Novel Fluorinated Ionomer for PEM Fuel Cells

Hui Xu (PI)

Giner, Inc., Newton, MA

DOE project award DE-SC0018597

June 6-8, 2022

DOE Hydrogen Program

2022 Annual Merit Review
and Peer Evaluation Meeting

Project ID
FC328

Project Goal

Develop high oxygen permeability ionomer (HOPI) for PEM fuel cell cathodes to reduce local oxygen transport loss, by engineering the polymer backbone to contain molecules with more open space available for gas transport

- Improve O_2 permeability by 5x compared to Nafion® Baseline
- Increase polymerization scale by 10x per batch
- Evaluate fuel cell performance, durability and local transport resistance

Outcomes: introduce alternative ionomer materials to the market, that enable higher power densities compared to state-of-the-art ionomers

Milestones	Composition	Completion
Q1	CMS proton conductivity at 80 ºC: 20 mS/cm at 50% RH, 40 mS/cm at 70% RH, and 90 mS/cm at 98% RH	100%
Q2	CMS Gas permeability: at least 4X increase compared to Nafion 1100EW ionomer measured under same conditions	100%
Q3	CMS Gas permeability: at least 5X increase compared to Nafion 1100EW ionomer measured under same conditions	100%
Q4	Fuel Cell performance: voltage is improved by 100 mV at 2.5 A/cm2 and current density @ 0.7 V is doubled, compared with Nafion® baseline. (Year 1 Go/No Go point)	100%
Q5	Fuel Cell performance: voltage improved by 150 mV at 2.5 A/cm2	100%
Q6	Fuel Cell performance: voltage improved by 200 mV at 2.5 A/cm2	100%
Q7	Local O_2 transport resistance: at least 4 times decrease compared to Nafion 1100EW ionomer measured under same conditions	70%
Q8	5 of 50-100cm^2 MEAs to be delivered to GM and Ballard (they wanted just ionomer not MEAs)	N/A

Project Overview

Timeline

- Project Start Date: 5/28/2019
- Project End Date: 8/27/2021

Budget

- Total Project Value:

  $ 999,595
- Funds Spent: $ 999,996

Barriers Addressed

- PEM fuel cell transport loss at low Pt loadings and high-power densities

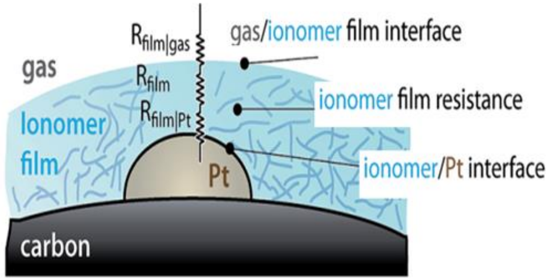
Collaborators

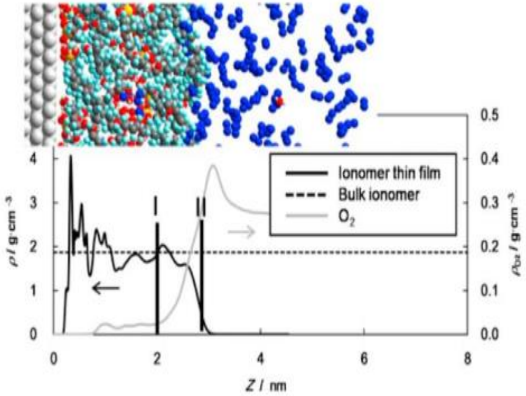
- Project Lead: Giner, Inc.
  - Shirley Zhong, Natalia Macauley, Hui Xu
- Subcontractors:
  - Compact Membrane Systems: Dr. Dan Lousenberg
  - University of Connecticut: Prof. Jasna Jankovic, Sara Pedram
  - University of California Irvine: Dr. Iryna Zenyuk, Yongzhen Qi, Andrea Perego

Relevance

Objective: Maximize catalyst performance by synthesizing and incorporating high oxygen permeability ionomer (HOPI) in fuel cell cathodes and meet 2020 DOE HFTO MYRDD Catalyst and heavy-duty MEA targets.

- High local O_2 transport resistance occurs due to thin ionomer film surrounding Pt particles
- High local O_2 transport resistance leads to low O_2 concentration on Pt surface thus inferior fuel cell performance
- Reduce local oxygen transport resistance by increasing ionomer permeability in cathode

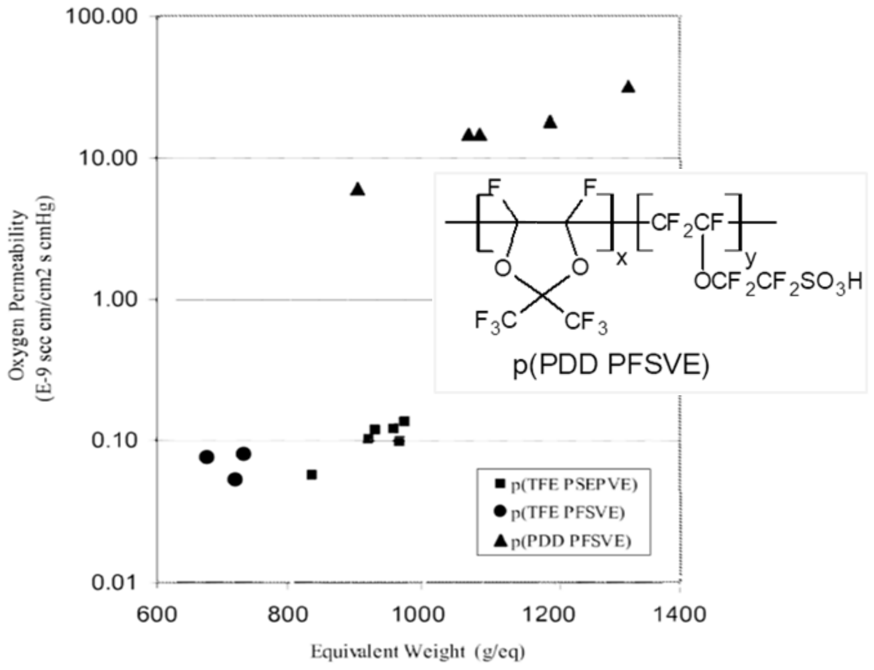




J. Phys. Chem. Lett. 7, 1127 (2016)
Macromolecules, 45, 7920 (2012)

Approach

Dry O_2 permeability of PDD copolymers vs. p(TFE PSEPVE) "Nafion®" or p(TFE PFSVE) "Aquivion®"



United States Patent Application 20130245219 A1

Ionomer development and characterization: Synthesize HOPIs with varied EW, and molecular weight and identify best composition for fuel cell performance. Characterize gas permeability and conductivity

Electrode integration: Vary the solid to liquid content, ionomer to carbon ratio; optimize mixing and coating method. Use rheology, laser diffraction particle size analysis, and zeta potential to monitor ink properties from batch to batch

MEA testing: Optimize MEA fabrication, membrane, gas diffusion layer, flow field, cell assembly (compression), conditioning and recovery protocols; measure local O_2 resistance

