Advanced AEMs with Tunable Water Transport for PGM-Free AEMFCs

PI - Michael Hickner, Penn State University
co-PIs - William Mustain, University of South Carolina
Bryan Pivovar, NREL
Michael Yandrasits, 3M Corporation

Project ID # FC308

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline and Budget

- ❖ Project Start Date: 10/01/18
  Agreement authorized 12/17/2018
- ❖ Project End Date: 09/30/20
- ❖ Total Project Budget: $1,276,286
  - Total Federal Share: $997,944
  - Total Recipient Share: $278,342
  - Total DOE Funds Spent*: $165,068

* As of 05/01/20

Barriers

A. Durability – focused on demonstrating moderate durability of AEMFCs based on understanding of water transport
B. Cost – enabling AEMFCs will lower the cost of the catalysts and the membranes
C. Performance – understanding water transport is key to high performance AEMFCs

Funded Partners

- ❖ Penn State University
- ❖ University of South Carolina
- ❖ National Renewable Energy Laboratory
- ❖ 3M Corporation

Relevance

<u>Objectives</u>: Over the course of this 24-month program, our team will:

❖ Develop novel poly(olefin) AEM chemistries with tunable water transport. In order to facilitate high AEMFC performance, they will have the following properties:

- OH^- conductivities greater than 60 mS/cm at 60 °C, 100 % RH
- Less than 10% degradation in conductivity after 5000 hours in 1 M NaOH at 60 °C and 2000 hours in 1 M NaOH at 80 °C
- Water diffusion coefficient > $5*10^{-6}$ cm^2/s (50% improvement over existing AEMs)

❖ Incorporate these novel ionomers into mechanical supports and integrate the resulting membranes into AEMFCs. During operation inside the AEMFC, the membranes will have:

- ASR values less than 100 $mOhm \cdot cm^2$ over 2000 hour operation
- Water flux greater than $2*10^{-5}$ mol $H_2O/cm^2 \cdot s$ – in order to be able to back-diffuse 80% of produced + electro-osmotic water from anode to cathode @ 600 mA/cm^2

❖ Demonstration of all of the following DOE metrics in a single MEA with H_2/O_2 fuel:

- Greater than 2000 hours of AEMFC operation at 600 mA/cm^2
- Operating voltage greater than 0.6 V with less than 10% decay over 2000 hours
- Operating $T \geq 60$ °C and $P \leq 1.5 atm_a$ with PGM loading less than 0.125 mg_{PGM}/cm^2

Approach

Focus on improved water management in AEMFCs

- ❖Synthesize new polyolefin-based membranes with high water diffusion coefficients (2x of current AEMs, >5*10^{-6} cm^2/s by PFG-NMR) and thicknesses of ~ 20 microns using support structures.
- ❖Optimize electrode formulation to pair with new membranes using current state-of-the-art knowledge on AEMFC electrodes.
- ❖Control cell conditions and measure water balance to develop a full understanding of how water transport influences cell performance and durability.
- ❖Use neutron radiography and cell water balance measurements to develop water transport-durability correlations.

