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

Hui Xu (Primary Contact), Brian Rasimick, Robert Stone, Shuai Zhao and Litao Yan
Giner, Inc.
89 Rumford Ave.
Newton, MA 02466
Phone: (781) 529-0573
Email: hxu@ginerinc.com

DOE Manager: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

Contract Number: DE-SC0007471

Subcontractor:
National Renewable Energy Laboratory, Golden, CO

Vendor:
3M Company, St. Paul, MN

Project Start Date: April 21, 2015
Project End Date: October 20, 2017

Overall Objectives

- Scale-up catalyst synthesis to short production (20 g/batch).
- Transfer the selected catalysts to membrane electrode assembly (MEA) in a large-scale fabrication platform.
- Build a sub-megawatt electrolyzer using selected catalysts with low-platinum group metal loading.
- Demonstrate sub-megawatt electrolyzer performance and durability.
- Perform economic analysis of the cost savings provided by the new catalysts at the megawatt-scale.

Fiscal Year (FY) 2017 Objectives

- Resolve the catalyst instability issue arising from catalyst scale-up.
- Scale-up catalyst synthesis to short production (>10 g/batch).
- Construct a 36-cell stack using developed catalysts and test its initial performance and durability.
- Extend catalyst durability tests to 2,000-hour testing in a short electrolyzer stack.

Technical Barriers

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

(F) Capital Cost: High platinum group metal catalyst loading (Ir loading >2 mg/cm^2) due to low catalytic activity for the oxygen evolution reaction and prohibitive proton exchange membrane (PEM) electrolysis cost

(G) System Efficiency and Electricity Cost: Low system efficiency (i.e., high electricity usage) due to significant anode overpotential

Technical Targets

The target of this project is to develop high-performance and long-lifetime oxygen evolution reaction 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 2017 Accomplishments

- Two approaches to producing durable Ir/$W_xTi_{1-x}O_2$ catalyst for the scale-up of catalyst synthesis have been identified:
  - Heat treatment of the $W_xTi_{1-x}O_2$ supports.
  - Formation of addition layer of IrO_2 surface sites.
- Two low-Ir loading (0.4 mg/cm^2 and 0.2 mg/cm^2) cells using scale-up Ir/$W_xTi_{1-x}O_2$ catalysts demonstrate significant durability over 1,000 h.
- A 36-cell 65-kW stack using baseline Ir black, Giner Ir/$W_xTi_{1-x}O_2$ and 3M Ir–nano-structured thin film (NSTF) has been designed and is ready to be assembled.

INTRODUCTION

Hydrogen production for mobility and energy storage from PEM water electrolysis is attractive due to its efficiency, ability to quickly cycle up and down, and delivery of hydrogen with high and differential pressure. However, capital costs are high due to expensive materials, especially the membrane and catalyst. Though membrane costs are predicted to decrease, precious metal catalysts costs will

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 Multi-Year Research, Development, and Demonstration (MYRDD) Plan. [2] Production Only.
[3] Utilizing H2A Ver.2. [4] Utilizing H2A Ver.3 (Electric consts increased to).075/kW from 0.039$/kW). [5] Stack Only
LHV – lower heating value;

come to dominate capital costs as this technology matures. Decreasing the precious metal requirement for PEM electrolysis is therefore vital for the widespread use of this technology. The overall objective of the Phase IIB project is to commercialize the low-precious-metal-loading, high-performance catalysts for PEM water electrolysis that we have successfully developed in our Phase II project, which may significantly lower the capital cost of water electrolyzers. Both Giner's Ir/$W_xTi_{1-x}O_2$ and 3M's Ir–NSTF catalysts developed under this project have been successfully scaled-up for commercialization and are currently being tested for durability and performance.

APPROACH

In the Phase IIB project, Giner aims to transition this game-changing, innovative catalyst technology to successful commercialization. In the previous efforts, Ir/$W_xTi_{1-x}O_2$ catalyst became less stable during the catalyst scale-up. We have identified two strategies to enhance the catalyst stability upon its scale-up. One is the adoption of a precisely controlled reactor, which enables better temperature control and uniform mixing during catalyst synthesis. The other is the surface modification of the $W_xTi_{1-x}O_2$ support to form better interaction between the catalyst and its support. The scale-up catalysts have demonstrated significant durability over 1,000 hours. In addition, we have completed the design of a 36-cell stack using both Giner's Ir/$W_xTi_{1-x}O_2$ and 3M's Ir–NSTF catalysts, on the basis of Giner's 300 cm^2 commercial PEM water electrolyzer platform.

