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: $1,278,452
  - Total Federal Share: $1,000,000
  - Total Recipient Share: $278,452
  - Total DOE Funds Spent*: $165,068

* As of 3/01/19

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 ≥ 60 °C and P ≤ $1.5atm_a$ 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.

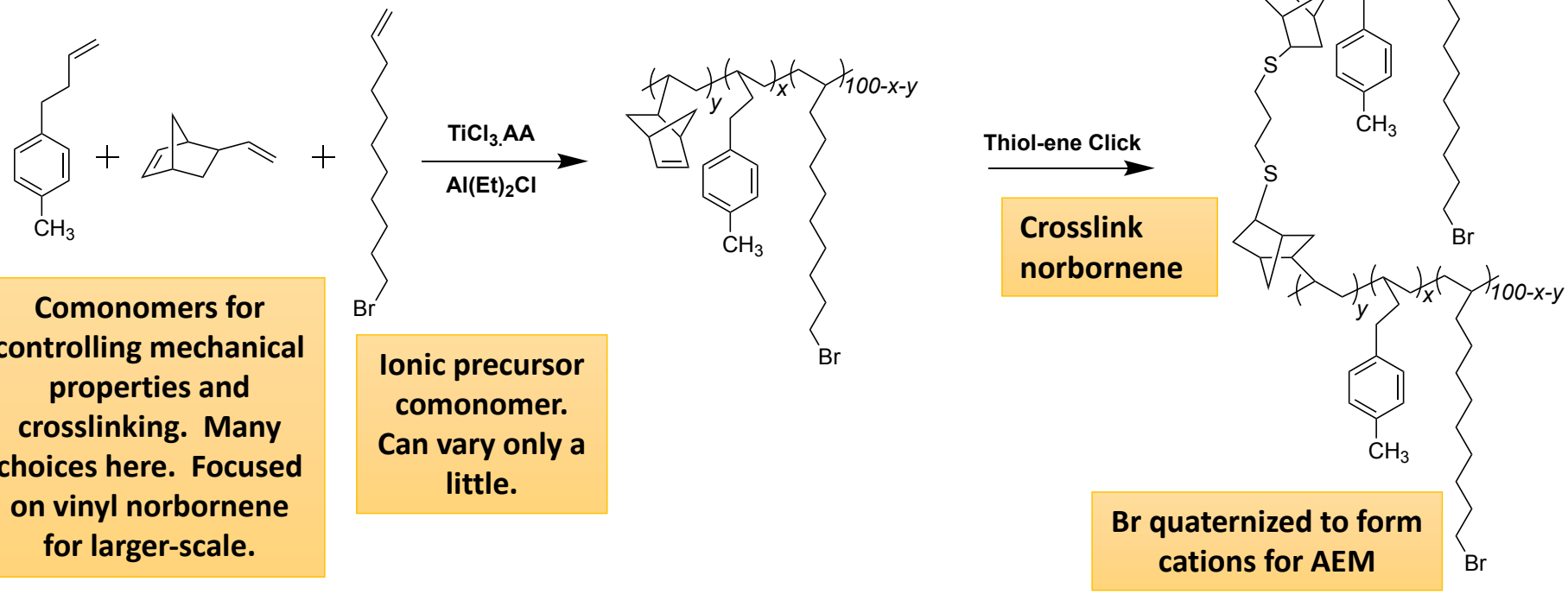
Major Milestones and Go/No-Go

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: Can achieve M6 performance metrics with first-generation membranes. Currently working on measuring membrane water diffusion coefficients and optimizing supported membranes. Will begin lifetime testing in M7.

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

M3/Q1	Membrane Milestone	≥ 2 AEM compositions with conductivity greater than 40 mS/cm at 60 °C in liquid water and water diffusion coefficient greater than $2*10^{-6}$ cm^2/s fabricated and delivered for cell testing
M3/Q1	Progress Measure	≥ 2 ionomer dispersions/powder samples sent to USC/NREL for cell testing

Accomplishments and Progress: Polymerization Batches

Control AEM – 3 batches	M.W.	eq	mass (g)
11-bromo-1-undecene	233.19	1	1.063
4-phenyl-1-butene	132.20	2	3.52
TiCl3·AA 75%	198.72		0.05
		1 mL/mg	
$AlEt_2Cl$ pure	120.56	TiCl3	
Toluene (anhydrous)			50 mL

