FC333

NIKOLA

ADVANCED MEMBRANES FOR HD FC TRUCKS

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Award DE-EE0009243

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PROJECT GOAL

Improve the performance and durability of membrane electrode assemblies (MEAs) in heavy duty (HD) fuel cell systems by developing membranes with optimized architectures which incorporate thermally-stable ionomers and immobilized radical scavengers

Realizing these proposed advances can:

- Reduce radical scavenger transport
- Limit performance losses due to excess cations
- Reduce durability losses due to depleted radical scavengers
- Reduce HD fuel cell TCO

OVERVIEW

Timeline & Budget

- Project Start: 10/1/2021
- Project End: 10/1/2024
- Total project budget: $1,281,134
  - Total Federal Share: $998,376
  - Cost Share: $282,758
  - Total DOE funds spent*: $30,348
  - Cost Share Funds Spent*: $8,605
  - * As of 4/25/2022

Partners

- Nikola Corporation, Project Lead
- The Chemours Company, Ionomer Synthesis

COLLABORATION & COORDINATION

Chemours™

- Monomer/polymer synthesis
- Reinforced membrane preparation

NIKOLA™

- Membrane evaluation
- MEA integration and evaluation

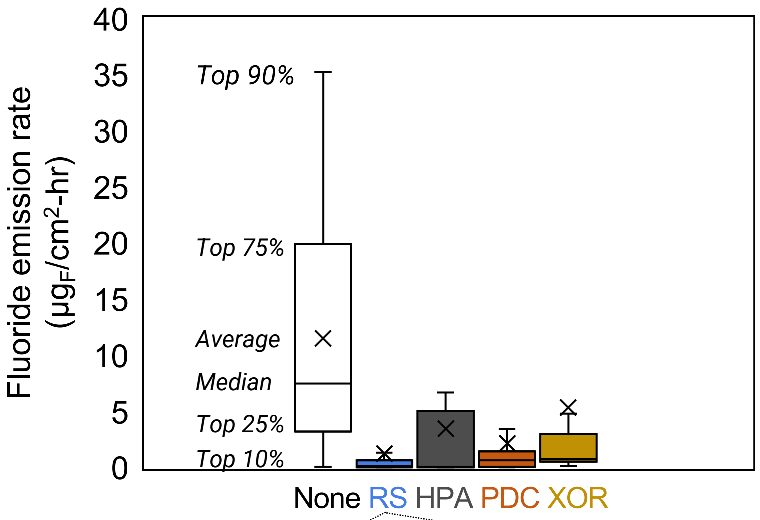
- Polymer & membrane characterization
- Membrane AST development

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

- **Develop optimized membrane for HD applications**
- Validate ion-immobilizing polymer concept
- Refine membrane AST for HD conditions

RADICAL SCAVENGER EFFECTIVENESS

RELEVANCE



Radical scavengers (RS)

- Ce and Mn ions and oxides

Heteropolyacids (HPA)

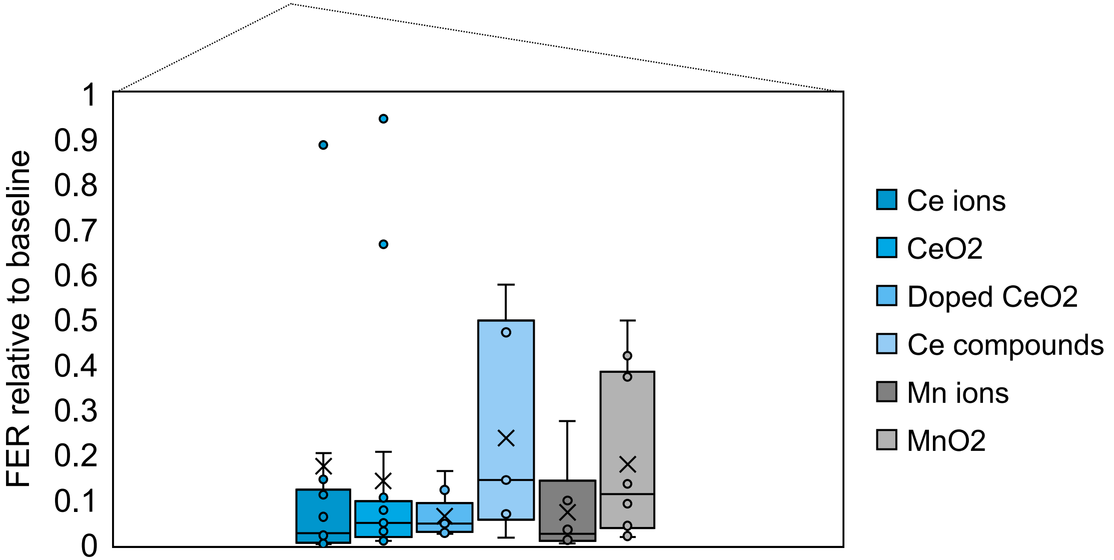
- Silicotungstic acid
- Phosphotungstic acid
- Polymerized HPAs

Peroxide decomposition catalysts (PDC)

- Si, Sn, Ti, Zr oxides

Crossover reducers (XOR)

- Graphene, hexagonal boron nitride
- Precious metal nanoparticles



All references listed in Backup Slides

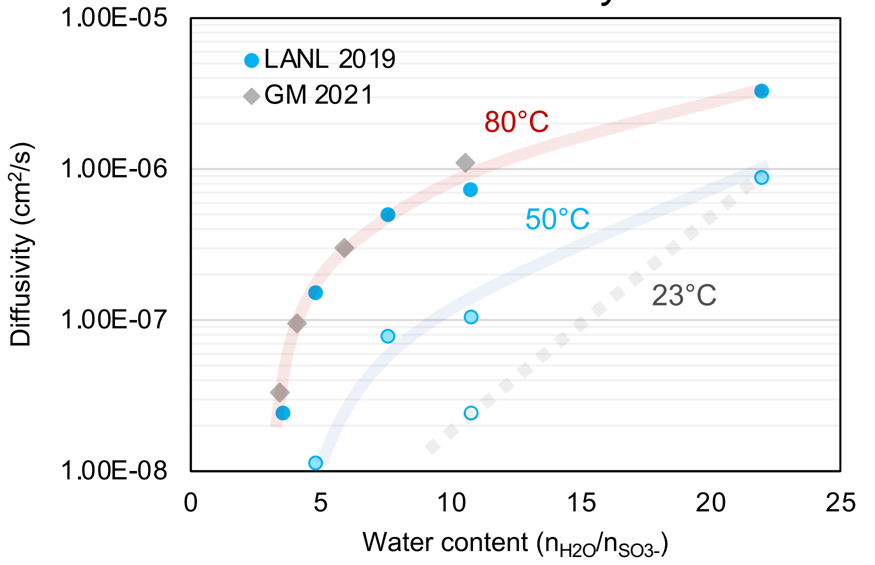
Radical scavenger additives significantly reduce fuel cell MEA degradation

- Reduced fluoride emission rates (FER)

The most effective scavengers are soluble and easily move around the MEA, especially at high temperatures

