Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells
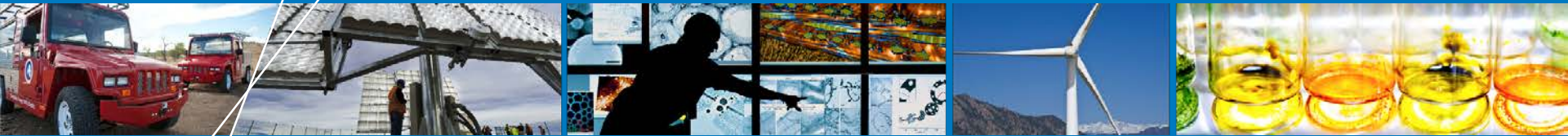
2016 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

June 8, 2016

FC147

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

Overview

Timeline
- **Start: Oct 2015**
- **End: Oct 2018**
- **% complete: ~10%**

Barriers
A. **Durability**
B. **Cost**
C. **Performance**

Budget ($K)

- FY16 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 ^{o}C.

- **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 ^{o}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^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).

Approach
FY 16 Milestones

| Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q1	12/31/2015	Quarterly progress measure	Synthesis of ≥30g of novel PF AEM for incorporation into membranes and dispersions for further characterization and MEA studies (Gen 1 PF AEM).	Completed
Q2	3/31/2016	Quarterly progress measure	Quantification of water uptake as function of relative humidity (RH), conductivity as a function of RH and temperature, and NMR self-diffusion coefficient for Gen 1 PF AEM.	Completed
Q3	6/30/2016	Quarterly progress measure	Quantification of degradation rate of Gen 1 PF AEM due to hydroxide attack at T≥80ºC.	Completed
Q4	9/30/2016	Milestone	In support of AEMFC Q2, 2017 milestone, Demonstrate conductivity of PF AEM >20 mS/cm after 500 hours of exposure to 1 M NaOH at 80°C.	TBD

Approach
PF AEM Materials – Targeted Linkages and Specific Chemistries
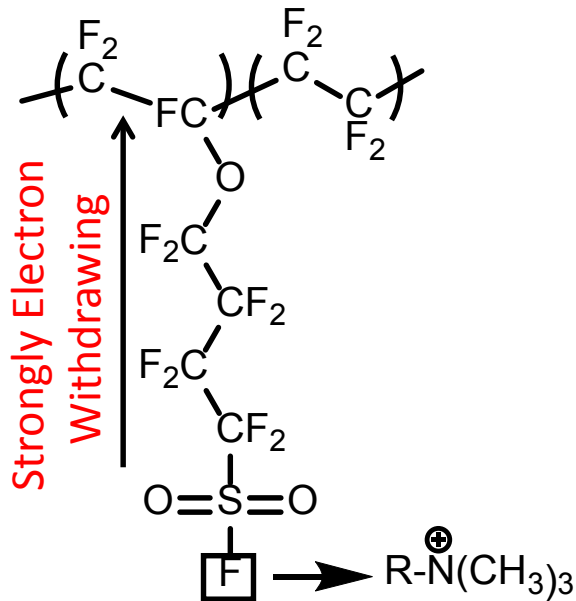
Synthesis: Perfluoro (PF) polymer electrolytes exhibit chemical robustness, enhanced water transport and conductivity properties compared to hydrocarbon polymers.

While PF chemistry improves PF sulfonic acid (PFSA) acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available perfluoro sulfonyl fluoride precursor (PF-SFP), different strategies can be employed to tether cations to the PF-SFP and have been investigated.
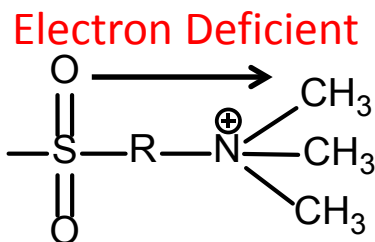
**Characterization**: Evaluate novel polymers for performance and durability

Fuel Cell Performance and Modeling Optimization: Use diagnostics and models to understand and minimize losses in AMFC performance and durability.
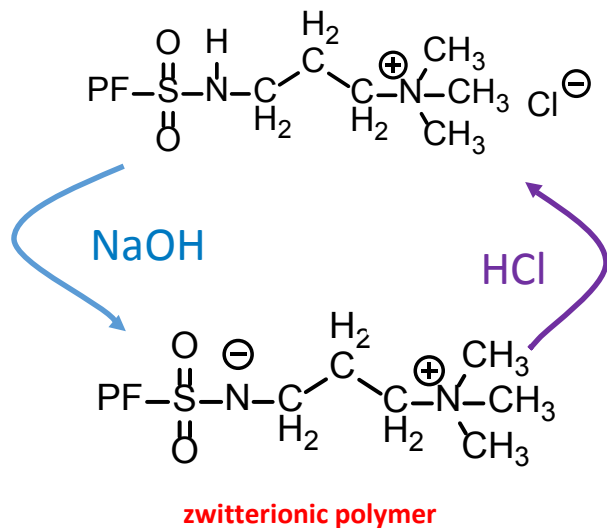
Approach (Background)
## Reactivity, Zwitterion Formation, and Solubility Issues (2015 AMR)

'Target' methylated sulfonamide

10%

Protonated sulfonamide

90%
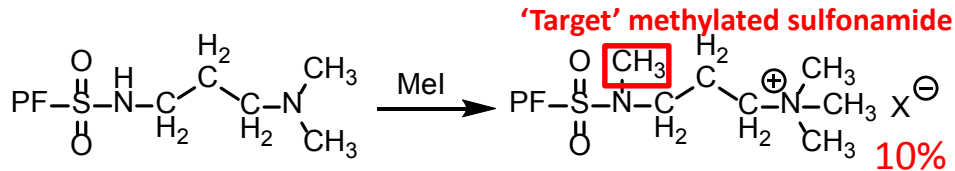
Reactivity: Incomplete reactions on polymer system
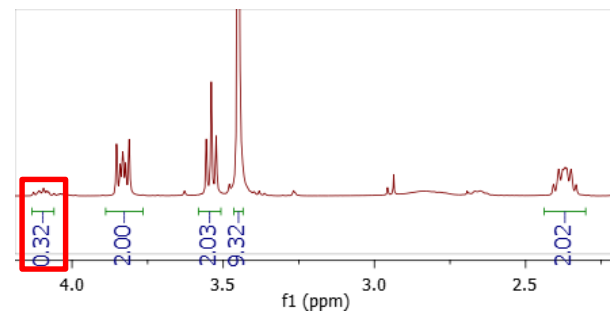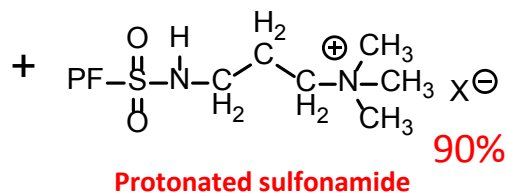
Zwitterion Formation: Acidic protons left behind in select synthesis routes resulted in poor hydroxide conductivity.

NaOH

HCl

zwitterionic polymer

Solubility of Reagents & Polymer (precursor/product): PF polymers have limited solubility and finding systems where reagents, precursors, and products remained soluble has been a significant challenge.

Swollen PF-SFP

PF-SFP

Crude Product

Dried product

Heterogeneous pressed film
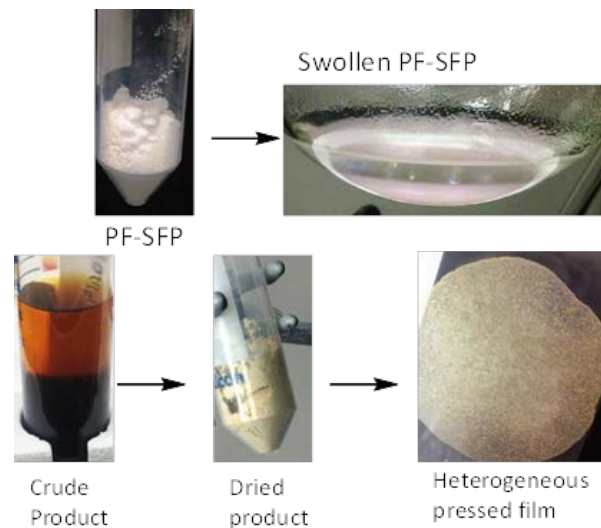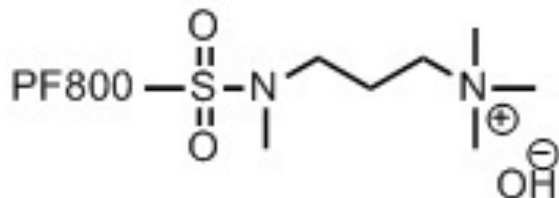
Accomplishments and Progress
Full Methylation (non-Zwitterionic Polymer)

