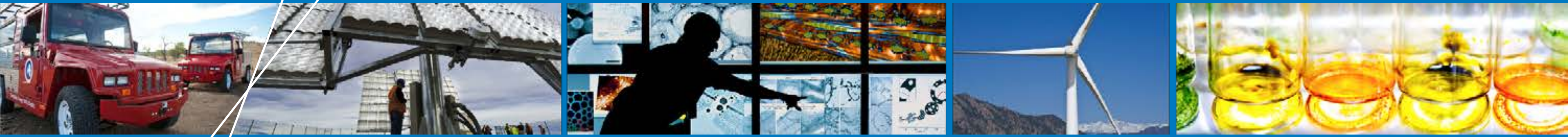
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Extended Surface Electrocatalyst Development



2017 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

June 7, 2017

FC142

Overview

Timeline

- Start: December 2015
- End: September 2018
- % complete: ~35%

Budget ($K)

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

	DOE Budget plan ($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

*through 3/1/17

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)[a]	g / kW (rated)	0.19[b]	0.125	0.125
Platinum group metal (pgm) total loading[a]	mg PGM / cm² 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 cm² 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 cm² 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.

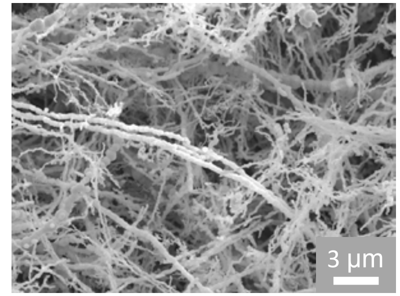
[d] Durability measured in a 25-50 cm² MEA during a hold at 1.2 V in H_2/N_2 at 80°C, 150 kPa absolute, 100% relative humidity. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (http://www.uscar.org/commands/files_download.php?files_id=267), 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

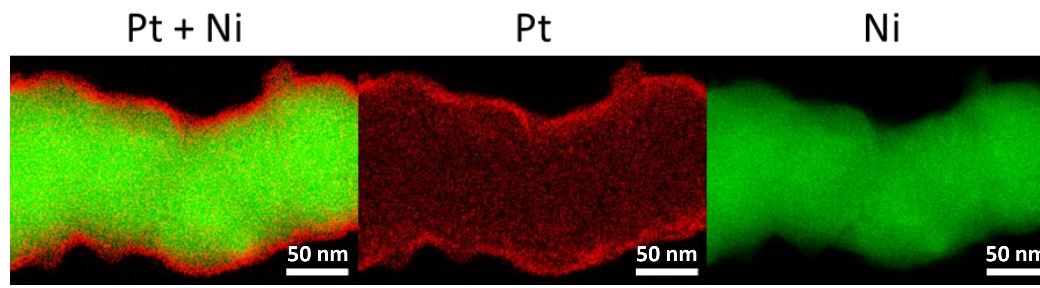
Extended Thin Film Electrocatalyst Structures(ETFECS)/Membrane Electrode Assemblies(MEAs)

Novel extended Ni nanotemplates (Delaware)
no-go decision (5% Effort, 100% Complete);
focus on commercial supplier.

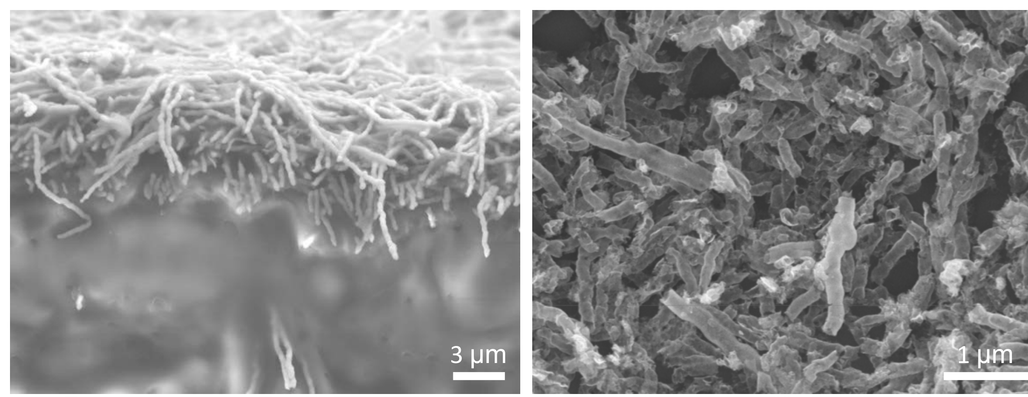


Ni NWs
(as received)

Focus on ALD synthesis of PtNi Nanowires (NWs), due to demonstrated performance but limitations (composition, batch size, reproducibility) of spontaneous galvanic displacement (SGD). Optimization of ALD process and post-processing. (NREL, CU, ALDN) (50% Effort, 50% Complete)



MEA optimization and testing including multiple architectures, compositions and operating conditions. (NREL)
(45% Effort, 10% Complete)



PtNi NW MEAs

CSM provides characterization in all areas above.

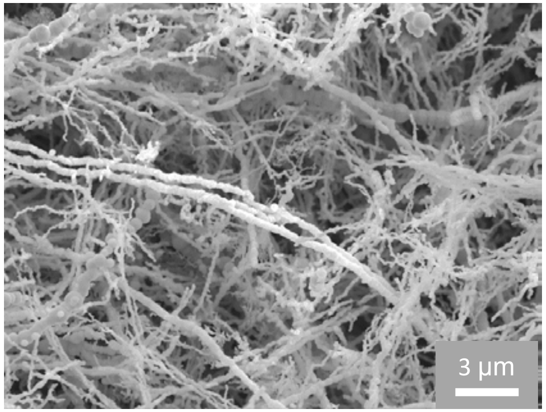
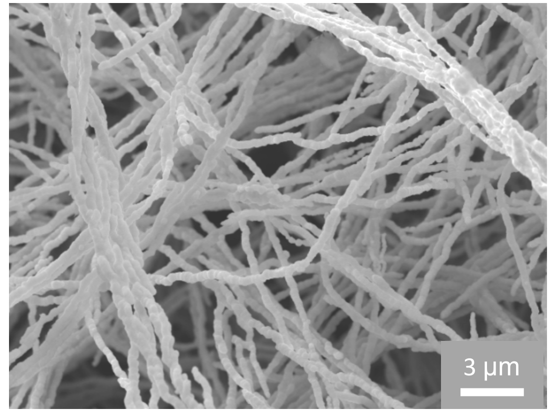
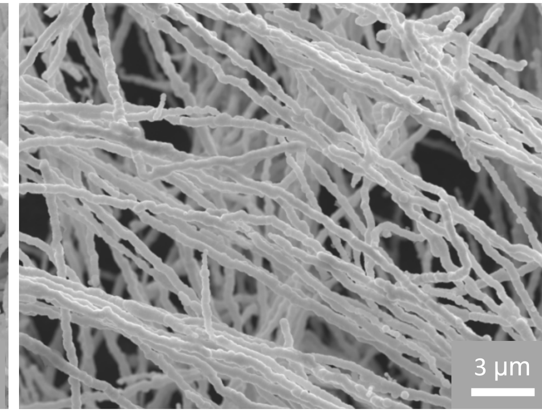
Approach

Project Schedule/Milestones

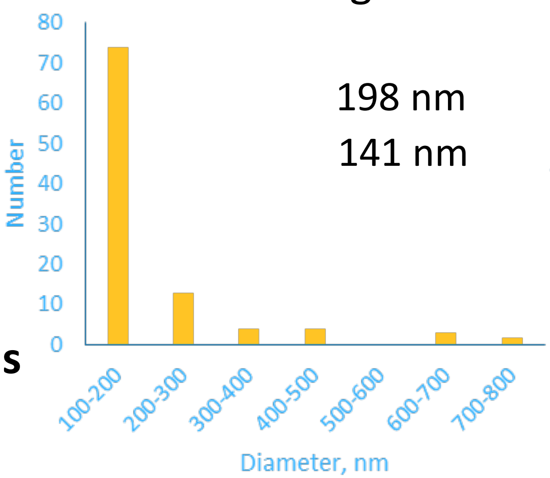
Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Type	Status
Q1	12/31/2016	Regular	Determine (using experimental measurements and developed models) and report overpotential losses associated with unique features of extended surface electrodes include protonic and electronic resistances of electrodes, and mass transfer losses including $R_{O2,local}$.	Quarterly Progress Measure	Met 12/16
Q2	3/31/2017	Regular	Quantify and report increase in catalytic performance (both specific activity and mass activity at 0.9V IR corrected) for shape/surface controlled nanostructures relative to standard Ni NWs. (NREL/Delaware)	Quarterly Progress Measure	No-go decision
Q3	6/30/2017	Regular	Demonstrate less than 40% loss in mass activity (following 30,000 voltage cycles performed according to Appendix E Table E1, DOE 2020 Target) for a cell with initial mass activity of >440 mA/mg_{Pt} at 0.9V (DOE 2020 Target) in fuel cell tests.	Quarterly Progress Measure	TBD
Q4	9/30/2017	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.	Annual Milestone	Best yet ~240 mA/mg

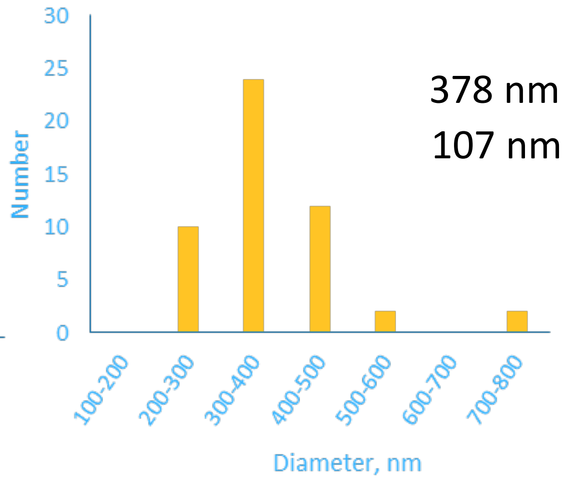
Accomplishments and Progress (2016)

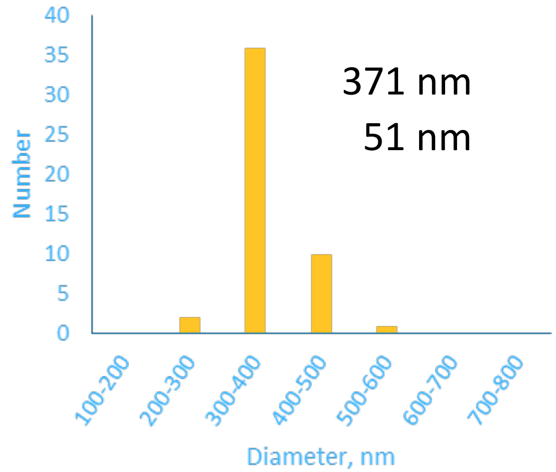
Nickel nanowire template – supply concerns

	1 g (2014)	50 g (2015)	100 g (2016)
SEM			
Fe Content	0.4%	0.8%	0.5%
BET (SA)	6.1 $m^2\ g^{-1}$	2.0 $m^2\ g^{-1}$	1.1 $m^2\ g^{-1}$
Pt (ECA) - SGD	~90 $m^2\ g^{-1}$	~50 $m^2\ g^{-1}$	>40 $m^2\ g^{-1}$
Average	198 nm	378 nm	371 nm
Std. Dev.	141 nm	107 nm	51 nm

Diameter Histograms







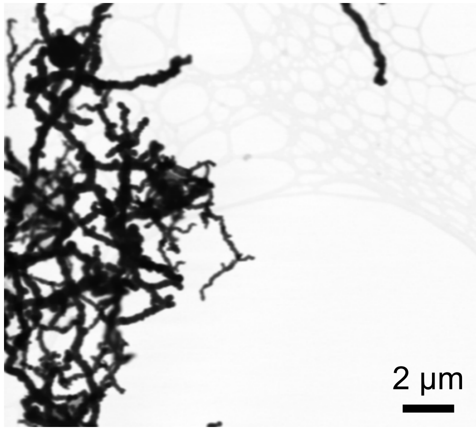
Changes in NiNWs likely resulted in lower Pt ECAs.

