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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

2010 DOE Hydrogen Program Fuel Cell Project Kick-Off

Venue: Washington D.C.

Presenter: John Turner

Organization: NREL

Date: Sept 28th, 2010

Overview

Timeline

- Project 05/01/2010
- Project 04/30/2014
- Percent Complete:10%

Barriers

- Durability
- Cost
- Performance

Budget

- Total project funding: $3.3M
  - DOE share - $3.05M
  - Contractor Share - $275k
- Funding received in FY10: $500k
- Funding for FY11: $550k

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, Shyam Kocha

DOE Electrocatalyst Targets

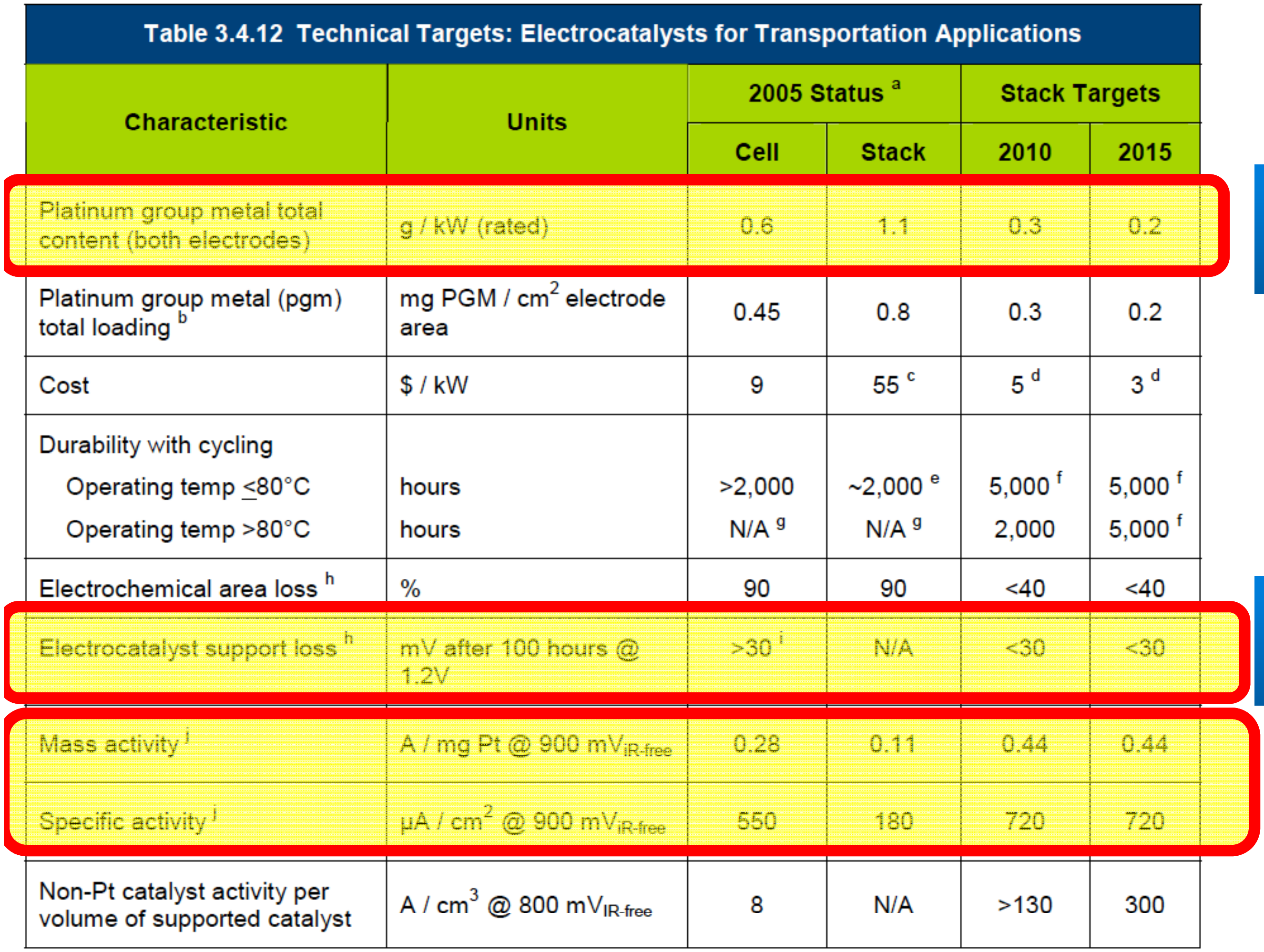


Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

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

~0.1 g/kW or 10g per 100kW stack

Based on mitigated start-stop

4x Activity enhancement

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

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 target (5000h/10y).
  - **Lower support corrosion**
    - lower Pt agglomeration due to support corrosion
  - **Lower peroxide concentration**
    - Lower membrane degradation
  - **Enhance Pt anchoring to support; Pt-support interaction**
    - lower loss in ECA
    - enhance catalyst activity
  - **Lower costs**
    - simplify & lower system cost through increased durability under start-up/shut-down
- Show that the combination of HPAs and tungsten oxides as co-catalysts and catalyst supports is the most versatile pathway to meeting the DOE goals for fuel$_{\text{ce}}$ ll MEA costs and performance.

Relevance: Automotive Fuel Cell Operation

Open Circuit Potential (OCV)

- Highest (H_2|Air) potential ~0.96 V @ OCV (80°C)

  Possible Air|Air potential ~ 1.1 V (80°C)
- Pt band formation in the membrane
- Peroxide generation

Idling

- Idling @ 0.85-0.96 V

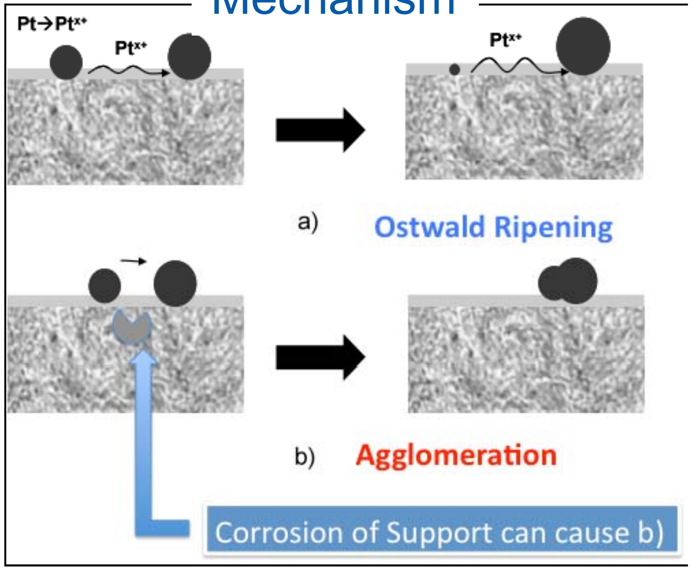
Start-up/Shutdown

- Highest potential ~1.5 V on cathode
- Highest potential after mitigation ~ 1.1 V (Air|Air)

Hydrogen Fuel Starvation

- High localized potentials on anode

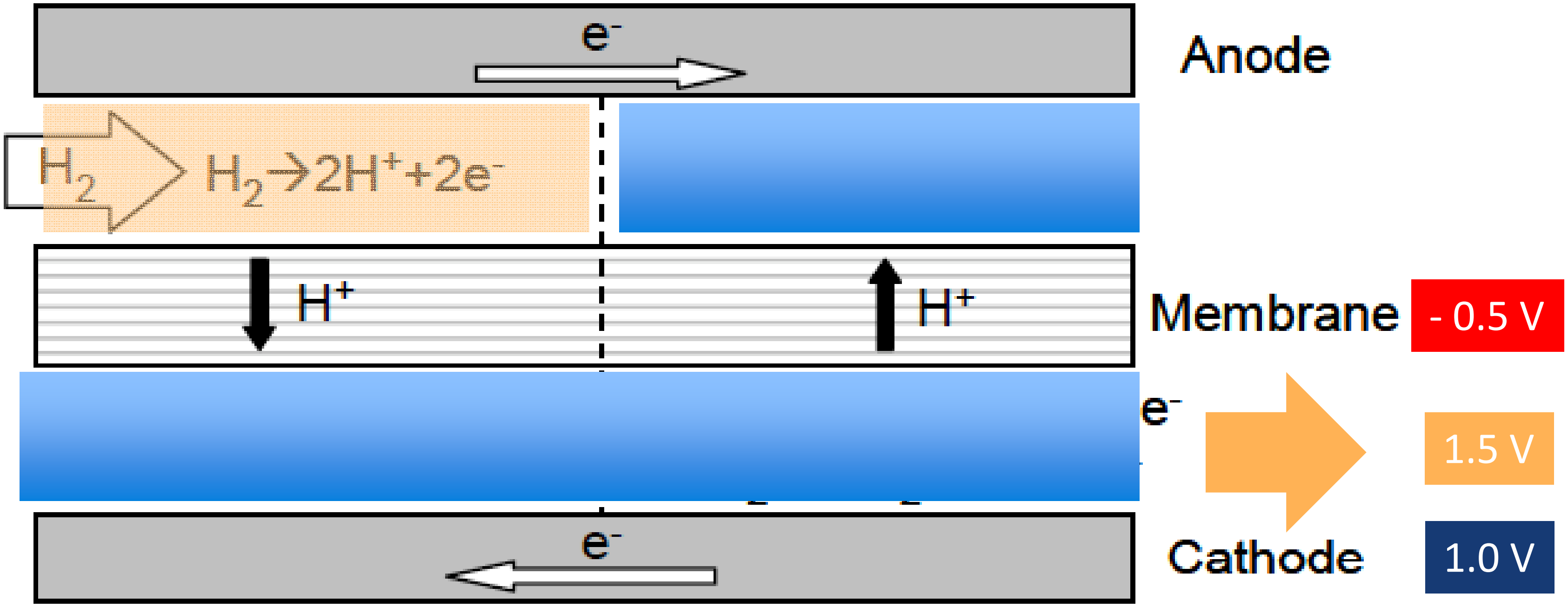
Mechanism



Corrosion of Support can cause b)

Unmitigated Start-up/Shutdown

~ 30,000 Start-up/Shut-down cycles over 10 years, 5000 h life of automotive PEMFC



Originally discovered by UTC Fuel Cells and reported in several patents.

Partially Mitigated Start-up/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)

These complex operations mitigate the losses partially.

