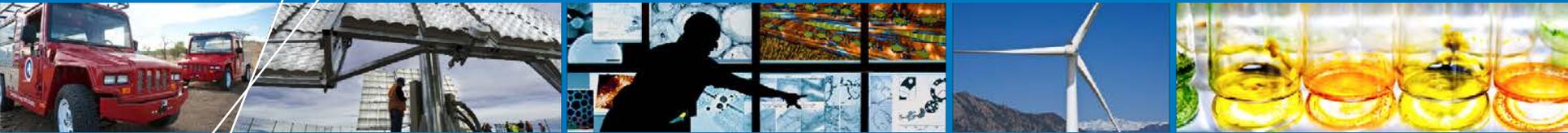


Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes



**2015 DOE Hydrogen and Fuel
Cells Program Review**

Bryan Pivovar (PI)

June 9, 2015

FC007

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

Overview

Timeline

- Start: July 2009
- End: September 2015
- % complete: ~95%

Budget (\$K)

DOE Cost Share	Recipient Cost Share	TOTAL
9,816	868	10,684

Budget (\$K)

FY 2014	782
FY 2015	650

Barriers

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

Partners – Principle Investigators

Oak Ridge National Laboratory (ORNL) – Dave Cullen

University of Delaware (Delaware) – Yushan Yan

Colorado School of Mines (CSM) – Dave Diercks, Svitlana Pylypenko

Tanaka Kikinokogyo (TKK) – Fumiaki Ogura
GM – Anusorn Kongkanand

Past project collaboration denoted in gray – not included in FY 15 work scope to date.

Current (year) collaboration denoted in black

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 / 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-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, H₂ at 200 sccm and N₂ 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 H₂/N₂ 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.

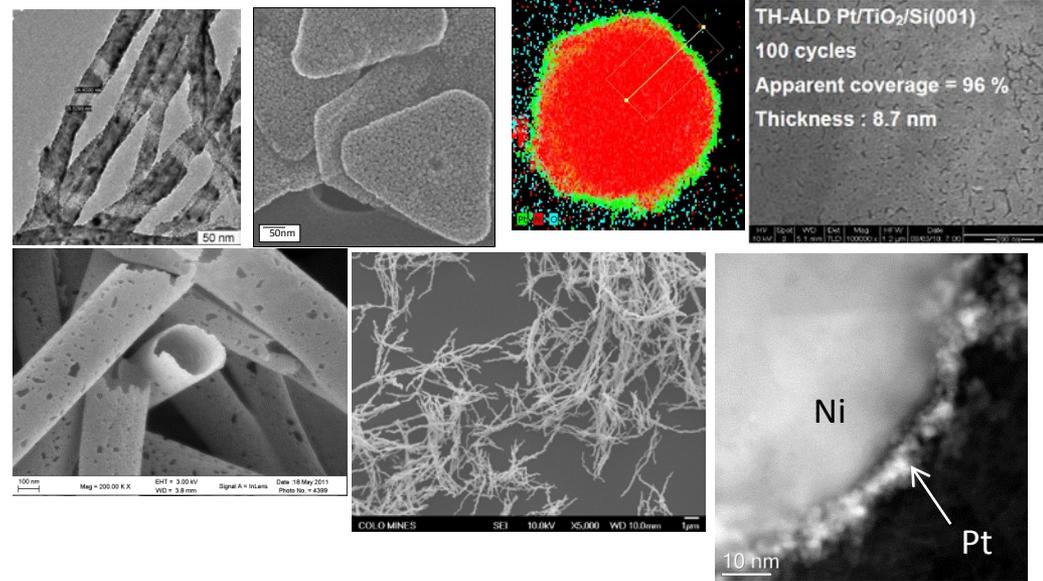
^e Test at 80°C H₂/O₂ in MEA; fully humidified with total outlet pressure of 150 KPa; anode stoichiometry 2; cathode stoichiometry 9.5 (as per Gasteiger et al. Applied Catalysis B: Environmental, 56 (2005) 9-35).

Approach

Extended Thin Film Electrocatalyst Structures (ETFECS)/ Electrodes

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

Current focus is on Pt/Co and Pt/Ni nanowires, due to demonstrated performance. Focus on post-processing (annealing and acid leaching) and ALD synthesis.

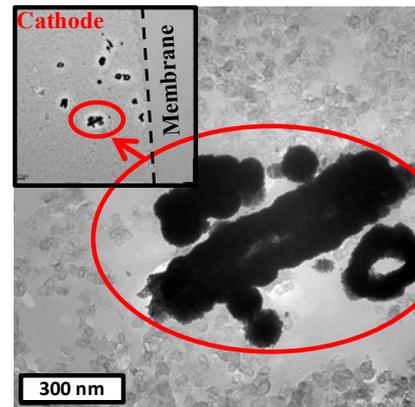


TH-ALD Pt/TiO₂/Si(001)
100 cycles
Apparent coverage = 96 %
Thickness : 8.7 nm

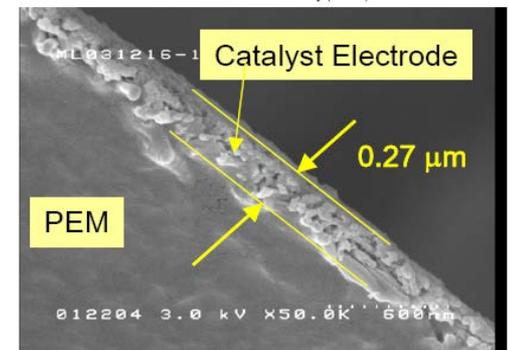
Efforts to translate catalytic improvements demonstrated in RDE studies over to fuel cells.

Multiple catalysts tested in MEAs.
Multiple fabrication techniques, operating conditions, and compositions investigated. (optimization studies)

NREL ETFECS



3M NSTF



http://www.hydrogen.energy.gov/pdfs/review04/fc_4_debe.pdf

Approach

Project Milestones

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q3	6/30/2014	Go/No-Go	Validate annealing as a potential route for improved mass activity and/or durability (No go if mass activity gain is less than 10% of unannealed samples and durability gain is less than 25% compared to unannealed samples.)	Go Decision
Q4	9/30/2014	Stretch	Demonstrate fuel cell performance using novel electrocatalysts of 0.44 A/mg Pt @900 mV (IR free) (DOE 2020 Target).	Unmet (stretch milestone)

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q2	3/31/2015	Annual Milestone (Regular)	Using pre-leaching on top performing novel electrocatalysts to reduce transition metal dissolution impact on durability, demonstrate a mass activity of 880 mA mgPt ⁻¹ at 0.9V (2x DOE 2020 Target) and less than a 5% loss after durability testing (30k cycles, mass activity) in RDE tests with a total transition metal dissolution of less than 1% of initial catalyst mass (current high performance materials experience dissolution rates up to 7 mass% under these conditions).	Complete
Q3	6/30/2015	Annual Milestone (Stretch)	Aligned with DOE's 2020 targets, 1,000 mW/cm ² at rated power and less than 40% loss in catalytic activity, develop MEAs with 100% improvement in initial mass activity when compared to baseline Pt/C catalysts at rated power (5 A/mgPt at 0.75V IR corrected) using novel electrocatalysts. Demonstrate less than 40% loss of mass activity at rated power (0.75 V IR free) 80°C, 100% RH after 30,000 potential cycles between 0.6 and 1.0V at 500mV/s.	On track

Accomplishments and Progress

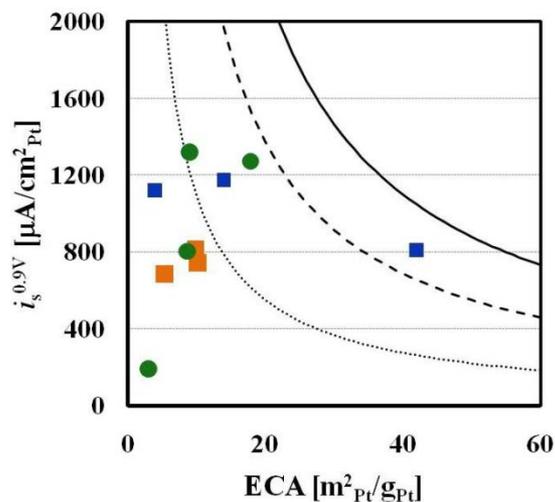
Responses to Previous Year (2014 AMR) Reviewer's Comments

- **Reviewer Comment:** It is still unclear if it is real to make both durable and highly active Pt-coated Ni nanowires. Ni nanowires are not stable when partially coated with Pt, and they are not very durable while fully coated with Pt.
- **Reviewer Comment:** The study on the oxide layer does provide good insights into the effect of oxidation of the catalyst. However, this was not the best area on which to focus the resources of last year. The effects of oxide layers on catalysts are relatively well known in the literature. They do provide protection for the non-oxidized part of the catalyst, but they are temporary layers that get dissolved again during low potentials.
- **Response:** Multiple comments addressed our prior year's work investigating an oxide layer and the value of this effort, and concerns about obtaining durable catalysts with high mass activity. This year's presentation contains current year results where both highly active and highly durable materials have been demonstrated. For our current, best of class materials, an O₂ annealing step, has been a critical post-processing step to increase durability and activity. It is unlikely we would have gained the insight of the potential importance and benefit of such a step without these past oxide studies.
- **Reviewer Comment:** The approach certainly has its merits, because it focuses on increasing available active sites on the catalyst. However, it is not clear how this would help reduce degradation, which is currently the main problem with catalysts...does not provide certainty that the catalyst will be durable in an MEA under automotive conditions (e.g., including start-up/shutdown cycles).
- **Response:** This comment suggests an activity connection only between ECA and durability, where extended surface materials can also have significant deviation from nanoparticle based materials even at high ECA due to a reduction in low coordination sites, and to the potentially reduced impact of dissolution/re-precipitation and agglomeration in extended surface catalysts. We have investigated durability for both Pt/dissolution and start/stop conditions and found advantages of our extended surface catalysts in both cases.
- **Reviewer Comment:** One critical point is that progress toward developing high-activity MEA electrodes is not nearly as advanced and remains a key barrier.
- **Response:** Agreed. Materials demonstrated/developed prior to this year didn't have intrinsic properties of both high activity and high durability. This made studying this area and progress more difficult. It remains a key challenge for taking advantage of these highly promising materials.

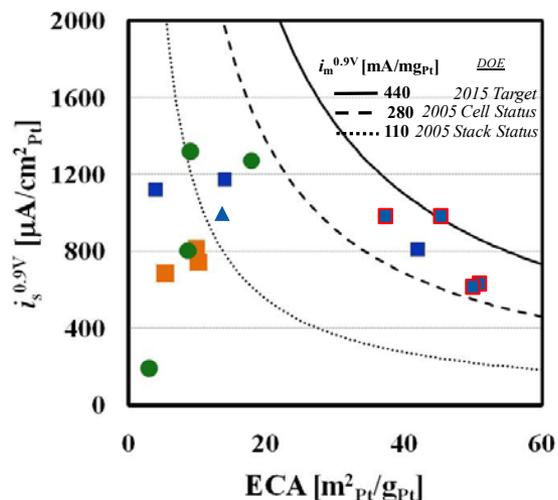
Accomplishments and Progress

Achieving high mass activity – Galvanic displacement (2014 AMR)

