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:	$1.073MM*
Cost Share Percentage:	23.72%

*Includes DOE, contractor cost share and FFRDC funds as of 3/31/17

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 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 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, atomic-scale electrocatalyst modeling, and advanced physical characterization to guide and accelerate development.

BP1 Milestones and Go/No-Go

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	100%	0
3.1 HT Fabrication	M3.1.1	HT Catalyst Deposition Process Reproducible	100%	1
	M3.1.2	HT Catalyst Treatment Process Reproducible	60%	2
3.2 HT Characterization	M3.2.1	HT EC Characterization Reproducible	100%	2
	M3.2.2	HT XRD Characterization Reproducible	100%	3
3. HT Development	M3.1	HT Activity, Area Agrees w/ Homogenous MEA	65%	3
3.2. HT Characterization	M3.2.3	HT EXAFS/XANES Characterization Reproducible	100%	4
2.1 KMC Refinement	G2.1.1	KMC predicts specific area and composition trends of Pt_xNi_{1-x} (≥3 mole fractions) during EC dealloying.	100%	4
2.2 DFT Refinement	G2.2.1	DFT predicts specific activity trends of Pt_xNi_{1-x} (≥3 mole fractions).	100%	5
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).	100%	4

- Validation of high throughput catalyst development largely complete; delay in (key) M3.1 resolved; now progressing.
- Refinement of KMC and DFT models complete; models validated.
- Project BP1 GNG (activity and durability) achieved.

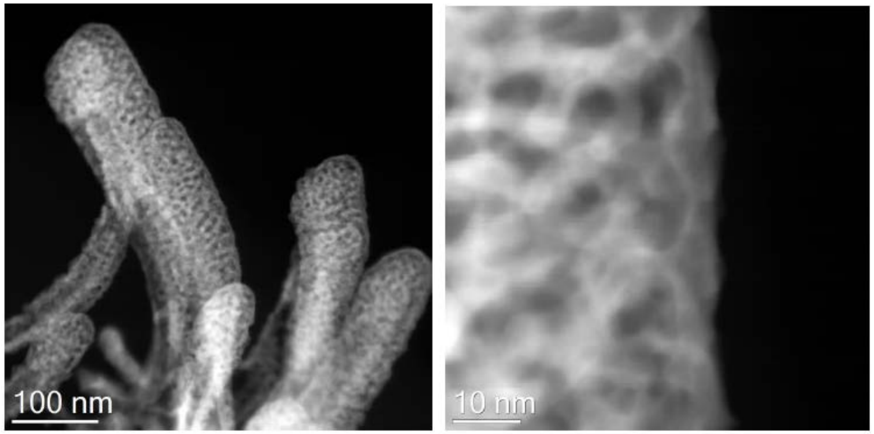
BP2 Milestones and Go/No-Go

Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
3.2 HT Characterization	M3.2	Combinatorial/HT Physical Char. Agrees w/ Homogenous Catalyst	60%	6
2.3 New NPTF Simulation	M2.3.1	Model(s) predict ≥2 new NPTF alloys w/ ≥30m^2/g area	40%	6
2.4 New UTF Simulation	M2.4.1	Model(s) predict ≥2 new UTF alloys w/ ≥4mA/cm^2 activity	50%	7
2.5 Dur. Cat. Simulation	M2.5.1	Model(s) predicts ≥4 alloys w/ ≤ 30% loss under ASTs.	0%	8
2. Catalyst Simulation	M2.1	Model(s) predict ≥4 alloys w/ ≥0.8A/mg and ≤ 20% loss w/ ASTs.	0%	8
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	85%	8

- BP2 milestones mostly reflect KMC and DFT simulations of new alloy candidates with improved activity, area, and durability.
- BP2 Go/No-Go reflects increased activity, durability, and MEA performance.
- Current BP2 GNG status (UTF PtNi) is 85%: 0.37A/mg_{PGM}, 43% loss, and 0.13g/kW.

Approach – Two Distinct Thin Film Electrocatalyst Morphologies

Nanoporous Thin Film (NPTF)

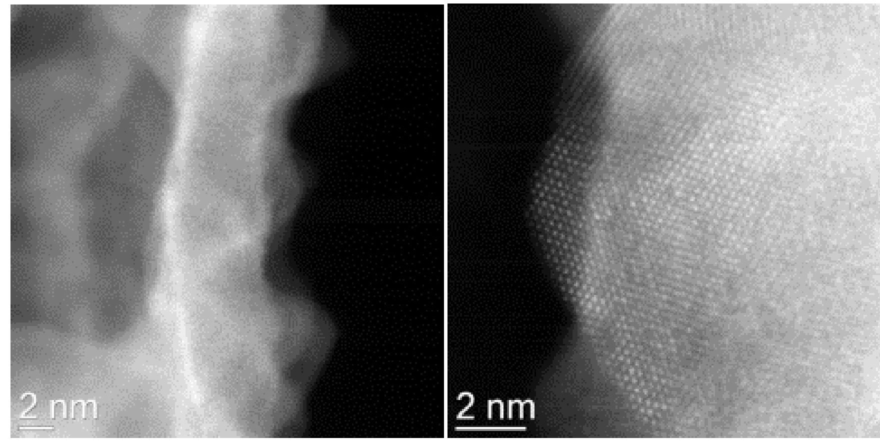


NPTF Approach:

1. **Maximize area and minimize leachable TM** by structure, composition, and process optimization.
2. **Stabilize** against **nanopore coarsening and TM dissolution** via additives.

NPTF PtNiIr "#3"		
	Status	Project Target
Mass Activity (A/mg_{PGM})	0.38	0.80
Specific Area (m^2/g_{PGM})	19.3	30
Spec. Activity (mA/cm^2_{Pt})	2.1	2.6
Mass Act. Change (%)	-45	-20

Ultrathin Film (UTF)



UTF Approach:

1. **Develop active, stable and thin surface facets** by structure, composition, and process optimization.
2. **Increase catalyst absolute area** by integration with higher area NSTF supports to enable increased absolute power density.

UTF PtNiIr "#2"		
	Status	Project Target
Mass Activity (A/mg_{PGM})	0.44	0.80
Specific Area (m^2/g_{PGM})	16.1	20
Specific Activity (mA/cm^2_{Pt})	2.7	4.0
Mass Act. Loss (%)	-45	-20

Status versus DOE and Project Targets

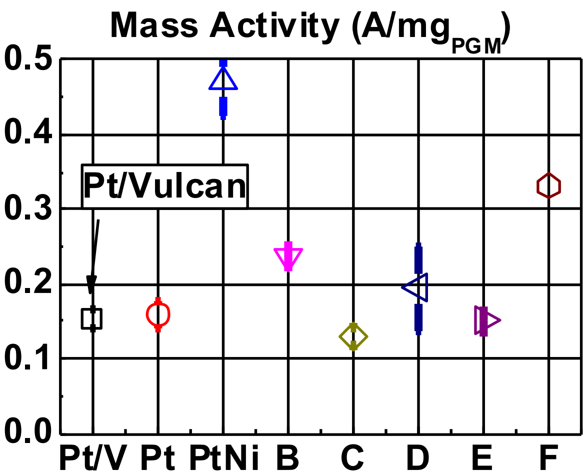
	2020 Target and Units	Project Target	UTF PtNi, PtNiIr		NPTF PtNiIr	
			2016	2017	2016	2017
Platinum group metal (PGM) total content (both electrodes)	0.125 g/kW ($Q/\Delta T \leq 1.45$)	0.1 (@ 0.70V)	NA	0.13[2]	0.18	0.151[1]
PGM total loading (both electrodes)	0.125 mg/cm^2	0.10	NA	0.077[2]	0.127	0.122[1]
Loss in catalytic (mass) activity	40 %	20	NA	45[4]	40	45[3]
Loss in performance at 0.8 A/cm^2	30 mV	20	NA	23[4]	28	21[3]
Loss in performance at 1.5 A/cm^2	30 mV	20	NA	NA	NA	NA
Mass activity @ 900 $mV_{iR\text{-}free}$	0.44 A/mg (MEA)	0.80	0.31	0.44[4]	0.24	0.38[3]

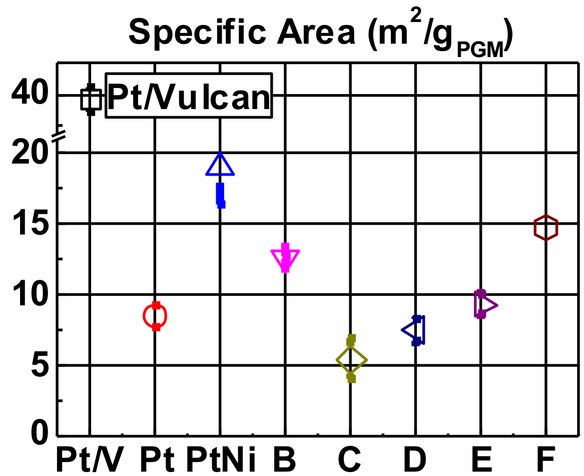
[1] 2017(Jan.) NPTF BOC MEA. 0.016mg_{Pt}/cm^2 NSTF anode, 0.090mg_{PGM}/cm^2 NPTF PtNiIr cathode, 0.016 mg_{Pt}/cm^2 cathode interlayer.
[2] 2017 (Jan.) UTF BOC MEA. 0.015mg_{Pt}/cm^2 NSTF anode, 0.046mg_{PGM}/cm^2 UTF PtNi cathode, 0.016 mg_{Pt}/cm^2 cathode interlayer.
[3] NPTF PtNiIr/NSTF cathode from 2017 (Jan.) NPTF BOC MEA, 0.09mg_{PGM}/cm^2 after 30k Electrocatalyst AST cycles.
[4] UTF PtNiIr. BOL and after 30k Electrocatalyst AST Cycles
PGM content values at 90°C cell, 1.5atmA H_2/Air, 0.70V ($Q/\Delta T$ = 1.41kW/°C)
GREEN: Meets or exceeds DOE 2020 target. YELLOW: Within ca. 15% of DOE 2020 target.

- 2017 catalysts approaching or meeting many DOE 2020 catalyst and MEA targets.
- PGM content and loading values include cathode interlayers (16μg/cm^2) for operational robustness.

