

V.D.4 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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mass and specific activity and electrochemical surface area for best performing, high-yield ETFECS.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program's Multi-Year Research, Development and Demonstration Plan:

- (A) Durability (of catalysts and membrane electrode assemblies)
- (B) Cost (of catalysts and membrane electrode assemblies)
- (C) Performance (of catalysts and membrane electrode assemblies)

Technical Targets

This project synthesizes novel ETFECS and incorporates these catalysts into electrodes with and without carbon for further study. The project has targets outlined in the Multi-Year Research, Development and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.13) and membrane electrode assemblies (MEAs) (Table 3.4.14). The specific targets and status of highest relevance are presented in Table 1.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2017/2020 Targets	Status
Mass Activity (150 kPa H ₂ /O ₂ 80°C 100% RH ^a)	A/mg-Pt @ 900 mV	0.44/0.44	0.45
Electro catalyst support stability	% mass activity loss	<10/<10	<10 ^b
Loss in initial catalytic activity	% mass activity loss	<40/<40	<10 ^b

^a relative humidity

^b measured in rotating disk electrode (RDE), following 30,000 cycles between 0.6 and 1 V.

Fiscal Year (FY) 2012 Objectives

- Produce novel extended thin film electrocatalyst structures (ETFECs) with increased activity and durability, moving towards meeting all 2020 DOE catalyst targets.
- Further increase electrochemically available surface area (ECA) and mass activity of extended surface catalysts.
- Scale up novel ETFECs synthesis to gram quantities.
- Quantify impact in rotating disc electrode of potential cycling, and carbon and ionomer content on observed

FY 2012 Accomplishments

- Joule Milestone - Maintained greater than 30 m²/g Pt and 720 micro amps/cm² (at 900 mV internal resistance-free) - DOE 2015 target, in scale up of ETFECs synthesis to gram quantity.
- Quantified impact in RDE of potential cycling, and carbon and ionomer content on observed mass and specific activity and ECA for best performing, high yield ETFECs.

- Demonstrated mass activities of ETFECS as high as 450 mA/mg-Pt @ 900 mV.
- Demonstrated high durability of ETFECS in potential cycling between 0.6 and 1 V for 30,000 cycles.
- Screened >5 substrates and/or adhesion layers for their applicability to yield fast nucleation rates and form thin continuous films by atomic layer deposition (ALD).
- Screened carbon blacks for inclusion in electrode compositions containing extended surface Pt nanostructures based on ability to produce dispersed electrodes and electrochemical stability up to 1.5 V.



Introduction

Conventional nanoparticle Pt/C electrocatalysts (2–5 nm) used in automotive fuel cells appear to have plateaued in terms of electrochemical area and catalytic activity. ETFECS offer the possibility of higher specific activities comparable to that of bulk poly-Pt. ETFECS typically exhibit lower ECAs and consequently lower mass activities. By investigating a number of alternative synthesis techniques, we expect to raise the ECA to deliver the benefits of both a high specific and mass activity. An additional benefit of ETFECS is that larger Pt structures are less susceptible to oxidation and dissolution thus leading to a highly active, durable and low-cost electrocatalyst system.

Approach

Our overall approach towards developing extended surface Pt catalysts for their high mass activity and durability, and incorporating these structures into robust, high efficiency MEAs is multipronged and includes: i) Synthesis of novel ETFECS—Pt nanoparticles with continuity over 10s of nms or more have demonstrated enhanced specific activity and exceptional durability (3M [1], others [2]). In our work we examine vapor deposition including sputtering, chemical vapor deposition (CVD) and ALD as well as wet chemistry methods that include spontaneous galvanic displacement (SGD); ii) focus on increased Pt mass activity—low Pt ECAs have (~10 m²/gPt) resulted in limited mass activity in the past; iii) electrode studies involving ETFECS—effective incorporation of extended Pt catalysts into electrodes. Studies with Pt Black as an unsupported surrogate, expanded to ETFECS, including carbon incorporation; and iv) modeling—of catalyst particles, electrode structure and electrode performance.