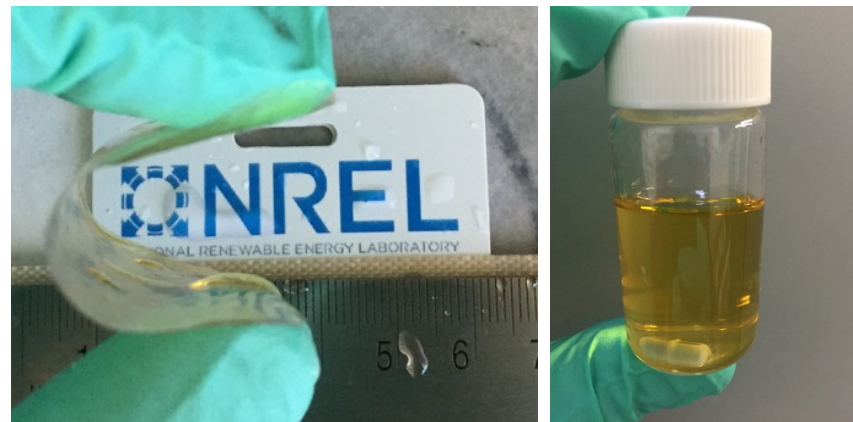Reaction chemistries demonstrated for amide linkages.
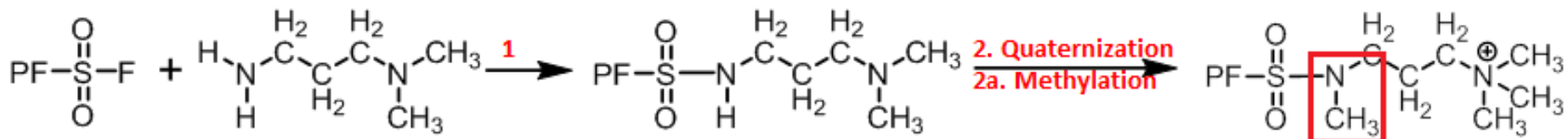
Several batches of 25-50g synthesized

Gen 1 PF AEM Polymer

Improved synthesis increased methylation of sulfonamide target to ~100%. Elimination of zwitterion, high and repeatable hydroxide ion conductivity.

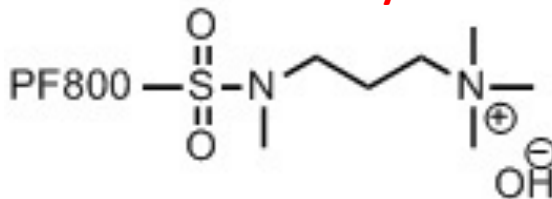| Counterion Form	Conductivity (mS/cm) in Water at 23°C
Cl⁻	17
OH⁻	55
Cl⁻ (after OH⁻)	17

Membranes are strong and ductile in both the dry and hydrated states
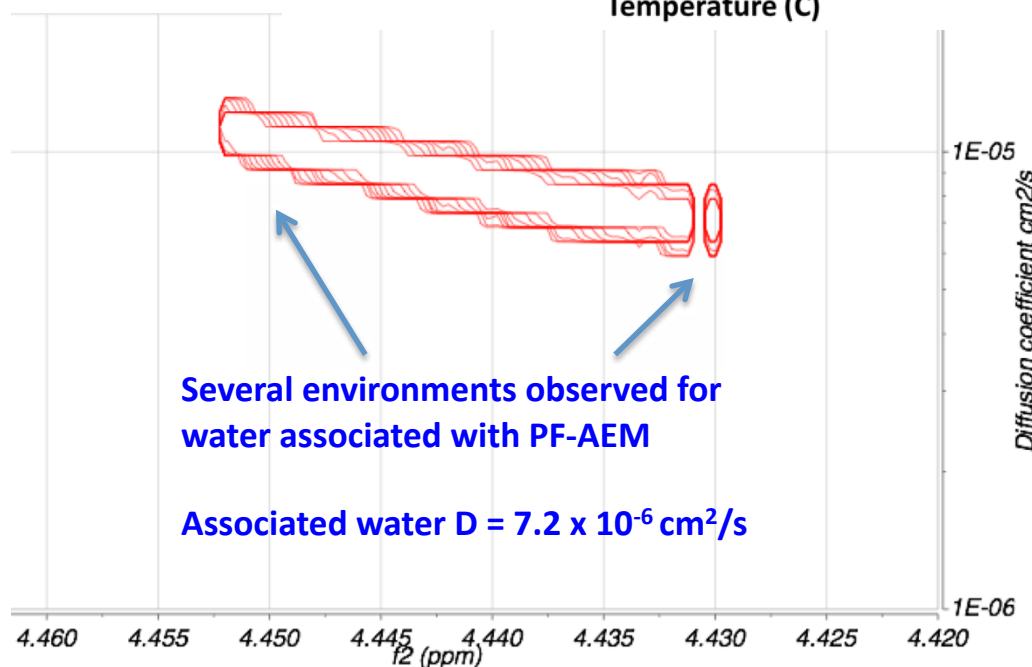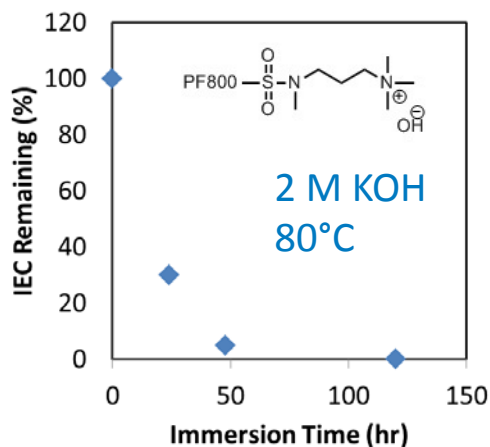

Polymer fully soluble in DMAc/DMF

Gen 1 PF AEM Polymer

Gen 1 PF AEM shows reasonable water uptake and good conductivity (Colorado School of Mines).

The water self-diffusion coefficient is high compared to other AEMs (University of Tennessee/Oak Ridge).
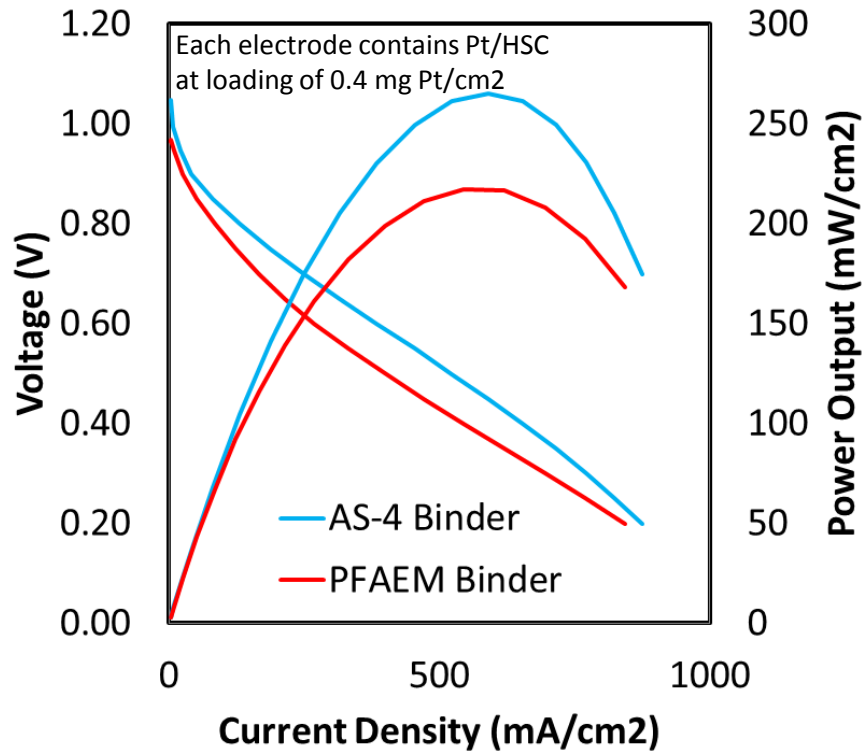
Poor chemical stability (NREL), but sufficient for short-term fuel cell testing.

2 M KOH 80°C

Several environments observed for water associated with PF-AEM

Associated water D = 7.2 x 10^{-6} cm^2/s
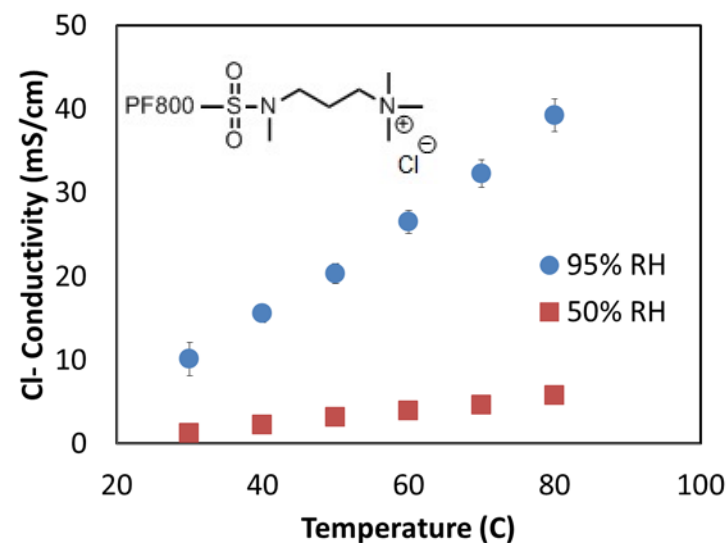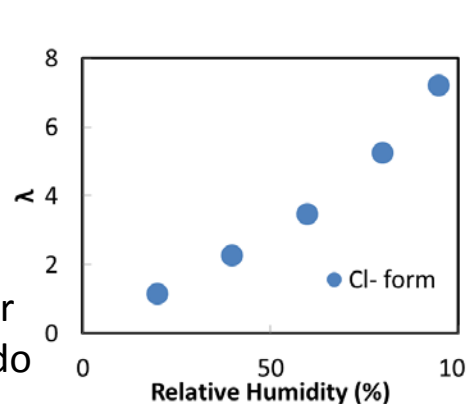
Accomplishments and Progress
PF AEM MEAs

