Novel ionomers and electrode structures for improved PEMFC electrode performance at low PGM loadings

DoE Annual Merit Review

Washington, DC, June 6, 2017

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Team:

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FCPAD: LBNL (A. Weber, A. Kusoglu), NREL (KC Neyerlin), ORNL (K. More), LANL (R. Borup), ANL (D. Myers)

OVERVIEW

Timeline

- Project start date: 10/1/16
- Project end date: 9/30/19
  - 6 of 36 months complete

Barriers addressed

- Cost, durability, performance
- Operational robustness

Budget

- Total Project Budget: $3,245,349
  - Total Recipient Share: $649,071
  - Total Federal Share: $2,596,278
- Total DOE Funds Spent*: $320,000

* As of 3/31/17

** Sub expenses as of 3/31 also

Partners

- Tufts University
- Michigan Technical University
- FCPAD
  - LBNL, LANL, ANL, ORNL, NREL

Relevance & OBJECTIVES

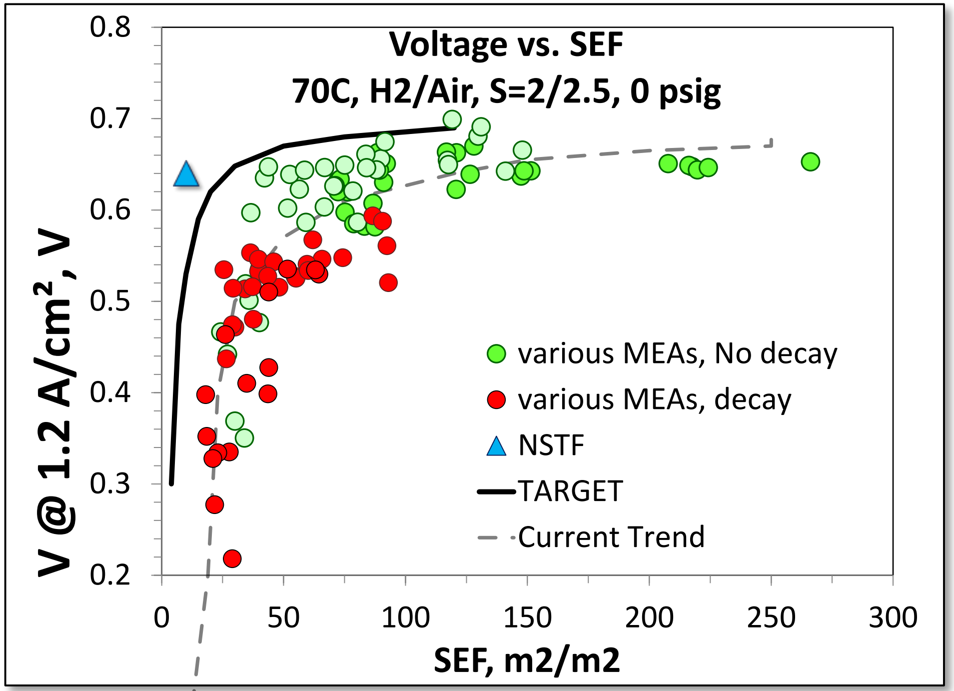
- Novel, electrode-focused ionomers will be generated, focusing on **combining conductivity with improved O_2 transport**
- **Understand and Optimize** cathodes utilizing **NSTF catalyst powder**
- **Integrate** ionomers with NSTF powder electrocatalyst to develop an advanced cathode of high activity and durability
- **Guide** development with state of the art and **novel characterization & modeling** techniques, including in-operando nano-CT and electrode pore network models.

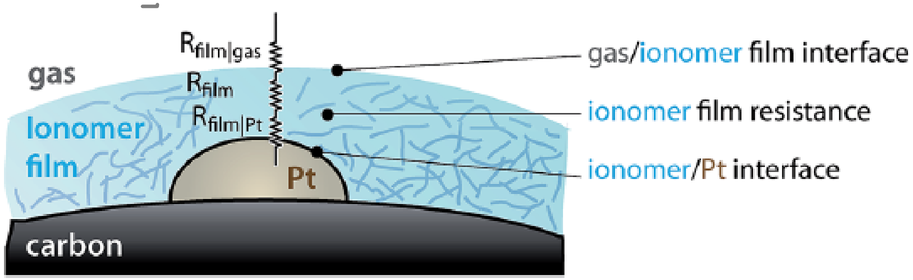
METRIC	2020[1] Target	Integrated Cathode	PRO-GRESS
PGM total loading, mg/cm^2	0.125	0.125	0.102[2]
PGM total loading, g / kW [150 kPa abs]	0.125	0.125	0.172[2]
Mass activity @ 900 mV iR-free, A/mg	0.44	0.44+	0.28
SUSD AST, %ECSA loss	<20 %	<20	N/A
SUSD AST, mV loss @ 1.2 A/cm^2	< 5%	< 5%	N/A
Support AST, % mass activity loss	< 30	< 30	28% (Pt)
Electrocatalyst AST, mV loss @ 1.5 A/cm^2	< 30	< 30	NA
Electrocatalyst AST, % Mass activity loss	< 40	< 40	45% (Pt)
MEA Robustness (cold/ hot / cold transient)	0.7/0.7/0.7	>0.7/>0.7/>0.7	0.6/NA/0.6[3]

[1] All metrics and DOE 2020 targets are taken from DE-FOA-0001412
[2] Assume using 0.025 mgPt/cm2 anode
[3] 3M transient protocols used for NSTF testing

APPROACH: Key Barrier
Cathode Transport limitations

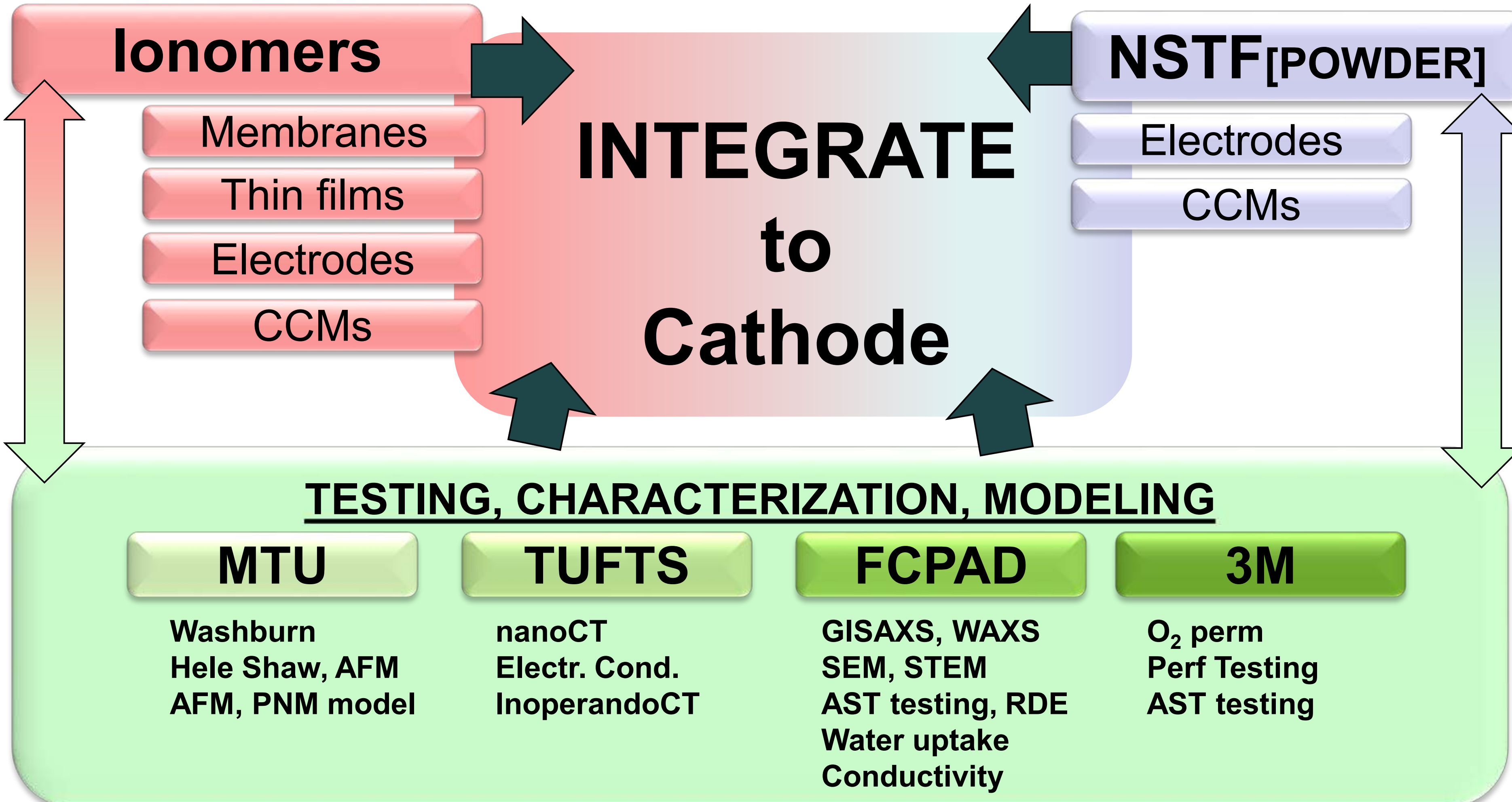
- Cathodes **at SEF's below 100 cm^2_{PGM}/cm^2_{planar}**,
  - Transport losses become significant
- NSTF cathodes break this trend
  - SEF's as low as 10.
- Likely that ***oxygen transport through ionomer*** near the reaction site is a key limitation
- FC155 goal is to
  - understand and improve Ionomer, bulk & local electrode transport
  - Maintain NSTF activity and durability





