Novel Fluorinated Ionomer for PEM Fuel Cells

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Giner, Inc., Newton, MA

DOE project award DE-SC0018597

June 7-11, 2021

2021 DOE H_2 and Fuel Cell
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

Project Overview

Timeline

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

Budget

- Total Project Value:

  $ 999,595
- Funds Spent: $ 867,702

  * As of 04/01/2021

Barriers Addressed

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

Collaborators

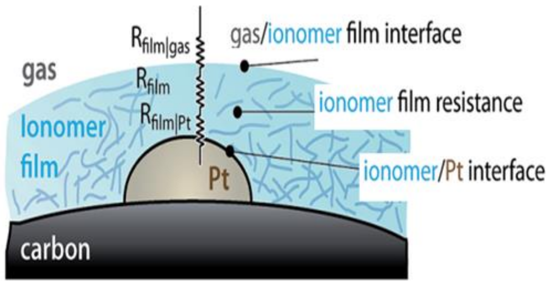
- Project Lead: Giner, Inc.
  - Shirley Zhong and Natalia Macauley
- Subcontractors:
  - Compact Membrane Systems: Dr. Dan Lousenberg
  - University of Connecticut: Prof. Jasna Jankovic, Sara Pedram
  - University of California Irvine: Dr. Iryna Zenyuk, Yongzhen Qi, Andrea Perego

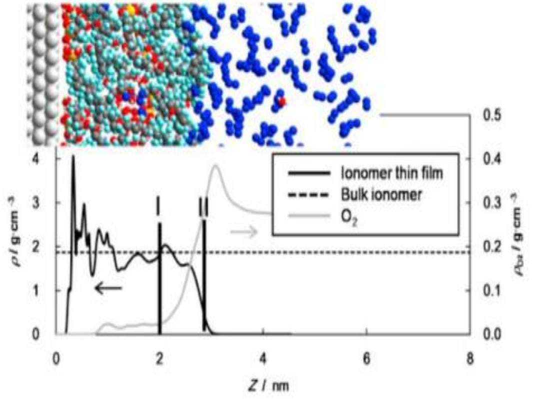
Relevance

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.

CHARACTERISTIC	UNITS	2020 TARGETS
Mass activity	A/mg PGM @ 900 $mV_{IR\text{-}free}$	0.44
Loss in initial catalytic activity	% mass activity loss	<40
Loss in performance at 0.8 A/cm^2	mV	<30
Loss in performance at 1.5 A/cm^2	mV	<30
MEA performance @ 0.800 V	mA/cm^2_{geo}	≥300
MEA performance @ rated power (150 kPa_{abs})	mW/cm^2_{geo}	≥1000

- 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





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

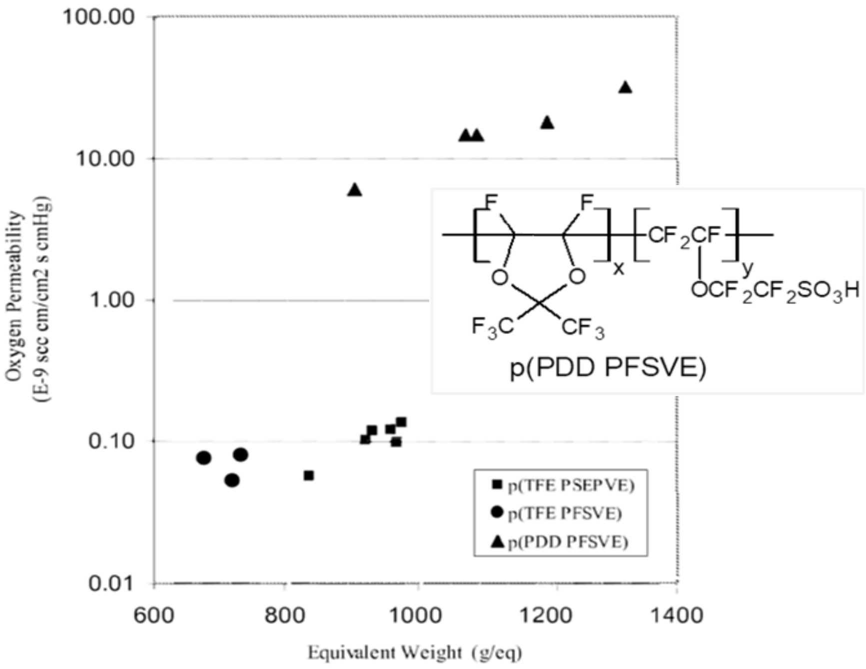
GOAL: Reduce local oxygen transport resistance by increasing ionomer permeability in cathode

Approach

Compact Membrane Systems

GINER

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

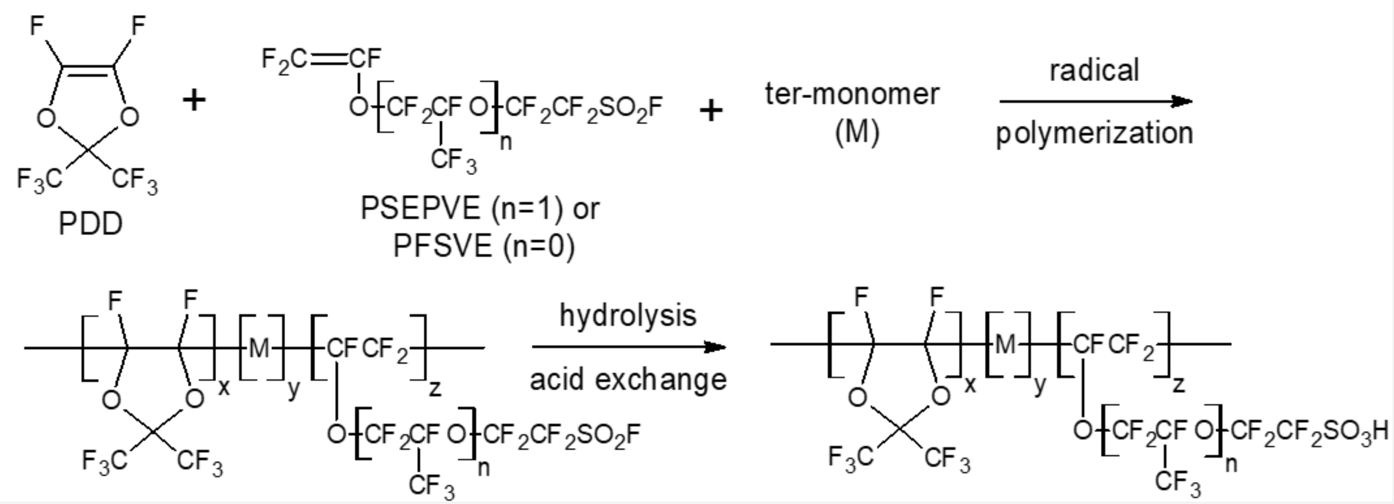
- **MEA testing:** Optimize MEA fabrication, membrane, gas diffusion layer, flow field, cell assembly (compression), conditioning and recovery protocols; measure local O_2 resistance

