FC327

Durable High-Power Density Fuel Cell Cathodes for Heavy-Duty Vehicles

Shawn Litster

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Pittsburgh, PA

DE-EE0008822

Overview

Timeline and Budget

- Project Start Date: 10/01/2019
  *Fully executed agreement on 4/30/2020
- Project End Date: 1/31/2023
- Total Project Budget: $2,500,00
  - Total Recipient Share: $500,000
  - Total Federal Share: $2,000,000
  - Total DOE Funds Spent: $34,839

Barriers

B. Cost

➢ Reduce PEM fuel cell costs by reducing PGM loading

C. Performance

➢ Increase catalyst activity, utilization, and effectiveness by increasing solubility and permeability of ionomers

A. Durability

➢ Increase the lifetime of PEM fuel cells by reducing the loss of efficiency and power

Project Lead

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– PI: Shawn Litster
– Co-PI: Zack Ulissi

Partners

The Chemours Company

– PI: Andrew Park

Ballard Power Systems, Inc.

– PI: Devproshad Paul
– Co-PI: Alan Young
– Co-PI: Shanna Knights

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Project Team and Scope

Carnegie Mellon University (University prime)

Shawn Litster (PI), Zack Ulissi (Co-PI), Jonathan Braaten

Electrode design, electrode fabrication, fuel cell testing, X-ray and electron imaging, AST development, multi-scale modeling, molecular-scale modeling, project management.

The Chemours Company (Industry sub)

Andrew Park (Chemours co-PI), Gerald Brown(Chemours co-PI)

Ionomer and dispersion development, synthesis, and experimental characterization.

Ballard Power Systems (Industry sub)

Devproshad Paul (Ballard PI), Alan Young, Shanna Knights

MEA fabrication scale-up analysis and demonstration, testing, AST development, and durability forecasting

Fuel Cell Performance and Durability Consortium

Collaboration with FC-PAD National Lab members on ionomer characterization , electron microscopy, electrode coating, durability measurements

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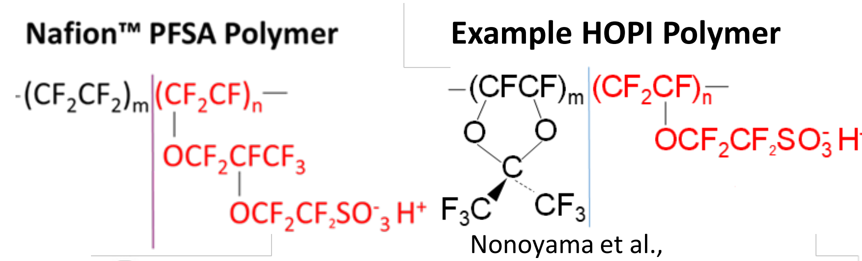
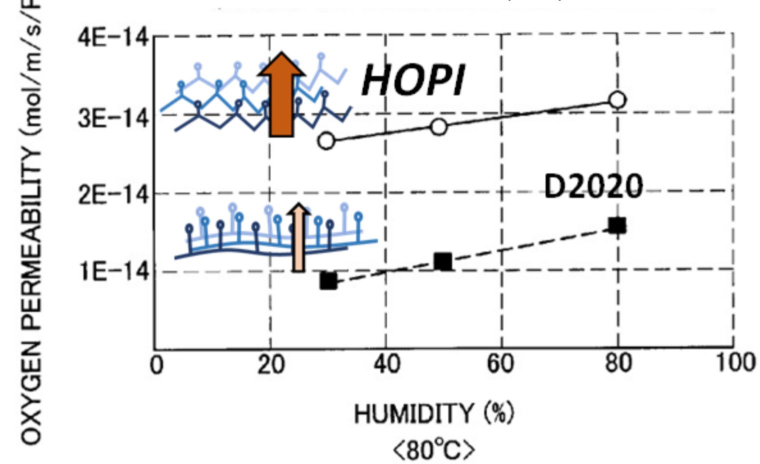
High Oxygen Permeability Ionomer (HOPI)

- Heavy duty vehicles requires high efficiency and long lifetimes at moderate Pt loading
  - Increase mass activity for high voltage efficiency
  - Reduce local Pt O_2 voltage loss with reductions in ECSA over long stack lifetimes
- Prior work indicates HOPIs reduce O_2 transport resistance and ***increase air mass activity***:[1]
  - 20% increase in current at 0.75 V
  - 50% increase in 0.85 V mass activity
- HOPIs with 3X greater O_2 permeability over baseline D2020 Nafion ionomer have been developed by Chemours
- Developed to address voltage losses due to thin ionomer film coatings of catalyst
- Emergent HOPI technology requires development of optimum integration for durability and manufacturability (e.g., mitigation of cracking during electrode casting).



Nonoyama et al., US Patent 9,431,661 B2.

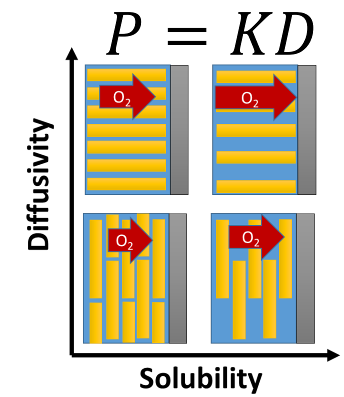


1. Shimizu et al, J. Electrochem. Soc., 2018

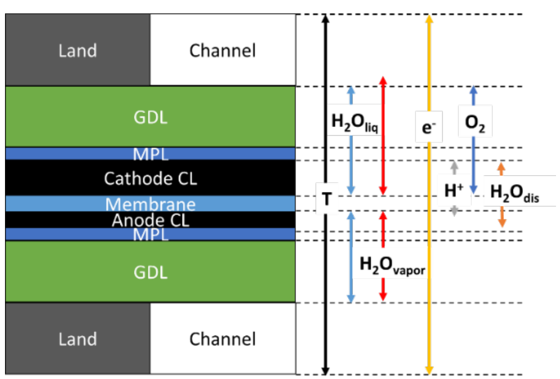
Relevance

Cell Modeling of HOPI Impact

- Permeability is the product of solubility and diffusivity
- Ionomer permeability can be increased in two ways:
    - Higher diffusivity through greater porosity, lower tortuosity, and favorable gas-polymer interactions
    - Higher solubility through favorable solvation and polymer interaction as well as greater porosity
- Approaches to increased permeability can have distinct impacts on fuel cell performance
    - Higher diffusivity yields higher O_2 concentrations at the Pt catalyst at high current density and increases maximum power density
    - Higher solubility increases O_2 concentration at the Pt interface with ionomer at <u>ALL</u> currents, increasing <u>efficiency and power density</u>
- Cell-scale modeling to understand impact of ionomer properties
- CMU's cathode model accounts for the following aspects related to HOPIs
    - Fraction of external Pt in contact with ionomer
    - Transport resistance to internal Pt through carbon support
    - Reduced activity of ionomer in contact with ionomer due to possible anionic poisoning
    - Solubility of O_2 in ionomer and water
    - Local resistance of ionomer due to:
        1. Diffusion through bulk ionomer film
        2. Diffusion through densified interfacial zones due to ionomer-Pt interaction