A. Weber, J. Mater. Chem. A, 2014, 2, 17207–17211

APPROACH: Team & Collaboration



APPROACH: Project Breakdown

NO -NOGO in RED

	TASK	OWNER	4	1	2	3		4	1		2	3		4	1	2	3
			BP1					BP2						BP3			
				2017					2017						2019		
IONOMER	**TASK 1: Ionomer development/evaluation**		o	o	o	o	o	o	o	o	o	o	o	o	o		
	1.1: Develop, clean, characterize ionomers with improved O2 transport & conductivity	3M	x	x	x	x		x	x		x	x		x	x		
	1.1.0: Baselines. PFSA 825 EW. PFIA (3M825 backbone)	3M	x	x													
	1.1.1: Phase 1. 3+ different Rf groups, sidechain imid content, x=0 and 1	3M		x	x	x		x									
	1.1.2: Phase 2. 1+ MASc (x>1), 3+ different Rf groups.	3M				x		x	x		x						
	1.1.3: Phase 3. 1+ more advanced ionomer.	3M							x		x	x		x			
	1.2: Ex-situ thin film characterization, RDE characterization of ionomer on Pt	FCPAD/MTU			x	x		x	x		x	x		x	x		
	1.3: Fabricate electrodes, CCMs and MEAs with new ionomer and Pt/C catalyst	3M		x	x	x		x	x		x	x		x	x		
	1.4. Ex-situ bulk characterization of ionomer films and electrodes	3M/Tufts/MTU			x	x		x	x		x	x		x	x		
	1.5: Extract electrode pore size distributions and contact angles vs ionomer type	Tufts/MTU			x	x		x	x		x	x		x	x		
	1.6: In-situ ionomer vs. electrode HCD, durability, water distribution, O2 permeability	3M/Tufts/MTU/ FCPAD		x	x	x		x	x		x	x		x	x		
	TASK	**OWNER**	4	1	2	3		4	1		2	3		4	1	2	3
NSTF	**TASK 2: NSTF electrode Development**		o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	2.1: Manufacture NSTF powder catalyst, NSTF powder electrodes, and MEAs	3M	x	x	x	x		x	x		x	x		x	x		
	2.1.1: Pt only NSTF	3M	x	x	x	x		x	x								
	2.1.2: Pt-alloy NSTF	3M			x	x		x	x		x	x		x	x	x	
	2.2: Evaluate impacts key structural variables (whisker, ionomer, ECA) on water content, location, and permeability	MTU			x	x		x	x		x	x		x			
	2.3: Evaluate performance and transport limitations vs. key NSTF electrode variables	3M/Tufts/MTU /FCPAD		x	x	x		x	x		x	x		x			
	2.4: Analyze NSTF electrode structure using tomography, STEM, in-operando nanoCT	Tufts/FCPAD		x	x	x		x	x		x	x		x			
	2.5: Evaluate NSTF electrode durability vs ECAs and catalyst compositions	3M/FCPAD				x		x	x		x	x		x	x		
	2.6: Evaluate activity, durability, performance impact of best-in class NSTF alloys	3M/MTU/FCPAD				x		x	x		x	x					
INTEGRATE	**TASK 3: Electrode Integration**							o	o	o	o	o	o	o	o	o	o
	3.1: Evaluate ionomers with optimal characteristics for NSTF electrode operation.	3M/TUFTS/MTU						x	x		x	x		x	x		
	3.2: NSTF modification for peak powder electrode operation	3M							x		x	x		x	x	x	
	3.3: water imbibition, structural characterization of new and decayed electrodes	Tufts/MTU/FCPAD									x	x		x	x	x	
	3.4: Optimized NSTF+new ionomer electrode MEA integration.	3M										x		x	x	x	x
MODEL	**TASK 4: Model development**		o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
	4.1: Adaptation of PNM to electrode	MTU	x	x	x	x											
	4.2: Link PNM to MEA model	MTU/Tufts/FCPAD		x	x						x	x				x	x
	4.3: Input new physics, and parameters, validate	MTU/Tufts		x	x	x		x	x		x	x		x	x	x	x
	TASK 5: Project Management	3M	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o

Progress and Objectives

Milestone Summary Table

TASK	TYPE	Milestone Description (Go/No-Go Decision Criteria)	Verification Process	DATE Q/M	%
1,1, 2.1	MLS	Synthesize first ionomer containing bis(sulfonyl)imide only containing protogenic groups devoid of sulfonic acids – at least 100g of > 10% solids in water alcohol solution. 20 grams of baseline 25 μg Pt/cm^2[geometric] NSTF powder prepared.	ICP, Conductivity for ionomer	**1/3**	**100% ICP**
1.6, 2.3	MLS	Setup and validation of DoE AST tests, electrode performance and O_2 transport script, and carbon-ionomer dual layer test script. Test TKK 10V50E catalyst with 3M825 ionomer at 3 IC ratios and 3 cathode Pt loadings.	DOE AST's, report	**2/6**	**100%**
1.2, 1.4, 2.2	MLS	Complete characterization of baseline ionomer, Pt/C, and powder NSTF Pt electrode materials. Characterizations to include wettability testing / water imbibition, capillary pressure and breakthrough pressure, percolation testing as a function of RH, and electrode layer analysis using SEM/EDS, TEM, and AFM.	Report	**3/9**	**66%**
2.6	MLS	NSTF powder electrode achieves mass activities >= 0.30 A/mg Pt	DOE AST	**4/12**	**96%**
1.4, 1.5, 2.4	MLS	Develop nano CT method and test baseline & NSTF materials & provide pore and ionomer distributions.	Report on morphology of baseline vs. NSTF electrodes	**4/12**	**66%**
4	MLS	PNM adapted to the electrode with the model delivering predictions at 40 ^{o}C and 80^{o}C.	Report/ demonstration	**4/12**	**50%**
1, 2	**GNG**	1) NSTF powder electrode ECSA >= 15 m^2/g and SEF > 40 m^2/ m^2 , 0.7 robustness factor and 2) Ionomer material developed exceeds the bulk O_2 permeability of the baseline 3M825 ionomer, with similar or better proton conductivity to 3M825	1) Evaluated in MEA using DOE protocols/ASTs 2) 3M O_2 permeability method(s)	**4/12**	**95% / 70%**
4.3	MLS	Reaction-kinetics model is consistent across full potential range & converges within PNM framework. PNM-continuum model framework converges and predicts polarization curves for baseline and NSTF electrodes for two temperatures T = 40 ^{o}C and 80^{o}C.	Report including predictions at DOE AST	**5/15**	

Progress and Objectives

Milestone Summary Table					
Recipient Name:		3M CORPORATION / Energy Components Program			
Project Title:		Novel ionomers and electrode structures for improved PEMFC electrode performance at low PGM loadings			%
TASK	TYPE	Milestone Description (Go/No-Go Decision Criteria)	Verification Process	DATE Q/M	
2	MLS	NSTF Cathode ECSA >= 25 m^2/g.	DOE ASTs	6/18	100
4.1, 4.2	MLS	MTU/Tufts: Baseline structures input to PNM. Electrochemistry connected. Initial fitting completed. PNM delivering initial predictions.	Report on initial predictions	7/21	
2	MLS	NSTF activity >=0.4 A/mg Pt in an electrode. 0.2 g/kW with NSTF containing electrode.	DOE ASTs	8/24	
1,2	**GNG**	Ionomer exceeds 3M825 O_2 perm by 33% with similar or improved conductivity. 0.35 A/mg Pt, 0.175 g/kW power output	3M O_2 perm	8/24	40%
4.3	MLS	MTU/Tufts: PNM - continuum predicts pol curves for T = 40 and T = 80C within 10% for NSTF and baseline electrodes. Capillary pressure diagrams vs ionomer predict within 10%	Report	9/27	
2.4	MLS	Tufts: In-operando Nano-CT experiments for visualizing water distribution, local hydrophobic and hydrophilic regions. Electrode capillary pressure diagrams generated and provided to PNM/MEA model and report prepared.		9/27	
4	MLS	PNM predicts pol curves for T = 40 and T = 80C within 10% for NSTF and baseline	Report/ DEMO	9/27	
3	MLS	Support cycle stability DoE targets achieved. < 40 % activity loss during catalyst cycling AST.	DOE ASTs	10/30	
3	MLS	Cathode activity >=0.44 A/mg PGM in an electrode. Metal stability <=30% activity loss. 0.125 g/kW with NSTF powder containing electrode.	DOE ASTs	12/36	

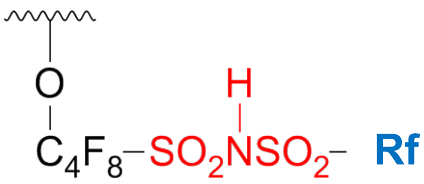
APPROACH: ELECTRODE Ionomers

2 methods to attack transport limitations

Improve electrode **ionomer O_2 permeability**

3M Perfluoroimides (IMIDE 1,2,etc)

Increase O_2 perm,
May reduce catalyst poisoning



Additional New Proprietary Ionomers

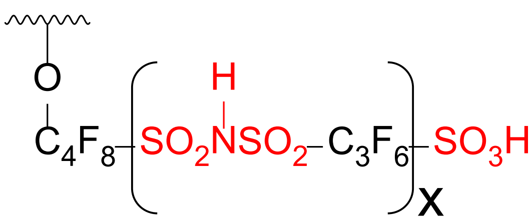
GOAL: increase O_2 permeability

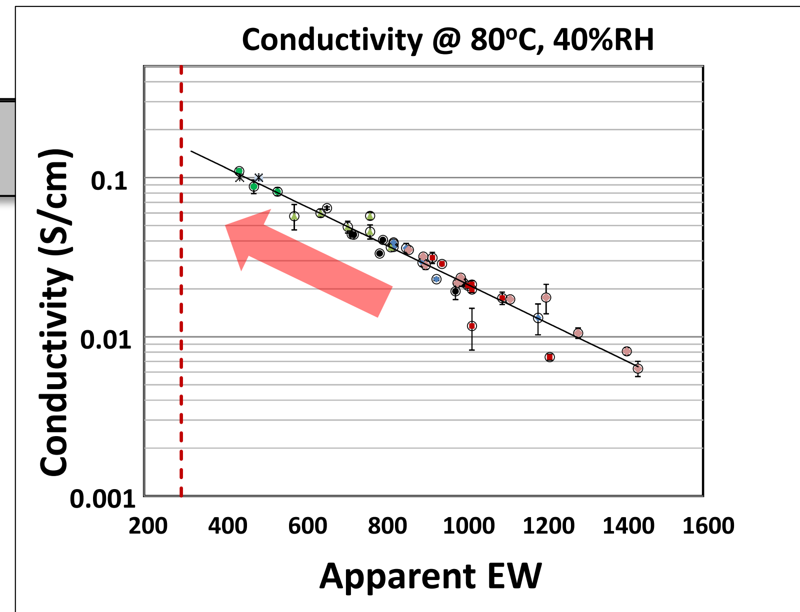
Improve electrode **ionomer H+ conductivity**

