High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis

Hui Xu (PI)
Giner Inc.
Newton, MA

Project ID#: PD103

This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

- Project Start Date: 4/21/2015
  Project End Date: 10/20/2017
- Percent Complete: 80%

Budget

- Phase IIB
  - Total Project Value: $ 999, 926
  - Total Funding Spent: $ 809,474*
- Cost Share Percentage:
  0% (SBIR)

* as of 4/26/17

Giner Researchers

Shuai Zhao, Bob Stone, Jason Willey, and Litao Yan

Partners

- NREL: Dr. Bryan Pivovar (Co-PI)
- 3M: Dr. Krzysztof Lewinski(Vendor)
- ORNL: Dr. Karren More (collaborator)

Barriers Addressed

- High platinum group metal (PGM) loading (Ir loading >2mg/cm^2)
  - Low catalytic activity for oxygen evolution reaction (OER)
- Low system efficiency
  - Significant anode over-potential
- High PEM electrolysis cost

Relevance

- **DOE H_2 Production Target for Electrolysis**

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

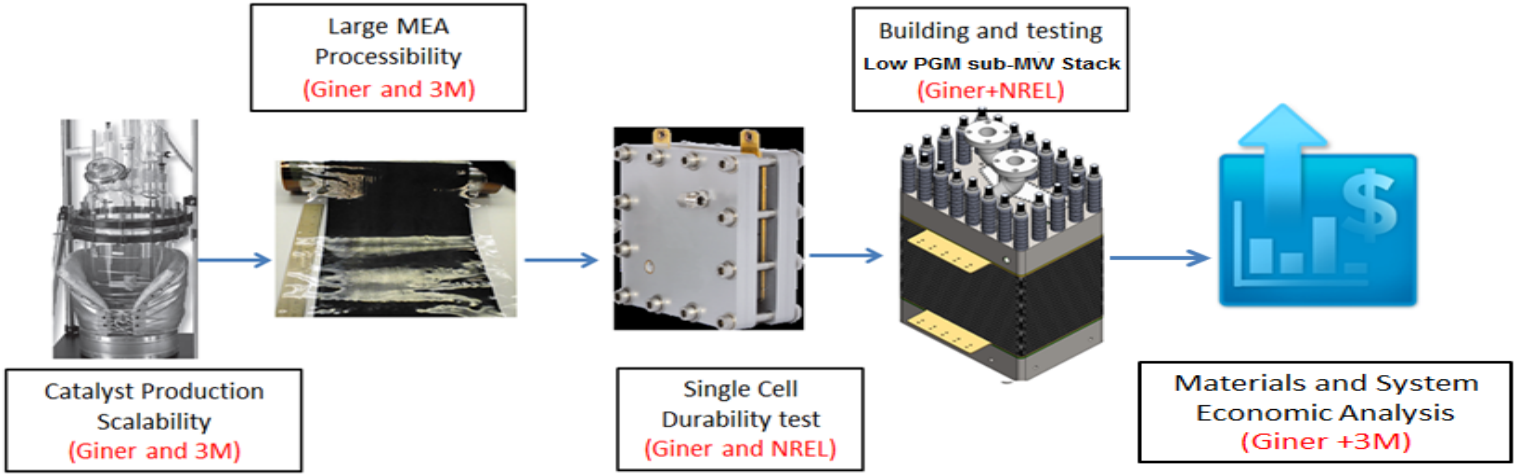
- **Phase 2 Accomplishments**

- Giner and 3M developed two OER catalysts, Ir/W_xTiO_{1-x} and Ir-NSTF, respectively , which lowered anode PGM loading by a factor of 5-8 while retaining the baseline performance (3 mg PGM/cm^2)
- Both catalysts successfully passed 1000-hour test with 20 mV voltage decay

- **Objectives**

- Scale-up and commercialize low PGM loading OER catalysts using Giner electrolyzer platform
- Evaluate the impact of newly developed catalysts on the PEM electrolyzer efficiency and cost

