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 (NREL)
Golden, CO

Vendor
3M Company, Minneapolis, MN

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

Overall Objectives

- Scale up catalyst synthesis to short production (>20 g/batch).
- Extend electrolyzer catalyst durability tests using accelerated stress test (AST) and steady-state operation up to 5,000 h.
- 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 (PGM) 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) 2016 Objectives

- Scale up catalyst synthesis to short production (>20 g/batch).
- Extend catalyst durability tests to 5,000-h testing in a short electrolyzer stack.
- Establish an AST protocol to study the degradation of oxygen evolution reaction (OER) catalyst and MEA.

Technical Barriers

This project addresses the cost barriers of the Hydrogen Production section of the Multi-Year Research, Development, and Demonstration (MYRDD) Plan.

(F) Capital Cost

- By 2020, reduce the cost of distributed production of hydrogen from water electrolysis to <$2.30/gge (≤$4.00 delivered and dispensed)
- By 2020, reduce the cost of central production of hydrogen from water electrolysis using renewable power to ≤$2.00/gge at plant gate

Technical Targets

The target of this project is 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	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 $0.057/kW from 0.039$/kW) . [5] Stack Only

LHV – lower heating value

FY 2016 Accomplishments

- 3M has realized roll-to roll production of Ir-supported nanostructured thin film (NSTF) (anode) and Pt-NSTF (cathode) and delivered a variety of catalyst decals and catalyst-coated membranes (CCMs) to Giner.
- Giner built six-cell short stacks using 3M NSTF anode catalyst and successfully completed a 2,000-h durability on one stack with minimal performance loss.
- Larger production of $Ir/W_xTi_{1-x}O_2$ catalyst was conducted at Giner. The catalyst-based anode demonstrated comparable performance to the standard anode but with one order of magnitude lower Ir loading.
- AST was performed to establish "Catalyst Durability Test" protocol for water electrolysis. The microstructures of aged MEAs under different AST conditions and stages were characterized and their correlation to performance analyzed.

INTRODUCTION

Hydrogen production for mobility and energy storage from polymer electrolyte membrane (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 come to control 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. The Phase IIB catalyst commercialization plan is illustrated in Figure 1. First, we will scale up the catalyst synthesis process to make small production runs (30 g). Second, we will develop an effective MEA fabrication process to make reproducible, full-sized MEAs. Small pieces cut from full MEAs will be subjected to extensive durability tests via accelerated stress and electrolyzer durability tests. These MEAs will be subsequently integrated into Giner's low-PGM loading sub-megawatt electrolyzers to test their performance and durability. The degradation study for MEAs after ASTs and electrolyzer tests will be aided by scanning electron microscopy–energy-dispersive X-ray spectroscopy mapping and transmission electron microscopy. Finally, detailed economic analysis of catalyst production costs and the impact of the catalysts on electrolyzer operations will be performed..

RESULTS

First, Giner's $Ir/W_xTi_{1-x}O_2$ catalyst (Ir; 45 wt%) has been scaled up and built into a short stack, as shown in Figure 2a. There were three groups of cells in the short stack: Group 1