Gen 1 PF AEMs have been fabricated into MEAs w/ PF AEM or Tokuyama AS-4 ionomer binder

Each electrode contains Pt/HSC at loading of 0.4 mg Pt/cm2

— AS-4 Binder
— PFAEM Binder

- PFAEM-Pt/C anode
- PFAEM-PtRu/C anode 0.5::1
- PFAEM-PtRu/C anode 0.6::1
- PFAEM-PtRu/C anode 0.8::1

60°C (100% RH)
H_2/O_2 gas flows of 0.2 slpm

PF AEM electrode performance not yet equivalent to AS-4.
PF AEM as electrode binder in inks only successful with DMAc – further optimization is required.
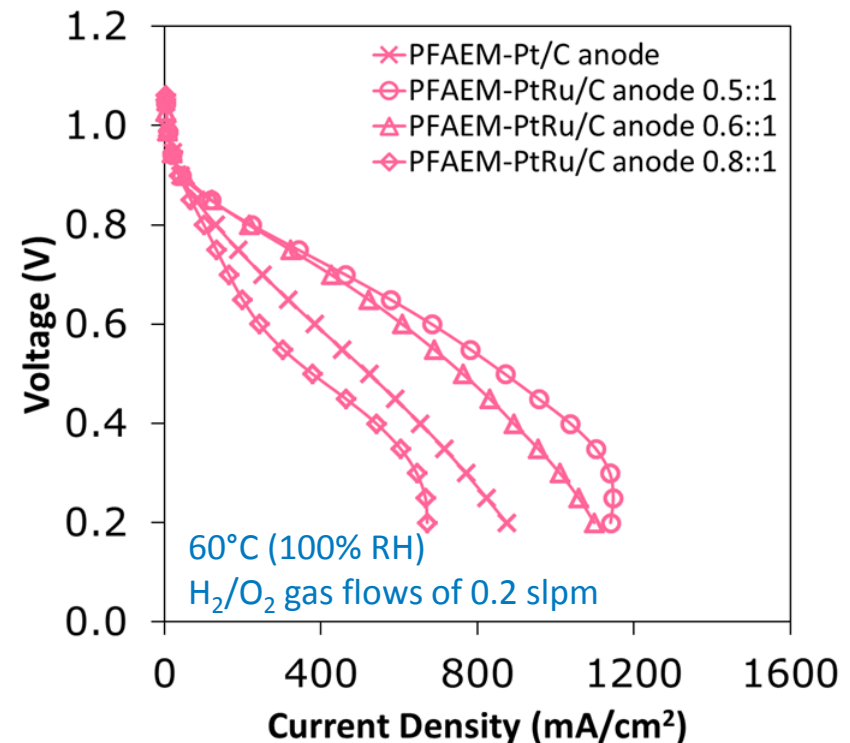
Initial anode optimization for PF AEM MEAs performed using AS-4 binder.
PtRu/Vulcan catalyst at an ionomer:carbon ratio of 0.5 to 1 gave best AMFC performance

Accomplishments and Progress
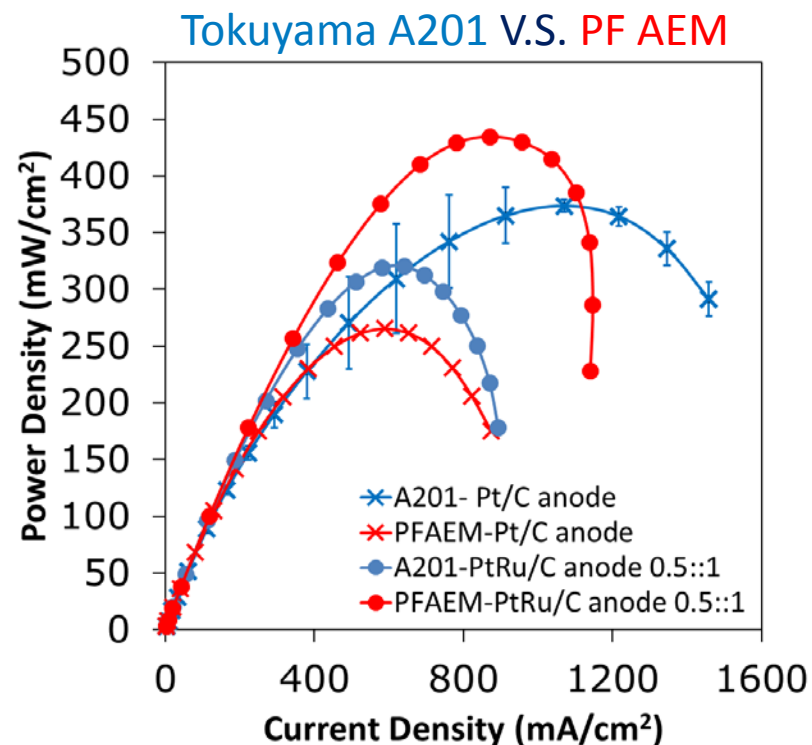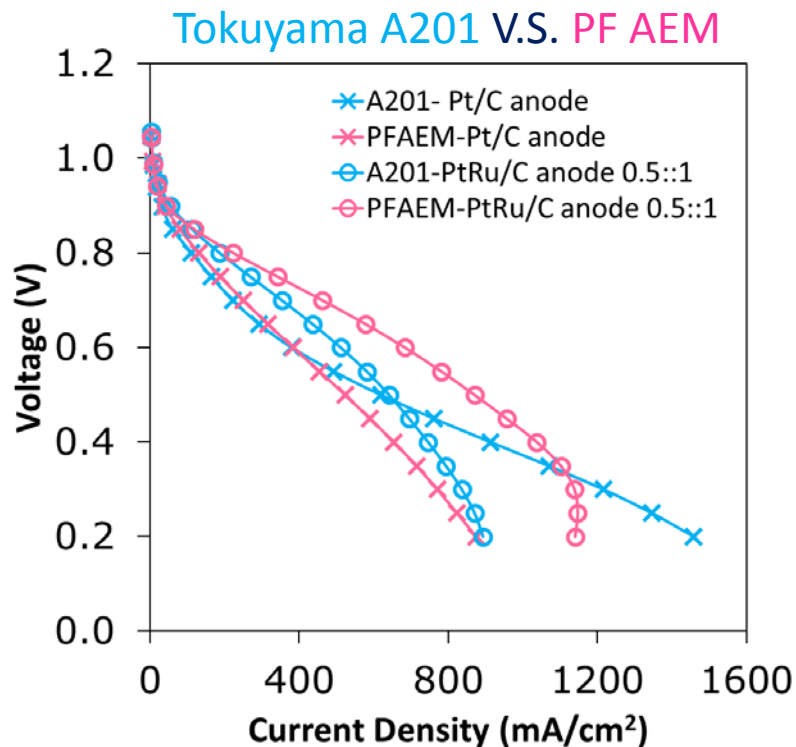## PF AEM MEA Performance

Tokuyama A201 V.S. PF AEM

Tokuyama A201 V.S. PF AEM

0.32 mg Pt/cm² for each cathode (0.8:1 ionomer:carbon)
0.32 mg Pt/cm² Pt/C anode; 0.30-0.35 mg PtRu/cm² anode
60°C cell temp with H_2/O_2 gas flows of 0.2 slpm (100% RH)
Tokuyama AS-4 electrode binder used in all MEAs

