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

DoE Annual Merit Review

Washington, DC, June 14, 2018

Project ID # FC155: PI: Andrew Haug, 3M

Team:

3M M. Lindell, F. Sun, J. Abulu, M. Yandrasits, A. Steinbach, M. Kurkowski, G. Weatherman, G. Thoma, I. Khan, M. Guerra, S. Smith, G. Dahlke, M. Priolo

Tufts University

Iryna V. Zenyuk, D. Sabarirajan, S.Normile, J. Liu, Y. Qi

Michigan Technological University

J. Allen, K. Tajiri, E. Medici, S. Abbou

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

BUDGET & Status

Timeline

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

Budget

- Total Project Budget: $3,245,349
  - Total Recipient Share: $649,071
  - Total Federal Share: $2,596,278
- Total Project Costs:* $1,225,000
  - Current Recipient Share: $245,000
  - Current DOE Share: $980,000

* As of 3/31/18

** Sub expenses as of 2/28/18

Barriers addressed

- Cost, durability, performance
- Operational robustness

Partners

- SUBCONTRACTORS
  - Michigan Technological University
  - Tufts University
  - FCPAD:
    - LBNL, ORNL, NREL, LANL, ANL
- PROJECT LEAD: 3M

Key Barrier Cathode Transport limitations

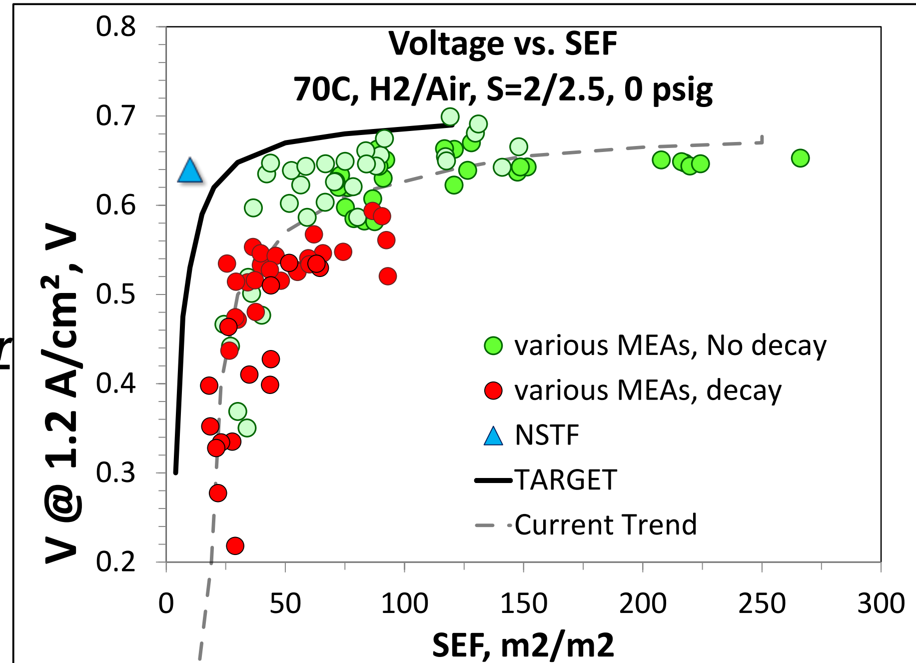
Dispersed Cathodes **at SEF's below 100 cm^2_{PGM}/cm^2_{planar}**,

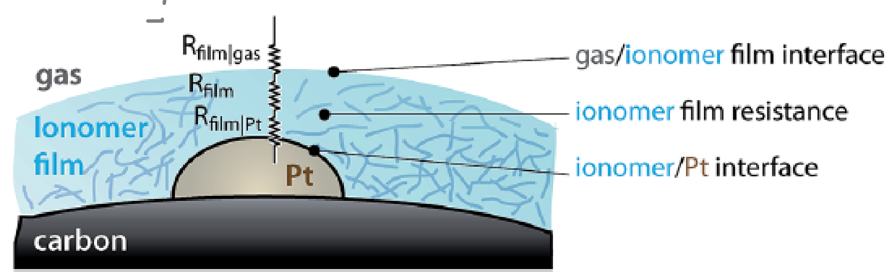
- Transport losses become significant

Traditional 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





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

FC155 goal is to

- Understand and improve
  Ionomer, bulk & local electrode transport
- Integrate NSTF into a dispersed electrode
- Maintain NSTF activity and durability
- Achieve high performance and robustness

Improved Ionomer

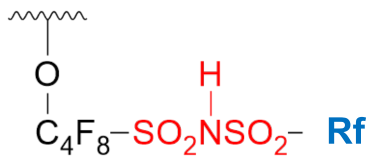
Dispersed NSTF

2 methods to improve transport

Improve electrode **ionomer O_2 permeability**

3M Perfluoroimides (IMIDE 1,2,etc)

Increase O_2 perm,
May reduce catalyst poisoning



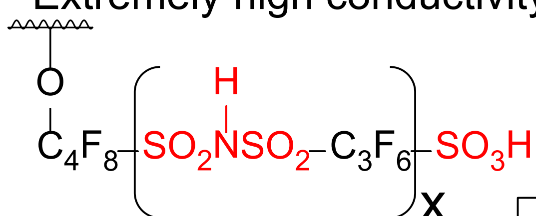
New ionomers specific to O_2 transport

Improve electrode **ionomer H+ conductivity**

- Less ionomer = better transport

MASC (MultiAcid Side Chain**): PF imide acids**

- Extremely high conductivity

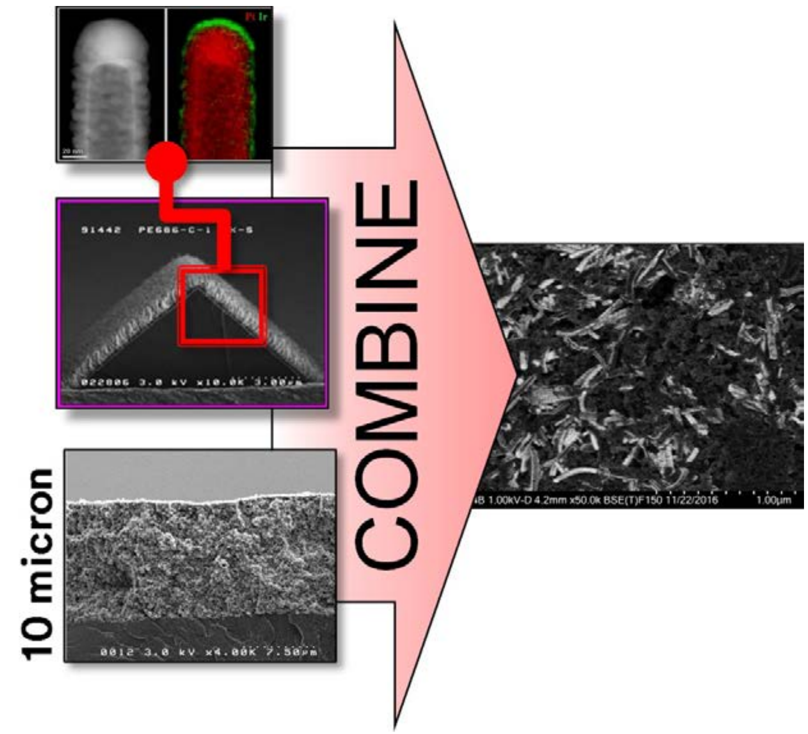


M. Yandrasits. DoE AMR (2015).

<650EW

Incorporate NSTF into powdered electrode

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



Relevance, Objectives & Status

METRIC		2020[1] Target	FC155 Target	3/2017	3/2018
PGM total loading, mg/cm^2		0.125	0.125	0.102[2]	0.102[2]
PGM total loading, g / kW [150 kPa abs]	NSTF	0.125	0.125	0.172[2]	0.172[2]
	Ionomer				0.125[2,4]
Mass activity @ 900 mV iR-free, A/mg		0.44	0.44+	0.28+	
SUSD AST, %ECSA loss		<20 %	<20	N/A	N/A
SUSD AST, mV loss @ 1.2 A/cm^2		< 5%	< 5%	N/A	N/A
Support AST, % mass activity loss	NSTF	< 30	< 30	28% (Pt)	<10% (Pt)
Electrocatalyst AST, mV loss @ 1.5 A/cm^2	NSTF	< 30	< 30	NA	80[5]
	Ionomer				134[5]
Electrocatalyst AST, % Mass activity loss	NSTF	< 40	< 40	45% (Pt)	40% (Pt)
	Ionomer			83% (Pt)	54.5%
MEA Robustness (cold/ hot / cold transient)	NSTF	0.7/0.7/0.7	>0.7/>0.7/>0.7	0.83/0.79/>1.0	0.93/0.84/0.90
	Ionomer				0.97/0.90/0.94
Ionomer Conductivity (S/cm, 80C, 50%RH)		---	0.087	0.050	0.070
Ionomer Bulk O_2 perm ($mol\text{-}cm\text{-}s^{-1}\text{-}cm^{-2}\text{-}kPa^{-1}$), 80C, 50RH		---	1.8E-13	2.0E-13	2.3E-13

1 All metrics and DOE 2020 targets are taken from DE-FOA-0001412
2 0.025 $mgPt/cm^2$ anode
3 3M transient protocols used for NSTF testing
4 At 0.65V, 80/68/68C. 7.5 psig
5 At 70/70/70C, 0 psig

OJBECTIVE

- 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

Collaboration & Coordination

Ionomers
- Membranes
- Thin films
- Electrodes
- CCMs

INTEGRATE to Cathode

NSTF[POWDER]
- Electrodes
- CCMs

TESTING, CHARACTERIZATION, MODELING

MTU
- Washburn
- Hele Shaw, AFM
- AFM, PNM model
- STEM

TUFTS
- nanoCT
- Electr. Cond.
- InoperandoCT
- Electrode Cond.

