

Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes



**Bryan Pivovar (PI),
National Renewable
Energy Laboratory**

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Review and Peer
Evaluation Meeting**

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FC007

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

Start: July 2009

End: September 2013

% complete: 7%

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
\$8,384,342	\$867,763	\$9,252,105*
91%	9%	100%

Budget (\$K)

FY 2009	1480
FY 2010	1203
FY 2011	2177
FY 2012	2015
FY 2013	1508

*Final award amounts are subject to appropriations and award negotiations.

Barriers

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2005 Status ^a		Stack Targets	
		Cell	Stack	2010	2015
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
Mass activity ⁱ	A / mg Pt @ 900 mV _{IR-free}	0.28	0.11	0.44	0.44
Specific activity ⁱ	μA / cm ² @ 900 mV _{IR-free}	550	180	720	720

Partners

Oak Ridge National Laboratory (ORNL)
 Los Alamos National Laboratory (LANL)
 University of California-Riverside (UC-R)
 State University of New York – Albany (CNSE)
 Stanford University (Stanford)
 University of Tennessee (Tenn)
 University of Texas-Austin (Texas)
 Nissan Technical Center North America* (NTCNA)
 Cabot Fuel Cells* (Cabot)
 Tanaka Kikinzoku Kogyo* (TKK)

*non-subcontracted collaborators

*Project Kickoff Meeting 7/27/09

Relevance (I)

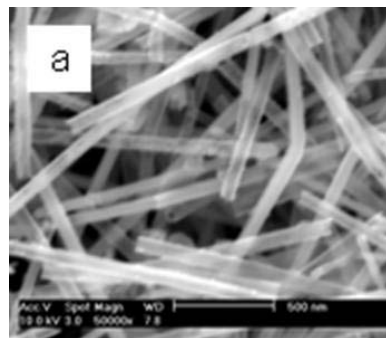
Extended, Continuous Pt Nanostructures

Novel Synthesis

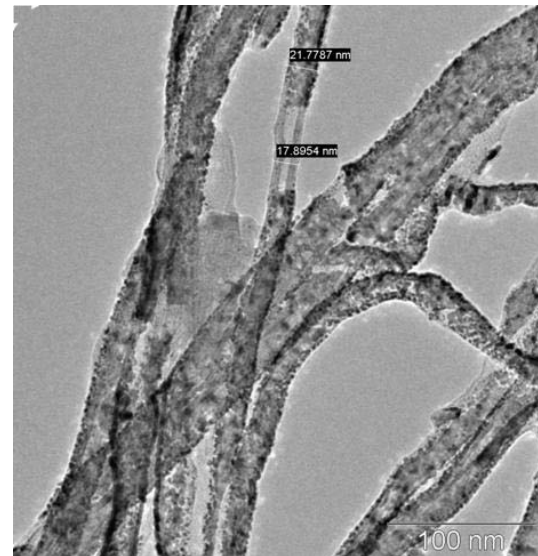
Objective: Produce novel catalysts based on extended Pt surfaces with increased activity and durability

3M's (and others) demonstrated improvements in specific activity and durability (bottom center and right) using similar materials have shown significant promise.

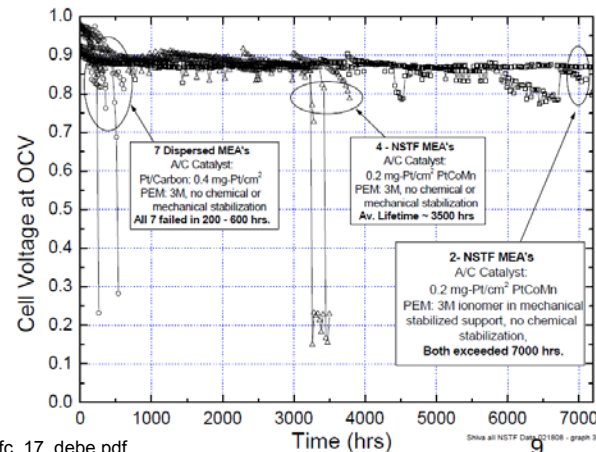
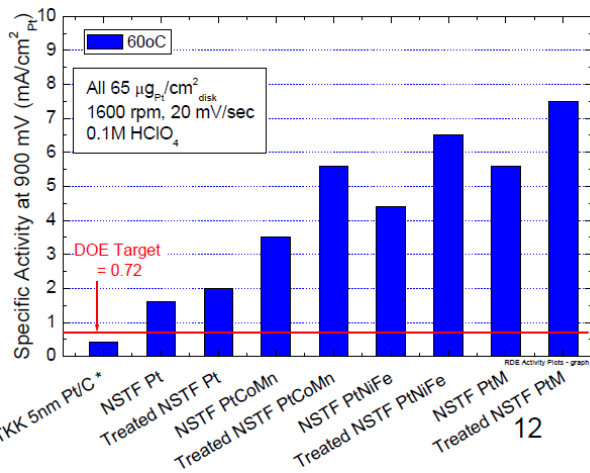
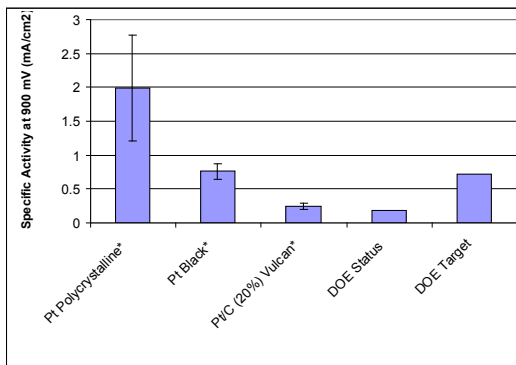
This project focuses on limitations in terms of mass activity and water management (next 2 slides).



Pt nanotubes (UC-R)



Pt coated carbon nanotubes (NREL)



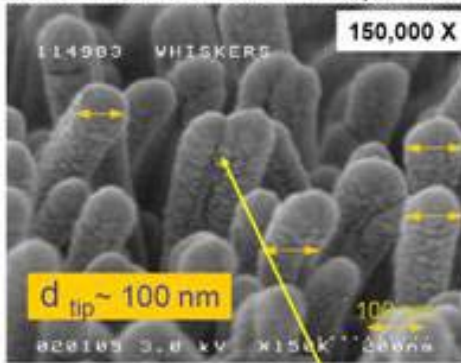
*Gasteiger et al., *Appl. Catal. B: Environ.*, 56, 9-35 (2005)

*http://www.hydrogen.energy.gov/pdfs/review09/fc_17_debe.pdf

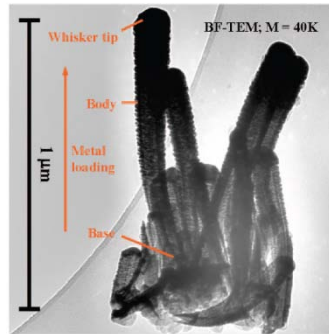
Relevance (II): Improved mass activity

Project Summary : Status Against DOE Targets – March, 2009

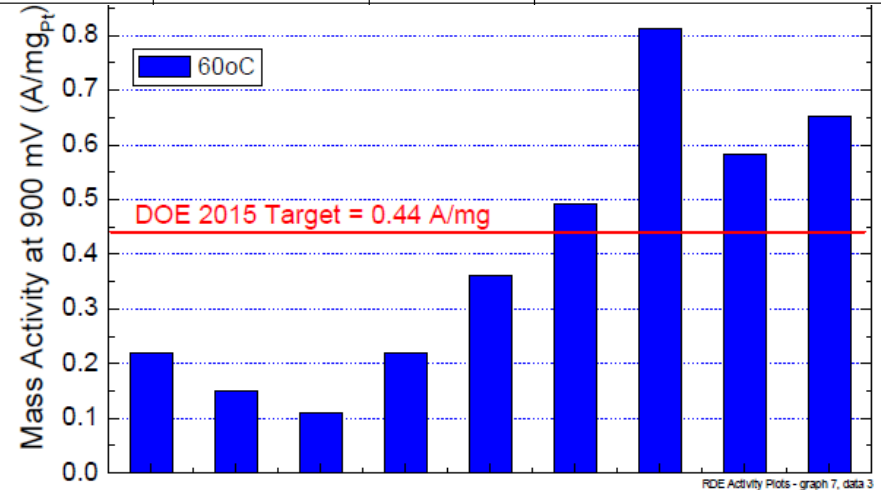
Subtask 1.1 NSTF surface area optimization



Surface Roughness Factor may be : $\Gamma_f \sim 1.5$ to 2 ?
 Tip diameter : $d_{tip} \sim 100$ nm
 Base diameter : ~ 50 nm of bare whisker
 Mean diameter over length taken as average of base and tip: $d_{av} \sim 75$ nm



Characteristic	Units	Targets	3M Status – 3/09
		2010 / 2015	(mfg'd roll-good)
Mass Activity (150kPa H ₂ /O ₂ 80°C. 100% RH)	A/mg-Pt @ 900 mV, 150kPa O ₂	0.44 / 0.44	0.16 A/mg in 50 cm ² w/ PtCoMn 0.33A/mg in 50 cm ² with new Pt _x M _y



Particle	Pt Shells	Surface Pt
2 nm cubooctahedron	5	52%
5 nm cubooctahedron	12	24%
12.5 nm Pt coated(50 nm core) cylinder	29	~5%

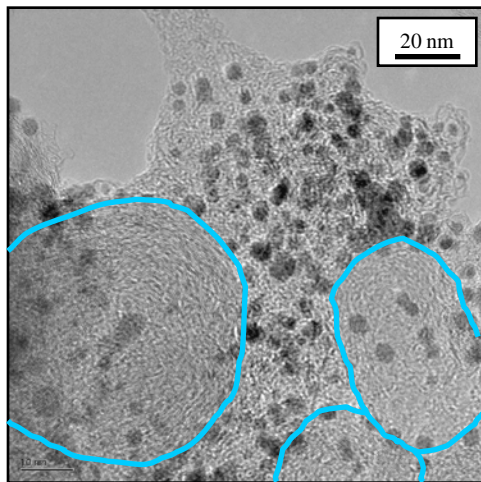
Objective: Further increase mass activity of extended surface catalysts

Mark Debe, 3M, DOE Annual Merit Reviews
http://www.hydrogen.energy.gov/pdfs/review07/fcp_25_debe.pdf,
http://www.hydrogen.energy.gov/pdfs/review09/fc_17_debe.pdf
 Gancs et al. *Chem. Mater.* **2008**, *20*, 2444–2454

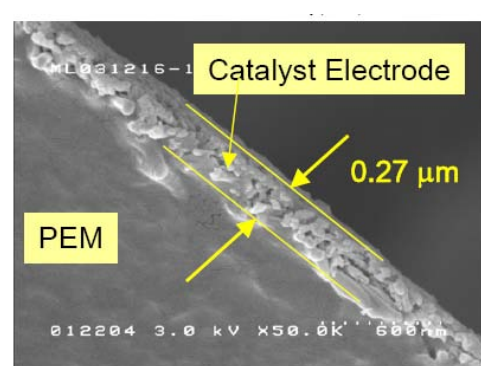
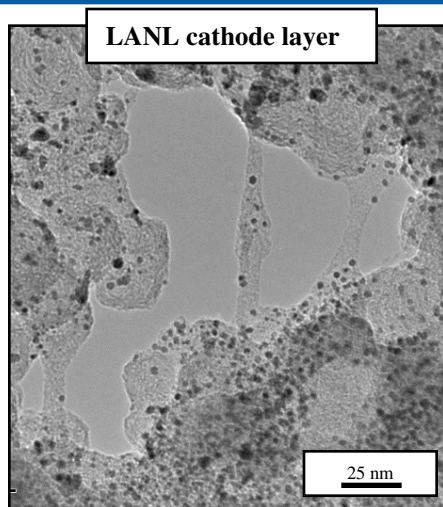
3M's approach (while exceptionally promising) has limits related to the use of nonconductive substrates and line of sight deposition process.

Relevance (III)

Dispersed Electrode Studies

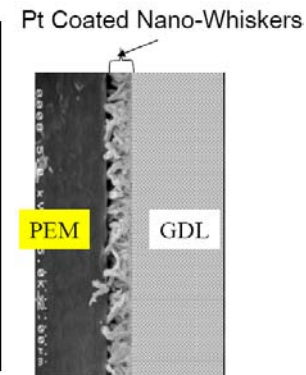


HR-TEM Karren More ORNL



SEM of 3M's NSTF MEA

http://www.hydrogen.energy.gov/pdfs/review04/fc_4_debe.pdf



Z ~ 0.5 micron

Electrode Studies

Objective: Effectively incorporate extended Pt catalysts into more traditional dispersed electrodes for mass transport/water management

Dispersed (traditional) electrodes (~10 μm) have shown exceptional tolerance over wide ranges of operating conditions, including those relevant for transportation applications (hot/dry and cold/wet). To date, such structures have not been demonstrated with extended Pt surfaces. Inherent electronic connectivity may help overcome “particle-size” related effects. Ionomer inclusion in catalyst layer may help cold start.

Table 3.4.13 Technical Targets: MEAs				
Characteristic	Units	2005 Status ^a	2010	2015
Operating temperature	°C	<80	<120	<120
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Cost ^b	\$/kW	60 ^c	10	5
Durability with cycling				
At operating temp of ≤80°C	hours	~2,000 ^d	5,000 ^e	5,000 ^e
At operating temp of >80°C	hours	N/A ^f	2,000	5,000 ^e
Unassisted start from low temperature	°C	-20	-40	-40
Performance @ ¼ power (0.8V)	mA / cm ² mW / cm ²	200 160	300 250	300 250
Performance @ rated power	mW / cm ²	600	1,000	1,000
Extent of performance (power density) degradation over lifetime ^g	%	5 ^h	10	5
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

Approach: Overview

1. Novel Synthesis
 - a. Core/Templates
 - b. Pt Deposition
2. Electrode Studies
3. Modeling

Project Timeline (Table of associated Milestones and Decision Points follows)

Task*	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16
1ai	M			MG				M				MG				
1aii	M	G				MG			M							
1aiii	M					MG		M			M					
1aiv	M					MG				M						
1bi ^a	M	M				MG										
1bi ^b						M				M		M		MG	MG	
1bii	M			M		M				M				MG	MG	
2a				M				MG				M				
2b				M						M				MG	MG	MG
3 ^c				M						M						M
3 ^d						M				M						M

*Task descriptions can be found in *Work Plan Outline*. ^aPVD coatings; ^bALD coatings; ^ccatalyst modeling; ^delectrode modeling
 Q represents quarter from start date; M represents Milestones; G represents go/no-go decisions
 Milestones due and go/no-go decisions enacted at end of quarter in which they appear
 active task during quarter; active task during quarter pending go/no-go decision; inactive task

Go/no-go decisions focus primarily on down selection of substrates and deposition processes to those of novel structures showing targeted/improved performance and durability.

Milestones

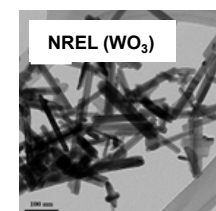
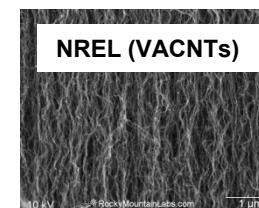
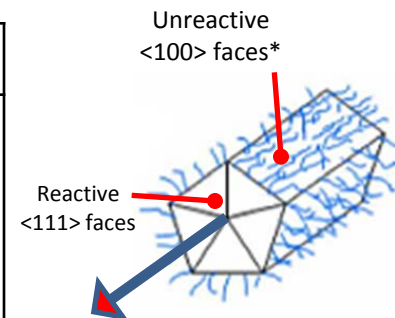
Supply first generation carbon nanotubes, metal oxide nanoparticles, and whiskers for initial platinum deposition studies.	09/09 Complete
Synthesize 1st generation Pt coated nanostructures by physical vapor deposition for electrochemical characterization.	09/09 Complete
Supply 1st generation Pt nanotubes synthesized from Ag nanowires for electrochemical testing and electrode studies.	09/09 delayed due to sub-contracting issues
Go/no-go decision for 1st generation CNTs. Based on initial studies of CNTs by coating techniques if continuous coatings are not obtained begin 2nd generation CNT synthesis.	12/09 Complete
Complete parametric study of PtNT production as influenced by Pt supplied, reaction time, Pt surface area, and resulting wall thickness.	05/10
Demonstrate (at least 3) 1st generation continuous nanostructured Pt catalysts in fuel cell testing.	09/10

Approach

(1a) Core/Templates

*adapted from Majidi, E., & Gates, B. (2007), *mrs.org*, 1017.

