
Highly Active, Durable, and Ultra-Low-Platinum-Group-Metal Nanostructured Thin Film Oxygen Reduction Reaction Catalysts and Supports

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Subcontractors:

- Johns Hopkins University, Baltimore, MD
- Purdue University, West Lafayette, IN
- Oak Ridge National Laboratory, Oak Ridge, TN
- Argonne National Laboratory, Lemont, IL

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Project End Date: December 30, 2019

Overall Objectives

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

- Mass activity of 0.50 A/mg_{PGM} or higher
- Platinum group metal (PGM) total content (both electrodes) of ≤ 0.1 g /kW
- 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) 2019 Objectives

- Develop new layered ultra-thin-film (UTF) catalysts toward achievement of activity, durability, and cost objectives, with a focus on reducing PGM content in underlayers.
- Employ advanced composition and structural analysis to guide and accelerate electrocatalyst development, including high-angle annular dark-field scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray absorption fine structure spectroscopy.
- Utilize density functional theory (DFT) and kinetic Monte Carlo (kMC) models to predict novel electrocatalyst concepts with improved activity and durability.
- Determine mechanism(s) negatively impacting break-in conditioning rate of project electrocatalysts and improve conditioning rate through material modification.

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 Plan¹:

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

Contribution to Achievement of DOE Milestones

This project will contribute to achievement of the following DOE milestones from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Milestone 2.7: Develop catalysts with 0.125 $\text{g}_{\text{PGM}}/\text{kW}$ at rated power. (4Q, 2017)
- Milestone 3.9: Demonstrate MEA performance of 1,000 mW/cm^2 at rated power at a high-volume projected cost of \$9/kW. (1Q, 2017)

FY 2019 Accomplishments

- Identified an optimal composition of UTF layered Pt/Ir catalysts that resulted in achievement of a PGM mass activity of 0.46 $\text{A}/\text{mg}_{\text{PGM}}$, which exceeds the DOE target and approaches the project target.
- DFT modeling predicted enhanced ORR activity for new class of Pt and Pd nanosheet catalysts due to optimal surface compression obtained with tuned nanosheet thicknesses. Key model predictions were validated experimentally by project collaborators at Johns Hopkins University and University of California, Irvine, which demonstrated up to a 14x activity enhancement vs. nanoparticle counterparts in acid.
- Identified three UTF layered PtNi/Ir catalyst compositions with PGM mass activities of 0.38 $\text{A}/\text{mg}_{\text{PGM}}$ or higher and <20% specific area loss after accelerated durability testing.
- Developed an improved electrocatalyst kMC durability model that incorporated DFT-

determined Pt diffusion barriers and constituent bond energies, and which accurately simulated Pt oxidation, Pt reduction, and Pt surface roughening during cycling. The model additionally confirmed the stabilization of Pt by the presence of an Ir underlayer.

- Developed a new class of UTF layered Pt/Ta catalysts with enhanced mass activity and specific area. An UTF Pt/Ta catalyst has achieved a mass activity of 0.41 $\text{A}/\text{mg}_{\text{PGM}}$ with a specific area of 22 $\text{m}^2/\text{g}_{\text{PGM}}$ with optimal processing, guided by advanced characterization, which enabled reduced oxygen content in the Ta layer. Modification of the Ta underlayer composition resulted in demonstration of a UTF Pt/TaX catalyst with mass activity of 0.44 $\text{A}/\text{mg}_{\text{PGM}}$ and specific area of 28 $\text{m}^2/\text{g}_{\text{PGM}}$.
- Identified a materials-based improvement for conditioning of UTF catalysts, reducing the time required to achieve peak performance. Studies revealed the presence of a contaminant species that elutes from the cell during break-in conditioning and that the contaminant is a significant ORR catalyst poison. A treatment was implemented that resulted in faster break-in conditioning rates and higher mass activity than an untreated baseline.

INTRODUCTION

State-of-the-art proton exchange membrane fuel cell membrane electrode assemblies (MEAs) utilized in today's 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. Relatively few state-of-the-art carbon-supported Pt nanoparticle catalysts have recently achieved the required performance in MEAs at the required catalyst loadings, but the catalyst and support durability remain generally insufficient to meet commercial requirements.

