
Platinum Monolayer Electrocatalysts

Jia Wang (Primary Contact), Miomir Vukmirovic,
Kotaro Sasaki
Brookhaven National Laboratory
Upton, NY 11973-5000
Phone: (631) 344-2515
Email: jia@bnl.gov

DOE Manager: Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractor:
Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: July 1, 2015
Project End Date: September 30, 2018

Overall Objectives

- Synthesize high-performance electrocatalysts for the oxygen reduction reaction (ORR) consisting of about one-monolayer (ML) Pt shell on cores made of stable, inexpensive metal, metal alloy, nitride, phosphide, or carbide nanoparticle cores.
- Increase activity and stability of Pt ML core-shell catalysts and stability of carbon supports while reducing noble metal contents.

Fiscal Year (FY) 2018 Objectives

- Design and synthesize new types of core-shell catalysts.
- Screen metal alloy, nitride, and phosphate as inexpensive core materials for high stability and promoting effect for ORR to improve Pt ML catalysts.
- Scale up syntheses of selected catalysts.
- Evaluate synthesized catalysts by membrane electrode assembly (MEA) tests.

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:

- Durability
- Cost
- Performance.

Technical Targets

This project focuses on improving durability and enhancing platinum group metal (PGM) mass activity while simplifying the synthetic processes for meeting/exceeding the DOE 2020 targets listed in Table 1.

FY 2018 Accomplishments

- Designed and synthesized dozens of non-noble-metal nanostructures in the form of alloys, nitrides, phosphides, carbides, and oxides. Four of them showed promise as suitable core material for enhancing PGM activity and durability of Pt ML catalysts.
- Demonstrated that both catalyst and support stability targets can be met using novel nanostructures.
- Delivered gram-scale synthesized catalyst samples for MEA tests.
- Exceeded 2020 DOE targets for catalyst durability (19% versus <40% loss) with PGM activity (0.37 A mg⁻¹) close to the target of 0.44 A mg⁻¹ in MEA tests.
- Gained new insight in structural advantages of Pt ML skin catalysts with Ni-rich nitride cores.

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

Table 1. Progress Toward Meeting DOE 2020 Technical Targets for Electrocatalysts and Supports

Characteristic	Units	Target	PtNiN/C	Pt _{ML} /Pd _{NS} ^a /WNi/C	Pt-NbO _x C
Mass activity	A mg ⁻¹ PGM at 0.9 V	0.44	0.91 RDE ^b 0.37 MEA	0.22 RDE 0.07 MEA	0.56 RDE
Catalyst stability (0.6–0.95 V)	Activity loss after 30K cycles	<40%	18% RDE 19% MEA	0% RDE	4% RDE
Loss at 0.8 A/cm ² (0.6–0.95 V)	mV, cell voltage after 30,000 cycles	<30	0 MEA	4 MEA ^c	
Support stability (1–1.5 V)	Activity loss after 5,000 cycles	<40%		0% RDE	0% RDE

^a NS – nanosheet^b RDE – rotating disk electrode^c Test result after 3,000 cycles

INTRODUCTION

Further enhancing activity and durability of fuel cell catalysts while reducing the PGM content is necessary for accelerating polymer electrolyte membrane fuel cell application in the automotive industry. While Pt ML catalyst maximizes Pt utilization, the core material and structure are critically important for high performance and durability of the core-shell catalysts. Our research aims at meeting the DOE target for electrocatalysts by reducing or eliminating PGM content in core materials and enhancing core durability. Inexpensive and stable materials are synthesized into various nanostructured materials and used as cores with or without a PGM interlayer for improved activity and durability of Pt ML catalysts.

APPROACH

Our approaches to improving Pt ML catalysts in FY 2018 include (1) using metal alloy, nitride, and phosphide to stabilize Ni or Co in cores; (2) promoting formation of favorable (111) facet on Pd nanosheet that acts as the interlayer with WNi or NbN particles; and (3) embedding NbO into the surface pores of carbon support with Pt covering on top. These approaches were supported by studies for gaining insight and understanding of the effect of crystalline facets on chemical and structural properties of metal compounds. Scale-up syntheses were carried out by developing new or simplified procedures and optimized protocols.