Accomplishments and Progress

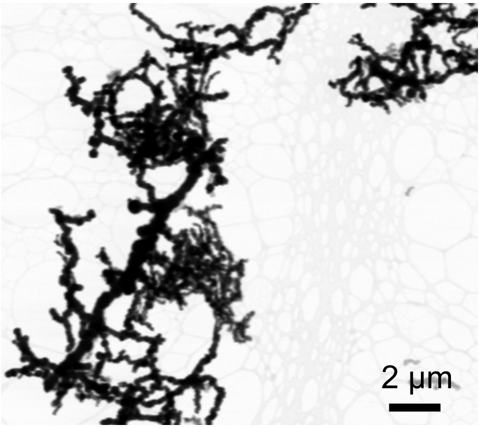
Working with vendor for custom nickel nanowires

- **Negotiated with upstream nanowire vendor**
- **Delivered multiple 20 g batches of different wire types for screening**

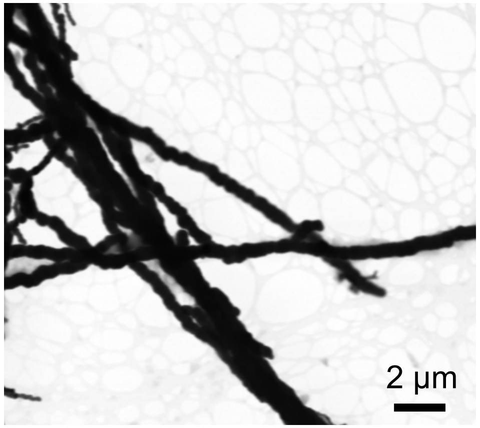
Type 4



Type 3



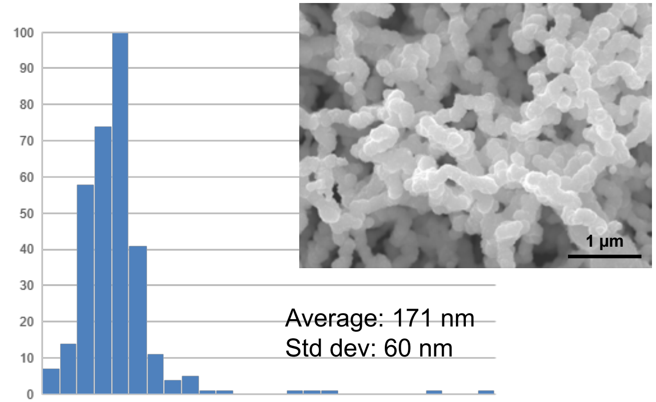
Type 2

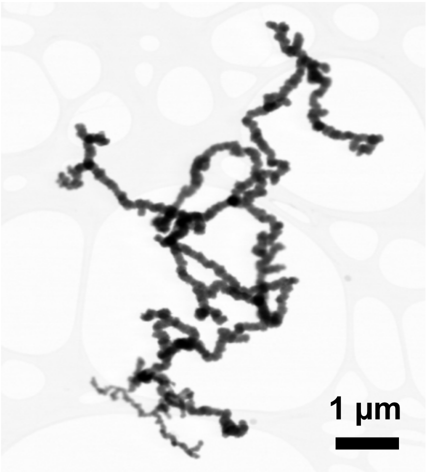


new Type 4

Down selected Type 4, have 100g batch that has shown good properties/ performance

BET: 4 m^2/g

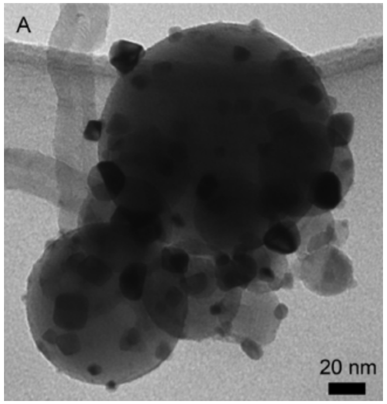




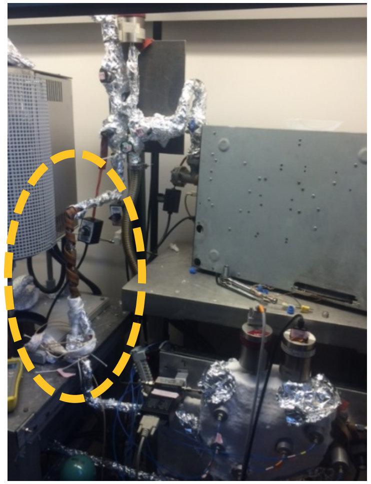
Accomplishments and Progress

Atomic layer deposition (ALD) – Pt onto Ni NWs

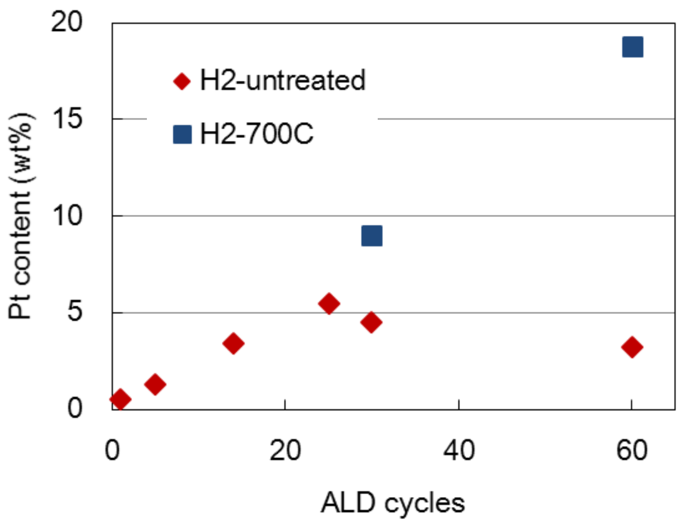
We have explored H_2 and O_2 based chemistry for Pt ALD.



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



Packed bed reactor initially capable of 500 mg batches.



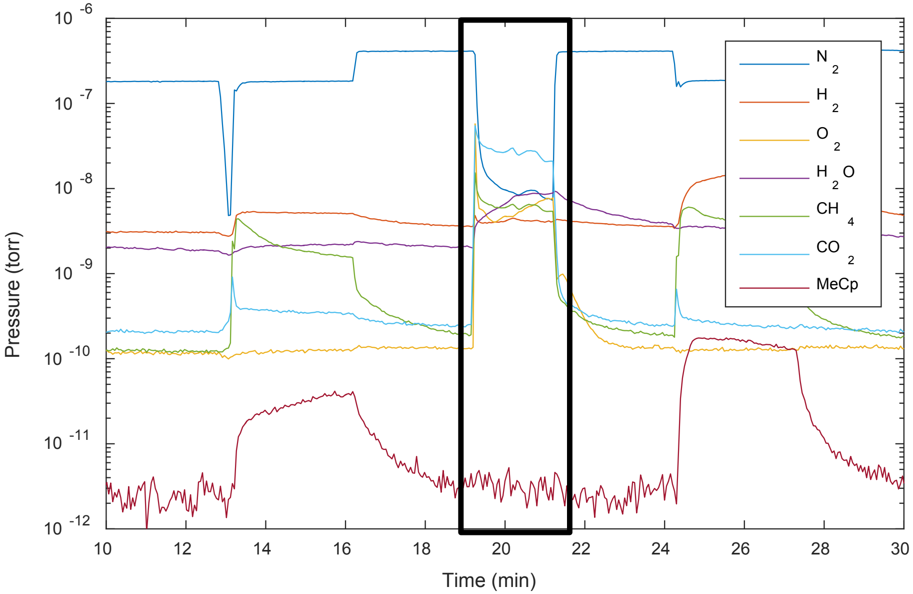
Pt deposition w/H_2 resulted in samples with significant carbon residue at targeted Pt content. This impacted digestion for ICP and observed electrochemical properties.

Higher temperatures allowed for removal of carbon.

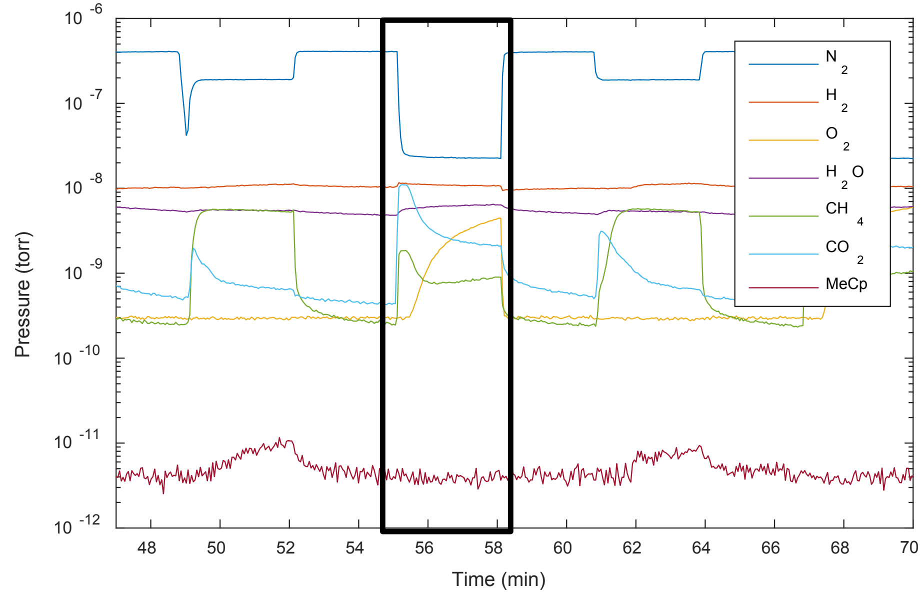
Accomplishments and Progress

Atomic layer deposition – excessive oxidation

Pure (100%) O_2 dose



5% O_2 in He dose



Dilute O_2 prevented excess oxidation, and resulted in improved properties/performance

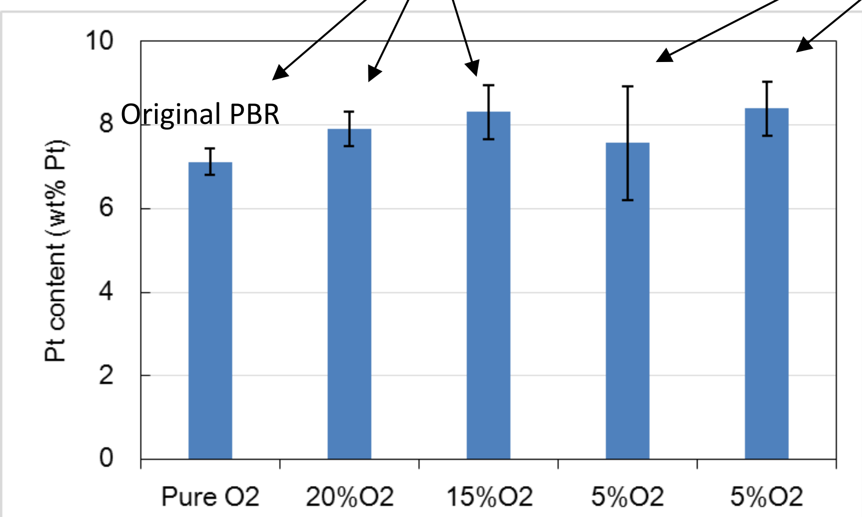
Accomplishments and Progress

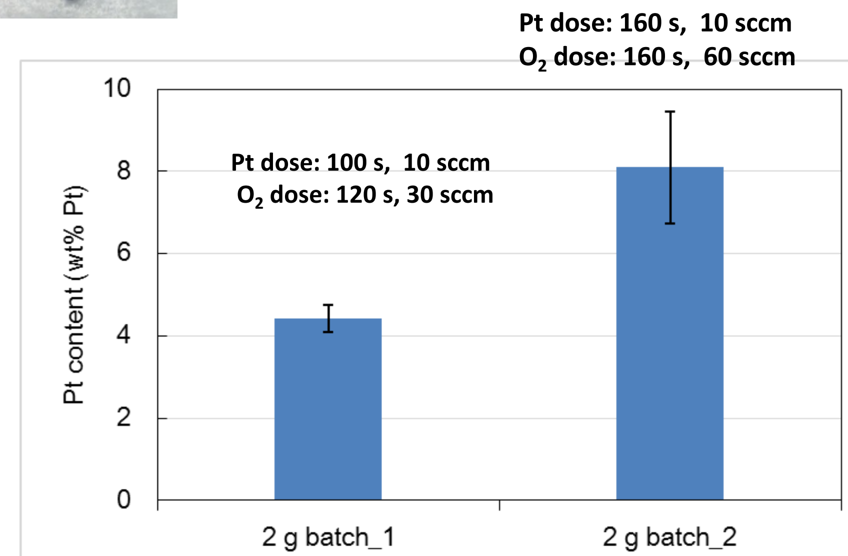
Atomic layer deposition – Scaled Up Batch Sizes

- New packed bed reactor (PBR) built for 10g batch size
- **30 cycles Pt-O_2** ALD reproducibility tested
  - Optimizing O_2 dose content with 0.5 g batches
  - Optimizing 2 g batches with 5% O_2 dose

Oxidation present on all high-oxygen samples

No visible oxidation with 5% O_2





Target Pt content (7-10 wt.%) achieved

Reaction condition modification was necessary for larger reactor/batch size.

