

Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes



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Overview

Timeline

- •Start: July 2009
- •End: September 2014
- •% complete: ~95%

Barriers

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

Budget (\$K)

DOE Cost Share	Recipient Cost Share	TOTAL
9,166	868	10,034

	Budget (\$K)
FY 2013	1949

782

Partners – Principle Investigators

Oak Ridge National Laboratory (ORNL) – Dave Cullen Los Alamos National Laboratory (LANL) – Rangachary Mukundan University of Delaware (Delaware) – Yushan Yan State University of New York – Albany (CNSE) – Eric Eisenbraun Stanford University (Stanford) – Stacey Bent University of Tennessee (Tenn) – Tom Zawodzinski Colorado School of Mines (CSM) – Dave Diercks, Svitlana Pylypenko Nissan Technical Center North America* (NTCNA) – Nilesh Dale Cabot Fuel Cells* (Cabot) – Paolina Atanassova Tanaka Kikinzoku Kogyo* (TKK) – Fumiaki Ogura GM – Anusorn Kongkanand

Past project collaboration denoted in gray, Current (year) collaboration denoted in black

FY 2014

Review Period Objectives:

• Pt catalysis remains a primary limitation for fuel cells. We have pursued synthesis of novel <u>extended thin film electrocatalyst</u> 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	Unito	2011 Status	Targets					
Characteristic	Units	2011 Status	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				

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

 M. Debe, U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Merit Review Proceedings, May, 2011, (<u>http://www.hydrogen.energy.gov/pdfs/review11/fc001_debe_2011_o.pdf</u>)

- ⁵ 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 (<u>http://www.uscar.org/commands/files_download.php?files_id=267</u>), 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 (<u>http://www.uscar.org/commands/files_download.php?files_id=267</u>), 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.

- Past years focused on several routes, these have been down-selected to most promising.
- Current focus is on Pt galvanically displaced samples from Co and Ni templates, due to demonstrated performance.



Increased 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



Approach Project Milestones (FY 14)

Qtr	Due Date	Туре	Milestones, Deliverables, or Go/No-Go Decision	Status
Q1	12/31/2013	Regular	For oxygen annealed samples using extended structure electrocatalysts in rotating disc electrodes demonstrate an initial performance of > .660 A/mg Pt @900 mV (IR free) (a 50% increase over the DOE 2020 Target), and <30% loss in initial mass activity (25 % improvement on DOE 2020 Target	Completed on time
Q2	3/31/2014	Regular	Aligned with DOE's 2020 target, develop MEAs using novel electrocatalysts that show less than 10% mass activity loss in electrocatalyst support stability tests	Completed on time
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 unannealled 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).	

Achieving high mass activity – Galvanic displacement



Responses to Previous Year (2013 AMR) Reviewer's Comments

- **Reviewer Comment:** While the initial design of the project was excellent, difficulties in growing real continuous layers (rather than aggregates of Pt nanoparticles) and in achieving the mass activity target have led the project into down-selects that make the remaining efforts essentially an investigation of Pt blacks, either unsupported (Pt/CoNW) or supported on a corrodible metal (Pt/NiNW), with limited structural control of the active Pt particle layer.
- **Reviewer Comment:** In other aspects, the progress of this project is disappointing. Real continuous layers, rather than clusters of nanoparticles, have not been achieved. Some of the structural control of the substrate that was achieved with the crystallographically defined Ag and Cu substrates has been lost in the shift to the less well-defined commercial Ni and Co nanowires. Only a modest start has been made in learning how to make effective MEA electrodes with catalysts other than the standard Pt/C or Pt alloy/C materials.
- **Response:** Both reviewers use the term 'real continuous layers', which on first inspection could be a logical, model system for the extended surface catalysts we have pursued. In our early consideration of the topic, we had shared a similar view of trying to obtain model catalyst systems with well controlled surface properties only to come to the realization that this was exceptionally difficult, that the surfaces obtained would have decreased surface area available, and they likely would not translate well to 3-d nanoparticles. While the current systems under study are less controlled (and therefore more challenging to study for fundamental properties/relationships), they have been able to achieve exceptionally high activities (suggesting ultra smooth surfaces with lower stability are not required) and are more scalable in their production routes.
- **Reviewer Comment:** There should be a focus on the oxide passivating layer on the Ni; it is unclear if it is a good thing (explaining the durability) or a bad thing (eliminating alloying and reducing performance). It is also unclear if it can be produced on the Co nanowires. There should be a big effort to get the fuel cell performance up. The structure of the catalyst layer needs to be fully addressed. It is possible that existing ink coating technologies are not going to work with these materials. This is a much longer-term activity that should perhaps be considered for a second phase of funding.
- **Response:** As we proposed in last years future work, we had a strong focus on the role of the oxide passivating layer in this year, investigating both pre- and post-galvanic displacement annealing impacts on structure and properties. These results clear show that oxidation can be used to improve resistance to corrosion, but it remains unclear if these improvements can be improved to a sufficient extent for use in durable fuel cells. We agree completely that the catalyst layer needs further study. This has become a much larger effort of our studies, and certainly merits additional investigation in our opinion.

