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

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Newton, MA

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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: 4/20/2017
- Percent Complete: 50%

Budget

- Phase IIB
  - Total Project Value: $ 999, 926
  - Total Funding Spent: $ 519, 006*
- Cost Share Percentage:
  0% (SBIR)

* as of 3/31/15

Giner Researchers

Brian Rasimick, Shuai Zhao, Zach Green and Bob Stone

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

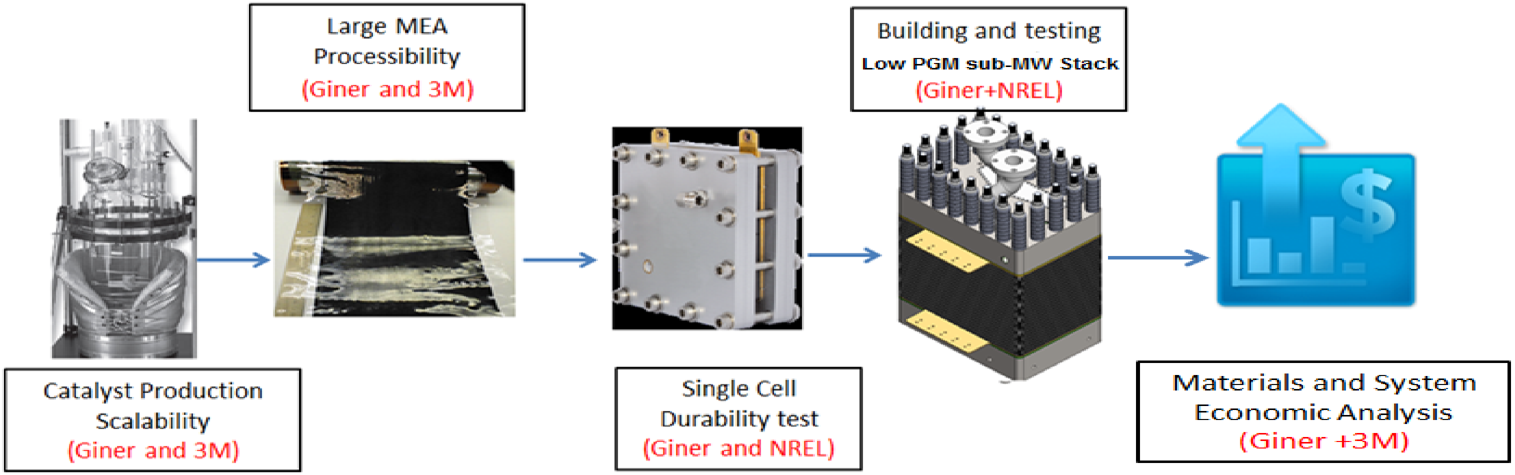
- **Phase 2 Accomplishments**

  - 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**

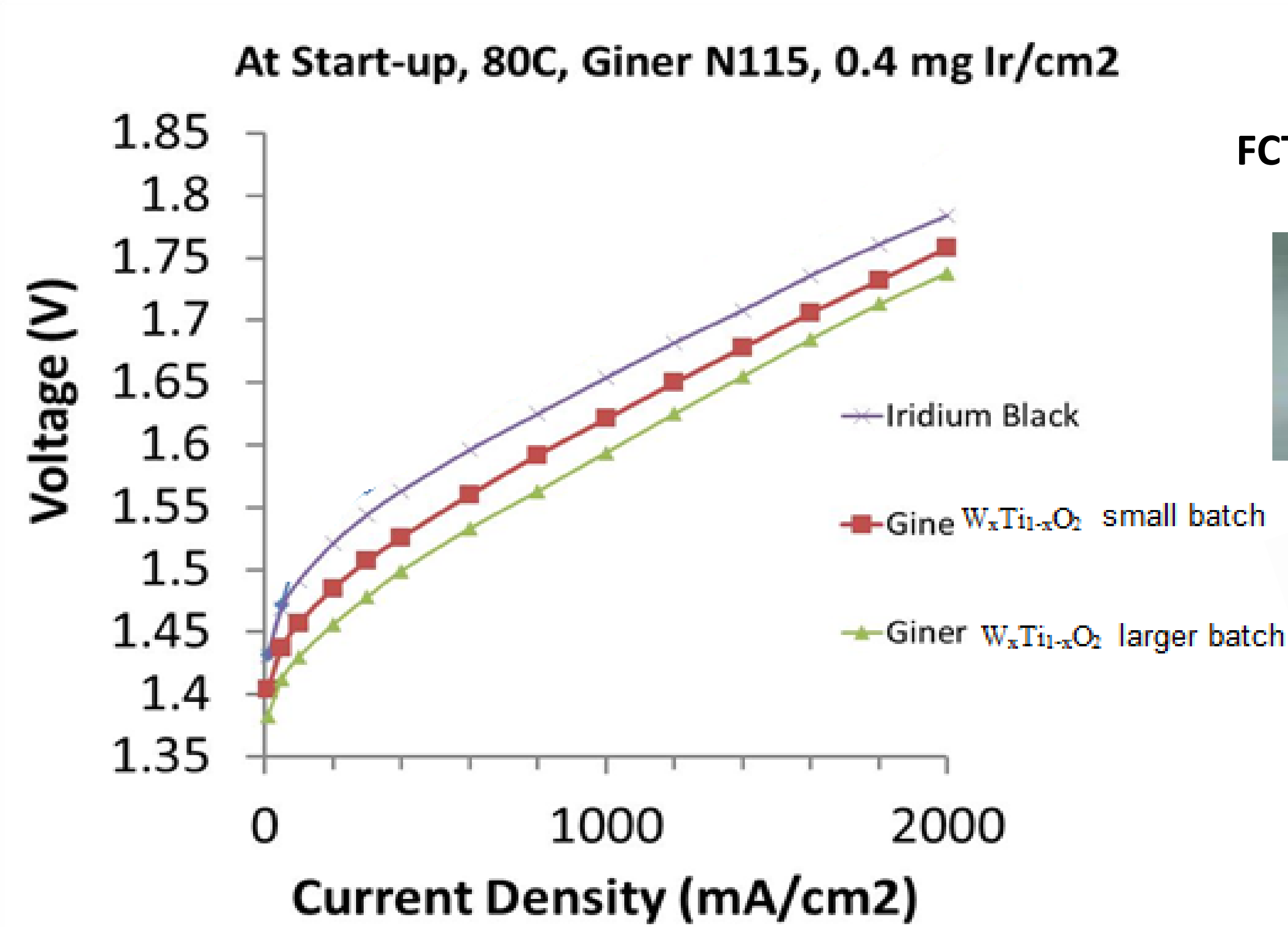
  - Scale-up and commercialize low PGM loading OER catalysts using Giner electrolyzer platform
  - Evaluate the impact of newly developed catalysts on the PEM electrolyzer efficiency and cost

Phase IIB Project Task and Milestones



			Year 1						Year 2					
Completion	ID	Task Name	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												
70%	M3.1	Obtain < 30 mV performance decay (at 2 A/cm2) after 30,000 cycles during AST												
40%	**M3.2**	Obtain < 50 mV performance (at 2 A/cm2) after 4,000 hours during electrolyzer testing												
	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												

Accomplishment 1: Ir/$W_x TiO_{1-x}$ Scale-Up



FCT 50cm² hardware

- the catalyst scaled up from 0.5 g/batch to 5 g/batch
- Scaled-up catalyst demonstrates higher activity than small batch one

Short Stack Design of 50cm² MEA

End Cell

- Group 1
  - Cell1: Giner standard Anode
  - Cell2: Giner standard Anode
- Group 2
  - Cell3: 0.5mg/cm2 Ir black
- Group 3
  - Cell4: 0.25mg/cm2 Ir/W-TiO2
  - Cell5 : 0.25mg/cm2 Ir/W-TiO2
  - Cell6: 0.25mg/cm2 Ir/W-TiO2

