Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID #FC147

Overview

Timeline and Budget

- Project start: October 2015
- Project end: Sept 2019
- % complete: ~ 85%

- DOE Budget plan
  - FY 2016 - 2019 $3,200k
  - Cost Share Percentage – 0%

Barriers

- Durability
- Cost
- Performance

Partners

- LBNL – Adam Weber
- 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

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).

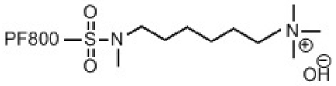
Model Development - Apply models to AMFCs to determine and minimize losses (water management, electrocatalysis, and carbonate related).

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

Approach

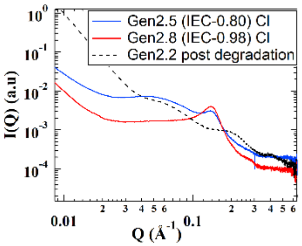
Membrane Synthesis, Electrode Optimization, and Fuel Cell Testing

Novel Polymer Synthesis



PF AEM Synthesis

NREL: provide current material for further testing

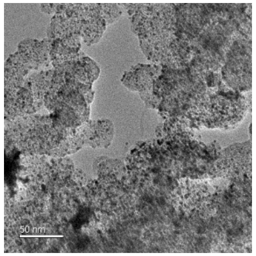


Characterization

NREL: conductivity, IEC

CSM: structure, carbonate

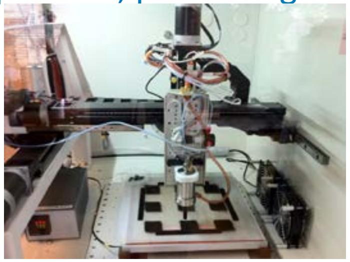
ORNL/UTK: microscopy, NMR



Fuel Cell Optimization

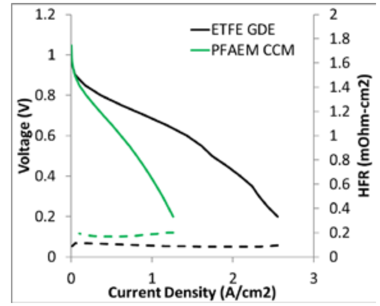
MEA Fabrication/Optimization

NREL: composition, processing



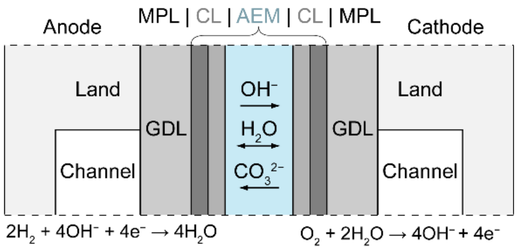
Fuel Cell Diagnostics

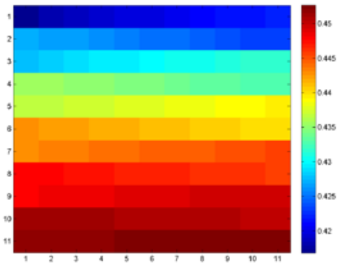
NREL: performance, durability, transport

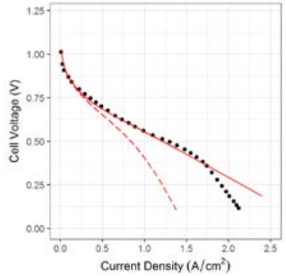


AMFC Modeling

LBNL: water, carbonate management, spatial effects







Approach

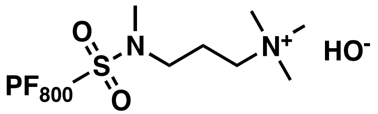
Project Schedule/Milestones

Quantify stability of Gen 2+ small molecule analogue in comparison to Gen 2 small molecule analog.	12/31/2017	Quarterly Progress Measure	**Complete**
Demonstrate in line CO2 sensors on anode and cathode exhaust in CO2 containing fuel cell tests to perform CO2 balance measurements and explore self-purging rates in operating cells.	3/31/2018	Quarterly Progress Measure	**Complete**
Demonstrate modeling of carbonate impacts on AMFC performance under dynamic operation and validate findings with fuel cell performance.	6/30/2018	Quarterly Progress Measure	**Modeling Complete**
Aligned with AEMFC Q2, 2019 milestone: Demonstrate alkaline membrane fuel cell performance of 0.6 V at 600 mA/cm2 on H2/air (maximum pressure of 1.5 atma) at T>60 C for >2000 hours, targeting <10% voltage degradation.	9/30/2018	Annual Milestone	**TBD**

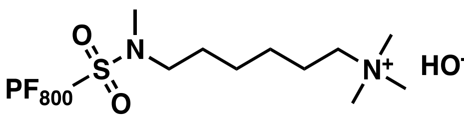
Accomplishments
PF AEM Efforts

Gen 2 PF AEM Synthesis Optimization

Gen 1 PF AEM Polymer

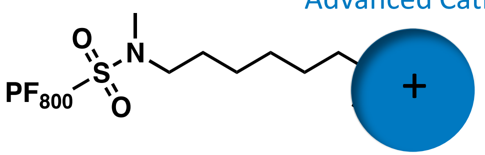


Gen 2 PF AEM Polymer



Gen 2+ PF AEM Polymer

Advanced Cation

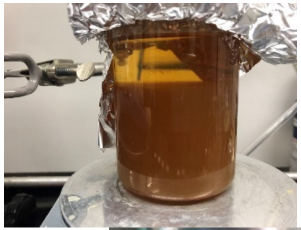


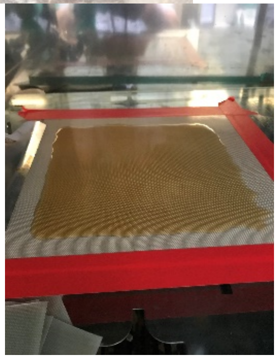
Gen 2 Status

- >400 g Gen 2 PF AEM polymer has been produced to date
- Properties consistent with PFSA analogues
- Polymer samples provided to over 30 research groups

Gen 2+ Status

- Established synthesis route
- Optimization underway
  - Ionomer appears to have improved solubility during synthesis.
  - Lower conversion of sulfonamide to tethered cation (low IEC)
  - Exploring stoichiometry, concentration and reaction time to improve conversion



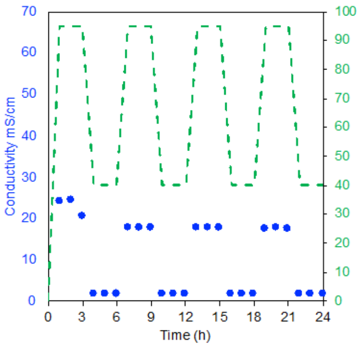


A.M. Park et al, *ECS Trans.* 2017 **80(8)**: 957-966; doi:10.1149/08008.0957ecst

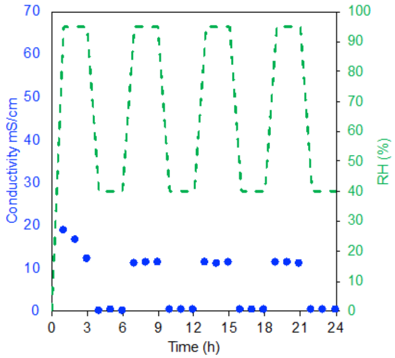
Accomplishments and Progress
PF AEM Characterization/Ex-situ Durability Studies

Conductivity (RH, T)

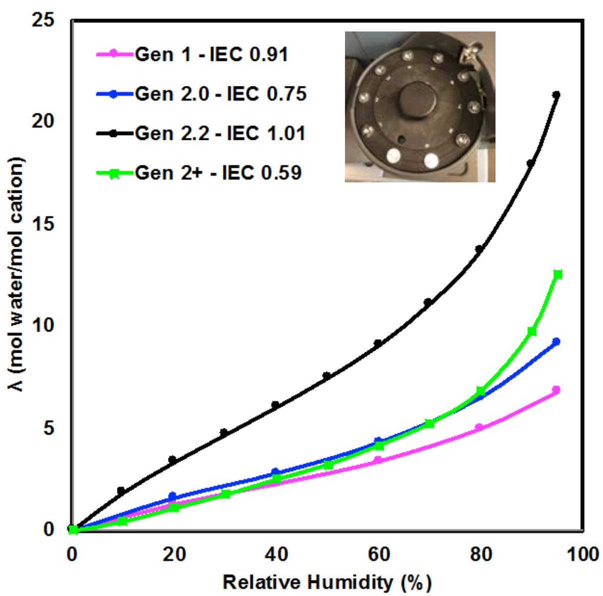
Gen 2 – Cl$^-$

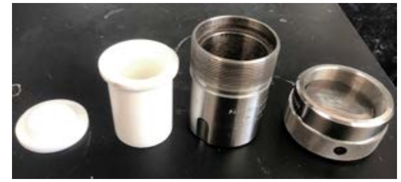


Gen 2+ – Cl$^-$



Water Uptake - DVS





Degradation

- Teflon-lined Parr reactors (20 mL)
- Dry samples of ~100 mg in Cl$^-$ form
- 1 M KOH (10 mL)
- 80 °C in oven for 1000 h
- IEC tested before/after
- RT Liquid H_2O Cl$^-$ Conductivity tested before/after

