FC327

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

Shawn Litster

Carnegie Mellon University
Pittsburgh, PA

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DE-EE0008822

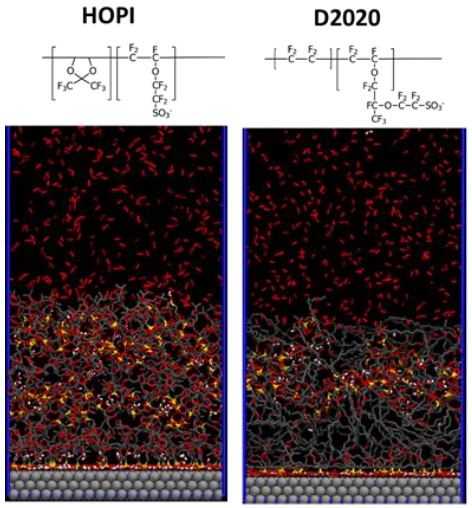
Technical overview and impact

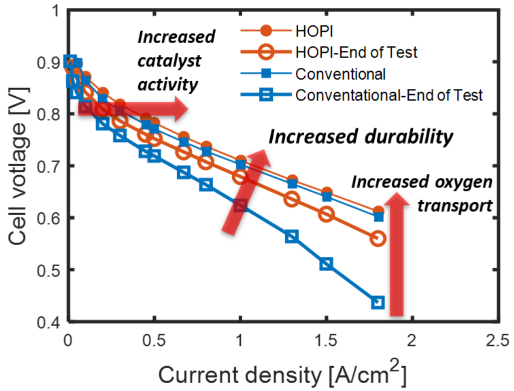
PROJECT GOALS

- Facilitate low platinum loadings in an advanced fuel cell membrane electrode assembly (MEA) cathode catalyst layer (CCL) for heavy-duty vehicles (HDVs).
- Synthesize and implement electrode-specific ionomers that permit enhanced oxygen transport to the platinum surface for improved performance and durability.
- Demonstrate the ionomer approach will yield required reduction in oxygen transport resistances in an MEA.
- Optimize the design of the ionomer for commercialization, demonstrating significant reductions in CCL platinum content while targeting ≤0.2 mg/cm^2 Pt catalyst loading and 25,000 hr lifetime set point.

IMPACT

- New ionomers developed specifically for electrode demands
- New insights on HOPI-Pt interfacial structure
- Significant increase in BOL performance due to increased mass activity and reduced local oxygen transport resistance
- Significant reductions in degradation rates and extended lifetimes





Overview

Timeline and Budget

- Project Start Date: 10/01/2019
- Project End Date: 1/31/2023
- Total Project Budget: $2,500,000
  - Total Recipient Share: $500,000
  - Total Federal Share: $2,000,000
  - Total DOE Funds Spent*: $974,243

*As of 12/31/2021

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

Carnegie Mellon University

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

Partners

The Chemours Company

- PI: Andrew Park
- co-PI: Gerald Brown

Ballard Power Systems, Inc.

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

M2FCT Consortium

Project Team and Scope

Carnegie Mellon University (University prime)

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

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)

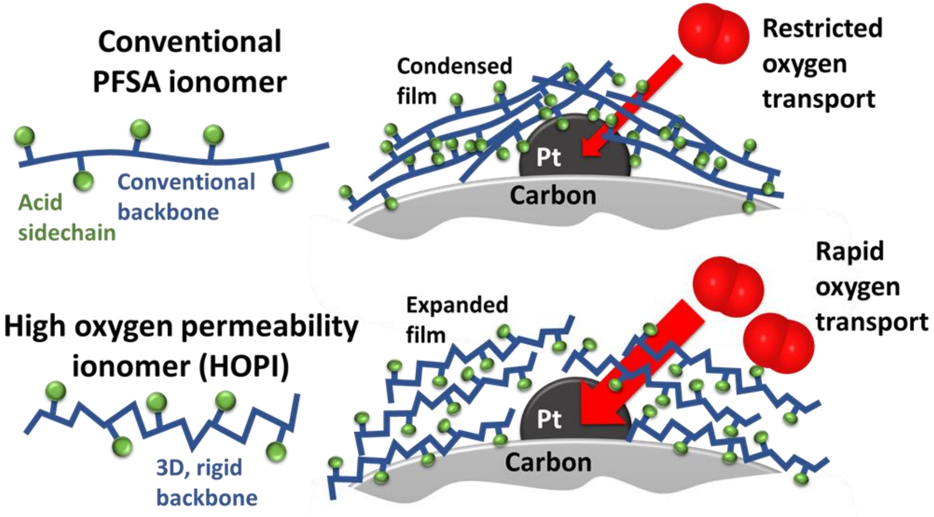
Andrew Park (Chemours co-PI), Gerald Brown(Chemours co-PI)

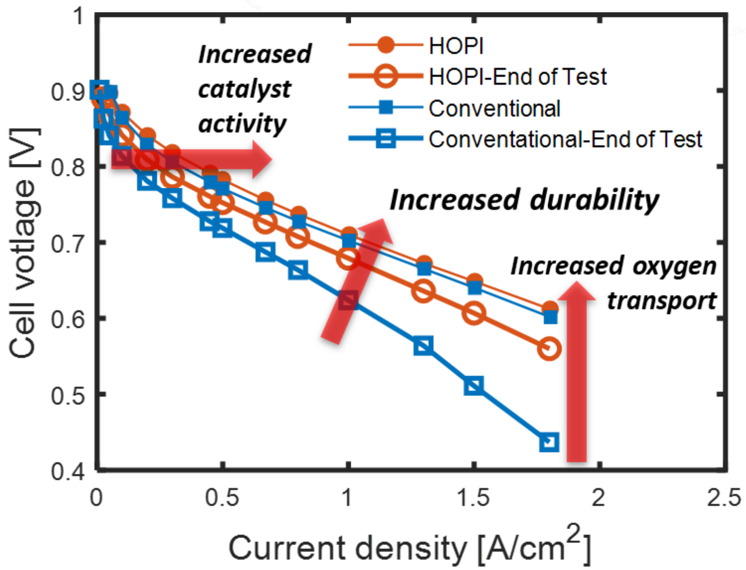
High Oxygen Permeability Ionomer (HOPI) and dispersion development, synthesis, and experimental characterization.

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





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

BERKELEY LAB

NREL Transforming ENERGY

Argonne NATIONAL LABORATORY

OAK RIDGE National Laboratory

Los Alamos NATIONAL LABORATORY

Carnegie Mellon University

Technical Targets, and Status

	DOE/Project Target	D2020 Baseline		HOPI Status	
		Pt/LSAC	Pt/HSC	**Pt/LSAC**	**Pt/HSC**
Mass activity (A/mg$_{Pt}$)[1]	>0.44	0.16	0.30	**0.23**	**0.48**
Performance at 0.8V(A/cm^2)[2]	0.3	0.33	0.55	**0.41**	**0.58**
Performance loss at 0.8 A/cm^2 (mV)[2,3,5]	<30	62	78	**29**	**53**
Local RO$_2$ (s/cm)[4]	9	16	21	**9**	**4**
CCL Resistance (mOhm.cm^2)[1,5]	N/A	110	103	**100**	**93**
Degradation rate (µV/cycle)[3,5]	N/A	2.1	2.3	**0.8**	**1.3**

[1] 80°C, 100%RH, [2] 80°C, 100%RH, 1.5barg, [3] 35K AST Cycles, [4] 80°C, 60%RH, [5] 0.2mg/cm^2 catalyst loading

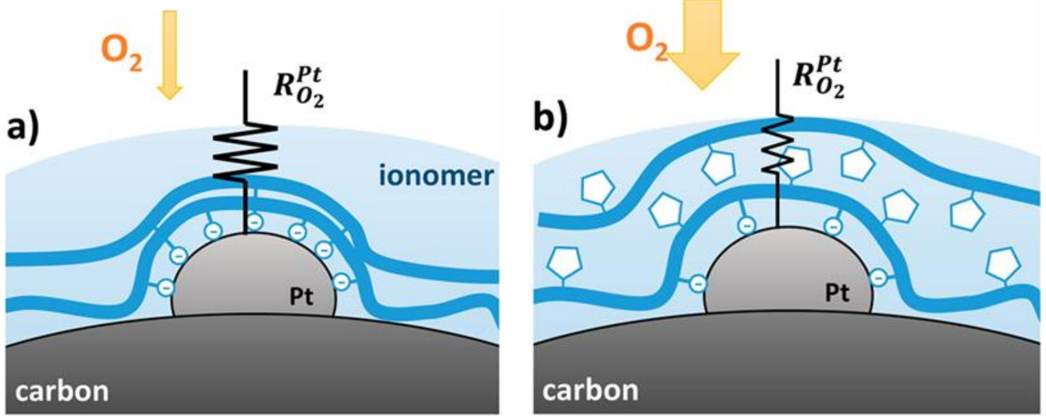
Year 1 & 2 Milestones and Go/No-Go Decision Points

Milestone Number* (Go/No-Go Number)	Milestone Description (Go/No-Go Decision Criteria)	Quarter	Percent complete	Progress notes
M1.1	Delivery of >200 mL (>10% solids) HOPI dispersion to project partners for thin-film characterization, ink studies, and MEA development	1	100%	350 ml of HOPI delivered to project partners this quarter.
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).	2	100%	Baseline D2020 protocol for 0.05-0.3 mgPt/cm2 defined in this report
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.	3	100%	Baseline D2020 MEA testing has been completed at Ballard and CMU.
M1.4	Selection of two HOPI dispersions for 50 cm^2 MEA fabrication and testing based on Task 1.1 and 1.2 findings	4	100%	Completed.
GNG 1	Demonstrate reduction of in-situ local oxygen transport resistance to 9 s/cm with no increase in cathode protonic sheet resistance.	4	100%	Target of 9 s/cm local O2 resistance has been met.
M2.1	Synthesis of improved HOPI scaled-up to 100 g to support expanded MEA testing	5	50%	Underway with new 1 L batch of ionomer dispersion delivered to Ballard
M2.2	Durability analysis comparing MEAs with HOPIs versus baseline Nafion D2020 for Pt and PtCo. Final output will be a report including failure mode analysis.	6	50%	Pt completed in Year 1
M2.3	Demonstrate single cell with HOPI-enhanced cathode with 0.2 mg Pt/cm^2 having a mass activity of 0.44 mA/mg PGM at 0.9 $V_{IR\text{-}free}$	7	100%	Achieved with Pt/HSC
M2.4	Define ASTs for input into forecasting performance at 25,000 h using durability models	8	100%	Existing ASTs demonstrated. Forecasting underway
GNG 2	Demonstrate a 2X increase in forecasted lifetime hours using HOPI versus a baseline using D2020 Nafion under identical test conditions with 0.2 mg Pt/cm^2 loading. The lifetimes of the HOPI and baseline D2020 cases will be defined as time until the power density at 0.7 V decreases to that when the baseline D2020 Nafion electrode had decreased by 10% and will be evaluated by AST characterization and forecasted durability modeling.	8	100%	Reduced degradation with HOPI demonstrated

Approach

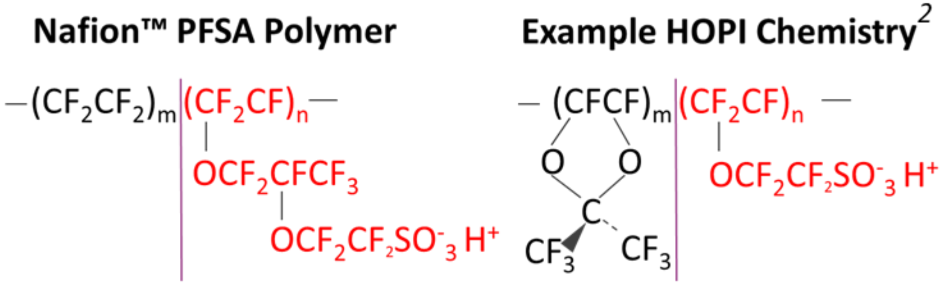
Chemours™

High Oxygen Permeability Ionomer (HOPI)

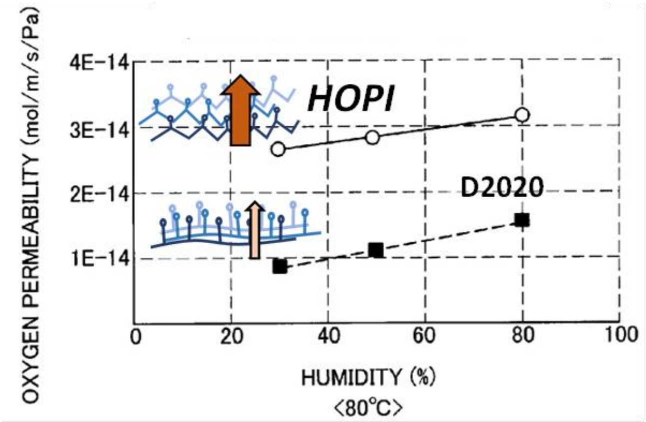

Traditional PFSA Ionomers[1]

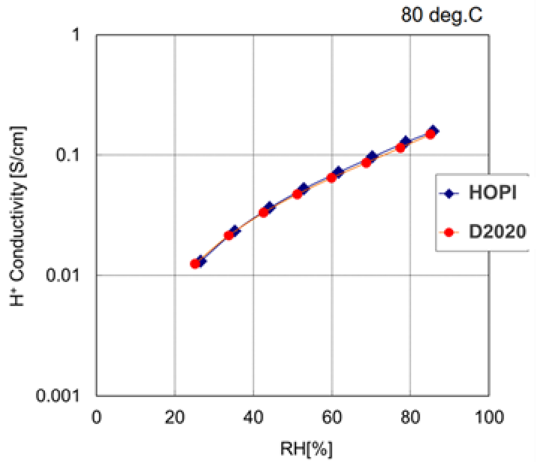
HOPI-type PFSA

Reprinted with permission from A. Kongkanand and M.F. Mathias, *J. Phys. Chem. Lett.* **2016** *7* (7), 1127-1137. Copyright 2016 American Chemical Society.


