

II.B.2 High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis

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Subcontractors

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- Examine the performance of synthesized OER catalysts in operating PEM electrolyzers
- Test the durability of selected OER catalysts in 1,000-hour PEM electrolyzer operations
- Characterize structure changes of selected catalysts after durability tests to analyze their degradation mechanisms
- Evaluate the scalability and processability of catalyst synthesis via short production runs of selected catalysts

Technical Barriers

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

(F) Capital Cost

(G) System Efficiency and Electricity Cost

Technical Targets

The targets of this project are to develop high performance and long lifetime OER catalysts that may help meet the technical targets of DOE distributed forecourt water electrolysis as shown in Table 1. Included in this table is Giner's status as of 2013.

TABLE 1. Technical Targets: Distributed Forecourt Water Electrolysis [1]

Characteristics		Units	2015 ¹	2020 ¹	Giner Status (2013)
Hydrogen Levelized Cost ²		\$/kg-H ₂	3.90	<2.30	3.64 ³ (5.11) ⁴
Electrolyzer Cap. Cost		\$/kg-H ₂	0.50	0.50	1.30 (0.74) ⁵
Efficiency	System	%LHV (kWh/kg)	72 (46)	75 (44)	65 (51)
	Stack	%LHV (kWh/kg)	76 (44)	77 (43)	74 (45)

¹ 2012 MYRDD Plan. ² Production Only. ³ Utilizing H2A Ver.2. ⁴ Utilizing H2A Ver.3 (Electric costs increased to \$0.057/kWh from 0.039\$/kWh). ⁵ Stack Only
 LHV - lower heating value

Overall Objectives

- Develop various synthetic routes to make iridium (Ir) based oxygen evolution reaction (OER) catalysts with enhanced surface area, oxidation resistance, performance and durability
- Screen the OER catalyst powders via rotating disk electrode (RDE) to determine corrosion resistance and initial catalytic activity
- Physically characterize the catalysts with good RDE activity using microscopy and X-ray techniques to elucidate their structure and particle size distribution
- Evaluate the performance and the durability of membrane electrode assemblies (MEAs) (1,000 hours) in Giner's laboratory commercial proton exchange membrane (PEM) electrolyzers
- Determine the category of catalyst that is most efficient and economically feasible

Fiscal Year (FY) 2015 Objectives

- Further develop synthetic routes to make Ir-based OER catalysts to lower Ir loading or enhance PEM electrolysis efficiency

Accomplishments

- Ir supported on tungsten doped titanium dioxide (Ir/W_xT_{1-x}O₂) reduced anode PGM loading by an order of magnitude while retaining performance comparable to the industry standard (with high PGM loading).
- Ir deposited on nanostructured thin film (Ir/NSTF) anode catalyst significantly lowered the catalyst loading

while enabling the water electrolysis operations at extremely high current density ($>10 \text{ A/cm}^2$).

- Both $\text{Ir/W}_x\text{T}_{1-x}\text{O}_2$ and Ir/NSTF anode catalysts demonstrated minimal performance decay after 1,000-hour PEM electrolyzer tests.
- Ir-metal (Ni or Co) nanowire OER catalysts simultaneously enhanced mass activity and specific activity compared to commercial Ir black in RDE tests.
- Structures of $\text{Ir/W}_x\text{T}_{1-x}\text{O}_2$ catalyst based anodes were characterized after durability tests, providing some insights on catalyst degradation mechanisms.
- Roll-to-roll production of Ir/NSTF catalysts was achieved, showing processability and scalability of catalyst synthesis.



INTRODUCTION

Current hydrogen production from electrolysis is only a small fraction of the global hydrogen market, due to the high cost that results from expensive materials (membrane, catalyst, and bipolar plate) and electricity consumption. The two largest efficiency losses in PEM electrolysis are the anode over-potential and the ohmic losses from the membrane resistance. Anode over-potential is a source of major inefficiency in the entire region of current densities, originating from poor OER kinetics. The only way to lower the over-potential at the anode is to utilize a better catalyst, increase the catalyst loading, or operate at a higher temperature. Iridium and its oxide (IrO_2) represent the current state of the art for oxygen evolution catalysts in electrolysis applications where both performance and durability are important. State-of-the-art PEM electrolyzers relying heavily on Ir black have high Ir loading and low system efficiency (high electricity consumption/per kilogram hydrogen). Therefore, our project aims to develop advanced Ir-based catalysts that enhance OER catalysis and the efficiency of PEM electrolyzers.