Phase IIB Project Task and Milestones

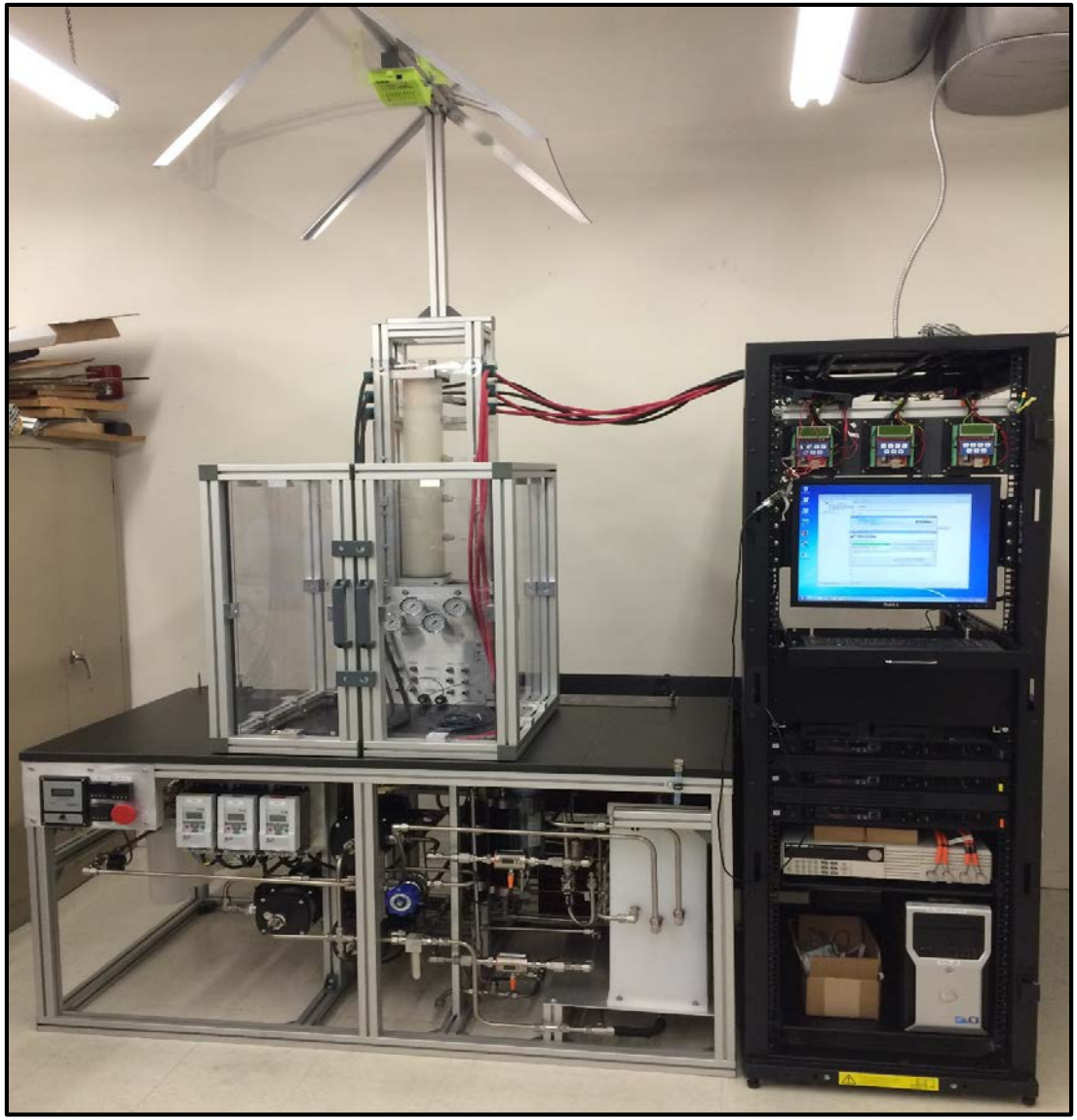


Completion	ID	Task Name	Year 1						Year 2					
			M2	M4	M6	M8	M10	M12	M14	M16	M18	M20	M22	M24
	1	**Task 1: Scale up the Production of Selected Catalysts**												
	2	Ir/W-TiO2 synthesis scale-up												
	3	IrNSTF synthesis scale-up												
100%	M1.1	Demonstrate the capability of producing 30g catalyst/batch with comparable performance to Giner standard: 1.75V at 2A/cm^2												
	4	**Task 2: Fabrication of Composite Electrolytes**												
	5	Ir/W-TiO2 based MEA fabrication												
	6	IrNSTF based MEA fabrication												
90%	M2.1	Demonstrate the capability of fabricating full-sized MEAs (1400 cm^2) with reproducing performance from batch to batch												
90%	M2.2	Deliver 10 m^2 IRNSTF based CCMs to Giner												
	7	**Task 3: Extend durability Tests of Selected Catalysts**												
	8	AST via Voltage Cycling												
	9	Electrolyzer Endurance Test												
90%	M3.1	Obtain < 30 mV performance decay (at 2 A/cm2) after 30,000 cycles during AST												
80%	**M3.2**	Obtain < 50 mV performance (at 2 A/cm2) after 4,000 hours during electrolyzer testing												
25%	10	**Task 4: Build low-PGM loading sub-MW stack (Giner)**												
0%	M4.1	Complete the construction of sub MW unit												
	11	**Task 5: Evaluate and Demonstrate sub-MW Electrolyzer**												
0%	M5.1	Obtain sub-MW unit 2,000 hours data												
	12	**Task 6: Perform Catalyst and System Economics**												
20%	M6.1	Analyze cost of catalyst materials and electrolyzer to reach 5% to 10% stack cost reduction by using the developed catalyst												
		Program Management												

Major Task Left :

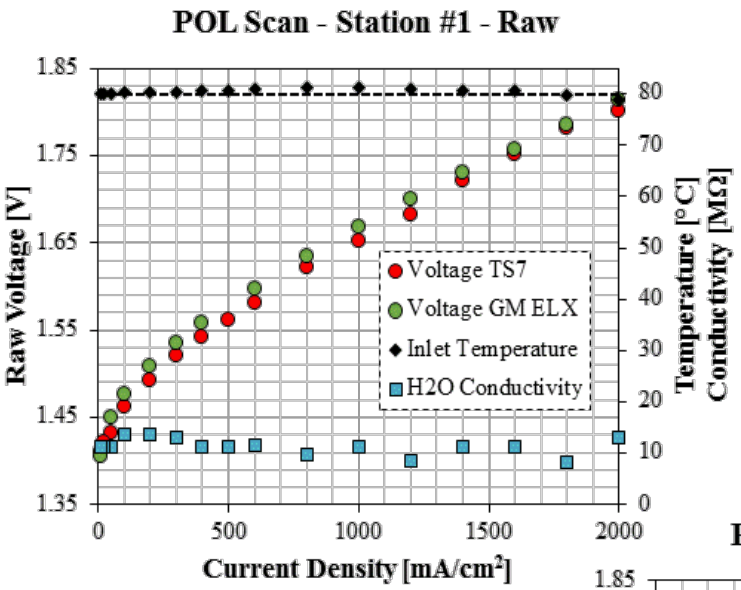
Assembly and Test of a sub-MW Stack

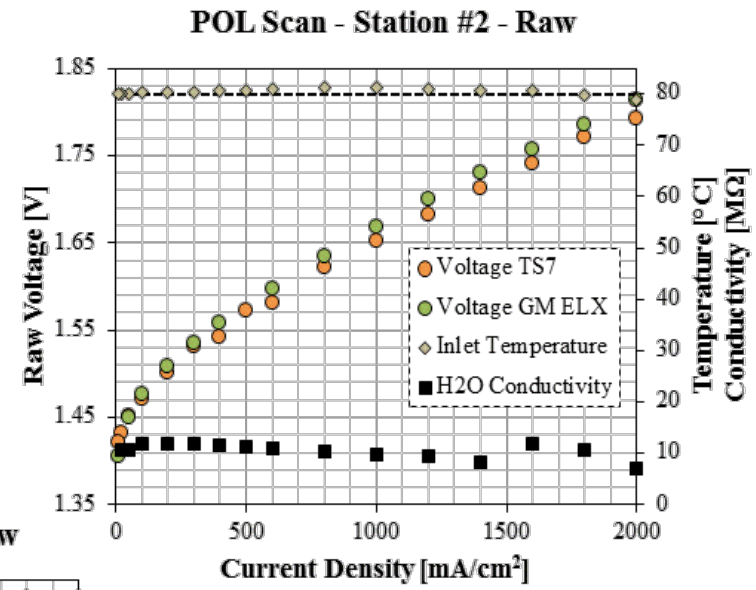
Accomplishment 1: New Electrolyzer Test Station to Expand Cell Testing Capacity

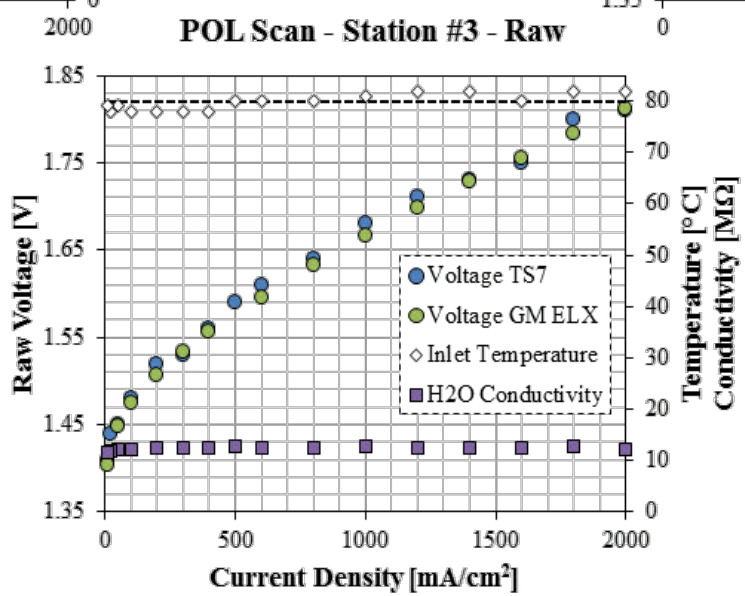


- Three cells can be tested simultaneously
- Up to 5000 mA/cm^2 for 50 cm^2 cell
- HFR embedded to measure cell resistance
- Remote control and H2 sensor

