

# Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells

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Project ID #FC147

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## Overview

## **Timeline and Budget**

- Project start: October 2015
- Project end: March 2019
- % complete: ~ 70%
- DOE Budget plan
  - FY 2016 2018 \$ 2,600k
  - Cost Share Percentage 0%

## **Barriers**

- Durability
- Cost
- Performance

## Partners

- LBNL Adam Weber
- ORNL/UTK Tom Zawodzinski
- Colorado School of Mines Andy Herring
- (in-kind) 3M Mike Yandrasits

# Relevance/Impact DOE (Preliminary) Milestones for AMFCs\*

- Q2, 2017: Develop anion-exchange membranes with an area specific resistance ≤ 0.1 ohm cm<sup>2</sup>, maintained for 500 hours during testing at 600 mA/cm<sup>2</sup> at T >60 °C.
- **Q4, 2017:** Demonstrate alkaline membrane fuel cell peak power performance > 600 mW/cm<sup>2</sup> on  $H_2/O_2$  (maximum pressure of 1.5 atma) in MEA with a total loading of  $\leq 0.125 \text{ mg}_{PGM}/\text{cm}^2$ .
- Q2, 2019: Demonstrate alkaline membrane fuel cell initial performance of 0.6 V at 600 mA/cm<sup>2</sup> on H<sub>2</sub>/air (maximum pressure of 1.5 atma) in MEA a total loading of < 0.1 mg<sub>PGM</sub>/cm<sup>2</sup>, and less than 10% voltage degradation over 2,000 hour hold test at 600 mA/cm<sup>2</sup> at T>60 °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<sup>2</sup> 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).

# Approach

Membrane Synthesis, Electrode Optimization, and Fuel Cell Testing

#### **Novel Polymer Synthesis**



Gen 2 Synthesis NREL: provide current material for further testing

## Fuel Cell Optimization

MEA Fabrication/Optimization NREL: composition, processing



# $\begin{array}{c} 10^{\circ} & Gen2.5 (IEC-0.80) CI \\ Gen2.8 (IEC-0.98) CI \\ Gen2.8 (IEC-0.98) CI \\ Gen2.8 (IEC-0.98) CI \\ Gen2.8 (IEC-0.98) CI \\ Gen2.8 (IEC-0.80) CI \\ Gen2.8$

Characterization NREL: conductivity, IEC CSM: structure, carbonate ORNL/UTK: microscopy, NMR



#### Fuel Cell Diagnostics NREL: performance, durability, transport



#### Gen 3 Synthesis NREL: develop improved stability tether



#### AMFC Modeling <sup>0</sup> current Densit LBNL: water, carbonate management, spatial effects





## Approach Project Schedule/Milestones

Name	Description	Criteria	Status
Mid-Project Decision Point (go/ no-go)	Meet FCTO MYPP 2017 Q2 Milestone for AEMFCs	Develop anion-exchange membranes with an area specific resistance of $\leq 0.1$ ohm cm2 (after correction for cell electronic losses), maintained for 500 hours	Complete
(go/ no-go)	AEMFCs	for cell electronic losses), maintained for 500 hours during testing at 600 mA/cm2 at T >60°C.	

Milestone Name/Description	End Date	Туре	Status
Verify durability improvement toward hydroxide attack of Gen 3 chemistry in small molecule studies.	12/31/2017	Quarterly Progress Measure	Complete
Provide experimental results to LBNL for model verification of 1+2D model.	3/31/2018	Quarterly Progress Measure	Complete
Demonstrate capability of achieving Gen 3 chemistry in polymer membranes with greater than 80% conversion of side chains to cation form.	6/30/2018	Quarterly Progress Measure	TBD
Aligned with AEMFC Q2, 2019 milestone: Demonstrate alkaline membrane fuel cell initial performance of 0.6 V at 600 mA/cm2 on H2/air (maximum pressure of 1.5 atma) at T>60 C for >500 hr.	9/30/2018	Annual Milestone	TBD