FCPAD
- GISAXS, WAXS
- SEM, STEM
- AST testing, RDE
- Water uptake
- Conductivity

3M
- O_2 perm
- Perf Testing
- AST testing

Collaborative results shown in upcoming slides

Progress and Objectives

		Milestone Summary Table	Q/M	%
BP1		Go/NoGo: NSTF electrode **ECSA >= 15 m²/g, 40 cm²/ cm², 0.7 robustness.** Ionomer bulk O2 perm + conductivity > 3M825 baseline		100
TASK	1,2	Synthesize IMIDE#1, Make 20+ grams of NSTF 25 ugPt/cm2 powder.	1/3	100
TASK	1,2,4	Validate DoE AST tests, specialty tests, run baseline with 3 ICs, 3 loadings..	2/6	100
TASK	1, 2	Characterize ionomer, Pt/C, and powder NSTF (SEM, TEM, NanoCT, etc)	3/9	100
TASK	1,2,4	NSTF powder electrode >= 0.30 A/mg Pt, NanoCT disp NSTF,	4/12	100
BP2		Go/NoGo: Ionomer exceeds 3M825 O_2 perm by 33% with similar or improved conductivity. 0.35 A/mg Pt, 0.175 g/kW power output		**75**
TASK	**4**	Reaction-kinetics model added to PNM framework. PNM predicts pol curves at T = 40 °C and 80°C.	5/15	100
TASK	**2**	NSTF Cathode ECSA >= 25 m²/g.	6/18	100
TASK	**4**	MTU/Tufts: Baseline structures, electrochem input to PNM, delivering initial predictions.	7/21	80
TASK	**2**	NSTF activity >=0.35 A/mg Pt in an electrode. 0.2 g/kW with NSTF containing electrode.	8/24	70
BP3		END: See Targets slide		**60**
TASK	**4**	MTU/Tufts: PNM - continuum predicts pol curves for T = 40 and T = 80C within 10%	9/27	33
TASK	**1-3**	Support AST targets achieved. Metal cycle AST <40% activity loss.	10/30	100
TASK	**1**	Ionomer with 50% greater O_2 permeability and 50% greater H+ conductivity than 3M825	11/33	75
TASK	**1-3**	>=0.44 A/mg PGM in electrode. Metal AST <=30% activity loss. 0.125 g/kW.	12/36	40

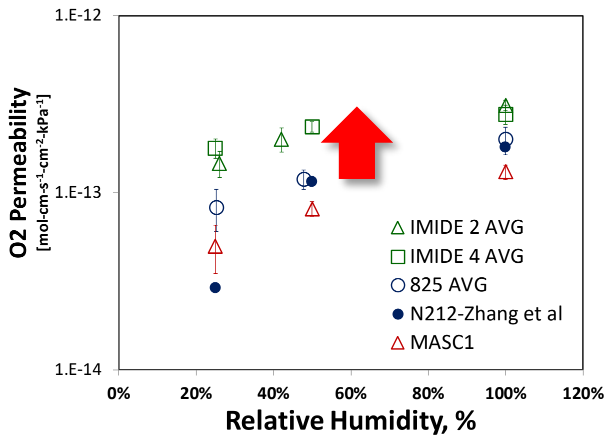
3M

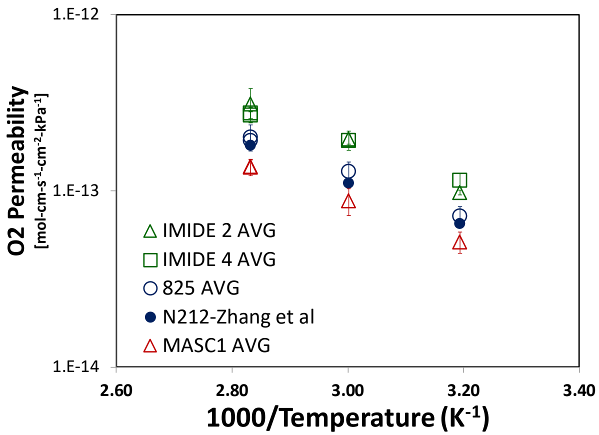
TASK1: Novel Ionomer Development Ex-Situ

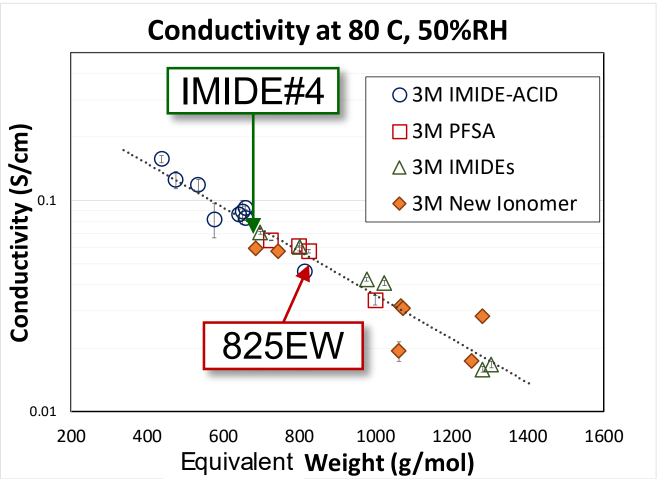
Bulk O_2 perm characterization
- GM (Zhang ECS 2013) method

Imide 2,4 (vs 825): **+37-50%** at 80C, 100% RH
Imide 4 (vs 825): **+92%** at 80C, 50% RH

MASC ionomers show high conductivity
IMIDE#4: 22% more conductive vs 3M825
NEW IONOMERS can exceed baseline conductivity





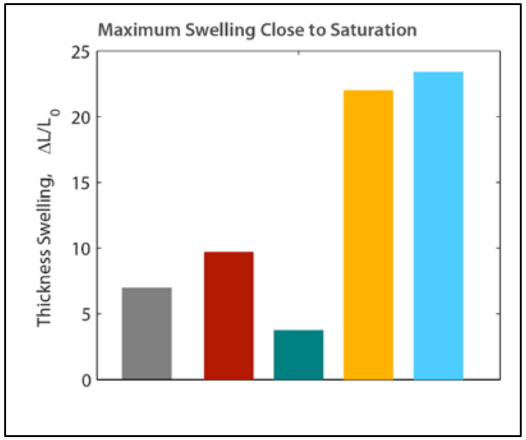


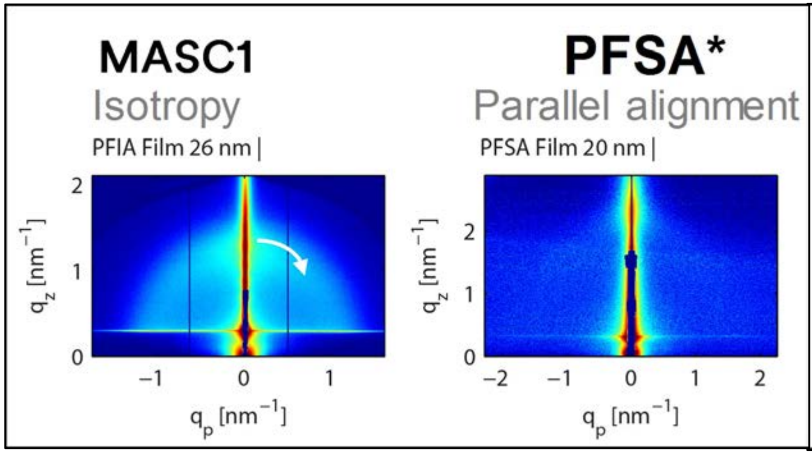
- IMIDE #4: +92% O_2 perm., +22% conductivity vs. 825EW (80C,50%RH)

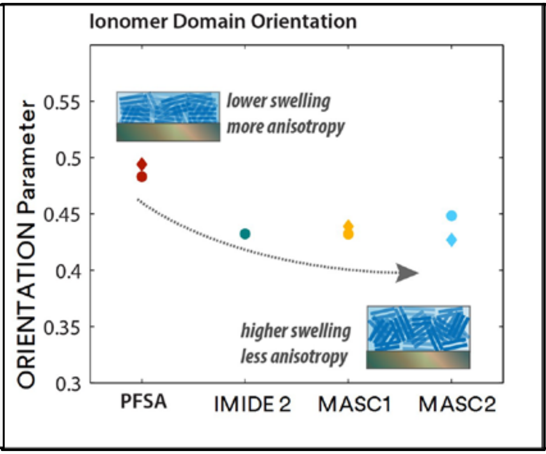
  BP1 GNG achieved. BP2 GNG achieved
- NEW Ionomer structures made with good conductivity

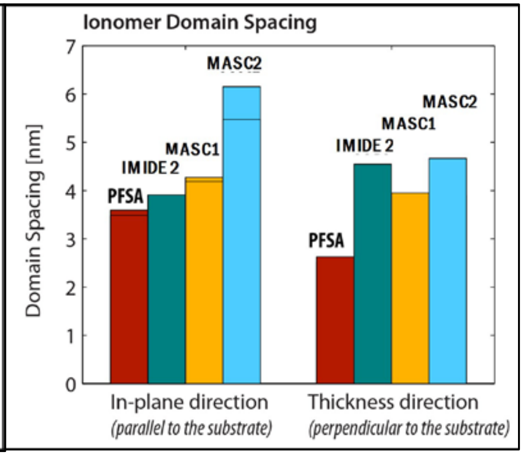
TASK1: Ionomer Evaluation THIN FILM

- GISAXS (LBNL): MASCs, IMIDEs less oriented than PFSA's as a thin film (lower orientation parameter)
- Ionomer domain spacing
  - MASCs > IMIDEs > PFSA
- Thin film swelling:
  - Consistent with EW
- Goal:
  - Link ionomer properties to electrode performance
  - Incorporate into the PNM









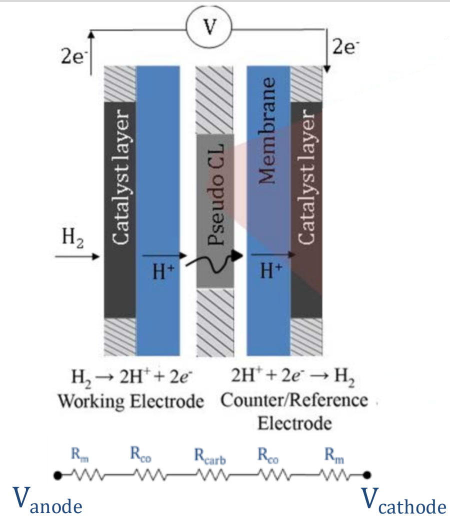
TASK1: Ionomer Evaluation ELECTRODE

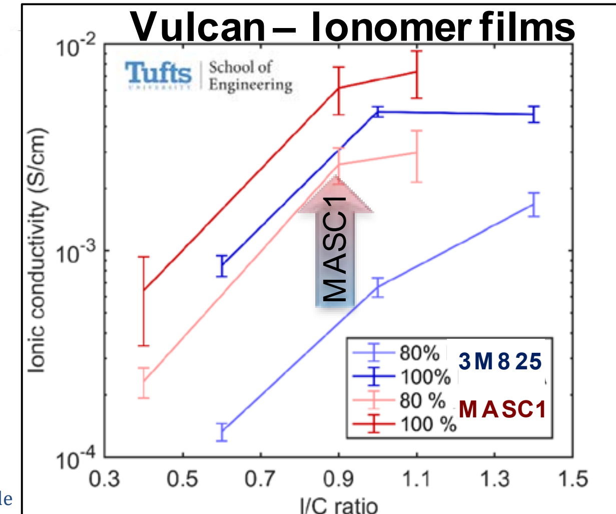
Tufts evaluating ionomer conductivity in electrodes

