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

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Project FC143

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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:	$2.599MM*
Cost Share Percentage:	23.72%

*Includes DOE, contractor cost share and FFRDC funds as of 3/31/18

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 0.8A/cm^2:	< 30 mV
Loss in performance at 1.5A/cm^2:	< 30 mV
Mass activity (0.90V$_{IR\text{-}FREE}$):	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

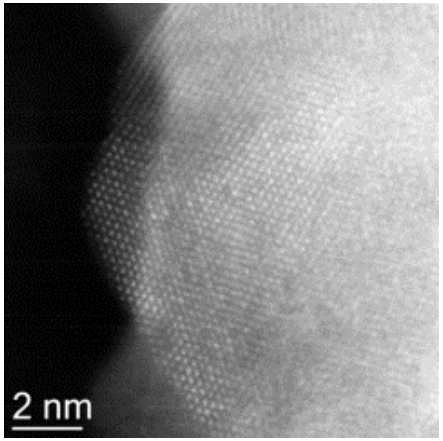
Establish relationships between electrocatalyst functional response (activity, durability), **physical properties** (bulk and surface structure and composition), **and fabrication processes** (deposition, annealing, dealloying) **via systematic investigation**.

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

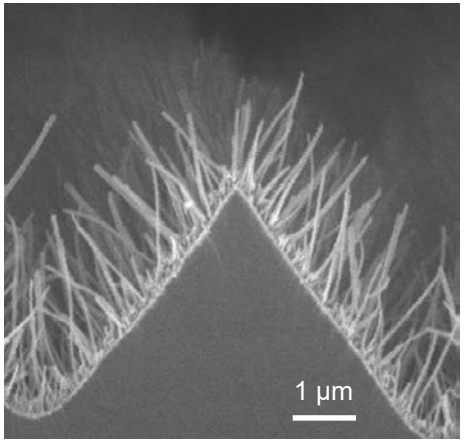
Approach – Active, Stable Ultrathin Film Electrocatalysts

Ultrathin Film (UTF) Catalyst on NSTF Supports

UTF Catalyst



NSTF Support



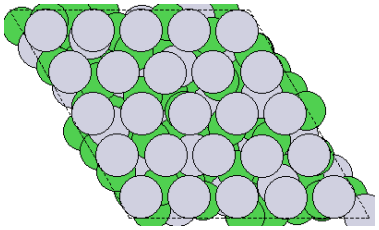
1. **Develop active and stable thin film catalysts** on durable supports via structure, composition, and process optimization.
2. Utilize **atomic and mesoscale modeling and advanced physical characterization** to accelerate development.
3. **Increase catalyst absolute area** by integration with higher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

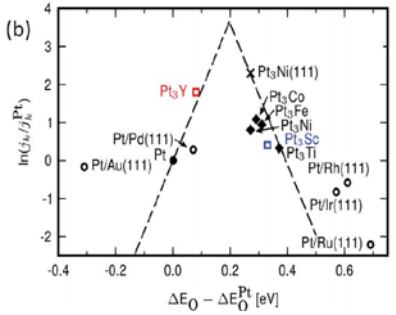
- Per project plan, NPTF approach de-emphasized in July ‘17

Electrocatalyst Modeling

Density Functional Theory (Purdue)

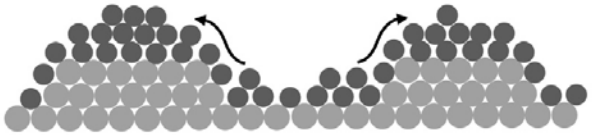
Stability and activity calculations of Pt skins on Pt alloys

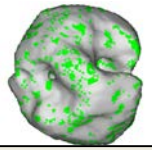




Kinetic Monte Carlo (Johns Hopkins)

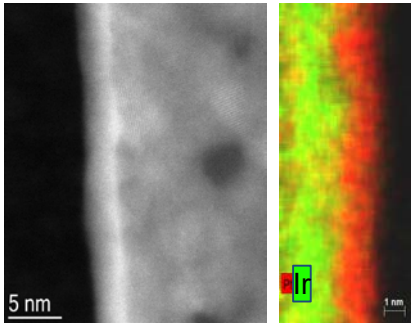
Structure, composition evolution predictions



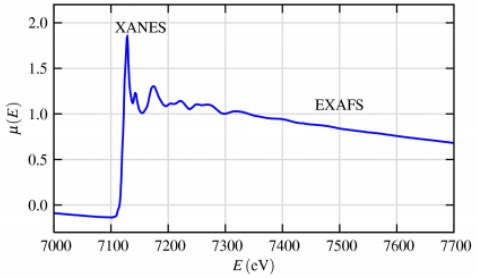


Advanced Characterization

TEM/EDS (ORNL)



XAFS (ANL)



BP2 Milestones and Go/No-Go

Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
3 HT Characterization	M3.1.2	Combinatorial Catalyst Treatment Process Reproducible	60%	5
3 HT Characterization	M3.1	Combinatorial/HT Activity, Area Agrees w/ Homogenous MEA	75%	3
3 HT Characterization	M3.2	Combinatorial/HT Physical Char. Agrees w/ Homogenous Catalyst	100%	6
2 Catalyst Simulation	M2.3.1	Model(s) predict ≥2 new NPTF alloys w/ ≥30m^2/g area	100%	6
2 Catalyst Simulation	M2.4.1	Model(s) predict ≥2 new UTF alloys w/ ≥4mA/cm^2 activity	100%	7
2 Catalyst Simulation	M2.5.1	Model(s) predicts ≥4 alloys w/ ≤ 30% loss under ASTs.	50%	8
2 Catalyst Simulation	M2.1	Model(s) predict ≥4 alloys w/ ≥0.8A/mg and ≤ 20% loss w/ ASTs.	75%	8
1.5 Catalyst Integration	G1.5.1 (PROJ)	Electrocatalyst achieves: 1) Loss in catalytic (mass) activity of 30% or less, and 2) Loss in performance at 0.8 A/cm^2 of 25 mV or less, and 3) Loss in Performance at 1.5A/cm^2 of 25 mV or less, and 4) either Mass activity of 0.44 A/mg_{PGM} or PGM total content (both electrodes) of 0.125 g/kW at Q/ΔT=1.45kW/°C.	96% 100% (5) 100% (20) 100% (<5) 0.28A/mg 0.15g/kW	9

- BP2 milestones largely reflect modeling efforts to predict new catalysts with potential for improved activity and durability.
- BP2 GNG (activity and durability, average of each clause) at 96%, based on 31Pt/26Ir UTF catalyst.
- Unanticipated difficulties with some HT tasks, especially EC characterization (seg. FC and flow cells).

Status versus DOE and Project Targets

	2020 Target and Units	Project Target	Ultrathin Film	
			2017	2018
Platinum group metal (PGM) total content (both electrodes)	0.125 g/kW ($Q/\Delta T \leq 1.45$)	0.1 (@ 0.70V)	0.12 (DOE) 0.13 (Proj.)	0.11[1] (DOE) 0.13[1] (Proj.)
PGM total loading (both electrodes)	0.125 mg/cm^2	0.10	0.077	0.098[1]
Loss in catalytic (mass) activity	40 %	20	45	5[2]
Loss in performance at 0.8 A/cm^2	30 mV	20	23	20[2]
Loss in performance at 1.5 A/cm^2	30 mV	20	NA	< 5[2]
Mass activity @ 900 mV$_{iR\text{-}free}$	0.44 A/mg (MEA)	0.80	0.44	0.39[3] 0.57[4]

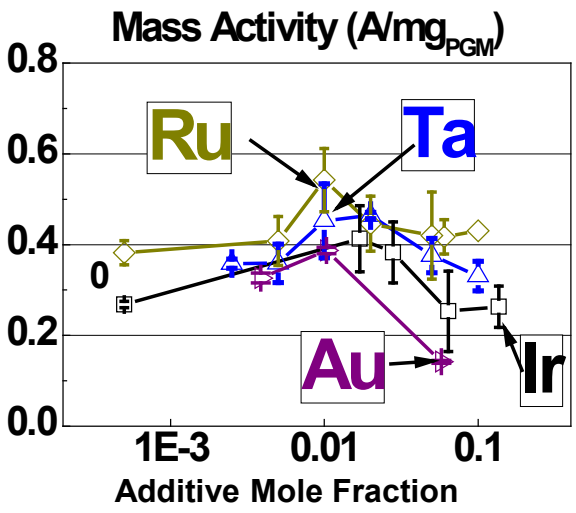
GREEN: Meets or exceeds DOE 2020 target. YELLOW: Within ca. 15% of DOE 2020 target.

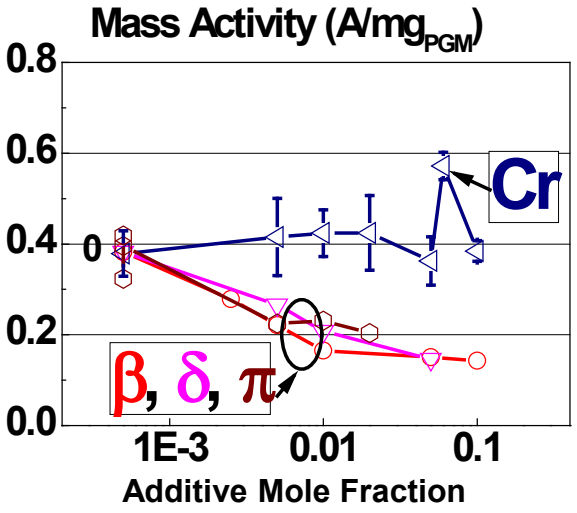
[1]2018 (May) UTF BOC MEA *with cathode interlayer (16*µg/cm^2).
Anode: UTF 9Pt/11Ir. Cathode: UTF 50Pt/11Ir. PEM: 3M-S 14µm 725EW PFSA w/ additive.
[2]UTF 31Pt/26Ir. [3]UTF 28Pt$_B$Ni$_{1-B}$/xIr. [4]UTF 28PtNi+Cr.
2018 DOE PGM content values at 95°C cell, 40%RH, 150kPa H_2/Air, $Q/\Delta T$ = 1.45kW/°C (0.663V)

- 2018 catalysts have achieved 6 of 6 DOE 2020 targets addressed and 4 of 6 project targets.
- DOE PGM content target exceeded with Pt catalyst with an Ir "underlayer" (between Pt and support).
- Pt catalysts with Ir underlayers are highly durable, meeting or exceeding 3 DOE and project targets.
- DOE mass activity target achieved with 3 surface-modified UTF PtNi catalysts w/ optimal compositions.

Accomplishments and Progress – Surface Modified UTF PtNi

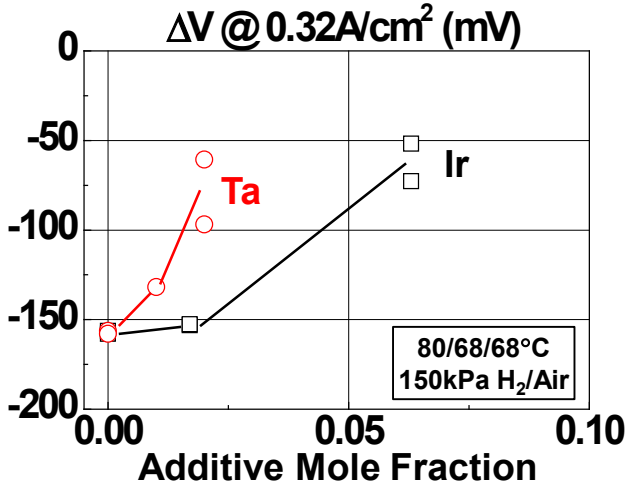
Beginning of Life Activity vs. Surface Additive. 0.025-0.030mg$_{PGM}$/cm^2. 50cm^2 MEA Format.