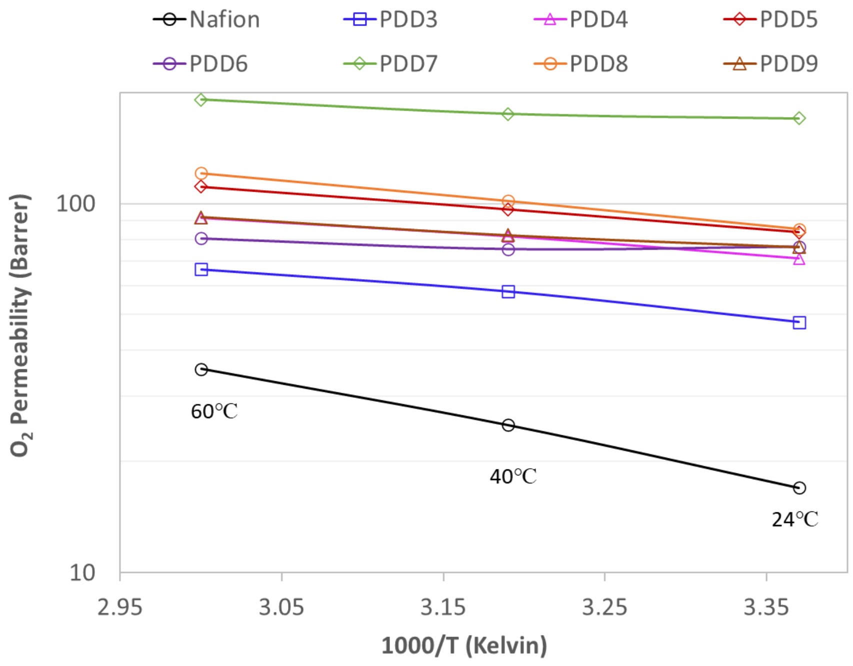
- Fluoro-ionomers with perfluoro-2,2-dimethyl-1,3-dioxole (PDD) have **two orders of magnitude higher dry O_2 permeability** from increased free volume imparted by the **PDD** repeat unit
- Develop next generation of fluorinated ionomers for PEM fuel cell cathodes with reduced local O_2 transport losses:
  - Highly conductive amorphous ionomers with higher free volume than Nafion®
  - Enhanced O_2 permeance to the PGM catalyst will improve overall performance

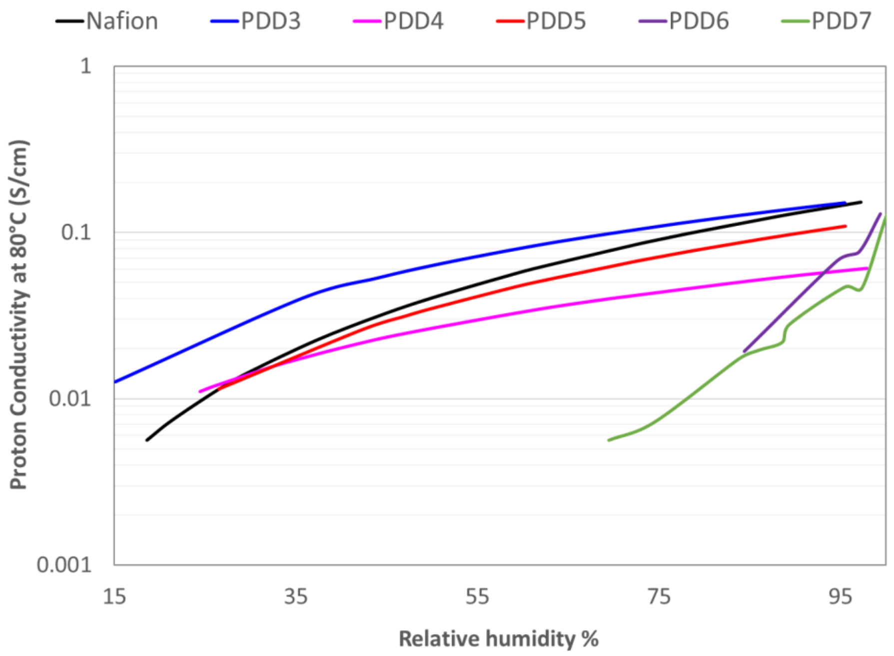
HOPI Synthesis

Ionomer	Composition	PDD content (mole%)	EW (g/mole)	Intrinsic Viscosity (dL/g)	O_2 Permeability (Barrer)	
					24°C	60°C
PDD1	PDD/PSEPVE/M	24 – 30	847	0.53	22	41
PDD2	PDD/PFSVE/M	30 – 36	864	0.51	12	27
PDD3	PDD/PFSVE/M	62 – 68	754	0.20	48	66
PDD4	**PDD/PFSVE/M**	**67 – 73**	**863**	**0.31**	**71**	**91**
PDD5	PDD/PFSVE/M	67 – 73	859	0.31	84	111
PDD6	PDD/PFSVE/M	70 – 76	953	0.20	77	81
PDD7	PDD/PFSVE/M	70 – 76	967	0.38	170	191
PDD8	PDD/PFSVE/M	67 – 73	789	0.28	85	121
PDD9	PDD/PFSVE/M	67 – 73	836	0.18	75	93
Nafion™ (control)	PSEPVE/TFE	0	930	N/A	17	36

- Copolymerization of **PDD**, **PFSVE** (or PSEPVE), and a ter-monomer (**M**)
- Synthesized ionomers with varied composition, EW, and molecular weight
- Identified and scale up the most promising high-PDD ionomer, **PDD4**
  - Transitioned to semi-batch polymerization for scale up
  - PDD8 and PDD9 are replicas of PDD4

O_2 Permeability and Proton Conductivity



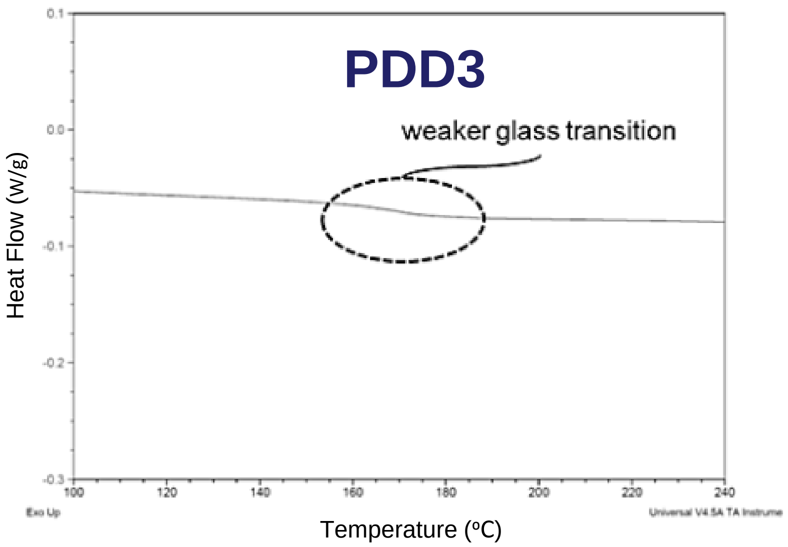


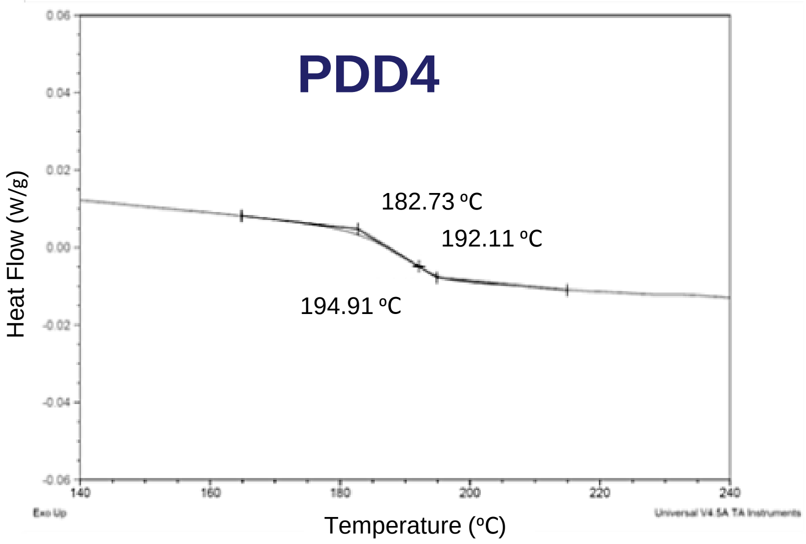
Permeability improvement vs Nafion							
T (℃)	**PDD 3**	**PDD 4**	**PDD 5**	**PDD6**	**PDD7**	**PDD8**	**PDD9**
24	3x	**4x**	**5x**	**5x**	**10x**	**5x**	**4x**
60	2x	3x	3x	2x	5x	3x	3x

