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

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Giner Inc.
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: 4/22/2013
  Project End Date: 4/21/2015
- Percent Complete: 99%

Budget

- Phase 2
  - Total Project Value: $999,983
  - Total Funding Spent: $902,915*
- Phase 2b
  - Total Project Value: $ 999,999
  - Start on April 22, 2015
- Cost Share Percentage:
  0% (SBIR)

* as of 3/31/15

Partners

- NREL: Dr. Bryan Pivovar (Co-PI)
- 3M: Dr. Krzysztof Lewinski(Co-PI)
- UMass-Lowell: Dr. Zhiyong Gu
- ORNL: Dr. Karren More

Barriers Addressed

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

Relevance

- DOE H_2 Production Target for Electrolysis

Technical Targets: Distributed Forecourt Water Electrolysis[1]

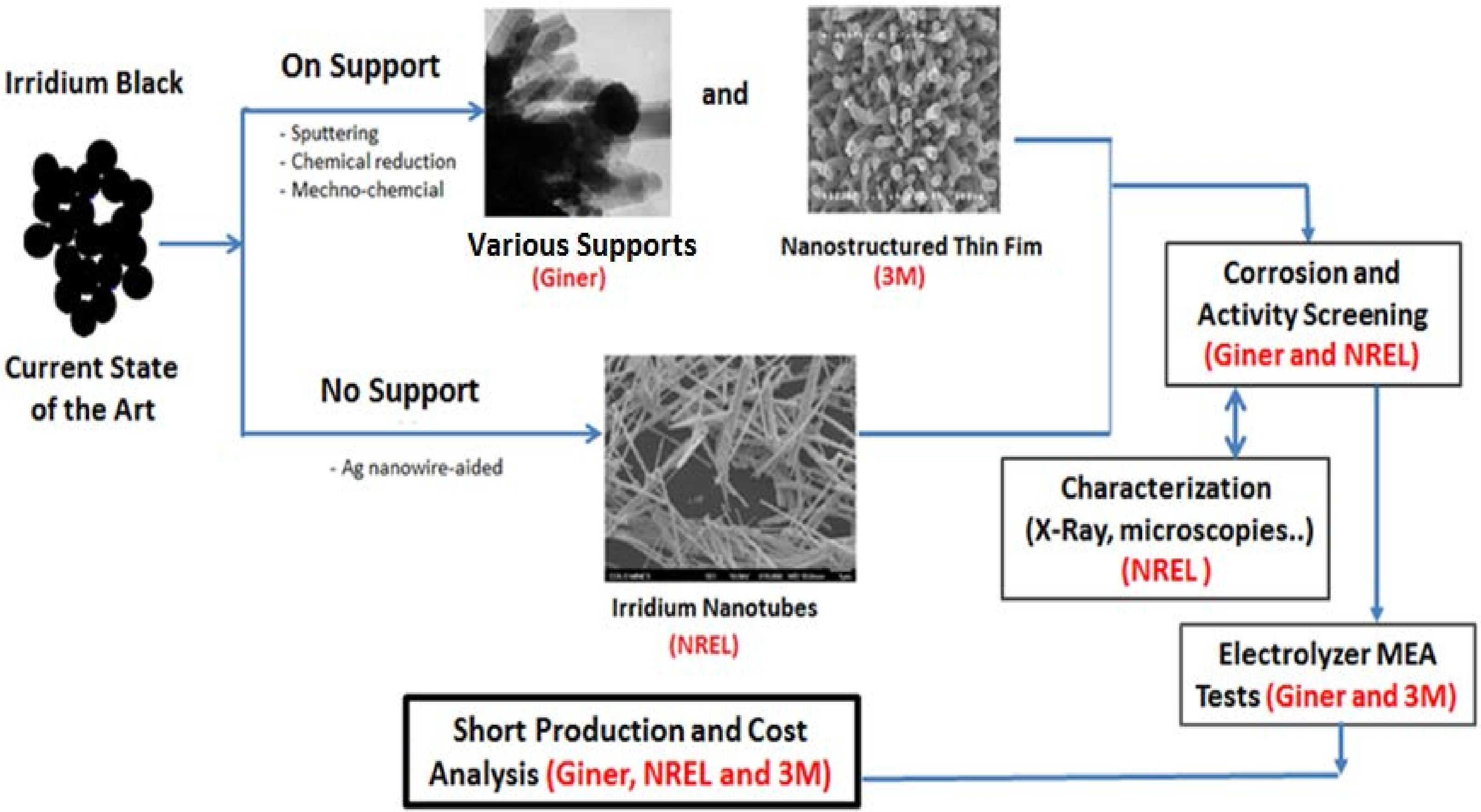
Characteristics		Units	2015	2020	Giner Status (2013)
Hydrogen Levelized Cost[2]		\$/kg-H_2	3.90	<2.30	3.64[3] (5.11)[4]
Electrolyzer Cap. Cost		\$/kg-H_2	0.50	0.50	1.30 (0.74)[5]
Efficiency	System	%LHV (kWh/kg)	72 (46)	75 (44)	65 (51)
Efficiency	Stack	%LHV (kWh/kg)	76 (44)	77 (43)	74 (45)

[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

- Objectives

- Develop advanced, low PGM loading catalysts for high-efficiency and long lifetime PEM water electrolysis
  - Improved both mass and specific activity
- Evaluate the impact of newly developed catalysts on the PEM electrolyzer efficiency and cost
  - Materials and system cost analysis

