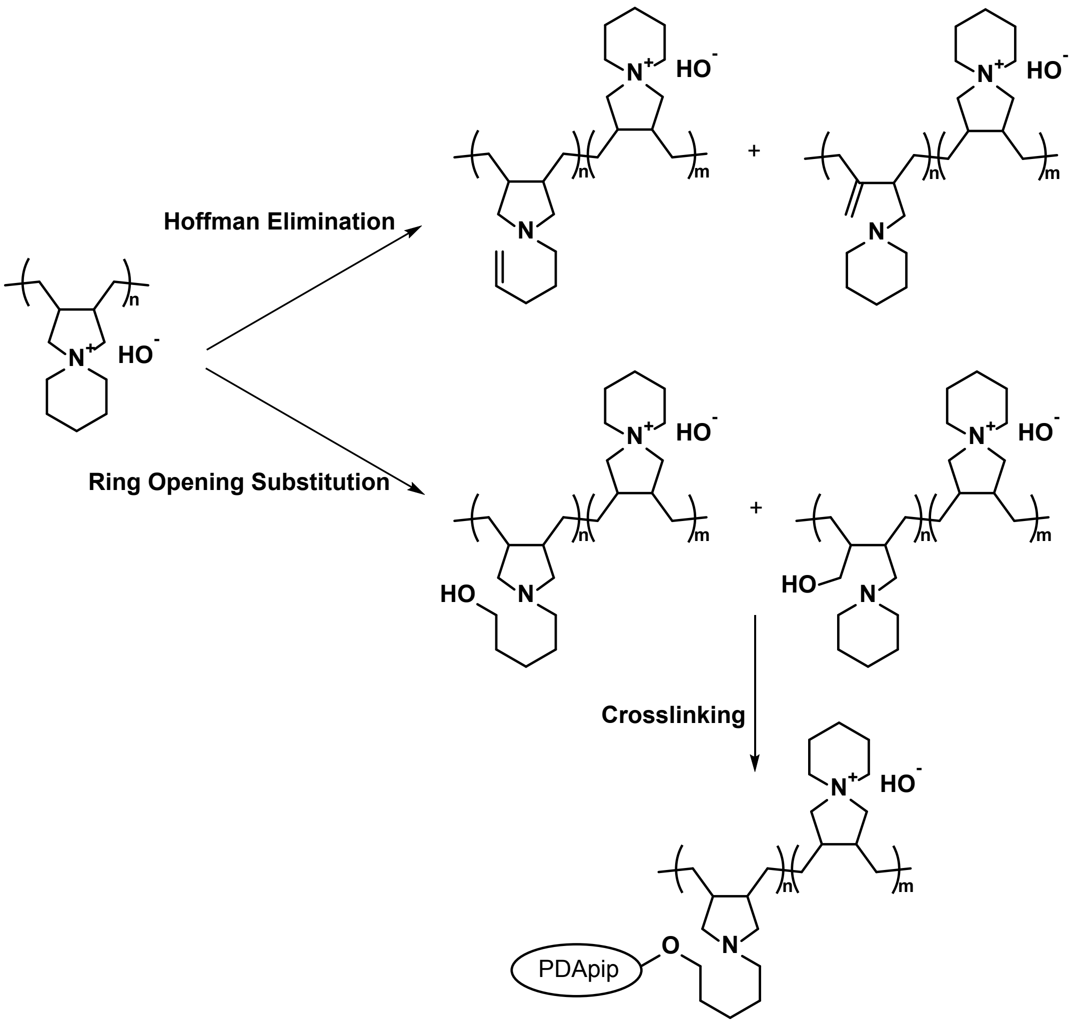
Technical Backup Slides

Accomplishments and Progress

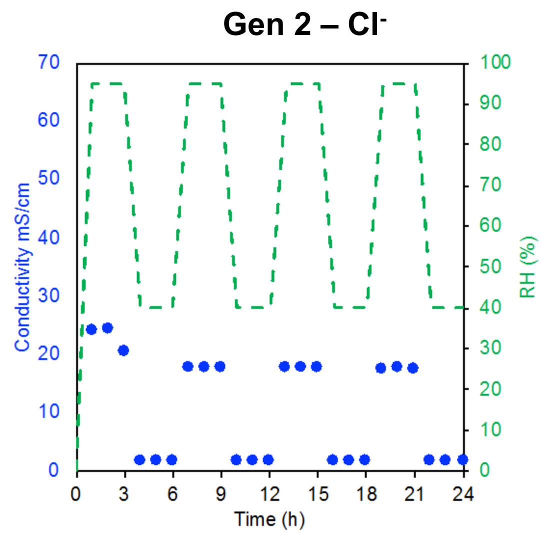
Degradation Pathways – Accelerated testing

