FC333

Advanced Membranes for Heavy Duty Fuel Cell Trucks

DOE Hydrogen Program
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Award DE-EE0009243

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Project Goal

Improve the lifetime efficiency of membrane electrode assemblies (MEAs) in heavy duty (HD) fuel cell systems by developing membranes with optimized architectures which incorporate thermally-stable ionomer chemistries and immobilized radial scavengers

Realizing the advances proposed in this work can:

- Reduce lifetime operational expenses of HD fuel cell systems
- Improve their commercial viability to displace diesel energy sources

Project Overview

Timeline
(anticipated)

- ❖ Project Start: Q3 2021
- ❖ Project End: Q3 2024

Budget

- ❖ Total project budget: $1,281,134
  - ➢ Total Federal Share: $998,376
  - ➢ Total Recipient Share: $282,758
  - ➢ Total DOE funds spent*: $0

* As of 4/12/2021

Barriers

- ❖ Durability
- ❖ Performance
- ❖ Cost

Partners

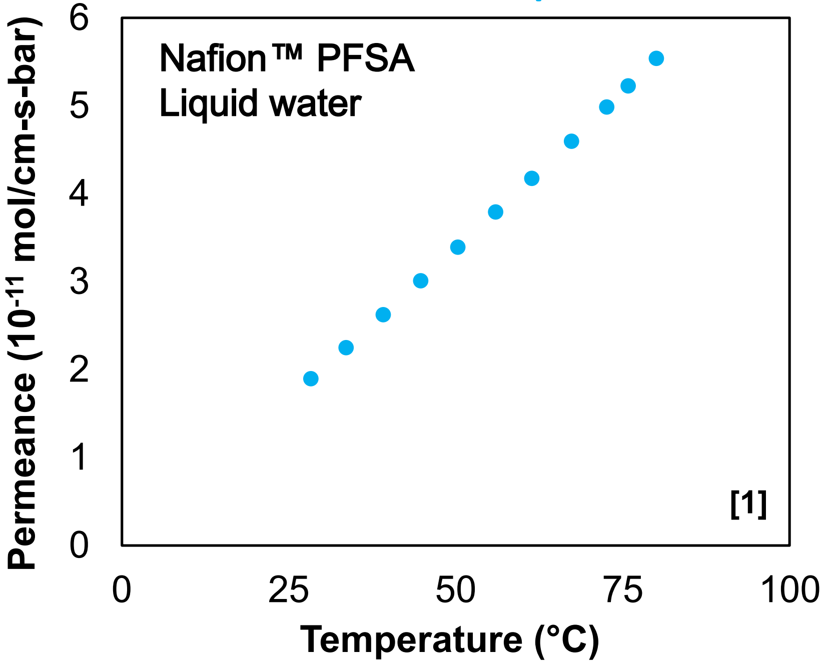
- ❖ The Chemours Company
  - ➢ Ionomer synthesis
  - ➢ Membrane preparation
  - ➢ Scale-up
- ❖ M2FCT Consortium
  - ➢ Ionomer/membrane characterization
  - ➢ AST development
  - ➢ Post-mortem characterization

Gas Crossover and Conductivity Loss

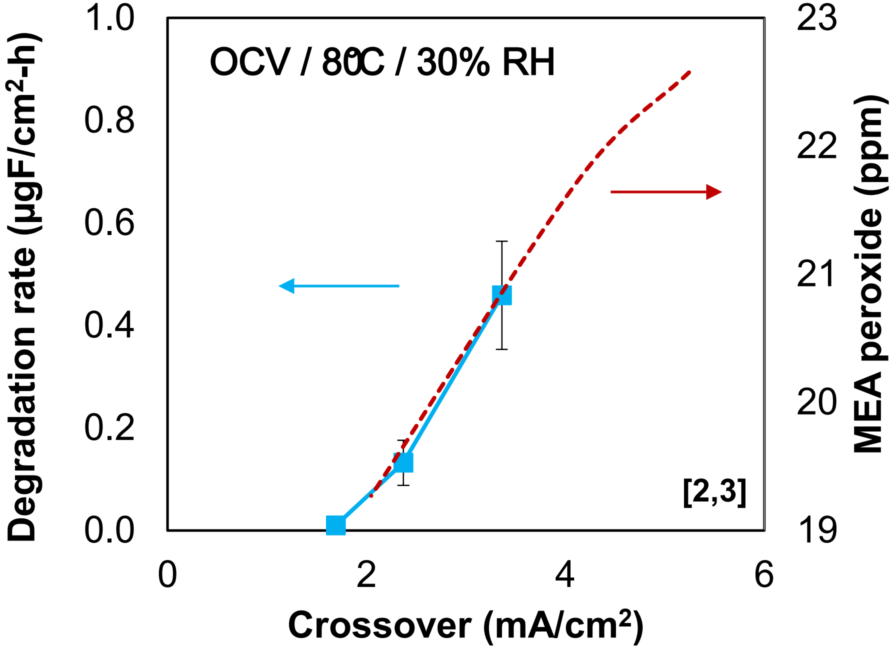
Relevance

Increased crossover can lead to a cascade of effects which reduce lifetime efficiency

Crossover vs. temperature



Degradation vs. crossover



Conductivity and crossover should be maintained at or better than SOA levels in an HD-specific membrane design

1. M. Schalenbach, et al., *J. Phys. Chem. C* 119, 25145–25155 (2015).
2. M. Zhao, et al., *Electrochim. Acta* 153, 254–262 (2015).
3. W. Liu and D. Zuckerbrod, *J. Electrochem. Soc.* 152, A1165–A1170 (2005).