- 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

Accomplishment: HOPI Synthesis

Compact Membrane Systems

GINER



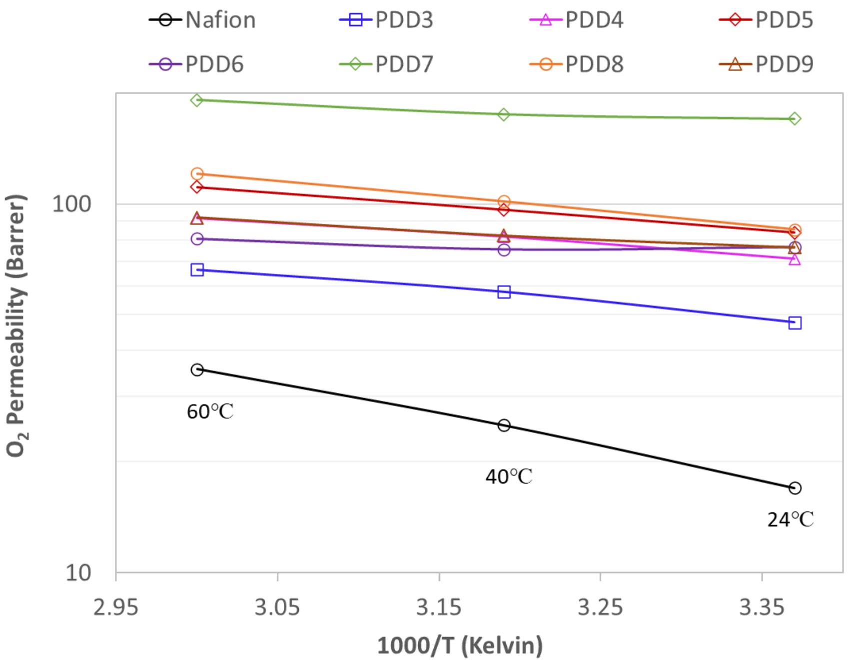
- Copolymerization of **PDD**, **PFSVE** (or PSEPVE), and a ter-monomer (**M**)
- Synthesized ionomers with varied composition, EW, and molecular weight
- Scale up the most promising high-PDD content ionomer, PDD4
- Transitioned to semi-batch polymerization for scale up of best ionomer
- Note: PDD8 and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

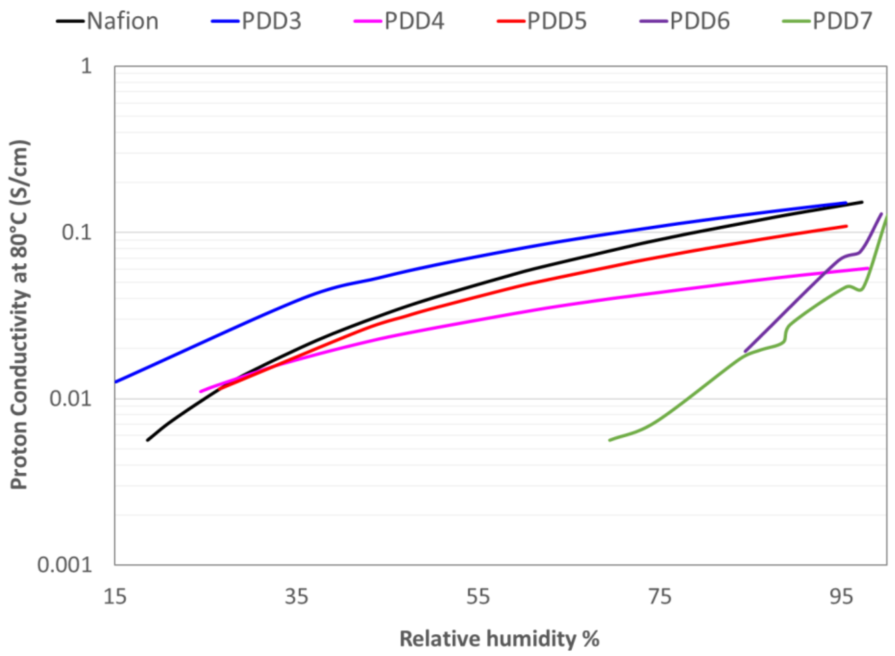
Ionomer	Composition	PDD content (mole%)	EW (g/mole)	Intrinsic Viscosity (dL/g)	O_2 Permeability (Barrer)	
					24°C	60°C
PDD1	PDD/PSEPVE/M	24 – 30	847	0.53	22	41
PDD2	PDD/PFSVE/M	30 – 36	864	0.51	12	27
PDD3	PDD/PFSVE/M	62 – 68	754	0.20	48	66
PDD4	**PDD/PFSVE/M**	**67 – 73**	**863**	**0.31**	**71**	**91**
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

O_2 Permeability and Proton Conductivity

Compact Membrane Systems

GINER



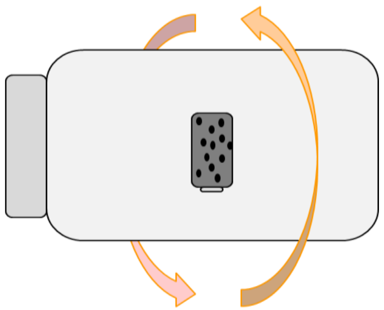


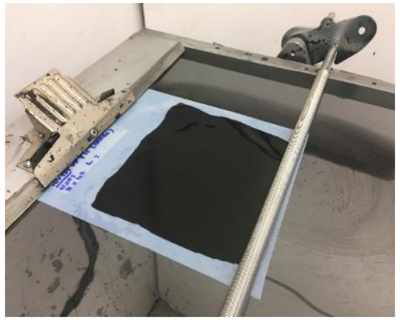
Permeability improvement vs Nafion							
T (℃)	PDD 3	PDD 4	PDD 5	PDD6	PDD7	PDD8	PDD9
24	3x	4x	5x	5x	10x	5x	4x
60	2x	3x	3x	2x	5x	3x	3x