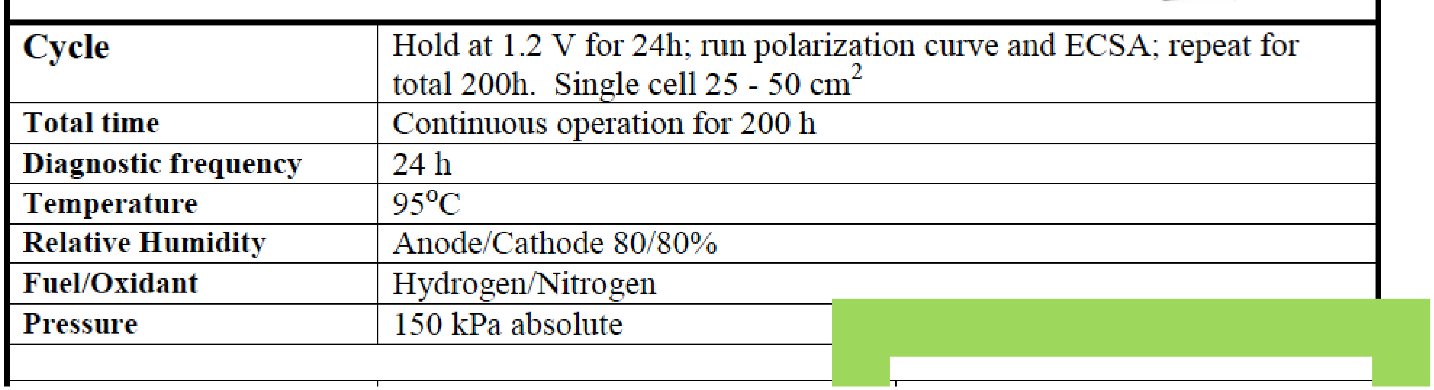
- **Material Control**
  - Selective HOR electrocatalyst that is a poor ORR catalyst
  - Selective electrocatalyst for H_2O splitting over C corrosion
  - New support materials that are corrosion-resistant

Can materials solutions eliminate need for complex operations?

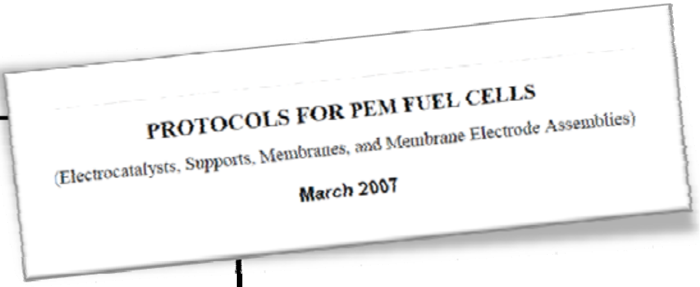
DOE Protocol (subscale cells, OCV hold)

Based on mitigated start-stop

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

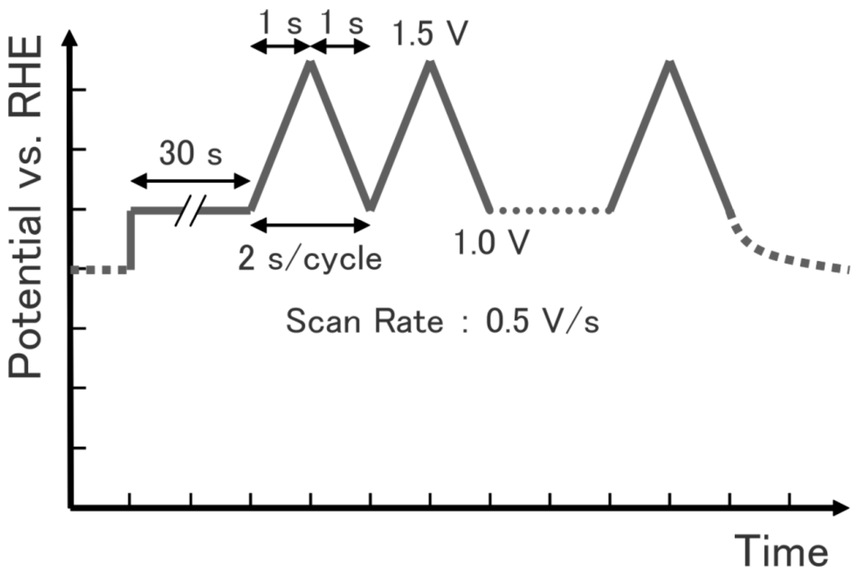


PROTOCOLS FOR PEM FUEL CELLS
(Electrocatalysts, Supports, Membranes, and Membrane Electrode Assemblies)
March 2007

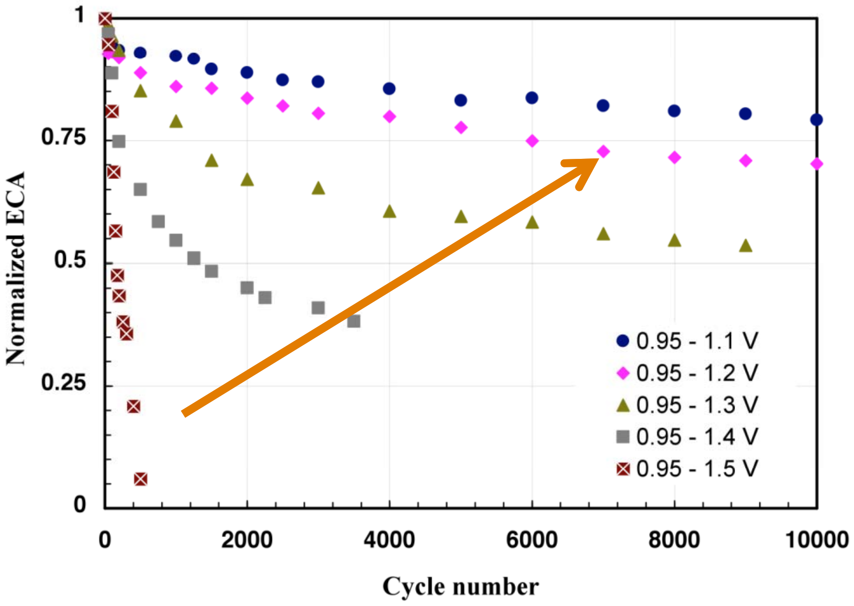
http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Protocol for unmitigated startup–shutdown cycling

Protocol (1–1.5 V potential cycles)



Unmitigated 1-1.5 V Simulated Start-up/Shut-down Cycle Protocol

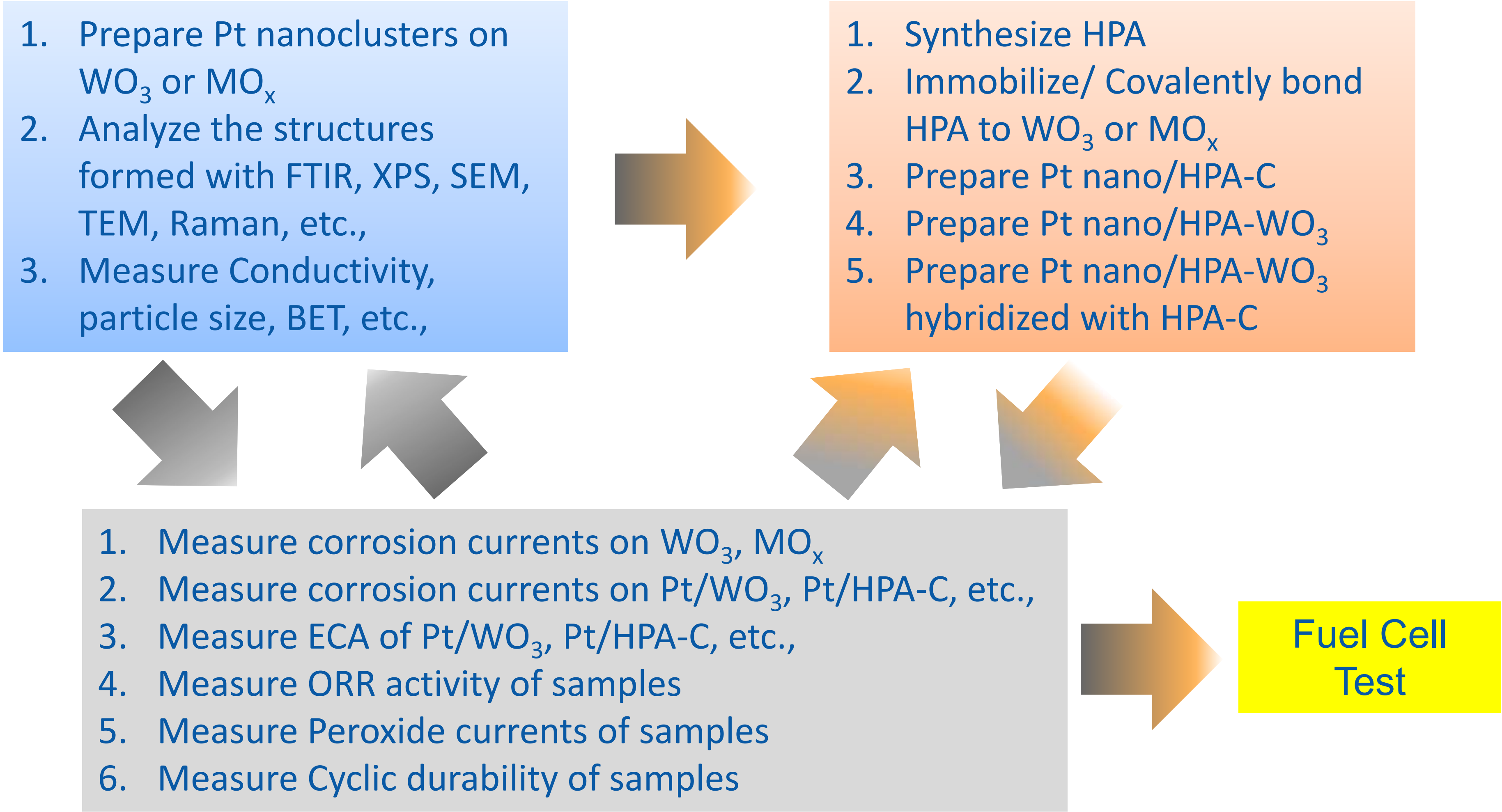


Effect of Upper Potential on loss of Electrochemical Surface Area

NREL will test new materials for durability using both protocols.

Overall Approach

Use the Team's synthetic expertise to explore a broad range of oxide based molecules (HPAs) and tungsten oxide catalysts to develop non-carbon supports and a catalyst layer for the ORR with improved performance at low loadings of Pt.



