

V.A.7 Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports

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Contract Number: DE-EE0007270

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Project Start Date: January 1, 2016
Project End Date: March 31, 2019

- Employ advanced composition and structural analysis to guide electrocatalyst development, including transmission electron microscopy, energy dispersive X-ray spectroscopy (EDS), and X-ray adsorption spectroscopy (XAFS).
- Initiate density functional theory (DFT) and kinetic Monte Carlo (kMC) model refinement efforts, towards enabling predictive capability of novel electrocatalyst concepts.
- Develop and validate high throughput electrocatalyst fabrication and characterization methods, towards acceleration of project electrocatalyst development.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

Table 1 summarizes 2016 project status against the relevant 2020 DOE targets and 2019 project targets. All reported status values are measurements made in membrane electrode assembly (MEA) format. PGM total content and PGM total loading are reported for two MEAs, the project baseline and an MEA with an improved durability “NPTF+M” cathode catalyst. The two MEAs, evaluated in Best of Class format (including a cathode interlayer for operational robustness), achieved 0.16 g/kW (at 0.70 V) with PGM total loading of 0.105 mg_{PGM}/cm² and 0.18 g/kW (at 0.70 V) with 0.127 mg_{PGM}/cm², respectively. Durability status is assessed with a NPTF PtNi+”M” cathode catalyst containing 0.109 mg_{PGM}/cm² which achieved 42% loss in mass activity after the DOE electrocatalyst accelerated stress test (AST) and performance at 0.8 A/cm² and 1.5 A/cm² increased by 8 mV and 68 mV, respectively. Beginning of life mass activity status is reported for three electrocatalysts, ranging from 0.28 A/mg_{PGM} for NPTF PtNi+M, 0.39 A/mg_{PGM} for UTF “A”, and 0.47 A/mg_{PGM} for baseline NPTF PtNi.

FY 2016 Accomplishments

- Initiated development of first UTF electrocatalyst series (“A”), including composition and fabrication processing optimization. Best UTF “A” electrocatalyst mass

Overall Objectives

The overall objective is development of improved thin film oxygen reduction reaction (ORR) catalysts on nanostructured thin film (NSTF) supports which achieve:

- Mass activity of 0.80 A/mg_{PGM} or higher
- Platinum group metal (PGM) total content (both electrodes) of ≤0.1 g/kW @ 0.70 V
- PGM total loading (both electrodes) <0.1 mg_{PGM}/cm²
- Mass activity durability of <20% loss
- Loss of performance <20 mV @ 0.8 and 1.5 A/cm².

Fiscal Year (FY) 2016 Objectives

- Initiate project at 3M and partner organizations.
- Develop new ultra-thin film (UTF) and nanoporous thin film (NPTF) electrocatalysts, towards achievement of first year project targets.

TABLE 1. Status Against Technical Targets

Characteristic	2020 Target and Units	Project Target	2016 Status
PGM total content (both electrodes)	0.125 g/kW	0.1 (0.70 V)	0.16 ¹ 0.18 ²
PGM total loading (both electrodes)	0.125 mg/cm ²	0.10	0.105 ¹ 0.127 ²
Loss in catalytic (mass) activity	40%	20	42 ³
Loss in performance at 0.8 A/cm ²	30 mV	20	-8 ³
Loss in performance at 1.5 A/cm ²	30 mV	20	-68 ³
Mass activity @ 900 mV _{iR-free}	0.44 A/mg (MEA)	0.80	0.28 ³ (NPTF "M") 0.47 ⁴ (NPTF) 0.39 ⁵ (UTF)

¹0.015 mg_{Pt}/cm² NSTF anode, 0.075 dealloyed PtNi/NSTF cathode, 0.015 mg_{Pt}/cm² cathode interlayer.

²0.02 mg_{Pt}/cm² NSTF anode, 0.091 mg_{PGM}/cm² NPTF "M" cathode, 0.016 mg_{Pt}/cm² cathode interlayer.

³NPTF "M" cathode, 0.109 mg_{PGM}/cm² after 30,000 electrocatalyst AST cycles.

