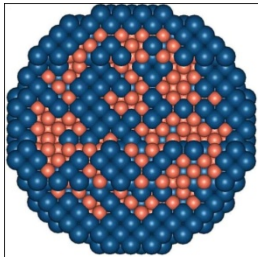
High-Activity Dealloyed Catalysts

M is one or
more non-
precious metals

precursor dealloying catalyst

$PtM_3/C \xrightarrow{\text{dealloying}} Pt_{1.5-3}M/C$


Cross section, Pt in blue

Lattice compression of surface Pt layer

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FC087

Overview

Timeline

- Project start date: 1 Aug 2010
- Project end date: 30 Nov 2013
- Percent complete: 30%

Budget

- Total project funding:$5,952,827
  - DOE share: $4,762,313
  - Contractor share: $1,190,514
- Funding received in FY11: $480,000
- Planned Funding for FY12: $750,000

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

Relevance

- Objectives:
  - 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
  - Demonstrate durability of the kinetic mass activity against DOE-specified voltage cycling tests in fuel cells
  - 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$^2_{geo}$
  - Scale up to full-active-area fuel cells, to be made available for DOE testing
  - Demonstrate durability of high current density performance
  - Determine where alloying-element atoms should reside with respect to the catalyst-particle surface for best durable activity

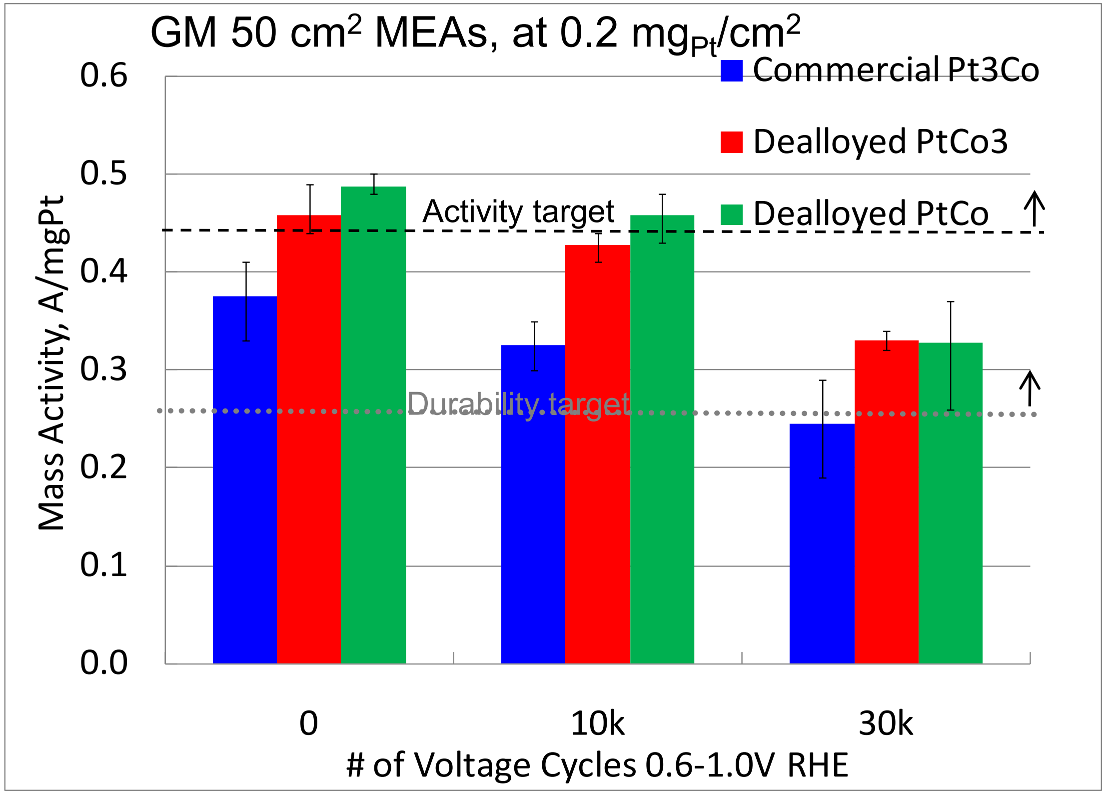
Reduce catalyst cost while achieving the required durable performance, allowing fuel cells to become economically competitive with other power sources.

Approach: Milestones and Go/No Go

Month/Year	Milestone or Go/No-Go Decision	Status
May-2012	Milestone 1: ORR mass activity >0.44 A/mg_{PGM} reliably achieved with 0.1 mg_{PGM}/cm^2 loading in at least two labs, at least one at scale of 49 cm^2 (or larger) MEA.	Numerically satisfied at GM by dealloyed JM $PtNi_3$ and (but at 0.2mg_{PGM}/cm^2) by GM D-PtCo and D-$PtCo_3$. Still need to achieve MEA result in second lab.
Oct-2012	Milestone 2: Durability of kinetic activity. ≥60% of initial mass activity maintained in two labs after 30,000 cycles 0.6-1.0V RHE in fuel cells	Numerically satisfied by GM D-PtCo and D-$PtCo_3$ at 0.2mg_{PGM}/cm^2. Still need to achieve with JM-sourced materials at 0.1 mg_{PGM}/cm^2 and in second lab.
Oct-2012	Go/No-Go: Simultaneously achieve Milestones 1 and 2 with one material	GM D-$PtCo_3$ satisfies, with above caveats. Still need to achieve with large-batch JM material and in 2nd lab
Dec-2012	Milestone 3: Initial high-current-density performance in H_2/air at cathode loaded ≤0.1 mg_{Pt}/cm^2 at least 560 mV at 1.5A/cm^2 in 50 cm^2 cell	D-$PtNi_3$ satisfies at GM. Still need to test in 2nd lab.
Nov-2013	Milestone 4: Scaleup and durability of high-current-density performance in full-active-area short stack in H_2/air under accelerated durability testing	Can't start until previous tasks are further along

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

Technical Accomplishment:
GM Dealloyed-$PtCo_3$ numerically satisfies both activity and durability milestones (but tested at $0.2 mg_{PGM}/cm^2$)



Provides existence proof for a dealloyed catalyst meeting the durability requirement

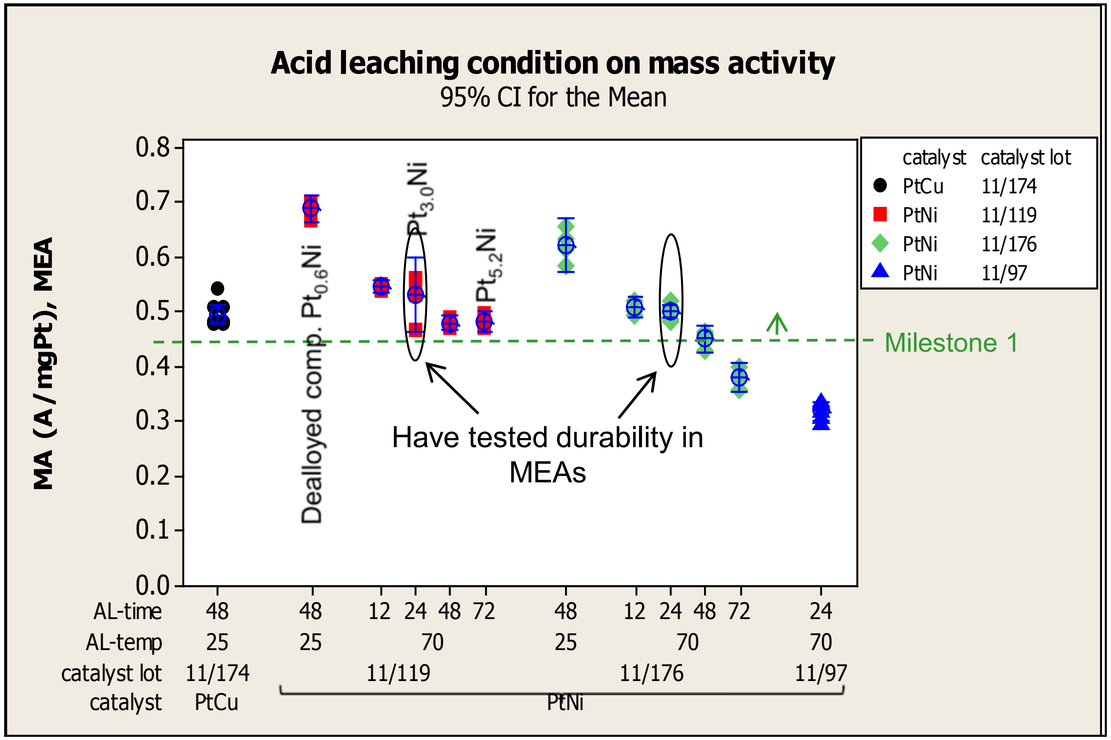
Caveats:

- •GM-made (2 g scale), not large (100 g) JM batch
- • Not tested in 2nd lab
- •Modernized MEA testing conditions (4 min/point, pretreatment)
- •130% of activity of commercial alloy, not intended doubling

Technical Accomplishment:

JM large-batch $PtCu_3$ and $PtNi_3$ satisfy initial activity target when dealloyed and MEA-tested at GM

GM 50 cm^2 MEAs, H_2/O_2, at 0.1 mg_{Pt}/cm^2



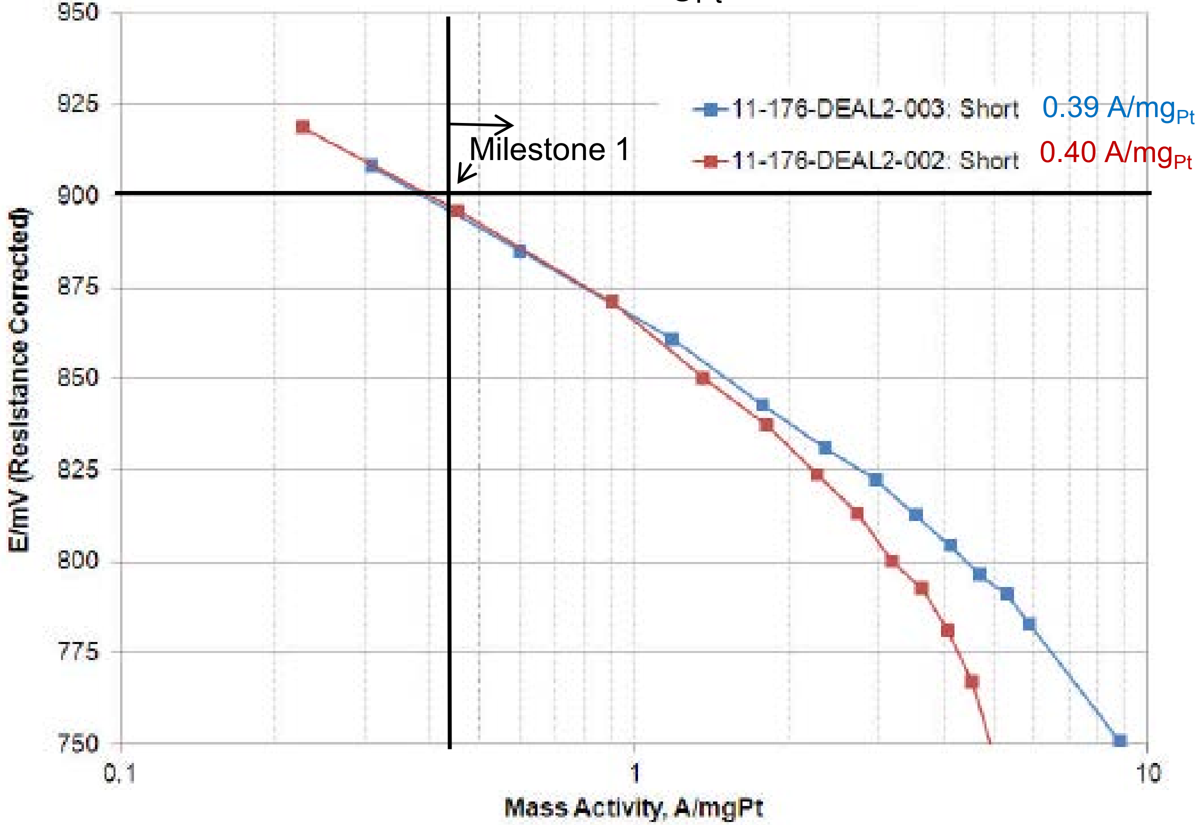
- Initial kinetic activity decreases with increasing severity of acid leaching (AL)
- individual data points are for separate MEAs (4-7 for each type)
- error bars show 95% confidence intervals for the mean
- All precursors from JM. 11/97 is early small batch. All others are large batches (~100 g)

- These are also 4 min/polarization curve point (averaging over last minute)
  - ➢11/119 24h 70°C also tested with old protocol (13min/pt, without prereduction) and passed milestone 1)
- After break-in (~7 h for D-$PtNi_3$)

Technical Accomplishment:

JM MEA tests of D-PtNi$_3$ activity close to, but below, Milestone 1

JM 49 cm^2 MEAs, at 0.1 mg$_{Pt}$/cm^2, 4 min holds



= current density (A/cm^2) / Pt loading (mg$_{Pt}$/cm^2)

JMFC data

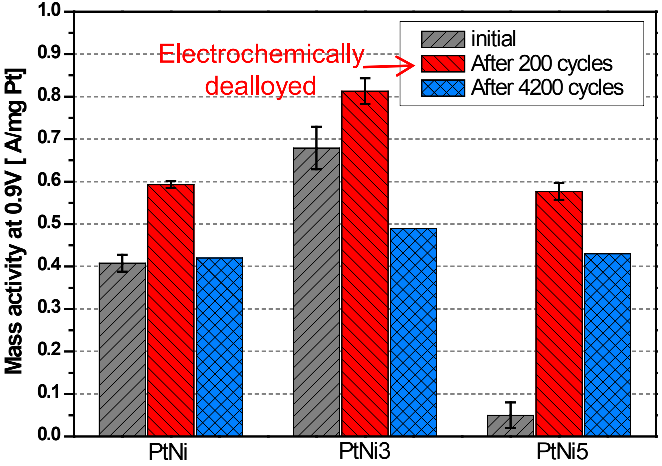
- for JM-dealloyed large-batch JM 11/176 PtNi$_3$
- two different ink formulations from same catalyst
- previous measurement for this catalyst had shown 0.37 A/mg$_{Pt}$

➔ 0.39 ±0.04

- other ink types and dealloying procedures have given lower activities

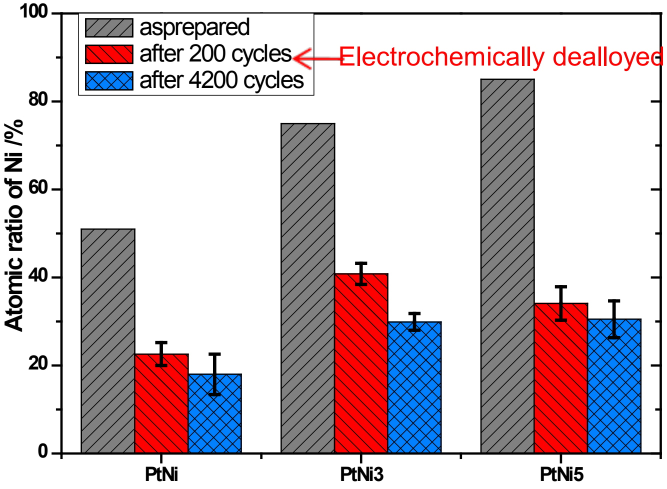
- JM is switching to full-active-area test stands, which they consider more reliable, for further work under this project

