Extended Surface Electrocatalyst Development

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

Project ID #FC142

Overview

Timeline and Budget

- Project start: December 2015
- Project end: March 2019
- % complete: 95%

- Total project budget: $ 3399k
  - Total recipient share: $ 399k
  - Total DOE share: $ 3000k

- DOE Budget plan
  - FY 2016 $ 1000k
  - FY 2017 $ 1000k
  - FY 2018 $ 1000k

Barriers

- Durability
- Cost
- Performance

Partners

- 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

*through 3/1/17

Relevance

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)[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

[a] PGM content and loading targets may have to be lower to achieve system cost targets.

[b] 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)

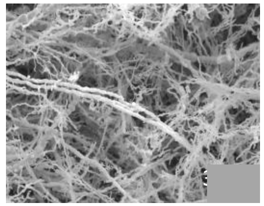
[c] Durability measured in a 25-50 cm^2 MEA during triangle sweep cycles at 50 mV/s between 0.6 V and 1.0 V at 80°C, atmospheric pressure, 100% relative humidity, H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (http://www.uscar.org/commands/files_download.php?files_id=267), Electrocatalyst Cycle and Metrics (Table 1). Activity loss is based on loss of mass activity, using initial catalyst mass, at end of test.

[d] Durability measured in a 25-50 cm^2 MEA during a hold at 1.2 V in H_2/N_2 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), Catalyst Support Cycle and Metrics (Table 2). Activity loss is based on loss of mass activity, using initial catalyst mass, at end of test.

[e] Test at 80°C H_2/O_2 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).

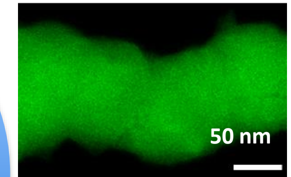
Approach

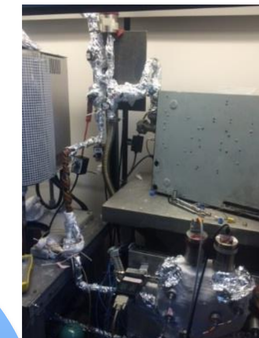
Catalyst and Membrane Electrode Assembly Development



Ni Nanowires
Commercial

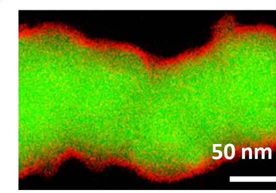
Ni

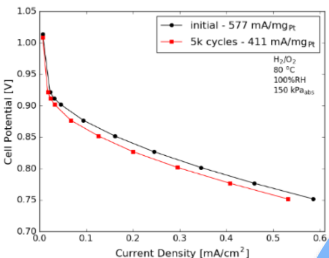




Atomic Layer Deposition (ALD)
CU: initial studies/novel chemistry;
ALD Nanosolutions: scale up

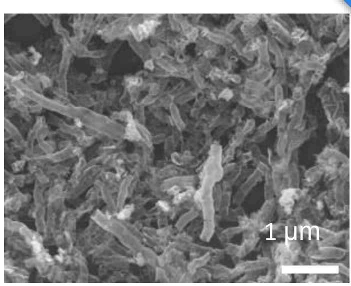
Pt + Ni

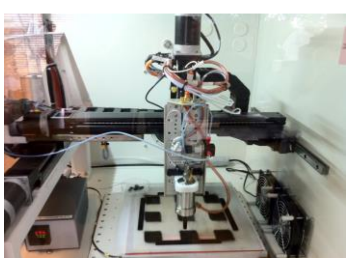




Fuel Cell Diagnostics
NREL: performance, durability, transport

Characterization
NREL: electrochemical
CSM: microscopic

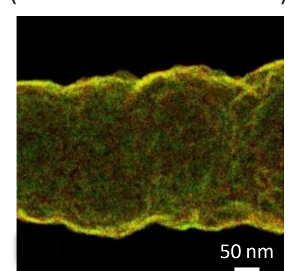




MEA Fabrication/ Optimization
NREL: composition, processing

Catalyst Post-Processing
NREL: annealing, leaching

Pt + Ni
(annealed and leached)



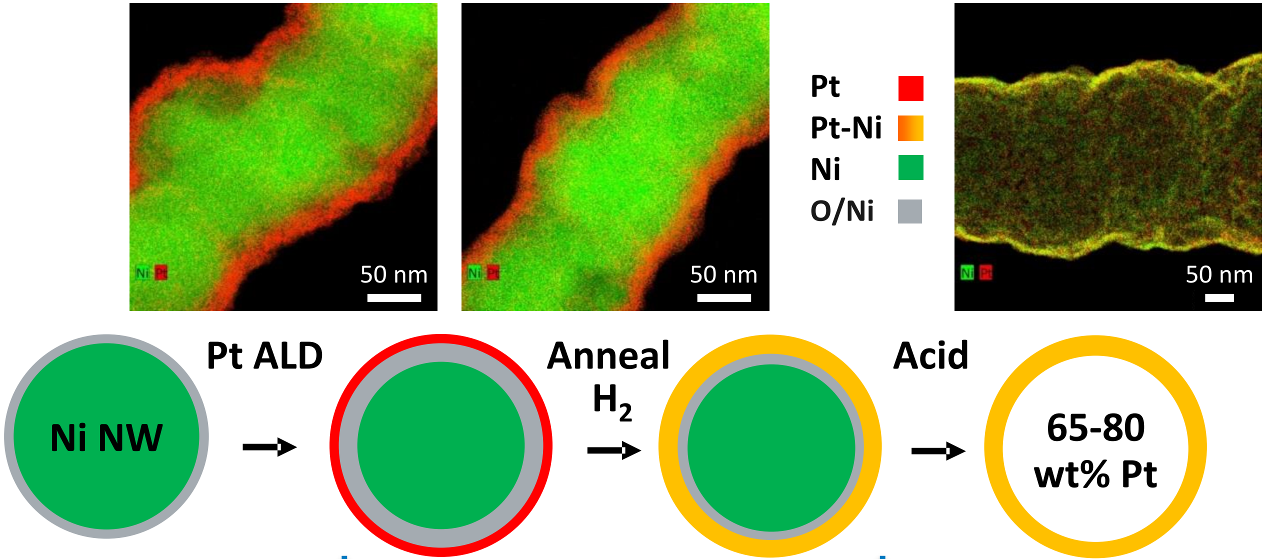
Approach

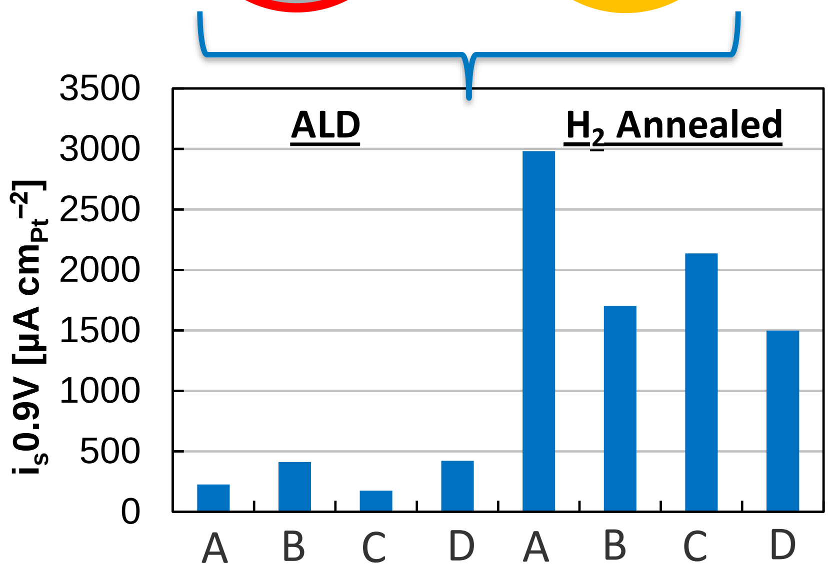
Project Schedule/Milestones

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No Go Decision	Type	Status
Q3	6/30/2018	Regular	Quantify the non-Fickian O_2 transport resistance of at least 3 unique electrodes containing PtNiNW electrocatalysts, a key metric for achieving high performance at low loading.	Quarterly Progress Measure	Met
Q1	12/31/2018	Regular	Demonstrate synthesis of at least 5 batches of PtNiNW samples by ALD synthesis at quantities of 10g or greater.	Quarterly Progress Measure	Met
Q2	3/31/2019	Regular	Demonstrate MEA performance that exceed the DOE 2020 mass activity target (440 mA/mgPt) for ALD batch sizes greater than 10g.	Annual Milestone	Met

Approach

ALD Synthesis of High Activity Platinum Nickel Nanowires (2018)

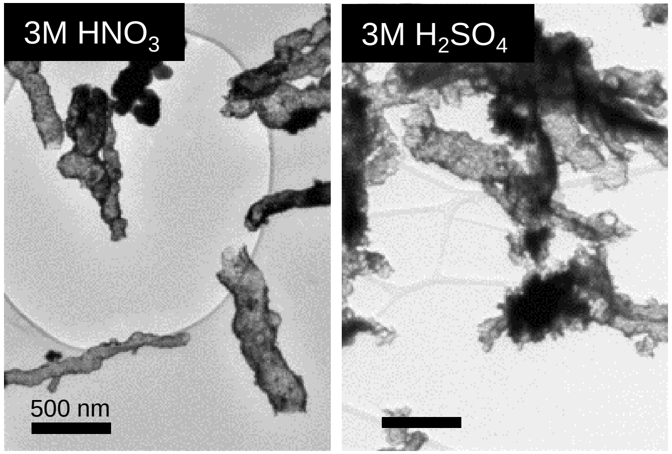




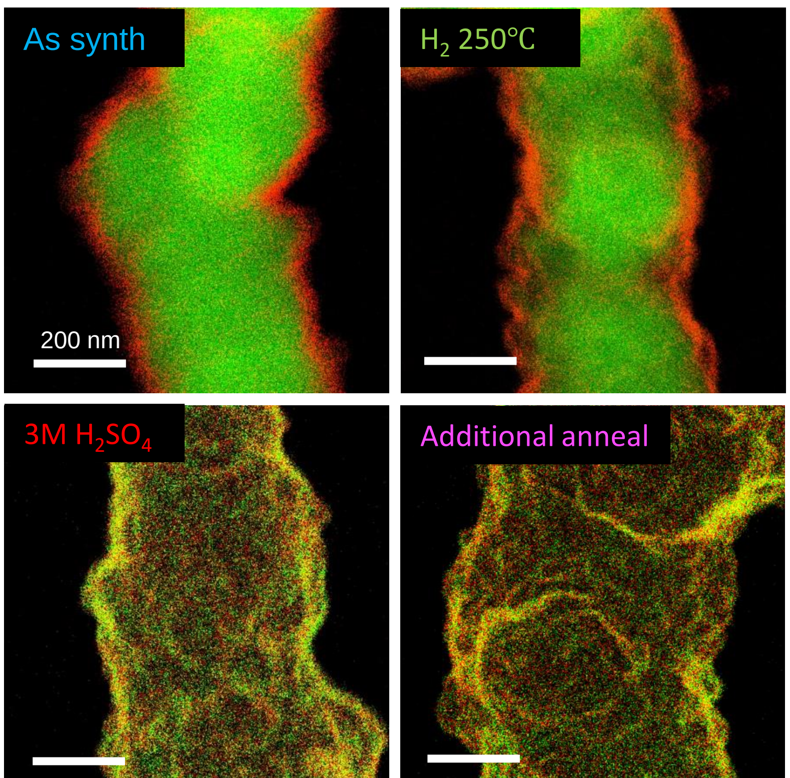
- H_2 annealing key to increasing alloying/specific activity.
- Reasonably high surface areas obtained (40+ m^2/g)
- Acid leaching removes excess Ni (poisoning concern)