– Less ionomer = better transport

MASC: Perfluoroimide acids

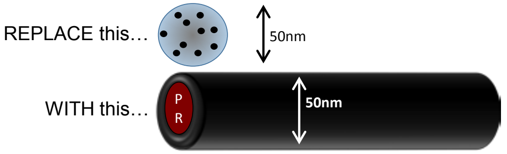
- Extremely high conductivity





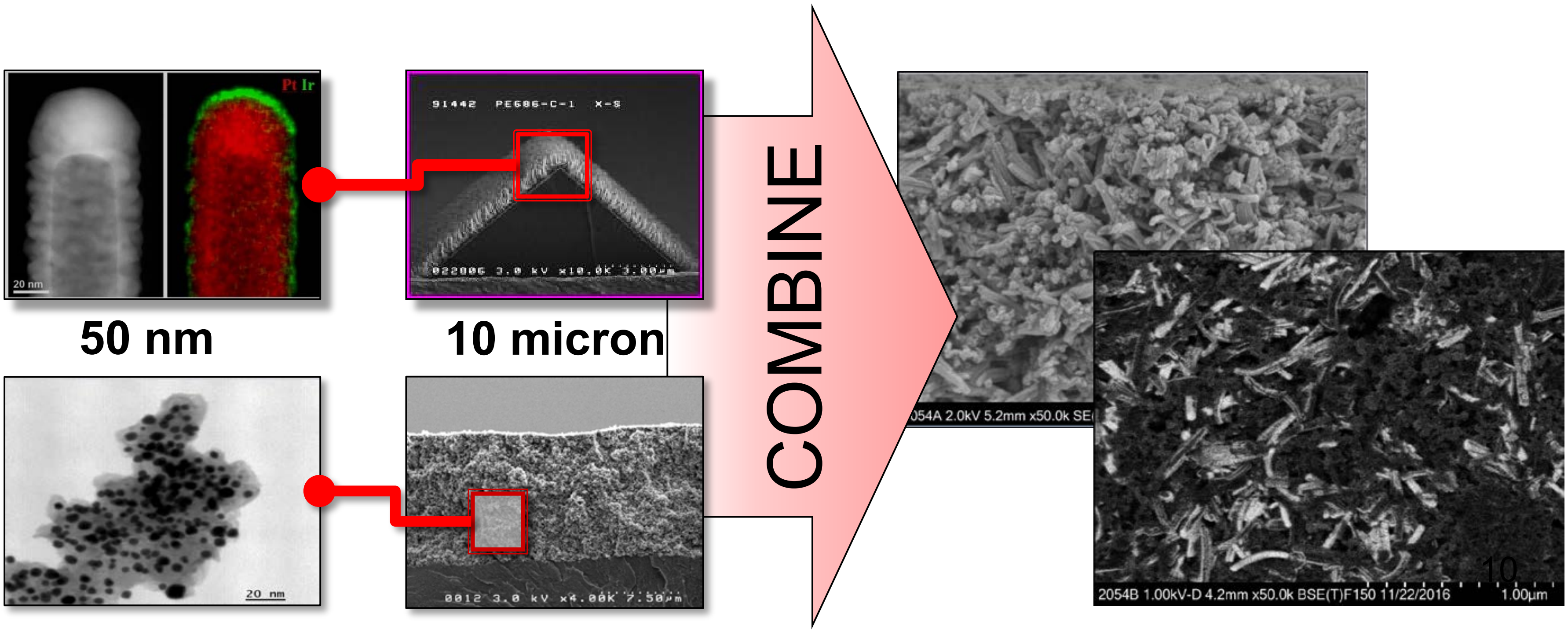
M. Yandrasits. DoE AMR (2015).

APPROACH: Powdered NSTF



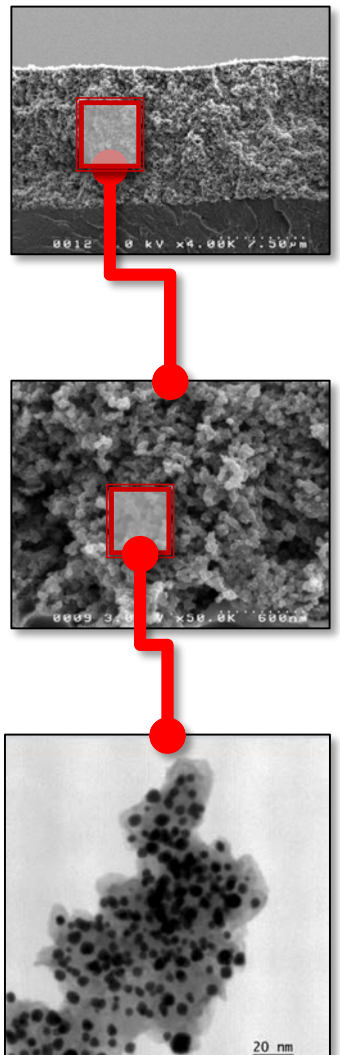
- Utilize powdered NSTF (Task 2)
- Utilize a dispersed electrode "package" (Task 1)
- Optimize in Task 3

- Powdered NSTF electrode
  - 10-100X thicker than NSTF
  - Contains ionomer
  - Improved operational robustness
  - Not constrained to liner NSTF loadings

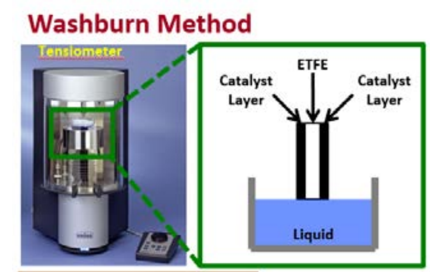


APPROACH: Test Methods (Vision)

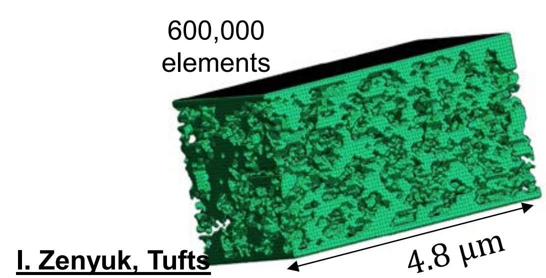
<u>Characterize electrode transport: in-situ/ex-situ</u>



- BULK level
  - Ionomer O_2 perm — GM Method (Zhang et al, 2013) / 3M
  - Electrode gas: — Carbon ionomer films atop CCM / 3M
  - Electrode H+ — C-Ionomer films between CCM / Tufts
  - Performance/robustness/AST's — LANL/NREL/3M/MTU
- Intermediate
  - Water imbibition — MTU Washburn method
  - NanoCT — Tufts
  - In-operando NanoCT — Tufts

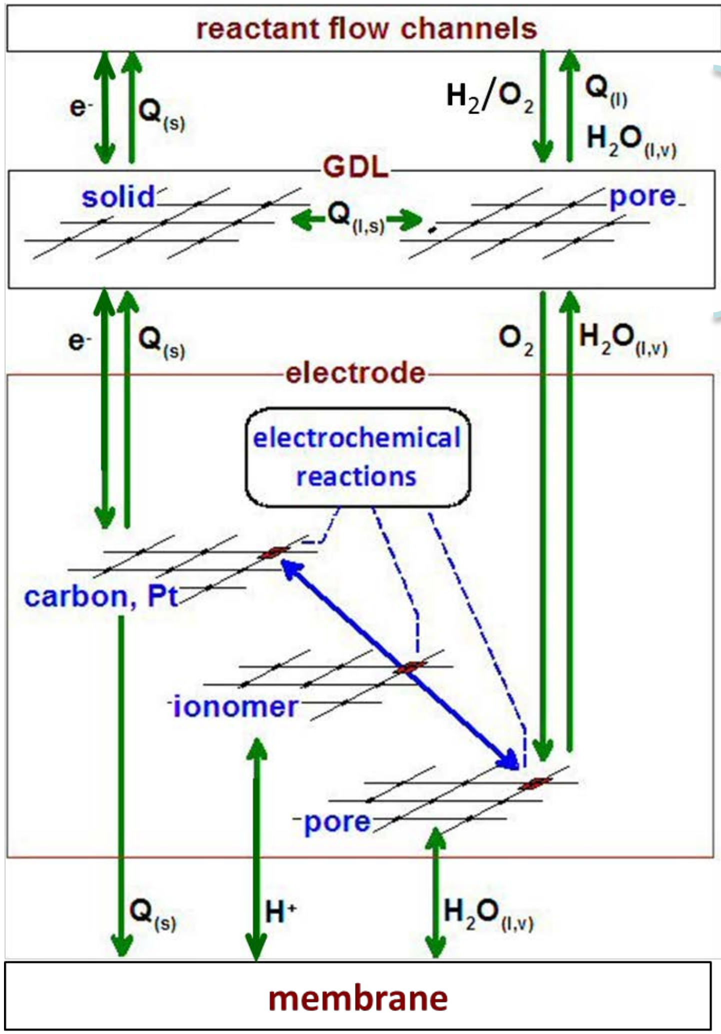


- LOCAL transport
  - Differential O_2 xport — 3M / NREL
  - Ionomer thin film — LBNL / MTU
    - GISAXS, WAXS, etc
  - STEM, etc — ORNL
  - Catalyst — ANL



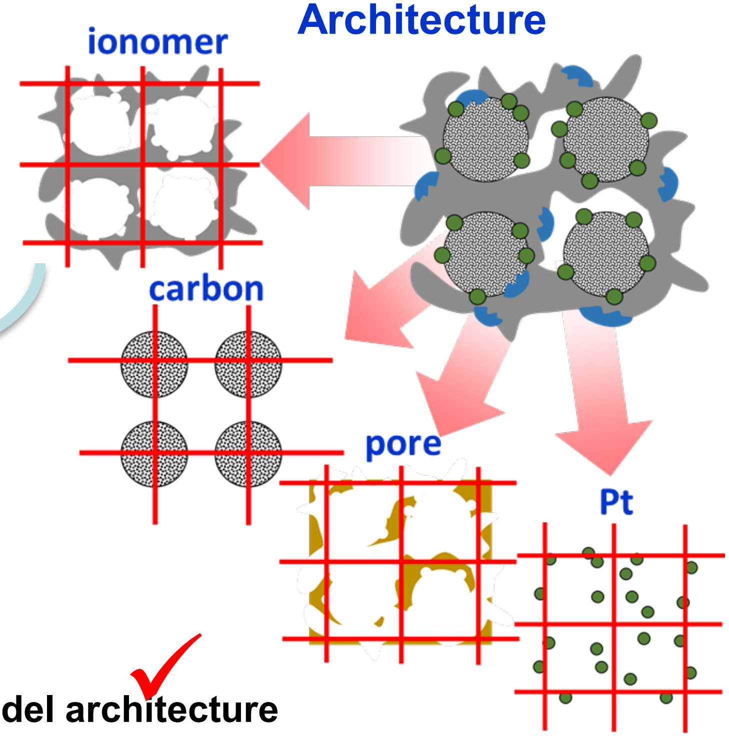
APPROACH: Pore Network Model

Catalyst Layer transport model between the membrane and the GDL transport model



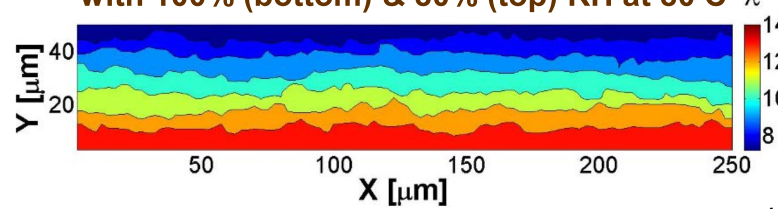
GDL model completed on previous DOE contract.

