

II.B.4 High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis

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Subcontractors

- National Renewable National Laboratory (NREL), Golden, CO
- 3M Company, St. Paul, MN

Project Start Date: April 22, 2013
Project End Date: April 21, 2015

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 and commercial electrolyzers
- Determine one category of catalyst that is most efficient and economically feasible

Fiscal Year (FY) 2014 Objectives

- Develop three synthetic routes to make Ir-based OER catalysts that may help to lower Ir loading or enhance

proton exchange membrane (PEM) water electrolysis efficiency

- Screen the OER catalysts via RDE to determine corrosion resistance and initial catalytic activity
- Characterize the catalysts with good RDE activity using microscopy and X-ray techniques to elucidate their structure and particle size distribution
- Evaluate the performance of catalysts synthesized from three routes in operating PEM electrolyzers and select the best catalysts for future short production

Technical Barriers

This project addresses the following technical barriers from the Production section of 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.

FY 2014 Accomplishments

- Synthesized Ir supported on tungsten (W)-doped titanium dioxide (TiO_2) that demonstrated excellent oxidation resistance (up to 1.8 V) and 3 times higher OER activity compared to commercial Ir black in RDE tests.
- Developed Ir/metal (Ag, Fe or Co) nanowire OER catalysts that enhance mass activity and specific activity simultaneously by 4 times, compared to commercial Ir black in RDE tests.
- Giner's Ir/W- TiO_2 catalysts demonstrated excellent performance in a PEM electrolyzer:
 - Catalytic activity increased by 3 times compared with standard Ir black
 - Matches Giner baseline performance with reduced Ir loading by 5 times
- 3M Ir NSTF demonstrated superior performance in a PEM electrolyzer:

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

Characteristics		Units	2015	2020	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

- Comparable performance with Giner baseline but at 8 times lower Ir loading
- Stable operation for 100 hours: 1.675 V at 1.5 A/cm²



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 overpotential and the ohmic losses from the membrane resistance. Anode overpotential is a source of major inefficiency in the entire region of current densities, originating from poor OER kinetics. The only way to

lower the overpotential at the anode is to utilize a better catalyst, increase the catalyst loading, or operate at a higher temperature. Iridium and its oxide (IrO₂) 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/kg H₂). Therefore, our project aims to develop advanced Ir-based catalysts that may enhance OER catalyst and the efficiency of PEM electrolysis.

APPROACH

This project is a strong collaboration between Giner, 3M, and NREL. Giner, NREL, and 3M will each develop a different approach to synthesize the OER catalysts, which will be compared to select the best catalysts for short production (see Figure 1).

