NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Extended Surface Electrocatalyst Development

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National Renewable Energy Laboratory
June xx, 2018

DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

Project ID #FC142

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

Overview

Timeline and Budget

- Project start: December 2015
- Project end: March 2019
- % complete: ~ 70%

- 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)

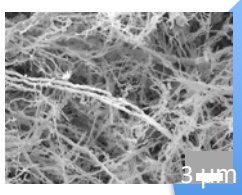
[c] Durability measured in a 25-50 cm^2 MEA during triangle sweep cycles at 50 mV/s between 0.6 V and 1.0 V at 80°C, atmospheric pressure, 100% relative humidity, H_2 at 200 sccm and N_2 at 75 sccm for a 50 cm^2 cell. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and 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).

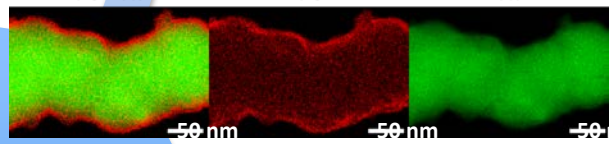
Approach

Catalyst and Membrane Electrode Assembly Development



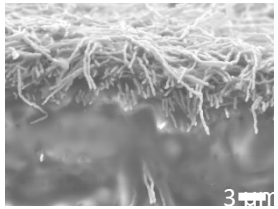
Ni Nanowires
Commercial

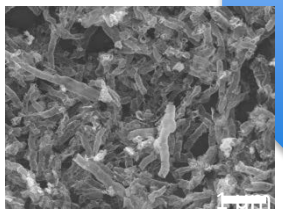
Atomic Layer Deposition (ALD)
CU: initial studies/novel chemistry;
ALD Nanosolutions: scale up



Catalyst Post-Processing
NREL: annealing, leaching

MEA Fabrication/ Optimization
NREL: composition, processing





Fuel Cell Diagnostics
NREL: performance, durability, transport

Characterization
NREL: electrochemical
CSM: microscopic

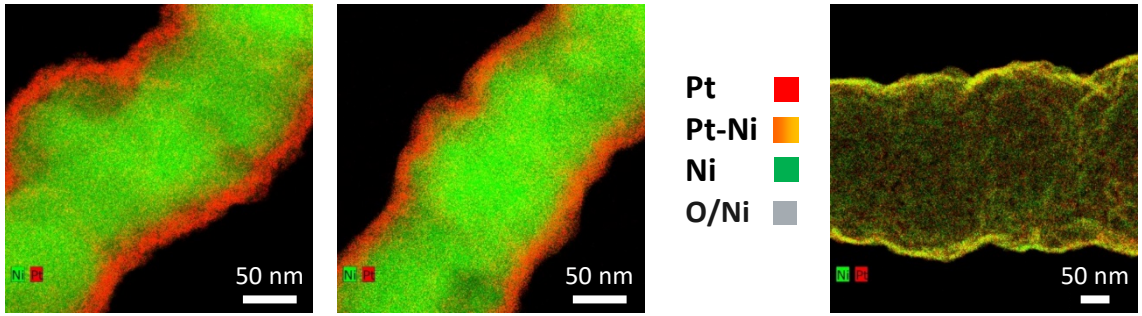
Approach

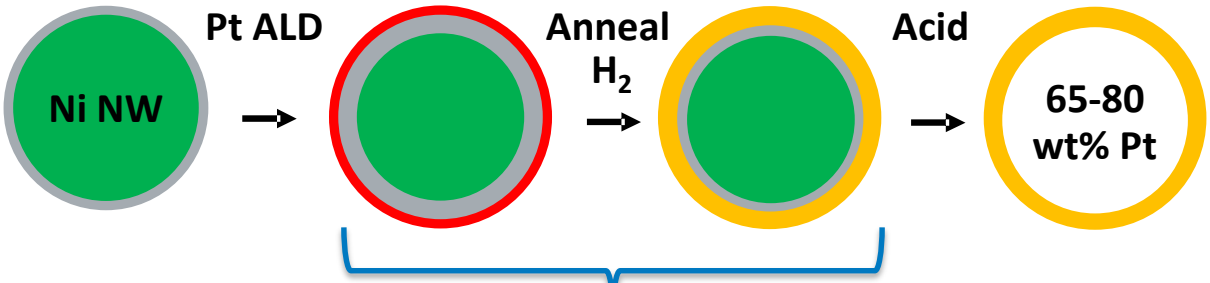
Project Schedule/Milestones

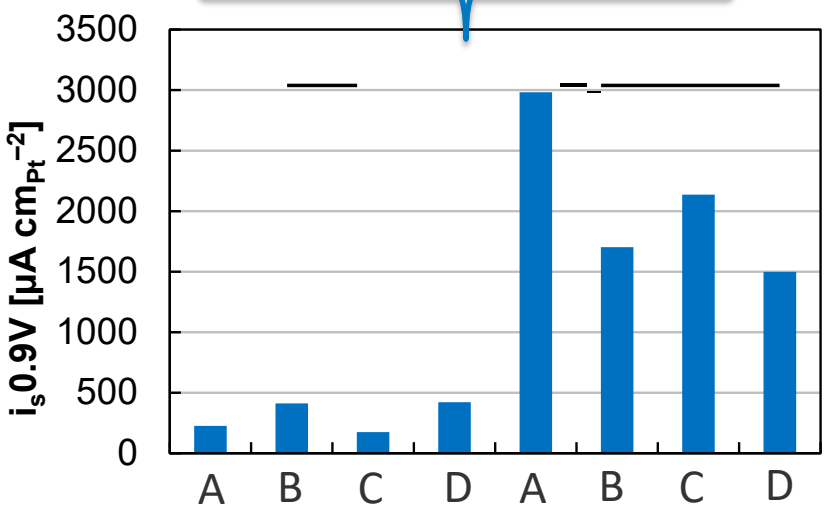
Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Type	Status
Q4	9/30/2017	Go/no go	Demonstrate a mass activity of >440 mA/mgPt at 0.9V (DOE 2020 Target) in fuel cell tests while also meeting at least one of FCTO's MEA durability targets.	Annual Milestone	Met
Q1	12/31/2017	Regular	Demonstrate ALD batch synthesis at >10g per batch scale.	Quarterly Progress Measure	Met
Q2	3/31/2018	Regular	Synthesis of >5g of ALD deposited PtNWs of acceptable quality (>500 mA/mg Pt) for MEA testing.	Quarterly Progress Measure	Met
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	On track
Q4	9/30/2018	Regular	In alignment with the DOE 2020 target for rated power (1,000 mW/cm2), demonstrate 600 mW/cm2 at rated power (cathode 3x improvement for electrodes based on PtNiNWs.	Annual Milestone	TBD

Approach

ALD Synthesis of High Activity PtNiNWs (2017 AMR Results)



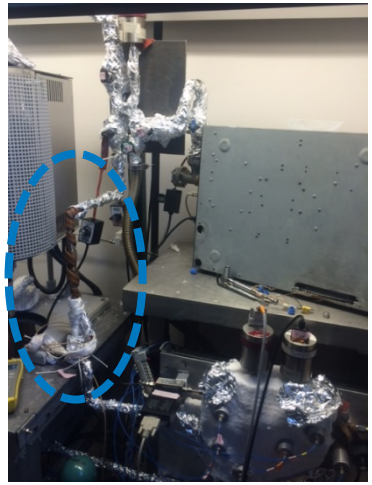




- H_2 annealing key to increasing alloying/specific activity.
- Reasonably high surface areas obtained (40+ m^2/g)
- Acid leaching removes excess Ni (poisoning concern)