Electrode Model Architecture



Ionomer model architecture completed; includes osmotic drag and diffusion

Example of water diffusion in membrane with 100% (bottom) & 80% (top) RH at 80 C

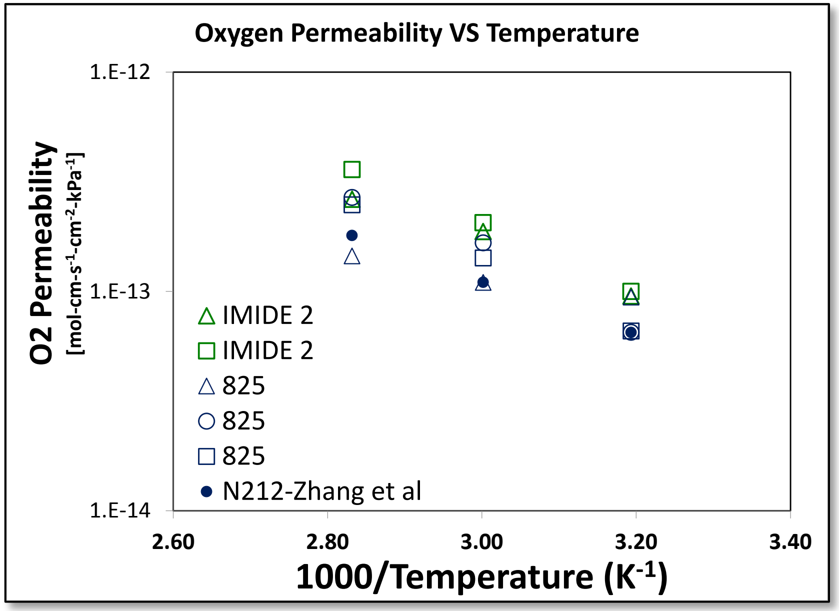


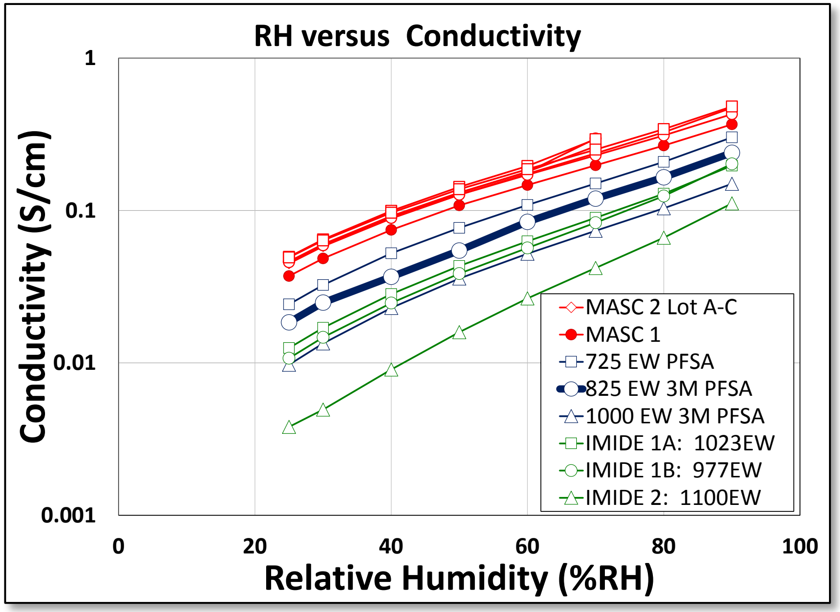
RESULTS: Novel Ionomer Development

- Bulk O_2 perm characterization
  - Validated GM (Zhang ECS 2013) method
- Imide 2 showing possible improvement of 3M825 baseline
- **MASC** ionomers show high conductivity, as expected
- Initial novel **IMIDE** ionomers approaching baseline conductivity

Combined results leading toward **BP1 GNG** deliverable for Task 1

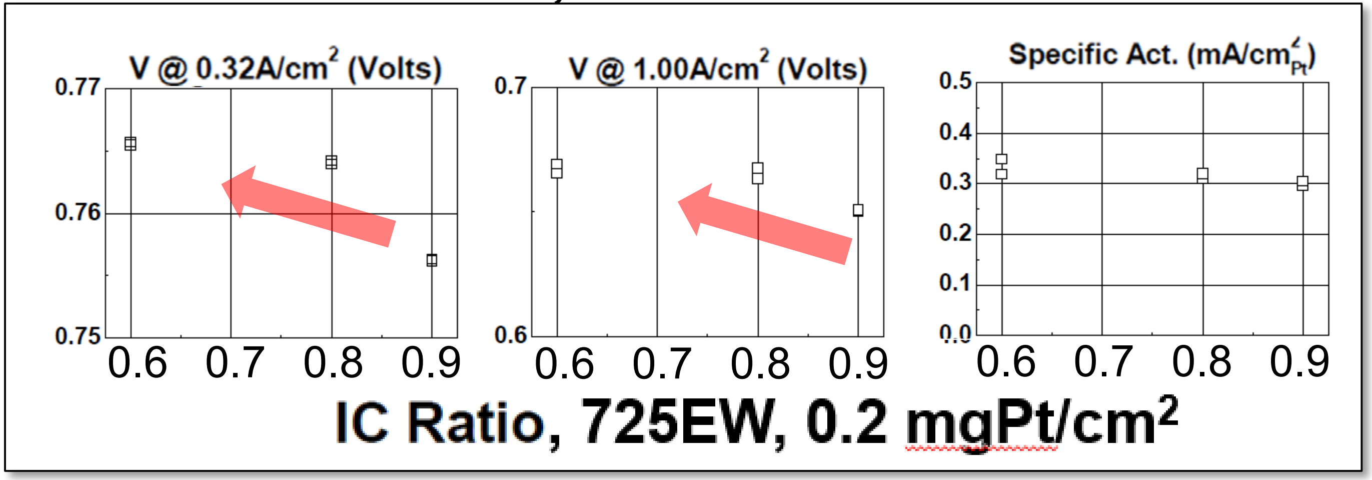
"BP1 GNG: Exceed 3M825PFSA and bulk O2 perm simultaneously, or demonstrate path toward such"



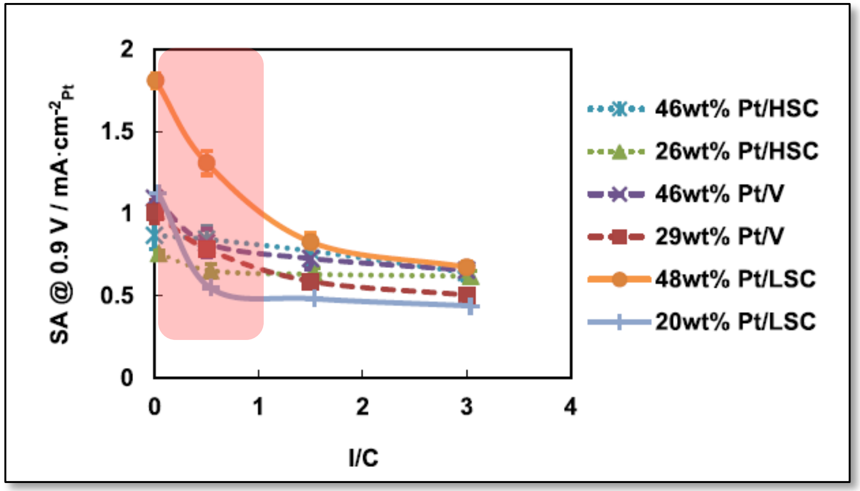


RESULTS: Novel Ionomer Development

- Testing with TKK 10V50E: **Baselines, trends**
  - 5 loadings
  - 4 I/C's
  - 4+Ews
  - **MLS Q2 met**



- Increased performance @ lower I/C
- Little to no specific activity gain between I/C=0.6 – 0.9
  - Broadening EW+ I/C range
  - FCPAD look into ionomer coverage at low IC ratios



K. Shinozaki et al. / JPS 325 (2016) 745

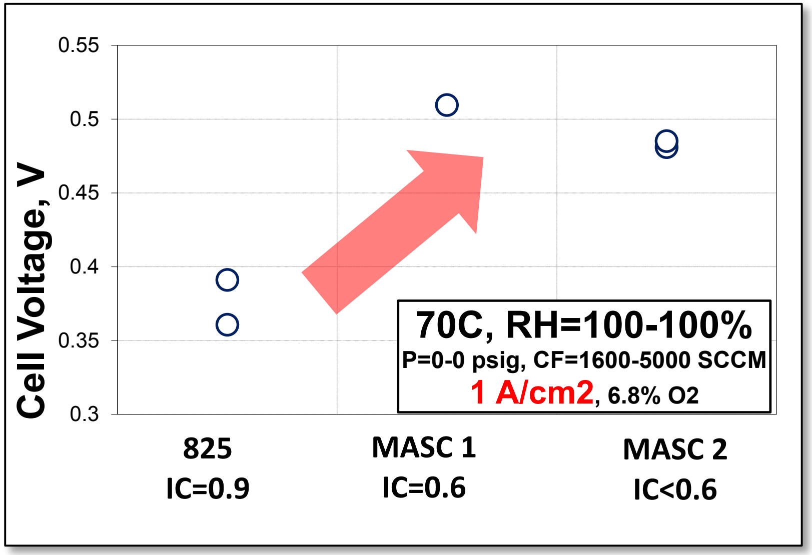
- **Task 2 GOAL: Improved transport, activity, performance with reduced ionomer amount**

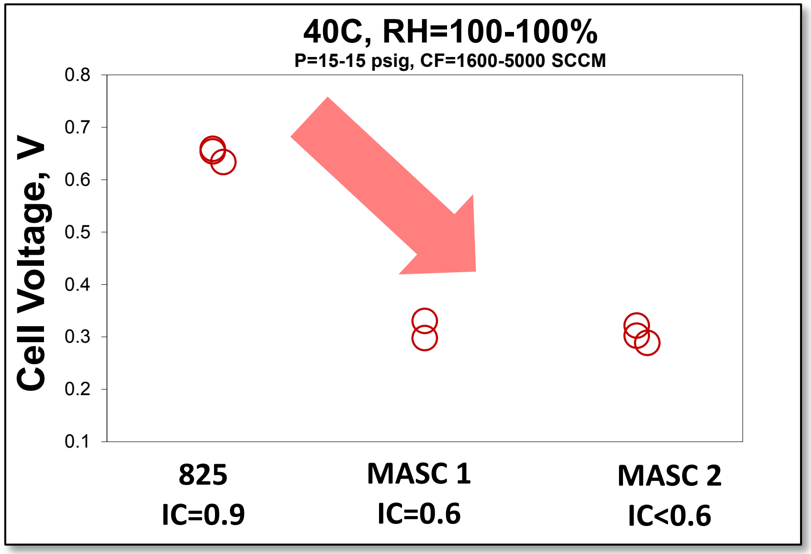
RESULTS: Novel Ionomer Development

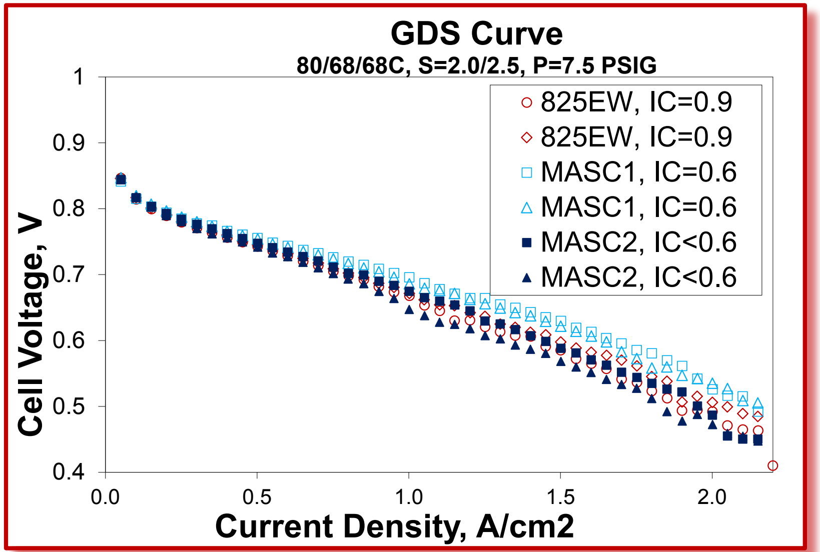
Tested with MASC ionomers

- **Task 1, MLS Q2/4/6**

- Low IC+EW = improved performance
- Reduced O_2 sensitivity
- Can be low T performance losses
  - Flooding