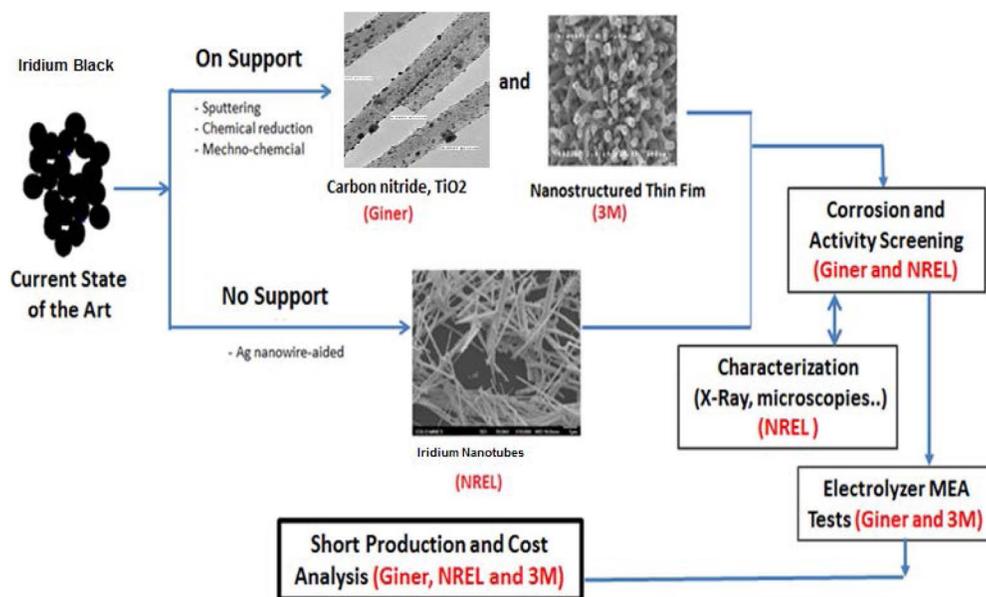


FIGURE 1. Illustration of Synergistic PEM Electrolysis Catalyst Development

The first approach is IrO₂ dispersed on a corrosion-resistant support (e.g. carbon nitride, doped titanium oxide) (Giner). The second approach is iridium nanostructured thin film (NSTF) from 3M that is derived from their platinum NSTF successfully used in PEM fuel cells. The third approach uses NREL's iridium nanotube technology, which may be used to greatly improve performance and/or decrease loading while maintaining high durability at higher electrode loadings. The developed catalysts will be first 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. Finally, scaled-up production of selected catalysts will be conducted and the cost of the catalysts as a function of production volume will be analyzed.

RESULTS

Giner has investigated a broad variety of supports for iridium, including titanium nitride, titanium carbide,

indium tin oxide (ITO), TiO₂, W-doped TiO₂ (W-TiO₂), carbon nitrides. W-TiO₂ (W_{0.1}Ti_{0.9}O₂) nanoparticles and TiO₂ nanowires have been selected as supports. In particular, W-TiO₂ not only demonstrates high oxidation resistance, but also possesses fair electronic conductivity. Ir nanoparticles were deposited on these supports via chemical reduction of Ir precursors and the resulted particle size of 2-3 nm was confirmed by transmission electron microscopy. The activity and durability of supported catalysts are shown in Figure 2.

In the RDE tests, the Ir/W-TiO₂ catalyst improves the OER activity by a factor of 3 compared with commercial Ir black (Figure 2a). The Ir/W-TiO₂ catalyst also demonstrates good stability during voltage cycling from 1.4 to 1.8 V; it retains 95% of its original OER activity even after 10,000 cycles (Figure 2b). Ir/W-TiO₂ also exhibits outstanding performance in a real PEM electrolyzer (Figure 2c). At 0.4 mg/cm² Ir loading, it nearly matches the performance of a Giner standard anode (2 mg/cm² Ir + 2 mg/cm² Pt) while reducing Ir loading by a factor of 5 and precious metal

