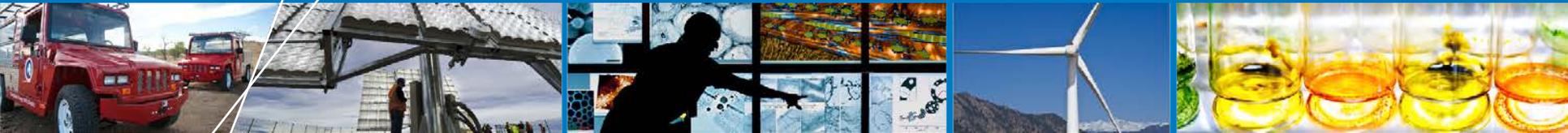


# Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes



**2013 DOE Hydrogen and Fuel  
Cells Program Review**

**Bryan Pivovar (PI)**

**May 16, 2013**

**FC007**

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

# Overview

## Timeline

- Start: July 2009
- End: September 2013
- % complete: ~80%

## Barriers

- A. Durability
- B. Cost
- C. Performance

## Budget (\$K)

DOE Cost Share	Recipient Cost Share	TOTAL
8384	868	9252

## Budget (\$K)

FY 2009	1480
FY 2010	1203
FY 2011	2177
FY 2012	1575
FY 2013	1949

## Partners – Principle Investigators

Oak Ridge National Laboratory (ORNL) – Dave Cullen  
Los Alamos National Laboratory (LANL) – Rangachary Mukundan  
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  
Colorado School of Mines (CSM) – Dave Diercks, Svitlana Pylypenko  
Nissan Technical Center North America\* (NTCNA) – Kev Adjemian  
Cabot Fuel Cells\* (Cabot) – Paolina Atanassova  
Tanaka Kikinzoku Kogyo\* (TKK) – Fumiaki Ogura

\*non-subcontracted collaborators

# Relevance

## ETF ECS/Dispersed Electrodes

### Review Period Objectives:

- Synthesis and characterization of novel extended thin film electrocatalyst structures (ETF ECS) with increased activity and durability, moving towards meeting all 2015 DOE catalyst targets simultaneously.

- Incorporation of ETF ECS with highest potential to meet DOE targets into MEAs for fuel cell testing of performance and durability.

**Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications**

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

<sup>a</sup> PGM content and loading targets may have to be lower to achieve system cost targets.

<sup>b</sup> M. Debe, U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Merit Review Proceedings, May, 2011, ([http://www.hydrogen.energy.gov/pdfs/review11/fc001\\_debe\\_2011\\_o.pdf](http://www.hydrogen.energy.gov/pdfs/review11/fc001_debe_2011_o.pdf))

<sup>c</sup> Durability measured in a 25-50 cm<sup>2</sup> MEA during triangle sweep cycles at 50 mV/s between 0.6 V and 1.0 V at 80°C, atmospheric pressure, 100% relative humidity, H<sub>2</sub> at 200 sccm and N<sub>2</sub> at 75 sccm for a 50 cm<sup>2</sup> cell. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols ([http://www.uscar.org/commands/files\\_download.php?files\\_id=267](http://www.uscar.org/commands/files_download.php?files_id=267)), Electrocatalyst Cycle and Metrics (Table 1). Activity loss is based on loss of mass activity, using initial catalyst mass, at end of test.

<sup>d</sup> Durability measured in a 25-50 cm<sup>2</sup> MEA during a hold at 1.2 V in H<sub>2</sub>/N<sub>2</sub> at 80°C, 150 kPa absolute, 100% relative humidity. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols ([http://www.uscar.org/commands/files\\_download.php?files\\_id=267](http://www.uscar.org/commands/files_download.php?files_id=267)), Catalyst Support Cycle and Metrics (Table 2). Activity loss is based on loss of mass activity, using initial catalyst mass, at end of test.

<sup>e</sup> Test at 80°C H<sub>2</sub>/O<sub>2</sub> in MEA; fully humidified with total outlet pressure of 150 KPa; anode stoichiometry 2; cathode stoichiometry 9.5 (as per Gasteiger et al. Applied Catalysis B: Environmental, 56 (2005) 9-35).

# Approach

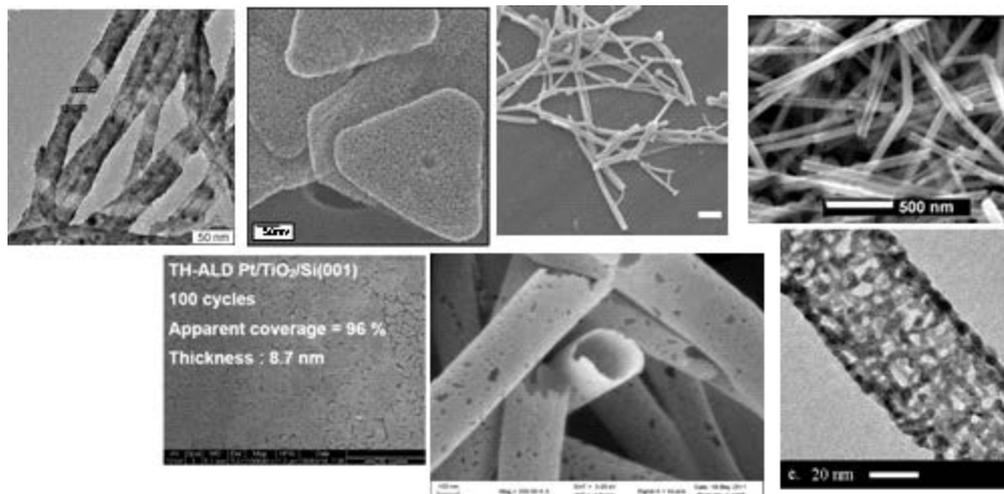
## Extended Thin Film Electrocatalyst Structures (ETFECS)/ Electrodes

Synthesis/Screening of novel catalysts (70%)

Pt catalysis remains a primary limitation to cost and durability targets, extended surfaces have shown promise in activity and durability.

Evaluate multiple synthesis techniques for relevance.

Focus on increased Pt mass activity  
Low Pt ECAs (electrochemically accessible surface areas) have been common in ETFECS, resulting in limited mass activity, increased surface accessible Pt has been a key focus.



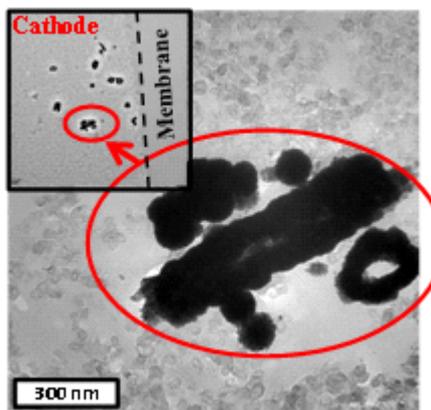
Particle	Pt Shells	Surface Pt
2 nm cubooctahedron	5	52%
5 nm cubooctahedron	12	24%
12.5 nm Pt coated(50 nm core) cylinder	29	~5%

Optimization of electrodes/Fuel cells (30%)

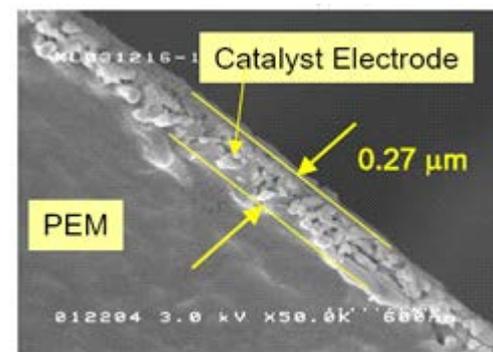
Effectively incorporate ETFECS into optimized, high performance electrodes.

Optimize ionomer and carbon content, dispersion quality, and loading.

### NREL ETFECS



### 3M NSTF



[http://www.hydrogen.energy.gov/pdfs/review04/fc\\_4\\_debe.pdf](http://www.hydrogen.energy.gov/pdfs/review04/fc_4_debe.pdf)

# Approach

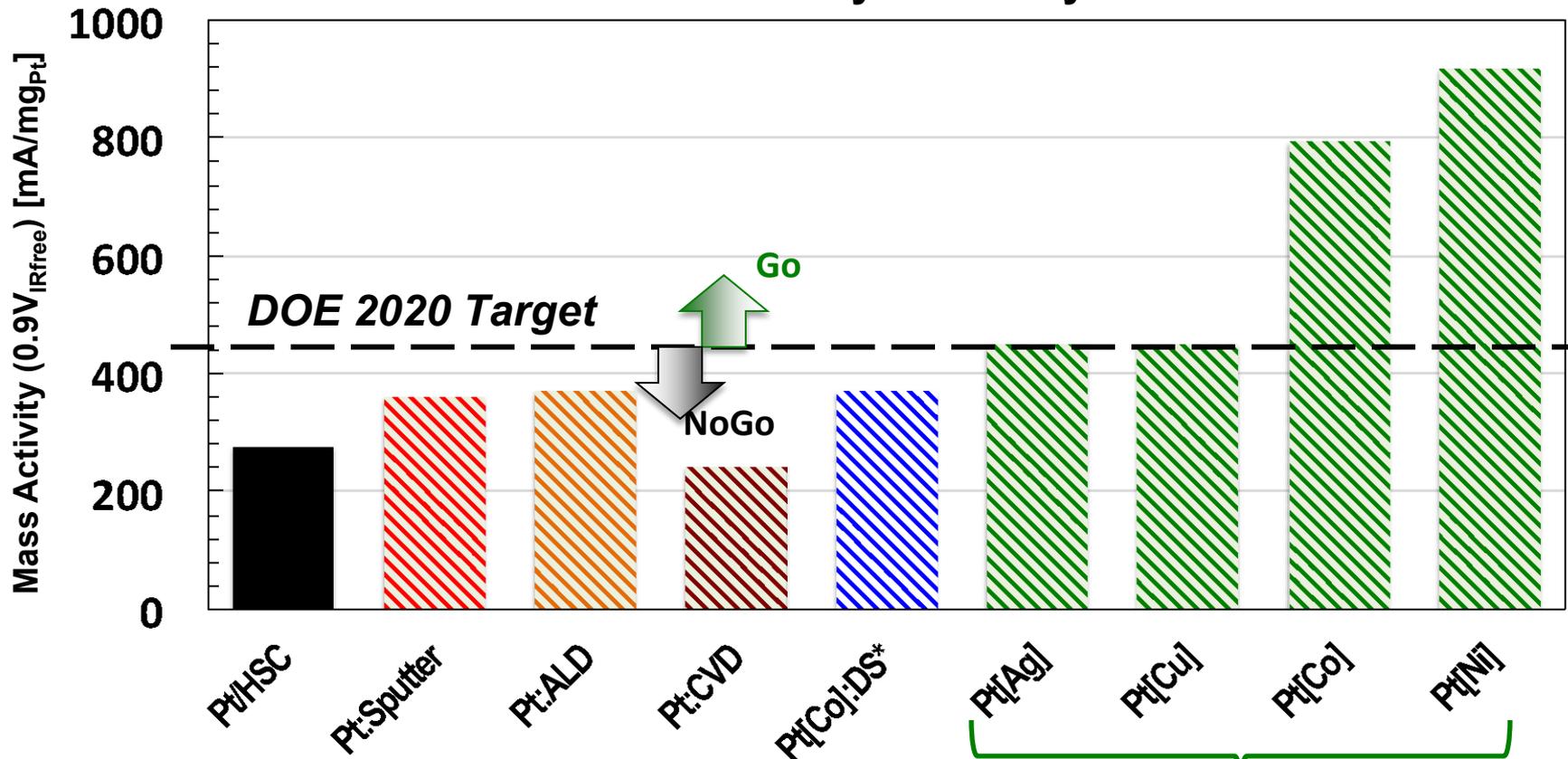
## Project Milestones (FY 12-13)

