NATIONAL RENEWABLE ENERGY LABORATORY

Innovation for Our Energy Future

WO_3 and HPA based system for ultra-high activity and stability of Pt catalysts in PEMFC cathodes

2011 DOE AMR

May 10, 2011

John Turner

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Project: FC084

Overview

Timeline

- Start Date: 05/01/2010
- End Date: 04/30/2014
- Percent Complete: 13%

Barriers

- Durability
- Cost
- Performance

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

Partners

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

Project lead – NREL

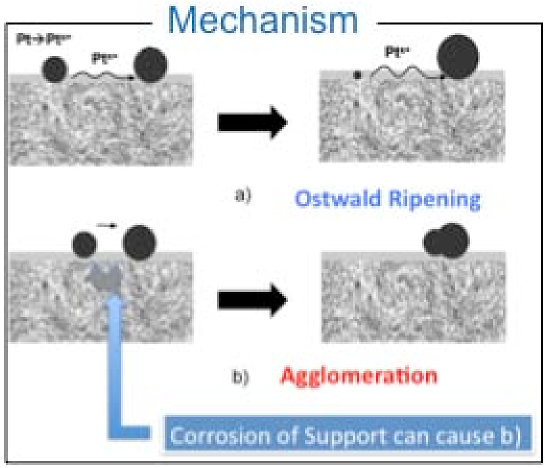
(John Turner, Anne Dillon, Katie Hurst, Bryan Pivovar, K.C. Neyerlin, Jason Zack, and Shyam Kocha)

Relevance: Objectives

Improve electrocatalyst, MEA durability, and activity through the use of Pt/WO_3 and HPA modification to approach automotive PEMFC activity (4x increase) and durability targets (5000h/10y).

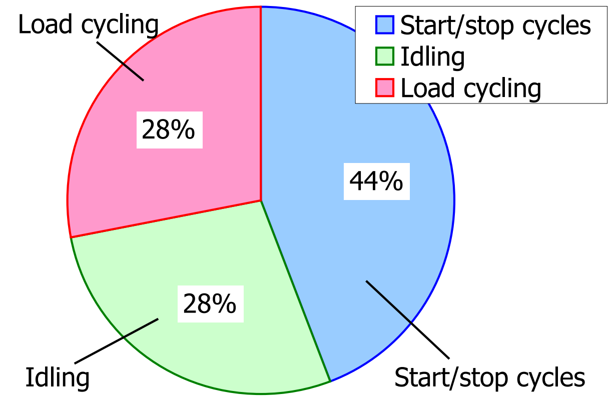
- **Enhance Pt anchoring to support**
  - Suppress loss in Pt ECA under load cycling operations
  - Enhance electrocatalytic activity
- **Lower support corrosion**
  - Increased durability under automotive startup/shutdown operation.
  - Suppress Pt agglomeration/electrode degradation

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 H_2-Air front time (time @ high V)
  - Trickle flow of H_2 @ shutdown
    - Maintains H_2 in anode for longer period
  - Low RH air purge @ shutdown
    - Suppression of C corrosion (less H_2O)
- **Material Control**
  - Selective HOR electrocatalyst that is a poor ORR catalyst
  - Selective electrocatalyst for H_2O splitting over C corrosion
  - Need new support materials that are corrosion resistant



R. Shimoi, 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

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]	%	90	90	<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 $mV_{iR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [j]	μA / cm^2 @ 900 $mV_{iR\text{-}free}$	550	180	720	720
Non-Pt catalyst activity per volume of supported catalyst	A / cm^3 @ 800 $mV_{iR\text{-}free}$	8	N/A	>130	300

PROTOCOLS FOR PEM FUEL CELLS

(Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies)

March 2007

Protocol based on OCV hold In Subscale Cells

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**	**Target**
CO_2 release	On-line	**<10% mass loss**
Catalytic Activity*	Every 24 h	≤60% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm^2**	Every 24 h	≤30mV loss at 1.5 A/cm^2 or rated power
ECSA/Cyclic Voltammetry	Every 24 h	≤40% loss of initial area

*Activity in A/mg @ 150kPa abs backpressure at 900mV iR-corr

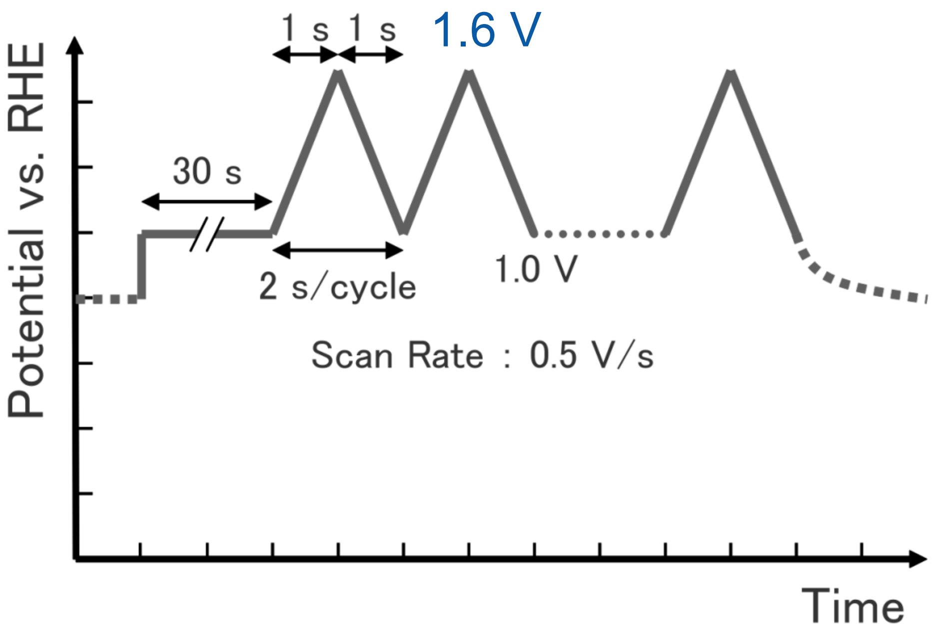
**Polarization curve per USFCC "Single Cell Test Protocol" Sec

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

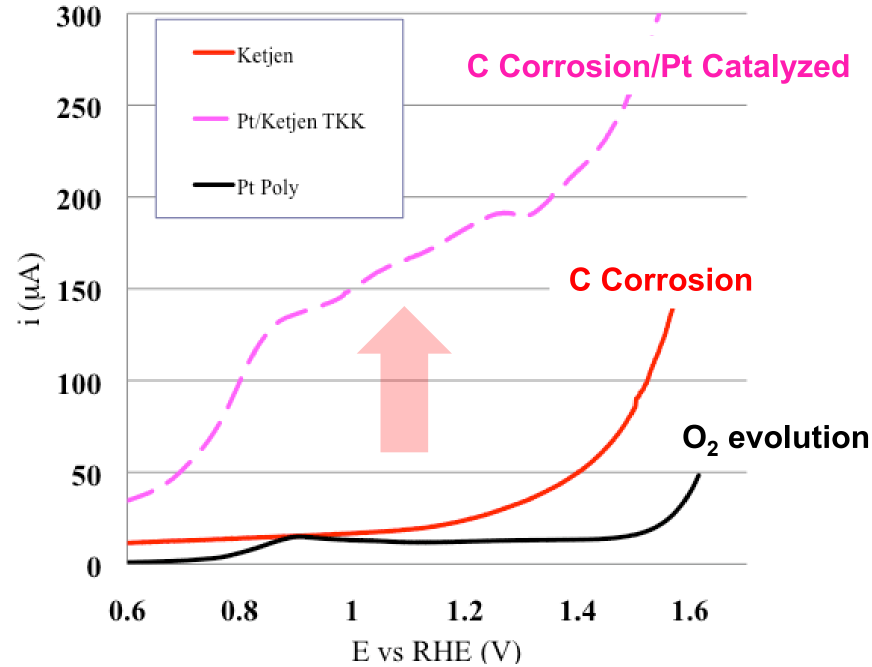
http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Accelerated Stress Test Protocol* — Alternative supports.