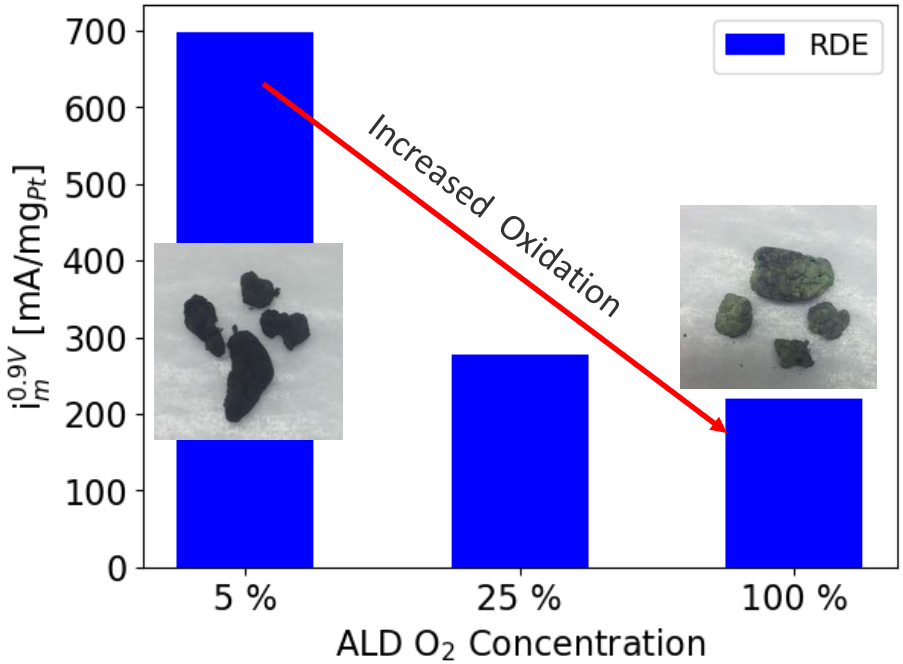
Accomplishments and Progress

ALD (CU) – Optimization of reaction conditions and supply of materials

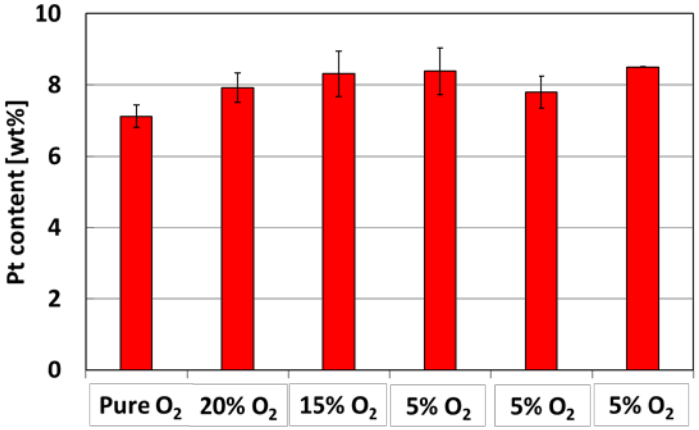


Packed bed reactor

Acid Leached Catalyst Performance



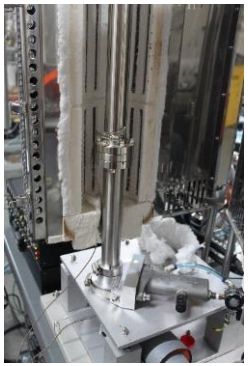
- Packed bed reactor used to develop O_2 Pt ALD chemistry at 0.5 and 2 g batch sizes.
- O_2 concentration found to be key parameter for improved properties.
- Multiple batches supplied for MEA testing (>5 g total of PtNiNWs, Q2 quarterly progress measure, see back up slide), with reasonable consistency.



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

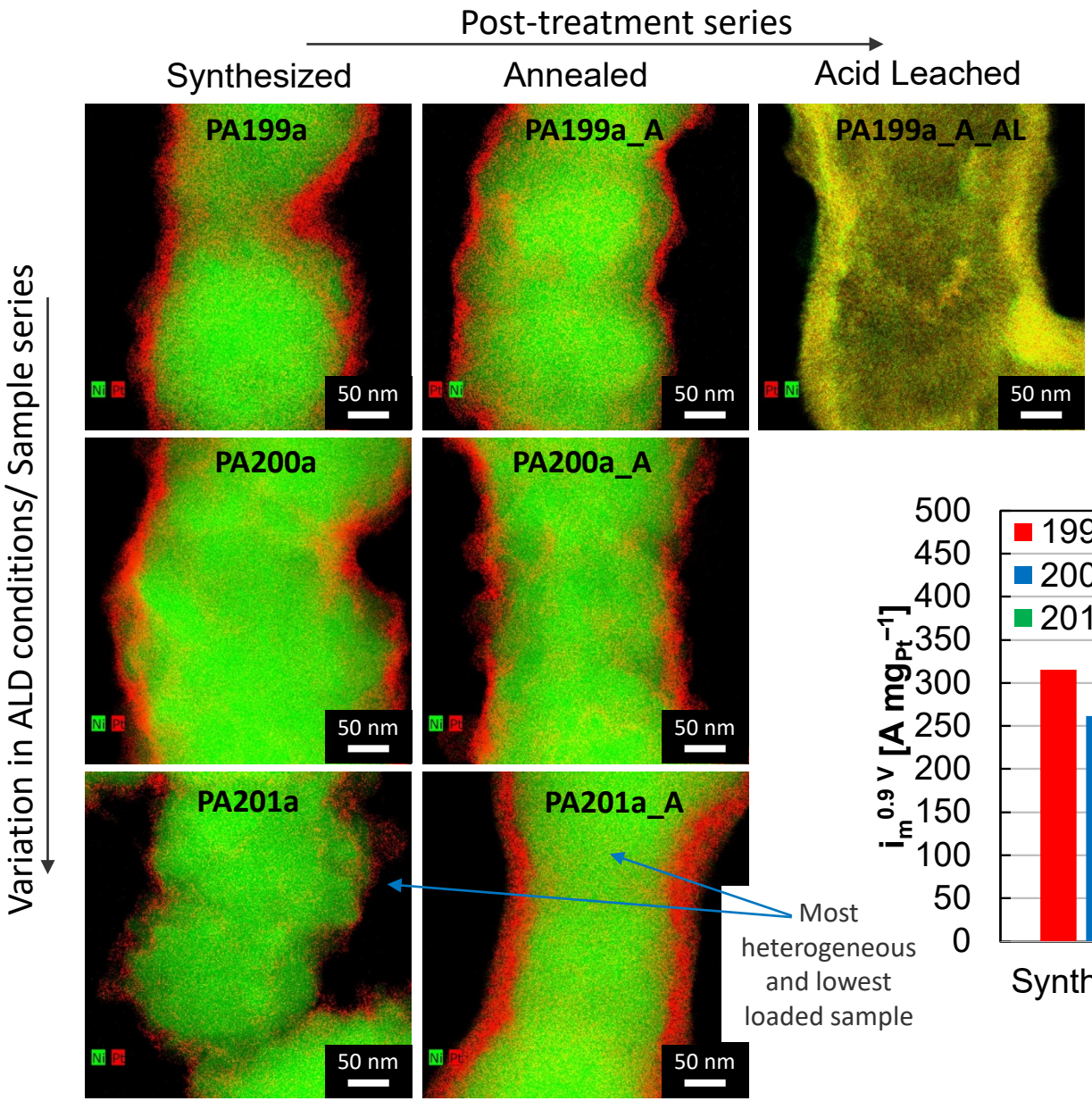
1-50 kg
Pilot Rotary Blender

g Pt Precursor	ICP Pt (Wt%)	Theoretical Pt (wt%)
3.1	8.76	11
2.2	8.11	8.2
1.2	6.03	4.5

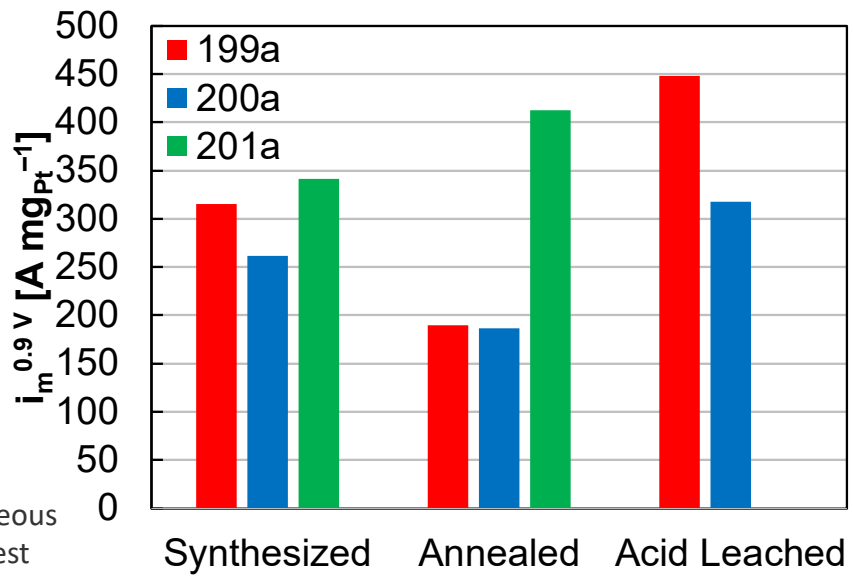
- ALD NanoSolutions has multiple reactors and scales from 5g batch to 3 mt/day continuous.
- Research Fluidized Bed Reactor was used to synthesize 15g catalyst batches (Q1, QPM).
- Target Pt loadings (7-10 wt%) were obtained in initial synthesis runs.
- Initial evaluation of chemistry efficiency is highly promising for full scale production.

