



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

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Project ID #P186

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# Project Overview

## Project Partners

Andrew Park (PI), Chemours  
Rod Borup (co-PI), Los Alamos Nat'l Lab

## Project Vision

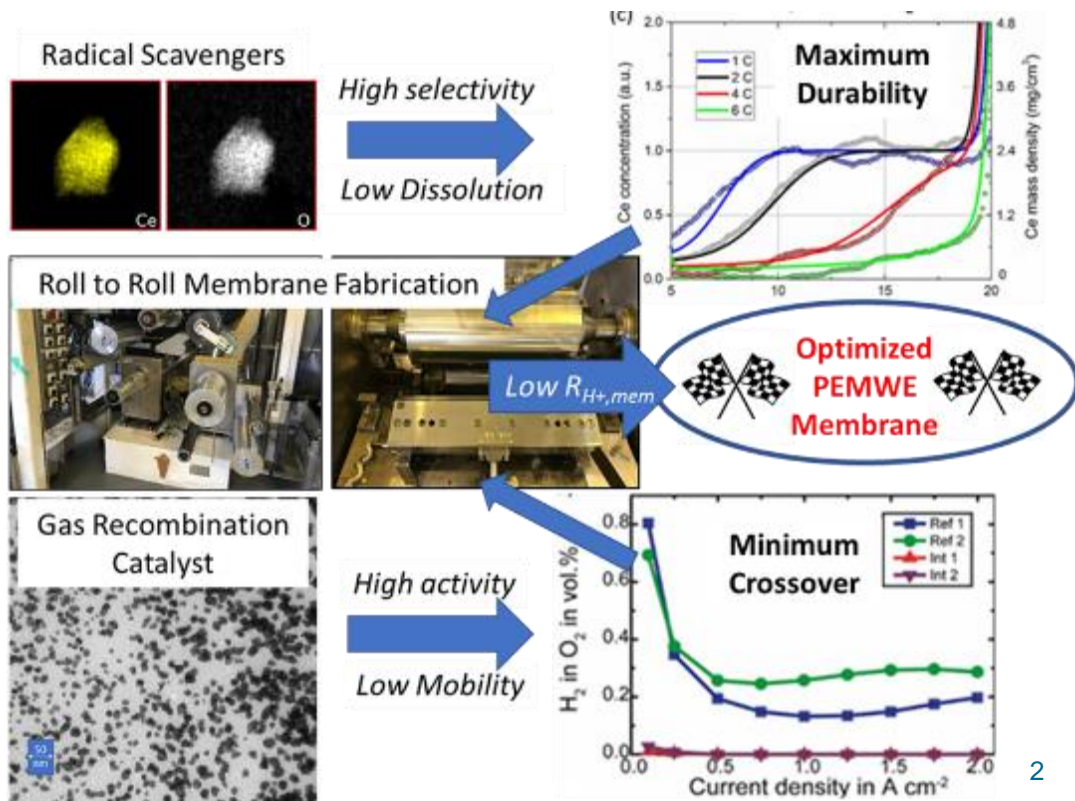
Thin, reinforced membrane with performance and durability additives that enables high current density and long lifetime in PEMWE systems.

## Project Impact

High performance commercial membranes will directly and indirectly reduce PEMWE costs, facilitating  $H_2$  @  $< \$4/gge$

Award #	EE0001859
Start/End Date	03/01/2020–02/28/2023
Total Project Value*	\$1.25M (DOE+Cost Share)
Cost Share %	20%

\* this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)





# Approach- Summary

## Project Motivation

This project was created with the vision of transforming PEMWE systems via high performance membranes. It unites the manufacturer of Nafion™ PFSA membranes (Chemours) and the leader in fuel cell performance and durability investigations (LANL).

