NREL
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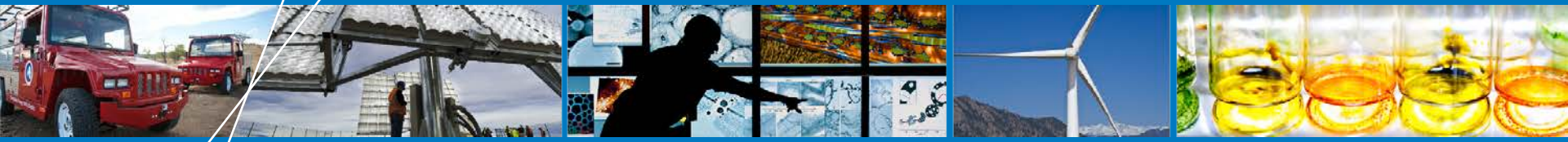
Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes



2012 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

May 15, 2012

FC007

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

- Start: July 2009
- End: September 2013
- % complete: ~60%

Barriers

A. Durability (catalyst; MEA)
B. Cost (catalyst; MEA)
C. Performance (catalyst; MEA)

Budget ($K)

DOE Cost Share	Recipient Cost Share	TOTAL
8384	868	9252

DOE funding	Budget ($K)
FY09	1480
FY10	1203
FY11	2177
Planned FY12	1575
Planned FY13	1949

Partners – Principle Investigators

Oak Ridge National Laboratory (ORNL) – Kelly Perry
Los Alamos National Laboratory (LANL) – Rod Borup
University of Delaware (Delaware) – Yushan Yan
State University of New York – Albany (CNSE) – Eric Eisenbraun
Stanford University (Stanford) – Stacey Bent
University of Tennessee (Tenn) – Tom Zawodzinski
University of Texas-Austin (Texas) – Jeremy Meyers
Nissan Technical Center North America* (NTCNA) – Kev Adjemian
Cabot Fuel Cells* (Cabot) – Paolina Atanassova
Tanaka Kikinzoku Kogyo* (TKK) – Fumiaki Ogura

*non-subcontracted collaborators

Relevance

ETFECS/Dispersed Electrodes

Review Period Objectives:

- Produce novel extended thin film electrocatalyst structures (ETFECS) with increased activity and durability, moving towards meeting all 2015 DOE catalyst targets simultaneously.

- Expand studies of electrode incorporation of ETFECS with highest potential to probe potential for meeting MEA Targets. Pursued studies with Pt Black as an unsupported surrogate, expanded to ETFECS, including carbon incorporation.

Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2011 Status	Targets	
			2017	2020
Platinum group metal total content (both electrodes)[a]	g / kW (rated)	0.19[b]	0.125	0.125
Platinum group metal (pgm) total loading[a]	mg PGM / cm^2 electrode area	0.15[b]	0.125	0.125
Loss in initial catalytic activity[c]	% mass activity loss	48[b]	<40	<40
Electro catalyst support stability[d]	% mass activity loss	<10[b]	<10	<10
Mass activity[e]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.24[b]	0.44	0.44

Table 3.4.14 Technical Targets: Membrane Electrode Assemblies

Characteristic	Units	2011 Status [a]	2017 Targets	2020 Targets
$Q/\Delta T_i$[b]	kW/°C	–	1.45	1.45
Cost[c]	$ / kW	13 (without frame and gasket) 16 (including frame and gasket)[d]	9	7
Durability with cycling	hours	9,000[e]	5,000[f]	5,000[f]
Performance @ 0.8 V[g]	mA / cm^2	160	300	300
Performance @ rated power	mW / cm^2	845[h]	1,000	1,000

Approach

ETFECS/Dispersed Electrodes

Synthesis of novel ETFECS (60%)

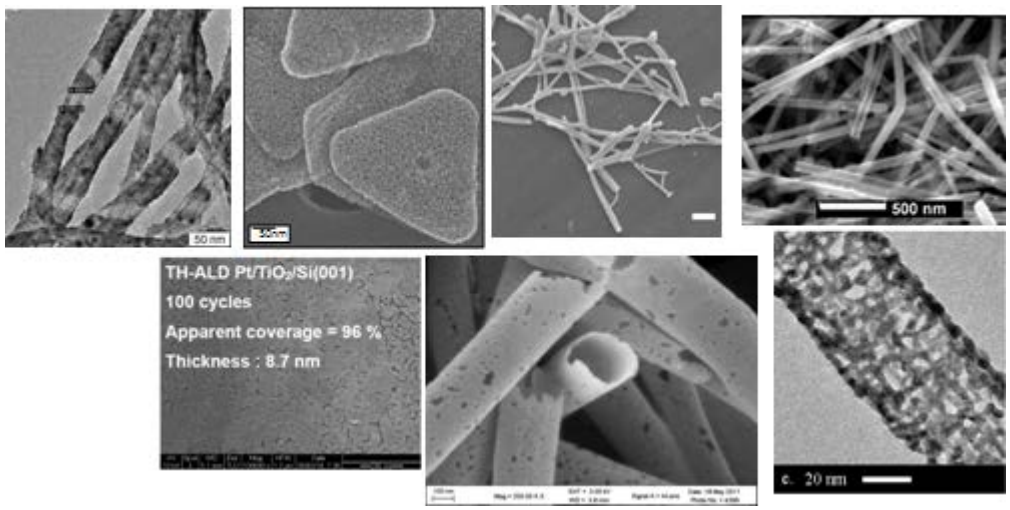
- Pt nanoparticles with continuity over 10's of nms or more. These materials have demonstrated enhanced specific activity and exceptional durability (3M, others).
- Screen multiple synthesis template (previous work) and Pt deposition (current year) techniques for relevance.
- Focus on increased Pt mass activity
  - Low Pt ECAs (electrochemically accessible surface areas) have been common (~10m^2/g_{Pt}), resulting in limited mass activity.

Electrode studies involving ETFECS (35%)

- Effectively incorporate extended Pt catalysts into electrodes. Pursued studies with Pt Black as an unsupported surrogate, expanded to ETFECS, including carbon incorporation.

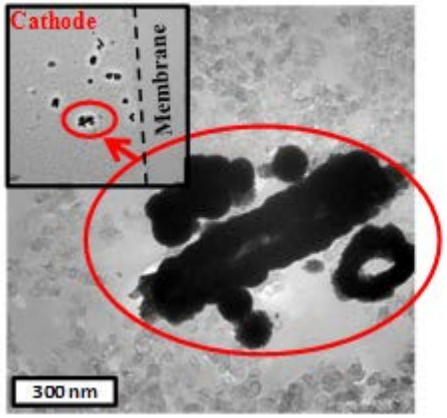
Supplemental modeling (5%)

- Modeling of catalyst particles, electrode structure and electrode performance.

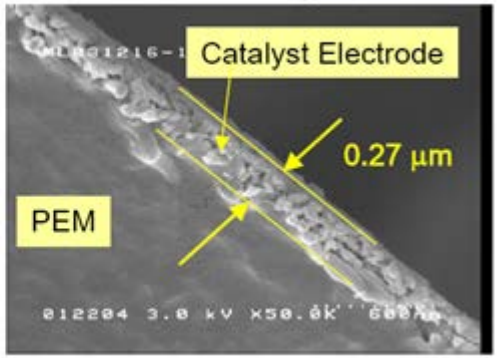


Particle	Pt Shells	Surface Pt
2 nm cubooctahedron	5	52%
5 nm cubooctahedron	12	24%
12.5 nm Pt coated(50 nm core) cylinder	29	~5%

NREL ETFECS



3M NSTF



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

Approach

Project Milestones

Demonstration of 2nd generation VACNTs, analogous to 3M's NSTF whiskers, based on low packing density and heights less than 2 microns.	12/10 Complete
DOE 2nd Quarter "Joule" Milestone for 2011 Budget: Demonstrate continuous Pt nanostructured catalyst with specific activity > 720 μA / cm^2 @ 900 mViR-free	3/11 Complete
Screening of at least 5 substrates and/or adhesion layers for their applicability to yield fast nucleation rates and form thin continuous films by ALD.	05/11 Complete
Go/no-go decision for down selection of carbon blacks included in electrode compositions containing extended surface Pt nanostructures based on ability to produce dispersed electrodes and electrochemical stability up to 1.5 V.	09/11 Complete

DOE 1st Quarter "Joule" Milestone for 2012 Budget: Maintain greater than 30 m^2/g Pt and 720 micro amps/cm^2 (at 900 mV IR free) in scale-up of ETFECS synthesis to gram quantity.	12/11 Complete
Quantify impact in rotating disc electrode of potential cycling, and carbon and ionomer content on observed mass and specific activity and electrochemical surface area for best performing, high yield ETFECS.	5/12 Complete
Quantify durability of top performing ETFECS relative to commercial Pt/C in fuel cell accelerated stress test (AST).	09/12 On track

Accomplishments and Progress

Pt Templates*/ Pt Deposition

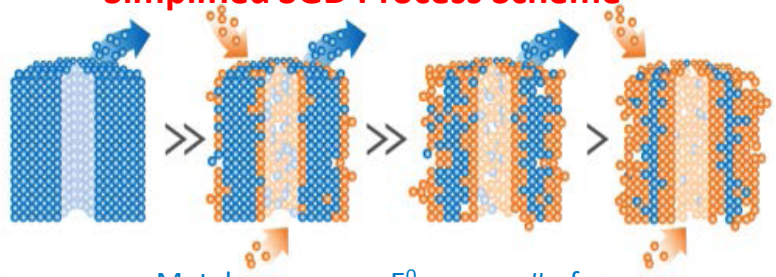
Vapor Deposition (evaporation, PLD)

- sputtering (NREL)*
- CVD (Tennessee)
- ALD: atomic layer deposition (NREL, Stanford, CNSE)

Solution Deposition (electrochemical, spontaneous, underpotential)

- spontaneous galvanic displacement (SGD) (NREL, UC-R/Delaware)

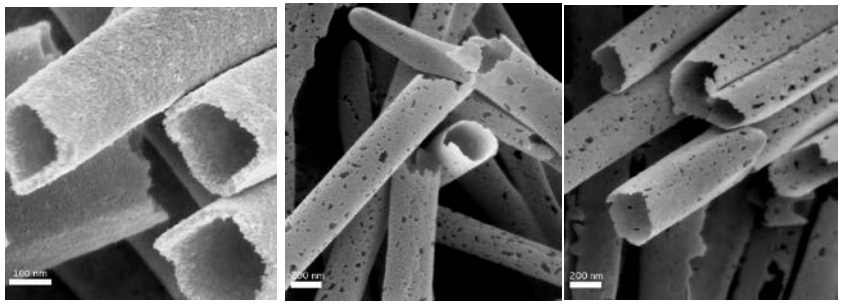
Simplified SGD Process Scheme



Metal	E^0	# of e^-
$Au^{3+} + 3\ e^- \leftrightarrow Au$	1.498	3
$Pt^{2+} + 2\ e^- \leftrightarrow Pt$	1.180	2
$Pd^{2+} + 2\ e^- \leftrightarrow Pd$	0.951	2
$Ag^{+} + e^- \leftrightarrow Ag$	0.800	1

* See supplemental slides for more detail

Pt CVD nanotubes



no anneal 500°C anneal 750°C anneal

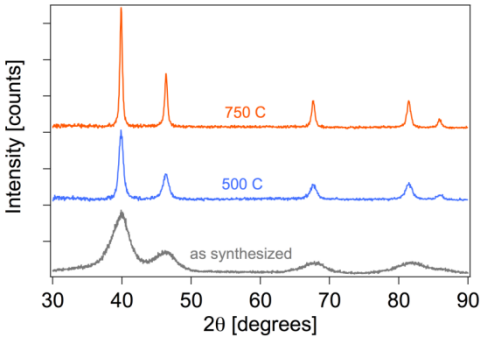
A wide array of different structures and compositions were obtained including nanoplates (NPs), nanowires (NWs), and nanotubes (NTs).