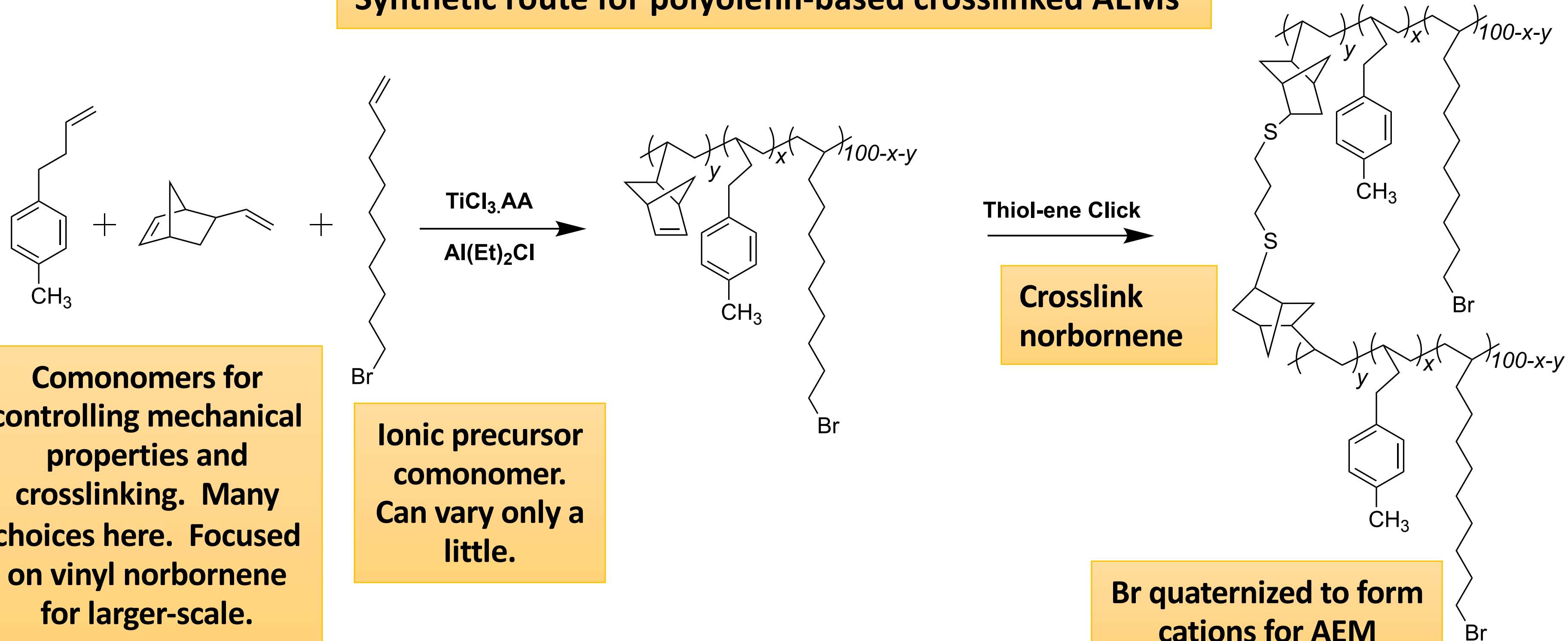
Major Milestones and Go/No-Go

Month/Quarter		
M6/Q2	Performance Milestone	AEMFC steady-state operation at 600 mA/cm^2. Cell Voltage > 0.6 V. H_2/O_2 reacting gases; Cell T ≥ 60°C; Pressure ≤ 1.5 atm$_a$
M12/Q4	Go/No-Go	500h AEMFC operation at 600 mA/cm^2. Cell Voltage > 0.6 V. Anode/Cathode feed gas: H_2/O_2; Cell T ≥ 60°C; Anode/Cathode pressure ≤ 1.5 atm$_a$
M18/Q6	Performance Milestone	500 h AEMFC operation at 600 mA/cm^2. Cell Voltage > 0.6V. Anode/Cathode feed gas: H_2/O_2; Cell T ≥ 60°C; Anode/Cathode pressure ≤ 1.5 atm$_a$. Total MEA PGM loading ≤ 0.125 mg/cm^2. 5 cm^2 active area
M21/Q7	Progress Measure	500h AEMFC operation at 600 mA/cm^2. Cell Voltage >6V. H_2/Air(CO_2-free); Cell T ≥ 60°C; Anode/Cathode Pressure ≤ 1.5 atm$_a$
M24/Q8	Performance Milestone	AEMFC steady-state operation at 600 mA/cm^2 with cell voltage > 0.6 V. H_2/Air (400 ppm CO_2) feed gases; Cell T ≥ 60°C; Anode/Cathode pressure ≤ 1.5 atm$_a$
M24/Q8	End-of-Project Goal	2000 h AEMFC continuous operation at 600 mA/cm^2. Cell Voltage > 0.6 V, less than 10% voltage fade. Anode/Cathode feed gases: H_2/O_2; Cell T ≥ 60°C; Anode/Cathode pressure ≤ 1.5 atm$_a$; Total MEA PGM loading ≤ 0.125 mg/cm^2; 50 cm^2 active area.

Current status: Have demonstrated M12 performance metrics with PSU membranes. Currently working on M18 electrode loading requirements. Continuing to measure membrane water diffusion coefficients and optimizing supported membranes. Projected to meet M24 End-of-Project Goals.

Accomplishments and Progress: Polymer Synthesis

Synthetic route for polyolefin-based crosslinked AEMs



Comonomers for controlling mechanical properties and crosslinking. Many choices here. Focused on vinyl norbornene for larger-scale.

Ionic precursor comonomer. Can vary only a little.

Crosslink norbornene

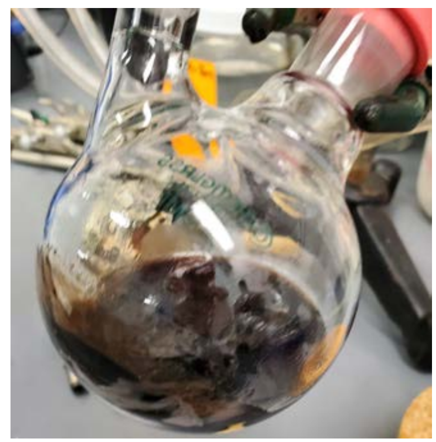
Br quaternized to form cations for AEM

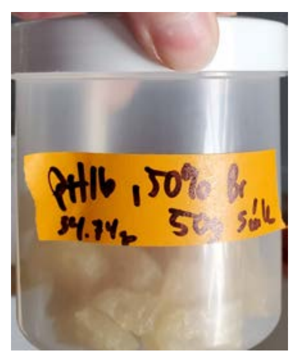
M15/Q5	Milestone	≥ 1 polymer electrolyte synthesized at 100 g scale to create supported membranes with: > 60 mS/cm at 60 °C; water diffusion coefficient > $5*10^{-6}$ cm^2/s
M21/Q7	Milestone	Downselect two supported membranes with in-cell ASR < 100 $mOhm\text{-}cm^2$ and OH^- conductivity and in-cell water flux > $2*10^{-5}$ mol H_2O/cm^2-s

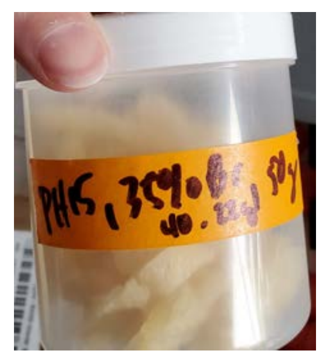
Accomplishments and Progress: Suite of Membrane Samples and Polymerization at 100 g Scale

Sample name	Feed % of 11-bromoundecene	% of 11-bromoundecene by NMR	^{1}H NMR IEC (meq/g)	Thickness (µm)
Ph3A	25	32	2.01	218
Ph5A	25	36	2.22	222
Ph5B	25	36	2.22	233
Ph5C	25	36	2.22	219
Ph6A	30	31	1.96	160
Ph6B	30	31	1.96	192
Ph6C	30	31	1.96	180
PH5E2	25	36	2.22	37
PH5E1	25	36	2.22	39
Ph5F1	25	36	2.22	84
Ph5F2	25	36	2.22	94
Ph5F3	25	36	2.22	61
FPH2A	25	32	1.89	59
FPH2B	25	32	1.89	68
PH5G	25	36	2.22	82
PH5H	25	36	2.22	71
PH5I	25	36	2.22	131
PH5O	25	36	2.22	97
PH5P	25	36	2.22	137
PH5Q	25	36	2.22	152
PH6M	30	31	1.96	120
PH6N	30	31	1.96	92
PH6O	30	31	1.96	135
FPH2K	25	32	1.89	77
FPH2L	25	32	1.89	69
FPH2M	25	32	1.89	47

