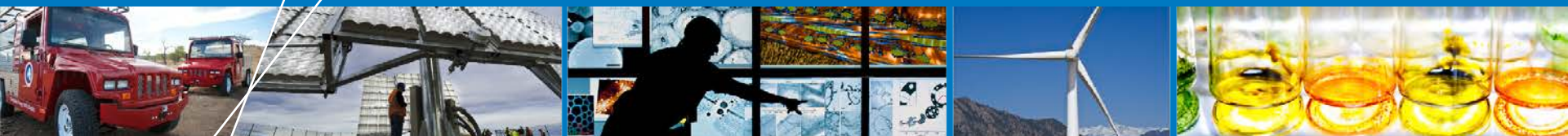


WO_3 and HPA based systems for durable Pt catalysts in PEMFC cathodes



2014 DOE Hydrogen and Fuel Cells Program Review

John Turner

June 18th, 2014

FC084

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start date: 05/01/2010
- End date: 04/30/2014
- Percent complete: 100%

Budget

- Total funding spent: \$2.9M
- Total Project value: \$2.9M
- Cost Share percentage: 9%

Barriers

- Durability
- Cost
- Performance

Partners

- S. George: UC Boulder
- A. Herring: CSM
- S. Hamrock: 3M
- K. Adjemian: NTCNA
- Tanaka Kikinzoku Kyogo (TKK)

Project lead – NREL

(John Turner, Anne Dillon,
Katie Hurst, Bryan Pivovar,
K.C. Neyerlin, Jason Zack, and Shyam
Kocha)

Relevance: Objectives

Improve electrocatalyst, MEA durability, and activity through the use of Pt/WO₃ and Heteropoly Acid (HPA) modification of carbon support to approach automotive PEMFC activity (**0.44 mA/mg_{Pt}**) and durability targets (5000h/10y).

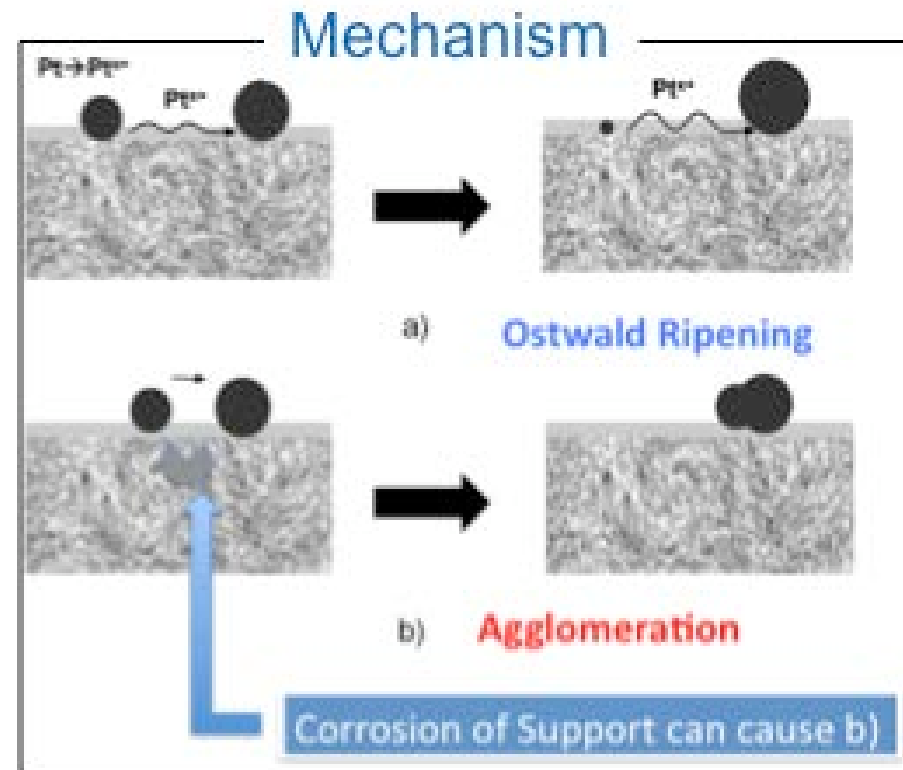
Enhance Pt anchoring to support

- Suppress loss in Pt ECA under load cycling operations
- Enhance electrocatalytic activity

Lower support corrosion

- Increased durability under automotive startup/shutdown operation.
- Suppress Pt agglomeration/electrode degradation

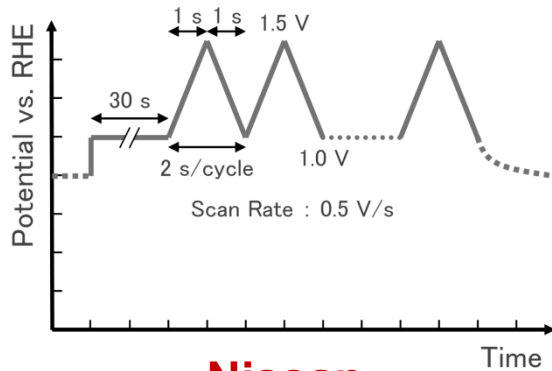
Simplify and lower system cost



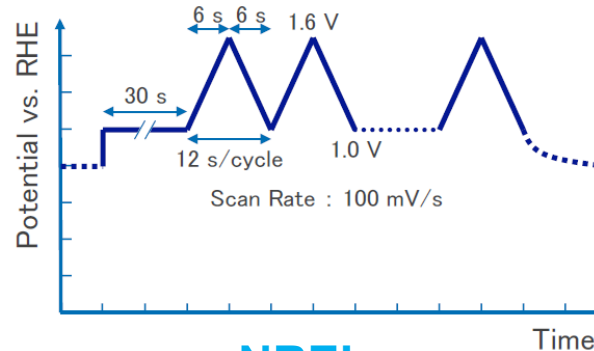
Develop Accelerated Tests for Durability Support- Protocols



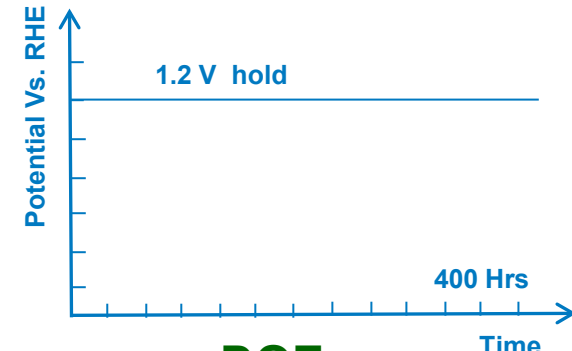
RDE Accelerated Test for Support Corrosion



Nissan



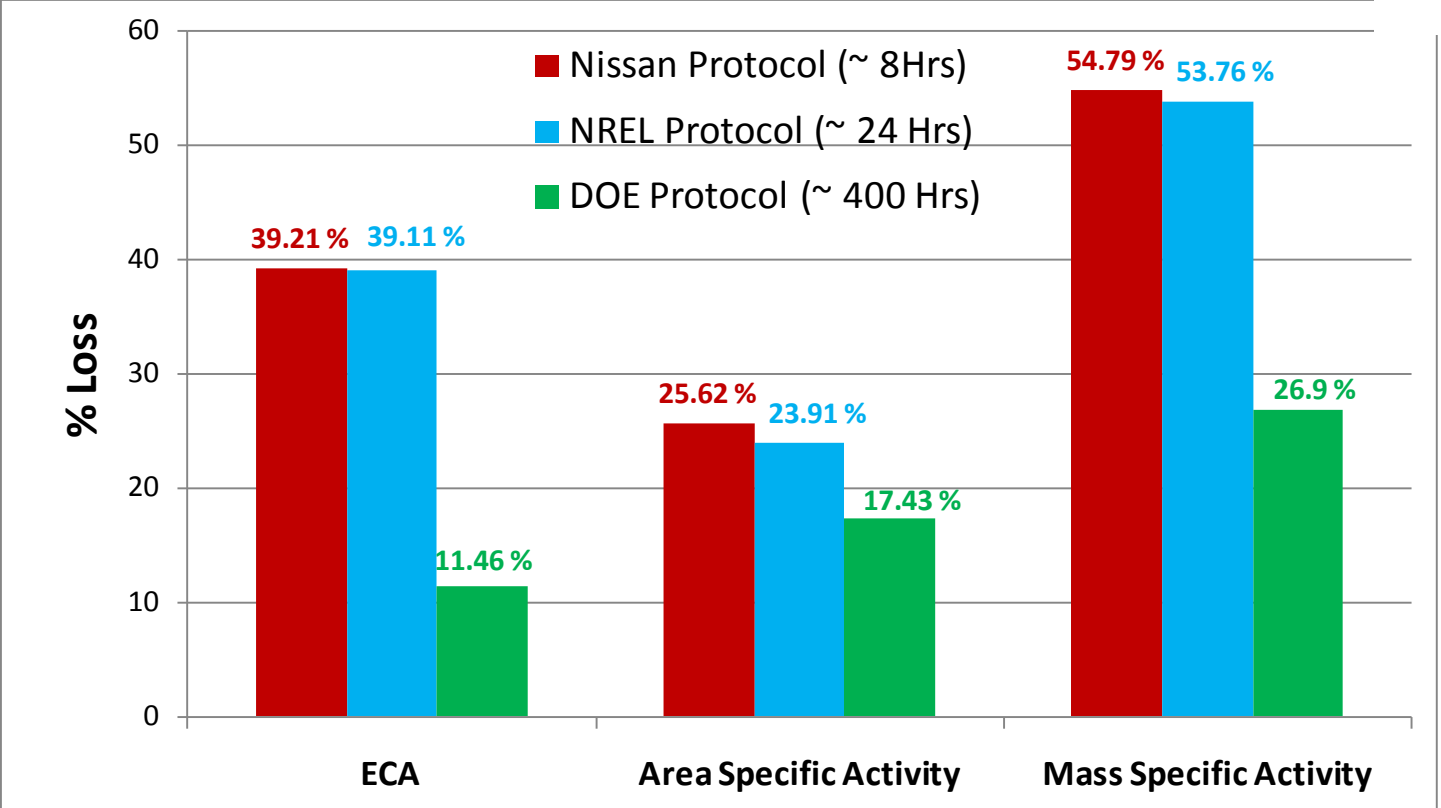
NREL



DOE

	Nissan	NREL	DOE
Temp	60°C	Room Temp	Room Temp
Scan Rate	500 mV/s	100 mV/s	1.2 V Hold
No of Cycles	5000 Cycles	6000 Cycles	No Cycles
Time to complete the test	~ 8 Hrs	~ 24 Hrs	~ 402 Hrs

Protocol Comparisons – Pt/C Results



- Nissan and NREL protocols result in comparable losses for ECA, i_s and i_m .
- Nissan protocol (60°C) takes only 8h due to higher temperature accelerant
- NREL protocol is conducted at RT and takes 24 h using low scan rate accelerant.

Approach

Synthesize WO₃

NREL

Supply WO₃ to CU for Pt ALD deposition

Supply WO₃ to CSM for HPA modification and Pt deposition

Charac. WO₃ & Pt/WO₃ for
- Conductivity
- BET surface area
- TEM



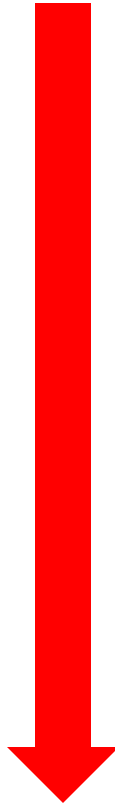
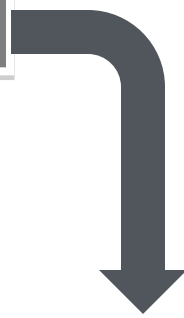
CU – Steve George

1. Prepare Pt nanoclusters on WO₃
2. Analyze the structures formed using FTIR, XPS, SEM, TEM, Raman, etc.,
3. Measure Pt particle size, BET, etc.,
4. Provide samples to CSM & NREL



CSM – Andy Herring

1. Synthesize HPA
2. Immobilize HPA to Pt/C
3. Prepare Pt nano/C
4. Immobilize HPA to C
5. Prepare Pt nano/HPA-C
6. Immobilize/ Covalently bond HPA to WO₃
7. Prepare Pt nano/HPA- WO₃
Prepare Pt nano/HPA- WO₃ hybridized with HPA-C
8. Alternative WO₃ synthesis

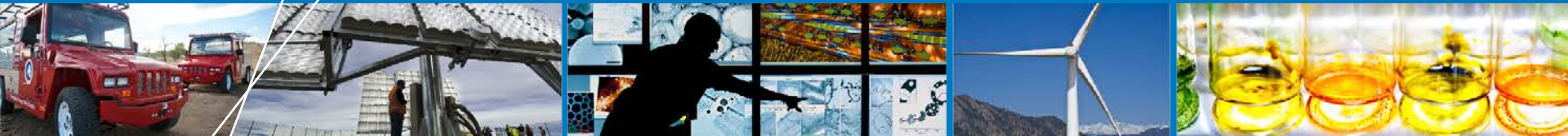


NREL

Electrochemical Characterization



Pt/WO_x Electrocatalysts

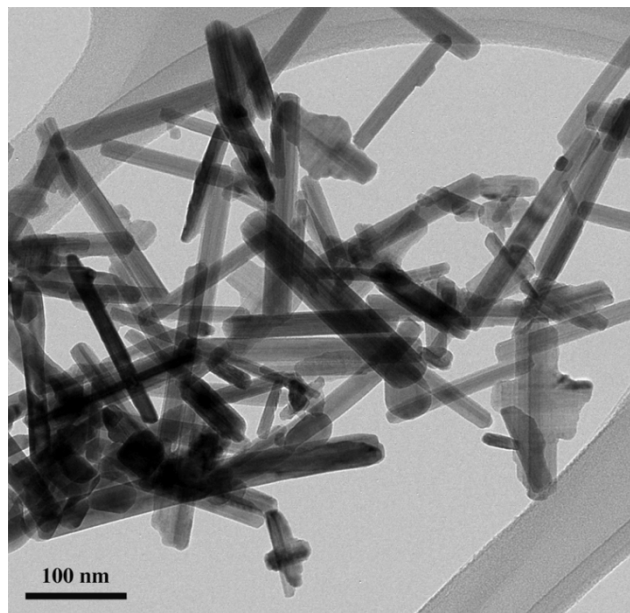


Accomplishments

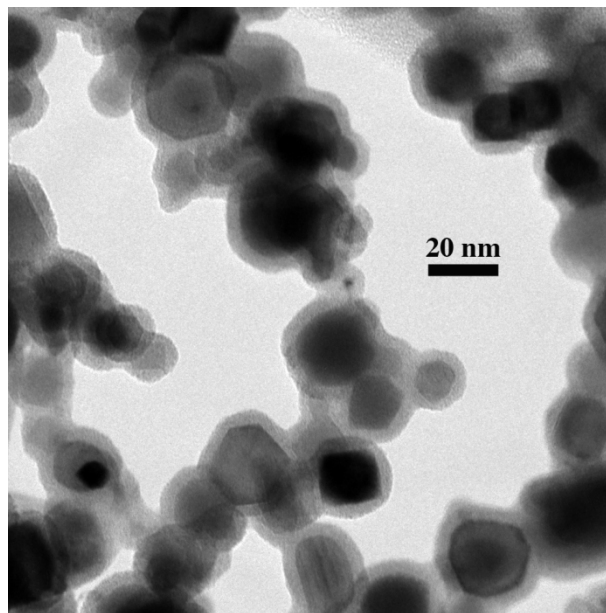
Other oxides, carbide and nitrides were also screened.