Challenges in High Temp. HD Membranes

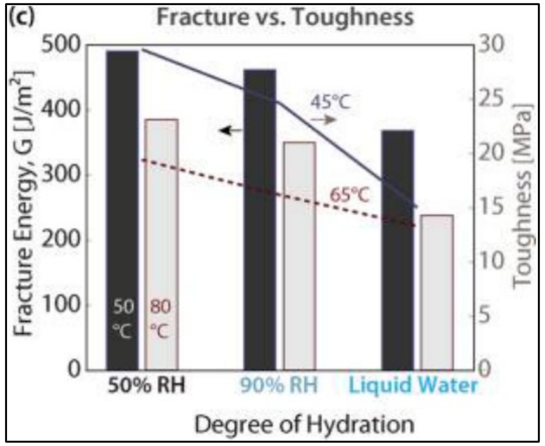
Relevance

Increased iron contamination

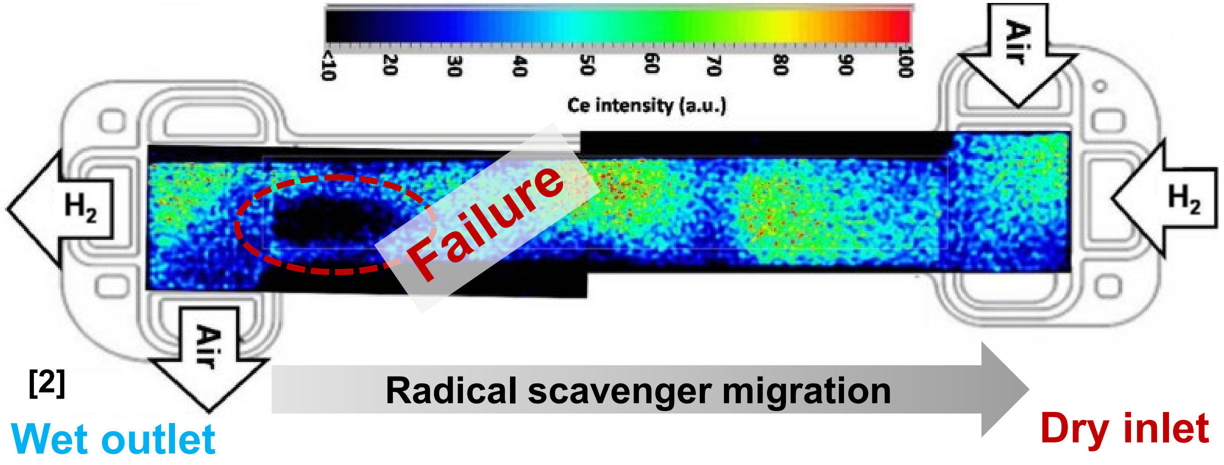
(especially during HD lifetime requirement)

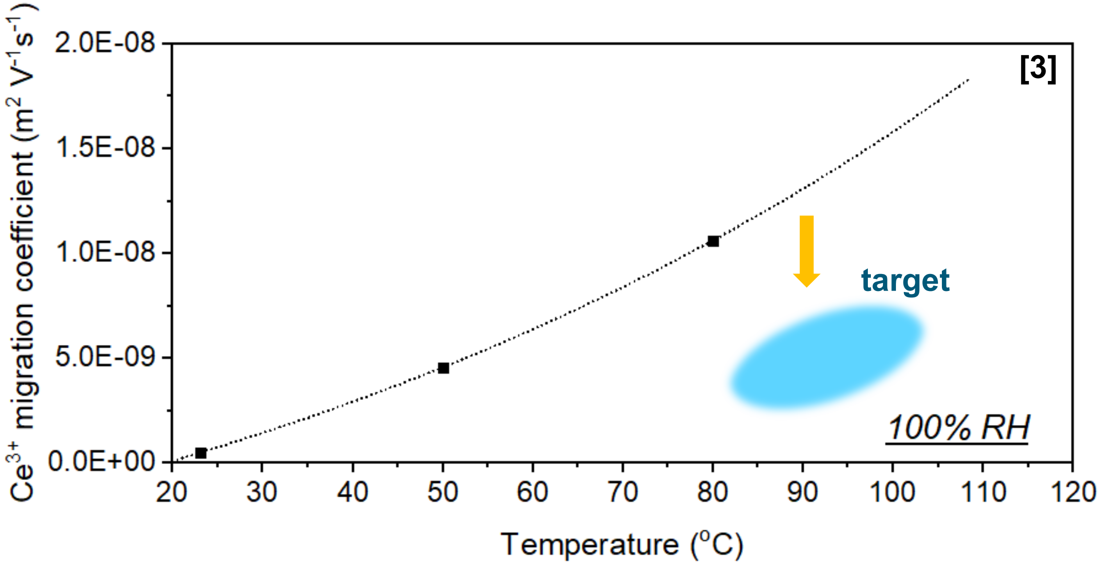
Decreased PFSA properties[1]

- Creep
- Elastic modulus
- Fracture energy
- Toughness



Increased radical scavenger migration





1. A. Kusoglu and A. Z. Weber, *Chem. Rev.*, **117**, 987–1104 (2017).
2. Y.-H. Lai, et al., *J. Electrochem. Soc.*, **165**, F3217–F3229 (2018).
3. A. M. Baker, et al., *ECS Trans.*, **92**, 429–438 (2019).

