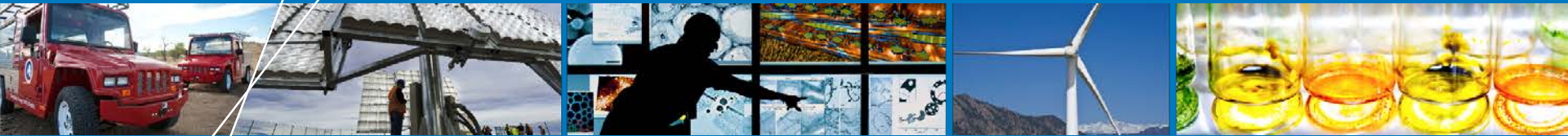


# Extended Surface Electrocatalyst Development



**2016 DOE Hydrogen and Fuel  
Cells Program Review**

**Bryan Pivovar (PI)**

**June 7, 2016**

**FC142**

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

# Overview

## Timeline

- **Start: December 2015**
- **End: September 2018**
- **% complete: ~10%**

## Budget (\$K)

DOE Cost Share	Recipient Cost Share	TOTAL
3,000	399	3,399

## DOE Budget (\$K)

FY 2016	1,000
FY 2017	1,000
FY 2018	1,000

## Barriers

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

## Partners – Principal Investigators

Colorado School of Mines (CSM) – Svitlana Pylypenko

University of Delaware (Delaware) – Yushan Yan

University of Colorado – Boulder (CU) – Al Weimer

ALD Nanosolutions (ALDN) – Karen Buechler

\*General Motors (GM) – Anusorn Kongkanand (consultant)

# Relevance

## ETFECS/Dispersed Electrodes

### Review Period Objectives:

- Pt catalysis remains a primary limitation for fuel cells. We have pursued synthesis of novel extended thin film electrocatalyst structures (ETFECS) for improved cost, performance, and durability.

- Incorporation of ETFECS to meet DOE MEAs targets for fuel cell 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

## Project Schedule/Milestones

Task	Task description	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1	<b>Synthesis of Ni nanostructures (Delaware)</b>	G1, D1											
Task 2	<b>Catalyst synthesis (NREL, CU, ALDN)</b>												
Subtask 2.1	ALD synthesis	M1				M5		G2, D2					
Subtask 2.2	Post-processing optimization												
Task 3	<b>Characterization (NREL, CSM, CU)</b>												
Subtask 3.1	Electrochemical characterization		M2 M3										
Subtask 3.2	Non-electrochemical characterization												
Task 4	<b>MEA testing and optimization (NREL, GM)</b>												
subtask 4.1	Initial Performance					M4 M6							
subtask 4.2	Durability								M7 M8		G3, D3		
Task 5	<b>Tech to market plan (NREL, GM, ALDN)</b>									M9			

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Type	Status
Q1	12/31/2015	Regular	Hold kick off meeting with project partners to set schedule and scope priorities	Quarterly Progress Measure (Regular)	Met 12/10/15
Q2	3/31/2016	Regular	Using extended surface catalysts prepared by ALD, demonstrate initial mass activity in RDE >2200 mA/mg Pt (900 mV IR free) (5x DOE MEA target).	Quarterly Progress Measure (Regular)	Met 3/16 See slide 8
Q3	6/30/2016	Regular	Demonstrate a mass activity of 880 mA mgPt <sup>-1</sup> at 0.9V (2x DOE 2020 Target) and less than a 5% loss after durability testing (30k cycles, mass activity) in RDE tests with a total transition metal dissolution of less than 1% of initial catalyst mass.	Annual Milestone (Regular)	On-track
Q4	9/30/2016	Stretch	Demonstrate a mass activity of >440 mA mgPt <sup>-1</sup> at 0.9V (DOE 2020 Target) in fuel cell MEA tests (Stretch goal) and demonstrate synthesis of Ni nanostructures with Ni (111) surface-faceted, extended surfaces with aspect ratios >50.	Quarterly Progress Measure (Stretch)	TBD

18 month go/no-go decision based on MEA performance (mass activity 440mA/mg and durability stability to cycling)

# Approach

## Extended Thin Film Electrocatalyst Structures (ETF ECS)/ Electrodes

Extended surface catalyst as exceptionally promising approach to meeting catalyst targets.

Parallel efforts:

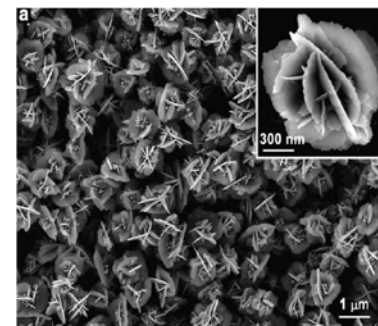
Novel extended nanotemplates (Delaware)

Focus on ALD synthesis of PtNi Nanowires (NWs), due to demonstrated performance and limitations of galvanic displacement (composition, batch size, reproducibility). Focus on ALD process (Pt and Ni), and post-processing (annealing and acid leaching). (NREL, CU, ALDN)

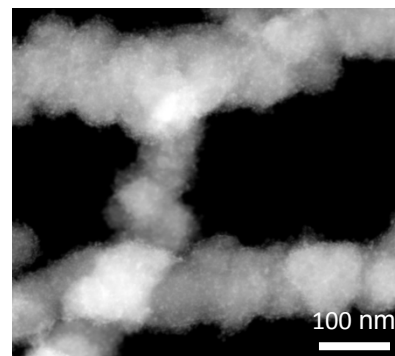
MEA optimization and testing including multiple architectures, compositions and operating conditions. (NREL, GM)

CSM provides characterization in all areas above.

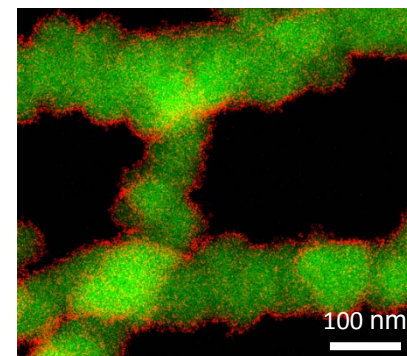
SEM: Ni  
'nanoflowers'



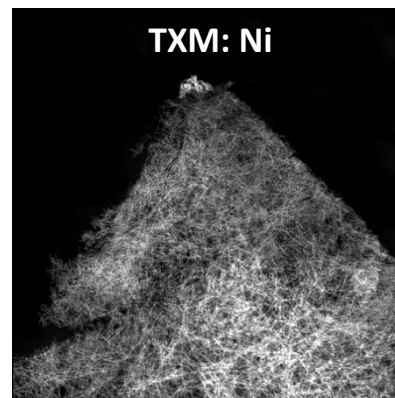
STEM: PtNi nanowires



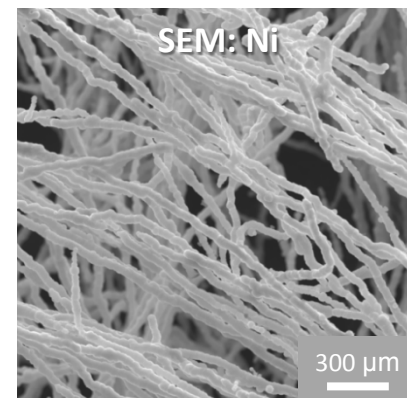
EDS: Pt + Ni



TXM: Ni



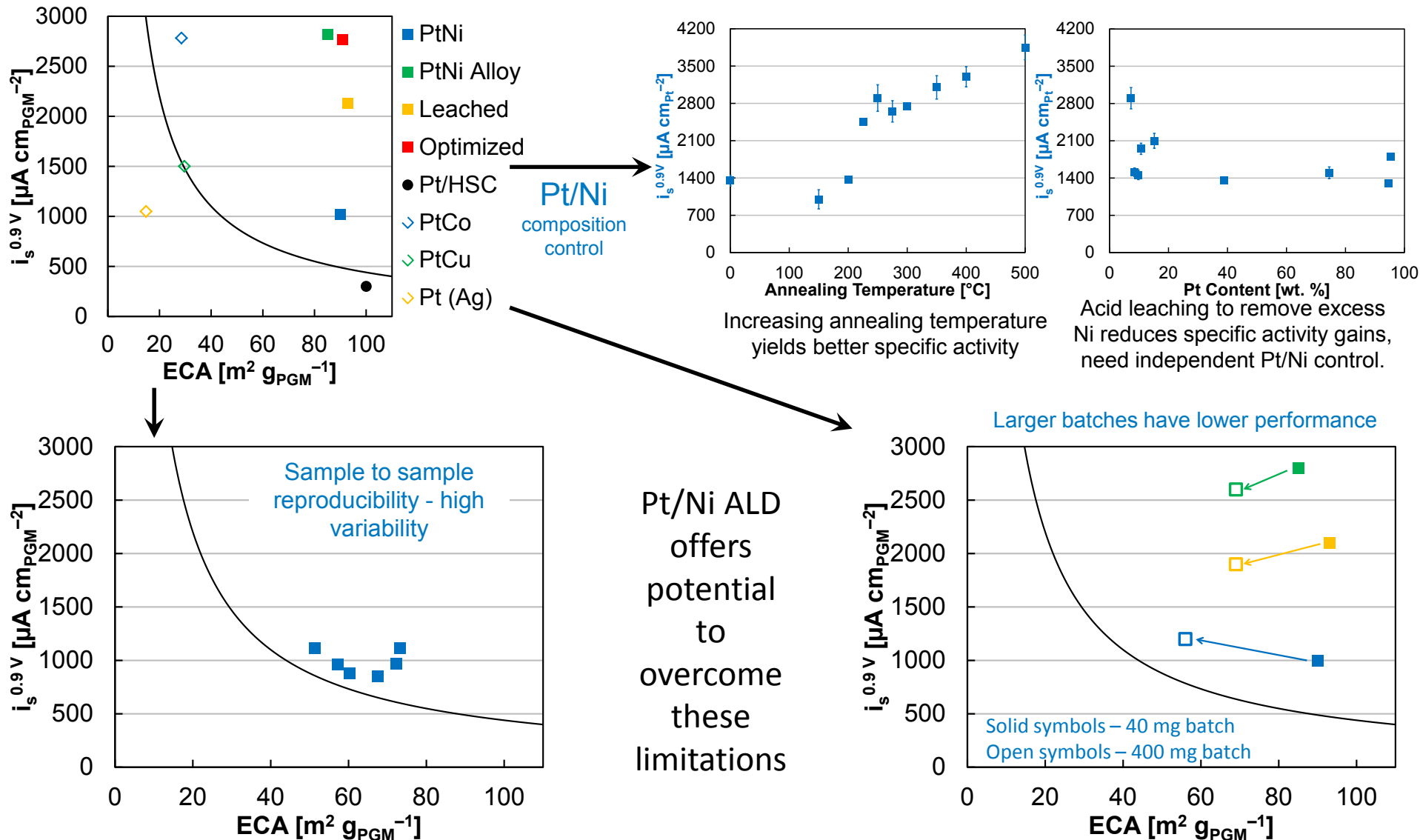
SEM: Ni



# Approach

## Moving from galvanic displacement to atomic layer deposition

Galvanic displacement produced high performance materials, but showed limitations with:

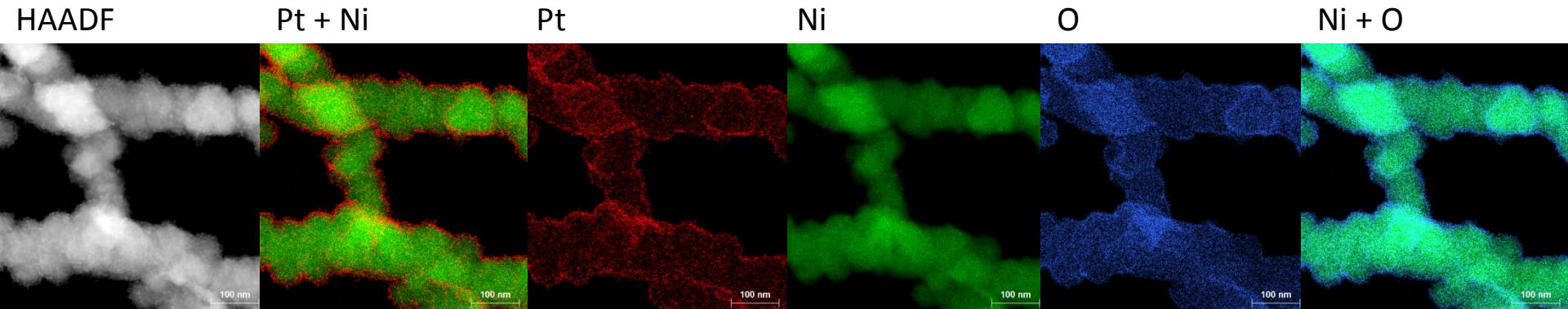




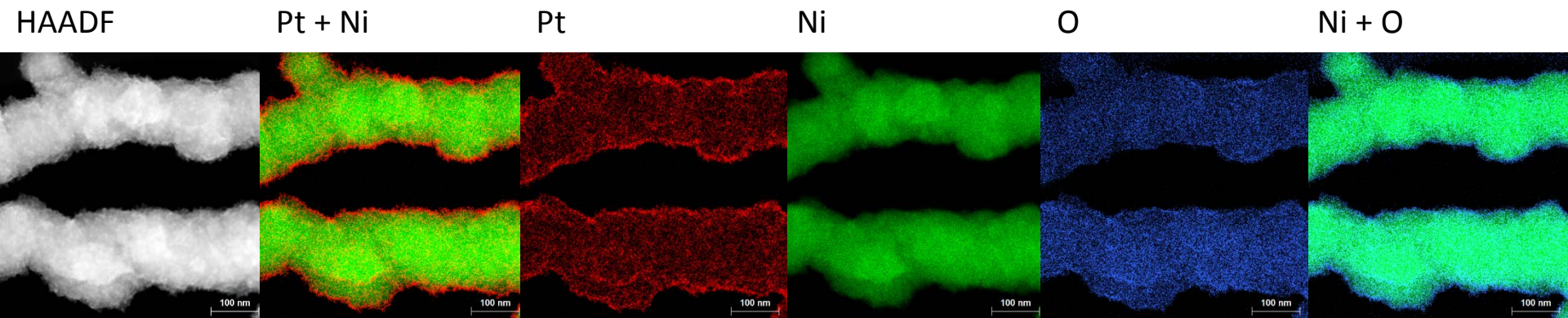
# Accomplishments and Progress

## Atomic layer deposition – oxygen chemistry (plus H<sub>2</sub> annealing)

### As-synthesized



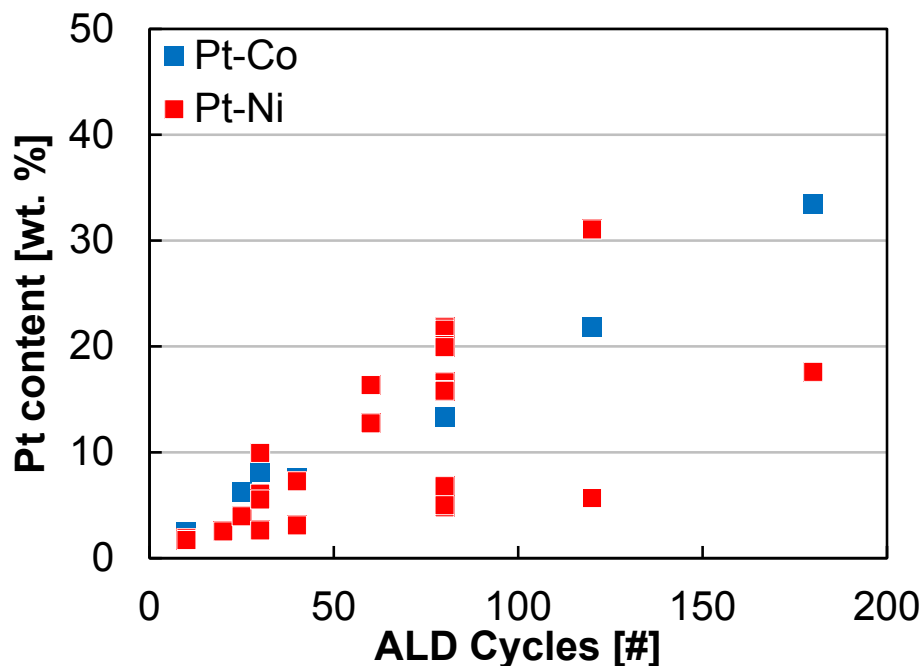
### Annealed



**Pt appeared to form a surface coating during oxygen atomic layer deposition and appeared to remain a surface coating following hydrogen annealing (required to increase specific activity) .**

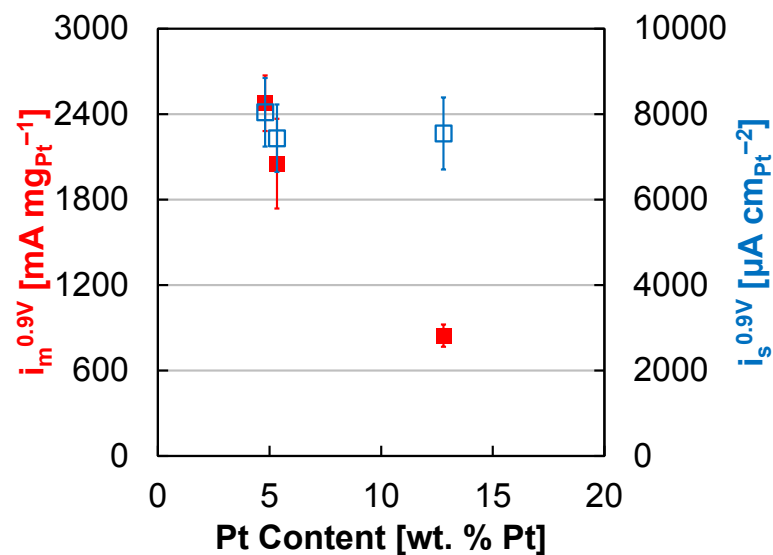
# Accomplishments and Progress

## Atomic layer deposition – oxygen chemistry (optimizing properties)

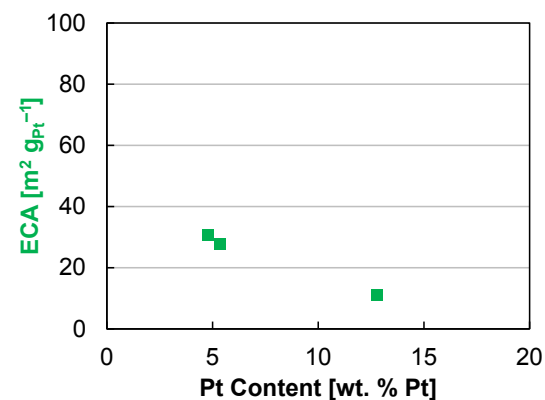


Pt deposition was probed on Co and Ni nanowires as a function of number of cycles and operating conditions.

Select samples probed for electrochemical properties.



Exceptionally high  $i_s$  above 8000  $\mu\text{A}/\text{cm}_{\text{Pt}}^2$  was obtained resulting in high mass activity, ~5x DOE 2020 MEA target in RDE.



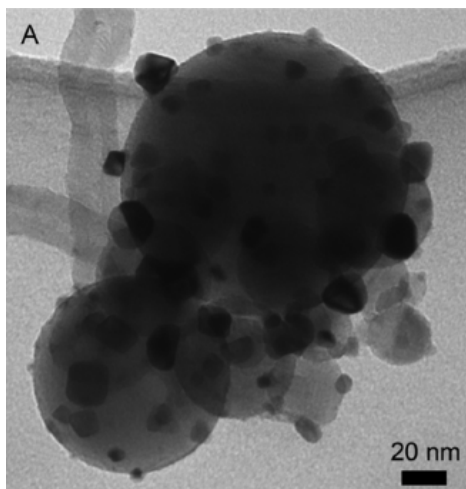
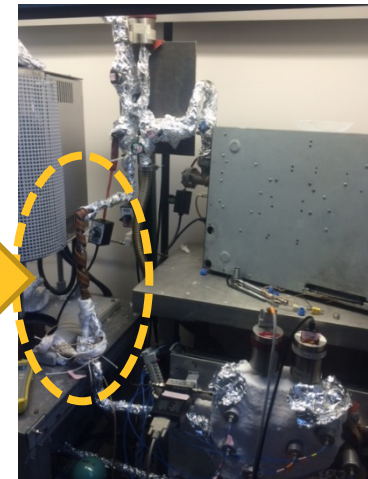
ECAs obtained were low relative to values obtained in earlier studies.



# Accomplishments and Progress

## Platinum deposition by hydrogen atomic layer deposition

Approach is being explored for its ability to co-deposit Pt and Ni (not rely on H<sub>2</sub> annealing step to control composition and the integration of Pt and Ni lattices).



Gould, T.D., *et al.* Applied Catalysis A: General 492 (2015) 107-116.

Packed bed reactor capable of several hundred mg to several g scale batches.

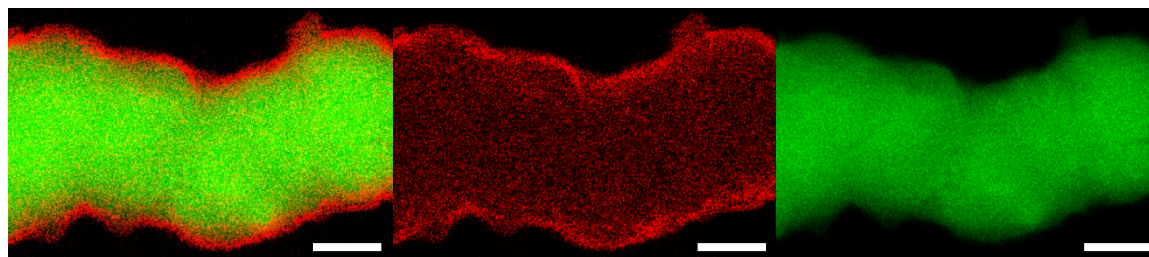
Atomic layer deposition with hydrogen has produced Pt-Ni nanowires up to 6 wt. % Pt.