- Too many: conductivity loss
- Too few: durability loss

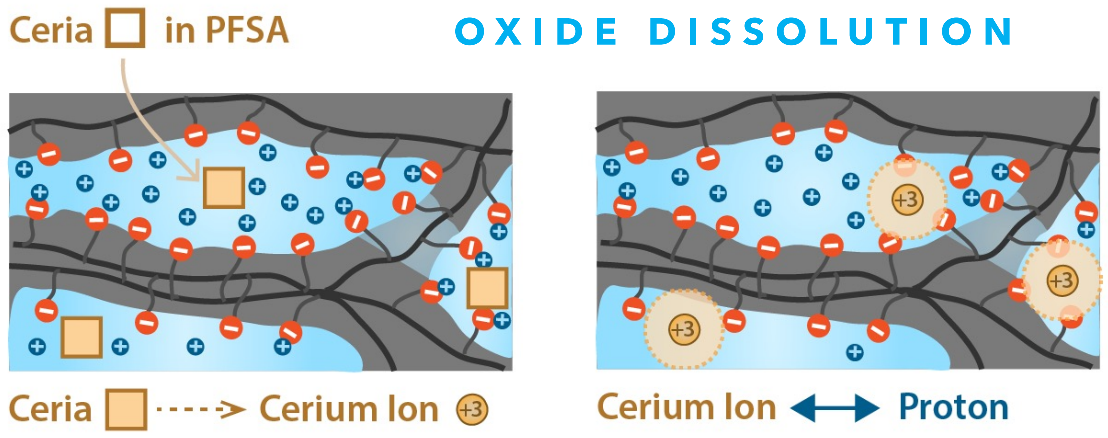
Ce cation diffusivity in PFSA



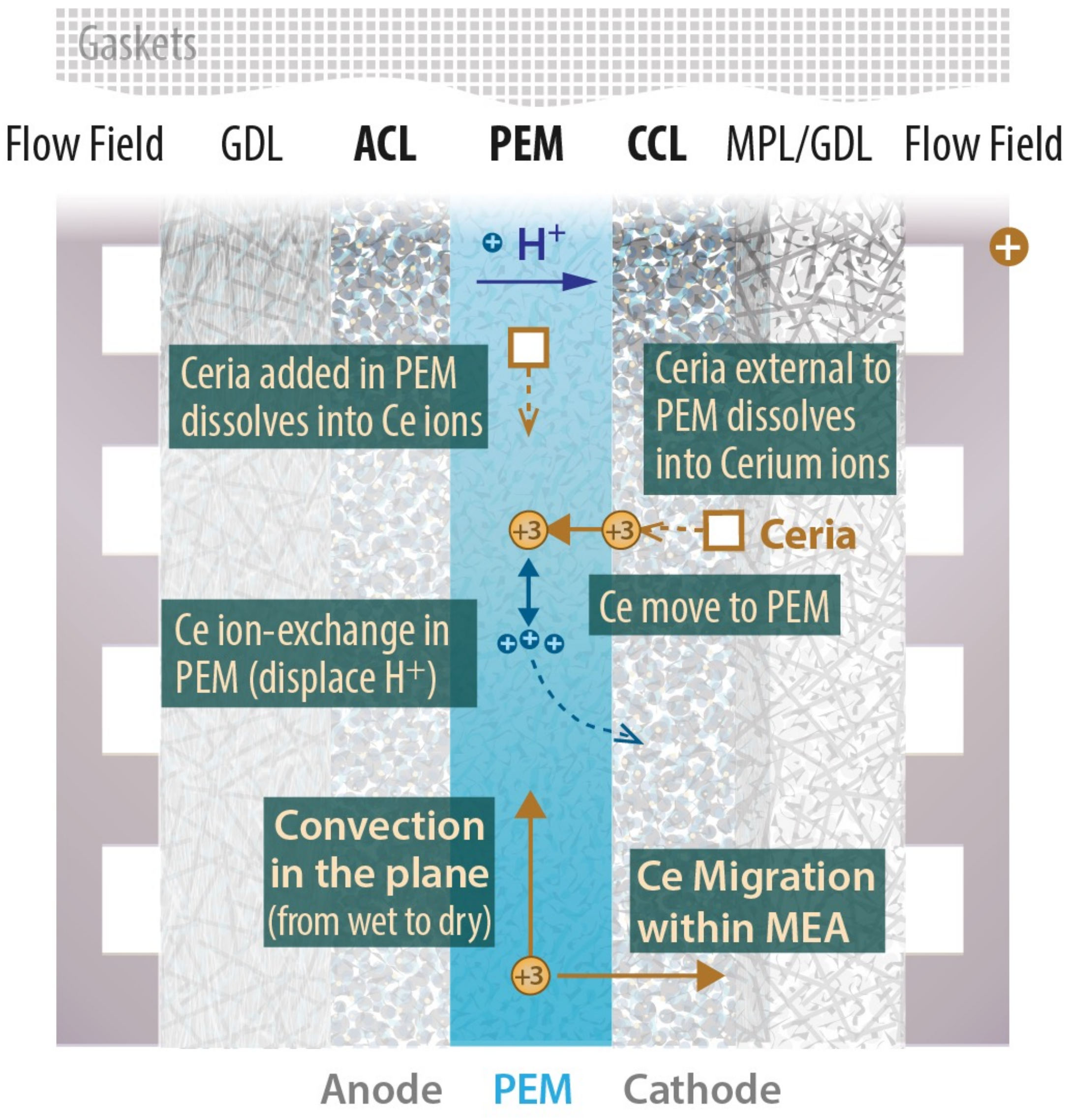
RADICAL SCAVENGER TRANSPORT MECHANISMS

RELEVANCE

OXIDE DISSOLUTION



CATION TRANSPORT



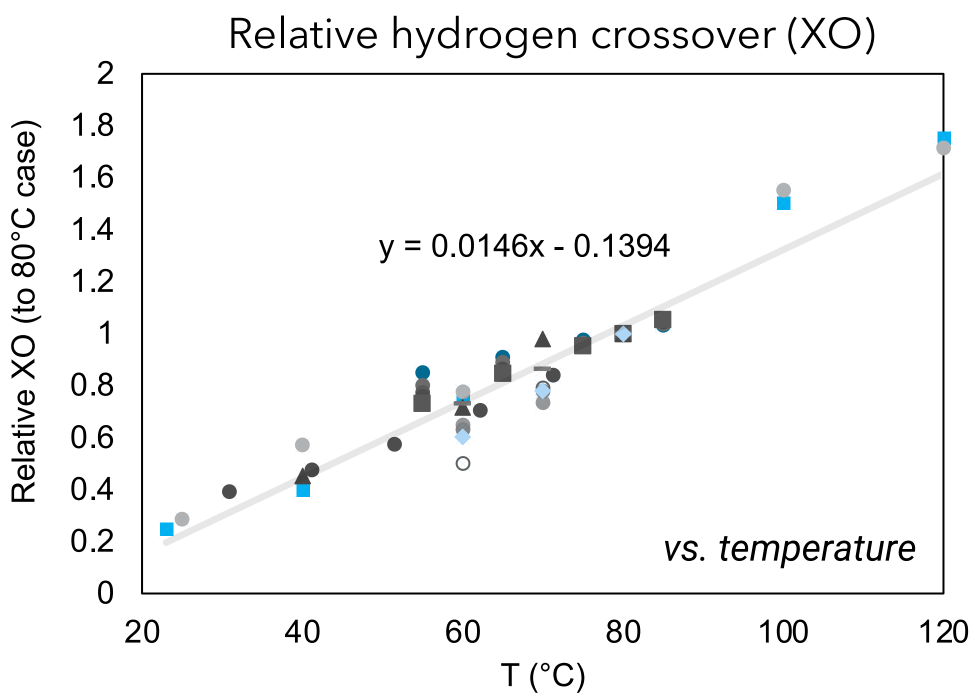
- **In-plane convection** due to water gradients[1-2]
- **Through-plane migration** due to potential gradients[3]
- **Self-diffusion** after gradients are removed[4]
- Cations stays in the cell: **no "washout"**[2]

