

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

## U.S. DOE 2019 Annual Merit Review and Peer Evaluation Meeting

Washington, DC

April 30, 2019

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## Project FC143

# Project Overview

## Timeline

**Project Start:** 1/1/2016  
**Project End:** 6/30/2019

## Barriers

- A. Durability
- B. Cost
- C. Performance

## Budget

**Total DOE Project Value:** \$4.360MM\*  
**Total Funding Spent:** \$3.274MM\*  
**Cost Share Percentage:** 23.72%

\*Includes DOE, contractor cost share and FFRDC funds as of 1/31/19

## DOE 2020 Technical Targets

**PGM total content (both elec.):** 0.125 g/kW  
**PGM total loading:** 0.125 mg/cm<sup>2</sup>  
**Loss in initial catalytic activity:** < 40%  
**Loss in performance at 0.8A/cm<sup>2</sup>:** < 30 mV  
**Loss in performance at 1.5A/cm<sup>2</sup>:** < 30 mV  
**Mass activity (0.90V<sub>IR-FREE</sub>):** 0.44 A/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 have intrinsically high specific activity and support durability, and approach many DOE 2020 targets *in state-of-the-art MEAs*.

**Project electrocatalysts will be:**

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

## Overall Approach

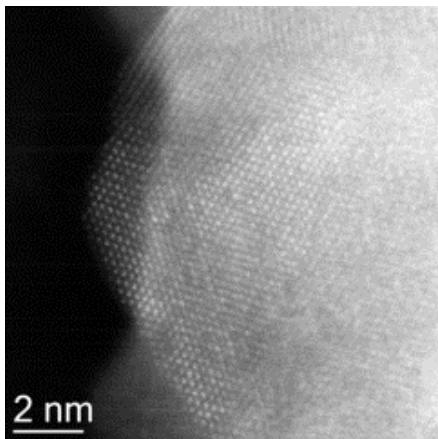
**Establish relationships between electrocatalyst functional response** (activity, durability), **physical properties** (bulk and surface structure and composition), and **fabrication processes** (deposition, annealing, dealloying) **via systematic investigation.**

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

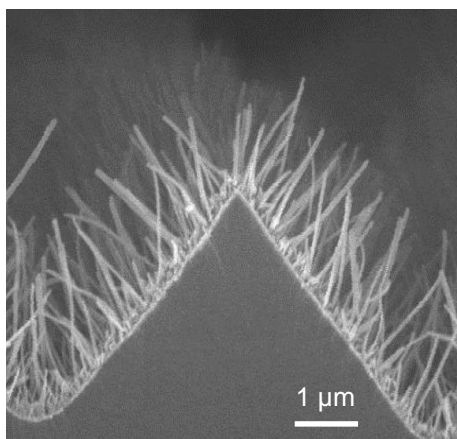
# Approach – Active, Stable Ultrathin Film Electrocatalysts

## Ultrathin Film (UTF) Catalyst on NSTF Supports

### UTF Catalyst



### NSTF Support

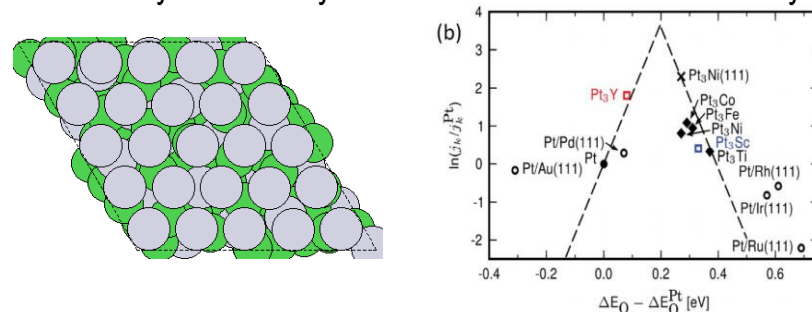


1. **Develop active and stable thin film catalysts** on durable supports via structure, composition, and process optimization.
2. Utilize **atomic and mesoscale modeling** and **advanced physical characterization** to accelerate development.
3. **Increase catalyst absolute area** by integration with higher area supports.

## Electrocatalyst Modeling

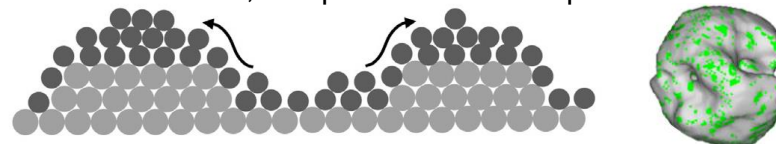
### Density Functional Theory (Purdue)

Stability and activity calculations of Pt skins on Pt alloys



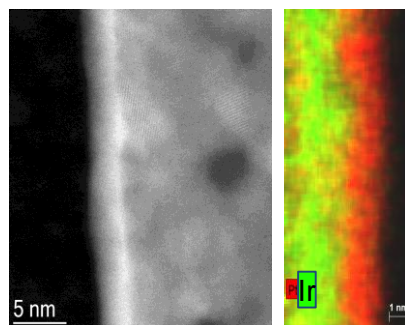
### Kinetic Monte Carlo (Johns Hopkins)

Structure, composition evolution predictions

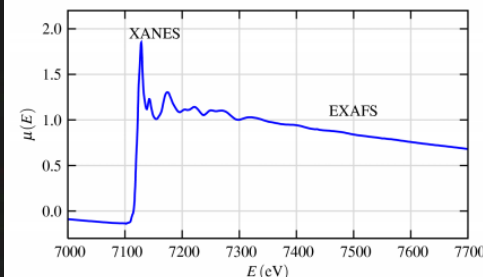


## Advanced Characterization

### TEM/EDS (ORNL)



### XAFS (ANL)



# Status versus DOE and Project Targets

	2020 Target and Units	Project Target	2018	2019
Platinum group metal (PGM) total content (both electrodes)	0.125 g/kW (Q/ΔT ≤ 1.45)	0.1	0.110 <sup>1</sup> , 150kPa 0.087 <sup>1</sup> , 250kPa	0.106 <sup>5</sup> , 150kPa 0.086 <sup>5</sup> , 250kPa
PGM total loading (both electrodes)	0.125 mg/cm <sup>2</sup>	0.10	0.098 <sup>1</sup>	0.094 <sup>5</sup>
Loss in catalytic (mass) activity	40 %	20	20 <sup>1</sup>	16 <sup>5</sup>
Loss in performance at 0.8 A/cm <sup>2</sup>	30 mV	20	22 <sup>1</sup>	25 <sup>5</sup>
Loss in performance at 1.5 A/cm <sup>2</sup>	30 mV	20	< 5 <sup>1</sup>	< 5 <sup>5</sup>
Mass activity @ 900 mV <sub>iR-free</sub>	0.44 A/mg (MEA)	0.50	0.39 <sup>2</sup> , Ir UL 0.27 <sup>3</sup> , Ta UL 0.57 <sup>4</sup> , PtNi+Ru,Cr	0.41 <sup>6</sup> , Ir UL 0.42 <sup>7</sup> , Ta UL 0.57 <sup>4</sup> , PtNi+Ru,Cr

**YELLOW: Achieved DOE target. GREEN: Exceeded DOE Target and Achieved Project target.**

<sup>1</sup>UTF 50Pt/11Ir. <sup>2</sup>UTF 28Pt<sub>B</sub>Ni<sub>1-B</sub>/6Ir. <sup>3</sup>UTF 40Pt/8Ta. <sup>4</sup>UTF 28PtNi+Cr or Ru. <sup>5</sup>UTF 31Pt/26Ir/NSTF. <sup>6</sup>UTF 28Pt<sub>C</sub>Ni<sub>1-C</sub>/6Ir. <sup>7</sup>UTF 10Pt/8Ta. PGM total content and loadings evaluated in "Best of Class" MEAs which include a low PGM anode (UTF 9Pt/11Ir), 14μm supported 3M PFSA membrane, and robustness-optimized diffusion media with a cathode interlayer (16μg<sub>Pt</sub>/cm<sup>2</sup>). PGM total content values at 95°C cell, 150kPa or 250kPa H<sub>2</sub>/Air, 2.0 and 2.5 H<sub>2</sub> and Air stoichiometry, Q/ΔT = 1.45kW/°C (0.663V).

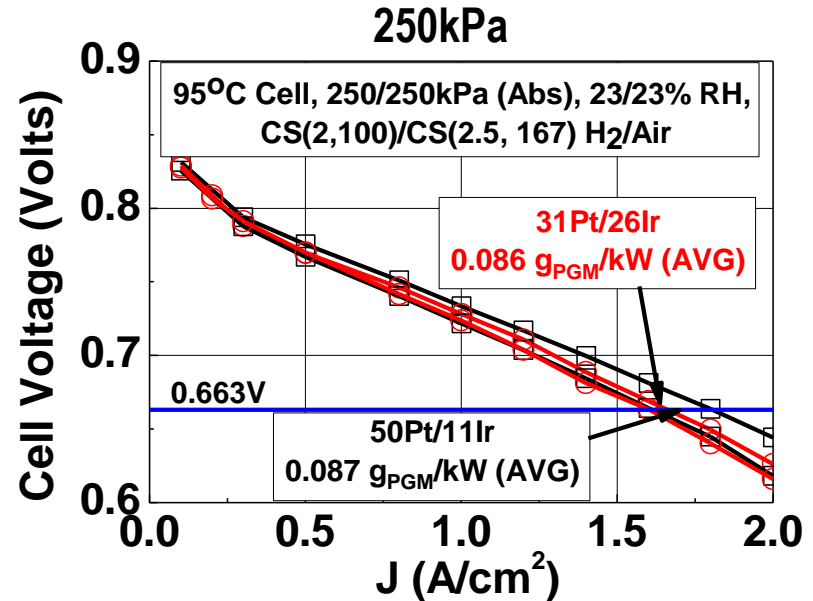
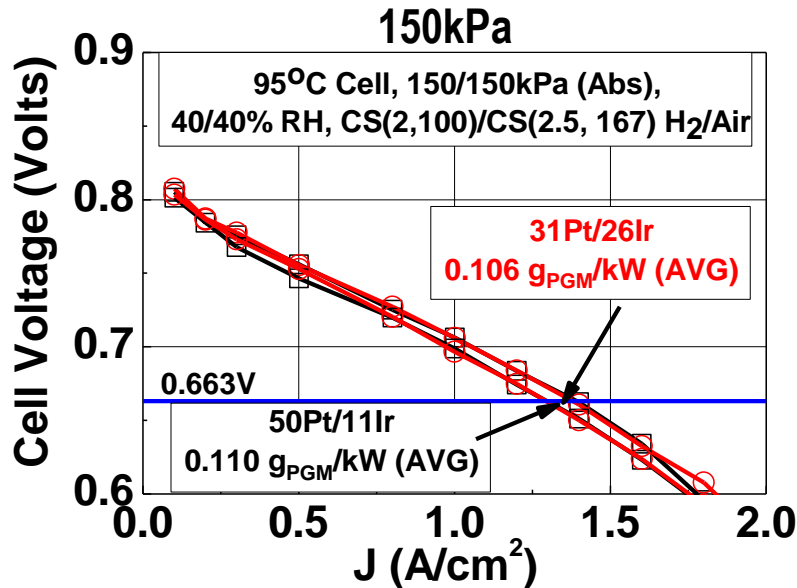
- 2019 catalysts have achieved 6 of 6 DOE 2020 targets addressed and 4 of 6 project targets.
- Two UTF Pt catalysts with Ir underlayers have each met 5 of 6 DOE targets.
- DOE mass activity target approached with UTF Pt/Ir, PtNi/Ir and Pt/Ta catalysts.
- Project mass activity target exceeded with UTF PtNi catalysts with surface modification by Cr or Ru.