Project Targets

Relevance

#	Metric		SOA status	Project target
1	Area specific resistance [Ω-cm^2]	95°C, 36% RH	0.08[a]	0.1
		80°C, 100% RH	0.016[a]	0.02
2	Gas crossover [mA/cm^2]	80°C, 100% RH	2[a]	2
3	Radical scavenger mobility [m^2/Vs]	95°C, 36% RH	~6.2×10^{-10} [b]	3.1×10^{-10}
		80°C, 100% RH	1.9×10^{-8} [b]	9.5×10^{-9}
4	Membrane chemical/mechanical AST lifetime[c] [h]		>660[a]	1000
5	Refined HD membrane AST lifetime [h]		n/a	TBD

[a] Nafion™ NC700 data from Chemours
[b] 5% Ce^{3+} in Nafion™ NR-211 from A. M. Baker, et al., *ECS Trans.*, **92**, 429–438 (2019).
[c] Table P.5, U.S. DOE MYRDD Plan, Section 3.4 Fuel Cells, p. 50, (2016)

Collaboration

Project Workflow and Collaborations

- Monomer/polymer synthesis
- Reinforced membrane preparation

Chemours™

NIKOLA™

- Membrane evaluation
- MEA integration and evaluation

- Polymer & membrane characterization
- Membrane AST development

MILLION MILE FUEL CELL TRUCK — U.S. DEPARTMENT OF ENERGY

LSU (no cost partner)

- **Develop optimized membrane for HD applications**
- Refine membrane AST for HD conditions

Project Participants and Roles

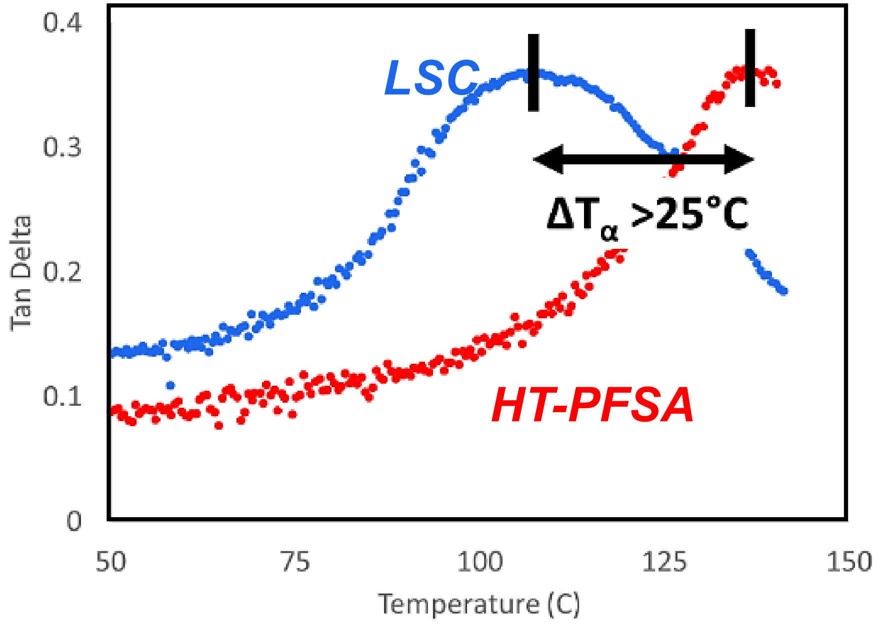
Collaboration

Institution	Roles
Nikola (prime) • Andrew Baker • John Slack • Bahareh Tavakoli • Vivek Murthi	• Measure radical scavenger migration rates using H_2 pump • Evaluate membrane conductivity and crossover *in situ* • Prepare MEAs using standard M2FCT electrodes • Analyze MEAs using representative testing
Chemours (sub-recipient) • Andrew Park • Allen Sievert • Todd Sayler	• Synthesize monomers (HT-PFSA, novel immobilizer) • Synthesize polymers containing various compositions of advanced monomers • Prepare membranes of different composition (t, EW, additive)
Louisiana State University (no cost partner) • Chris Arges	• Measure solubility of CeMOx nanoparticles (NPs) • Quantify effectiveness of radical scavengers and membranes containing them *in situ* and in *operando*
M2FCT Consortium	• Develop and refine HD-specific membrane AST (all) • Model voltage loss breakdown & tradeoffs (NREL & ANL) • Evaluate of nanoparticle morphology and surface chemistry (ORNL) • Perform fundamental polymer/membrane characterization (LBNL & LANL)

Optimizing Membrane Composition

Approach

Increase stability of ionomer



- HT-PFSA is more crystalline than LSCs at lower equivalent weights (EWs)[1]
- Lower feasible EW bound for HT-PFSA

1. A. Kusoglu and A. Z. Weber, *Chem. Rev.*, **117**, 987–1104 (2017).

Evaluate and model effects of parameters on durability

- Thickness
- EW
- Side chain
- Additive type and %

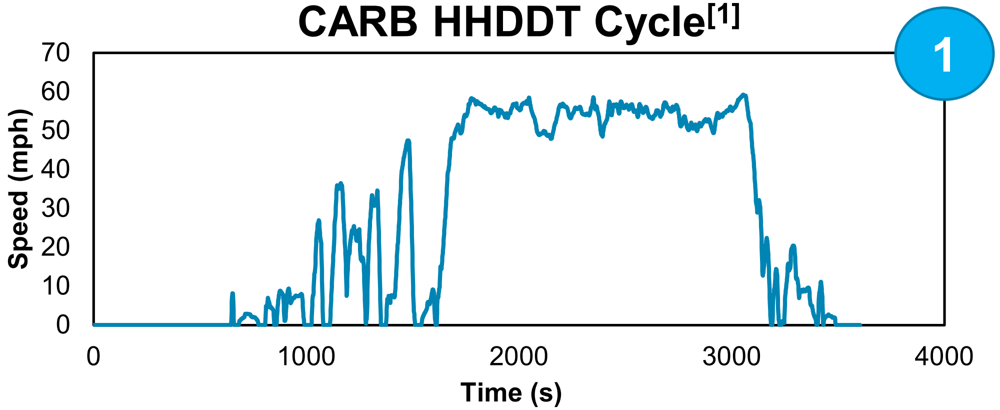
Advanced reinforcements

Ionomer chemistry and compositional changes will be evaluated in MEAs under representative HD test protocols and modeled to maximize lifetime efficiency

