High-Activity Dealloyed Catalysts

2010 DOE Hydrogen Program Fuel Cell

Project Kick-Off

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Overview

Timeline

- Project start date: 1 Sept 2010
- Project end date: 31 Aug 2013
- Percent complete: 0%

Budget

- Total project funding:$5,952,827
  - DOE share: $4,762,313
  - Contractor share: $1,190,514
- Funding received in FY10: $1,350,000
- Funding received in 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 A/mg_{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
  - 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
  - Correlate atomic-scale structure with activity and durability
  - 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.

Approach

- Pt alloyed with non-noble transition metals M, usually with a stoichiometry around Pt_3M, has typically given oxygen reduction Pt-mass activities ~2 times those of Pt alone (0.2 A/mg_{Pt} vs. 0.1A/mg_{Pt} [H_2/O_2 80ºC, 100% RH, P=150 kPa_{abs} (p_{O2}=100kPa_{abs})]
- But if one starts with much higher concentration of the alloying element, often PtM_3, and removes M down to a stoichiometry of $Pt_{(2-3)}M$ (6 to 9-fold reduction of M), higher activities can be achieved
    - Koh, S.; Strasser, P. Electrocatalysis on Bimetallic Surfaces: Modifying Catalytic Reactivity for Oxygen Reduction by Voltammetric Surface Dealloying. *J. Am. Chem. Soc.* **2007**, *129*, 12624-12625.
    - Some previous claims of perhaps-similar effects, but with very low reported activities for baseline catalysts: Toda, T.; Igarashi, H.; Uchida, H.; Watanabe, M. Enhancement of the Electroreduction of Oxygen on Pt Alloys with Fe, Ni, and Co. *J. Electrochem. Soc.* **1999**, *146*, 3750-3756.
- These activity improvements have been ascribed to residual compression of the Pt lattice, but inhomogeneities in the catalysts complicate interpretation
- This project seeks to better define the mechanisms of this effect, to scale up synthesis of such materials, to evaluate and improve the durability of the activity enhancement, to develop electrodes giving good high-current-density performance in air, and (if appropriate) to test dealloyed catalysts in short stacks under realistic conditions
    - General Question: ***Where should alloying-element atoms be in a Pt-based catalyst for maximum durable activity?***

Milestones and go/no go

- Milestone 1
  - Sept 2011 Initial kinetic mass activity in H_2/O_2: >0.44 A/mg_{Pt} *reliably* achieved in at least two labs, at least one at scale of 50 cm^2 (or larger) MEA. (status – achieved with $PtCu_3$, but need more durability)
- Milestone 2
  - Apr 2012 Durability of kinetic activity: At least 0.24 A/mg_{Pt} maintained after 30k cycles per DOE-mandated protocol (0.6-1.0 V?) in at least two labs; at least one at $50cm^2$ (or larger) scale. (status: major problems seen for $PtCu_3$; promise seen for other alloys)
- Go / no go decision
  - Apr 2012: meet Milestones 1 and 2. (status: simultaneous activity and durability remain a major challenge)
- Milestone 3
  - Sept 2012 Initial high-current-density performance in air: at least 560mV at 1.5 A/cm^2 at 0.1 mg_{Pt}/cm^2 in $50cm^2$ cell (status – still far short)
- Milestone 4
  - Aug 2013 (end of project) Scaleup and durability of high-current-density performance: At least 560 mV at 1.5 A/cm^2 at 0.1mg_{Pt}/cm^2 achieved in full-active-area short stack under H_2/air, 80ºC, 100%/50% RH, 150 kPa_{abs} outlet pressure, 2/2 stoich after accelerated durability testing. (status –not started)

Collaborations (subcontractors)

- Technical University Berlin (TUB) (university)– Prof. Dr. Peter Strasser
  - née Univ. of Houston
  - Selection of new candidate catalyst systems, pre-fuel-cell evaluation
- Johnson Matthey Fuel Cells (JMFC) (industry) – Dr. Rachel O'Malley
  - Scaleup of synthesis, incorporation in 50 cm^2 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 will work through iterative cycles of synthesis, scaleup, performance evaluation, and characterization

GM (prime, industry) activities on project

- Overall technical coordination
  - Correlation of performance and characterization data
- Intermediate-scale development of dealloying methods
- MEA preparation and 50 cm^2 fuel cell testing of candidate catalysts
- Short-stack testing
- Coordination of x-ray absorption spectroscopy
  - Soon-to-be-augmented industrial access to beam time at Advanced Photon Source (ANL)
- Coordination of electron microscopy
  - Help out using GM Cs-corrected TEM as needed (e.g., elemental mapping of individual particles using electron energy loss spectroscopy)
- Project administration

Technical Univ. Berlin activities

- Primary choice of systems for study, drawing on BES and NSF-supported projects and concluded GM-funded project
- Small-scale synthesis of candidate catalysts (including small-scale dealloying processes)
  - e.g., effects of deposition order
- Rotating disk electrode (RDE) evaluation of catalysts for oxygen reduction reaction (ORR) activities
- Downselect of materials to be evaluated by other partners and/or scaled up by JMFC

Johnson Matthey Fuel Cells activities

JM
Johnson Matthey Fuel Cells
the power within

- Professional scaleup of precursor synthesis and supporting characterization
  - Preparation of more homogeneous samples to allow more conclusive correlations between activity and physical properties
  - If possible, preparation of materials with and without ordered superlattices
  - 20, then 100g samples available for MEA testing
- Scaleup of dealloying techniques
- Posttreatment of dealloyed materials
  - e.g., mild thermal annealing
- Preparation and testing of MEAs for oxygen reduction activity, durability, and high-current-density performance
- Feed back ideas for catalyst improvements

MIT activities

- Carry out electron microscopy, including use of HRTEM facilities at ORNL, of precursors, freshly-dealloyed catalysts, catalysts from broken-in MEAs, and catalysts from durability-tested MEAs
- Detailed evaluation of microscopic data, drawing on previous experience with other alloy-catalyst systems
- Small-scale preparation of alternate catalyst structures for comparison with dealloyed catalysts
- Feed back ideas for catalyst improvements

Northeastern U. activities

Northeastern
UNIVERSITY

- X-ray absorption spectroscopy (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near-Edge Structure) analyses of precursors, freshly-dealloyed catalysts, catalysts from broken-in MEAs, and catalysts from durability-tested MEAs
- Electrochemical cells for in situ experimentation
- *Cells for in-operando studies of operating fuel cells*
- Carry most of the XAS data-analysis load
- Feed back ideas for catalyst improvements