APPROACH

Three distinct catalyst approaches have been explored in this project. The first approach is iridium dispersed on tungsten-doped titanium oxide ($\text{Ir/W}_x\text{T}_{1-x}\text{O}_2$) at Giner. The second approach is iridium nanostructured thin film from 3M (Ir/NSTF). The third approach uses NREL's iridium on Ni or Co nanowire technology (IrCo or IrNi); the developed catalysts have been screened by RDE for corrosion resistance and activity and selected catalysts will be made into MEAs and tested in Giner's state-of-the-art electrolyzer test stations to evaluate their performance and durability. Scaled-up production of selected catalysts was conducted.

RESULTS

Giner efforts have focused on increasing mass-specific activity by dispersing Ir nanoparticles (NPs) on appropriate supports, similar to what has been achieved with carbon supported Pt for fuel cells (see Figure 1a). One example is $\text{Ir/W}_x\text{T}_{1-x}\text{O}_2$ catalyst that have been characterized by high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) images (see Figure 1b) at Oak Ridge National Laboratory (ORNL). Figure 1b demonstrates typical morphology of Ir NPs (bright areas) on surfaces of agglomerated $\text{W}_x\text{T}_{1-x}\text{O}_2$ support plates. Most of the $\text{W}_x\text{T}_{1-x}\text{O}_2$

