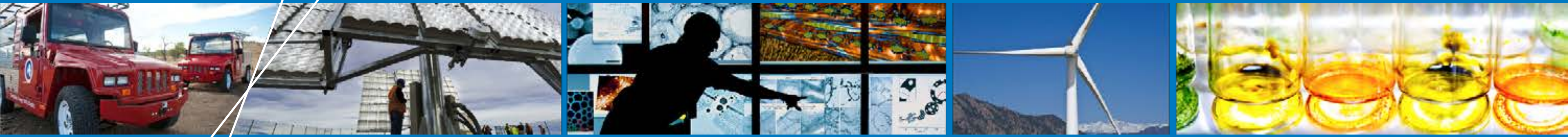
NATIONAL RENEWABLE ENERGY LABORATORY

Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells



2017 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

June 8, 2017

FC147

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

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

- **Start: Oct 2015**
- **End: Oct 2018**
- **% complete: ~35%**

Barriers

A. Durability
B. Cost
C. Performance

Budget ($K)

- FY17 DOE Funding: $1M
- FY16-FY18 at $1M/yr
- Total Project Value: $3M
- Cost Share Percentage: 0%

Partners – Principal Investigators

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^2, maintained for 500 hours during testing at 600 mA/cm^2 at T >60 ^oC.
- **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 ≤ 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 ^oC. 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

Improve novel perfluoro (PF) anion exchange membrane (AEM) properties and stability.

Employ high performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells (AMFCs).

Apply models and diagnostics to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate related).

*taken from D. Papageorgopoulos presentation AMFC Workshop, Phoenix, AZ, April 1, 2016

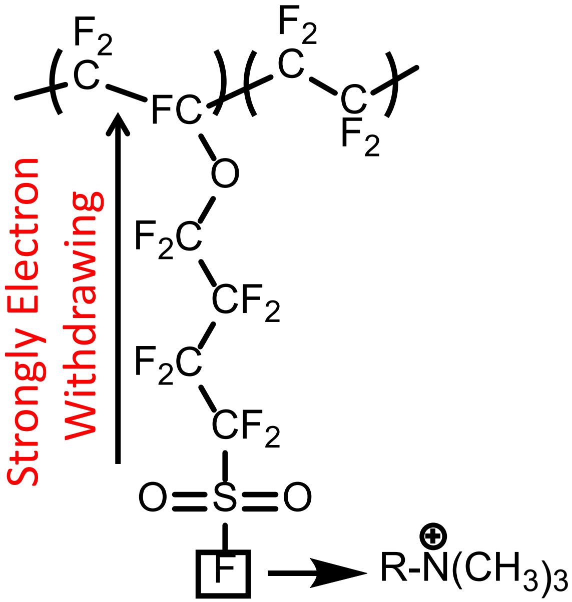
Approach
FY 17 Milestones

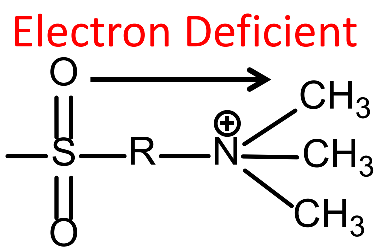
Milestone Name/Description	End Date	Type	Status	
Synthesis and membrane fabrication of ≥100g of novel (advanced cation) PF AEM for further characterization and MEA studies (Gen 2 PF AEM).	12/31/2016	Quarterly Progress Measure (Regular)	**Complete**	NREL
NMR studies comparing mobilities of carbonate, bicarbonate, hydroxide at varying RH.	3/31/2017	Quarterly Progress Measure (Regular)	**Complete**	UTK/ORNL
Determine carbonate uptake rates and equilibrium values at different CO_2 concentrations and temperatures for model incorporation.	6/30/2017	Quarterly Progress Measure (Regular)	**On track**	CSM
Develop and demonstrate model for carbonate in AEMFCs.	9/30/2017	Quarterly Progress Measure (Regular)	**Complete**	LBNL
Aligned with AEMFC Q4, 2017 milestone: Demonstrate alkaline-membrane-fuel-cell peak power performance > 600 mW/cm^2 on H_2/O_2 (maximum pressure of 1.5 atm abs) in MEA with a total loading of ≤ 0.125 $mgPGM/cm^2$.	9/30/2017	Annual Milestone (Regular)	**TBD**	NREL

Name	Description	Criteria	Status	
Mid-Project Decision Point	Meet FCTO MYPP 2017 Q2 Milestone for AEMFCs	Develop anion-exchange membranes with an area specific resistance of ≤0.1 ohm cm^2 (after correction for cell electronic losses), maintained for 500 hours during testing at 600 mA/cm^2 at T >60oC.	**Complete**	NREL

Approach

PF AEM Materials – Targeted Linkages and Specific Chemistries





Perfluoro (PF) polymer electrolytes exhibit chemical robustness, enhanced water transport and conductivity properties compared to hydrocarbon polymers, and form high performance electrodes.

1. Improved material development (Gen 2/ Gen 3 PF AEM chemistries) (NREL)

- Moving beyond sulfonamide tether due to inherent stability concerns

2. Characterization and AMFC implementation of materials on hand (NREL, CSM, UTK/ORNL)

- Membrane: Water uptake, conductivity, diffusivity, carbonate uptake
- MEA: Cell performance and durability

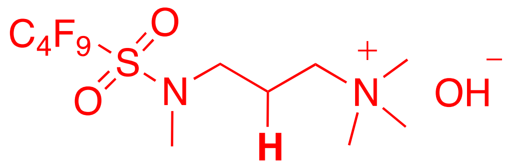
3. AMFC modeling and diagnostics (LBNL, NREL)

- Application of advanced diagnostic tools (impedance, limiting current, H2 pump)
- Effects of membrane thickness, water diffusivity, carbonate uptake being investigated

Accomplishments and Progress

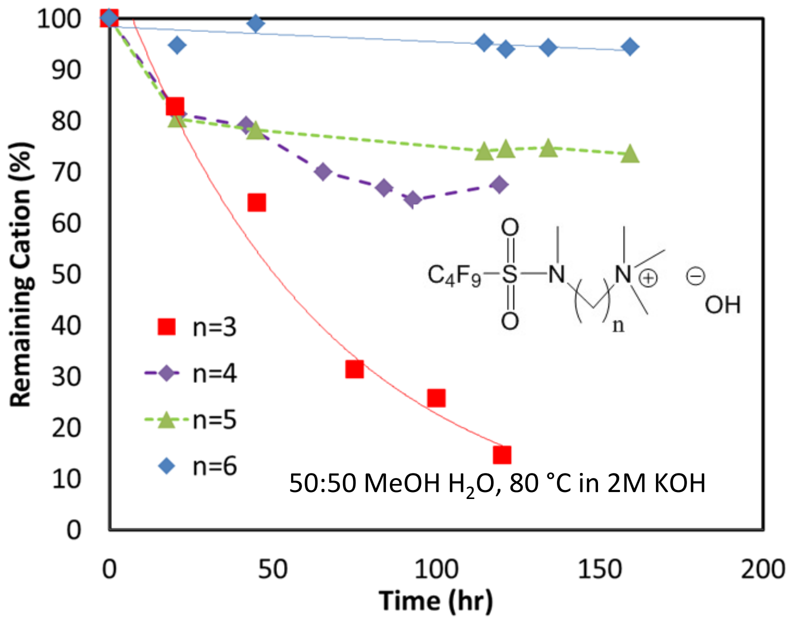
Leveraging Small Molecule Studies

Small Molecule Analog of Gen 1 PF AEM Polymer



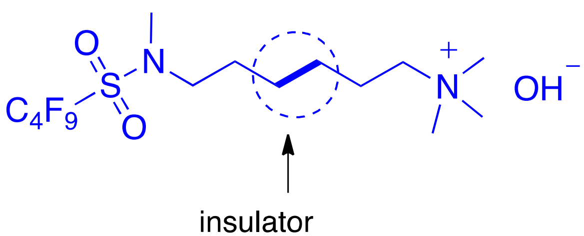
Shown to have poor durability due to proximity of cation and electron withdrawing sulfonamide to β-hydrogen. Only 10% of molecule is left after 125 hours at 80 °C

Small Molecule Analog Stability*



*Basic Energy Science funded work

Small Molecule Analog of Gen 2 PF AEM Polymer



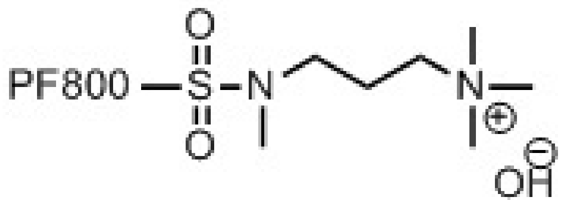
Significantly increased stability achieved through lengthening of the alkyl chain (n=6).
~5% degradation after 150 hours at 80°C (50% MeOH).

NMR shows sulfonamide linkage becomes the weak point at long (n=6) tether length. Limiting stability of this tethering route.

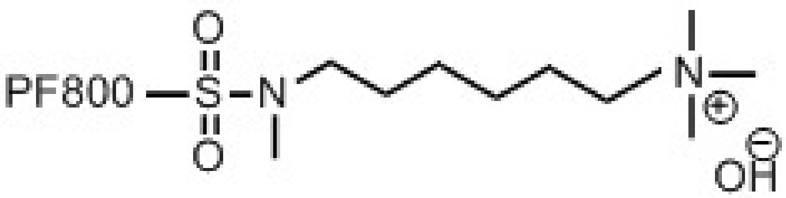
Accomplishments and Progress

Improved Chemical Stability (Gen 2)

Gen 1 PF AEM Polymer



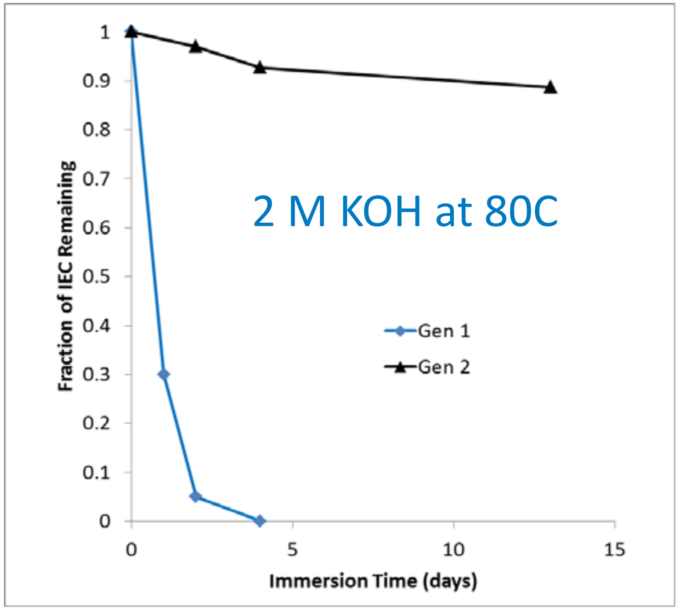
Gen 2 PF AEM Polymer



Polymer	IEC (measured/theoretical) [mmol/g]	OH^- Conductivity @23°C in Water [mS/cm]
Gen 1	0.91 (1.06)	55
Gen 2	0.77 (1.03)	43

Significantly increased stability (~30x) achieved through lengthening of the alkyl chain, while ion exchange properties largely retained.