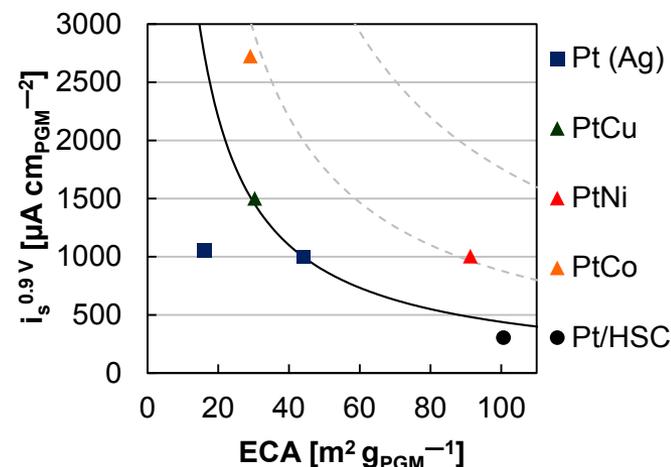
2011



2012



2013

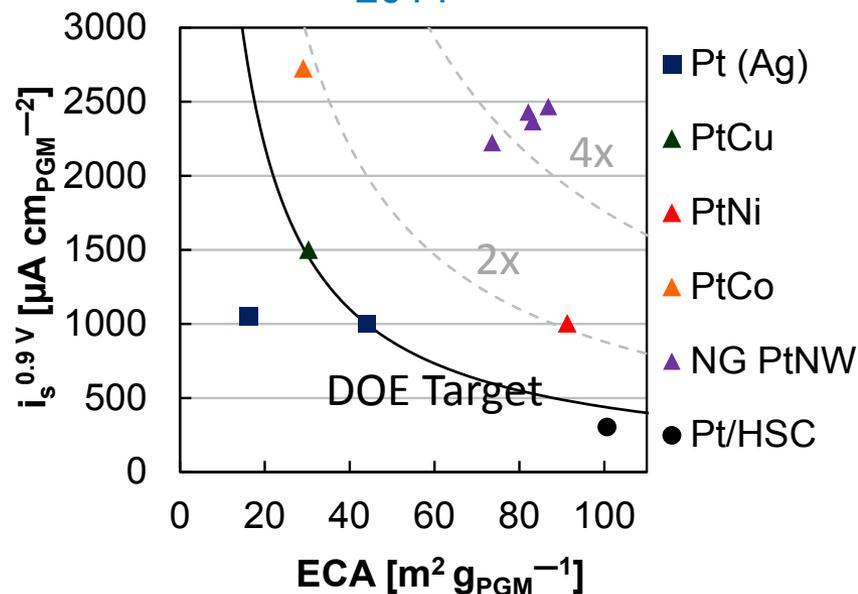


Electrochemically available surface area (ECA) has been limited in extended surface materials to low values ($\sim 10 \text{m}^2/\text{g Pt}$), we have reach ($\sim 90 \text{m}^2/\text{gPt}$ comparable to Pt/C)

Our efforts have seen consistent increases in both ECA and specific activity (i_s).

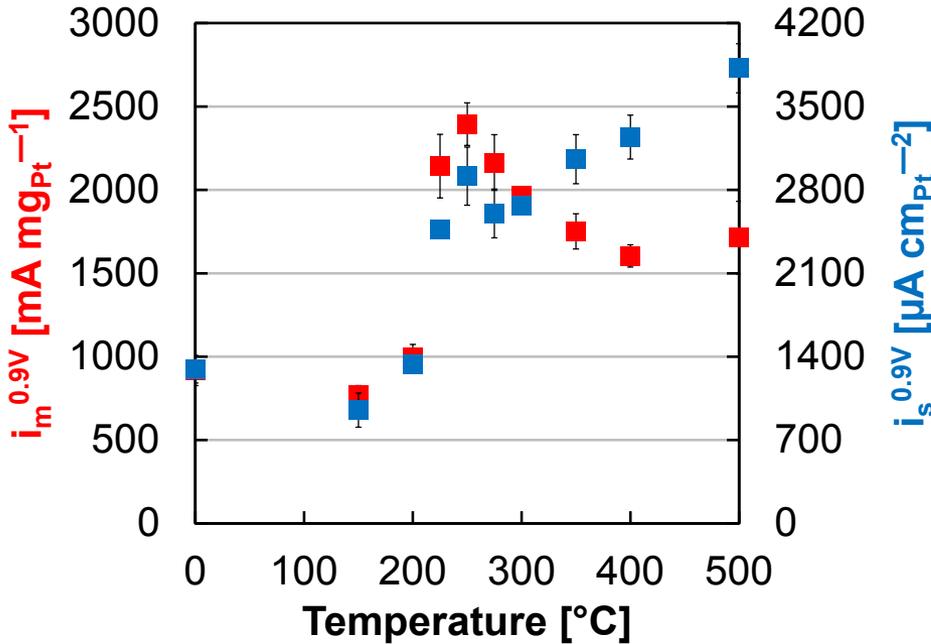
We have recently achieved both high ECA and i_s (resulting in exceptionally high mass activity, $\sim 5\text{x}$ DOE 2020 MEA target in RDE test). 2014 materials exhibited durability concerns related to transition metal ion leaching.

2014



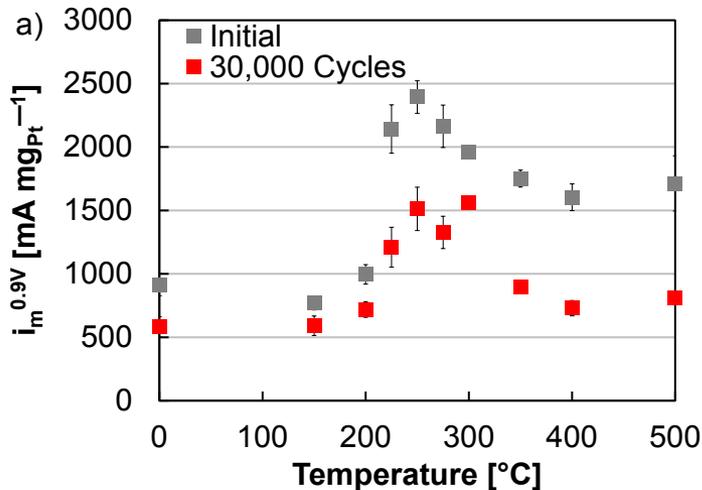
Accomplishments and Progress

Optimizing H₂ annealing for mass activity

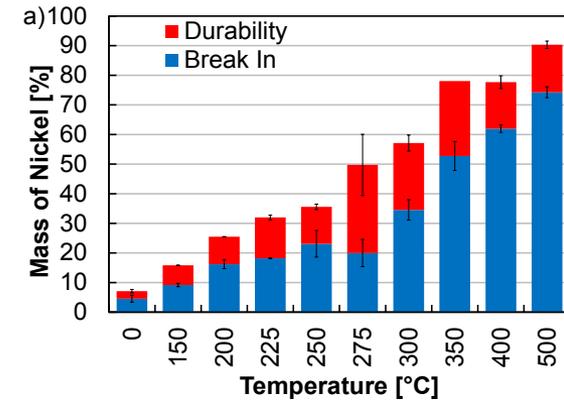


Annealing in a reducing atmosphere (H₂) was investigated/optimized to promote alloying thereby increasing activity.

Specific activity increased with increasing temperature. Mass activity peaked at 250°C, as Pt surface area (ECA) dropped above 250°C.



Highly performing samples showed durability losses following potential cycling (RDE, 30k cycles, 0.6-1.0V, 500 mV s⁻¹).



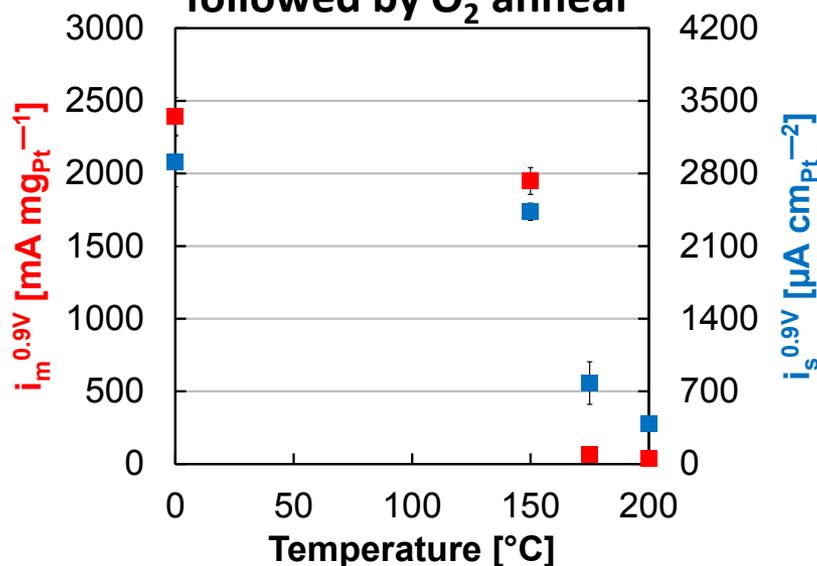
Ni dissolution rates increased with increasing annealing temperatures.

Highly active samples show poor durability, durable samples show lower activity.

Accomplishments and Progress

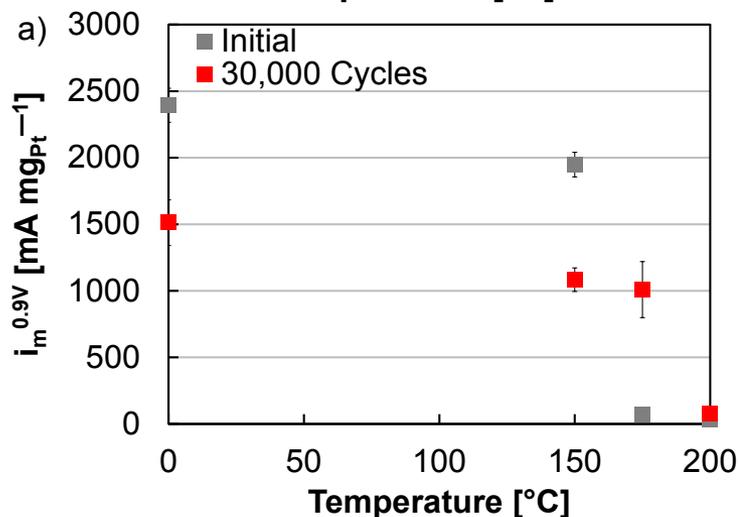
Addressing durability concerns of transition metal ion contamination

250°C H₂ anneal
followed by O₂ anneal

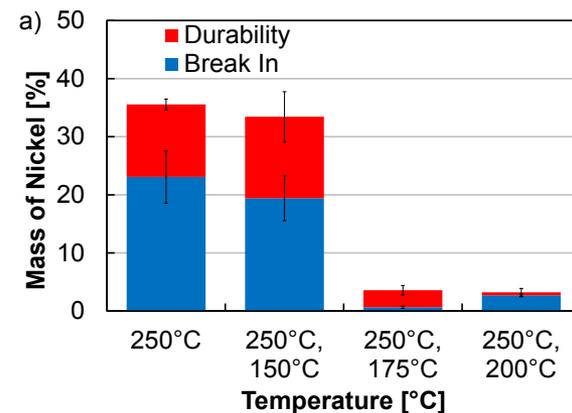


Multiple approaches/steps investigated, focus on annealing (oxidizing and/or reducing conditions) and acid leaching, efforts build on work presented previously.

O₂ anneal resulted in major losses in performance when applied above 150°C.



At 175°C performance improved significantly post cycling.



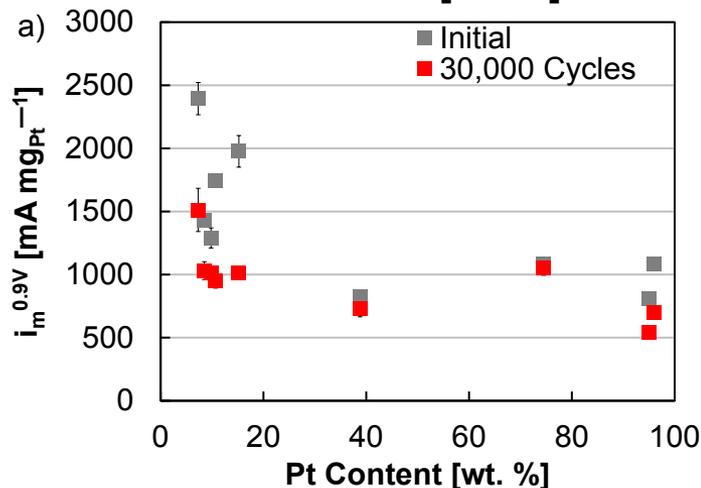
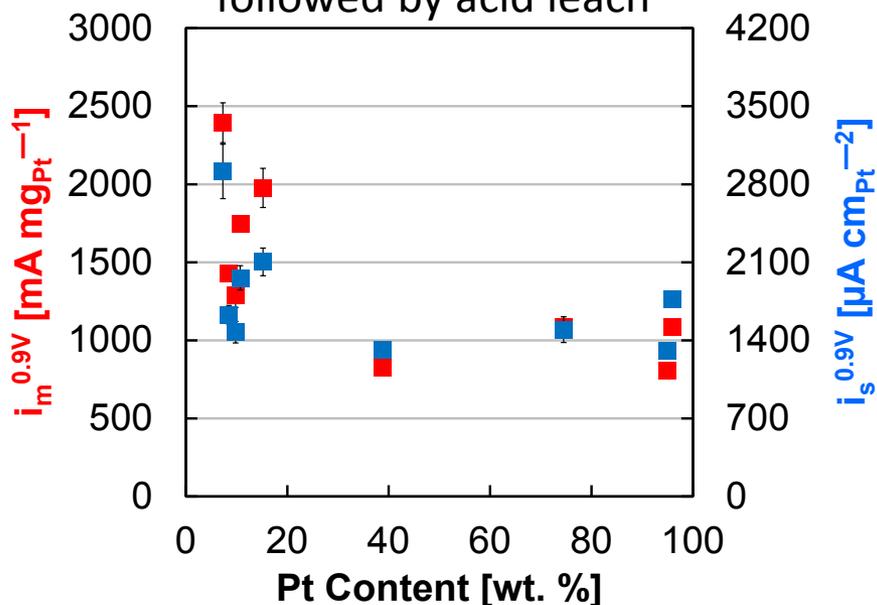
Ni dissolution rates decreased substantially above 150°C.