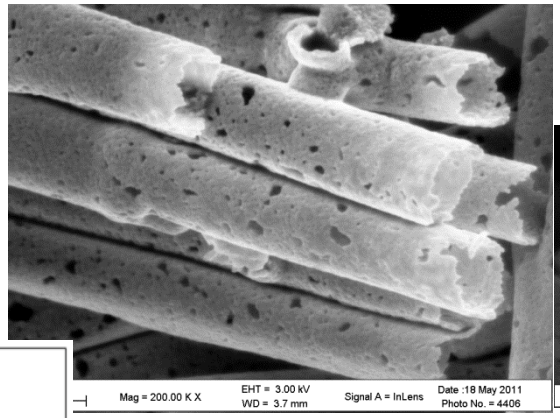
Focus on increasing ECA, specific (mass) activity, and durability:

- UC-R/Delaware: Multistep SGD (Pd, Pt, Au), template metal, stoichiometry
- NREL*: Displacement ion, template metal, template morphology, solvent system, reactant delivery, post processing, stoichiometry, temperature, scale up.

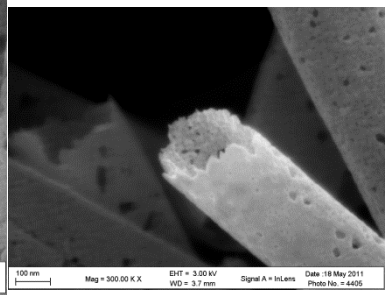
Accomplishments and Progress

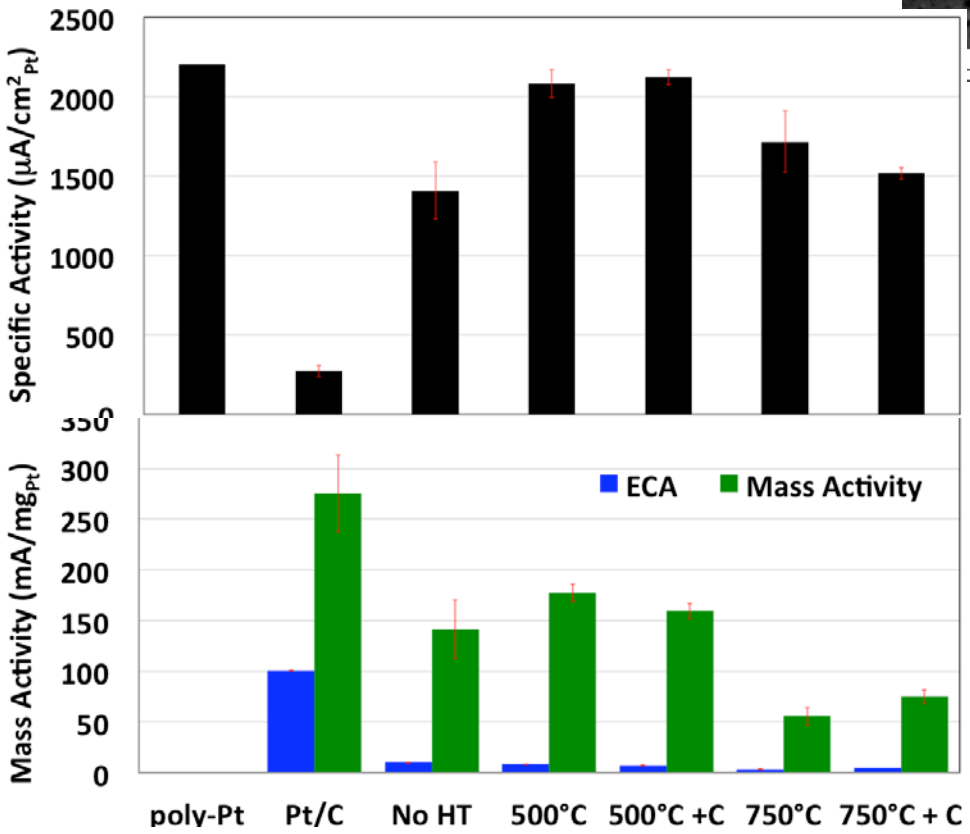
CVD Pt NT Characterization (Tennessee, NREL)





500°C





Specific activities for 500°C annealed samples essentially match that of polycrystalline Pt.

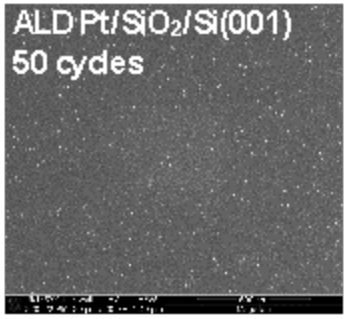
Carbon incorporation played little role on observed electrochemical properties.

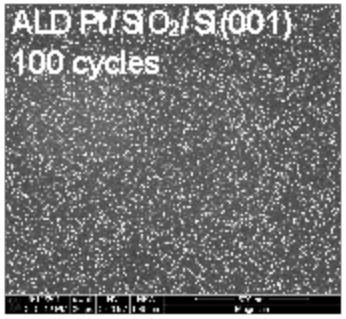
Surface areas (ECAs) are low resulting in low mass activities. May be improved by increasing ECA or specific activity.

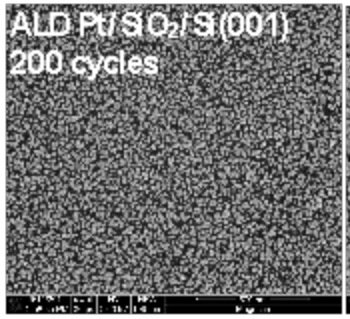
Accomplishments and Progress

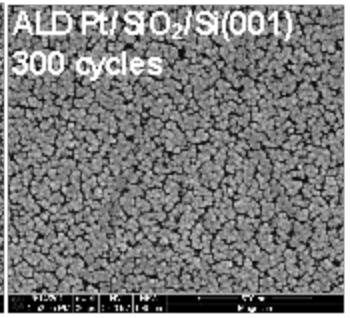
Pt Deposition (ALD): Ozone (Stanford)

