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

Hui Xu (PI)
Giner Inc.
Newton, MA

June 18, 2014

Project ID#: PD103

Project Overview

Timeline

- Project Start Date: 4/24/2013
  Project End Date: 4/23/2015
- Percent Complete: 55%

Budget

- Total Funding Spent: $337,130*
- Total Project Value: $999,983
- Cost Share Percentage: 0% (SBIR)

* as of 3/31/14

Partners

- NREL: Dr. Bryan Pivovar (Co-PI)
- 3M: Dr. Krzysztof Lewinski(Co-PI)

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]

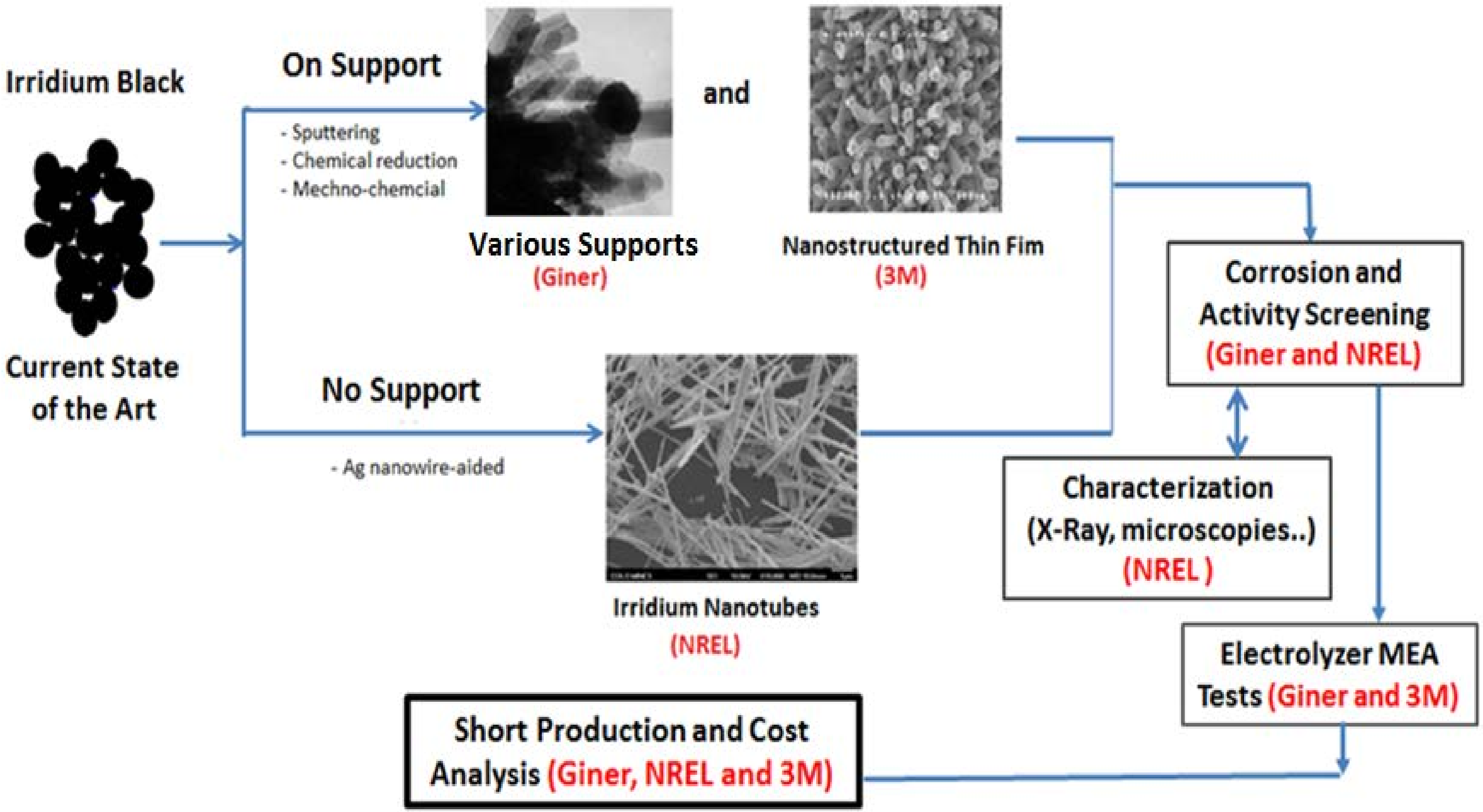
Characteristics		Units	2015	2020	Giner Status (2013)
Hydrogen Levelized Cost[2]		$/kg-$H_2$	3.90	<2.30	3.64[3] (5.11)[4]
Electrolyzer Cap. Cost		$/kg-$H_2$	0.50	0.50	1.30 (0.74)[5]
Efficiency	System	%LHV (kWh/kg)	72 (46)	75 (44)	65 (51)
Efficiency	Stack	%LHV (kWh/kg)	76 (44)	77 (43)	74 (45)

