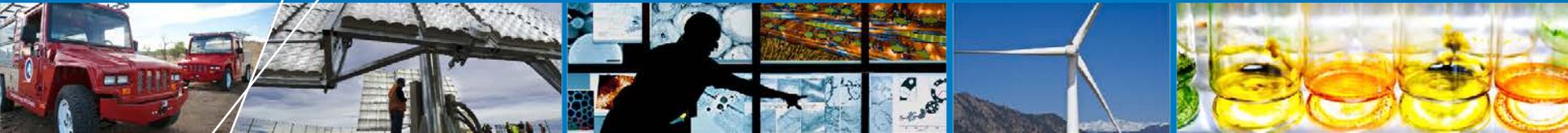


# $WO_3$ and HPA based systems for durable Pt catalysts in PEMFC cathodes



## 2013 DOE Hydrogen and Fuel Cells Program Review

John Turner

May 16<sup>th</sup>, 2013

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: 65%

## 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
- Funding received for FY12: \$975k
- Planned funding for FY13: \$816.6

## 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<sub>3</sub> and Heteropoly Acid (HPA) modification of carbon support to approach automotive PEMFC activity (**0.44 mA/mg<sub>Pt</sub>**) and durability targets (5000h/10y).

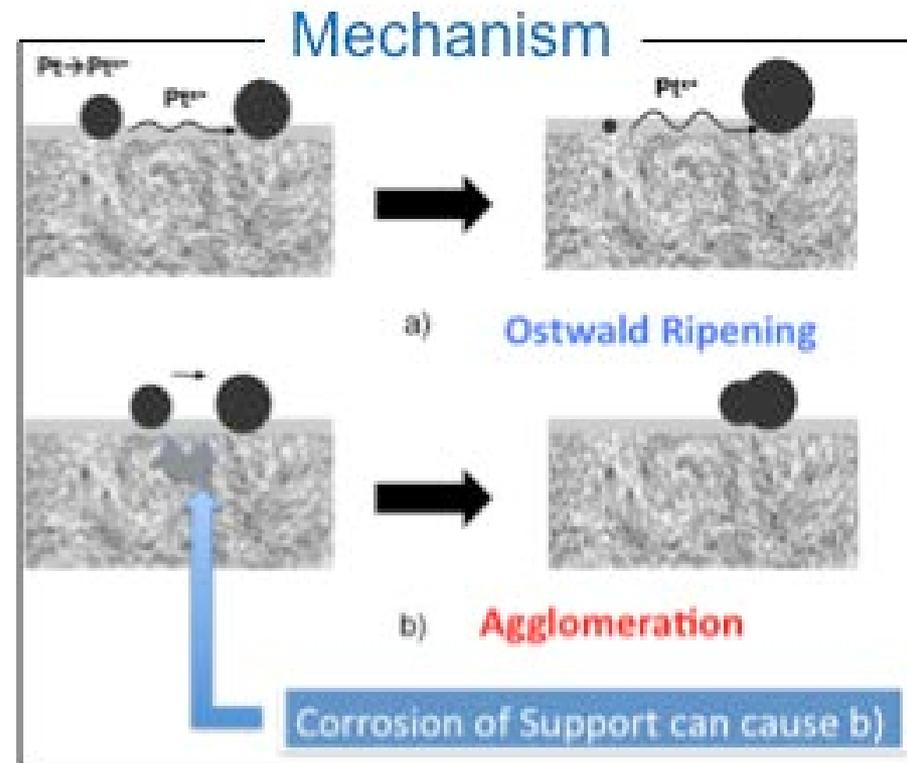
## Enhance Pt anchoring to support

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

## Lower support corrosion

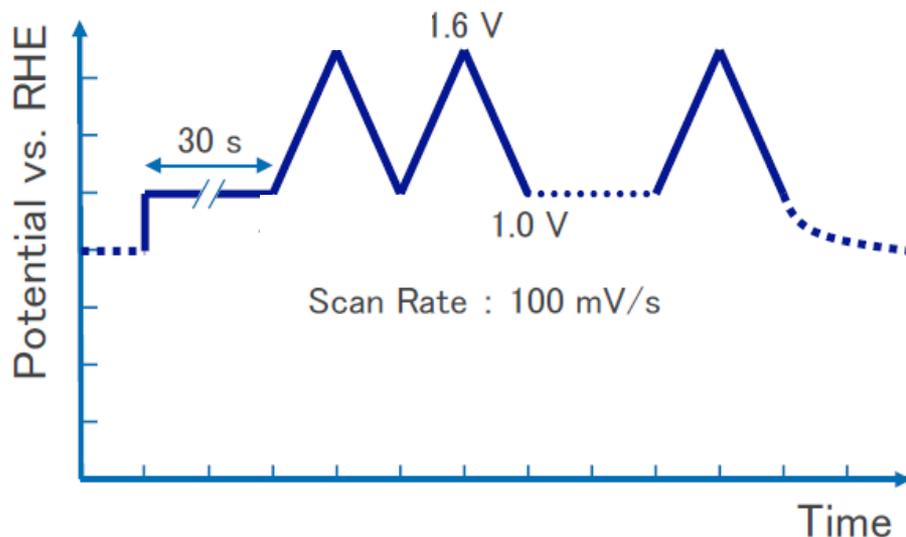
- Increased durability under automotive startup/shutdown operation.
- Suppress Pt agglomeration/electrode degradation

## Simplify and lower system cost



# Protocols for Electrocatalyst/Support Durability Evaluation

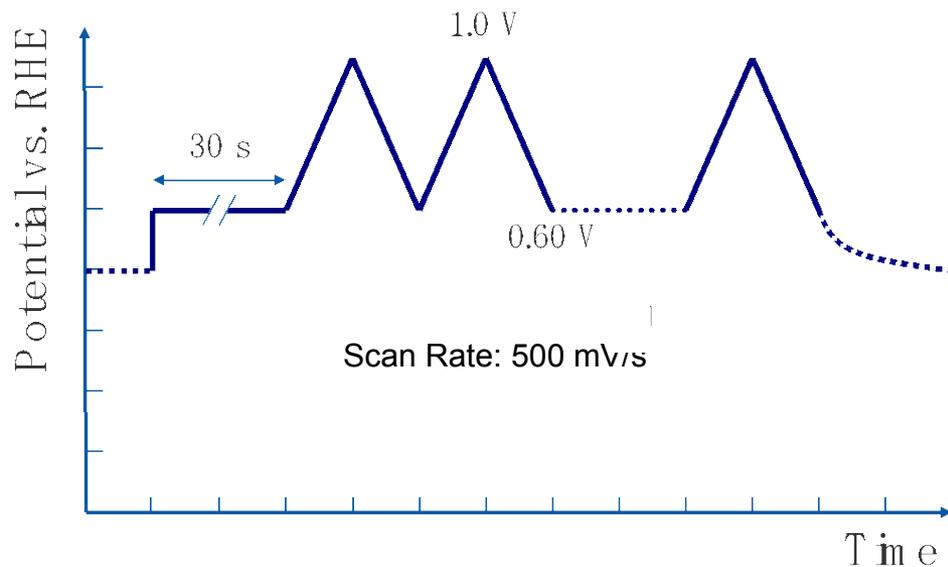
## 1.0–1.6 V Regime



### 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**

**Team for catalyst supports**

Shyam Kocha (NREL)—Lead

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

# Approach

Synthesize  $\text{WO}_3$

**NREL & CSM**

Hot wire  $\text{WO}_3$  to CU for Pt Atomic Layer Deposition (ALD)

Hot wire  $\text{WO}_3$  to CSM for HPA modification and Pt deposition

Characterize  $\text{WO}_3$  & Pt/ $\text{WO}_3$  for

- Conductivity
- Surface area
- TEM
- Wt %Pt

**CU – Steve George**

1. Prepare Pt nanoclusters on  $\text{WO}_3$
2. Analyze the structures formed using FTIR, XPS, SEM, TEM, Raman, etc.,
3. Measure Pt particle size, Brunauer-Emmett-Teller, etc.
4. Provide samples to NREL

**CSM – Andy Herring**

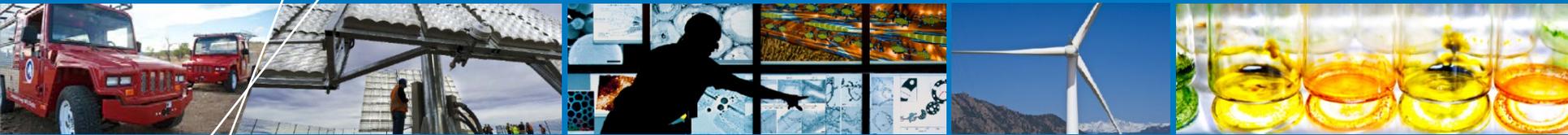
1. Synthesize HPA
2. Immobilize HPA carbon
3. Prepare Pt nano/C
4. Immobilize HPA to C
5. Prepare Pt nano/HPA-C
6. Immobilize/ Covalently bond HPA to  $\text{WO}_3$
7. Prepare Pt nano/HPA-  $\text{WO}_3$   
Prepare Pt nano/HPA-  $\text{WO}_3$  hybridized with HPA-C
8. Alternative  $\text{WO}_3$  synthesis

**NREL**

Electrochemical Characterization

# Official Milestones for FY 13

- 5.7.1 - Scale-up catalyst synthesis processes to generate >1 g of >20 wt% Pt on WO<sub>x</sub> for MEA evaluation  
**Completed 12/12**
- 5.7.2 - Select synthesis route (ALD Pt on WO<sub>x</sub>, Colloid Pt/WO<sub>x</sub>, Direct reduction of Pt on WO<sub>x</sub>, Colloidal Pt/HPA/C or Pt/other alternative non-carbon support) based on highest mass activity for further MEA preparation and evaluations **3/13**
- 5.7.3 - Prepare and evaluate MEAs based on selected and scaled-up Pt/support synthesis route and demonstrate cyclic durability of Pt/alt support to be 2x greater than that of baseline Pt/C in MEAs of subscale fuel cells **9/13**