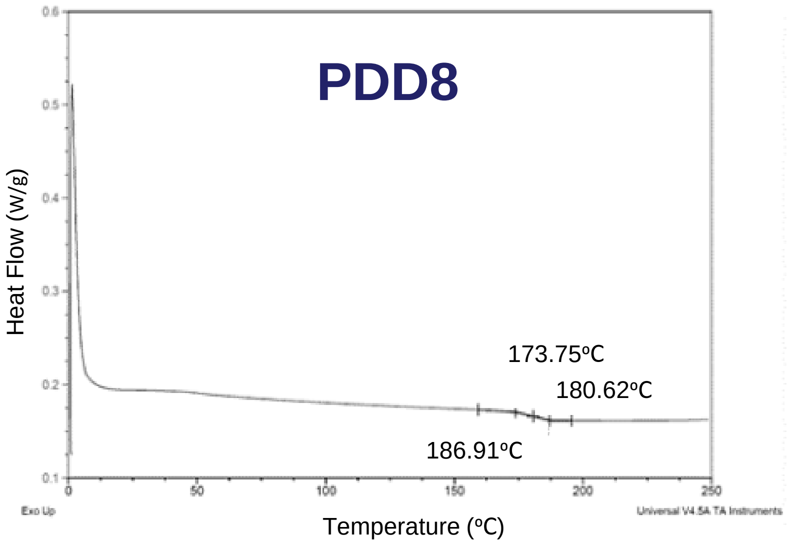
- PDD7 HOPI displays **10x** the permeability of Nafion due to high PDD content
- PDD3 has highest conductivity due to low EW
- PDD6 and 7 may have high variability in composition leading to immeasurable conductivity at low RH

Accomplishment

HOPI Glass Transition Temperature







- Evaluated T_g of various PDD ionomers with TGA to enable optimal processing of the ionomer for MEA fabrication
- T_g of PDD3 (754EW) was weaker, likely due to more compositional drift during synthesis, i.e., more non-uniformity
- PDD4 (863EW) has a measurable glass transition temperature, in the region of 183 °C
- PDD8 (789EW) also had a measurable glass transition temperature around 180 °C

IEC Tests and Fenton Test

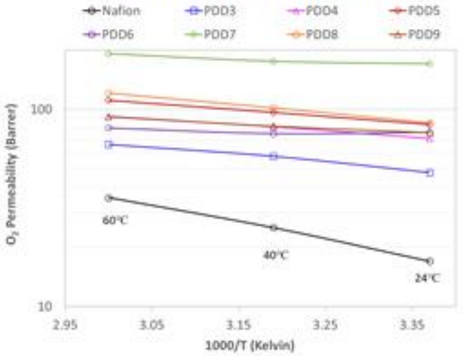
Sample ID	Average IEC (mol/g)	Average EW	Loss in EW
Nafion Fresh	0.973	1027	
Nafion Tested	0.803	1245	**21%**
PDD4 Fresh	0.964	1037	
PDD4 Tested	0.877	1141	**9%**

- PDD ionomer was cast into thin membrane on Kapton
  - Gently released from substrate by soaking in DI water
- 24h soak in Fenton's reagent (20% H_2O_2 + 10 ppm Fe^{2+}) at 80 ºC
- PDD4 showed 2x less degradation in Fenton test

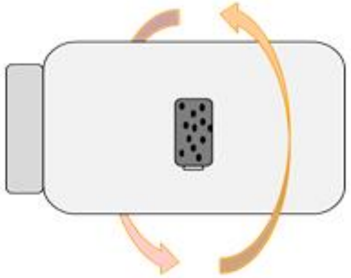
Accomplishment

Catalyst Ink/MEA Optimization

Ionomer Permeability

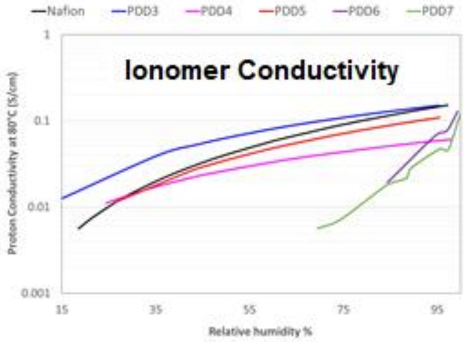


Ball Milling

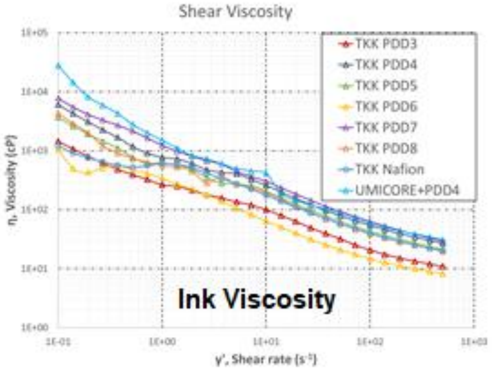


Mayer rod coating

Hot pressing

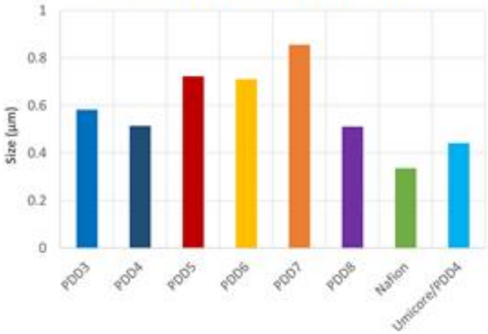


Ionomer Conductivity

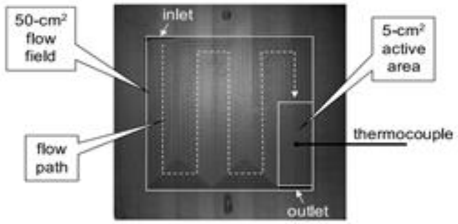


Ink Viscosity

Catalyst Agglomerate Size



5cm² in GM Differential cell

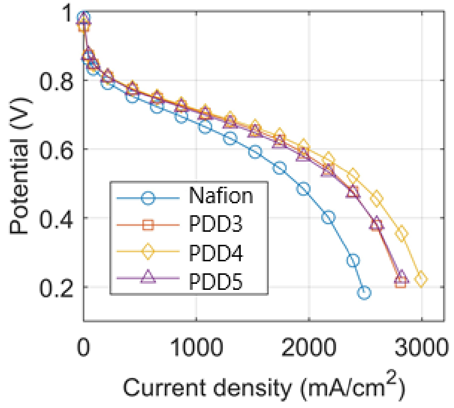


- TKK **TEC36F32** 30 wt.% **PtCo catalyst** in Water / Alcohol Solvent with I/C of 0.8, 0.9, 1
- Ink characterization with **rheology** for viscosity and **laser diffraction** for catalyst agglomerate size
- **Successfully coated homogenous catalyst layers** on Teflon or GDL using Mayer rod method
- Target loading of **0.1 mg/cm² Pt** at cathode + Commercial 0.2 mg/cm² Pt anode + Hot pressed to N211 membrane
- Variety of membranes: N211, Nafion HP, Permion

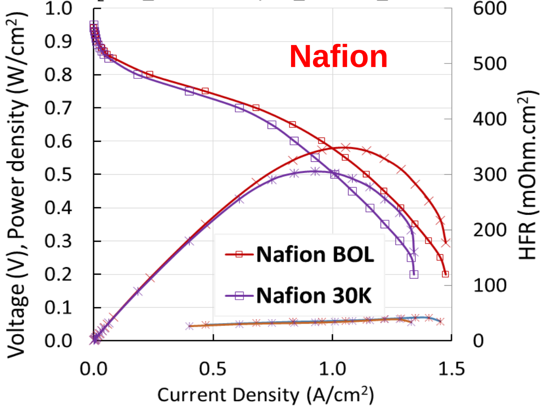
Accomplishment

Improved MEA Performance & Durability

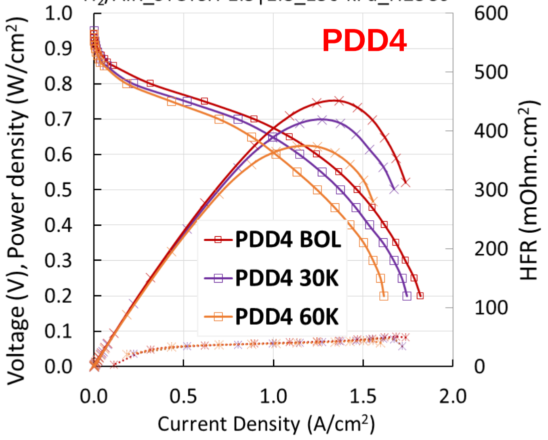
I-C=0.9_N211_0.1 mg/cm^2_80C_100%RH
H_2/AIR_1.5|3.0 SCCM _150 kPa_H23C6