Technical Approaches

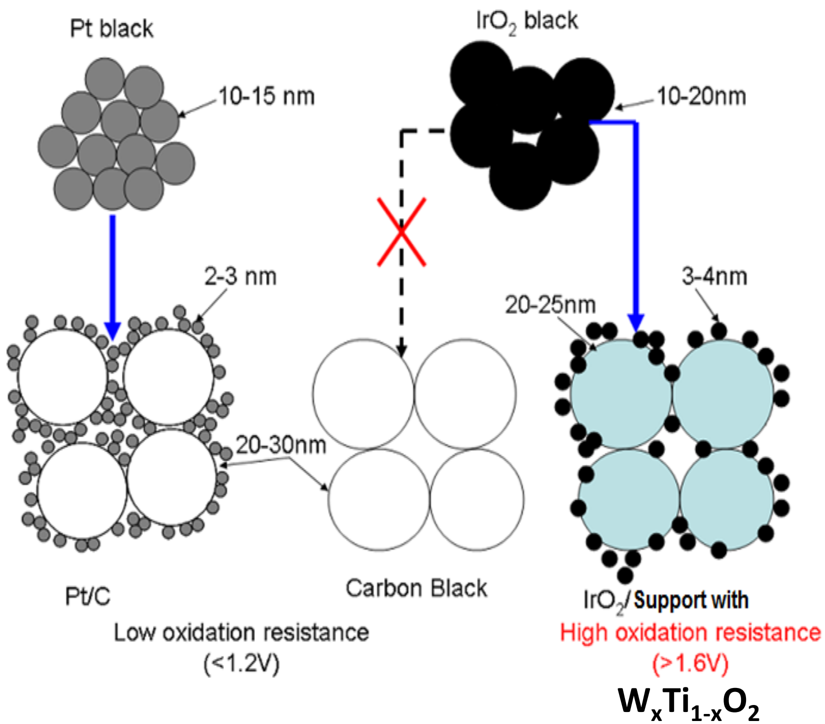


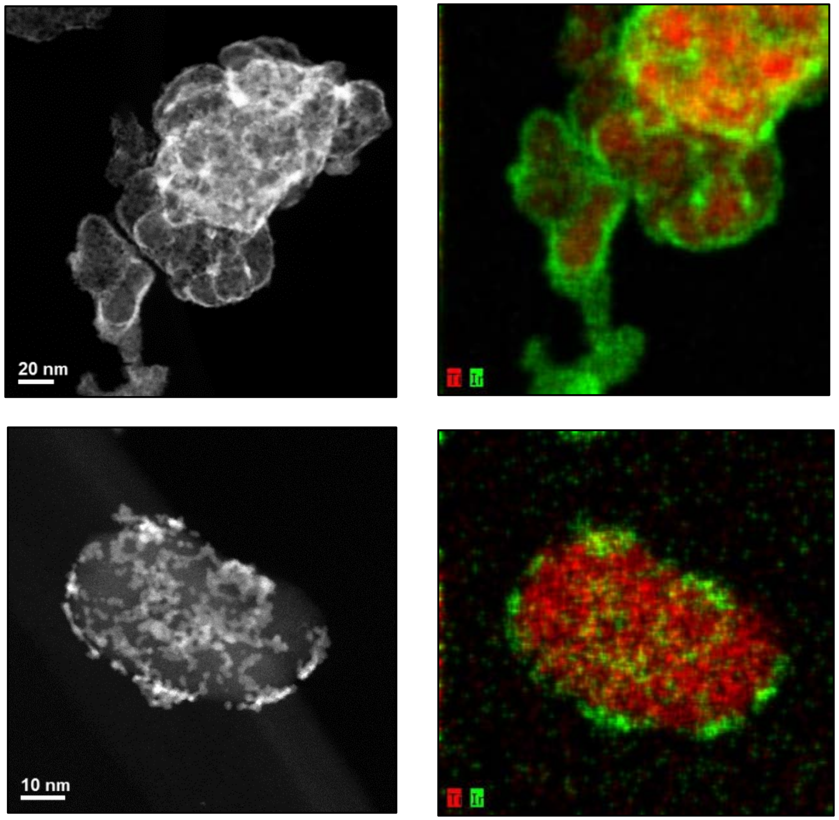
Fulfilled Milestones

Number	Milestones	Delivery Time	Completion
1	*SAMPLE PREPARATION*		
	3 samples of supported catalysts (5g for each)- Giner	10/31/2013	95%*
	5 samples of NSTF based MEAs (2g for each) – 3M	10/31/2013	100%
	5 samples of iridium nanotube catalysts (1g for each)-NREL	10/31/2013	95%*
2	*Corrosion/oxidation resistance ≥ 1.8 V*	1/31/2014	100%
3	*Performance Metrics*		
	PGM < 0.5 mg/cm^2	7/31/2014	100%
	1.7 V@ 1A/cm^2 target	7/31/2014	100%
	> 100 h at 1.5 A/cm^2	7/31/2014	100%
4	*Durability*		
	< 20 mV drop after 1000 hours at 1.5A/cm^2	1/31/2015	100%
5	*Commercialization*		
	Delivering 100' of roll-to-roll produced catalyst	1/31/2015	100%

* Not 100% completion due to large volume catalyst production needed

Achievement 1: $Ir/W_xTi_{1-x}O_2$ Catalyst (Giner)



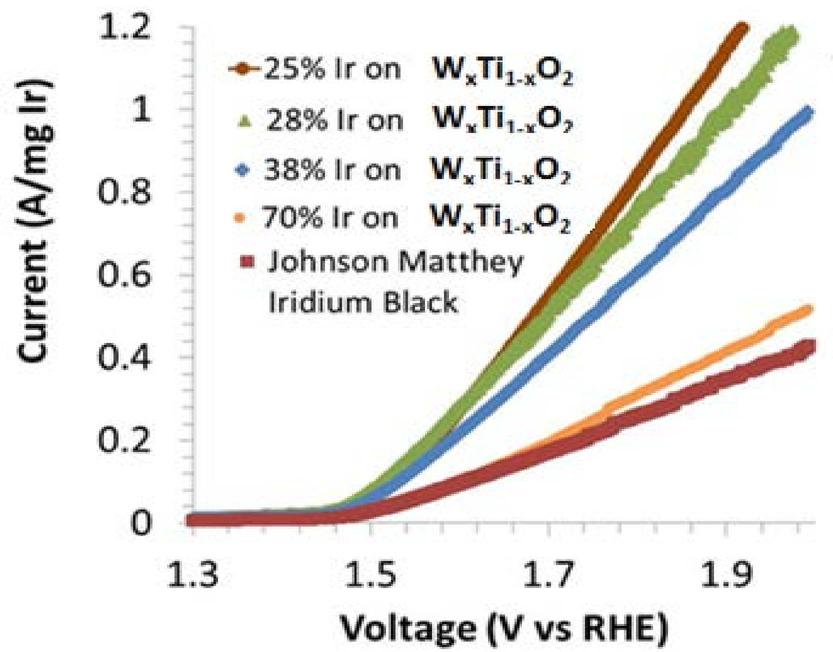


Images taken by Dr. Karren More at ORNL

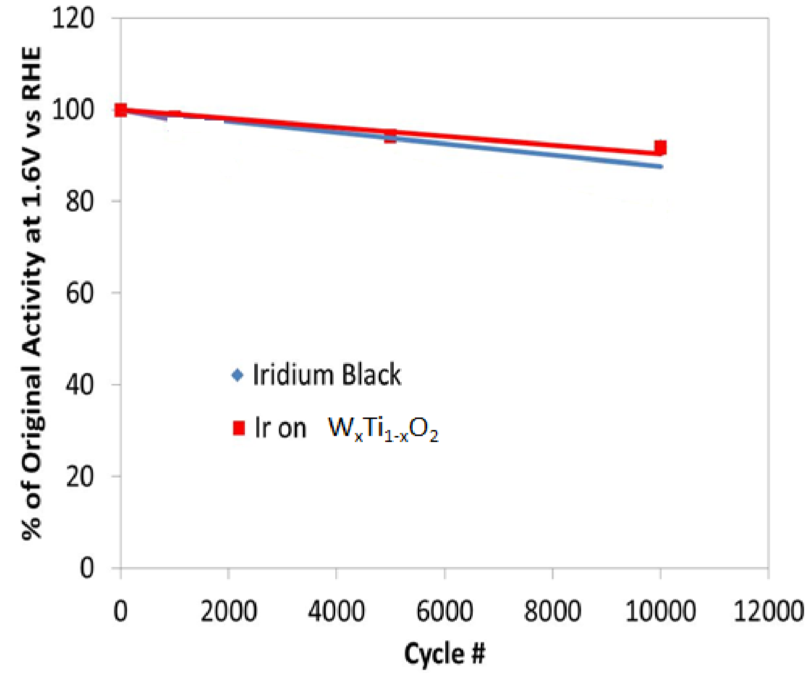
- Supports with high oxidation resistance needed as electrolyzers operate at high Voltage
- Ir NPs form a “chain-like” network of interconnected NPs on the surface of the $W_xTi_{1-x}O_2$