Gen 2

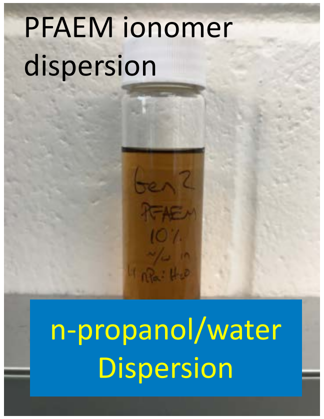
- More opaque color
- Still soft/flexible
- Broken/tears easily
- IEC ↓ 2.8%
- Conductivity ↓ 21%

Approach
Electrode Development (2018 AMR)

- We had focused on two specific electrode approaches:

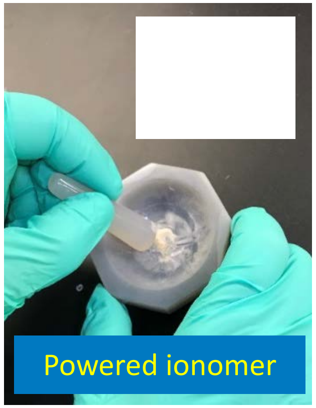
Ionomer Dispersion

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



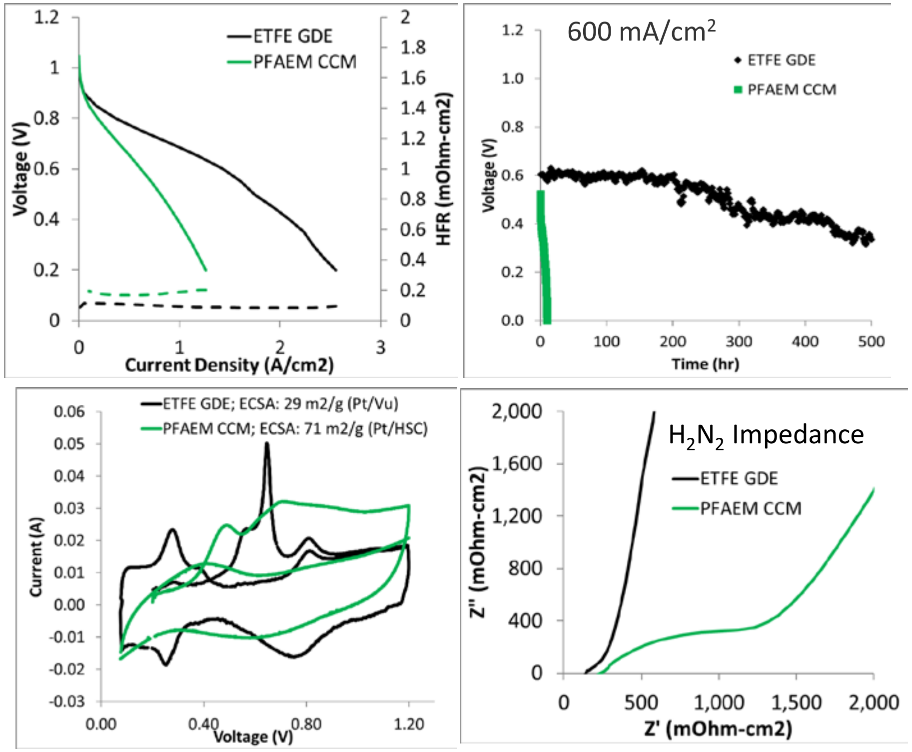
Ionomer Powder

- 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^2, 5A/cm^2), 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

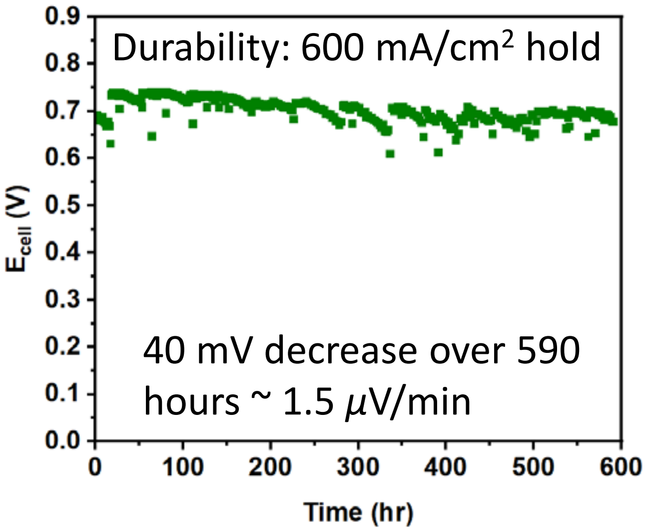
PFAEM Gen 2 membranes, 60^{o}C, H_2/O_2



- 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.

Durability Advances of AMFCs

NREL Gen2 PF AEM + USC Electrodes (H_2/ CO_2-free Air)

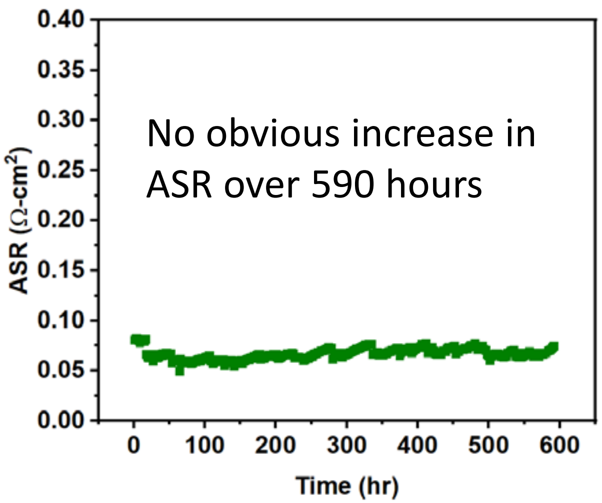


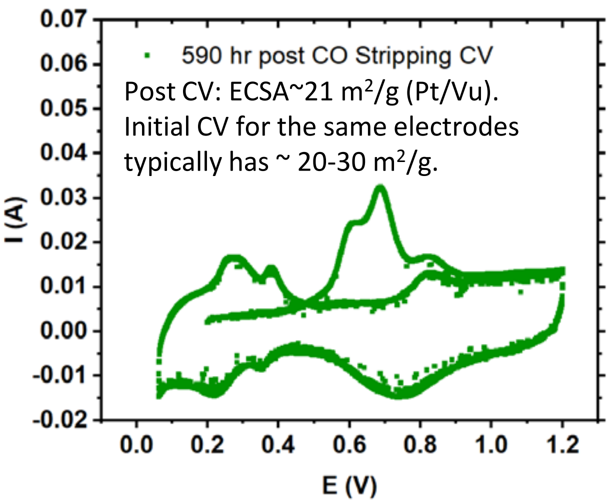
Annual milestone: 9/30/2018, Completed.

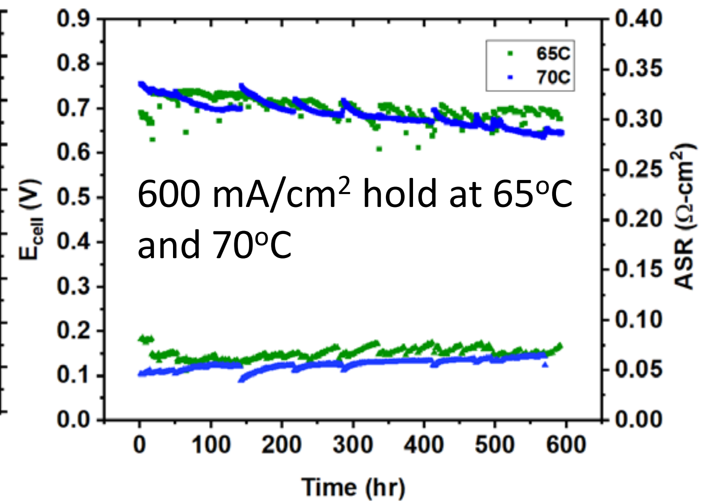
Demonstrate alkaline membrane fuel cell performance of 0.6 V at 600 mA/cm2 on H_2/air (maximum pressure of 1.5 atma) at T>60 C for >500 hours.