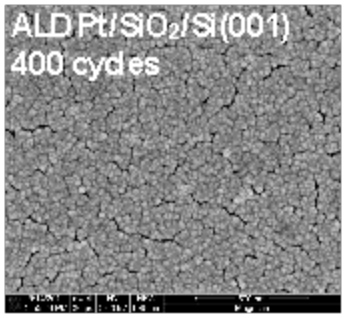
Air



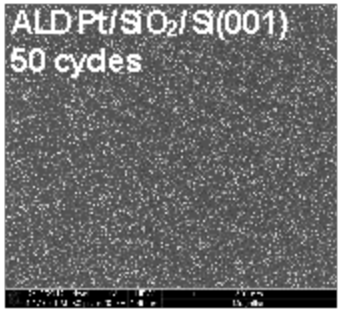


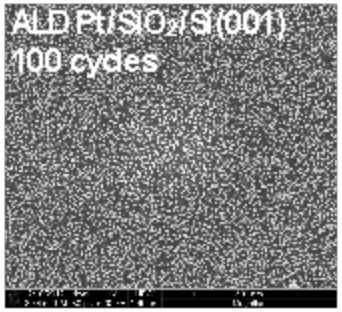


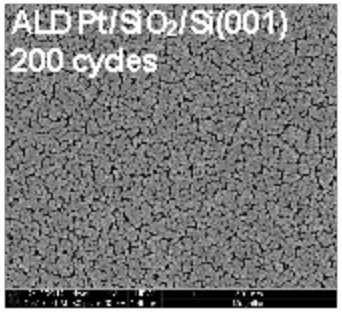


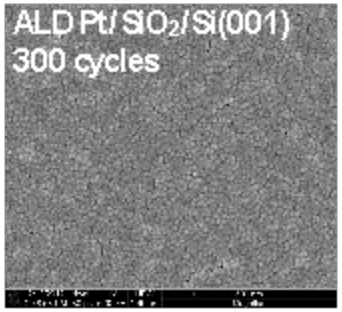


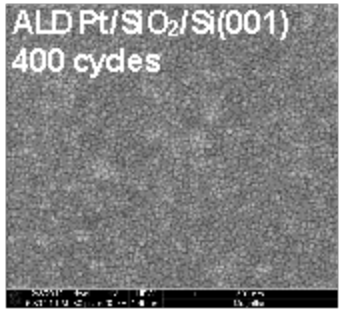
O_3





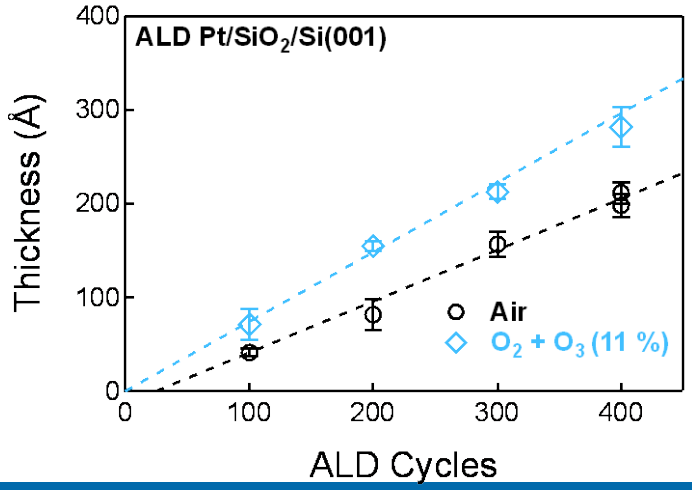






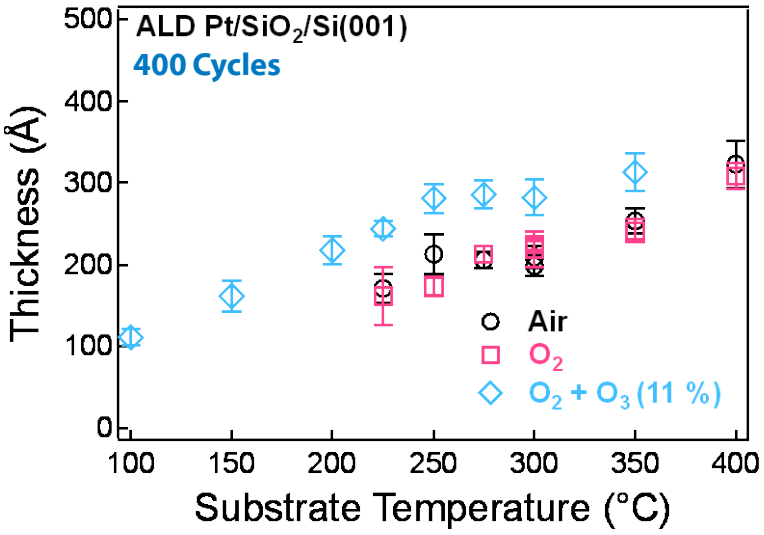
T= 300°C

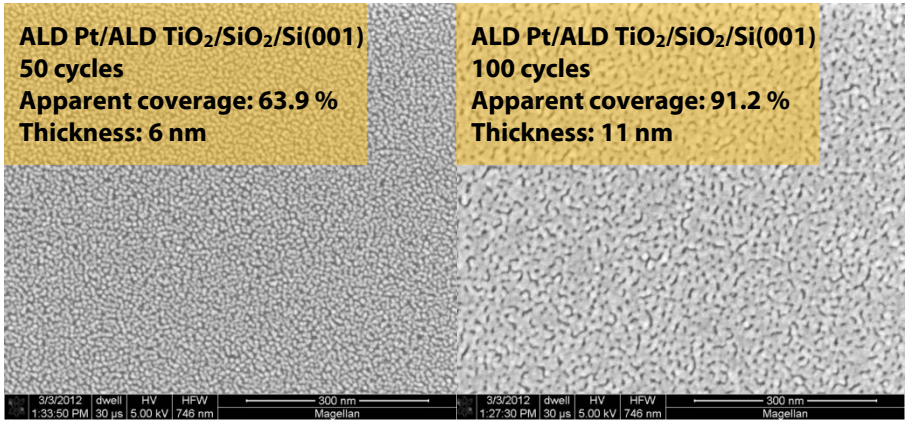
- Growth rate in O_3 is larger than in air
- Almost no nucleation delay in Pt ALD with O_3
- Nucleation delay in O_2 system: 25 cycles



Accomplishments and Progress

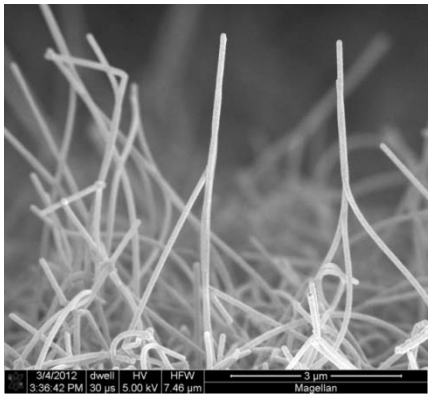
Pt Deposition (ALD): Ozone (Stanford/CNSE)

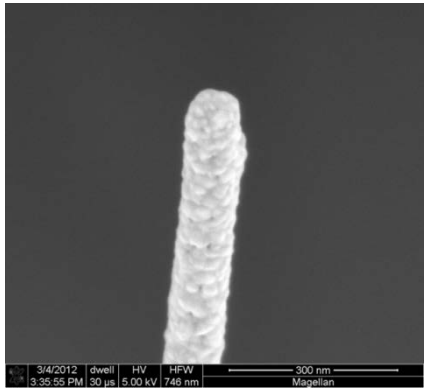




- Ozone has a tremendous impact on Pt deposition allowing significantly lower T deposition.
- TiO_2 coating shows better conformality at reduced thickness.
- Approach has been applied to nanostructures, next step electrochemical characterization.

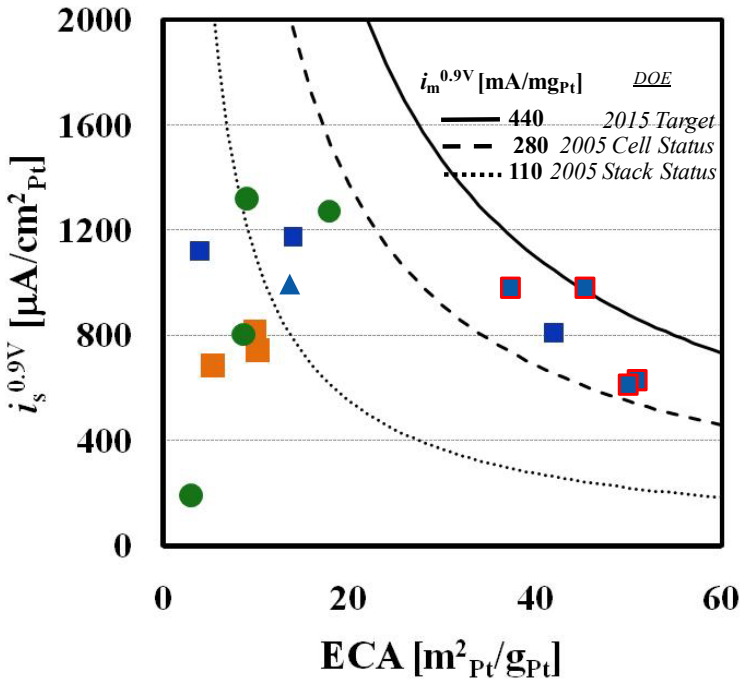
After TiO_2/Pt ALD





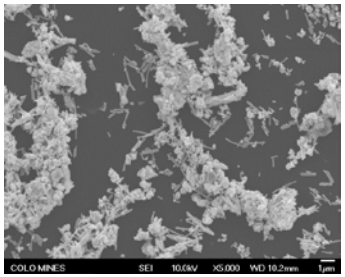
Accomplishments and Progress

Pt SGD: Scale Up (NREL)

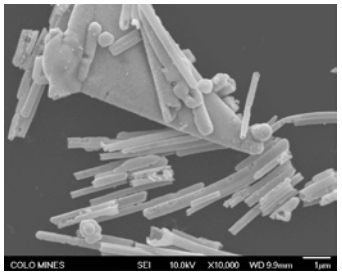


- Scale up of high performing SGD sample was performed to create increased catalyst quantities for characterization and electrochemical testing.
- High ECA and mass activity achieved, significant variability between batches.

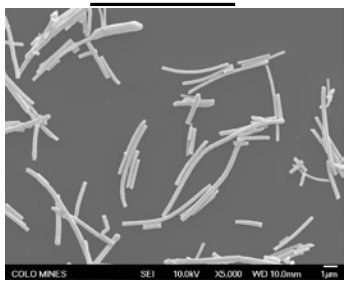
Batch 1



Batch 2



Batch 4

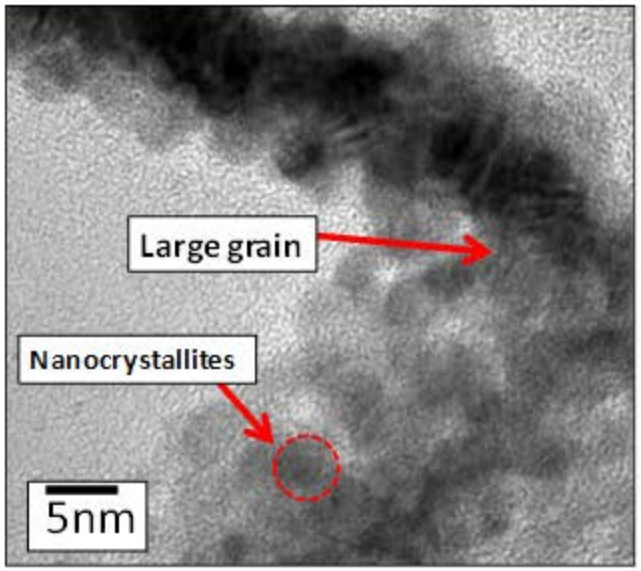


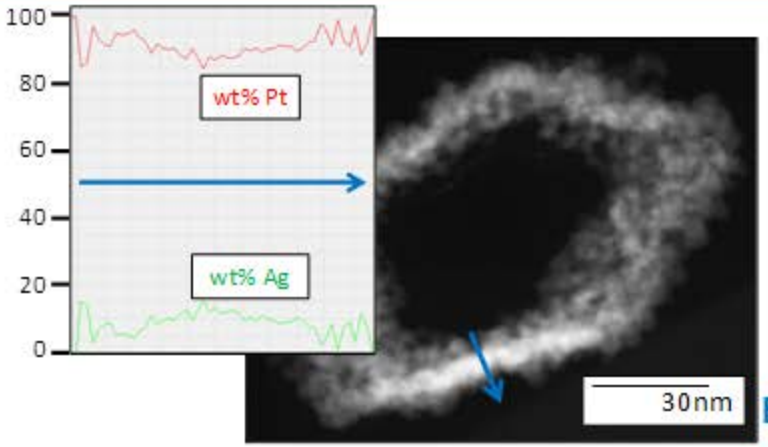
				Pt Wt %			
	ECA (m^2/g_{Pt})	$i_s^{0.9V}$ ($\mu A/cm^2_{Pt}$)	$i_m^{0.9V}$ (mA/mg_{Pt})	XRF (NREL)	XRF (LANL)	EDS (NREL)	EDS (ORNL)
Batch 1	38.6	1050	400	82	77.5	80-86	87-91
Batch 2	53.0	630	340	95	95	96-99	98-100
Batch 3	45.6	980	450	94	90	94-96	94-97
Batch 4	51.0	640	330	96	92	95-97	93-95
Average	47.0	820	390				

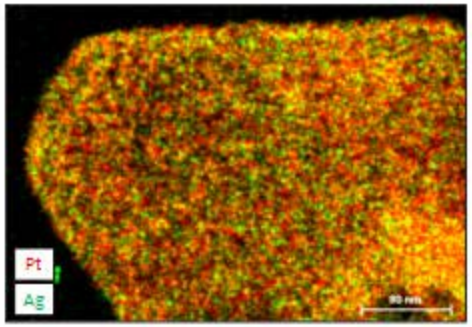
Batch 3

Accomplishments and Progress

Pt SGD: Scale Up Characterization (ORNL, LANL)