## 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

## Key Impact

Metric	State of the Art	Expected Advance
Membrane resistance [ $\Omega$ -cm <sup>2</sup> ]	0.2	<0.07
Membrane tensile strength (MPa)	25	>40
Gas Recombination Catalyst and Radical Scavenger in membrane	No	Yes

## Partnerships

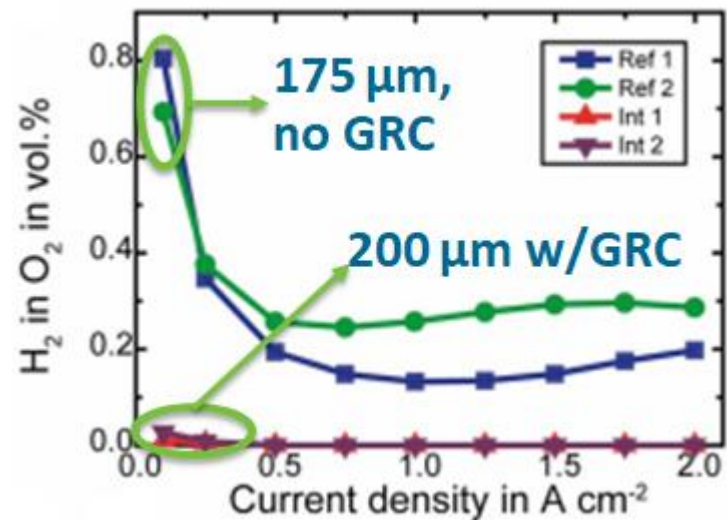
Chemours is the manufacturer of Nafion™ PFSA polymers and is the leading supplier of water electrolyzer membranes today

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

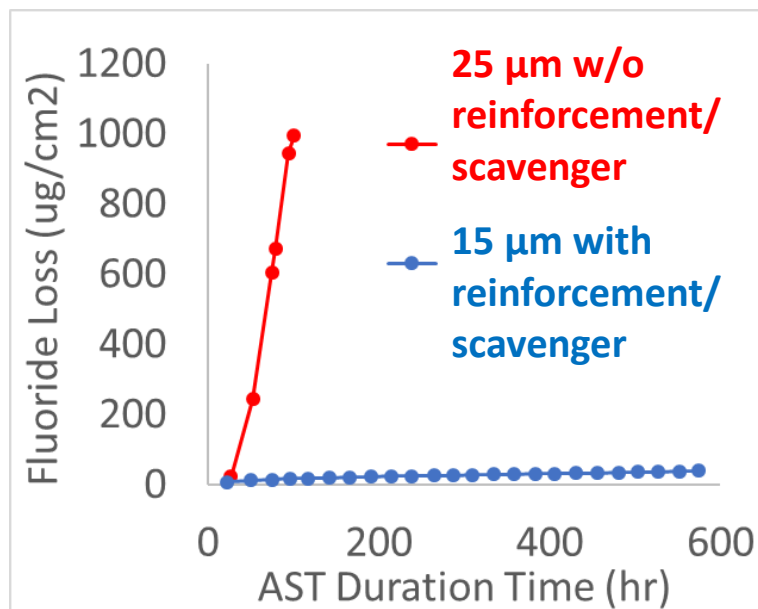


# Approach- Innovation

- Thin membranes exacerbate H<sub>2</sub> crossover, especially at high  $\Delta P$ .
- Membrane thinning, possibly due to radical attack on PFSA polymer, could be a concern
- These mechanisms will be studied and mitigated via gas recombination catalysts (GRCs) and radical scavengers.
- BP1 work will focus on making membranes with these additives and evaluating their activity/stability in the membrane.
- GNG 1 will show that GRCs can reduce the H<sub>2</sub> crossover in a membrane at given thickness by 50%, while maintaining high standards for performance

