# WO$_3$ and HPA based systems for durable Pt catalysts in PEMFC cathodes
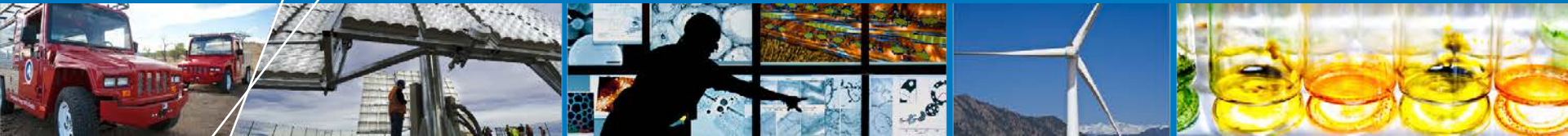
**2013 DOE Hydrogen and Fuel Cells Program Review**

**John Turner**

**May 16$^{th}$, 2013**

FC084

# 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 $Pt/WO_3$ and Heteropoly Acid (HPA) modification of carbon support to approach automotive PEMFC activity (**0.44 mA/mg$_{Pt}$**) and durability targets (5000h/10y).
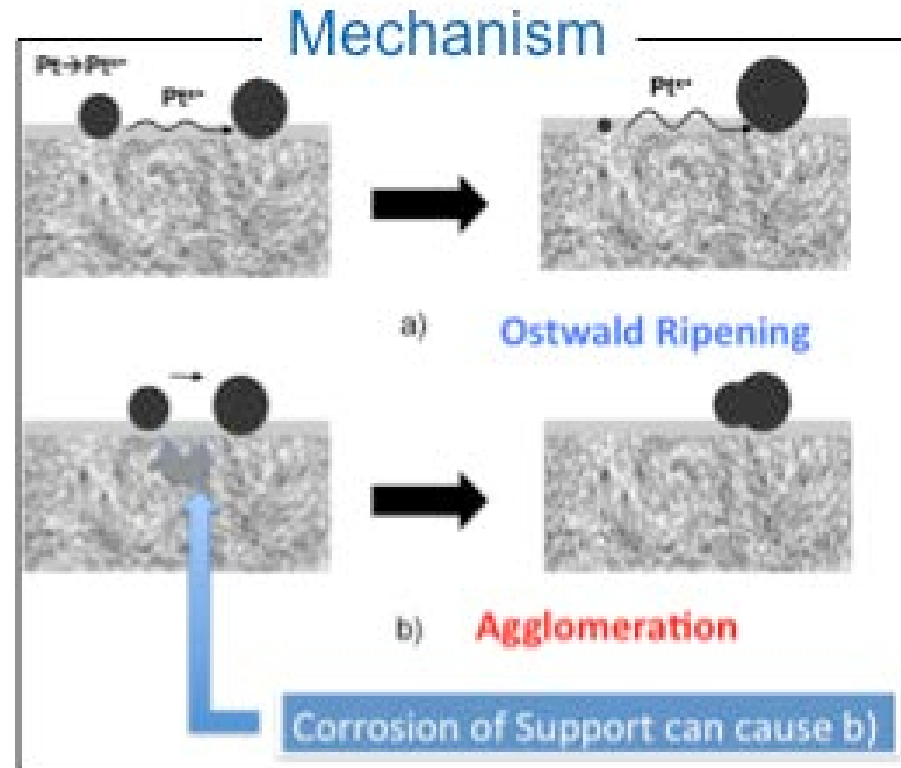
**Enhance Pt anchoring to support**

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

**Lower support corrosion**

- Increased durability under automotive startup/shutdown operation.

- Suppress Pt agglomeration/electrode degradation

**Simplify and lower system cost**



Mechanism

a) Ostwald Ripening

b) Agglomeration

Corrosion of Support can cause b)

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)

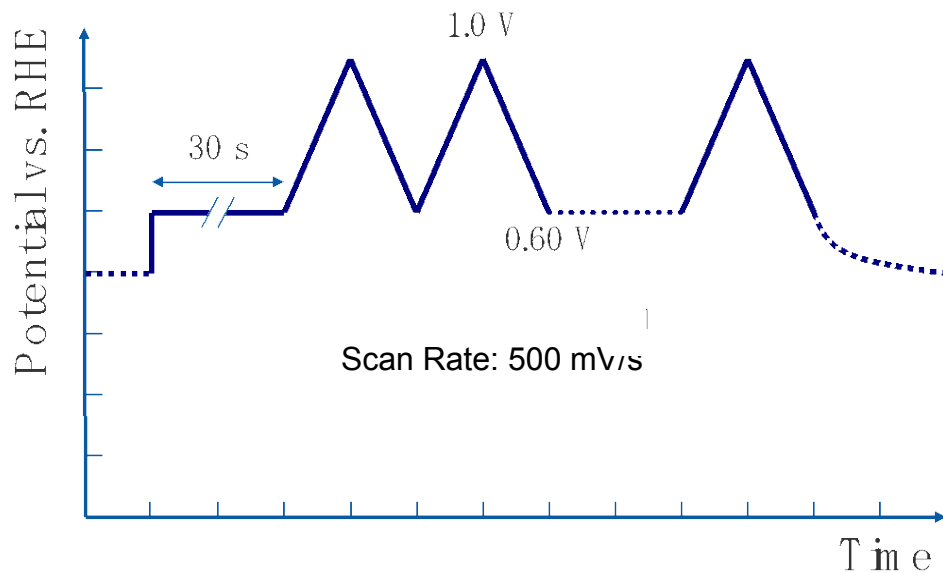# Protocols for Electrocatalyst/Support Durability Evaluation

## 1.0–1.6 V Regime
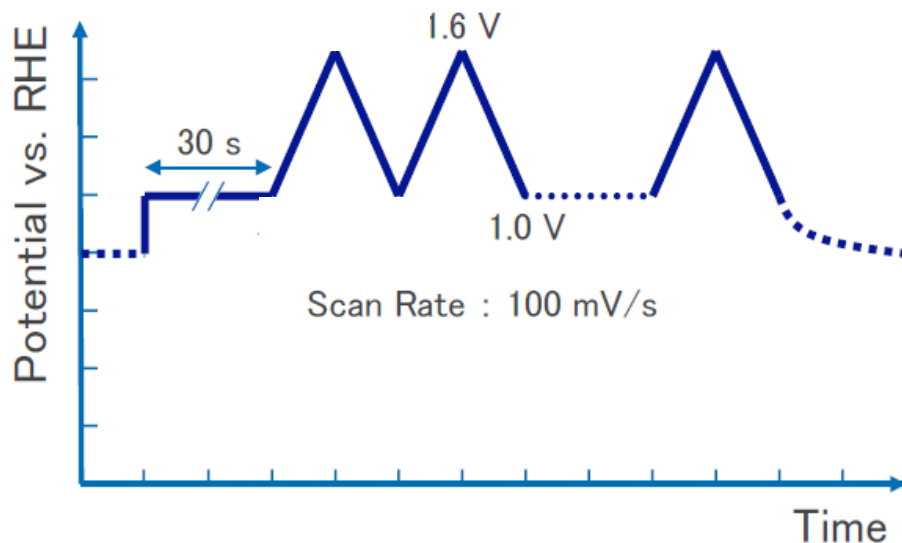


**Start-up/Shut-down Regime**
—Support degradation
—Pt agglomeration

## 0.60–1.0 V Regime



**Normal Operating Regime**
—Pt dissolution
—Pt agglomeration

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**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 WO$_3$     **NREL & CSM**

| Hot wire WO$_3$ to CU for Pt Atomic Layer Deposition (ALD) | Hot wire WO$_3$ to CSM for HPA modification and Pt deposition |
|---|---|

Characterize WO$_3$ & Pt/WO$_3$ for
- Conductivity
- Surface area
- TEM
- Wt %Pt

**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, 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 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 13

- **5.7.1 - Scale-up catalyst synthesis processes to generate >1 g of >20 wt% Pt on WOx for MEA evaluation Completed 12/12**

- **5.7.2 - Select synthesis route (ALD Pt on $WO_X$, Colloid Pt/$WO_X$, Direct reduction of Pt on $WO_X$, 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**
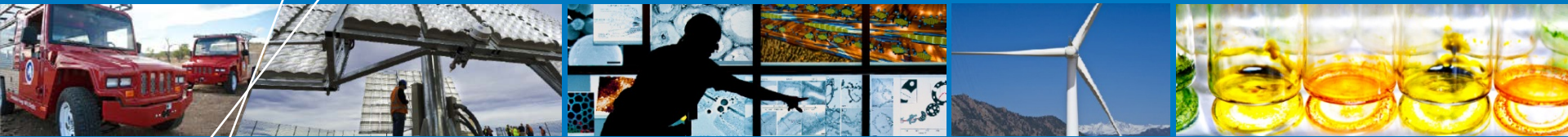
Synthesis

# 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$_{11}$ (wt% of support) | Pt(111) $\beta_{max}$ (°2$\theta$) | d-spacing (Angstroms) | $\delta_{Pt}$ – XRD (nm) | $i_m$ (mA/mg$_{Pt}$) |
|---|---|---|---|---|
| 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 |