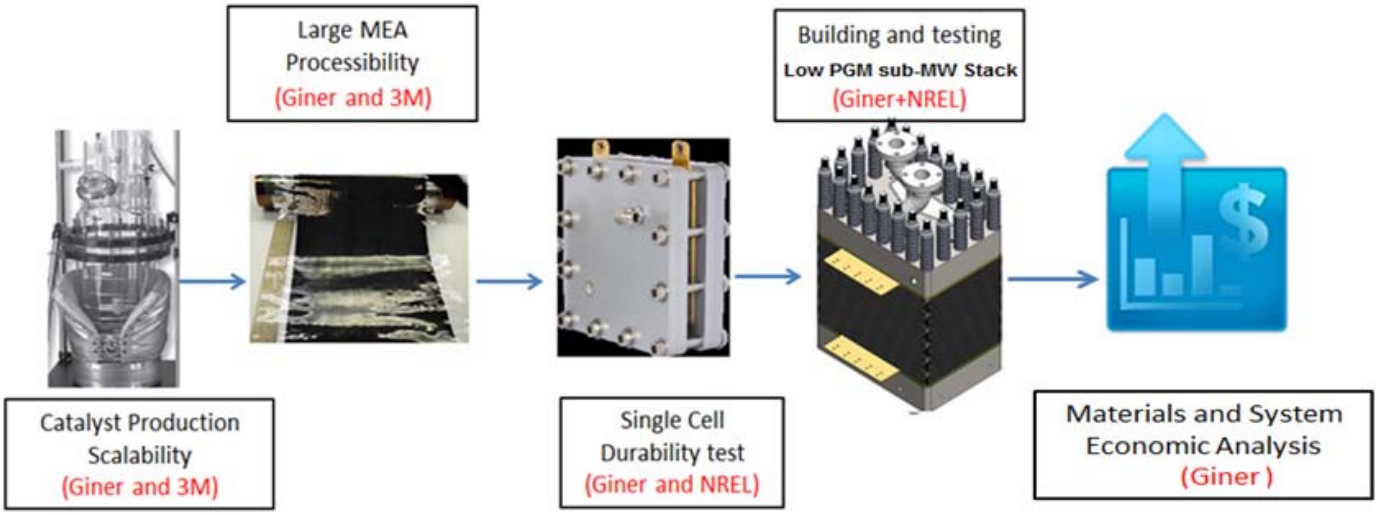

FIGURE 1. Catalyst development and commercialization approach

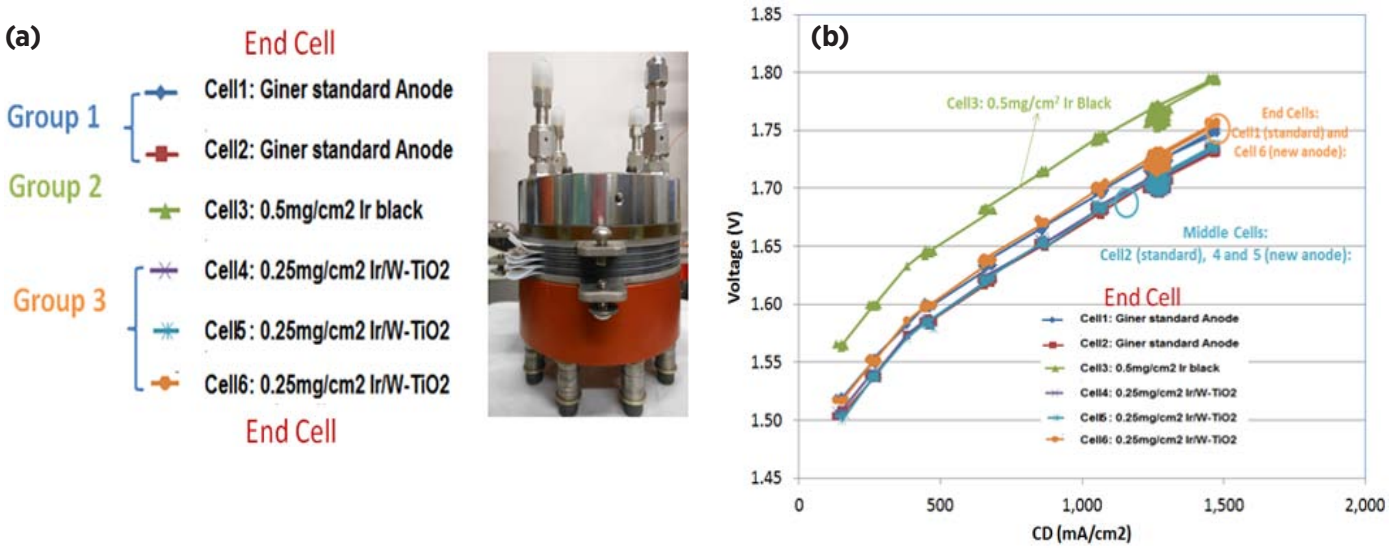

FIGURE 2. Short electrolyzer stack (a) and cell performance at 80°C (b) for Ir/$W_xTi_{1-x}O_2$ catalyst developed at Giner Inc. Membrane: Nafion 115; cathode: 0.4 mg/cm^2 Pt from Tanaka Pt/C; anode of standard MEA: 3 mg/cm^2 PGM.