Nafion™ PFSA Polymer

Example HOPI Chemistry[2]





- Heavy duty vehicles requires high efficiency and long lifetimes at moderate Pt loading
    - Increase mass activity for high voltage efficiency
    - Reduce local Pt O2 voltage loss with reductions in ECSA over long stack lifetimes
- Prior work indicates HOPIs reduce O2 transport resistance and increase air mass activity[3]
    - 20% increase in current at 0.75 V
    - 50% increase in 0.85 V mass activity
- Emergent HOPI technology requires development of optimum integration for durability and manufacturability

HOPI polymers have been specifically engineered for cathode catalyst layers to reduce mass transport losses associated with local O_2 flux on Pt

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1. Kongkanand and Mathias, J. Phys. Chem. Lett, 2016. 2. US Patent 9,431,661 B2, 3. Shimizu et al, J. Electrochem. Soc., 2018

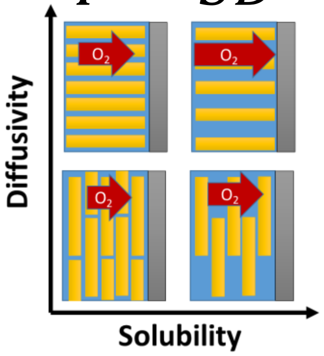
Relevance

Modeling the Impact of HOPI

- Permeability (P) is the product of solubility (S) and diffusivity (D)
- **Observed specific ORR activity of catalyst is proportional to O_2 solubility of adjacent electrolyte**
- CMU's multiphase MEA model: O_2 solubility and diffusivity of ionomer, catalyst aggregate size, fraction of internal/external Pt, anion adsorption, and local Pt O_2 resistance (see Technical Backup slides).
- Implemented with 3X permeability assuming 50/50 contribution of solubility and diffusivity (73% increased solubility and diffusivity)
- Provides consistent increase in mass activity and limiting current with literature and preliminary data[1]
- 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 (doubling of lifetime)
- Substantial increases in voltage efficiency and maximum power density with HOPI

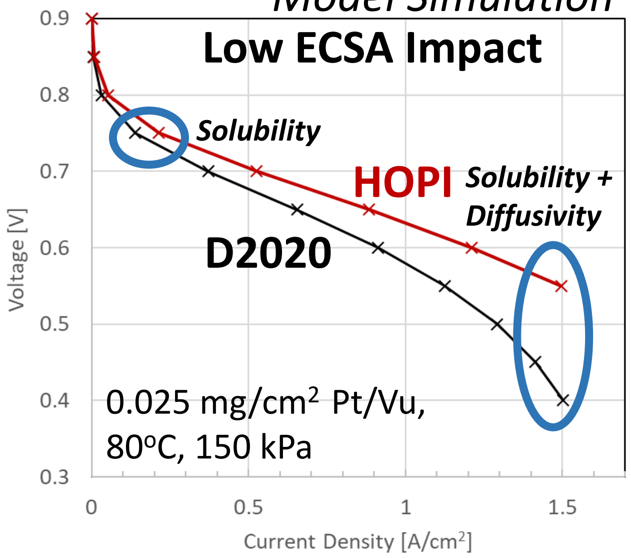
Permeability

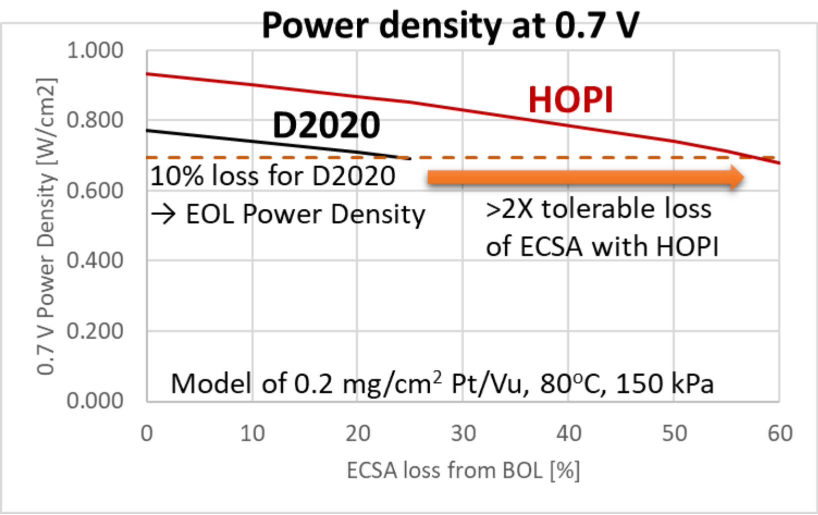
$$P = SD$$

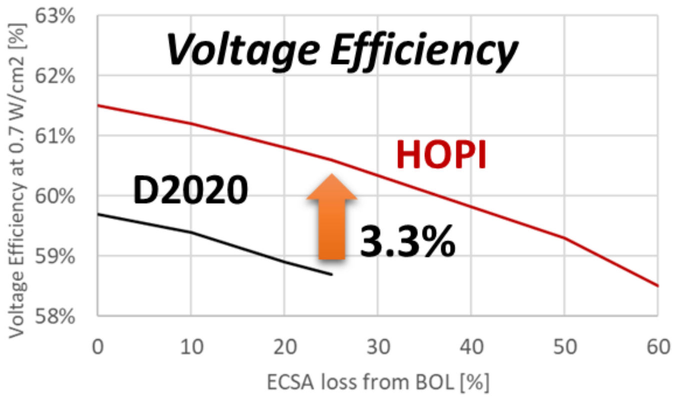


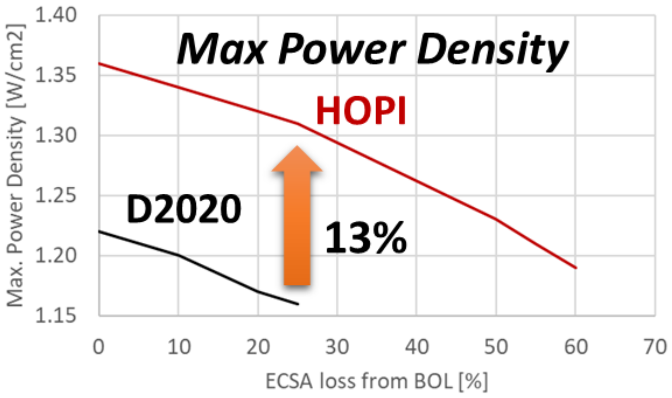
*Neutral gas/solid interaction case

Model Simulation









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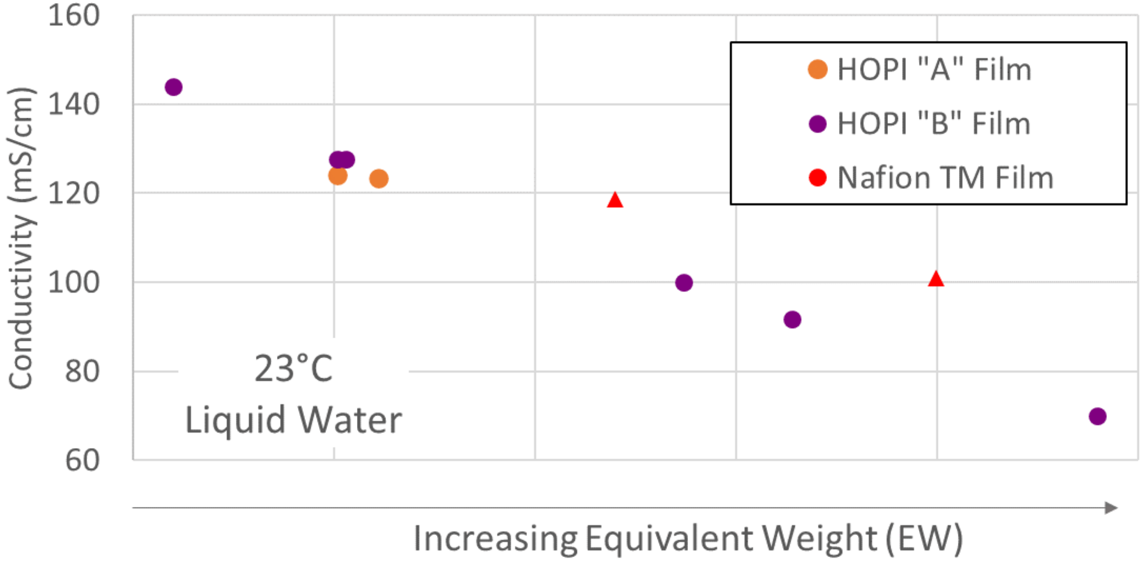
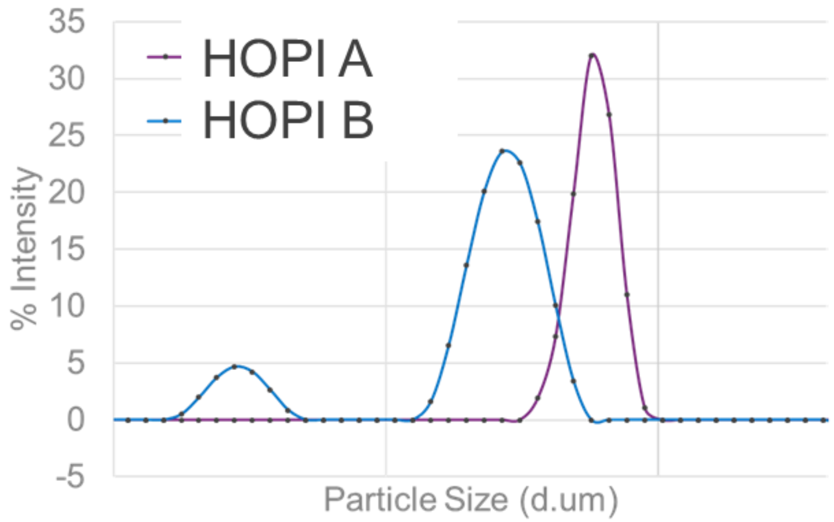
[1] Shimizu et al, *J. Electrochem. Soc.*, 2018

Effect of HOPI Side Chain Chemistry & EW

- HOPI dispersions with two different sulfonic acid monomers (“A” or “B”) were fabricated to understand impact of side chain and evaluate alternate chemistry’s effect on crack formation
- HOPI proton conductivity appears to be a strong function of EW, irrespective of sulfonic acid monomer moiety
- Zeta potential suggests both dispersions are stable, but that HOPI B may tend to agglomerate more than HOPI A
- A wide range of HOPI “B” equivalent weights have been synthesized to understand impact of EW/conductivity on performance of HOPI in electrode layers.

Dispersion	nPa:H2O ratio	Zeta Potential (mV)
HOPI “A”_1	70:30	-45.0
HOPI “A”_2		-41.0
HOPI “B”_1		-18.4
HOPI “B”_2		-23.5





N-Propanol Rich HOPI Dispersions Reduce or Eliminate Cracking of Films

X nPA: 1 H2O ratio	HOPI “A” Film Cracking (RED is extreme cracking)	HOPI “B” Film Cracking (RED is extreme cracking)
0	🟥	🟥
0.43	🟧	🟧
1	🟨	🟨
2.33	🟩	🟩
9	🟩	🟩