Template (Prioritized)	Advantages	Disadvantages
Metal (wires, tubes, etc) (UC-R, NREL)	Highly conductive Alloy improvements Galvanically displaceable Controlled surface structure	Catalytic inhibitors Stability under operating conditions Limited materials/ morphologies
Carbon Nanotubes (CNTs) (NREL)	Highly conductive High corrosion resistance Carbon abundance Dopants Surface modification	Cost (although still cheap compared to Pt) Poor wettability Processing Limited chemistries/ morphologies
Metal oxides* (CNSE, NREL)	Many different materials Many demonstrated structures	Conductivity/Corrosion resistance (in many cases)
Whiskers* (NREL)	Cost Corrosion resistant Demonstrated/Optimized in 3M's NSTF	Non-conductive Limited morphologies



*see supplemental slides 28-29 for more detail.

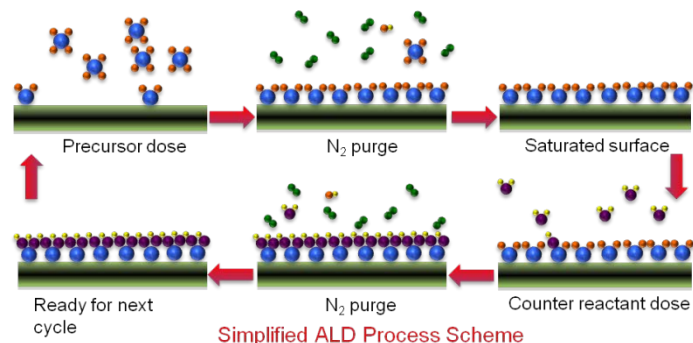
Approach

(1b) Pt Deposition/ Coating Techniques

Vapor Deposition (evaporation, CVD, PLD)

sputtering

atomic layer deposition* (ALD)



Solution Deposition (electrochemical, spontaneous, underpotential)

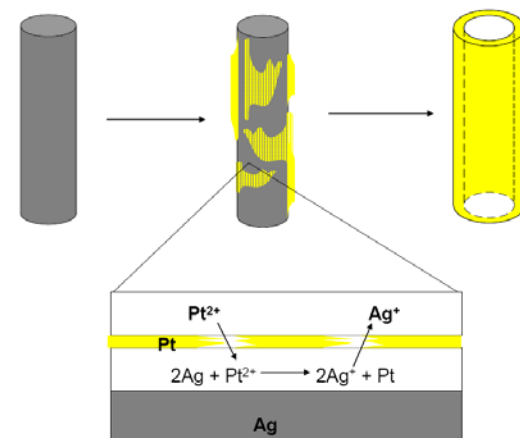
spontaneous galvanic displacement

Specific Issues Considered

Line of sight vs. non-line of sight

Inherent difficulty of forming continuous thin Pt skin*

Ag Nanowire (AgNW) Template Method



*see supplemental slides 30-34 for more detail.

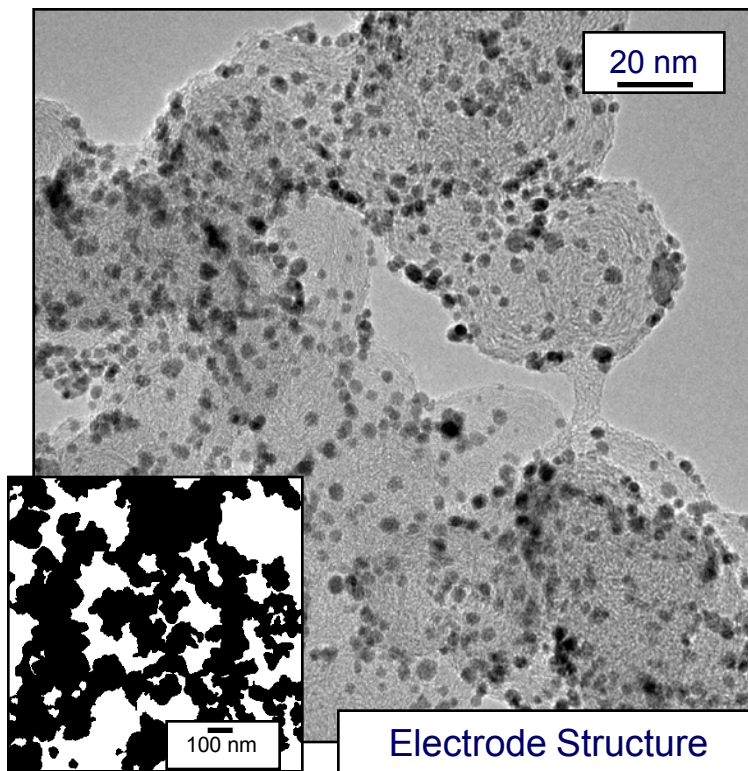
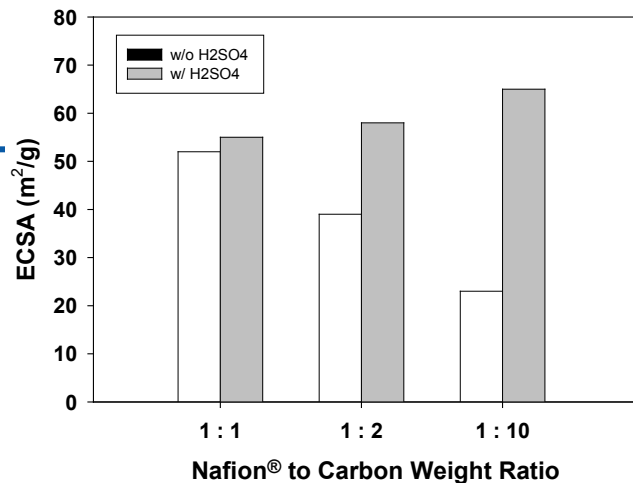
Approach

(2) Electrode Studies

We will perform electrode studies that specifically include extended-surface catalysts.

These studies will build off of work our team has performed on traditional systems, coupling electrochemical properties (ECSA, activity, durability with structure and composition).*

Factors investigated will include porosity, composition, processing, and architecture (to better assess performance and durability).



20% Pt/C
TEM, ORNL

*H. Xu, E. Brosha, F. Garzon, F. Uribe, M. Wilson, and B. Pivovar, *ECS Transactions*, 2007; 11, 1, 383.

*H. Xu, E. Brosha, K. More, F. Uribe, F. Garzon, B. Pivovar, in prep.

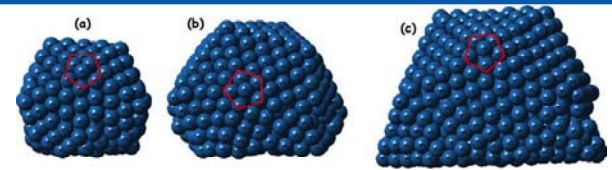
*see supplemental slides 41-43 for more detail.

Approach

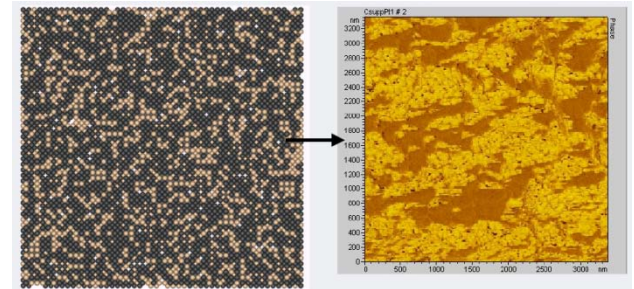
(3) Modeling Studies

Our development of novel catalysts and implementation in electrodes will be supported through (NREL) coordinated modeling efforts. 3 Thrusts*:

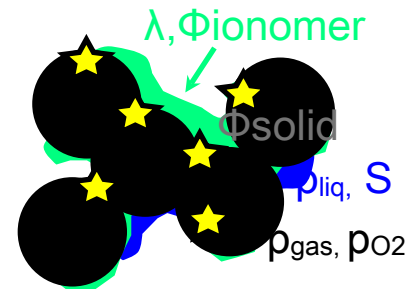
1. Simulations involving Pt film and extended Pt structure formation (Tenn).
2. Simulations of architectures based on extended Pt structures into “thick” electrode structures (Tenn).
3. Simulations of the performance of fuel cells based on thick electrodes with extended structure Pt catalysts (Texas).



Simulations developed to describe Pt particle size and structure on carbon supports will be expanded to include other approaches taken in the project.



3D simulations take into account composition of electrodes.



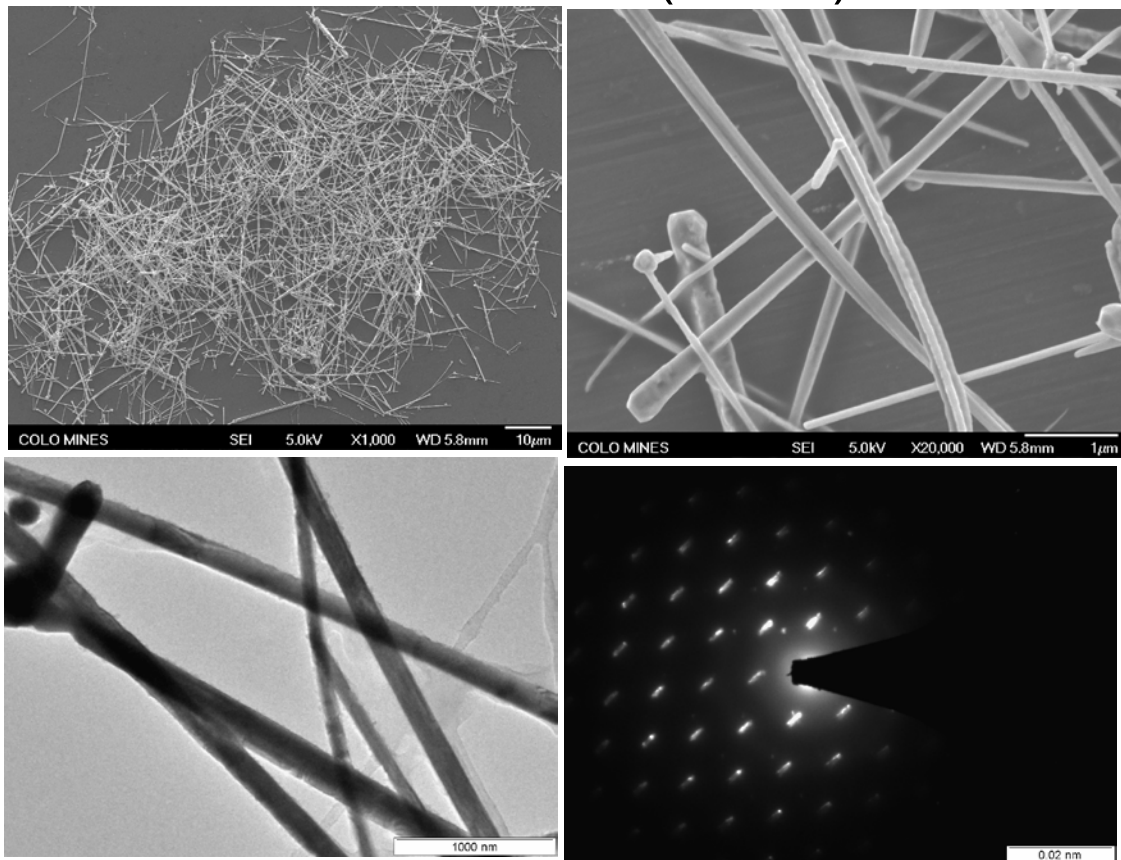
Extension of established porous electrode models to highlight issues critical to the incorporation of extended surfaces in thick, dispersed electrodes

*see supplemental slides 42-46 for more detail.

Technical Accomplishments and Progress

Metal Templates

Cu Nanowires (NREL)



Ag and Se nanowires demonstrated as templates for Pt and PtRu nanowires (UC-R).¹

Cu nanowires much less studied (NREL), we have developed novel (quicker, potentially cheap) route.

Cu has been used for similar galvanic displacements reactions.²

Pt-Cu alloys shown to be advantageous for activity.³

Microwave assisted surfactant mediated growth (wet chemical process)

[1] Z. Chen, W. Li, M. Waje, Y. S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060-4063.; VIP and Frontpiece Picture

[2] J. Zhang, F.H.B. Lima, M. H. Shao, K. Sasaki, J.X. Wang, J. Hanson, R. R. Adzic, *J. Phys. Chem. B*, 109 (2005) 22701-22704.

[3] R. Srivastava, P. Mani, N. Hahn, P. Strasser, *Angew. Chem. Int. Ed.* 46 (2007), 8988.

Technical Accomplishments and Progress

Carbon Nanotubes (CNTs)

Meaningful effort in this area. Included the investigation of single walled, multi-walled, and vertically aligned (VACNTs) CNTs

Investigated synthesis routes focusing on water assisted CVD (due to high purity, amorphous carbon etching, improved growth, and extended catalyst lifetime).

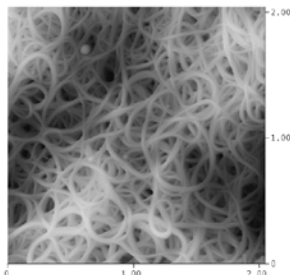
Focused on catalyst deposition as we found this key for reproducibility.*

Investigated the effect of Ar-plasma, O-plasma, ozone, and trimethyl aluminum pre-treatment on surface composition.

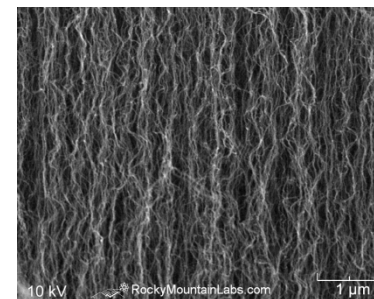
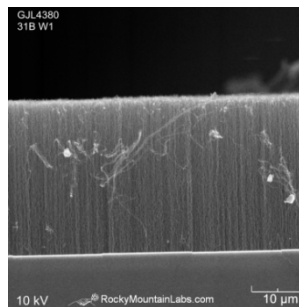
Investigated mats and VACNTs as deposition substrates.