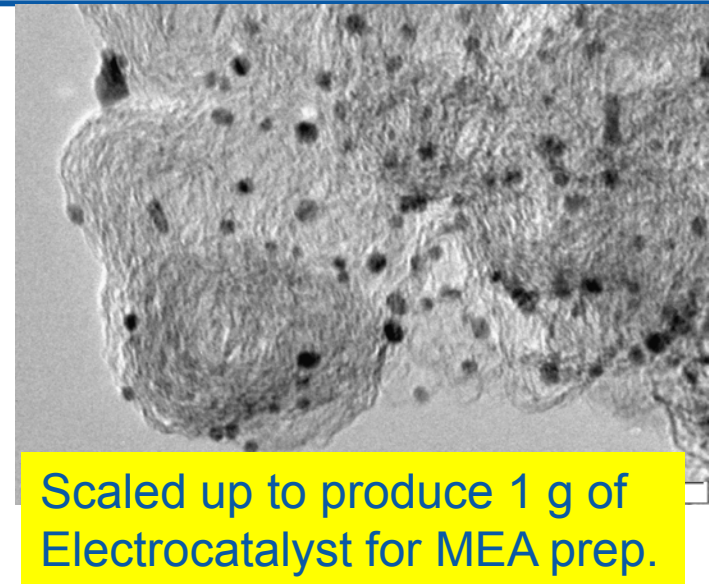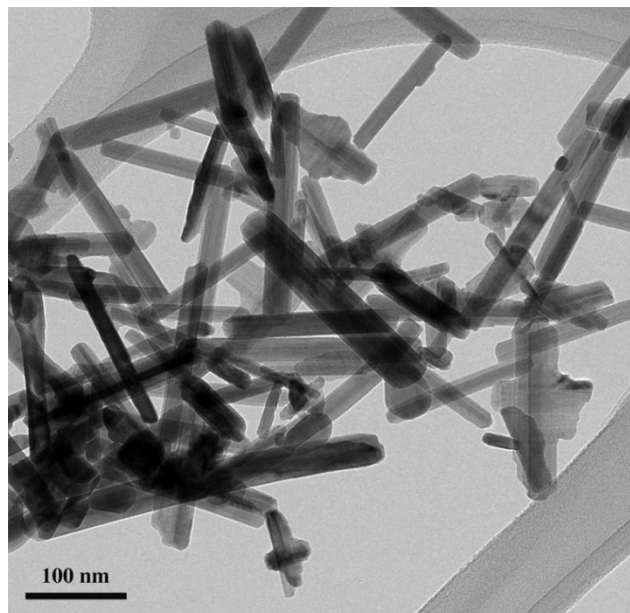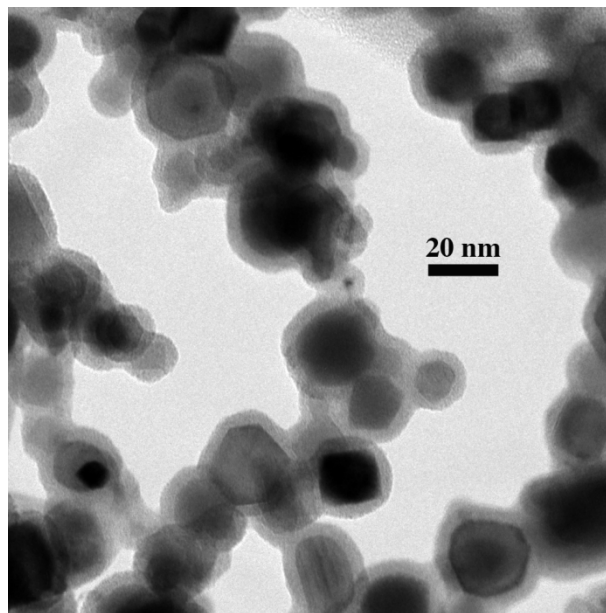Scaled up to produce 1 g of Electrocatalyst for MEA prep.
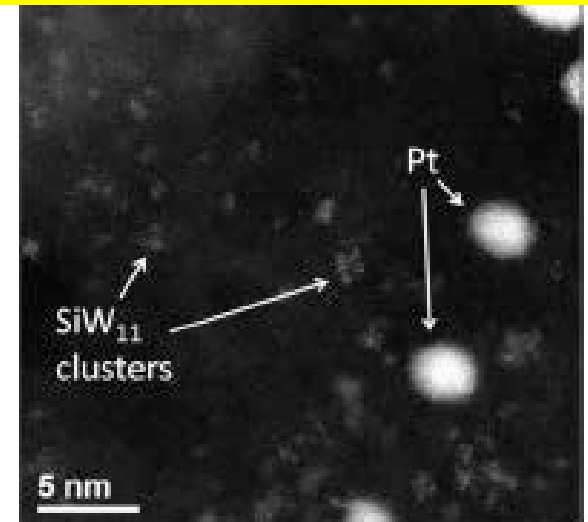
Figure 3: Z-contrast STEM image of Pt/SiW$_{11}$ -C showing spatial distribution of Pt (bright white spots ~3-5nm) and SiW$_{11}$ (~1nm dull gray spots)
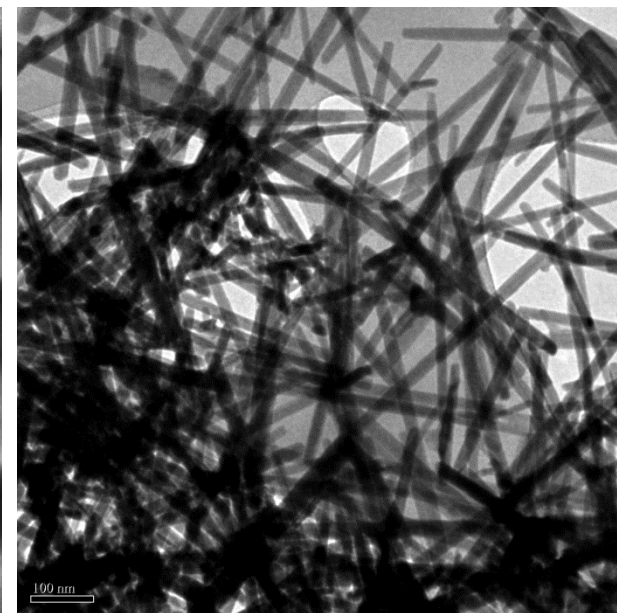
# HWCVD Production of Tungsten Oxide Nanostructures
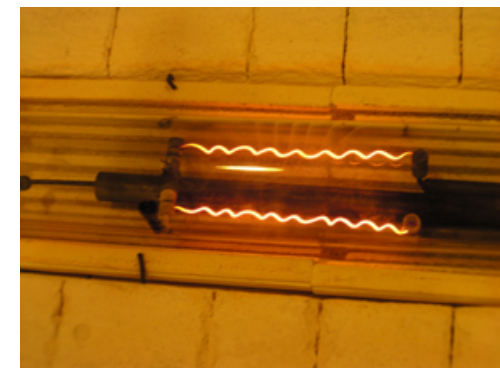## Synthesis at 150 Torr 4% O$_2$ in Ar, filament temperature ~ 2000°C



300°C              30°C             30°C

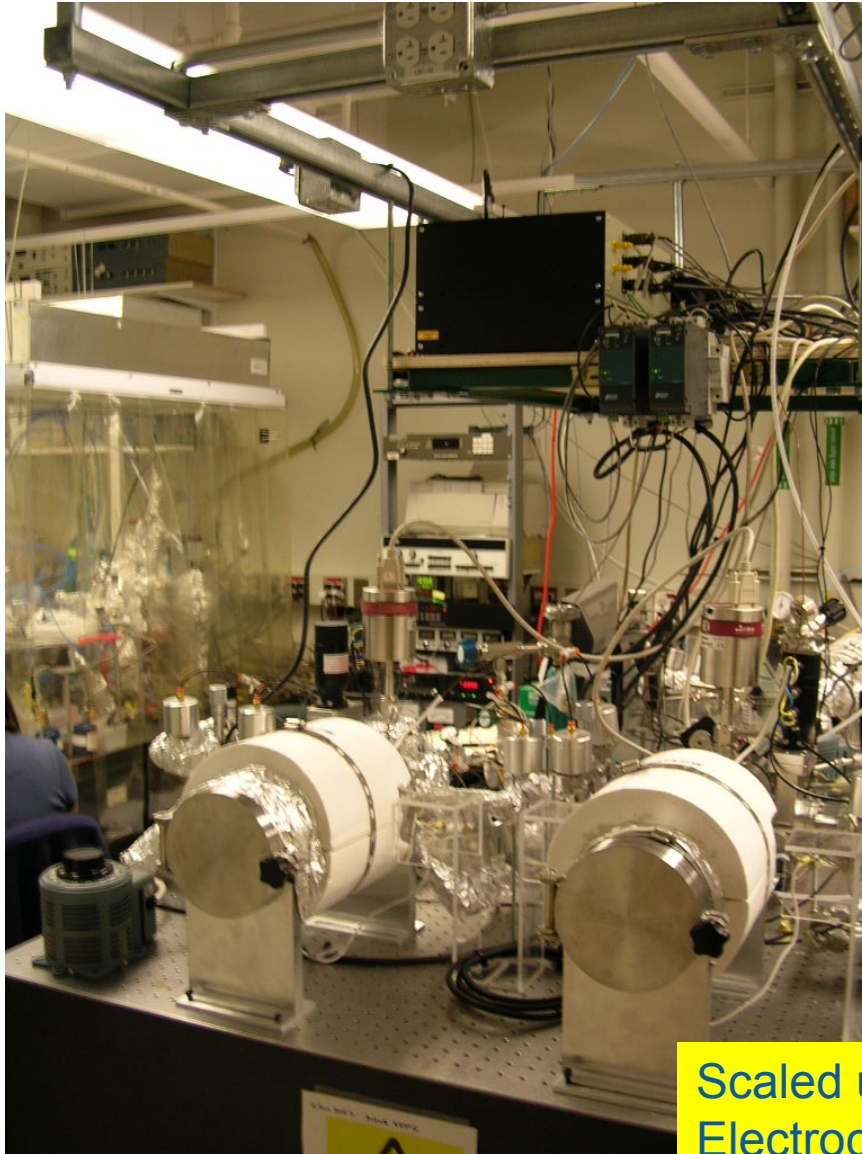**4 sequential depositions**

# 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.

# Pt ALD on WO$_3$ - Scaling with Dual Rotary Reactor



Dual rotary reactor demonstrates "proof of concept" 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.