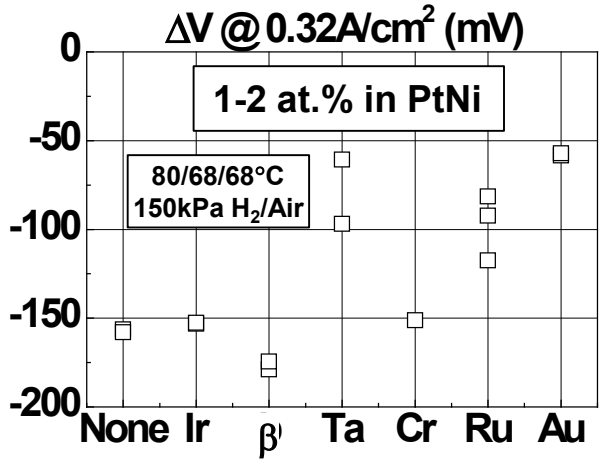




- Ir addition to surface of PtNi increased activity (last year).
- Ru, Ta, and Cr also effective at specific surface additive levels.
- Enhanced mass activity due to higher specific activity
  - Up to 3 mA/cm$^2_{Pt}$.
- Project activity status value: 0.57A/mg$_{PGM}$ with PtNi+Cr.

Electrocatalyst AST Durability vs. Surface Additive. 0.025-0.030mg$_{PGM}$/cm^2. 50cm^2 MEA Format.

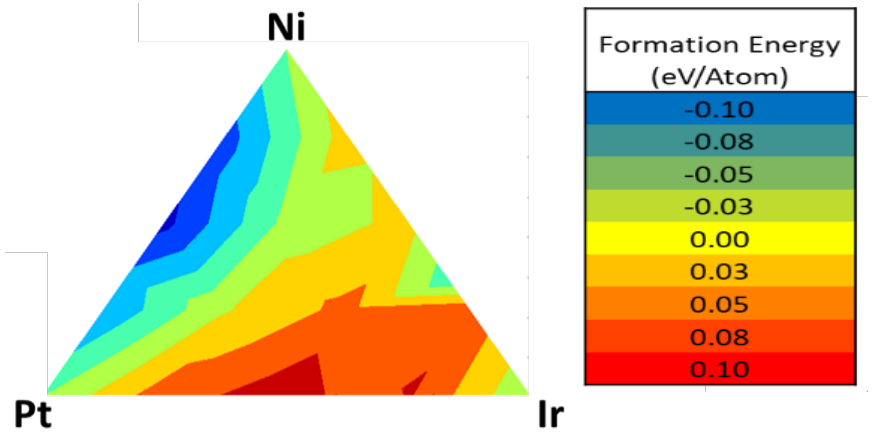




- Ta or Ir addition to UTF PtNi improves H$_2$/Air performance retention after AST.
  - Depends on additive level.
- Ru and Au also effective near 1-2 at. % surface additive level.
- Effective additives generally improved specific area durability.

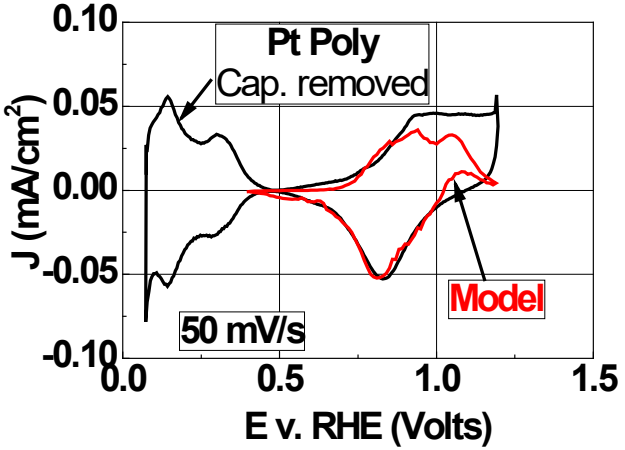
Accomplishments and Progress – Electrocatalyst Durability Modeling

DFT Pt-Ni-Ir Interaction Energies (Purdue)



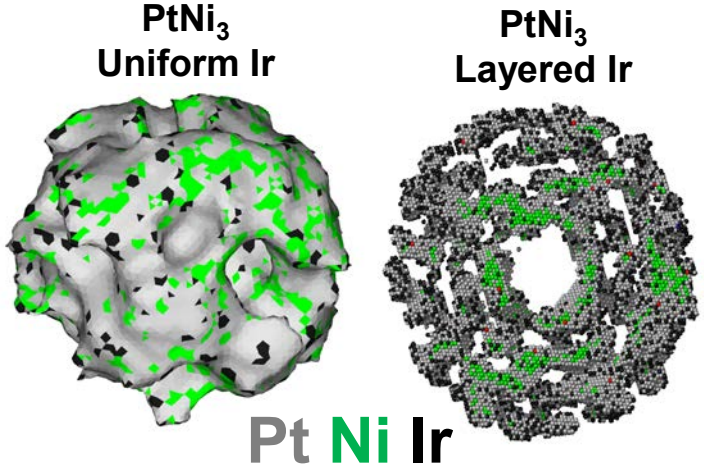
- Ir predicted to remain segregated from Pt, Ni.
- Ir, Pt surface diffusion barriers also calculated.

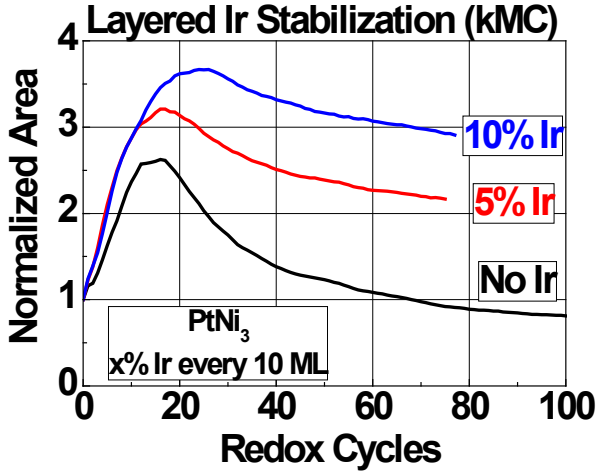
kMC Simulated Pt Oxidation/Reduction (JHU)



- kMC model updated to incorporate Pt redox and DFT interaction energies and diffusion barriers.

Simulated Nanoporous PtNiIr Durability (JHU, Purdue)





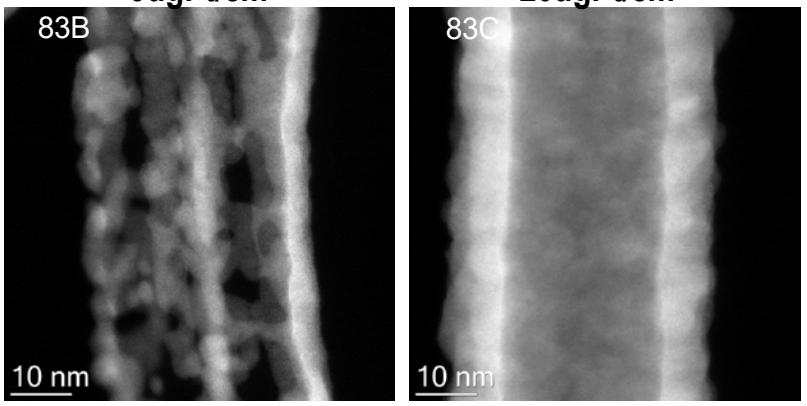
- Higher area and durability predicted with Ir in uniform or layered distributions.
- Mechanism: Low Ir mobility "pins" Pt, slowing structural degradation.
- Ta predicted to yield similar enhancement as Ir.

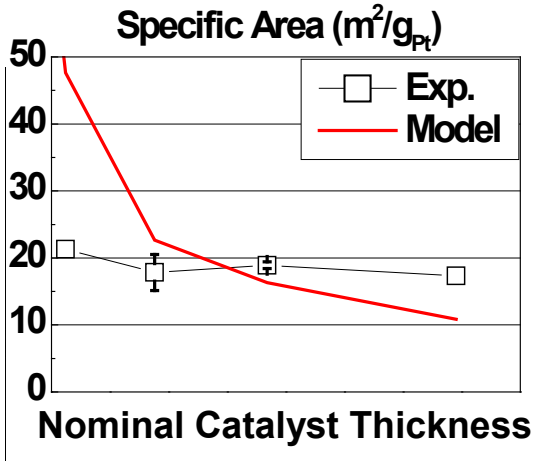
Accomplishments and Progress – Metal-Support Adhesion Modeling

Catalyst Dewetting from Support Limits Surface Area As Catalyst Thickness Decreases

UTF PtNi, Conditioned

9ugPt/cm^2 20ugPt/cm^2

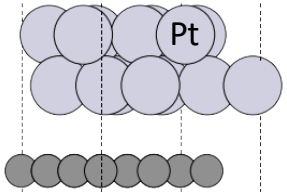




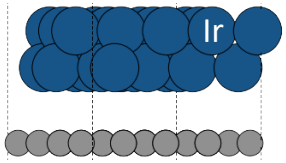
- Catalyst dewetting from support prevents expected specific area growth with decreasing catalyst film thickness.
- Significant degradation mechanism for nm-scale catalyst films.

Adhesion Modeling of Metals to Graphene, PR149 Supports (Purdue)

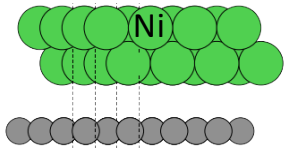
Pt/graphene



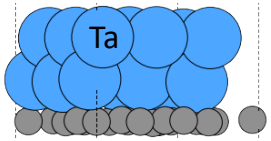
Ir/graphene



Ni/graphene

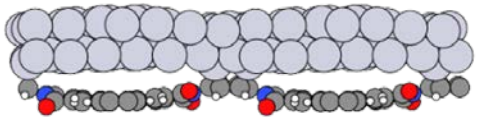


Ta/graphene



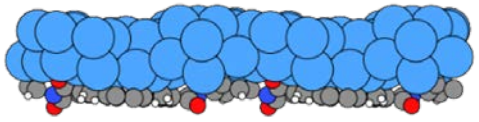
Pt/PR149

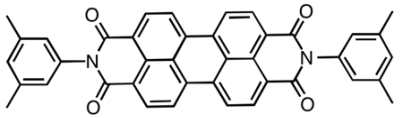
E_{adh}=-0.11 eV/Pt



Ta/PR149

E_{adh}=-0.55 eV/Ta

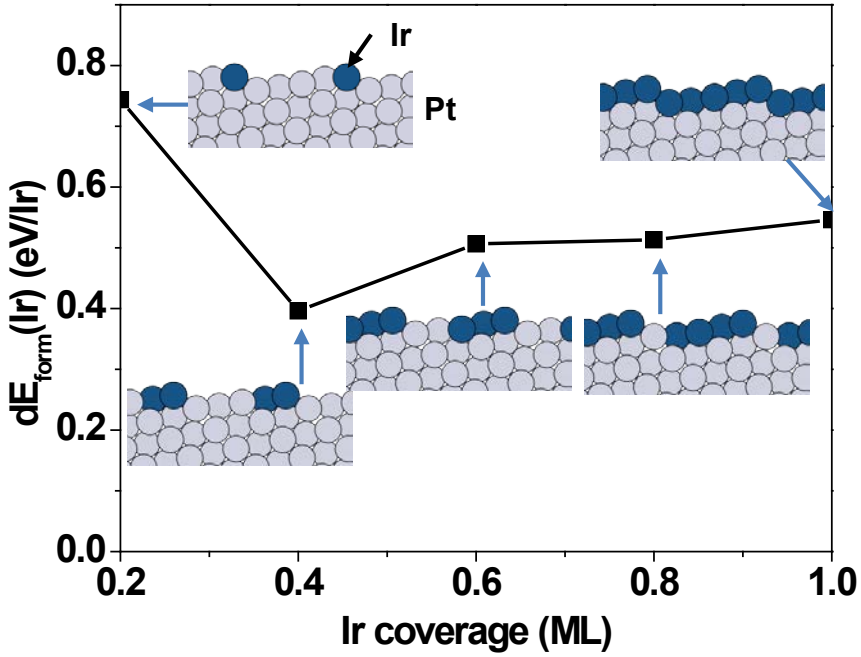




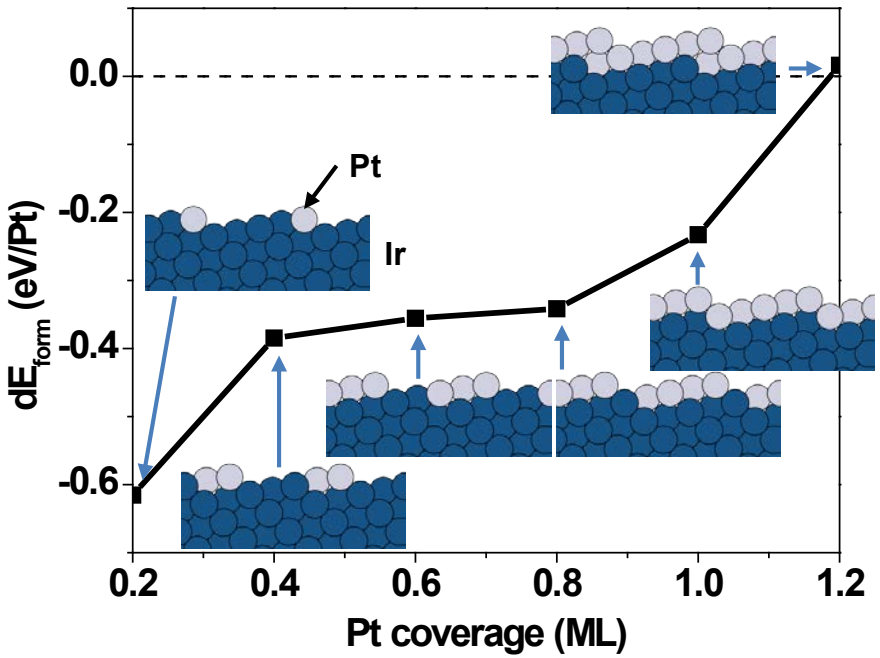
- Pt, Ir, and Ni adhesion to graphene (PR149 analogue) predicted to be weak, E_{adh} ~ 0eV/atom.
- Several materials identified with improved adhesion relative to Pt.
  - Ta/graphene: E_{adh} ~-0.63eV/Ta
- Periodic PR149 model also developed; consistent with graphene results.