⁴Annealed NPTF P4A Pt₃Ni₁/NSTF, 0.12 mg_{Pt}/cm²; adjusted from 0.900 V_{MEAS} (70 mV/dec)

⁵Best UTF "A", 0.027 mg_{PGM}/cm². Average of two MEAs.

"Best of Class" refers to the currently-determined optimal combination of components.

activity of 0.39 A/mg_{PGM} approaches DOE 2020 target (0.44 A/mg) in MEA format, and is 3.9X higher than UTF baseline Pt/NSTF. Significant correlations were identified between electrocatalyst activity, composition, and structure.

- Optimized integration of durability additive "M" into NPTF PtNi/NSTF. Best to-date PtNi+"M" NPTF electrocatalyst loses 42% mass activity after 30,000 electrocatalyst AST cycles (vs. 40% target), and H₂/air performance at 0.8 A/cm² and 1.5 A/cm² improved by 8 mV and 68 mV, respectively (vs. 30 mV loss target). When integrated into best of class format, resultant MEA achieves 0.18 g/kW at 0.70 V.
- Initiated DFT and kMC model refinement with baseline project electrocatalysts. DFT has determined trends in electrocatalyst activity and surface structure stability induced by bulk and near-surface composition variations. kMC model refinement has focused on incorporation of relevant physics for dealloying via potential cycling, and preliminary predictions of composition evolution with dealloying agree in trend with experiment.
- Method development for high throughput (HT) electrocatalyst fabrication, physical characterization, and electrochemical characterization has been initiated. HT fabrication and physical characterization methods are reproducible and validated.



INTRODUCTION

State-of-the-art proton exchange membrane fuel cell MEAs utilized in today's prototype automotive traction fuel cell systems continue to suffer from key technical and

economical limitations of high cost, insufficient durability, and low robustness to off-nominal operating conditions. State-of-the-art MEAs based on conventional carbon-supported Pt nanoparticle catalysts currently incorporate precious metal loadings which are significantly above those needed to achieve MEA cost targets; performance, durability, and/or robustness decrease significantly as loadings are reduced.

This project focuses on development of novel thin-film electrocatalysts based on 3M's NSTF catalyst technology platform. NSTF electrocatalysts and electrodes are a unique approach towards addressing key technical commercialization challenges. The thin film electrocatalyst structure imparts substantially higher ORR specific and mass activities (4.7 mA/cm²_{Pt} and 0.8 A/mg_{PGM} in rotating disk electrode, 2.5 mA/cm²_{Pt} and 0.47 A/mg_{PGM} in MEA) [1] and high resistance to electrocatalyst dissolution and sintering induced by electrochemical cycling [2]. The NSTF support is based on an oriented, sub-micron scale crystalline organic pigment whisker, not carbon nanoparticles, which enables exceptional resistance to corrosion in fuel cell and water electrolysis applications [3]. NSTF electrodes, which are a single layer of NSTF electrocatalyst particles partially embedded into an ion-conducting membrane, are ultrathin (<1 μm) and do not require ionomer for proton conduction [4]. When integrated into state-of-the-art, operationally robust MEAs, this electrode structure enables high absolute and specific power densities (0.89 W/cm² and 6.8 kW/g at 0.692 V cell voltage) at ultra-low MEA PGM loadings (0.13 mg_{PGM}/cm² total) [5].

APPROACH

The project approach is to establish relationships between electrocatalyst functional response (activity,

durability), physical properties (bulk and surface structure and composition), and fabrication processes (deposition, annealing, dealloying) via systematic investigation. Electrocatalysts will be generated in one of two distinct morphologies, NPTF and UTF, each with distinct pathways towards achieving project targets. Additionally, this project utilizes high throughput material fabrication and characterization, electrocatalyst modeling, and advanced physical characterization to guide and accelerate development.

RESULTS

Since project initiation in January 2016, significant progress has been made towards development of new, improved electrocatalysts with target activity, durability, and cost. This work has included development of new electrocatalyst compositions, fabrication process optimization, electrochemical and physical characterization, and modeling.