# Synthesis

# Pt/HPA-C Preparation

- Dispersion of HPA-C material in water via 20 min ultrasonication
- Addition of Pt colloid followed by ultrasonication for an additional 20 min
- Catalyst separation via Buchner filtration
- Drying at 200°C for 2 h

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

**Table I. Evaluation of lattice strain using Pt peak position measured by XRD.**

Loading SiW <sub>11</sub> (wt% of support)	Pt(111) $\beta_{max}$ (°2 $\theta$ )	d-spacing (Angstroms)	$\delta_{Pt}$ – XRD (nm)	$i_m$ (mA/mg <sub>Pt</sub> )
0	39.62	2.2750	4.4	316
3.2	39.55	2.2784	3.9	373
7.1	39.67	2.2717	3.4	334
15.9	39.64	2.2735	3.8	312

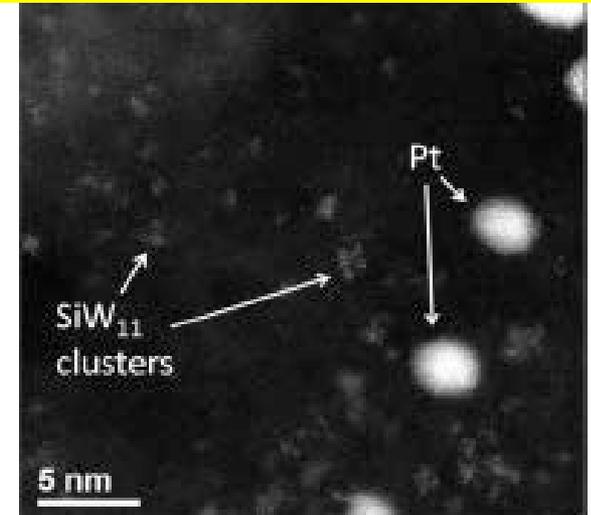
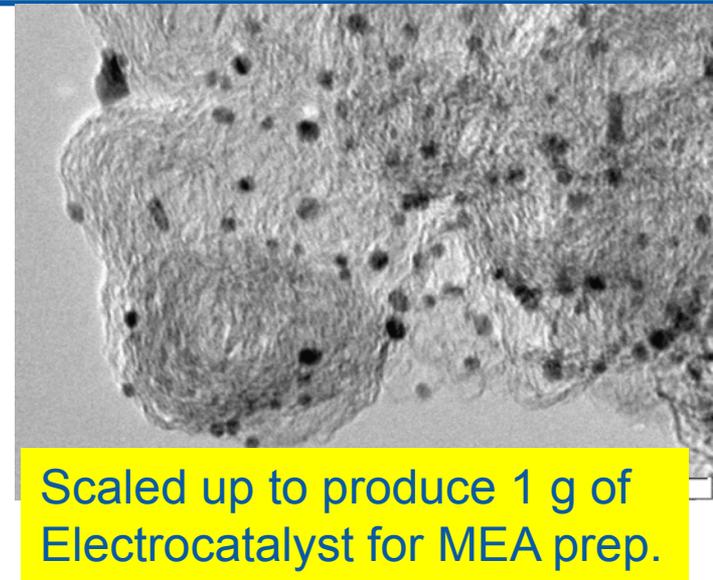
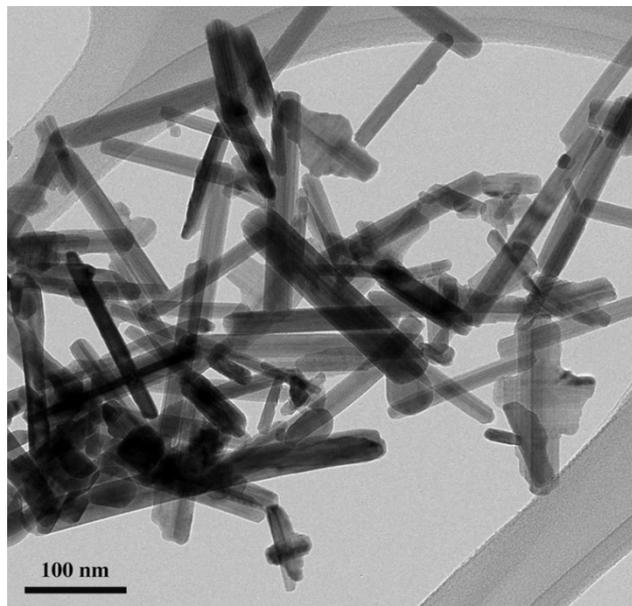


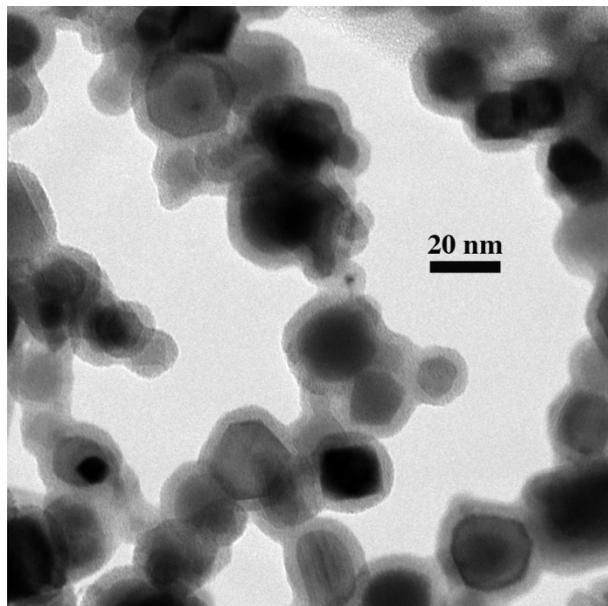
Figure 3: Z-contrast STEM image of Pt/SiW<sub>11</sub>-C showing spatial distribution of Pt (bright white spots ~3-5nm) and SiW<sub>11</sub> (~1nm dull gray spots)

# HWCVD Production of Tungsten Oxide Nanostructures

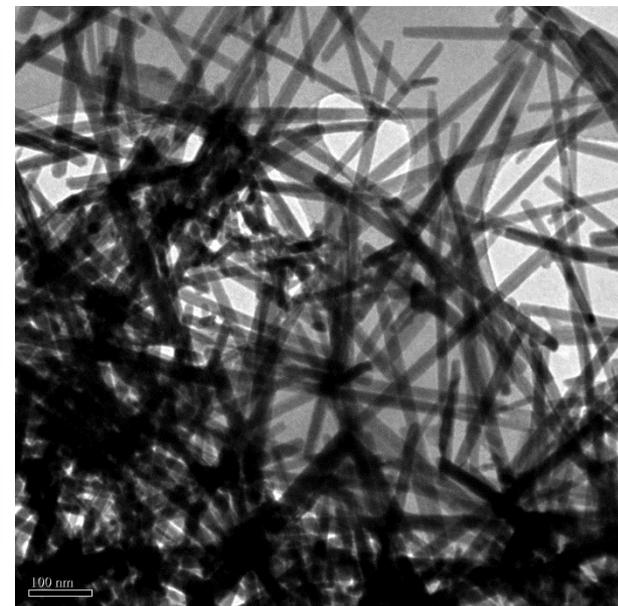
Synthesis at 150 Torr 4% O<sub>2</sub> in Ar, filament temperature ~ 2000°C



300°C



30°C

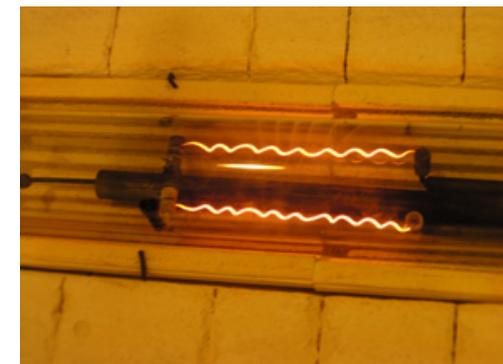


30°C

4 sequential depositions

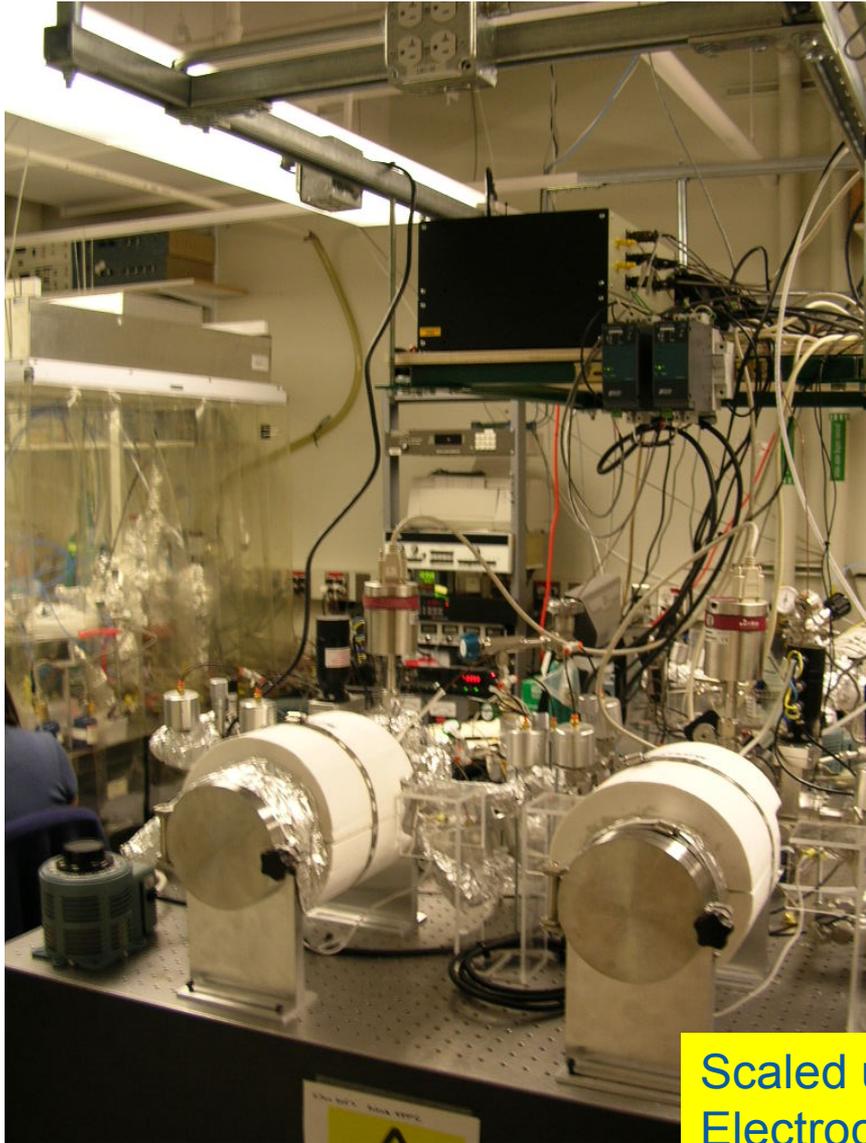
## Dramatic change in particle morphology

- 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.