Accomplishments and Progress

Characterization of large scale batches



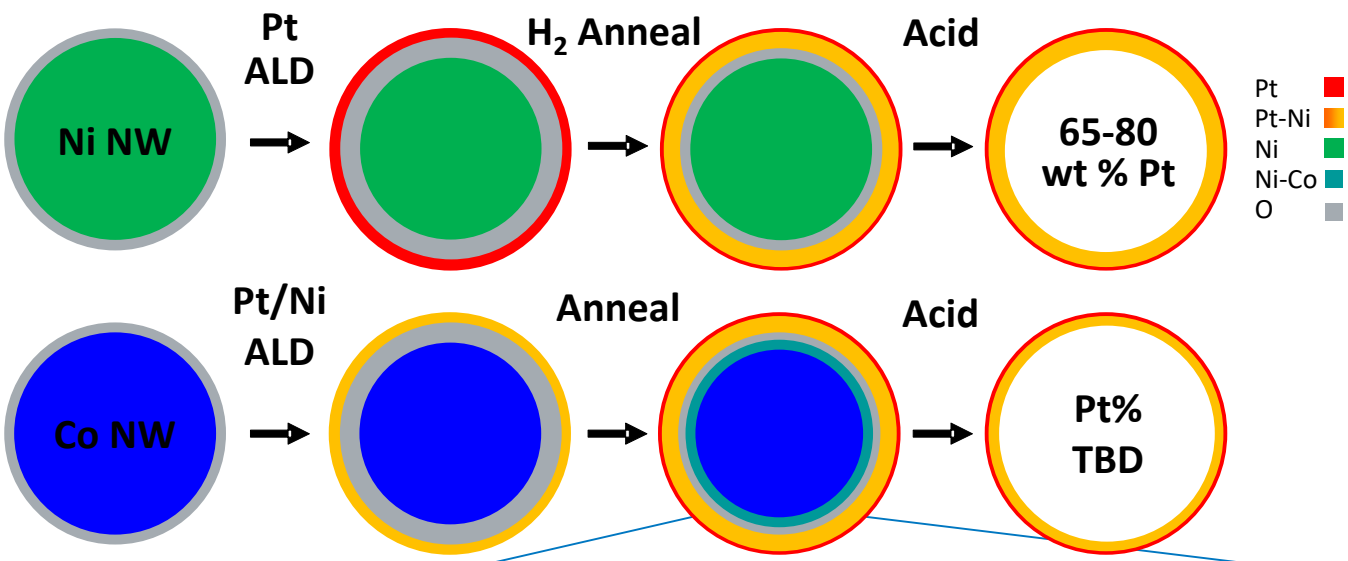
- Microscopy consistent with other approaches.
- Electrochemical (RDE) properties reasonable for first attempts.
- Further optimization efforts underway.



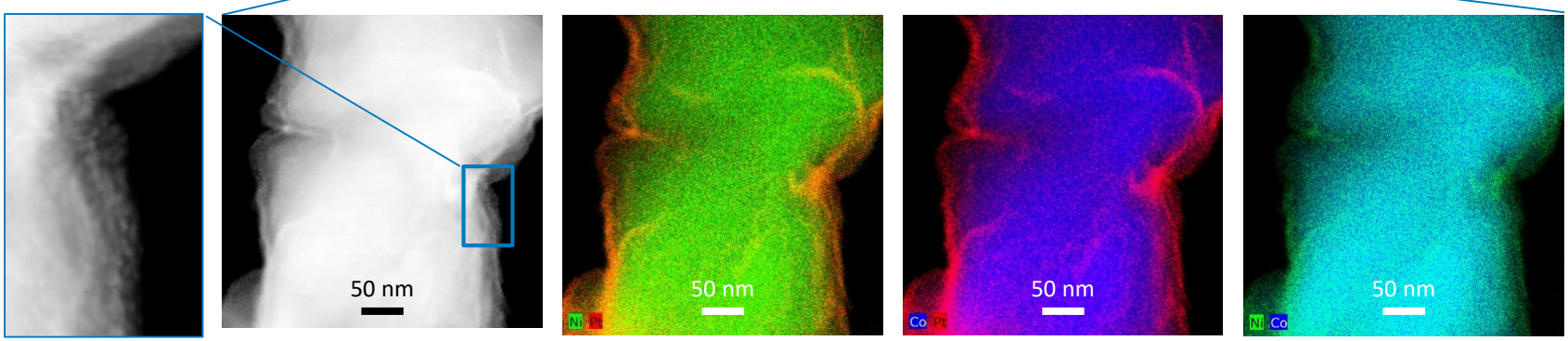
Accomplishments and Progress

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

- 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).



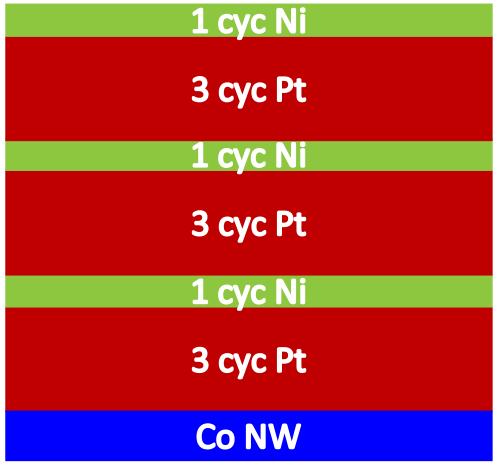
- Co-deposition of Pt and Ni by ALD potentially allows independent control over Ni content and more homogeneous composition.
- Co NWs employed to allow independent compositional analysis of Ni and Pt.



Accomplishments and Progress

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

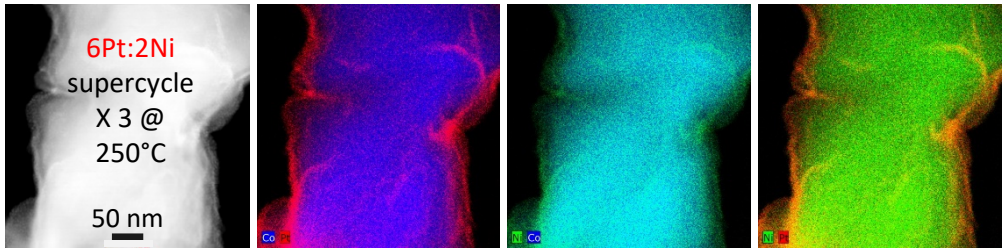
- Pt and Ni deposited by ALD w/ 5%O_2



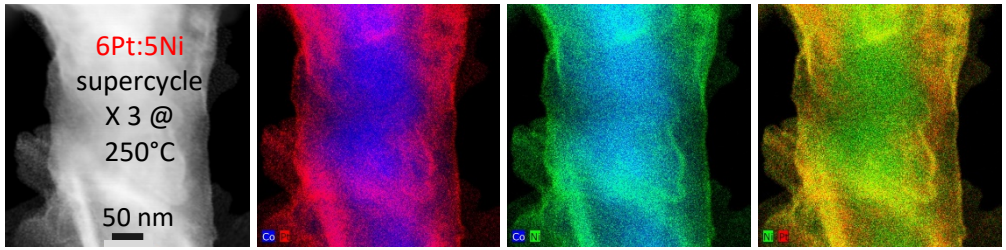
ICP	Co #6	Co #7	Co #8	Co #9	Co #10
T	295°C	250°C	210°C	250°C	250°C
Pt wt. %	10.4	4.5	3.8	10.3	14.9
Ni wt. %	2.7	0.68	0.83	1.3	4.2
Pt at. %	3.4	1.4	1.2	3.4	5.0
Ni at. %	3	0.72	0.87	1.4	4.8
Pt/Ni	1.1	2	1.4	2.4	

- Varied number of cycles of Pt/Ni deposition and reaction temperature
- Pt found to have slightly higher deposition rate than Ni
- Different Pt/Ni deposition extents and ratios obtained
- Microscopy reveals surface shell of Pt/Ni
- Electrochemical characterization underway.

Co #9



Co #10

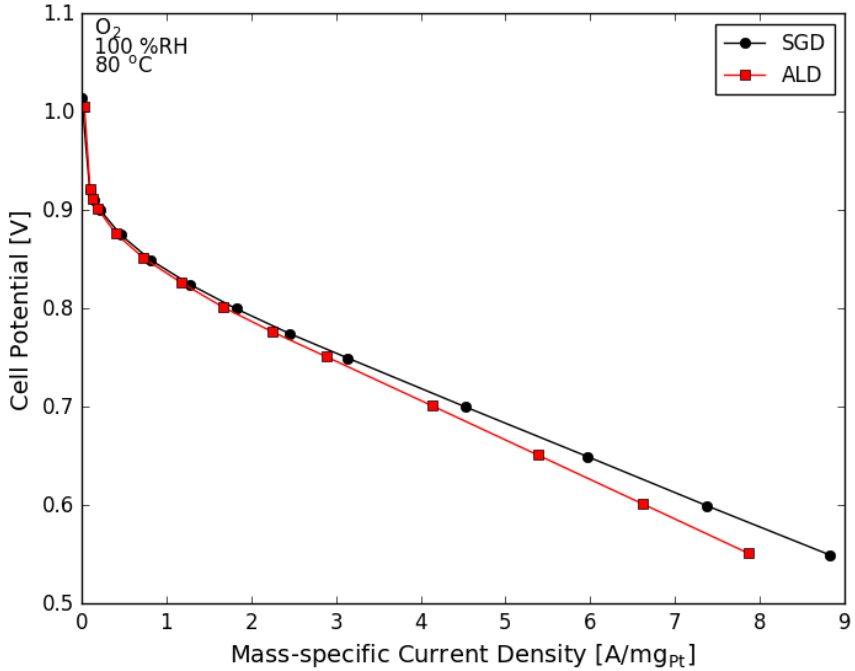


Accomplishments and Progress

PtNiNW Fuel Cell Performance (2017 AMR Status)