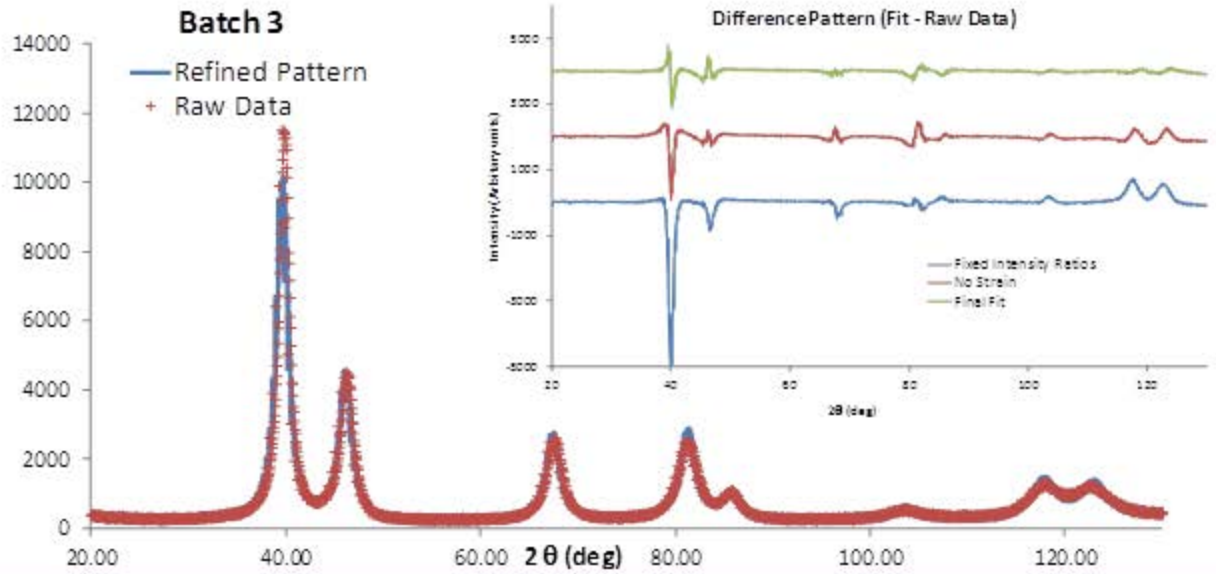






HR TEM consistently shows materials made up of agglomerates of small crystals/grains.

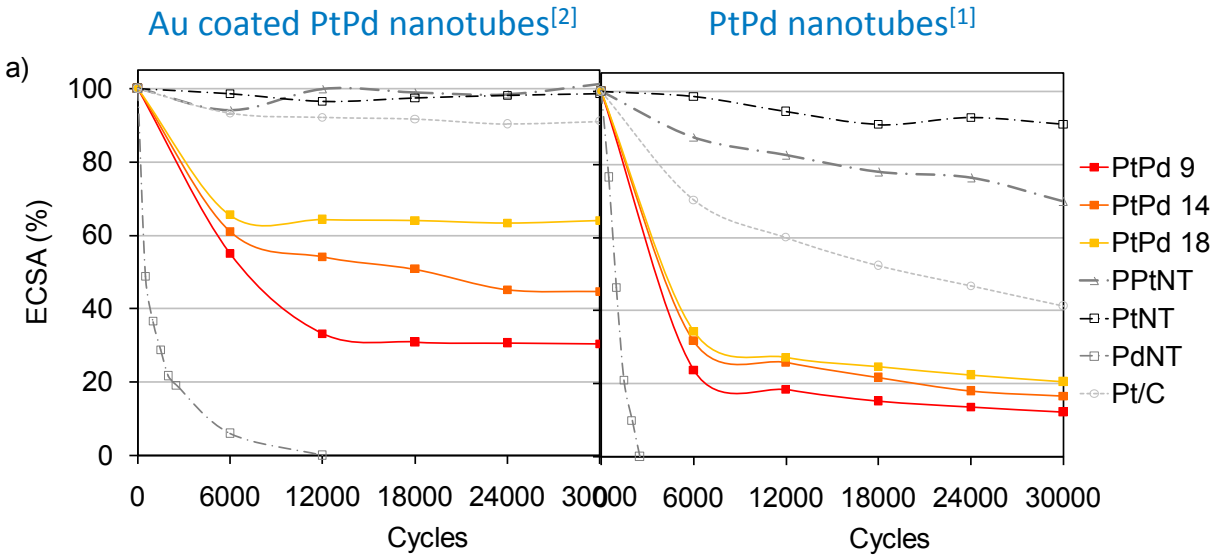
Elemental maps/line scans show homogeneous composition throughout structures.

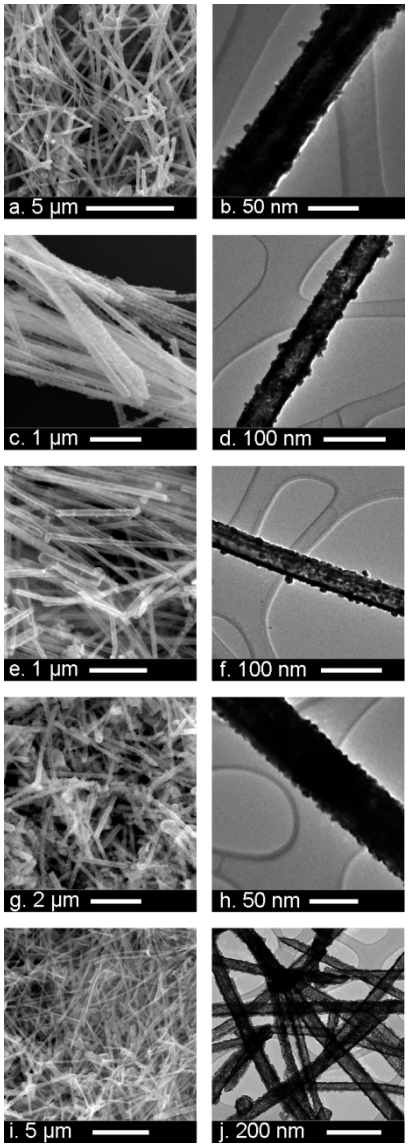


XRD fitting of catalysts show best fit with strain and preferred orientation, but are complicated and require further effort and technique refinement.

Accomplishments and Progress

Pt SGD: Multistep Pd, Pt, Au (UC-R/Delaware)





SEM and TEM images of a-b) PdNTs, c-d) PtPd 9, e-f) PtPd 14, g-h) PtPd 18, and i-j) PtNTs.

PtPd NTs and Au coated PtPd NTs investigated due to parallels with work of Adzic et al. and ability to be effectively investigated using SGD.

Specific activities can be very high, but mass activities low on a PGM basis (high on Pt basis).

Pd appears to be a poor choice for SGD catalyst support, Au may be promising for durability enhancements.

[1] J. Zhang, Y. Mo, M.B. Vukmirovic, R. Klie, K. Sasaki, R.R. Adzic *J. Phys. Chem. B* **2004**, 108, 10955.
[2] J. Zhang, K. Sasaki, E. Sutter, R.R. Adzic *Science* **2007**, 315, 220.