Scale bars: 50 nm

Pt + Ni

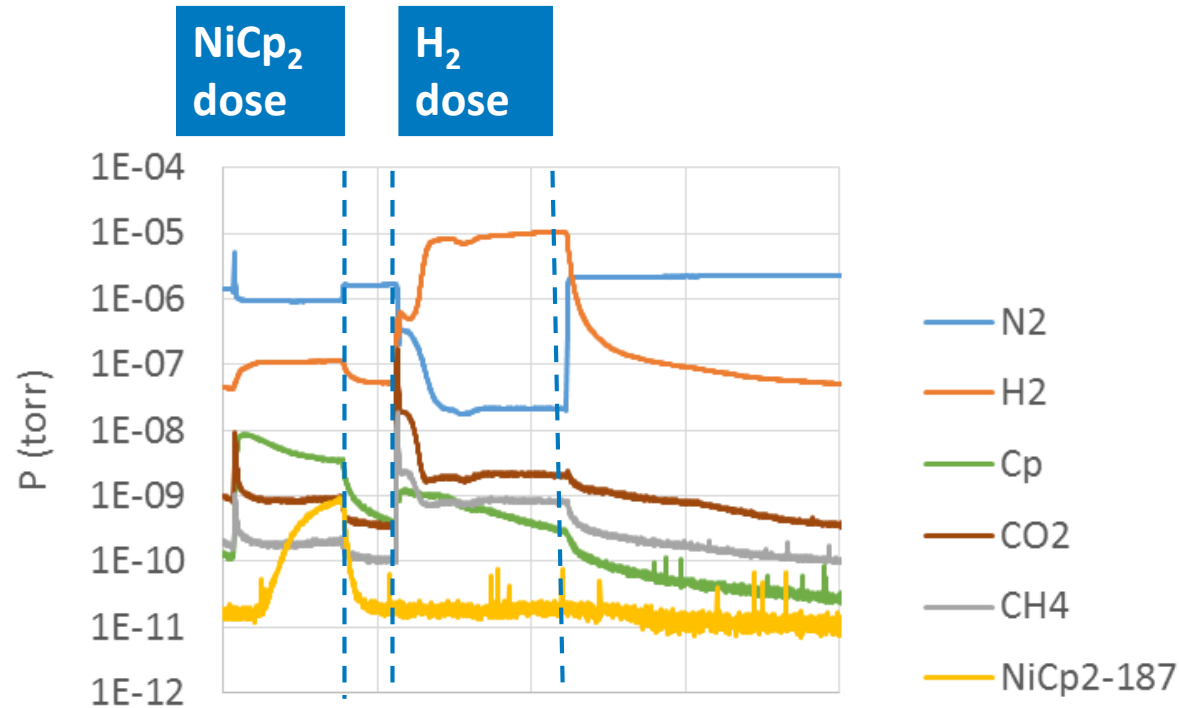
Pt

Ni



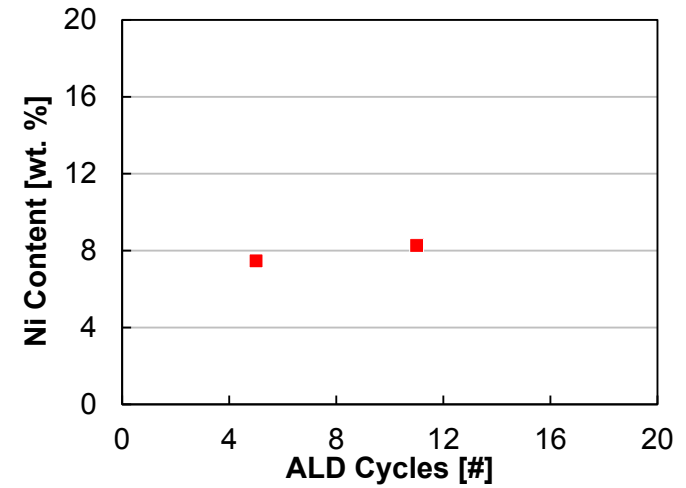
# Accomplishments and Progress

## Demonstrating Ni ALD



Mass spec data confirms ALD reactions as expected during Ni deposition.

## Ni ALD onto CoNWs

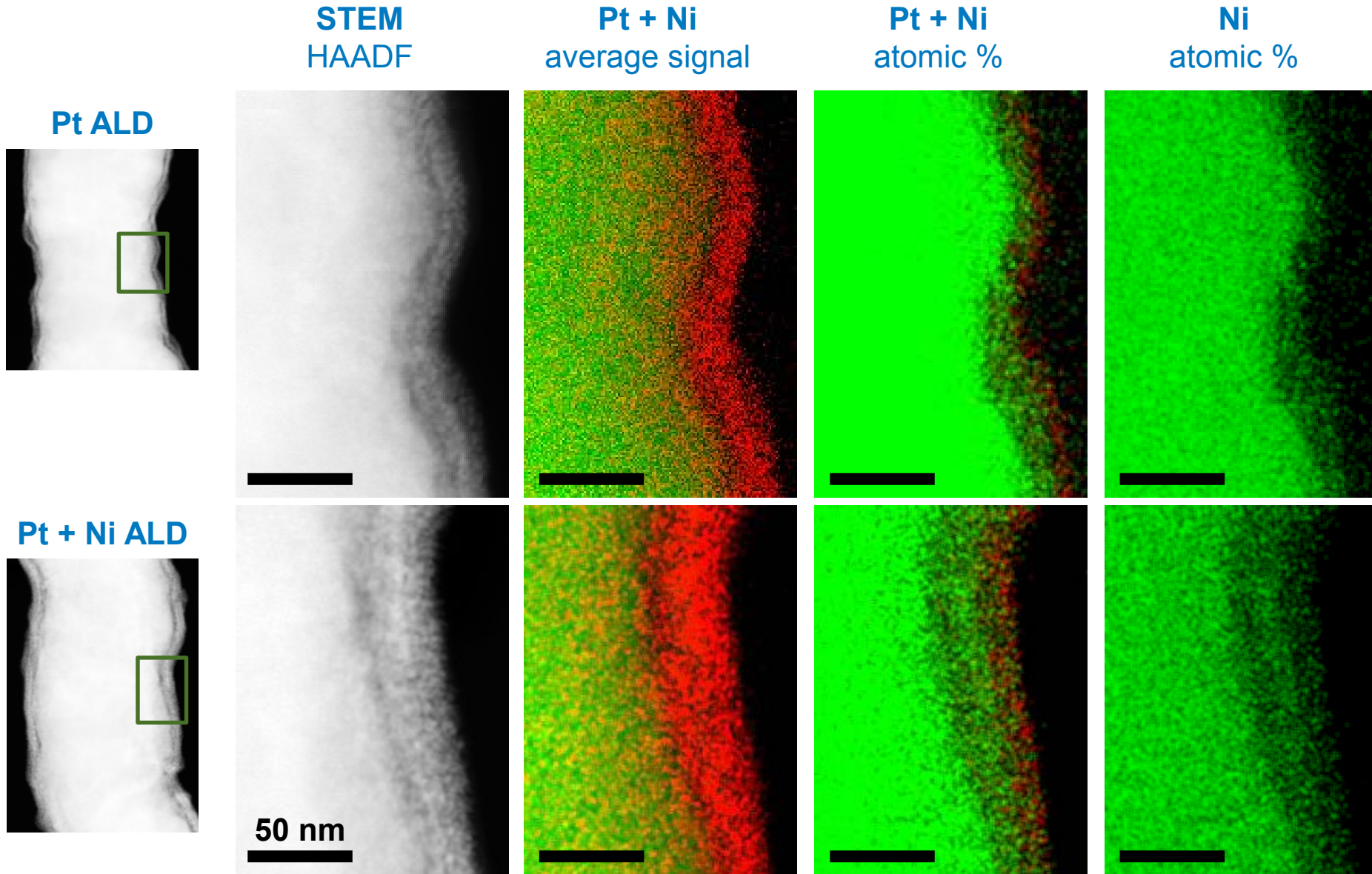


Cobalt nanowires used as a model, nanowire support to quantify Ni deposition.

Demonstrated 7.0-9.0 wt.% Ni on cobalt nanowires with limited cycling

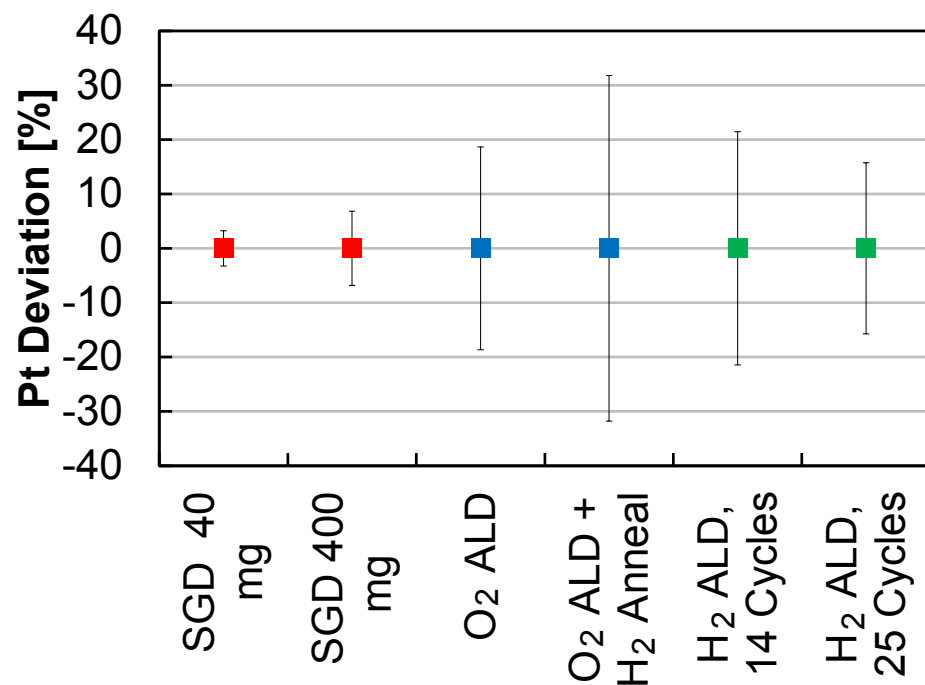
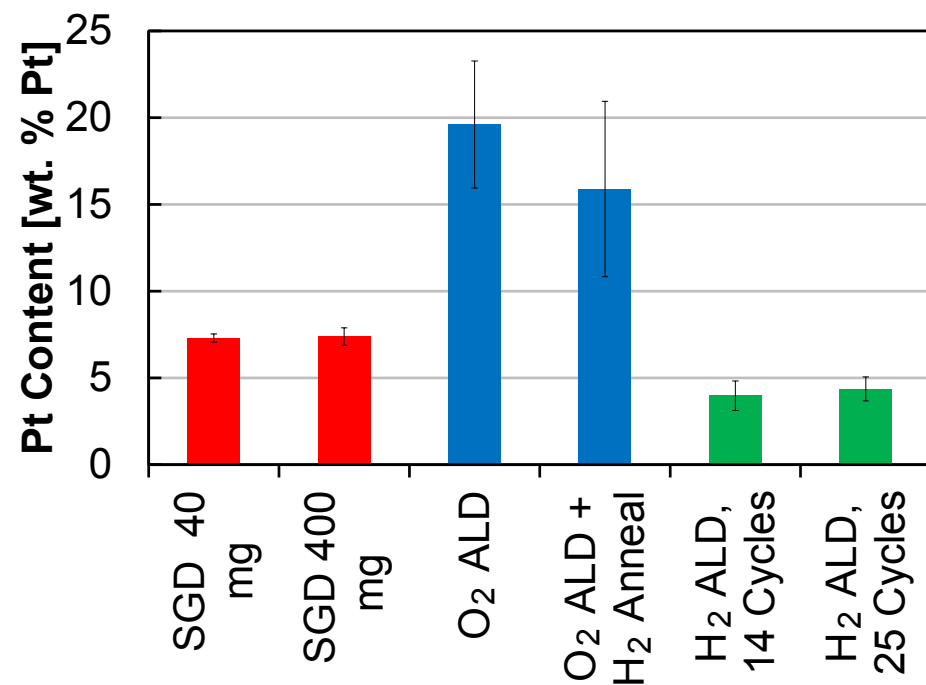
# Accomplishments and Progress

Pt and Ni deposition by hydrogen atomic layer deposition onto NiNWs



# Accomplishments and Progress

## Heterogeneity – comparing catalyst synthesis methods



**Atomic layer deposition gives a larger compositional distribution (ICP-MS) than previous spontaneous galvanically displaced (SGD) samples (data shown represent 6 digestions from a single synthesis).**