Synthesis	Maintain greater than 30 m <sup>2</sup> /g Pt and 720 micro amps/cm <sup>2</sup> (at 900 mV IR free) - DOE 2015 target, in scale-up of ETFECS synthesis to gram quantity.	12/11 Completed on time
RDE	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 Completed on time
Fuel Cell	Quantify durability of top performing ETFECS relative to commercial Pt/C in fuel cell accelerated stress test (AST).	09/12 Completed on time
Synthesis	Go/No-go decision for catalyst synthesis. No go all catalyst synthesis routes that have not demonstrated mass activities above 0.44 A/mg Pt @900 mV (IR free).	2/13 Completed on time
Fuel Cell	Demonstrate mass activity of 0.36 A/mg Pt @900 mV (IR free) with novel ETFECS in MEAs (a 50% improvement over 2011 status).	5/13
Fuel Cell	Demonstrate <40% mass activity loss in initial catalytic activity (DOE 2020 Target).	07/13
Fuel Cell	Go/No-go decision for delivery of short stack. If 2020 DOE targets of mass activity and loss in initial catalytic activity are met in a single cell, we will prepare short stack for further validation.	08/13

# Accomplishments and Progress

## Catalyst Synthesis Summary (Go/No-go Decision Point)

### RDE Mass Activity Summary



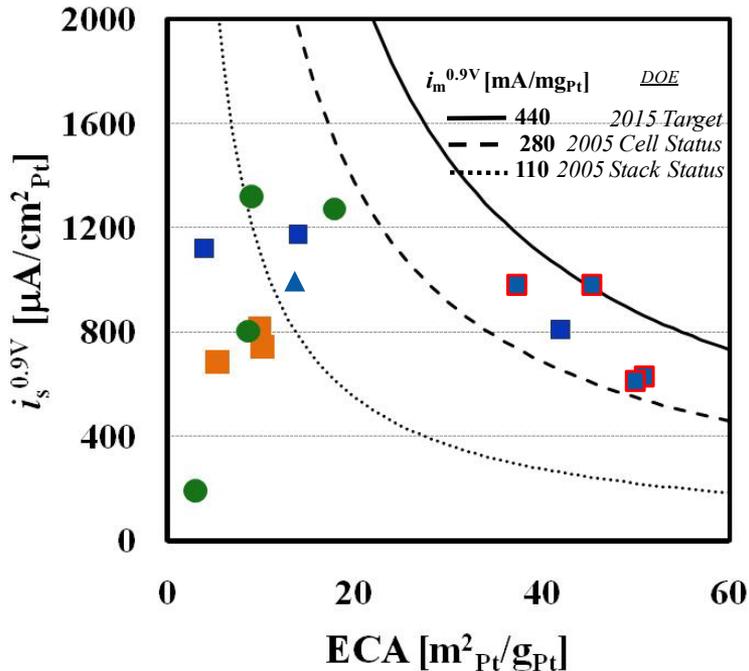
Electrocatalysts synthesized by galvanic displacement meet the DOE mass activity target.

\* AMR Poster FC100; Brian Larsen, NREL: High Aspect Ratio Nano-Structured Pt-based PEM Fuel Cell Catalysts

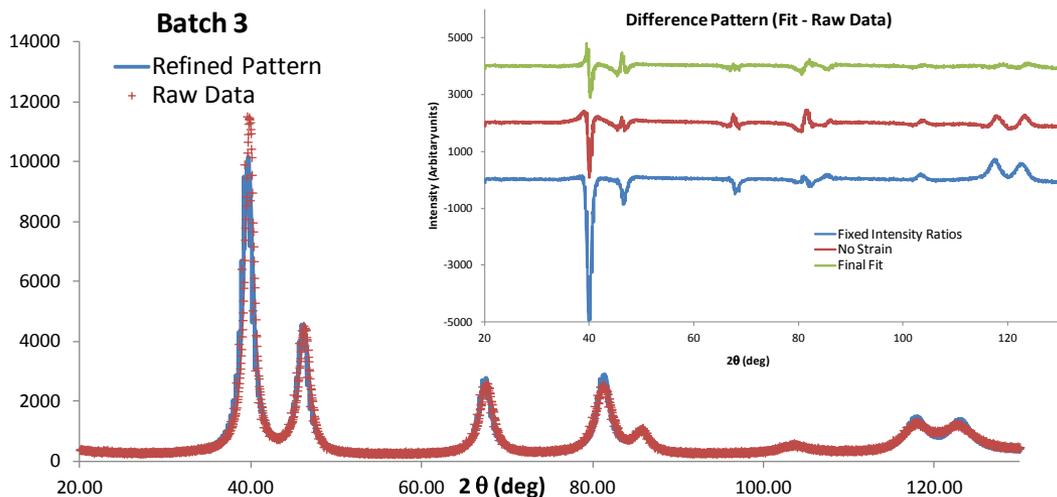
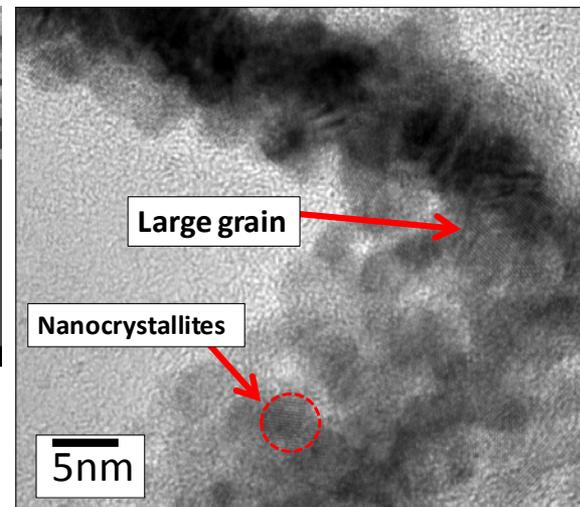
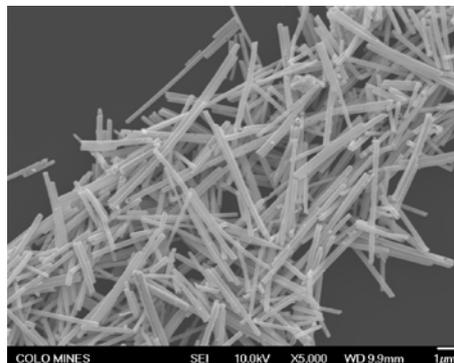
Supplementary synthesis discussion presented in Technical Back-up Slides 22-24

# Past Year Accomplishments

## PtAgNTs SGD: (2012 AMR)



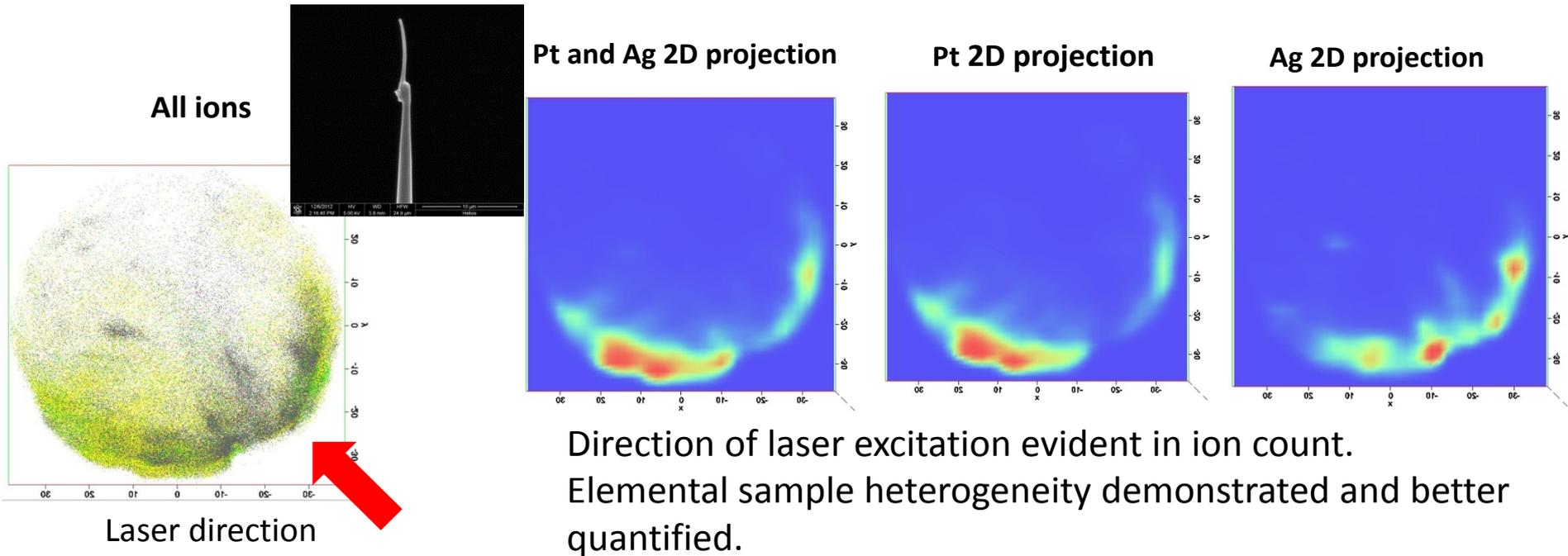
- Increased surface area of ETFECS (typically  $\sim 10 \text{ m}^2/\text{g Pt}$ ) to  $>50 \text{ m}^2/\text{g Pt}$ , while maintaining high specific activity ( $i_s$ )
- In depth: electrochemical, microscopic (ORNL) and x-ray characterization of highest performing sample.