HWCVD Production of Tungsten Oxide Nanostructures

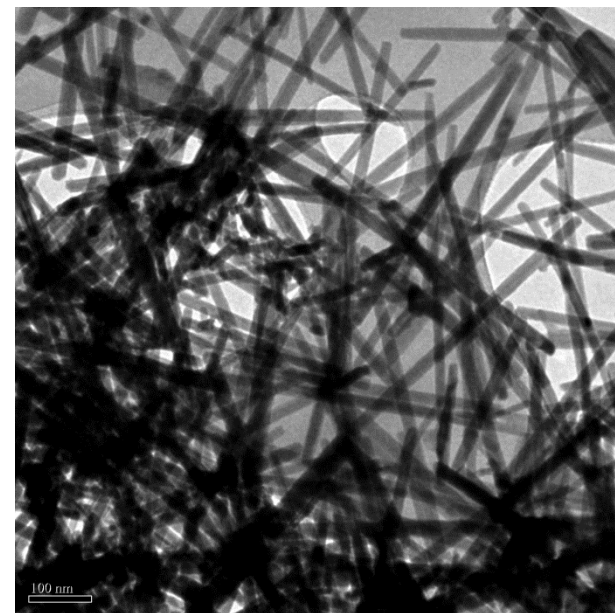
Synthesis at 150 Torr 4% O₂ in Ar, filament temperature ~ 2000 °C.



300 °C



30 °C

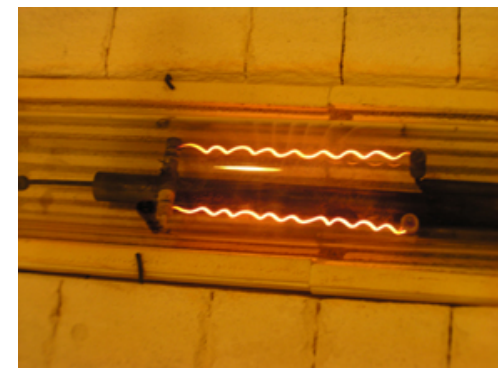


30 °C

4 sequential depositions

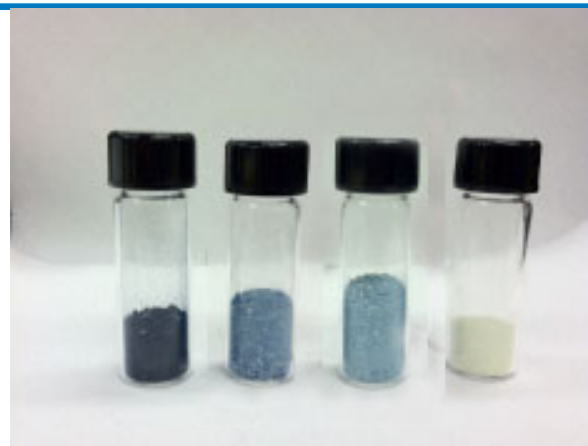
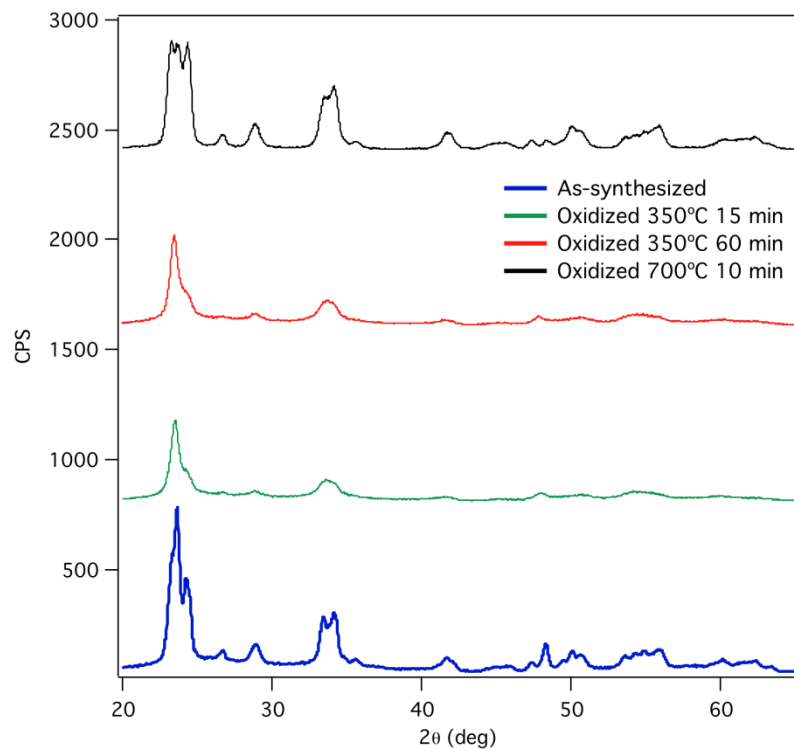
■ Dramatic change in particle morphology

- Lower furnace temperature
- Sequential depositions lead to rod growth



A.H. Mahan, P. A. Parilla, K.M. Jones and A.C. Dillon, *Chem. Phys. Lett.* 413 (2005) 88.

Controlling the stoichiometry of WO_x by subsequent oxidation in air.



58.7 m²/g
As-produced

58.7 m²/g
400°C
15 min

47.9 m²/g
400°C
60 min

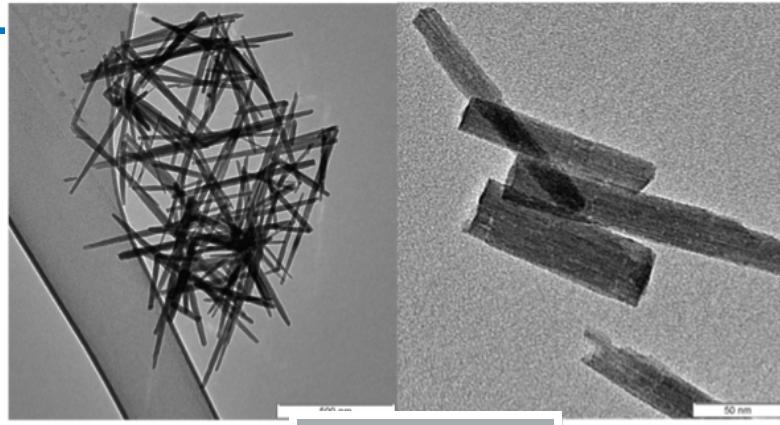
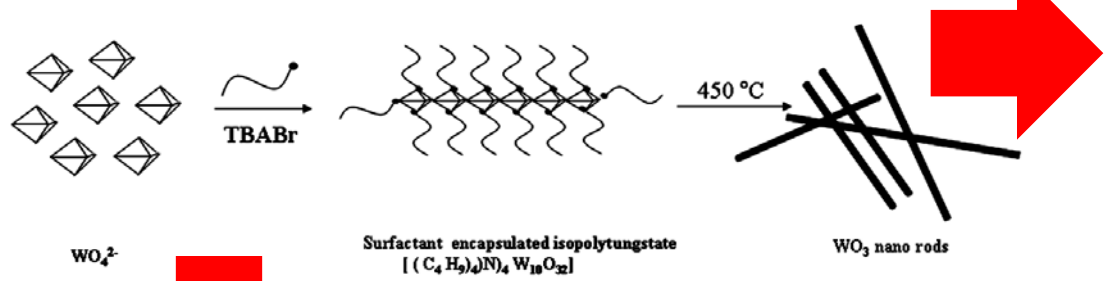
26.0 m²/g
700°C
10 min

Samples are heterogeneous

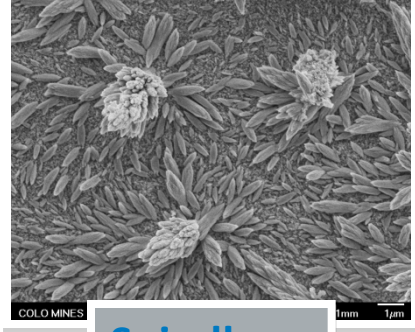
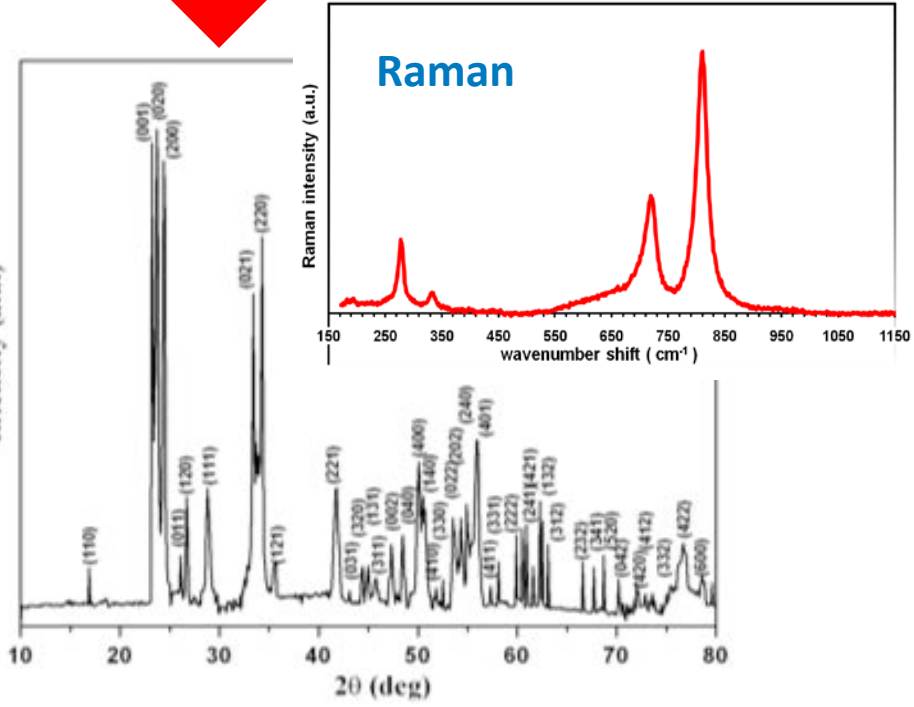
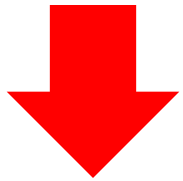
- Different oxide phases are made upon oxidation
- Sub-stoichiometric material should have higher conductivity
- The stoichiometry of WO_x may impact subsequent Pt deposition

Tungsten Oxide Wet Chemistry Synthesis

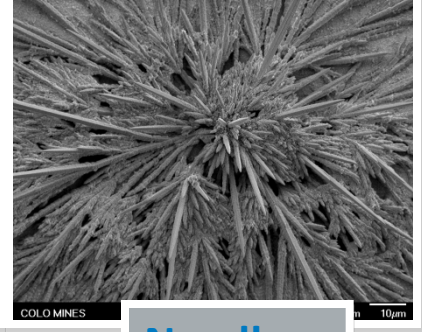
Pyrolysis of $((C_4H_9)_4N)_4W_{10}O_{32}$.



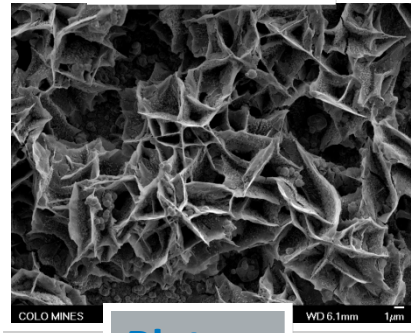
Nanorods



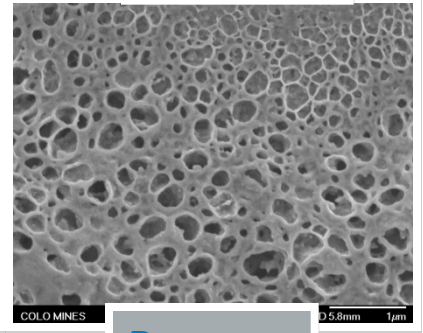
Spindles



Needles



Plates

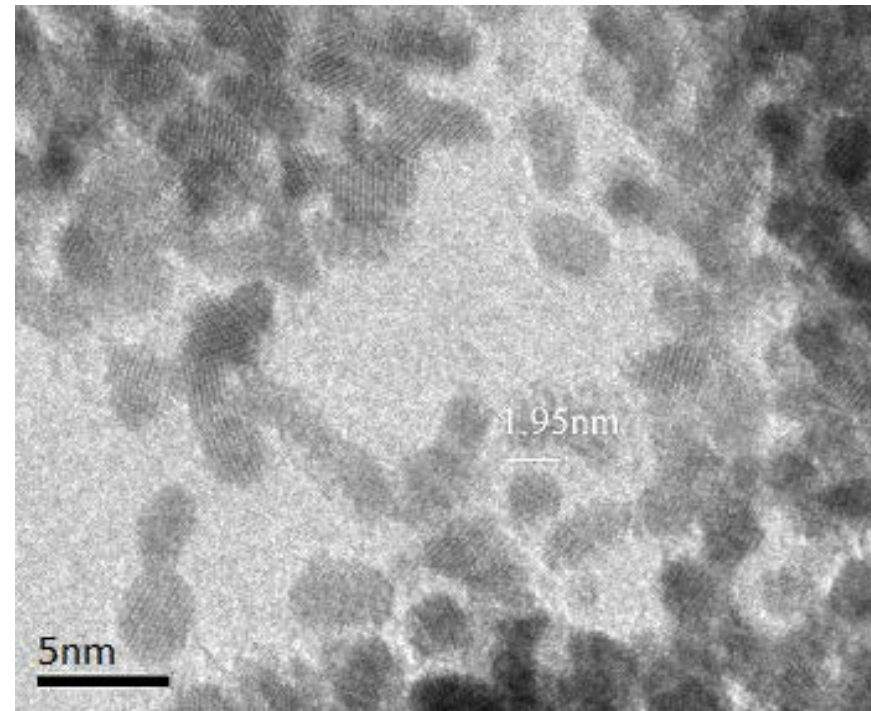
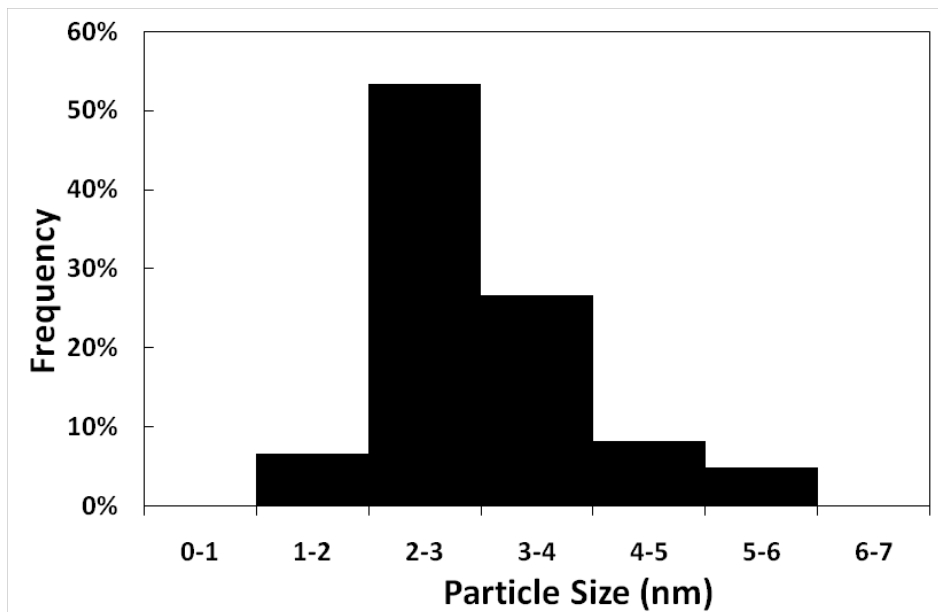


Porous

XRD pattern—as synthesized WO_3 nano rods.