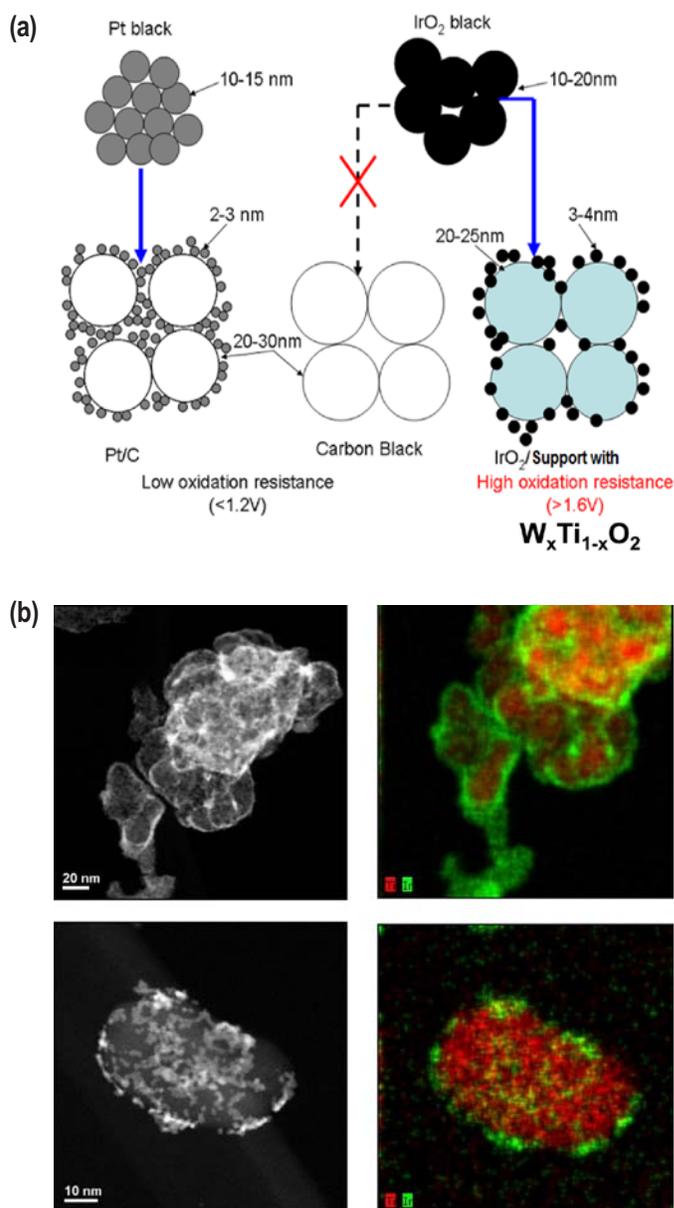


FIGURE 1. $\text{Ir/W}_x\text{T}_{1-x}\text{O}_2$ catalyst development at Giner. (a) Illustration of supported Ir nanoparticle catalyst development. (b) HAADF-STEM images of Ir supported on $\text{W}_x\text{T}_{1-x}\text{O}_2$ taken by Dr. Karren More at ORNL.

particles are thin plates and are “bean-shaped or elongated.” The corresponding EDS map (Ti = red, Ir = green) shows that Ir does not form a continuous coating on the surface of $W_xTi_{1-x}O_2$, but Ir NPs form a “lacey or chain-like” network of interconnected NPs (1.5–2.5 nm) on the surface of the $W_xTi_{1-x}O_2$.

The performance and durability of the Ir/ $W_xTi_{1-x}O_2$ catalyst are shown in Figure 2. The anode of Group 3 cells (4, 5, and 6) is made of Ir/ $W_xTi_{1-x}O_2$ catalyst with low Ir loading (0.25 mg/cm²) where Group 1 cells (1 and 2) use the industry standard anode (Pt+Ir loading 2 mg/cm²). Low loadings of the new catalyst performed significantly better than standard iridium black containing twice as much PGM and approached the performance of the Giner standard anode containing eight times the PGM loading (Figure 2a). A single

cell containing Ir/ $W_xTi_{1-x}O_2$ catalyst at the anode remained relatively stable during a 1,000-hour operation at 1.5 A/cm² with 20 mV voltage loss (Figure 2b). HAADF-STEM images of test MEAs (data not shown) indicate that partial Ir agglomeration and Ir migration into the membrane occur, which may account for the performance loss.

3M created a new NSTF anode that uses iridium without any platinum. The catalyst loading is 0.25 mg/cm². 3M anodes with this low Ir-loading (Ir/NSTF) demonstrated performance comparable to industry standard anodes. Furthermore, they also enabled extremely high current densities up to 16 A/cm² (Figure 3a). No signs of impending transport limitations have been observed at these very high current densities. The ability to operate at high current density is significant as it may help to reduce the size, and

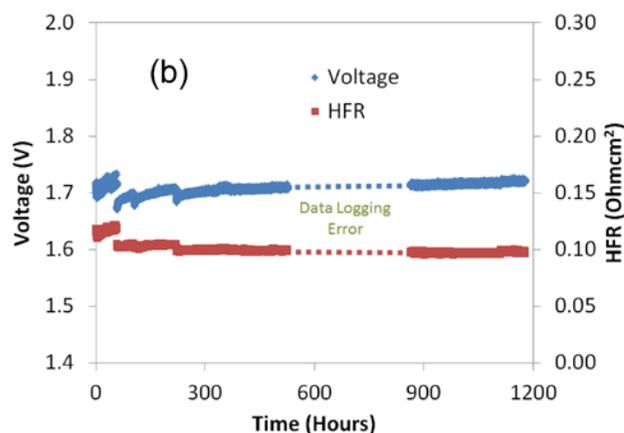
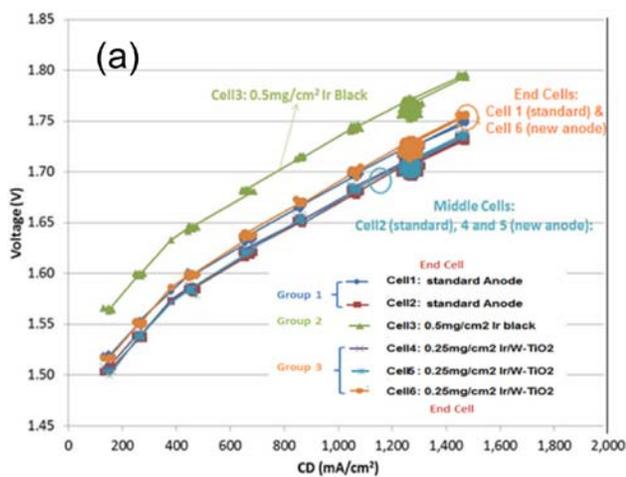


