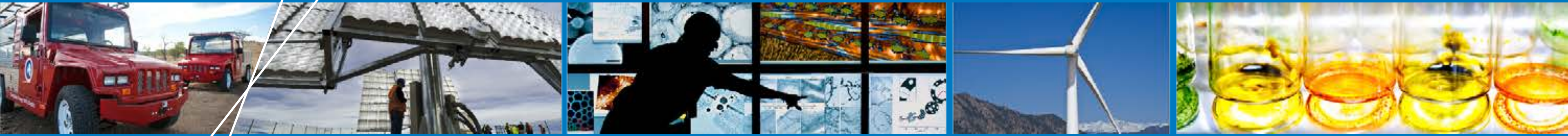
WO_3 and HPA based systems for durable Pt catalysts in PEMFC cathodes



2012 DOE Hydrogen and Fuel Cells Program Review

John Turner

May 15th, 2012

FC084

Overview

Timeline

- Start Date: 05/01/2010
- End Date: 04/30/2014
- Percent Complete: 40%

Budget

- Total project funding: $2.9M
  - DOE share: $2.6M
  - Cost share
    - CSM: $204,315
    - CU: $54,000
- Funding received in FY10: $500k
- Funding received in FY11: $550k
- Planned Funding for FY12: $975k

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)

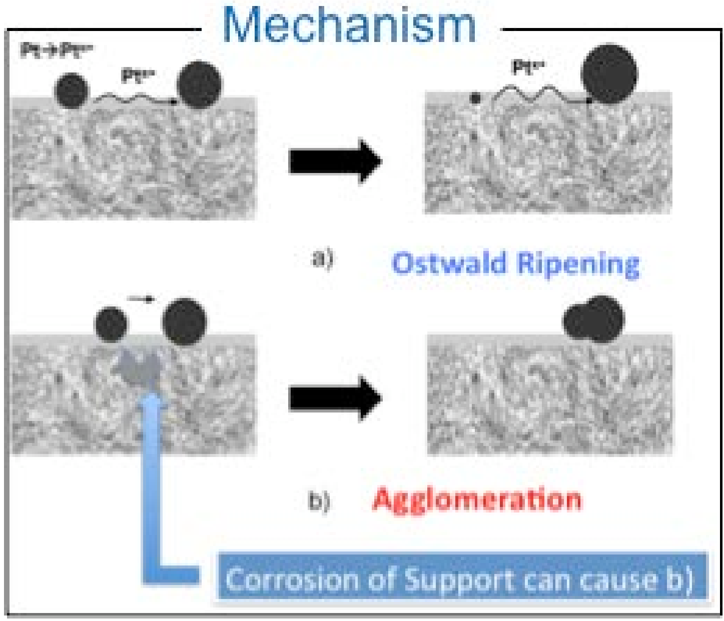
Relevance: Objectives

Improve electrocatalyst, MEA durability, and activity through the use of Pt/WO_3 and HPA modification 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

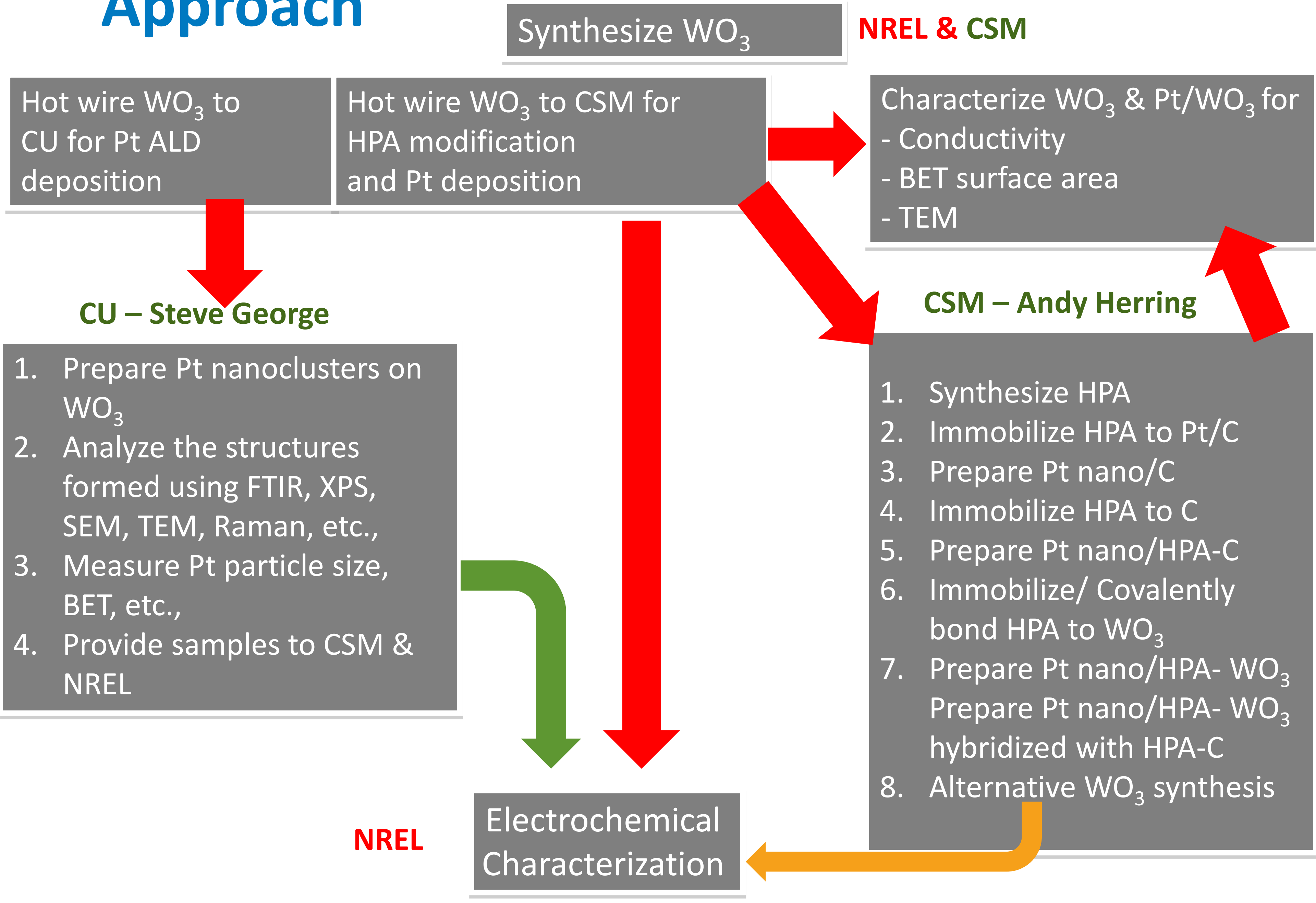
- **Lower support corrosion**
  - Increased durability under automotive startup/shutdown operation.
  - Suppress Pt agglomeration/electrode degradation

Simplify system and lower system cost



Polymer Electrolyte Fuel Cell Degradation, Editors: Matthew M. Mench, Emin Caglan Kumbur, T. Nejat Veziroglu, Chapter 3, S. Kocha, Electrochemical Degradation: Electrocatalyst and Support Durability (2012)

Approach



Synthesize WO_3

NREL & CSM

Hot wire WO_3 to CU for Pt ALD deposition

Hot wire WO_3 to CSM for HPA modification and Pt deposition

Characterize WO_3 & Pt/WO_3 for
- Conductivity
- BET surface area
- TEM

CU – Steve George

1. Prepare Pt nanoclusters on WO_3
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 WO_3
7. Prepare Pt nano/HPA- WO_3 Prepare Pt nano/HPA- WO_3 hybridized with HPA-C
8. Alternative WO_3 synthesis

NREL

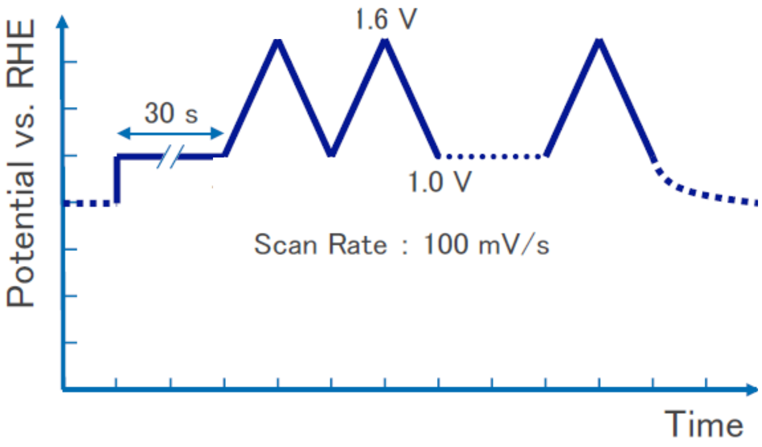
Electrochemical Characterization

Official Milestones for FY 12

- **5.7.1 - Establish at least 2 standard test protocols to evaluate and benchmark the durability of alternative Pt supports. 12/11 Completed**
- **5.7.2 - Obtain cyclic voltammograms (CVs) and mass activity for Pt on WO_3, HPA, or a combination of the two with electrochemical surface areas greater than 25 m^2/g Pt. 4/12 "yes"(ECA)**
- **5.7.3 - Demonstration of controlled nano-structured Pt placement and loading on WO_3, HPA, or a combination having mass activity (0.28 A/mg Pt @ 900 mV iR-free) comparable to baseline Pt/C (DOE Status). 9/12 Not yet**

Protocols for Electrocatalyst/Support Durability Evaluation

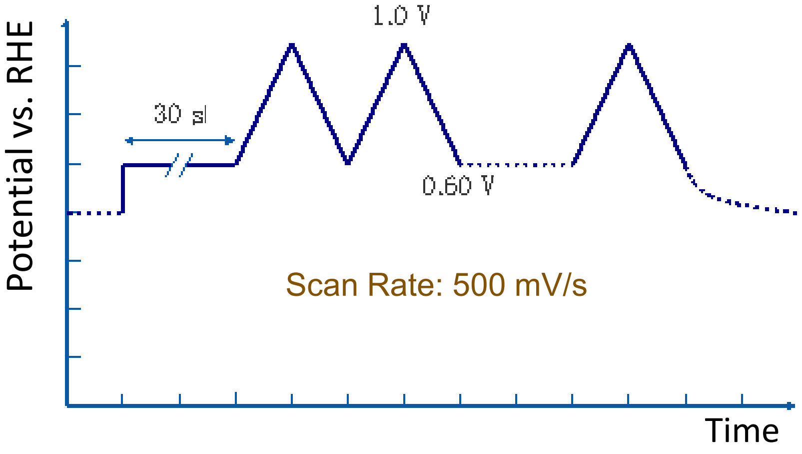
1.0–1.6 V Regime



Start-up/Shut-down Regime

—Support degradation
—Pt agglomeration

0.60–1.0 V Regime



Normal Operating Regime

—Pt dissolution
—Pt agglomeration

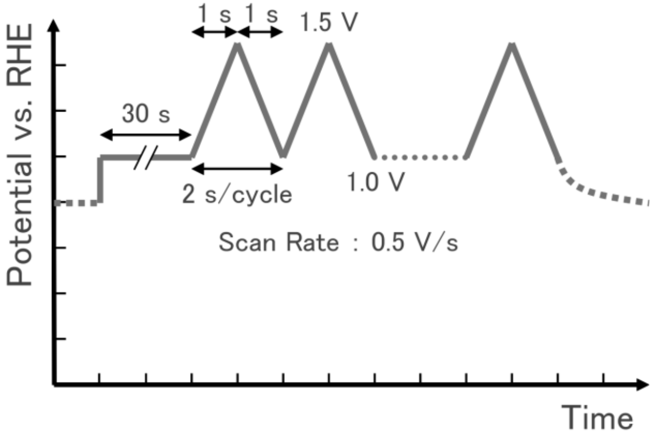
Durability Working Group Co-chairs: Debbie Myers & Rod Borup

<u>Team for catalyst supports</u>

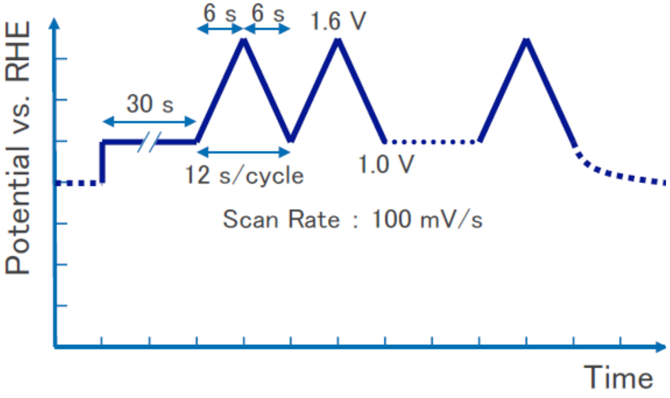
Shyam Kocha (NREL)—Lead

KC Neyerlin (NREL), Eric Brosha (LANL) , Mahlon Wilson (LANL), Lior Elbaz (LANL), Nilesh Dale (NTCNA), Vijay Ramani (IIT).

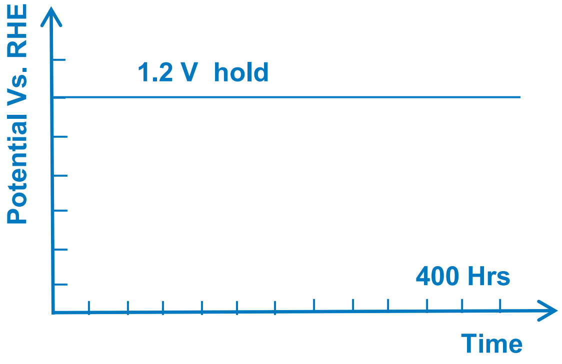
Accelerated Stress Test for Support Durability – Protocols tested at Nissan



Nissan



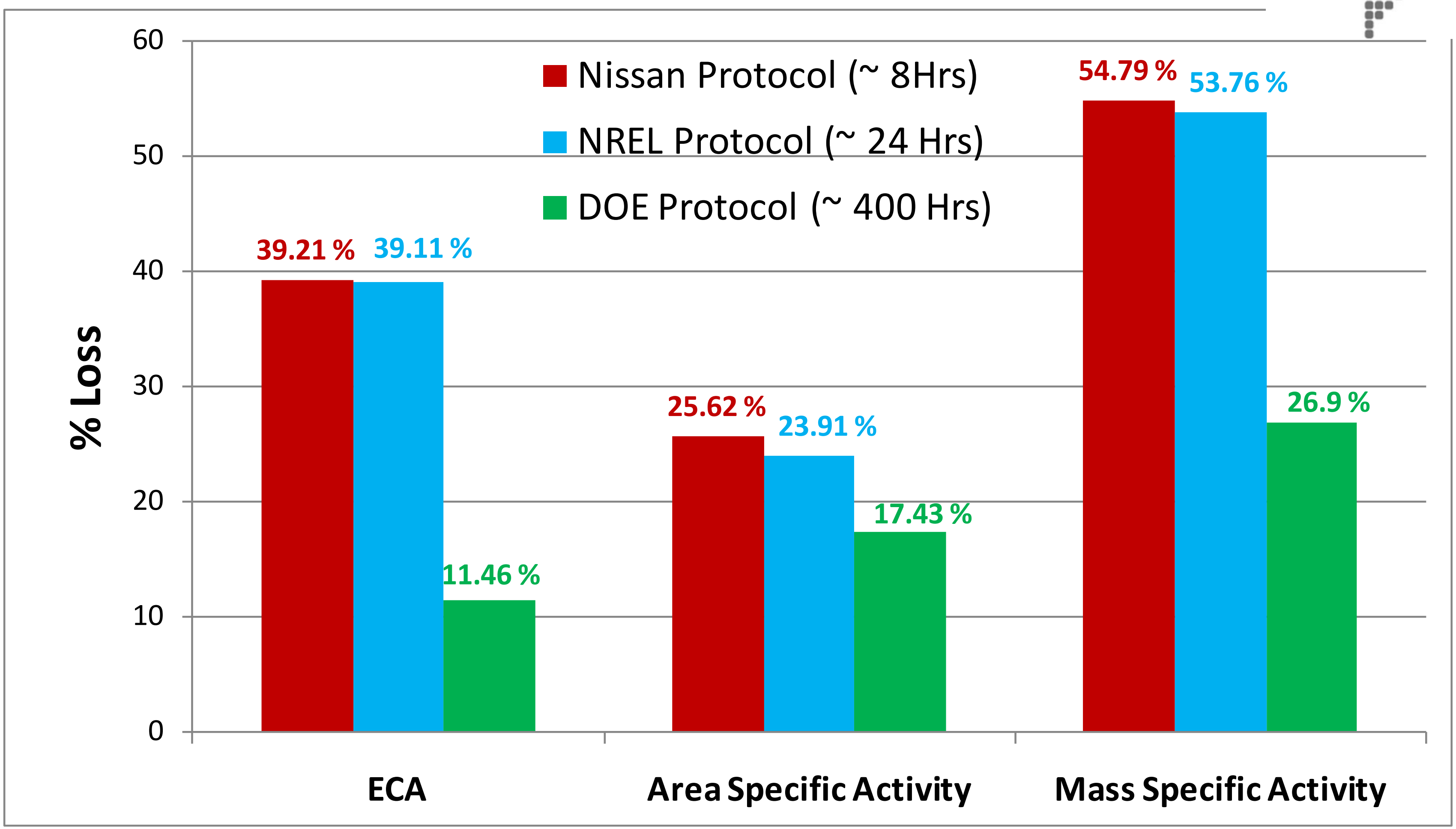
NREL



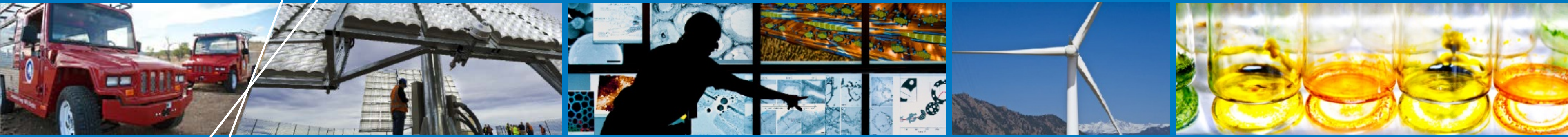
DOE

	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
Total time for test	~ 8 Hrs	~ 24 Hrs	~ 400 Hrs