Accomplishments and Progress – Pt/Ir Formation Energy, Activity Modeling

Formation Energy – Ir Added to Pt

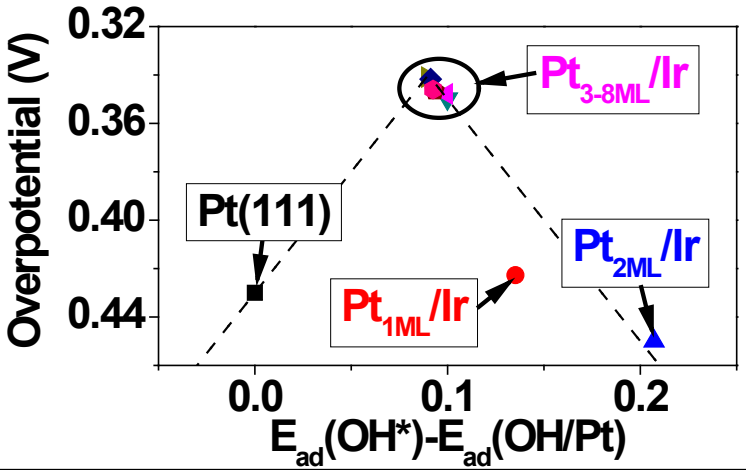


Formation Energy – Pt Added to Ir



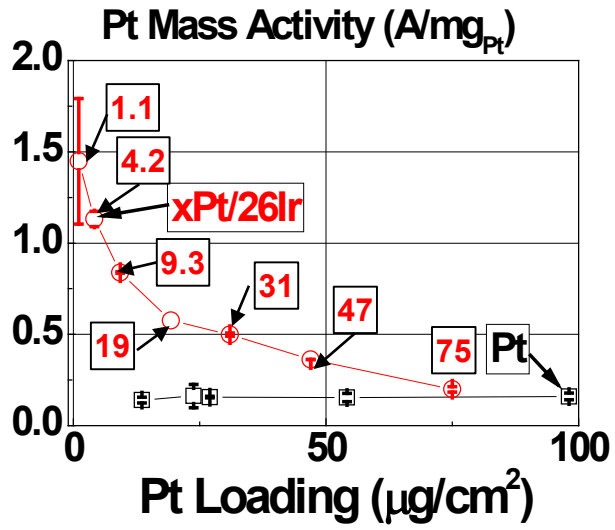
- Formation of Ir (sub)-monolayers on stepped Pt surface is energetically unfavorable.
- Pt (sub)-monolayers on Ir are favorable.
  - Additional Pt layers are energetically neutral.
- 3-8 Pt monolayers on Ir(111) are predicted to have up to 20x ORR activity vs. Pt(111)
  - Compressive strain of epitaxial Pt on Ir(111).

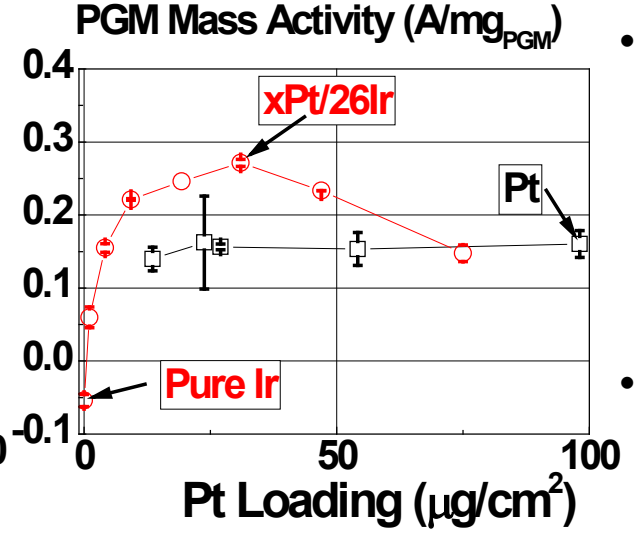
Activity – Pt Added to Ir



Accomplishments and Progress – UTF Pt Catalyst with Ir Underlayer

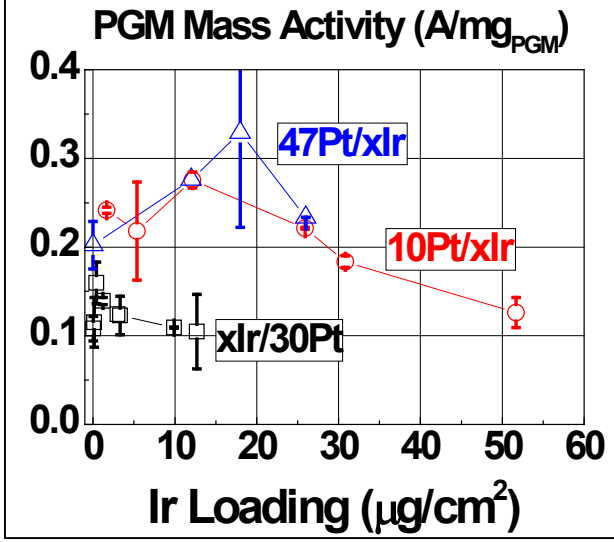
Pt and PGM Mass Activity for Various Pt Loadings with Fixed Ir Underlayer. 50cm² MEA Format.

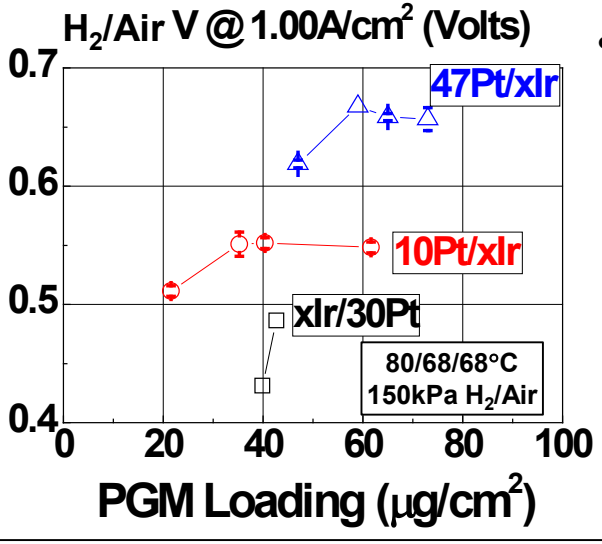




- Ir underlayer (between support and Pt surface layer) increased PGM and Pt mass activities.
  - Pt mass activity > 1A/mg at ~ monolayer Pt coverages.
  - Ir activity <<< Pt at 0.900V.
- *Increased mass activity due to higher area, not specific activity.*
  - Factor: H_{UPD} on Ir metal.

Mass Activity and H_2/Air Performance of Ir-Modified Pt (Surface vs. Underlayer). 50cm² MEA Format.

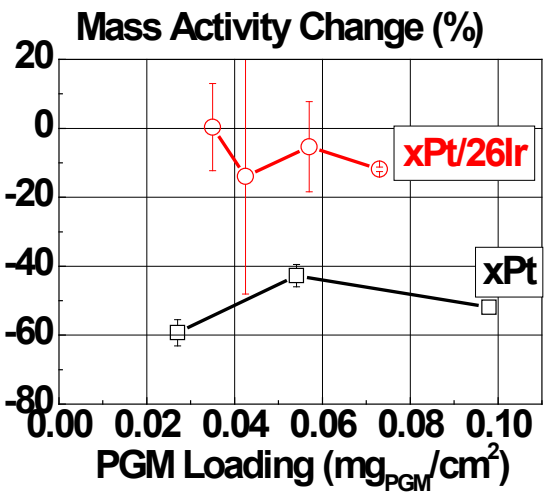


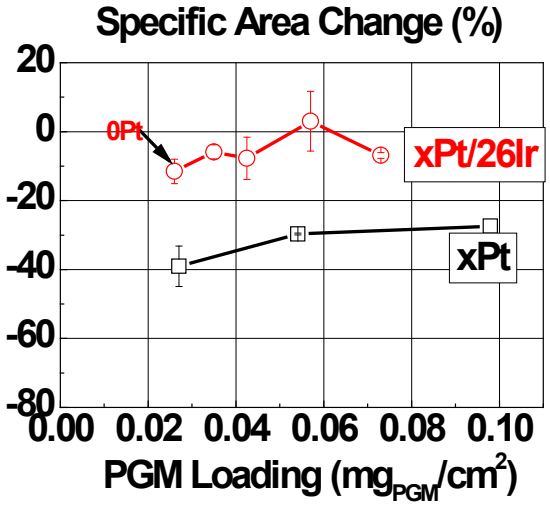


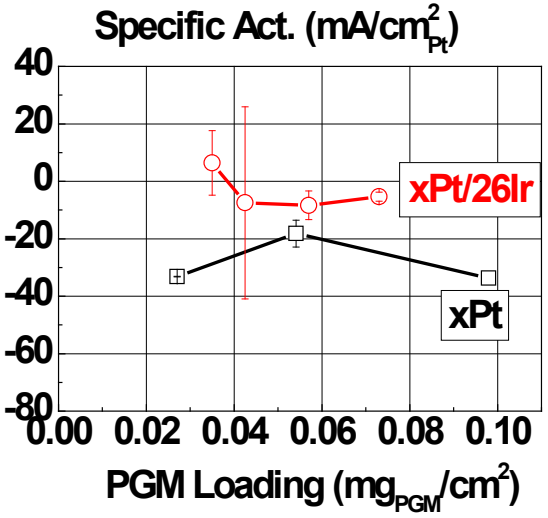
- With Pt, Ir underlayer yields superior peak mass activity and H_2/Air performance than Ir surface modification.
  - Pt/Ir mass activity depends on Ir content.
  - Pt/Ir H_2/Air performance increases with added Ir until optimal level incorporated.

Accomplishments and Progress – Pt/Ir Electrocatalyst Durability

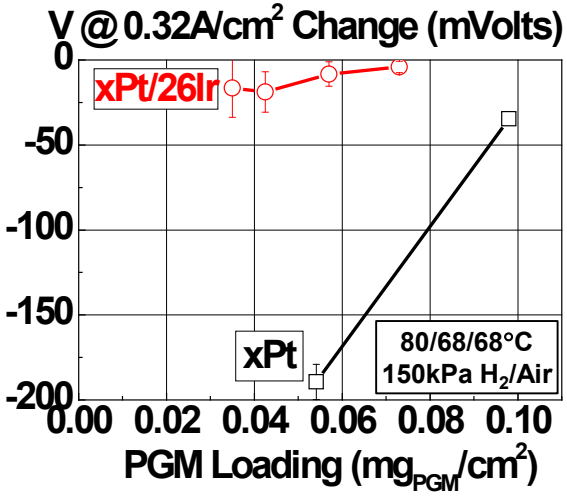
Electrocatalyst AST Durability (80°C, 30K Cycles, 0.60-1.00V). 50cm^2 MEA Format.