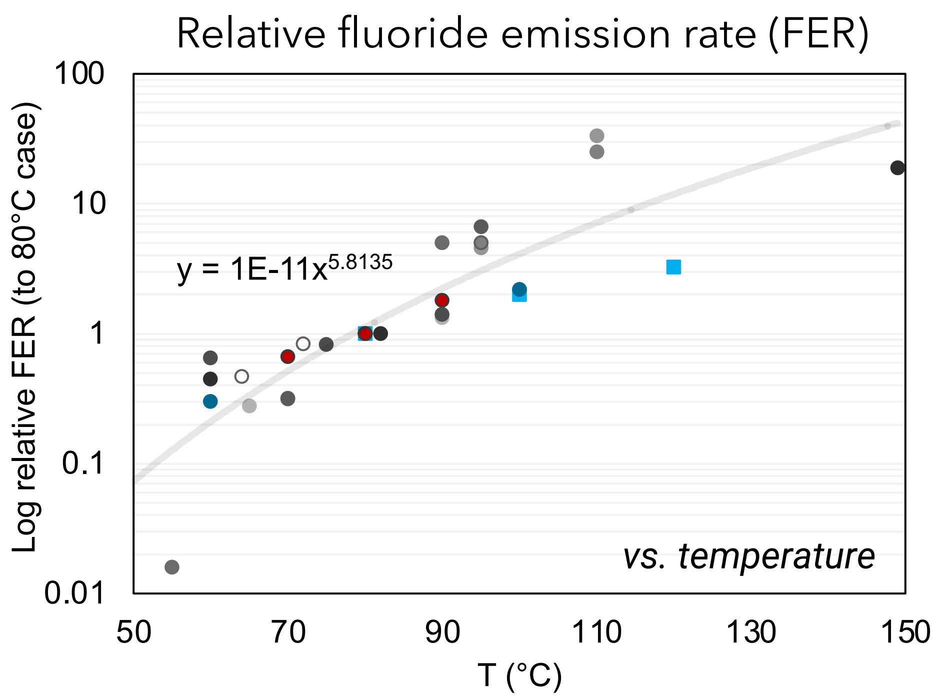
[1] Lai, et al., *J. Electrochem. Soc.*, **165**, F3217 (2018).
[2] Baker, et al., *J. Electrochem. Soc.*, **163**, F1023 (2016).
[3] Okada, et al., *Electrochim. Acta*, **43**, 3741 (1998).
[4] Goswami, et al., *J. Phys. Chem. B*, **105**, 9196 (2001).

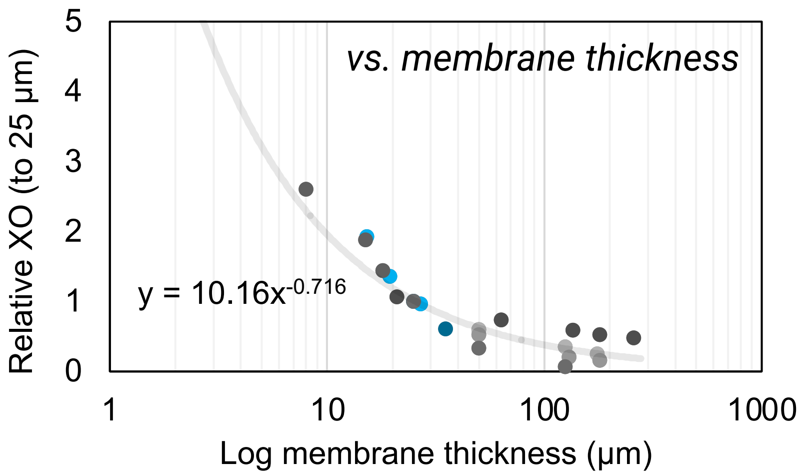
Illustrations courtesy of Dr. Ahmet Kusoglu (LBNL)

ADDITIONAL CHALLENGES AT HIGH TEMPERATURE

RELEVANCE







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

Conductivity and crossover should be optimized for an HD-specific membrane design without relying on reducing membrane thickness

All references listed in Backup Slides

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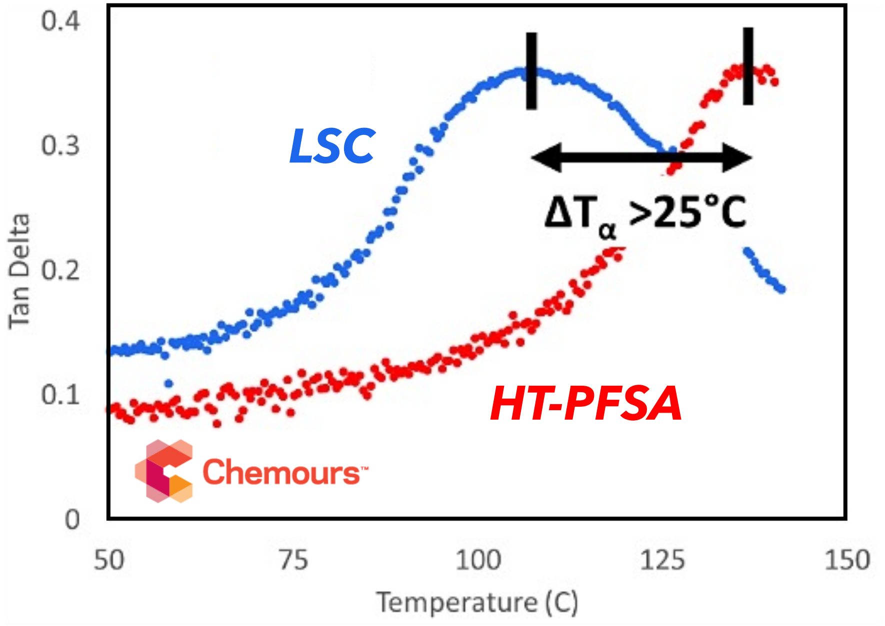
OPTIMIZING MEMBRANE CHEMISTRY & ARCHITECTURE

APPROACH

Increase stability of ionomer



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

Evaluate and model effects of parameters on durability:

- Thickness
- Equivalent weight (EW)
- Additive content

Evaluate ionomer chemistry and compositional changes under representative HD test protocols and derive empirical relationships which maximize lifetime efficiency