## Accomplishments and Progress Continued Improvement and Supply of Gen 2 PF AEM

#### Gen 2 PF AEM Synthesis Optimization

Polymer Gen	Excess Linker	IEC <sub>Theoretical</sub> [mmol/g]	IEC <sub>Measured</sub> [mmol/g]	σ <sub>οн-</sub> [mS/cm]
1.0	1.15	1.06	0.91	55
2.0	1.1	1.03	0.77	43
2.1	1.4	1.03	0.83	46.4
2.2	1.7	1.03	0.91	51.4

**Gen 1 PF AEM Polymer** 





Synthesis scale and reproducibility

- >300 g Gen 2 PF AEM polymer has been produced to date
- Gen 2 production scale is ~12 g per batch, limited by reactor volume
- 7 batches of Gen 2.2 produced with reasonable reproducibility (IEC = 0.9 ± 0.04 mmol/g)
- Properties consistent with PFSA analogues

Polymer distribution ~20 entities, including:

- 9 3M
- Pajarito Powder
- Giner
- pH Matter
- Oak Ridge
- Lawrence Berkeley <sup>-</sup>

- LSU
- Tennessee
- CO School of Mines
- UC-Merced
- South Carolina
- TUM

## Accomplishments and Progress PF AEM Durability Studies

#### Accelerated degradation conditions (140 °C, 2:1 MeOH:H<sub>2</sub>O, 2M KOH, 24 hr) Chosen for solubility, reaction times

#### Gen 2 PF AEM Polymer



#### **Membrane Durability**

- Membrane physically changed, conformed to reactor liner and became opaque and heterogeneous
- Couldn't be dissolved/recast, x-ray scattering showed significant change in structure, conductivity difficult to measure and low
- IEC decreased by only 13% compared to 62% of small molecule analogue





Pre Degradation

Post Degradation



## Accomplishments and Progress PF AEMs Moving Forward

#### Gen 2 with increased stability cations

- Small molecule degradation indicates stability limitation of the quaternary ammonium cation
- Cations with enhanced stability being pursued: imidazolium, phosphonium, and heterocyclic cations have shown promising stability.

#### **Gen 3 PF AEM Polymer**



#### **Gen 3 chemistry**

#### **Gen 2 PF AEM Polymer**



#### Imidazolium

- 1. Hugar et al. J. Am. Chem. Soc. 2015, 137 (27), 8730-8737.
- 2. Price et al. ACS Macro. Lett. 2014, 3 (2), 160-165.
- 3. Yang et al. Int. J. Hydrogen Energy 2015, 40 (5), 2363-2370.

#### Phosphonium

4. Gu et al. ChemSusChem 2010, 3 (5), 555-558.

5. Noonan et al. J. Am. Chem. Soc. 2012, 134 (44), 18161-18164.

#### Heterocyclic

6. Gu et al. *Macromolecules* 2014, 47 (19), 6740-6747.
7. Dang et al. *J. Mater. Chem. A* 2016, 4 (30), 11924-11938.

• Explore feasibility of a cation tether with an all carbon linkage (go/no-go 6/30/18)



## Accomplishments and Progress Probing Carbonate Equilibrium

• Carbonate is critical for cell performance and is getting better quantified (modeled).



#### Transient Conductivity in presence of Air/N2/Air



Carbonation happens quickly

Steady-state equilibrium between CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> Reproducibility/Experimental error relatively large



Slight decrease in  $HCO_3^{-}/CO_3^{2-}$  with increasing temperature

Transient conductivity of OH- sample in Air(400 ppm CO<sub>2</sub>) & N<sub>2</sub>(0 ppm CO<sub>2</sub>) 60°C & 85%RH in a Bekktech cell

- Equilibrium with local conditions happens quickly
- Conductivity drops when exposed to  $CO_2 \rightarrow$  absorption
- Conductivity rises when  $CO_2$  removed  $\rightarrow$  desorption
- Data reproducible between cycles