(VA)CNT growth modes investigated

Growth Method	Catalyst Source	Carbon Source	Carrier Gas	Morphologies
CVD (std)	Ferrocene	Xylene	Ar/H ₂	MWNTs
water-assisted CVD	Iron, sputtered	Ethylene	He/H ₂	MWNTs, SWNTs
ALD/water-assisted CVD	Ferrocene	Ethylene	He/H ₂	DWNTs, TWNTs



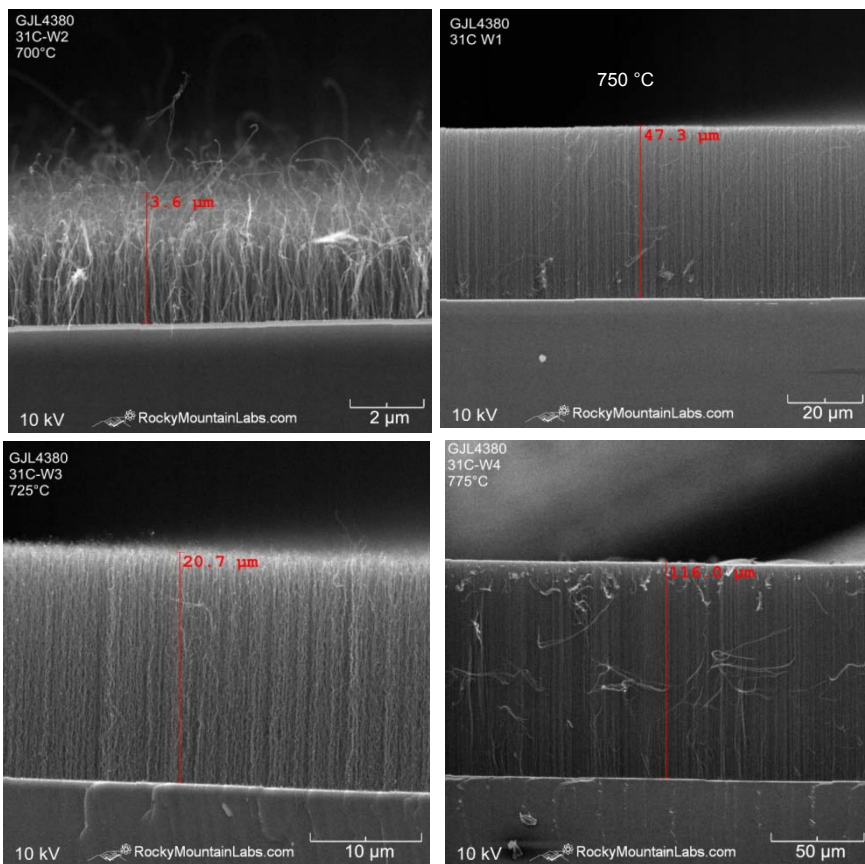
CNT mats



*see supplemental slides 26-27 for more detail.

Technical Accomplishments and Progress

Effect of Temperature on VACNT Growth



Temperature Dependence of the Average Height and Width for the VACNTs

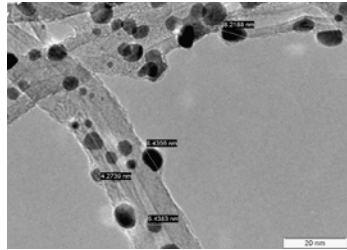
Temperature (°C)	CNT Width (nm)	Height (μm)
700	30	3-5
725	20	21
750	15	50
775	15	115
800	12	87

Significant changes were observed in CNT width, height, and tube-tube packing density with respect to changes in temperature.

We have at our availability a number of CNTs. Developmental work on VACNTs is focusing on short CNTs (<2 microns), less dense VACNTs as these are most appropriate for line of site deposition techniques. (3M NSTF analogues)

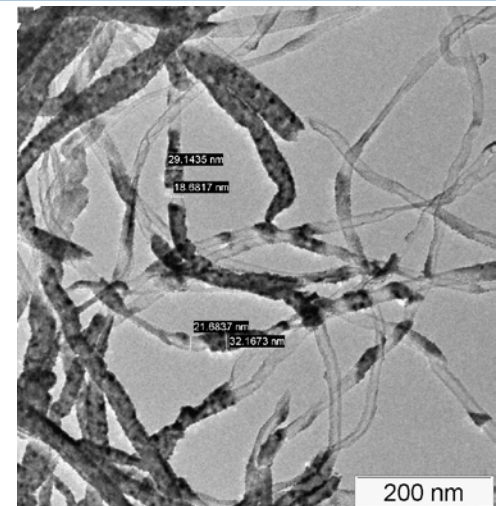
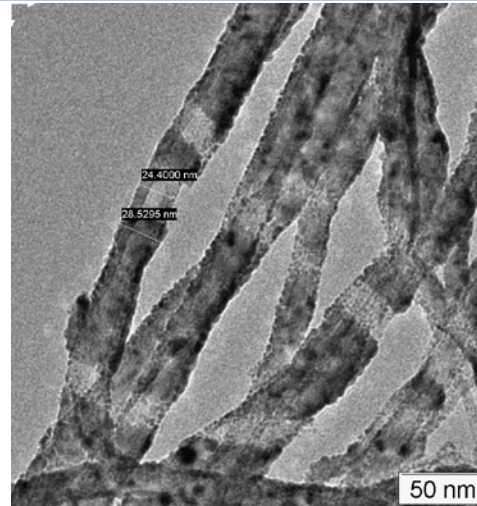
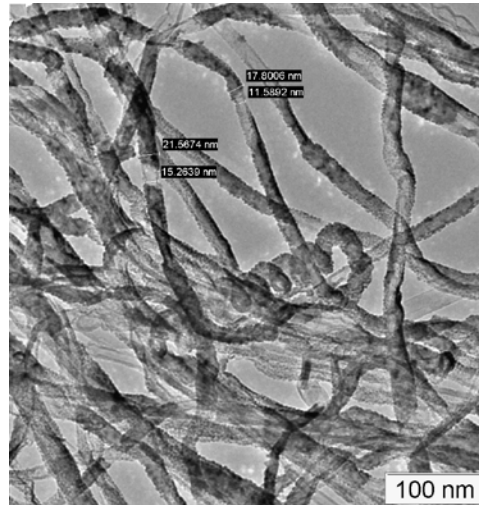
Technical Accomplishments and Progress

Initial Pt Deposition Results/Milestone



Typical Pt/CNTs

ISI literature search yielded >1300 hits for “carbon nanotubes” and “fuel cells”.

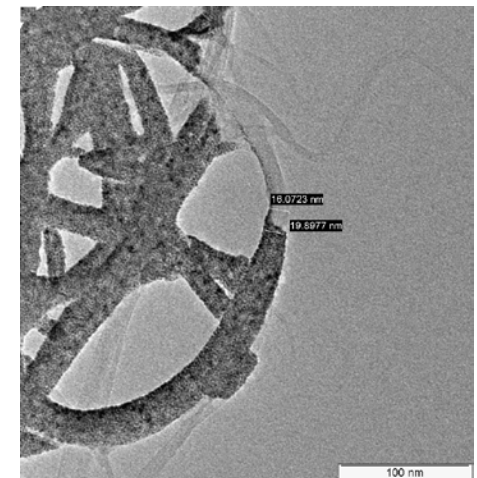


MWCNTs Increasing Deposition Time



- **Go decision:** Thin (perhaps, as low as 2 nm), continuous platinum coatings on first generation CNTs (water assisted CVD growth CNTs without surface pretreatment) were shown by transmission electron micrographs. Based on the ability to demonstrate conformal coatings on these first generation CNTs, investigations of these substrates are continuing while pursuit of 2nd generation CNTs (which would have included elemental doping and/or specific surface pretreatments) are being limited.

Based on high surface tension of Pt and the tendency of numerous Pt/CNT catalysts reported to form isolated particles, we expected difficulty in getting CNTs to coat with Pt the way we hoped. Still, plenty of issues exist (quantities, Pt distribution, scalability, etc.)

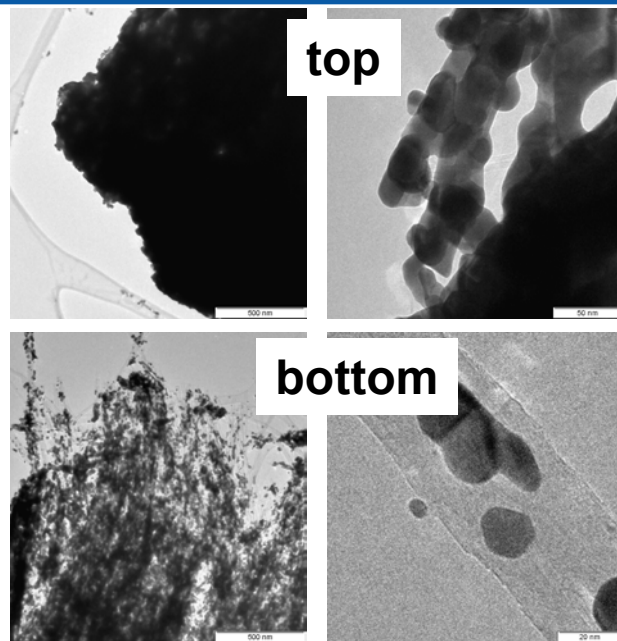
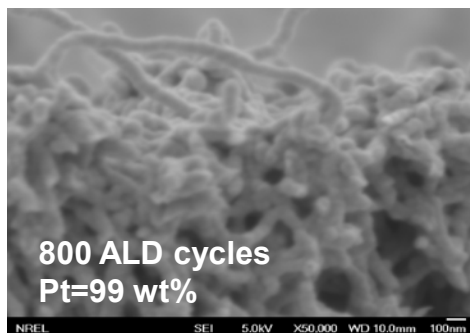
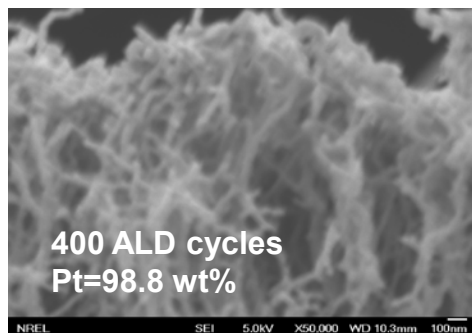
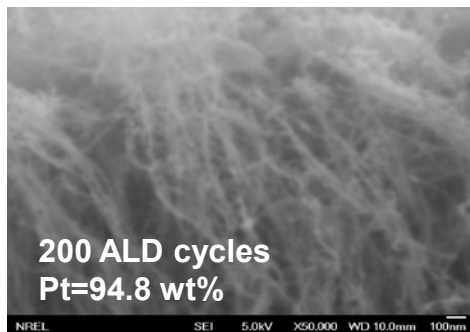
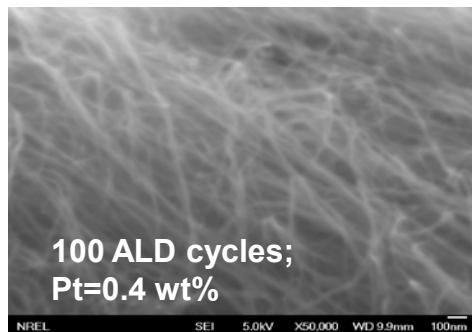


Laser purified Pt coated SWCNT

Technical Accomplishments and Progress

Pt Atomic Layer Deposition

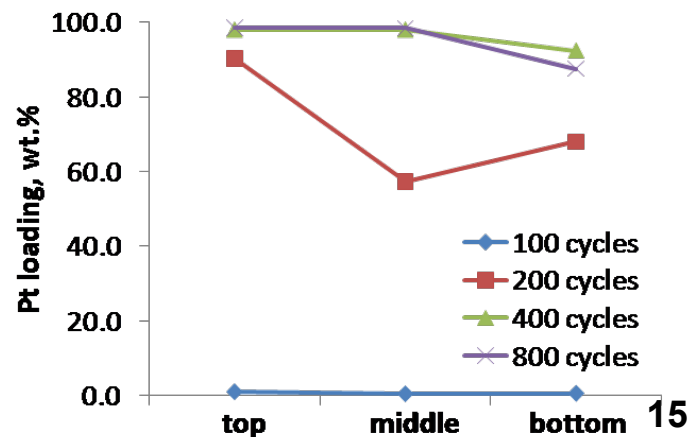
Effect of ALD cycles on Pt coverage for (~20 μm) VACNTs



Pt loading greatly accelerates after 100 ALD cycles (nucleation slow).

Significant heterogeneity occurs (even with ALD) along the length of the tube (we attribute this to variability along CNTs). Relatively long lengths and slow nucleation leads to lower conformal nature of coatings.

400 ALD cycles



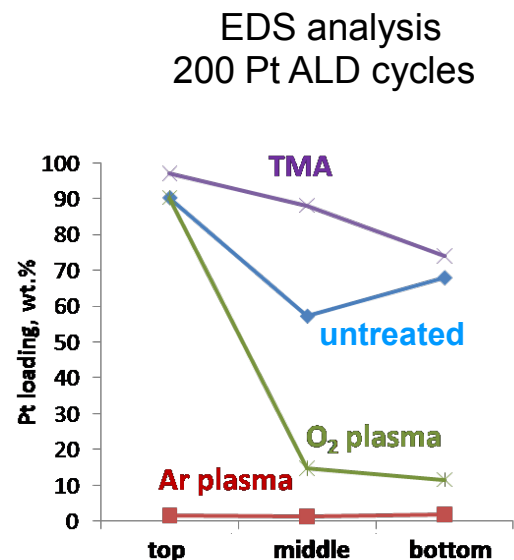
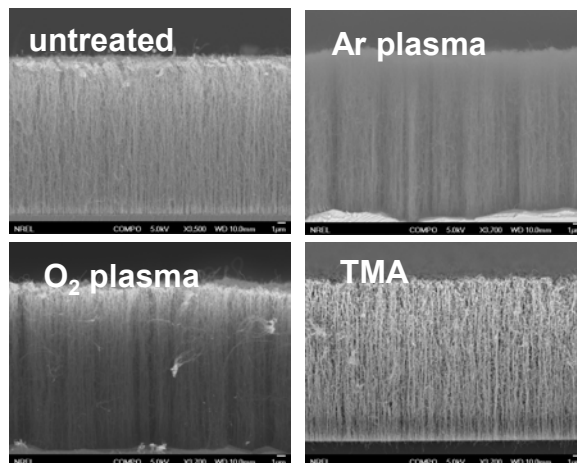
Technical Accomplishments and Progress

Pt Atomic Layer Deposition

Effect of functionalization of CNT's on Pt coverage

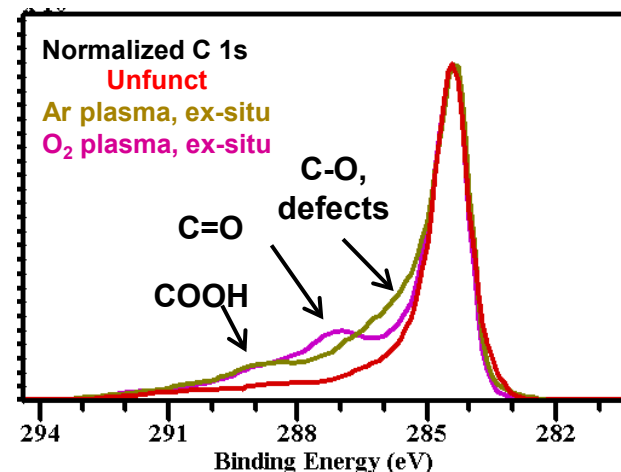
O₂ and Ar plasma surface pretreatments presented here decreased and/or made Pt deposition less uniform/slower.

Trimethylaluminum (TMA) adhesion layer enhanced nucleation but still resulted in uneven Pt deposition.



Focus on enhanced nucleation, reduced cycles for thinner, more even coatings.

XPS and Raman data have probed the composition of and surface groups of CNTs as a function of pretreatment.* This data is important for enhanced understanding of nucleation processes and differences observed between samples.



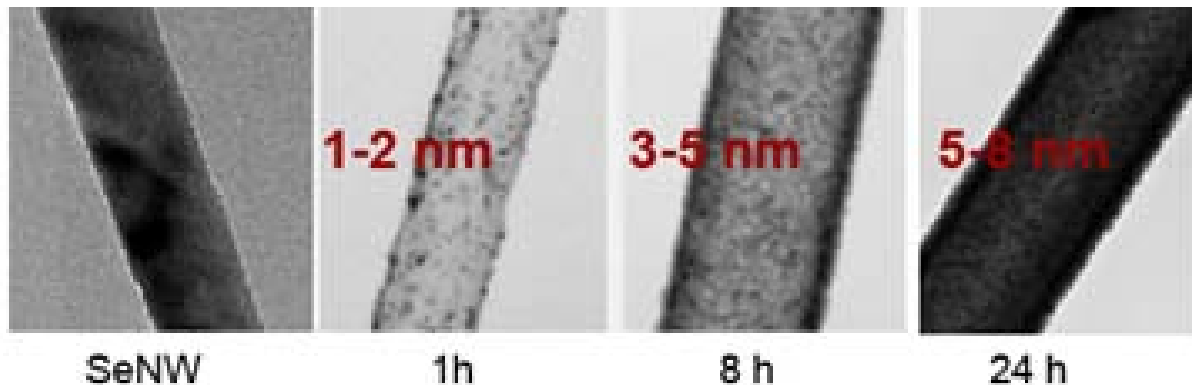
*See supplemental slide 36 for more detail.