Accomplishments and Progress

Acid leaching studies: ALD compared to SGD



SGD: broken wires after 3M acid treatment



ALD: wires intact, smooth, uniform even after harsh acid treatment

Pt L_3 edge EXAFS

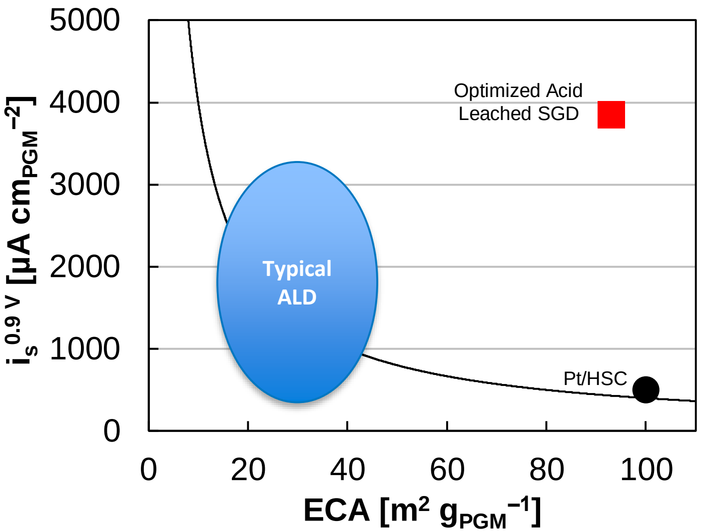
SGD	*Bond*	*N*	*R(Å)*
As synth	Pt-Pt	12	2.74
H_2 250°C	Pt-Pt	5.7	2.69
	Pt-Ni	5.7	2.56
H_2 250°C, 1M H_2SO_4	Pt-Pt	6.8	2.71
	Pt-Ni	3.24	2.60

ALD	*Bond*	*N*	*R(Å)*
As synth	Pt-Pt	11.2	2.74
H_2 250°C	Pt-Ni	10.5	2.57
H_2 250°C, 3M H_2SO_4	Pt-Pt	12	2.76
H_2 250°C, 3M H_2SO_4, H_2 250°C	Pt-Pt	5.7	2.69
	Pt-Ni	6.3	2.60

- ALD: lose PtNi alloy, reduced performance.
- But robustness of ALD wires allows us to try re-annealing step to regain activity.

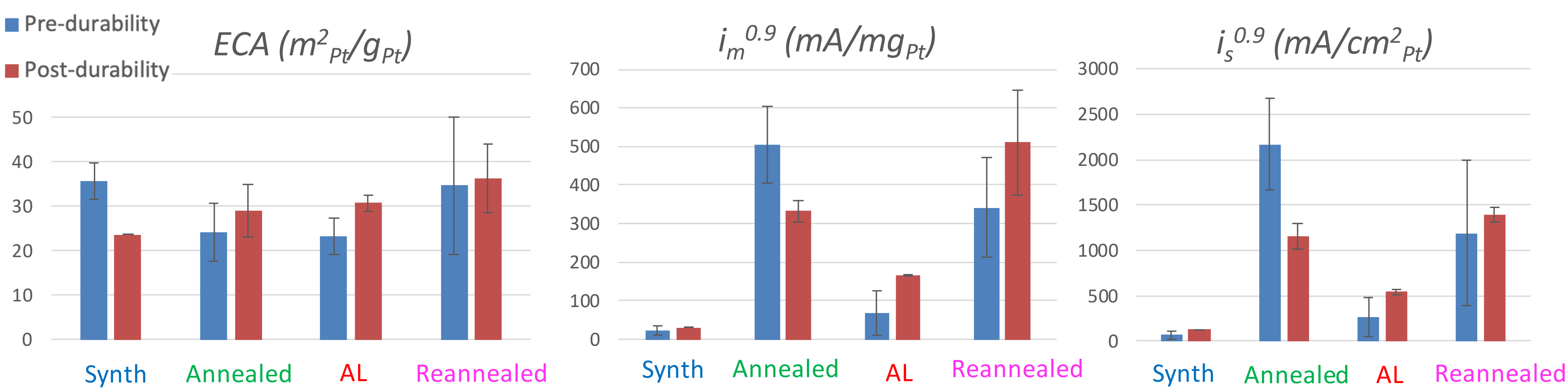
Accomplishments and Progress

Effect of Alloying on Acid Leached Nanowires



S.M. Alia, C. Ngo, S. Shulda, M.-A. Ha, A.A. Dameron, J. Nelson Weker, K.C. Neyerlin, S.S. Kocha, S. Pylypenko, B.S. Pivovar, *ACS Omega* **2017** 2 (4), 1408-1418.

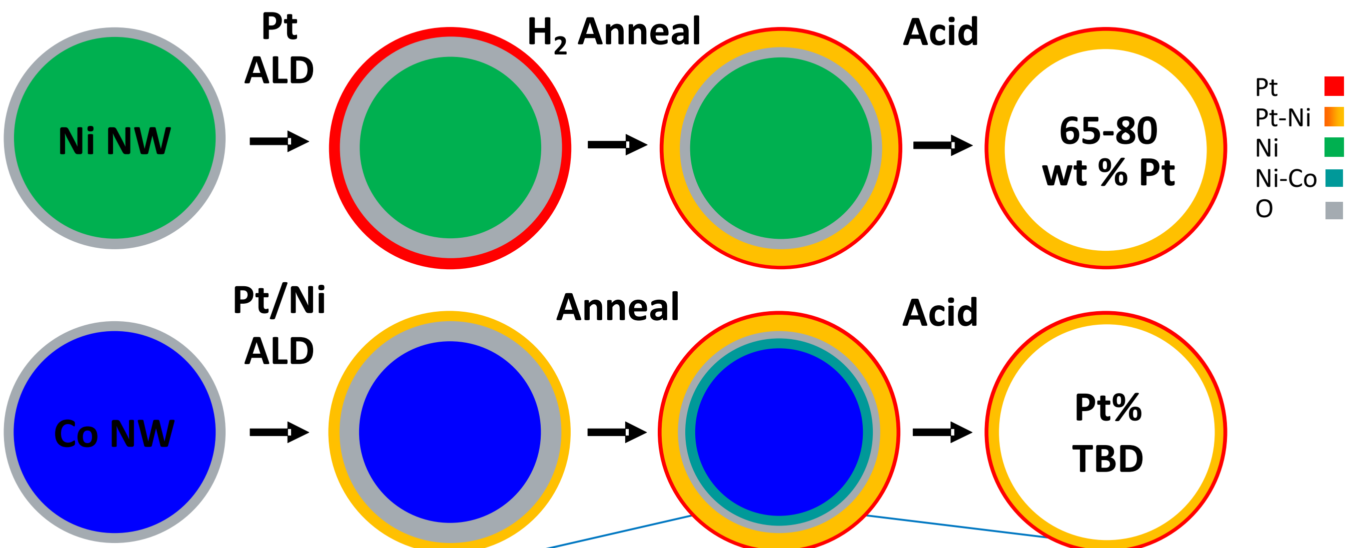
- Key differences noted between SGD, ALD synthesis and performance
- Lost ALD activity from acid leaching can be regained by reannealing



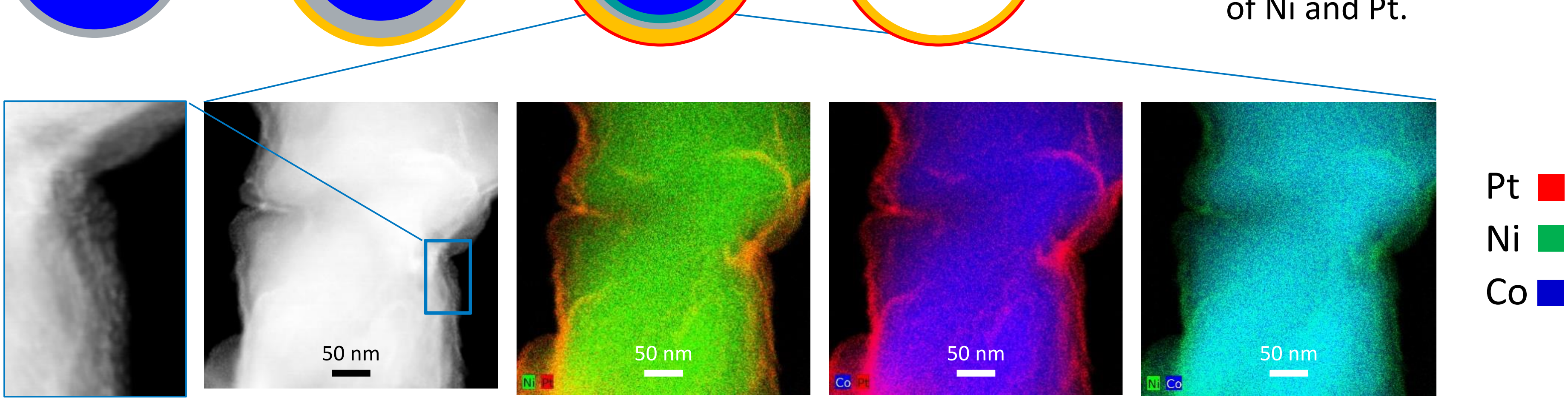
Accomplishments and Progress

ALD Synthesis (CU) with co deposition of Pt and Ni (2018)

- Established Pt ALD route has produced catalysts of reasonable activity, but has been limited because H_2 annealing step required for Ni incorporation into Pt lattice. Lack of control over Ni in Pt shell (ECA and specific activity limitations).



