

High-Activity Dealloyed Catalysts

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FC087



Overview

Timeline

- Project start date: 1 Aug 2010
- Project end date: 31 May 2013
- Percent complete: 10%

Budget

- Total project funding: \$5,952,827
 - DOE share: \$4,762,313
 - Contractor share: \$1,190,514
- Funding received in FY10: \$1,350,000 (very little actually spent)
- Funding for FY11: \$1,351,712

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 $0.44 \text{ A/mg}_{\text{PGM}}$ in H_2/O_2 fuel cells
 - 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 $<0.125 \text{ g}_{\text{Pt}}/\text{kW}$ and $<0.125 \text{ mg}_{\text{Pt}}/\text{cm}^2_{\text{geo}}$
 - 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

- Pt alloys, typically Pt_3M , have typically given 2x the oxygen reduction activity of Pt/C
- Strasser: If start instead with PtM_3 , voltage cycle to give a 6- to 9-fold reduction of M content, get activities exceeding DOE mass activity target of 0.44 A/mg_{Pt} @900mV
 - Koh, S. **Strasser, P.**, *J. Am. Chem. Soc.* **2007**, 129, 12624-12625.
 - Some previous claims of perhaps-similar effects, but with very low reported activities for baseline Pt catalysts: Toda, T.; Igarashi, H.; Uchida, H.; Watanabe, M., *J. Electrochem. Soc.* **1999**, 146, 3750-3756.
- Improved activity ascribed to lattice compression (M smaller than Pt) (Strasser et al., Nature Chemistry 2 (2010) 454-460)
 - Can such compression be thermodynamically stable against dissolution/redeposition of top Pt layer?
 - LEED of Pt layers on Cu(111) showed compression up to 15 monolayers
 - Relative importance of lattice compression vs. direct ligand effects of M?
- This project:
 - Develop manufacturable methods of catalyst synthesis and dealloying (prior to incorporation in MEA)
 - Avoid negative effects of transition metal ions in ionomer
 - Improve durability while maintaining high initial activity.
 - Achieve steady-state structures that maintain high activity; proper choice of composition
 - Develop electrodes that give good high-current-density performance in H₂/air with these catalysts
 - Answer a fundamental question: ***Where should alloying-element atoms be in a Pt-based catalyst particle for maximum durable activity?***

Approach: Milestones and Go/No go

Month/Year	Milestone or Go/No-Go Decision	Status
Sep-2011	Milestone 1: ORR mass activity >0.44 A/mgPt reliably achieved in at least two labs, one in ≥ 50 cm^2 fuel cell	Achieved with PtCu_3 but need more durability; close for PtCo_3
Apr-2012	Milestone 2: Durability of kinetic activity. $\geq 60\%$ of initial mass activity maintained in two labs after 30,000 cycles 0.6-1.0V RHE	Major problems for PtCu_3 , achieved (one lab) for PtCo_3
Apr-2012	Go/No-Go: Simultaneously achieve Milestones 1 and 2 with one material	TBD: combine properties conferring activity with those conferring durability
Sep-2012	Milestone 3: Initial high-current-density performance in H_2/air at cathode loaded ≤ 0.1 $\text{mg}_{\text{Pt}}/\text{cm}^2$ at least 560 mV at $1.5\text{A}/\text{cm}^2$ in 50 cm^2 cell	Still far short – need catalyst development and electrode optimization
Aug-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	Not started

Collaborations (subcontractors)

- GM



- Overall project guidance, testing of catalysts and MEAs, characterization

- 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



Johnson Matthey Fuel Cells
the power within

- Scaleup of synthesis, improved manufacturability of dealloying, incorporation and testing in 50 cm² and larger fuel cells

- Massachusetts Institute of Technology (MIT) (university) – Prof. Yang Shao-Horn

- Electron microscopy, dealloying interpretation, preparation of alternate 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