*Neutral gas/solid interaction case



External Pt ORR Model

ECSA — Film diffusion — Pt interface

$$j = \frac{a_{Pt} 4F p_{O2}}{H_{O2}} \left[\frac{1}{\frac{i_{0,c}(T)}{4FC_{O_2,ref}}(1-\theta_{PtO})\exp\left(\frac{\theta_{PtO}\omega_{PtO}}{RT}\right)\exp\left(\frac{\alpha_{c,c}F}{RT}\eta_c\right)} + \frac{l_{Naf}}{D_{O2,Naf}} + \frac{1}{k_{local}} \right]^{-1}$$

Ionomer solubility

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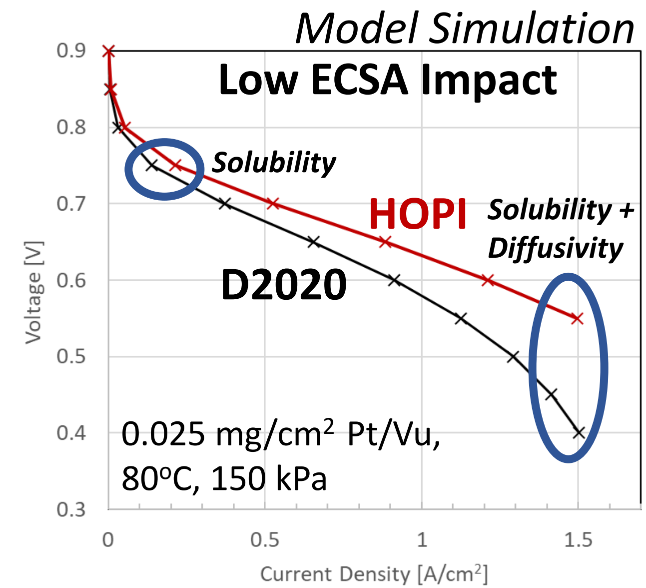
Modeling the Impact of HOPI

- Model implemented with 3X permeability for ionomer
- Assumed 50/50 contribution of solubility and diffusivity to increased permeability
  - 73% increase in solubility and ionomer diffusivity and interface resistance
- Provides consistent increase in mass activity and limiting current with literature and preliminary data[1]
- Experimentally observed large performance increases[1] at >0.75 V not predicted without solubility increase
  - Precise breakdown of solubility and diffusivity of HOPIs in future work



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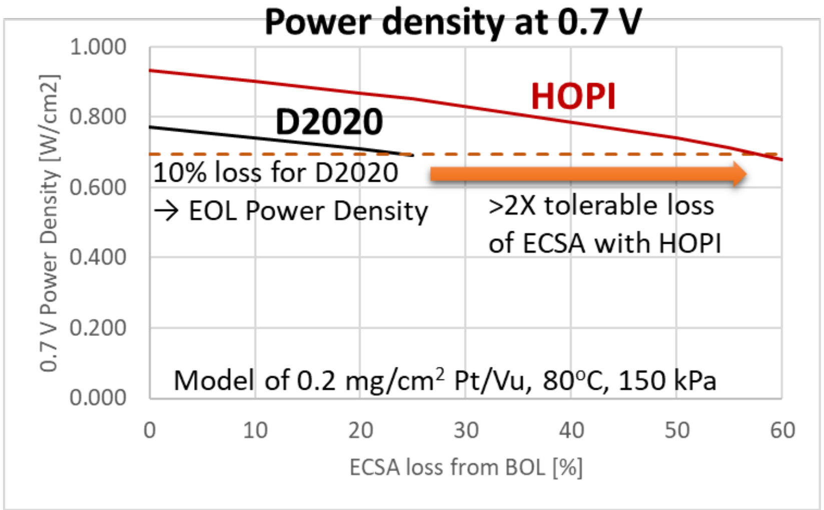
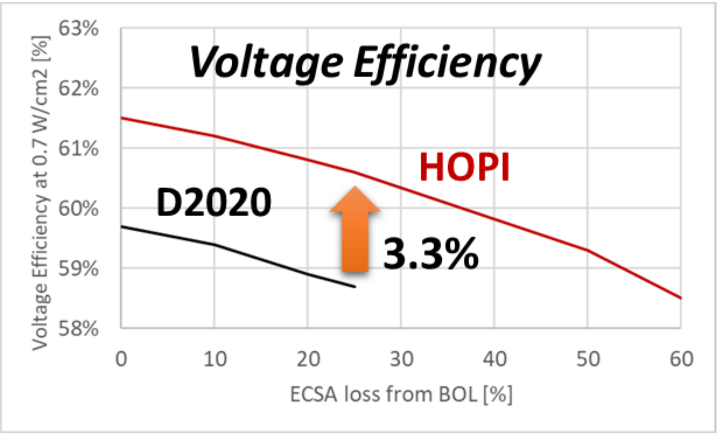
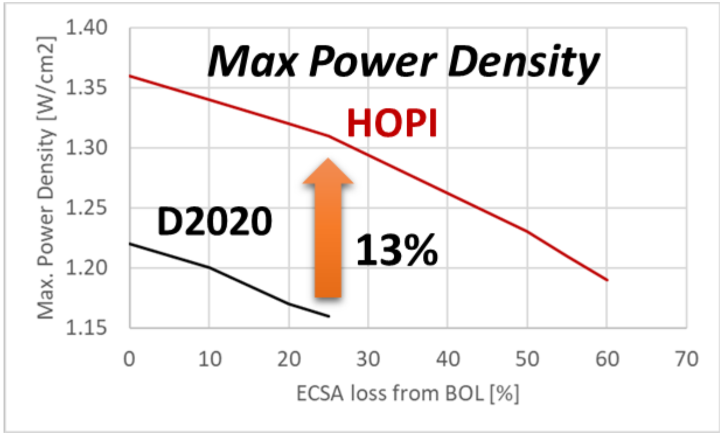
1. Shimizu et al, J. Electrochem. Soc., 2018