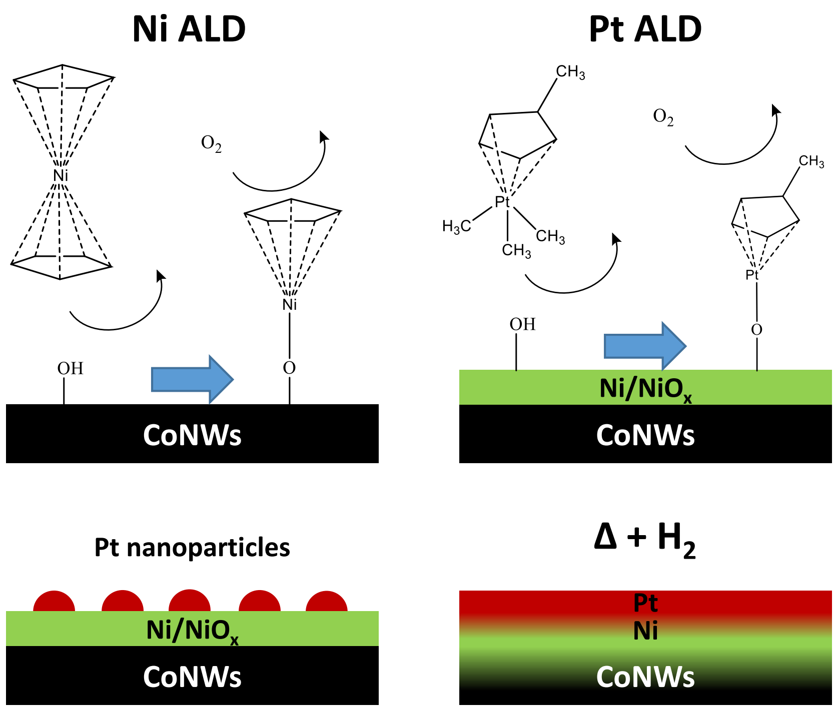
- Co-deposition of Pt and Ni by ALD potentially allows independent control over Ni content and more homogeneous composition.
- Co NWs employed to allow independent compositional analysis of Ni and Pt.



Accomplishments and Progress

ALD Synthesis with co deposition of Pt and Ni (CU)

Schematic of bimetallic ALD process:

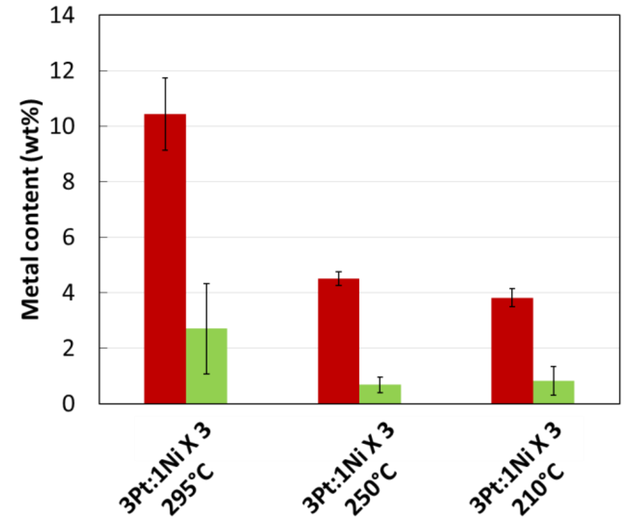


supercycle [x cycle Ni-O_2 / y cycle Pt-O_2

Annealing for lattice contraction and oxide reduction

ALD examined with variety of process conditions

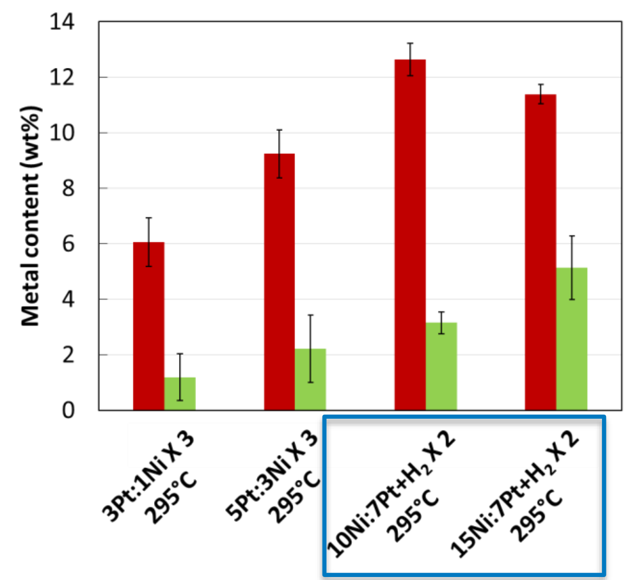
Varying ALD temperature changes growth rate



wt%Pt
wt%Ni
* balance Co

Varying supercycle ratio used to control Pt and Ni wt%

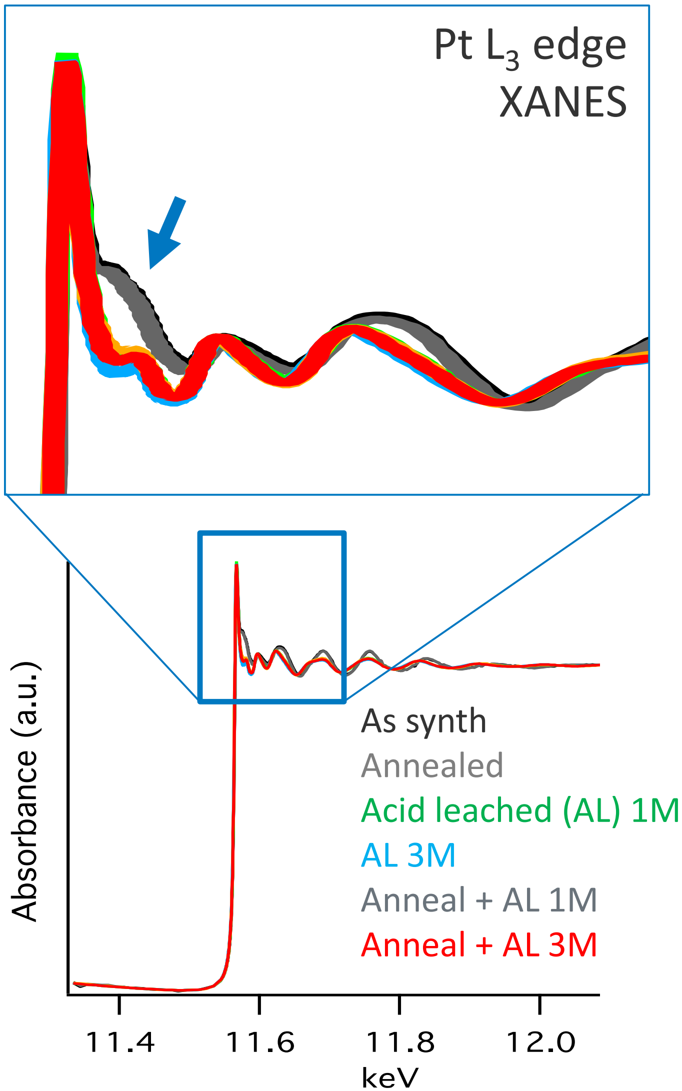
In situ H_2 annealing added between supercycles

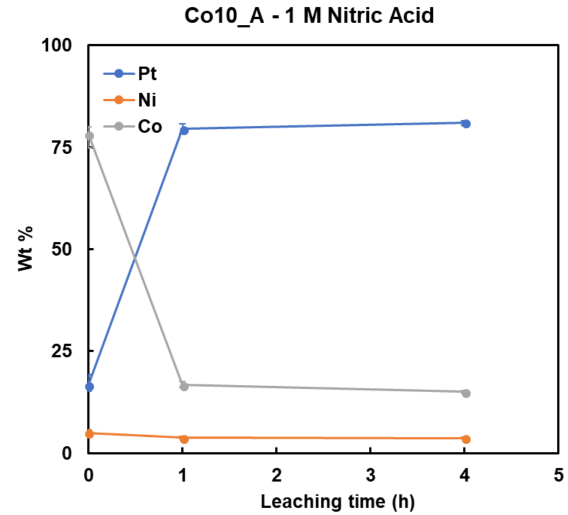


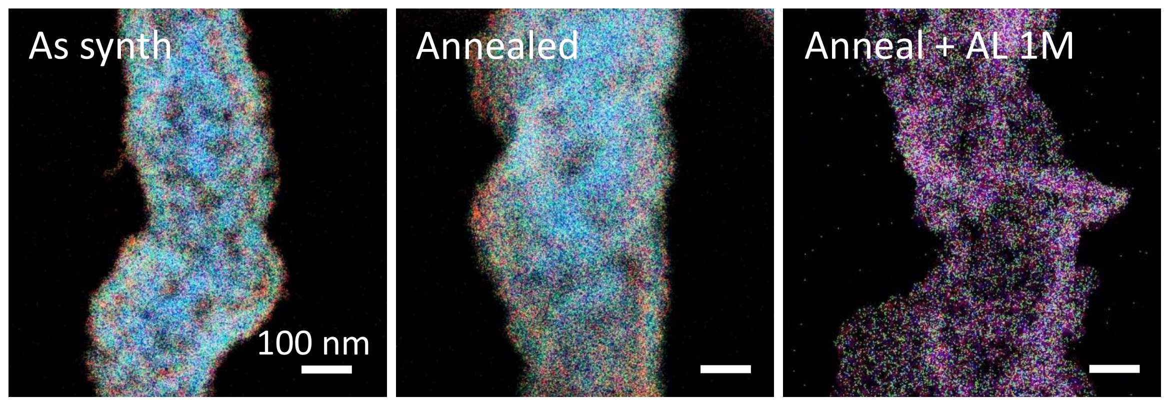
Accomplishments and Progress

Characterization of nanowires made by ALD co deposition of Pt and Ni

EDS maps (right) show overlays of Pt + Ni + Co.