(1–1.6 V potential cycles)



(0.6–1.6 V corrosion sweep)



<u>Possible Accelerated Stress Test</u>

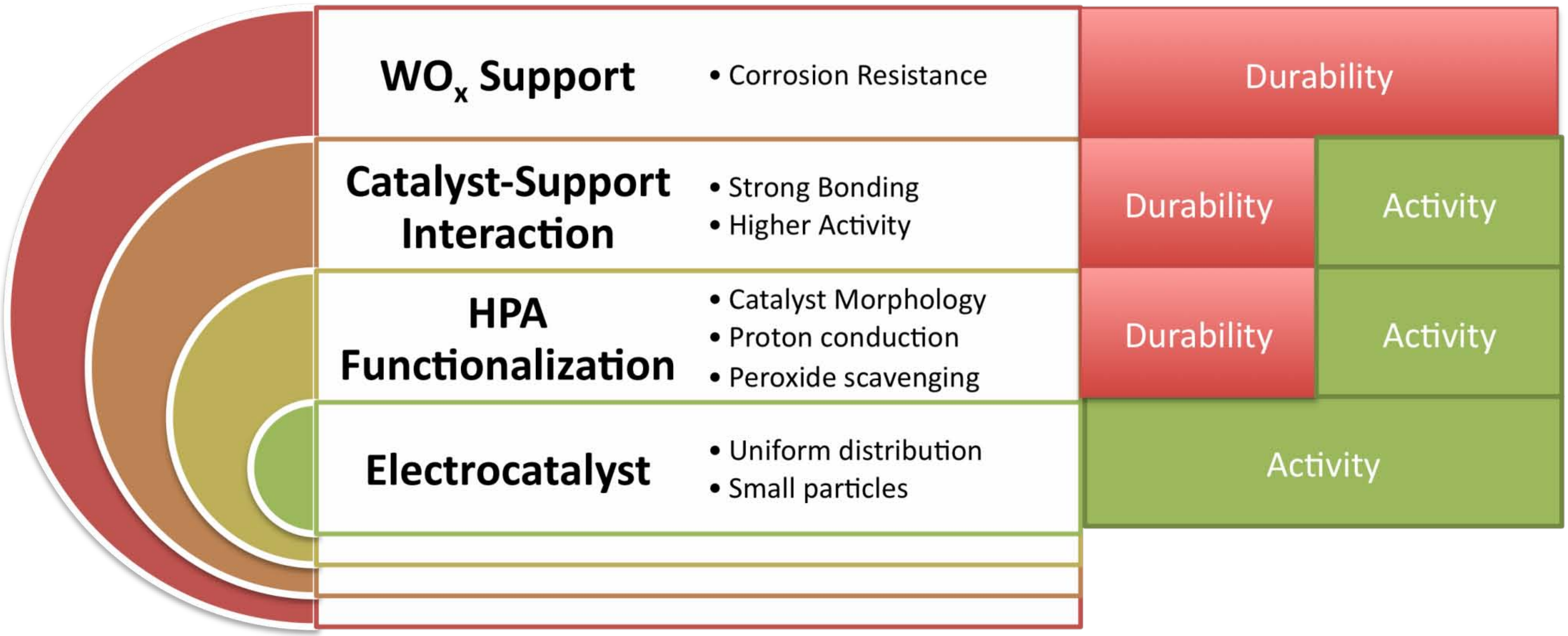
- Simulated start-stop regime
- 10,000 cycles, $H_2|N_2$
- RDE & MEA tests possible

<u>Screening Corrosion Test</u>

- Fast–RDE only, 0.1 M $HClO_4$
- 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—*Univ. Greenwich,* UK	**10wt% $Pt/WO_3/C$** 0.5M H_2SO_4; PTFE electrodes	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 Na_2WO_4 impreg. into C, HCl	**ORR activity $Pt–WO_3/C$ = x3 to 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 $Pt/W_{18}O_{49}$ = x4 to 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 to 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**

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

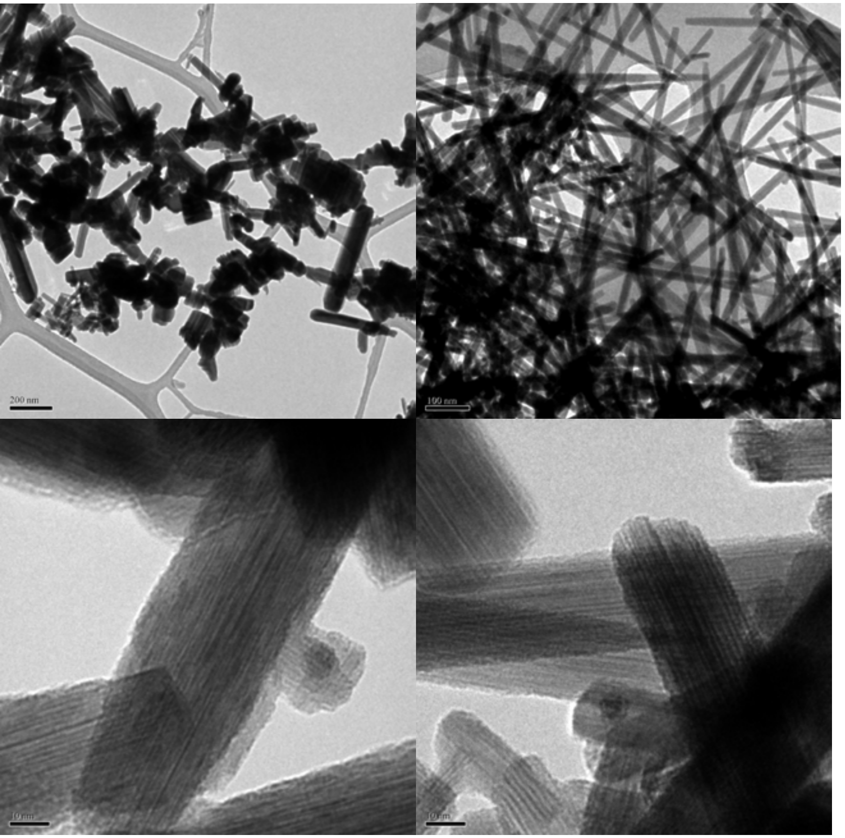
1. Prepare Pt nanoclusters on WO_3
2. Analyze the structures formed using FTIR, XPS, SEM, TEM, Raman, etc.,
3. Measure Pt particle size, BET, etc.,
4. Provide samples to CSM & NREL