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

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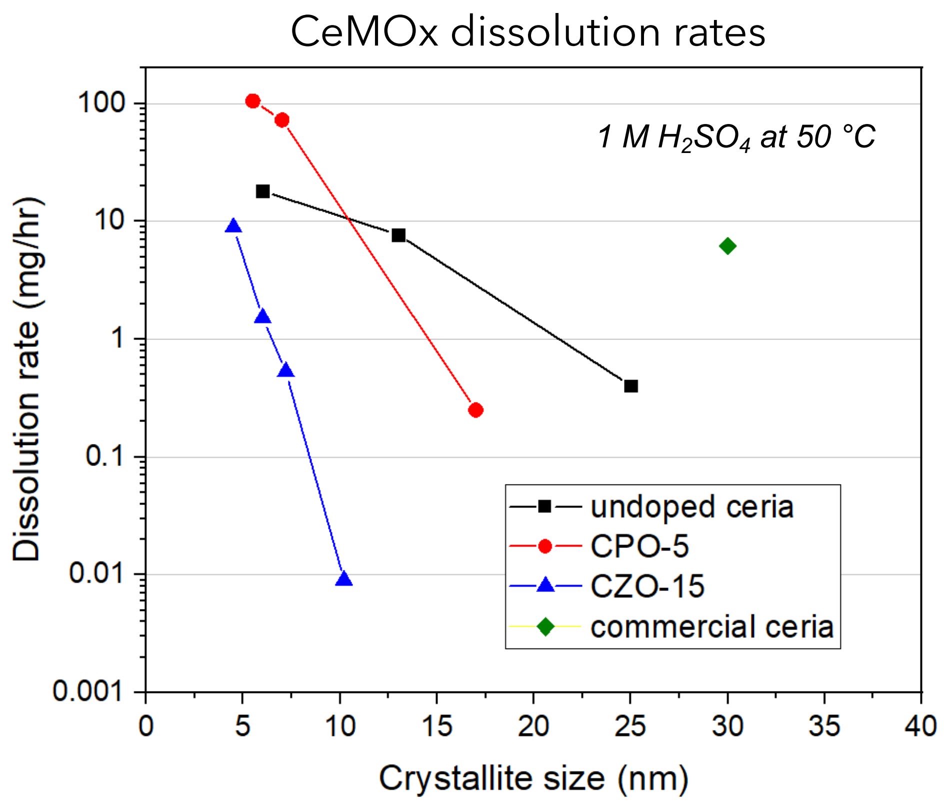
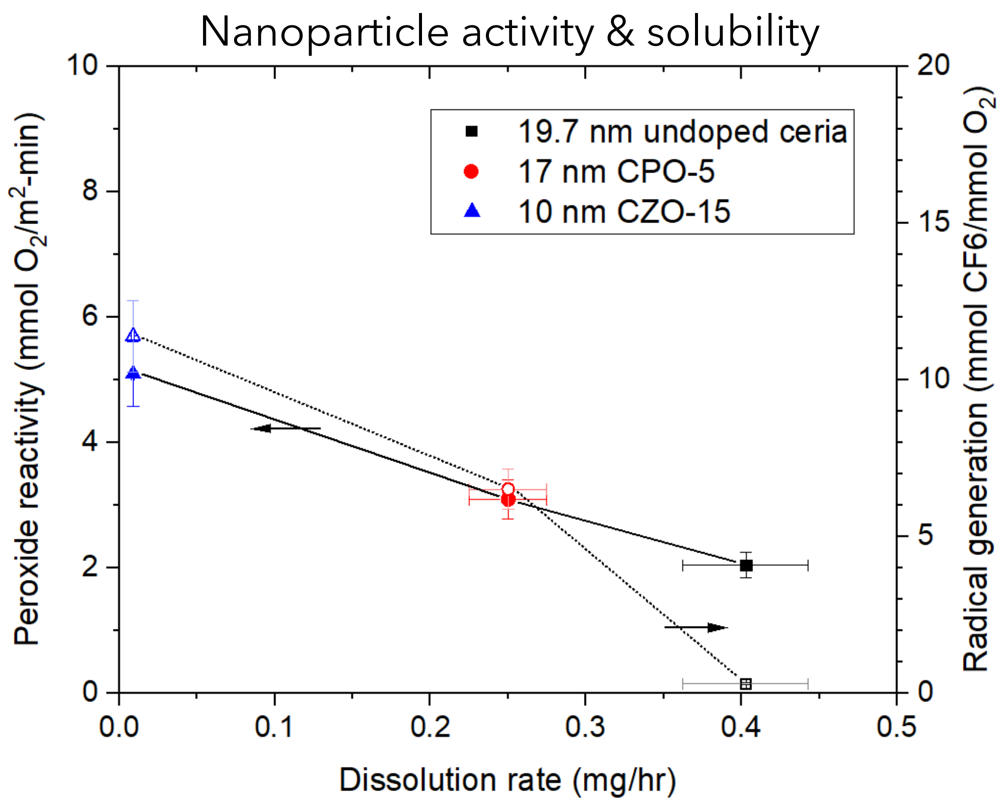
METAL-DOPED CERIA NANOPARTICLES

APPROACH



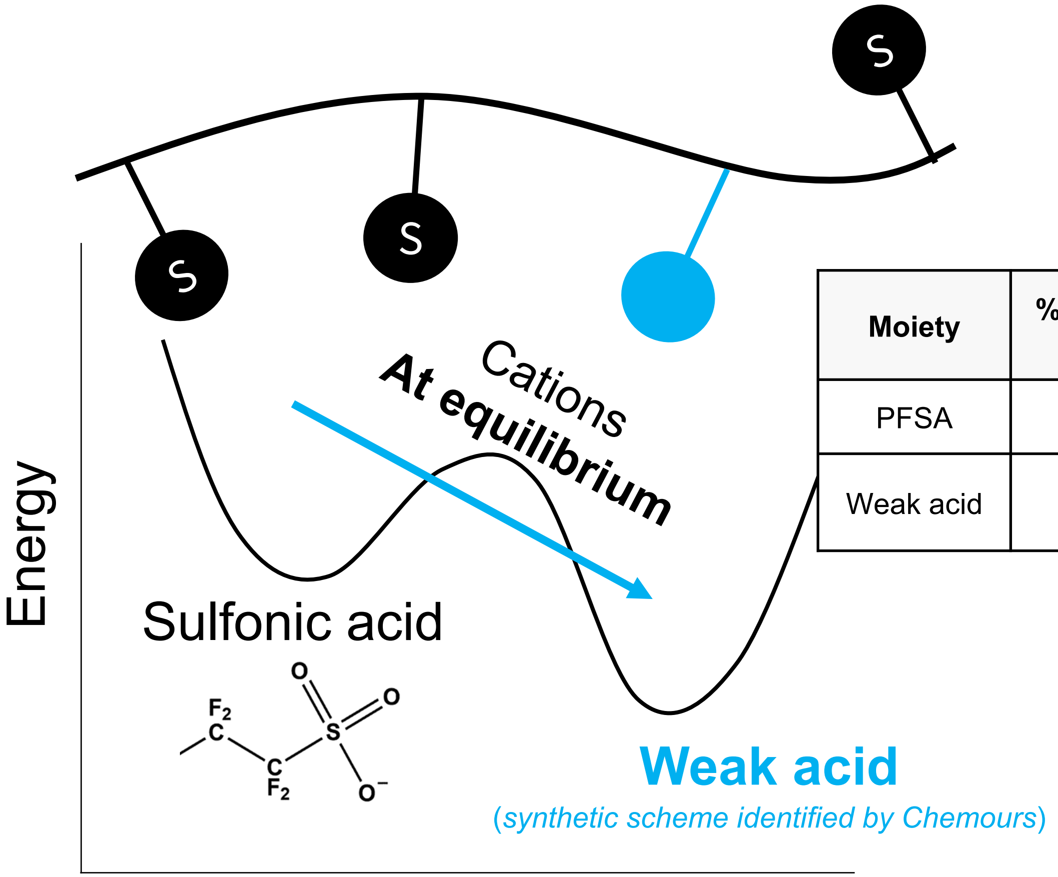


- Insolubility of metal-doped ceria (CeMOx) attributed to internal porosity (CPO) or agglomeration (CZO)
- Enhanced peroxide decomposition activity attributed to higher concentration of surface O_2 vacancies
- **State of agglomeration not clear in membrane; solubility/activity not assessed *in situ***

Baker, et al., *J. Electrochem. Soc.*, **168**, 024507 (2021).