**XRD fit (LANL) with simple strain and preferred orientation is insufficient to get complete match, does not incorporate sample heterogeneity.**

# Accomplishments and Progress

## Atom Probe Characterization (CSM)

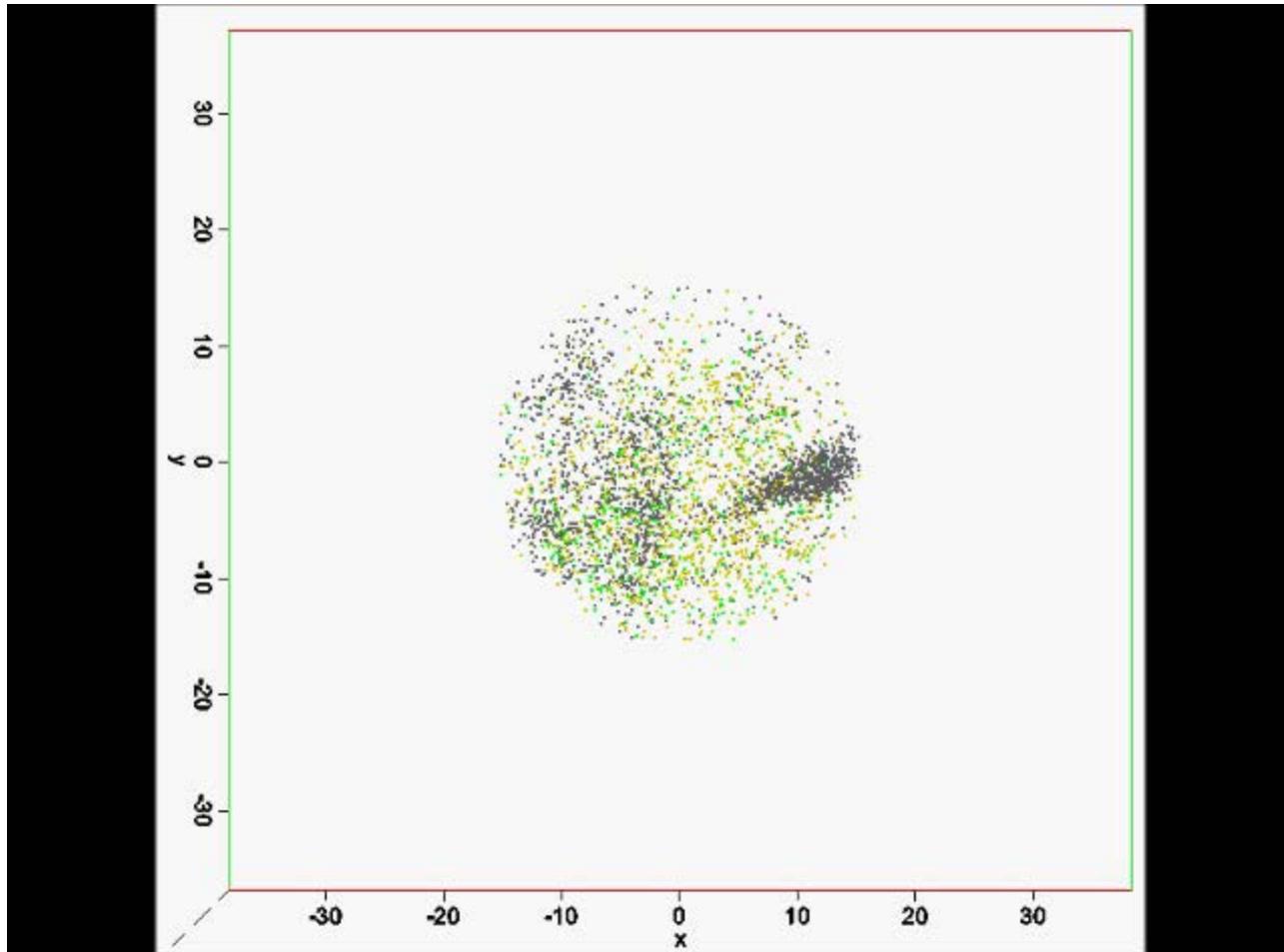


			Pt Wt %				
ECA (m <sup>2</sup> /g <sub>Pt</sub> )	$i_s^{0.9V}$ (μA/cm <sup>2</sup> <sub>Pt</sub> )	$i_m^{0.9V}$ (mA/mg <sub>Pt</sub> )	XRF (NREL)	XRF (LANL)	EDS (NREL)	EDS (ORNL)	ICP-MS (NREL)
45.6	980	450	94	90	94-96	94-97	94

Single atom probe measurement of nanotube tip, resulted in significantly lower Pt composition (84wt%) than other elemental analysis.

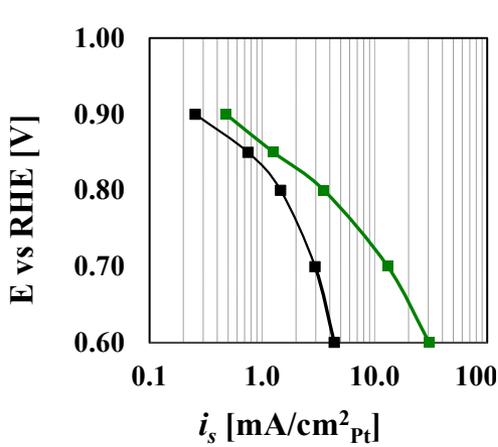
# Accomplishments and Progress

## Atom Probe Depth Profile

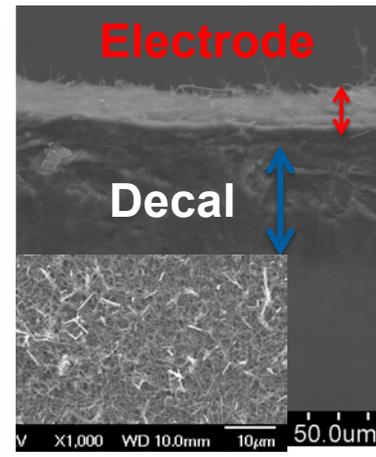
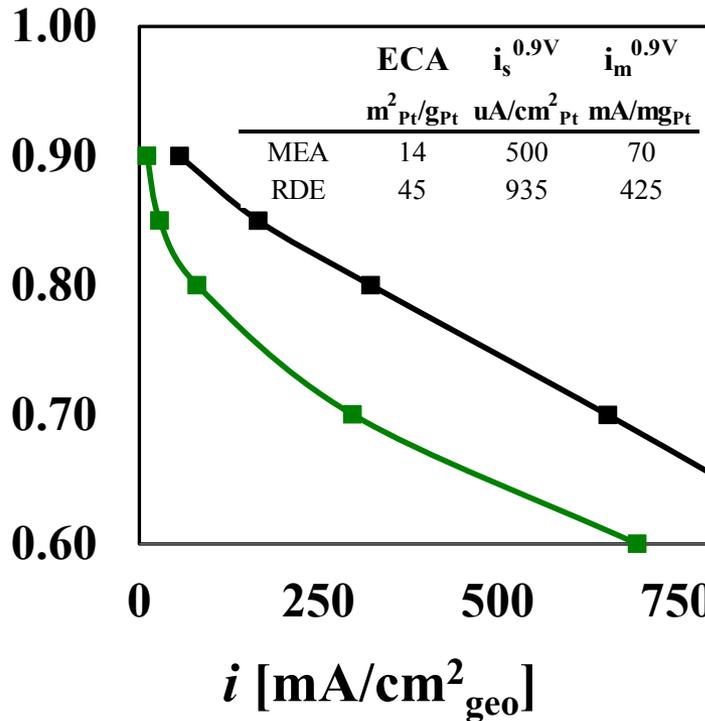


# Accomplishments and Progress

## PtAgNT MEA Preparation and Fuel Cell Testing

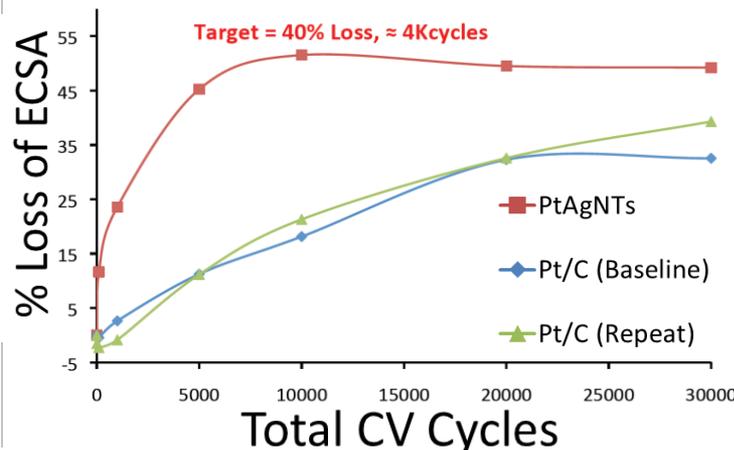


PtAgNTs (initial tests) showed significantly reduced surface area and specific activity vs RDE (modest mass activity). High specific activity vs. Pt/HSC baseline.

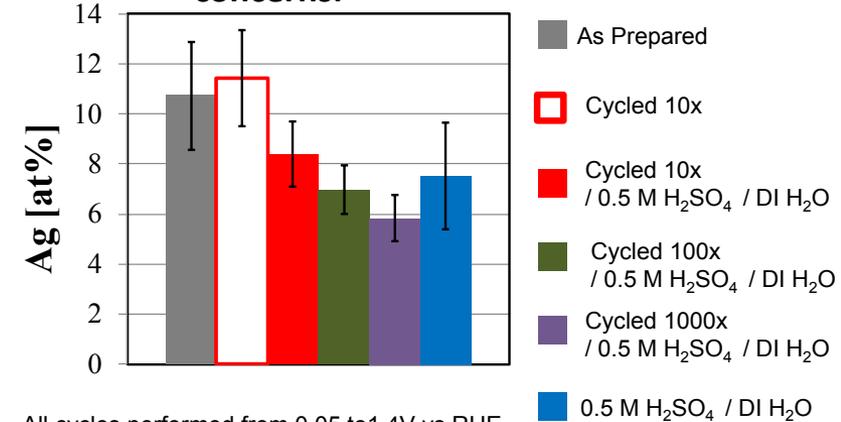


**Experimental Conditions**  
 5cm<sup>2</sup>-single serpentine FF  
 80°C 100% RH  
 H<sub>2</sub>/O<sub>2</sub> 150/300 sccm  
 150 kPa (~100 kPa H<sub>2</sub>/O<sub>2</sub>)  
 N212 Membrane  
 15 min per point –Anodic Sweep  
 JM-GDE (Anode)/SGL25BC Cathode  
 0.28 mg<sub>Pt</sub>/cm<sup>2</sup><sub>elec</sub> –Pt/HSC  
 0.16 mg<sub>Pt</sub>/cm<sup>2</sup><sub>elec</sub> –PtAg w/GCNF2

Ex-situ acid leaching and potential cycling were explored and showed promise to reduce Ag dissolution concerns.



Accelerated stress testing (LANL) showed increased surface area losses quickly, but losses stabilized after 5000 cycles (little change in fuel cell performance).