RESULTS

Enhanced Durability by PGM-Free Cores of Metal Alloy, Phosphide, and Oxide

We used various synthesis methods to explore suitable core materials and structures for improving Pt ML catalysts—for example, ternary PdNiMo nanoparticles made by sonolysis, Pd₂Ir mixed interlayers covering Ni cores, and small particles of nitrides and carbides of Ti, V, Cr, Nb, Mo, Ta, and W. Among non-PGM metals, Ni, Co, and Fe are ORR-activity promoters, and others are studied mainly for enhancing durability. Below we discuss one example of metal alloy (WNi), one example of phosphide (Co₂P), and one example of metal oxide (NbO_x). In all three cases, distinct nanostructures play important roles in enhancing durability and activity.

WNi nanoparticles on Vulcan-XC72R (VC) carbon support were synthesized by ammonolysis, followed by thermal annealing in hydrogen gas. Pd was deposited on WNi/C in the form of a nanosheet (NS) by using CO gas as a facet-shape control agent. The strong and preferential chemisorption of CO on Pd (111) leads to the formation of Pd NS by preventing growth on the (111) basal plane. Pt ML was deposited via galvanic replacement of an underpotentially deposited Cu monolayer on the Pd nanosheets. The layered structure of Pt_{ML}/Pd_{NS}/WNi/C catalyst is schematically illustrated in Figure 1a. Measured on RDE, the mass activity of the Pt_{ML}/Pd_{NS}/WNi/C catalyst is 0.24 A mg⁻¹ PGM. After 30,000 potential cycles between 0.6 and 1.0 V, the ORR measurements showed no loss in activity. There is also no activity loss after 5,000 potential cycles between 1.0 V and 1.5 V at 500 mV/s (Figure 1b). Replacing WNi by NbN resulted in similar durability enhancement for the Pt_{ML}/Pd_{NS} catalysts. In contrast, Pt_{ML}/Pd_{NS}/C is unstable. These results indicate that WNi and NbN are highly effective in enhancing durability.

Pt-Co₂P nanorod catalyst was studied in collaboration with Prof. Zen Zhang at University of Virginia; the catalyst was made by facet-controlled syntheses to promote the formation of Pt(111) facet on Co₂P(010)-rich nanorods. Density functional theory calculations found this interface is the most favorable for ORR. Nanorods having (010) at the sides and (001) at the ends provide a large portion of the surface area with the desirable (010) facet (Figure 1c). A thin Pt layer was uniformly coated on Co₂P nanorods in the presence of Fe(CO)₅. Released CO stabilizes Co₂P against surface oxidation and facilitates the growth of close-packed Pt(111) thin layer (Figure 1d). On RDE, Pt mass activity of 0.96 A mg⁻¹ is more than twice that of PtCo/C. After 10,000 potential cycles, the mass activity decreased to 0.70 A mg⁻¹ but was still higher than 0.44 A mg⁻¹. Because the shape and morphology were retained, the durability may be further improved by higher Pt coverage on Co₂P nanorods.

Nb oxides are acid stable but electrical conductivity decreases with higher oxidation states. We verified the formation of small NbO_x (x ≤ 1) particles by X-ray diffraction (Figure 1e) for samples made with Ketjenblack