ECSA-based Lifetime Increase with HOPI

- Preliminary evaluation of increased performance and extended lifetime using ECSA loss as a metric of lifetime
- Evaluation of 0.7 V power density and ECSA loss associated with 10% power density reduction with D2020
  - D2020 experiences 10% drop with ~25% ECSA loss
  - HOPI reduces to same power density at ~60% ECSA loss
- Based on ECSA, HOPI doubles lifetime to EOL power density at 0.7 V
- Substantial increases in voltage efficiency and maximum power density with HOPI







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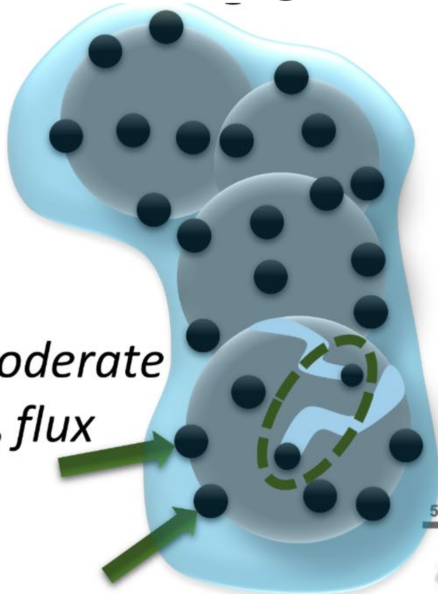
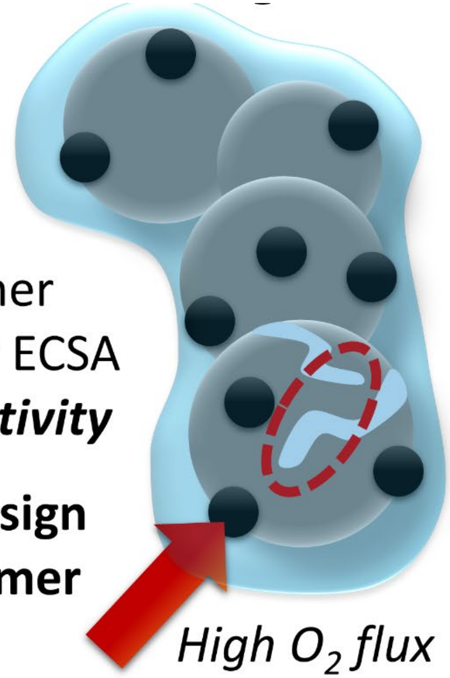
Durable High Performance with Advanced Ionomer Integration



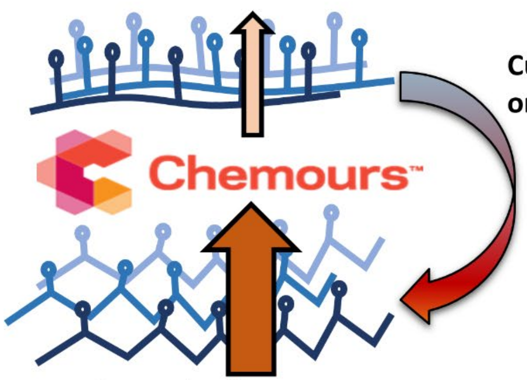
25,000 hours

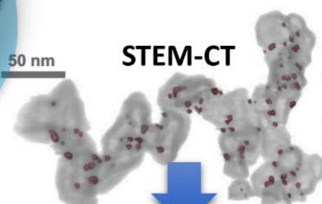
- Outer Pt coarsens
  →Loss of ECSA
- Inner Pt redeposits at ionomer
  → Loss of high activity inner ECSA
- ***High O_2 resistance & low activity***



Higher solubility ionomer to increase efficiency for HDVs

1. Short side chain high O_2 perm. ionomers





2. Integrated design of catalyst-ionomer

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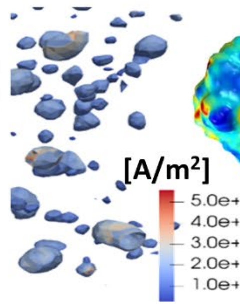
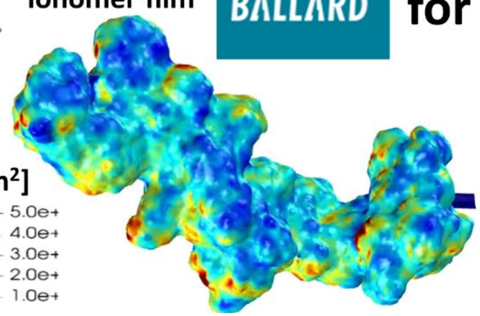
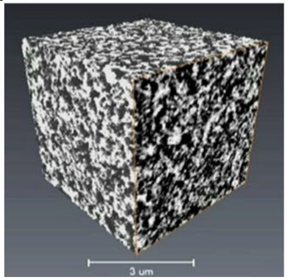




3. Durable electrode fabrication strategy for O_2 perm. ionomers



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Year 1 Milestones and Go/No-Go