## BP3 Milestones and **Project Deliverable**

Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
1.6 Pwr. Dur.	M1.6.1	Electrocatalyst demonstrates < 50mV loss at 1.5A/cm <sup>2</sup> .	100%	9
1.2 Cat. EC. Char.	M1.2.2	Electrocatalyst demonstrated with ≥ 0.50A/mg mass activity	100%	9
	M1.2.3	Electrocatalyst demonstrated with ≤ 20% mass activity loss	100%	10
1.5 Cat. Int.	M1.5.2	Electrocatalyst achieves ≥ 0.50A/mg, ≤ 20% loss, and PGM content ≤ 0.11 g /kW @ Q/ΔT=1.45kW/°C.	85%	11
1.3 Cat. Char.	M1.3.1	TEM/EDS and XAFS characterization of NSTF catalyst in at least three conditioning states completed.	100%	11
1.6 Pwr. Dur.	M1.6.2	Electrocatalyst demonstrates < 30mV loss at 1.5A/cm <sup>2</sup> .	100%	9
1.5 Cat. Int.	M1.5.3	Catalyst demonstrated which achieves 80% of entitlement rated power in less than 5 hours using system-friendly activation protocol.	80%	12
<b>1.5 Cat. Int.</b>	<b>D1.5.4</b>	<b>A set of MEAs (6 or more, each with active area ≥ 50 cm<sup>2</sup>) which achieve all project targets is made available for independent testing at a DOE-approved location.</b>	<b>91%</b>	<b>13</b>

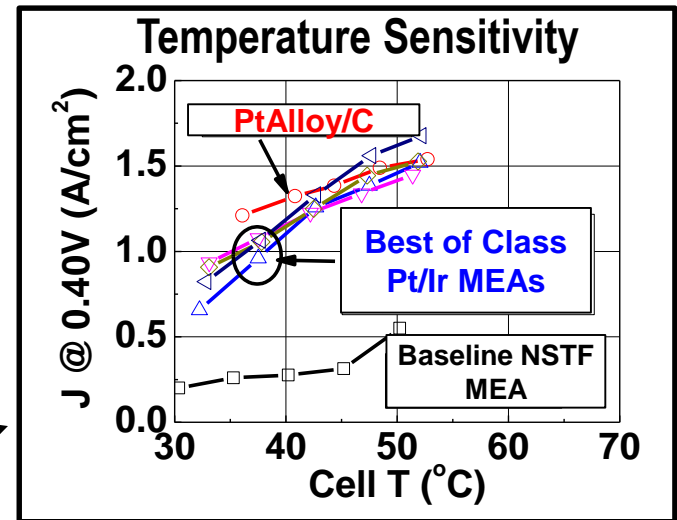
- BP3 milestones target demonstrating catalysts which meet project targets individually, then collectively approach final project targets, then collectively reach all project targets.
  - M1.3.1, M1.5 statuses are 85 and 91%, based on UTF 50Pt/11Ir.
- Focused efforts to address NSTF break-in conditioning added last year; good progress to date.
- Activities towards deliverable to be initiated in Q2 CY19.

# Accomplishments and Progress – UTF Pt/Ir Exceeds PGM Targets



- Two Pt/Ir catalysts (50Pt/11Ir, 31Pt/26Ir) exceeded PGM loading and content targets at 150kPa.
- At 250kPa, PGM contents improved to 0.086-0.087 g/kW

	Total PGM Loading (mg/cm <sup>2</sup> )	Total PGM Content @ 150kPa (g/kW)	Total PGM Content @ 250kPa (g/kW)
DOE 2020 Target	0.125	0.125	0.125
2018 (May) UTF 31Pt/26Ir	0.094	0.106	0.086
2018 (May) UTF 50Pt/11Ir	0.098	0.110	0.087

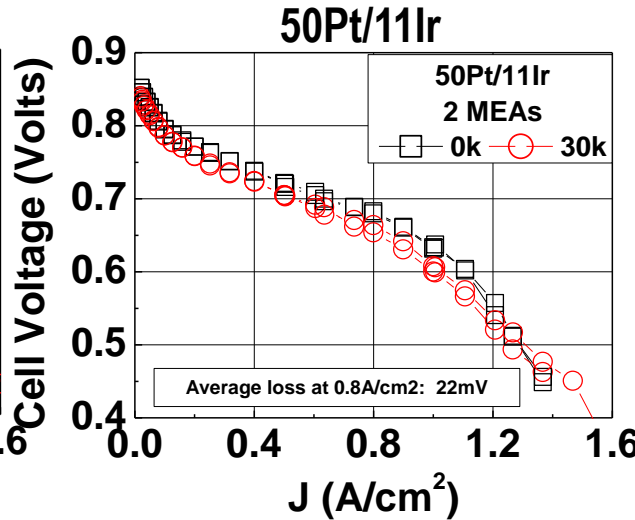
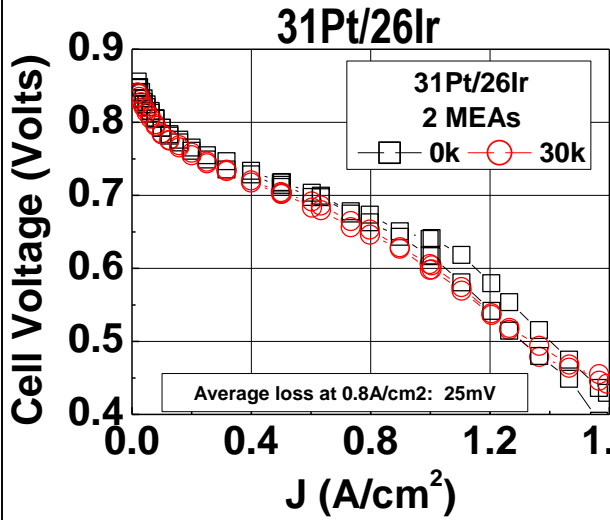


- MEAs are operationally-robust; improved vs. traditional NSTF electrodes; approaches dispersed electrodes

Best of Class MEAs include cathode interlayer (16 $\mu$ g<sub>PGM</sub>/cm<sup>2</sup>) and optimized anode GDL for operational robustness

# Accomplishments and Progress – UTF Pt/Ir Exceeds Durability Targets

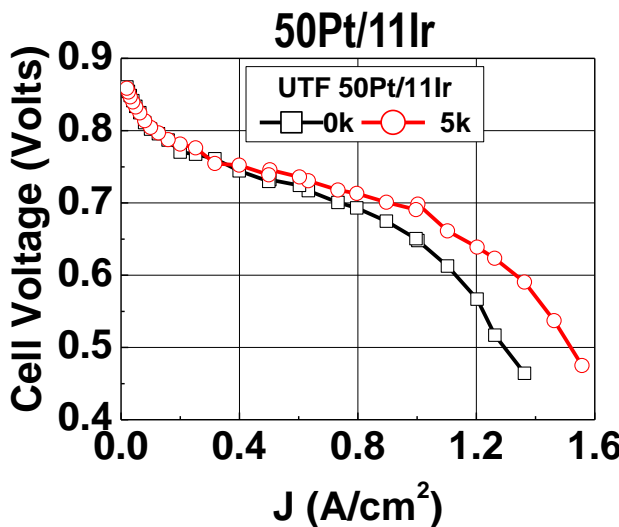
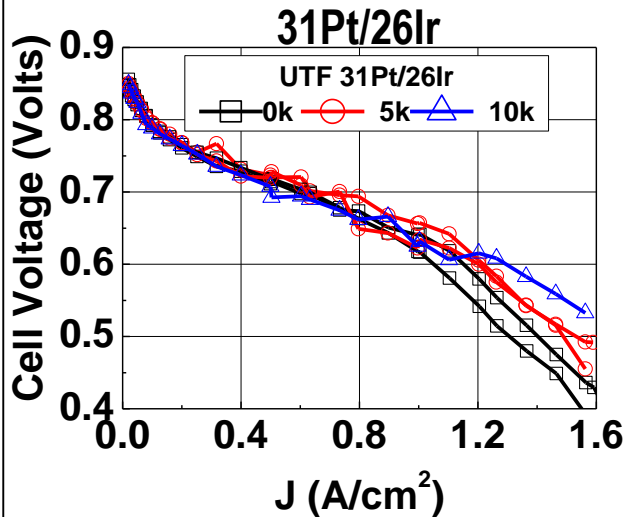
## Electrocatalyst AST Durability (80°C, 30K Cycles, 0.60-1.00V). 50cm<sup>2</sup> MEA Format.



- Mass activity losses  $\leq 20\%$
- $\leq 25\text{mV}$  loss at  $0.8\text{A}/\text{cm}^2$
- Minimal performance loss near limiting current density.

	Mass Act. Change (%)	$\Delta V$ @ $0.8\text{A}/\text{cm}^2$ (mV)
DOE Target	-40	-30
UTF 31Pt/26Ir	$-16 \pm 3$	$-25 \pm 12$
UTF 50Pt/11Ir	$-20 \pm 1$	$-22 \pm 5$

## Support AST Durability (80°C, 5K Cycles, 1.00-1.50V). 50cm<sup>2</sup> MEA Format.



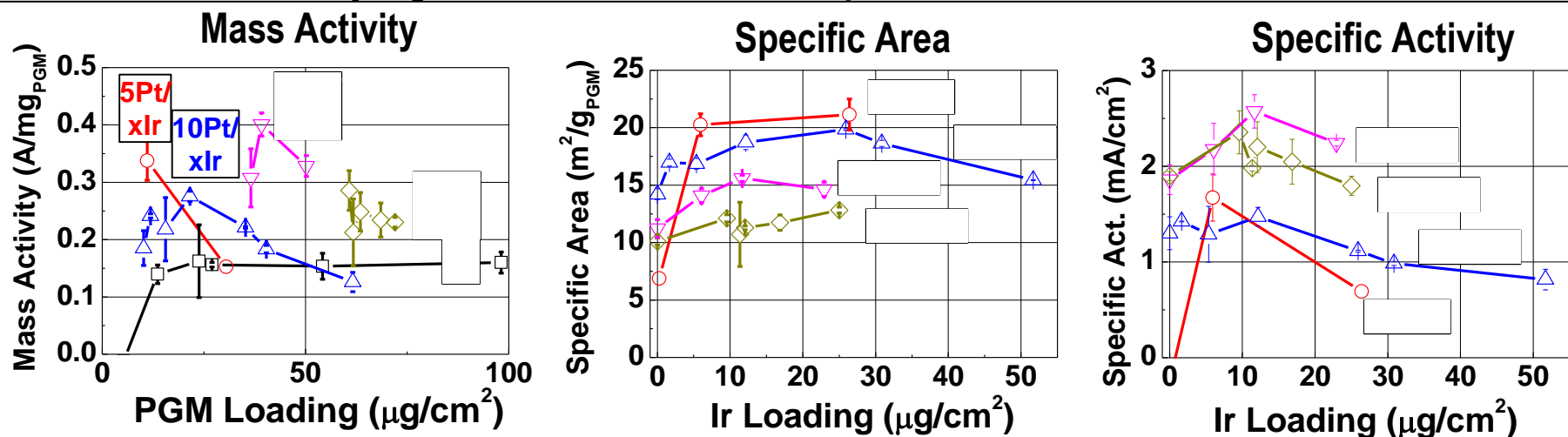
- Performance steady or improved after 5 or 10k cycles.
- ECSA changes  $< 2\%$ .

	$\Delta V$ @ $1.5\text{A}/\text{cm}^2$ (mV)	ECSA Change (%)
DOE Target	-30	NA
UTF 31Pt/26Ir	$< -5$	+2
UTF 50Pt/11Ir	$< -5$	-2

UTF Pt/Ir durability exceeds DOE targets;  $< 30\text{mV}$  loss,  $0-1.5\text{A}/\text{cm}^2$

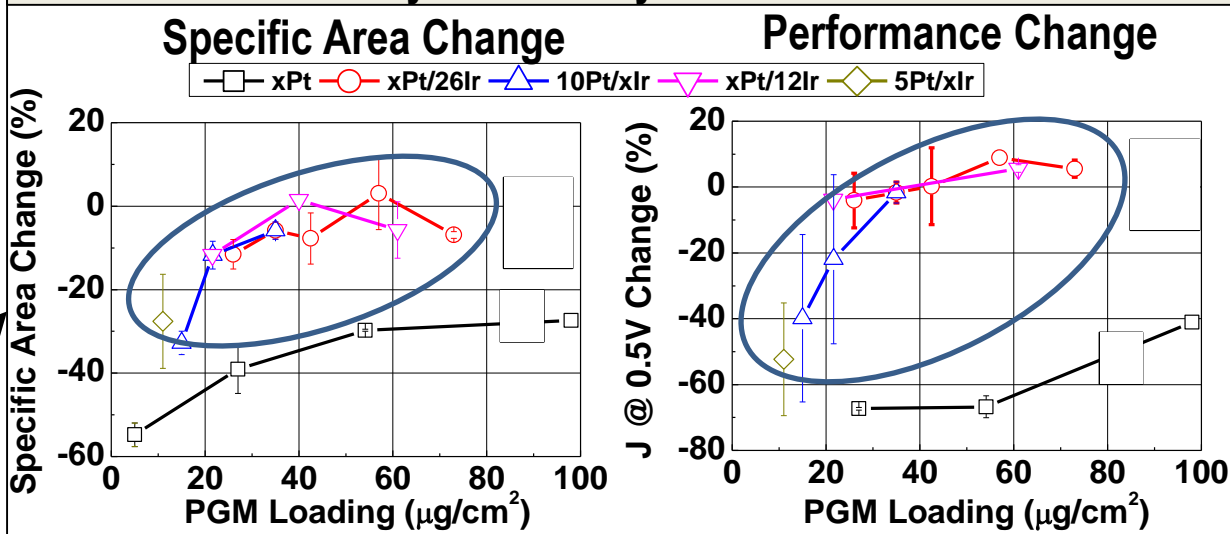


## Activity, H<sub>2</sub>/Air Performance vs. Composition. 50cm<sup>2</sup> MEA Format.



- Ir underlayer enhances PGM mass activity, up to 2.5x vs. Pt.
- Specific area: enhanced with as little as 2-5 μg<sub>Ir</sub>/cm<sup>2</sup>.
- Specific activity: optimal between 5-15 μg<sub>Ir</sub>/cm<sup>2</sup>.
- High activity Pt/Ir catalysts also durable: specific area and H<sub>2</sub>/Air performance.