PtNi/PtCo NWs Results (2013 AMR)

Both PtNi and PtCo NWs showed high mass activity, including after potential cycling.

Surprising differences in the way the two samples behaved.

Extent of reaction without added acid.

Durability upon exposure to

acid.







PtCo NWs – more in depth studies



"Full" Pt displacement of oxygen annealed Ni NWs

Oxidation treatment of Ni NWs results in decreased Pt displacement with increasing oxidation time (Ni oxide layer thickness), excess Pt supplied.

Performance decreased with increasing oxidation, little impact on durability.

XRD, XPS, and microscopy (including atom probe) have been used to probe the oxide layer.



10

8

6

4

2

0

Mass of Nickel [%]

Post-oxidation of partially displaced PtNi NWs

PtNi NWs were investigated for post oxidation and exhibited improved durability as the Ni oxide layer thickness was increased with thickness. Performance losses were observed in initial activity.



Durability improvements correlated to decreasing amounts of Ni leached from the catalyst during electrochemical breakin/durability and greater ECA retention.

Next generation Pt based NWs



Advances in synthesis and processing have resulted in a significant performance breakthrough with mass activities above 2200 mA/mg Pt.

This has been achieved through high specific activity and high ECA.

Durability remains a concern, but mass activity remains high even after potential cycling.



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.

Optimization of ETFECS fuel cell performance



0.55

0.05

0.50

 $i_m [A/mg_{Pt}]$

Successive tests of related materials have yielded continuous improvements in performance as we have improved our MEA fabrication techniques and optimized compositions. Specific and mass activity plots show shifts in activity and different voltage dependencies.

5.00

Summary of current ETFECS fuel cell performance vs RDE

	MEA			RDE			
Catalyst	ECA	i _s ^{0.9V}	i _m 0.9V	ECA	i _s ^{0.9V}	i _m 0.9V	
	$[m^2_{Pt}/g_{Pt}]$	[µA/cm ² _{Pt}]	[mA/mg _{Pt}]	$[m^2_{Pt}/g_{Pt}]$	[µA/cm ² _{Pt}]	[mA/mg _{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	36	254	91	69	2600	1800	

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

Impact of transition metal leaching



ETFECS fuel cell performance vs. Pt/C



Performance of NGPtNW when normalized for Pt mass or measured Pt surface area behaves differently than Pt/C, showing gains at higher current densities, perhaps due to the impact of transition metal ion related contaminants.

While removal of transition metal ions is a key focus, comparisons at 0.9V may penalize these materials.

0.65

 (\mathbf{r})

n

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (PI), Shaun Alia, KC Neyerlin, Arrelaine Dameron, Jason Zack, Jeremy Leong, C. 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, focus on oxide layer
Colorado School of Mines (CSM): Svitlana Pylypenko, Dave Diercks	Sub; Materials characterization using XPS, microscopy and atom probe techniques.
Oak Ridge National Lab (ORNL): Dave Cullen	Sub; High resolution microscopy and advanced sample preparation
Tanaka Kikinzoku Kogyo: Fumiaki Ogura	In-kind partner; Provide baseline catalyst material; Consultation on catalyst synthesis
General Motors LLC (GM): Anusorn Kongkanand	In-kind partner; Consultation on transition metal impacts and MEA fabrication

Interactions: Participate 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 durability and the role of transition metals.

- Continued investigation of oxide layer role in passivation of transition metal components.
- Selective removal of transition metals to limit impact of performance loss.

Fuel cell studies:

Optimization of fuel cell performance (ECA and is) 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, kinetic losses).

Durability studies to quantify and reduce impact of performance loss with specific emphasis on transition metal leaching.

Summary

- **<u>Relevance</u>**: 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 exceptionally high surface area and specific activity catalysts that offer the potential to dramatically decrease required Pt loadings through exceptionally high mass activities (>2200 mA/mg Pt), and demonstrated good durability under select (potential cycling, both RDE and MEA) conditions of these materials. The project has advanced the performance of these materials in MEAs and demonstrated the need for further understanding and development in this area.
- **<u>Collaborations</u>**: We have a diverse team of researchers including 2 national labs, 2 universities, and 2 industry.
- **Proposed Future Research:** Novel synthesis is focused on durability concerns of high performance transition metal containing materials. Fuel cell efforts are focused on optimized electrode structures of complex catalysts.