Task Number	Task or Subtask (if applicable)	Milestone Number* (Go/No-Go Decision Point Number)	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Anticipated Quarter
1.1	Ionomer development and synthesis	M1.1	Delivery of >200 mL (>10% solids) HOPI dispersion to project partners for thin-film characterization, ink studies, and MEA development	Receipt of ionomer	1
1.3	Scale-able fabrication and testing of MEAs with HOPI-enhanced cathodes	M1.2	Define ink processing protocol with concept level ink mixing/coating equipment for 0.05-0.20 $mgPt/cm^2$ cathode catalyst coated membranes (CCM).	Report to DOE FCTO in quarterly update	2
1.3	Scale-able fabrication and testing of MEAs with HOPI-enhanced cathodes	M1.3	Define baseline PFSA ionomer (D2020) capability with 0.20 $mgPt/cm^2$ Pt or PtCo catalyst, optimized for ionomer loading. Output will be a metrics table with full analysis of CCL transport properties.	Performance characterization in report to DOE FCTO in quarterly update	3
1.3	Scale-able fabrication and testing of MEAs with HOPI-enhanced cathodes	M1.4	Selection of two HOPI dispersions for 50 cm^2 MEA fabrication and testing based on Task 1.1 and 1.2 findings	Report to DOE FCTO in Quarterly update	4
1.3	Scale-able fabrication and testing of MEAs with HOPI-enhanced cathodes	GNG 1	Demonstrate reduction of in-situ local oxygen transport resistance to 9 s/cm with no increase in cathode protonic sheet resistance.	Limiting current and N2/H2 EIS and Nyquist plot analysis reported to DOE FCTO in quarterly update	4

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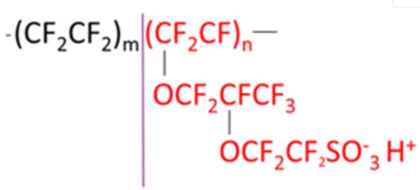
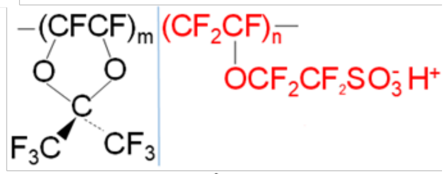
HOPI Development

Ionomer Synthesis

Nafion™ PFSA Polymer



Example HOPI Polymer



Nonoyama et al.,
US Patent 9,431,661 B2.

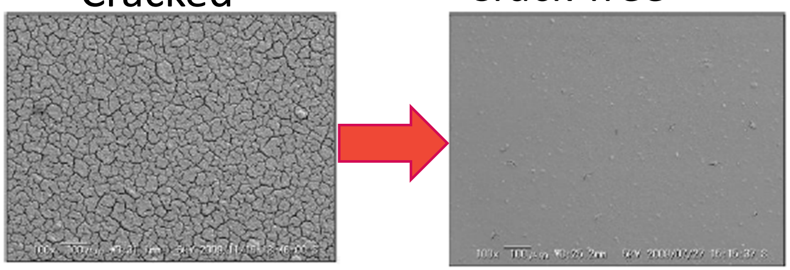
Ionomer & Dispersion Preparation

- Tuning dispersion of ionomer in solvent for ink integration
- Solvent selection
- Weight content
- Characterization of agglomeration

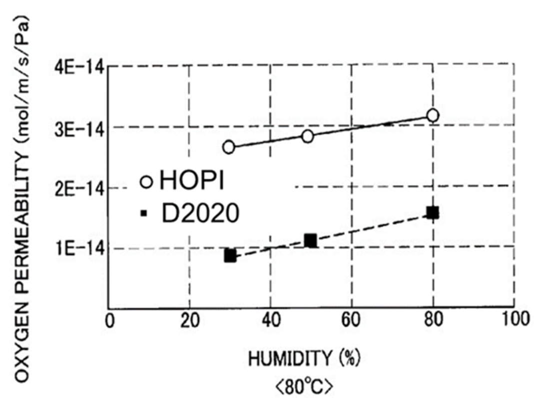
Electrode Coating Quality

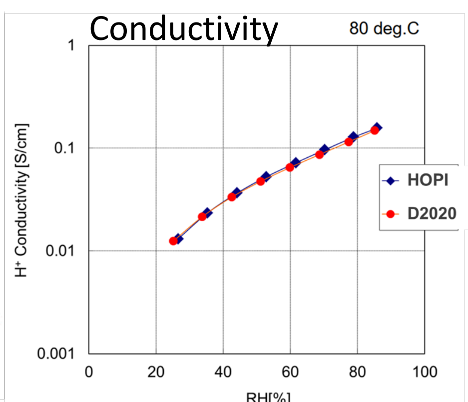
Tuning ionomer and dispersion for high quality films with HOPI

Cracked Crack-free



Ionomer & Dispersion Characterization





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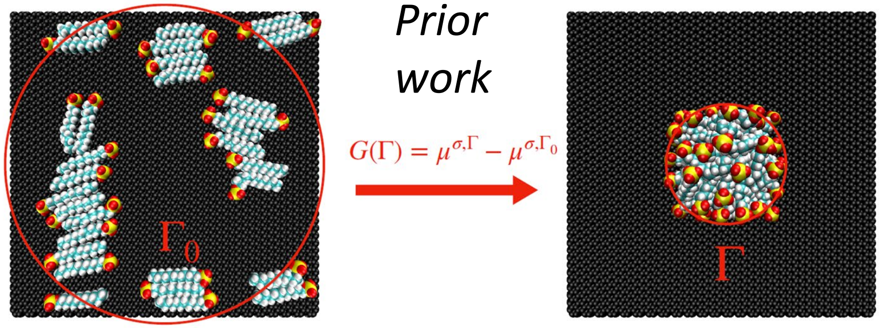
Molecular Simulation

MD, DFT, and ML to understand ionomer dispersion, ionomer-solid interaction, and ionomer transport properties including solubility and diffusivity

Ionomer packing on Pt and Carbon surface

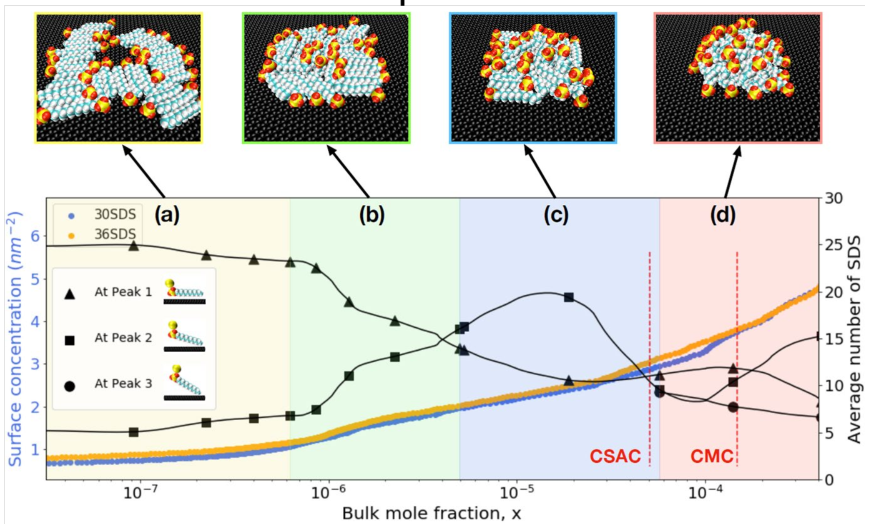
(Low surface concentration) **(High surface concentration)**