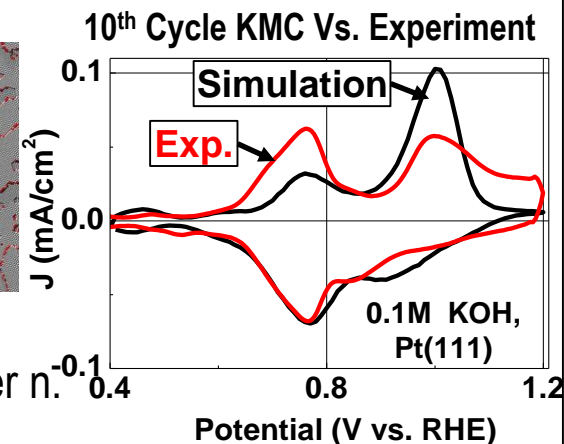
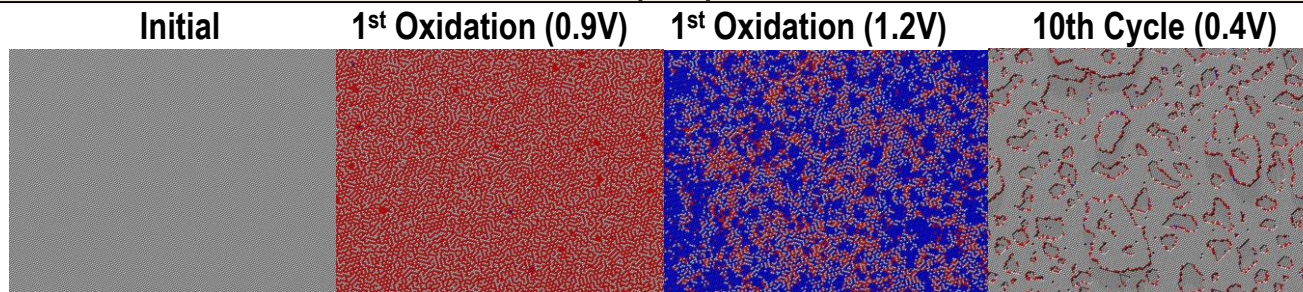
## Electrocatalyst Durability. 50cm<sup>2</sup> MEA Format.



**Pt/Ir Optimization: 40% improved activity vs. last year; durability maintained.**

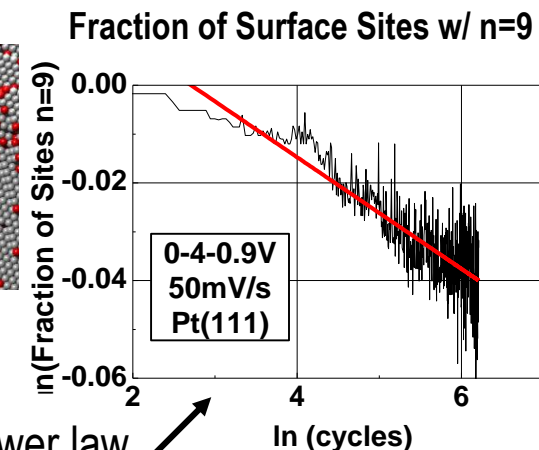
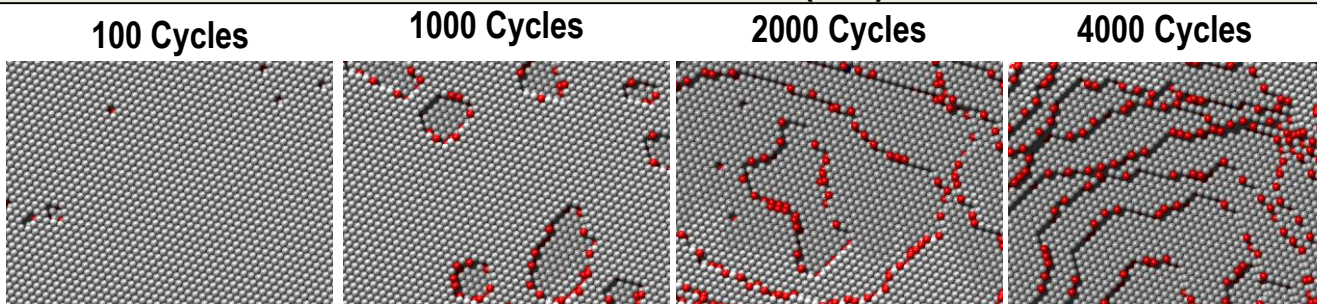
# Accomplishments and Progress – KMC Durability Modeling (Purdue, JHU)

## KMC Simulation of Pt(111) CV Predicts Pt Redox and Surface Roughening



- Initial scan to 0.90 V forms hydroxylated surface network
- Terrace sites ( $n=9$  coordination) 2<sup>nd</sup> oxidation at 1.20V; lower E for lower  $n$ .
- Roughening occurs upon oxide reduction; step edges remain oxidized.
- “Steady state” simulation captures key Pt redox features.

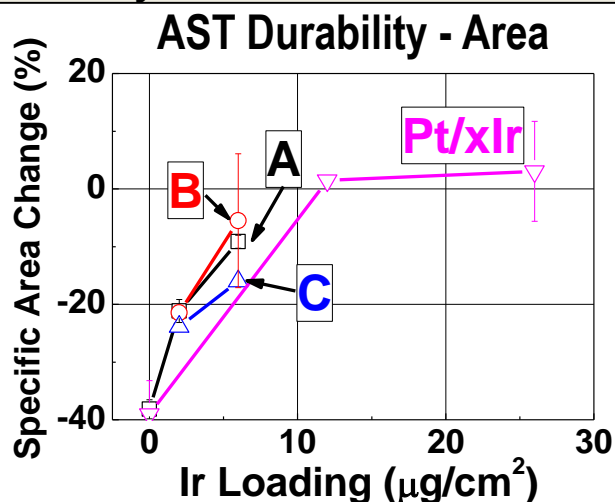
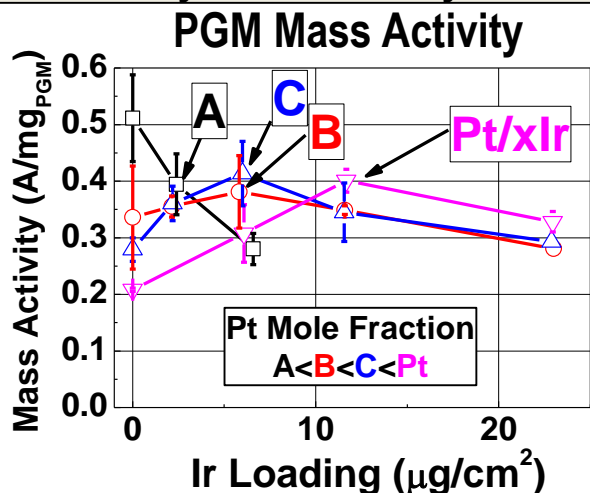
## KMC Simulation of Pt(111) Under Accelerated Stress Test



- Roughness forms via “vacancy islands”, which expand with cycling
- Step edges, once formed, remain oxidized; likely inactive for ORR.
- Simulation predicts continuous roughening through 1000s of cycles – power law.
- Next steps: Simulations of alloys, layered structures, and nanoparticles.

# Accomplishments and Progress – Pt, PtNi Integration with Ir Underlayer

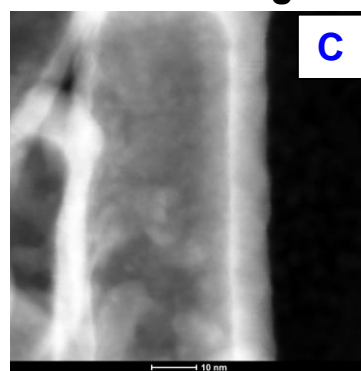
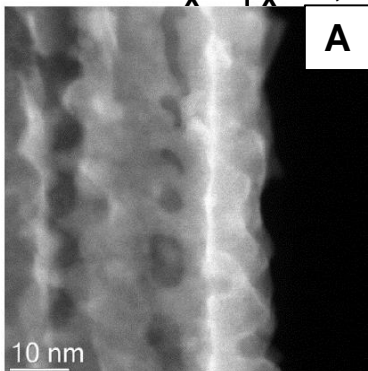
Activity, Electrocatalyst AST Durability vs Pt:Ni, Pt:Ir Ratios.  $30\mu\text{g}_{\text{Pt}}/\text{cm}^2$ .  $50\text{cm}^2$  MEA Format.



- Last year - integration of high activity UTF PtNi (A) onto Ir – severely reduced activity.
- This year - Ni, Ir content optimization - 4 catalysts with mass activity  $\geq 0.38 \text{ A}/\text{mg}_{\text{PGM}}$
- Electrocatalyst durability enhanced with  $\geq 2\mu\text{g}_{\text{Ir}}/\text{cm}^2$ .

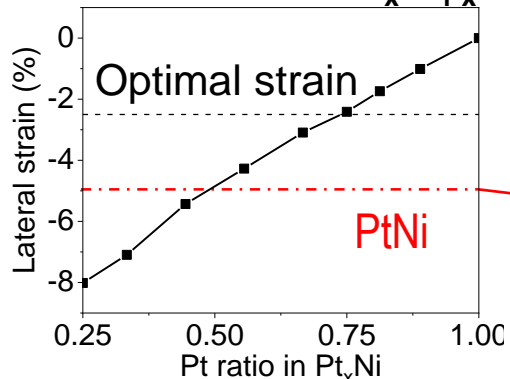
Possible PtNi Activity Loss Mechanism w/ Ir – Thin film instability; Pt skin over-compression?