End Cell

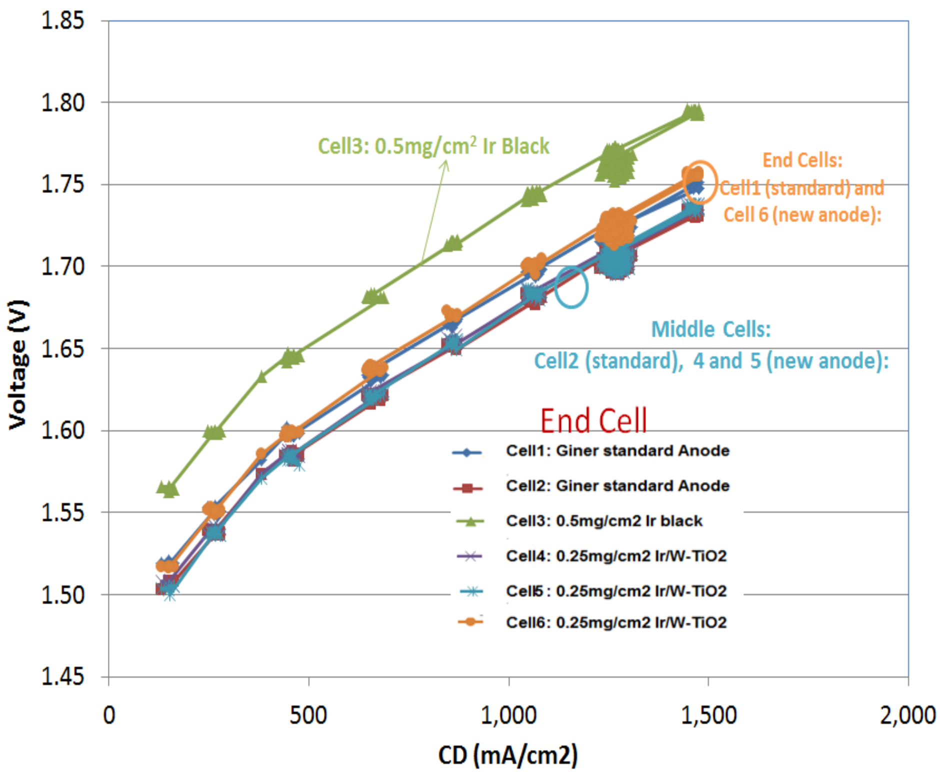
Anode DM

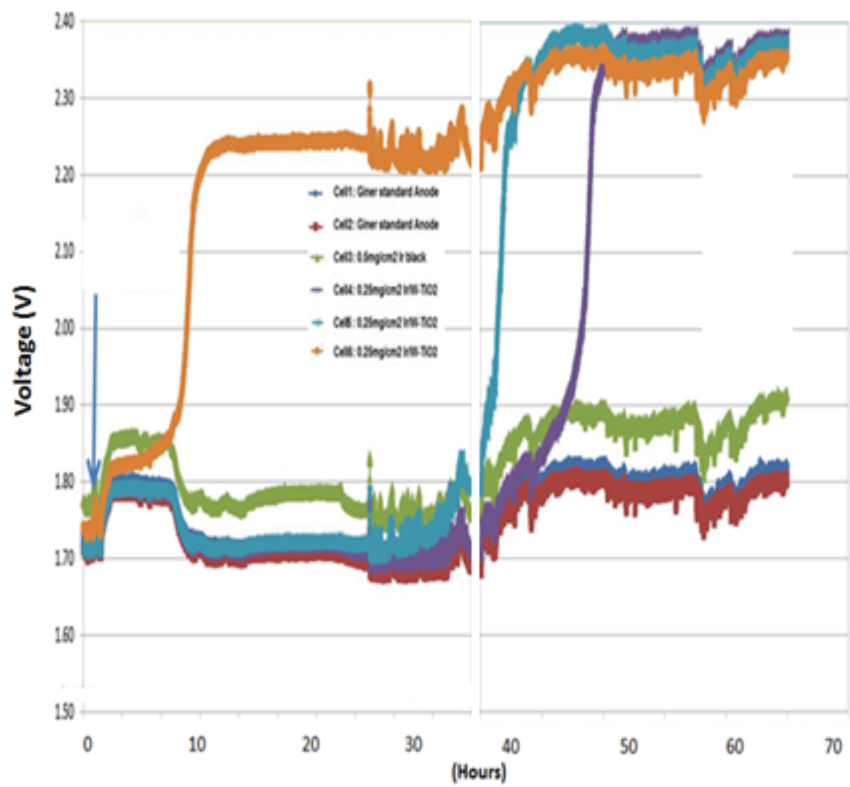
MEA (50cm²)

Current Collector

Giner proprietary 50cm² hardware

Performance and Durability of MEA



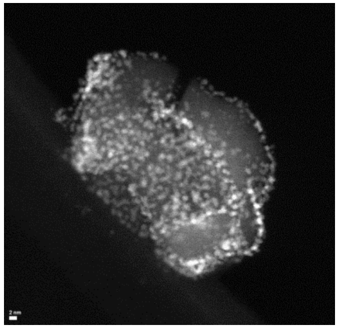


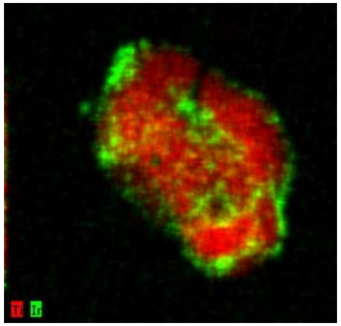
- **Scaled-up catalyst demonstrates initially high activity;**
- **Ir/W_xTiO_{1-x} Catalyst Cell 4 , 5 and 6 started to decay at different times**

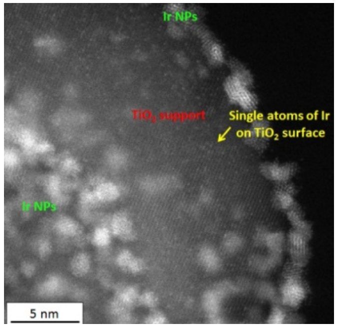
MEA Instability Analysis

- Low PGM loading MEA more vulnerable to environmental oscillation
- Catalyst structure changes partially due to scale-up of catalyst production (catalyst anchoring, catalyst morphology particle size)

Large-Batch

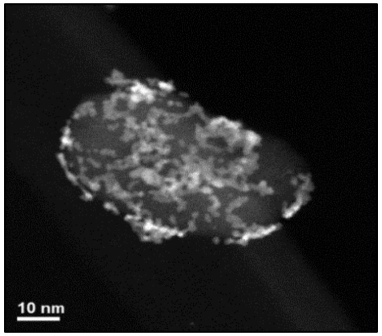


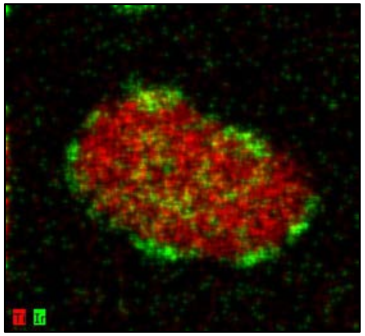




- Particle Size ~ 1 nm and Ir atoms
- Isolated Ir nano – particles (NPs)

Small-Batch





- Particle Size ~ 2-3 nm
- Ir NPs form a “chain-like” network of interconnected NPs

Small particle size starts with high activity but end up with poor durability

Precise Controlled Catalyst Synthesis

1. Factors leading to Catalyst Instability of Large-batch Synthesis

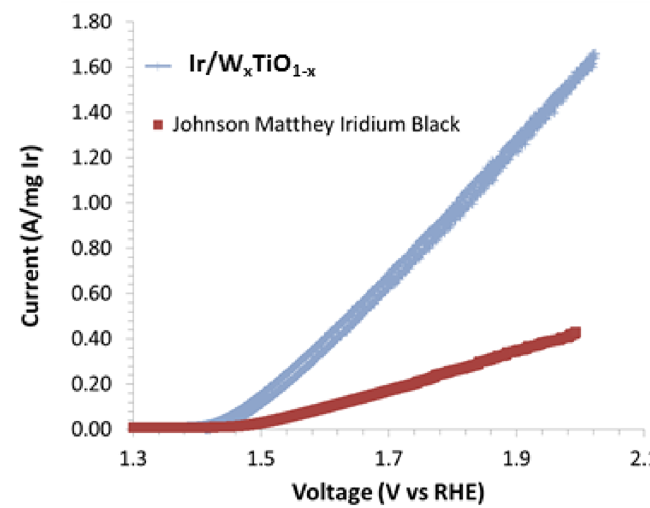
- Heating ramp cannot be precisely controlled
- pH condition is a limiting factor
- Poor anchoring of Ir on the support

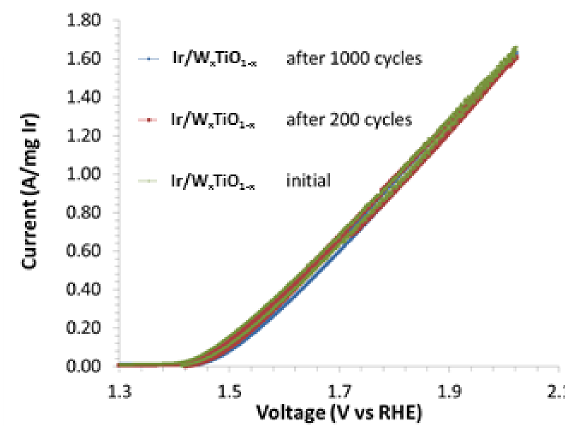
2. Path-forwards

- Purchase of a well-controlled reactor
  - Jacketed reactor for well-controlled cooling and heating
  - Electrical rotator for uniform mixing
- Decayed MEAs to be characterized by Dr. Karren More

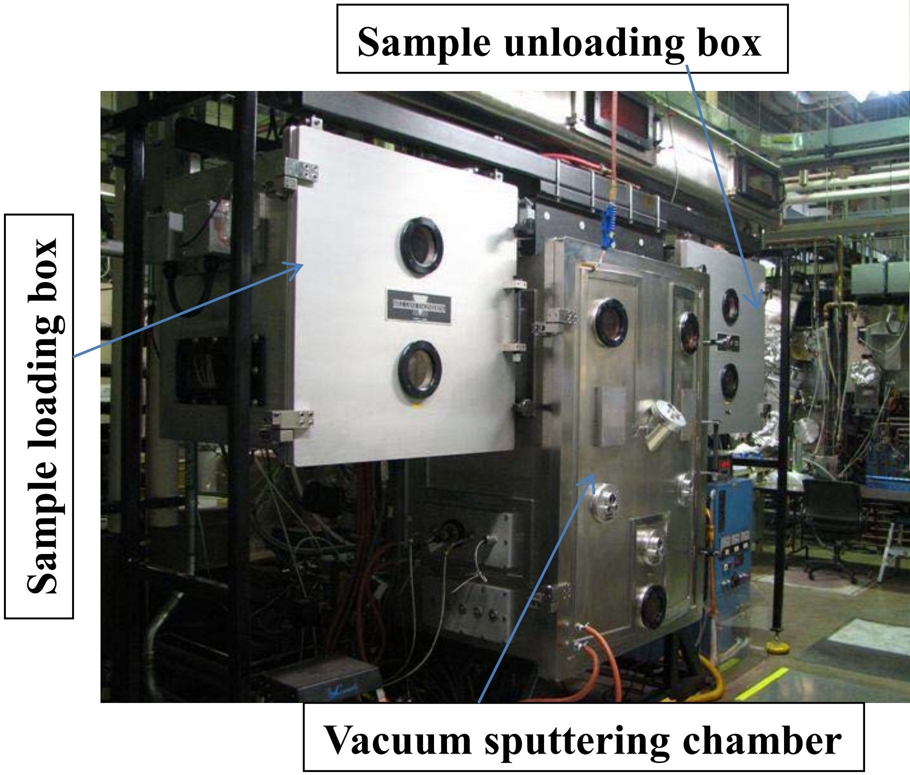
3. **New batches of catalyst** demonstrated high activity and good stability in RDE

