Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

# Performance and Durability Investigation of Thin, Low Crossover Proton Exchange Membranes for Water Electrolyzers

**Andrew M. Park**

**The Chemours Company**

**DOE Project Award #DE-EE0008836**

**June 8, 2021**

Chemours™

Nafion™

Project ID #P186

DOE Hydrogen Program 2021 Annual Merit Review and Peer Evaluation Meeting

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

NREL Transforming ENERGY | BERKELEY LAB Bringing Science Solutions to the World | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory

# Project Overview

## Project Partners

Andrew Park (PI), Chemours
Siddharth Komini Babu, Los Alamos Nat'l Lab

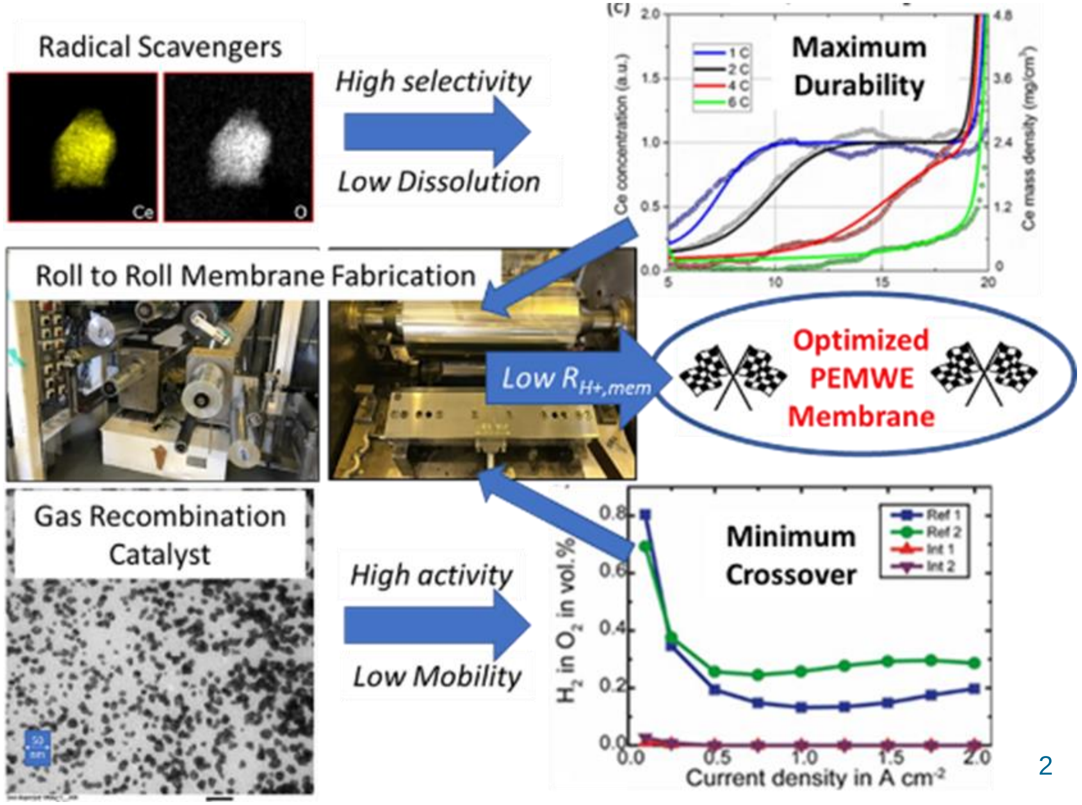
## Project Vision

Thin, reinforced membrane with performance and durability additives that enables high current density and long lifetime in PEMWE systems.

## Project Impact

High performance commercial membranes will directly and indirectly reduce PEMWE costs, facilitating $H_2$ @ < \$2/kg

| | |
|---|---|
| Award # | EE0008836 |
| Start/End Date | 03/01/2020 – 02/28/2023 |
| Project Funding* | \$1.25M (DOE + Cost Share) |




*this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

# Approach – Summary

## Project Motivation

This project aims to transform PEMWE systems via high performance membranes. It unites the manufacturer of Nafion™ PFSA membranes (Chemours) and the leader in performance and durability investigations of polymer electrolyte materials (Los Alamos National Lab (LANL)).

## Key Impact

| Metric | State of the Art | Expected Advance |
|---|---|---|
| Membrane resistance [Ω-cm²] | *0.2* | *<0.07* |
| Membrane tensile strength (MPa) | *25* | *>40* |
| Gas Recombination Catalyst and Radical Scavenger in membrane | *No* | *Yes* |

## Barriers

Manufacturability: These membranes will be constructed on roll-to-roll systems for easy transition to the commercial scale

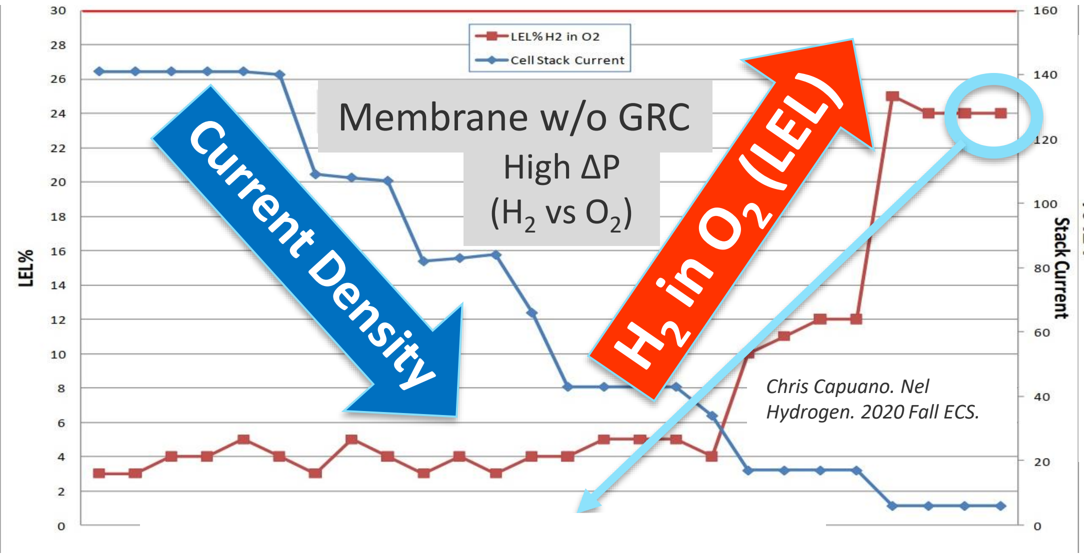
Durability: The additives envisioned to enable thin membranes can move, agglomerate, or leave the system entirely, which will be studied and mitigated

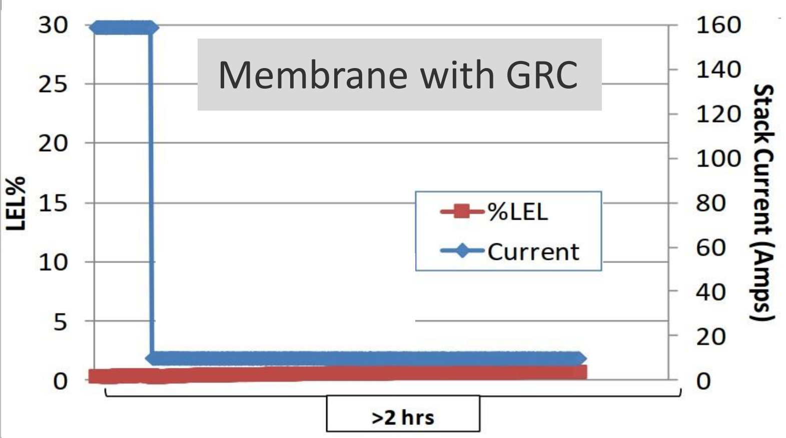
## Partnerships

Chemours is the manufacturer of Nafion™ PFSA polymers and is the leading supplier of water electrolyzer membranes today

Los Alamos National Lab has studied the fundamental mechanisms of PFSA membrane durability for >10 years and has significant relevant experience/equipment.