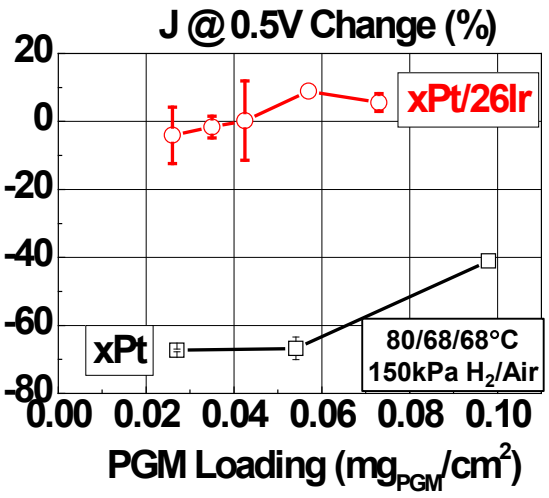






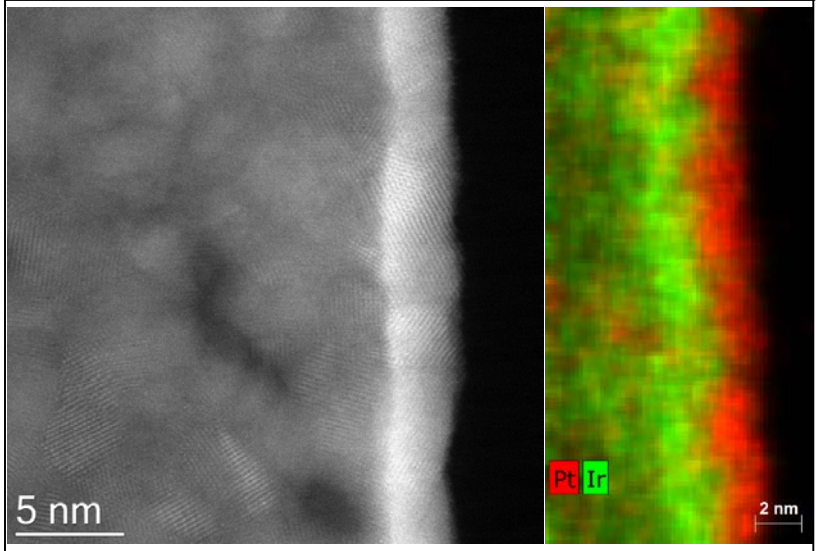
- Ir underlayer substantially improved durability of low-loaded, thin film Pt catalysts.
  - Activity, area losses < 20%.
- Relative to underlayer-free, H_2/Air performance with Ir underlayer was substantially stabilized at low and high J.
  - < 30mV loss at all J.



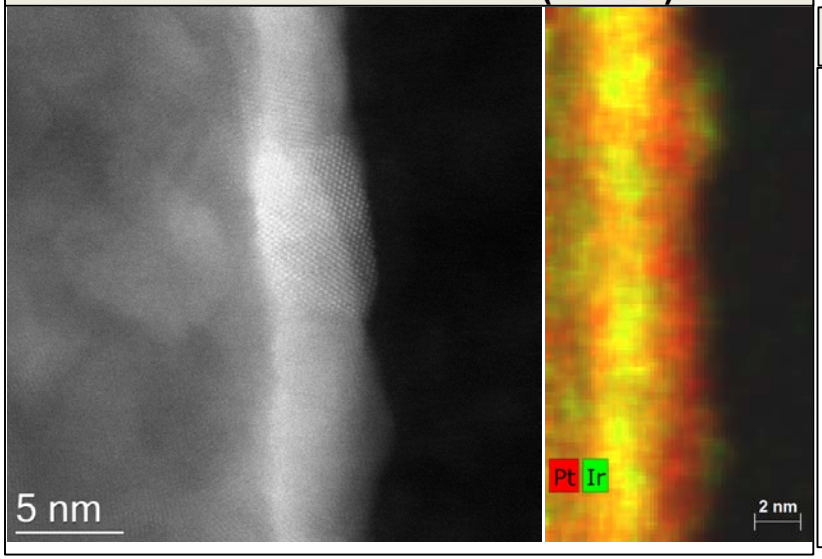


Accomplishments and Progress – Pt/Ir Physical Characterization

10Pt/12Ir – Before FC Testing (ORNL)

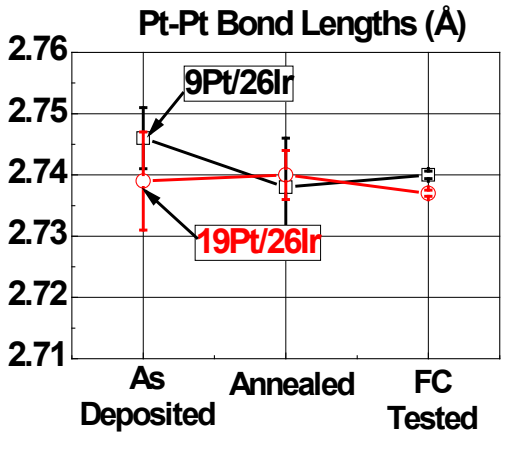


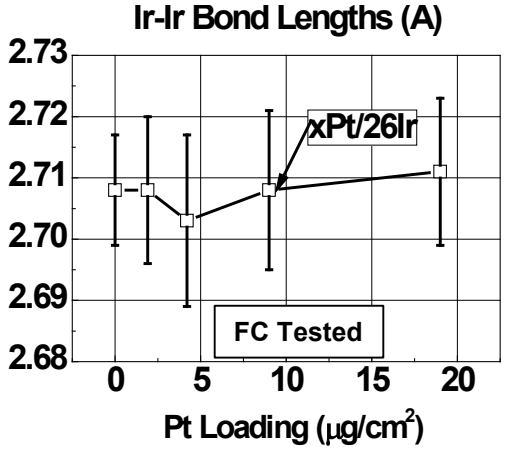
10Pt/12Ir – After AST (ORNL)



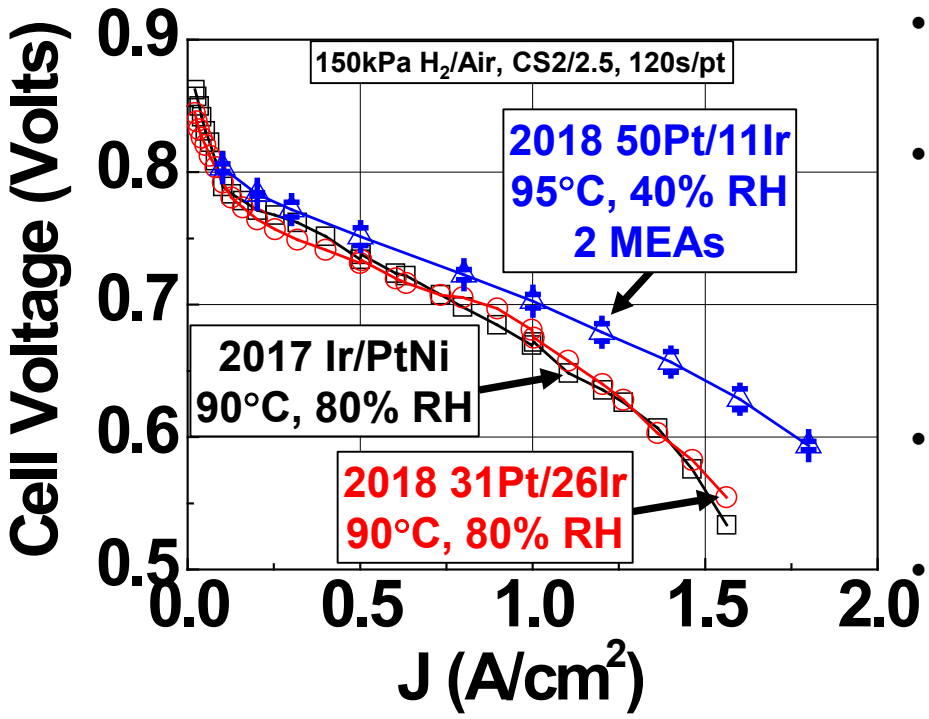
- Ir underlayer promotes formation of nm-scale Pt skin
- Thin film structure maintained after Electrocatalyst AST.
  - Ir may migrate towards surface with fuel cell testing or after AST; depends upon construction.
- Pt/Ir is compositionally stable (10Pt/12Ir).
  - Pt mole fraction before testing: 0.40 ± 0.07
  - Pt mole fraction after AST: 0.40 ± 0.01
- Little evidence of Pt-Ir interaction based on XAFS (through FC-tested state).
  - Pt-Pt bond lengths change modestly with state.
  - Ir-Ir bond lengths independent of Pt content.
  - Ir is primarily metallic in as-deposited and tested states.

Pt/Ir XAFS (ANL)





Accomplishments and Progress – PGM Content Assessment



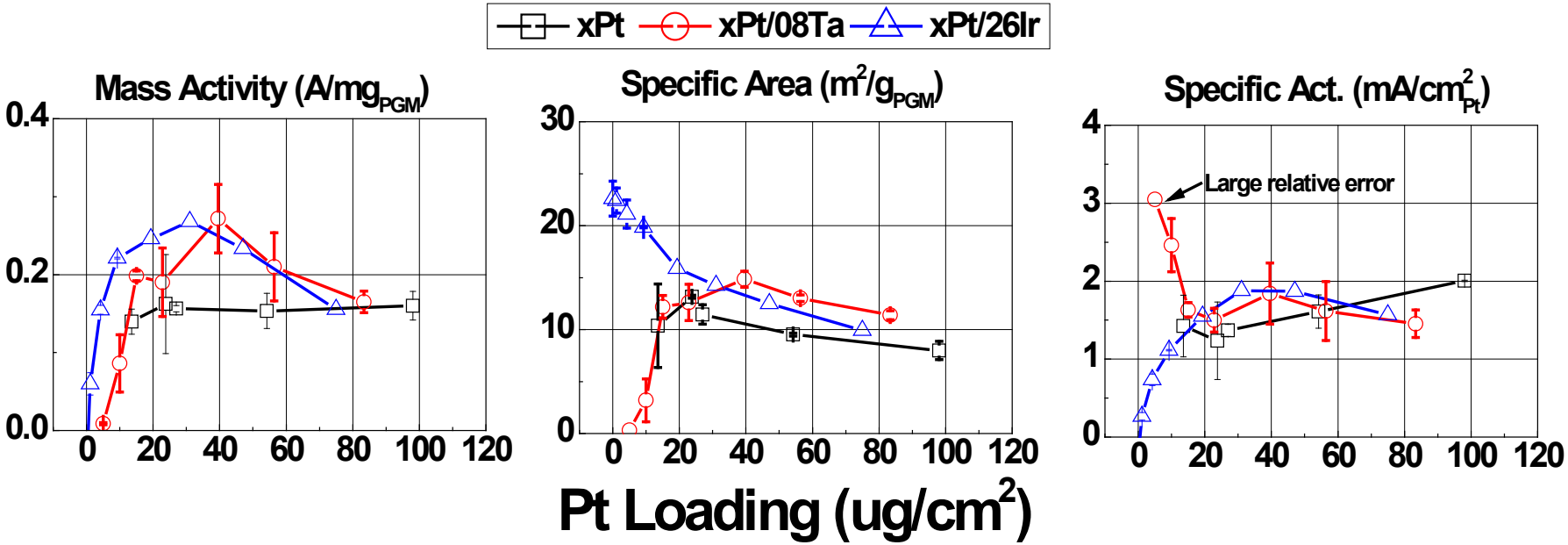
- MEAs with Pt/Ir catalysts assessed for rated power and PGM content at Q/ΔT target (1.45kW/°C).
- With 2018 50Pt/11Ir cathode, PGM content improved with optimized T and RH.
  - 90°C, 80% RH: 0.137 g/kW.
  - 90°C, 44% RH: 0.125 g/kW. **DOE target achieved.**
  - 95°C, 40% RH: 0.110 g/kW. **DOE target exceeded.**
- Electrocatalyst and support AST targets exceeded with 31Pt/26Ir – assessment of 50Pt/11Ir in progress.
- **Achievement of Project Mass Activity and PGM Content targets will likely require:**
  1. **Reduced PGM or PGM-free underlayers**
  2. **Increased specific activity (alloys).**