George Washington U. activities

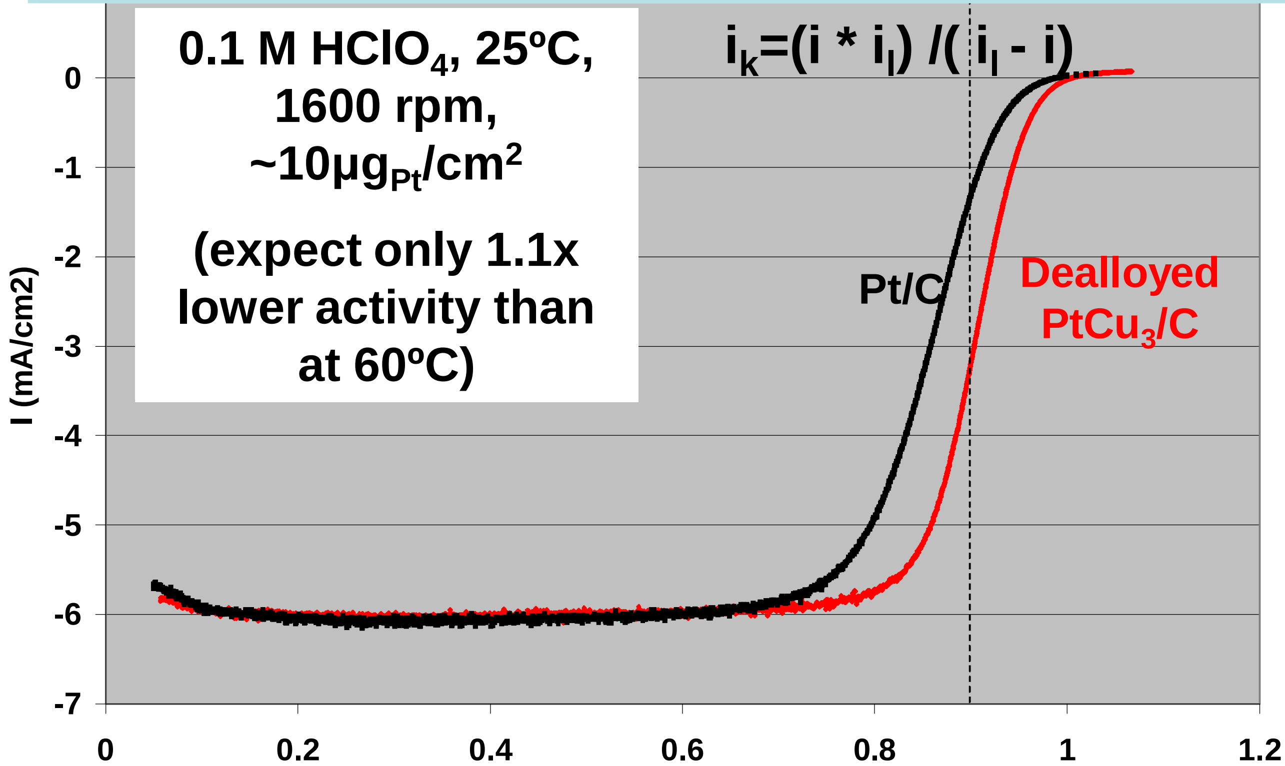
THE GEORGE
WASHINGTON
UNIVERSITY
WASHINGTON DC

- Theoretical support of x-ray absorption spectroscopy efforts
  - Calculate signals expected from different postulated catalyst compositions and structures
- Δμ XANES to determine potential-dependent coverages and binding-site geometries of oxygen-containing adsorbates
  - Experimental tests of proposed ORR mechanisms
- Feed back ideas for catalyst improvements

Technical Accomplishments

- Note: The pre-project accomplishments of the subcontractors in relevant areas are underrepresented in this presentation due to the the discouragement of the use of previously-copyrighted graphics.

University of Houston showed high activity for their $PtCu_3$ dealloyed and evaluated on rotating disk electrode



$0.1\ M\ HClO_4$, 25ºC, 1600 rpm, ~10$\mu g_{Pt}/cm^2$

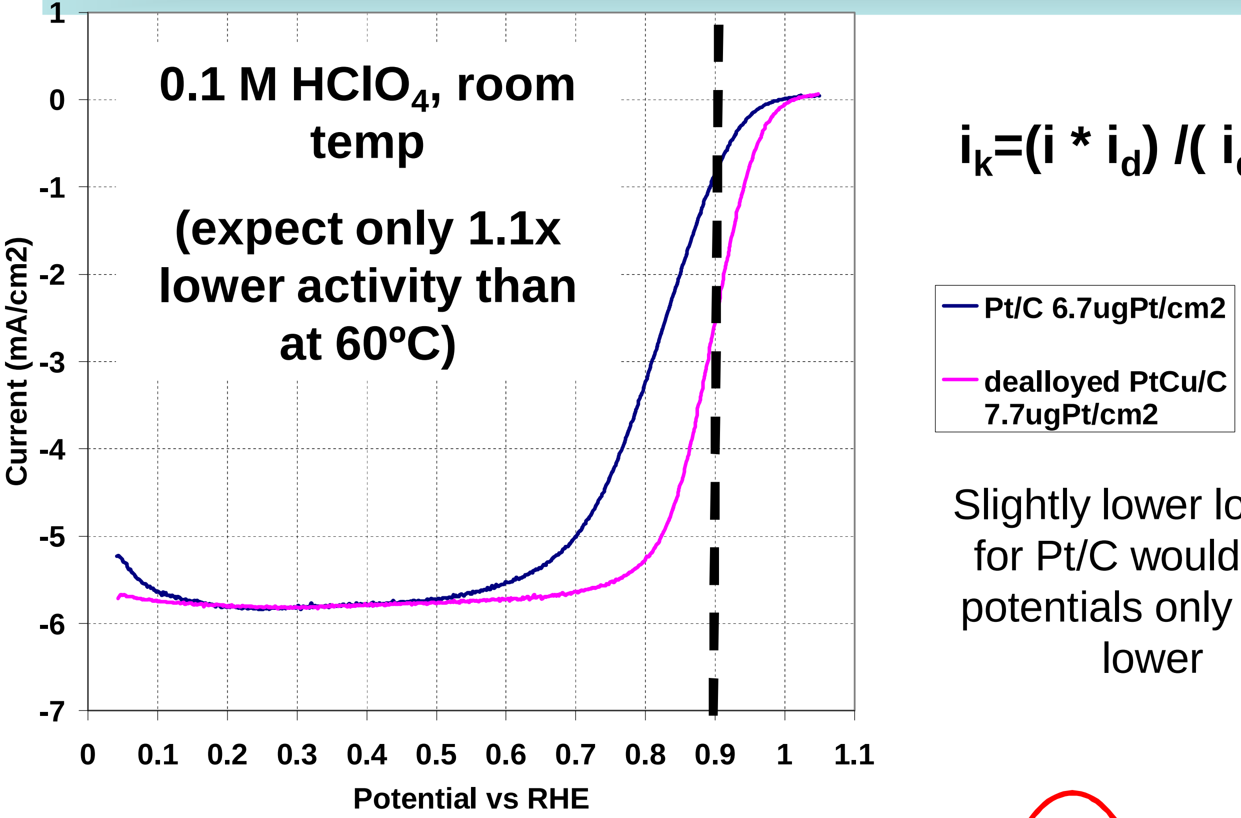
(expect only 1.1x lower activity than at 60ºC)