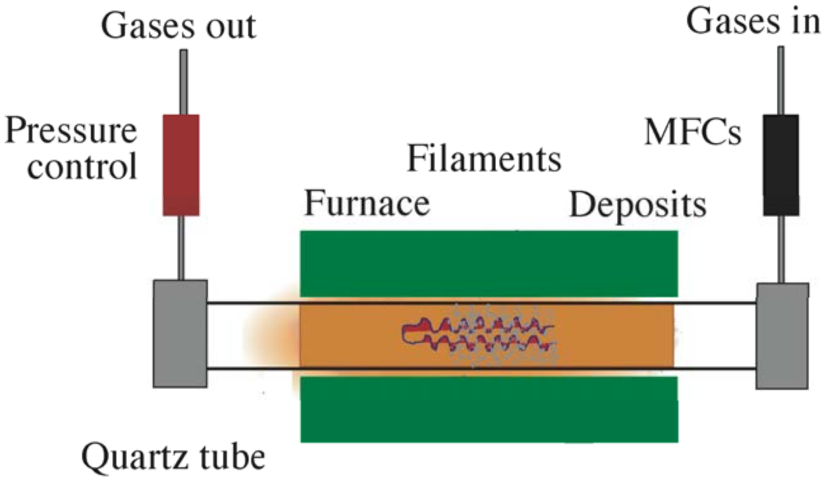
1. Prepare Pt nanoclusters on WO_3 or MO_x
2. Analyze the structures formed with FTIR, XPS, SEM, TEM, Raman, etc.,
3. Measure Conductivity, particle size, BET, etc.,

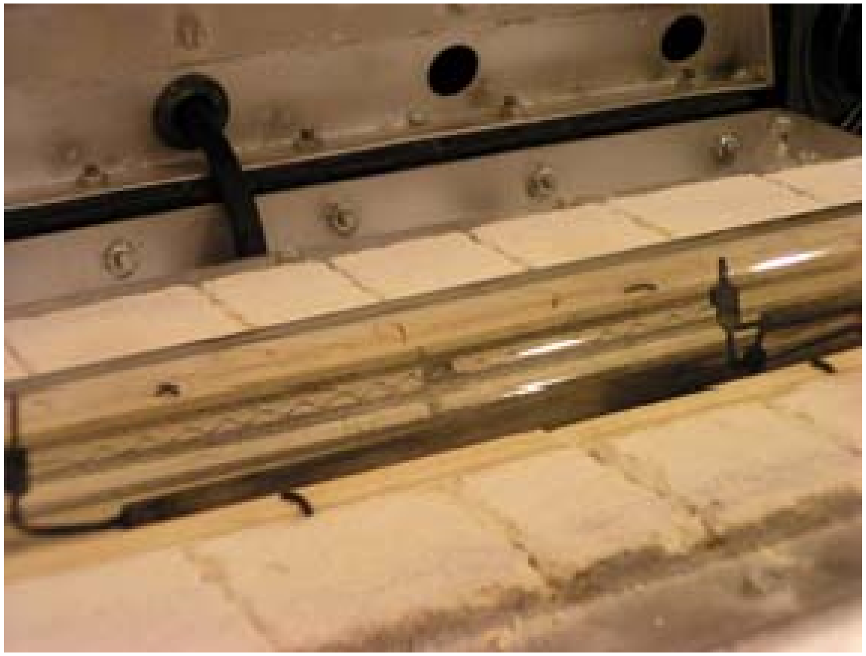
1. Synthesize HPA
2. Immobilize/ Covalently bond HPA to WO_3 or MO_x
3. Prepare Pt nano/HPA-C
4. Prepare Pt nano/HPA-WO_3
5. Prepare Pt nano/HPA-WO_3 hybridized with HPA-C

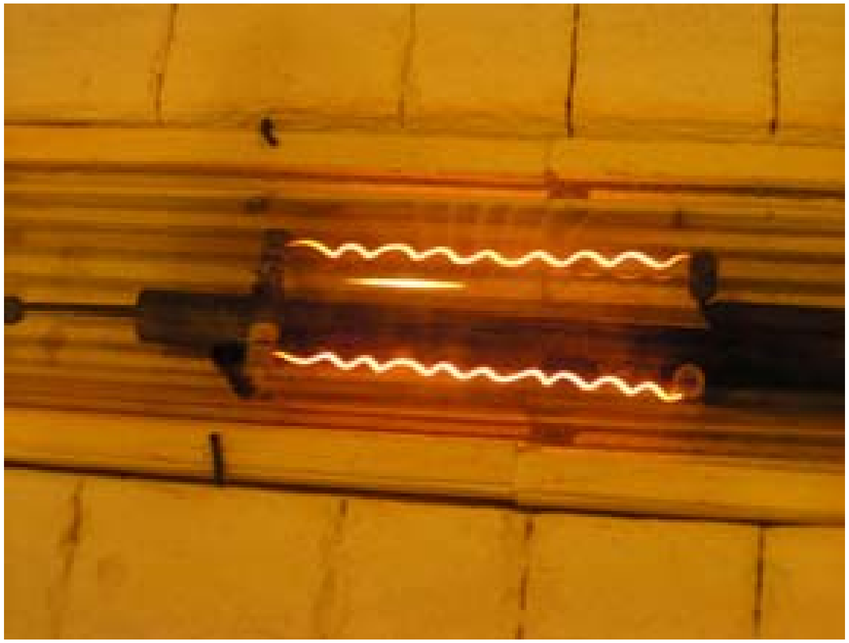
1. Measure corrosion currents on WO_3, MO_x
2. Measure corrosion currents on Pt/WO_3, Pt/HPA-C, etc.,
3. Measure ECA of Pt/WO_3, Pt/HPA-C, etc.,
4. Measure ORR activity of samples
5. Measure Peroxide currents of samples
6. Measure Cyclic durability of samples

Fuel Cell Test

Hot-Wire Chemical Vapor Deposition (HWCVD) — Synthesis of Metal Oxide Nanoparticles



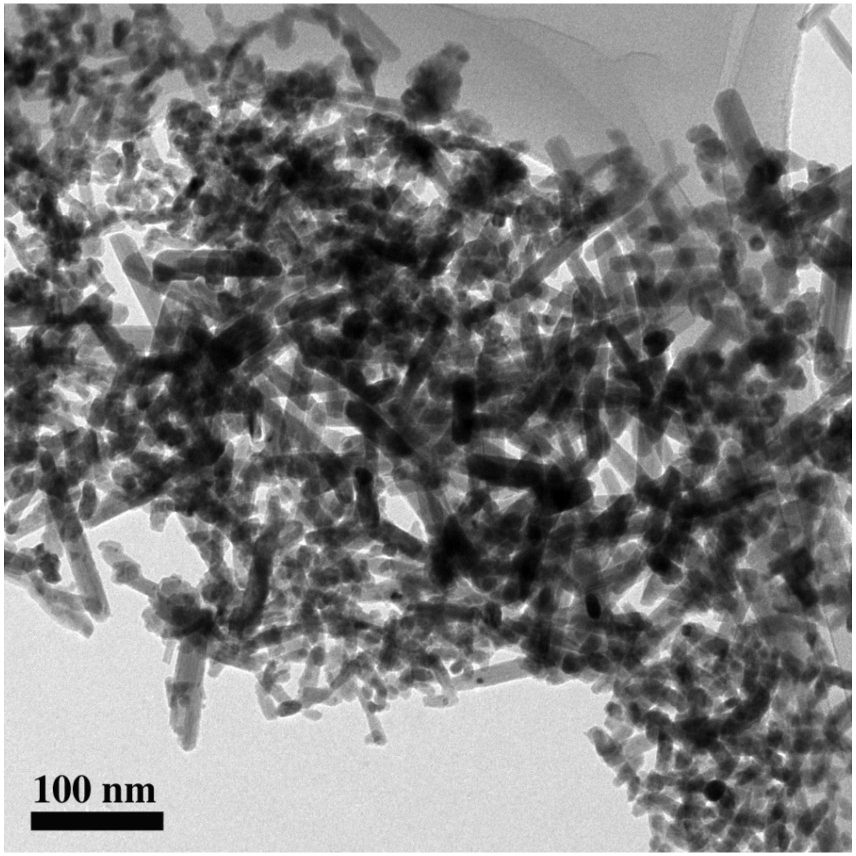




The filament is oxidized with a small O_2 partial pressure in Ar to form crystalline nanostructures.

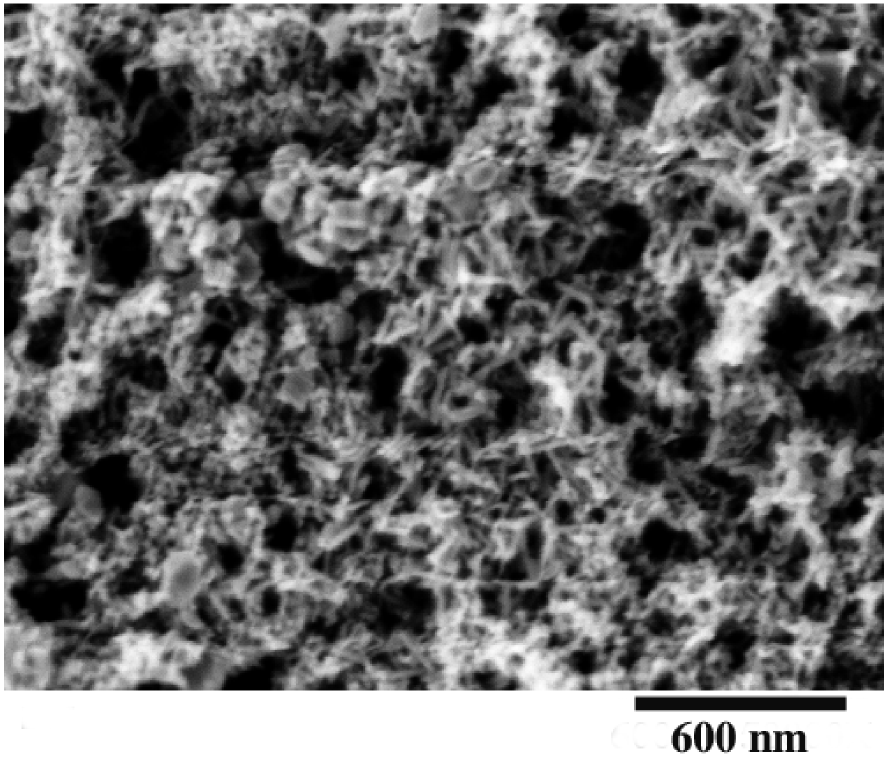
A Microscopic View

TEM



Starting Material

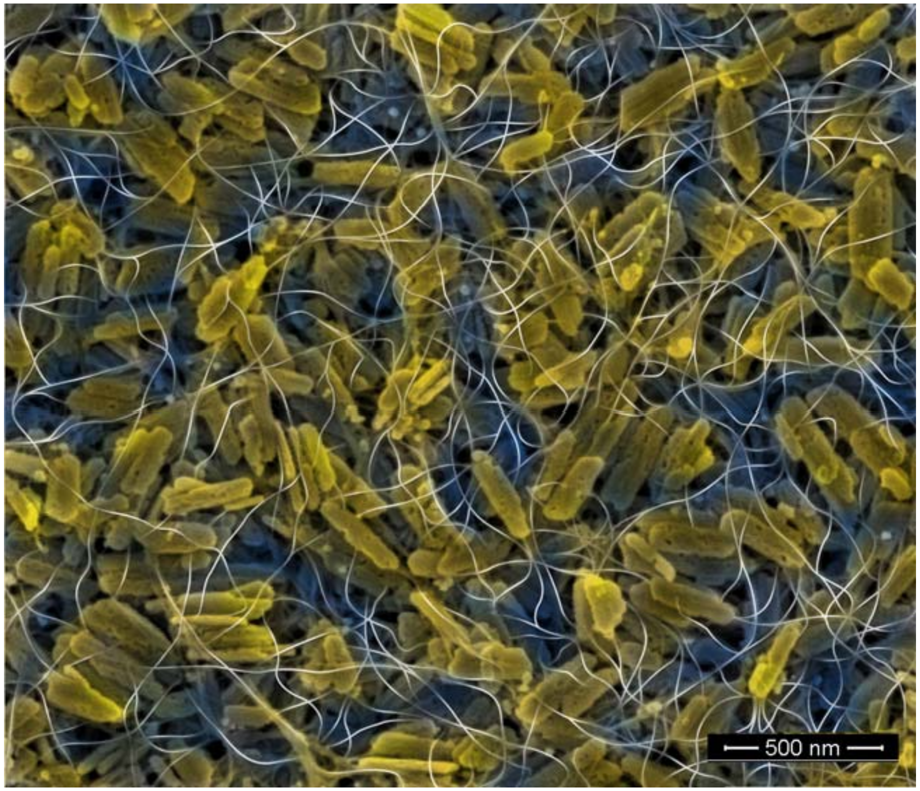
SEM



Porous Film via Electrophoresis

A high surface area porous film can be created on a variety of surfaces (e.g. transparent conducting oxide coated glass or polymers).