Protocol Comparisons – Nissan Results



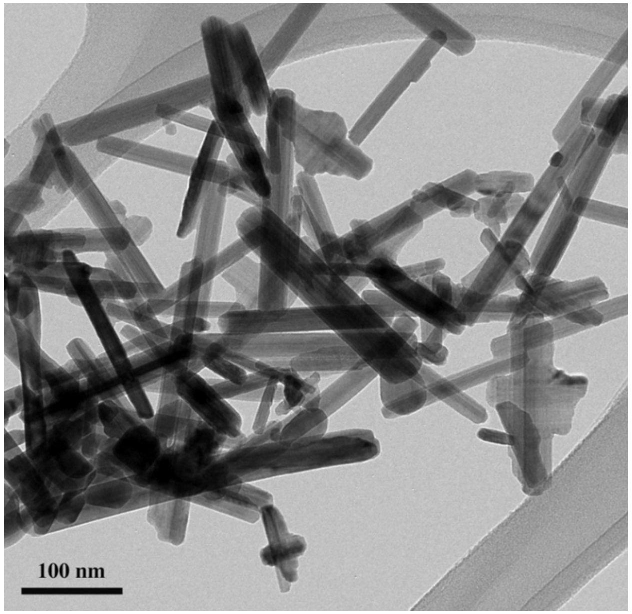
- Nissan and NREL protocols result in comparable losses for ECA, i_s and i_m.
- Nissan protocol (60^{o}C) takes only 8h due to higher temperature accelerant
- NREL protocol is conducted at RT and takes 24 h using low scan rate accelerant.



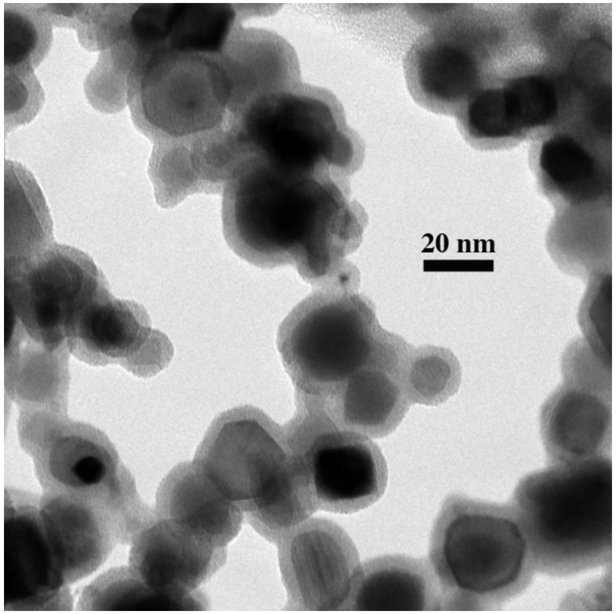
Synthesis

HWCVD Production of Tungsten Oxide Nanostructures

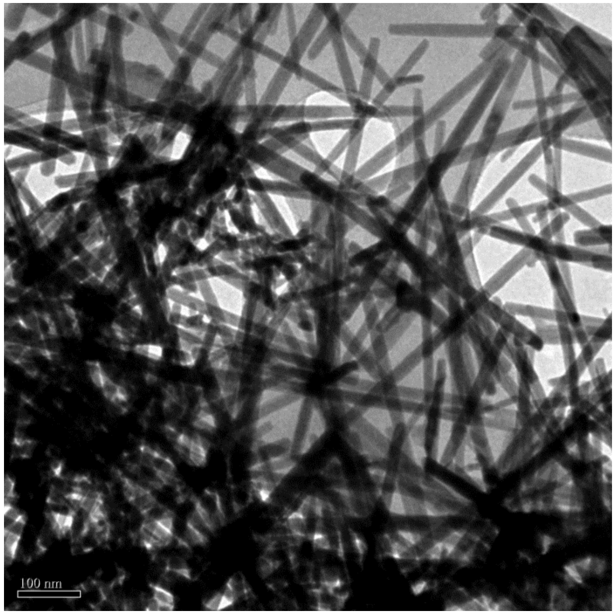
Synthesis at 150 Torr 4% O_2 in Ar, filament temperature ~ 2000˚C.



300 ˚C

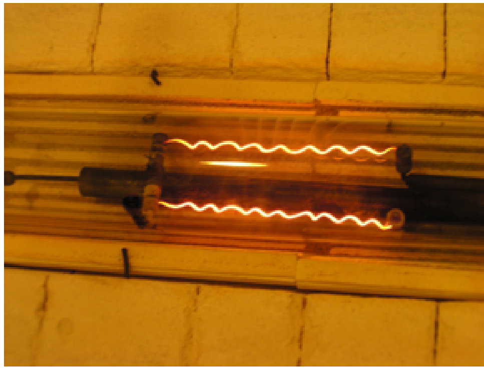


30 ˚C



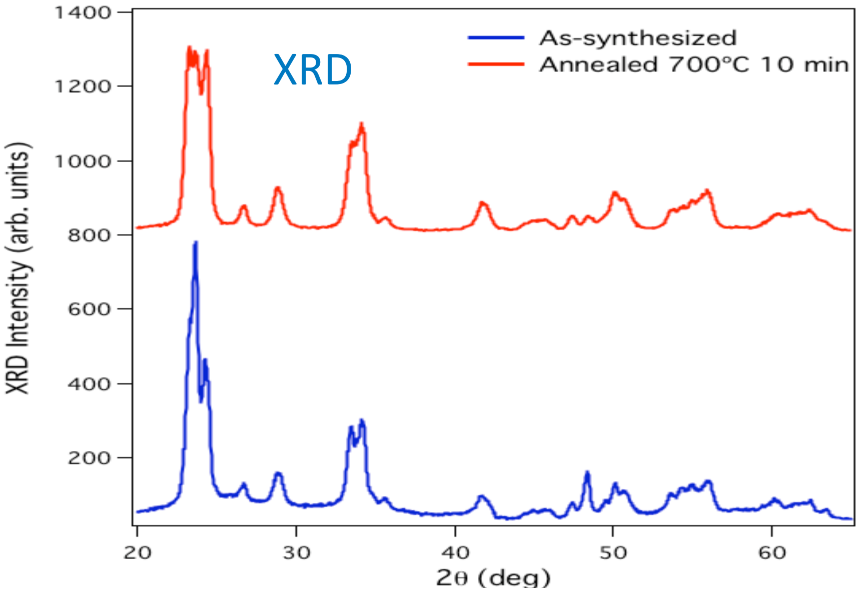
30 ˚C
4 sequential depositions

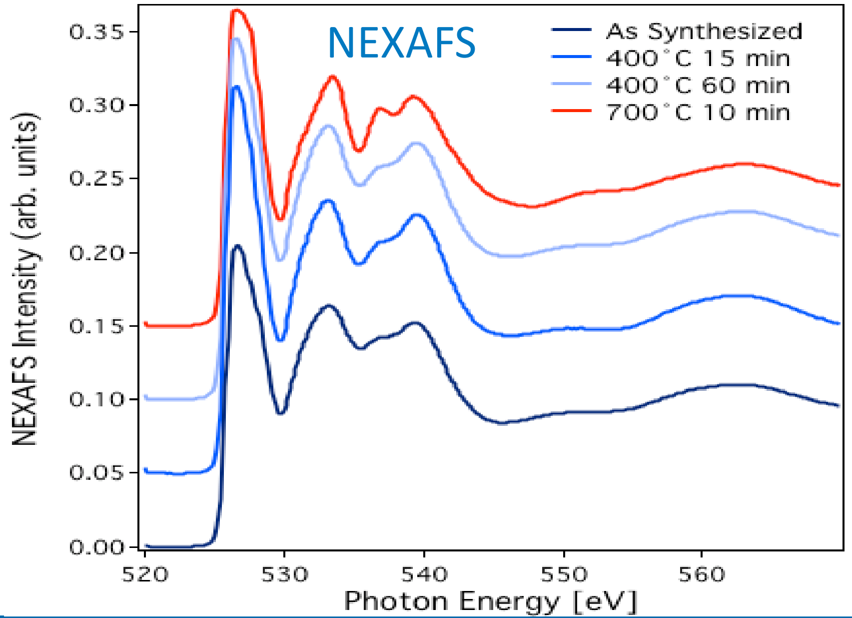
- **Dramatic change in particle morphology**
  - **Lower furnace temperature**
  - **Sequential depositions lead to rod growth**

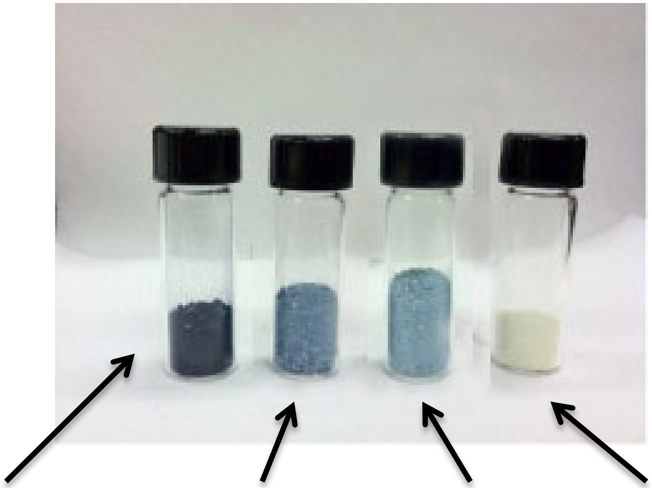


A.H. Mahan, P. A. Parilla, K.M. Jones and A.C. Dillon, *Chem. Phys. Lett.* 413 (2005) 88.

Stoichiometry of WO_x Controlled by Oxidation in Air







58.7 m^2/g_{WOx}
No anneal

49.0 m^2/g_{WOx}
400°C
15 min

47.9 m^2/g_{WOx}
400°C
60 min

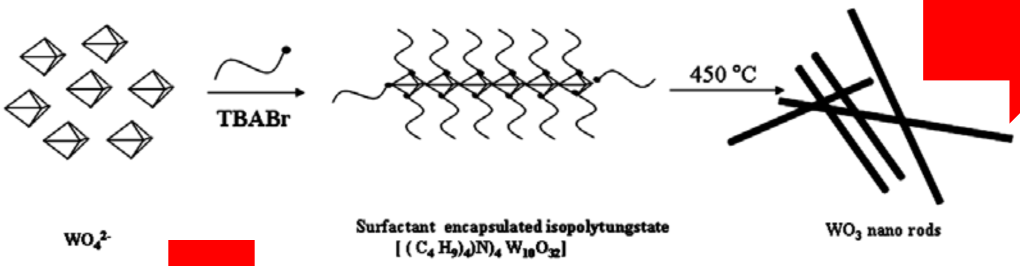
26.0 m^2/g_{WOx}
700°C
10 min

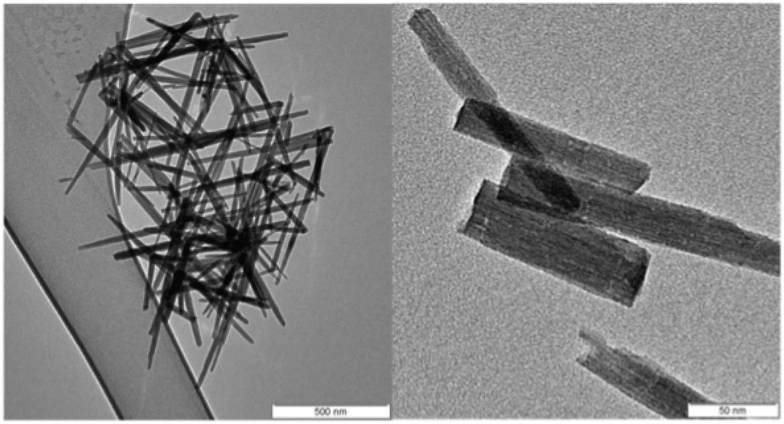
Different oxide stoichiometries are made by annealing in air. Hot-wire grown at RT is $WO_{1.7}$ (TGA)

NEXAFS data from SLAC to give us oxygen bonding

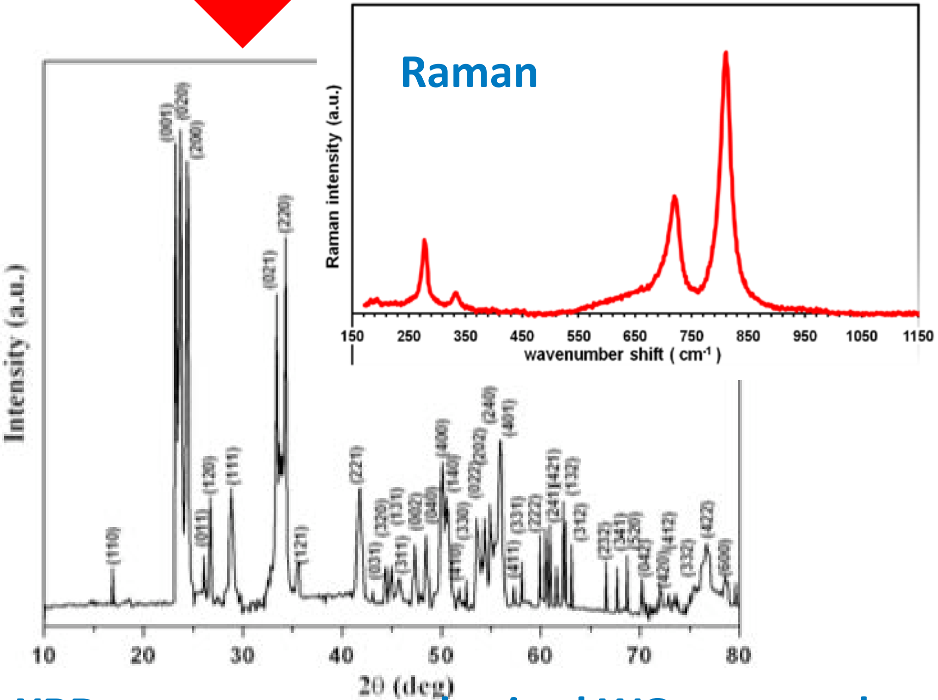
Tungsten Oxide Wet Chemistry Synthesis

Pyrolysis of $((C_4H_9)_4)N)_4W_{10}O_{32}$.
(Tetrabutylammoniumdecatungstate)

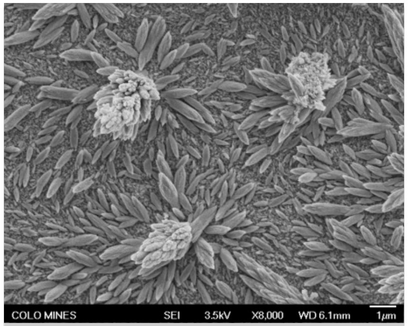




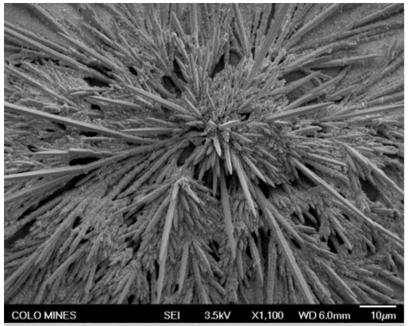
Nanorods



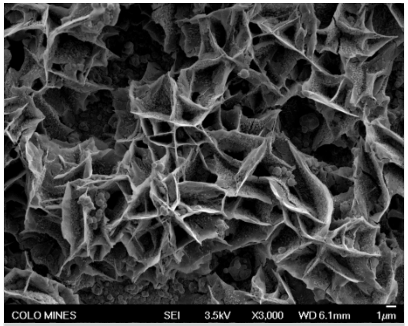
XRD pattern—as synthesized WO_3 nanorods.