		ECA (m^2/g)	$i_m^{0.9V}$ (mA/mg_{Pt})	$i_s^{0.9V}$ ($\mu A/cm^2_{Pt}$)
SGD	RDE	21	518	2502
	MEA	22	**238**	1151
ALD	RDE	11	219	1936
	MEA	9.8	**228**	2320

Both materials were pre-leached to 80 wt% Pt

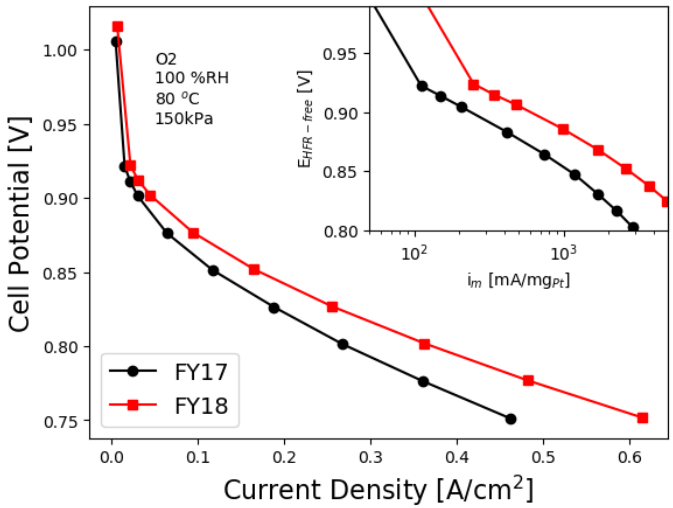


- MEAs showed reasonable performance for mass activity, but fell short of DOE target.
- ECA measurements between MEA and RDE were consistent.
- 2017 AMR ALD samples were limited to low ECA.

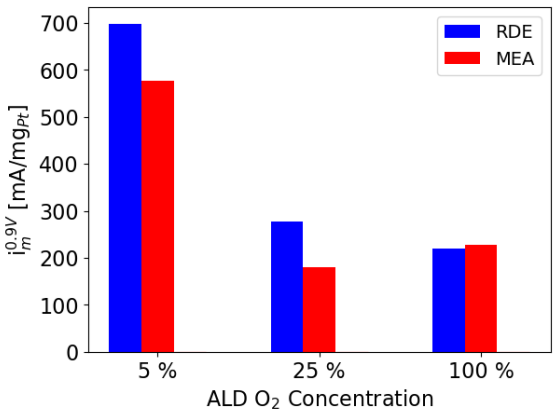
Accomplishments and Progress

Project mid-point go/no-go milestone

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



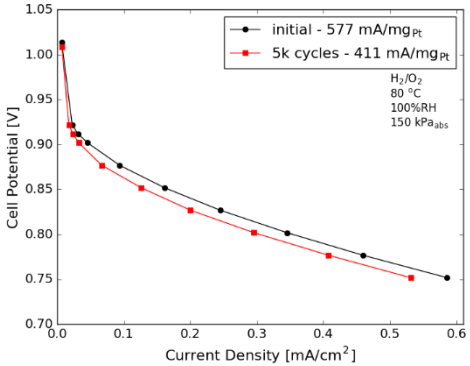
- Mass activity improvement from 2017 AMR, now meets DOE mass activity target.
- Activity trend with ALD O_2 concentration consistent between RDE and MEA.