Test Station Validation



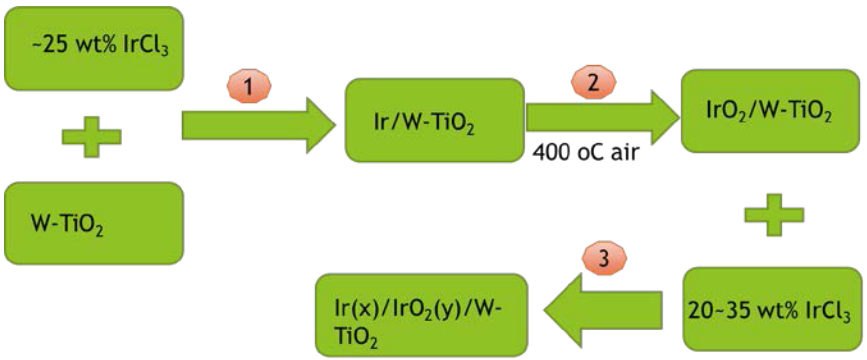




Accomplishment 2: Ir/$W_xTi_{1-x}O_2$ Catalyst Improvement and Scale-up

1. Modify the catalyst synthesis

- Heat treatment of support materials W_xTiO_{1-x} to modify its surface groups
- Introduction of IrO_2 between Ir and W_xTiO_{1-x}



x,y: weight percentage for Ir and IrO_2, respectively

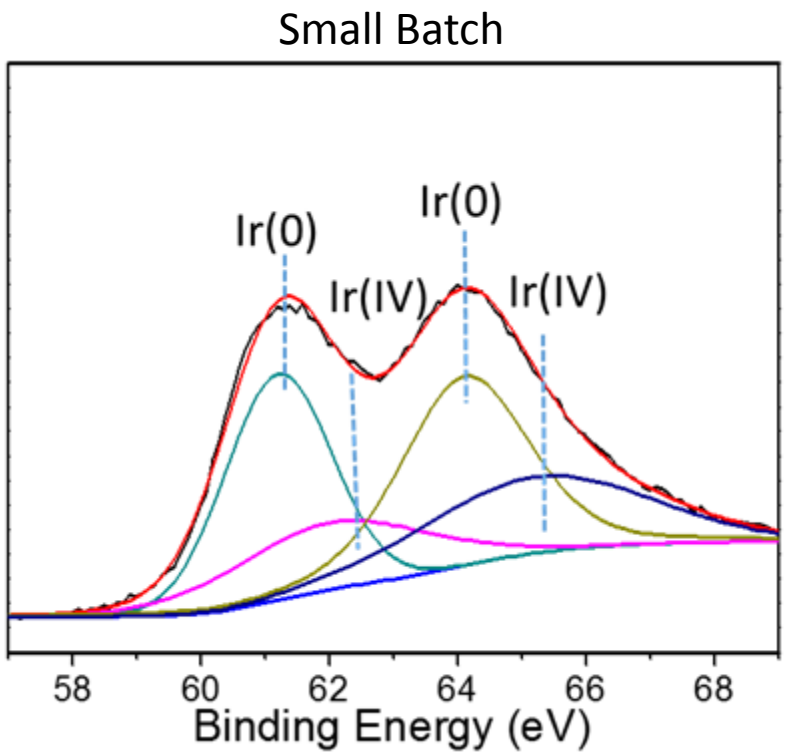
2. More precise synthesis process control

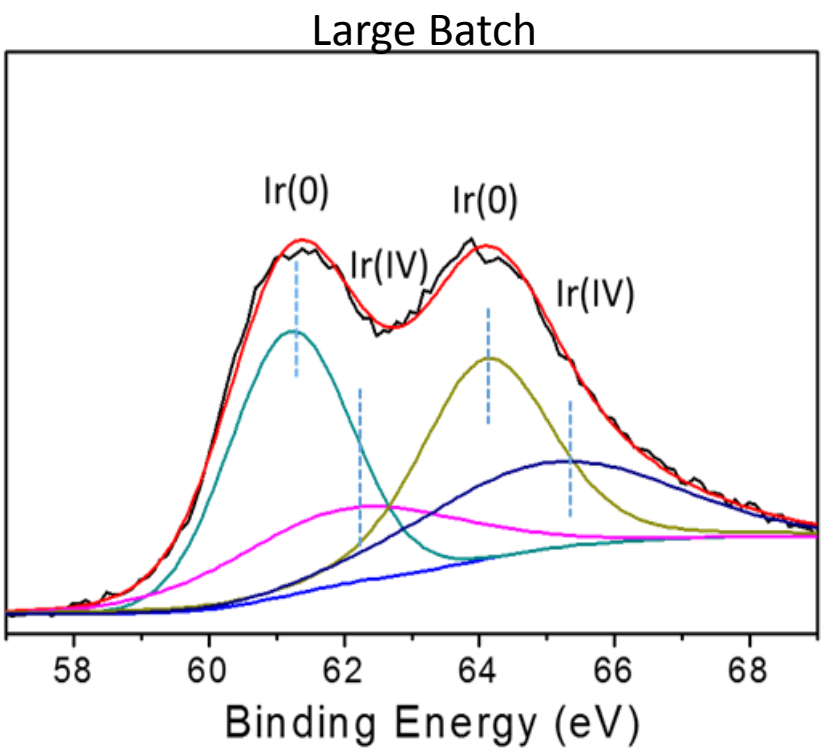
- Purchase of a well-controlled reactor
  Jacketed reactor for well-controlled cooling and heating
- Electrical rotator for uniform mixing

➢ Scale-up from 0.5 g/batch to 5-10 g/batch

Bench-scale and Scale-up Catalysts (XPS)

Catalyst: $Ir/Ti_{1-x}W_xO_2$ (45 wt% Ir loading)

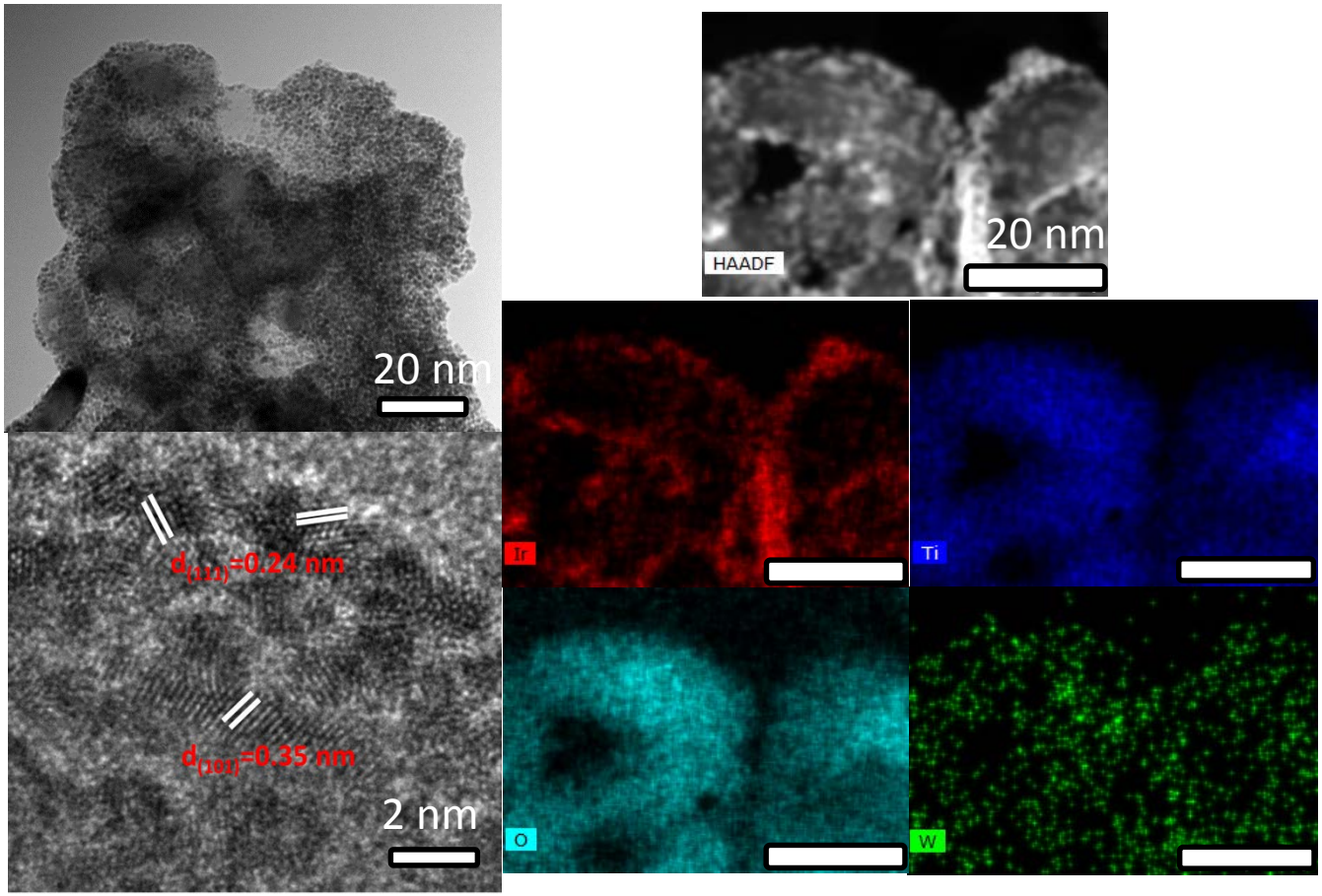




- From XPS spectra of Ir scaled up batch of $Ir/Ti_{1-x}W_xO_2$, the composition of Ir element was similar to small batch, with a majority of metallic Ir