Equilibrium Reactions:  $CO_{2(aq)} + OH^{-} \leftrightarrow HCO_{3}^{-}$  $HCO_{3}^{-} + OH^{-} \leftrightarrow CO_{3}^{2^{-}} + H2O$ 

Divekar et al., ECS Trans. 2017 80(8): 1005-1011; doi:10.1149/08008.1005ecst

## Accomplishments and Progress Electrode Preparation

- Few groups have shown high AMFC (~1W/cm2) performance.
- We have focused on two specific electrode approaches:

#### PF AEM Gen 2

- Employed NREL Gen 2 PF AEM dispersion properties fairly consistent with typical PFSA dispersions for PEM
- Performance fairly average (100's mW/cm<sup>2</sup>), but durability very poor (~10 hours)



#### ETFE - based

- Solid ionomer powder (Prof. John Varcoe, Univ. of Surrey), dry mixed with catalyst, sprayed on GDL
- Electrode fabrication and optimization by Mustain, U. So. Carolina)
- Have demonstrated record performances in AMFCs (~2W/cm<sup>2</sup>, 5A/cm<sup>2</sup>), with good durability



L. Wang et al, *Green Chem.*, 2017, **19**, 831 T.J. Omasta, et al., *Journal of Power Sources* (2017) T.J. Omasta, et al., *Energy Environ. Sci.*, 2018, **11**, 551

Anode Type:	IC	BC	EC
Pt Loading, mg cm <sup>-2</sup>	0.47	0.47	0.50
C Loading, mg cm <sup>-2</sup>	0.75	1.07	1.76
Carbon weight %	41.4 %	48.0 %	56.0 %
AEI weight %	17.2 %	20.0 %	20.0%
AEI:C ratio	*0.417	*0.417	0.357

## Accomplishments and Progress High Performance AMFCs (2017 AMR Status)



- PF AEM Gen 2 membrane used in both cases, only difference is electrodes.
- Performance and durability of ETFE electrodes much higher than PF AEM.
- Performance, durability, voltammetry, and impedance all show strong dependence on electrodes.
- Extreme sensitivity to RH/water management for ETFE GDEs.

# Accomplishments and Progress

Continuing Work with Gen 2 PF AEM



- Fully humidified and low RH (67%) showed lowest performance.
- HFR shows expected trend with RH, 100% RH shows much lower HFR but suffers due to (anode) mass transport limitation.
- HFR decreases with increasing current density, as water produced at anode back diffuses to cathode.

<sup>1</sup>Omasta, T. J. et al. Energy Environ. Sci. **11**, 551–558 (2018).

## Accomplishments and Progress ETFE GDE/PFAEM CCM Asymmetric MEAs



• ETFE electrodes at anode enables high initial performance



- HFR trends are also insightful, they show increasing HFR for PF AEM at anode and decreasing HFR for ETFE at anode with current density.
- Input provided for modeling efforts.

#### Membrane Electrode Assembly

- Cell Temp: 60°C
- Membrane: Gen 2 PFAEM (32 μm)
- lonomer: ETFE or PFAEM
- GDL: Toray H-060 or SGLBC29
- Gases: H<sub>2</sub> var°C, O<sub>2</sub> var°C, 1.0 slpm
- Active Area: 5 cm<sup>2</sup>
- Pressure: 121 kPa abs
- Anode: 0.5 mg/cm<sup>2</sup> Pt/HSC
- Cathode: 0.5 mg/cm<sup>2</sup> Pt/HSC
- Relative Humidity: 80% RH

## Accomplishments and Progress ETFE GDE/PFAEM CCM Asymmetric MEAs





- Asymmetric MEAs also interesting for looking at durability trends.
- PF AEM at cathode shows extremely poor durability, while ETFE at cathode even with PF AEM at anode show better durability.
- HFR not impacted by durability over the time investigated, not correlated to performance loss.
- ETFE electrode necessary at anode for performance
- ETFE electrode necessary at cathode for durability