Technical Accomplishment:
Tech. Univ. Berlin found (1) broad maximum in activity at initial composition of $PtNi_3$ (RDE data), (2) nonlinear correlation between initial and dealloyed compositions



Electrochemically dealloyed

x-axis labels: composition before dealloying



Electrochemically dealloyed

From Energy-Dispersive Spectroscopy

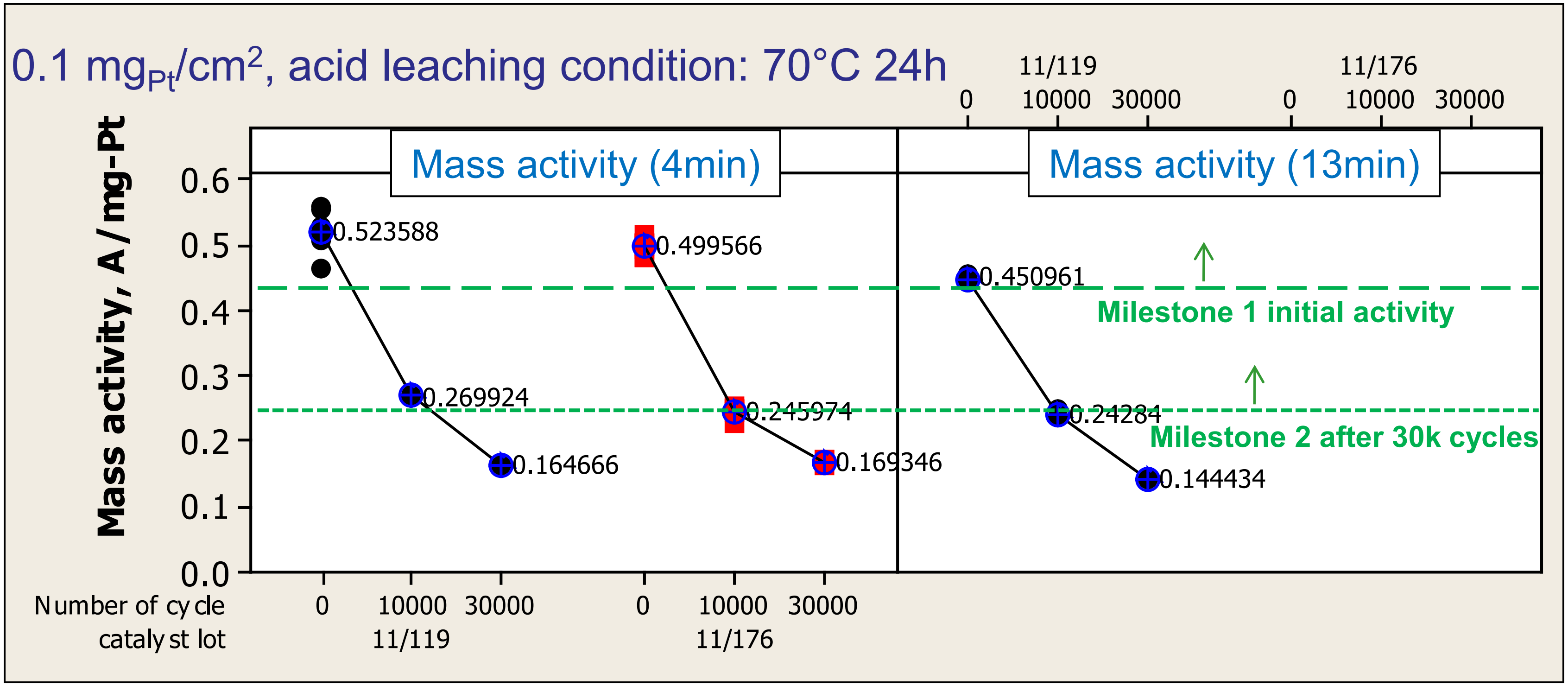
- $PtNi_3$ gave highest mass (and specific) activities
  - At initial composition
  - After electrochemical dealloying (200 cycles 0.6-1.0 V)
  - After “RDE durability” test (additional 4000 cycles 0.5-1.0 V
  - Other compositions also checked; no sharp maximum as reported by 3M for NSTF

- More Ni in precursor does not necessarily mean more Ni remaining
  - After electrochemical dealloying (200 cycles 0.6-1.0 V)
  - After “RDE durability” test (additional 4000 cycles 0.5-1.0 V
- Higher initial Ni content gives more access of acid to particle interiors

TUB has prepared 2 g of low-temperature codeposited $PtNi_3$ for MEA testing by GM and JM

Technical Non-accomplishment to Date:

Durabilities of catalysts dealloyed (by one method) from 2 large batches of JM D-$PtNi_3$ have proven inadequate in GM 50 cm^2 testing



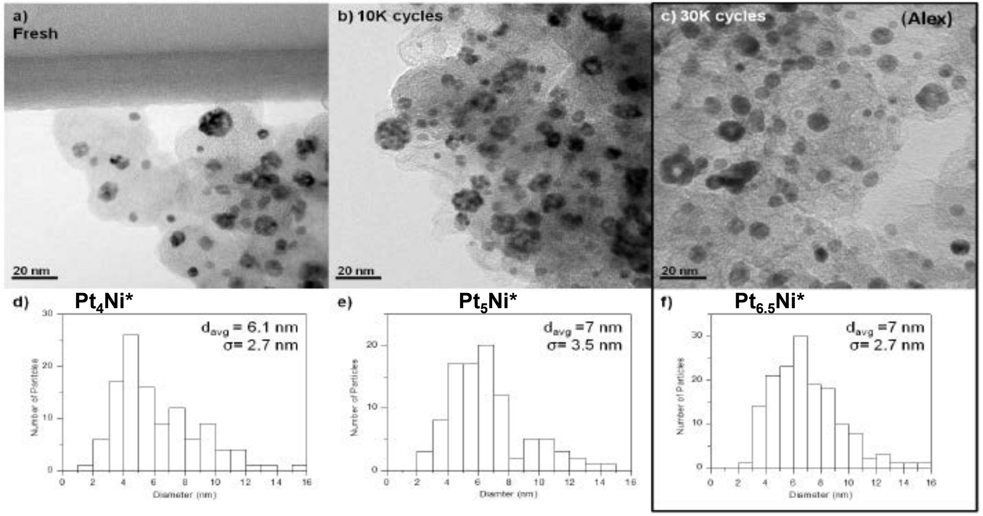
0.1 mg_{Pt}/cm^2, acid leaching condition: 70°C 24h

- lost 66-68%% of initial activity at 30,000 cycles 0.6-1.0V, not the ≤40% of Milestone 2
- Significantly worse than GM D-$PtCo_3$ (tested at 0.2mg_{Pt}/cm^2)
- Running detailed characterization to find origins of durability inferior to GM D-$PtCo_3$
  - ➢Ni and Co should have similar corrosion chemistries and Pt-M interaction strengths

Technical Accomplishment:

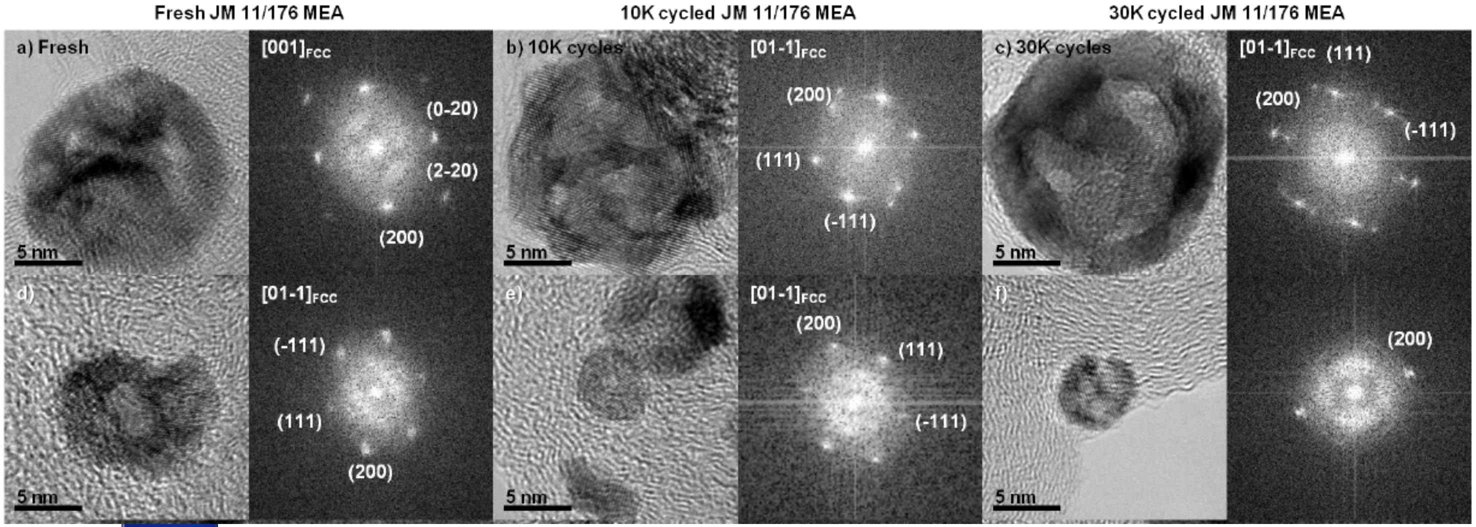
Electron microscopy suggests reasons for poor durability of the tested D-$PtNi_3$

MIT micrographs of 11/176 D-$PtNi_3$ MEAs cycled at GM

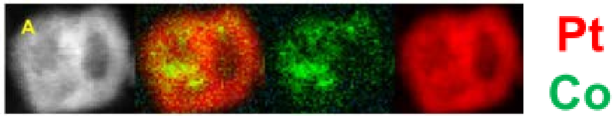


- 11/176 $PtNi_3$ shows
  - − unusually broad and non-normal particle size distribution
    - ➢ JM had focused on single-phase, with and without superlattice
  - −contrast within particles *of all sizes*
    - ➢In contrast to MIT experience with commercial Pt_3Co, where only large particles were spongy
    - ➢ can see through to turbostratic carbon – are holes

*** Compositions estimated from EXAFS coordination numbers**



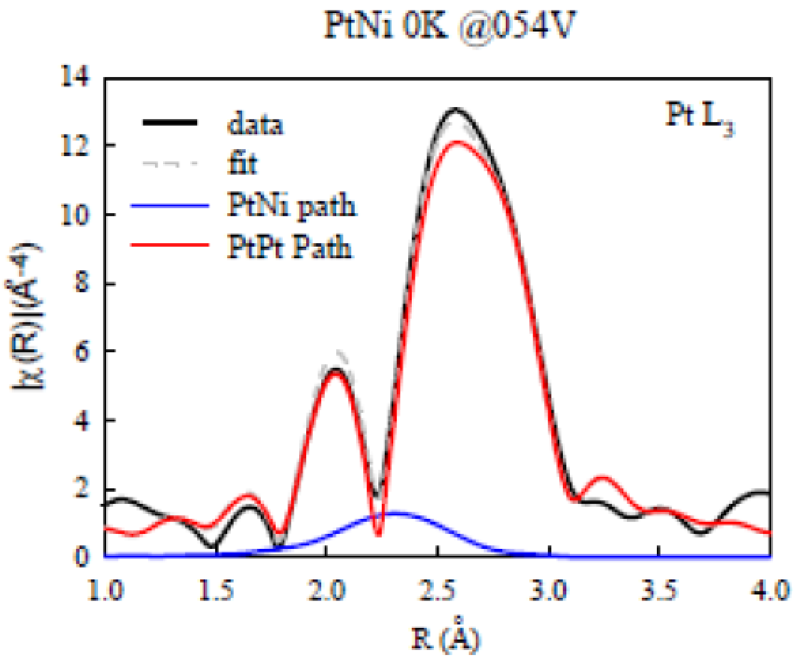
- •Fourier transform shows each particle is a single crystal, despite holes
- **•Smaller versions of Erlebacher crystalline ligament/pore networks?**

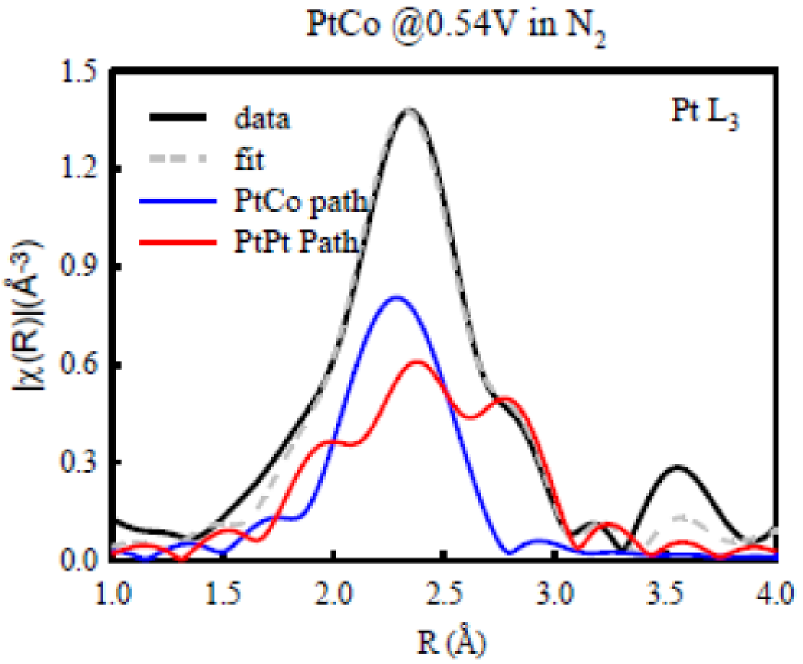


Last year, showed more durable D-$PtCo_3$ had Co-rich cores as well as holes. Other durable catalysts have just single cores.

