

WO₃ and HPA based system for ultra-high activity and stability of Pt catalysts in PEMFC cathodes



2011 DOE AMR

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Project: 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: 13%

Budget

- Total project funding: \$2.9M
 - DOE share: \$2.6M
 - Contractor share
 - CSM: \$204,315
 - CU: \$54,000
- Funding received in FY10: \$500k
- Funding for FY11: \$500k

Barriers

- Durability
- Cost
- Performance

Partners

- S. George: UC Boulder
- A. Herring: CSM
- S. Hamrock: 3M
- K. Adjemian: NTCNA

Project lead – NREL

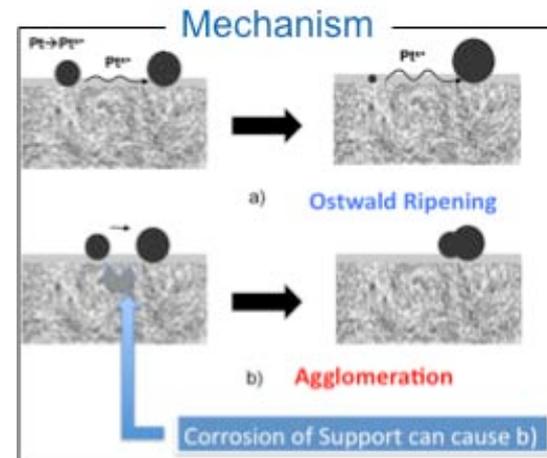
(John Turner, Anne Dillon, Katie Hurst, Bryan Pivovar, K.C. Neyerlin, Jason Zack, and Shyam Kocha)

Relevance: Objectives

Improve electrocatalyst, MEA durability, and activity through the use of Pt/WO₃ and HPA modification to approach automotive PEMFC activity (4x increase) 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



Partial Mitigation of Startup/Shutdown

•Electrical Control

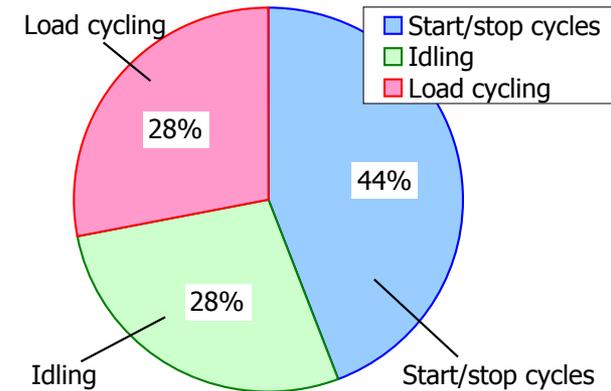
- Voltage Limiting Device or Shorting Resistor
 - Can limit upper potential to ~ OCV

•Gas Flow Control

- Fast gas purge
 - Reduces H₂-Air front time (time @ high V)
- Trickle flow of H₂ @ shutdown
 - Maintains H₂ in anode for longer period
- Low RH air purge @ shutdown
 - Suppression of C corrosion (less H₂O)

•Material Control

- Selective HOR electrocatalyst that is a poor ORR catalyst
- Selective electrocatalyst for H₂O splitting over C corrosion
- Need new support materials that are corrosion resistant



R. Shimoï, A. Takahashi, A. Iiyama, Development of fuel cell stack durability based on actual vehicle test data: Current status and future work, SAE International 2009-01-1014 (2009).

These complex operations mitigate the losses partially.

Can materials solutions eliminate need for complex operations?

DOE Catalyst Support Target & Protocols

Electrocatalyst Support Loss Based on OCV hold

PROTOCOLS FOR PEM FUEL CELLS
(Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies)
March 2007

Protocol based on OCV hold In Subscale Cells

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2005 Status ^a		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal total content (both electrodes)	g / kW (rated)	0.6	1.1	0.3	0.2
Platinum group metal (pgm) total loading ^b	mg PGM / cm ² electrode area	0.45	0.8	0.3	0.2
Cost	\$ / kW	9	55 ^c	5 ^d	3 ^d
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 ^e	5,000 ^f	5,000 ^f
Operating temp >80°C	hours	N/A ^g	N/A ^g	2,000	5,000 ^f
Electrochemical area loss ^h	%	00	00	<40	<40
Electrocatalyst support loss ^h	mV after 100 hours @ 1.2V	>30 ⁱ	N/A	<30	<30
Mass activity ^j	A / mg Pt @ 900 mV _{iR-free}	0.28	0.11	0.44	0.44
Specific activity ^j	μA / cm ² @ 900 mV _{iR-free}	550	180	720	720
Non-Pt catalyst activity per volume of supported catalyst	A / cm ³ @ 800 mV _{iR-free}	8	N/A	>130	300

Table 2
Catalyst Support Cycle and Metrics

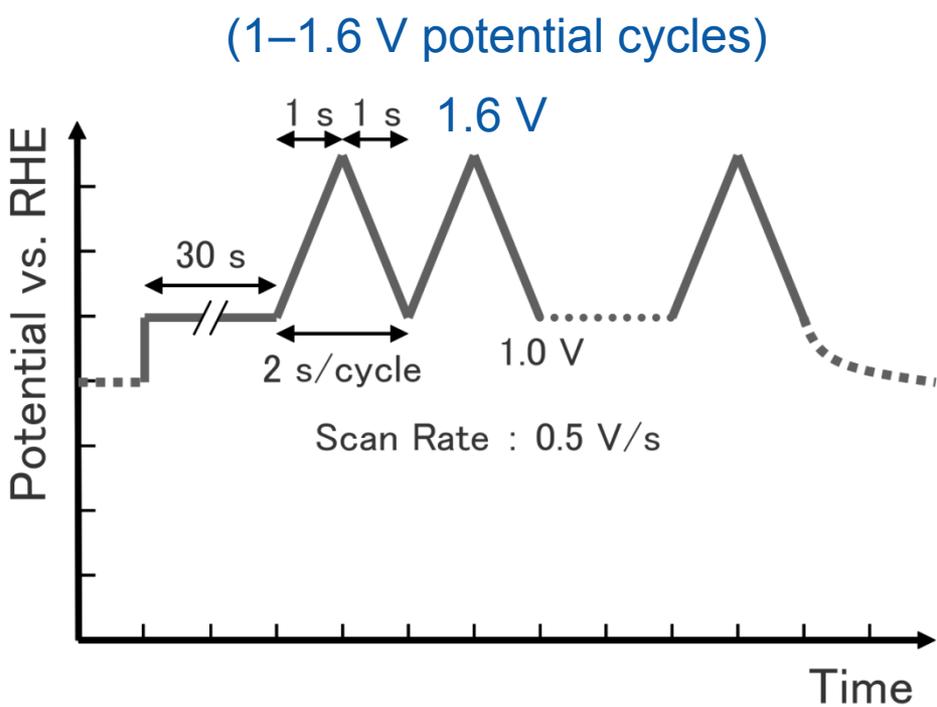
Cycle	Hold at 1.2 V for 24h; run polarization curve and ECSA; repeat for total 200h. Single cell 25 - 50 cm ²
Total time	Continuous operation for 200 h
Diagnostic frequency	24 h
Temperature	95°C
Relative Humidity	Anode/Cathode 80/80%
Fuel/Oxidant	Hydrogen/Nitrogen
Pressure	150 kPa absolute
Metric	Frequency
CO₂ release	On-line
Catalytic Activity*	Every 24 h
Polarization curve from 0 to ≥1.5 A/cm²**	Every 24 h
ECSA/Cyclic Voltammetry	Every 24 h
*Activity in A/mg @ 150kPa abs backpressure at 900mV iR-comp	
**Polarization curve per USFCC "Single Cell Test Protocol" Sec	

Target
<10% mass loss
≤60% loss of initial catalytic activity
≤30mV loss at 1.5 A/cm ² or rated power
≤40% loss of initial area