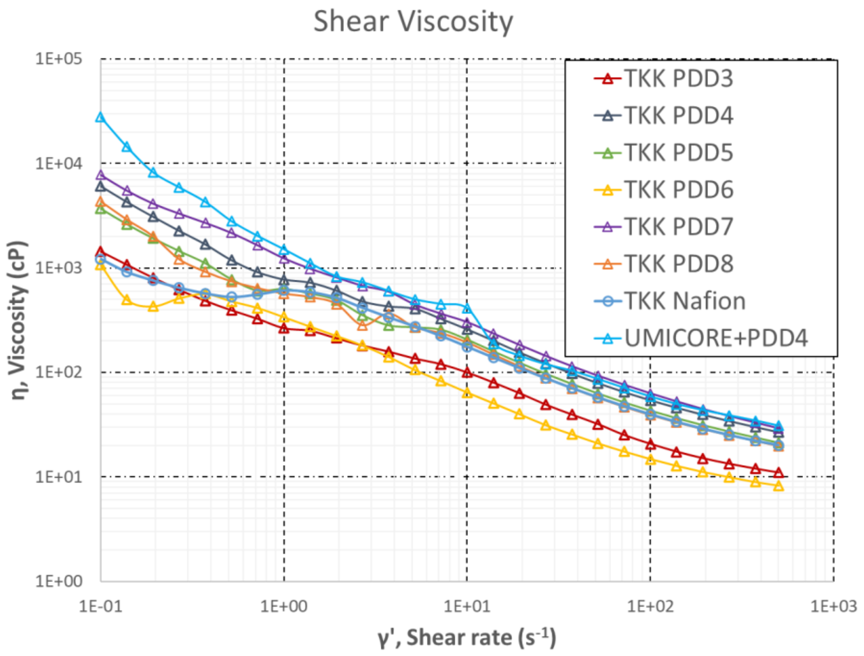
- PDD7 HOPI displays **10x** the permeability of Nafion due to high PDD content
- PDD3 has highest conductivity due to low EW
- PDD6 and 7 may have high variability in composition leading to immeasurable conductivity at low RH

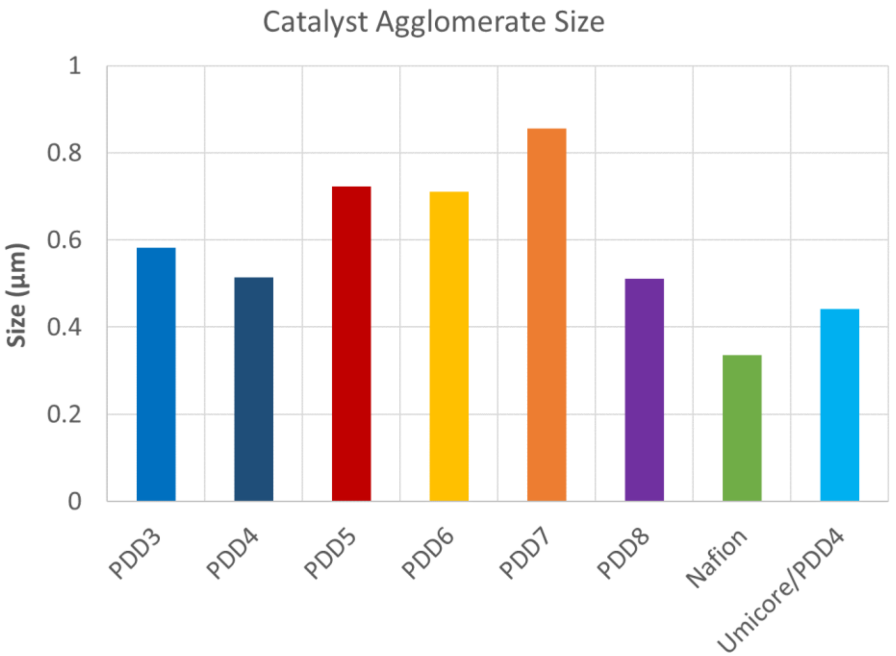
✓ Q1: CMS proton conductivity at 80 ºC: 20 mS/cm at 50% RH, 40 mS/cm at 70% RH, and 90 mS/cm at 98% RH
✓ Q2: CMS Gas permeability: at least 4X increase compared to Nafion 1100EW ionomer measured under same conditions
✓ CMS Gas permeability: at least 5X increase compared to Nafion 1100EW ionomer measured under same conditions