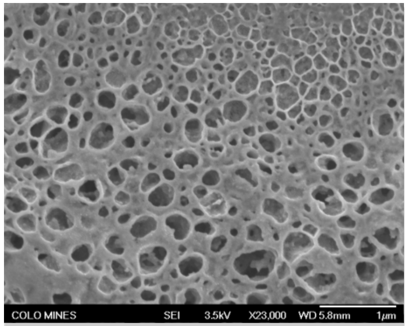
Spindles



Needles



Plates

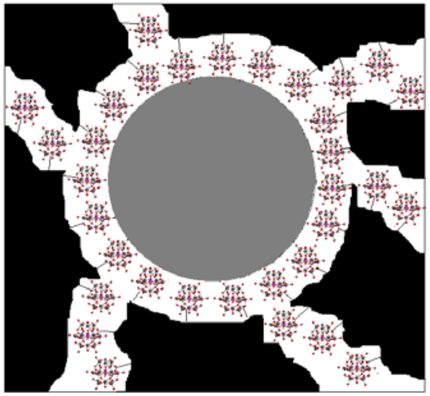


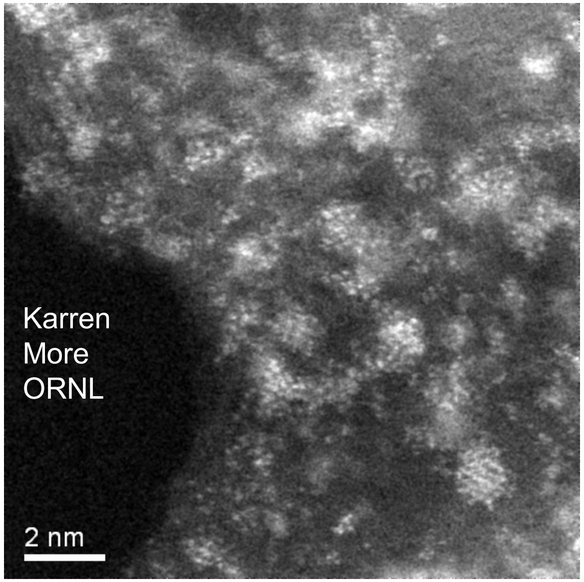
Porous

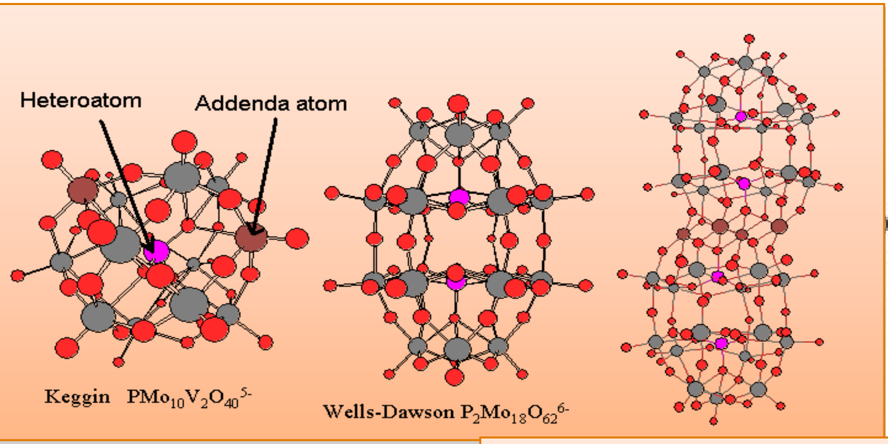
HPA Functionalization of Carbon and WO_3

Immobilized HPAs as Catalyst Supports

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





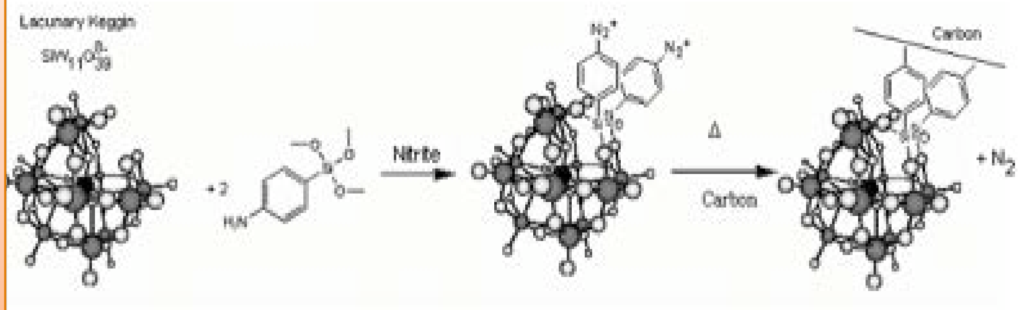


Keggin $PMo_{10}V_2O_{40}^{5-}$

Wells-Dawson $P_2Mo_{18}O_{62}^{6-}$

Wells-Dawson Sandwich

$Fe_4^{II}(H_2O)_2(P_2W_{15}O_{56})_2^{16-}$

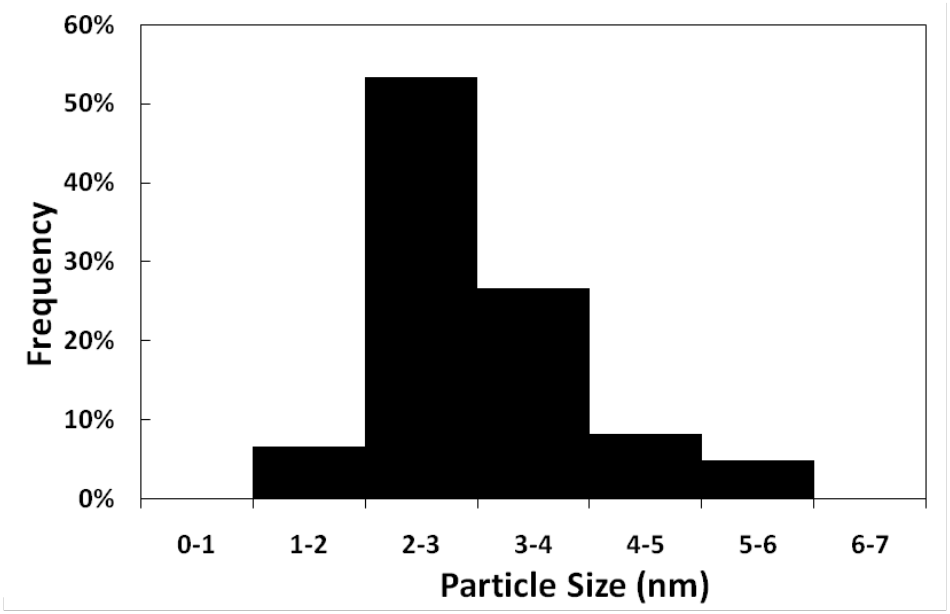


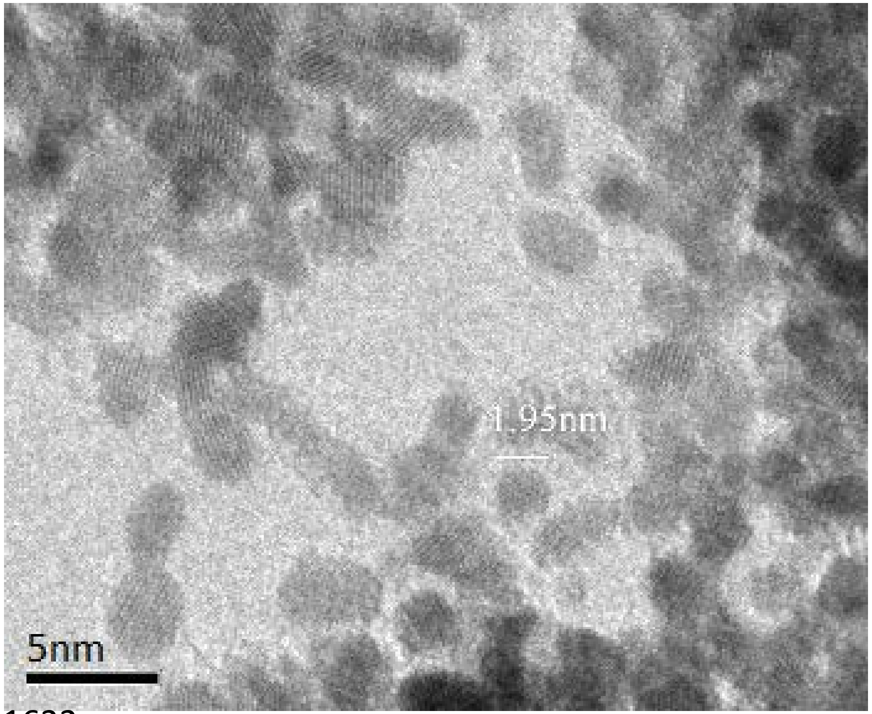
HPA functionalization of Carbon black confirmed by EDX spectra.

Pt Colloid Synthesis

A literature recipe* was modified significantly to synthesize size-controlled Pt nanoparticles by:

- Decreasing the temperature to 80˚C
- Bubbling dilute CO into solution
- Gradually adding 0.25M NaOH over 3h

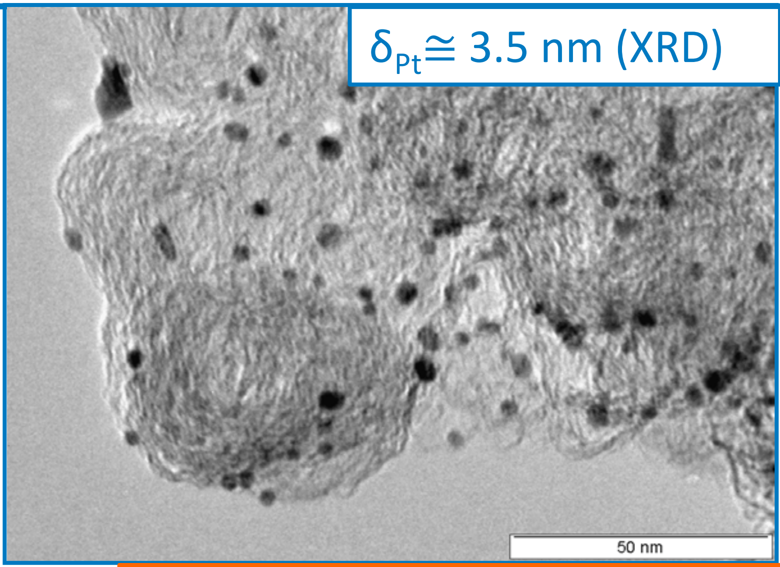




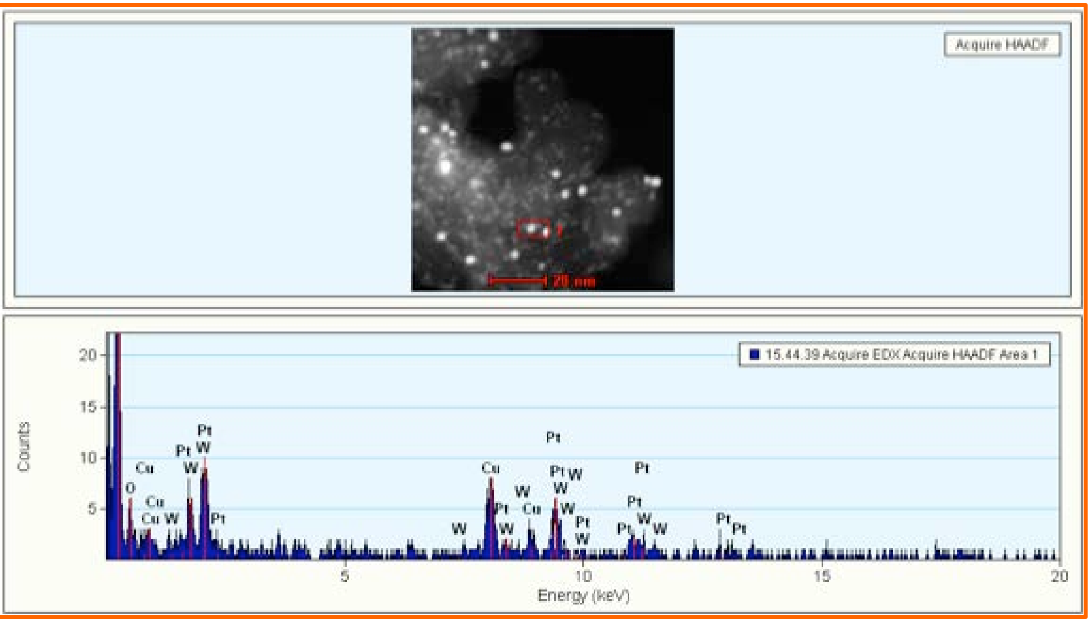
*Wang, Y.; Ren, J.; Deng, K.; Gui, L.; Tang, Y. *Chem. Mater.* **2000**, *12*, 1622.