Metal Oxide Nanorods in a Carbon Nanotube Net



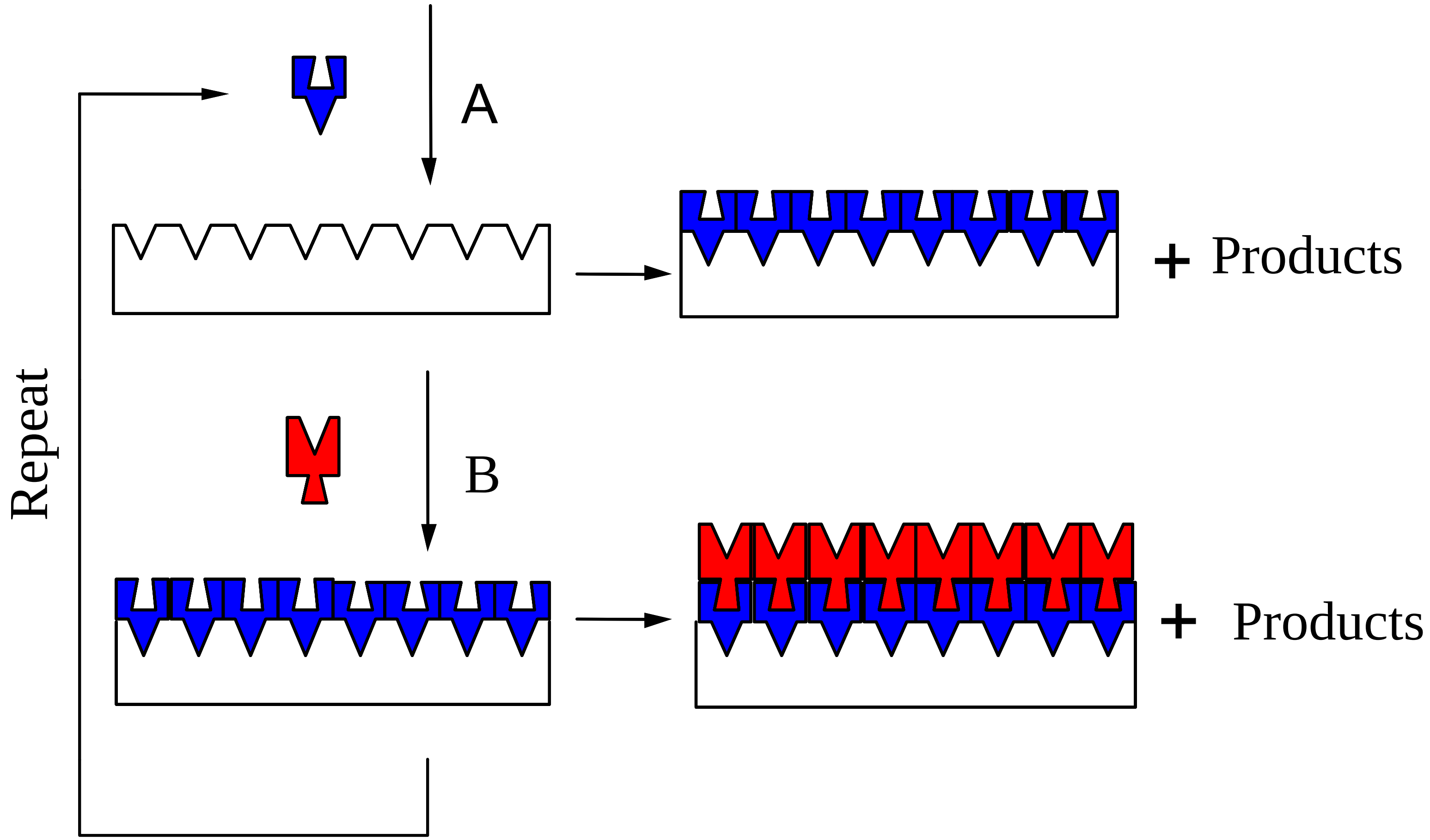
Metal oxide nanoparticles : yellow and blue
Carbon nanotubes: white

Reference :Advance Energy Materials

- •Metal oxide nanorods suspended with 5wt% carbon single-walled nanotubes.
- •Suspension subject to vacuum filtration.
- •Film may be transferred to various substrates.
- •Mild heat treatment may be required

WO_3 is not very conductive and may require the addition of conductive material

Atomic Layer Deposition (ALD) Based on Sequential, Self-Limiting Surface Reactions



Atomic Layer Deposition (ALD)

Layer by layer conformal Al_2O_3 coatings with sequential surface reactions

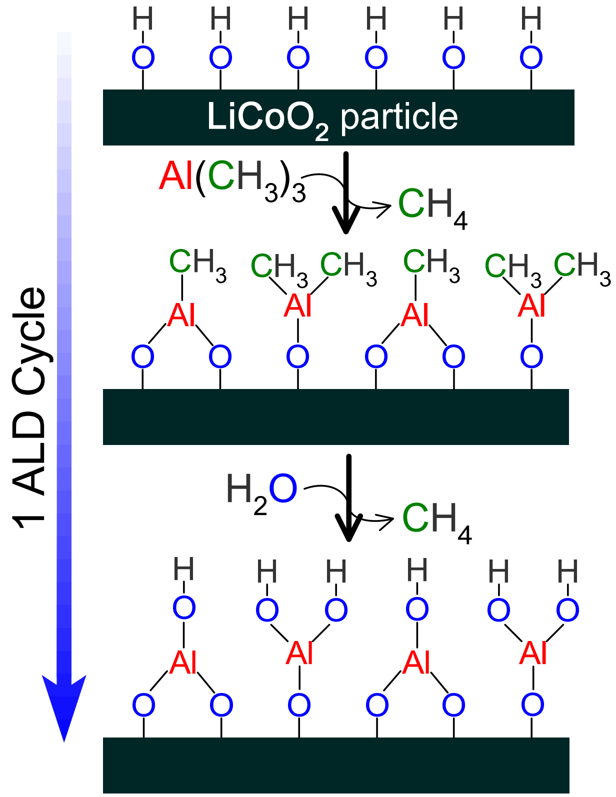
A) Surface-OH + $Al(CH_3)_3$

$\longrightarrow$ Surface-O-$Al(CH_3)_2$ + CH_4

B) Surface-O-$Al(CH_3)_2$ + 2 H_2O

$\longrightarrow$ Surface-O-$Al(OH)_2$ + 2 CH_4

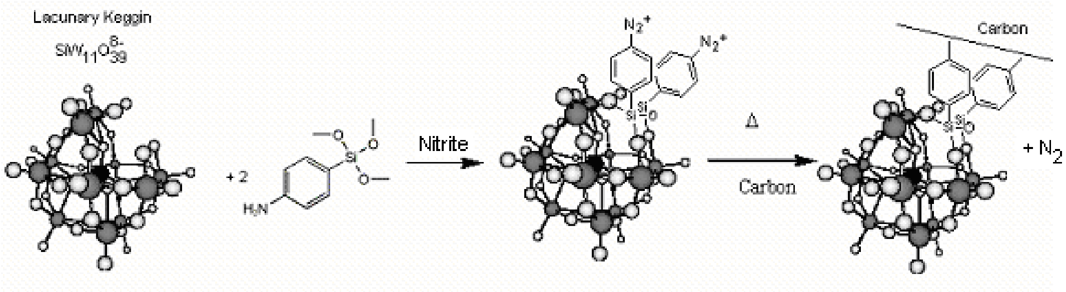
- No solvent, no excessive amount of precursors, No post-heat-treatment at high-temperature
- Sequential & self-limiting surface reaction, Conformal coating & Atomic thickness control

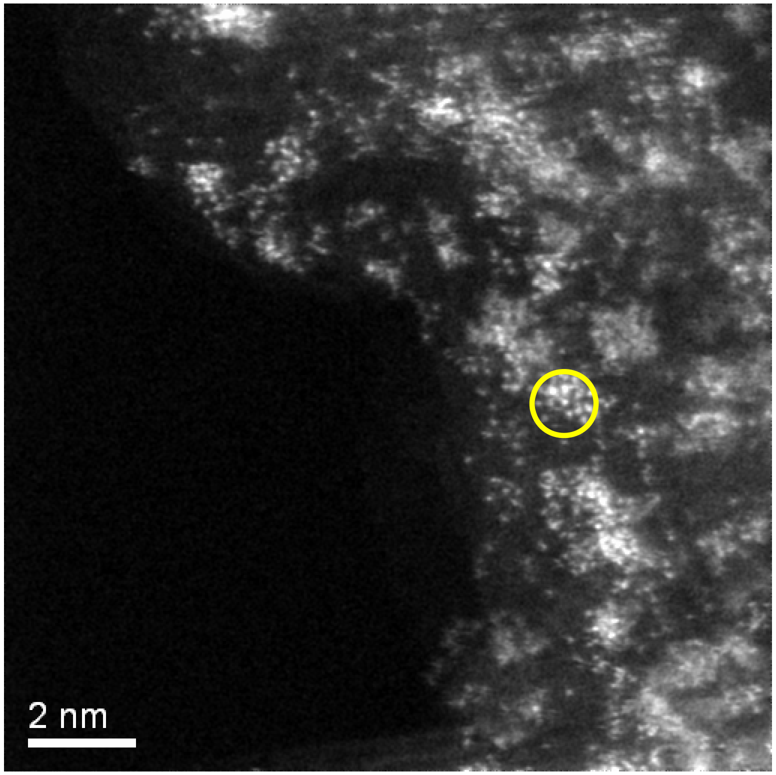


A.C. Dillon, A.W. Ott, J.D. Way and S.M. George *Surface Sci*. 322 (1995) 230.