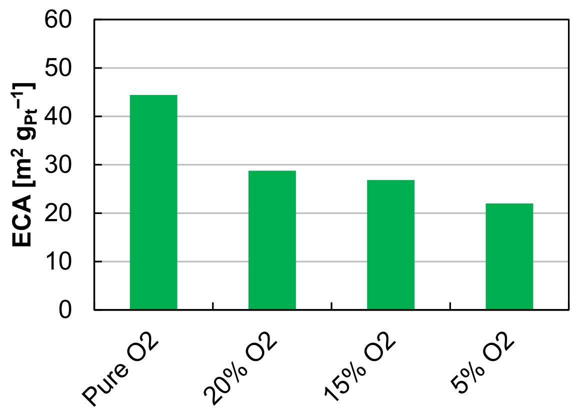
Note: error bars are standard deviation across each batch

Accomplishments and Progress

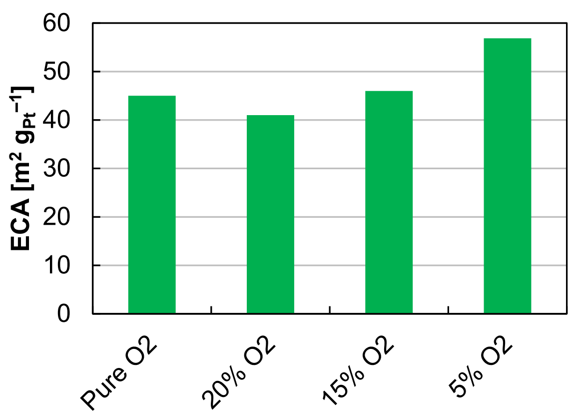
Atomic layer deposition – H_2 annealing

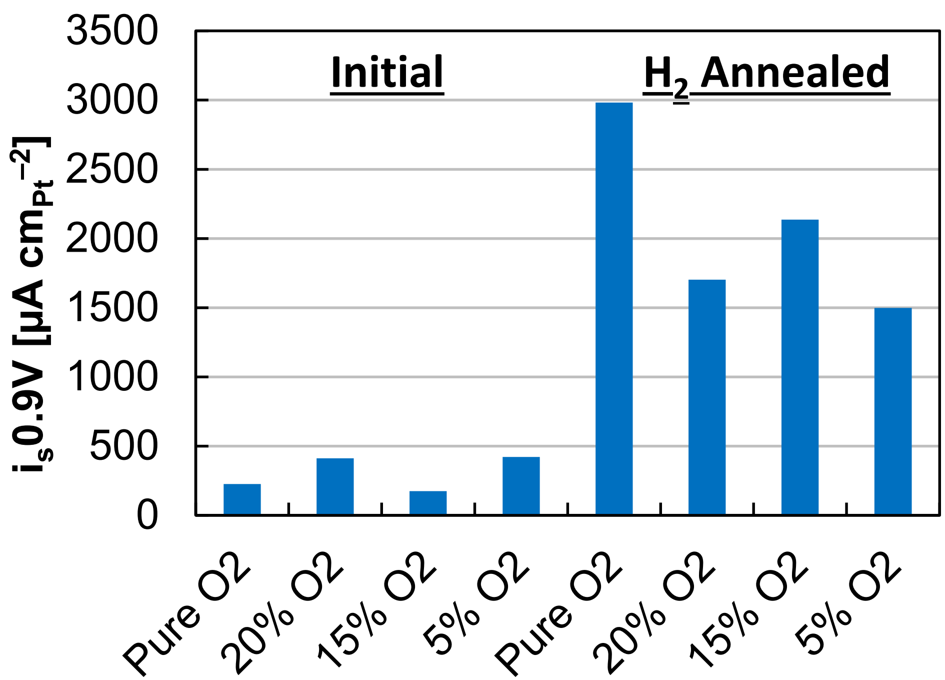
- Reasonable surface areas consistently achieved > 40 $m^2\ g_{Pt}^{-1}$
- H_2 annealing has improved electrochemical surface area (ECA)
- H_2 annealing has even larger role on specific activity (i_s)

ALD – initial



H_2 Annealed



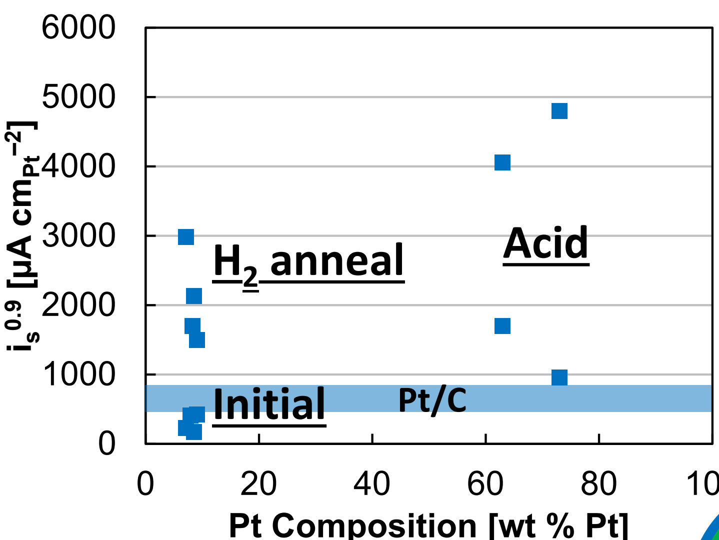


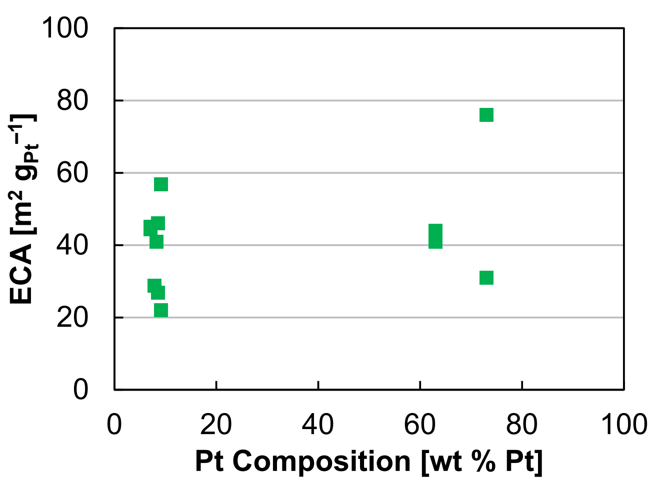
High specific activity achieved

Accomplishments and Progress

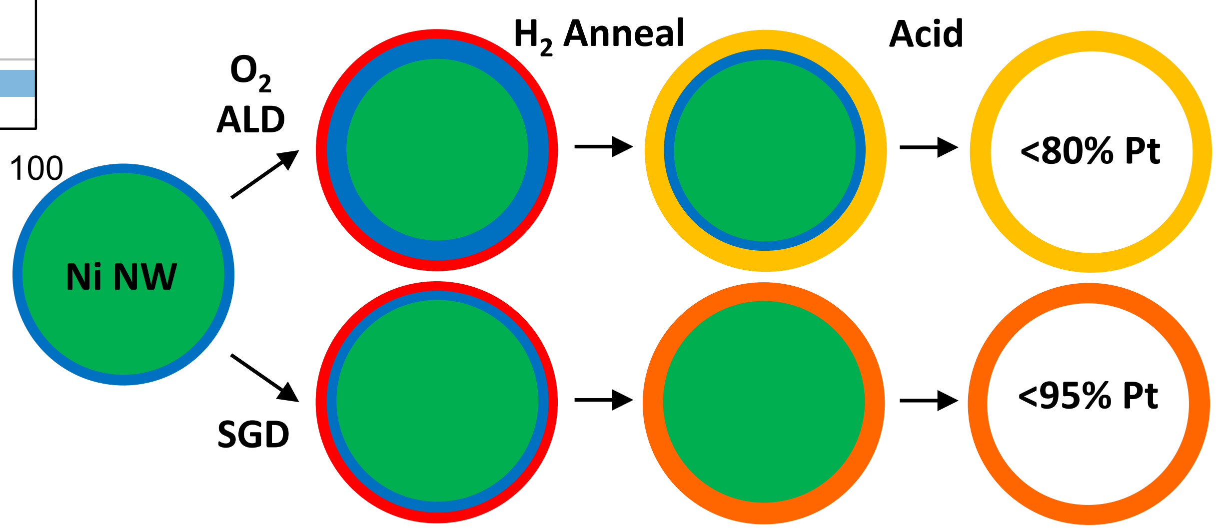
Atomic layer deposition – Acid Leaching

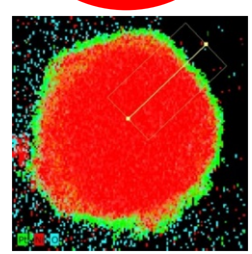
ALD - Summary





- Acid leaching removes majority of nickel
- Target properties of specific activity and ECA roughly maintained, in contrast to SGD where acid leaching led to significant decreases in specific activity.