All cycles performed from 0.05 to 1.4V vs RHE. 0.5 M H<sub>2</sub>SO<sub>4</sub> and DI H<sub>2</sub>O treatments were for 2 hrs each at 80°C

# Accomplishments and Progress

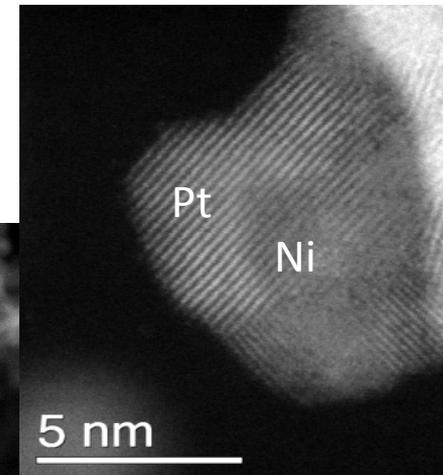
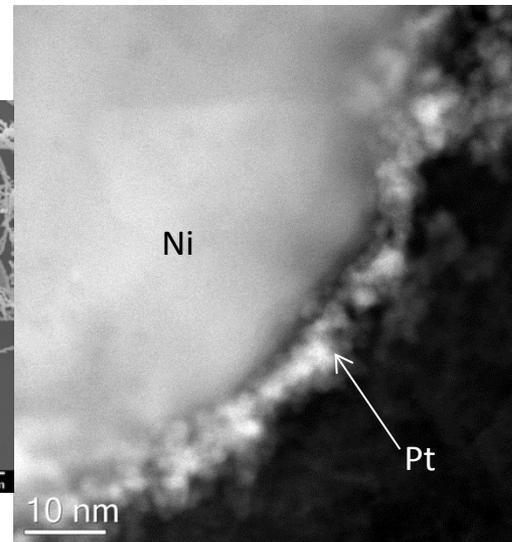
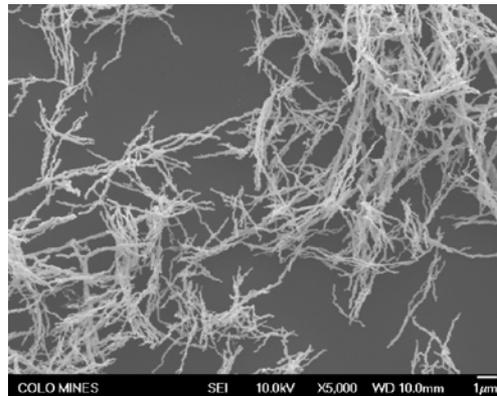
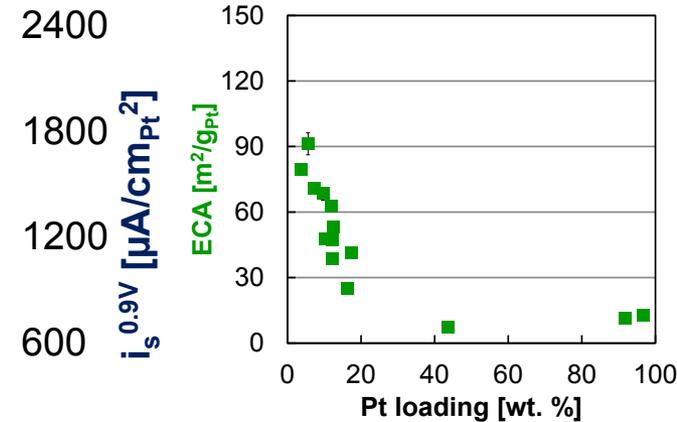
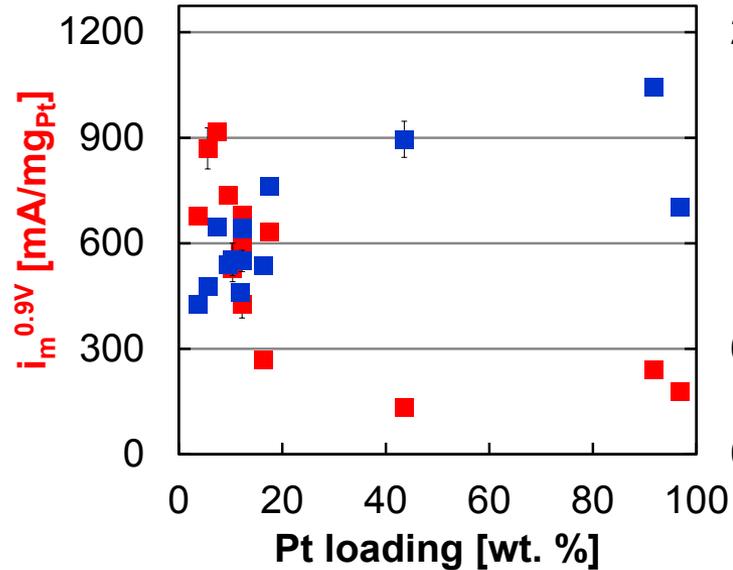
## Galvanic Displacement - PtNiNWs

Galvanic Displacement work transitioned to Ni and Co nanowire (NW) substrates due to reduced contamination concern and potential alloying benefits.

Mass activities as high as 900 mA/mg Pt obtained (2x DOE 2020 target).

High mass activity obtained at low Pt displacement levels due to high ECAs (90 m<sup>2</sup>/gPt). Little evidence of specific activity alloy advantage at low Pt %.

Ni/Co NWs used lack well defined shape of Ag/Cu NWs used in earlier synthesis.



# Accomplishments and Progress

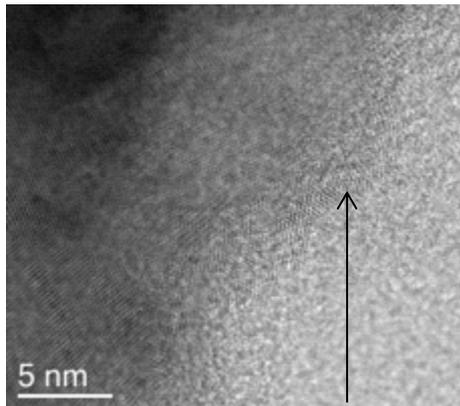
## PtNiNWs Oxide Investigation

Galvanic Displacement from Ni and Co nanowires (NWs) can be impacted by the role of oxides.

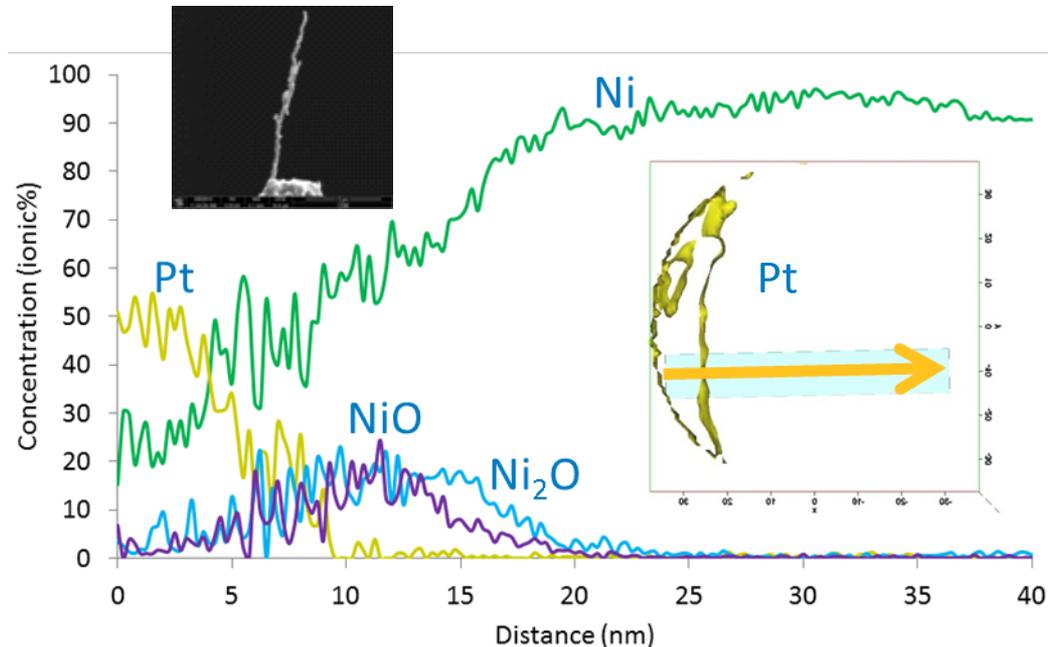
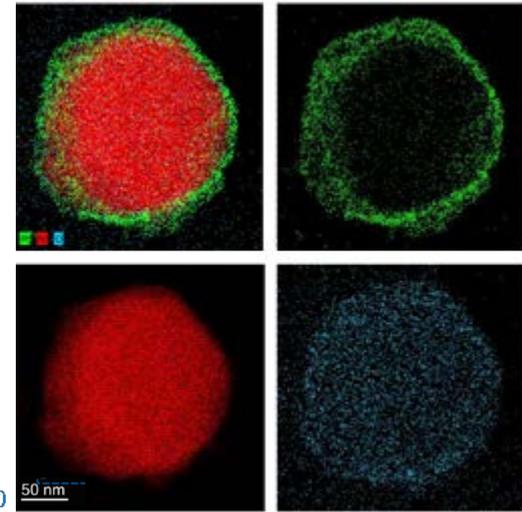
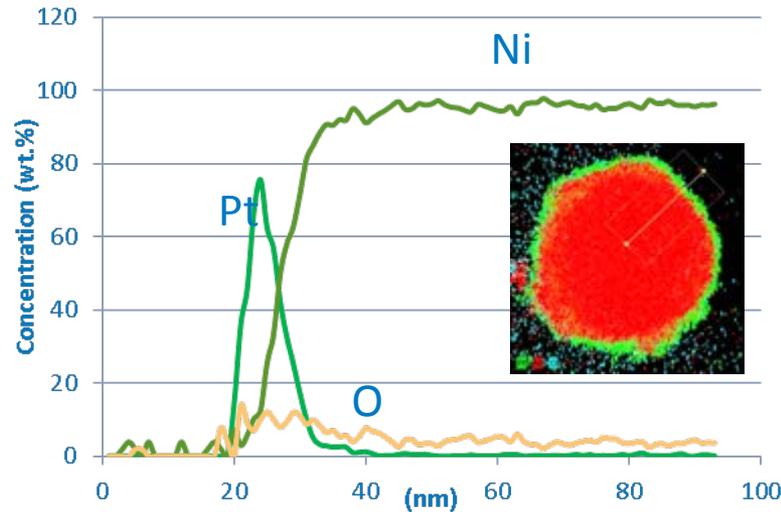
Changes in specific activity and degree of alloying/displacement are highly dependent on the oxide layer.

Cross-sectional TEM (ORNL) and atom probe (CSM) yield insight into the high activity, core-shell structures generated at low-displacement, and the presence of NiO<sub>x</sub> species, thickness, and location.