Accomplishments and Progress – New NPTF Alloy Development

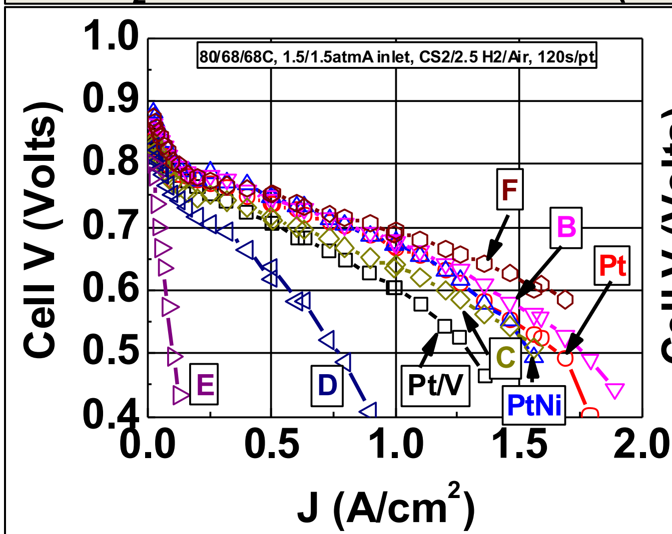
NPTF Status Values. 6 Alloys(Ni, B-F) x 3 Mole Fractions. 0.08-0.10mg_{PGM}/cm^2. 50cm^2 MEA Format.

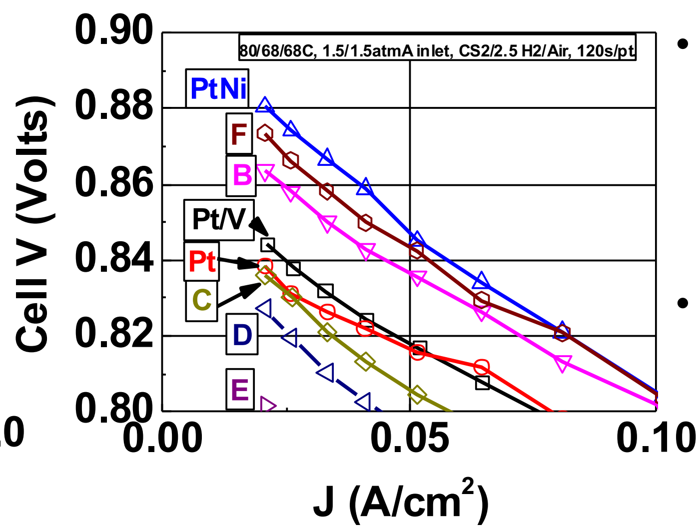




- Status values reflect current optimal composition and processing for each alloy.
- Highest mass activity (0.47A/mg_{PGM}) to date with annealed, dealloyed PtNi.
- Mass activity variation mostly due to ca. 4x variation in specific area.

H_2/Air Performance - NPTF (0.08-0.09 mg_{PGM}/cm^2) vs. Pt/V (0.10mg_{PGM}/cm^2). 80°C, 1.5atmA.

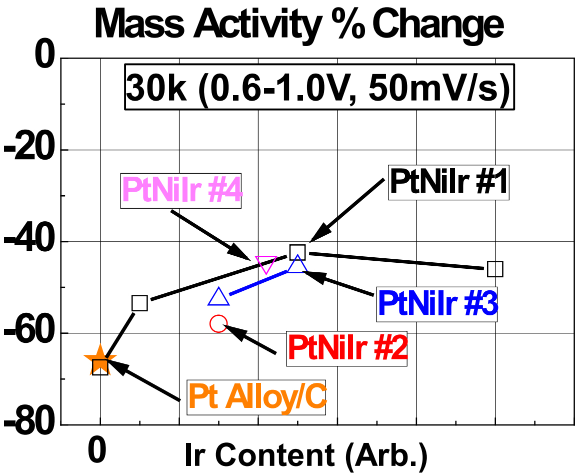


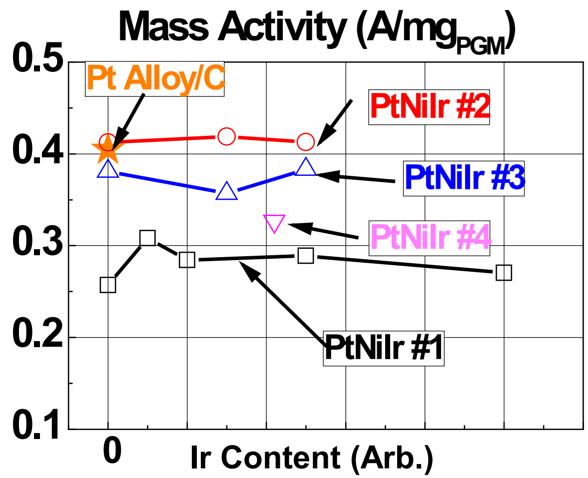


- At lower loading, several NPTF candidates yield improved performance vs. Pt/V.
  - Up to 90mV @ 1A/cm^2.
  - Up to 35mV @ 0.02A/cm^2
- New alloys "B", "F" have improved high current H_2/Air performance over PtNi, but lower kinetic performance.

Accomplishments and Progress – NPTF PtNi Stabilization via Ir

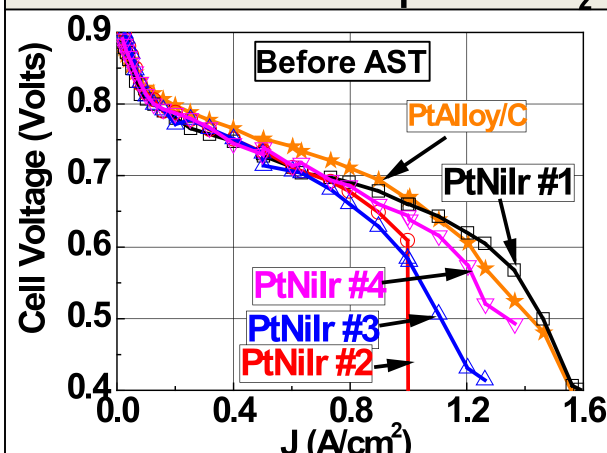
Ir Impact on BOL Activity and DOE Cat. AST Durability. 0.08-0.11mg_{PGM}/cm^2. 50cm^2 MEA Format



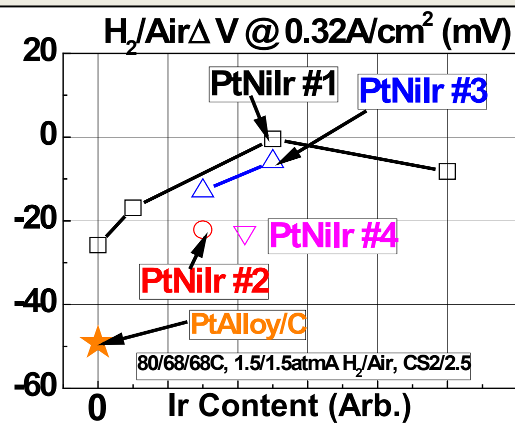


- Ir integration with NPTF PtNi reduces mass activity loss after Electrocatalyst AST.
  - 70% loss (Ir-free) to as little as 45% loss (w/ Ir).
  - Ir primarily improves specific activity retention.
- Beginning of life PGM mass activity varies from 0.28-0.42A/mg_{PGM}; depends on Ir integration method.

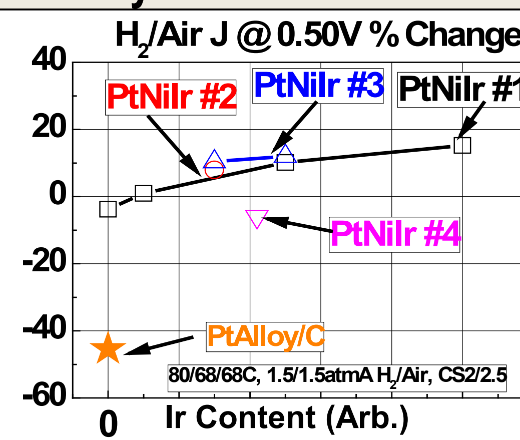
Ir Impact on H_2/Air Performance Retention After Electrocatalyst AST



- Pre-AST performance depends on Ir integration method (impacts dealloying).



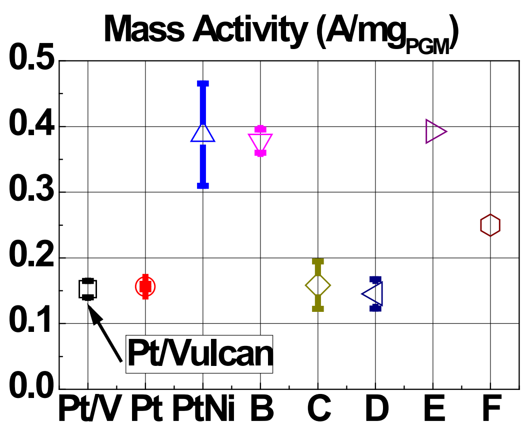
- Monotonic improvement w/ Ir content for #1, #3 integration; all < 30mV loss.
- PtAlloy/C: 50mV loss.

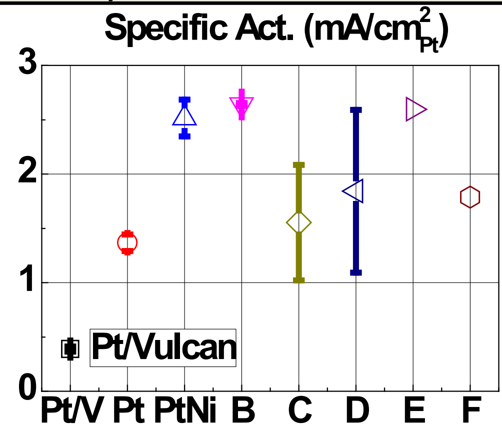


- PtNi, PtNiIr limiting current density change: -10% to +15% (*improves*).
- PtAlloy/C: -45% (local transport)

Accomplishments and Progress – New UTF Alloy Development

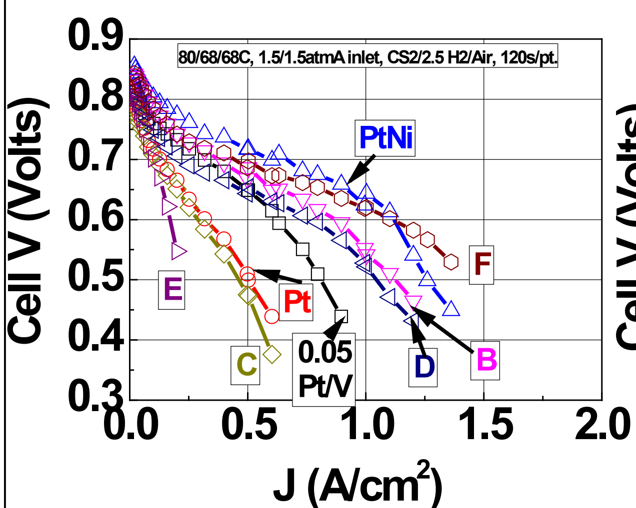
UTF Status Values. 6 Alloys (Ni, B-F) x 4 Mole Fractions. 25-30μg$_{PGM}$/cm^2. 50cm^2 MEA Format.