Accomplishment: Catalyst Ink Optimization





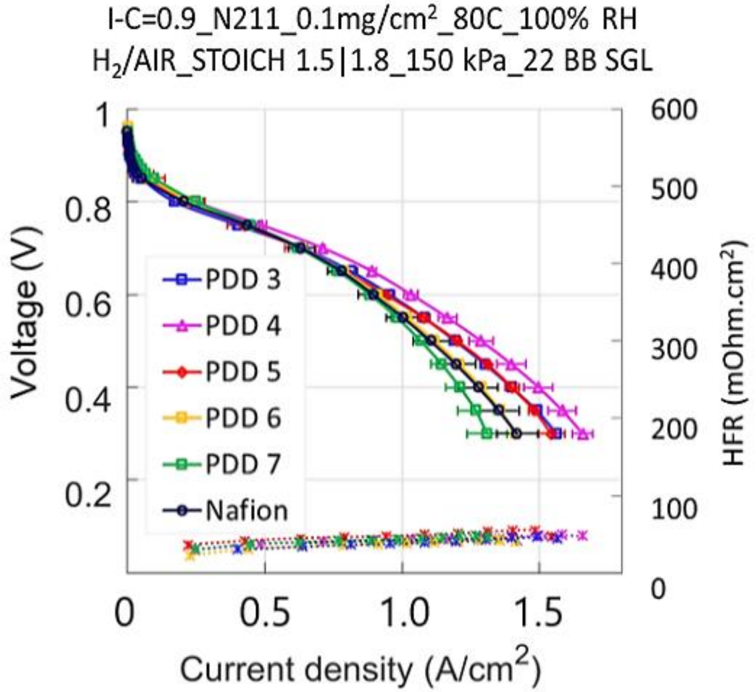


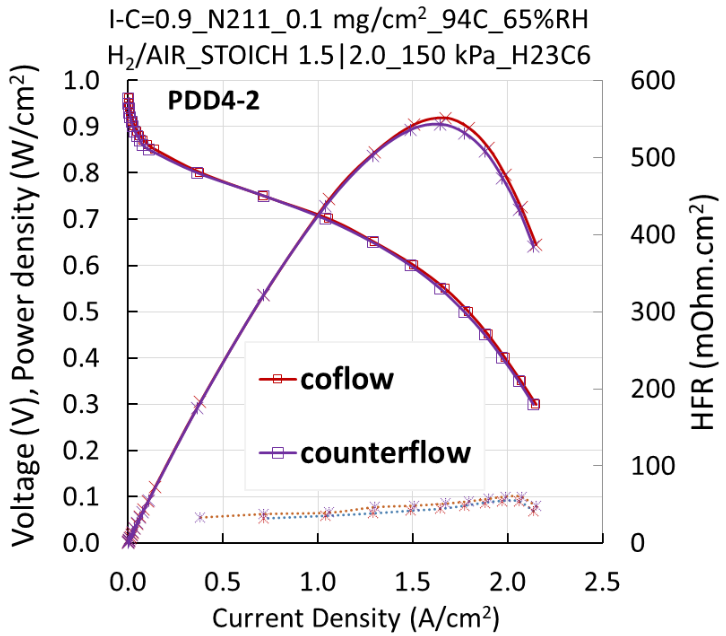


- TKK **TEC36F32** 30 wt.% **PtCo catalyst** in Water / Alcohol Solvent with I/C of 0.8, 0.9, 1
- Other catalysts evaluated: UMICORE Elyst Pt30 0690, TKK TEC36E32, TEC36E52
- Ink characterization with **rheology** for viscosity and **laser diffraction** for catalyst agglomerate size
- **Successfully coated homogenous catalyst layers** on Teflon or GDL using Meyer rod method
- Target loading of **0.1 mg/cm^2 Pt** at cathode + Commercial 0.2 mg/cm^2 Pt anode + Hot pressed to N211 membrane