CATION-CHELATING PFSA ENDGROUPS

APPROACH

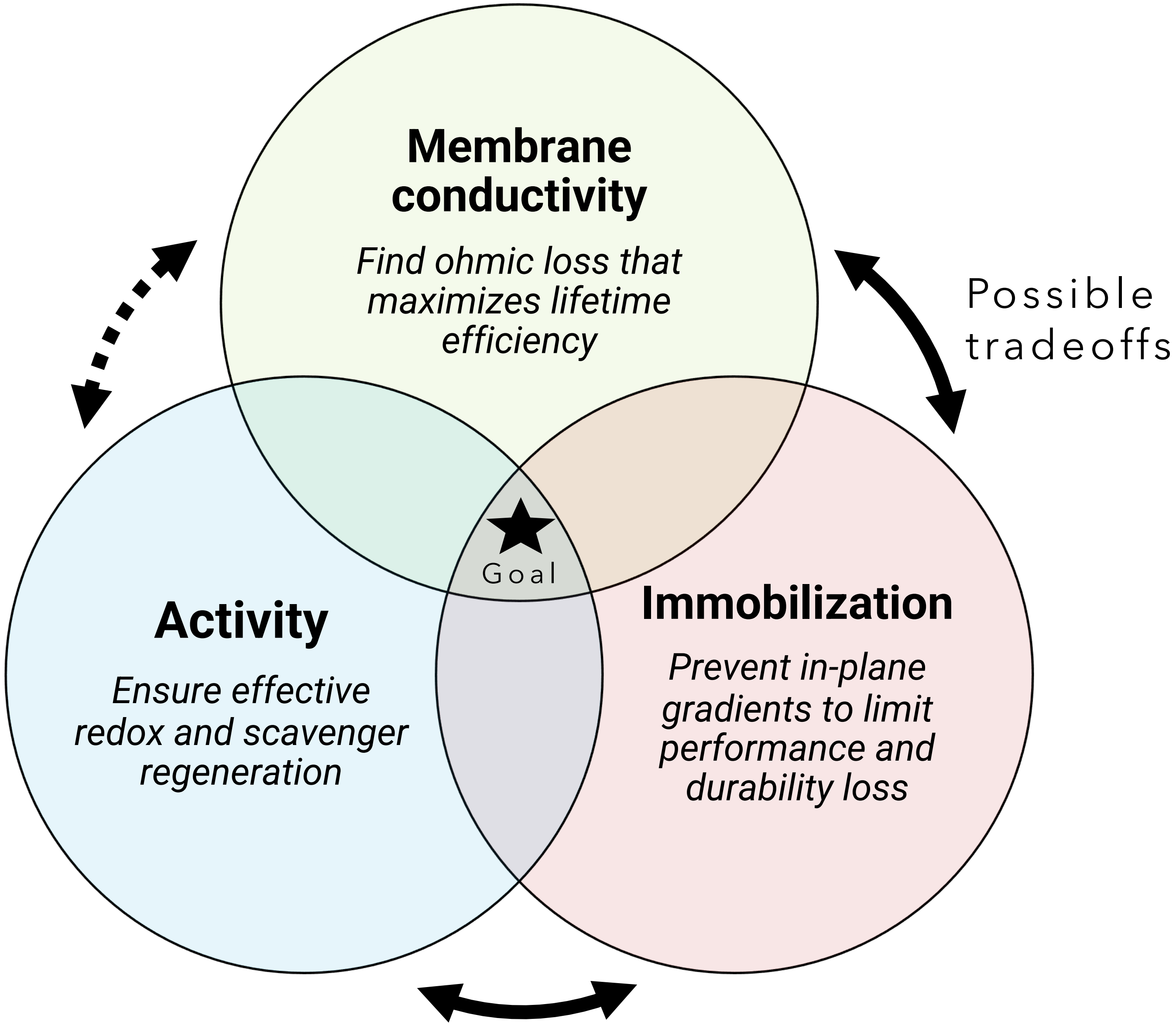


Moiety	% Associated Ions
PFSA	1×10^{-12}
Weak acid	99 to 75 (*estimated*)

- Use membrane containing periodic weak acid (i.e. strong cation-associating) end groups to mitigate radical scavenger migration and reduce contamination/depletion effects
- Necessary to evaluate tradeoffs in membranes containing proposed immobilization schemes

RADICAL SCAVENGER DESIGN PHILOSOPHY

APPROACH



PROJECT TARGETS & STATUS

APPROACH

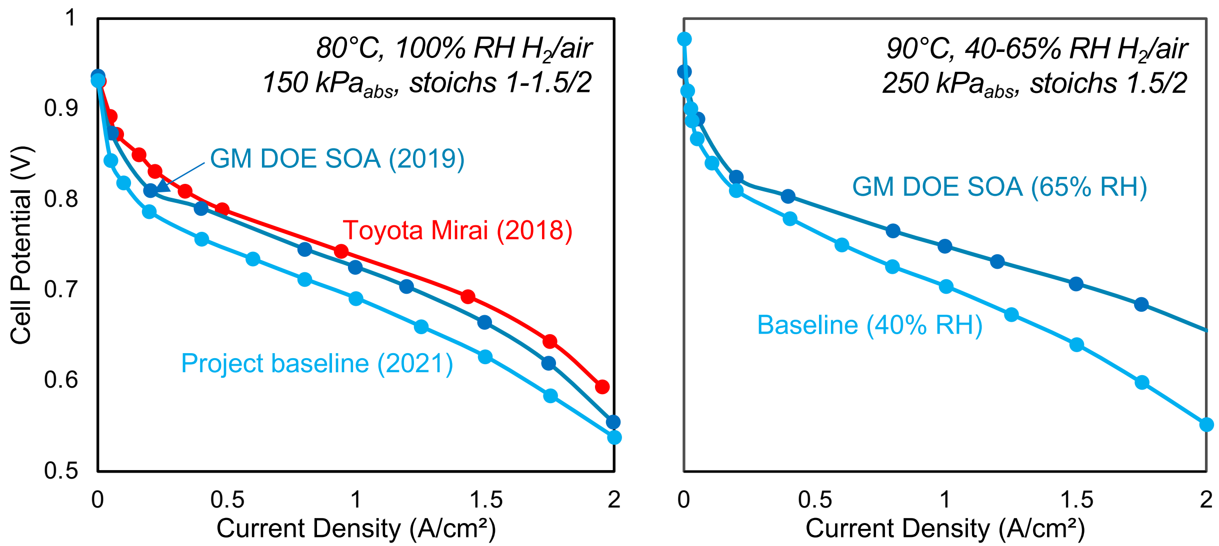
#	Metric		SOA status	Status	Project target
1	Area specific resistance [Ω-cm^2]	95°C, 36% RH	0.065[a]	0.045[e]	0.1
		80°C, 100% RH	0.016[a]	0.013[e]	0.02
2	Gas crossover [mA/cm^2]	80°C, 100% RH	2[a]	1.7[e]	2
3	Radical scavenger mobility [m^2/Vs]	95°C, 36% RH	~$6.2x10^{-10}$ [b]	n/a	$3.1x10^{-10}$
		80°C, 100% RH	$1.9x10^{-8}$ [b]	n/a	$9.5x10^{-9}$
4	Membrane chemical/mechanical AST lifetime[c] [h]		>660[a]	n/a	1,000
5	HAST (aggressive current cycling) lifetime[d] [h]		650[d]	n/a	TBD