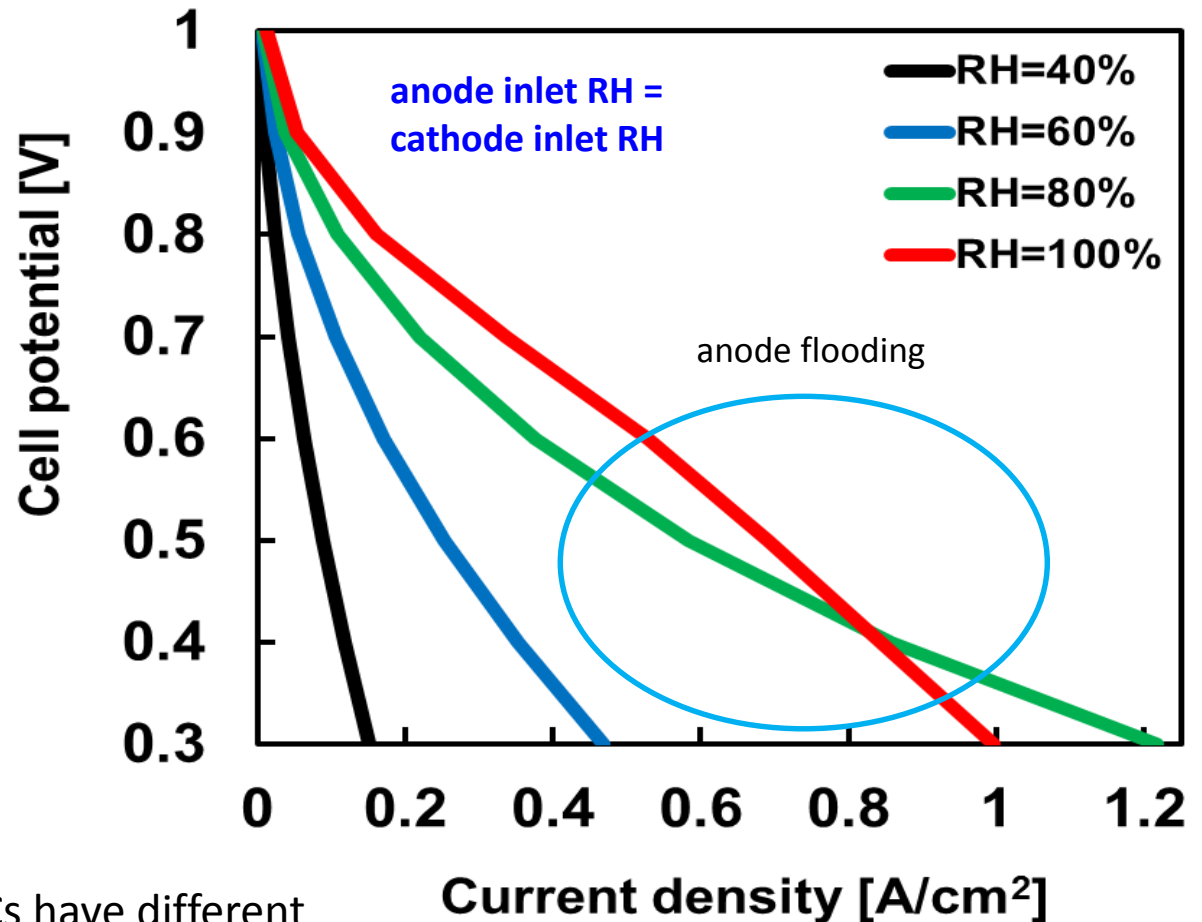| Membrane	Ionomer to Carbon %	Anode	OCV (V)	HFR ($m\Omega \cdot cm^2$)
A201	0.8:1	Pt/C	> 1	184
PF AEM	0.8:1	Pt/C	1.05	155
A201	0.5:1	PtRu/C	> 1	134
PF AEM	0.5:1	PtRu/C	1.03	155

Gen 1 PF AEM has higher beginning of life fuel cell performance than Tokuyama A201.

Accomplishments and Progress
## Modeling of AMFC Performance (LBNL)

Modeling of AMFC performance is an area that has been far behind that of PEMFCs. We (LBNL) are pursuing to provide insight into observed performance and to minimize losses.

These efforts will allow for limitations of water transport, carbonate formation and electrode performance to be better understood.

anode inlet RH = cathode inlet RH

anode flooding

—RH=40%
—RH=60%
—RH=80%
—RH=100%

Cell potential [V] vs Current density [A/cm²]

Unlike PEMFC systems, AMFCs have different water management concerns, the modeling data presented here highlights RH concerns, including the potential for anode flooding.

See backup slides for more information.
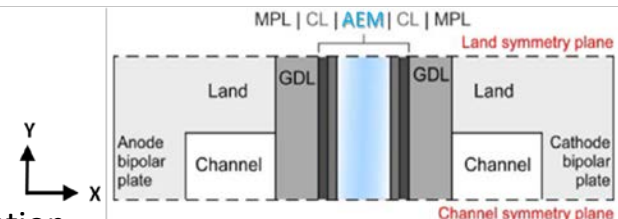
Accomplishments and Progress
Effects of Membrane Thickness and Water Diffusivity (LBNL)

Modeling highlights the advantages of going to thinner membranes where water management concerns are alleviated (better hydration due to back-diffusion). (Team member 3M is key for targeting thinner membranes).

Additionally, higher water diffusivity improves high current density operation (part of our team's rationale for pursuing PF AEMs).

Effect of AEM thickness

AEM Water diffusivity
$D = (1.5 \times 10^{-6} \text{ cm}^2/\text{s}) \times \text{scale factor}$
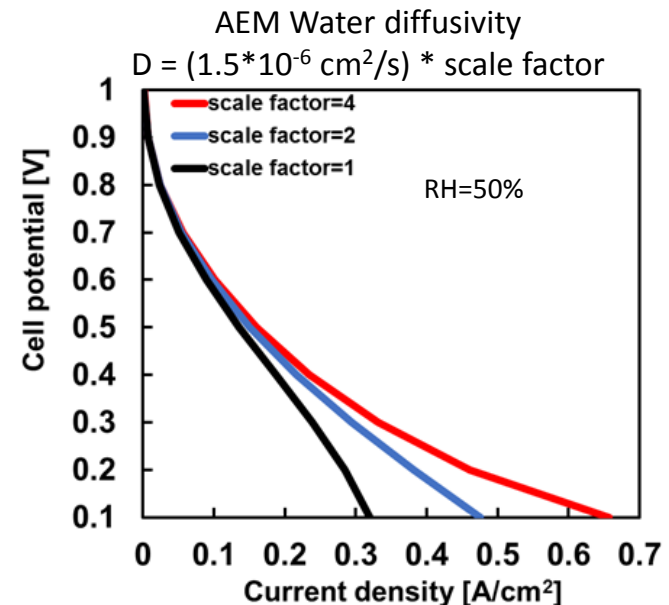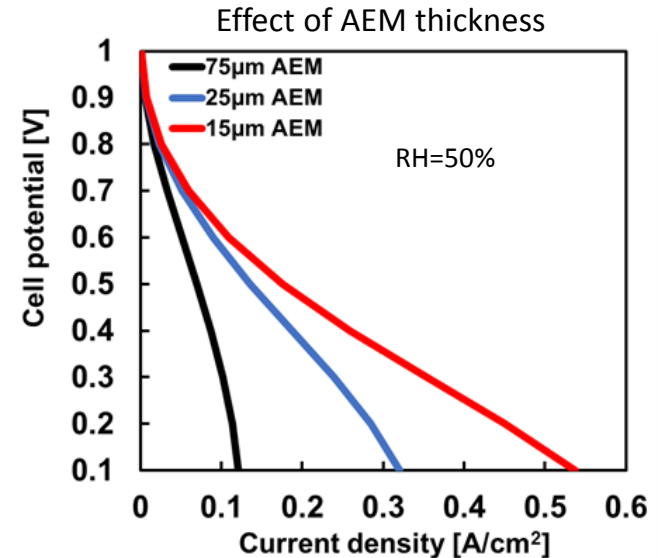
Accomplishments and Progress
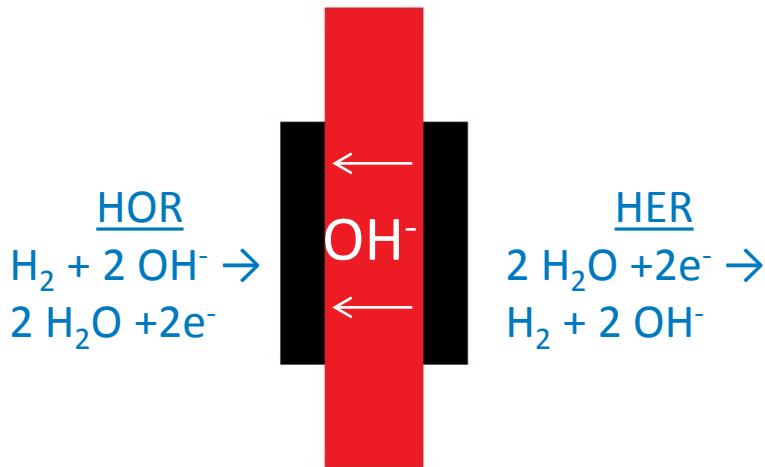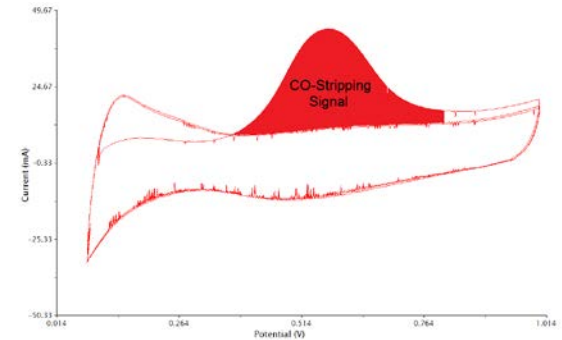## Experimental Diagnostic Tools for AMFC (NREL)

Much like modeling of AMFCs, diagnostics is also an area that has been far behind that of PEMFCs. We are applying diagnostics with modeling to better understand performance losses and limitations.

Carbon Monoxide Stripping

For electrochemical surface area (ECA) determination, H_{UPD} cannot be used for AMFCs (no ionomer H^+ conduction), therefore a CO-stripping technique has been used. Standard PEM CO stripping conditions had to be modified for AMFC conditions.