Progress aided by an improved understanding of reactions/solubility.



>200g of Gen 2 synthesized to date.

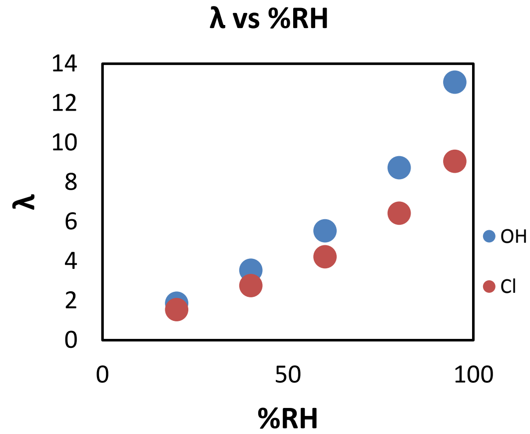
Distributed to >10 collaborators including:

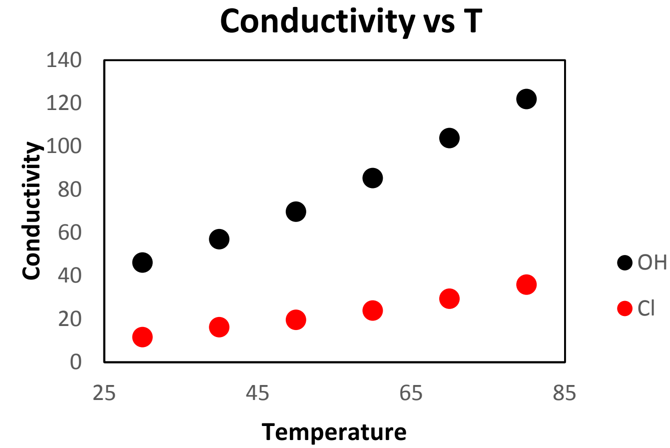
- 3M
- Pajarito Powder
- Giner
- pH Matter
- Oak Ridge
- Lawrence Berkeley
- LSU
- Tennessee
- CO School of Mines
- UC-Merced
- UConn
- TUM

Accomplishments and Progress

Characterization of PFAEM Gen 2

Gen 2 PFAEM exhibits high conductivity in OH^- form – 122 mS/cm at 80°C and 95%RH – with reasonable water uptake (similar to PFSAs). (CSM)





Water self-diffusion coefficients slightly lower for PFAEM compared to commercial membrane (Tokuyama A201) with higher IEC (1.98 mmol/cm^3 vs 1.28 mmol/cm^3 for Gen 2). (UTK/ORNL)

Comparison of Water Diffusion Rates

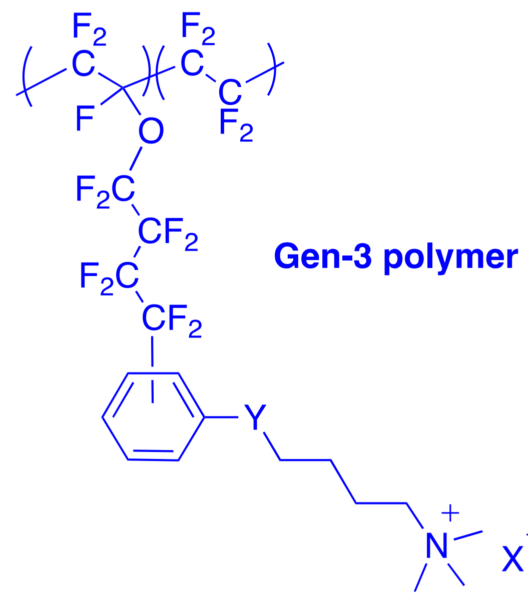
		$D(H2O)(m^2/s)$
	Gen-2	5.28E-10
OH^- form	A201	8.22E-10
	Gen-2	1.78E-10
HCO_3- form	A201	4.46E-10
	Gen-2	1.56E-10
Cl form	A201	3.30E-10

*water in Nafion(bulk) ~9 x 10^{-10} m^2/s

Accomplishments and Progress

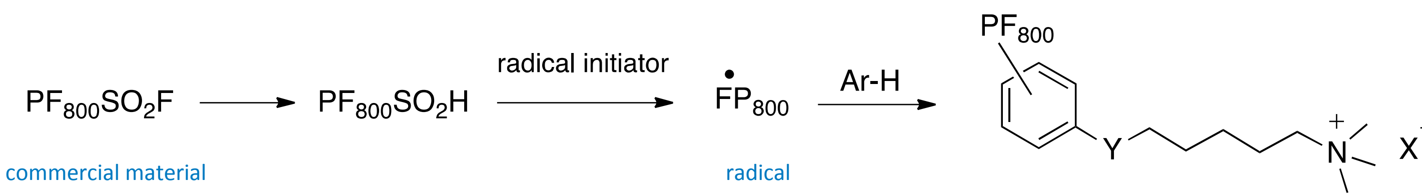
Gen 3 PFAEM Development

Alternate tether required for further stability improvements. Gen 3 approach targets perfluoroalkyl linkage avoiding sulfonamide.



Gen-3 polymer

- Perfluoroalkyl **PF_{800}** (Gen-3) is significantly weaker electron-withdrawing group then $PF_{800}SO_2$ (Gen-2)
- Aromatic linker with **PF_{800}** is NOT susceptible for OH^- attack
- PF_{800} small molecule analogues show improved base stability
- Various cations under consideration
- Solubility and extent of reaction are primary concerns. Synthesis is underway.

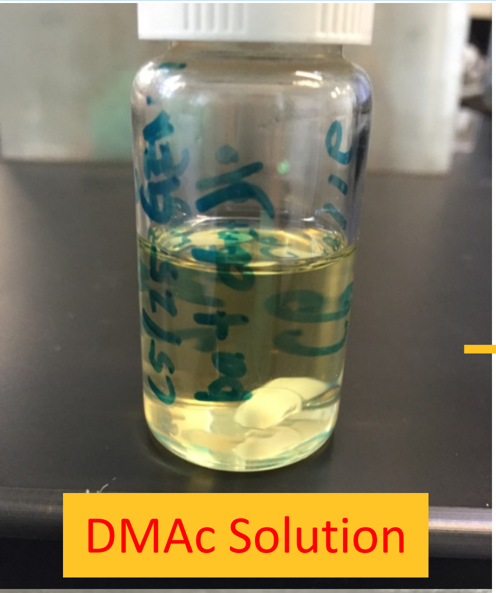


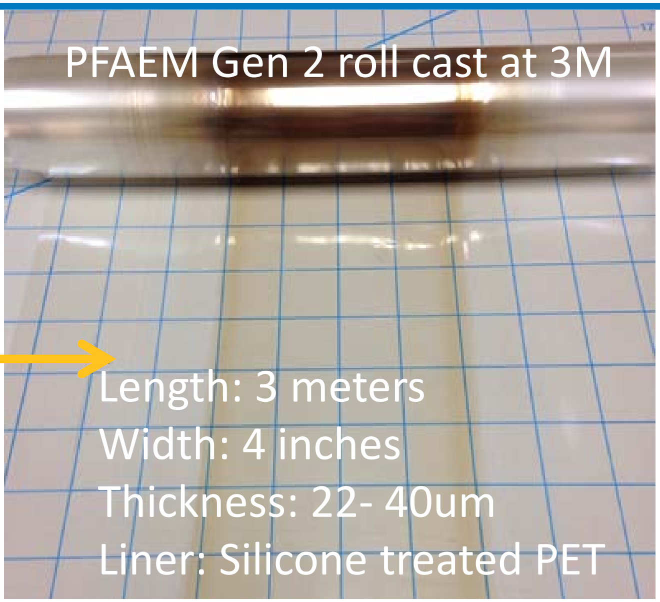
Y = CH_2; NR

Gen-3 polymer

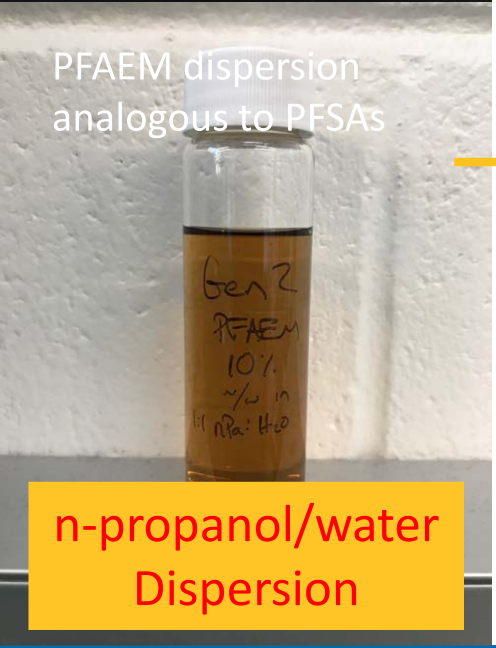
Accomplishments and Progress

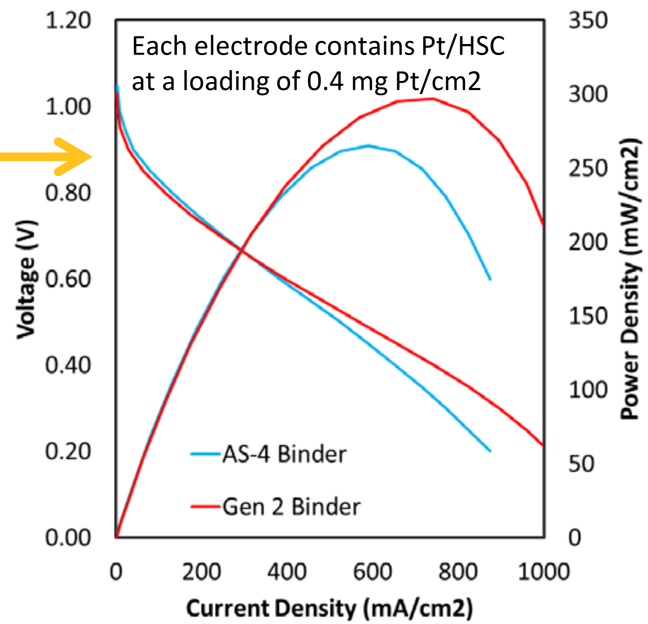
Gen 2 PFAEM Solutions and Dispersions





Improved reaction conversion and polymer processing knowledge have led to improved/larger quantities of Gen 2 materials.