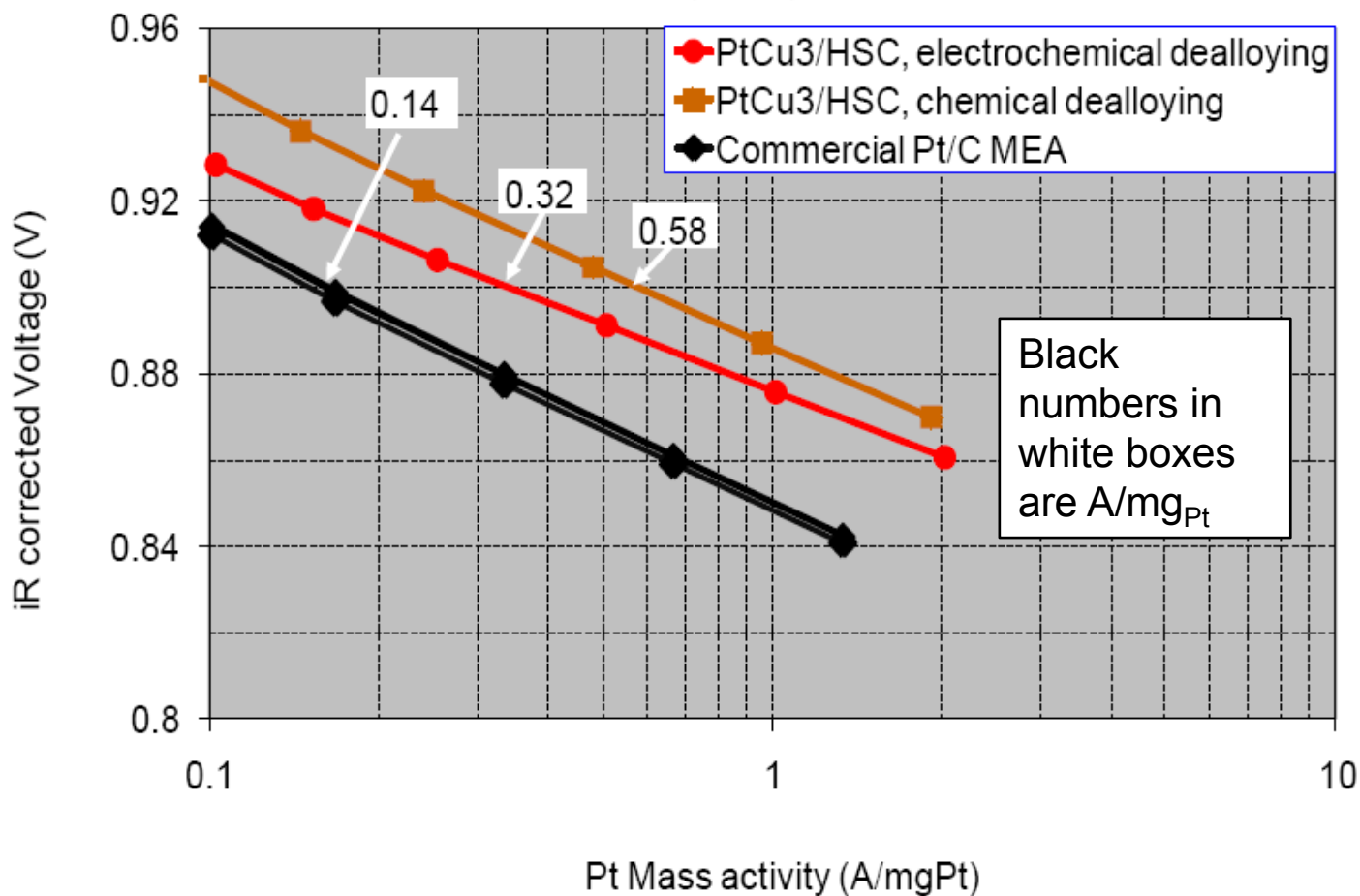


Tech transfer: University → Catalyst manufacturer → Stack integrator

Technical Progress: Demonstrated initial mass activity $>0.44 \text{ A/mg}_{\text{Pt}}$ in GM 50 cm^2 fuel cells made with manufacturable dealloying processes

Pt mass activity, H_2/O_2 , Stoich 2/9.5;
100% RH; 80°C ; 150 kPa

(pre-project data)

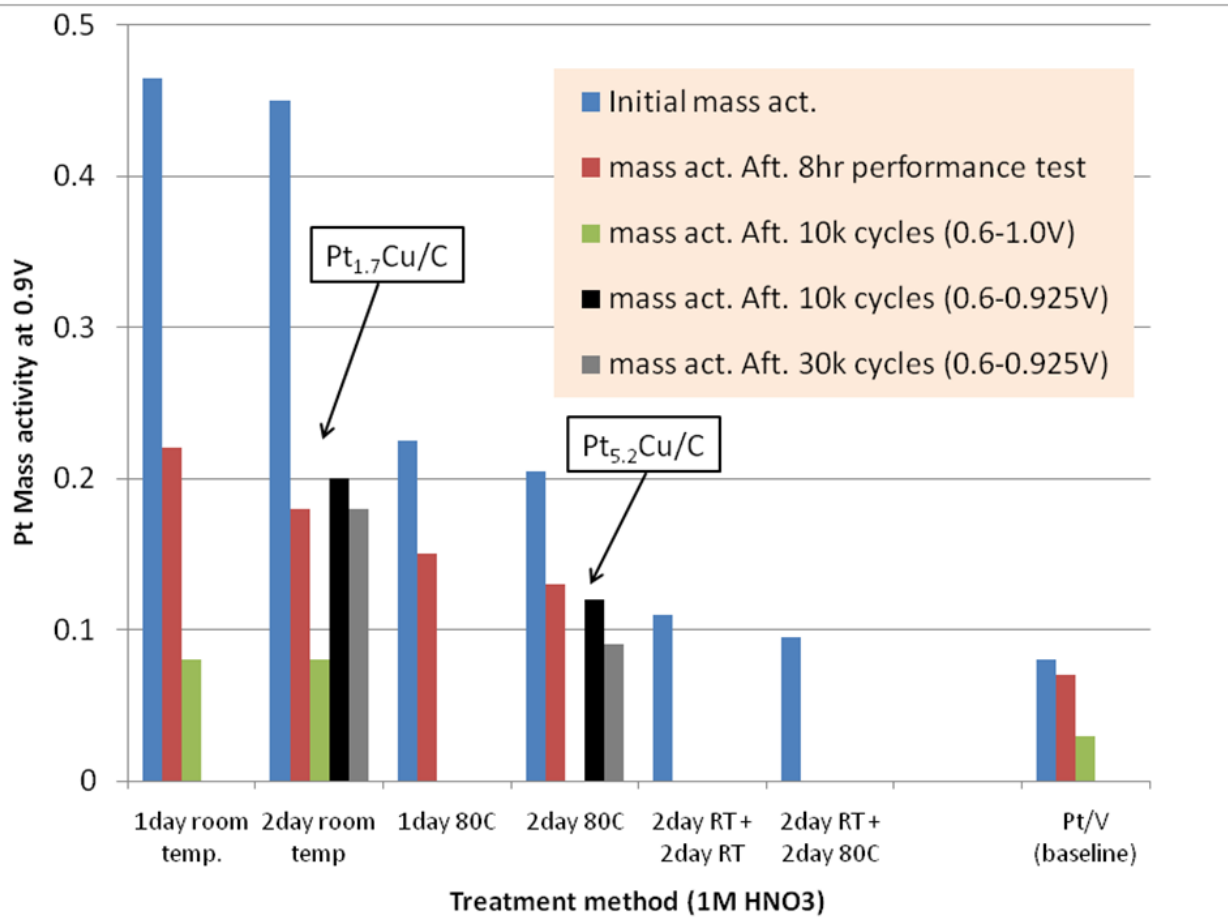


- In pre-project work, GM developed methods to dealloy U of Houston PtCu_3 precursor in powder form (before making electrodes)
- 15 min/point, ascending current densities

Technical Progress: Residual Cu content is critical; identified durability issues with GM-dealloyed UofH PtCu₃ in 50 cm² fuel cells

(Most of these data were prior to this project, but cycling to 0.925V under project)