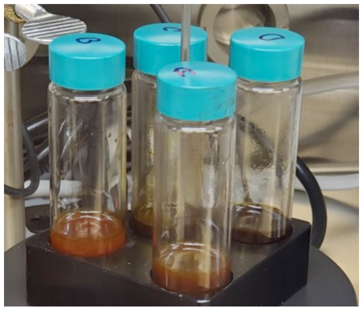
Experiment	Yield (%)
Penn State 50 g trial – 35% Br monomer feed	80
Penn State 50 g trial – 50% Br monomer feed	69
3M 100 g trial – 15 % Br monomer feed	75





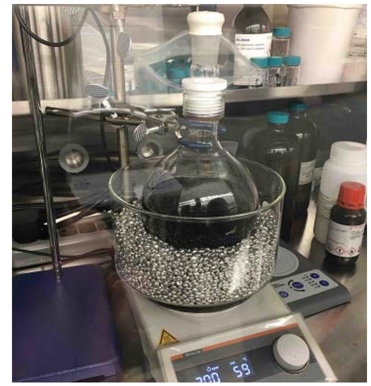


Accomplishments and Progress: Polymerization at 100 g Scale

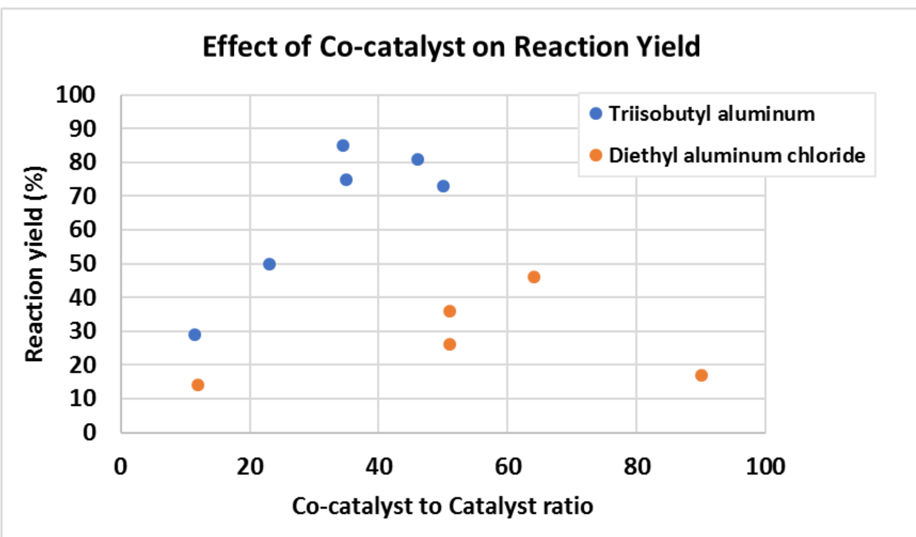


2g scale reactions
14%→ 75% Yield

10g scale polymers
58% → 85% Yield



100g scale reaction
(October 2019) - 75% Yield

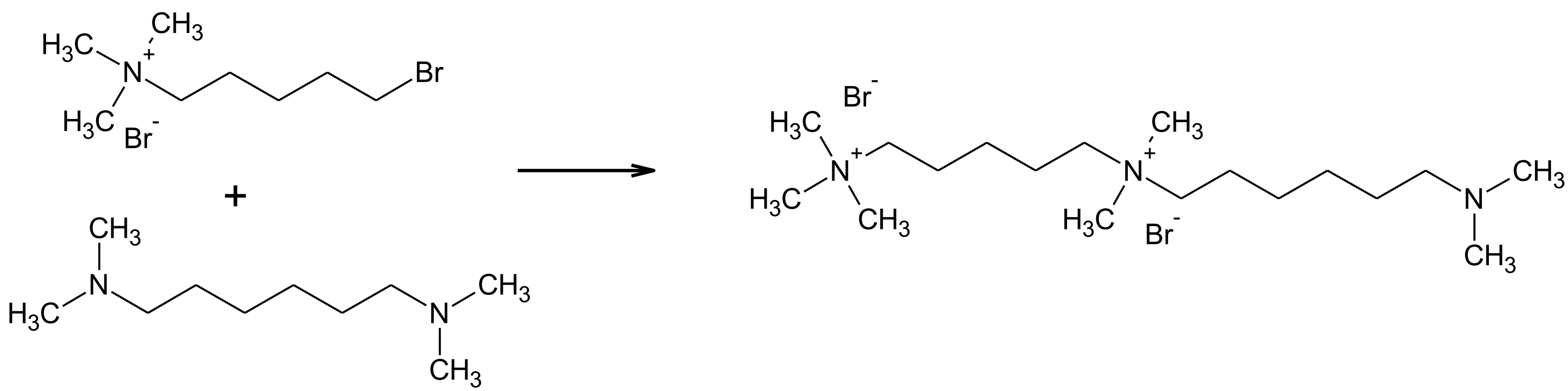


100 g reaction (3M-H15C9):

- Copolymer ratio 85:15 (PB:BrUD)*
- Serves as basis for solution quaternization and coating. solution/dispersion development.
- Cocatalyst optimization shows >80% yield possible.
- Additional reactions planned.