Accomplishments and Progress

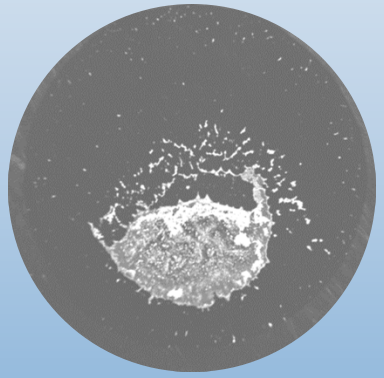
Pt Black in RDE w/Carbon (NREL)*

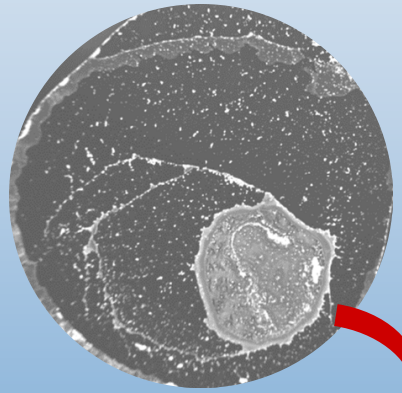
Pt Black
44 ug_{Pt}/cm^2_{elec}

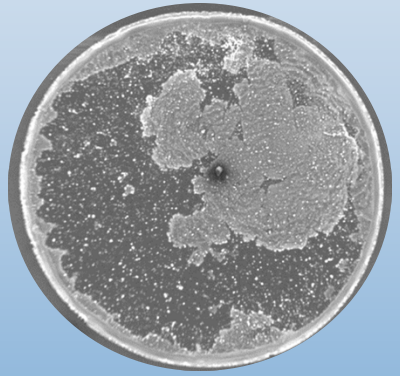
75 wt% Pt Black
38 ug_{Pt}/cm^2_{elec}

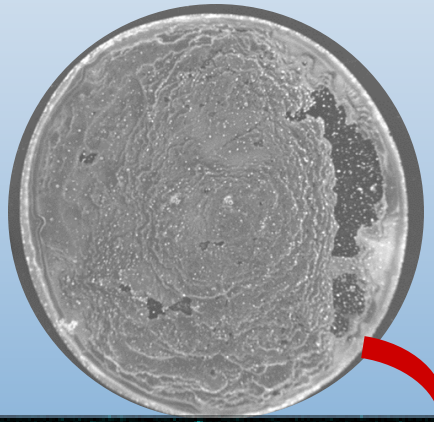
50 wt % Pt Black
26 ug_{Pt}/cm^2_{elec}

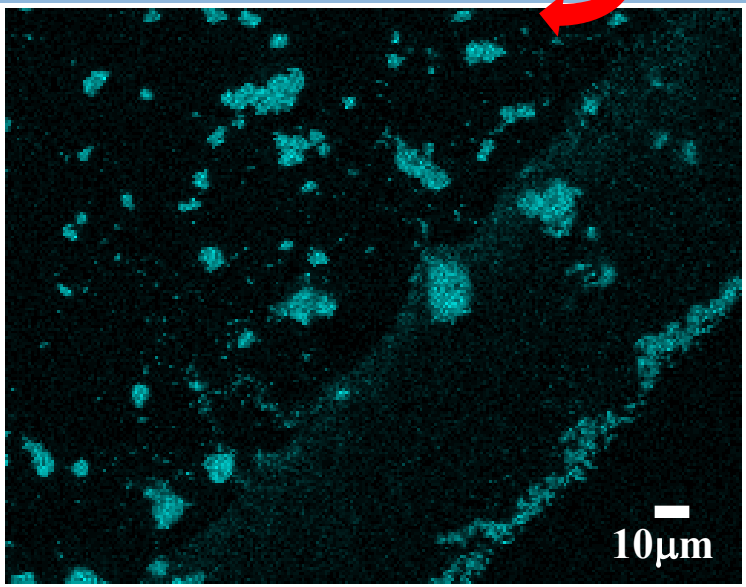
25 wt% Pt Black
13 ug_{Pt}/cm^2_{elec}

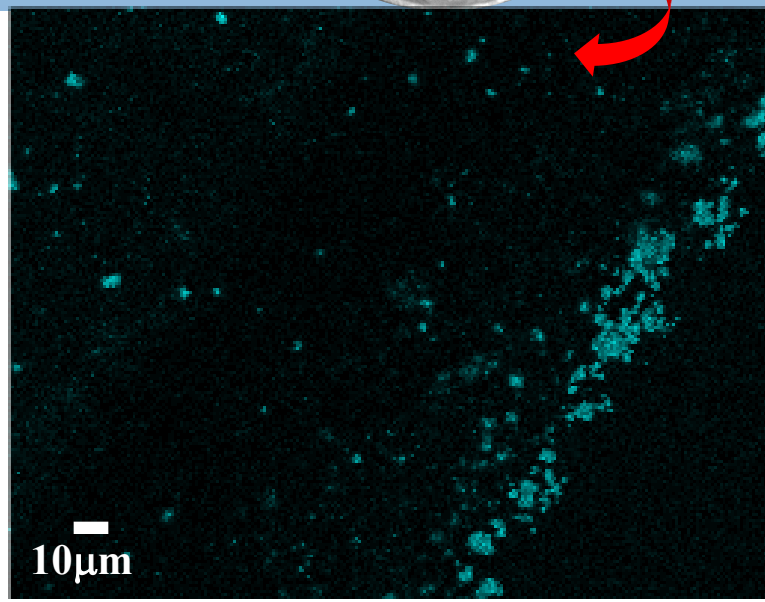








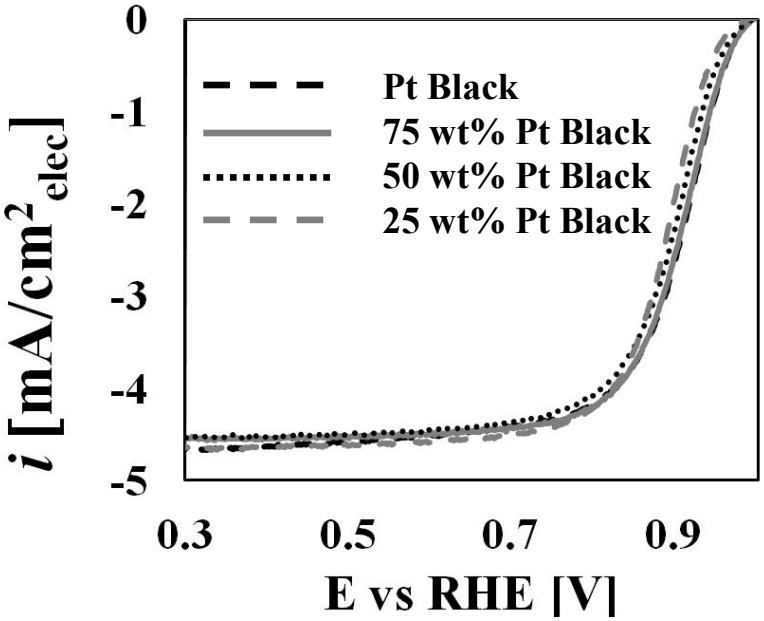


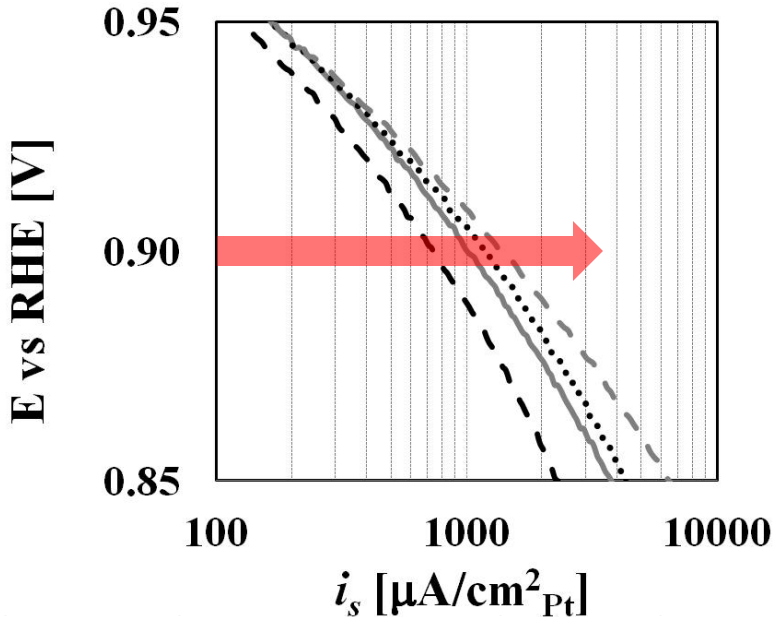


* See supplemental slides for more detail

Accomplishments and Progress

Pt Black in RDE w/Carbon (NREL)



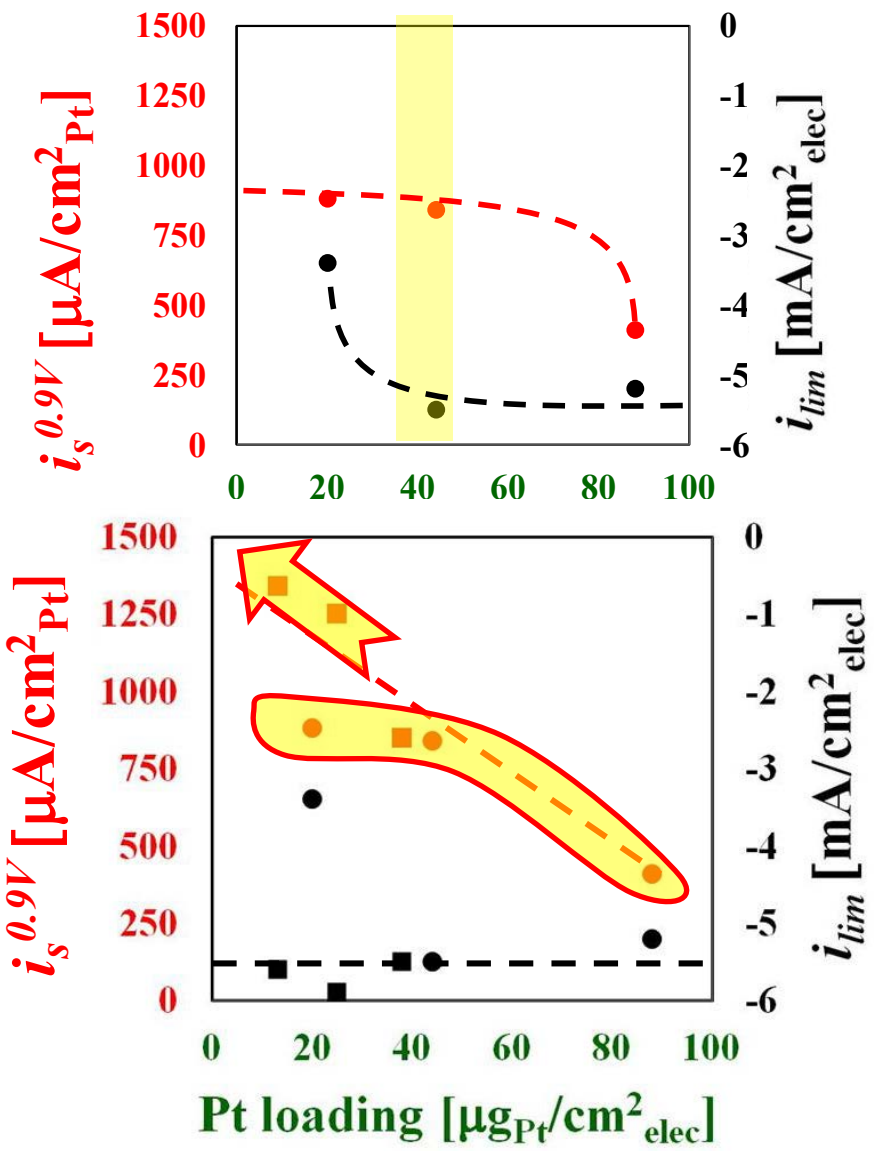


Catalyst	Pt Loading [$\mu g_{Pt}/cm^2_{elec}$]	ECA [m^2_{Pt}/g_{Pt}]	i_{lim} [mA/cm^2_{elec}]	Sweep rate [mV/sec]	$i_s^{0.9V}$ [$\mu A/cm^2_{Pt}$]	$i_m^{0.9V}$ [mA/mg_{Pt}]	elec [#]	Reference
Pt Black (Umicore AG)[1]	14	13	-	50	1200	150	-	[a]
Pt Black (Aldrich)[2]	41	19	-	10	250	50	-	[b]
Pt Black (HiSpec 1000, JM)	44	6	-	20	860	50	2	[c]
Pt Black (TKK)	44	25	-5.5	20	840	200	7	this work
75 wt % Pt Black w/Vu	38	21	-5.5	20	850	180	3	this work
50 wt % Pt Black w/Vu	25	20	-5.9	20	1250	250	5	this work
25 wt % Pt Black w/Vu	13	26	-5.6	20	1340	350	3	this work

[a] M. Nesselberger et al. *JACS*, **133**, 17428-17433 (2011) [b] B. Lim et al. *Science*, **324**, 1302-1305 (2009)
[c] H. A. Gasteiger et al. *Applied Catalysis B: Environmental*, **56**, 9 (2005)

Accomplishments and Progress

Pt Black in RDE w/Carbon (NREL)



RDE limiting current can be a useful indicator of insufficient disc coverage, but particularly in the case of unsupported catalysts, does not guarantee a good dispersion.

Specific activity measurements are intended to be assessments of the (intrinsic) activity of surface accessible Pt sites towards ORR.

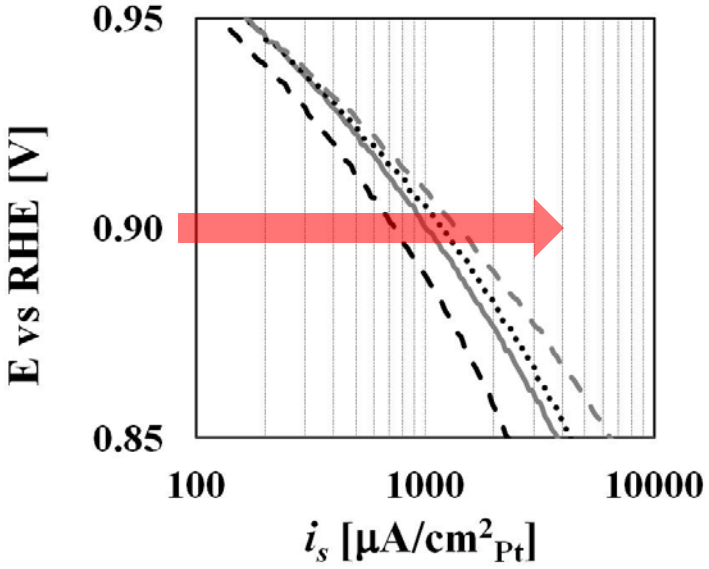
Incorporation of C improves the Pt black dispersion and gives a "truer" intrinsic activity. However, we suspect even our numbers are below a "true" specific (intrinsic) activity.