# Pt ALD on $\text{WO}_3$ - Scaling with Dual Rotary Reactor



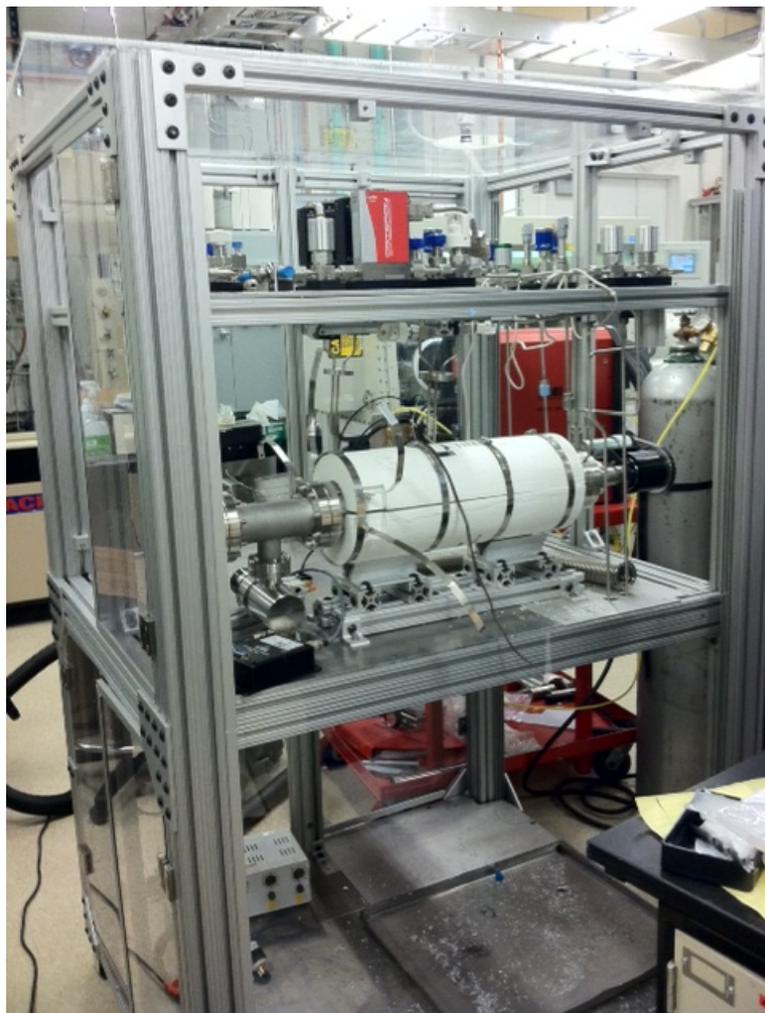
Dual rotary reactor demonstrates “proof of concept” for uniform Pt particle growth on  $\text{WO}_3$  nanorods at large scale.

- Computer controlled spinning enables uniform deposition.
- This system can hold a volume of  $60 \text{ cm}^3$ .
- Based on the powder density of  $\text{WO}_3$ , This corresponds to  $\sim 420 \text{ g / deposition}$ .

Scaled up to produce 1 g of Electrocatalyst for MEA prep.



# New NREL Rotary ALD system for uniform scalable Pt deposition on $\text{WO}_x$ Powders



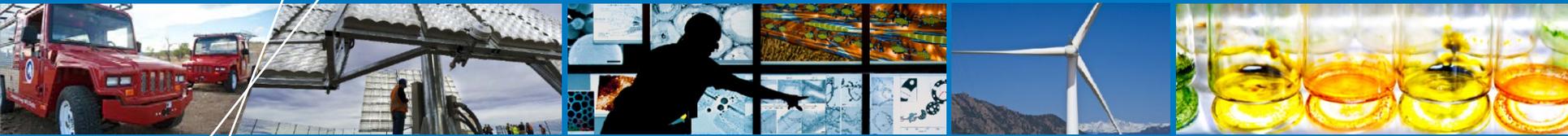
Able to coat powders or flat surfaces

Equipped for two heated and two room temperature precursors

Reactor volume  $\sim 100 \text{ cm}^3$

Produced highest mass activity (85mA/mg Pt) so far at 50 wt% Pt/ $\text{WO}_x$ .

Funded by NREL LDRD

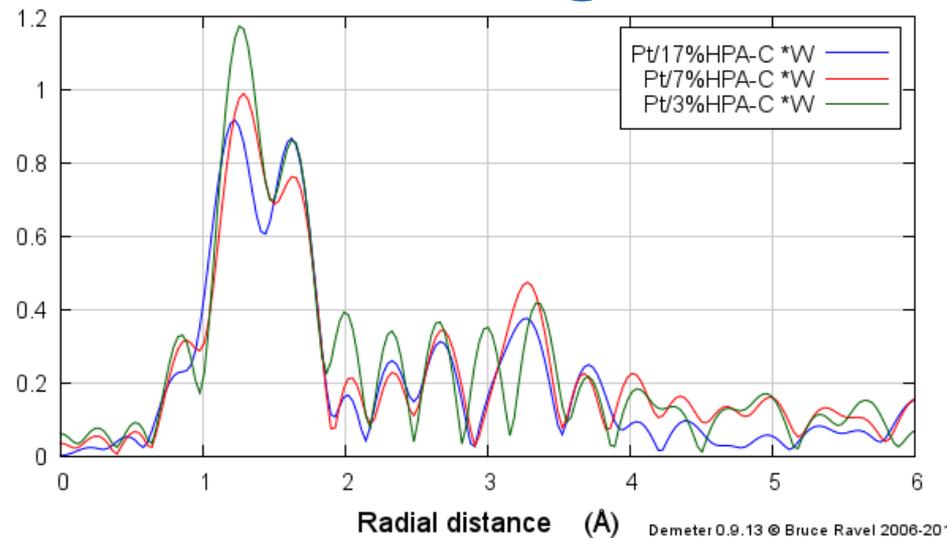
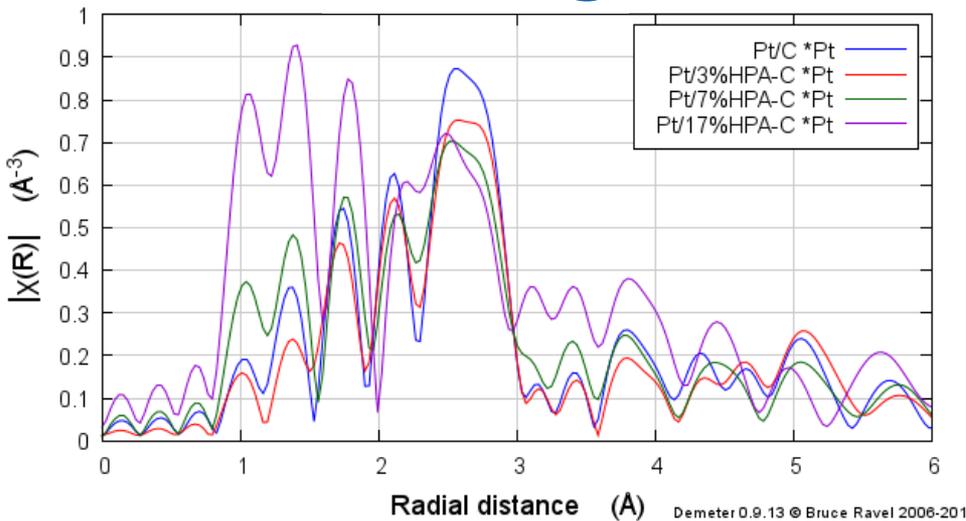