Not intended/designed for non-carbon supports/unmitigated start-stop

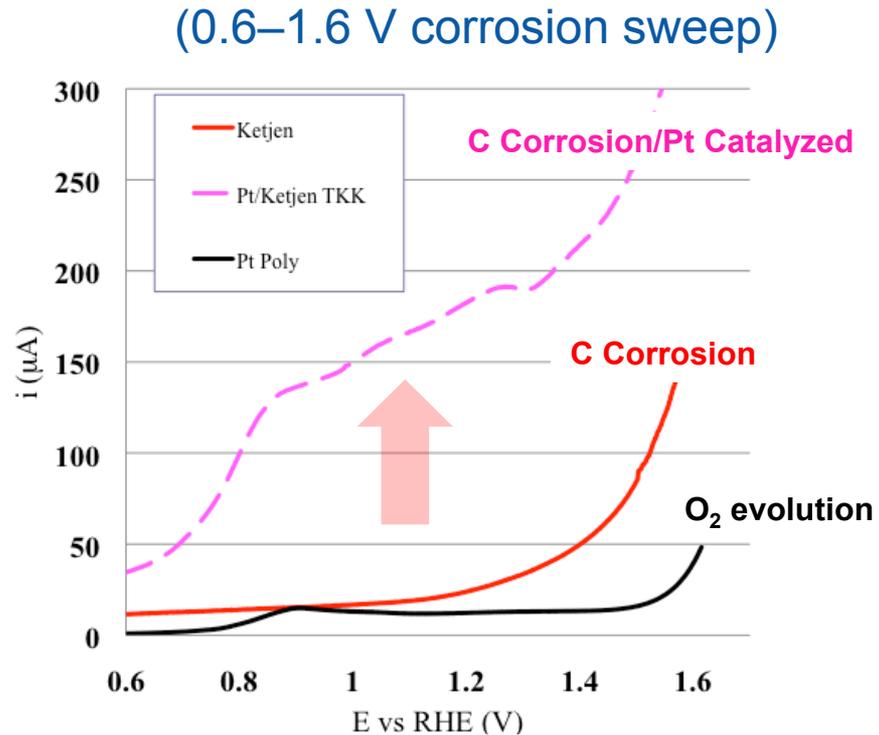
http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Accelerated Stress Test Protocol* — Alternative supports.



Possible Accelerated Stress Test

- Simulated start-stop regime
- 10,000 cycles, H₂|N₂
- RDE & MEA tests possible

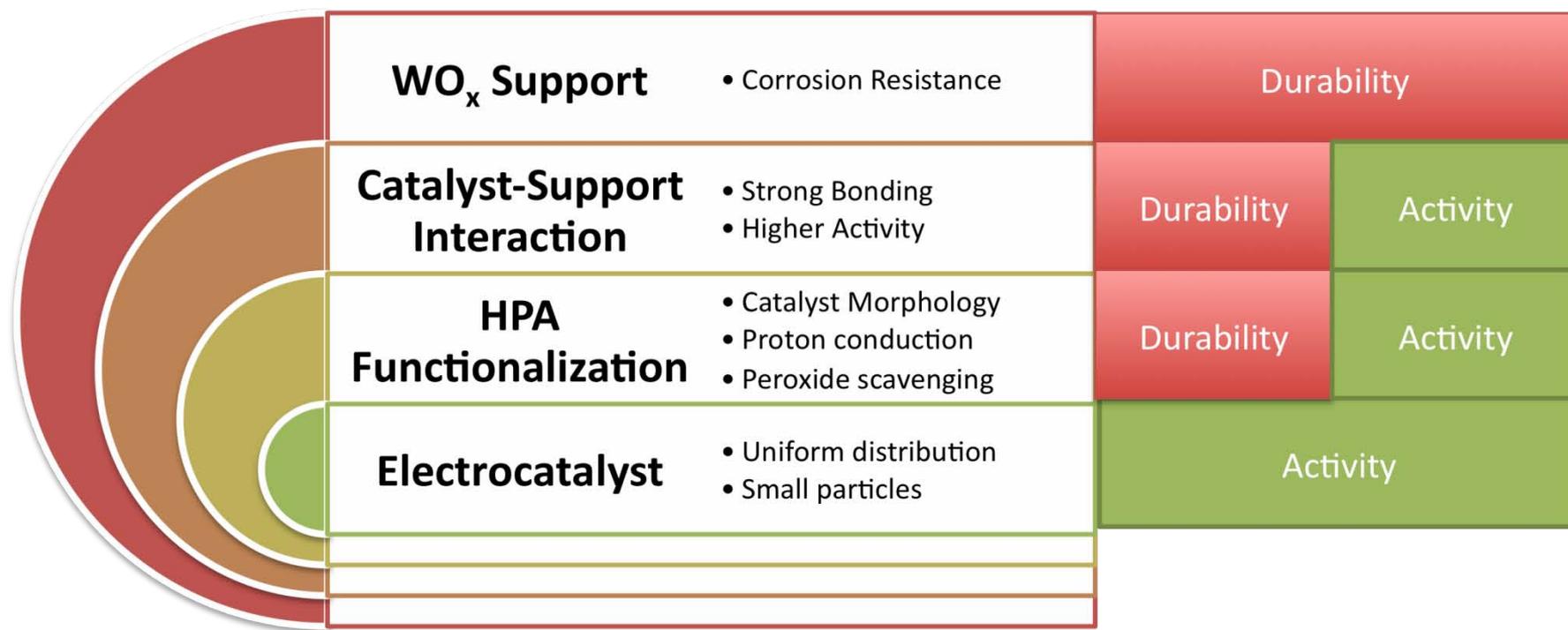


Screening Corrosion Test

- Fast-RDE only, 0.1 M HClO₄
- Evaluation of both support & Pt/support

*DOE Durability Group—subteam for catalyst supports:
 Shyam Kocha (NREL), Eric Brosha and Mahlon Wilson (LANL)

Electrocatalyst System — Approach



Approach involves strategies to counter electrode degradation under startup/shutdown operation, Pt agglomeration under normal automotive load cycles, and improved activity that together will help **reduce Pt loading and hence lower PEMFC stack cost.**

Select Literature on Oxide Supports

Reference	System Evaluated	Key Results: d_p , ORR Activity
Z. Sun, H. C. Chiu, A.C.C. Tsueng— <i>Univ. Greenwich, UK</i>	10wt% Pt/WO₃/C 0.5M H ₂ SO ₄ ; PTFE electrodes	$d_p = 1\text{--}3\text{ nm}$ ORR Activity Pt/WO₃/C > Pt/C
Shim, Lee, Lee, Cairns <i>LBNL—2001</i>	Pt–WO₃/C; Pt–TiO₂/C PEMFC Na ₂ WO ₄ impreg. into C, HCl	ORR activity Pt–WO₃/C = x3 to Pt/C
Saha, Banis, Zhang, Li, Sun, Cai, Wagner— <i>General Motors</i>	15 mm long, 20–60 nm dia Nanowires W₁₈O₄₉ Grown on carbon microfiber paper	$d_p = 2\text{--}4\text{ nm}$ ORR activity Pt/W₁₈O₄₉ = x4 to Pt/C
Suzuki, Nakagawa, Ishihara, Mistushima, Ota— <i>Yokohama Nat’nl Univ.</i>	Pt/WO ₃ ; Pt/V ₂ O ₅ , Pt/SnO ₂ ; Pt/Cr ₂ O ₃ ; Pt/GC RF Sputtering onto C	ORR activity Pt/V₂O₅ > Pt/WO₃ = Pt/C
Savadogo and Beck <i>Ecole Polytech, Quebec</i>	5%Pt- 40%WO₃ PAFC, 180°C	ORR activity = x2 to Pt/C
Huang, Ganeshan, Popov; — <i>Univ. S. Carolina</i>	Rutile Phase–Nb_{0.25}Ti_{0.75}O₂ 0.5M H ₂ SO ₄ ; RDE	$d_p = 3\text{--}4\text{ nm}$ ORR Activity Pt/Nb_{0.25}Ti_{0.75}O₂ = x1 Pt/C

8

Increased electrocatalytic activities reported in the literature—Suggests possible “Support–Catalyst Interaction”

