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14. ABSTRACT The objective of this project is the development of next generation fuel cell catalyst systems purposely “engineered” using dopant-mediated growth and stabilization. This “dopant engineering approach” reflects the fact that the activity and stability of a nanoparticulate catalyst supported on a high-surface area electrode material (such as a carbon nanotube support) can be enhanced by purposely doping, or chemically modifying, the support surface. In comparison to the conventional approach using a non-modified carbon support, the dopant-engineering approach employs heterovalently doped carbon support materials decorated by catalyst nanoparticles. The dopant atoms are					
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Report Title

Final Report: Next generation Catalyst Engineering via Support Modification

ABSTRACT

The objective of this project is the development of next generation fuel cell catalyst systems purposely “engineered” using dopant-mediated growth and stabilization. This “dopant engineering approach” reflects the fact that the activity and stability of a nanoparticulate catalyst supported on a high-surface area electrode material (such as a carbon nanotube support) can be enhanced by purposely doping, or chemically modifying, the support surface. In comparison to the conventional approach using a non-modified carbon support, the dopant-engineering approach employs heterovalently-doped carbon support materials decorated by catalyst nanoparticles. The dopant atoms are purposefully used to influence the size, density, distribution, and perhaps even the activity of the overlying catalyst nanoparticles. Compared to the current catalyst system, this dopant-engineered catalyst system could provide enormous improvements in catalyst utilization, activity, and durability. Dopant engineering may also provide an intriguing route to magnify the activity of non-platinum based catalyst nanoparticles, or even enable the creation of entirely new oxide-based catalysts. Our effort focuses on identifying dopant/catalyst combinations to enhance the performance of direct methanol fuel cells. We are specifically focused on the development and characterization of nitrogen-doped catalysts in membrane electrode assemblies (MEAs) for single-cell acid and alkaline direct methanol fuel cell (DMFC) testing. We have demonstrated significant improvements in performance from catalysts doped with nitrogen after deposition of PtRu. These results highlight the significant potential of this support “engineering” approach for producing catalysts with exceptional activity and durability.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
01/21/2016 31.00	A. A. Dameron, P. Joghee, G. Bender, R. O'Hayre, S. Pylypenko, K. N. Wood. Nitrogen Post Modification of PtRu/Carbon Catalysts for Improved Methanol Oxidation Reaction Performance in Alkaline Media, <i>Journal of the Electrochemical Society</i> , (06 2015): 913. doi: 10.1149/2.0011509jes
03/27/2012 6.00	Arrelaine A. Dameron, , Tim S. Olson, , Steven T. Christensen, , Jennifer E. Leisch, , Katherine E. Hurst, , Svitlana Pylypenko, , Justin B. Bult, , David S. Ginley, , Ryan P. O'Hayre, , Huyen N. Dinh, , Thomas Gennett. Pt-Ru Alloyed Fuel Cell Catalysts Sputtered from a Single Alloyed Target, <i>American Chemical Society</i> , (10 2011): 0. doi:
03/27/2012 12.00	T. Fabian, R. O'Hayre, S. Litster, F.B. Prinz, J.G. Santiago. Active water management at the cathode of a planar air-breathing polymer electrolyte membrane fuel cell using an electroosmotic pump, <i>Journal of Power Sources</i> , (06 2010): 0. doi: 10.1016/j.jpowsour.2009.12.025
03/27/2012 11.00	Tibor Fabian, Ryan O'Hayre, Dan Clark, Bryan Babcock, A. J. Tupper. Optimization of Passive Air Breathing Fuel Cell Cathodes, <i>Journal of Fuel Cell Science and Technology</i> , (04 2010): 0. doi: 10.1115/1.3177381
03/27/2012 10.00	Yingke Zhou, Timothy Holme, Joe Berry, Timothy R. Ohno, David Ginley, Ryan O'Hayre. Dopant-Induced Electronic Structure Modification of HOPG Surfaces: Implications for High Activity Fuel Cell Catalysts, <i>The Journal of Physical Chemistry C</i> , (01 2010): 0. doi: 10.1021/jp9088386
03/27/2012 9.00	Yingke Zhou, Timothy Holme, Joe Berry, David Ginley, Robert Pasquarelli, Ryan O'Hayre. Improving PEM fuel cell catalyst activity and durability using nitrogen-doped carbon supports: observations from model Pt/HOPG systems, <i>Journal of Materials Chemistry</i> , (11 2009): 0. doi: 10.1039/b910924b
03/27/2012 8.00	Yingke Zhou, Robert Pasquarelli, Ryan O'Hayre, Timothy Holme. First principles study of doped carbon supports for enhanced platinum catalysts, <i>Physical Chemistry Chemical Physics</i> , (12 2010): 0. doi: 10.1039/b927263a
03/27/2012 7.00	Thomas Gennett, Zongping Shao, Ryan O'Hayre, Huyen N. Dinh, Yingke Zhou, Kenneth Neyerlin, Tim S. Olson, Svitlana Pylypenko, Justin Bult. Enhancement of Pt and Pt-alloy fuel cell catalyst activity and durability via nitrogen-modified carbon supports, <i>Energy & Environmental Science</i> , (10 2010): 0. doi: 10.1039/c003710a
07/13/2014 28.00	Svitlana Pylypenko, Albina Borisevich, Karren L. More, April R. Corpuz, Timothy Holme, Tim S. Olson, Huyen N. Dinh, Thomas Gennett, Ryan O'Hayre, Arrelaine A. Dameron. Nitrogen: unraveling the secret to stable carbon-supported Pt-alloy electrocatalysts, <i>Energy & Environmental Science</i> , (06 2013): 0. doi: 10.1039/c3ee40189h
07/13/2014 26.00	Kevin N. Wood, Ryan O'Hayre, Svitlana Pylypenko. Recent progress on nitrogen/carbon structures designed for use in energy and sustainability applications, <i>Energy & Environmental Science</i> , (07 2014): 0. doi: 10.1039/c3ee44078h
07/13/2014 27.00	Kevin N. Wood, Svitlana Pylypenko, Arrelaine A. Dameron, Prabhuram Joghee, Tim S. Olson, Guido Bender, Huyen N. Dinh, Thomas Gennett, Ryan M. Richards, Ryan O'Hayre, April R. Corpuz. Effect of nitrogen post-doping on a commercial platinum–ruthenium/carbon anode catalyst, <i>Journal of Power Sources</i> , (02 2014): 0. doi: 10.1016/j.jpowsour.2013.09.067