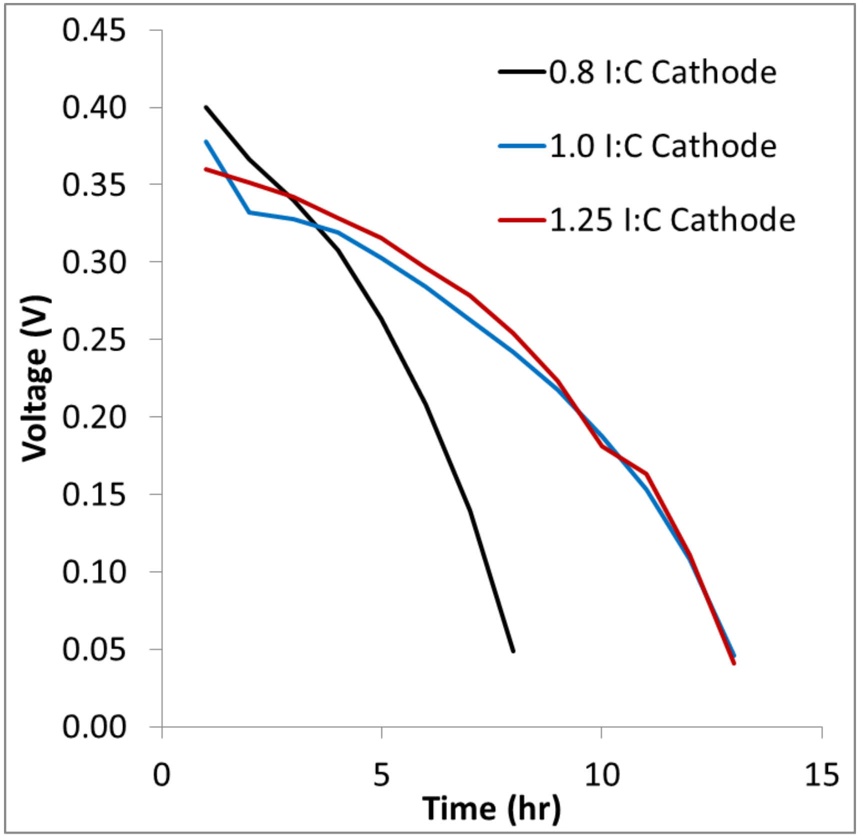


PFAEM Gen 2 ionomer electrode performance surpasses commercial Tokuyama AS-4 ionomer in MEAs with PFAEM membrane.

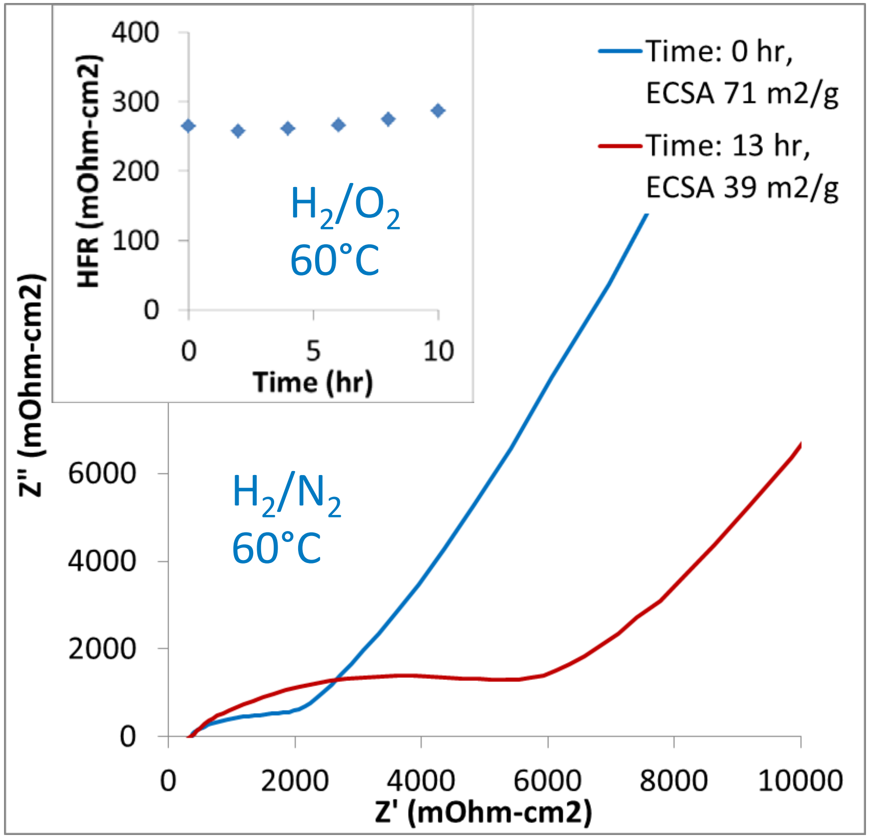
Accomplishments and Progress

Durability of Gen 2 PFAEM MEAs

Current Hold at 0.4 A/cm²



Cathode Impedance, 1.0 I:C



Gen 2 PFAEM MEAs degraded quickly when operated under high humidification at constant current

Durability losses associated with electrodes through impedance and voltammetry.

Accomplishments and Progress

Implementation of High Performance GDEs

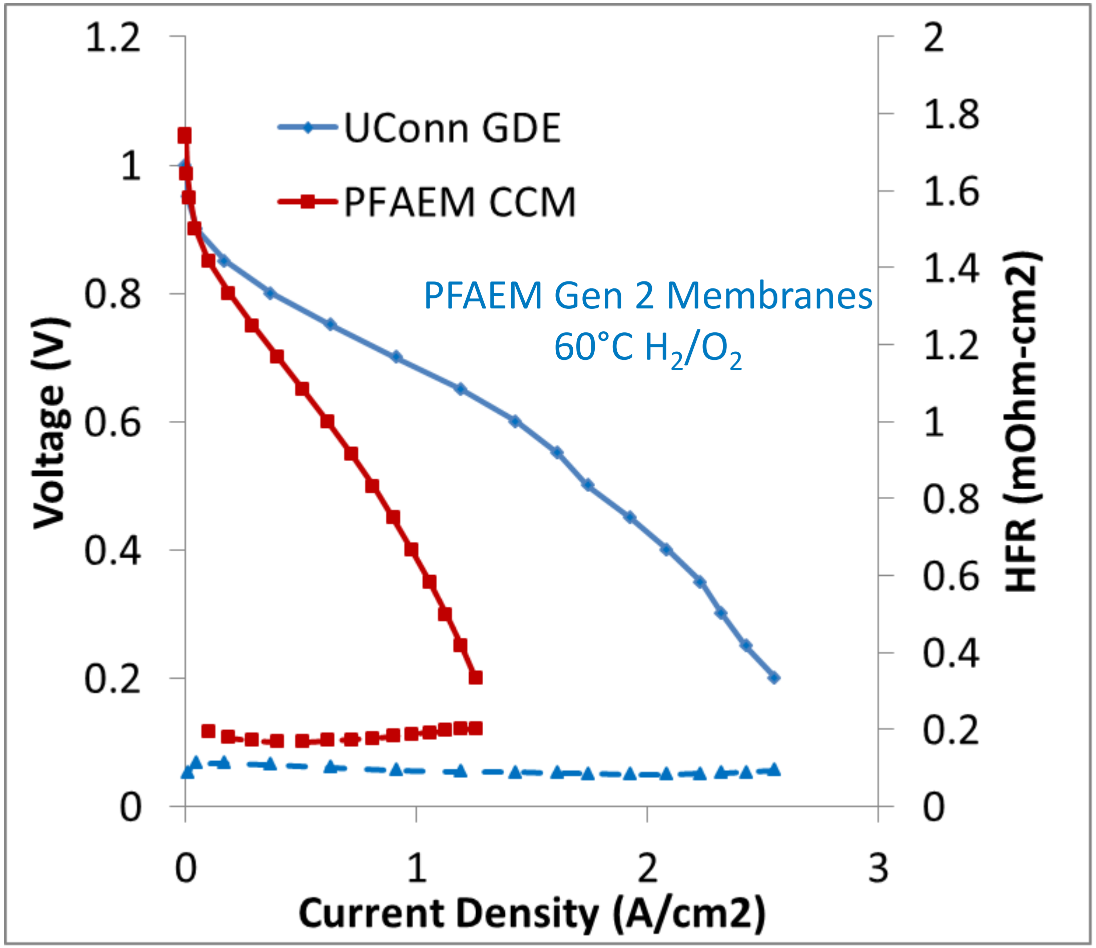
Few groups have shown high AMFC (~1W/cm²) performance in the literature (~300mW/cm² much more common).

UConn (Bill Mustain's) group has shown >1W/cm2 in AMFCs and initially supplied us with GDEs.

Later Andrew Park(NREL) spent 1 week at UConn fabricating GDEs and obtaining GDE fabrication knowledge.

Composition:

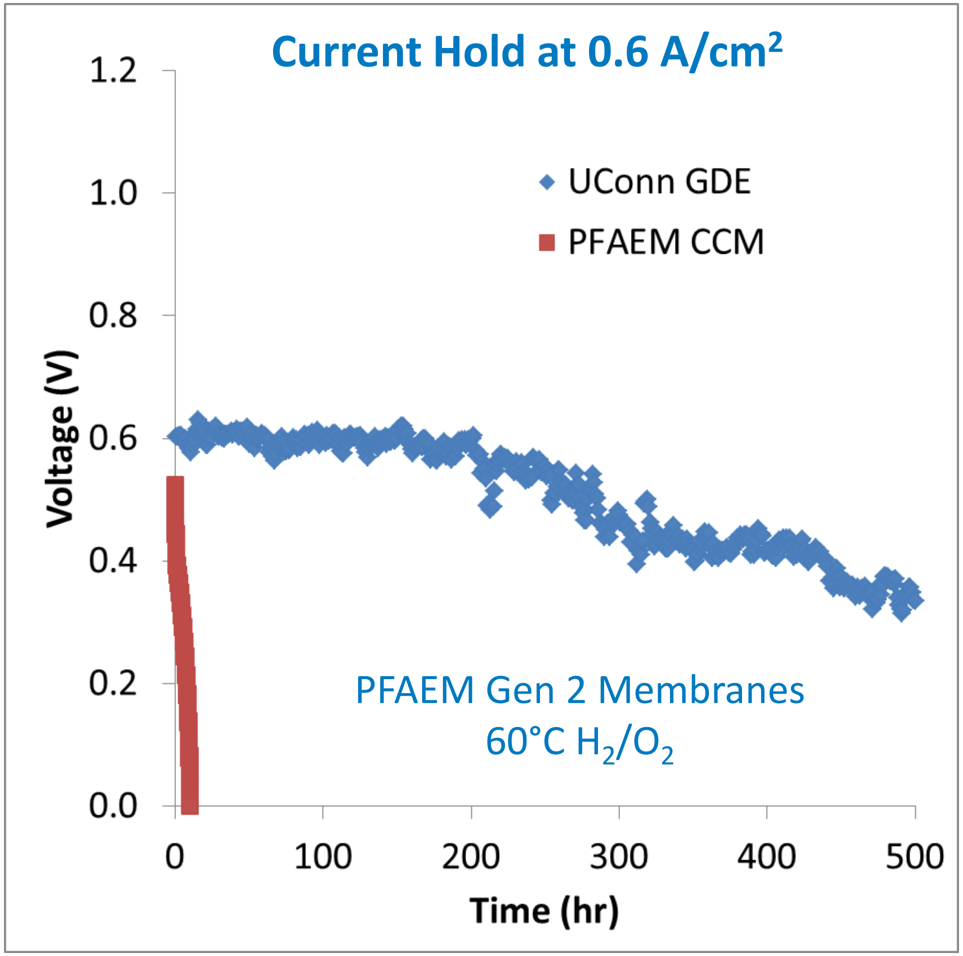
- Solid ionomer powder (Prof. John Varcoe, Univ. of Surrey), mixed with catalyst, sprayed on GDL (Toray H-060)
- Cathode: Pt/Vu (0.4 mg/cm²)
- Anode: PtRu/Vu (0.67 mg/cm²)