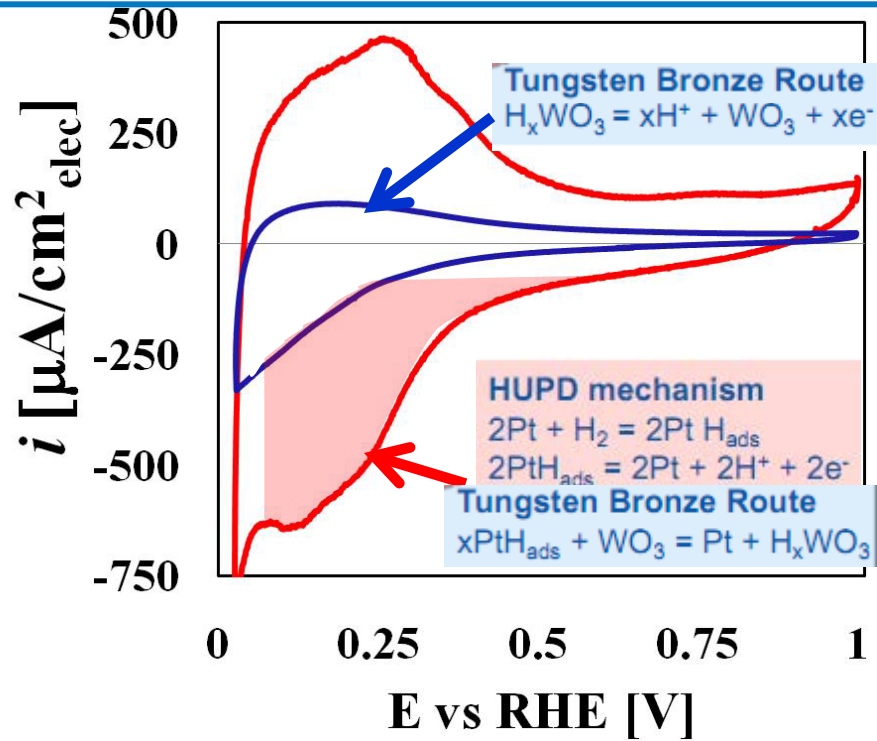
Pt Colloid Synthesis (outcome)

- A literature recipe* was modified significantly to synthesize Pt nanoparticles of controlled size by:
 - Decreasing the temperature to 80°C
 - Bubbling dilute CO into solution
 - Gradually adding 0.25M NaOH over 3h



*Wang, Y.; Ren, J.; Deng, K.; Gui, L.; Tang, Y. *Chem. Mater.* **2000**, *12*, 1622.

Tungsten Bronze Formation Interferes with Standard Electrochemical Surface Area Measurements Techniques



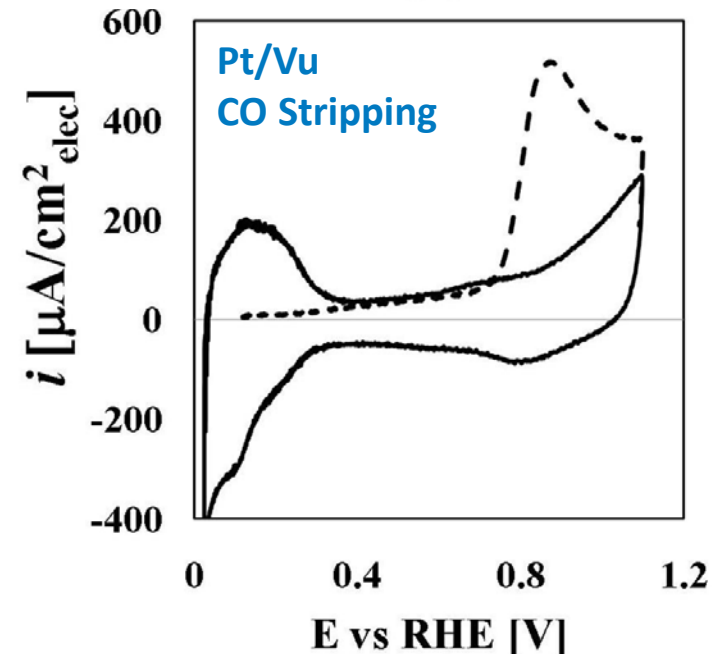
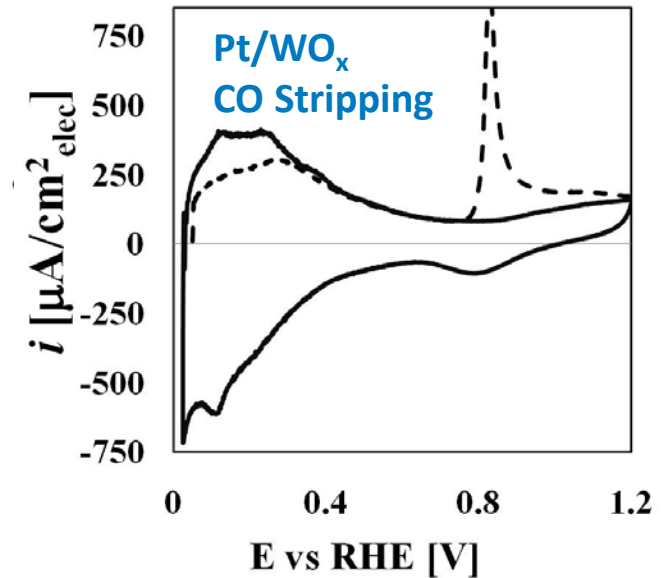
Formation of Hydrogen Tungsten Bronzes
 ($H_{0.18}WO_3$ and $H_{0.35}WO_3$)
 $WO_3 + xH^+ + xe^- = H_xWO_3$ ($0 < x < 1$)

Formation of Substoichiometric Oxides
 $WO_3 + 2yH^+ + 2ye^- = WO_{3-y} + yH_2O$ ($0 < y < 1$)

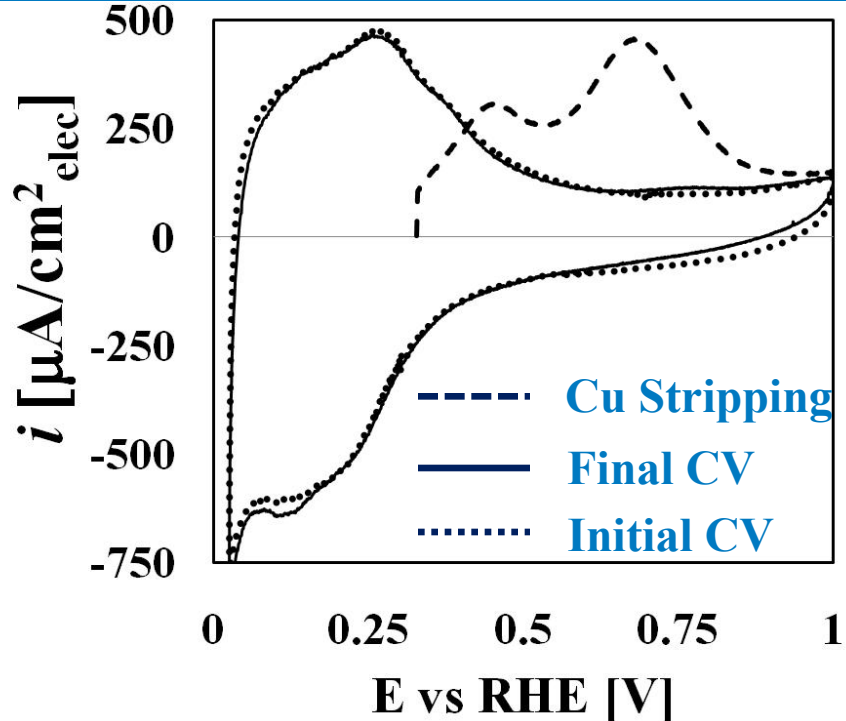
P. J. Kuleza, L.R. Faulkner, J. Am. Chem. Soc.
 110 (1988) 4905

HUPD

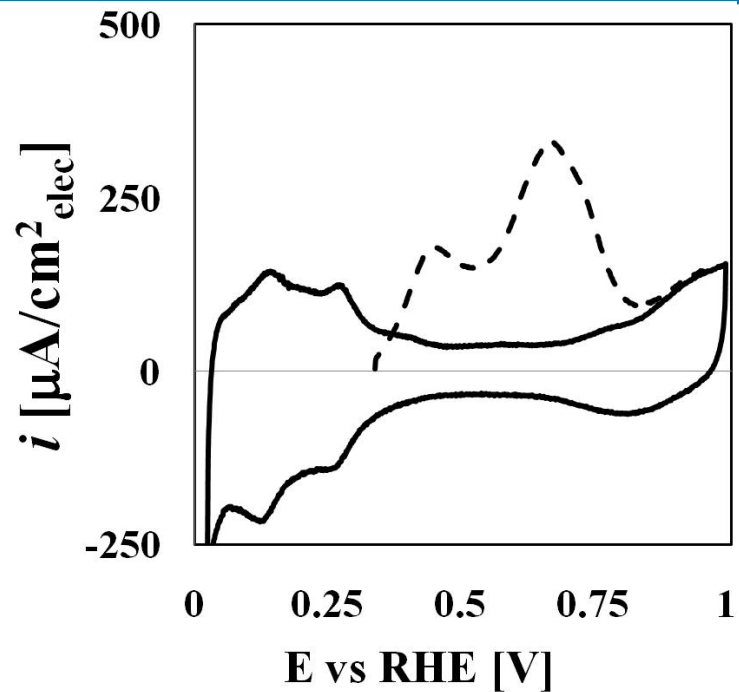
ECA
 $[m^2/g_{Pt}]$
 125



Cu UPD on Pt/WO_x Electrocatalysts



a) ALD Deposited Pt on HWD WO_x Nanorods



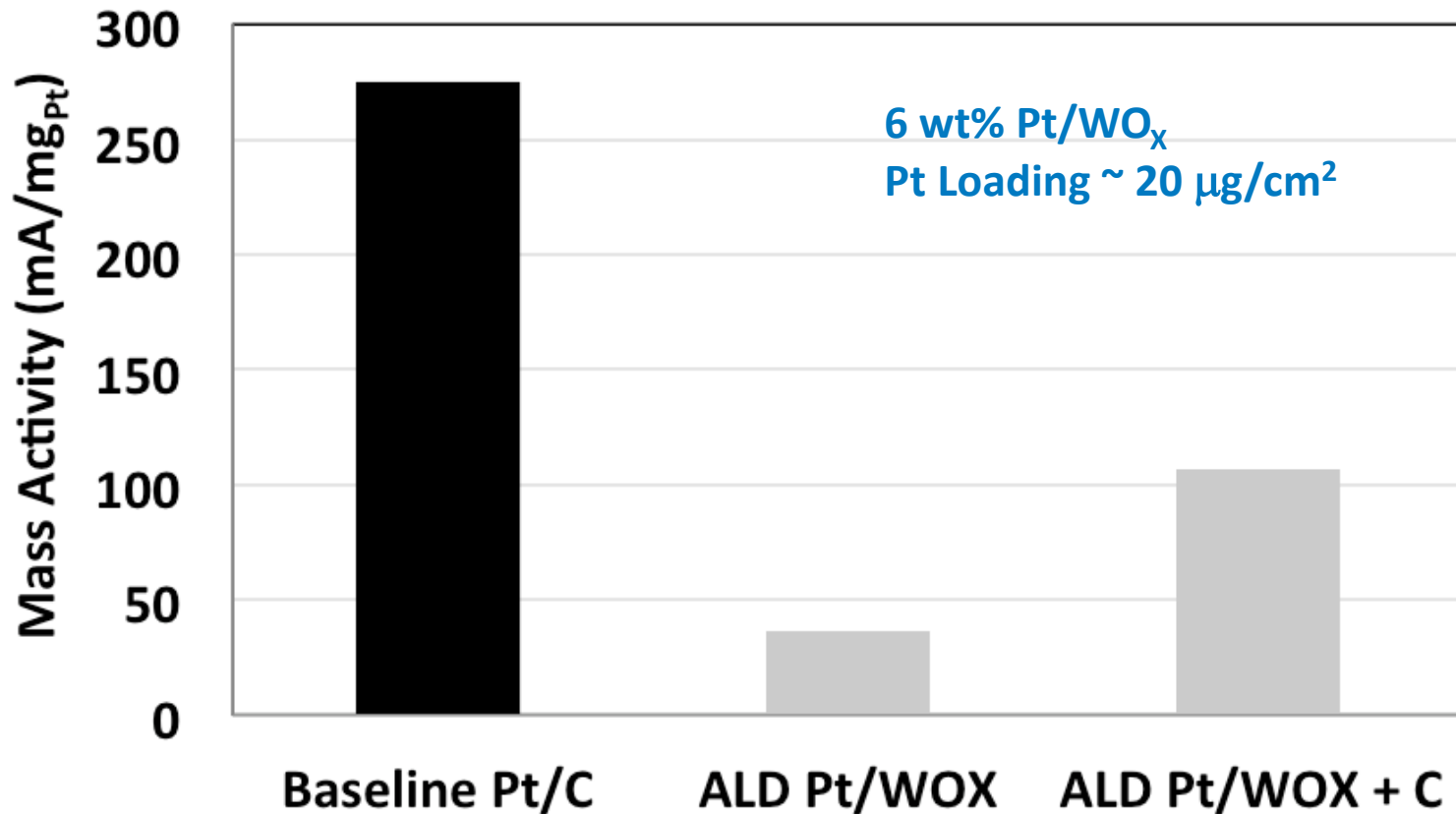
b) Wet Chemistry Pt/WO_x

Catalyst	Cu UPD	ECA			δ _{particle} [nm]	ECA predicted
		[m ² /g _{Pt}]	CO	HUPD*		
23 wt% Pt/WO _x ^a	53	30	65	5 ^c	56	
22 wt% Pt/WO _x ^b	16	12	16	9 ^d	31	