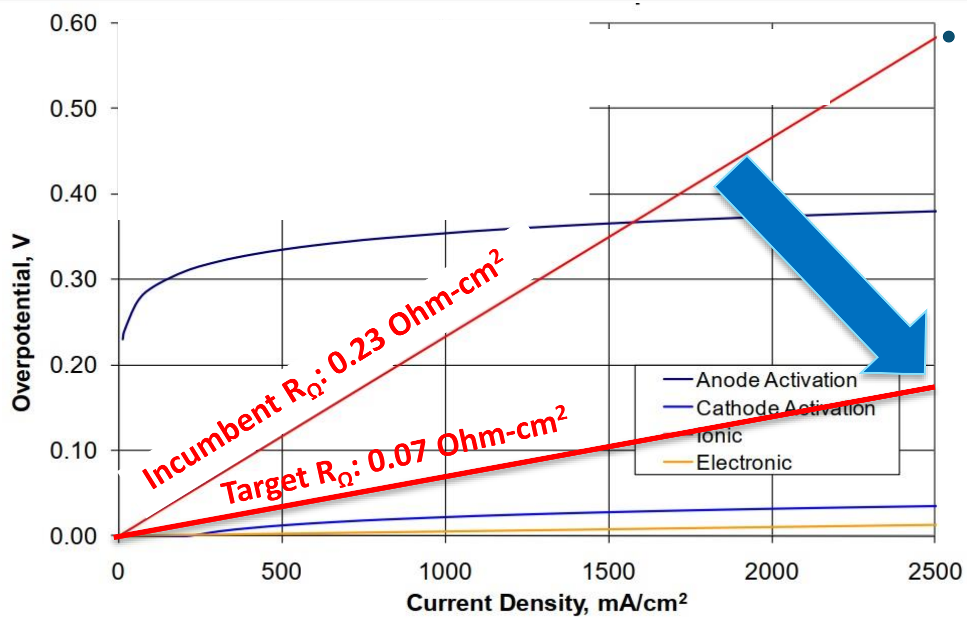
# Approach – Innovation: Combining Several Benefits Into One Membrane



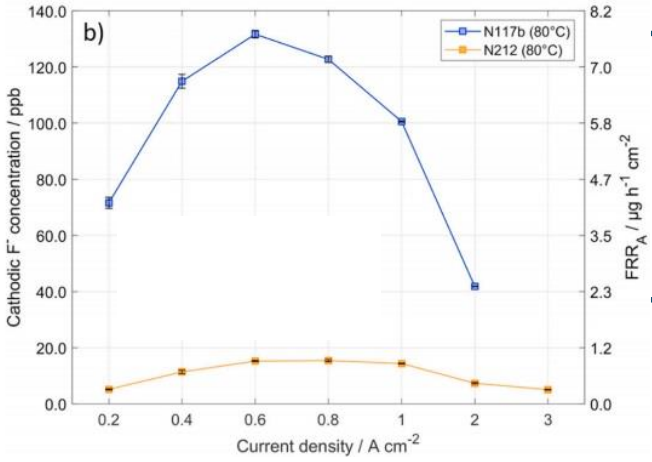




- Pursuit of cheap electricity (feedstock) will require usage of intermittent energy
- Current density will follow varying electrical load
- Low current density results in high $H_2$ in $O_2$ content (safety concern – LEL = 4%)

***GRCs enable safe stack operation for load-following applications, especially at high ΔP with a thin membrane***




- Reinforcing thin membranes is preferred for several benefits:
  1. Handleability (especially at scale)
  2. Mechanical Properties
  3. Low x-y expansion
  4. Enables low EW ionomers




- Fluoride ions have been quantified in PEMWE cell effluent
- Fluoride loss exacerbated at high temps

***Radical scavengers will be investigated to understand impact on PEMWE degradation***

# Approach and Collaborations: Project Team

| Project Partner | Role | Key Personnel | Activities |
|---|---|---|---|
| Chemours | Project Lead | Andrew Park (PI), Ryan Gebhardt, Dave Manion, Ben Wright, Sam Bartuska, Tim Hopkins | Membrane manufacturing (lab and pilot scale), raw materials sourcing, durability testing, project management and reporting |
| Los Alamos National Laboratory | Project Member | Siddharth Komini Babu (sub PI), Rod Borup, C. Evan van Pelt, Chung Hyuk Lee | Ex-situ measurements of hydrogen permeation and additive mobility, durability testing, GRC and scavenger synthesis |
| NREL Transforming ENERGY | HydroGEN Collaborator | Guido Bender (node PI), Jacob Wrubel, Jason Zack, Ellis Klein | In-situ PEMWE MEA and gas crossover testing, failure analysis, fluoride release quantification |
| Berkeley Lab | HydroGEN Collaborator | Adam Weber, Ahmet Kusoglu, and Nem Danilovic (node PIs), Arthur Dizon | Cell modeling, membrane behavior with additives |

- Team is well integrated, and has met biweekly to discuss results and future work

# Relevance and Impact

- PEMWE devices are the most proven technology to drive the adoption of H2@Scale. Reducing areal resistance of membranes in PEMWE environments is a critical contributor to their envisioned cost reduction toward \$2/kg $H_2$.

- Understanding durability implications of gas recombination catalysts and radical scavengers will enable “moving on” from incumbent thick membranes in PEMWE.

- EMN nodes bring capabilities that Chemours does not currently have in-house, facilitating advancement in materials availability.

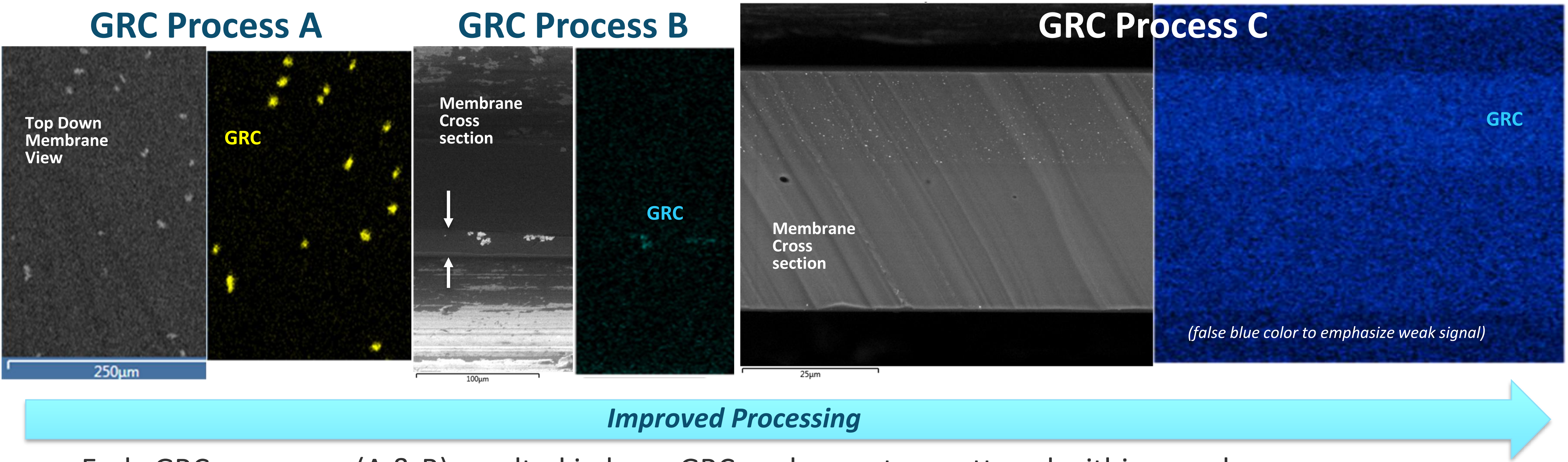
- The expected project outcome – significant progress toward a commercial PEMWE-specific membrane – ensures a USA-based supplier of these critical raw materials.