- 07/14/2014 30.00 Prabhuram Joghee, Svitlana Pylypenko, Kevin Wood, Guido Bender, Ryan O'Hayre. High-Performance Alkaline Direct Methanol Fuel Cell using a Nitrogen-Postdoped Anode, *ChemSusChem*, (06 2014): 0. doi: 10.1002/cssc.201400158
- 07/22/2011 1.00 S. Pylypenko, A. Queen, T. Olson, A. Dameron, K. O'Neill, K. Neyerlin, B. Pivovar, H. Dinh, D. Ginley, T. Gennett, R. O'Hare. Tuning Carbon-Based Fuel Cell Catalyst Support Structures via Nitrogen Functionalization. I. Investigation of Structural and Compositional Modification of Highly Oriented Pyrolytic Graphite Model Catalyst Supports as a Function of Nitrogen Implantation, *Journal of Physical Chemistry C*, (07 2011): . doi:
- 07/22/2011 2.00 S. Pylypenko, A. Queen, T. Olson, A. Dameron, K. O'Neil, K. Neyerlin, B. Pivovar, H. Dinh, D. Ginley, T. Gennett, R. O'Hayre. Tuning Carbon-Based Fuel Cell Catalyst Support Structures via Nitrogen Functionalization. II. Investigation of Durability of Pt₁Ru Nanoparticles Supported on Highly Oriented Pyrolytic Graphite Model Catalyst Supports As a Function of Nitrogen Implantat, *Journal of Physical Chemistry C*, (07 2011): . doi:
- 08/07/2012 13.00 Fritz B. Prinz, Wonyoung Lee, Xi Chen, S. Nonnenmann, Dawn A. Bonnell, Ryan P. O'Hayre. Nanoscale impedance and complex properties in energy-related systems, *MRS Bulletin*, (07 2012): 659. doi: 10.1557/mrs.2012.145
- 08/07/2012 16.00 T.S. Olson, P. Joghee, S. Pylypenko, A.A. Dameron, H.N. Dinh, K.J. O'Neill, K.E. Hurst, G. Bender, T. Gennett, B.S. Pivovar, A.R. Corpuz, R.M. Richards, R.P. O'Hayre. Effect of a nitrogen-doped PtRu/carbon anode catalyst on the durability of a direct methanol fuel cell, *Journal of Power Sources*, (11 2012): 142. doi: 10.1016/j.jpowsour.2012.06.012
- 08/07/2012 15.00 Thomas Gennett, Arrelaine A. Dameron, Tim S. Olson, Steven T. Christensen, Jennifer E. Leisch, Katherine E. Hurst, Svitlana Pylypenko, Justin B. Bult, David S. Ginley, Ryan P. O'Hayre, Huyen N. Dinh. Pt–Ru Alloyed Fuel Cell Catalysts Sputtered from a Single Alloyed Target, *ACS Catalysis*, (10 2011): 1307. doi: 10.1021/cs200200s
- 08/07/2012 14.00 Kevin N. Wood, Steven T. Christensen, Svitlana Pylypenko, Tim S. Olson, Arrelaine A. Dameron, Katherine E. Hurst, Huyen N. Dinh, Thomas Gennett, Ryan O'Hayre. In situ small-angle x-ray scattering analysis of improved catalyst—support interactions through nitrogen modification, *MRS Communications*, (07 2012): 0. doi: 10.1557/mrc.2012.13
- 08/10/2013 18.00 Yuanyuan Zhao, Yingke Zhou, Bin Xiong, Jie Wang, Xia Chen, Ryan O'Hayre, Zongping Shao. Facile single-step preparation of Pt/N-graphene catalysts with improved methanol electrooxidation activity, *Journal of Solid State Electrochemistry*, (12 2012): 1089. doi: 10.1007/s10008-012-1968-0
- 08/10/2013 23.00 P. Joghee, S. Pylypenko, T. Olson, A. Dameron, A. Corpuz, H. N. Dinh, K. Wood, K. O'Neill, K. Hurst, G. Bender, T. Gennett, B. Pivovar, R. O'Hayre. Enhanced Stability of PtRu Supported on N-Doped Carbon for the Anode of a DMFC, *Journal of the Electrochemical Society*, (09 2012): 768. doi: 10.1149/2.063211jes
- 08/10/2013 22.00 Prabhuram Joghee, Svitlana Pylypenko, Kevin Wood, April Corpuz, Guido Bender, Huyen N. Dinh, Ryan O'Hayre. Improvement in direct methanol fuel cell performance by treating the anode at high anodic potential, *Journal of Power Sources*, (01 2014): 37. doi: 10.1016/j.jpowsour.2013.06.105
- 08/10/2013 21.00 T. S. Olson, A. A. Dameron, K. Wood, S. Pylypenko, K. E. Hurst, S. Christensen, J. B. Bult, D. S. Ginley, R. O'Hayre, H. Dinh, T. Gennett. Enhanced Fuel Cell Catalyst Durability with Nitrogen Modified Carbon Supports, *Journal of the Electrochemical Society*, (02 2013): 389. doi: 10.1149/2.062304jes
- 08/10/2013 20.00 Bin Xiong, Yingke Zhou, Yuanyuan Zhao, Jie Wang, Xia Chen, Ryan O'Hayre, Zongping Shao. The use of nitrogen-doped graphene supporting Pt nanoparticles as a catalyst for methanol electrocatalytic oxidation, *Carbon*, (02 2013): 181. doi: 10.1016/j.carbon.2012.09.019
- 08/10/2013 19.00 Yingke Zhou, Ryan O'Hayre, Bin Xiong, Zongping Shao. Facile single-step ammonia heat-treatment and quenching process for the synthesis of improved Pt/N-graphene catalysts, *Applied Surface Science*, (02 2013): 433. doi: 10.1016/j.apsusc.2012.12.053