UTF development has focused on optimization of a single Pt alloy system, termed UTF “A”. Optimization work has included studies to evaluate the influence of composition

and annealing. Figure 1 summarizes key initial findings relating mass and specific activities, measured in MEA, to electrocatalyst composition and structure. Unannealed and annealed electrocatalysts were initially evaluated in fuel cell for mass and specific activity in MEA, with areal PGM loadings of $28 \pm 2 \mu\text{g}_{\text{PGM}}/\text{cm}^2$, substantially below the DOE 2020 target. Tested catalysts were then evaluated for atomic-scale structure by Z-contrast scanning transmission electron microscopy (STEM) imaging and bulk composition by EDS at Oak Ridge National Laboratory and for Pt-Pt bond lengths by XAFS at Argonne National Laboratory. Figure 1A shows that as the Pt mole fraction decreased, mass activity generally increased for both unannealed and annealed UTF “A”. Annealing was especially beneficial for relatively lower Pt fractions, achieving 0.29 A/mg at the minimum Pt mole fraction evaluated.

Figure 1B and Figure 1C compares the influence of annealing on the resultant electrocatalyst structure after fuel cell testing at a single initial composition. The annealed, tested catalyst’s structure (Figure 1C) is largely similar to the unannealed, tested catalyst (Figure 1B), but the annealed catalyst’s surface appears moderately smoother, suggestive of larger surface facets. Figure 1D shows that the specific