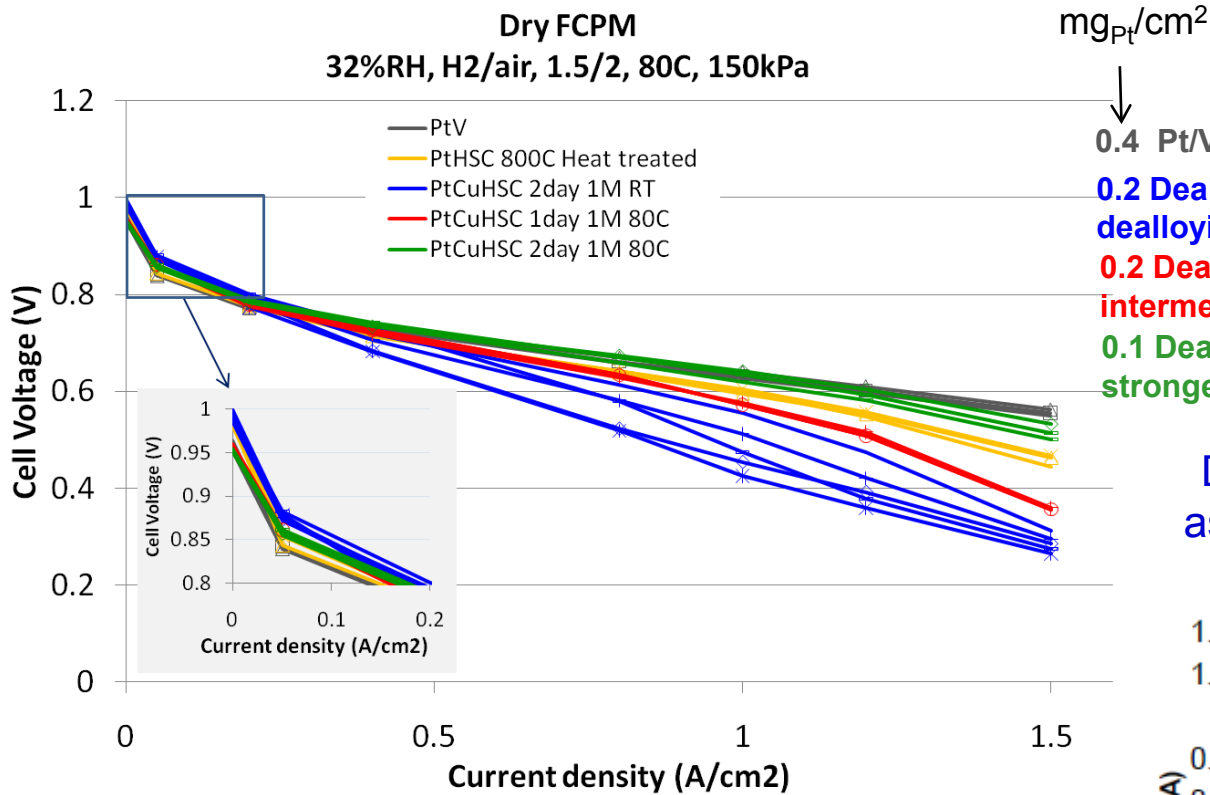
- Higher initial kinetic activity with higher initial Cu content
- Disappointing durability
- Suppressing upper voltage cycling limit significantly reduces losses



More copper removed →

Develop strategies to leave, and maintain, just the right amount of the right alloying element(s) in the right places

Technical progress: identify issues with initial high current density performance in air (50cm²) for UofH PtCu₃



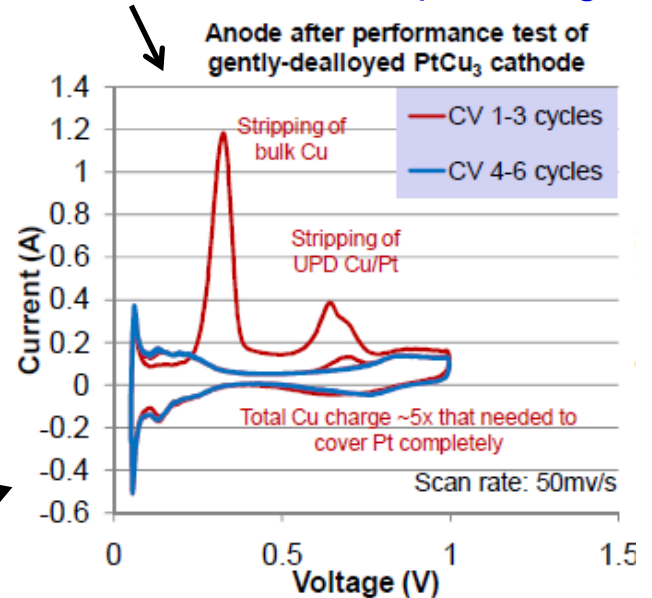
0.4 Pt/Vulcan

0.2 Dealloyed PtCu₃/HSC, weakest dealloying

0.2 Dealloyed PtCu₃/HSC, intermediate dealloying

0.1 Dealloyed PtCu₃/HSC, strongest dealloying

Dissolved excess Cu²⁺ plated as metal on anode, poisoning it



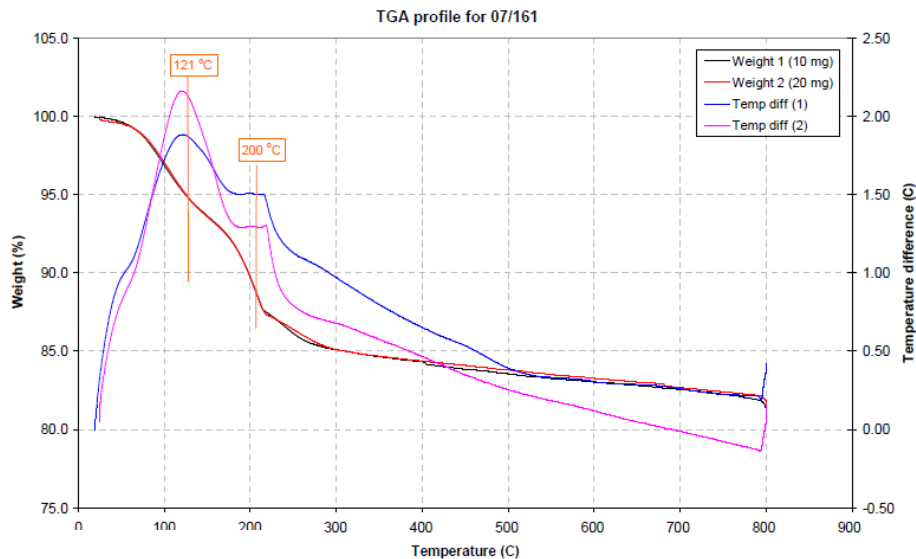
Opposite trends at low and high current density performance

• Excessive remaining Cu decreases high-current-density performance in air

- Cu²⁺ displaces H⁺ in ionomer (general for M)
 - Migration to cathode at high current density, starve ORR of H⁺ (Greszler et al., Fuel Cell Handbook V.6, Wiley 2009)
- Cu plates out on anode (unique to Cu)

Technical Progress: scale-up of production of catalyst precursor

- After deposition of Pt and alloying element, need to anneal
 - Improve mixing of Pt and M, in some cases reduce M precursor
 - Increase homogeneity of the active particles
- U of Houston / Tech. Univ. Berlin had annealed in batches <0.5 g