$28\text{Pt}_x\text{Ni}_{1-x}/6\text{Ir}$ , After Conditioning

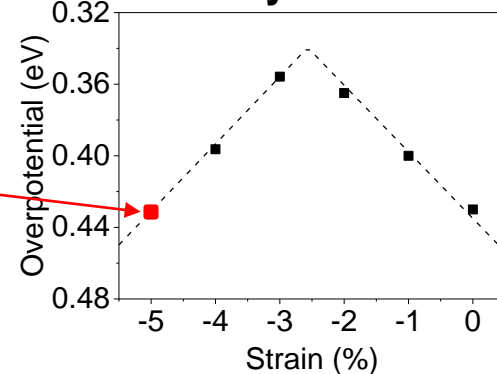


Higher Ni content PtNi catalysts on Ir were structurally unstable

DFT Strain of  $\text{Pt}_x\text{Ni}_{1-x}$



DFT Activity vs. Strain



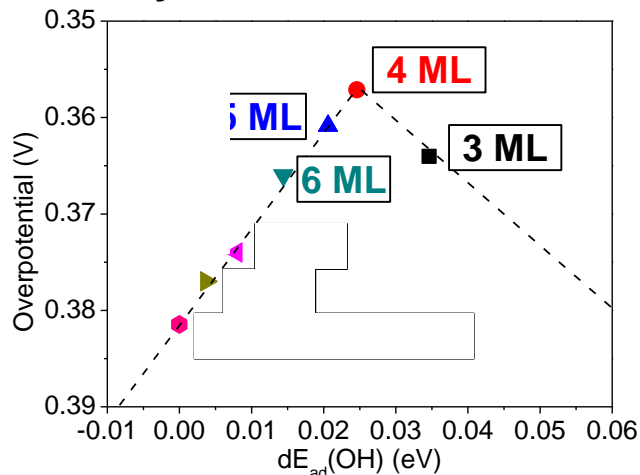
Ir increases Ni retention, leading to Pt skins on Ni-richer alloys such as Pt-skin/**PtNi**, which has too large of a strain for ORR

**Strain optimized PtNi/Ir yields enhanced activity and durability.**

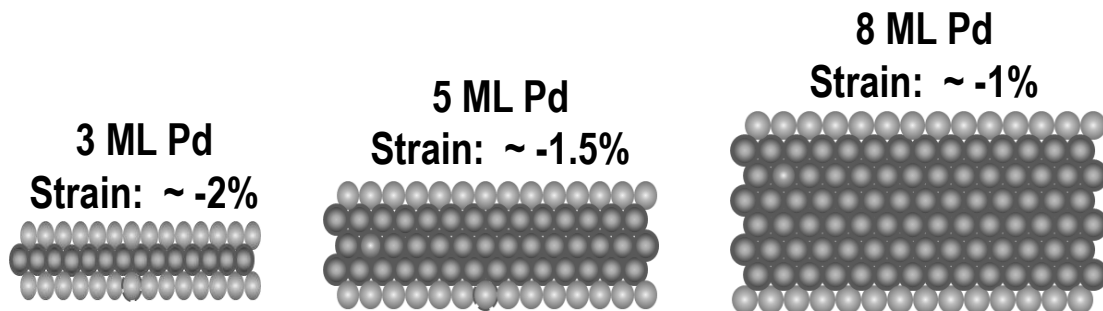
# Accomplishments and Progress – Monometallic Nanosheet Catalysts

## DFT Predictions – Enhanced Performance through Pure Strain Effects on Pt/Pd Nanosheets (Purdue)

### Activity vs. Nanosheet Thickness

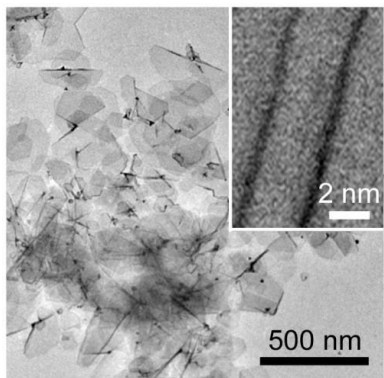


- Quasi-two dimensional nanosheets predicted to exhibit compressive strains which depend upon the nanosheet thickness.
- 4-5 ML Pd nanosheets predicted to have superior ORR activity.
- Optimal Pt nanosheets predicted to have very similar activity.

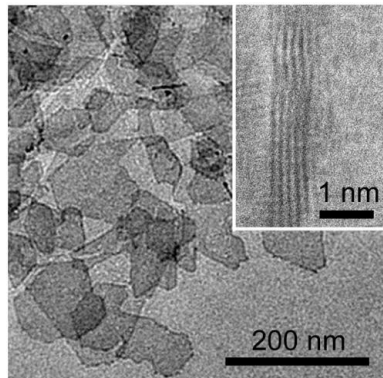


## Experimental Synthesis and Characterization of Pd Nanosheets (JHU (C. Wang), UC Irvine))

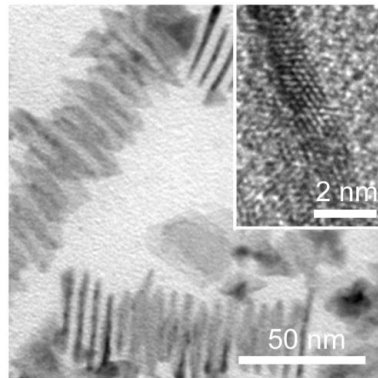
3 ML Pd Nanosheet  
1.5% Strain



5 ML Pd Nanosheet  
1.2% Strain



8 ML Pd Nanosheet  
0.3% Strain

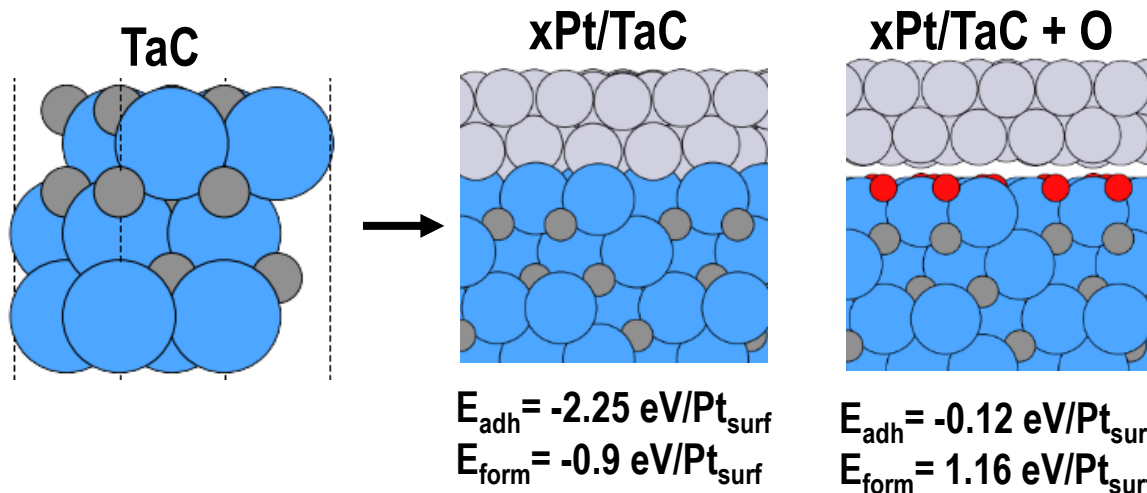


- Experimental Pd nanosheets exhibit strain in trend with DFT.
- **Multi-fold activity gains vs. Pd nanoparticles in acid or alkaline:**
  - 10, 14, 5x for 3, 5, and 8 ML Pd in 0.1M HClO<sub>4</sub>.
  - 18, 15, 2x for 3, 5, and 8 ML Pd in 0.1M KOH.

L. Wang, Z. Zeng, W. Gao, T. Maxson, D. Raciti, M. Giroux, X. Pan, C. Wang, J. Greeley, Science, 363 (6429), 870-874 (2019)

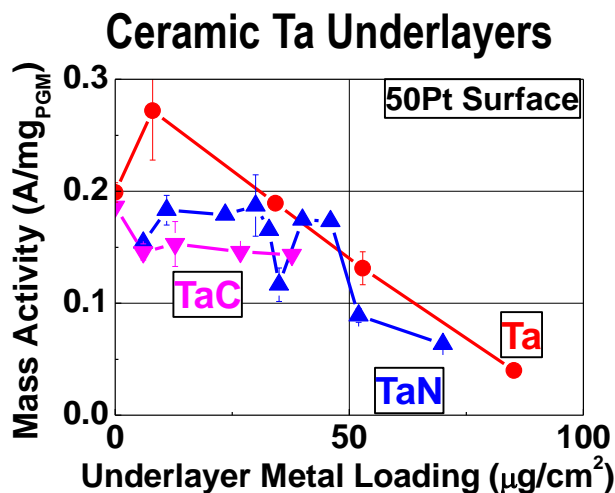
# Accomplishments and Progress – Pt Integration on Non-PGM Underlayers

## DFT Pt Adhesion Modeling to TaC (Purdue)

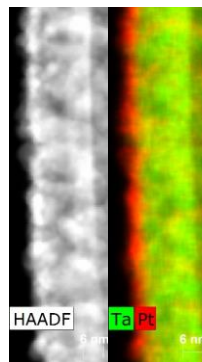


- This year – significant effort for non-PGM underlayers (backup)
- One area – Ta ceramics
- DFT predicted strong Pt adhesion to TaC (and TaN).
- Oxidation Concern:
  - Refractory metals are oxophilic.
  - Surface oxide weakens Pt adhesion, promoting dewetting.

## Impact of Underlayer Composition, Loading. Baseline Process Level “B”. 50cm<sup>2</sup> MEA Format.



### EDS Analysis 16Pt/50TaN, After Test

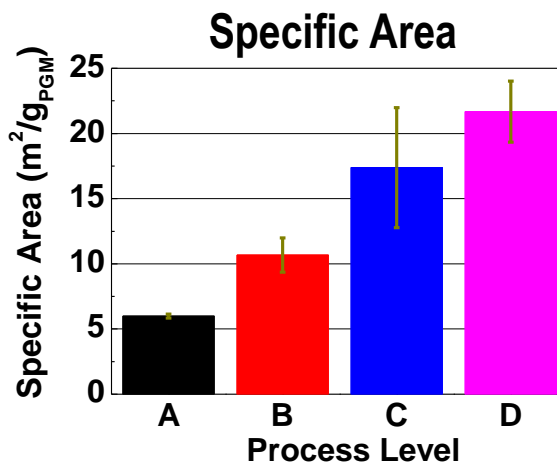
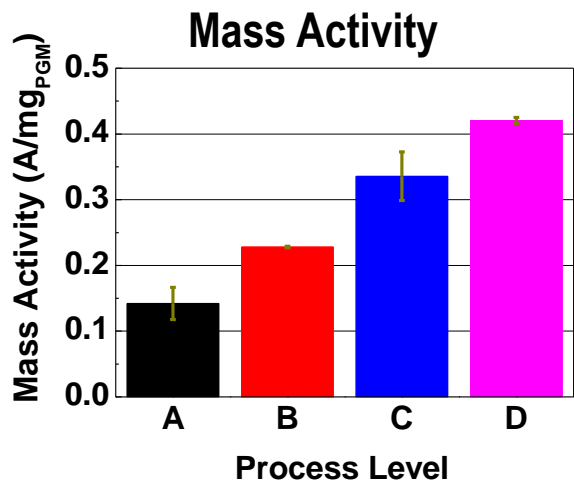


- Pt catalysts on TaN and TaC have similar or lower activity than Pt/Ta.
- TEM/EDS analysis (after FC test):
  - Thin, largely contiguous Pt surface
  - *N:Ta ratio of 0.5 (less than ~1.0 target)*
  - *O:Ta ratio of 2.6 (much higher than typically observed with Ta alone).*

**Oxidation is a key challenge for non-PGM refractory underlayers.**

# Accomplishments and Progress – Pt/Ta Fabrication Optimization

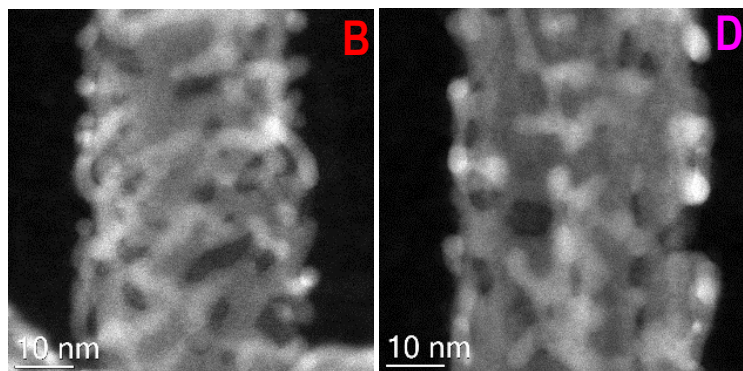
Process and O Content Critical for Mass Activity, Area of 10Pt/8Ta. 50cm<sup>2</sup> MEA Format.



- Fabrication process modified towards decreased oxygen content of Ta underlayer.
- Modification effective at increasing mass activity and specific area:
  - Mass activity: up to 0.42 A/mg (2.5x).
  - Specific area: up to 22 m<sup>2</sup>/g (3.5x).