contained two standard cells with an anode PGM loading of 3 mg/cm^2; Group 2 had one cell using commercial (Johnson Matthey) Ir catalyst at low loading, 0.5 mg/cm^2; and Group 3 contained three cells using Ir/$W_xTi_{1-x}O_2$ catalyst at extremely low loading, 0.25 mg/cm^2. The membrane is Nafion 115 and the active area is 50 cm^2. The performance of these cells operated at 80°C is shown in Figure 2b. First, the cells with low Ir loadings from the Ir/$W_xTi_{1-x}O_2$ catalyst performed significantly better than that with the commercial iridium black as the former has a 50 mV lower overpotential. Second, the cell performance of the Ir/$W_xTi_{1-x}O_2$ anode approached the performance of the Giner standard anode even the former anode had one order of magnitude lower Ir loading. The significantly higher activity of the Ir/$W_xTi_{1-x}O_2$ has been demonstrated. The durability of the short stack has also been tested, but the data is not shown because the malfunction of test station caused the fast decay of the cell performance.

3M has delivered a few batches of NSTF decals and CCMs to Giner for short stack testing. The most successful CCM is NSTF (cathode: 0.25 mg/cm^2 Pt from Tanaka Pt/C; anode: 0.5 mg/cm^2 Ir from Ir-NSTF) deposited on 3M 100 μm 800 equivalent weight membrane. This CCM was built into a short stack compared to standard cells using Nafion 115 and anode PGM loading of 3 mg/cm^2. The performance of these cells operated at 80°C is shown in Figure 3a. It can be seen that NSTF cells demonstrated much better performance than standard cells, as the former had 150 mV lower overpotential at 5,000 mA/cm^2. The superior performance of the NSTF cells is due to their high catalyst activity and thinner membrane with low equivalent weight resulting in less ohmic loss. The durability of this short stack was shown in Figure 3b. The durability test has passed 2,000 h and NSTF cells demonstrate significant durability without any performance loss.

In this project, we have also made great efforts to establish an AST protocol for the OER catalysts and elucidate the cause of performance decay after ASTs. As shown in Figure 4a and 4b, NREL evaluated the stability of a series of commercially available catalysts under rotating disk electrode conditions, which includes Johnson Matthey Ir black and Umicore Ir supported on TiO_2. It clearly shows that most catalysts lost their activity after the hold at 1.6 V for 13.6 h. Giner performed voltage cycling from 1.4–2.0 V using an MEA containing 0.1 mA/cm^2 Ir black. It can be seen from Figure 4c that as the cycle number increases, the overpotential of the tested cell continuously goes up, indicating decreasing MEA performance. The decreased MEA performance can be due to catalyst agglomeration and more pronouncedly, Ir migration. The latter is clearly displayed in Figure 4d, where a number of Ir particles are seen in the membrane, leading to the loss of the catalyst from the anode.

CONCLUSIONS AND FUTURE DIRECTIONS

Several conclusions can be drawn:

- Giner's Ir/IrO_2/$W_xTi_{1-x}O_2$, Ir/$W_xTi_{1-x}O_2$, and 3M's Ir-NSTF anode catalysts have been scaled up and tested in short stacks (5–6 cells, 50 cm^2).
- Giner's Ir/$W_xTi_{1-x}O_2$-based anode demonstrated superior performance to standard anode in short-term testing.
- 3M's Ir-NSTF on 100 μM low equivalent weight membrane demonstrates great performance and durability after 2,000 h of testing.
- Catalyst durability AST protocol developed through a cohesive collaboration between NREL and Giner and a variety of OER catalysts have been characterized.