Heteropoly Acid (HPA) Immobilization

1. Adsorption onto carbon, or
2. Better — attachment to carbon via chemical bonding, one example below…





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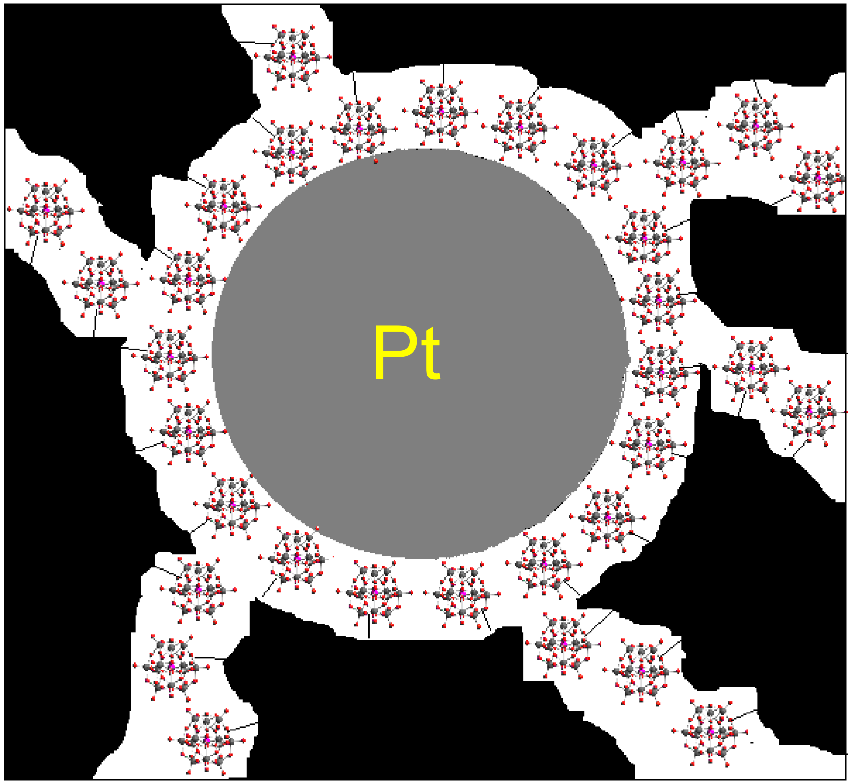
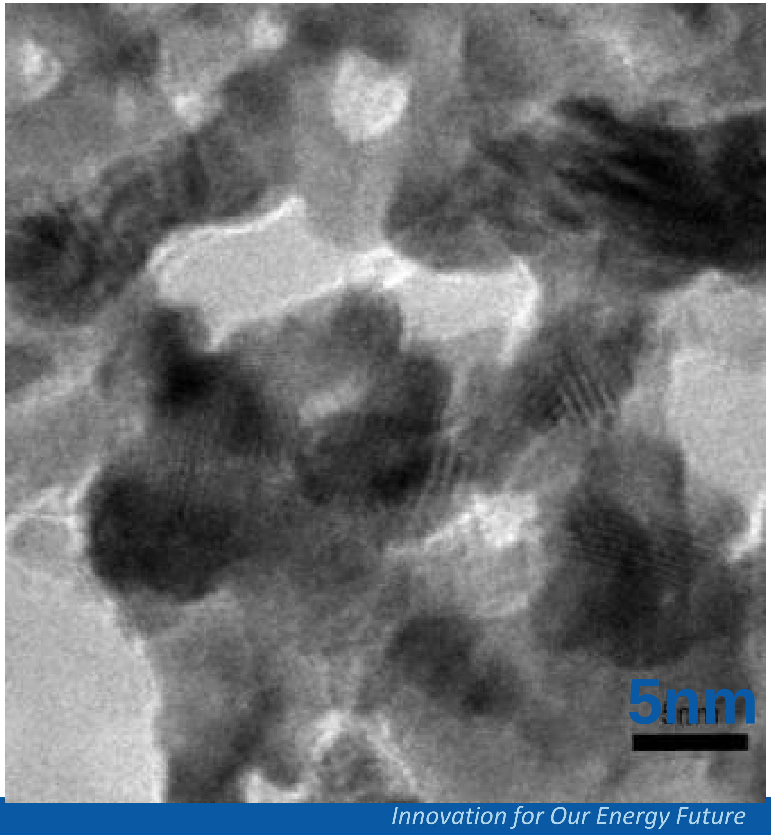
Immobilized HPAs as Catalyst Supports

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





Tungsten oxide nanowires grown on carbon paper as Pt electrocatalyst support for high performance proton exchange membrane fuel cells

Madhu Sudan Saha[a,1], Mohammad N. Banis[a], Yong Zhang[a], Ruying Li[a], Xueliang Sun[a,*],
Mei Cai[b], Frederick T. Wagner[c]

[a] Department of Mechanical and Materials Engineering, The University of Western Ontario, 1151 Richmond Street N, London, Ontario, N6A 5B9, Canada
[b] General Motors Research and Development Center, Warren, MI 48090-9055, USA
[c] General Motors Research and Development, Honeoye Falls, NY 14472-1039, USA

2.1. Growth of W18O49 nanowires

Before the growth of W18O49 NWs on carbon paper substrate, a thin tungsten film was first deposited on carbon microfibers of a carbon paper by RF magnetron sputtering using a tungsten target (purity 99.99%) in high purity argon (purity 99.999%). The chamber pressure was maintained at 4.6 × 10−3 Torr. After the sputtering, a thin 450 nm thick W film was obtained on carbon paper substrate. Subsequently, the sputtered carbon paper was placed in the middle part of a quartz tube, which was mounted horizontally inside a tubular furnace without using vacuum system. A carrier gas of high purity argon (99.999%) was passed through the quartz tube at a rate of 300 sccm (standard cubic centimeters per minute) through a hot water (90 °C) bath. After 20 min, the system was heated to 750 °C and was kept at this temperature for 30 min. Then the furnace was cooled down to room temperature in the flowing carrier gas. After the experiment, the colorless W film was observed to change to a dark purple-blue film; analysis of this film showed it to be an oxide, likely formed from reaction with adventitious air and/or water in the inert gas stream.

2.2. Deposition of Pt nanoparticles on W18O49 NW/carbon paper

Pt nanoparticles supported on W18O49 NW/carbon paper composites were prepared by the reduction of Pt precursors with glacial acetic acid as described previously [31]. In a typical preparation, the required amount of Pt precursor was added into 25 ml of glacial acetic acid, which was then agitated in an ultrasonic bath for 10 min. The W18O49 NWs/carbon paper was then soaked in the above solution, was heated to a temperature of 110 ± 2 °C, and was then kept at that temperature for about 5 h under constant stirring. Afterward, the Pt nanoparticles supported on W18O49 NWs/carbon paper (Pt/W18O49 NWs/carbon paper) composites were washed with deionized water and dried at 85 °C overnight in a vacuum oven. The Pt loadings of the Pt/W18O49 NW/carbon paper composites were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The morphologies of the composites were determined using a scanning electron microscope (SEM) (Hitachi S-2600 N) and transmission electron microscope (TEM) (Philips CM10). X-ray diffraction (XRD) analysis was also carried out with an X-ray diffractometer (Rigaku-MiniFlex) using Cu Ka radiation at 30 kV.

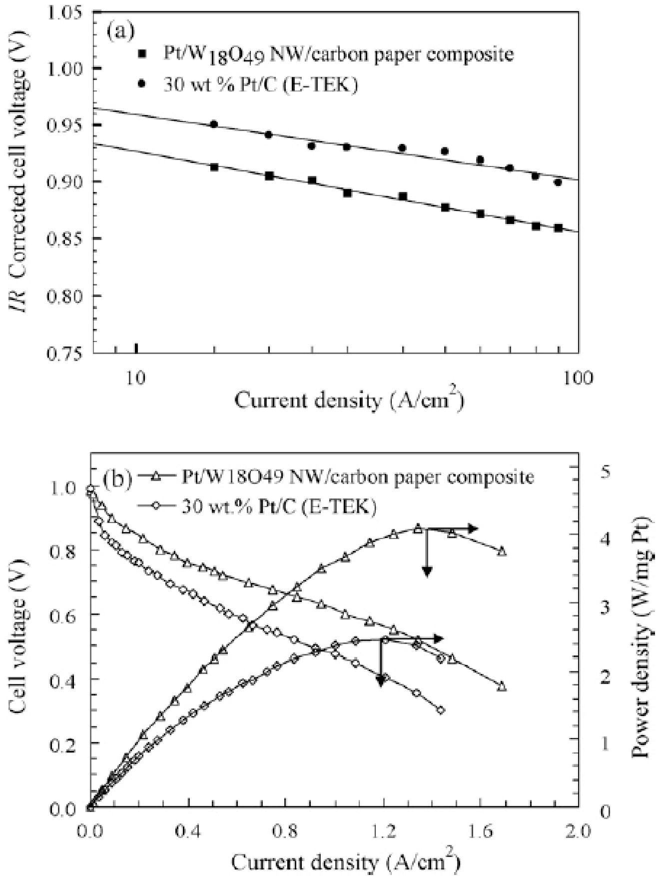


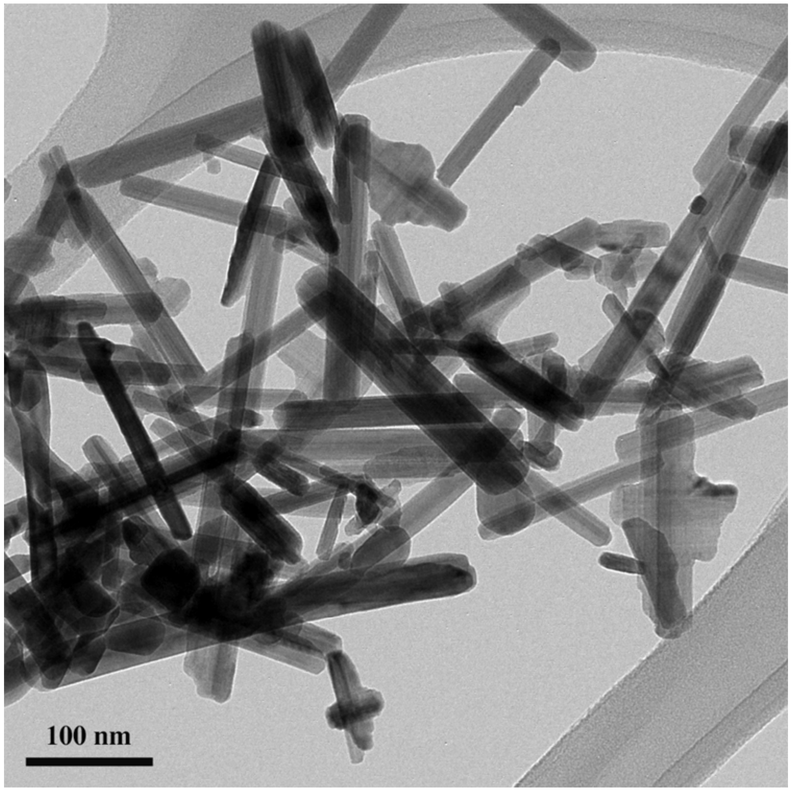
Fig. 5. (a) Comparison of the *iR*-free Tafel plots for oxygen reduction reaction. (b) Polarization curves and power density curves in single cell PEMFC of MEA's made with Pt/$W_{18}O_{49}$ NW/carbon paper composite (0.17 $mg_{Pt}\,cm^{-2}$) and conventional Pt/C electrode (0.20 $mg_{Pt}\,cm^{-2}$) as cathodes for H_2/O_2 at 80 °C, Nafion 112 membrane, 25/30 psig anode and cathode back pressure, respectively. Anodes were E-TEK gas diffusion electrode with a Pt loading of 0.5 $mg_{Pt}\,cm^{-2}$.