CSM – Andy Herring

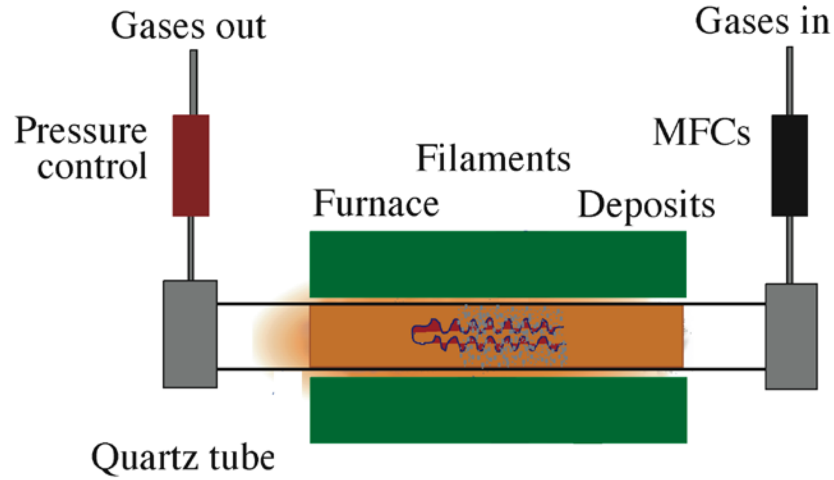
1. Synthesize HPA
2. Immobilize HPA to Pt/C
3. Prepare Pt nano/C
4. Immobilize HPA to C
5. Prepare Pt nano/HPA-C
6. Immobilize/ Covalently bond HPA to WO_3
7. Prepare Pt nano/HPA-WO3
8. Prepare Pt nano/HPA-WO3 hybridized with HPA-C

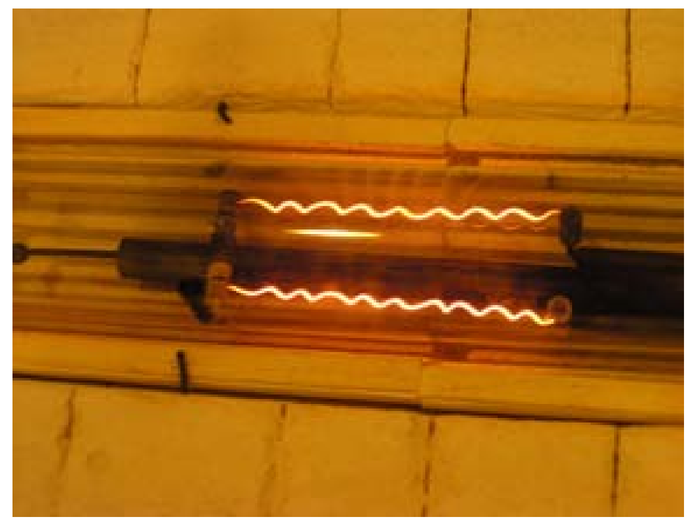
NREL Electrochemical Characterization

Technical Accomplishments: Hot-Wire Chemical Vapor Deposition (HWCVD) — Synthesis of WO_3 Metal Oxide Nanoparticles



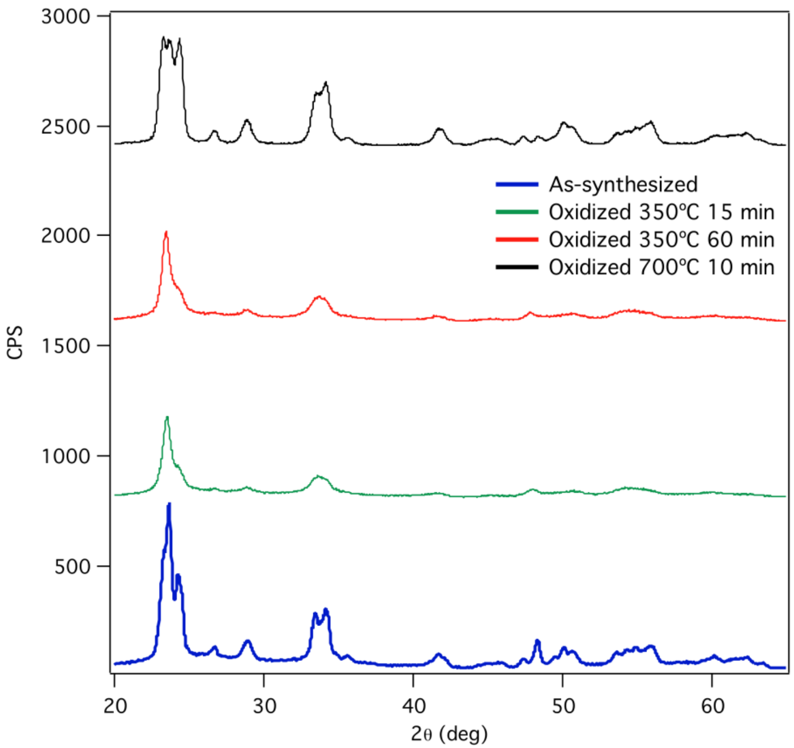
KEH474870 **300 C** KEH474878 **RT**





The filament is oxidized with a small O_2 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