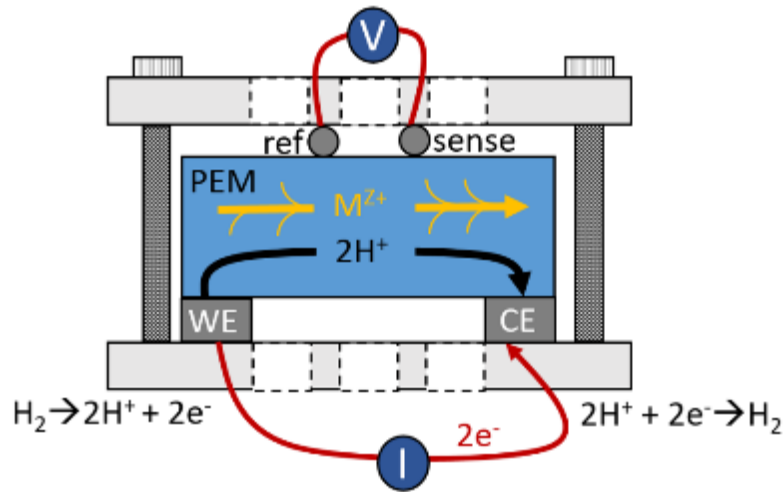


Thiele and co-workers, J ECS, 165(16) F1271-F177 2018

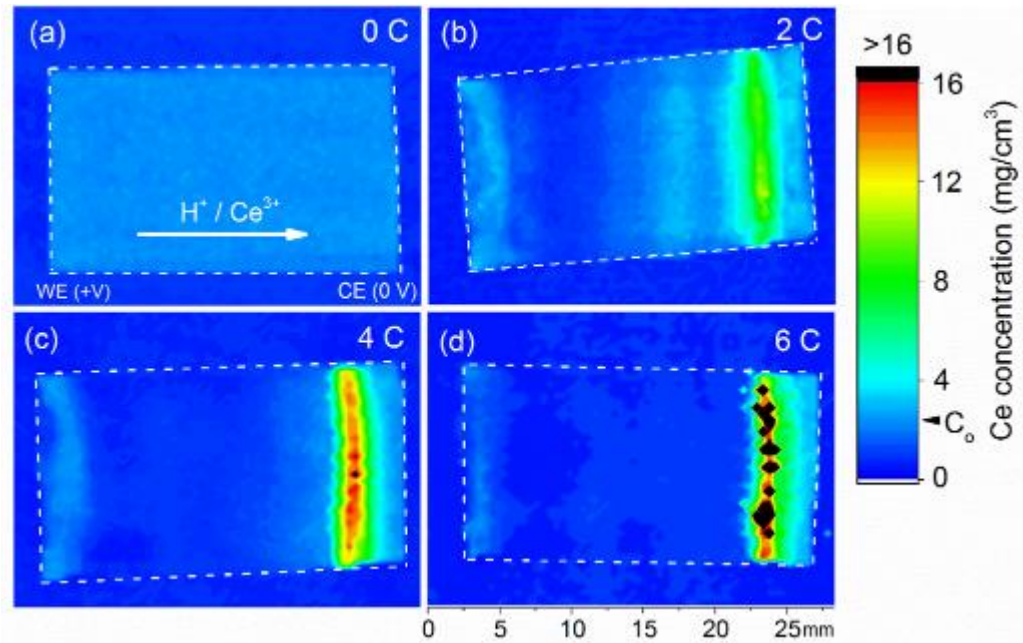




# Approach- Innovation



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



- BP1 will adapt cerium migration work for fuel cell membranes into water electrolyzer space to investigate movement of platinum GRC and radical scavenger in PFSA membrane in PEMWE conditions
- Mobility data will feed into fabrication efforts to optimize placement and composition of additives for reduced/eliminated mobility and/or dissolution



# Accomplishments

- New project starting 3/1/20; essentially all lab work delayed due to Covid-19 pandemic. Milestone M1 largely complete remotely.