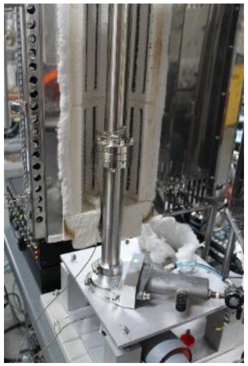


- As synth already shows PtNi alloy (see arrow) due to annealing step during ALD.
- Loss of Ni, Co, PtNi alloy with acid leaching
- Difficulty in retaining Ni

Accomplishments and Progress

ALD (ALDN) Scale up of catalyst synthesis

Fluidized Bed Reactors



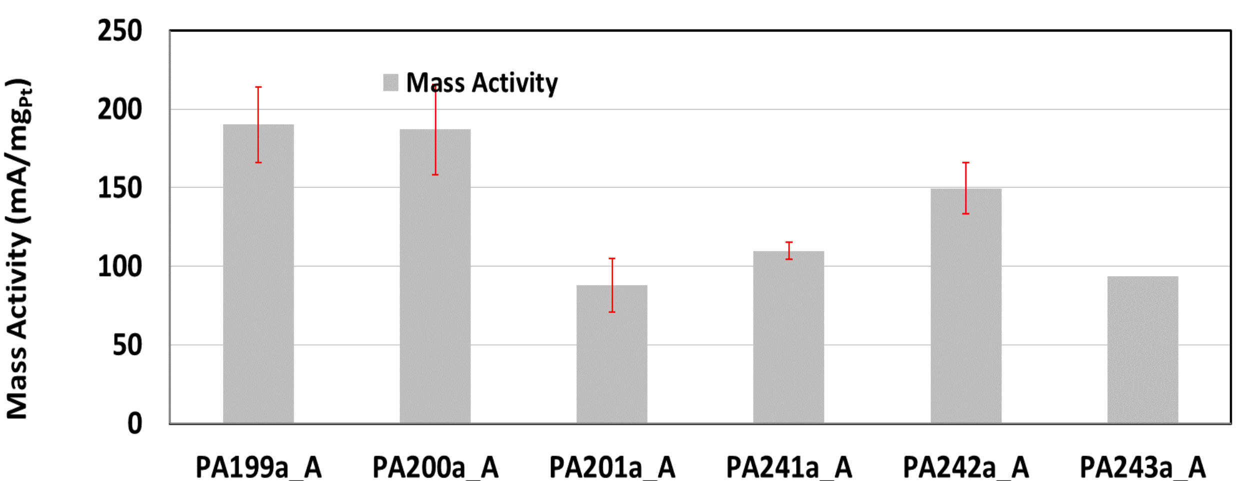
10-200 g
Research FBR

1-10 kg
Pilot FBR

Vacuum Rotating Drum Reactors

5-50 g
Research Rotary Drum

1-50 kg
Pilot Rotary Blender

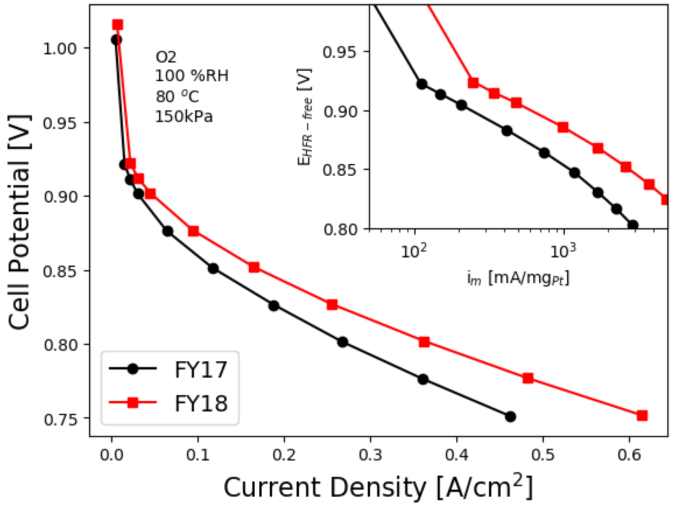


- ALD NanoSolutions has multiple reactors and scales from 5g batch to 3 mt/day continuous.
- Research FBR used to synthesize 15g catalyst batches.
- Show reasonable RDE activity and pursing acid leaching, MEA testing.
- Additional nanowire order has been ordered to continue large scale synthesis and testing.

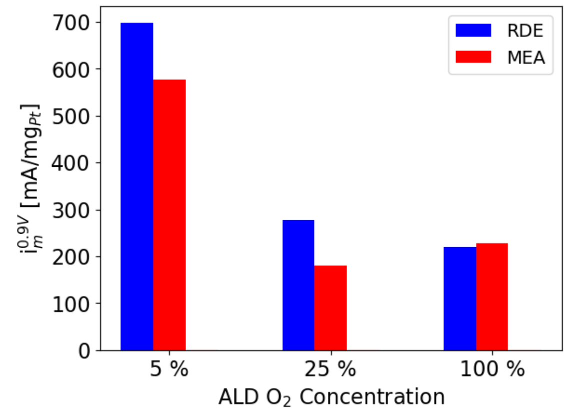
Accomplishments and Progress

Project mid point go/no go milestone (2018)

Go/No-go: Demonstrate a mass activity of >440 mA/mg_{Pt} at 0.9V (DOE 2020 Target) in fuel cell tests while also meeting at least one of FCTO's MEA durability targets



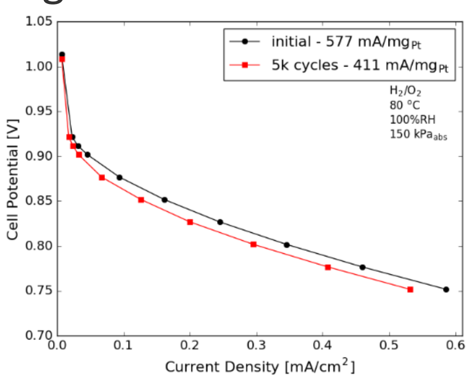
- Mass activity improvement from 2017 AMR, now meets DOE mass activity target.
- Activity trend with ALD O_2 concentration consistent between RDE and MEA.



Durability Testing

Protocol: Triangle sweep cycle, 5000 cycles, 500 mV/s, 1.0-1.5 V

Target: <40% loss in initial catalytic activity



Cycles	$i_m^{0.9V}$ [mA/mg]
0	577
5000	411*
% Loss	28.8

$i_m^{0.9V}$ > 440 mA/mg ✔

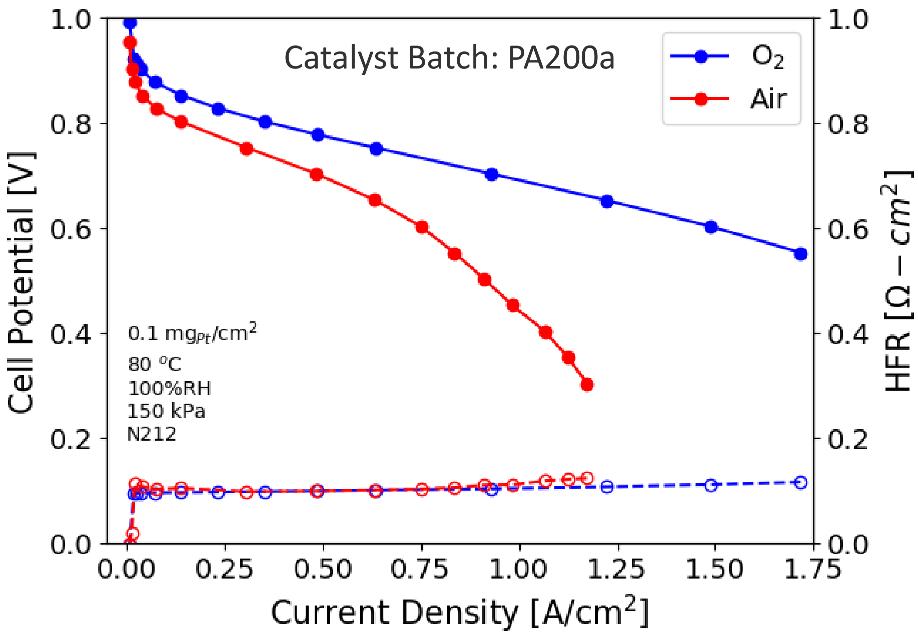
DOE Durability Target ✔

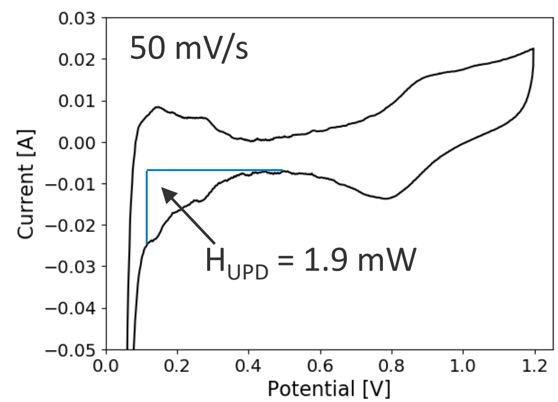
*following voltage recovery

Accomplishments and Progress

Accomplished FY19 Annual Milestone

Demonstrate MEA performance that exceed the DOE 2020 mass activity target (440 mA/mg_{Pt}) for ALD batch sizes greater than 10 g.





$i_m^{0.9V}$	**463 mA/mg_{Pt}**
ECSA	35.5 m^2/g_{Pt}
$i_s^{0.9V}$	1226 µA/cm^2_{Pt}

PtNi mixed with Vulcan XC72
PtNi:C – 2:1 (w/w)
I/C – 0.5

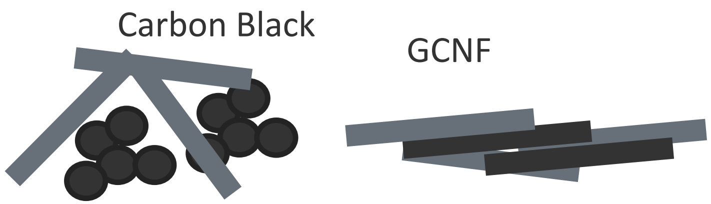
Ionomer and carbon dispersed separately from PtNi

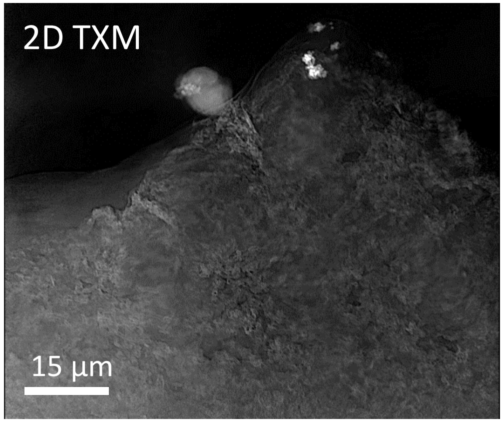
PtNi mixed with carbon/ionomer prior to coating