NiNW (no Pt)



Thin oxide 'skin' on NW



# Accomplishments and Progress

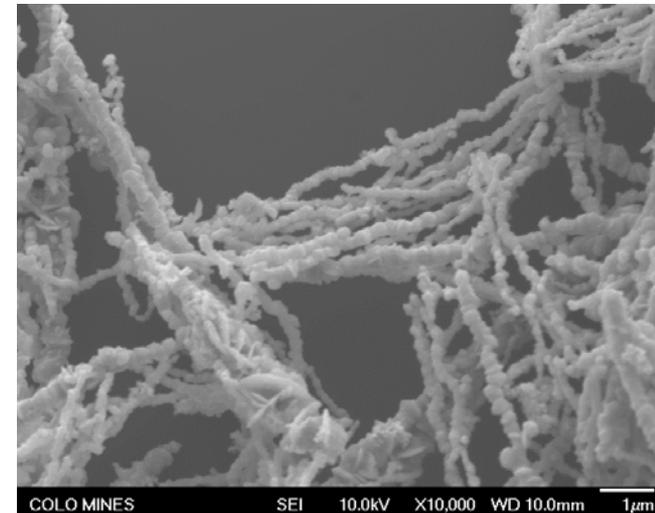
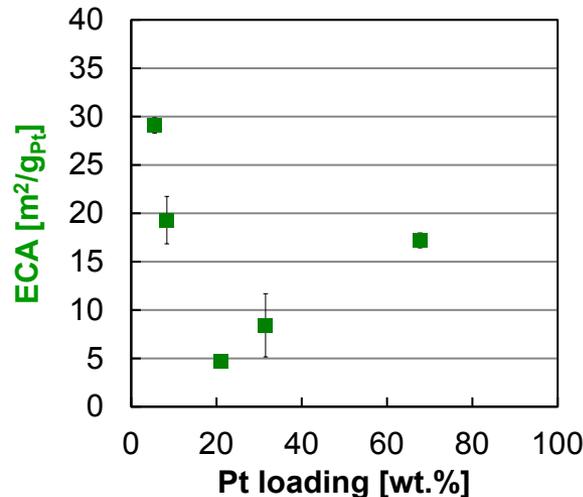
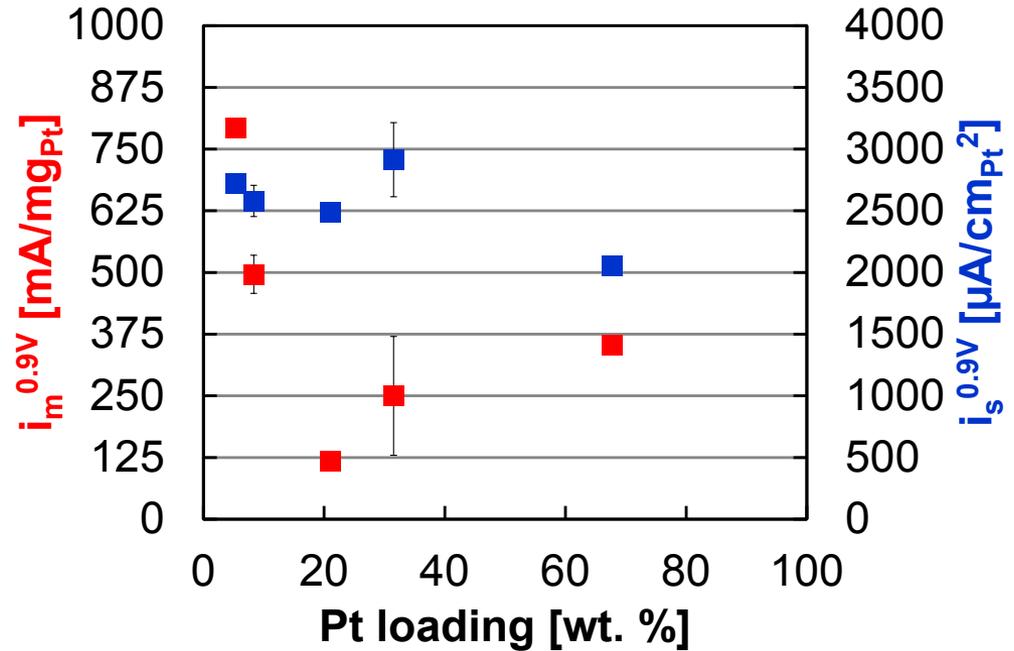
## Galvanic Displacement - PtCoNWs

PtNi and PtCo NWs have behaved much differently quite possibly due to the role of oxide.

Initial experiments verified that Ni displacement was possible, although limited to 30% without added acid that could attack the oxide layer. Co displacement proceeded much further.

Specific activities of Co samples much higher (suggesting alloying).

ECAs much lower, particularly at low Pt displacements.



# Accomplishments and Progress

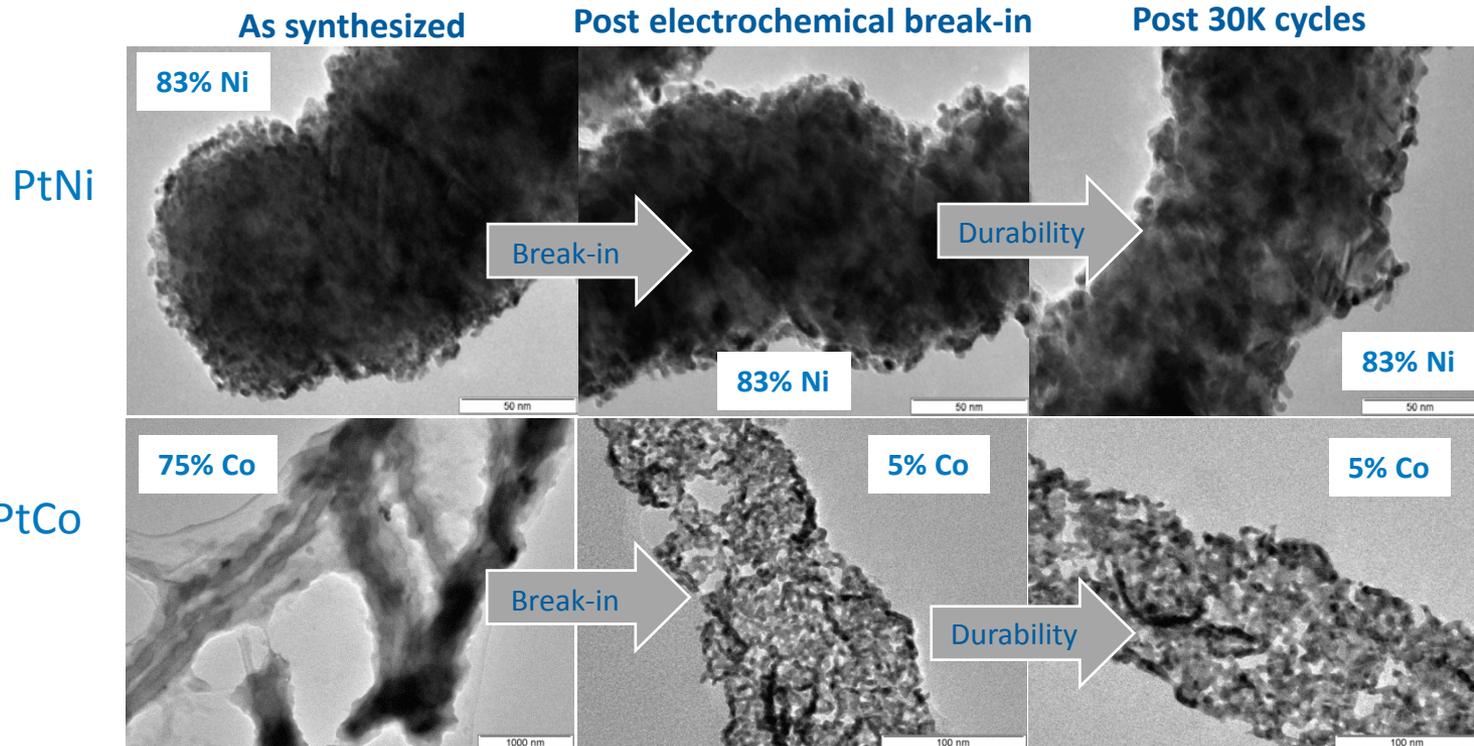
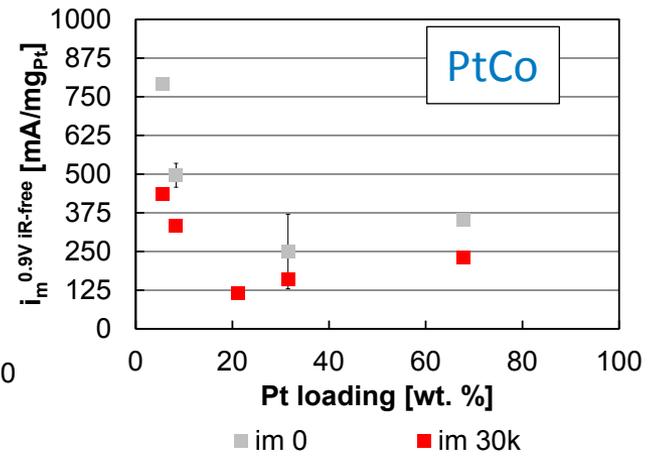
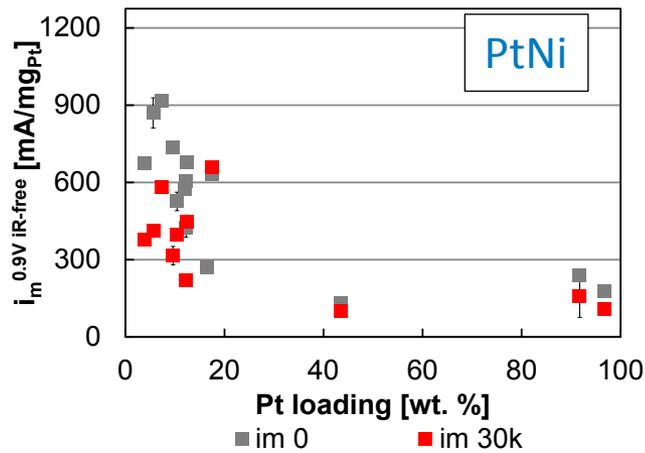
## PtNi/PtCo NWs Durability

Both PtNi and PtCo NWs showed loss of performance due to cycling.

Specific PtNi samples were able to maintain mass activity >600 mA/mgPt even after cycling.

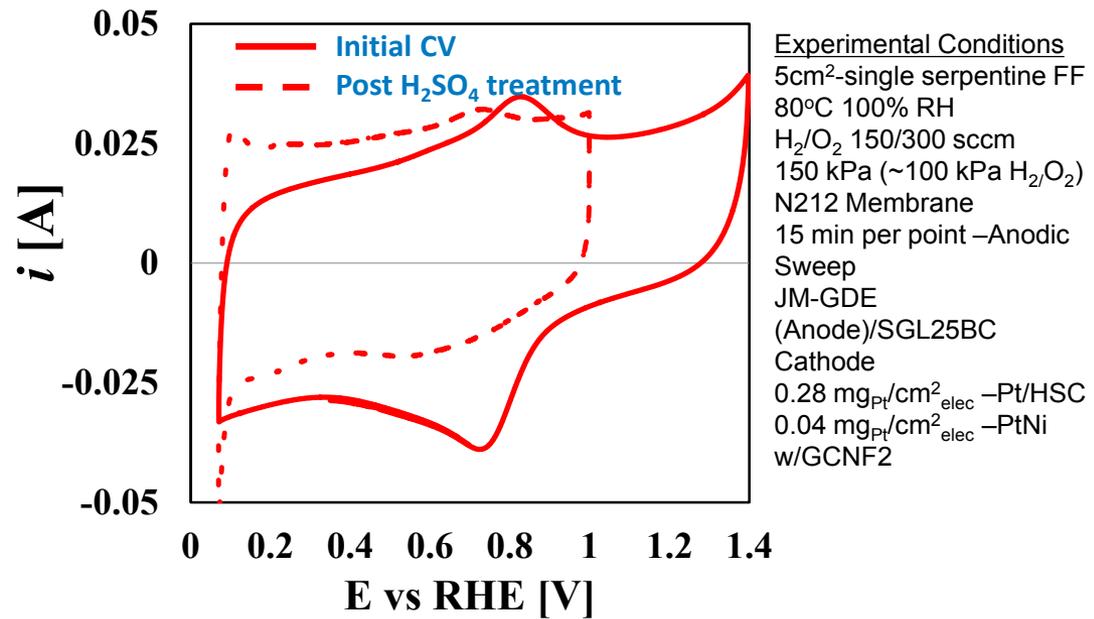
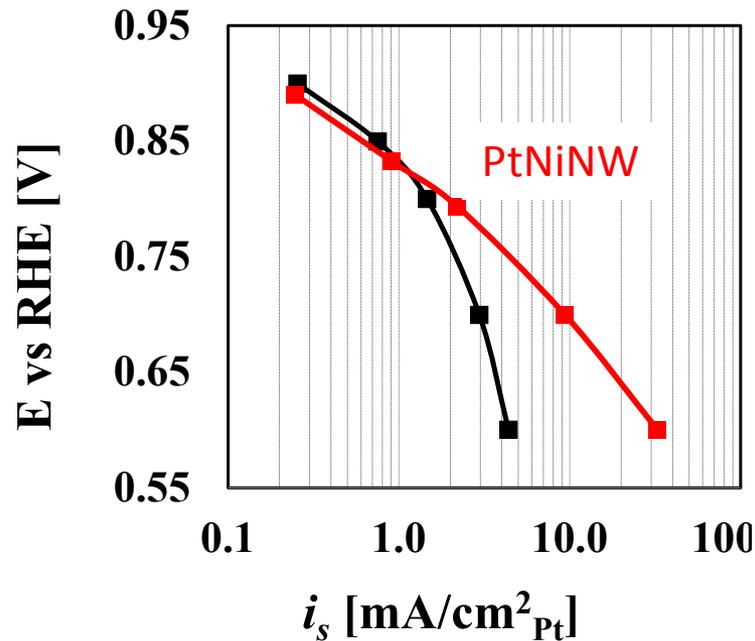
Microscopic analysis of PtNi and PtCo NWs showed dramatic differences in durability and resistance to dissolution (again oxide layer importance).