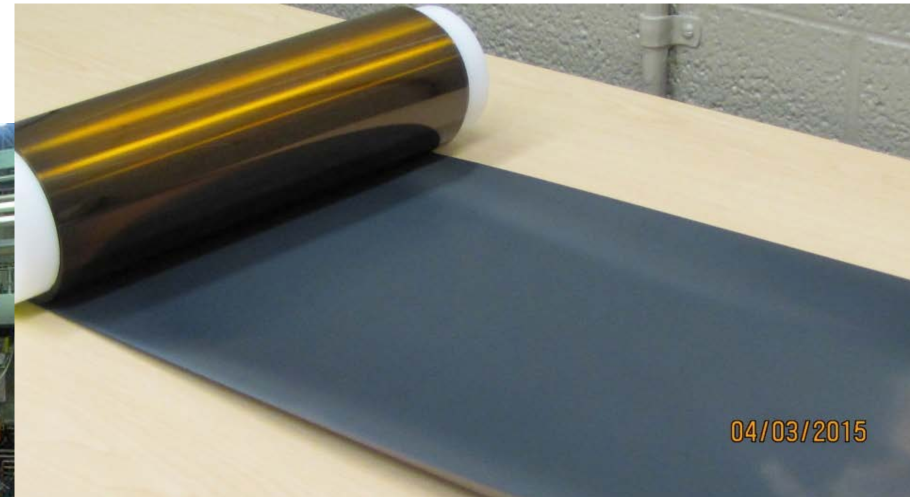
New Batches of Catalysts



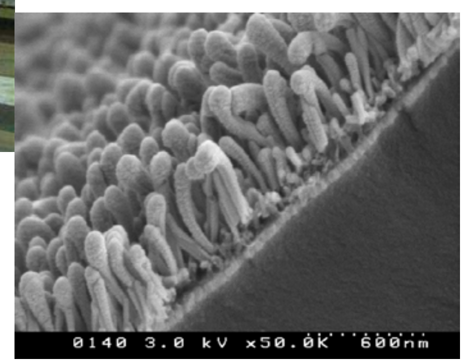


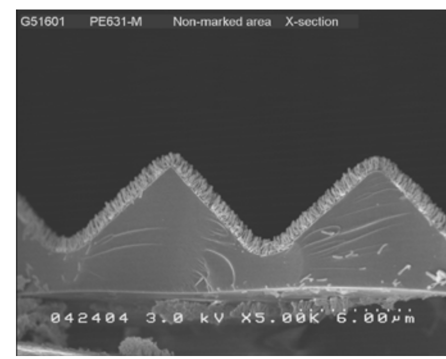
Accomplishment 2: 3M Ir-NSTF Scale-up





Iridium #3





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

Decals or CCMs Provided by 3M

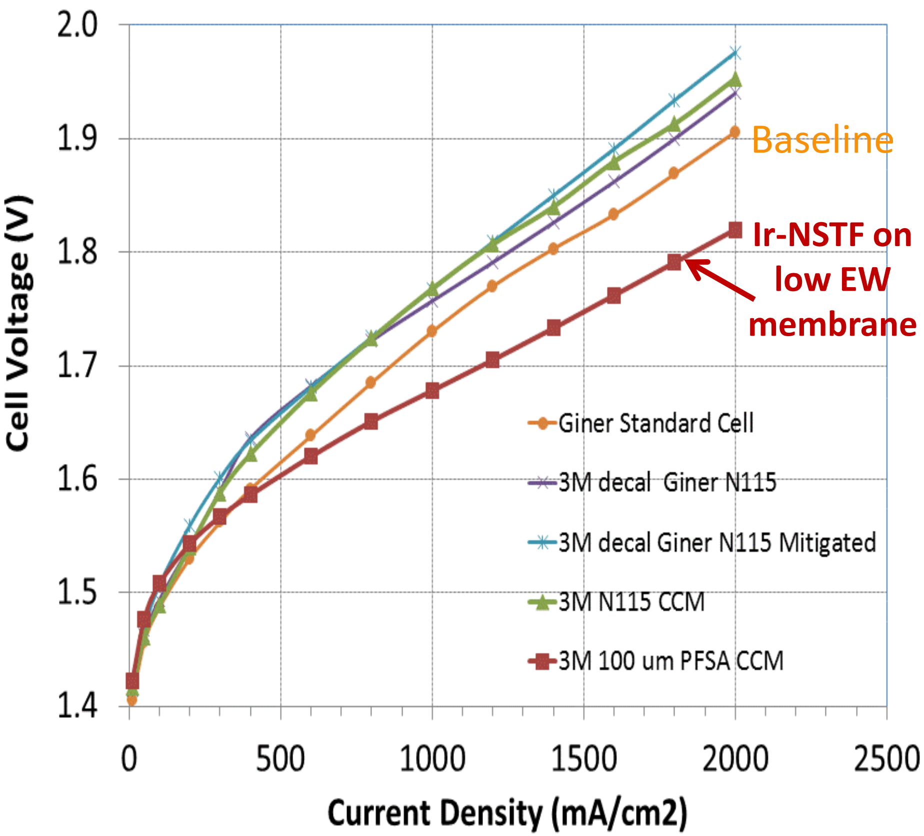
Batch	Anode (Ir) (mg/cm^2)	Cathode (Pt) (mg/cm^2)	Membrane	Comment
1	0.25	0.25		Decal only
2	0.50	0.25	Nafion 115	Non-H_2 crossover mitigated membrane
3	0.50	0.25	3M 50 μm 800EW	Non-H_2 crossover mitigated membrane
4	0.50	0.25	3M 100 μm 800EW	Non-H_2 crossover mitigated membrane

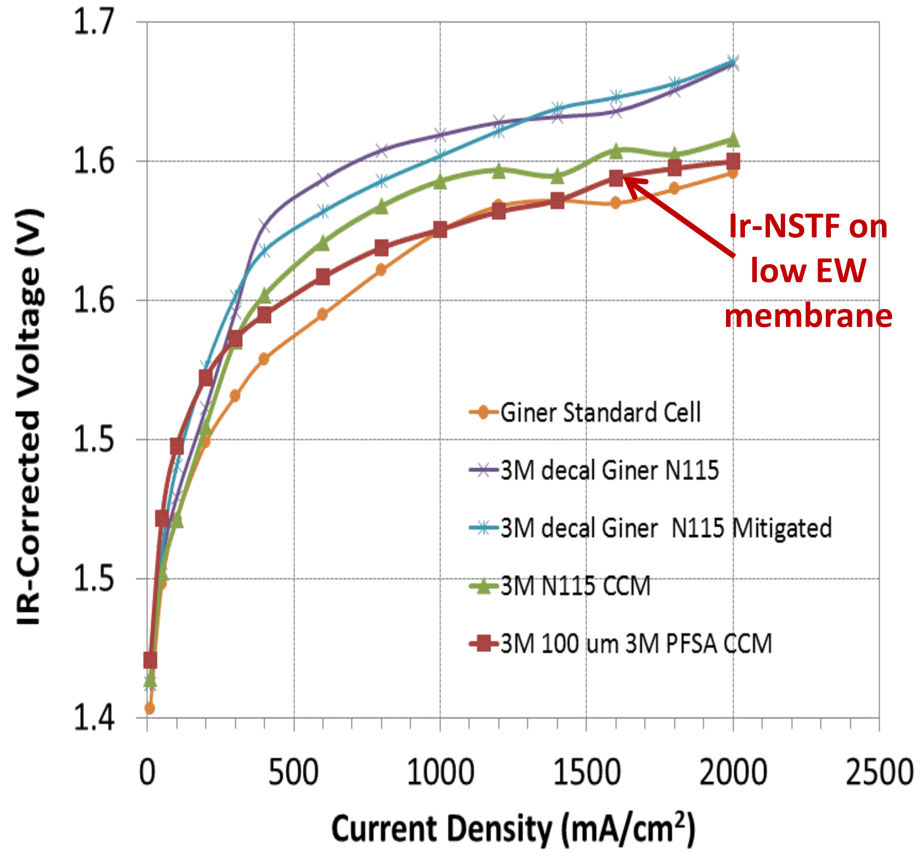
Giner standard cells: Ir loading 2-3 mg/cm^2, N115 membrane

- Single Cell performance test
  - Crossover mitigation (Giner)
- Hydrogen crossover measurement
- Short stack tests

All these tests were performed at Giner Inc.