Higher alcohol content reduces tendency of neat HOPI cast films to crack

Effect correlates well with early observed trends in catalyst layers


Crack-Free film

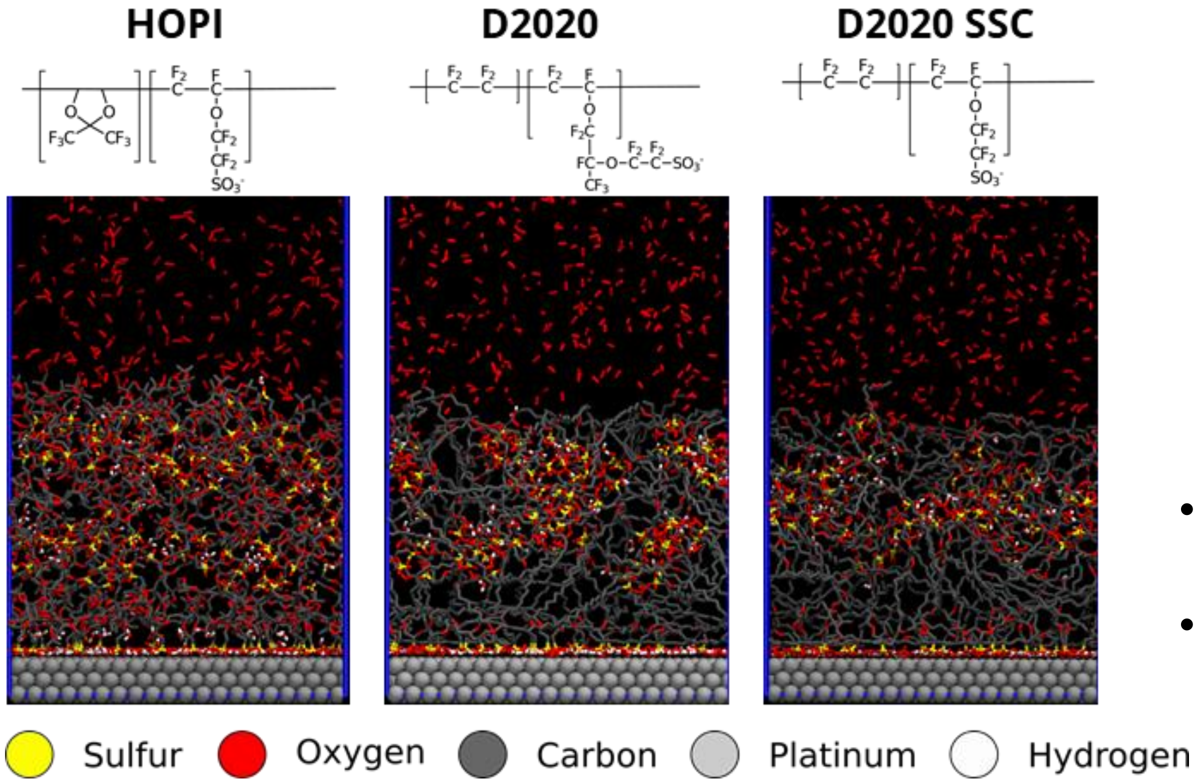

Film with some cracking

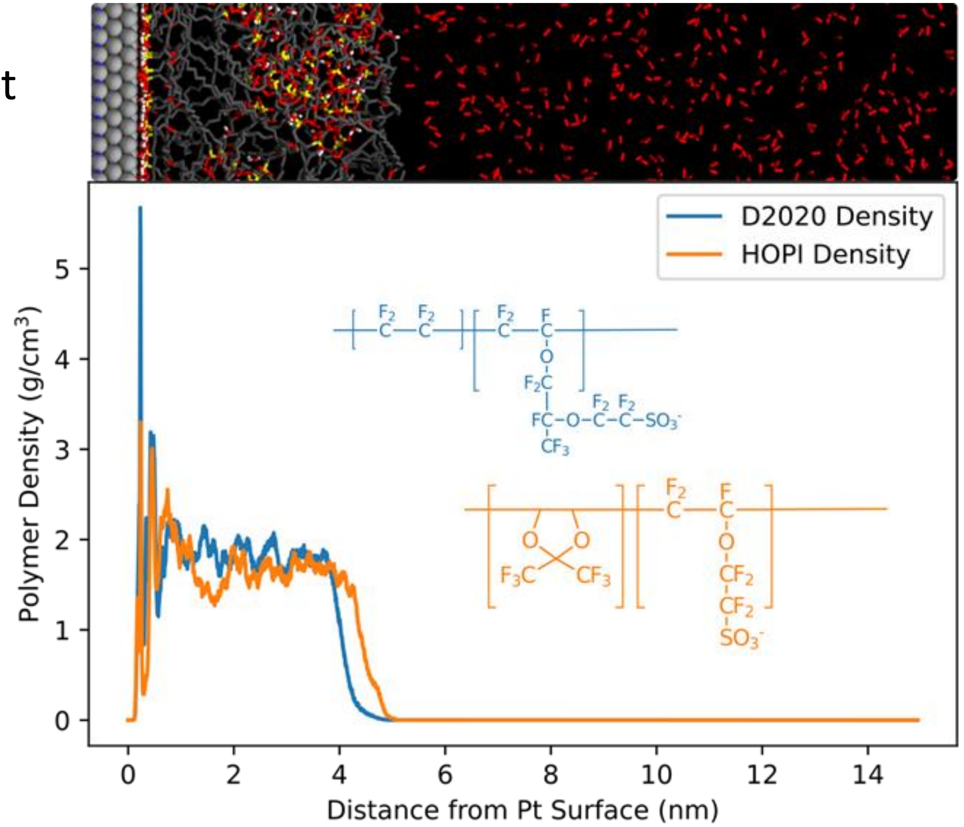
In the remainder of this project, Chemours aims to:

- Continue to understand fundamentals of HOPI catalyst layer cracking
- Prepare additional HOPI variations (EW / polymer composition) as guided by catalyst application testing
- Plan for continued scale up demonstrations of polymerization capability

All-atom MD of Ionomer-Pt Interface

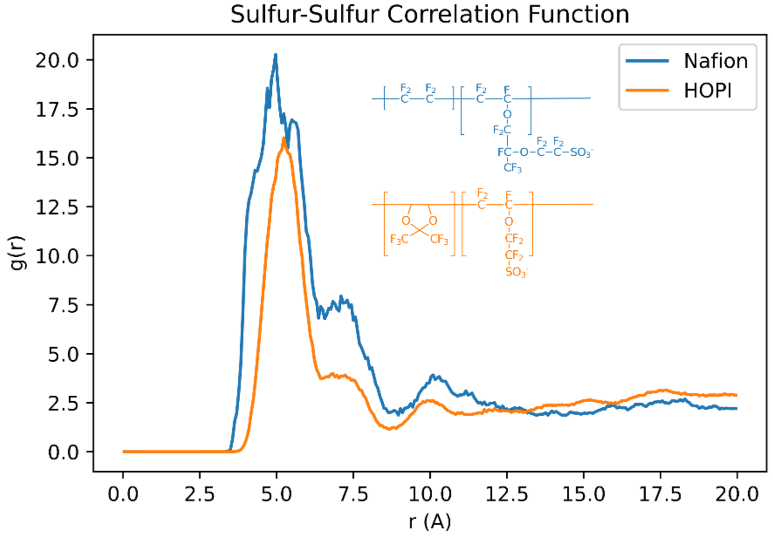
- MD simulations of ionomer-platinum interfaces
- Comparison of HOPI and D2020 and alternative D2020 with short side chain (SSC) chemistry
- HOPI exhibits least amount of hydrophilic clustering
- More amorphous structure of HOPI layer
- Increased thickness (lower density) for HOPI relative to D2020

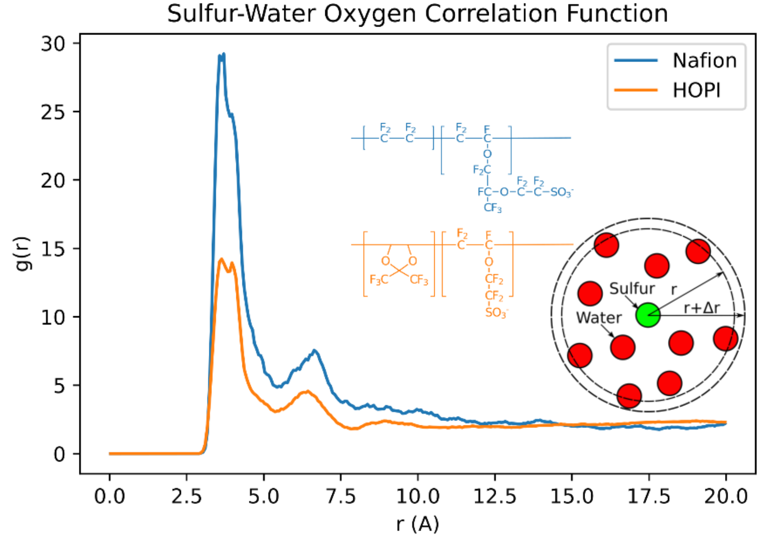




- Density of polymer at the platinum interface is significantly higher for D2020 compared to HOPI
- This will likely result in improved oxygen solubility/diffusivity at the interface

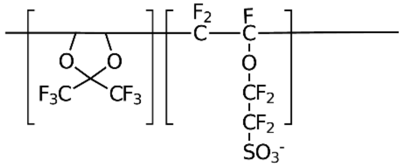
Water clustering and pore-network visualization

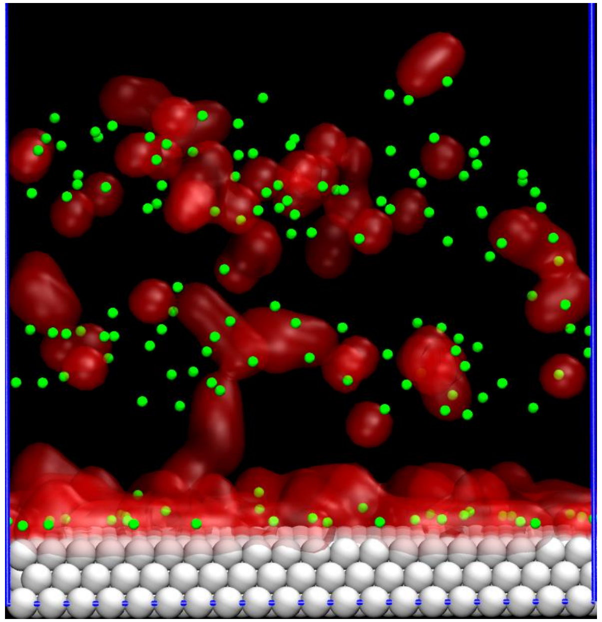

Sulfur-Sulfur Correlation Function


Sulfur-Water Oxygen Correlation Function

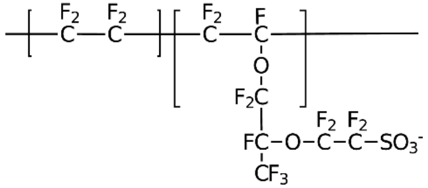
- Water clusters in HOPI are more disperse compared to D2020
- D2020 exhibits more continuous pores compared to HOPI

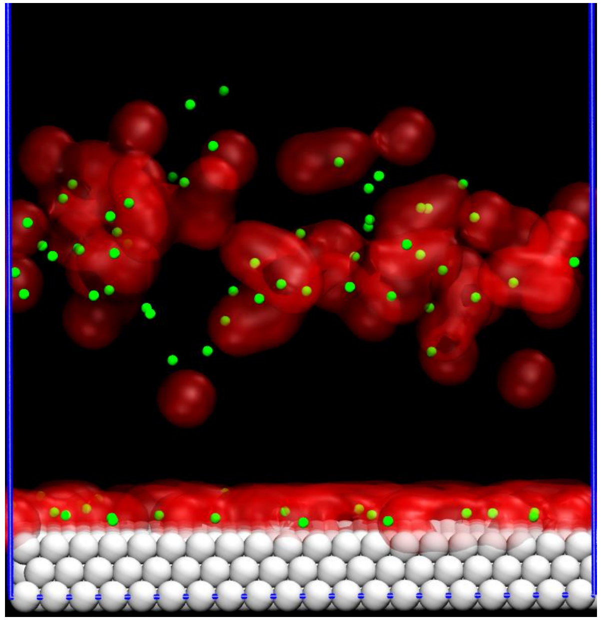
HOPI





D2020



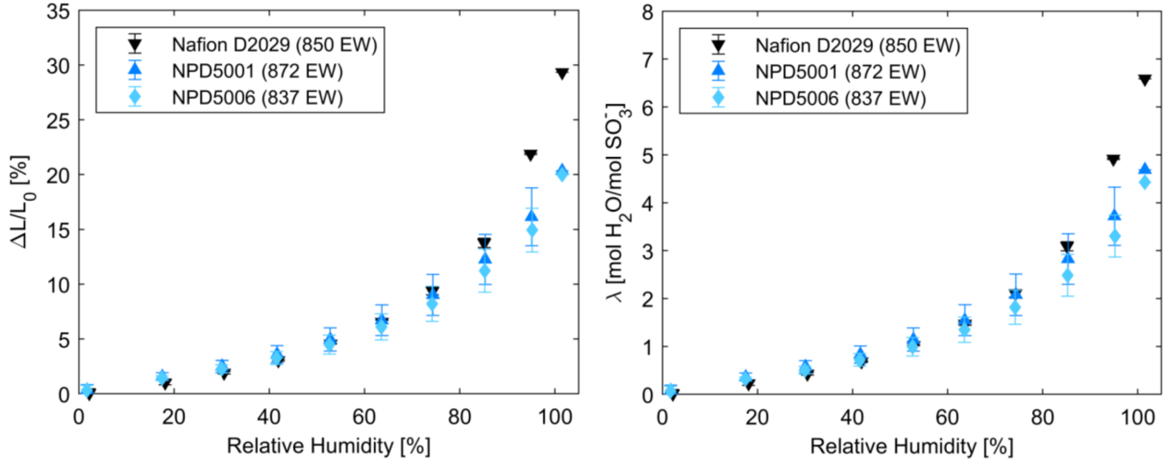


● Water
● Sulfur

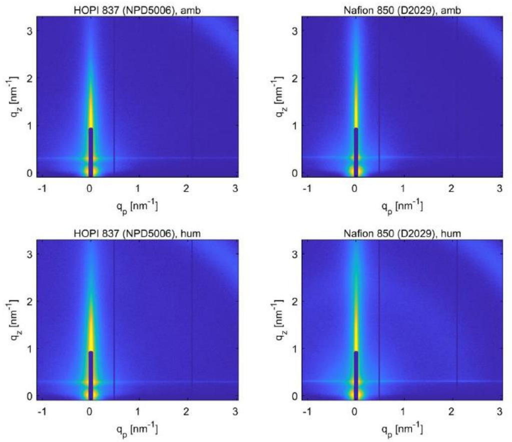
Technical Accomplishment

Thin-film Characterization

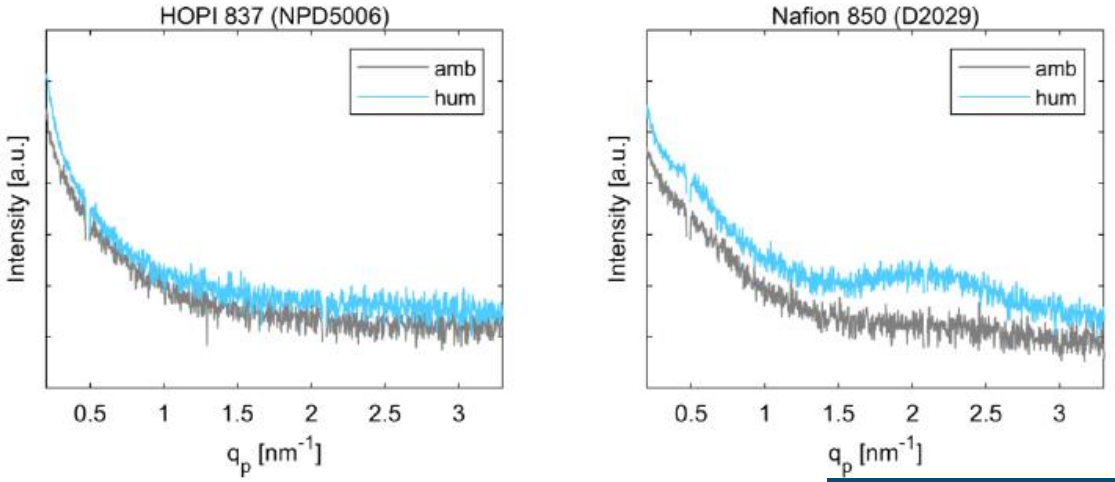
- HOPI and Nafion D2029 (~900 EW) control analyzed by GISAXS at LBL
- HOPI ionomer films show weaker phase separation compared to Nafion
  - Likely result of 3D bulky backbone chemistry
- Similar swelling and water content between HOPI and D2029 at <60% RH
- Reduced swelling and decreased water content at higher relative humidity
- Indicates the more rigid structure of the HOPI ionomer
- May explain the less pronounced RH sensitivity of MEA R_{O2} to RH with HOPI vs D2020