Results of Pt/HPA-C Preparation

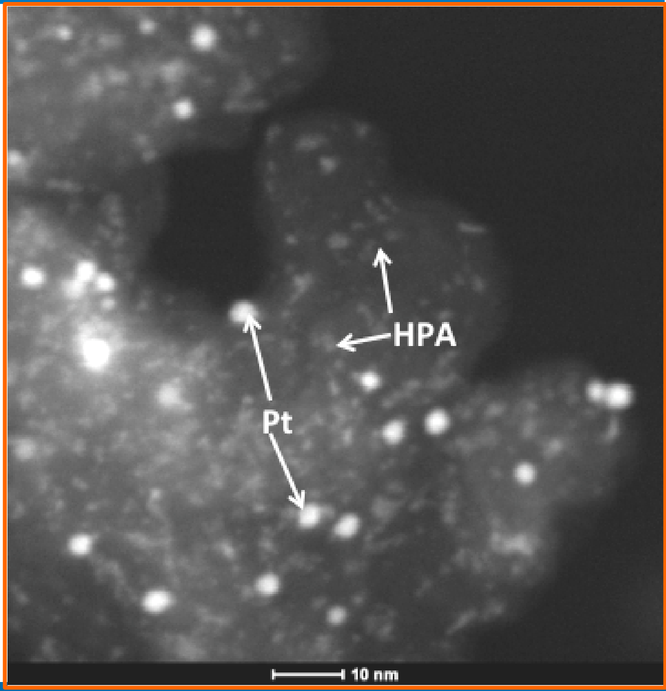
- **Dispersion of HPA-C material in water via ultrasonication (20 minutes)**
- **Addition of Pt colloid followed by ultrasonication for an additional 20 min**
- **Catalyst separation via Buechner filtration**
- **Drying at 200˚C for 2 h**



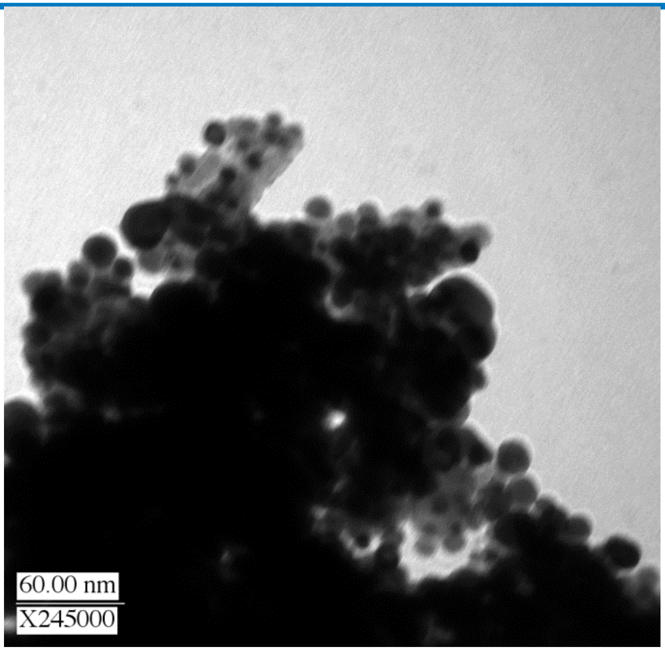
$\delta_{Pt} \cong 3.5$ nm (XRD)



STEM EDX analysis, FEI F20 UT, 200 kV, spot size 7, from red square area



Progress of Pt ALD on WO_x materials

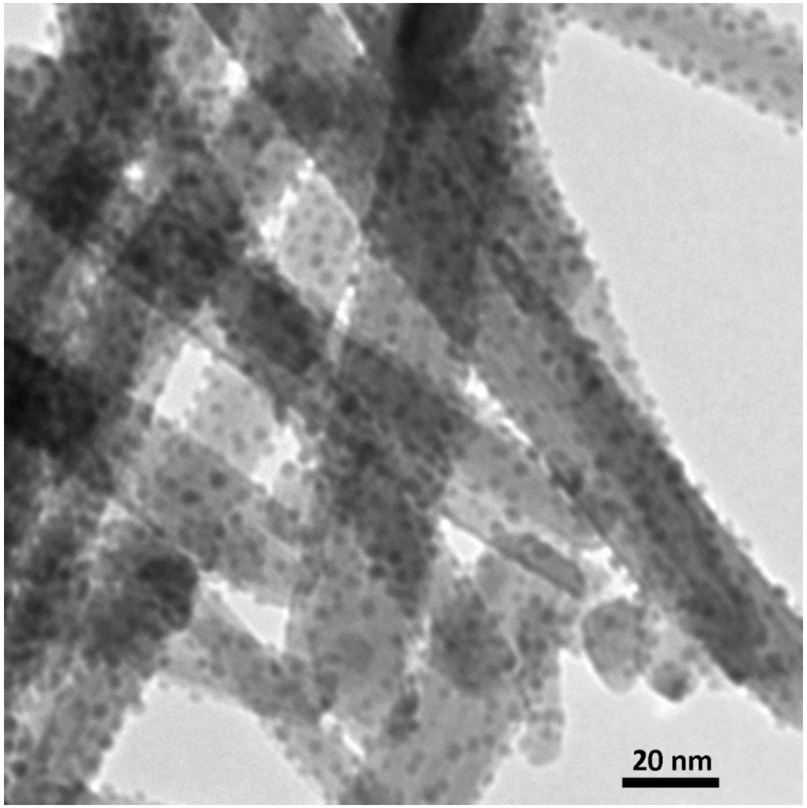


Initial ALD resulted in high Pt loading with large particle sizes.

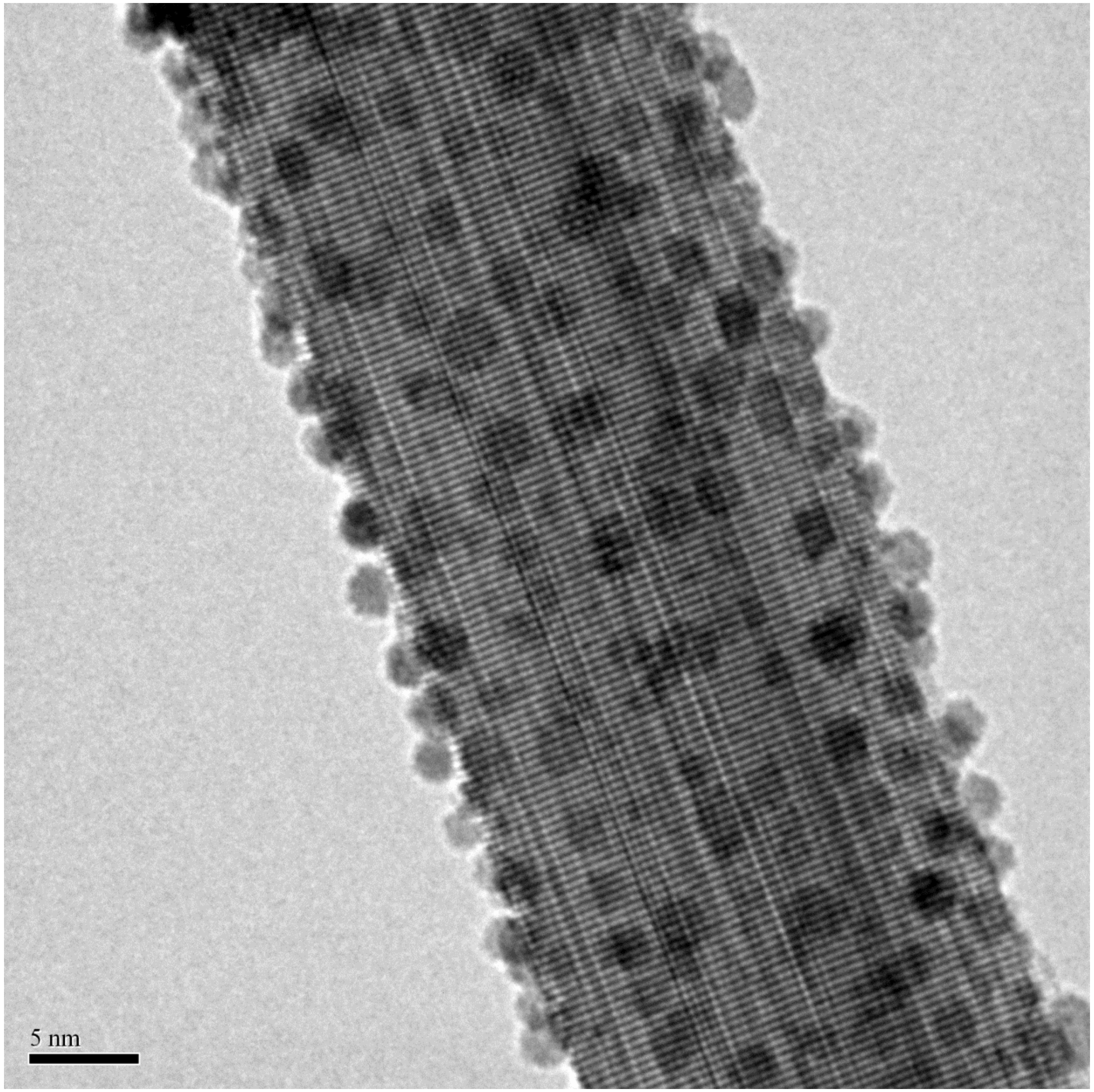
With a higher flux (higher precursor temp) the nucleation was more uniform, leading to smaller particles throughout the sample.

Saturated exposure leads to more uniform coverage

60 Cycles
Pt precursor temperature = 70°C
(14.1 wt% Pt)



NREL Atomic Layer Deposition of Pt

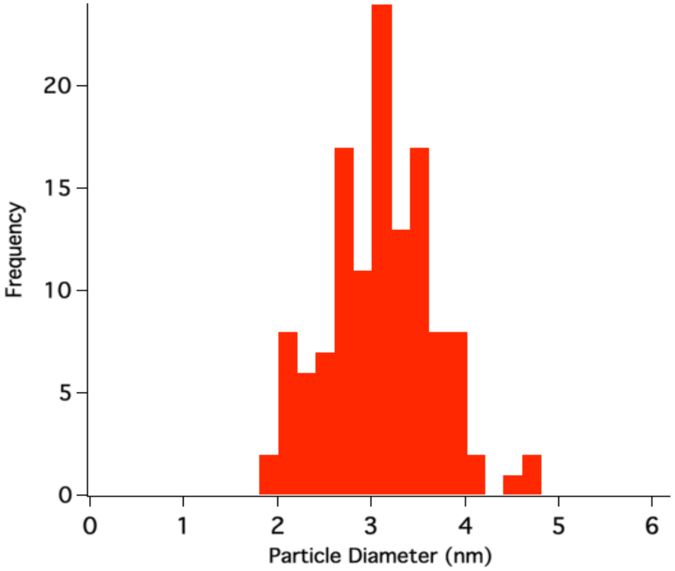


Current deposition capabilities

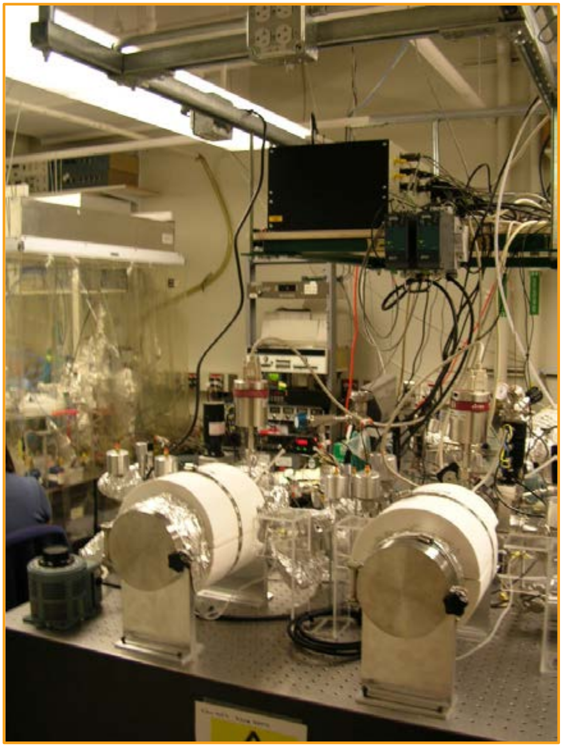
Smaller Pt particle size

Demonstrated Pt loading 1 – 23 wt% (not controlled)

Continue to increase the uniformity of Pt coverage.



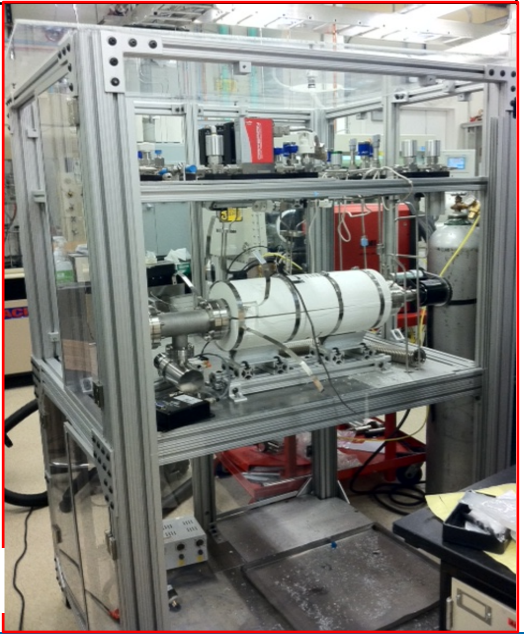
Pt ALD on WO_3 – Scaling with Dual Rotary Reactor



Dual rotary reactor for uniform Pt particle growth on WO_3 nanorods at large scale.

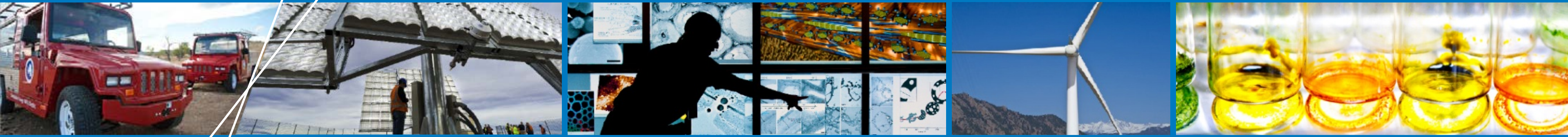
- Computer controlled spinning enables uniform deposition.
- This system can hold a volume of 60 cm^3.
- Based on the powder density of WO_3, This corresponds to ~ 420 g / deposition.

New NREL Rotary ALD system for uniform scalable Pt deposition on WO_x Powders



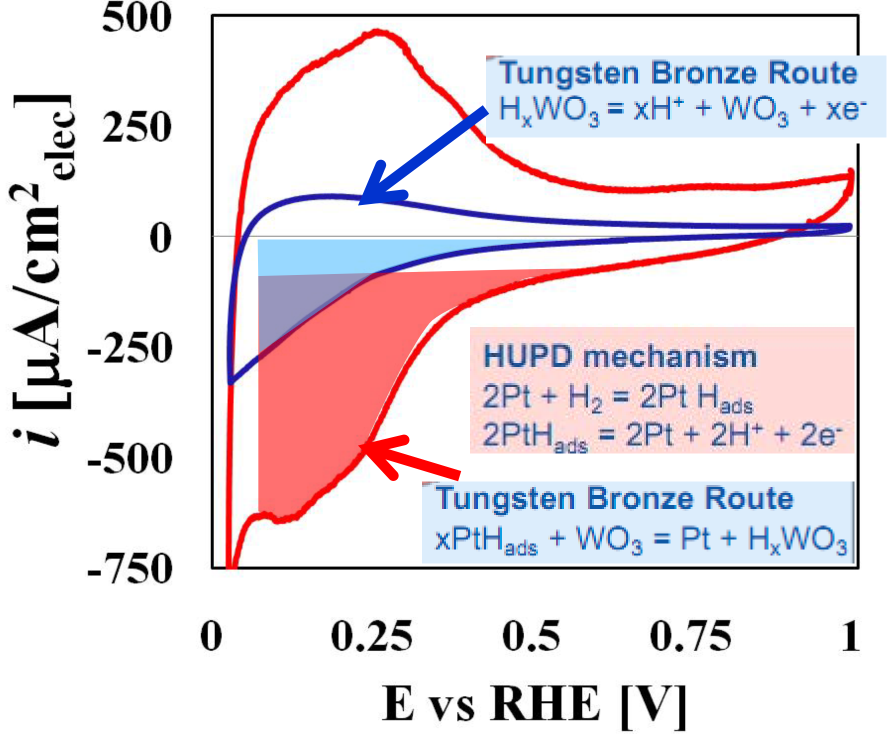
Able to coat powders or flat surfaces
Equipped for two heated and two room temperature precursors
Reactor volume ~100 cm^3