# Accomplishments: Milestones Achieved

| Milestone Type and Number | Milestone Description | Verification Process | Anticipated Date (Months from Start) | Approximate Percent Complete |
|---|---|---|---|---|
| Milestone (M1) | Define initial electrolysis membrane MEA material sets and ASTs which are capable of providing performance of at least 2 A/cm$^2$ at 1.9 V | Chemours/LANL | 3 | 100% |
| Milestone (M2) | Establish test for gas crossover ($H_2$ in $O_2$ content) for electrolyzer MEAs, and acquire baseline crossover/performance for N115, N117, NR212-containing MEAs | Chemours/LANL | 6 | 100% |
| Milestone (M3) | Manufacture membranes with at least 3 different additives for gas recombination and radical scavenging and evaluate their activity for $H_2$ and $O_2$ recombination/radical scavenging by monitoring $H_2$ in $O_2$ content and FER, respectively, at beginning of life (BoL) targeting 2% $H_2$ in $O_2$ for all current densities between 0.5 and 2 A/cm$^2$ and an FER <0.25 µg/cm$^2$-hr, a factor of 40x lower than NR211 in the DOE fuel cell combined chemical/mechanical AST. | LANL | 9 | 100% |
| Go/No-go (G1) | A ≤50 µm thick PFSA-based membrane with gas recombination catalyst layer (GRC PGM maximum loading of 0.1 mg/cm$^2$) demonstrates at least 50% reduction in $H_2$ in $O_2$ (outlet) content (maximum of 2% $H_2$ in $O_2$ for all current densities between 0.5 and 2 A/cm$^2$) compared to membrane with equivalent thickness without GRC layer. Membrane resistance must be <0.07 Ω-cm$^2$ and current density must reach 2 A/cm$^2$ at <1.9V, with all targets to be met in a PEMWE MEA at 60°C and with a differential pressure of 1-10 bar. | Chemours/LANL | 12 | 75% |

- Significant COVID-related delays to developing/validating experimental cells/protocols have been mitigated by recent progress
- GNG 1 expected to be reached with short no-cost extension

# Accomplishments:
# Successful GRC and Radical Scavenger Membrane Inclusion




- Early GRC processes (A & B) resulted in large GRC agglomerates scattered within membrane area
  - Likely ineffective recombination via low surface area to volume ratio of GRC
- Improved processing (C) yields membrane where GRC is uniformly dispersed in PFSA matrix
  - Though composition is not yet fixed, GRC inclusion process should be able to be leveraged across different compositions/chemistries
- Radical scavenger easily included in membrane (not shown)

***Optimized processes facilitate GRC and radical scavenger inclusion in PEM***

# Accomplishments:
# Reinforced Membrane Prototype and MEA Testing

| Membrane | Dry Thickness (µm) | Reinforced? | GRC or Radical Scavenger? | Areal Resistance in 23°C $H_2O$ [mΩ-cm$^2$] | Ultimate Tensile Strength [MPa] | | Liquid $H_2O$ Expansion [%] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | MD | TD | MD | TD |
| N 117 | 178 | No | No | 217 | 25 | 25 | 13 | 22 |
| N 115 | 127 | No | No | 156 | 31 | 28 | 11 | 19 |
| NR 212 | 50 | No | No | 78 | 32 | 32 | 20 | 20 |
| NDP 4006 | 50 | Yes | No | 81 | 43 | 42 | 13 | 8 |