	Total PGM Loading (mg/cm^2)	Spec. Power @ Q/ΔT=1.45 (kW/g_{PGM})	Rated Power @ Q/ΔT=1.45 (W/cm^2)	ORR Mass Activity (A/mg_{PGM})	Electrocatalyst AST (NSTF Cathode Only)		Support AST (NSTF Cathode Only)
					Mass Act. Change (%)	ΔV @ 0.8A/cm^2 (mV)	ΔV @ 1.5A/cm^2 (mV)
DOE 2020 Target	0.125	8.0	1.000	0.44	-40	-30	-30
2017 (Mar.) UTF Ir/PtNi	≤ 0.089	≥ 6.6	0.58	0.44	-45	-23	NA
2018 (Mar.) UTF 31Pt/26Ir	≤ 0.094	≥ 6.5	0.64	0.28	-5	-20	< -5
2018 (May) UTF 50Pt/11Ir	≤ 0.098	≥ 8.9	0.89	0.28	TBD	TBD	TBD

Best of Class MEAs include cathode interlayer ($16ug_{PGM}/cm^2$) and optimized anode GDL for operational robustness (see backup)

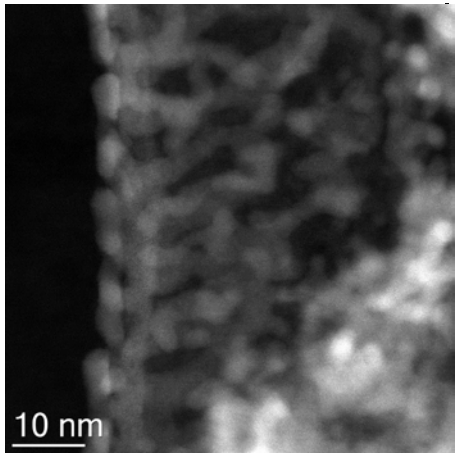
Accomplishments and Progress – Pt with Non-PGM Underlayer (Ta)

Activity, Area Dependence on Pt Content with Ir and Ta Underlayers. 50cm² MEA Format.

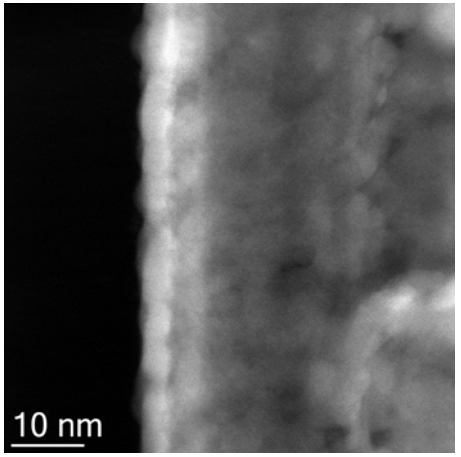


- Ta and Ir yield similar peak mass activity.
- Activity loss as Pt thickness on Ta decreased, due to specific area loss – different than w/ Ir.
- At low Pt loadings, Pt coating is discontinuous.
- EDS and XPS: Ta is oxidized (Ta:O ~ 1:1).
  - TaO is ~100x more resistive than metal.
- (One) hypothesis: unutilized Pt at low loading due to electronic disconnection.
- Conductive underlayers in development.

10Pt/8Ta, After FC

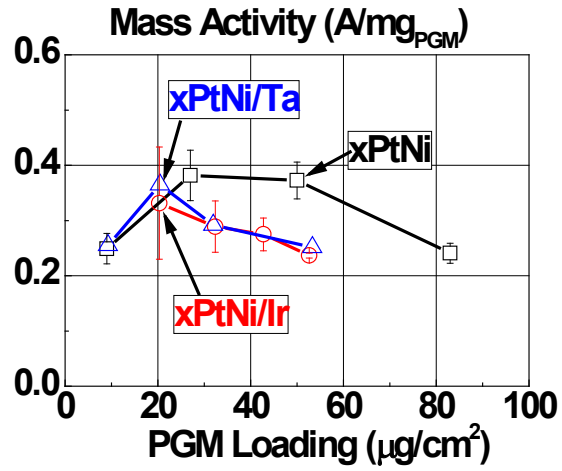


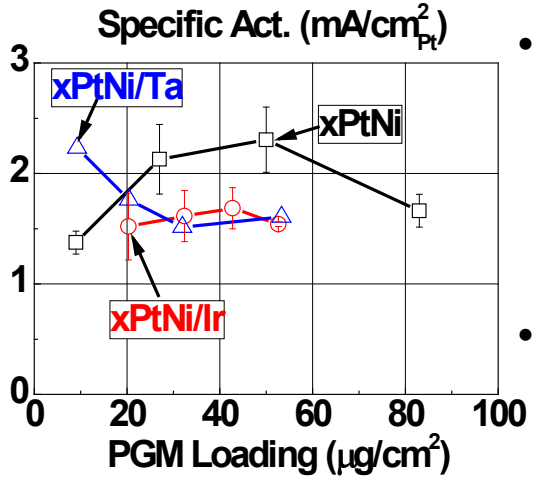
20Pt/8Ta, After FC



Accomplishments and Progress – Alloy Integration onto Underlayers

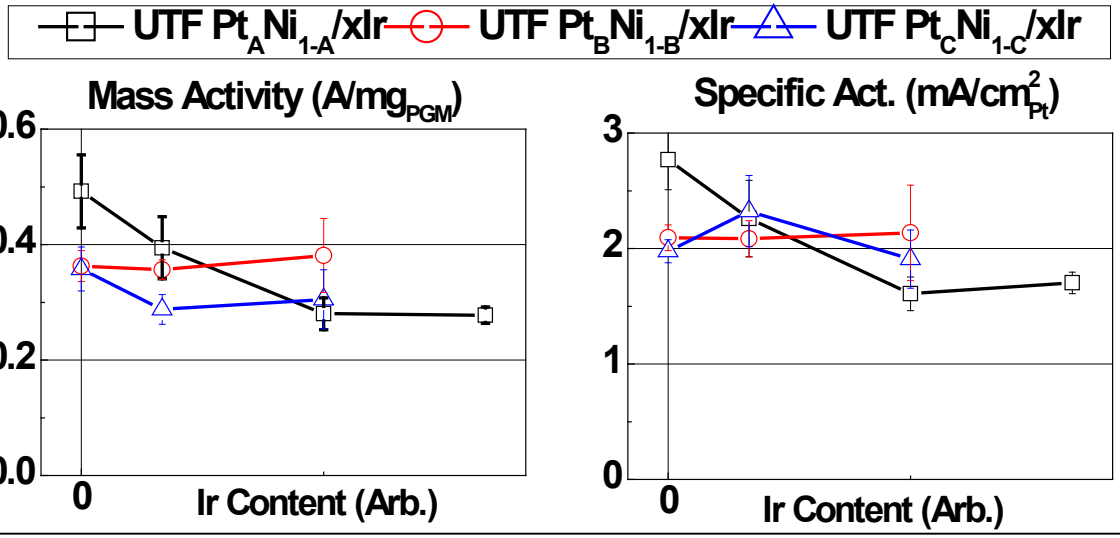
PtNi Alloy Integration onto Ir or Ta Underlayers. 50cm² MEA Format.





- With fixed Ir or Ta underlayers, PtNi mass activity *decreased* as PGM loading increased from 20 to 50 ug/cm^2.
  - Similar response with either Ta or Ir.
  - Specific activity suppressed.
- Mass activity dependence on PtNi content different than with Pt.
  - *Pt activity higher with underlayer than without, over similar Pt content range.*

PtNi Alloy Optimization on Ir Underlayer. 50cm² MEA Format.



- With PtNi (A), activity decreases rapidly with increasing Ir content.
- UTF PtNi with compositions (B, C) are less sensitive to Ir content.
- Status value for UTF PtNi/Ir: 0.39A/mg$_{PGM}$ with Pt$_B$Ni$_{1-B}$/Ir.
- High activity ORR catalyst integration with underlayers in progress.

Collaborations

- **3M - Electrocatalyst Fabrication and Characterization, Electrode and MEA Integration, HT Development**
  - A. Steinbach (PI), C. Duru, G. Thoma, J. Petrin, A. Haug, K. Lewinski, M. Kuznia, C. Bedoya, D. Rowe, J. Bender, M. Stephens, M. Brostrom, 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

Dual Pathway Approach: "The project keeps two approaches … NPTF and UTF. …no clear explanation about the relationship… unclear why two approaches are necessary."

- *Both approaches were initially assessed as having reasonable probability of achieving project targets.*
- *The dual approach allowed for comparative analyses for impacts of new alloy compositions and additives with significantly different catalyst morphologies, broadening the applicability of key findings.*
- *The original project plan included an informal approach downselect near mid-project. Based on assessment and plan for downselect, 3M de-emphasized the NPTF approach in project Q6.*

Collaboration: "The collaborative aspects … were not explained well. …collaborations … not fully justified, especially for tasks during the upcoming year. For example, it is unclear how the HT development at JHU was coupled with a similar task at ANL."

- *Agreed. Early BP1 model work at JHU and Purdue focused on model validation. Reporting of results on proprietary material concepts could not be reported last year. It is our hope that this year, the collaboration and impact on results are evident.*
- *JHU and ANL (and 3M) were independently addressing HT electrochemical characterization methods for gradient composition catalysts via independent approaches, as this aspect was recognized as the key HT challenge.*

Operational Robustness: "A complete change in direction that has been requested by reviewers for many years is necessary. The catalyst layer needs to be modified so that its mass transport is improved… comparable to traditional Pt/C electrodes"

- *Agreed that operational robustness is important. The focus of this project is development of catalysts with improved activity and durability, capable of being integrated into robust dispersed electrodes (FC155, A. Haug) or MEAs (previous project FC104). While both methods are effective, the dispersed electrode approach has substantially reconciled robustness concerns.*

Remaining Challenges and Barriers

1. The mass activity of UTF alloy catalysts with durable Ir underlayers do not meet DOE targets. The high specific activity PtNi catalysts (with and without surface modification), optimized without underlayers, may need to be re-optimized for use with underlayers.
2. Ir content needs to be reduced to be compatible with the relative abundance of Ir to Pt.
3. Non-PGM underlayers may have high electronic resistance, preventing entitlement specific areas and mass activities with thin ORR catalyst coatings.
4. Achievement of rated and specific power targets will require integration of high specific activity ORR catalyst onto thicker, reduced-PGM, conductive underlayers.
5. Experimental specific activities are approximately 10x below entitlement model prediction of catalysts with well-defined and optimally-strained Pt skins.
6. Development of high throughput electrochemical characterization of catalysts has been plagued by poor reproducibility and/or lower-than expected sensitivity.
7. Break-in conditioning of NSTF cathode electrodes is longer and more complex than many carbon supported Pt nanoparticle cathode electrodes.
8. Rated power loss is generally the key lifetime-limiting factor for NSTF cathode MEAs.

Key Future Work – 2Q18-1Q19

- Integrate higher specific activity UTF alloys onto reduced PGM-content, Ir-containing underlayer, to achieve activity and durability targets simultaneously (BP2 GNG).
- Develop higher thickness, electronically-conductive, PGM-free underlayers for improved mass activity, specific area, and H_2/Air performance at relevant electrode PGM loadings.
- Determine mechanism of PtNi specific activity suppression in presence of Ir or Ta underlayers through characterization and modeling.
- Continue durability model development, including assessment of activity after simulated electrocatalyst AST cycling.
- Generate publications re: surface modified catalysts and underlayer catalysts.
- Demonstrate quantitative HT electrochemical characterization method via segmented fuel cells and/or flow cells.
- Optimize third generation project electrocatalysts to achieve project targets
  - Project Target: ≥ 0.80A/mg_{PGM}, ≤ 20% loss, and MEA PGM content ≤ 0.10 g/kW @ 0.70V.
  - '18 Status: 0.28A/mg_{PGM}, 5% loss, and MEA PGM content < 0.15g/kW @ 0.70V.
- 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

- **Task 1 - ORR Electrocatalyst, Support, and Fabrication Process Development**

  2018 catalysts have met or exceeded 6 of 6 DOE targets.