600 JD (KB) that differs from VC in having many ~ 4 nm pores on the carbon surface. These pores were used to contain the particle size and uniform coverage on carbon support. Without surface pores, it is difficult to reduce Nb(5+) precursor to low oxidation state because higher temperature is needed, causing particles to grow in size and to retain higher oxidation state. Thus, the sharp X-ray diffraction peaks at low angles corresponding to highly oxidized large Nb_2O_5 and NbO_2 particles on the sample made with VC are not seen for the sample made with KB. This indicates the formation of largely amorphous small particles on KB. The weak and broad peaks in Figure 1e correspond to NbC. Thus, the average number of O per Nb is ≤ 1 . Nearly complete reduction of Nb made these embedded particles a reducing agent for Pt spontaneous deposition on top of NbO_x . As shown by the structural model in Figure 1f, embedded NbO_x anchors down Pt particles on the carbon surface and minimizes Pt-carbon contact, which can reduce carbon corrosion and agglomeration of Pt particles. Excellent durability was achieved. A Pt-NbO_xC catalyst with Pt:Nb molar ratio 1:2 showed a PGM activity of 0.52 A mg^{-1} after 50,000 potential cycles between 0.6 V and 1 V and no loss after 5,000 cycles between 1 V and 1.5 V.

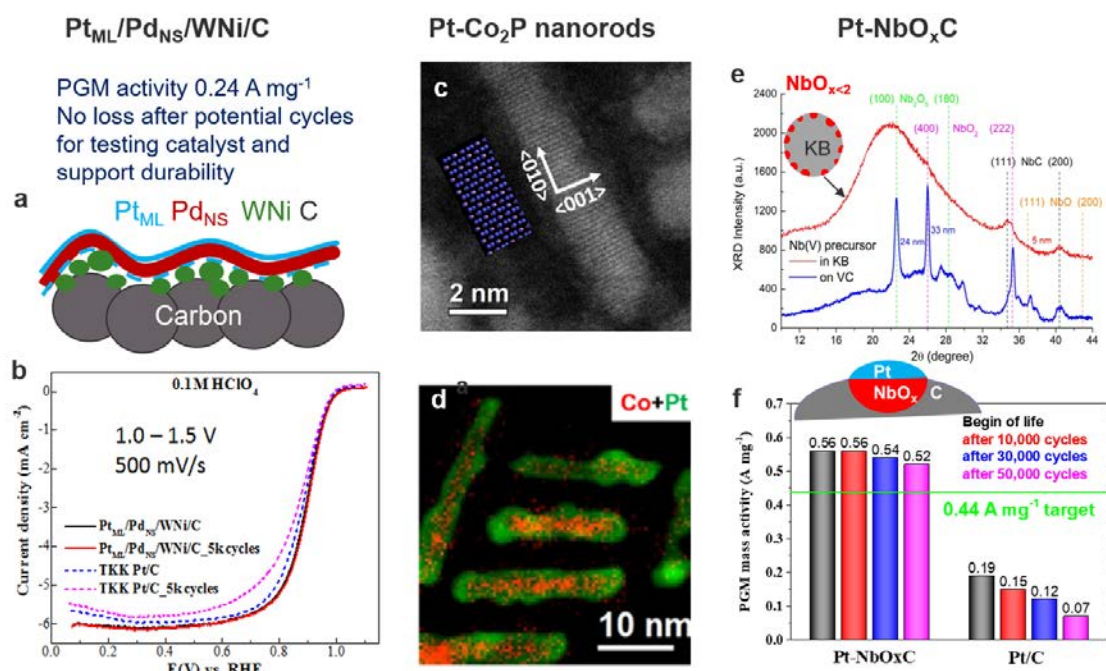


Figure 1. (a) Structural model of Pt_{ML}/Pd_{NS}/WNi/C, (b) ORR polarization curves measured on RDE for Pt_{ML}/Pd_{NS}/WNi/C compared with Pt/C before and after 5,000 cycles for testing support durability, (c) transmission electron microscopy image of Co₂P nanorods, (d) scanning transmission electron microscopy–electron energy loss spectroscopy elemental mapping of Pt-coated Co₂P nanorods, (e) XRD diffraction of NbO_xC made using KB compared to Nb₂O₅ and NbO₂ particles made using VC as supports, and (f) Pt mass activities of Pt-NbO_xC compared to Pt/C