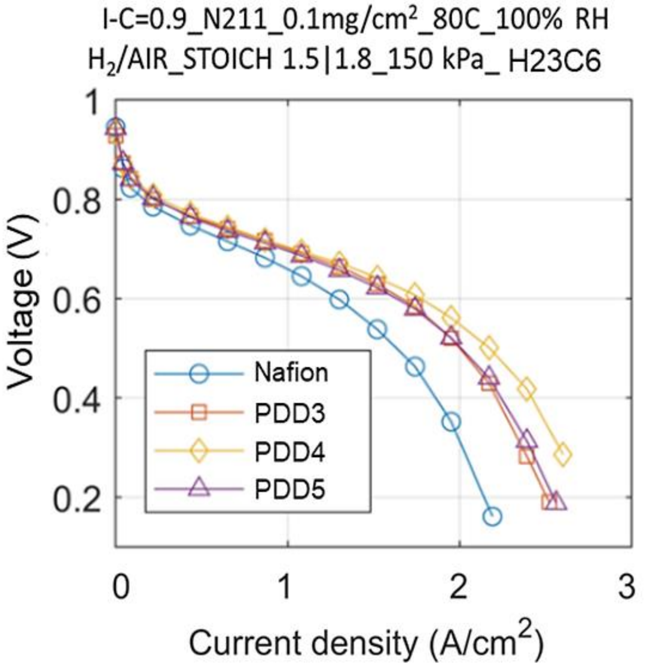
Accomplishment: MEA Performance

3-serpentine flow field





14-serpentine flow field

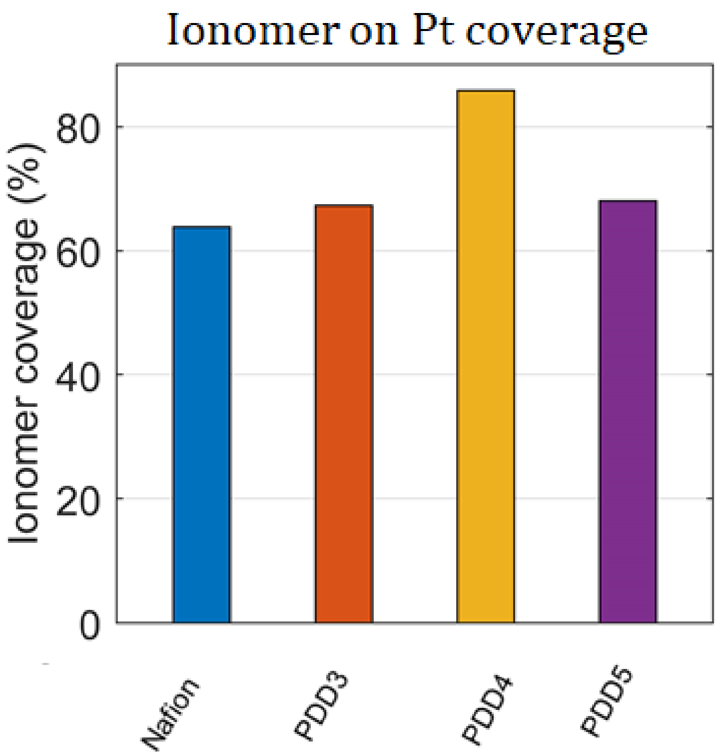


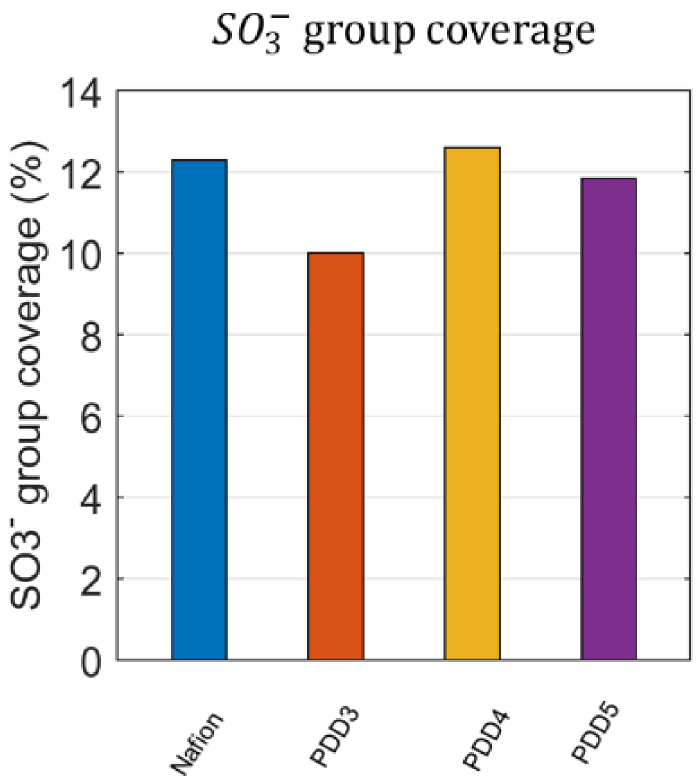
- MEAs using PDD3,4,5 outperform Nafion in the high current density region due to high permeability
- Consistent trend observed with different flow fields, 3- vs. 14-channel, GDLs and operating conditions
- **OPTIMAL PDD content and EW identified in MEA PDD4: 67 – 73 mole% and 836EW**
- No difference in co-flow vs. counterflow operation at heavy duty operating conditions

✓ **Q4:** Fuel Cell performance: voltage improved by 100 mV at 2.5 A/cm^2
✓ **Q5:** Fuel Cell performance: voltage improved by 150 mV at 2.5 A/cm^2

TEC36F32, 25 cm^2

Ionomer and SO_3^- group Coverage



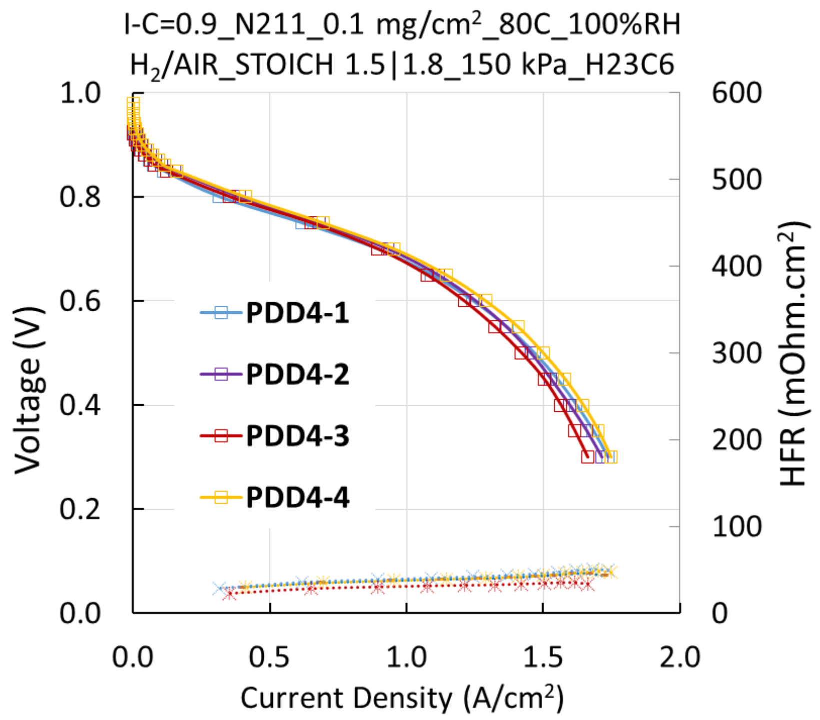


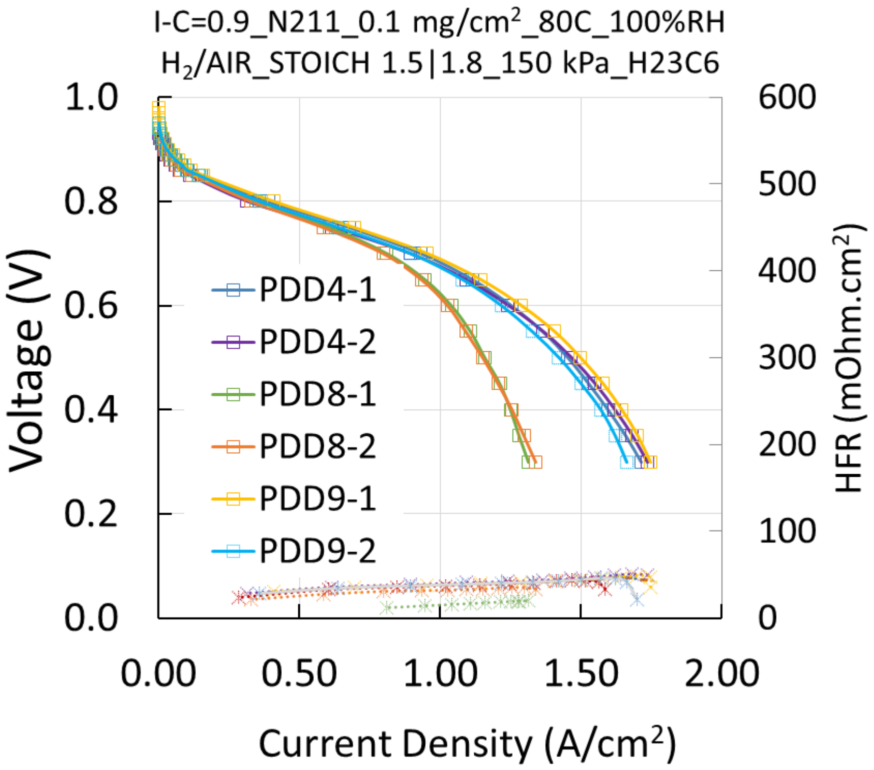
Journal of Electroanalytical Chemistry, **708,** 87-94 (2013)