M.S. Saha et al. / Journal of Power Sources 192 (2009) 330–335

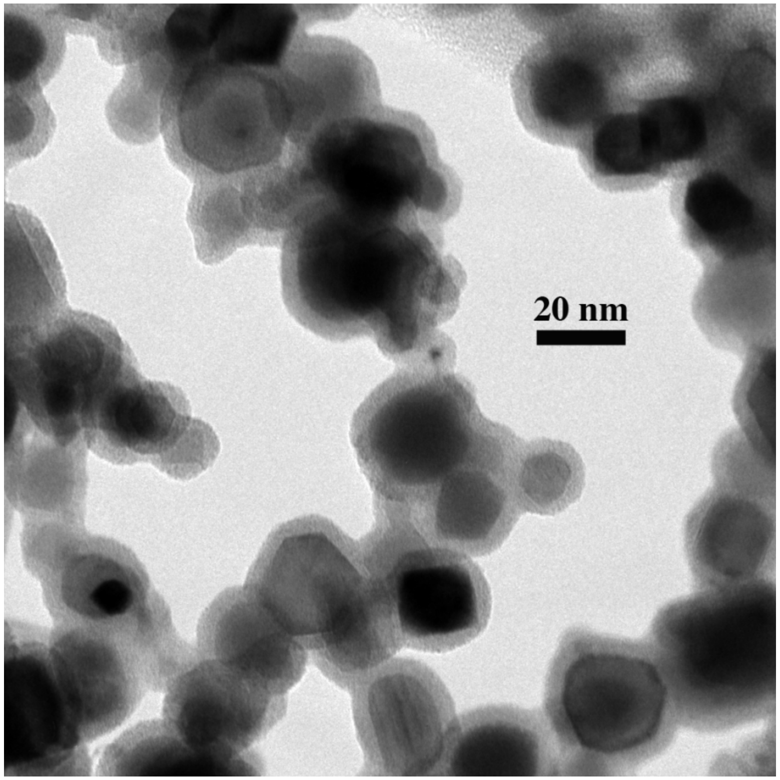
Accomplishments: Summary

- Project started at NREL and CU.
  - WO_3 nanoparticles grown using HWCVD @ NREL.
  - Pt deposited on WO_3 using ALD @ CU.
  - Baseline poly-Pt and Pt/C catalysts evaluated using rotating disk electrode @ NREL.
- Subcontract & SOW with Steve George/CU completed.
- Subcontract & SOW for Andy Herring nearing completion.

HWCVD Production of WO_3 Nanostructures



300 ˚C

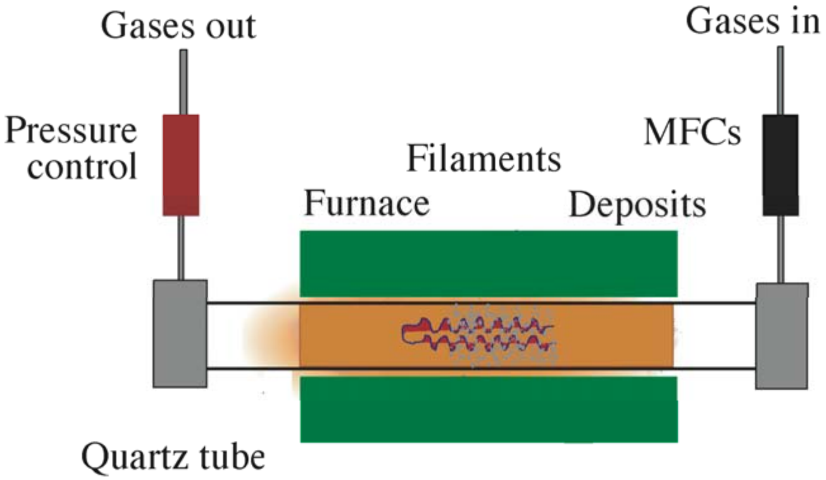


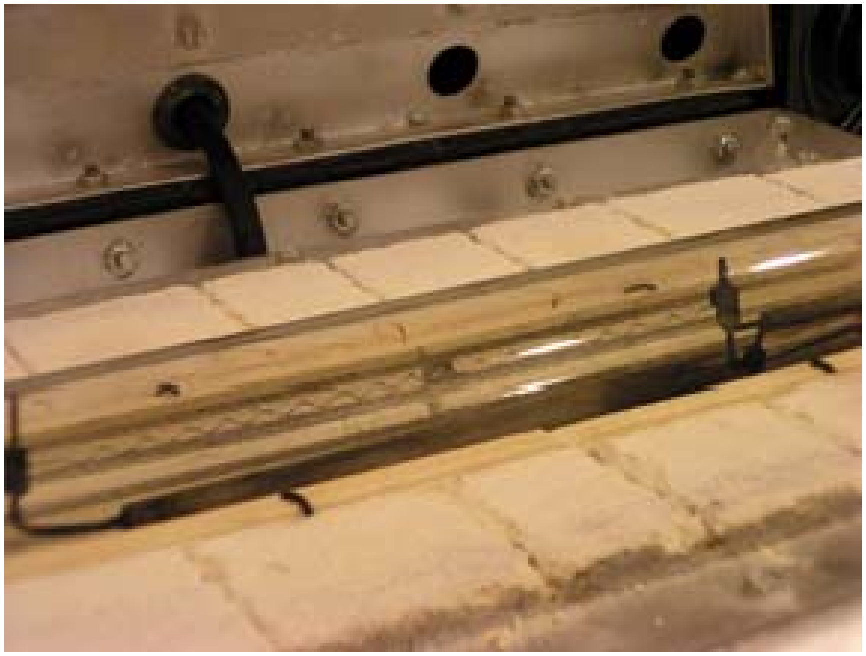
30 ˚C

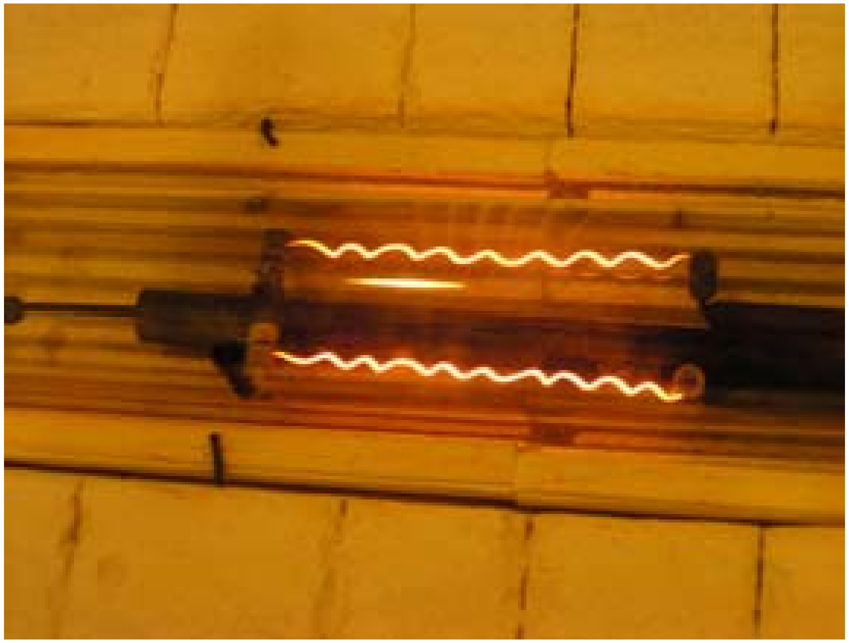
Synthesis at 150 Torr 4% O_2 in Ar, filament temperature ~ 2000˚C. Dramatic change in particle morphology by changing furnace temperature.

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

Hot-Wire Chemical Vapor Deposition (HWCVD) — Synthesis of Metal Oxide Nanoparticles