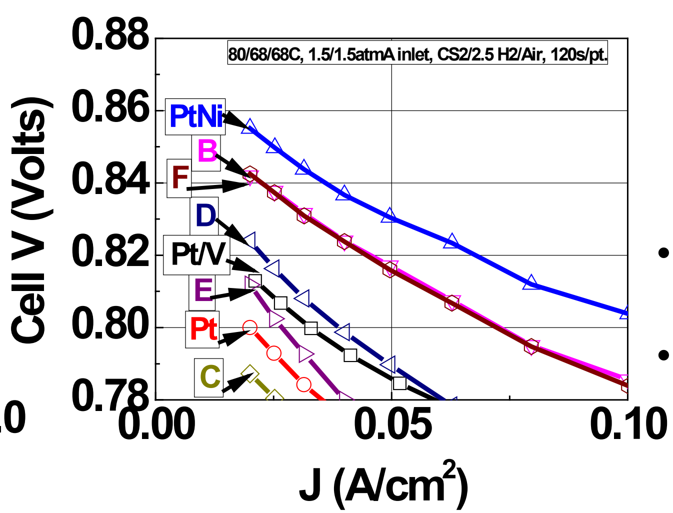




- Status values reflect optimal composition and processing for each alloy.
- Three alloys identified with >0.38A/mg$_{PGM}$ and > 2.5mA/cm$^2_{Pt}$.
  - ~7x higher specific activity than Pt/V.
- 50% specific activity gain needed to achieve 0.8A/mg project target.
  - Approach: Pt skin optimization.

H_2/Air Performance - UTF (0.025-0.030 mg$_{PGM}$/cm^2 vs. Pt/V (0.05mg$_{PGM}$/cm^2). 80°C, 1.5atmA

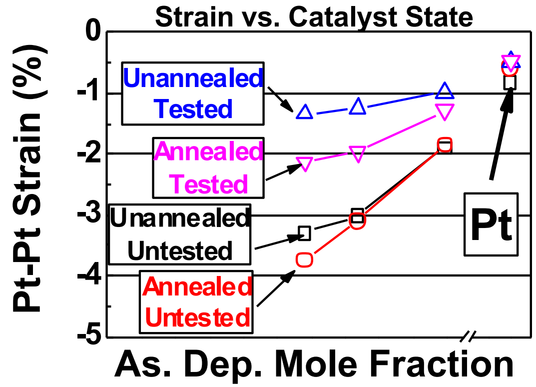




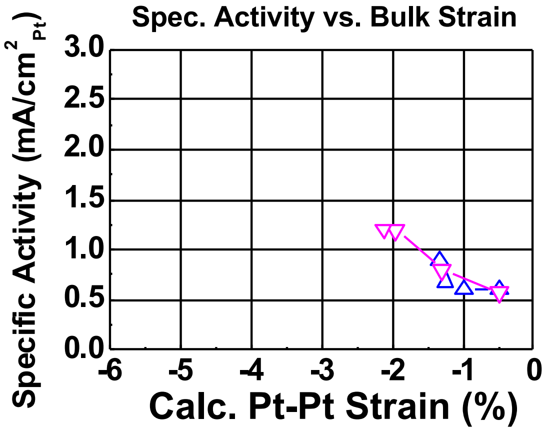
- Four UTF alloys yield improved performance vs. Pt/V, with 40-50% less PGM loading.
  - Up to 69mV @ 0.5A/cm^2
  - Up to 43mV @ 0.02A/cm^2.
- Absolute performance increase needed to achieve targets.
- UTF development phases:
  1. Optimize electrocatalyst (activity, durability, ECSA).
  2. Integrate with higher area supports to allow increased loading (0.08mg/cm^2) and absolute cathode surface area.

Accomplishments and Progress –UTF PtNi Property Correlations

Structure-Activity Correlations (Composition) - ANL

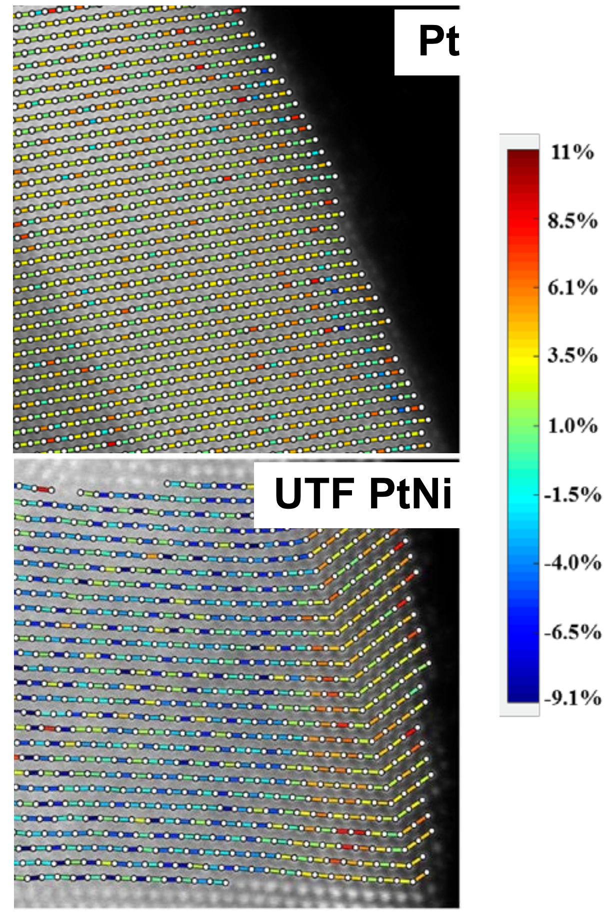


- Bulk strain increases w/ alloy fraction.
- Strain relaxes after FC testing.
- Annealed catalysts retain more strain.



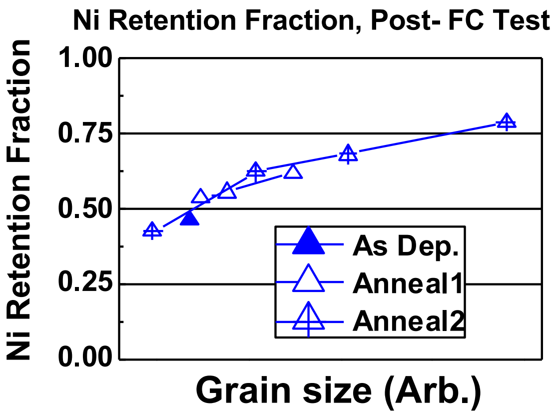
- Activity of annealed and unannealed Pt_xNi_{1-x} correlates with bulk strain.

Surface Strain Mapping-ORNL

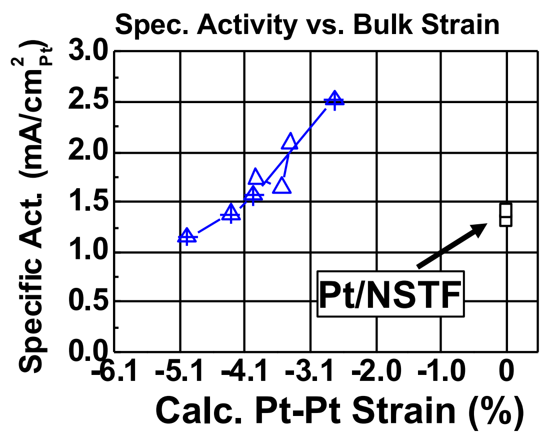


- (One example): Pt skin on PtNi is thick and relaxed relative to bulk.
- Challenging measurement/analysis.
- Not representative of all UTF PtNi.

Structure-Composition-Activity Correlations (Process) - ORNL



- UTF PtNi compositional stability varies with grain size (anneal process).



- Activity correlates with post-test composition (bulk strain).

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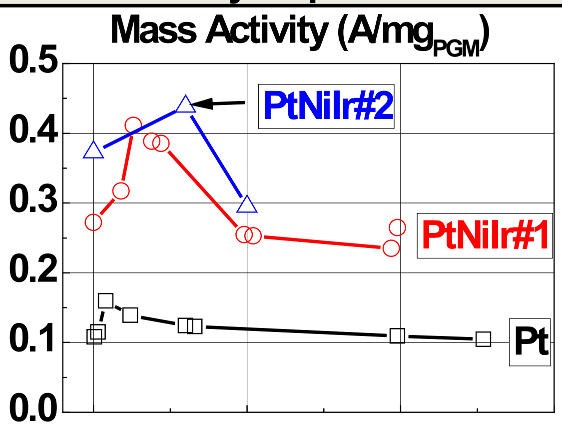
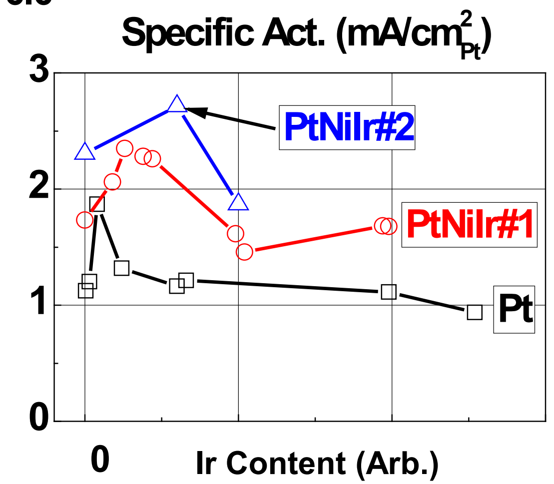
Accomplishments and Progress – Ir Integration into UTF Pt, PtNi

