Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports

FC143

Andrew J. Steinbach

3M Company, St. Paul, MN

U.S. DOE 2016 Annual Merit Review and Peer Evaluation Meeting

Washington, DC

June 7, 2016

Project Overview

Timeline

Project Start: 1/1/2016
Project End: 3/30/2019

Barriers

A. **Durability**
B. **Cost**
C. **Performance**

Budget

Total DOE Project Value:	$4.360MM*
Total Funding Spent:	$0.073MM*
Cost Share Percentage:	23.72%

*Includes DOE, contractor cost share and FFRDC funds as of 2/28/16

DOE 2020 Technical Targets

PGM total content (both elec.):	0.125 g/kW
PGM total loading:	0.125 mg/cm^2
Loss in initial catalytic activity:	< 40%
Loss in performance at 0.8 A/cm^2:	< 30mV
Loss in performance at 1.5 A/cm^2:	< 30mV
Mass activity (0.90 $V_{IR\text{-}FREE}$):	0.44A/mg

Partners

Johns Hopkins University (J. Erlebacher)
Purdue University (J. Greeley)
Oak Ridge National Laboratory (D. Cullen)
Argonne National Laboratory (D. Myers, J. Kropf)

Project Objective and Relevance

Overall Project Objective

Develop *thin film* ORR electrocatalysts on 3M Nanostructured Thin Film (NSTF) supports which exceed all DOE 2020 electrocatalyst cost, performance, and durability targets.

Project Relevance

ORR catalyst activity, cost, and durability are key commercialization barriers for PEMFCs.

3M NSTF ORR catalysts are one leading approach which approach many DOE 2020 targets *in state-of-the-art MEAs*.

Project electrocatalysts will be:

- compatible with scalable, low-cost fabrication processes.
- integrated into advanced electrodes and MEAs which address traditional NSTF challenges: operational robustness, contaminant sensitivity, and break-in conditioning.

Overall Approach

Establish relationships between electrocatalyst functional response (activity, durability), physical properties (bulk and surface structure and composition), and fabrication processes (deposition, annealing, dealloying) via systematic investigation.

Utilize high throughput material fabrication and characterization, electrocatalyst modeling, and advanced physical characterization to guide and accelerate development.

Status versus DOE and Project Targets

	2020 Target and Units	Project Target	Status (Apr. '16)
Platinum group metal (PGM) total content (both electrodes)	0.125 g/kW	0.1 (0.70V)	0.16[1] 0.18[2]
PGM total loading (both electrodes)	0.125 mg/cm^2	0.10	0.105[1] 0.127[2]
Loss in catalytic (mass) activity	40 %	20	40[3]
Loss in performance at 0.8 A/cm^2	30 mV	20	28[3]
Loss in performance at 1.5 A/cm^2	30 mV	20	NA
Mass activity @ 900 $mV_{iR\text{-}free}$	0.44 A/mg (MEA)	0.80	0.24[3] (NPTF "M") 0.47[4] (NPTF) 0.31[5] (UTF)

[1]0.015mg_{Pt}/cm^2 NSTF anode, 0.075 dealloyed PtNi/NSTF cathode, 0.015 mg_{Pt}/cm^2 cathode interlayer.
[2]0.02mg_{Pt}/cm^2 NSTF anode, 0.091mg_{PGM}/cm^2 NPTF "M" cathode, 0.016 mg_{Pt}/cm^2 cathode interlayer.
[3]NPTF "M" cathode, 0.091mg_{PGM}/cm^2 after 30k Electrocatalyst AST cycles.
[4]Annealed NPTF P4A Pt_3Ni_7/NSTF, 0.12mg_{Pt}/cm^2; adjusted from 0.900V_{MEAS} (70mV/dec)
[5]UTF "#4", 0.025mg_{PGM}/cm^2.

Milestones (BP1), Project Go/No-Gos, and Deliverable

Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
4.1 Proj. Management	M4.1	Intellectual Property Management Plan Completed, Signed	90%	0
3.1 HT Fabrication	M3.1.1	HT Catalyst Deposition Process Reproducible	70%	1
	M3.1.2	HT Catalyst Treatment Process Reproducible	0%	2
3.2 HT Characterization	M3.2.1	HT EC Characterization Reproducible	35%	2
	M3.2.2	HT XRD Characterization Reproducible	10%	3
3. HT Development	M3.1	HT Activity, Area Agrees w/ Homogenous MEA	25%	3
3.2. HT Characterization	M3.2.3	HT EXAFS/XANES Characterization Reproducible	0%	4
1.2 Catalyst EC Characterization	G1.2.1 (PROJ)	Electrocatalyst achieves (≥0.44A/mg and ≤50% mass activity loss) or (≥0.39A/mg and ≤ 40% mass activity loss).	80%	4
1.5 Catalyst Integration	G1.5.1 (PROJ)	Electrocatalyst achieves ≥ 0.6A/mg, ≤ 30% loss, and MEA PGM content ≤ 0.13 g/kW @ 0.70V	60%	8
1.5 Catalyst Integration	D1.5.3	A set of MEAs (6 or more, each with active area ≥ 50 cm^2) which achieve all project targets is made available for independent testing at a DOE-approved location.		12

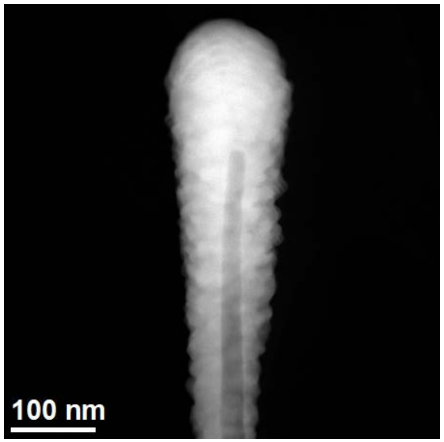
3M Science. Applied to Life.™

Approach – Two Distinct Thin Film Electrocatalyst Morphologies

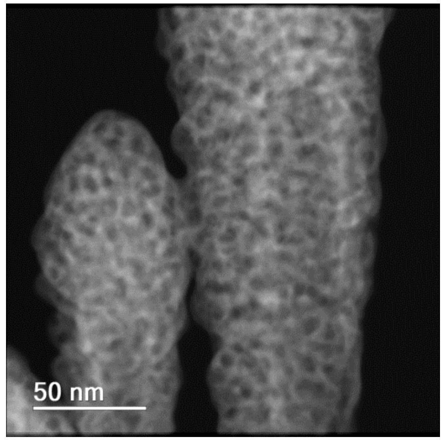
Nanoporous Thin Film (NPTF)

MEA Conditioning State

Before



After (Dealloyed)



NPTF Approach:

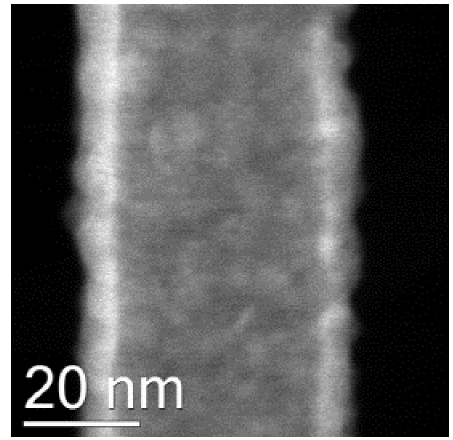
1. Structure/composition/process space optimization to maximize area and minimize leachable TM.
2. Proprietary stabilization approaches to minimize coarsening and TM dissolution.

NPTF PtNi/NSTF, "P4A, TFA"		
	Status	Target
Mass Activity (A/mg)	0.47	0.80
Specific Area (m^2/g)	19	30
Spec. Activity (mA/cm^2_{Pt})	2.5	2.6

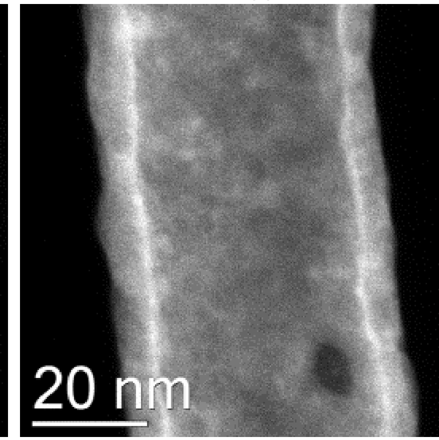
Ultrathin Film (UTF)

MEA Conditioning State

Before



After



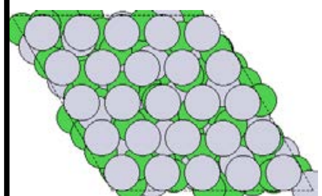
UTF Approach:

1. Structure/composition/process space optimization to develop highly active, stable, and thin surface facets.
2. Maximize NSTF support surface area.