Highly active samples show poor durability, durable samples show lower activity.

Accomplishments and Progress

Addressing (Improving) durability concerns of transition metal ion contamination

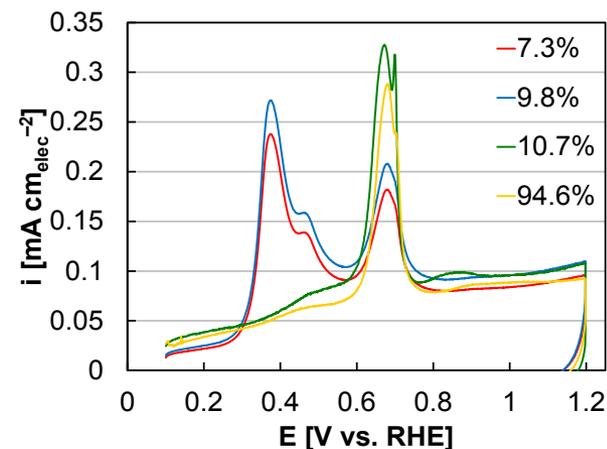
250°C H₂ anneal
followed by acid leach



Durability improved for samples with increased Pt wt%.

Acids of different types, concentrations, and exposure times were used to pre-leach transition metal (Ni⁺) ions from catalysts.

Decreasing performance (primarily due to specific activity loss) found as increasing leaching strength (increased Pt wt%)

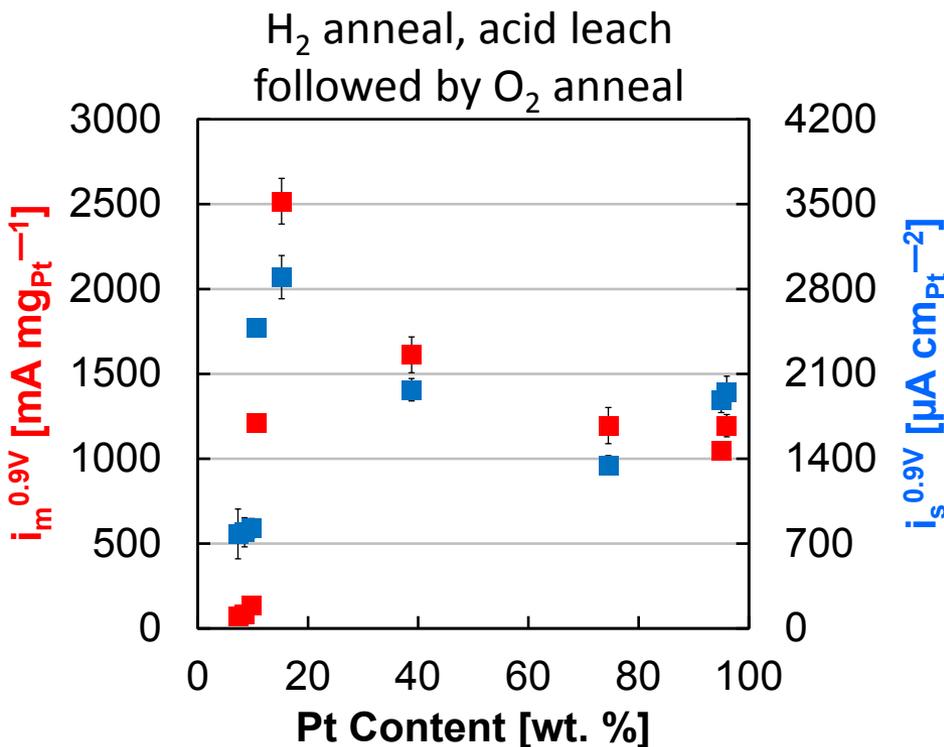


Below 10 wt% Pt, CO stripping shows presence of surface Ni.

Highly active samples show poor durability, durable samples show lower activity.

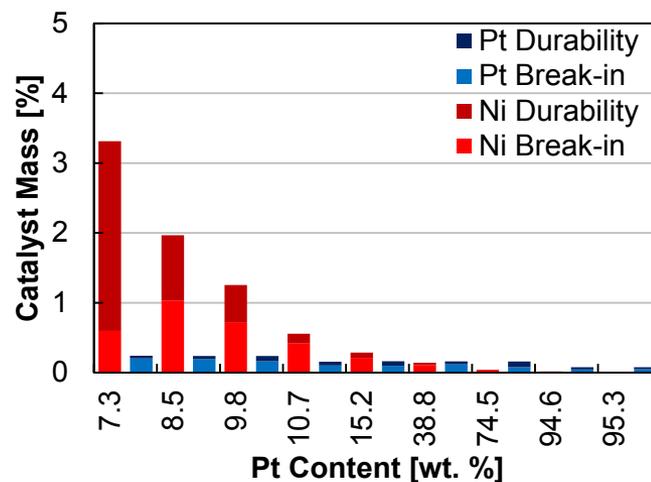
Accomplishments and Progress

Addressing (Improving) durability concerns of transition metal ion contamination



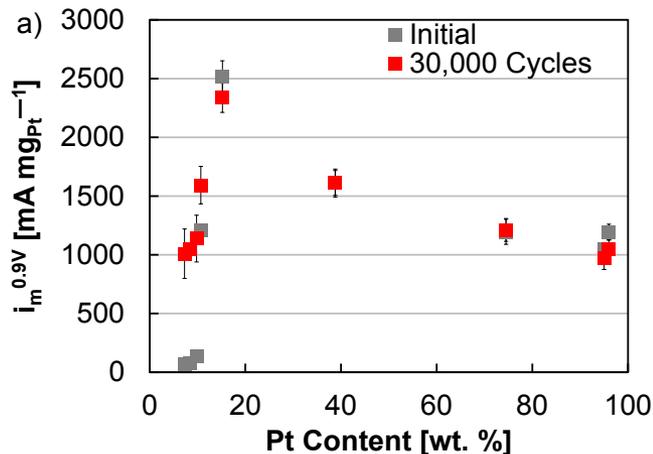
O₂ annealing was applied to acid leached samples to explore durability improvements.

O₂ annealing post-acid leaching resulted in high mass activity samples at higher Pt wt%. Ni contamination reduced at higher Pt content.



Exceptional durability demonstrated for potential cycling.

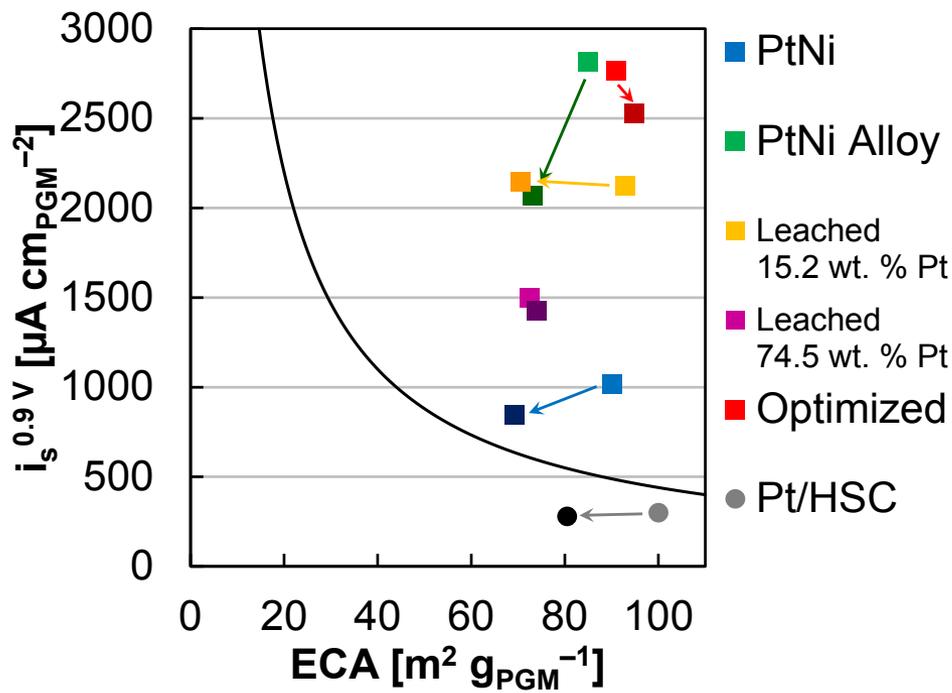
Above 10 wt% Pt, metal dissolution rates are very low.



Highly active samples also show high durability !!!

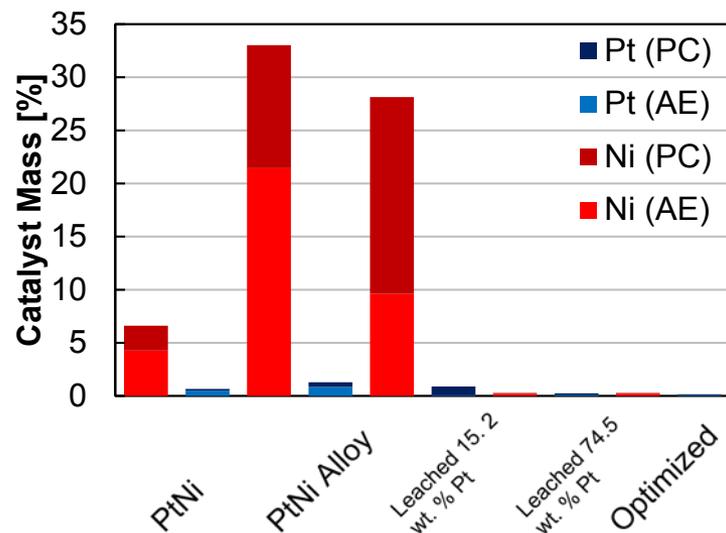
Accomplishments and Progress

Galvanic displacement PtNiNW performance summary/comparison



Initial performance and performance after cycling shown for a series of different PtNiNW catalysts. Current generation materials show improved performance and durability.

Leached and optimized samples also show low losses of Pt and Ni through electrochemical tests and enabling MEA fabrication without transition metal leaching concerns.