# Characterization

# Pt/HPA-C EXAFS

## Pt Edge

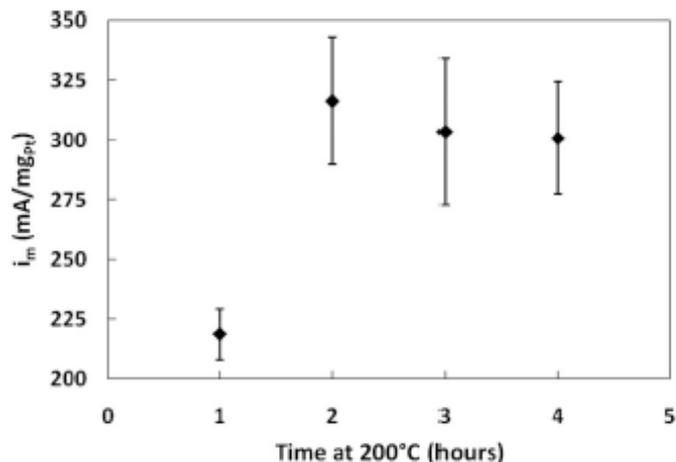
## W Edge



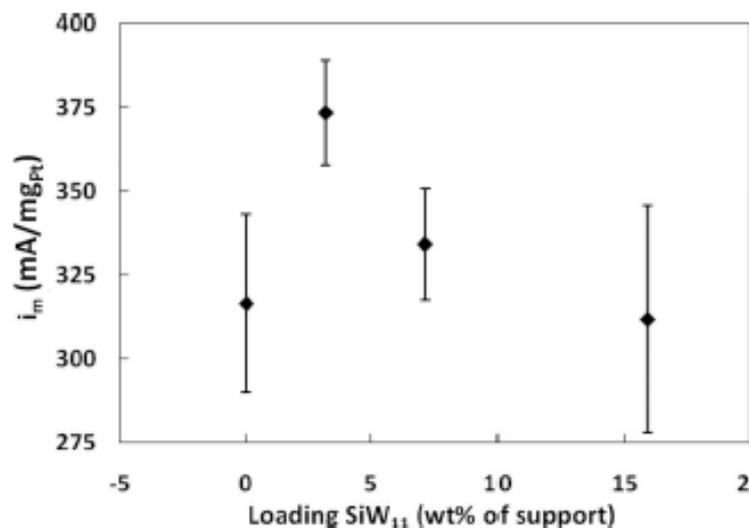
The strong effect on the Pt edge with increasing HPA loading implies that Pt is preferentially binding at the HPA locations. In contrast, there is very little change in the W edge implying that the Pt-W interaction remains approximately unchanged as HPA loading is increased.

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.

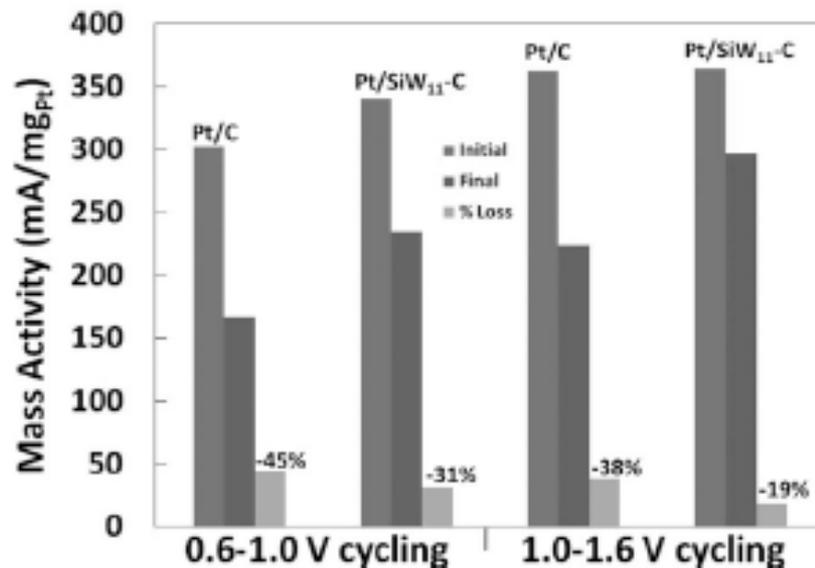
# Pt/C-HPA: Results Summary



**Figure 1.** ORR mass activity measured at 900 mV of Pt/C catalysts as a function of post-synthesis heat-treatment time, measured in 0.1 M HClO<sub>4</sub>.



**Figure 5.** ORR mass activity measured at 900 mV of Pt/SiW<sub>11</sub>-C catalysts as a function of SiW<sub>11</sub> loading, measured in 0.1 M HClO<sub>4</sub>.



**Figure 7.** ORR mass activity measured at 900 mV of Pt/C and Pt/SiW<sub>11</sub>-C catalysts before and after 0.6–1.0 V cycling (left) and 1.0–1.6 V cycling (right).



the society for solid-state  
and electrochemical  
science and technology

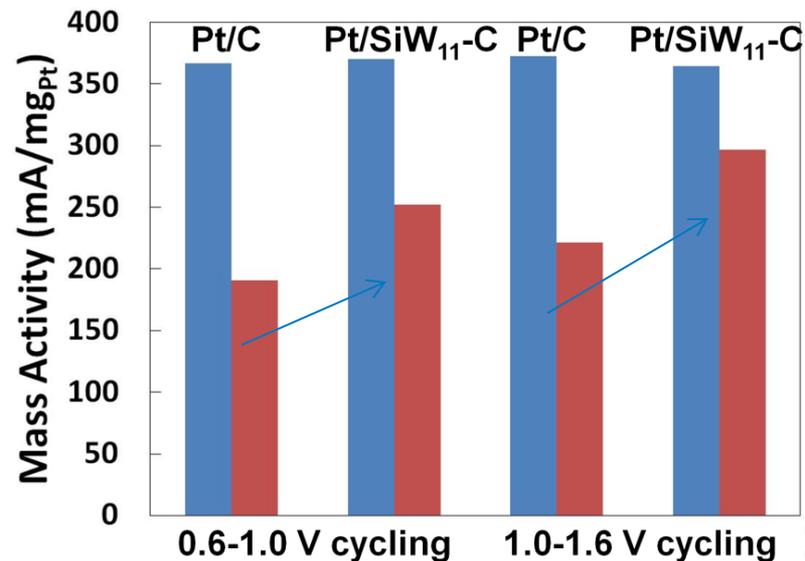
Journal of The Electrochemical Society

## Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction

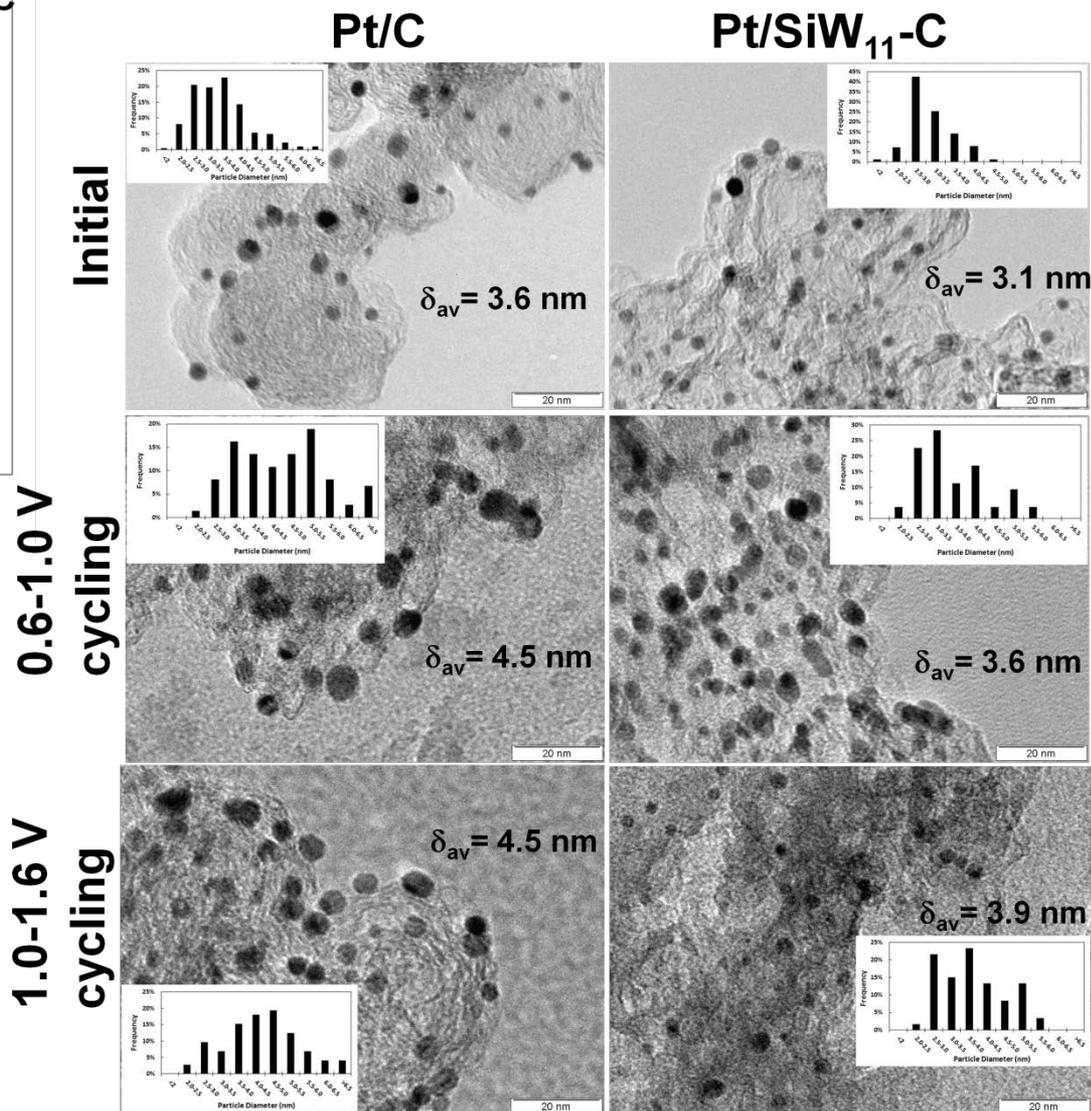
K. Sykes Mason, Kenneth C. Neyerlin, Mei-Chen Kuo, Kiersten C. Horning, Karren L. More and Andrew M. Herring

*J. Electrochem. Soc.* 2012, Volume 159, Issue 12, Pages F871-F879.  
doi: 10.1149/2.068212jes