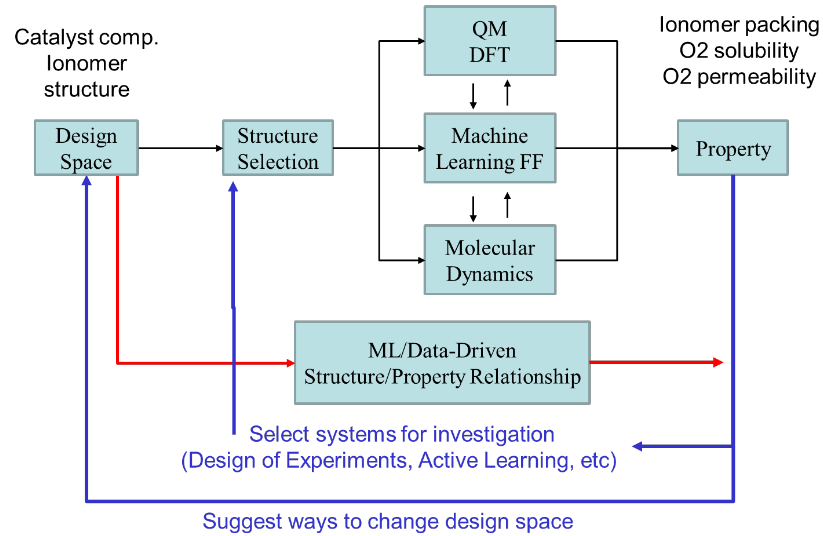
$$\mu^{\sigma,\Gamma_0} = \mu^{\sigma,id} = \mu^{\sigma,0} + k_B T \ln(\eta_0)$$

$$\mu^{\sigma,\Gamma} = \mu^{\sigma,id} + f(\Gamma) = \mu^{\sigma,0} + k_B T \ln(\eta) + f(\Gamma)$$

SDS at a Graphene Surface



Surrogate-Based Materials Design



Theory ionomer studies integrated with Chemours vast library of available monomers and chemistry

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Yoon and Ulissi, Langmuir, 2020

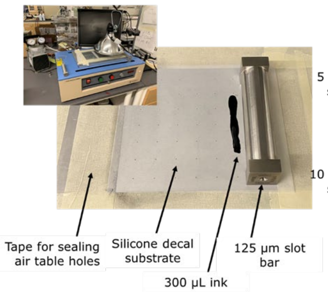
Technical Accomplishments

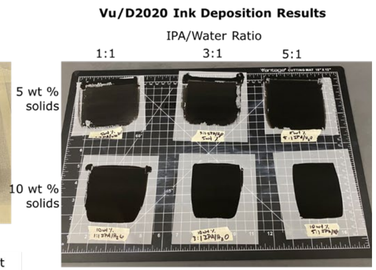
Diagnostics & Modeling

Ionomer, Ink, & Electrode Studies

Ink colloidal studies *Ionomer O_2 transport*

Small scale electrode coating & testing

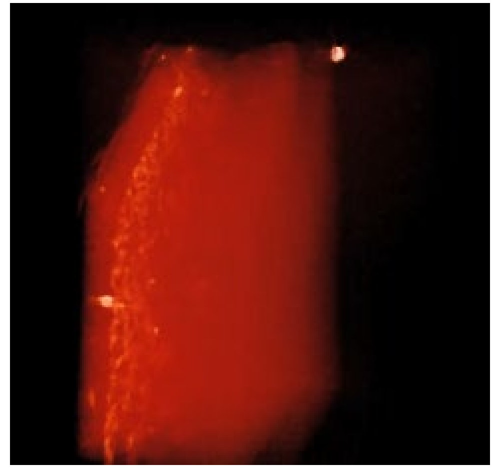


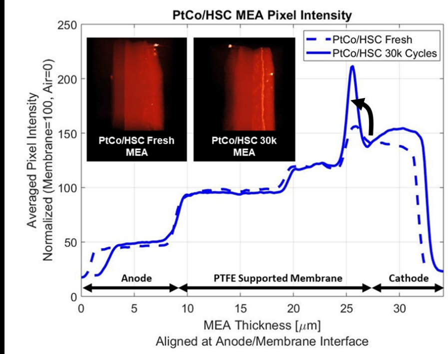


Preliminary results of ink coating on decals

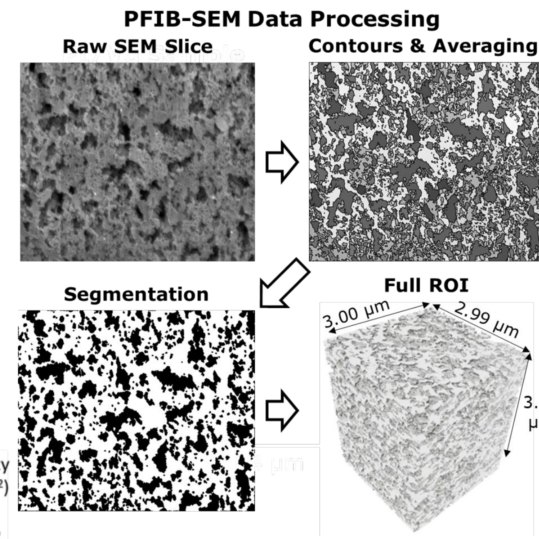
Imaging & Materials Characterization

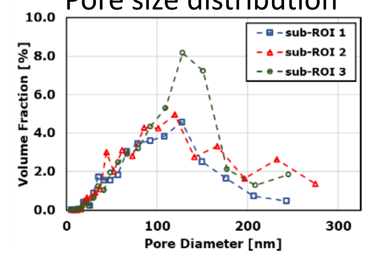
3D Pt redistribution





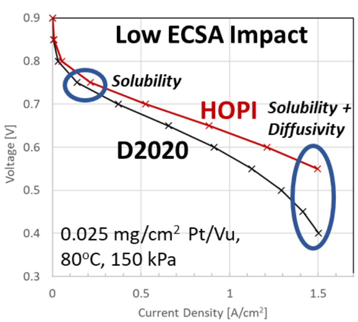
Plasma FIB-SEM (BOL & EOL)