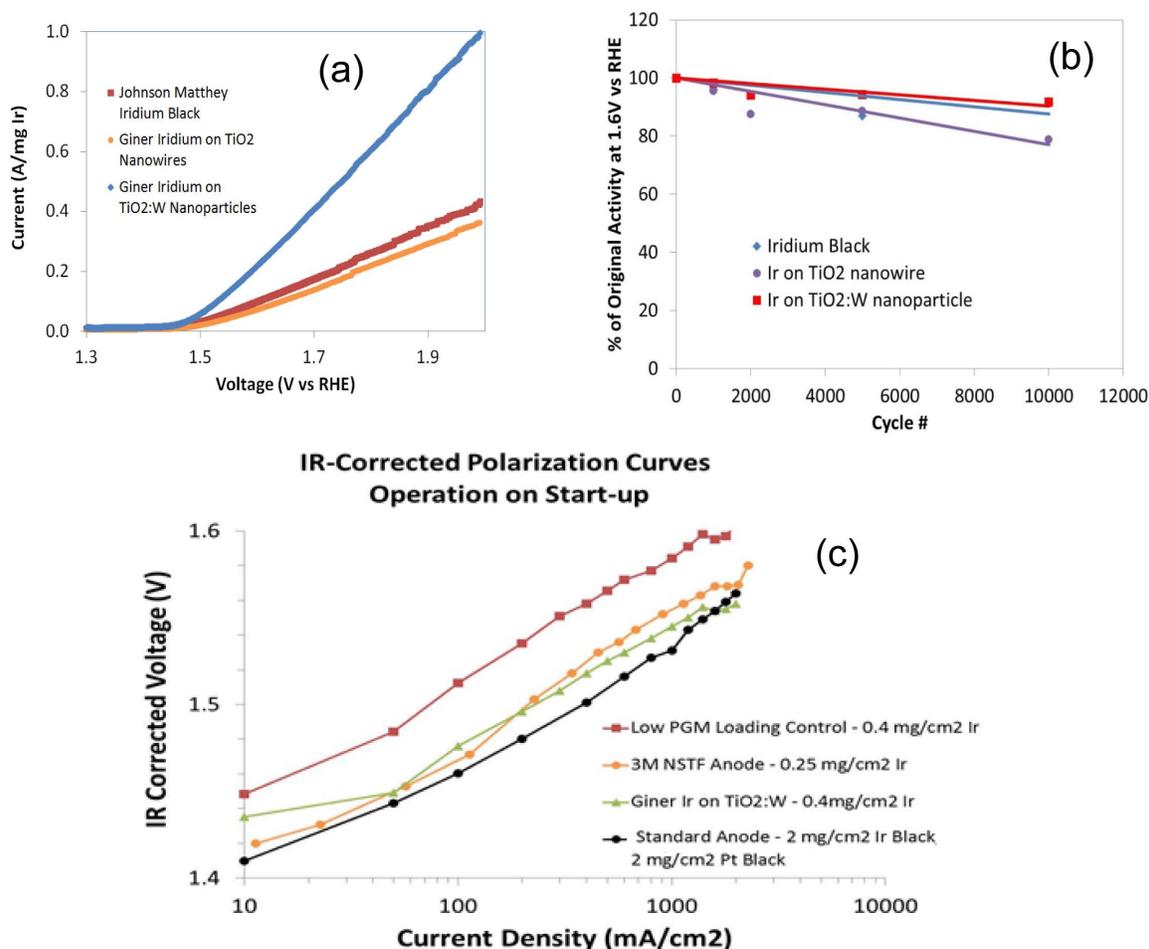


FIGURE 2. Performance of Giner Ir supported on two TiO₂ supports (a) OER activity of in a RDE (scan rate: 20 mV/s; RPM: 2,500 rpm; Ir loading: 40 μg/cm² 0.1 M HClO₄); (b) catalyst durability during voltage cycling from 1.4 V to 1.8 V vs RHE; (c) PEM electrolyzer performance of Ir/W-TiO₂ at 80°C