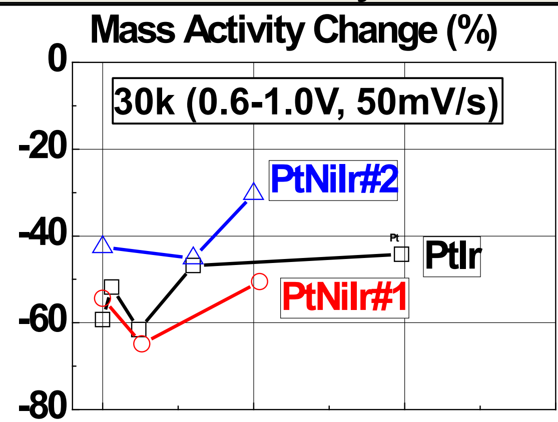
Activity Impact of Ir

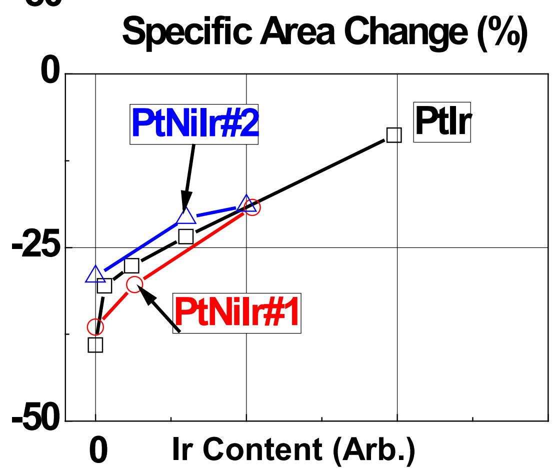


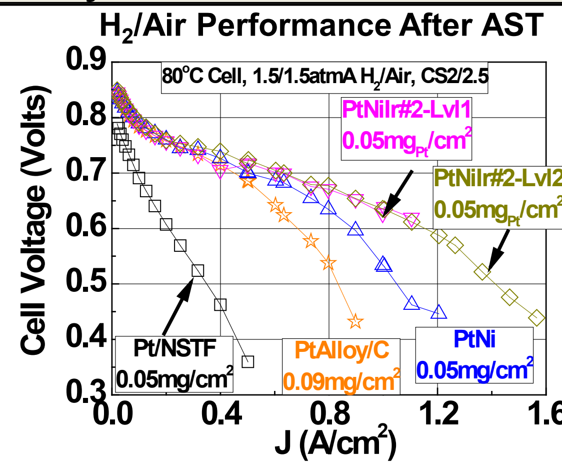


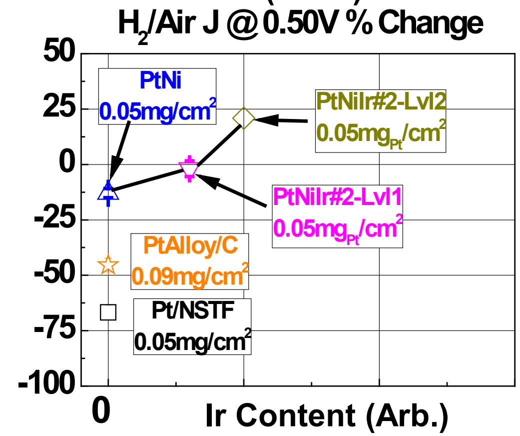
- At optimal content, Ir increases UTF Pt and PtNi PGM mass activity due to increased specific activity.

Electrocatalyst AST Durability of UTF PtIr, PtNiIr





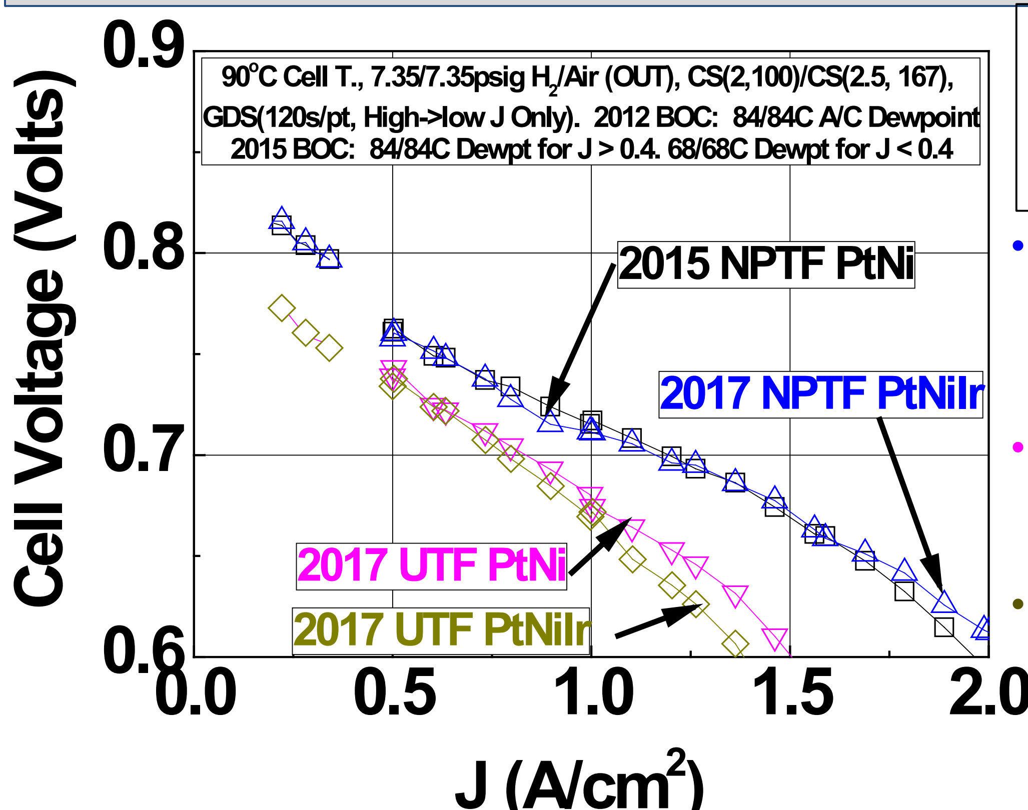




- Ir impact on mass activity retention after AST is unclear.
- Specific area retention increases monotonically with Ir content.

- Ir improves post-AST H_2/Air limiting current densities of UTF PtNi.
  - PtNiIr has ~75% higher limiting current than PtAlloy/C, with ~40% less PGM.
- PtNiIr > PtNi >> Pt.

Accomplishments and Progress – Best of Class MEAs



"Best of Class" MEA format

- Low PGM anode; 3M-S 725EW PFSA 14µm w/ additive.
- Optimized anode GDL, cathode interlayer for operational robustness.

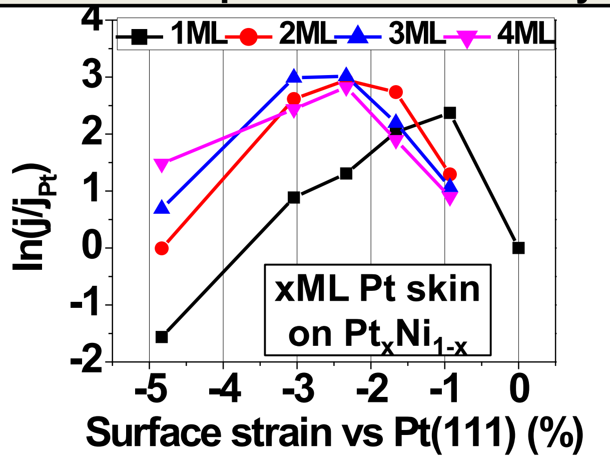
- **2017 NPTF PtNiIr MEA (0.122mg$_{PGM}$/cm^2 total)**
  - Improved specific power, durability over 2015 status.
  - MEA achieves total loading and ¼ power targets.
  - NPTF cathode achieves H_2/Air performance loss target.
- **2017 UTF PtNi MEA (0.077mg$_{PGM}$/cm^2 total)**
  - MEA achieves specific power and total loading targets.
  - UTF cathode loading is ultra-low 46µg/cm^2.
- **2017 UTF PtNiIr MEA (< 0.09mg$_{PGM}$/cm^2)**
  - Improved durability and activity vs. PtNi, but reduced BOL H_2/Air performance.
  - UTF cathode achieves DOE mass activity target.

	Total PGM Loading (mg/cm^2)	Spec. Power @ Q/ΔT=1.45 (kW/g$_{PGM}$)	Rated Power @ Q/ΔT=1.45 (W/cm^2)	1/4 Power (A/cm^2 @ 0.80V)	ORR Mass Activity (A/mg$_{PGM}$)	Electrocatalyst AST Durability (NSTF Cathode Only) Mass Act. Loss (%)	Electrocatalyst AST Durability (NSTF Cathode Only) ΔV @ 0.8A/cm^2 (mV)
DOE 2020 Target	0.125	8.0	1.000	0.300	0.44	40	30
2015 (Sept.) NPTF PtNi	0.131	6.8	0.891	0.310	0.39	~65	NA
2017 (Jan.) NPTF PtNiIr	0.122	7.3	0.897	0.308	0.40	45	21
2017 (Jan.) UTF PtNi	0.077	8.1	0.626	NA	0.37	43	50
2017 (Mar.) UTF PtNiIr	< 0.089	>6.6	0.584	< 0.200	0.44	45	23

3M Science. Applied to Life.™ GREEN: Meets or exceeds DOE 2020 target. YELLOW: Within ca. 10% of DOE 2020 target

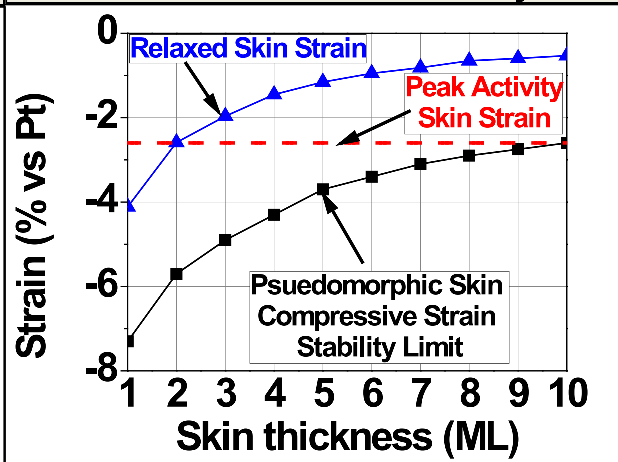
Accomplishments and Progress – UTF PtNi DFT Modeling

Pseudomorphic Pt Skin Activity



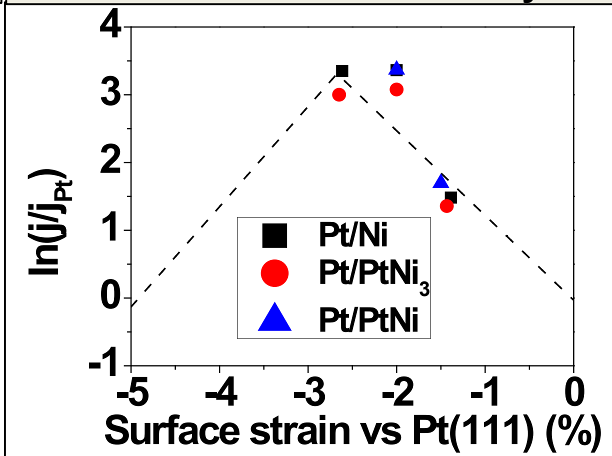
- Activity peak between 2-3% strain for 2-4ML Pt skins on Pt_xNi_{1-x}.
- Activity at high strain depends on skin thickness.