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

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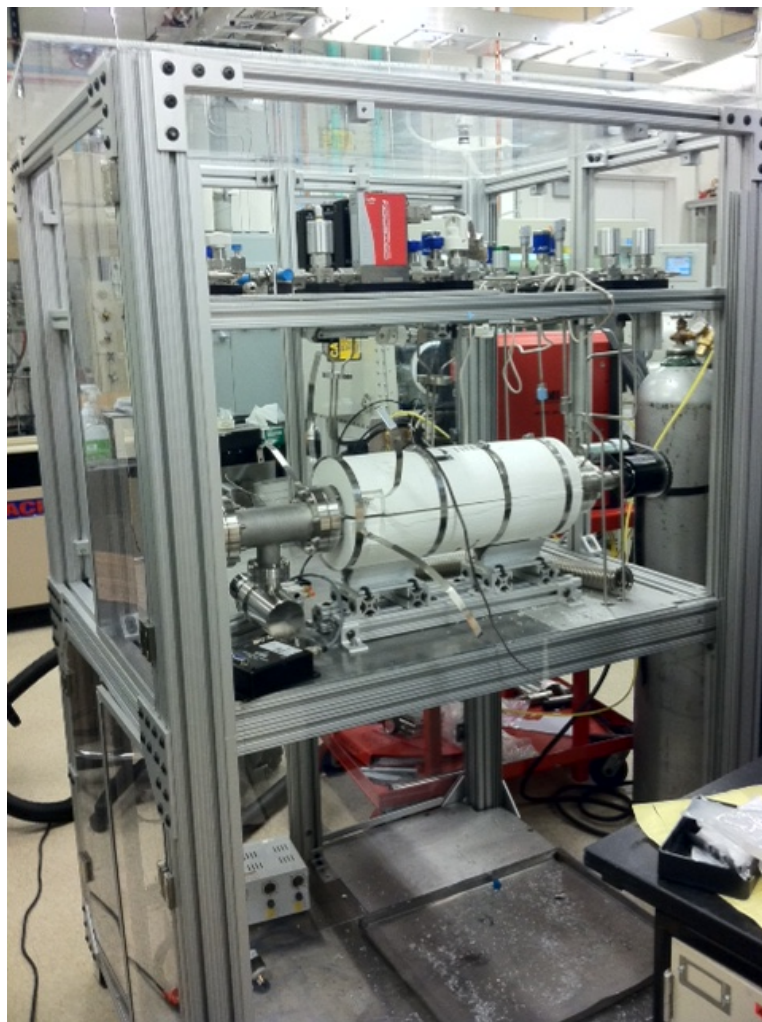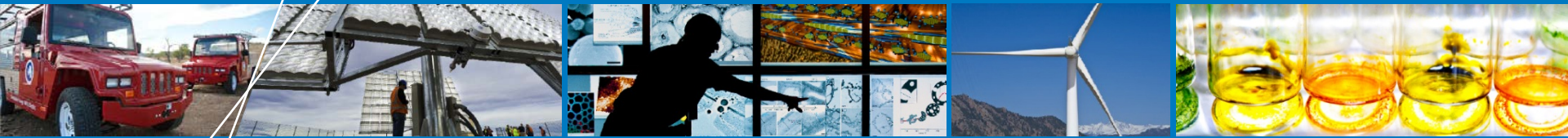


Able to coat powders or flat surfaces

Equipped for two heated and two room temperature precursors

Reactor volume ~100 cm$^3$

Produced highest mass activity (85mA/mg Pt) so far at 50 wt% Pt/WO$_x$.
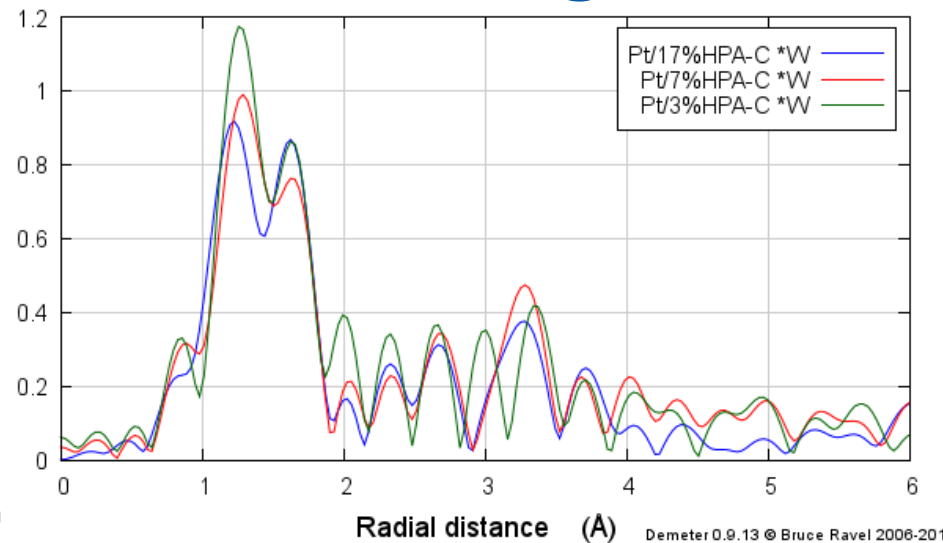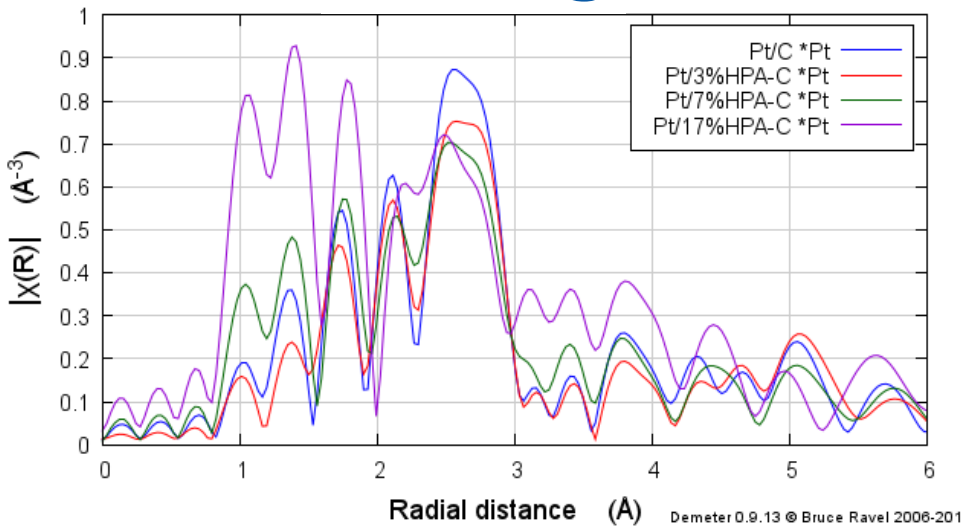
Funded by NREL LDRD