Representative HD Test Protocols

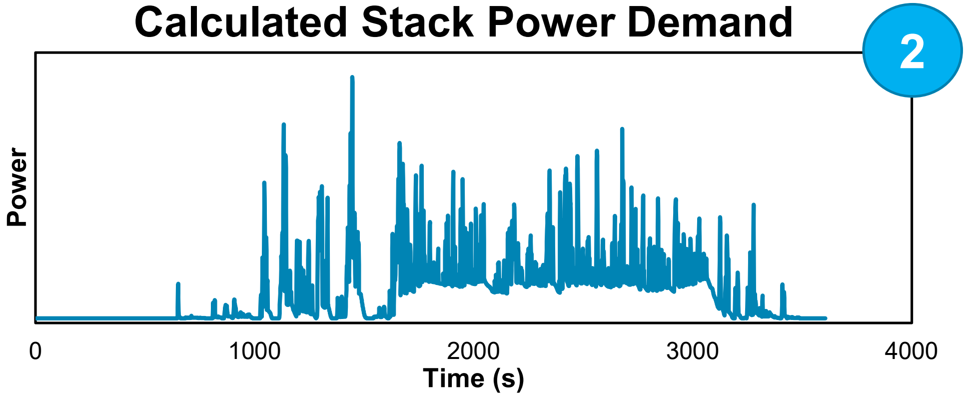
Approach

CARB HHDDT Cycle[1]



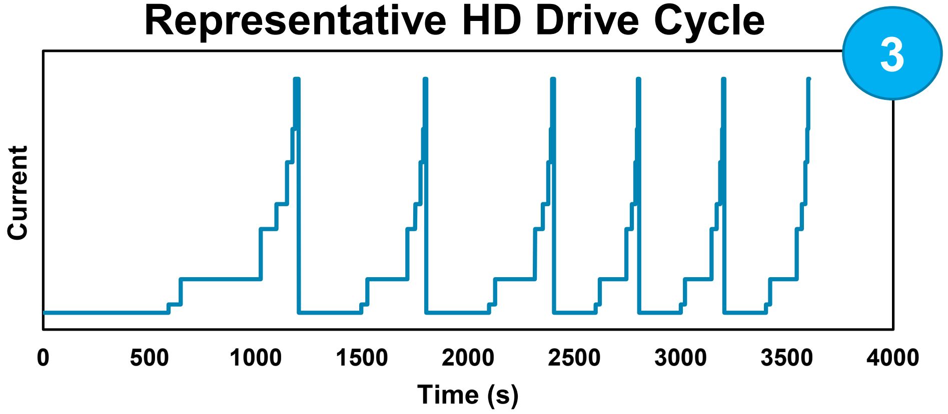
- Based on routes for target customer applications
- Representative use case → lab-scale AST cycle

Calculated Stack Power Demand



- Hybridization strategy & control logic
- Road/vehicle parameters (grade, GVW, CdA)

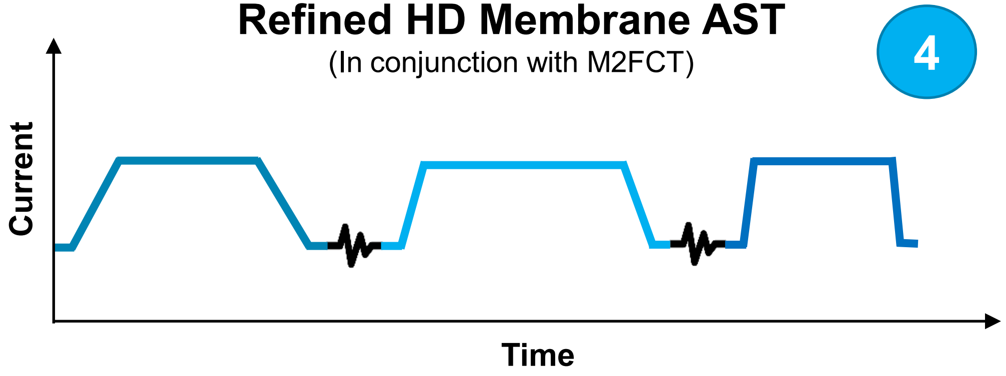
Representative HD Drive Cycle



- Smoothed to eliminate transient current spikes
- Filtered to capture relevant voltage sweeps
- Incorporates voltage clipping

Refined HD Membrane AST

(In conjunction with M2FCT)