^c) From TEM, ^d) from XRD

Mass activity of ALD Pt/WO_x is low due to low conductivity of WO_x

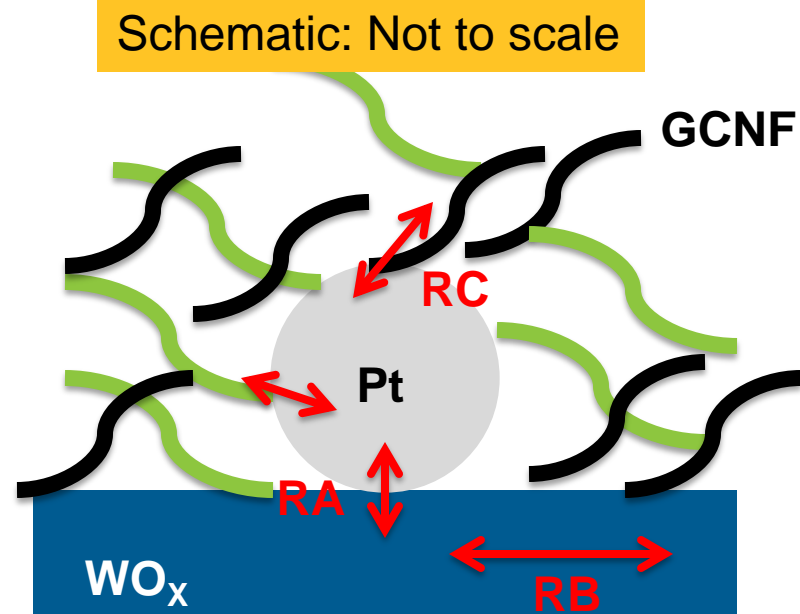
Adding carbon (graphite nanofibers – GNF) improves conductivity, but still far short of baseline



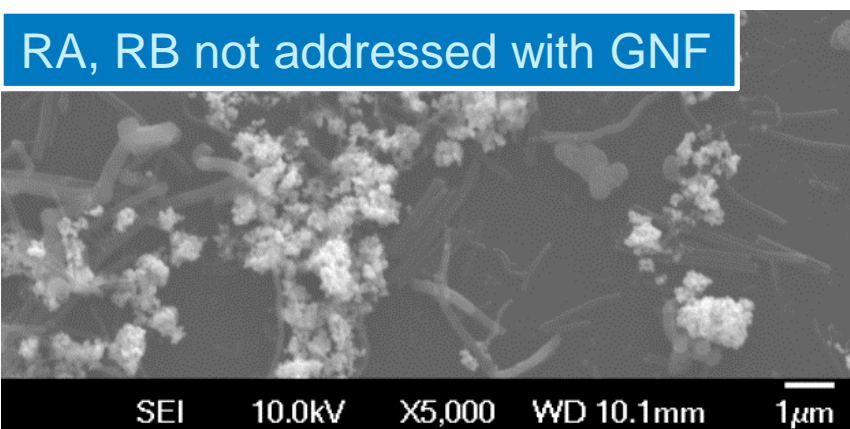
From NREL ALD

Challenges: Electronic Conductivity

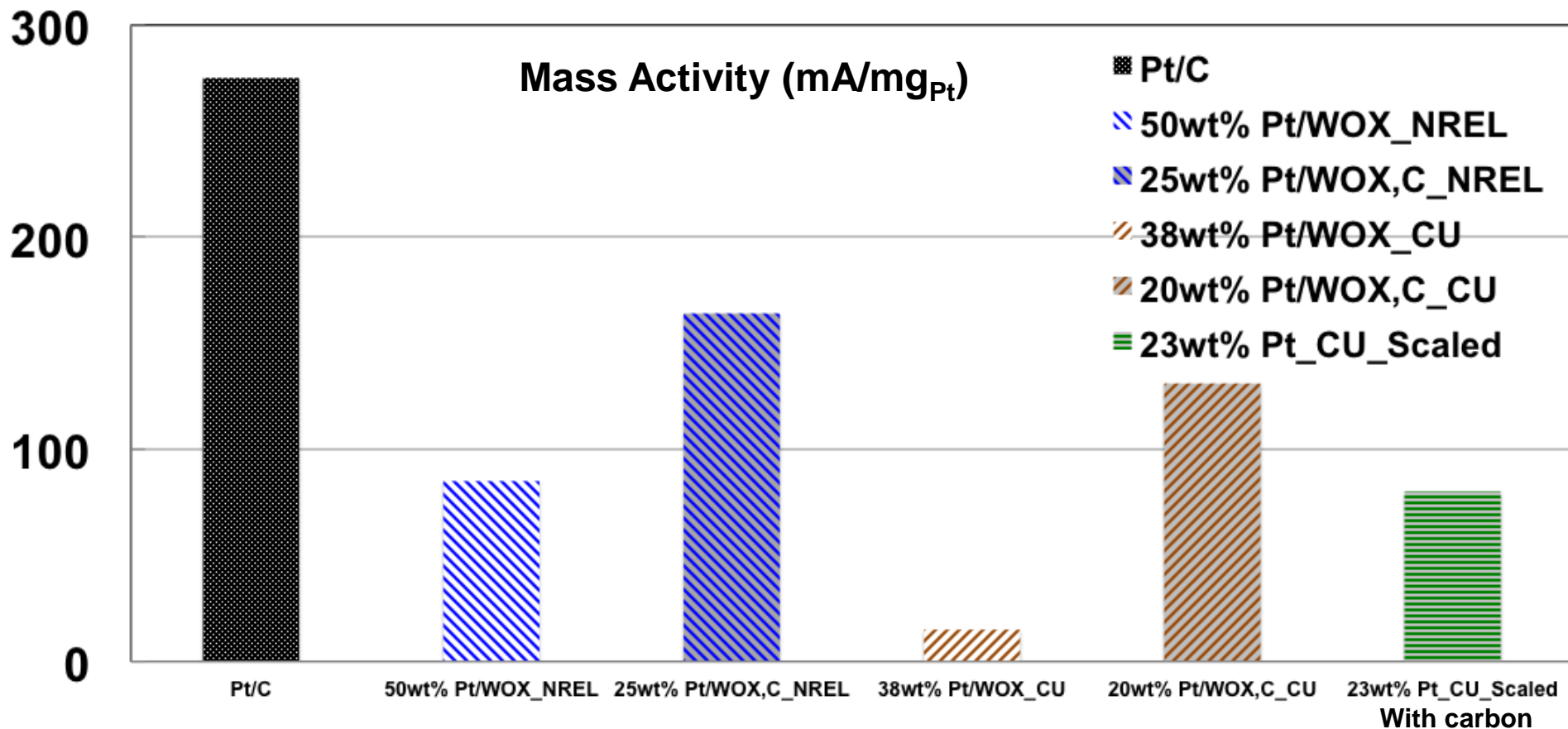
- Oxides supports have low electronic conductivity
- Addition of carbon matrix enhances the overall conductivity
- 3 electron pathways
 - Contact point between Pt and support: **RA**
 - Electronic conductivity through the support: **RB**
 - Electronic conductivity through the added carbon matrix: **RC**
 - Coating of Nafion[®] ionomer on Pt and WO_x and C not shown: **R_{Nafion}**



Actual Micrograph



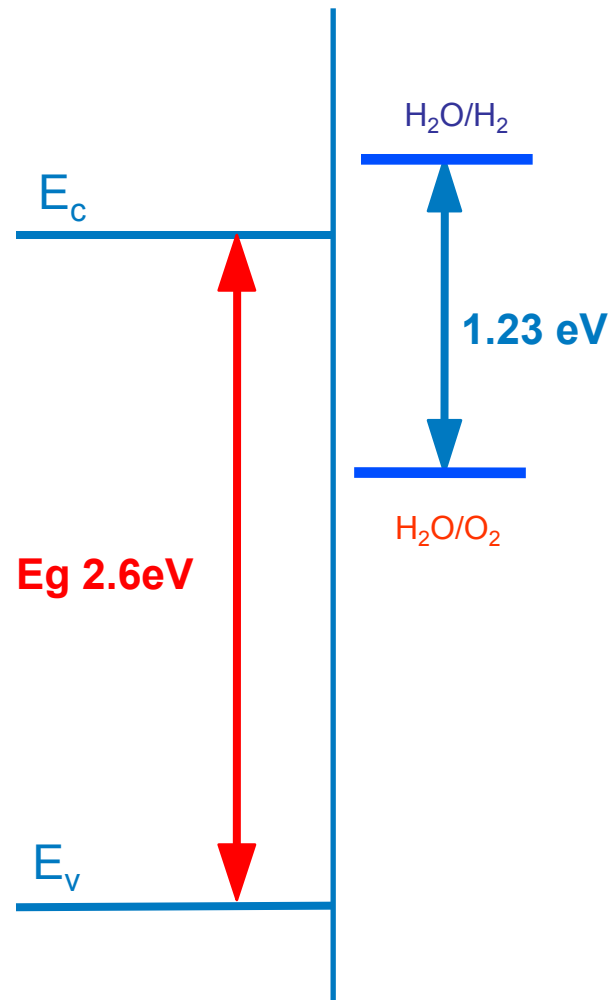
Mass Activity of Pt/C vs. ALD Pt/WO_x



WO_x based electrocatalysts did not meet Pt/C baseline activity

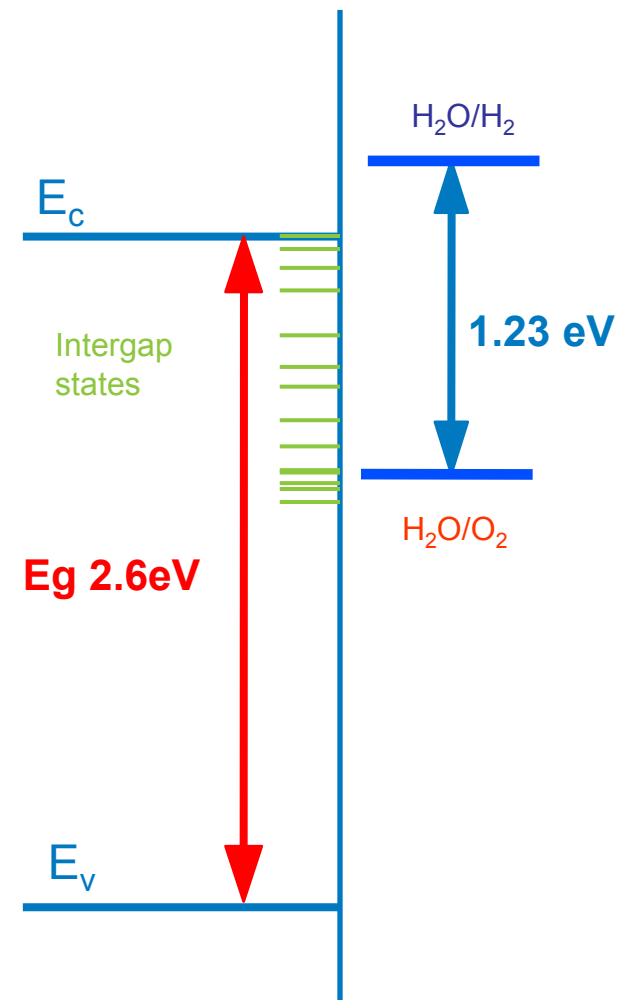
WO₃ Semiconductor Energetics

Blocking

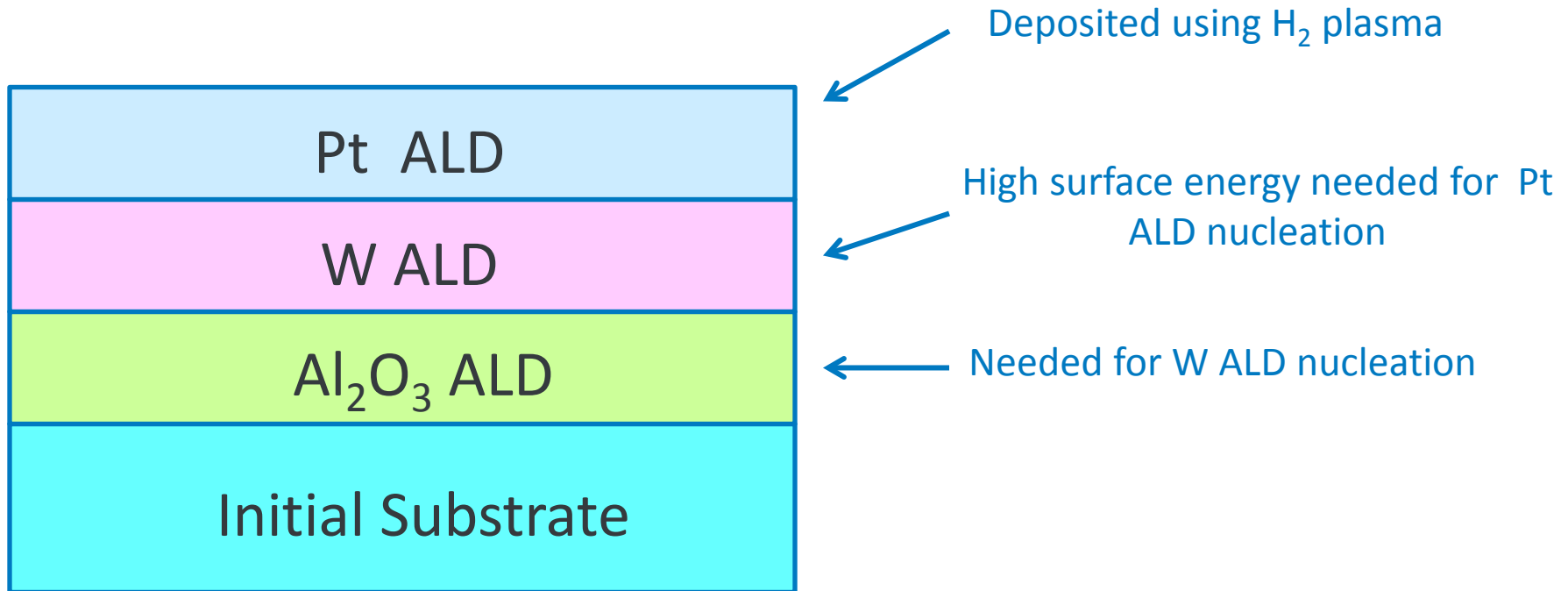


- WO₃ will block carrier transport for reactions in the gap.
- Sub-stoichiometric WO₃ doesn't provide conductive path.
- To obtain good conductivity, states must be created in the gap via alloying.
- Impact of alloying on the stability is unknown