**O<sub>2</sub> ALD was run on a mat of wires, H<sub>2</sub> ALD was run in a packed bed.**

**Heterogeneity and loading are potential concerns related to low ECA observed.**

# Accomplishments and Progress

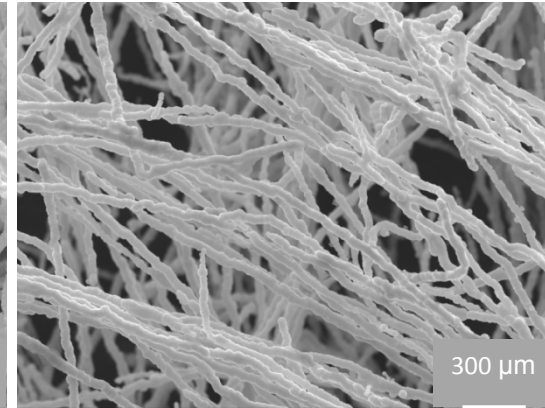
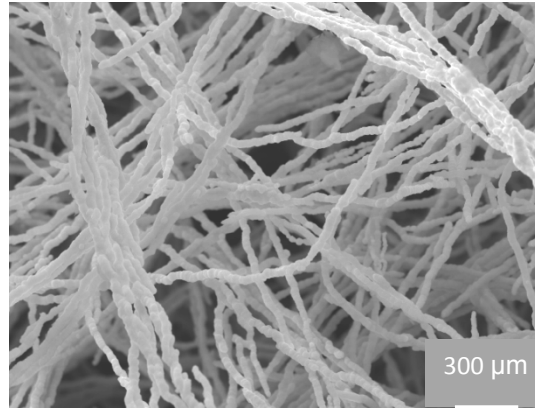
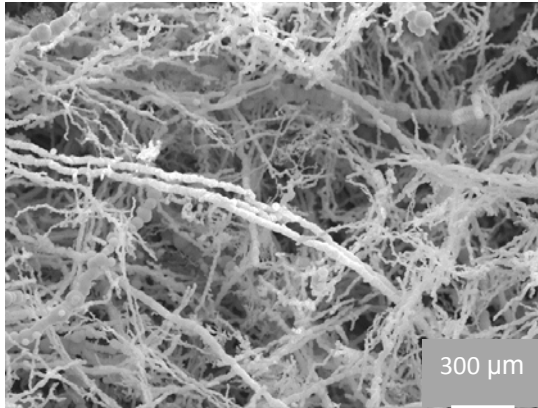
## Changes in the Upstream Nickel Nanowires

1 g (2014)

50 g (2015)

100 g (2016)

SEM



Fe Content  
BET (SA)  
Pt (ECA)

0.4%  
 $6.1 \text{ m}^2 \text{ g}^{-1}$   
 $\sim 90 \text{ m}^2 \text{ g}^{-1}$

0.8%  
 $2.0 \text{ m}^2 \text{ g}^{-1}$   
 $\sim 50 \text{ m}^2 \text{ g}^{-1}$

0.5%  
 $1.1 \text{ m}^2 \text{ g}^{-1}$   
TBD

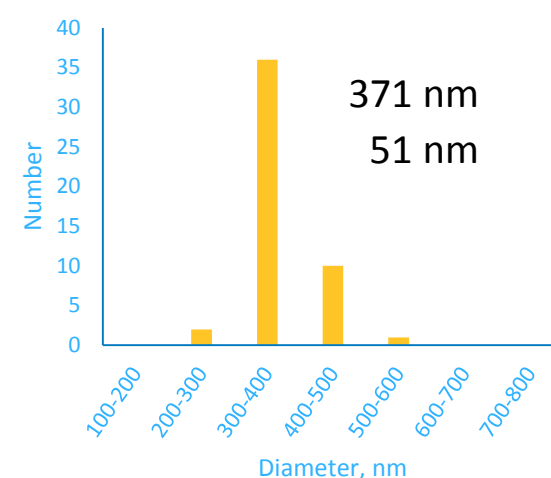
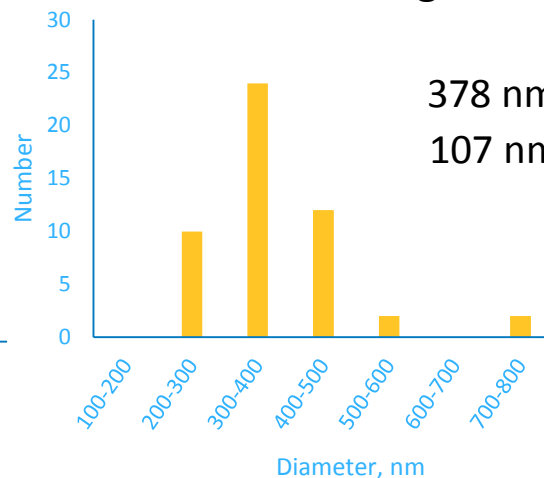
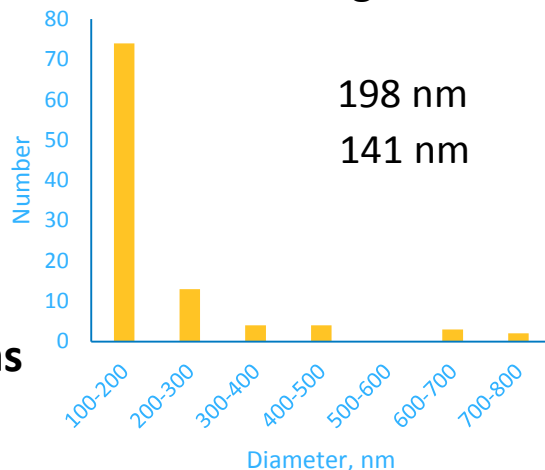
Average  
Std. Dev.

198 nm  
141 nm

378 nm  
107 nm

371 nm  
51 nm

Diameter  
Histograms



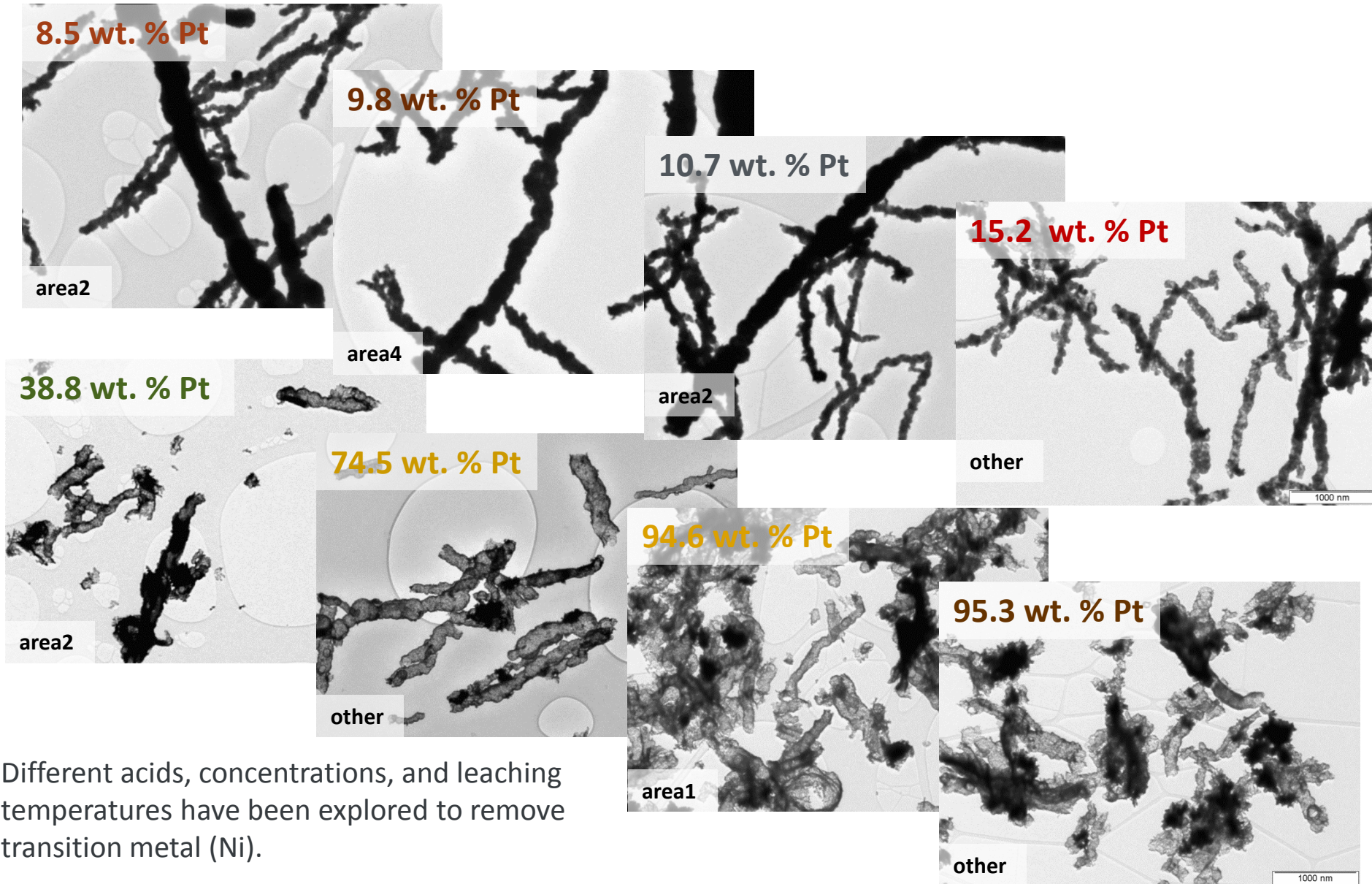
Changes in upstream template may account for lower Pt ECAs following synthesis.

Exploring novel nanotemplates (Delaware) and working with vendor.



# Accomplishments and Progress

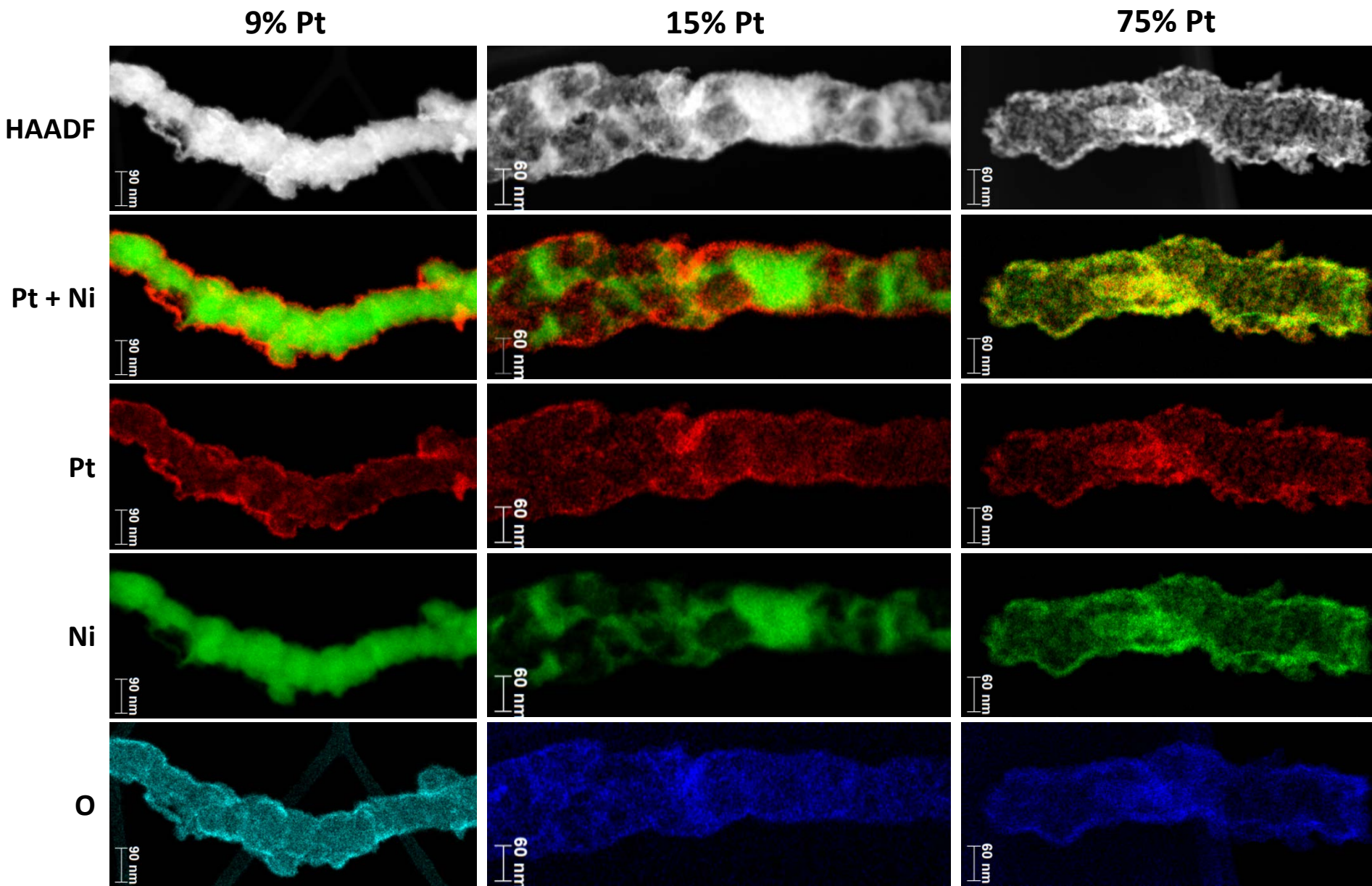
## Acid leaching – impact of post processing (morphology)



Different acids, concentrations, and leaching temperatures have been explored to remove transition metal (Ni).