RESULTS

Figures 1a and 1b show the transmission electron microscope (TEM) images of Ir(45)/$Ti_{1-x}W_xO_2$ and IrO_2(25)/$Ti_{1-x}W_xO_2$, which represent 45 wt% and 25 wt% Ir in the catalyst, respectively. For the Ir(45)/$Ti_{1-x}W_xO_2$ sample, the iridium nanoparticles with size of 3 nm was uniformly deposited on the $Ti_{1-x}W_xO_2$ support. The observed conductive inter-connected Ir chain can enhance the electronic transfer and thus the electrolyzer performance. The distance of 0.24 nm of iridium (1 1 1) planes is confirmed by high resolution TEM image (Figure 1c), which further verify the existence of iridium. The distance of 0.35 nm of anatase $Ti_{1-x}W_xO_2$ phase (1 1 1) plane is also indexed. High-angle annual dark field–energy dispersive X-ray spectroscopy mapping (Figures 1 d–h) demonstrated the distribution of various elements including Ti, W, O and Ir. For the Ir(20)/$Ti_{1-x}W_xO_2$ sample, there was no conductive inter-connected Ir chain, indicating the significance of optimizing the Ir content on the support.

Single MEAs were prepared using the Ir/$W_xTi_{1-x}O_2$ as the anode catalyst, commercial Nafion® 115 membranes, and commercial Pt as the cathode catalyst. The electrolyzer stability was significantly enhanced by the heat treatment of the $W_xTi_{1-x}O_2$ support, which could be due to the modification of the support surface and subsequent increase in the binding between Ir nanoparticles and their support. The MEA performance of Ir/$W_xTi_{1-x}O_2$ with heat treatment was 1.76 V at a current density of 2 A/cm^2, which was close to initial performance of Ir/$W_xTi_{1-x}O_2$ without heat treatment. However, the Ir supported on heat treated $W_xTi_{1-x}O_2$ support showed little performance decay after 233 hours of operation (Figure 2a); in contrast, the performance of the catalyst that was not heat treated decayed substantially under the same operating conditions for the same operating hours (Figure 2b).

The MEAs were tested for their durability in a new test station (Figure 3) at 2 A/cm^2. The MEA loading was 0.4 mg/cm^2. The MEA is quite stable and barely without voltage increase after 1,500 h. The top line shows the average feeding water temperature (80°C) since the real temperature oscillated over the course of durability test. The figure also recorded all the incidences including power supply shutdown and heat failure, demonstrating robustness of the cell subjects to multiple incidences.