08/22/2011 5.00 Abhishek Dhanda, Heinz Pitsch, Ryan O'Hayre. Diffusion Impedance Element Model for the Triple Phase Boundary, Journal of the Electrochemical Society, (04 2011): 877. doi: 10.1149/1.3596020

09/09/2013 17.00 Kevin N. Wood, Svitlana Pylypenko, Tim S. Olson, Arrelaine A. Dameron, Kevin O'Neill, Steven T. Christensen, Huyen N. Dinh, Thomas Gennett, Ryan O'Hayre. Effect of Halide-Modified Model Carbon Supports on Catalyst Stability, ACS Applied Materials & Interfaces, (12 2012): 0. doi: 10.1021/am301898e

TOTAL: 26

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

INVITED TALKS:

1. R. O'Hayre, "Fuel Cells for Energy Conversion", Invited Lecture, Pusan National University, Pusan, South Korea, August 14th, 2015.
2. R. O'Hayre, C. Duan, M. Sanders, D. Clark, M. Shang, D. Diercks, B. Gorman, S. Ricote, and J. Tong, "Materials for Electrochemical Energy Conversion", Invited Seminar, Korea Institute of Materials Science, South Korea, August 10th, 2015.
3. R. O'Hayre, C. Duan, M. Sanders, D. Clark, M. Shang, D. Diercks, B. Gorman, S. Ricote, and J. Tong, "Materials for Electrochemical Energy Conversion", Invited Seminar, Korea Tech, South Korea, August 6th, 2015.
4. R. O'Hayre, "Fuel Cells for Energy Conversion", Invited Lecture, Korea Tech, South Korea, August 6th, 2015.
5. R. O'Hayre, "Fuel Cells for energy conversion", Invited Lecture, 2015 International School on Materials For Energy and Sustainability, Golden, CO. July 12-19th, 2015.
6. R. O'Hayre, "Triple-conducting cathodes for proton-conducting ceramic fuel cells", Invited Presentation, International Workshop on Proton Conducting Ceramics, Oslo, Norway, March 24-27th, 2015.
7. R. O'Hayre, "Materials for Electrochemical Energy Conversion", Invited Presentation, University-Industry Electrochemistry Workshop, DeNora Inc., Concord, Ohio, November 11-12th, 2014.

CONTRIBUTED TALKS

1. Jason Christ, Tim Batson, Chris Cadigan, Jianhua Tong , Ryan O'Hayre , Svitlana Pylypenko, "Oxygen reduction reaction electrocatalysts based on perovskite oxides", 249th American Chemical Society National meeting, Denver, Colorado, March, 2015
2. S. Pylypenko, P. Joghee, K. Wood, A. Corpuz, J. Christ, G. Bender, R. O'Hayre, "Effect of nitrogen functionalization on stability and performance of carbon-supported PtRu electrocatalysts in acid and alkaline media.", 249th ACS National Meeting, Denver, Colorado, March 22-26th, 2015.

Number of Presentations: 9.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

08/10/2013	25.00	Wonyoung Lee, Minh Hwan Lee, Ryan O'Hayre, Fritz Prinz. Nanoscale Electrochemistry in Energy Related Systems using Atomic Force Microscopy", in Scanning Probe Microscopy for Energy Research: Materials, Devices, and Applications, World Scientific. ISBN-13: 978-9814434706 , Singapore: World Scientific, (03 2013)
TOTAL:		1

Received

Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

CSM Outstanding Faculty Research Award- Colorado School of Mines. 2015

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Joghee Prabhuram	0.75
FTE Equivalent:	0.75
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

The results from our project have created serious interest within the electrochemical industry. Our ARO project results have led in a recent funded project with DeNora Industries Inc. This exploratory project, which started in Feb. 2015 aims to determine whether our nitrogen-doping method can be used to improve the performance of their industrial electrocatalysts used for chlor-alkali electrochemistry.

**Project Final Report - Grant #W911NF-09-1-0528
(Reporting Period: September 2009 – September 2015)**

Final Report: Next Generation Catalyst Engineering via Support Modification

Ryan O'Hayre
Metallurgical and Materials Engineering
Colorado School of Mines, Golden, CO. 80401

Objective

The objective of this project is the development of next generation fuel cell catalyst systems purposely “engineered” using dopant-mediated growth and stabilization. This “dopant engineering approach” reflects the fact that the activity and stability of a nanoparticulate catalyst supported on a high-surface area electrode material (such as a carbon nanotube support) can be *enhanced* by purposely doping, or chemically modifying, the support surface. In comparison to the conventional approach using a non-modified carbon support, the dopant-engineering approach employs heterovalently-doped carbon support materials decorated by catalyst nanoparticles. The dopant atoms are purposefully used to influence the size, density, distribution, and perhaps even the activity of the overlying catalyst nanoparticles. Compared to the current catalyst system, this dopant-engineered catalyst system could provide enormous improvements in catalyst utilization, activity, and durability. Dopant engineering may also provide an intriguing route to magnify the activity of *non-platinum* based catalyst nanoparticles, or even enable the creation of entirely new oxide-based catalysts. Our effort focuses on identifying dopant/catalyst combinations to enhance the performance of direct methanol fuel cells. We are specifically focused on the development and characterization of nitrogen-doped catalysts in membrane electrode assemblies (MEAs) for single-cell acid and alkaline direct methanol fuel cell (DMFC) testing. We have demonstrated significant improvements in performance from catalysts doped with *nitrogen after deposition* of PtRu. These results highlight the significant potential of this support “engineering” approach for producing catalysts with exceptional activity and durability.