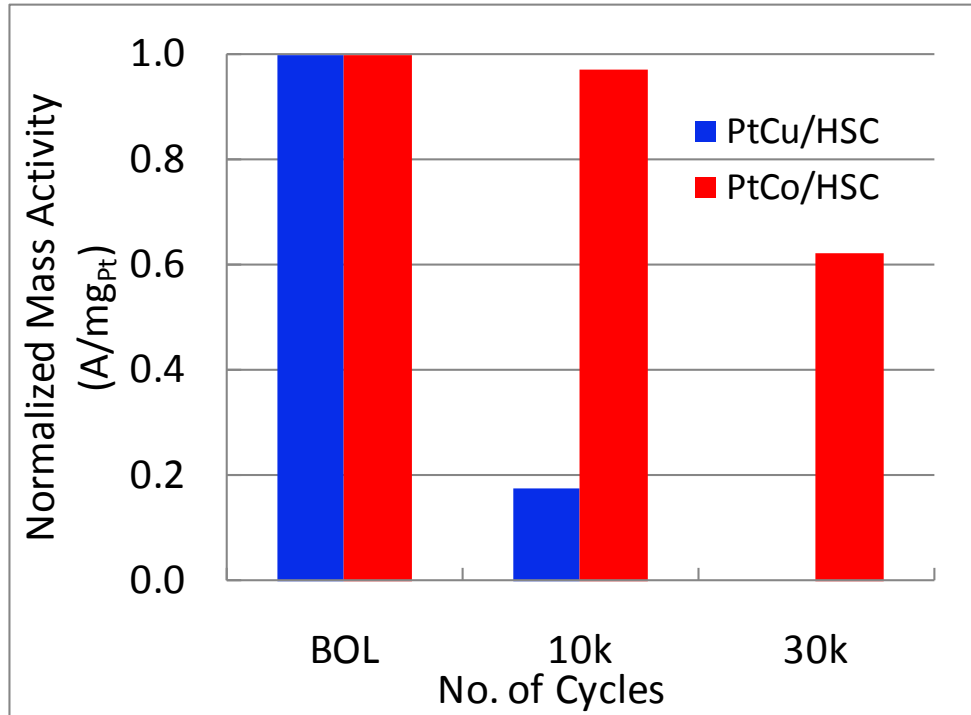
- JMFC had previously produced 1-10 g batches similar to Strasser's
- Initial JMFC 190 g anneals of PtCu₃ did not reproduce earlier small batches
 - Specific surface areas of 5-12 m²/g_{Pt} vs. 26 for 5 g batch
 - X-ray diffraction pattern did not show residual pure-Cu phase

- JMFC Differential thermal analysis showed exotherm at 121 and 200 °C
- If due to autocatalytic processes, could account for sintering of large batches

Revision of procedures recently yielded ~100 g batches with proper precursor surface area >20 m²/g_{Pt}

Technical Progress: Dealloyed GM PtCo₃ retains its activity better than dealloyed UofH PtCu₃

GM 50 cm² fuel cells; cycling 0.6-1.0V 50mV/s



catalyst	Initial mass activity (A/mg _{Pt})
GM-dealloyed UofH PtCu ₃	0.69
GM-dealloyed GM PtCo ₃	0.37

Use detailed characterization to identify drivers for activity and for durability – learn to get both simultaneously

Is the greater stability of PtCo due to

- chemistry differences between Cu and Co?
- differences between particle structures?

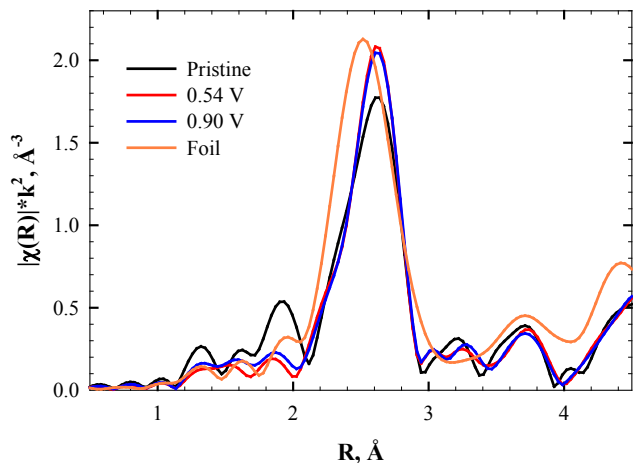
Preliminary TUB data suggest dealloyed PtNi₃ even more stable than PtCo₃

Technical Progress: What is the local structure of active dealloyed PtCu₃? – GM *in situ* electrochemical Extended X-ray Absorption Fine Structure (EXAFS)

PtCu/Vulcan

Pre-project data

Representations consistent with EXAFS data

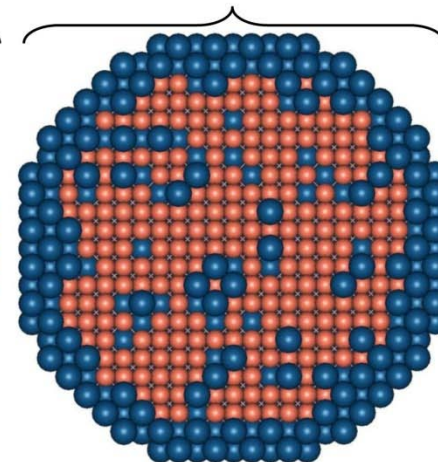
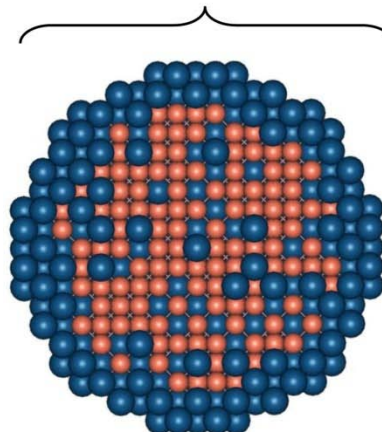


Cu K Edge

- $R_{\text{Cu-M}} > R_{\text{Cu-Cu}}$ in Foil (2.55 Å)
- 0.54 V \approx 0.90 V (Cu is buried)
- $N_{\text{Cu-Cu}} = 6.0$
- $N_{\text{Cu-Pt}} = 2.9$