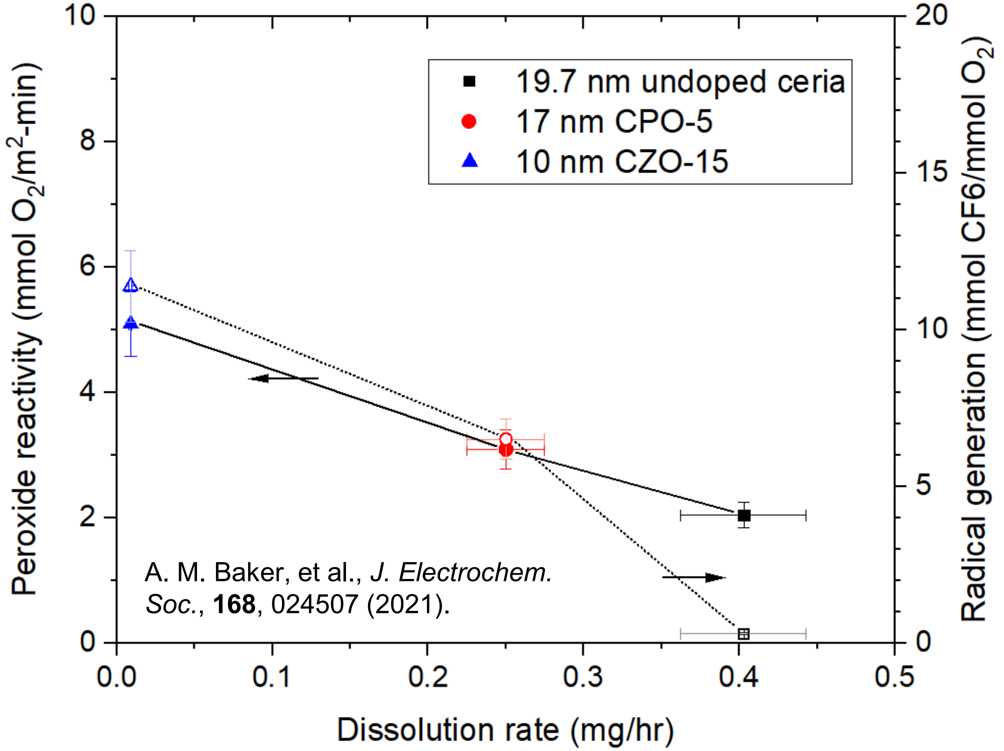
- Stressors balanced and accelerated
- Humidity cycling induced with current cycles
- Potential and water gradients present

1. NREL DriveCAT - Chassis Dynamometer Drive Cycles. (2018)

Radical Scavenger Immobilization

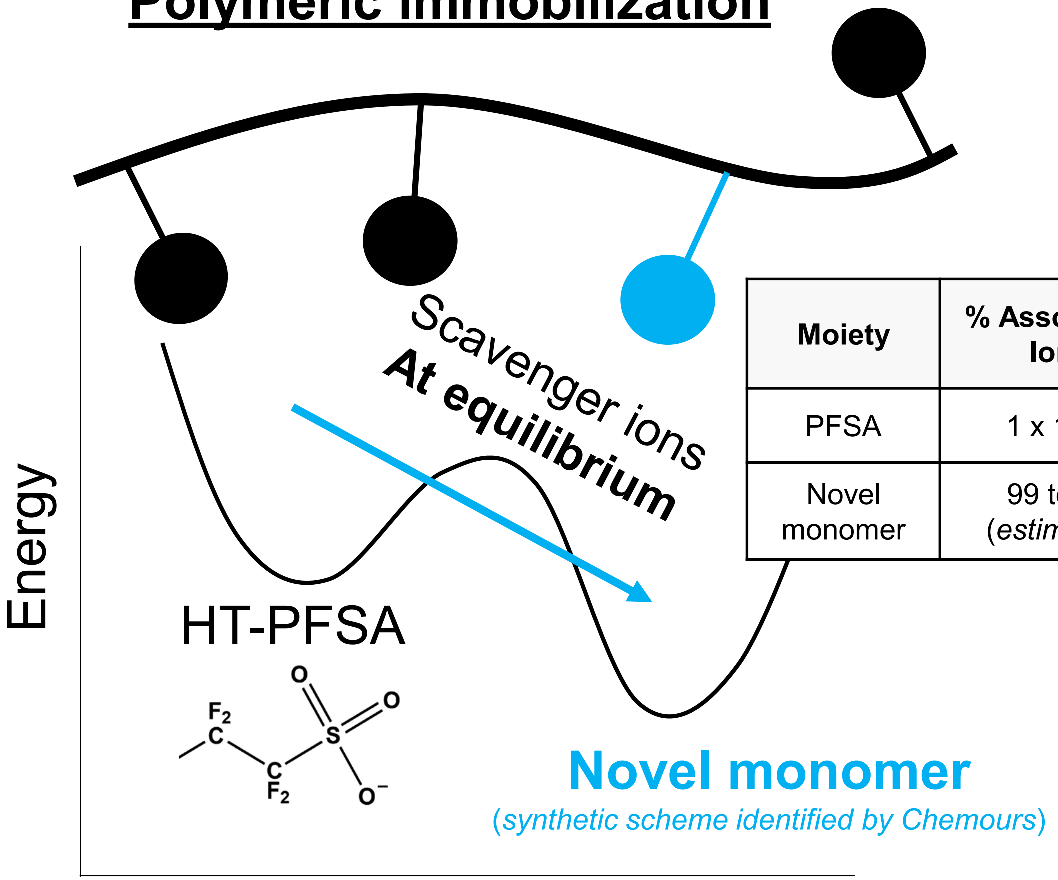
Approach

Metal-doped ceria (CeMOx) NPs



- Internal porosity + agglomeration → insolubility
- d_{np}, dopants → $vO_{2,surface}$ → peroxide scavenging
- Solubility/scavenging not assessed *in situ*