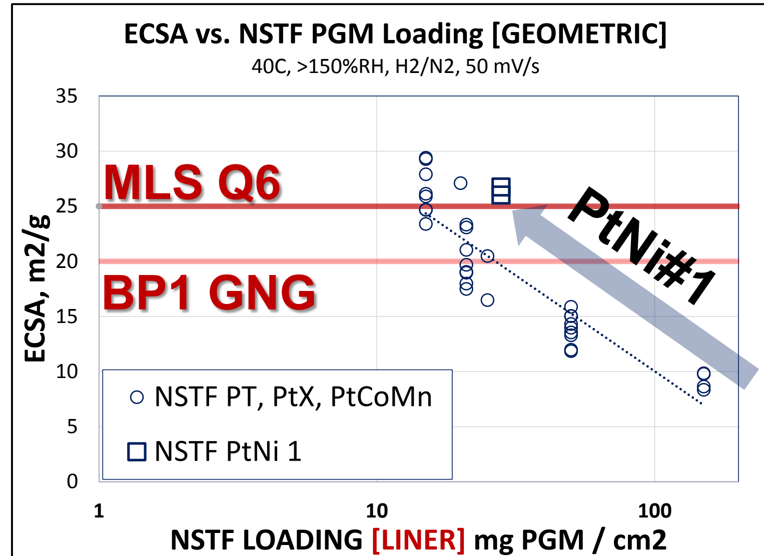




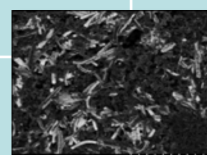


RESULTS: Powdered NSTF

- Powdered NSTF
  - Eliminates geometric constraint
  - Requires new variables (Wh/S, I/S)
- **Task 2 BP1 GNG Targets met**
  - **ECSA**

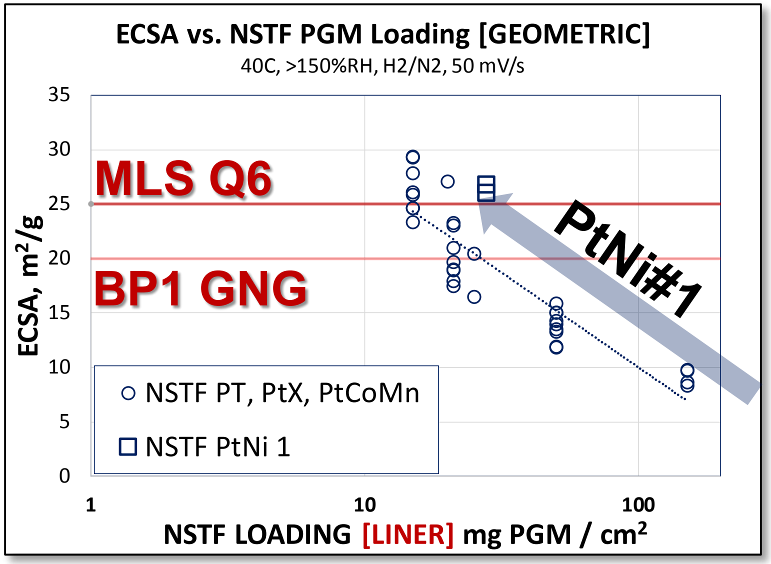


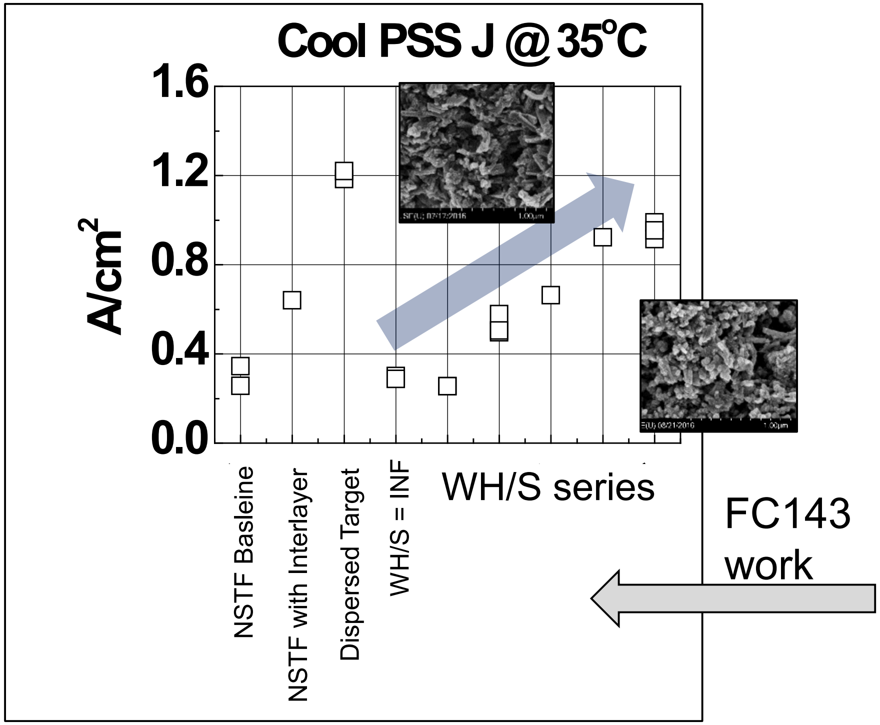
PtNi#1 : Showing higher area than similar PtX loadings

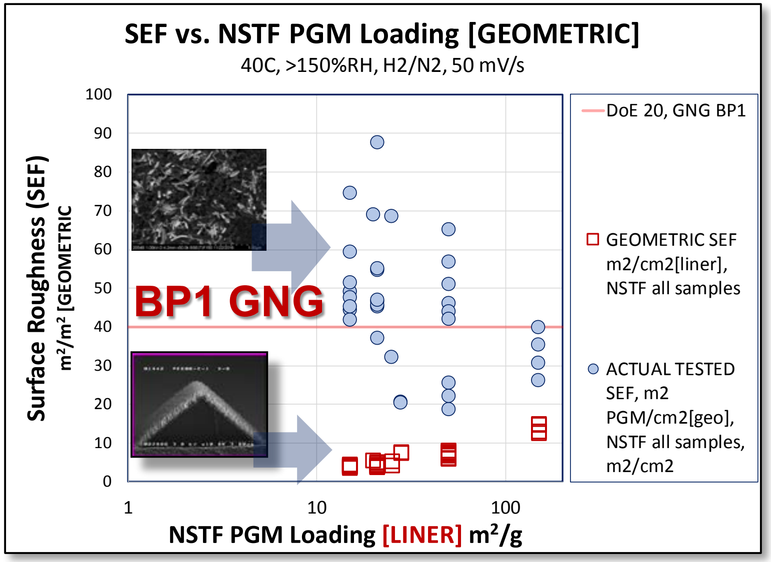
TYPE	Desired load	NSTF on liner	ECSA	SEF	Wh/S	I/S
	mg / cm2	mg / cm2 [geo]	m2/g	m2/ m2[geo]		
NSTF	0.15	0.15	7	10.5	---	---
NSTF	0.05	0.05	14	7	---	---
dNSTF	0.15	0.05	14	**21**	**Optimi-zing**	
dNSTF	0.15	0.025	20	**30**		
dNSTF	0.15	0.028	26	**39**		

RESULTS: Powdered NSTF

- Powdered NSTF
  - Eliminates geometric dependence
  - **Allows thicker electrodes**
  - **Leads to enhanced robustness**
- **Task 2 BP1 GNG Targets met**
  - **ECSA**
  - **SEF**
  - **Robustness**



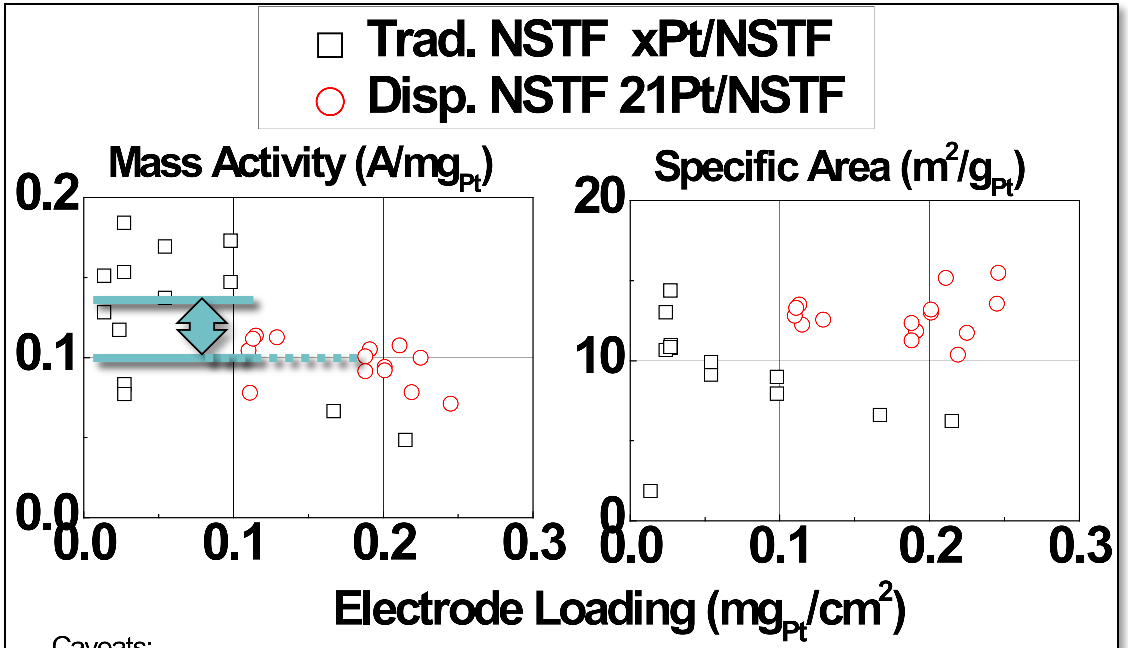




RESULTS: Powdered NSTF

- Initial mass activities of Pt-dNSTF
  - Pt: 0.09 to 0.17 A/mg
  - PtCoMn: 0.26 – 0.28 A/mg Pt
    - O_2 Tafel extraction
- **MLS Q4 = 0.30 A/mg Pt**

- There may be some activity loss compared to NSTF
  - **Retains ~70% classic NSTF activity**



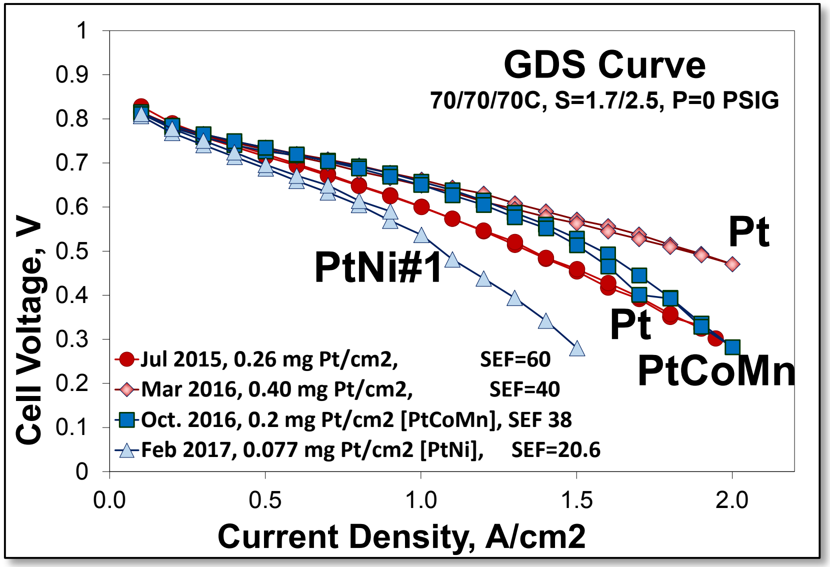
Caveats:
1). Trad. NSTF from several different stations
2). ECSA determination challenging for ultra low absolute SEFs
3). ORR Activity corrections for short, crossover may not be valid for low absolute activities