[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

Approaches


Irridium Black
Current State of the Art
On Support
- Sputtering
- Chemical reduction
- Mechno-chemcial
and
Various Supports
(Giner)
Nanostructured Thin Fim
(3M)
No Support
- Ag nanowire-aided
Irridium Nanotubes
(NREL)
Corrosion and Activity Screening
(Giner and NREL)
Characterization
(X-Ray, microscopies..)
(NREL)
Electrolyzer MEA Tests (Giner and 3M)
Short Production and Cost Analysis (Giner, NREL and 3M)

Milestones

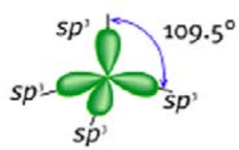
Number	Milestones	Delivery Time	Completion
1	*SAMPLE PREPARATION*		
	3 samples of supported catalysts (5g for each)- Giner	10/31/2013	95%*
	5 samples of NSTF based MEAs (2g for each) – 3M	10/31/2013	100%
	5 samples of iridium nanotube catalysts (1g for each)-NREL	10/31/2013	95%*
2	*Corrosion/oxidation 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	Ongoing
5	*Commercialization*		
	Delivering 100' of roll-to-roll produced catalyst	1/31/2015	Not started yet

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

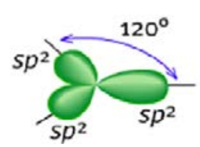
Achievement 1: Various Catalyst Supports (Giner)

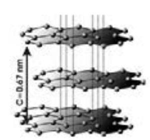
Material	Conductivity	Electrochemical Stability
Titanium Carbide	**High**	Poor
ITO (90% In_2O_3: 10% SnO_2)	**High**	Poor
Titanium Nitride	**Medium**	Poor
W-doped TiO_2 ($Ti_{0.9}W_{0.1}O_2$)	**Medium**	**Good**
TiO_2 Nanowire	Low	**Good**
Graphitic-Carbon Nitride	Low	Poor
Beta (β)-Carbon Nitride	Low	Poor

Sp^3 hybrid orbitals



Sp^2 hybrid orbitals





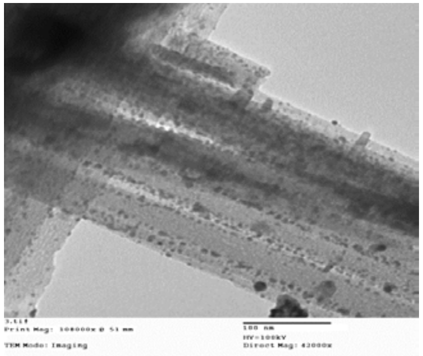
http://www.physik.fu-berlin.de/einrichtungen/ag/ag-reich/lehre/Archiv/ss2011/docs/Gina_Peschel-Handout.pdf

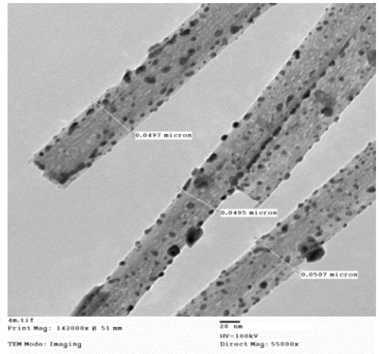
Conductivity: high (>0.1 S/cm); medium (0.001-0.1 S/cm); low: <0.001 S/cm
Stability: Voltage cycling performed between 1.2 to 1.8V

- Original Target: β-carbon nitride, but low conductivity and instability
- Good supports for oxygen reduction reaction (ORR) catalysts not necessarily applicable for OER catalysts due to high voltage for electrolysis operations
- Doping TiO_2 with other metals (W, or Ta) may gain good conductivity and stability