FIGURE 2. PEM electrolyzer performance and durability of Giner Ir/ $W_xTi_{1-x}O_2$ catalyst at 80°C. (a) PEM electrolyzer performance of a short stack of six cells with various anode catalysts. (b) 1,000-hour durability test at 1.5 A/cm². Membrane: Nafion® 115; cathode catalyst: Pt/C, Pt loading 0.4 mg/cm²; anode catalyst: Ir/ $W_xTi_{1-x}O_2$, Ir loading 0.4 mg/cm².

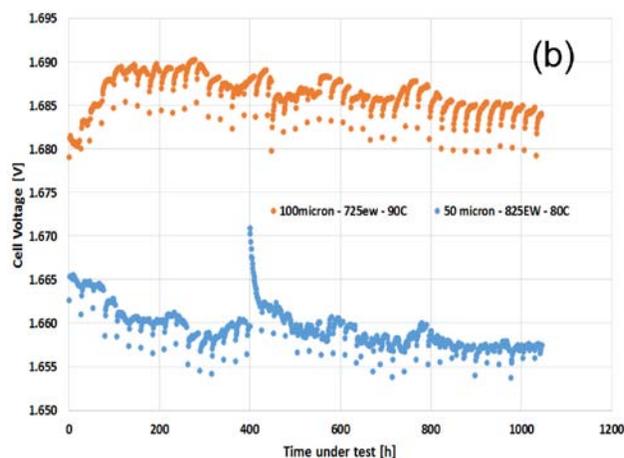
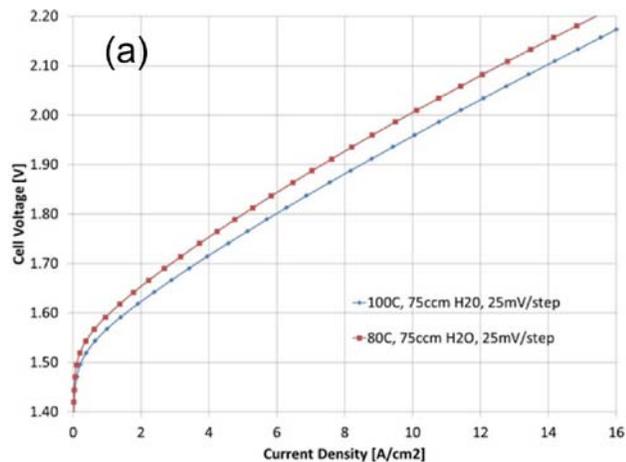


FIGURE 3. PEM electrolyzer performance and durability of 3M Ir/NSTF catalyst. (a) High current density operation of Ir/NSTF catalysts. (b) Durability of two 3M Ir/NSTF anode catalyst-based MEAs up to 1,500 hours. Cathode: 0.25 mg/cm². Pt Anode: 0.25 mg/cm² Ir. Test cycle: cycling from 1.4 V to 2.0 V, hold for 24 h at 1.5 A/cm².

hence cost, of PEM water electrolyzers. Durability testing of the Ir/NSTF was also conducted by 3M. Two MEAs were subjected to multiple hour long cycles of operation at 1.5 A/cm^2 , one has a $100\text{-}\mu\text{m}$ thick membrane operated at 90°C ; the other has $50\text{-}\mu\text{m}$ thick operated at 80°C . Both MEAs showed extremely stable performance over 1,500 hours of testing (Figure 3b).

