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

Overview to DOE Catalysis Working Group
Argonne National Laboratory
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Project Objective and Relevance

Overall Project Objective

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

Project Relevance

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

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

Project electrocatalysts will be:

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

Overall Approach

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

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

Status Against DOE 2020 and Project Targets

Table 1. Status Against Targets			
Characteristic	**2020 Target and Units**	**Project Target**	**2016 Status**
Platinum group metal (PGM) total content (both electrodes)	0.125 g/kW	0.1 (0.70V)	0.16[1] 0.18[2]
PGM total loading (both electrodes)	0.125 mg/cm^2	0.10	0.105[1] 0.127[2]
Loss in catalytic (mass) activity	40 %	20	42[3]
Loss in performance at 0.8 A/cm^2	30 mV	20	-8[3]
Loss in performance at 1.5 A/cm^2	30 mV	20	-68[3]
Mass activity @ 900 mV$_{iR\text{-}free}$	0.44 A/mg (MEA)	0.80	0.28[3] (NPTF "M") 0.47[4] (NPTF) 0.39[5] (UTF)

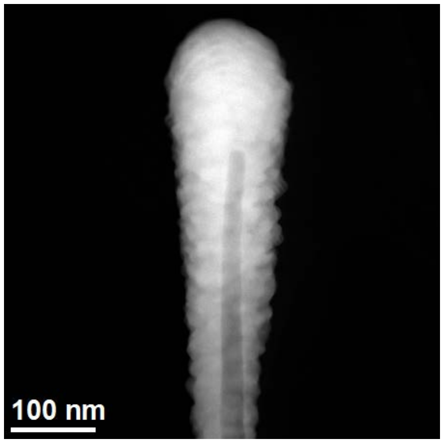
[1]0.015mg$_{Pt}$/cm^2 NSTF anode, 0.075 dealloyed PtNi/NSTF cathode, 0.015 mg$_{Pt}$/cm^2 cathode interlayer.
[2]0.02mg$_{Pt}$/cm^2 NSTF anode, 0.091mg$_{PGM}$/cm^2 NPTF "M" cathode, 0.016 mg$_{Pt}$/cm^2 cathode interlayer.
[3]NPTF "M" cathode, 0.109mg$_{PGM}$/cm^2 after 30k Electrocatalyst AST cycles.
[4]Annealed NPTF P4A Pt_3Ni_7/NSTF, 0.12mg$_{Pt}$/cm^2; adjusted from 0.900V$_{MEAS}$ (70mV/dec)
[5]Best UTF "A", 0.027mg$_{PGM}$/cm^2. Average of two MEAs.

Approach – Two Distinct Thin Film Electrocatalyst Morphologies

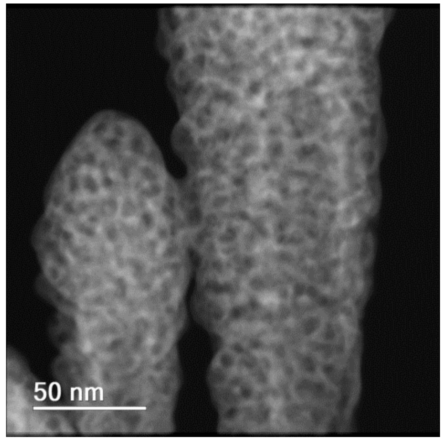
Nanoporous Thin Film (NPTF)

MEA Conditioning State

Before



After (Dealloyed)



NPTF Approach:

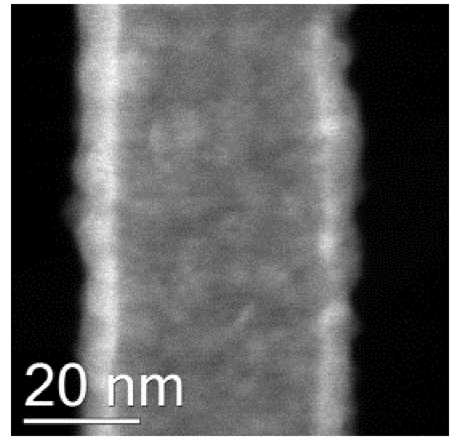
1. Structure/composition/process space optimization to maximize area and minimize leachable TM.
2. Proprietary stabilization approaches to minimize coarsening and TM dissolution.

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

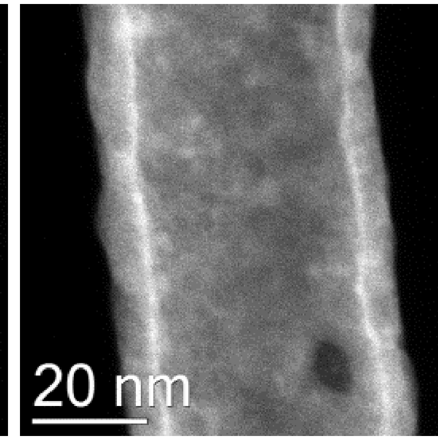
Ultrathin Film (UTF)

MEA Conditioning State

Before



After



UTF Approach:

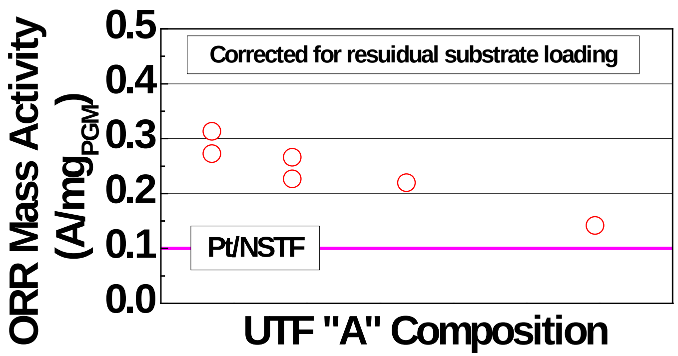
1. Structure/composition/process space optimization to develop highly active, stable, and thin surface facets.
2. Maximize NSTF support surface area.