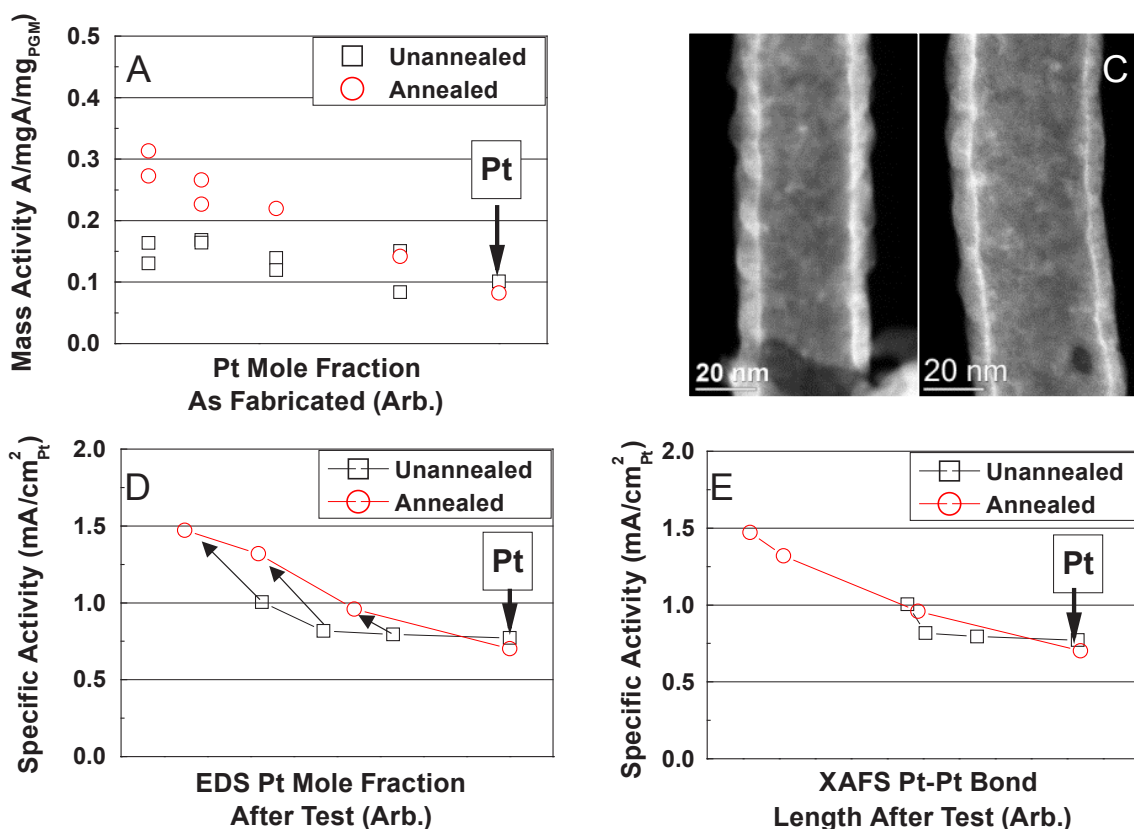


FIGURE 1. (A) Influence of composition and annealing on UTF “A” mass activity. (B, C) Z-contrast STEM of tested unannealed and annealed catalysts, respectively. (D, E) Specific activity dependencies on Pt mole fraction (EDS) and Pt-Pt bond distances (XAFS), determined after fuel cell testing.

activity increases monotonically as the EDS-determined Pt mole fraction in the tested electrocatalyst decreases, and annealed electrocatalysts have higher specific activity than unannealed at a given Pt mole fraction. Figure 1E suggests that the specific activity differences between annealed and unannealed catalysts with varying initial Pt mole fractions may be rationalized by the Pt-Pt bond distance in the catalyst after evaluation, as determined by XAFS.

One UTF “A” composition from the preceding series was annealed at a variety of conditions and evaluated for mass activity in MEA (Figure 2). All annealed UTF “A” catalysts achieved higher mass activity than unannealed, and mass activity decreased with increased annealing extent. The average mass activity of UTF “A” at the optimal annealing conditions was 0.39 A/mg, 3.9X higher than Pt. Further annealing optimization is in progress.

We have previously reported that one NPTF alloy system, PtNi, is insufficiently stable to achieve the DOE durability targets when evaluated under the electrocatalyst AST. [6] In pre-project work, we have identified that incorporation of durability additive “M” into the PtNi electrocatalyst greatly improved the durability, but MEA H_2 /Air performance was suppressed as compared to the “M”-free catalyst. Initial NPTF development in this project has focused on optimization of “M” integration for improved durability and performance. To date, four different “M” integration methods have been evaluated for beginning of life mass activity and performance with dealloyed PtNi catalyst, with PGM contents ranging from ca. 0.09–0.11 mg_{PGM}/cm^2 . For each integration method, several method-dependent integration variables have also been evaluated. Figure 3A and 3B show that beginning of life mass activity and H_2 /air performance depend strongly on the integration method (A–D) and integration method variables (0–20). Methods “C” and “D” yielded the overall highest beginning of life mass activity, achieving as high as 0.30 A/ mg_{PGM} , but



FIGURE 2. Mass activity sensitivity vs. annealing extent for single UTF “A” composition

Method “D” yielded appreciably higher H_2 /air performance at 1 A/ cm^2 . Series “D” samples, with varying “M” content, were evaluated under the DOE electrocatalyst AST; changes in mass activity and H_2 /air performance are summarized in Figure 3C. Without “M” (Level 0), mass activity loss was 70% and H_2 /Air loss at 1 A/ cm^2 was 44 mV after the AST. With level 5 “M” content, mass activity loss after the AST was reduced to 42% and H_2 /air performance at 1 A/ cm^2 increased by 7 mV. NPTF PtNi “M” catalysts can also generate high rated power performance when integrated with improved MEA components. Figure 3D summarizes H_2 /air performance at 90°C cell temperature vs. reactant pressures for Series “A”, Level 5 NPTF PtNi+“M” cathode catalyst, in best of class MEA format, including a cathode interlayer for operational robustness. [5] At 0.70 V, specific power values of 5.3 kW/g, 6.3 kW/g, and 7.0 kW/g are obtained at 1.5 atmA, 2.0 atmA, and 2.5 atmA reactant pressures.