RDE Based Activity and Stability of Ir/ $W_xTi_{1-x}O_2$

Initial OER Activity



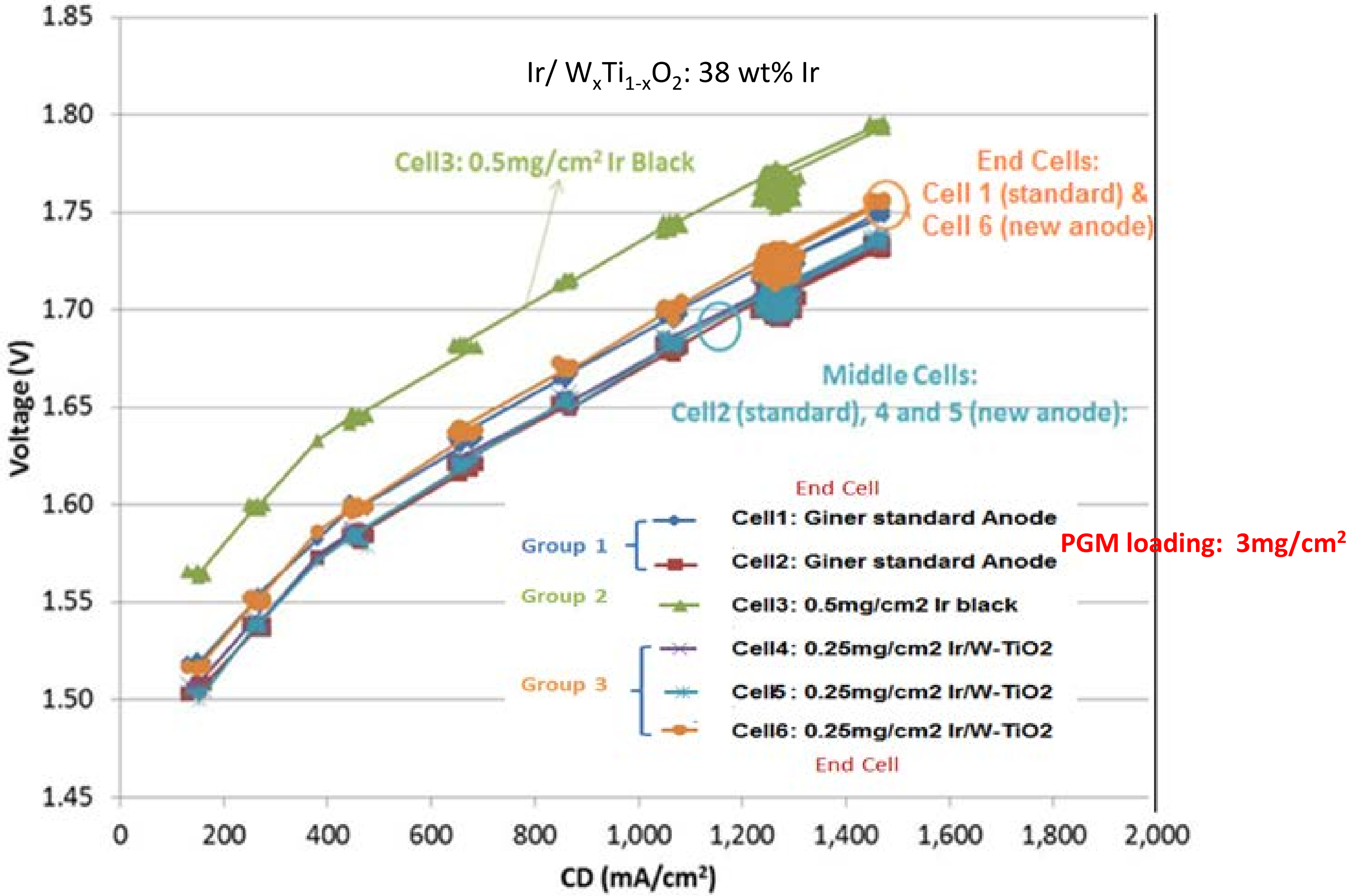
Voltage cycling from 1.4 to 1.8V



Scan rate: 50 mV/s; **RPM:** 1960 rpm; **Ir loading**:40-80 μg/cm^2; **Solution:** 0.5M H_2SO_4

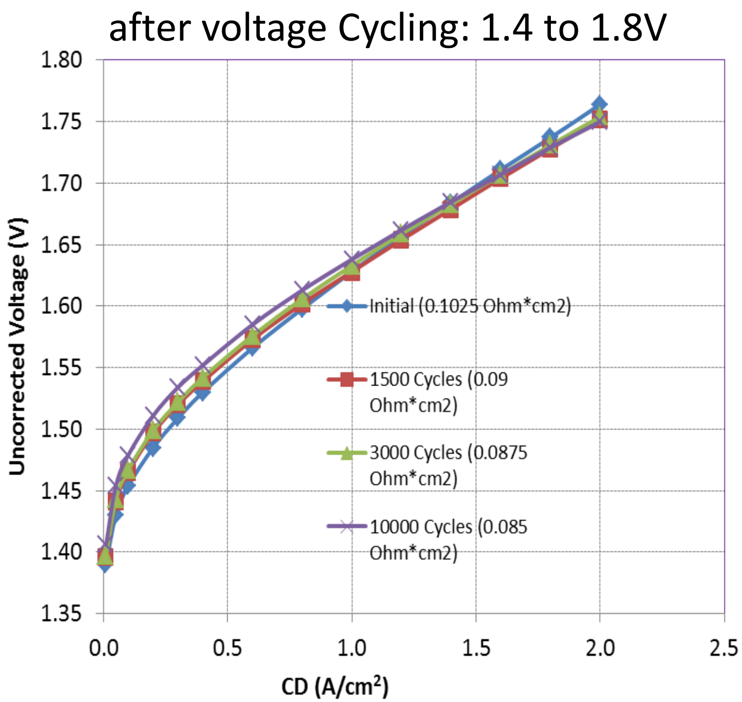
- Ir/ $W_xTi_{1-x}O_2$ achieves 3x higher activity than baseline Ir black (at 2.0V)
- Ir/ $W_xTi_{1-x}O_2$ also demonstrates excellent stability during voltage cycling
- Ir mass activity increases as Ir loading decreases

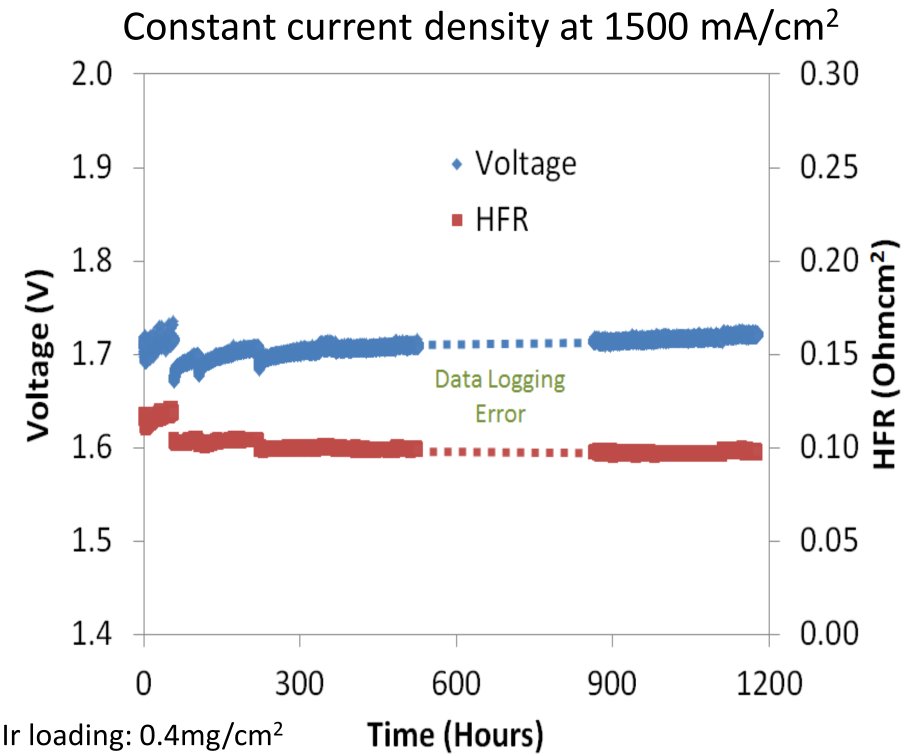
Stack MEA Performance Using Ir/ $W_xTi_{1-x}O_2$ Catalyst



- 0.25 mg/cm^2 Ir/ $W_xTi_{1-x}O_2$ demonstrates comparable performance to standard (2.5 mg/cm^2 PGM)-reduced PGM loading by 10x;
- 0.25 mg/cm^2 Ir/ $W_xTi_{1-x}O_2$ shows 65 mV lower voltage than 0.5 mg/cm^2 Ir black

Durability of Ir/ $W_xTi_{1-x}O_2$ Catalyst



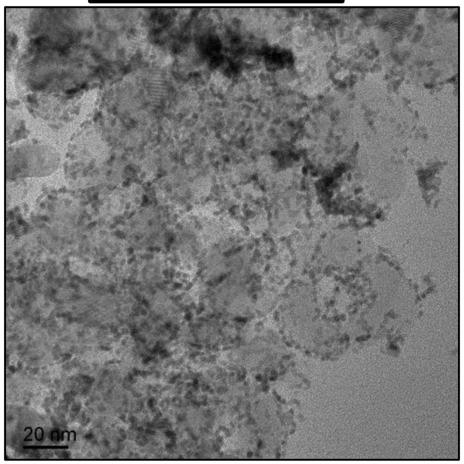


38 % Ir/ $W_xTi_{1-x}O_2$: Ir loading: 0.4mg/cm^2

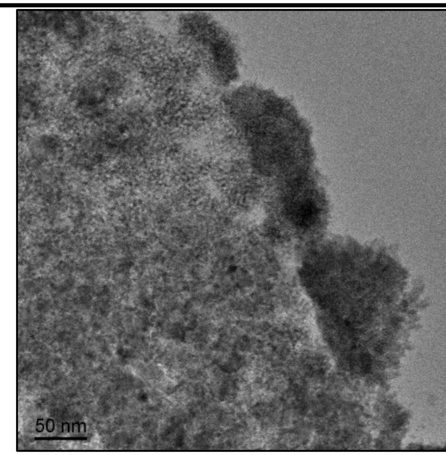
- Minimal voltage loss after cycling from 1.4 to 1.8V
- 1000 hours durability tested completed with only 20 mV performance decay
  - Passed Milestone 4