Lower ECAs relative to PEM measurements (identical catalyst)

Hydrogen Pump

HOR
$H_2 + 2\ OH^- \rightarrow$
$2\ H_2O + 2e^-$

HER
$2\ H_2O + 2e^- \rightarrow$
$H_2 + 2\ OH^-$

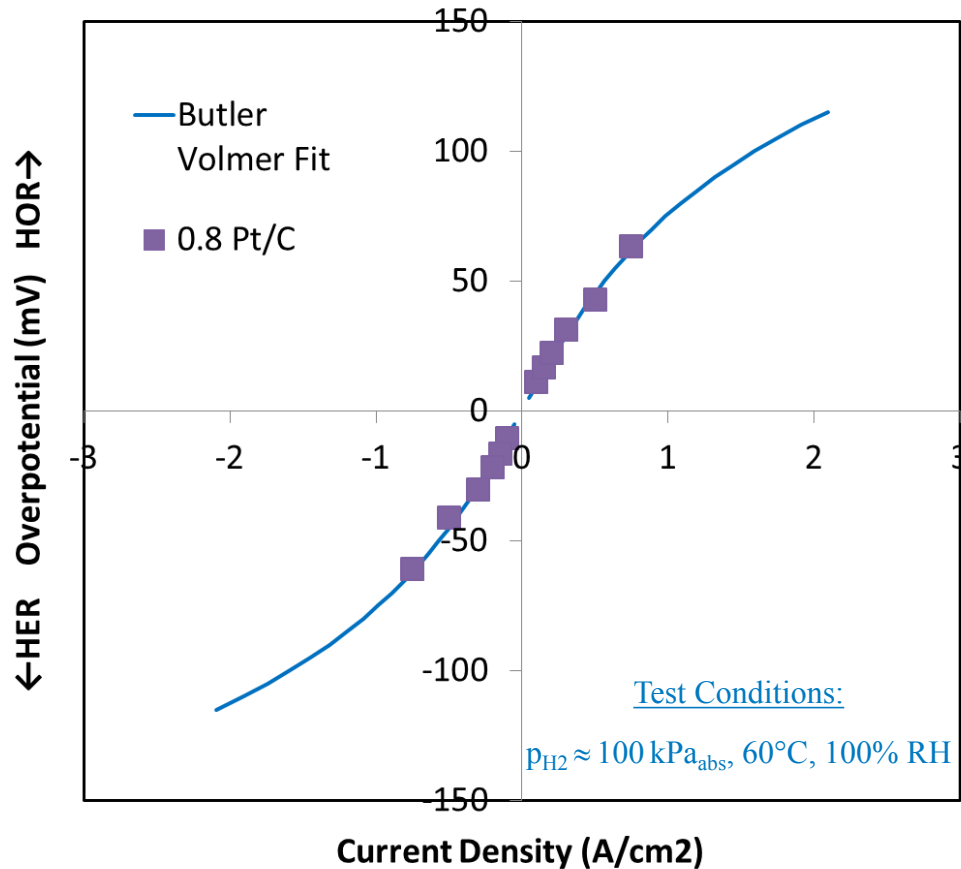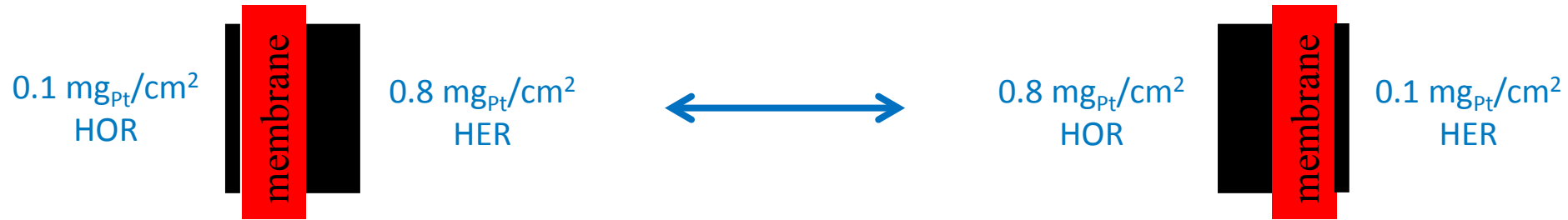In order to optimize individual cell components, it is critical to understand how each is performing. AMFC performance is complicated due to the high HOR overpotentials encountered (relative to PEM systems). Reference electrodes remain a potential strategy to decouple loss mechanisms, however we have initially employed hydrogen pump experiments.

Assymetric MEAs (loadings and catalysts).

See backup slides for more information.

Accomplishments and Progress
## Determination of HOR/HER Exchange Current Density and Voltage Losses

0.1 mg$_{Pt}$/cm² HOR | membrane | 0.8 mg$_{Pt}$/cm² HER

↔

0.8 mg$_{Pt}$/cm² HOR | membrane | 0.1 mg$_{Pt}$/cm² HER

$\alpha_{a,c}$	i$_{o,HER}$ (mA/cm²)	i$_{o, HOR}$ (mA/cm²)
0.5	1.23	1.28

Exchange current density for HOR on Pt/C determined successfully from AMFC MEA with at least one high loaded electrode by fitting data with Butler-Volmer kinetic model, data agrees reasonably with RDE data

— Butler Volmer Fit

■ 0.8 Pt/C

HOR → Overpotential (mV) ← HER

Current Density (A/cm2)

Test Conditions:
$p_{H2} \approx 100$ kPa$_{abs}$, 60°C, 100% RH

Reference	Catalyst	i$_{o,HOR}$ (mA/cm²)
Strmcnik et al., 2013	Pt/C	~1.0
"	Pt(0.1)Ru(0.9)/C	>6.5
Durst et al., 2014	Pt/C	1.0
Wang et al., 2014	Pt/C	0.3
"	Pt(0.6)Ru(0.4)/C	0.7
St. John et al., 2015	Pt/C	0.49
"	Pt(0.8)Ru(0.2)/C	1.42
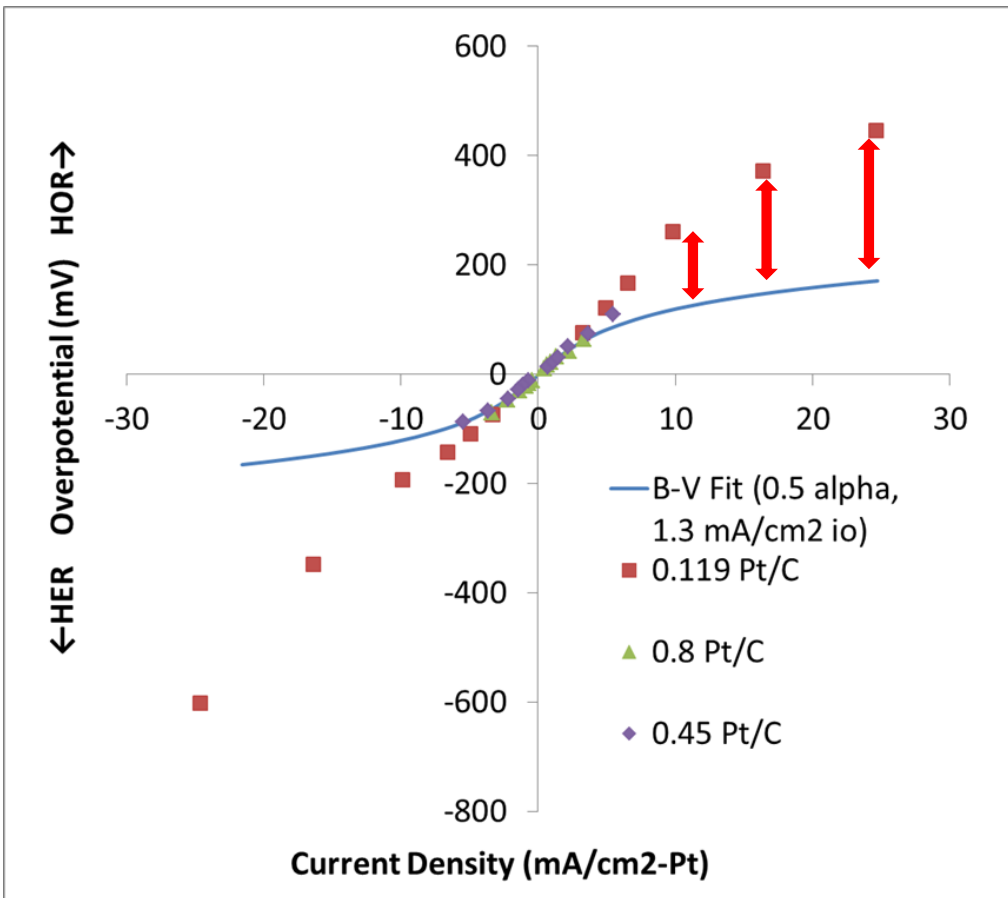
When normalized to platinum area, uncompensated resistance appears for low loaded electrodes (or high current density per platinum area).
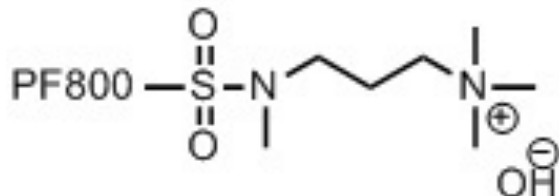
Overpotential losses are substantial.
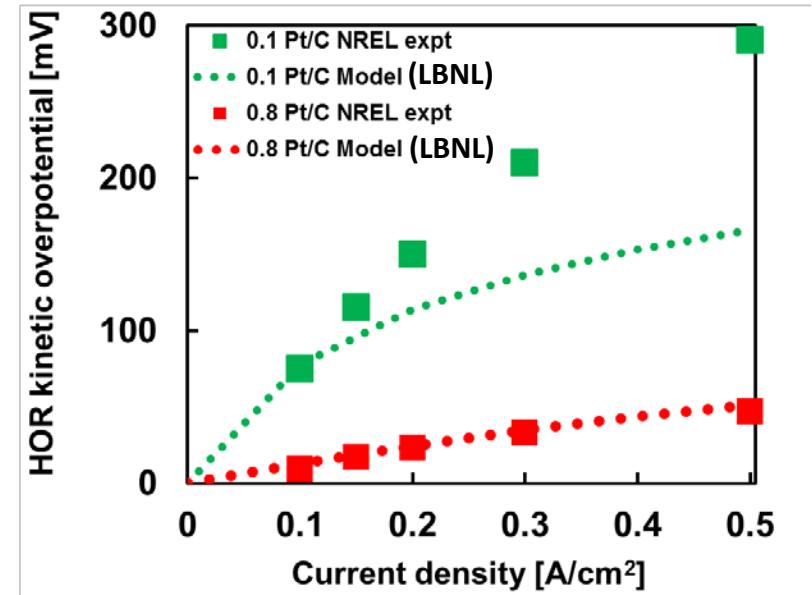
Modeling of hydrogen pump system agrees with experimental data at high loading, deviates at low. Will be critical for meeting performance/loading requirements of AMFCs.
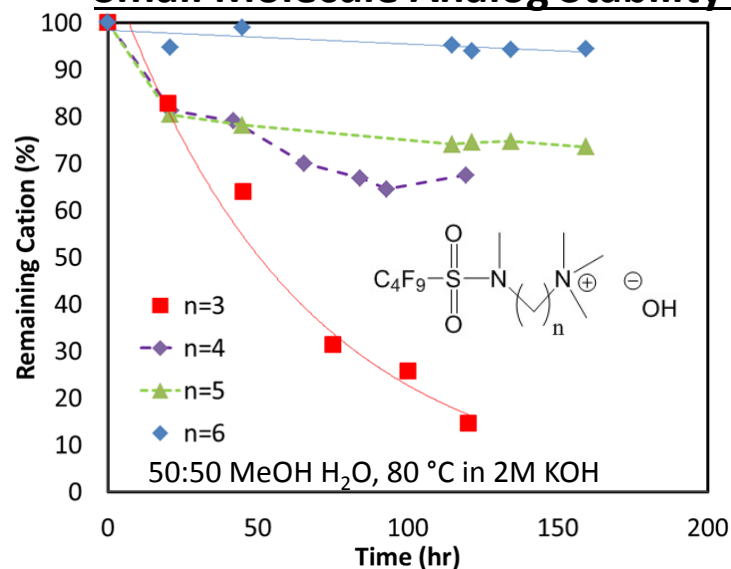
Accomplishments and Progress
Improving PF AEM Stability