Accomplishments and Progress

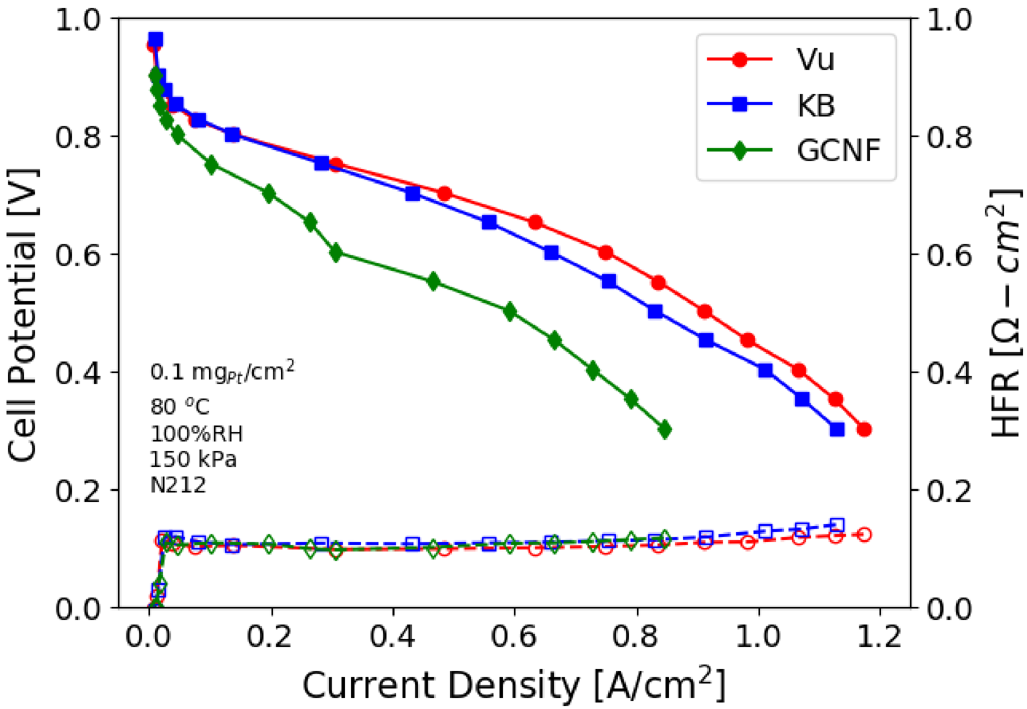
Incorporation of Carbon Blacks

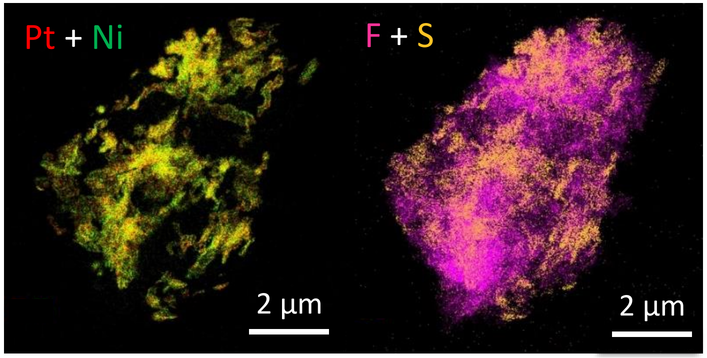
- Ketjenblack improved high-current-density performance (2018)
- Carbon types incorporated into large-batch ALD MEAs to study effect: Ketjenblack (KB), Vulcan XC72 (Vu), Graphitized Carbon Nanofibers (GCNF)
- In-situ performance suggests carbon shape may be important for electrode structure
- Evaluating **alternative fabrication process, coating Pt-Ni, C/ionomer separately**





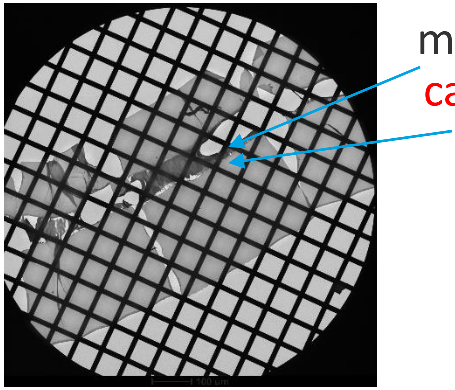
Pt-Ni ALD MEA (small scale batch). Wires appear most distributed in 2:1 ratio (best performer). Working toward 3D reconstructions.

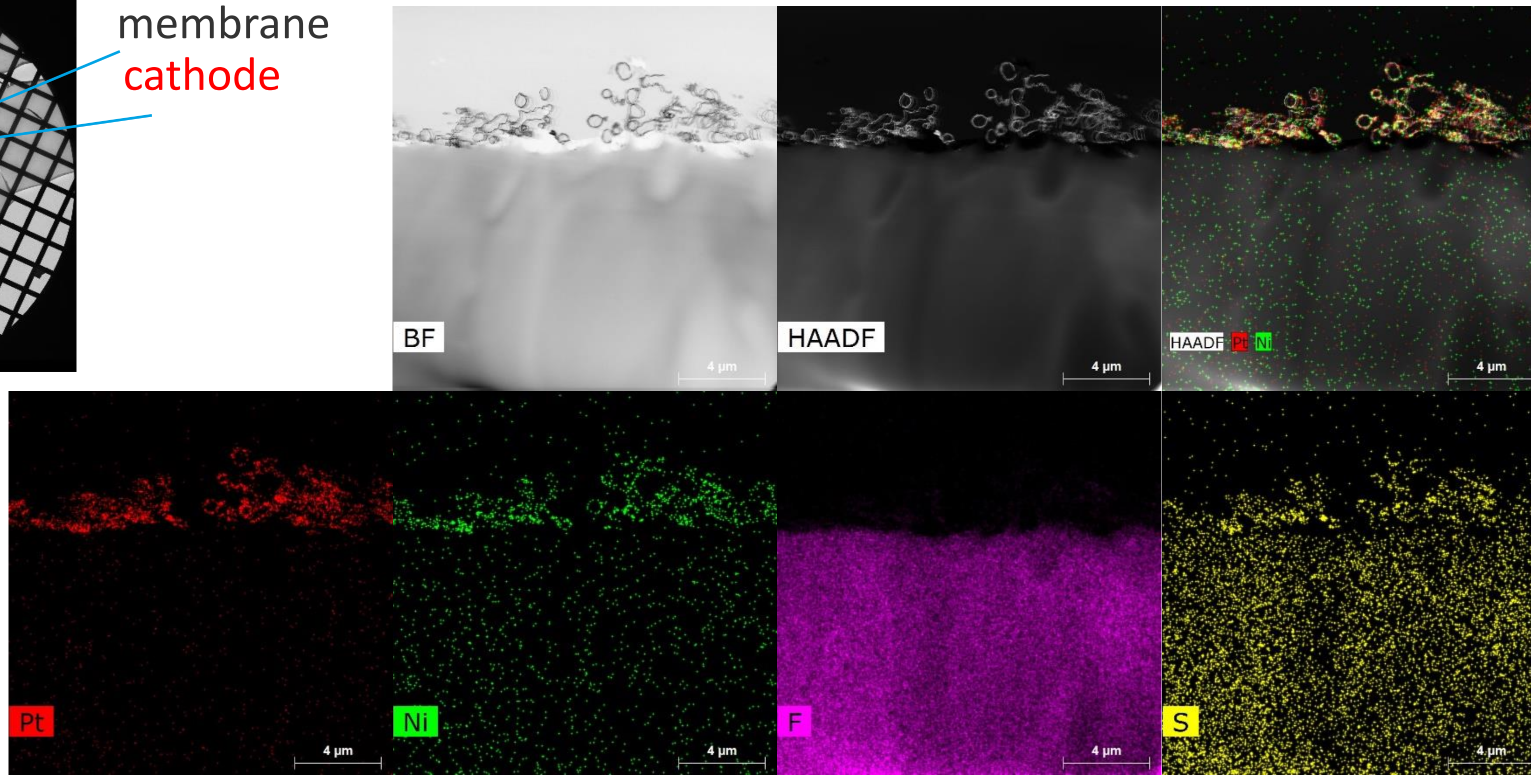




Accomplishments and Progress

Evaluation of Nickel Leaching





- Low magnification STEM images and EDS maps show small amounts of Ni in membrane
- Higher magnification of PtNi nanowires show Pt and Ni in catalyst layer

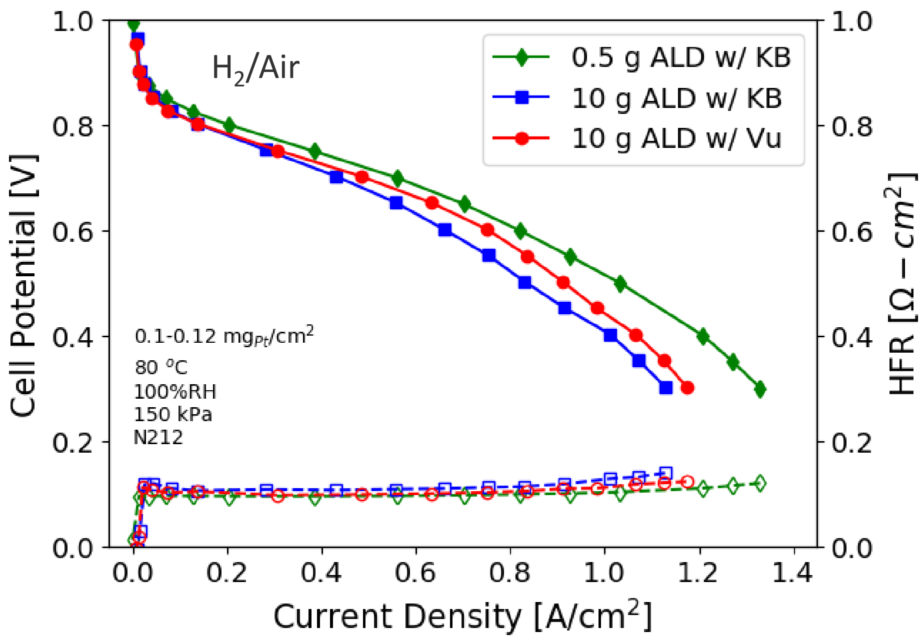
Element	[norm. wt.%]	[norm. at.%]
Fluorine	96.20	97.81
Sulfur	3.03	1.82
Potassium	0.71	0.35
Nickel	0.06	0.02

0.02 at% Ni in membrane
Trace K contaminant

Accomplishments and Progress

Large batch catalyst MEAs similar to small batch MEA

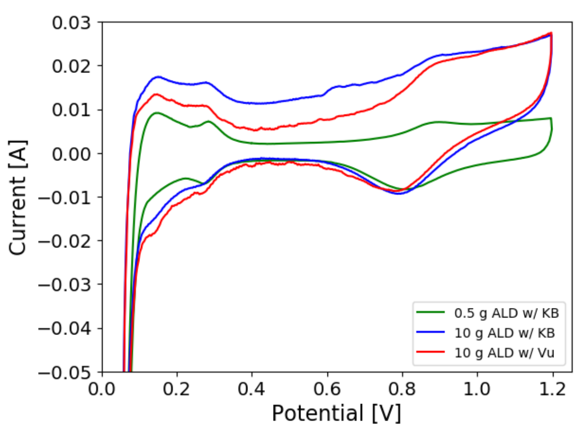
- Large-batch ALD synthesis/scalable coating MEAs result in similar performance small-batch ALD synthesis/spray-coating MEAs