# Pt/HPA-C Durability



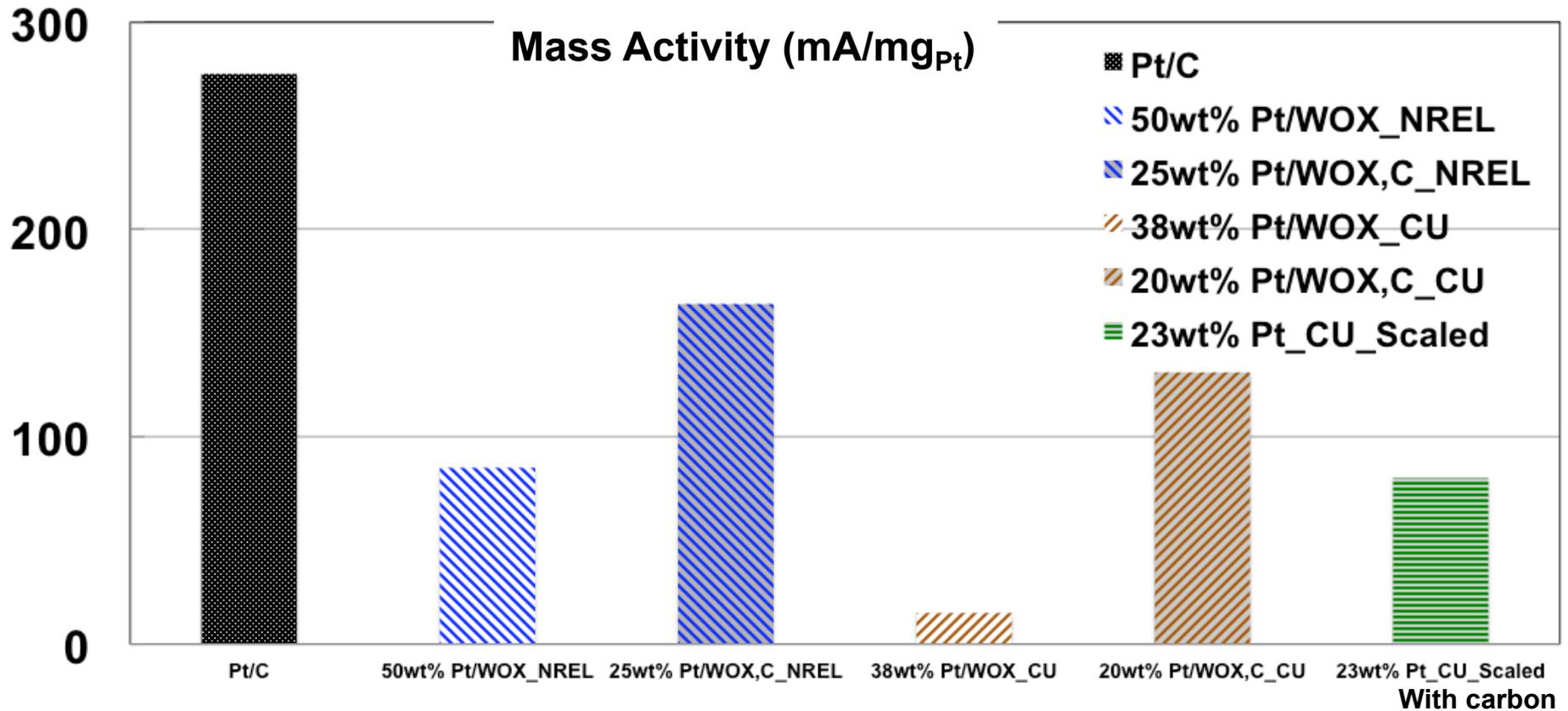
The 0.6-1.0 V cycling (30,000 cycles, 500 mV/s) was used to evaluate Pt dissolution, while 1.0-1.6 V cycling (6,000 cycles, 100 mV/s) evaluated support corrosion. HPA loading was chosen such that initial activity was near equal to Pt/C. In both cases, HPA helped maintain catalyst activity by slowing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



\*All scale bars are 20 nm.

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

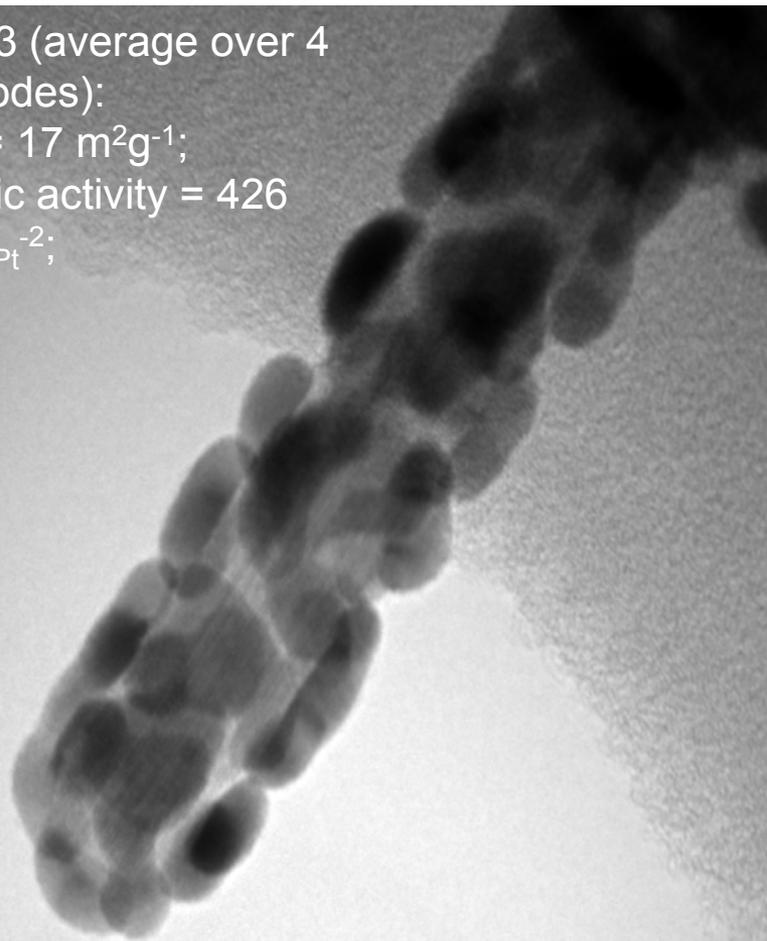
# Mass Activity of Pt/C vs. ALD Pt/WO<sub>x</sub>



# KEH93 and VRA128 TEM Comparison

KEH93, 47% Pt

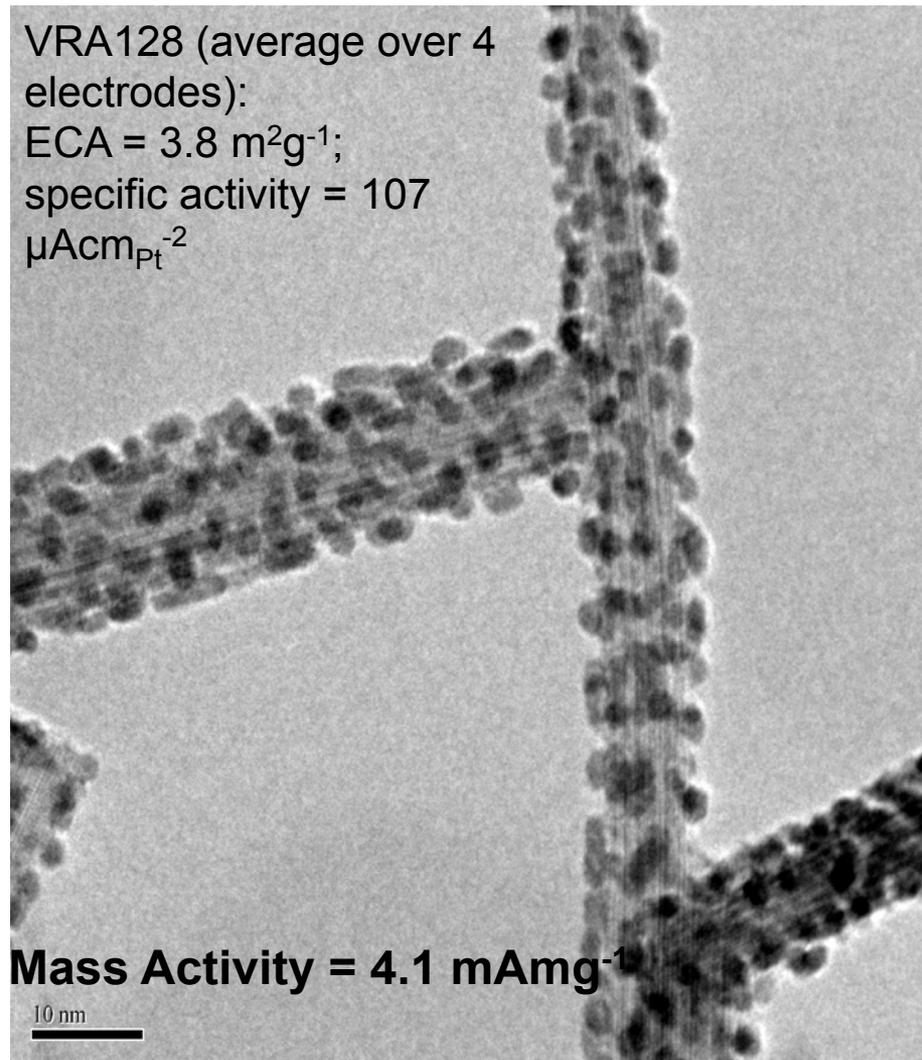
KEH93 (average over 4 electrodes):  
ECA =  $17 \text{ m}^2\text{g}^{-1}$ ;  
specific activity =  $426 \mu\text{Acm}_{\text{Pt}}^{-2}$ ;



**Mass Activity =  $75 \text{ mA mg}^{-1}$**

VRA128, 54% Pt

VRA128 (average over 4 electrodes):  
ECA =  $3.8 \text{ m}^2\text{g}^{-1}$ ;  
specific activity =  $107 \mu\text{Acm}_{\text{Pt}}^{-2}$