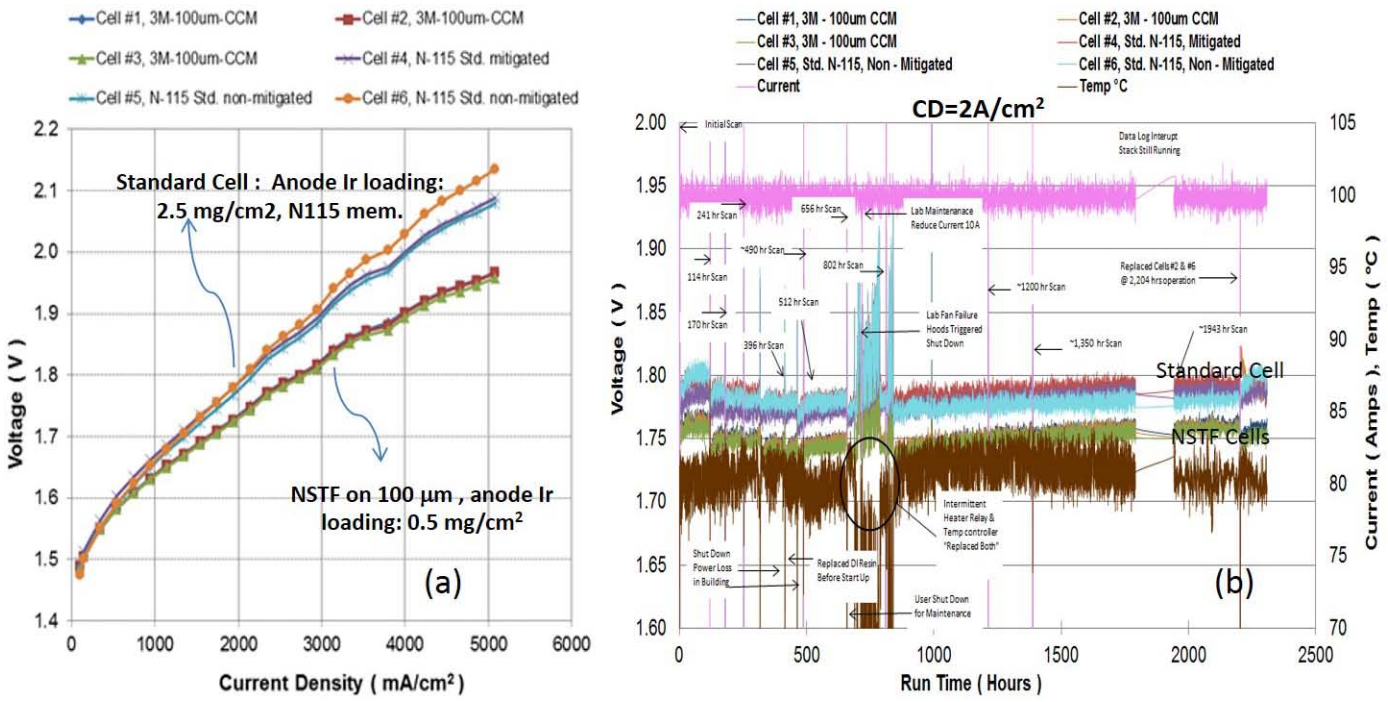

FIGURE 3. The comparison of 3M's NSTF MEAs with standard MEAs at 80°C. Standard MEA (anode: 3 mg/cm^2 PGM; membrane: Nafion 115; cathode: 0.4 mg/cm^2 Pt from Tanaka Pt/C), NSTF MEA (anode: 0.5 mg/cm^2 Ir from Ir/NSTF; membrane: 3M 100 µm 800 equivalent weight membrane; cathode: 0.4 mg/cm^2 Pt from Tanaka Pt/C).

Future work includes:

- Complete AST durability test protocols and correlate with real performance test.
- Complete 5,000-h stack durability of selected Giner and 3M catalysts.
- Select catalysts for Giner sub-megawatt electrolyzer stack construction.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Xu, H., C. Mittelsteadt, B. Rasimick, and A. Stocks, "Anode Catalyst Suitable for Use in an Electrolyzer," US 2015/0368817A1.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Invited talk: "Advanced Oxygen Evolution Catalysts for Water Electrolysis," presented at the 250th ACS Meeting, Division of Energy and Fuels, Boston, MA, August 18, 2015.

2. "Studies of MEA Durability in Proton Exchange Membrane Water Electrolysis," Abstract #1516, presented at the 228th ECS Meeting, Phoenix, AZ, October 11–15, 2015.

3. Invited Talk: "Water Electrolysis: from Components to Systems," presented in TechConnect World Innovation Conference, Washington, D.C., May 22–25, 2016.

4. "High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis," presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review Meeting, Washington, D.C., June 4–8, 2016.

5. Shaun M. Alia, Brian Rasimick, Chilan Ngo, K.C. Neyerlin, Shyam S. Kocha, Svitlana Pylypenko, Hui Xu, and Bryan S. Pivovar, "Activity and Durability of Iridium Nanoparticles in the Oxygen Evolution Reaction," J. Electrochem. Soc. 2016 163(11): F3105-F3112; doi:10.1149/2.0151611jes.

6. Shaun M. Alia, Katherine E. Hurst, Shyam S. Kocha, and Bryan S. Pivovar, "Mercury Underpotential Deposition to Determine Iridium and Iridium Oxide Electrochemical Surface Areas," J. Electrochem. Soc. 2016 163(11): F3051-F3056; doi:10.1149/2.0071611jes.