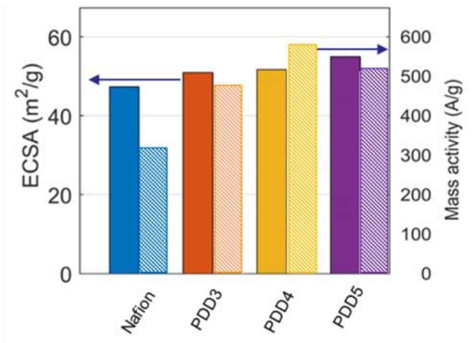


I-C=0.9_N211_0.1 mg/cm^2_80C_100%RH
H_2/AIR_STOICH 1.5|1.8_150 kPa_H23C6



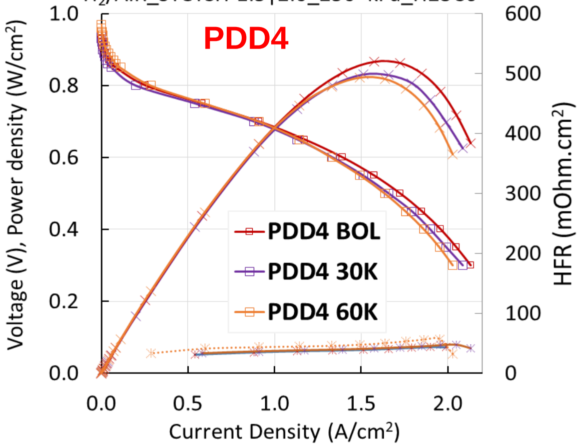
I-C=0.9_N211_0.1 mg/cm^2_80C_100%RH
H_2/AIR_STOICH 1.5|1.8_150 kPa_H23C6





80°C, 100%RH @ 30K	Nafion	PDD4
0.8 A/cm^2 Loss (mV)	40	16
MA Loss (%)	31	31
Anode FER (μg/h-cm^2)	0.0047	0.0012
Cathode FER (μg/h-cm^2)	0.0034	0.0022

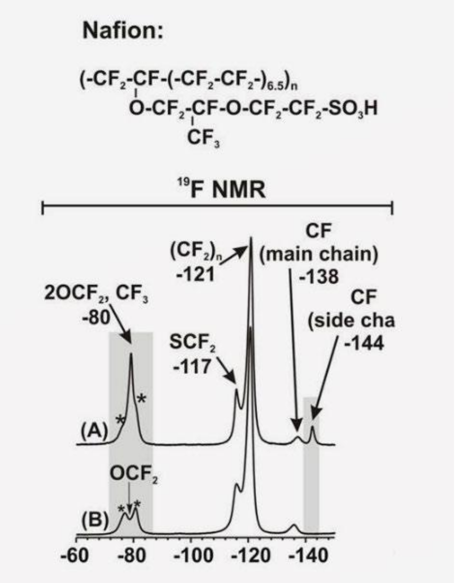
I-C=0.9_N211_0.1 mg/cm^2_94C_100%RH
H_2/AIR_STOICH 1.5|2.0_250 kPa_H23C6

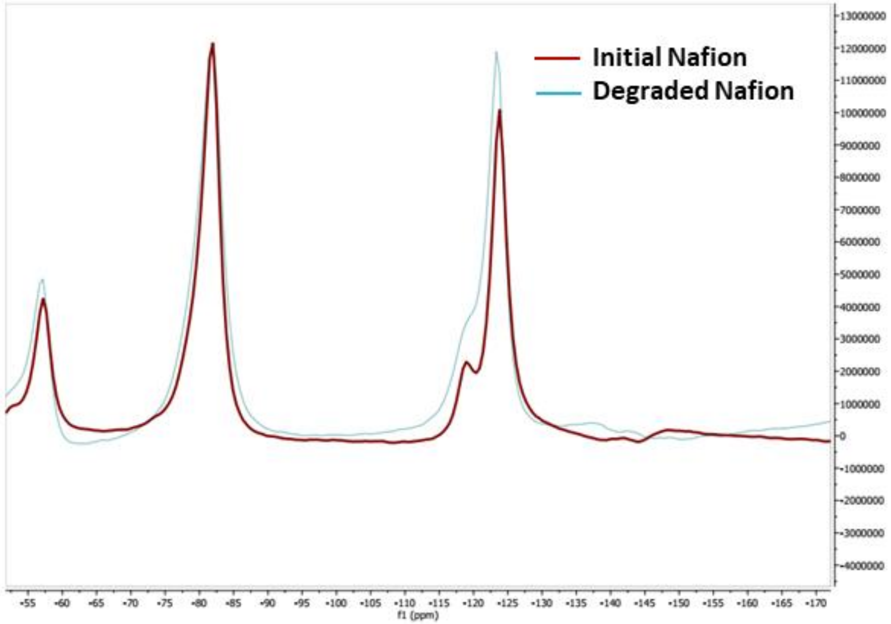


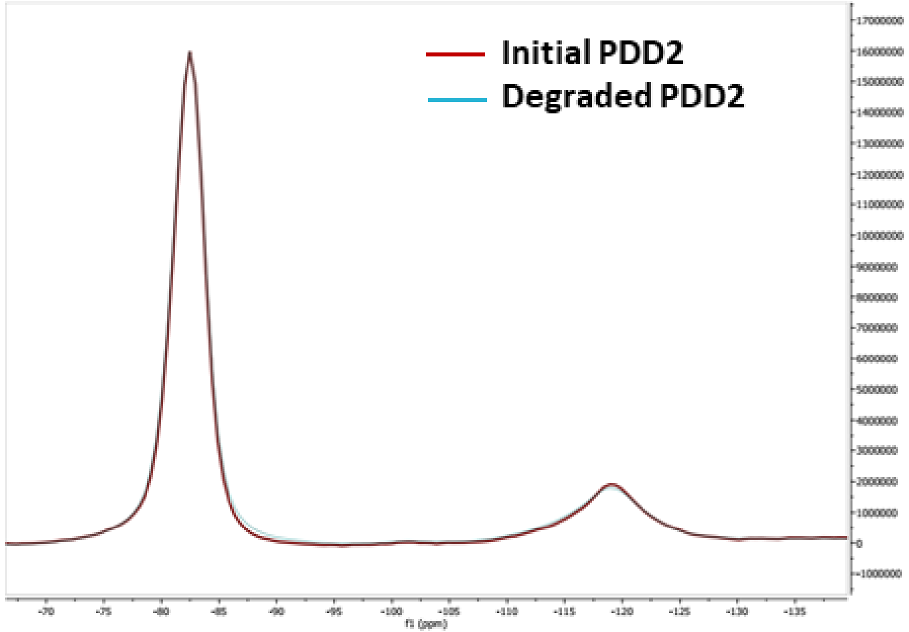
Almost no loss @ Heavy-duty conditions

- Tested different CCMs and GDEs with 5 cm^2 and 25 cm^2 active area
- Variety of GDLs and flow field designs (e.g., 25 cm^2 3-serpentine)
- Top left: 25 cm^2 CCM in 50 cm^2 14-serpentine flow field with fixed flows achieves 1.2 W/cm^2