PtNi samples suggest oxide may allow passivation, PtCo samples suggest preleaching necessary.



# Accomplishments and Progress

## PtNiNWs Initial MEA Performance

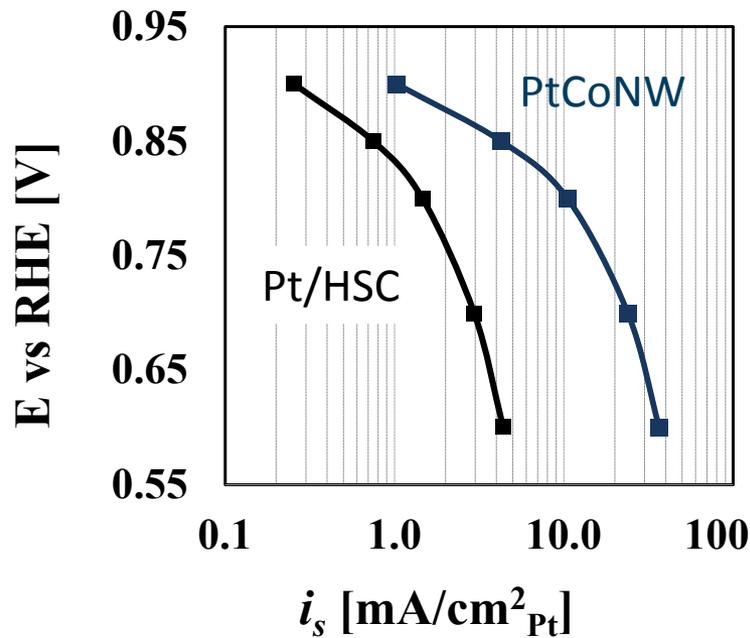


Initial results show high specific activity at high current after acid washing. These studies point to a number of concerns for this system that we need to address (see Slide 17):

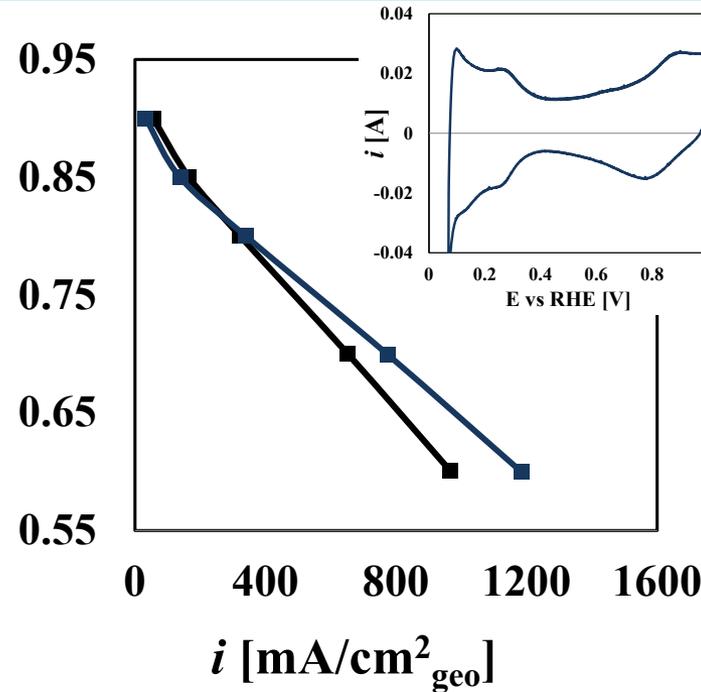
- Ni dissolution (not apparent in RDE), lack of Pt features in initial CV
- Decreased surface areas (relative to RDE)
- Low Pt content and Ni as a magnetic element impact MEA fabrication

# Accomplishments and Progress

## PtCoNWs MEA Performance



Pt/HSC	ECA	$i_s$ corr	$i_m$ corr
	m <sup>2</sup> <sub>Pt</sub> /g <sub>Pt</sub>	uA/cm <sup>2</sup> <sub>Pt</sub>	mA/mg <sub>Pt</sub>
RDE	100	275	275
MEA	77	250	200



PtCoNW	ECA	$i_s$ corr	$i_m$ corr
	m <sup>2</sup> <sub>Pt</sub> /g <sub>Pt</sub>	uA/cm <sup>2</sup> <sub>Pt</sub>	mA/mg <sub>Pt</sub>
	17	2200	370
	14	1050	150

**Experimental Conditions**  
 5cm<sup>2</sup>-single serpentine FF  
 80°C 100% RH  
 H<sub>2</sub>/O<sub>2</sub> 150/300 sccm  
 150 kPa (~100 kPa H<sub>2</sub>/O<sub>2</sub>)  
 N212 Membrane  
 15 min per point –Anodic Sweep  
 JM-GDE  
 (Anode)/SGL25BC  
 Cathode  
 0.28 mg<sub>Pt</sub>/cm<sup>2</sup><sub>elec</sub> –Pt/HSC  
 0.22 mg<sub>Pt</sub>/cm<sup>2</sup><sub>elec</sub> –PtCo w/GCNF2

Directly synthesized PtCoNWs exhibited surface areas approaching those of RDE and well defined Pt CV. Specific activity in fuel cell was about half of that of RDE, fuel cell mass activity competitive with Pt/HSC baseline.

# MEA Fabrication Challenges

## MEA Fabrication



**Pt loading:** Measured using XRF, weighing and calculation Pt wt in ink. Values did not always agree.

**Decal:** Occasional trouble with decal transfers with thicker electrodes

**Subscale Cell:** 5 cm<sup>2</sup> cell hardware has increased uncertainty (edge effects)

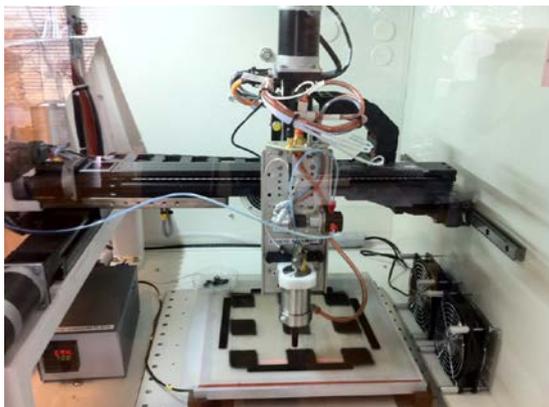
**Leaching:** Avoiding base metal removal at MEA stage (slide 10)

### Fabrication Methods thus Far:

- Direct spraying, decal spray with transfer, filtering with transfer, and direct painting

### Ink Formulation:

- Supportless electrocatalysts behave differently than traditional Pt/C catalysts and Pt blacks.
- Catalyst dispersions (inks) and MEA fabrication significantly more complicated
- We have investigated different ink agitation approaches, we typically can use a magnetic stir bar, however not for PtNi, sonic syringe not powerful enough to maintain dispersion for spray system
- Preliminary investigations suggest, solvent choices can aid in improving dispersions.



CCM preparation by spray-coating of electrocatalyst ink directly onto the membrane or by decal method was carried out.

# Collaborations

## Key Investigators/Major Participants

**National Renewable Energy Lab: Bryan Pivovar (PI), Shyam Kocha, Arrelaine Dameron, Jason Zack, KC Neyerlin, Justin Bult, Brian Larsen, Jeremy Leong**

**Oak Ridge National Laboratory: Dave Cullen**

**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**

**Colorado School of Mines: Svitlana Pylypenko, Dave Diercks**

**Nissan Technical Center North America: Nilesh Dale**

**Cabot Fuel Cells: Paolina Atanassova**

**Tanaka Kikinzoku Kogyo: Fumiaki Ogura**

## **Additional Collaborators:**

**Stanford Linear Accelerator (SLAC): Mike Toney**

# Future Work

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## Electrocatalyst synthesis:

Focus on galvanic displacement (NREL, Delaware), all other synthesis routes no-goed within project: Focus on PtNi, PtCo.

PtNi: Focus on oxide passivating layer, effects of annealing and attempting to further increase specific activity.

PtCo: Focus on increasing surface area, leaching of excess Co. Advanced characterization of materials (CSM, ORNL).

## Fuel cell studies:

Projects primary focus is on improving catalyst performance in MEAs with a focus on MEA fabrication using down-selected electrocatalysts.

Explore factors impacting observed ECAs, activity, and durability.

# Summary

- **Relevance:** Focused on overcoming the cost, performance and durability barriers for fuel cell commercialization by increasing Pt mass activity.
- **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 down-selected catalyst synthesis route to galvanic displacement due to the high mass activities achieved 900 mA/gPt. Have demonstrated exceptionally high surface areas up to 90m<sup>2</sup>/gPt. Have tested galvanically displaced samples in fuel cells.
- **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 into highly performing MEAs. Investigation of oxide layer and increased specific activity.