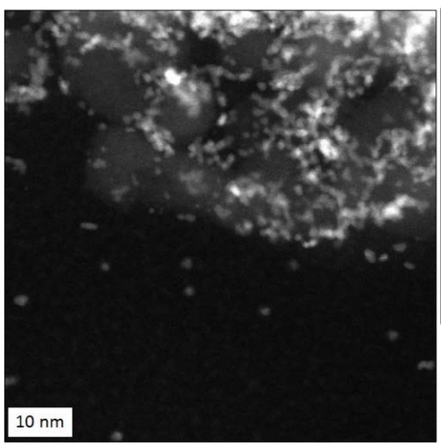
Fresh and Tested MEA Structure

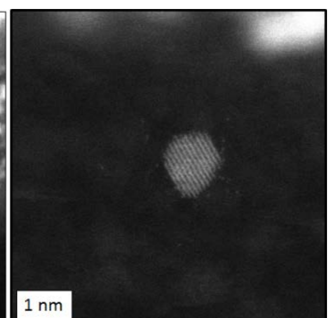
Fresh MEA

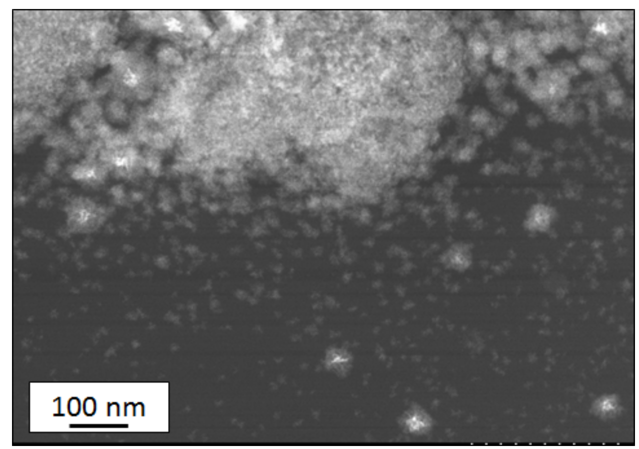


Test MEA (after 1000-h)





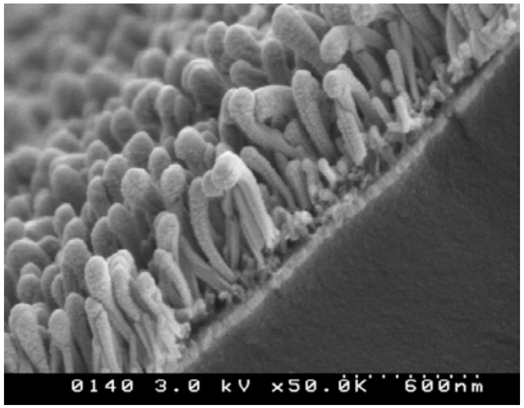


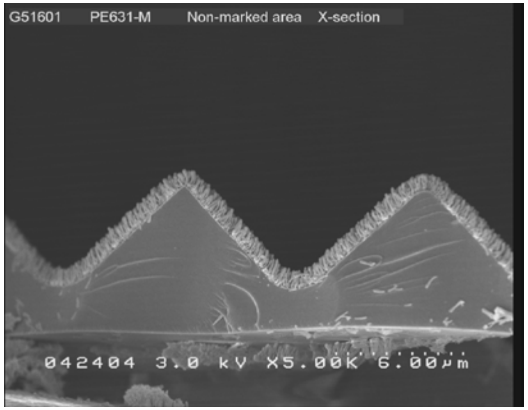


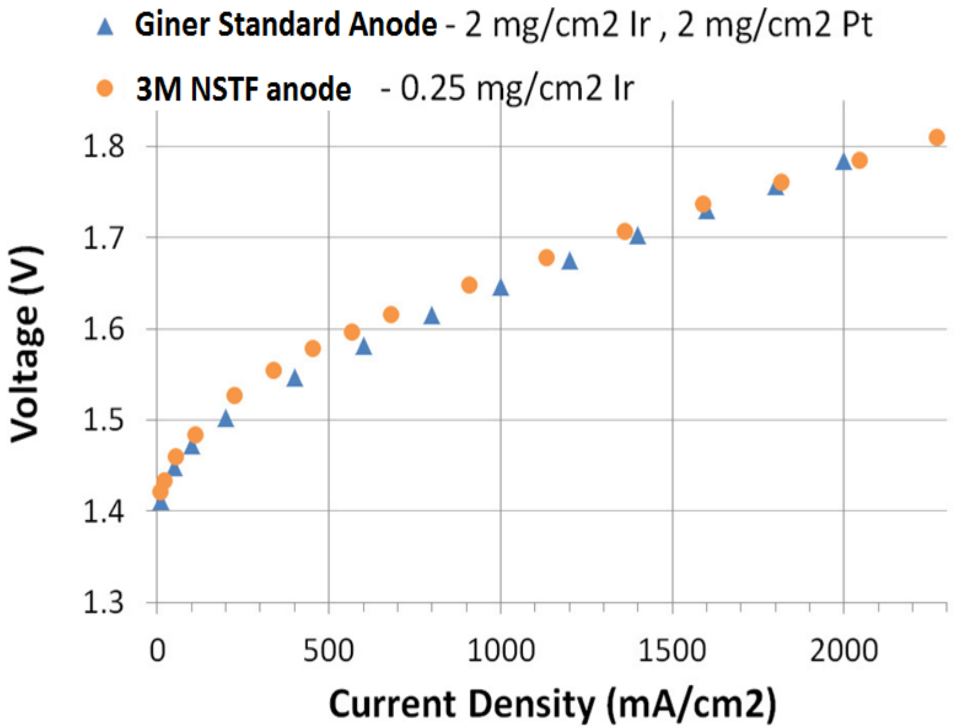
Images taken by Dr. Karren More at ORNL

- Some Ir NP precipitate in membrane after testing (to distance of ~2 μm)
- Ir NPs agglomeration occurs due to Ir dissolution and migration to surfaces

Achievement 2: Ir Coated Whiskers on Nano-Structured Substrate (3M)