$$i_k = (i * i_l) / (i_l - i)$$

- activating pretreatment removed most copper
- but Pt-Pt XRD spacing still that of a PtCu alloy (smaller)

	A/mg_{Pt}	m^2/g_{Pt}
Dealloyed $PtCu_3/C$	0.52	88
Pt/C	0.12	77

GM rotating disk measurements also showed high activities for UofH $PtCu_3$ precursor dealloyed on disk



0.1 M $HClO_4$, room temp

(expect only 1.1x lower activity than at 60ºC)

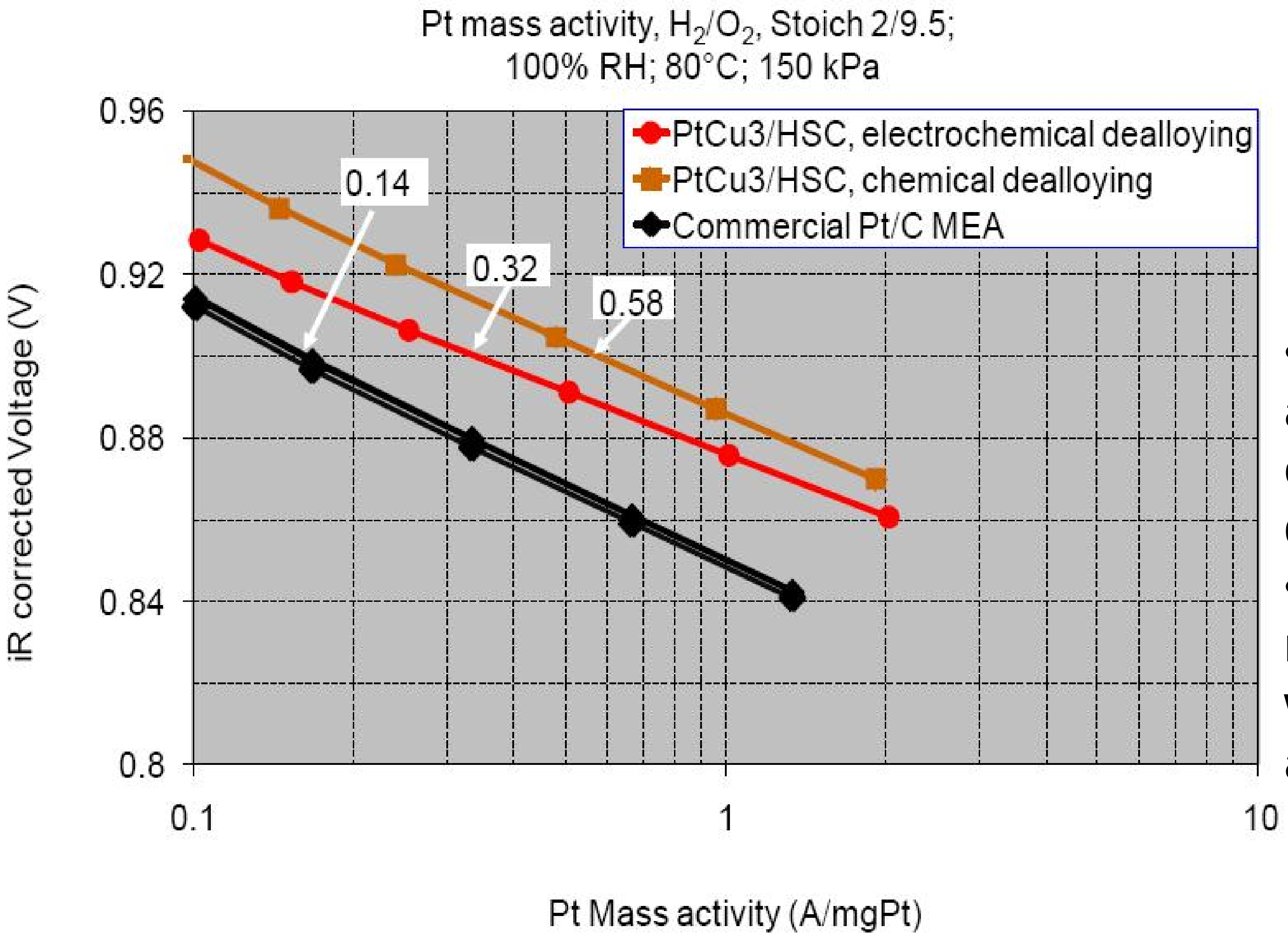
$$i_k=(i * i_d) /(i_d - i)$$

Slightly lower loading for Pt/C would give potentials only 4 mV lower

	HAD (m^2/g_{Pt})	A/mg_{Pt} (0.9V, 5mV/s, RT C)	uA/cm^2_{Pt} (0.9V, 5mV/s, RT C)	
22%PtCu/HSC SK-C104 Ink Made by GM	91	0.390	436	average of 3 electrodes
22%PtCu/HSC SK-C158 Ink Made by UH	112	0.494	504	average of 6 electrodes
Pt/C reference (1 sig. dig.)	60	0.1	200	

Need more manufacturable dealloying process :