Results

Moving beyond template synthesis development, our current year's work focused on Pt deposition and scale up of

high performing materials. We have continued our focus on ALD, and SGD, have added CVD as a technique and have de-emphasized sputtering. While sputtering is still deemed to be of merit (including for commercial processes), sputtering is not being currently pursued within the project due to cost of implementation for roll to roll processes, specialty equipment, and time - as well as promise of other approaches.

ALD work largely led by Stanford has focused on lower temperature deposition processes and the use of ultraviolet exposure to samples and the use of ozone as a more powerful oxidant in the reaction process. The use of ozone in particular has shown major improvements in lowering the reaction temperature and allowing thinner (single nm) continuous Pt coatings to be obtained. CVD work implemented at the University of Tennessee in the past year has resulted in free-standing Pt nanotubes from deposition into, followed by dissolution of, anodized aluminum oxide templates. The resultant catalyst structures have shown specific activities approaching that of polycrystalline Pt and far higher than other pure Pt nanostructures. These materials are limited in terms of low ECAs, and current focus is being spent exploring increasing ECA and exploring Pt alloys.

SGD continues to be a route that shows high promise and that we are pursuing with significant efforts. The work at UC-Riverside has stopped and has transitioned to the University of Delaware with the relocation of project co-PI, Yushan Yan. Based on the high performance of these materials, we performed scaled up synthesis to produce gram quantities for expanded studies in electrodes. Table 2 show the result of four batch synthesis where each batch consisted of between 250 and 400 mg of catalyst. We also distributed these samples to ORNL and LANL for advanced characterization to supplement and compare to measurements made at NREL. Table 1 summarizes the properties obtained for scaled up ETFECS. Most notably the ECAs for these materials are unusually high for extended surface catalysts and retain high specific activities, resulting in mass activities at or near DOE 2020 Targets.

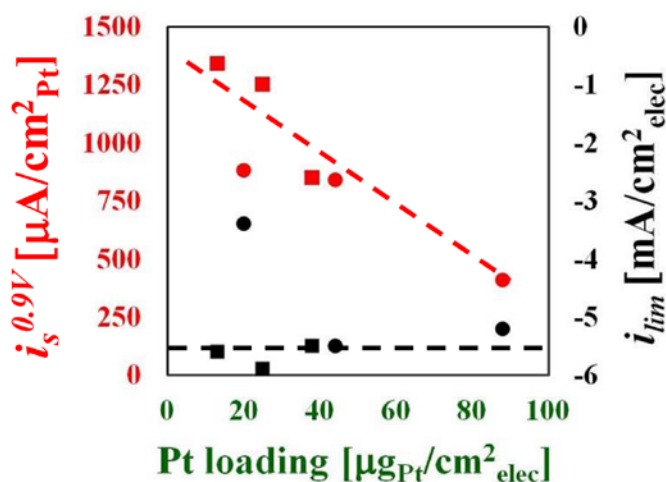
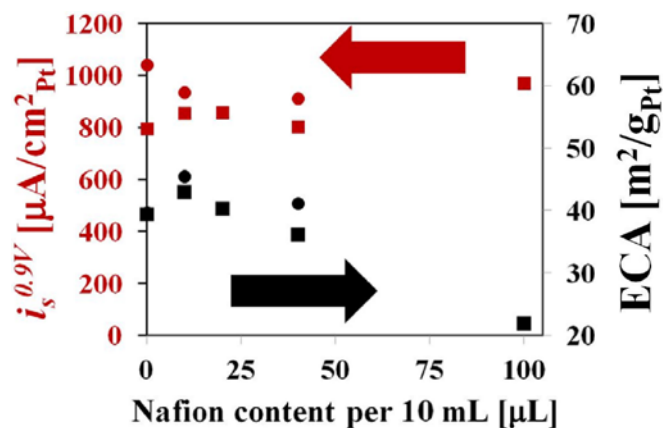
In the area of electrochemical characterization and electrode studies, we focused at first on Pt black as a surrogate for advanced ETFECS. The focus on Pt black allowed us to study catalyst dispersions and performance with and without carbon inclusion. Figure 1 shows the impact of carbon inclusion (squares) on specific activity (i_s) and limiting current as a function of RDE loading. These results demonstrate the importance of carbon in obtaining good dispersions to achieve high specific activity.