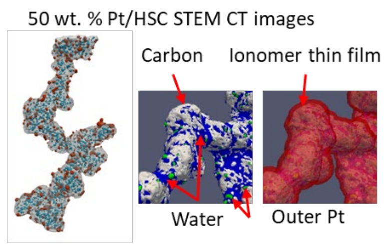




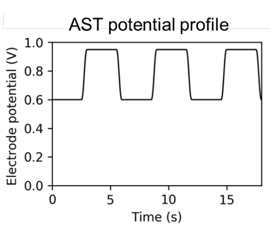
High resolution, high-throughput imaging

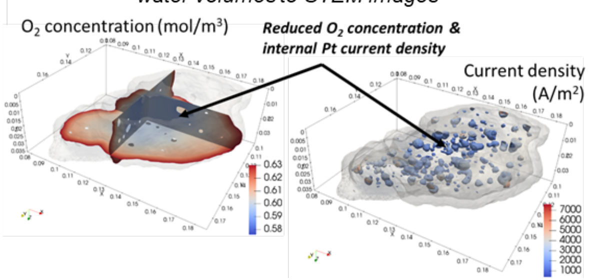
Performance & Durability Modeling





Synthetic addition of ionomer and water volumes to STEM images





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Prior work from DE-EE0007271

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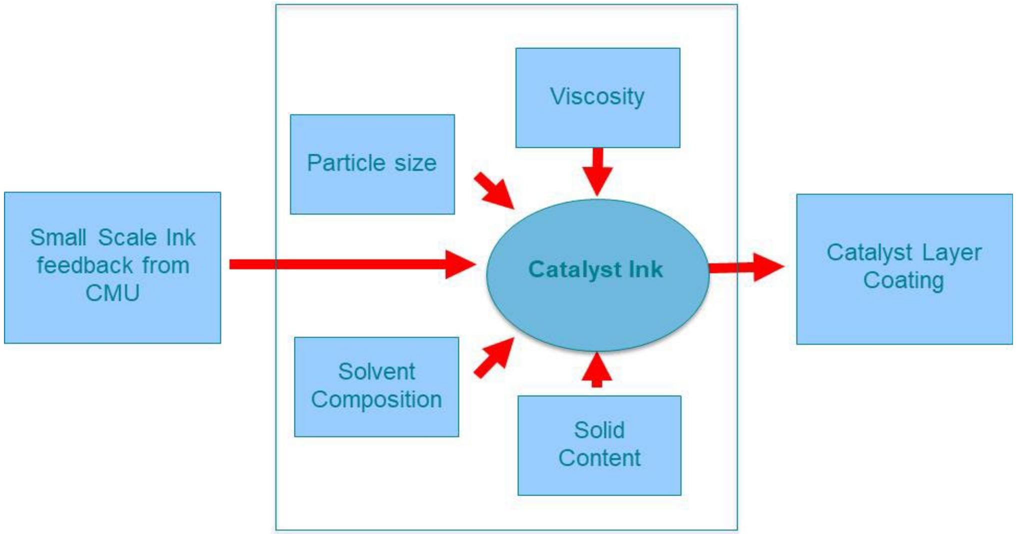
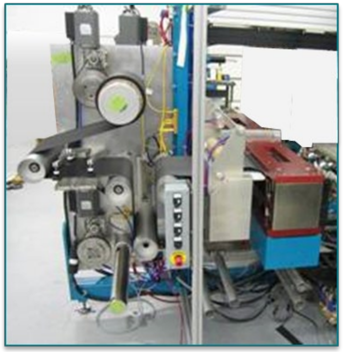
CCM Fabrication Approach

Ink Scale-up Process

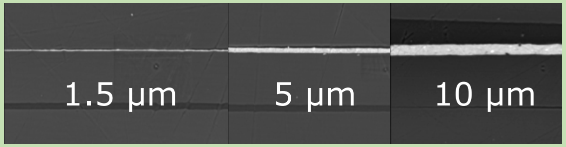


Roll-to-Roll Coating Processes



Ballard Capabilities

- Scalable mixing & coating technology
- Roll-to-roll coating processes
- Catalyst layer in-line QA and QC capability
- Coating capability down to very low catalyst loadings



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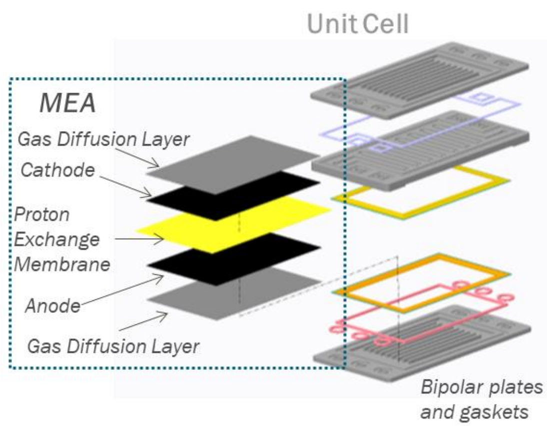
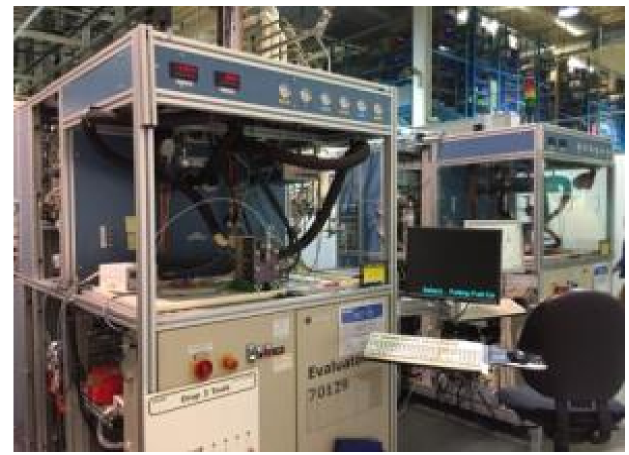
MEA Evaluation Approach