Technical Accomplishments and Progress

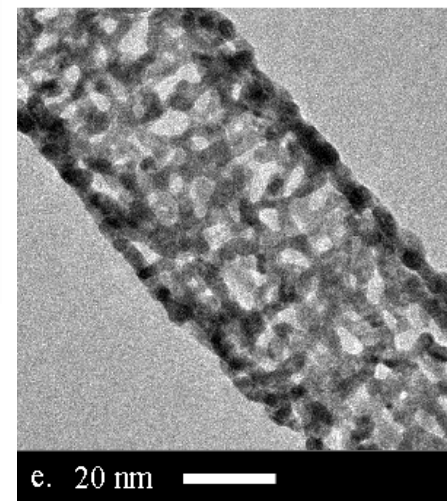
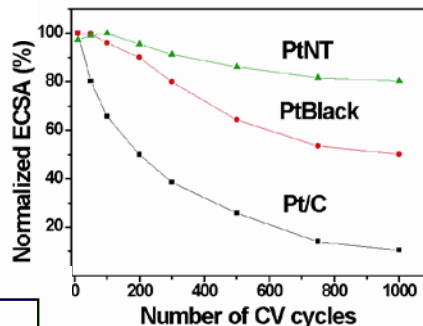
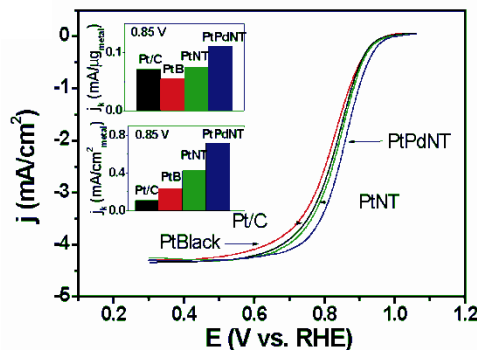
Spontaneous Galvanic Displacement (SGD)

SGD studies involving Cu nanowires have begun at NREL. Initial x-ray diffraction (XRD) results suggest that Cu has been incorporated into the Pt nanowires.

Future studies (reflected by the examples shown) will focus on elucidation of the SGD reaction, and in-depth (structural and electrochemical) characterization of the resultant materials.



SGD as a function of time with SeNW



Z. Chen, W. Li, M. Waje, Y. S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060-4063.

Collaborations

Key Investigators/Major Participants

National Renewable Energy Lab: Bryan Pivovar (PI), Shyam Kocha, Huyen Dinh, Lin Simpson, Chai Engtrakul, Arrelaine Dameron, Tim Olson, KC Neyerlin, Svitlana Pylypenko, Justin Bult, Brian Larsen, Jeremy Leong

Oak Ridge National Laboratory: Karren More

Los Alamos National Laboratory: Rod Borup

University of California-Riverside: Yushan Yan

State University of New York – Albany: Robert Geer

Stanford University: Stacey Bent

University of Tennessee: Tom Zawodzinski

University of Texas-Austin: Jeremy Meyers

Nissan Technical Center North America: Kev Adjemian

Cabot Fuel Cells: Paolina Atanassova

Tanaka Kikinzoku Kogyo: Fumiaki Ogura

Novel Material Synthesis and Characterization (NREL, CNSE, UC-R)

Continuous coating of Pt on substrates (NREL, Stanford, UC-R)

Electrode/Fuel Cell Studies (NREL, LANL, ORNL, Nissan, Cabot, Tanaka)

Modeling of Catalysts and Electrodes (NREL, CWRU, Texas)

Proposed Future Work

Templates/Cores (1a)

Focus on advancement of Cu based nano-templates (4/10 – 10/10)

Development of short, less dense VACNTs (4/10 – 7/10)

Investigation of metal oxide supports (4/10 – 4/11)

Pt deposition (1b)

Sputtering onto mats (4/10 – 10/10)

ALD studies investigating adhesion layers, nucleation, growth (4/10 – 10/11)

Optimization of SGD displacement process, resultant structures/composition, and electrochemical performance and durability (4/10 – 10/11)

Electrode studies (2)

Electrochemical screening (specific and mass activity) of novel catalysts (4/10 – TBD)

Incorporation of highest performing catalysts into electrode studies. (7/10 – TBD)

MEA fabrication and fuel cell testing of novel catalysts (7/10 – TBD)

Modeling (3)

Advancement of models and correlation of experimental data with models involving Pt wetting on surfaces, electrode structure and performance (on-going)

Summary

Relevance: Focused on overcoming the most critical barriers for fuel cell MEA development.

Approach: Developing extended surface Pt catalysts for their high mass activity and durability, and incorporating these structures into robust, high efficiency MEAs.

Technical Accomplishments and Progress: The project has identified and synthesized novel materials with target Pt structures. We have demonstrated for the first time conformal Pt coatings on CNTs, and Pt nanostructures from Cu nanowires. We have performed controlled growth of CNTs. We have investigated Pt ALD, sputtering, SGD and other solution based routes as Pt deposition techniques.

Collaborations: We have a diverse team of researchers from several institutions including 2 national labs, 5 universities, and 3 industry.

Proposed Future Research: Strongly focused on the materials demonstrated with Pt extended surfaces: targeting improvements in mass activity, high voltage cycling stability, and water management.

Additional Slides

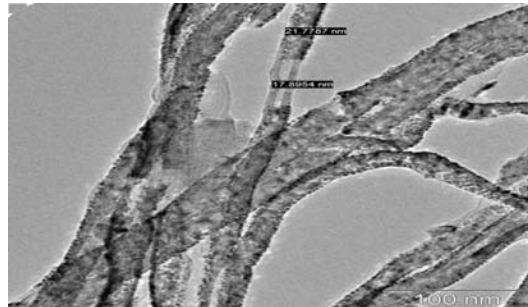
Fundamental Concept/Pathway

Catalyst film on support

- High Specific Activity
- Low Mass Activity (thickness)
- Geometric Area
- Low Dissolution
- Support : Catalyst Interaction

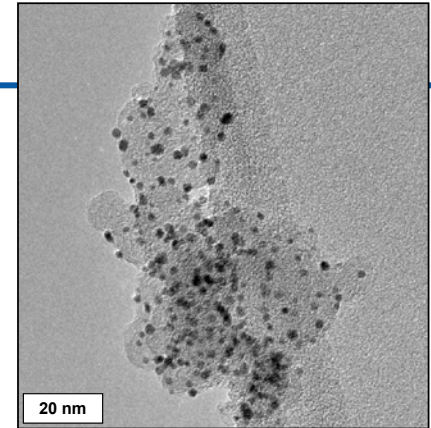
Nanoparticle Pt on carbon support

- Low Specific Activity
- Moderate Mass Activity
- High Surface Area
- Good Mass Transport & Water management
- High Dissolution
- Support corrosion



Pt coated carbon nanotube support

- High Specific Activity
- High Mass Activity
- High Durability
- Good Mass Transport & Water management
- Support : Catalyst Interaction



Remaining/Continuing Issues

How do Pt particles nucleate on different structures,
How does Pt wet extended surface templates

Importance of exposed crystal faces, role of oxides, low
coordination sites

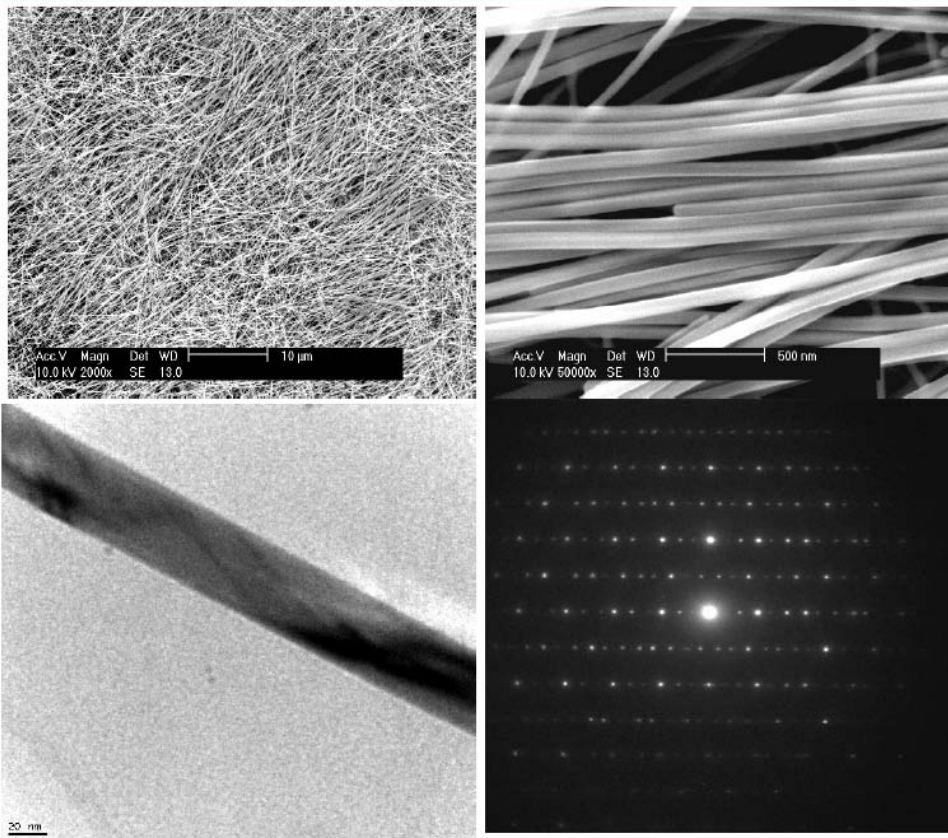
Alloy improvements

Durability of thin skins

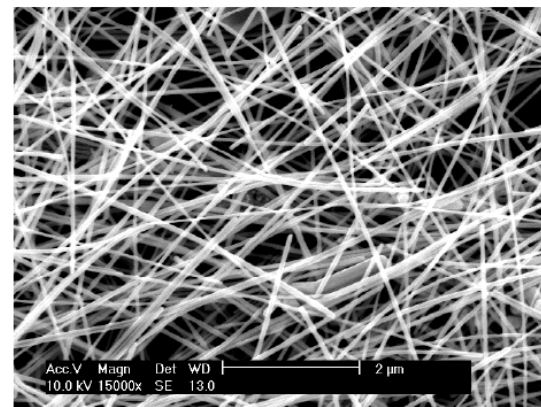
Mechanism of SGDR

Metal Templates (UC-R)

Ag Nanowire (AgNW)



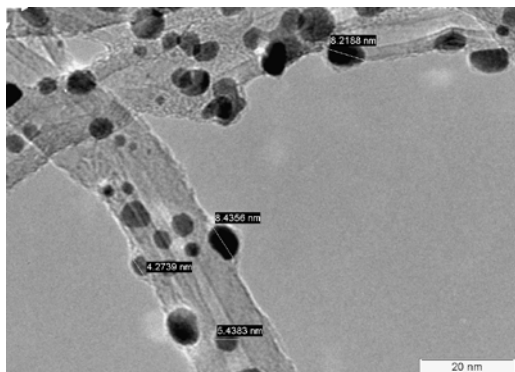
Se Nanowire



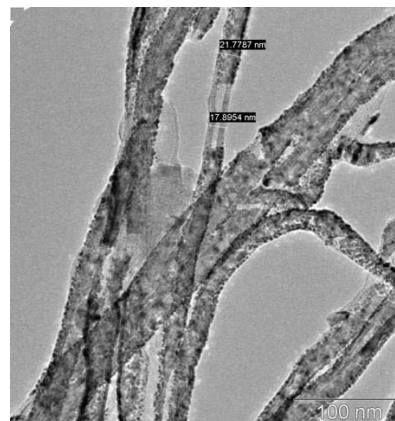
UC-R has demonstrated Ag and Se as PtNT or PtRuNT Templates.

Carbon Nanotubes (NREL)

ISI literature search yielded 350 hits from 2007 and before for “carbon nanotubes” and “fuel cells”, now >1300.



Typical

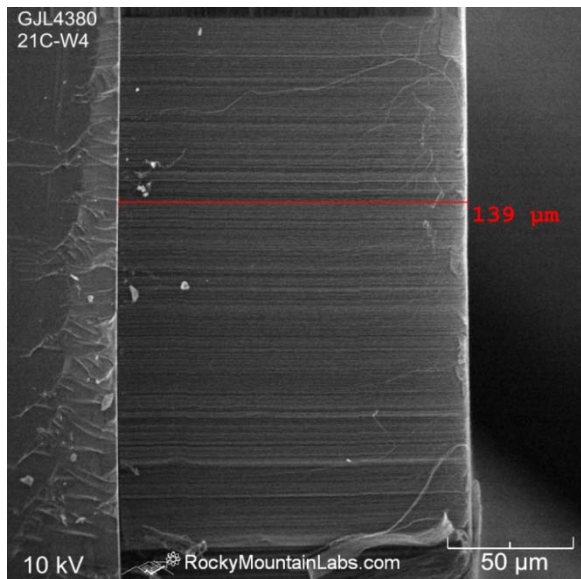


Unique

Unique Position

- Significant expertise stemming in part from DOE’s Hydrogen Storage Center of Excellence
- Synthesis methods available at NREL: laser vaporization, arc-discharge, CVD, ALD/CVD, plasma-enhanced CVD, hot-wire CVD
- Variety of non-standard CNT materials currently available at NREL

Controlling Fe Catalyst Morphologies: Effect of Catalyst Annealing Conditions



Standard Synthesis Conditions:

Pressure = 760 Torr

Flow rates = 540 sccm He (~ 175 ppm H_2O), 360 sccm H_2 , 100 sccm C_2H_4

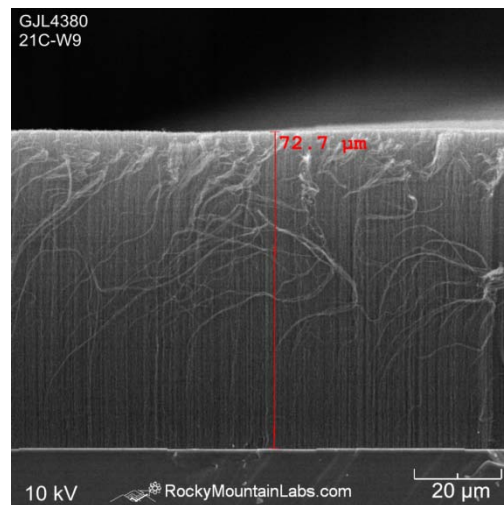
Temperature = 750 $^\circ\text{C}$

Growth Time = 5 min

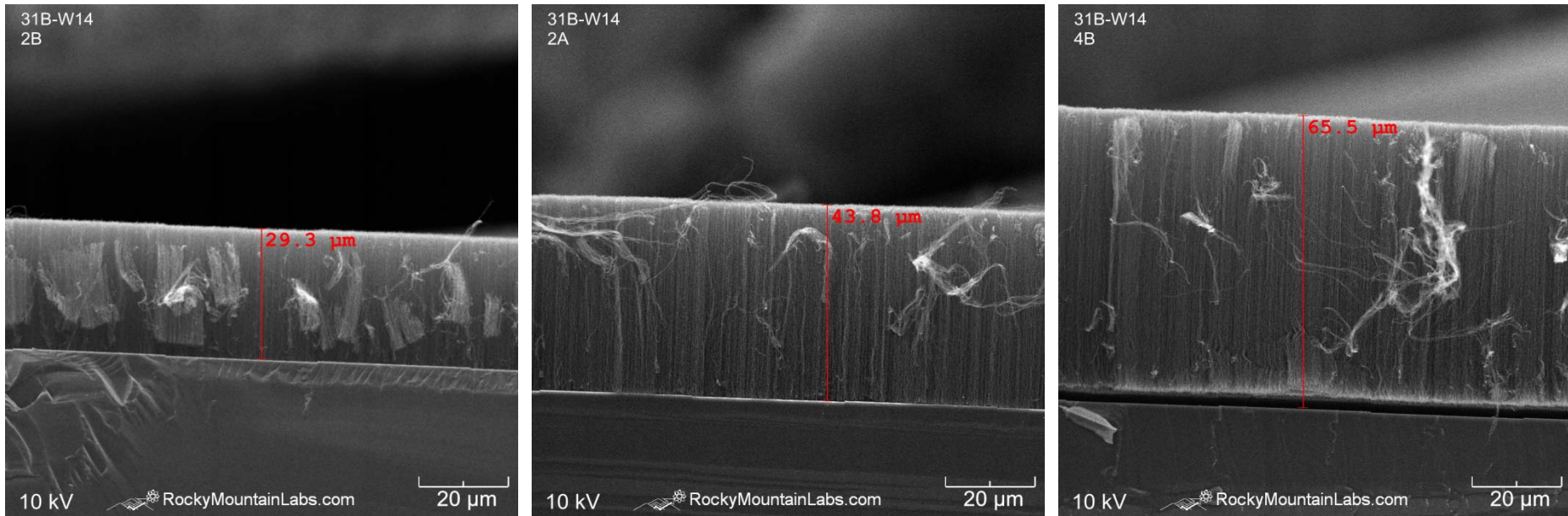
Notes: (1) Substrates consist of SiO_2 (111) wafer with 100 nm thermal oxide, ~ 60 nm Al_2O_3 , and ~ 1 nm Fe. (2) Prior to growth, the catalyst was either thermally annealed in H_2 alone (20 min) or with water (15 min in H_2 and 5 min in $\text{H}_2/\text{H}_2\text{O}$).