PtNiN/C—Simplified Synthesis Procedure and Promising MEA Test Results

For scale-up synthesis of PtNiN/C catalysts, we developed a facile synthesis procedure that combines reduction and nitriding steps into one thermal treatment of Ni and Pt precursors with ammonia gas. Tested on RDE, the PtNiN/C catalyst exhibited the Pt mass activity of 0.91 A mg^{-1} , higher than that (0.86 A mg^{-1}) obtained previously. After 30,000 potential cycles between 0.6 V and 1.0 V at 50 mV/s, the losses measured were small: mass activity (-18%), electrochemical surface area (-13 %), and $E_{1/2}$ (-13 mV). MEA test of the PtNiN/C catalyst was performed at General Motors. Figure 2a shows H₂/O₂ polarization curves at 80°C before and after 10,000 and 30,000 potential cycles. The Pt mass activity (0.37 A mg^{-1}) is higher than that of Pt/C (0.17 A mg^{-1}) but slightly lower than the target. After 30,000 potential cycles, the losses in activity (-19%) and

electrochemical surface area (~21%) were only ~1/3 those of Pt/C (-66% and -76%, respectively), and the DOE targets of <40% loss were met (Figure 2b and 2c).

Another MEA test of PtNiN/C sample was performed with H₂/air at Los Alamos National Laboratory. Figure 2d shows no loss of cell voltage at 1 A cm⁻² after 30,000 potential cycles, and the current at 0.6 V is more than twice that of Pt/C (Figure 2e). More MEA tests are planned to optimize MEA fabrication for reducing the gap between the PGM activities measured in MEA and on RDE and maximizing high-current-density performance with H₂/air.