- Significant improvements in durability achieved.
- Relatively stable HFR.
- Relatively stable electrodes.
- Temperatures stability established up to 70°C

- 1.0 slpm, 5 cm², 100-132 kPa_{abs}
- Anode: 0.7 mg/cm² PtRu/Vu
- Cathode: 0.6 mg/cm² Pt/Vu

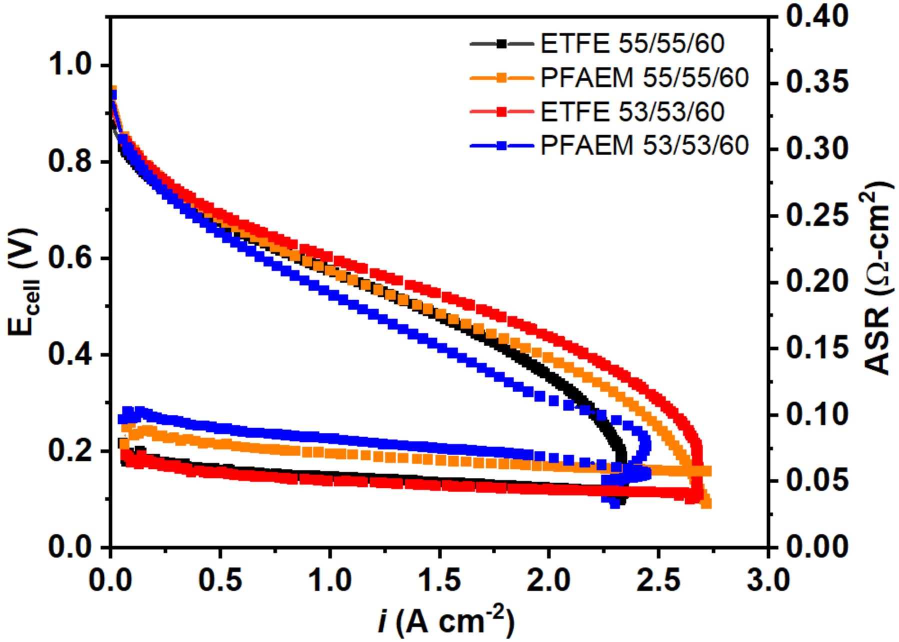




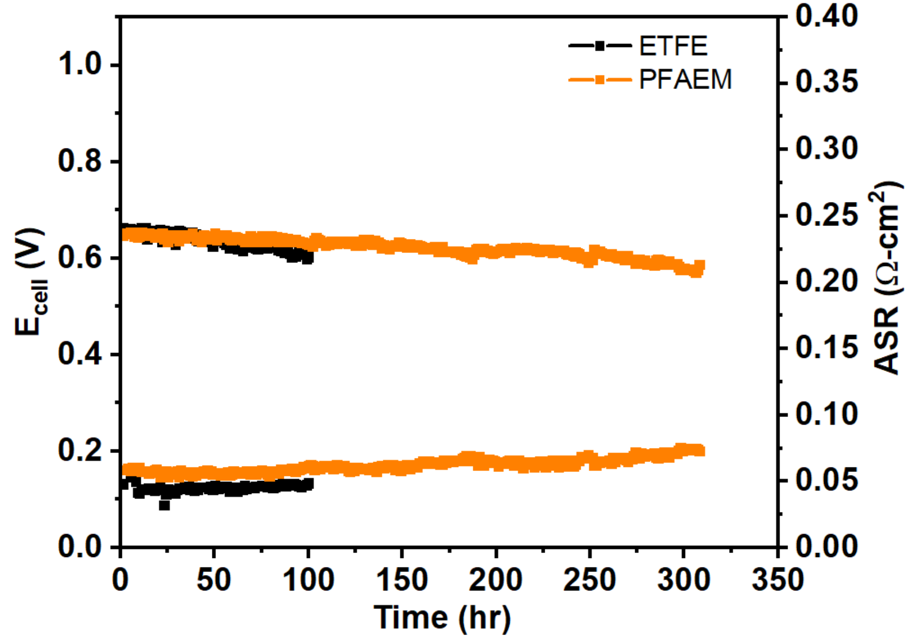


Accomplishments and Progress
Improved PF AEM Electrode Performance

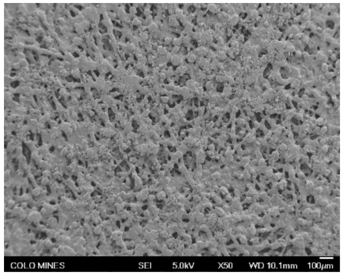
- Solid polymer (GDE) approach adapted to PF AEM
- A side-by-side comparison of optimized PF AEM and ETFE electrodes (~ 0.4 mg cm^{-2} Pt/Vu anode and cathode)



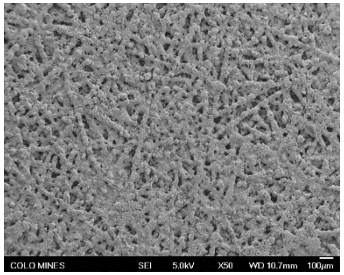
600 mA/cm^2 hold durability test, H_2/O_2, 60°C, 121 kPa_{abs}, 95%RH



PFAEM electrode



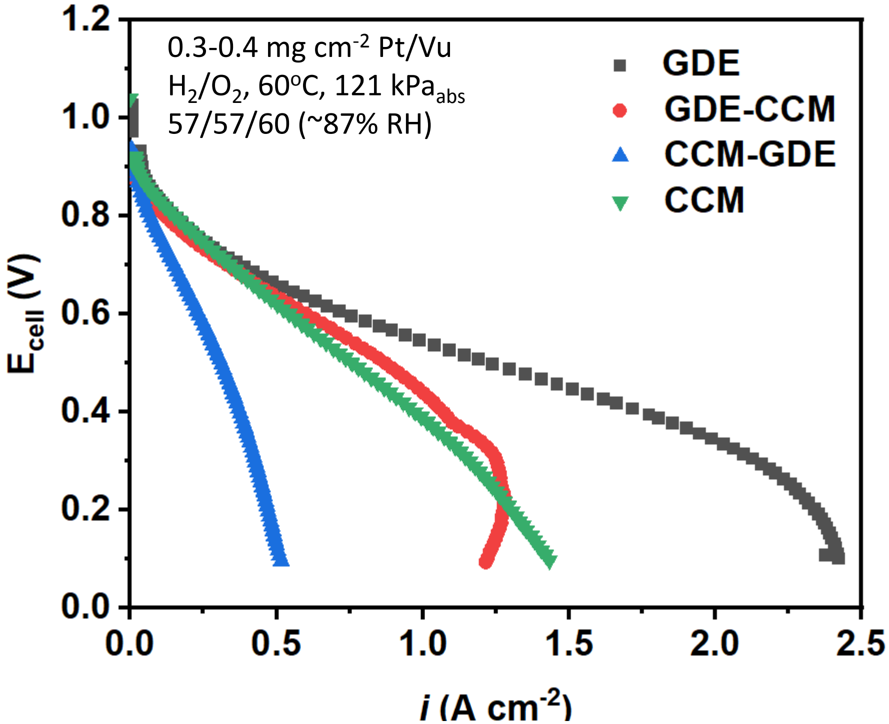
ETFE electrode

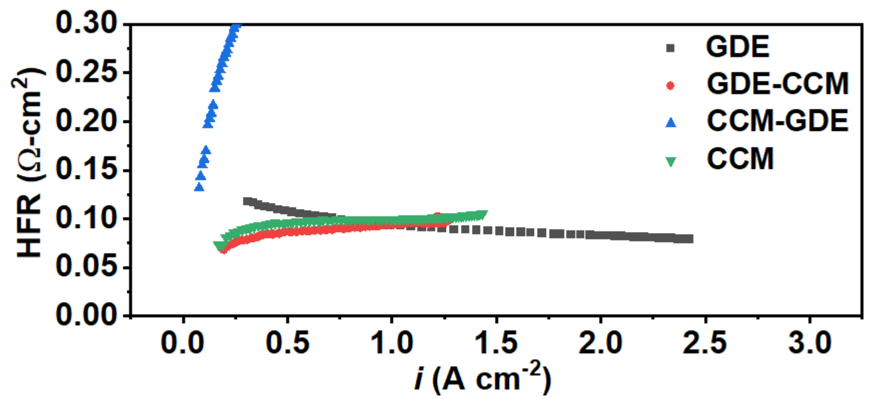


- ✓ Equivalent performance and durability achieved.
- ✓ HFR higher for PF AEM electrodes.
- ✓ Similar visual appearance.
- ✓ Slight differences depending on RH, PF AEM electrodes slightly better wet, ETFE electrodes slightly better dry.
- ✓ Processing conditions found more important than polymer structure.