Performance of 3M Decals/CCMs





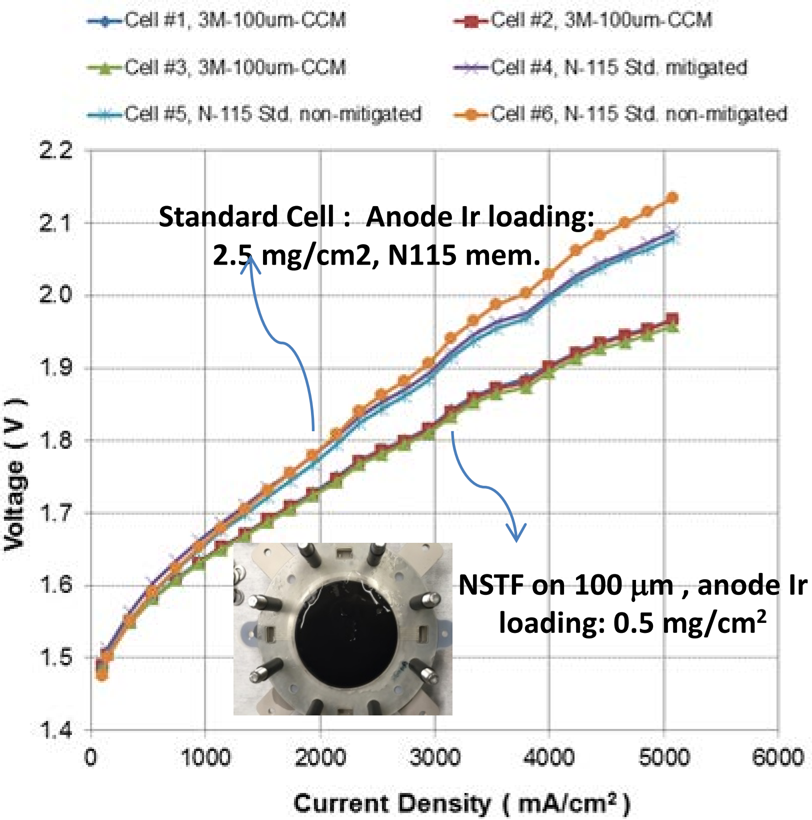
- Ir-NSTF on low EW 100 μm PFSA demonstrated the best performance, in part due to lower membrane resistance (0.1 Ohm-cm^2 vs 0.125 Ohm-cm^2 for N115);
- IR-corrected performance comparable to that of standard cell with much higher Ir loading (2-3 mg/cm^2)

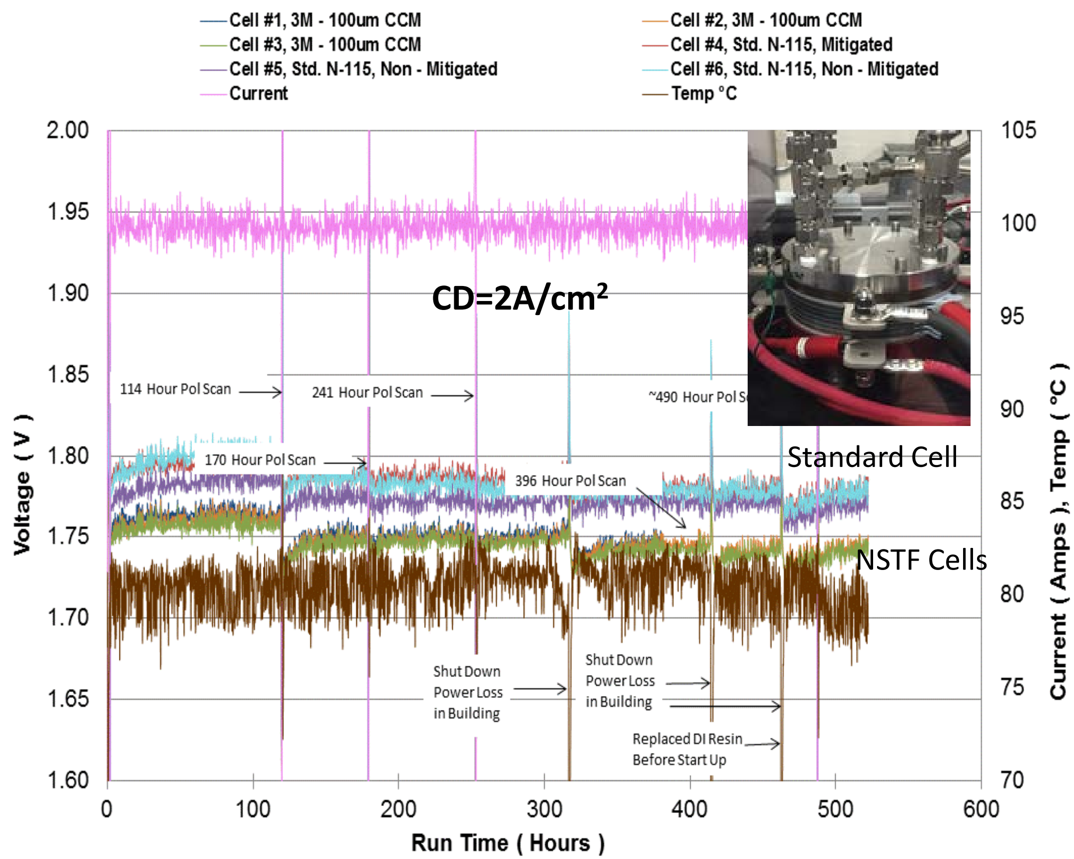
H_2 Crossover Testing

NSTF decal on unmitigated N115 80 °C			
Pressure (bar H2/bar O2)	A/cm2	mol% H2 in O2	Cell V
0/0	0.1	>4%	1.544
0/0	0.5	>4%	1.663
0/0	1	3.88%	1.766
0/0	2	2.36%	1.947
NSTF decal on mitigated N115 80 °C			
Pressure (bar H2/bar O2)	A/cm2	mol% H2 in O2	Cell V
0/0	0.1	< 0.10%	1.536
0/0	0.5	< 0.10%	1.656
0/0	1	< 0.10%	1.756
0/0	2	< 0.10%	1.925
10/0	1	< 0.10%	1.763
20/0	1	< 0.10%	1.771
30/0	0.5	< 0.10%	1.779
30/0	0.25	< 0.10%	1.677
30/0	0.1	0.16%	1.564

- **In-situ H_2 crossover at various conditions measured at Giner**
- **H2 crossover significantly reduced after using mitigated membrane**