- MASC1 8X conductivity at 80%RH in electrode

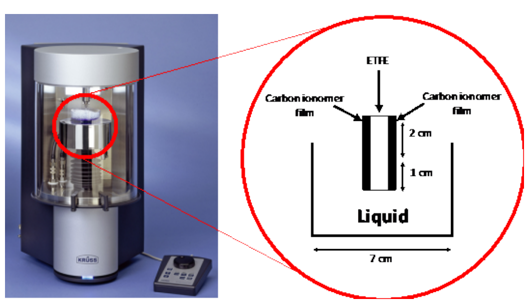
MTU: decreasing contact angle with EW

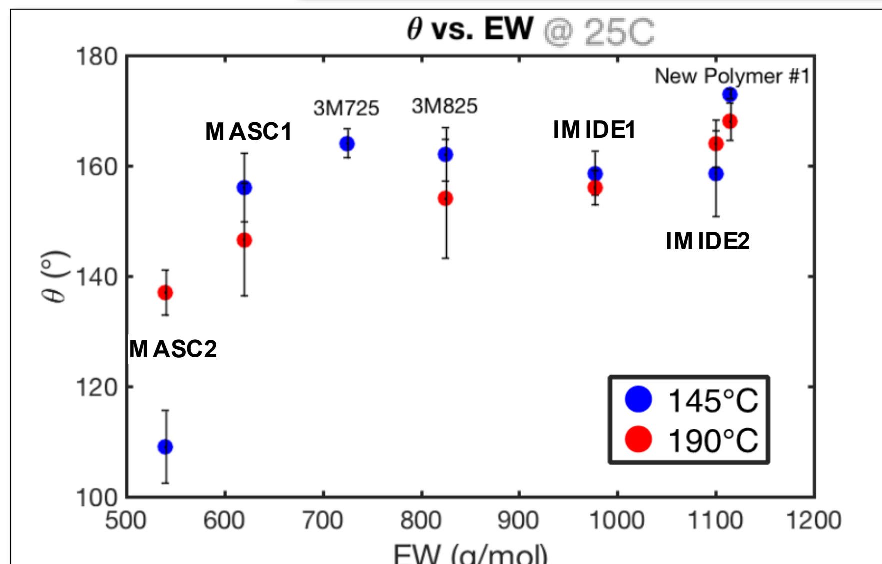
- Defining electrode window of operation
- New ionomers may break PFSA curve





Washburn method

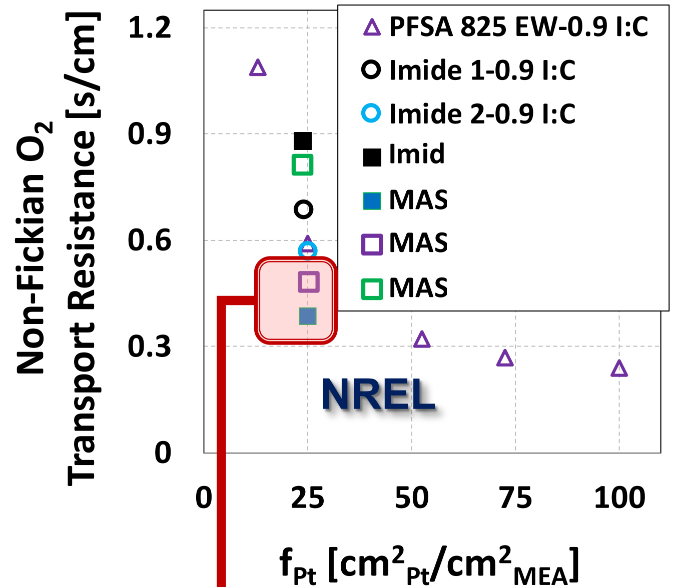


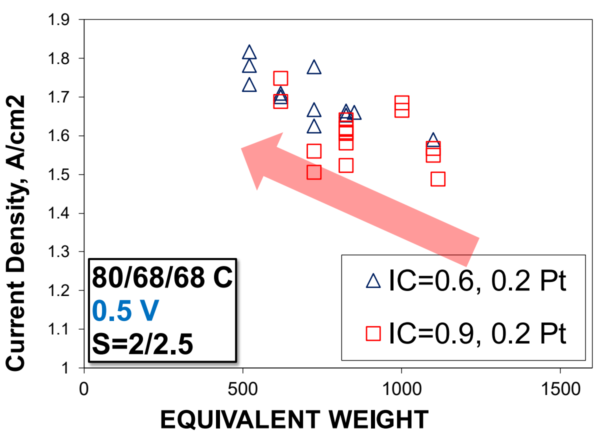


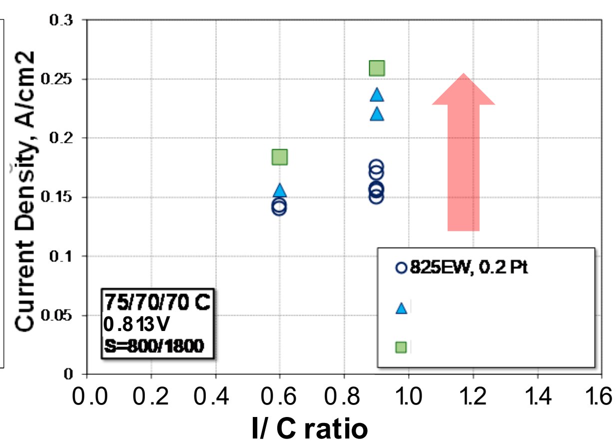
TASK1: Ionomer Evaluation CCM/MEA

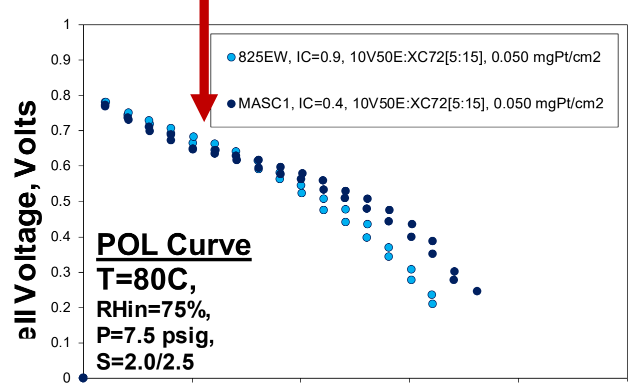
- MASC allows
  - low I/C
  - lower local transport losses
- MASC improves high current operation
  - [BACKUP] MASC robustness good at low I/C
- IMIDEs show increased H_2/Air activity

FUTURE: Combine benefits



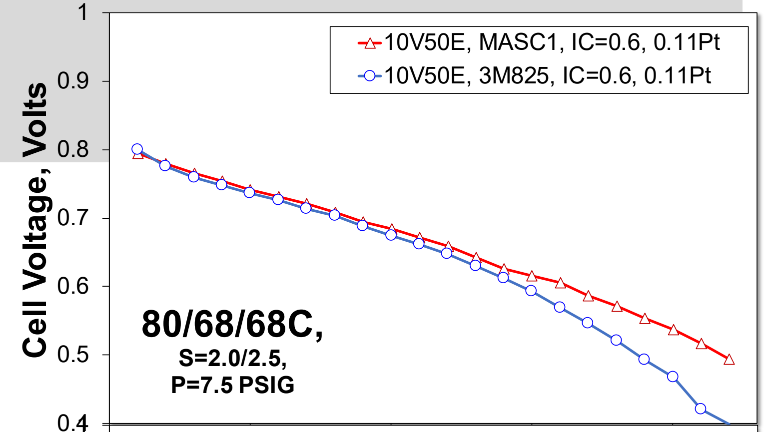


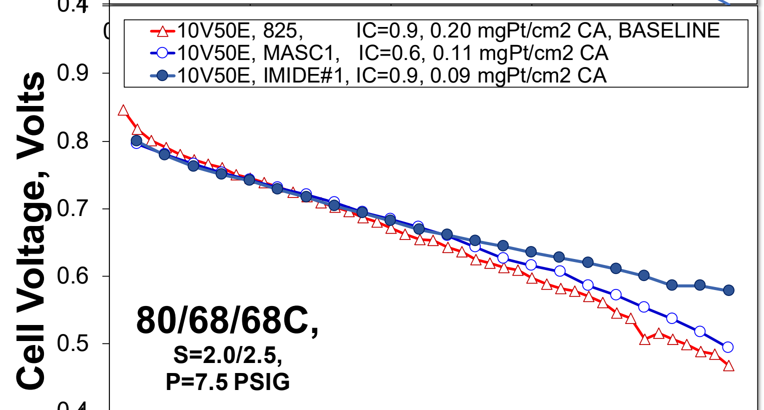


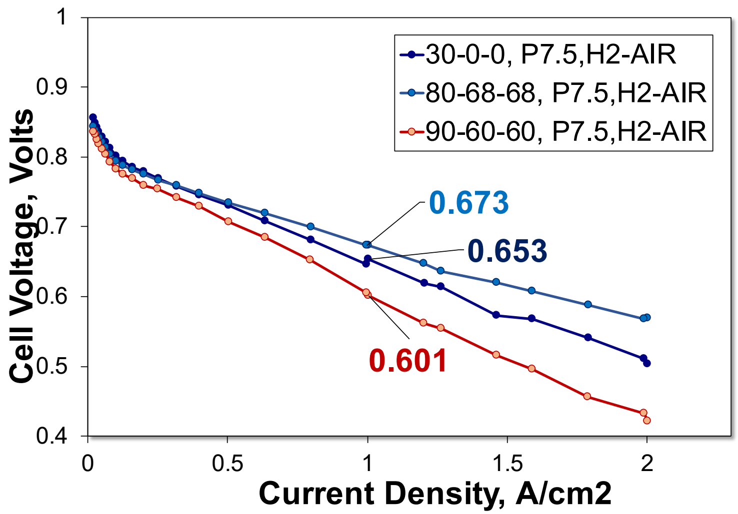


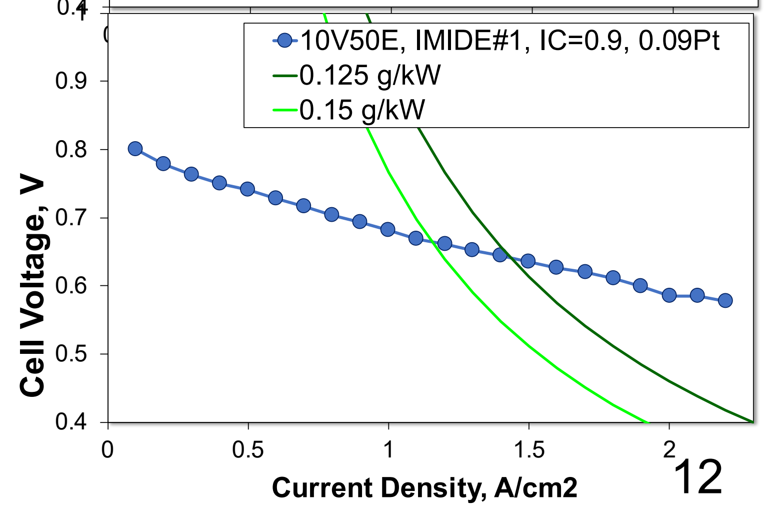
Task 1: BEST in CLASS

- SPECS:
  - 0.025 mg Pt/cm² anode
  - Better membrane, GDL
- Latest crosses 0.125 g/kW @ 0.647V
  - Imide#1, I/C=0.9, above AN/MEM/GDL
- Wide operating range
- FUTURE GAINS:
  - IMIDE#4, Better catalyst,
  - New Ionomers