REFERENCES

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

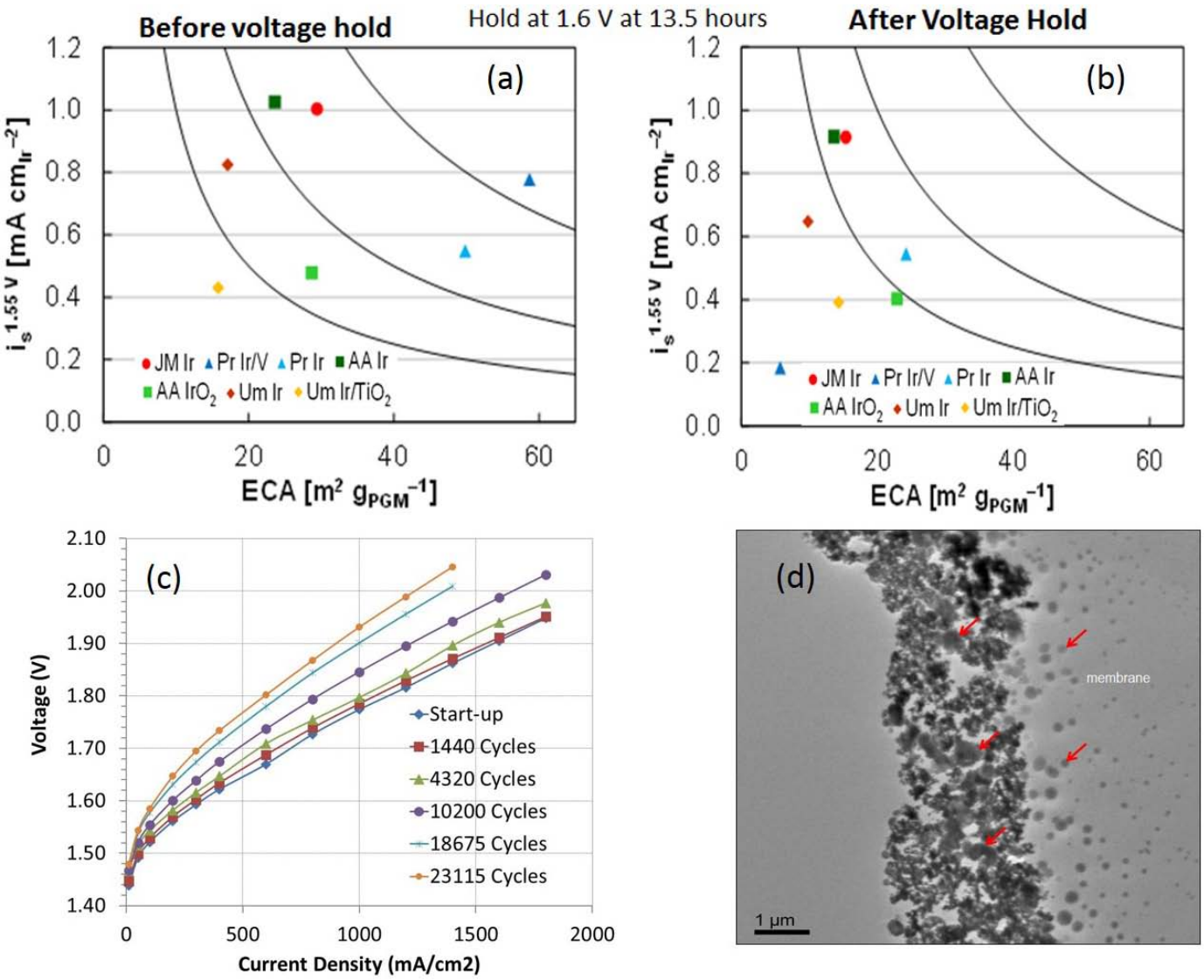

FIGURE 4. AST for catalyst degradation studies and structure characterization. (a) and (b): hold at 1.6 V for 13.5 h; (c) voltage cycling from 1.4 V to 2.0 V with 0.1 mg/cm^2 Ir black at the anode; (d) structure of anode and adjacent membrane after voltage cycling from (c), transmission electron micrograph taken by Dr. Karren More at Oak Ridge National Laboratory.