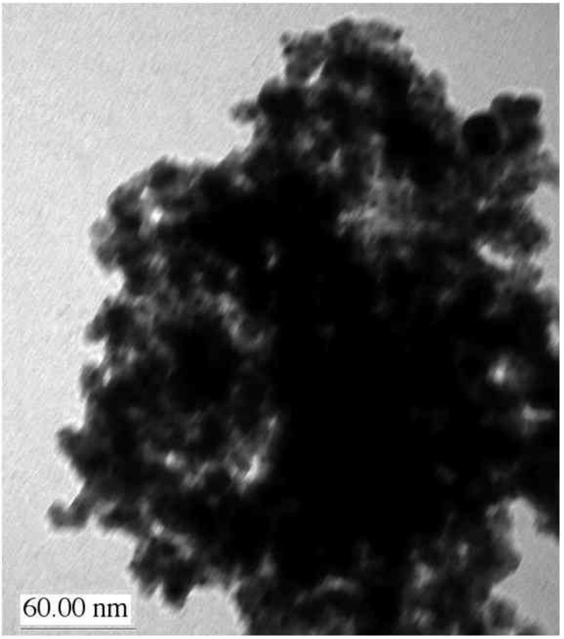
Samples are heterogeneous

-Different oxide phases are made upon oxidation

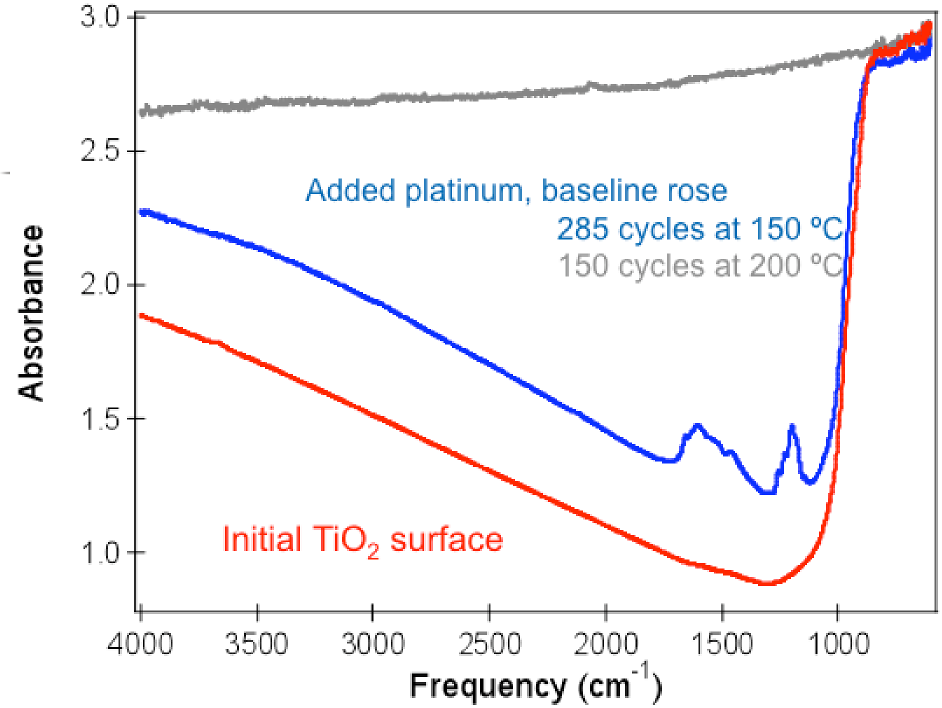
-The stoichiometry of WO_x may impact subsequent Pt deposition

Technical Accomplishments: Initial ALD of Pt/WO_3

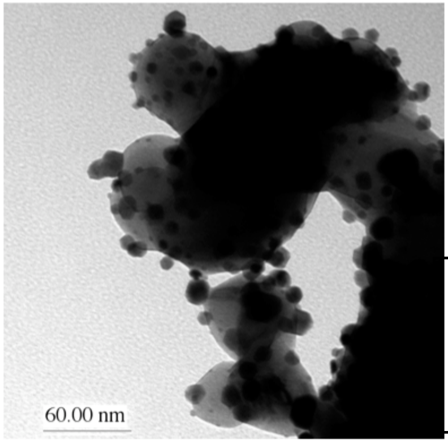
- **Initial experiments with WO_3 revealed it is very absorptive in IR**



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

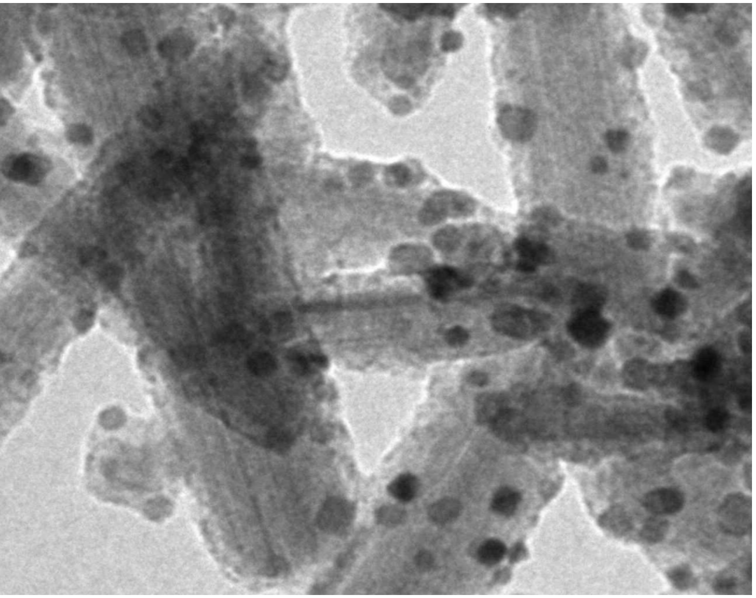


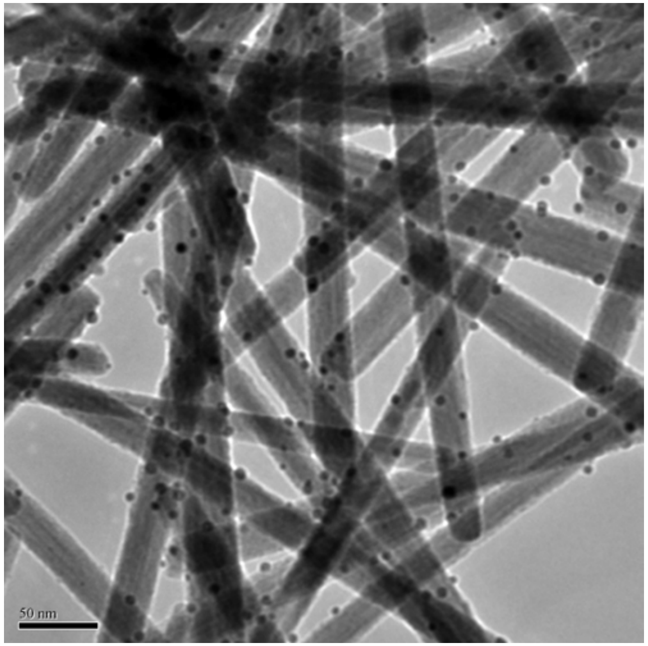
FTIR Background Absorbance Monitors Metal Deposition



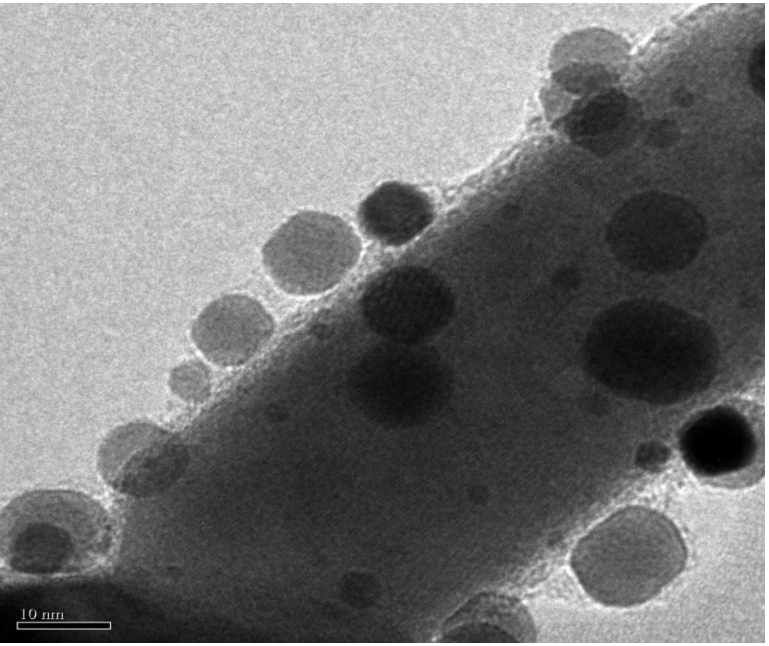
TEM of Pt ALD on TiO_2 IR-Absorbance Change >1.0