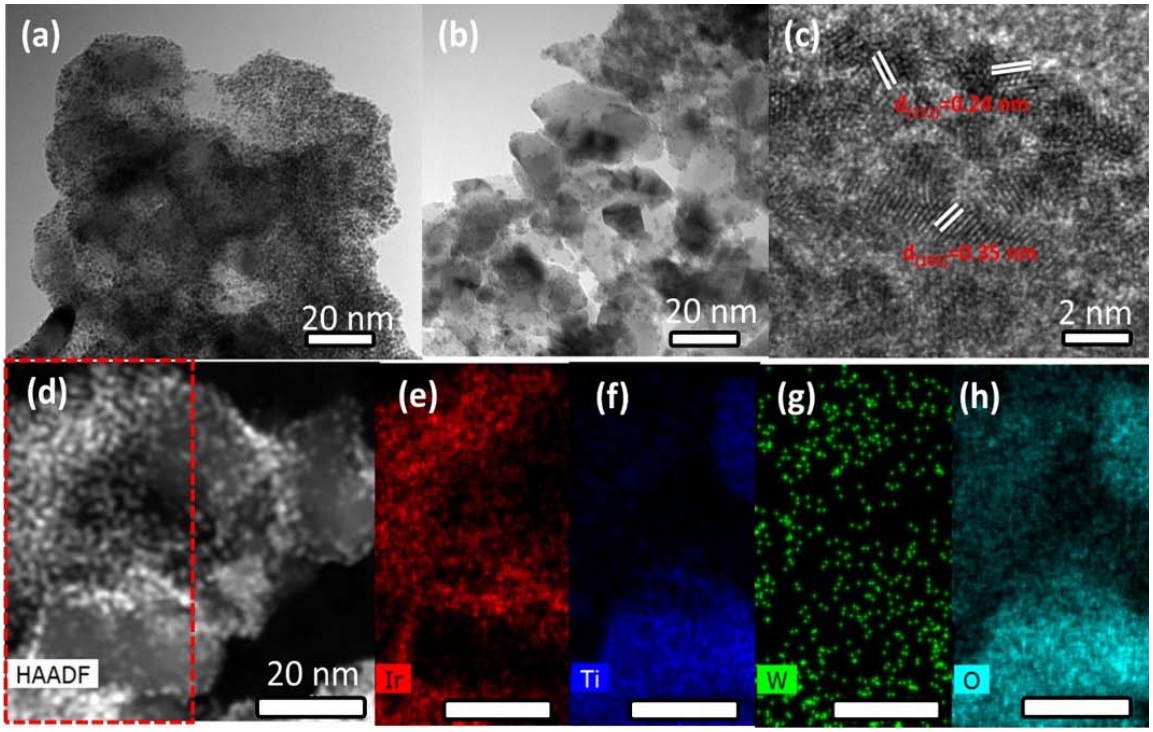
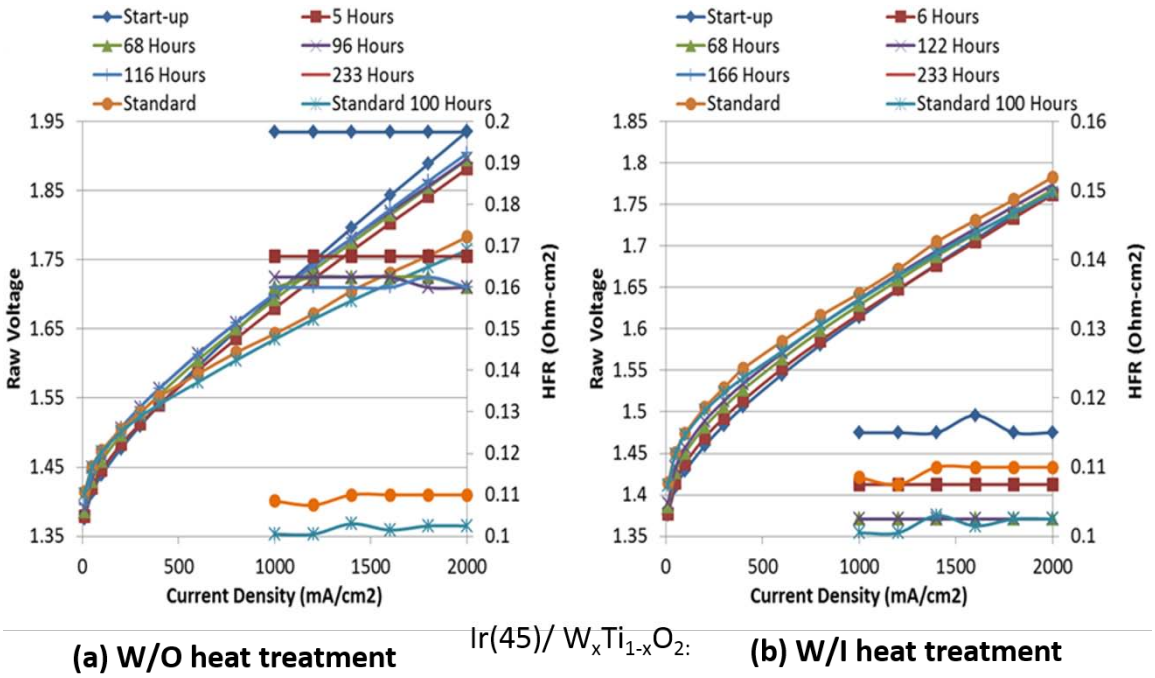


FIGURE 1. TEM images of (a) Ir(45)/$Ti_{1-x}W_xO_2$; (b) IrO_2(25)/$Ti_{1-x}W_xO_2$; (c) high resolution TEM of Ir(45)/$Ti_{1-x}W_xO_2$; (d–h) high-angle annual dark field–energy dispersive X-ray spectroscopy mapping of Ir(45)/$Ti_{1-x}W_xO_2$



Ir(45)/ $W_xTi_{1-x}O_2$:

FIGURE 2. The electrolyzer performance and short durability of Ir(45)/$W_xTi_{1-x}O_2$, (a) without support heat treatment, and (b) with support heat treatment