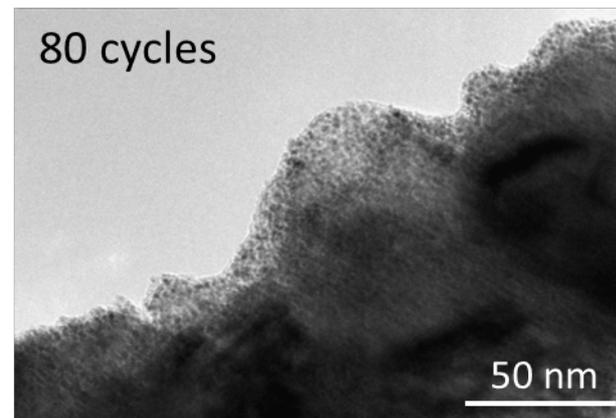
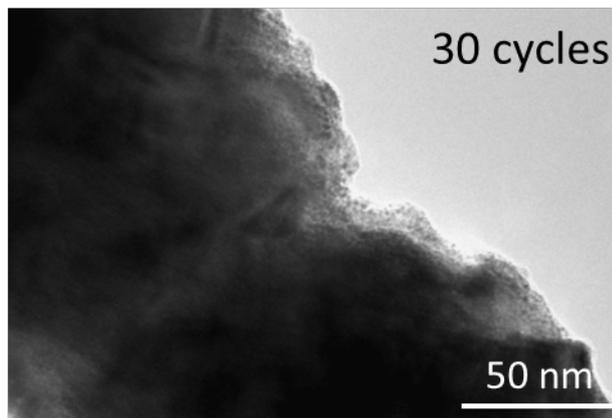
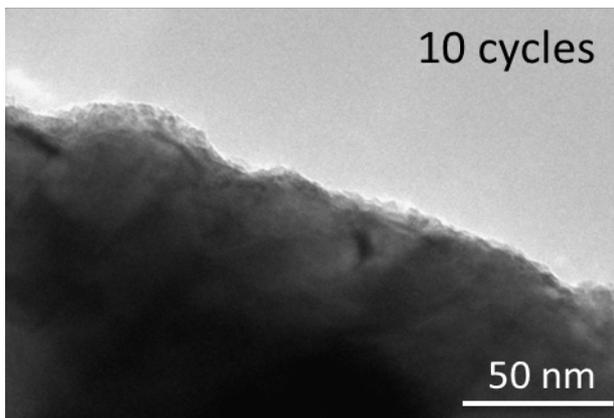
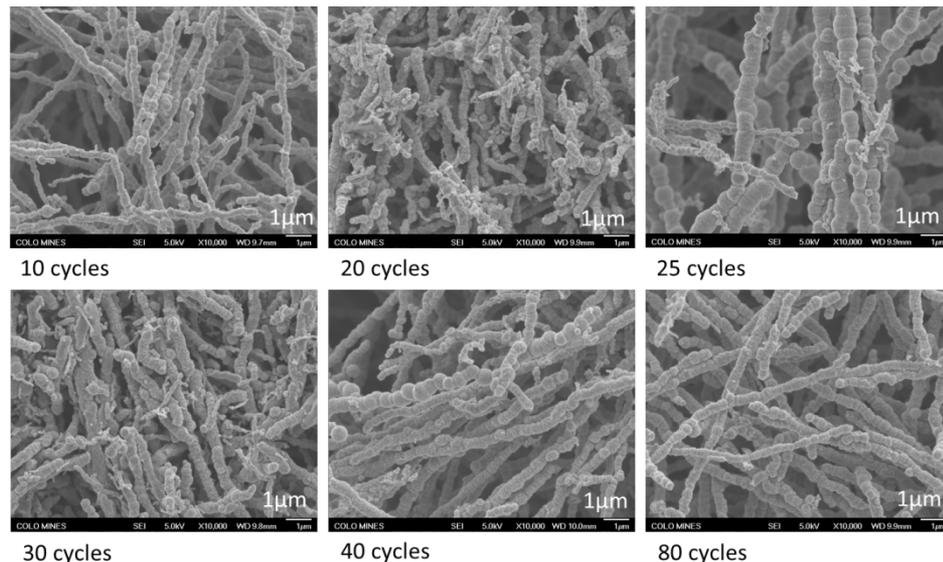


Accomplishments and Progress

Investigation of Atomic Layer Deposition (ALD) for Pt alloy NW synthesis

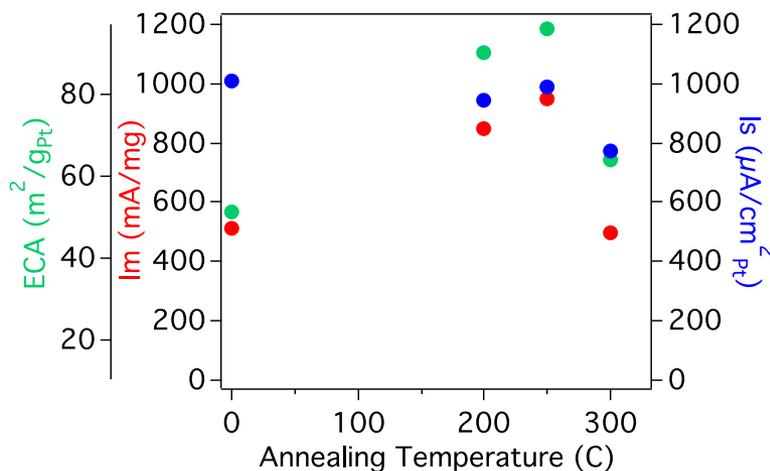
- Batch sizes of several (perhaps 100's of) grams synthesized easily with our equipment
- Synthesis much quicker and easier
- Higher reproducibility expected
- Target structures and processing steps already optimized by galvanic displacement
- Have investigated ALD reaction conditions for O_2 exposure and subsequent H_2 annealing of materials.

Morphologies and structures obtained similar to galvanic displacement and uncoated Ni NWs.

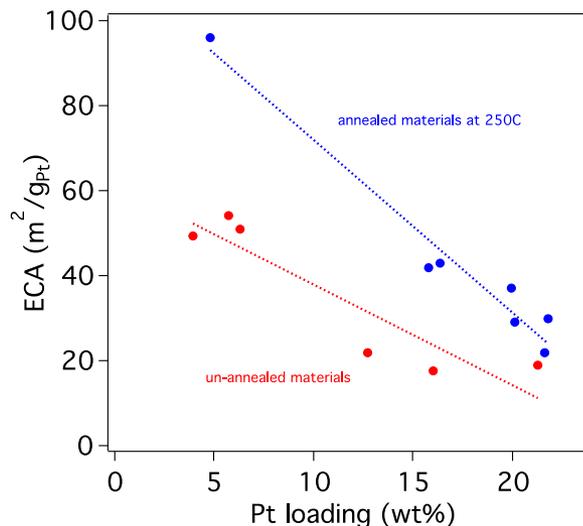


Accomplishments and Progress

Investigation of Atomic Layer Deposition (ALD) for Pt alloy NW synthesis

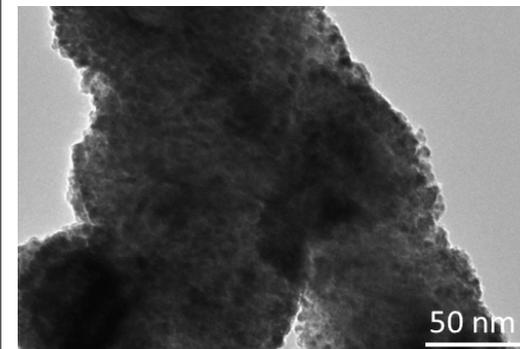


Annealing temperature of 250°C found to be optimal in limited temperature study, consistent with galvanically displaced samples.

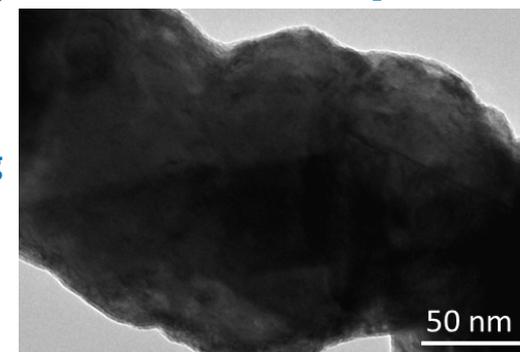


H_2 annealing found to dramatically increase surface area (ECA), >90 m^2/g Pt achieved.

Pt on Ni – 60 ALD cycles



Pt on Ni – 60 ALD cycles H_2 annealed



Current approach (non-agitated samples) has resulted in intra- and inter-batch heterogeneity.

80 cycles -4 different batches

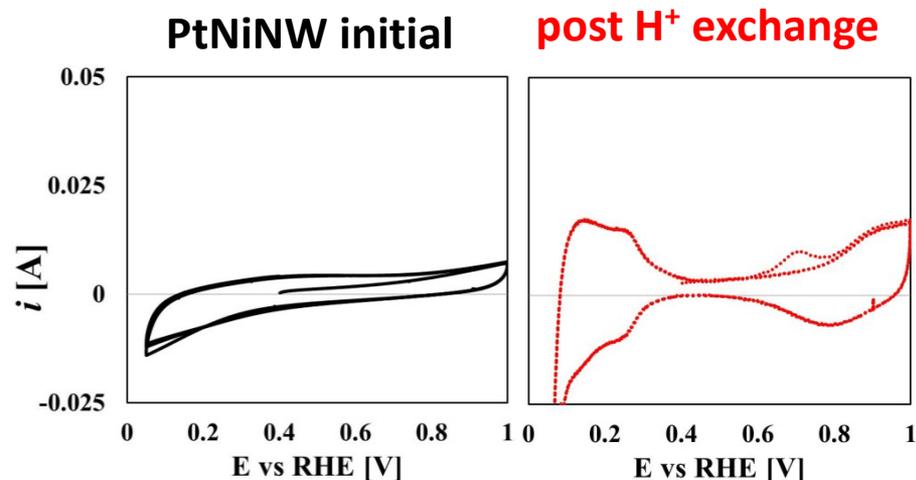
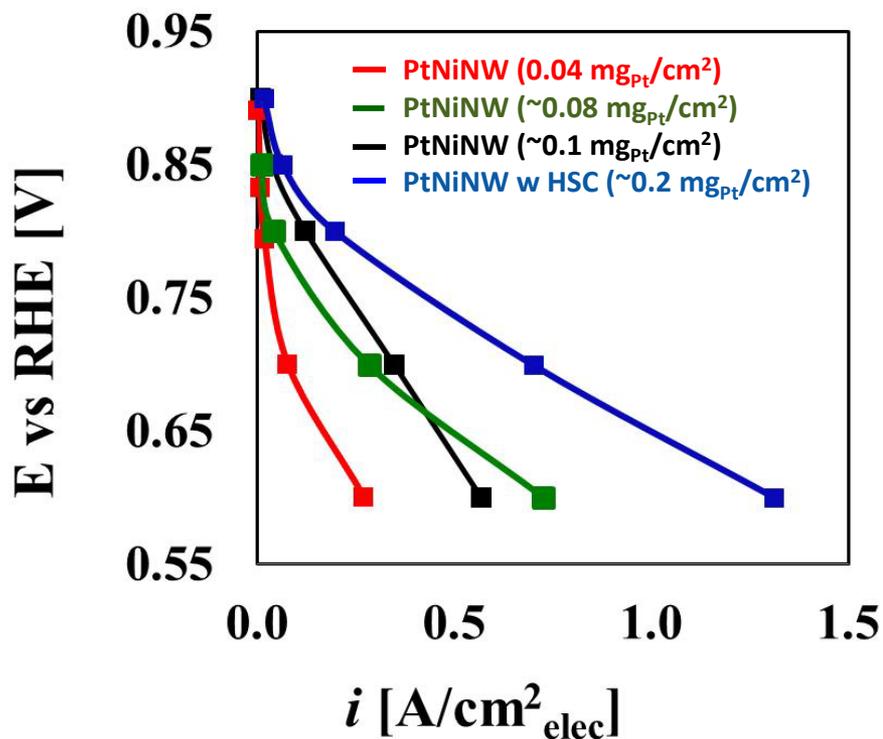
I_s ($\mu A/cm^2_{Pt}$)	I_m (mA/mg _{Pt})	ECA (m^2/g_{Pt})
2134	879	41
1921	426	22
1549	444	29
1814	663	37

Annealing found to smoothen surface (decrease roughness), but also resulted in increased Pt ECA.

High ECAs obtained, specific activity still lower than galvanic displacement.

Accomplishments and Progress

Optimization of ETFECS fuel cell performance (2014 AMR)



Transition metal ion leaching was a problem for this generation of materials and required an acid wash step after MEA fabrication to remove nickel ion contamination from the MEA.

Successive tests of related materials yielded continuous improvements in performance as we have improved our MEA fabrication techniques and optimized compositions.