Technical Backup Slides

PtCoNWs – additional data and studies











Figure S.3. (a) Dark- and (b) bright-field STEM images of cross-sectioned PtCoNWs (5.5 wt % Pt). (c) Composite, (d) Co, (e) oxygen, and (f) Pt EDS maps of the same cross-section.

Figure S.4. (a) Dark- and (b) bright-field STEM images of cross-sectioned PtCoNWs (5.5 wt % Pt). (c) Composite, (d) Co, (e) oxygen, and (f) Pt EDS maps of the same cross-section.

Table S.1. XPS of CoNWs and PtCoNWs (wt. %, by ICP-MS). Compositions are presented in atomic percentage. Standard deviation denoted Std. Dev.

	CoNW	PtCo	PtCo	PtCo	PtCo	PtCo	PtCo
		2.1%	5.5%	8.4%	21.1%	31.5%	67.7%
Со	100	99.6	86	76.9	56.7	48.7	53.1
Pt	0	0.4	14	23.1	43.3	51.4	46.9
Std. Dev.	0	0.5	0.6	5.3	3.4	0.9	1.2

The core shell nature of the materials studied is obvious from microscopy.

XPS results compare surface compositions to bulk (ICP) compositions













Figure S.5. (a) Dark- and (b) bright-field STEM images of PtCoNWs (5.5 wt % Pt). (c) Composite, (d) Co, (e) oxygen, and (f) Pt EDS maps of the same cross-section.

PtNiNWs – Additional data on impact of oxidation pre-galvanic displacement



Figure S.6. Percentage of (a) Ni and (b) Pt originally on the working electrode in RDE half-cells lost intro the liquid electrolyte following electrochemical break in and durability testing. Percentages were determined by ICP-MS and data was presented as a function of annealing temperature. NiNWs were annealed in oxygen prior to attempting maximum Pt displacement. Durability testing was completed by potential cycling (0.6 - 1.0 V vs. RHE) 30,000 times in a RDE half-cell.

prior to attempting maximum Pt

displacement.

MEA Fabrication Challenges

MEA Fabrication



Pt loading: Measured using XRF, weighing and calculation Pt wt in ink. Values did not always agree. Decal: Occasional trouble with decal transfers with thicker electrodes

Subscale Cell: 5 cm² cell hardware has increased uncertainty (edge effects)

Leaching: Avoiding base metal removal at MEA stage

Fabrication Methods thus Far:

• Direct spraying, decal spray with transfer, filtering with transfer, and direct painting



Ink Formulation:

- Supportless electrocatalysts behave differently than traditional Pt/C catalysts and Pt blacks.
- Catalyst dispersions (inks) and MEA fabrication significantly more complicated
- We have investigated different ink agitation approaches, we typically can use a magnetic stir bar, however not for PtNi, sonic syringe not powerful enough to maintain dispersion for spray system
- Preliminary investigations suggest, solvent choices can aid in improving dispersions.

Fuel cell tests of carbon-free catalysts

Pt Black has been used as a dense, carbon-free surrogate for advanced ETFECS repeatedly within the project due to ETFECS materials limitations (reproducibility, sample size, availability, ever-evolving optimized compositions).

Here we show investigations of Pt Black MEAs over a range of compositions and show that some trends (although lower in performance remain constant.

Specific activity remains relatively constant while ECA changes with ionomer content.



NGPtNW

ionomer content	ECA	i _s 0.9V	0.9V i _m	ionomer content	ECA	i _s ^{0.9V}	i _m 0.9V
[wt%]	m ² _{Pt} /g _{Pt}	uA/cm ² Pi	t mA/mg _{Pt}	[wt%]	m ² _{Pt} /g _{Pt}	uA/cm ² _{Pt}	mA/mg _{Pt}
5	15	212	32	5	-	-	-
10	21	271	56	10	36	254	91
30	12	261	31	30	27	285	78
50	4	-	-	50	-	-	- ,
15 w Pt-HSC (20-80)	28	289	82	15 w NGPtNW-HSC (20-80)	28	288	82
10 µm				60 µm			

Pt Black

Pt/C baseline performance 5 and 25 cm² cells (47 wt% Pt/HSC)



Consistent, repeatable baseline Pt/HSC kinetic performance regardless of testing platform. (3 different inks and fabrication times and 9 different MEAs total)

All performance data taken @ 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)

- $5 \text{ cm}^2 200/200 \text{ sccm H}_2/O_2$ (single serpentine)
- \circ 25 cm² 1000/1000 sccm H₂/O₂ (triple serpentine)

All surface area measurements taken @ 35oC 150 kPa, 100 %RH, 150/100 sccm H₂/N₂

100 mV/sec