Intergap states could provide conducting pathway



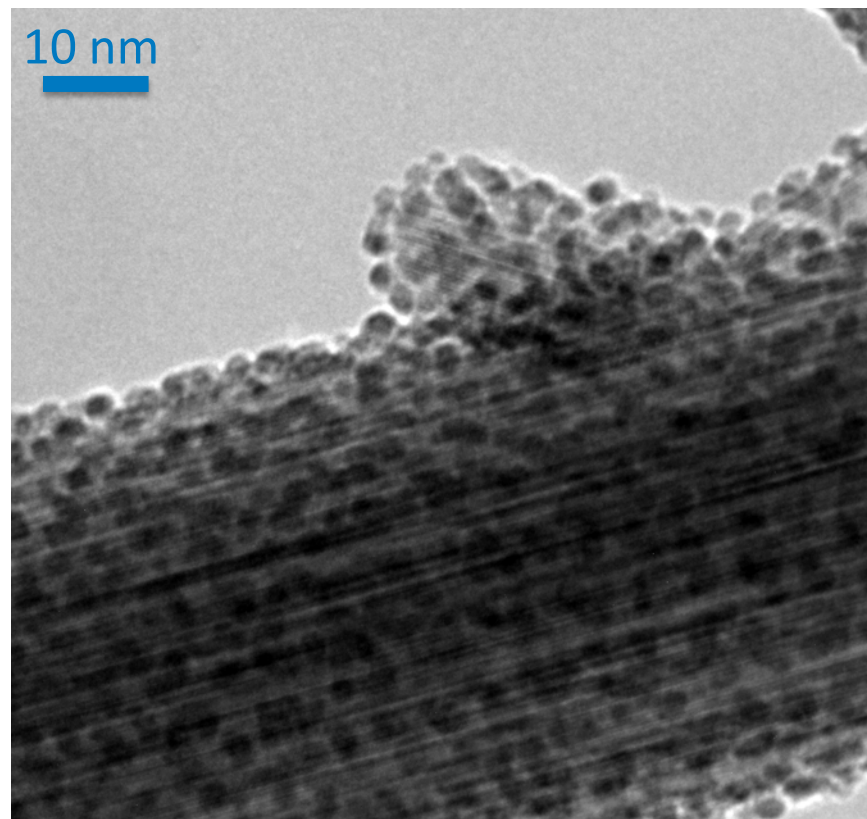
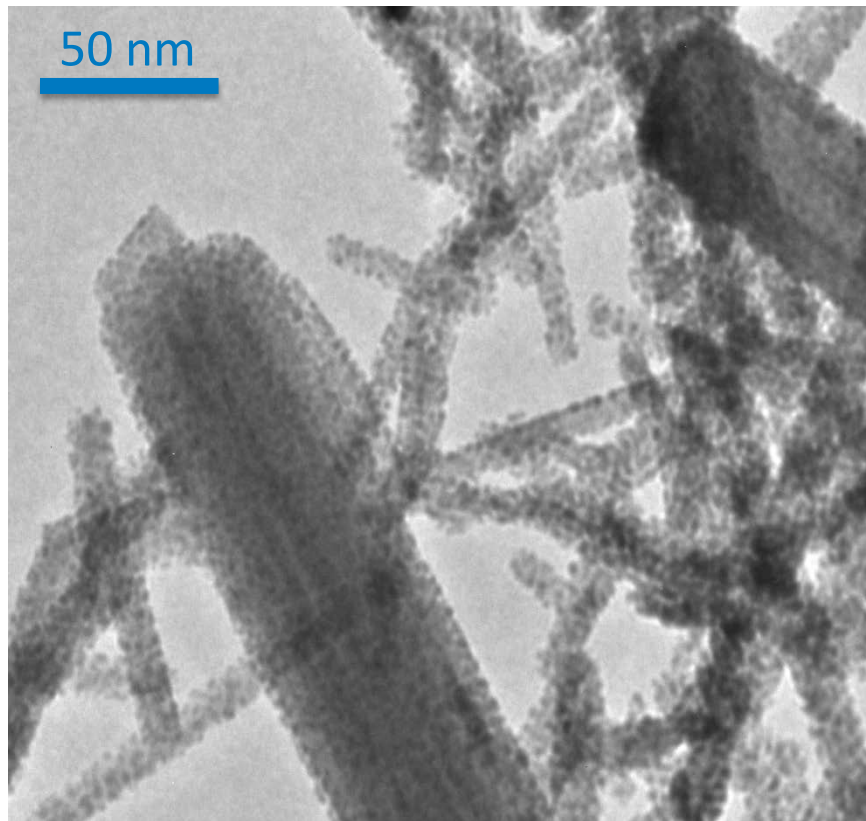
Strategy for Continuous Pt ALD Films Using W Adhesion Layer



Continuous film of Pt would help conductivity, but needs a continuous W adhesion layer. Attempted to make a W film via a hydrogen plasma, but didn't work for mesostructured WO₃

Results for Pt ALD on WO_x Particles in Plasma Reactor used for Flat Substrates

200 cycles - $MeCpPt(IV)Me_3$ with H_2 plasma at $120^\circ C$



Attempt to produce a W film via a hydrogen plasma to make a continuous film of Pt, but didn't work for mesostructured WO_3 Pt particles are still the result.

Atomic Layer Deposition of Platinum Nanoparticles on Titanium Oxide and Tungsten Oxide Using Pt(hfac)₂ and Formalin as the Reactants

Virginia R. Anderson,¹ Noemi Leick,² Joel W. Clancey,¹ Katherine E. Hurst,³ Kim M. Jones,³
Anne C. Dillon³ and Steven M. George^{1,4}

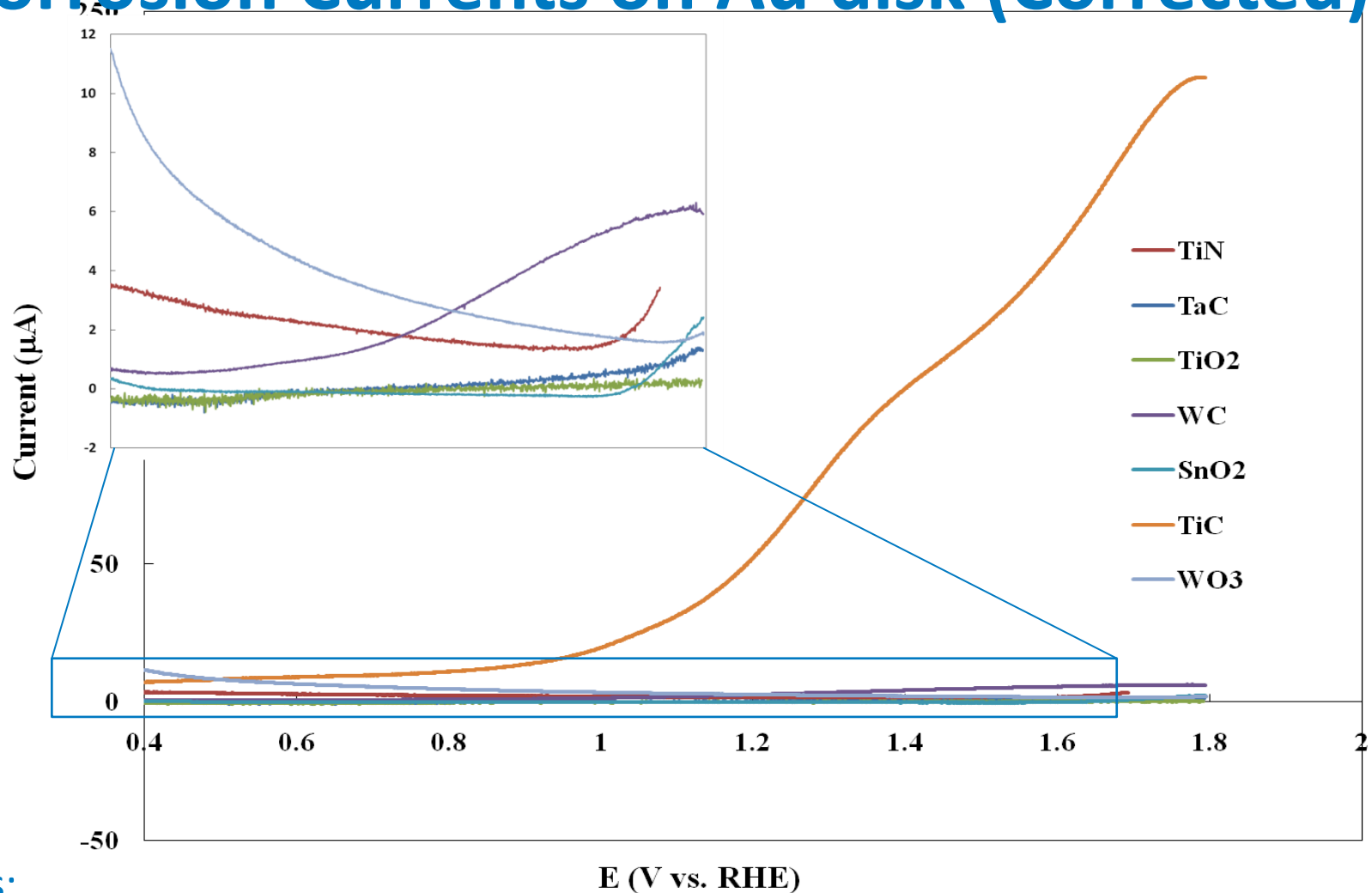
¹Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309;

²Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB Eindhoven; ³National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, Colorado, 80401; ⁴Dept. of Mechanical Engineering, University of Colorado, Boulder, Colorado, 80309

ACKNOWLEDGEMENTS

This work is dedicated to Dr. Anne C. Dillon who was a former student and collaborator. Her early passing took away a colleague with deep insight and infectious enthusiasm. This work was funded by the DOE under the EERE Fuel Cell Technology Program. We thank Dr. Andrew Cavanagh for X-ray photoelectron spectroscopy (XPS) sample analysis. We also appreciate useful conversations on Pt ALD with Dr. Layton Baker who is now at the Jet Propulsion Laboratory.

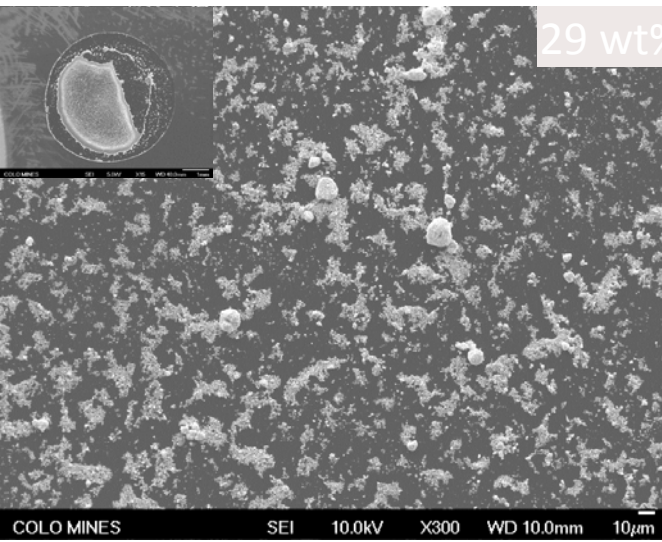
Corrosion Currents on Au disk (Corrected)



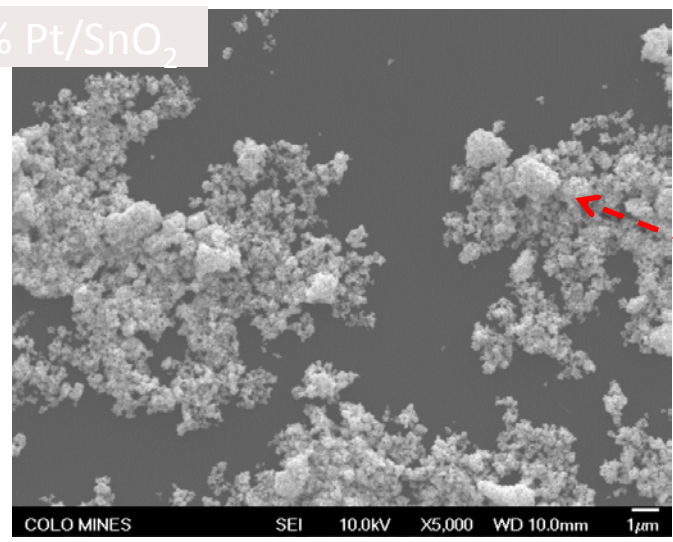
Results:

- TiC is the worst. From the inset WC is also less than ideal, and TiN is questionable
- TiO₂, TaC, and WO₃ appear to be the best for corrosion resistance.