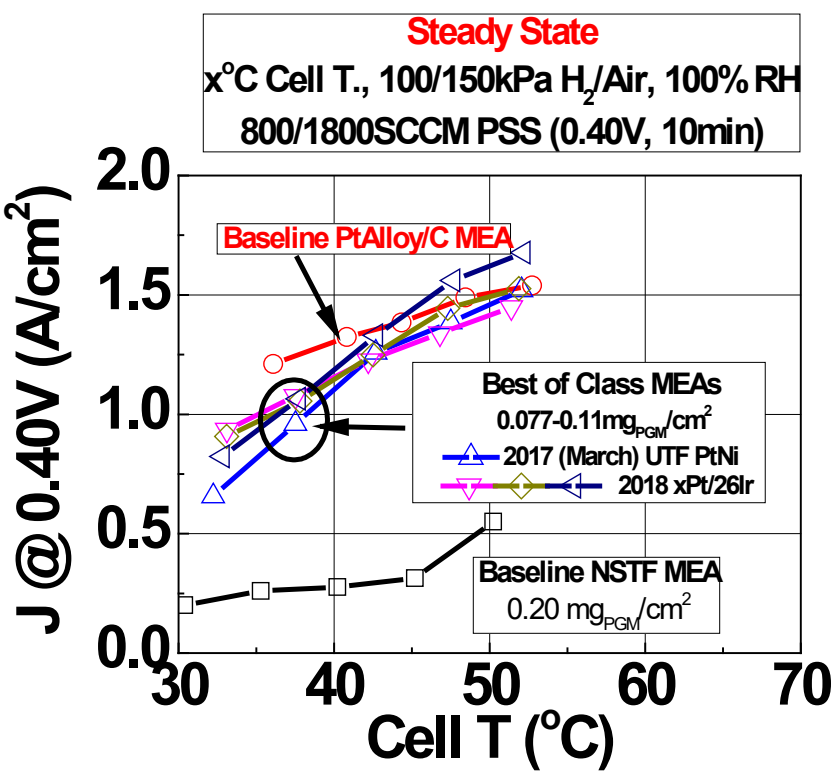
  - **UTF Surface Modification**
    - Ir, Cr, Ru, and Ta yielded enhanced mass activity vs. unmodified PtNi, ranging from 0.40 to 0.57 A/mg_{PGM}, due to improved specific activity, as high as 3mA/cm^2_{Pt}.
    - Activity enhancements at specific composition ranges for each additive.
    - Ir, Ta, Ru, and Au additives effective at improving electrocatalyst durability (activity, area, and/or H_2/Air performance).
  - **UTF Underlayers**
    - 4 of 6 project targets met or exceeded.
    - Pt/Ir catalysts have Pt mass activity as high as 1.4A/$mg_{Pt,}$ and improved H_2/Air performance vs. Pt at ultra-low PGM contents.
    - Pt/Ir catalysts are durable, meeting/exceeding project targets.
    - Ir and Ta underlayers are effective at increasing PGM mass activity of Pt catalyst due to increased specific area vs. underlayer-free.
    - Re-optimization of high activity PtNi alloy may be required for integration with Ta or Ir underlayers.
- **Task 2 - Electrocatalyst Simulation**

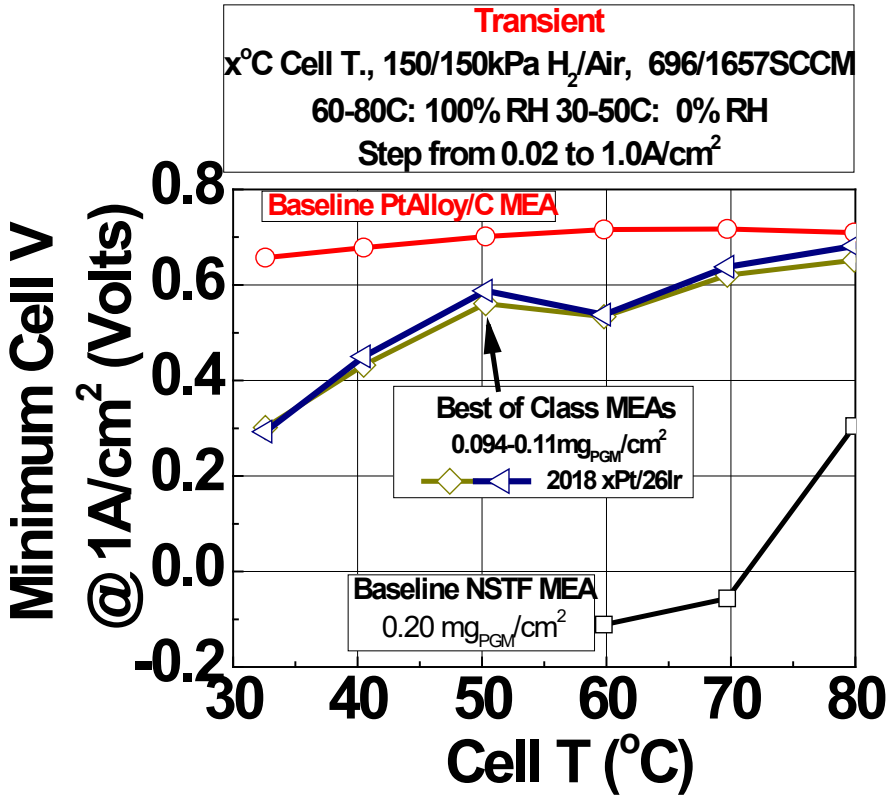
  Catalyst Durability Modeling
  - Pt, Ni, and Ir interaction energies completed, revealing tendency for Ir to segregate from PtNi.
  - DFT-determined surface diffusion barriers of Pt, PtO, and Ir indicate high stability of Ir surface clusters.
  - kMC model has been updated to include redox cycling and to incorporate DFT-determine interaction energies and diffusion barriers towards development of a modeled accelerated stress test.

  Underlayer Modeling
  - Pt monolayers on Ir predicted to have high specific activity, as much as 20x higher than Pt(111).
  - Pt on Ir predicted to be thermodynamically stable.
  - Underlayer adhesion modeling to PR149 and graphene substrates indicates relatively neutral adhesion of Pt, Ir, and Ni but high adhesion of Ta.

Technical Backup Slides

Technical Backup Slides – Operational Robustness

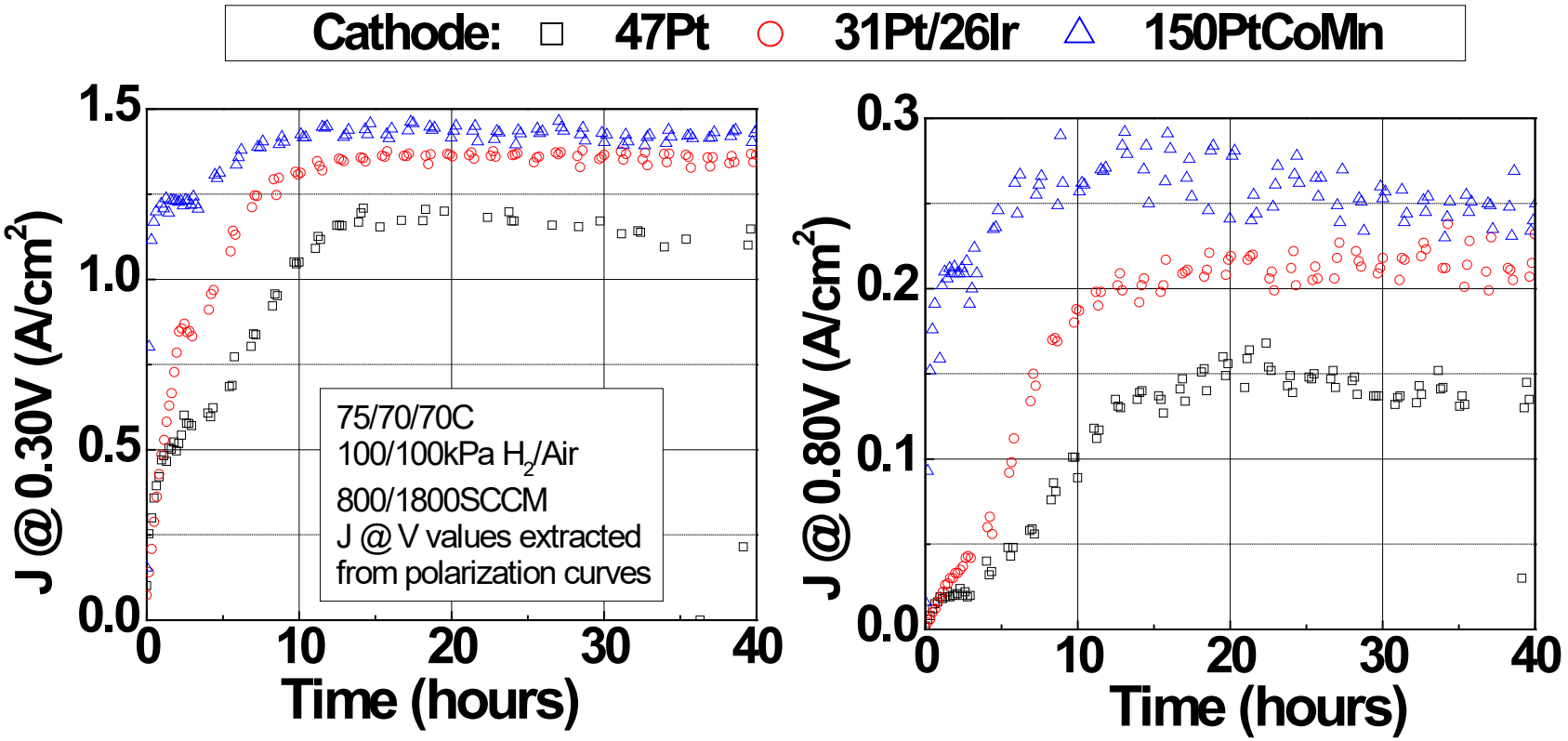




Improved Operational Robustness via Optimized Components

- Best of Class MEAs with xPt/26Ir have comparable operational robustness to previous Best of Class MEAs developed in FC104.
  - Optimized, liquid water permeable anode GDL
  - Cathode GDL with interlayer (Pt/C electrode with 16 $\mu g_{Pt}/cm^2$).
- Significantly improved over traditional NSTF electrode MEAs without optimized components, but not as robust as Pt Alloy/C electrode.

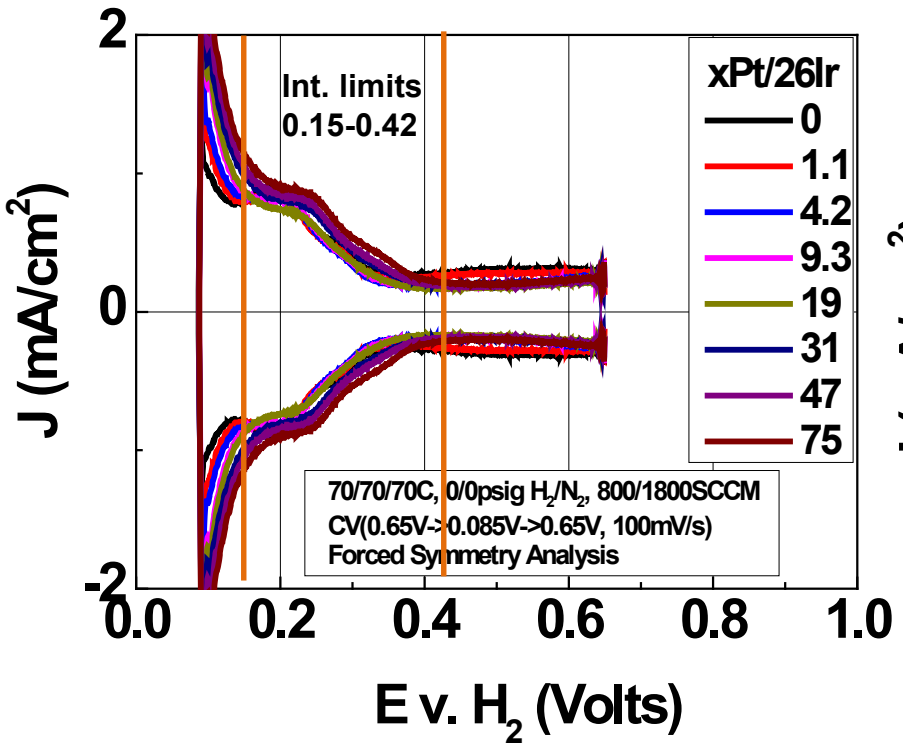
Technical Backup Slides – Break-in Conditioning