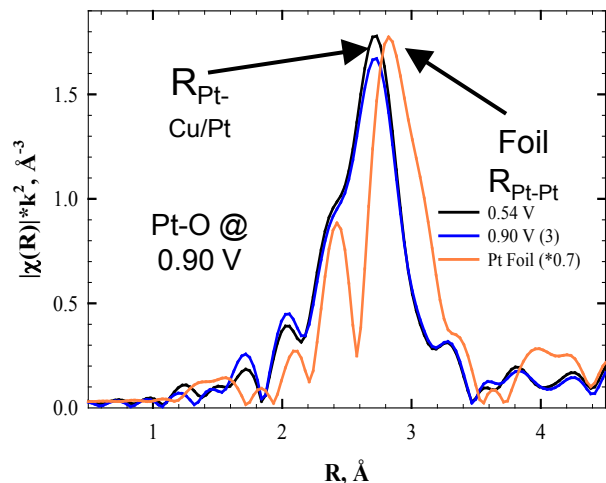
d (nm): 2.85_{core} 3.5_{total}

d (nm): 3.73_{core} 4.5_{total}



Pt-PtCu_{1.6}/Vulcan

Pt-PtCu_{1.8}/HSC



Pt L₃ Edge

- $R_{\text{Pt-M}} < R_{\text{Pt}}$ in Foil (2.77 Å)
- 0.54 V \neq 0.90 V (some Pt on surface)
- Obvious Pt-O @ 0.90 V (some Pt on surface)

Cu content of cores is still sufficiently high that one would expect dissolution if shell were penetrated

- Pt-Pt distances
 - average: 2.70 Å
 - shell: 2.74 Å
 - > 1.1% compression
- Pt-Cu 2.64 Å

Relatively thin (2-3 atom-thick) Pt shell leaves open the possibility that ligand effects, as well as the observed lattice compression, contribute to the enhanced activity.

Does activity correlate best with Pt-Pt compression or core M content (from EXAFS), or with d-band vacancies (from XANES) ?

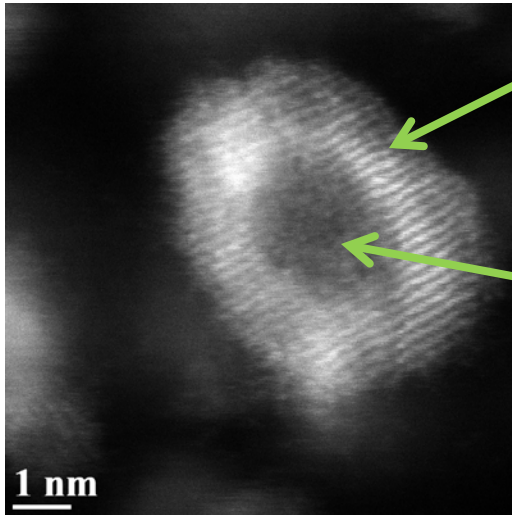


In situ EXAFS at Brookhaven NL synchrotron (NSLS), using beamtime under DE-AC02-98CH10886

HAADF “Z-contrast” TEM (at GM) for dealloyed PtCu₃ shows both

core-shell and “Swiss Pt” particles

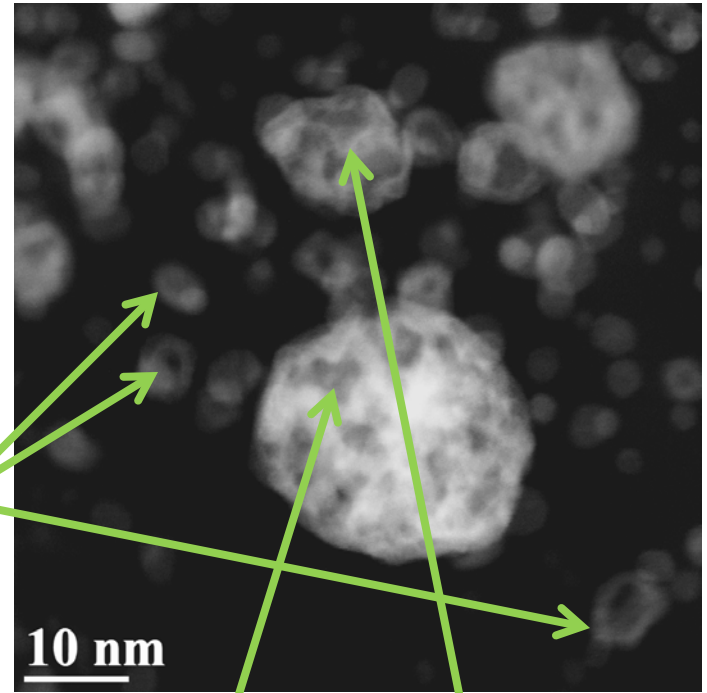
(High Angle Annular Dark Field)



Pt shell

Pre-project data

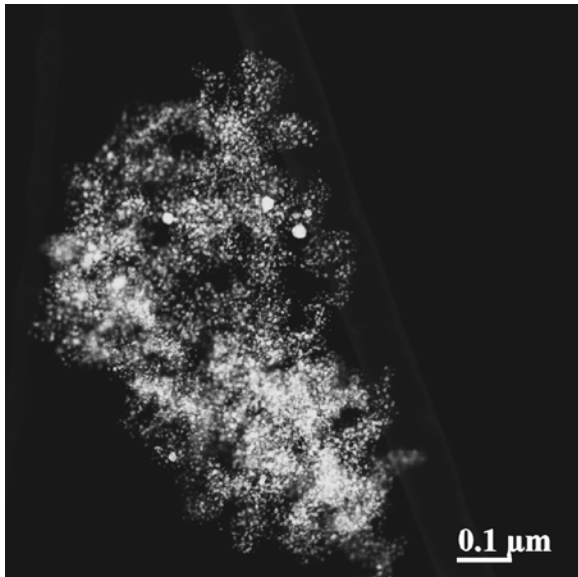
Pt-Cu Core



Many core-shells

Adapted in part with permission from F.T. Wagner, B. Lakshmanan, and M.F. Mathias, J. Phys. Chem. Lett. 1 (2010) 2204. Copyright 2010 American Chemical Society