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

PDD4 Repeatability

3-serpentine flow field

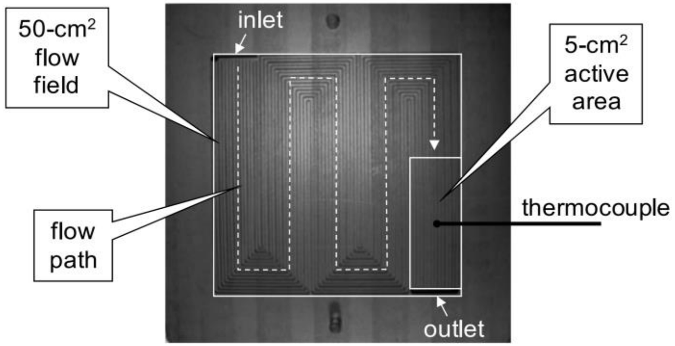




- Good repeatability in performance for multiple MEAs with PDD4 cathodes
- PDD8 and PDD9 are replicas of PDD4: both have the same PDD content but different EW
- **Successfully repeated PDD4's performance with newly synthesized ionomer PDD9**

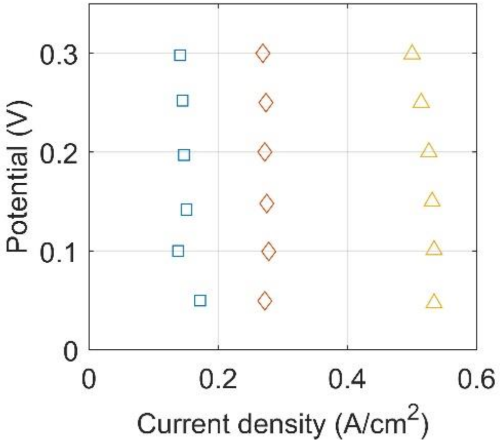
Accomplishment: Local O_2 Transport Resistance

5cm² GM Differential cell



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

100 kPa

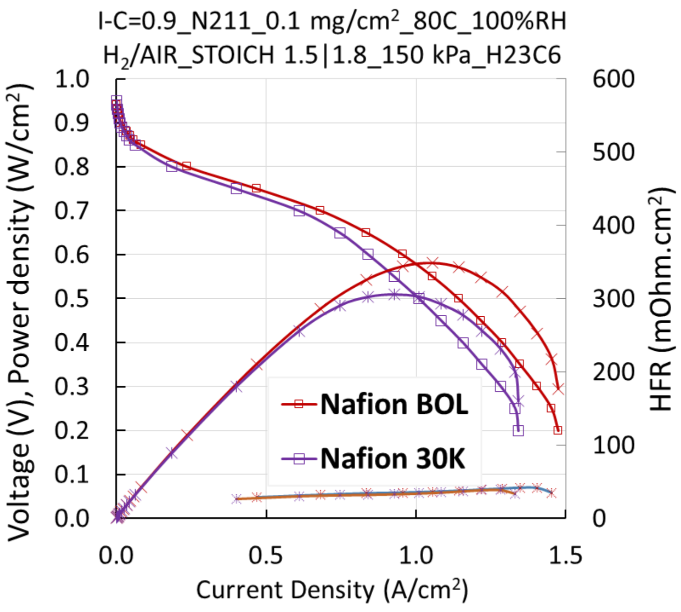


PtCo/HSC 75% RH	RO_2 Local NF (s/cm)
Nafion	0.079
PDD3	0.157
PDD4	0.049
PDD5	0.083
Pt/Vulcan 90% RH	
Nafion	0.209
PDD4	0.091

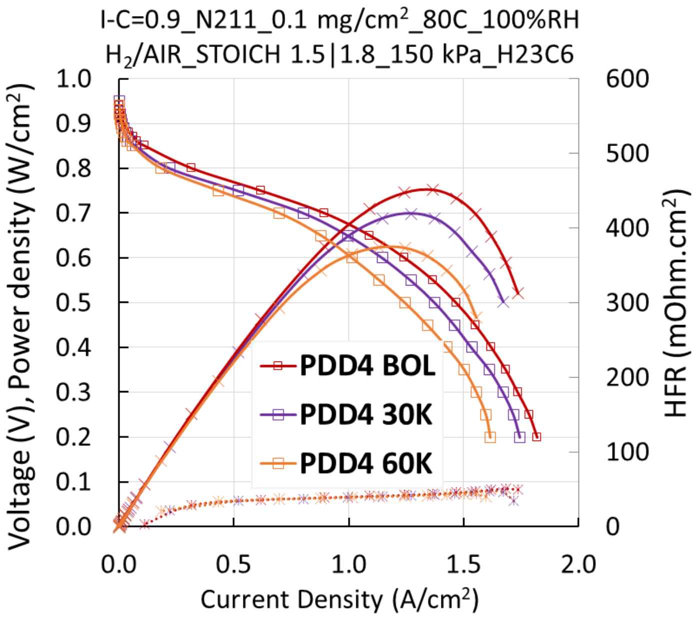
- A limiting current approach was used to measure the transport resistance: $R_T = R_{ch} + R_{DM} + R_{MPL} + \boldsymbol{R_{other}}$
- 1%, 2% and 4% O_2 in He and variety in back pressures (100 kPa, 125 kPa, 150 kPa, 200 kPa)
- Current densities at 0.1-0.2 V were used for local oxygen transport analysis
- **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

