High-Activity Dealloyed Catalysts

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General Motors Global Product Development,
Fuel Cell Activities

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FC087

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Overview

Timeline

- Project start date: 1 Aug 2010
- Project end date: 30 Sep 2014
- Percent complete: 90%

Budget

- Total Funding Spent as of 3/31/14: $5.4M
- Total DOE Project Value: $5.95M
- Cost Share: 20%

Barriers

- Barriers addressed
  - B. Cost
    - Decrease required loading of precious metals including platinum
  - A. Durability
    - Maintain kinetic activity, and later high current density performance, after appropriate accelerated tests
  - C. Performance
    - Achieve and maintain high current densities at acceptably-high voltages

Partners

- Subcontractors:
  - Technical University of Berlin
  - Johnson Matthey Fuel Cells
  - Massachusetts Institute of Technology
  - Northeastern University
  - George Washington University
- Project lead: GM

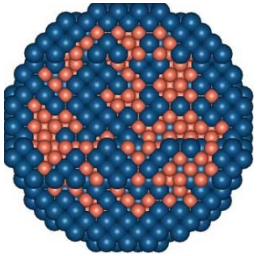
Approach: Basic Concept

M is one or more non-precious metals

precursor **dealloying** catalyst

PtM_3/C ----------> $Pt_{1.5\text{-}5}M/C$

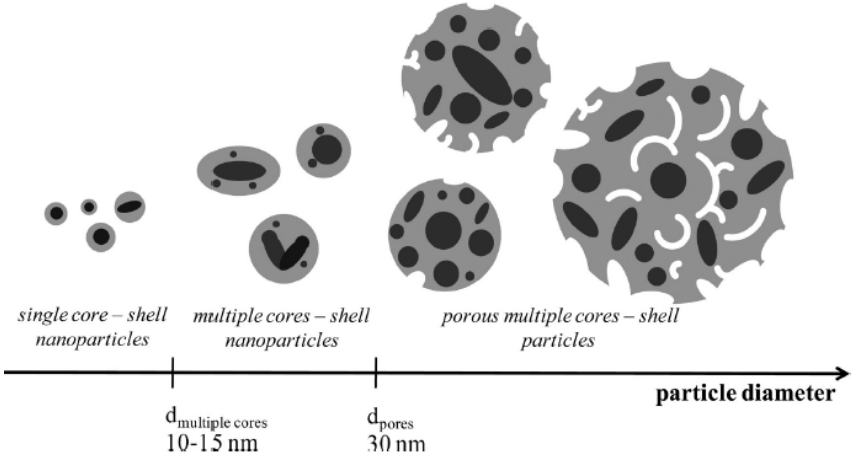
e.g., acid leaching, electrochemically dissol'n



Cross section, Pt in blue

Lattice compression of surface Pt layer

- Erlebacher dealloying of continuous films showed ligament/pore network controlled by relative rates of nonnoble-element dissolution and noble atom *surface* diffusion → tune to improve durability
- Shao-Horn pre-project work suggested high initial non-noble atom concentration generate porous structure
- Strasser pre-project work suggested particle morphology determined by particle size (below)



From M. Oezaslan, M. Heggen and P. Strasser, J. Am. Chem. Soc. 134 (2012) 514 with permission from ACS

Question to be answered

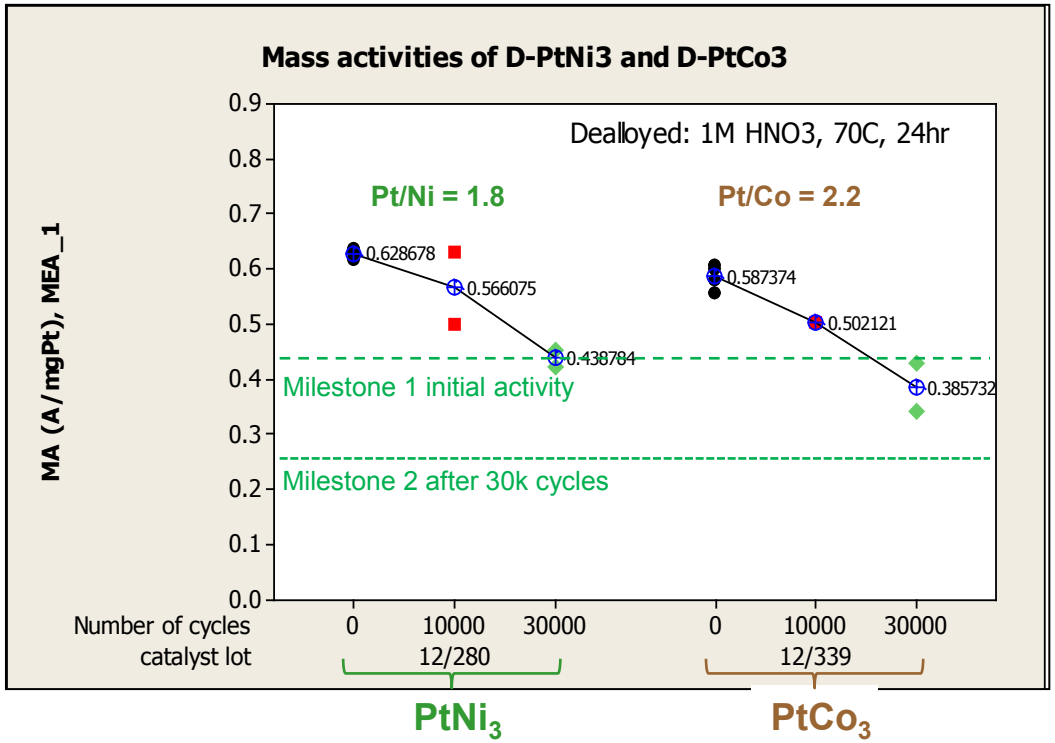
- Activity-morphology relationship
- Desired structure, elements, and composition for durability
- Activity-durability trade-off

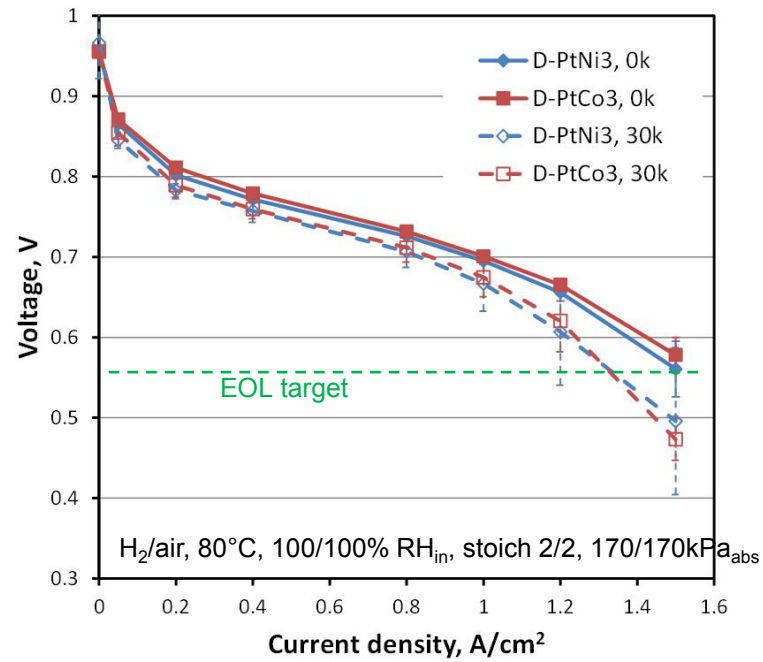
Relevance

- **Cost**
  - Demonstrate reliable oxygen reduction reaction kinetic mass activities > DOE target 0.44 A/mg_{PGM} in H_2/O_2 fuel cells, using **manufacturable** synthesis and dealloying procedures
  - Achieve high-current-density performance in H_2/air fuel cells adequate to meet DOE heat rejection targets and Pt-loading goals of <0.125 g_{Pt}/kW and <0.125 mg_{Pt}/cm^2_{geo}
- **Durability**
  - Demonstrate durability of the kinetic mass activity against DOE-specified voltage cycling tests in fuel cells
  - Determine where alloying-element atoms should reside with respect to the catalyst-particle surface for durable activity
- **Performance**
  - Demonstrate durability of high-current-density performance
  - Scale up to full-active-area fuel cells, to be made available for DOE testing

Reduce catalyst cost while achieving the required durable performance, allowing fuel cells to become economically competitive with other power sources.

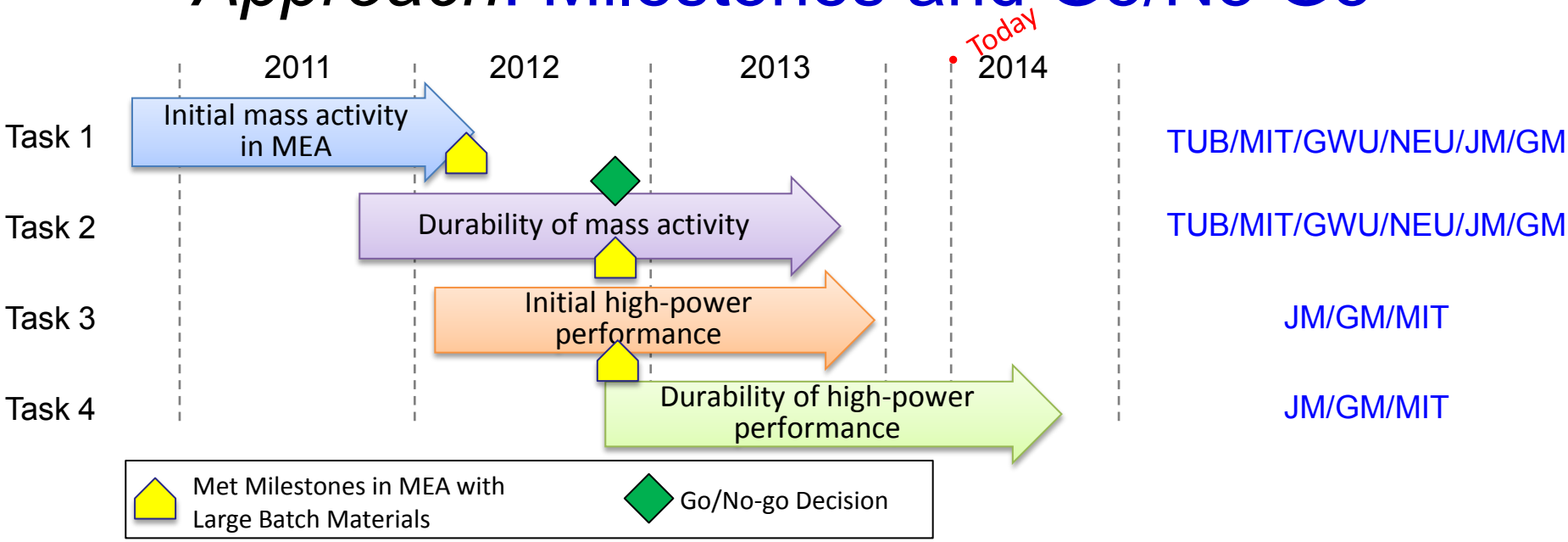
D-$PtNi_3$ vs D-$PtCo_3$ from JM Large-Batch Precursors





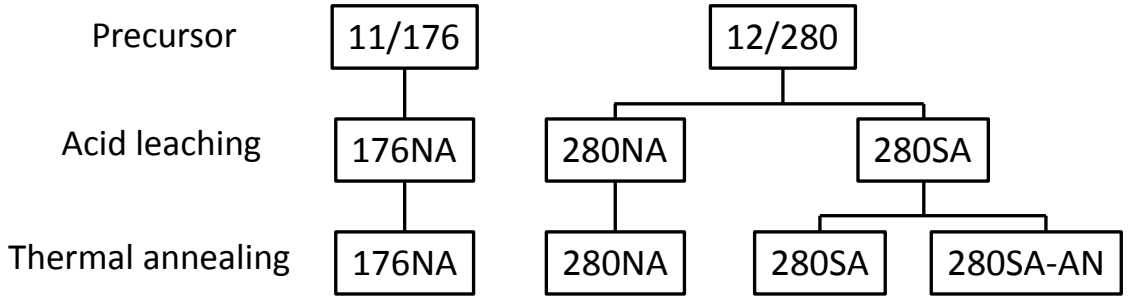
- Met all DOE 2017 cathode durability of activity target in multiple large-batch catalysts (>100g) for both PtNi and PtCo using several different acid-leaching and thermal annealing treatments.
- Met Milestone 3 (initial high-power performance) but not 4 (durability of high-power performance).