Bench-scale Catalyst (TEM)

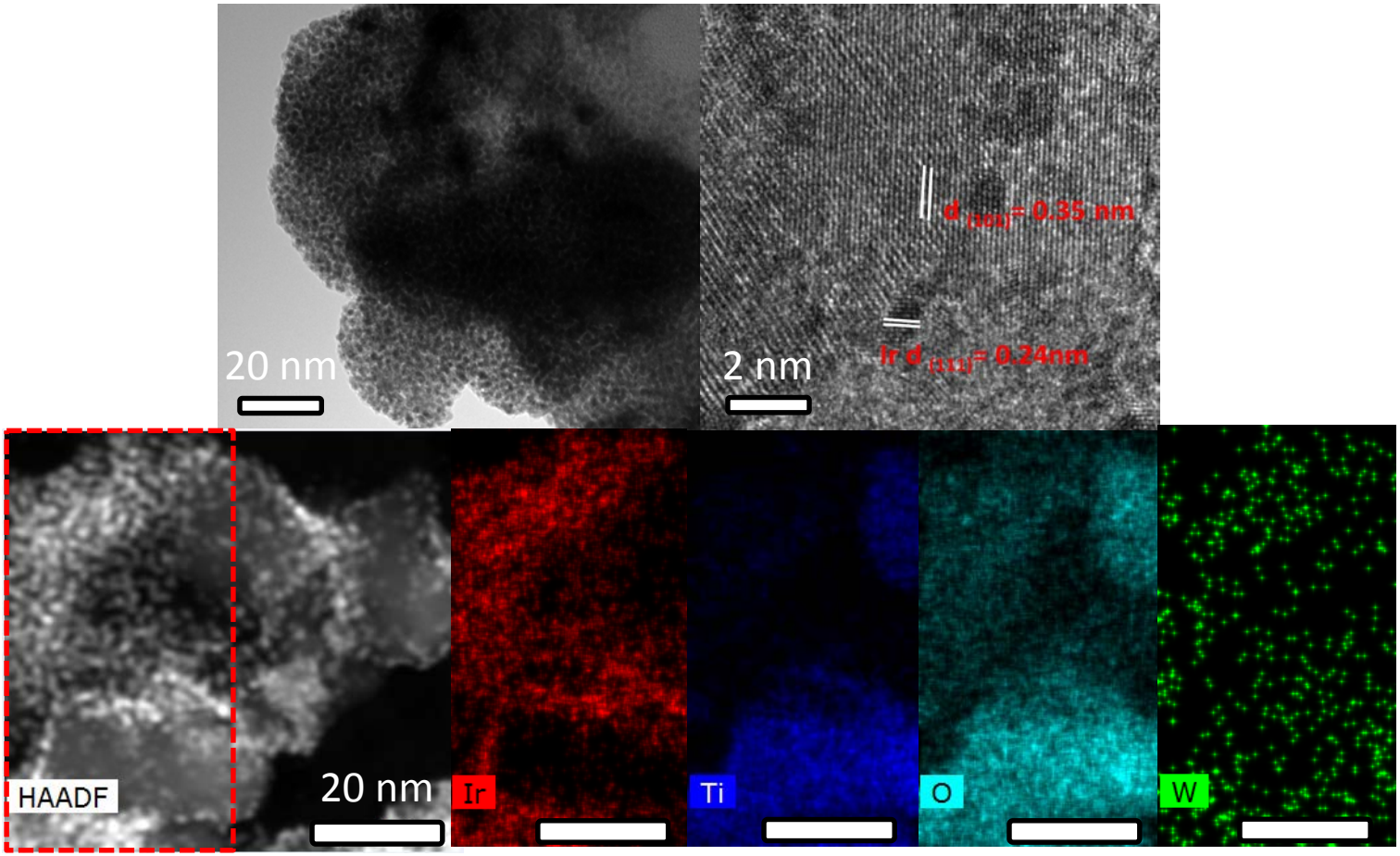
TEM image, HAADF image and element mapping of Ir/$Ti_{1-x}W_xO_2$45 wt% loading



- The Ir nanoparticles with size of 3 nm is uniformly deposited on $Ti_{1-x}W_xO_2$ support, interconnected,
- The d-spacing of Ir (1 1 1) planes (0.24 nm) confirmed by HRTEM image, and the d-spacing of anatase $Ti_{1-x}W_xO_2$ (1 0 1) facets (0.35 nm) also indexed
- EDX mapping demonstrated that Ti, W, O and Ir were homogeneously distributed and formed conductive network of iridium

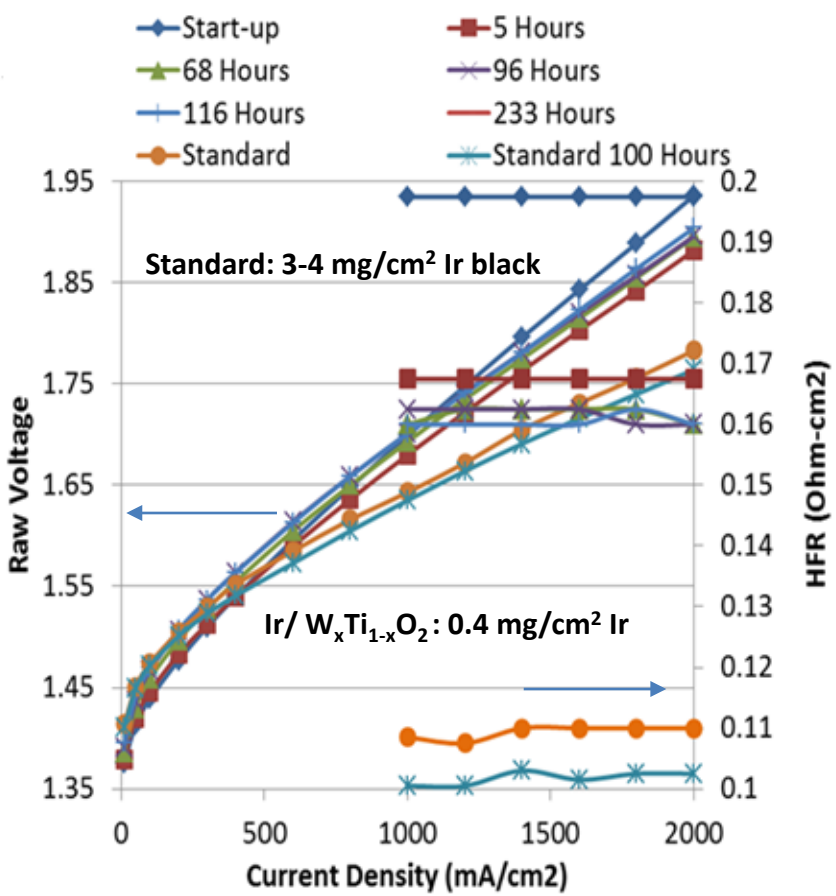
Scale-up Catalyst (TEM)