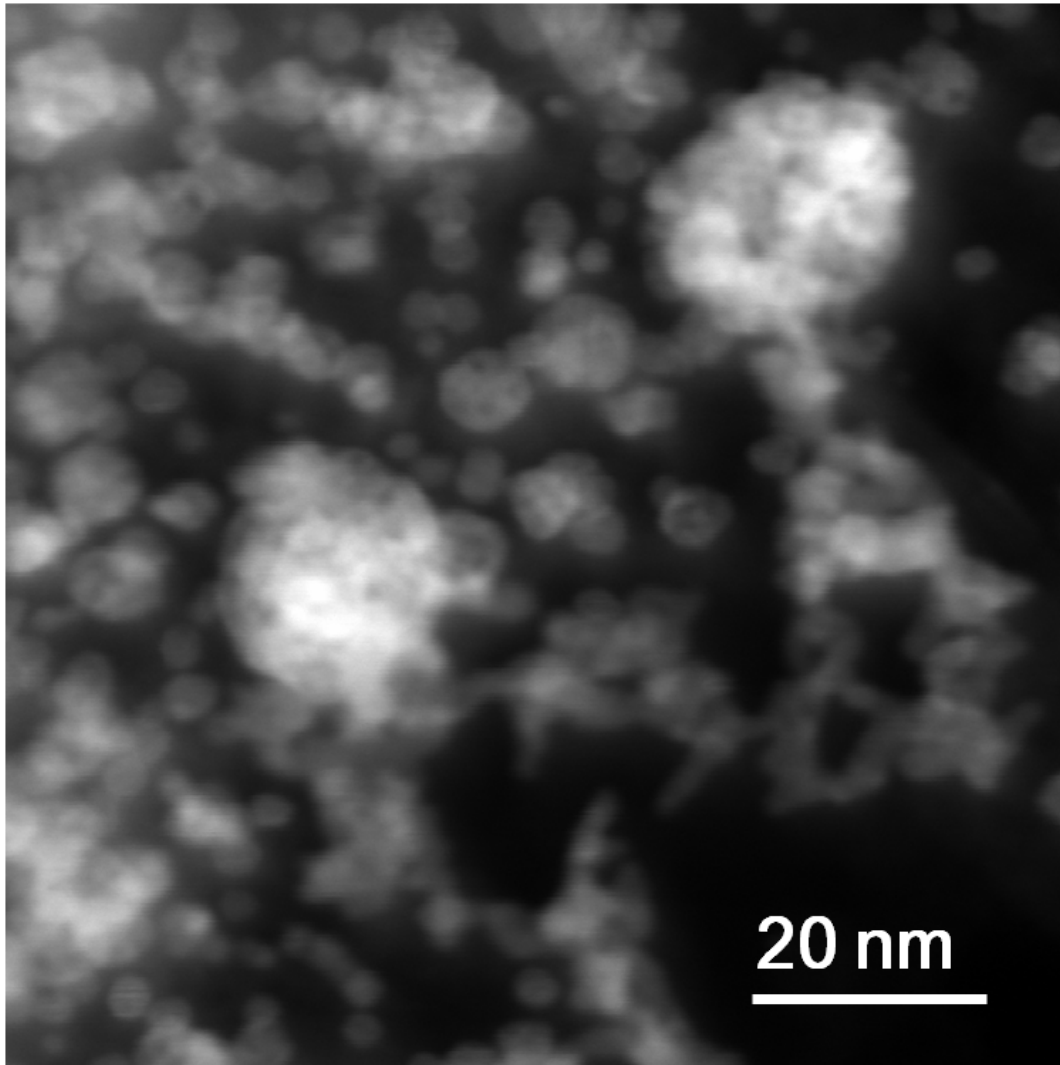
A few “Swiss Pt catalyst” – EELS/EDAX shows little Cu



•Further work needed to determine:

- Relative contributions of different types of particles to activity/durability
- How far can alloying element be below surface and still influence activity? (lattice compression vs. ligand effects)
- Is 200keV e-beam damage distorting the images? (D.A. Muller and J. Silcox, Phil. Mag. 71 (1995) 1375)
- Do different alloying metals give different structures?

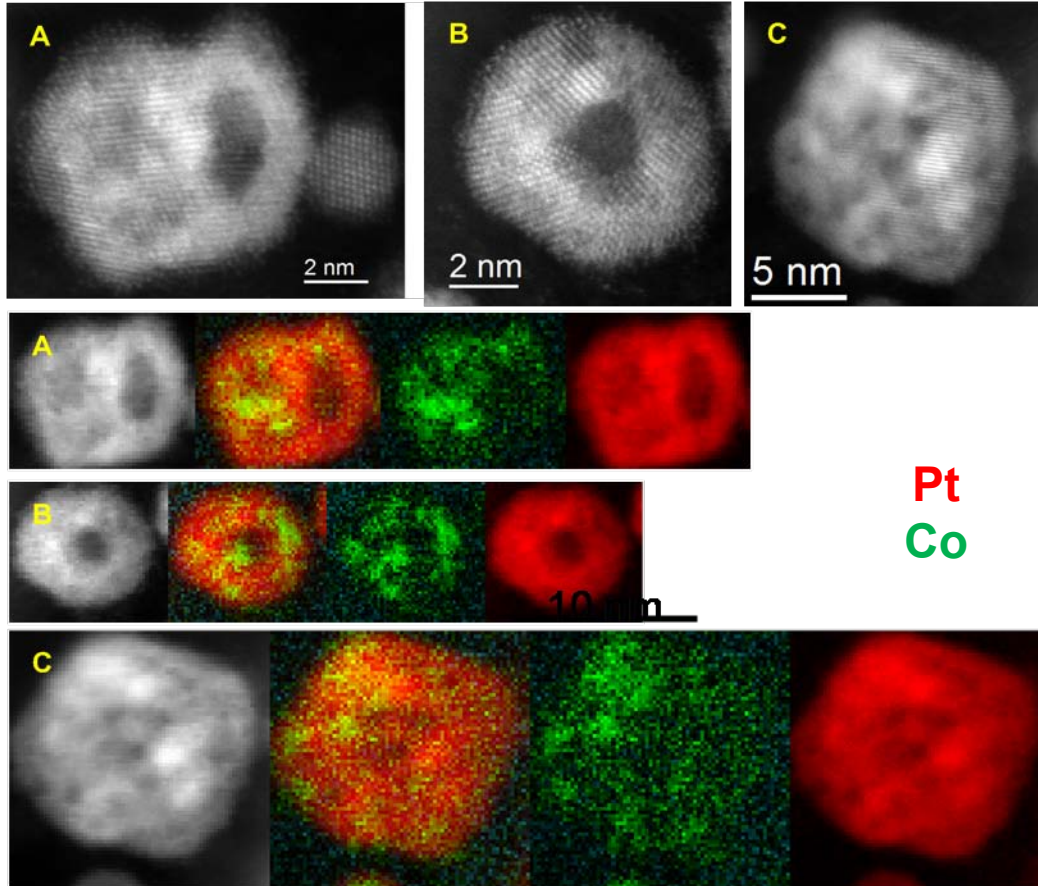
Technical Progress: Dealloyed GM Pt_{Co} (with enhanced durability): almost all particles show multiple dark spots in HAADF TEM



- intensity from thickness and square of atomic number
- dark spots could be (1) voids or (2) Co-rich cores
- same structure seen for the two separate syntheses examined
- same structure seen after 30,000 cycles 0.6-1.0V RHE

Microscopy by Vic Liu of GM, using (non-Cs-corrected) TEM at U. of Rochester

Technical Progress: EELS mapping identifies origins of dark spots for GM dealloyed PtCo₃



- HAADF STEM and Electron Energy Loss Spectroscopy elemental mapping
 - Prof. David Muller, Cornell U.
- 29 particles, ~100 dark spots analyzed in detail
- ~1/2 of dark spots are Co-rich cores
 - **multiple cores in many particles**
- ~1/2 of dark spots are voids or pits
- some Co-rich cores appear adjacent to voids

Might presence of multiple cores in a particle promote durability?