Surface Strain Stability



- Highly-strained Pt skins are not thermodynamically stable.
- High-strain skins will reconstruct (Moiré), reducing surface strain.

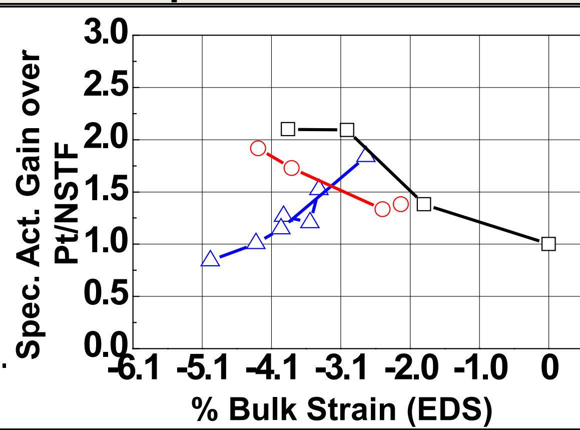
Relaxed Pt Skin Activity



- After relaxation, Pt skin surface strain (and activity) depends on resultant skin thickness and less on bulk composition.

Model Validation – Experimental UTF PtNi

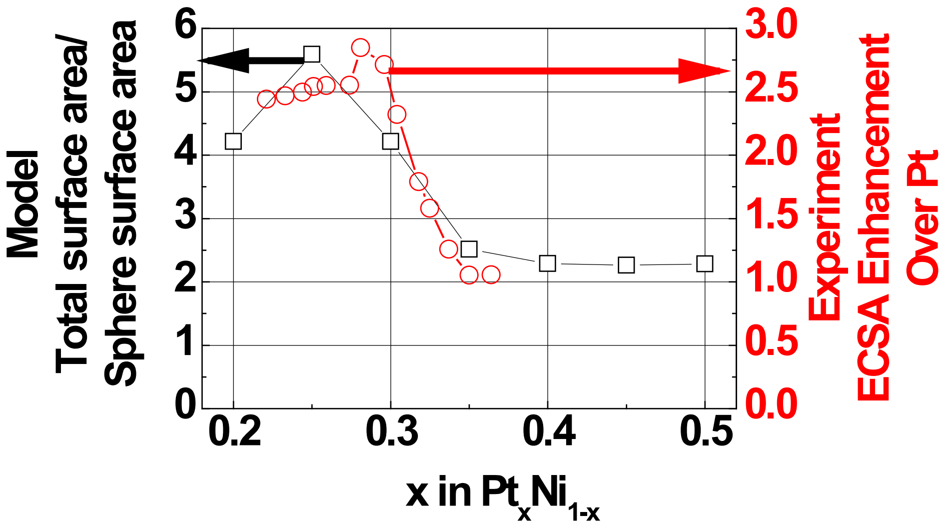
- Experimental activity trends with bulk strain consistent with model predictions, but not magnitude.
  - Exp.: 2x vs. Pt. Model: ~20x vs. Pt(111).
- Discrepancy may be due to non-optimal Pt skin thickness, near-surface defects, and actual surface strain of experimental materials.
  - Difficult to quantify.



	Thickness	Comp	Anneal
□	Fixed	Var	Fixed
○	Var	Fixed	Fixed
△	Fixed	Fixed	Var.

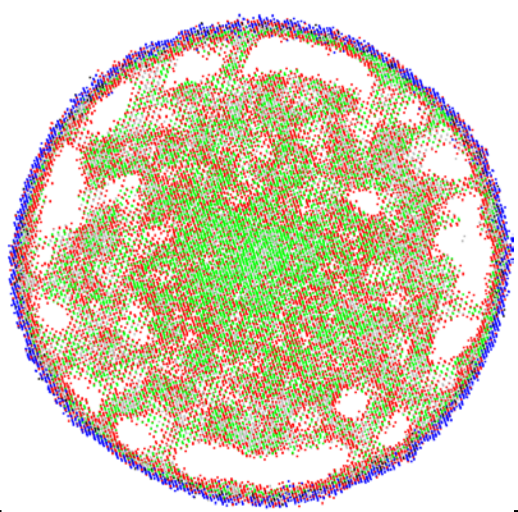
Accomplishments and Progress – NPTF Modeling

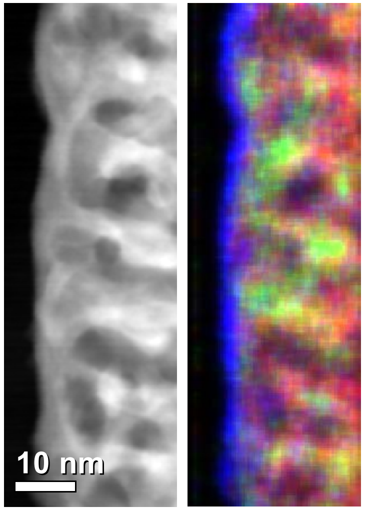
Kinetic Monte Carlo Model Refinement, Validation (JHU)



- KMC model refined to include dealloying via oxidation/reduction cycles (akin to dealloying in FC)
- Refined model accurately captures onset of nanoporosity formation with composition
- Model surface areas 2x experiment values.
  - Some ECSA loss during break-in.

Density Functional Theory and Kinetic Monte Carlo Modeling of NPTF PtNiIr (JHU, Purdue)

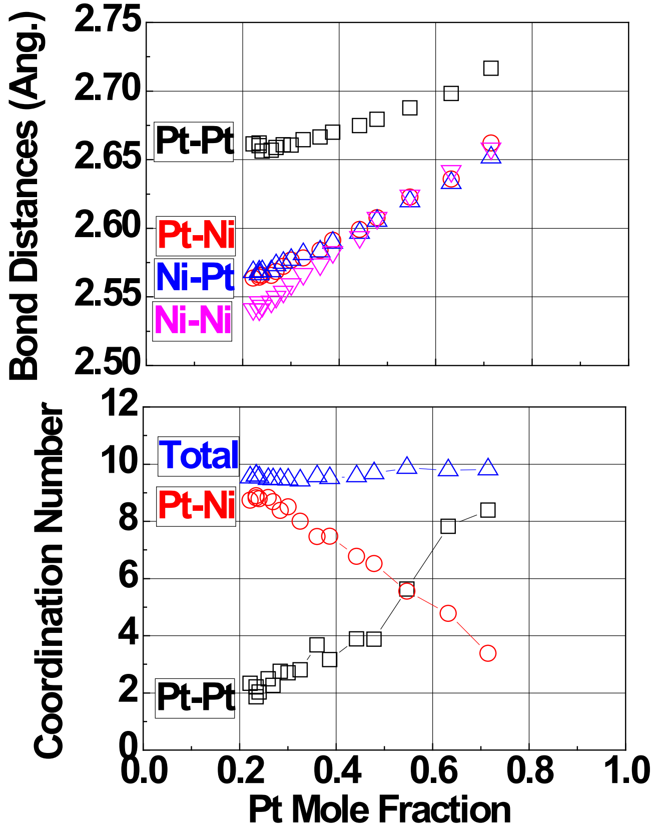




- Using DFT-estimated interaction parameters, kMC-predicted structure strikingly similar to experiment.
- Ir is relatively immobile in simulation and experiment.
- Suggested stabilization mechanism - capillary wetting of Pt, Ni onto Ir.

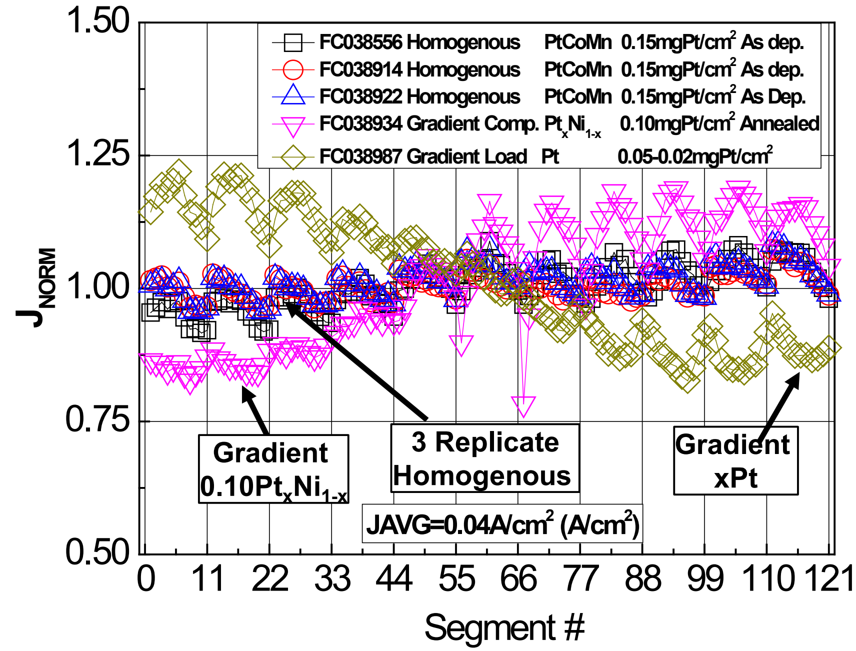
Accomplishments and Progress – High Throughput Catalyst Development

XAFS of Gradient Composition Pt_xNi_{1-x} (ANL)



- XAFS conducted on gradient PtNi NSTF catalyst on fabrication substrate
- Bond distances and coordination numbers vary monotonically with Pt mole fraction, as expected.
- All HT physical characterization methods validated: XRF, XRD, WAXS, XAFS.

Segmented Fuel Cell ORR Activity (3M)



- Good sample-sample and segment-segment reproducibility with homogenous electrodes.
- Absolute activity variation of gradient electrodes correct in trend, but not in magnitude.
  - PtNi: 3-4x activity variation expected vs. 1.5x observed
  - Pt: 2.5x activity variation expected vs. 1.5x observed
- Lateral electronic conduction reduces sensitivity; optimization continues.

Collaborations

- **3M - Electrocatalyst Fabrication and Characterization, Electrode and MEA Integration, HT Development**
  - A.Steinbach (PI), C. Duru, A. Hester, S. Luopa, A. Haug, J. Abulu, G. Thoma, K. Lewinski, M. Kuznia, I. Davy, 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
- **Purdue University – DFT Modeling of Electrocatalyst Activity, Durability**
  - J. Greeley (PI), Z. Zeng, 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, D. Yang
- **University of Hawaii, NREL – NSTF Transport Studies**
  - J. St. Pierre, T. Reshetenko, K. C. Neyerlin
- **FC-PAD Consortium**
  - MEAs to be provided annually.