Performance and Durability of Short Stack



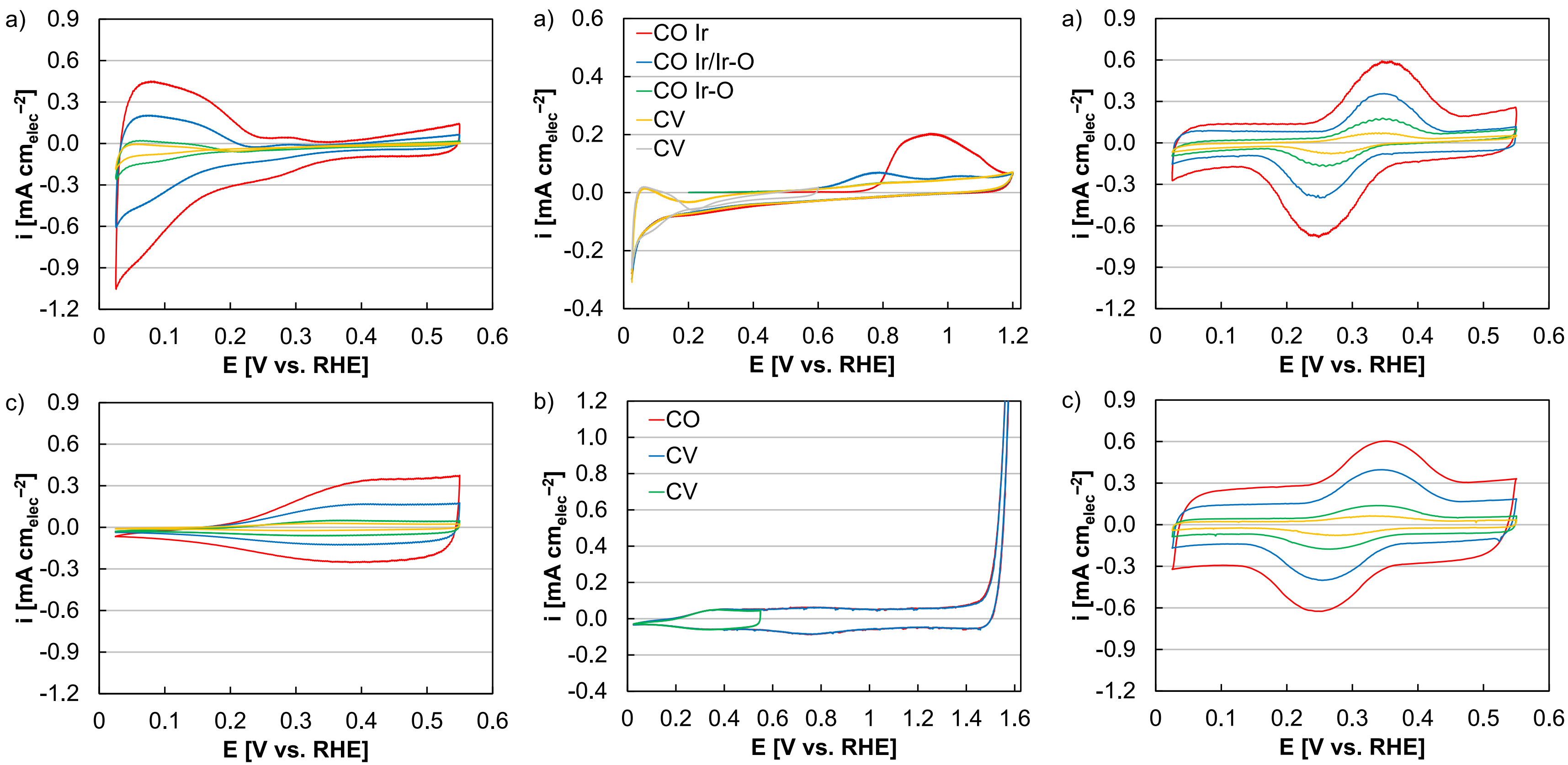


Active Area: 50 cm² @ Ambient Pressure and ~ 80 °C

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

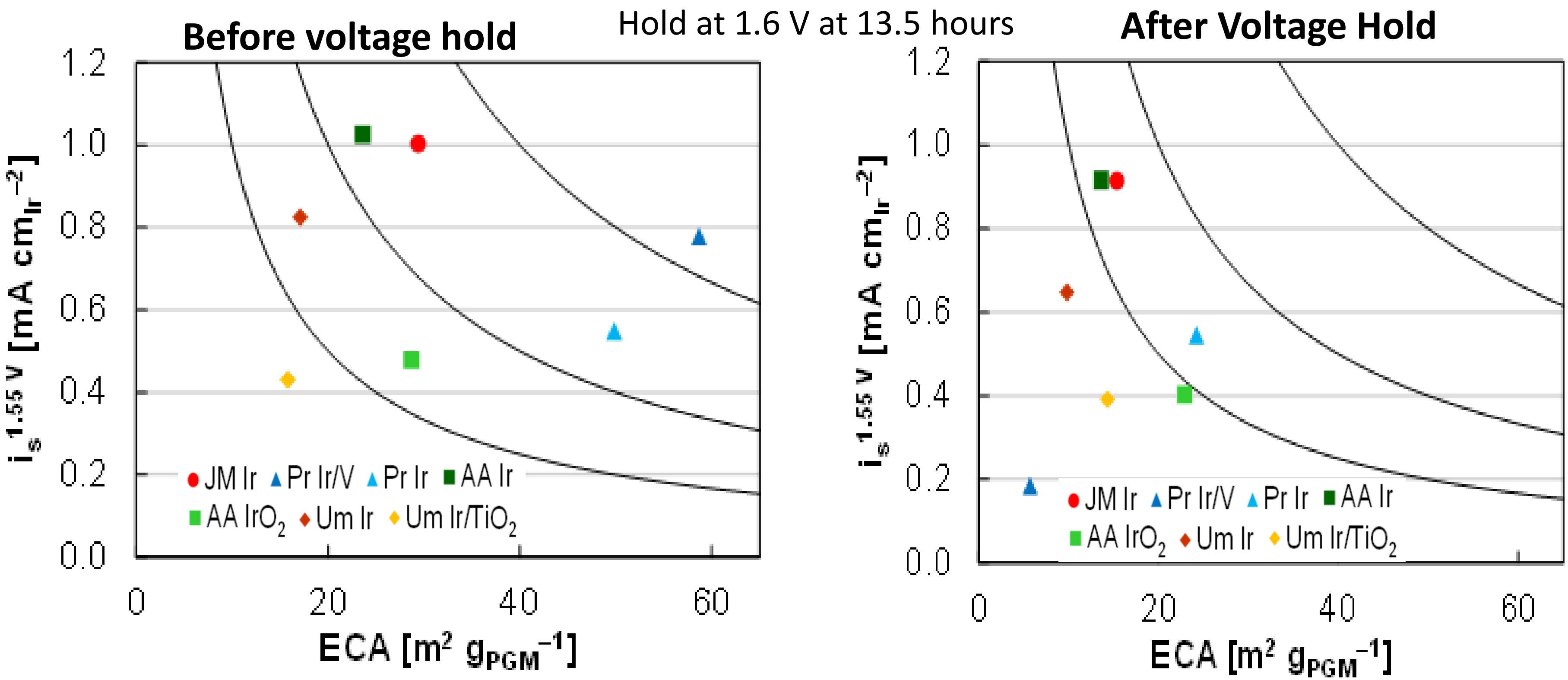
Accomplishment 3: Ir ECS Protocol Development

	H_2-UPD	CO Stripping	Mercury UPD
Ir			
Ir Oxide			



- H_2-UPD can be used on Ir, but not oxides
- CO stripping is more sensitive to the formation of surface oxides
- Only mercury could be used on both metals and oxides

Baseline Ir Catalysts (RDE)



- Mass activities (solid lines) of 0.1, 0.2, and 0.4 A mg_{Ir}^{-1}
- Loss of ECA after voltage hold
- Mass activity decreases after voltage hold

Accomplishment 4: MEA Degradation Studies

Anode Catalyst	Ir Black (JM)	$Ir/W_xTi_{1-x}O_2$
Fresh MEA	✓	✓
Voltage cycling (> 10, 000 cycles)	1.4 V to 2.0 V 1.4 to 1.8 V	1.4 V to 1.8 V
Constant voltage hold (48 hours)	2.0 V	1.8 V
Long-term durability test (1000-h test)	2 A/cm^2	1.5 A/cm^2
Ir Loading (mg/cm^2)	2, 0.4, 0.1	2, 0.4, 0.1

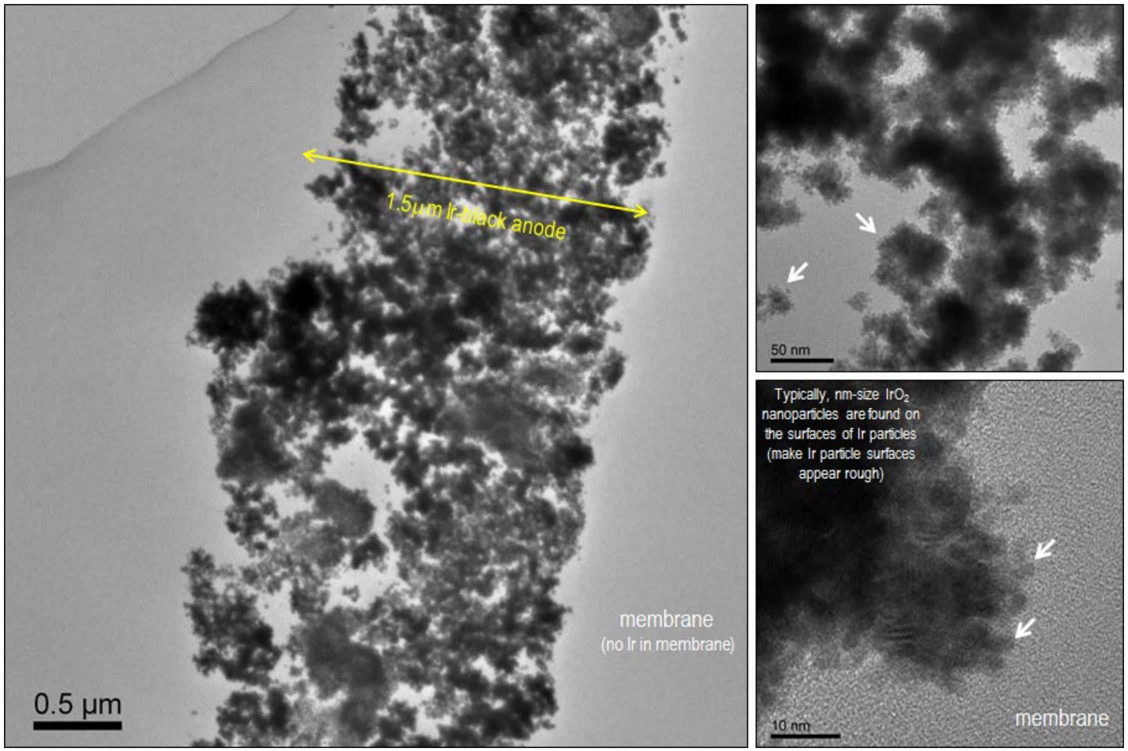
- Polarization curves acquired after individual stress tests
- MEA characterized at ORNL to elucidate microstructural changes

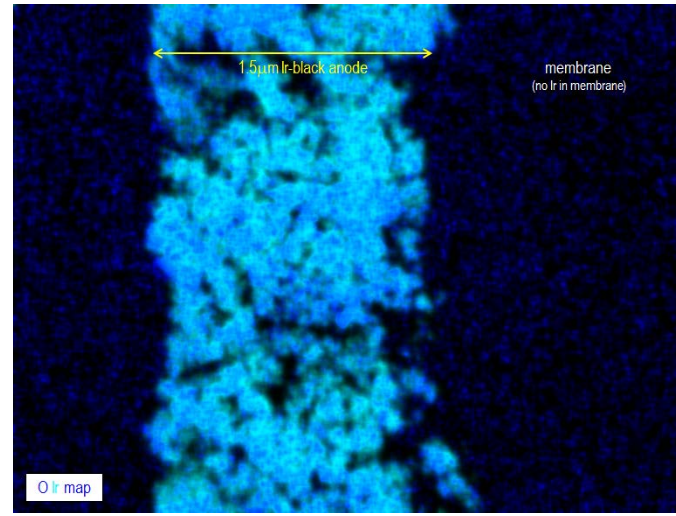
Correlation between electrochemical stability and microstructural changes?