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# Technical Backup Slides

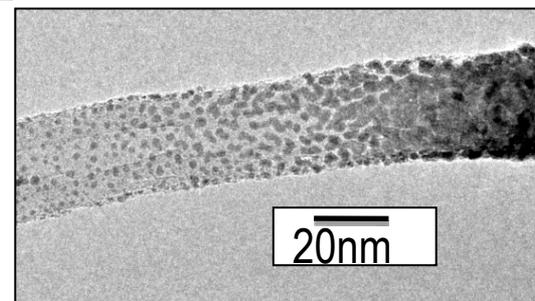
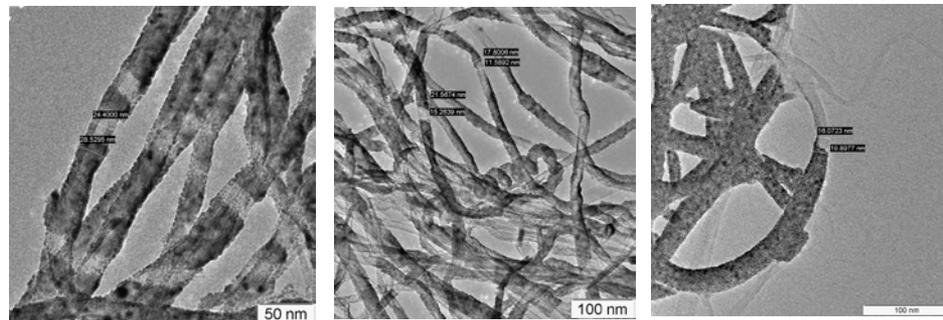
# Accomplishments and Progress

## Catalyst Synthesis - Sputtering (NREL)

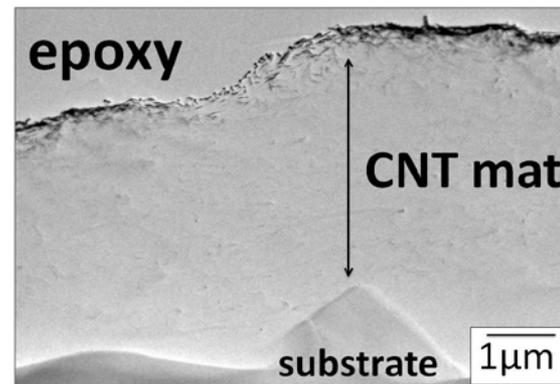
- **Sputtering has yielded targeted structures (thin Pt layers on substrates – NSTF(3M), CNTs(NREL))**

In our studies, homogeneity of material and yield on carbon nanotubes yielded some target structures (shown) in low quantities. The material quantities and heterogeneity prevented proper electrochemical characterization.

Sputtering processes (as investigated within the project) needed significant effort and capital investment in order to increase throughput, reproducibility, and control. Due to cost of implementation, specialty equipment, and time, this effort was stopped (No-goed) in 2011.

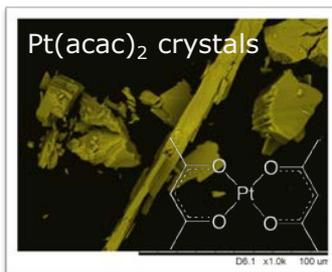
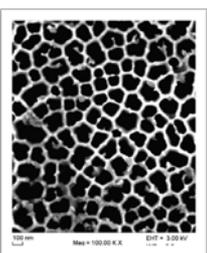
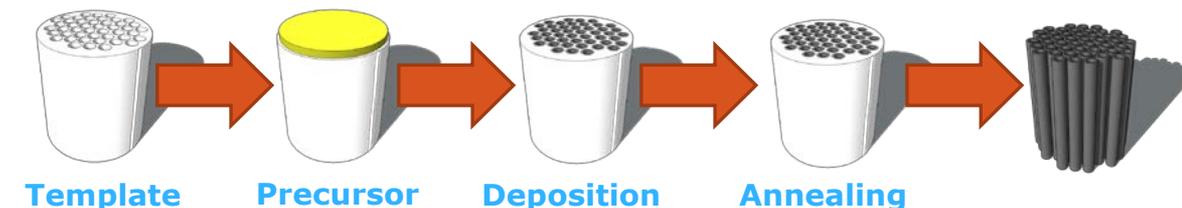


K. Perry (ORNL)



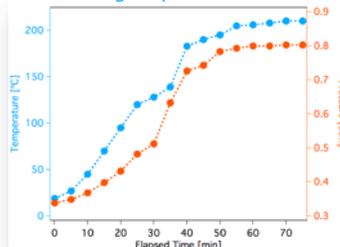
# Accomplishments and Progress

## Catalyst Synthesis - CVD (Tennessee)



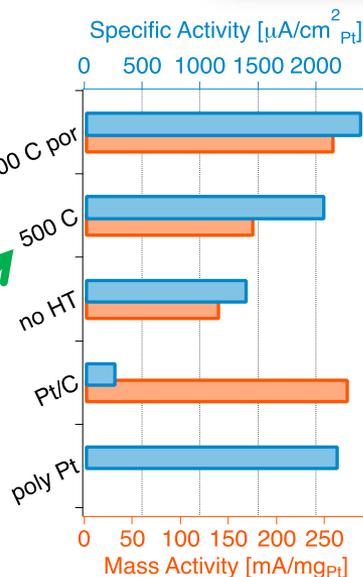
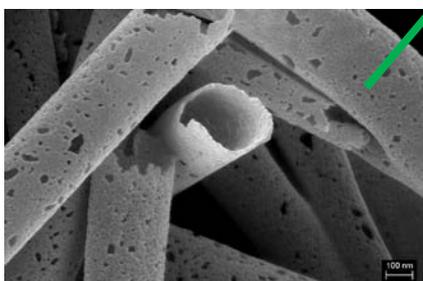
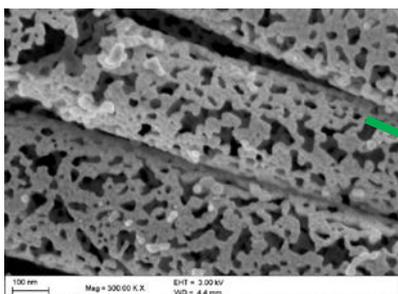
- Common MOCVD, solution phase precursor
- Vaporizes ~140 °C
- Decomposes ~250 °C (in inert atmosphere)

Temperature and Pressure of Reactor During Deposition



- Chemical Vapor Deposition (CVD) has yielded targeted structures in alumina templates

The specific activities of materials generated reached the level of polycrystalline Pt. Unfortunately surface areas were low.

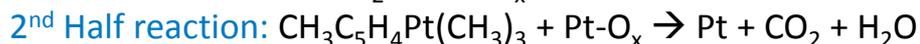
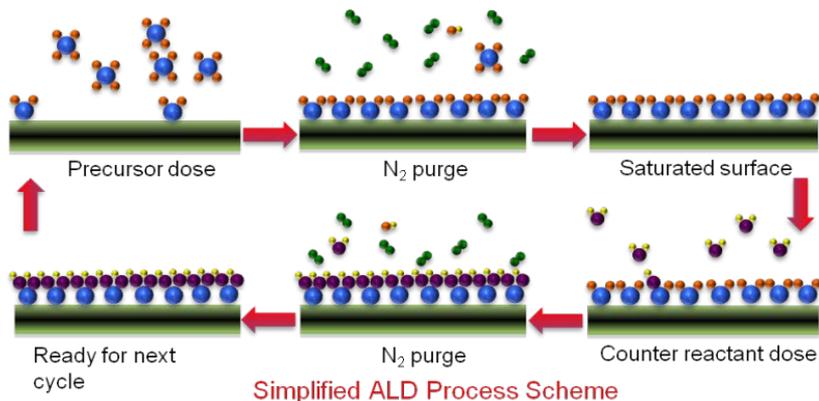


Efforts to increase surface area resulted in porous tubes with slightly improvements in surface area, but further gains in surface area are required.

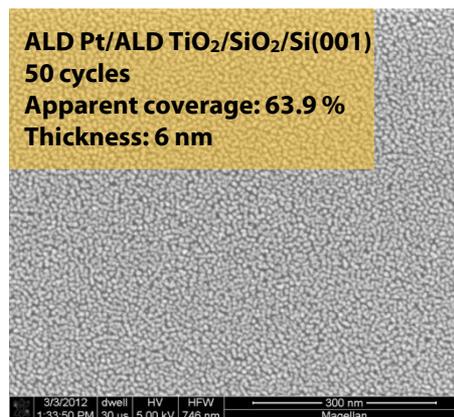
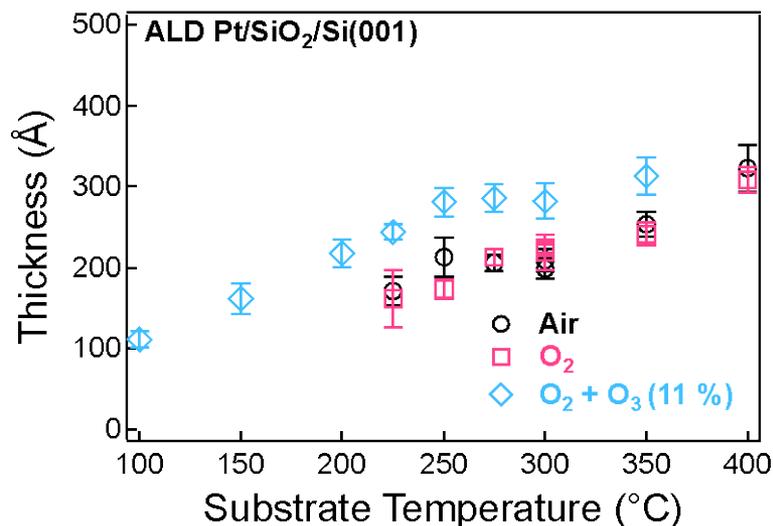
This effort was stopped (no-goed) in February 2013.

# Accomplishments and Progress

## Catalyst Synthesis - ALD (Stanford, SUNY-Albany)



- We have focused atomic layer deposition (ALD) synthesis on oxidative chemistry due to simplicity and system limitations.
- We have investigated flat (model) systems and nanostructures (CNTs, inorganic nanowires), different reaction conditions (temperature, reactants, pulse length) and substrate composition/adhesion layers.