Alternate carbons have shown similar effect.

These results have strong implications on conventional thinking regarding extended surfaces and particle size effects.

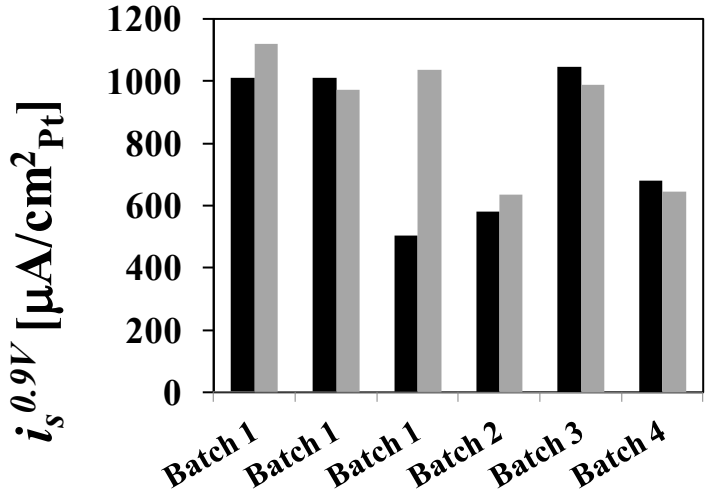
Accomplishments and Progress

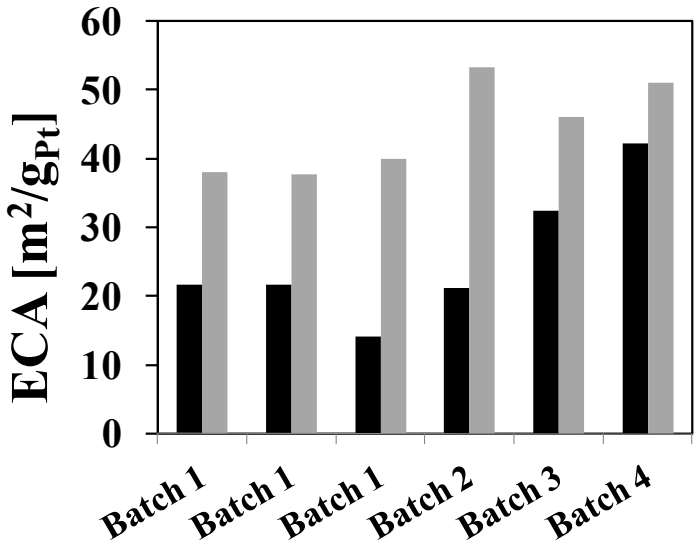
Carbon Incorporation with Pt ETFECS (NREL)



- Pt Black
- 75 wt% Pt Black
- 50 wt% Pt Black
- 25 wt% Pt Black

Previously demonstrated an ↑ $i_s^{0.9V}$ w/ an ↑ in carbon wt% and lower Pt loading due to improved electrocatalyst dispersion

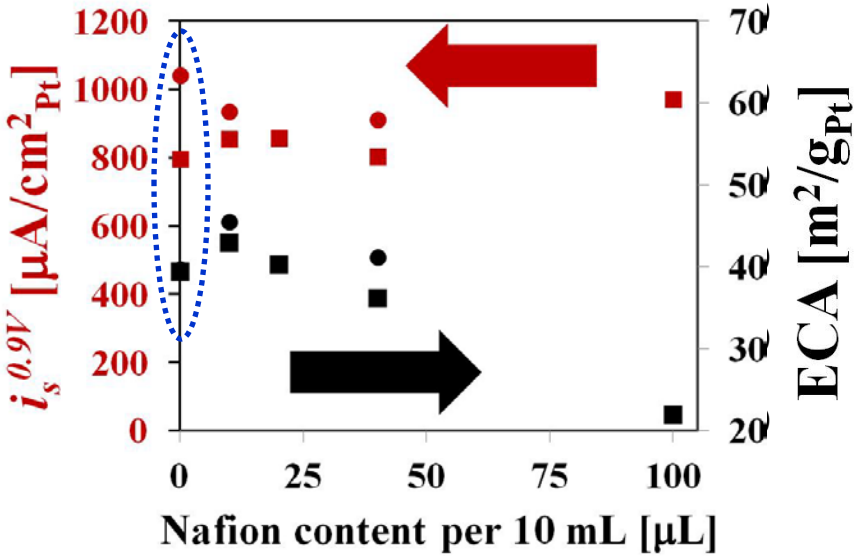




- Little or no improvement in $i_s^{0.9V}$
- significant (>20%) increase in ECA
- Could Nafion® content be affecting electrocatalyst properties?

Accomplishments and Progress

Ink Formulation Effects on ETFECS (NREL)



- Appears to be an optimum Nafion content for ECA
  - independent of carbon content
- Carbon helps with ECA when Nafion is present
  - ECA identical at zero Nafion content
- $i_s^{0.9V}$ is increased when carbon is present
  - Most evident at zero Nafion content

30,000 cycles from 0.6 to 1.0V

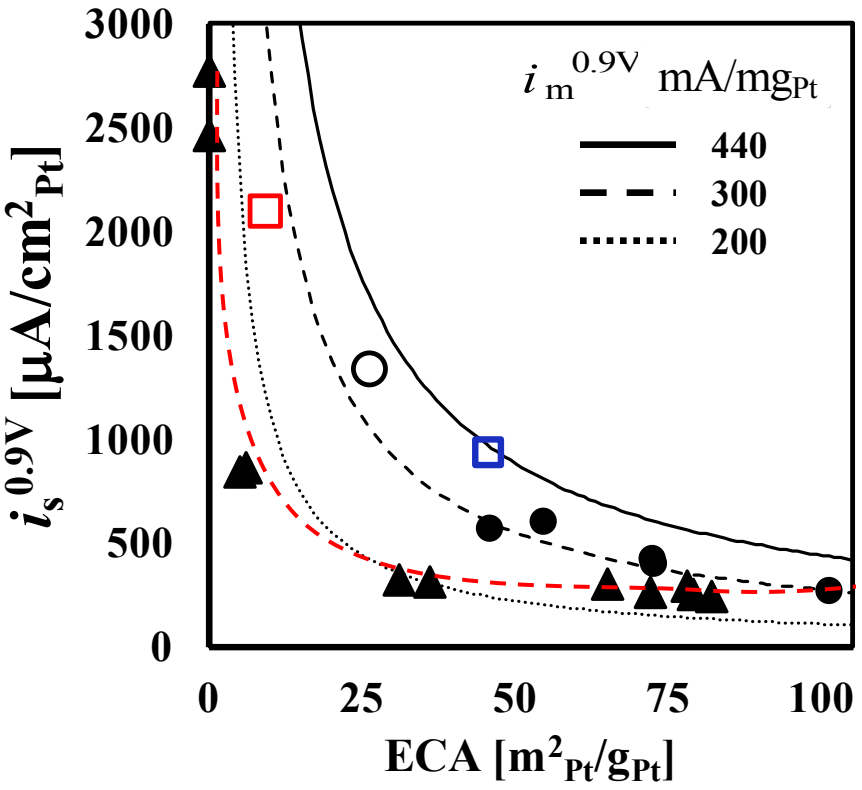
(10 μL Nafion)

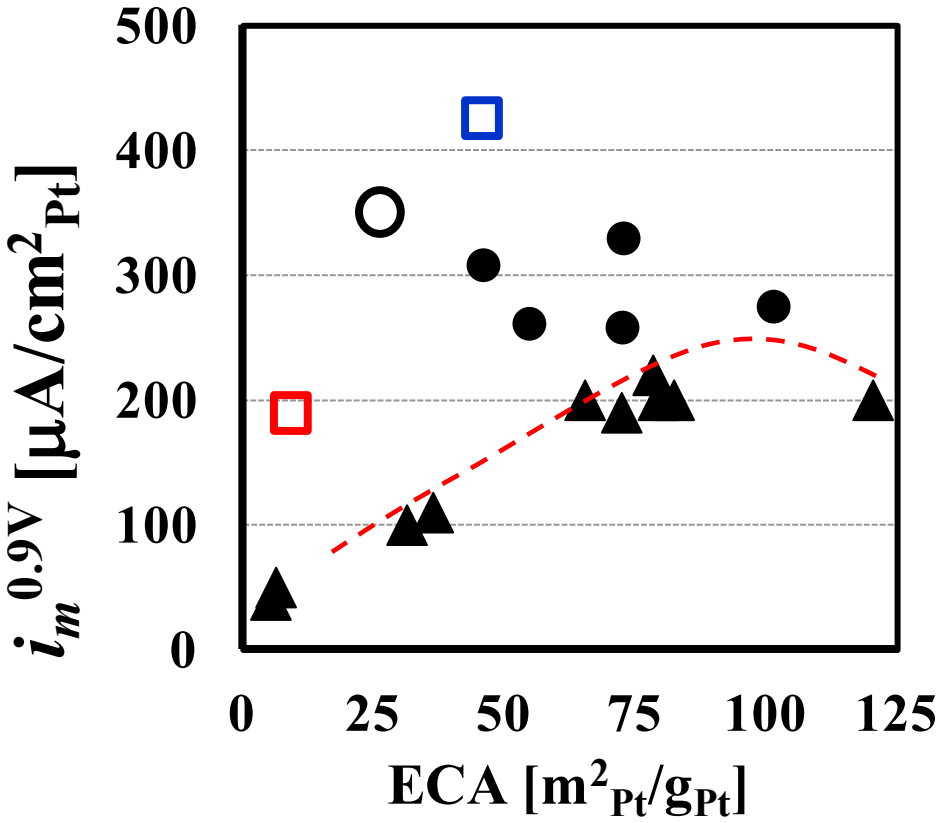
Nafion content μL/10 mL	i_{lim} mA/cm2 elec	ECA m^2_{Pt}/g_{Pt}	$i_s^{0.9V}$ uA/cm^2_{Pt}	$i_m^{0.9V}$ mA/mg_{Pt}
0	5.2	40	1042	414
10	5.1	45	935	425
40	4.8	41	912	379