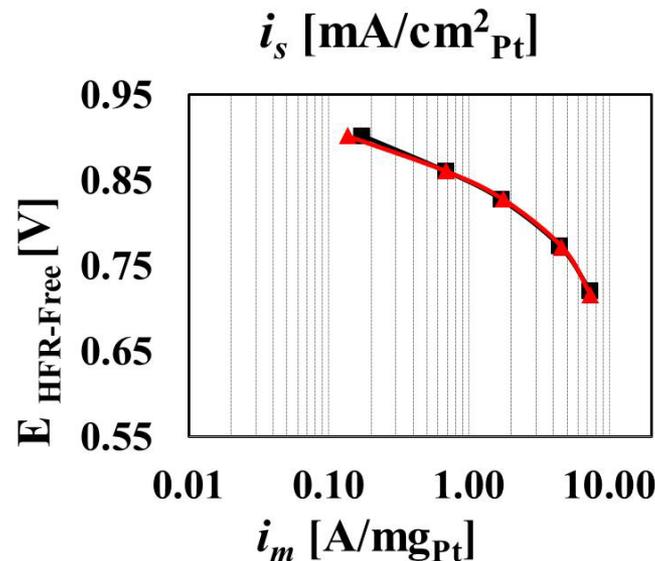
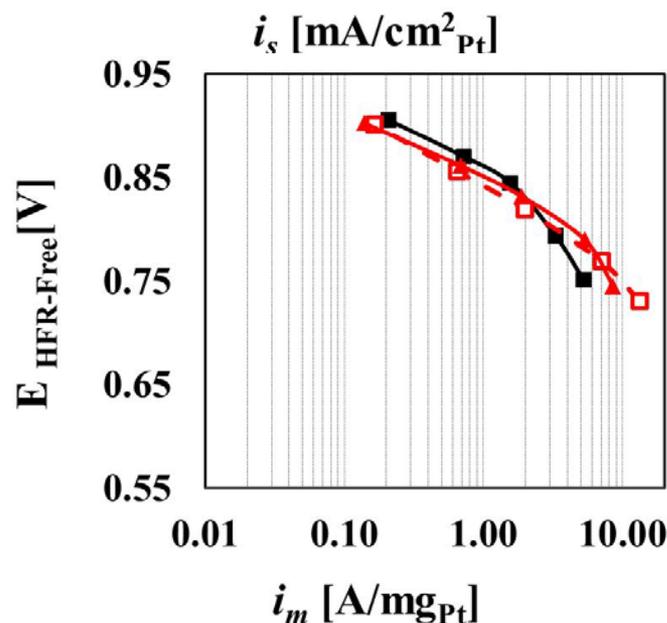
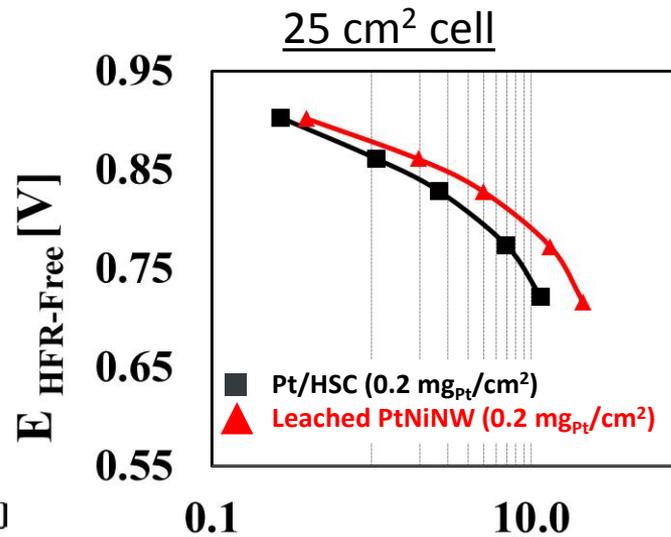
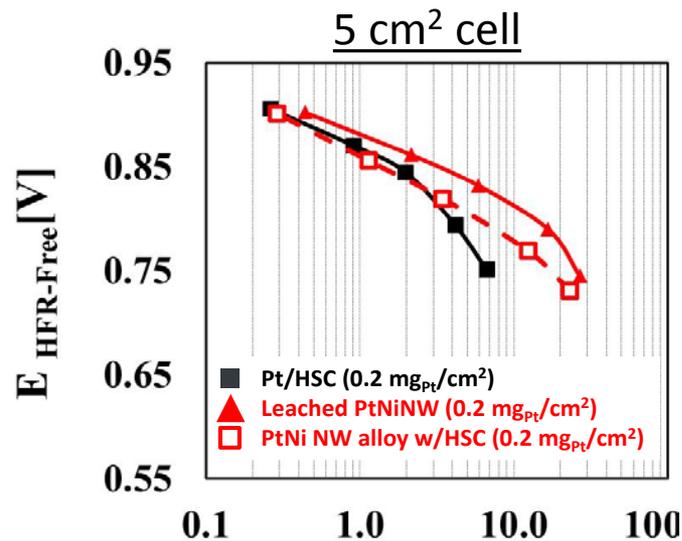
Accomplishments and Progress

ETFECS fuel cell performance

MEA performance of PtNiNWs showed similar performance and higher specific activity when compared to Pt/C baseline MEAs. Leached PtNiNWs did not require an acid wash step and was demonstrated in 5 and 25 cm² cells.

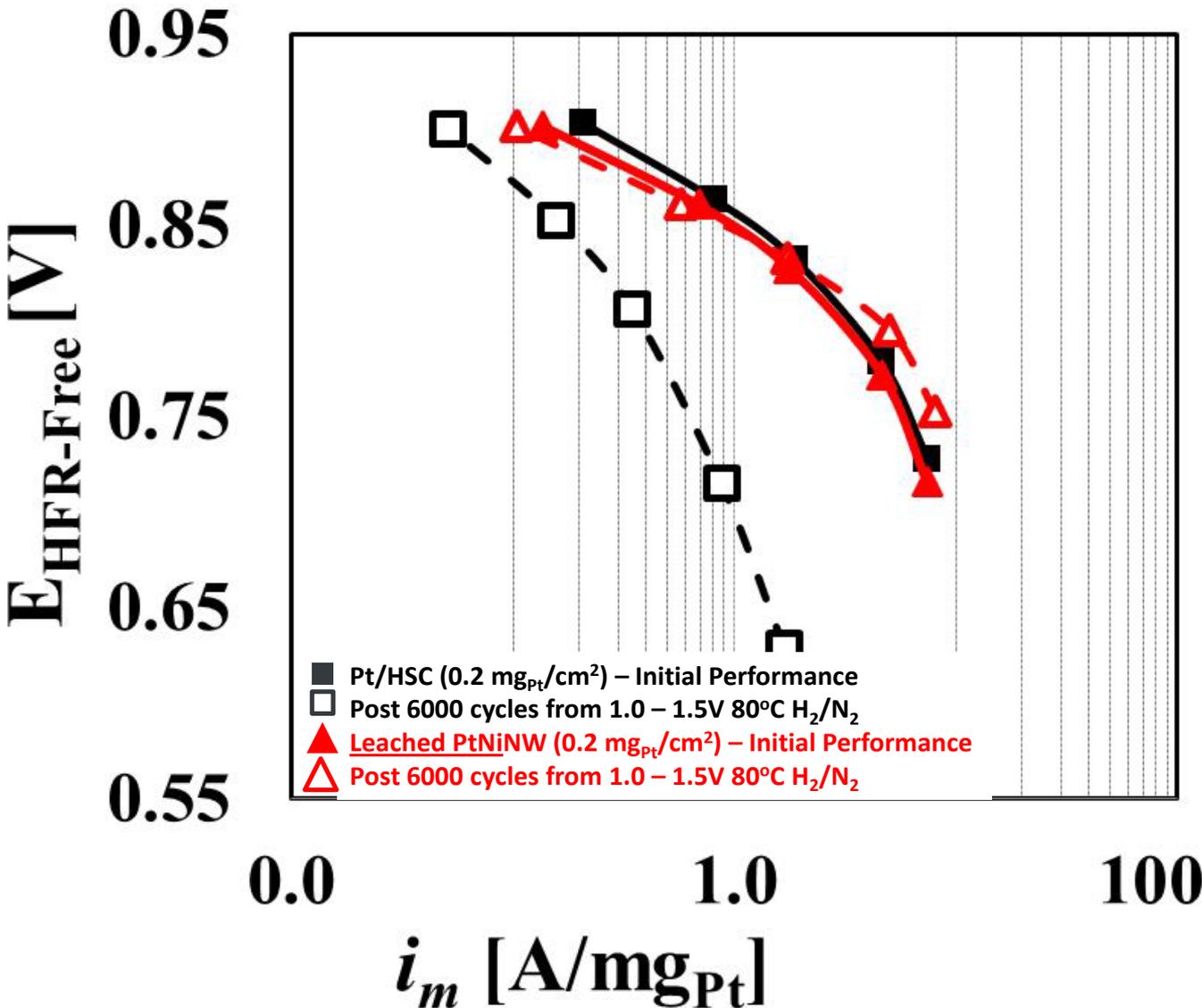
Determination of optimum synthesis conditions had limited MEA tests. Optimized catalyst scaled up and focus of current tests.

5 cm² single serp. 80°C 100% RH 150 kPa
 H₂/O₂ Constant E, 15 min per point
 25 cm² triple serp. 80°C 100% RH 150 kPa
 H₂/O₂ constant E, 15 min per point



Accomplishments and Progress

ETFECS fuel cell durability



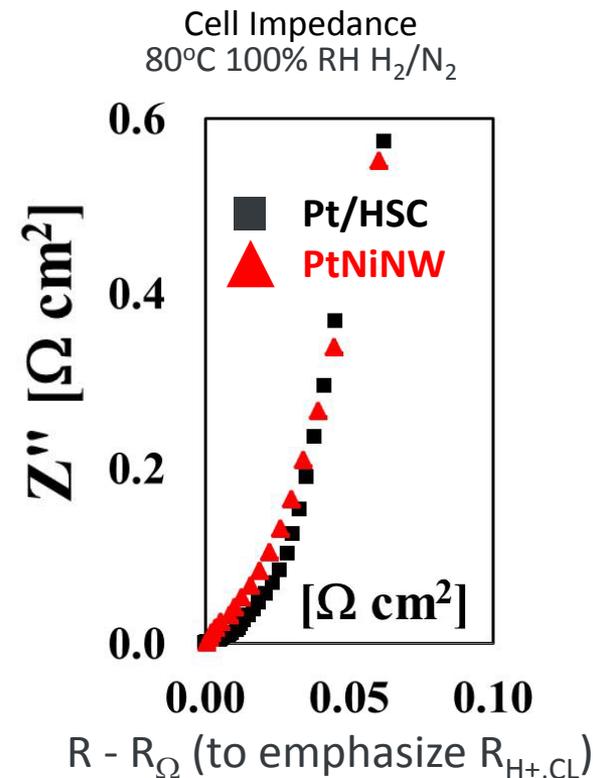
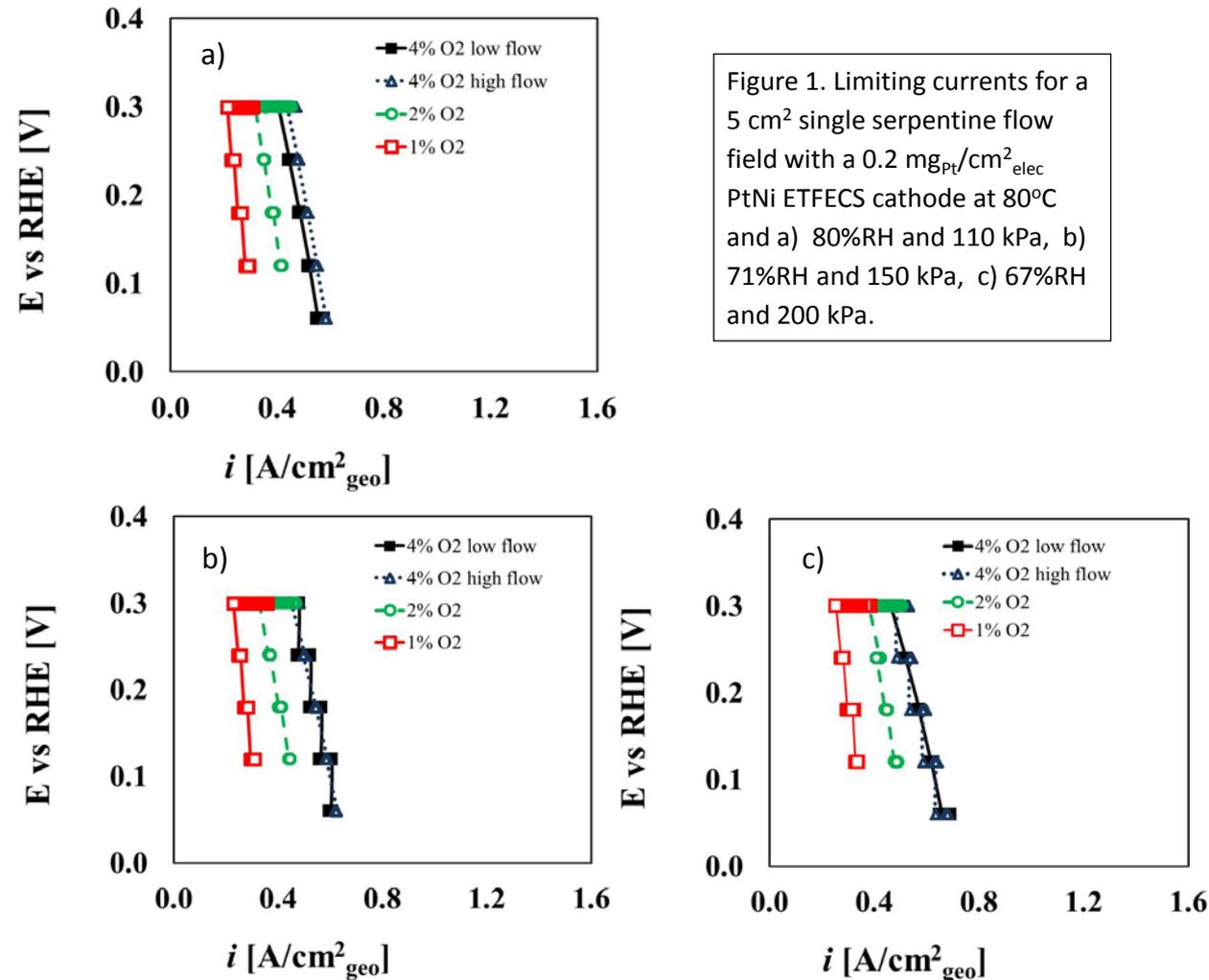
PtNiNWs show greatly improved stability compared to Pt/C when studied with potential cycling between 1-1.5V.