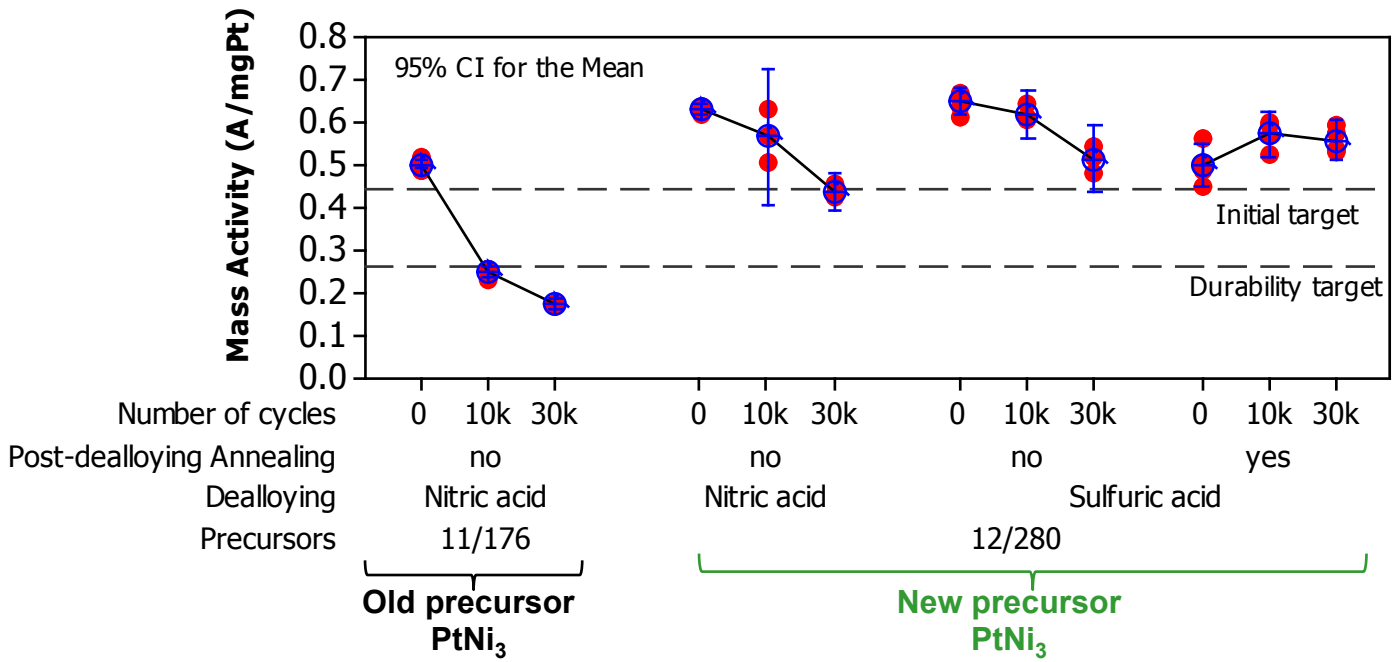
Approach: Milestones and Go/No Go



Time	Milestone or Go/No-Go Decision	Status
May-2012	Milestone 1: Initial ORR mass activity.	Satisfied at two labs with large batches catalysts
Oct-2012	Milestone 2: Durability of mass activity.	Satisfied at two labs with large batches catalysts
Oct-2012	Go/No-Go: Simultaneously achieve Milestones 1 and 2 with one material	Passed
Dec-2013	Milestone 3: Initial high-current-density performance with Milestone 2-compliant material.	Satisfied at two labs with large batches catalysts
Mar-2014	Milestone 4: Durability of high-current-density performance with Milestone 2-compliant material.	Demonstrated durability in 50cm^2 either by (1) using more realistic upper-limit voltage suppression on 0.1mg/cm2 electrode or (2) using DOE 1V cycling test at higher loaded (0.15mg/cm2) electrode. Shortstack test is on-going.

Selected MEA-tested Catalysts for Characterization



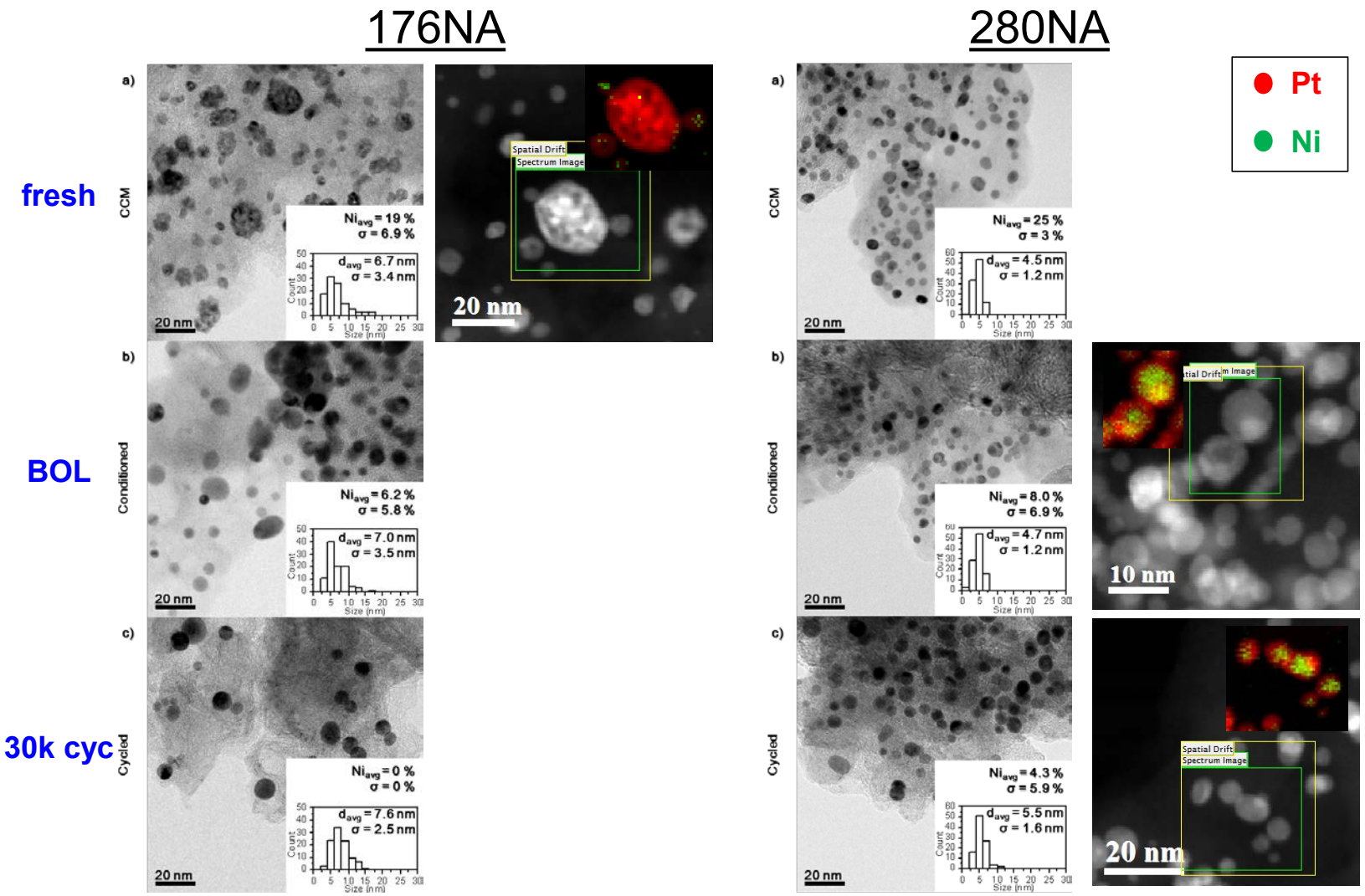


Cycling:
0.6-1.0V
50mV/s, H_2/N_2, 80 C, 100% RH
Cathode loadings:
0.082-0.100 mg_{Pt}/cm^2
Thermal annealing:
5% H_2/N_2 at 400 C for 4hrs

- Advanced characterization (TEM at MIT, STEM at GM, EXAFS at NEU, and XANES at GWU) were all done on the same MEA sample set generated at GM. (4 types x 3 stages)

Technical Accomplishment:

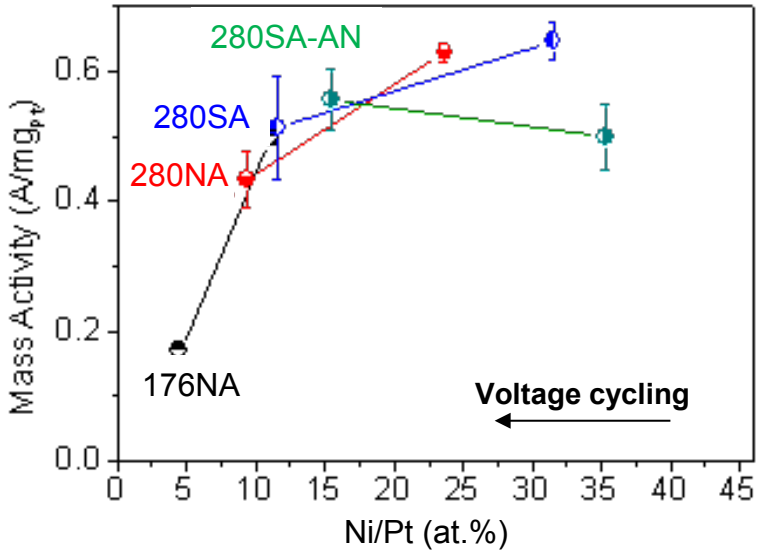
11/176-derived catalysts show porous structure and hold less Ni



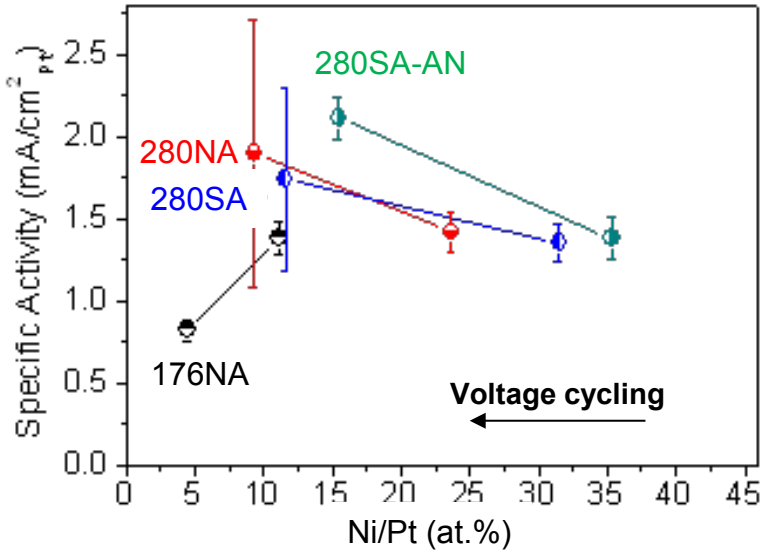
- 176NA clearly has wider particle-size distribution and retains less Ni when compared with 12/280-derived catalysts.