[a] Nafion™ NC-700 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)
[d] Lai, et al., *J. Electrochem. Soc.*, **165**, F3217 (2018).
[e] HT-PFSA membrane in this study, no weak acid incorporated

PERFORMANCE & DURABILITY OF BASELINE MEMBRANES

ACCOMPLISHMENTS & PROGRESS (TASK 2.2)

50 cm^2 single cell tests



HAST Durability Testing[3]

Current cycling @ 90°C, 30% RH, 300 kPa_{abs}

Current density	Voltage decay rate
0.05 A/cm^2	0.06 ± 0.02 mV/hr
1.2 A/cm^2	0.53 ± 0.18 mV/hr

Project baseline MEAs

MEA	Membrane	Cathode Catalyst	Anode Catalyst	mg_{Pt}/cm^2 (Cath./An.)
Project baseline (NREL spray coat)	NC-700 (15 μm)	50% Pt/Vu	50% Pt/HSC	0.25/0.1
GM DOE SOA[1]	12 μm PFSA	30% PtCo/HSC	10% Pt/C	0.1/0.025
Toyota Mirai[2]	10 μm PFSA	PtCo/AB	Pt/C	0.32/0.1

Lower performance than other SOA MEAs

- Slightly thicker membrane
- Pure Pt instead of alloy
- Low surface area C support
- Lower loading than Mirai MEA

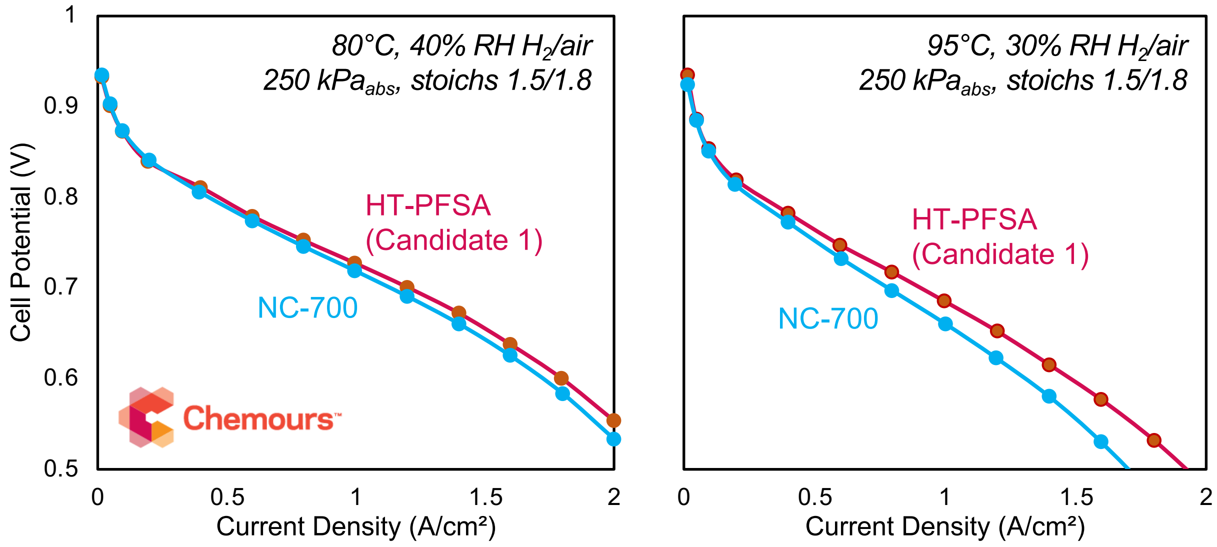
Durability experiments performed on baseline MEAs

[1] Kumaraguru, *U.S. DOE H2&FC Annual Merit Review* (2019).
[2] Borup, More, and Myers, Report LA-UR-18-24454 (2018).
[3] Lai, et al., *J. Electrochem. Soc.*, **165**, F3217 (2018).

PERFORMANCE OF HT-PFSA MEMBRANES

ACCOMPLISHMENTS & PROGRESS (TASK 2.2)

25 cm^2 single cell tests



MEAs prepared by Chemours

- Anodes: 0.1 mg/cm^2 Pt/HSC
- Cathode: 0.4 mg/cm^2 PtCo/HSC

- At 95°C, 30% RH, the lower EW HT-PFSA improves on the baseline
  - 25 mV improvement at 1 A/cm^2
  - >20% reduction in HFR
- Durability effect still needs to be confirmed

WEAK ACID MONOMER SYNTEHSIS

ACCOMPLISHMENTS & PROGRESS (TASK 1.2)

- Novel monomer designed for implementation in PFSA polymer for reduced cerium mobility
- Monomer synthesis a target in Budget Period 1
  - 5g monomer targeted in Summer 2022
- 3-step monomer synthesis plan in place
- **Successful demonstration of 3 mmol quantity of target monomer completed**
- Refining steps/yields underway toward 5 g target