Approach

Synthesize WO_3

NREL

Supply WO_3 to CU for Pt ALD deposition

Supply WO_3 to CSM for HPA modification and Pt deposition

Charac. 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

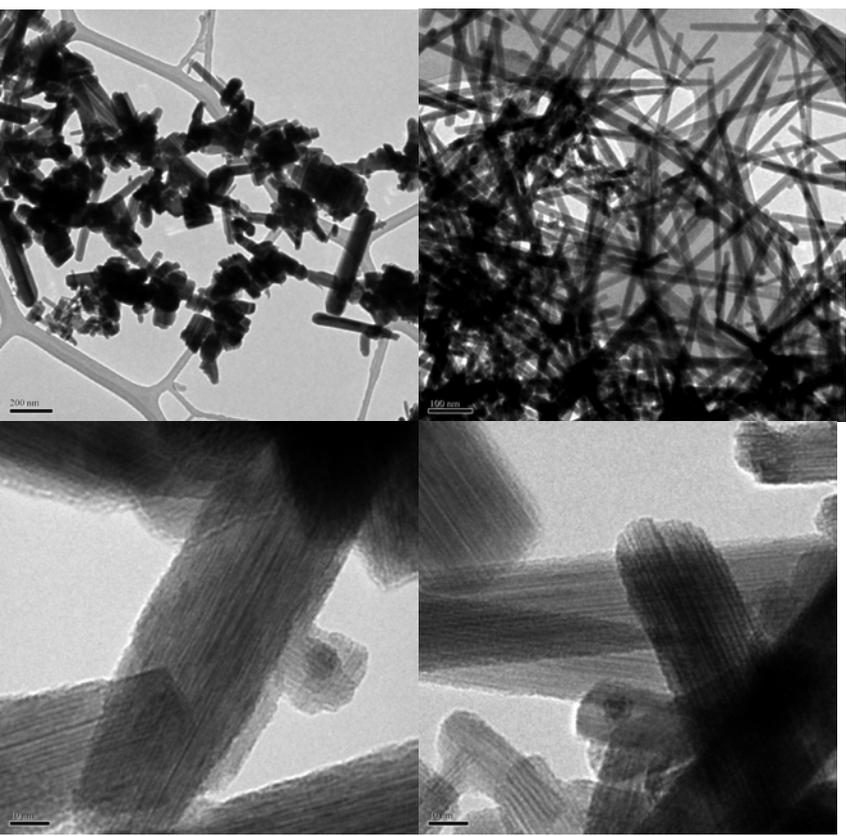
CSM – Andy Herring

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
8. Prepare Pt nano/HPA- WO_3 hybridized with HPA-C

NREL

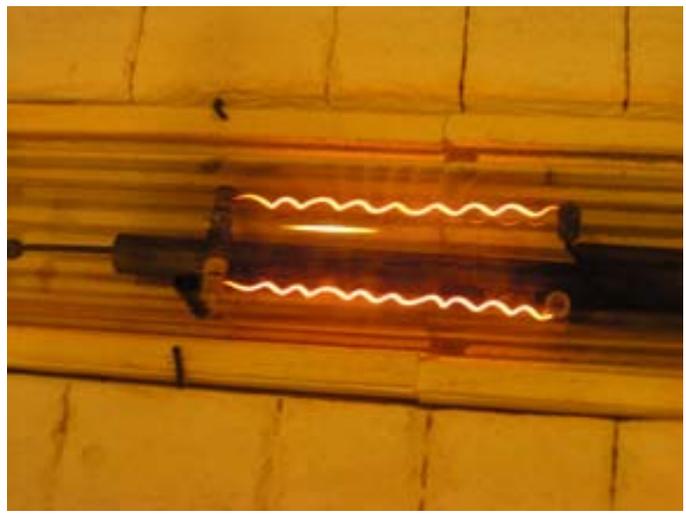
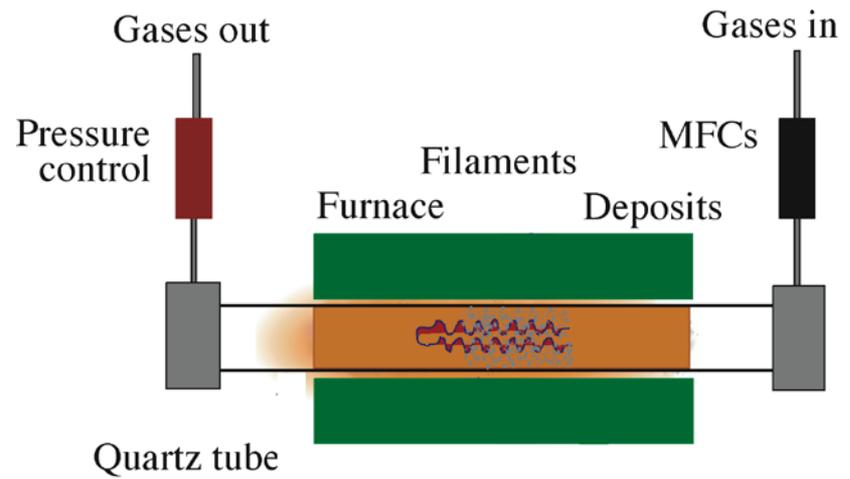
Electrochemical Characterization

Technical Accomplishments: Hot-Wire Chemical Vapor Deposition (HWCVD) — Synthesis of WO₃ Metal Oxide Nanoparticles



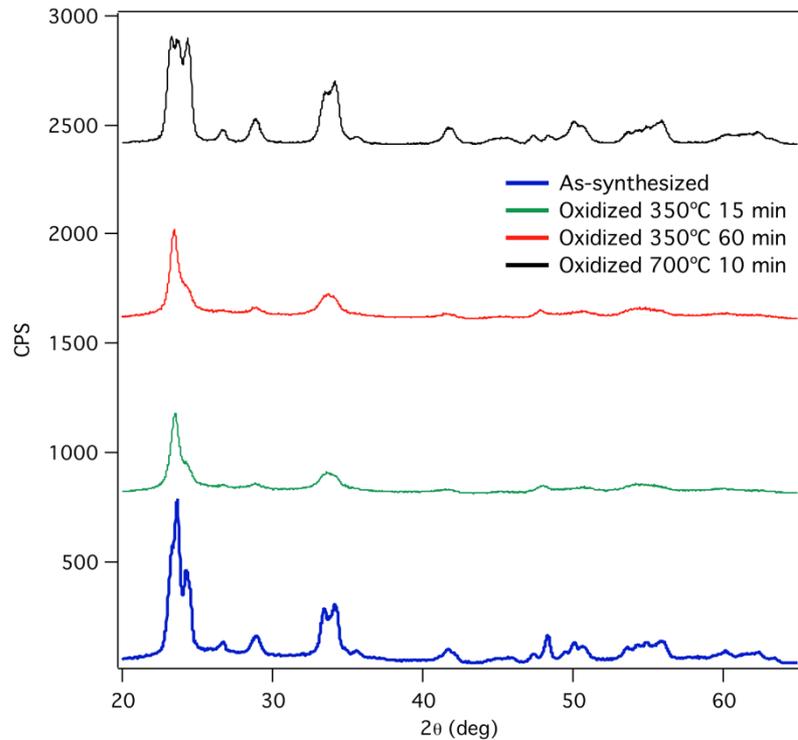
KEH474870 300 C

KEH474878 RT



The filament is oxidized with a small O₂ partial pressure in Ar to form crystalline nanostructures.