Bulk Ni Content and Activity

Mass activity



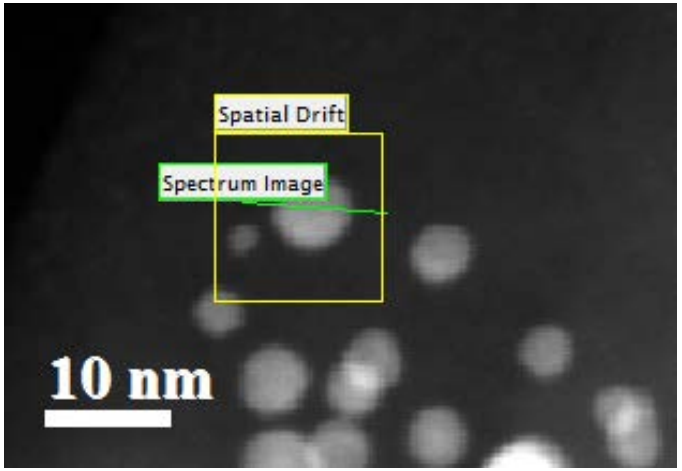
Specific activity

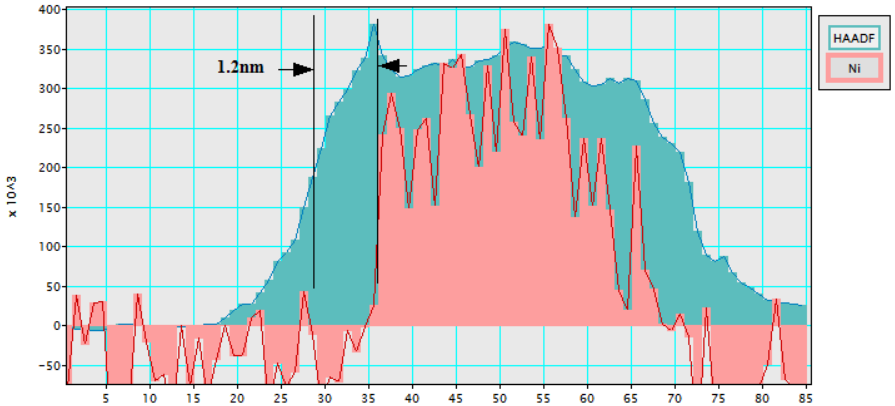


- Ni contents in tested catalysts were measured using EPMA in conjunction with TEM-EDS.
- In most cases (except for 280SA-AN), mass activity decreases with voltage cycling in part due to loss of surface area.
- In contrast to increasing specific activities observed in 12/280-derived catalysts, 176NA lost specific activity.
- Therefore, bulk Ni content provides some indication of ORR activity but there are also other factors.

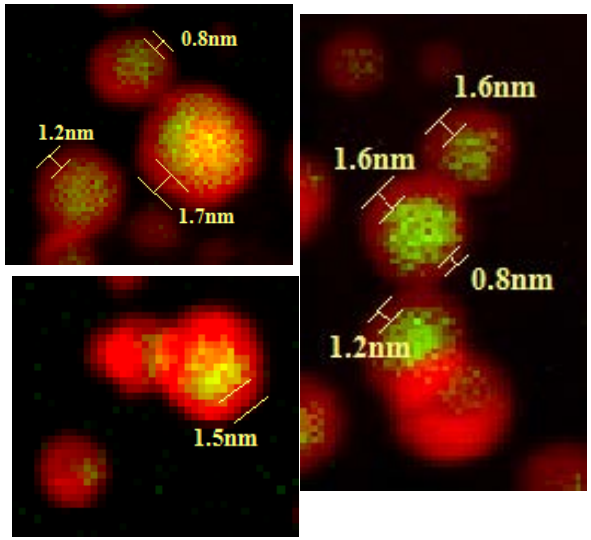
Technical Accomplishment:

Pt Shell Observation





280SA-EOT



Pt-Shell thickness in nm with one st.dev.

	BOL	Cycled
280SA	1.16±0.57	1.59±0.55
280SA-AN	1.27±0.32	1.62±0.49

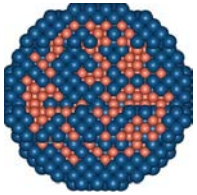
- Pt shell estimation was done using HAADF-STEM and EELS.
- Pt shell thicknesses were ~1.2 at BOL and ~1.6nm at 30k cycles.

XAFS Overview

Purpose of these studies

Utilize *in situ* XAS on operating dealloyed PtM electrocatalysts in order to:

1) identify where the alloying element needs to be in order to impart maximum activity, and
2) how these structures correlate with durability

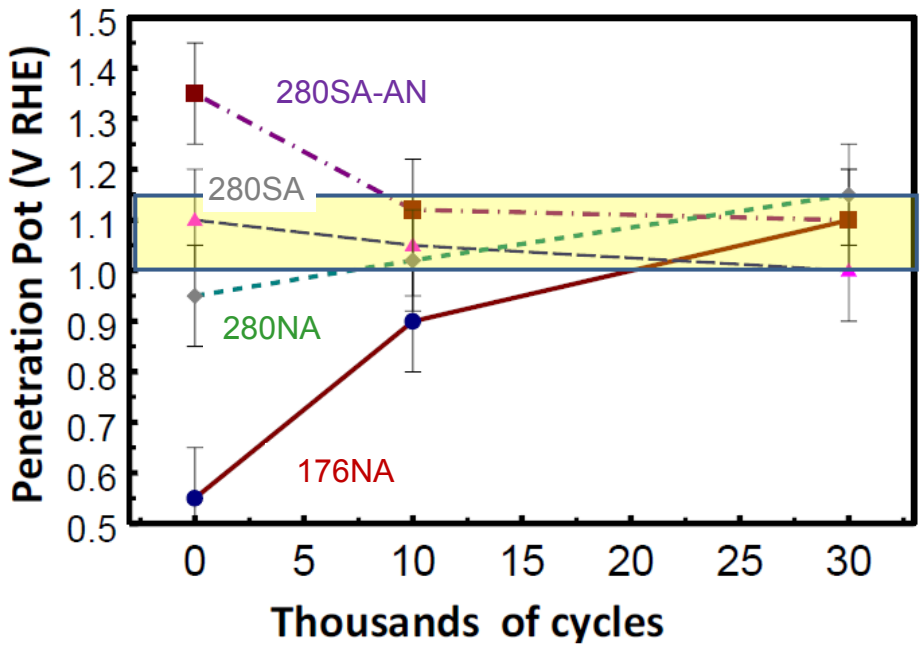


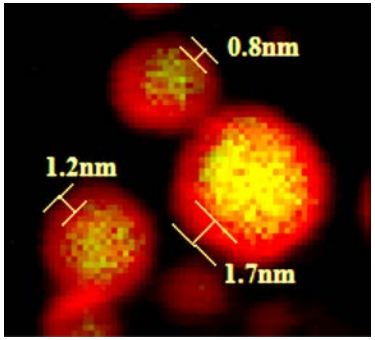
Project achievements

1. <u>Findings regarding PtM dealloyed core-shell particles</u>
   a. Effect of second metal: the compression effect is much more important than the ligand effect.
   b. Importance of having non-porous Pt shell
   c. Importance of leaving more Ni in dealloyed catalysts

2. <u>New techniques</u>
   a. FEFF calculations from derived structures to determine shifts in the Pt d-band centers
   b. Use of $\Delta\mu$ technique at M-edge to follow Pt skin thickness on Pt-M core-Pt shell nanoparticles
   c. Use of $\Delta\mu$ technique at Pt-edge to confirm Sabatier principle and dual volcano contribution in total activity

Pt-Shell Property: penetration potentials (V_{pen})





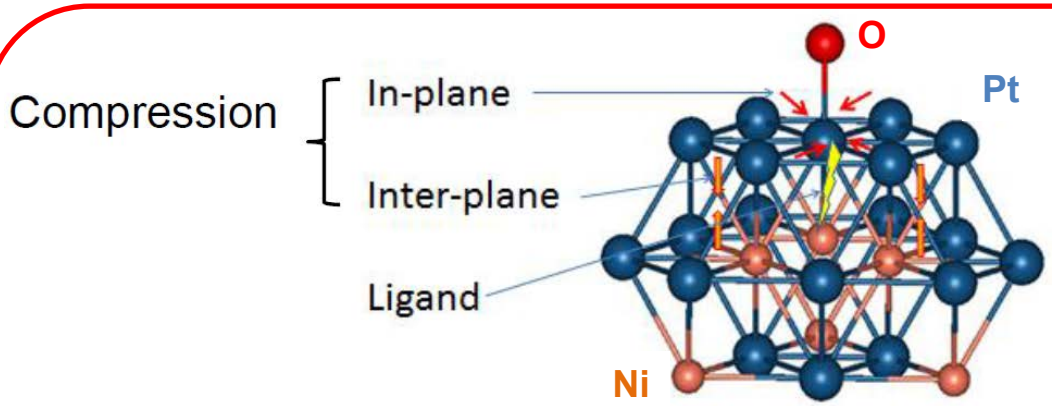
Pt-Shell thickness (nm)

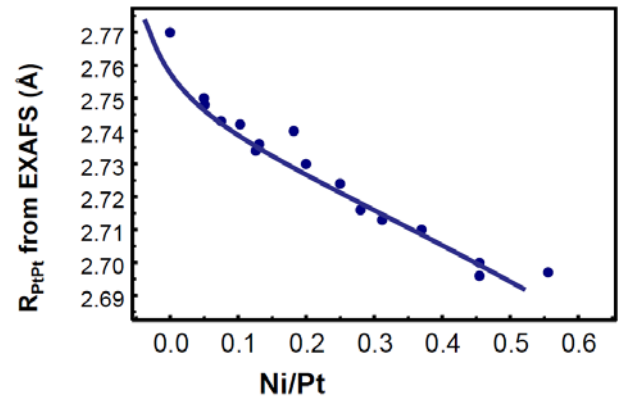
	BOL	Cycled
280SA	1.16±0.57	1.59±0.55
280SA-AN	1.27±0.32	1.62±0.49

- One can evaluate how resistance Pt shell is by monitoring characteristic Ni K edge Δμ peak that indicates direct Ni-O interaction. V_{pen} indicates potential where O penetrates Pt shell and meets Ni in the core.
- $PtNi_3$ (11/176) starts with a low V_{pen} (porous).
- SA-dealloyed materials are more resistant than the NA-dealloyed variety.
- After voltage cycling, V_{pen}s of all four $PtNi_x$ catalysts approach the same value, indicating a characteristic skin thickness. → Supported by GM STEM-EELS Pt-shell measurement.
- **V_{pen} correlates with thickness and porosity**

Technical Accomplishment:

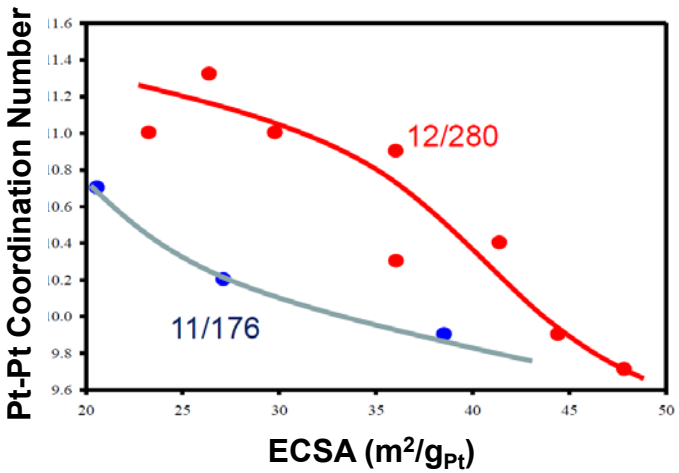
Compression, Shell Porosity



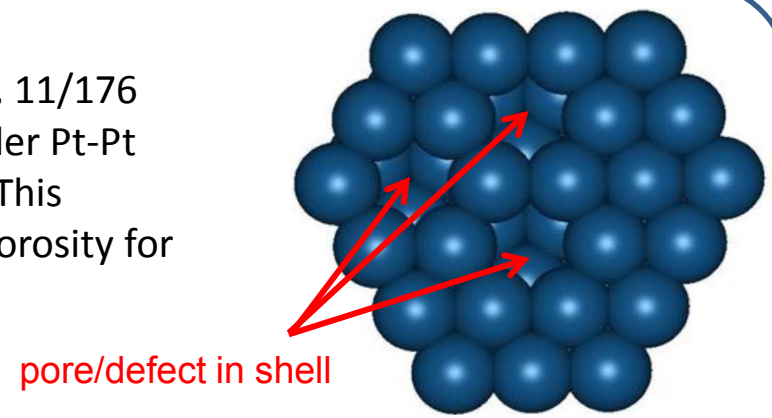


Effect of alloying metal: the compression effect is much more important than the ligand effect

- Uniform volcano plot vs. Ni/Pt ratio
- $R_{Pt\text{-}Pt}$ (EXAFS) follows the Ni/Pt ratio