Approach

In order to investigate the effects of dopant-support modification on catalyst system activity and durability, a combination of theoretical studies (DFT), model catalyst systems based on geometrically well-defined highly oriented pyrolytic graphite (HOPG) substrates and high-surface area electrochemical and MEA-based studies are used. Details of our approach:

- 1) **Model studies:** In order to fundamentally study the effects of potential dopants, various candidate dopants, including N, Ar, CF₄, and I, are doped via a vacuum implantation technique onto HOPG substrates. Dopant dosage is controlled by implantation voltage, beam current, and implantation time. Catalyst nanoparticles (such as Pt or PtRu) are subsequently sputter deposited onto the dopant-implanted HOPG substrates in the same chamber (without breaking vacuum). The electrocatalytic activity and morphology of the model catalyst systems are examined before, during, and after electrochemical cycling by a variety of techniques including XPS, TEM, SEM, CV, and CO—stripping (to measure ECSA).
- 2) **High surface area catalysts:** Based on insights from model studies, high surface area analogues of the best dopant/catalyst combinations are produced using the same implantation/sputtering system with a rotary wheel that ensures uniform implantation and catalyst decoration of high-surface area carbon support materials. These high surface area doped catalysts are studied before, during, and after electrochemical cycling using the same suite of techniques discussed above.
- 3) **MEA studies:** Large batches of the best performing high-surface area doped catalysts are used to make MEAs for fuel cell testing. Long terms (>500 hr) fuel cell testing of doped and undoped catalysts are used to evaluate whether the benefits of the doping process translate to better performance and durability in a real fuel cell device.

Relevance to Army

Support-doping could improve precious-metal based methanol fuel cell catalytic activity and durability by 3-10x, thereby decreasing catalyst costs by more than 50% (or increase power-density and efficiency by more than 20% at level cost), and increasing fuel cell lifetime by 100-300%. In addition, the application of this technology to other

electrocatalytic systems beyond fuel cells is particularly intriguing for both the military and civilian sector. Based on our results, a global industrial electrochemistry company, DeNora Industries Inc., recently contracted with our research team to see if our N-doping approach can be used to improve the performance of their electrocatalysts, which are used in industrial electrochemistry applications such as the chlor-alkali process.

Accomplishments During the Project

During its duration, this project resulted in the publication of **30 papers in peer-reviewed journals**, including high-impact publications in *Energy and Environmental Science*, *Advanced Functional Materials*, and *ChemSusChem*. Results of our ARO research were featured on **3 journal covers**. In addition, **43 invited talks and 38 contributed talks** were given by the PI and associated students and postdocs over the course of the project. **4 masters degrees and 2 PhD degrees** were funded by the project. All have found positions in industry or academia. **Two of the postdocs employed by the project have gone on to tenure track faculty positions**. We are currently working with industrial electrochemistry company DeNora Industries, Inc. to explore potential **commercial applications** of our nitrogen-doping technology for the commercial chlor-alkali electrocatalysts.

The following numbered paragraphs briefly summarize our major scientific accomplishments over the duration of the entire project (2009-2015).

1) Determined the optimal range and type of nitrogen functionalization for greatest enhancement of catalyst durability using the model HOPG system.

Detailed studies using the HOPG/PtRu model catalyst system, as documented in papers published in *J. Phys. Chem. C* were used to determine the optimal range and type of nitrogen functionalization that leads to the best enhancement of catalyst durability. Specifically, we used microscopy and XPS analysis to establish the role of nitrogen in the durability of PtRu/HOPG model catalyst system. **Figure 1** shows PtRu nanoparticles on N-doped HOPG samples before and after 300 cycles between 0 and 1.1 V vs. Ag/AgCl for different levels of N-doping. Before cycling, the TEMs show that PtRu coverage and composition are independent of the amount of nitrogen present. After cycling to 1.1 V, low implantation dose (5- 15 s) resulted in poor stability while high implantation dose (45, 100s) seemed to have greatly increased particle stability. The results indicate that a high amount of N is needed to form clustered multi-N-defects, which appears to minimize coalescence/migration of the PtRu catalyst. Density functional theory (DFT) was used to infer the effect of specific N functionalities on the stability of PtRu. *DFT calculations show that N-defects such as pyrrolic and pyridinic N enhance the stability of Pt in PtRu and that pyrrolic N improves the stability of PtRu by stabilizing both Pt and Ru. Hence, a balance between pyrrolic and pyridinic N is needed to stabilize PtRu catalyst.* **These results were published in the following papers:** Y. Zhou, R. Pasquarelli, T. Holme, J. Berry, T. Ohno, D. Ginley, R. O'Hayre, "Dopant-induced electronic structure modification of HOPG surfaces: implications for high activity fuel cell catalysts *Journal of Physical Chemistry C*, **114**, 506-515 (2010); S. Pylypenko, A. Queen, K. Neyerlin, T. Olson, A. Dameron, K. O'Neill, D. Ginley, B. Gorman, S. Kocha, H. Dinh, T. Gennett, and R. O'Hayre, "The role of Nitrogen Doping on Durability in the Pt-Ru/HOPG System", *ECS Transactions*, **33**(1), 351-357, (2010); S. Pylypenko, A. Queen, T. S. Olson, A. Dameron, K. O'Neill, K. Neyerlin, B. Pivovar, H. N. Dinh, D. S. Ginley, T. Gennett, and R. O'Hayre, "Tuning carbon-based fuel cell catalyst support structures via nitrogen functionalization. Part I: Investigation of structural and compositional modification of highly oriented pyrolytic graphite model catalyst supports as a function of nitrogen implantation dose", *J. Physical Chemistry C*, **115**(28), 13676-13684 (2011). S. Pylypenko, A. Queen, T. S. Olson, A. Dameron, K. O'Neill, K. Neyerlin, B. Pivovar, H. N. Dinh, D. S. Ginley, T. Gennett, and R. O'Hayre, "Tuning carbon-based fuel cell catalyst support structures via nitrogen functionalization. Part II: Investigation of durability of Pt-Ru nanoparticles supported on highly oriented pyrolytic graphite model catalyst supports as a function of nitrogen implantation dose", *J. Physical Chemistry C*, **115**(28), 13667-13675 (2011)