Membrane Electrode Assembly Cell Temp: 60°C; RH: 80% RH Membrane: Gen 2 PFAEM (32 μm) Ionomer: Varcoe AEI or PFAEM Gases: H<sub>2</sub> var°C, O<sub>2</sub> var°C, 1.0 slpm Active Area: 5 cm<sup>2</sup>

- GDE: 0.35 mg/cm<sup>2</sup> Pt/HSC
- CCM: 0.40 mg/cm<sup>2</sup> Pt/HSC

## Accomplishments and Progress Performance Losses and Carbon Corrosion Concerns

As-prepared PF AEM CCM

Post-test Cathode (13 hours)

Post-test Anode (13 hours)



Clear signs of Pt agglomeration and carbon corrosion in both anode or cathode, but more pronounced in cathode. Major changes in voltammetry and impedance observed. As- prepared PF AEM electrodes look like standard PFSA PEMFC electrodes



## Accomplishments and Progress AMFC Modeling (2017 AMR Status)



- 2017 AMR Status:
  - 2D model developed to explore water and carbonate management
  - Performance is highly sensitive to RH variations



## Accomplishments and Progress Role of Water Back Diffusion



- Feedback from NREL experiments: cathode RH does not need to be very high for good performance
- Water back-diffusion replaces consumed water at AEMFC cathode
  - At  $\beta = 0.5$ , water flux from anode to cathode equals water consumption by ORR
- Faster water diffusion allows for more even catalyst utilization in cathode CL



## Accomplishments and Progress Effects of CO<sub>2</sub> contamination



- NREL demonstrated rapid reduction in conductivity when OH-form PFAEM exposed to air containing  $\mathrm{CO}_2$ 
  - Model uses high CO<sub>2</sub> absorption and desorption rates suggested by NREL expt.
- Down the channel, average  $CO_3^{2-}$  concentration in MEA increases slightly, but ASR decreases overall due to hydration effects.

Models use air cathode (+400 ppm  $CO_2$ ),  $H_2$  anode, 80% RH. Cell voltage of 0.7 V, temperature 60 °C.

## Accomplishments and Progress Responses to Previous Year (2017 AMR) Reviewer's Comments

- Reviewer Comment: Cost has been ignored. Analogies, or at least attempts to compare and rationalize cost improvements, should be presented. Cost mock-up through film formation should be taken into account.
- Response: While the primary focus of this work has not been cost, the use of perfluorinated ionomers tends to have much higher cost than that of hydrocarbon ionomers. The premise of using the PFSA precursor in these tests was to focus on an established larger scale production as a platform for evaluating the technology, specifically the potential benefits as a durable, high conductivity, high water transport membrane or as an ionomer. While advantages in water transport and conductivity have been demonstrated, durability and electrode performance are still lacking. These factors, plus the in flux of hydrocarbon polymers with high performance may limit our pursuit of these materials to the remaining time of this project. We have already pivoted toward a higher focus on the electrodes for the impact that they have shown on device performance.
- Reviewer Comment: The project still utilizes PGM catalysts, while the raison d'etre for alkaline fuel cell work is the potential for PGM-free fuel cells.
- **Response:** We have done this because this has been a polymer development project, but have followed work of others showing very positive strides in this direction and have included some preliminary work on backup slide 30. This area is of high interest but would merit another project of similar scale.
- **Reviewer Comment:** The only deficit: had a fuel cell fluoropolymer chemist(s) been involved, the compositional design/progression of the tether could have been identified immediately, and unnecessary work would have been eliminated.
- Response: Our team has world class chemists, and some of the best fluoropolymer chemists through our interactions with 3M that is highly active in the project. While significant experience in this area has greatly aided the project, one of the biggest surprises has been some of the difficulties associated with solubility and reactivity of the approaches employed. One of the easiest areas to overlook was the significant synthetic challenges to perform the select chemistries employed on the polymers used. While we respect the reviewers comment, we think this is a greater reflection of the difficulties of our chosen routes and perhaps limitations or mistakes made in the literature when employing similar approaches rather than a lack of involvement or skill on our team's part.

# Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (PI), Andrew Park, Derek Strasser, Chris Antunes, Ami Neyerlin, K.C. Neyerlin, Shaun Alia, Hai Long, Zbyslaw Owczarczyk	Prime; Oversees the project, PF AEM synthesis and stability characterization, MEA optimization, and fuel-cell testing
Lawrence Berkeley National Laboratory (LBNL) Adam Weber, Huai-Suen Shiau, Mike Gerhardt	Sub; Fuel cell modeling including water transport and carbonate issues
Oak Ridge National Laboratory/University of Tennessee (ORNL/UT): Tom Zawodzinski, Ramez Elgammel, Zhijiang Tang	Sub; Polymer characterization (water self- diffusion coefficient and electro-osmotic drag)
Colorado School of Mines (CSM): Andy Herring, Ashutosh Divekar	Sub; Membranes characterization (water uptake, conductivity, structure).
<b><u>3M (3M):</u></b> Mike Yandrasits, Krzysztof Lewinski, Steve Hamrock	In-kind; Consulting on novel chemistries; preparation of solutions and dispersions; membrane fabrication.

University of South Carolina: Bill Mustain, Travis Omasta; advanced electrode/GDE University of Surrey: John Varcoe, ETFE membrane and ionomer Many others whom have used/studied Gen 2 PF AEM

# Remaining Challenges and Barriers/Future Work

- Polymer Synthesis:
  - Increased stability
  - Focus on increased stability cations and Gen 3 polymer development
- Characterization:
  - Membrane and electrode properties (including stability)
  - Continuing studies on stability, structure, water transport, carbonate
- AMFC implementation, Modeling, and Diagnostics:
  - Improved performance and durability in cells, closing the gap between experimental and modeling efforts
  - Electrode optimization and diagnostic studies focused on further characterization of electrodes and elucidating performance loss and durability.
    - In-situ: limiting current, RH studies, CV, segmented cell, air performance, and impedance
    - Ex-situ: microscopic, electrochemical, and spectroscopic analysis
  - Continued integration of modeling efforts with cell testing
    - Further elucidation of the impact of operating conditions (T, RH, current density, CO<sub>2</sub> concentration)

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

# Technology Transfer Activities

- Highly focused on engagement of project partner 3M, leaders in the areas of PF membranes and materials. Through technical advances, the materials being developed could lead to commercial products.
- Involvement with multiple projects leveraging core membrane technology being developed (Incubator projects with Giner, Inc (Reversible Fuel Cells) and University of Delaware (Redox Flow Battery) and SBIR Project with pHMatter, Inc (Reversible Fuel Cells). SBV project with Midwest Energy Group. As well as supply of polymer materials to ~20 entities.
- Co-led AMFC Workshop, May 1, 2016 involving over 50 participants from academia, industry and government. Contributed to/Co-led Workshop Report. Participation with ARPA E IONICS program.

2016 AMFC Workshop Report http://energy.gov/eere/fuelcells/downloads/2016-alkaline-membrane-fuel-cell-workshop

# Summary

- **<u>Relevance</u>**: AMFCs offer promise for improved performance and decreased cost.
- <u>Approach</u>: Synthesize, characterize and optimize membrane and fuel cell performance and durability using modeling and advanced diagnostic/ characterization techniques.
- Accomplishments and Progress: This year saw significant advances in technology by quantify the degradation of Gen 2 and Gen 3 small molecule analogues. The focus on electrodes has allowed us to elucidate the importance of water management on performance, particularly the role of back diffusion of water. Durability improvements due to ETFE electrodes were found to be significant. Model development provided insight into the role of water and carbon dioxide allowing the performance potential and limitations of AMFCs to be better understood.
- **Collaborations:** We have a diverse team of researchers including 3 national labs, 2 universities, and 1 industry participant that are leaders in the relevant fields of PF polymer electrolytes (3M), characterization (ORNL/UTK, CSM), and modeling (LBNL).
- **Proposed Future Research**: Focused on further improving polymer properties, and improving fuel cell performance and durability with an emphasis on electrode issues.