- **~1 W/cm² achieved with UConn GDEs, approaching state-of-the-art performance for AMFC**

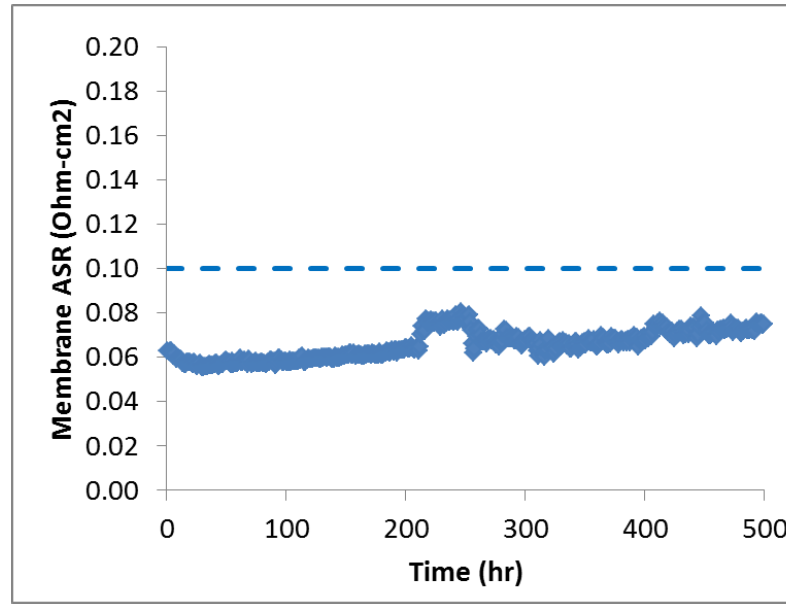
Accomplishments and Progress

Durability of PFAEM with UConn GDEs



Mid Project Decision Point - Completed

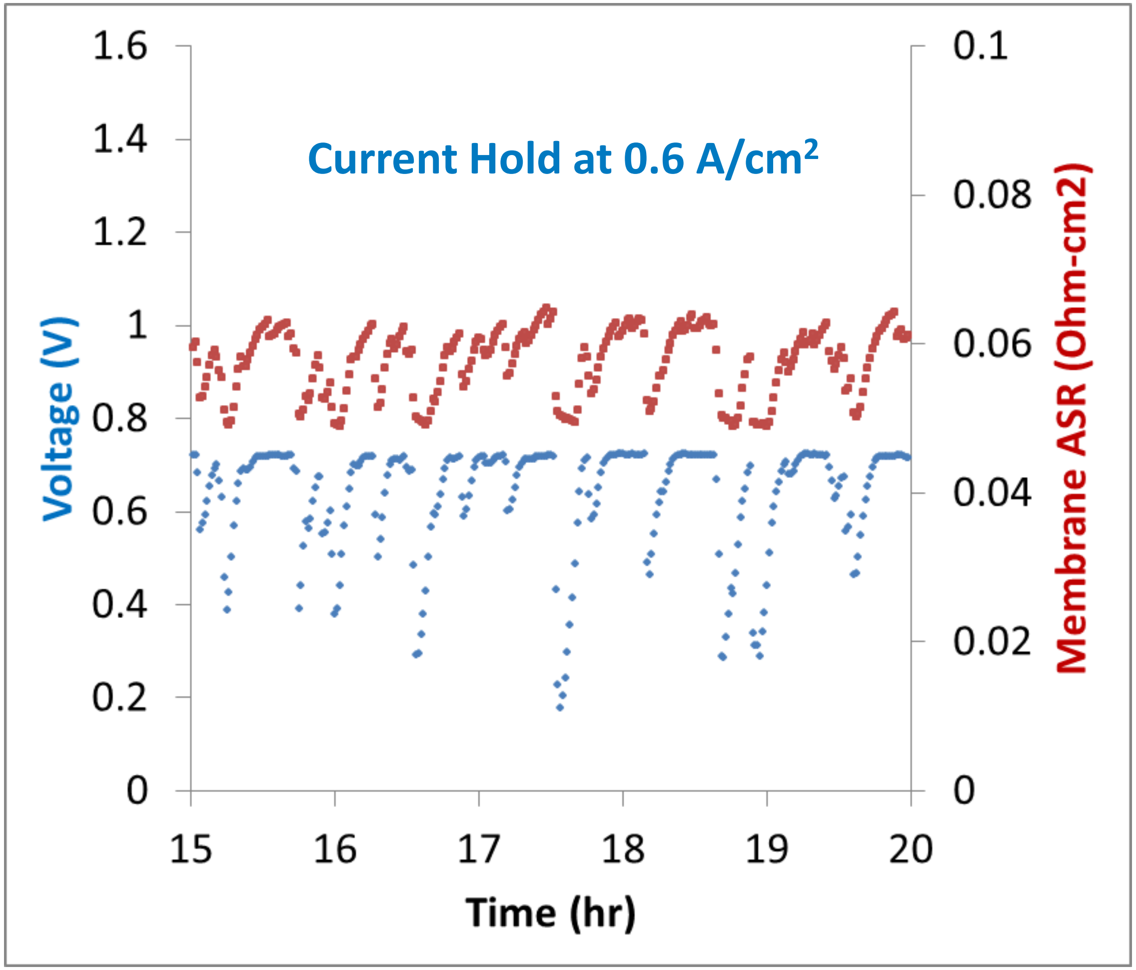
Develop anion-exchange membranes with an area specific resistance of ≤0.1 ohm cm2 (after correction for cell electronic losses), maintained for 500 hours during testing at 600 mA/cm2 at T >60°C.



- **Demonstration of FCTO MYPP 2017 Q2 Milestone for AEMFCs**

Accomplishments and Progress

Extreme Sensitivity to Water Management



Membrane Electrode Assembly

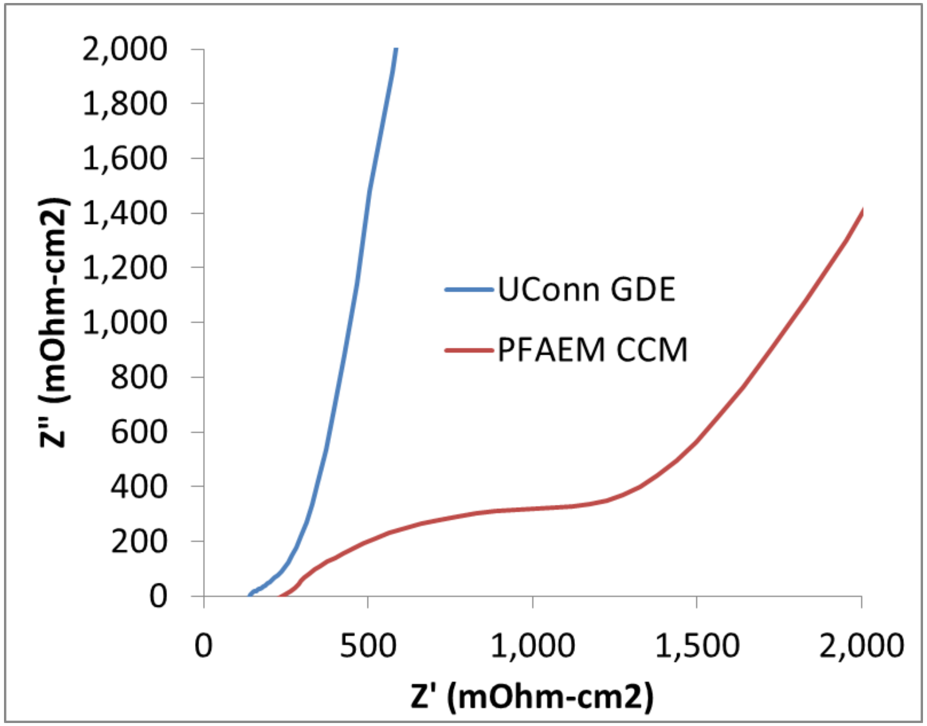
- Cell Temp: 60°C
- Membrane: Gen 2 PFAEM (30 µm)
- Ionomer: Varcoe AEI
- GDL: Toray H-060
- Gases: **H_2 55.3°C, O_2 56.0°C**, 1.0 slpm
- Active Area: 5 cm^2
- Pressure: 200 kPa abs
- Anode: 0.8 mg/cm^2 Pt/Vu
- Cathode: 0.5 mg/cm^2 Pt/Vu

- **Performance highly dependent on slight variations in RH (not shown).**
- **Periodic transient (flooding) events witnessed.**
- **This sensitivity not seen in PEMs or other AMFCs we have tested.**