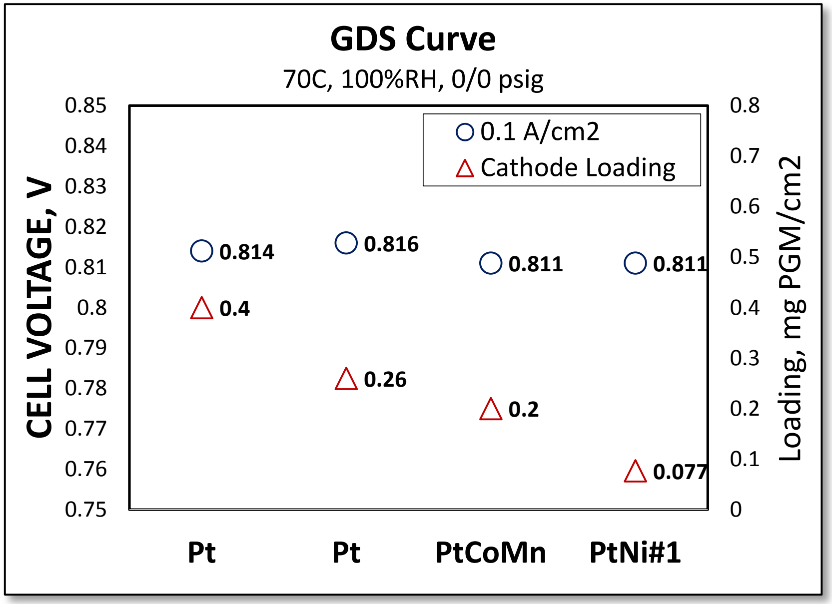
RESULTS: Powdered NSTF

- First alloy downselect from FC143 tested (Task#2)
  - PtNi#1
- Good activity
  - 3-4.5X Pt reduction with 0-5 mV performance loss @ 0.1 A/cm^2
  - **GNG BP1, MLS Q6**
- Good performance
  - 0.171[2] g/kW
  - **MLS Q6, GNG BP2**

  [2]assumes 0.025 mgPt/cm^2 anode

  [2]0.6V, 80/68/68C, 7.5 psig H_2/Air
- Continue to optimize electrode package to accept transition metals





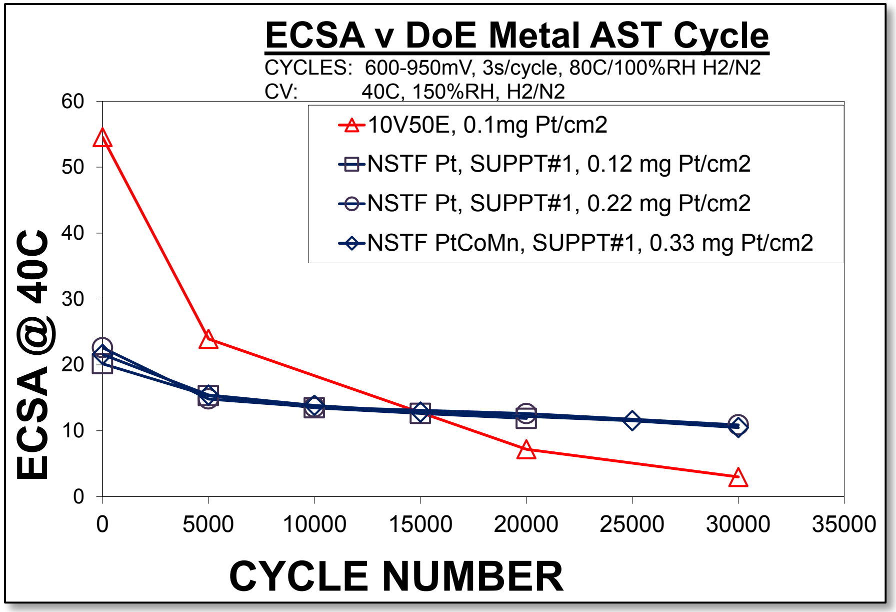
RESULTS: Powdered NSTF DoE AST

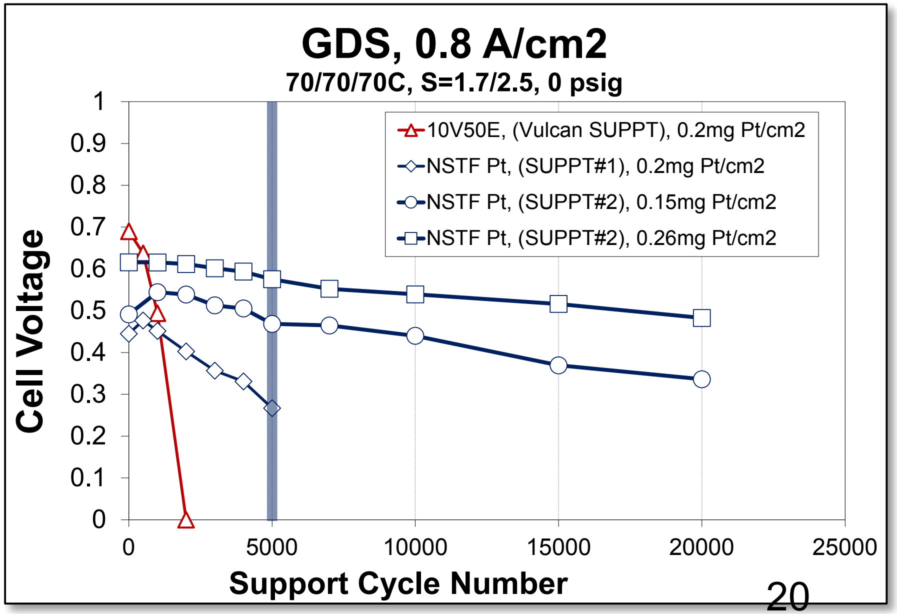
METAL AST just begun

- 10V50E loses 90+% ECSA
- NSTF 25Pt (as Pt or alloy) loses ~40-45%
- FC143 downselect improvements will be evaluated in 2017 & 18

SUPPORT AST

- Dispersed NSTF shows better stability than 10V50E
  - SUPPORT#2 survived 20K cycles
  - **MLS Q10 achieved**

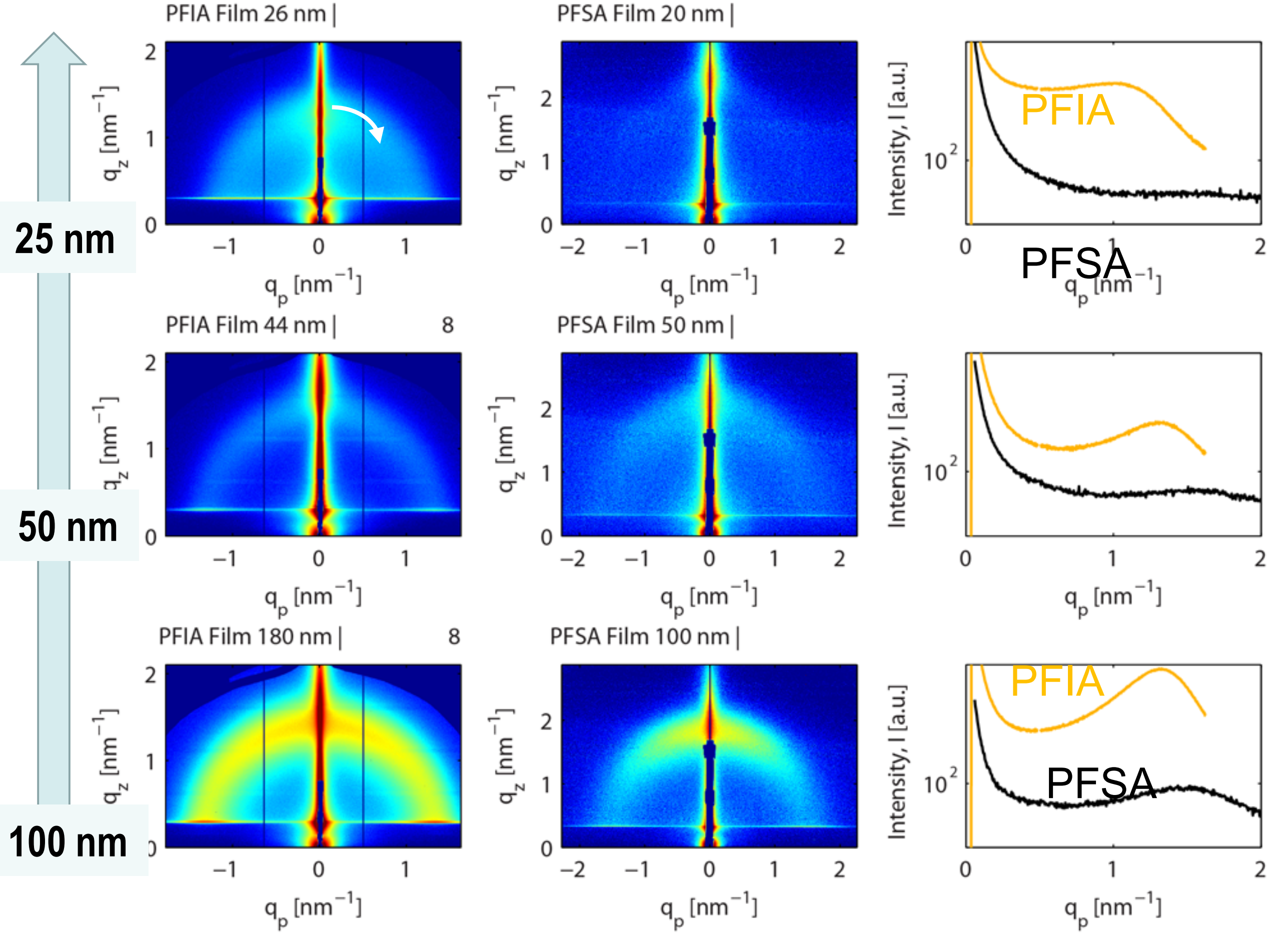




RESULT: Morphology of 3M Ionomer GISAXS

PFIA
Isotropy

PFSA*
Parallel alignment



- PFSA:
  - Weak phase-separation
  - Some domains are parallel to the substrate
    - O.P. = 0.50 – 0.60
    - Could be a proxy for transport limitation