**MEA Components**

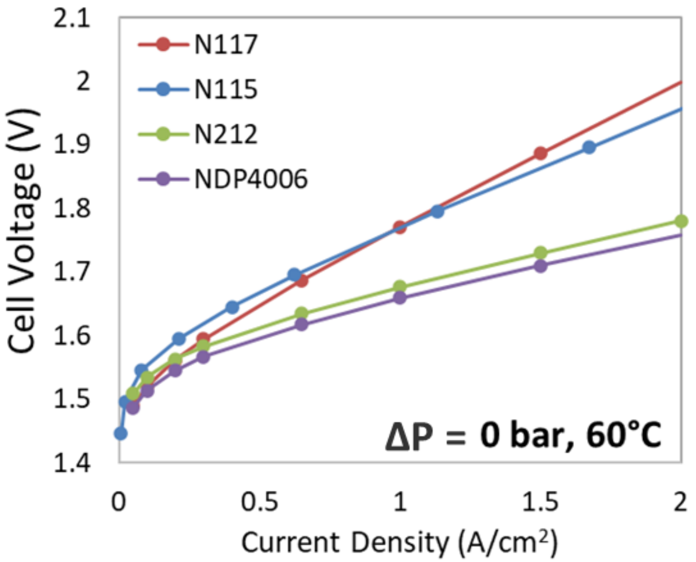
*Anode:* IrOx at 0.32-0.4 mg/cm$^2$

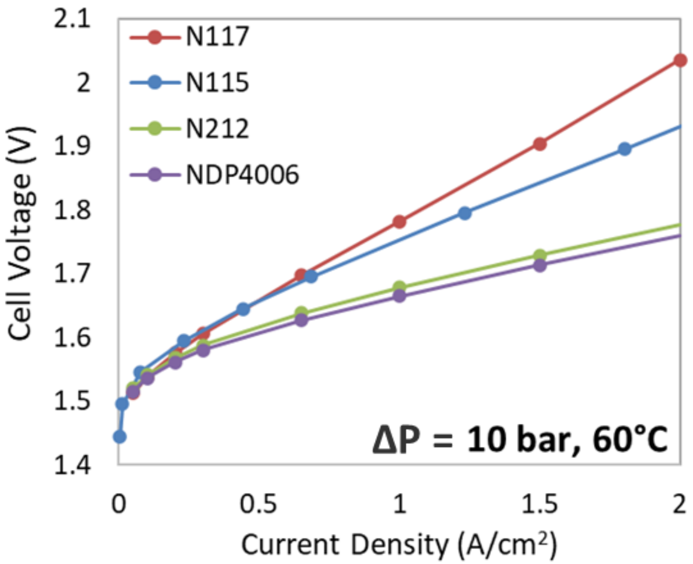
*Cathode:* Pt/HSC at 0.1 mg/cm$^2$

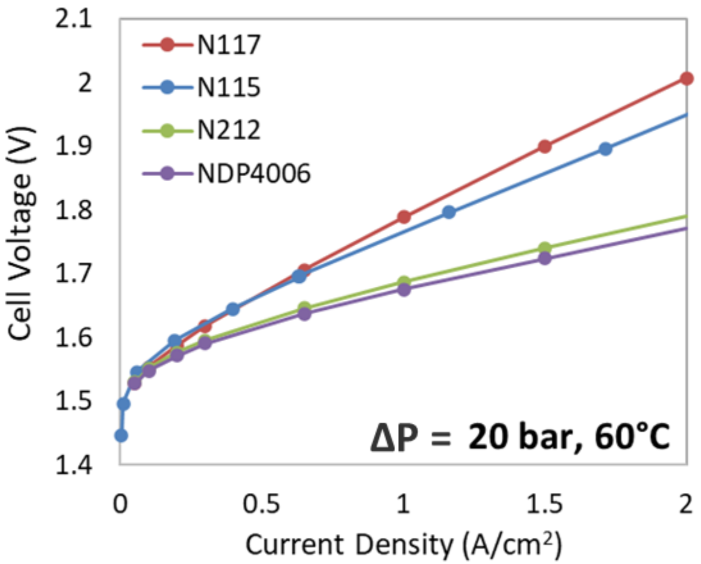
*Temperature:* 60°C

*Pressure:* 0-20 bar $H_2$, Ambient $O_2$

*Water flow:* 300 mL/min

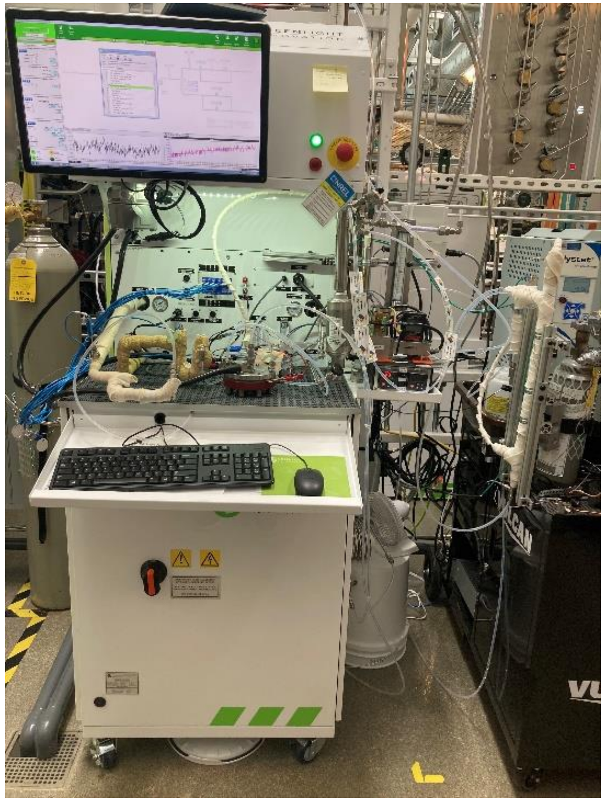


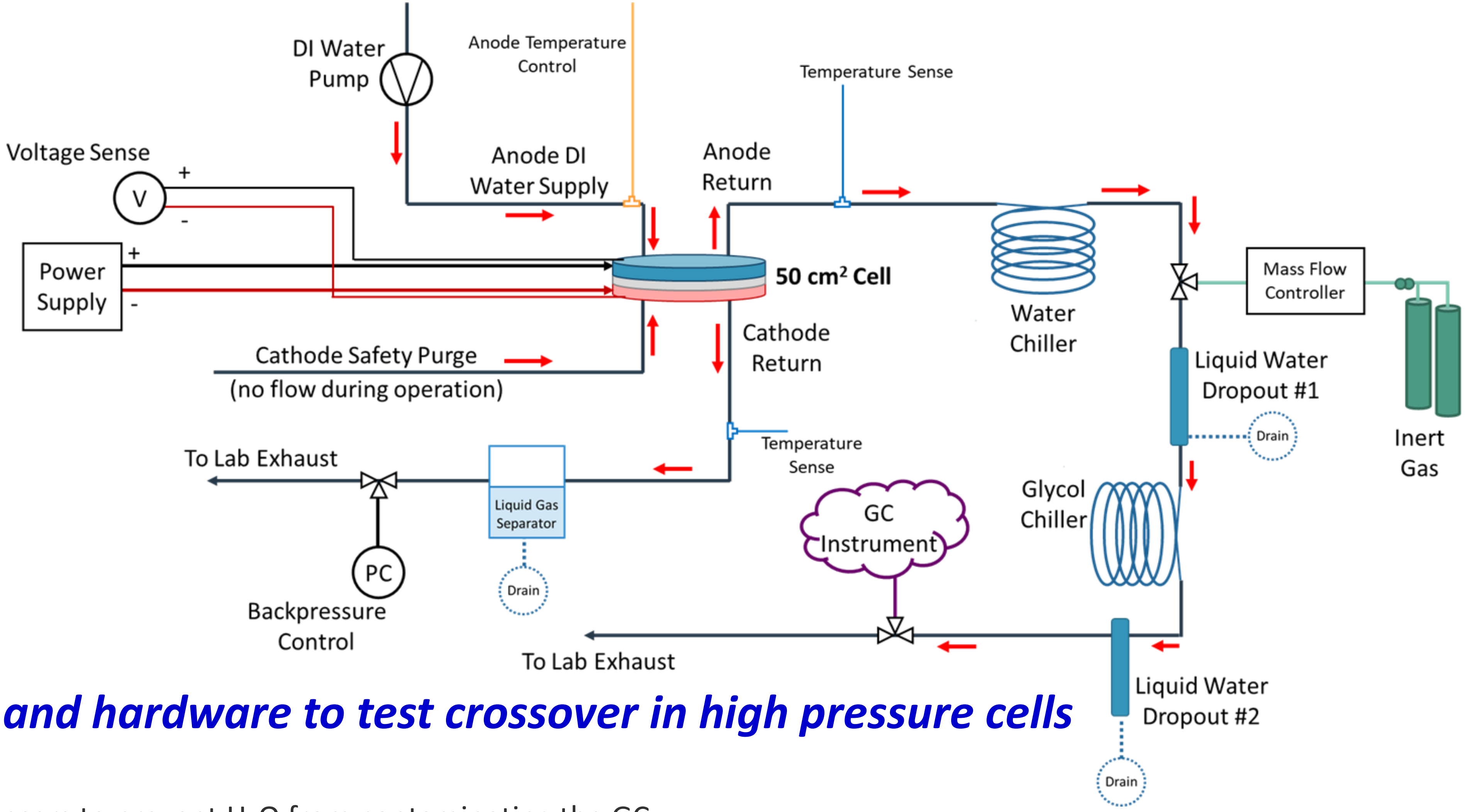




***Reinforced prototype membrane matches NR212 performance, with higher strength and reduced planar expansion***

# Accomplishments: Testing Anode Exhaust Stream from Operating MEA






## *Developed new process and hardware to test crossover in high pressure cells*

- Capable of testing up to 30 bar
- Liquid water dropouts & condensers to prevent $H_2O$ from contaminating the GC
- System designed with inert dilution gas to keep $H_2$:$O_2$ < 1% LFL

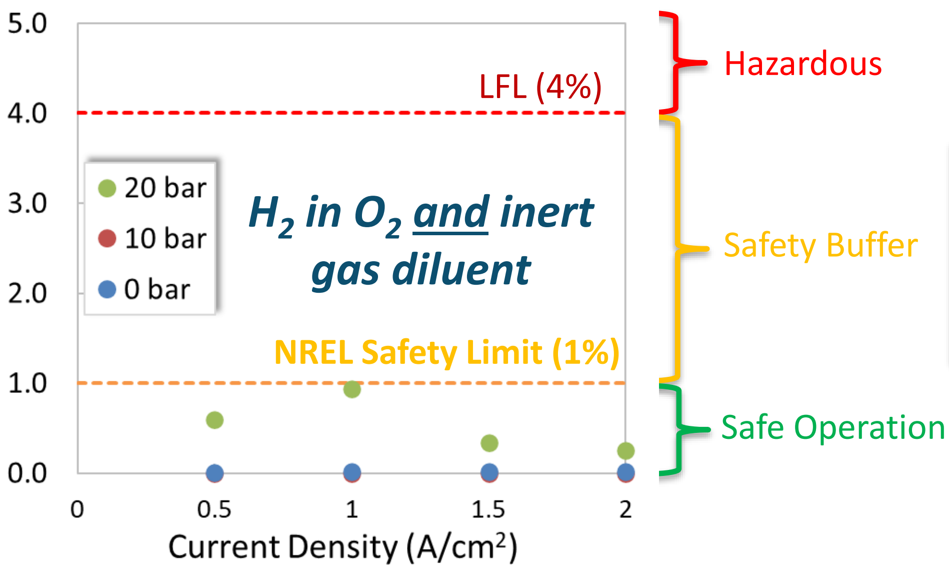
# Accomplishments: Ensuring Safe Crossover Testing With Inert Gas Dilution

NREL Transforming ENERGY

- Operating safely: lower flammability limit of $H_2$ in $O_2$ is 4%
  - NREL safety limit is 1%
  - Hydrogen crossover can create a flammability hazard at our operating conditions after the water is removed
  - A monitored dilution stream of inert gas was added for safe operation
  - $H_2$ in $O_2$ content is extracted from the GC analysis of the diluted stream