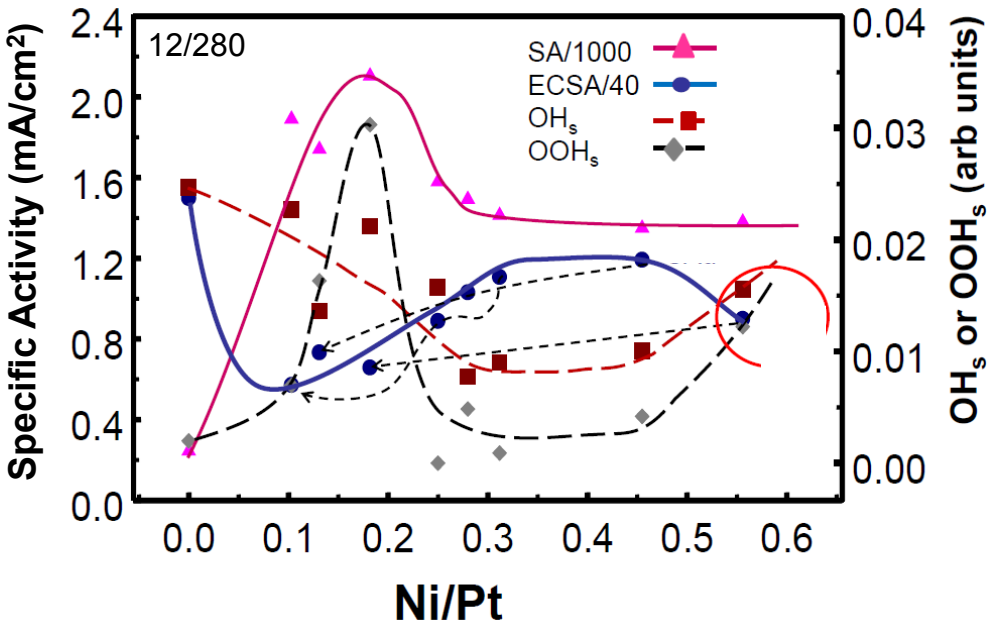
At the same ECSA, 11/176 shows much smaller Pt-Pt CN than 12/280. This indicates higher porosity for 11/176.



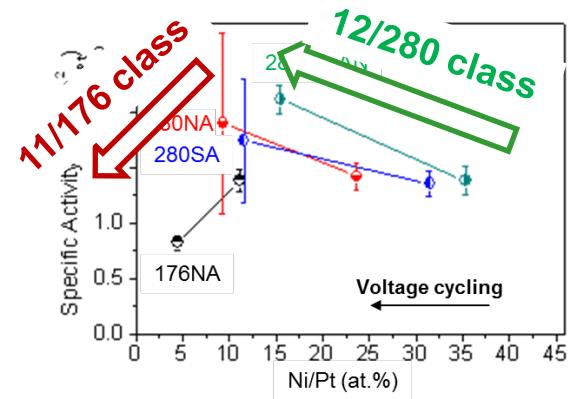
Lower shell porosity = higher activity, durability

Technical Accomplishment:

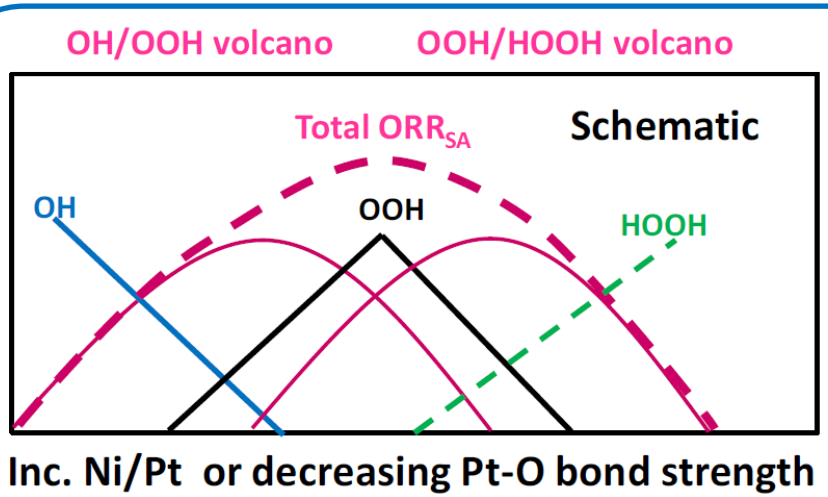
Sabatier Principle Confirmation



Specific activities as Ni decreases



- To make a durable catalyst, one wants to start from high Ni content.

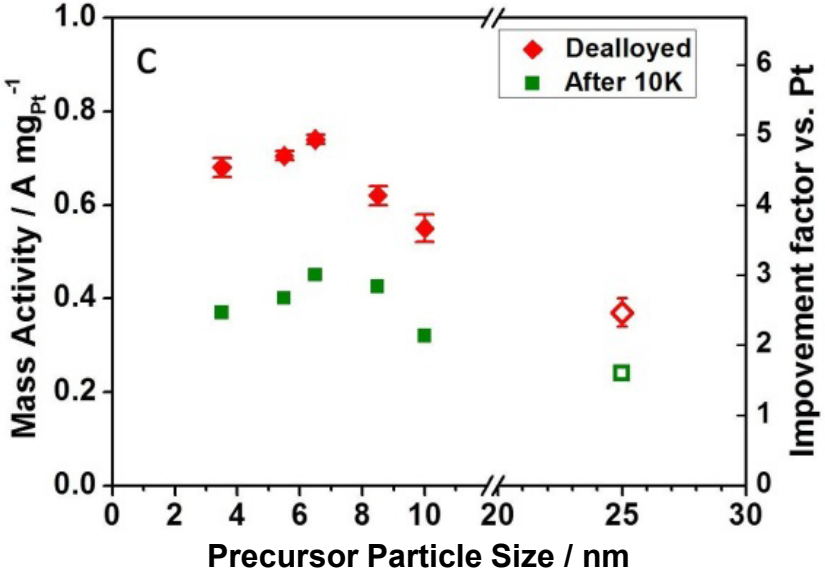


Specific activity correlates with OOH surface species in lieu of OH dominating. This points to a relatively lower Pt-O bond strength.

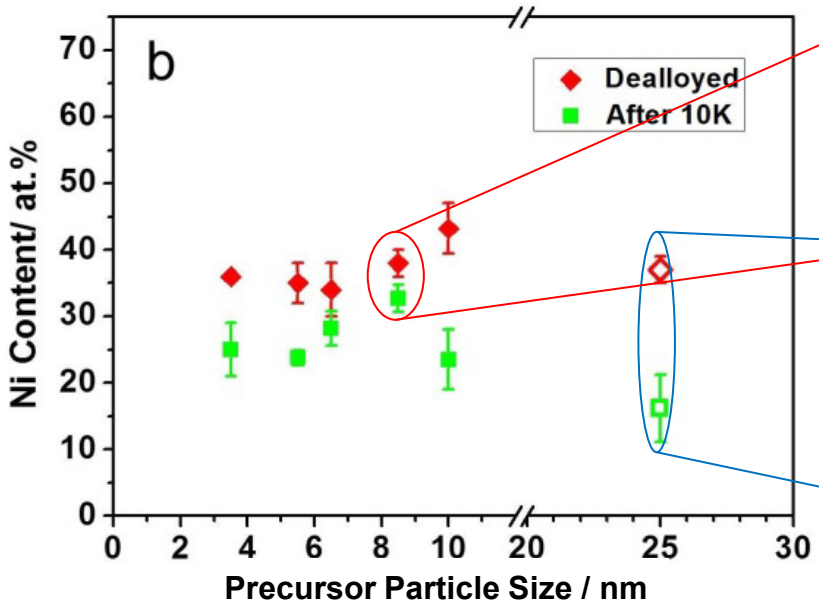
* Ni/Pt ratios from EPMA studies of MEA cathode

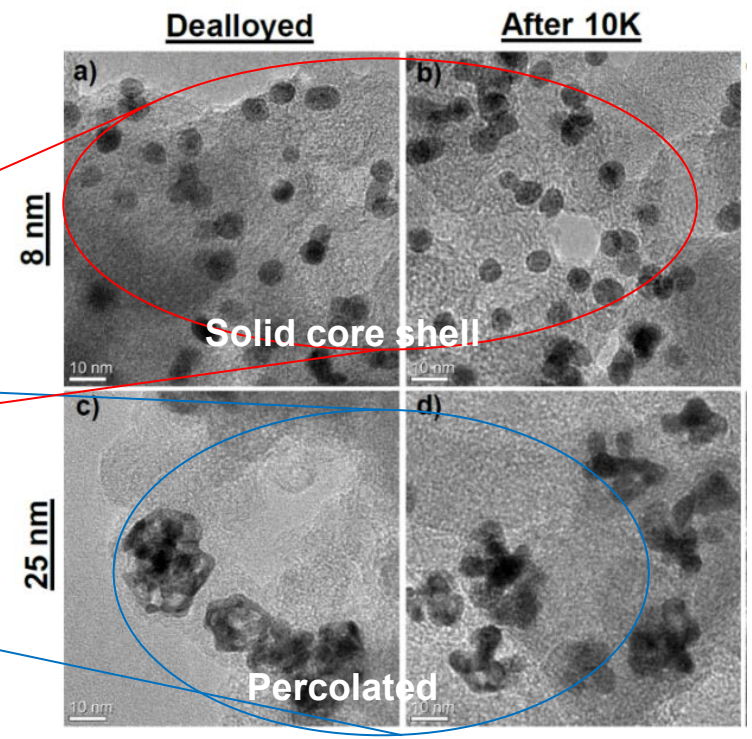
Technical Accomplishment:

New Catalyst Design: Precursor Size



- Use new synthesis to produce size-selective monodispersed $PtNi_3$ precursors. 3 - 25nm.
- There appeared to be an optimal precursor size for activity.
- Precursor size of 6-8 appeared to be the best in retaining Ni.

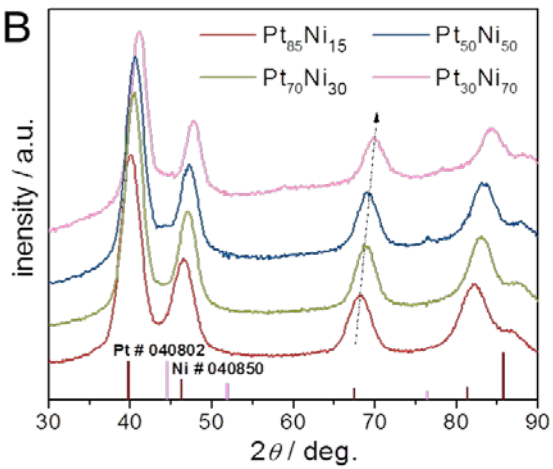


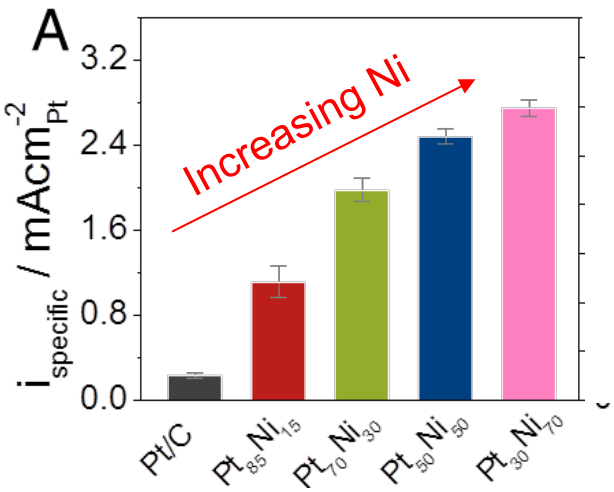


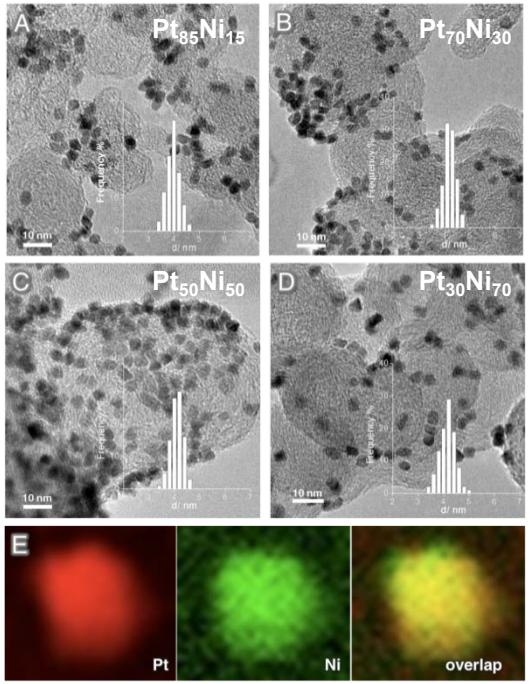
Technical Accomplishment:

Precursor Composition

- Controlling particle size through CO confinement







Cui, et al. *JACS* 2014, 136, 4813
Cui, et al. *Nature Mater.* 2013, 12, 765

- TUB made precursor with different Pt/Ni composition but all with the same particle size (4nm).
- Found that initial activity increased with Ni content.