*PB = Phenyl Butene, Br = Bromoundecene

Accomplishments and Progress: Optimization of Multi-cation Synthesis



Trial	Reaction Solvent	Hexanediamine Equivalents	% Yield*
1	CHCl3	35.5	52
2	CHCl3	8.8	76
3	ACN	1	na
4	ACN	3	60
5	ACN	5	47
6	ACN	1	39

Accomplishments and Progress: Ionomer Solutions and Cast Membranes

3M-H15C9 (pre-quaternized) in toluene (top phase) and water (bottom phase).

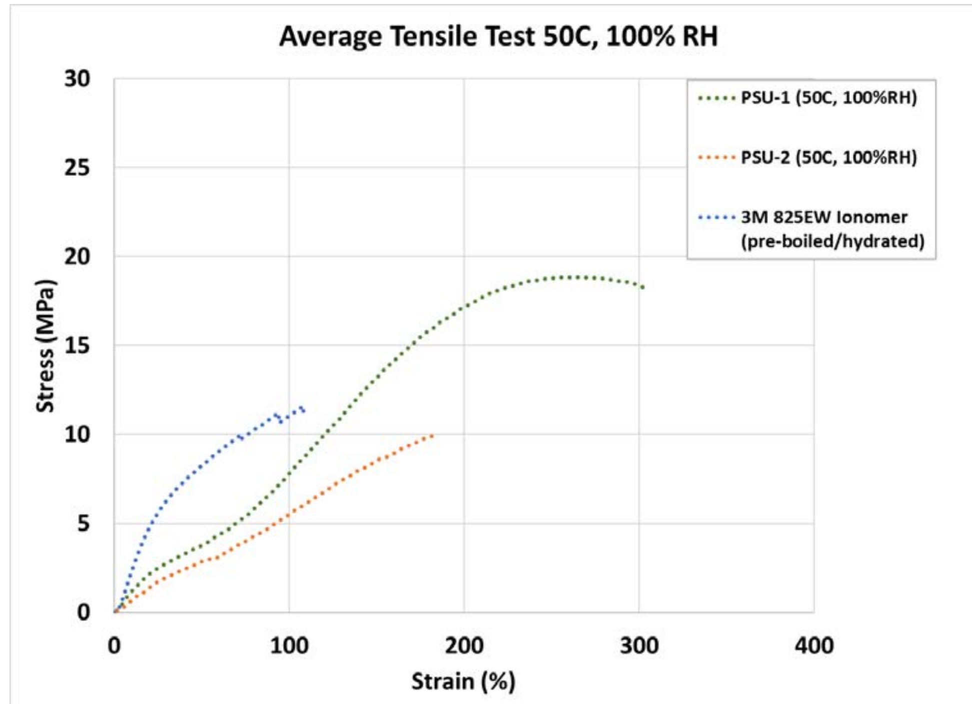
3M-H15C9 (quaternized) with trimethyl amine shows potential for dispersion.

- 3M Lab scale membrane (4”x4” – no support)
- Solution quaternized and cast from THF:Methanol

<u>Next Steps for improving solubility/dispersibility:</u>

- Increase bromoundecene ratio (increase IEC)
- Functionalize 3M-H15C9 with multi-cation side chain
- Identify stable post-quaternization solution/dispersion composition
- Cast ePTFE supported membranes in quaternary amine form

Accomplishments and Progress: Membrane Characterization



Key Observation:

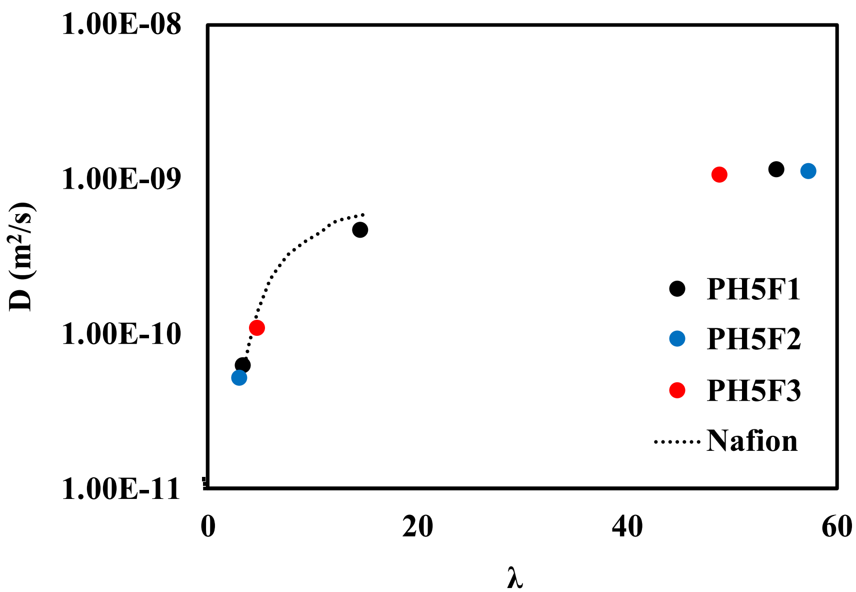
- PSU membranes have comparable tensile properties to 3M 825EW Ionomer