# Accomplishments and Progress

## Acid leaching – impact of post processing (compositional analysis)

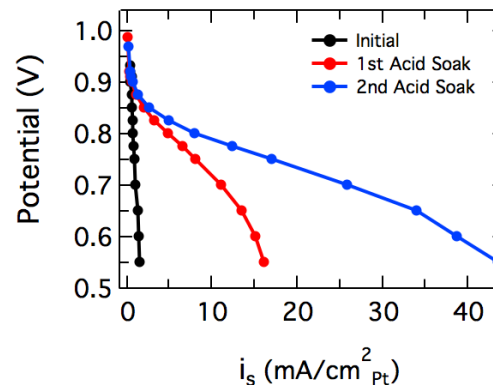
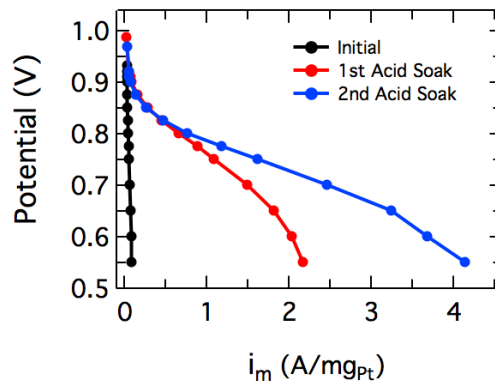
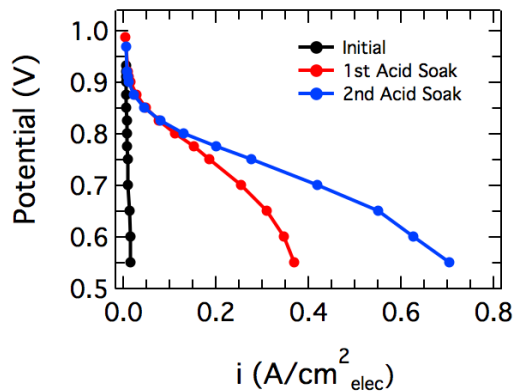




# Accomplishments and Progress

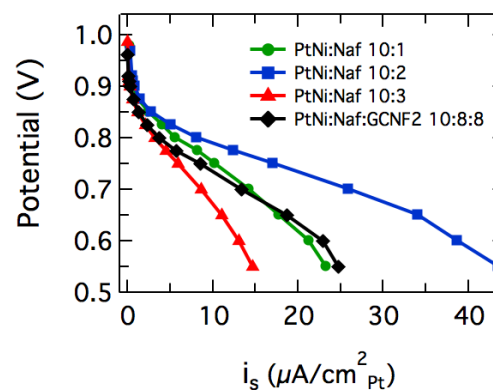
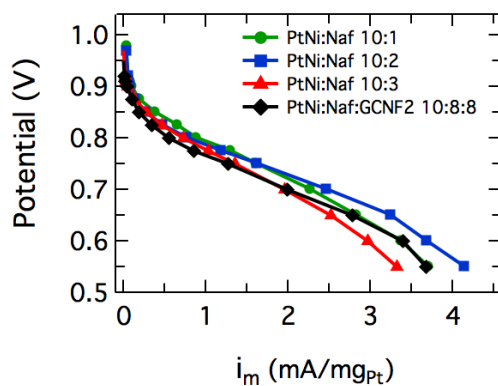
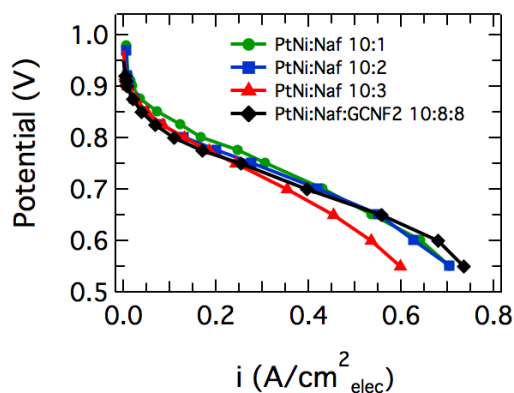
## MEA – Effect of processing on open circuit potentials and surface areas

### PtNi:Naf 10:2



Pt Loading: 0.16-0.2 mg/cm<sup>2</sup>  
Cell Temp: 80 °C  
Humidity: 100 % RH  
Back Pressure: 150 kPa<sub>abs</sub>  
Anode/Cathode Gas: H<sub>2</sub>/O<sub>2</sub>

### All MEAs after 2<sup>nd</sup> Acid Soak

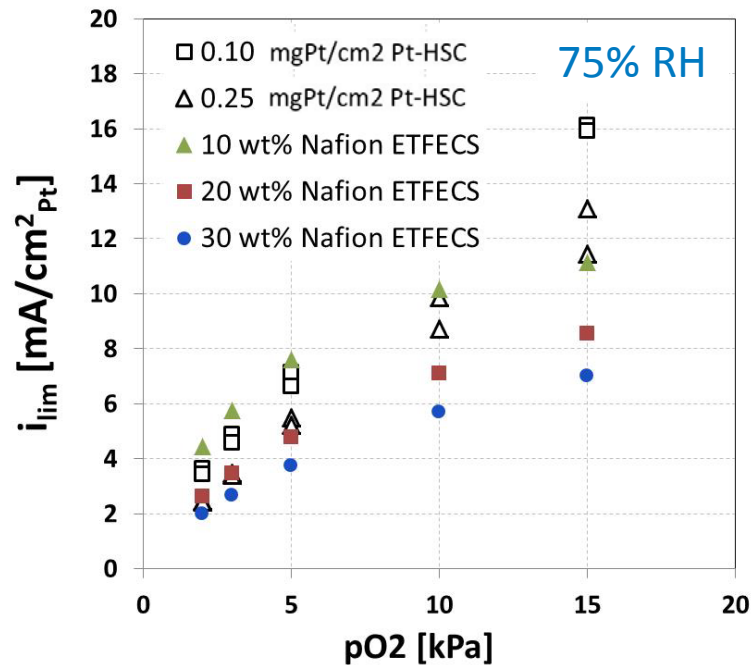


In parallel to our catalyst development, we have used galvanically displaced catalysts to explore MEA performance and optimization.

Acid washing has been used to address excess Ni contamination concerns. Future studies will have a focus on pre-leached catalysts.

# Accomplishments and Progress

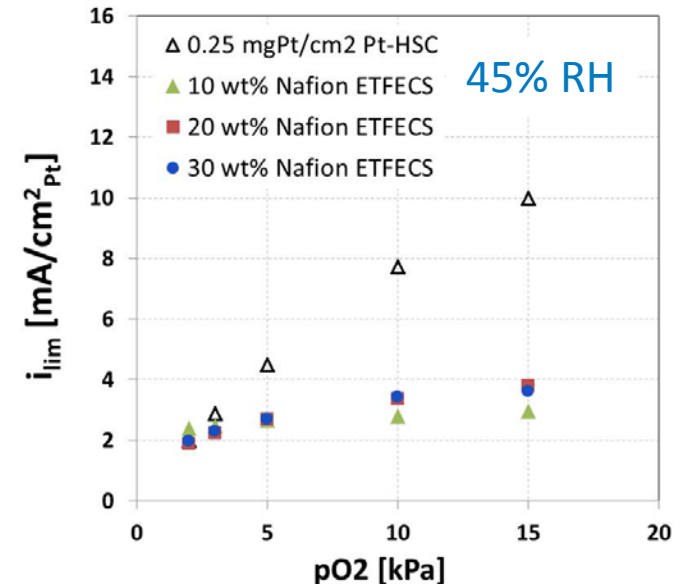
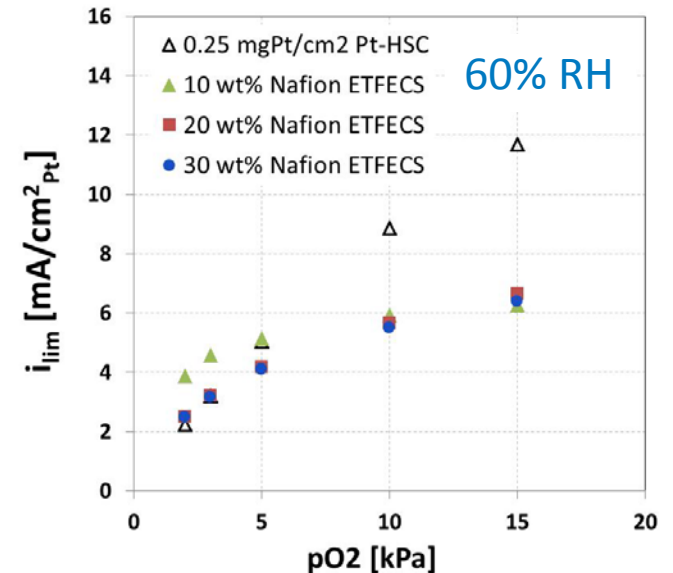
## MEA – Diffusion limited currents



Nafion content plays a large role in ETFECS limiting current ( $i_{lim}$ ) at high RH, but a minor role at decreased RH.

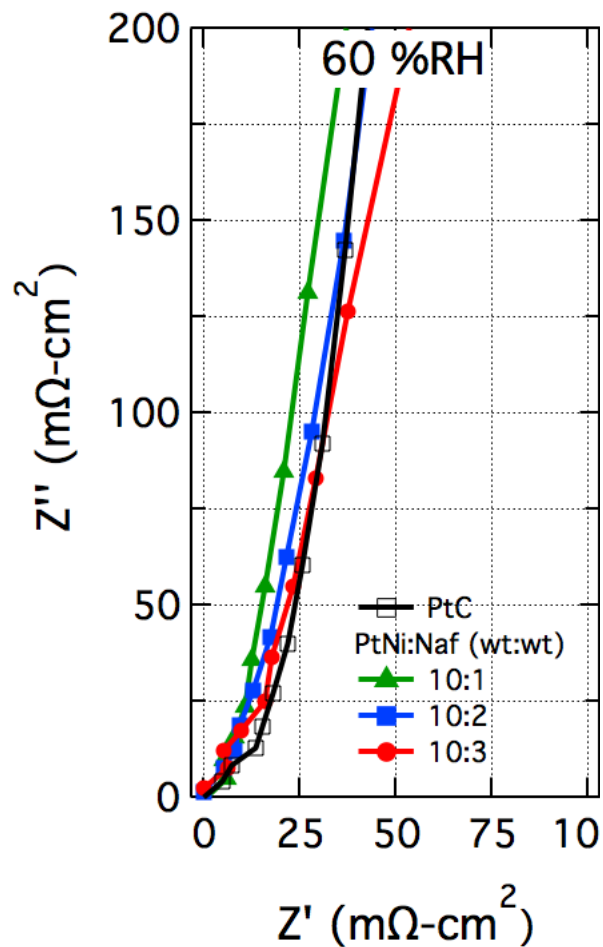
At high RH, 10 wt% Nafion ETFECS has similar limiting current to that of Pt/C. Begins to deviate at high pO<sub>2</sub>. For low RH samples, ETFECS deviates from Pt/HSC at much lower pO<sub>2</sub>.