Accomplishment: Improved Durability

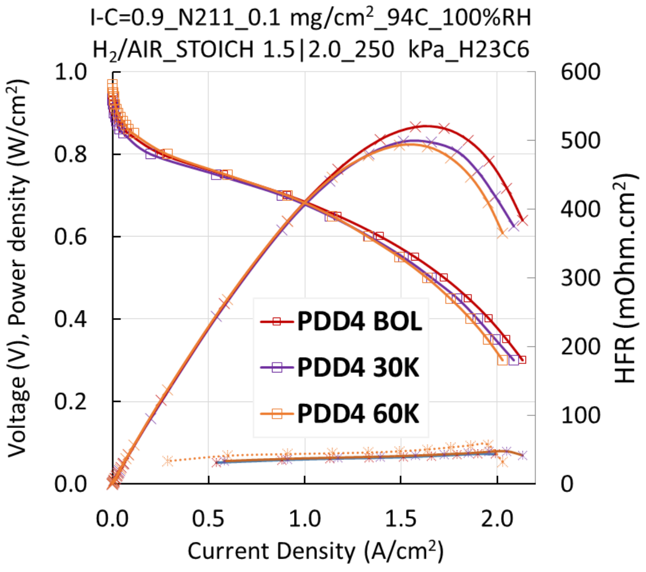
Nafion



PDD4



PDD4, Heavy Duty Condition



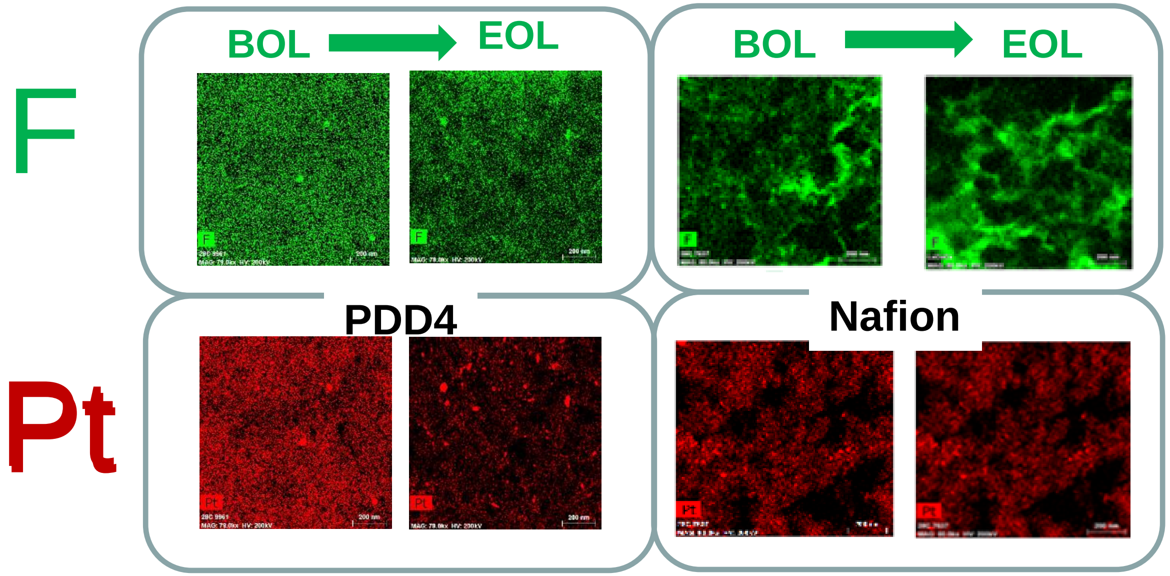
- **30K-60K Square Wave AST (0.6 – 0.95 V)** was used to degrade MEAs
- Previously **PDD4** MEA displayed best durability among PDD MEAs
  - Highly durable at heavy duty operating conditions: 94ºC, 65% RH, 250kPa
- **Fluoride Emission Rate (FER)** measured with hydrocarbon membrane (**Permion**)
  - 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/cm² Loss (mV)	40	16
MA Loss (%)	31	31
Anode FER (µg/h-cm²)	0.0047	0.0012
Cathode FER (µg/h-cm²)	0.0034	0.0022

TEM and Nano CT

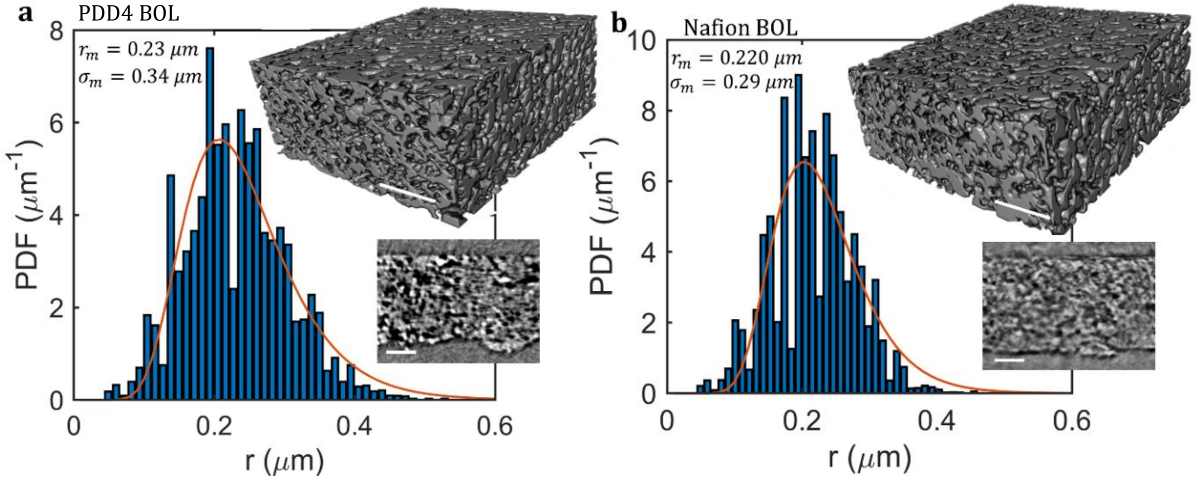
BOL = Beginning of Life

EOL = End of Life



Scale bar = 200 nm

Scale bar = 3 µm



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%)**

- 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

Responses to Previous Year Reviewers' Comments

This project was not reviewed in 2020

Collaboration and Coordination

- **CMS (**subcontractor**):** Dr. Dan Lousenberg**.** Synthesized HOPI samples for MEA design and testing; also provides ionomer permeability data
- **UCI** (subcontractor): **Prof. Iryna Zenyuk.** Performed ionomer and SO_3^- group coverage, some O_2 transport resistance and Nanoscale Computer Tomography
- **UConn** (subcontractor): **Prof. Jasna Jankovic.** Provided microstructure analysis with SEM and TEM: ionomer, Pt, Co distributions and particle size
- **General Motors**: Dr. Craig Gittleman. Provided flow field to measure local O_2 transport resistance