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 toward addressing key technical barriers. The thin-film electrocatalyst structure imparts substantially high ORR specific activities and high resistance to electrocatalyst dissolution and sintering induced by electrochemical cycling [2]. The NSTF support is based on an oriented, submicron-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 ultra-thin (<1 μm) and do not require additional ionomer for proton conduction [4]. When integrated into state-of-the-art operationally robust MEAs, the NSTF electrode structure enables high absolute and specific power densities [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. Additionally, the project utilizes electrocatalyst modeling and advanced physical and chemical characterization to guide and accelerate development.

RESULTS

Table 1 summarizes 2019 project status against the relevant DOE targets and more stringent project targets. The PGM content and PGM loading values were from measurements made in 50-cm² MEAs constructed with a 14- μ m supported 3M PFSA membrane and robustness-optimized diffusion media with a cathode interlayer (16 μ g Pt/cm²). The remaining targets were measured in 50-cm² MEAs with 20- μ m unsupported PFSA membranes with 3M standard diffusion media without a cathode interlayer.

Table 1. Status Against Technical Targets

Characteristic	Target and Units	Project Target	2019 Status
PGM total content (both electrodes)	0.125 g/kW ($Q/\Delta T \leq 1.45$)	0.10	0.106 ^a , 150kPa 0.086 ^a , 250kPa
PGM total loading (both electrodes)	0.125 mg/cm ²	0.10	0.094 ^a
Loss in catalytic (mass) activity	40%	20	16 ^a
Loss in performance at 0.8 A/cm ²	30 mV	20	25 ^a
Loss in performance at 1.5 A/cm ²	30 mV	20	<5 ^a
Mass activity @ 900 mV _{IR-free}	0.44 A/mg	0.50 (in MEA)	0.46 ^b , 0.44 ^c , 0.57 ^d
^a UTF 31Pt/26Ir. ^b UTF 20Pt/8Ir. ^c UTF 5Pt/50TaX. ^d UTF 28PtNi+Cr. PGM total content and loadings evaluated in “Best of Class” MEAs, which include a low-PGM anode (UTF 9Pt/11Ir). PGM total content values at 95 °C cell, 150 kPa or 250 kPa H ₂ /air, 2.0 and 2.5 H ₂ and air stoichiometry, $Q/\Delta T = 1.45$ kW/ °C (0.663V).			

A project electrocatalyst, UTF 31Pt/26Ir, exceeded five of the six DOE targets that this project addresses and additionally has met three of six of the project targets. The electrocatalyst is based on a stabilized, layered catalyst structure consisting of a surface Pt layer and an “underlayer” of Ir between the Pt surface layer and the NSTF perylene red 149 whisker support. The catalyst, comprising 31 μ g_{Pt}/cm² and 26 μ g_{Ir}/cm², demonstrated PGM total contents of 0.106 g_{PGM}/kW at 150 kPa (absolute) reactant pressures and 0.086 g_{PGM}/kW at 250 kPa (absolute) reactant pressures when integrated into an MEA with a PGM total loading of 0.094 mg/cm², exceeding the respective DOE targets. Additionally, the catalyst was exceptionally durable and demonstrated a loss in catalytic (mass) activity of 16%, loss in performance at 0.8 A/cm² of 25 mV, and loss in performance at 1.5 A/cm² of less than 5 mV, all of which exceed the three respective DOE targets. The mass activity of this catalyst was 0.27 A/mg_{PGM}, below the DOE target of 0.44 A/mg_{PGM}.

The project status values for mass activity are provided for three catalysts. Two layered catalysts, one with an Ir underlayer and the second with a composition-modified Ta underlayer (“TaX”), yielded PGM mass activities of 0.46 and 0.44 A/mg_{PGM}, respectively, exceeding and meeting the DOE target and approaching the project target. A third catalyst, consisting of a UTF PtNi alloy with a chromium surface additive, achieved 0.57 A/mg_{PGM}, exceeding DOE and project targets.