Technical Accomplishments: TEMs of improved ALD Pt/ WO_3





140 cycles
Room temp
KEH474894

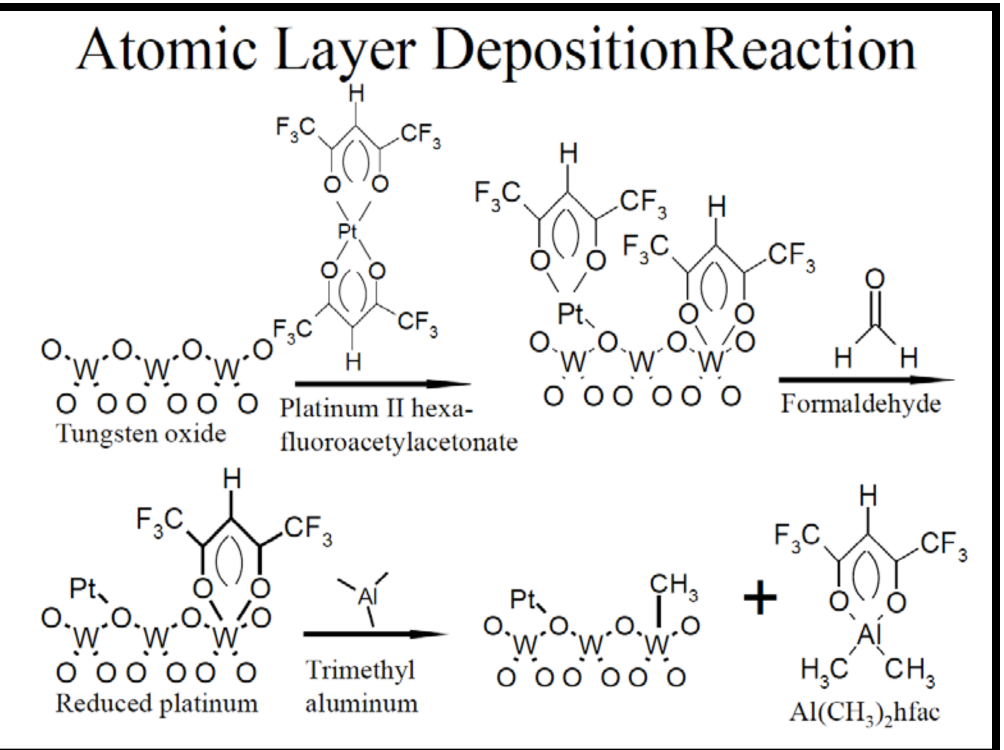


Improved Pt deposition on WO_3; Further iterations needed to reduce particle size.

- **Non-uniformity of Pt deposition may be due to the mixed W phase material.**

- **Uniformity higher for WO_3 compared to substoic WO_X.**

Pt–ALD on WO_X



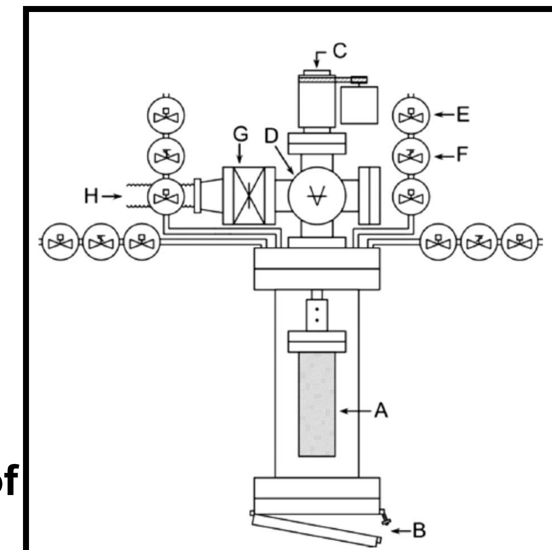
Roll to roll (R2R) coating for large area film coatings

Scale-up: Companies

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

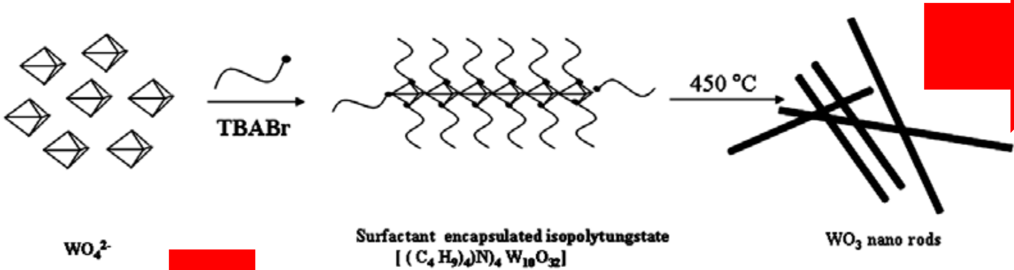
http://www.sundewtech.com/

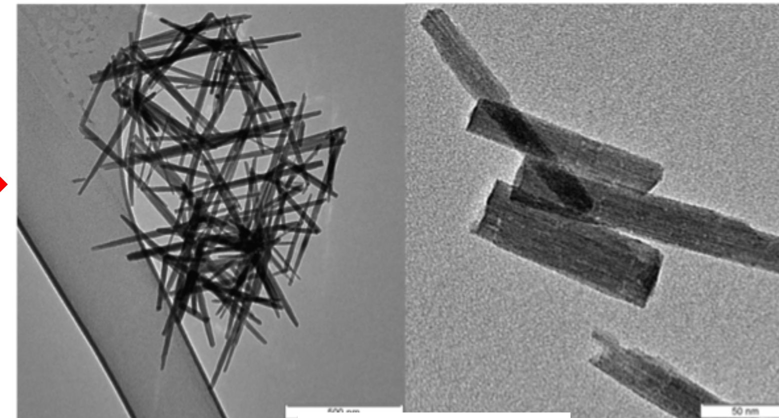
Rotary reactor for ALD coating of large batches of particles



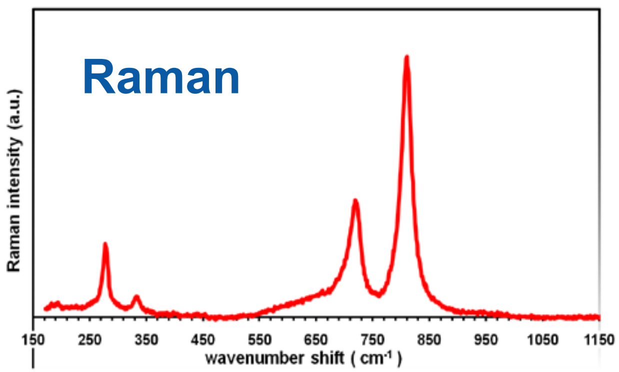
Technical Accomplishments: Tungsten Oxide Wet Chemistry Synthesis

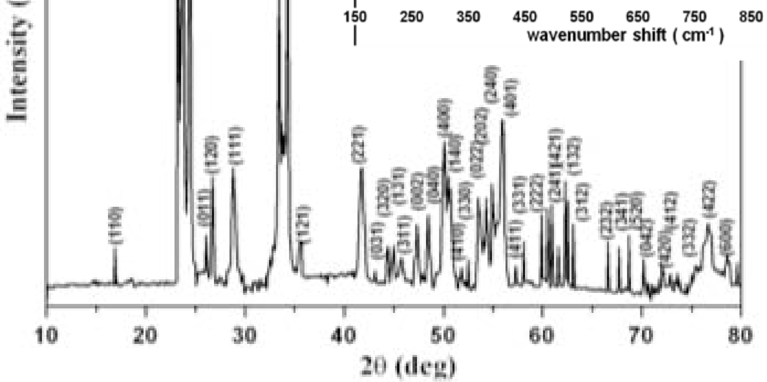
Pyrolysis of $(((C_4H_9)_4)N)_4W_{10}O_{32}$