Task or Subtask	Milestone Type and Number	Milestone Description	Verification Process	Anticipated Date (Months from Start)	Approximate Percent Complete
1.1	Milestone (M1)	Define initial electrolysis membrane MEA material sets and ASTs which are capable of providing performance of at least 2 A/cm <sup>2</sup> at 1.9 V	Chemours/LANL	3	90%
3.1	Milestone (M2)	Establish test for gas crossover (H <sub>2</sub> in O <sub>2</sub> content) for electrolyzer MEAs, and acquire baseline crossover/performance for N115, N117, NR212-containing MEAs	Chemours/LANL	6	5%
2.1	Milestone (M3)	Manufacture membranes with at least 3 different additives for gas recombination and radical scavenging and evaluate their activity for H <sub>2</sub> and O <sub>2</sub> recombination/radical scavenging by monitoring H <sub>2</sub> in O <sub>2</sub> content and FER, respectively, at beginning of life (BoL) targeting 2% H <sub>2</sub> in O <sub>2</sub> for all current densities between 0.5 and 2 A/cm <sup>2</sup> and an FER <0.25 μg/cm <sup>2</sup> -hr, a factor of 40x lower than NR211 in the DOE fuel cell combined chemical/mechanical AST.	LANL	9	1%
2.2	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 <sup>2</sup> ) demonstrates at least 50% reduction in H <sub>2</sub> in O <sub>2</sub> (outlet) content (maximum of 2% H <sub>2</sub> in O <sub>2</sub> for all current densities between 0.5 and 2 A/cm <sup>2</sup> ) compared to membrane with equivalent thickness without GRC layer. Membrane resistance must be <0.07 Ω-cm <sup>2</sup> and current density must reach 2 A/cm <sup>2</sup> 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	1%



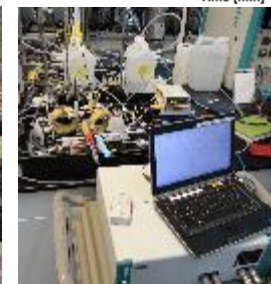
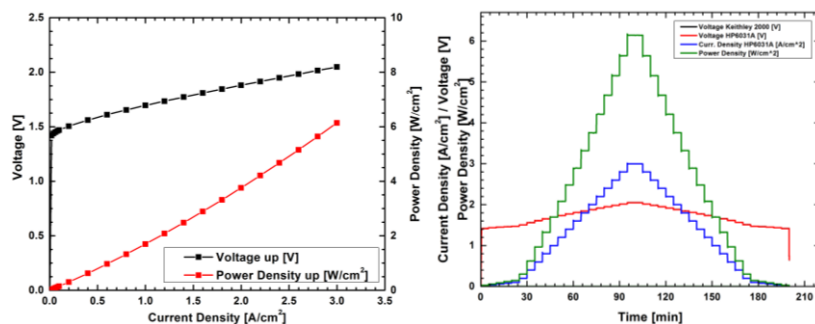
## Relevance & Impact

- Thin membranes are made on roll to roll equipment and use far less PFSA polymer, for less cost per unit area.
- A successful commercial membrane would represent a step change in performance and efficiency for the most mature renewable hydrogen generation space.
- The partners have unique capabilities that enable an impactful research area.
- The membrane developed here can be used in future projects as a durable, high performance baseline for the consortium community



# Collaboration: Effectiveness

- NREL: Guido Bender - In Situ Testing Capabilities for Hydrogen Generation (1 W-250 kW)
- 3 way project meetings held to discuss equipment needs and sampling schedule
- 2x commercial test systems and 6x NREL built single PEM/AEM electrolyzer
  - $\Delta p_{\max}$  up to 50 bar enables differential pressure tests for new project membrane application and verification
  - Anode and cathode product gas analyzers for safety and gas crossover quantification
- Ex-situ measurement of fluoride emission from PEMWE MEA effluent to be developed



1) G. Bender et al., "Initial Approaches in Benchmarking and Round Robin Testing for Proton Exchange Membrane Water Electrolyzers", International Journal of Hydrogen Energy, 44 (2019) 9174-9187