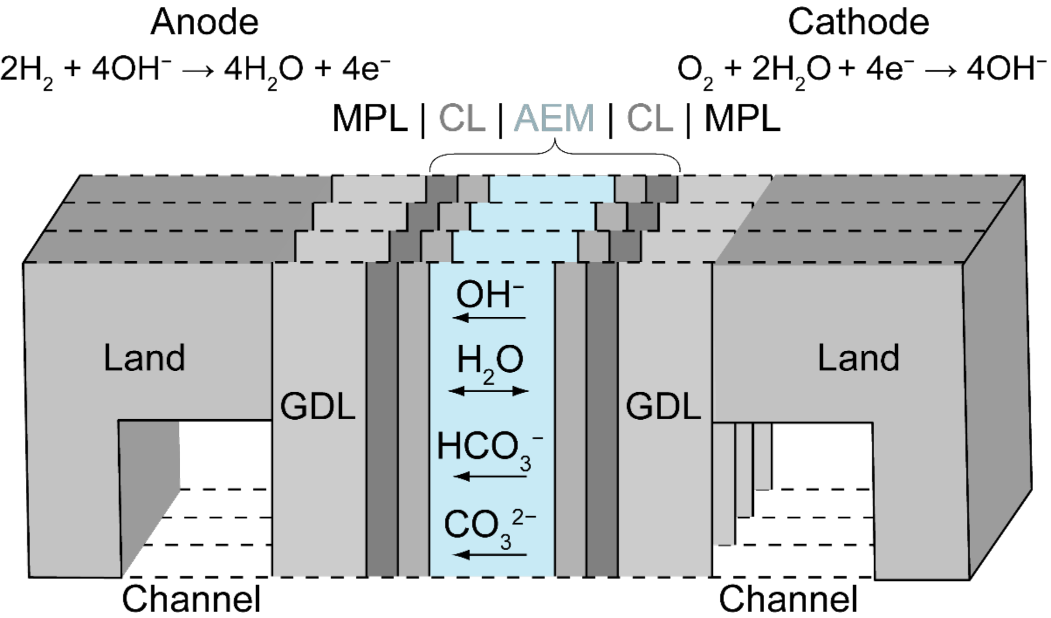
Accomplishments and Progress
Asymmetric MEAs by Applying PF AEM CCM and GDE Electrodes

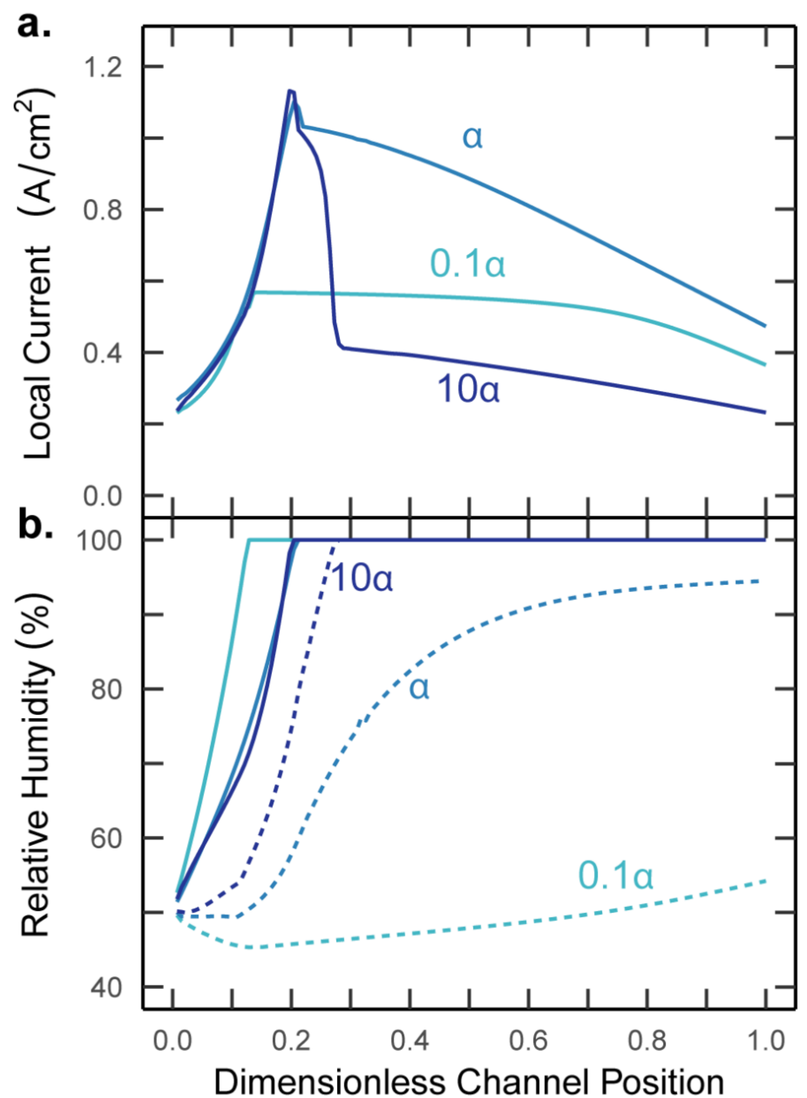
- Optimum anode and cathode will be different.
- As NREL has multiple electrode capability (processing, deposition, access to materials), we performed investigations of symmetric and asymmetric MEAs :
- Presented here is an investigation of GDE vs CCM processing of PF AEM electrodes, where we have found:
  - Symmetric GDE approach offers highest performance
  - CCM (anode) - GDE (cathode) showed poor performance, HFR suggests membrane dry out key issue.
  - Other cells configurations show intermediate performance, trends in HFR with current density provide water management information.





Accomplishments and Progress
Modeling Approach and Results (LBNL)





- **Last time:** Model shows importance of anode-to-cathode water flux
- **New work:** Extended model down channel to study carbonate and water transport effects
- Membrane water transport properties are critical
  - Too fast (high α) and cathode floods
  - Too slow (low α) and cathode dries out

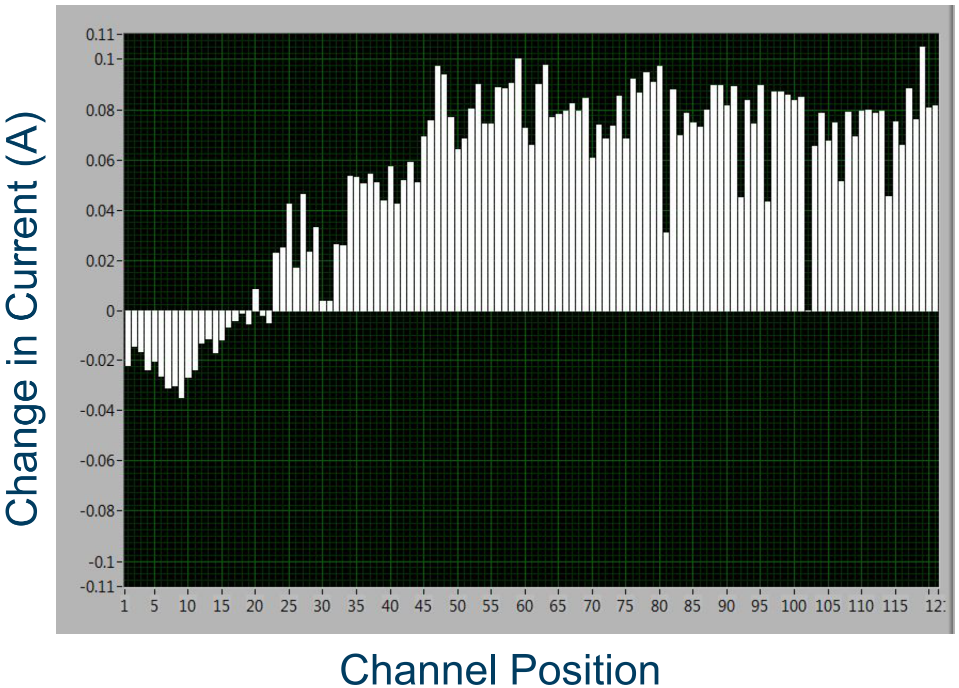
α = membrane water transport coefficient

Water flux $N_{H_2O} \sim \alpha \nabla \mu_{H_2O}$

Accomplishments and Progress
Model Validation for Down Channel Water Management

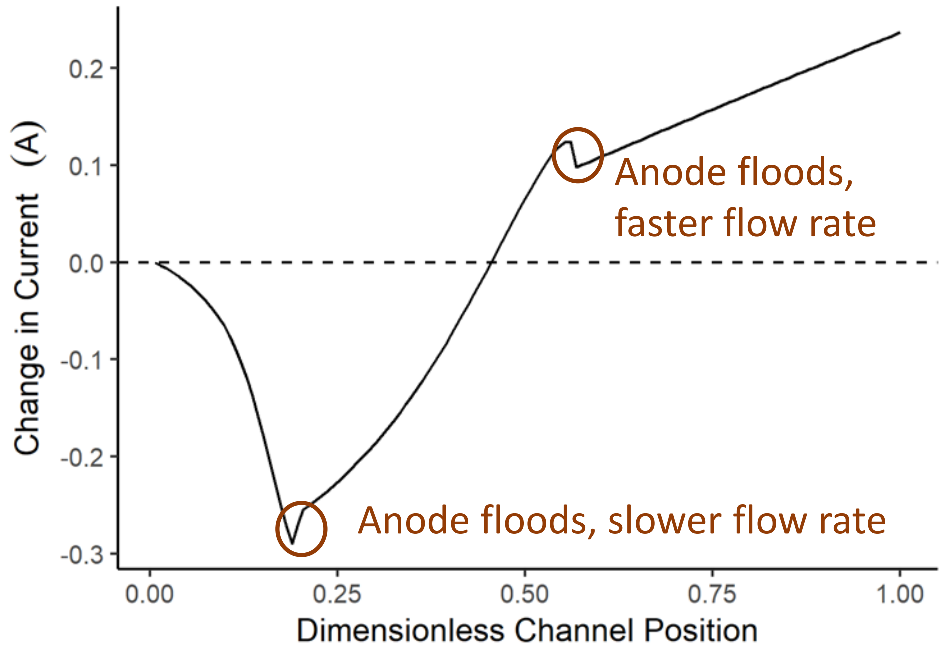
NREL Segmented Cell Experiment

Change in current density upon increasing flow rate (0.75 – 1.00 slpm)