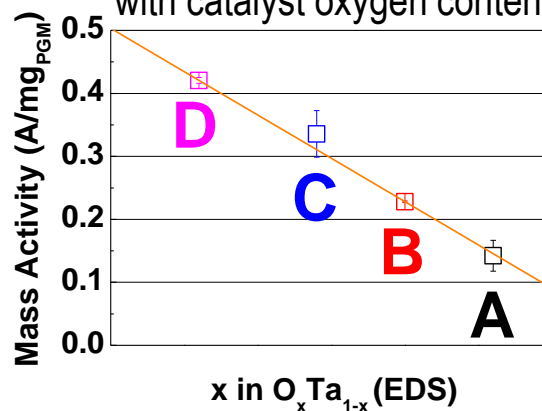
### TEM After FC Test

- Connected Pt fibrils on TaO<sub>x</sub>
- No clear structural correlation w/ activity



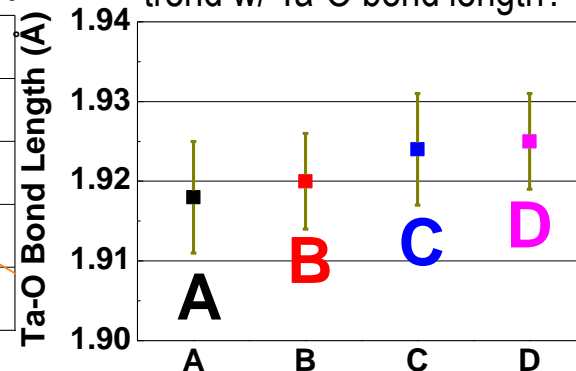
### EDS

- Activity (and area) correlate with catalyst oxygen content

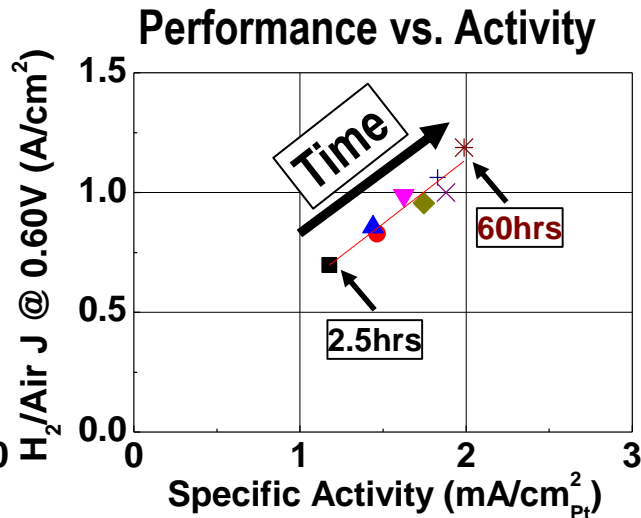
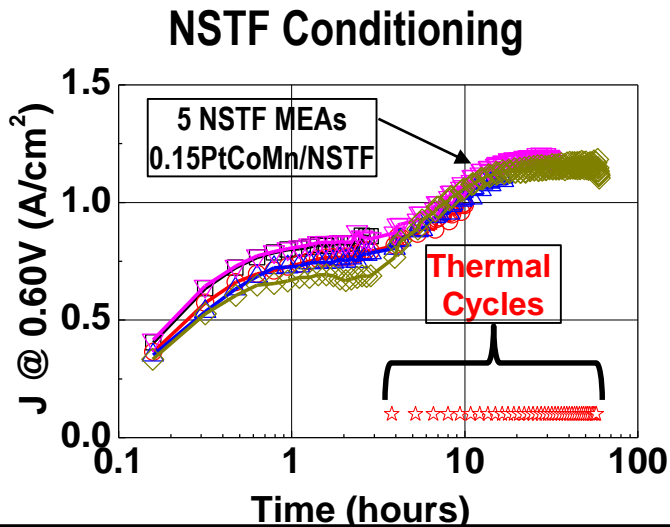


### XAFS

- Ta primarily as Ta<sup>5+</sup>; slight trend w/ Ta-O bond length?



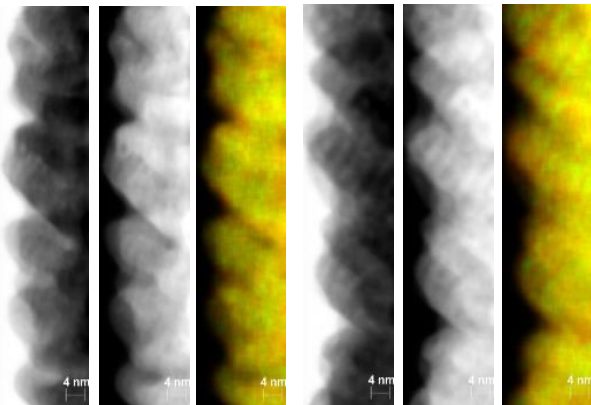
DOE mass activity target approached with PGM-free underlayer. Plausible material factor and process identified. Optimization continues.



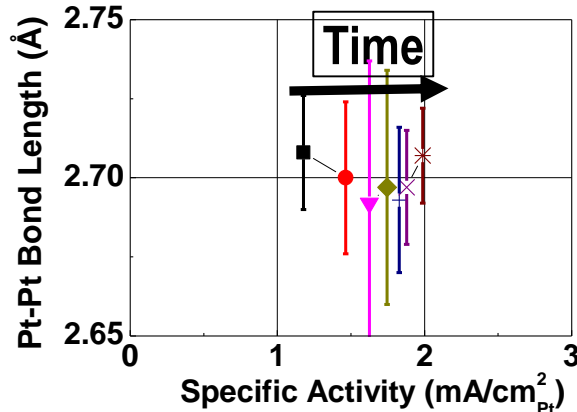
- Entitlement performance requires extended, complex conditioning (repeated “thermal cycles”).
- **Key finding:** H<sub>2</sub>/Air performance correlates with specific activity, which improves during conditioning.

2.5hrs  
78at% Pt

60hrs  
83at% Pt



### XAFS Pt-Pt Bond Lengths

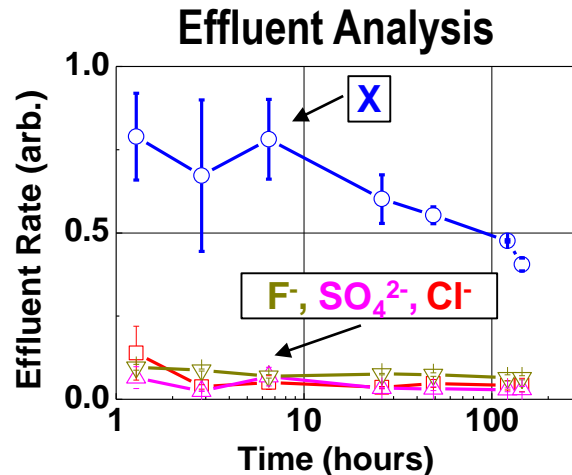
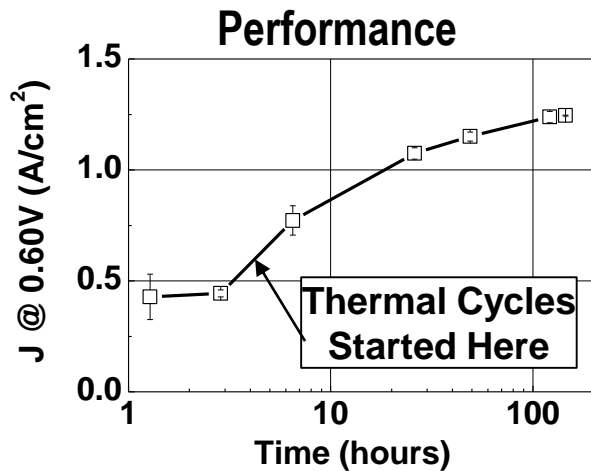


- **TEM/EDS:** Modest grain growth, composition change.
- **EXAFS:** Relatively small changes of Pt-Pt bond lengths; poor correlation with activity.



# Accomplishments and Progress – Addressing NSTF Conditioning

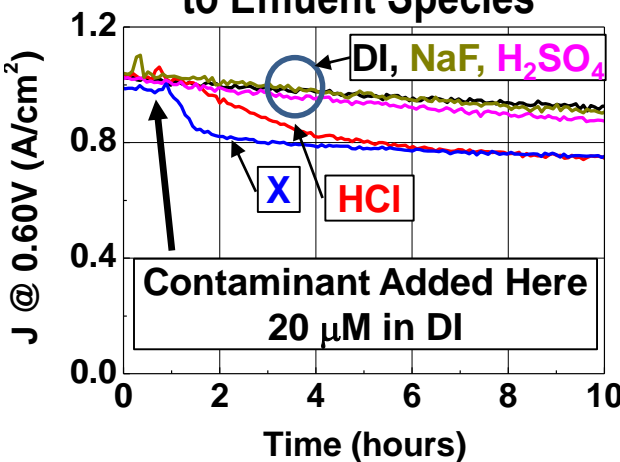
## Analysis of Cell Effluent During Conditioning. 150PtCoMn/NSTF. 50cm<sup>2</sup> MEA Format.



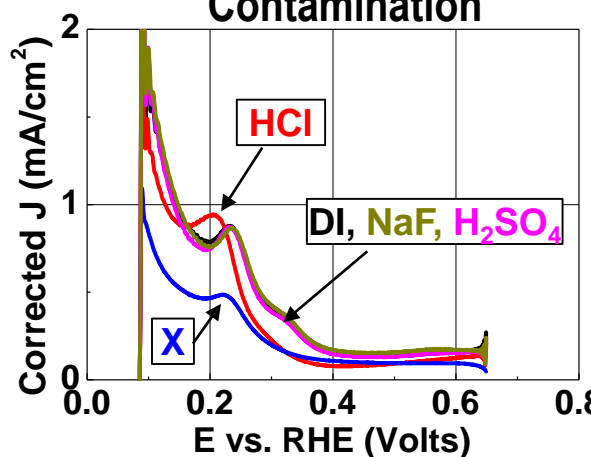
- Hypothesis: Slow conditioning by slow contaminant removal.
- Cell liquid effluent during conditioning analyzed.
- “X”: highest concentration; correlation with performance.
- F-, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>: low concentration; poor correlation with performance.

## Contaminant Sensitivity Studies. 150PtCoMn/NSTF. 50cm<sup>2</sup> MEA Format.

### H<sub>2</sub>/Air Performance Sensitivity to Effluent Species



### Voltammetry After Contamination



- Species detected in effluent assessed for impact on performance and voltammetry
- F-, SO<sub>4</sub><sup>2-</sup>: no effect; similar to DI
- Cl<sup>-</sup>: significant effect; H<sub>UPD</sub> onset shift
- “X”: most rapid decay; H<sub>UPD</sub> onset shift and site blockage
- Losses reversible by thermal cycling or contaminant removal.

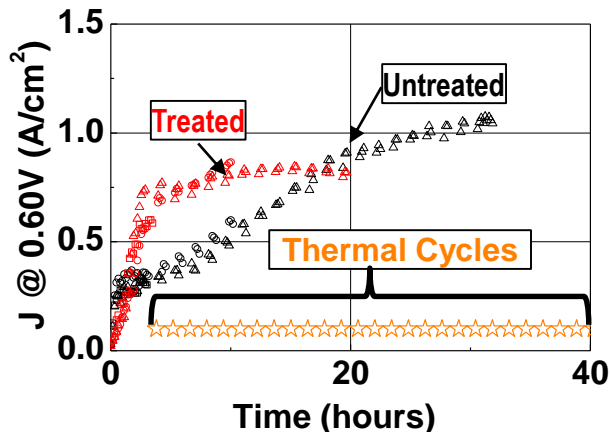
Potential source of slow NSTF conditioning identified - contaminant.



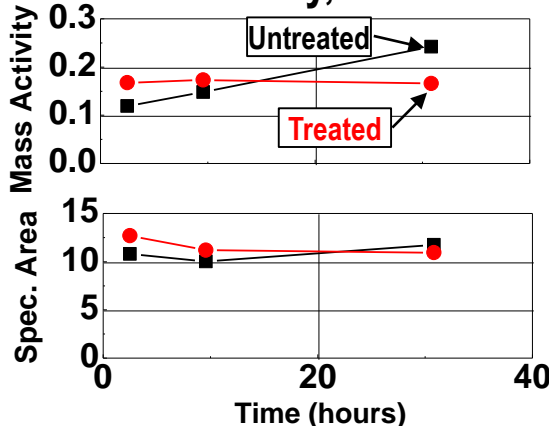
# Accomplishments and Progress – Addressing NSTF Conditioning

Treatment Decreases Conditioning Time. UTF Pt, 58  $\mu\text{gPt}/\text{cm}^2$ . 50 $\text{cm}^2$  MEA Format.