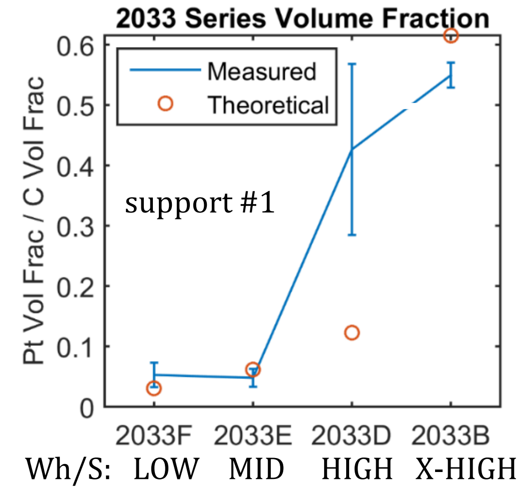
PFIA:
  - Stronger phase-separation
  - Well-defined morphology (i.e. Hydrophilic domains)
  - Closer to random alignment
    - O.P. = 0.40 – 0.45
    - **Favorable for transport**

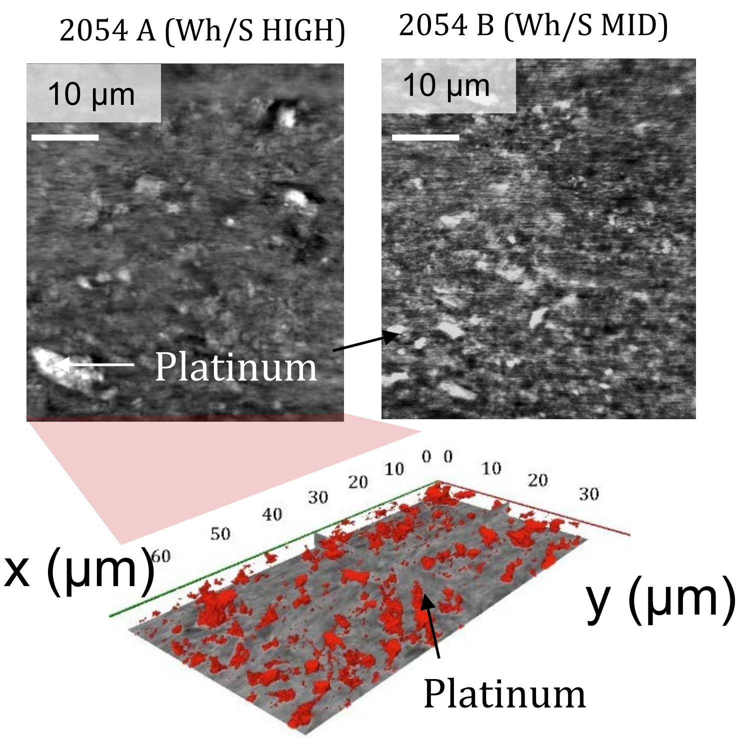
* Both ionomers have the same backbone length.
Thin films spin cast on Si. GISAXS under saturated conditions.

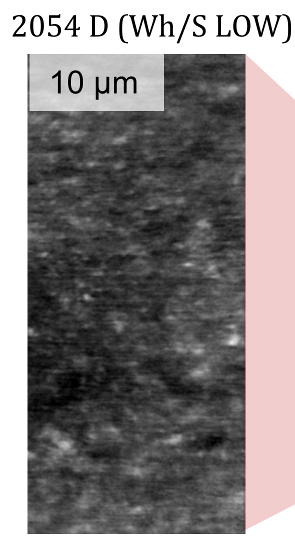
PFSA data from: Kusoglu et al. Adv. Functional Materials, 26 (2016) 4961–4975

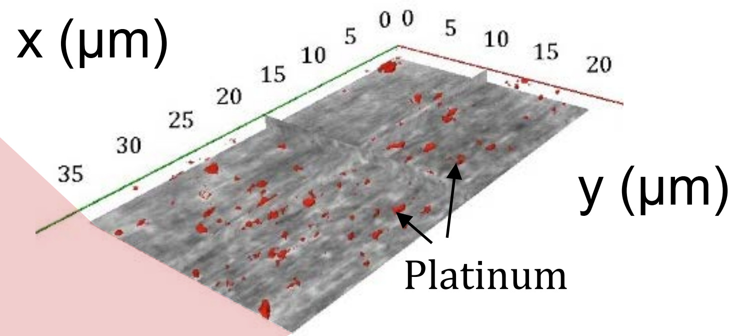
Results: Tufts NanoCT

- Examining key variables
  - Whisker / support ratio
  - Ionomer / support ratio
  - Extract trends and relate to performance and transport data









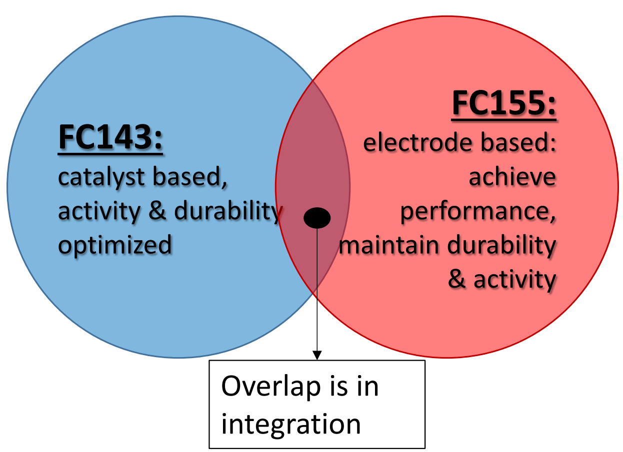
- Nano-CT shows increase in Pt and whisker volume fraction with Wh/S ratio for both supports

COLLABORATIONS

DoE FC155

- **3M**: A. Haug, M. Lindell, T. Matthews, J. Abulu, M. Yandrasits, A. Steinbach, M. Kurkowski, G. Weatherman, G. Thoma, I. Khan, 3M CRL
- **Tufts U.**: NanoCT, H+ conductivity, modeling
  - Iryna V. Zenyuk, D. Sabarirajan, Stanley Normile
- **Michigan Tech.:** Water transport, model development, performance testing
  - Jeffrey Allen, K. Tajiri, E. Medici, and team
- **FCPAD:** STEM, GISAXS, WAXS, AST testing, differential testing, RDE
  - Adam Weber (PoC), LBNL, LANL (R. Borup), ORNL (K. More), ANL, NREL (K. Neyerlin)

- **FC143: Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports**
  - Johns Hopkins, Purdue University
  - ORNL, ANL, NREL, FCPAD
- **FC144: Highly-Accessible Catalysts for Durable High-Power Performance**
  - **General Motors,** 3M, Carnegie Mellon, Cornell University, Drexel University, NREL
- **NREL**
  - 3M PFSA CCMs for differential testing and development



SUMMARY

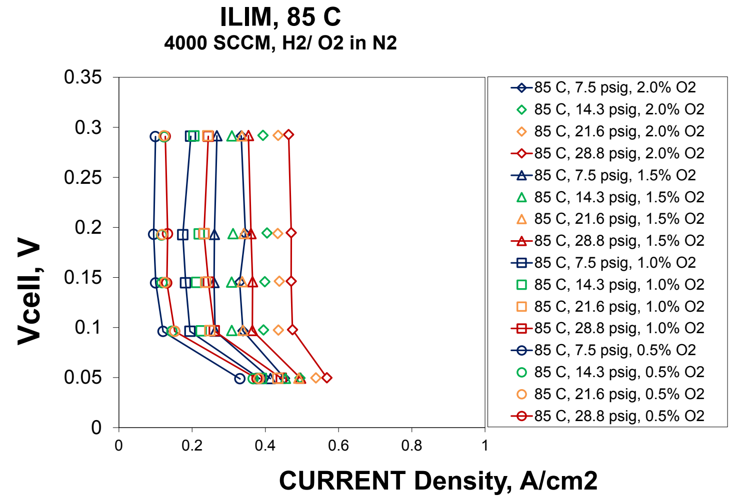
- Significant materials generated for this project (MLS Q1, Q2)
  - NSTF and Ionomers
- Ionomers showing paths toward BP1 GNG (O_2 permeability and conductivity)
  - MASC: Increased performance, Lower IC = Better transport
  - IMIDE: As good/better bulk permeability
- Dispersed NSTF
  - Excellent ECSA & areas meeting BP1 GNG, MLS Q6
  - Metal/support durability gains show path to durability milestones
    - NSTF durability largely remains
  - Good activity & performance approaching BP1 GNG, MLS Q6
- Characterizations & Collaborations
  - Underway and at or ahead of Q3 and Q4 milestones
- Model
  - Framework developing toward Q4 deliverable

FUTURE Work

- Ionomers
  - Continue IC series testing through Q3
  - Combine with alternative Pt/C catalyst
    - Lower loading than 10V50E
    - Surface carbon
  - Enhance IMIDE conductivity by close of Q4
- dNSTF
  - Examine transport characteristics with differential testing by Q4
  - Integrate with best dispersed package (ionomer+support)
  - Transition metal analysis in Q3 and Q4
- AST testing
  - Complete for all baselines by Q3
- FCPAD
  - Examine dNSTF baseline with STEM
  - Examine IMIDE#2, MASC#2 with GISAXS, differential testing, RDE
  - Examine low I/C ratio vs. standard I/C ratio structural differences
  - STEM of dispersed NSTF to evaluate ionomer coverage (Q3-Q4), impact of support type (Q5-6), effect of operation and decay (Q6-7)
  - Baseline AST testing, differential testing (Q3-Q8)
- Tufts
  - nanoCT, in-operando CT developments
  - Hydrogen conductivity vs. I/C and ionomer type
    - Compare to nanoCT data for ionomer
- MTU
  - Complete PNM framework (Q4)
  - Provide water imbibition and transport data for key series (I/C and EW) (Q3-4)

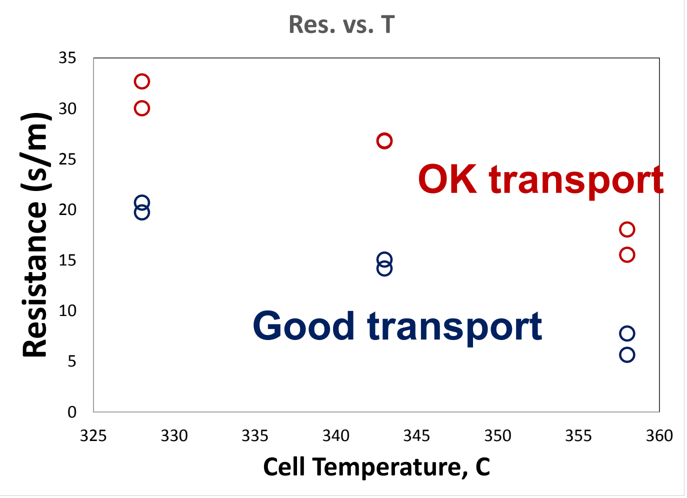
Technical Back-Up Slides

APPROACH: Test METHODS

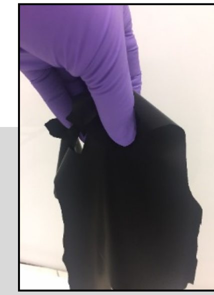


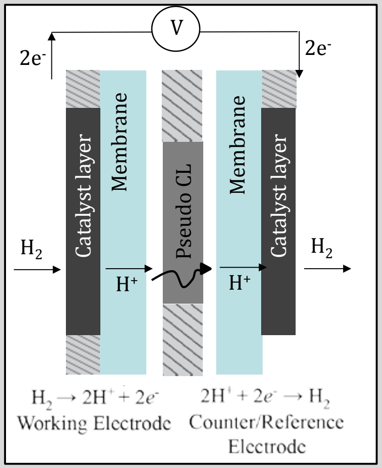
METHODS

- Differential cell testing
- Status: UNDERWAY
  - Extract local limitations UNDERAY
- Use with
  - dNSTF electrodes
  - Standard electrodes
  - Different ionomers in electrodes
  - Carbon-ionomer films atop electrodes