LBNL Model

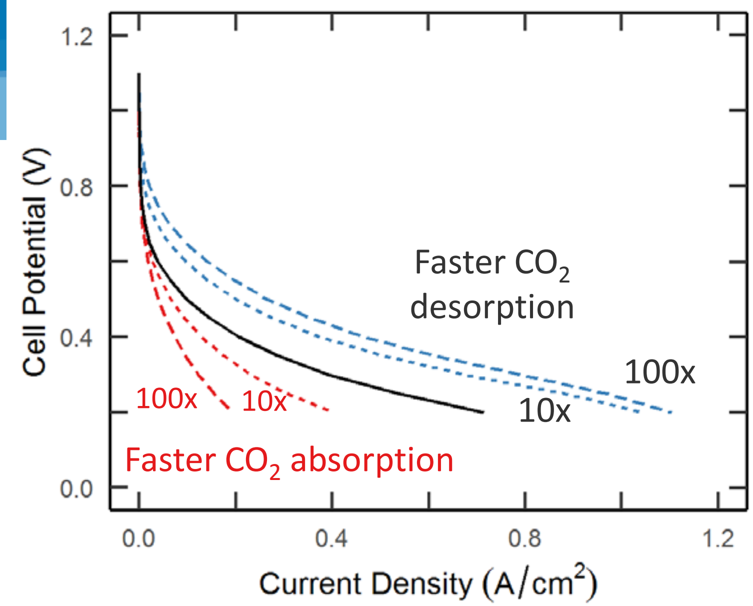
Change in current density upon increasing flow rate (0.32 – 1.00 slpm)

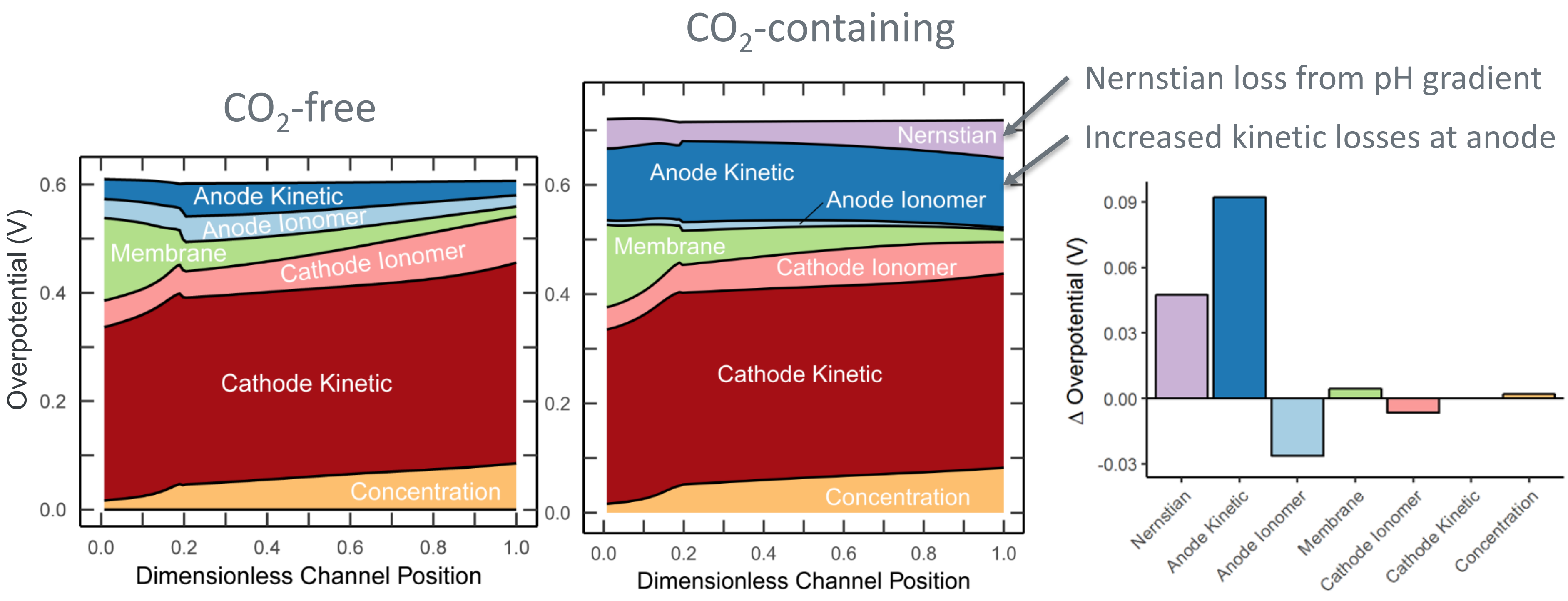


- Higher flow rate reduces membrane hydration initially, causing current decrease
- Mass transport improves further down channel, causing current increase
- Continuing to work on quantitative agreement between model and experiment

Accomplishments and Progress Modeling CO_2 effects on AEMFCs

- CO_2 absorption and desorption kinetics impact AEMFC performance
- CO_2 related performance losses can be quantified in terms of importance with Nernstian and anode kinetics dominating.





Models run at 60 °C with H_2 and air at 50% RH, 1.2x stoich flow, 0.72 A/cm^2 average current density

Accomplishments and Progress
Responses to Previous Year (2018 AMR) Reviewer's Comments

- Reviewer Comment: The Gen 2 polymer did not work well as an electrode binder compared to an ETFE material that has been developed and tested by others. Fuel cell tests with a PF-AEM catalyst-coated membrane were lackluster.
- Response: We have greatly advanced the performance of all PF-AEM MEAs, specifically by optimizing the composition and processing parameters associated with MEA fabrication, and we currently have shown PF-AEM electrodes with comparable performance to ETFE electrodes. This is a significant advancement of science in this area as demonstrating that other ionomers are capable of achieving these high levels of performance with proper processing potentially opens up options for electrode materials, design and development.

- Reviewer Comment: The most critical barriers, such as membrane stability in an alkaline environment and anion-exchange membrane fuel cell (AEMFC) performance and durability issues, have been addressed. However, more fundamental barriers for the application, such as the impact of carbonate/bicarbonate formation and its impact on membrane properties, including stability, and on fuel cell performance and durability, have been addressed only to some extent./It is unclear how AMFC modeling is being used to support development; there is no model validation with data.
- Response: We have included more effort in the past year focusing on carbonate/bicarbonate. This includes modeling work, some of which we have begun validating with experimental results. On carbonate specifically, we have identified the specific loss mechanisms and have publications submitted and/or published on the topic.

- Reviewer Comment: The work addresses the performance and durability of AEMFCs. A PF-based AEMFC provides some potential advantages for phase separation to improve conductivity and for water management. The project still appears to focus on alkylammonium cations, even though the work indicates these cationic groups are degrading and more stable cationic groups have been identified in previous work.
- Response: In the past year we have developed Gen 2+ chemistry that moves beyond ammonia cations and includes advanced cations. Initial results have shown good durability over the first 165 hours of operation using Gen 2+ membranes.

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**
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; supply of precursor polymers.**

University of South Carolina: Bill Mustain, Xiong Peng, Travis Omasta; advanced electrode/GDE
University of Surrey: John Varcoe, ETFE membrane and ionomer
Colorado School of Mines (CSM): Svitlana Pylypenko and Samantha Medina; SEM images
Many others whom have used/studied Gen 2 PF AEM

Remaining Challenges and Barriers

- Polymer Synthesis:
  - Increased stability, decreased catalyst ionomer interactions
- Characterization:
  - Membrane and electrode properties (including stability)
- AMFC implementation, Modeling, and Diagnostics:
  - Improved performance and durability in cells, power density no longer driver
    - Low PGM loading
    - CO_2
    - Robustness (water management)
  - Closing the gap between experimental and modeling efforts

Future Work

- Polymer Synthesis:
  - Improving IEC of Gen 2+ materials through reaction optimization studies
- AMFC implementation, Modeling, and Diagnostics:
  - Electrode optimization and diagnostic studies focused on further characterization of electrodes and elucidating performance loss and durability.
    - Low PGM studies
    - Robustness studies
    - CO_2 impact quantification
    - Application of advanced diagnostics
      - 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_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.