Anode Ir; cathode Pt/C; membrane: Nafion® 115

Fresh MEA

Anode: 0.4 mg/cm^2 Ir
Cathode: 0.4 mg/cm^2 Pt

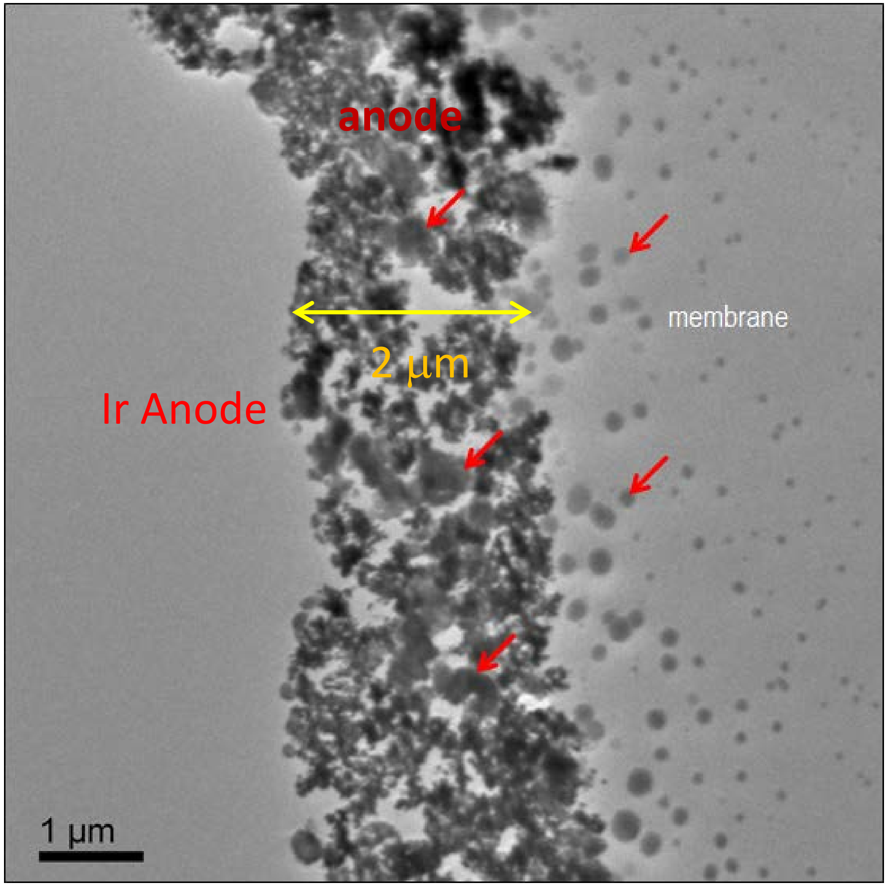




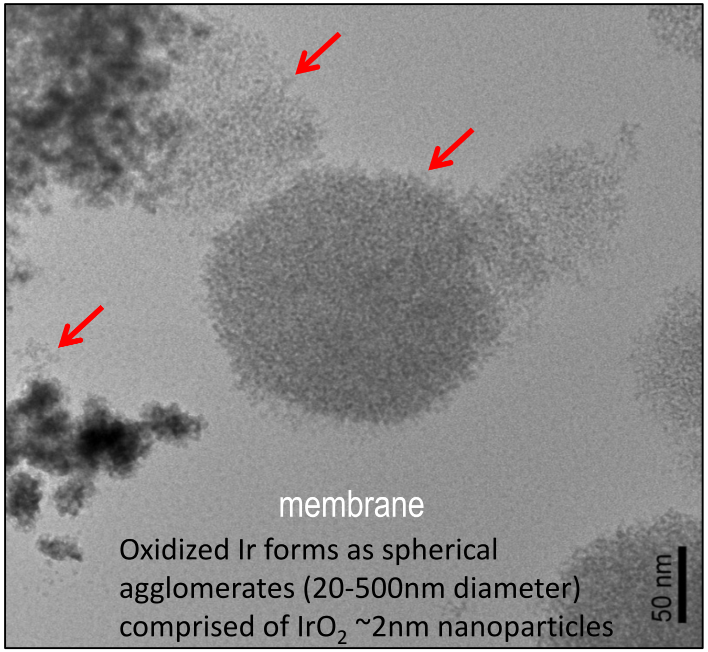
- **Ir black layer comprised nm-sized, agglomerated Ir particles**
- **Some IrO_2 identified on the surfaces of Ir particles**
- **No Pt or Ir particle in the membrane**

Aged MEA : Near Anode

1.4 V (30 sec.) to 2.0 V (3.0 sec.), 10, 000 cycles,

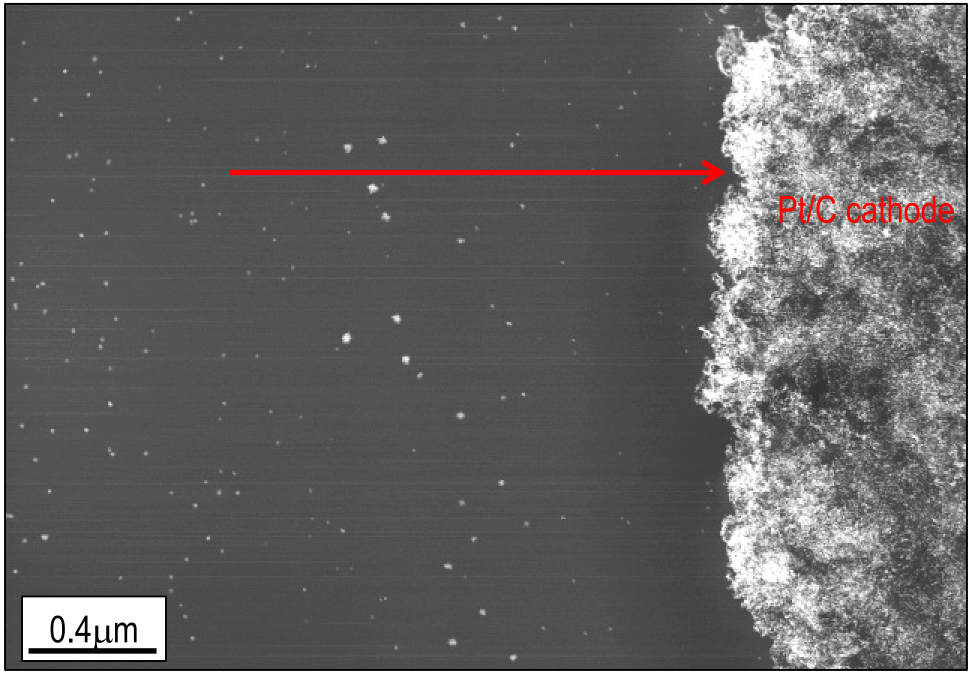


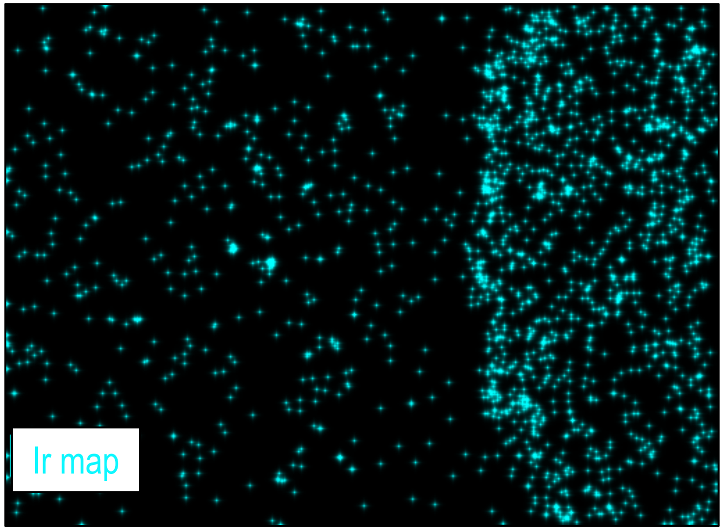
Anode: 0.4 mg/cm^2 Ir
Cathode: 0.4 mg/cm^2 Pt

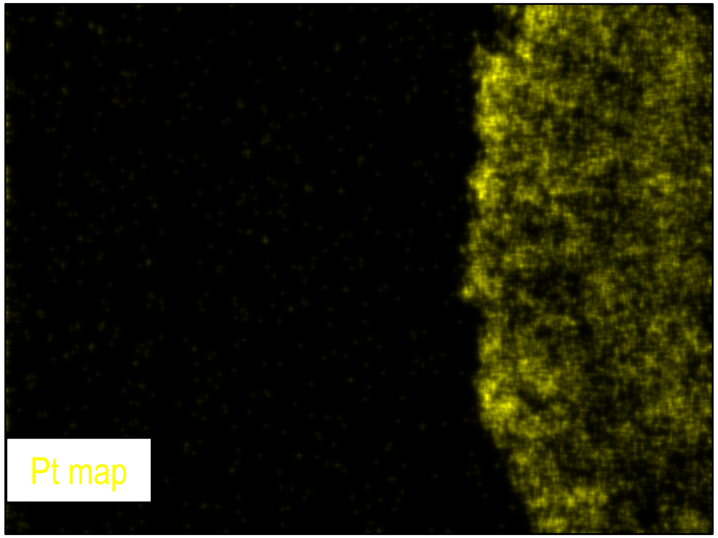


- **Significant Ir oxidation occurs at anode/membrane interface and within anode pores**
- **Spherical nanoparticle agglomerates clearly formed in the membrane(red arrows)**

Aged MEA : Near Cathode







- **Ir migrated from anode across membrane to cathode that can lead to electrical shorting of the membrane-catastrophic !**
- **No distinct Pt particles in membrane adjacent to cathode**

Project Summary

- Both Giner Ir/$W_xTi_{1-x}O_2$ and 3M Ir-NSTF anode catalysts have been scaled up and tested in short stacks (5-6 cells, 50 cm^2)

- Giner scale-up Ir/$W_xTi_{1-x}O_2$ catalyst based anode demonstrated superior performance to standard anode, but fast performance decay:
  - Catalyst morphology structure changes upon scale-up (Ir particle size, Ir dispersion)
  - Precisely-controlled catalyst synthesis helped to stabilize the catalyst

- 3M scale-up Ir-NSTF on 100 µM low EW membrane demonstrates great performance
  - Lower over-potential than Giner Standard Cells
  - Excellent durability upon constant current test at 2 A/cm^2

- Catalyst durability AST protocol investigated on cohesive collaboration between NREL and Giner and a variety of OER catalysts have been characterized.

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	Subcontractor; fundamental studies of MEA degradation; standard protocol establishment
3M Company (3M) Krzysztof Lewinski, Sean Luopa	Vendor; IrNSTF based catalyst development, short production, cost analysis
Oak Ridge National Laboratory (ORNL) Karren More	Collaborator: catalyst and MEA structure characterization

Great team with complementary expertise leads to project success!