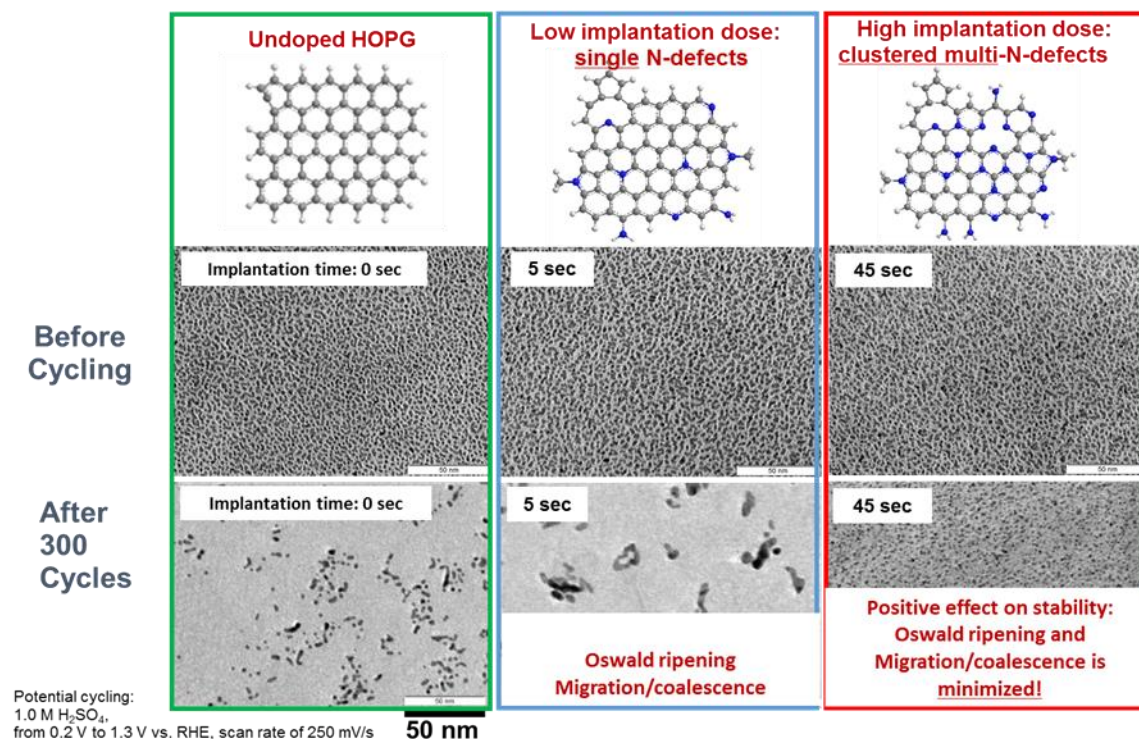


Figure 1. Transmission electron microscopy (TEM) images showing the effect of N-dosage on catalyst durability following potential cycling. High N-dosage results in clustered multi-N-defects, which have a positive effect on the stability of PtRu nanoparticles on N-doped HOPG.

2) Developed (with partners at NREL) a novel ion-implantation/sputter system to enable dopant functionalization via ion-implantation of high-surface area carbon support materials followed directly (without breaking vacuum) by sputter deposition of the PtRu catalyst nanophase. (See Figure 2). The results obtained from this novel ion-implantation/sputter system was published in the following paper: A.A. Dameron, T.S. Olson, S.T. Christensen, J.E. Leisch, K.E. Hurst, S. Pylypenko, J.S. Bult, D.S. Ginley, R. O'Hayre, H.N. Dinh, T. Gennett, "Compositional Control of Pt₁-xRu_x Thin Films Sputtered from a Single Alloyed Target", *ACS Catalysis*, **1**, 1307-1315 (2011);

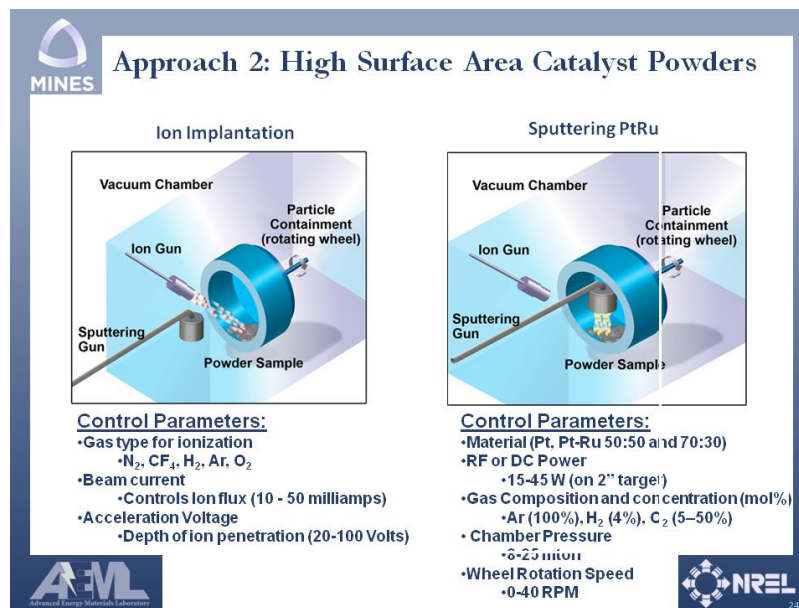


Figure 2. Combined ion-implantation/sputter system for simultaneous dopant functionalization and PtRu loading of high-surface area carbon support materials for DMFC catalysts.