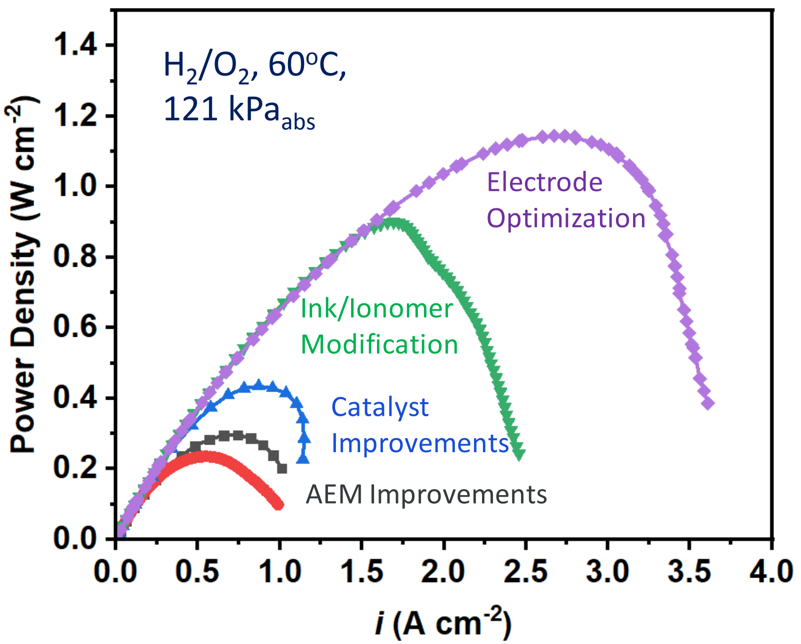
- Involvement with multiple projects leveraging core membrane technology being developed have included (Incubator projects with Giner, Inc (Reversible Fuel Cells) and University of Delaware (Redox Flow Battery) and SBIR Project with pHMatter, Inc (Reversible Fuel Cells). SBV project with Midwest Energy Group. As well as supply of polymer materials to over 30 entities.

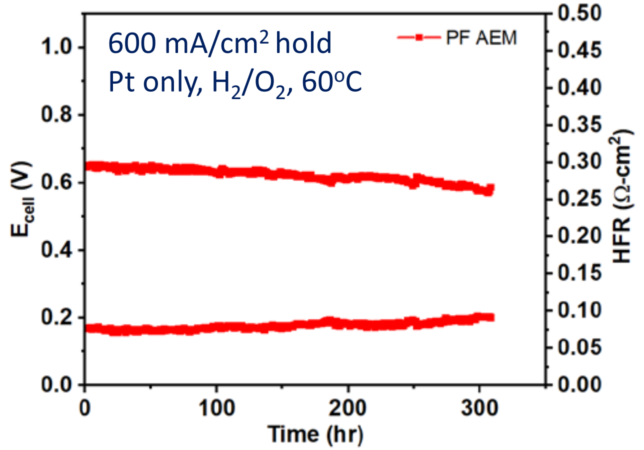
- Sponsoring and co-organizing Anion Exchange Membrane Workshop, May 30, 2019, Dallas, TX.

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 we advanced Gen 2+ chemistry. We made significant advances in performance and durability focusing on electrode optimization, demonstrating high performance with fully PF AEM MEAs. 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, 1 university, and 1 industry participant that are leaders in the relevant fields of PF polymer electrolytes (3M), characterization (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.

Gen2 PF AEM + Ionomer Electrodes

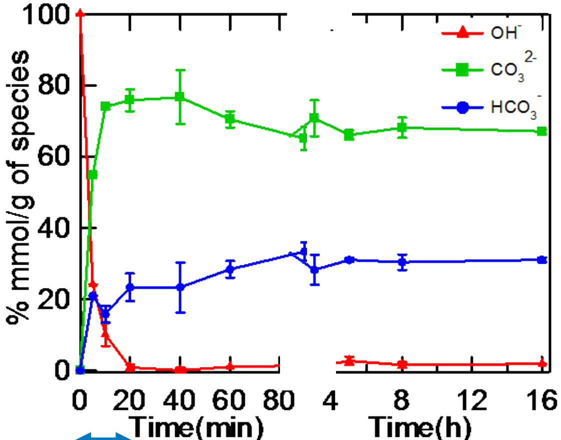


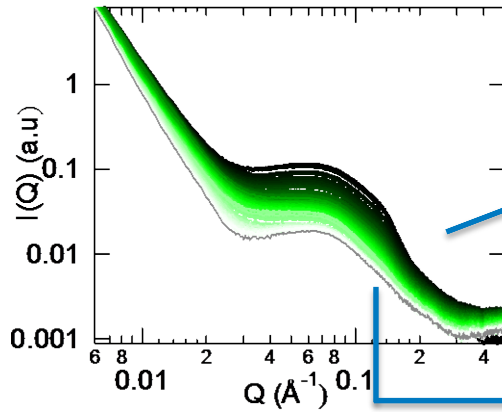


Technical Backup Slides

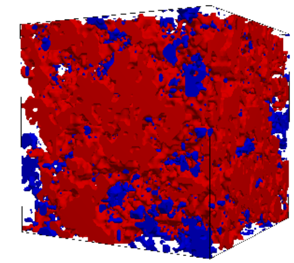
Accomplishments and Progress
Probing Carbonate and Structure (CSM)

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

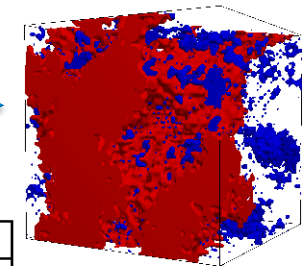




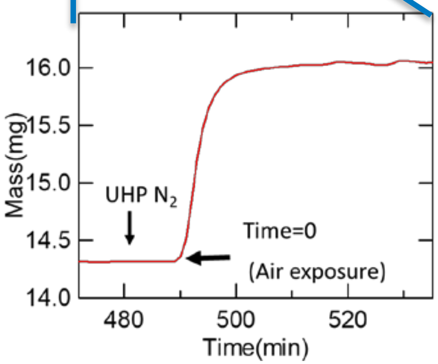
Transient Small angle x-ray scattering of OH- sample in Air(400 ppm CO_2)



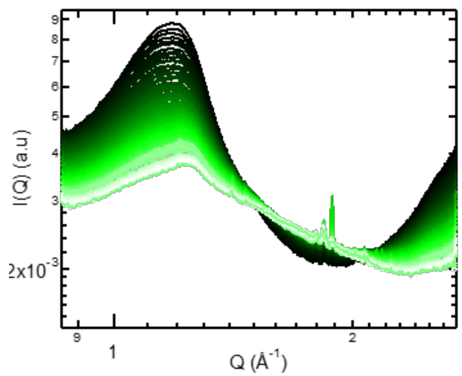
OH^- form



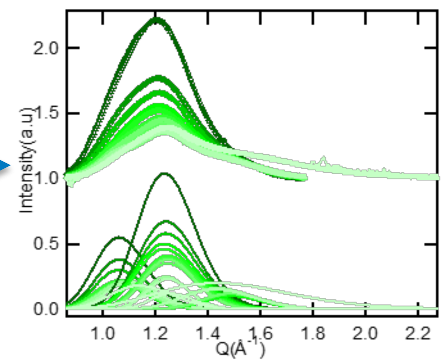
HCO_3^-/CO_3^{2-} form



Transient change in mass when exposed to air(400 ppm CO_2)



Wide-angle x-ray scattering to study changes in backbone crystallinity



Equilibrium Reactions:

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

$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$

- Carbonation leads to increase in mass of AEM
- Changes in small-angle x-ray scattering will help us understand the transition of 3D-morphology
- Wide-angle x-ray scattering data indicates the polymer is loosing crystallinity

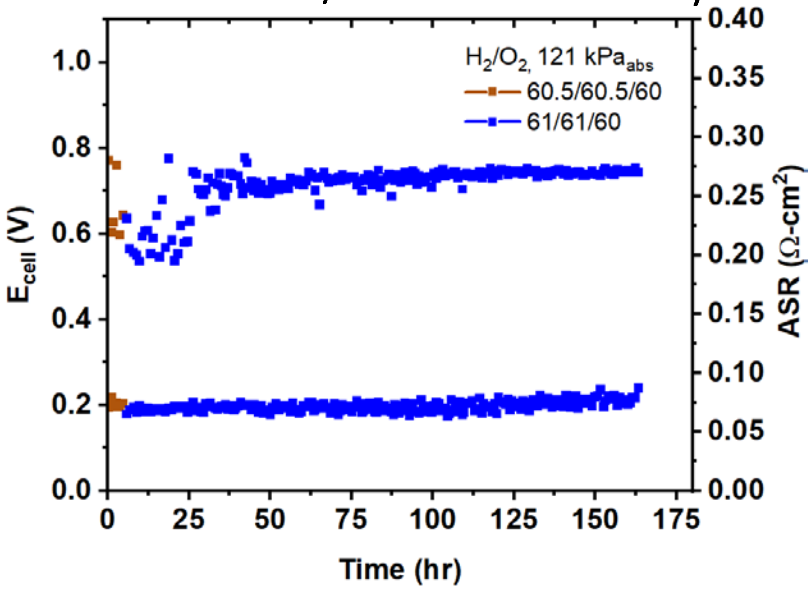
Divekar et al.,, ECS Trans. 2017 80(8): 1005-1011; doi:10.1149/08008.1005ecst