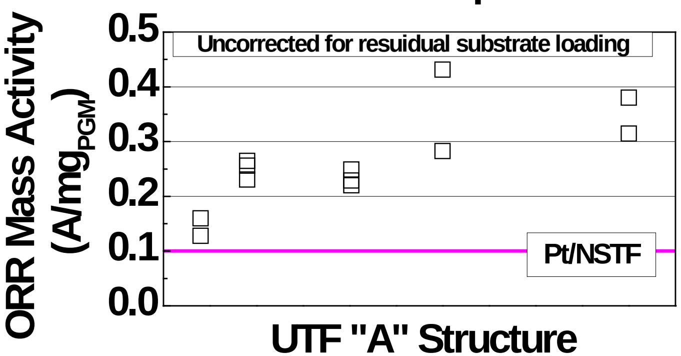
UTF "A"/NSTF, *Proprietary Process*		
	Status	**Target**
Mass Activity (A/mg)	**0.39**	**0.80**
Specific Area (m^2/g)	**15**	**20**
Specific Activity (mA/cm^2_{Pt})	**2.5**	**4.0**

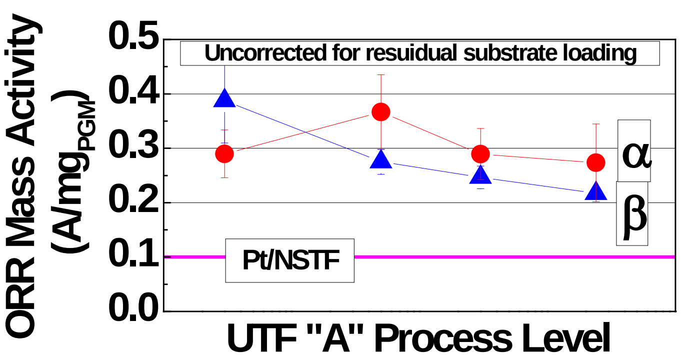
UTF Electrocatalysts

UTF "A" Electrocatalyst MEA Mass Activity

Cathode electrode PGM loading: ≤ 0.05mg_{PGM}/cm^2

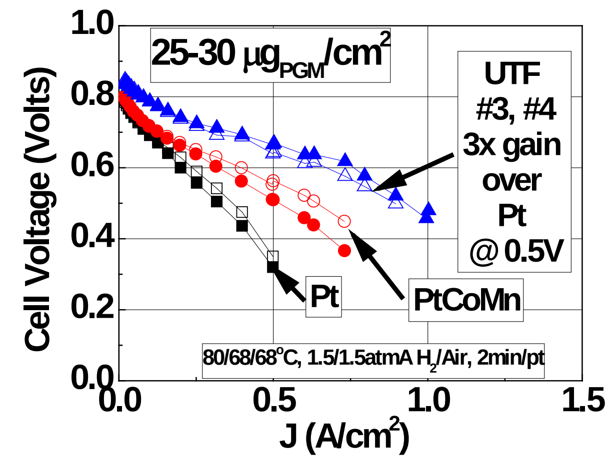




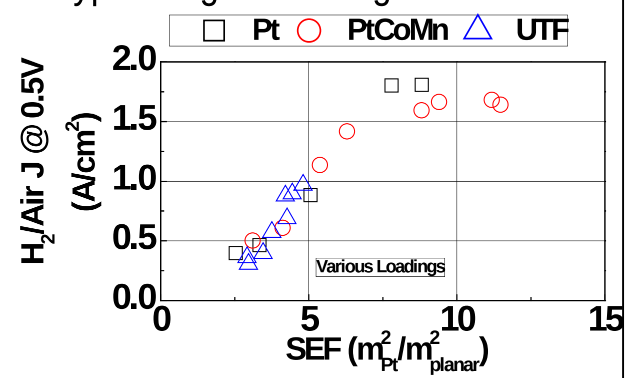


- "A": First single alloy system
- Initial work - systematic study of composition, structure, and fabrication process levels.
- Mass activity largely monotonic function of key variables.
- To date, best MEA mass activity approaches 0.39A/mg, ~4x higher than Pt/NSTF.
- Characterization by TEM, EDS, EELS, XAFS in progress. Correlations developing.
- Durability evaluation initiated.