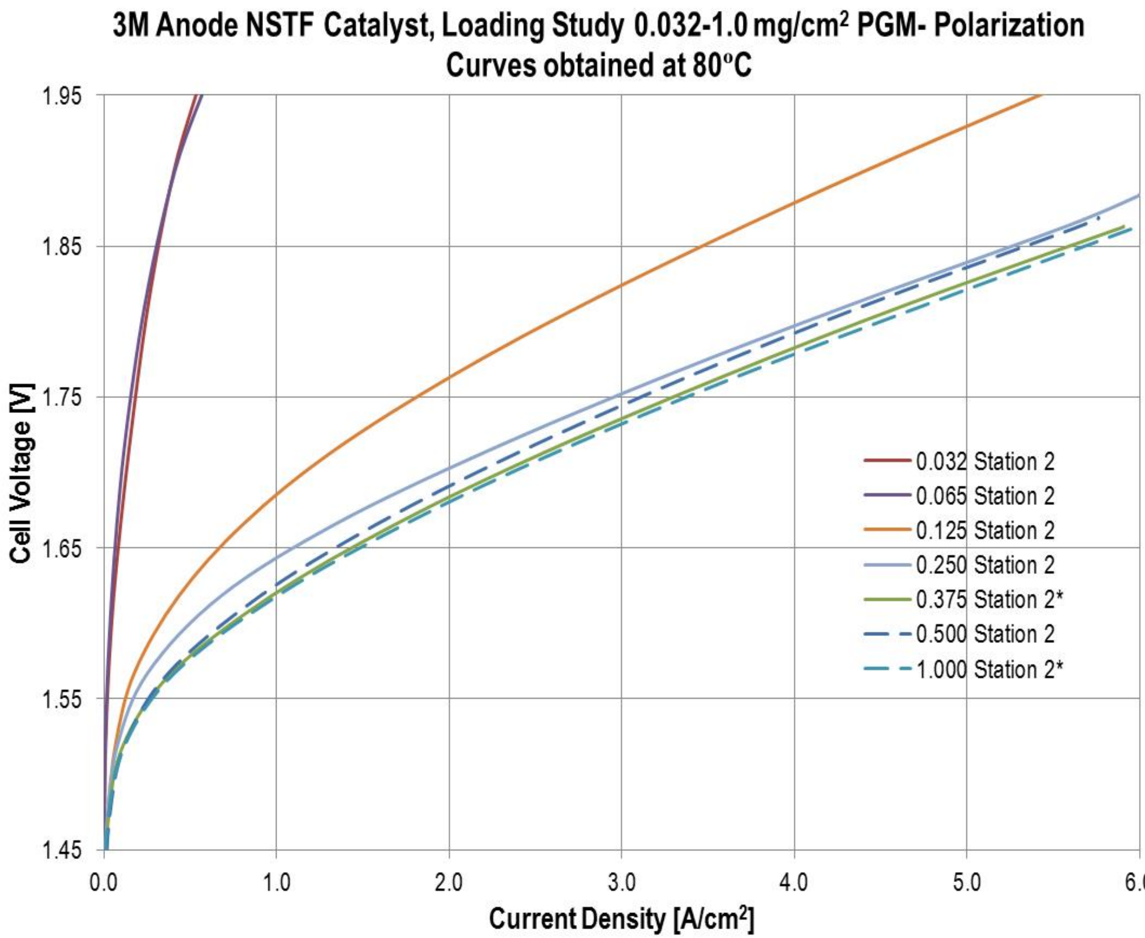






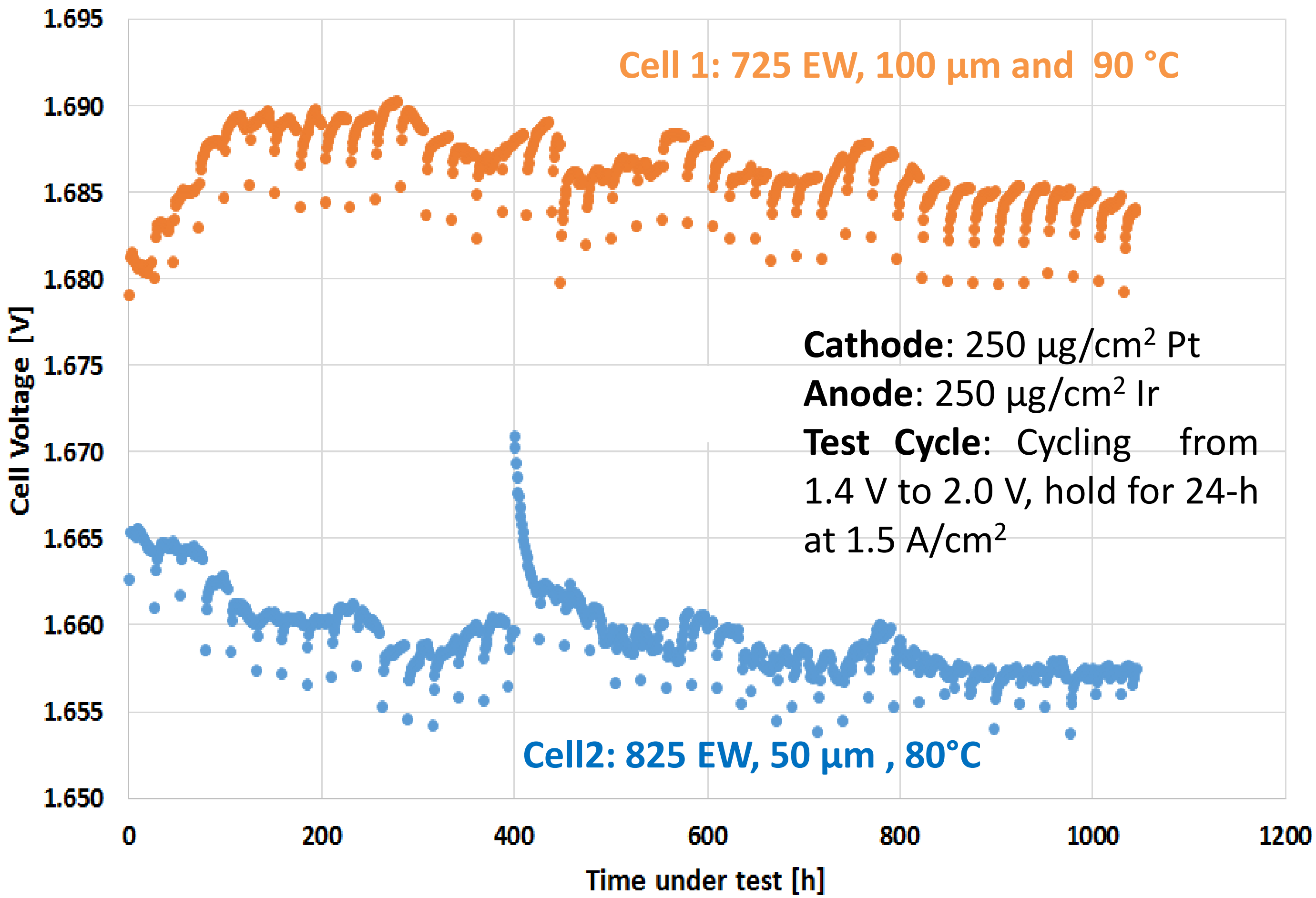
- ♦Ir-NSTF anode demonstrates comparable performance to standard anode but at 1/8 Ir loading and 1/16 PGM loading

Impact of Ir Loading on Performance of Ir-NSTF MEAs



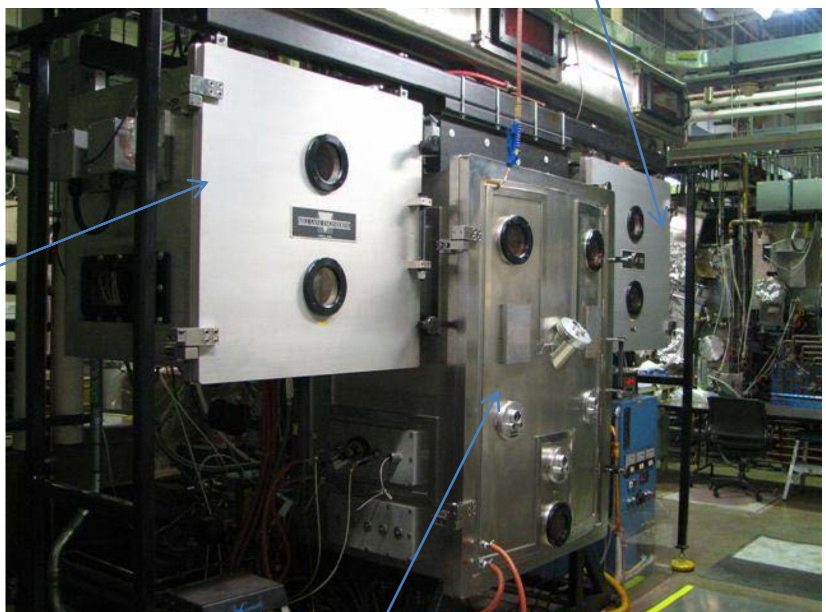
- Optimum catalyst loading from the performance point of view appears to be around 0.2-0.4 mg/cm^2 PGM.