UTF "#4"/NSTF, *Proprietary Process*		
	Status	Target
Mass Activity (A/mg)	0.31	0.80
Specific Area (m^2/g)	19	20
Specific Activity (mA/cm^2_{Pt})	1.7	4.0

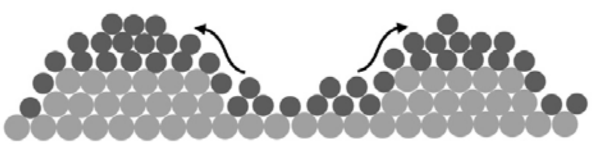
Approach – Electrocatalyst Modeling

1. Atomistic determination of catalyst surface structures

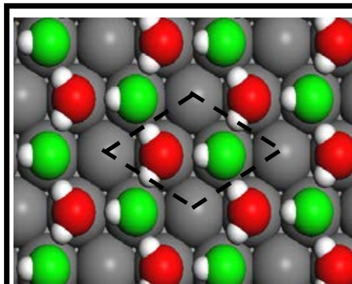


DFT
Surface energy calculations of Pt skins on Pt alloys

Kinetic Monte Carlo
Alloy surface structure predictions

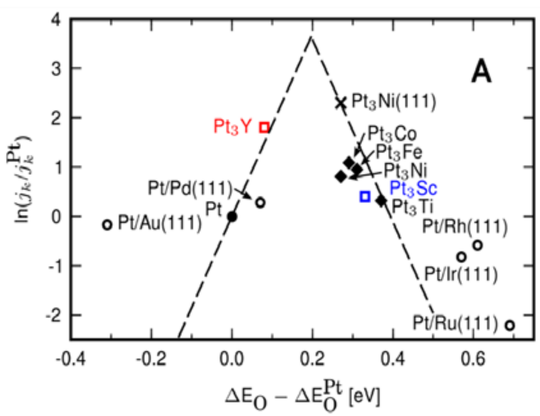


2. Activity predictions of optimized surface structures



DFT
Descriptor binding energies on optimized surface structures

Kinetic predictions of ORR currents from volcano plots and free energies



3. Model Validation

Electrocatalyst Fabrication
PVD Deposition
Proprietary dealloying and annealing processing

Activity Characterization
MEA
RDE
Flow cell

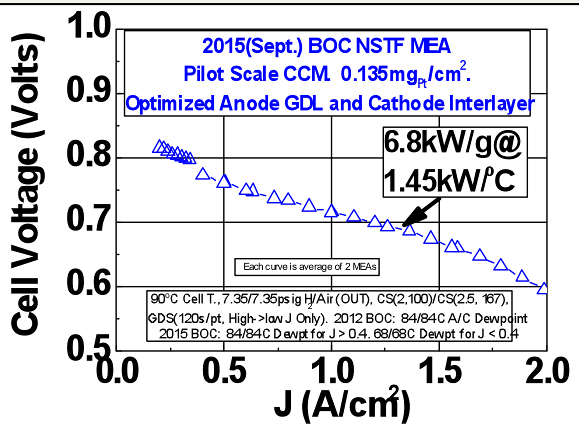
Structure/Composition Characterization
HAADF-STEM
STEM+EDS
XAFS / Δμ-XANES
WAXS
XRD
XRF

HT Methods When Validated

4. Characterization Feedback for Model Refinement

Approach – Advanced NSTF Electrode

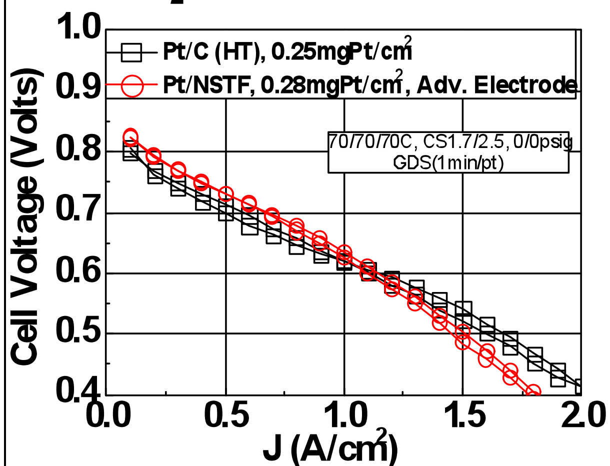
Traditional NSTF Electrode



- NSTF electrode thickness is sub-micron, enabling high rated power at low Pt loading.
- Challenges:
  - Lower area than Pt/C (higher contam. sensitivity, slower break-in).
  - Lower robustness (flooding); mitigation by optimized DM and cathode interlayers.

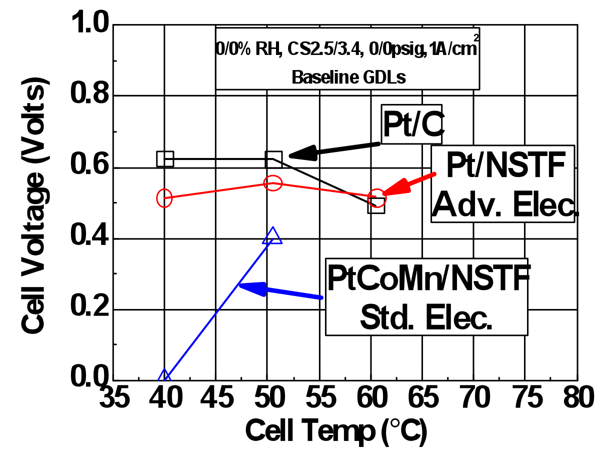
Advanced NSTF Electrode (Early Work)

H_2/Air Performance



- Similar specific activity, specific area as traditional NSTF electrodes.
- Pt/NSTF adv. electrode has higher activity than heat-treated Pt/C, but transport loss at high J.

Operational Robustness



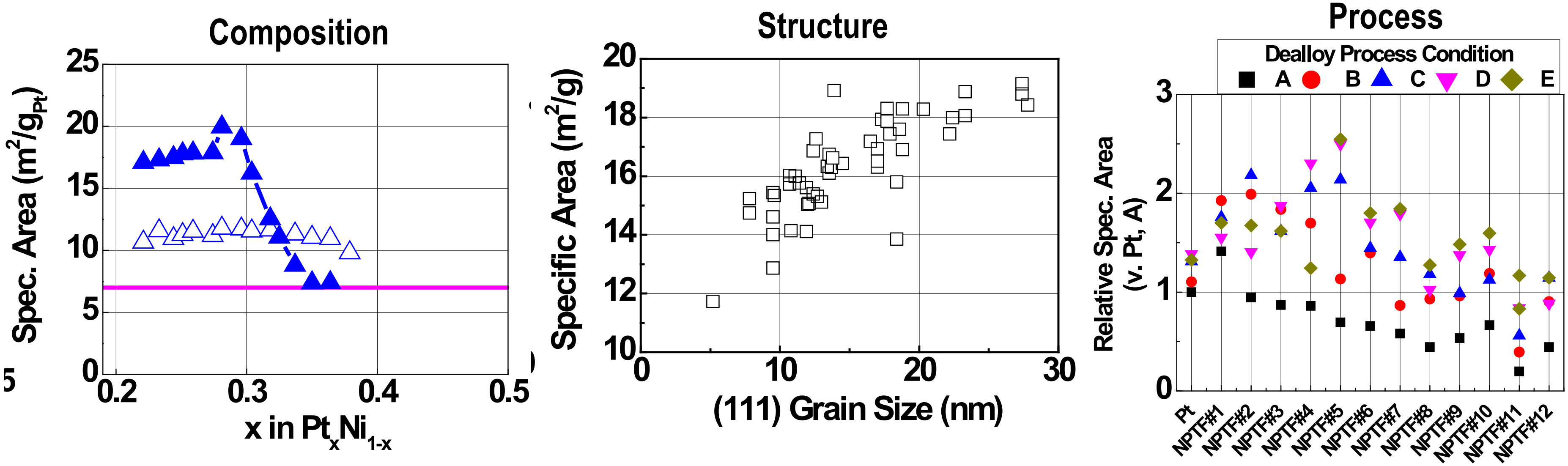
- Similar temperature sensitivity as Pt/C electrodes.
- Significantly improved over traditional NSTF electrodes.

- Advanced NSTF electrode has potential to address key challenges with NSTF MEAs, and enables evaluation of entitlement electrocatalyst concepts in MEA.
- **Key Question**: Will specific power targets be attainable?

Per FOA, **limited** advanced NSTF electrode development will be conducted within the project to enable evaluation of entitlement project electrocatalysts in MEA.