As indicated in the preceding sections, ultimate electrocatalyst performance and durability depend strongly upon composition and fabrication parameters, including electrocatalyst deposition method, annealing method, and dealloying method. These parameters in combination represent a large, time-consuming variable space to simultaneously optimize, and HT electrocatalyst development can result in substantial acceleration. Method development for HT electrocatalyst fabrication, physical characterization, and electrochemical characterization by segmented fuel cell has been initiated. To date, HT electrocatalyst fabrication consists of physical vapor deposition of Pt and another alloying element where the other element deposition rate varies monotonically across the NSTF substrate. Figure 4 (left) summarizes loading and composition analysis of three replicate gradient binary alloy electrocatalysts fabricated with identical conditions. Composition analysis consisted of scanning X-ray fluorescence with 1 mm spatial resolution. The relative standard deviation for Pt loading vs. position was on average 3.4% (maximum 11%) and for Pt mole fraction was on average 2.6% (maximum 6.5%), both exceeding expectations and the project milestone. Figure 4 (right) summarizes HT electrocatalyst structural characterization by wide angle X-ray scattering (WAXS), conducted at Argonne National Laboratory. WAXS spectra were analyzed to determine the FCC lattice constant and (111) grain size. The WAXS-determined lattice constants agreed well with expectation, decreasing with decreasing Pt mole fraction and were generally similar to Vegard’s law predictions. (111) grain sizes were constant with Pt mole fraction, also consistent with expectation.

A new kMC simulation package has been developed that incorporates oxidation and reduction cycles, surface diffusion, and electrochemical dealloying. The physical features incorporated into this code include (a) potential-dependent dissolution of a first base metal, (b) potential-dependent oxidation or reduction of all surface species, and