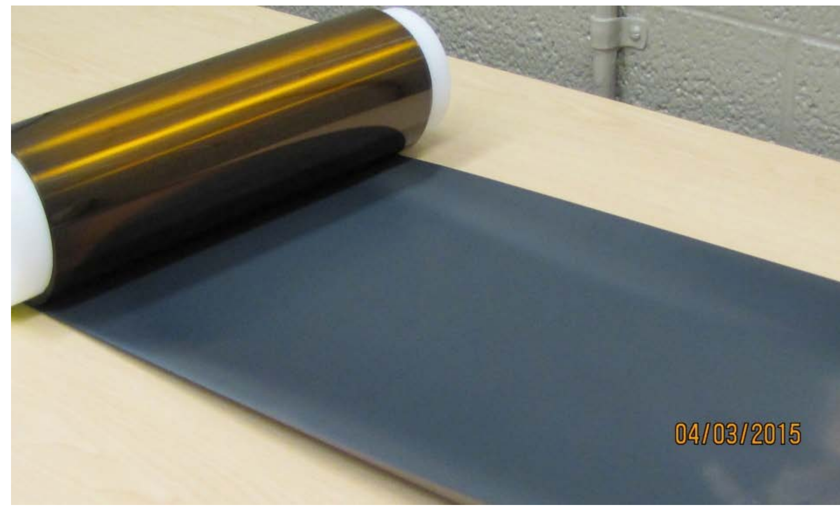
Durability of Ir-NSTF Catalyst



- 1000 hours durability completed nearly without performance decay
  - Passed Milestone 4
- Cycling from 1.4 V to 2.0V demonstrates the stability of Ir-NSTF catalyst

Roll-to-Roll Production of Ir-NSTF Catalysts



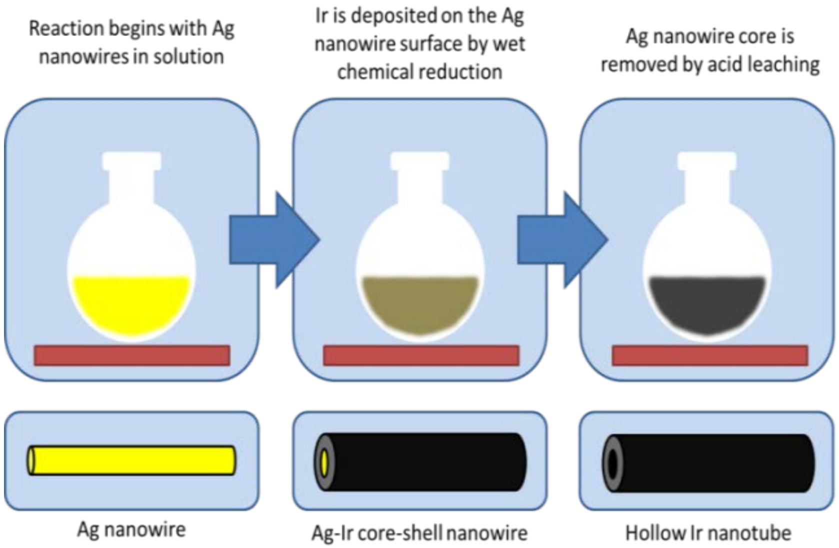


Iridium #3

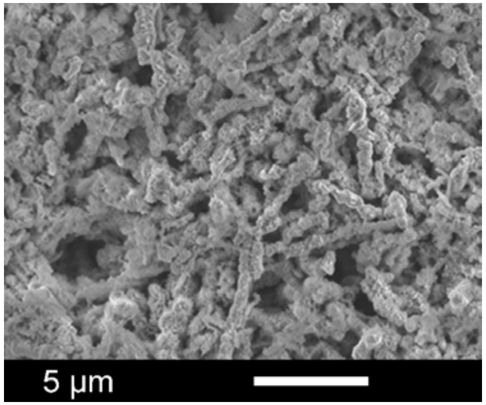
- Roll-to-roll production of Ir-NSTF has been successfully completed

Achievement 3: Ir/Metal Nanowires (NREL)

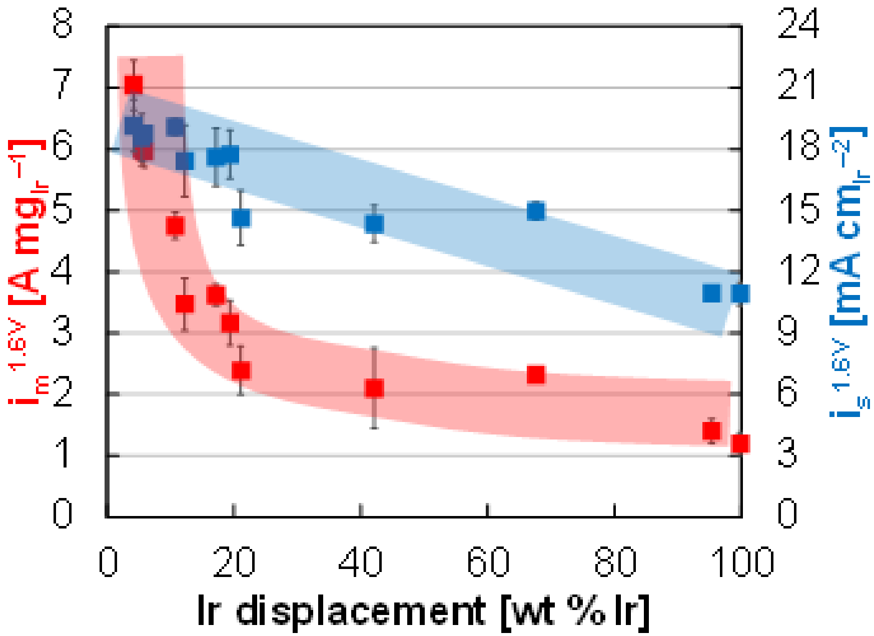
- Extended Continuous Nano-Structured Catalysts
- Partial Galvanic Displacement
  - "Thrifting" of the iridium layer
  - Various metal templates (Ag, Ni or Co)
- Ir Loading can be further controlled by acid leaching