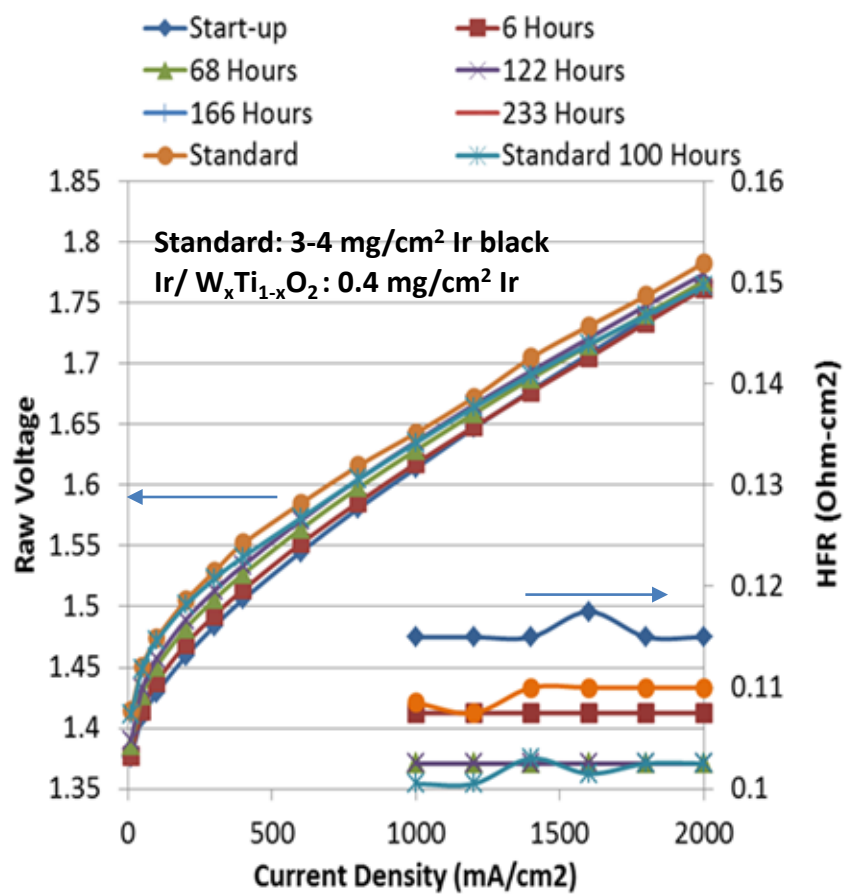
TEM image, HAADF image and element mapping of $Ir/Ti_{1-x}W_xO_2$45 wt% loading



- Similar Ir nanoparticle distribution and conductive network formation were observed in scaled up batch of with size $Ir/Ti_{1-x}W_xO_2$

Impact of Support Heat Treatment

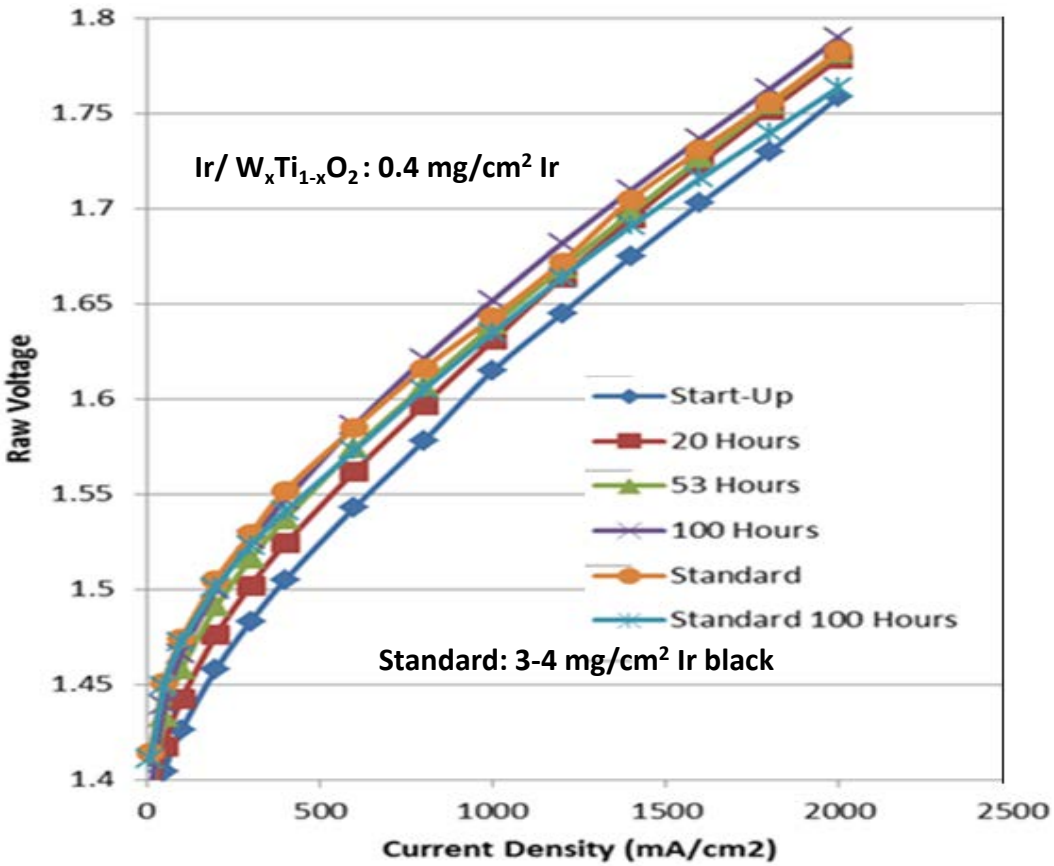


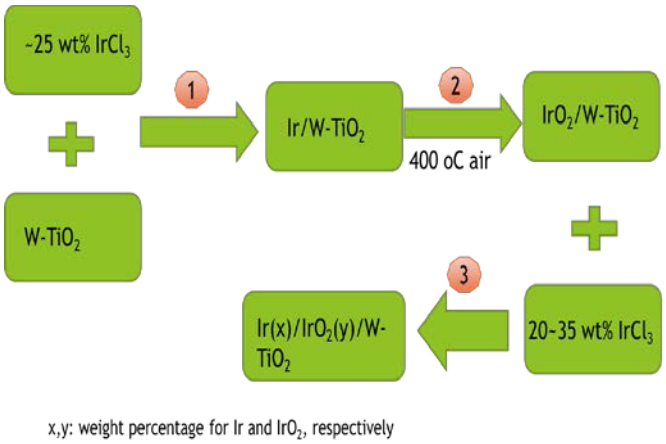


W/O heat treatment Ir(45)/ $W_xTi_{1-x}O_2$: **W/I heat treatment**

- Heat treatment of $W_xTi_{1-x}O_2$ at air for 1-2 hours significantly improves catalyst durability likely due to enhanced Ir particle inter-connection and anchoring on the support.