The role of carbon inclusion and the dependence of Nafion[®] on observed properties of ETFECS were also probed. Figure 2 shows examples of increasing Nafion[®] content in RDE studies with (circles) and without (squares) carbon. The role of both carbon and Nafion[®] in improving dispersion can be seen at low levels of Nafion[®] content. However, high Nafion[®] contents led to a systematic trend of decreasing ECA. Carbon incorporation always had a positive or neutral effect.

TABLE 1. Characterization of Scaled Up ETFECS Synthesis

	ECA (m ² /g _{Pt})	$i_s^{0.9V}$ ($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	$i_m^{0.9V}$ (mA/mg _{Pt})	Pt Wt%			
				XRF (NREL)	XRF (LANL)	EDS (NREL)	EDS (ORNL)
Batch 1	38.6	1050	400	82	77.5	80-86	87-91
Batch 2	53.0	630	340	95	95	96-99	98-100
Batch 3	45.6	980	450	94	90	94-96	94-97
Batch 4	51.0	640	330	96	92	95-97	93-95
Average	47.0	820	390				

XRF - X-ray fluorescence spectroscopy; EDS - energy-dispersive X-ray spectroscopy

**FIGURE 1.** Specific activity and limiting current of Pt black as a function of RDE loading with (squares) and without carbon (circles)**FIGURE 2.** Specific activity and ECA of ETFECS as a function of Nafion® content with (circles) and without carbon (squares)

Durability of the samples was also tested and showed high promise for the ETFECS approach. Data are presented in Table 2 for 30,000 cycles between 0.6 and 1.0 V for ETFECS samples with and without carbon. ECA decreased

TABLE 2. Durability Cycling of ETFECS With and Without Carbon Inclusion

	ECA	NECA	$i_s^{0.9V}$	$N i_s^{0.9V}$	$i_m^{0.9V}$	$N i_m^{0.9V}$
	m ² /g _{Pt}	m ² /g _{Pt}	$\mu\text{A}/\text{cm}^2_{\text{Pt}}$		mA/mg _{Pt}	
Pt only (pre)	41		964		393	
Pt only (post)	33	81	1071	111	355	90
Pt + C (pre)	39		1078		420	
Pt + C (post)	30	78	1330	123	405	96

NECA - normalized electrochemical surface area

by approximately 20% in both cases, but was accompanied by a modest (11 to 23%) increase in specific activity. The resulting mass activity was 90 to 96% of the initial activity, a remarkably high result, much better than that of conventional Pt/C and highly supportive of our approach to improved cost, durability and performance of fuel cell catalysts. The reported mass activities approach DOE 2020 targets and show exceptionally good durability.

Conclusions and Future Directions

The project has synthesized many novel catalysts using materials, geometries, and approaches not previously demonstrated. We have reached poly crystalline Pt specific activity in nanostructures using CVD, and have demonstrated continuous ALD Pt coatings down to single nm thickness. We have met the 2020 DOE mass activity target without alloying advantages and commonly produce extended surface catalysts with >40 m²/g ECA. We have shown good cyclic durability, and elucidated the role of carbon in RDE studies of unsupported catalysts. Future work, broken down by topical area, includes:

- Pt deposition
 - CVD (Tennessee): Systematic studies involving wall thickness, annealing T, co-deposition of metals with potential alloy benefits (Ni, Co).
 - ALD (Stanford, Center for Nanoscience and Engineering, NREL): Further studies involving ozone with a focus on low-temperature ALD, application of developed techniques to nanostructured substrates and removable RDE

- tips (highly-ordered pyrolytic graphite, edge-plane pyrolytic graphite, gas chromatograph).
- SGD (NREL, Delaware): further process optimization focusing on reproducibility and characterization of initial samples.
- Electrode studies (NREL)
 - Incorporation of highest performing catalyst into MEA electrodes.
 - Expanded MEA fabrication and fuel cell testing of ETFECS.
- Modeling
 - Colloidal interactions to probe dispersions and inks of ETFECS (Tennessee).
 - RDE models to investigate specific activity, limiting current and electrochemical surface area (Texas).