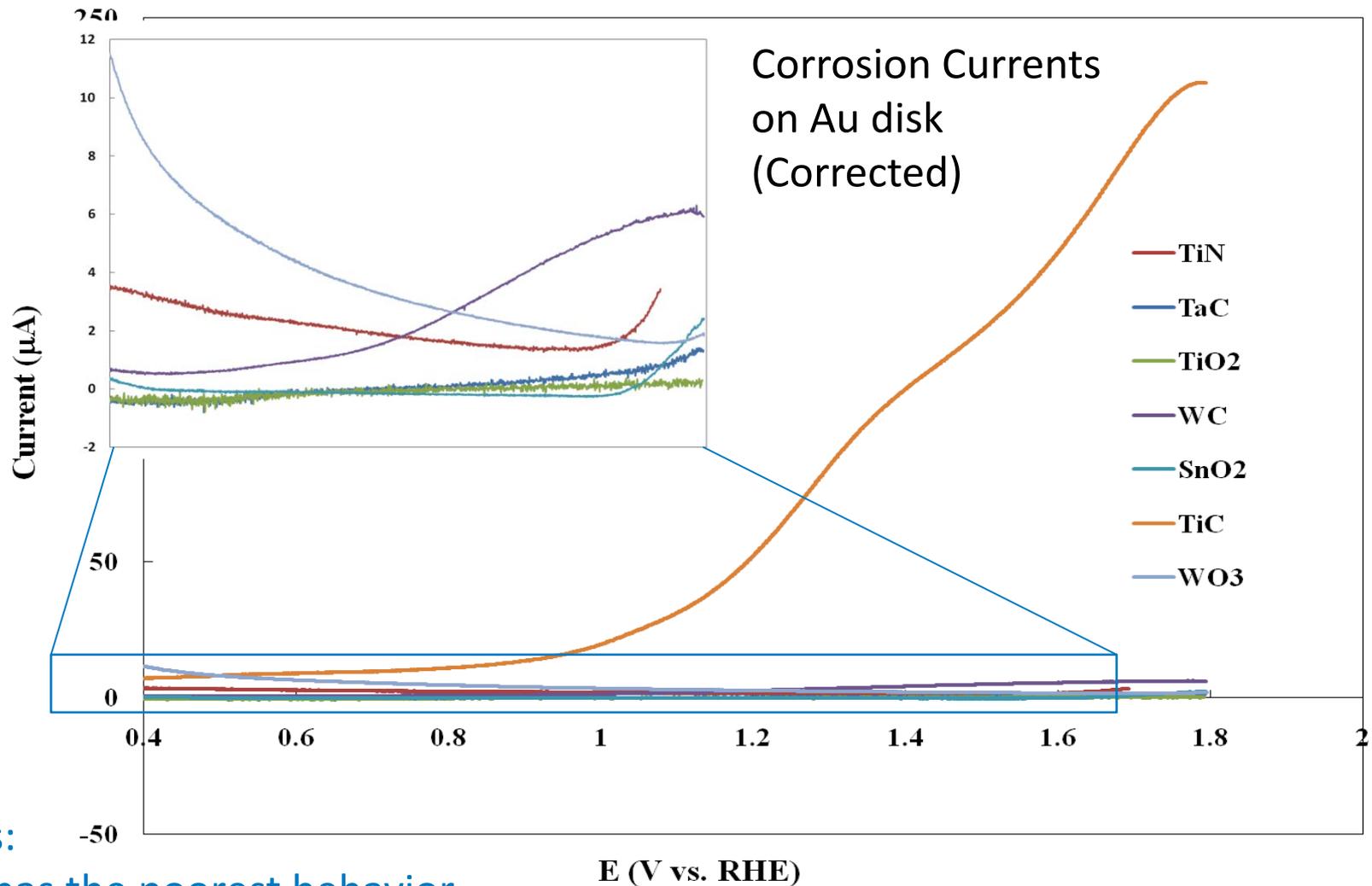


**Mass Activity =  $4.1 \text{ mA mg}^{-1}$**

# Alternative Supports

- **Gram quantities available**
- **Conductivity measurements of powders**
  - MX have higher conductivity than oxides
- **Relative corrosion currents measured in RDE**
  - MX have reasonable corrosion resistance
- **Can also be used as a metal matrix in place of carbon black support to provide conductivity**
- **Will deposit Pt nanoparticles on these materials using wet chemistry**
- **Will evaluate activity and ECA in RDE to determine if they are suitable for tests in subscale cells**

# Alternative Supports



## Results:

- TiC has the poorest behavior.
- WC is also less than ideal, and TiN is questionable.
- TiO<sub>2</sub>, TaC, and WO<sub>3</sub> appear to be the best for corrosion resistance.

# Conclusions

## 1. ALD Pt/WO<sub>x</sub> + C system

1. Scaled up to 1g quantities of ~ high wt% Pt/WOX
2. Does not meet activity benchmark of Pt/C in RDE
3. CCMS will not be prepared
4. Will not be evaluated in subscale cells

## 2. Colloidal Pt/C—HPA

1. Scaled up to 1g quantities of ~ 17 wt% Pt/C-HPA
2. Meets activity benchmark of Pt/C in RDE
3. CCMS will be prepared
4. Will be evaluated in subscale cells

## 1. Pt black + WO<sub>x</sub> + C system

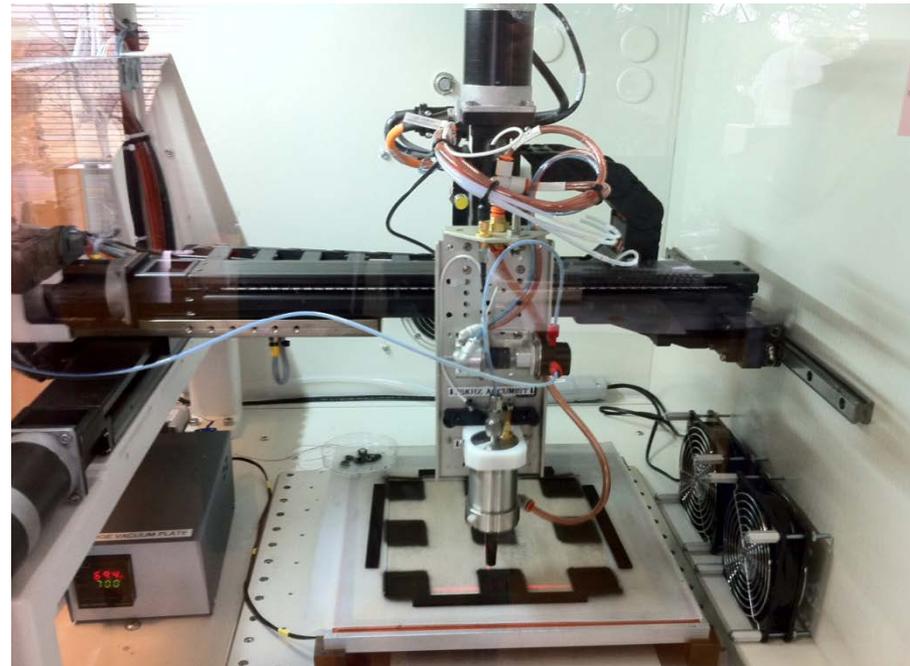
1. Intended to understand system
2. Does not meet activity benchmark of Pt/C in RDE
3. CCMS will not be prepared
4. Will not be evaluated in subscale cells

## 2. Pt/SnO<sub>x</sub> + C system

1. Gram quantities of ~ 28 wt% Pt/SnO<sub>2</sub>-GCNF available
2. Meets activity benchmark of Pt/C in RDE
3. CCMS prepared —1<sup>st</sup> iteration
4. Evaluated in subscale cells—1<sup>st</sup> iteration

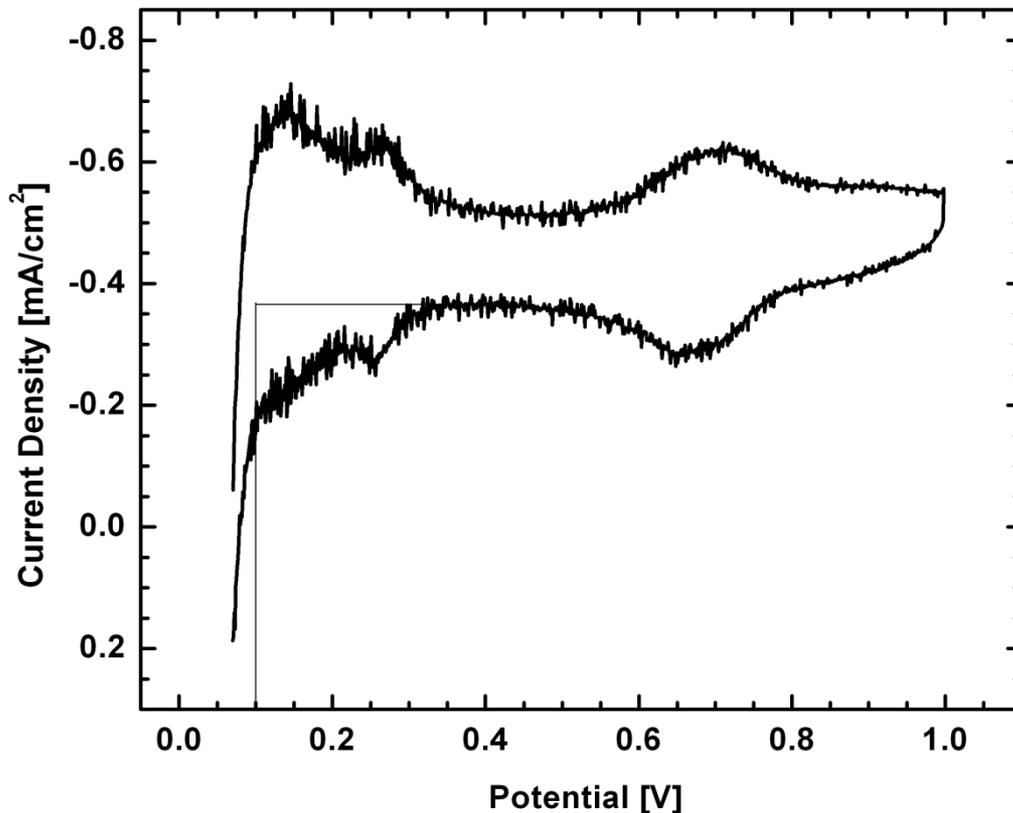
Activity benchmark of Pt/C (w Nafion®) in RDE studies in 0.1 M perchloric acid, at 25°C and 100 kPa O<sub>2</sub> is ~275 mA/mg<sub>Pt</sub>

# MEA Preparation



CCM preparation by spray-coating of electrocatalyst ink directly onto the membrane was carried out. A total of 9 Pt/C anodes were prepared and 3 Pt/SnO<sub>2</sub> cathodes were deposited. One CCM is currently under test.