Approach - High Throughput (HT) Electrocatalyst Development

Motivation – Large Variable Space



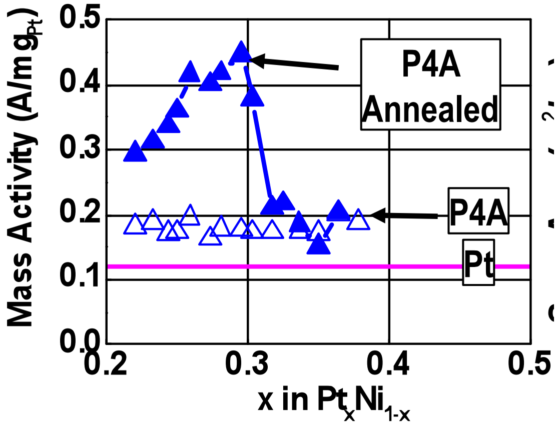
- Ultimate electrocatalyst performance and durability often has significant interdependencies on composition, structure, and processing conditions.
- Variable space: 5 comp. x 3 structure x 3 process levels = 45 unique electrocatalysts (one binary system)

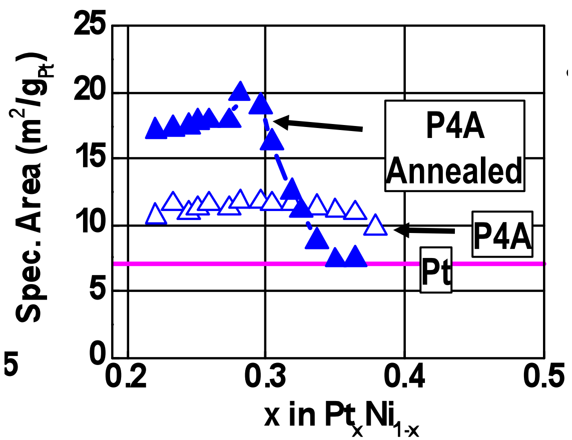
HT Electrocatalyst Fabrication	HT Electrochem. Characterization	HT Physical Characterization	HT Data Management
Deposition - Feasible Dealloying - TBD Annealing - TBD	**Segmented FC - Feasible** Multi-channel flow cells - TBD	**XRF - Validated** **XRD/WAXS – Feasible/Validated** XAFS - TBD	**Custom analysis software – Validated/In Progress** Storage in SQL DB - TBD

Significant first year effort to develop and validate HT methods.

Pre-Project Background – NPTF Pt_xNi_{1-x}/NSTF

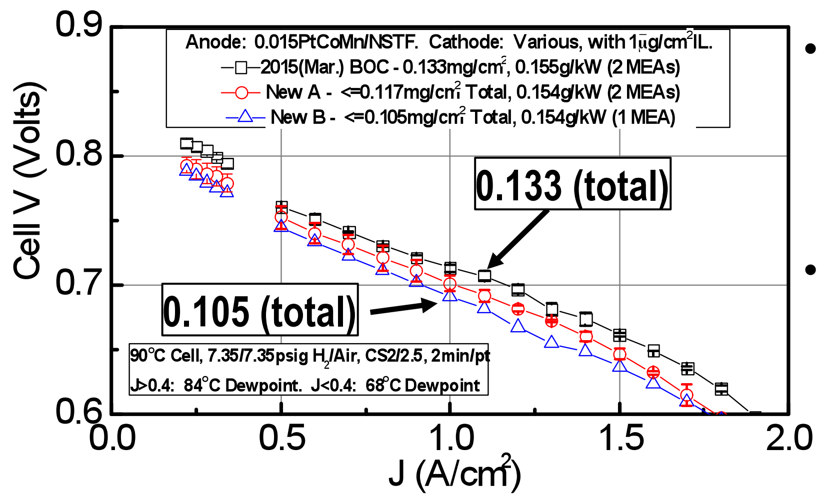
Composition, Structure





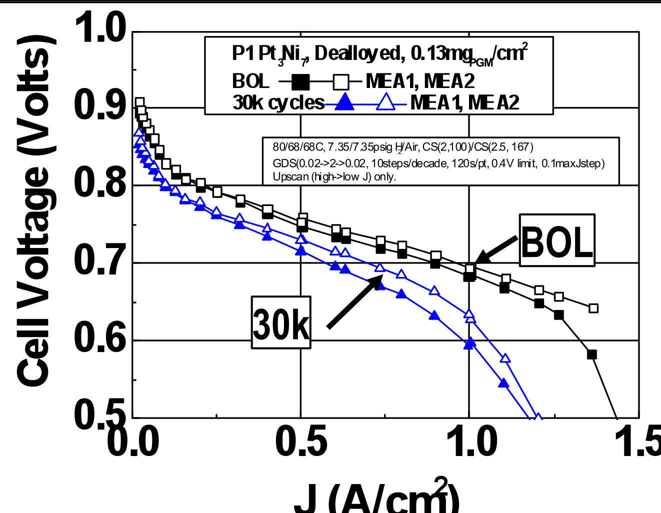
- NPTF mass activity and specific area (in MEA) depend strongly on composition and structure induced by annealing.

H_2/Air Performance at Low PGM



- Dealloyed NPTF PtNi can yield high specific power w/ 0.105 mg_{PGM}/cm^2_{MEA}.
- Mass activity improvement needed to achieve MEA ¼ power and rated power targets.

NPTF PtNi Electrocatalyst Durability Insufficient



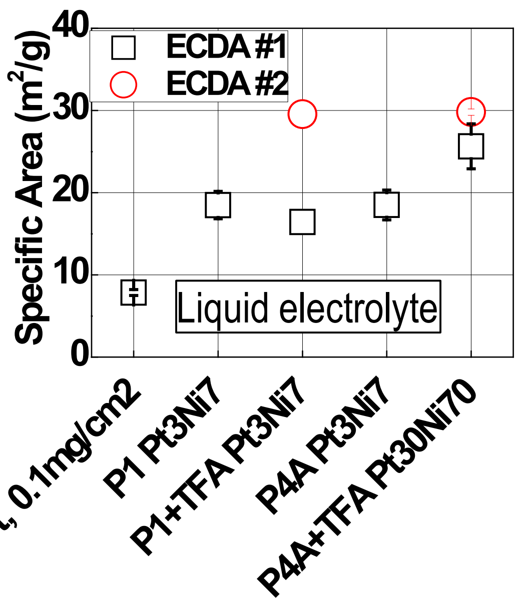
Metric	Change/DOE Tgt
Mass Activity (A/mg)	-64 / -40%
V @ 0.8A/cm^2	-47mV/-30mV
Surf. Area (m^2/g)	-40% / NA

- Substantial losses after 30k DOE Electrocatalyst AST cycles.

1. Specific area (coarsening)
2. Specific activity (Ni loss)

Accomplishments and Progress – NPTF Dealloying Optimization

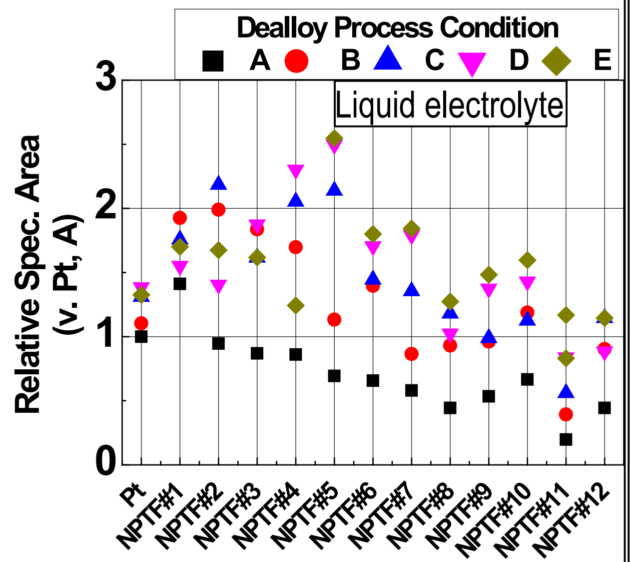
Structure, Process



- Specific area of Pt_3Ni_7 increases 50% (to 30m^2/g) after annealing and optimized dealloying.

Pre-project work

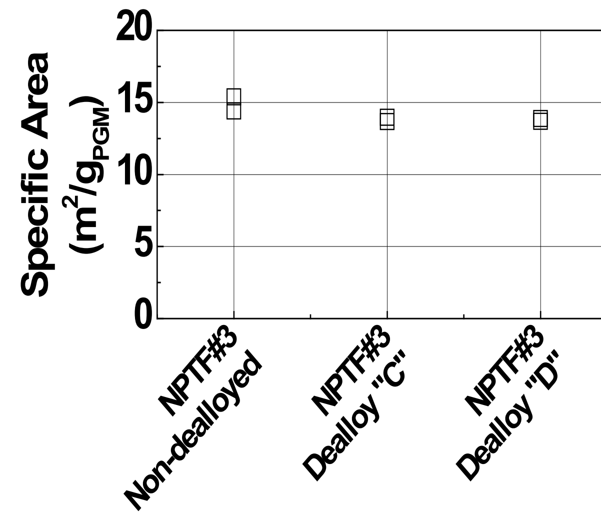
Composition, Process



- NPTF specific area has strong sensitivity to composition and dealloying process conditions.