Nuclear Magnetic Resonance



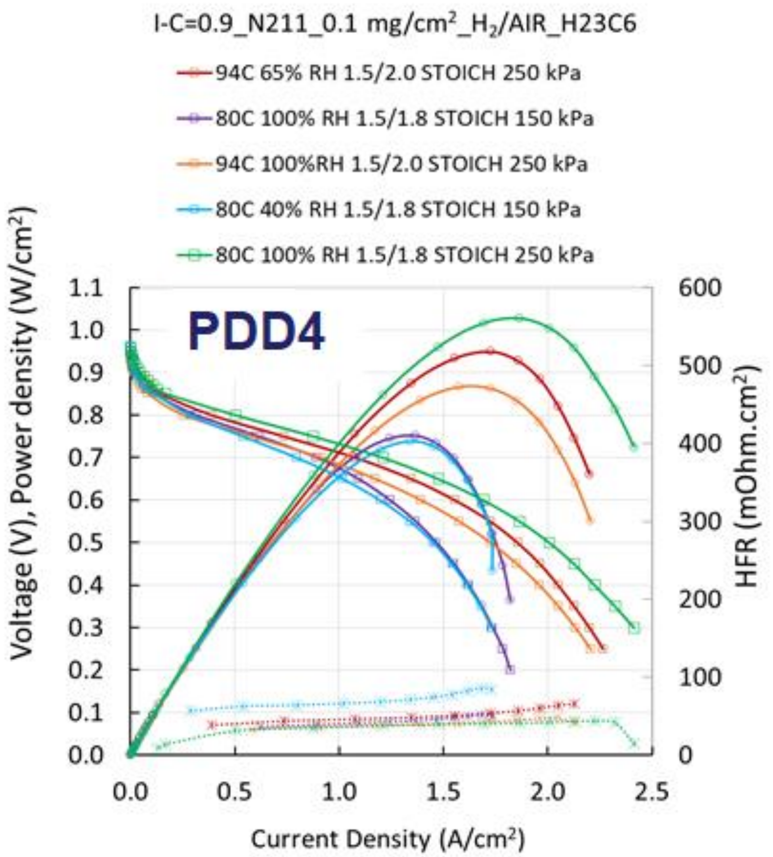


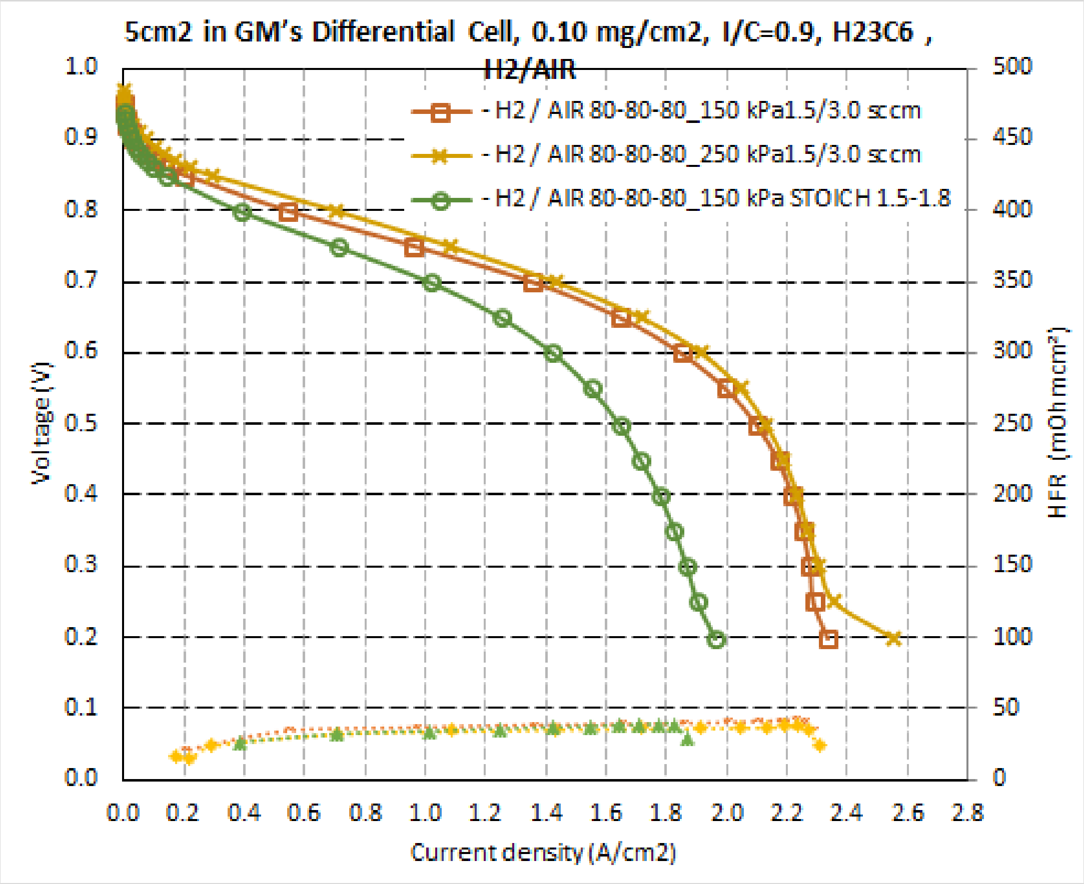


- Fresh and Fenton degraded Nafion, and PDD4
- PDD4 showed the smallest changes between fresh and degraded sample