UTF H_2/Air Performance

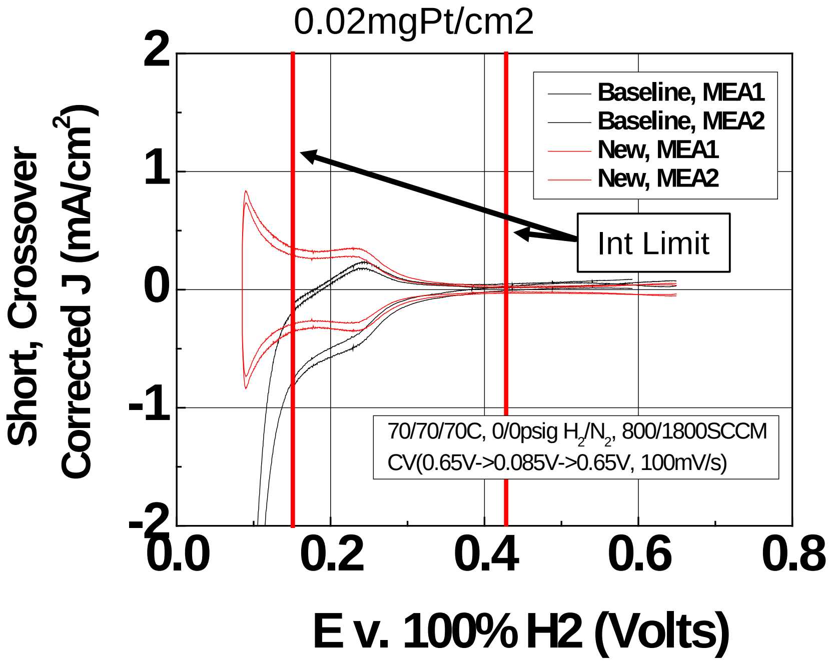


- UTF performance >> Pt
- High J performance suppressed v. typical higher loadings

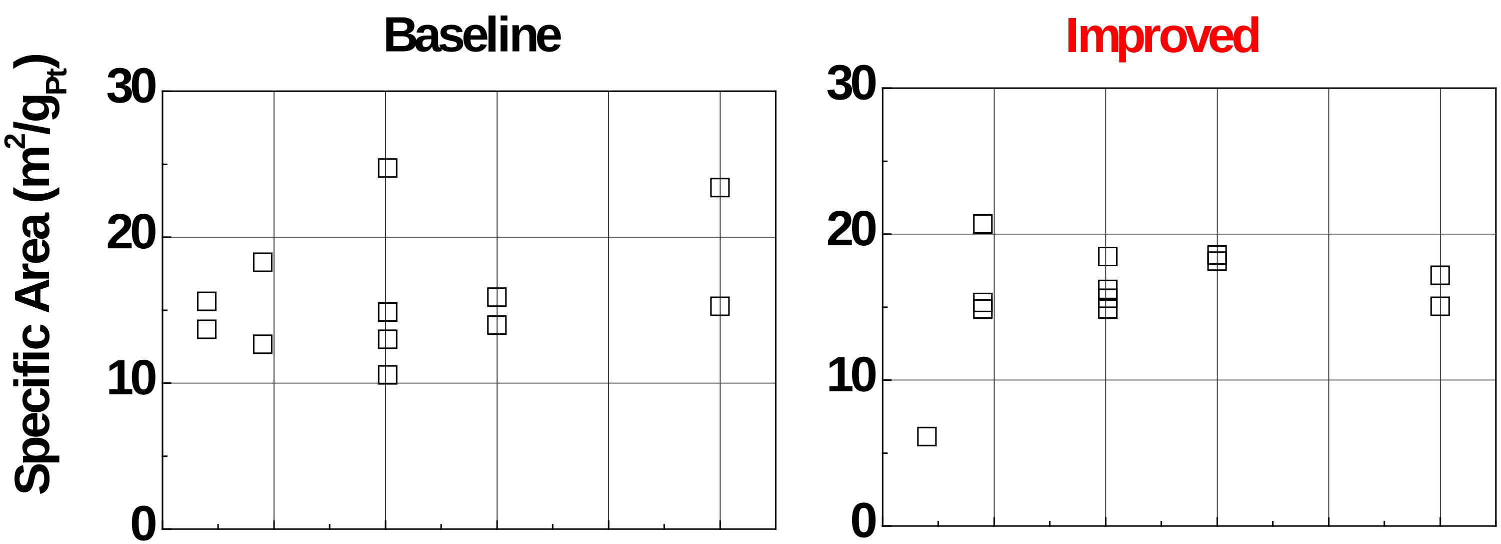


- High J performance dictated by absolute cathode surface area
- UTF TGT: >20m^2/g, 0.075mg/cm^2

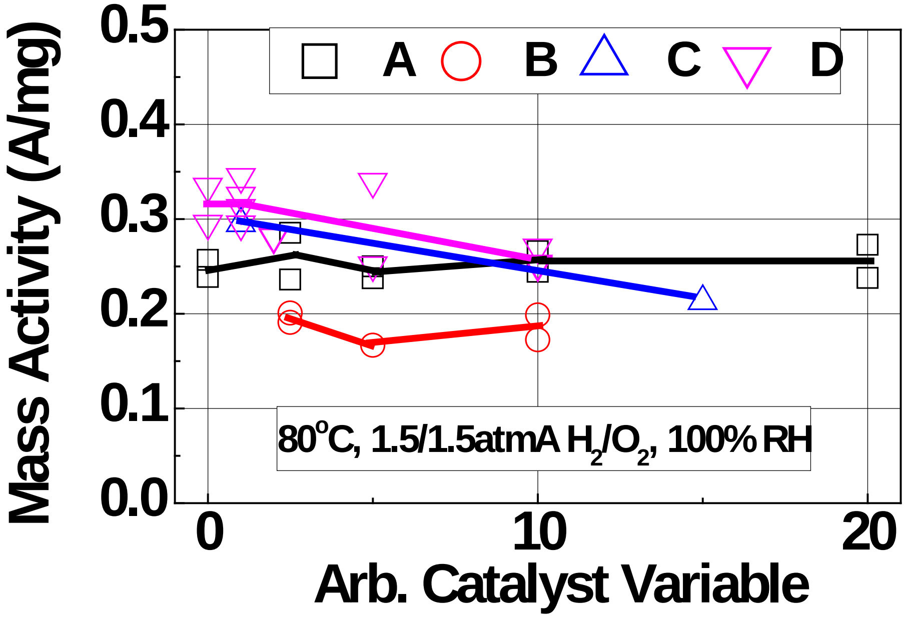
Challenges w/ FC Measurements at Ultralow PGM