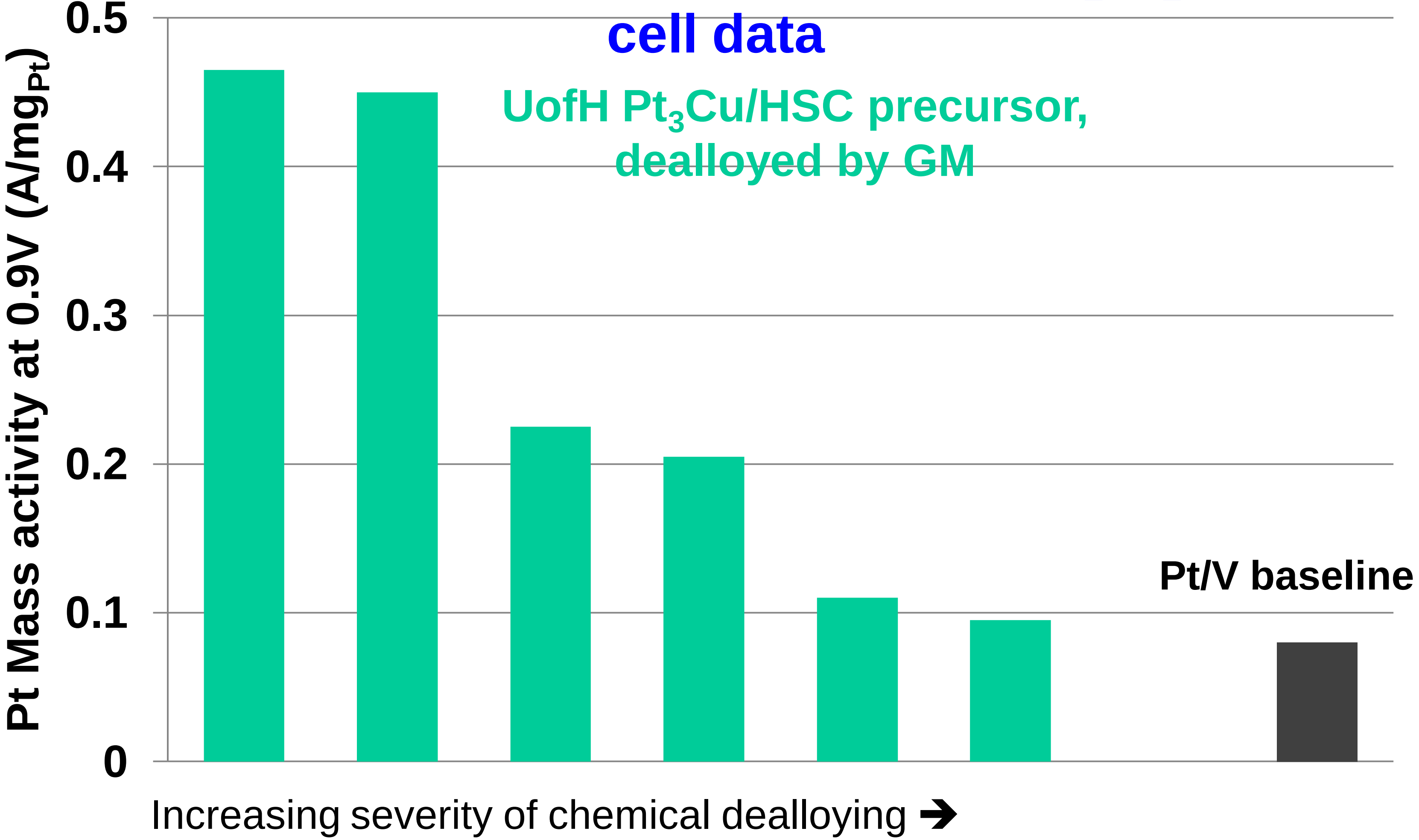
- UH precursor synthesis involved annealing in 0.5 g batches
    - Generation of quantities for MEA testing was tedious
- Electrochemical dealloying (voltage cycling 0.05-1.2V RHE) on rotating-disk electrode produced only ~10 µg quantities
- Electrochemical dealloying after membrane-electrode assembly is made consumes proton-exchange capacity of membrane and ionomer in electrodes with dissolved-metal cations
    - Subsequent acid treatment of MEA causes excessive wrinkling
- GM developed preliminary powder-dealloying processes (both chemical and electrochemical) – applied before making MEA
- Further development of dealloying processes is needed to remove optimal amount of alloying element



- 15 min/point, ascending current densities
- Black numbers in white boxes are A/mg_{Pt}

GM-dealloyed U. Houston precursor $PtCu_3$: GM confirmed high mass activities in 50 cm^2 MEAs for both electrochemical and chemical dealloying

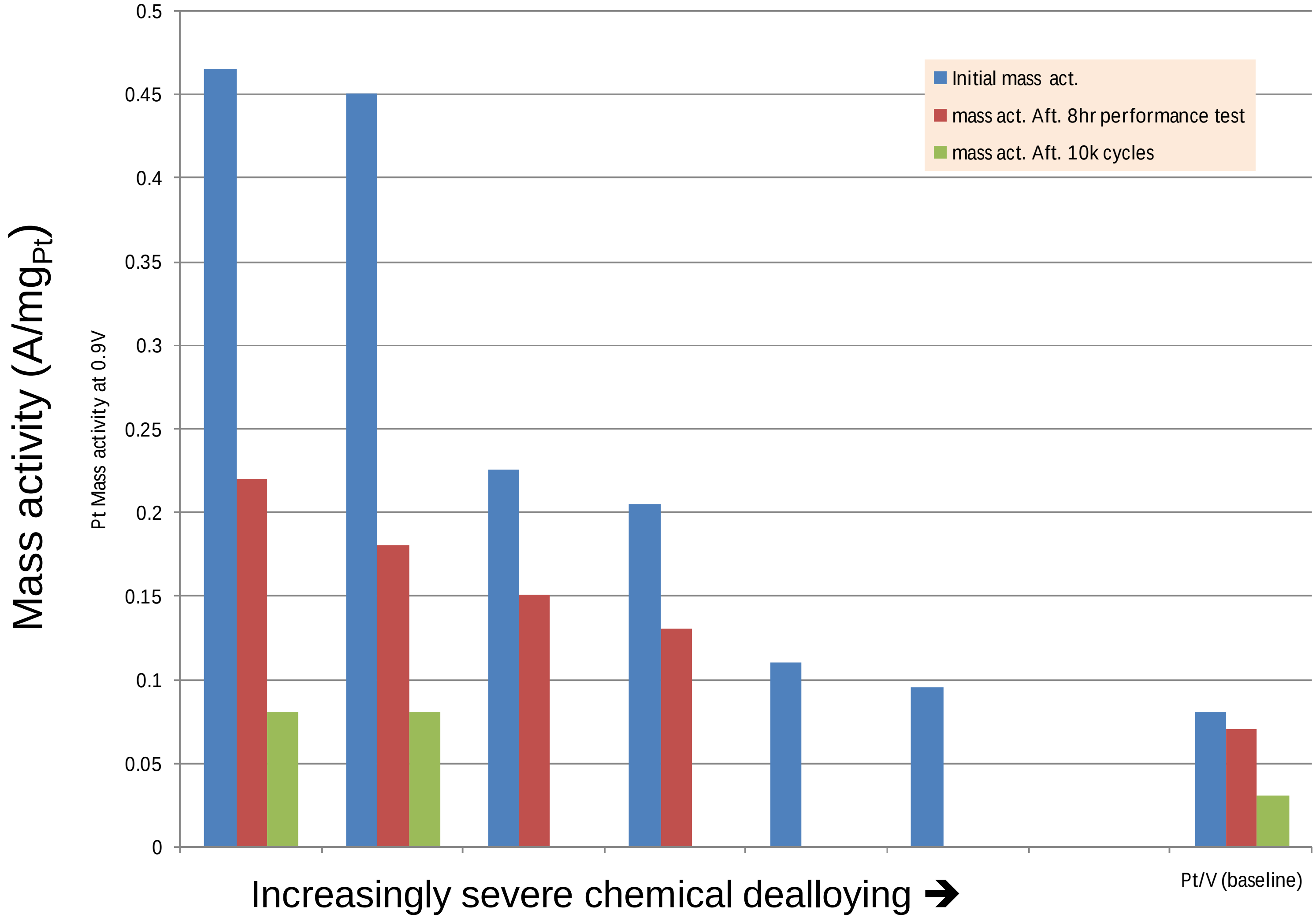
Different chemical treatments: GM 50cm^2 H_2/O_2 single fuel cell data