MEA Performance and Durability of Gen2+ AEM

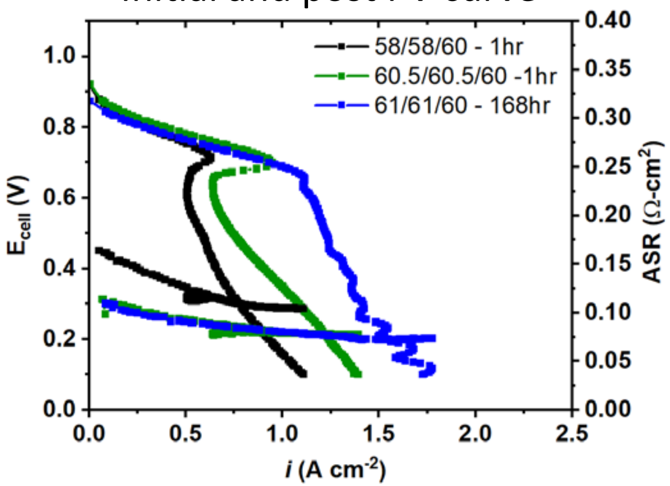
NREL Gen2+ PF AEM + USC Electrodes (H_2/O_2)

- Over 168 hr in-situ durability test hold at 600 mA/cm^2, no loss in cell voltage.
- Due to low IEC value of Gen2+ AEM, initial performance was low at RH% ≤ 100%; after increasing RH% to be oversaturated ~ 103% RH, performance increased obviously and held over 168 hr.

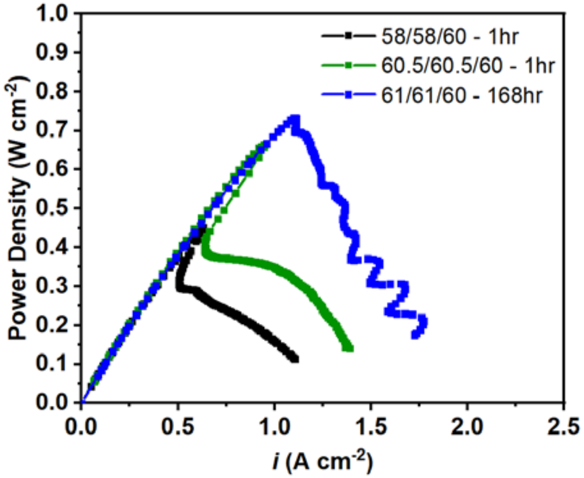
600 mA/cm^2 hold durability



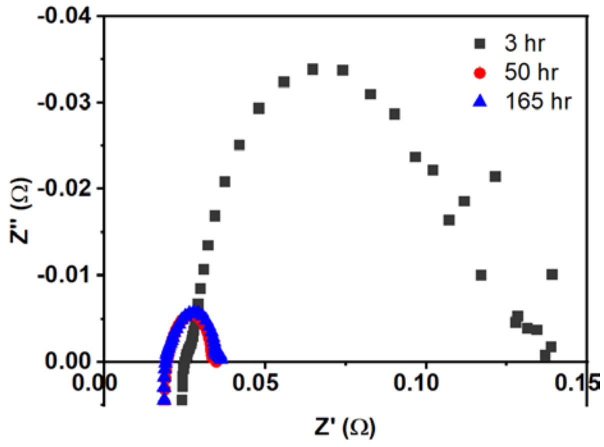
Initial and post PV curve



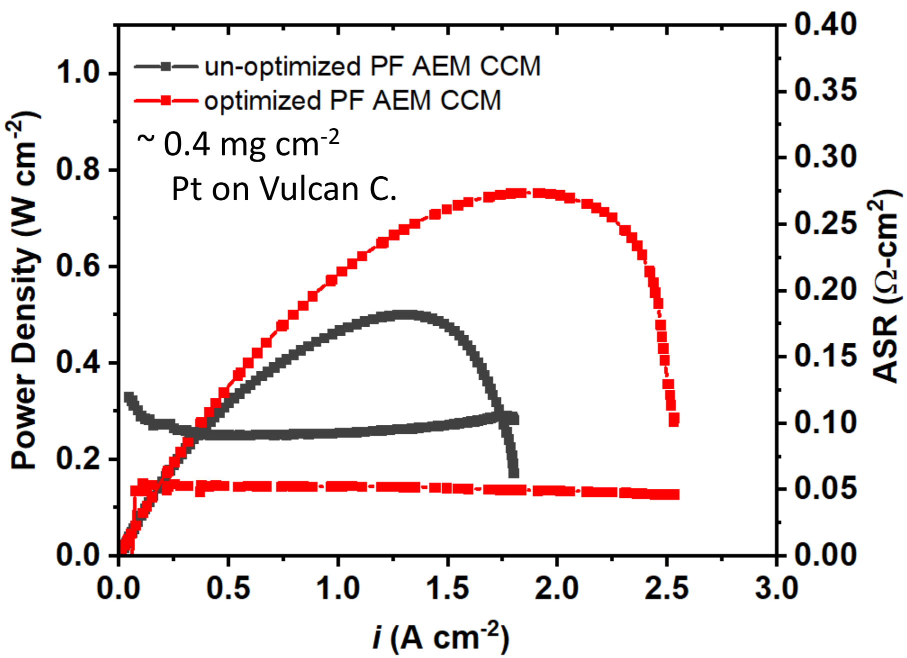
Initial and post power density



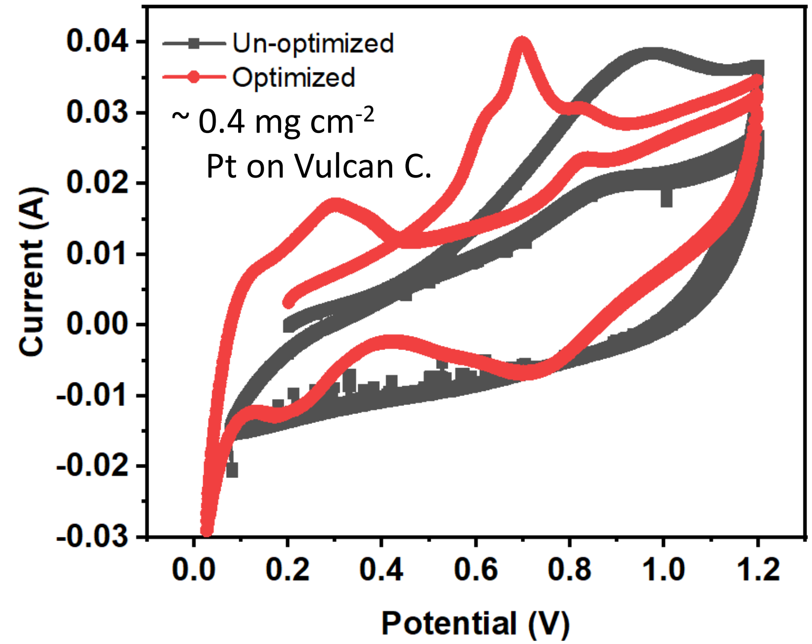
H_2/O_2 full frequency impedance



Electrode Optimization of PF AEM Dispersion Ionomer CCM



CO-Stripping Cyclic Voltammetry

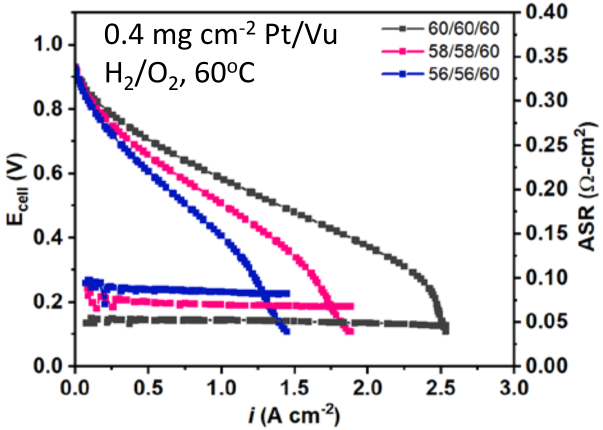


- Efforts were focused on optimizing CCM electrodes (details not shown here, manuscript in preparation)
- Optimized CCM has much higher performance and lower ASR.