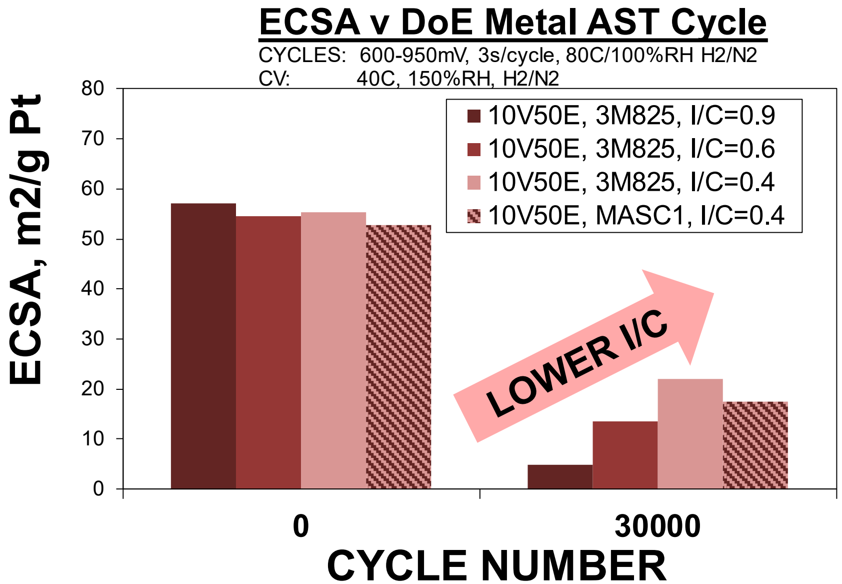




3M

TASK1: Ionomer Future Work

- IMIDES & MASCs & PFSAs
  - New imides will likely be made after IMIDE #4
  - Path possible to greater O_2 perm
  - Go lower I/C for performance & durability
- NEW IONOMER PATH [Backup slide]
  - Incorporate new O_2 permeable monomers
  - Several prepared, tested, in queue
  - Additional materials every 2-3 months
- Key challenges
  - Gain 50+50 (O_2 perm + conductivity) ionomer
- Linking:
  - bulk/measurable properties
  - To ionomer characteristics
  - To improved fuel cell performance
- Optimizing for dispersed NSTF system



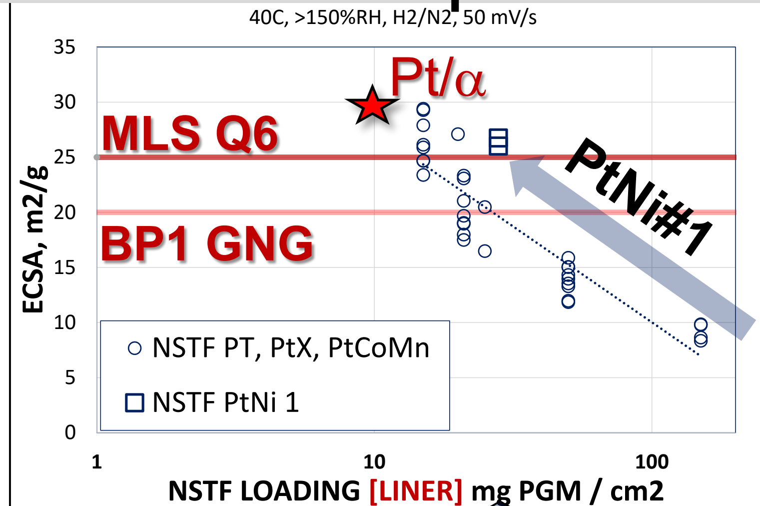
TASK2: Powdered NSTF Powder Properties

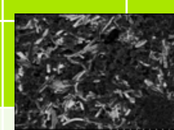
Powdered NSTF

- Eliminates geometric constraint
- Requires new variables (Wh/S, I/S)

Task 2 BP1 GNG Targets met

- **ECSA, Surface roughness**



TYPE	Desired load	NSTF on liner	ECSA	SEF	Wh/S	I/S
	mg / cm^2	mg / cm^2 [geo]	m^2/g	cm^2/ cm^2[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**		
dNSTF	0.15	0.010 Pt / 0.010 α	**60** Pt / **30** PGM	**90**		

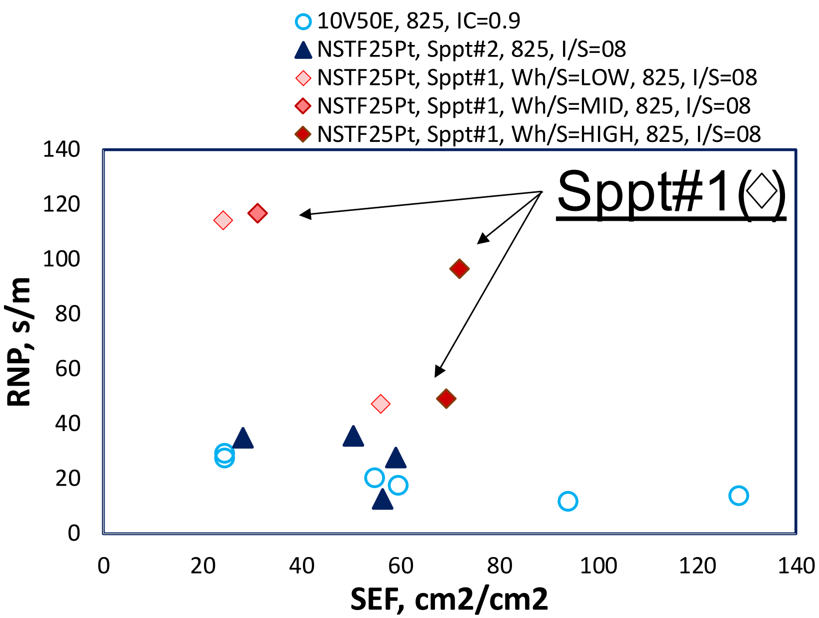
PtNi#1 :

Showing higher area than similar PtX loadings

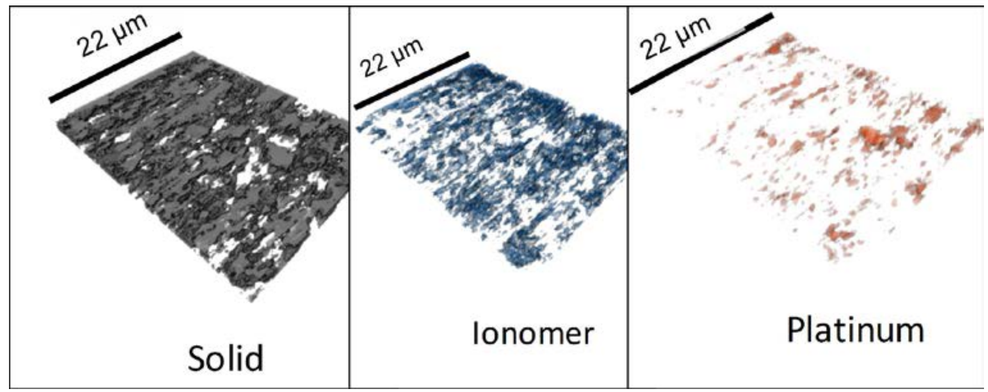
Equivalent to stacking 15 layers of NSTF 0.010 mg Pt/ cm^2 sheets

TASK2: Powdered NSTF Electrode Properties

- TRANSPORT TESTING
- NANO-CT Evaluation
- Bringing understanding to disp. NSTF parts



NSTF 25 Pt, SPPT#2, Very Low Wh/S



Sample	Wh/S	Porosity	In Plane Tortuosity	Thru Plane Tortuosity
Sppt#2	HIGH	0.59	1.96	1.58
	VERY LOW	0.59	2.03	1.74
Sppt#1	HIGH	0.51	2.63	2.24
	VERY LOW	0.52	2.42	2.29

TASK2: Powdered NSTF 10Pt/10α ug/cm²

New NSTF Catalyst from FC144 (Steinbach PI)
- ECSA is 59 m²/g Pt, 30 m²/g PGM

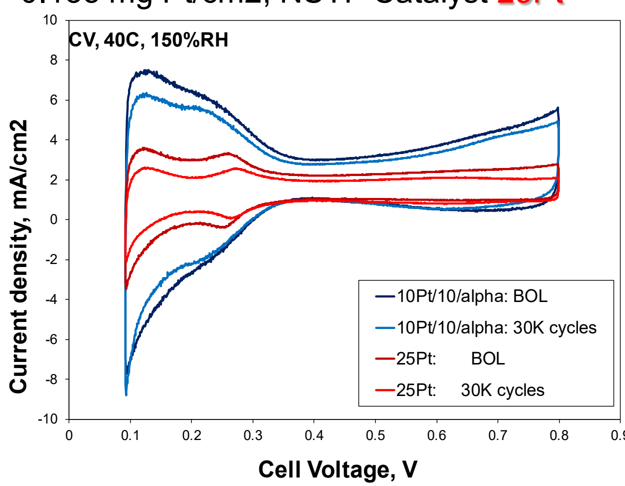
0.135 mg Pt/cm² electrode made
- H_2/O_2 Mass & spec. activity lower than expected

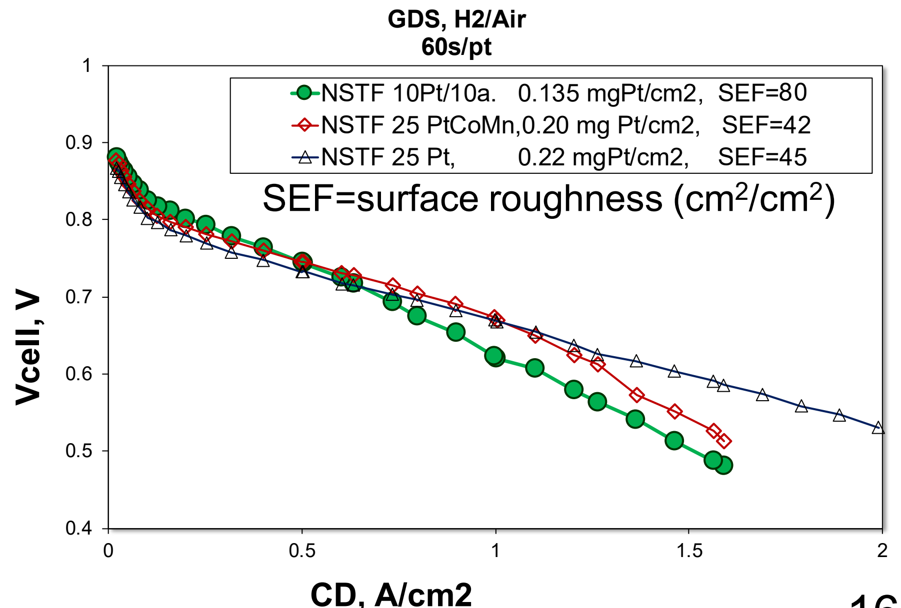
H_2/Air low current:
- 25mV gain vs best Pt @ 0.8V with 40% less Pt