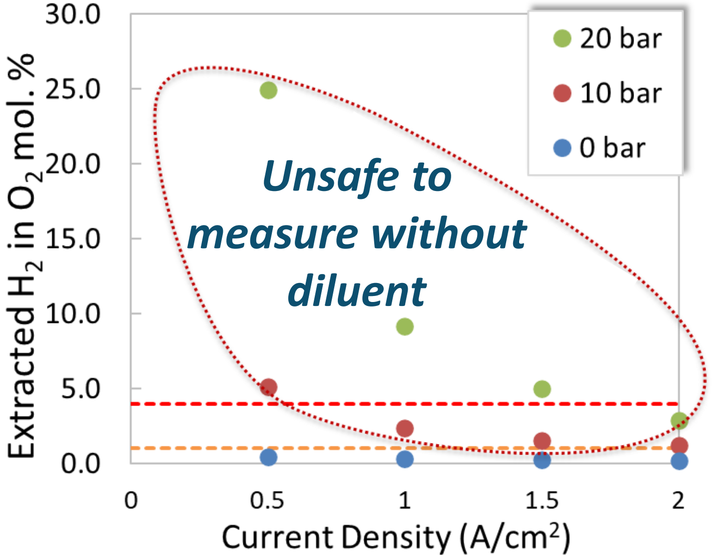
**Nafion 212, 60°C**

**As measured ($H_2$ in total gas)**




***$H_2$ and $O_2$ content extracted from inert gas in GC***

**Extracted $H_2$ in $O_2$ Data**

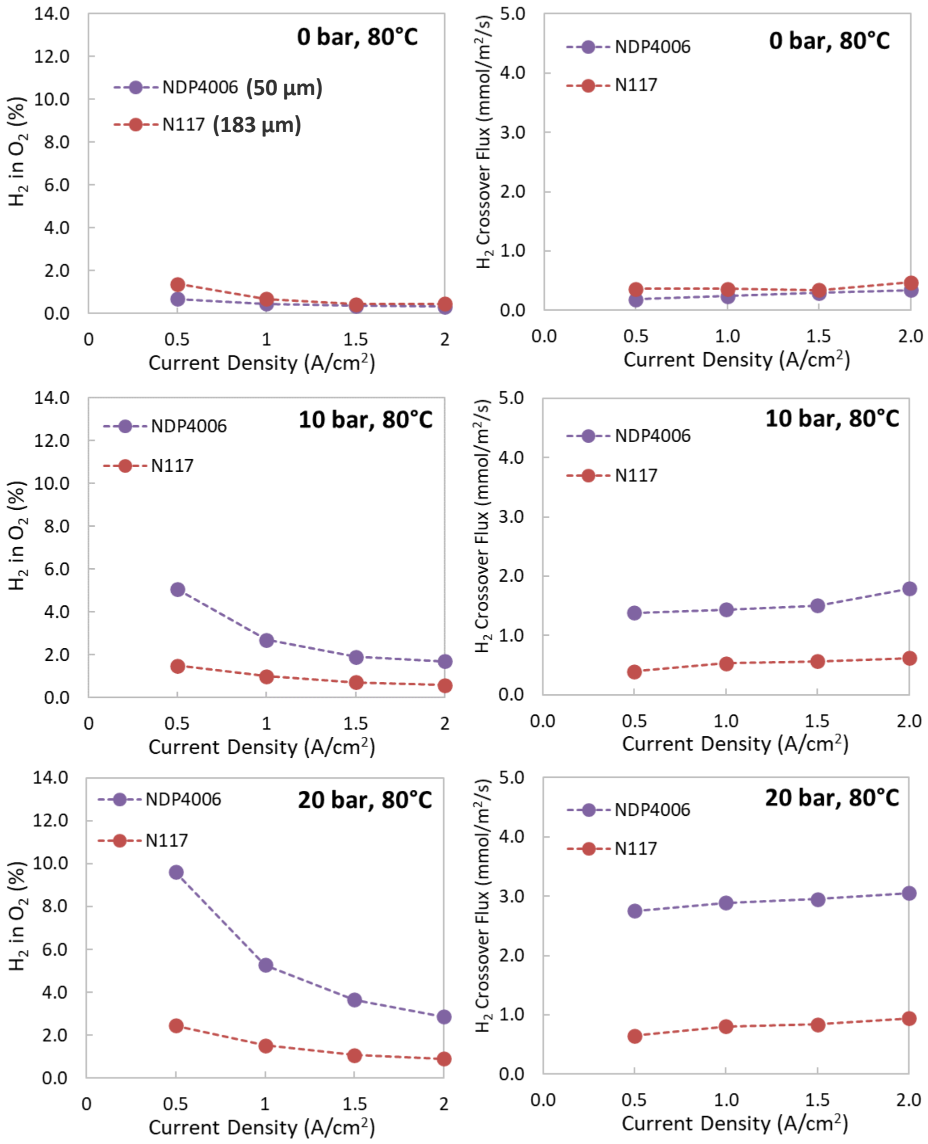



***High $H_2$ content in $O_2$ stream mitigated with inert carrier gas, enabling safe measurement of high gas crossover***

# Accomplishments: Hydrogen Crossover as Function of Backpressure

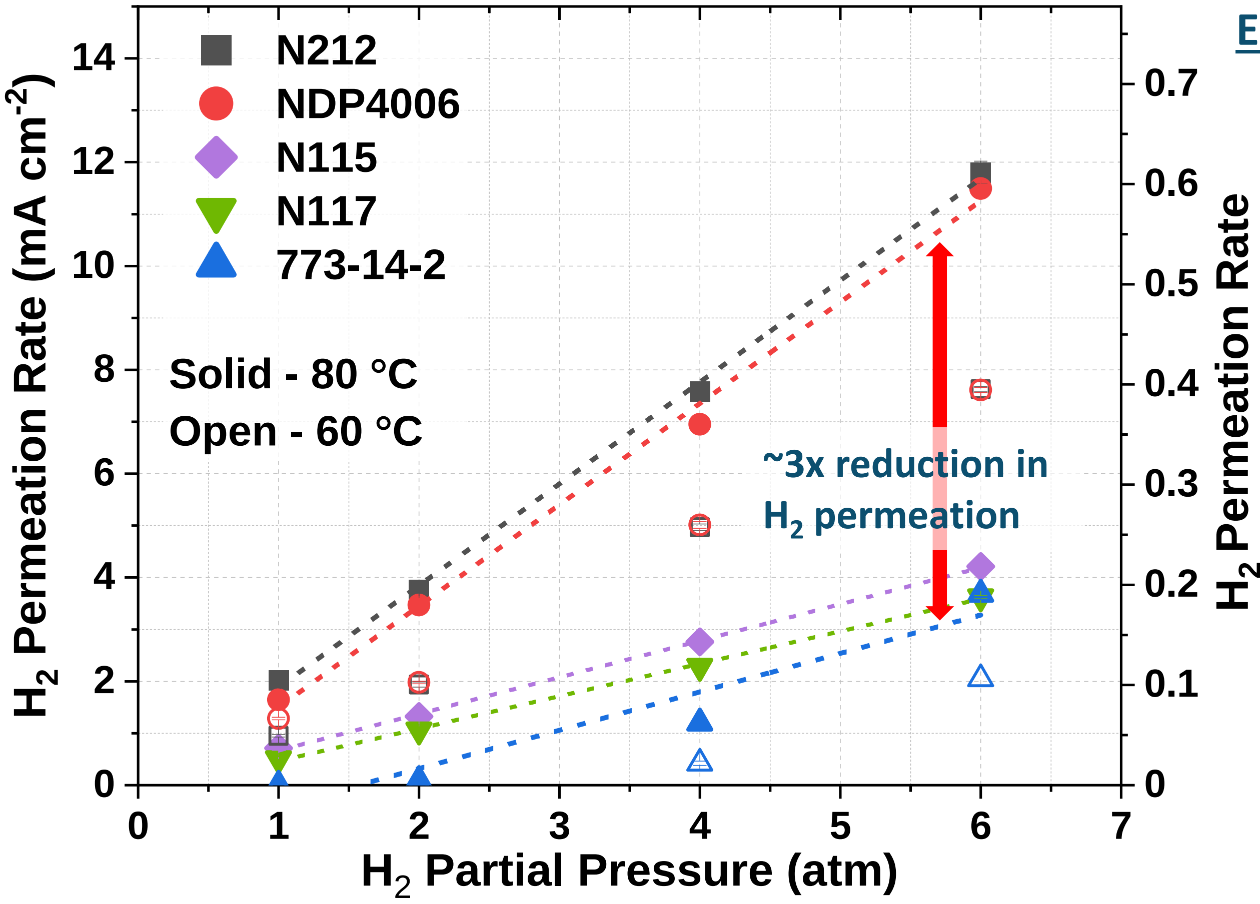
- Tested baseline cells for $H_2$ crossover at 3 different $H_2$ pressures **(0 bar, 10 bar, 20 bar)** and 2 different temperatures **(60℃, 80℃)**
- $H_2$ percent in $O_2$ decreases with current density because the OER produces $O_2$ more than $H_2$ crosses over
- Crossover flux vs. current density can provide insights about the crossover mechanism(s):
  - Increasing the current increases the concentration gradient, driving diffusion
  - Increasing backpressure increases the pressure-driven flux (suggested to be negligible for Nafion™)
  - Electroosmotic drag could mitigate crossover (water moves from anode to cathode), which may be an interesting effect to explore/quantify in the coming quarters (subject to funding)

$$N_{H_2}^{tot^*} = \underbrace{\frac{D_{H_2}^{eff} S_{H_2} p_{H_2}^C}{t_{mem}}}_{\text{Diffusion}} + \underbrace{\frac{k_{mem} S_{H_2} p_{H_2}^C \Delta p_{H_2}}{\eta_{H_2O} t_{mem}}}_{\text{Pressure-driven}} - \underbrace{\frac{S_{H_2} p_{H_2}^C}{c_{H_2O}} \frac{n_{H_2} i}{F}}_{\text{Electro-osmotic Drag}}$$



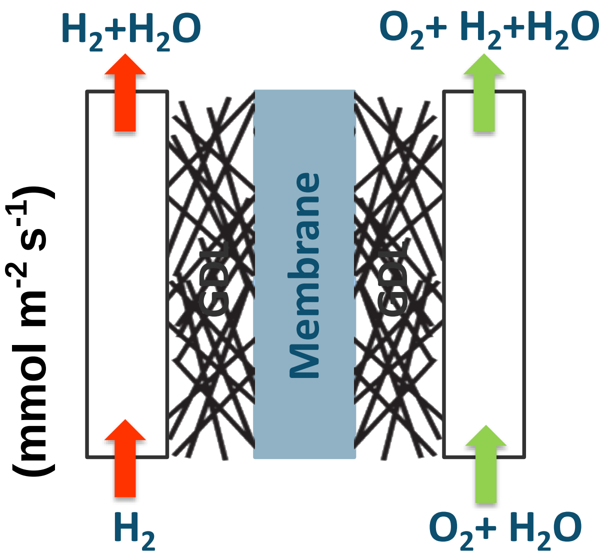

*M. Bernt *et al.*, J. Electrochem. Soc., **165**, 2018

# Accomplishments: $H_2$ Permeation Reduction with GRC




Active area: 50 cm², Cell temperature: 80 °C, $O_2$ partial pressure: 1 atm, titanium single serpentine flow field