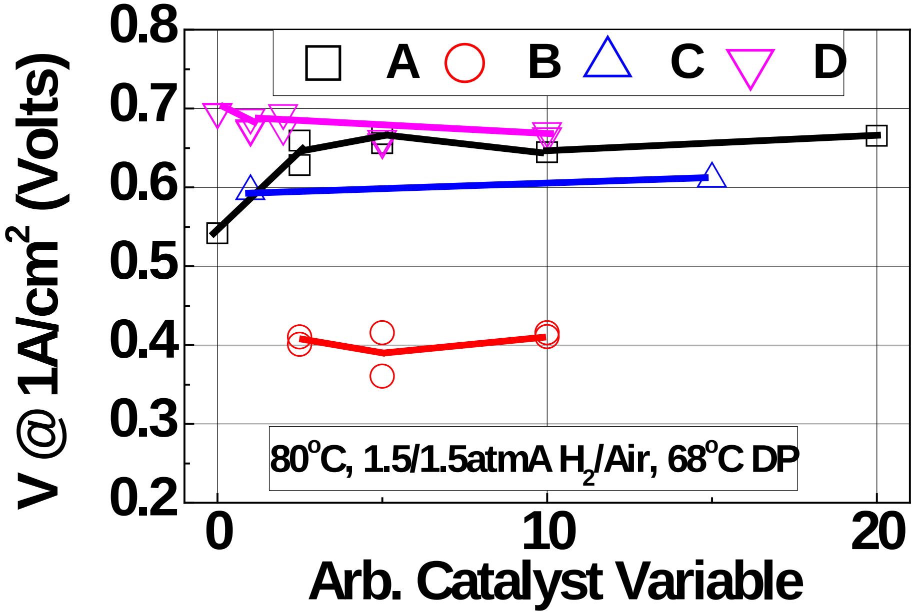


- At ultra-low PGM, CV curvature (HER?) makes MEA H_{UPD} integration values questionable.
- New method developed which greatly improves S:N of ECSA as determined by H_{UPD}
- ECSA values calculated with same integration limits with both methods.
- CO stripping may be an alternative; have not evaluated.



Task 1 – NPTF Development – Stabilization with "M"