Results not particularly surprising due to the absence of carbon in the PtNiNW samples.

25 cm₂ triple serp. 80°C 100% RH 150 kPa H₂/O₂ constant E, 15 min per point

Accomplishments and Progress

Fuel cell diagnostics oxygen limiting current experiments and impedance



Oxygen limiting current measurements have been made on PtNiNWs. This data will be used to elucidate oxygen transport resistance local to the Pt surface. It will be investigated as a function of electrode fabrication conditions (ionomer/catalyst ratio, loading, carbon loading), and compared to Pt/C results to understand and minimize transport resistance.

Cell impedance has been used to determine H⁺ resistance of the catalyst layer (R_{H+,CL}) inside of PtNiNW electrodes and compare this to Pt/C electrodes. For the cases shown 12 μm Pt/C electrodes (30 wt% Nafion) shows similar R_{H+,CL} to 2 μm PtNiNW electrodes (10 wt% Nafion)., tradeoff between thickness and ionomer content. Further PtNiNW studies are underway.

Accomplishments and Progress

Summary of MEA vs RDE results

Catalyst	MEA			RDE		
	ECA	$i_s^{0.9V}$	$i_m^{0.9V}$	ECA	$i_s^{0.9V}$	$i_m^{0.9V}$
	$[\text{m}^2_{\text{Pt}}/\text{g}_{\text{Pt}}]$	$[\mu\text{A}/\text{cm}^2_{\text{Pt}}]$	$[\text{mA}/\text{mg}_{\text{Pt}}]$	$[\text{m}^2_{\text{Pt}}/\text{g}_{\text{Pt}}]$	$[\mu\text{A}/\text{cm}^2_{\text{Pt}}]$	$[\text{mA}/\text{mg}_{\text{Pt}}]$
47 wt% Pt/HSC	83	263	216	100	275	275
Pt Black (decal)	21	270	56	22	800	176
PtCo [co-deposited]	14	1050	150	17	2200	370
PtCrCo [co-deposited]	21	550	115	26	1800	470
Pt-AAO template (Decal)	10	340	34	8	1250	100
Pt-AAO template (Filter)	7	400	28			
PtNi (Filter)	55	76	41	56	1200	660
NGPtNW	57	290	165	69	2600	1800
NGPtNW (pre-leached)	45	440	200	69	1900	1300

MEA data versus RDE data show reasonable agreement between ECA values for all except NGPtNW (this electrode is much thicker than others 60 μm vs 10 μm). Specific activity values at 0.9V for transition metal containing samples show greater decreases in MEA values versus RDE than Pt only samples.

Collaborations

Institutions	Role
<u>National Renewable Energy Laboratory (NREL):</u> Bryan Pivovar (PI), Shaun Alia, KC Neyerlin, Katie Hurst, Jason Zack, Clay Macomber, Shyam Kocha	Prime, Oversees the project, lead catalyst synthesis and characterization; lead electrode fabrication and fuel cell testing
<u>University of Delaware (Delaware):</u> Yushan Yan, Jarrid Wittkopf	Sub; Support work in catalyst synthesis by galvanic displacement
<u>Colorado School of Mines (CSM):</u> Svitlana Pylypenko, Dave Diercks, Ami Neyerlin, Jeremy Leong	Sub; Materials characterization using XPS and microscopy, electrospinning of polymers.
<u>General Motors LLC (GM):</u> Anusorn Kongkanand	In-kind partner; Consultation on transition metal impacts, fuel cell performance, and MEA fabrication

Interactions: Related collaborative work with SLAC (Mike Toney) and Colorado University (Will Medlin) Participation in the DOE catalysis working group Past year(s) project participants have included LANL, CNSE, Stanford, Tennessee, NTCNA, Cabot.

Future Work/Remaining Challenges

Electrocatalyst synthesis:

Focus on reproducibility/increased batch size.

Galvanic displacement to produce materials of target performance in increased quantity.

Further post-processing studies of ALD synthesized materials, use of rotary to improve intra- and inter- batch reproducibility.

Electrode structure/fuel cell studies:

Optimization of electrode structure/fuel cell performance using ETFECS with a focus on catalyst ink dispersions and composition.

Isolation of overpotential losses in MEA electrodes made with ETFECS materials (separation of mass transfer, ohmic, and kinetic losses).

Durability studies to quantify performance loss with specific emphasis on transition metal leaching.

Summary

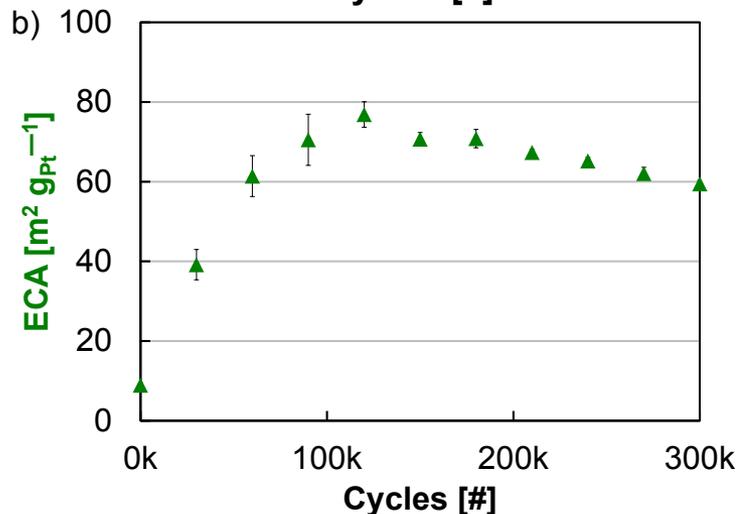
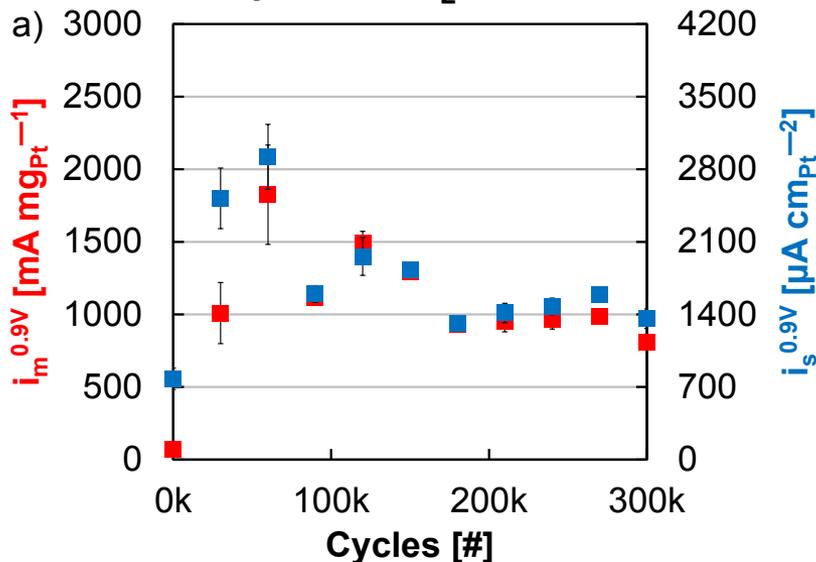
- **Relevance:** Focused on overcoming the cost, performance and durability barriers for fuel cell commercialization by increasing Pt mass activity and durability.
- **Approach:** Developing durable, high mass activity extended surface Pt catalysts , and optimize MEA performance/durability for these materials.
- **Accomplishments and Progress:** The project has demonstrated extended surface catalysts with remarkably high surface area and specific activity that offer the potential to dramatically decrease required Pt loadings through exceptionally high mass activities (>2500 mA/mg Pt). These materials have also demonstrated good durability under select (potential cycling, both RDE and MEA) conditions, including dramatically reduced transition metal dissolution rates. The project has advanced the performance of these materials in MEAs and demonstrated the need for further understanding and development in these areas.
- **Collaborations:** We have a diverse team of researchers including 2 universities, and 1 industrial participant.
- **Proposed Future Research:** Fuel cell efforts are focused on optimized electrode structures of complex catalysts.

Technical Backup Slides

Accomplishments and Progress

Addressing durability concerns of transition metal ion contamination

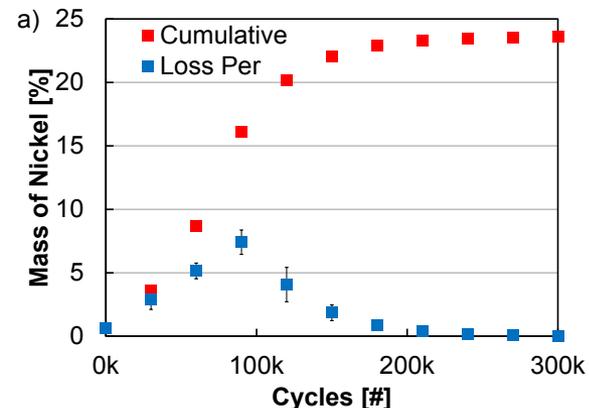
250°C H₂ anneal followed by 175°C O₂ anneal



Extended durability (RDE) investigated to study recovery of previous high activity.

Specific activity and mass activity improve for this highly oxidized sample, presumably due to removal of Ni oxide species from the surface, up to 100k cycles.

ECA shows initial increase with cycle number as well (RDE, 30k cycle experiments, 300k cycles in total, 0.6-1.0V, 500 mV s⁻¹).