Impact of Additional IrO_2 Layer

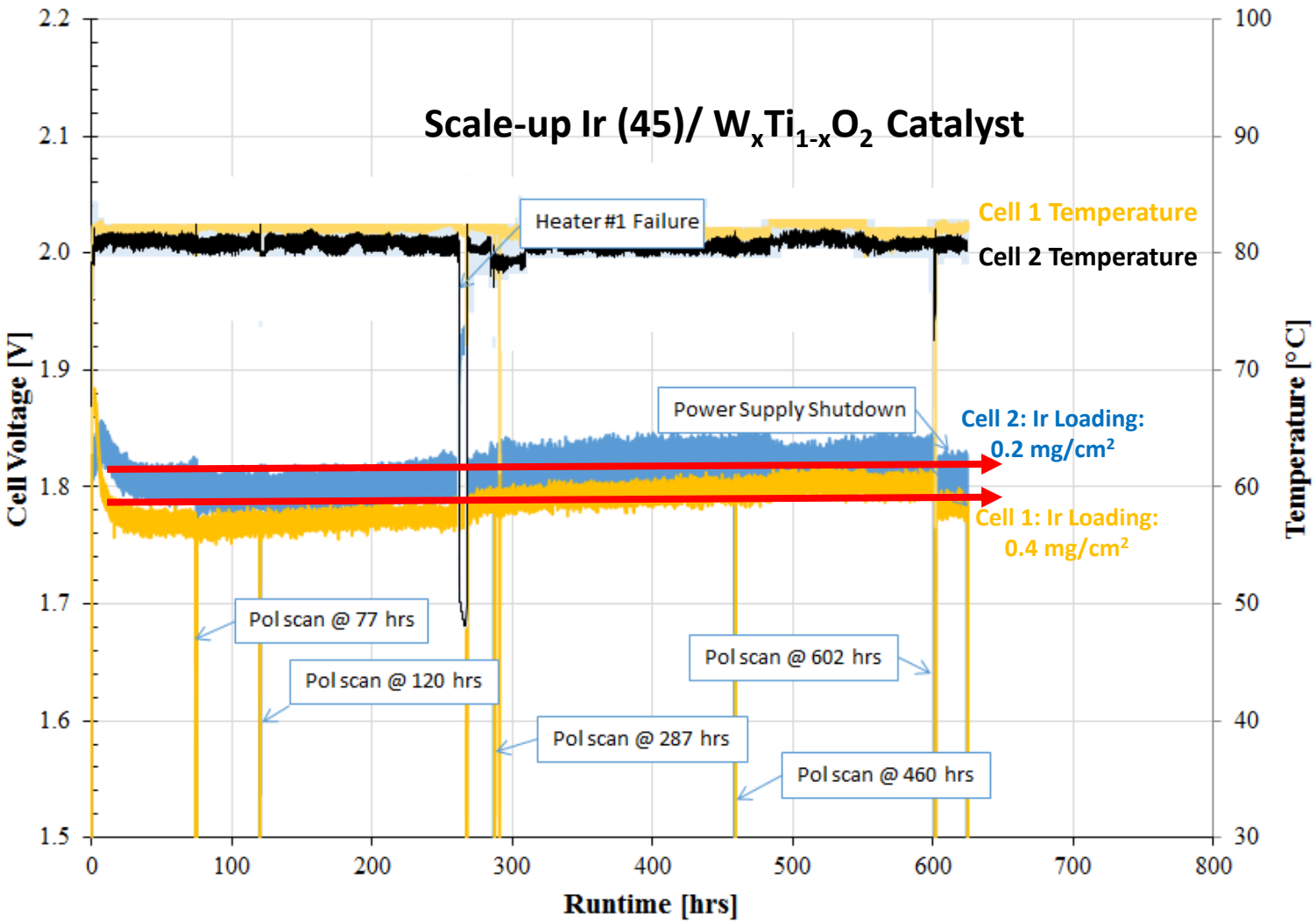




Ir(35)/IrO_2(25)/$W_xTi_{1-x}O_2$

- Introduction of addition IrO_2 layer has also improved the catalyst durability

Durability Test of Ir (45)/ $W_xTi_{1-x}O_2$ Catalyst

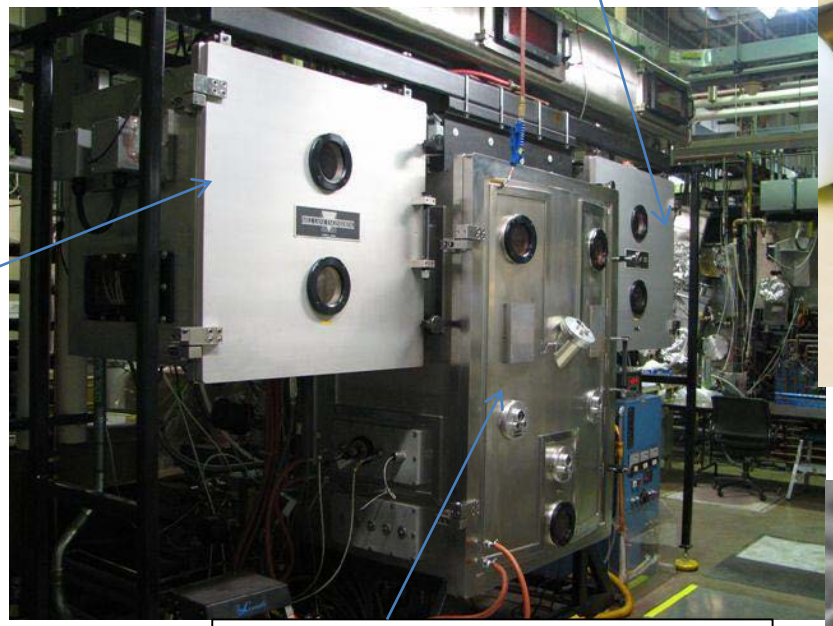


- Two low Ir loading (0.4 mg/cm² and 0.2 mg/cm²) cells demonstrate significant durability over 600 hours