Pre-project and current project work

MEA Measurements

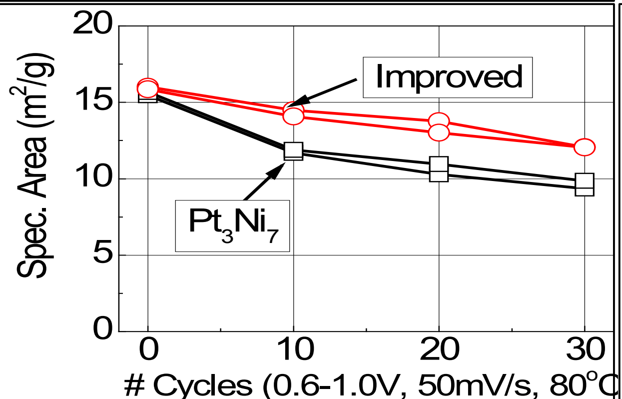


- After MEA conditioning, pre-dealloyed NPTF specific area is *lower* than non-dealloyed.
  - ~ 50% of liq. values.
- Studies in progress to determine discrepancy source.

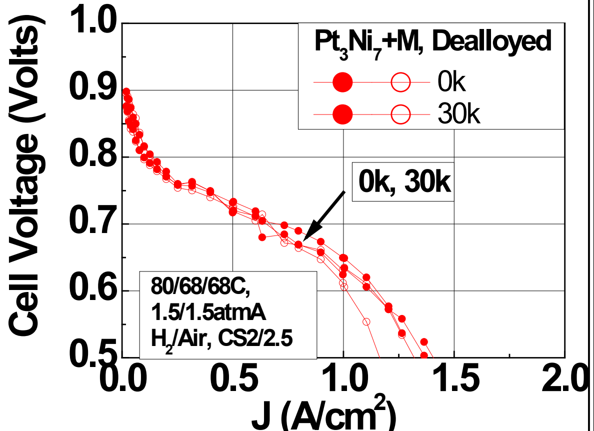
Pre-project work

Accomplishments and Progress – Durable NPTF Development

NPTF Stabilization – "M"



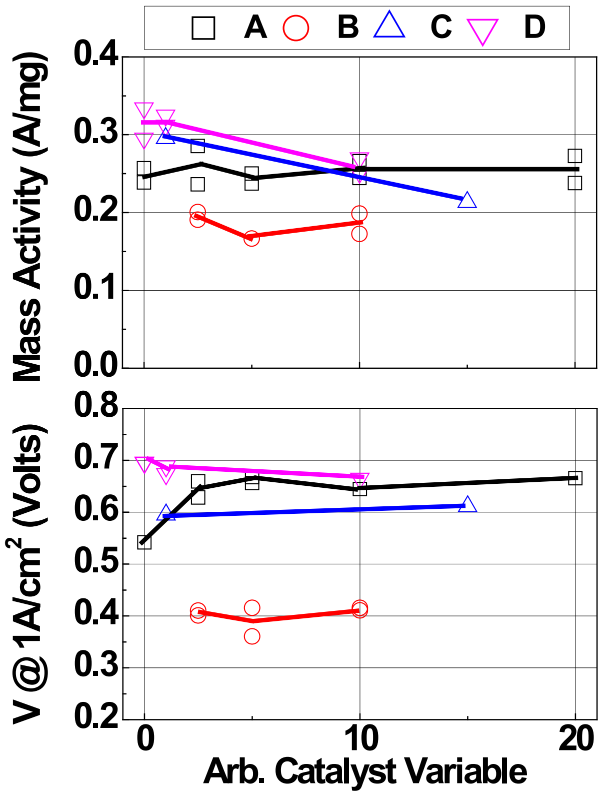
- Specific area loss reduced from -38 to -24% w/ "M".



- Substantial deactivation; performance optimization needed.

Pre-project work

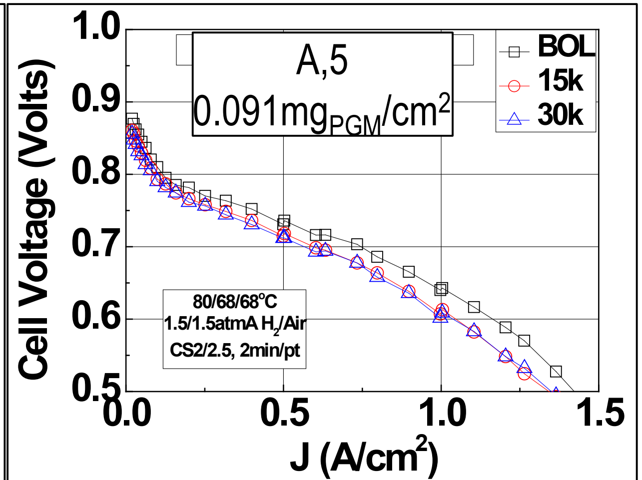
"M" Performance Optimization



- Activity, performance optimization in progress via 4 approaches.
- Composition, process variables influential.

Current project

"M" Electrocatalyst Durability



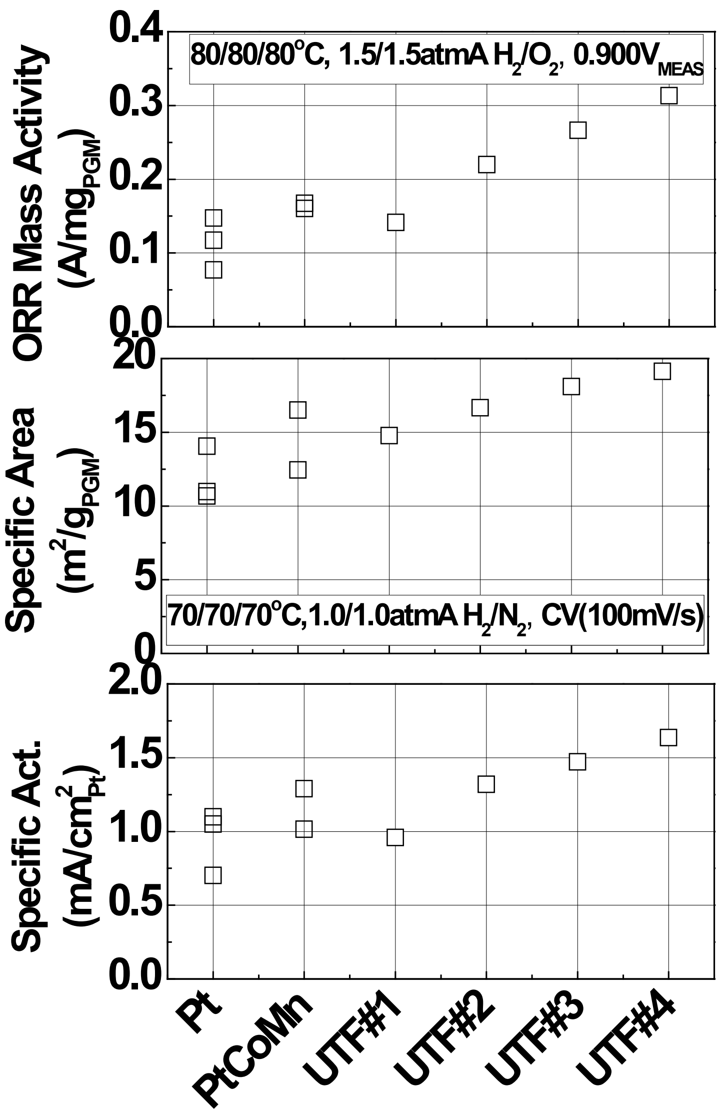
Metric	Change/DOE Tgt
Mass Activity (A/mg)	-40±0.8 / -40%
V @ 0.8A/cm²	-28±1.4 /-30mV
Surf. Area (m²/g)	-14±0.15 / NA %

- DOE 2020 electrocatalyst AST targets achieved.
- 60% mass activity improvement needed to achieve BP1 GNG.
- Durability evaluation of other approaches in progress.

Current project

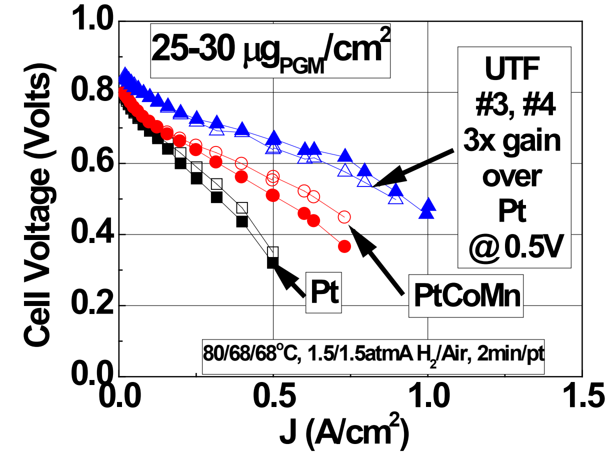
Accomplishments and Progress – UTF Electrocatalysts

New UTF Electrocatalysts Activity, Area (MEA)

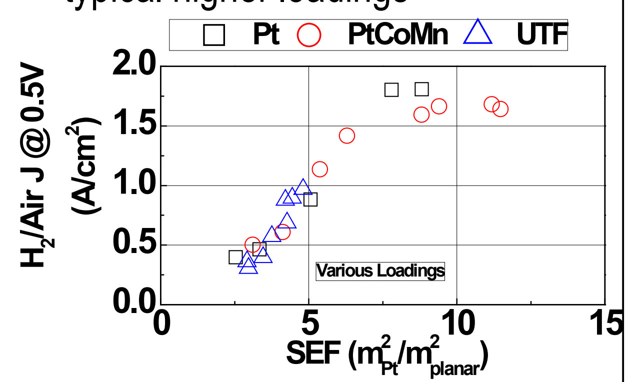


- Activity of initial 4 UTF catalysts is promising.
- UTF mass activity as much as ~ 2x Pt
- Specific area approaches $20 m^2/g$, close to UTF target.
- Specific activity 60% higher than Pt, but less than half of approach target ($4 mA/cm^2_{Pt}$).
- In-depth physical characterization in progress for input to modeling effort.