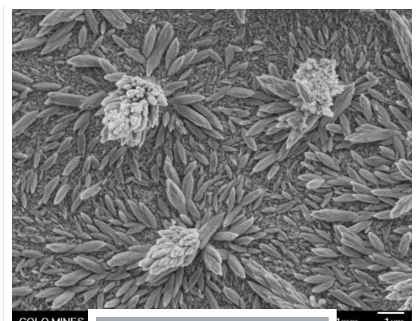


Nanorods

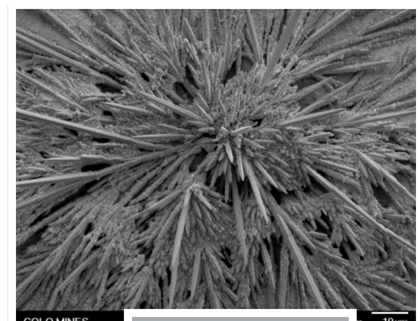




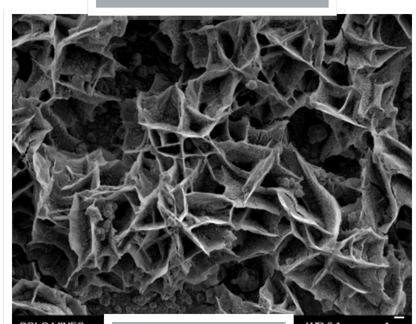
XRD pattern—as synthesized WO_3 nanorods.