Technical Accomplishment:

NEU/GWU EXAFS shows fewer Pt-M interactions in 11/176 D-$PtNi_3$ than in D-$PtCo_3$





- **$PtNi_3$: least alloying-element atoms in the neighborhood of each Pt atom**
  - In MEA, D-$PtNi_3$ to date looks like porous Pt particles with segregated Ni

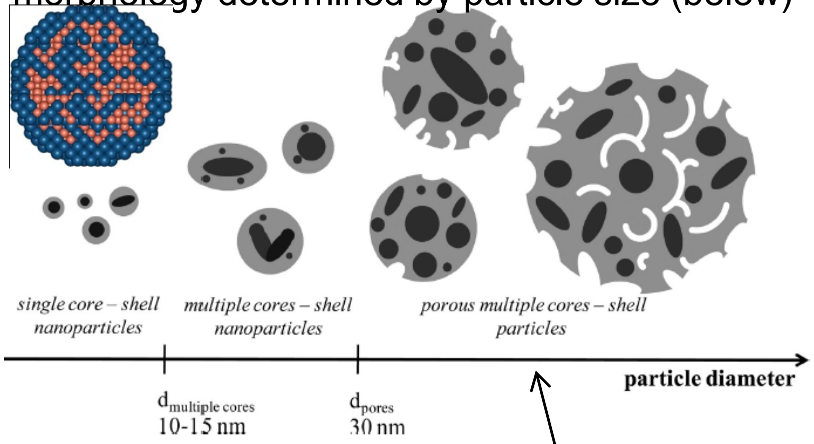
New XAS capabilities

- Developed method to do in-situ XAS of used fuel cell electrodes
  - Separate used catalyst-coated diffusion medium from membrane, build into liquid cell
- Δμ XANES evidence for –OO(H) adsorbate or for M atoms directly below Pt with adsorbed oxygen (M in immediate subsurface layer)

Future work:

Control relative rates of Ni dissolution and Pt surface diffusion during dealloying to improve durability

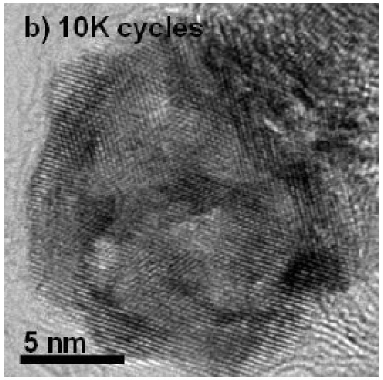
- Dissolution proceeds from surface inwards along domains with sufficiently-large clusters of non-noble atoms
- Shao-Horn pre-project work suggested porous networks from high initial non-noble atom concentration
  - our starting non-noble concentration above threshold for percolation
- Strasser pre-project work suggested particle morphology determined by particle size (below)



For small particles, Pt need surface-diffuse over only short distances to encapsulate remaining alloy, avoid pores

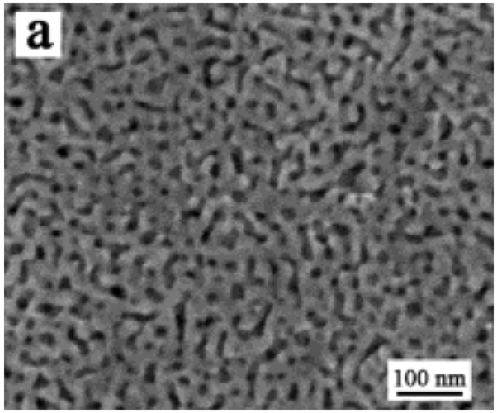
From M. Oezaslan, M. Heggen and P. Strasser, J. Am. Chem. Soc. 134 (2012) 514, used with permission from the American Chemical Society

In 11-176 D-$PtNi_3$, got little encapsulation – Ni dissolution too fast vs. Pt surface diffusion?



Nanoparticle version of Erlebacher-type pore formation?

- Erlebacher dealloying of continuous films showed ligament/pore network controlled by relative rates of nonoble-element dissolution and noble atom *surface* diffusion



Surface diffusion lengths too long for Pt to encapsulate remaining alloy, get porous network of nearly pure noble metal maintaining original lattice

From Y. Ding and J. Erlebacher, J. Am. Chem. Soc. 125 (2003) 7772, used with permission from the American Chemical Society

Future work:

Steps to improve durability

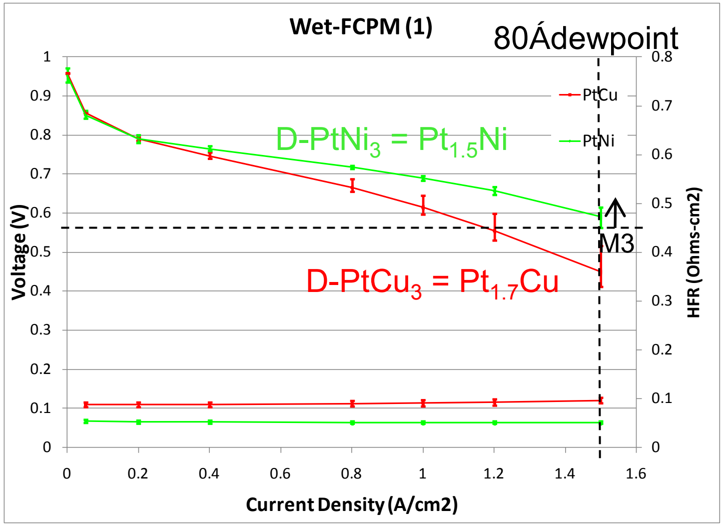
- Want more core/shell, less pores, but with high M content in cores
  - Decrease M dissolution rate vs. Pt surface diffusion rate during dealloying
    - Use less aggressive chemical leachant to slow M dissolution and/or higher temperature and/or added complexing ions to increase Pt surface diffusion rate
- Start with more uniform particle sizes
  - JM running 6 different $PtNi_3$ preparation methods
  - TUB low-temperature codeposited $PtNi_3$ (2g) being tested in MEAs by GM and JM
- Is $PtCo_3$ intrinsically more corrosion-resistant than $PtNi_3$?
  - Seems unlikely from known corrosion properties and heats of mixing, but JM will make a $PtCo_3$ analog
  - Note: TUB had looked at a wide range of alternate alloying elements in preproject work
- Ternary systems
  - GM has added Au or Ir in bulk, TUB has added Au or Pd on surface
    - To date, no very encouraging results
  - Additional component to increase flux of diffusing Pt adatoms during dealloying
  - JM exploring addition of passivating elements

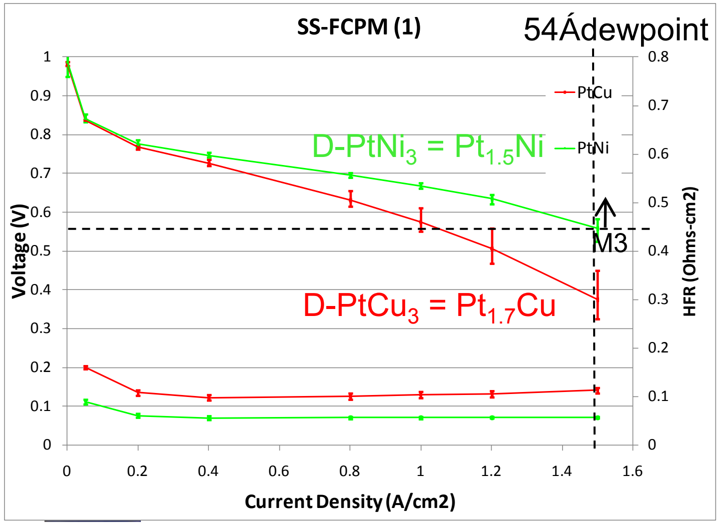
Technical Accomplishment:

Air performance for D-$PtNi_3$ improved vs. D-$PtCu_3$ with similar dealloyed stoichiometries ($Pt_{1.7}Cu$ and $Pt_{1.5}Ni$), meets Milestone 3 criterion at 1.5 A/cm^2

GM 50 cm^2 MEAs, at 0.1 mg_{Pt}/cm^2

Conditions: H_2/air, 80ÁC, dewpoints as noted, backpressure 170 kPa_{abs}, stoichs 2/2