- a single penetration of Pt shell would no longer lead to complete loss of alloying-element atoms

Pathways to durable activity and performance: alloying elements where they are needed and nowhere else

Choice of alloying metal(s) (M)

- Avoid plating of anode
- Change chemical balance during dealloying
- Change electronic structure
- Ternaries

Control of M concentration in core

- Homogeneity of precursor particles
- Extent of alloy mixing and ordering prior to dealloying
- Tuned dealloying procedures
- Initial M concentration in precursor

Control of Pt shell thickness

- Intensity of dealloying
- M choice and concentration
- Post-treatments (e.g., thermal or electrochemical annealing)
- Deposition order
- Post-dealloying Pt deposition

Structural control

- Single- vs. multiple-core particles
- Compactness and orientation of Pt shell surface

Future Work (FY2011)

* *Reliable* means attention to sensitivity to test conditions and to durability from the start

- **Establish *reliable** initial mass activities above the 0.44A/mg_{Pt} target**
 - JMFC to scale up synthesis of baseline PtCu₃ and PtNi₃ precursors
 - TUB to select at least two alternate compositions/structures (based on rotating-disk electrode (RDE) testing)
 - Avoid Cu deposition onto anode
 - Change order of deposition
 - Compare miscible/phase-separated alloy systems, with and without ordered superlattices
 - TUB, JMFC, and GM to further develop more facile (manufacturable) means of dealloying, pursue post-dealloying surface treatments
 - Thermal and/or electrochemical annealing
 - Control shell thickness and morphology
 - GM (and JM) to evaluate initial ORR activities in 50 cm² single fuel cells
 - Determine sensitivities to test conditions (e.g., time at potential)
 - MIT to determine particle morphologies by transmission electron microscopy
 - Structure, and surface and subsurface compositions
 - NEU, GWU to determine local atomic coordination (EXAFS), chemical state (XANES) and O-adsorbate coverage/form as function of potential and gas content ($\Delta\mu$ XANES)
 - GM to lead correlation of ORR activity data with physical characterization

Future Work (FY 2012)

- Task 2: Small-scale demonstration of durability of mass activity
 - Considerable work already in 1st year, as preliminary work shows problems that must be surmounted
 - Durability as function of multicore vs. single-core, shell thickness, shell structure, alloying-element concentration in core
 - Synthesis must be scaled up to at least 5g level to allow testing at a scale no smaller than 50 cm² fuel cells
- Go/no go decision on Milestones 1&2. Phase 1 → Phase 2
- Task 3: Demonstration of beginning-of-life power density in MEAs
 - Modifications to structures of electrode layers to address local mass-transport issues
 - Address general problem seen for low-loaded electrodes at high current density
 - Possible additional hurdles as area-specific activity increases
 - Compare low-area and high-area catalysts with similar mass activities

Summary

Relevance: Reduce loading of platinum group metals required in fuel cells to levels needed for cost-competitive commercial applications.

Approach: Synthesis of catalysts with excess non-noble components, most of which are removed before use in fuel cell, giving unique near-surface structure/composition. Iterative process with detailed characterization to give active and durable structures.

Technical Accomplishments and Progress: Demonstrated required initial kinetic activity in oxygen, demonstrated required durability in a different catalyst, identified challenges in durability and high-current-density performance in air

Technology Transfer/Collaborations: Within project, University → Catalyst Manufacturer → Stack Integrator (prime). Publications/presentations to come.

Proposed Future Research: Develop controlled structures and composition profiles through iterative cycles of synthesis, post-treatment, testing, and characterization, seeking steady-state structure with durable high activity.

Summary Table

PGM = Platinum-group metal

Metric	units	2010	2011	2015 DOE target
Mass activity	A/mg _{PGM} @ 900mV _{iR-free}	Hadn't started	0.6 (PtCu ₃) 0.37 (PtCo ₃)	≥ 0.44
Loss in catalytic (mass) activity	% lost after 30k cycles 0.6-1.0V		38%(PtCo ₃) 83% (PtCu ₃)	≤ 40%
PGM Total Content	g _{PGM} /kW _{rated}		0.19 @1.5A/cm ² in H ₂ /air	≤0.125
PGM Total Loading	mg _{PGM} /cm ² _{geo}		0.15	≤ 0.125
Specific activity	μA/cm ² _{PGM}		860	720
Catalyst support stability	% mass loss of support		TBD	< 10%