The BET surface areas of ETFECS (~ 6m<sup>2</sup>/g) are much lower than Pt/HSC (>300m<sup>2</sup>/g), and may lead to thicker Nafion coating layers. By diluting traditional electrodes with carbon at lower loadings we have been able to increase the limiting current per Pt site, and will explore this approach and electrospun ionomer incorporation to improve limiting currents.



# Accomplishments and Progress

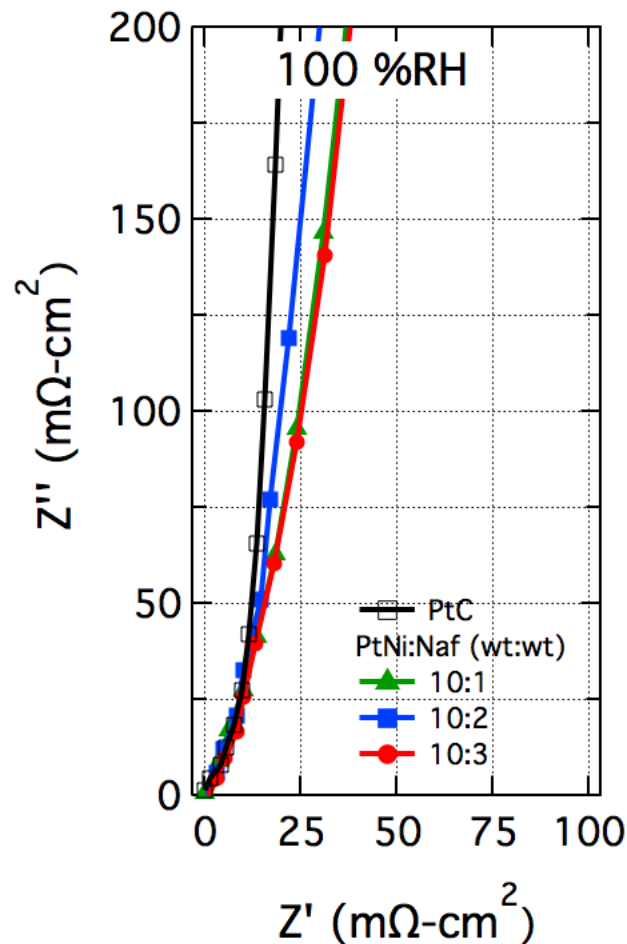
## MEA – Impedance spectroscopy



Cell Temp: 80 °C

H<sub>2</sub>/N<sub>2</sub> flow: 200 sccm

Back Pressure: 150 kPa<sub>abs</sub>



Impedance has been applied to probe the importance of proton conduction within ETFECS electrodes and compare with traditional electrodes.

The data shows basically no changes in electrode conductivity as a function of ionomer content down to 10:1 (catalyst: ionomer). We are exploring lower ionomer contents and alternative ionomer incorporation.



# Collaborations

Institutions	Role
<b><u>National Renewable Energy Laboratory (NREL):</u></b> Bryan Pivovar (PI), Shaun Alia, KC Neyerlin, Katie Hurst, Jason Zack, Scott Mauger, Shyam Kocha	<b>Prime, Oversees the project, lead catalyst synthesis and characterization; lead electrode fabrication and fuel cell testing</b>
<b><u>University of Delaware (Delaware):</u></b> Yushan Yan, Jarrid Wittkopf	<b>Sub; Support work in providing Ni nanostructures</b>
<b><u>Colorado School of Mines (CSM):</u></b> Svitlana Pylypenko, Sarah Shulda, Chilan Ngo	<b>Sub; Materials characterization using spectroscopy and microscopy</b>
<b><u>University of Colorado-Boulder (CUB):</u></b> Al Weimer, Will Medlin, Wilson McNeary	<b>Sub; ALD synthesis including both Pt and Ni using both oxidative and reductive chemistry</b>
<b><u>ALD Nanosolutions (ALDN):</u></b> Karen Buechler, Joe Spencer	<b>Sub; ALD consultation, scale up and business-case analysis</b>
<b><u>General Motors LLC (GM):</u></b> Anusorn Kongkanand	<b>In-kind partner; Consultation on transition metal impacts, fuel cell performance, and MEA fabrication</b>

Beam time at SLAC (Johanna Nelson Weker)

Mai-Ahn Ha (UCLA) Office of Science SCSGR awardee joining (6/20)

# Future Work/Remaining Challenges

## Nanotemplate synthesis:

Develop routes to novel Ni nanostructures and demonstrate at useful scale. Focus on clean, well-shape controlled nanowires and nanoflowers.

## Electrocatalyst synthesis:

ALD – controlled co-deposition of Pt/Ni onto nanotemplates.

Post-processing optimization of resultant catalysts (annealing and acid leaching)

Characterization and optimization (electrochemical and structural studies)

## Fuel cell testing:

Optimization of electrode structure/performance (including electrospinning/spraying and incorporation of different geometry carbons).

Isolation and minimization of overpotential losses in MEA electrodes (separation of mass transfer, ohmic, and kinetic losses).

Durability studies to quantify and minimize performance losses.

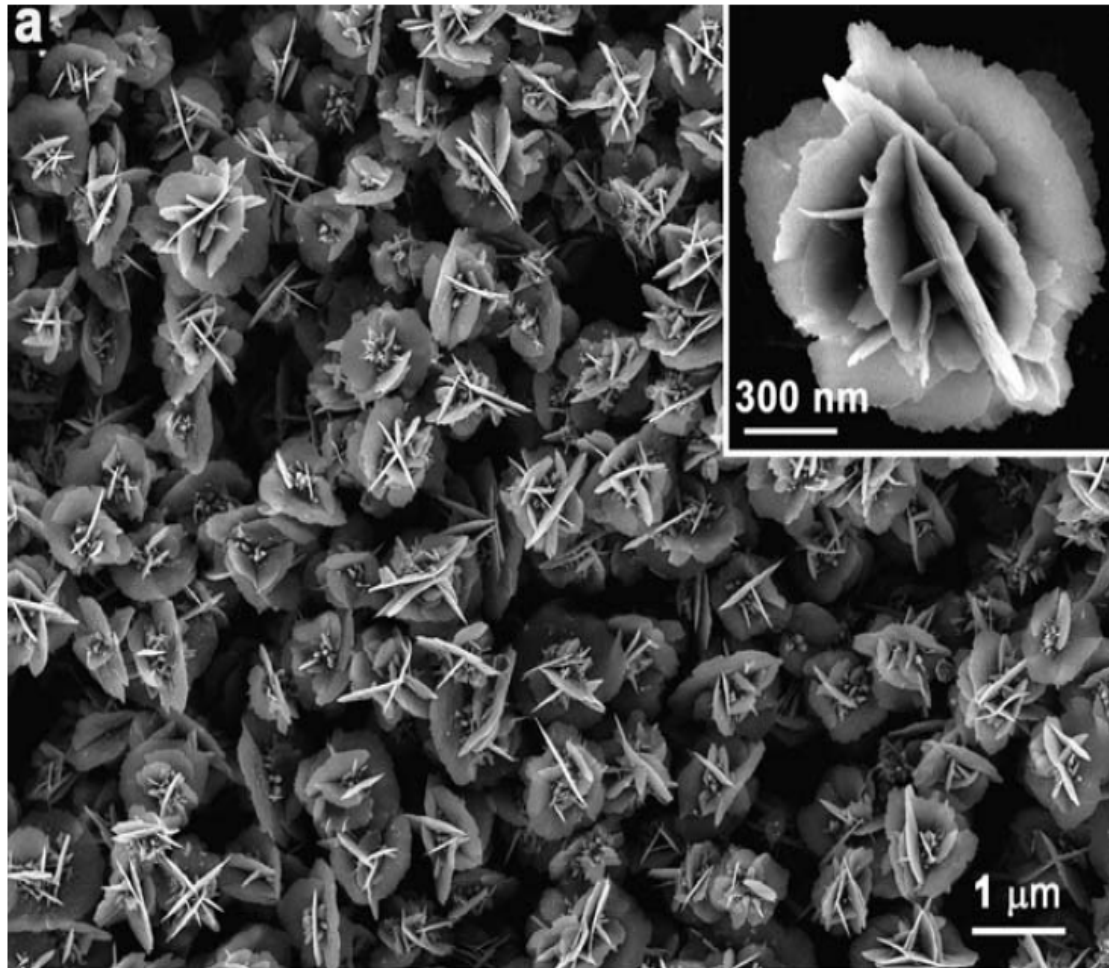
# Summary

- **Relevance:** Focused on overcoming the cost, performance and durability barriers for fuel cell commercialization by increasing Pt mass activity and durability.
- **Approach:** Developing durable, high mass activity extended surface Pt catalysts , and optimize MEA performance/durability for these materials.
- **Accomplishments and Progress:** The project has demonstrated the ability to deposit both Pt and Ni by ALD onto extended surface nanostructures. Surface areas of **90m<sup>2</sup>/g Pt** and specific activities of **8 mA/cm<sup>2</sup> Pt** (0.9V IR free) have been reached although not in the same sample, mass activity Pt of **2400 mA/mg Pt** has been demonstrated. ETFECS materials have incorporated into MEAs showing greatly improved performance with acid leaching. Diagnostic studies including limiting current and impedance have been applied to elucidate performance losses and optimized structures.
- **Collaborations:** We have a diverse team of researchers including 3 universities, and 2 industrial participants.
- **Proposed Future Research:** See previous slide.