UofH Pt_3Cu/HSC precursor, dealloyed by GM

- Initial ORR activity declined as more aggressive acid leaching removed more copper from UofH $PtCu_3$ precursor
- But performance at high current density in air improved as dealloying severity increased (not shown)

To date, chemically dealloyed $PtCu_3$ seems unstable to both standard pol curves and to 0.6-1.0V voltage cycling in $50cm^2$ cells

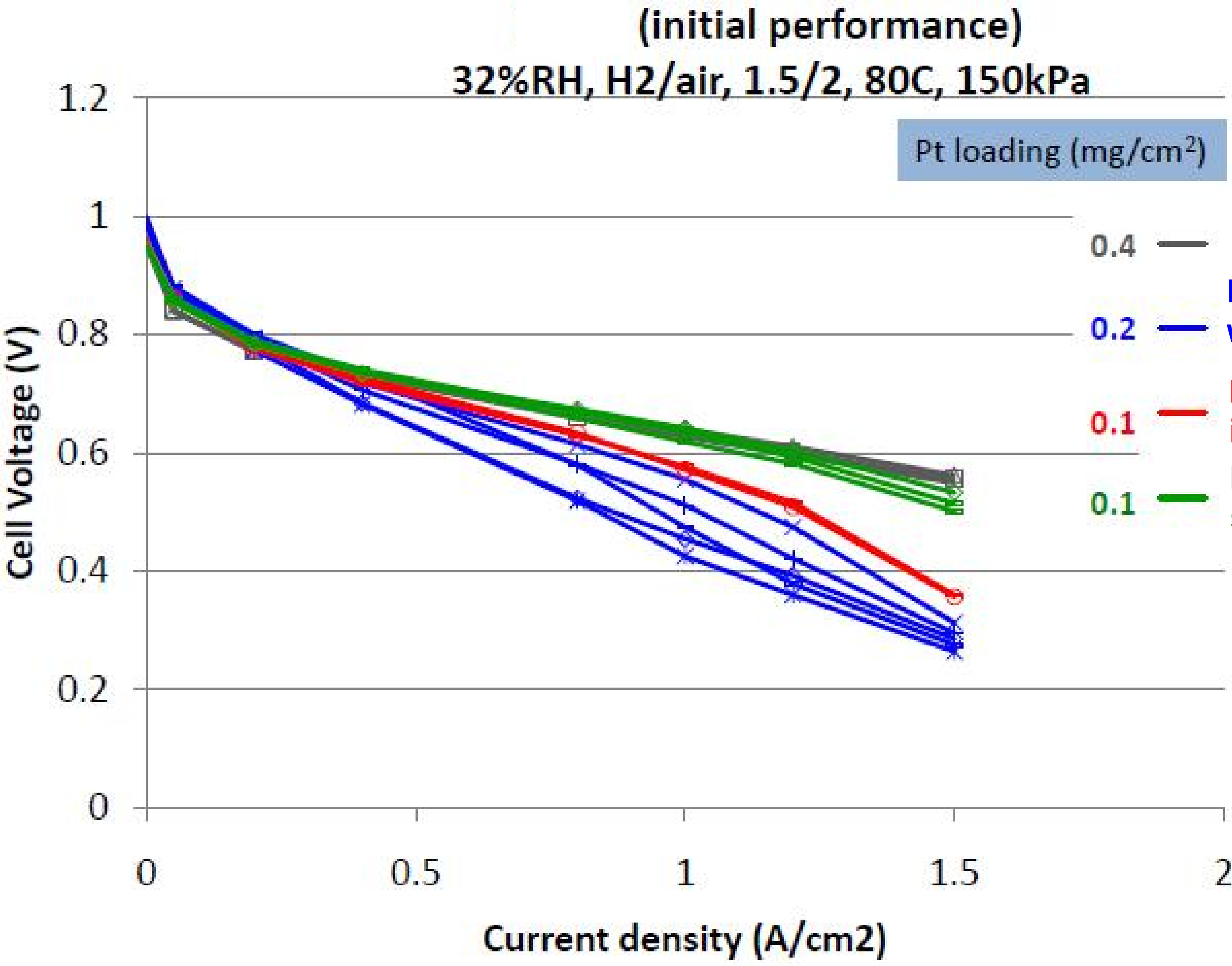


Dealloyed PtM_3 looking more stable than $PtCu_3$ in GM 50cm^2 MEAs, but is less active

precursor	BOL A/mg$_{Pt}$	10k 0.6-1.0V A/mg$_{Pt}$	30k 0.6-1.0V A/mg$_{Pt}$	precursor by	activity by
$PtCu_3$	0.45*/1.0**	0.07		U of Houston	GM
PtM_3	0.42**	0.39**	0.26**	GM	GM