# 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.
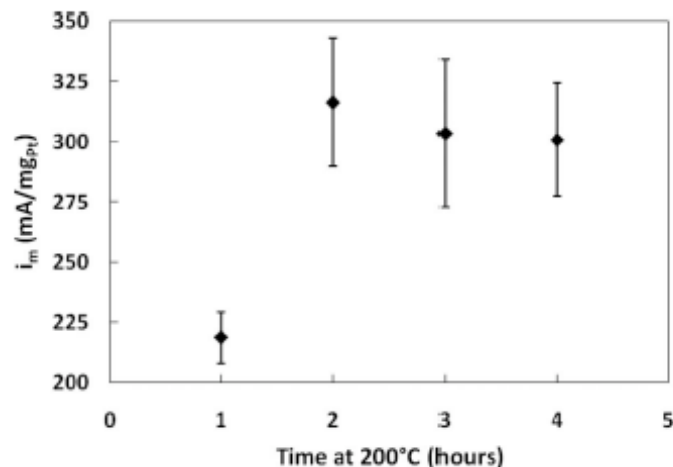
**Figure 1.** ORR mass activity measured at 900 mV of Pt/C catalysts as a function of post-synthesis heat-treatment time, measured in 0.1 M $HClO_4$.
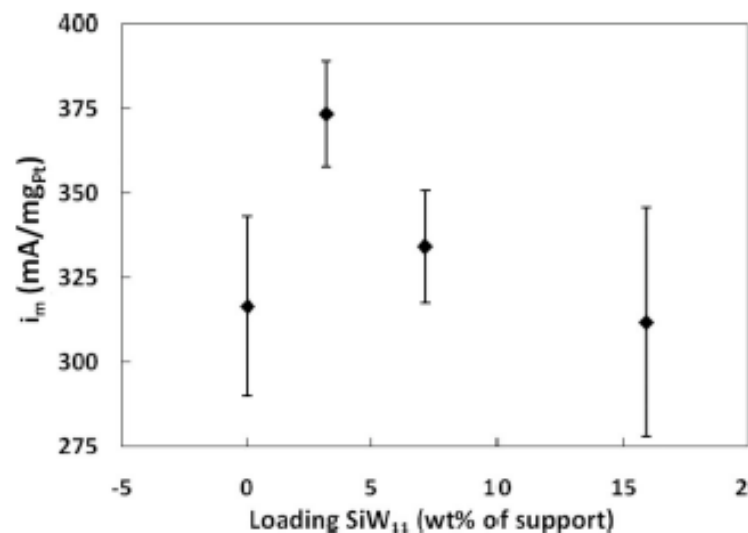


**Figure 5.** ORR mass activity measured at 900 mV of Pt/SiW$_{11}$-C catalysts a function of SiW$_{11}$ loading, measured in 0.1 M $HClO_4$.
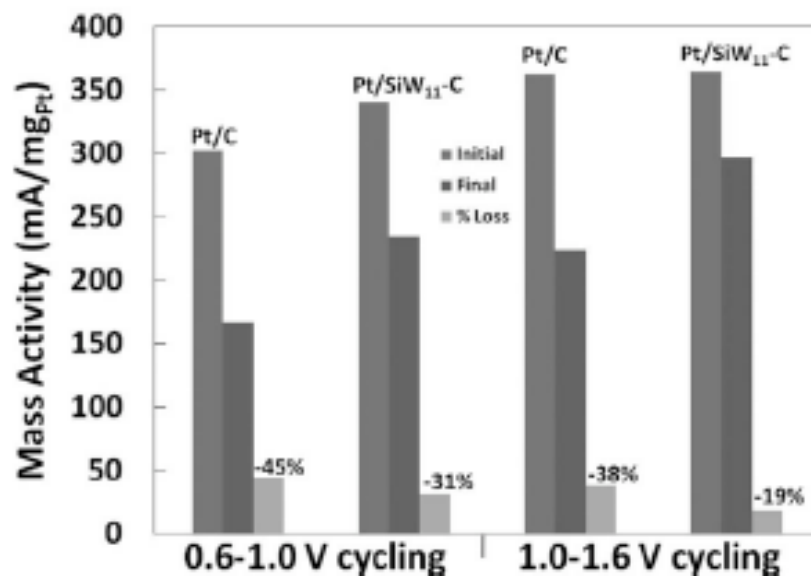


**Figure 7.** ORR mass activity measured at 900 mV of Pt/C and Pt/SiW$_{11}$-C catalysts before and after 0.6–1.0 V cycling (left) and 1.0–1.6 V cycling (right).
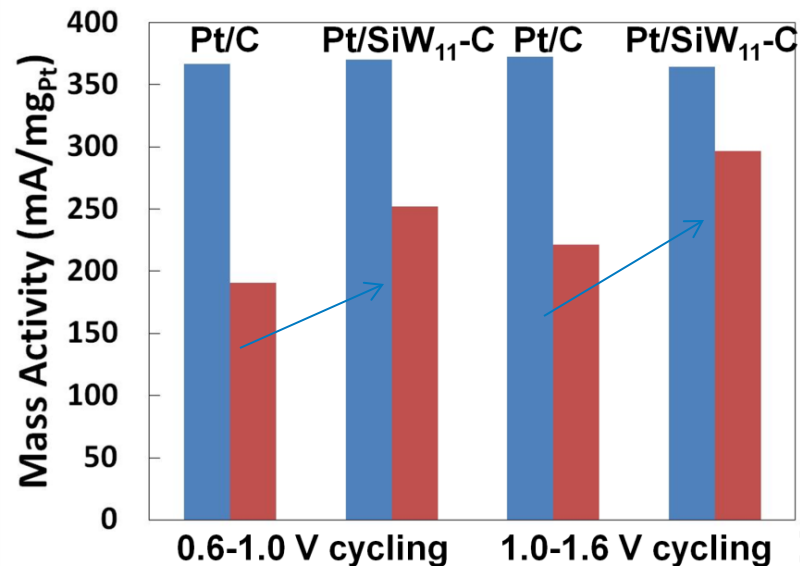
## Investigation of a Silicotungstic Acid Functionalized Carbon on Pt Activity and Durability for the Oxygen Reduction Reaction

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

# 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.
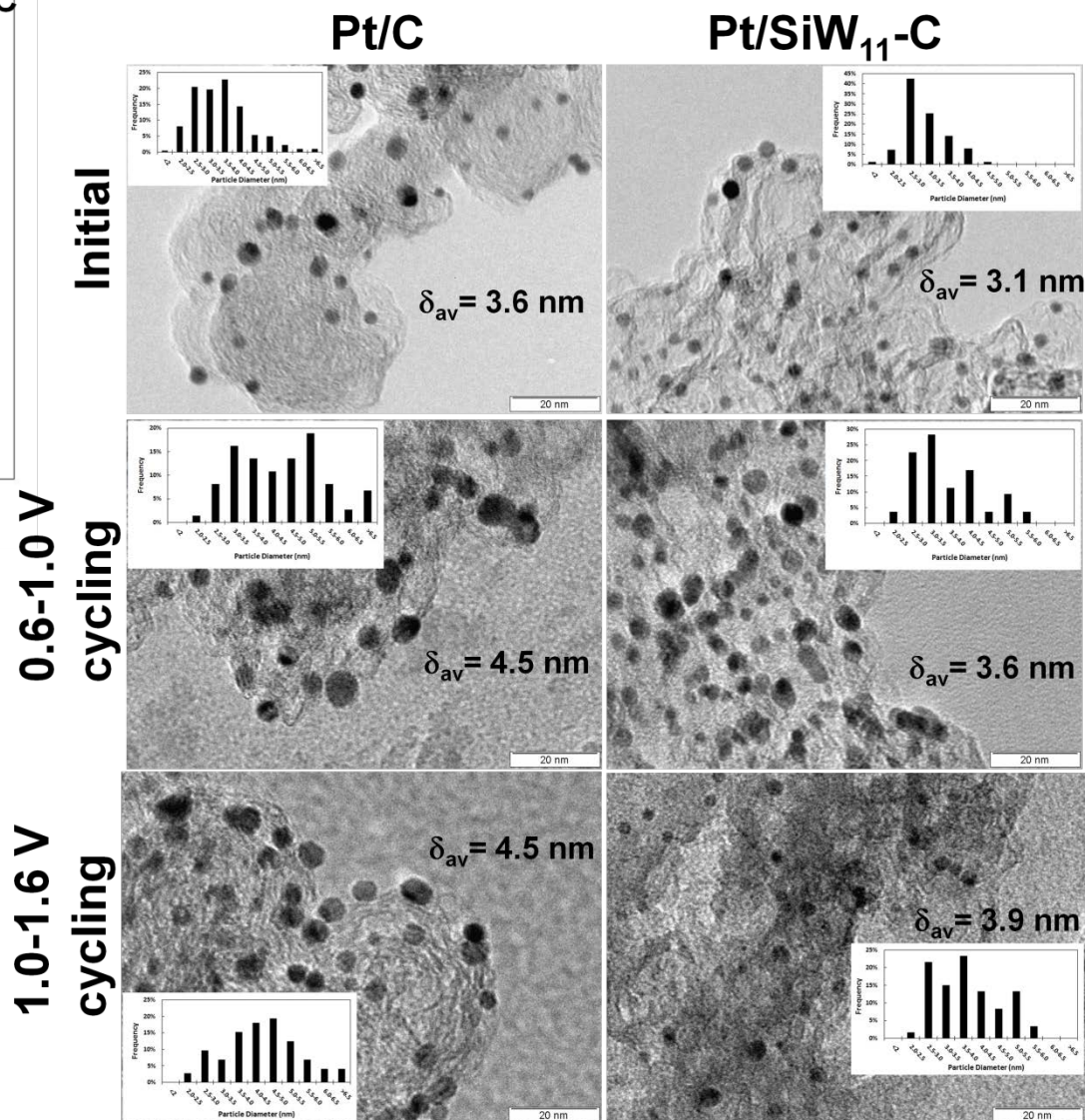
*All scale bars are 20 nm.
**Insets show Pt particle size distribution in 0.5 nm increments starting from 1.5 nm.