## Ex-situ $H_2$ Permeation Measurement



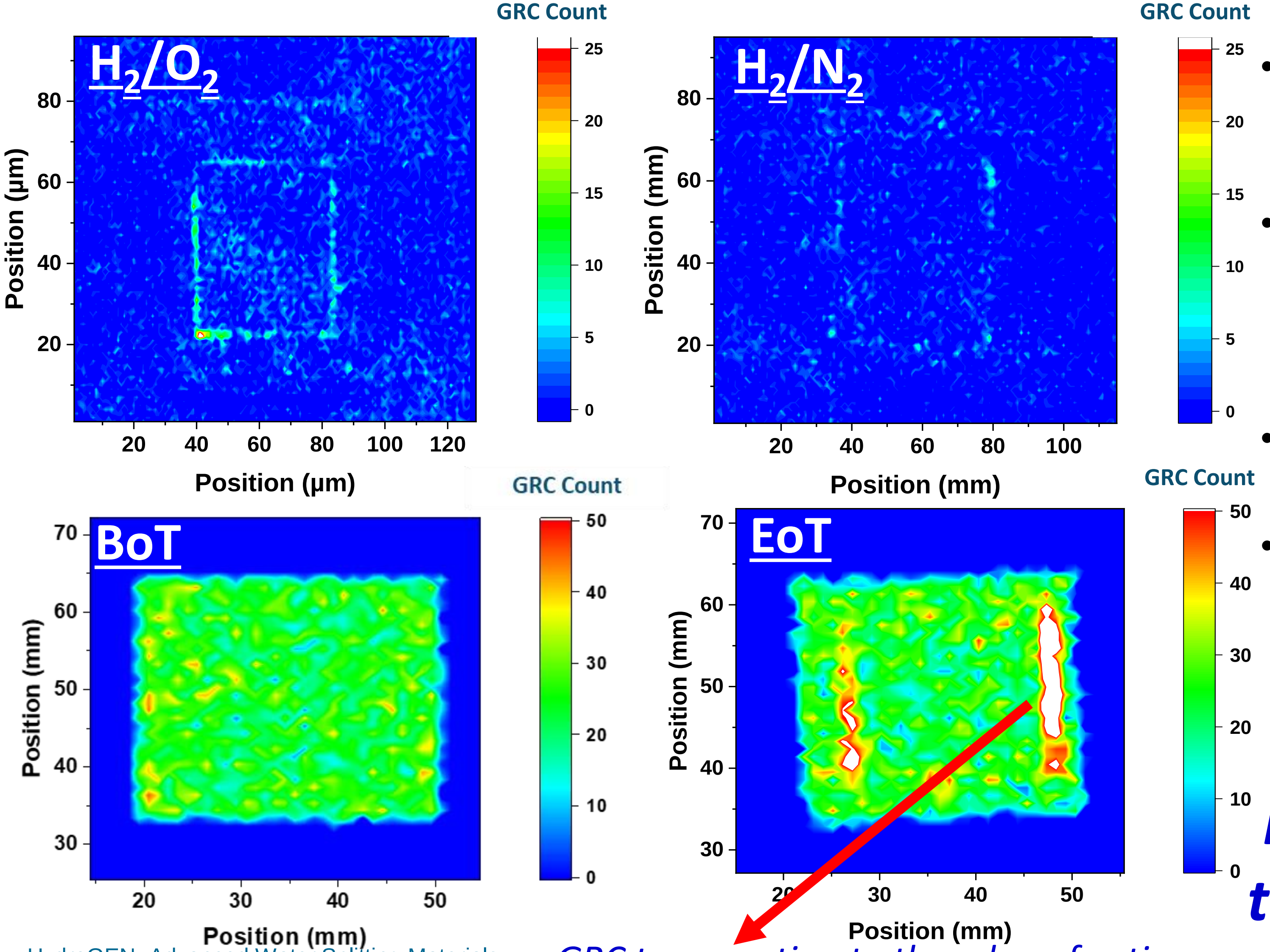

- $H_2$ crossover measurement in $H_2/O_2$ environment in cell with membrane and PTLs (no electrodes)
- Oxygen supersaturated to simulate PEMWE conditions
- Cell max ΔP = 5 atm. New cell hardware to be purchased for BP2 (subject to funding)

| Membrane | Thickness (µm) | GRC Loading (mg/cm²) | $H_2$ Permeation rate (mmol m$^{-2}$ s$^{-1}$ atm$^{-1}$) |
|---|---|---|---|
| NR212 | 50 | n/a | 0.10 |
| NDP 4006 | 50 | n/a | 0.10 |
| N115 | 125 | n/a | 0.04 |
| N117 | 175 | n/a | 0.03 |
| 773-14-2 | ~56 | <<0.1 | 0.04 |

***~50 µm membrane with GRC shows ~3x reduction in effective $H_2$ crossover between 1-6 atm $p_{H2}$***

# Accomplishments:
# XRF Mapping of GRC Migration in Ex-situ Cell

**Cell temp: 65 ˚C, Cathode: Dry $H_2$ at 2.75 kPa, Anode: $N_2/O_2$ at 300 % RH and 0.75 kPa + 3 ml/min $H_2O$**




*GRC transporting to the edge of active area*

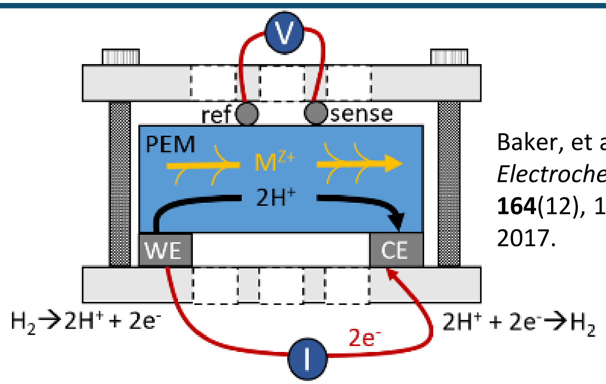
- End of test XRF (top row) of first GRC-containing membrane prototype shows tendency of GRC to migrate to perimeter of "active" (hydrated) area
- Effect does not occur in $H_2/N_2$ environment, suggesting active recombination promotes movement of GRC

- Refined prototype (bottom row) shows uniform GRC distribution at beginning of $H_2/O_2$ cell test.
- At end of test, some GRC movement to edges of hydrated area is obvious. Average GRC content in membrane appears lower, but still substantial.

***XRF capability to map in-situ movement of GRC will be critical to ensure durability of membrane***

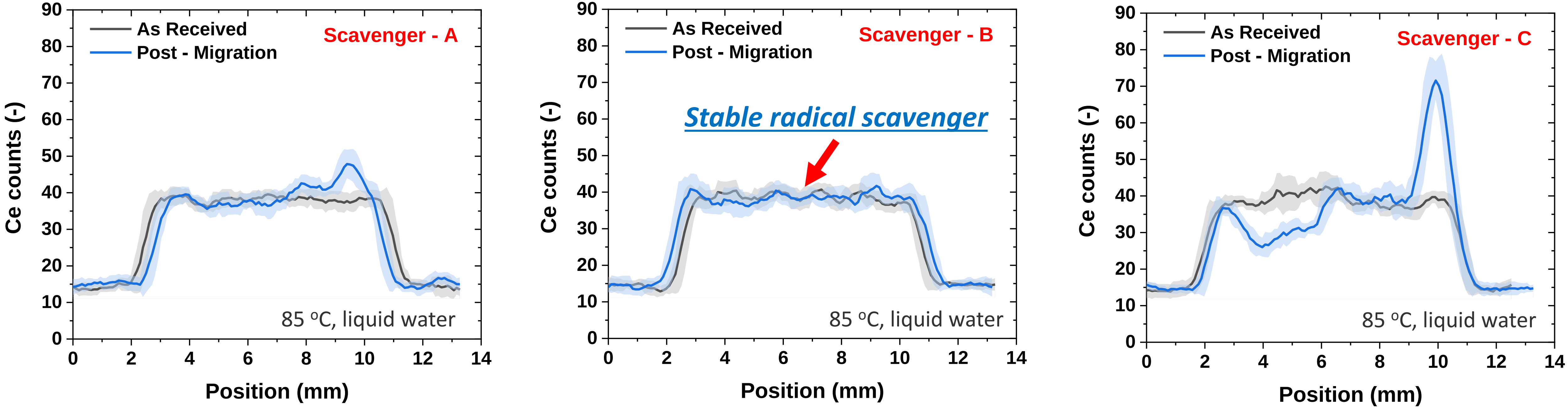
# Accomplishments: Mitigation of Radical Scavenger Migration

- As with GRCs, radical scavengers are a risk to move within/out of the membrane during PEMWE operation
- Utilizing cerium migration approach in PEMWE-relevant environment reveals tendency of scavenger to migrate




Baker, et al., *J. Electrochem. Soc.*, **164**(12), 1272-1278, 2017.