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# Technical Backup Slides

# Synthesis of Ni Nanostructures (Delaware)



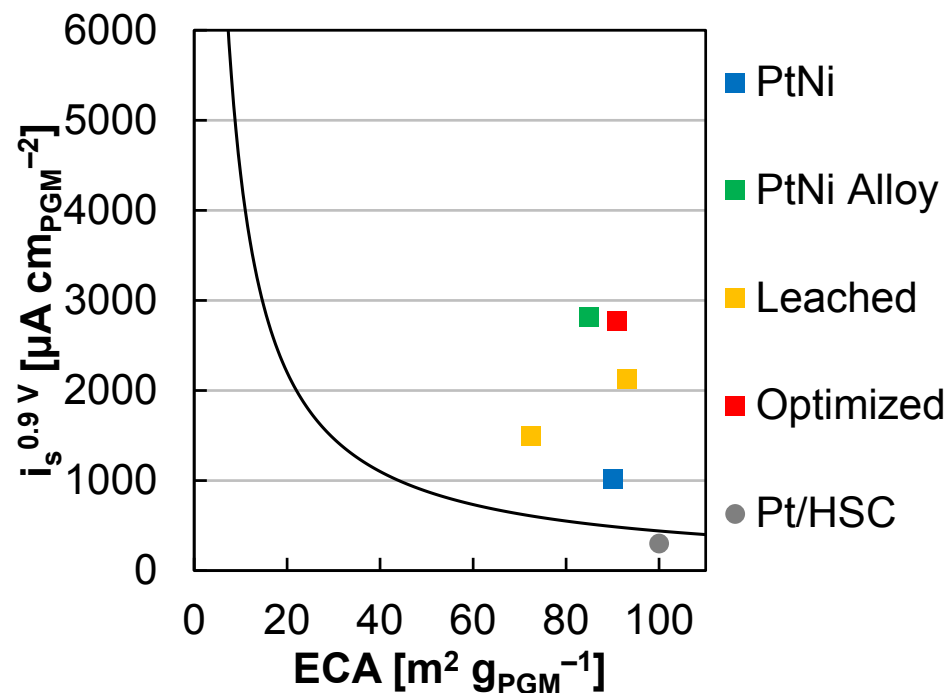
- Ni(111)
- Pt(111) is the most active
- Synthesis
- Galvanic displacement for ORR tests
- Provide Ni samples to the team



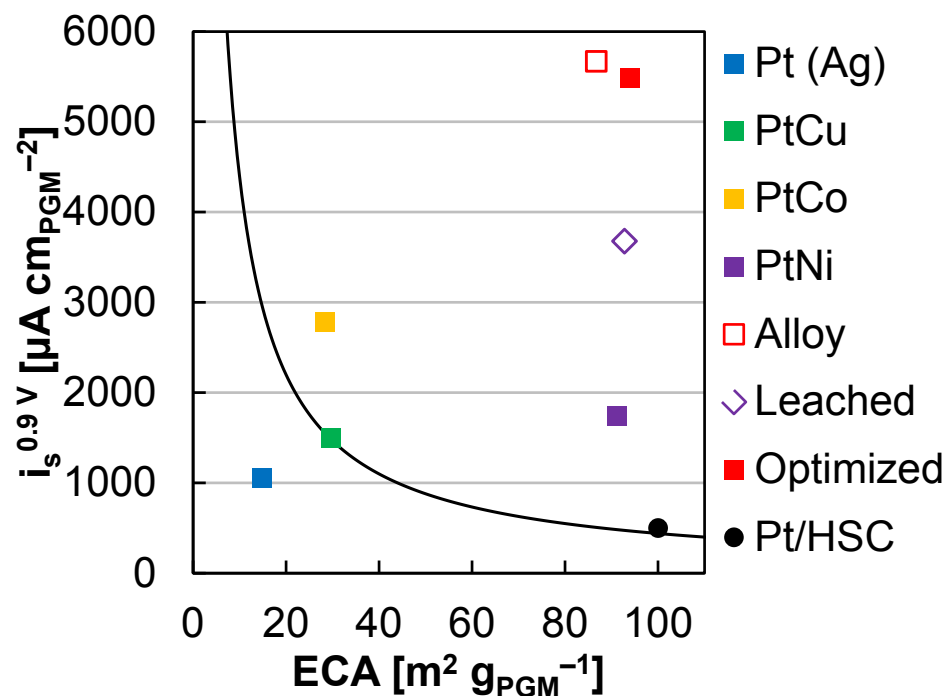
# Accomplishments and Progress

## Achieving high mass activity – Galvanic displacement

2015



2016



Rotational air drying method was used to coat ex-situ working electrodes, update electrochemical methods.

ECAs exceed  $90 \text{ m}^2/\text{g}_{\text{Pt}}$  and is above  $5000 \mu\text{A}/\text{cm}_{\text{Pt}}^2$  resulting in exceptionally high mass activity,  $\sim 12\text{x}$  DOE 2020 MEA target in RDE.

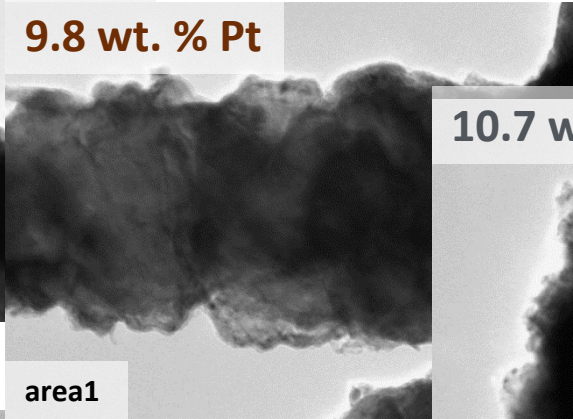
# Accomplishments and Progress

## Acid leaching – Galvanic displacement

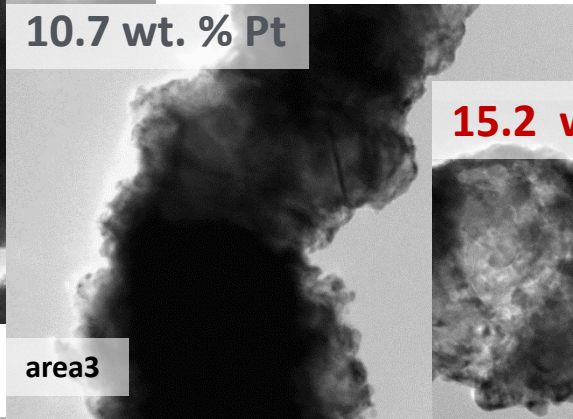
8.5 wt. % Pt



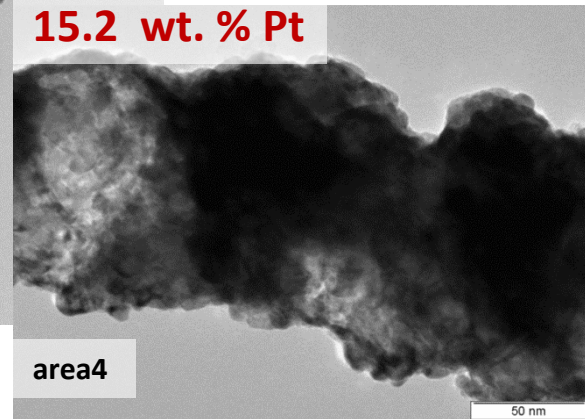
9.8 wt. % Pt



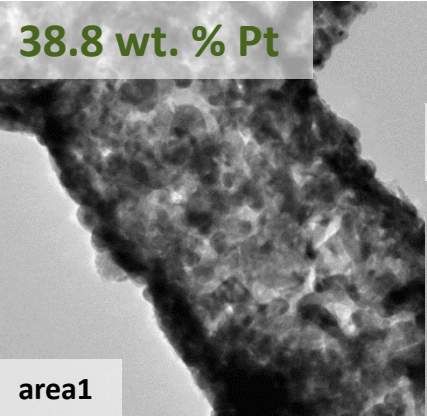
10.7 wt. % Pt



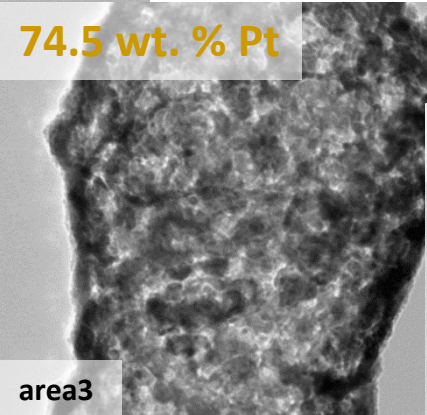
15.2 wt. % Pt



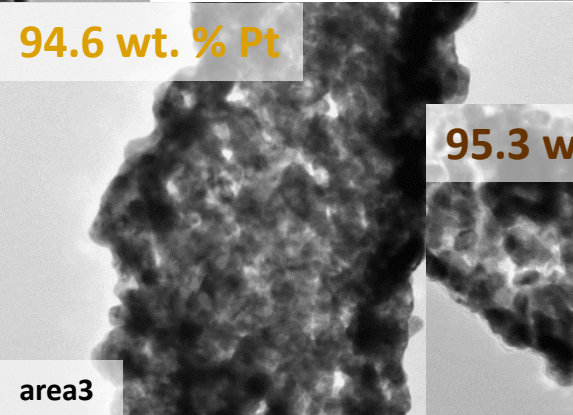
38.8 wt. % Pt



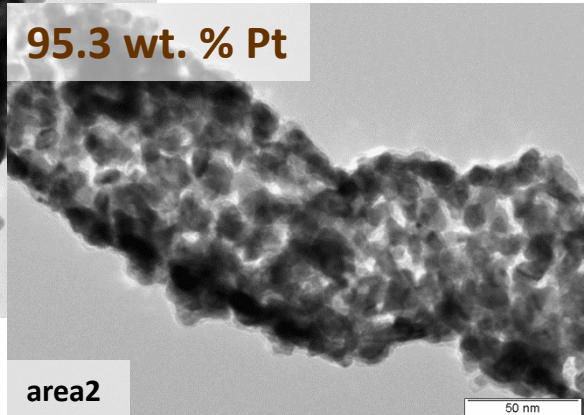
74.5 wt. % Pt



94.6 wt. % Pt



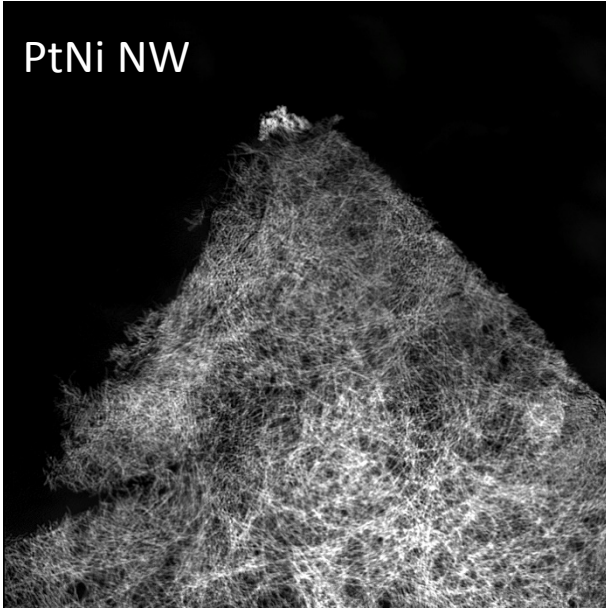
95.3 wt. % Pt



# Accomplishments and Progress

## Integration into membrane electrode assemblies

PtNi NW



Transmission x-ray microscopy has been used to study electrode composition and structure.

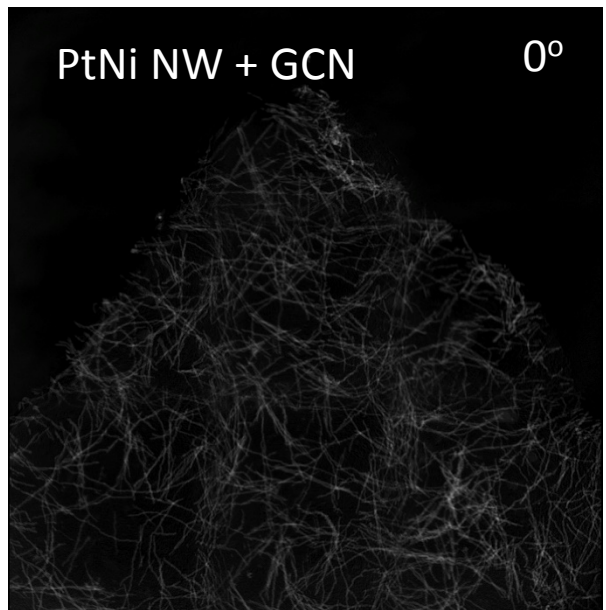
Top: MEA prepared with PtNi nanowires, Nafion and polyacrylic acid.

Bottom: MEA prepared with PtNi nanowires, Nafion, polyacrylic acid, and graphitized carbon nanofibers.