# Mass Activity of Pt/C vs. ALD Pt/WO$_X$



Mass Activity (mA/mg$_{Pt}$)

Legend:
- Pt/C
- 50wt% Pt/WOX_NREL
- 25wt% Pt/WOX,C_NREL
- 38wt% Pt/WOX_CU
- 20wt% Pt/WOX,C_CU
- 23wt% Pt_CU_Scaled

With carbon
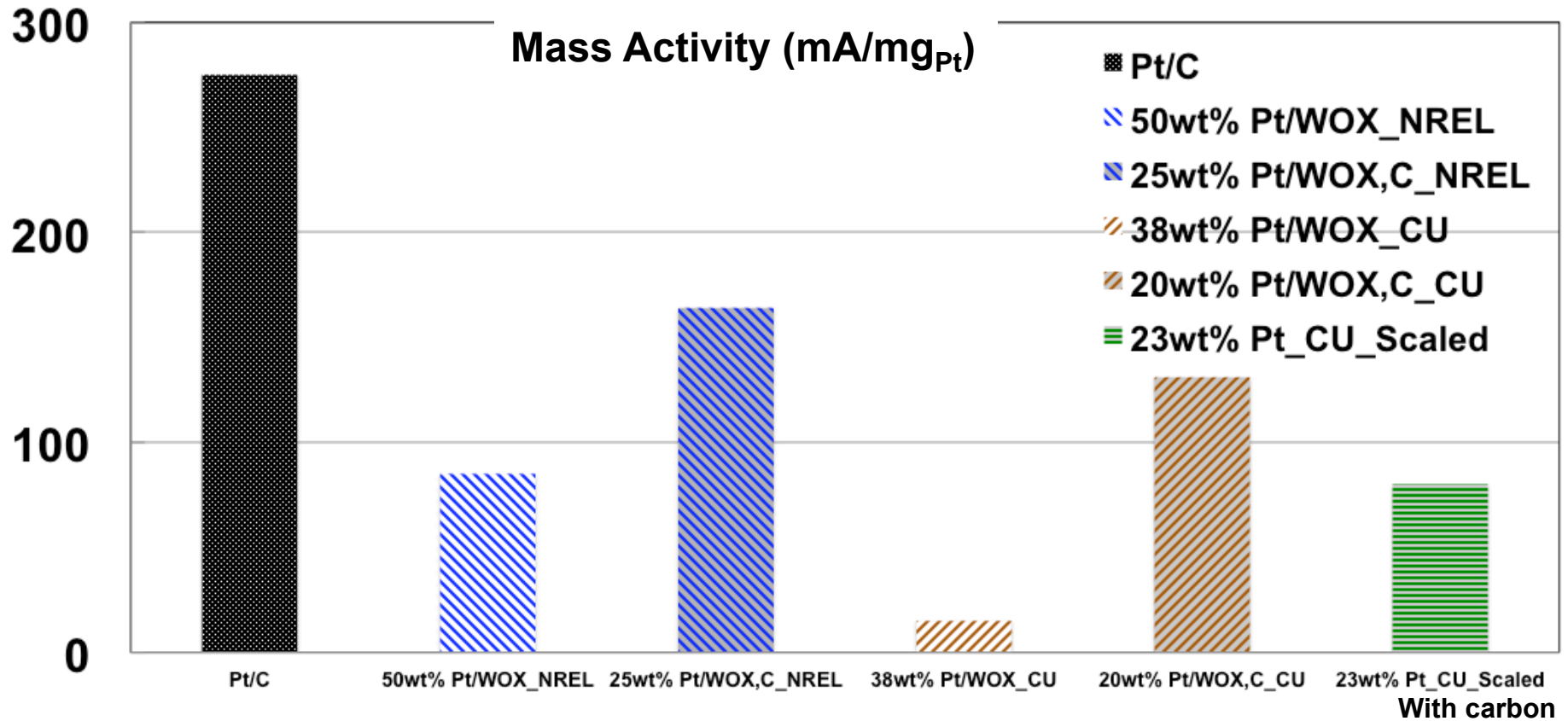
# KEH93 and VRA128 TEM Comparison

KEH93, 47% Pt

VRA128, 54% Pt



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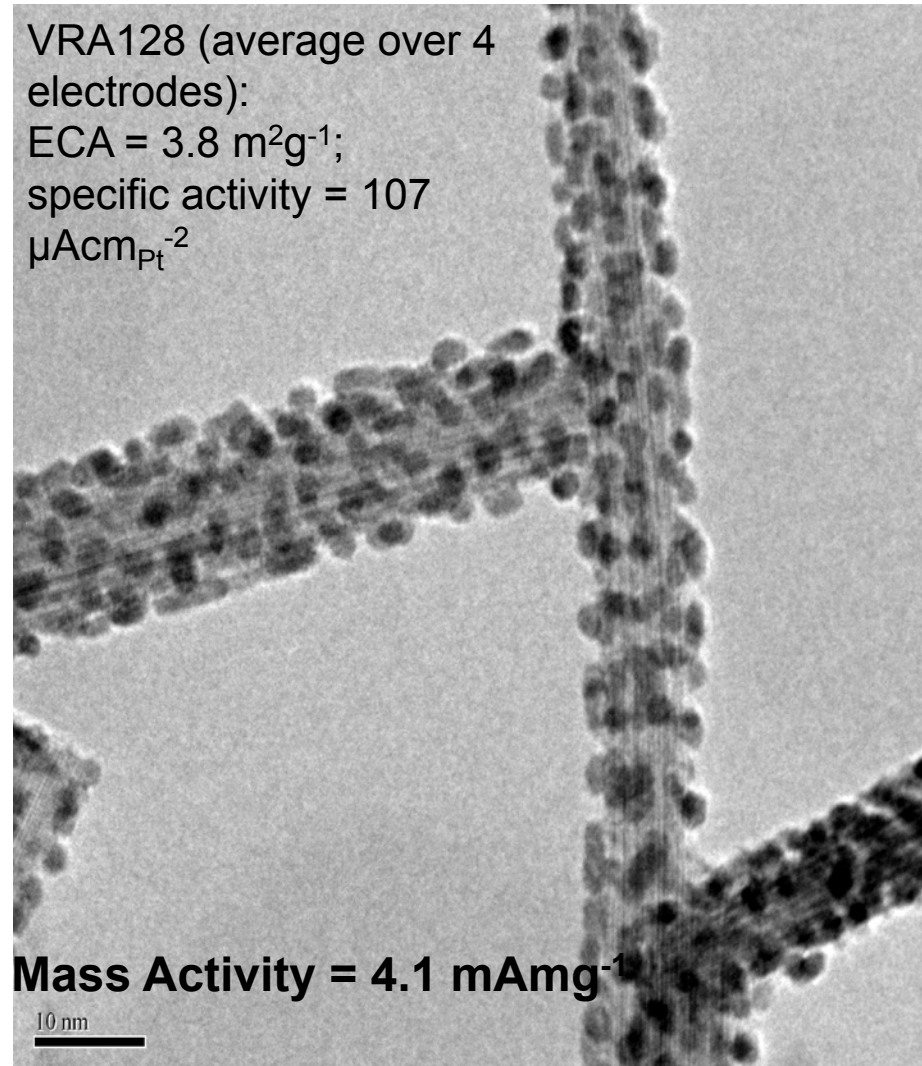ECA = 17 $m^2g^{-1}$;
specific activity = 426 $\mu Acm_{Pt}^{-2}$;

10 nm
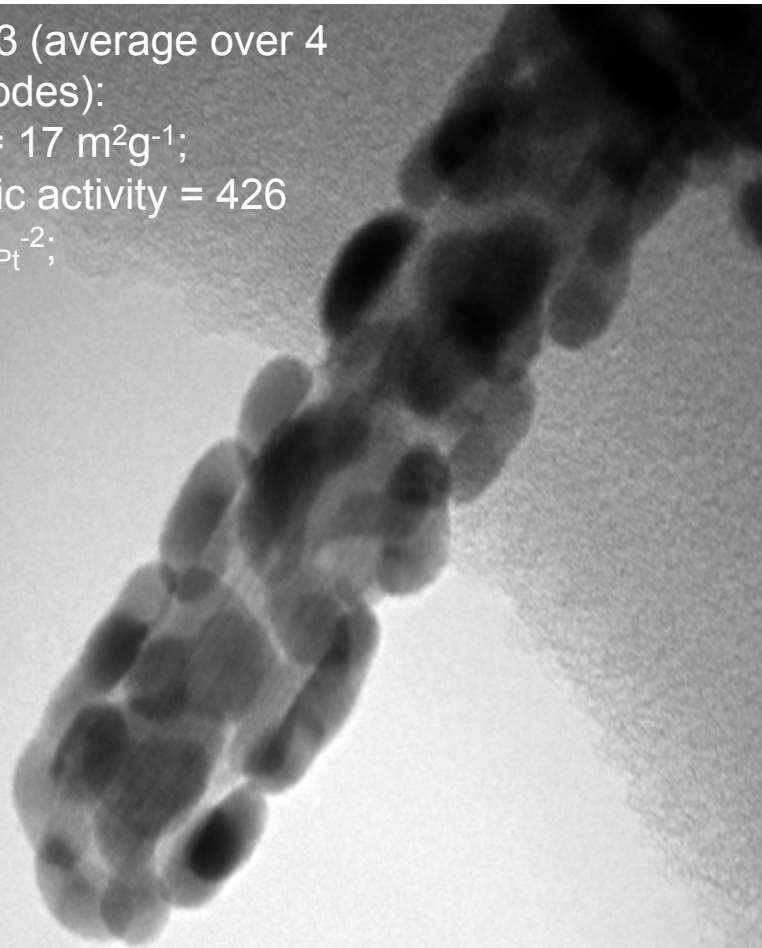
**Mass Activity = 75 mAmg$^{-1}$**