**Cerium concentration profiles across the membrane pre- and post-migration experiment**

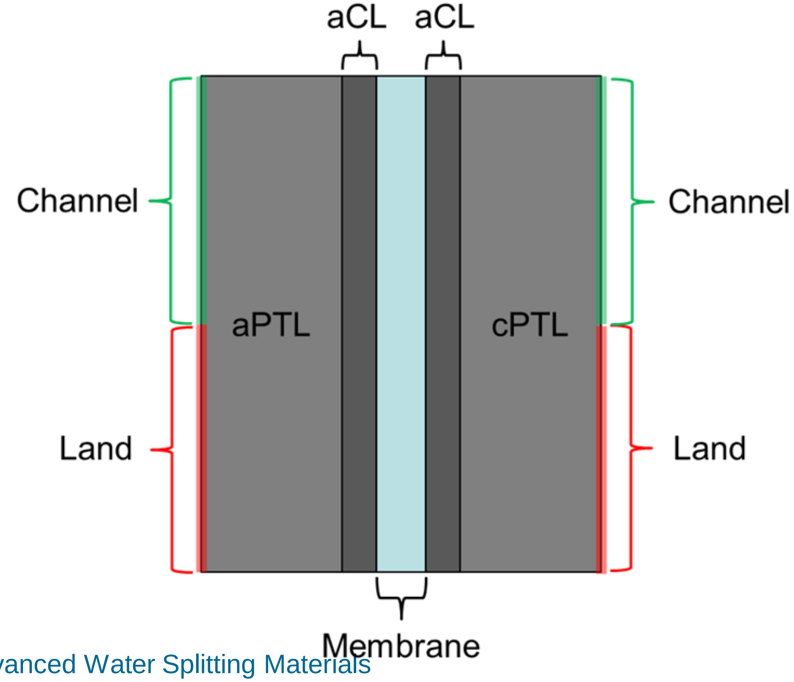



***Scavenger morphology/composition has a significant impact on their mobility in a PEMWE environment***

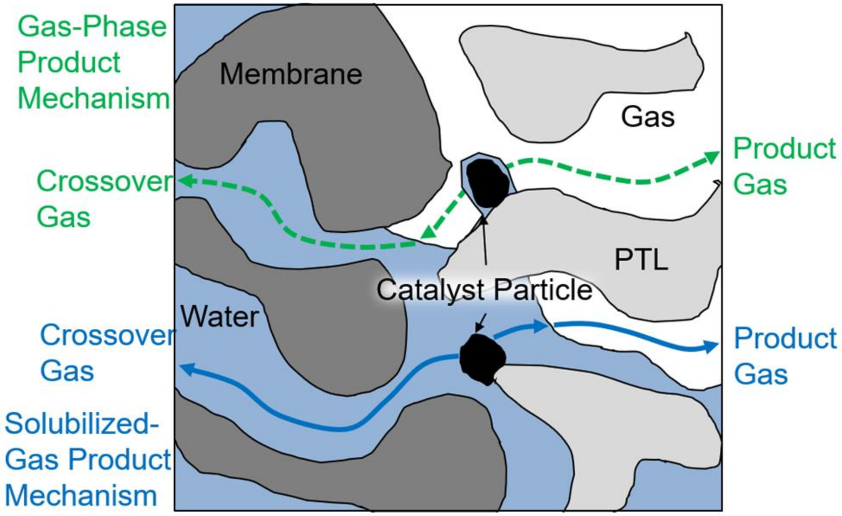
# Accomplishments:
# Mathematical Model for PEMWE

## 2D finite-element method (FEM) model

- Physics / Governing Equations / Domain
  - Porous gas and liquid flow / Darcy's Law ■ ■ ■
  - Gas transport / Stefan-Maxwell equations ■ ■ ■
  - Electrochemistry / Butler-Volmer kinetics ■
  - Membrane transport / Conc. solution theory




## Development of Crossover Mechanisms



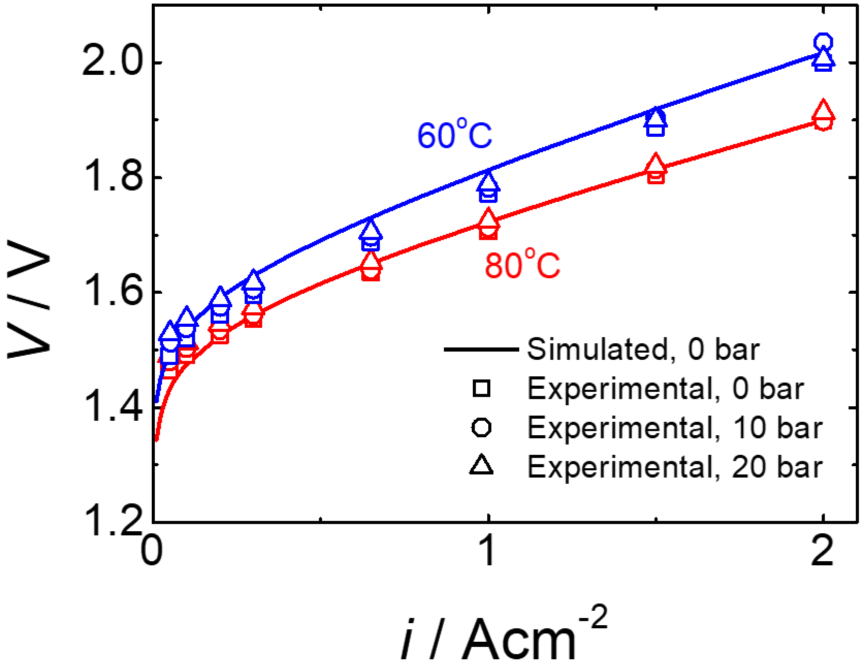

- Two mechanisms for gas evolution
  - Gas-Phase product (green)
    - Product gas generated directly into gas phase
    - Assumes quick bubble formation kinetics
  - Solubilized Gas product (blue)
    - Product gas generated directly into liquid phase
    - Allows for high-concentrations in liquid phase

# Accomplishments:
# Using Model to Understand Baseline Performance

BERKELEY LAB

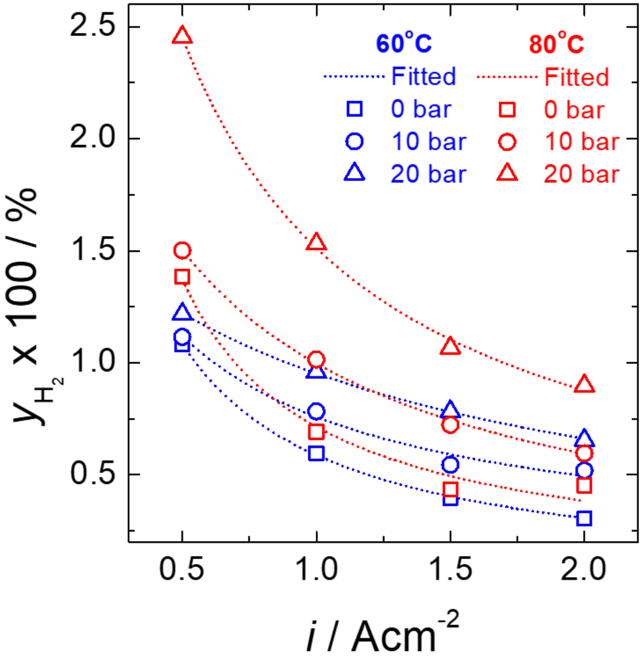
## Polarization Curve Model Fit

- FEM model output compares well to experimental measurements from NREL on N117 membrane




## Hydrogen Crossover Model Fit

- Crossover model is also able to fit data generated by NREL on N117 membrane as a function of temperature and pressure




***FEM model appears to accurately predict experimental results, and will be used to aid in membrane design in BP 2 (subject to funding).***

# Collaboration: Effectiveness

- Chemours has provided prototype membranes samples to LANL and NREL, and to LBNL in the near future.
- LANL has built new capabilities and extended existing ones into the PEMWE space to feed back ex-situ data on membranes with GRC and radical scavengers to Chemours. Permeability and other data are sent to LBNL for modeling. New additive compositions are in development for integration with Chemours in BP2 (subject to funding).
- NREL has built an in-situ gas crossover testing platform (0-30 bar) and has tested MEAs made with Chemours' membranes. Feedback goes to Chemours for membrane design and LBNL for modeling.
- LBNL models have established a platform to assist with design of prototype membranes.
- Many developed protocols can be merged into the benchmarking/protocols 2b scope
- Work on thin membranes will provide significant fundamentals to HydroGEN members as well as H2NEW efforts to explore scale-up considerations based on state of the art materials.