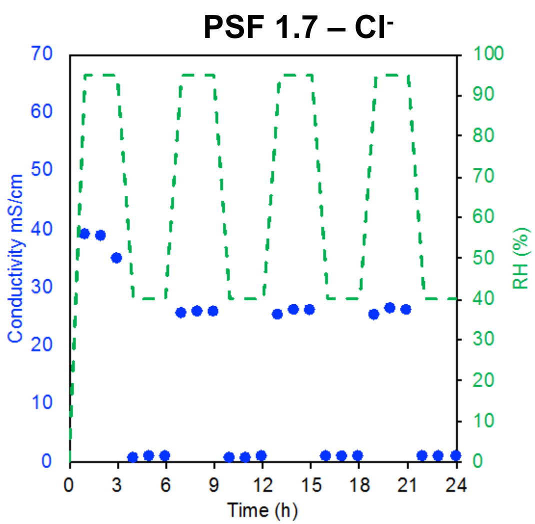
- After 144 hours some insoluble material was left behind in the reactor

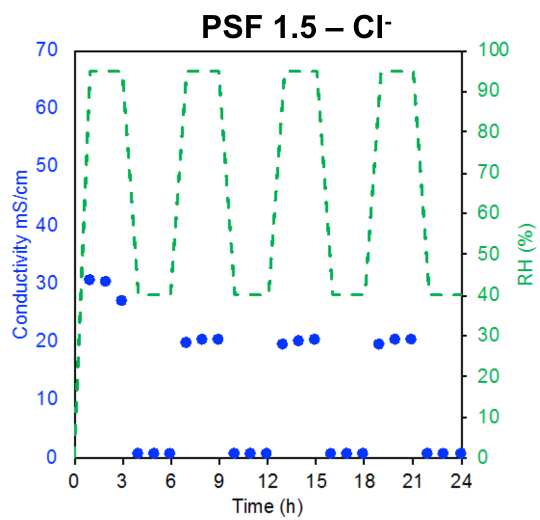
- Insolubility indicates crosslinking resulting from ring opening attack of hydroxyl degradation products