UTF H_2/Air Performance



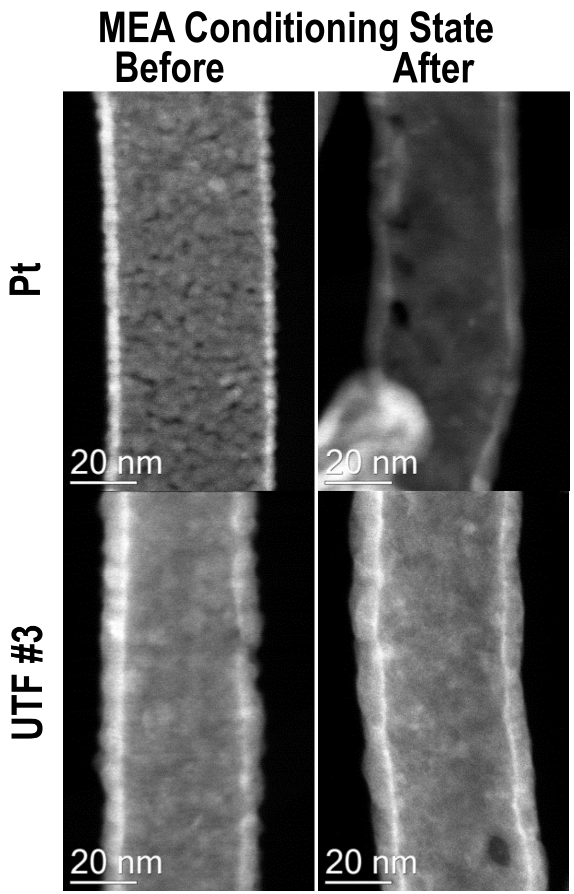
- UTF performance >> Pt
- High J performance suppressed v. typical higher loadings



- High J performance dictated by absolute cathode surface area
- UTF TGT: $>20m^2/g$, $0.075mg/cm^2$

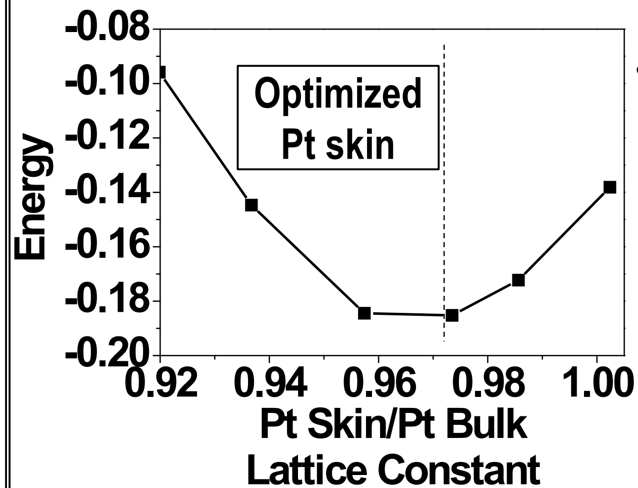
Accomplishments and Progress – UTF Electrocatalyst Analysis, Modeling

UTF STEM Analysis (ORNL)

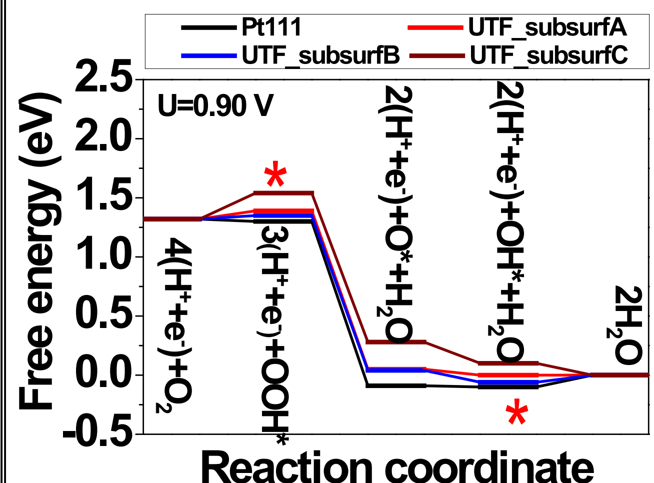


- Before testing, UTF is somewhat smoother than Pt (still not ideal, atomically smooth surface facets).
- After MEA conditioning, UTF morphology relatively unchanged but significant comp. change likely reduces specific activity.

UTF DFT Modeling (Purdue)



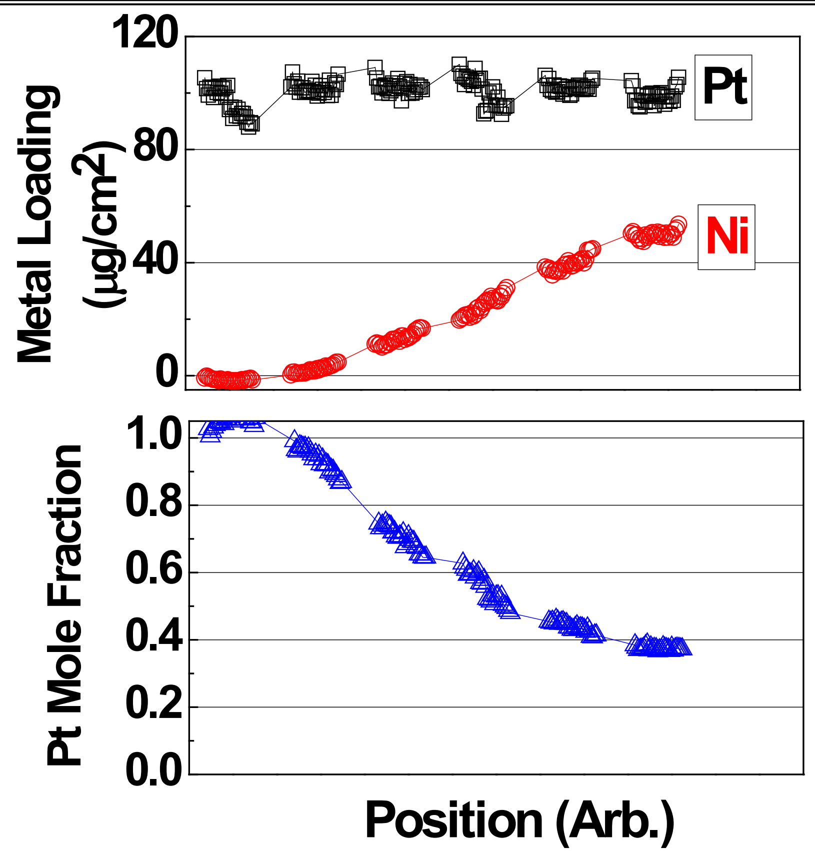
- Pt skin surface energy minimization of model UTF



- Two possible energy barriers identified for different model UTF sub-surface compositions
- Comparison between experiment and model on-going.

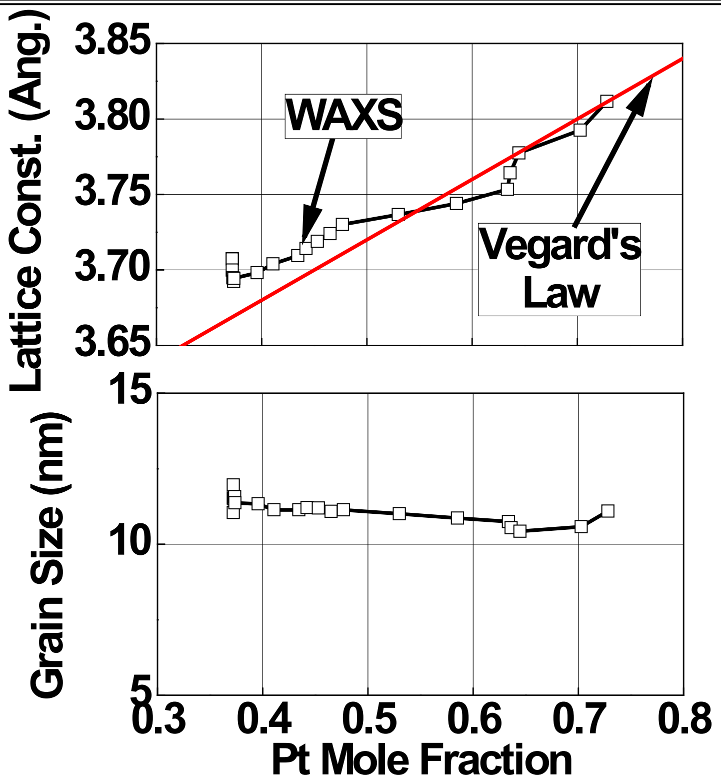
Accomplishments and Progress – High Throughput Development

Composition Analysis of Gradient PtNi



- Pt_xNi_{1-x}/NSTF fabricated w/ gradient composition across NSTF growth substrate.
- Composition analysis by XRF conducted across gradient w/ 1mm spatial resolution.