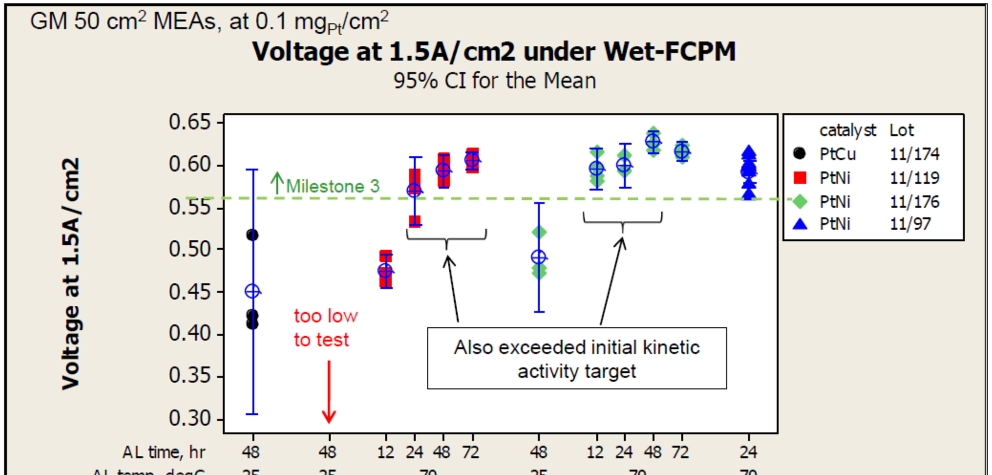
- Last year showed worse high-current air performance with more Cu remaining after dealloying, and showed that Cu plated on anode
- 1.5 A/cm^2 performance better for D-$PtNi_3$ than D-$PtCu_3$ despite slightly more Ni in the electrode
- Ni required elevated-temperature dealloying to remove about the same amount of non-noble metal as was removed at room temperature for Cu

Note: Fuel Cell Tech Team Pol Curve has 59ÁC dewpoint

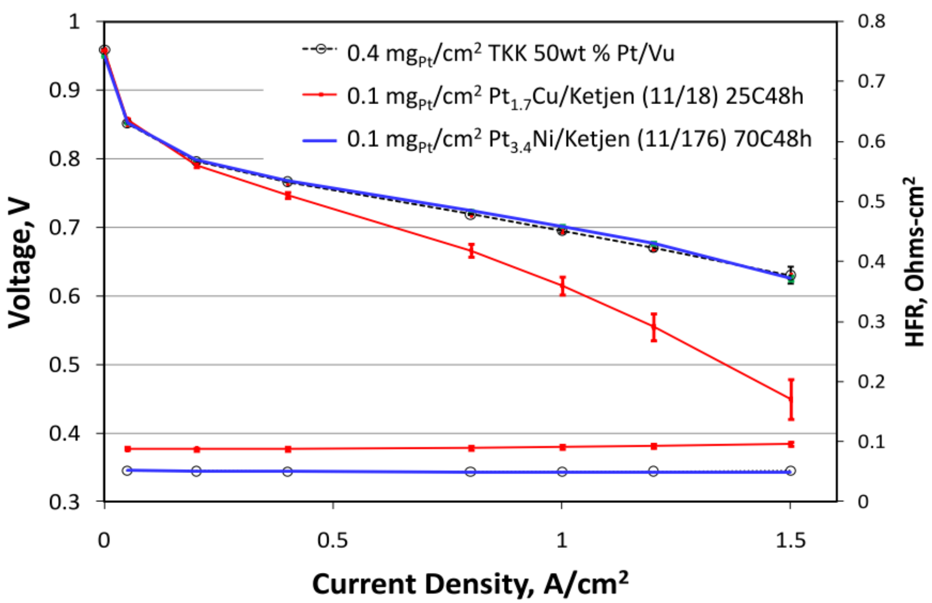
Data for earlier 11/97 JM small-batch D-$PtNi_3$ with inferior kinetic activity

Technical Accomplishment:

D-PtNi$_3$ range of dealloying conditions that give adequate high-current air performance overlaps conditions giving adequate kinetic activity



- part of PtCu losses due to metallic plating of Cu on anode
- 25°C D-PtNi3 (Pt0.6-0.8Ni) also gave poor air performance: no anode plating, but more non-noble metal remained after dealloying to cause problems when dissolved into ionomer (vs. Pt$_{1.7}$Cu)



D-PtNi$_3$ at 0.1mg$_{PGM}$/cm^2 matches performance of Pt at 0.4mg$_{PGM}$/cm^2 over entire H$_2$/air pol curve

- big improvement at high current over D-PtCu$_3$ with similar initial kinetic activity

Future work:

- Durability improvements
  - Alternate $PtNi_3$ syntheses at JM and TUB
  - Already-discussed changes in dealloying to control Ni dissolution vs. Pt surface diffusion at JM, TUB, and GM
- Continue improvements to activities
  - Alternate prep methods for $PtNi_3$ at JM and TUB
  - Alternate dealloying methods, posttreatments at JM, GM, and TUB
- Advanced characterization
  - Performance/structure correlations from good/bad pairs of durability-tested MEAs at NEU, GWU and MIT
    - Pt shell thicknesses and lattice compressions, core alloying-element concentrations, subsurface layer alloying atom concentrations and movement, changes in oxygen adsorbates
- Initial high current density performance in air at GM and JM
  - Durability improvements should reduce transition ions in ionomer
  - Drive toward higher surface area
- Start testing durability of high-current-density performance at GM and JM

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
  - Scaleup of synthesis, improved manufacturability of dealloying, incorporation and testing in 49 cm^2 and larger fuel cells
- 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, Δμ XANES

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

Tech transfer: University ➔ Catalyst manufacturer ➔ Stack integrator

Summary:

- Project has moved from D-$PtCu_3$ to large-batch JM D-$PtNi_3$
  - ➢Enabled us to match, at 0.1 mg_{PGM}/cm^2 in GM 50cm^2 MEAs, both kinetic and high-current air performance of Pt/C at 0.4 mg_{PGM}/cm^2
- D-$PtNi_3$ to date has shown poor durability
  - ➢Believe this is due to structural shortcomings that we have plans to alleviate
    - −GM small-batch D-$PtCo_3$ shows that dealloyed systems can meet the durability criterion

PGM = Platinum-group metal

Metric	units	2011	2012	2015 DOE target
Mass activity	A/mg_{PGM} @ 900mV$i_{R\text{-free}}$	0.6 ($PtCu_3$) 0.37 ($PtCo_3$)	0.46($PtCo_3$) 0.52 ($PtNi_3$)	≥ 0.44
Loss in catalytic (mass) activity	% lost after 30k cycles 0.6-1.0V	38%($PtCo_3$) 83%($PtCu_3$)	28%($PtCo_3$) 69% ($PtNi_3$)	≤ 40%
PGM Total Content	g_{PGM}/kW_{rated}	0.19($PtCu_3^*$) @1.5A/cm^2 in H_2/air	0.16 ($PtNi_3$) @1.5A/cm^2 in H_2/air	≤0.125
PGM Total Loading	mg_{PGM}/cm^2_{geo}	0.15($PtCu_3$)	0.15 (anode still 0.05)	≤ 0.125
Specific activity	$\mu A/cm^2_{PGM}$	860 ($PtCu_3$)	1460 ($PtNi_3$)	720
Catalyst support stability	% mass loss of support	TBD	TBD	< 10%

Note: some 2011 $PtCu_3$ numbers were for differently-dealloyed catalysts*; all 2012 $PtNi_3$ numbers are for the same MEAs