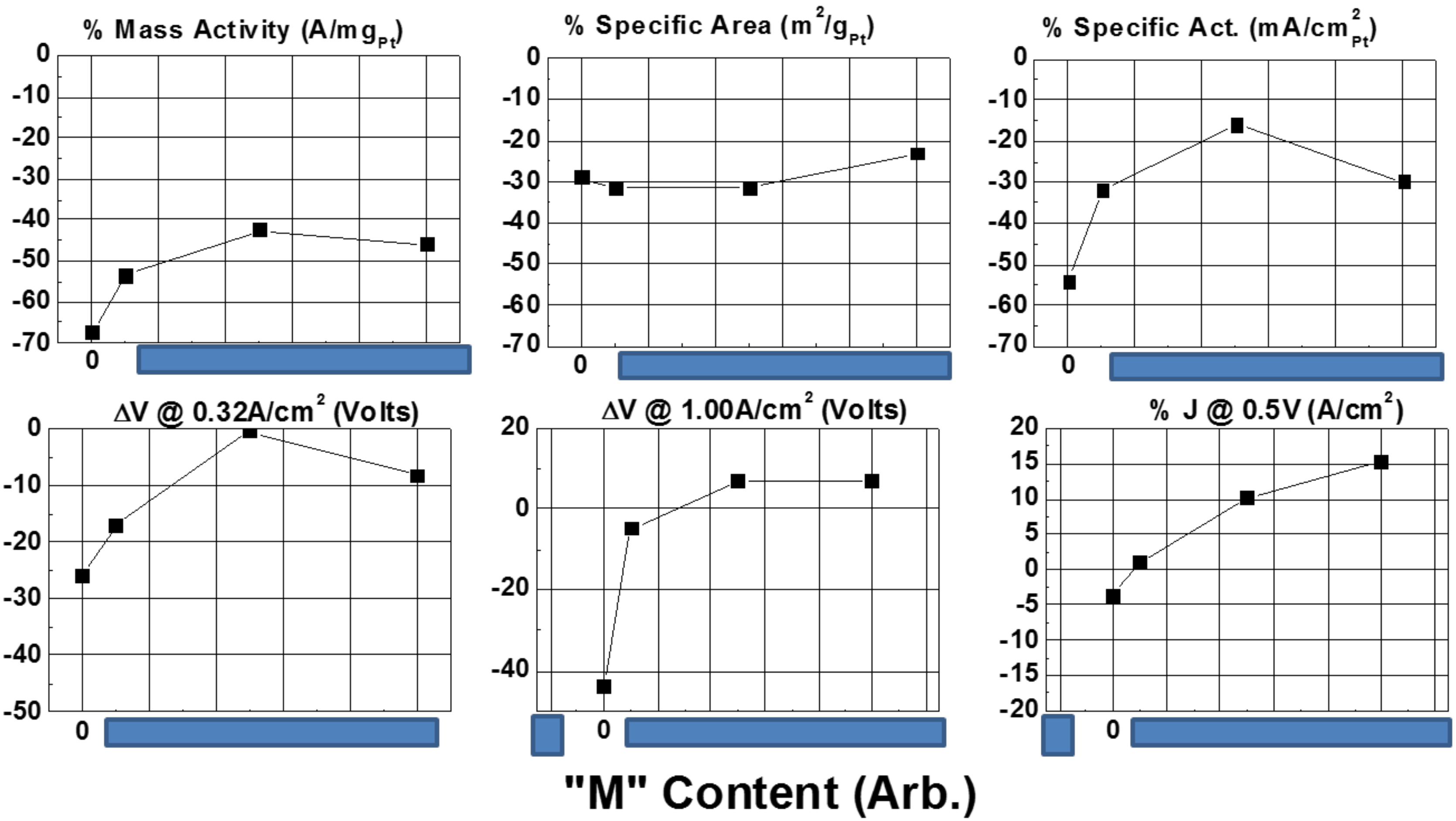


Impact of "M" Integration Method on NPTF PtNi Activity, Performance

- Four different "M" integration methods, with several variations within each method.
- Mass activity and H_2/Air performance @ 1A/cm^2 depend strongly on integration method and level.

- To date, method "D" yielding best combination of BOL activity and performance.

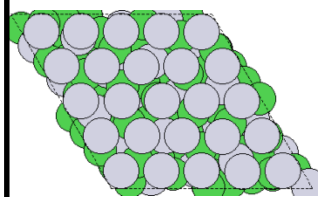
“M” Integration (Type D) Electrocatalyst AST



- With one “M” integration method, conducted Electrocatalyst AST vs. “M” content
- With no “M” (0), > 60% mass activity loss and >40mV loss at 1A/cm^2 after AST
- With “M”, close to target durability attained and performance for J >0.8A/cm^2 improved.

Approach - Electrocatalyst Simulation

1. Atomistic determination of catalyst surface structures

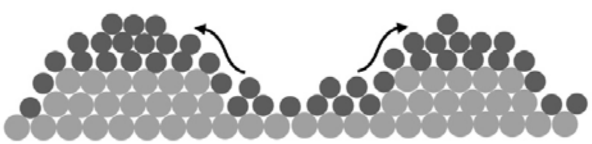


DFT

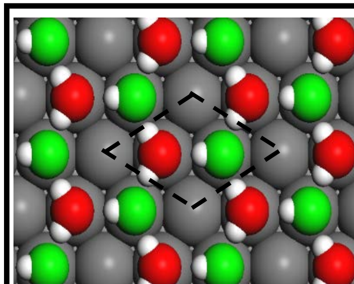
Surface energy calculations of Pt skins on Pt alloys

Kinetic Monte Carlo

Alloy surface structure predictions



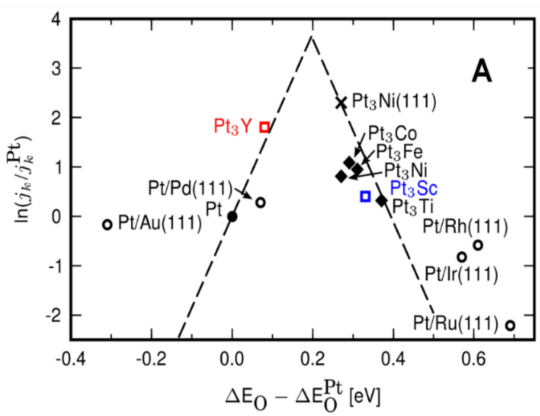
2. Activity predictions of optimized surface structures