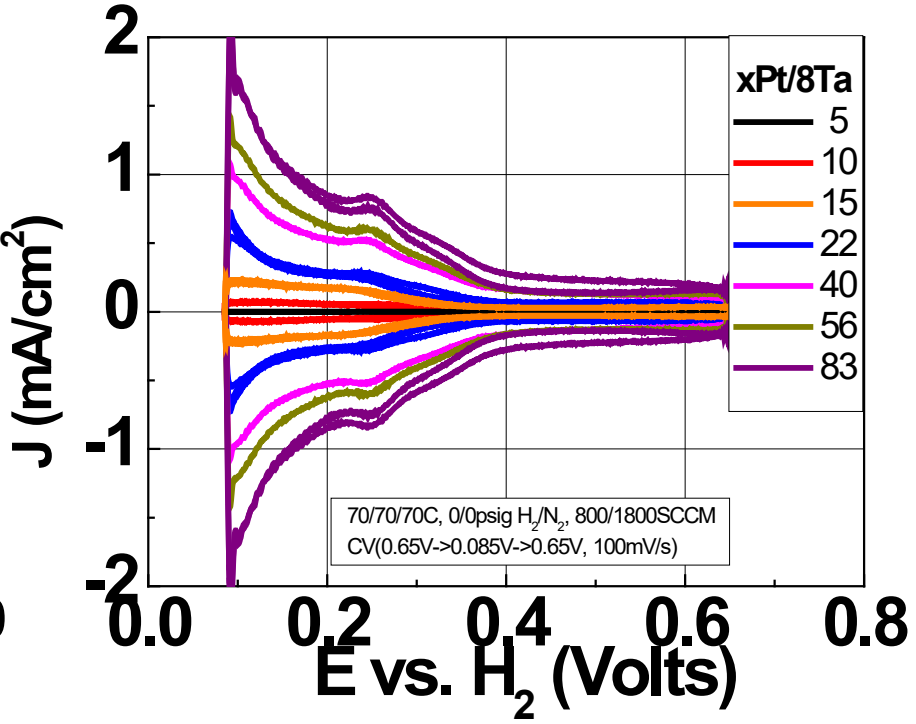


Break-in Conditioning of UTF Catalysts with Ir Underlayer

- Conditioning time of project Pt/Ir catalysts is generally similar or improved vs. pure Pt NSTF catalysts at similar loadings, but slower than much higher loaded PtCoMn/NSTF.
- Catalyst composition, structure, processing, and surface area are all influential factors for both conditioning time and performance prior to conditioning.
- Conditioning used here consists of several repeated temperature and potential cycles.

Technical Backup Slides – Voltammetry of Underlayer Catalysts

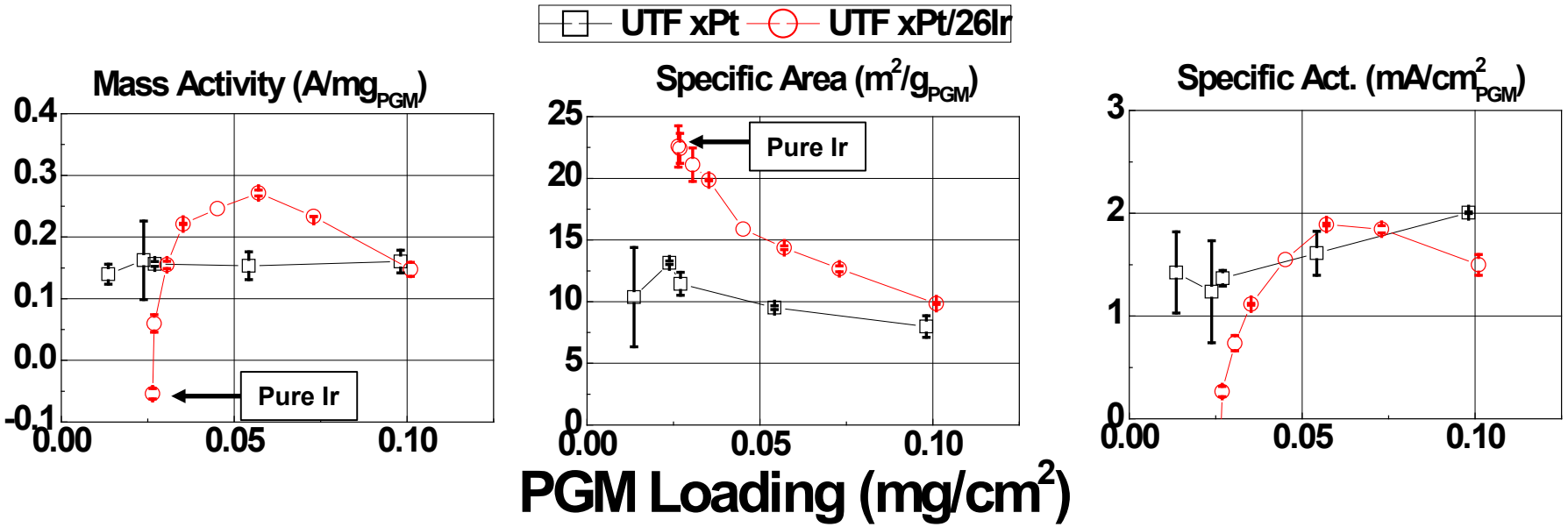




Voltammograms Reveal Pt Utilization Differences vs. Underlayer Type

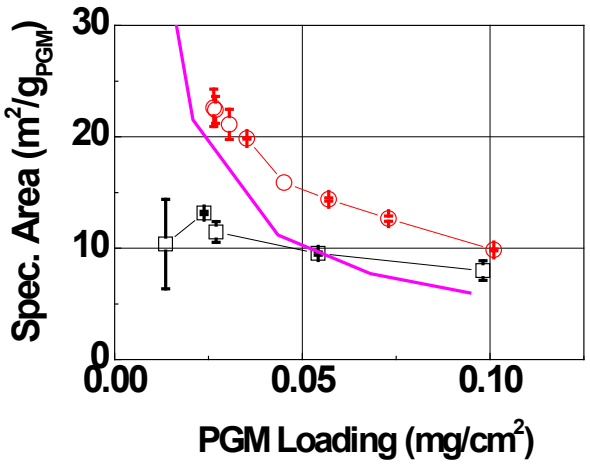
- Pt/Ir voltammograms transition from Ir (metal)-like to Pt-like with addition of 4 µg/cm^2 Pt to 26 µg/cm^2 Ir.
  - Literature for poly Ir specific charge has wide range.
  - Area analysis in this presentation assumes 220 µC/cm$^2_{Pt\ and/or\ Ir}$
- Pt/Ta voltammograms indicate Pt deactivation for Pt loadings < 22 µg/cm^2.
- As part of analysis, CVs are forced to be symmetric about J=0. Required for reliable analysis of ultra-low area catalysts.
  - Assumes H_{UPD} kinetics are highly reversible.

Technical Backup Slides - UTF Catalysts with Ir Underlayers

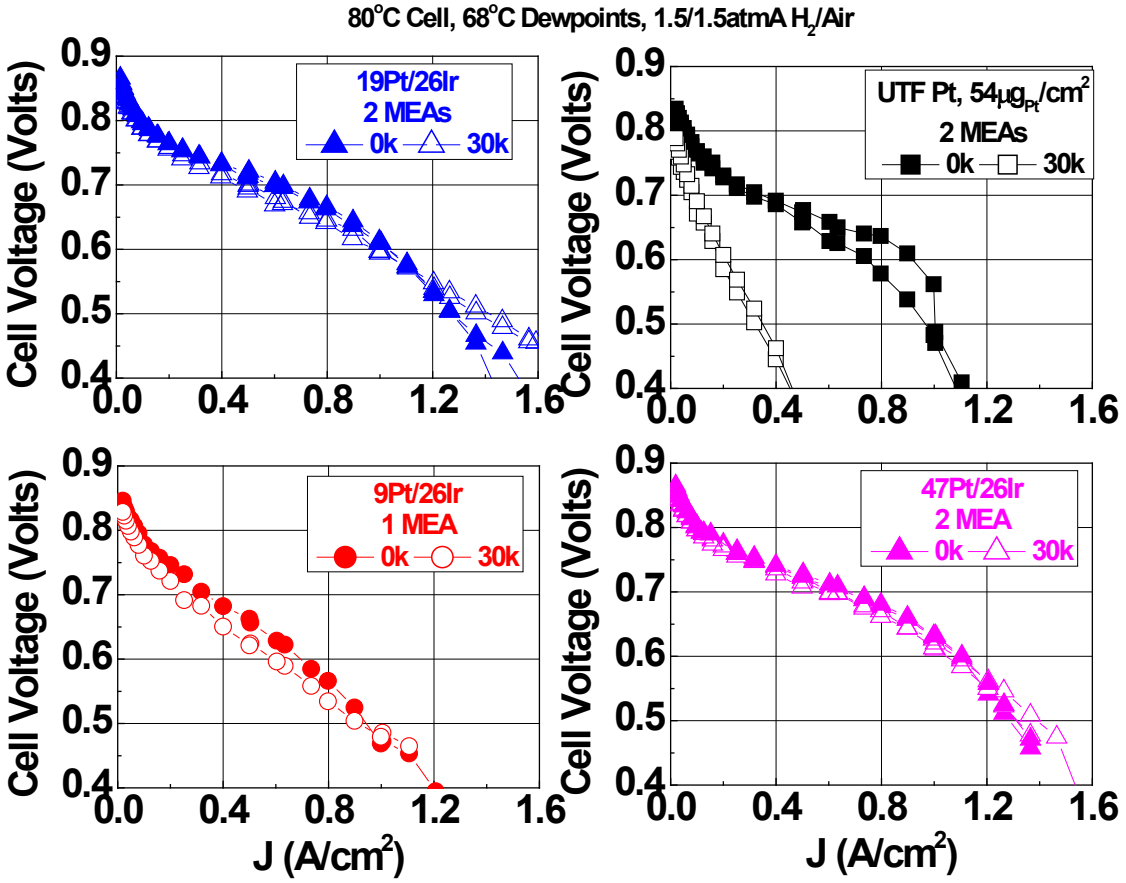


Impact of Pt Loading with Fixed Ir Underlayer

- Improved PGM mass activity is due primarily to increased specific area.
- Area increases monotonically as Pt content on Ir decreases, similar in trend with simple model projection.
- Overall specific activity ranges from 0 to essentially Pt-like
  - Absolute activity normalized by total (Pt+Ir) measured area.
  - How to measure **Pt** specific activity of Pt sub-monolayer on Ir?