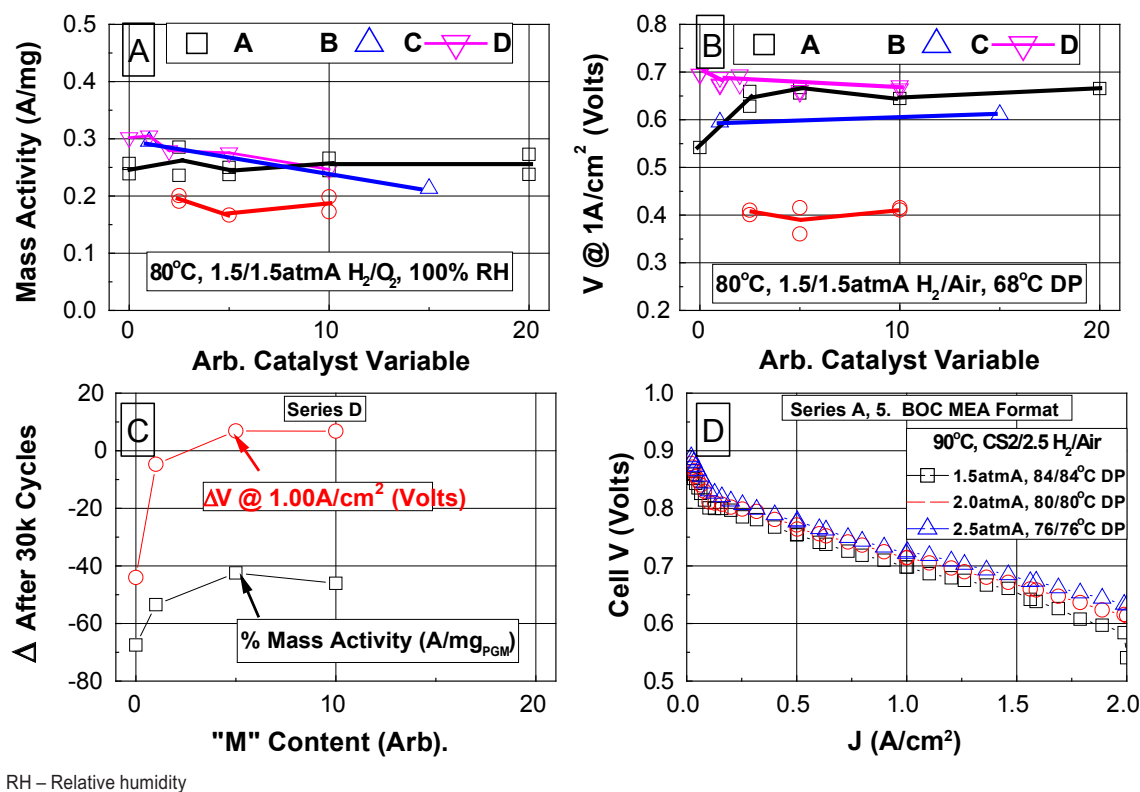


FIGURE 3. NPTF PtNi "M" integration. Top row: Beginning of life mass activity (A) and H₂/air performance (B) vs. "M" integration method (A-D) and integration variable (0-20). (C) Mass activity and H₂/air performance change after 30,000 DOE electrocatalyst AST cycles. (D) PtNi+M in best of class MEA format, with 0.13 mg_{PGM}/cm² total loading.

(c) surface diffusion of all surface species. The code is being optimized so that input parameters lead to behavior that is approximately similar to the behavior of real Pt alloys. Figure 5 compares compositional evolution of experimental NSTF catalyst to preliminary representative output of the package versus the number of oxidation/reduction cycles. Composition evolution with cycling is similarly sigmoidal for both the simulation and experiment data, and final average composition agrees reasonably. It is relevant, and perhaps surprising, that even after 100 cycles and the development of full porosity, there is still significant residual base metal on the surface of the simulated material.

To complement our efforts in experimental electrochemical reactivity measurements, characterization, and kMC modeling, we have begun a program of detailed DFT modeling to predict the atomic-scale structures, stability, and ORR reactivity of UTF "A" alloy surfaces under electrochemical conditions. The alloys are modeled with periodic boundary conditions, and smooth surfaces, which have been found to be most active for ORR, are considered (Figure 6). To estimate the stability of the surfaces with Pt skins, we calculate the average surface stress for different Pt mole fractions and for different thicknesses of platinum skins. Surfaces with low stress values are identified, and

these surfaces are considered for additional analysis of ORR activity. The ORR rate estimates, in turn, are plotted as a function of the amount of strain in the surface platinum layers. Alloys with Pt skins thicknesses of approximately three layers are found to be very active for the ORR, while thicker or thinner skins show modestly reduced activity. These predictions are currently being calibrated against the experimental results on ultrathin films that we have recently measured and will provide a target for future synthesis efforts in our program. In addition, the structural models of the alloy surfaces will be refined using the results of detailed kMC simulations, which can provide dynamical information about catalyst structures under reaction conditions.

CONCLUSIONS AND FUTURE DIRECTIONS

New NSTF electrocatalysts have been developed which are approaching several DOE 2020 targets based on two electrocatalyst morphologies: ultra-thin film and nanoporous thin films. UTF "A" electrocatalysts have demonstrated mass activity as high as 0.39 A/mg, 3.9X higher than the pure Pt/NSTF baseline. Analysis of UTF "A" electrocatalysts by STEM+EDS and XAFS reveal dependencies of catalyst activity on compositional and structural parameters.