Polymeric immobilization

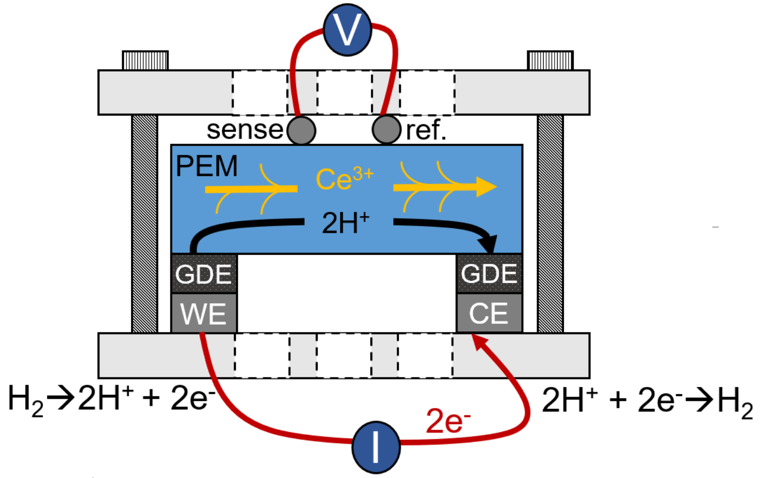


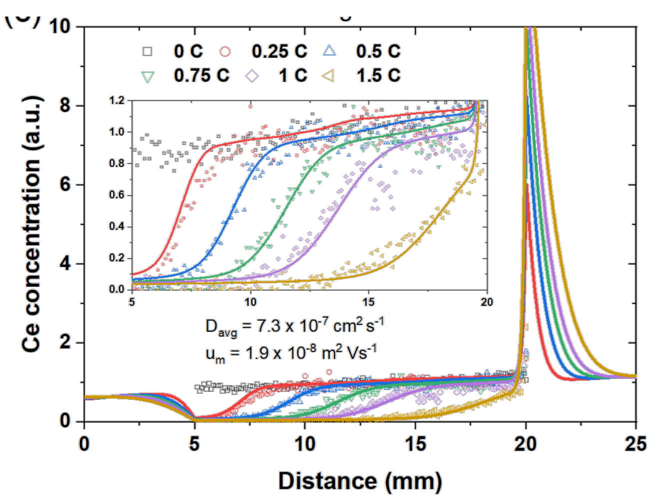
Moiety	% Associated Ions
PFSA	1×10^{-12}
Novel monomer	99 to 75 (*estimated*)

Necessity to evaluate degree of migration reduction and radical scavenging efficacy *in situ* in membranes containing proposed immobilization schemes

Measuring Radical Scavenger Migration Rate

Approach



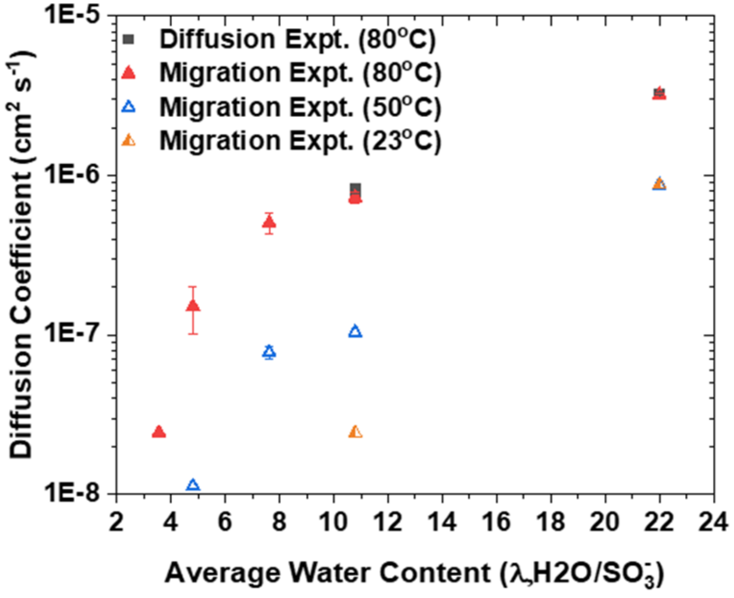


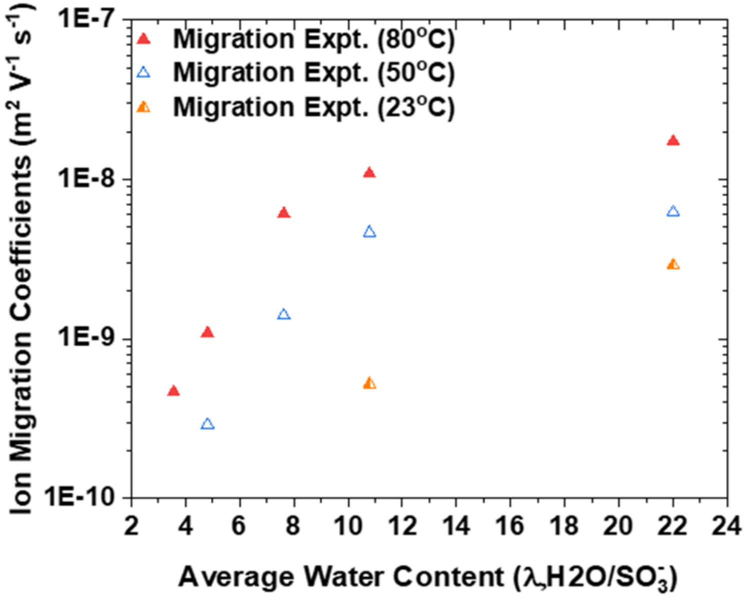
Experiment modeled with the Nernst-Planck equation:

$$\frac{\partial c}{\partial t} = \nabla.\left(\boldsymbol{D_o}\lambda\nabla c_{Ce} + \boldsymbol{u_m}c_{Ce}\nabla\phi_{ionic}\right)$$