Pt/SnO₂ Electrocatalysts: SEM

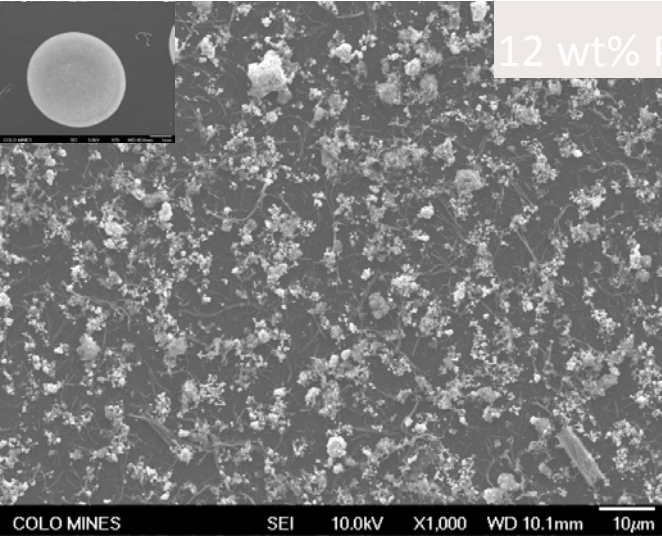


29 wt% Pt/SnO₂

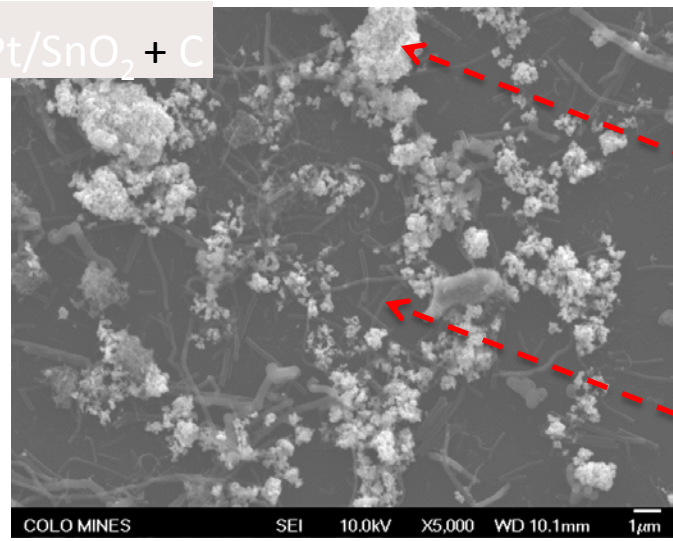


Pt/SnO₂

Better dispersion

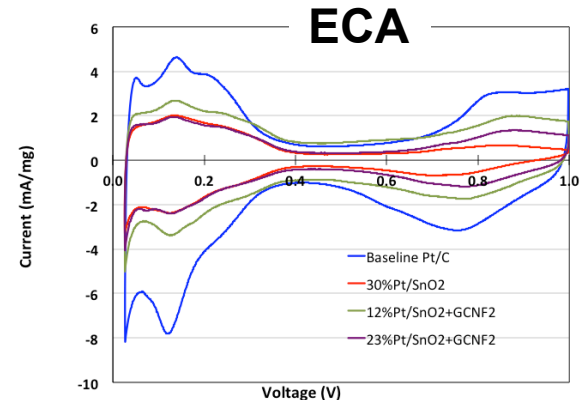
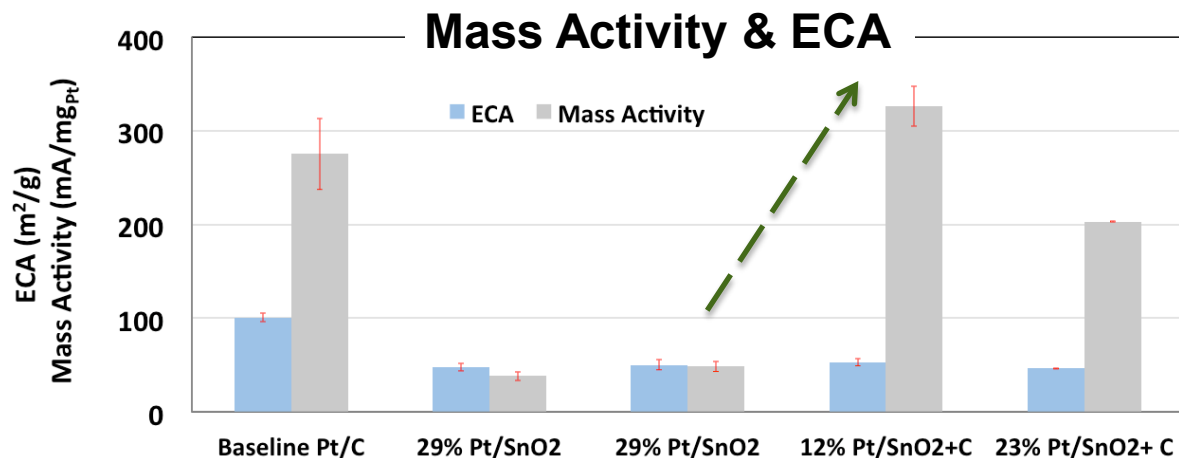
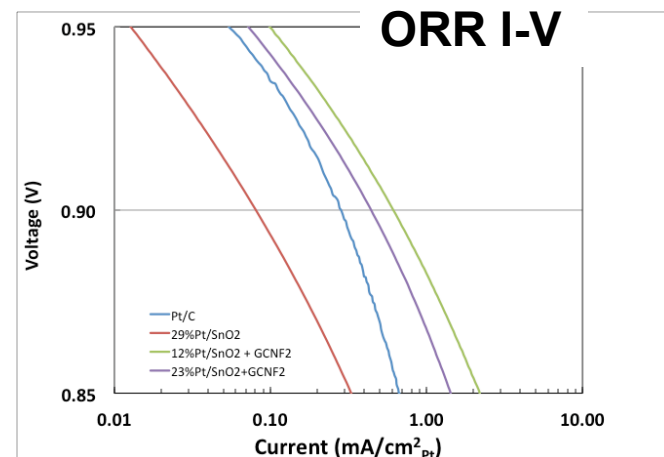
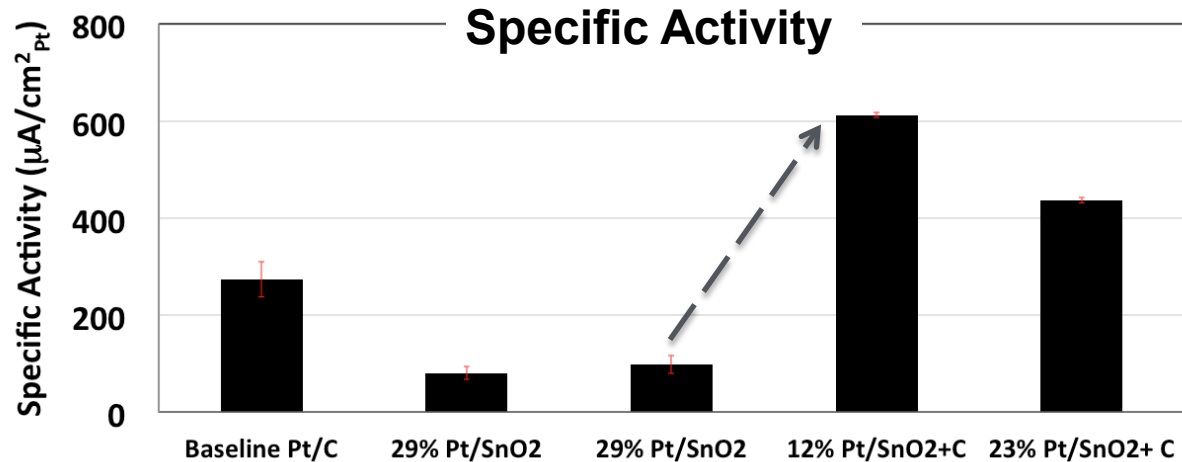


12 wt% Pt/SnO₂ + C



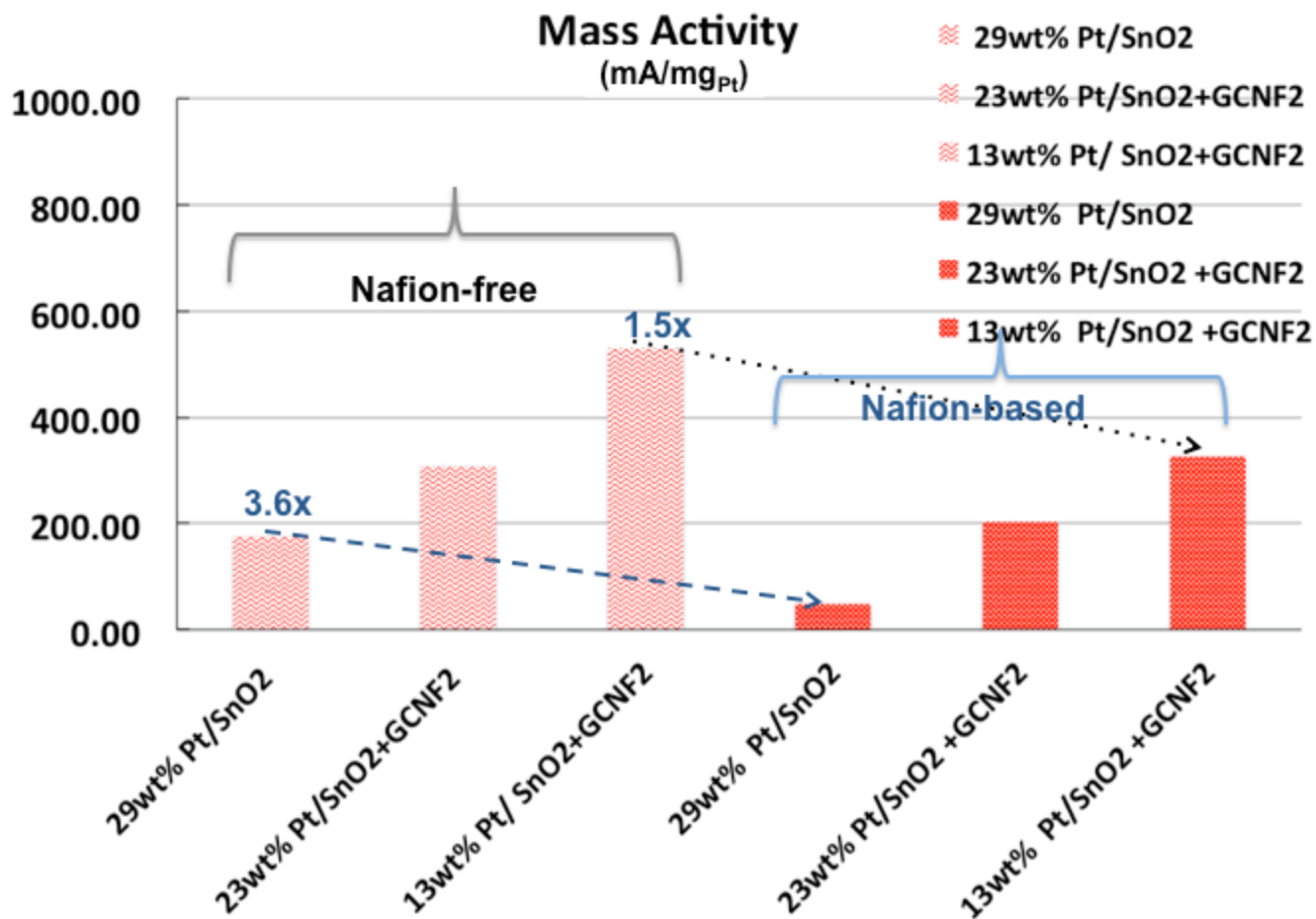
Pt/SnO₂
Carbon nanofibers providing interconnects

Pt/SnO₂ Electrocatalysts: ORR Activity



Lower electronic conductivity—one of the causes for lower activity of Pt/SnO₂ electrocatalysts; the other being electrode dispersion.

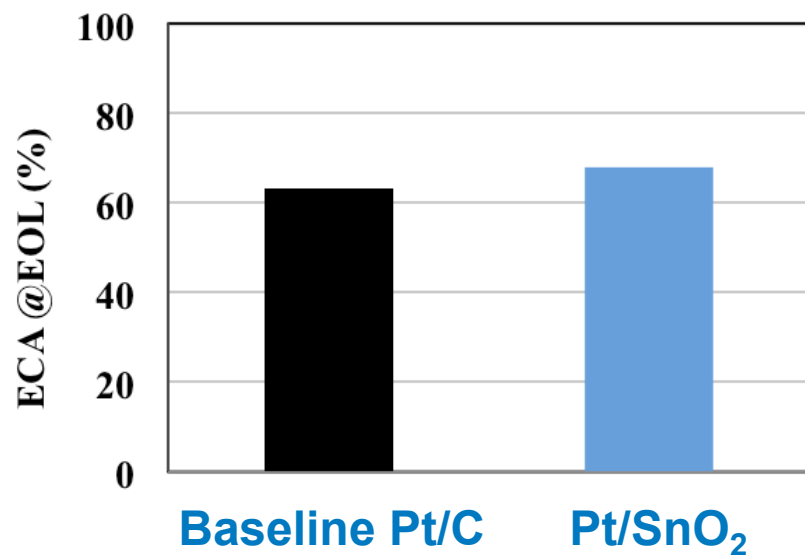
Results—Pt/SnO₂



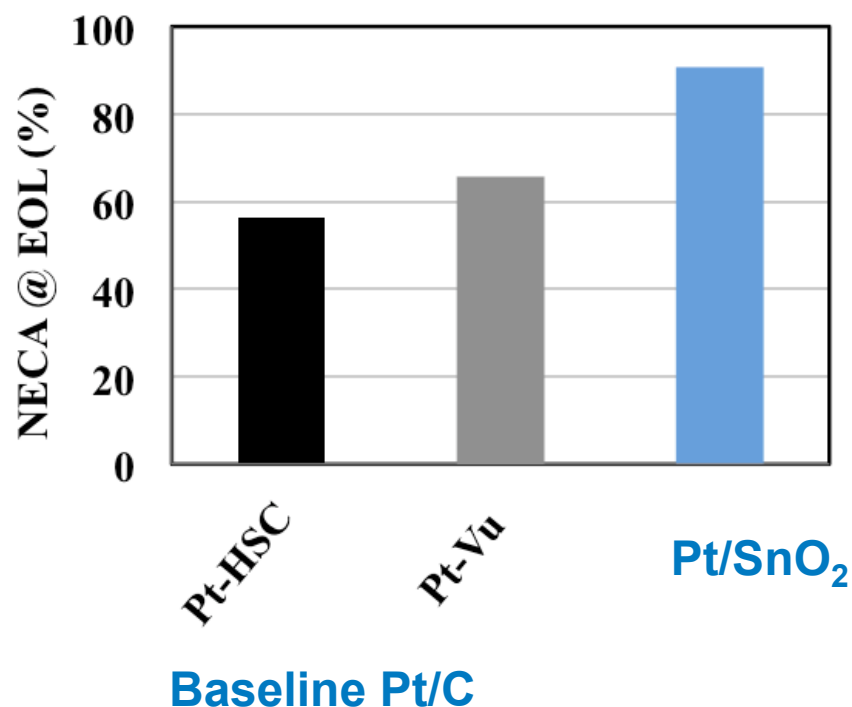
Nafion-free results are better due to Nafion blocking or slowing down oxygen diffusion. Note: this only works for an RDE.

Pt/SnO₂ Electrocatalysts: Cyclic Durability

0.6- 1.0V, RT, 500 mV/s

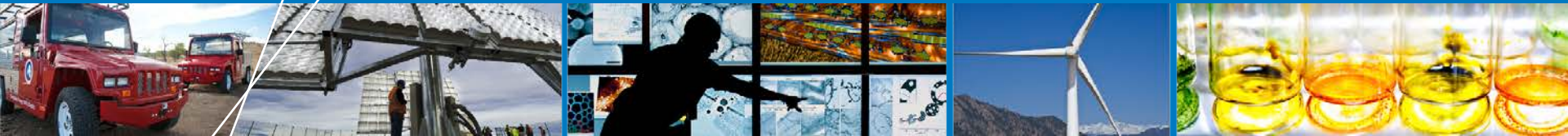


1.0V- 1.6V, RT, 100 mV/s



- Protocol (0.6–1.0V, RT, 500 mV/s) applied to baseline Pt/C and Pt/SnO₂ show similar losses in ECA. Losses are likely to be due to Pt dissolution which is independent of the support.
- Protocol (1.0V–1.6V, RT, 100 mV/s) applied to baseline Pt/C and Pt/SnO₂ show higher losses for Pt/C catalysts since the SnO₂ support is more corrosion resistant.