# Subscale Fuel Cell Testing Pt/SnO<sub>2</sub>/C



Loading = 0.06 mg/cm<sup>2</sup>

ECA = 5 m<sup>2</sup>/g<sub>Pt</sub>

Initial MEAs exhibited double the resistance as Pt/C MEAs.

ECAs were low and actual cathode loading was ~1/10 the targeted amount (0.2 mg<sub>Pt</sub>/cm<sup>2</sup>) based on XRF measurements.

Currently, diagnostics are being conducted to resolve these issues.

# Accomplishments and Progress

- $\text{WO}_x$  preparation was scaled up to gram levels for ALD platinum deposition.
- CU-Boulder deposited ALD Pt/ $\text{WO}_x$  scaled up to g quantity.
- Mass activity of scaled up ALD Pt/ $\text{WO}_x$  was low.
- Pt colloids were prepared (CSM) that were subsequently deposited on HPA functionalized C. This was scaled up to generate 1 g quantity.
- Pt/ $\text{SnO}_2$  obtained from a commercial catalyst supplier (TKK). These materials are available in gram quantities.
- Pt/ $\text{SnO}_2$  was evaluated in RDE with and without Nafion<sup>®</sup>.
- Pt/ $\text{SnO}_2$  CCMs were prepared and subscale testing is underway.
- Alternative support materials were studied for conductivity and corrosion resistance.
- Subscale test run comparing Pt/C MEA to a Pt/HPA-C MEA.

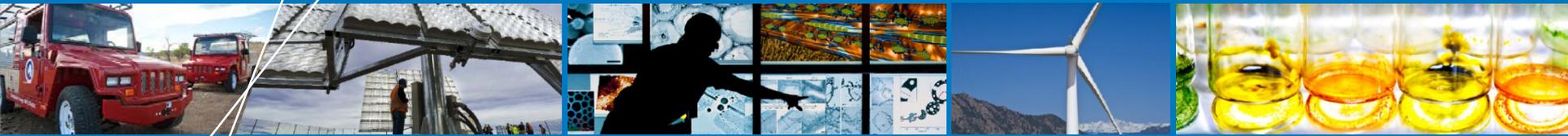
# Future work

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- **Finish up Pt/SnO<sub>2</sub> in subscale cell – NREL**
- **Test Pt/C-HPA in subscale cell – NREL/CSM**
- **Test Pt/C-HPA with other forms of graphitized carbon supports – NREL/CSM**
- **Wet chemistry Pt deposition of alternative support carbides, etc and evaluation in RDE – NREL**

# Collaborations

- **CU Boulder: subcontractor – University**
  - ALD growth of Pt on  $WO_x$
- **CSM: subcontractor – University**
  - 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**



# Supplemental Slides

# MEA and RDE Data for HPA-C

RDE data

Catalyst	ECA (m <sup>2</sup> /g)	Specific Activity (μA/cm <sup>2</sup> Pt)	Mass Activity (mA/mg Pt)
Pt/C	45	710	310
Pt/3%HPA-C	61	610	370
Pt/HSC (TKK)	100	270	270

Activity measured at 0.9 V vs RHE using linear sweep voltammetry

MEA data\* – 5 cm<sup>2</sup> cell, Pt/HSC anode, H<sub>2</sub>/O<sub>2</sub>

Catalyst	Cathode loading (mg Pt/cm <sup>2</sup> )	ECA (m <sup>2</sup> /g)	Specific Activity (μA/cm <sup>2</sup> Pt)	Mass Activity (mA/mg Pt)
Pt/C	0.192	55	210	120
Pt/3%HPA-C	0.136***	62	220	140

Activity measured at 0.9 V vs anode reference using potential hold method\*\*

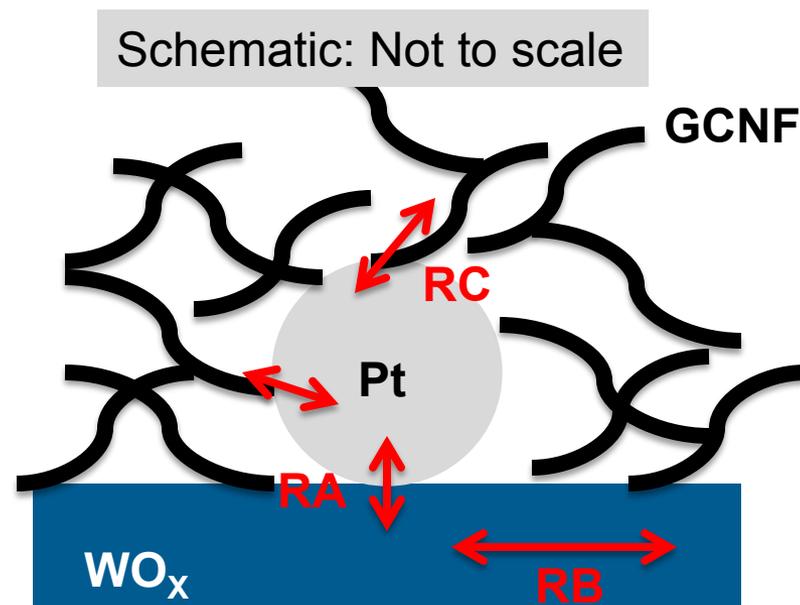
\*has only been tested once, no optimization (loading, ionomer:C ratio, etc.)

\*\*average of last 5 minutes of a 15 minute hold

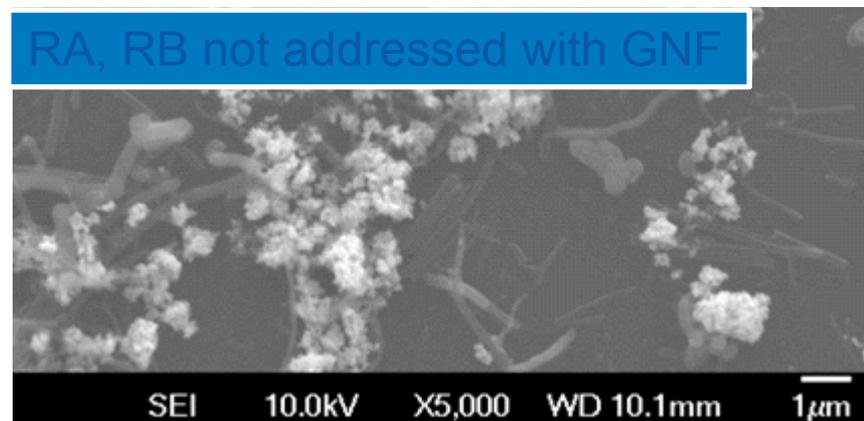
\*\*\*measured by weight, XRF gave spurious results

# Challenges: Electronic Conductivity

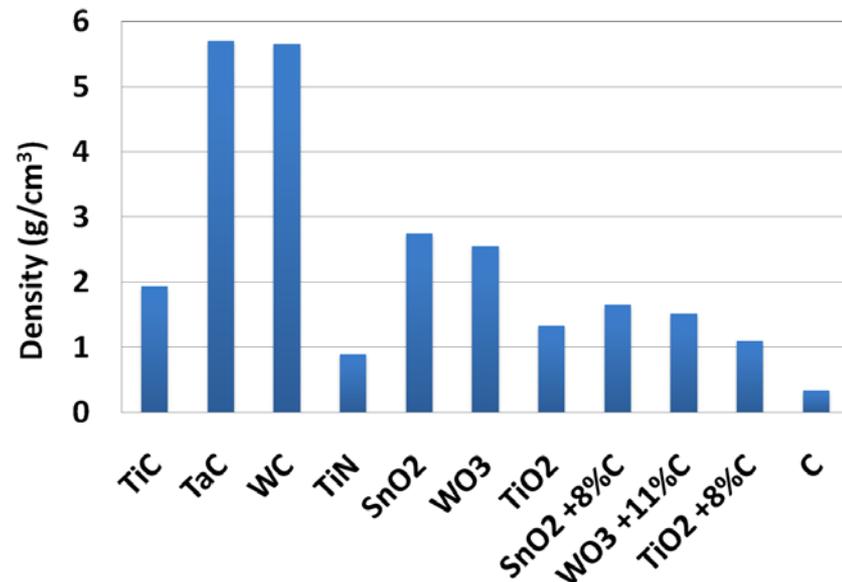
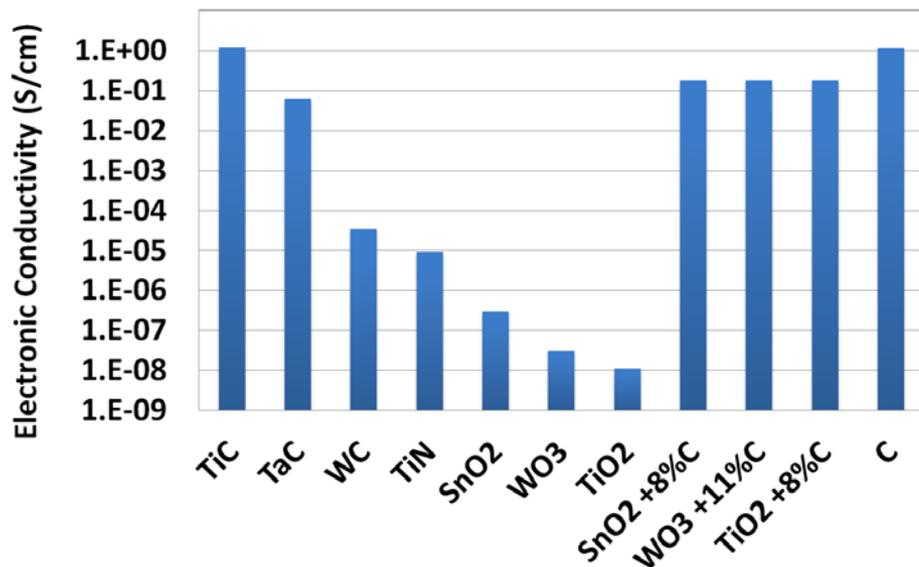
- Oxides supports have low electronic conductivity
- Addition of carbon matrix enhances the overall conductivity
- 3 electron pathways
  - Contact point between Pt and support:  $RA$
  - Electronic conductivity through the support:  $RB$
  - Electronic conductivity through the added carbon matrix:  $RC$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