*Initial activity of 1.0A/mgPt ("10x") when measured using recent protocol – shorter time since surface oxide was reduced
** measured using the more recent protocol

- Project will determine cause of activity and durability differences between alloys with different metals
  - Structural effects?
  - Ligand effects?
- Project will improve balance of activity and durability



Pt/Vulcan

Deal. PtCu$_3$/HSC, weakest dealloying

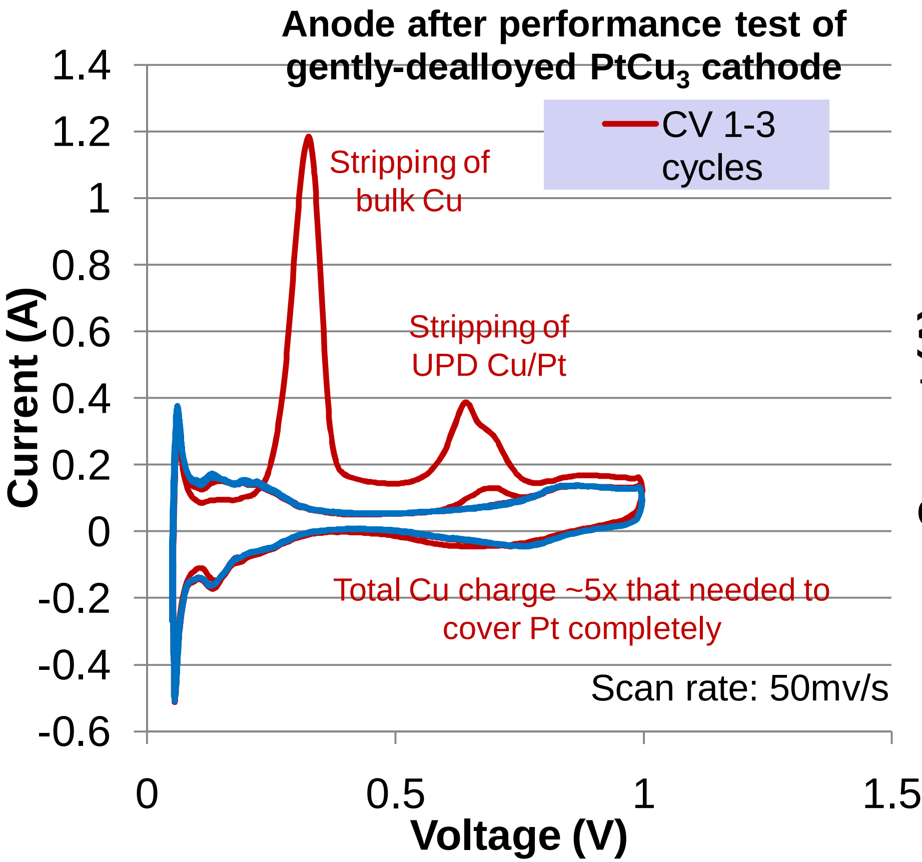
Deal. PtCu$_3$/HSC, intermediate dealloying

Deal. PtCu$_3$/HSC, strongest dealloying

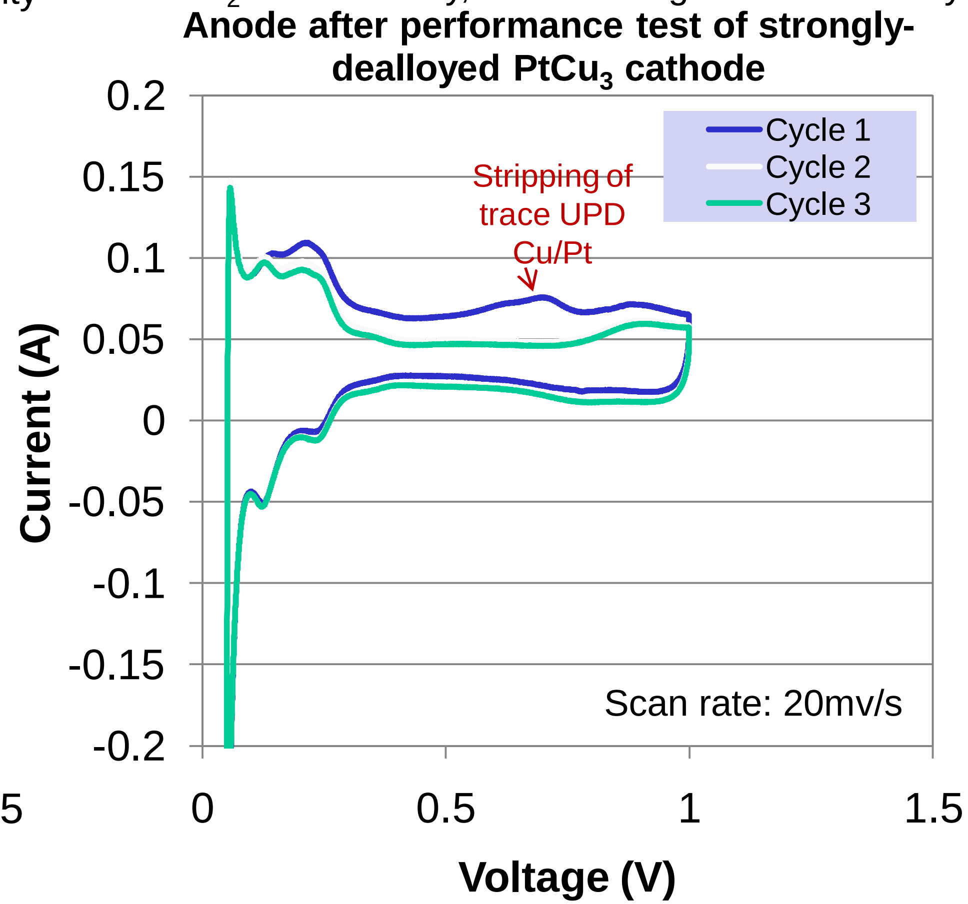
Excessive remaining Cu decreases high-current-density performance in air