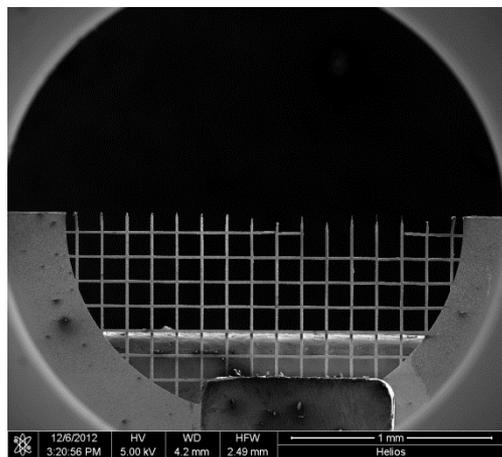
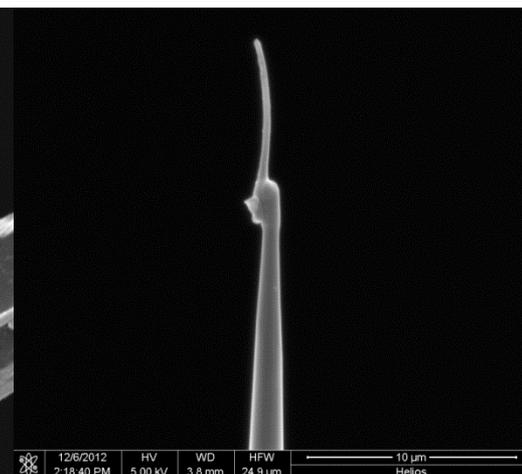
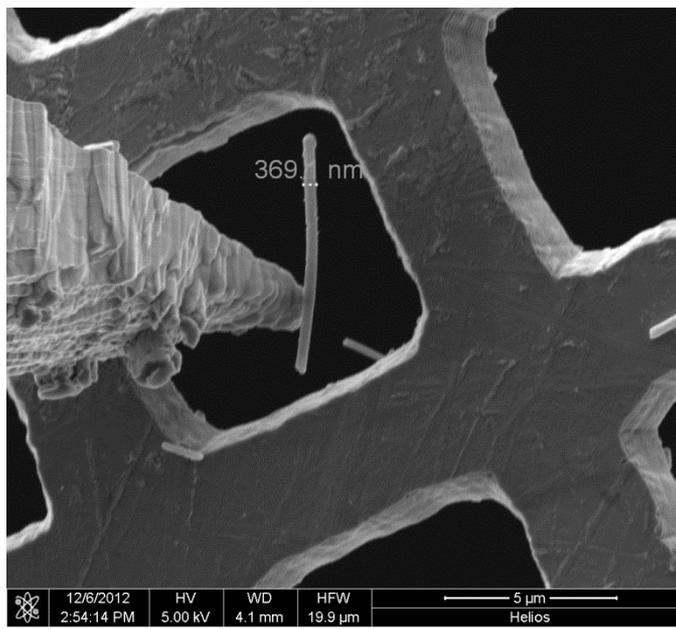
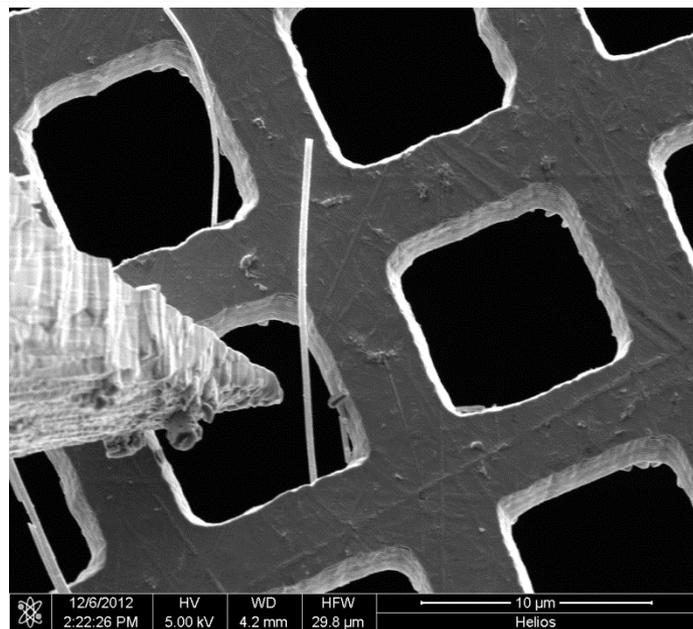


- We have shown ozone as the oxidant offers advantages in nucleation and growth temperature.
- Even with advances in chemistry and surface modification, we were unable to get conformal Pt coatings below 5 nm, although we were able to improve significantly from the 20 nm continuous coatings initially obtained.

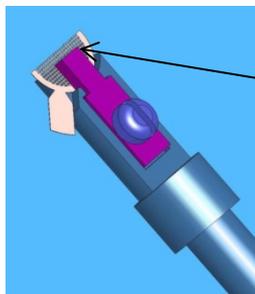
This effort was stopped (no-goed) in February 2013.

# Accomplishments and Progress

## Sample Prep Atom Probe (CSM)



Grid Prepped for Sample Connection



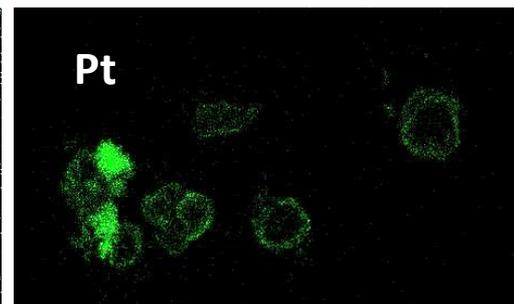
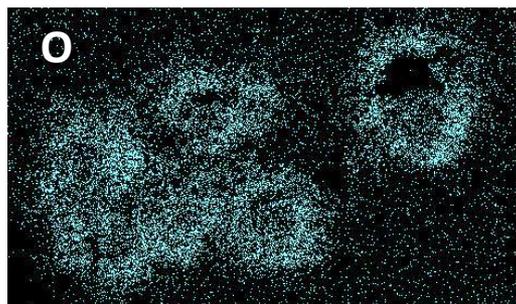
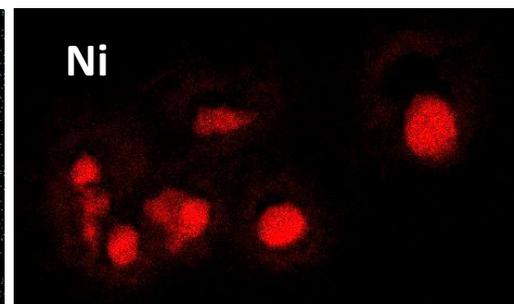
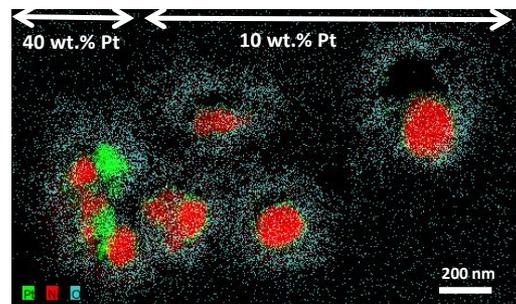
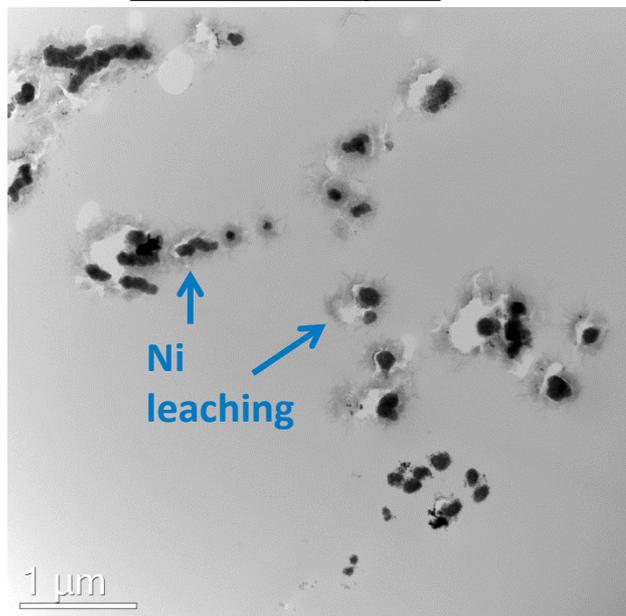
Removable Grid Holder Tip

Nanotube or nanowire samples drop cast onto grid and then mounted individually onto another grid prepped (by focused ion beam) for sample connection. Sample tested in slide 8 and 9 shown (top, right).

# Accomplishments and Progress

## PtNiNWs (supplemental microscopy, ORNL)

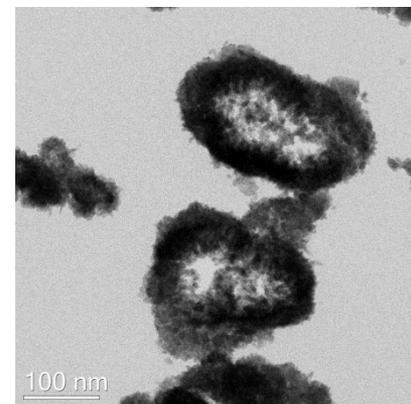
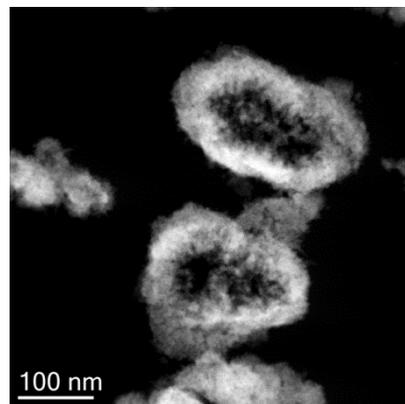
### 20% Pt Samples



At low levels of displacement (<20% Pt), large Pt agglomerates and Ni leaching into epoxy (used for sample preparation) were not observed.

At near full displacement, PtNi nanotubes were formed, similar to PtAg, but with much lower surface areas (AgCl precipitate suspected to aid in increasing surface area).

### 95% Pt Samples



# Accomplishments and Progress

## Electrode Studies (experimental summary)

Extended structure catalysts outside of this project have not been studied in detail within electrodes.

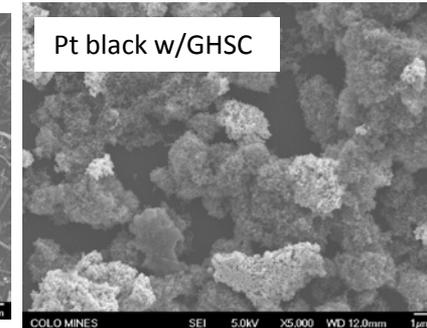
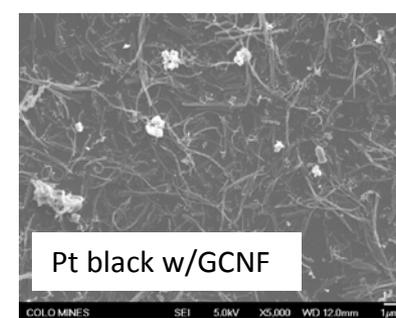
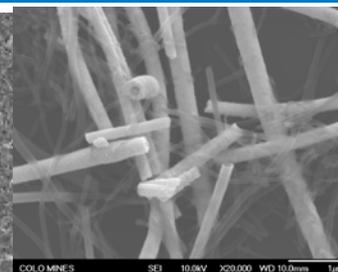
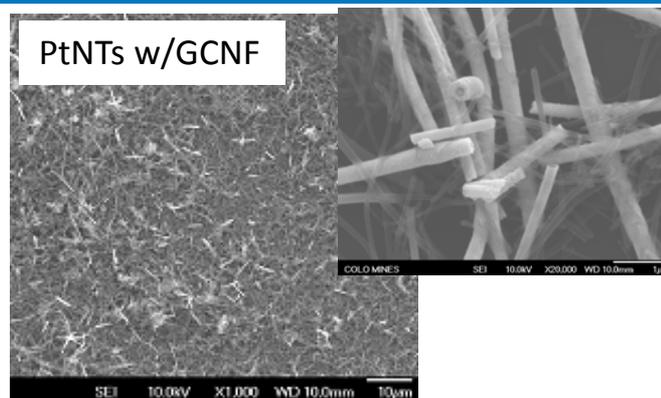
### Significant effort in RDE\* studies

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

### Carbon investigated for

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

	RDE Loading	Nafion Content	Carbon type	Carbon Loading	Durability
<b>Pt Black</b>	X	X	X	X	X
<b>Pt/C (Vulcan®, HSC)</b>	X	X	X		X
<b>PtAgNTs</b>	X	X	X	X	X
<b>PtNiNWs</b>	X	X		X	X
<b>PtCoNWs</b>	X	X		X	



Through our significant studies of novel ETFECS, Pt Blacks, and Pt/C we have established a world leading position regarding the impact of different parameters on observed electrochemical performance in RDE and the impact of ink dispersion/loading/preparation. This expertise has been/is being directed toward the development of MEAs based on these materials.