The stoichiometry of WO_x can be controlled 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

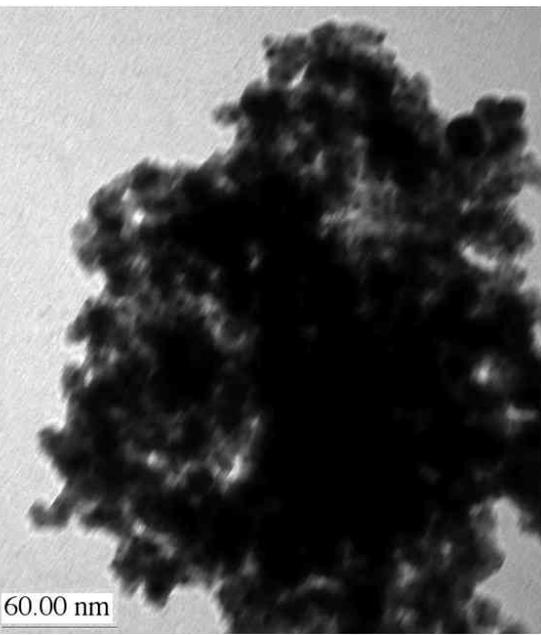
Samples are heterogeneous

-Different oxide phases are made upon oxidation

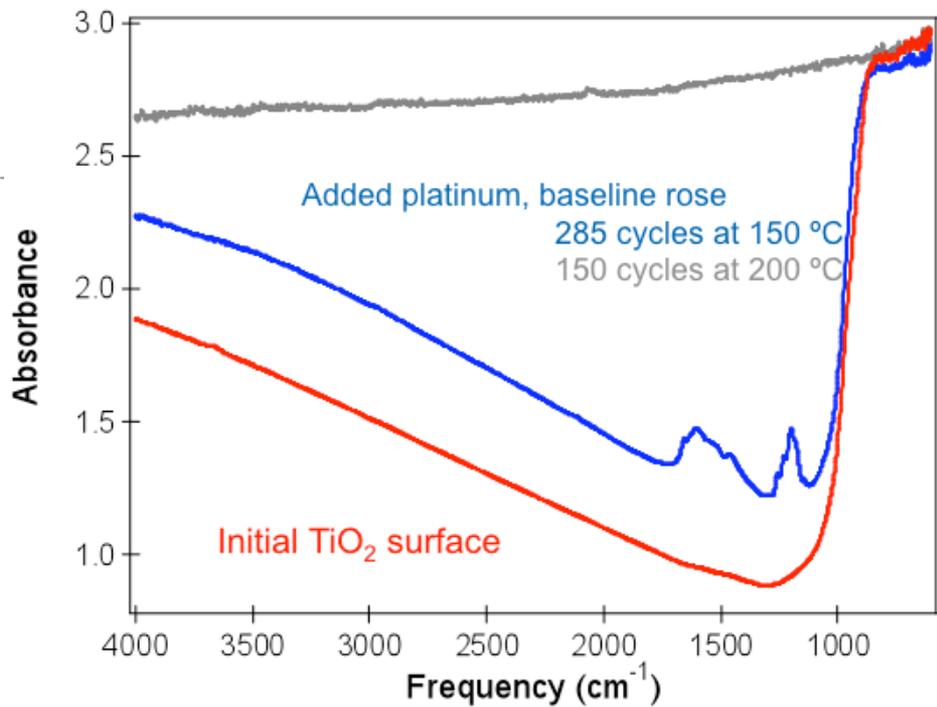
-The stoichiometry of WO_x may impact subsequent Pt deposition

Technical Accomplishments: Initial ALD of Pt/WO₃

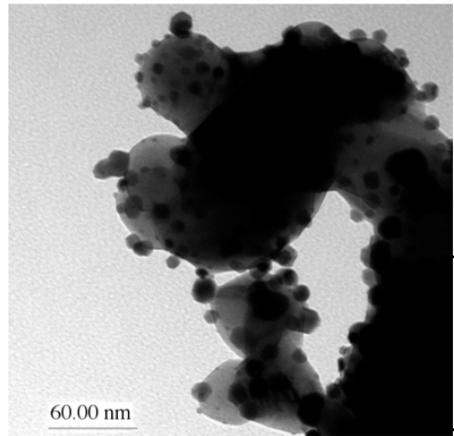
Initial experiments with WO₃ revealed it is very absorptive in IR



Excessive Pt deposition and large agglomerated Pt particles— TEM images.

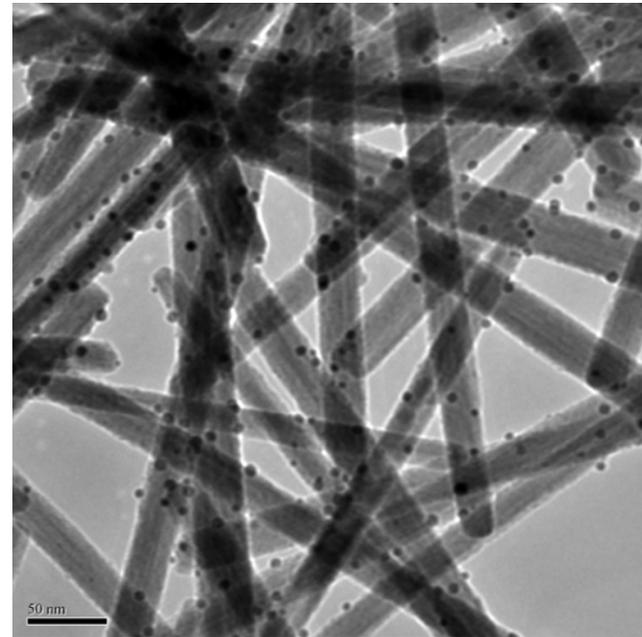
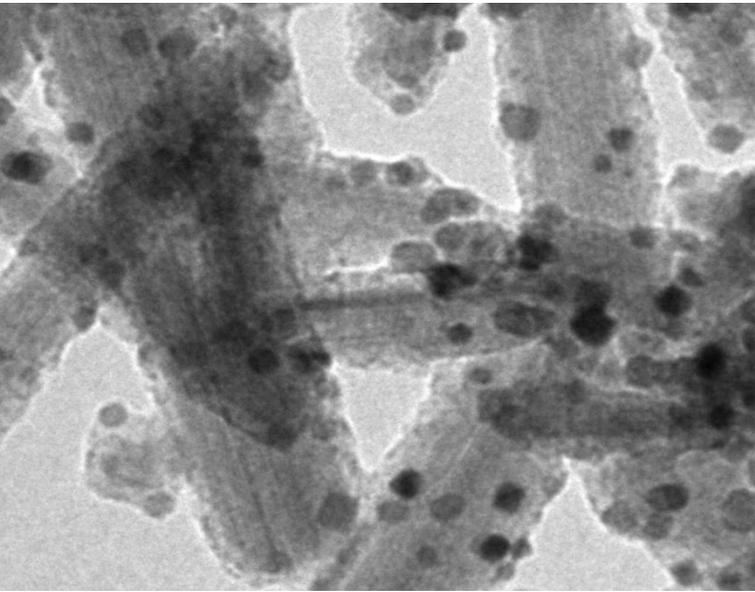