Future Research

- Identify and resolve durability issue of Ir/ $W_xTi_{1-x}O_2$ catalyst upon scale-up;
- Complete AST durability test protocols and correlate with real performance test
- Complete 5000-h Stack durability of selected Giner and 3M catalysts
- Select catalysts for Giner sub-MW electrolyzer stack construction

Acknowledgments

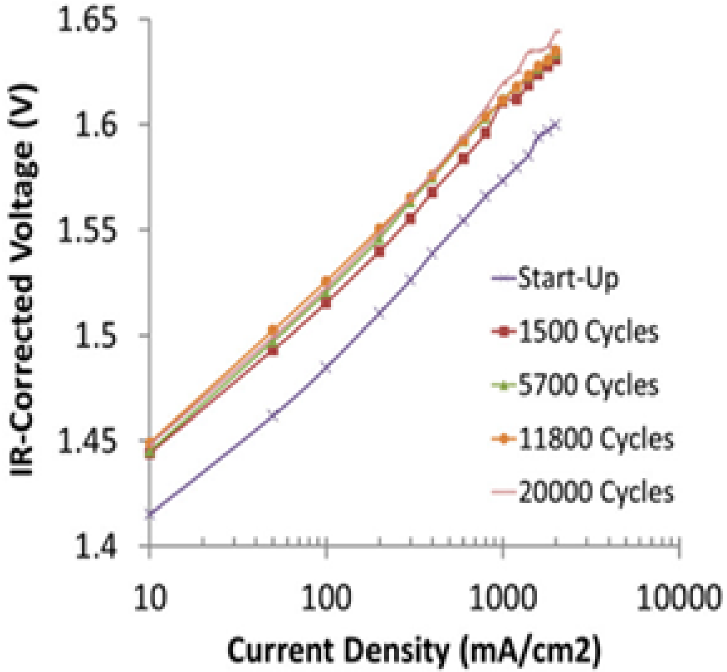
- Financial support from DOE SBIR/STTR program under the contract # DE-SC0007471
- DOE Fuel Cell Technologies Office
  - Dr. David Peterson
- Giner Personnel

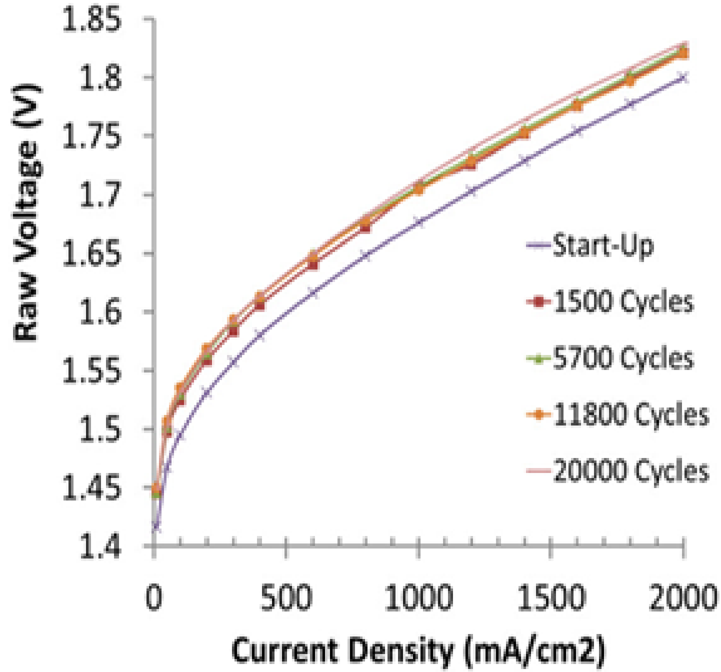
  Monjid Hamden, Tim Norman, and Corky Mittelsteadt
- NREL: Bryan Pivovar, Shaun Alia, K. C. Neyerlin; Shyam Kocha
- 3M: Krzysztof Lewinski and Sean Luopa
- ORNL: Karren More

Appendix

AST of 3M N115 Decals

Anode: Ir-NSTF (Ir: **0.25** mg/cm^2); Cathode: standard, 80 ° C, Nafion ® 115



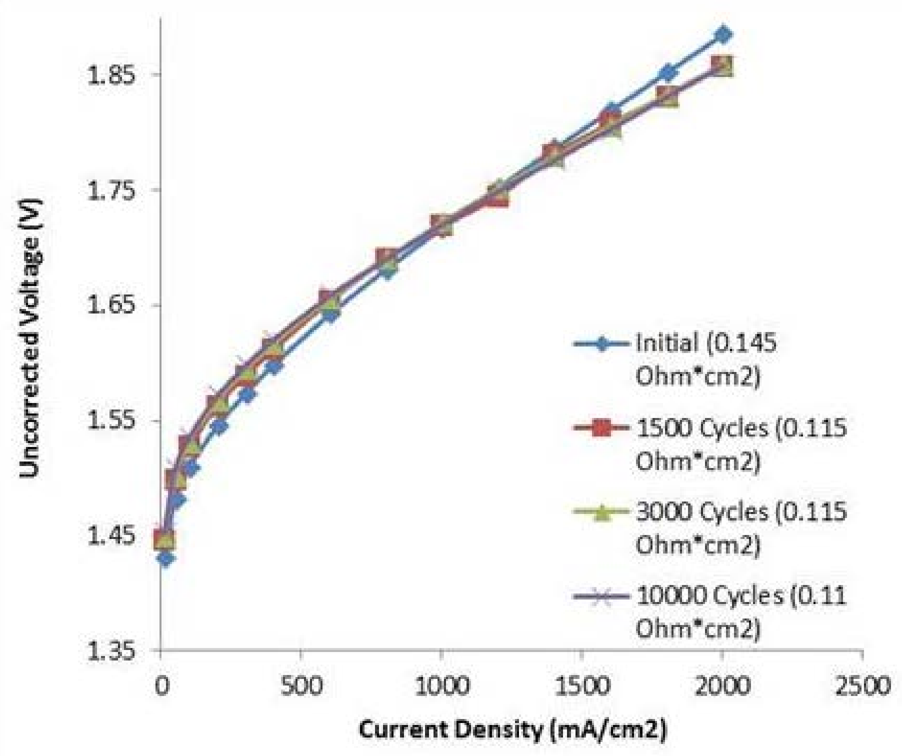


AST: voltage cycling from 1.4 V to 2.0V, 30 min for each voltage, square wave

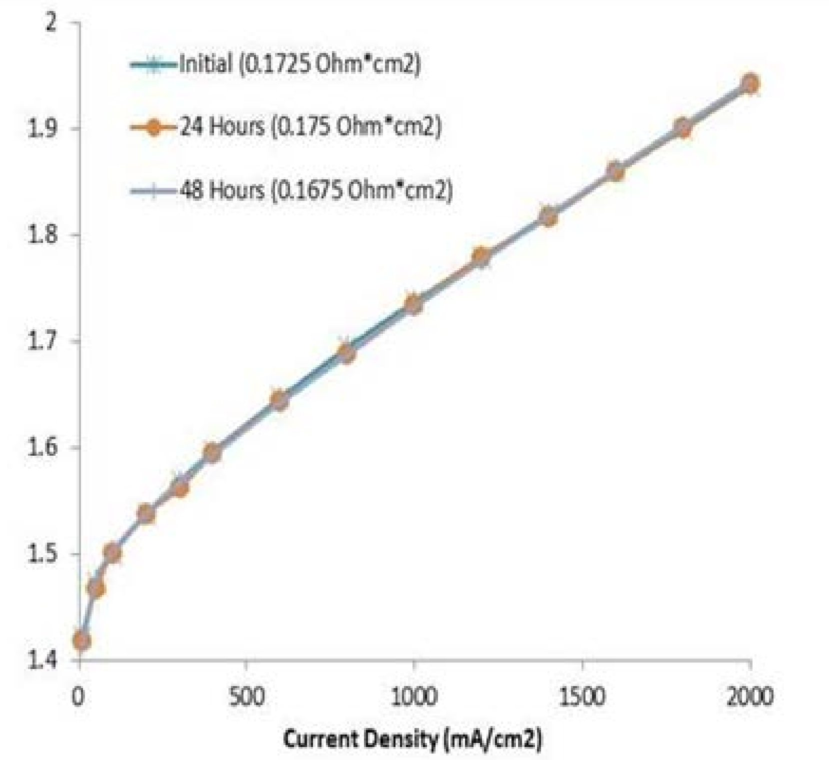
- Good durability demonstrated in a single cell test after initial conditioning