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

10 nm

**Mass Activity = 4.1 mAmg$^{-1}$**

# 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



Corrosion Currents on Au disk (Corrected)

Legend: TiN, TaC, TiO2, WC, SnO2, TiC, WO3

Axes: Current (µA) vs E (V vs. RHE)
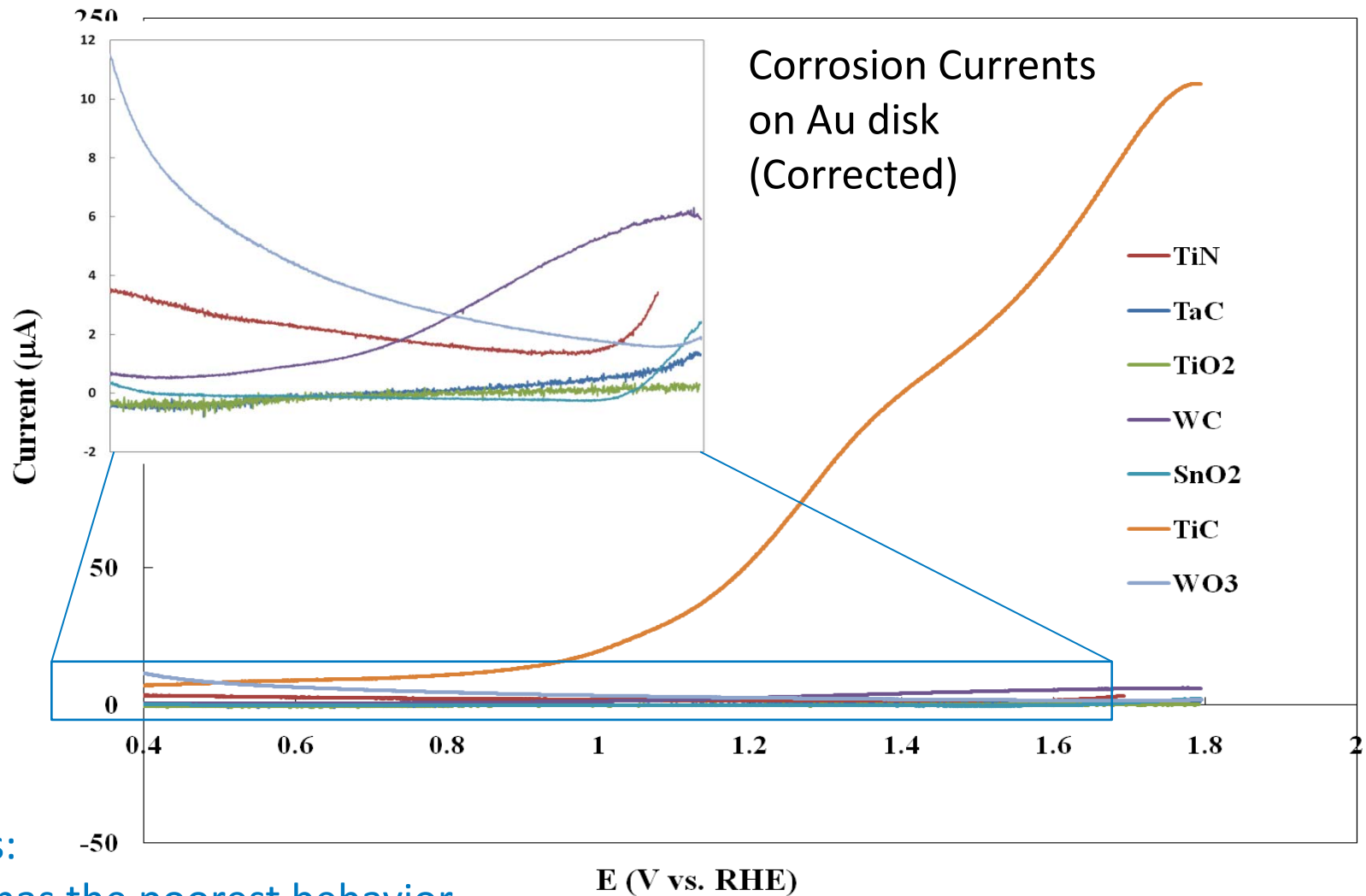
Results:
- TiC has the poorest behavior.
- WC is also less than ideal, and TiN is questionable.
- TiO$_2$, TaC, and WO$_3$ appear to be the best for corrosion resistance.

# Conclusions

1.  **ALD Pt/WO$_X$ + 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$_X$ + 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/SnOx + C system**

    1.  Gram quantities of ~ 28 wt% Pt/SnO$_2$-GCNF available

    2.  Meets activity benchmark of Pt/C in RDE

    3.  CCMS prepared —1st iteration

    4.  Evaluated in subscale cells— 1st iteration

**Activity benchmark of Pt/C (w Nafion®) in RDE studies in 0.1 M perchloric acid, at 25$^o$C and 100 kPa O$_2$ is ~275 mA/mg$_{Pt}$**

# MEA Preparation
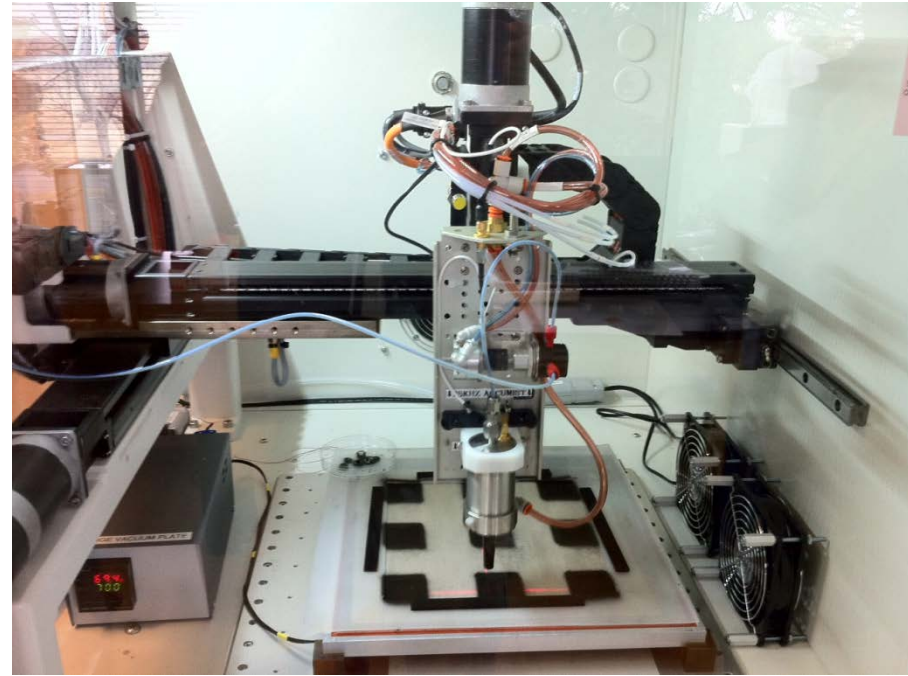


CCM preparation by spray-coating of electrocatalyst ink directly onto the membrane was carried out. A total of 9 Pt/C anodes were prepared and 3 Pt/SnO$_2$ cathodes were deposited. One CCM is currently under test.