Batch Size	Carbon Type	$i_m^{0.9V}$ [mA/mg$_{Pt}$]	ECSA [m^2/g$_{Pt}$]
0.5 g	Ketjen	507	22.6
10 g	Ketjen	469	30.8
10 g	Vulcan	463	35.5

PtNi:C – 2:1 (w/w)

Refinements in ALD synthesis and coating procedure likely to improve performance of scalable MEAs



Accomplishments and Progress

Responses to Previous Year (2018 AMR) Reviewer's Comments

- Reviewer Comment: One primary challenge is that it is unclear whether the ETFECS structure with the hollow core (after dealloying) will be stable against electrochemical cycling, which does not appear to have been assessed to any significant extent. Another aspect of concern is that there appears to be relatively little MEA testing with exposure to hydrogen/air with state-of-the-art components (e.g., thin polymer electrolyte membrane [PEMs]); this testing process is critical for assessing impacts of residual transition metals.
- Response: Multiple reviewers noted that durability was an issue that hadn't yet been probed in detail. We have previously demonstrated that we were able to meet the stop-start durability target and meet the project mid-point go/no-go decision. We have focused remaining project resources in obtaining higher performing MEAs prior to probing durability.

- Reviewer Comment: The team needs to come up with a verified process, such as the acid-leaching step, to make the MEA fabrication process viable. It is well known in the PEM technical community that any leftover Ni in the electrode will quickly destroy the membrane, significantly decrease cell performance, and affect durability. This project does not define a method for verifying that Ni does not and will not leach out of this catalyst.
- Response: We have focused on MEA testing of materials approximately 70 wt. % Pt or higher to improve the viability of MEA fabrication and durability. We have verified low Ni leaching rates with ICP-MS in half-cell testing and found significantly less Ni dissolution compared to unleaded materials.

- Reviewer Comment: Performance variations are very high for both types of testing, suggesting that significant additional efforts on optimization of both the catalyst and the catalyst layer will be required.
- Response: We have shifted focus to larger scale batches (10 g) for testing to mitigate variability performance variability.

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (co-PI), Shaun Alia (co-PI), KC Neyerlin, Katie Hurst, Jason Zack, Scott Mauger, Ahmad Mayyas	**Prime, Oversees the project, lead catalyst synthesis and characterization; lead electrode fabrication and fuel cell testing; techno-economic analysis**
University of Delaware (Delaware): Yushan Yan, Jarrid Wittkopf	**Sub; Support work in providing Ni nanostructures**
Colorado School of Mines (CSM): Svitlana Pylypenko, Sarah Zaccarine, Chilan Ngo, Samantha Medina	**Sub; Materials characterization using spectroscopy and microscopy**
University of Colorado-Boulder (CUB): Al Weimer, Will Medlin, Wilson McNeary	**Sub; ALD synthesis including both Pt and Ni using both oxidative and reductive chemistry**
ALD Nanosolutions (ALDN): Karen Buechler, Joe Spencer	**Sub; ALD consultation, scale up and business-case analysis**

Beam time at SLAC (Johanna Nelson Weker)
Mai-Anh Ha (UCLA) Office of Science SCSGR awardee
Shawn Litster (Carnegie Mellon)

Remaining Challenges/ Proposed Future Work

Electrocatalysts:

- ALD – Optimization of scale-up batches at 10 g batch size and beyond.
- Pt/Ni ALD co-deposition
- Post-processing optimization (annealing and acid leaching)
- Characterization and optimization (electrochemical and structural studies)

MEA Fabrication and Optimization:

- Optimization of electrode structure/performance using ALD materials.
- Isolation and minimization of overpotential losses in MEA electrodes.
- Evaluation and minimization of local oxygen transport and proton transport resistances to improve high current density performance.
- Durability studies to quantify and minimize performance losses.

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

Intellectual Property

- Nanowires have been IP protected.
- Continual development of additional IP.

Industrial Interactions:

- ALD NanoSolutions as an appropriate industrial partner for synthesis due to the importance of ALD reactions and reactors.
- Small business interactions involving NWs for related applications have included. Small Business Voucher program: Oorja; SBIR program: Giner, pH Matter – pH Matter is getting trained to synthesize NWs and has been approached about licensing options.
- Large business interactions: Includes OEMs and component suppliers.

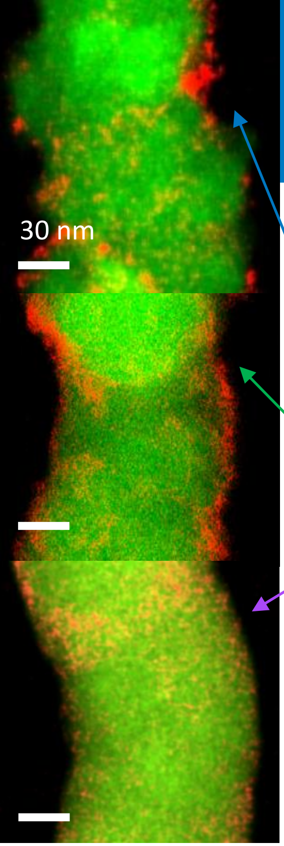
Summary

- **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 achieve high performance of ALD synthesized PtNi NWs in reasonable scale (up to 10g batches) and reproducibility. Pt/Ni co-deposition by ALD has been demonstrated. Post-treatment has allowed significant gains in performance and removed Ni leaching concerns. MEAs now demonstrate mass activity above DOE targets 440 mA/mg_{Pt} . MEA optimization has shown potential to improve high current density performance.
- **Collaborations:** We have a diverse team of researchers including 3 universities, and an industrial participant.
- **Proposed Future Research:** See previous slide.

Technical Back-Up Slides

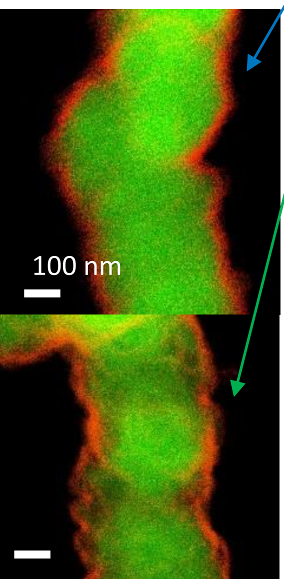
Accomplishments and Progress

ALD compared to SGD (Pt on Ni NWs)

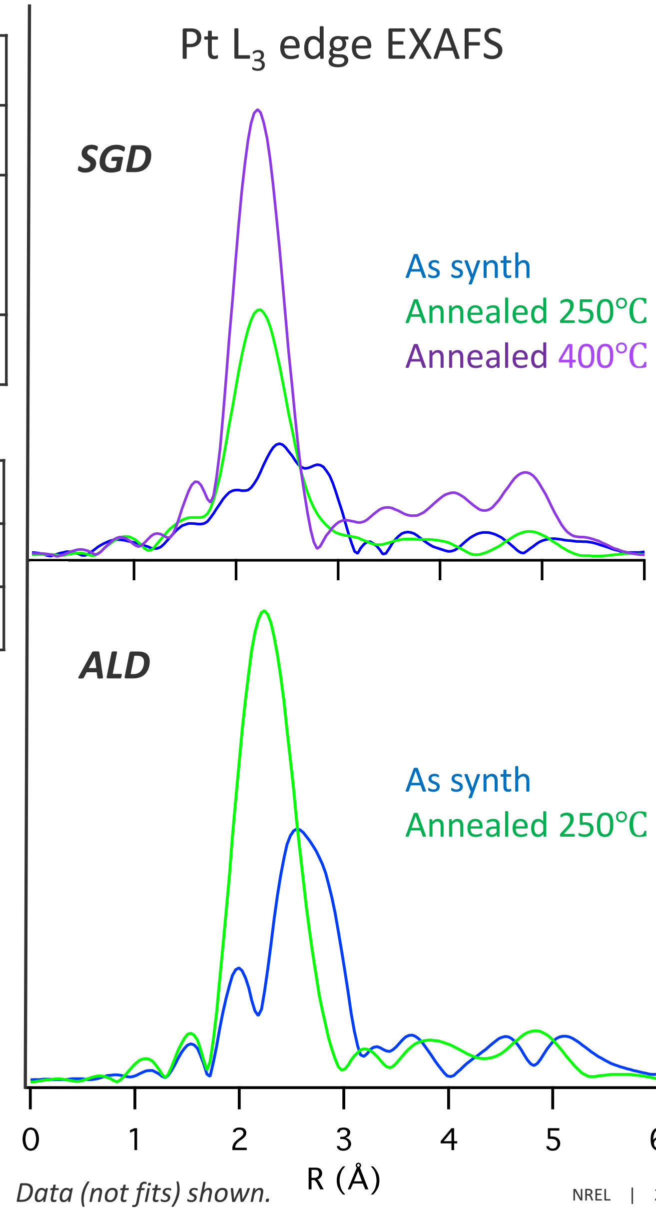


SGD	*Bond*	*N*	*R(Å)*	*σ^2x10^3*	*R-Factor*
As synth	Pt-Pt	12	2.74	7.97	0.016
H_2 250°C	Pt-Pt	5.7	2.69	7.2	0.001
	Pt-Ni	5.7	2.56	5.4	0.001
H_2 400°C	Pt-Ni	10.4	2.55	4.7	0.005

ALD	*Bond*	*N*	*R(Å)*	*σ^2x10^3*	*R-Factor*
As synth	Pt-Pt	11.2	2.74	6.5	0.011
H_2 250°C	Pt-Ni	10.5	2.57	6.8	0.008