<u>Durability Testing</u>

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

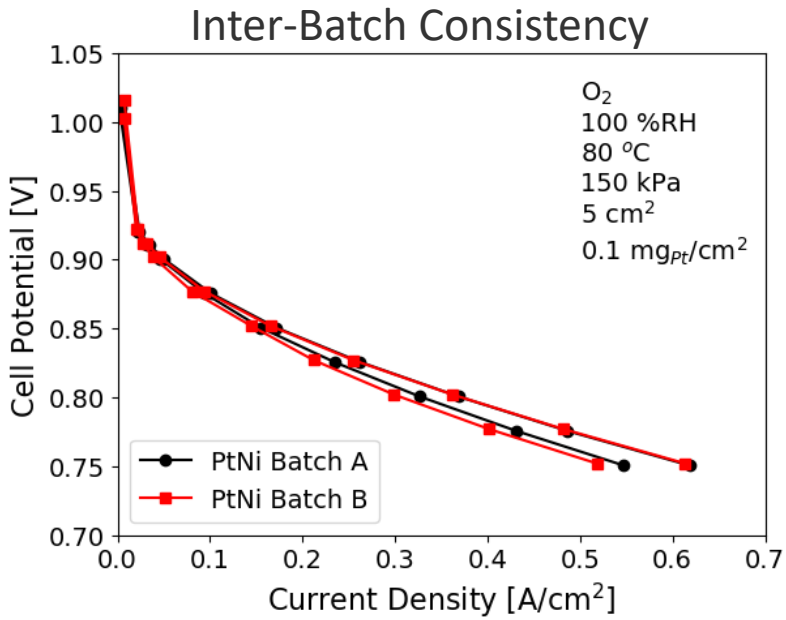
$i_m^{0.9V}$ > 440 mA/mg ✓

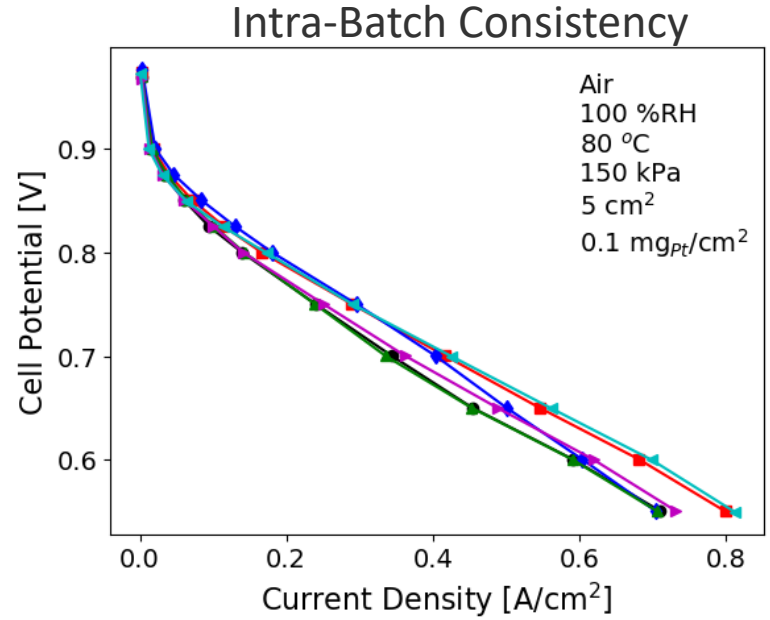
DOE Durability Target ✓

*following voltage recovery

Accomplishments and Progress

intra- and inter-batch PtNiNW consistency in MEAs



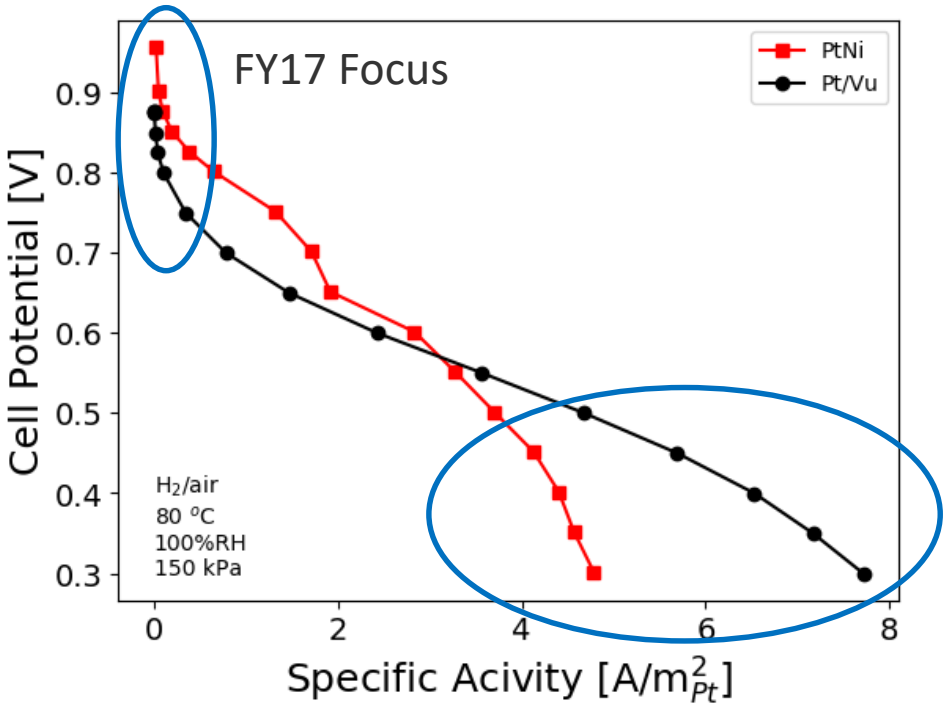


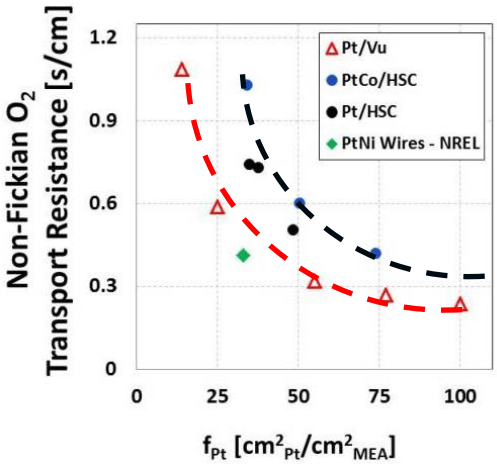
- MEAs have been demonstrated from multiple synthesis batches with similar cell performance
- MEAs from a single batch have also shown reasonable consistency
- We have met mass activity target repeatedly
- Higher ECAs from ALD materials in fuel cell tests than 2017 AMR

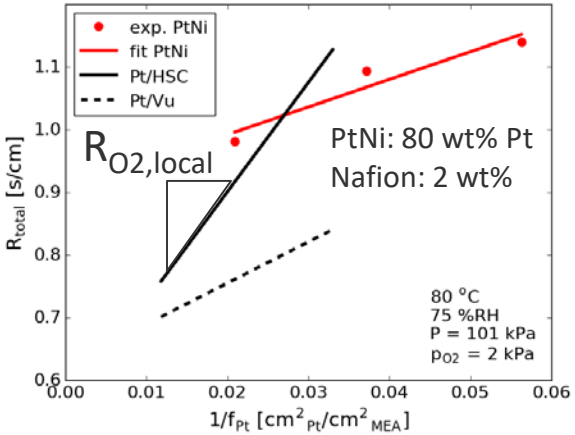
Loading (mg/cm^2)	ECA (m^2/g)	$i_m^{0.9V}$ (mA/cm2)
0.105		489
0.131	22.7	440
0.150		431
0.108		509
0.107	19.6	428
0.111	18.1	393
	Average	**448**

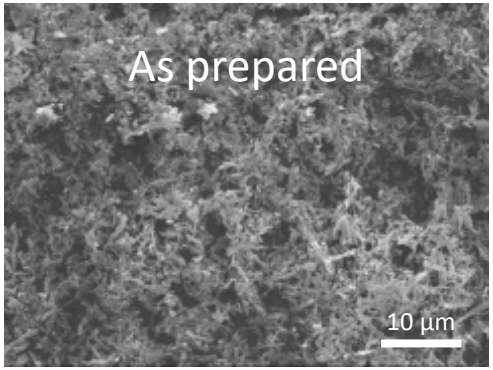
Accomplishments and Progress

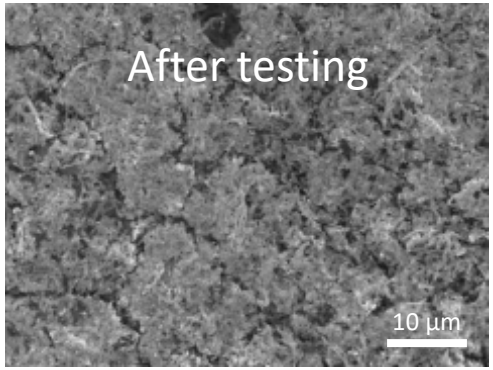
Moving beyond mass activity to address rated power











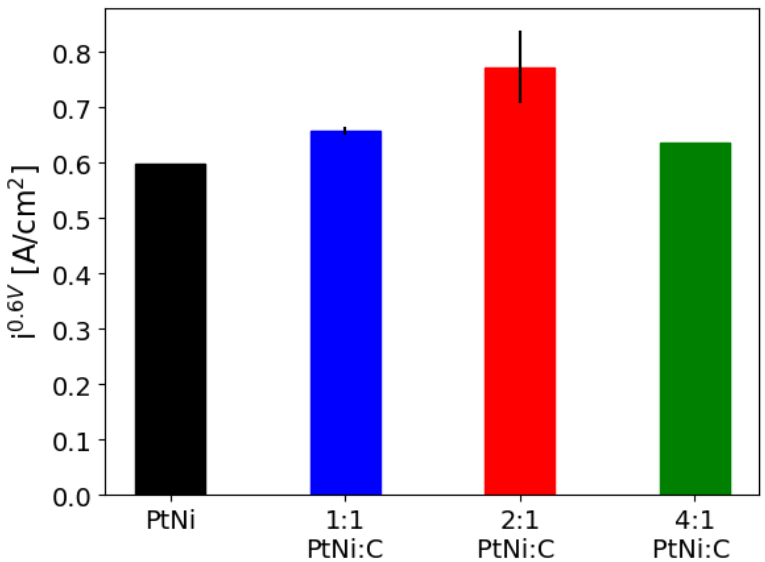
- Mass activity success
- Limited high current performance
- Local mass transport not limiting
- Electrode structure may be limiting

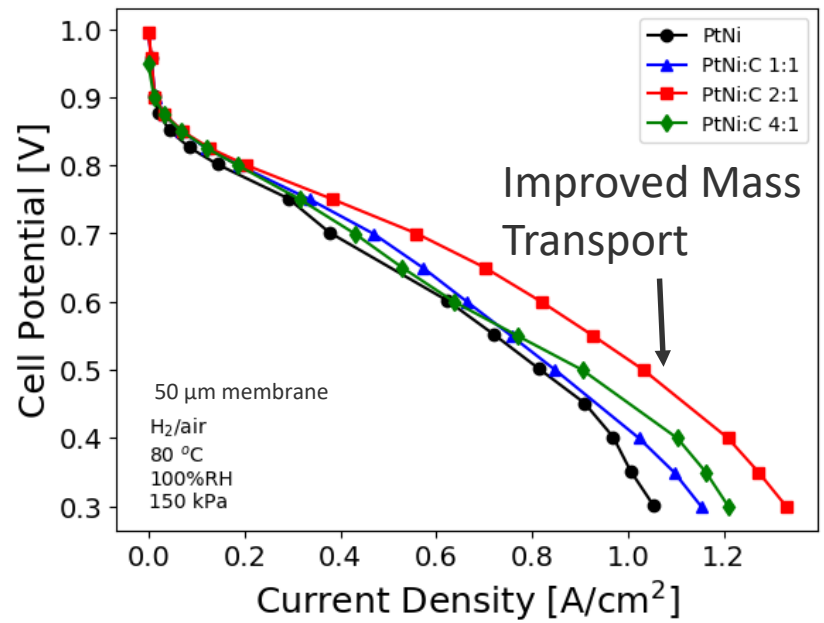
Accomplishments and Progress

Incorporating carbon to address mass transport concerns

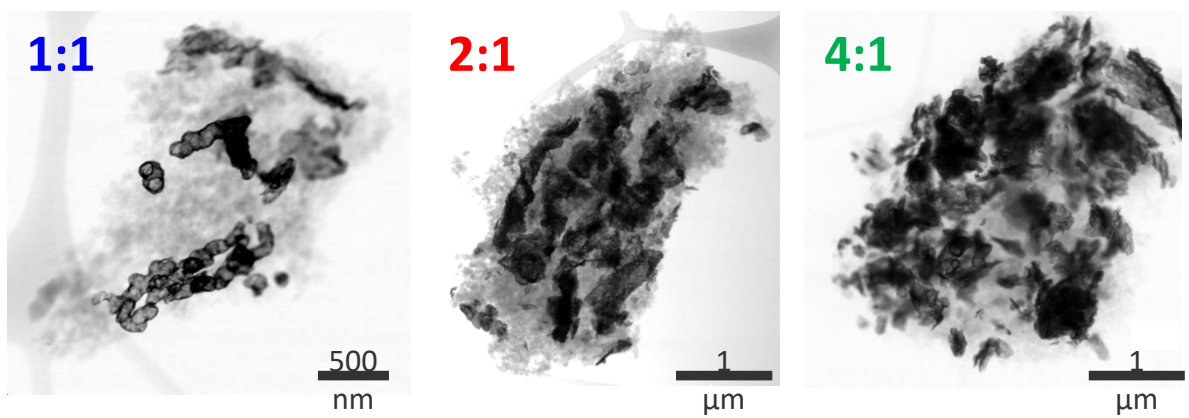
PtNi to Carbon (Ketjenblack) ratio varied

Ionomer to Carbon ratio fixed at 0.9





- Mass activity/kinetic region relatively unchanged
- Improved high current density performance with 2:1 PtNi:C incorporation
- Microscopy has been used to study catalyst layer morphology and ionomer



Accomplishments and Progress

Responses to Previous Year (2017 AMR) Reviewer's Comments

- Reviewer Comment: 1) However, the performance of the extended catalysts is still significantly lower than the target, and significant effort will be needed to bring the performance up. 2) it is questionable whether the project team will achieve its go/no-go decision metric of 440 mA/mg at 0.9 V by 9/30/2017, 3) the pathway to higher mass activity is still unclear; 4) The mass activity target is yet to be achieved.
- Response: Multiple reviewers have noted that achieving the mass activity targets had not been achieved and that this was a significant barrier. We have been able to meet the MEA targets in multiple tests. We continue trying to further improve performance through increased catalyst performance and have also moved into durability and high current density performance.