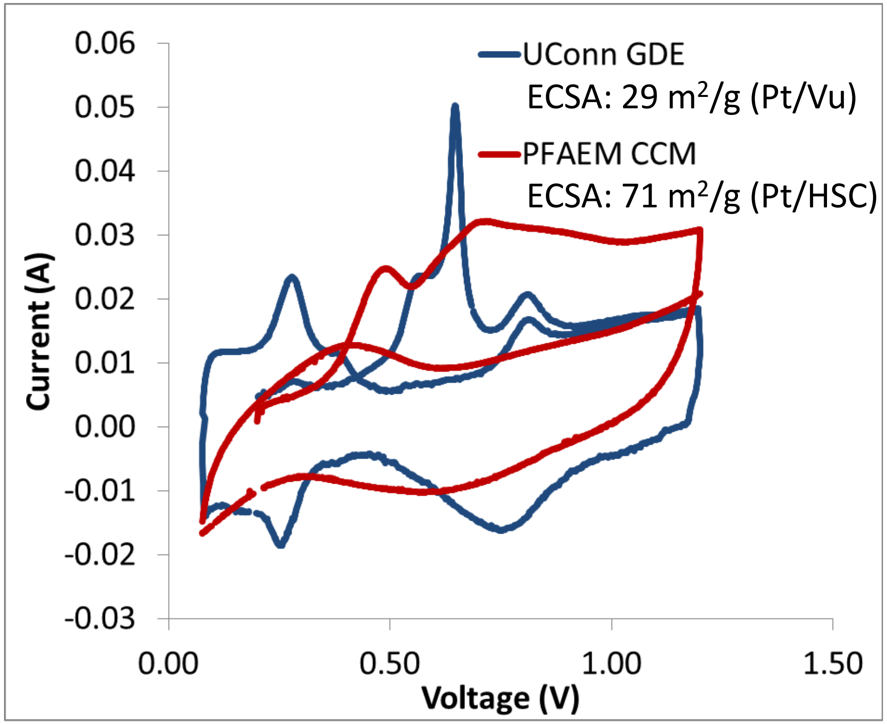
Accomplishments and Progress

MEA Diagnostic Comparisons between PFAEM CCM and UConn GDE

H_2/N_2 Impedance

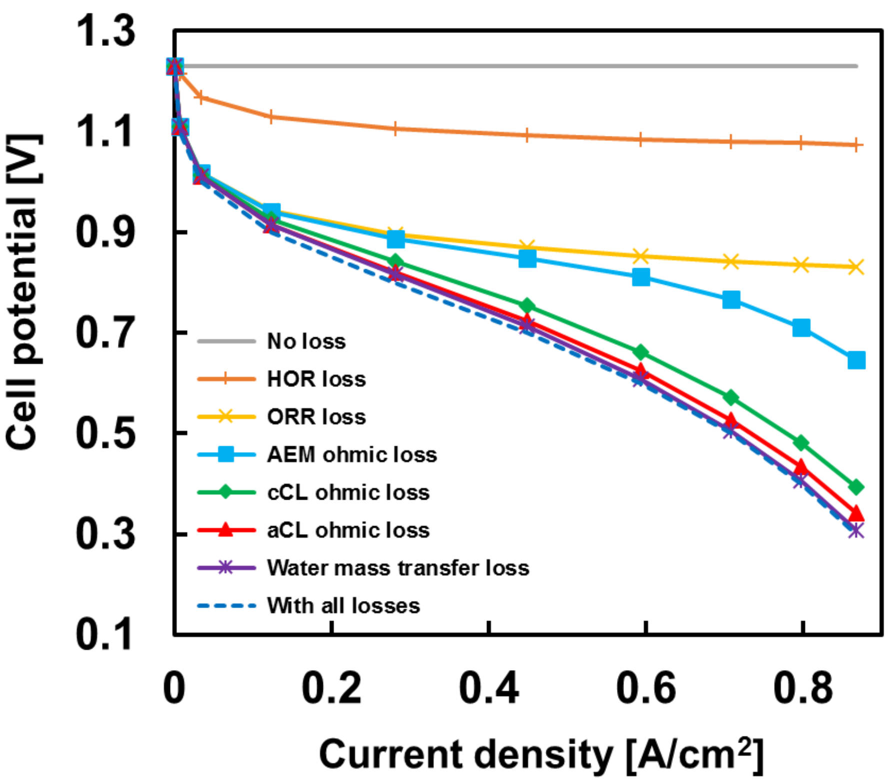


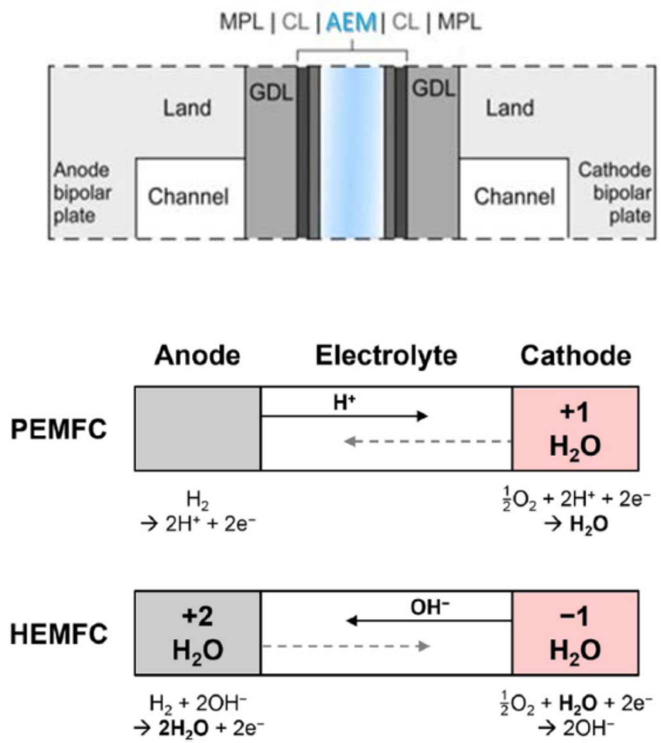
Cyclic Voltammetry w/CO Stripping



- **Impedance and CV data show striking differences.**
- **Impedance shows significant electrode resistance for PFAEM CCM.**
- **Voltammetry shows significant difference in ionomer-catalyst interactions – PFAEM has higher ECA, but less distinct Pt features.**

Accomplishments and Progress
AMFC Model Development





cCL dehydration

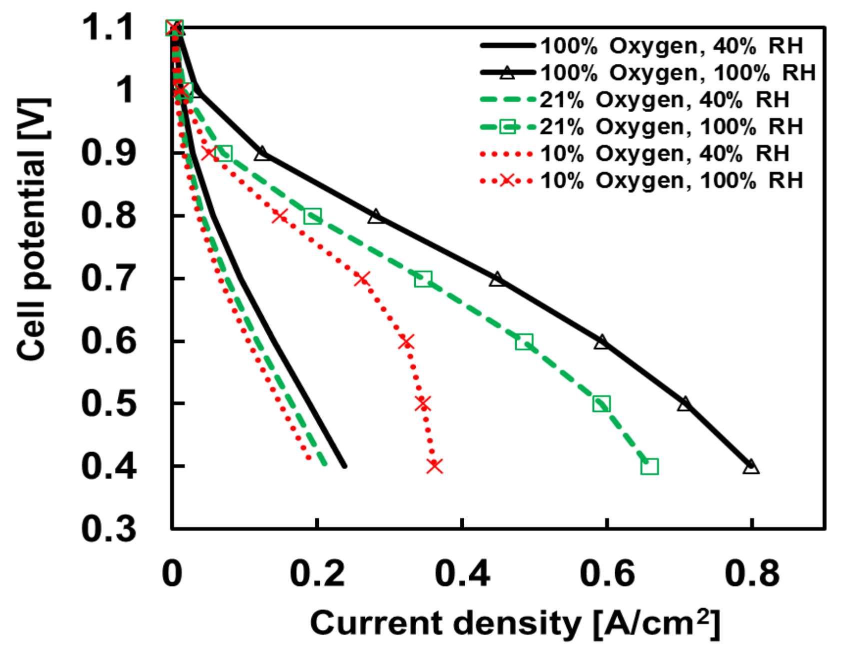
- LBNL – addressing **major** gap - AMFC models developed based on literature data of Tokuyama materials presented at 2016 AMR.
- These efforts have been extended to probe performance losses with emphasis on water and carbon dioxide management.

H-S. Shiau, I.V. Zenyuk, and A.Z. Weber, J. Electrochem. Soc., submitted (2017).

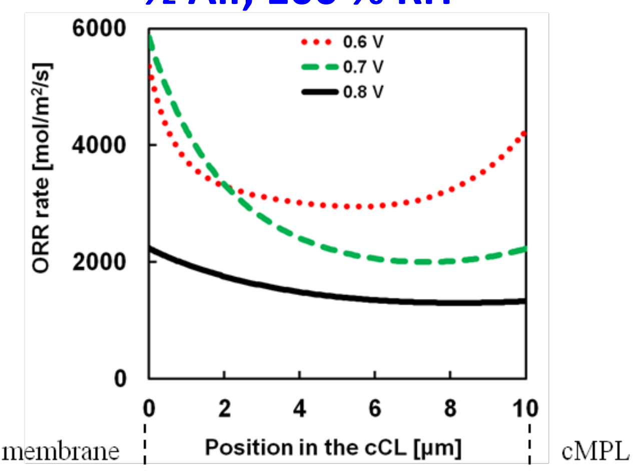
Accomplishments and Progress

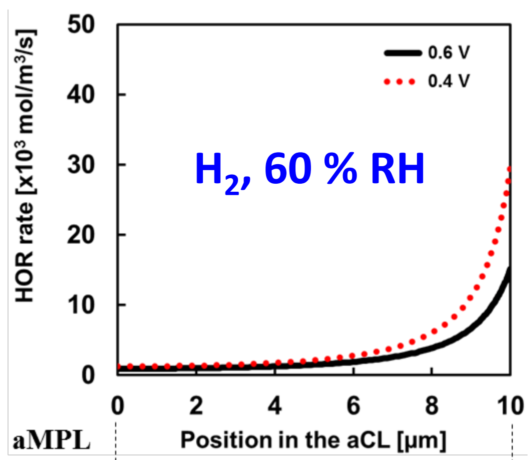
Impact of RH/Oxygen Concentration

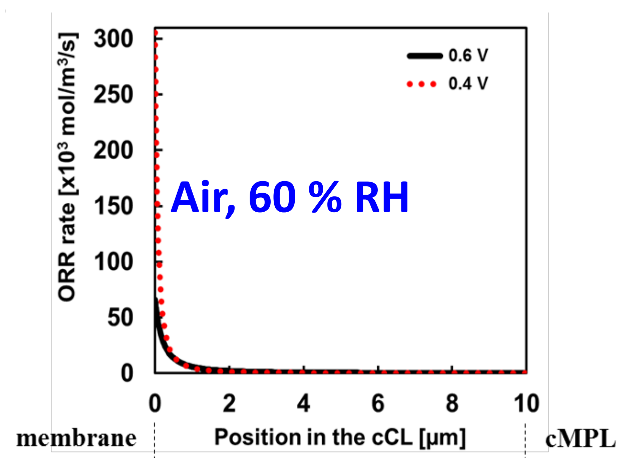
- Models had focused on pure O_2, high RH
- At low RH, narrow electrode reaction distributions observed
  - Ohmically limited
  - Poor catalyst utilization
- At low oxygen concentrations
  - Mass-transport limitations