Overall Approach

Cell Assembly & Leak Test → BOL Diagnostics → AST ⇄ In-situ Diagnostics → EOL Diagnostics → Failure Analysis





- **Extensive testing capability including**
  - Test station scalability from single cell MEA to full system
  - Highly Accelerated Life Testing (HALT) and Highly Accelerated Stress Screening (HASS)
  - Advanced characterization tools
  - Materials analysis
- **Experienced with automotive, bus and rail standards**

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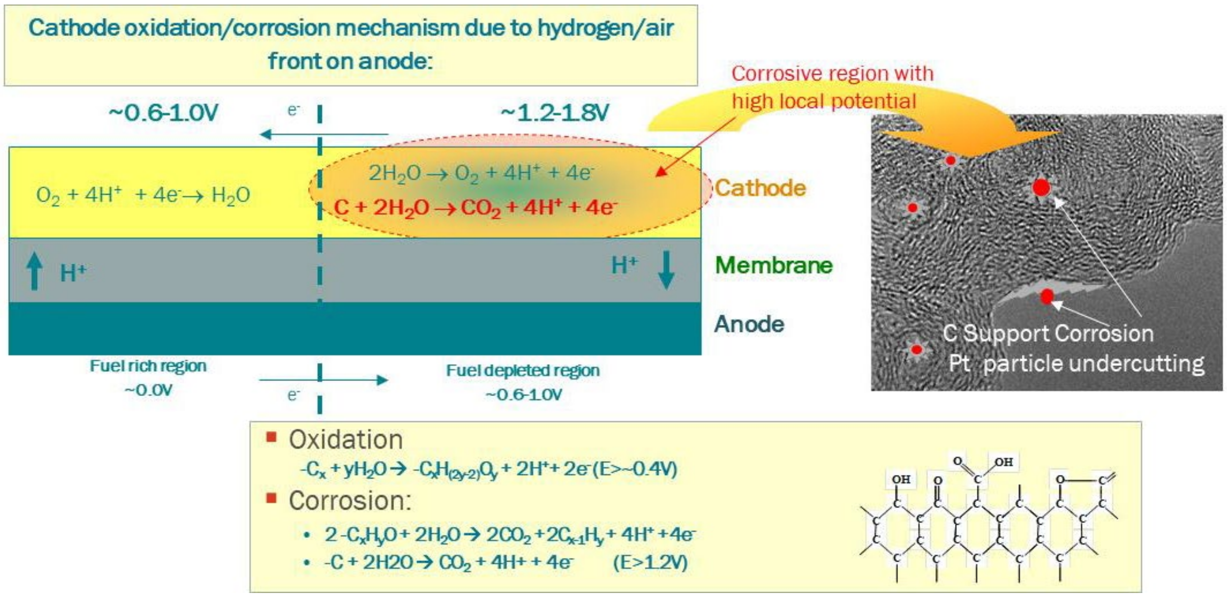
Carbon Corrosion AST (Air to Air Start-Up/Shut-Down AST)

Cycling Summary

Air-Air SU/SD AST

- 100% RH
- 30°C or 80°C
- 0.6V (30 s)
- Air-Air State (60 s)

Carbon Corrosion Mechanism



Air/air starts cause high cathode over potentials (~1.3V and higher), accelerating platinum dissolution and resulting in particle growth and migration, and catalyst carbon support corrosion

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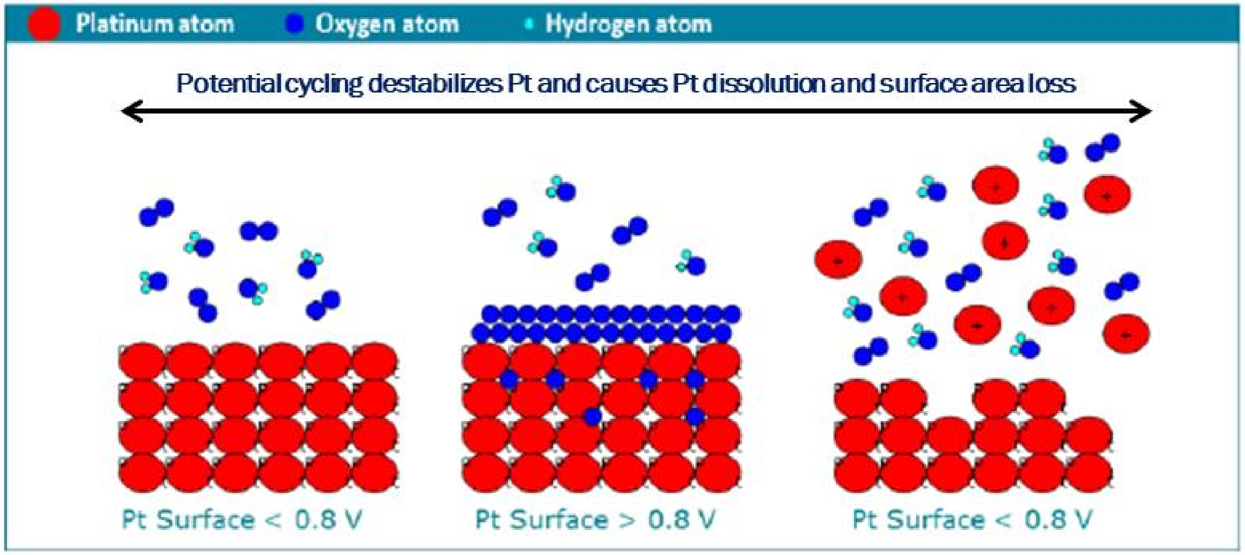
Pt Dissolution AST

Cycling Summary

Pt Dissolution AST

- 100% RH
- 80°C
- 0.6V (5 s)
- 1.0V (5 s)
- Cathode (air)/Anode (H_2)

Pt dissolution Mechanism



A square wave voltage profile will be chosen to maximize time at upper potential limit (UPL) while minimizing overall test duration