# **Technical Backup Slides**

# Accomplishments and Progress

Small Molecule Gen 3 durability

#### **Gen 3 PF AEM Polymer Target**



- *Para* substitution is projected to be one of two major products (*meta* position being the other) in the modified polymer
- *Ortho* substitution is presumed to be minor due to steric hindrance with the polymer
- Durability is presumed to be highest at the *meta* position
- Gen 3 small molecule degradation
  - After heating at 140 °C for 24 hrs in 2:1 methanold<sub>3</sub>:KOH 1H NMR indicated the QA cation degraded 64%



# •<sup>19</sup>F NMR employed to detect changes in fluorine environments

- Spectra indicates three fluorine signals with integration values proportional to the number of fluorine atoms in each environment.
- Post degradation the integration values indicated the same proportionality and the addition of a peak for fluoride



#### •Gen 3 small molecule conclusions

- QA cation stability is comparable to the sulfonamide
- Gen 3 tether linkage indicates enhanced stability

# Accomplishments and Progress

Change in Morphology due to CO2 Uptake



Intensity and d-spacing of the spectrum drops when exposed to air indicating CO<sub>2</sub> reaction and loss of water

- Drop in intensity follows a double exponential decay behavior.
- The time of equilibration is faster at lower %RH

[1] Divekar et.al, ECS Transactions, 80, 8(2017)

## Accomplishments and Progress MEA Diagnostics for ETFE GDE/PFAEM CCM Asymmetric MEAs



Surface area decreases after durability tests

## Accomplishments and Progress ETFE GDE MEAS



- Highest performance obtained with PF AEM Gen 2 membrane is 1.4 W/cm<sup>2</sup>.
- Impedance showing slight change after 13 hour test.

# **Accomplishments and Progress**

MEA Performance: PFAEM Solid Ionomer GDE vs PFAEM Dispersion Ionomer CCM



#### Membrane Electrode Assembly

- Cell Temp: 60°C
  - Membrane: Gen 2 PFAEM (33 μm)
- GDL: Toray H-060
- Gases:  $H_2$  ,  $O_2$  1.0 slpm
- Active Area: 5 cm<sup>2</sup>
- Pressure: 121 kPa abs
- Anode is controlled with Mustain/Varcoe ETFE GDEs, 0.6 Ptmg/cm2 Pt/HSC.
- Cathode:
- C: 0.25 mg/cm<sup>2</sup> Pt/Vu, PFAEM dispersion ionomer (CCM), 100RH
- C: 0.25 mg/cm<sup>2</sup> Pt/Vu, PFAEM solid ionomer (GDE), 90RH
  - PFAEM GDE cathode has almost twice higher HFR than PFAEM CCM cathode

## Accomplishments and Progress Silver Cathode GDE Performance



• Ag cathode yields reasonable performance, but with low OCV

# Accomplishments and Progress

**Coupling Modeling and Experimental Results** 



- Similar trend to experiment for polarization curve performance
- HFR decreases at high current density as the membrane hydrates
- Model currently seems to overestimate HFR increase at low RH

## Accomplishments and Progress Modeling Down-the-channel Effects in AEM Fuel Cells

Iterate 2-D model along channel



Model used O<sub>2</sub> cathode, H<sub>2</sub> anode, 60% RH. 0.1 std L/min flow rate. Cell voltage of 0.7 V, temperature 60 °C.

- Iterate 2-D model down the channel for cell-scale impacts
- NREL experiments demonstrated flooding on anode and cathode depending on operating conditions. Updated water transport modeling in membrane to match observations.
- Cell self-hydrates down the channel, leading to reduced membrane resistance
- High flow rates avoid flooding but reduce membrane water content, leading to reduced conductivity



## Accomplishments and Progress Modeling Down-the-channel Effects in AEM Fuel Cells





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- Cell self-hydrates down the channel, leading to reduced membrane resistance
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Models use air cathode,  $H_2$  anode, 80% RH. Cell voltage of 0.7 V, temperature 60 °C.