DFT

Descriptor binding energies on optimized surface structures

Kinetic predictions of ORR currents from volcano plots and free energies



3. Model Validation

Electrocatalyst Fabrication

PVD Deposition

Proprietary dealloying and annealing processing

Activity Characterization

MEA

RDE

Flow cell

Structure/Composition Characterization

HAADF-STEM

STEM+EDS

XAFS / Δμ-XANES

WAXS

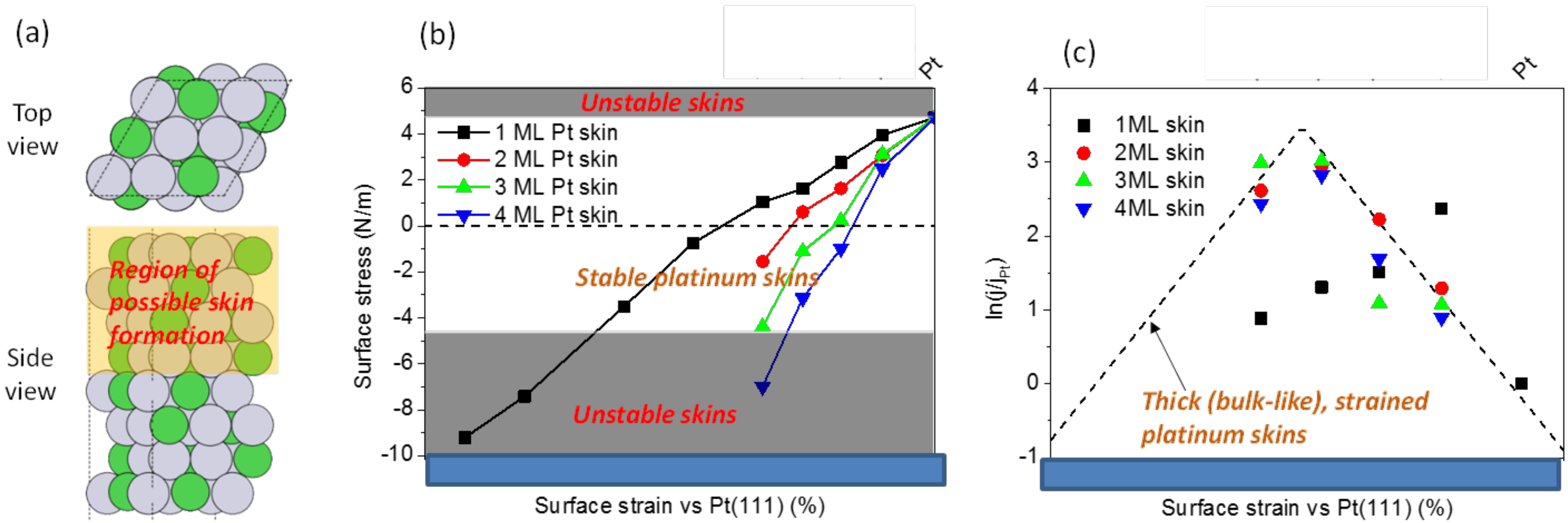
XRD

XRF

HT Methods When Validated

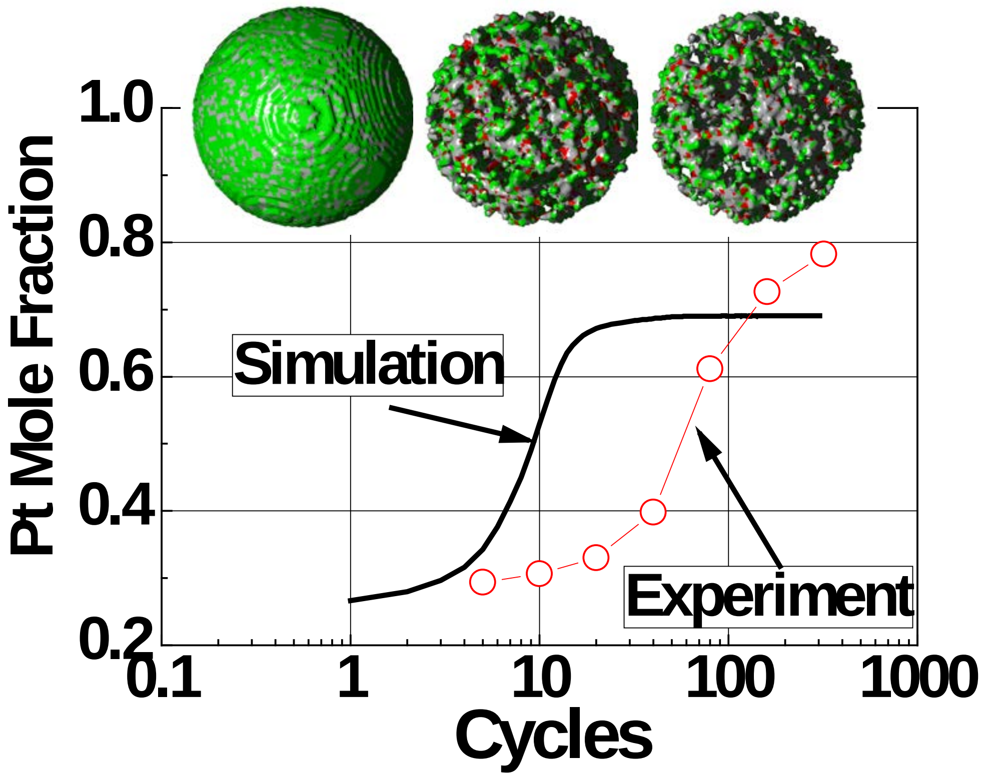
4. Characterization Feedback for Model Refinement

Electrocatalyst Simulation – DFT of UTF "A"



- Purdue has initiated DFT analysis of the stability and activity of UTF "A" catalysts vs. composition and Pt skin thickness.
- Large surface stresses can develop if substantially strained; depends on Pt skin thickness
- Activity also depends on surface strain and skin thickness ~ up to 20x higher than Pt predicted.
- Model will be tuned based on extensive UTF "A" electrochemical and physical characterization. If validated, will be used for property predictions in new systems.

Electrocatalyst Simulation – KMC of NPTF PtNi



Comparison of composition evolution of experimental NSTF catalyst to simulated average composition of a ~20nm Pt binary alloy sphere as a function of oxidation/reduction cycle number.
(silver) Pt;
(red) oxidized Pt;
(green) Ni.

- Johns Hopkins has initiated Kinetic Monte Carlo modeling of composition and structure (surface area) evolution of PtNi during electrochemical dealloying (oxidation/reduction cycles).
- Preliminary model results qualitatively consistent with experiment:
  - Similar sigmoidal composition evolution, slope in transition region, and final composition
- Model will be tuned based on extensive NPTF PtNi dataset. If validated, will be used for property predictions in new systems.