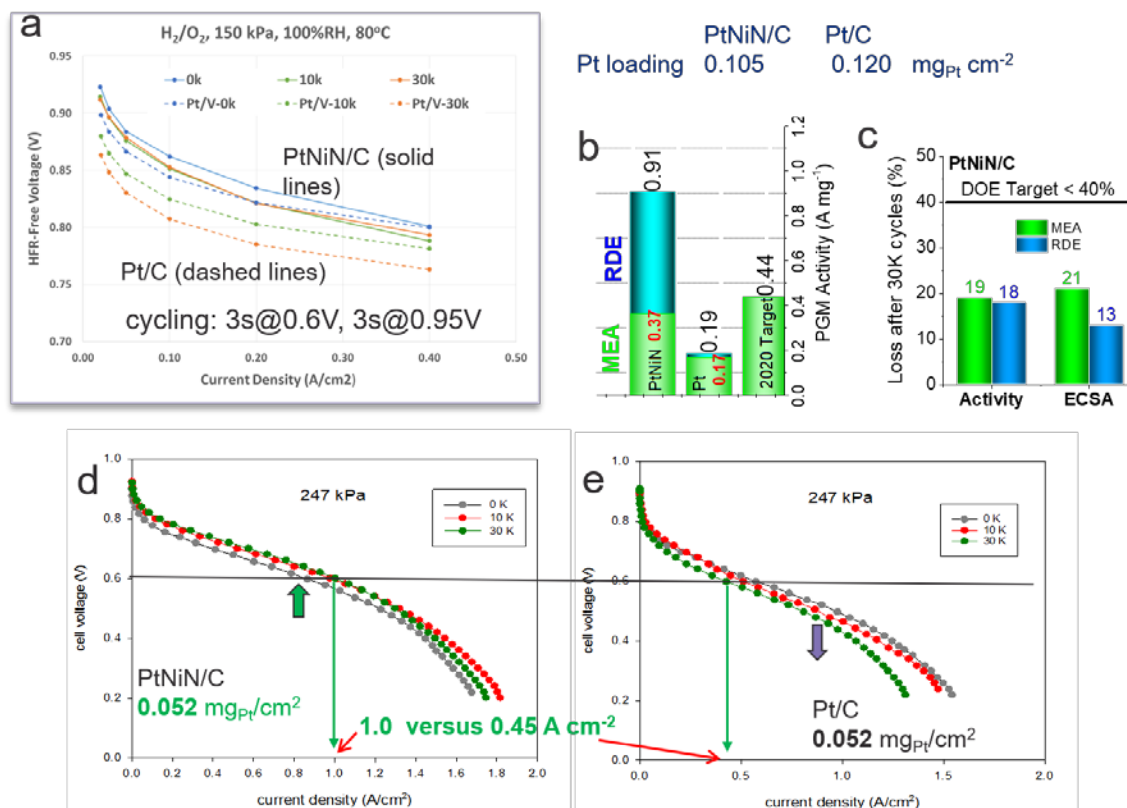


Figure 2. (a) H₂/O₂ polarization curves for cathode catalyst PtNiN/C in comparison with Pt/C before and after 10,000 and 30,000 potential cycles, (b) PGM activities for PtNiN/C catalyst measured by MEA and RDE compared to the DOE target for PGM activity, (c) durability test results for PtNiN/C after 30,000 potential cycles on RDE and in MEA, and (d, e) H₂/air polarization curves measured before and after 10,000 and 30,000 potential cycles for PtNiN/C and Pt/C

More recent MEA tests for Pt_{ML}/Pd_{NS}/WNi/C and Pt-NbO_xC showed considerable gaps between the activities measured in MEA and on RDE. Some improvement is expected by optimizing MEA fabrication. For the Pt-NbO_xC catalyst, the high NbO_x-to-C content ratio likely resulted in significant reduction of electronic conductivity. The ultrathin catalyst layer on RDE is not as sensitive as in MEA to such an effect. New carbon material with the same ~4 nm pore size but lower density may help in improving MEA performance.

PtNiN/C—Structural Advantages of Pt Monolayer Skin Catalyst with Nitride Cores

As the MEA results showed the promise of PtNiN/C in meeting activity and durability targets concurrently, we further studied the intrinsic advantage of nitriding. We found that fcc-structured Ni₄N phase is particularly suitable as the core for PGM skin catalysts. For example, Figures 3a and 3b show the X-ray diffraction of Pt-Ni samples prepared in hydrogen and ammonia, respectively. The alloy particles formed in hydrogen exhibited two sets of diffraction peaks corresponding to a Pt-rich phase (sharper peaks at lower angles) and a Ni-rich

phase (smaller peaks at larger angles). In contrast, single-phase particles were formed by nitriding Pt-Ni with ammonia. The latter is preferred for making uniform catalysts. The distinct structural behavior can be attributed to the smaller lattice mismatch between Pt and Ni₄N (4.56%) than that between Pt and Ni (10.2%).

When Pt segregates to the surface, a Pt_x-(Pt_{1-x}Ni_{1/4})_{core} structure forms. For a 4 nm particle with 1:1 Pt:Ni molar ratio, $x = 0.7$ corresponds to about 1-ML-thick Pt skin as illustrated by the schematic model in Figure 3. In comparison, acid-treated PtNi skin catalysts form multilayer skin on smaller Ni-rich cores because a large portion of Ni is leached out. A thinner Pt skin yields a higher surface area per Pt mass, which is important for high-current-density-performance where kinetic barrier is less a limiting factor. Thus, it is very significant that good durability of as-synthesized PtNiN/C catalysts is demonstrated by MEA tests, which indicates that Ni-rich nitride core is quite stable and effective in enhancing the surface area of Pt and specific activity for ORR via moderate strain effect.