FTIR Background Absorbance Monitors Metal Deposition

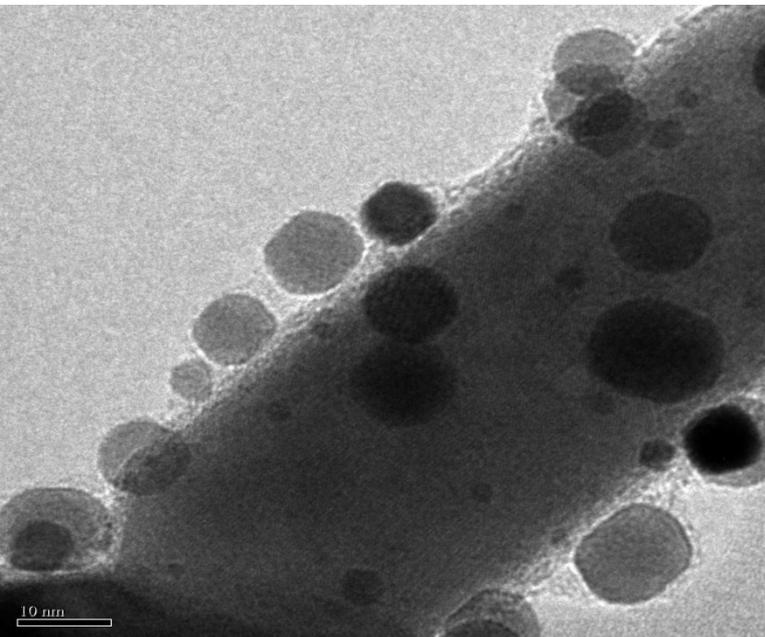


TEM of Pt ALD on TiO₂ IR-Absorbance Change >1.0

Technical Accomplishments: TEMs of improved ALD Pt/ WO₃



140 cycles
Room temp
KEH474894

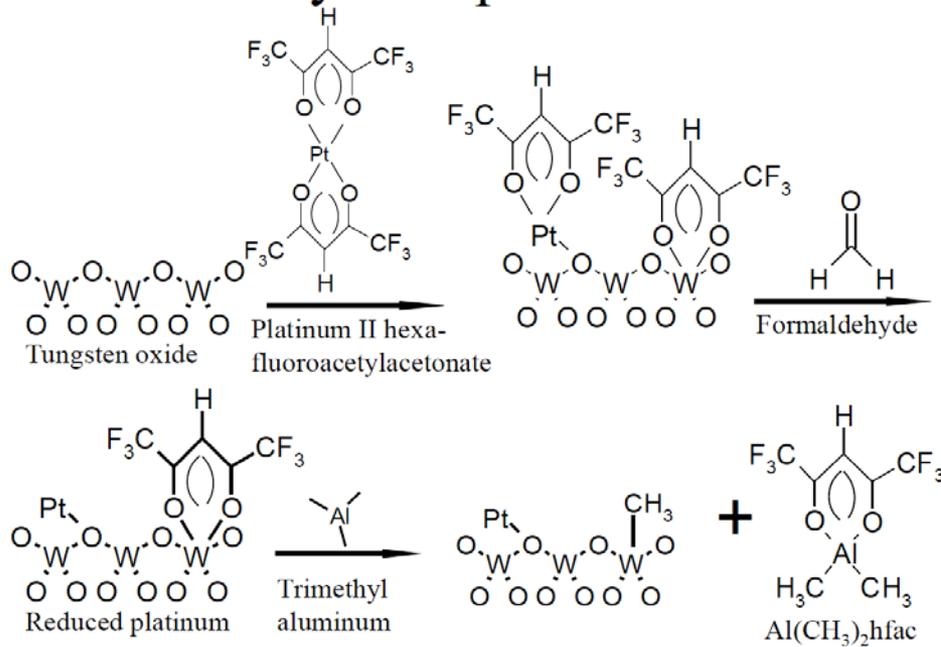


**Improved Pt deposition on WO₃;
Further iterations needed to
reduce particle size.**

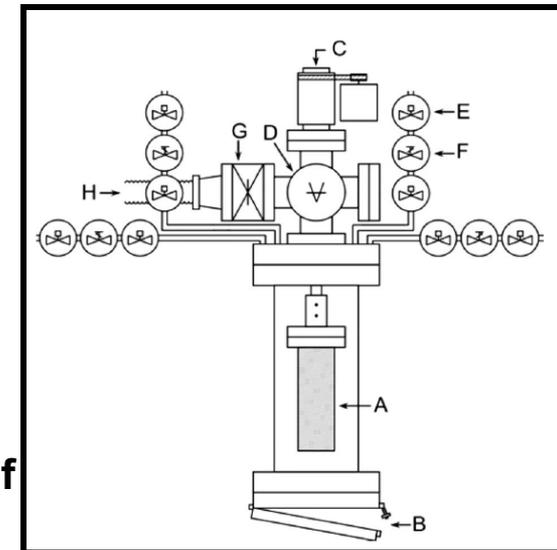
- **Non-uniformity of Pt deposition may be due to the mixed W phase material.**
- **Uniformity higher for WO₃ compared to substoic WO_x.**

Pt-ALD on WO_x

Atomic Layer Deposition Reaction



Roll to roll (R2R) coating for large area film coatings



Rotary reactor for ALD coating of large batches of particles

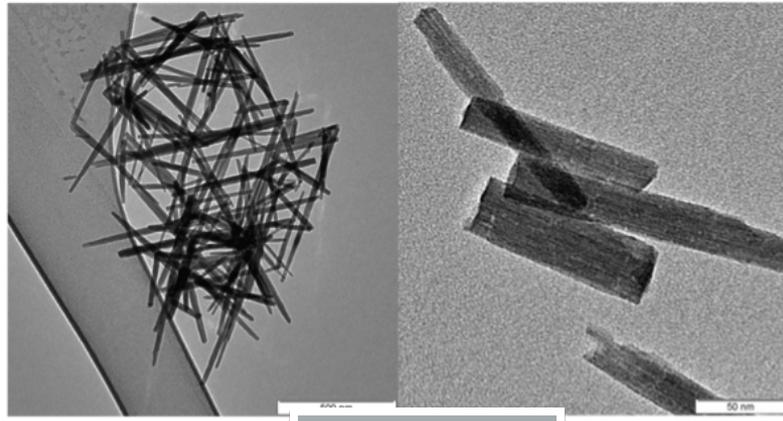
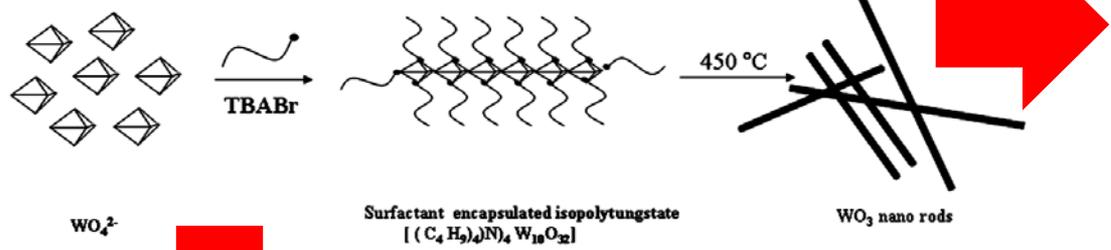
Scale-up: Companies

<http://www.aldnanosolutions.com/markets/>

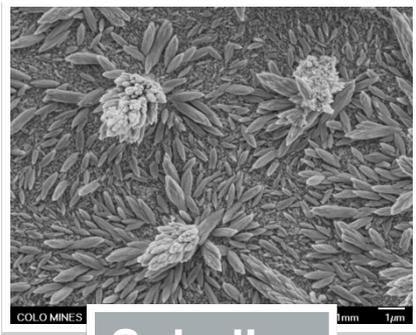
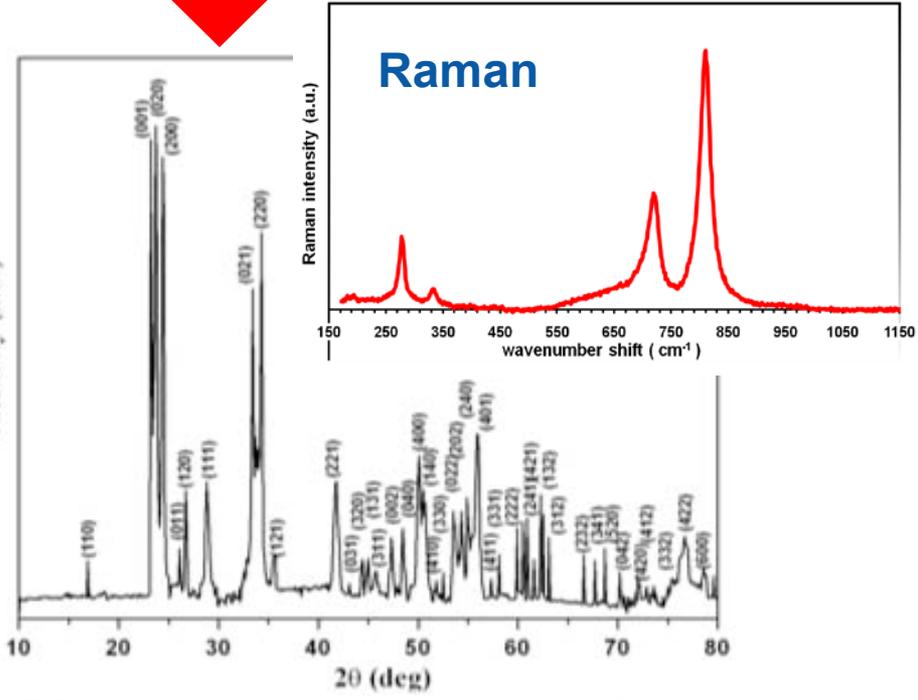
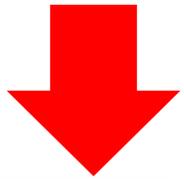
<http://www.sundewtech.com/>