Performance



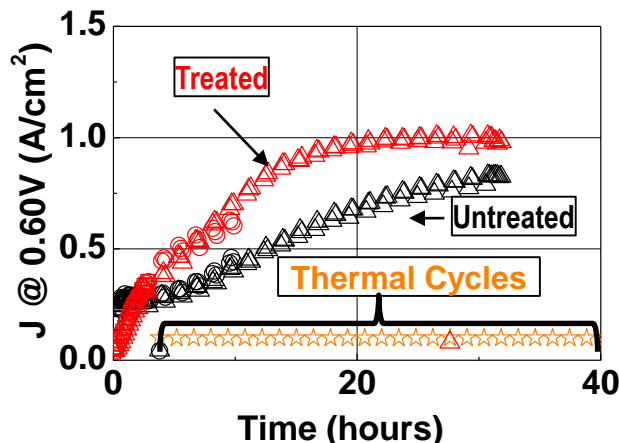
Activity, Area



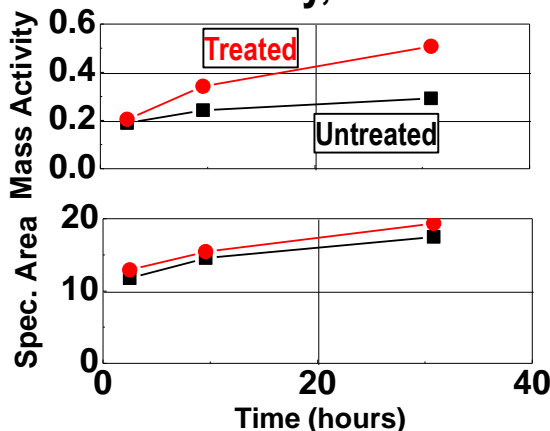
- Treatment increased pre-TC performance and activity, and decreased conditioning time.
- However, treatment suppressed:
  - performance for  $t \leq 1$  hour
  - entitlement performance and activity
- Metrics for treated MEA:
  - Pre-TC performance: 87%(2.5 hours)
  - ... vs. “entitlement”: 70%(30 hours)

Treatment Effective with High Activity UTF PtNi, 30  $\mu\text{gPt}/\text{cm}^2$ . 50 $\text{cm}^2$  MEA Format.

Performance



Activity, Area



- Treatment effective for high activity UTF PtNi catalyst with low PGM loading and absolute surface area.
- Unclear if treatment impacts contaminant “X” (measurements planned Q2CY19).

Treatment promising. Mechanism validation, optimization in progress.

# Collaborations

- **3M - Electrocatalyst Fabrication and Characterization, Electrode and MEA Integration**
  - A. Steinbach (PI), C. Duru, G. Thoma, K. Struk, A. Haug, K. Lewinski, M. Kuznia, J. Bender, M. Stephens, J. Phipps, and G. Wheeler.
- **Johns Hopkins University – Dealloying Optimization, kMC Modeling, HT Development**
  - J. Erlebacher (PI), L. Siddique, E. Benn, A. Carter and T. Pounds
- **Purdue University – DFT Modeling of Electrocatalyst Activity, Durability**
  - J. Greeley (PI), Z. Zeng, and J. Kubal
- **Oak Ridge National Laboratory – Structure/Composition Analysis**
  - D. Cullen (PI)
- **Argonne National Laboratory – XAFS and HT Development**
  - D. Myers (PI), A. J. Kropf, and D. Yang
- **FC-PAD Consortium**
  - MEAs to be provided annually.

# Response to Reviewers' Comments

**Durability:** 3M has been working on Pt and Pt-alloy catalysts deposited on NSTF supports for a long time, and it looks like the team still has issues to solve in terms of meeting the mass activity durability targets.

- ***New this year were several project catalysts with Ir underlayers which exceed the DOE and project electrocatalyst and support durability targets.***

**Modeling:** ... The research is well supported through density functional theory (DFT) calculations and Monte Carlo simulation studies done by university partners.

- ***Simulations at Purdue and Johns Hopkins have been critical towards elucidating activity and stabilization mechanisms of Ir and many other underlayer concepts.***

**Operational Robustness and MEA Conditioning:** The project is aimed at mass activity, which is more related to catalyst activity. However, one of the most critical barriers of this type of non-ionomer catalyst layer is operational robustness, particularly hydration sensitivity. Any attribute of this barrier was not addressed in the project, and neither was any approach discussed. The requirement of long-time MEA conditioning is also a significant problem.

- ***Operational robustness of traditional NSTF electrodes is largely resolved by interlayers and liquid permeable anode GDLs. Best of Class MEAs with these layers also have high performance, exceeding DOE PGM content and loading targets.***
- ***Operational robustness issues of NSTF appear to be completely resolved with dispersed NSTF electrodes (A. Haug, FC155).***
- ***As of 2018, the project is formally emphasizing catalyst factors of conditioning. Recent progress towards understanding the underlying cause(s) provides optimism that this issue can be resolved in the near-term***

## Remaining Challenges and Barriers

1. The mass activity of UTF alloy catalysts with durable Ir underlayers approach, but do not meet, DOE and project targets.
2. Experimental specific activities are approximately 10x below entitlement model prediction of catalysts with well-defined and optimally-strained Pt skins.
3. Ir content needs to be reduced to be compatible with the relative abundance of Ir to Pt.
4. Refractory underlayers may have high electronic resistance and insufficient stability against oxidation, preventing entitlement specific areas, mass activities, and durability with thin ORR catalyst coatings.
5. Break-in conditioning of NSTF cathode electrodes is longer and more complex than many carbon supported Pt nanoparticle cathode electrodes.
6. Rated power loss is generally the key lifetime-limiting factor for NSTF cathode MEAs.

## Key Future Work – 1Q19-2Q19

- Finalize Ir underlayer optimization towards achievement of remaining mass activity target.
- Validate O-content mechanism for improved non-PGM refractory underlayers, and apply to “entitlement” Pt and underlayer catalysts.
- Finalize conditioning studies, including mechanism validation and treatment optimization (“X” mitigation).
- Generate publications re: surface modified UTF catalysts and UTF underlayer catalysts.
- Project deliverable: 6 or more MEAs meeting project targets provided to DOE-approved location.

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

# Summary – Project Catalysts have achieved 6 of 6 DOE Targets

## UTF Pt/Ir catalysts

- Two UTF Pt/Ir catalysts independently exceeded DOE PGM content, loading, electrocatalyst and support durability targets. Catalysts achieve 5 of 6 DOE targets
- UTF Pt/Ir optimization resulted in 40% increase of PGM mass activity and durability was maintained.
- Mass activities of UTF PtNi/Ir of 0.38-0.41A/mg<sub>PGM</sub> achieved (3 catalysts) via Ni and Ir content optimization to minimize overcompression predicted by DFT. Assessment for PGM content in progress.

## UTF Pt Catalysts with Low/No-PGM Underlayers

- Extensive examination of multiple underlayer concepts to improve Pt utilization, including refractory metals, alloys/mixtures, multi-layers, and Ta ceramics. Ceramic underlayers had high oxygen content.
- UTF Pt/Ta fabricated by improved processing resulted in up to a 2.5x mass activity gain, to 0.42A/mg. Activity gain due to increased Pt utilization, plausibly due to increased underlayer conductivity.

## NSTF Conditioning

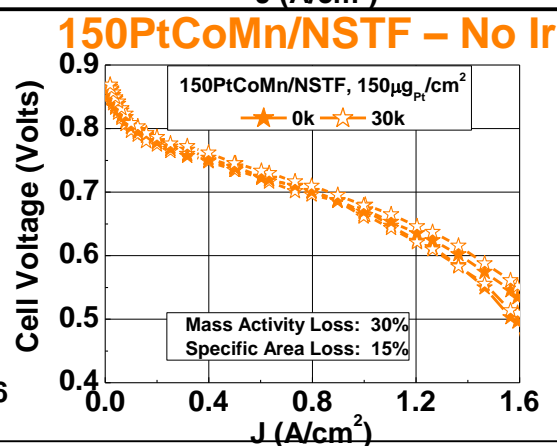
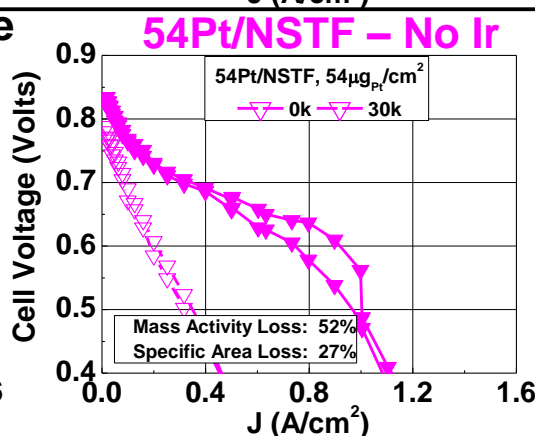
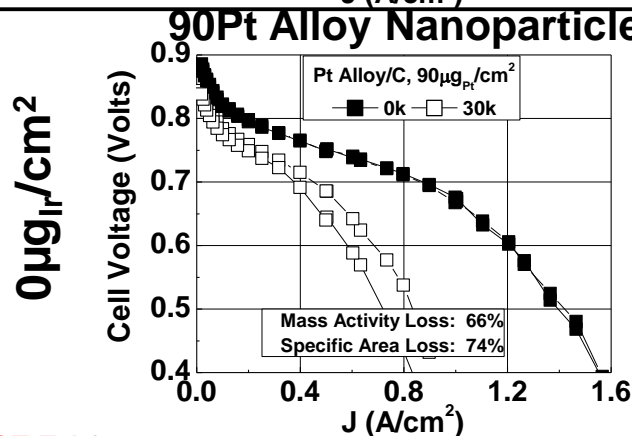
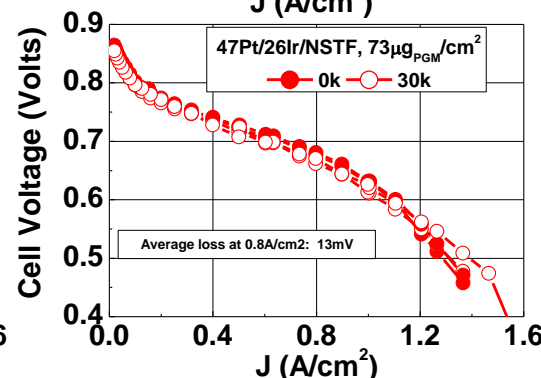
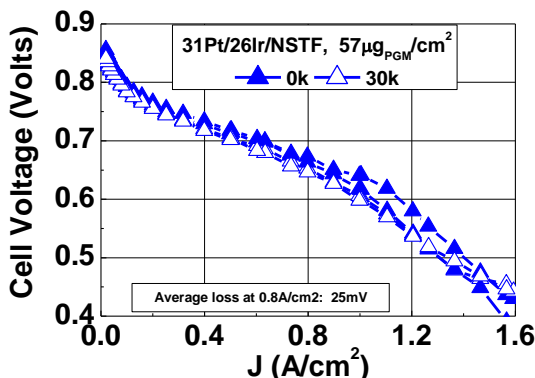
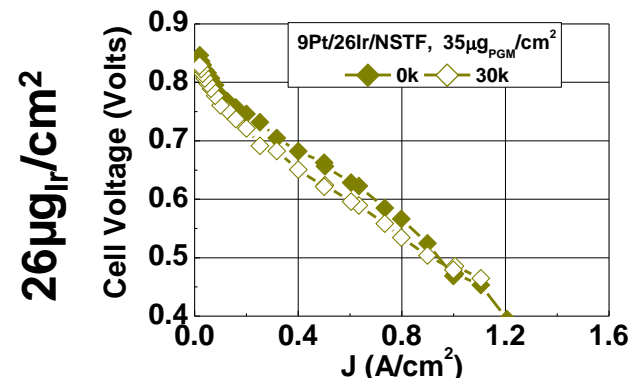
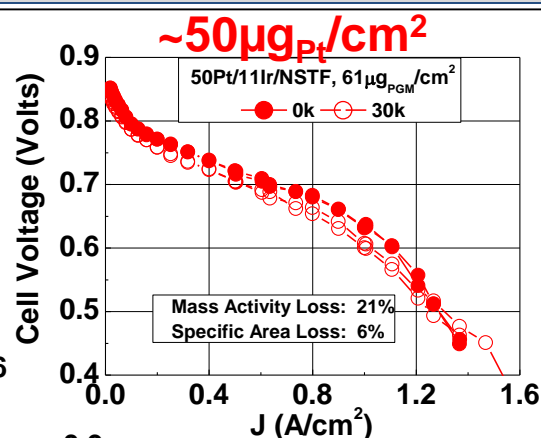
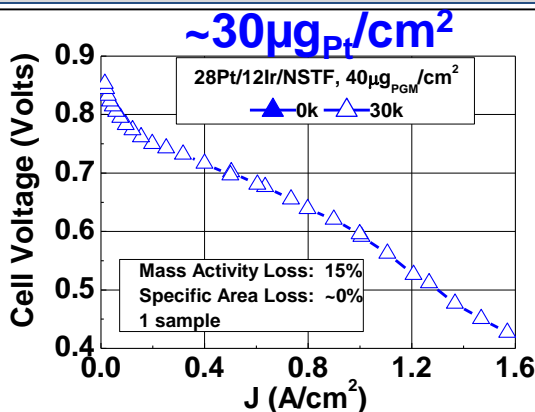
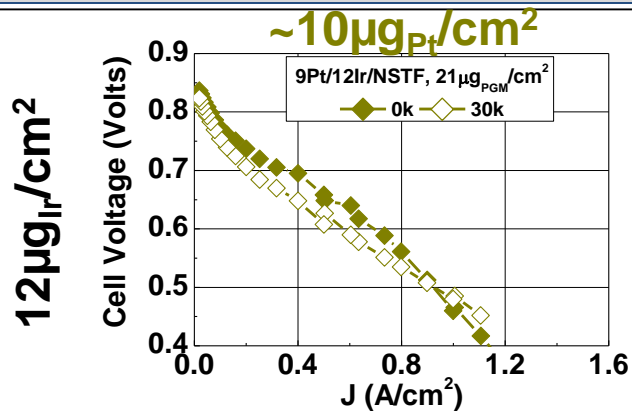
- Potential material source of slow conditioning of NSTF identified, a catalyst contaminant which is slowly removed from the cell during conditioning.
- A treatment process improved the conditioning rate of UTF catalyst MEAs, but suppressed entitlement performance and activity. Optimization and validation across material sets is in progress.