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 best performance demonstrating repeatability in HOPI polymerization process
- PDD HOPIs show 2x lower local oxygen transport resistance than Nafion
- PDD HOPIs in catalyst layers have more SO_3^- groups in contact with Pt than Nafion
- Microstructural analysis in agreement with performance and durability results
  - Porosity changes, Pt and Co loss, particle size growth

Future Direction

- **Scale up PDD4 polymerization process**
  - Transition from batch to semi-batch process
- **MEA performance Improvement**
  - Use higher quality membranes from 3M and Gore
    - 15 µm supported membrane with doped Ce
  - Adopt advanced flow field and GDL
- **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

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

Acknowledgments

- Financial support from DOE SBIR/STTR Program under award DE-SC001859

- Technical Manager
  - Dr. Dimitrios Papageorgopoulos

- Collaborators
  - Jasna Jankovic (Univ. of Connecticut)
  - Iryna Zenyuk (Univ. of California, Irvine)
  - Dan Lousenberg (CMS)
  - General Motors (flow field to measure local O_2 transport resistance)

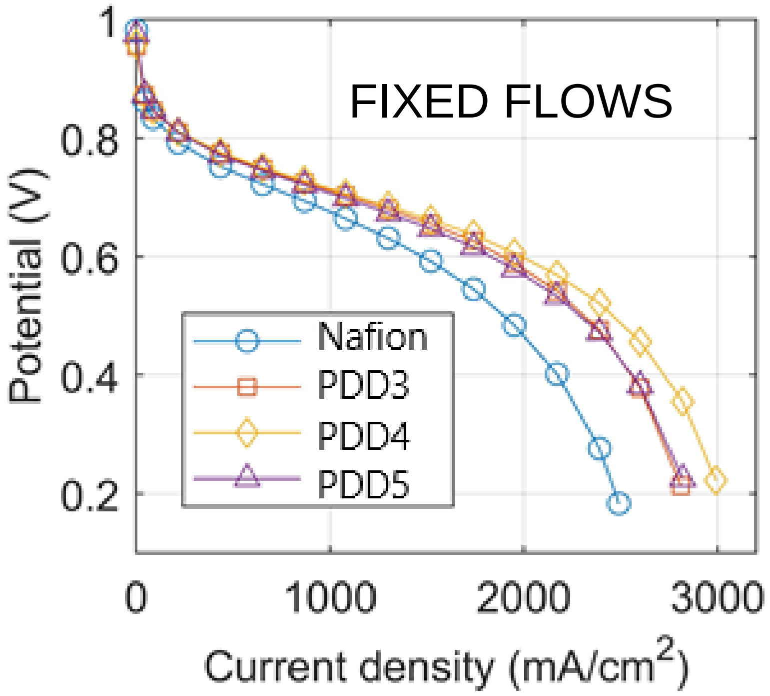
Technical Backup and Additional Information

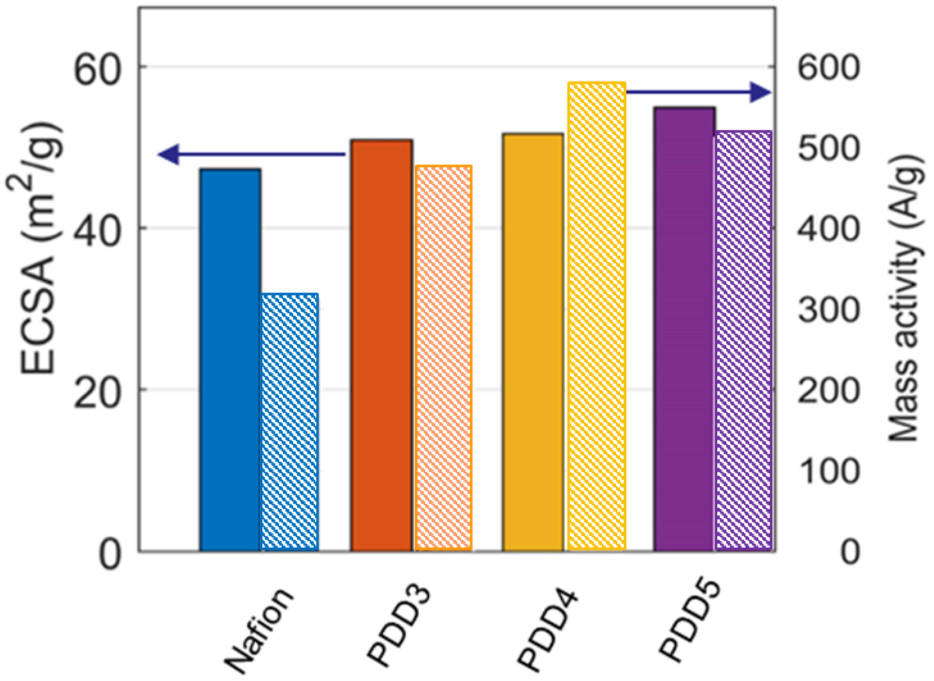
Technology Transfer Activities

- Secure multiple supports from potential ionomer users
  - GM
  - Nikola
  - Ballard
  - Plug Power
- License ionomer technology from CMS to provide products for fuel cell and other 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
  - 0.2 mg/cm^2 Pt for heavy duty vehicles

PDD vs Nafion Performance and ECSA

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





- 14-serpentine flow field with fixed flows achieves 1.2 W/cm^2

Progress toward DOE Targets

- Met the following DOE 2020 performance and durability targets

DOE Fuel Cell Electrocatalyst and MEA Technical Targets

CHARACTERISTIC	UNITS	PROJECT STATUS	2020 TARGETS
Mass activity	A/mg PGM @ 900 $mV_{IR\text{-}free}$	1.15	0.44
Loss in initial catalytic activity	% mass activity loss	11	<40
Loss in performance at 0.8 A/cm^2	mV	5	<30
Loss in performance at 1.5 A/cm^2	mV	50	<30
MEA performance	mA/cm^2_{geo} @ 800 mV	315	≥300
MEA performance	mW/cm^2_{geo} @ 668 mV	940	≥1000

- Some targets can be achieved using state-of-the-art PEMs from Gore

Publications and Presentations

- ECS Prime 2020 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, Session I01B-2219, 6 October 2020, 20:00 - 20:20

- Manuscript submission to Nature Energy:

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