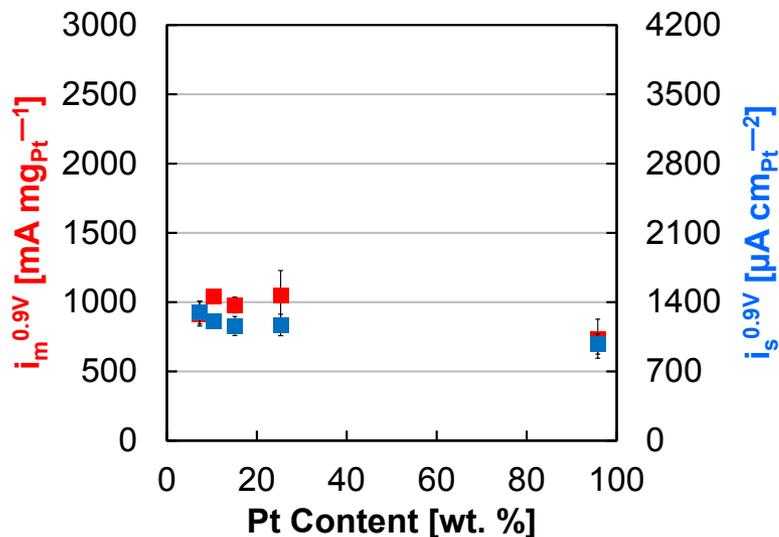
Ni dissolution levels off after several successive durability tests.

Material reaches peak activity following 60k cycles, and is fairly stable above 200k cycles.

Accomplishments and Progress

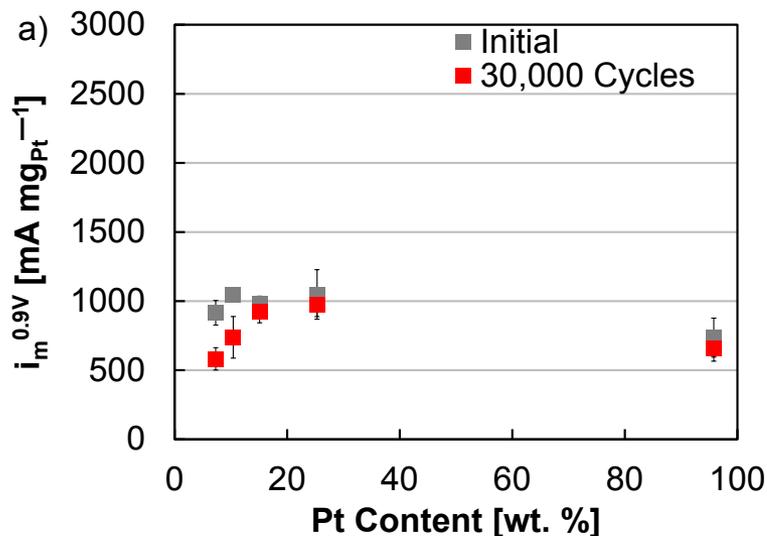
Addressing durability concerns of transition metal ion contamination

Acid leach



Acids of different types, concentrations, and exposure times were used to pre-leach transition metal (Ni⁺) ions from catalysts.

Modest performance changes witnessed when only acid leaching was performed.



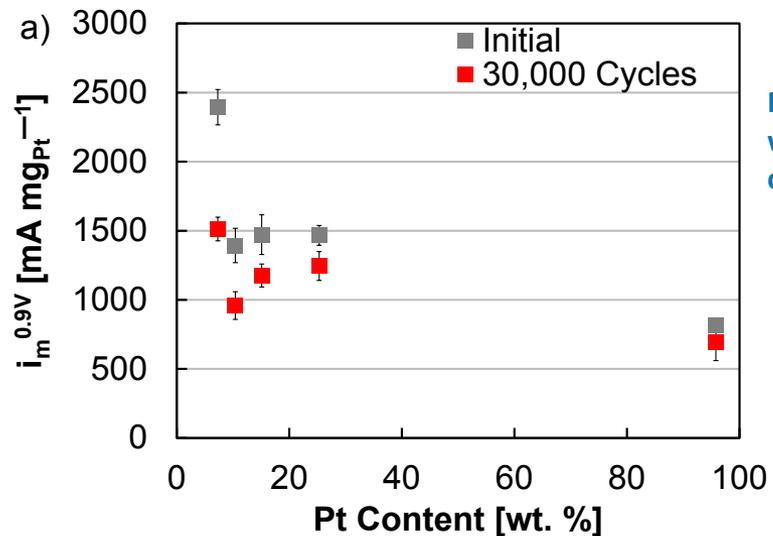
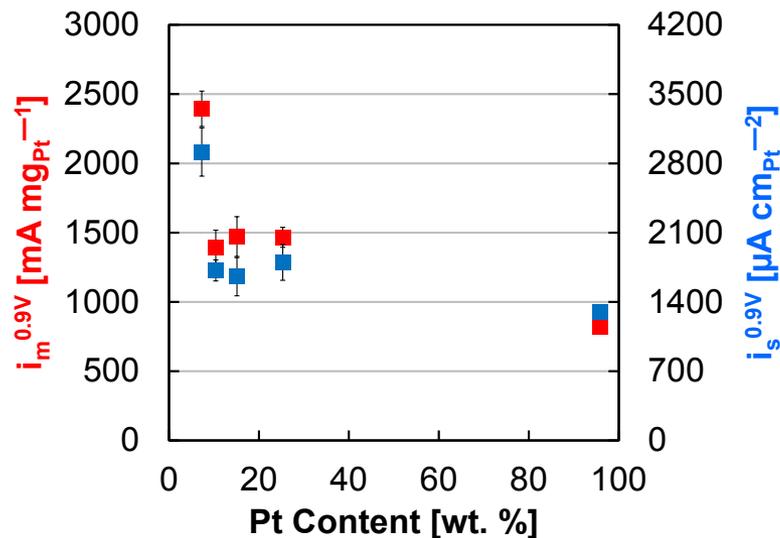
Low leaching levels showed slightly decreased durability results.

Sample activities consistent regardless of Ni content. Durability improved with Ni leaching.

Accomplishments and Progress

Optimizing H₂ annealing for mass activity

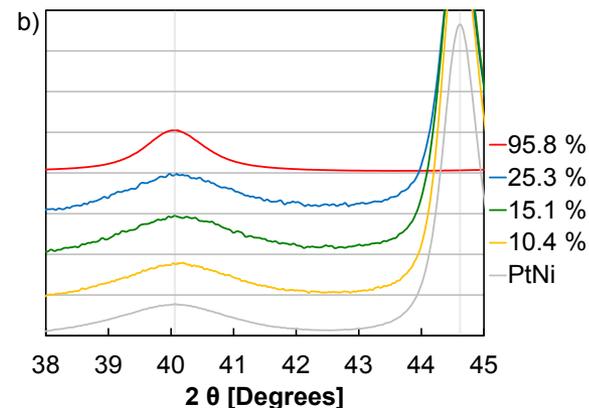
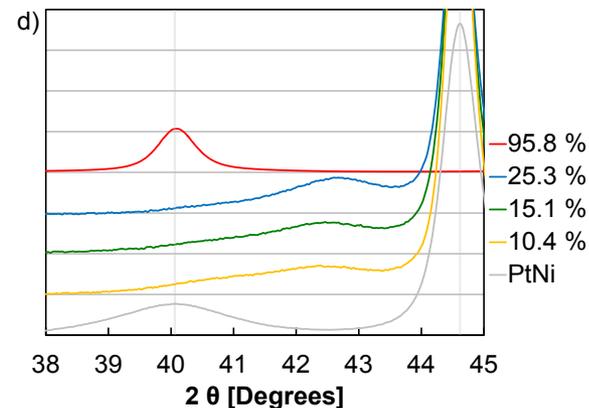
Acid leach followed by
250°C H₂ anneal



Durability decreased
with increasing Ni
content.

Annealing in a reducing atmosphere (H₂)
was investigated/optimized to promote
alloying thereby increasing activity.

Pt lattice
compression
less severe
at higher Pt
content.

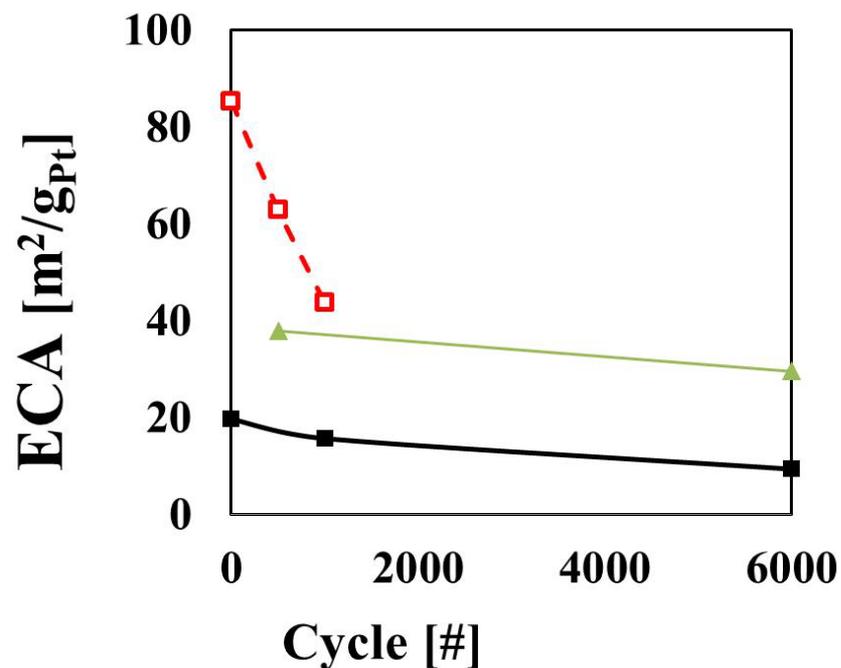
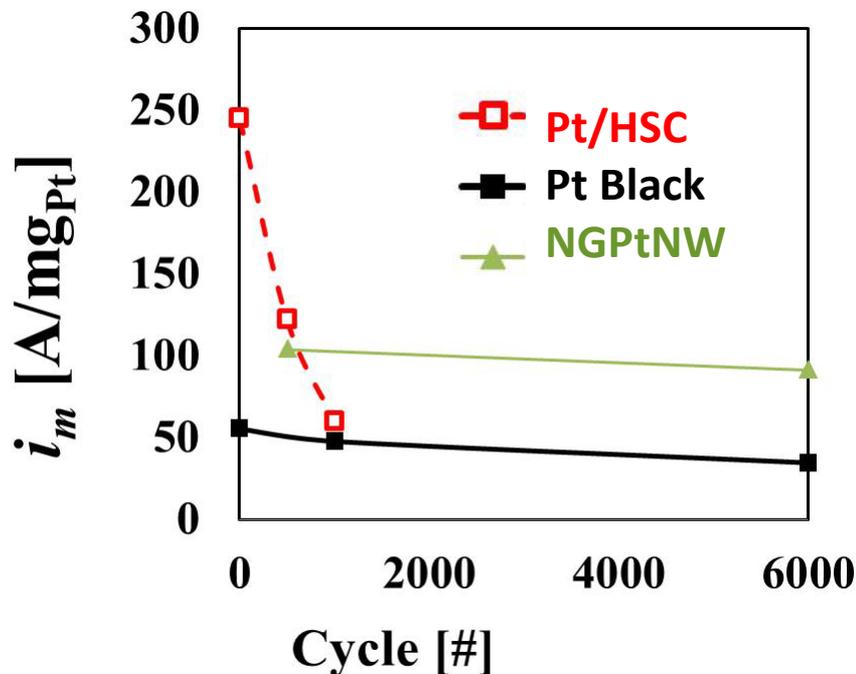


Increasing Ni removal resulted in lower activity
following H₂ anneal, improved durability.