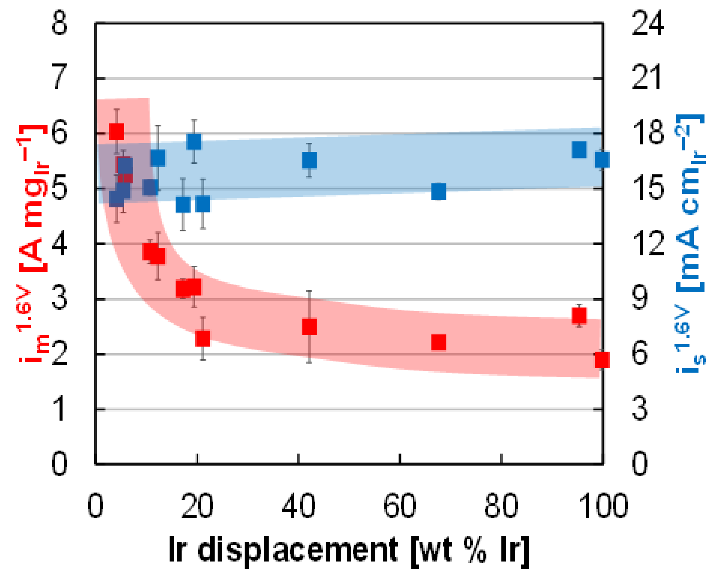
IrCo Nanowires



Ir/Co Nanowire Optimization



Acid Leached Samples

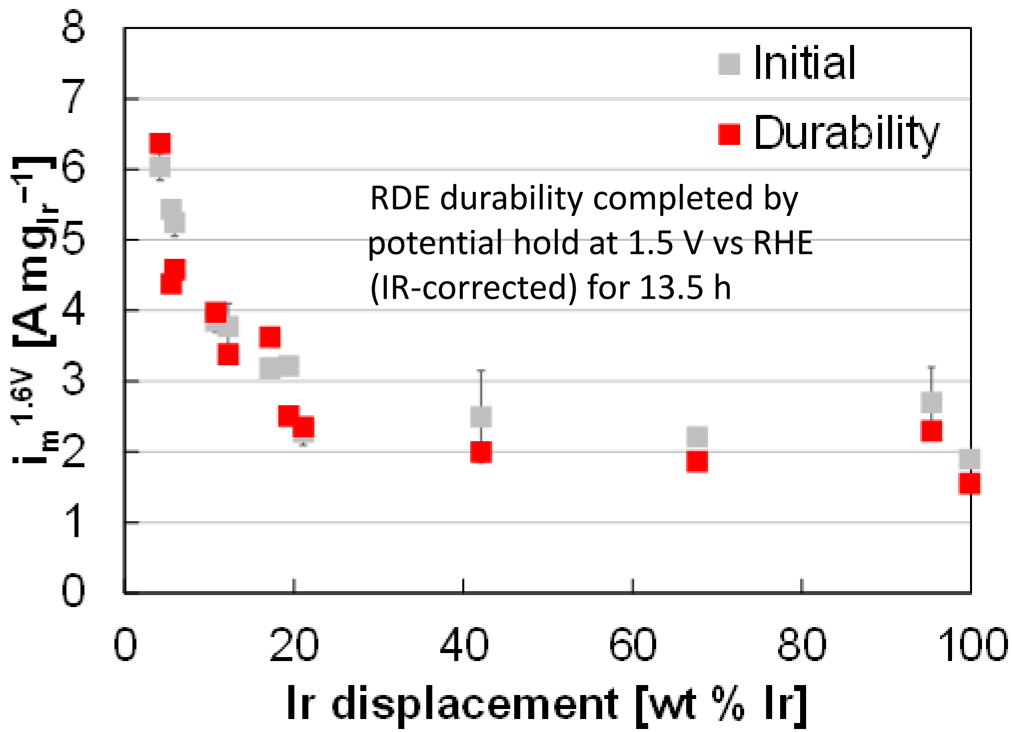


Acid leaching completed by exposure material (30 mg) to 3 M sulfuric acid (15 ml) for 16 h at room temperature.

- Increased compositions of IrCoNWs were investigated
- Trends for higher mass and specific activity at lower displacement levels
- Majority of Co leaches out

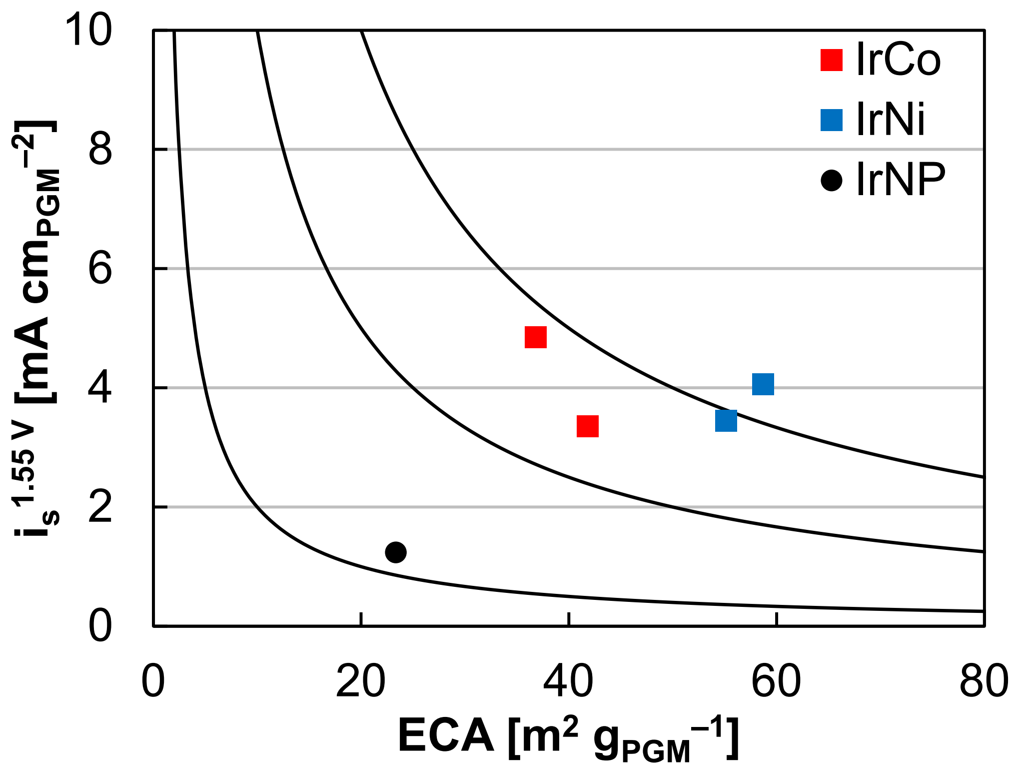
- Acid leached samples showed similar performance, but much better durability (next slide)

Ir/Co Nanowire Durability



- Almost no loss in mass activity for acid leached samples
- Greatly reduced Ir and Co dissolution rates when measured by ICP-MS.

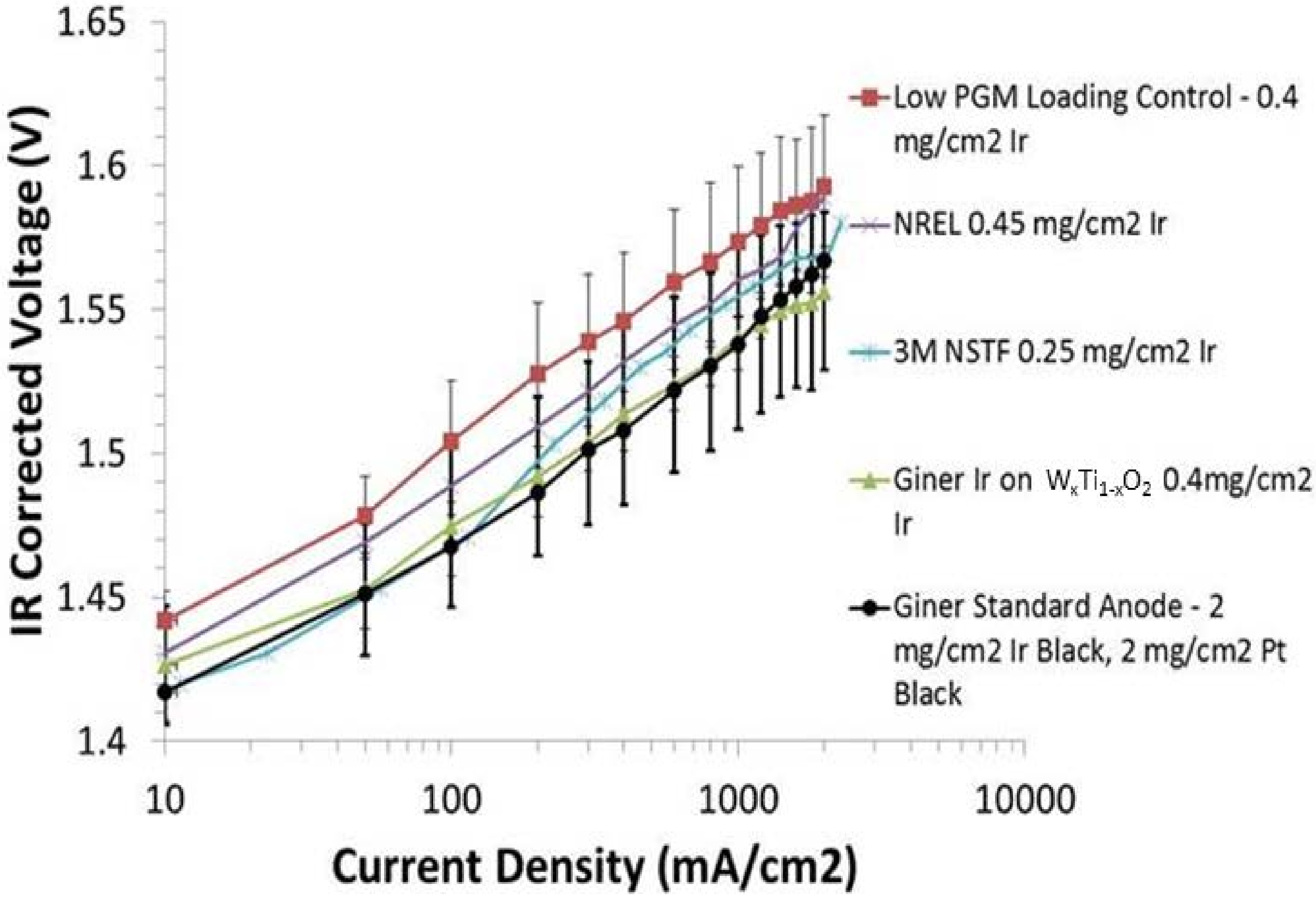
Ir/Co and Ir/Ni Nanowire Performance



Lines (black) of constant mass activity at 0.2, 1, and 2 A mg_{Ir}^{-1}

- Both IrCo and IrNi NWs show greatly increased activity (~10x) compared to iridium nanoparticles