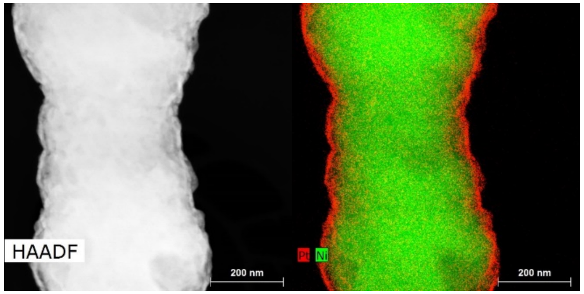


SGD PtNiNW cross-section, D. Cullen, ORNL

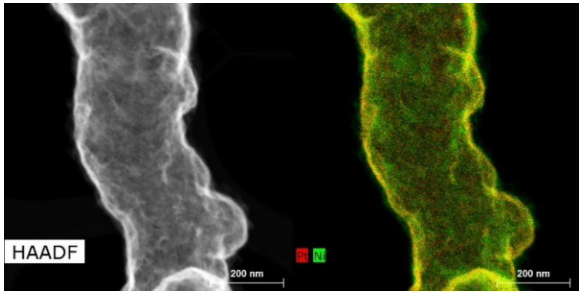
Accomplishments and Progress

Atomic layer deposition – PtNi NWs

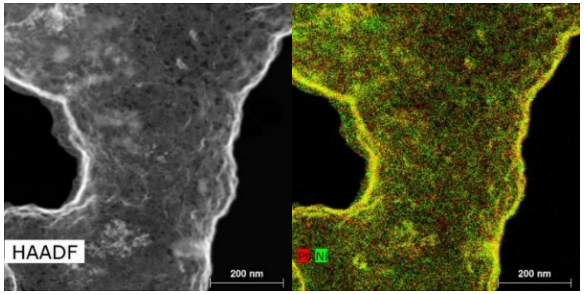
PtNi, 8 wt. % Pt



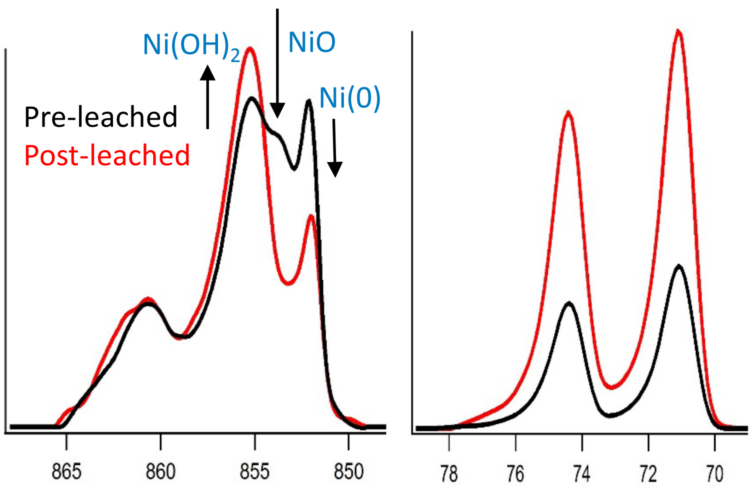
PtNi, 63 wt. % Pt



PtNi, 73 wt. % Pt

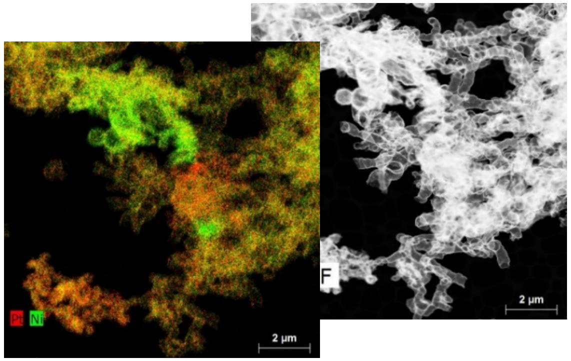


In acid-leached samples majority of nanowires are hollow



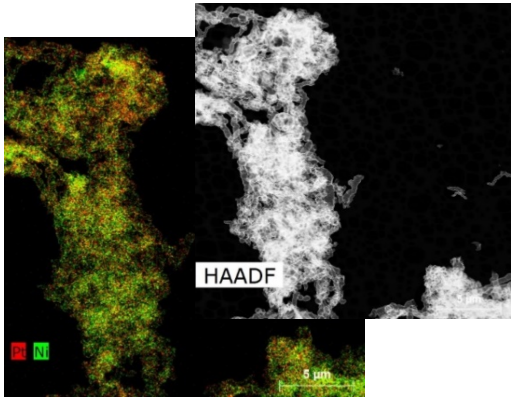
XPS shows alteration of Ni speciation, Pt unchanged.

PtNi, 63 wt. % Pt



Still heterogeneous distribution of Ni

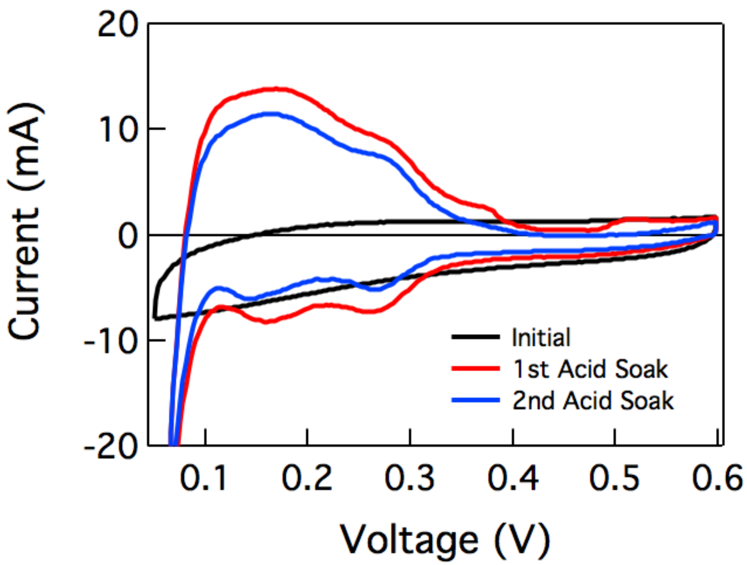
PtNi, 73 wt. % Pt

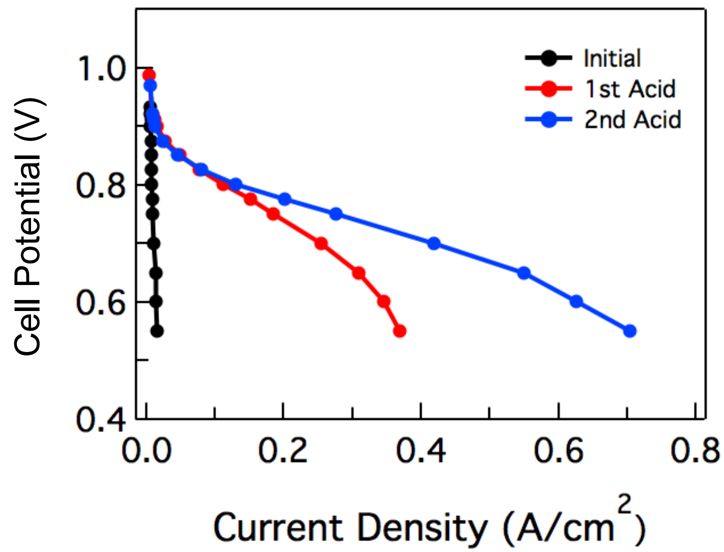


More homogeneous distribution of Ni

Accomplishments and Progress (2016)

Identification of Ni contamination impacts of MEA performance (SGD)

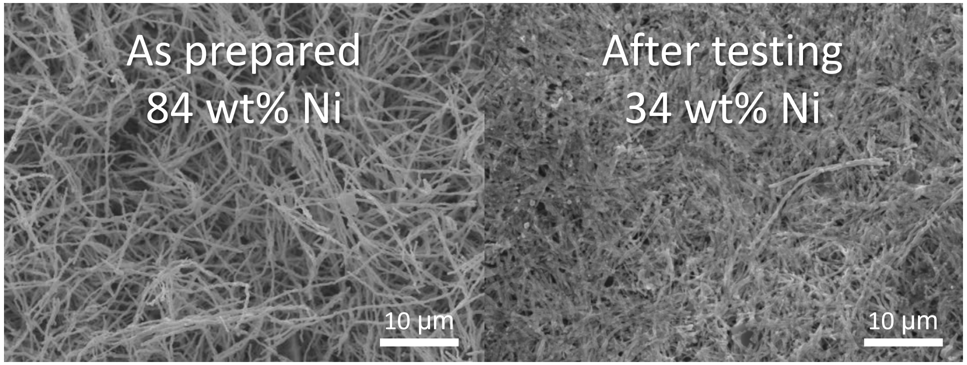


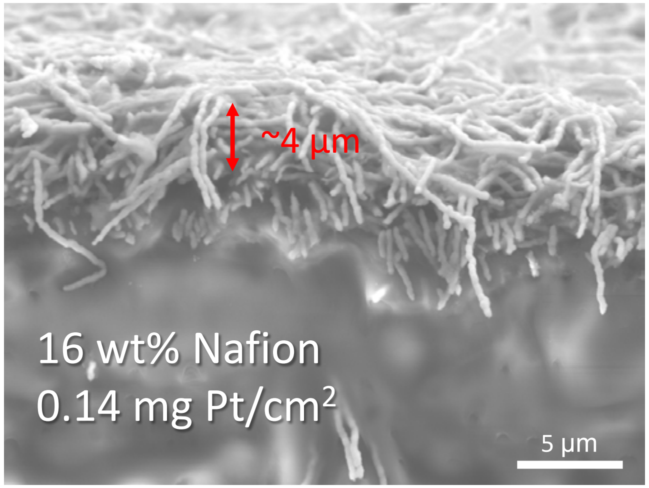


Nafion wt%	$i_m^{0.9V}$ (mA/mg_{Pt})
9	133
16	92
23	81

Reduced ionomer content beneficial

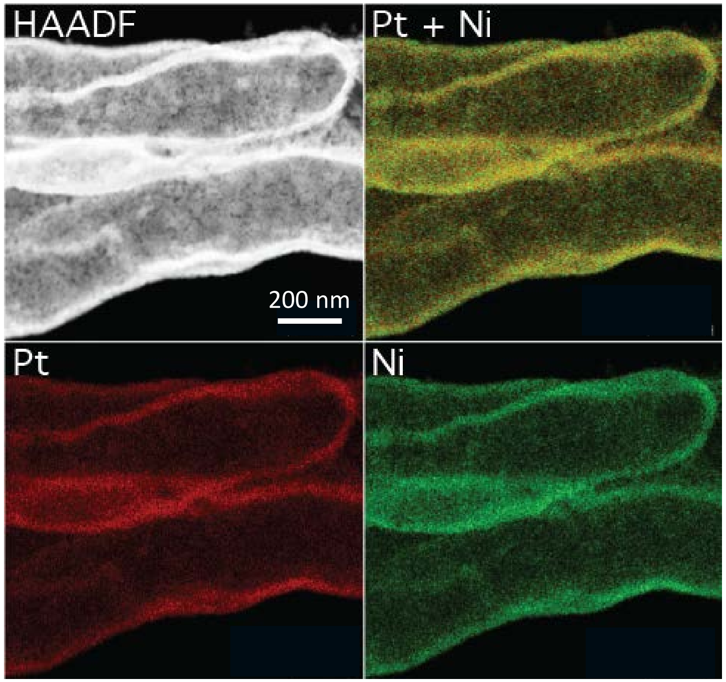
- Performance limited by Ni contamination
- Removing Ni by post acid effective, but not viable commercially



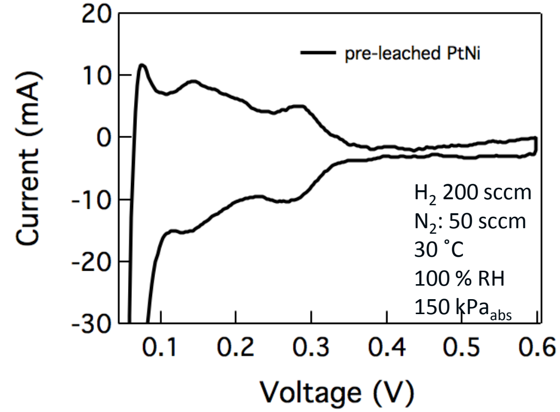


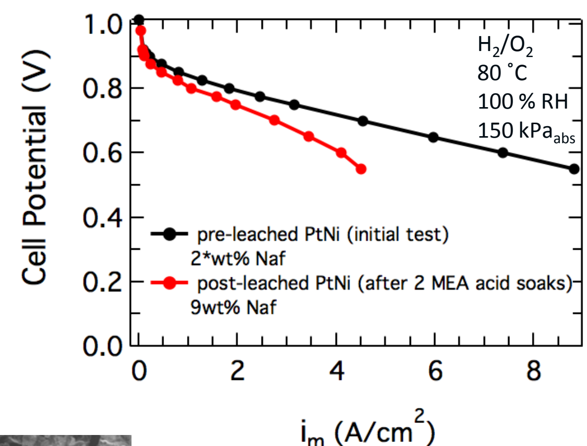
Accomplishments and Progress

Pre-leached PtNi (SGD) results in higher activity without MEA acid wash



81 wt% Pt

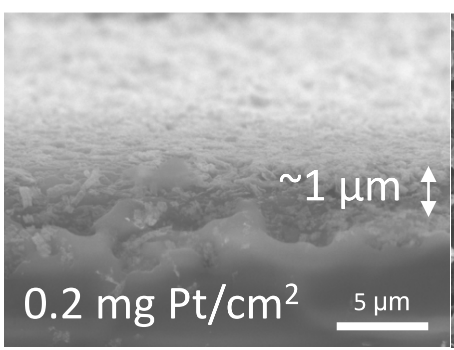


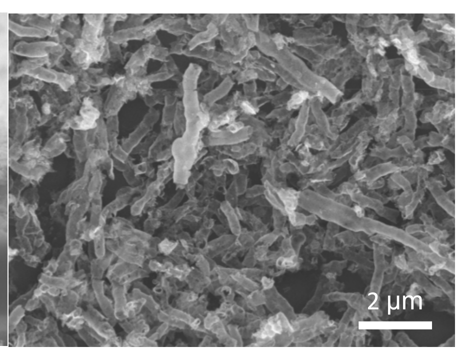


Pre-leached PtNi results in:

- higher activity than un-leached PtNi (with ex-situ leaching)
- no need for soaking MEAs in acid

pre-leached PtNi MEA 2 wt% Nafion

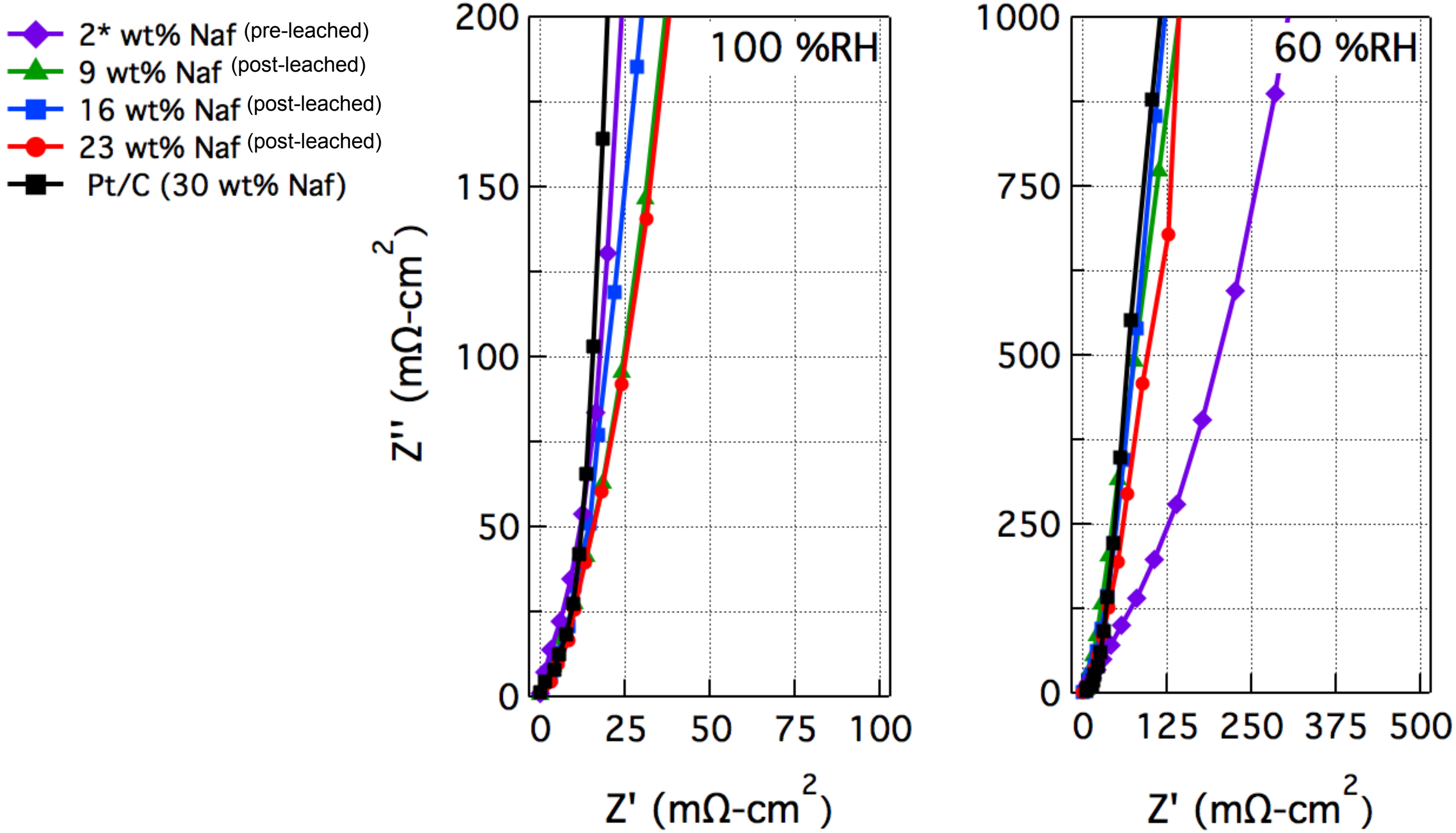




	Sample Type	ECA m^2/g	$i_m^{0.9V}$ mA/mg_{Pt}	$i_s^{0.9V}$ $\mu A/cm_{Pt}^2$
Pre-leached PtNi (initial)	MEA	22	238	1103
	RDE	21	518	2502
Post-leached PtNi (after 2nd acid soak)	MEA	19	133	697
	RDE	54	1400	2600

Accomplishments and Progress

MEA impedance spectroscopy

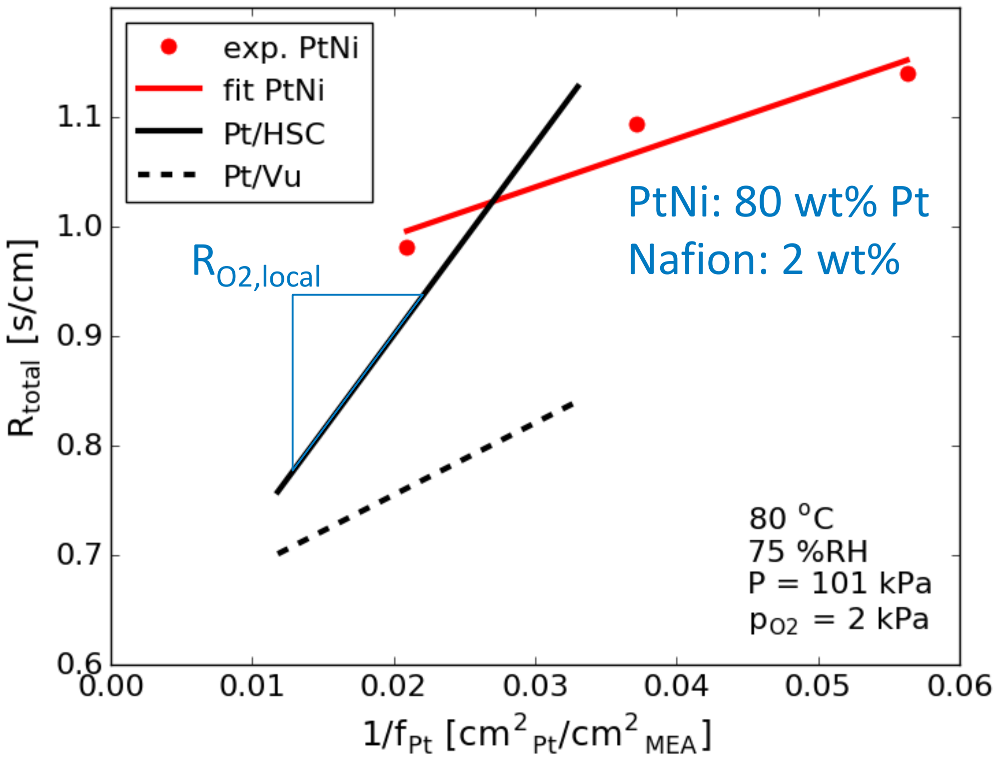


Cell Temp: 80 ˚C
H_2/N_2: 200 sccm
Back Pres.: 150 kPa_{abs}

- At 100% RH, PtNi NWs exhibit impedance behavior similar to that of Pt/C, regardless of leaching conditions or ionomer content.
- At 60% RH, only low loaded, pre-leached PtNi NWs show significantly different impedance behavior – suggesting (RH dependent) metal-surface proton conduction is important
- Low ionomer content offers potential benefits in O_2 transport resistance and activity

Accomplishments and Progress

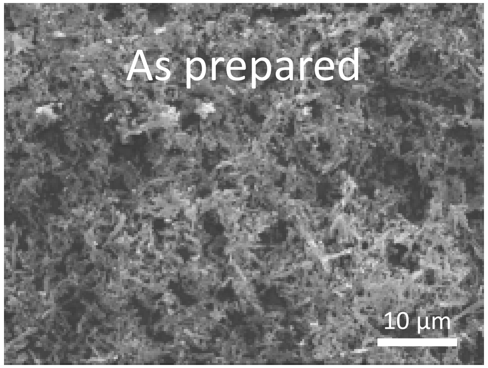
Low local oxygen transport resistance ($R_{O2,Local}$) of pre-leached PtNiNW MEAs (SGD)

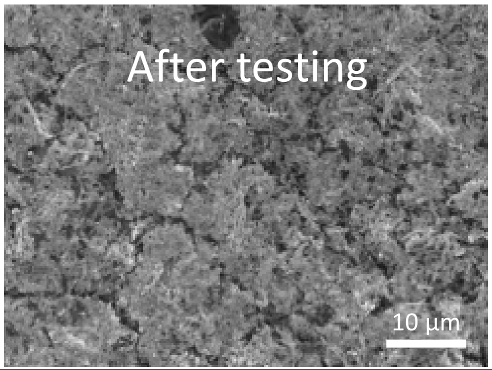


Catalyst	$R_{O2\ local}$ [s/cm]
PtNi	4.4
Pt/HSC	17.1*
Pt/Vu	6.28*

*K. C. Neyerlin, et al., *ECS Meeting Abstracts*, **MA2016-02** (38), 2492 (2016).