New Monomer Work

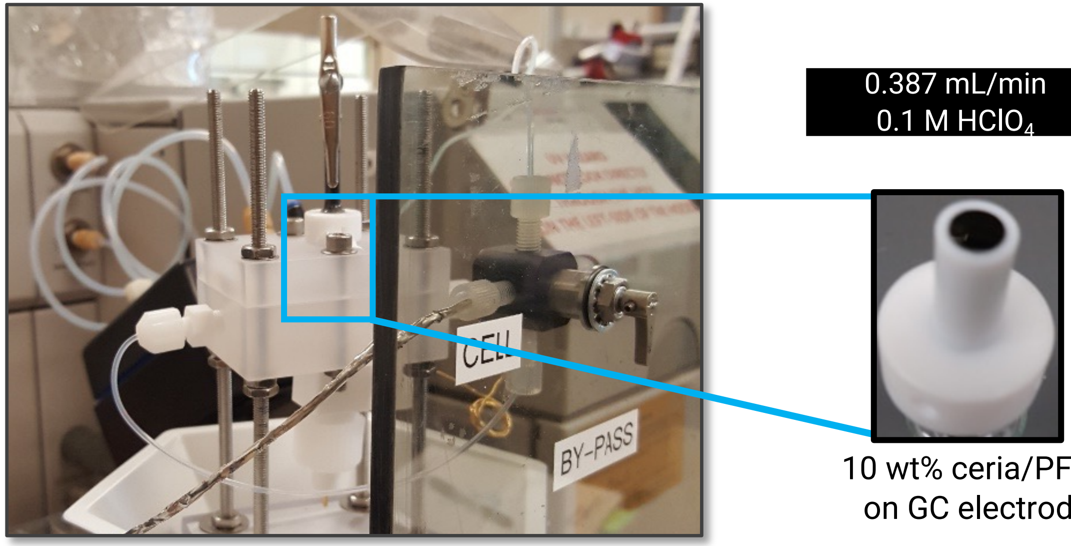
$$CF_2{=}CF{-}R_f{-}X$$

Where,
R_f = perfluoro side chain
X = novel end group moiety

CERIUM OXIDE NANOPARTICLE DISSOLUTION

ACCOMPLISHMENTS & PROGRESS (TASK 2.3)

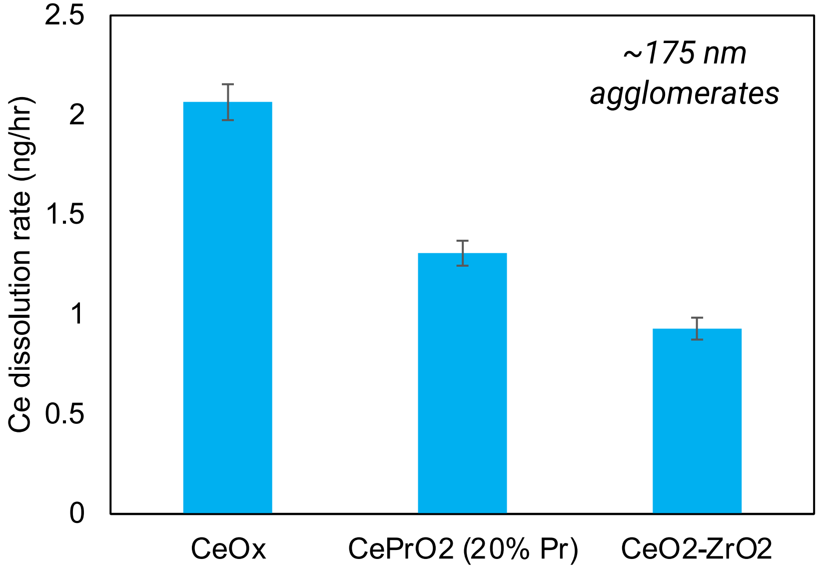
Online ICP-MS



0.387 mL/min
0.1 M $HClO_4$

10 wt% ceria/PFSA
on GC electrode

Ce dissolution rates

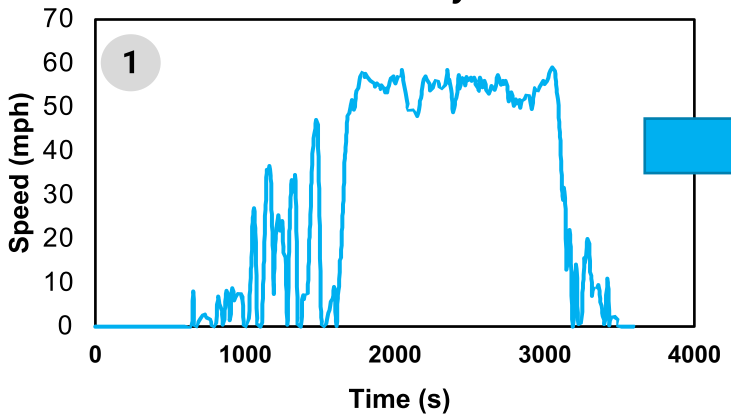


- Ce cation dissolution rates of 3 commercial ceria powders measured using on-line ICP-MS
  - Average agglomerate sizes of ~175 nm measured via Zetasizer
- Dissolution rates qualitatively match previous trends: Undoped > Pr-doped > Zr-doped
  - State of agglomeration in membrane still unknown
- Presently investigating dissolution as a function of potential by adding carbon to electrodes

AST DEVELOPMENT PLAN (IN COLLABORATION WITH M2FCT)

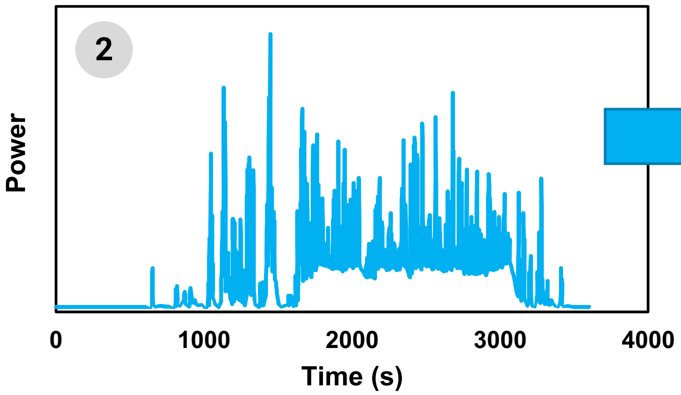
ACCOMPLISHMENTS & PROGRESS (TASK 4.1)

CARB HHDDT Cycle[1]



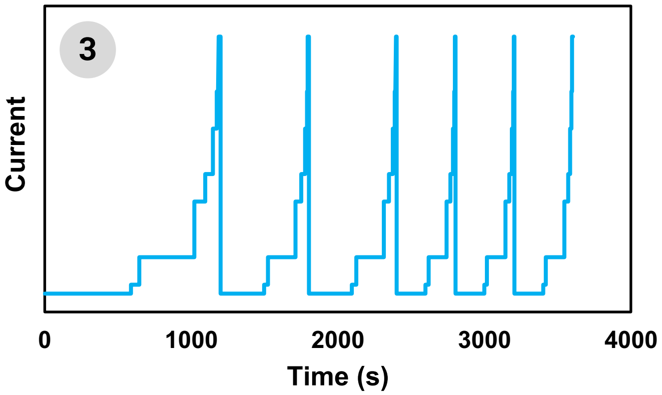
- Based on routes for target customer applications

Stack Power Demand



- Hybridization strategy & control logic
- Battery sizing & chemistry
- Incorporates grade, GVW, CdA