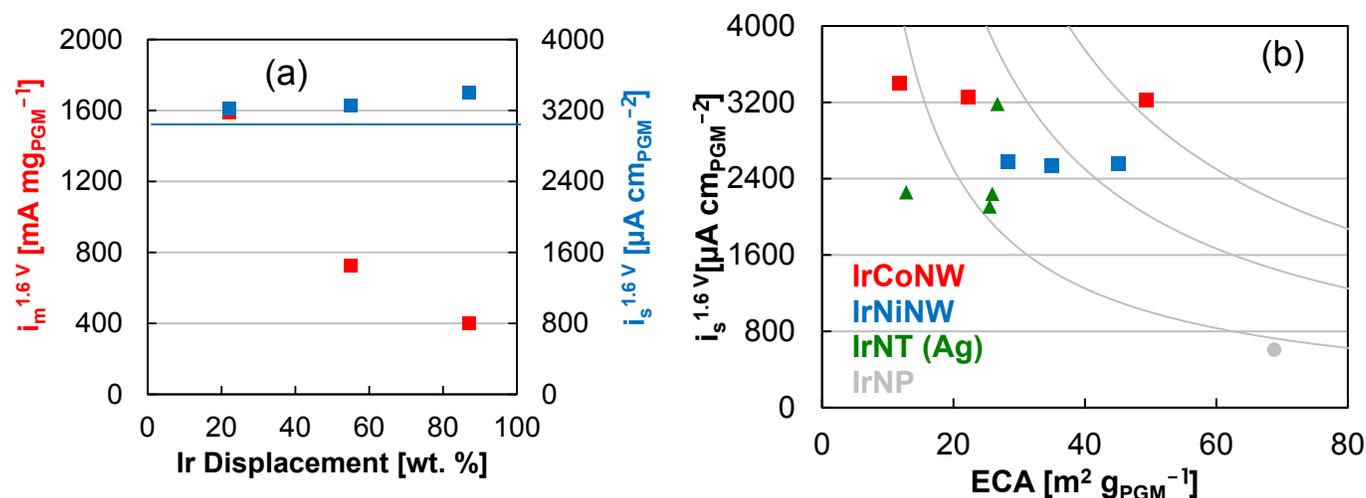


FIGURE 3. Performance of NREL Ir/metal nanowires in RDE tests (a) OER activity of Ir/Co nanowire vs. Ir loading in the nanowire; (b) OER activity comparison of different Ir/metal nanowires vs. the Ir ECSA

loading by a factor of 8. In a comparison with 0.4 mg/cm^2 Ir black, Ir/W-TiO₂ improves the OER activity (current density at a fixed voltage 1.8 V) by a factor of 3. The improved OER activity is directly correlated to decreased Ir particle size. Ir is well dispersed on W-TiO₂ which may increase the electrochemical surface area (ECSA) of Ir particles.

NREL attempted to make iridium nanotubes using different nanowires as a scaffold material. Iridium was deposited onto metal nanowire (Ag, Co or Ni) using partial galvanic displacement. In a typical experiment, iridium cobalt nanowires were synthesized by the galvanic displacement of cobalt with iridium chloride. Synthesis was completed in water to ensure that all iridium reduction occurred at the expense of cobalt. Excess iridium precursor was supplied and experiments were conducted with and without the presence of nitric acid. Iridium content in the cobalt nanowires can be varied. The addition of nitric acid increased the iridium content to 98.4 wt%. The OER activity of these Ir/metal nanowires is shown in Figure 3. Figure 3a illustrates the impact of Ir displacement in the Ir/Co nanowire on the mass and specific activity using a RDE. It can be seen that, as the Ir loading increases, the mass activity of the Ir/Co nanowire catalyst increases but its specific activity remains nearly constant. Figure 3b plots the OER activity of Ir/various metal (Ag, Ni or Co) nanowires against the Ir ECSA that was measured by a mercury under-potential deposition [2]. Contour lines are of constant mass OER activity (500 , 1000 , 1500 mA mg_{PGM}^{-1}) and Y-axis represents the specific activity. Ir/Co nanowire catalyst demonstrates the highest activity: 3.8 times greater specific activity than Ir black and 3 times greater mass activity than Ir black. The durability of these catalysts was also measured by the voltage cycling and it was found that the higher Ir loading, the lower OER activity, the better durability (data not shown). The acid leaching of the Ir/metal nanowire catalysts increase their durability.

3M has created a new NSTF anode that uses iridium without any platinum. This is different from the first generation NSTF anode, where iridium is supported on platinum deposited on the NSTF. The catalyst loading is 0.25 mg/cm^2 . The novel anode is pressed onto a MEA along with a NSTF cathode containing 0.25 mg/cm^2 platinum. The membrane material was a 50 - μm thick sheet of 3M 800 equivalent weight ionomer. The MEA is assembled in Giner's proprietary electrolyzer hardware (flow field and diffusion media) and tested performance is shown in Figure 4. The effect of Ir loading on the electrolyzer performance is shown in Figure 4a and found that the optimum Ir loading appears to be around 0.2 - 0.4 mg/cm^2 PGM. In comparison, the NSTF MEA performed nearly as well as a standard MEA despite having only 25% of the iridium and 12.5% of the total PGM. Preliminary durability testing of the NSTF was also conducted by 3M. Two MEAs were subjected to extended operation at 1.65 V. Both MEAs showed no sign of significant performance degradation after 200 hours (Figure 4b). This has met Milestone 3: PGM loading of less the 0.5 mg/cm^2 ; electrochemical stability at 1.8 V; voltage below 1.7 V @ 1 A/cm^2 .