In collaboration with Johanna Nelson Weker, SLAC

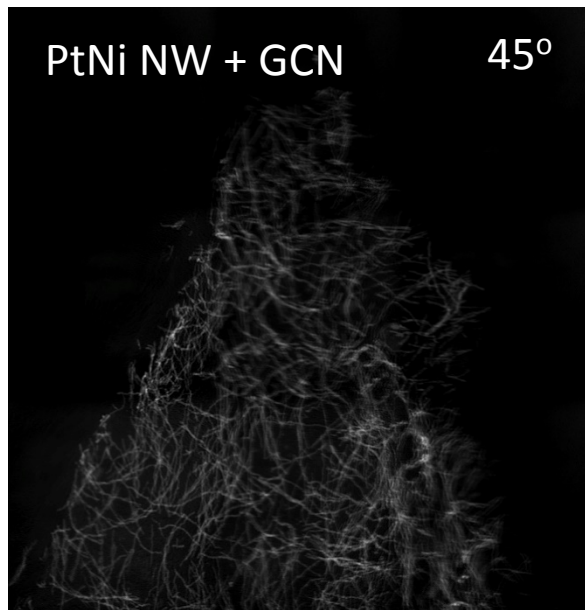
PtNi NW + GCN

0°



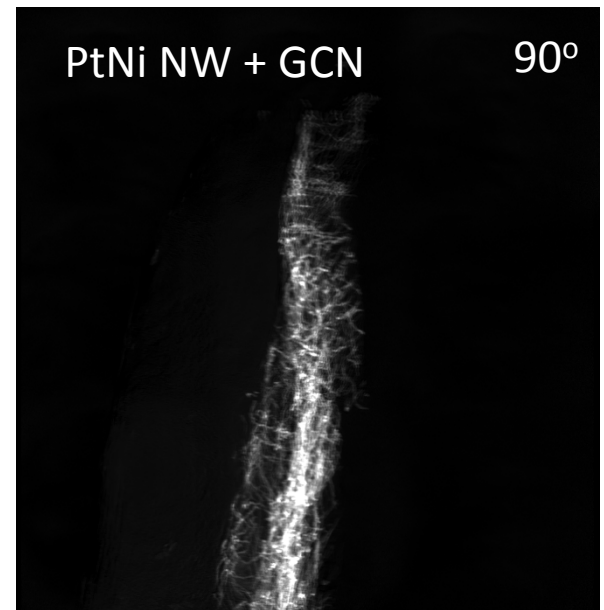
PtNi NW + GCN

45°



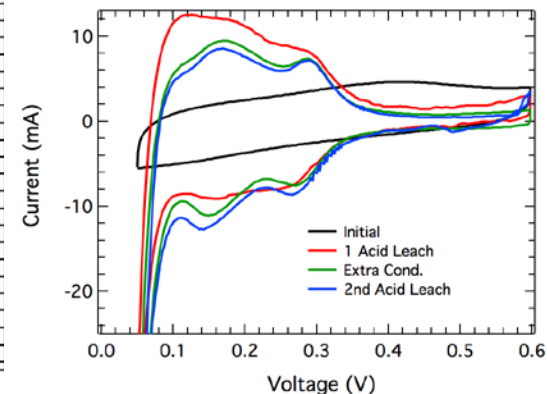
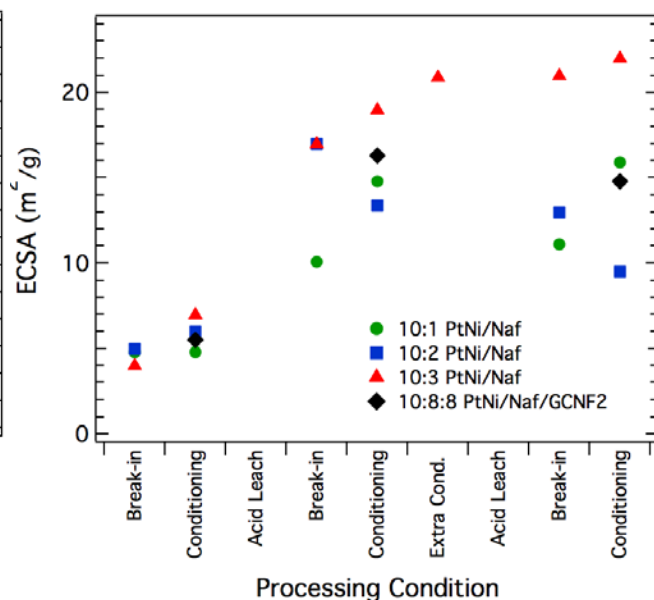
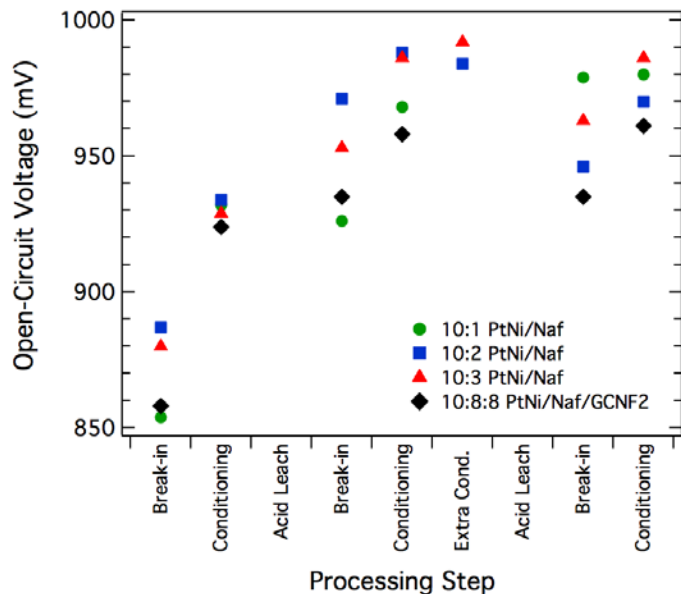
PtNi NW + GCN

90°



# Accomplishments and Progress

## MEA – Effect of processing on open circuit potentials and surface areas



Processing of membrane electrode assemblies required to clean Pt surfaces and improve open circuit potentials (Ni contamination). Acid soaking of MEAs for 15 hours in 0.01 m H<sub>2</sub>SO<sub>4</sub> (20°C).

ECAs greater than 20  $m^2/g_{Pt}$ , eventually are obtained, and Pt features become clear in cyclic voltammograms. Still far below ECA values obtained in RDE (55  $m^2/g$  Pt in RDE)

Treatment	Pt Content			
	10 wt% Nafion	20 wt% Nafion	30 wt% Nafion	10wt% Nafion w/GCNF2
Initial	12.7	12.9	12.1	13.0
Acid Soak 1	50.3	49.1	47.8	51.0
Acid Soak 2	52.6	63.0	53.6	56.3

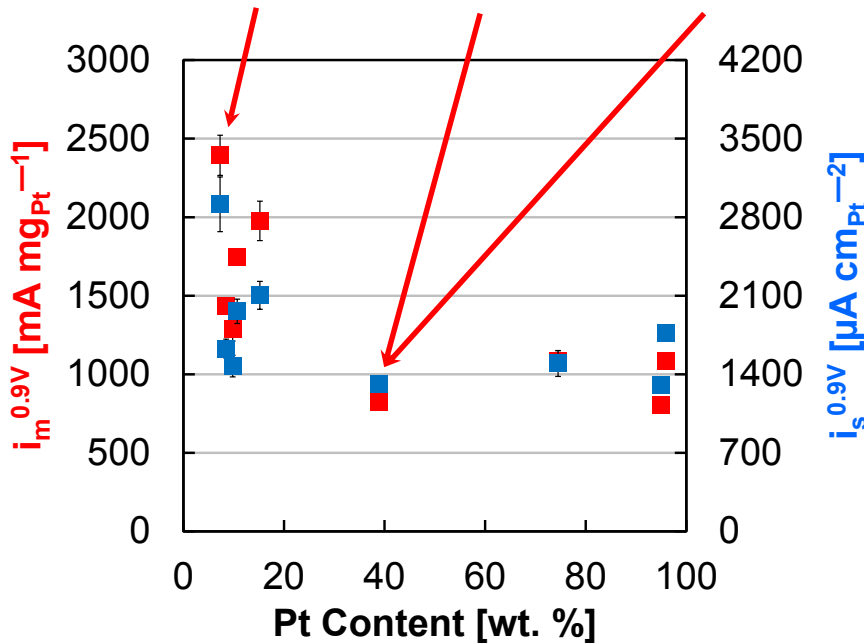
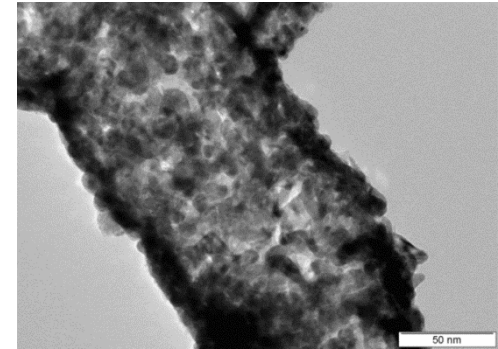
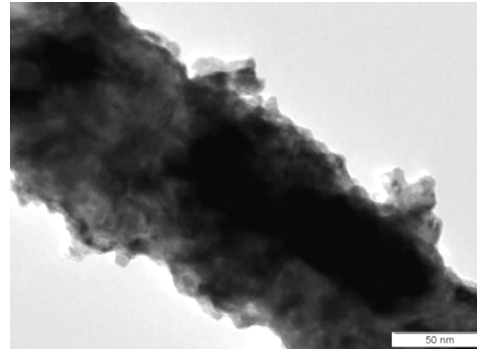
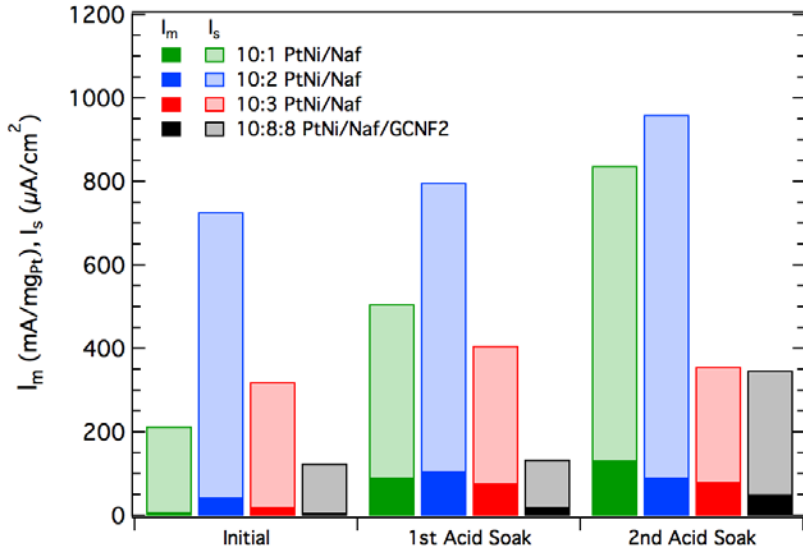
400 mg batch galvanic displacement (RDE)

- Specific activity = 2600  $\mu A cm_{Pt}^{-2}$
- Mass activity = 1400  $mA mg_{Pt}^{-1}$
- ECA = 54  $m^2 g_{Pt}^{-1}$



# Accomplishments and Progress

## Integration into membrane electrode assemblies



### 400 mg batch galvanic displacement (RDE)

- Specific activity =  $2600 \mu\text{A cm}_{\text{Pt}}^{-2}$
- Mass activity =  $1400 \text{ mA mg}_{\text{Pt}}^{-1}$
- ECA =  $54 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$

ECA and mass activities improve with acid washing, specific activity relatively constant

Membrane electrode assembly with a mass activity  $\sim 150 \text{ mA/mg}_{\text{Pt}}$  eventually obtained.