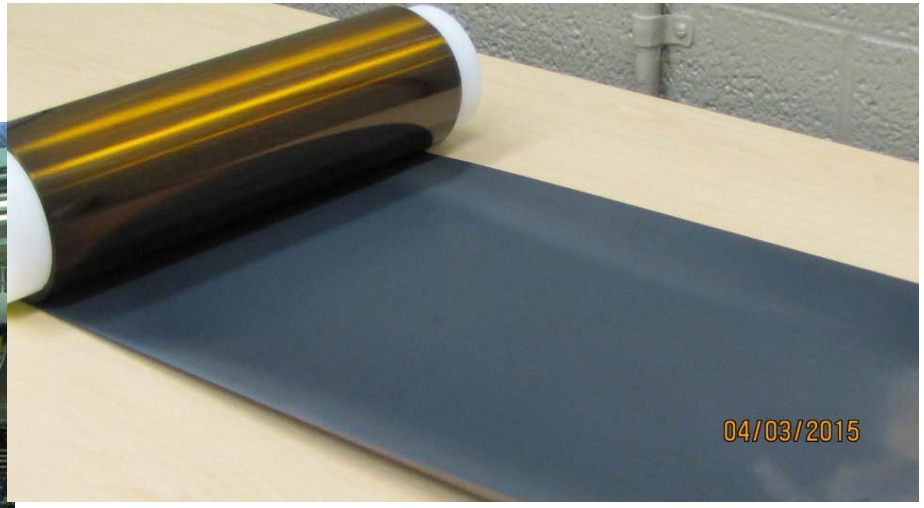
Accomplishment 3: 3M Ir-NSTF Scale-up

Sample unloading box

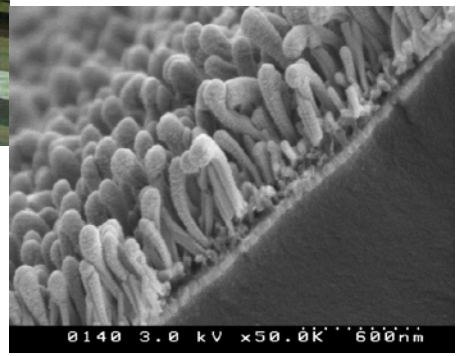
Sample loading box

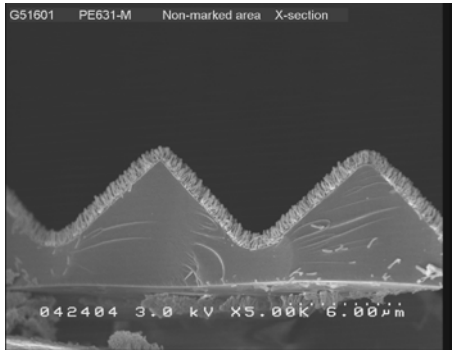


Vacuum sputtering chamber



Iridium #3





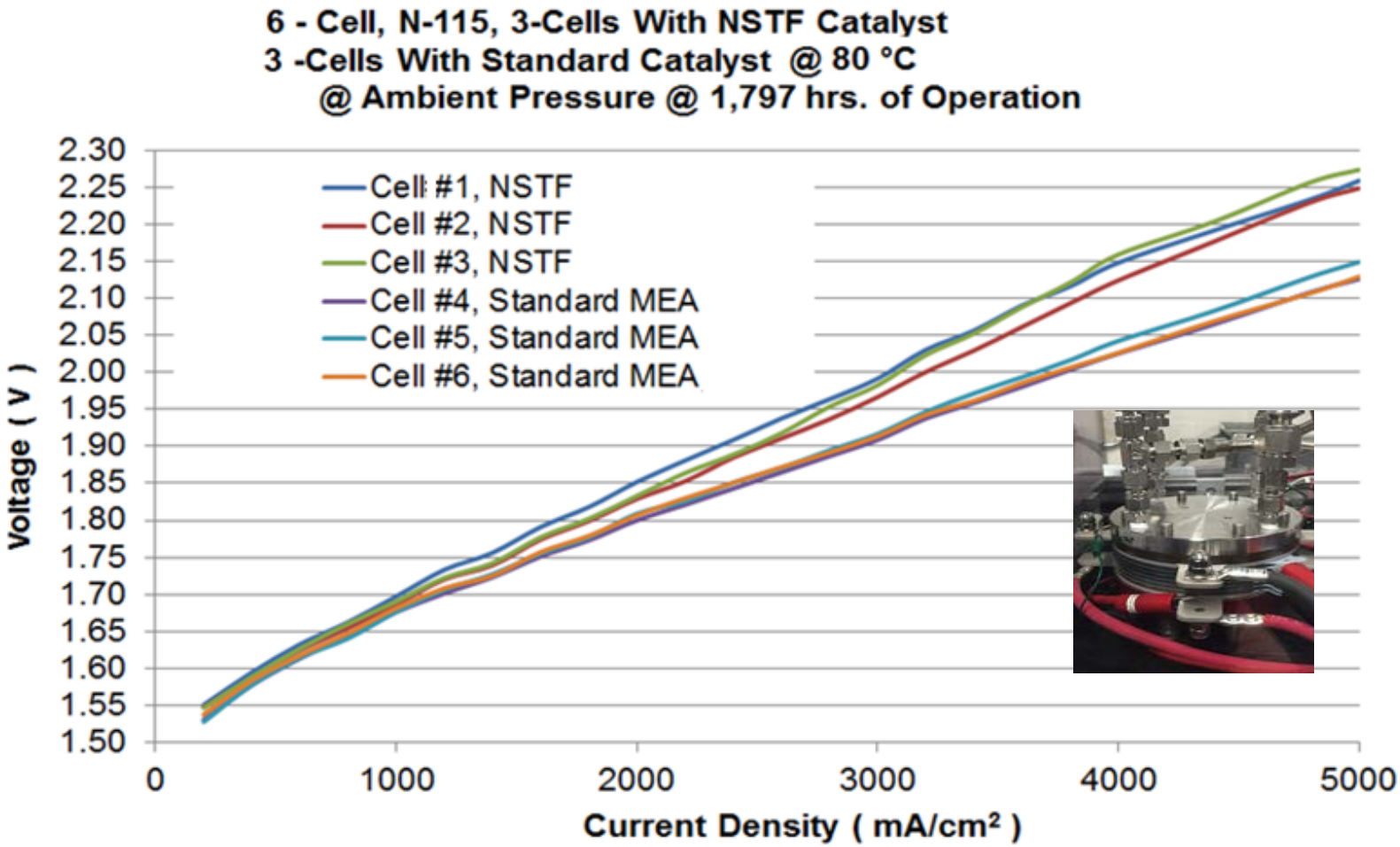
- Roll-to-roll production of Ir-NSTF has been successfully completed

Assembled MEAs Using 3M CCMs

Name	Anode	Cathode	Membrane	Mitigated*	Pressed At
50 um 3M PFSA	0.5 mg/cm^2 Ir NSTF	0.25 mg/cm^2 Pt NSTF	50 μm 3M PFSA	No	3M
100 um 3M PFSA	0.5 mg/cm^2 Ir NSTF	0.25 mg/cm^2 Pt NSTF	100 μm 3M PFSA	No	3M
N115 CCM	0.5 mg/cm^2 Ir NSTF	0.25 mg/cm^2 Pt NSTF	Nafion 115	No	3M
N115 Giner	0.25 mg/cm^2 Ir NSTF	0.25 mg/cm^2 Pt NSTF	Nafion 115	No	Giner
N115 Giner Mitigated	0.25 mg/cm^2 Ir NSTF	0.25 mg/cm^2 Pt NSTF	Nafion 115	Yes	Giner
Giner Standard Cell	1.5 mg/cm^2 Ir black & 1.5 mg/cm2 Pt black	0.4 mg/cm^2 Pt on carbon	Nafion 115	Yes	Giner

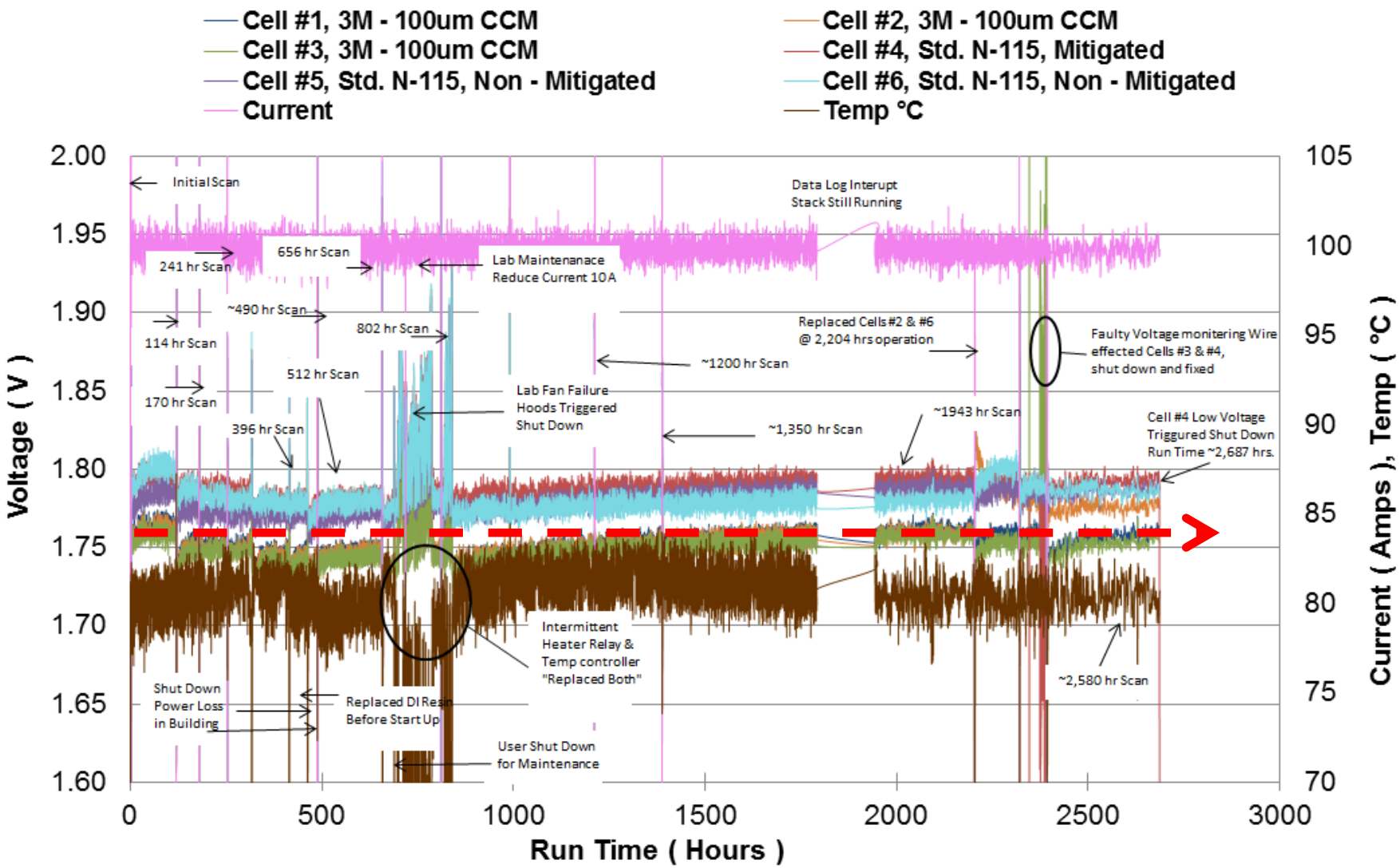
* Membrane mitigation to reduce H_2 crossover