Gen 1 PF AEM Polymer

Shown to have poor durability. Not surprising due to proximity of cation and electron withdrawing side chain.

Gen 2 PF AEM Polymer

97% of IEC retained after 48 hr in 2 M KOH at 80°C

Significantly increased stability (30x) achieved through lengthening of the alkyl chain. Stability concerns remain due to the sulfonamide linkage (alternative tethering strategies are being investigated).

Small Molecule Analog Stability*

50:50 MeOH H_2O, 80 °C in 2M KOH

*Basic Energy Science funded work (above) focused on cation and tether stability being leveraged.

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 and conductivity).**
3M (3M): Mike Yandrasits, Krzysztof Lewinski	**In-kind; Consulting on novel chemistries; preparation of solutions and dispersions; membrane fabrication.**

Remaining Challenges and Barriers

- ## Polymer Synthesis:
  - Improved stability still required. Gen 2 polymer seems adequate for limited applications.

- ## Modeling and Fuel Cell Diagnostics
  - Understand limits and minimize losses of water management, carbonate poisoning, and electrode performance.

- ## Fuel Cell Testing:
  - Optimize electrode performance using PF AEM electrode binder
  - Demonstrate durability/long term performance in CO2-free and ambient air testing.

Future Work

- Membrane Synthesis:
    - Gen 3 polymer development (avoiding sulfonamide linkage)
    - Gen 2 polymer Scale up

- Characterization
    - Conductivity, stability, water transport, carbonate.

- Modeling
    - Parametric studies exploring operating conditions (T, RH, current density, CO_2 concentration)
    - Coupling ORR kinetics to water transport, and elucidation of water transport within the cell.

- Fuel Cell Testing:
    - Improved performance and durability through optimization of individual component performance.

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).

- Co-led AMFC Workshop, May 1, 2016 involving over 50 participants from academia, industry and government.

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:** The project has successfully synthesized PF AEM sulfonamide-linked chemistries for highly OH- conductive AEMs. Extensive characterization has been performed on the polymer. Implementing this polymer into devices yields reasonable AMFC power densities that surpass those for commercial AEMs. Modeling and diagnostic techniques are being performed to advance/optimize AMFC architecture.

- **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.

Technical Backup Slides

Relevance
Benefits of Perfluoro electrolytes vs Hydrocarbon electrolytes

Our approach focuses on achieving **higher-temperature, higher-power-density AMFC operation** through implementation of **novel alkaline perfluoro (PF) membranes and ionomeric dispersions**. The PF materials proposed are expected to enhance water transport capabilities and electrode performance/durability significantly, thereby enabling higher temperature and power density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO_2, potentially enabling complete tolerance to ambient CO_2.
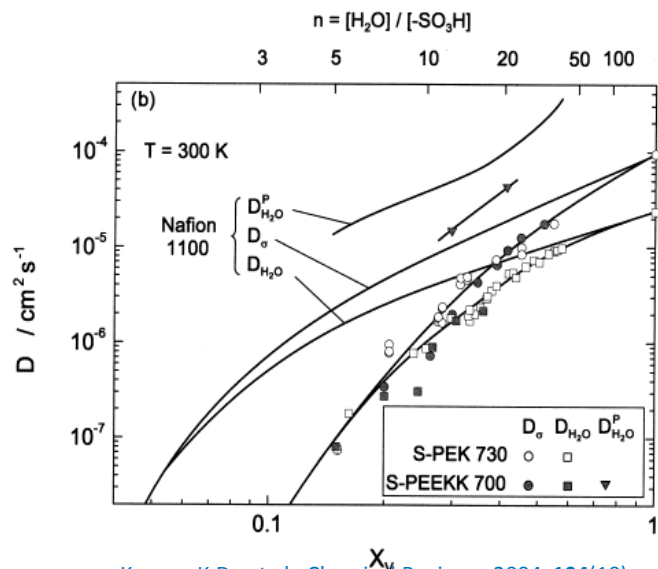
Kreuer, K.D., et al., Chemical Reviews, 2004. **104**(10): p. 4637-4678

Most AEMs are based on hydrocarbon polymer chemistry. From significant work in the area of PEMs, water transport and conductivity has been shown to be **significantly higher in PF polymers**, particularly at lower hydration levels.

While perfluoro membranes are electron withdrawing, as long as cations remain chemically stable, hydroxide is a free cation and should not have losses associated with decreased basicity compared to hydrocarbon membranes.

Perhaps the most exciting advance in the AEM area in the past decade has come from the high hydroxide stabilities of covalently tetherable cations recently reported. At this point in time, we feel clear that cations with high hydroxide stability have been demonstrated. Demonstrating these cations in high performance polymers is the remaining challenge

Our team through BES funded efforts in cation stability have quantified benzyltrimethyl ammonium (BTMA$^+$) stability at 80°C of less than 10% degradation after 5,000 hours, and a half-life of over 4 years. Stability capable of enabling several applications.
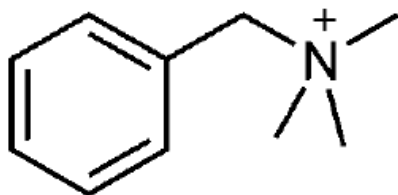
Kreuer and Marino have shown multiple cations with increased stability relative to BTMA$^+$, with 6-azonia-spiro[5.5]undecane showing a 20x improvement in base stability.

BTMA$^+$
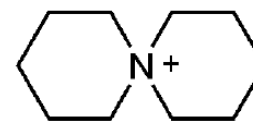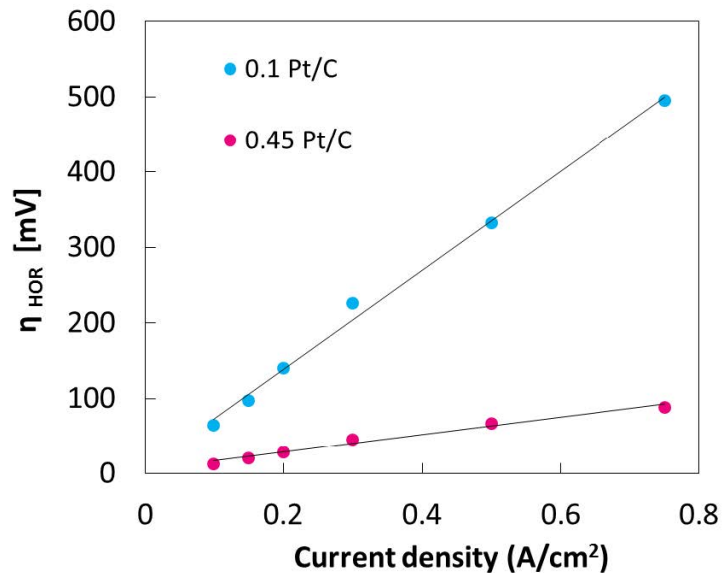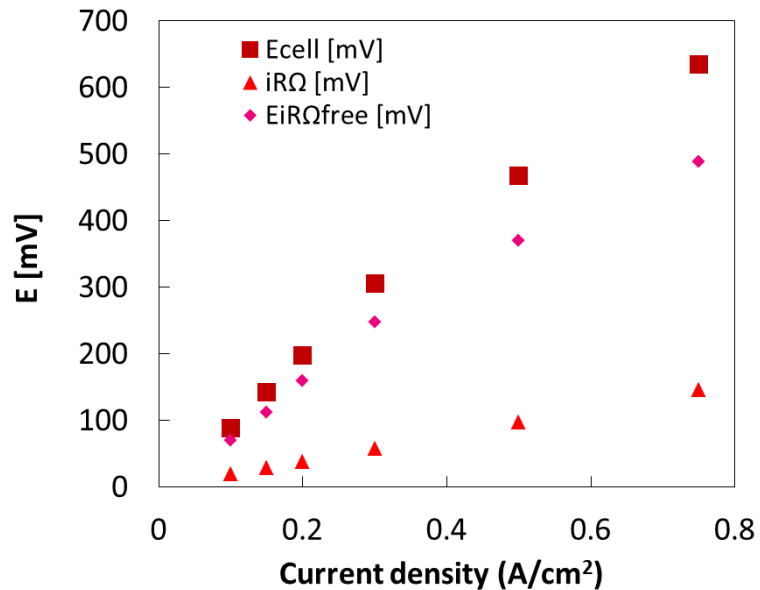