Funded by NREL LDRD



Electrochemical Characterization

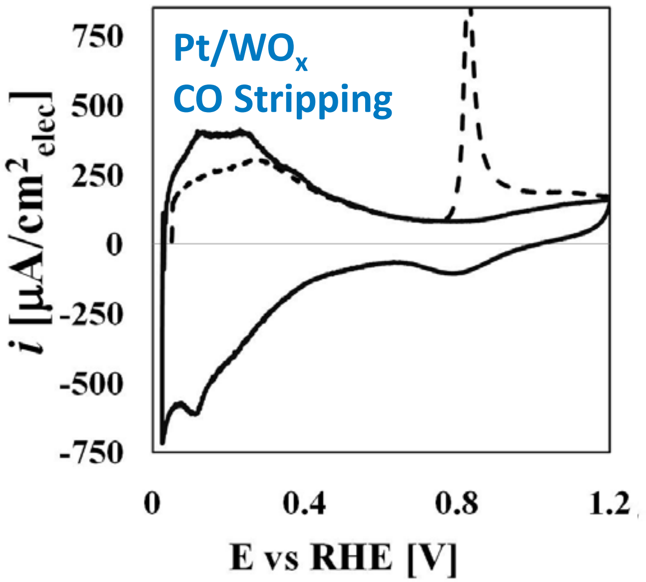
Results: ECA Determination of Pt/WO_x

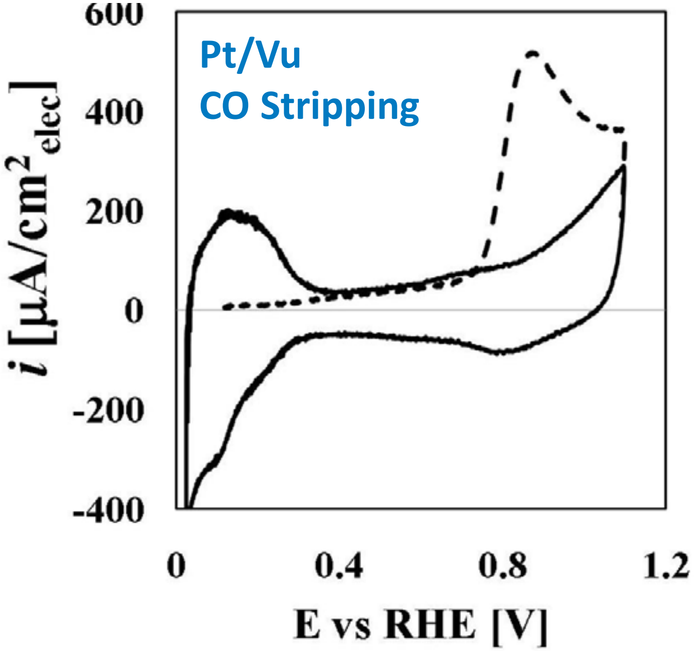


Tungsten Bronze Route
$H_xWO_3 = xH^+ + WO_3 + xe^-$

HUPD mechanism
$2Pt + H_2 = 2Pt\ H_{ads}$
$2PtH_{ads} = 2Pt + 2H^+ + 2e^-$

Tungsten Bronze Route
$xPtH_{ads} + WO_3 = Pt + H_xWO_3$





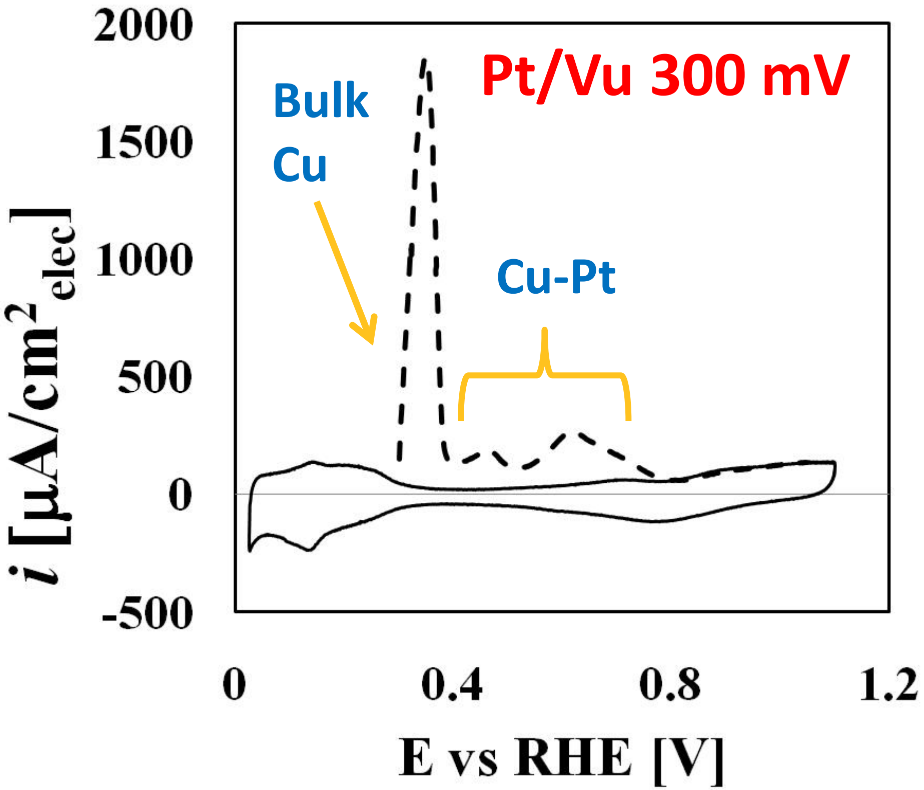
	ECA [m^2/g_{Pt}]
HUPD	125

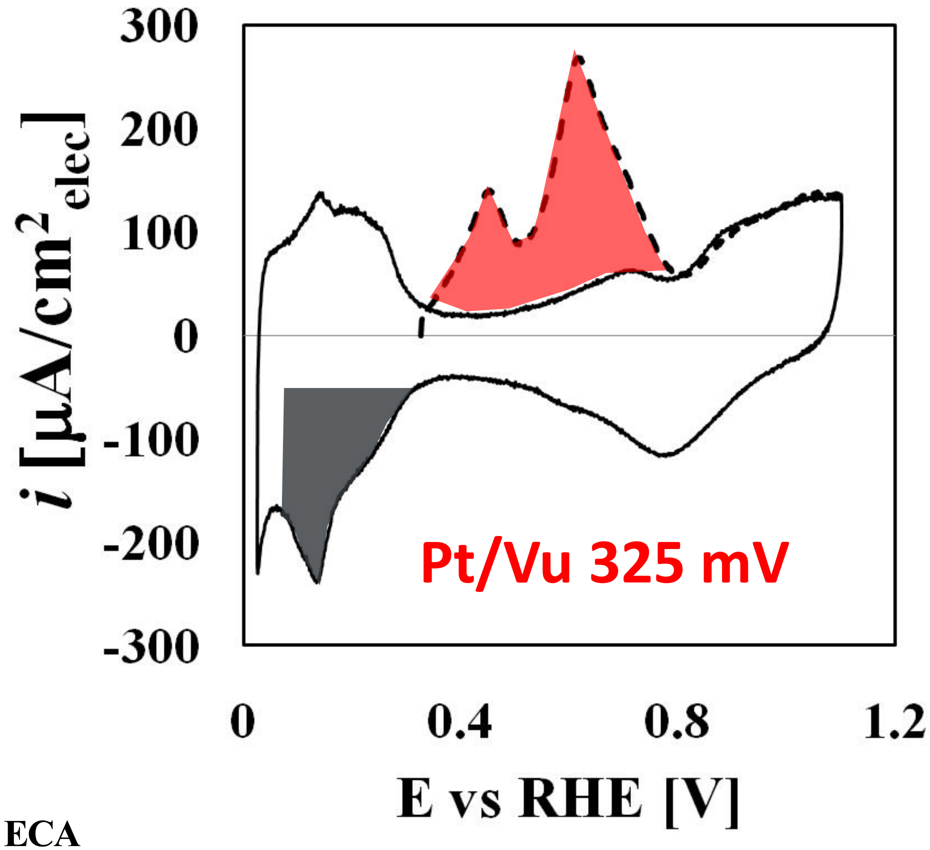
Formation of Hydrogen Tungsten Bronzes
($H_{0.18}WO_3$ and $H_{0.35}WO_3$)
$WO_3 + xH^+ + xe^- = H_xWO_3$ ($0 < x < 1$)

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

Results of Cu UPD on Pt/Vu Electrocatalysts

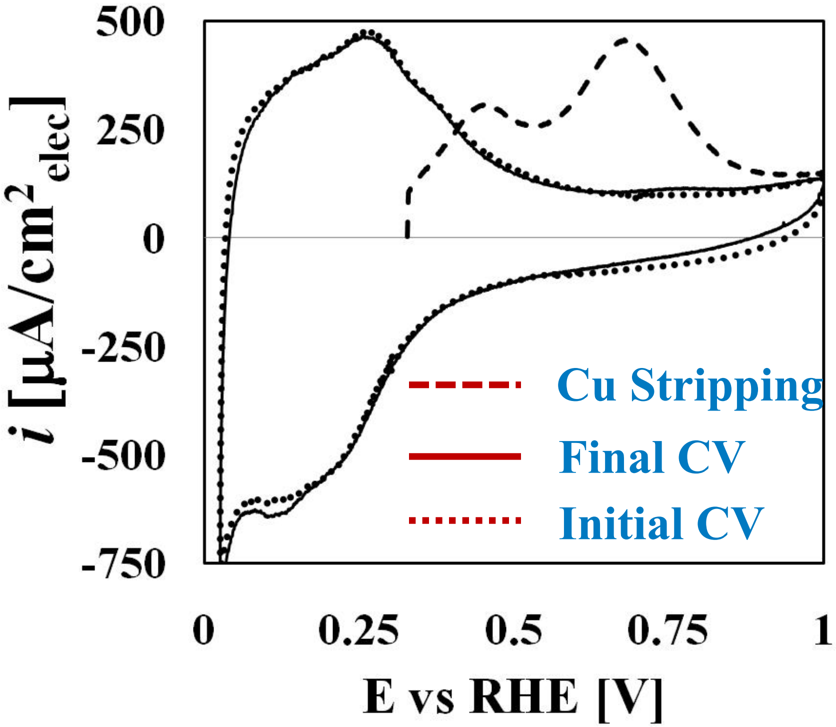




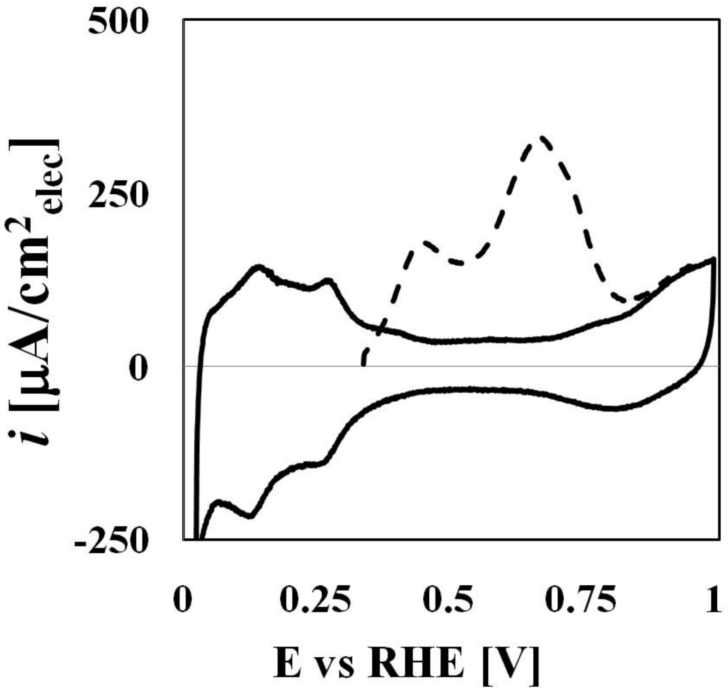
	ECA [m^2/g$_{Pt}$]		
Catalyst	**Cu UPD**	**CO**	**HUPD**
47 wt% Pt/Vu	65		68
Pt Black	19	17	17

65 vs. 68 m^2/g$_{Pt}$

Cu UPD on Pt/WO_x Electrocatalysts



a) ALD Deposited Pt on HWD WO_x Nanorods

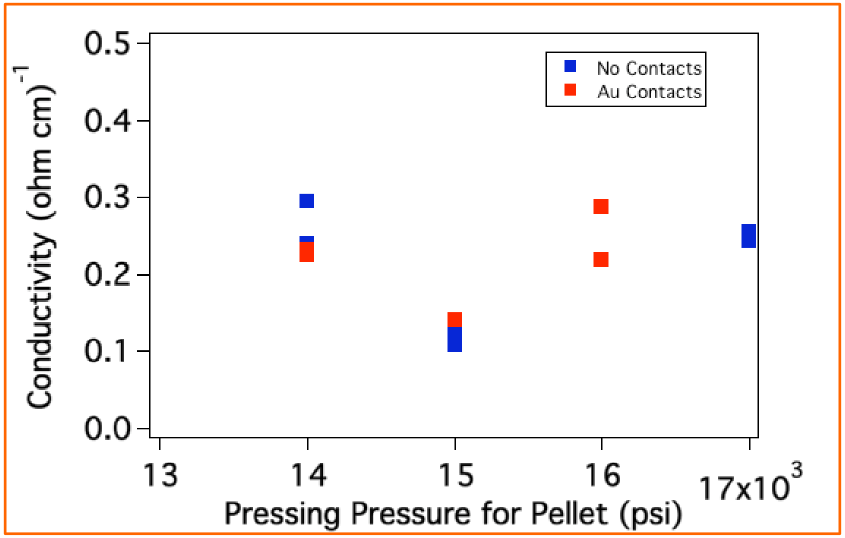


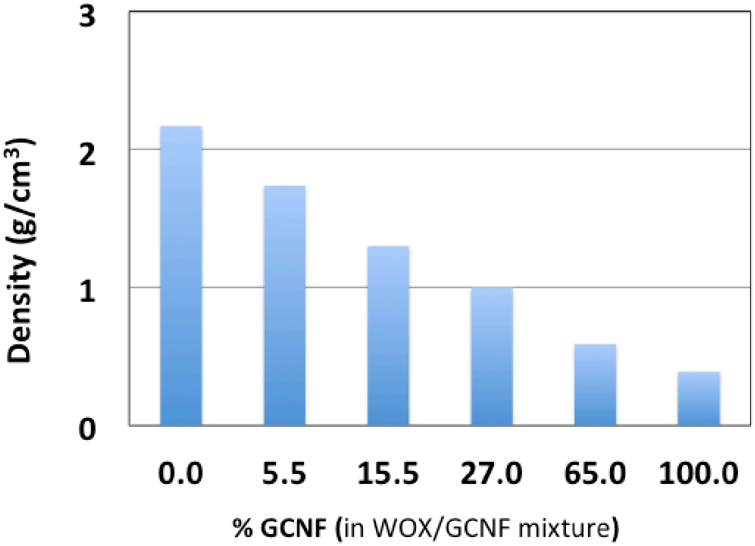
b) Wet Chemistry Pt/WO_x

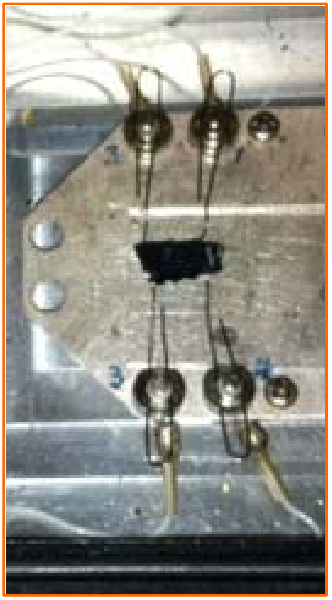
	ECA $[m^2/g_{Pt}]$			$\delta_{particle}$	ECA
Catalyst	**Cu UPD**	**CO**	**HUPD***	**[nm]**	predicted
23 wt% Pt/WOx[a]	53	30	65	5[c]	56
22 wt% Pt/WOx[b]	16	12	16	9[d]	31