3) Demonstration of improved catalyst-support interactions for iodine and nitrogen-fluorine co-doped system

A major goal of our project was to examine whether other dopants could offer similar benefits as nitrogen. Among the various dopants we examined, we determined that iodine and fluorine dopants provided the most beneficial effects, in some cases exceeding the benefits of nitrogen doping. Furthermore, we discovered that the benefits of a carefully tuned support system modified with fluorine and nitrogen surpass those obtained with nitrogen only (no fluorine) modification. Ion implantation of iodine into HOPG results in a consistent amount of structural damage to the carbon matrix, regardless of dose. For this modification, improvements in stability are similar to nitrogen modification; however, the benefit is only observed at higher dose conditions. This indicates that a mechanism different than the one associated with nitrogen may be responsible for the improved durability in iodine-functionalized materials. This work identified iodine as a potential alternative dopant with similar catalyst durability benefits as nitrogen. This work also identified co-doped nitrogen-fluorine dopants as potential alternative dopants with potentially even better catalyst durability benefits than nitrogen alone. These results were published in the following paper: K. N. Wood, S. Pylypenko, T.S. Olson, A.A. Dameron, K.O'Neill, S.T. Christensen, H.N. Dinh, T. Gennett, and R. O'Hayre, "The effect of halide-modified model carbon supports on catalyst stability", *ACS Appl. Mater. Interfaces*, **4** (12), 6728-6734 (2012)

4) Demonstration of Improved Durability Using a Nitrogen-doped PtRu/Carbon Anode Catalyst in a Direct Methanol Fuel Cell

We evaluated the electrochemical performance and durability of PtRu supported on our optimized N-doped Vulcan catalyst material in the anode of a single-cell direct methanol fuel cell (DMFC). This study demonstrated significant enhancement in catalyst durability (more than 2X enhancement) for the N-doped C/PtRu catalyst compared to the undoped C/PtRu catalyst. This work was detailed in the following publication: P. Joghee, A.R. Corpuz, T.S. Olson, S. Pylypenko, A.A. Dameron, H.N. Dinh, T. Gennett, B.S Pivovar, R. O'Hayre, "Enhanced stability of PtRu supported on N-doped carbon for the anode of a DMFC", *J. Electrochem. Soc.*, **159**, F768-F778 (2012)

We also further investigated the effect of a high anodic potential treatment protocol on the performance of a direct methanol fuel cell (DMFC). DMFC membrane electrode assemblies (MEAs) with PtRu/C (Hi-spec 5000) anode catalyst were subjected to anodic treatment (AT) at 0.8 V vs. DHE using potentiostatic method.

Despite causing a slight decrease in the electrochemical surface area (ECSA) of the anode, associated with ruthenium dissolution, AT resulted in significant improvement in DMFC performance in the ohmic and mass transfer regions and increases the maximum power density by ~15%. Furthermore, AT improved the long-term DMFC stability by reducing the degradation of the anode catalyst. From XPS investigation, it is hypothesized that the improved performance of AT-treated MEAs is related to an improved interface between the catalyst and Nafion ionomer. Among potential explanations, this improvement may be caused by incorporation of the ionomer within the secondary pores of PtRu/C agglomerates, which generates a percolating network of ionomer between PtRu/C agglomerates in the catalyst layer. Furthermore, the decreased concentration of hydrophobic CF₂ groups may help to enhance the hydrophilicity of the catalyst layer, thereby increasing the accessibility of methanol and resulting in better performance in the high current density region. These results have been summarized in the following publication: P. Joghee, S. Pylypenko, K. Wood, A. Corpuz, G. Bender, H.N. Dinh, R. O'Hayre, "Improvement in DMFC performance by treating the anode at high anodic potential, *J. Power Sources*, **245**, 37-47 (2014)

5) Effect of post-doping of PtRu/Carbon Anode Catalyst on the Durability of a Direct Methanol Fuel Cell

In order to demonstrate our N-doping approach on real, commercial catalysts, we then studied the effects of *after-the-fact* chemical modification of a state-of-the-art commercial carbon-supported PtRu catalyst for direct methanol fuel cells (DMFCs). A commercial PtRu/C (JM HiSPEC-10000) catalyst was post-doped with nitrogen by ion-implantation, where "post-doped" denotes nitrogen doping after metal is carbon-supported. Overall, implantation at high dosage results in 16% higher electrochemical surface area and enhances performance, specifically in the mass transfer region. Rotating disk electrode (RDE) results show that after 5000 cycles of accelerated durability testing to high potential, the modified catalyst retains 34% more electrochemical surface area (ECSA) than the unmodified catalyst. The benefits of nitrogen post-doping were further substantiated by DMFC durability studies (carried out for 425h), where the MEA with the modified catalyst exhibits higher surface area and performance stability in comparison to the MEA with unmodified catalyst. *These results demonstrated that post-doping of nitrogen in a commercial PtRu/C catalyst is an effective approach, capable of improving the performance of available best-in-class commercial catalysts (Figure 3).* These results were summarized in the following publication: A.N. Corpuz, K. Wood, S. Pylypenko, A.A. Dameron, P. Joghee, T.S. Olson, G. Bender, H.N. Dinh, T. Gennett, R.R. Richards, R. O'Hayre, "Effect of nitrogen post-doping on a commercial platinum-ruthenium/carbon anode catalyst" *J. Power Sources*. **248**, 296-306, (2014).

6) Demonstrated durability enhancement in an alkaline direct methanol fuel cell by post-doping the PtRu/Carbon anode catalyst with nitrogen.