6-azonia-spiro[5.5]undecane

Marino, M.G. and K.D. Kreuer, Chemsuschem, 2015. **8**(3): p. 513-523

M Sturgeon, C Macomber, C Engtrakul, H Long, and B Pivovar, J. Electrochem. Soc., 162 (4) F366-F372 (2015).

$$E_{cell}$$
$$= \frac{RT}{2F} \ln\left(\frac{pH_2, ca}{pH_2, an}\right) - iR_\Omega - iR^{eff}_{OH^-,ca} \quad (1)$$
$$- iR^{eff}_{OH^-,an} - |\eta_{HER}| - \eta_{HOR}$$

$$E_{iR_{\Omega free}} = E_{cell} - iR_\Omega = \eta_{HER} + \eta_{HOR} \quad (2)$$

Critical Assumption: $\eta_{HOR} = \eta_{HER}$ for given electrode

$$\eta_{HOR} = E_{iR_{\Omega free}} \times \frac{(cm2 - Pt)_{HER}}{(cm2 - Pt)(_{HER_+HOR})} \quad (3)$$

Linearized Butler-Volmer equation
$$i_{o,s}(\alpha_a + \alpha_c) = \frac{i}{\eta}\frac{RT}{F}\frac{1}{L10A_{Pt,el}} \quad (4)$$

$\alpha_{a,c}$ = 0.5, 1.0, or 2.0

Hydrogen pump conditions: @60°C, 100% RH H_2 at a total pressure of 121kPa for 5cm^2 MEA area

Equations for the AEMFC model (LBNL)

Electrode kinetics

➢ **Butler-Volmer kinetics:**

$$i_{HOR} = A_{Pt} i_{0,HOR}^{ref} \left(\frac{p_{H_2}}{p_{ref}}\right) a_{vapor} \left[\exp\left(\frac{\eta_a F}{RT}\right) - \exp\left(\frac{-\eta_a F}{RT}\right)\right] \qquad i_{0,HOR}^{ref} = 10^{-3} \frac{A}{cm^2}$$

$$A_{Pt} = 10^7 \left(\frac{1}{m}\right) \quad p_{ref} = 10^5 (Pa)$$

$$i_{ORR} = A_{Pt} i_{0,ORR}^{ref} \left(\frac{p_{O_2}}{p_{ref}}\right) a_{vapor} \left[\exp\left(\frac{-\eta_c F}{RT}\right) - \exp\left(\frac{\eta_c F}{RT}\right)\right] \qquad i_{0,ORR}^{ref} = 10^{-6} \frac{A}{cm^2}$$

Membrane properties

➢ **OH⁻ conductivity:**

Vapor-equilibrated:
$$\kappa_V = \begin{pmatrix} 0.1334 - 3.882\times10^{-4}T + (0.01148T - 3.909)a_0 - (0.06690T - 23.01)a_0^2 \\ + (0.1227T - 42.61)a_0^3 - (0.06021T - 21.80)a_0^4 \end{pmatrix}$$

Liquid-equilibrated:
$$\kappa_L = 10\exp\left[\frac{15,000}{R}\left(\frac{1}{273.15} - \frac{1}{T}\right)\right]$$

➢ **AEM water diffusivity:**

Vapor-equilibrated:
$$D_V = (0.0051\lambda T - 1.44\lambda)\times10^{-10}$$

Liquid-equilibrated:
$$D_L = (-79.8 + 17.9\lambda - 1.33\lambda^2 + 0.033\lambda^3)\times10^{-10}$$

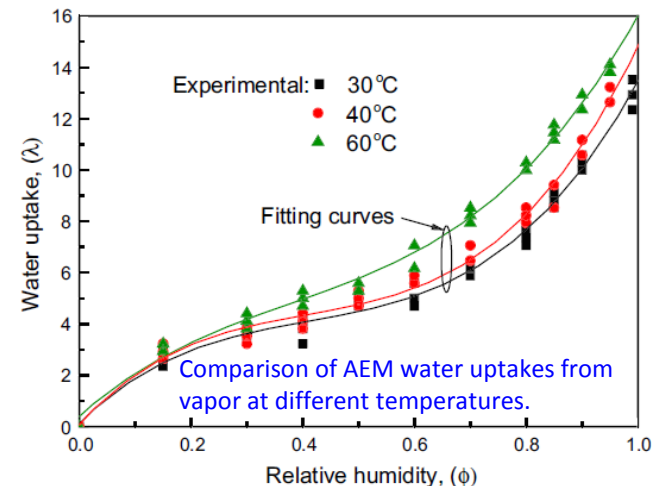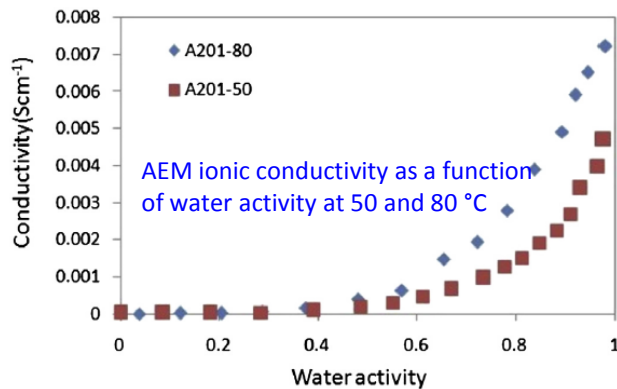➢ **Electro-osmotic coefficient:**
$$\xi = 0.183\lambda + 1.3$$

➢ **Membrane water content:**

$$\lambda_V = (-0.6a_0^3 + 0.85a_0^2 - 0.2a_0 + 0.153)\times(T - 313) + 39a_0^3 - 47.7a_0^2 + 23.4a + 0.117$$

$$\lambda = \lambda_V + S(19 - \lambda_V)$$

AEM ionic conductivity as a function of water activity at 50 and 80 °C

Comparison of AEM water uptakes from vapor at different temperatures.
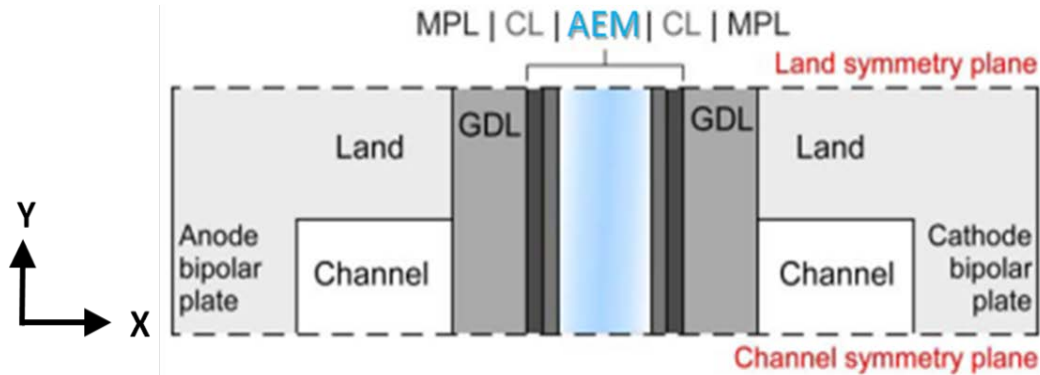
Source of AEM data and properties: (1) Q. Duan et al. *Journal of Power Source* 243 (2013) 773 - 778
(2) Y.S. Li et al. *International Journal of Hydrogen Energy* 35 (2010) 5656 - 5665

(1) Model parameters
# (2) Model validation against experimental polarization curve