½ Air, 100 % RH





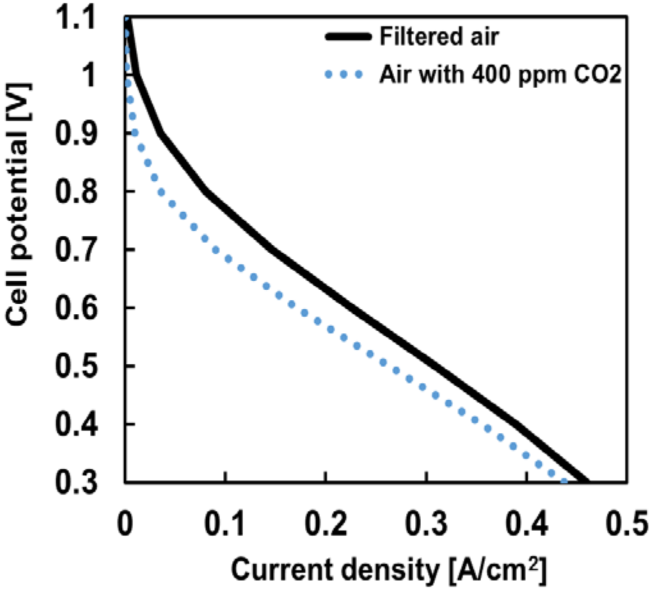


Accomplishments and Progress

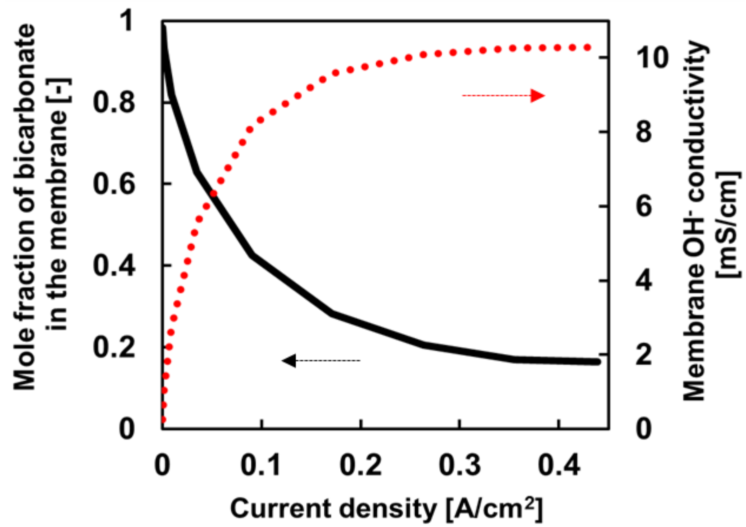
Role of Carbon Dioxide (Carbonate Formation)

- **The membrane in CO_3^{2-} form can be restored to OH^- form at high current density due to OH^- generation and thus self-purge of CO_2 at anode**

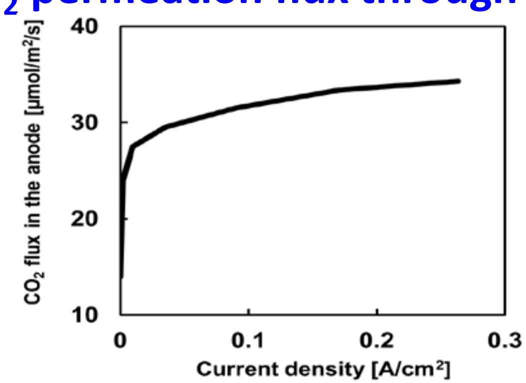
Polarization curve



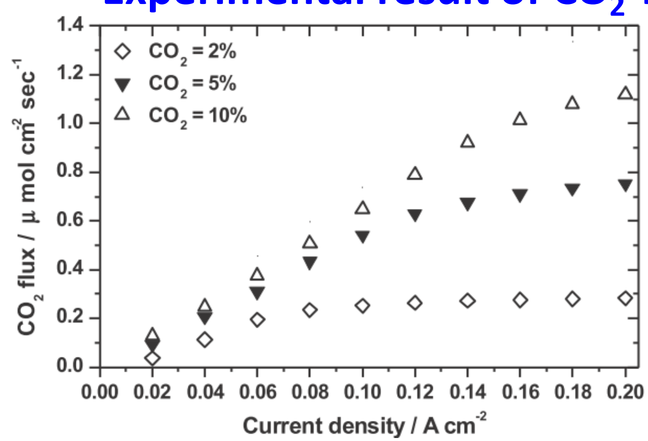
Fraction of CO_3^{2-} in the AEM



CO_2 permeation flux through AEM



Experimental result of CO_2 flux*



*S. Suzuki et al. / Electrochimica Acta 88 (2013) 552– 558

Accomplishments and Progress

Responses to Previous Year (2016 AMR) Reviewer's Comments

- **Reviewer Comment:** The impact of the AEM membrane work will be dependent on whether an effective PGM-free anode catalyst material can be developed or whether the anode and catalyst loadings can be reduced below those currently observed in PEMFC systems.
- **Reviewer Comment:** It is unclear whether AMFCs will ultimately achieve commercial relevance because of poor HOR kinetics and lower conductivity than PEMFCs.
- **Response:** **Both reviewers highlight the concerns of HOR and the ability to use non PGM catalysts and/or ultra low PGM loadings. While these are critical concerns for AMFCs, this project is focused on the membrane development part (and doesn't have adequate funding to include these other critical areas). Significant research is going on in other projects and we have continued interest in this area and would look to leverage work of others for improved electrode/catalysis. All that said, our upcoming milestones include lower catalyst loadings and these will be areas we are beginning to investigate, but the primary focus for this project involves polymer development and implementation.**

- **Reviewer Comment:** AEMFC systems in general are not as well developed as PEMFC systems, so the ultimate limits of what can be done are not known. It may be that there are power limits, or durability limits, or other as-yet unidentified limits that will ultimately make AEM systems not competitive. This is a potential weakness of this general area, but it will take projects such as this one to determine whether AEM systems can be competitive.
- **Response:** **We completely agree.**

- **Reviewer Comment:** A project weakness is the lack of details on MEA fabrication.
- **Response:** **We have tried to include more detail in this year's presentation, however there is a challenge for conveying this type of information in this format and so we also point to references for more detailed information along these lines.**

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (PI), Andrew Park, Matt Sturgeon, Ami Neyerlin, K.C. Neyerlin, Shaun Alia, Logan Garner, 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	**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).**
3M (3M): Mike Yandrasits, Krzysztof Lewinski, Steve Hamrock	**In-kind; Consulting on novel chemistries; preparation of solutions and dispersions; membrane fabrication.**

University of Connecticut (UConn): Bill Mustain, Travis Omasta; advanced electrode/GDE

Remaining Challenges and Barriers/Future Work

- Polymer Synthesis:
  - Avoid sulfonamide linkage
  - Focus on Gen 3 polymer development
- Characterization:
  - Obtaining information about membrane properties (including stability)
  - Continuing studies on stability, conductivity, 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, and impedance (and water management)
    - Ex-situ: microscopic, electrochemical, and spectroscopic analysis
  - Integration of modeling efforts with cell testing
    - Further elucidation of the impact of operating conditions (T, RH, current density, CO_2 concentration)

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.
- Currently involved in 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.
- Co-led AMFC Workshop, May 1, 2016 involving over 50 participants from academia, industry and government. Contributed to/Co-led Workshop Report.

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

Summary

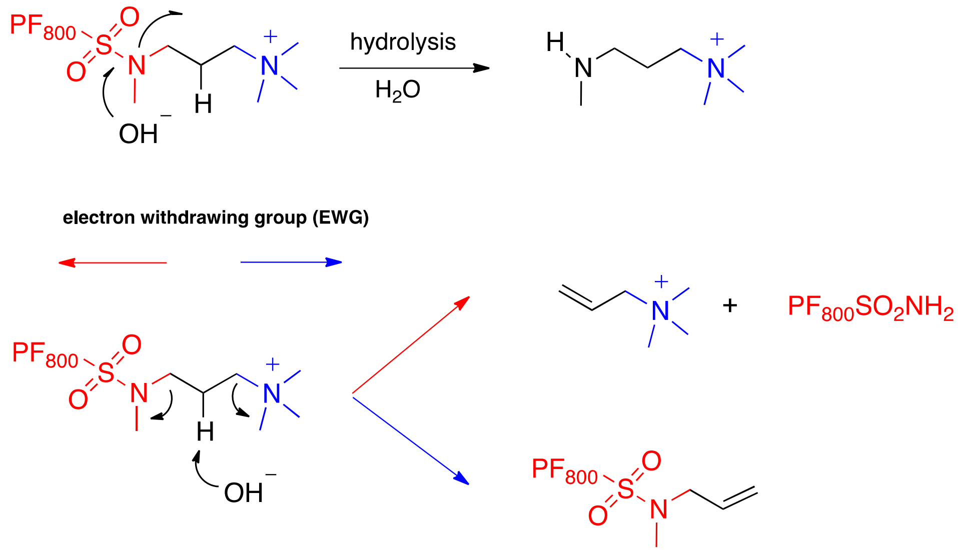
- **Relevance:** AMFCs offer promise for improved performance and decreased cost.
- **Approach:** Synthesize, characterize and optimize membrane and fuel cell performance and durability using modeling and advanced diagnostic/ characterization techniques.
- **Accomplishments and Progress:** This year saw significant advances in technology by the improved performance, durability and processing of **Gen 2 PFAEMs**. The implementation of these materials plus UConn GDEs has allowed us to demonstrate performance **~1W/cm^2** and durability beyond **500 hours** (demonstrating a 2017 Q2 DOE milestone). Model development is providing insight into the role of **water and carbon dioxide** in these systems. 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