UTF Layered Pt/Ir Catalysts

This year, several sets of UTF Pt/Ir/NSTF catalysts were fabricated and characterized, where the Ir loading on the support whisker was fixed in each set and the Pt loading on the Ir typically varied stepwise from 5 to 50 μ g/cm². Figure 1 summarizes PGM mass activity, specific area, and specific activity for these sets, and the metrics are plotted as a function of Pt loadings. For each set of Pt/Ir/NSTF catalysts, optimal PGM mass activity generally occurred with Pt loadings between 10 and 30 μ g/cm². With the xPt/8Ir series, the PGM mass activity increased monotonically from 0.30 to 0.46 A/mg_{PGM} as the Pt loading increased from 3 to 20.5 μ g/cm², and then it decreased monotonically to 0.25 A/mg_{PGM} as the Pt loading increased further to 55 μ g/cm². In

contrast, the mass activity of the UTF Pt catalyst without an Ir underlayer was minimally sensitive to Pt loadings between 14 and 98 $\mu\text{g}/\text{cm}^2$.

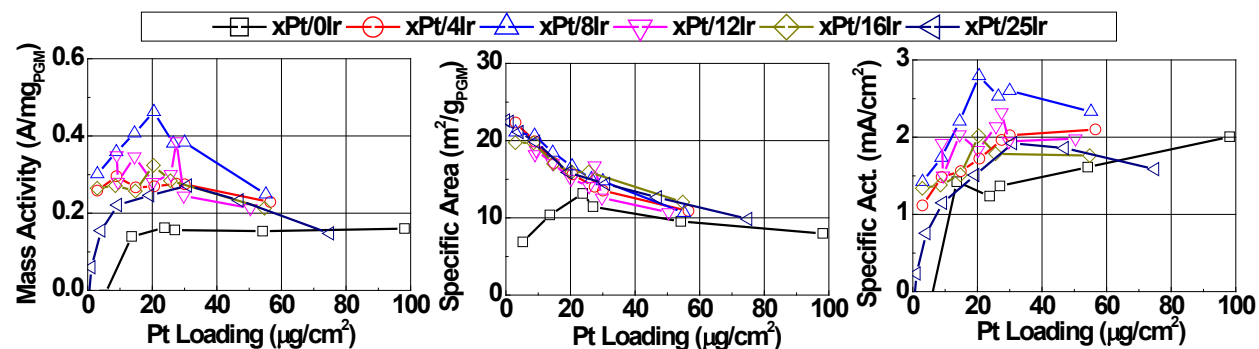


Figure 1. PGM mass activity, specific area (PGM-normalized), and ORR specific activity vs. Pt loading for several sets of UTF Pt/Ir/NSTF catalysts with 0, 4, 8, 12, 16, or 25 $\mu\text{g}/\text{cm}^2$ of Ir in the underlayer. Mean values shown; error bars excluded for clarity.

Figure 1 (middle) summarizes the specific area dependence on Pt loading, where the measured surface area (by cyclic voltammetry) was normalized to total PGM loading. For all of the UTF Pt/Ir/NSTF catalysts assessed, the specific area increased monotonically and similarly as the Pt loading decreased from about 55 to about 5 $\mu\text{g}/\text{cm}^2$. Figure 1 (right) summarizes the specific activity dependences on Pt loading. For all Pt/Ir/NSTF catalysts assessed, the specific activity was found to increase monotonically as the Pt loading increased from 5 to about 20–30 $\mu\text{g}/\text{cm}^2$, with no further improvement as the Pt loading increased further. As such, the observation of peak UTF Pt/Ir/NSTF catalyst mass activity with Pt loadings of 10–30 $\mu\text{g}/\text{cm}^2$ is due to the balance of optimal specific activity level (requiring ~ 20 $\mu\text{g}/\text{cm}^2$ of Pt or more) and optimal specific area (monotonically increasing as Pt loading decreases).