Approach - High Throughput (HT) Electrocatalyst Development

HT Electrocatalyst Fabrication

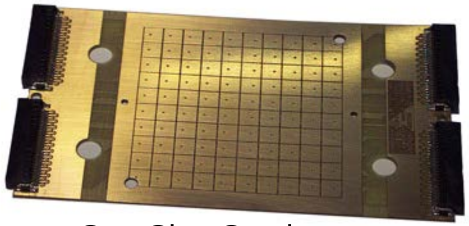
Deposition
- Physical vapor deposition with appropriate masks.

Dealloying – TBD
- Use multi-channel flow cell which incorporates NSTF catalyst on growth substrate
- Use multi-channel potentiostat to independently dealloy each segment.
- To be developed at JHU.

Annealing – TBD
- Proprietary 3M process.

HT Electrochem. Characterization

Segmented fuel cell



S++ Sim. Services

- Uses effectively same hardware as standard 50cm^2 test cell
- Allows evaluation after standard testing (conditioning, ASTs) with no translation (ideally).

Multi-channel flow cells – TBD
- Surface area, ORR activity determination.
- On growth substrate (JHU/3M) and with catalyst powder (ANL).

HT Physical Characterization

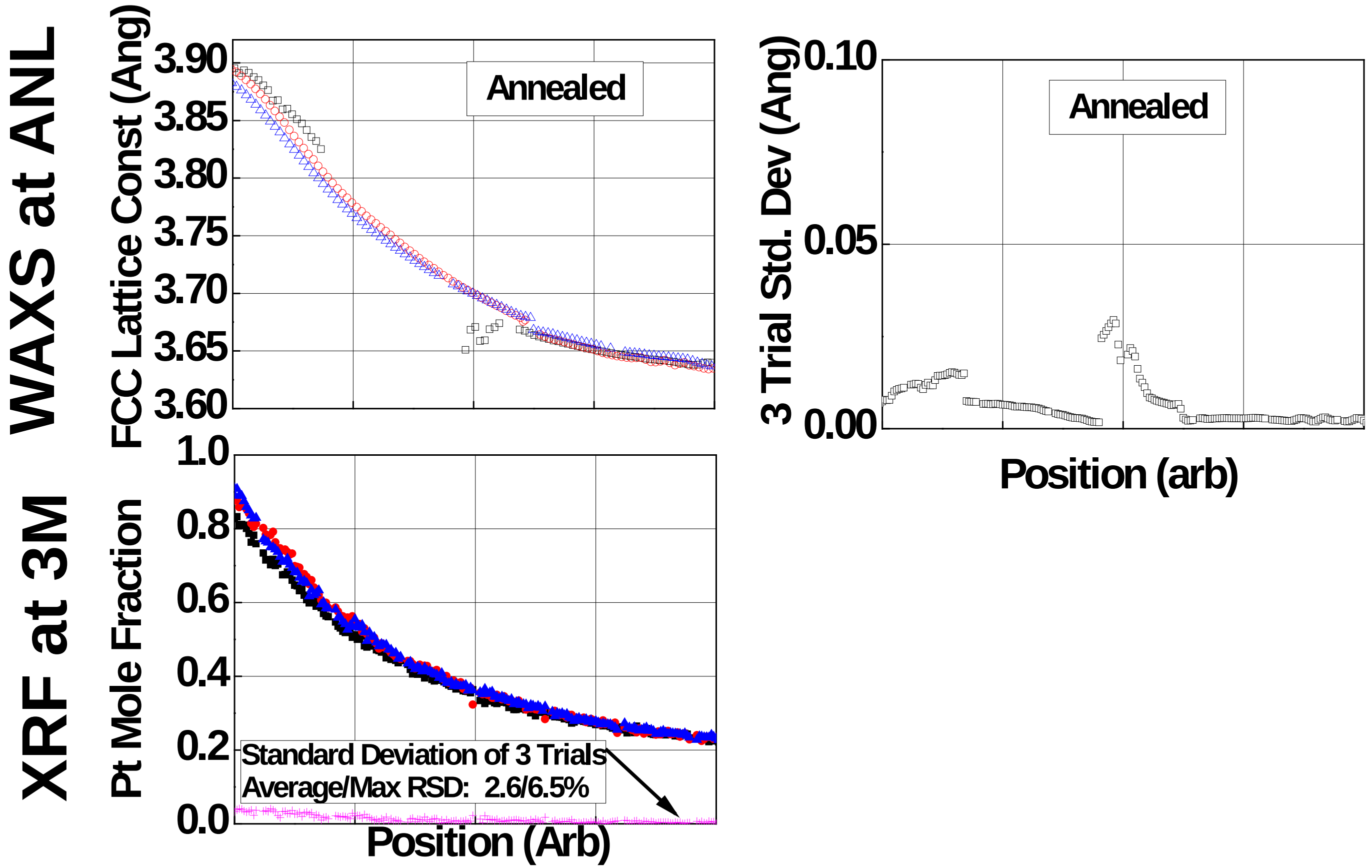
XRF (comp.)
- 1mm resolution

XRD/WAXS (struct.)
- WAXS at ANL APS demonstrated
- XRD via benchtop/lab instruments in development at ANL.