[c] From TEM, [d] from XRD

Results: Conductivity of WO_x

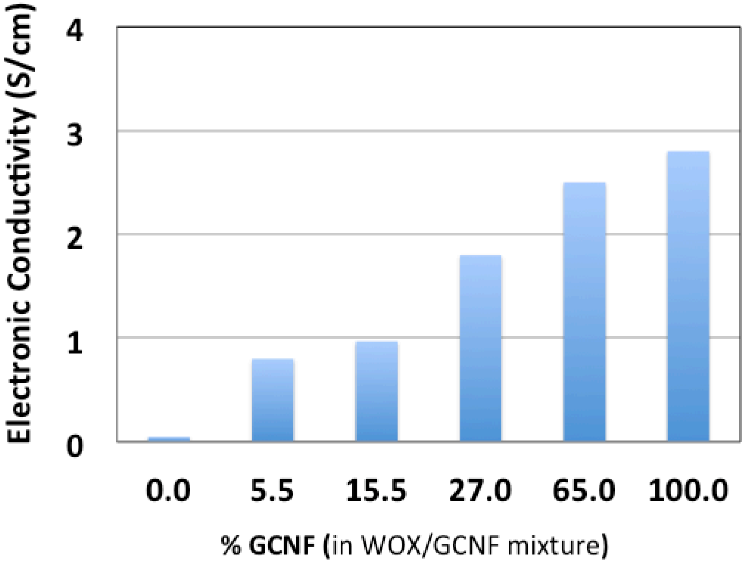




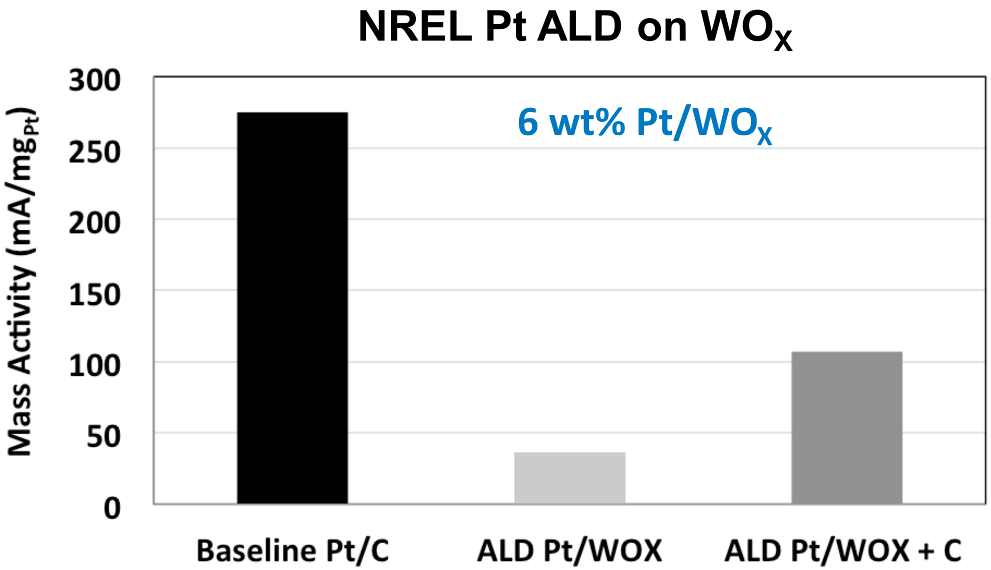


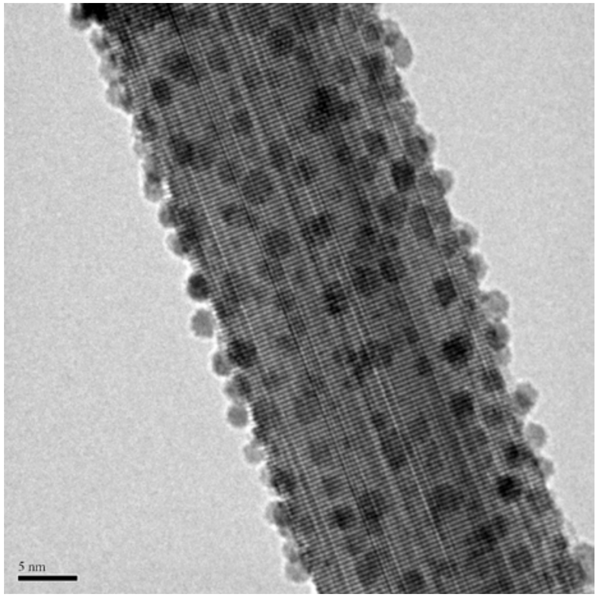
HWCVD
4 point
probe for
pellets

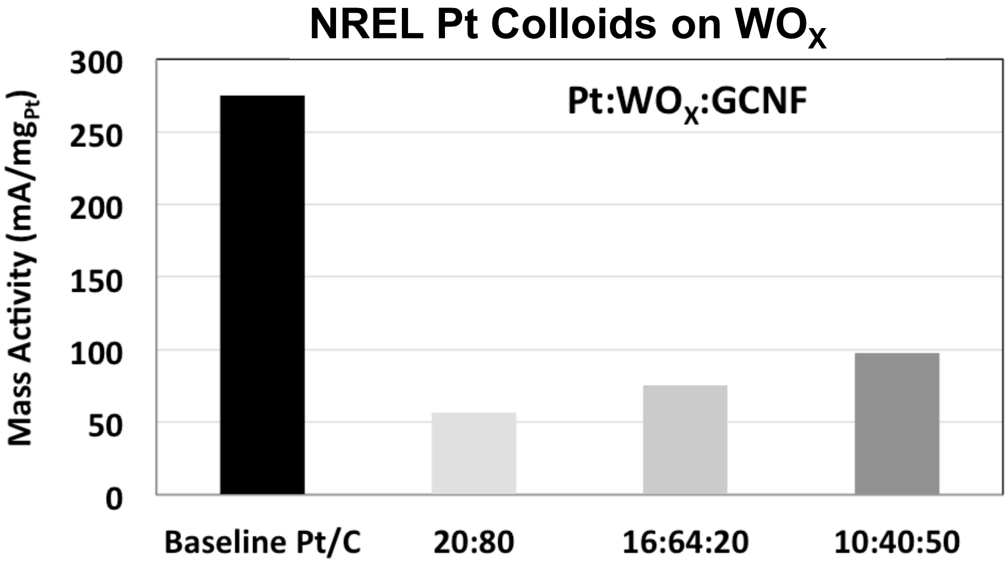
WO_x powders from wet chemistry @ RT, 500 N/cm^2 , Au coated Cu plates

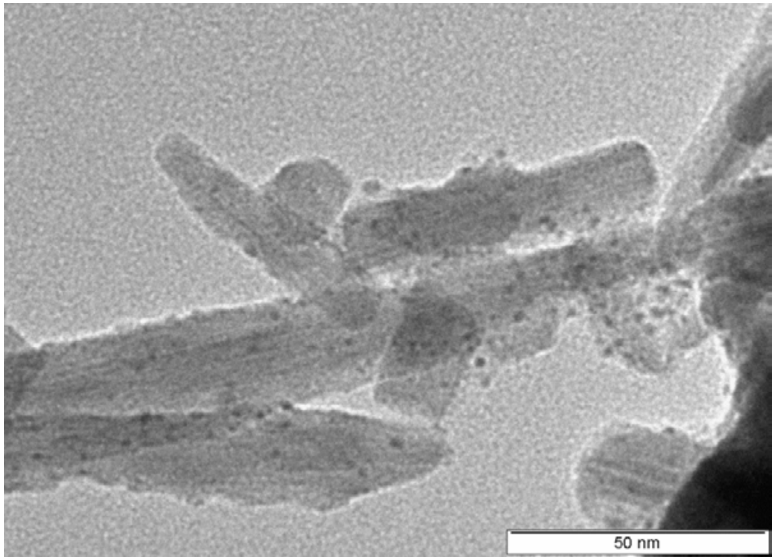


Results for Mass Activity: Pt/WO_X

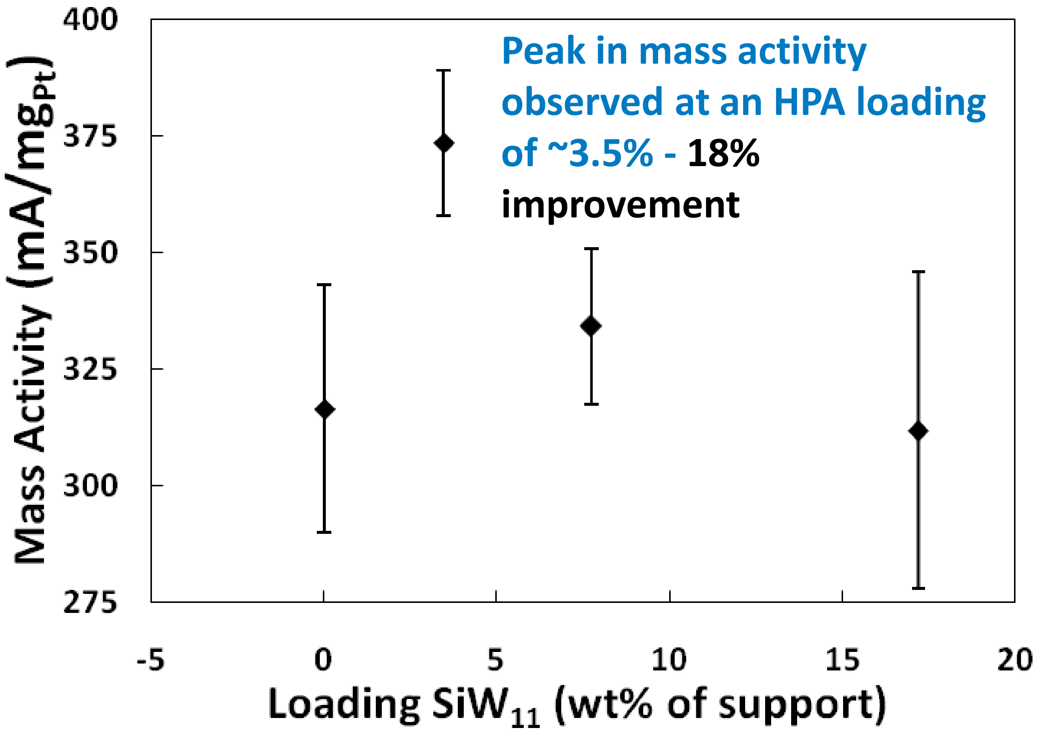








Results: Impact on Mass Activity for HPA Loading on Carbon

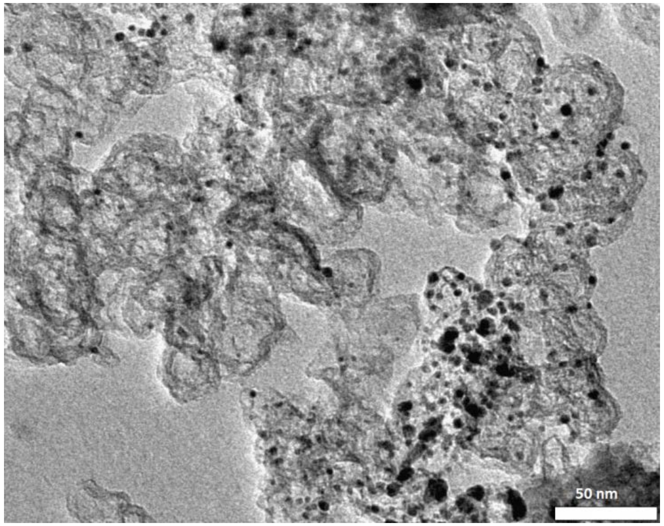


Peak in mass activity observed at an HPA loading of ~3.5% - **18% improvement**

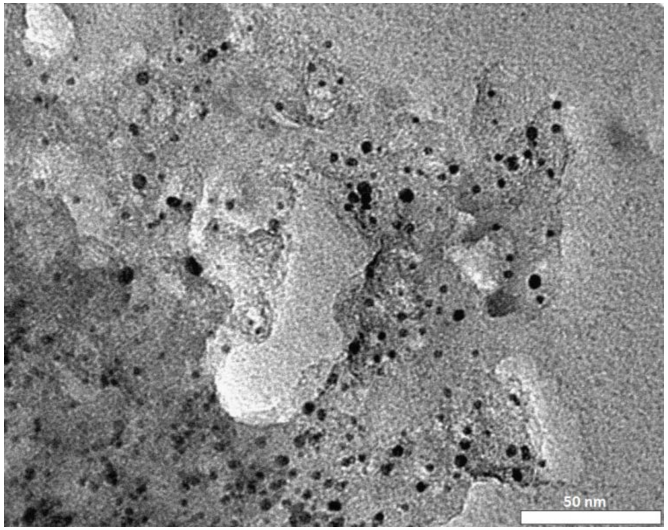
	6,000 cycles	30,000 cycles
	1.0-1.6 V	0.6-1.0 V
Pt/C	57%	52%
Pt/HPA-C	92%	71%

7% HPA on carbon, mass activity retention (NREL Protocol)

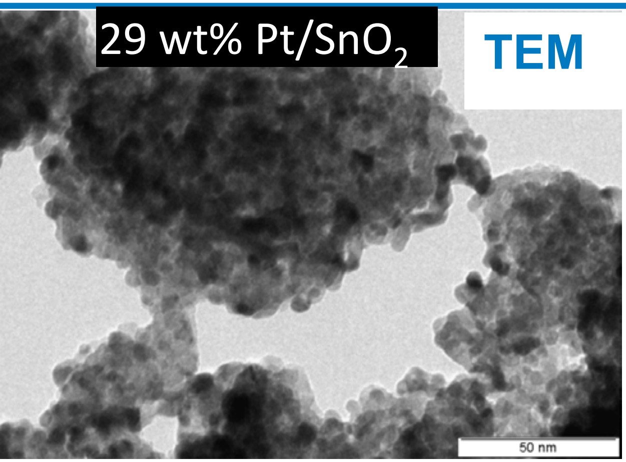
Pt/C after 0.6-1.0 V cycling



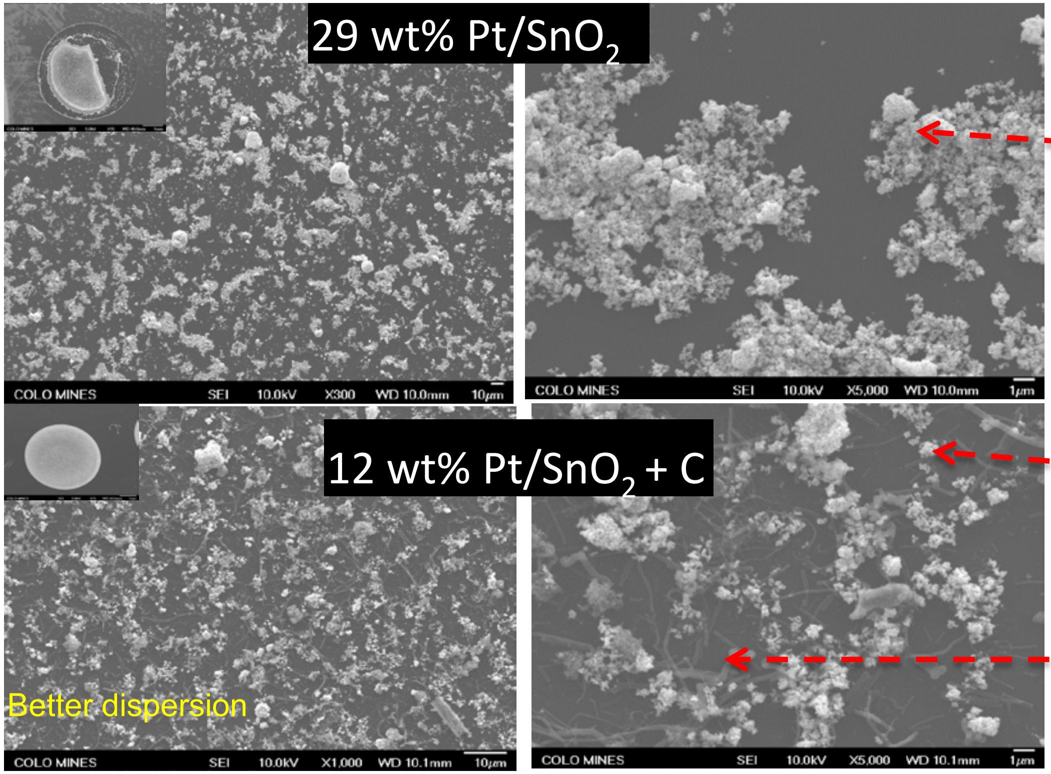
Pt/HPA-C after 0.6-1.0 V cycling



Pt/SnO_2 Electrocatalysts



Sample ID	Electrode Loading (mg/cm^2)	Wt % Pt
Pt/SnO_2	18	29
Pt/SnO_2	18.8	29
Pt/SnO_2 + C	9.2	12
Pt/SnO_2 + C	9.4	23