Annealing Conditions	Height (μm)	CNT Width (nm)
H_2/He	139	30
$\text{H}_2/\text{He}/\text{H}_2\text{O}$	73	10

Annealing the Fe catalyst in a $\text{H}_2/\text{H}_2\text{O}$ atmosphere before CNT growth inhibited Ostwald ripening and resulted in shorter CNTs. Average heights were cut in half. In addition, the VACNTs were more densely packed and the CNT widths decreased by a factor of 3.



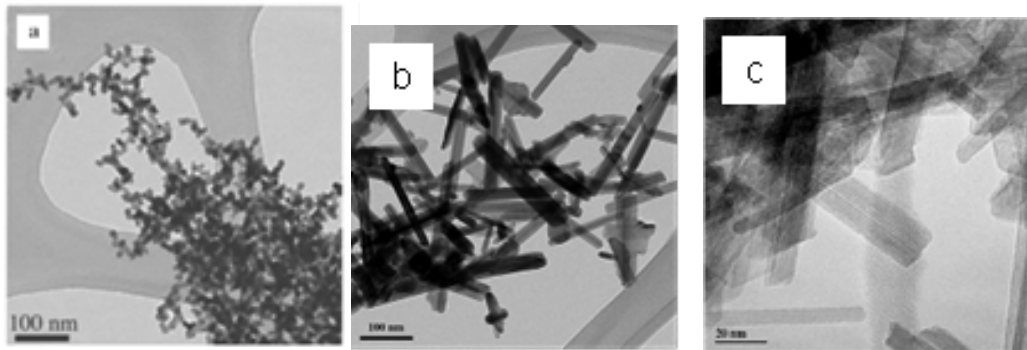
Inhomogeneities in the Fe Catalyst Layer: Non-Uniform CNT Growth Lengths



- DC magnetron sputtering is unable to control the uniformity of the Fe catalyst layer (~1 nm) on a substrate greater than 1"
- CVD reactor not optimized for high-throughout studies
- Heights of the VACNTs varied by a factor of ~2 (from 30 to 65 μm)
- Non-uniform growth rates, early growth termination

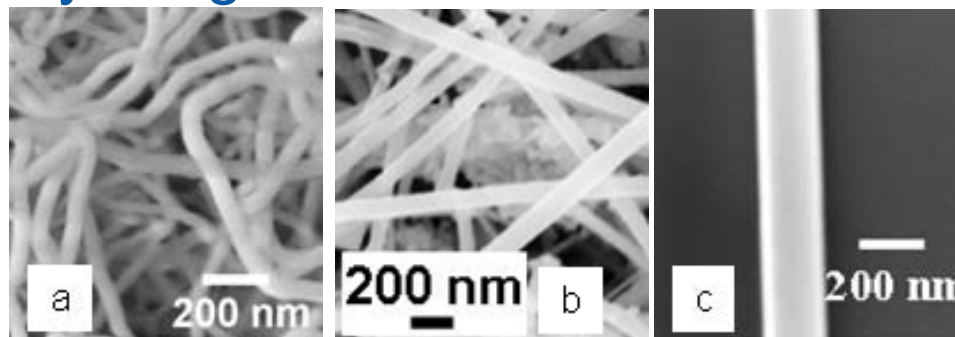
Metal-oxide nano-structures (CNSE, NREL)

NREL has strong background in this area due to the role of these materials in areas such as advanced solar devices and batteries.



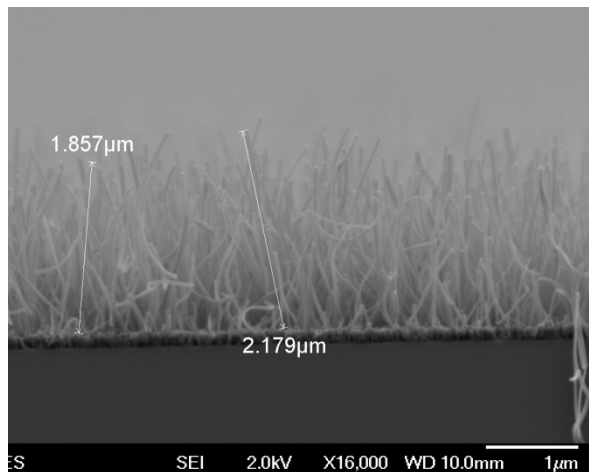
NREL synthesized nanostructured oxides:
a) MoO_3 ;
b) WO_3 ;
c) MnO_2

Center for Nanoscale Science and Engineering (CNSE) will play a significant role in this area of templates.

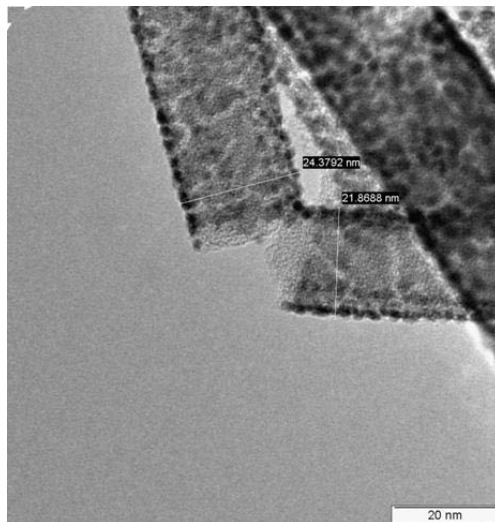


CNSE synthesized:
a) amorphous SiO_2 ;
b) crystalline SiO_2 ;
c) SnO_2 .

Perylene Red based nanostructures (NREL)



Cross-section SEM of Pt coated PR nanowhiskers (TEM shown above).

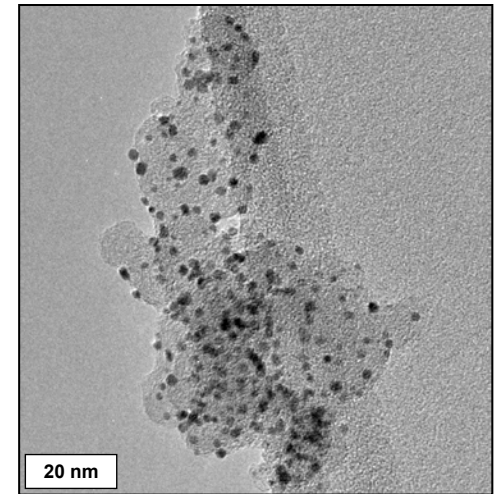


Pt coated perylene red whiskers

- These structures highly studied (optimized) by 3M
- Hope to leverage 3M's work
 - Visit to 3M (Nov), M. Debe suggested materials could be shared under an NDA
- Cheap templates, mass manufacturable
- Focus on thin film electrodes

Pt nanostructure formation

- Traditional wet chemical/aerosol based routes
 - Commonly employed
 - Tend to discrete particles (spheres, icosahedron, cubooctahedron, etc.)
 - Adaptable to scale up, give high surface area to volume



20% Pt/C, TEM ORNL

With inherently increased specific activity and durability what routes make sense for extended Pt nanostructures? (keep in mind manufacturability)

Inherent difficulty in Extended Pt

- Surface Tension

- Pt has just about the highest surface tension (scales roughly with melting temperature).

W: 2.9 J/cm²

Pt: 2.3 J/cm²

Cu: 1.67 J/cm²

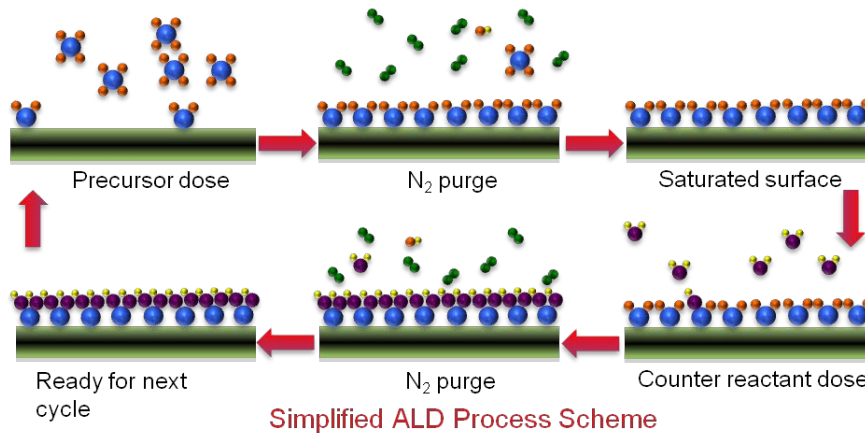
Ag 1.1 J/cm²

- Work needed to increase/decrease surface is

$$W = \gamma dA$$

Pt does not want to coat other materials/surfaces, prefers itself. How do we overcome this?

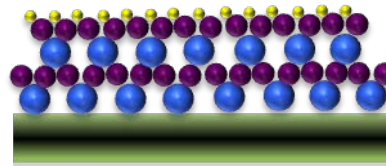
Atomic Layer Deposition (ALD)



- Atomic layer deposition (ALD) is a vapor phase process like chemical vapor deposition
- ALD is based on alternating surface reactions, where each reaction step is self-limiting.
- Deposition achieves 0.1 - 3Å/cycle

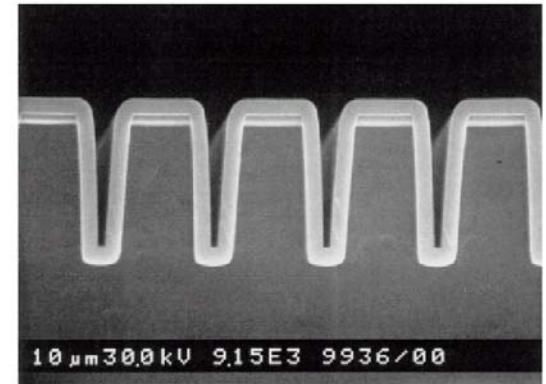
Advantages to ALD:

- Excellent conformality possible
- Excellent uniformity possible
- Elimination of detrimental gas phase reactions



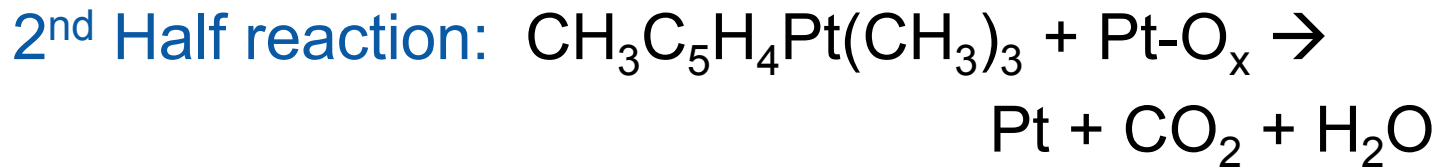
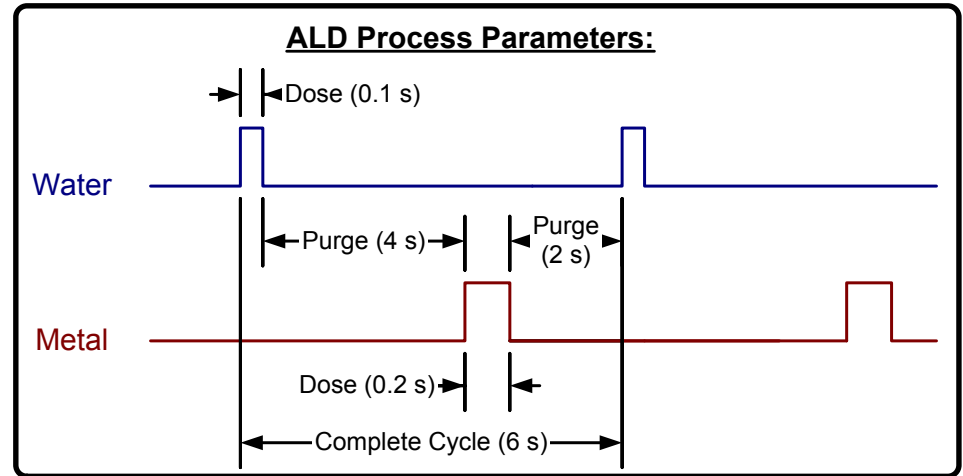
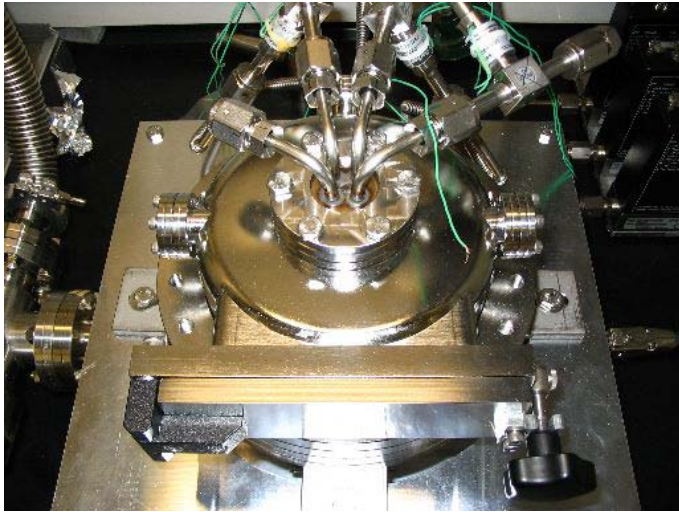
Major disadvantage:

- Slow deposition rate (100-300 nm/hr typical)
- Limitations with Pt



From Ritala and Leskela

Pt ALD (Stanford, NREL)



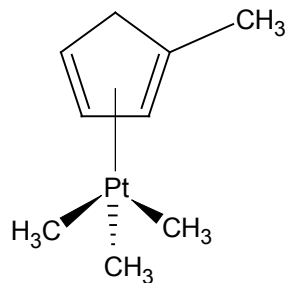
Pt ALD (Stanford)

Precursors:

(MeCpPtMe₃) 99%; O₂ from dry air

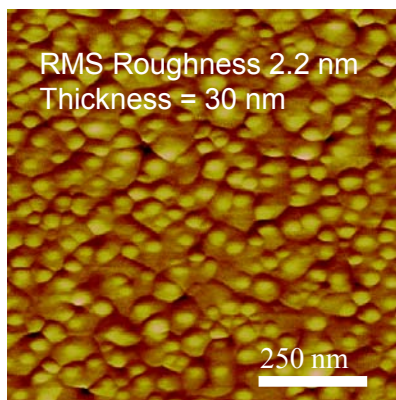
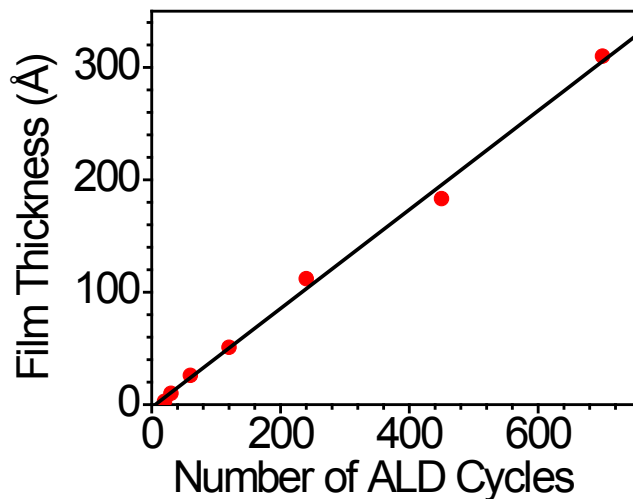
Carrier and purging gas:

Nitrogen (99.9999%)

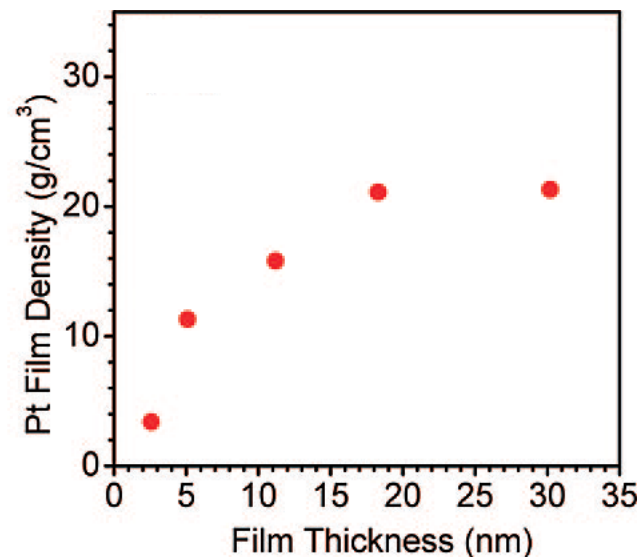


Optimized Pt ALD parameters:

- Substrate Temp.: 245~300°C
- Pt precursor Temp.: 50°C
- Air dose time: 2 s
- Pt dose time: 2 s
- N₂ purging time: 12s (30 s)
- Growth rate of ~0.43 Å/cycle



Resistivity at 30 nm: 18 $\mu\Omega\text{-cm}$
(Bulk Pt value 10.8 $\mu\Omega\text{-cm}$)

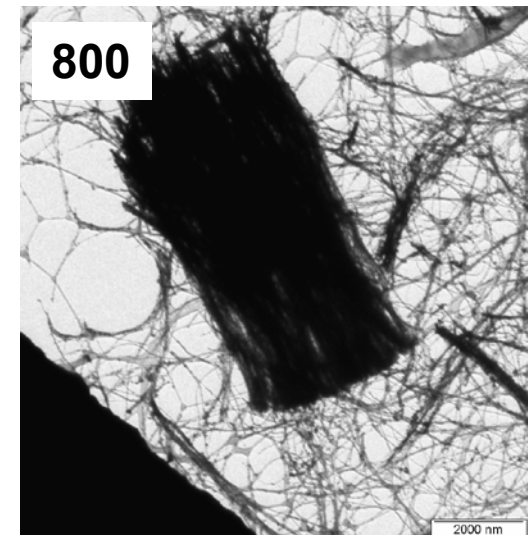
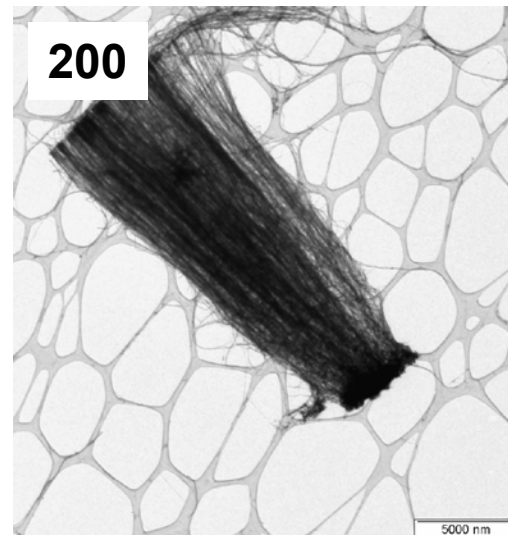
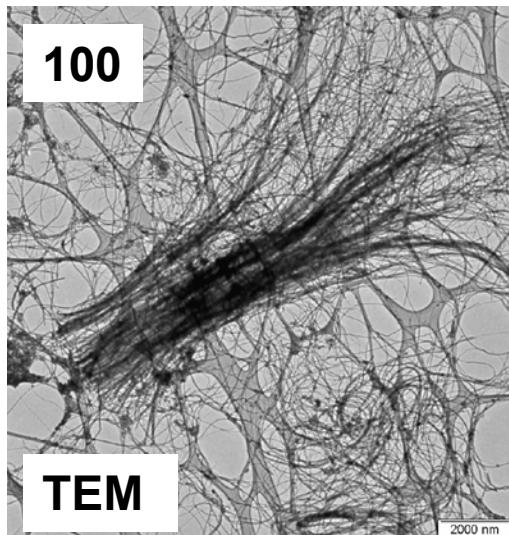
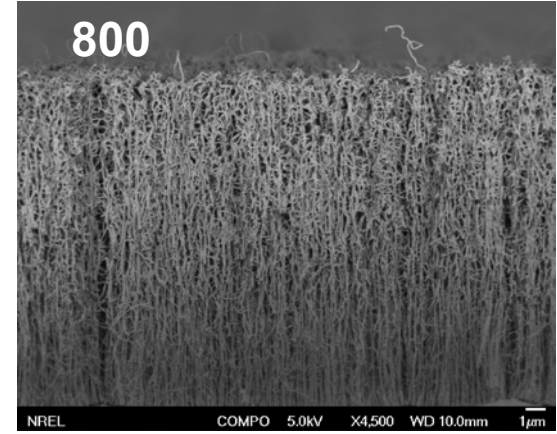
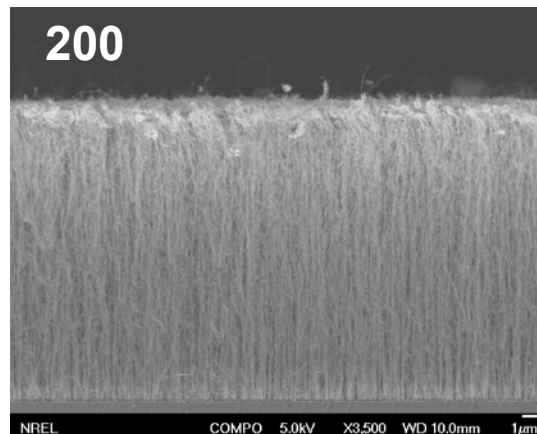


Christensen et al. in Chem. Mater. 2009, 21, 516–521 conclude that film closure occurs at ~40 Pt ALD cycles on SrTiO₃

Bent group, Stanford

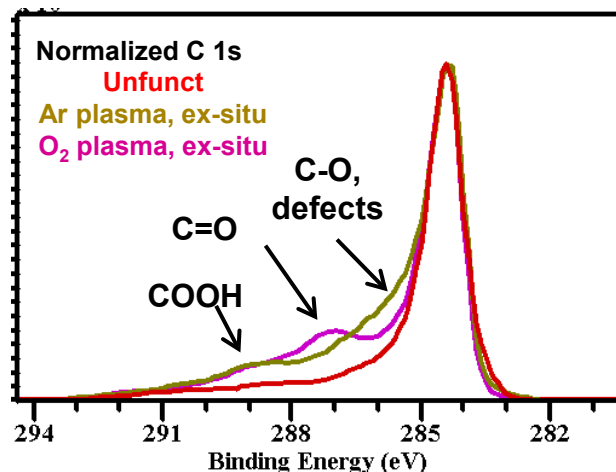
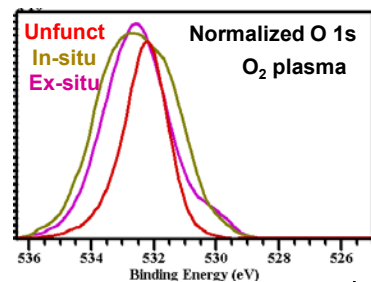
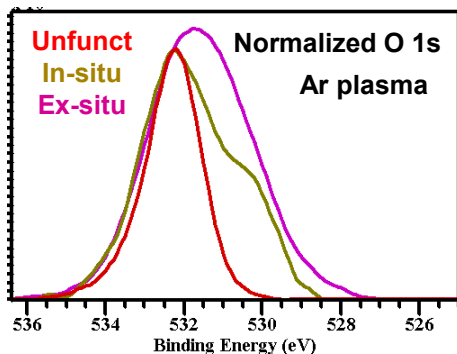
Pt ALD (NREL)

Effect of ALD cycles: Pt coverage, Pt gradient and Pt/CNT's dispersion



Effect of Surface Treatments on VACNTs

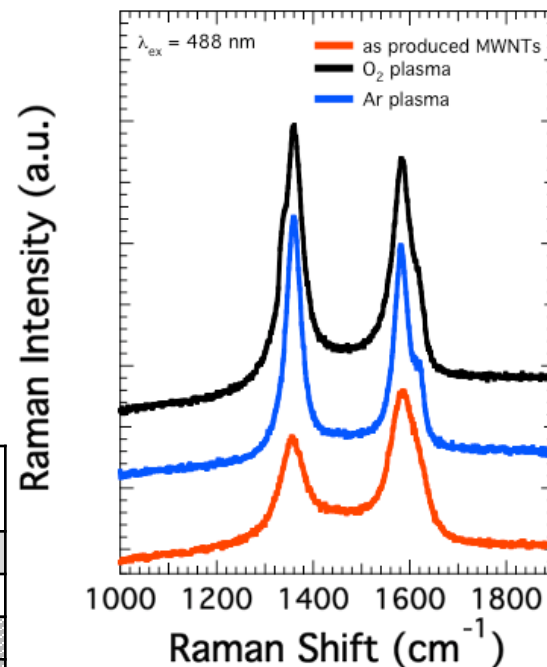
XPS data: Shows significant changes in C-O composition as a function of surface treatment



Surface oxygen concentration measured by XPS

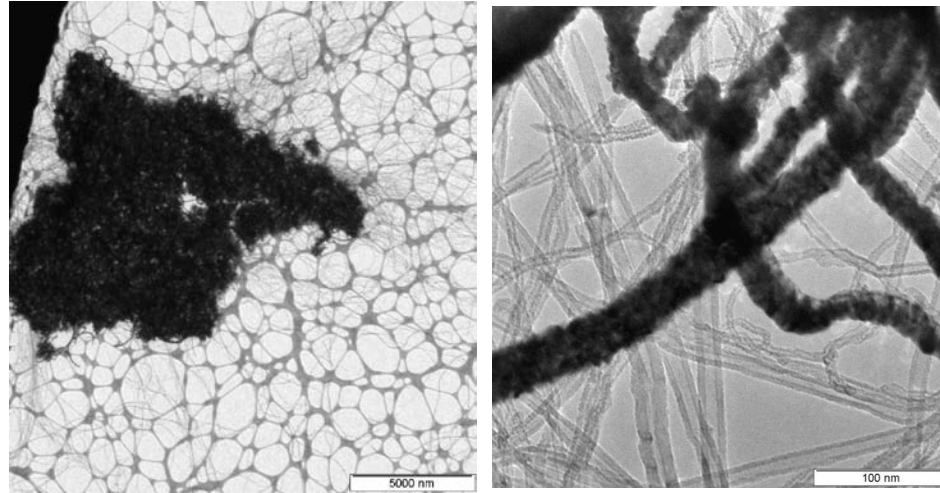
Time	Unfunc	O ₂	Ar	Ar+O ₂	TMA
0 sec	22.5				
in-situ 5 min		5.4		4.4	6.8
ex-situ 5 min		12.1	15.3	12.8	
ex-situ 30 min		21.0	42.3	17.5	

Raman data: Shows shifts in D-G band peaks intensity for ex-situ samples decreased graphitic content/ increasing defects reflected by changes in peak intensity with plasma treatment.