MEA Performance at Different Conditions

25cm^2
3-Serp

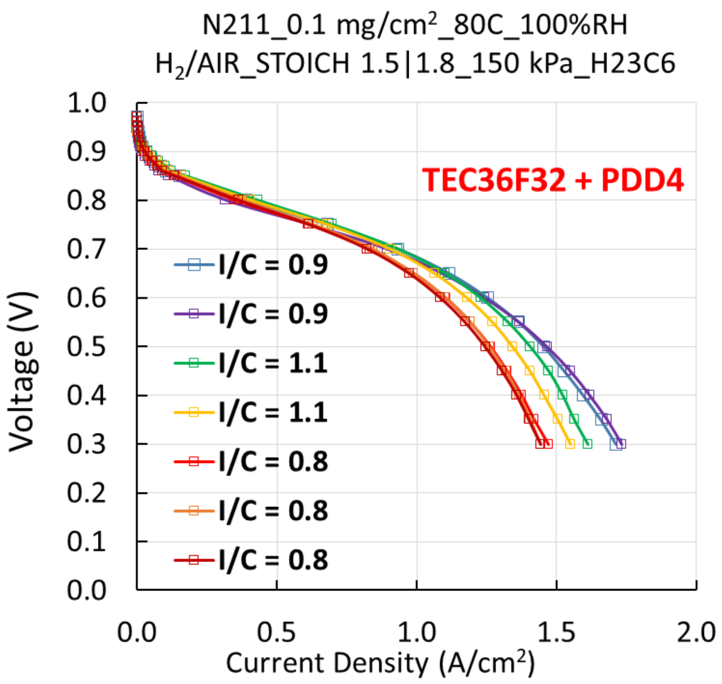


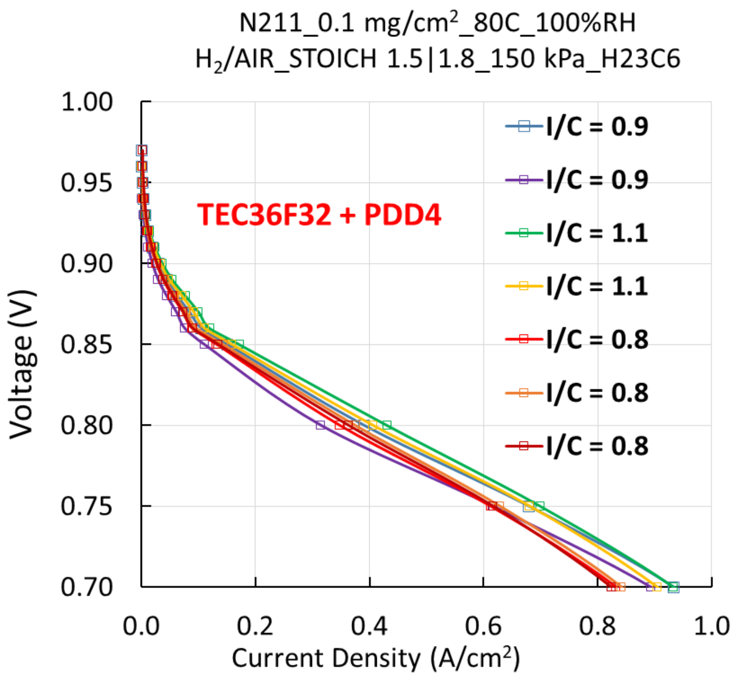


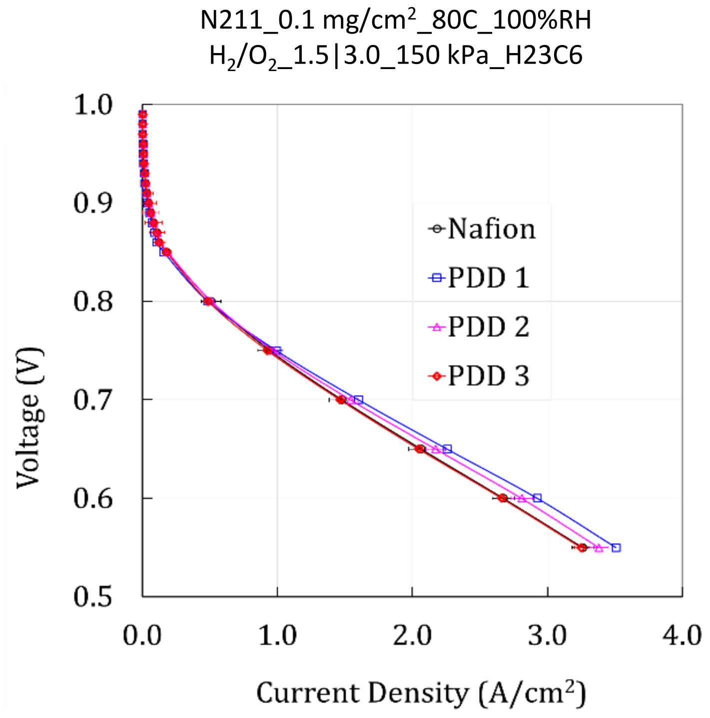
- Best performance seen at 80C, 100% RH, 250 kPa
- Achieves 1.435 A/cm^2 at 0.7V in GM's Differential Cell (80C, 100% RH, 250 kPa)

Accomplishment

Various I/C and H_2/O_2 Operation







- Lower EW PDD HOPI performs better in pure O_2
- Higher I/C resulted in better kinetic performance but worse mass transport – similar at 0.7 V

Collaboration and Coordination

- **Giner (Prime): Drs. Hui Xu and Natalia Macauley, Shirley Zhong.** Overall project management, HOPI integration with fuel cell electrodes
- **CMS (**subcontractor)**: Dr. Dan Lousenberg.** Synthesized HOPI samples for MEA design and testing; also provided ionomer permeability data
- **UCI** (subcontractor): **Prof. Iryna Zenyuk Group.** Performed ionomer and SO_3^- group coverage, some O_2 transport resistance and Nanoscale Computer Tomography
- **UConn** (subcontractor): **Prof. Jasna Jankovic Group.** Provided microstructure analysis with SEM and TEM: ionomer, Pt, Co distributions and particle size; Nicholas Eddy did NMR
- **General Motors**: **Dr. Craig Gittleman and Anusorn Kongkanand**. Provided flow field to measure local O_2 transport resistance

Remaining Challenges and Barriers

- Challenges remain in the area of scale up: high cost of low volumes of component materials such as PDD and PFSVE
  - Only cheap when bough in large volumes
- Polymer inhomogeneity issues seen during batch copolymerization
  - During synthesis PDD is more reactive than the vinyl ether monomer (having the sulfonate group) and it is therefore difficult to control PPD incorporation at higher PDD concentrations (i.e. higher EW > 800 g/mol)
  - We have addressed by transitioning from batch to semi-batch copolymerization

Responses to Previous Year Reviewers' Comments

- There are no major project weaknesses noted for this project. The presenter stated that some automation within the synthesis may improve composition reproducibility. In general, achieving tight composition control in free radical reactions is challenging.
    - Response: During synthesis PDD is more reactive than the vinyl ether monomer, it is therefore difficult to control PPD incorporation at higher PDD concentrations . We have addressed this by transitioning from batch to semi-batch copolymerization (not automation)

- Subscale-size MEAs do not shed light on the overall mass transfer and current distribution issues in real world HD applications. A larger MEA (200 cm2) should be tested under similar test conditions. Ionomer thickness in the catalyst layer, and its effects on overall performance and durability, is necessary to arrive at an optimal catalyst layer ionomer content, as well as to understand cost and durability tradeoffs
    - Response: We agree that 200 cm2 larger MEA will help to better study mass transfer issue. We are working with OEMs and funding agencies to secure additional funding to work on this. If funding becomes available, we will also optimize catalyst layer ionomer content, and study cost and long-term durability.

- Unfortunately, the actual materials did not meet expectations and did not meet DOE Hydrogen and Fuel Cell Technologies Office milestones
    - Response: In this project, we used commercial mediocre Pt/C catalysts that did not show high catalytic activity. This could be the reason that some DOE milestones have not been meet. In fact, when we adapted highly active catalysts in another project FC#356, the adaption of HOPI exceeded DOE milestones.

- This project has almost ended, but any future funding to this technical approach to improve oxygen transport using PDD-based ionomers should include a scalability study, both for manufacturing ionomers and for testing larger-platform MEAs.
    - We are working with OEMs and funding agencies to secure additional funding to work on this. If funding becomes available, we will perform scalability study, for both manufacturing ionomers and testing larger-platform MEAs

Future Work

- **Synthesize more scaled up PDD4 HOPI for use in other projects and for distribution to OEMs**
  - using semi-batch process
- **MEA performance Improvement**
  - Use higher quality membranes from 3M and Gore
    - Gore's 12 µm supported membrane
    - 15 µm supported membrane with doped Ce
- **Understanding ionomer durability**
  - NMR after Fenton's test to identify ionomer degradation mechanism
  - H_2O_2 vapor cell testing
- **Evaluate MEAs by OEMs and FC-PAD**
  - Send 50-100 cm^2 MEAs with best ionomer
  - Extensive and harsh FC vehicle operation conditions

    (Transients, Sub-freezing operations, heavy-duty applications and corresponding AST)
  - FC-PAD for ionomer/MEA evaluation – MEAs were sent and await evaluation

Any proposed future work is subject to change based on funding levels

Summary

- Successfully synthesized the first of its kind HOPIs with 2-10x higher O_2 permeability than Nafion
- HOPIs demonstrated pronounced fuel cell performance and durability improvement compared to Nafion
    - Met DOE Mass Activity and Durability targets
- Successfully replicated the best-performed HOPI polymerization process
- PDD HOPIs showed 2x lower local oxygen transport resistance than Nafion

Acknowledgement

- Financial support from DOE SBIR/STTR Program under award DE-SC0018597

- Technical Manager
  - Dr. Dimitrios Papageorgopoulos

- Collaborators
  - Jasna Jankovic (Univ. of Connecticut)
  - Iryna Zenyuk (Univ. of California, Irvine)
  - Dan Lousenberg (CMS)
  - Craig Gittleman (General Motors for loaning differential flow field)

Technical Backup and Additional Information

Technology Transfer Activities

- Secured multiple support letters from potential ionomer users
    - GM, Nikola, Ballard, and Plug Power
- Discussed licensing ionomer technology from CMS to provide products for fuel cell community
- Utilize ionomer for Giner’s commercial products
- Collaboration with commercial coating company to explore roll-to-roll (R2R) production of PDD based catalyst layers