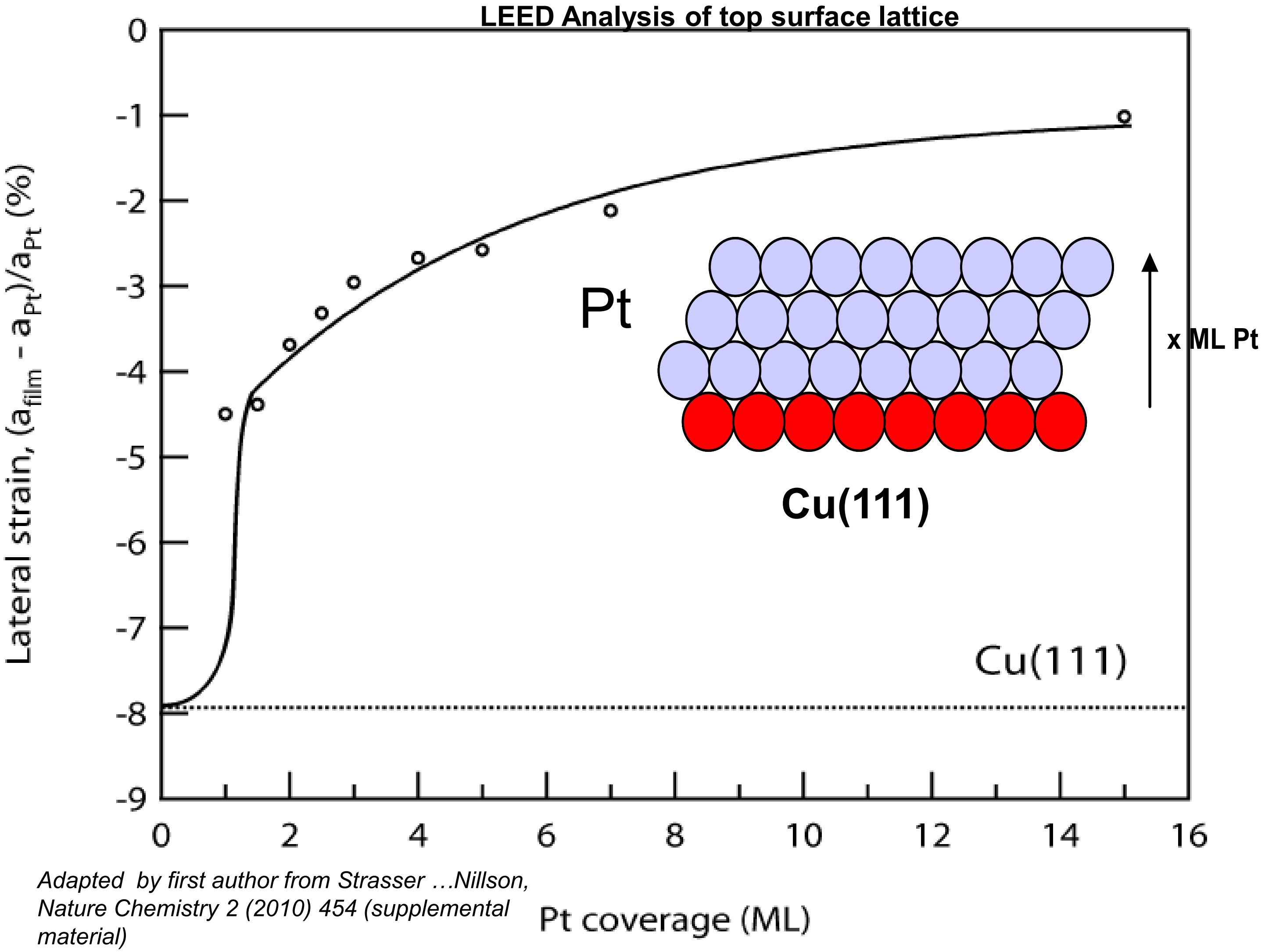
* In 2011, to get decent air performance at 1.5 A/cm^2, needed to remove more Cu than would satisfy mass activity target, as noted on Table in 2011

- data from pre-project $PtCu_3$ precursor (small batch) in red
- $PtNi_3$ is from JM large-batch precursor
- $PtCo_3$ is from GM small-batch precursor

Technical Back-Up Slides

Background information: Compressive strain in (111) model ‘Cu core – Pt shell’ structures

- LEED study shows that *lattice strain is longer range than ligand effects*, > 10 layers
- **surface compression can be thermodynamically stable**



Also used as a backup slide for last year’s AMR presentation

Adapted by first author from Strasser …Nillson, Nature Chemistry 2 (2010) 454 (supplemental material)

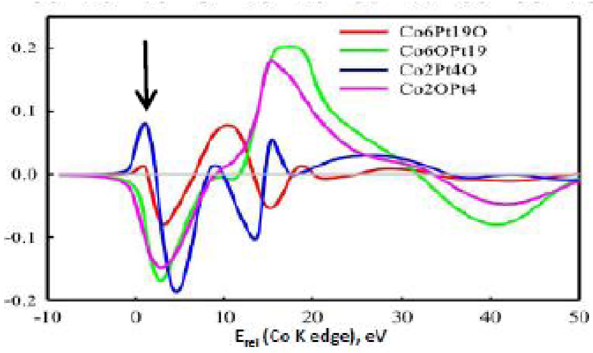
Technical Accomplishment:

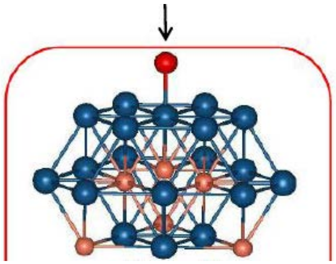
Northeastern U. and George Washington U. data

X-ray Absorption Spectroscopy Refined as Tool for Characterizing Atomic-Scale Structure and Composition of Catalysts Used in MEAs

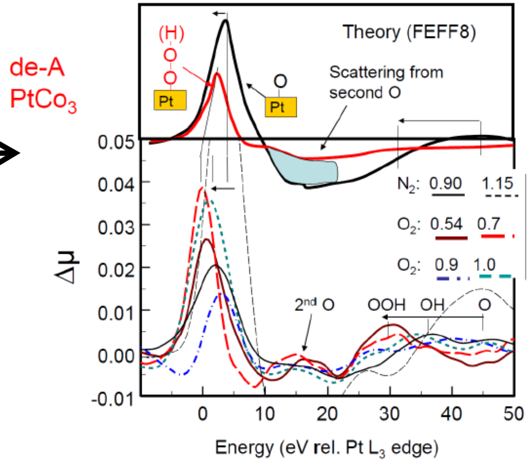
- Developed methodology for electrochemical XAS of used cathode electrodes from MEAs
  - ions dissolved into the membrane had confounded analysis
  - run durability of catalyst coated diffusion media (CCDM), separate CCDM from membrane, build CCDM into $HClO_4$ electrochemical cell

- Δμ XANES signature identified for oxygen bound to Pt atom above alloying elements in second layer
  - chance to quantify, in practical nanoparticles, alloying-element atoms in positions with strongest effects on activity
  - chance to quantify near-surface motion of alloying-element atoms