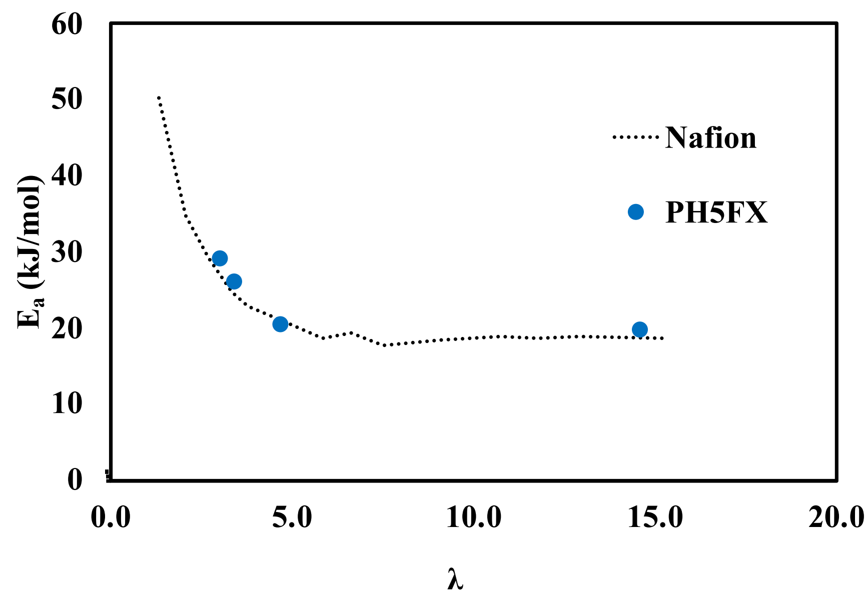
Next Steps

- Test 3M made membranes (unsupported and supported)

Accomplishments and Progress: Membrane Characterization

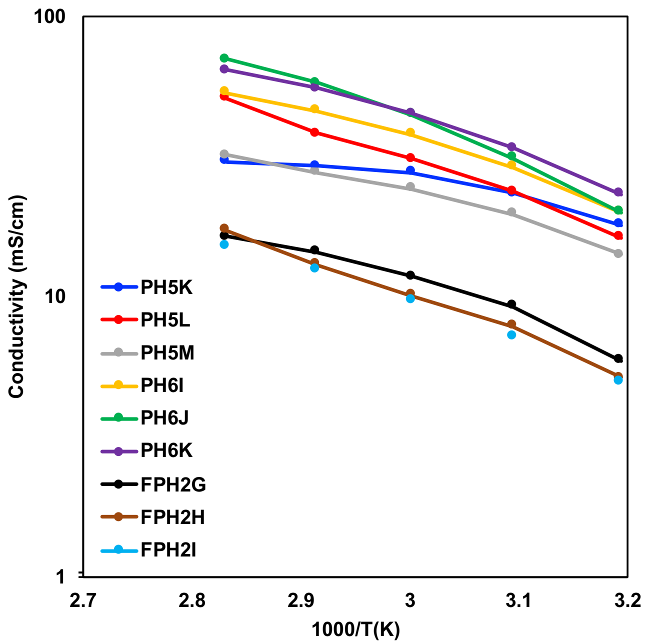
^{1}H PFG-NMR shows that water diffusion in polyolefin membranes is similar to that of PFSAs over a range of water contents.