HD "Drive Cycle"/Life Test

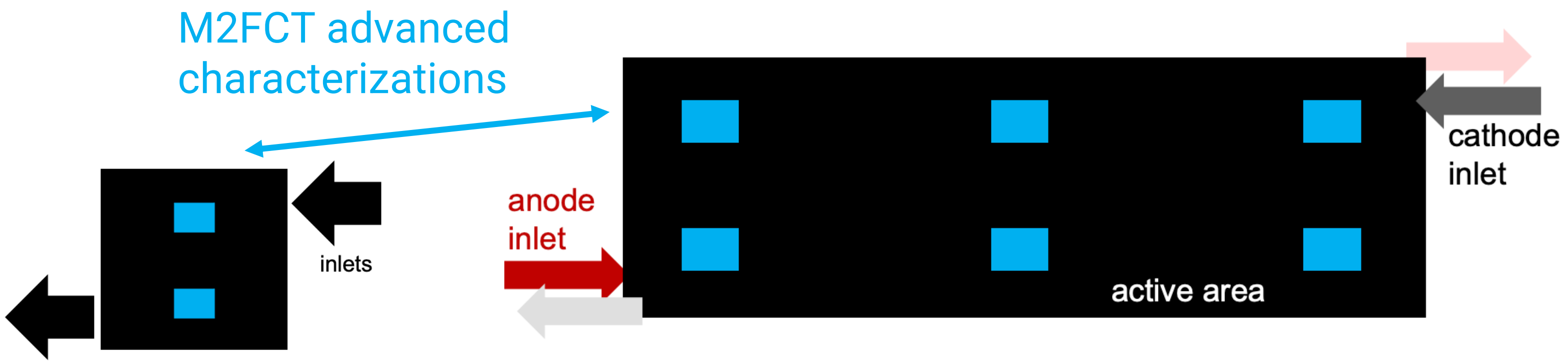


- Smoothed transient current spikes
- Relevant redox events captured
- Incorporates voltage clipping

- Run 2 test protocols in parallel
- Periodically remove cells from short stack
- Compare property changes in various locations
- Identify any acceleration factors between tests
- Refine single cell protocol

M2FCT "H_2/air AST AST"

Short Stack "Drive Cycle"



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

RESPONSES TO REVIEWERS' COMMENTS

ACCOMPLISHMENTS & PROGRESS

2021 AMR Comment	Response
"The project should define appropriate targets and ASTs early in the project"	We adopted the HAST protocol for primary membrane evaluations, with an initial target that meets or exceeds baseline. Future AST development later in the project will involve multiple, synergistic MEA stressors.
"It is not clear that the identified mobility target is enough to reach U.S. DOE targets for HD application"	We agree that this relationship has not been definitively established in the literature, however we believe that any improvement over the baseline is meaningful if it improves overall lifetime efficiency.
"The project should determine whether scavengers can be regenerated"	Radical scavenger regeneration will be explicitly measured using *in situ* fluorescence experiments.
"The task lists have too many parameters to choose and optimize"	The task list has been shortened to focus only on EW, thickness and additive content.
"It looks like the project is targeting only a small improvement"	This project aims to enabling longer operation at high T/low RH excursions, as well as preventing conductivity & durability loss due to in-plane radical scavenger gradients.

REMAINING CHALLENGES & BARRIERS

Challenge	Resolution
Effectiveness of immobilization during polarization: *Will weak acids help Ce cations resist electric fields?*	• Use X-ray fluorescence to intermittently measure in-plane radical scavenger gradients during *ex situ* migration experiments • Water gradient resistance expected to be similar to diffusion
Effectiveness of radical scavenging in immobilized systems: *Will Ce redox when associated with weak acid?*	• Quantify radical scavenging rate both in situ and in operando • Optimize amount of “free” Ce relative to associated Ce
Negative effects of ionic crosslinking on membrane conductivity: *Is there a nonlinear decrease due to weak acids?*	• Tune weak acid content in membrane • Offset conductivity loss by using low EW ionomers

YEAR 1 MILESTONES AND PROGRESS

SUMMARY

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

Relevance: Reduce TCO of HD PEM fuel cell systems by increasing the MEA lifetime efficiencies

Approach: Develop a HD-specific architecture containing advanced reinforcements, thermally-stable ionomers, and immobilized radical scavengers

PROGRESS

Milestone	Period	Progress	
Define initial MEA material set and test protocols	Q1	Complete	✓
Evaluate the performance and durability of a membrane with the new HT-PFSA and compare to Nafion™ NC700	Q2	Initial performance testing complete Baseline durability testing completed, awaiting subcontract agreement for further testing	✓ ⌛
Synthesize 5 g of novel monomer	Q3	3 mmol quantity synthesized	⌛
Measure dissolution and migration of CeM_yO_x in PFSA and compare it to Ce^{3+}	Q4	Improved dissolution resistance of CPO and CZO demonstrated	⌛

PROPOSED 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

TECHNICAL BACKUP & ADDITIONAL INFORMATION

TECHNOLOGY TRANSFER ACTIVITIES

Patents: n/a

Tech-to-market activities

Commercialization of membrane technology is anticipated if proposed advances are realized

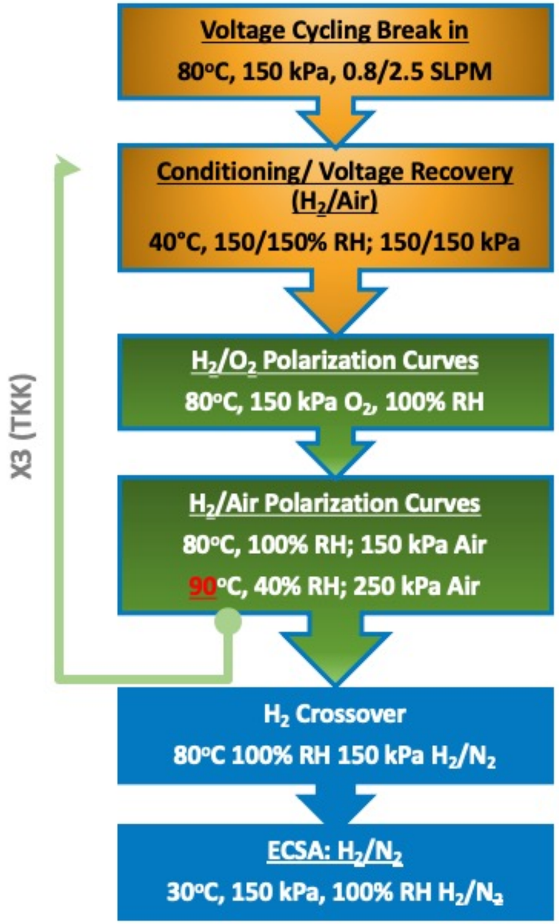
Future/Additional Funding: n/a

INITIAL MEA MATERIAL SET AND TEST PROTOCOLS

MILESTONE M1

Milestone M1 (Q4 2021): Define initial MEA material sets and test protocols.

- Hardware: 50 cm^2 quad/quad serp, co-flow
- Membrane: Nafion™ NC-700
- Catalysts: 50% Pt/HSC (TKK) / 50% Pt/Vu (TKK) [Anode/Cathode]
- Catalyst loading: 0.1 / 0.3 mg_{Pt}/cm^2 [Anode/Cathode]
- GDL: AvCarb GDS3250 @ ~20% compression
- Subgasket: 25 µm PTFE
- Break-in: 50 cm^2 M2FCT protocol, see right
- Polarization: see right (constant stoich's of 1.5/2)
- AST: OCV RHC // GM HAST (90C, 30% RH, 300 kPa_{abs} 0.05-1.2 A/cm^2)
- Intermittent diagnostics: VIR, EIS(HFR), LSV/ECSA, FER (when available)
- Post mortem/EOT: thinning via SEM, in plane XRF for Ce migration, XY failure localization



SLIDE 6 REFERENCES

ADDITIVE FIGURE (TOP LEFT)

Radical Scavengers – See Slides 29 & 30

Heterpolyacids

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