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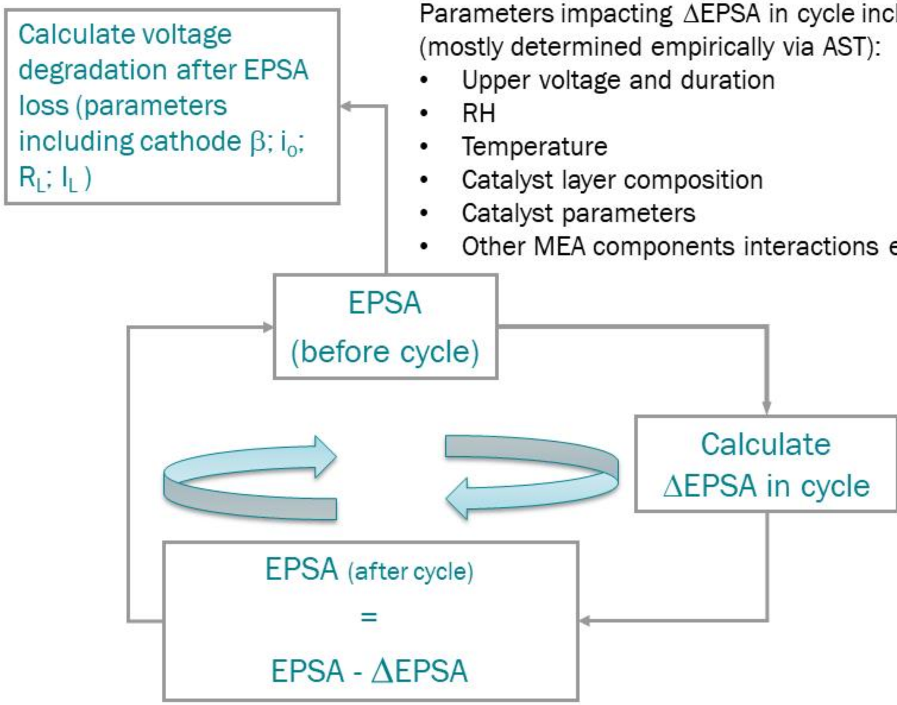
Lifetime Forecasting Model

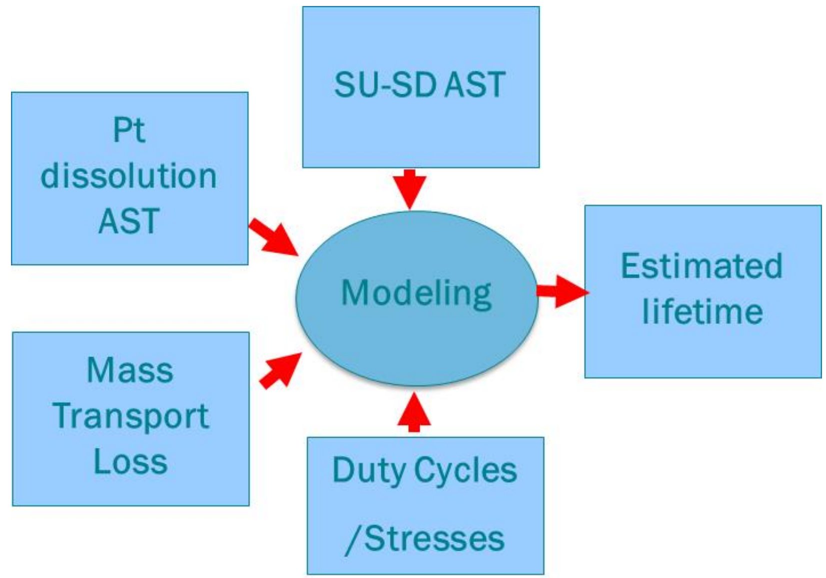
Model Input Calculation

Parameters impacting ΔEPSA in cycle include (mostly determined empirically via AST):

- Upper voltage and duration
- RH
- Temperature
- Catalyst layer composition
- Catalyst parameters
- Other MEA components interactions effects



Model Estimation



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Reponses to Last Year AMR Reviewers' Comments

Project was not reviewed last year

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Future Work

Year 1 HOPI development and HOPI-enhanced cathode performance

Focus on establishing the baseline HOPI synthesis, characterization, performance modeling, and performance testing.

Year 2 HOPI-enhanced cathode performance and durability

HOPI and cathodes will be refined for performance and there is increased focus on durability.

Year 3 Optimizing Performance and Durability for HDVs with HOPIs

Focus on synthesizing an optimized HOPI and fabricating HOPI-enhanced cathodes capable of meeting HDV performance and durability targets.

Summary

Approach

An integrated approach to advancing HDV fuel cell efficiency and durability with advanced electrode ionomers

1. **HOPIs for durable high efficiency with low Pt loading** through higher solubility and diffusivity. Tuning of ionomer synthesis and dispersions with guidance from molecular modeling and colloidal studies.
2. **Optimization of the catalyst|ionomer interface** through colloidal studies, small-scale electrode testing, cell to molecular-scale modeling.
3. **Scale-able high-performance electrode fabrication with HOPIs** through small-scale evaluation and medium-scale electrode casting in an industry format.
4. **ASTs and 25,000 hr performance forecasting** to guide the development of fuel cells with adequate performance and lifetime for HDVs.

Accomplishments and Progress to date

- Prime award fully executed 04/30/2020
- Delivery of D2020 and membrane from Chemours to Ballard for baseline MEA benchmarking.
- Delivery of D2020 and HOPI to CMU for ink and electrode studies.
- Initial ink (DLS, rheometer) and electrode studies at CMU for small-scale casting using automatic coater.
- Initial cell scale modeling of HOPI impact on performance and durability.

Collaboration and Coordination with Other Institutions

- Experienced industrial partners in fuel cells for HDVs and PFSA ionomers coupled with advanced diagnostics, modeling, and imaging.
- Tight coordination of ionomer development with requirements for industry-scale MEA fabrication.
- Integration of industry PFSA chemistry library and synthesis with molecular simulation to investigate promising material sets.

Relevance/Potential Impact

- HOPIs yield longer lifetimes by minimizing voltage loss as ECSA decreases over longer HDV lifetimes.
- Reduce loss in maximum power density with ECSA loss
- New HOPI chemistries with high O_2 solubility provide a catalyst independent pathway to higher efficiency through higher apparent mass activity.

Proposed Future Work

- Upcoming Year 1 efforts focused on establishing baseline MEA for benchmarking and then establishing first generation HOPI-enhanced cathodes
- Subsequent efforts on advancing initial HOPI chemistry and cathodes
- Development of HDV-specific ASTs and 25,000 hr durability forecasting.

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