Response to Reviewers' Comments

Rated power stability of NSTF MEAs

"… if membrane improvements **lessen NSTF degradation by membrane fragments**), they could **enable the full cyclic durability promise of NSTF** to finally be realized in fuel cell applications. There is a **significant possibility that the changes generated by this project will provide only incremental improvements** that are insufficient to get NSTF into significant fuel cell applications."

- *Project is addressing several catalyst-specific factors of rated power loss. Factors directly addressed:*
  1. *PFSA decomposition product accumulation on the NSTF cathode catalyst surface (PEM decomp. rate, ECSA).*
  2. *ECSA loss where the NSTF cathode electrode roughness factor drops below ~$10 cm^2_{Pt}/cm^2_{planar}$*
  3. *Transition metal loss from the cathode electrocatalyst to the PEM*
- *Impact of new alloys on PFSA decomp. rate and rated power loss will be assessed.*
- *Non-catalyst modifications are under development (outside this project).*

Operational robustness of NSTF MEAs

"While quite solid, **it is unclear whether performance and durability should be the primary focus** (as laid out in the project) **or whether "operational robustness," the historic Achilles' heel of NSTF, should have more emphasis**."

- *Improved operational robustness is important, but out of scope for a catalyst project.*
- *While not formal project criterion, operational robustness is being assessed with downselected catalysts.*
- *Electrode-extrinsic approaches developed in previous MEA integration project are effective with new catalysts.*
- *Electrode-intrinsic approaches are promising and under development in 3M Electrode project (FC155).*
- *See backup slide for summary figure.*

Remaining Challenges and Barriers

1. Further improved electrocatalysts will require optimization of large composition/process space. HT electrochemical characterization necessary for acceleration not yet validated.

2. Experimental specific activities approximately 10x below entitlement model prediction of catalysts with well-defined and optimally-strained Pt skins.

3. Break-in conditioning of NSTF MEA cathodes is longer and more complex than many carbon supported Pt nanoparticle MEA electrodes.

4. Rated power loss is generally key lifetime-limiting factor for NSTF cathode MEAs.

Key Future Work – 2Q17-1Q18

- Validate HT electrochemical characterization; implement HT electrocatalyst development.
- UTF Development
  - Composition, process optimization of downselected alloys towards increased specific activity.
  - Optimize Pt skin on stable UTF base electrocatalysts towards increased specific activity.
  - Initiate integration onto higher area supports for improved rated power.
- NPTF Development
  - Composition, process optimization of downselected alloys towards increased specific area and rated power capability.
  - Additive integration optimization for further improved durability.
- Electrocatalyst Modeling
  - Complete modeling studies of durability additives.
  - Complete modeling of new electrocatalyst concepts for improved activity and durability.
- Rated Power Durability
  - Evaluate impact of new catalysts on MEA-level rated power durability (load cycle, F^- emission).

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

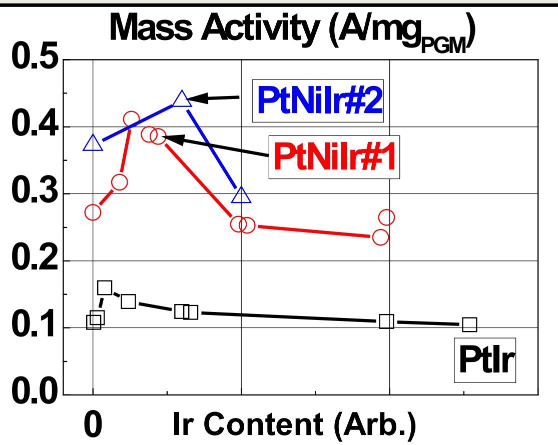
Summary

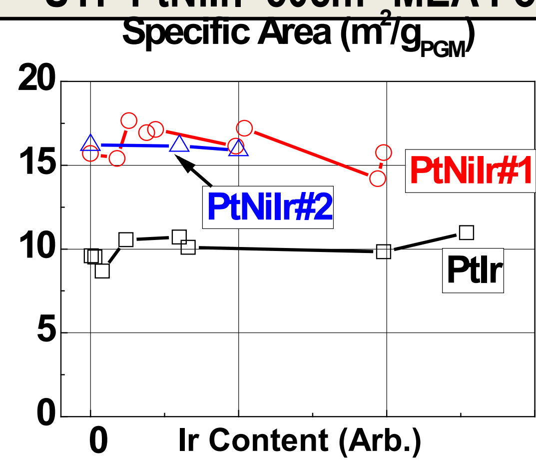
- New Electrocatalyst Development
  - 6 UTF and 6 NPTF Pt alloy series have been fabricated and characterized. Several improved candidates identified for further optimization.
  - Relationships between electrocatalyst functional response, physical properties, and fabrication processes have been established for UTF PtNi catalyst.
  - Ir integration improves many durability characteristics of NPTF and UTF PtNi catalysts.
  - Durable UTF and NPTF PtNiIr catalysts can yield high specific power in MEA.
- Electrocatalyst Modeling
  - Refined Kinetic Monte Carlo model predicts composition and structure during dealloying consistent with experimental NPTF PtNi.
  - Refined Density Functional Theory model predicts activity trends vs. strain consistent with UTF PtNi. Significant gap in magnitude between model and experiment (experimental char. gap).
  - Models are providing insight into mechanism of Ir stabilization.
- High Throughput Development
  - Approaches for HT electrocatalyst fabrication and physical characterization (composition, bulk structure, atomic structure) have been validated.
  - HT electrochemical characterization (seg. cell) is reproducible and correct in trend, but magnitude of response is muted.

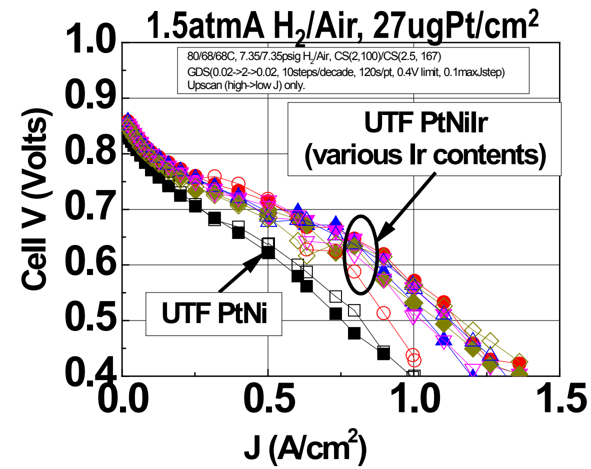
Technical Backup Slides

NPTF, UTF PtNiIr

UTF PtNiIr. 50cm² MEA Format.

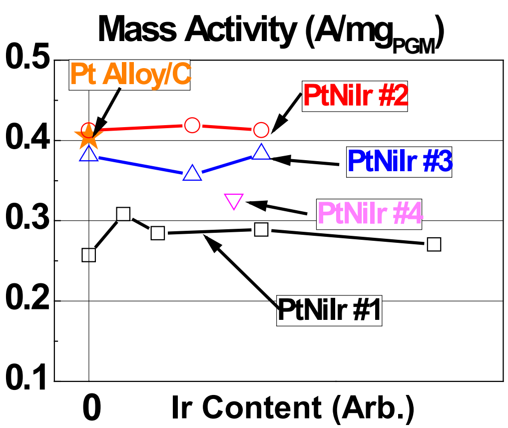


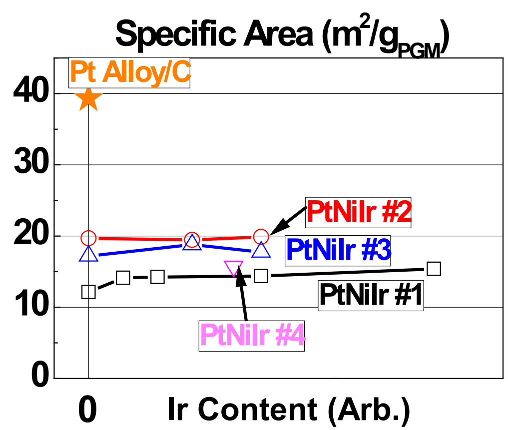


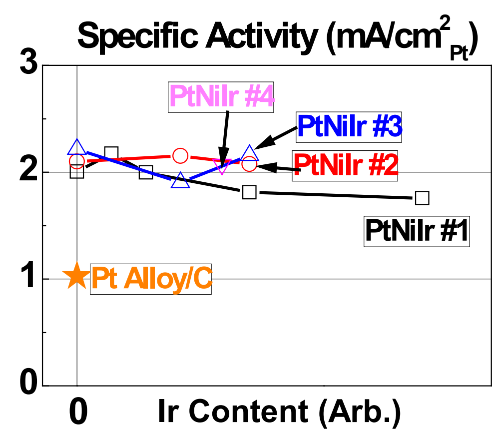


- With UTF, Ir does not strongly impact PGM-specific area.
- H_2/Air: UTF PtNiIr > UTF PtNi

NPTF PtNiIr. 50cm² MEA Format.



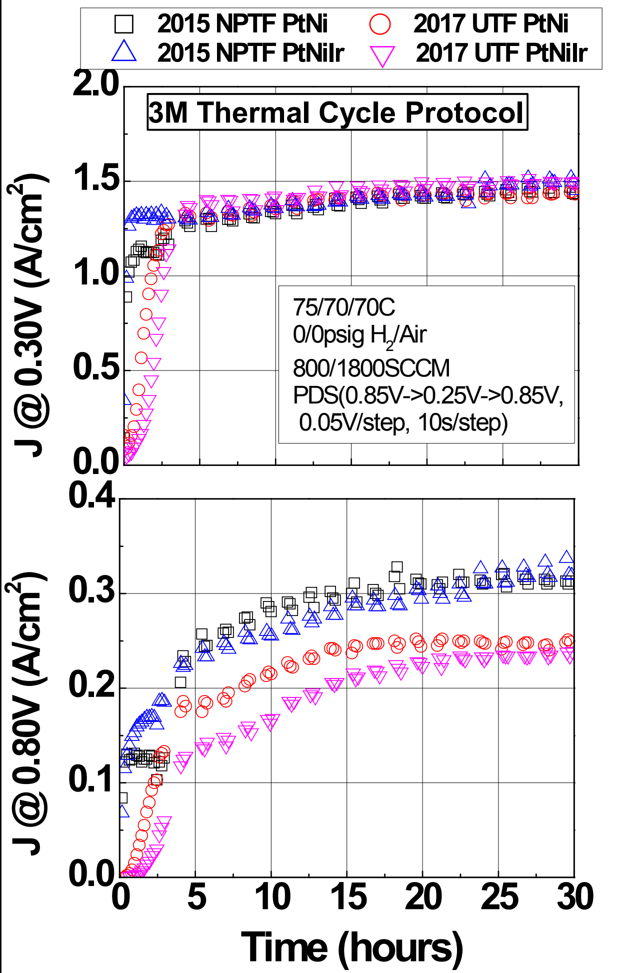




- With NPTF PtNi, Ir does not strongly impact PGM-specific area or specific activity.