2D computational domain

AMFC model validation

Model parameters

OH⁻ conductivity at 100% RH at 65 °C (mS/cm)	45
Thicknesses of GDL, MPL, CL and Membrane (µm)	190, 45, 10 and 25
Volume fraction of ionomer in CL	0.112
Porosities of GDL, MPL and CL	0.8, 0.3 and 0.38
Saturated permeabilities of GDL, MPL and CL (m^2)	1E-11, 1E-15 and 6E-17
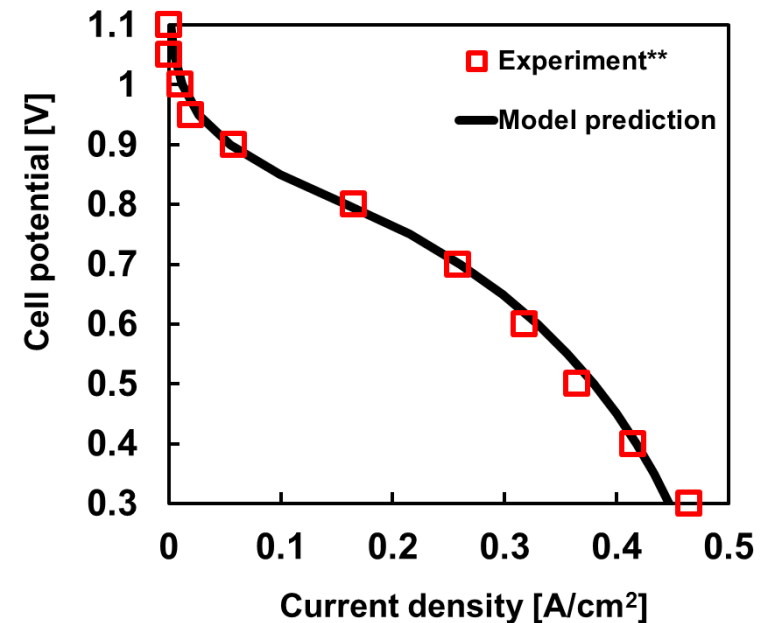
**Experimental data at 100% RH, 65 °C and 1 atm (from Yu Seung Kim's group at LANL)
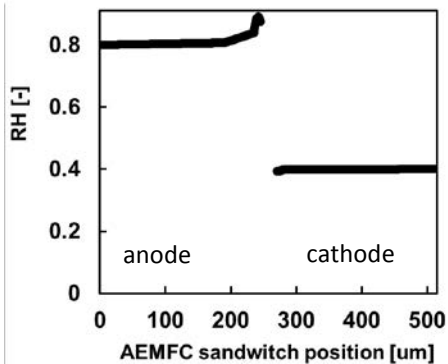
Accomplishments and Progress
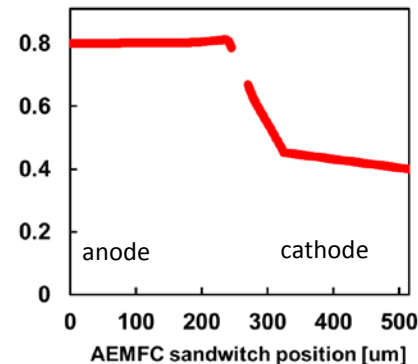## Modeling of AMFC Water Balance with Differential Inlet %RH (LBNL)

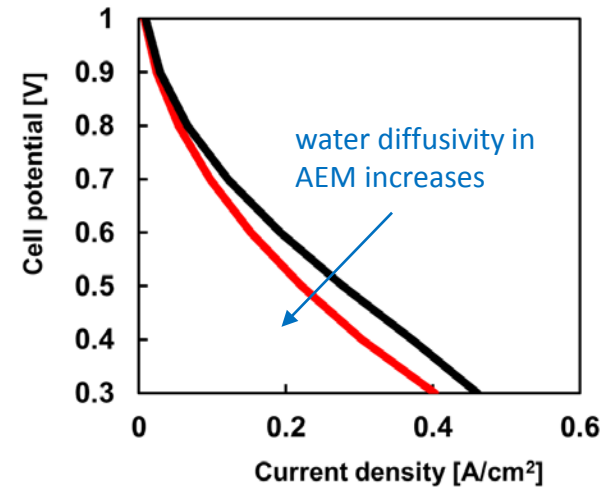**wet anode inlet (80% RH), dry cathode inlet (40% RH)**

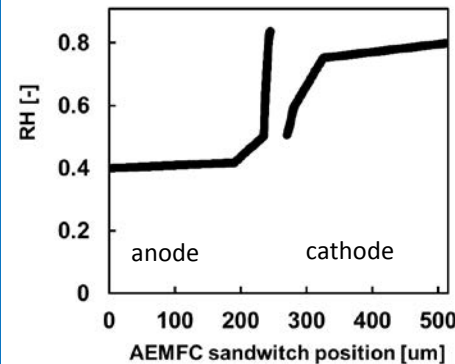water diffusivity in AEM increases

Low D_{water} in AEM   High D_{water} in AEM

Performance is *improved* with higher water diffusivity in AEM, suggesting that the cathode dehydration and water-consuming ORR kinetics are limiting factors when the cathode inlet is drier than the anode inlet.
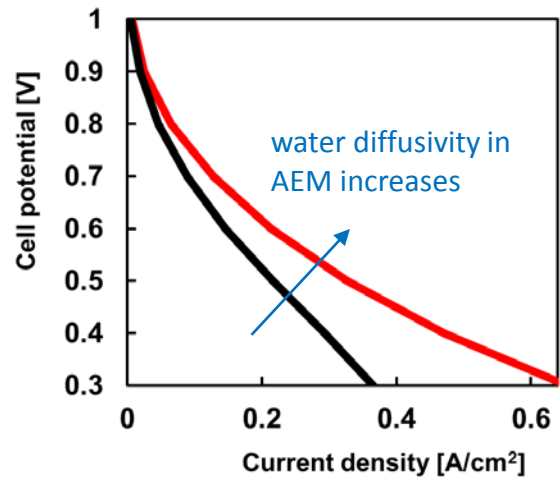
dry anode inlet (40% RH), wet cathode inlet (80% RH)

water diffusivity in AEM increases

Low D_{water} in AEM   High D_{water} in AEM

Performance is *reduced* with higher water diffusivity in AEM, suggesting that the anode dehydration (high OH$^-$ ohmic resistance) is more limiting than the water-consuming ORR kinetics when the anode inlet is drier than the cathode inlet.

Accomplishments and Progress
Modeling of AMFC Cathode Catalyst Layer Resistance (LBNL)
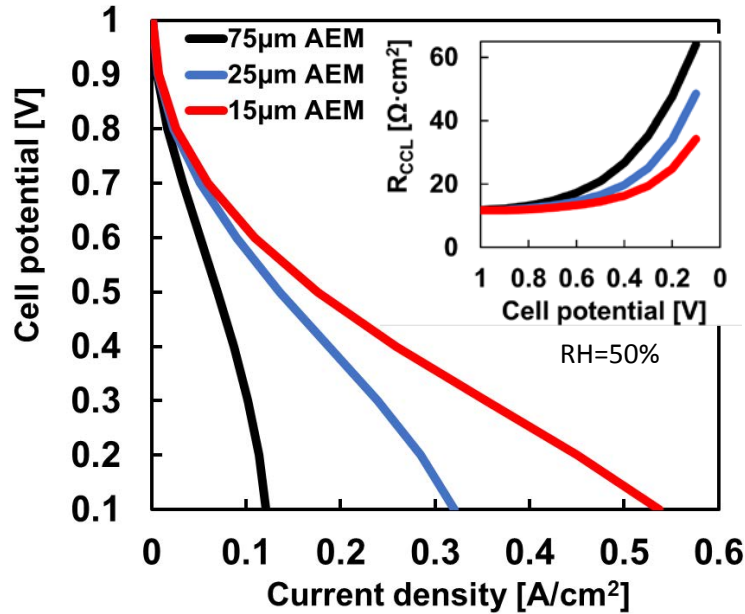
Thinner AEM helps decrease CCL ionic resistance by enhancing water diffusion from anode to cathode.
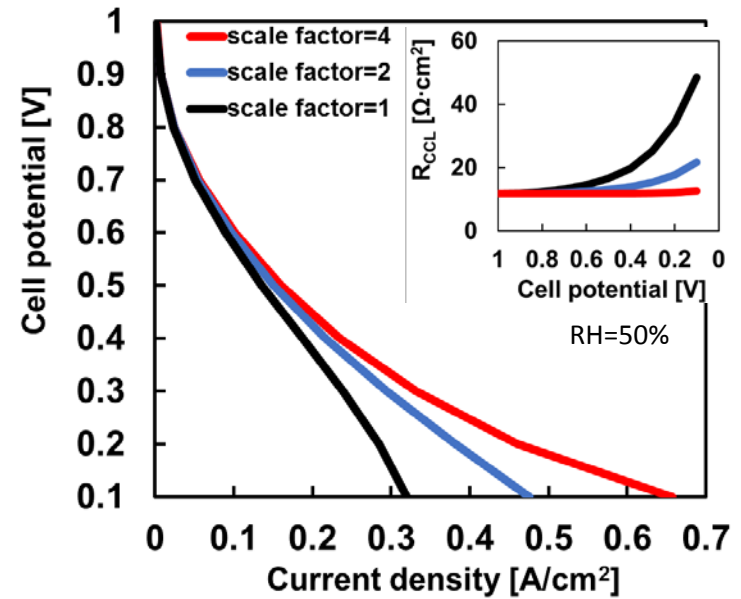
Higher AEM water diffusivity is more effective to uniformly distribute water, as indicated by uniform CCL ionic resistance

At very low potential (high current density), ORR rate becomes non-uniform in cathode catalyst layer due to uneven distribution of water content. Water management at cathode critically important

spatial distribution of reaction rate in CCL

Normalized reaction rate

at 0.4 V   *AEM/CCL interface*   at 0.2 V   *CCL/GDL interface*