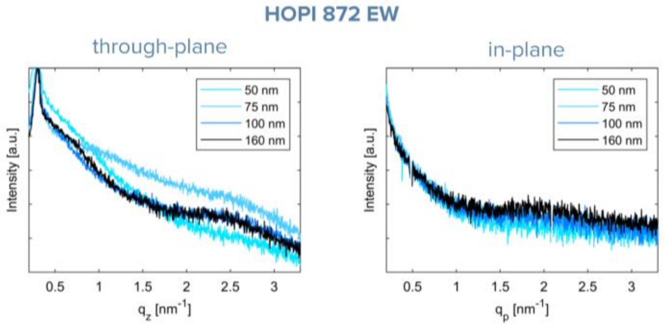
Silicon substrates



RH Effect



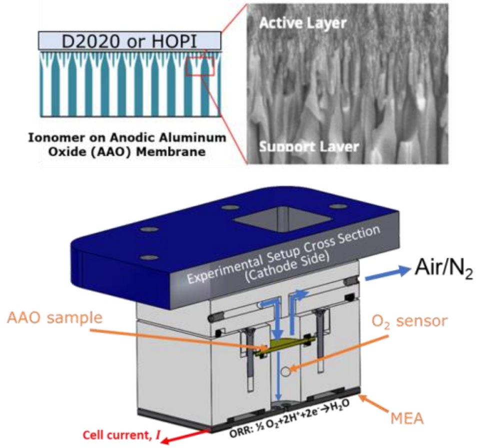
Thickness Effect



Technical Accomplishment

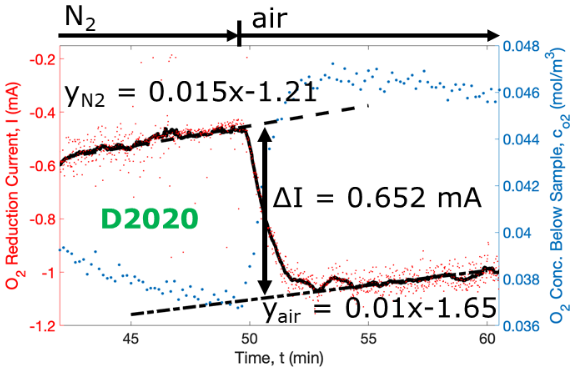
HOPI vs D2020 Permeability

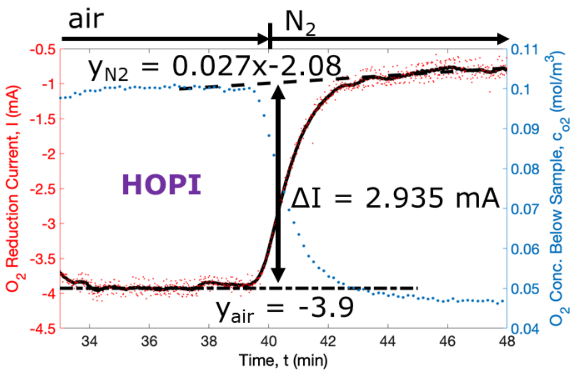
- New improved apparatus with integrated oxygen sensor for improved accuracy with high permeability films and substrates
- Measures permeability of a quasi-free-standing film by supporting the layer on a nano-porous substrate without a polarized electrode surface (*vs.* Pt surface of RDE, films, etc.)
- Permeability based on current difference between air and N_2 flowing
- Measurements performed with HOPI and D2020 films
- As fabricated film thickness measured in dry condition by profilometer due to sample to sample and ionomer to ionomer variability
- Increased permeability of 2.6X for HOPI over D2020
- Significant increase in bulk film permeability and not only a Pt-surface interface effect



Method and apparatus

1. H. Liu, W. K. Epting, and S. Litster, "Gas Transport Resistance in Polymer Electrolyte Thin Films on Oxygen Reduction Reaction Catalysts," *Langmuir*, vol. 31, no. 36, pp. 9853–9858, 2015.
2. J. P. Braaten, X. Xu, Y. Cai, A. Kongkanand, and S. Litster, "Contaminant Cation Effect on Oxygen Transport through the Ionomers of Polymer Electrolyte Membrane Fuel Cells," *J. Electrochem. Soc.*, vol. 166, no. 16, pp. F1337–F1343, 2019.



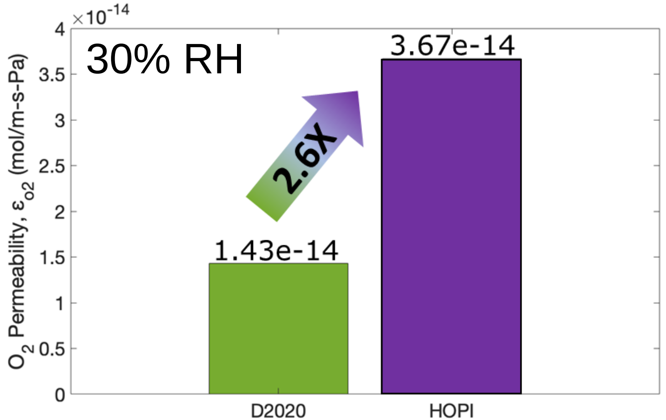


$T_{sample} = 50.0 \pm 0.1°C$, p = 1 atm
Air or N_2, 0.2 l/min, 29%RH

Material	D2020	HOPI
thickness*, µm	9.65	5.40

*Measured by CMU nanofab staff by using Profilometer

$$\varepsilon_{O_2} = \frac{Il}{nAF\Delta P_{O2}} = \frac{Il}{nAF\Delta C_{O2}RT}$$



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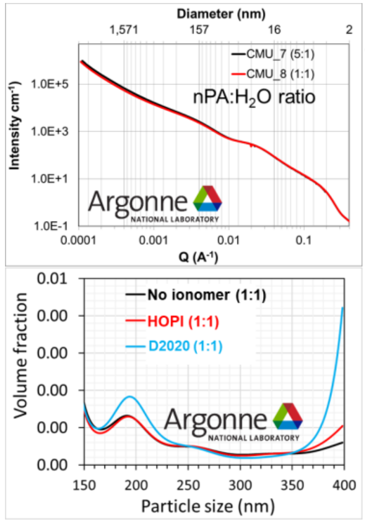
Technical Accomplishment

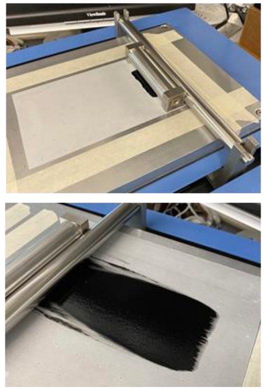
Ink and electrode optimization

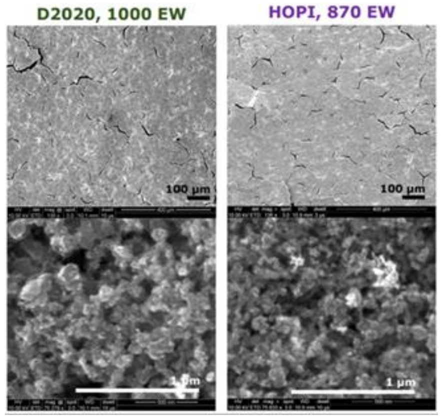
- Study of ink composition on agglomeration and coating quality
  - Ionomer type effect: D2020 (1000EW) *vs.* HOPI (870EW)
  - EW effect: DE2029 (880 EW) *vs.* D2020 & HOPI
- CMU ink agglomeration characterized by USAXS
  - No strong effect of nPA:H2O ratio on agglomeration
  - Less agglomeration with HOPI vs. D2020
- Coating studies at CMU
  - Greater degree of cracking with HOPI vs. D2020/DE2029
  - Greater ionomer agglomeration with low nPA:water ratios
- Studies on effect of ionomer, solvent, and I/C ratio on performance
- Significant 67% increase in mass activity with HOPI over D2020
- Significant reduction in total non-Fickian (p-indep) oxygen transport resistance with HOPI

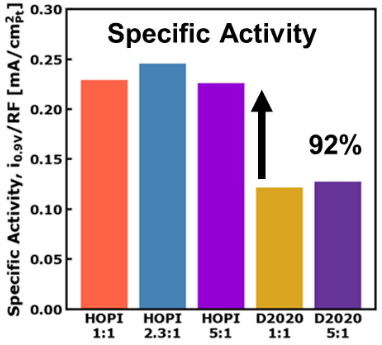
Ink SAXS

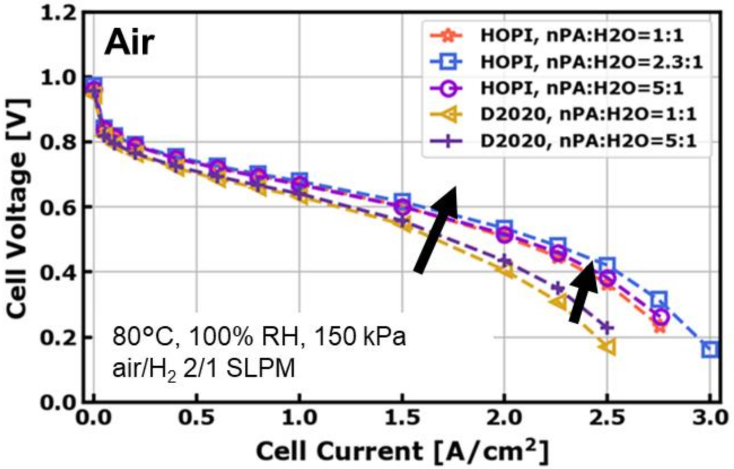


Decal coating with automatic wet film coater

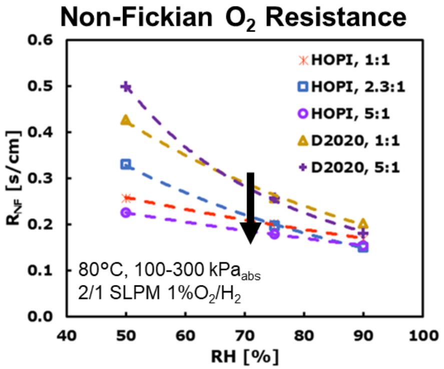








TKK EA 50 (46 wt % Pt/LSAC),
I/C=0.6, 0.20±0.02 mg_{Pt}/cm^2 (est.)



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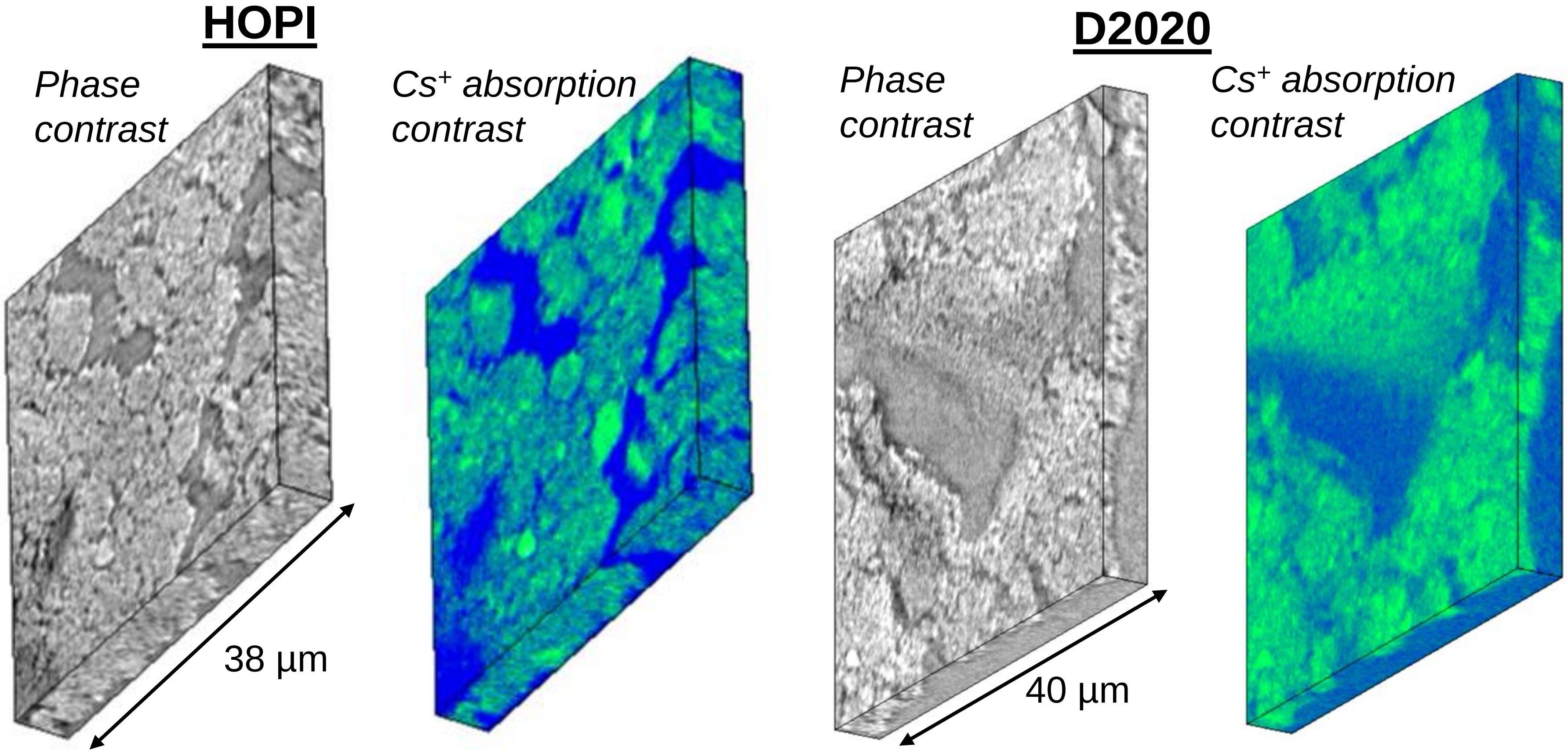
Nano-CT Imaging of Catalyst Layers