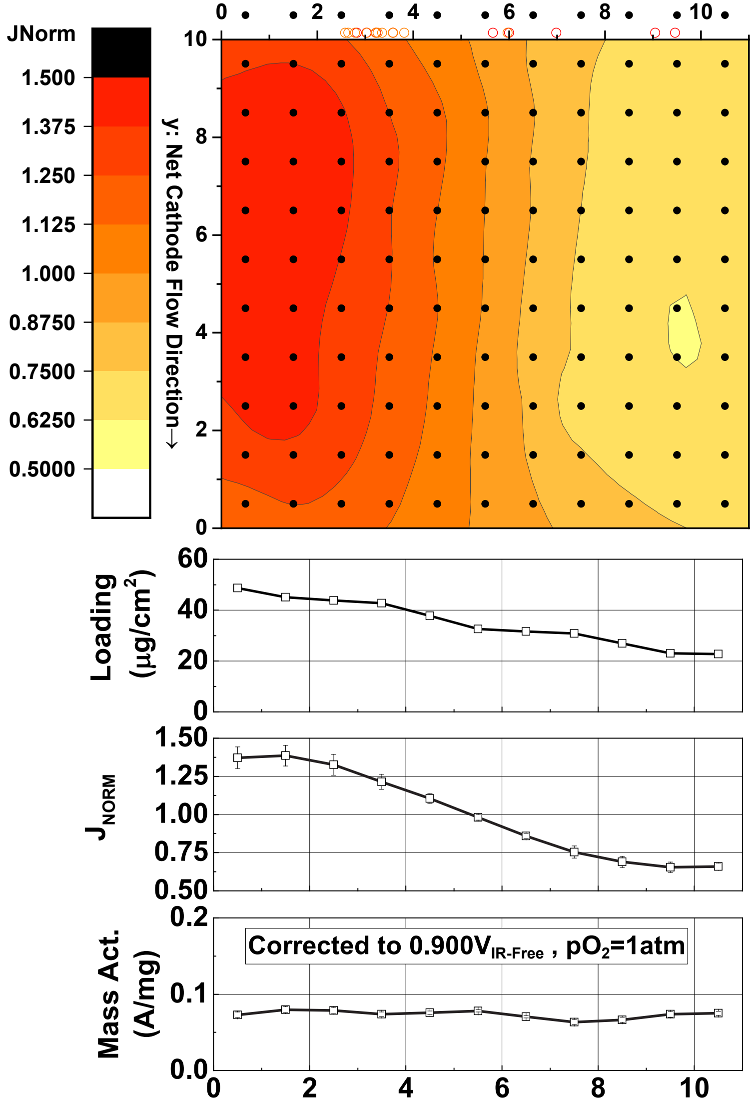
Wide Angle Xray Scattering (ANL)

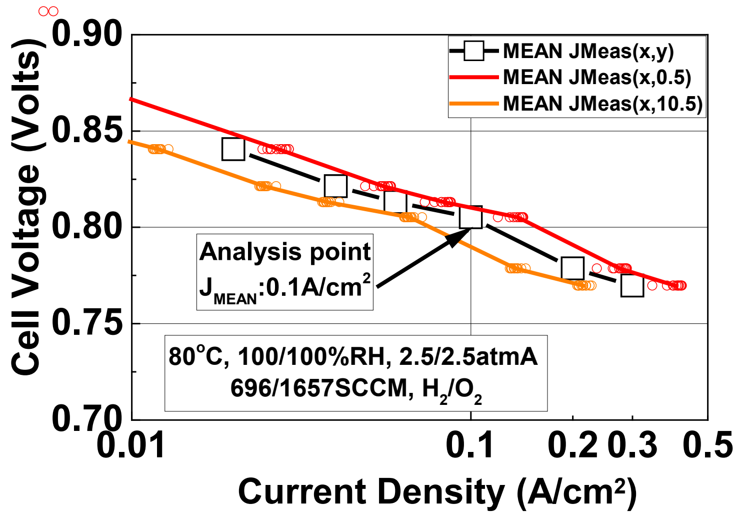


- WAXS allowed for relatively rapid measurement of key bulk structural characteristics.
- Lattice constants largely as expected.
- Grain sizes larger than determined with *similar* homogenous catalysts by XRD

Accomplishments and Progress – High Throughput Development

Segmented Cell MEA Activity of Loading-Gradient Pt/NSTF Electrode





- Successfully evaluated mass activity of gradient NSTF electrode MEA in 121 segment, 50cm^2 test cell.
  - Pt load gradient: 48→22µg/cm^2
- J gradient consistent w/ loading gradient
- Mass activity @ 0.900$V_{IR\text{-}FREE}$ similar to homogenous catalysts.
- Application to gradient alloy electrocatalyst in progress.

Collaborations

- **3M - Electrocatalyst Fabrication and Characterization, Electrode and MEA Integration, HT Development**
  - Energy Components Program: A.Steinbach (PI), A. Hester, C. Duru, S. Luopa, A. Haug, J. Abulu, A. Komlev, K. Lewinski, M. Kuznia, and I. Davy.
  - Corporate Analytical Laboratory: J. Bender, M. Stephens, M. Brostrom, A. Gharachorlou
- **Johns Hopkins University – Dealloying Optimization, kMC Modeling, HT Development**
  - J. Erlebacher (PI), L. Siddique
- **Purdue University – DFT Modeling of Electrocatalyst Activity, Durability**
  - J. Greeley (PI), Z. Zeng
- **Oak Ridge National Laboratory – Structure/Composition Analysis**
  - D. Cullen (PI)
- **Argonne National Laboratory – XAFS and HT Development**
  - D. Myers (PI), J. Kropf

- **FC-PAD Consortium**
  - MEAs to be provided annually.

Barriers

1. Significantly improved electrocatalysts will require optimization of large composition/process space.

2. Electrocatalyst AST durability of UTF electrocatalysts is not known; may be insufficient to achieve DOE and project targets.

3. Minimum stable UTF electrocatalyst thickness on support, fabricated with scalable-processes, is not known.

Key Future Work – 2Q16-1Q17

1. Continue characterization studies of several new NPTF and UTF electrocatalysts to establish functional relationships between electrocatalyst physical properties, fabrication process parameters, and functional response.

2. Establish reliable high throughput electrocatalyst fabrication and characterization methods to accelerate development.

3. Refine kMC and DFT models to capture experimentally-observed trends for baseline NPTF and UTF electrocatalysts, to enable predictive capability for new electrocatalyst concepts.

4. Optimize first generation project “M” electrocatalysts to achieve project G/NG
   - NPTF or UTF ORR electrocatalyst achieves:
     (≥ 0.44 A/mg PGM and ≤ 50% mass activity loss) or
     (≥ 0.39 A/mg PGM and ≤ 40% mass activity loss).

5. Incorporate first generation electrocatalysts into advanced NSTF electrodes and evaluate for performance, operational robustness and durability at loadings approaching DOE and project targets.

Response to Reviewers' Comments

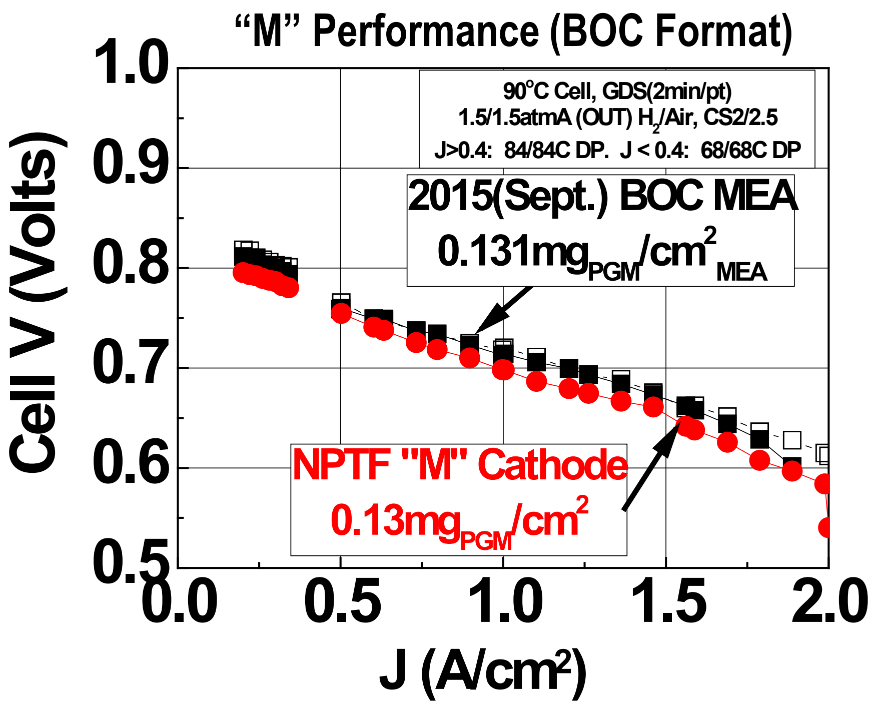
- This project has not yet been reviewed.