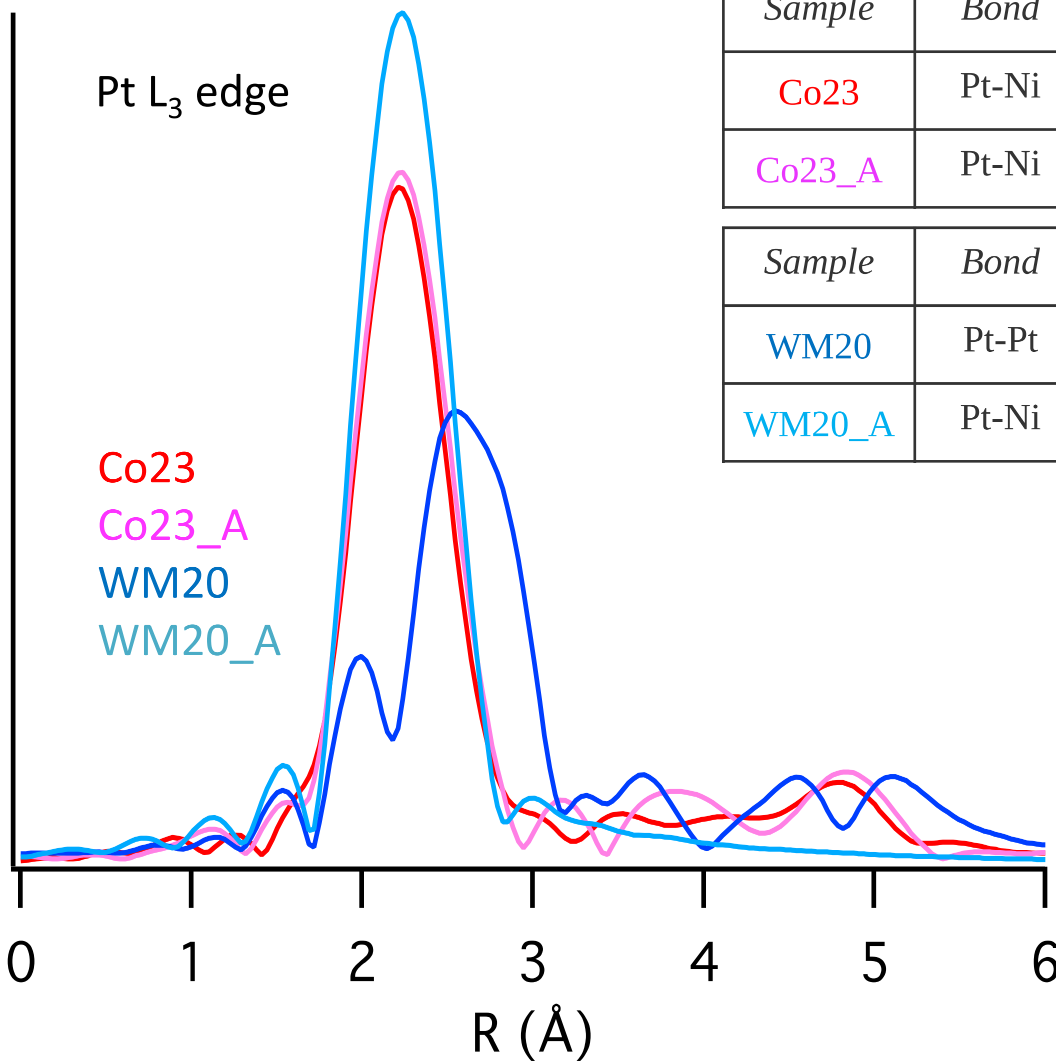
- SGD samples require higher annealing temp (400°C) to form full PtNi alloy.
- ALD wires are easier to alloy (lower T).
  - Visible in homogeneous coating on wire.



Data (not fits) shown.

Accomplishments and Progress

Platinum nickel Alloying with Cobalt Template



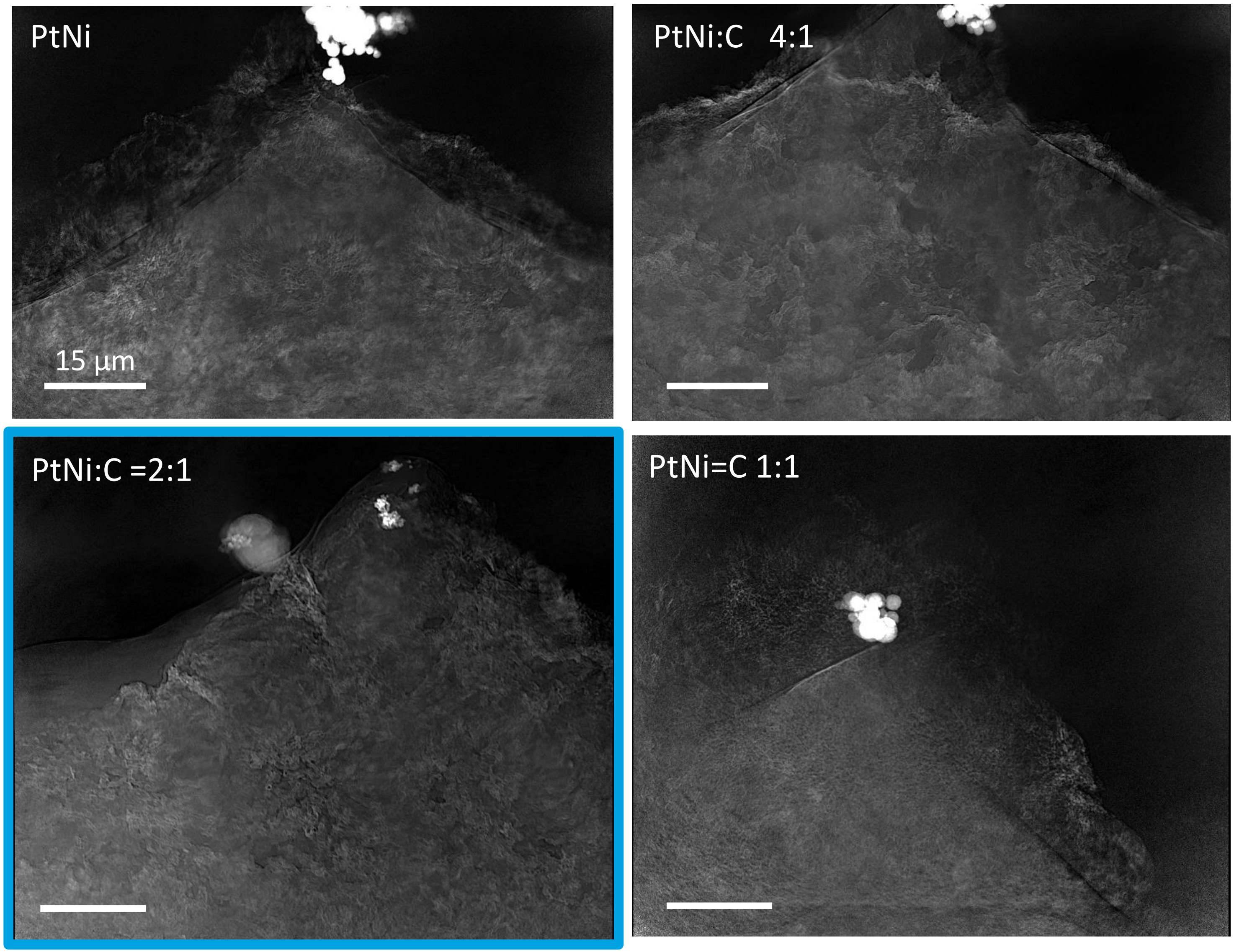
Sample	Bond	N	R(Å)	$\sigma^2 x10^3$	R-Factor
Co23	Pt-Ni	11.08	2.57	9.4	0.021
Co23_A	Pt-Ni	11.06	2.57	8.8	0.011

Sample	Bond	N	R(Å)	$\sigma^2 x10^3$	R-Factor
WM20	Pt-Pt	11.2	2.74	6.5	0.011
WM20_A	Pt-Ni	10.45	2.57	6.8	0.008

- Co23 as prepared sample already shows full PtNi alloy, due to annealing step during ALD synthesis.
- Both annealed samples show full PtNi alloy.
- Co23 shows similar PtNi CN in as prepared sample, higher CN for annealed sample.

Accomplishments and Progress

Incorporated Carbon to Improve Mass Transport   Constant I:C



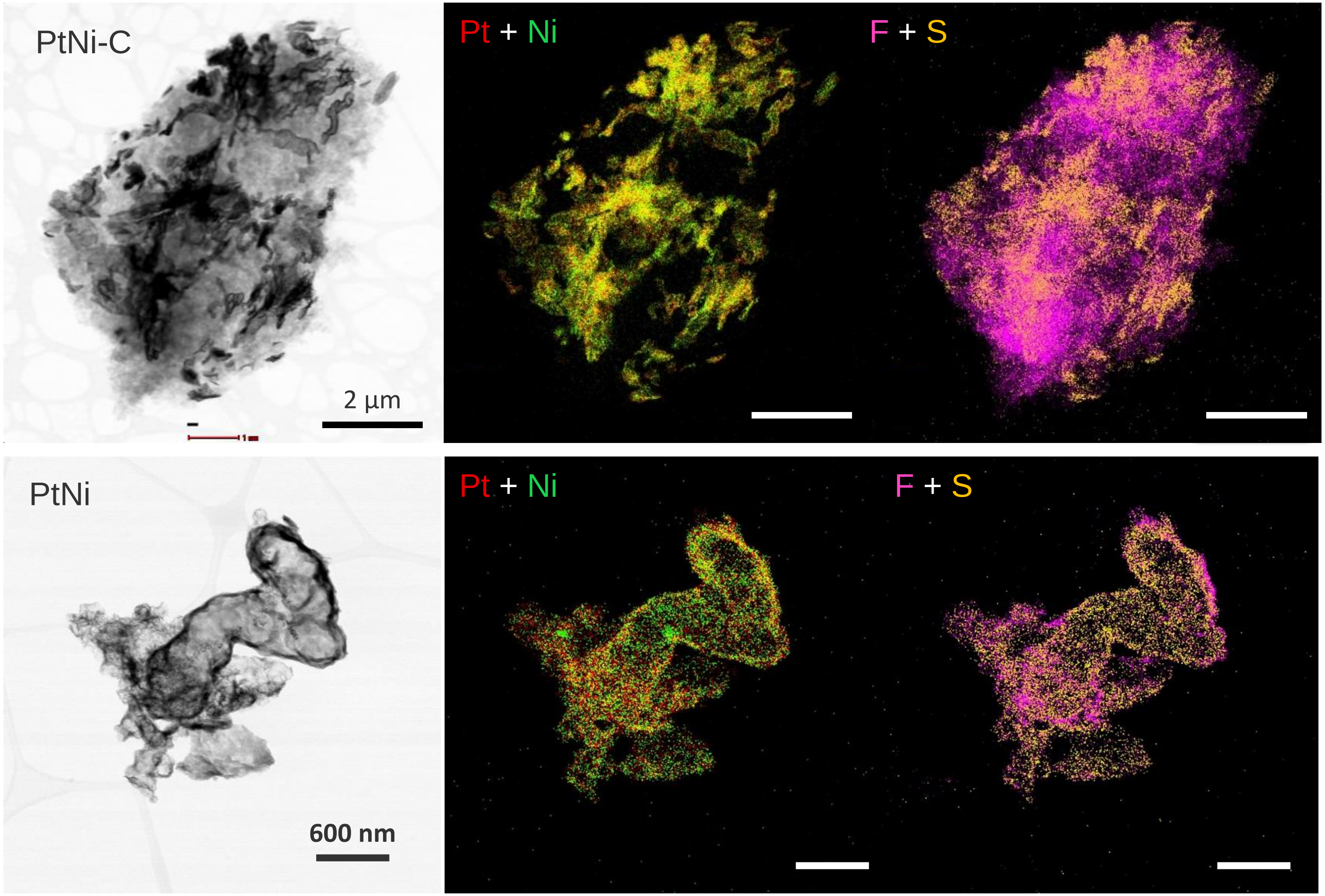
2D TXM data:

- Energy: 8355 eV (right above Ni K edge, both Pt and Ni absorb here).
- As expected, less dense amounts of wires as ratio goes down.
- Wires look most distributed in 2:1 ratio; and this was the best performer.