Main Degradation Routes of Gen-1 and Gen-2 PFAEM

Gen-1 PFAEM

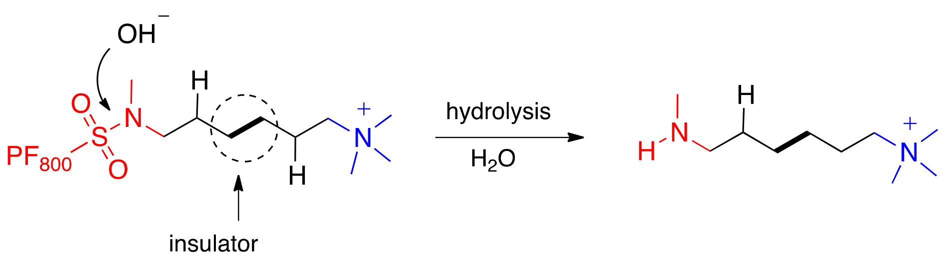


sulfonamide degradation

sulfonamide degradation
via β-elimination of sulfonamide

cation degradation via
Hofmann elimination of amine

Gen-2 PFAEM

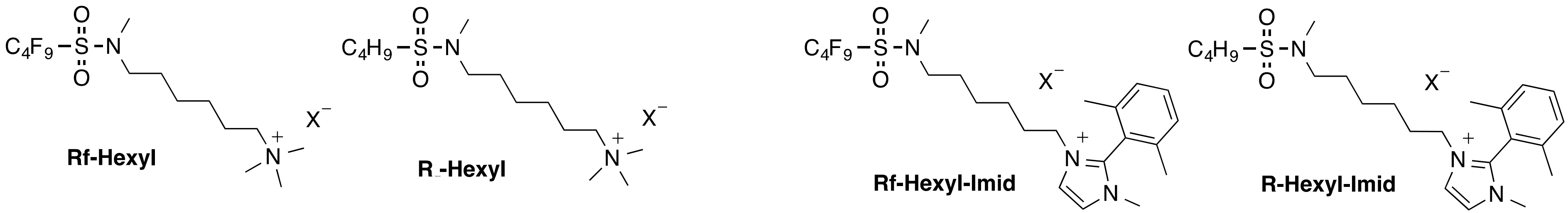


sulfonamide degradation only

Longer alkyl chain in Gen-2 acts as an insulator which suppress electrons movement and cation degradation

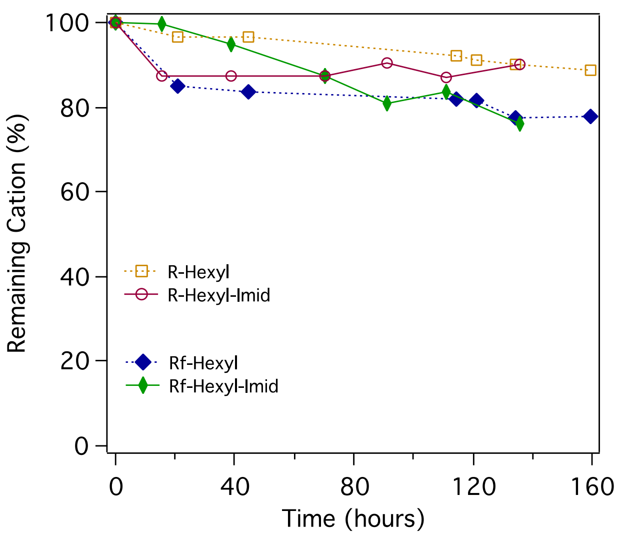
Accomplishments and Progress

Blocking Hoffman Degradation Provides Key Info about Stability of Sulfonamide Linker

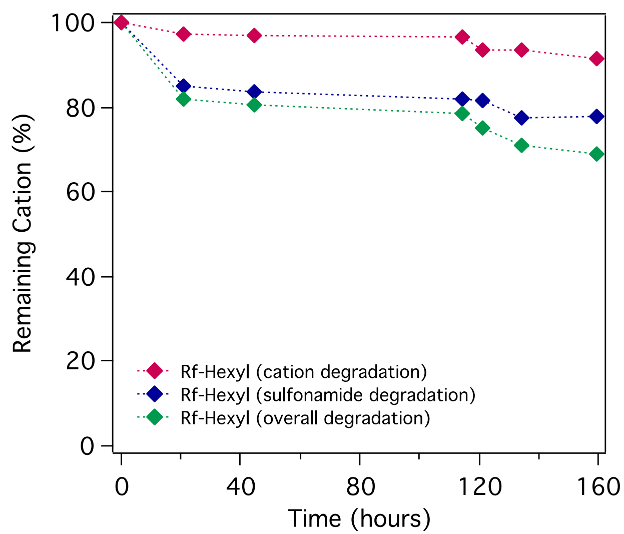


Rf-Hexyl **R-Hexyl** **Rf-Hexyl-Imid** **R-Hexyl-Imid**

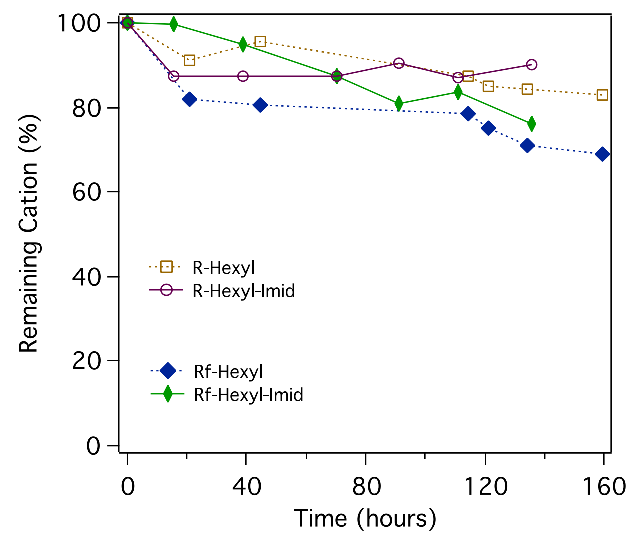
Sulfonamide linker degradation only:



Contributions of multiple deg. routes (**Rf-Hexyl**):



Comparison of overall degradation:



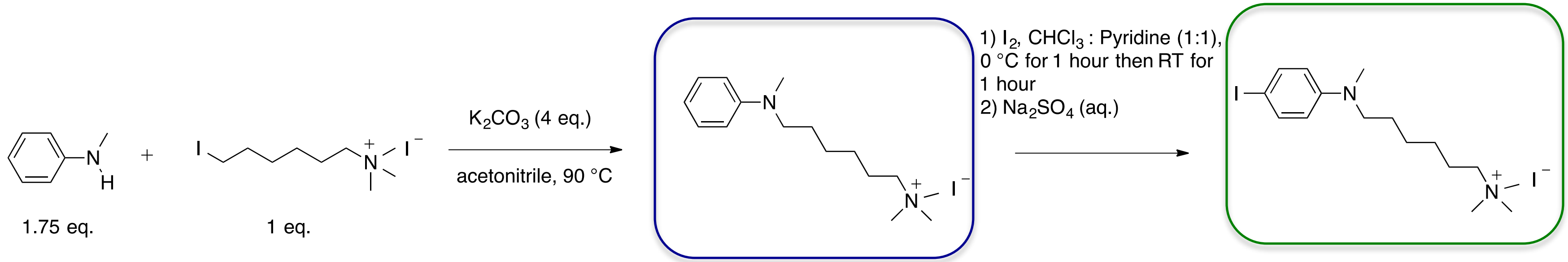
With Gen 2 PFAEM, dominant route of degradation occurs at sulfonamide linker – improving cation stability (with novel imidazolium) does not markedly improve polymer stability. Future small molecule efforts will focus on alternate linkages.

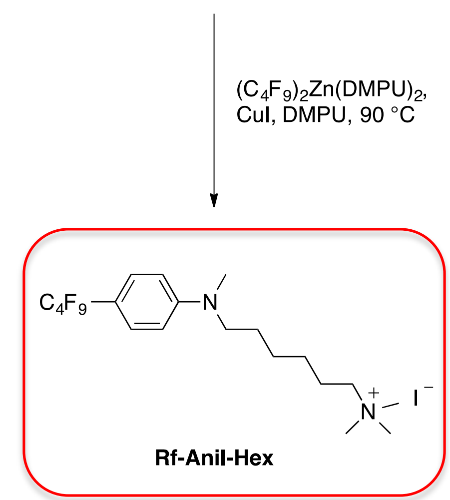
Accomplishments and Progress

Synthesis of New Non-sulfonamide Model Cation (Gen 3)

Very pure material obtained in high >95% yield

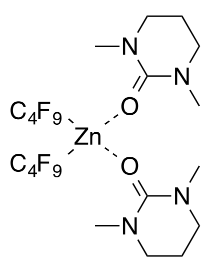
Very pure product obtained in ~95% yield



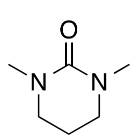


Key reagent and solvent of final reaction step:

$(C_4F_9)_2Zn(DMPU)_2$ =



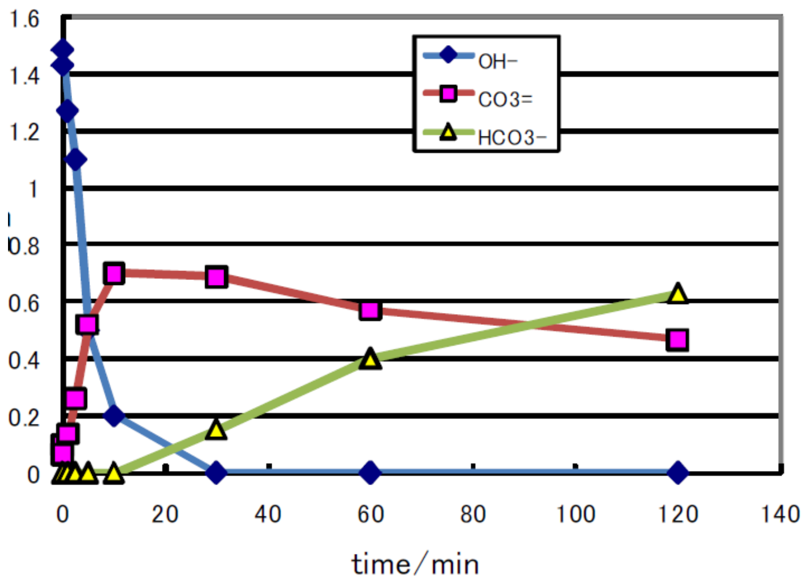
DMPU =



Accomplishments and Progress

Carbon-dioxide uptake of PFAEM Gen2

Collaborators from Colorado School of Mines attempt to study the carbonate(s) formation from OH^- ions when exposed to air containing CO_2.
Our goal is to investigate the kinetics and equilibrium concentration of carbonate and bicarbonate ions when exposed to air at different concentrations of CO_2 and different temperatures.