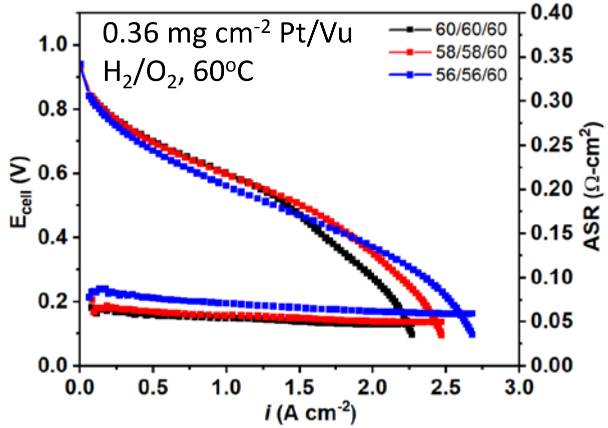
- Voltammetry shows significant difference in ionomer-catalyst interactions – optimized CCM shows more distinct Pt features.
- Un-optimized CCM ~ 37 m^2/g ECSA
- Optimized CCM ~ 37 m^2/g ECSA
- We are still learning how to improve voltammetry measurements and process to understand and gain better in-situ CV data.

Accomplishments and Progress
Electrode Development of PF AEM Ionomer: Dispersion CCM vs Solid GDE

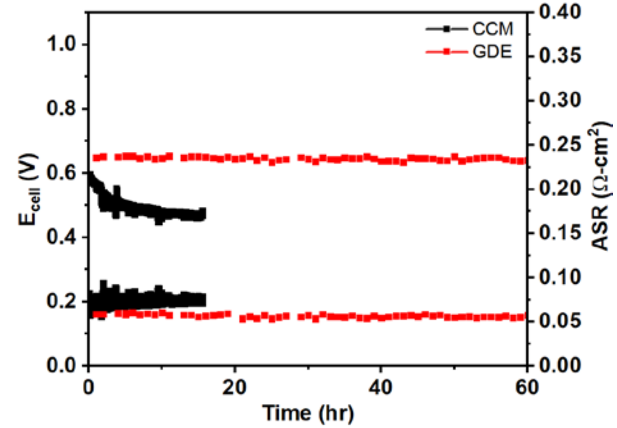
CCM



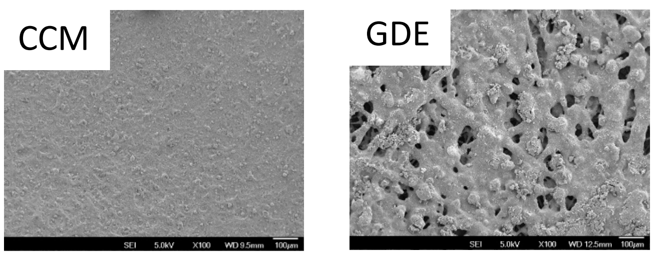
GDE

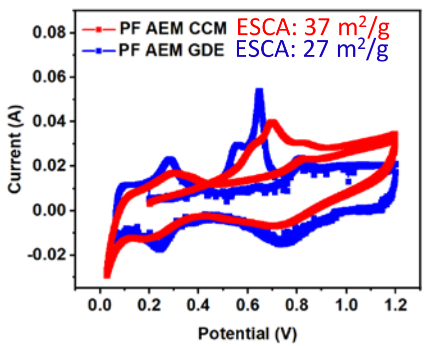


600 mA/cm^2 hold durability test, H_2/O_2, 60^{o}C, 121 kPa$_{abs}$, 100%RH

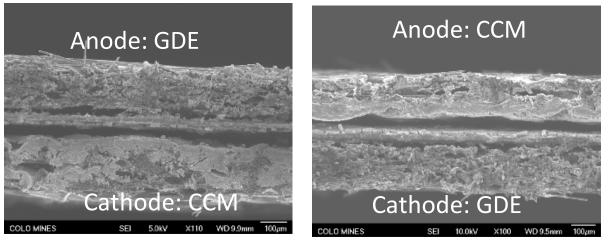


Initial MEAs, Top-down SEM Images





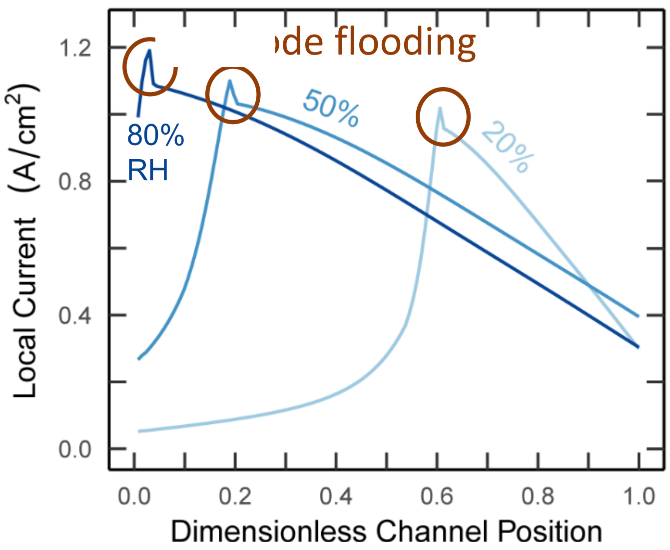
Post MEAs, Cross-sectioned SEM Images



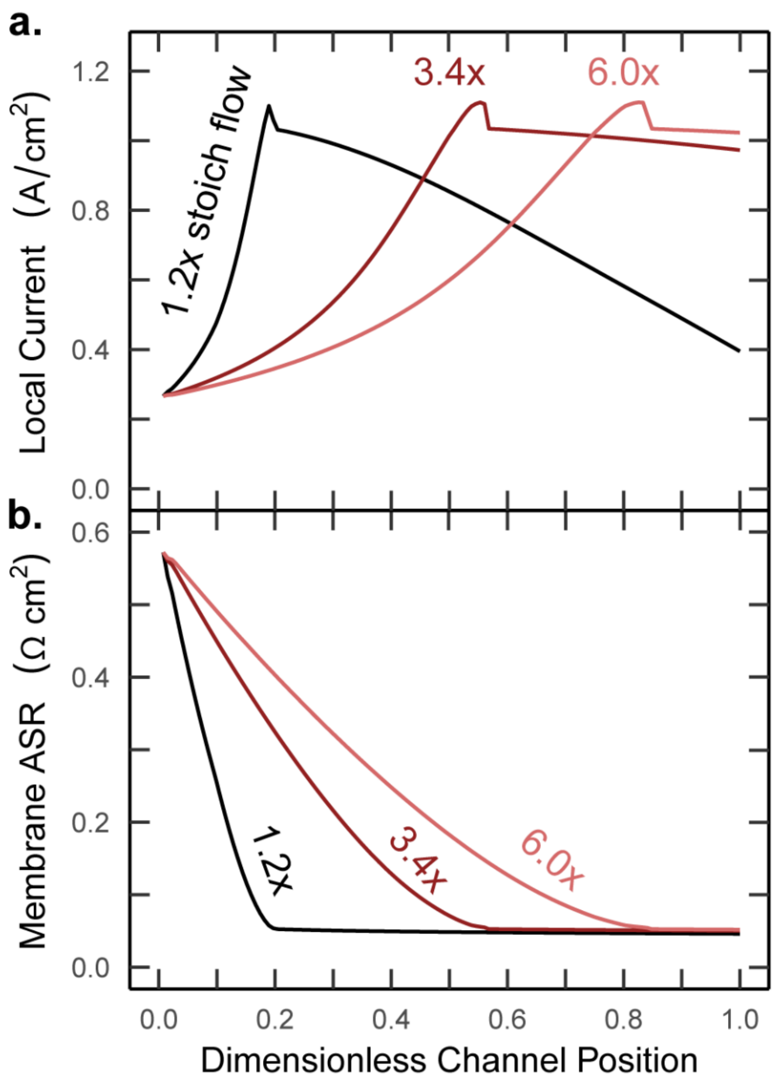
- Striking differences in water management in CCM and GDE
- CCM: RH conditions cause a large impact in both kinetic and transport regions.
- GDE: RH conditions cause less of the impact in both regions.
- CCM shows highest performance at 100% RH; GDE has higher tolerance at < 100% RH
- GDE shows much stable durability performance; while CCM degrades much faster
- GDE CV shows more Pt features but slightly lower ESCA.

Accomplishments and Progress
Down Channel Water Modeling

Varying inlet RH



Varying stoich flow rates



- Inlet RH affects current profile and flooding behavior throughout cell
- Discontinuities in current density due to anode flooding, which reduces gas transport
- Increasing flow rates improves mass transport at end of cell but extends dryout near cell inlet

Models run with at 60 °C with H_2 and CO_2-free air at 50% RH and 0.6 V, 1.2x stoich flow

Accomplishments and Progress
Down Channel CO_2 Modeling

- CO_2 in cathode reacts with OH− to form HCO_3^-/CO_3^{2-}. Carbonates accumulate at anode, resulting in voltage losses due to:
  - Reduction in anode catalyst utilization
  - pH gradient
  - Stoichiometry effects