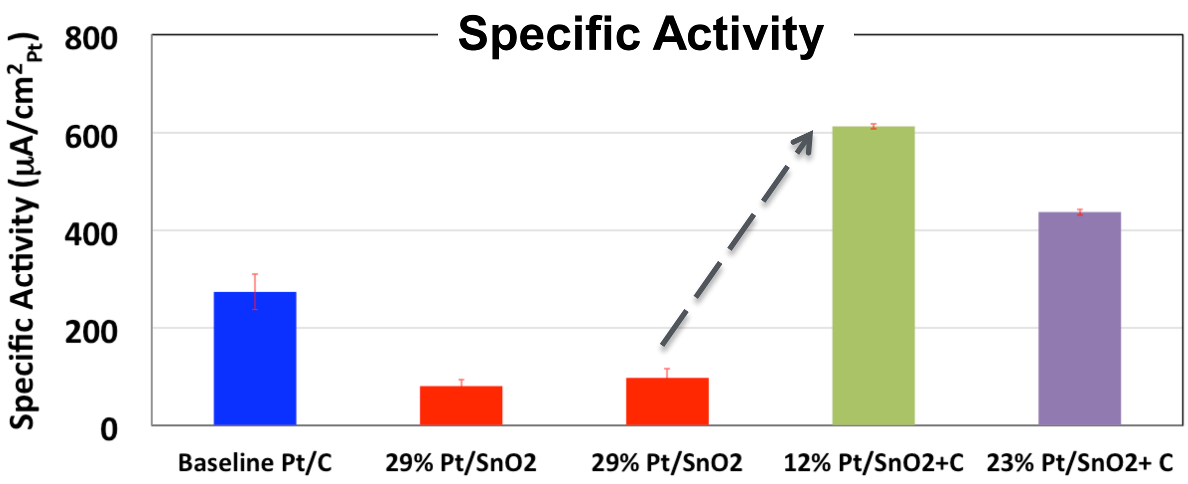
Pt/SnO_2

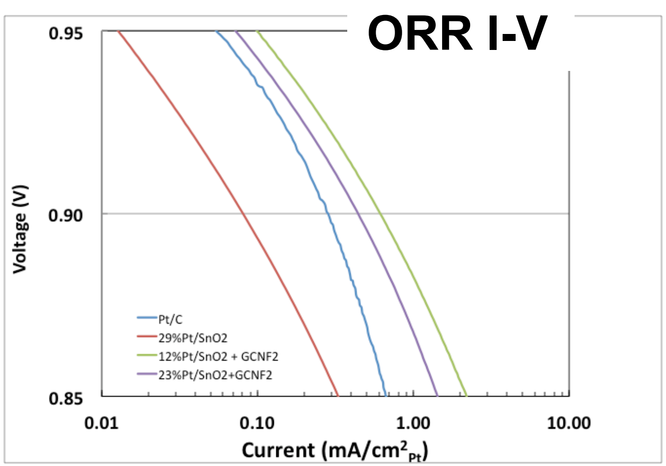
Pt/SnO_2

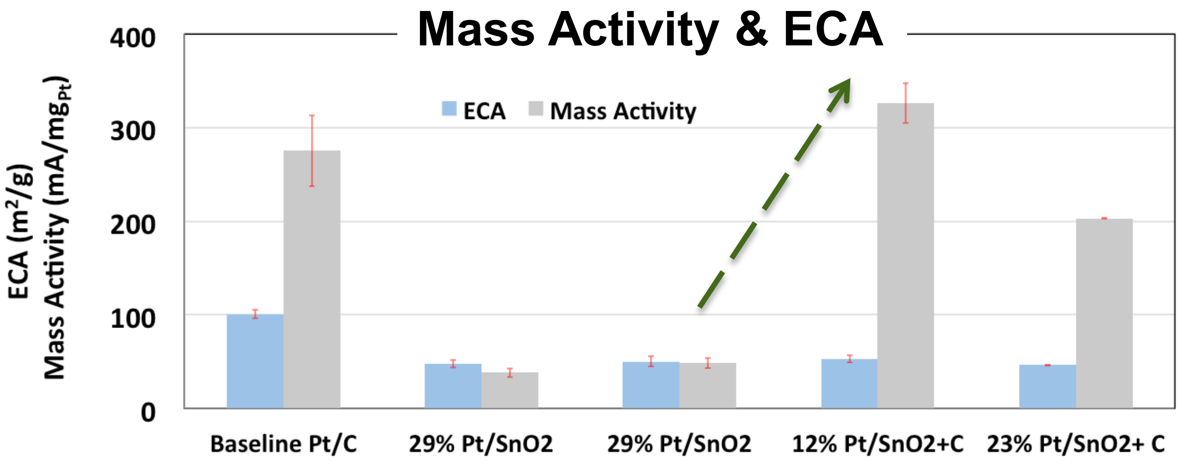
Carbon nanofibers providing interconnects

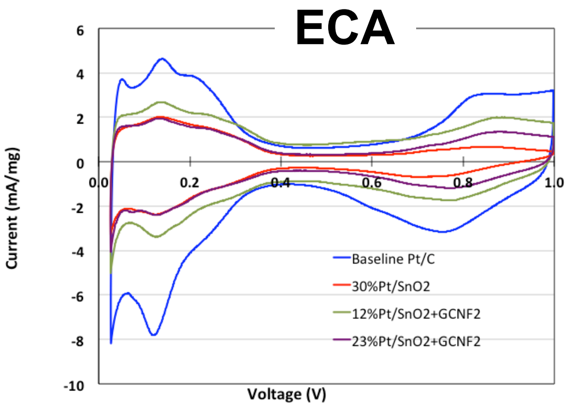
Electrocatalysts were evaluated in RDEs ‘as is’ as well as with 2 different amounts of added carbon black (GCNF) to increase the electronic conductivity of the catalyst layer. GCNF was used as it is a more durable carbon black than Ketjen black®.

Pt/SnO_2 Electrocatalysts: ORR Activity





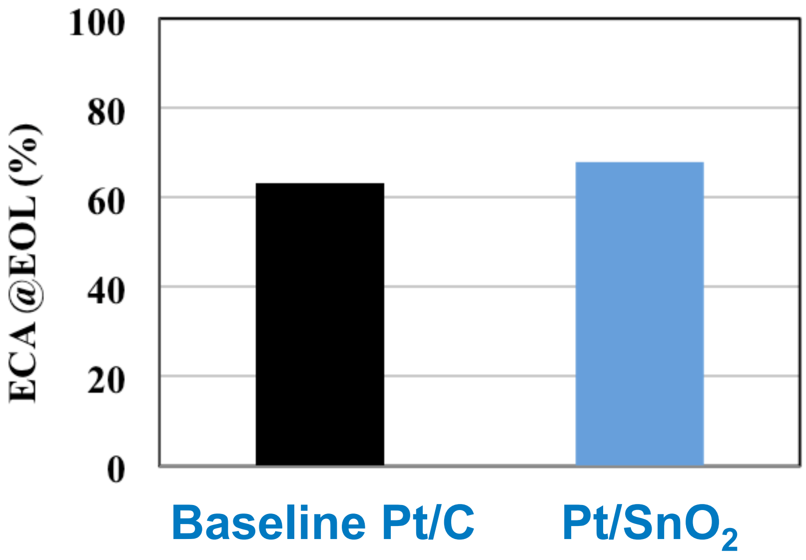




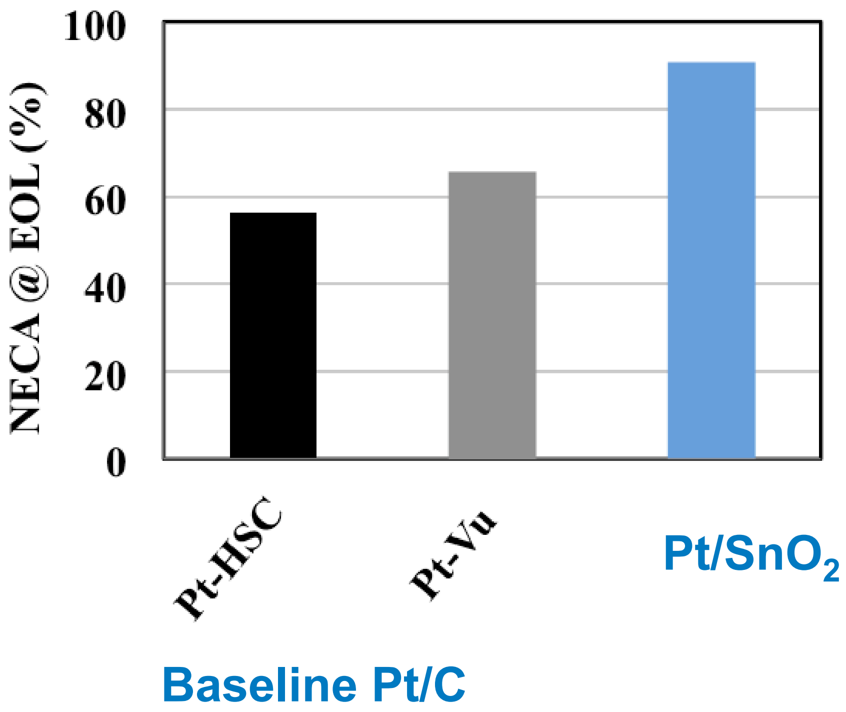
Lower electronic conductivity—one of the causes for lower activity of Pt/SnO_2 electrocatalysts; the other being electrode dispersion.

Pt/SnO_2 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/SnO_2 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/SnO_2 show higher losses for Pt/C catalysts since the SnO_2 support is more corrosion resistant.

Collaborations

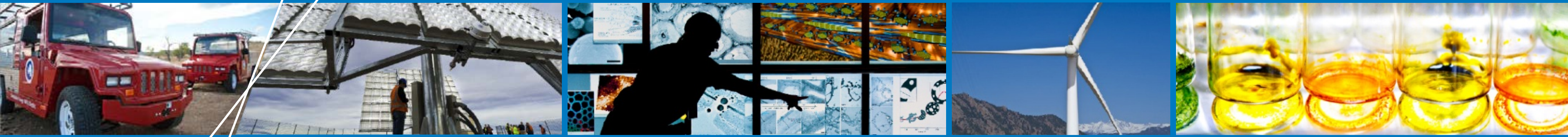
- **CU Boulder: subcontractor – University**
  - ALD growth of Pt on WO_x
- **CSM: subcontractor – University**
  - Synthesis of WO_3 and preparation and attachment of HPA to Pt/WO_3
- **3M: subcontractor – Company**
  - Advice on thin films electrocatalysts
- **NTCNA: consultant – Automotive Company**
  - Support on fuel cell testing & AST protocols
- **Tanaka Kikinzoku Kyogo (TKK) — Commercial Electrocatalyst Manufacturer**

Future Work (2012)

1. Complete a systematic conductivity of WO_X films with and without conductive matrices to guide catalyst ink formulations.
2. Improve wet-chemistry Pt deposition and ALD Pt deposited on WO_X and characterize electrochemically with and without a conductive matrix to obtain mass activities <u>comparable to Pt/C</u>
   - Decision on ALD Pt/WO_X vs. wet-chemistry Pt/WO_X for meeting program goals (December 2012)
3. Evaluate alternative catalysts such as Pt-alloys (on WO_X + conductive matrix) in RDE for higher activities. (2013)
4. Scale-up selected electrocatalyst system synthesis process to prepare Pt/WO_X + conductive matrix in gram quantities for MEA preparation (2013, 2014)
5. Evaluation of HPA incorporation into catalyst layers of MEA to ascertain proton conduction and durability impacts (2013, 2014)
6. Optimize catalyst inks for MEA preparation and evaluation in subscale cells. (2013, 2014)

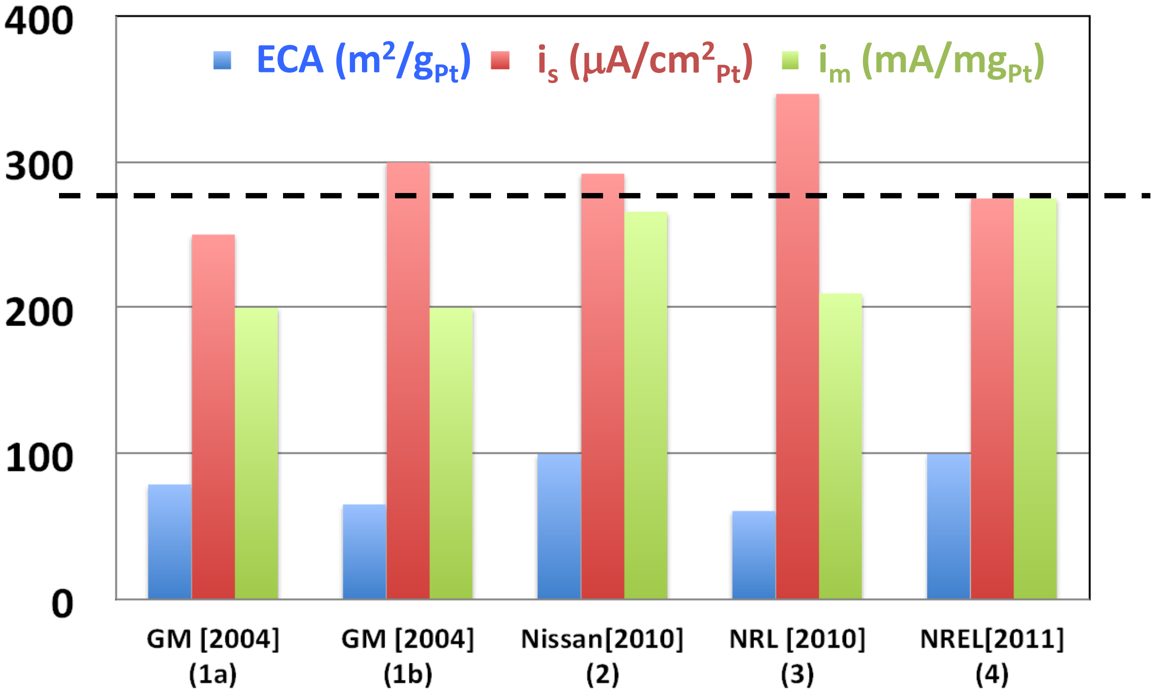
Summary

1. WO_X was prepared using HWCVD having BET surface area of ~ 50 m^2/g; WO_X also prepared using wet-chemistry techniques
2. CU-Boulder deposited Pt using ALD:
   - These materials did not initially produce small and uniform particles of Pt/WO_X
   - On refinement of the ALD conditions, smaller particles of Pt were obtained
   - The wt% of Pt/WO_X is still very low and not suitable for electrochemical characterization
   - A rotary system is being used currently to increase the yield of ALD Pt/WO_X and improve the Pt particle distribution
3. NREL also attempted ALD of Pt/WO_X; these materials had a reasonable Pt wt % and electrochemical characterization resulted in a mass activity of ~100 mA/mg (ALD Pt/WO_X with inclusion of carbon black)
4. Conductivity of WO_X pellets was measured using Vander Paw technique as well powders in an in-house conductivity cell.
5. AST protocols for evaluating durability of alternative supports were developed with the DWG
6. ECA issues were addressed using three different protocols.
7. Pt colloids were prepared (CSM) that were subsequently deposited on HPA functionalized C; these materials were electrochemically characterized and exhibited ~15–20% higher mass activity that Pt/C and improved durability under cycling.
8. Pt/SnO_2 obtained from a commercial catalyst supplier (TKK) was evaluated in RDE. These catalysts also achieved activities comparable to baseline Pt/C after the inclusion of graphitized carbon black to the ink formulation. These materials demonstrated higher cyclic durability compared to baseline Pt/C



Supplemental Slides

Pt/C Activity Benchmarks: RDE, 0.1M $HClO_4$, Nafion®-based Inks



(1a) TKK 47 wt% Pt/HSC, 60°C, 20 mV/s, no iR comp

(1b) E-TEK 20 wt% Pt/V, 60°C, 20 mV/s, no iR comp

(2) TKK 47 wt% Pt/HSC, 30°C, 10 mV/s, no iR comp

(3) E-TEK 20 wt% Pt/V, 25°C, 20 mV/s, no iR comp

(4) TKK 47 wt% Pt/HSC, 25°C, 20 mV/s, iR comp

1. **Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs,** H Gasteiger, S Kocha, B Sompalli, F Wagner, Applied Catalysis B Environmental (2005), Volume: 56, Issue: 1-2, Publisher: ELSEVIER SCIENCE BV, Pages: 9-35.
2. **Examination of the activity and durability of PEMFC catalysts in liquid electrolytes,** Ikuma Takahashi, Shyam S Kocha, Journal of Power Sources (2010) Volume: 195, Issue: 19, Publisher: Elsevier B.V., Pages: 6312-6322.
3. **Experimental methods for quantifying the activity of platinum electrocatalysts for the oxygen reduction reaction,** Yannick Garsany, Olga A Baturina, Karen E Swider-Lyons, Shyam S Kocha, Analytical Chemistry (2010) Volume: 82, Issue: 15, Publisher: AMER CHEMICAL SOC, Pages: 6321-6328.
4. K.C. Neyerlin, Jason Zack, Bryan Pivovar, Shyam Kocha, NREL ECS Abstracts and Meetings 2010, 2011.