UTF Layered Pt/TaX/NSTF Catalysts

Previously, we reported initial results from a body of work aimed at developing UTF layered catalysts where the underlayer contained little or no precious metal. In that work, several Pt catalysts with Ta underlayers were found to have significantly improved mass activities and specific areas relative to Pt catalysts without underlayers [5]. Additionally, the method by which the catalyst was fabricated also strongly influenced the resultant catalyst properties, where optimal processing resulted in Pt/Ta catalysts with mass activities as high as 0.41 A/mg and specific areas exceeding 20 m^2/g [5]. The processing parameter variation was hypothesized to influence the electronic conductivity of the Ta layer, enabling utilization of the surface Pt layer when it becomes discontinuous at very low loadings.

This year, several UTF Pt catalysts with composition-modified Ta underlayers were generated and characterized, with the objective of improving the conductivity of the non-PGM underlayer toward enabling increased Pt catalyst utilization at ultra-low Pt contents and enhancing specific area and mass activity. Figure 2 compares the mass activity, specific area, and specific activity for Pt (“xPt”), Pt on Ta underlayers with 8 $\mu\text{g}/\text{cm}^2$ areal Ta loading (“xPt/8Ta”), and Pt on composition-modified Ta underlayers with 45 $\mu\text{g}/\text{cm}^2$ areal Ta loading (“xPt/45TaX”), plotted as a function of Pt loading. As the Pt loading of the xPt/8Ta and xPt/45TaX catalysts decreased to about 10 $\mu\text{g}/\text{cm}^2$ (approximately 1 nm thick), the mass activity, specific area, and specific activity increased significantly relative to higher Pt loadings. As the Pt loading decreased from 10 to about 5 $\mu\text{g}/\text{cm}^2$, the mass activity and specific area of the xPt/45TaX increased further, achieving 0.44 A/mg and 28 m^2/g . In contrast, the specific area of the xPt/8Ta catalyst decreased from 22 to ~ 0.4 m^2/g as the Pt loading decreased from 10 to 5 $\mu\text{g}/\text{cm}^2$, and the mass activity was not measurable. This result is consistent with the TaX underlayer enabling improved Pt utilization relative to Ta as the Pt thickness decreases below about 1 nm.

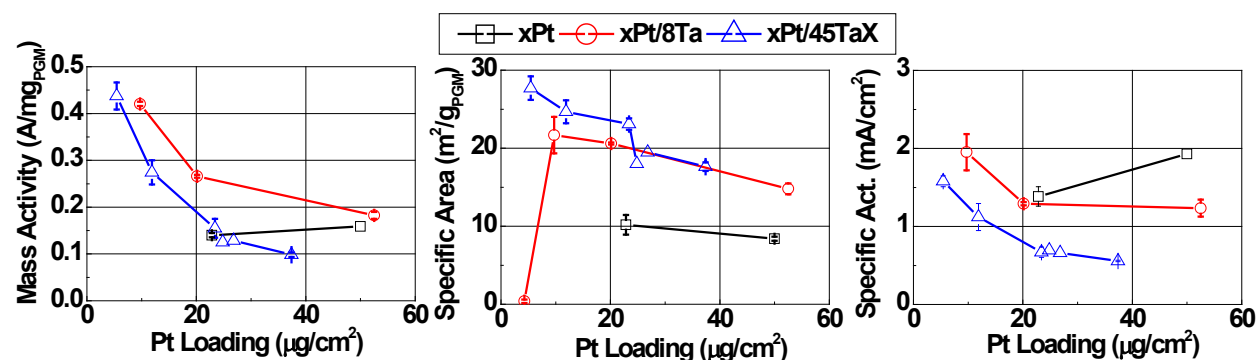


Figure 2. Mass activity, specific area, and specific activity for UTF Pt, UTF Pt on $8 \mu\text{g}/\text{cm}^2$ Ta, and UTF Pt on composition-modified $45 \mu\text{g}/\text{cm}^2$ Ta. Catalysts fabricated with optimum process level “D” from preceding section.

One concerning aspect with the Ta and TaX underlayers is that they may suppress specific activity. Figure 2 (right) shows that with Pt loadings of 20–25 $\mu\text{g}/\text{cm}^2$, the specific activities of Pt, xPt/8Ta, and xPt/45TaX were 1.4, 1.3, and 0.7 $\text{mA}/\text{cm}^2_{\text{Pt}}$, respectively. As the loadings increased, the specific activity of Pt increased and the specific activities with the underlayers decreased. Work is ongoing to characterize these catalysts to determine possible causes for the suppressed specific activity, including migration of Ta and/or X into the Pt layer and nonoptimal Pt-Pt compressive strain.