	ECA m^2_{Pt}/g_{Pt}	NECA	$i_s^{0.9V}$ uA/cm^2_{Pt}	N $i_s^{0.9V}$	$i_m^{0.9V}$ mA/mg_{Pt}	N $i_m^{0.9V}$
Pt only (pre)	41		964		393	
Pt only (post)	33	81	1071	111	355	90
Pt + C (pre)	39		1078		420	
Pt + C (post)	30	78	1330	123	405	96

Accomplishments and Progress

Impact of Current Results





▲ Gasteiger et al. *Appl. Catal.B*, **56**, 9 (2005)

● **TKK-Pt**

○ **TKK-Pt Black w/C**

□ **NREL-Pt(Ag)w/C [SGD]**

□ **UT-Pt [CVD] w/C**

Collaborations

Key Investigators/Major Participants

National Renewable Energy Lab: Bryan Pivovar (PI), Shyam Kocha, Huyen Dinh, Lin Simpson, Chai Engtrakul, Arrelaine Dameron, Jason Zack, Tim Olson, KC Neyerlin, Justin Bult, Brian Larsen, Niccolo Aieta, Jeremy Leong
Oak Ridge National Laboratory: Kelly Perry
Los Alamos National Laboratory: Rod Borup
University of Delaware: Yushan Yan
State University of New York – Albany (CNSE): Eric Eisenbraun
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

Additional Collaborators:
Stanford Linear Accelerator (SLAC): Mike Toney
Johns Hopkins University: Jonah Ehrlebacher
Colorado School of Mines: Svitlana Pylypenko, Ryan Richards

Future Work

- **Pt deposition:**
  - CVD (Tennessee): Systematic studies involving wall thickness, annealing T, co deposition of metals with potential alloy benefits (Ni, Co)
  - ALD (Stanford, CNSE, NREL): Further studies involving ozone with a focus on low temperature ALD, application of developed techniques to nanostructured substrates (including NSTF) and electrochemical characterization
  - SGD (NREL, Delaware): further process optimization focusing on reproducibility and characterization of initial samples

- **Electrode studies (NREL):**
  - Continued electrode studies of highest performing catalysts and role of carbon, including durability studies and catalyst utilization studies
  - Expanded MEA fabrication and fuel cell testing of ETFECS

- **Modeling *:**
  - Colloidal interactions to probe dispersions and inks of ETFECS (Tennessee)
  - Rotating disc electrode (RDE) models to investigate specific activity, limiting current and electrochemical surface area (Texas)

* See supplemental slides for more detail

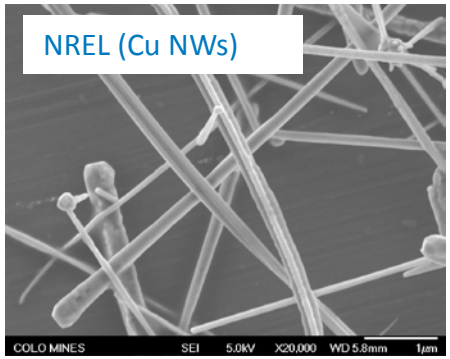
Summary

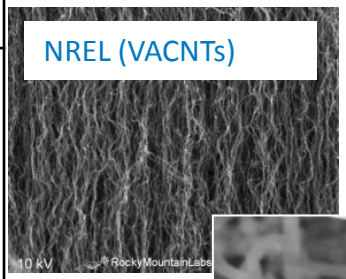
- **Relevance: Focused on overcoming the most critical barriers for fuel cell MEA development.**
- **Approach: Developing extended surface Pt catalysts for their high mass activity and durability, and explore incorporating these structures into robust, high efficiency MEAs.**
- **Accomplishments and Progress: The project has synthesized many novel catalysts using materials, geometries, and approaches not previously demonstrated. Have reached poly crystalline Pt specific activity in nanostructures using CVD. Have demonstrated continuous ALD Pt coatings down to single nm thickness. Have met 2020 DOE mass activity target without alloying advantages, commonly produce extended surface catalysts with >40m^2/g ECA. Have shown common perception of Pt Black and extended surfaces to be flawed. Have shown good cyclic durability, and elucidated the role of carbon in RDE.**
- **Collaborations: We have a diverse team of researchers from several institutions including 2 national labs, 5 universities, and 3 industry. We have added collaborators with specific strengths.**
- **Proposed Future Research: Focused on incorporating materials with improved mass activity and voltage cycling stability into highly performing electrodes. Seeking further improvements in mass activity targeting alloy advantages.**

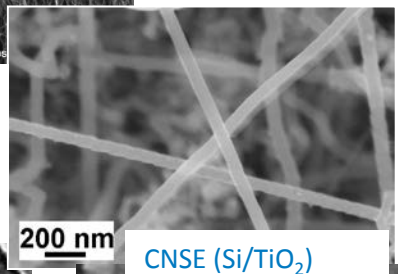
Technical Backup Slides

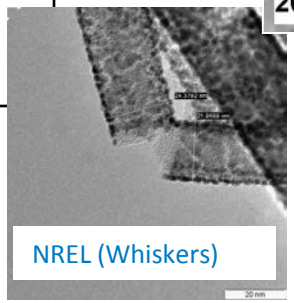
Approach
Templates

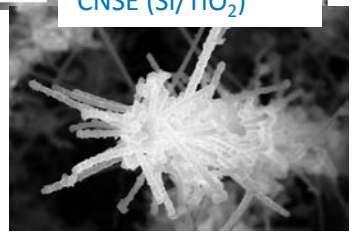
Template	Status
Metal (wires, tubes, etc) NREL, UC-R/Delaware	Cu nanowires synthesized routinely Ag nanowires have been synthesized, now commercially obtained Ag nanoplates synthesized
Carbon Nanotubes (CNTs) NREL	Continuous thin films only obtained by sputtering Down selected work in synthesis to short, dispersed tubes.
Metal oxides (CNSE, NREL)	Focus on TiO_2 coated Si nanowires.
Whiskers	3M NSTF









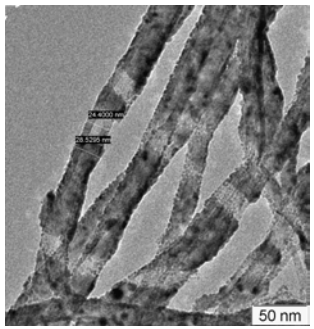


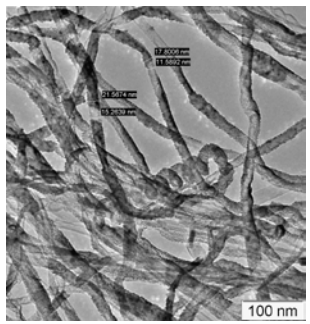
Discovery synthesis of cores/templates is complete.
See last year's AMR Presentation for details.

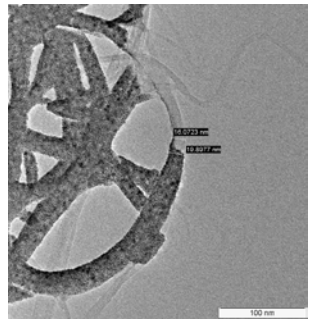
Accomplishments and Progress

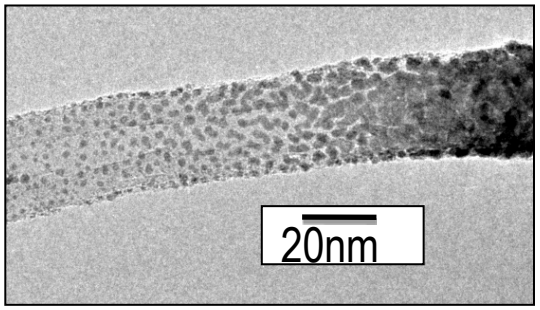
Sputtering (NREL)

- **Sputtering has yielded targeted structures (thin Pt layers on substrates – NSTF(3M), CNTs(NREL))**





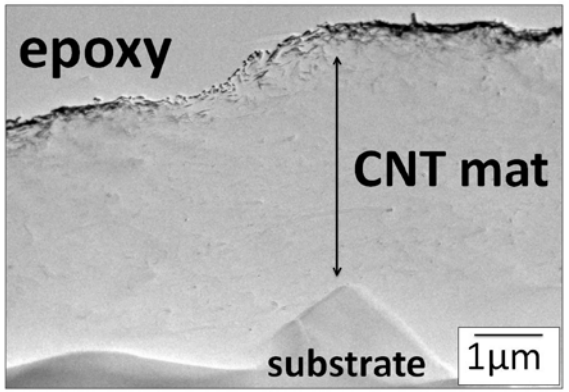




K. Perry (ORNL)

Homogeneity of material and yield prevented meaningful electrochemical characterization.

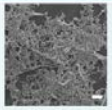
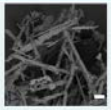
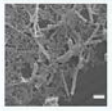
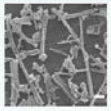
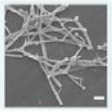
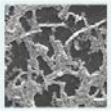
Roll to roll processes (including thin mat fabrication or vertically aligned substrates and continuous sputtering) necessary to improve yield. While deemed to be of merit (including for commercial processes), sputtering is not being currently pursued (within project) due to cost of implementation, specialty equipment, and time - as well as promise of other approaches.



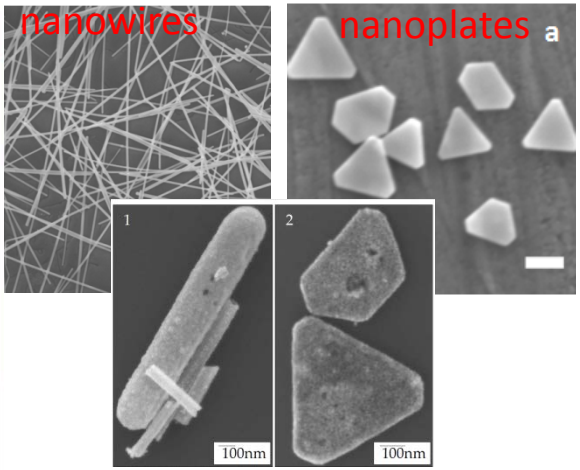
Accomplishments and Progress

Examples of Reaction Variable Investigated for Pt SGD (NREL)

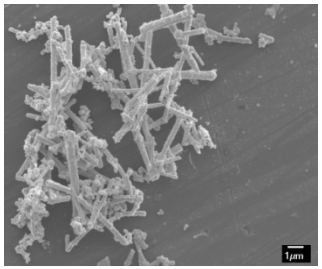
Temperature/ Reactant Delivery

Instant. Pt delivery	Product		Metered Pt delivery*	Product	
280°C	Long Pt-Cu wires and Pt particles		280°C	Long Pt coated Cu wires and Pt-Cu particles	
200° C	Long Pt-Cu wires and Pt particles		200° C	Shortened Pt-Cu wires and Pt-Cu particles (~18 m^2_{Pt}/g_{Pt})	
93° C	Long smooth Pt-Cu wires		93° C	Shortened Pt-Cu wires with rough porous surfaces (~9 m^2_{Pt}/g_{Pt})	
22°C	Shortened Pt-Cu wires		Note: all scale bars are 1 micron *Pt delivery over 15 hours (.1 mL/hr of 10 mMol H_2PtCl_6 in CHP)		