Accomplishments and Progress

Fuel cell accelerated stress tests (support corrosion)

1-1.5V @ 500 mV/sec, 80°C, 100%RH, H₂/N₂



Conditions for all fuel cell data reported: 80°C, 150 kPa, 100 %RH – (47 kPa P_w, 100 kPa gas pressure) – 0.2 mg_{Pt}/cm²

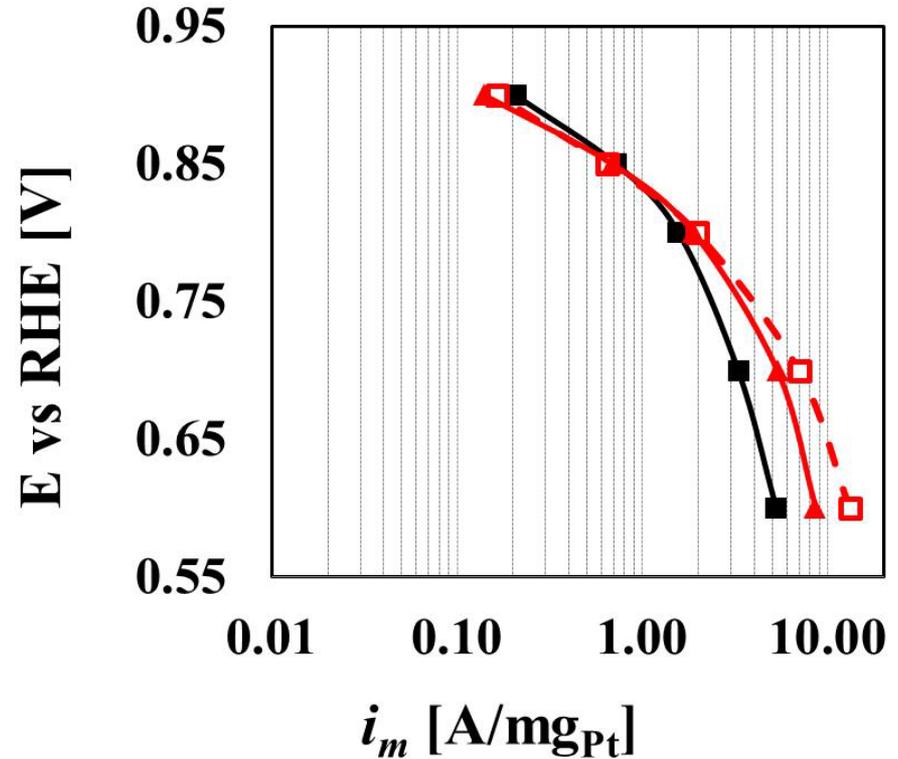
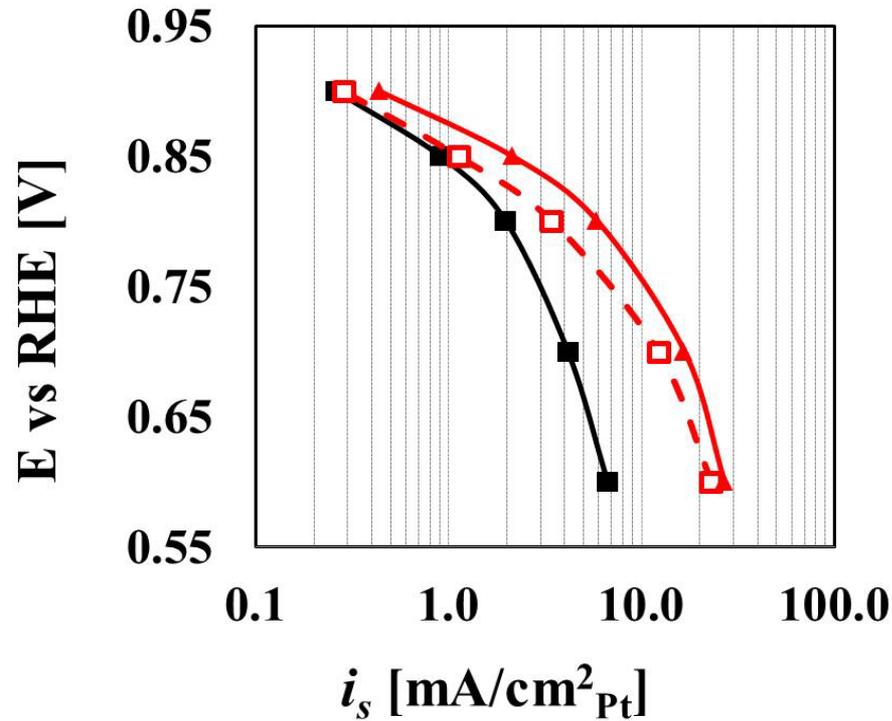
15 min per point (0.6, 0.7, 0.8, 0.85, 0.9V)

ECA @ 35°C 150 kPa, 100 %RH, 150/100 sccm H₂/N₂ (100mV/sec)

High potential, support corrosion cycling experiments (for start-stop conditions) showed promising results in terms of retained performance compared to Pt/C. Our most advanced catalyst showed higher performance and improved durability compared to Pt black under identical conditions.

Present Year Accomplishments and Progress

Optimization of ETFECS fuel cell uncorrected performance - (5 cm²)

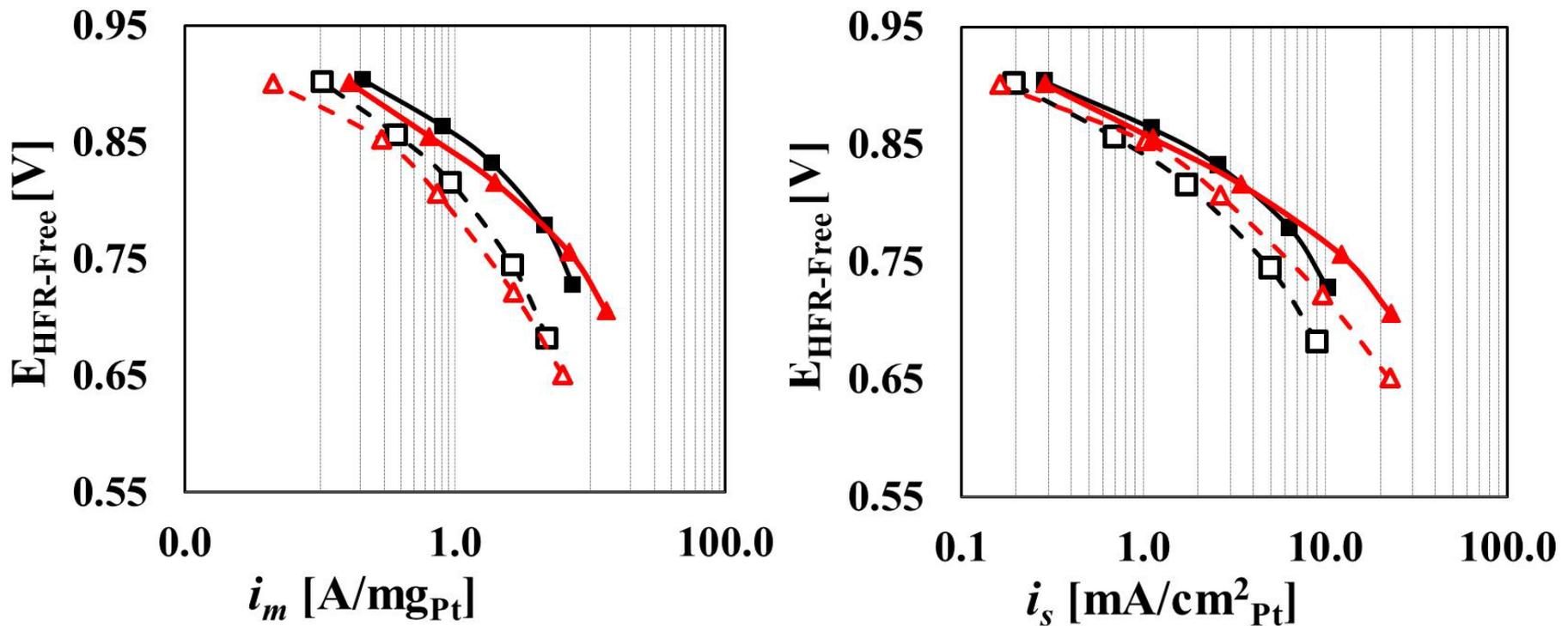


- Pt/HSC (0.2 mg_{Pt}/cm²)
- ▲ Pre-treated PtNi (0.2 mg_{Pt}/cm²)
- PtNi w/HSC (0.2 mg_{Pt}/cm²)

5 cm₂ single serp. 80°C 100% RH 150 kPa H₂/O₂
Constant E, 15 min per point

Accomplishments and Progress (25 cm²)

ETFECS fuel cell durability – effect of carbon incorporation



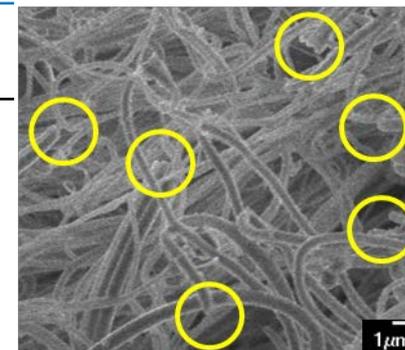
- Pt/HSC (0.2 mg_{Pt}/cm²) – Initial Performance
- Post 1000 cycles from 1.0 – 1.5V 80°C H₂/N₂
- ▲ PtNi w HSC (0.2 mg_{Pt}/cm²) – Initial Performance
- △ Post 1000 cycles from 1.0 – 1.5V 80°C H₂/N₂

25 cm₂ triple serp. 80°C 100% RH 150 kPa
H₂/O₂ constant E, 15 min per point

Accomplishments and Progress

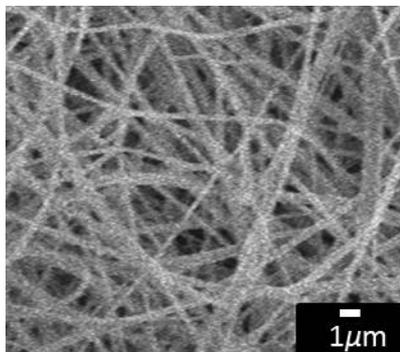
Electrospinning of polymer nanowires for electrode incorporation

Samples	Electric Field (kV/cm)	Observation	Diameter (nm)
Nafion (20 wt PAA)	10/15	Fiber mat	340 ± 4
Fractured Nafion ^a	10/15	Fiber mat	466 ± 38
Fractured Nafion after dispersed in solution ^b	10/15	Partially dissolved	-
PFSA (2 wt PEO)	10/15	Fiber mat	173
Fractured PFSA ^a	10/15	Fiber mat	316
Fractured PFSA after dispersed in solution ^b	10/15	Partially dissolved	-

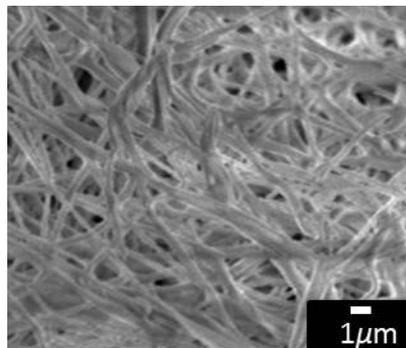


Fractured Nafion

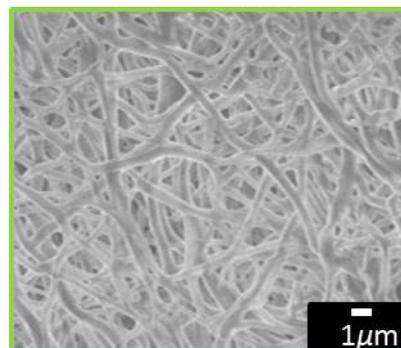
Electrospinning of Nafion has been undertaken in order to provide ionic pathways through electrodes without requiring complete catalyst coverage of Pt sites (looking to take advantage of conduction properties of extended surface electrocatalysts). Fibers have been spun and fractured at liquid N₂ temperatures. Annealing has been employed to improve solvent tolerance.



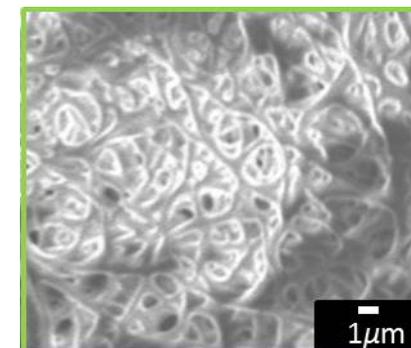
PFSA
(2 wt PEO)



No thermal treatment
before dispersing in H₂O



Annealing at 110°C
before dispersing in H₂O



Annealing at 140°C
before dispersing in H₂O
* Structure is altered at 140°C