Technical Accomplishment:

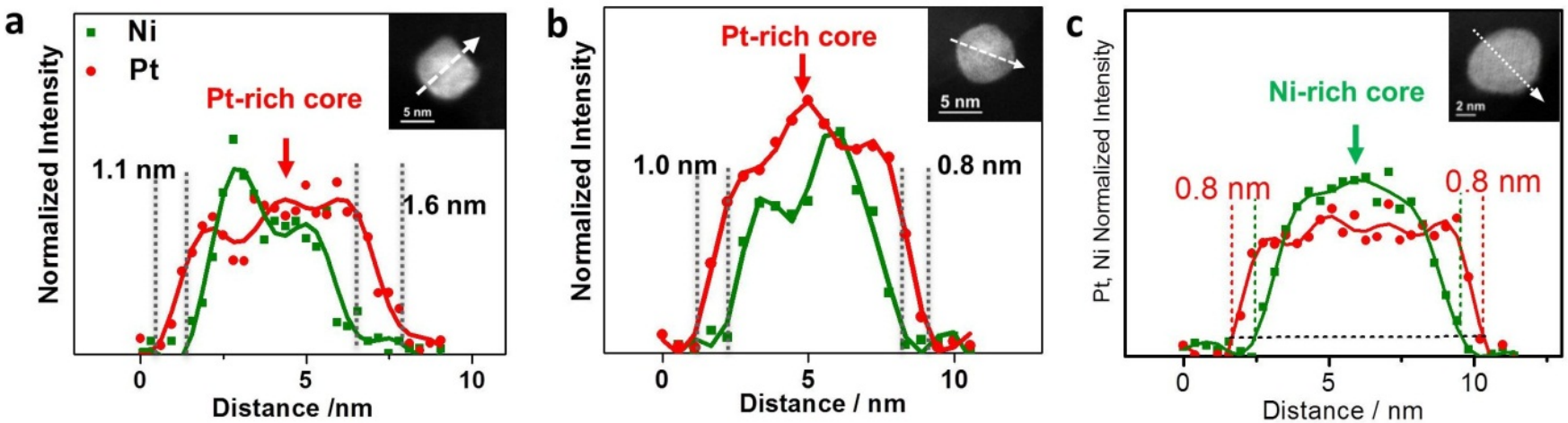
Catalyst Local Composition

Aberration-corrected STEM/EELS

TUB
180°C, air-annealed D-$PtNi_3$

TUB
400°C, H_2-annealed D-$PtNi_3$

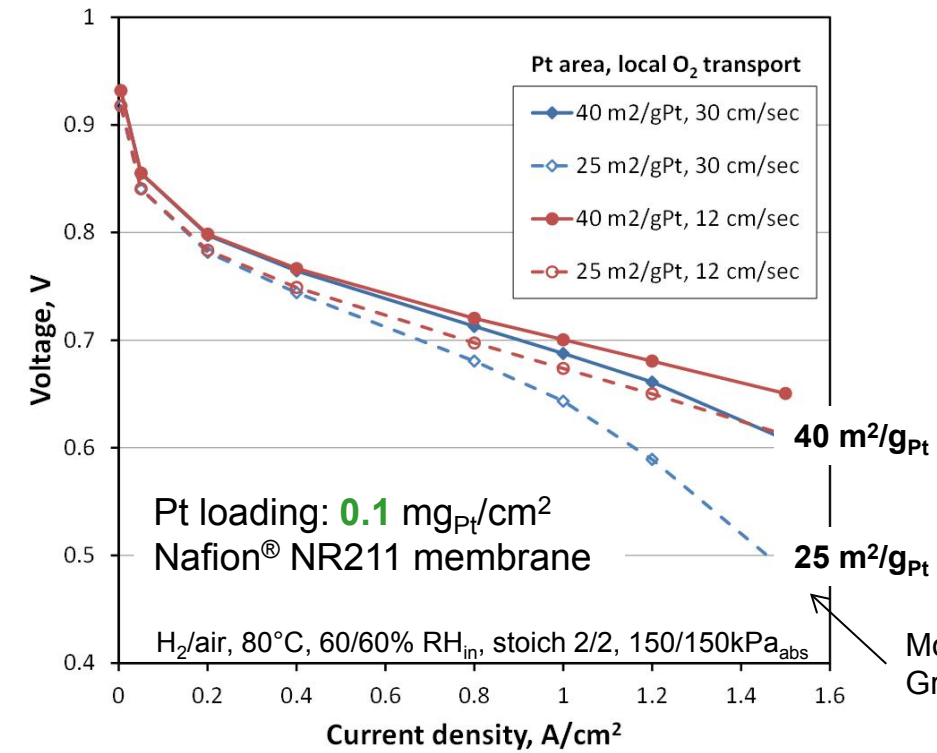
JM
D-$PtNi_3$, 12/280



- TUB compared catalysts prepared using electrochemically-dealloyed TUB precursors with two different heat treatment with JM's acid-dealloyed catalyst.
- TUB made catalysts have Pt-rich cores but JM catalyst has a Ni-rich core.
- Durability of JM catalyst was superior to TUB catalysts despite similar precursor particle size (8nm).
- Hypothesized that heat treatment might be important for durability.
- Observed that mass activity after 4k cycles in RDE increased with heat treatment time.

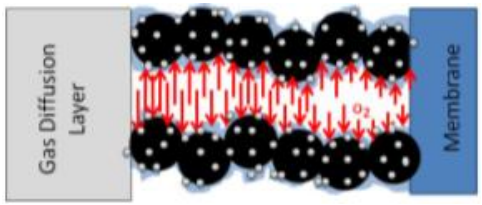
Last year AMR

Local O_2 Transport Resistance and Pt Surface Area

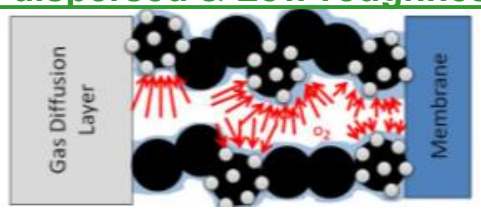


Modeled by Greszler, *et al.*, *J. Electrochem. Soc.*, F831 (2012)

Well-dispersed & High roughness factor



Poorly-dispersed & Low roughness factor

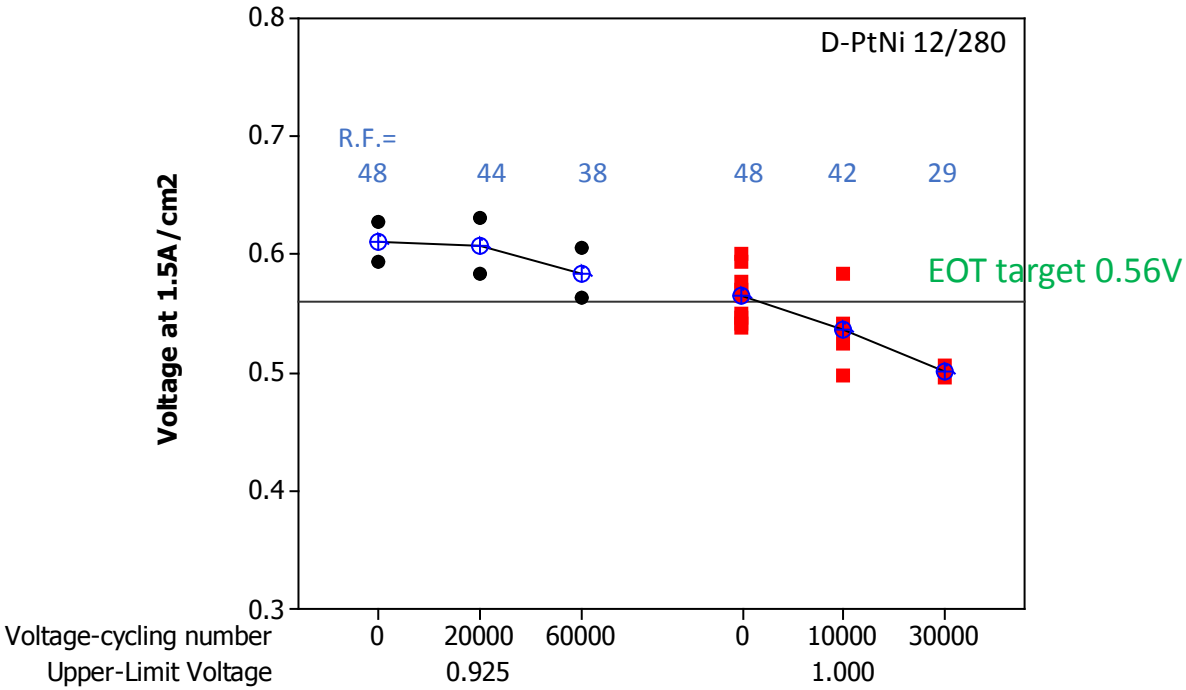


Cartoon from DOE transport proj, Wenbin Gu

- In fact, because the electrodes we've developed have low Pt roughness factor (Pt loading Pt-specific surface area) the 'local O_2 transport resistance' described by other groups begins to become relevant.
- May require 'electrode' development which was out of the original scope of our project.
- 0.6-1.0V cycling is more aggressive than that in vehicle operation.

Technical Accomplishment:

Decreasing Upper-Limit Voltage (but longer test) could Enable Dealloyed Catalysts



Measurement:
H_2/air, 80°C, 100/100% RH_{in}, stoich 1.5/2, 170/170kPa_{abs}

Cycling:
0.6-1.0V or 0.6-0.925V
50mV/s, H_2/N_2, 80°C, 100% RH

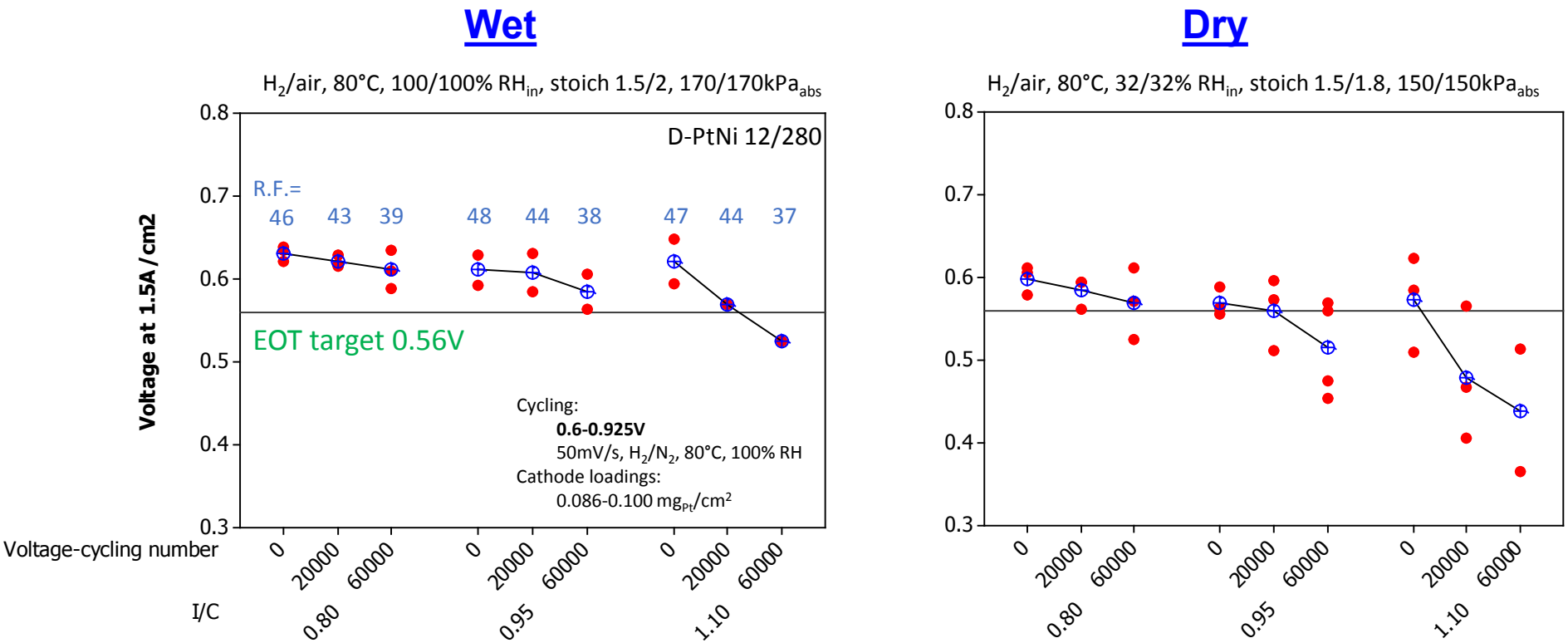
Cathode loadings:
0.086-0.100 mg_{Pt}/cm^2

- Reducing upper-limit voltage from 1.0 to 0.925 V (but twice as many cycles) reduced performance decay to an acceptable level.