Based on the impressive performance and durability results we demonstrated with nitrogen-doping for *acid*-based DMFCs, we wanted to see if similar positive effects could be created in *alkaline*-based DMFCs. A commercial PtRu/C (JM HiSPEC-10000) catalyst was post-doped with nitrogen by ion-implantation, where "post-doped" denotes nitrogen doping after metal is carbon-supported. Overall, implantation at high dosage resulted in 32% higher electrochemical surface area and enhances performance, specifically in the ohmic and mass transfer region. For example, the N-doped PtRu/C MEA delivered a maximum power density of 140 (oxygen) and 110 mWcm⁻²(air), whereas the undoped PtRu/C MEA delivered a maximum power density of 117 (oxygen) and 100 mWcm⁻² (air). This represented a 10–17% improvement in performance for the N-doped PtRu/C MEA compared to the undoped PtRu/C MEA. The increased performance of PtRu/C after doping with nitrogen is at least partially attributed to its higher ECSA. Our previous results demonstrated the improved performance and durability of the nitrogen-doped PtRu/C in acid-based DMFCs. These new results demonstrate that post-doping of nitrogen in a commercial PtRu/C catalyst is also an effective approach to improve the performance of best-in-class commercial catalysts in **alkaline media (Figure 4, Table 1). Moreover, this work demonstrated some of the best ADMFC performance metrics ever reported in the literature.** These results have been summarized in the following publications: P. Joghee, S. Pylypenko, K. Wood, G. Bender, R. O'Hayre, "High performance alkaline direct methanol fuel cell employing a nitrogen post-doped PtRu/C anode", *ChemSusChem*, **7**, 1854-1857 (2014). DOI: 10.1002/cssc.201400158 (2014); K. N. Wood, A. A. Dameron, P. Joghee, G. Bender, R. O'Hayre and S. Pylypenko, "Nitrogen Post-Modification of PtRu/Carbon Catalysts for Improved Methanol Oxidation Reaction Performance in Alkaline Media", *J. Electrochem. Soc.* **162** (8), F913-F918 (2015).

7) Investigation of catalyst-support interactions in the graphene-supported materials.

The unique structure and properties of graphene nanosheets make them a very promising alternative to carbon black supports. From our earlier studies we concluded that one of the biggest challenges associated with the graphene supports is poor dispersion of this material during electrode preparation. This issue was addressed by conducting a systematic study of the performance of catalysts supported on graphene-based materials, combining their evaluation in RDE with SEM analysis. We have identified specific solvents and aging treatments that greatly improve the performance of catalyst-inks based on graphene (to be published). Another major issue is poor dispersion of material during metal deposition (sputtering). In the last years of the project, we focused on synthesis of PtRu/graphene and PtRu/N-doped graphene

samples using templated graphene as support. The morphology of the templated graphene allowed to limit agglomeration of graphene sheets during metal deposition and therefore resulted in metal loadings higher than those achieved on graphene nanosheets. This work is currently being prepared for publication.

8) Benchmark reviews of direct methanol fuel cells and N-doped carbon-based materials for energy applications.

In the final year and a half of the project, we have also written two comprehensive literature reviews.

The first review paper focuses on the area of N-doped carbon-based materials for energy applications. It was published in *Energy and Environmental Science*: K. Wood, R. O'Hayre and S. Pylypenko, "Recent progress on nitrogen/carbon structures designed for use in energy and sustainability applications", *Energy Environ. Sci.*, **7**, 1212-1249 (2014). This review provides a comprehensive overview of advances in the last half decade on state-of-the-art carbon modification with nitrogen heteroatoms. Improvements in well-established fabrication/modification processes are discussed as well as novel strategies. Additionally, recent theoretical and experimental findings related to the benefits and effects of nitrogen modification for specific applications in the energy and environmental fields were reviewed. Applications of N-doped carbon materials, discussed in this review include fuel cells, batteries, supercapacitors, hydrogen storage, CO₂ capture, chemical production, photocatalysis, and biosensing.

The second review paper focuses on the current scientific and commercial status of direct methanol fuel cell technology as a whole. This benchmark, invited review was published in *MRS Energy and Sustainability* in 2015: P. Joghee, J. Nekuda Malik, S. Pylypenko, R. O'Hayre, "A review on direct methanol fuel cells - in the perspective of energy and sustainability", *MRS Energy and Sustainability*, **2**, E3 (2015)

Collaborations and Technology Transfer

- The results from our project have created serious interest within the electrochemical industry. Our ARO project results have led in a recent funded project with DeNora Industries Inc. for \$77,000. This exploratory project, which started in Feb. 2015 aims to determine whether our nitrogen-doping method can be used to improve the performance of their industrial electrocatalysts used for chlor-alkali electrochemistry.

Resulting Journal Publications During the Most Recent Reporting Period (Sept 2014-Sept 2015)

Listed below are only publications from the final year of the project. Previous publications have already been detailed in prior annual progress reports.

- P. Joghee, J. Nekuda Malik, S. Pylypenko, R. O'Hayre, "A review on direct methanol fuel cells - in the perspective of energy and sustainability", *MRS Energy and Sustainability*, **2**, E3 (2015)
- K. N. Wood, A. A. Dameron, P. Joghee, G. Bender, R. O'Hayre and S. Pylypenko, "Nitrogen Post-Modification of PtRu/Carbon Catalysts for Improved Methanol Oxidation Reaction Performance in Alkaline Media", *J. Electrochem. Soc.* **162** (8), F913-F918 (2015)

Graduate Students Involved During Reporting Period

- Kevin Wood (PhD, graduated)