## Electrocatalyst Simulation

- KMC modeling has successfully simulated Pt (111) oxidation and reduction and Pt surface roughening during cyclic voltammetry, and has simulated an AST consisting of 1000s of cycles.
- DFT modeling predicted PtNi catalysts on Ir result in an unstable, highly-strained Pt surface which is prone to instability and reconstruction, similar to experiment.
- Extensive DFT modeling has investigated multiple reduced-PGM content underlayer concepts for Pt activity, Pt adhesion, support adhesion and oxidation sensitivity.

# Technical Backup Slides

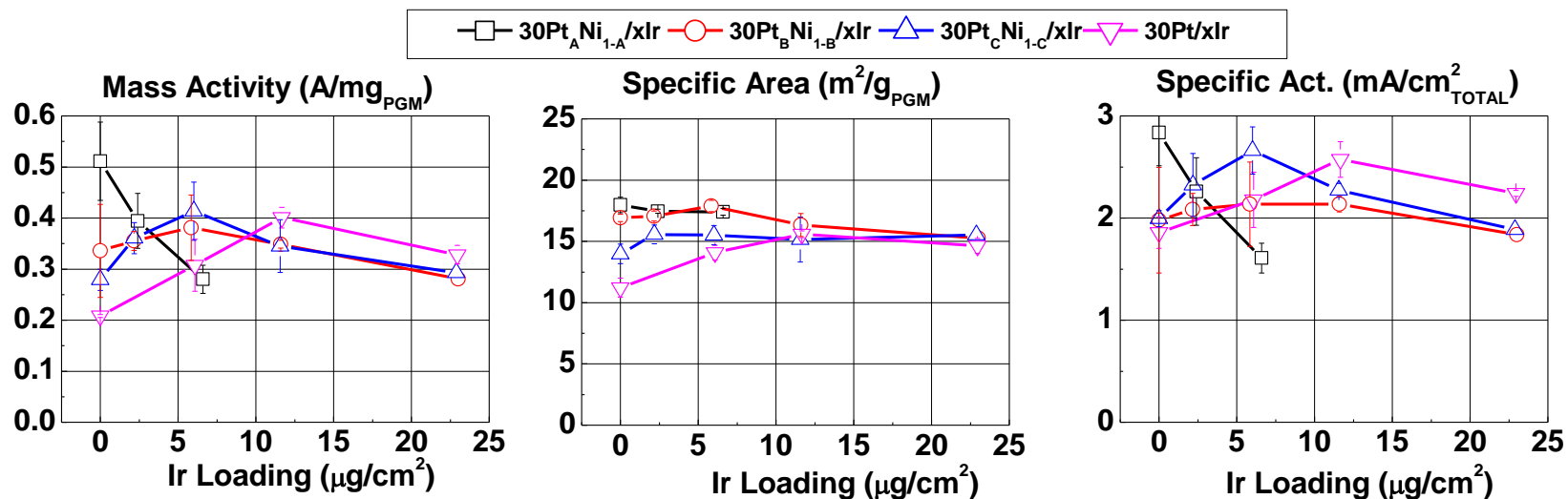
# Technical Backup – Electrocatalyst AST Durability of UTF Pt/Ir



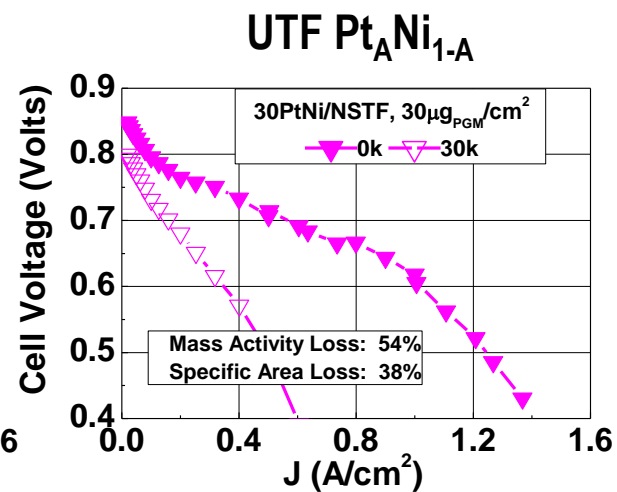
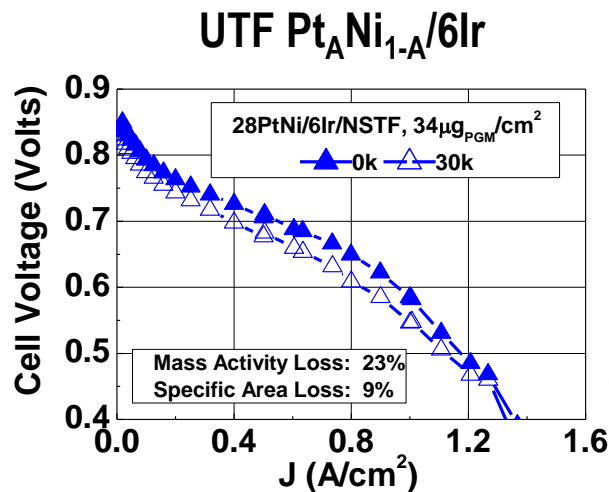
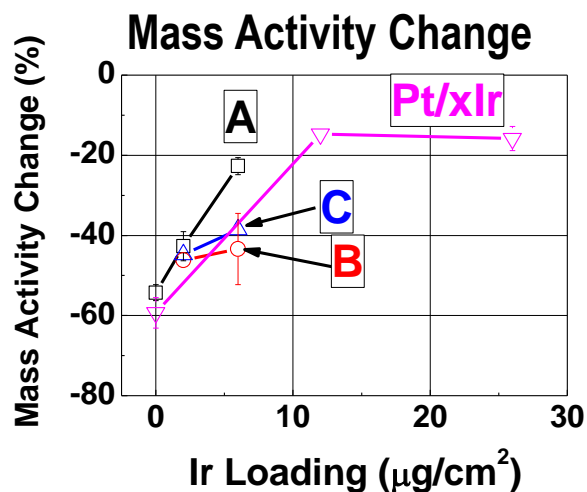


# Technical Backup – UTF PtNi/Ir

Mass Activity, Specific Area, Specific Activity.  $30\mu\text{gPt}/\text{cm}^2$ .  $50\text{cm}^2$  MEA Format.

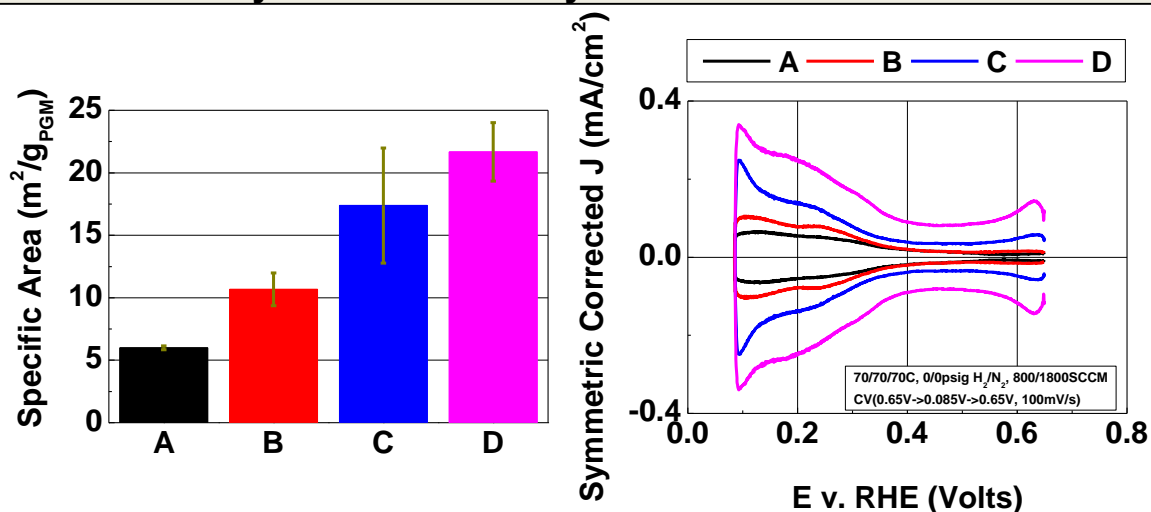


Electrocatalyst Durability.  $30\mu\text{gPt}/\text{cm}^2$ .  $50\text{cm}^2$  MEA Format.