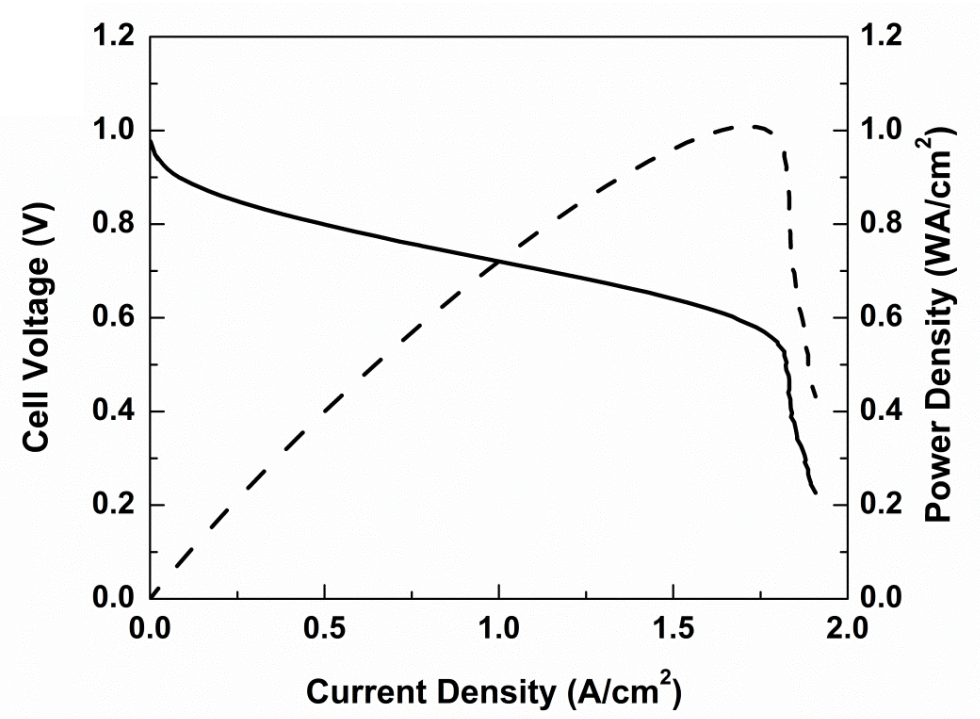
Novel AEM – Low IEC – 2 batches	M.W.	eq	mass (g)
11-bromo-1-undecene	233.19	1	2
5-vinyl-1-norbornene	120.19	5	5.2
TiCl3·AA	198.72		0.05
		1 mL/mg	
$AlEt_2Cl$ 1.0 M in hexanes	120.56	TiCl3	
Toluene (anhydrous)			50 mL

Novel AEM – High IEC – 3 batches	M.W.	eq	mass (g)
11-bromo-1-undecene	233.19	1	2
5-vinyl-1-norbornene	120.19	5	5.2
TiCl3·AA	198.72		0.05
		1 mL/mg	
$AlEt_2Cl$ 1.0 M in hexanes	120.56	TiCl3	
Toluene (anhydrous)			50 mL

- Over 80 polymerization batches conducted.
- 8 successful, on target batches shown at left.
- Yields approaching 60 %
- IECs between 1.5 and 12.5 meq/g targeted.
- Membrane IEC, conductivity, water transport, and stability currently being measured.
- 4 g batch of polymer shown below. Increasing scale currently.

Current status: Working on supported membranes with larger polymer batches. More samples being sent to project partners.

Accomplishments and Progress: Cell Testing Demonstrations



- Powdered ionomer in electrodes
- Cathoode: 0.50 mg_{Pt}/cm^2 Alfa Aesar HiSPEC 4000, Pt nominally 40%wt., supported on Vulcan XC-72R carbon
- Anode: 0.70 $mg_{Pt\text{-}Ru}/cm^2$ Pt-Ru catalyst (Alfa Aesar HiSPEC 10000, Pt nominally 40%wt., and Ru, nominally 20%wt., supported on Vulcan XC-72R carbon
- 60 °C cell temperature, H_2/O_2 reacting gases at 1.0 L/min.

Current status: Membrane testing for durability in progress to meet next milestone. Electrode work in progress to meet project goals.

Responses to Previous Year Reviewers' Comments

- New project commenced in late 2018.
- Project not reviewed last year.

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

- Need larger-scale polymer synthesis for coating and supported membranes. Working with vinyl norbornene and single cations to keep synthesis simple.

- 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 1 Go/No-Go.

- 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

❖ Rest of this year - FY19

- 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 1 Go/No-Go 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.

❖ Next year - FY20

- Fabrication of high-performance supported membranes and optimization of electrode structures and cell conditions will allow for progress on Year 2 milestones.
- Develop strategies for increasing durability through modifying cell water transport.
- Develop wholistic picture of water transport in AEMFCs using neutron radiography.

- 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 metrics. Still catalyst layer work and cell conditions to optimize for meeting loading and durability targets.
- We have demonstrated 100s of hours of lifetime at 600 mA/cm^2 with previous polyolefin membranes in a collaboration between Penn State and U. South Carolina. Working to solidify the lifetime testing on current membranes with lower catalyst loadings.
- Larger scale synthesis is underway and will enable more membrane coating studies and lifetime testing.
- Work underway to meet Year 1 Go/No-Go.

M12/Q4	Go/No-Go	500h 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$_a$