Publications and Presentations

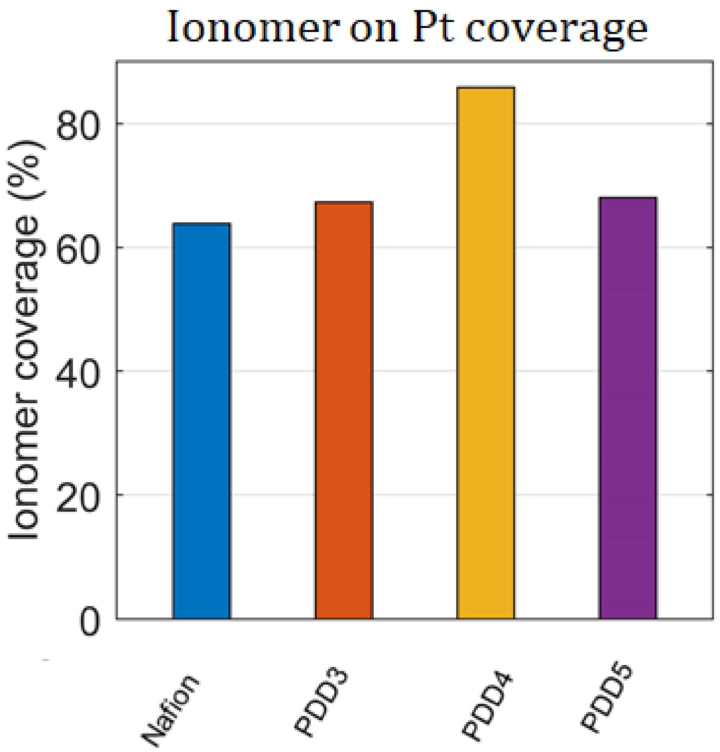
- ECS Prime 2021 Conference Presentation :

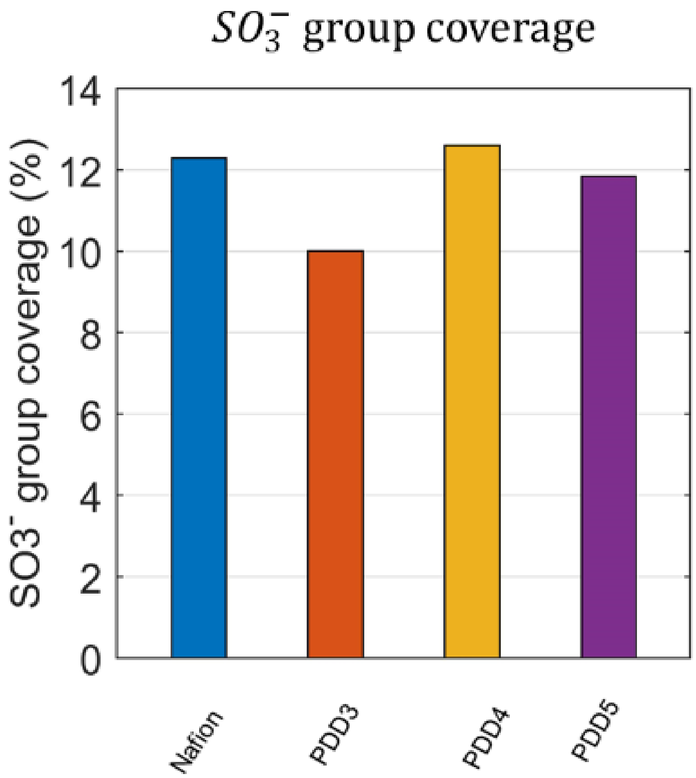
N. Macauley, M. Spinetta, S. Zhong, F. Yang, D. Lousenberg, J. Jankovic, S. Pedram, I. Zenyuk, Y. Qi, H. Xu, High Oxygen Permeability Novel Fluorinated Ionomers for Proton Exchange Membrane Fuel Cells, October 2021

- Manuscript submitted to Advanced Energy Materials is under review:

N. Macauley, M. Spinetta, S. Zhong, F. Yang, D. Lousenberg, W. Judge, V. Nikitin, A. Perego, Y. Qi, S. Pedram, J. Jankovic, I. V. Zenyuk, H. Xu, High Oxygen Permeability Novel Fluorinated Ionomers for Proton Exchange Membrane Fuel Cells

Ionomer and SO_3^- Group Coverage



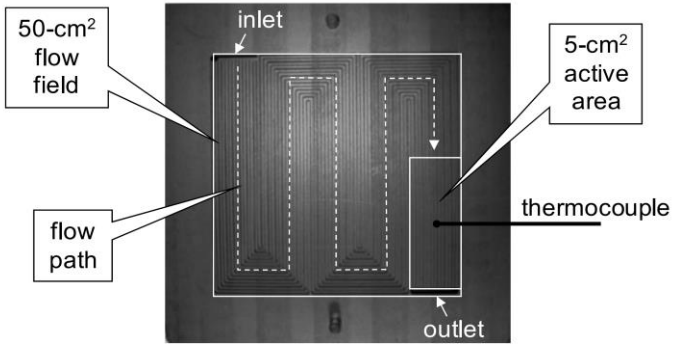


Journal of Electroanalytical Chemistry, **708,** 87-94 (2013)

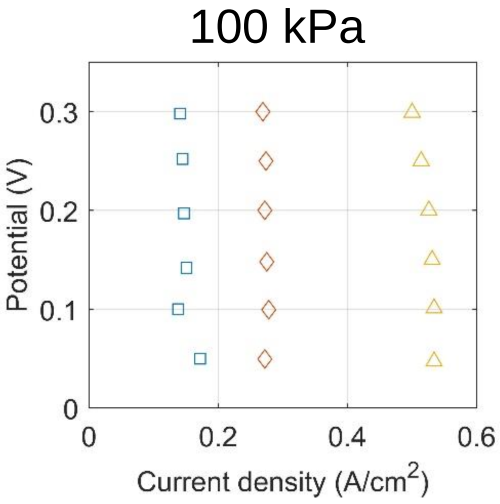
- PDD4 has highest ionomer and SO_3^- coverage
- Indicates good dispersion of ionomer in catalyst layer

Local O_2 Transport Resistance

5cm^2 GM Differential cell



Baker et al, J. Electrochem. Soc. 156, B991 (2014)

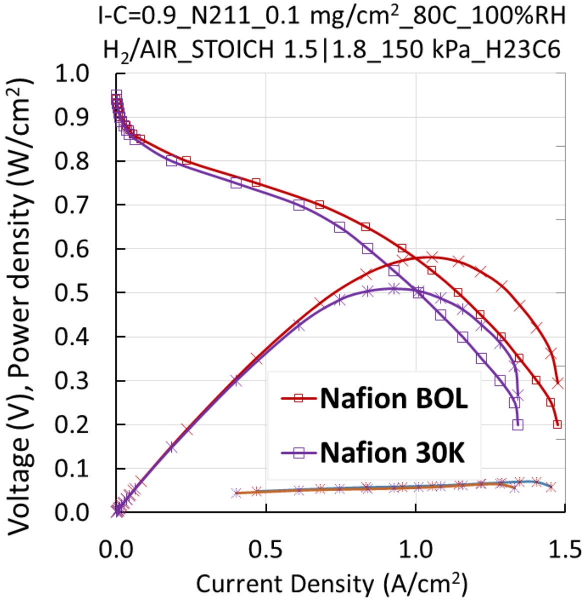


PtCo/HSC 75% RH	**RO_2 Local NF (s/cm)**
Nafion	0.079
PDD3	0.157
PDD4	0.049
PDD5	0.083
Pt/Vulcan 90% RH	
Nafion	0.209
PDD4	0.091