NREL fabricated iridium nanotubes starting with various nanowire scaffolds. Iridium was deposited onto the nanowire surface using galvanic displacement. The galvanic displacement process occurs when the support material

oxidizes and reduces iridium ions in solution to metallic iridium resulting in an iridium/iridium alloy coating on the support surface. During NREL's syntheses, the amount of iridium precursor supplied was varied to explore catalysts of various Ir loading and composition. After deposition, the nickel and cobalt nanowire supports were selectively exposed to acid leaching conditions to remove transition metals to various extents. The performance of select IrNi and IrCo nanowires evaluated by RDE are shown in Figure 4. The lower Ir content, the higher OER activity (Figure 4a). Mass activity improvements were found to be the result of both

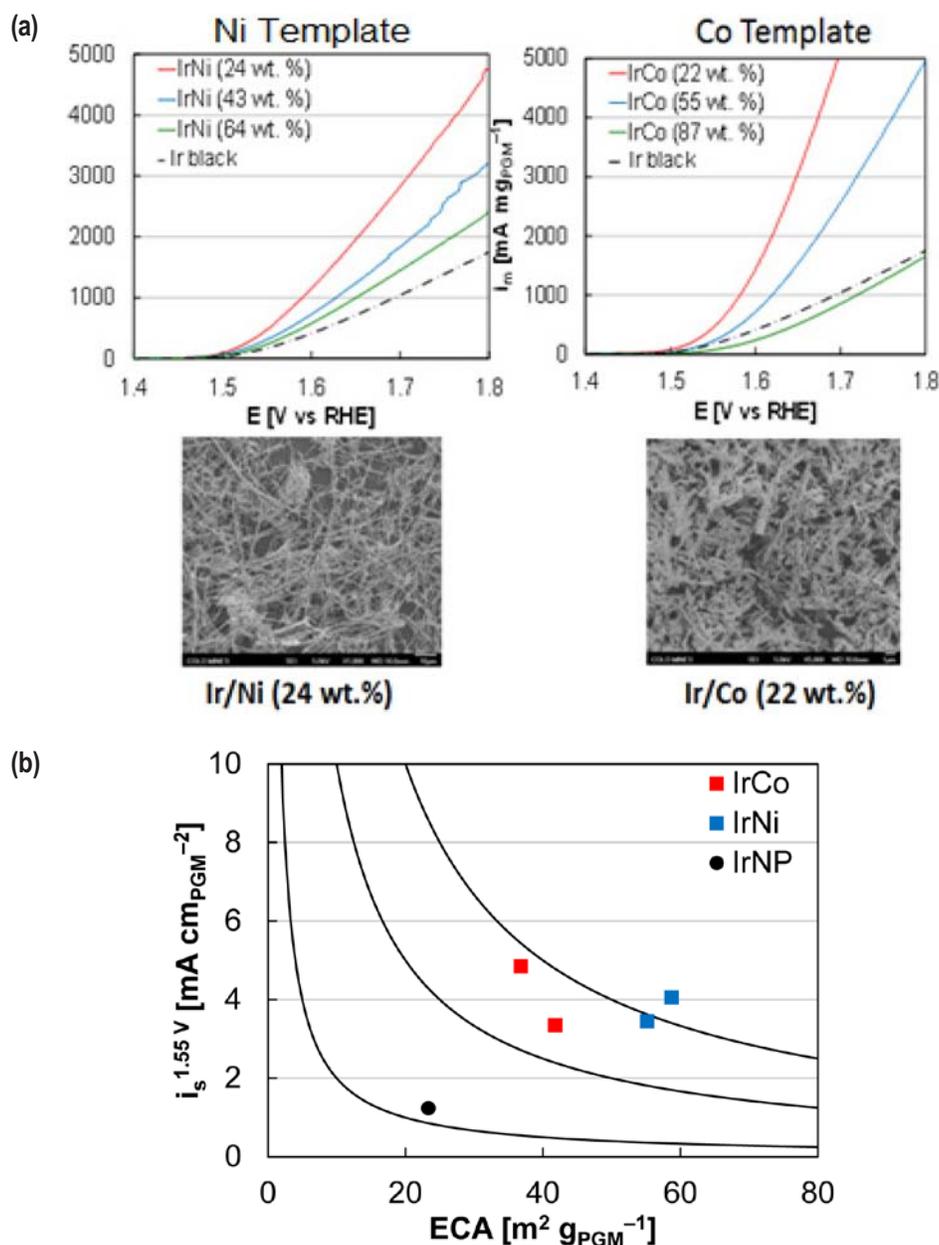


FIGURE 4. Catalytic activity of NREL IrNi and IrCo catalysts using RDE. (a) Ir/metal nanowires based on various templates. (b) ECSA and areal current density (i_s) of various batches of NREL's iridium-coated nanowires and nanotubes. The contour lines (right to left) are of constant mass OER activity of 200, 1,000, and 2,000 mA/mg Ir .