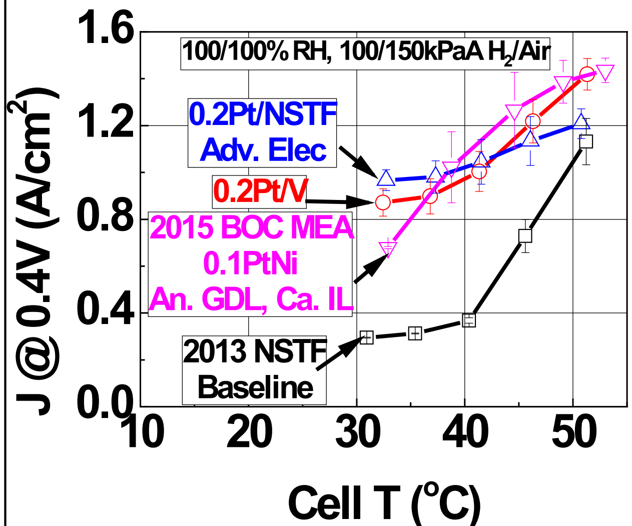
Break-in Conditioning, Operational Robustness, Area Determination

BOC MEA Conditioning



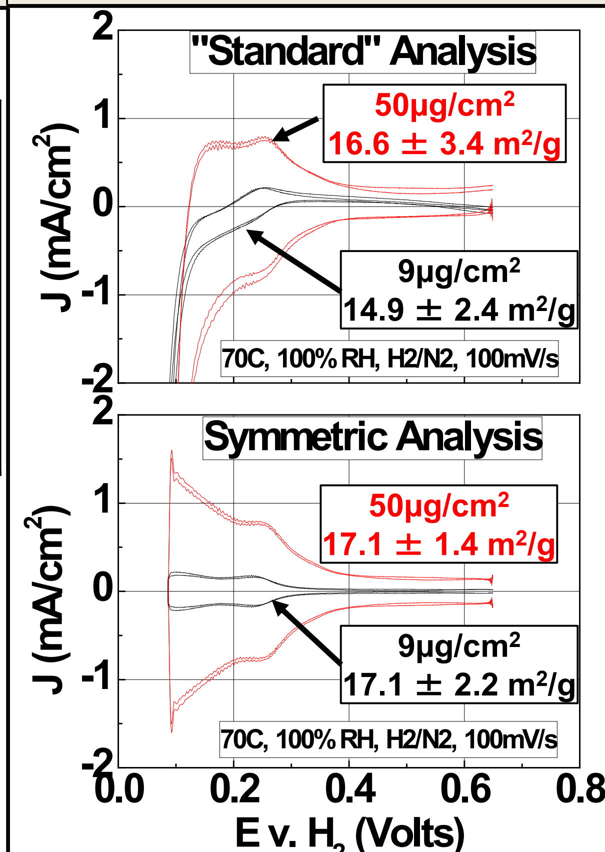
- UTF modestly slower than NPTF.
- Ir has little effect.
- Processing variations are influential.

Operational Robustness



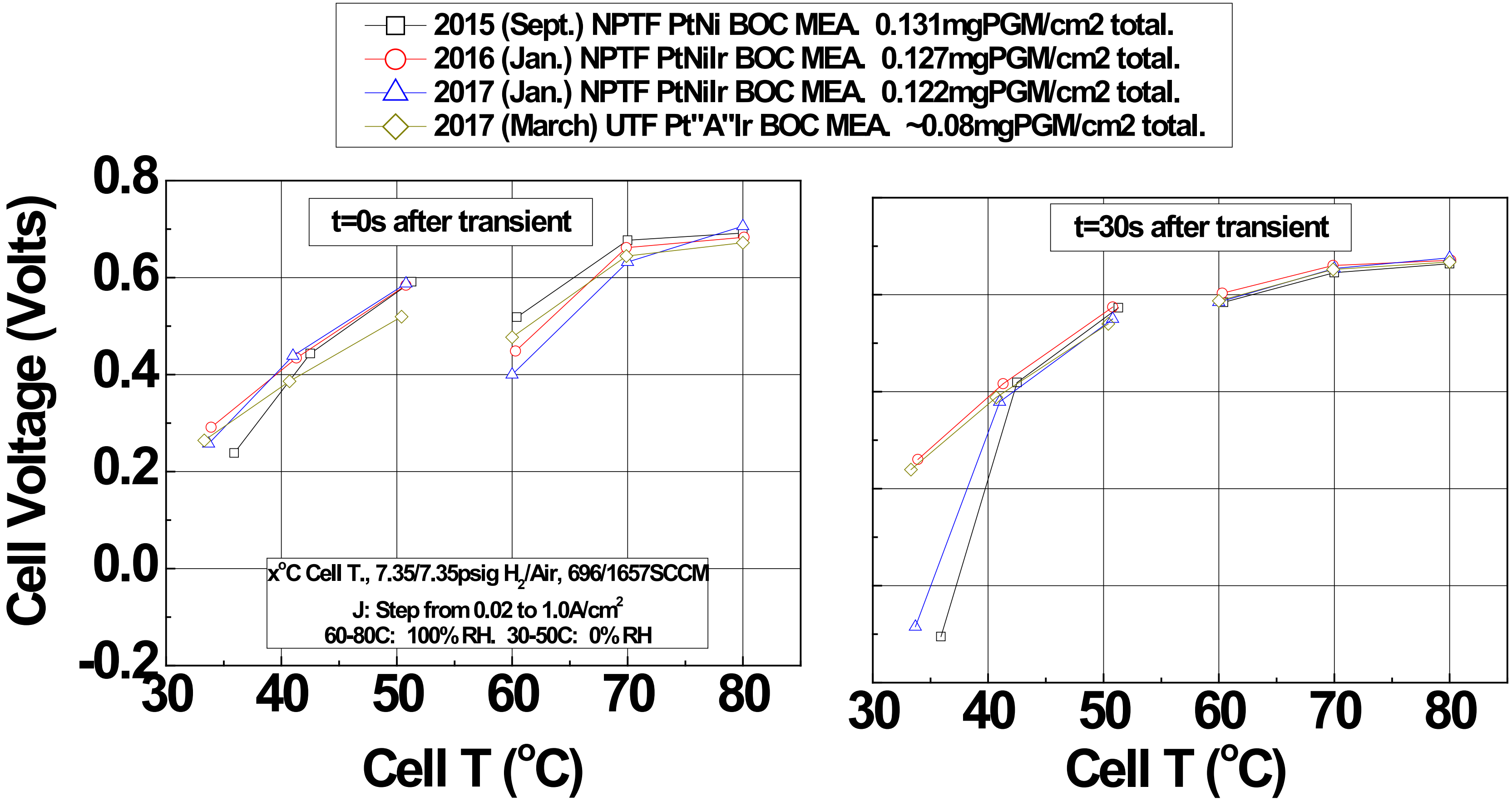
- Two approaches are effective towards improved NSTF operational robustness (performance sensitivity to temperature)
  1. Electrode extrinsic – anode GDL and cathode interlayer (2015 BOC, prev. 3M MEA integration project)
  2. Electrode intrinsic – advanced NSTF electrode (FC155).

ECSA Determination at Low Load



- CVs from ultra-low load MEAs have apparent "other" reductive processes.
  - H_{UPD} integration error-prone.
- "Forced" symmetry approach removes questionable H_{UPD} integration.

Best of Class MEAs – Operational Robustness



Anode GDL, Cathode Interlayer Approaches Effective w/ 2017 BOC MEAs

- 2016, 2017 BOC MEAs achieve stable 1A/cm2 operation down to 42C cell temperature or lower, similar to or improved vs. 2015 NPTF PtNi Best of Class MEA.
- Target is stable 30C operation.

Kinetic Monte Carlo (kMC) Simulations

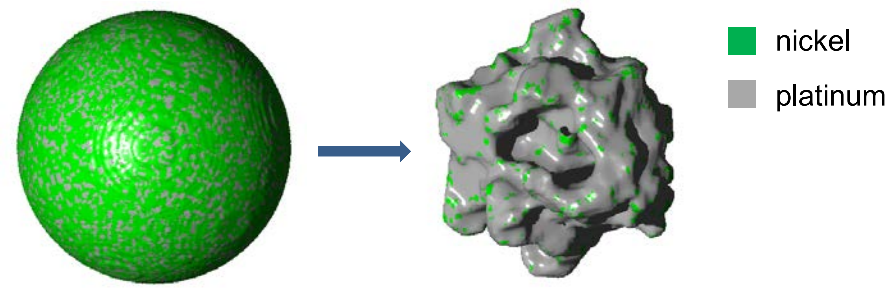
Atom-Scale Simulations of Dealloying and Coarsening

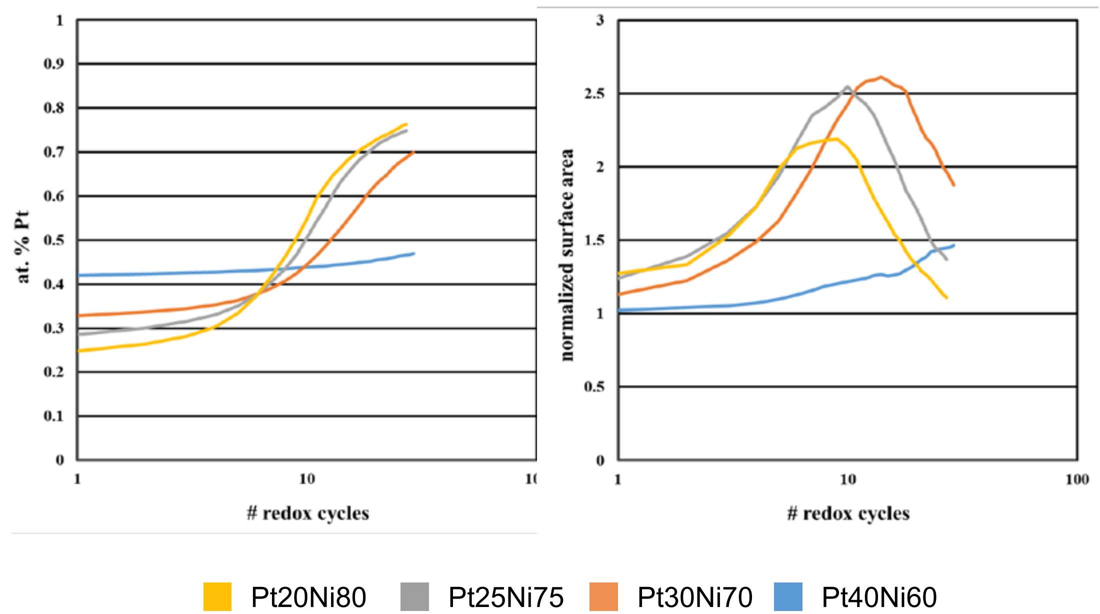
Novel kMC Simulation inputs:

- DFT-based activation barriers for Ni-Pt-Ir bond energies
- Oxidation and reduction transitions to simulate cyclic voltammetry

Primary Conclusions to date:

- Dealloying/short time scales
    - Porosity evolution is controlled by creating mobile Pt atoms during surface redox cycling
    - Composition vs redox cycle follow experimental trends in base alloy composition
- Coarsening/long time scales
    - Ir has low mobility
    - Ni and Pt wetting of relatively immobile Ir clusters slows coarsening





dealloying simulations show correct composition and surface area trends vs. # of redox cycles

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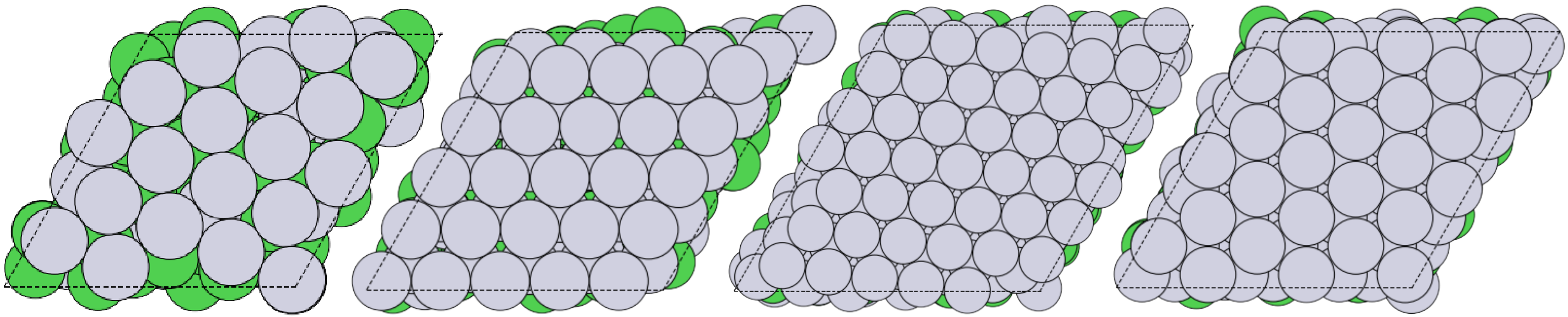
DFT - Pt/$PtNi_3$ Moiré Reconstructions ; PtIr Interactions

Pt skin strain (and activity) on relaxed surfaces depends on skin thickness

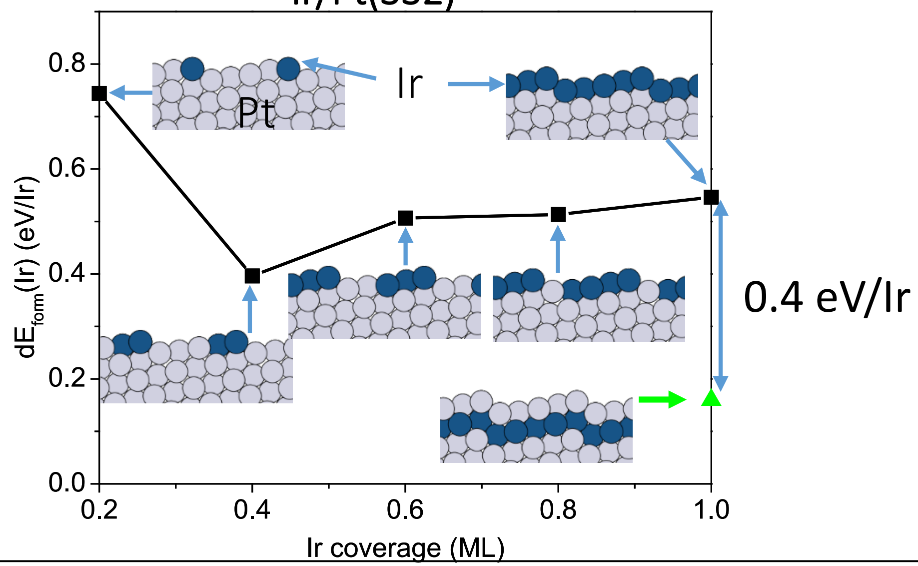
RT19 on RT21 | RT25 on RT28 | RT43 on RT49 | RT27 on RT31



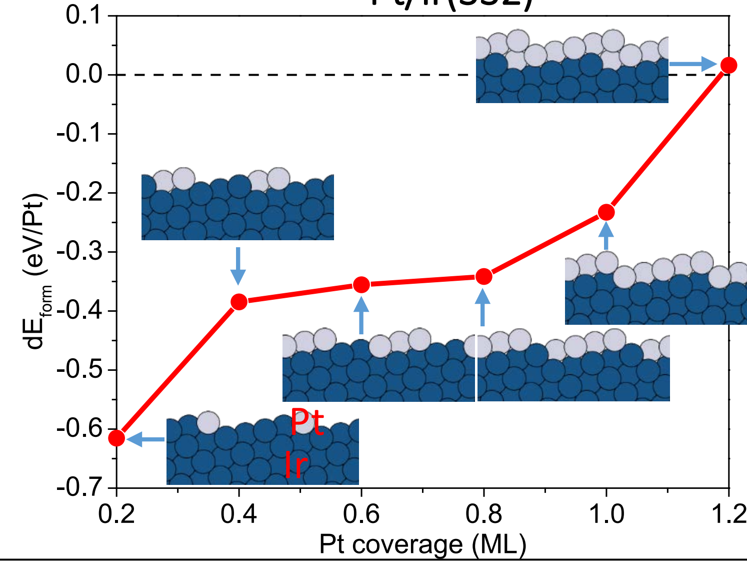
(1ML skin, -4%) | (2ML skin, -2.5%) | (3ML skin, -2.0%) | (4ML skin, -1.5%)

Pt on Ir is more energetically favorable than Ir on Pt.

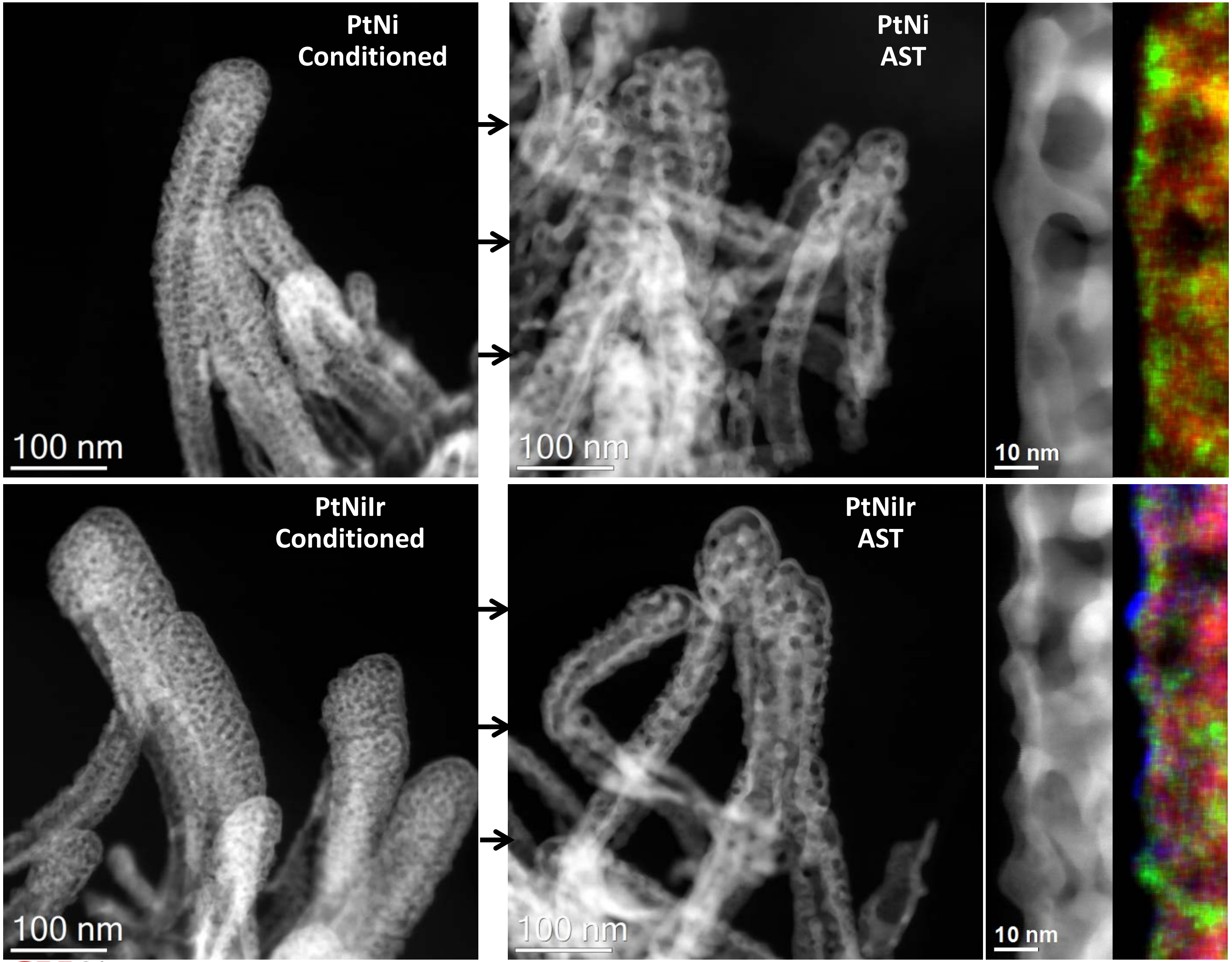
Ir/Pt(332)



Pt/Ir(332)



Electron Microscopy Reveals Highly Durable Ir Coatings on PtNi NPTF



Oak Ridge National Laboratory

- Minimal Ir dissolution observed following ASTs.
- Ir remains as a surface layer on the underlying PtNi alloy