Technical Accomplishments: Tungsten Oxide Wet Chemistry Synthesis

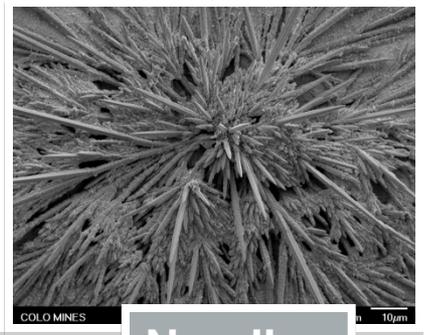
Pyrolysis of $((C_4H_9)_4N)_4W_{10}O_{32}$



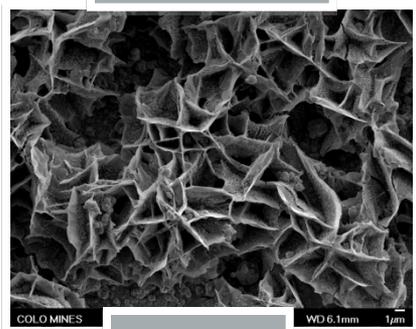
Nanorods



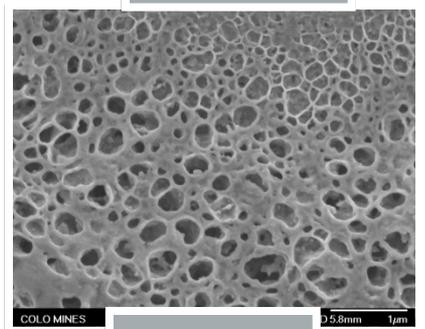
Spindles



Needles



Plates



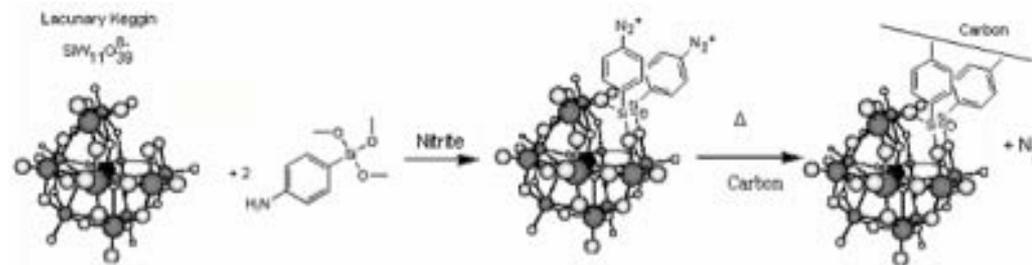
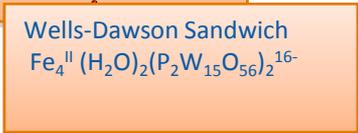
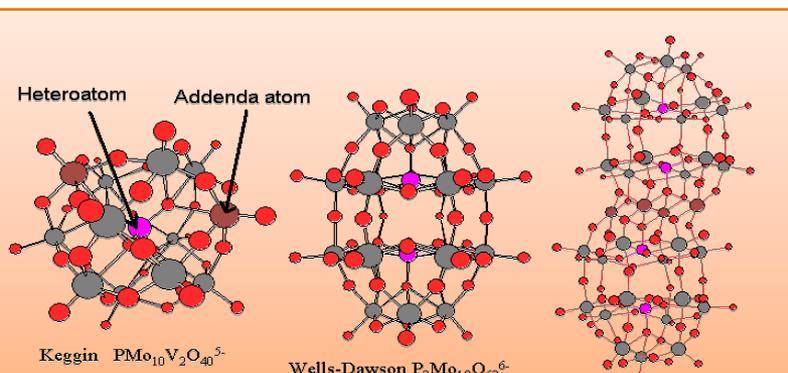
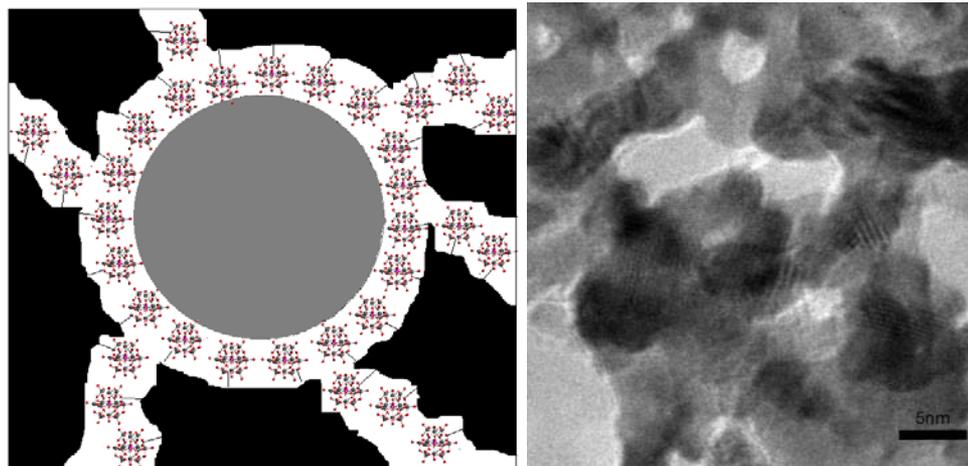
Porous

XRD pattern—as synthesized WO_3 nano rods.

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

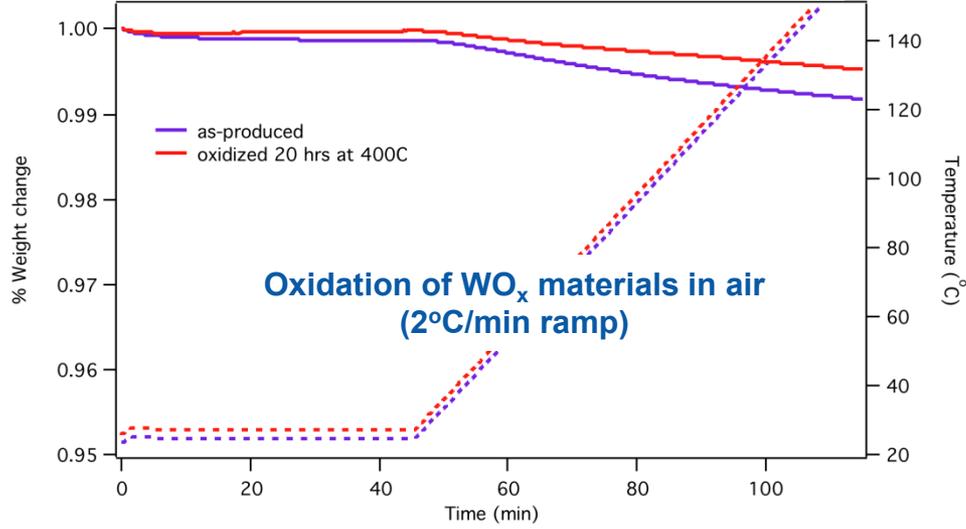
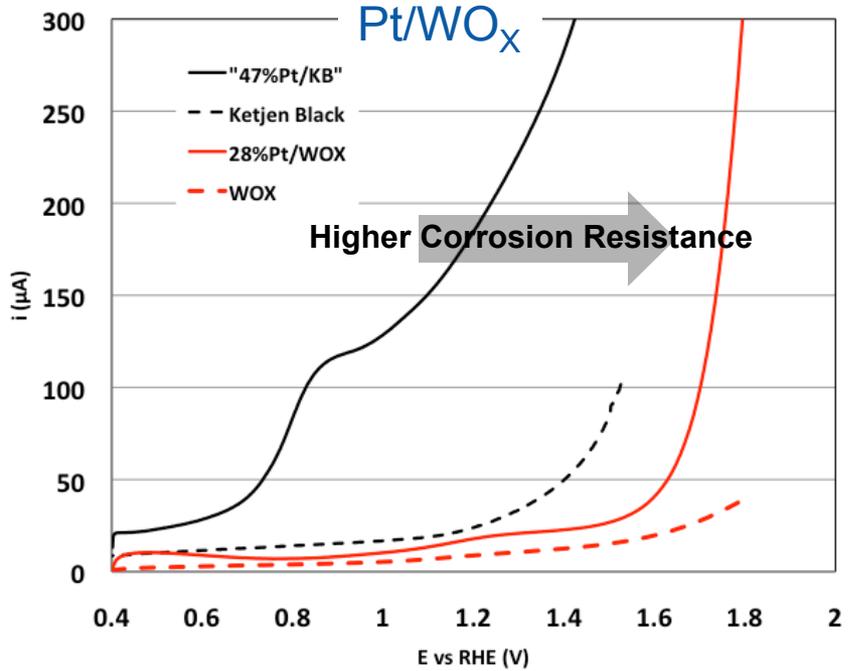
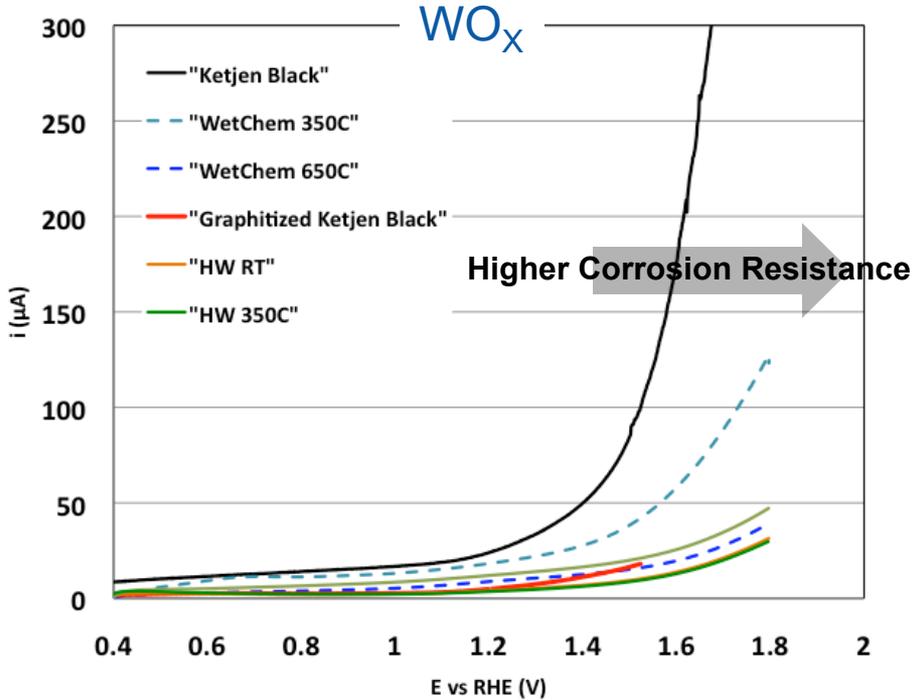
- Stabilize nano-metallic particles
- Decompose peroxide
- Alter electrochemistry on Pt surface
- Conduct protons