- Reviewer Comment: 1) The following are weaknesses: durability is still a question, 2) Long-term durability of the catalyst must also be addressed. 3) Durability and stability of acid leaching to remove Ni core nanowire to make hollow tubes is still in question
- Response: A few reviewers noted that durability was an issue that hadn't yet been probed in detail. We present durability data in this presentation, including demonstrating that we were able to meet the stop-start durability target and meet the project mid-point go/no-go decision.

- Reviewer Comment: The team needs to come up with an effective post-processing step, especially the acid-leaching step to make the MEA fabrication process viable. Any leftover of Ni in the electrode will diminish the cell performance and affect its durability.
- Response: Our focus has become MEA testing of materials approximately 70 wt. % Pt or higher to improve the viability of MEA fabrication and durability. The project focus is centered around MEA testing and durability, and supplying materials to that effort.

- Reviewer Comment: The team also needs to ensure a supply of nanotemplates with consistent quality for this project. Any variability in nanotemplate quality may slow down the progress of the project.
- Response: We have worked with our supplier determine optimal templates. We have placed orders at large batch sizes (up to 200 g).

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 Shulda, Chilan Ngo	**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.
- 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 Backup Slides

Accomplishments and Progress

Repeated Production of High Activity Samples (Annealed, RDE)

Mass by Batch	Specific Activity	Mass Activity	ECA (m2/g)
0.5	1703	697	41
0.5	2410	685	29
0.5	2019	1029	51
0.5	1956	892	46
0.5	723	845	118
2.0	2828	607	21
0.5	3087	780	25
5.5 (total)	2104 (ave)	791 (ave)	47 (ave)

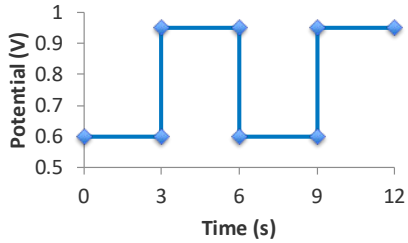
2018, Q2, QPM: Synthesis of >5g of ALD deposited PtNWs of acceptable quality (>500 mA/mg Pt) for MEA testing.

Predominantly from 100 g NiNW precursor batch

Accomplishments and Progress

Electrocatalyst Durability Testing

Square wave cycle with steps between 0.6 V (3 s) and 0.95 V (3 s)

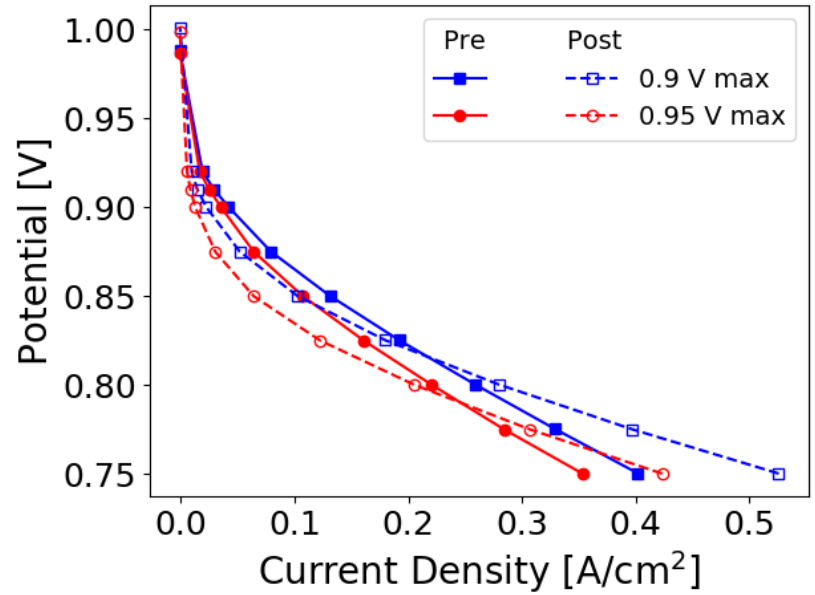


Metric	Target
ECSA	< 30% loss of initial area
$i_m^{0.9V}$	< 40% loss of initial catalytic activity

Max Potential		ECSA (m^2/g)	$i_m^{0.9V}$ (mA/mg)
0.9	Pre	15.35	295[1]
	Post[2]	10.1	165
	Loss	**34.4 %**	**44.1 %**
0.95	Pre	19.6	282[1]
	Post[2]	14.0	114
	Loss	**28.6 %**	**60 %**