Awards, Honors and Appointments

- CSM Outstanding Faculty Research Award- *Colorado School of Mines. 2015*

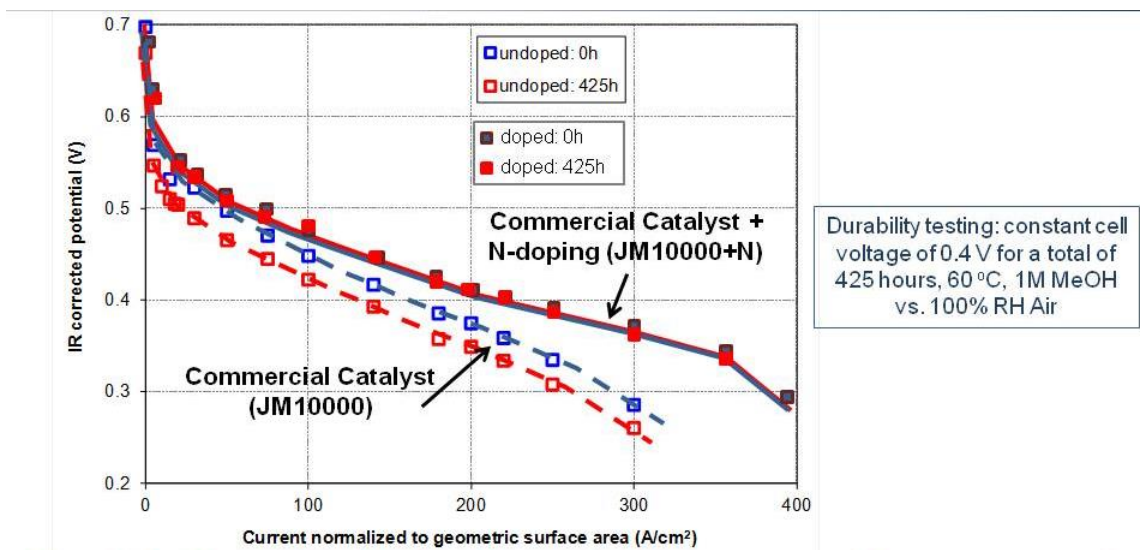


Figure 3. Nitrogen-modification of a state of the art commercial direct methanol fuel cell catalyst (JM10000) leads to a 40% increase in fuel cell performance and an even more significant increase in durability.

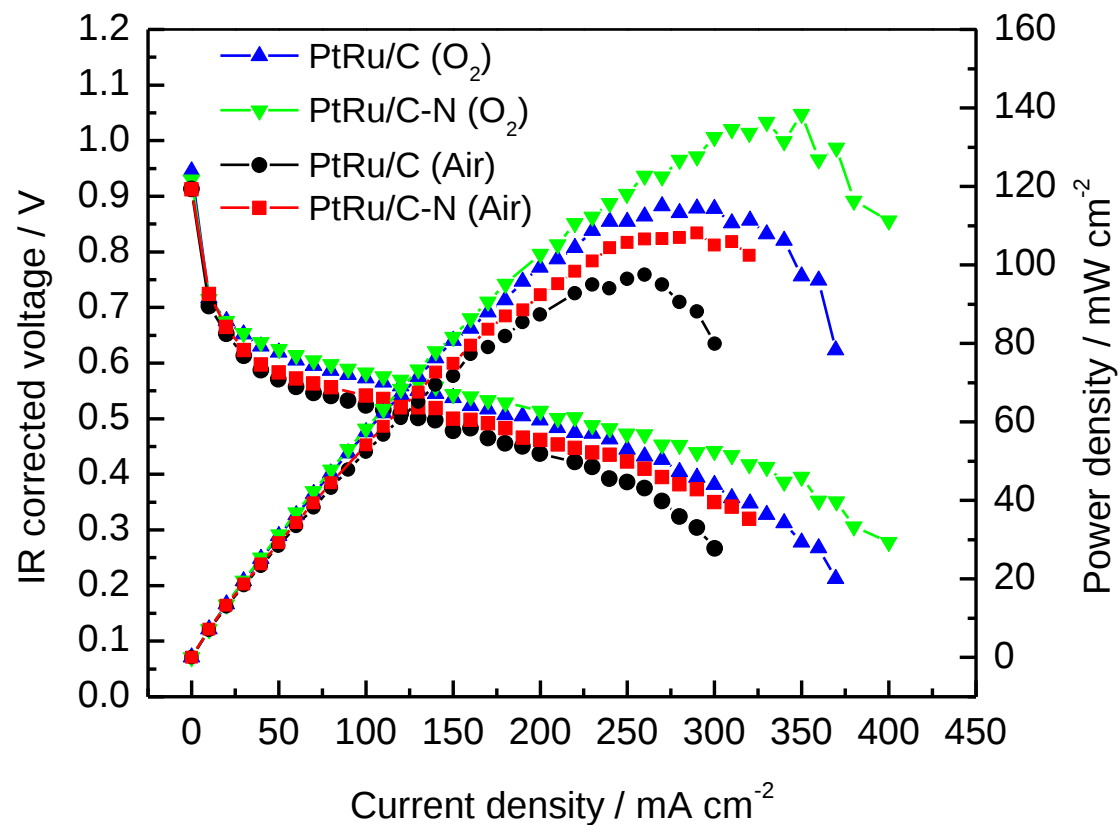


Figure 4. Performance of alkaline-based direct methanol fuel cells employing N-doped PtRu/C and undoped PtRu/C catalysts in 2M NaOH + 2M CH_3OH at 80°C. The N-doped catalyst leads to a ~15-20% increase in max power density. **These results represent some of the best alkaline DMFC performance results ever reported in the literature (as further detailed in Table 1 below).**

Table 1. Comparison of our ADMFC performance with some of the literature data				
Ref.	Anode catalyst	Fuel	Temp. (C°)	Max.PD (mW cm ⁻²)
Our data	PtRu/C (3mgcm ⁻²)	2MNaOH/2M CH ₃ OH	80	100(air) 117 (O ₂)
Our data	PtRu/C-N (3mgcm ⁻²)	2MNaOH/2M CH ₃ OH	80	110(air) 140 (O ₂)
[24]	PtRu (1mgcm ⁻²)	1M CH ₃ OH	80	2.6 (O ₂)
[25]	PtRu (4mgcm ⁻²)	1MKOH/1M CH ₃ OH	50	6.0(air)
[9]	PtRu (8mgcm ⁻²)	2MKOH/1M CH ₃ OH	90	160 (O ₂)
[26]	PtRu (1mgcm ⁻²)	0.5MKOH/1M CH ₃ OH	80	60 (O ₂)