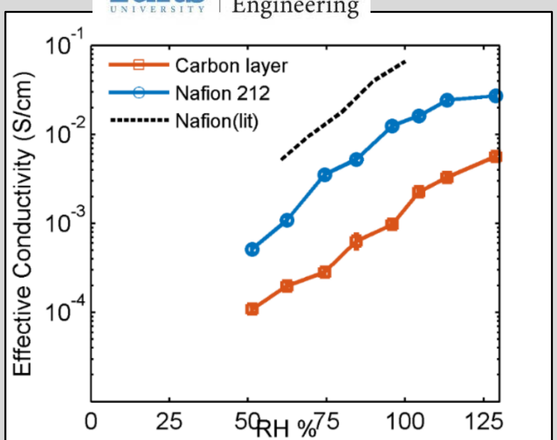


APPROACH: TEST Methods / Carbon-Ionomer layers

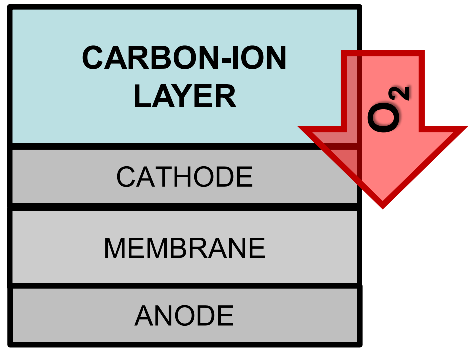


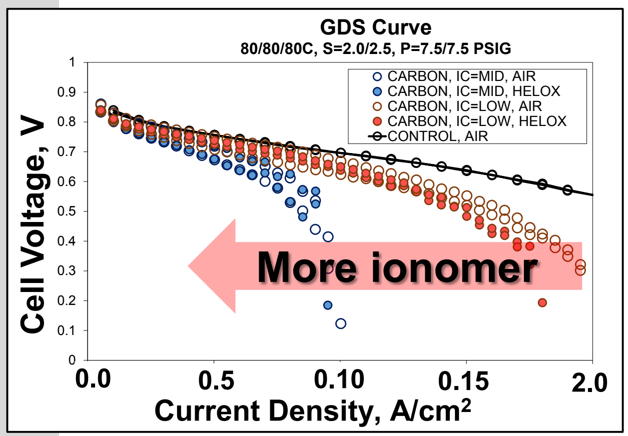


Tufts University School of Engineering



PROTON TRANSPORT

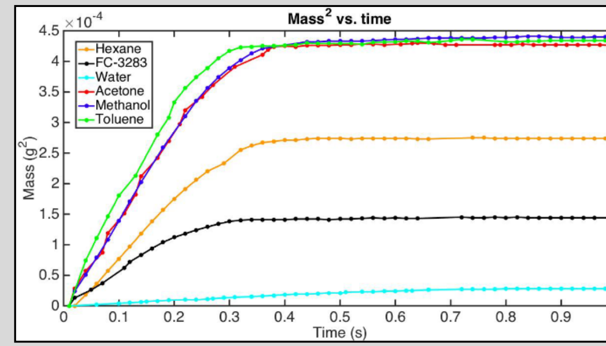




GAS TRANSPORT

Washburn Method

- Effective Surface Energy
- Pore Volume
- Ionomer Uptake
- Liquid Permeability



Hele-Shaw Method

- Gas Permeability
- Liquid Permeability
- Capillary Pressure
- Percolation Pressure
- Ionomer Uptake

WATER TRANSPORT

APPROACH: Test METHODS

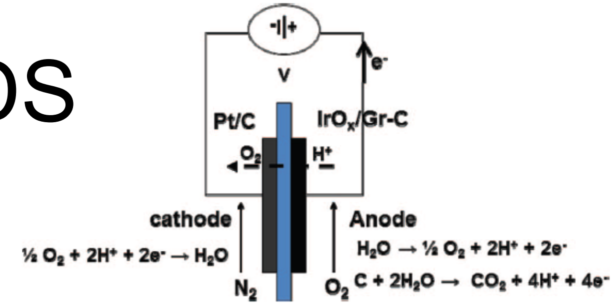
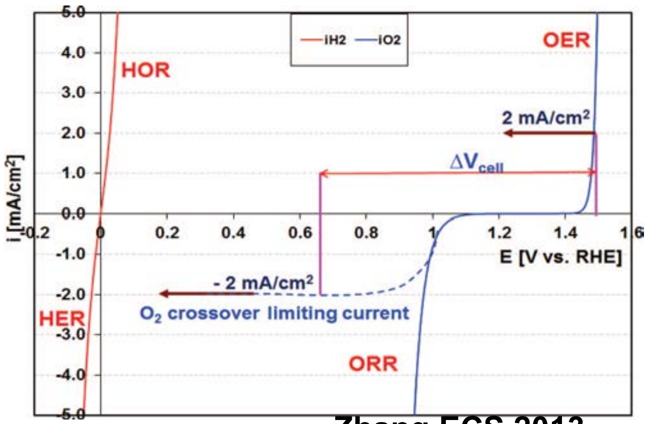


Figure 1. Schematic illustration of the experimental setup for the electrochemical measurement of the O_2 permeability through a polymer electrolyte membrane.

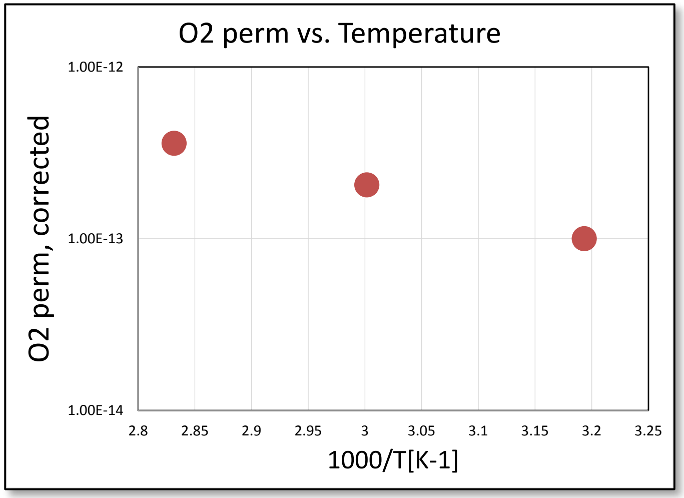


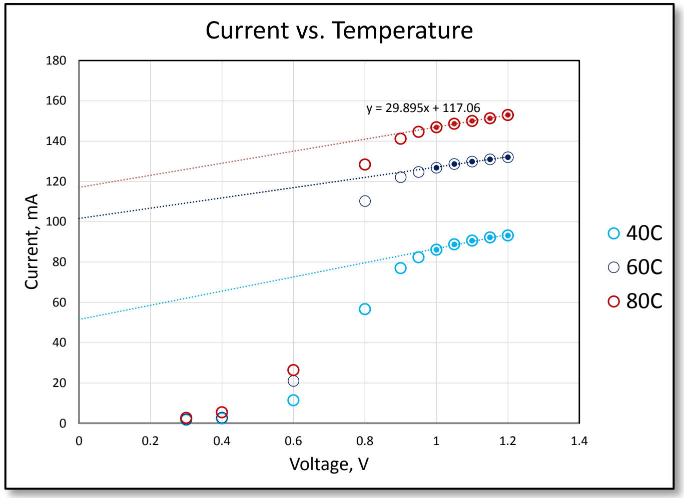
Zhang ECS 2013

METHODS

- Bulk O_2 permeability
- Use with
  - Ionomer development

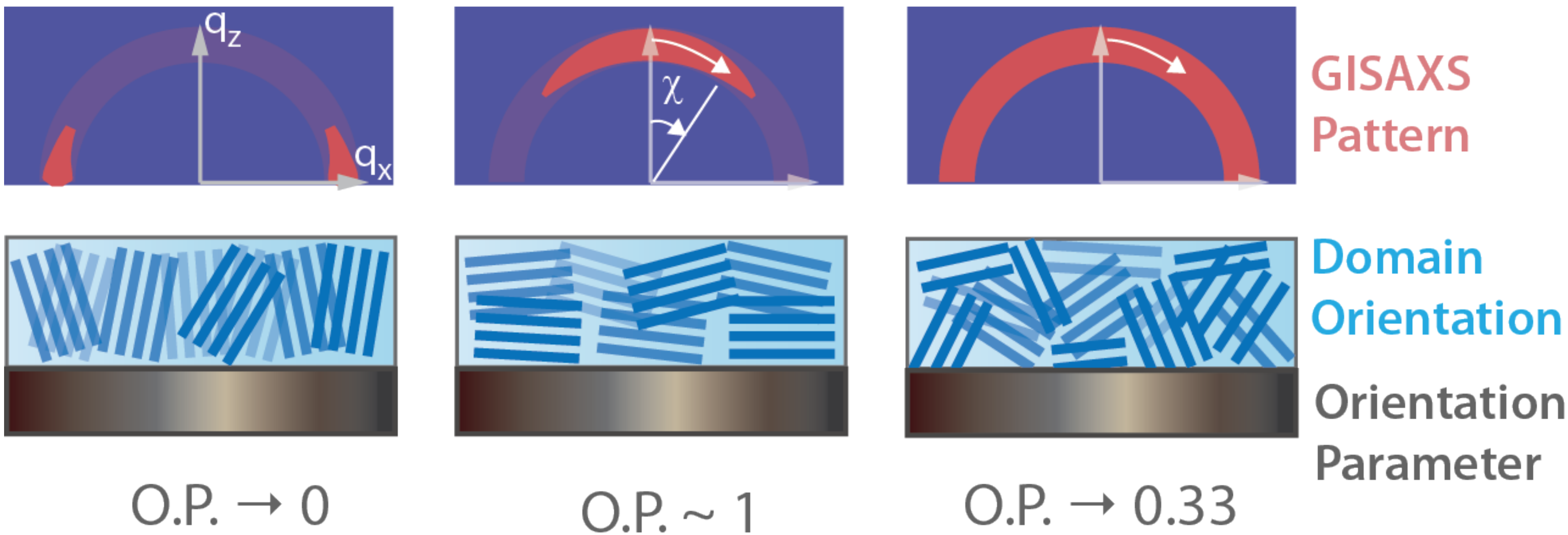
- Key attributes
  - Pt and Ir electrodes
  - Allows in-cell testing: T, RH, xO_2





APPROACH: GISAXS

- GISAXS images and orientation parameter



PFSA is more like this one (but still with some random orientation)

PFIA is like this one

For Transport, it is believed that lower O.P.'s are less inhibitive for transport