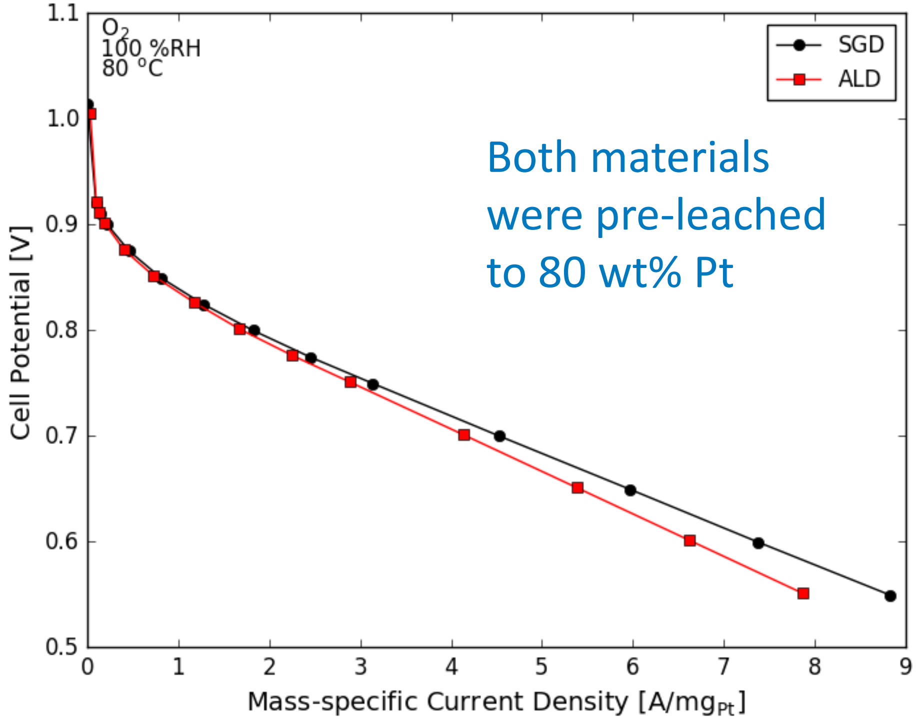
- Extended surface catalyst enables low ionomer content which can lead to lower $R_{O2,local}$
- High R_{total} needs further investigation, could be related to compact electrode (options exist)





Accomplishments and Progress

Equivalent MEA performance for SGD and ALD PtNiNWs



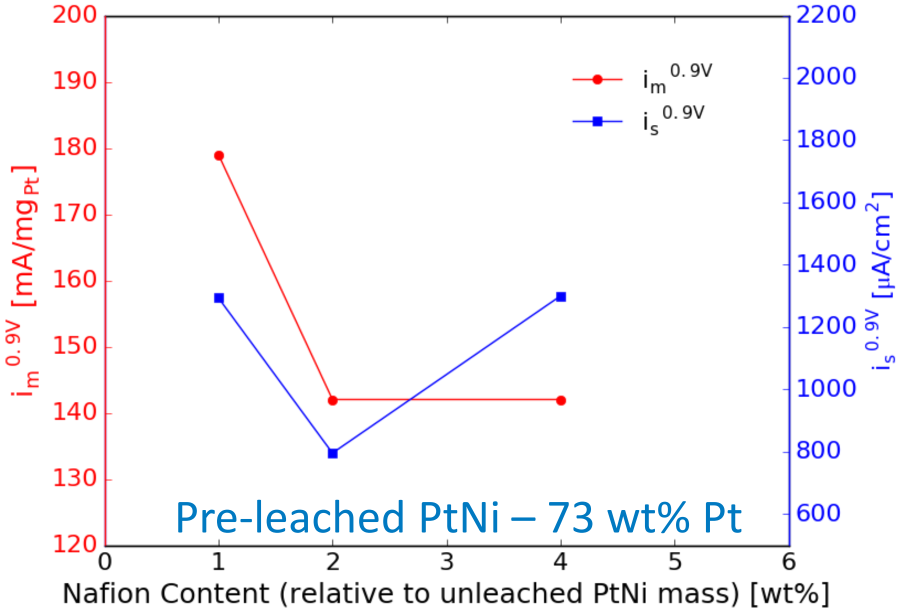
Similar performance between MEAs with SGD and ALD materials

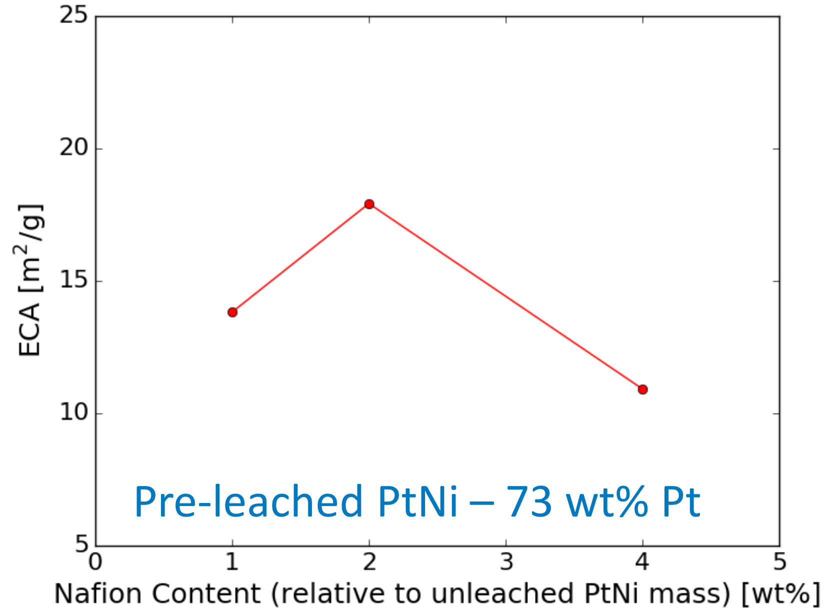
		ECA (m^2/g)	$i_m^{0.9V}$ (mA/mg_{Pt})	$i_s^{0.9V}$ ($\mu A/cm^2_{Pt}$)
SGD	RDE	21	518	2502
	MEA	22	**238**	1151
ALD	RDE	11	219	1936
	MEA	9.8	**228**	2320

MEAs maintain RDE-measured ECA for both catalyst preparation methods
ALD samples maintain specific activity, focus on higher ECA samples.

Accomplishments and Progress
Optimization of Pt and Nafion Content (ALD)

- **High performing, larger ALD synthesized batches have begun enabling parametric studies of catalyst pre-treatment and electrode composition**
- **Will provide increased statistical relevance and broader parameter space to be explored**





Accomplishments and Progress

Responses to Previous Year (2016 AMR) Reviewer's Comments

- **Reviewer Comment:** The project approach of optimization of Pt overcoated Ni nanowires is generally effective. The approach is lacking in development of improved Ni-leaching mitigation strategies in the MEA. The Ni loading in MEA electrodes is very concerning; it would appear that even if a small fraction leaches, significant fractions of the MEA ion exchange capacity (IEC) will be consumed. More effort toward quantifying and improving is needed.
- **Reviewer Comment:** However, these samples imply that an extraordinary concentration of Ni will be entering into the process of fabricating MEAs and eventually into fuel cells themselves where the Ni will contribute to aggregating the nanowires in ink (based on findings from FC-106), displacing protons in the membrane, and increasing the hydrophilicity of all porous layers. The researchers understand that Ni needs to be leached, but no data have been shown so far to ensure that activity is preserved after nanowire leaching.
- **Response: Both reviewers highlight the concerns of using large amounts of Ni in MEAs. This was both a focus of last year's presentation and this year's; however, in this year we showed significant advancement of pre-leaching of Ni as a route to high performance catalyst that can effectively be incorporated into highly performing MEAs.**

- **Reviewer Comment:** …especially a project premised on ALD, which is widely thought to be a low-throughput means of producing catalyst batches.
- **Reviewer Comment:** Some perspective should be reported on the cost implications of this and whether ALD would represent a practical commercial process.
- **Reviewer Comment:** There does not yet appear to be a contribution from ALD NanoSolutions on the business case analysis, although it would be very interesting to hear more about the business case for ALD.
- **Response: Multiple comments were made in relevance to the applicability of ALD as a catalyst synthesis route, as well as a single comment on ALD NanoSolutions contributions from a business case perspective. ALD Nanosolutions has demonstrated 50 kg batch sizes of materials synthesized by ALD and see potential to scale beyond this size which is already relevant for catalyst production. We performed techno-economic analysis which suggests when done at large scale that synthesis of the catalyst through ALD would add less than 10% to the cost of Pt in the final catalyst material. A few slides are presented in the back-up material.**

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (PI), Shaun Alia, KC Neyerlin, Katie Hurst, Jason Zack, Scott Mauger, Shyam Kocha, 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-Ahn Ha (UCLA) Office of Science SCSGR awardee
Shawn Litster (Carnegie Mellon)

Remaining Challenges/ Proposed Future Work

Nanotemplates:

Validation of targeted performance from commercial supplier.

Electrocatalysts:

ALD – scale-up to 10 g batch size. Further increase of ECA and specific activity. Co-deposition of Pt and Ni/Co.

Post-processing optimization (annealing and acid leaching)

Characterization and optimization (electrochemical and structural studies)

Fuel cell testing:

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.

Demonstrate a mass activity of >440 mA mgPt–1 at 0.9V (DOE 2020 Target) in fuel cell tests while also meeting at least one of FCTO's MEA durability targets.

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

Technology Transfer Activities

Intellectual Property

B.S. Pivovar, S.M. Alia, “Platinum Nickel Nanowires as Oxygen Reducing Electrocatalysts and Methods of Making the Same” US Patent 20160126562 May 5, 2016.

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. 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.

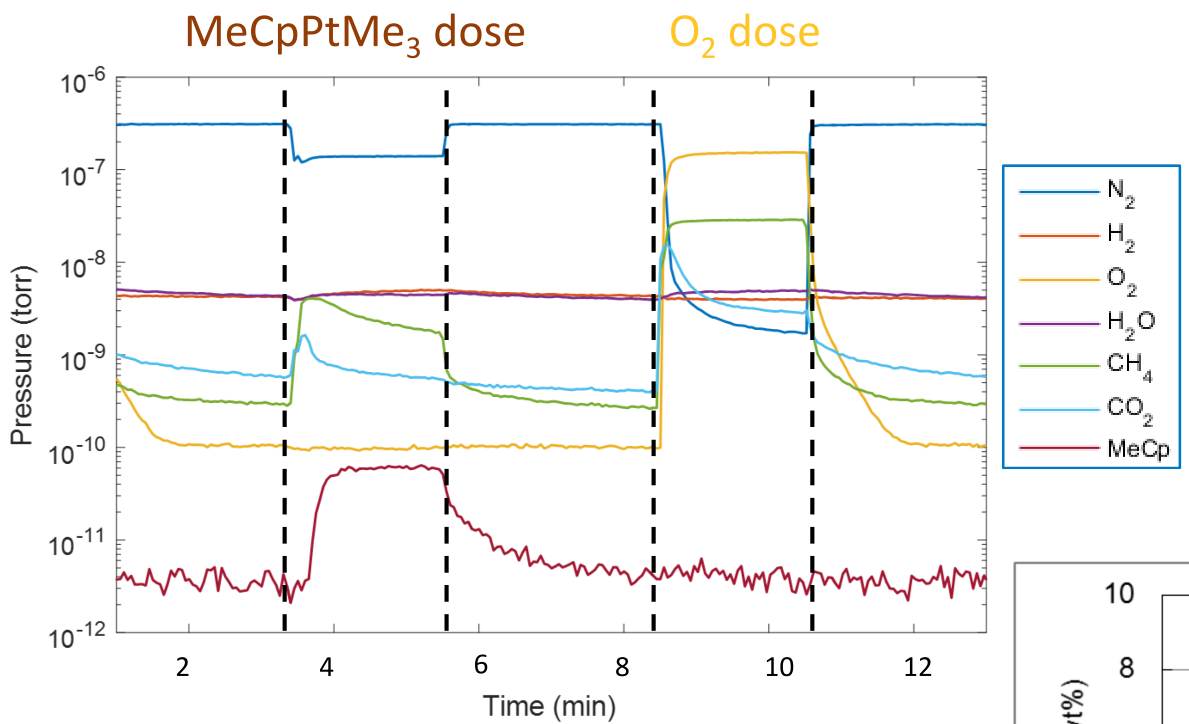
Summary

- **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 and reproducibility. Performance and durability have been significantly improved with annealing and pre-leaching. MEAs with pre-leached ETFECS (SGD and ALD) demonstrate mass activity Pt ~**240 mA/mg_{Pt}** with low ionomer content. Limiting current measurements show very low $R_{O2,local}$ for ETFECS MEAs.
- **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