# Subscale Fuel Cell Testing Pt/SnO$_2$/C
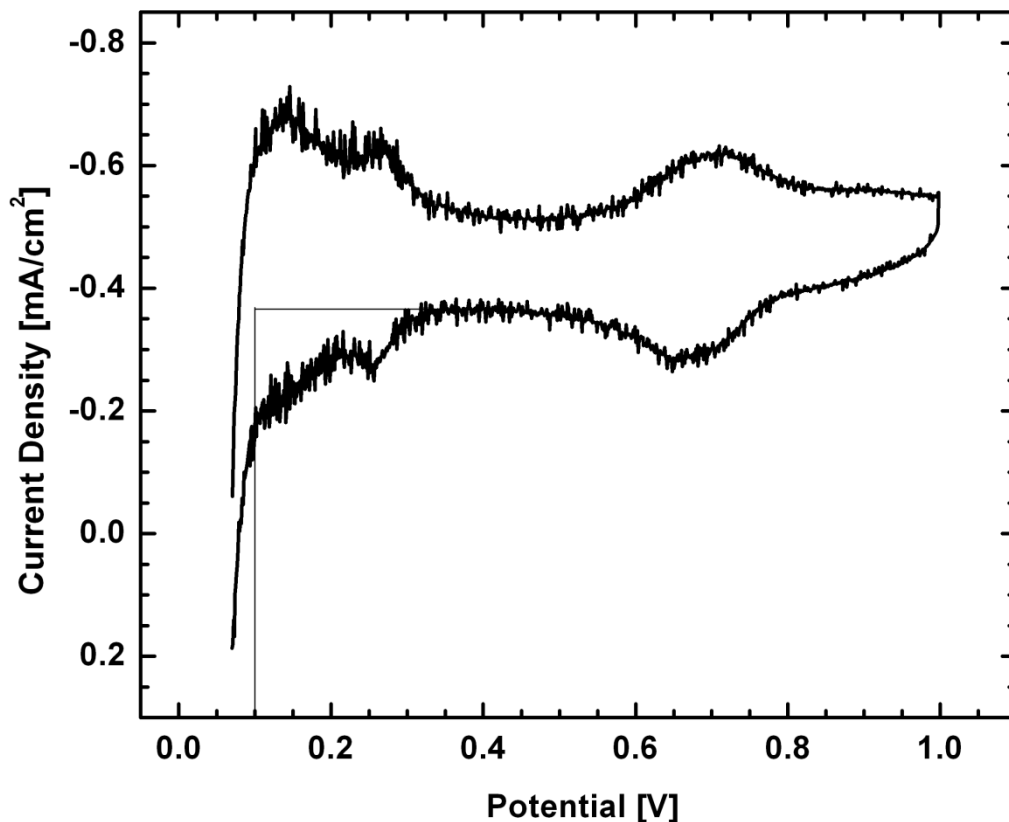


Loading = 0.06 mg/cm$^2$
ECA = 5 m$^2$/g$_{Pt}$

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$_{Pt}$/cm$^2$) based on XRF measurements.

Currently, diagnostics are being conducted to resolve these issues.
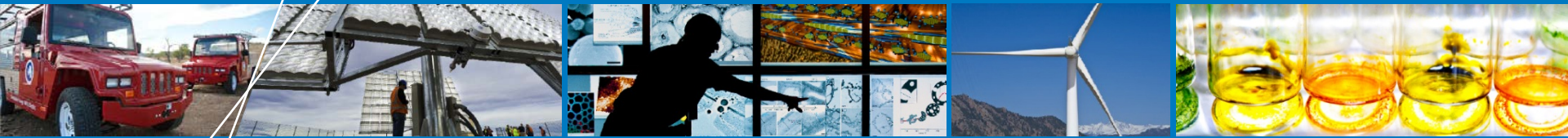
# Accomplishments and Progress

- $WO_X$ preparation was scaled up to gram levels for ALD platinum deposition.

- CU-Boulder deposited ALD $Pt/WO_X$ scaled up to g quantity.

- Mass activity of scaled up ALD $Pt/WO_X$ was low.

- Pt colloids were prepared (CSM) that were subsequently deposited on HPA functionalized C. This was scaled up to generate 1 g quantity.

- $Pt/SnO_2$ obtained from a commercial catalyst supplier (TKK). These materials are available in gram quantities.

- $Pt/SnO_2$ was evaluated in RDE with and without Nafion®.

- $Pt/SnO_2$ 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

- **Finish up Pt/SnO$_2$ 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 (m2/g) | Specific Activity (µA/cm² 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 cm² cell, Pt/HSC anode, $H_2/O_2$

| Catalyst | Cathode loading (mg Pt/cm²) | ECA (m2/g) | Specific Activity (µA/cm² 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**
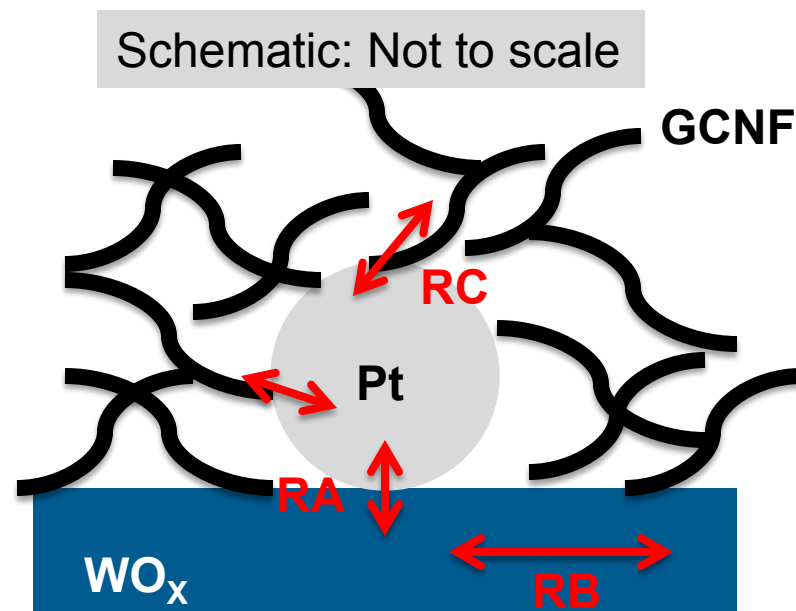
*has only been tested once, no optimization (loading, ionomer:C ratio, etc.)
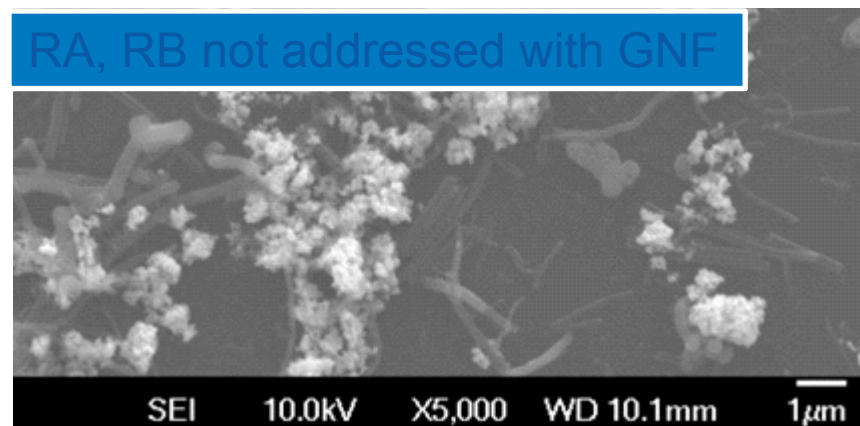**average of last 5 minutes of a 15 minute hold
***measured by weight, XRF gave spurious results

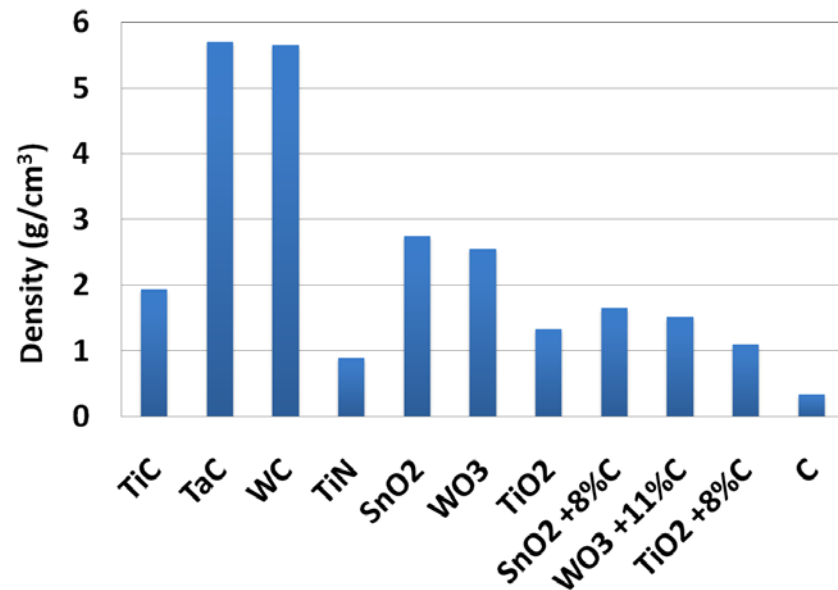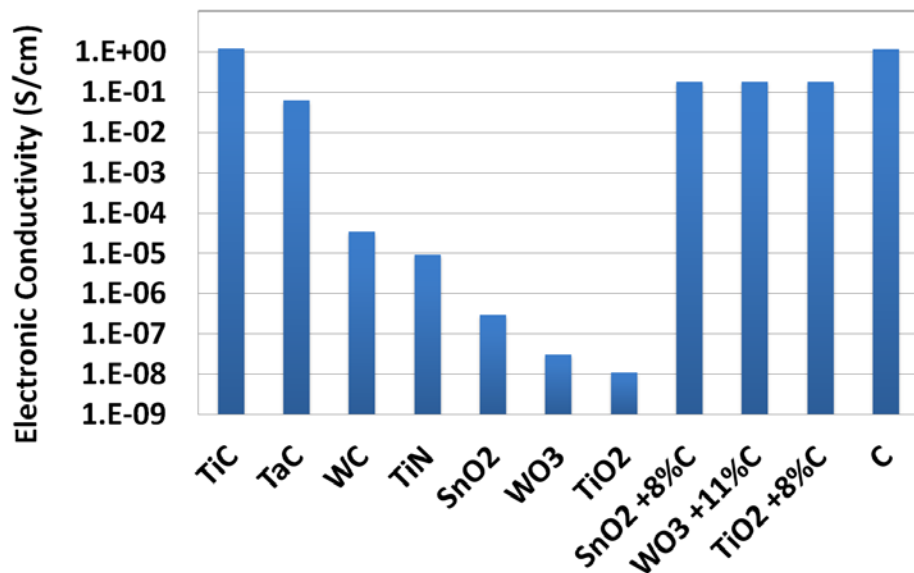# Challenges: Electronic Conductivity