MEA Performance of Three Catalysts



- All three categories of catalysts demonstrated better performance than low PGM loading control 0.4mg/cm^2 Ir black

Project Summary

- **Ir-based OER catalysts for PEM electrolysis have been successfully synthesized**
  - Giner: Ir/$W_xTi_{1-x}O_2$
  - 3M: Ir-NTSF
  - NREL: IrCo and IrNi nanowires (NWs)
- **Giner:** Ir/ $W_xTi_{1-x}O_2$ catalyst based MEA demonstrated excellent performance
  - A 6-cell electrolyzer stack test: The catalyst matched Giner baseline but reduced Ir loading by 10x
  - Single cell test: successfully passed 1000-h test with 20 mV voltage decay
  - Catalyst and MEA structures were obtained
- **3M: D**urability test and mass production of IrNSTF catalysts
  - Comparable to standard anode with 8x lower PGM loading
  - Two MEAs passed 1000-h test nearly with negligible performance loss
  - Roll-to- roll production of IrNSTF catalysts accomplished
- **NREL:** Activity and Durability of Ir-metal nanowires investigated
  - RDE data shows that both IrCo and IrNi NWs had 10x activity compared to Ir nanoparticles
  - Acid leaching significant improved the catalyst IrCo and IrNi NWs durability

Collaborations

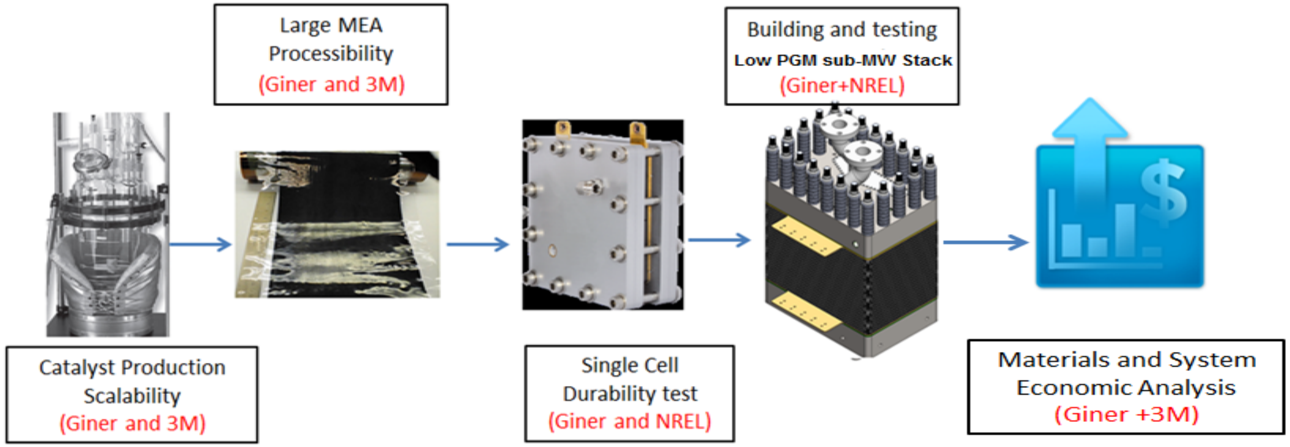
Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Brian Rasimick, Allison Stocks, and Michael Smith	Prime, oversees the project; broad screening of catalyst supports; electrolyzer hardware design and validation; electrolyzer cell tests, cost analysis; catalyst and MEA test protocol
National Renewable Energy Laboratory (NREL) Bryan Pivovar, Shaun Alia, K. C. Neyerlin	Sub; iridium/metal nanowires development, iridium surface area characterization; catalyst and MEA test protocol
3M Company (3M) Krzysztof Lewinski, Sean Luopa	Sub; IrNSTF based catalyst development, electrolyzer cell tests, short production, cost analysis
Oak Ridge National Laboratory (ORNL) Karren More	Collaborator: catalyst and MEA structure characterization
Univ. of Massachusetts at Lowell (UMass-Lowell) Zhiyong Gu and Gao Fan	Collaborator: catalyst composition and structure analysis

Great team with complementary expertise leads to a big success of project !

Future Research

- Test Ir/ $W_xTi_{1-x}O_2$ catalyst at high Ir loading (1-2 mg/cm^2) to study its effect on over-potential;
- Further improve the performance and durability of Ir/ $W_xTi_{1-x}O_2$ by varying Ir deposition approaches ;
- Test the MEA durability of three developed catalysts at more harsh conditions and extended hours;
- Select catalysts for Giner sub-MW electrolyzer stack construction

Phase 2B Project Work Plan



		Year 1						Year 2					
ID	Task Name	M2	M4	M6	M8	M10	M12	M14	M16	M18	M20	M22	M24
1	**Task 1: Scale up Selected Catalyst Production**												
2	Ir/W-TiO_2 synthesis scale-up												
3	IrNSTF synthesis scale-up												
4	**Task 2: Fabrication of Composite Electrolytes**												
5	Ir/W-TiO2 based MEA fabrication												
6	IrNSTF based MEA fabrication												
7	**Task 3: Extend Durability Tests of Selected Catalysts**												
8	AST via Voltage Cycling												
9	Electrolyzer Endurance Test												
10	**Task 4: Build low-PGM loading sub-MW Stack (Giner)**												
11	**Task 5: Evaluate and Demonstrate sub-MW Electrolyzer**												
12	**Task 6: Perform Catalyst and System Economics**												
	Program Management												

Acknowledgments

- Financial support from DOE SBIR/STTR program under the contract # DE-SC0007471
- DOE Fuel Cell Technologies Office
  - Dr. David Peterson
- Giner Personnel
  Brian Rasimick, Michael Smith, 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
- UMass-Lowell: Drs. Zhiyong Gu and Gao Fan

Answers to Reviewers' Comments

- There was a lack of focus on the best performing catalyst. Working with Ir puts the project at a cost disadvantage

  Answer: *Two metals, Ir and Ru, exhibit high OER activity for acid-based water electrolysis; but Ru is very unstable. Therefore, Ir is the most appropriate OER catalyst for PEM water electrolysis in terms of activity and stability. Our efforts have reduced the Ir loading by a factor of 10 thus significantly lowering the capital cost associated with Ir usage.*

- The researchers need to better understand the catalyst support interaction. Longer-term testing is needed, as well as cycle testing. The cycle testing is particularly important because the electrolyzer will be turned on and off repeatedly. They need to focus more on increasing the catalyst activity.

  Answer: *Both long-time test (1000 hours) and accelerated tests have been applied to study the durability of the developed catalysts. High resolution TEM images have been obtained with the help of Dr. Karren More at ORNL to understand support interaction.*

- The RDE measurement should also be extended to NSTF catalysts if possible. TiO2-supported Ir catalysts with a higher Ir-loading (>60 wt.%) should be tested.

  Answer: *TiO2-supported Ir catalysts with a higher Ir-loading (>60 wt.%) has been synthesized . RDE of NSTF catalyst ha s not been performed due to some experimental restriction.*

- Significant progress was made during the past year. However, the different types of catalysts should be compared on the same basis. one of the other speakers indicated that NSTF had durability issues. Fabrication difficulties and costs were not addressed. If

  Answer: *On Slide 19, all the three categories of catalysts are compared in one figure under similar electrolyzer operating conditions. NSTF demonstrated excellent durability based on 1000-hour tests.*

Publications/Reports

- **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.
- **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 2014
- **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, August 2014.
- **Xu**, H., "Novel Oxygen Evolution Catalysts for Proton Exchange Membrane Water Electrolysis", to be presented in in 224th meeting of ECS, Abstract #1239, Cancun, Mexico, October 2014