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- Ir-based OER catalysts for PEM electrolysis have been successfully synthesized and characterized at NREL, 3M, and Giner and RDE data show promising activity of developed catalysts compared to commercial Ir black:
 - Giner: various supports and Ir nanotubes
 - NREL: Ir/metal nanowires

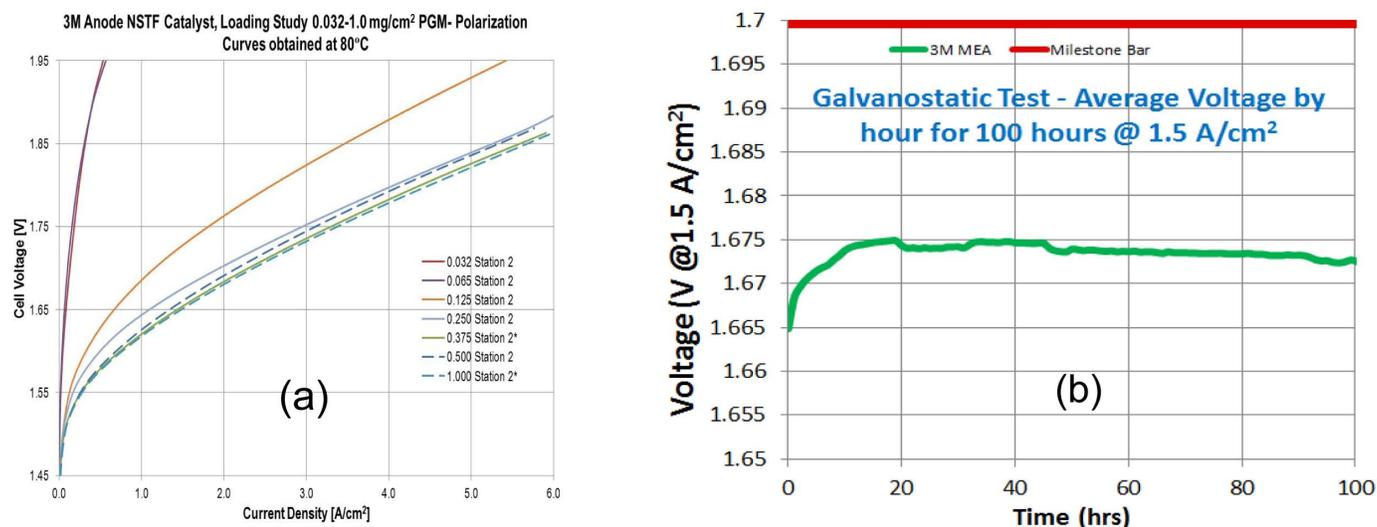


FIGURE 4. Performance of 3M Ir NSTF catalysts (a) impact of Ir loading in the IrNSTF on the electrolyzer performance; (b) a 100-hour durability test of the IrNSTF catalyst (at a current density of 1.5 A/cm²)

- 3M: Ir NSTF
- 3M NSTF catalyst-based MEA demonstrates superior performance:
 - Comparable performance to standard Ir black catalyst but at 8 times lower Ir loading
 - 1.675 V at 1.5 A/cm² for 100 hours, with Ir loading <0.5 mg/cm²
 - Significantly exceeding the milestone set for July 2014
- Giner Ir/W-TiO₂ catalyst MEA demonstrates excellent performance:
 - Catalytic activity increased by 3 times compared with Ir black with same loading
 - Nearly matches Giner baseline performance but reduce Ir loading by 5 times
 - Approaches the performance of 3M NSTF OER catalyst

Future Directions

- Test the durability of the developed catalysts in PEM electrolyzers
- Develop economic analysis of materials and system:
 - Catalyst and MEA cost from short production
 - Electrolyzer system cost and efficiency

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Xu, H., “High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis”, Presentation in DOE Hydrogen and Fuel Cell merit review meeting, Arlington, VA, June 2014.
2. Xu, H, B Rasimick, A Stocks, S Alia, B Pivovar, “High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis” Prog Rpt, DOE Phase II DE-SC0007471, August 2013.
3. 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, January 2014.

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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).