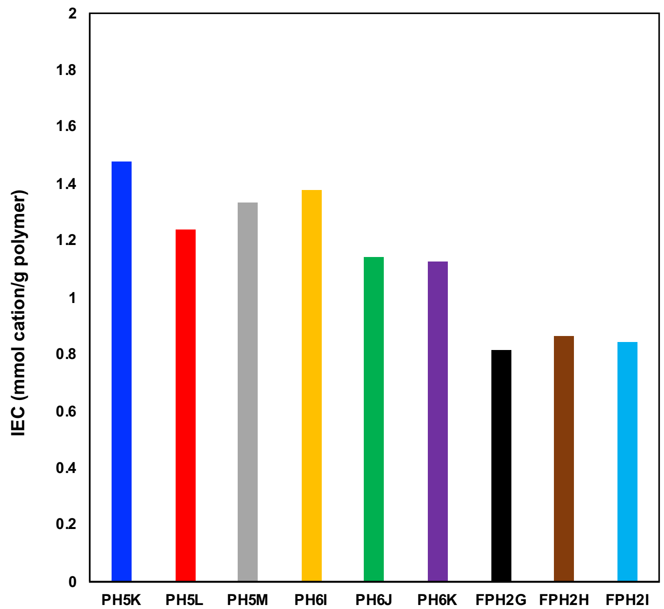


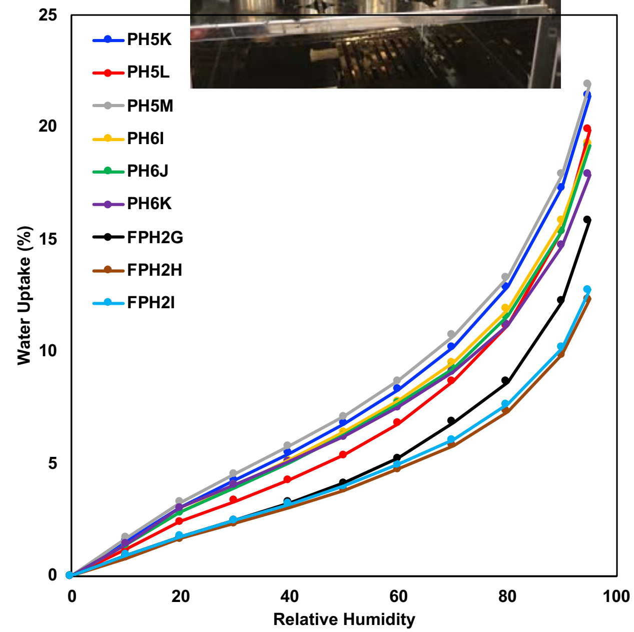


In collaboration with Lou Madsen, VT

Accomplishments and Progress: Membrane Characterization



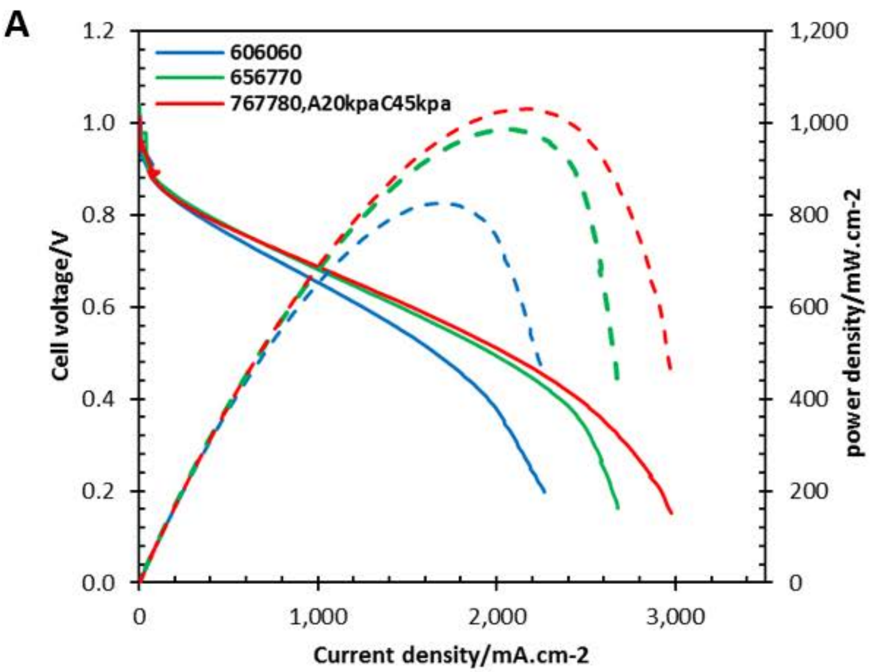




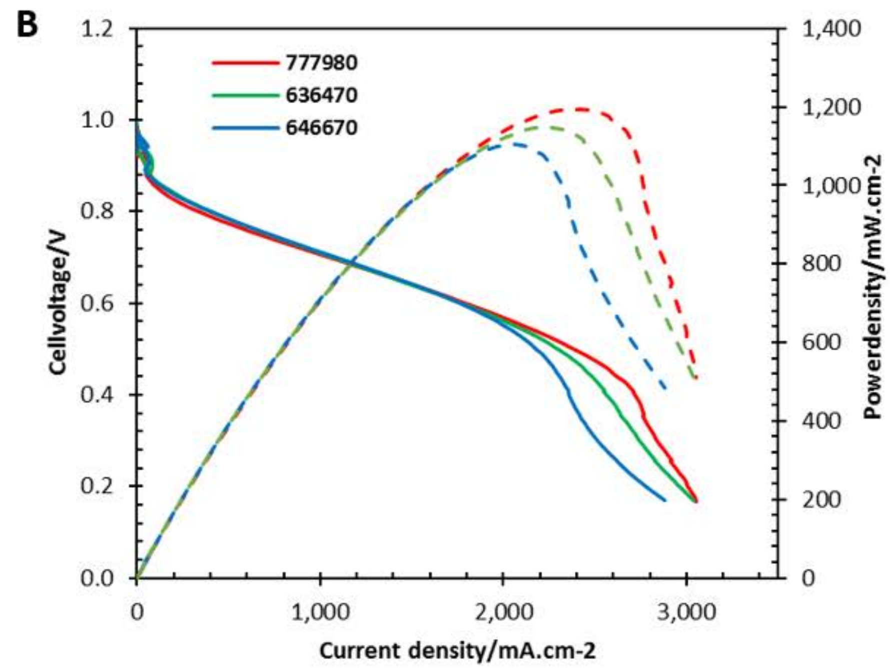
- High Cl^- conductivities reaching 70 mS cm^{-1} at 95% RH, 80 °C
- Similar overall results for PH5 and PH6 series
- Lower IEC for FPH2 series results in lower water uptake and conductivity

Accomplishments and Progress: Cell Performance

Quarter 4 (without PTFE content)

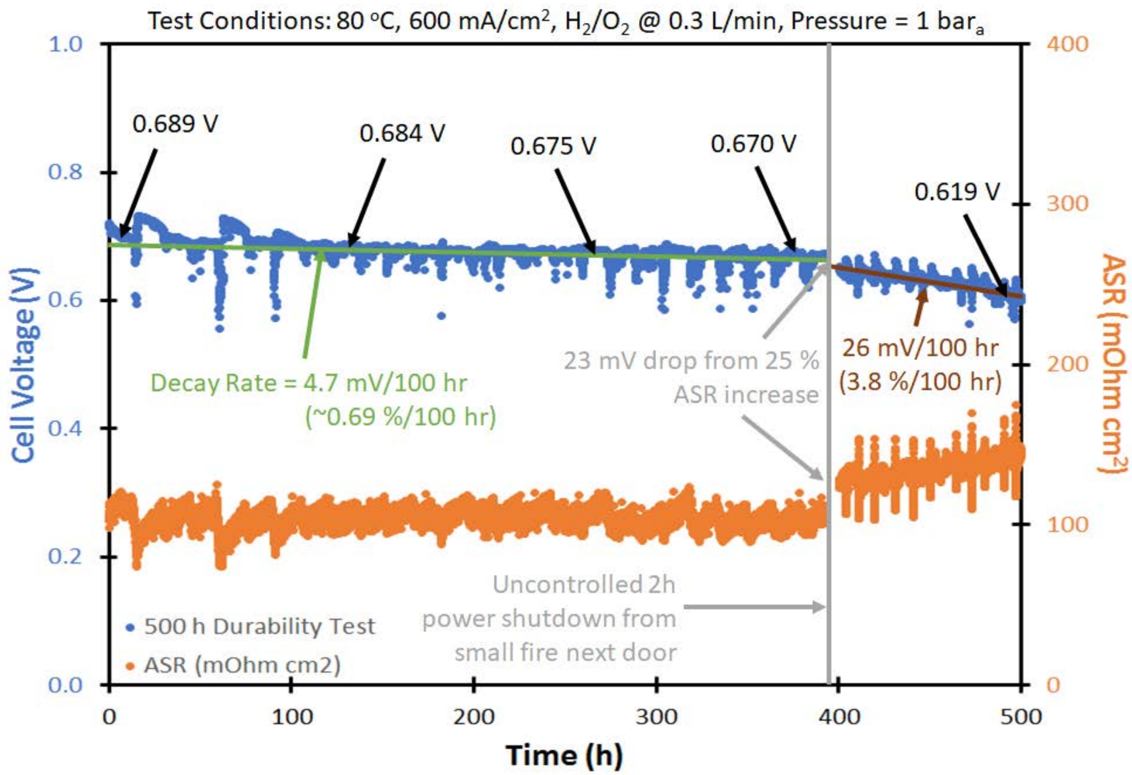


Quarter 5 (8% PTFE in anode with a constant ionomer/carbon ratio of 0.4)