Immobilized HPAs as Catalyst Supports



HPA functionalization of Carbon black confirmed by EDX spectra

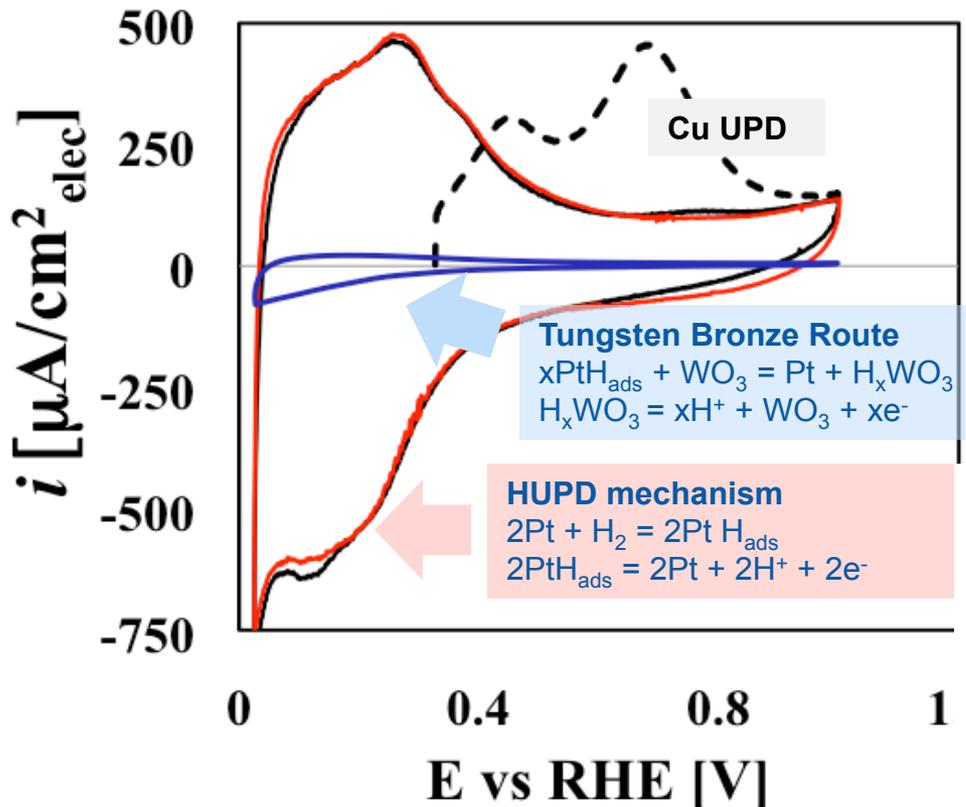
Corrosion Resistance of WO_x and Pt/ WO_x



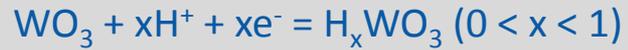
- Corrosion Resistance $WO_x > C$
- Corrosion Resistance $Pt/WO_x > Pt/C$

- WO_x material does not decompose
- Less than 1 wt% H_2O is desorbed from the material
- WO_x stable within the fuel cell regime

Technical Accomplishments: CVs & Electrochemical Area



Formation of Hydrogen Tungsten Bronzes
 ($H_{0.18}WO_3$ and $H_{0.35}WO_3$)

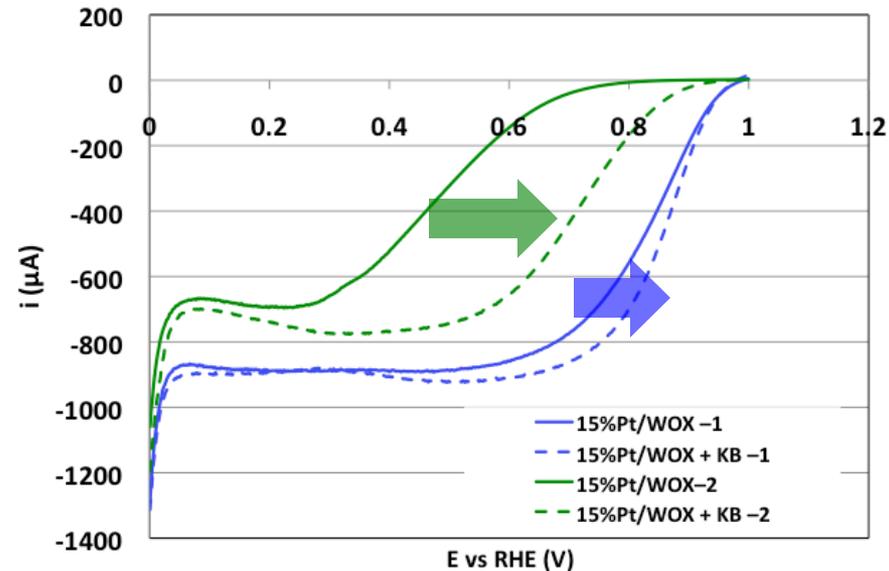


Formation of Substoichiometric Oxides



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

Cu UPD might give a better estimate of ECA, because HUPD region includes charge due to formation of H_xWO_3 as well as spillover effects.



ORR I-V Curves: RDE electrode ink modification improves activity.