Performance Upon Durability Tests

Ir Black: 1.4-2.0V Cycled MEA



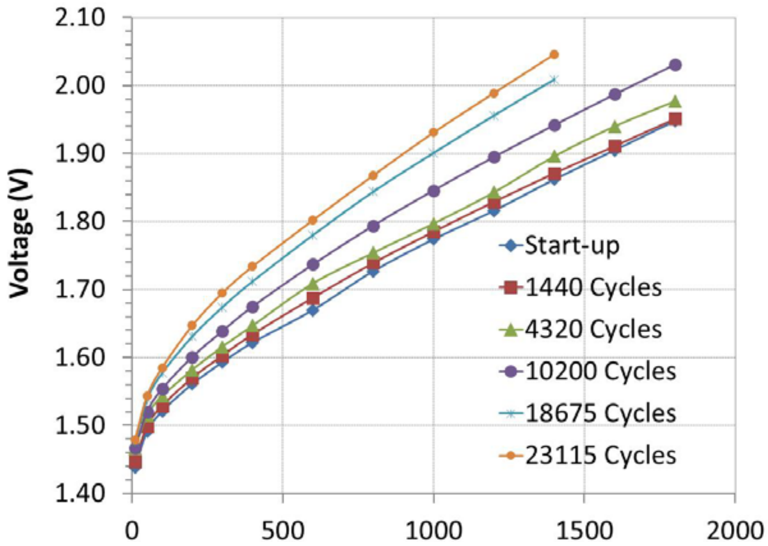
Ir Black: 2.0 V-hold MEA

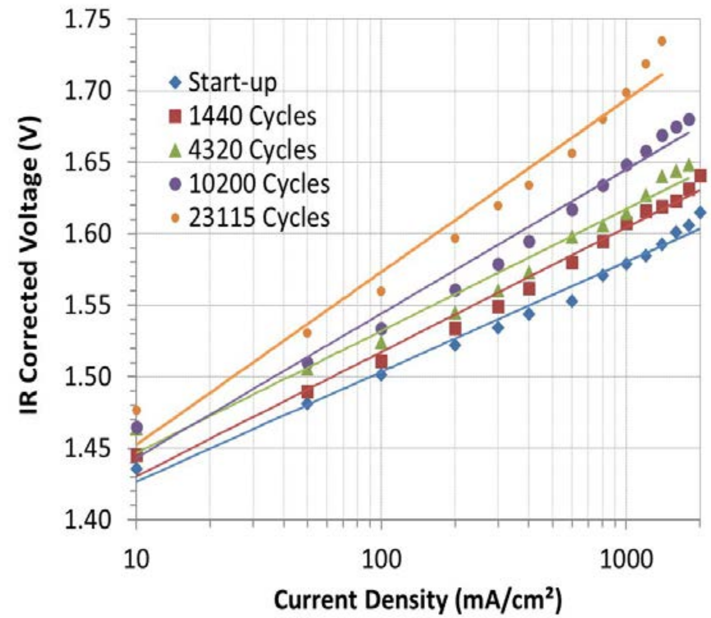


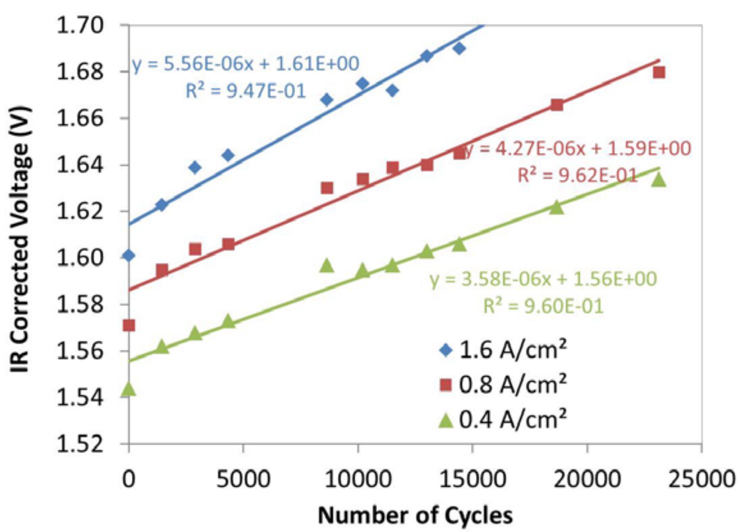
- **MEA degradation due to Ir agglomeration and migration/deposition does NOT MANIFEST in electrochemical performance - More aggressive stress protocols**
- **High Ir loading (0.4 mg/cm^2) obscures the catalyst degradation nature?**

Durability Tests w/ Extreme Low Ir Loading

Anode: 0.1 mg/cm² Ir black; Cathode: 0.4 mg/cm² Pt



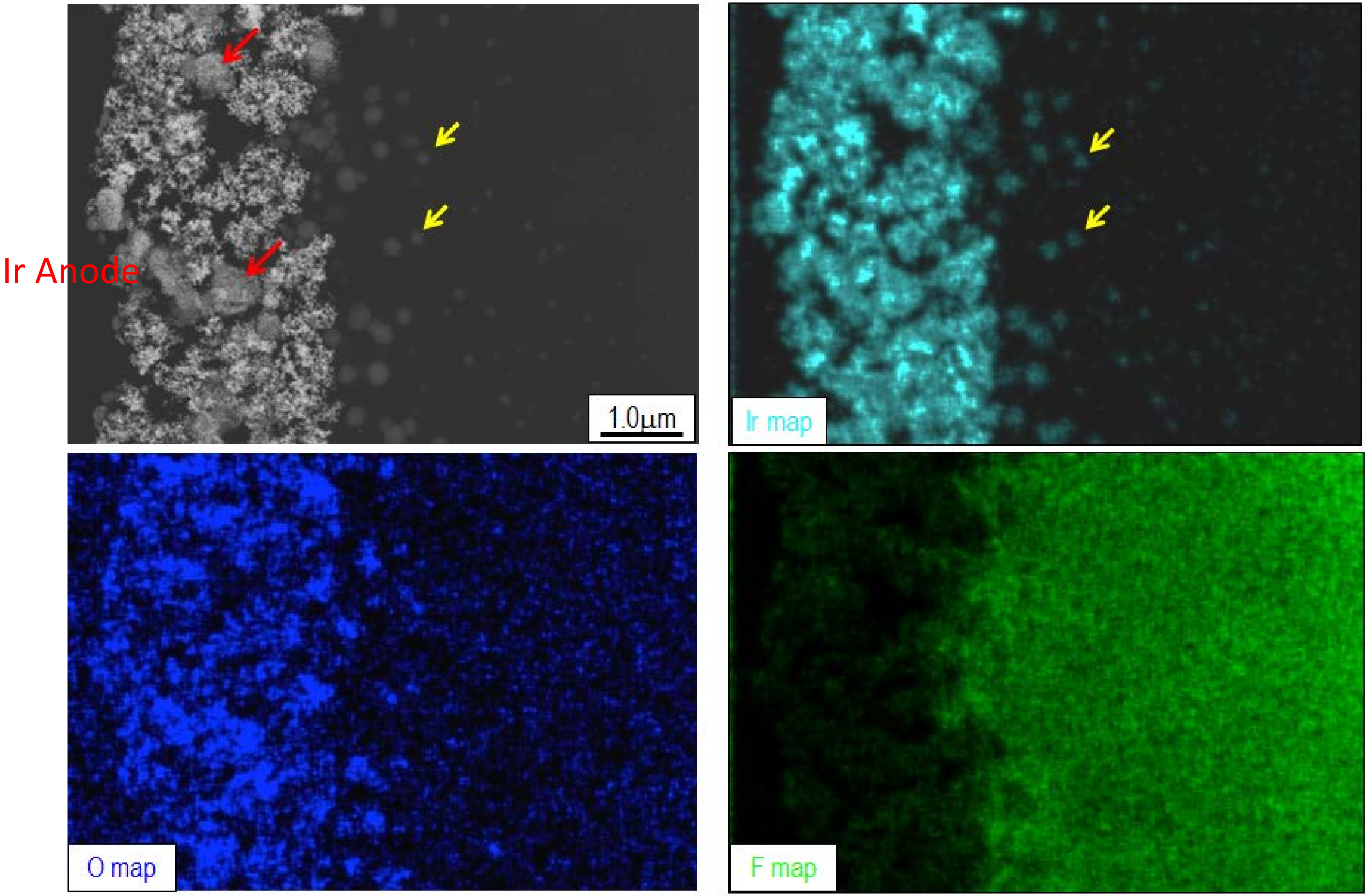




- **Electrochemical performance loss clearly observed at 0.1 mg/cm² loading !**
  - Sample to be characterized

- **While increasing Ir loading to 2.0 mg/cm², no apparent performance decay again**

Aged MEA After Voltage Cycling 1.4 to 2.0 V



- **Significant Ir oxidation within porous regions of anode (red arrows);**
  - **Migration of Ir/IrO_2 into membrane forming agglomerates**

Publications/Reports

- **Lewinski**, K, and S.M. Luopa, invited talk "High Power Water Electrolysis as a New Paradigm for Operation of PEM Electrolyzer", L09: Oxygen or Hydrogen Evolution Catalysts for Water Electrolysis Session, Talk 1948, 227th Meeting of the Electrochemical Society, Chicago, IL, USA, May 24-28 (2015).

- **Xu**, H, Rasimick, B and More, K., "High-Performance, OER Catalysts for Proton Exchange Membrane Electrolysis, Invited talk at L09: Oxygen or Hydrogen Evolution Catalysts for Water Electrolysis Session, 227th Meeting of the Electrochemical Society, Chicago, IL, USA, May 24-28 (2015).

- **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)

- **Xu**, H , Advanced Catalyst for Water Electrolysis", Invited talk presented in in 250th meeting of ACS, Energy and Fuels Division, Boston, August 16-2,(2015)

- **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 IIB Grant No. DE-SC0007471, August (2015)

Answers to Reviewers' Comments

- The milestones might have been originally written to be lax. *Answer: the millstones were discussed with DOE SBIR Program Manager and considered reasonable. In the Phase II B project, we have re-polished the milestones to make them more specific and measurable*

- The graph on slide 19 for the Ir NSTF approach shows a polarization curve that deviates from the shape of the other catalyst curves. This should be explained. The error bars on slide 19 are considerable and obscure comparisons between the catalysts. While perhaps this amount of potential error is unavoidable, consideration should be given to how this might be improved.
  Answer: These data represented initial tests that may need to be repeated . This aspect has been improved in this new presentation. A better comparison can be seen from new data on Slide 12 (single cell) and Slide 14 (stack) in this presentation.

- A project weakness is the lack of an approach to gain a fundamental, molecular-level understanding of the catalyst surface and its effect on performance.
  Answer: We tried to understand our catalyst in a fundamental and molecular level. Due to the SBIR project nature, however, we did not have much time and resource to complete this goal . Despite this , we collaborated with Dr. Karren More at ORNL to gain the understanding of our catalysts via high resolution TEM images.