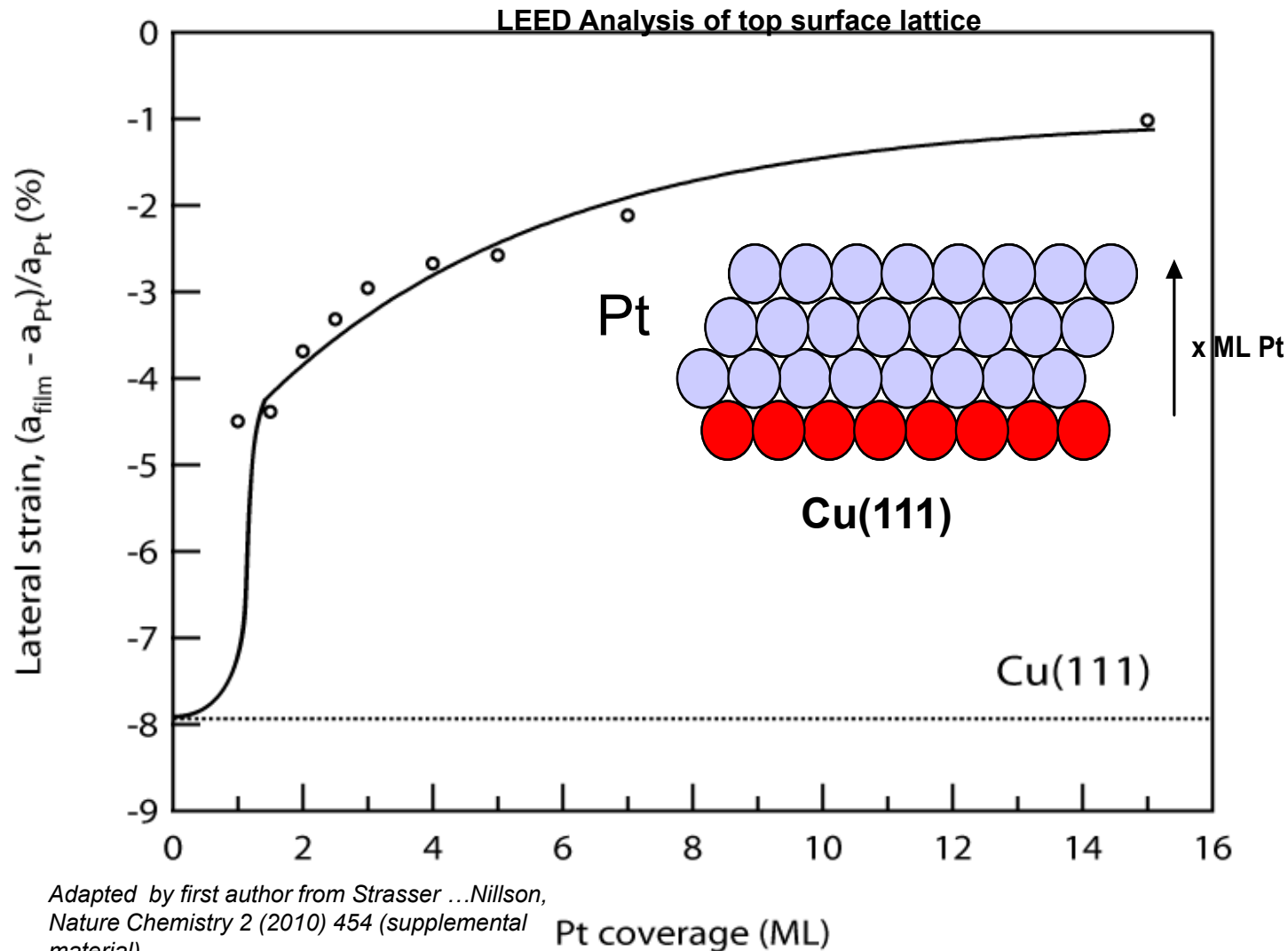
For more highly dealloyed PtCu₃

Note: not all 2011 status numbers are for the same catalyst or the same electrode – future aim is simultaneous satisfaction of all metrics with one MEA

Technical Back-Up Slides

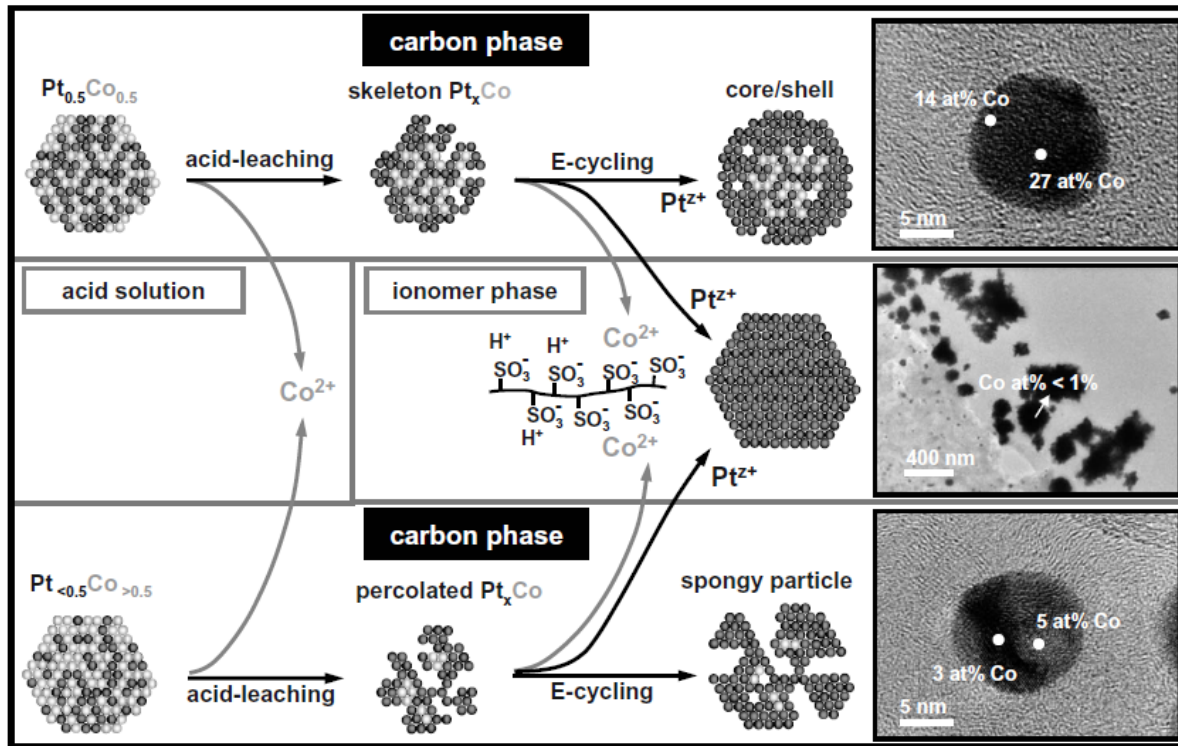
Background information: Compressive strain in (111) model 'Cu core – Pt shell' structures

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

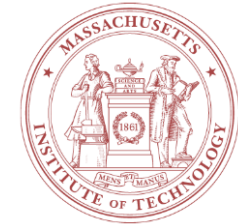


Adapted by first author from Strasser ...Nillson,
Nature Chemistry 2 (2010) 454 (supplemental
material)

MIT proposed that, for commercial Pt₃Co, final PtCo structure depends on initial local Pt/Co ratio



S. Chen, H.A. Gasteiger, K. Hayakawa, T. Tada and Y. Shao-Horn, J. Electrochem. Soc. 157 (2010) A82. Reproduced by permission of The Electrochemical Society.



MIT background work

In this project we need to determine:

- which types of particles are most active
 - Why are they most active?
- how to control which types of particles we get
- how the particles evolve with use