- Nano-CT (CMU) of catalyst layers by phase contrast for pore/crack structure and Cs^+-stained absorption contrast for 3D ionomer mapping
- High agglomeration of electrode structure and ionomer with HOPI
- Cracks present between agglomerations with HOPI
- Mostly continuous film with D2020 with more uniform ionomer distribution


HOPI

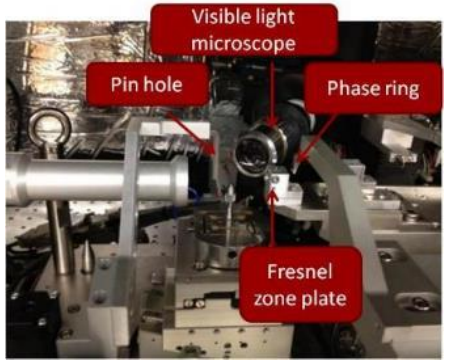
Phase contrast

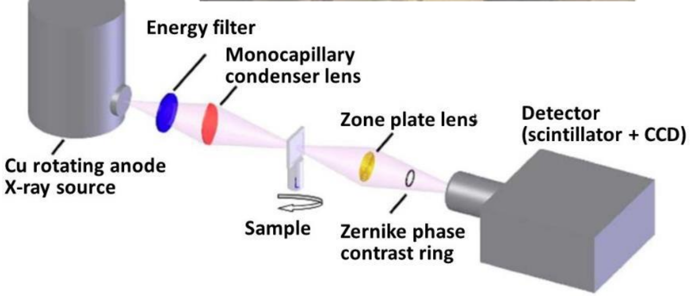
Cs^+ absorption contrast

D2020

Phase contrast

Cs^+ absorption contrast





Max. resolution of 50 nm (16 nm voxels)
Large-field-of-view imaging with 150 nm resolution (65 nm voxels) shown here
User facility available to industry, nat'l labs, and universities.

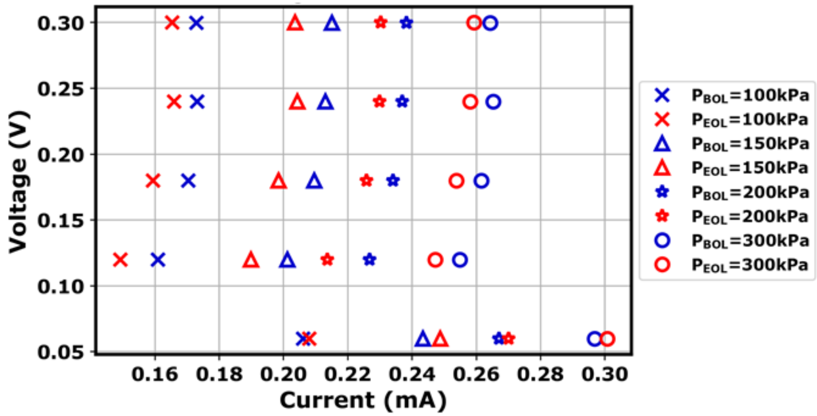
Carnegie Mellon University

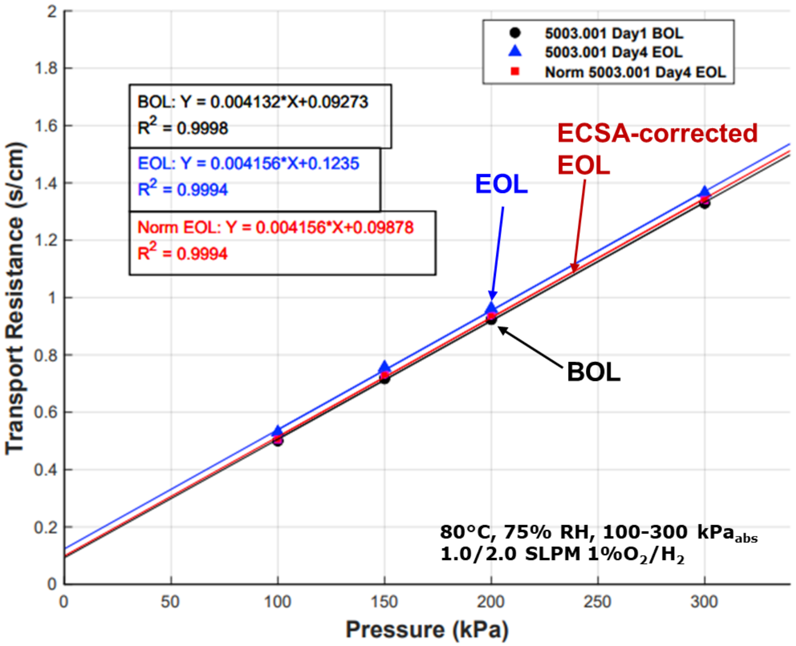
Green intensity ~ volumetric density of ionomer

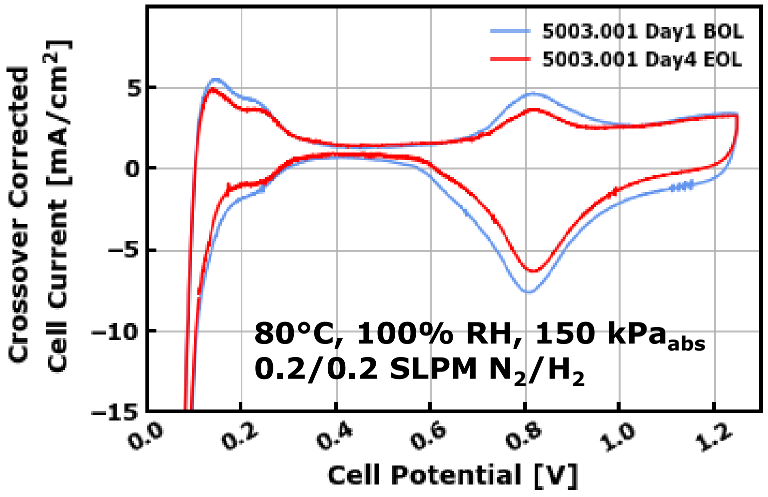
Ionomer stability and AST

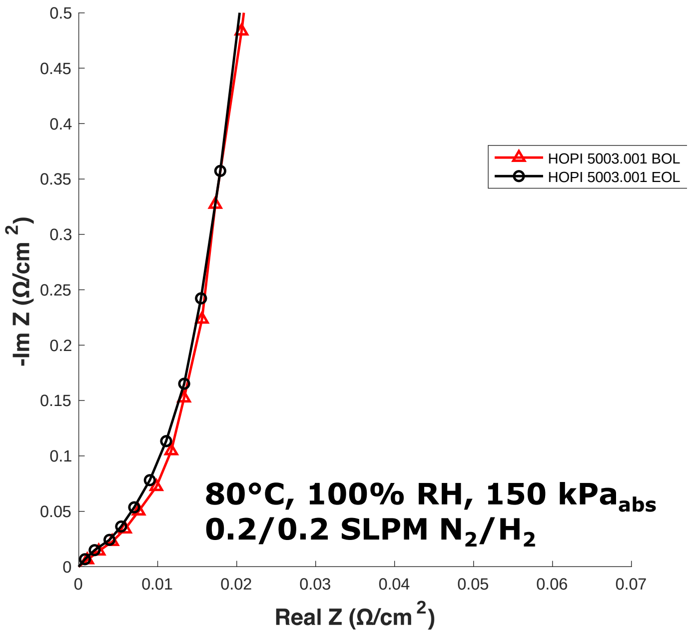
- Evaluate chemical stability of HOPI via chemical degradation with OCV holds (28 hr in preliminary test)
- CV ECSA shows the initial loss in surface area over 5 days of testing
- No increase in electrode proton conduction resistance
- No change in pressure-dependent slope of oxygen transport resistance
- No change when pressure-independent resistance is corrected for ECSA loss

$$R_{total} = \frac{C_{O2}^{channel,in} - C_{O2}^{electrode}}{Oxygen\ Flux} = \frac{4FP_{O2}^{channel,in}}{i_{\lim}RT}$$





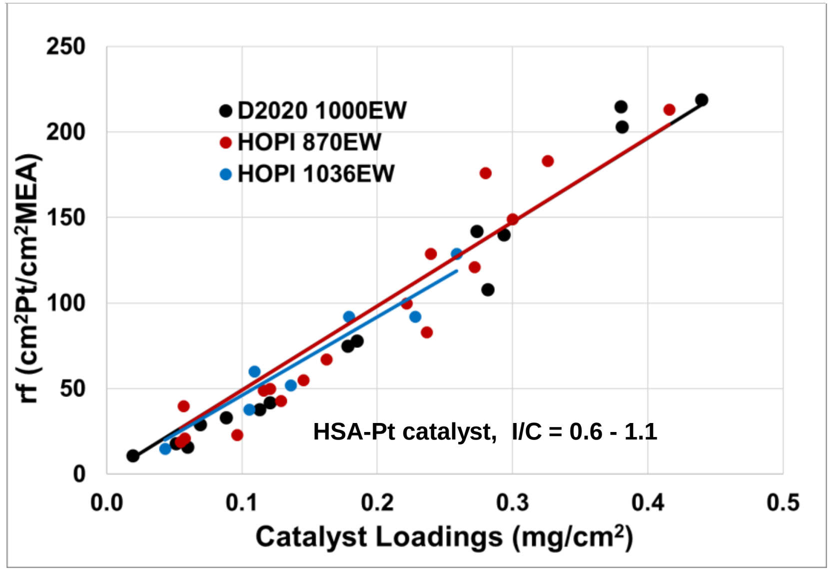




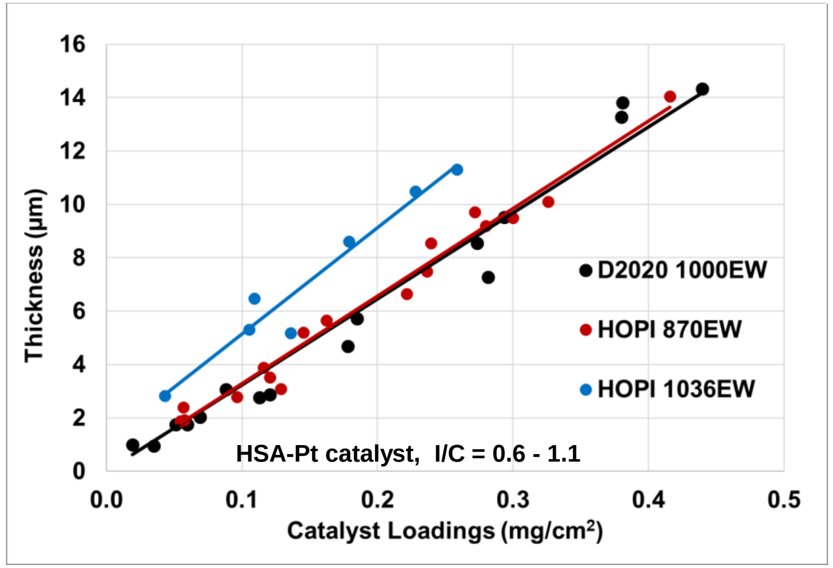
Technical Accomplishment

Scale-able Electrode Fabrication

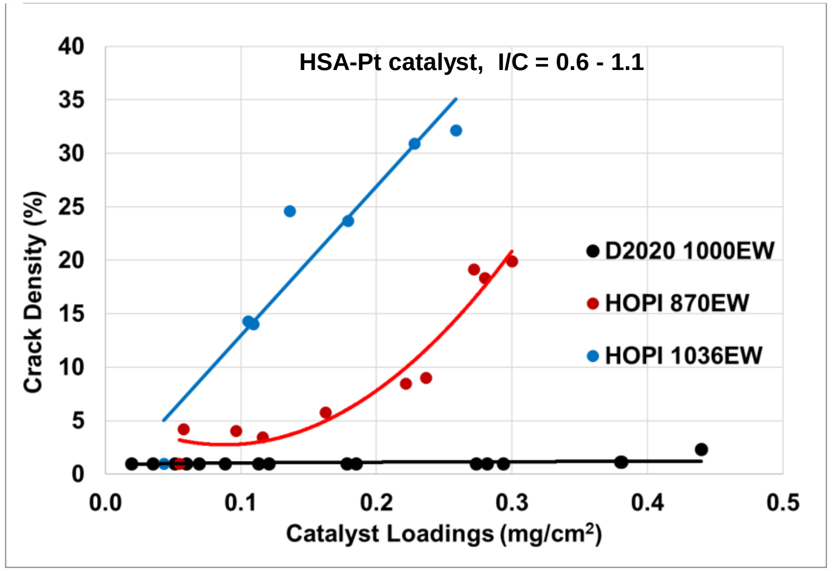
Catalyst Layer Roughness Factors (rf) vs. Catalyst Loadings