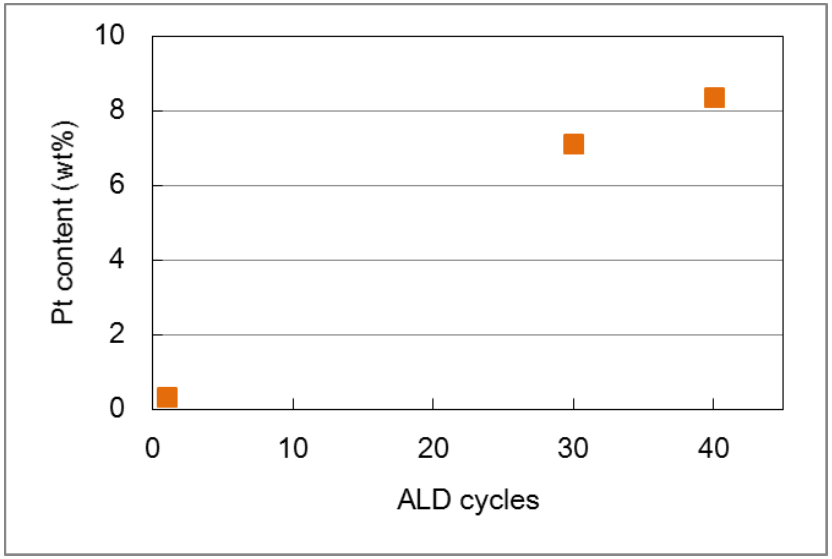
Atomic layer deposition – Pt/O_2 chemistry



Pt/O_2 chemistry results in efficient oxidation of the $MeCpPtMe_3$ ligands

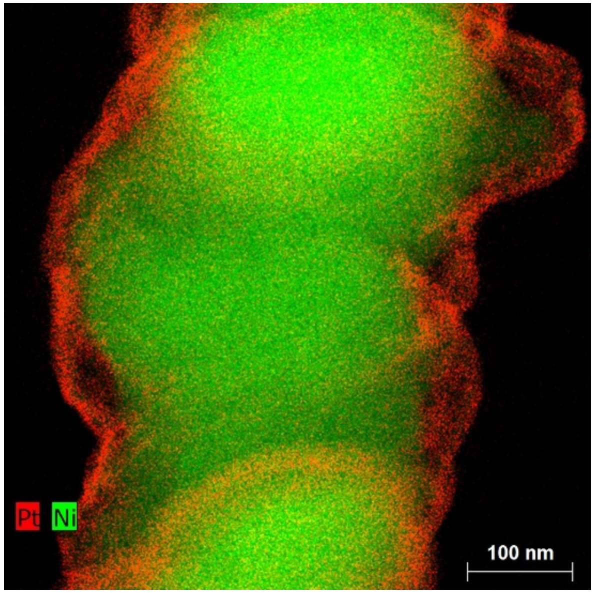
Faster reaction times enable significantly shorter cycle times

- Linear growth curve
- Complete digestion of materials for ICP
  (No residual carbon)
- 30 ALD cycles Pt-O_2 chosen for electrochemical testing and scale up



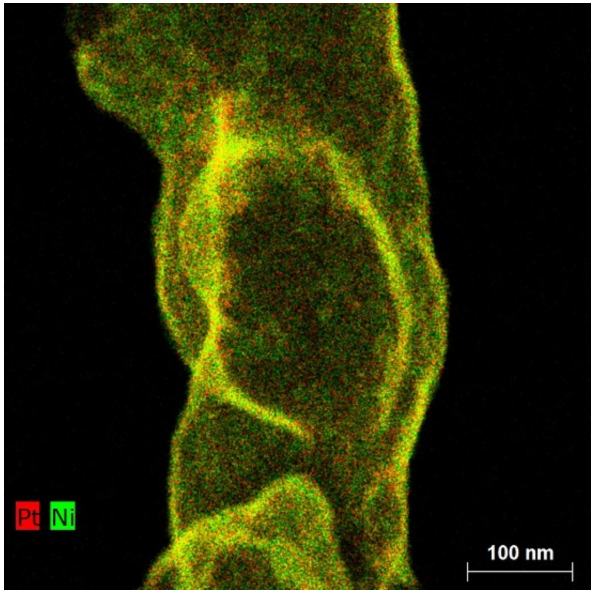
Pt ALD on type 4 Ni NWs

PtNi, 8 wt. % Pt (ICP)



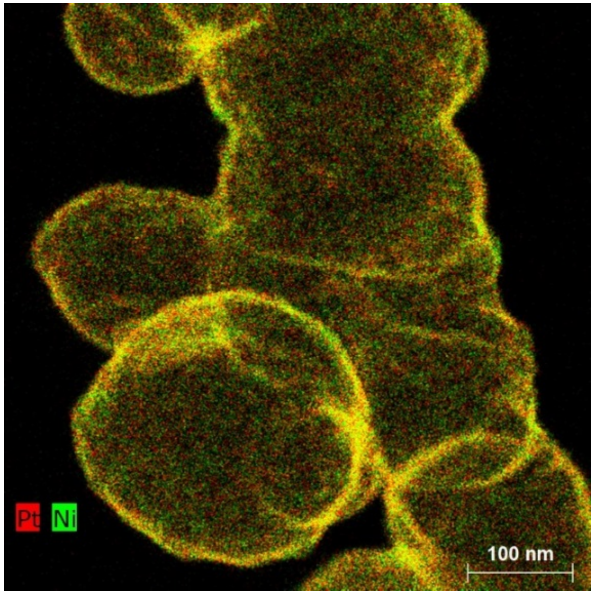
EDS	wt.%	at.%	XPS	at.%
Pt	6.0	1.9	Pt	26.8
Ni	94.0	98.1	Ni	73.2

PtNi, 63.4 wt. % Pt (ICP)



EDS	wt.%	at.%	XPS	at.%
Pt	51.1	24.2	Pt	13.5
Ni	48.9	75.8	Ni	86.5

PtNi, 72.7 wt. % Pt (ICP)



EDS	wt.%	at.%	XPS	at.%
Pt	70.8	42.3	Pt	50.5
Ni	29.2	57.7	Ni	49.5

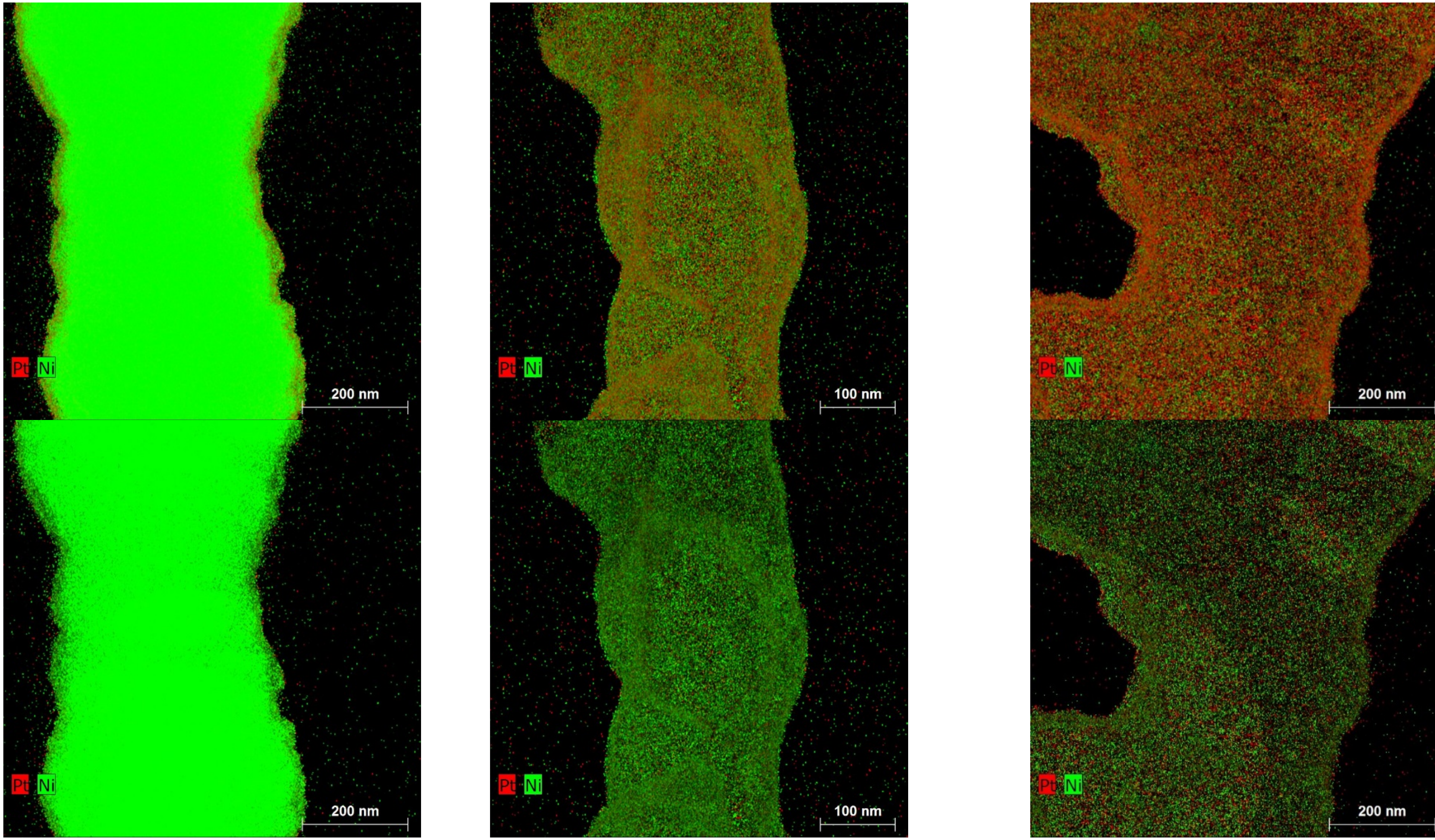
Amount of Ni relative to Pt is different

Pt ALD on type 4 Ni NWs (quantified maps)

PtNi, 8 wt. % Pt | PtNi, 63.4 wt. % Pt | PtNi, 72.7 wt. % Pt

mass %

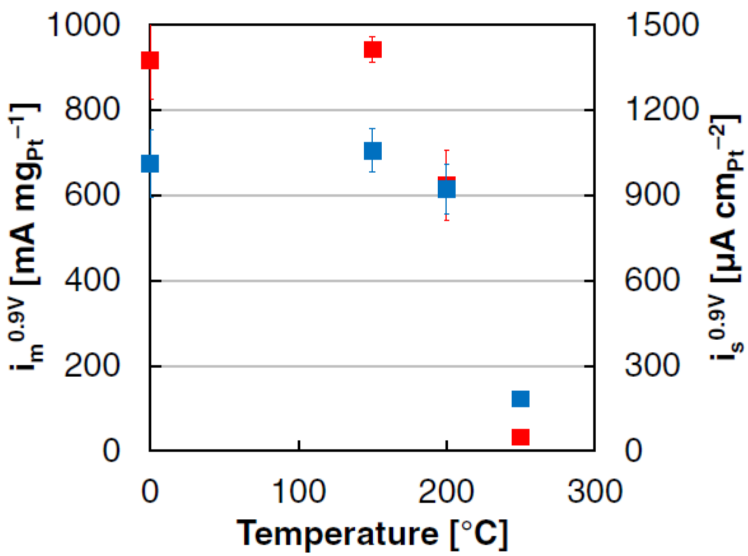
atomic %



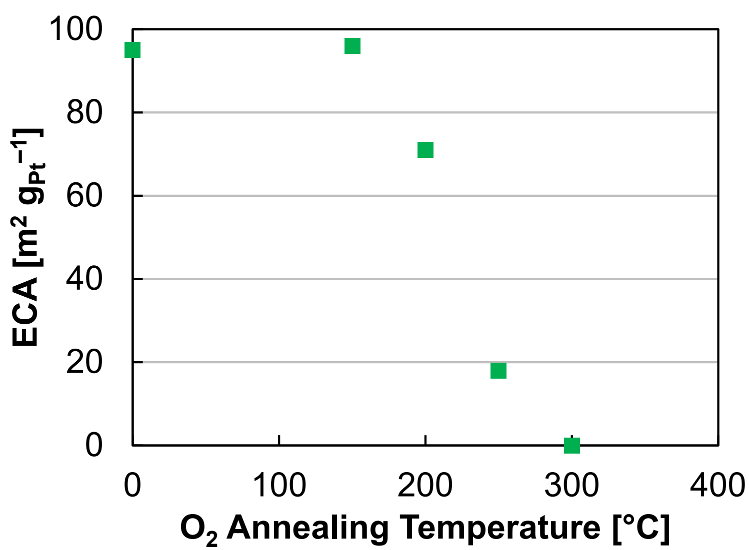
Amount of Ni relative to Pt is different in the two acid leached samples; each acid-leached sample has certain regions that are more rich in Pt