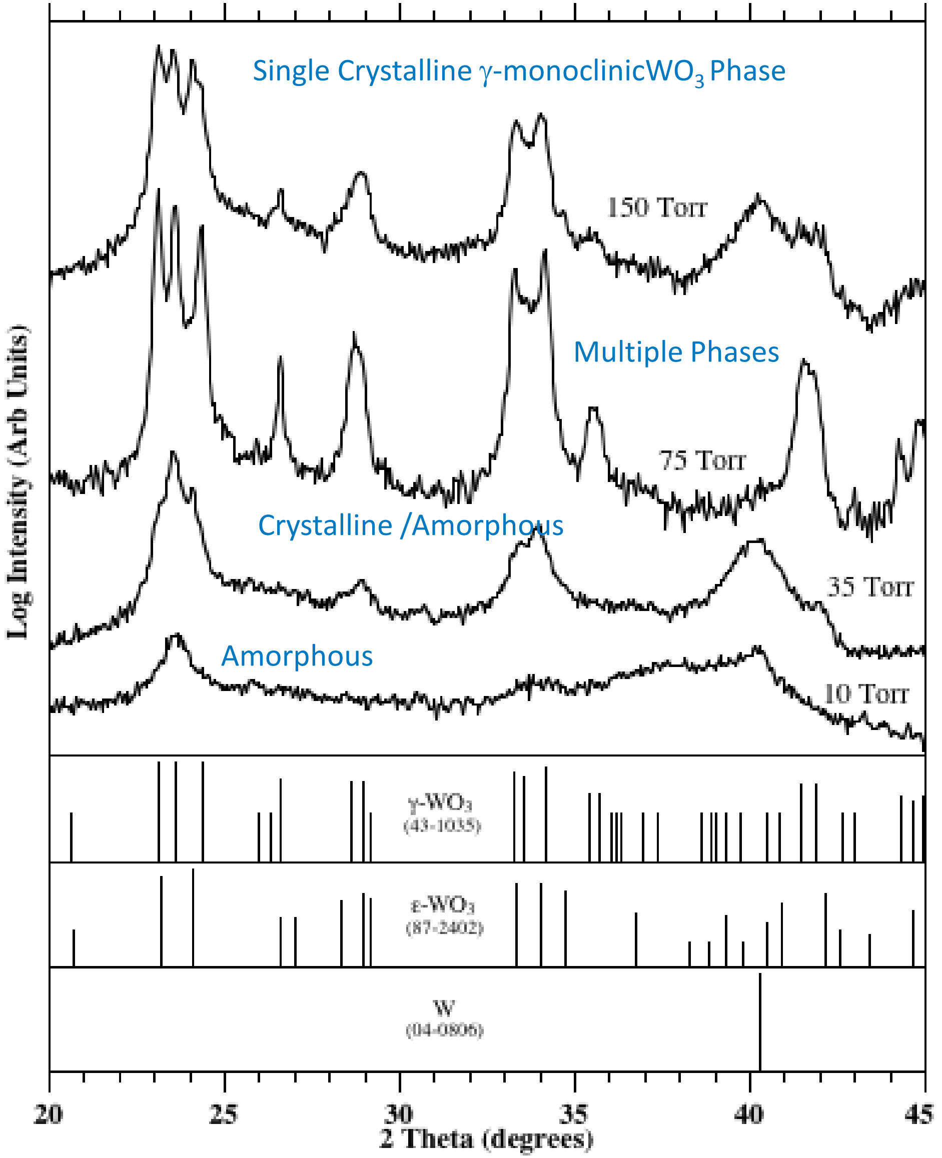
Literature on Oxide Supports 2012

Reference	System Evaluated	Key Results: d_p, ORR Activity, e-conductivity
Z. Sun, H. C. Chiu, A.C.C. Tsueng—*Univ. Greenwich,* UK	**10wt% Pt/WO_3/C** 0.5M H_2SO_4;	d_p = 1–3 nm **ORR Activity Pt/WO_3/C > Pt/C**
Shim, Lee, Lee, Cairns *LBNL—2001*	**Pt–WO_3/C; Pt–TiO_2/C** PEMFC	**ORR activity Pt–WO_3/C = x3 Pt/C**
Saha, Banis, Zhang, Li, Sun, Cai, Wagner—*General Motors*	**15 mm long, 20–60 nm dia Nanowires $W_{18}O_{49}$** **Grown on carbon microfiber paper**	d_p = 2–4 nm **ORR activity Pt/$W_{18}O_{49}$ on C = x4 Pt/C**
Suzuki, Nakagawa, Ishihara, Mistushima, Ota—Yokohama Nat'nl Univ.	Pt/WO_3; Pt/V_2O_5, Pt/SnO_2; Pt/Cr_2O_3; Pt/GC **RF Sputtering onto C**	**ORR activity Pt/V_2O_5 > Pt/WO_3 = Pt/C**
Savadogo and Beck Ecole Polytech, Quebec	**5%Pt- 40%WO_3** PAFC, 180°C	**ORR activity ~ x2 Pt/C**
Huang, Ganeshan, Popov; — *Univ. S. Carolina*	**Rutile Phase–$Nb_{0.25}Ti_{0.75}O_2$** 0.5M H_2SO_4; RDE	d_p = 3–4 nm **ORR Activity Pt/$Nb_{0.25}Ti_{0.75}O_2$ = x1 Pt/C**

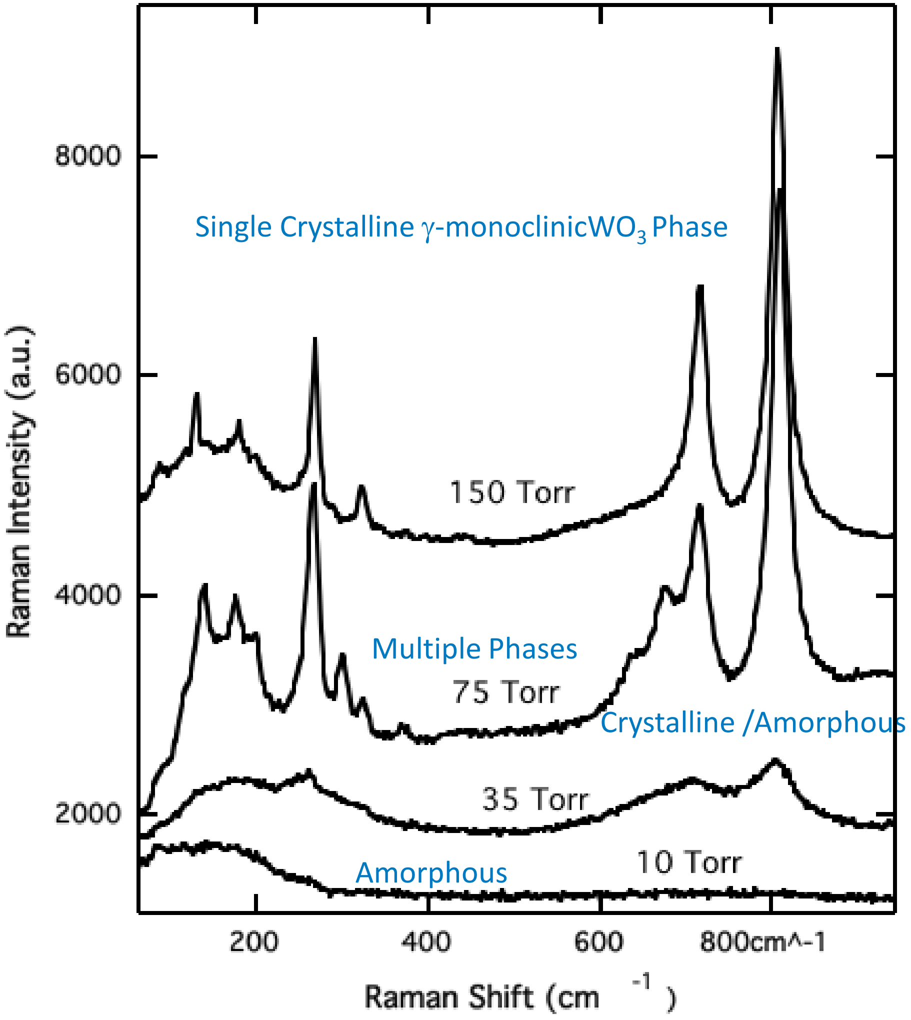
Equal or enhanced ORR electrocatalytic activities have been reported in the literature–generally requiring a conductive matrix like carbon black or doping of the oxide support and often have been compared to Pt/C that have lower values than obtainable today for commercial electrocatalysts.

Optimal Synthesis Conditions Result in a Single Crystalline Phase

X-ray Diffraction (XRD)



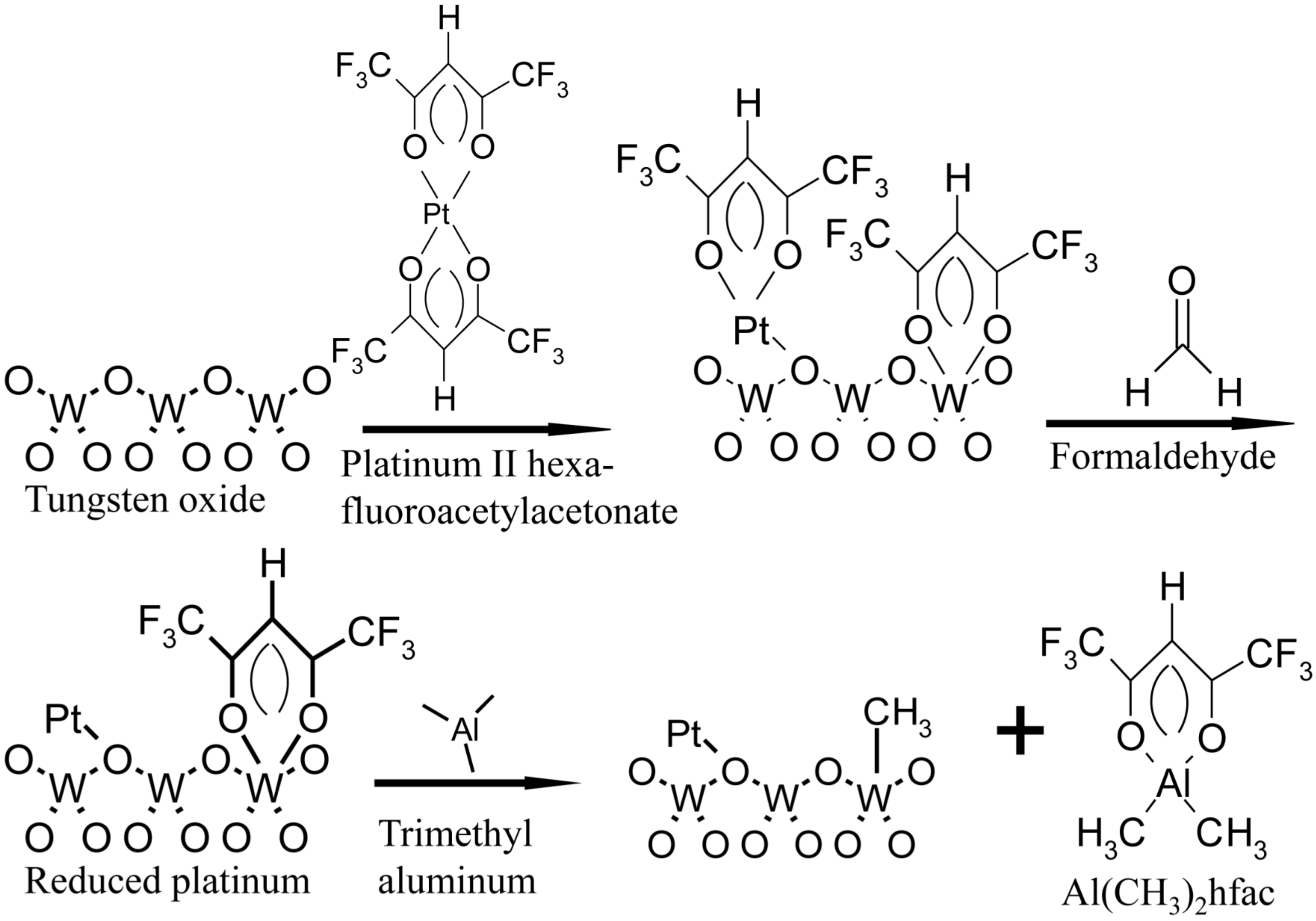
Raman Spectroscopy



300˚C, 4% O$_2$ in Ar, filament ~ 2000˚C

35

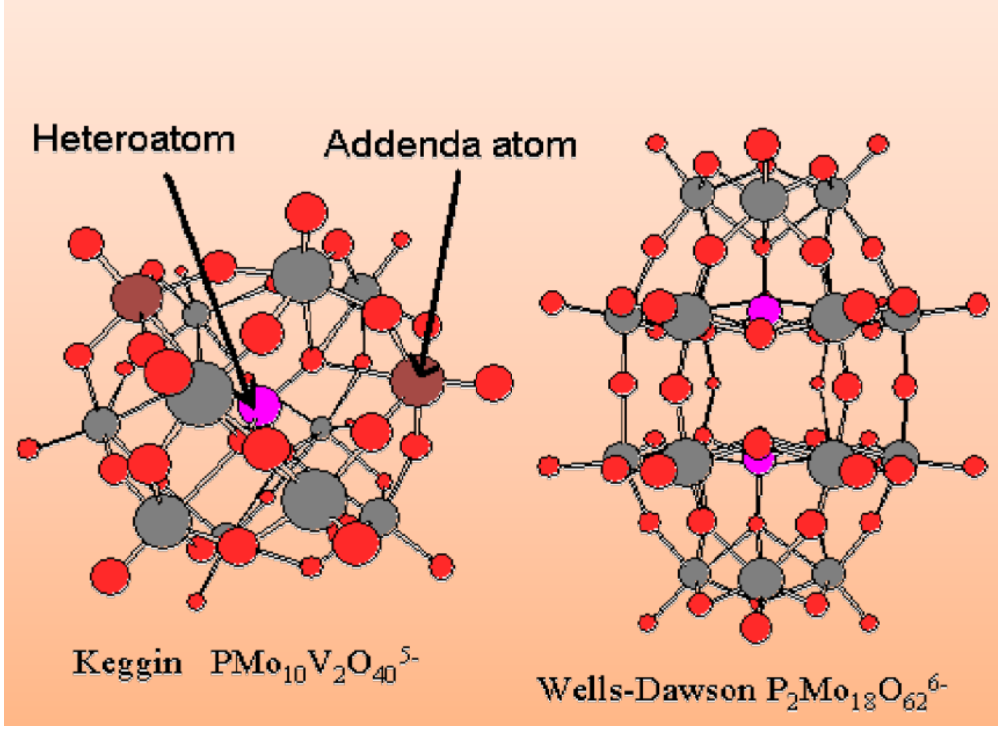
Pt ALD Reaction Sequence



D.N. Goldstein, S.M. George *Appl. Phys. Lett*. 143106 (2009) **95**
D.N. Goldstein, S.M. George *Thin Solid. Film*. 5339 (2011) **519**

HPA Background

- **Benefits**
  - Acts like 1 nm spheres of WO_x
  - Enhances the ORR
  - Stabilizes Pt nano-particles
  - Decomposes peroxide
  - Improves CO tolerance
  - Excellent proton conductors
- **Challenges**
  - Soluble in water
  - Possible mass transport issues



Challenges may be overcome by immobilizing HPA via covalent linkages to the carbon

Wlodarczyk, R.; Chojak, M.; Miecznikowski, K.; Kolary, A.; Kulesza, P. J.; Marassi, R. *Journal of Power Sources* **2006**, *159*, 802.
Guo, Z.; Han, D.; Wexler, D.; Zeng, R.; Liu, H. *Electrochimica Acta* **2008**, *53*, 6410.