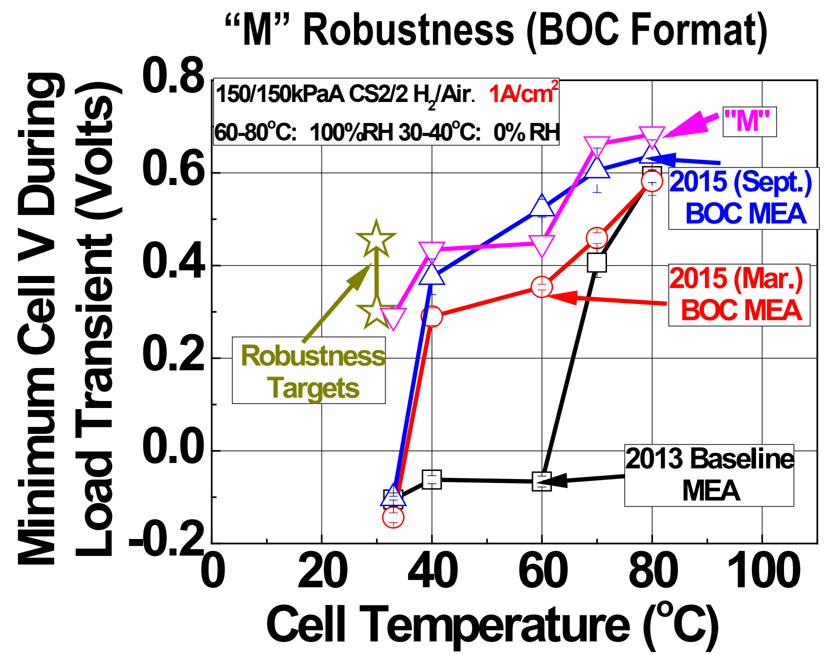
Summary

- NSTF ORR electrocatalyst development is based on two distinct thin film morphologies.
  1. Nanoporous thin film
     - Current status (in MEA): 0.47A/mg, 19m^2/g, 0.091mg$_{PGM}$/cm^2
     - Sensitive to composition, structure, and dealloying process conditions
  2. Ultrathin film
     - Current status (in MEA): 0.31A/mg, 19m^2/g, 0.025mg$_{PGM}$/cm^2
     - H_2/Air performance is transport limited; need 2x higher absolute area.
     - Durability assessments initiated
- Stabilization approach ("M") has enabled electrocatalyst which achieves DOE 2020 durability target but activity low; further optimization in progress.
- High throughput electrocatalyst development has good prospects for significantly accelerating project development timeline.
  1. HT Fabrication
     - Deposition demonstrated
  2. HT Electrochemical Characterization
     - Segmented cell promising.
  3. HT Composition/Structure Characterization
     - Bulk composition and structure analysis demonstrated.

Technical Backup Slides

Backup Slide – "M" Best of Class MEA



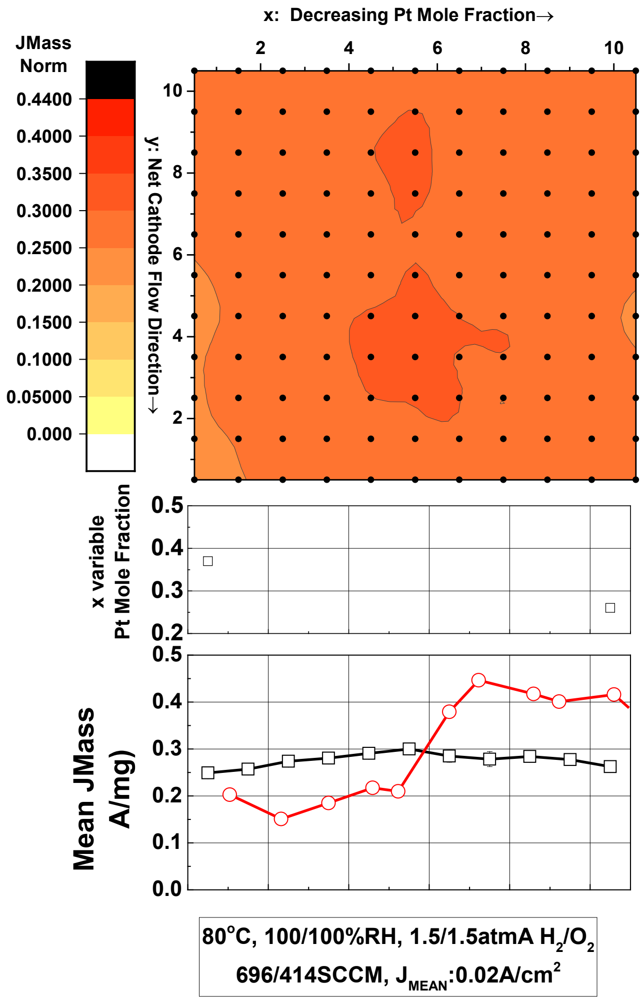


- "M" integrated into BOC MEA format (FC104) and evaluated for performance and operational robustness.
- Compared to 3M 2015(Sept.) BOC MEA (FC104), first "M" BOC MEA has:
  - Lower BOL mass activity (0.28 v. 0.39A/mg)
  - Lower rated and specific power (5.7 v. 6.8 kW/g)
  - Similar/improved operational robustness

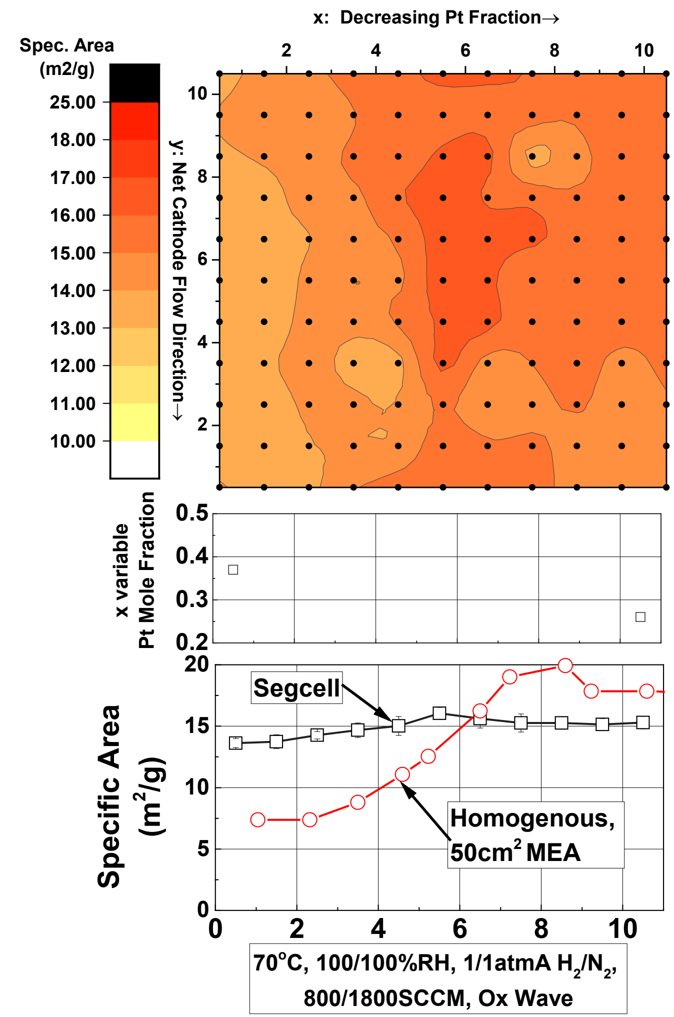
Both MEAs include identical "X3" anode GDL, "B" cathode interlayer (16µg/cm² Pt/C), 3M-S 725EW 14µ PEM, and FF2 from FC104. Loadings are total MEA (anode, cathode, and interlayer).