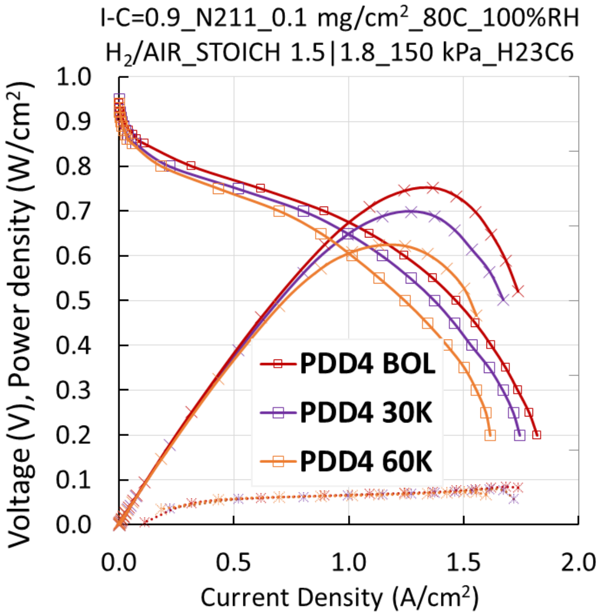
- A limiting current approach was used to measure the transport resistance: $R_T = R_{ch} + R_{DM} + R_{MPL} + \boldsymbol{R_{other}}$
- 1%, 2% and 4% O_2 in He and variety in back pressures (100 kPa, 125 kPa, 150 kPa, 200 kPa)
- Current densities at 0.1-0.2 V were used for local oxygen transport analysis
- **Improved performance of PDD4 cathode is partially due to 2x lower local RO_2 than Nafion**
- Bulky PDD molecule creates void space for O_2 transport

Improved Durability

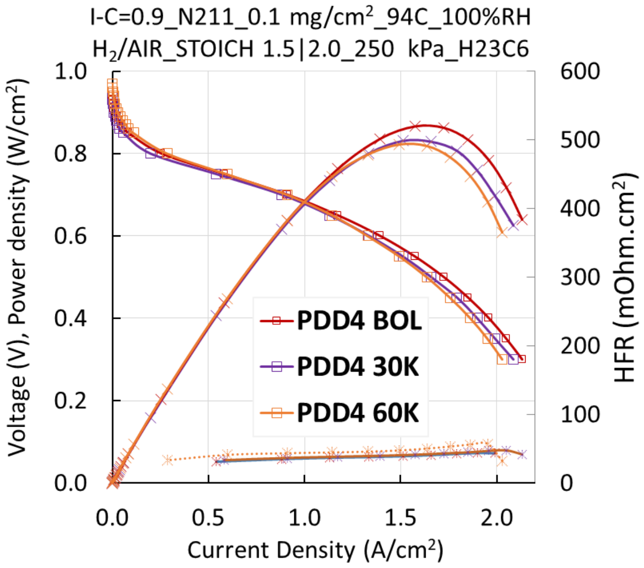
Nafion



PDD4



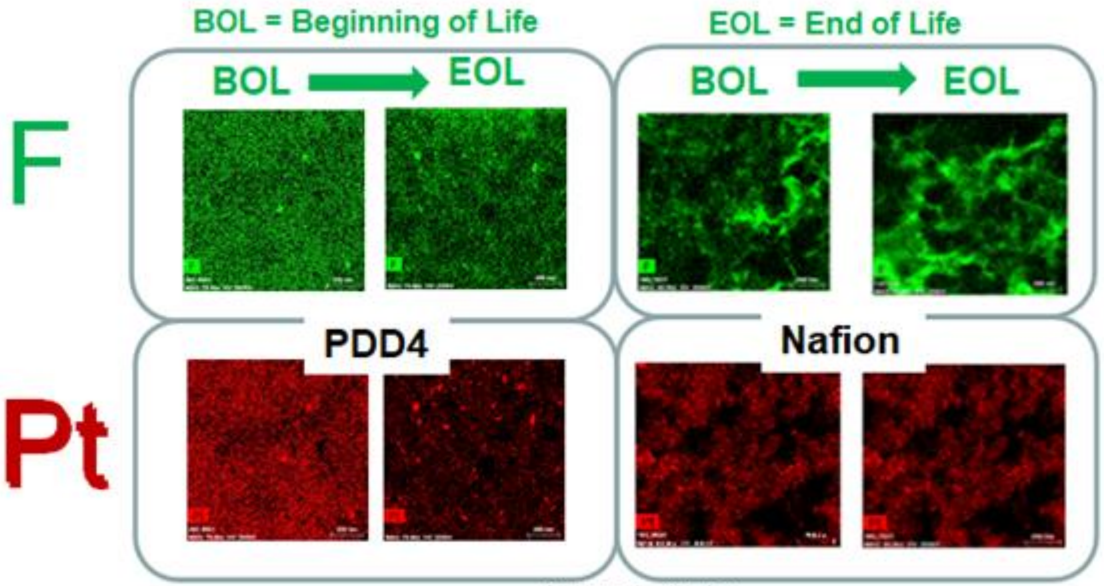
PDD4, Heavy Duty Condition



- **30K-60K Square Wave AST (0.6 – 0.95 V)** was used to degrade MEAs
- Previously **PDD4** MEA displayed best durability among PDD MEAs
  - Highly durable at heavy duty operating conditions: 94ºC, 65% RH, 250kPa
- **Fluoride Emission Rate (FER)** measured with hydrocarbon membrane (**Permion**)
  - Isolated fluoride from the ionomer, and eliminated membrane fluoride
- **PDD4** MEA displayed a visibly lower FER than Nafion

80ºC, 100%RH @ 30K	Nafion	PDD4
0.8 A/cm^2 Loss (mV)	40	16
MA Loss (%)	31	31
Anode FER (µg/h-cm^2)	0.0047	0.0012
Cathode FER (µg/h-cm^2)	0.0034	0.0022

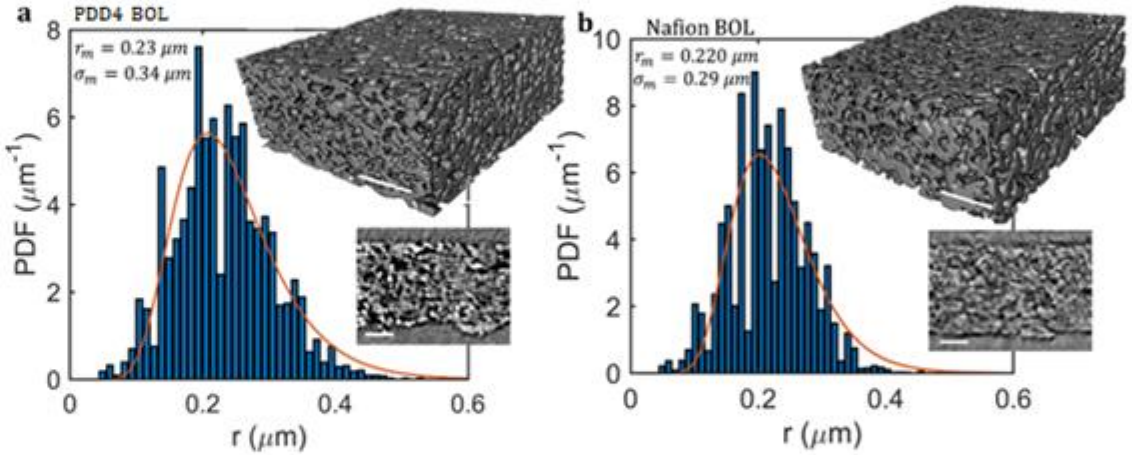
TEM and Nano CT



Scale bar = 200 nm

Sample ID	Primary porosity	Secondary porosity	Pt/Co Atomic	Average Particle size (nm)	Co count
PDD4 BOL	25%	**64%**	8.4	3.98±1.25	0.007
PDD4 EOL	36%	47%	16.9	4.43±1.04 **(+11%)**	0.004 (-43%)
Nafion BOL	39%	45%	6.3	6.25±1.86	0.033
Nafion EOL	39%	44%	19.5	9.04±3.93 (+45%)	0.015 **(-53%)**

Scale bar = 3 µm



- Ionomer and Pt distributions become more agglomerated and non-uniform at EOL
- **Nafion** displays more visible agglomeration at BOL
- PDD4 shows the least agglomeration at BOL and EOL
- Electrode **PDD4** has the smallest particle size growth
- Less cobalt leached from PDD4 cathode - Pt/Co atomic ratio
- Nano x-ray CT showed slightly higher porosity of a) PDD4 vs. b) Nafion at BOL