H_2/Air low HIGH current performance is poor
- Root causing

Catalyst	Activity Disp. NSTF	%Retained vs. Classic NSTF
Pt	0.09	66-70%
PtCoMn	0.2-0.25	64-75%
Pt/α	0.10	~30%

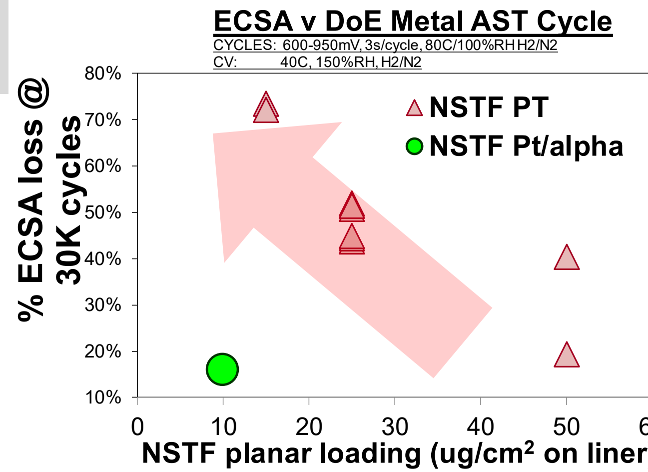
0.135 mg Pt/cm2, NSTF Catalyst 10Pt/10α
0.135 mg Pt/cm2, NSTF Catalyst 25Pt





TASK2: Metal AST

- NSTF decay rates scale with loading on whiskers
  - Similar to standard (non-dispersed) NSTF
- **<u>10Pt/10α shows exceptional stability</u>,**
  - 15% ECSA loss



METAL AST Testing

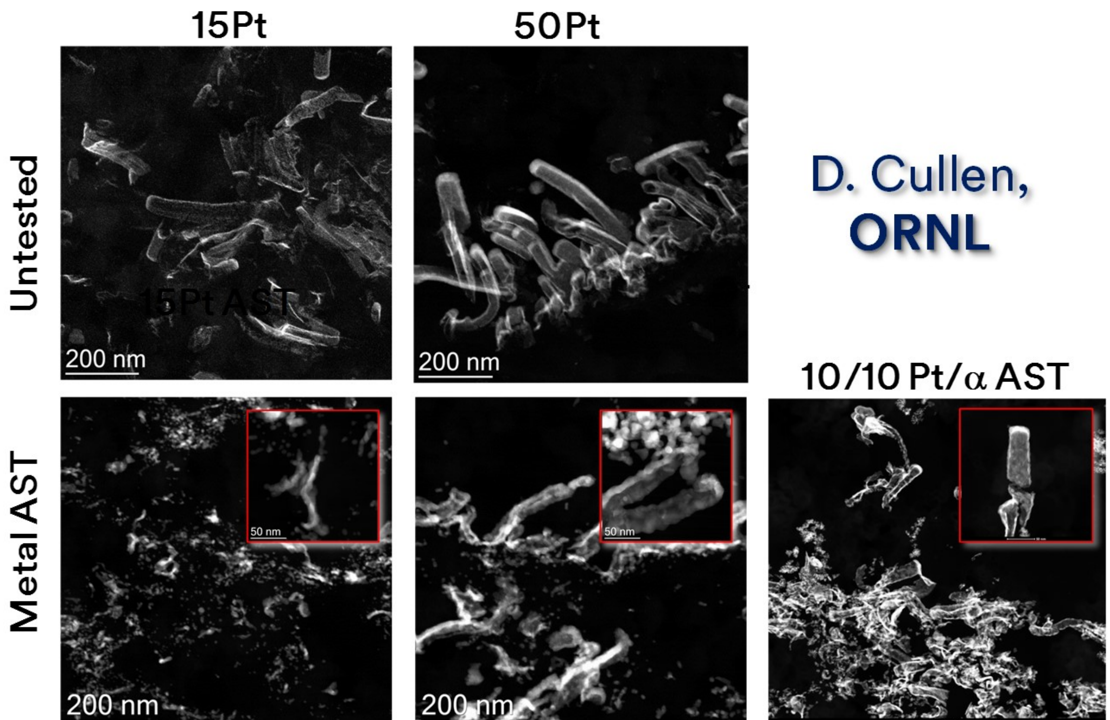
- Thinner NSTF coatings lose whisker shape after AST

IMPLICATIONS

- Disconnected metal coating disintegrates
- Lost NSTF area/activity

MITIGATIONS Available

- 10/10 Pt/α is an example
- Thin film structure maintained

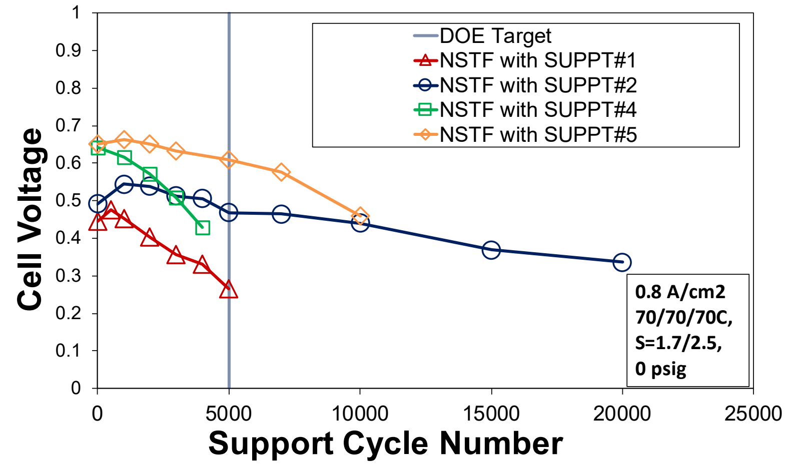


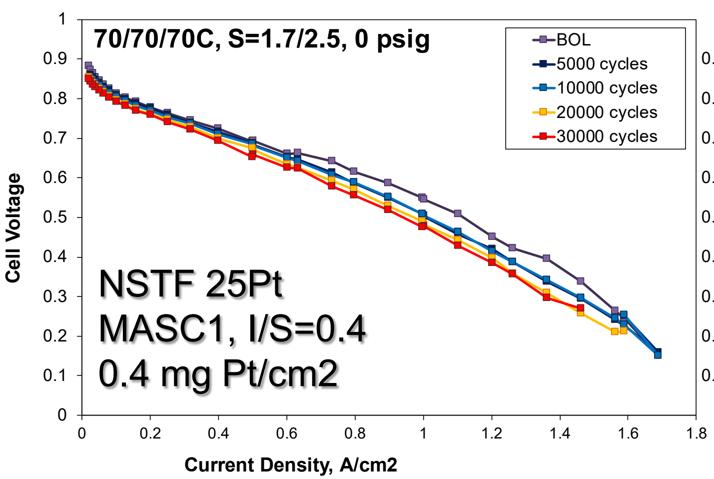
D. Cullen, ORNL

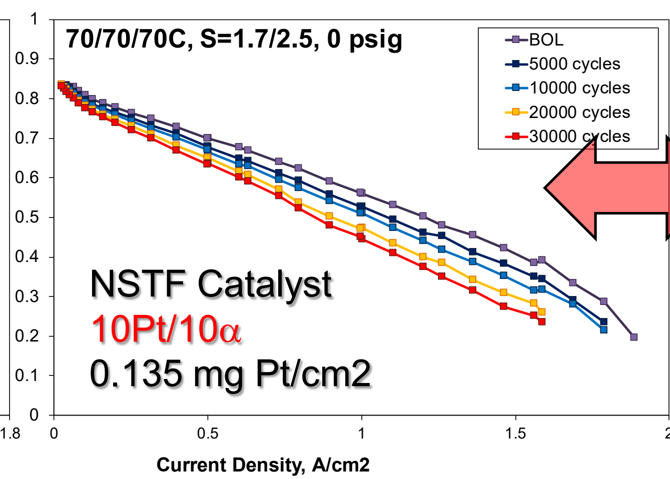
TASK2: Metal & Support AST

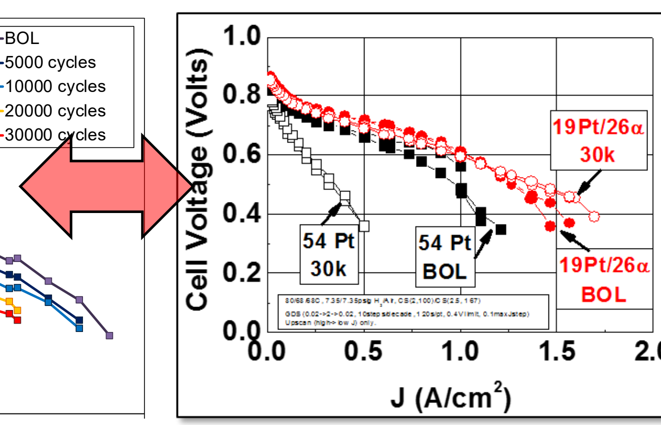
- NSTF samples **exceed Support AST targets**
  - Supports #2, 5
- Metal AST performance decay minimal with sufficient surface roughness
- **10Pt/10a shows exceptional stability**
  - Meets **metal AST targets**
  - & Sppt AST targets w/Sppt #4,5
  - AST Performance loss greater than expected
    - Root causing / reoptimizing