# Proposed Future Work

| Task or Subtask | Milestone Type and Number | Milestone Description | Responsible | Anticipated Date (Months from Start) | Approximate Percent Complete |
|---|---|---|---|---|---|
| 1.1 | Milestone (M5) | Begin AST testing of roll to roll fabricated reinforced membranes | Chemours/LANL | 15 | 0% |
| 3.1 | Milestone (M6) | Manufacture and evaluate series (minimum 5 different samples) of membranes with different thicknesses and GRC layer compositions | Chemours | 18 | 0% |
| 2.1 | Down-Select #1 | Finalize selection of ePTFE reinforcement and additive composition | Chemours | 18 | 0% |
| 2.2 | Milestone | Achieve $H_2$ in $O_2$ content of <2% for all current densities between 0.5 and 2 A/cm$^2$ for a membrane with a GRC layer | Chemours/LANL | 21 | 0% |
| | Go/No-Go (G2) | i. Reinforced roll-to-roll dispersion cast membrane with GRC and radical scavenging additives demonstrates a $H_2$ in $O_2$ content of < 2% for all current densities between 0.5 and 2 A/cm$^2$.<br>ii. Voltage in an MEA at 2 A/cm2 must be < 1.9 V and membrane resistance/gas crossover must not increase more than 2% of BoL value after 500 hr of continuous operation at 60°C and differential pressure of 30 bar. | Chemours/LANL | 24 | 0% |

- Budget Period 2 work will focus on integrating membrane, gas recombination catalyst, and radical scavenger into “complete” membrane prototypes
- Membranes will begin to be tested for durability as well as initial performance, culminating in GNG 2.

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

# Project Summary

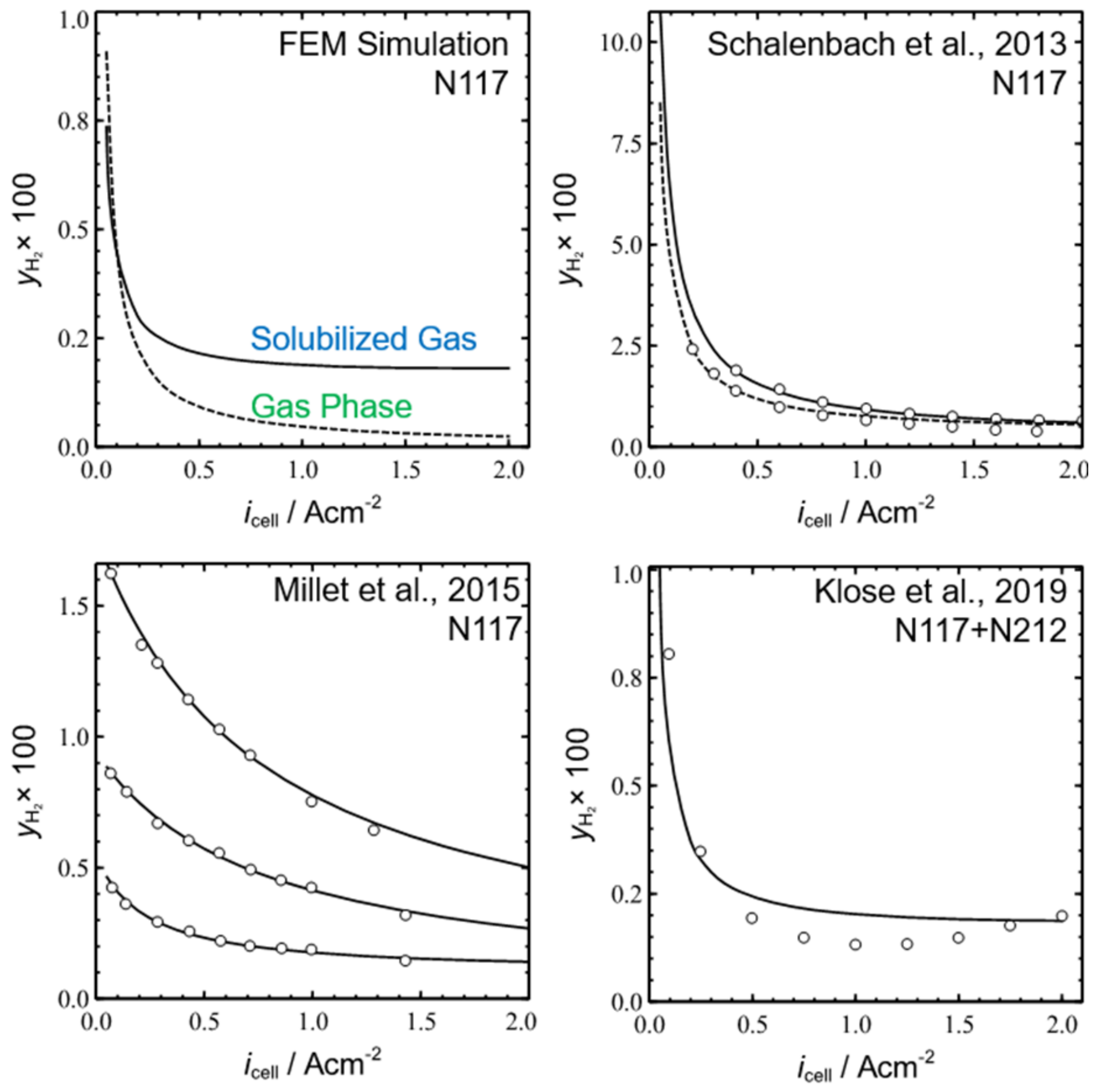
- Budget period 1 work has focused on individual aspects of the envisioned final membrane
- A thin, reinforced membrane prototype has demonstrated equal or better performance than NR 212 with higher strength and lower expansion
- GRCs appear to be effective in reducing hydrogen in oxygen content by ~3x compared to baseline PFSA membranes. This effect will be verified in an MEA for GNG 1.
- Radical scavengers have been made to be immobile in the PEMWE environment.
- Budget period 2 will merge all workstreams to create “all-in-one” complete prototype membranes and evaluate them in ASTs.

# Technical Backup Slides

# Subtask 1.1 (Milestone M1): Define Baseline MEA Materials Sets

| Component | Condition | Material/Amount |
|---|---|---|
| Membranes | | N117<br>N115<br>NR212<br>NDP 4006 |
| Electrode Catalyst | Anode | Iridium Oxide |
| | Cathode | Platinum on High Surface Area Carbon |
| Electrode Loading | Anode | 0.4 $mg/cm^2$ (same as H2NEW) |
| | Cathode | 0.1 $mg/cm^2$ |
| Gas Diffusion Layer | Cathode | 0% PTFE Carbon Paper (Toray) |
| Porous Transport Layer | Anode | Pt-Sputtered Titanium Felt (Bekaert)<br>2GDL5-0,125 or 2GDL6-0,25 |
| Gaskets | Ambient Pressure | Polytetrafluoroethylene (PTFE) |
| | Differential Pressure | Proprietary |

# Accomplishments:
# Comparing Product Gas Mechanisms to Literature




- Simulation Results
  - (top-left) Simulation results showing the difference between the crossover of the two mechanisms
    - Solubilized gas (solid line)
    - Gas phase (dashed line)
  - (top-right, bottom row) Comparison of simulated and published crossovers
    - The solubilized gas mechanism can explain high-current density crossover better