Performance of Short Stack



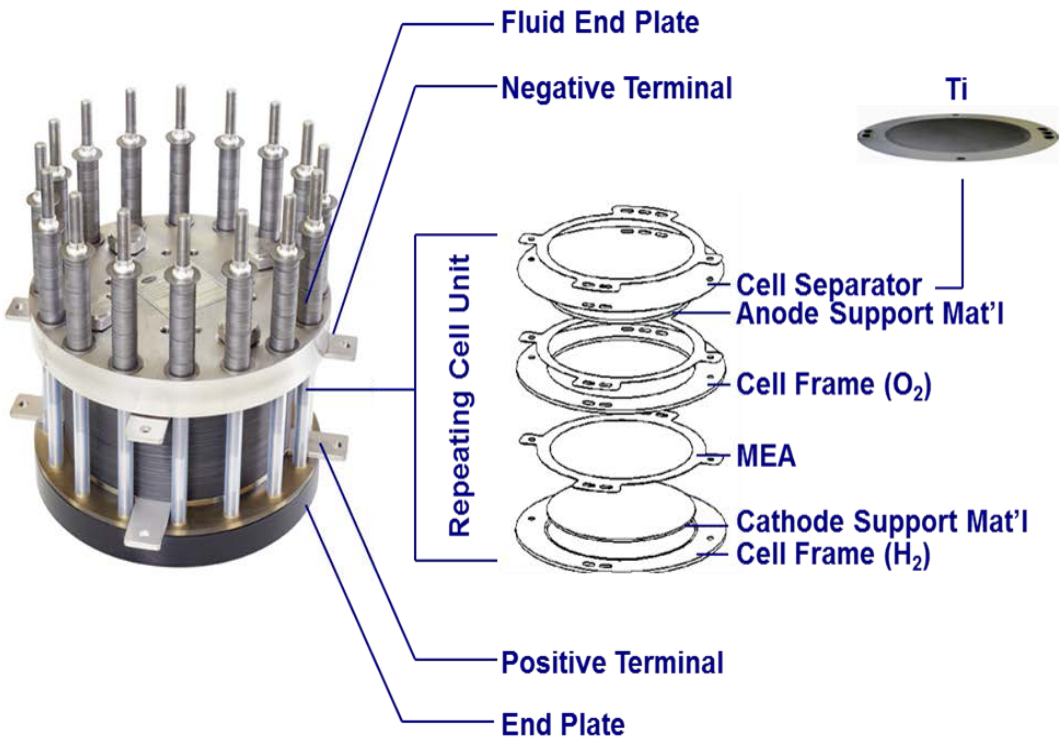
- **Low Ir loading NSTF cells exhibit good performance**

Durability of Short Stack



- **Low Ir loading NSTF cells exhibit good durability**

Accomplishment 4: Stack Design and Construction



Items	Specifications
Cell Area	200 cm^2
Cell #	36 cells
1-6	Baseline Ir black
7-18	3M IrNSTF
19-30	Giner Ir (45)/ $W_xTi_{1-x}O_2$
31-36	Baseline Ir black
CD	3000 mA/cm^2
Voltage	2.0 V
Power	40 KW

- Stack design completed in December 2016
- Stack assembly postponed to June 2017 due to Giner's large backlog of commercial electrolyzer orders (approved by program manager)

Summary

- Two approaches to producing durable $Ir/W_xTi_{1-x}O_2$ catalyst for catalyst synthesis scale-up have been identified and adopted:
  - Heat treatment of the $W_xTi_{1-x}O_2$ support
  - Formation of IrO_2 surface sites before Ir deposition
- Two low-Ir loading (0.4 mg/cm^2 and 0.2 mg/cm^2) cells using scale-up $Ir/W_xTi_{1-x}O_2$ demonstrate significant durability over 600 hours
- Giner built 6-cell short stacks using 3M NSTF anode catalyst and successfully completed a 2500-hour durability barely with performance decay
- A 36-cell 40-kW stack using baseline Ir black, Giner $Ir/W_xTi_{1-x}O_2$ and 3M IrNSTF has been designed and assembly will be completed in June 2017

Collaborations

Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Brian Rasimick, Allison Stocks, and Michael Smith	Prime, oversees the project; $Ir/W_xTi_{1-x}O_2$ catalyst scale-up; single and short stack tests, cell tests, cost analysis; catalyst and MEA test protocol
National Renewable Energy Laboratory (NREL) Bryan Pivovar, Shaun Alia, K. C. Neyerlin	To test short stack and perform TEA
3M Company (3M) Krzysztof Lewinski	Vendor; IrNSTF based catalyst development, short production, cost analysis
Oak Ridge National Laboratory (ORNL) Karren More	Collaborator: catalyst and MEA structure characterization

Future Research

- Complete the assembly of the 36-cell 40-kW electrolyzer short stack;
- Achieve the durability test of the short stack at NREL
  - Current density 3 A/cm^2
  - 200 hours
- Deliver technical-economical analysis report basing on catalyst and MEA cost reduction

Acknowledgments

- Financial support from DOE SBIR/STTR program under the contract # DE-SC0007471
- DOE Fuel Cell Technologies Office
  - Dr. David Peterson
- Giner Personnel

  Monjid Hamden, Tim Norman, and Corky Mittelsteadt
- NREL: Bryan Pivovar, Shaun Alia, K. C. Neyerlin; Shyam Kocha
- 3M: Krzysztof Lewinski and Sean Luopa
- ORNL: Karren More

AMR Review

Project strengths:

- Giner is a leader in the electrolysis field. Other strengths include attempts to develop accelerated stress tests for electrolysis and a method to measure ECSA for metals and oxides.
- Project strengths include the ability to do scale-up and testing with a clear path to commercialization of promising leads.
- This is a strong team working on interesting problems.
- This is an interesting project and idea.

Project weaknesses:

- The researchers need to work on the durability of their catalyst. They need to validate the accelerated testing protocols. They should look to the PEM fuel cell protocols for any additional durability tests. They need to do a techno-economic analysis (H2A) to determine the projected impact of their work on hydrogen cost.
- It would be beneficial to perform an H2A model analysis and compare results with other similar technologies because, notably, the use of Ir seems prohibitive in practice.

Recommendations for additions/deletions to project scope:

Understanding the role of particle migration/sintering upon cycling (and dependence on size and initial dispersion) for these Ir systems would be helpful for this project and others with similar PGM minimization objectives.