- $\lambda = 10.5 - 2.1f_{Ce}$
- $\sigma_{ionic} = 10.5e^{100f_{Ce}-0.02}\left[\frac{mS}{cm}\right]$

Diffusivity (D_o) and migration (u_m) simultaneously fit from a single H_2 pump experiment:

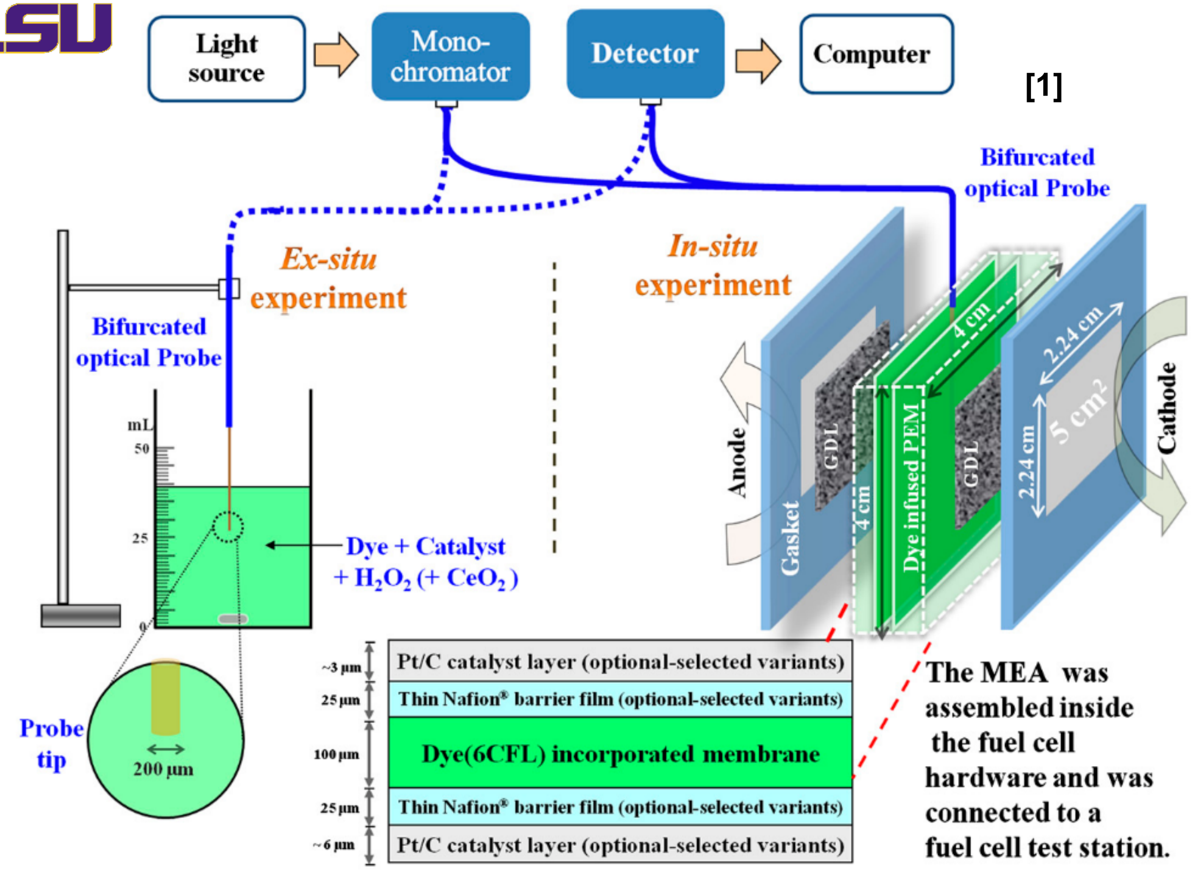


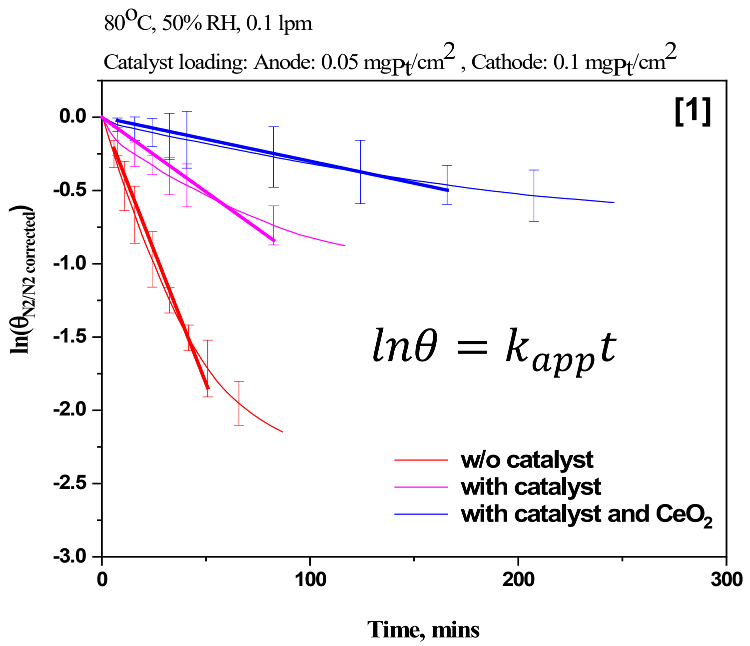


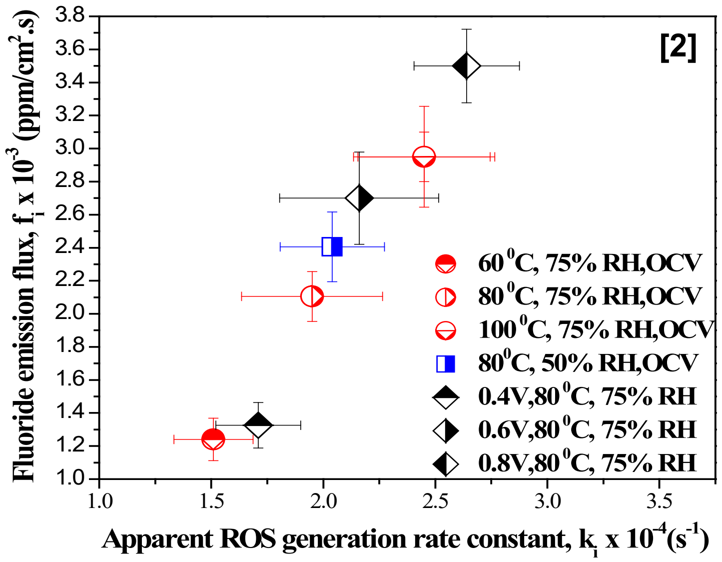
A. M. Baker, S. Komini Babu, et al., *ECS Trans.*, **92**, 429–438 (2019).

Measuring Radical Scavenger Efficacy

Approach







Fluorescence spectroscopy can be used to quantify the radical scavenging efficacy of proposed immobilization schemes both *ex situ* and in *operando*

1. V. Prabhakaran, C. G. Arges, and V. Ramani, *Proc. Natl. Acad. Sci. U. S. A.*, **109**, 1029–34 (2012).
2. V. Prabhakaran, C. G. Arges, and V. Ramani, *Phys. Chem. Chem. Phys.*, **15**, 18965–18972 (2013).

Accomplishments and Progress

Progress

This project was not reviewed last year and has an anticipated start date of Q3 2021

Advantages of the Proposed Approach

Relevance

- **Membrane parameters optimized specifically for HD FC trucks** to maximize lifetime efficiency in long haul applications
- **Two-pronged approach to radical scavenger stabilization** mitigates risk associated with new polymer development
- **Analysis of CeMOx surface chemistry and morphology** can reveal mechanisms of solubility resistance and peroxide/radical scavenging
- **Novel monomer may enable more optimal localization of radical scavengers** and could be tailored to enable in-plane variations (e.g. near wet outlets) while mitigating performance losses

Milestones and Decision Points

Future Work

Selected milestones and expected results (Q1-4):

- Synthesize 5 g of novel radical scavenger immobilization monomer
- Measure performance and durability of membranes containing HT-PFSA ionomer
- Evaluate *ex situ* radical scavenger migration in membranes containing metal-doped ceria (CeMOx)

Go/No-Go Decision Point (Q6): Demonstrate a reinforced membrane with HT-PFSA that exhibits an area specific resistance of <0.1 Ω-cm^2 at 95°C, 36% RH and <0.02 Ω-cm^2 at 80°C, 100% RH while maintaining a gas crossover of <2 mA/cm^2.

Anticipated Challenges

Future Work

Challenge	Resolution