  →only ~20% losses of surface area and mass activity compared to ~40% losses for the 1V upper limit.

Technical Accomplishment:

Electrode Optimization: Ionomer Content



- Durability of high-power performance improved with decreasing ionomer-to-carbon ratio.
- The trend was even more obvious in dryer condition. →flooding is unlikely.
- Similar results were observed in the transport project (2013 AMR) on 0.05 mg_{Pt}/cm^2 Pt/V electrodes. It was attributed to local oxygen transport resistance.

Stack Demonstration

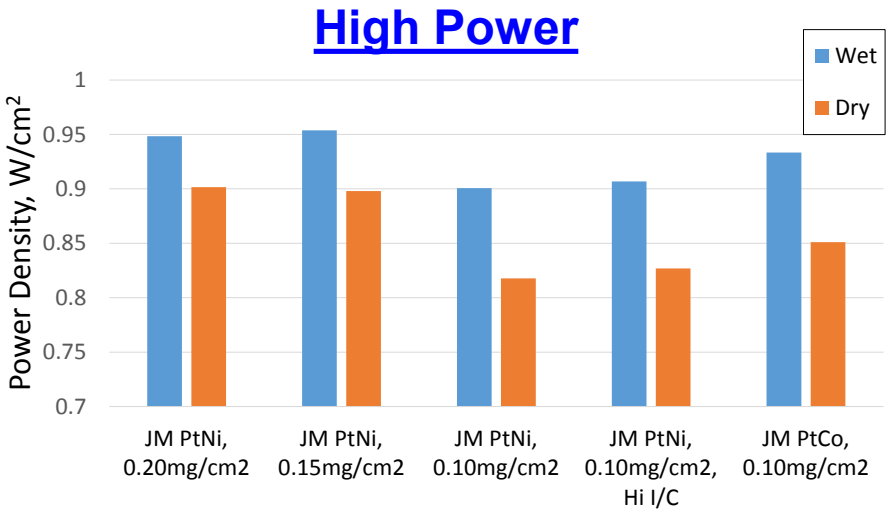
JM Precursors $PtNi_3$ and $PtCo_3$ (analogous to 12/280)

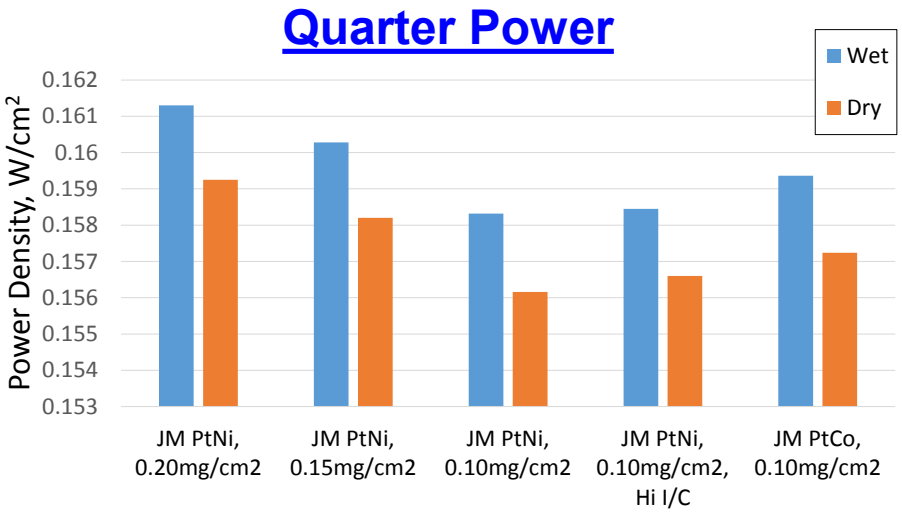
Type	Description	Pt loading (mg_{Pt}/cm^2)	I/C	Cathode ECA (m^2/g_{Pt})
1	GM Pt alloy/CB	0.20	Standard	
2	JM 30% PtNi/HSC (14/12)	0.20	Standard	45
3	JM 30% PtNi/HSC (14/12)	0.15	Standard	48
4	JM 30% PtNi/HSC (14/12)	0.10	Standard	45
5	JM 30% PtNi/HSC (14/12)	0.10	High	46
6	JM 30% PtCo/HSC (14/16)	0.10	Standard	49

- Catalyst powder arrived from JM early Feb. These are D-$PtNi_3$ and D-$PtCo_3$ catalysts analogous to 12/280. MEA are being fabricated.
- Built a full-active-area shortstack in Feb. Completed most initial fuel cell performance evaluation.
- Will be tested under DOE-recommended drive-cycle durability protocol.

Technical Accomplishment:

Initial Stack Performance



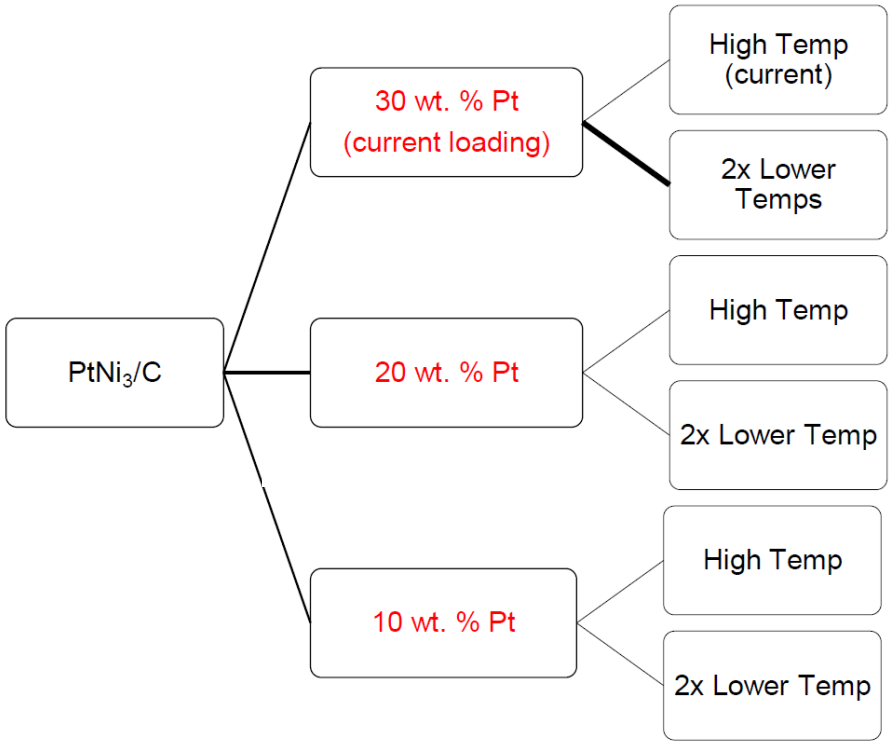


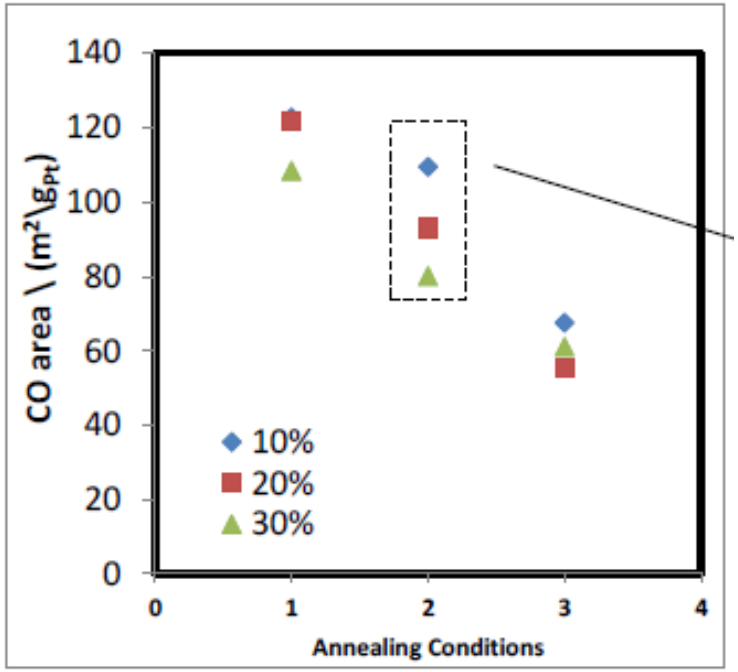
- Performance of 0.20 mg_{Pt}/cm^2 PtNi was slightly lower than expected but others performed well.
- PtCo slightly outperformed PtNi at the same loading.
- With 0.05 mg_{Pt}/cm^2 anode, now at 0.16 g_{PGM}/kW. Should get very close to 0.125 g_{PGM}/kW DOE target with lower-loaded anode.
- Ionomer distribution in electrode is key to closing gap at dry condition

Technical Accomplishment:

Catalyst Development for Improved Dispersion

Johnson Matthey Fuel Cells
the power within





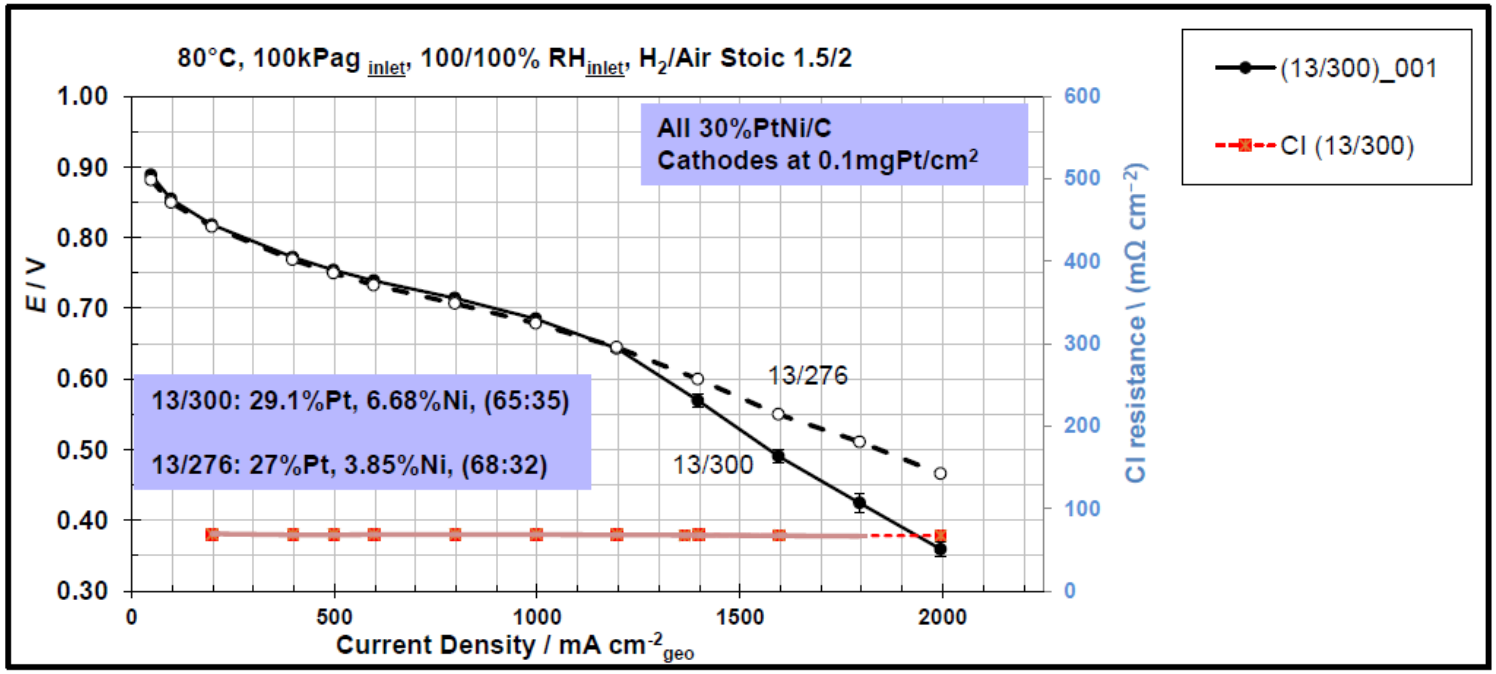
1: Low Temperature
2: Intermediate
3: High

- To improve dispersion of the catalyst precursor, JM attempted to reduce metal loading and heat treatment temperature.
- Metal loading had smaller impact than heat treatment temperature.
- However, at lower-temperature treatment gave incomplete alloying.
- JM continues to pursue different synthesis approaches.