Catalyst Layer Thickness vs. Catalyst Loadings



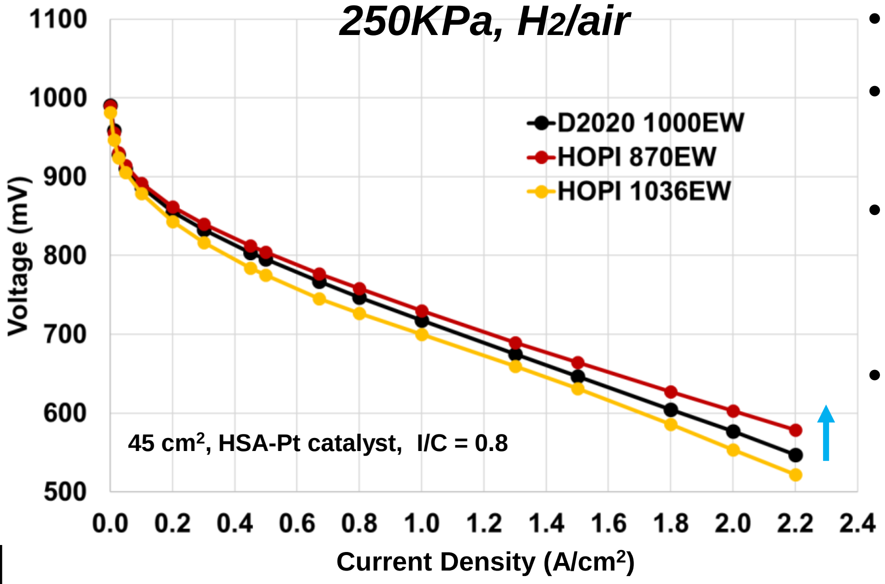
Catalyst Layer Crack Density vs. Catalyst Loadings



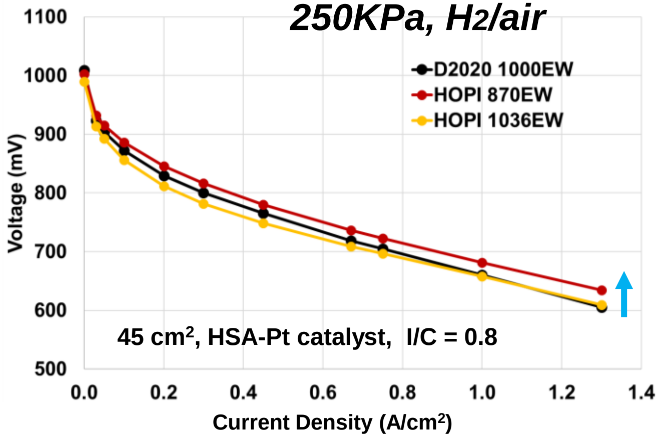
- Catalyst layer was fabricated in the roll-to-roll scale-able coating process
- Catalyst loadings had a good agreement with roughness factors (*rf)* and thicknesses except HOPI 1036EW deviated from loading vs thickness trend where high crack density may explain the higher thickness
- HOPI integrated catalyst layers (CLs) had higher crack density at higher catalyst loadings but decreased to similar to D2020 with decreasing catalyst loadings
- HOPI 870EW had comparatively lower crack density compare to high EW HOPI variant

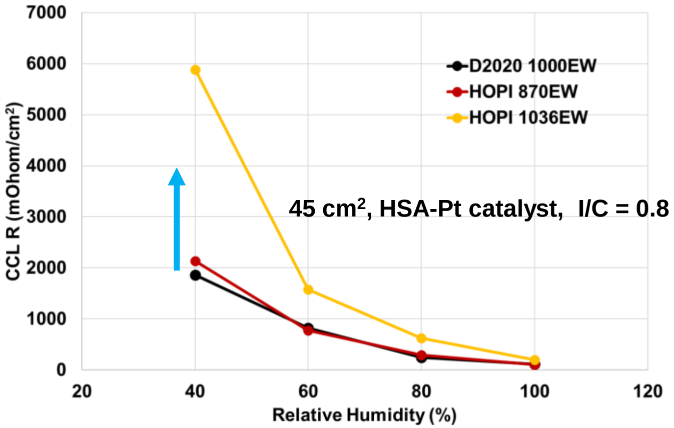
Electrode Performance – Ionomer Types

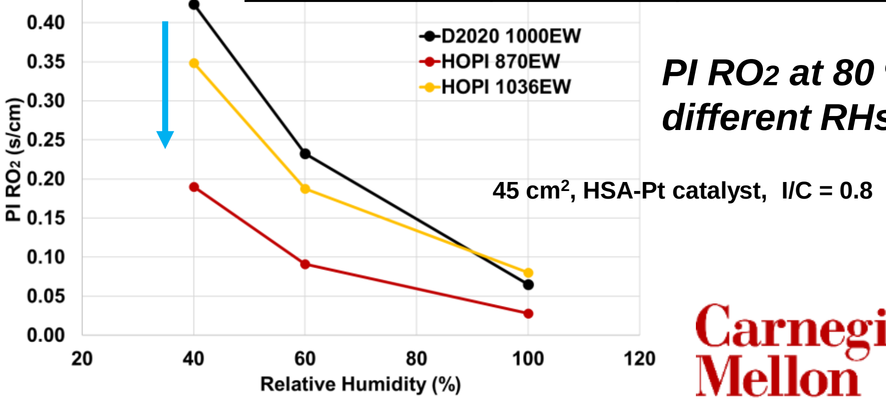
- Two HOPI variants were tested and compared performance with D2020 baseline.
- **HOPI 870EW variant was the top performing candidate over D2020 and HOPI 1036EW**
- HOPI 870EW variant showed similar cathode catalyst layer resistance (CCL R) but significant reduction of pressure independent (PI) oxygen transport resistance and 1.5 times higher mass activity than D2020
- HOPI 1036EW variant suffered with poor performance due to higher CCL proton & local oxygen transport resistance (EW & high crack density effect)


100% RH Performance at 80 ºC, 250KPa, H_2/air

Ionomer Types, EW	Roughness Factor	Mass Activity (A/mgPt at 0.9V)
D2020, 1000EW	108	0.3
HOPI, 870EW	83	0.48
HOPI, 1036EW	92	0.34


60% RH Performance at 80 ºC, 250KPa, H_2/air

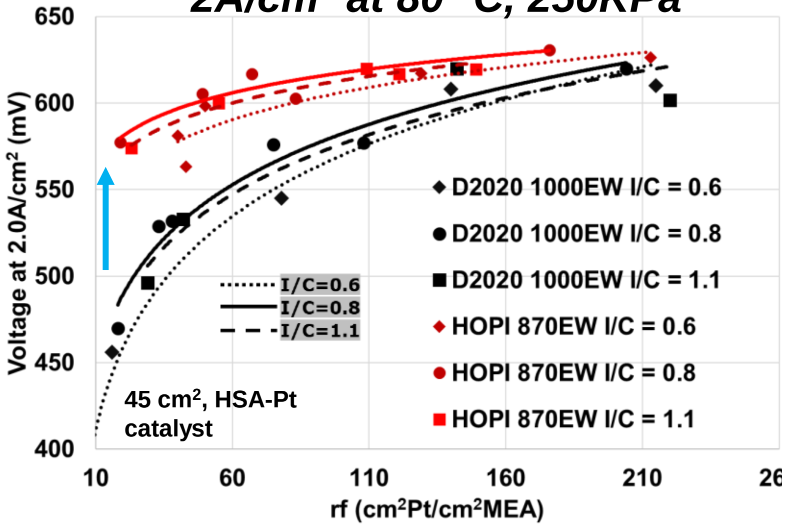

CCLR at 80 ºC, different RHs


PI RO_2 at 80 ºC, different RHs

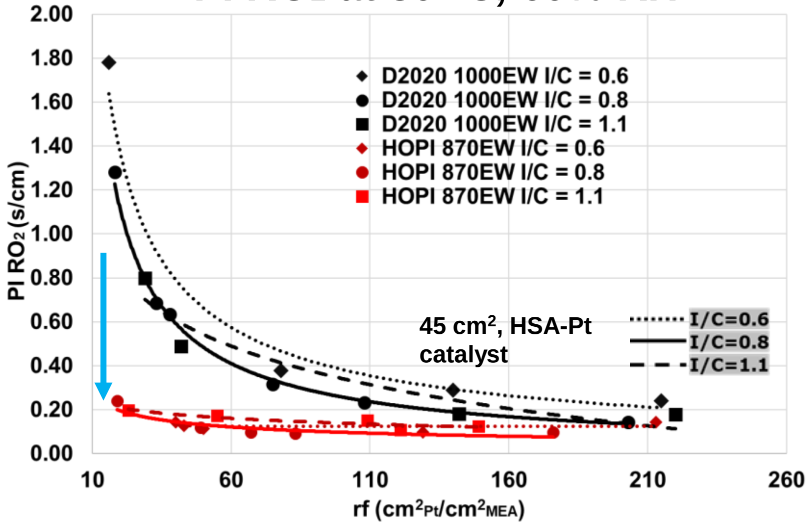
Technical Accomplishment

Performance – Catalyst & Ionomer Loadings

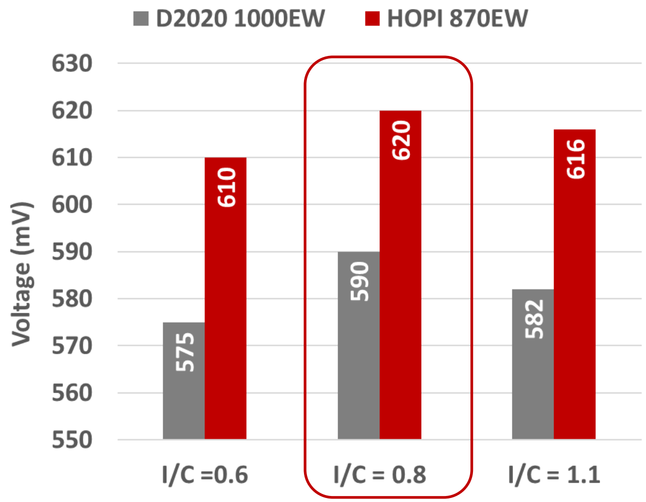
100% RH Performance at 2A/cm² at 80 °C, 250KPa



PI RO_2 at 80 °C, 60% RH



Performance comparison at rf = 110

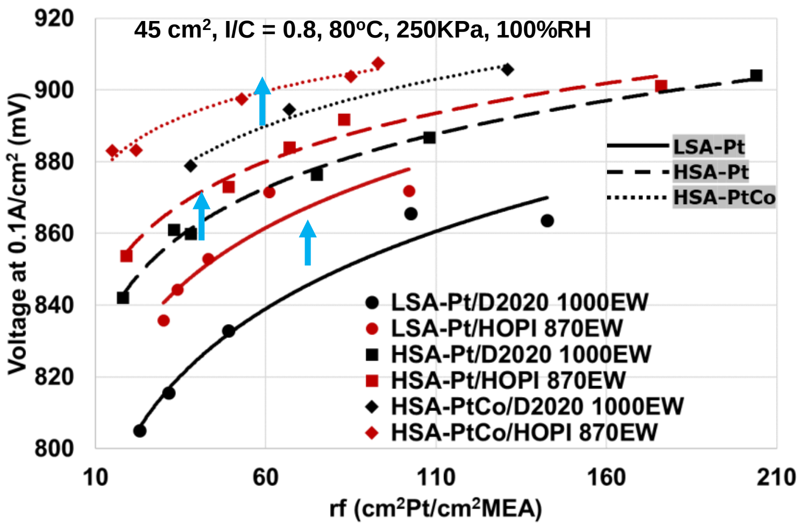


- Various catalyst loadings and three I/C ratios were investigated based on HSA-Pt catalyst
- **I/C = 0.8 was the optimum** for both D2020 and HOPI 870EW performance and PI RO_2

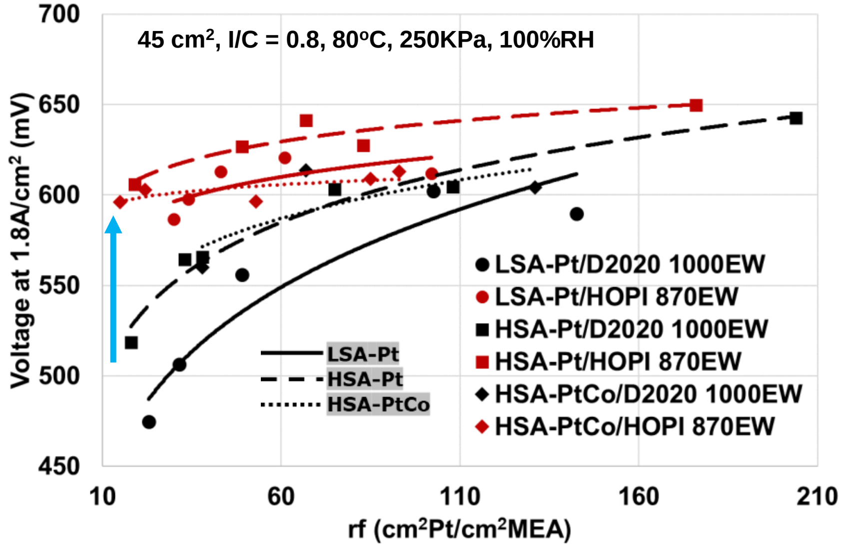
Compared to D2020 ionomer, HOPI 870EW showed:

- Performance gain at high current density and reduction of oxygen transport resistance with decreasing roughness factor
- 30 mV performance gain at rf=110 with optimum I/C ratio
- 60 mV performance gain at rf=30 with same optimum I/C ratio

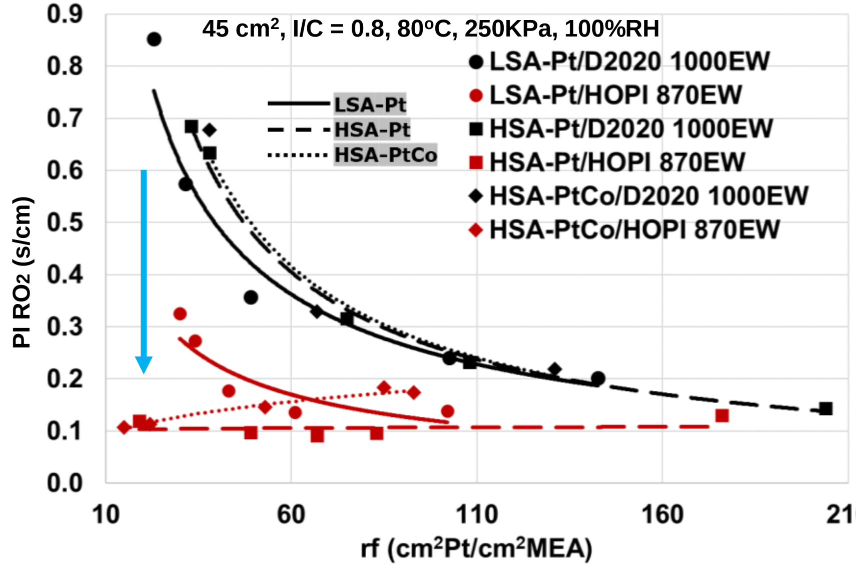
Electrode Performance – Catalyst Types



Low Current Density Performance

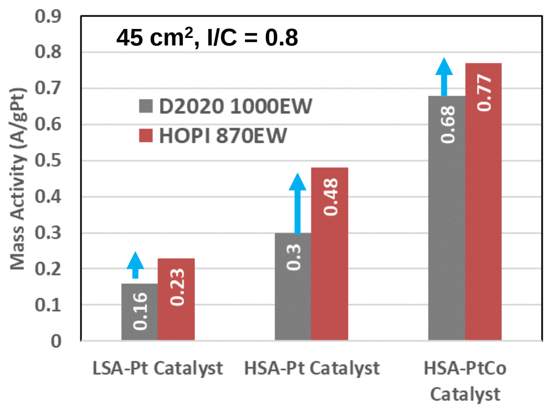


High Current Density Performance



PI RO2 Comparison

- Three catalysts including LSA-Pt, HSA-Pt, HSA-PtCo were investigated with both D2020 and HOPI 870EW ionomers
- **HSA-Pt catalyst is the top performer at high current density**
- Regardless of catalyst types, HOPI 870EW showed over D2020 -
  - 10-20 mV kinetic performance improvement due to the mass activity improvement
  - Significant mass-transport related high current density performance improvement due to reduction of PI RO2



Mass Activity Comparison

Technical Accomplishment

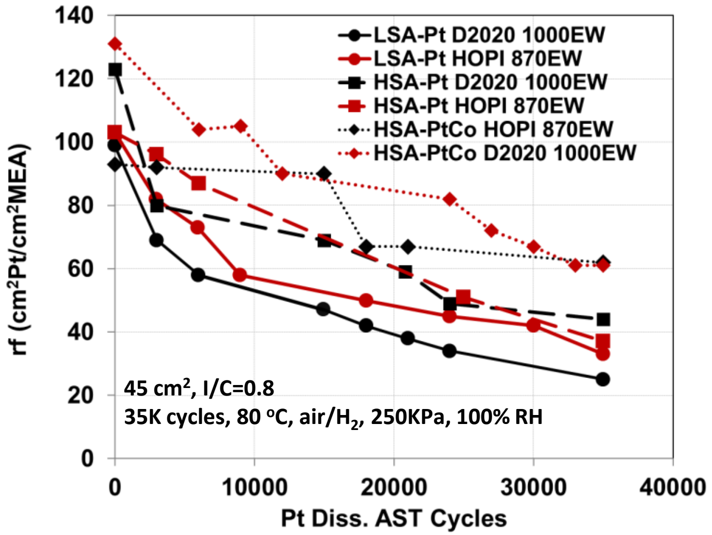
Electrode Durability

BALLARD™

In comparison to D2020, HOPI 870EW showed:

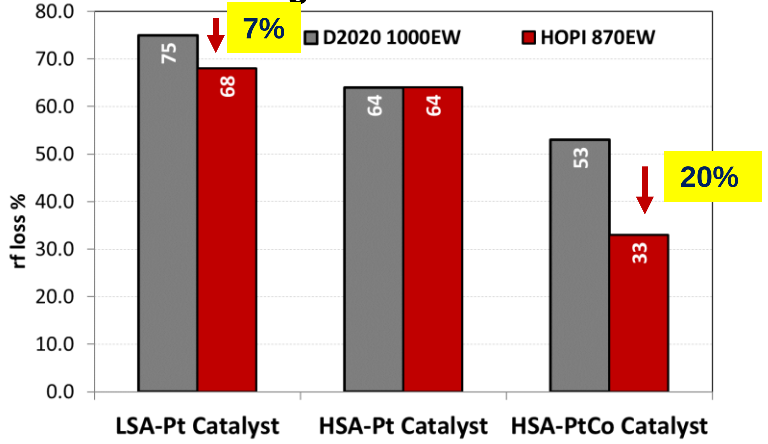
- Minor change in rf loss but major reduction of MEA performance degradation rate for both LSA-Pt and HSA-Pt catalyst
- For HSA-PtCo catalyst, major reduction in rf loss and performance degradation at 0.1A/cm^2 but negative impact on degradation at high current density, possibly due to faster changes of CL morphology during AST cycling because of high crack density: 32% in HSA-PtCo/HOPI vs 4% in HSA-PtCo/D2020

RF with Pt Dissolution AST Cycles

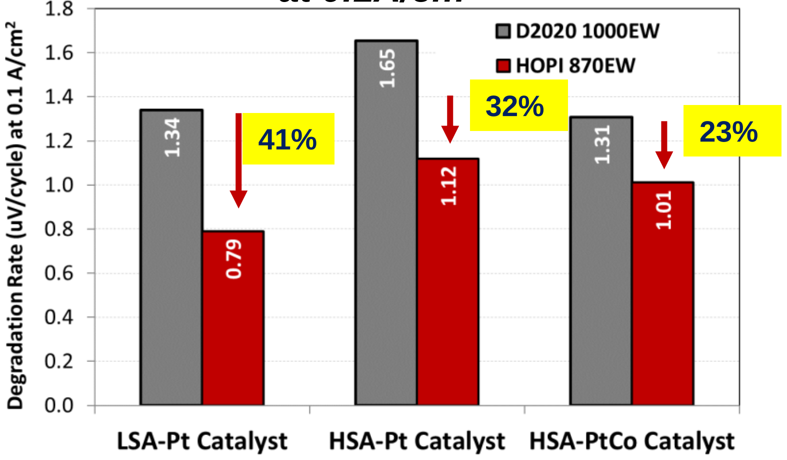


45 cm^2, I/C=0.8
35K cycles, 80 °C, air/H_2, 250KPa, 100% RH

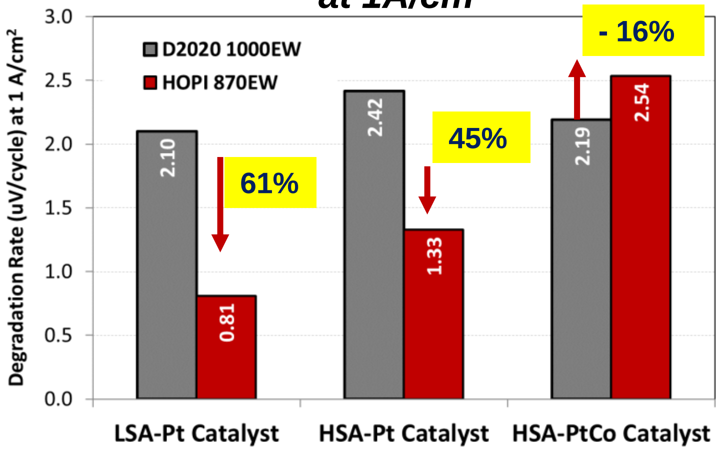
RF Degradation



Performance Degradation Rate at 0.1A/cm^2



Performance Degradation Rate at 1A/cm^2



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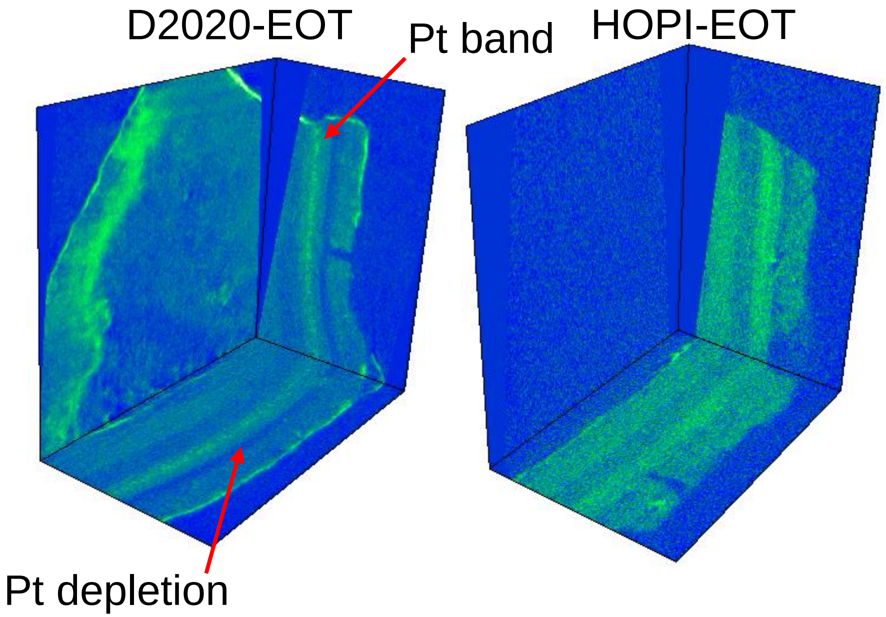
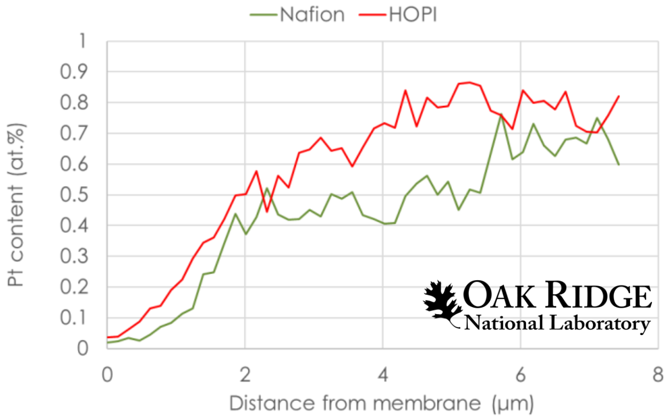
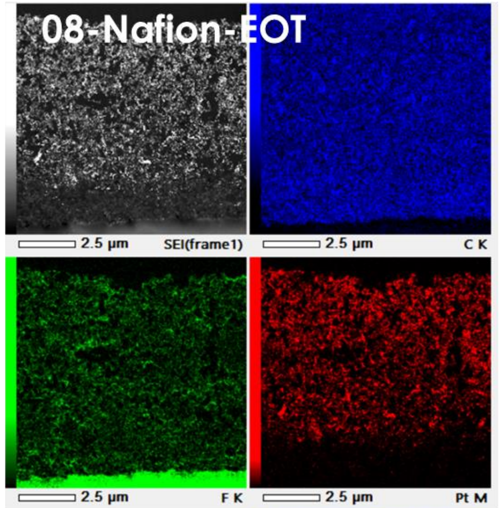
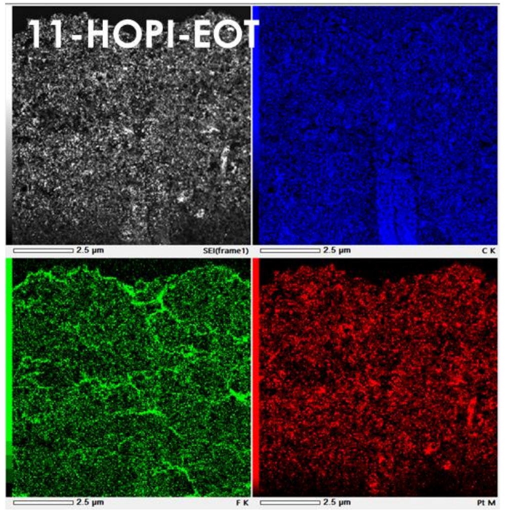
Microscopy Analysis of Degradation

- Microscopy studies on pristine and end of test (EOT) Pt/HSC samples from Ballard
  - X-ray nano-CT at CMU
  - Electron microscopy at ORNL
- Nano-CT shows more significant region of Pt depletion in D2020 sample as well as a more obvious Pt band
- Pt located on cathode side of membrane reinforcement layer
  - This AST performed in air results in more diffuse band located further from cathode than with N2 AST
- Electron microscopy with elemental mapping also shows enhanced depletion of Pt in first 2 µm of the cathode adjacent to the PEM
- Fluorine mapping by ORNL also shows the agglomeration of HOPI as observed by nano-CT