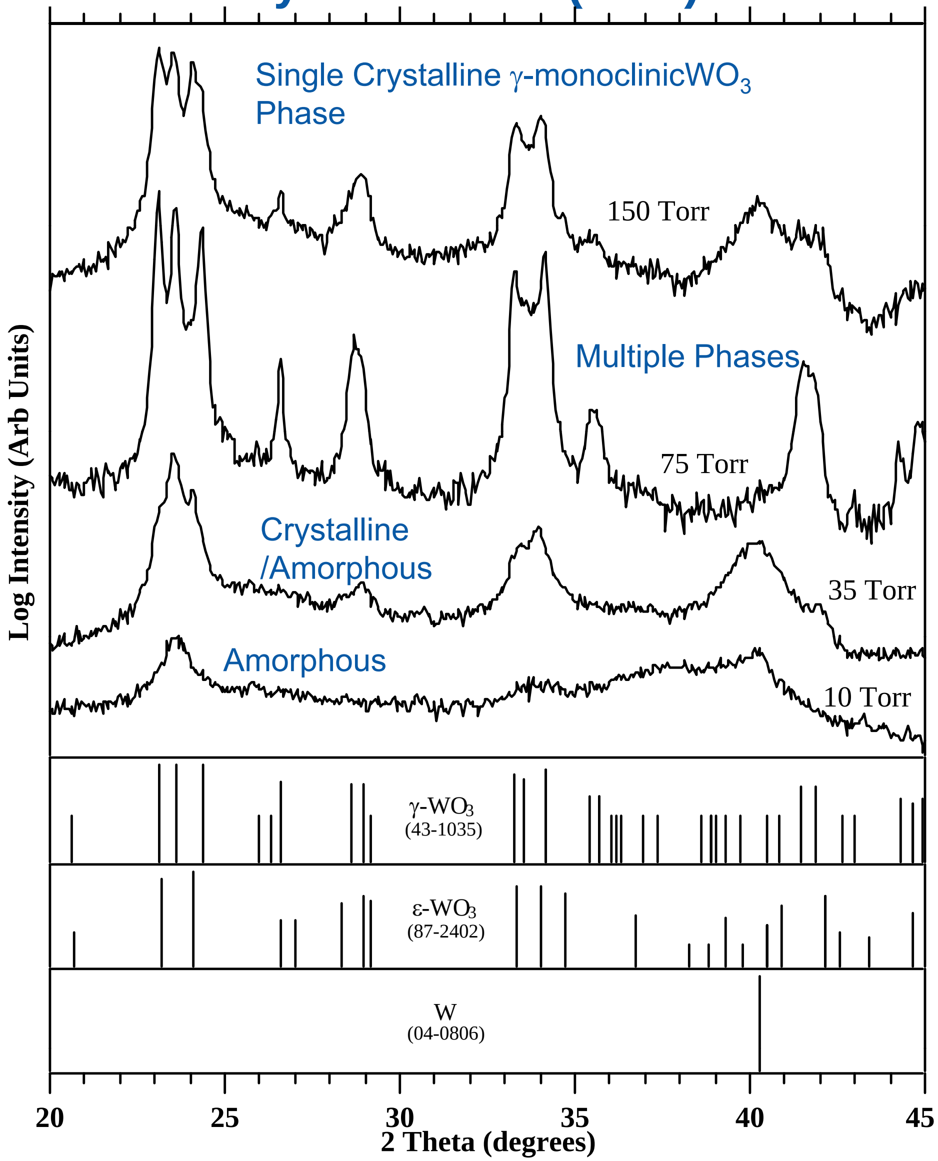




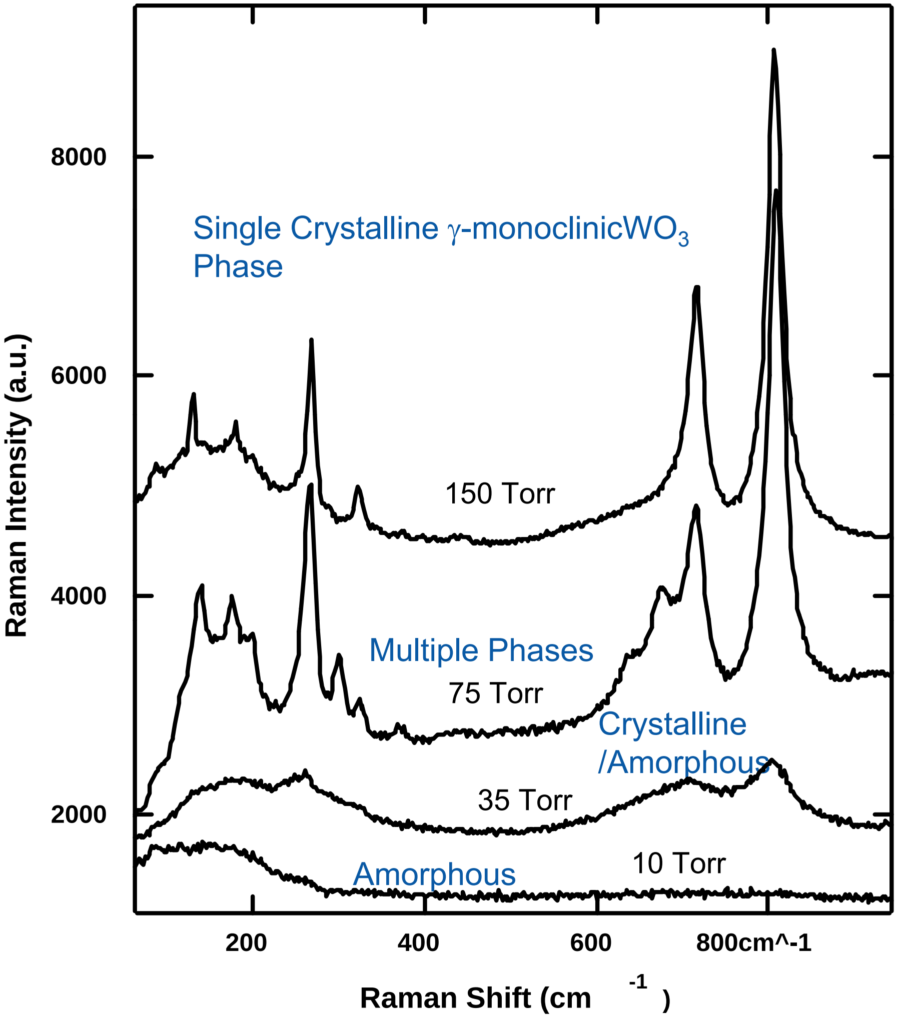
The filament is oxidized with a small O_2 partial pressure in Ar to form crystalline nanostructures.

Optimal Synthesis Conditions — Single Crystalline Phase

X-ray Diffraction (XRD)



Raman Spectroscopy



300˚C, 4% O_2 in Ar, filament ~ 2000˚C

Surface Chemistry for Pt ALD Using $MeCpPtMe_3 + O_2$

(A) $3O(ad) + 2(MeCp)PtMe_3(g) \rightarrow$

$2(MeCp)PtMe_2(ad) + CH_4(g) + CO_2(g) + H_2O(g)$

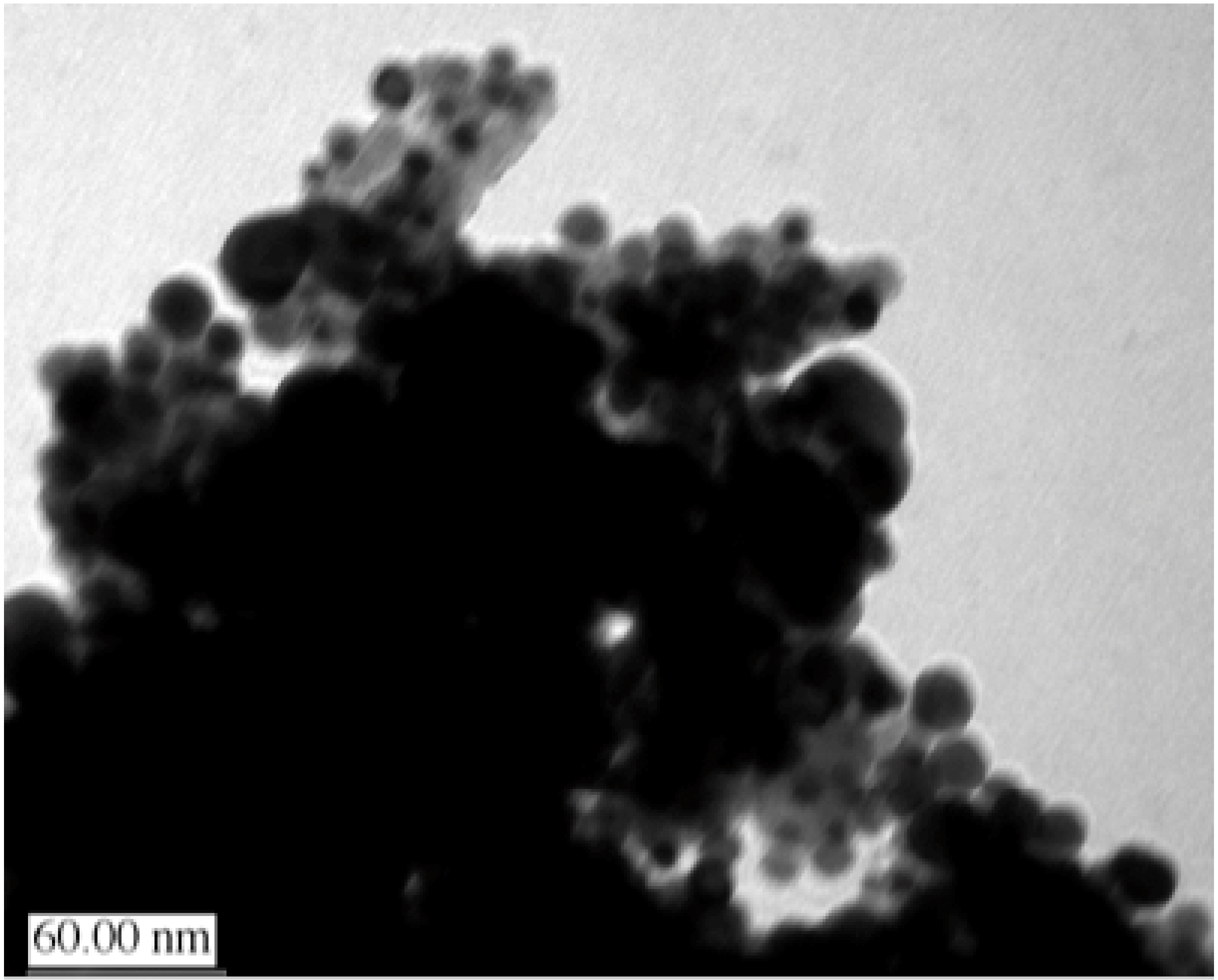
(B) $2(MeCp)PtMe_2(ad) + 24\ O_2(g) \rightarrow$

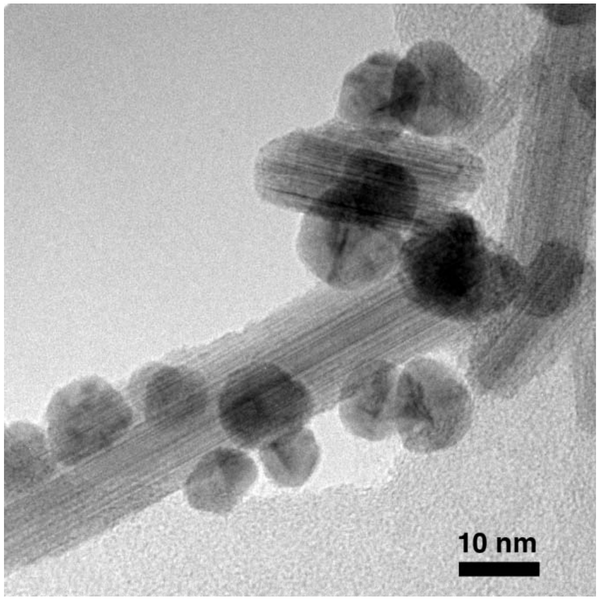
$2Pt(s) + 3O(ad) + 16CO_2(g) + 13H_2O(g)$

W.M.M. Kessels, *H.C.M. Knoops, SAF, Dielssen , A.J.M. Markus, M.C.M, van de SandenAppl. Phys. Lett. 95*, 013114 (2009)

Depositing metals with ALD requires more complex chemistries

Nanoparticles on WO_3 with ALD



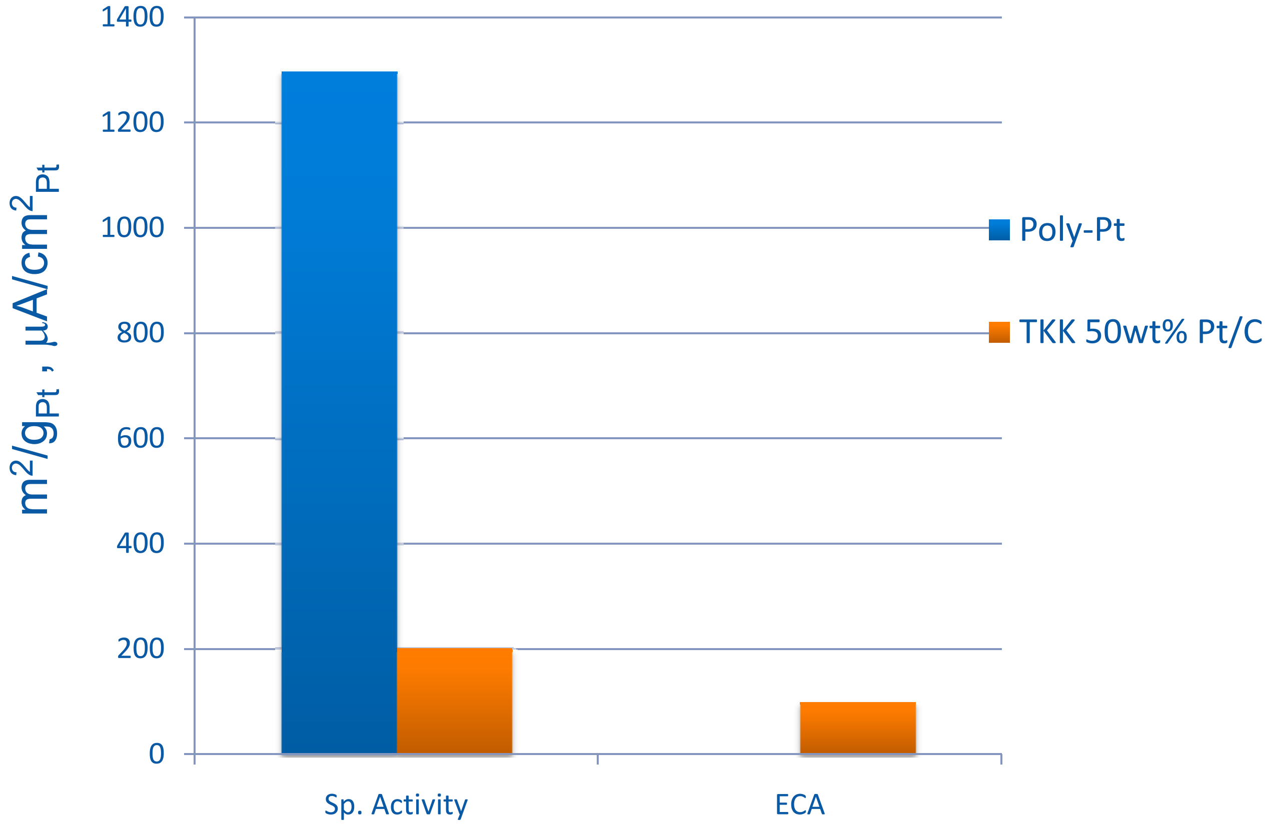


Next generation Pt nanoparticles will be targeted to approach 2-4 nm

COMPLETED:

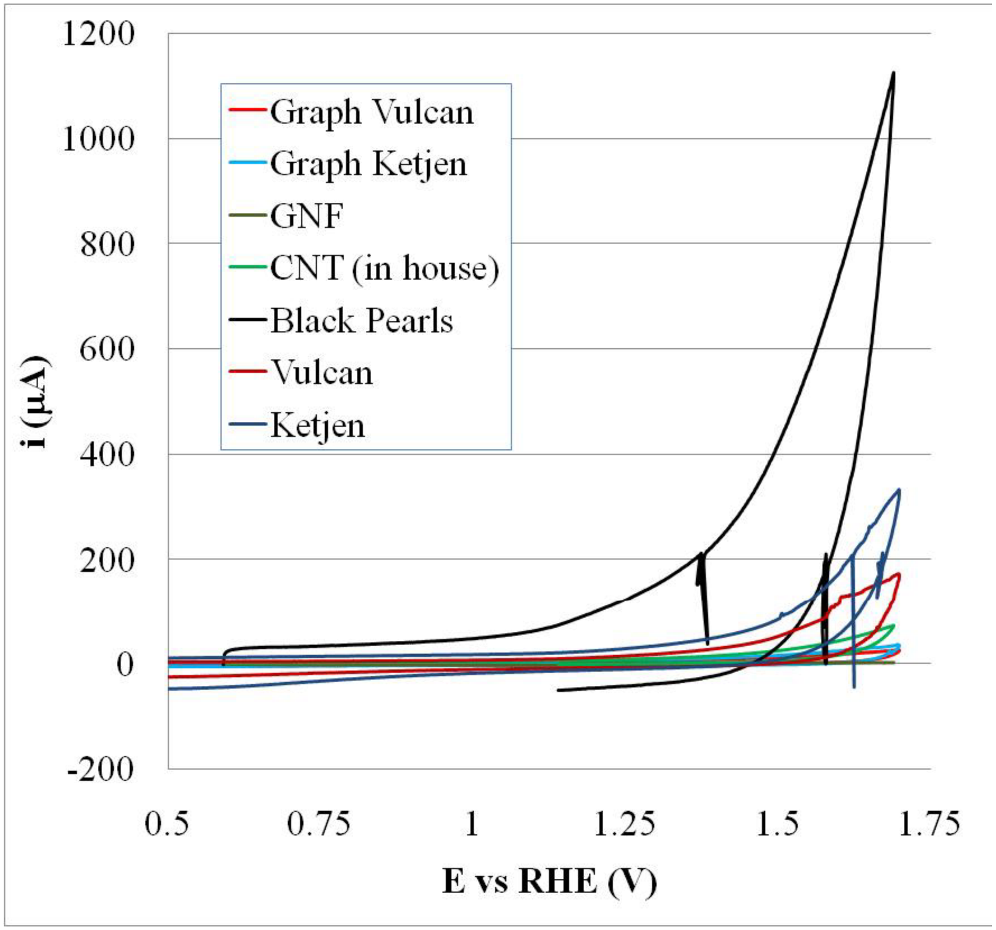
Demonstration of nano-structured Pt on WO_3, HPA, or a combination of the two. **09/2010.**

ORR Activity & ECA : RDE half-cell



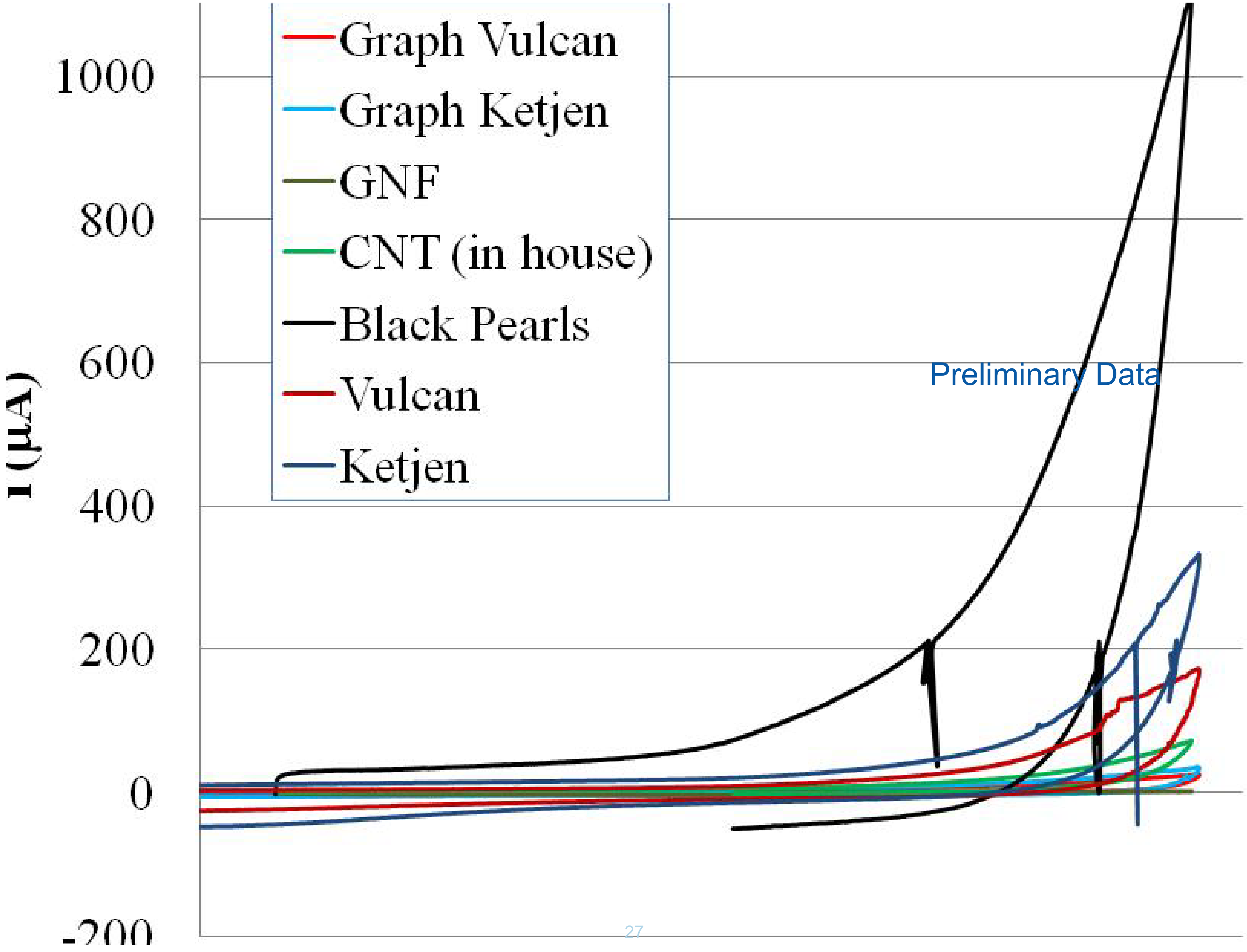
Preliminary Results using RDE in 0.1 M $HClO_4$ have been conducted on poly-Pt and TKK 50wt% Pt/C. Meet the ECA and activity benchmarks in literature.

Carbon Corrosion Onset: RDE half-cell



Preliminary Data

Graphitized and corrosion-resistant carbons exhibit positive shift of the onset of corrosion current.



Preliminary Data

Collaborations

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

Proposed Future Work

Sept – Dec 2010. Work will be continued on controlled nano-structured Pt placement and loading on WO_3, HPA, or a combination of the two. Microscopy and spectroscopy to characterize the materials will be conducted

Dec – Feb 2011. Conductivity of WO_3, Pt/WO_3 and Pt/WO_3 – HPA will be measured.

Jan – April 2011 High$_{sur}$ face area catalyst electrodes based on tungsten oxide and tungsten-based heteropoly acids (HPAs) will be prepared; they will be tested electrochemically in half-cells/corrosion cells. .

Jan – Sept 2011 Electrochemical area of Pt/WO_3 based on CVs in half-cells will be reported**..**

2011 – 2013 Variations of improved versions of Pt/WO_3 and Pt/WO_3 – HPA materials will be evaluated for ECA, ORR and peroxide currents in RDE experiments. Promising materials will be considered for testing as MEAs of subscale fuel cells.

Summary

The objective of this project is to enhance electrocatalyst & MEA durability and activity through the use of Pt/WO$_3$ and HPA modification to approach automotive PEMFC activity (4x increase) and durability target (5000h/10y).

At this time:

- Subcontract & SOW with CU has been completed.
- Subcontract & SOW for CSM nearing completion.
- WO$_3$ nanoparticles have been grown using HWCVD @ NREL.
- Pt has been deposited on WO$_3$ using ALD @ CU.
- Baseline poly-Pt and Pt/C catalysts have been benchmarked in RDE set-up.

Future on ongoing work will involve depositing small nanoparticles of Pt/WO$_3$ and Pt/WO$_3$ – HPA and evaluating them for conductivity, surface area, ORR activity and durability.

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Platinum tungsten oxide (Pt-WO_3) nanoparticles: their preparation in glycol and electrocatalytic properties

Kwok-Ying Tsang[a]; Tung-Chun Lee[a]; Jiawen Ren[a]; Kwong-Yu Chan[a]; Hengzhi Wang[b]; Huanting Wang[c]
[a] Department of Chemistry, The University of Hong Kong, Hong Kong, SAR, PR China [b] Department of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China [c] Department of Chemical Engineering, Monash University, Clayton, VIC 3800, Australia

2. Experimental

Colloidal platinum in ethylene glycol was prepared in a manner similar to previously reported [12, 18]. An ethylene glycol solution of $H_2PtCl_6 \cdot H_2O$ ($5.6\,\mathrm{mg\,mL^{-1}}$) was slowly added with stirring into a glycol solution of 0.5 M NaOH to obtain a transparent yellow platinum colloidal solution. This mixture was then heated at 160°C for 3 h, with flowing N_2 to take away water vapour and organic by-products. A transparent dark-brown homogeneous colloidal solution of Pt was obtained without any precipitation. Previously reported syntheses of WO_3 nanoparticles used tungstic acid dissolved in water. Here, we replaced the solvent with ethylene glycol so that it is compatible with the glycol synthesis of platinum nanoparticles. Another solution of 0.05 M tungstic acid together with 0.5 M NaOH in ethylene glycol was prepared and Vulcan XC-72 carbon powder was immersed in this solution to adsorb the tungsten precursor. Excess 2 M HCl solution was then added to the tungsten impregnated carbon suspension and kept at 80°C for 5 h. Tungsten oxide precipitated according to the reaction

$$WO_4^{2-} + H^+ \longrightarrow WO_3 + H_2O. \qquad (1)$$

The platinum colloidal solution was added afterwards and allowed to be adsorbed by the carbon and precipitated out in a period of 5 h. The Pt–WO_3 nanoparticle loaded carbon powder was collected by centrifugation and washed twice with ethanol. The amount of platinum precursor and tungsten precursor was predetermined and controlled. The dihydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot H_2O$) was supplied by Chempure Ltd and tungstic acid was supplied by Aldrich Chemical Company, Inc. Deionized water with 18.2 MΩ resistivity was produced by a Milli-Q ultrapure system. Organic solvents and other chemicals were analytical grade and used as received.