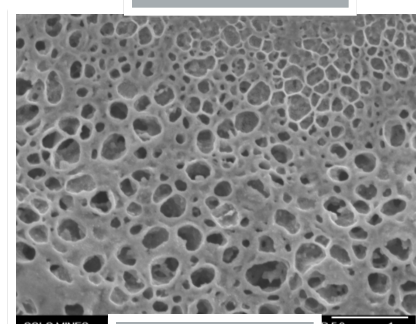
Spindles



Needles



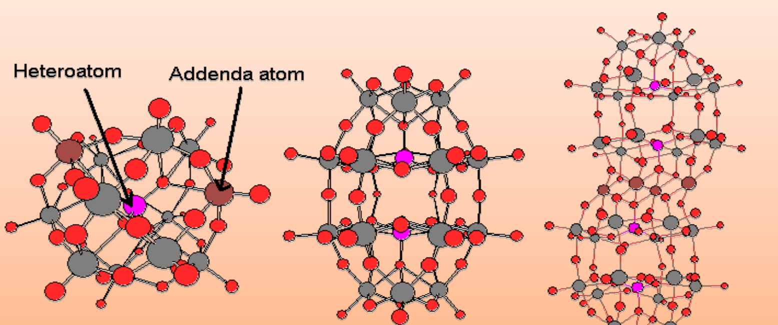
Plates



Porous

HPA Functionalization to C, Pt/C, WO_3 and Pt/WO_3

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

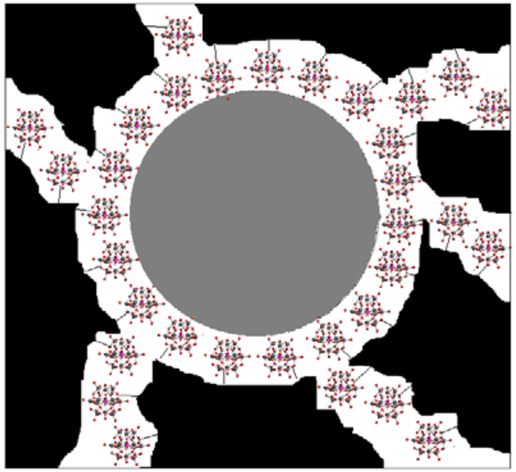


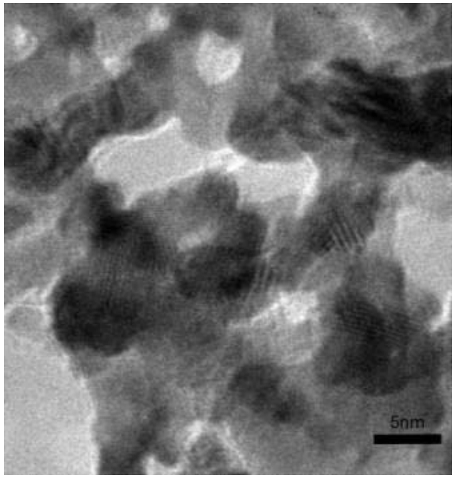
Keggin $PMo_{10}V_2O_{40}^{5-}$

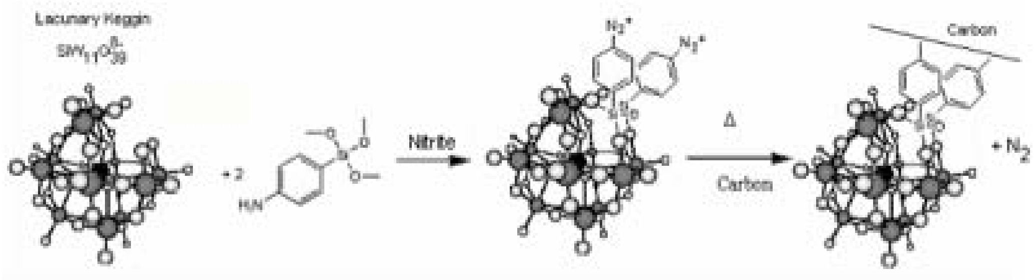
Wells-Dawson $P_2Mo_{18}O_{62}^{6-}$

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

Immobilized HPAs as Catalyst Supports

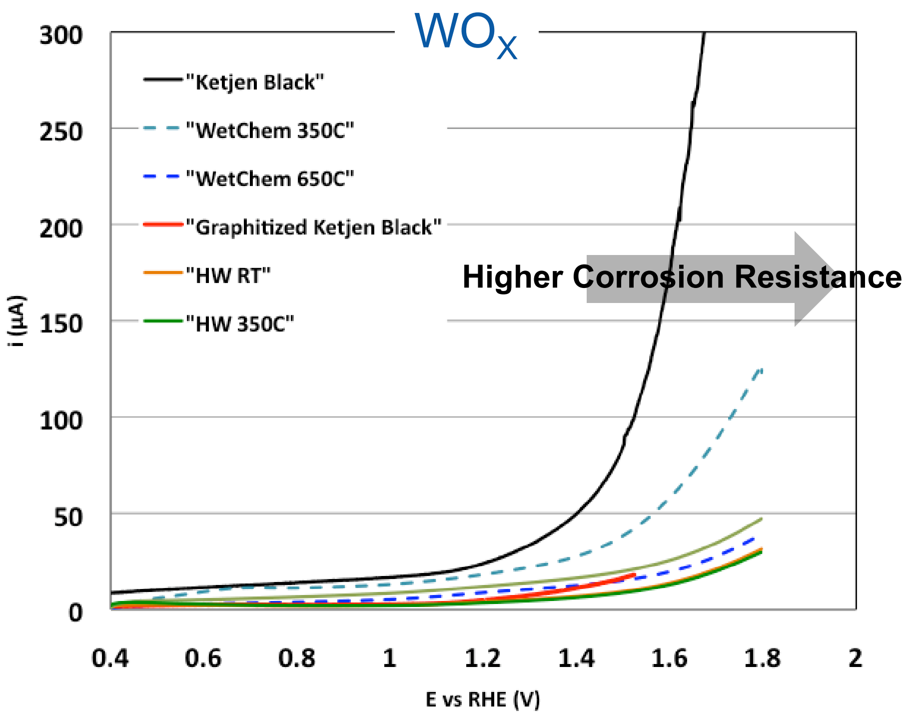


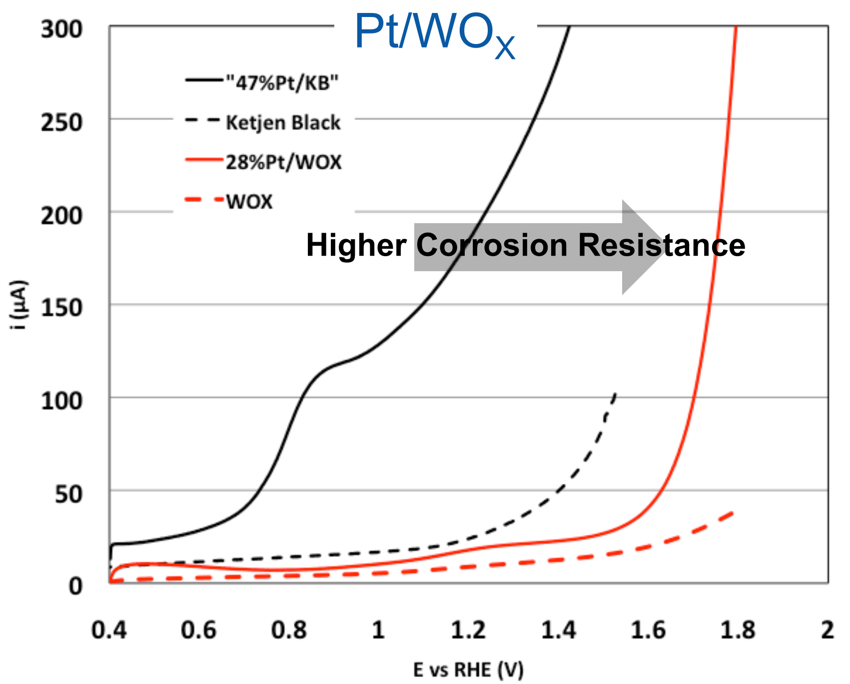


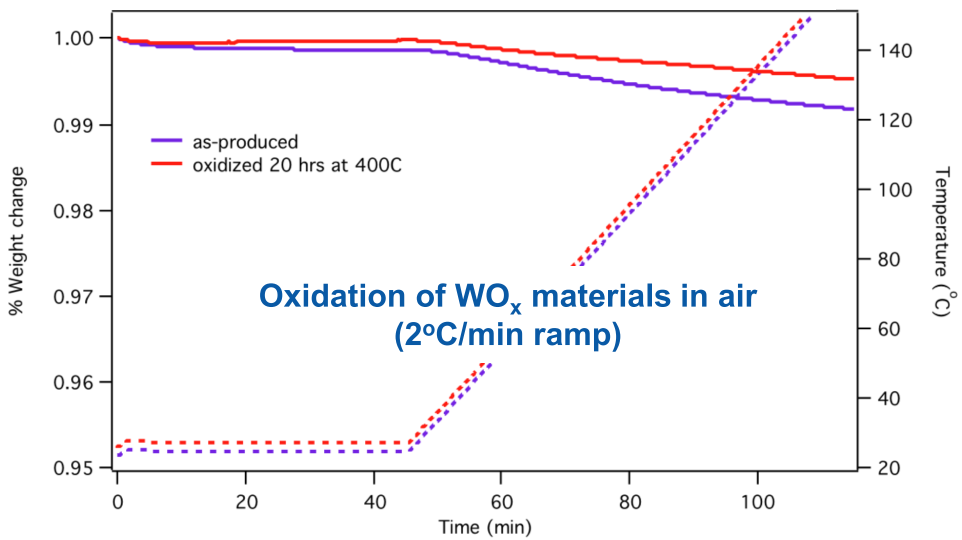


HPA functionalization of Carbon black confirmed by EDX spectra

Corrosion Resistance of WO_x and Pt/WO_x



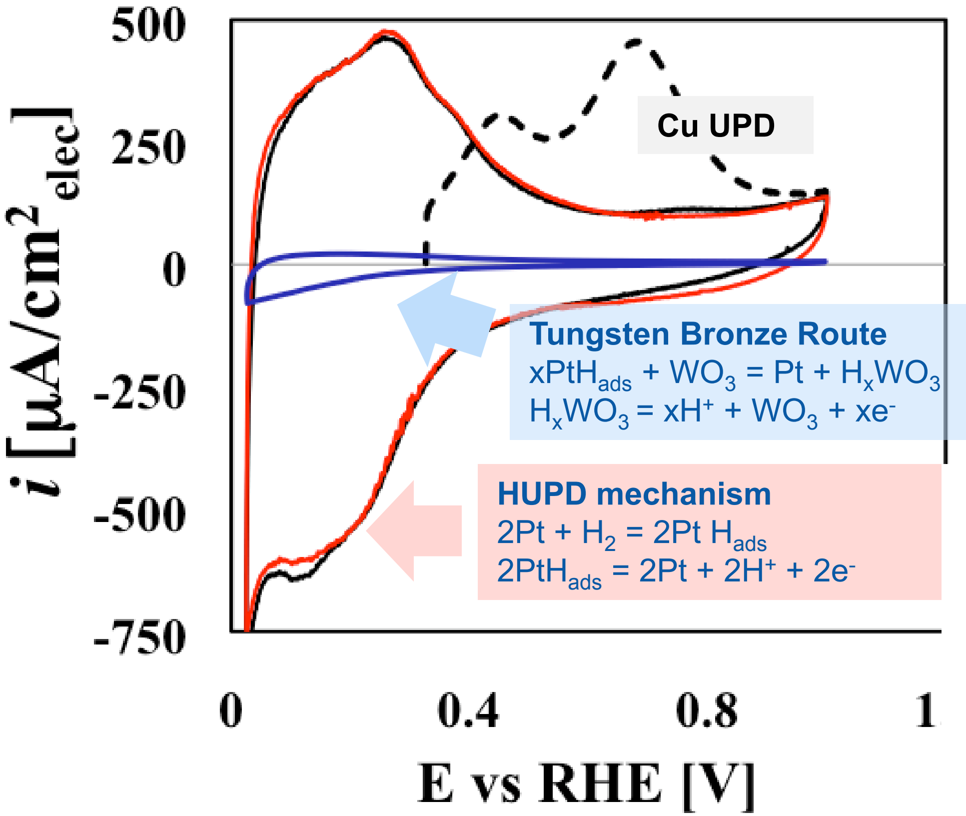




- **Corrosion Resistance WO_x > C**
- **Corrosion Resistance Pt/WO_x > Pt/C**

- 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 $H_{0.35}WO_3$)