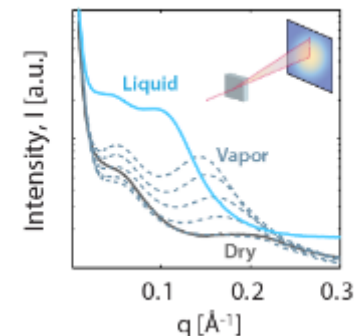




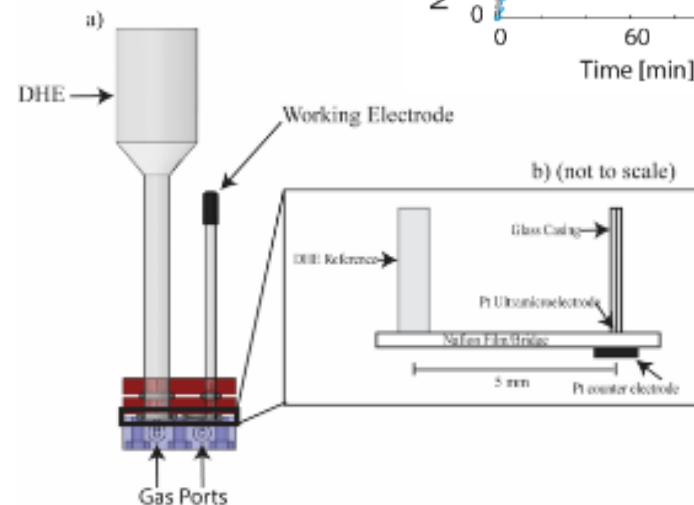
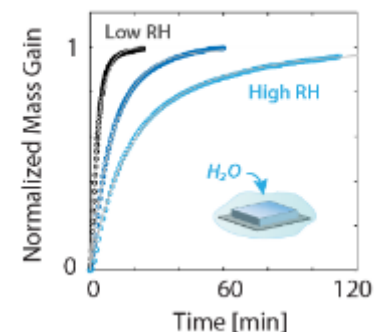
# Collaboration: Effectiveness

- LBNL: Adam Weber – Multiscale Modeling of Water-Splitting Devices
  - Leverage modeling to understand optimum placement of GRC and radical scavenger component in membrane
- LBNL: Ahmet Kusoglu – Thin Film and Bulk Ionomer Characterization
  - Understand effects of additives on membrane morphology
- LBNL: Nem Danilovic – Microelectrode Testing of LTE Electrocatalysts, Ionomers, and Their Interactions in the Solid State
  - Test for  $H_2/O_2$  permeabilities of baseline membrane components
- Kickoff meeting held between Chemours and LBNL to discuss sampling and timelines.

Small-Angle X-ray Scattering (SAXS)



Water Uptake & Kinetics





# Proposed Future Work

Task or Subtask	Milestone Type and Number	Milestone Description	Verification Process	Anticipated Date (Months from Start)	Approximate Date
2.2	Go/No-go (G2)	Reinforced roll-to-roll dispersion cast membrane with GRC (<0.075 mg PGM/cm <sup>2</sup> ) and radical scavenging additives demonstrates a H <sub>2</sub> in O <sub>2</sub> content of <2% for all current densities between 0.5 and 2 A/cm <sup>2</sup> where membrane thickness is ≤ 50 μm, membrane resistance is < 0.05 Ω-cm <sup>2</sup> , and hydrogen backpressure is 30 bar. Voltage in an MEA at 2 A/cm <sup>2</sup> 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	2/28/2022
4.3	Milestone (M10)	Demonstrate prototype manufacturing of > 100 linear meters of down-selected membrane design on Chemours' R2R manufacturing line with < 0.05 Ω-cm <sup>2</sup> membrane resistance, < 1% H <sub>2</sub> in O <sub>2</sub> content for all current densities in an MEA, > 10 mg/L Fe(III) tolerance, with additive nanoparticle mobility of < 2.1x10 <sup>-8</sup> m <sup>2</sup> /Vs, maintaining > 50% concentration in the membrane and improved lifetime after defined duty cycle/AST, with capacity to produce membranes at costs/rates comparable to Nafion™ XL	Chemours/LANL	36	2/28/2023

- Subsequent budget periods will involve production of high performance, reinforced, optimized membranes utilizing additive innovations on a pilot scale.
- Any proposed future work is subject to change based on funding levels



# Project Summary

- This membrane project addresses several critical impact areas to enable the further market penetration of PEM electrolysis for cheaper hydrogen production
  - Lower proton resistance via thin, reinforced architecture
  - Reduced gas crossover by gas recombination catalyst
  - Slowed PFSA thinning/degradation with radical scavengers
  - Roll-to-roll membrane production for facilitated MEA adoption
- Project partner Los Alamos contributes vital understanding to degradation modes and additive stability/migration
- Node partners NREL and LBNL contribute world-class evaluation, diagnostic, and modeling techniques.
- Project is new for March 2020, most work remains to be completed