Kinetics of CO_2 reaction using A201(wet condition) and temperature of20°C
Ref: Yanagi et.al,ECS Transactions, 16(2008)

Important Reactions:

$CO_{2(aq)} + OH^- \rightarrow HCO_3^-$

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H2O$

Equilibrium concentrations of Gen2 polymer after 24 h:(Assumption- no OH^- remaining)

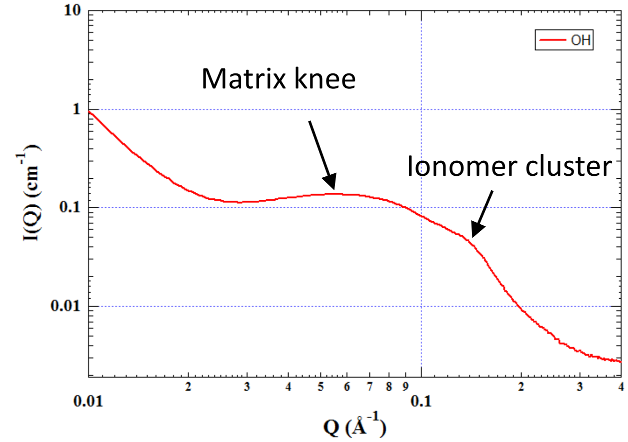
20 °C : CO_3^{2-}(52%) and HCO_3^-(48%) of the total IEC(0.75mmol/gm)

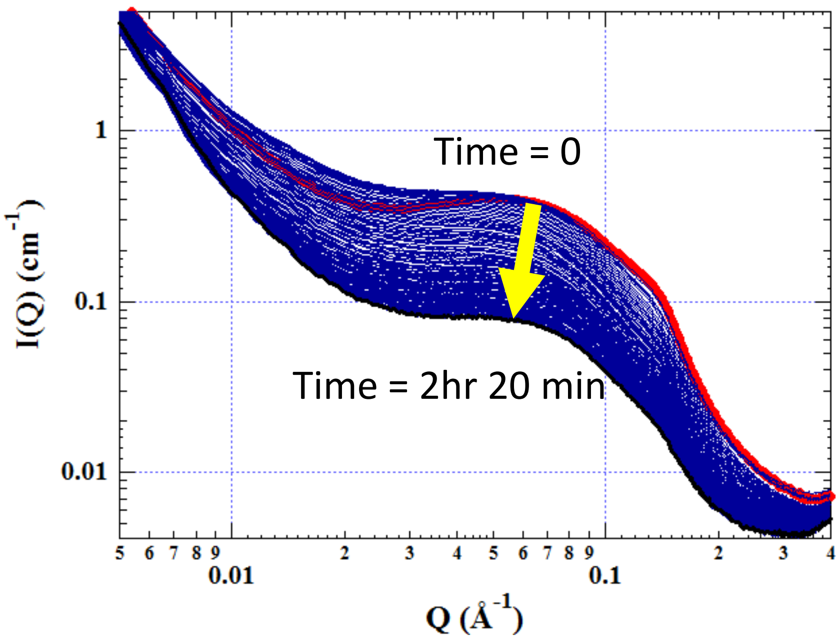
Tokuyama Data:
Last data point was collected at 2 hrs. The data suggests that there is no hydroxide and the only species remaining are carbonate(60%) and bicarbonate(40%). But 2 h is not sufficient to collect the equilibrium values

Accomplishments and Progress

Small angle x-ray scattering (SAXS) of PFAEM Gen2

SAXS data was collected to understand the structure and morphology of the polymer at Advanced Photon Source facility at Argonne National Laboratory, IL.
The scattering data shows 2 distinct features which closely resemble the matrix knee feature(11 nm) and ionomer cluster(4.4 nm) of 3M-PFSA.
The data was collected in different ionic forms to better understand the size of ionomer feature in each form.





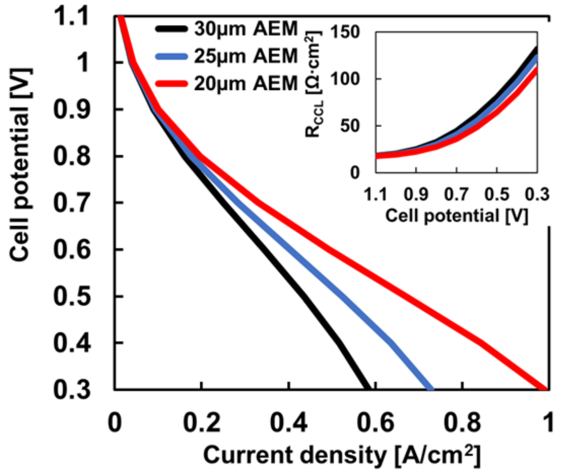
Transient SAXS(OH→HCO_3^-/CO_3^{2-}) at 60 °C & 50%RH

Transient SAXS data of OH^- form of Gen2 polymer when exposed to air was studied. Drop in intensity might correspond to the loss of water as carbonate/bicarbonates are formed. The polymer equilibrates quickly at a lower humidity.
Our goal is to track the peak location to understand the change in ionic domain size over time(Colorado School of Mines).

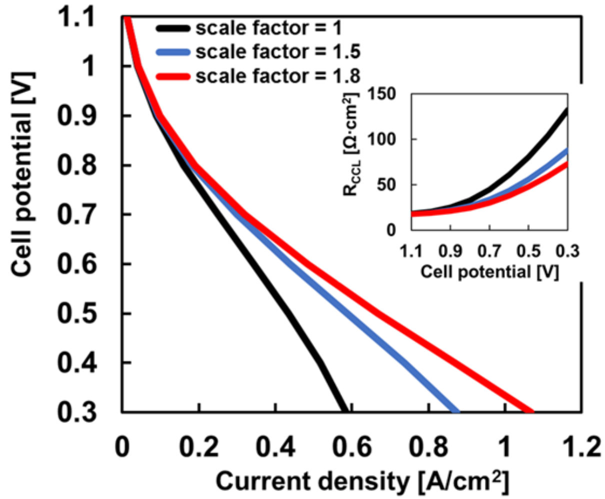
Accomplishments and Progress

AMFC Model Sensitity Studies

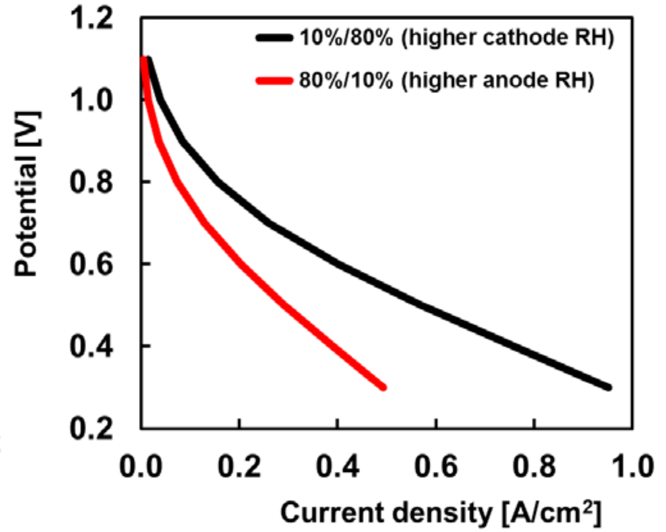
AEM thickness



AEM water diffusivity



Asymmetric humidification

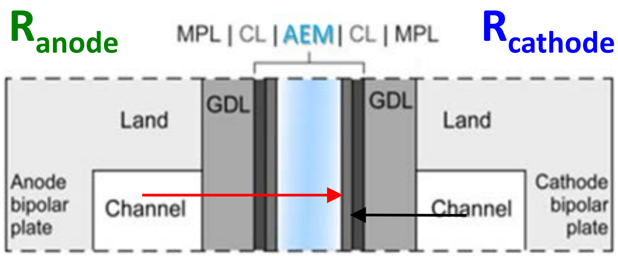


- **Getting more water to cCL is key**
  - Depends on governing resistances

H-S. Shiau, I.V. Zenyuk, and A.Z. Weber, J. Electrochem. Soc., submitted (2017).

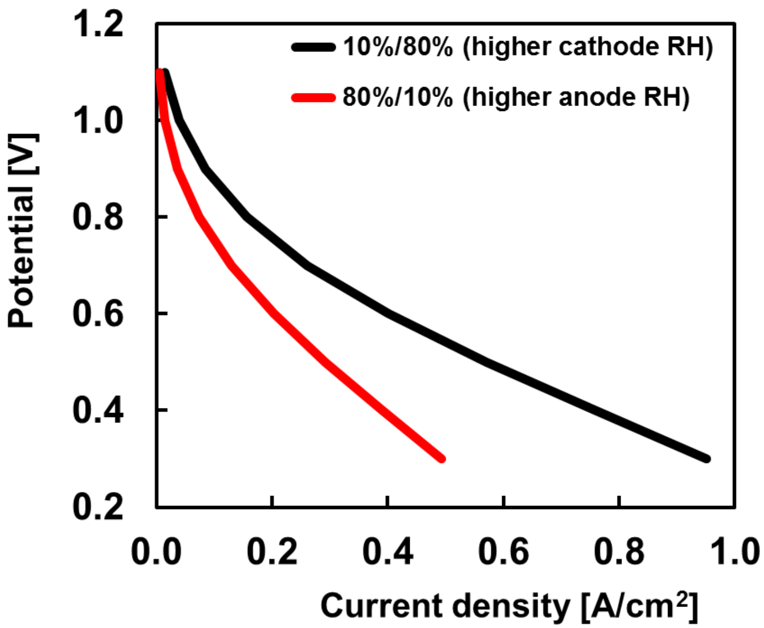
Accomplishments and Progress

Asymmetric Humidification and Transport Resistance to cCL

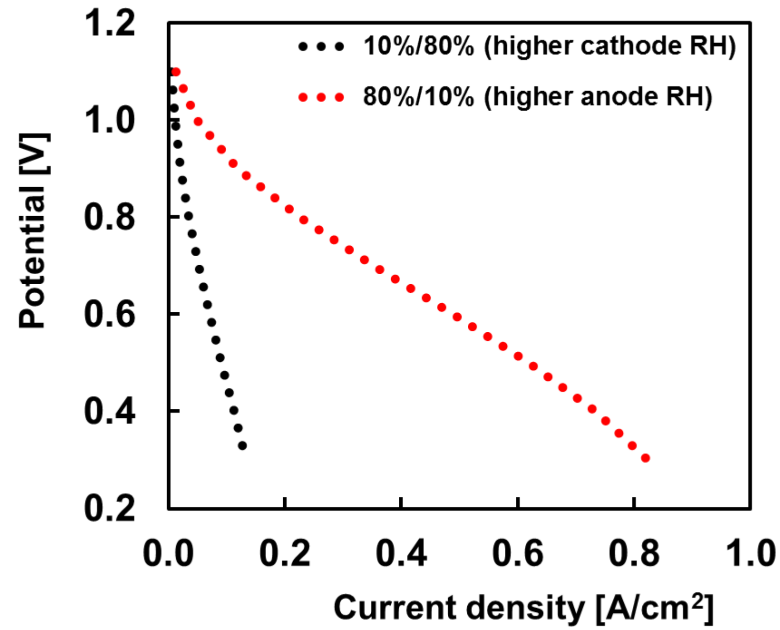


- If AEM has small water diffusivity, humidified cathode causes higher performance than humidified anode
- If AEM has large water diffusivity, humidified anode causes higher performance than humidified cathode

$R_{anode} > R_{cathode}$



$R_{anode} < R_{cathode}$



80%/10% RH $R_{anode} > R_{cathode}$

10%/80% RH $R_{anode} > R_{cathode}$

80%/10% RH $R_{anode} < R_{cathode}$

10%/80% RH $R_{anode} < R_{cathode}$