DOE Support AST,
80C, 100%RH, H2/N2, 1-1.5V, 2s per cycle







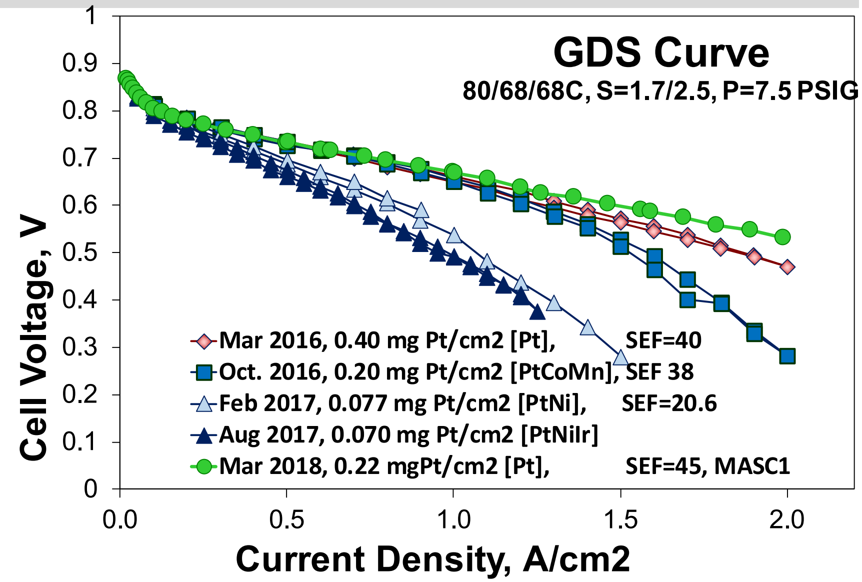


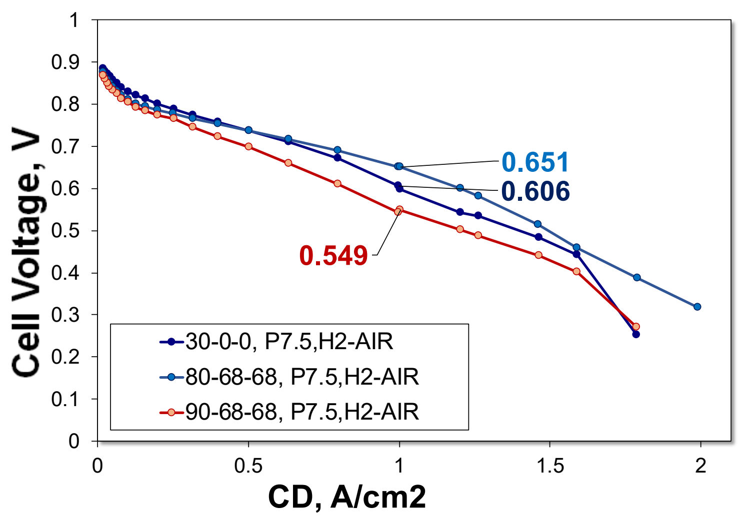
A. Steinbach et al, FC144

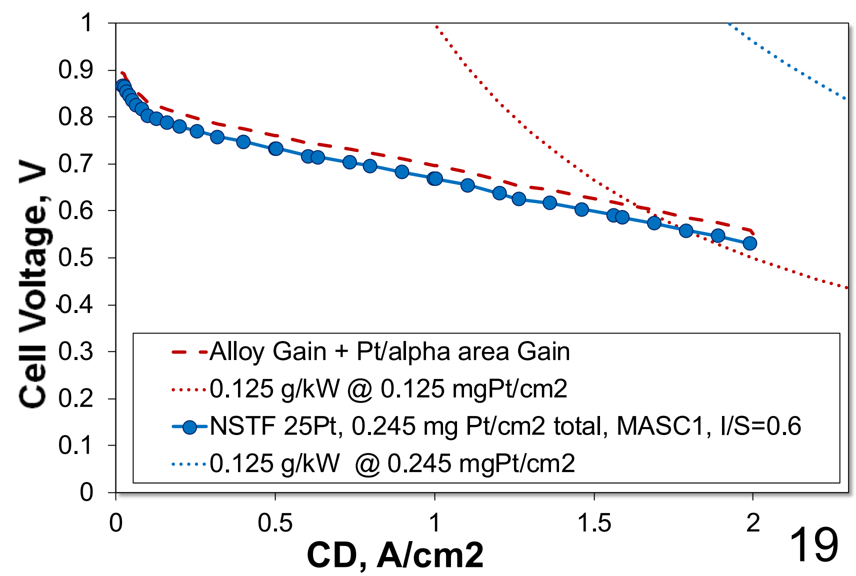
TASK 2: Best in Class performance

- NSTF 25Pt incorporating Task 1 ionomer knowledge
- Pt/alpha and PtXY catalysts offer ECSA and 30+ mV
- Ionomer, structure learnings to be incorporated in BP2, 3

vs. 80C, 68C Dpt	30C	90C, 68C Dpt	35-80C trans
TARGET	0.7	0.7	0.7
Oct. 2017	0.83	0.79	>1.0
Mar. 2018	0.93	0.84	0.90





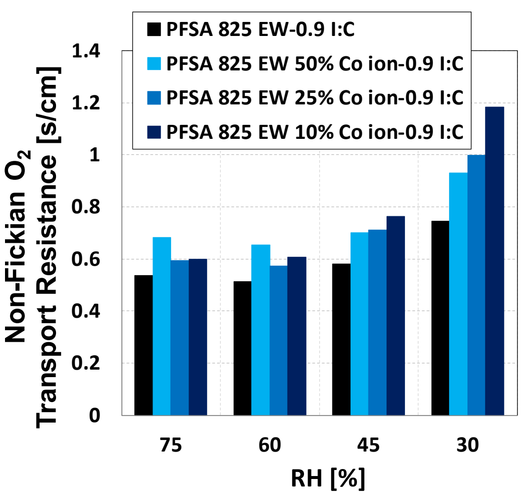


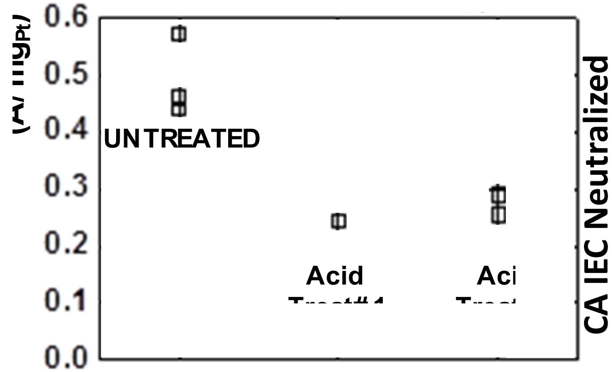
3M

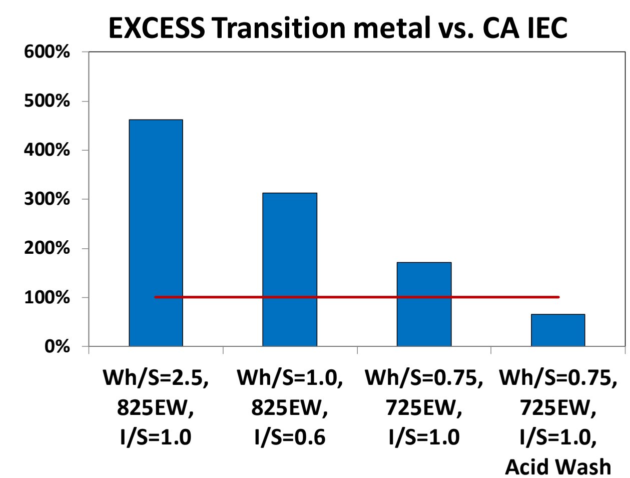
Task 3: Transition Metal Issue

- Ni and Co leach into electrode pre-test
  - PtNi Cathode ionomer is completely neutralized
- MITIGATION & Understanding Necessary
  - Increase electrode ionomer & IEC
  - Acid wash catalyst to remove excess Ni
  - TMI operating window (NREL local transport)
- Status: 1st Acid Treatments caused activity loss
  - Significant work ongoing

Catalyst	State	% Transition Metal Retained
PtCoMn	Powder	100 (Co)
	CCM/Untested	33
	Tested	20
PtNi	Powder	100 (Ni)
	CCM/Untested	72.5
	Tested	64

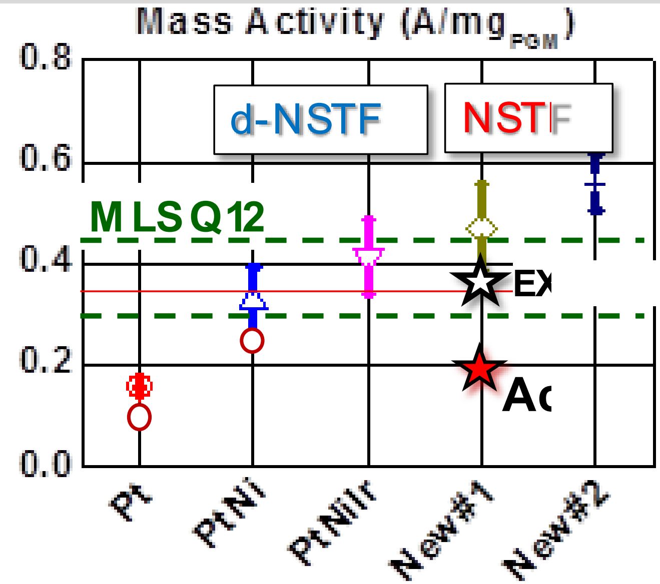






TASK 2,3: NSTF & Integration Next

- NSTF Alloy integration critical
  - PtNiRu lost more than 33%
  - Identify&expand TMI operating window
  - TMI impacts (Ex: Local O_2 transport)
  - Process development
- Test method requiring less NSTF
  - 10Pt/10α required 25+ feet of NSTF film
- Process development
  - TMI removal with minimal activity loss
- Integration with new ionomers
- Integration with downselected support

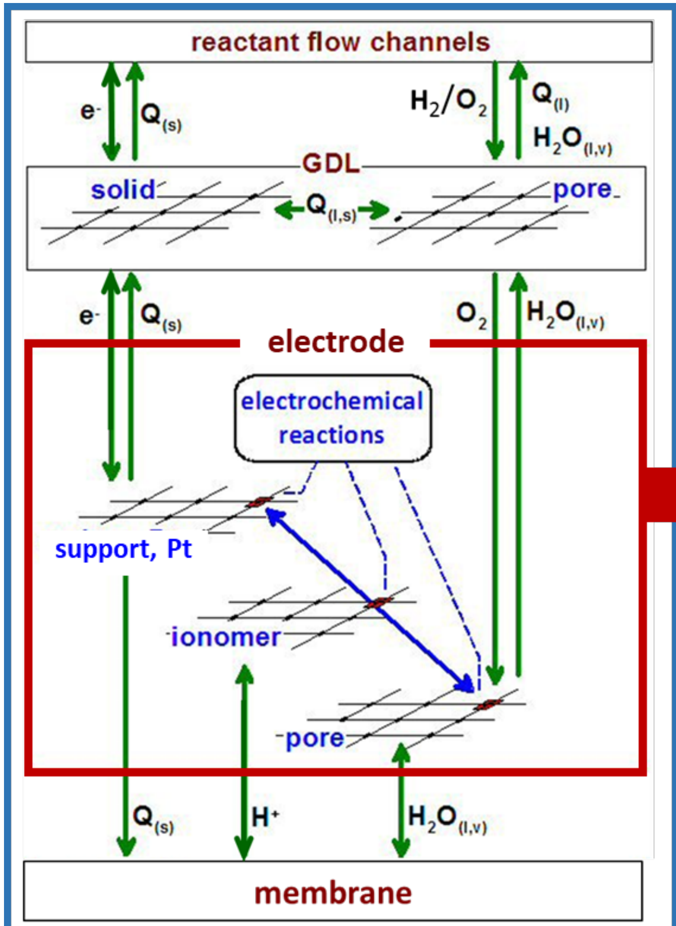


	Test date	Balance	Ionomer
PtNi	End Q2	Sppt 1	3M825
PtNiIr	End Q4	Sppt 2	3M825
PtNiRu	End Q5	Sppt 3	3M725
PtNiRu rpt	Q6-Q8	Process development	
New NSTF	Q7-Q9	Sppt 2 or 5	TBD