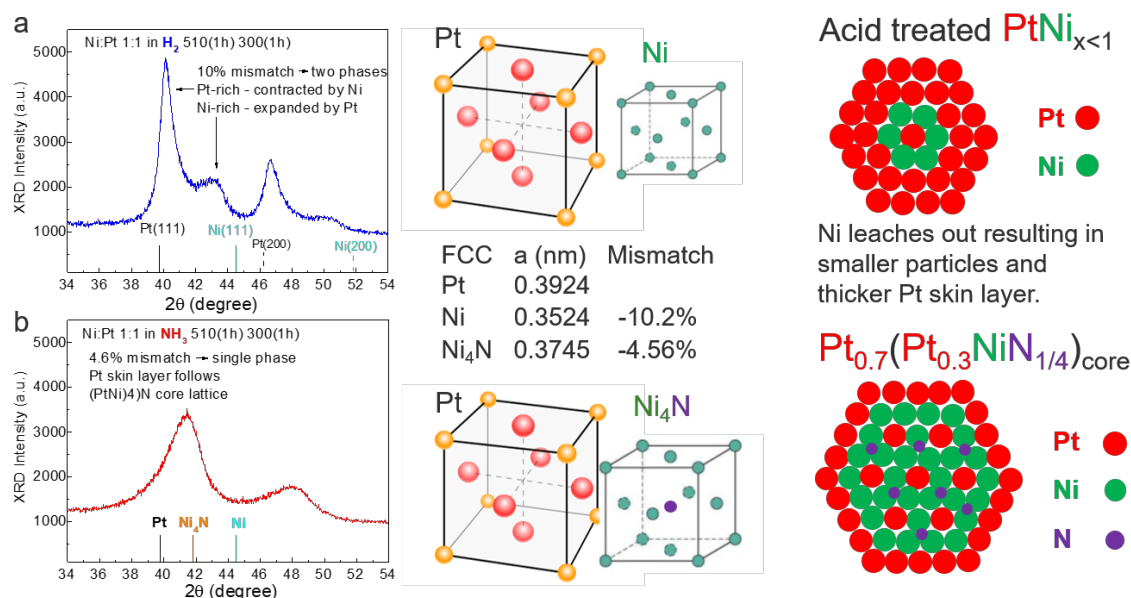


Figure 3. X-ray diffraction profiles of NiPt/C and PtNiN/C samples made by reducing metal precursors in hydrogen (a) and ammonia gas (b). Middle panel: lattice mismatch. Right panel: Structural models of Pt skin catalysts with Ni and NiN cores.

CONCLUSIONS AND UPCOMING ACTIVITIES

New results show that inexpensive metal alloy (WNi), nitride (NbN), and oxide (NbO_xC) are effective in enhancing durability and that PtNiN/C is currently more promising than Pt-Co₂P/C for meeting the targets of PGM activity and catalyst durability concurrently. We developed a facile procedure to synthesize grams-per-batch PtNiN/C catalyst. In MEA tests, PtNiN/C samples exceeded 2020 DOE targets for catalyst durability (20% versus <40% loss, no voltage loss at 0.8 A cm⁻² versus <30 mV loss) with PGM activity (0.37 A mg⁻¹) close to the target of 0.44 A mg⁻¹. In-depth structural analysis explained the advantages of nitride core for Pt ML skin catalysts.

Future work will improve PtNiN/C catalysts by optimizing synthesis parameters and looking into possible benefits of high-pressure nitriding and intermetallic ordered phases. New types of carbon supports will be studied for controlling particle size and distribution during synthesis and for beneficial effects on MEA performance. The feedback from ongoing MEA tests will be analyzed for optimization of catalysts and guiding exploration of new opportunities and approaches.