Technical Accomplishment:

Manufacturing-friendly Synthesis

Johnson Matthey Fuel Cells
the power within



Catalyst Number	Catalyst Description	Cathode Loading ($mgPt/cm^2$)	Surface Area (m^2/g_{Pt})	Roughness factor	Mass Activity 0.9V /(A/mgPt)	Spec Activity 0.9V /(A/mgPt)
13/300 n=3	Standard prep	0.1476± 0.01	56.05± 2.44	82.65± 2.32	0.62 ± 0.01	1106± 49
13/276, n=1	New Prep	0.1076	64.10	68.97	0.60	

- JM made progress on simplifying their catalyst precursor synthesis process to provide better manufacturability.
- Dealloyed catalyst from this precursor showed similar or better performance than the 12/280 at JM. Will be shipped to GM for validation.

GM

Responses to Last Year AMR Reviewers' Comments

- "does not explore any novel class or type of catalyst" "already known and do not add new insight into the functional properties of these catalysts"
  - Because the bulk composition is the same, it does not mean that the catalysts are the same. The class of catalyst we are working on has only been actively studied in the last several years. We've further developed it and demonstrated to be one of the most durable active catalysts in MEA. It is true that many known perspectives were found to apply to this catalyst class in order to make it durable. However, it is highly valuable to be able to prove it so.
- "catalyst lack of consistency in particle size and elemental distribution" "Why not adopt the synthetic path reported by the ANL"
  - Our objective is to develop a manufacturable synthesis approach to enable a successful technology transfer from academia to component supplier and then stack integrator. Adopting the ANL synthetic path may facilitate fundamental studies but will deviate from our approach.
- "How the efforts of NEU and GWU were leveraged in the rest of the project is unclear."
  - Results reported this year should be a good example for their contributions. Their results have reinforced our understanding in the structures needed for a durable active catalyst. Those include Pt shell quality/thickness and base-metal composition/location. These newly developed techniques will also be valuable for future catalyst development.
- "Lack of modeling capability to validate demonstrated performance change/durability related to material structure"
  - GM has a strong model capability and we place significant values on experimentally-validated model. Yet physical model for low-loaded electrode is still unclear. We will support ANL-led DOE electrode project who will use our catalyst in studying electrode structure-performance correlation.

Collaborations (subcontractors)

- GM
  - Overall project guidance, testing of catalysts, fabrication and testing of MEAs and fuel cells

- Technical University Berlin (TUB) (university)– Prof. Dr. Peter Strasser
  - née Univ. of Houston (UofH)
  - Selection of new candidate catalyst systems, pre-fuel-cell evaluation, tie-in to theory

- Johnson Matthey Fuel Cells (JMFC) (industry) – Dr. Rachel O'Malley
  - Scale-up of synthesis, improved manufacturability of dealloying, incorporation and MEA testing

- Massachusetts Institute of Technology (MIT) (university) – Prof. Yang Shao-Horn
  - Electron microscopy, dealloying interpretation, alternate preparations of core/shell structures

Northeastern University (NEU) (university) – Prof. Sanjeev Mukerjee
  - X-ray absorption spectroscopy (EXAFS, XANES)

George Washington University (GWU) (university) -- Prof. David Ramaker
  - Theoretical support of x-ray absorption spectroscopy, $\Delta\mu$ XANES

Project is working through iterative cycles of synthesis, scaleup, performance evaluation, and characterization

Tech transfer: University ➔ Catalyst manufacturer ➔ Stack integrator

Remaining Challenges and Future Work

- **Demonstration of durability of high-power performance**
  - Stack testing on-going. Will test any new promising catalysts. (GM/JM)

- **Still room to improve high-power performance and its durability**
  - Increasing catalyst surface area, particle size uniformity, and alloy quality are key.
    - Alternate $PtNi_3$ syntheses/treatments for improved PSD and high surface area. (JM/TUB)
    - Fine-tune dealloying and electrode fabrication for improved high-power performance (GM)
    - Continue development of binary and ternary dealloyed systems (TUB/JM/MIT)

- **Effects of base metal leaching on performance is unclear**
  - Can affect during ink making, electrode fabrication processes, as well as fuel cell performance.
    - Investigate effect of base metal leaching on performance (ANL project)
    - Investigate effect of base metal leaching on ink properties (ANL project)
    - Collaborate with DOE transport team. Fabrication and theory on low-Pt-loaded electrode. (GM)

** Out of the scope of original proposal. Unlikely to be completed*
** Will continue under ANL-led project*

Summary

- Met all DOE 2017 cathode catalyst targets in multiple large-batch catalysts.
- Performed advanced characterization at 5 institutions on the same set of samples to gain collective learning and ensure consistency.
- Developed XAFS techniques to enable characterization of Pt shell and subsurface metals under fuel cell-relevant environment that can be applied to future catalyst development.
- Catalysts with more Ni generally showed higher ORR activity although not necessary high-power performance.
- Despite similar initial activity, catalysts with better particle-size distribution and smaller particle size retained more Ni, and thus showed better durability of mass activity. This is due to the ability to form more uniform Pt shell over its core.
- Demonstrated that dealloyed catalysts developed under this project might be sufficiently durable if (1) we used higher cathode loading ($0.15 mg_{Pt}/cm^2$) or if (2) we suppressed the upper-limit voltage to 0.925V with $0.1 mg_{Pt}/cm^2$ cathode.
- Successfully transferred and further developed catalyst technology from academia, to catalyst supplier, and to stack integrator in ~3 years.

Acknowledgements

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- Alex Hawkins
- Brian Theobald

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- Lin Gan

MIT

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- Christopher E. Carlton
- Binghong Han

Northeastern University

- Sanjeev Mukerjee
- Qingying Jia

George Washington University

- David Ramaker
- Keegan Caldwell

Technical Back-Up Slides

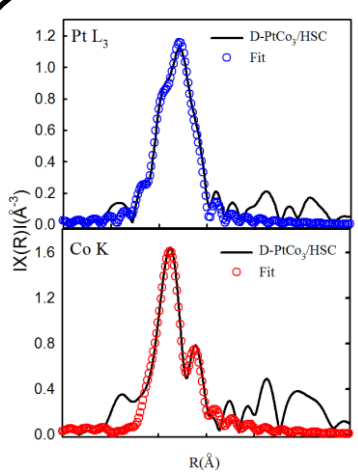
Technical Accomplishment:

Sample Overview

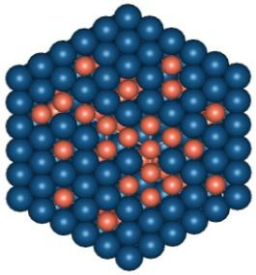
Precursor	cycles	d(nm)	Pt/M	Microstructure
PtCo/HSC	~100	3-5	2.2	Mostly SC-S
$PtCo_3$/HSC	~100	4.0	2.7	50% SC-S, 50% MC-PS
$PtNi_3$/HSC-176	BOL	7.0	8.0	MC-PS w M in PS
	10k			MC-PS w < M in PS
	30k	7.6	19.8	MC-PS w << M in PS
$PtNi_3$/HSC-280 SA-annealed	BOL	5.0	1.8	solid particles
	10k			
	30k	4.7	5.5	solid particles
$PtNi_3$/HSC-280 SA-unannealed	BOL	4.5	2.2	solid particles
	10k			
	30k	5.5	4.9	solid particles
$PtNi_3$/HSC-280 NA-unannealed	BOL	4.7	3.2	solid particles
	10k			
	30k	5.5	9.7	solid particles

(SC) single core
(MC) multiple-core
(S) solid shell
(PS) porous shell

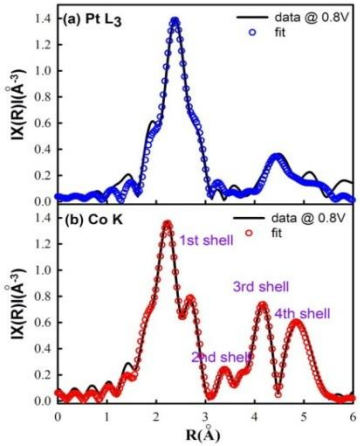
- Same sample set used in other studies.
- Particle size from MIT TEM. Pt/M from GM EPMA.



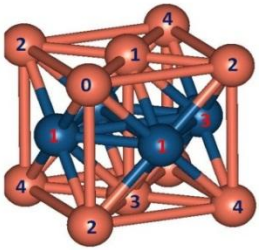
Disordered core



Pt_1Co_3/C



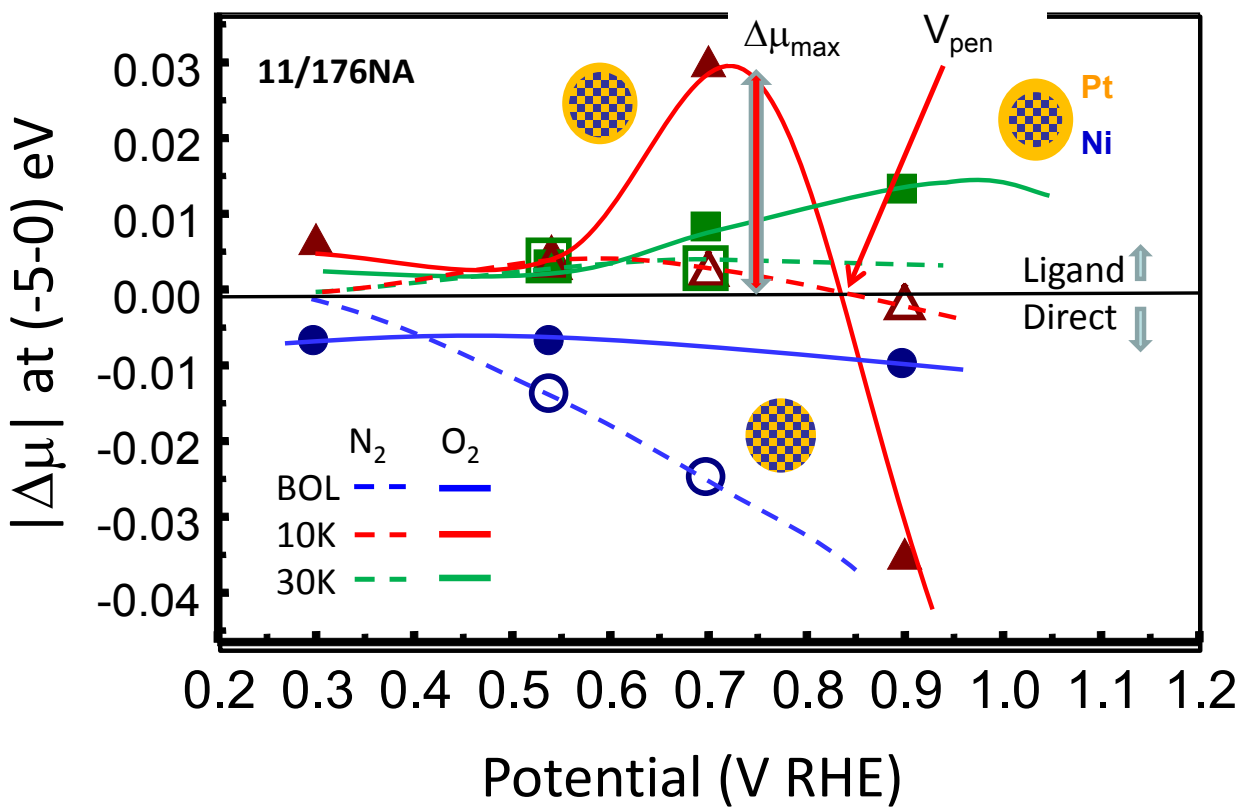
Ordered core



Pt_1Co_1/C

NOTES
All samples were cycled CCDMs from MEAs except for the (early) PtCox samples which were hand-painted electrodes on carbon cloth.