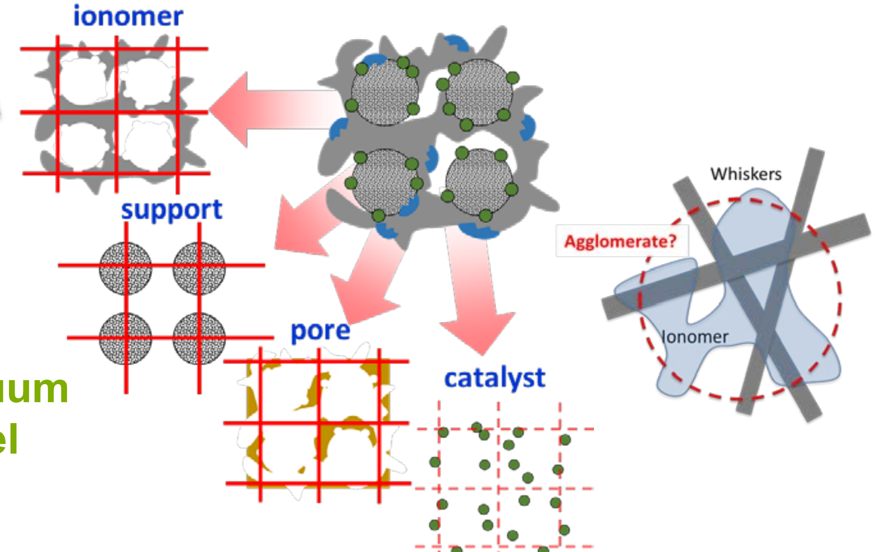
Any proposed future work is subject to change based on funding levels

Tufts-MTU Electrode Transport Model

Cathode/Anode transport fluxes Model between the membrane and the gas channel



Electrode network approach



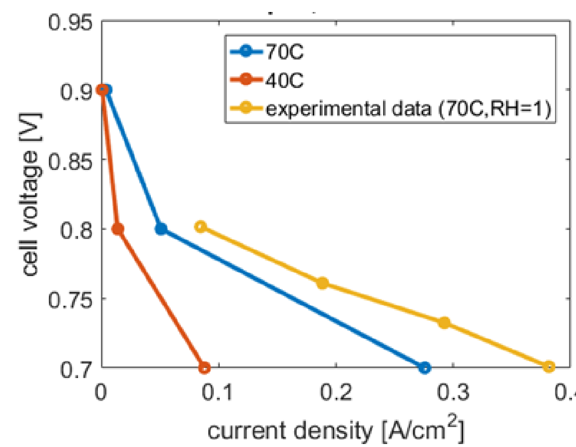
Continuum Model

Pore Network Model

Progress Status:

- **Development: 80%**
- **Calibration: 60%**
- **Validation: 40%**
- **Prediction: 0%**

Model Calibration at 70C



Reviewer comments: AMR 2017

- The specifics for next steps have not been presented in a clear, concise manner, nor are the key variables or learnings from the next steps presented in a way to lend confidence in obtaining positive results.
- A clearer experimental plan and next steps are needed.
  - It is hoped 3M achieved this in the annual review and in the 2018 AMR presentation
- It is not suitable to work only on materials development to meet the target. Investigating why it works (or does not work) is expected.
  - It is hoped the FC155 ***team*** has shown some background on NSTF and ionomer improvements
- The work on NSTF does not seem to have particularly high cell performance and seems to be significantly lower than the standard NSTF membrane electrode assemblies (MEAs)…the highest-performing NSTF samples would be of greater interest, as those studied to date do not appear to be the highest performers.
  - We have shown improved operation for Pt NSTF, but alloy integration requires effort that is budgeted for in Task 3.
- Annual review (paraphrasing): Clearer demonstration of meeting DoE operation range parameters should be shown for dispersed NSTF.
  - 3M has corrected this and demonstrated NSTF operating range more clearly in this presentation.

3M

Summary

- TASK 1
  - Ionomers developed exceeding BP1,2 O_2 permeability and conductivity targets
  - Ionomer thin film, bulk & electrode understanding focusing future work
  - Best in class ionomer showing promising performance
  - Lower ionomer content parts increasing metal stability
- TASK 2
  - Exceptional metal AST shown with 10Pt/10α NSTF electrodes
  - DoE support AST targets exceeded utilizing NSTF
  - Improved dispersed NSTF performance shown & path for improvement demonstrated
  - Dispersed NSTF fundamental understanding building
- TASK 3
  - Dispersed NSTF alloy incorporation work ongoing
- TASK 4: PNM model development in validation phase, predictions beginning

BACKUP

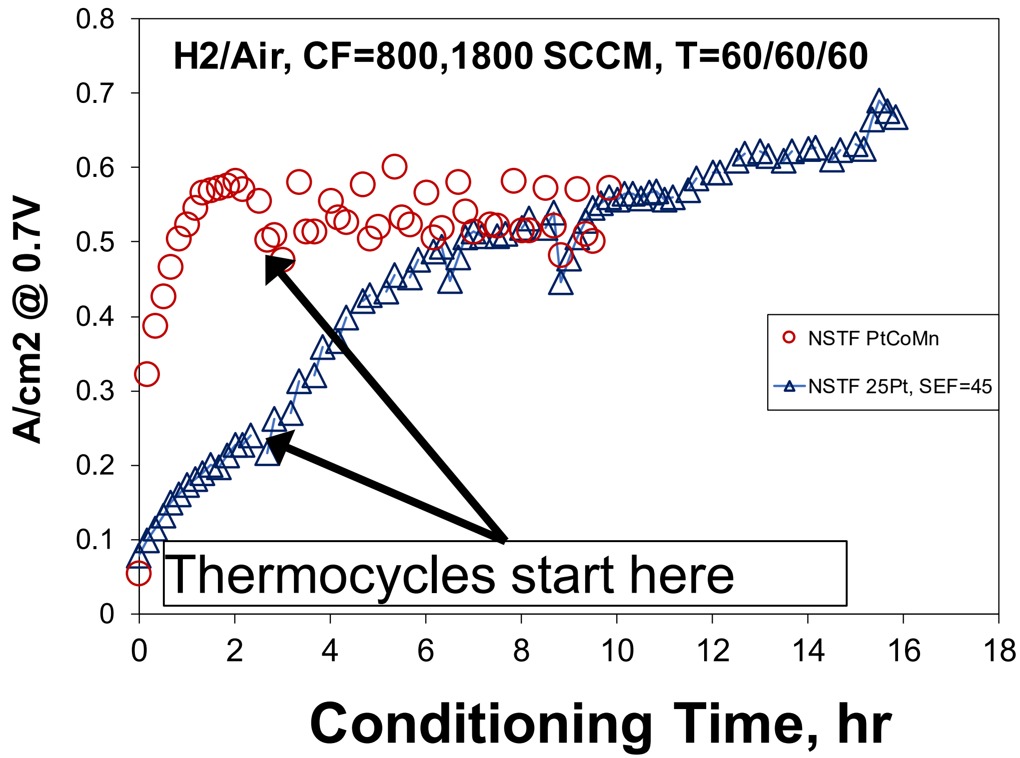
Acknowledgements

- 3M
  - M. Lindell
  - F. Sun
  - J. Abulu
  - M. Yandrasits
  - A. Steinbach, M. Kurkowski
  - G. Weatherman
  - G. Thoma
  - I. Khan
  - M. Guerra
  - S. Smith
  - G. Dahlke
  - M. Priolo
- Tufts University
  - I. V. Zenyuk
  - D. Sabarirajan
  - S. Normile
  - J. Liu
  - Y. Qi
- Michigan Technical University
  - J. Allen
  - K. Tajiri
  - E. Medici
  - S. Abbou
- FCPAD
  - LBNL (A. Weber, A. Kusoglu)
  - NREL (KC Neyerlin, S. Kabir)
  - ORNL (D. Cullen, K. More)
  - LANL (M. Mukundun, R. Borup)
  - ANL (D. Myers)

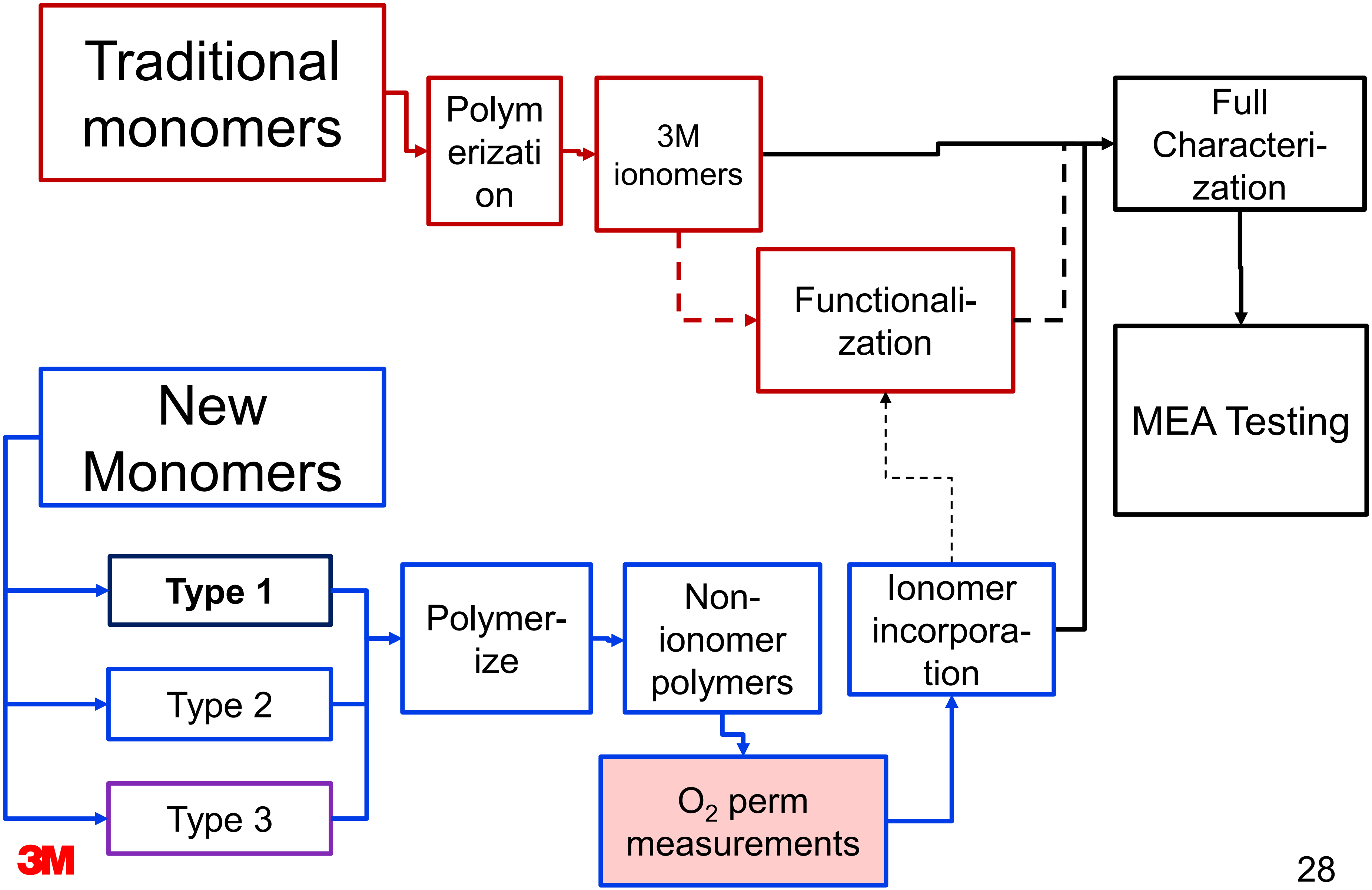
NSTF: Process development

- Two critical factors limit NSTF effectiveness
  - Operating range
  - Conditioning