AOP Milestones 2011

- Demonstrate controlled nano-structured Pt placement and loading on WO_3 , HPA, or a combination of the two. 12/10 (100% completed) ✓
- Obtain cyclic voltammograms (CVs) and mass activity for Pt on WO_3 , HPA, or a combination of the two. 2/28/11 (100% completed) ✓
- Prepare high surface area catalyst electrodes based on tungsten oxide and tungsten-based heteropoly acids (HPAs), test electrochemically in half-cells and compare to the corrosion of typical carbon blacks for PEMFCs up to 1.5 V. 7/31/11 (60% Completed) ✓
- 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 10 m^2/g Pt. 9/30/11 (50% Completed) ✓

Collaborations

- **CU Boulder:** subcontractor – University
 - Growth of Pt on WO_x
- **CSM:** subcontractor – University
 - Attachment of HPA to Pt/ WO_3
- **3M:** subcontractor – Company
 - Advice on thin films
- **NTCNA:** consultant – Auto Company
 - Support on fuel cell testing

Future Work

- **Deposit smaller more uniform Pt particles on WO₃ supports**
 - Continue to achieve better control of Pt nucleation and dispersion.
 - Achieve controlled ALD deposition of Pt particles that are ~2 nm in diameter.
- **Functionalize Pt/WO₃/C with HPA; morphological control of Pt with HPA**
 - Electrocatalysts will be built from the ground up. Nano-structured carbon to be functionalized by HPA to control nano-Pt.
 - Material will be fully characterized morphologically so that structure activity relationships can be established.
- **Electronic conductivity of WO_x**
 - Conductivity of WO_x of various stoics with and without addition of carbon will be systematically evaluated.
- **RDE electrochemistry**
 - Optimization of catalyst inks will be carried out to obtain the best dispersions and utilization of catalyst for ECA and ORR activity measurements
 - A careful study of the ECA measurement and contribution/overlap of hydrogen tungstates to the HUPD region will be carried out
 - HPA modified catalysts will be evaluated for ECA and ORR activity.

Summary

Relevance: Pt/WO_x addresses the key issues of support durability and catalyst activity for PEMFC commercialization

Approach: Use of a durable support and HPA functionalization that may provide catalyst-support interaction and raise the activity

Technical Accomplishments: Growth of WO_x nanorods and other shapes using HWD and wet chemistry, ALD deposition of Pt on WO_x, HPA attachment to carbon, preliminary electrochemistry on these materials.

Collaborations: Close collaboration with CU Boulder on Pt-ALD, with CSM on HPA functionalization and consulting with 3M and NTCNA.

Technical Back-up Slides

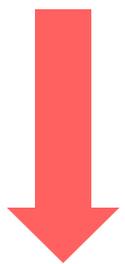
Automotive Operations Imposed on Catalyst Support

- **Startup/Shutdown**

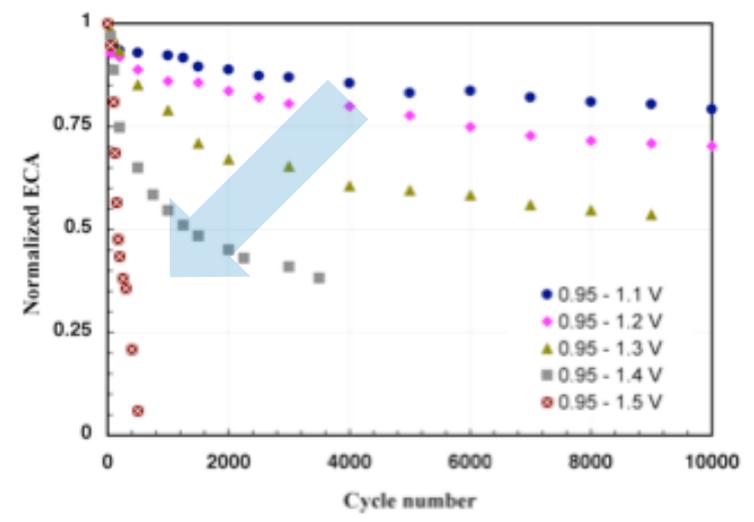
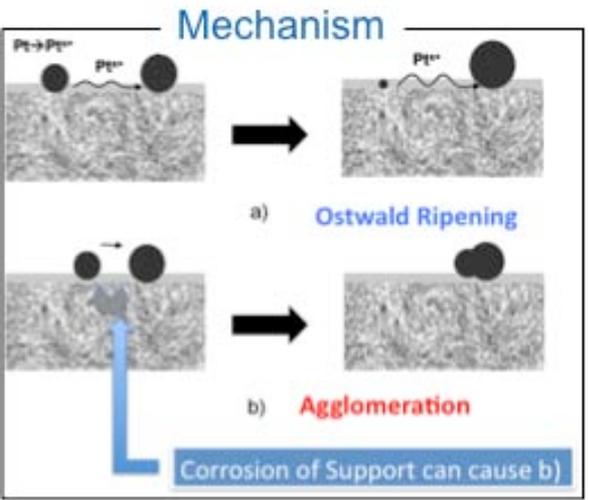
- Unmitigated
 - Anode : H₂-Air Front → 0 – OCV (0.95 V)
 - Cathode: Air → 0.95 V – 1.6 V **Severe C corrosion**
- Mitigated (Stack shorting)
 - Anode : H₂-Air Front → 0 – OCV (0.95 V)
 - Cathode : 0 V – OCV

- **Normal Operation**

- OCV (0.95 V) **Milder C corrosion**
- Load Cycling (0.60– 0.95 V)



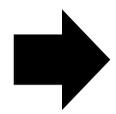
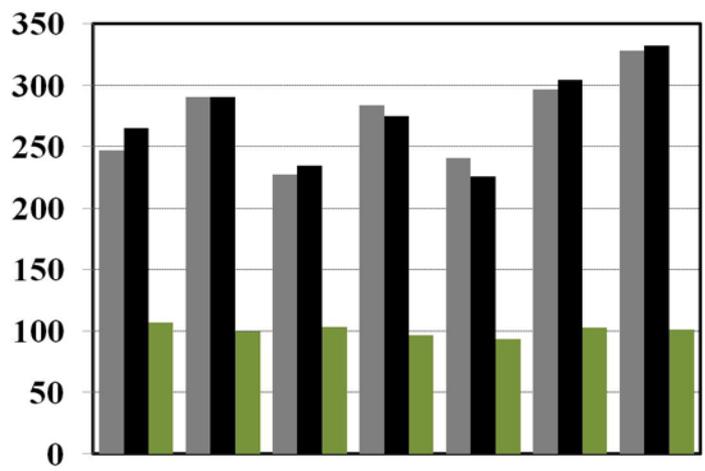
Effect of Upper Potential on loss of Electrochemical Surface Area



ECA & ORR Benchmarks for Baseline Pt/C Electrocatalysts

Rotating Disk Electrode Experiments

■ $i_s^{0.9V}$ [$\mu\text{A}/\text{cm}^2_{\text{Pt}}$]
 ■ $i_m^{0.9V}$ [$\text{mA}/\text{mg}_{\text{Pt}}$]
 ■ ECSA [$\text{m}^2/\text{g}_{\text{Pt}}$]



	$i_s^{0.9V}$ [$\text{mA}/\text{cm}^2_{\text{Pt}}$]	$i_m^{0.9V}$ [$\text{mA}/\text{mg}_{\text{Pt}}$]	ECA [$\text{m}^2_{\text{Pt}}/\text{g}_{\text{Pt}}$]	RF [$\text{cm}^2_{\text{Pt}}/\text{cm}^2_{\text{elec}}$]
Pt/HSC-TKK	270 ± 35	275 ± 35	100 ± 5	-
Poly Pt	2300 ± 100	-	-	1.5 ± 0.1

DOE Status and Targets & NREL Status for Pt/C

Table 1. NREL & DOE 2015 electrocatalyst Status & Targets.
 *RDE half-cells - 900 mV, 20 mV/s, 25°C, 0.1 M HClO₄;
 **MEAs - 900 mV, 50 cm² subscale fuel cells, 15 min/point, 150 kPa (PO₂ = 100 kPa), 80°C, 100% RH, Nafion membrane.

	Specific Activity [$\mu\text{A}/\text{cm}^2_{\text{Pt}}$]	Mass Activity [$\text{mA}/\text{mg}_{\text{Pt}}$]
DOE 2015 Target in MEA**	720	>440
DOE 2005 Pt/C Status**	180	110
NREL Pt/C status in MEA**	290±10	225±10
NREL Pt/C status in RDE*	270 ± 30	270±30