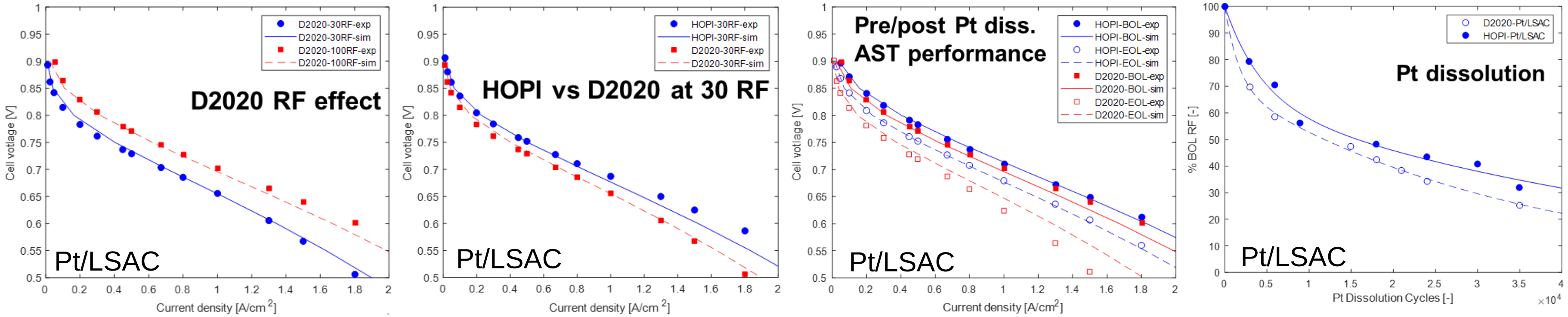


Technical Accomplishment

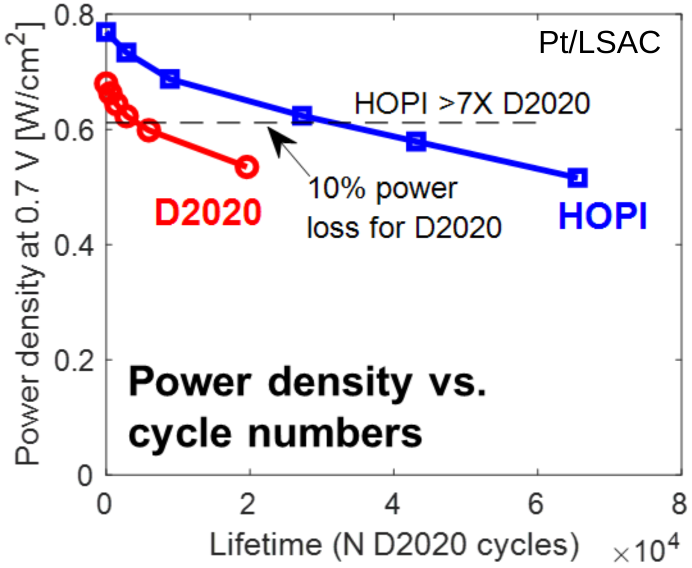
HOPI-enhanced lifetime forecast

- CMU MEA model validated and applied to Pt/LSAC lifetime forecasting based on Pt dissolution.
- **~7X** longer lifetime with HOPI to reach same EOL power density.
- Ballard lifetime forecasting for aggressive drive cycle with Pt/HSC for HOPI vs. D2020.
- For ~10% performance loss at 0.7 V cell voltage (equivalent roughly to 1.34 A/cm^2), HOPI MEAS showed **~4x** lifetime improvement

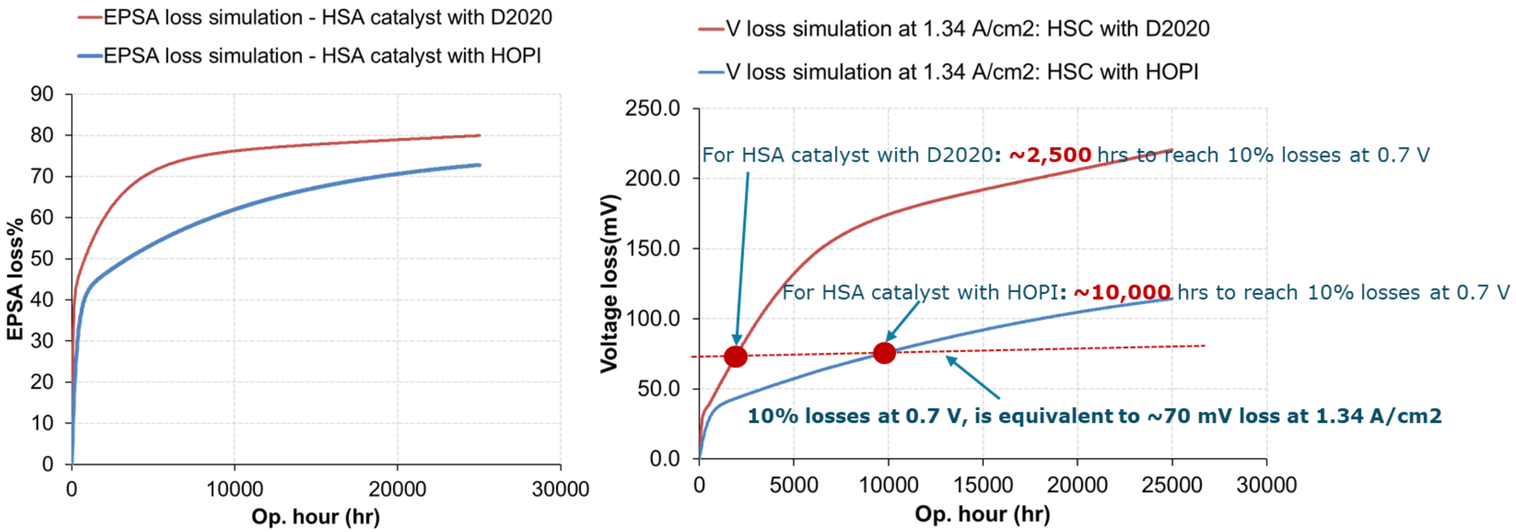
CMU MEA model validation for RF, ionomer and AST



Pt/LSAC estimation using CMU MEA model



Ballard lifetime forecasting model for Pt/HSA and aggressive drive cycle



For HSA catalyst with D2020: **~2,500** hrs to reach 10% losses at 0.7 V

For HSA catalyst with HOPI: **~10,000** hrs to reach 10% losses at 0.7 V

10% losses at 0.7 V, is equivalent to ~70 mV loss at 1.34 A/cm2

Reponses to Last Year AMR Reviewers' Comments

We thank the reviewers for the many positive comments. Below we address only questions, suggestions, and comments of concern.

"…primary unknowns of the approach are how central catalyst degradation will be in HD systems and how chemically robust the HOPIs are in use.", "…Additional studies investigating the HOPI membrane for bulk properties such as water uptake, permeability, conductivity, and durability to radical attack would be good inclusions.", "…inclusion of membrane studies on free-standing films of HOPIs would provide valuable insight", & "…HOPI ionomer chemistry adds additional ether linkages in the passive repeating unit of the polymer…effort should be focused on fully characterizing the stability of this ionomer against chemical/electrochemical degradation."

A new ionomer chemical AST has been established in the past year and preliminary results are encouraging showing no loss in ionomer performance. LBL has performed several characterizations of HOPI thin films. Oxygen permeability of quasi free-standing films has been measured.

"…unclear whether HOPIs are needed or helpful at 0.2 mgPt/cm^2. A significant impact would be expected at lower loadings (<0.1 mgPt/cm2). Modeling at lower loadings should also be considered." & "…at the end of the day for the high-roughness-factor MEAs was just not there …minute improvements over the D2020 baseline when the roughness factor is >100. This begs the question of whether some other factor is dominating the performance of the catalyst layer, such as the catalyst layer resistance being higher for the HOPI, or the optimal ionomer-to-catalyst ratio being different for the HOPI, as compared to D2020, possibly because the density of D2020 is higher."

Low loading has been modeled and validated in the past year. At 0.2 mgPt/cm^2 the benefits of HOPI are increased mass activity and retention of performance over the stack lifetime as RF decreases.

"…project should focus on high-surface-area-carbon-type (HSC-type) supports, as these work the best at a low loading.

Catalysts with HSC supports has been a major focus of the past year.

"…threefold improvement in oxygen permeability is meaningful, but it is not clear how well it will be maintained over time or whether there are other degradation phenomena that may be worse in HOPI than in other PFSAs. The HOPI approach also requires that Pt ECSA loss be treated as a significant degradation concern because it cannot be addressed either by novel catalysis approaches or by systems controls. This is a worthwhile project, but it is not enough by itself to fully cover durability concerns."

Startup/shutdown ASTs for carbon corrosion have also shown significant reductions in degradation rate despite same ECSA loss with D2020 and HOPI.

"…difficulty in performing all the needed catalyst layer optimizations to properly demonstrate the improvement in the catalyst layer performance using a HOPI."

This challenge is addressed by performing small-scale studies at CMU with larger parameter ranges in the ink composition and evaluation of loading at larger scale at Ballard.

"…they could provide direct evidence by looking at the MEA performance as a function of oxygen partial pressure in the cathode. This would prove that it is the high oxygen solubility/concentration in the ionomer that is the source of the performance enhancement. This is important, as it will guide further development of this ionomer, as well as others."

This is a good suggestion for an approach to addressing a key objective in Year 3.

"…HOPI will likely benefit light-duty applications in the near term. Constraining development to HD targets does not seem like a logical first step", "…should estimate the cost increase relative to D2020", and "…Since HD applications typically use higher Pt loadings, degradation studies are critical. For this application, the implementation of HOPI will be highly dependent on cost. Perhaps the investigators can discuss cost impacts in future disclosures."

Costs associated with the ionomer are an important consideration.

Future Work

Year 3 Optimizing Performance and Durability for HDVs with HOPIs

- Ink optimization for new HOPI variants with higher equivalent weight and chemistry
- Molecular dynamics simulations of alternative HOPI backbone and sidechain chemistries
- Separate quantification of diffusivity and solubility vs. permeability for HOPI
- Anion adsorption impact on activity analysis
- Crack mitigation strategies (solvents, drying, additives)
- Understanding HOPI impact on degradation with HSC supports and PtCo catalyst
- Completion of ionomer AST studies

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

- Synthesis of a chemstable HOPI and distribution to project partners.
- Evaluation of HOPI catalyst ink preparation and deposition and comparison with D2020 baseline.
- Scaled-up evaluation of HOPI-based cathodes prepared by roll-to-roll deposition.
- Significant reduction in local oxygen transport losses, meeting Year 1 goal.
- Up to 67% increase in mass activity for Pt on Vulcan and LSAC.
- 60-70% reduction in degradation rate with HOPI in Pt dissolution AST
- MD studies of HOPI and D2020 elucidating the open structure of HOPI films on Pt surfaces.

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.
- Collaboration with M2FCT for USAXS of inks (ANL), electrode fabrication and testing with PtCo/HSC (NREL), ionomer evaluation (LBNL – in progress), and upcoming imaging with ORNL.

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 mass activity.

Proposed Future Work

- Ink optimization for new HOPI variants
- MD simulations of alternative HOPI backbone and sidechain chemistries
- Separate quantification of diffusivity and solubility vs. permeability for HOPI
- Anion adsorption impact on activity analysis
- Crack mitigation strategies (solvents, drying, additives)
- Understanding HOPI impact on degradation with HSC supports and PtCo catalyst

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Austin Plymill

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Devproshad Paul (Ballard PI)
Alan Young
Shanna Knights

Million Mile Fuel Cell Truck (M2FCT) Consortium

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Oak Ridge National Laboratory

Dave Cullen

DOE Hydrogen and Fuel Cell Technologies Office

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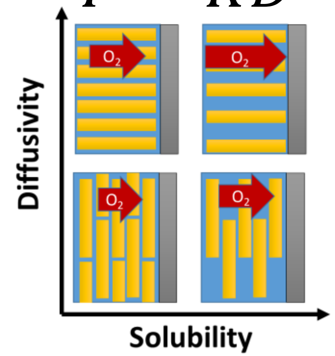
Elliot Padgett
Dimitrios Papageorgopoulos
Sunita Satayapal
Dan Berletti

Technical Backup and Additional Slides

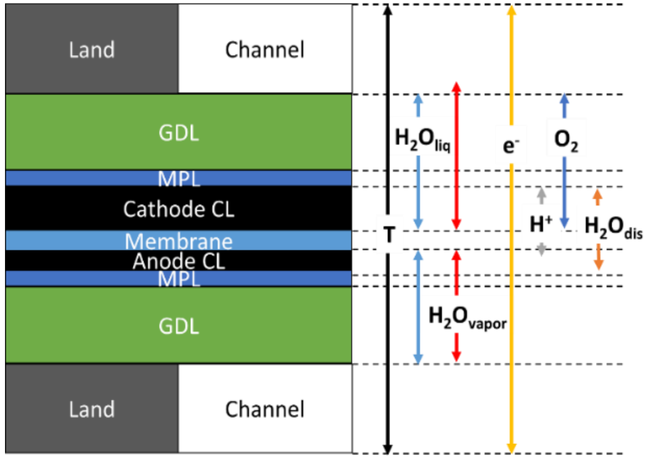
Cell Modeling of HOPI Impact

- 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 ALL currents, increasing efficiency and power density
- 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

$$P = KD$$



*Neutral gas/solid interaction case



External Pt ORR Model

Film diffusion

Pt interface

ECSA

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

Ionomer solubility

MD convergence evaluation

Time evolution of density peaks indicates whether the system is still equilibrating in simulation