FY 2018 PUBLICATIONS/PRESENTATIONS

Publications

1. C. Liu, Z. Ma, M. Cui, Z. Zhang, X. Zhang, D. Su, C.B. Murray, J.X. Wang, and S. Zhang, “Favorable core/shell interface within Co₂P/Pt nanorods for oxygen reduction electrocatalysis,” *Nano Letters* 18 (2018): 7870–7875.
2. N.S. Marinkovic, K. Sasaki, and R. R. Adzic, “Determination of Single- and Multi- Component Nanoparticle Sizes by X-ray Absorption Spectroscopy,” *J. Electrochem. Soc.* 165 (2018): J3222–J3230.
3. G. Chen, K.A. Kuttiyiel, M. Li, D. Su, L. Du, C. Du, Y. Gao, W. Fei, G. Yin, K. Sasaki, and R.R. Adzic, “Correlating the Electrocatalytic Stability of Platinum Monolayer Catalysts to Their Structural Evolution in the Oxygen Reduction Reaction,” *J. Materials Chemistry A* 6 (2018): 20725.
4. K.A. Kuttiyiel, S. Kattel, S. Cheng, J.H. Lee, L. Wu, Y. Zhu, G.-G. Park, P. Liu, K. Sasaki, J.G. Chen, R.R. Adzic, “Au-doped Stable L10 Structured Platinum Cobalt Ordered Intermetallic Nanoparticle Catalysts for Enhanced Electrocatalysis,” *ACS Applied Energy Materials* 1 (2018): 3771–3777.
5. L. Song, Z. Liang, Z. Ma, Y. Zhang, J. Chen, R. R. Adzic, and J. X. Wang, 2018. “Temperature-dependent kinetics and reaction mechanism of ammonia oxidation on Pt, Ir, and PtIr alloy catalysts,” *J. Electrochem. Soc.* 165 (2018): J3095–J3100.
6. Z. Ma, Y. Zhang, S. Liu, W. Xu, L. Wu, Y.-C. Hsieh, P. Liu, Y. Zhu, K. Sasaki, R.R. Adzic, J.N. Renner, K.E. Ayers, and J.X. Wang, “Reaction Mechanism for Oxygen Evolution on RuO₂, IrO₂, and RuO₂@IrO₂ Core-Shell Nanocatalysts,” *J. Electroana. Chem.* 819 (2018): 296–305.
7. B. Cai, R. Hübner, K. Sasaki, D. Su, C. Ziegler, M. Vukmirovic, B. Rellinghaus, R. Adzic, A. Eychmüller, “Core-shell structuring of pure metallic aerogels towards highly efficient Pt utilization for the oxygen reduction reaction,” *Angewandte Chemie International Edition* 57 (2018): 1–5.
8. C. Okoli, K.A. Kuttiyiel, K. Sasaki, D. Su, D. Kuila, D. Mahajan, and R.R. Adzic, “Highly Dispersed Carbon Supported PdNiMo Core with Pt Monolayer Shell Electrocatalysts for Oxygen Reduction Reaction,” *ECS Transactions* 85, no. 12 (2018): 67–89.
9. Y. Zhang, F. Liu, S. Liu, D. Lu, D. Su, M. Liu, Y. Zhang, P. Liu, J.X. Wang, R.R. Adzic, and O. Gang, “Oxygen Reduction on Gold Nanocrystal Surfaces in Alkaline Electrolyte: Evidence for Surface Proton Transfer Effects,” *ECS Transactions* 85 (2018): 93–110.
10. L. Song, M.B. Vukmirovic, and R.R. Adzic, “Enhanced Oxygen Reduction Reaction Activity on Pt-Monolayer-Shell PdIr/Ni-core Catalysts,” *ECS Transactions* 85, no. 12 (2018): 57–65.
11. N.S. Marinkovic, K. Sasaki, and R.R. Adzic, “Design of efficient Pt-based electrocatalysts through characterization by X-ray absorption spectroscopy,” *Frontiers in Energy* 11 (2017): 236–244.
12. F. Lu, Y. Zhang, S. Liu, D. Lu, D. Su, M. Liu, Y. Zhang, P. Liu, J.X. Wang, R.R. Adzic, and O. Gang, “Surface-Proton-Transfer-Promoted-Four-Electron Oxygen Reduction on Gold Nanocrystal Surfaces in Alkaline Solution,” *J. Am. Chem. Soc.* 139 (2017): 7310–7317.
13. K.A. Kuttiyiel, K. Sasaki, G.-G. Park, M.B. Vukmirovic, L. Wu, Y. Zhu, J.G. Chen, and R.R. Adzic, “Janus Structured Pt–FeNC Nanoparticles as a Catalyst for the Oxygen Reduction Reaction,” *Chemical Communications* 53 (2017): 1660–1663.