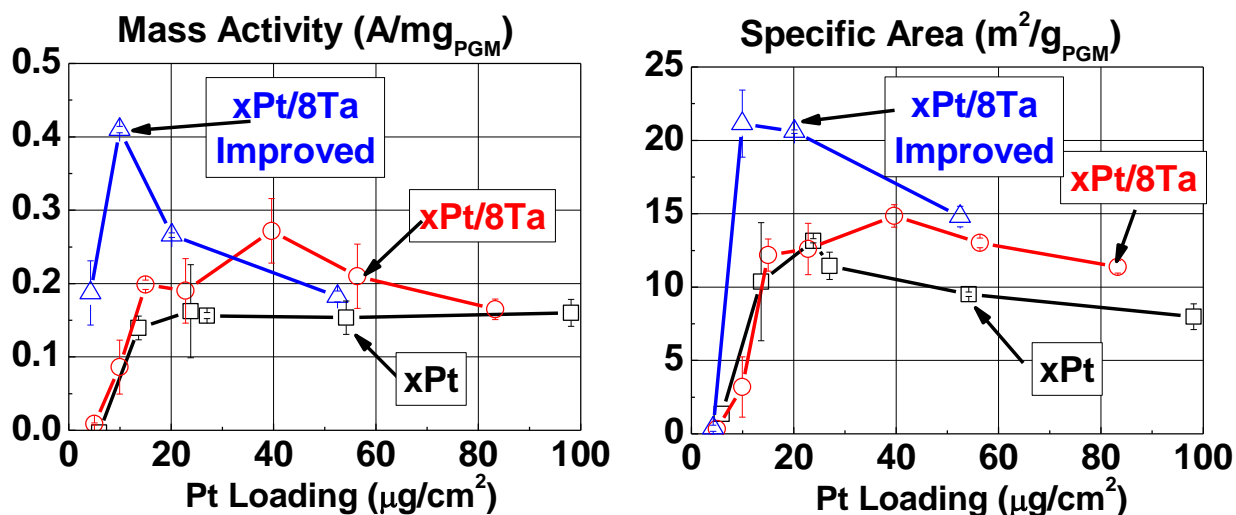


# Technical Backup – UTF Pt/Ta Optimization

## Specific Area and Cyclic Voltammetry vs. Process. 10Pt/8Ta. 50cm<sup>2</sup> MEA Format.

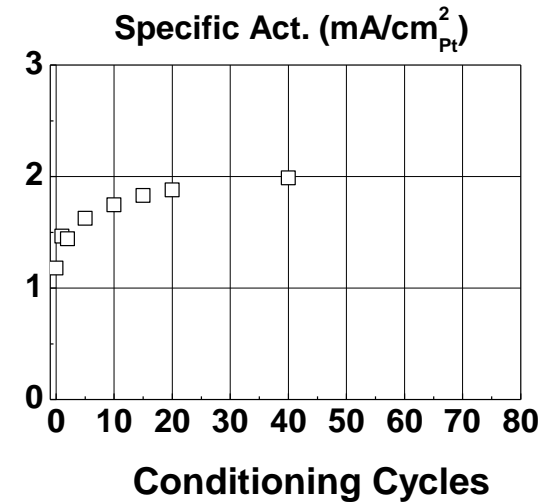
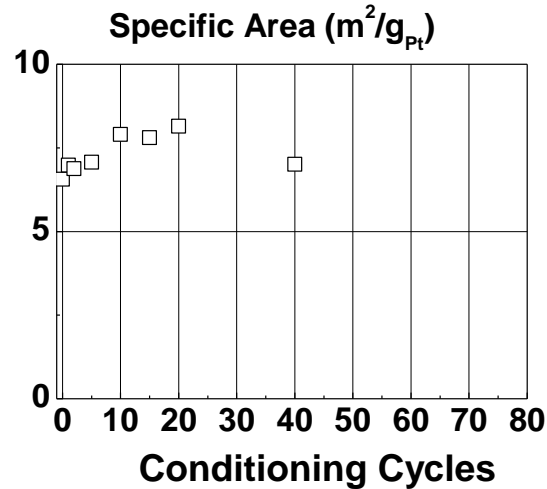
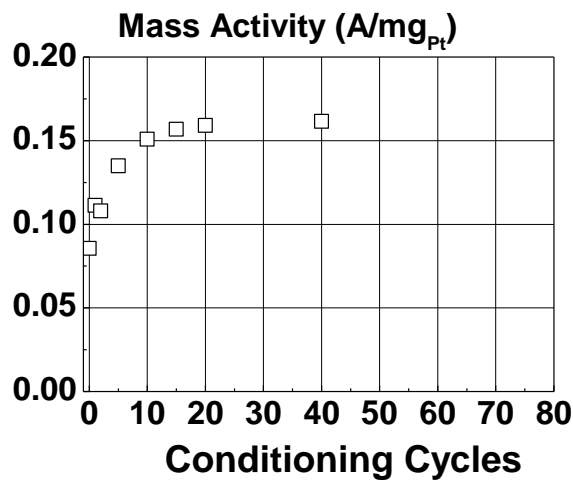


## Mass Activity, Specific Area vs. Pt Loading on 8Ta vs. Process. 50cm<sup>2</sup> MEA Format.

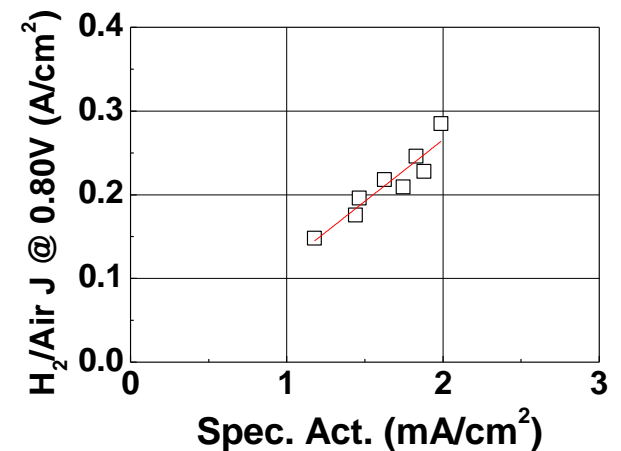
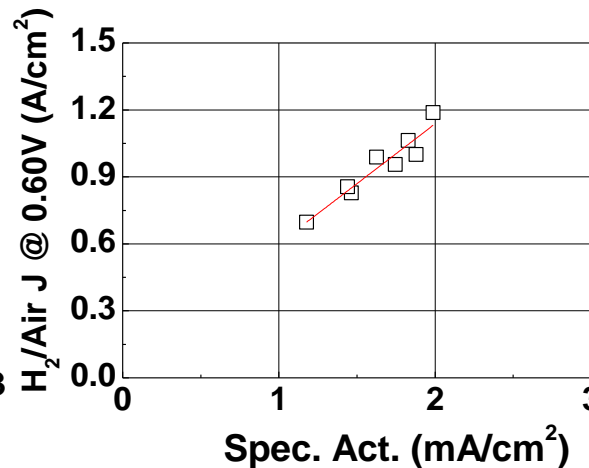
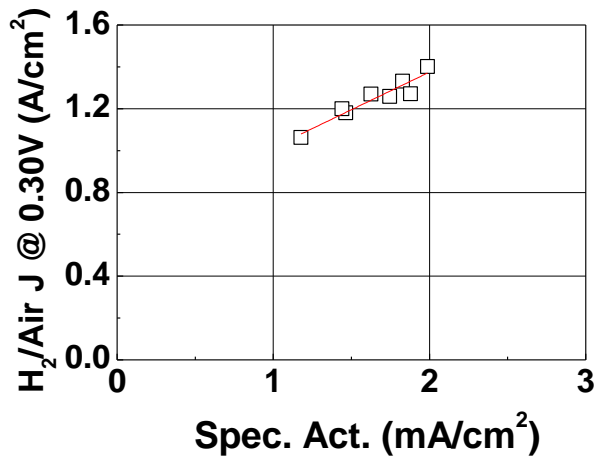


# Technical Backup – NSTF Conditioning - Baseline 150PtCoMn Study

## Evolution of Mass Activity, Specific Area, Specific Activity vs. Conditioning Cycles

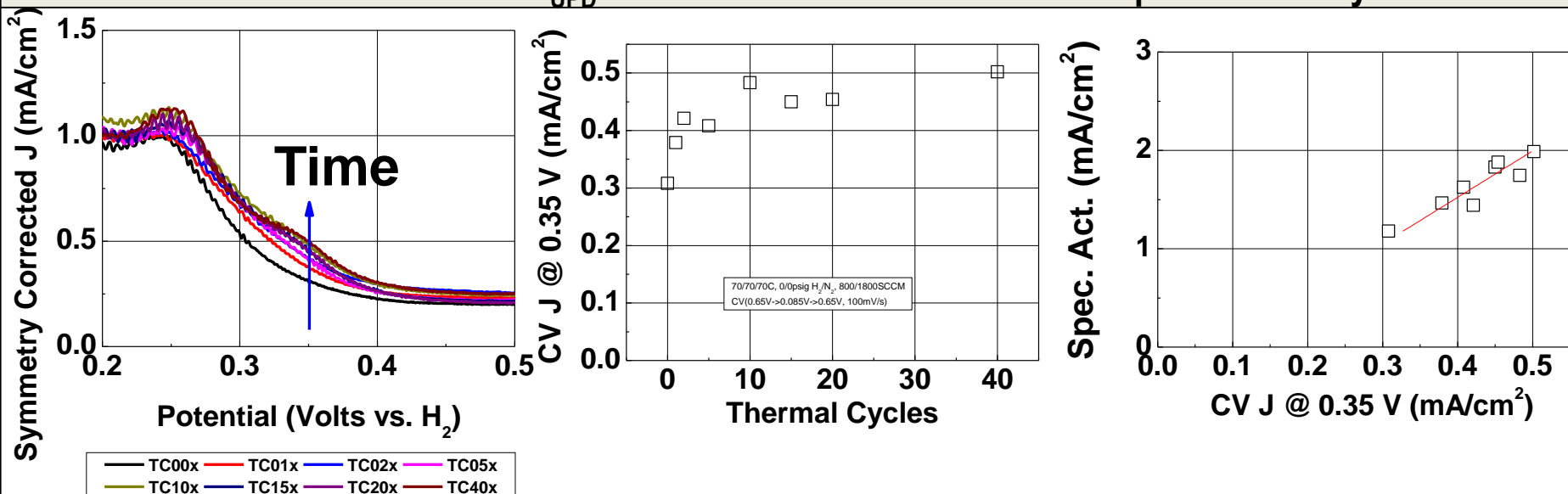


## $H_2$ /Air Performance Correlation with Specific Activity (Mass Activity Analogous)

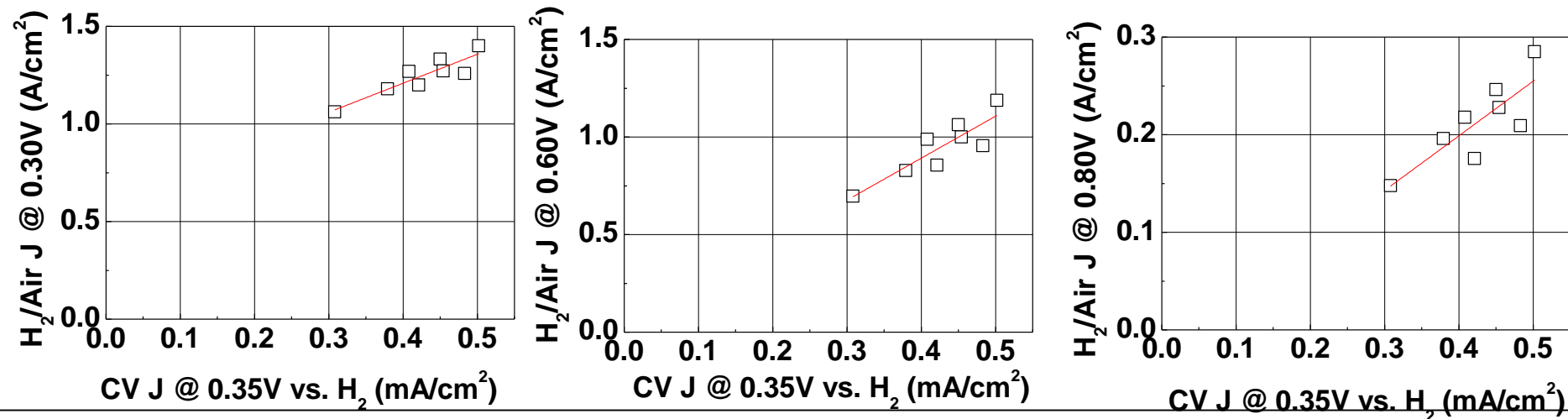


# Technical Backup – NSTF Conditioning - Baseline 150PtCoMn Study

## Slow Evolution of $H_{UPD}$ Onset Potential Correlates with Specific Activity

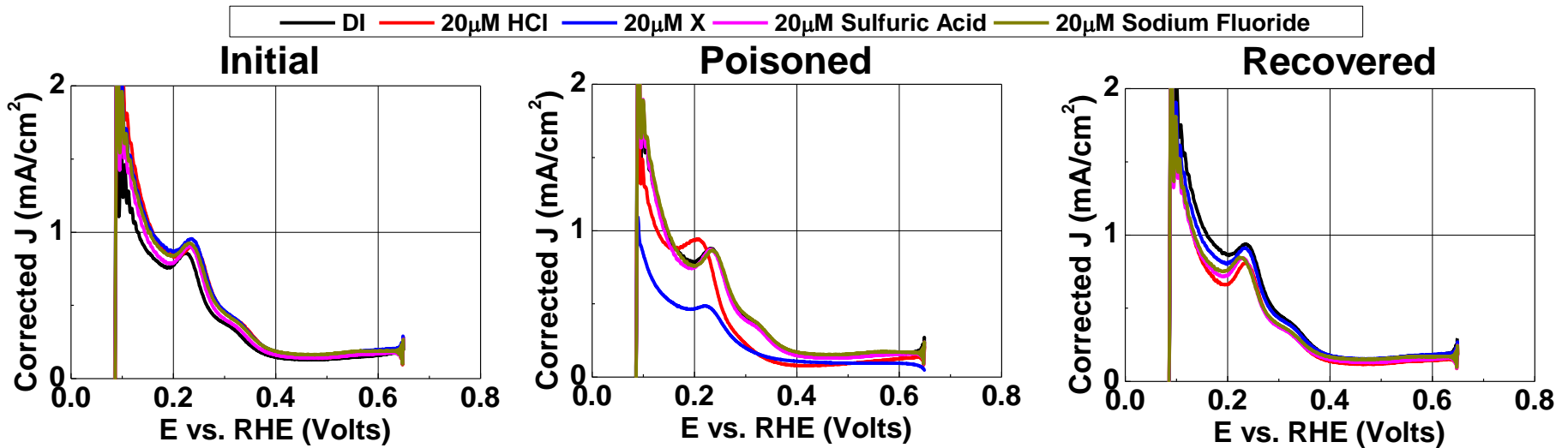


## $H_{UPD}$ Onset Potential Correlates with H<sub>2</sub>/Air Performance (Ambient Pressure)



# Technical Backup – NSTF Conditioning - Contamination Study

CVs vs. Contamination State. 150PtCoMn/NSTF. 50cm<sup>2</sup> MEA Format.



Mass Activity, Specific Area, Specific Activity vs. Contam. State. 50cm<sup>2</sup> MEA Format.