- Work on this project has led
  - to increased conditioning rates
  - And increased operating range



TASK1: Path to New Ionomers



3M

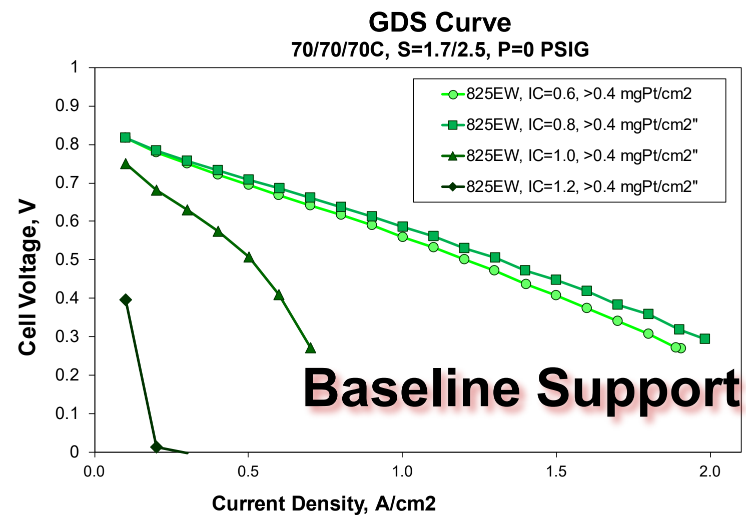
TASK 2: In cell tests

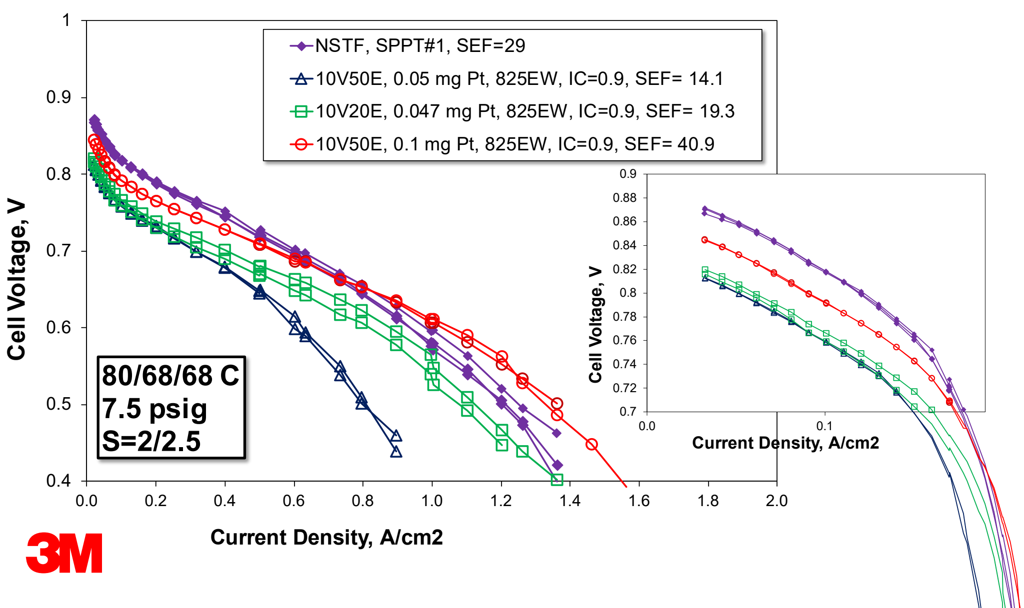
NSTF suppt#1 very sensitive to I/Sppt ratio

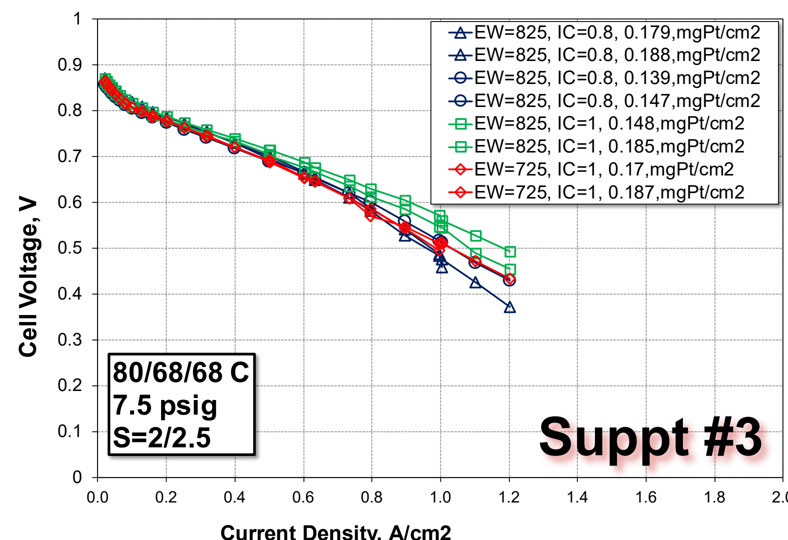
- Suppt #2 is less IC sensitive, accepts lower EW

NSTF 25 Pt showing 3.4X H_2/Air activity gains

- NSTF25Pt: SEF=29 cm^2/cm^2, 818 mV (+27 mV)
- 10V50E: SEF=40 cm^2/cm^2, 791 mV



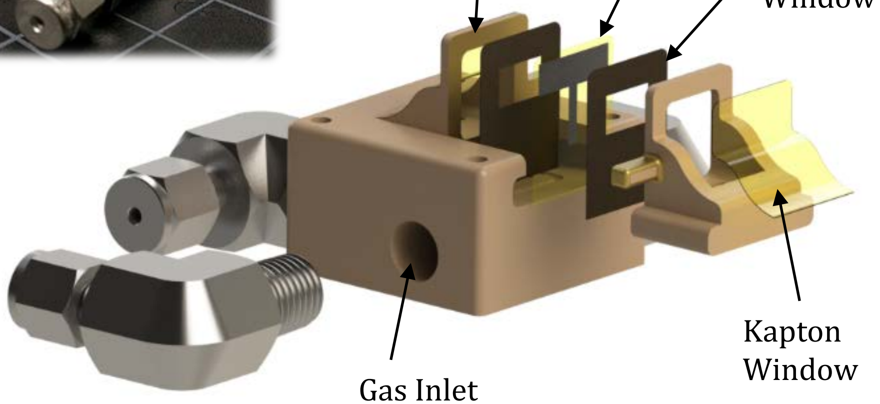


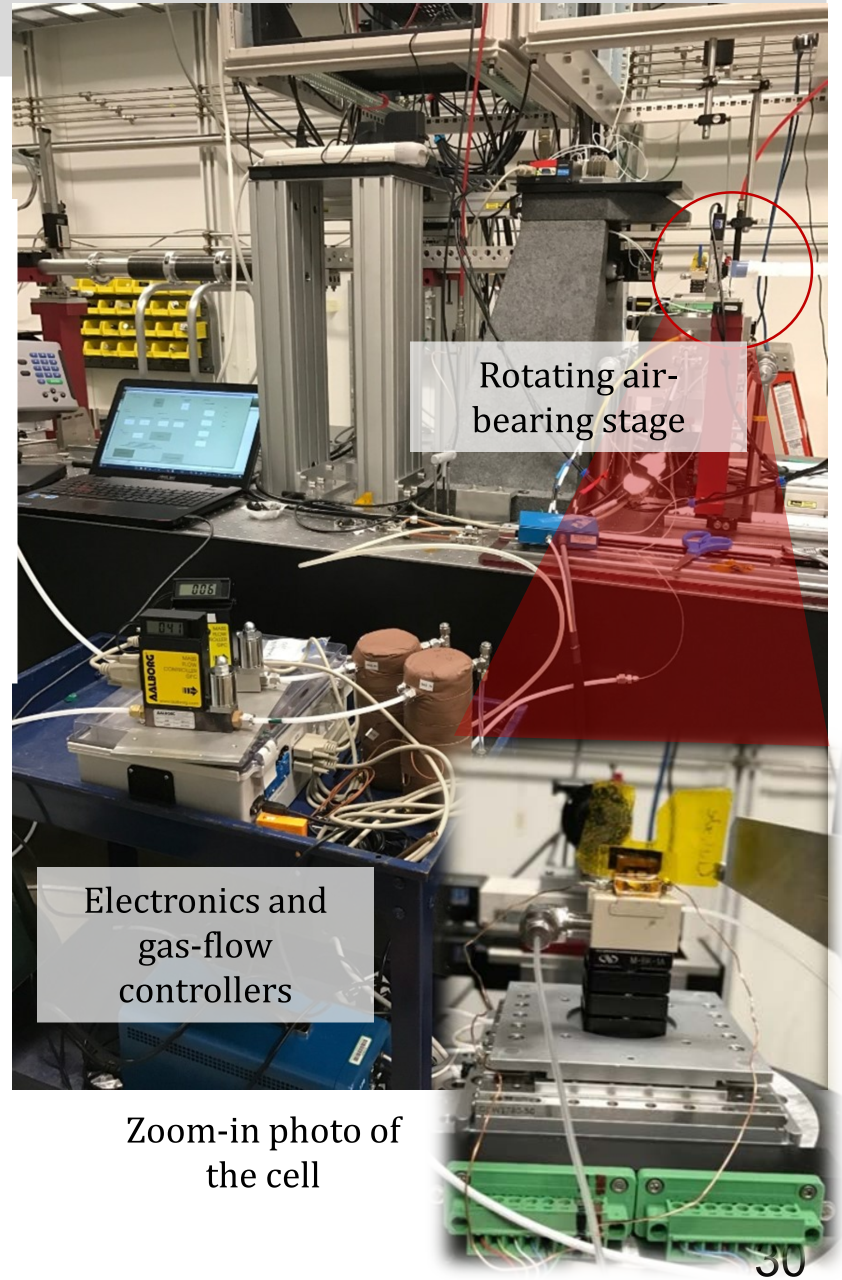


3M

Operando TXM nano-CT Cell

Tufts UNIVERSITY | School of Engineering





Zoom-in photo of the cell

- Visualize water formation and movement during FC operation
- Operando cell design for X-ray tomography is completed and the cell tested at three synchrotrons: APS, SSRL and ESRF
- Active area ~ 4 mm^2, the cell maintained constant 10 mA current
- Current challenges: beam damage at low energies

3M