- **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**
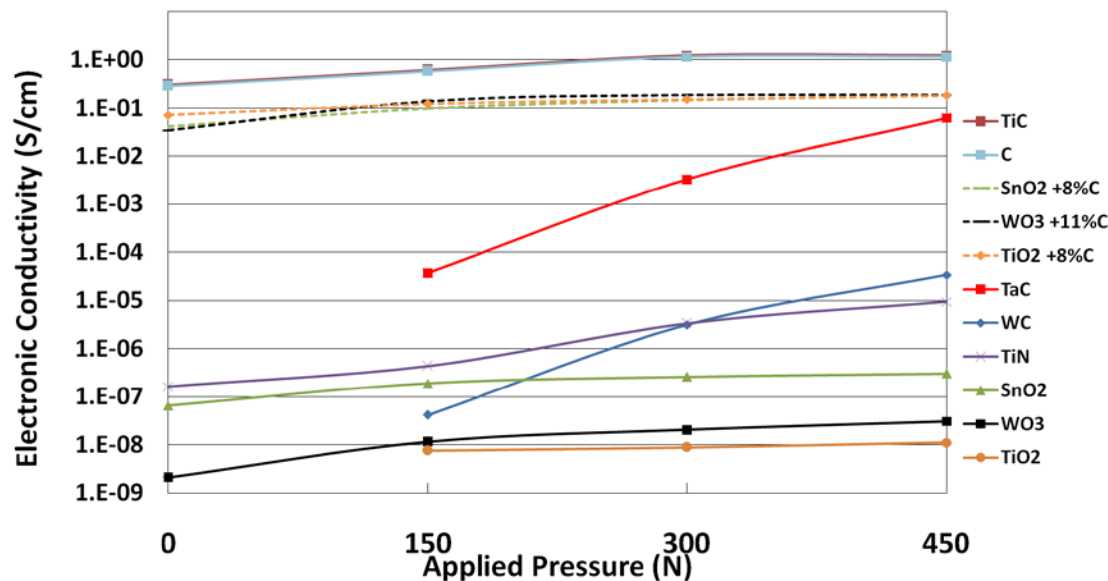  - Coating of Nafion ionomer on Pt and $WO_X$ and C not shown: $R_{Nafion}$



Schematic: Not to scale

GCNF

RC

Pt

RA

$WO_X$

RB

Actual Micrograph

RA, RB not addressed with GNF

SEI     10.0kV     X5,000     WD 10.1mm     1μm
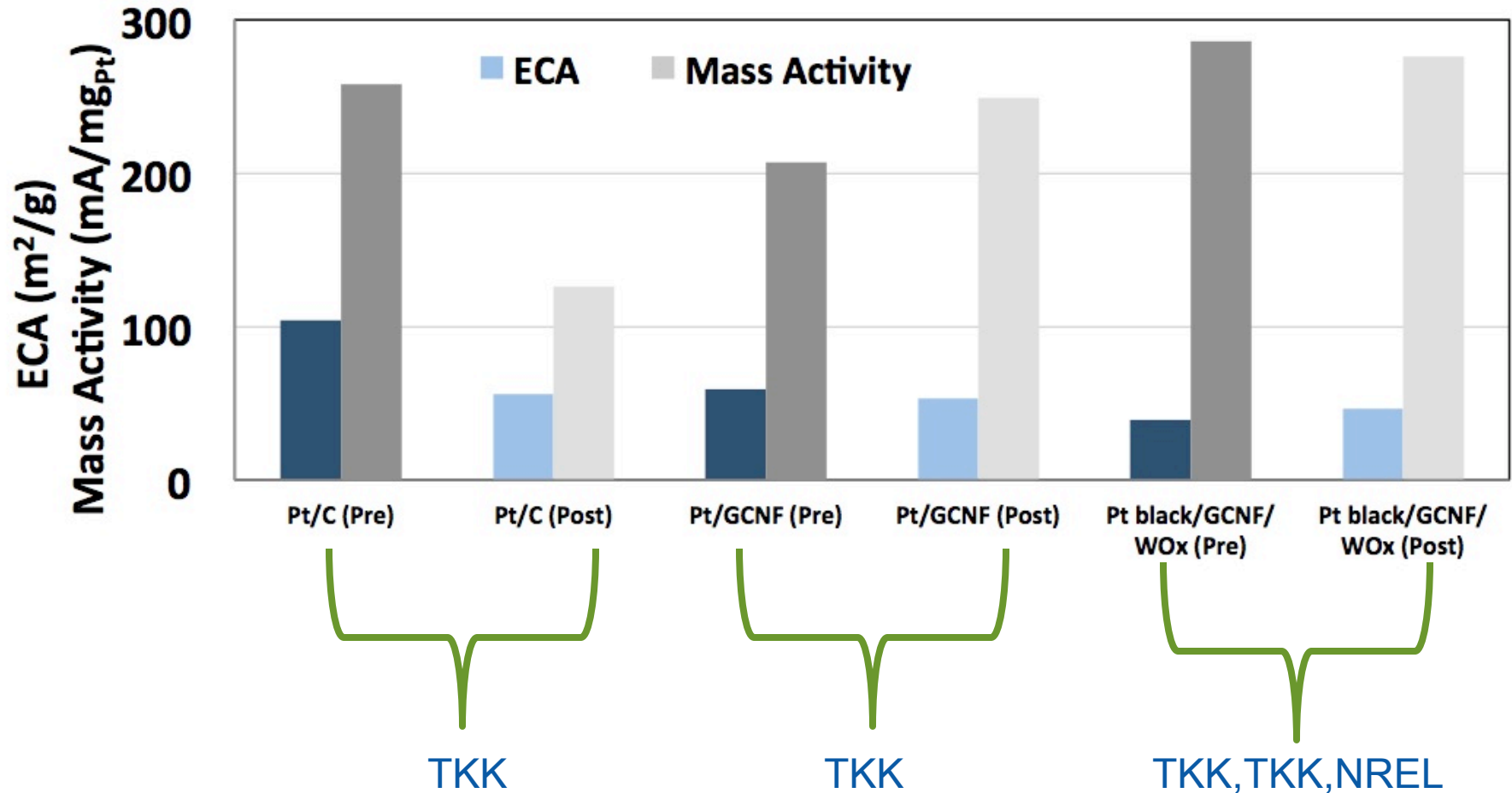
# Conductivity of Alternative Supports



Measured at an applied pressure of 450 N.

# Durability (Pt black + GCNF+ WO$_X$) System
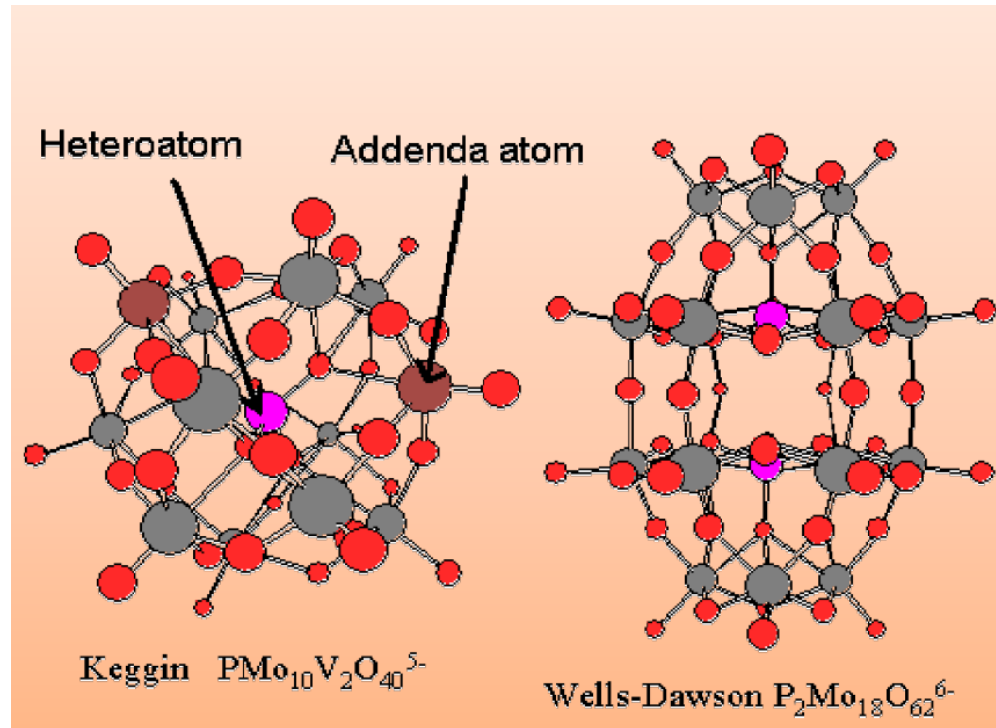
NREL 1.0V-1.6V protocol

# 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



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

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

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.