Presentations

1. K. Sasaki, “Recent Advances in Platinum Core-Shell Electrocatalysts for the Oxygen Reduction Reaction,” The 8th International Fuel Cell Workshop Yamanashi University, Koku, Japan, August 23, 2018.
2. K. Sasaki, N. Marinkovic, H.S. Isaacs, and R.R. Adzic, “Synchrotron-based *In Situ* Characterization of Nanostructured Electrocatalysts for Fuel Cell Applications,” ACS National Meeting, New Orleans, March 19, 2018.

3. N. Marinkovic, K. Sasaki, and R.R. Adzic, "Insights in measuring particle size of multiatomic nanoparticles by XAS," 233rd ECS Meeting, Seattle, WA, May 14, 2018.
4. K. Sasaki, K.A. Kuttiyiel, Dong Su, Zhixiu Liang, Liang Song, and R.R. Adzic, "Nitride-Stabilized Platinum Monolayer & Core-Shell Electrocatalysts for the Oxygen Reduction Reaction," 232nd ECS Meeting, National Harbor, Maryland, October 3, 2017.
5. Y. Cai, K. Sasaki, L. Song, A. Kongkanand, and R.R. Adzic, "MEA Studies of Transition Metal Nitride Core-Pt Shell Catalysts for Fuel Cell Applications," 233rd ECS Meeting, Seattle, WA, May 14, 2018.
6. J.X. Wang, L. Song, Z. Liang, Y. Zhang, and R.R. Adzic, "Reaction Mechanism of Ammonia Oxidation Reactions," Electrochemical Society Meeting, Seattle, May 17, 2018.
7. H.L. Xin, W. Xia, Z. Liang, K. Sasaki, D. Wang, and Radoslav Adzic, "Resolving noble metal redistribution and delocalized dealloying effect at the sub-nanometer scale in low-platinum fuel cell nanocatalysts by statistically significant 4D electron microscopy and Visualizing electrochemical reactions at the nanoscale by in-situ TEM," 233rd ECS Meeting, Seattle, WA, May 14, 2018.
8. Z. Liang, J. Fu, M.B. Vukmirovic, and R.R. Adzic, "Electrochemical CO₂ Reduction on Oxide-Derived Cu Surface with Various Oxide Thicknesses," 233rd ECS Meeting, Seattle, WA, May 17, 2018.
9. Y. Zhang, F. Lu, S. Liu, D. Lu, D. Su, M. Liu, Y. Zhang, P. Liu, J.X. Wang, R.R. Adzic, and O. Gang, "Oxygen Reduction on Gold Nanocrystal Surfaces in Alkaline Electrolyte: Effects of Surface Proton Transfer," 233rd ECS Meeting, Seattle, WA, May 15, 2018.
10. J. Chen, R. Manso, L. Song, Z. Liang, and J.X. Wang, "Synthesis of Nanostructured Bimetallic Catalysts for Oxidation Reactions in Alkaline Solution," 233rd ECS Meeting, Seattle, WA, May 17, 2018.
11. H. Yu, A. Poozhikunnath, M.B. Vukmirovic, J. Roller, L.J. Bonville, R.R. Adzic, and R. Maric, "Ternary Pt-Rh-SnO₂ Catalyst Synthesized from Vapor Phase for Ethanol Oxidation," 233rd ECS Meeting, Seattle, Washington, May 14, 2018.
12. L. Song, M.B. Vukmirovic, and R.R. Adzic, "Enhanced Oxygen Reduction Reaction Activity on Pt-Monolayer-Shell PdIr/Ni-core Catalysts," 233rd ECS Meeting, Seattle, Washington, May 14, 2018.
13. Z. Liang, J. Fu, M.B. Vukmirovic, N. Marinkovic, and R.R. Adzic, "Insights into Cu₂O-Based Catalysts for Electrochemical CO₂ Reduction via in-situ ATR-IR and Raman," 255th ACS National Meeting & Exposition, New Orleans, LA, March 20, 2018.