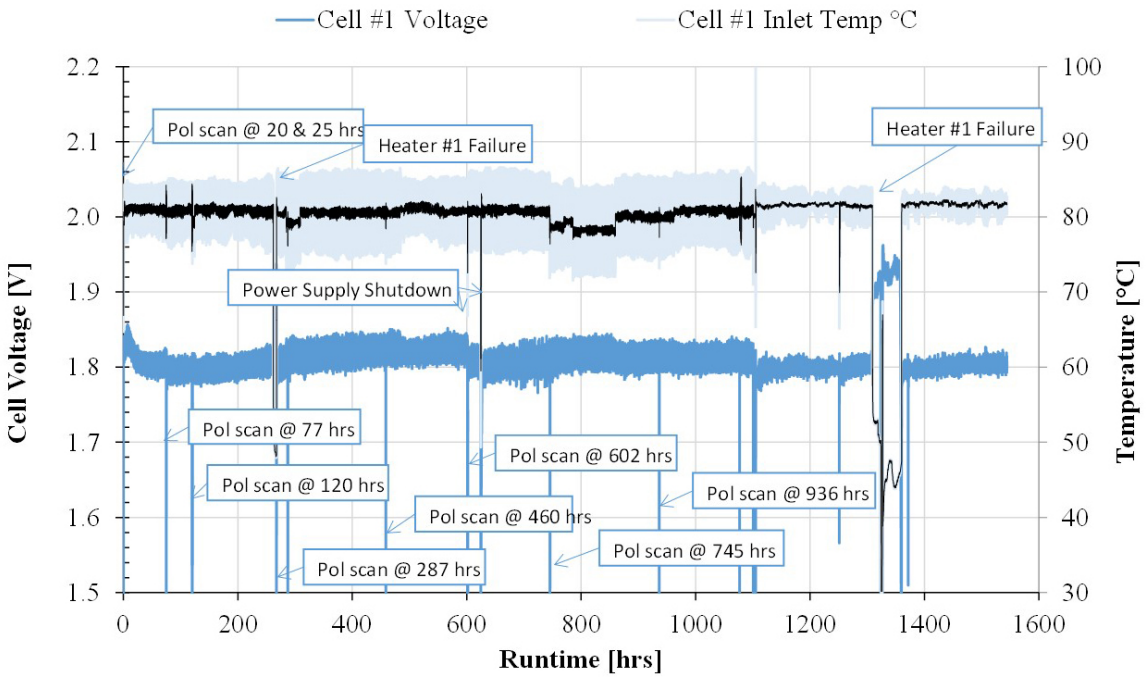


FIGURE 3. The 1,500-hour durability of Ir(45)/$W_xTi_{1-x}O_2$ catalyst with support heat treatment

Our final delivery is a 65 kW stack that consists of 36 cells with an active area of 300 cm^2 for each cell (Figure 4). These 36 cells are divided into three categories: Category 1: Cell 1 to 12 – commercial Ir black; Category 2: Cell 13 to 24 – Ir/$W_xTi_{1-x}O_2$ catalyst; Category 3: Cell 25 to 36 – 3M Ir–NSTF catalyst. The designed operating current density (CD) = 3 A/cm^2, voltage = 2.0 V, so the power = 3 (A/cm^2) x 2.0 V x 36 x (300 cm^2) = 65 kW. The stack design and hardware preparation for the 36-cell stack test has been completed.

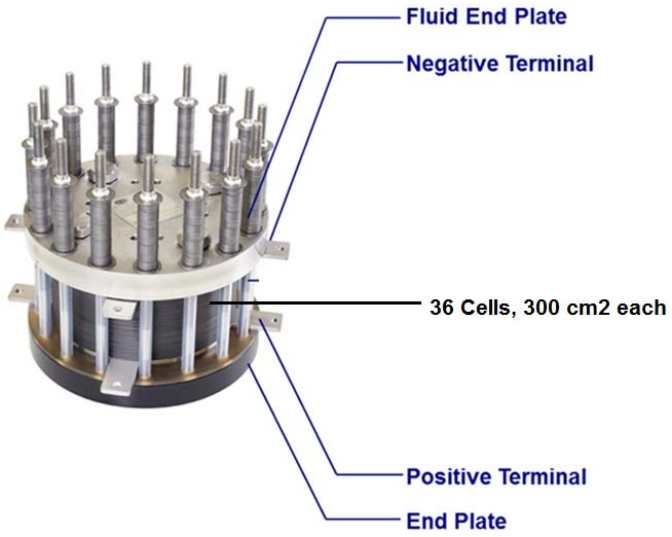


FIGURE 4. Schematic of 36-cell stack and anatomy of cell components

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions can be drawn:

- Giner's Ir/$W_xTi_{1-x}O_2$ anode catalysts have been scaled-up and catalyst instability from scale-up in the last year has been resolved via multiple strategies.
- Giner's Ir/$W_xTi_{1-x}O_2$-based anode demonstrates superior performance up to 1,500 h, barely with any performance decay.
- A 36-cell 65-kW stack using baseline Ir black, Giner Ir/$W_xTi_{1-x}O_2$, and 3M Ir–NSTF has been designed and prepared.

Upcoming activities include:

- Complete the assembly of 36-cell 65-kW stack.
- Test the durability of the 36-cell stack over 2,000 h.
- Perform techno-economic analysis of the stack cost.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Invited Talk: "Benchmarking Catalyst Development for PEM Water Electrolysis," presented at 1st International Conference on Electrolysis (ICE), Copenhagen, June 12–15, 2017.

2. "High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis," Presentation at DOE Hydrogen and Fuel Cells Program Annual Merit Review meeting, Washington, D.C., June 5–8, 2017.

REFERENCES

1. Hamden, M., "PEM Electrolyzer Incorporating an Advanced Low Cost Membrane," Presentation in DOE 2012 Hydrogen and Fuel Cells Program Annual Merit Review meeting, https://www.hydrogen.energy.gov/pdfs/review12/pd030_hamdan_2012_o.pdf (2012).