Both cells were operated with H_2/O_2 reacting gases. The anode and cathode catalyst loadings were 0.7 $mgPtRu/cm^2$ and 0.5 $mgPt/cm^2$, respectively. (The numbers on top of figures indicates anode, cathode and cell temperature, backpressures).

Accomplishments and Progress: Cell Durability

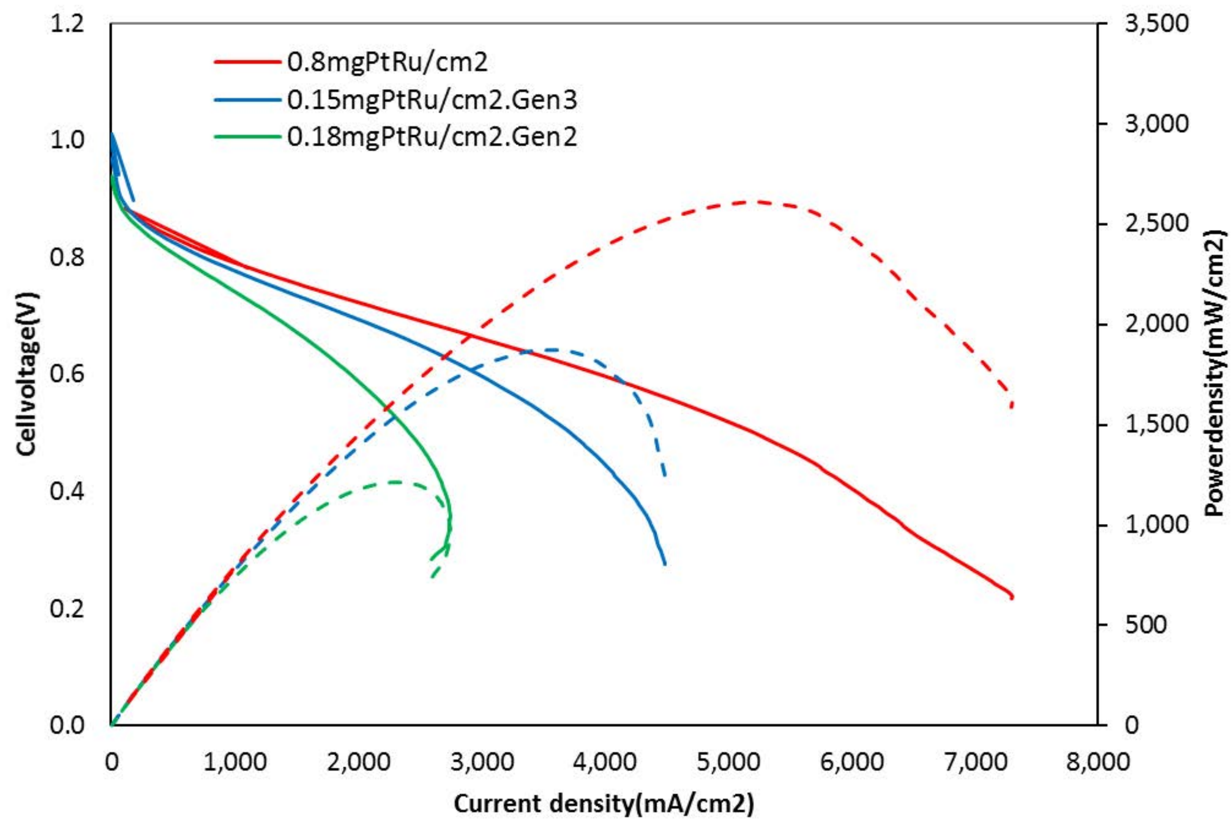


- Generation 3 electrodes
- Cell temperature: 80 ℃
- Anode
  - Loading : 0.66 $mg_{PtRu}cm^{-2}$
  - Dew Point: 75-77 °C
- Cathode
  - Loading: 0.61 $mg_{Pt}cm^{-2}$
  - Dew Point: 78-79 °C
- A/C Flowrate: 0.3/0.3 L min^{-1}
- A/C Back Pressurization: 0/0 kPa

Current status: Working on meeting M18 goals for electrode loading and M24 Year 2 2000 h lifetime. Cell testing ramping up with 100 g polymer synthesis.