XAFS – TBD
- Project will evaluate possibility of in-operando XAFS of gradient electrocatalysts (ANL)

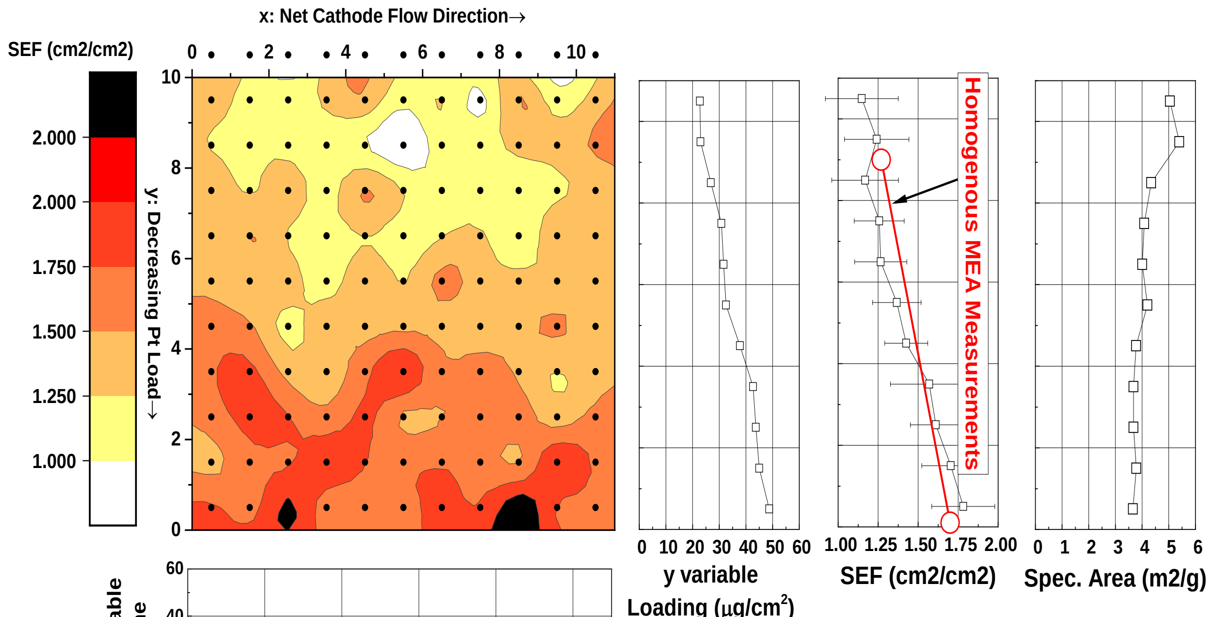
Significant first year effort to develop and validate HT fabrication and characterization methods.

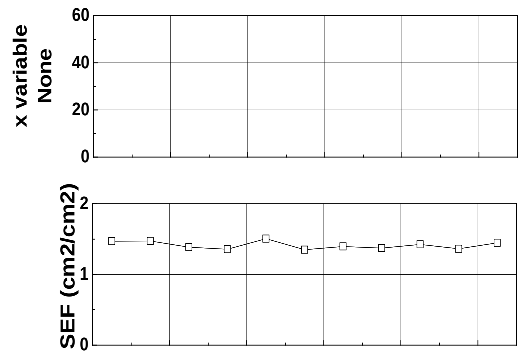
Combinatorial Fabrication and Char. Development



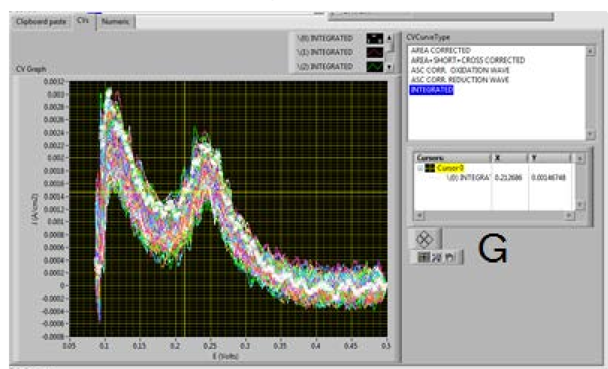
- Analysis of three replicate annealed PtNi gradient catalysts shows good agreement in lattice constant.
- One trial showed erroneous results over mid-section – cause TBD.
- Lattice constant decreases as Pt mole fraction decreases, as expected.
- Analysis for grain size of this series in progress.

Task 3 - Combinatorial Electrocatalyst Fabrication and Characterization Development – Segmented ECSA





CVs of 121 segments, homogenous MEA



- Pure Pt, loading gradient (20-50ug/cm2), bottom to top.
- Very low roughness factors of ~1-2cm^2_{Pt}/cm^2_{planar} required significant method development (software!)
- Detected roughness factor agrees well between segmented cell and homogenous cell.
- Some challenges with reliability of cell setup. Debugging in progress.

Summary

- **UTF and NPTF stabilization approaches are promising**
  - UTF "A": Up to 0.39A/mg, in MEA (ca. 4x Pt/NSTF). Significant sensitivities to composition, structure, processing. Durability assessments initiated.
  - NPTF PtNi+"M": Electrocatalyst AST durability target largely achieved. Mass activity improving.

- **Electrocatalyst Simulation**
  - **DFT**
    - Simulations of first Pt alloy system with varying subsurface compositions and Pt skin thicknesses revealing key trends in both stability and activity.
    - Correlations to project experimental data in progress.
  - **kMC**
    - Initial Pt_xNi_{1-x} surface area and composition evolution simulations agree reasonably well with experiment

- **HT Development**
  - HT electrocatalyst fabrication and composition and structural characterization methods validated.
  - HT electrochemical characterization development in progress. Showing good promise.