Electrocatalyst Modeling

In previous project work, Purdue University developed a DFT model to predict the activity of layered Pt on Ir catalysts. In that work, it was predicted that three or more monolayers of Pt adhered to an Ir(111) slab substrate could result in up to a 20x enhancement in activity over Pt(111) [5]. This predicted enhancement was largely due to the predicted compression of the Pt-Pt bond distance by approximately 2.5%–3% relative to bulk Pt, induced by pseudomorphic compressive strain of the surface Pt lattice on Ir(111), which has a smaller face-centered cubic (FCC) lattice constant (3.839 Å) than Pt (3.924 Å).

This year, the modeling work was extended to include analysis of *unsupported* Pt and Pd monolayers (“nanosheets”), including nanosheets with exposed hcp(0001), fcc(111), fcc(110), and fcc(100) facets. The model predicted that as the number of monolayers decreased from eight to three, the surface compressive strain would decrease from approximately -4% to -1.5% for Pt nanosheets and -2% to -1% for Pd nanosheets. Collaborators at Johns Hopkins University and University of California, Irvine experimentally synthesized and characterized Pd nanosheet catalysts based on this approach. The resultant Pd nanosheet catalysts with three, five, and eight monolayers were found to have Pd-Pd bond compression of -1.5%, -1.2%, and -0.3%, consistent with the model prediction. In rotating disk electrode studies, the Pd nanosheet catalysts with three, five, and eight Pd monolayers had activity enhancements of 10x, 14x, and 5x, respectively, vs. Pd nanoparticles in 0.1 HClO_4 , and 18x, 15x, and 2x in 0.1 M KOH. The nanosheet catalysts development resulted in a publication in *Science* [6].

As reported last year, the project is developing an electrocatalyst cyclic durability model based on kMC and DFT. DFT modeling at Purdue University was used to determine several key thermodynamic parameters, including detailed calculations of diffusion barriers for Pt surface atoms in the presence of adsorbed oxygen and hydroxide, and to determine Pt, Ni, and Ir bond energies as a function of self and other coordination numbers. At Johns Hopkins University, the kMC model was updated significantly to incorporate the DFT-determined thermodynamic parameters and to include Pt oxidation and reduction kinetics explicitly. The updated kMC model was then utilized to conduct simulations of various catalyst structures. The simulation was found to agree quite well with experiment regarding the onsets of the multi-step Pt(111) oxidation reactions and the broad Pt reduction process. Based on this development work, a manuscript has been prepared and submitted for publication [7].

The kMC model was then used to assess the impact of Ir underlayers on the stabilization of Pt under potential cycling. Two simulations were conducted, which consisted of simulated redox cycling of a cubic Pt particle on the surface of a larger pure Pt slab or a pure Ir slab. Simulated cycling of the Pt cube on the Pt slab resulted in relatively rapid formation of a highly defective surface consisting of multiple step edges and which continually roughened with cycles. In contrast, cycling of the Pt particle on the Ir slab resulted in rapid formation of a Pt monolayer on the Ir surface with relatively few defects, indicative of the higher stability observed experimentally. Due to the relatively lower surface defect density, the surface oxygen content of Pt on Ir was reduced relative to Pt on Pt, resulting in a higher overall surface specific ORR activity.

CONCLUSIONS AND UPCOMING ACTIVITIES

Over the past year, two new UTF layered electrocatalysts were developed that met or exceeded the DOE mass activity target of 0.44 A/mg_{PGM}. The first catalyst was based on composition optimization of the Pt/Ir system, where the Ir effectively enabled utilization of Pt at low surface coverages, enhanced the specific activity through optimal Pt surface compressive strain, and stabilized the catalyst against dewetting and surface area loss. The second catalyst was based on a composition- and process-optimized Pt/TaX catalyst that did not contain any PGM beyond the surface ORR Pt catalyst, and which resulted in catalysts with unprecedented NSTF specific surface areas as high as 28 m²/g. DFT modeling predicted a new class of PGM nanosheet catalysts that experimentally demonstrated Pd activity enhancement up to 14x that of nanoparticle counterparts in acidic electrolyte. A kMC durability model was developed that accurately predicted Pt oxidation and reduction during cycling and verified the mechanism of Pt stabilization with Ir underlayers. Lastly, studies revealed the presence and identity of a catalyst contaminant that was correlated to the break-in conditioning rate of NSTF MEAs, and a materials modification was implemented, which improved the conditioning rate.