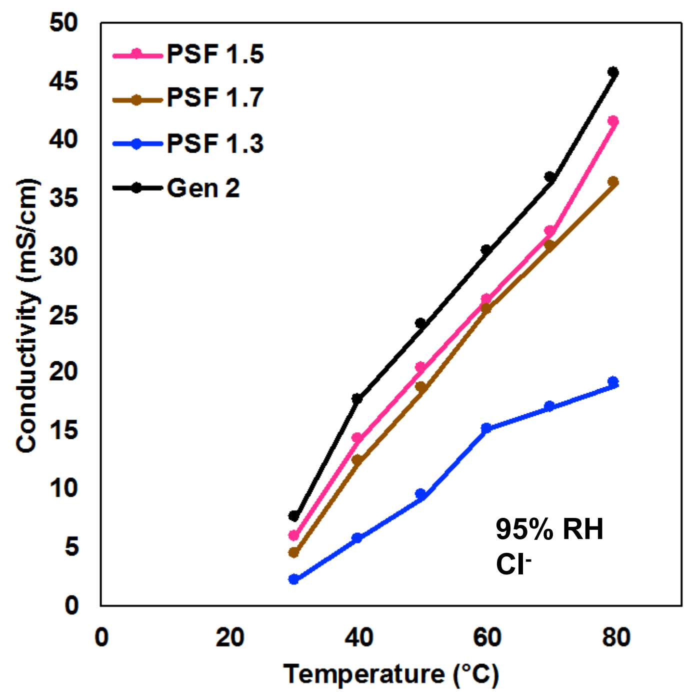


Characterization - conductivity

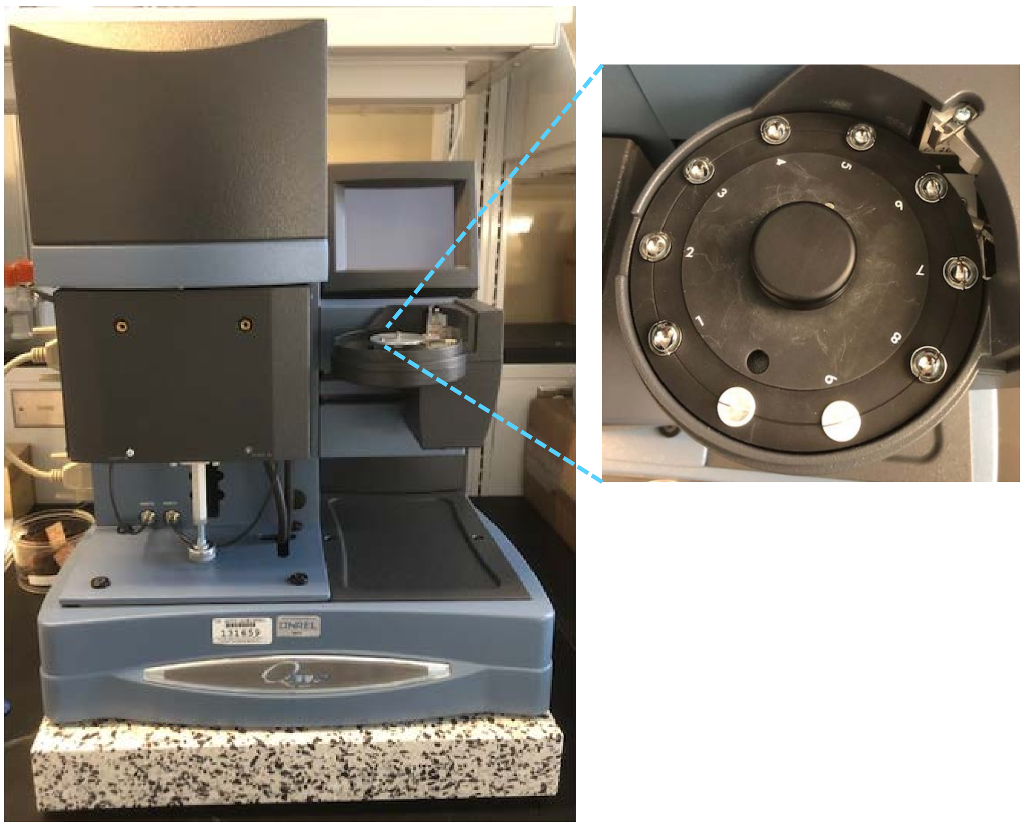


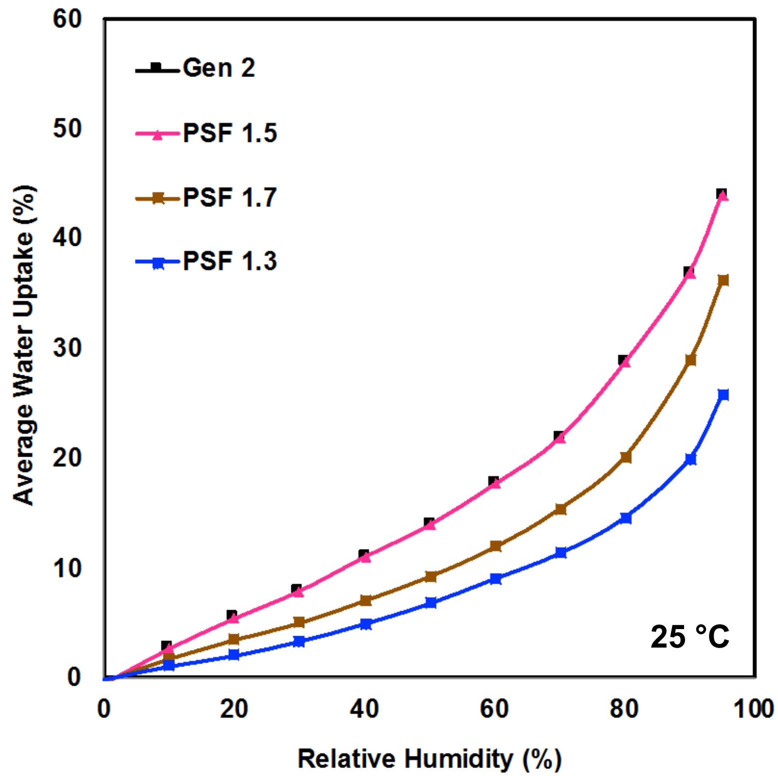






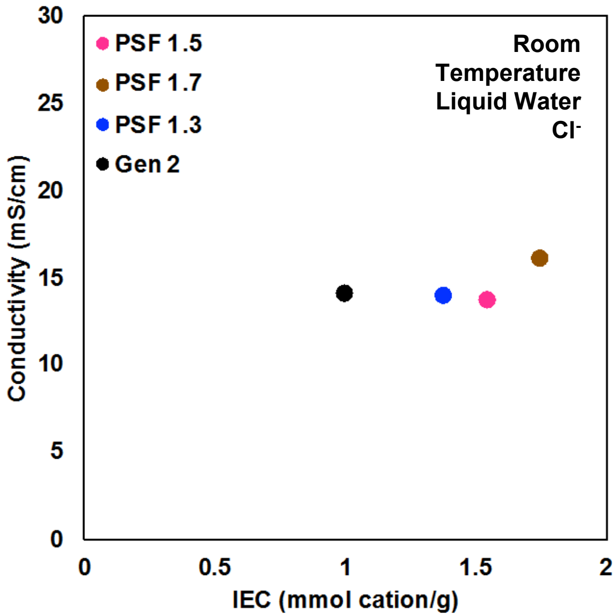
Characterization – water uptake

