Advanced AEMs with Tunable Water Transport for PGM-Free AEMFCs

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Project ID # FC308

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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.

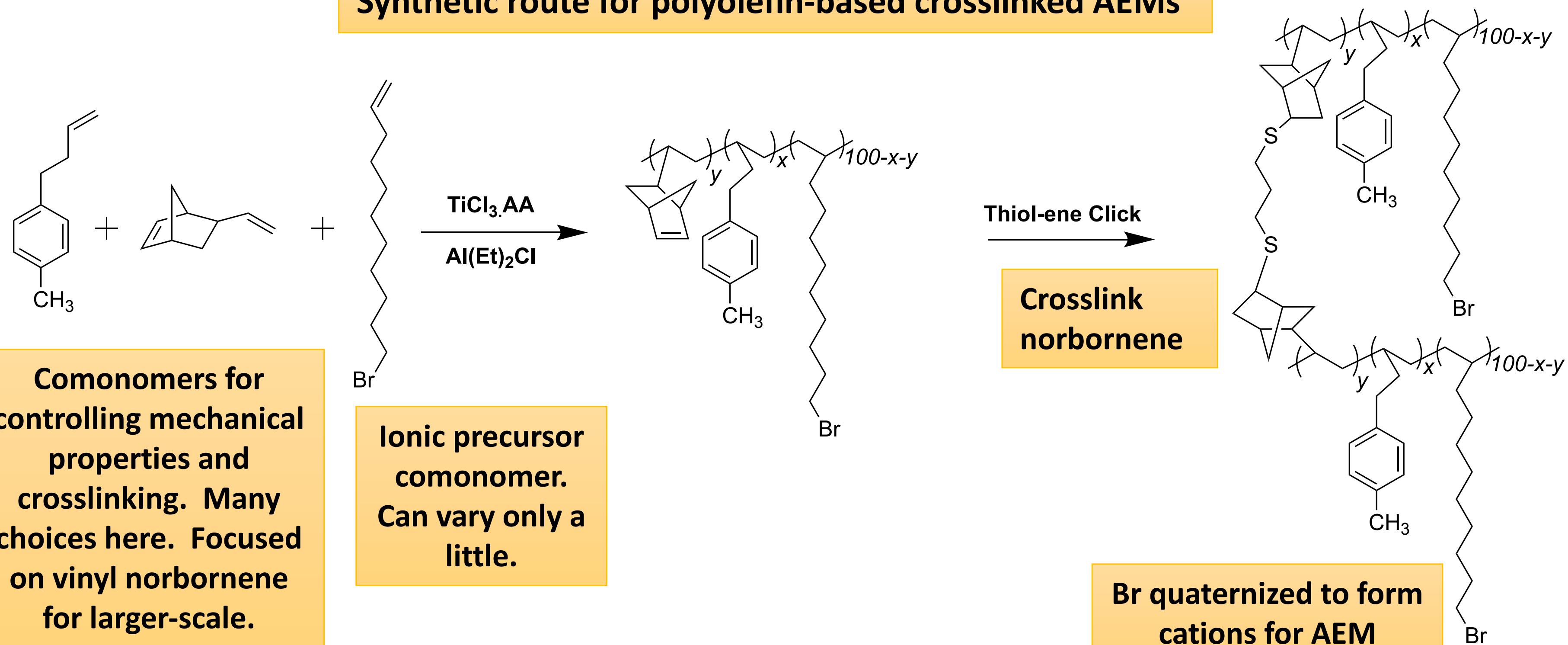
Major Milestones and Go/No-Go

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

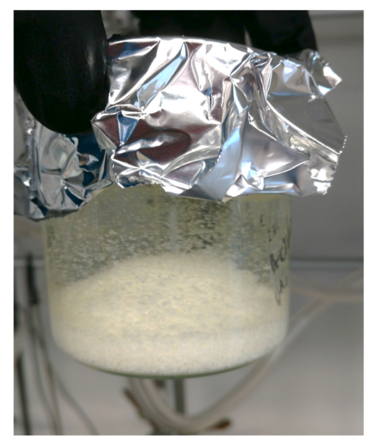
Control AEM – 3 batches	M.W.	eq	mass (g)
11-bromo-1-undecene	233.19	1	1.063
4-phenyl-1-butene	132.20	2	3.52
TiCl3·AA 75%	198.72		0.05
$AlEt_2Cl$ pure	120.56	1 mL/mg TiCl3	
Toluene (anhydrous)			50 mL

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
$AlEt_2Cl$ 1.0 M in hexanes	120.56	1 mL/mg TiCl3	
Toluene (anhydrous)			50 mL

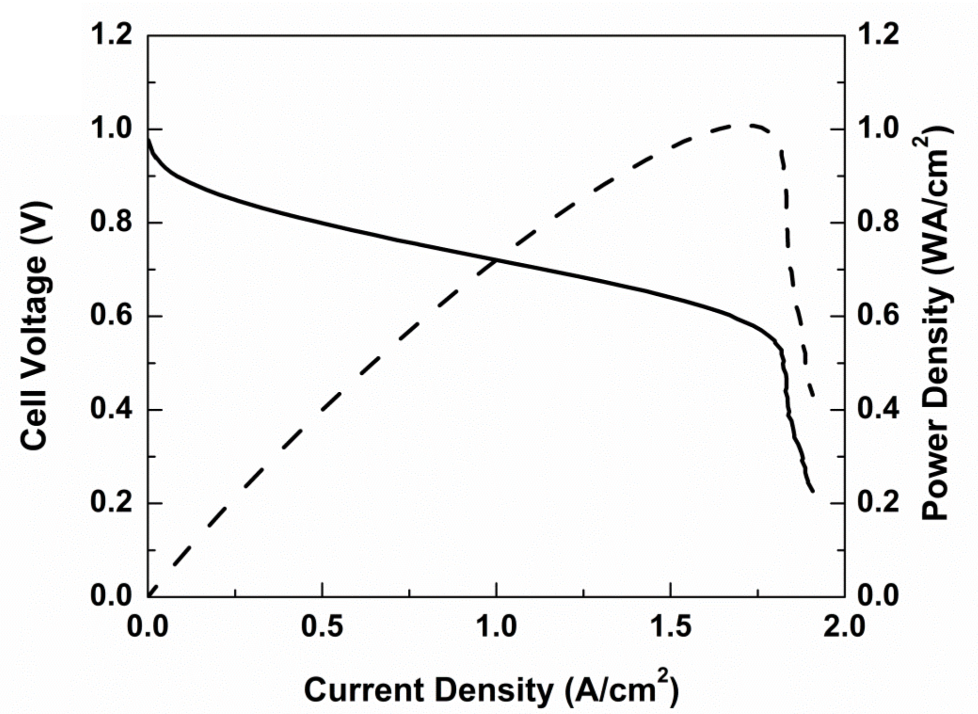
Novel AEM – High IEC – 3 batches	M.W.	eq	mass (g)
11-bromo-1-undecene	233.19	1	2
5-vinyl-1-norbornene	120.19	5	5.2
TiCl3·AA	198.72		0.05
$AlEt_2Cl$ 1.0 M in hexanes	120.56	1 mL/mg TiCl3	
Toluene (anhydrous)			50 mL

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

- ❖ 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.



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.

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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^{o}C; Anode/Cathode pressure ≤ 1.5 atm_a