GM cyclic voltammetry showed poisoning of *anode* by copper from $PtCu_3$

Better O_2 mass activity, worse air high current density

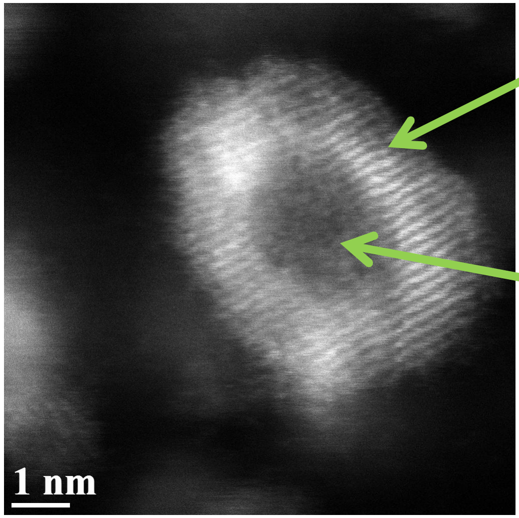


Worse O_2 mass activity, better air high current density



- More Cu remaining after dealloying ⇔ higher O_2 mass activity
- Excess Cu dissolves in ionomer, plates out on anode at H_2 potential
- Cu on anode poisons H_2 oxidation at high current density (see this in AC impedance as added high-frequency loop)
- **Use of a non-Pt metal other than Cu should avoid this anode poisoning (won't plate)**
- Mass-activity loss in previous slide likely due to other effects

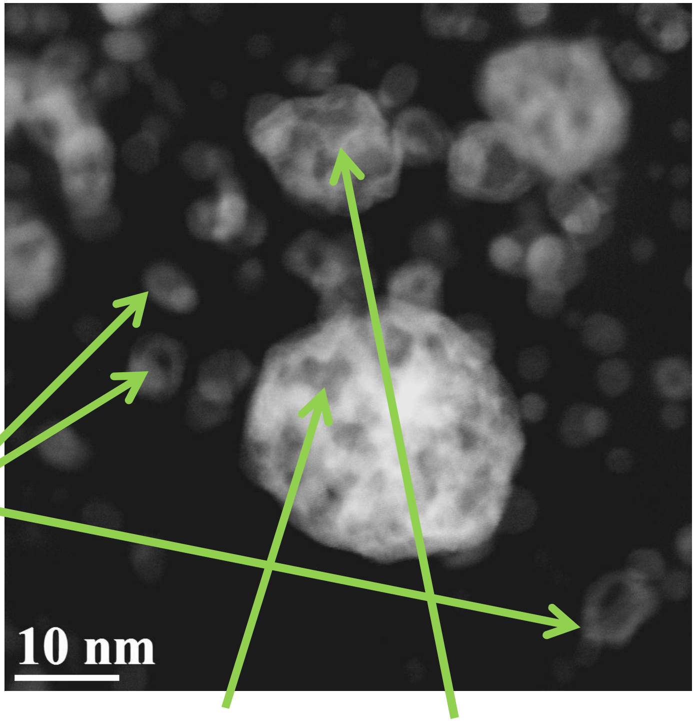
HAADF “Z-contrast” TEM (at GM) for dealloyed $PtCu_3$ shows both core-shell and “Swiss Pt” particles



Pt shell

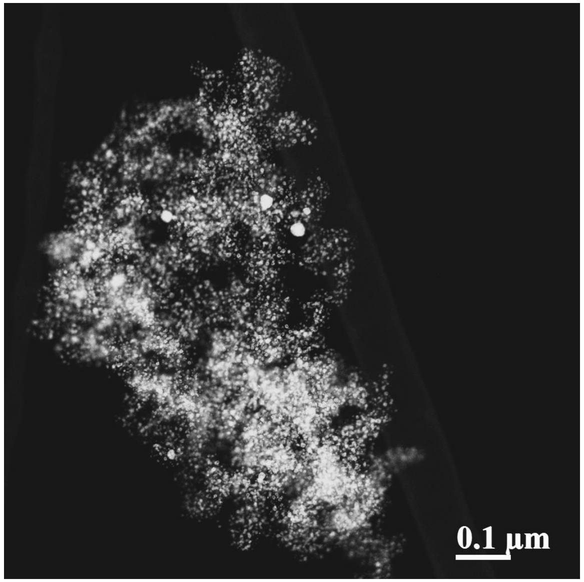
Pt-Cu Core

From F.T. Wagner, B. Lakshmanan, and M.F. Mathias, J. Phys. Chem. Lett. 1 (2010) 2204, used with permission from the Am. Chem. Soc.



Core-shell

“Swiss Pt catalyst” – EELS shows no 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?
  - Do different alloying metals give different structures?
    - Is e-beam damage distorting the images? (D.A. Muller and J. Silcox, Phil. Mag. 71 (1995) 1375)

Local vs. averaging techniques

- High resolution TEM looks at a single particle
  - Are the results representative as a whole?

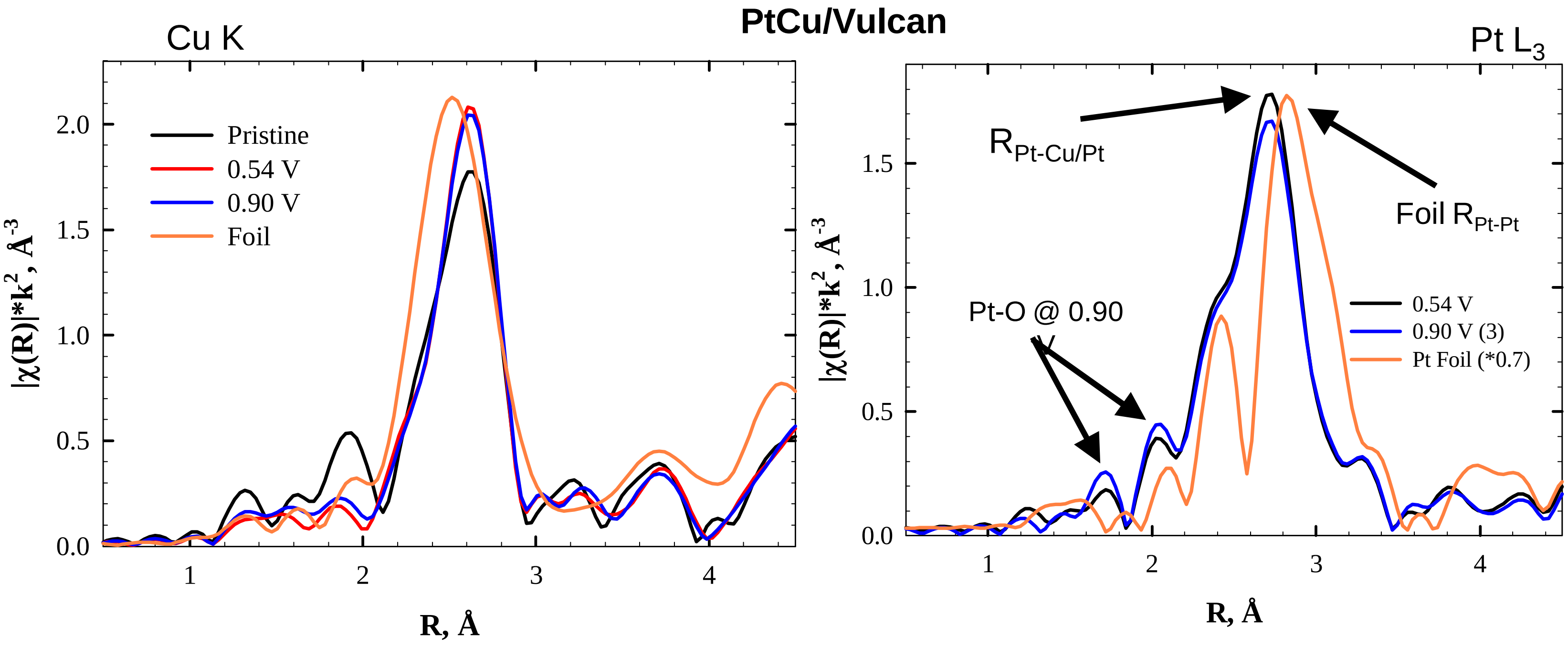
- High resolution TEM is an ex situ technique (vacuum)