This work is progressing towards 3D reconstructions.

Accomplishments and Progress

Platinum Nickel and Nafion interactions

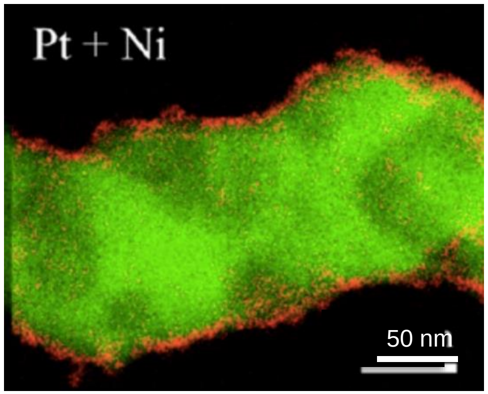


- Consistent observations of correlation between metal (Pt and Ni) maps with S map.
- Correlations between S and Ni are stronger than for Pt.
- Need alternative electrode fabrication process: PtNi NWs, C+ionomer deposited separately.

Accomplishments and Progress

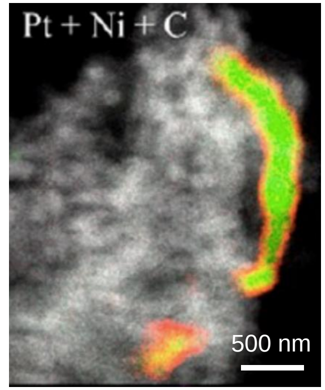
Acid leaching studies: electrodes

Wires (0.1M HNO_3 leached)



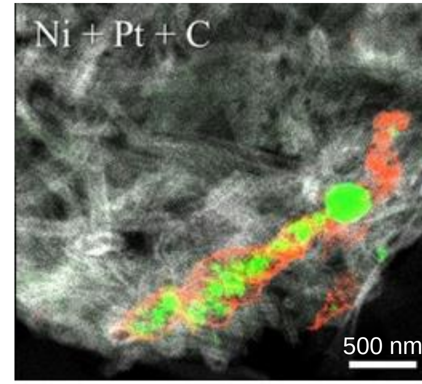
	N	*R(Å)*
Pt-Pt	6.4	2.72
Pt-Ni	3.7	2.58

Unleached electrode



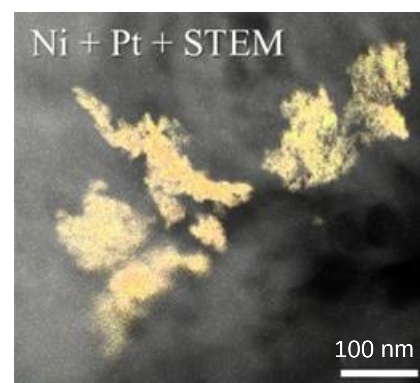
	N	*R(Å)*
Pt-Pt	6.4	2.72
Pt-Ni	3.7	2.58

1M H_2SO_4 at 25 ℃



	N	*R(Å)*
Pt-Pt	6.8	2.71
Pt-Ni	3.2	2.60

1M H_2SO_4 at 80 ℃



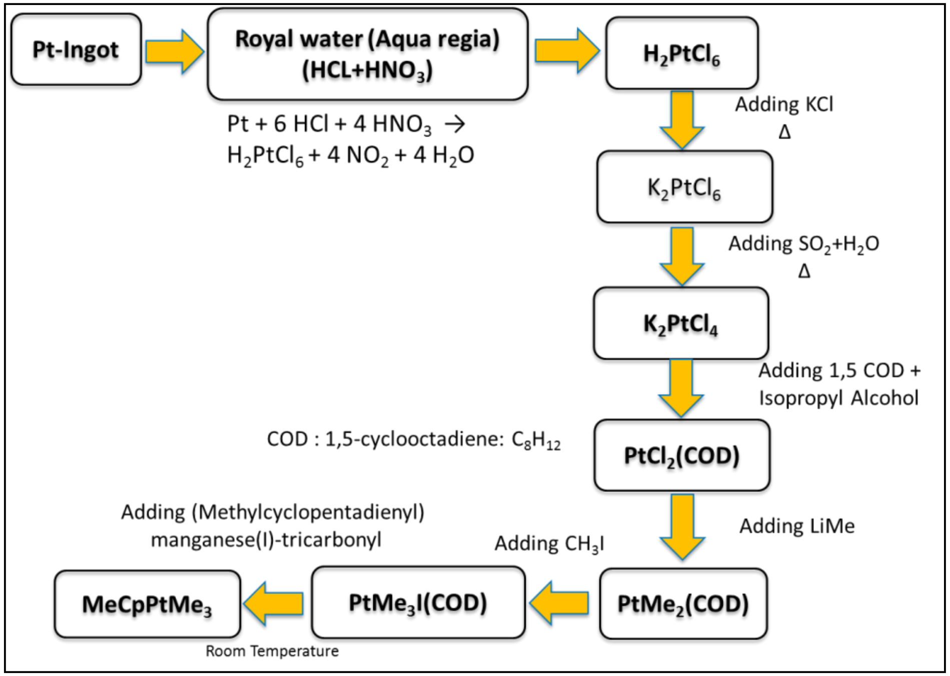
	N	*R(Å)*
Pt-Pt	7.5	2.70
Pt-Ni	2.2	2.60

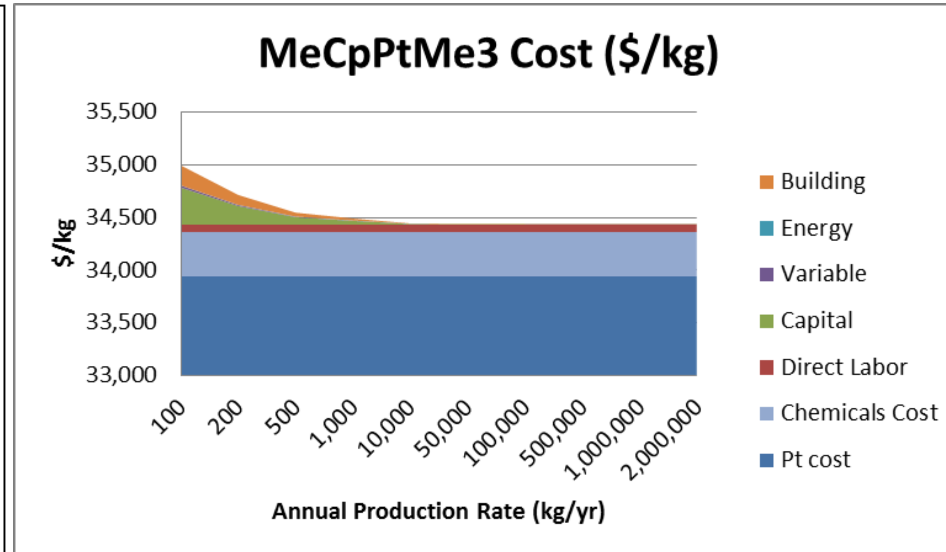
- Acid leaching preferentially removes bulk Ni
- But alloyed Ni is also removed
- Motivates further studies of acid leaching

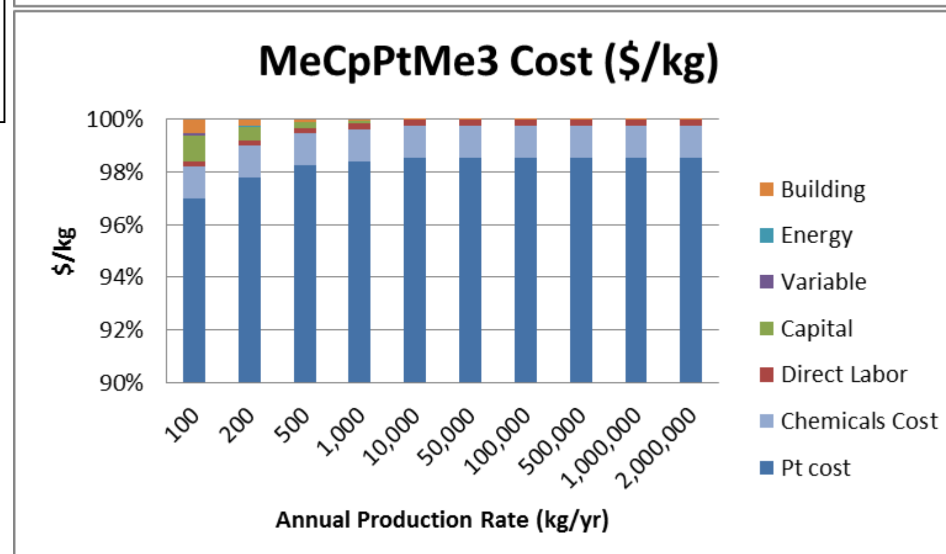
Note: these are SGD samples.

Accomplishments and Progress

Preliminary Techno economic Analysis MeCpPtMe3 Precursor







Although $MeCpPtMe_3$ Precursor is currently high cost (~4x Pt), at even modest production volume (100's of kg/yr), we project cost to only be a few % higher than Pt cost.

Accomplishments and Progress

Preliminary Techno economic Analysis ALD Reactors/Processing

Estimated Production Costs: Rotary Blender Reactor (ALDN)

Production Rate	1	10	100	Tons/yr
Reactor Size	2	9	20	ft^3
Required $MeCpMe_3Pt$	1750	17500	175000	Kg/yr
Required H_2	44	441	4410	Kg/yr
Production Cost (excluding $MeCpMe_3Pt$)	665	623	618	$/kg Product

ALD reactor costs and post-processing costs (annealing and acid leaching) are projected to be low as well. Pt would be used very efficiently and recycled in this operation at scale.

Resulting catalyst processing cost would be >10% than the cost of Pt.