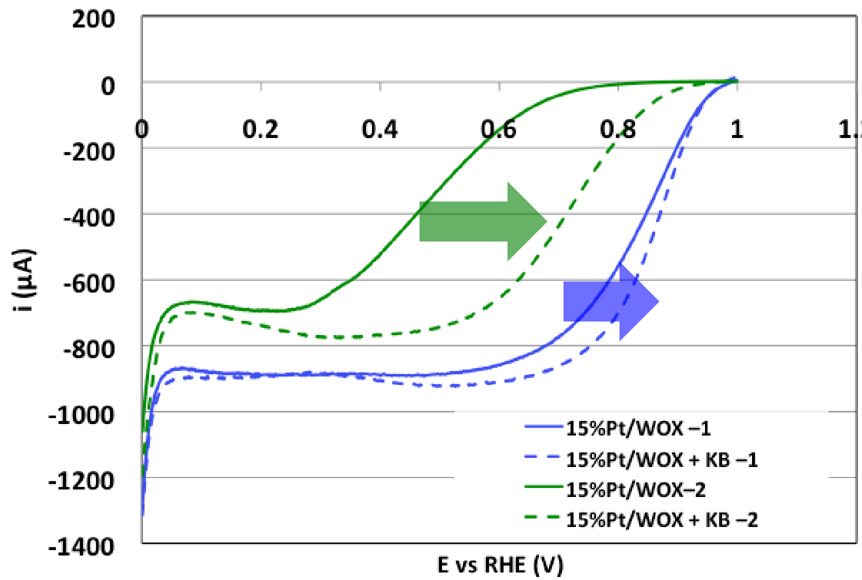
$WO_3 + xH^+ + xe^- = H_xWO_3$ $(0 < x < 1)$

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

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 WO_3 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/WO_3/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.

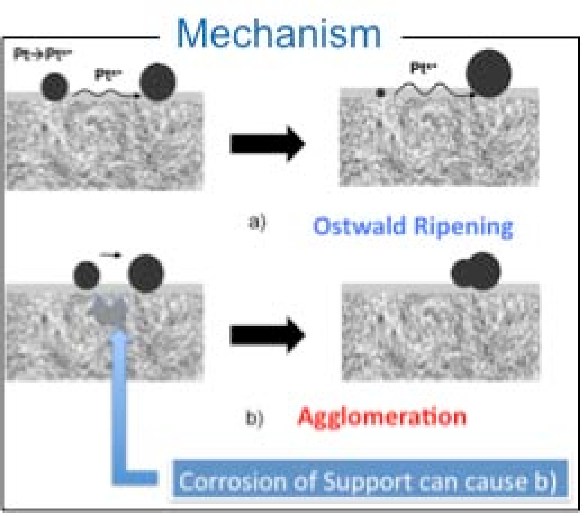
Technical Back-up Slides

Automotive Operations Imposed on Catalyst Support

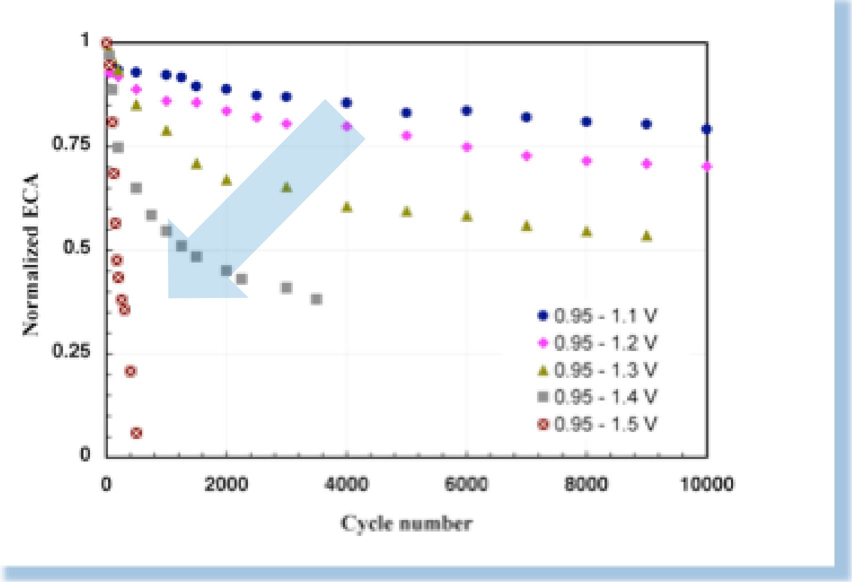
- **Startup/Shutdown**
  - Unmitigated
    - Anode : H_2-Air Front ➔ 0 – OCV (0.95 V)
    - Cathode: Air ➔ 0.95 V – 1.6 V
  - Mitigated (Stack shorting)
    - Anode : H_2-Air Front ➔ 0 – OCV (0.95 V)
    - Cathode : 0 V – OCV
- **Normal Operation**
  - OCV (0.95 V)
  - Load Cycling (0.60– 0.95 V)

Severe C corrosion

Milder C corrosion

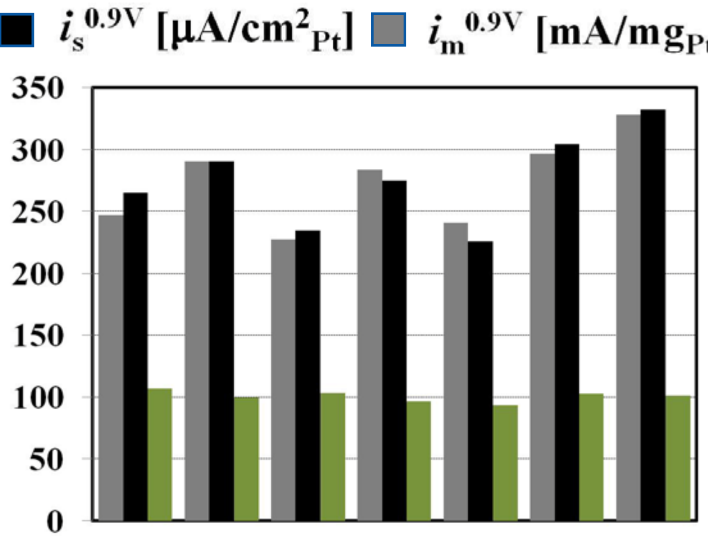


Effect of Upper Potential on loss of Electrochemical Surface Area



ECA & ORR Benchmarks for Baseline Pt/C Electrocatalysts

Rotating Disk Electrode Experiments



	$i_s^{0.9V}$ [mA/cm$^2_{Pt}$]	$i_m^{0.9V}$ [mA/mg$_{Pt}$]	ECA [m$^2_{Pt}$/g$_{Pt}$]	RF [cm$^2_{Pt}$/cm$^2_{elec}$]
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 $HClO_4$;*

***MEAs - 900 mV, 50 cm² subscale fuel cells, 15 min/point, 150 kPa (PO_2 = 100 kPa), 80°C, 100% RH, Nafion membrane.*

	Specific Activity [μA/cm$^2_{Pt}$]	Mass Activity [mA/mg$_{Pt}$]
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