- Can we get information about local atomic coordination from an averaging technique?

- Can we do so in an operating electrochemical cell or, better, in an operating fuel cell?

➔ X-ray absorption spectroscopy
  - Extended x-ray absorption fine structure (EXAFS)
    - Local bond distances and coordination numbers around a particular element
  - X-ray absorption near edge structure (XANES)
    - Total amounts and chemical states of particular elements
  - Potential difference electrochemical XANES (Δμ XANES)
    - Bonding geometries of adsorbates as a function of potential (if EXAFS shows that metal atoms don’t move)

What is the local structure of active dealloyed PtCu ? – GM in situ EXAFS



Cu K Edge

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

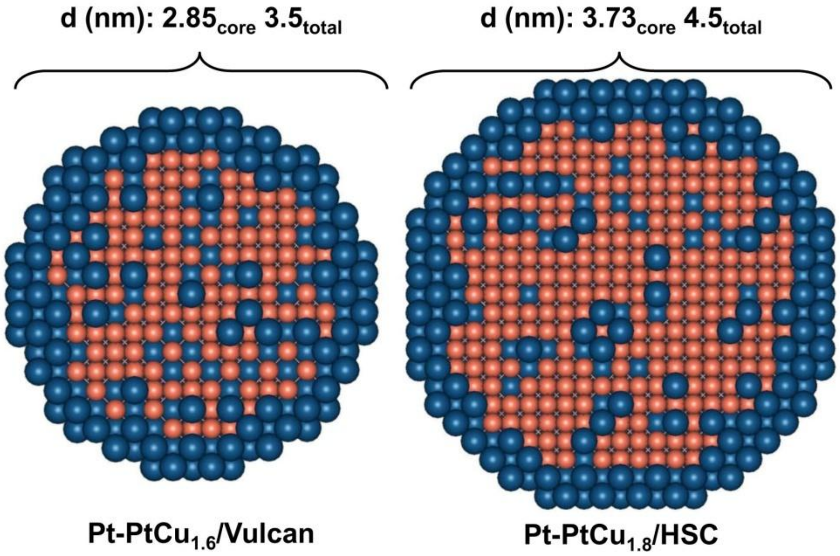
Pt L_3 Edge

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

In situ EXAFS at Brookhaven NL synchrotron (NSLS), using GM beamtime

Hypothesized cartoons of the proposal are being checked with microscopic images and with spectroscopically-supported average configurations

GM EXAFS data indicate average particle configurations with Cu-rich cores



Representations of the average Pt$_{(SHELL)}$PtCu$_{x,(CORE)}$ electrocatalyst morphologies ascertained from the modeling of the EXAFS analysis: (blue) Pt (orange) Cu.

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.

Future Work (FY2011)

- **Establish *reliable** initial mass activities above the 0.44A/mg$_{Pt}$ target**
  - TUB to select baseline precursor for dealloying (probably $PtCu_3$)
  - TUB to select at least two alternate compositions/structures (based on rotating-disk electrode (RDE) testing)
    - Avoid Cu deposition onto anode
    - Compare precursors with and without ordered superlattices
    - Compare miscible/phase-separated alloy systems (change order of deposition)
  - TUB, JM, and GM to further develop more facile (manufacturable) means of dealloying
  - JM to scale synthesis of baseline and at least two alternate precursors to at least 20g level
  - GM (and JM) to evaluate initial ORR activities in 50 cm^2 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 (Δμ XANES)
  - GM to lead correlation of ORR activity data with physical characterization

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

Future Work (FY 2012)

- Task 2: Small-scale demonstration of durability of mass activity
  - Some work already in 1st year, as preliminary work shows problems that must be surmounted
  - Probable need for structures/compositions more durable than baseline dealloyed $PtCu_3$
  - Synthesis must be scaled up to at least 5g level to allow testing at a scale no smaller than 50 cm^2 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
  - Address general problem seen for low-loaded electrodes at high current density
  - Possible additional hurdles as area-specific activity increases
  - Need for increased sophistication in description of ORR kinetics at low potentials (not a single Tafel slope)
  - Modifications to structures of electrode layers to address local mass-transport issues

Future Work (FY2013)

- Demonstration of durability of power density in full-active-area MEAs
  - Once good durable activity and good initial performance at high current density are achieved
    - Scale up synthesis and MEA preparation to allow testing in short stacks with full active area (300-400 cm^2/cell)
    - Test durability of both activity and power density in short stacks

Feedback between synthesis, performance evaluation, and detailed characterization to understand and surmount problems with durability of performance at high current density

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

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

Technology Transfer/Collaborations: Prime is industrial fuel cell developer; one sub is a commercial manufacturer of fuel cell catalysts; others are university. Publications/presentations to come.

Proposed Future Research: Iterative cycles of synthesis, performance evaluation, and atomic-scale characterization to simultaneously satisfy targets for kinetic activity in O_2, durability, and high-current-density performance in air

Supplemental Slides