electrochemical surface area (ECSA) and specific activity (Figure 4b). The ECSA was measured by Hg under-potential deposition [2]. The contour lines in Figure 4b are of constant mass OER activity of 200, 1,000, and 2,000 mA/mg Ir, and highlight the approximately order-of-magnitude improvement in activity of both IrCo and IrNi nanowires compared to commercial Ir NP.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- Ir-based OER catalysts for PEM electrolysis have been successfully synthesized
 - Giner: Ir/W_xTi_{1-x}O₂
 - 3M: Ir-NSTF
 - NREL: IrCo and IrNi nanowires
- Giner: Ir/ W_xTi_{1-x}O₂ catalyst-based MEA demonstrated excellent performance
 - A six-cell electrolyzer stack test: the catalyst matched Giner baseline but reduced Ir loading by 8x
 - Single cell test: successfully passed 1,000 h test with 20 mV voltage decay
- 3M: Durability test and mass production of Ir/NSTF catalysts
 - Enabled high current density (16 A/cm²) at 0.25 mg/cm² Ir loading
 - Two MEAs passed 1,000 h test with negligible performance loss
- NREL: Activity and durability of Ir-metal nanowires investigated
 - RDE data shows that both IrCo and IrNi nanowires had ~10x mass activity compared to Ir nanoparticles

Future Directions

- Test Ir/W_xTi_{1-x}O₂ catalyst at high Ir loading (1–2 mg/cm²) to study its effect on over-potential
- Test the catalyst durability of developed catalysts in a short stack under more harsh conditions and extended hours
- Select one category of catalyst with best durability for Giner sub-megawatt electrolyzer stack construction

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Xu, H., B. Rasimick, A. Stocks, B. Pivovar, and K. Lewinski, “High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis,” Progress Report, U.S. Department of Energy Phase II Grant No. DE-SC0007471, August 2014.
2. Xu, H., “Novel Oxygen Evolution Catalysts for Proton Exchange Membrane Water Electrolysis,” presented in 224th meeting of ECS, Abstract #1239, Cancun, Mexico, October 2014.
3. Xu, H., “Invited talk: High-Performance and Long-Lifetime Oxygen Evolution Catalysts for PEM Water Electrolysis,” presented in 225th meeting of ECS, Chicago, May 2015.
4. Xu, H., B. Rasimick, A. Stocks, B. Pivovar, and K. Lewinski, “High-Performance, Long-Lifetime Catalysts for PEM Electrolysis,” final report, U.S. Department of Energy Phase II Grant No. DE-SC0007471, May 2015.
5. Xu, H., “High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis,” presentation in DOE Hydrogen and Fuel Cell Merit Review Meeting, Washington, D.C., June 2015.
6. Shaun Alia, Shyam Kocha, Bryan Pivovar, “Establishing Baselines/Protocols Relevant for PEM Electrolysis,” IEA PEM Electrolysis Workshop, Herten, Germany, April 20–21, 2015.
7. K.A. Lewinski and S.M. Luopa, “High Power Water Electrolysis as a New Paradigm for Operation of PEM Electrolyzer,” L09: Oxygen or Hydrogen Evolution Catalysts for Water Electrolysis Session, #1948, 227th Meeting of the Electrochemical Society, Chicago, IL, May 24–28, 2015.

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1. Hamden, M., “PEM Electrolyzer Incorporating an Advanced Low Cost Membrane,” Presentation in DOE 2012 H2 and Fuel Cells AMR meeting, http://www.hydrogen.energy.gov/pdfs/review12/pd030_hamdan_2012_o.pdf (2012).
2. Kounaves, K.P., and Buffle, J. “Deposition and Stripping Properties of Mercury on Iridium Electrodes,” *J. Electrochem. Soc.* 13, 2495-2498 (1986).
3. Xu, H., “High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis,” Presentation in DOE Hydrogen and Fuel Cell Annual Merit Review Meeting, Washington, D.C., June 2014.