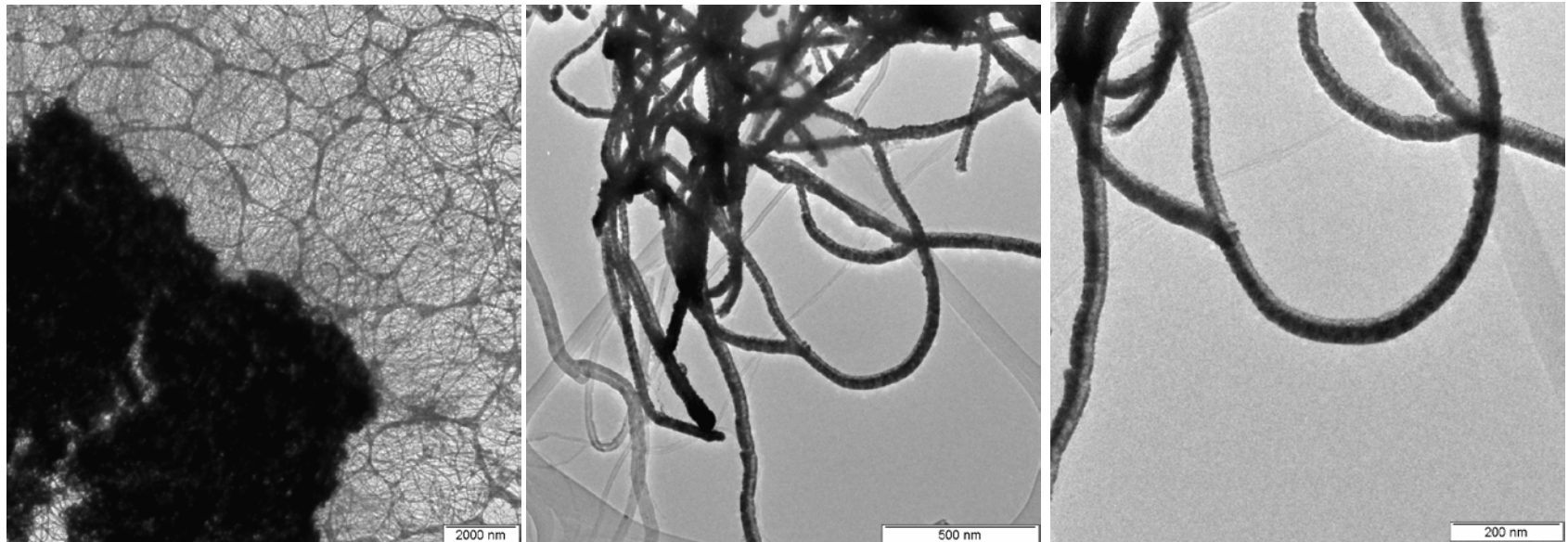


Sputter Deposition

Ex-situ O₂ plasma, 5 min



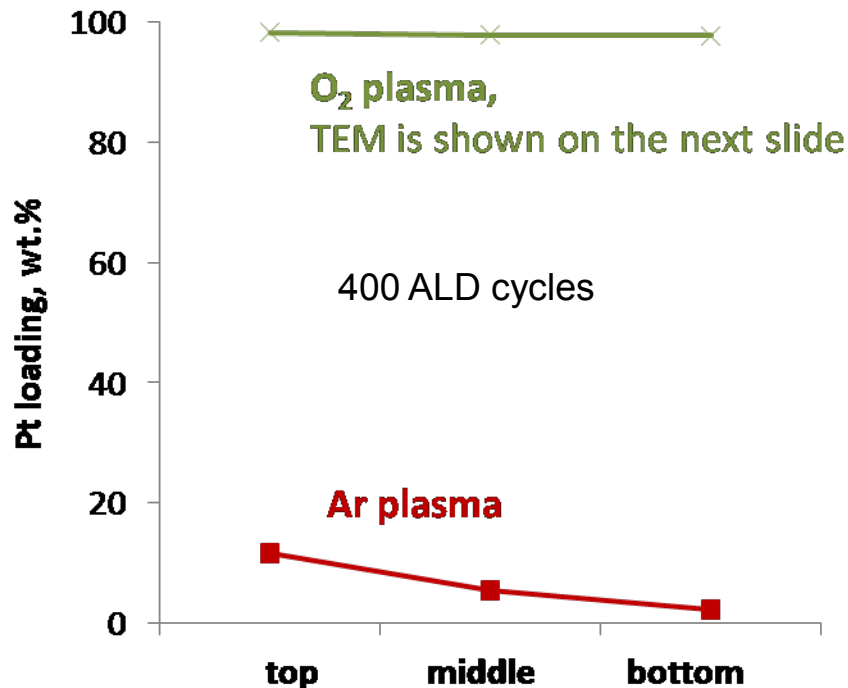
Ex-situ Ar plasma, 5 min



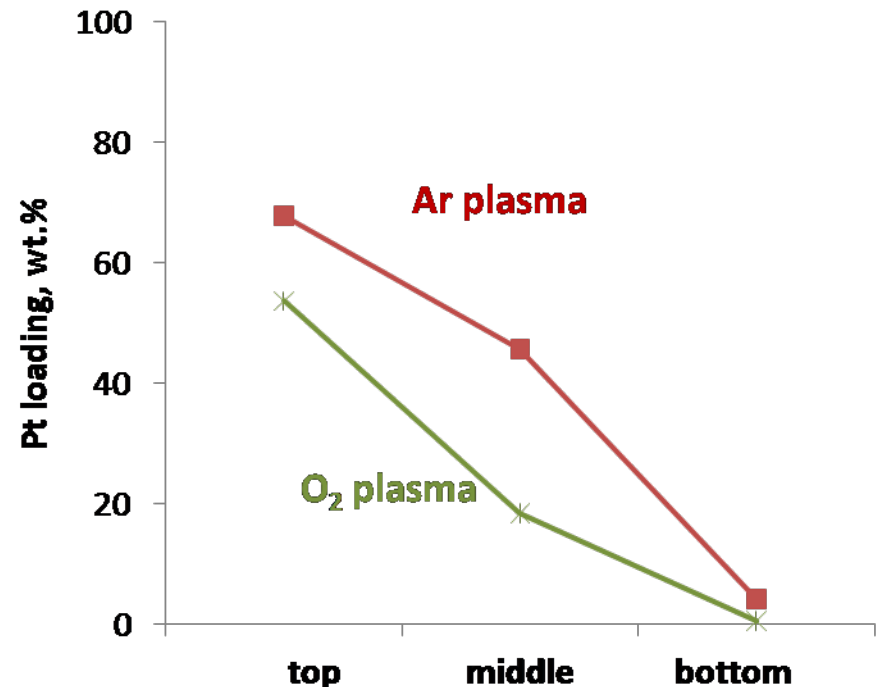
ALD vs. Sputter Deposition

Effect of Pt deposition method and ex-situ functionalization of CNT's

Atomic Layer Deposition

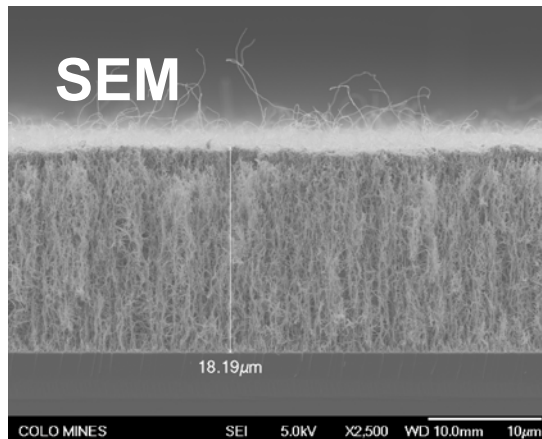
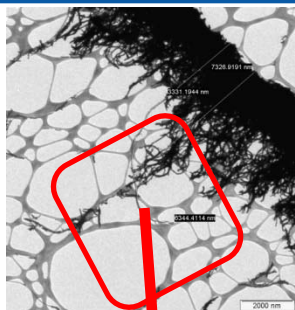


Sputtering Deposition



Sputtering, as could be expected, shows significant gradient in Pt coverage. Perhaps surprisingly ALD can show similar gradients.

Pt ALD on O₂ plasma treated CNTs

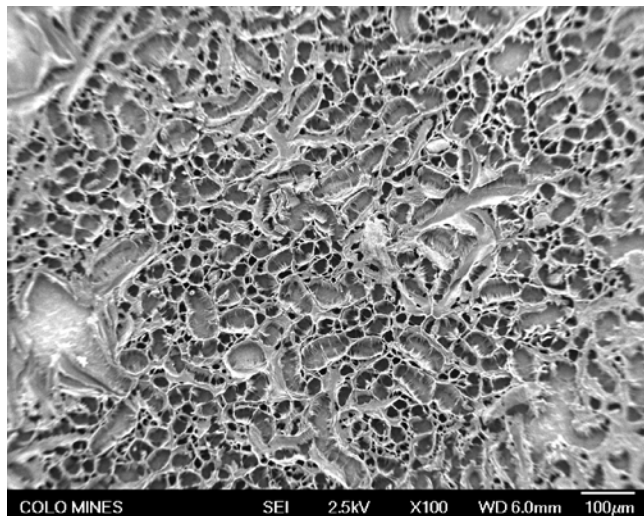


ex-situ functionalization of CNT's in O₂ plasma leads to decreased Pt coverage gradient, continuity seems to be less than desired.

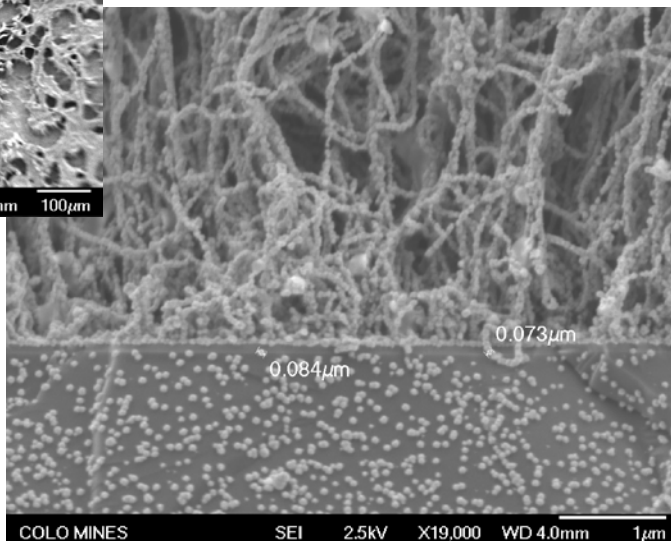


Solution Deposition on VACNTs

“Foaming” of VACNTs common, poor control over thickness and uniformity.

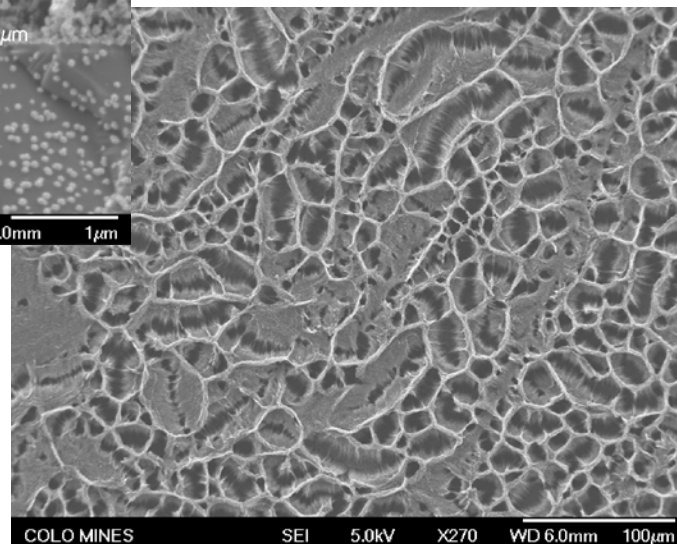


Microwave assisted Pt deposition



Spontaneous Pt deposition 4.7 mM sodium tetrachloroplatinate in ethanol (60 hours).

Spontaneous Pt deposition 2.4 mM sodium tetrachloroplatinate in ethanol (4 hours).



Background - Electrode History

‘GE’ style electrode: Pt black steam-bonded to membrane with Teflon[®] binder

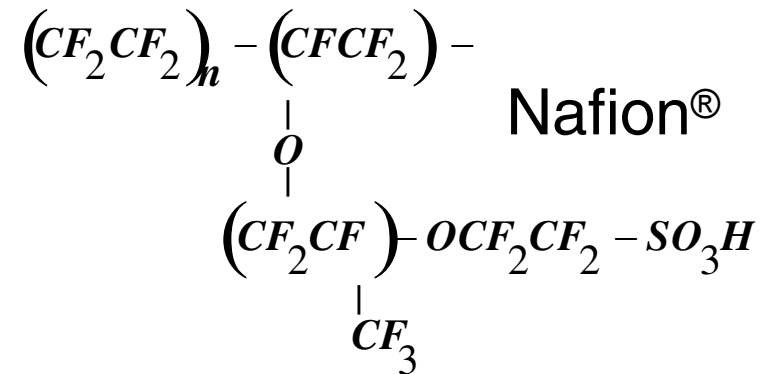
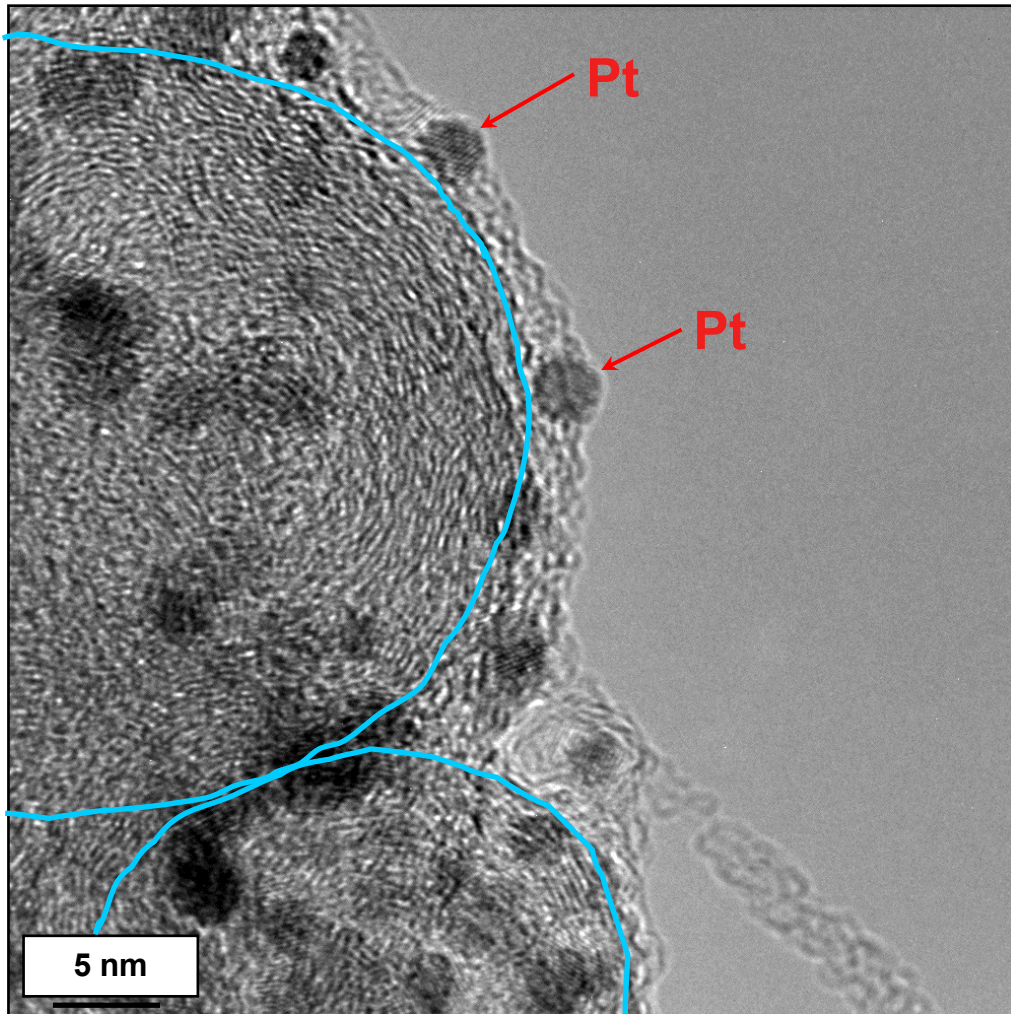
1986: Raistrick (LANL): Impregnated catalyzed Prototech electrode (ELAT)

1990: Wilson (LANL): Intimately mixed ionomer/catalyst ink applied to membrane

Mid 90’s – Present: Nanostructured electrodes (3M, carbon nanotubes)

Catalyst compositions often “empirically” optimized for best initial performance, still not much science/design involved.

Electrode Structure – text book

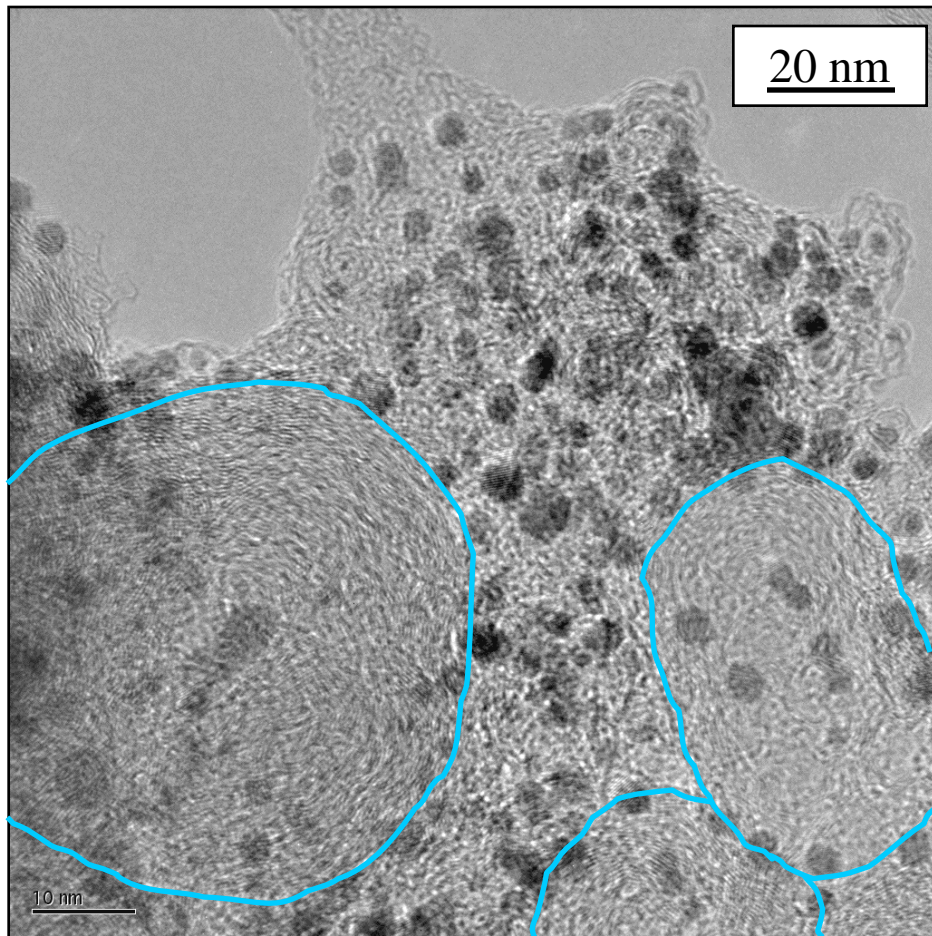


Triple phase boundary
(Nafion[®], carbon, Pt
and pore space) clear.