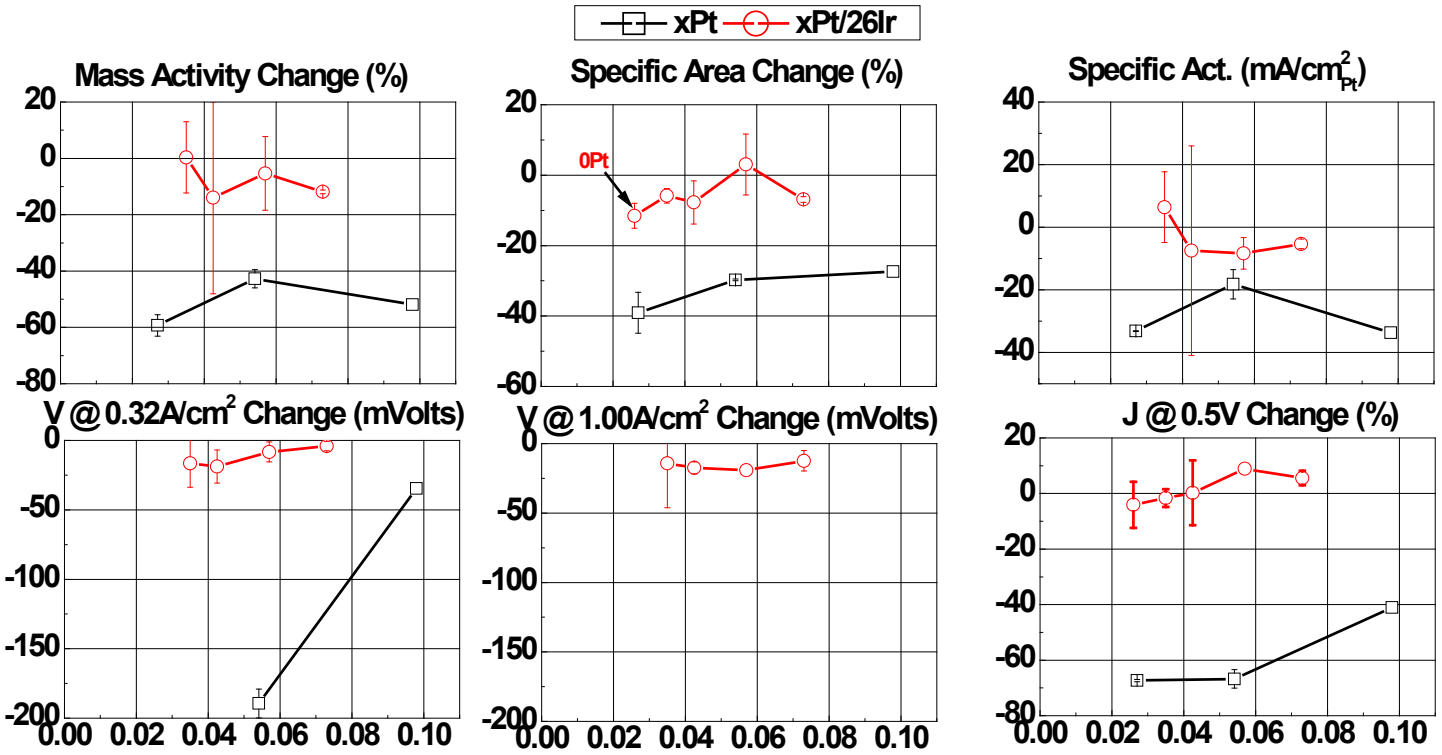
Technical Backup Slides – Electrocatalyst AST Durability of Pt/Ir Catalysts



Ir Underlayer Stabilizes H_2/Air Performance After Electrocatalyst AST

- Pure Pt (54 µg/cm^2) loses significant performance after Electrocatalyst AST
  - 30% surface area loss - performance strongly sensitive to area at low loadings
- Ir underlayer substantially stabilizes performance with variety of low Pt loadings and low areas.
  - < 30mV loss over entire polarization curve with Pt loadings of 9 to 47 µg/cm^2.

Technical Backup Slides - Electrocatalyst AST Durability of Pt/Ir Catalysts

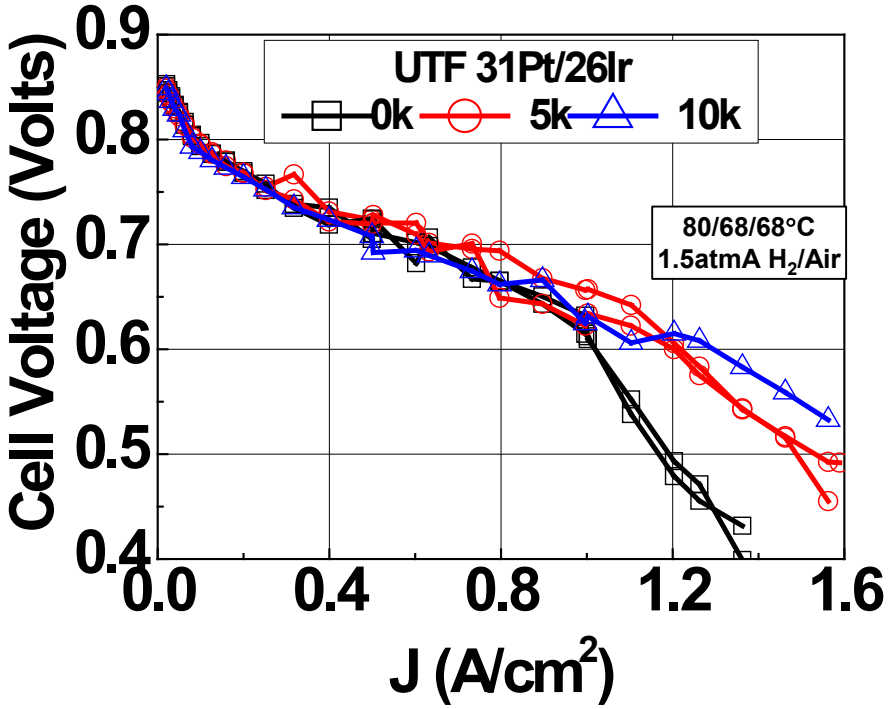


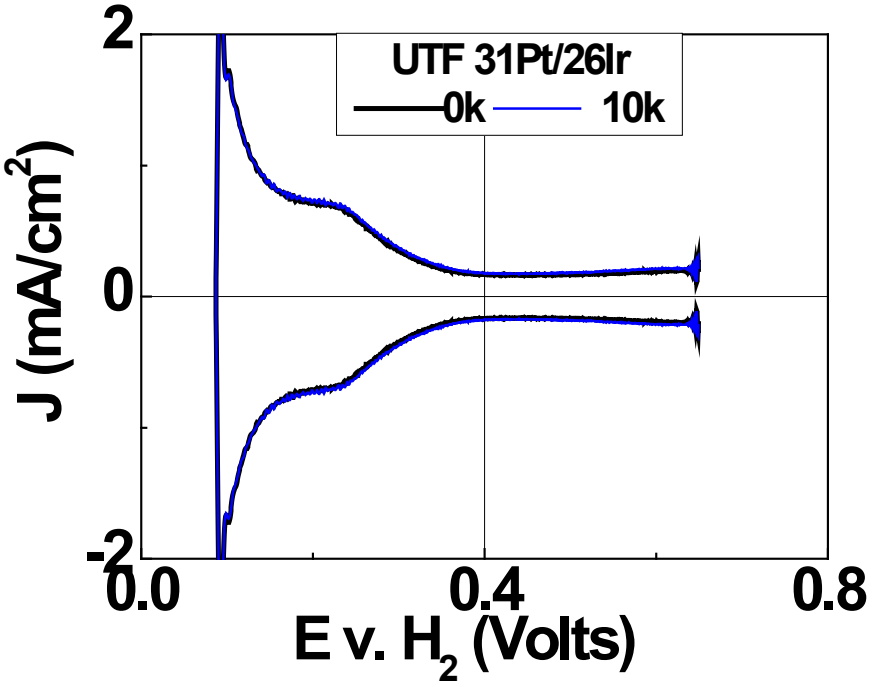
Ir Underlayer Stabilizes Activity, Area, and H_2/Air performance of UTF Pt.

- After Electrocatalyst AST, Pt/NSTF:
  - loses 40-60% mass activity and 30-40% surface area
  - H_2/Air performance losses increase monotonically with decreasing loading.
- Ir underlayer substantially stabilizes catalysts.
  - < 20% mass activity, specific area, specific activity losses.
  - < 15mV loss at 0.02A/cm², ≤ 20mV @ 1A/cm² , and < 10% loss in J @ 0.50V.

Technical Backup Slide – Support AST Durability of Pt/Ir Catalysts

Support AST Durability (80°C, 5K Cycles, 1.00-1.50V)

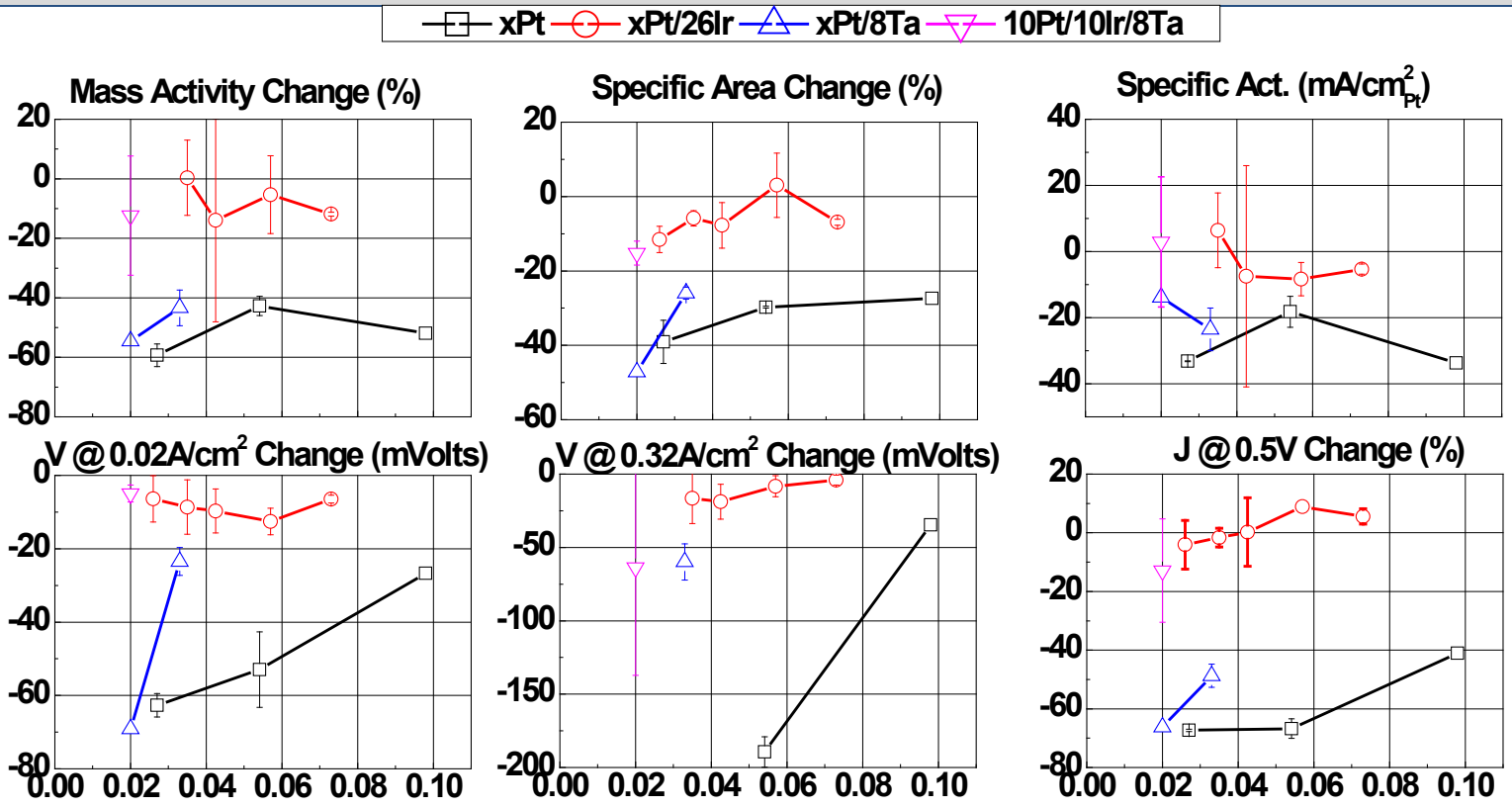




Oxidatively-Stable Activity, Area, and H_2/Air Performance of Pt/Ir Catalysts

- Performance loss < 5mV across entire polarization curve after 5k or 10k cycles.
- Performance at J ≥ 1A/cm^2 increased after 5k cycles.
  - Ir may suppress performance below 0.70V at beginning of life.
- Mass activity and specific area changes < 5% after AST.
  - CVs after 10k cycles essentially unchanged vs. 0k. Ir remains (largely) metallic after extended high E cycling.
- CVs forced to be symmetric to enable reliable analysis of ultra-low area catalysts.
  - Assumes reversible H_{UPD} kinetics

Technical Backup Slide – Durability of Pt/Ir, Pt/Ta, Pt/Ir/Ta Catalysts



Electrocatalyst Durability of Ta, Ir, Ir/Ta Underlayers

- 20Pt/Ta has generally similar durability as 28Pt with much higher losses than 20Pt/Ir.
- Stability with Ta underlayer may increase as Pt thickness increases.
- Ta appears stable (EDS): 0.69 ± 0.02 Pt mole fraction before testing, 0.63 ± 0.04 after AST (Ta more stable than Pt?).
- Incorporation of an Ir layer between Ta and Pt (generally) decreased losses.