M18/Q6	**Performance Milestone**	**500 h AEMFC operation at 600 mA/cm^2. Cell Voltage > 0.6V. Anode/Cathode feed gas: H_2/O_2; Cell T ≥ 60°C; Anode/Cathode pressure ≤ 1.5 atm$_a$. Total MEA PGM loading ≤ 0.125 mg/cm^2. 5 cm^2 active area**

Accomplishments and Progress: Low Loadings



- Anode/Cathode/Cell: 72/74/80 ℃
  - Anode/Cathode flow rates: 1 L min^{-1}
  - Anode/Cathode Back Pressurization: 0 kPa

- Reducing the catalyst loading increases sensitivity to water
- Need to optimize current density and dew points for low loadings
- Using Gen.3 electrodes (added PTFE) helps to mitigate flooding

- Upcoming work:
  - Adding a microporous layer to the anode
  - Pairing with PGM-free cathodes

Responses to Previous Year Reviewers' Comments

- The overall weakness is that the project is based on the idea that water transport is the single most important factor for AEMFC performance and durability. It may be true, but in case this is not the decisive factor, then the whole project may go in the wrong direction. The membrane milestone is not challenging (40 mS/cm at 60°C). Those targets with quaternized polyolefinic polymers have been achieved by a couple of projects. USC has demonstrated over 2 W/cm^2 peak power density with its polyolefinic membrane and ionomers. It is unknown how much better performance can be achieved with highly water-permeable, "more advanced" polyolefinic membranes. It is understood that this is not an AEMFC project but an AEM project. However, if the project does not achieve better performance, better durability (>2,000 hours in fuel cell operating conditions), or low PGM loading (<0.125 $mgPGM/cm^2$), the advantage of using the proposed AEMs for AEMFCs may be too small. A clear pathway for achieving those challenging targets is not apparent.
  - **This project was designed around the parameters of the DOE RFP in 2018 that specifically called for investigation into water transport in AEMs. In that spirit, we are advancing knowledge around this issue and filling an important gap in the field. A number of groups will continue to push on cell metrics and we will play our role in elucidating water transport phenomena as well as refining our membranes and electrodes.**
- The project team needs to quantify "larger-scale" batches. The current loading (as seen on slide 8) is way too high and needs to be lowered soon. It seems like the cell has some transport issues, even in oxygen. A systematic study of those limitations and how they can be overcome with advanced membranes should be added.
  - **We have not made multiple 100 g polymer batches.**
  - **Low loadings are being approached in Year 2 as reported in the slides.**

Responses to Previous Year Reviewers' Comments

The linkage between polymer structure and the desired AEM property improvements has not emerged from results to date. This may reflect the fact that the project is still in a synthesis-heavy phase, with the first round of feedback from measurements not yet completed.

- **We appreciate this comment and we are continuing to work in this area. Our end of project conclusions have not been reached, yet, but we will take the reviewer's advice on this.**

PGM-free catalysts are highly speculative, and an especially speculative idea is that there are ones that are durable.

- **Novel catalysts have been de-emphasized in this project and we have tended to stick with established catalysts to demonstrate low loadings.**

A recommended addition would be to the go/no-go decision point: an interim total PGM-loading target is needed. Regarding deletions, the target for the later stage of the project is overly challenging. Either the 500-hour H_2/air (CO_2-free) or 2000-hour H_2/O_2 target can be deleted and modified to some progress measure, e.g., 100-hour H_2/air (CO_2-free) for Q7 and 500-hour H_2/air (CO_2-free) for Q8.

- **We will weigh our progress against this suggestion in Year 2.**

The project team should forget about catalysts and do what they do best and check whether they can make durable membranes that operate under fuel cell operating conditions with low-PGM catalysts.

- **We agree. We are pursuing this strategy in Year 2.**

The project is off to a good start. Seeing the progress in the coming years is gladly anticipated.

- **Thanks!**

Collaboration & Coordination

- Project collaborators:
  - Prime – Penn State University
  - Sub Recipients
    - University of South Carolina
    - National Renewable Energy Laboratory
    - 3M Corporation
- University of South Carolina is responsible for electrode formulation, cell testing, and water transport studies – including neutron radiography.
- National Renewable Energy Laboratory is responsible for lifetime testing and water balance studies.
- 3M Corporation is responsible for membrane coating and supported membranes.
- Coordination is performed through regular meetings and teleconferences. All project partners have worked together previously and have joint publications.

PennState UNIVERSITY OF SOUTH CAROLINA NREL NATIONAL RENEWABLE ENERGY LABORATORY 3M Science. Applied to Life.™

Remaining Challenges and Barriers

- ❖Larger-scale samples will enable more lifetime testing and neutron radiography studies of water transport.
- ❖Lifetime still needs to be proven out at lower loadings to meet Year 2 Goal.
- ❖Electrode formulation, membrane thickness, and water transport studies will enable a wholistic understanding of how water transport in the cell influences performance and durability.

Proposed Future Work

❖ Through rest of project in FY20
- Synthesize larger-scale batches of polymer with vinyl norbornene motif and fabricate supported membranes.
- Continue to optimized electrode structures and cell conditions to meet milestones and Year 2 End-of-Project goal on performance and durability at required loadings.
- Measure water transport in membranes using PFG-NMR and connect to cell water transport observations using water balance measurements.

❖ Project ends at the end of FY20
- Risk will be mitigated by taking advantage of state-of-the-art catalyst for alkaline membranes that are reported.
- Major risks will be to approach required catalyst loadings while still reaching durability targets.

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

Technology Transfer Activities

- 3M and Penn State have filed joint IP under past programs. Considering joint IP on new material composition for this work.

Summary Slide

- Key early data indicates success in achieving performance and lifetime metrics. Still catalyst layer work and cell conditions to optimize for meeting loading and durability targets.
- We have demonstrated 500 hour lifetime at 600 mA/cm^2 with polyolefin membranes to meet Year 1 Go/No-Go metric. Working to solidify the lifetime testing on current membranes with lower catalyst loadings to meet Year 2 End-of-Project goal.
- Larger scale synthesis has been accomplished and will enable more membrane coating studies and lifetime testing.
- Work underway to meet Year 2 End-of-Project Goal.

M24/Q8	End-of-Project	2000 h operation at 600 mA/cm^2. V > 0.6 V, less than 10% voltage fade; H2/O2; T ≥ 60 ºC; P ≤ 1.5 atm$_a$; Total MEA PGM loading ≤ 0.125 mg/cm^2