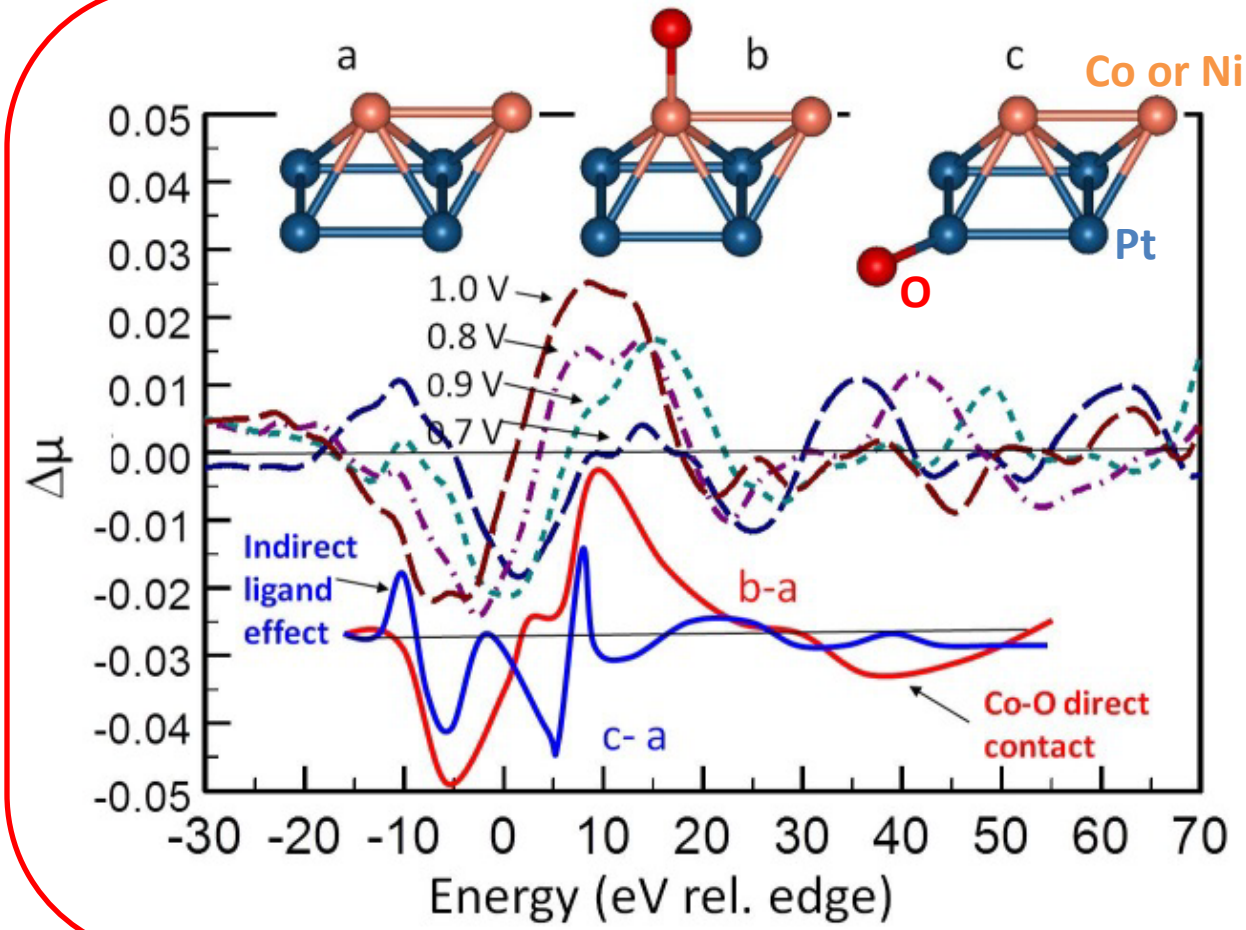
Direct and indirect Ni-O interaction



- Direct M-O interaction is only possible when O(H) has penetrated the Pt surface.
- This is easily followed, by monitoring the amplitude of the initial Ni K edge Δμ peak.
- Potential where O(H) can penetrate Pt surface (V_{pen}) illustrates Pt shell property.

Technical Accomplishment:

How Close is Ni to the Surface? Δμ at the Ni K edge



TOP: Pt_4Co_2-(O) clusters used for the FEFF8 calculations

MIDDLE: Experimental Co K edge Δμ data for dealloyed Pt_1Co_1/C at the indicated potentials

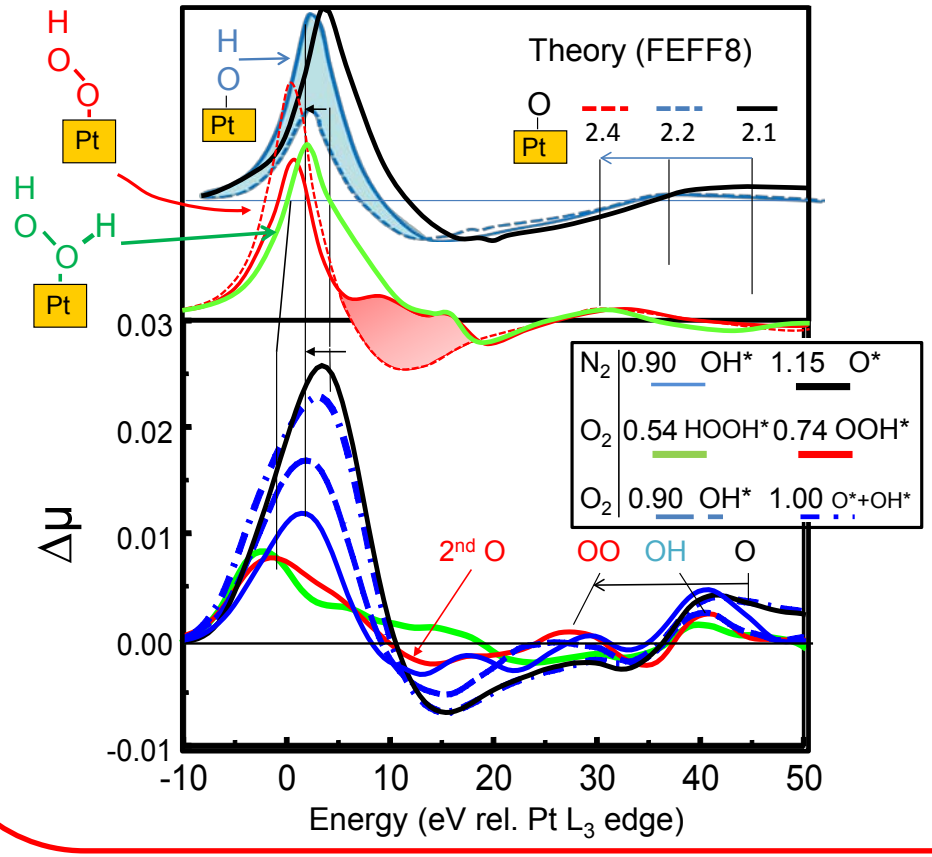
BOTTOM: FEFF8 calculated Δμ signals from the above models. Note that the amplitude of the first peak (positive or negative) serves as a marker for direct or indirect Co-O interactions

- Indirect Co-O (or Ni-O) interactions, a marker for adsorbates coming on the outer edge of the Pt skin, as seen by M atoms in the direct subsurface layer.
- Give opportunity, for first time, to observe immediate subsurface M under potential control

Technical Accomplishment:

Identify Oxygen Species with Δμ at the Pt L_3 edge

Dealloyed $PtNi_3$ (12/280), SA unannealed



$\Delta\mu = \mu(V, O_2 \text{ or } N_2 \text{ sparged}) - \mu(0.54, N_2 \text{ sparged})$ for catalyst SAu (BOL) at the indicated potentials. Also indicated are FEFF8 results for the indicated adsorbates with Pt-O bond lengths as indicated in Å producing the shifts of the 30-45 eV peak. The contribution from the second O in the OOH* is highlighted in red, that from the H in the OH in blue, as determined from the difference in Δμ with and without the second atom. The H "outside" the second O in OOH is not included in the FEFF8 calculations.

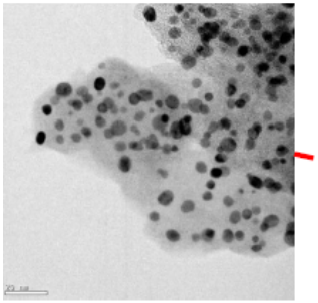
Absorbate chemistries and geometries serve as markers of Pt-O bond strength, and are correlated well with theory (Norskov, Adzic, etc.)

Technical Accomplishment:

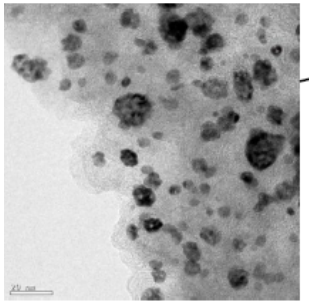
XAFS Final Observations

Our observations on real-life, operating nanoparticles correlate with literature on "ideal" surfaces measured by RDE.

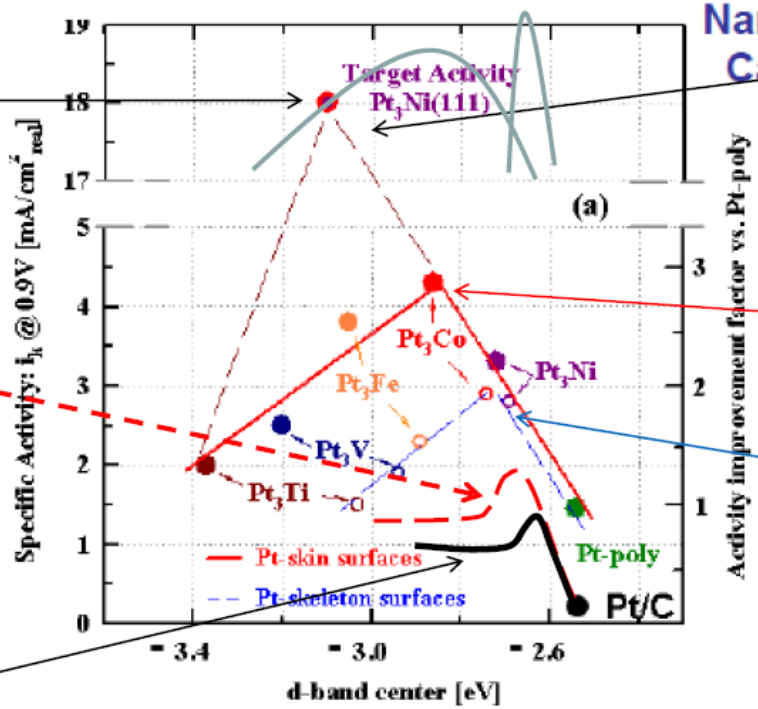
ε_d=-3.10 eV

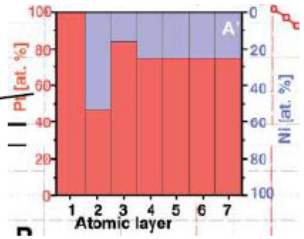


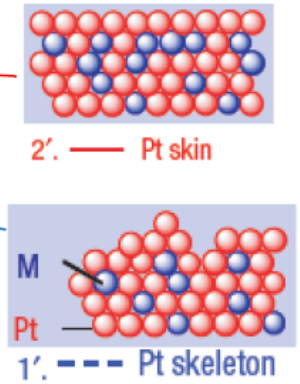
Solid NP



Porous NP







Polycrystals

d-band calc with FEFF by Jia

Our results overlaid on Markovic 2013 AMR

These results should serve as a roadmap for the rational design of new catalysts.