[1] Data from reassembled cells

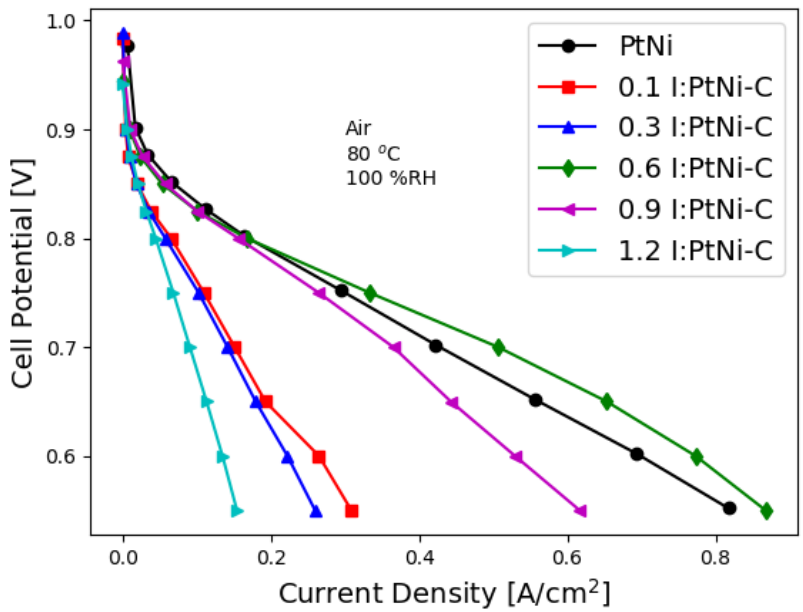
[2] following recovery step

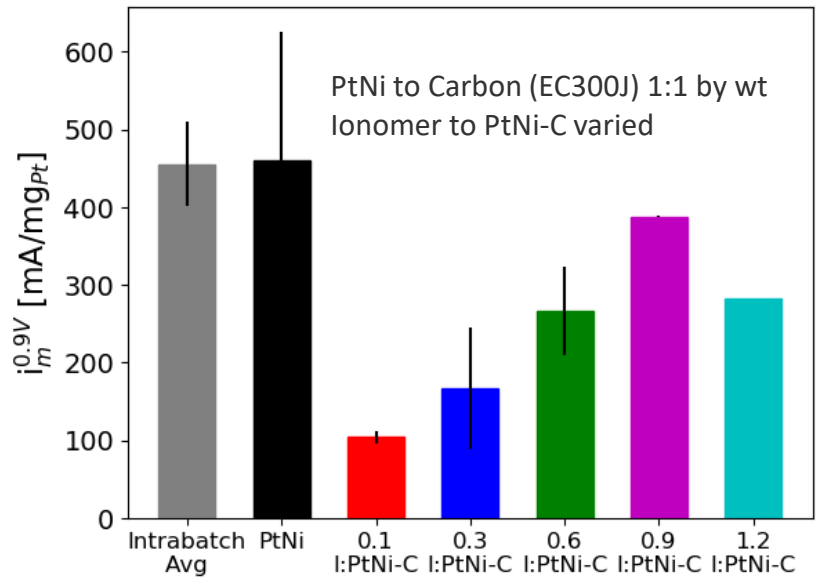


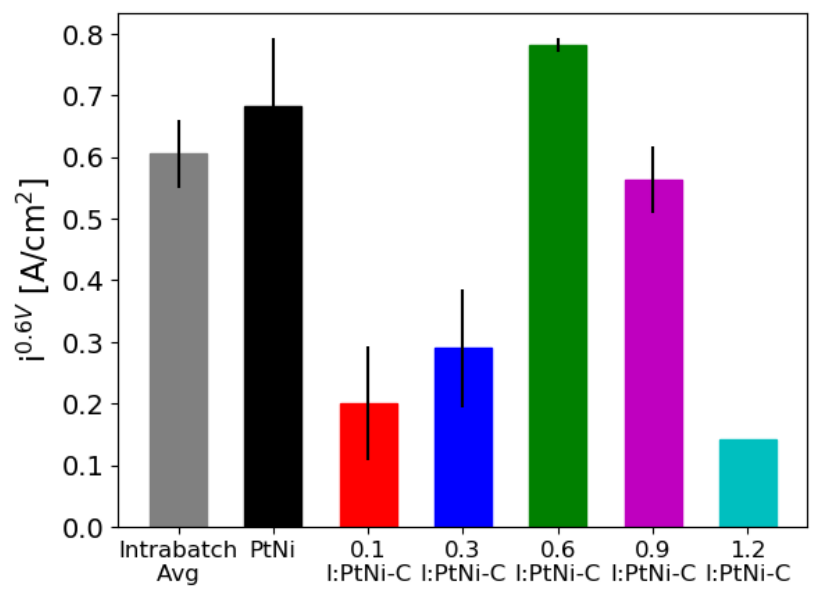
- Initial tests performed to investigate mass activity losses due to Pt dissolution cycling
- Durability targets not met, but results were reasonably consistent with other Pt alloy approaches
- More testing in this area needed.

Accomplishments and Progress

Varying Ionomer Content in MEAs







- The content of ionomer within electrodes was found to play a role on both mass activity and high current density performance.
- 0.9 was found to be optimal for mass activity.
- 0.6 was found to be optimal for high current performance.