Pt/HPA-Graphitized C Electrocatalysts



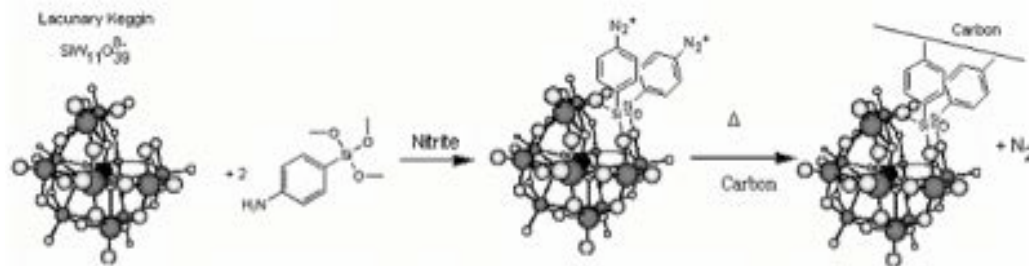
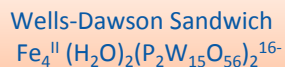
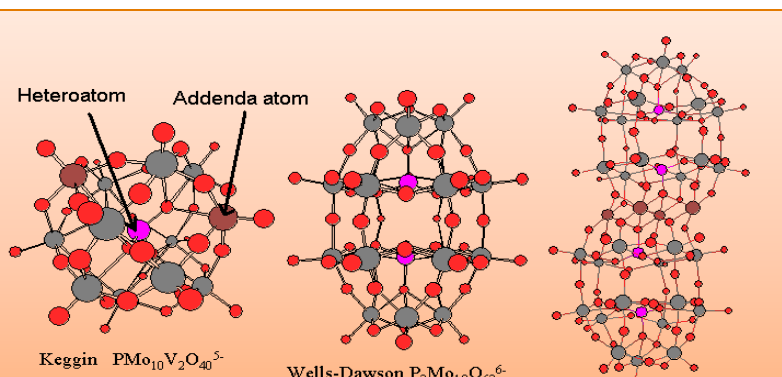
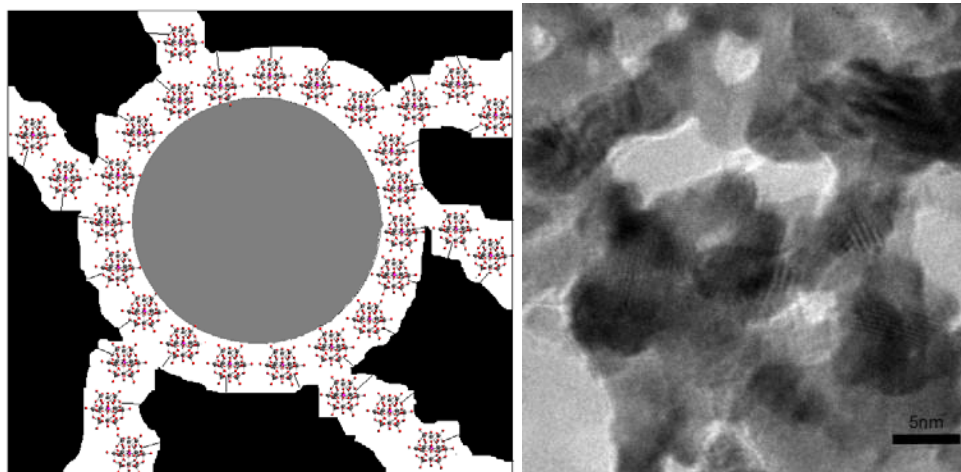
Accomplishments

Based on FY13 work on Pt/Ketjen Black-HPA, Fuel Cell Tech Team and DOE recommendation was to evaluate Pt/graphitized carbon-HPA.

HPA Functionalization to C, Pt/C, WO₃ and Pt/WO₃

- Stabilize nano-metallic particles
- Decompose peroxide
- Alter electrochemistry on Pt surface
- Conduct protons

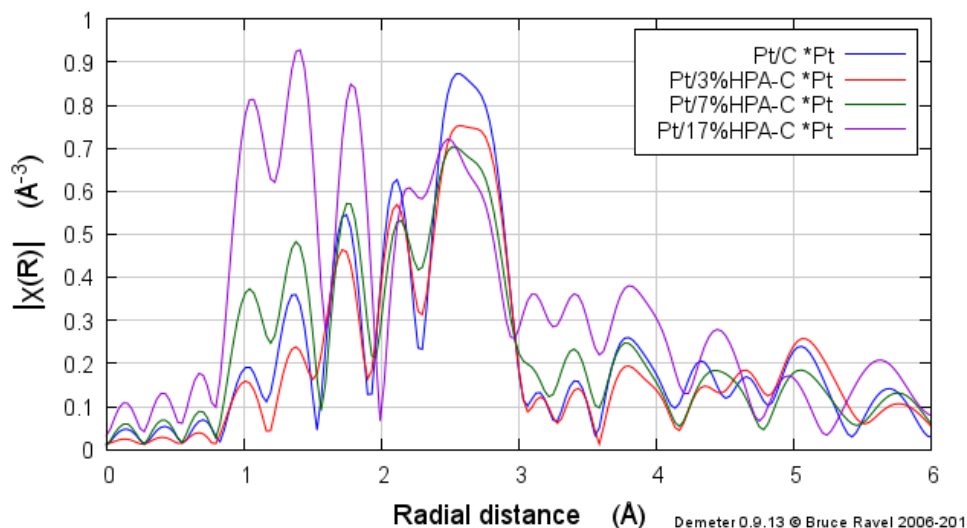
Immobilized HPAs as Catalyst Supports



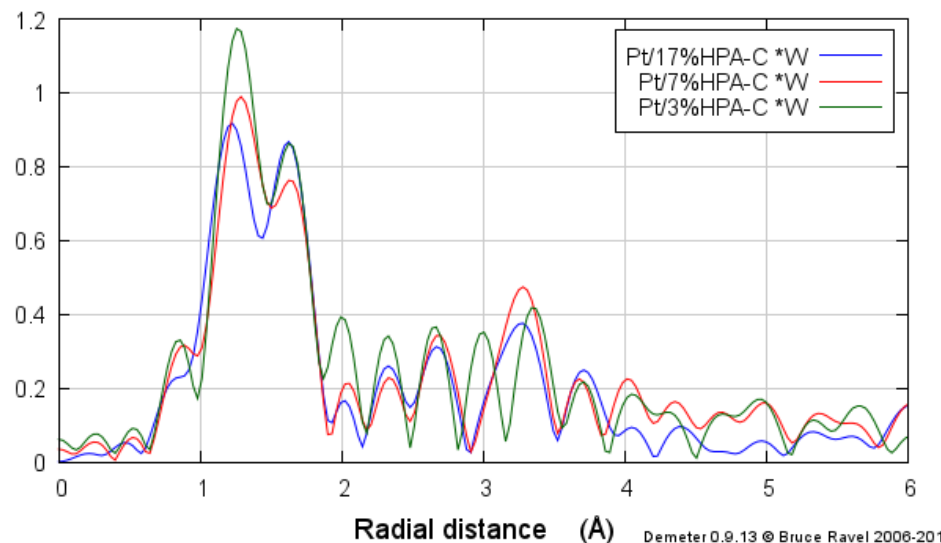
HPA functionalization of Carbon black confirmed by EDX spectra.

Pt/HPA-C EXAFS

Pt Edge



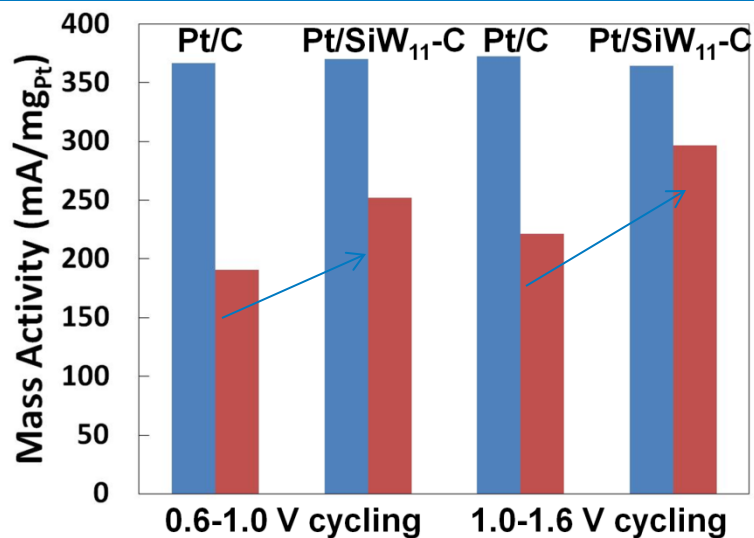
W Edge



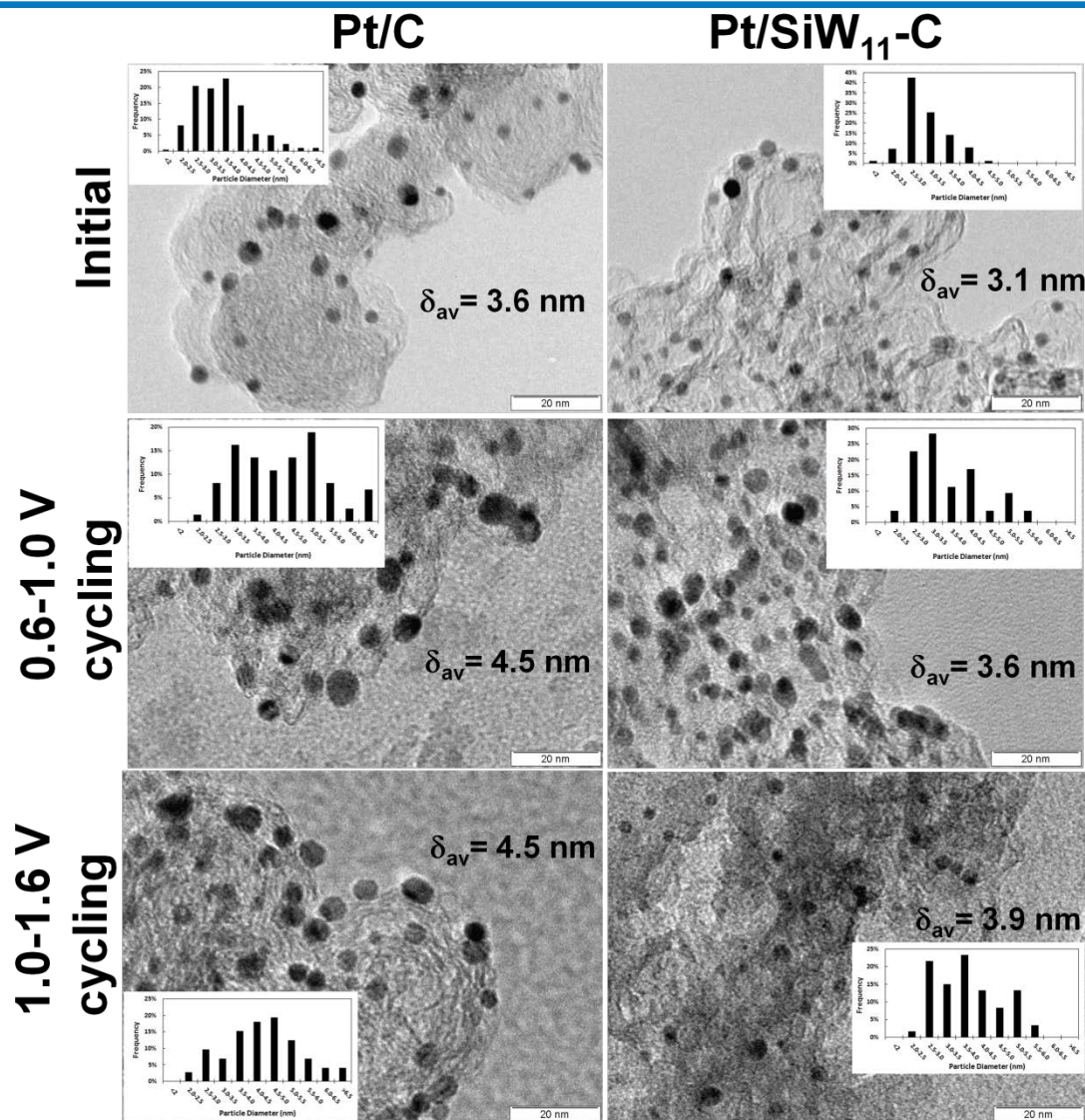
The strong effect on the Pt edge with increasing HPA loading implies to us that Pt is preferentially binding at the HPA locations. In contrast, there is very little change in the W edge implying that the Pt-W interaction remains approximately unchanged as HPA loading is increased.

The maximum observed in Pt mass activity is likely a result of competing effects of the Pt-W interactions shown here and occupation of preferential binding sites by the HPA.

Pt/HPA-C Durability



The 0.6-1.0 V cycling (30,000 cycles, 500 mV/s) was used to evaluate Pt dissolution, while 1.0-1.6 V cycling (6,000 cycles, 100 mV/s) evaluated support corrosion. HPA loading was chosen such that initial activity was near equal to Pt/C (blue bars). In both cases, HPA helped maintain catalyst activity by slowing particle growth (red bars).



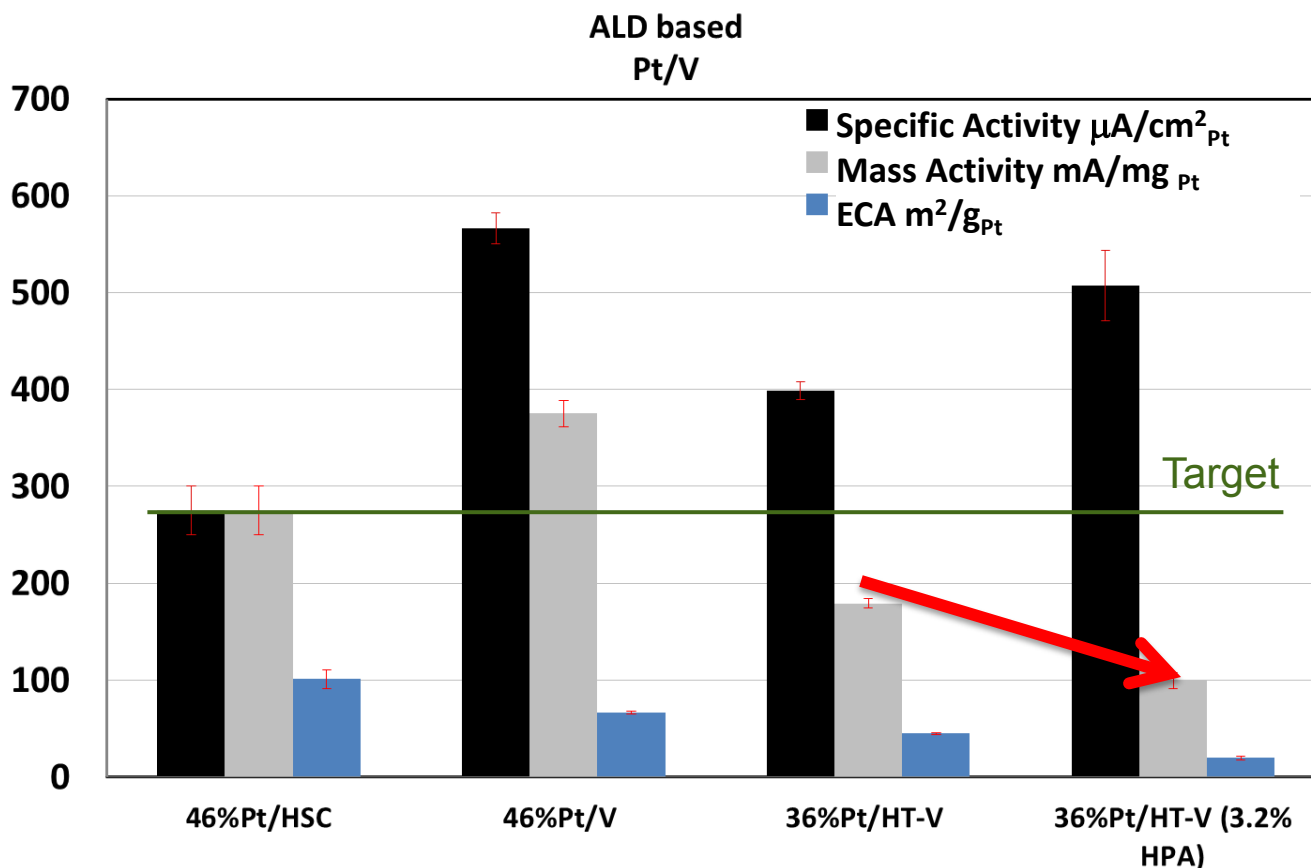
*All scale bars are 20 nm.