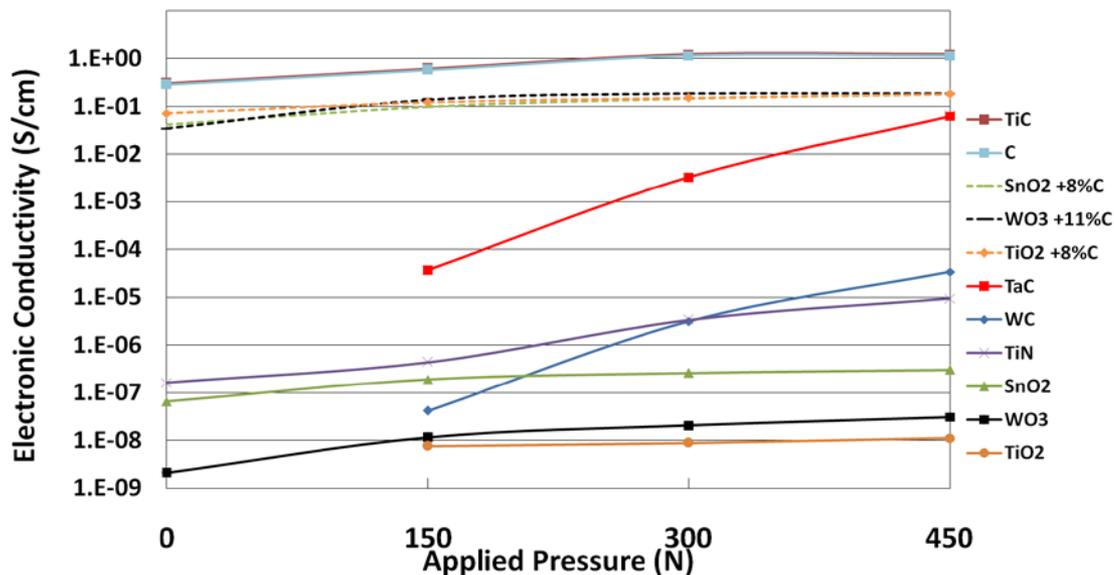
Actual Micrograph



# Conductivity of Alternative Supports

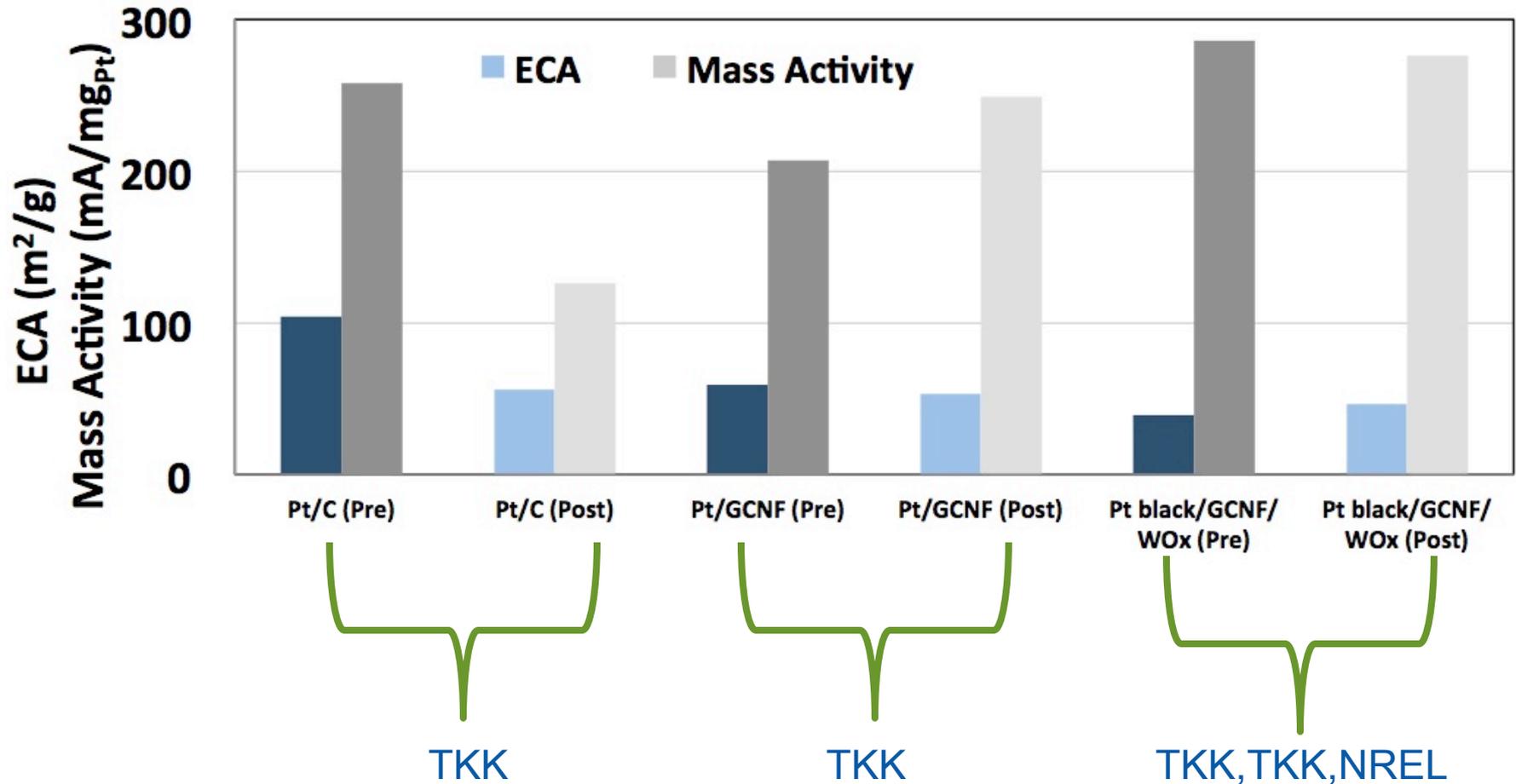


Measured at an applied pressure of 450 N.



# Durability (Pt black + GCNF+ WO<sub>x</sub>) System

NREL 1.0V-1.6V protocol



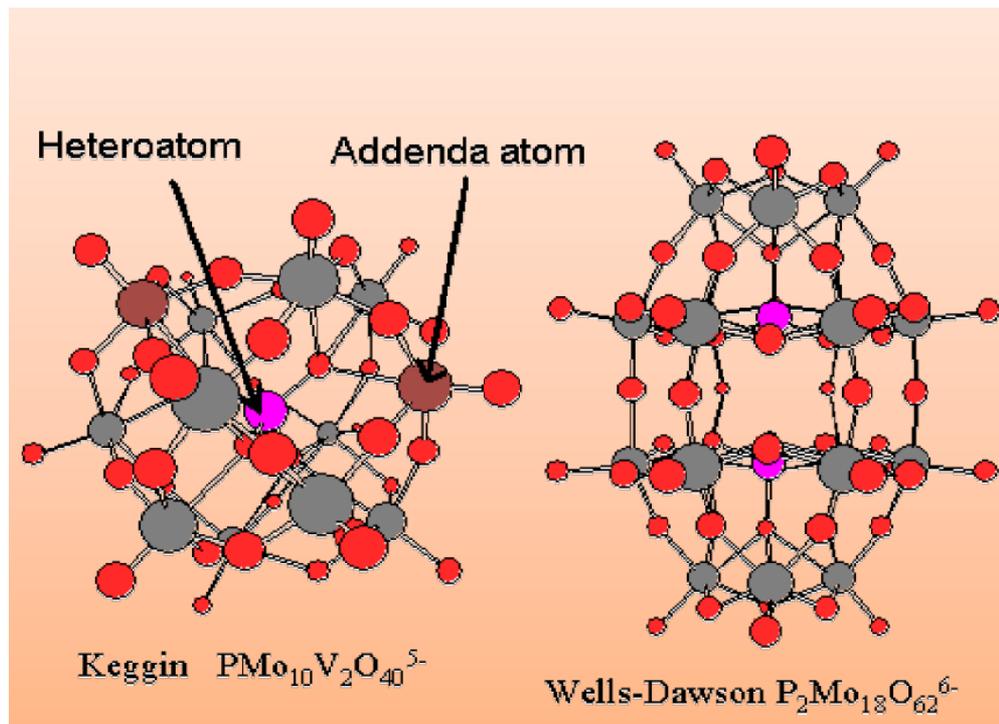
# HPA Background

- **Benefits**

- Acts like 1 nm spheres of  $\text{WO}_x$
- 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.