In future work, the project will continue development of one or more electrocatalysts that meet all DOE and project targets. Process and composition optimization of UTF catalysts on PGM-free underlayers will also continue toward achieving entitlement of absolute and specific areas and mass activities with the underlayer approach. Manuscripts will be generated based on the project catalyst development. Lastly, work will continue to identify and implement material solutions to break-in conditioning.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. L. Wang, Z. Zeng, W. Gao, T. Maxson, D. Raciti, M. Giroux, X. Pan, C. Wang, and J. Greeley, "Tunable Intrinsic Strain in Two-Dimensional Transition Metal Electrocatalysts," *Science* 363, no. 6429 (2019): 870–874.
2. L. Wang, Z. Zeng, C. Ma, F. Xu, M. Giroux, M. Chi, J. Greeley, and C. Wang, "Migration of Cobalt Species in Mixed Platinum-Cobalt Oxide Bifunctional Electrocatalysts in Alkaline Electrolytes," *Journal of The Electrochemical Society* 166, no. 7 (2019): F1–F5.
3. J. Erlebacher, J. Kubal, Z. Zeng, J. Greeley, K. Struk, and A. Steinbach, "Kinetic Monte Carlo Simulations of Electrochemical Oxidation and Reduction of Pt(111)," *submitted*.
4. "Self-Driven Strain Tuning in Transition Metal Nanocrystals for the Oxygen Reduction Reaction," (Contributed Talk) AiMES meeting, Cancun, Mexico (September 30–October 4, 2018).
5. "First Principles Calculations for Design of Heterogeneous Catalysts: Perspectives and Opportunities," (Invited Seminar) Department of Chemistry, University of Wisconsin-Madison (November 6, 2018).
6. "First Principles Studies of Heterogeneous Electrocatalysis: Incorporating Structural Complexity into Catalyst Reactivity and Screening Studies," (Invited Seminar) Department of Chemical Engineering, University of Notre Dame (February 5, 2019).
7. "Structure, Stability and Activity of the Supported Ultrathin Transition Metal and (Hydroxy)Oxide Electrocatalysts: A DFT Perspective," (Poster) Chemical Reactions at Surfaces, GRS and GRC, Ventura, CA (February 16–22, 2019).

8. D.A. Cullen, D. Myers, J. Greeley, J. Erlebacher, G. Thoma, and A.J. Steinbach, “Exploring the Activity and Stability of Pt-based Catalysts through Analytical Electron Microscopy,” *Microscopy & Microanalysis*, Baltimore, MD (August 5–9, 2018).

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4. M.K. Debe, “Tutorial on the Fundamental Characteristics and Practical Properties of Nanostructured Thin Film (NSTF) Catalysts,” *J. Electrochem. Soc.* 160, no. 6 (2013): F522–F534.
5. A.J. Steinbach et al., “Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports,” Presentation FC143, 2019 Annual Merit Review, DOE Hydrogen and Fuel Cells Program, Washington, DC (April 2019).
6. L. Wang, Z. Zeng, W. Gao, T. Maxson, D. Raciti, M. Giroux, X. Pan, C. Wang, and J. Greeley, “Tunable Intrinsic Strain in Two-Dimensional Transition Metal Electrocatalysts,” *Science* 363, no. 6429 (2019): 870–874.
7. J. Erlebacher, J. Kubal, Z. Zeng, J. Greeley, K. Struk, and A. Steinbach, “Kinetic Monte Carlo Simulations of Electrochemical Oxidation and Reduction of Pt(111),” *submitted*.