Special Recognitions & Awards/Patents Issued

1. Principal Investigator, Bryan Pivovar, has been awarded the 2012 Charles Tobias Young Investigator Award (Electrochemical Society).

FY 2012 Publications/Presentations

1. Han-Bo-Ram Lee and Stacey F. Bent, “Microstructure-Dependent Nucleation in Atomic Layer Deposition of Pt on TiO₂,” *Chem. Mater.* 2012, 24, 279–286.
2. Arrelaine A. Dameron, Svitlana Pylypenko, Justin B. Bult, K.C. Neyerlin, Chaiwat Engtrakul, Christopher Bochert, G. Jeremy Leong, Sarah L. Frisco, Lin Simpson, Huyen N. Dinh, Bryan Pivovar, “Aligned Carbon Nanotube Array Functionalization for Enhanced Atomic Layer Deposition of Platinum Electrocatalysts,” *Applied Surface Science*, 258 (13), 2012, 5212–5221.
3. Shaun M. Alia, Kurt O. Jensen, Bryan S. Pivovar, and Yushan Yan, “Platinum Monolayered Palladium Nanotubes as Oxygen Reduction Reaction Electrocatalysts,” *ACS Catal.*, 2012, 2 (5), pp 858–863.
4. Brian A. Larsen, K. C. Neyerlin, Justin Bult, Christopher Bochert, Jeffrey L. Blackburn, Shyam Kocha, Bryan Pivovar, “Platinum nanoplates as novel oxygen reduction reaction electrocatalysts” accepted *JACS* July, 2012.

5. Bryan Pivovar, “Extended Surface Catalysts,” Johns Hopkins University, December 13, 2011.
6. Bryan Pivovar, “ETFECs Development at NREL,” ACS Colorado Section, January 23, 2012.
7. Bryan Pivovar, “NREL’s Fuel Cell R&D/Extended Surface Catalysts”, GM, Honeoye Falls, NY June 13, 2011.
8. Bryan Pivovar, “3-D Catalyst Structures for PEM Fuel Cell Electrocatalysts,” Meet. Abstr. - Electrochem. Soc. 1201 558 (2012).
9. Brian A. Larsen, Christopher Chang, Svitlana Pylypenko, and Bryan Pivovar, “Spontaneous Galvanic Displacement Reactions: Effects of Template and Surface Ligand Interaction,” Meet. Abstr. - Electrochem. Soc. 1101 83 (2011).
10. K. Neyerlin, B. Larsen, J. Zack, S. Kocha, and B. Pivovar, “Incorporation of Carbon with Unsupported Pt Electrocatalysts,” 220th ECS Meeting - Boston, MA October 9 – October 14, 2011, Abstract No. 807.
11. K. Neyerlin, B. Larsen, T. Olson, S. Pylypenko, J. Zack, S. Kocha, and B. Pivovar, “Electrochemically Available Surface Area and Mass and Specific Activities of Extended Surface Pt Nanostructures,” 220th ECS Meeting - Boston, MA October 9 – October 14, 2011, Abstract No. 808.
12. S.M. Alia and Y. Yan, “Platinum Monolayered Palladium Nanotubes for the Oxygen Reduction Reaction,” 220th ECS Meeting - Boston, MA October 9 – October 14, 2011, Abstract No. 1059.
13. Brian A Larsen, K. C. Neyerlin, Justin Bult, Christopher Bochert, Jeffrey Blackburn, Shyam Kocha, Bryan Pivovar, “Platinum nanoplates as novel oxygen reduction reaction electrocatalysts,” 242nd ACS National Meeting, Fall 2011, Denver, Colorado, August 28 – September 1, Abstract No. 403.
14. Han-Bo-Ram Lee and Stacey F. Bent, “The Effects of TiO₂ Crystallinity on Nucleation in Atomic Layer Deposition of Platinum,” ALD 2011.

References

1. http://www.hydrogen.energy.gov/pdfs/review08/fc_1_debe.pdf.
2. Z. Chen, W. Li, M. Waje, Y.S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060-4063.