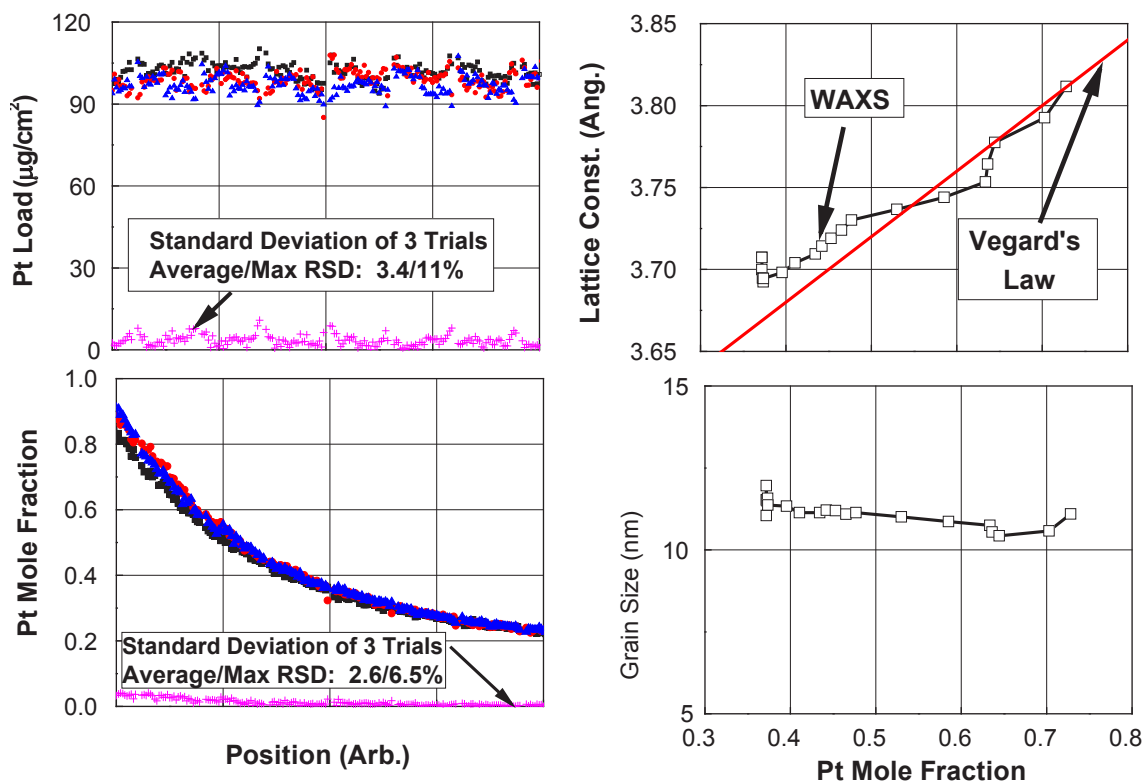


FIGURE 4. HT electrocatalyst composition (left) and WAXS structural characterization (right) for gradient composition electrocatalysts

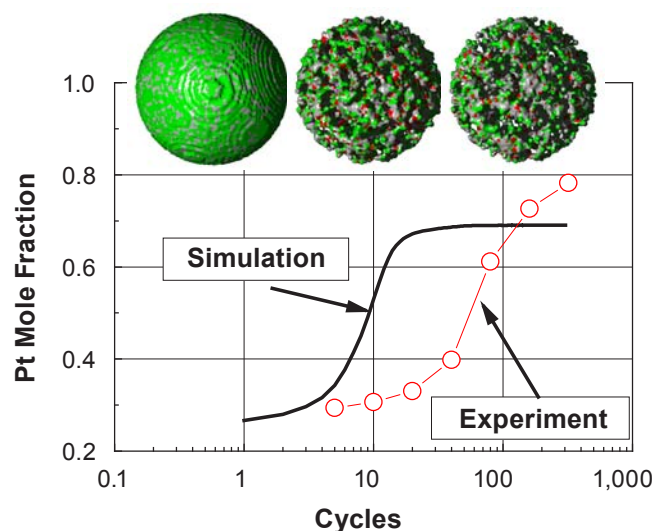


FIGURE 5. Comparison of composition evolution of experimental NSTF catalyst to simulated average composition of a ~20 nm Pt binary alloy sphere as a function of oxidation/reduction cycle number. (Silver) Pt; (red) oxidized Pt; (green) alloying element.

NPTF $\text{PtNi}+\text{M}$ electrocatalyst optimization has resulted in improving mass activity and H_2/air performance, and durability has approached DOE 2020 targets. DFT modeling

has provided insight into the influence of electrocatalyst subsurface composition and Pt skin thickness on electrocatalyst activity and stability of a first Pt alloy. kMC modeling of a first Pt binary alloy has predicted evolution of NPTF composition evolution during dealloying, with reasonable agreement with experimental results. Methods for HT electrocatalyst fabrication and composition and structure characterization have been validated.