Feasibility of proposed monomer and its processibility	• Synthetic scheme identified by Chemours which leverages their extensive monomer library • Optimize monomer % in terpolymer
Effectiveness of immobilization during polarization	• X-ray fluorescence will be used to intermittently measure in-plane location of radical scavenger • Impedance spectroscopy will be used to intermittently measure changes in cathode CL ionic resistance • Resistance to water gradients expected to be higher
Effectiveness of radical scavenging in immobilized systems	• The radical scavenging rate will be quantified both *in situ* and *in operando* • The active group in the novel monomer may be tuned to maximize scavenging

Summary

Objective: Fabricate a membrane with increased performance and durability at high temperatures

Relevance: Directly increase the performance and durability of MEAs in PEM fuel cell systems in order to reduce the overall costs of HD operation

Approach: Maximize lifetime efficiency by developing an HD-specific architecture containing advanced reinforcements, thermally-stable ionomers, and immobilized radical scavengers

Accomplishments: The anticipated start date of the project is Q3 2021

Technical Backup Slides
and Additional Information

Tech Transfer Activities

Patents: n/a

Tech-to-market activities: Commercialization of membrane technology is anticipated if proposed advances are realized

Future/Additional Funding: n/a

Progress Towards DOE Targets

CHARACTERISTIC	UNITS	2015 STATUS	2020 TARGETS
Maximum oxygen cross-over [a]	mA/cm^2	2.4	2
Maximum hydrogen cross-over [a]	mA/cm^2	1.1	2
Area specific proton resistance at:			
Maximum operating temperature and water partial pressures from 40–80 kPa	ohm cm^2	0.072 (120°C, 40 kPa)	0.02
80°C and water partial pressures from 25–45 kPa	ohm cm^2	0.027 (25 kPa)	0.02
30°C and water partial pressures up to 4 kPa	ohm cm^2	0.027 (4 kPa)	0.03
-20°C	ohm cm^2	0.1	0.2
Maximum operating temperature	°C	120	120
Minimum electrical resistance	ohm cm^2	>5,600	1,000
Cost	$/m^2	17	20
Durability			
Mechanical	Cycles*	23,000	20,000
Chemical	Cycles*	742	>500
Combined chemical/mechanical	Cycles*	–	20,000

*= >15 mA/cm^2 crossover or >20% loss in OCV

Objective: meet all 2020 DOE membrane technical targets and project targets specific to high T, HD systems