Quite atypical.

HR-TEMs courtesy of Karren More, ORNL

Electrode Structure – Representative?



Fresh cathode Pt catalyst particles

In typical TEM micrographs of electrodes, features such as ionomer “webs” and detachment of Pt from carbon/ Pt segregation can be observed.

Differences in performance between nanoparticle Pt and bulk crystals typically cited as particle size effects. Results of our studies suggest ohmic issues (electronic contacts at the nanoscale) are likely important.

Extended Surfaces

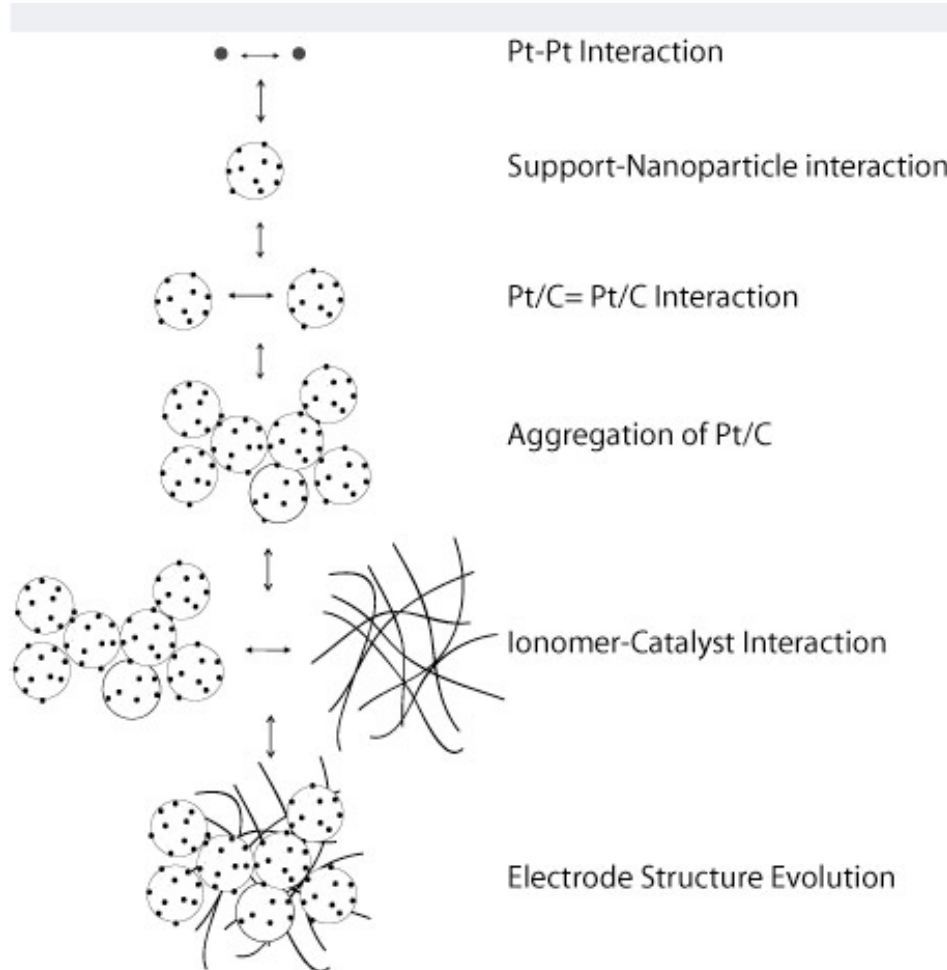
Create inherent electronic (and apparently ionic) pathways.

Are finding wide utility in several other EERE areas that NREL is ideally situated to leverage.

HR-TEMs courtesy of Karren More, ORNL

Catalyst/electrode structure modeling

Hierarchical Approach (Univ. of Tenn.)



• Interaction energies

- Obtained from Lifshitz formulation using optical properties

(UV-Vis-IR spectra, synthesis of nanoparticles)

• Nanoparticles

- Modeled using Molecular dynamics study

(HRTEM of nanoparticles, EMS)

• Supported catalyst and composite electrode

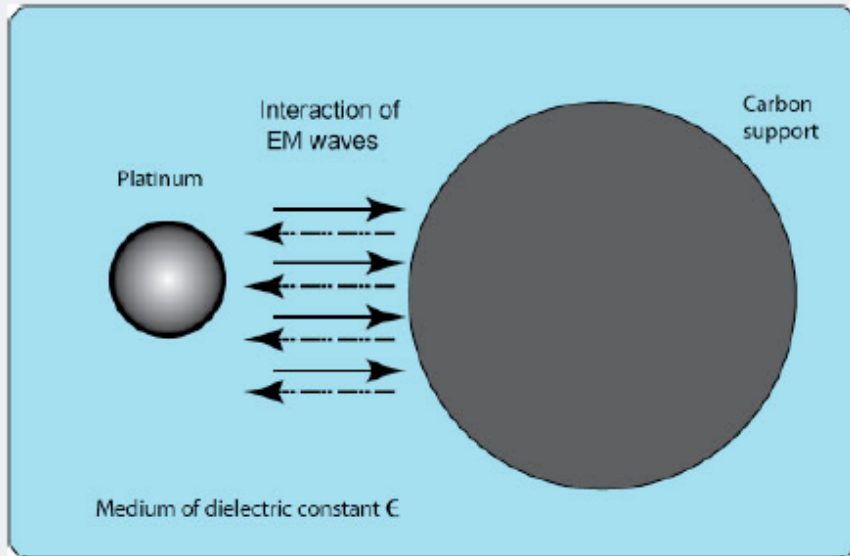
- Markov Chain Monte Carlo method

(Synthesis of supported catalyst, TEM of supported catalysts, AFM of electrode structures)

• Conductivities of electrode

- Percolation models

Principles of approach (Tenn)



➤ Electromagnetic 'fluctuations' between materials

- Casimir's and Lifshitz theories

➤ Dependant on the material properties of objects

➤ Relationship between absorption spectra and fluctuations

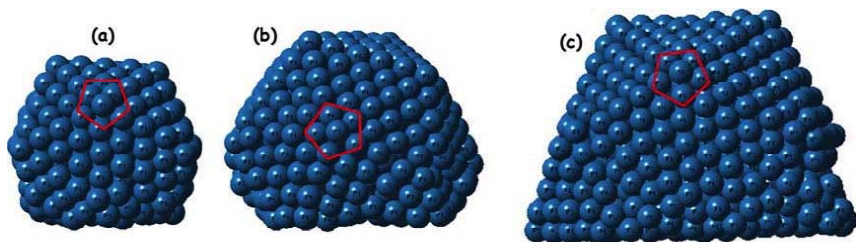
➤ Validity at macroscopic length scales **Geometric factor**

$$A_{132} = A(h, \epsilon_1, \epsilon_2, \epsilon_3)$$

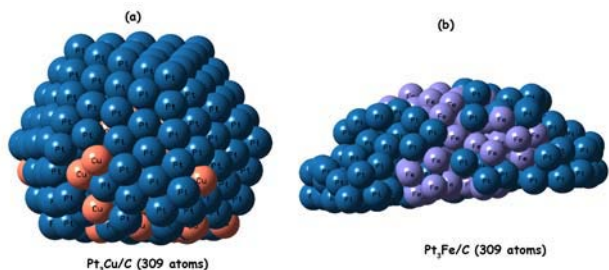
$$U(h) = \frac{-A}{6} \left[\frac{4r^2}{(2r+h)^2 - 4r^2} + \frac{4r^2}{(2r+h)^2} + \ln \left(\frac{(2r+h)^2 - 4r^2}{(2r+h)^2} \right) \right]$$

Initial Results/Examples (Tenn)

Pt Particle Simulations

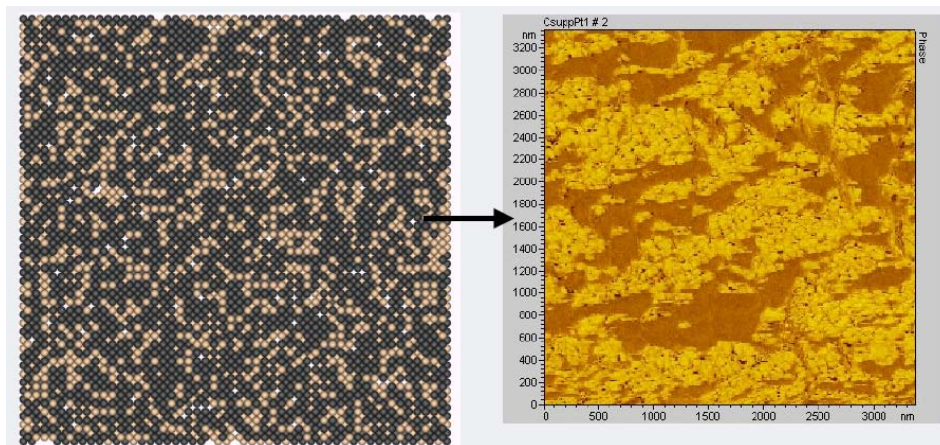


Simulations developed to understand Pt particle size and structure on carbon supports will be expanded to include other approaches taken in the project.



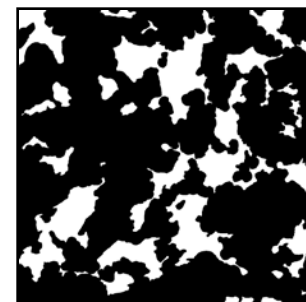
Approach has also been applied to alloys.

Electrode Simulations



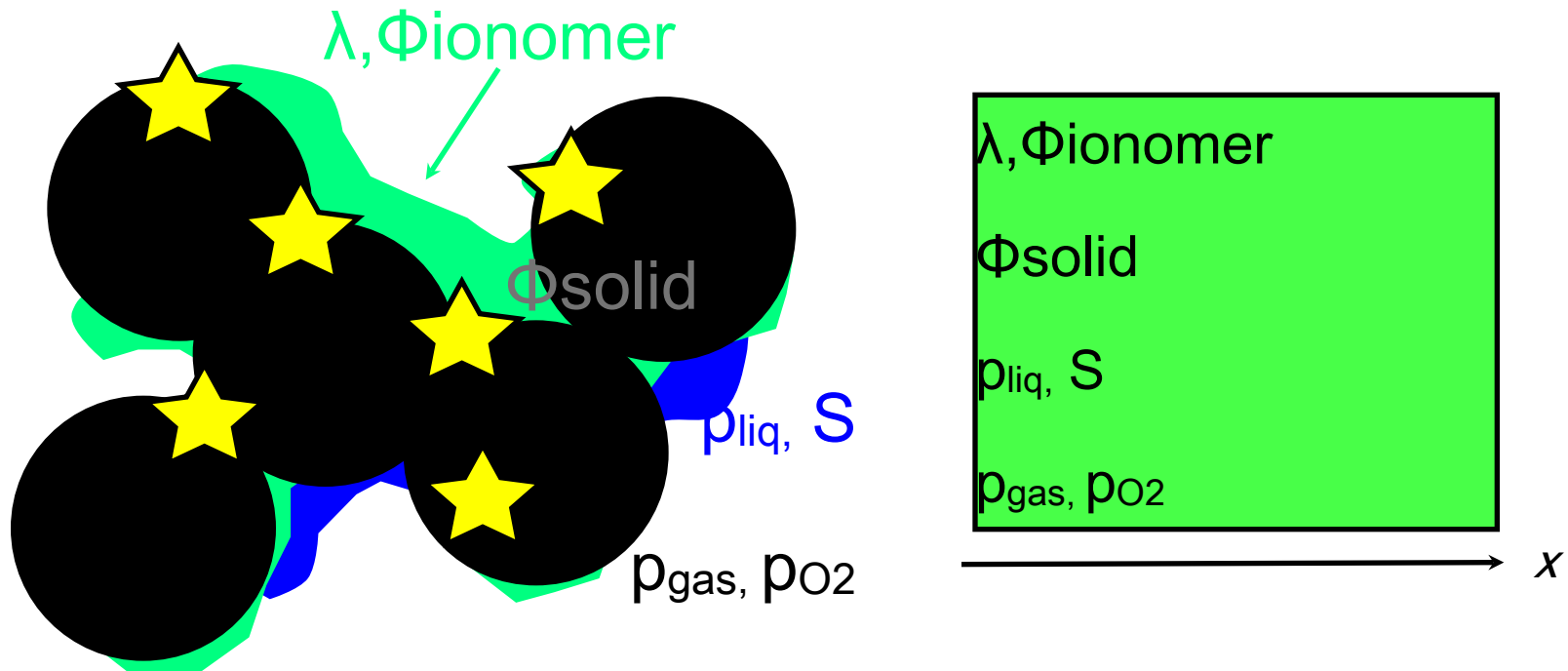
3D simulations take into account composition of electrodes.

Resultant structures mirror observed structures.



Porous Electrode Modeling (Texas)

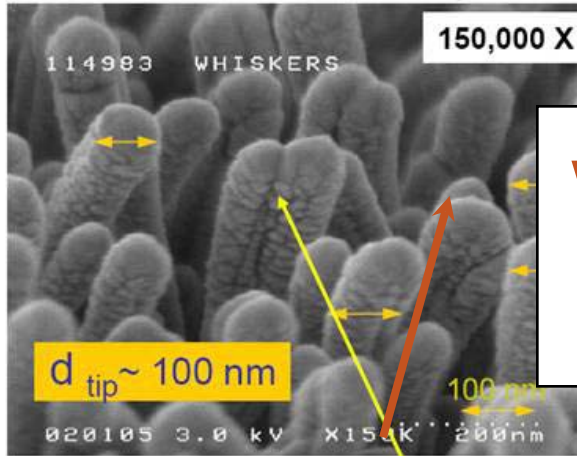
- Extend established porous electrode models to highlight issues critical to the incorporation of extended surfaces in thick electrodes.
- Use experimental data and modeling of electrode architecture to establish volume averaged parameters.



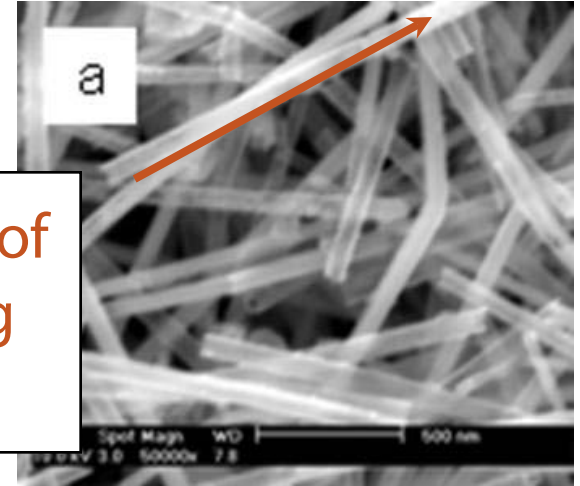
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Extended Continuous Surfaces

Subtask 1.1 NSTF surface area optimization



what is mechanism of ion transport along rod/ tube?



Pt nanotubes, Y. Yan, UC-Riverside.

Surface Roughness Factor may be : $\Gamma_f \sim 1.5$ to 2 ?
Tip diameter : $d_{tip} \sim 100$ nm
Base diameter : ~ 50 nm of bare whisker
Mean diameter over length taken as average of base and tip: $d_{av} \sim 75$ nm

http://www.hydrogen.energy.gov/pdfs/review07/fcp_25_debe.pdf

Need to add features to continuum model to address unique features

- Contact resistance
- Percolation threshold
- Film resistance

Impedance models/ ex-situ testing with blocking electrodes to characterize ion transport

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