Accomplishments and Progress

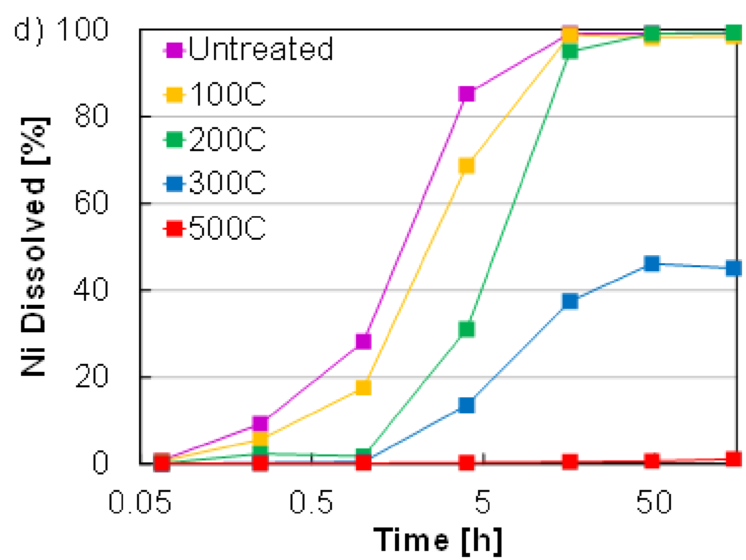
Spontaneous Galvanic Displacement – Role of Oxide Layer



- Annealing in oxygen increases the amount of Ni oxides near the surface
- Nickel oxides more difficult to dissolve, clean electrochemically
- Positive – increased durability (half-cell)
- Negative – lower ECA, activity



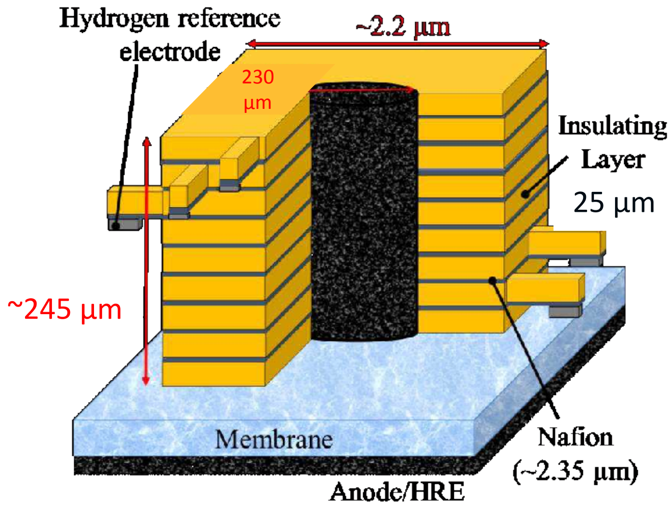
Ni NWs exposed to 3 M H_2SO_4



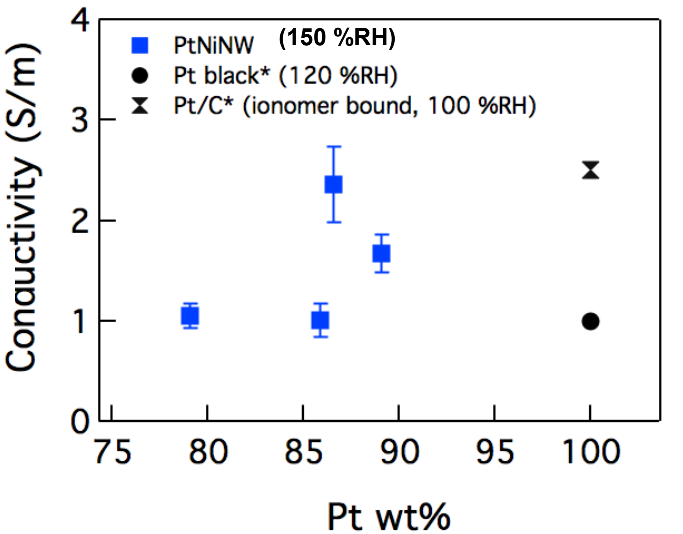
S.M. Alia, S. Pylypenko, A. Dameron, K.C. Neyerlin, S.S. Kocha, B.S. Pivovar *J. Electrochem. Soc.* **2016** *163*(3), F296.

Accomplishments and Progress:
ETFECS surface proton conductivity

Microstructured Electrode Scaffold

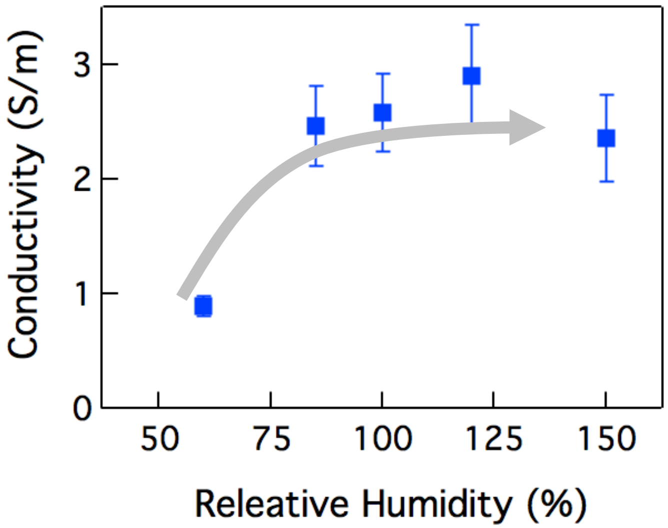


S. Komini Babu, et al. *ECS Trans.*, 69 (17) 23-33 (2015) doi:10.1149/06917.0023ecst



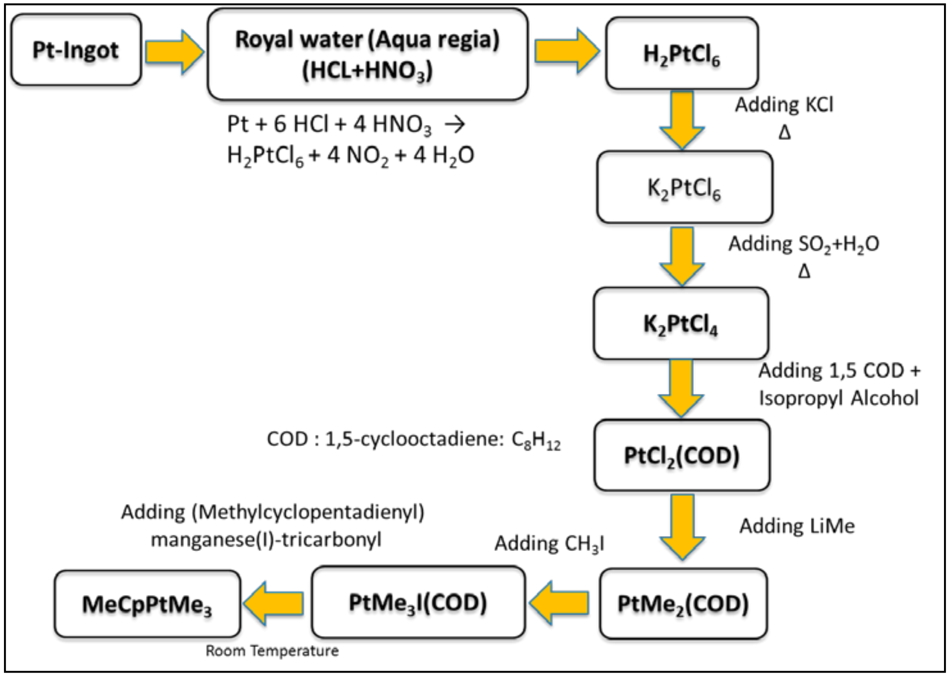
*An and Litster, *ECS Trans.*, 58(1), 831-839 (2013) Doi:10.1149/05801.0831ecst

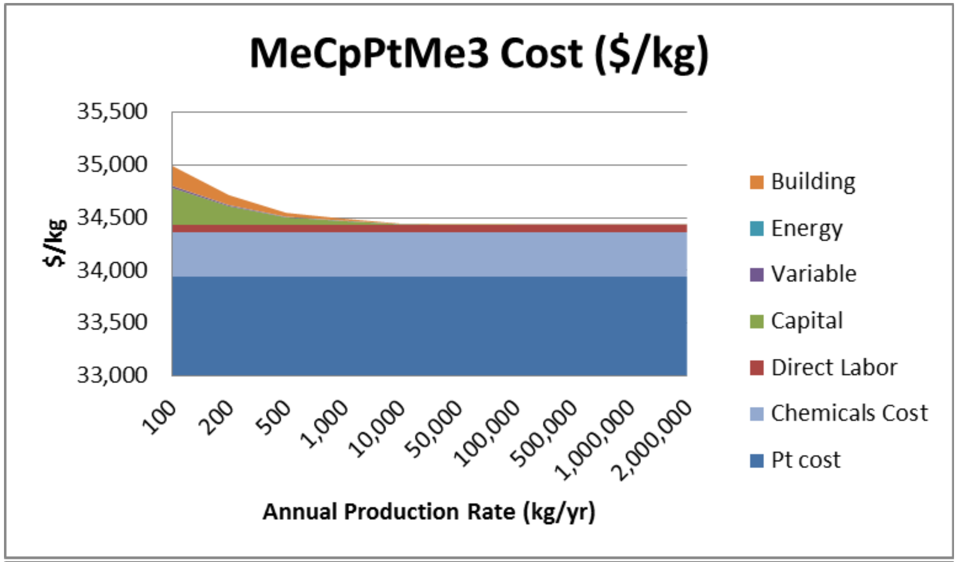
Proton conductivity of PtNiNWs consistent with Pt black (both without ionomer) and only slightly less ionomer bound Pt/C.

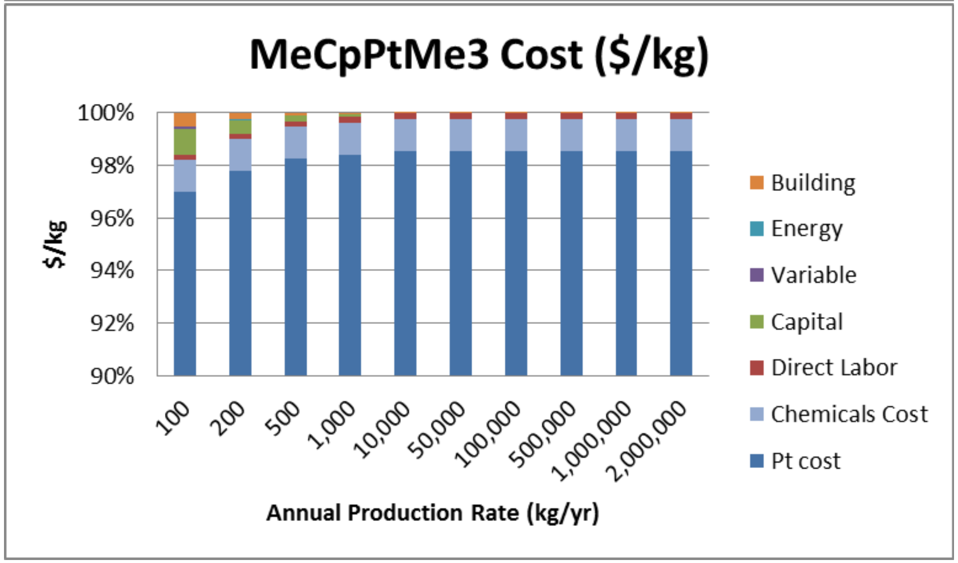


Accomplishments and Progress

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.