In future work, the project will fabricate and characterize several new NPTF and UTF electrocatalysts to establish functional relationships between electrocatalyst composition, physical properties, fabrication process parameters, and functional response. HT electrocatalyst processing and electrochemical characterization methods will be developed, validated, and utilized when available to accelerate development. kMC and DFT models will be refined to capture experimentally-observed trends for baseline NPTF and UTF catalysts, which will enable predictive capability for new electrocatalyst concepts. Highly durable $\text{PtNi}+\text{M}$ electrocatalysts will continue to be refined for further improved mass activity and H_2/air performance. Finally, project electrocatalysts will be incorporated into advanced NSTF electrodes and evaluated for performance, operational robustness, and durability.

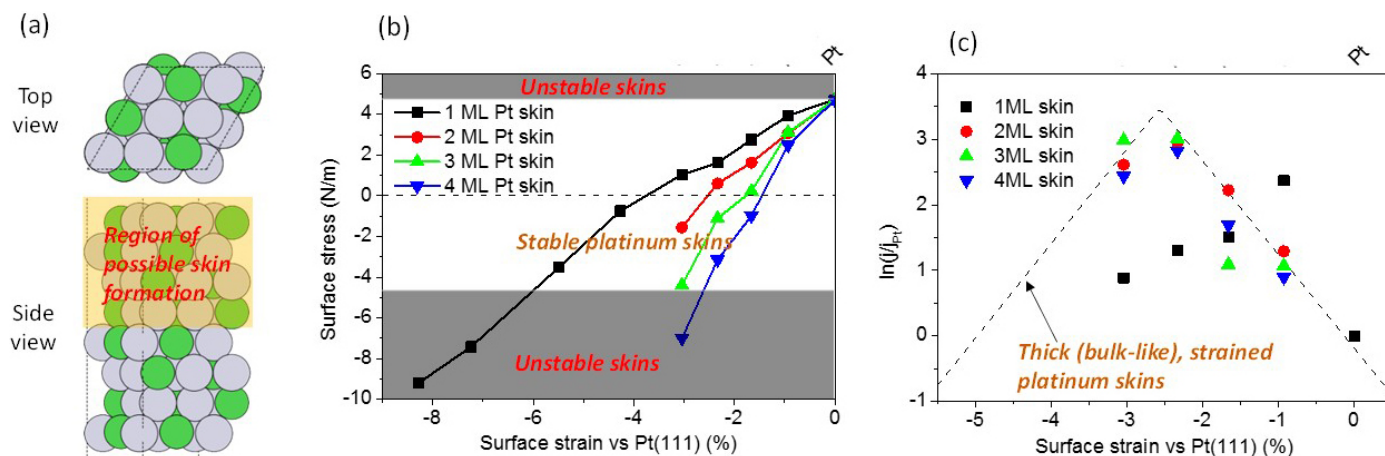


FIGURE 6. DFT predictions of stability and activity for platinum skins. (a) Schematic of Pt alloy structures, with highlighted region where formation of pure platinum skins is considered. (b) Stability map for pseudomorphic platinum skins on Pt alloy substrates. Skins with large positive or negative surface stresses are likely to be unstable. (c) Predicted oxygen reduction activities for platinum skins on Pt alloy substrates. Active skins are predicted to have approximately 3 ML of platinum. Predictions for very thick platinum skins are shown with the dashed line.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. A.J. Steinbach, Presentation FC143, 2016 U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review, June 2016, Washington, D.C.
2. A.J. Steinbach, "Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports," Presentation to DOE Catalyst Working Group, July 27, 2016.
3. A.J. Steinbach, "Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports," Presentation to USCAR Fuel Cell Tech Team, August 17, 2016.

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6. D.A. Cullen et al., "Linking morphology with activity through the lifetime of pretreated PtNi nanostructured thin film catalysts," *J. Mater. Chem. A*, **3** 11660–11667 (2015).