**Insets show Pt particle size distribution in 0.5 nm increments starting from 1.5 nm.

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Electrochemical Activity for ALD Catalyst (ALD—Pt/V)

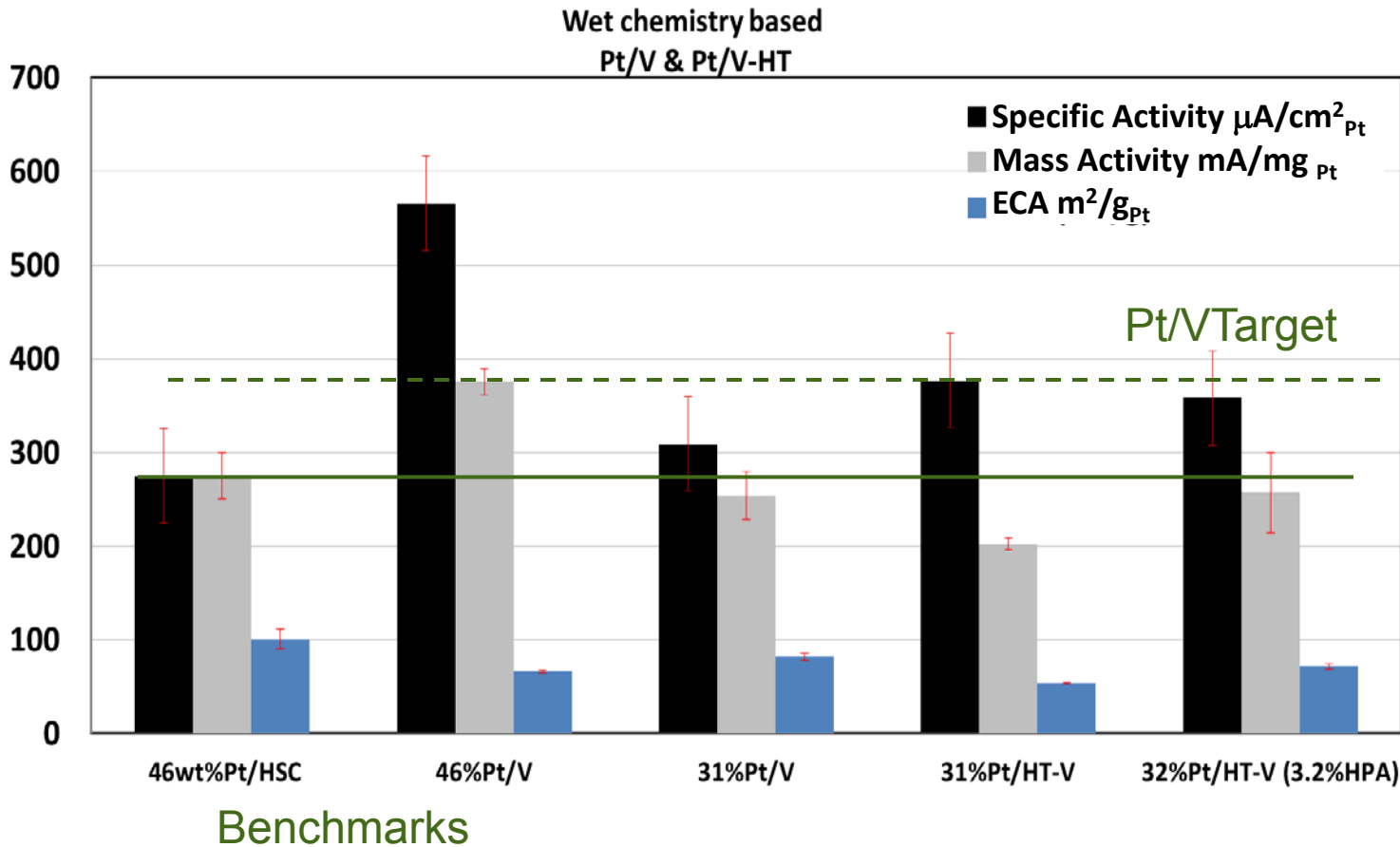
Mass Activity Target = 275 mA/mg_{Pt}



In this next set of experiments (to slide 34) however, this data shows a decrease in the activity after HPA modification. The reason for the difference is not clear.

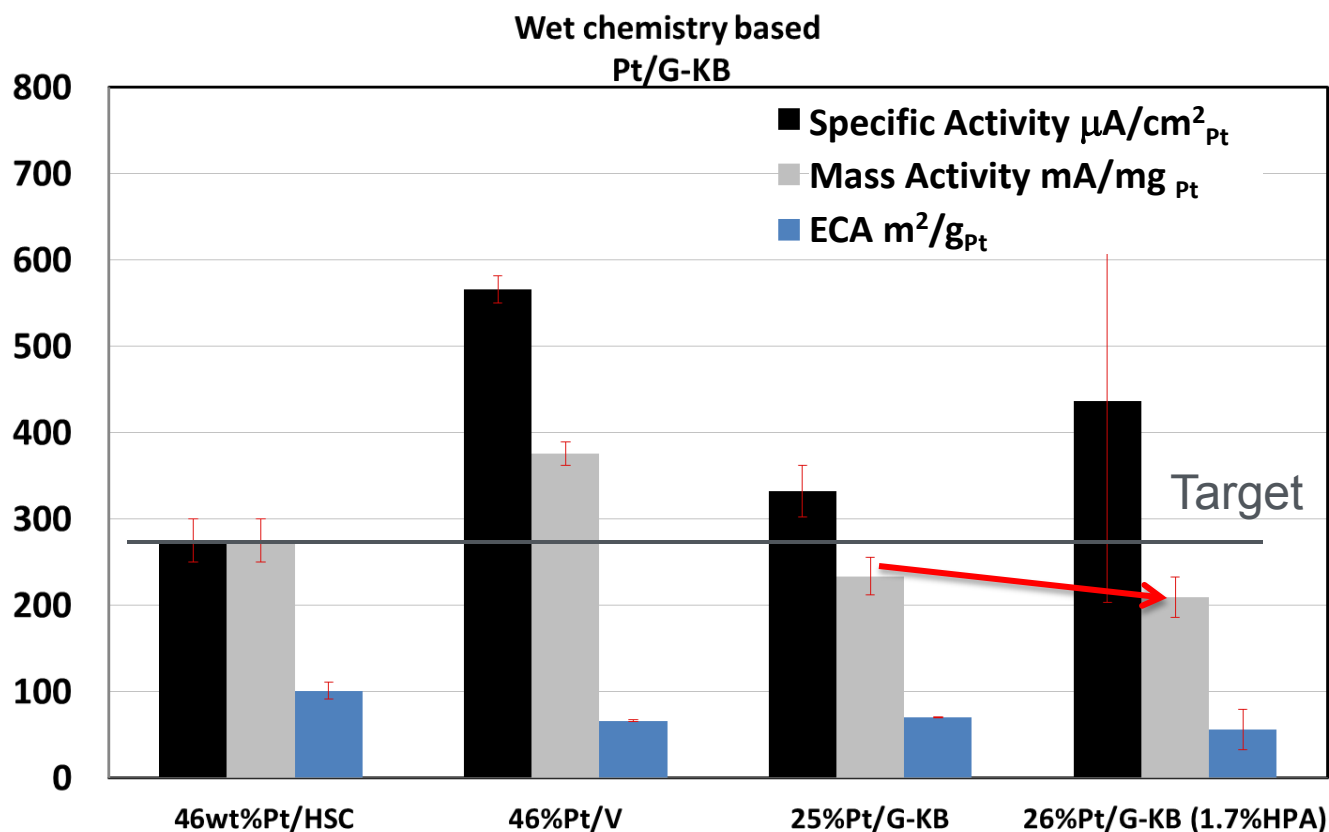
Electrochemical Activity for Wet Chemistry Catalysts (Pt/V, Pt/HT-V)

Mass Activity Target = 275 mA/mg_{Pt}; 380 mA/mg_{Pt}



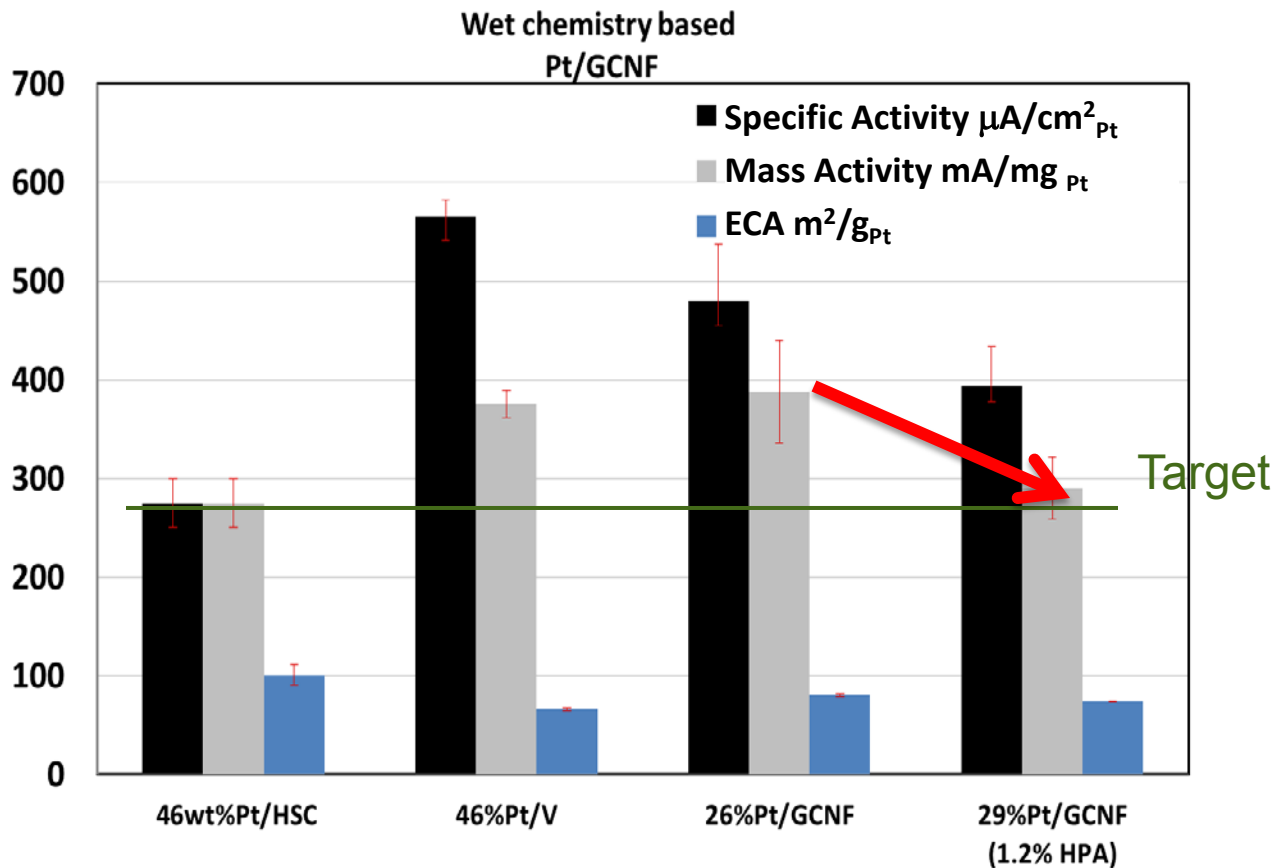
Electrochemical Activity for Wet Chemistry Catalysts (Pt/G-KB)

Mass Activity Target = 275 mA/mg_{Pt}



Electrochemical Activity for Wet Chemistry Catalysts (Pt/GCNF)

Mass Activity Target = 275 mA/mg_{Pt}



Cyclic Durability of Pt/C and Pt/C-HPA

ECA ($\text{m}^2/\text{g}_{\text{Pt}}$); ECA Loss (%)

Pt/Ketjen Black Baseline:

BOL= 100 $\text{m}^2/\text{g}_{\text{Pt}}$; EOL= 46 $\text{m}^2/\text{g}_{\text{Pt}}$; **39.5% Loss**

Pt/GCNF:

BOL= 82 $\text{m}^2/\text{g}_{\text{Pt}}$; EOL=71 $\text{m}^2/\text{g}_{\text{Pt}}$; **13.4% Loss**

Pt/GCNF-HPA:

BOL= 68 $\text{m}^2/\text{g}_{\text{Pt}}$; EOL=52 $\text{m}^2/\text{g}_{\text{Pt}}$; **23.5% Loss**

EOL @ 5000 cycles

Pt/GCNF exhibits improved durability compared to baseline, but for post-HPA treatment, the losses are slightly higher.

For these samples, the HPA treatment does not result in an improvement of the durability of the catalyst system.

FY 2014 1st Quarter Milestone

- Meet the Pt/C baseline activity of **275 mA/mg_{Pt}** mass activity at 0.90 V, 100 kPa with either the HPA modified carbons or the non-carbon supports, but show a **2x greater cyclic durability** in RDE tests.

12/31/2013

Milestone has been met; but HPA treatment itself does not cause any improvement in durability of a graphitized carbon support.

2nd and Final Quarter Milestone

- Evaluate remainder of the Pt/HPA treated carbons with RDE

MEA testing was a no-go and the program was ended early with some cost saving to DOE

3/31/2014