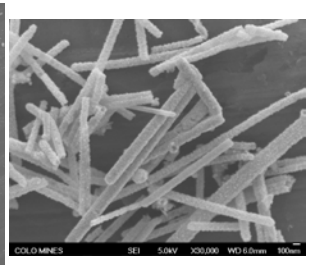
Template Morphology



Template Metal

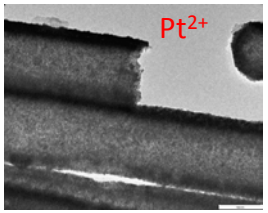


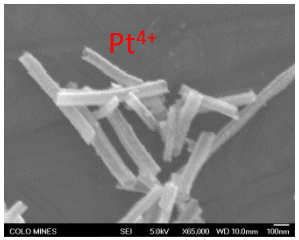
PtNTs from CuNWs



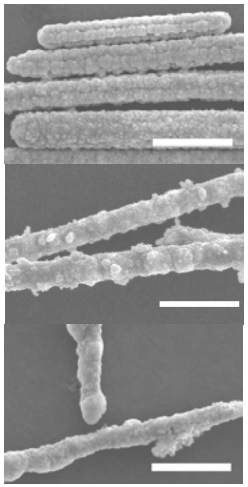
Pt NTs from AgNWs

Pt Precursor

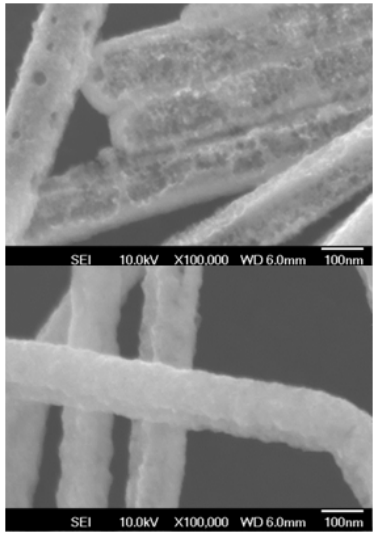




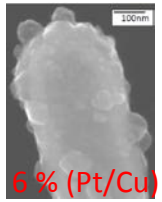
Surface Ligands

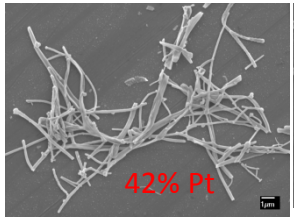


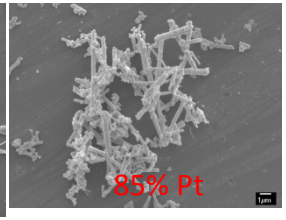
Reaction solvent



Displacement Extent (Stoichiometry)







Approach
Electrode Studies (NREL)

Extended structure catalysts have not been studied in detail within electrodes.

Effectively incorporating ETFECS into electrodes is expected to be a significant challenge. Material availability and reproducibility has been an issue. We therefore began studies using commercially available Pt black as a representative high density unsupported electrocatalyst, and obtained critical results.

Studies primarily in RDE* and have investigated

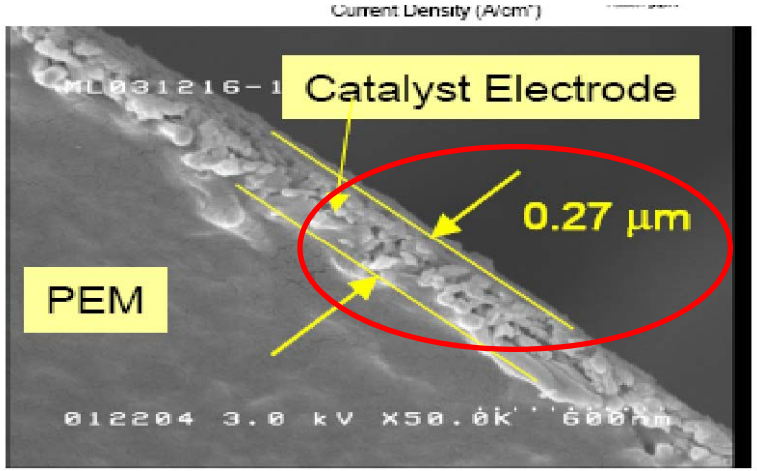
- Carbon incorporation (several types)
- Ink composition (loadings, composition)
- Activity, ECA, Durability

Carbon investigated for

- Transport issues (mass, e-, H+)
- Catalyst Dispersion

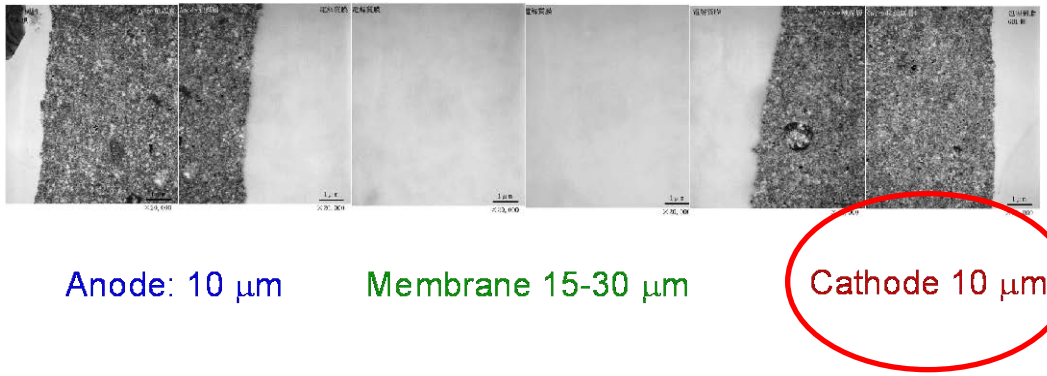
*RT, 0.1 M $HClO_4$
10-80 $\mu g_{Pt}/cm^2_{elec}$
20mV/sec CVs
20mV/sec LSV ORR

3M NSTF Electrocatalyst Layer



Mark Debe, "*Advanced Cathode Catalysts*", **2009** DOE Hydrogen Program Review, May 18-22

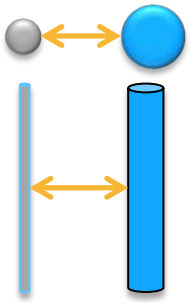
Conventional Pt/C Electrocatalyst Layers



Approach
Supplemental Modeling

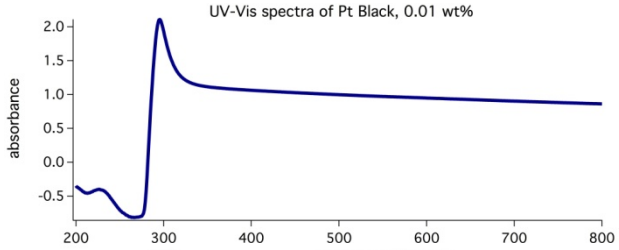
Colloidal interaction parameters (Tennessee)

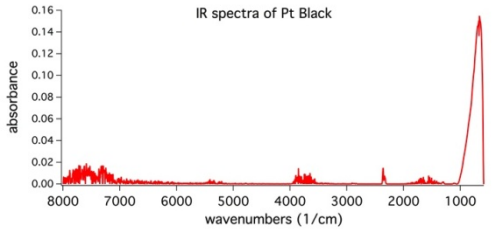
- Many of our catalyst particles have different interactions in inks and electrodes that are not well understood but critical for the successful integration of these materials into highly performing electrodes. Interactions of these particles can be modeled in terms of a Hamaker coefficient approach to better understand dispersion and interaction in solvents and electrodes from physically measurable properties including UV-Vis and IR spectra.

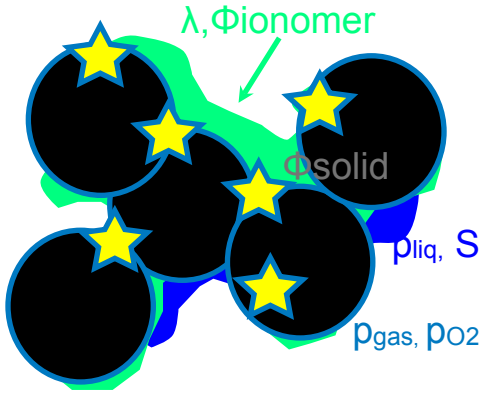
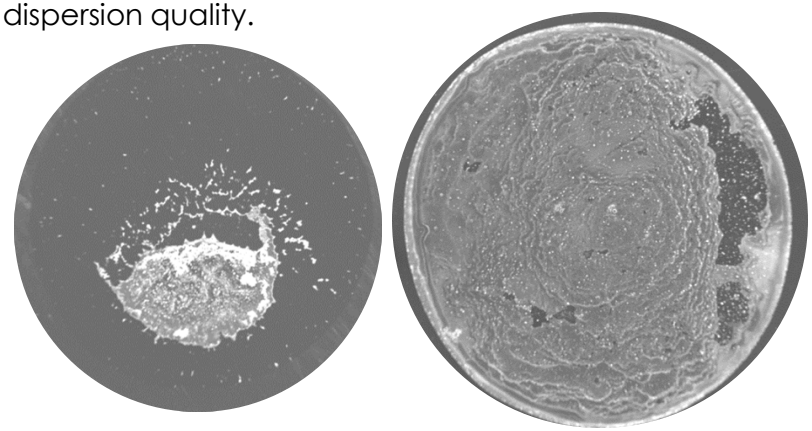


$$G_{ss}(z;R1,R2) = -\frac{A_{1m/2m}}{3}\left[\frac{R_1R_2}{z^2-(R_1+R_2)^2}+\frac{R_1R_2}{z^2-(R_1-R_2)^2}+\frac{1}{2}ln\frac{z^2-(R_1+R_2)^2}{z^2-(R_1-R_2)^2}\right]$$

$$G_{c||c}(z;R1,R2) = -\sqrt{\frac{2\pi R_1R_2}{R_1+R_2}}\frac{kT}{8\pi l^{3/2}}\sum_{n=0}^{\infty}{'r_n^{3/2}}\sum_{q=1}^{\infty}\frac{1}{q}\times\int_1^{\infty}p\left[(\bar{\Delta}_{Am}\bar{\Delta}_{Bm})^q+(\Delta_{Am}\Delta_{Bm})^q\frac{e^{-r_npq}}{\sqrt{pq}}\right]dp$$





Modeling of RDE results for extended surface catalysts (Texas)

- Expand established porous electrode models into RDE geometries to explain the performance of unsupported catalysts observed as a function of composition and dispersion quality.