Backup Slide – HT MEA Evaluation of NPTF Pt_xNi_{1-x} (First Trial)

Mass Activity



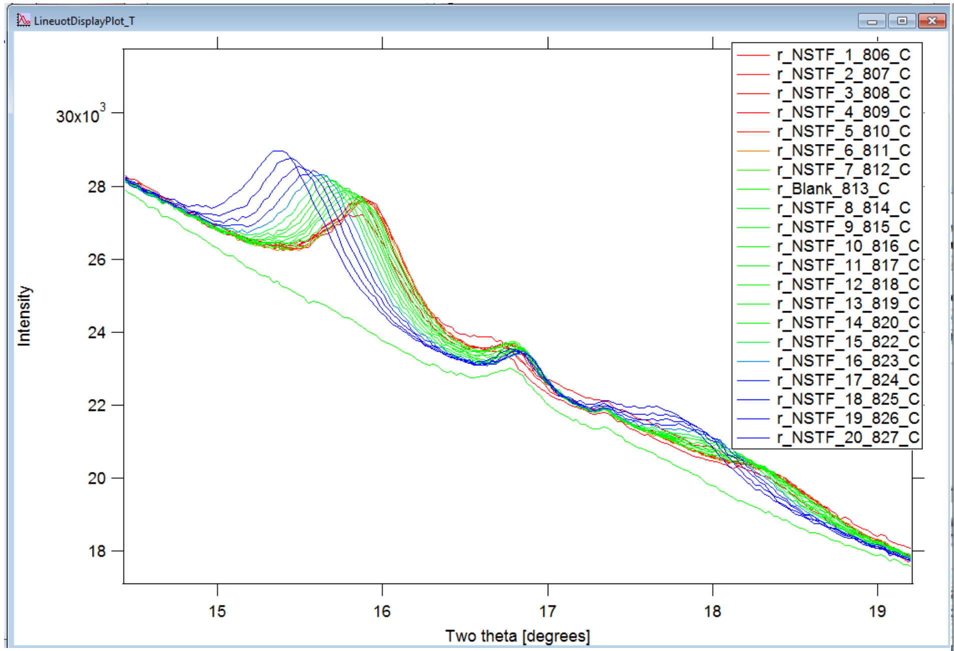
Specific Area



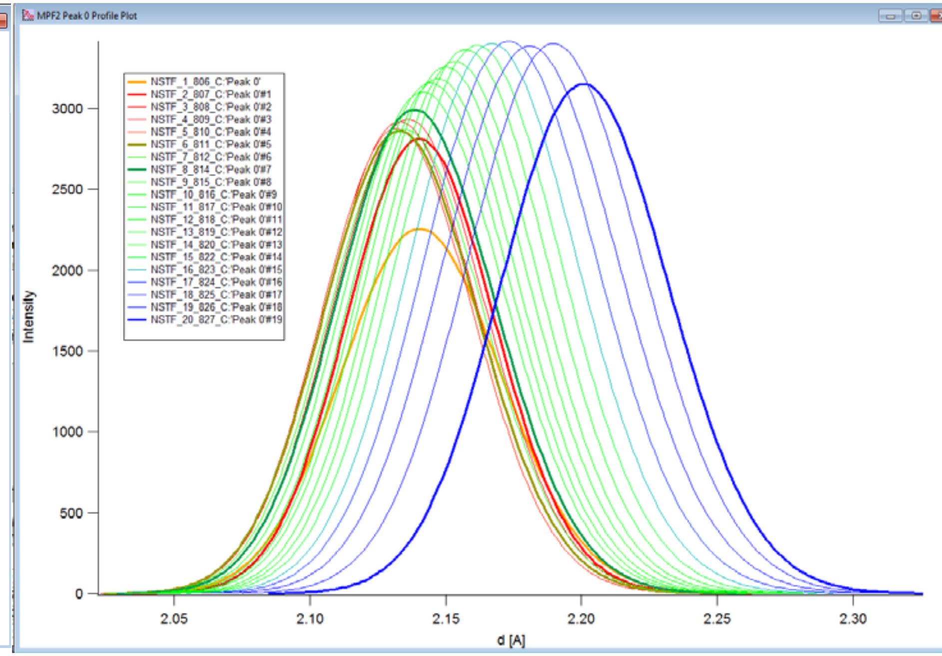
- Annealed NPTF PtNi in segmented cell does not show expected 2x transition in activity and area at Pt_3Ni_7
- Segmented cell "peak" approximately at right composition, but response is very muted.
- Diagnostic work in progress.

Backup Slide – WAXS of Gradient PtNi Electrocatalyst

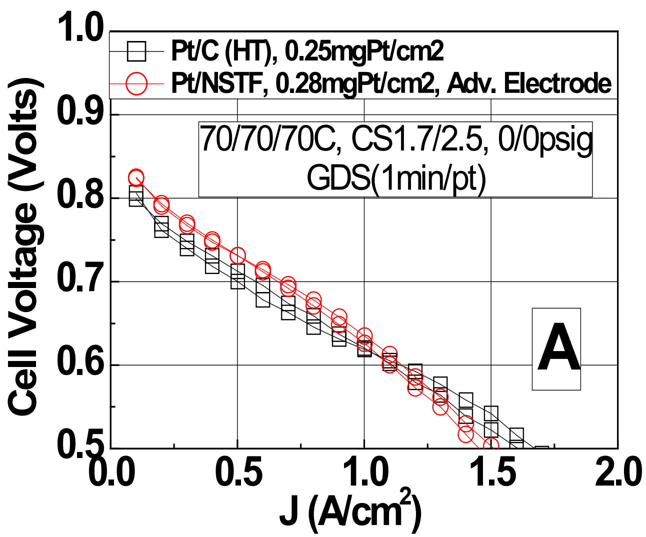
Measured WAXS Spectra v. Position

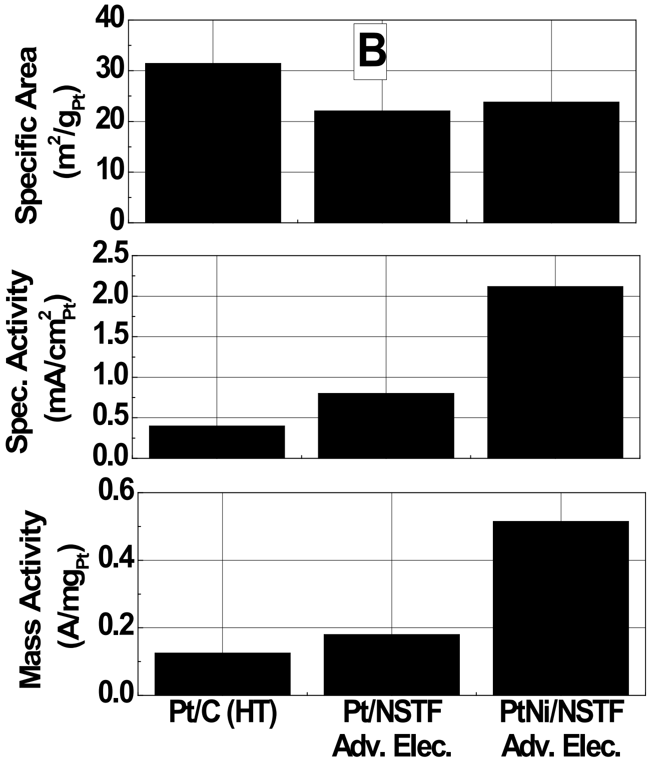


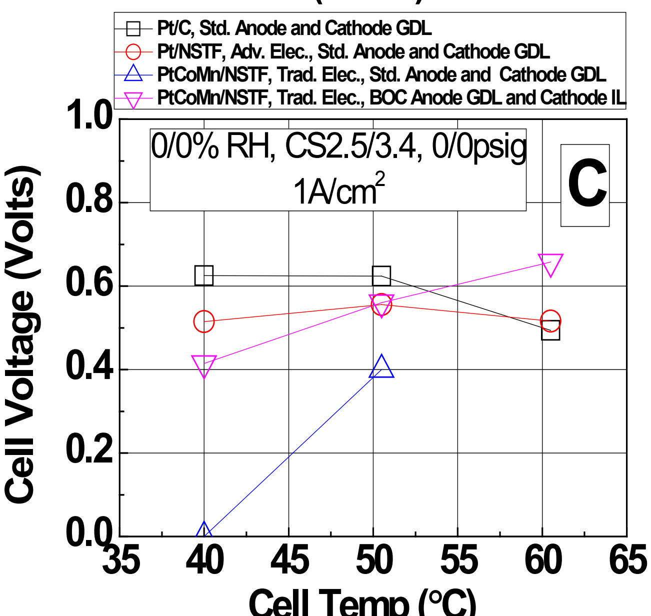
Peak Fitting



Backup Slide – Adv. Electrode Performance, Robustness, Activity







A. At similar loading, Pt/NSTF in advanced electrode yields higher kinetic but reduced transport performance.

B. Activity, area of Pt/NSTF and dealloyed NPTF PtNi/NSTF advanced electrodes compared to HT Pt/C; similar to traditional NSTF electrodes*; suggests little/no activity penalty in MEA electrode*.

C. Operational robustness (temperature sensitivity) of adv. NSTF electrode similar to Pt/C and traditional NSTF electrodes w/ optimized anode DM and cathode IL; significantly improved over traditional NSTF w/o optimized ad-layers.