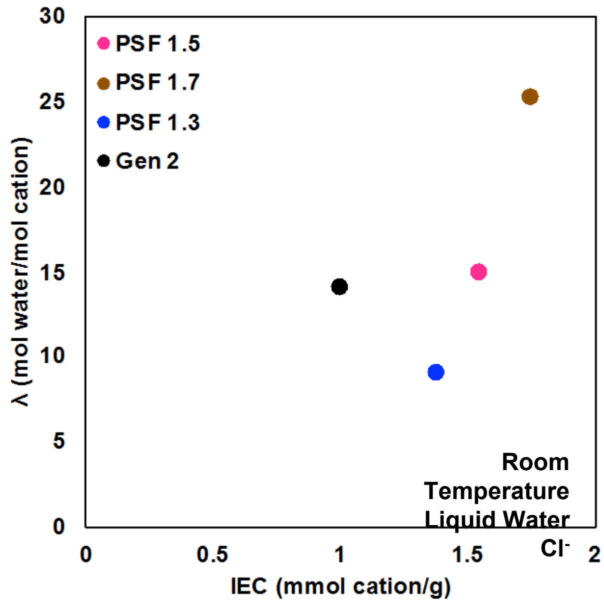


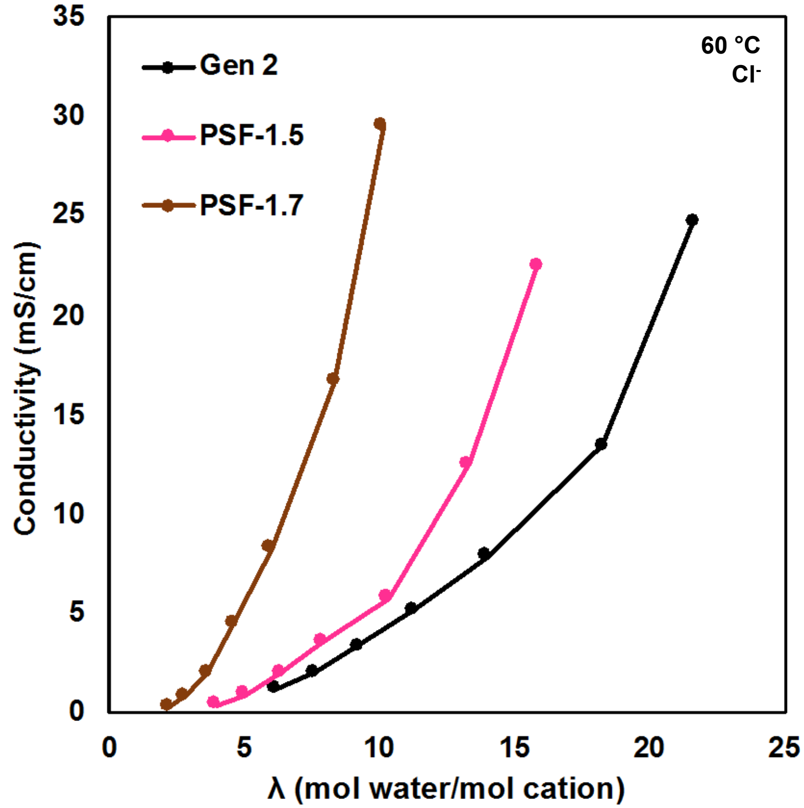


Accomplishments and Progress

Characterization



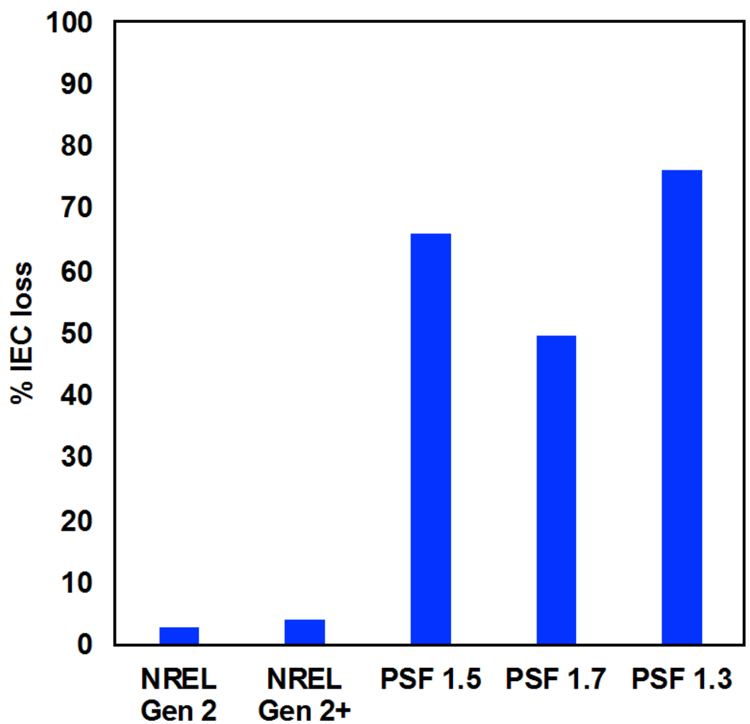


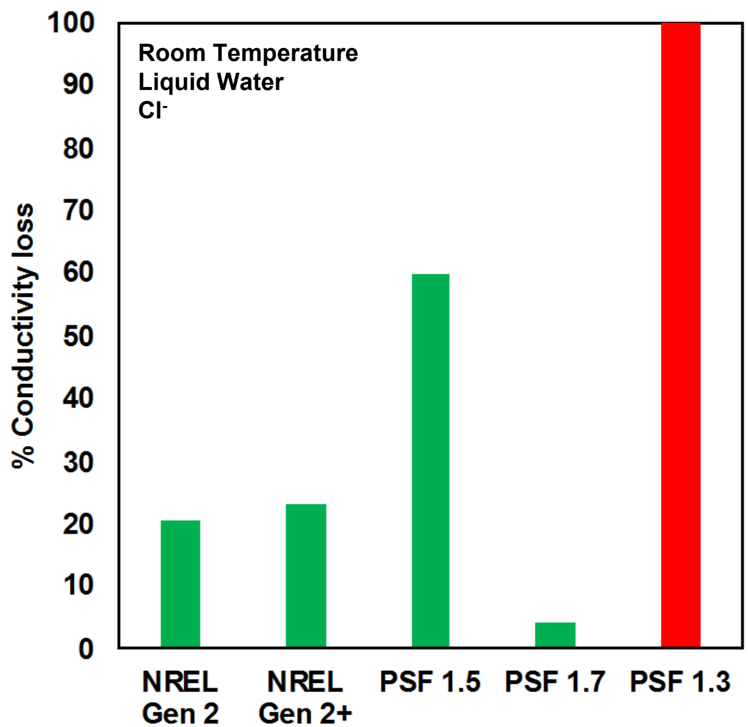


Accomplishments and Progress

Durability

Post 1000 h, 80°C Degradation Testing





- PSF 1.7 shows improved stability relative to PSF 1.5 and PSF 1.3

- PSF-1.3 could not be measured
- Some correlation between IEC and conductivity loss, however morphology changes also seem significant