Accomplishments and Progress

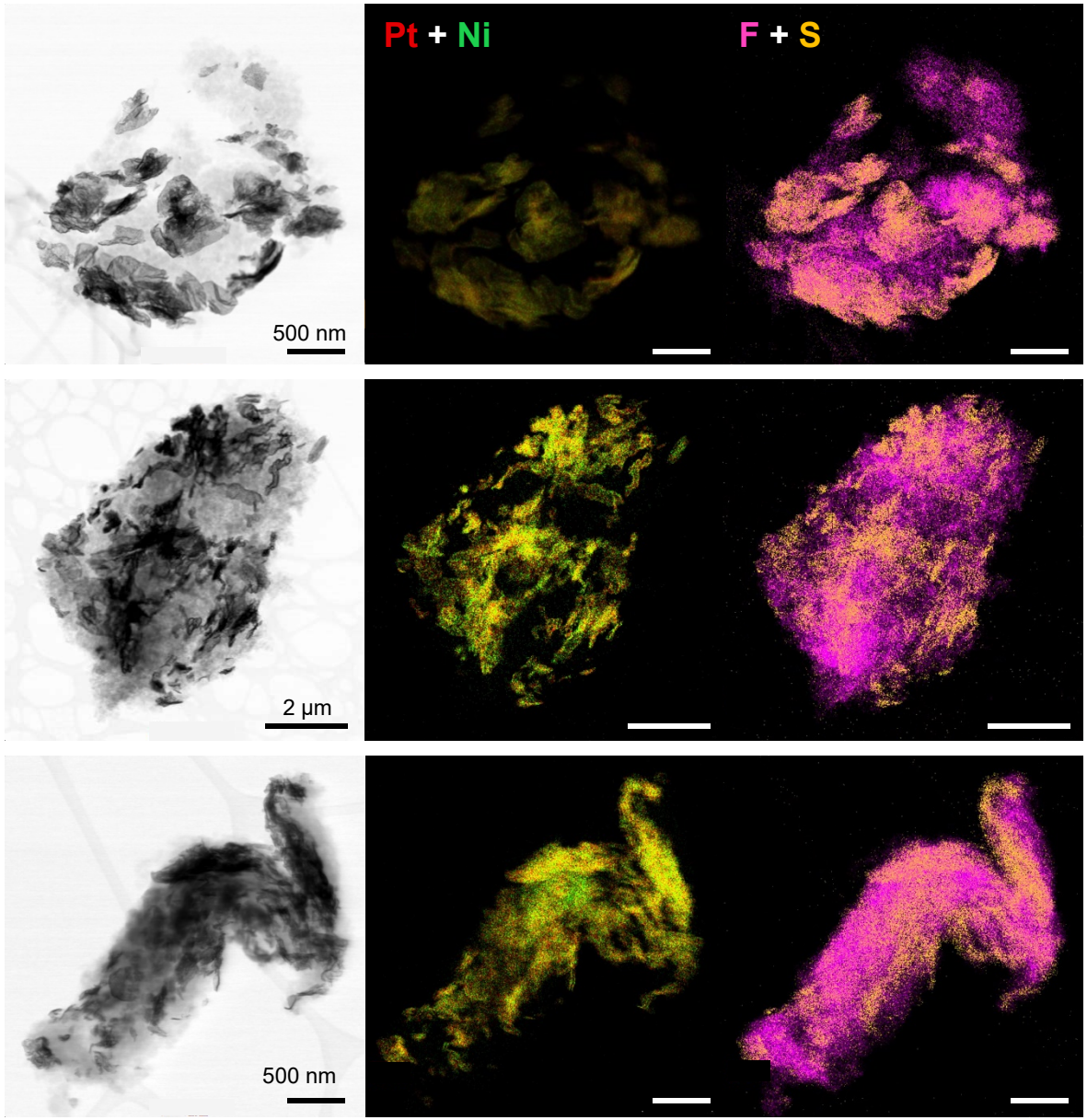
Varying Ionomer Content in MEAs

Varied ionomer-to-solids (I:S) ratio

I:S = 0.6

I:S = 0.9

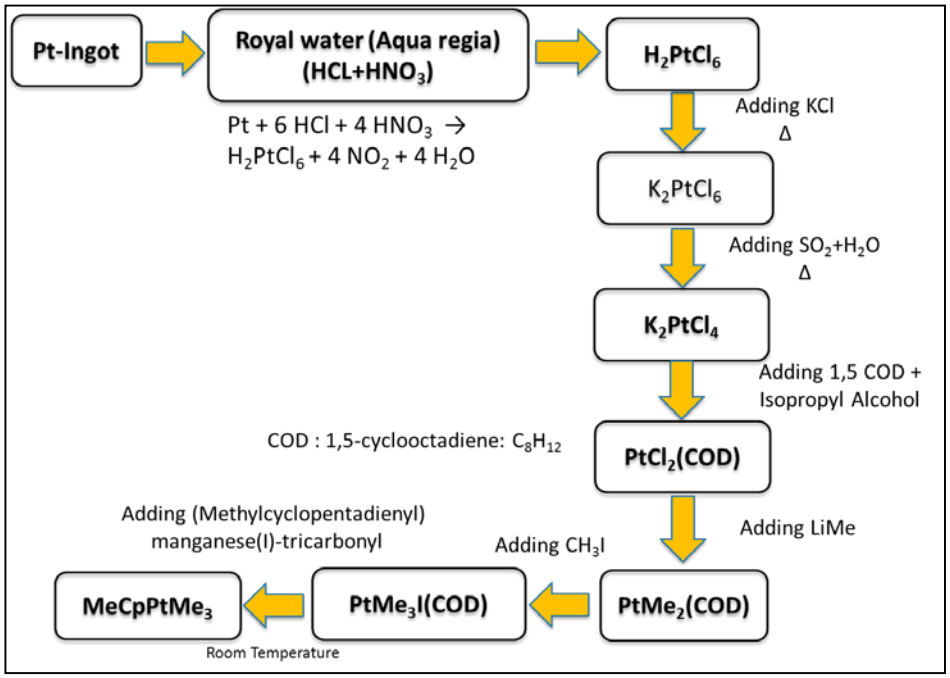
I:S = 1.2

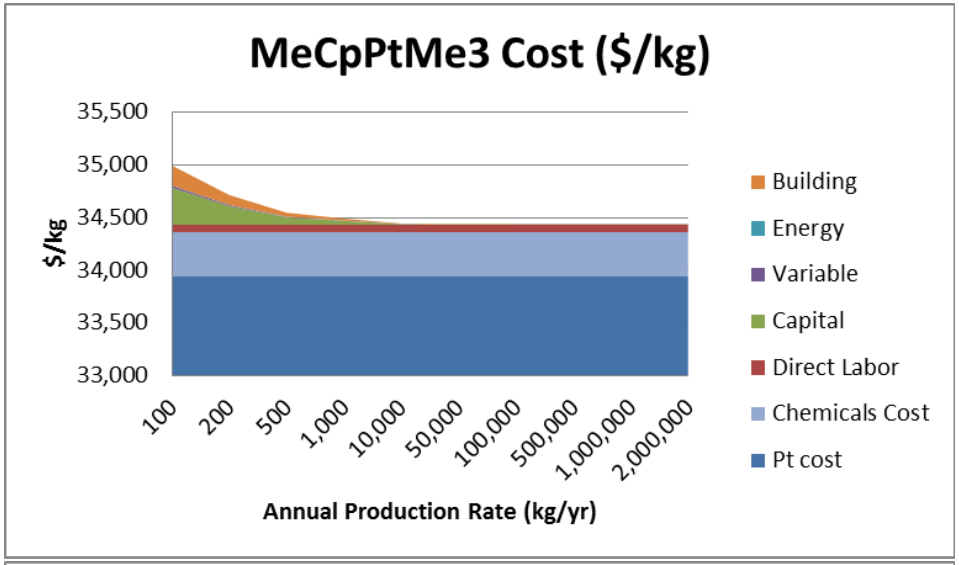


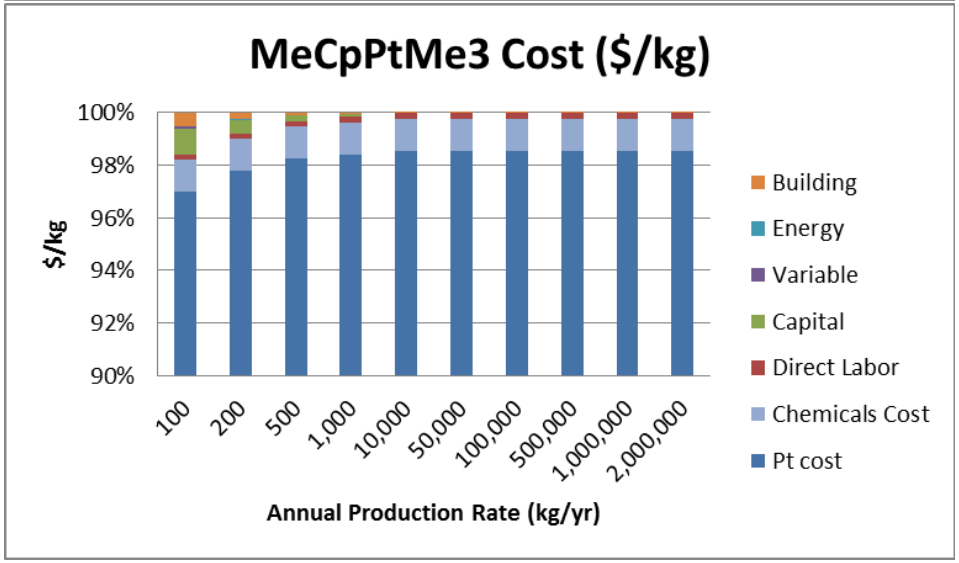
Microscopy used to study catalyst layer morphology and ionomer distribution

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.

Reviewer Only Slides

Data Management Plan

- This project will maintain compliance with data management requirements of the Department of Energy and abide by the Office of Energy Efficiency and Renewable Energy data sharing and preservation requirements.
- To the greatest extent and with the fewest constraints possible, this project will make digital research data available to, and useful for, the broader scientific community, industry, and the public.
- Technical reports, journal article accepted manuscripts, software, and scientific research datasets will be submitted to OSTI through the DOE Energy Link System. Data from this project deemed appropriate for public access will be made available through the NREL Data Catalog.
- Data in this public release will be in a machine-readable digital format (e.g., comma-delimited).
- This project will not generate or use Personally Identifiable Information (PII). Any data containing national security implications, business confidentiality, or intellectual property will not be released in accordance with all laws and DOE regulations, orders, and policies.

Critical Assumptions and Issues

- Critical assumption: The catalyst performance of ETFECS demonstrated in RDE by spontaneous galvanic displacement can be translated over to and improved upon by ALD.
- Potential solutions: To date, we have demonstrated high performance ALD synthesized samples reaching reasonable ECA (~40 m^2/g pt) and specific activity (~2,000 μA/cm^2 Pt). Continued optimization of the limited parameter space investigated, and the demonstrated performance of SGD synthesized materials makes this likely.

- Critical assumption: The catalyst performance of ETFECS demonstrated in RDE can be translated over to MEAs, enabling durable, high performance without significant losses due to mass transport, ionic, or electronic resistance.
- Potential solutions: To date, our highest performance materials have shown significantly lower performance in MEAs than RDEs. Our work to date has shown significant improvements in MEA and RDE performance through investigation of a few specific fabrication variables, including mixing conditions, ultrasonic spraying conditions, incorporation of carbon, and ionomer to carbon ration. We have begun a systematic approach investigating and mitigating losses associated with mass transport, ion and electron conduction. These will be an ongoing focus of the project, and we have a go/no-go decision based on reaching the MEA target performance.

- Critical assumption: We will be able to achieve our end of the FY go/no-go decision regarding performance and durability.
- Potential solutions: We have demonstrated 240 mA/mg Pt performance with a limited sample set and catalyst with limited ECA and specific activity. Assuming further gains in either (already demonstrated at the RDE level) or improvements in MEA incorporation, we feel optimistic that we will achieve this target.

Publications and Presentations

Publications

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, "Exceptional Oxygen Reduction Reaction Activity and Durability of Platinum-Nickel Nanowires Through Synthesis and Post-Treatment Optimization" ACS Omega 2017 2 (4), 1408-1418. doi: 10.1021/acsomega.7b00054

S.A. Mauger, K.C. Neyerlin, S.M. Alia, C. Ngo, S.K. Babu, K.E. Hurst, S. Pylypenkno, S. Lister, B.S. Pivovar "Fuel Cell Performance Implications of Membrane Electrode Assembly Fabrication with Platinum-Nickel Nanowire Catalysts" J. Electrochem. Soc. 2018 165 (3), F238-F245. doi:10.1149/2.1061803jes

C. Ngo, M.J. Dzara, S. Shulda, S. Pylypenko, Spectroscopy and Microscopy for Characterization of Fuel Cell Catalysts. Electrocatalysts for Low Temperature Fuel Cells: Fundamentals and Recent Trends 2017, 443.

Presentations

S. Pylypenko, Characterization of Electrocatalytic Materials: Challenges and Novel Approaches, New Mexico Chapter AVS symposium, Albuquerque, NM, May 16th, 2017

S. Pylypenko, Challenges and Novel Approaches in Multiscale Characterization of Active Materials, Forschungszentrum Juelich, Germany, July 12th, 2017

S.M. Shulda, J.N. Weker, C. Ngo, S.A. Mauger, S.M. Alia, K.C. Neyerlin, B.S. Pivovar, S. Pylypenko, "Chemical and Structural Investigation of Pt-Ni Extended Surface Catalyst Electrodes," 232nd ECS Meeting, October 4, 2017 National Harbor, MD.

S.M. Alia, K.C. Neyerlin, K. Hurst, J.W. Zack, S.A. Mauger, W.W. McNeary, A. Weimer, W. Medlin, S.M. Shulda, C. Ngo, S. Pylypenko, B.S. Pivovar, "Development and Implementation of Catalysts and Membrane Electrode Assemblies Based on Extended Thin Film Electrocatalysts," 232nd ECS Meeting, October 4, 2017 National Harbor, MD.

S. Pylypenko, Multi-scale characterization of nanowire-based electrocatalysts, Rocky Mountain ACS regional meeting, Loveland, CO, October 25-28th, 2017

W. McNeary, K. Hurst, S.M. Alia, S.A. Mauger, K.C. Neyerlin, C. Ngo, J.W. Medlin, A.W. Weimer, S. Pylypenko, K.J. Buechler, B.S. Pivovar, "Atomic Layer Deposition for Extended Surface Electrocatalyst Development," 2017 AIChE Annual Meeting, November 2, 2017, Minneapolis, MN.

W. McNeary, K. Hurst, S.M. Alia, S.A. Mauger, K.C. Neyerlin, C. Ngo, J.W. Medlin, A.W. Weimer, S. Pylypenko, K.J. Buechler, B.S. Pivovar, "Extended Thin Film Electrocatalyst Structures Via Pt Atomic Layer Deposition," 2017 AIChE Annual Meeting, November 2, 2017, Minneapolis, MN.

S. Zaccarine, C. Ngo, S. Shulda, S. Pylypenko, S. Mauger, S. Alia, K.C. Neyerlin, B. Pivovar, S. Pylypenko, "Characterization of extended surface catalysts for optimization of performance in polymer electrolyte membrane fuel cells", GRADS, CSM, April 2018

S. Zaccarine, C. Ngo, S. Shulda, S. Mauger, S. Alia, K.C. Neyerlin, B. Pivovar, S. Pylypenko, "Optimizing Extended Surface Catalysts and Electrodes through Multitechnique Multiscale Characterization" ISE 2018.