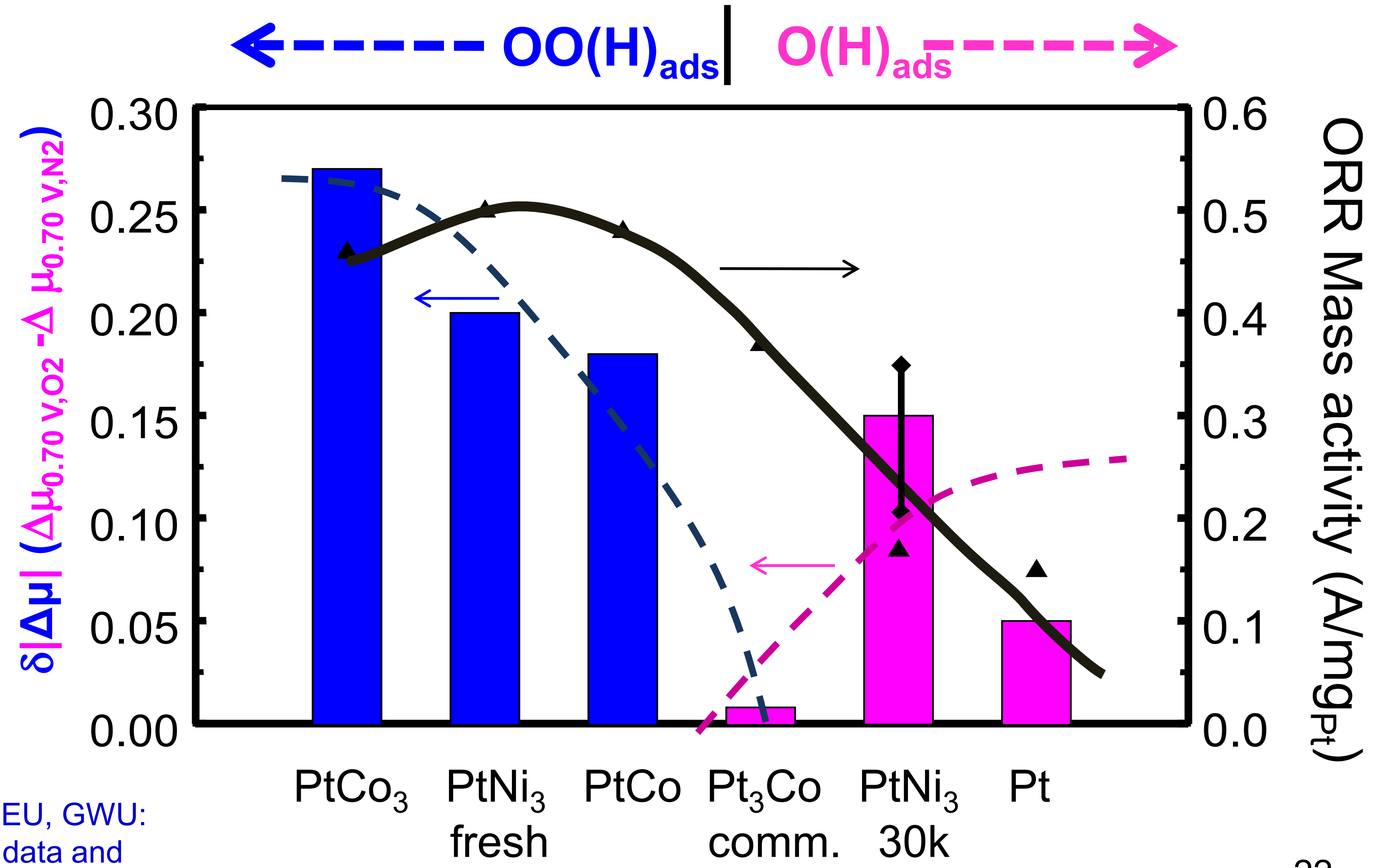




- Δμ XANES signature identified for adsorbed dioxygen species
  - correlate activity with surface concentration of a possible intermediate

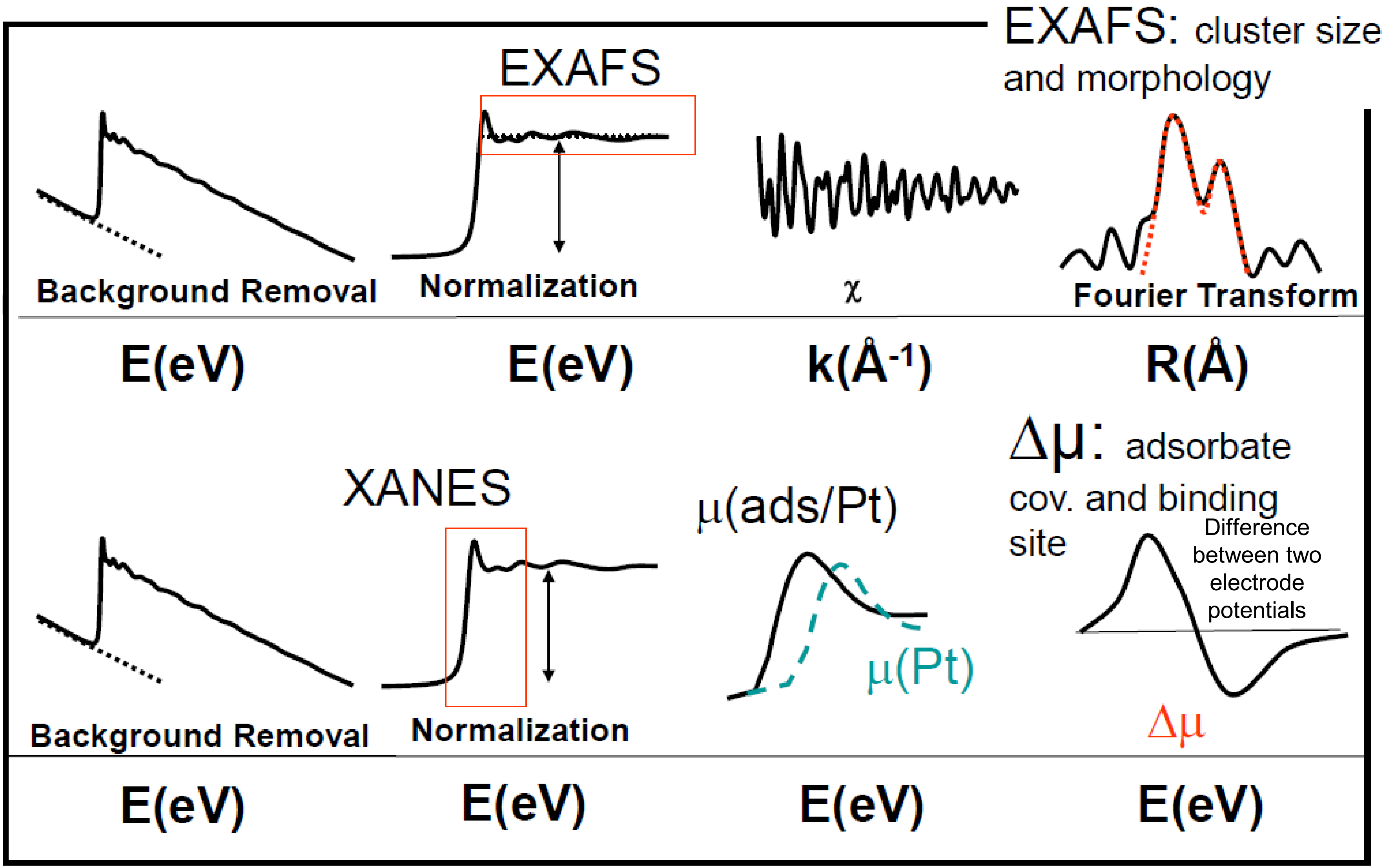


Oxygen adsorbates at 0.7 V RHE (O_2 sparging) from Δμ XANES correlated with ORR activity



NEU, GWU: data and analysis

Schematic illustration of XAS techniques



EXAFS: cluster size and morphology

Δμ: adsorbate cov. and binding site

Difference between two electrode potentials

Comparison of mass activities, specific activities, and surface areas

Catalyst	Dealloying	Cycles 0.6-1.0V RHE	Mass act. (A/mg_{Pt})	Spec. act. ($\mu A/cm^2_{Pt}$)	Echem. Surface Area (m^2/g_{Pt})
D-$PtCu_3$	25°C, 48h	0	0.58	1040	56
		10,000	0.10	270	37
D-$PtCo_3$	80°C, 24h	0	0.46	1000	46
		30,000	0.33	1030	32
D-$PtNi_3$ 11/119	70°C, 24h	0	0.52	1460	36
		30,000	0.16	940	17
D-$PtNi_3$ 11/176	70°C, 24h	0	0.50	1280	39
		30,000	0.17	810	21

Note: The two D-$PtNi_3$ datasets are for large precursor batches from JM; the D-$PtCu_3$ and D-$PtCo_3$ data are not. Precursor preparations are not all analogous; i.e., differences in performance need not be due to the differences between the metals used.