Iridium (Ir) on Various Supports

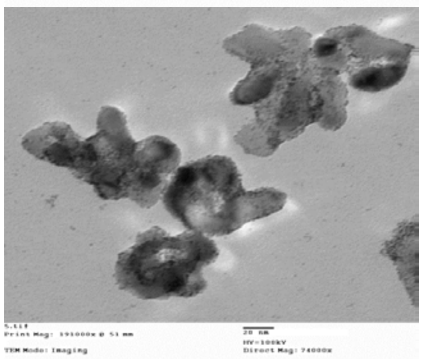
2-3 nm

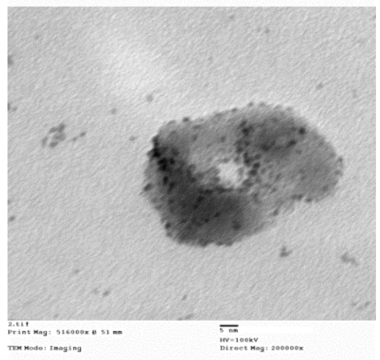




Ir/TiO_2 Nanowires (Ir: 48 w.t.%)

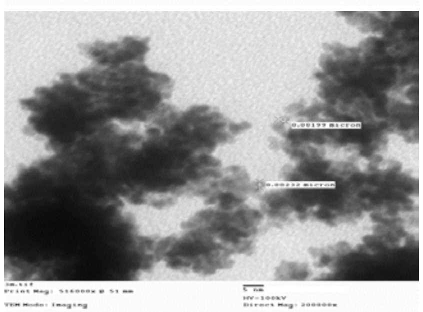
2-3 nm

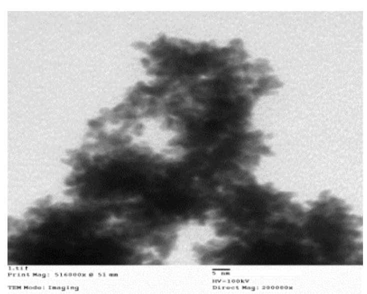




Ir /W-doped TiO_2 nanoparticles (Ir: 38 w.t.%)

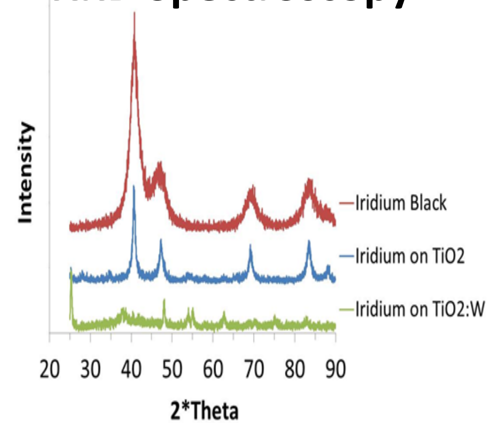
30 nm





Ir Black from JM (Ir: 99 w.t.%)

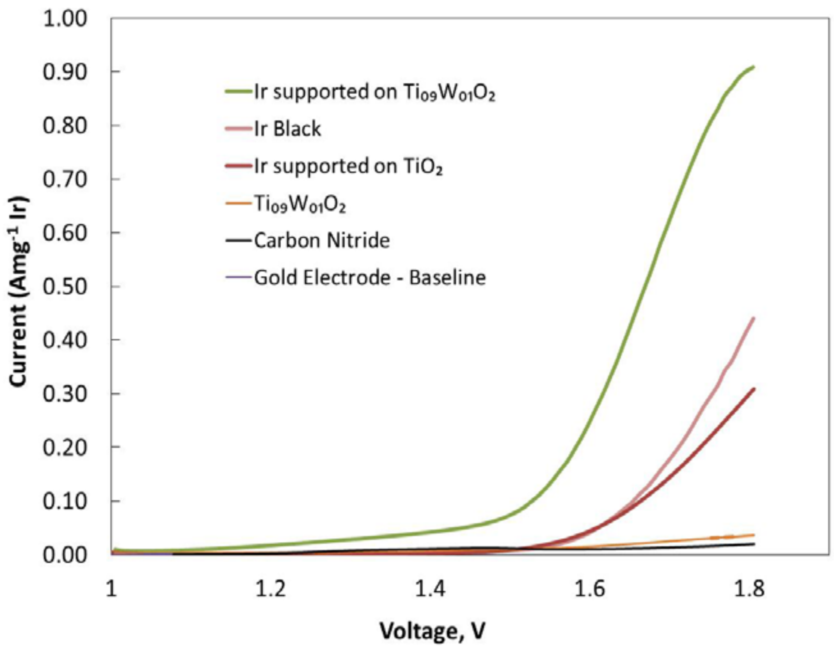
XRD Spectroscopy



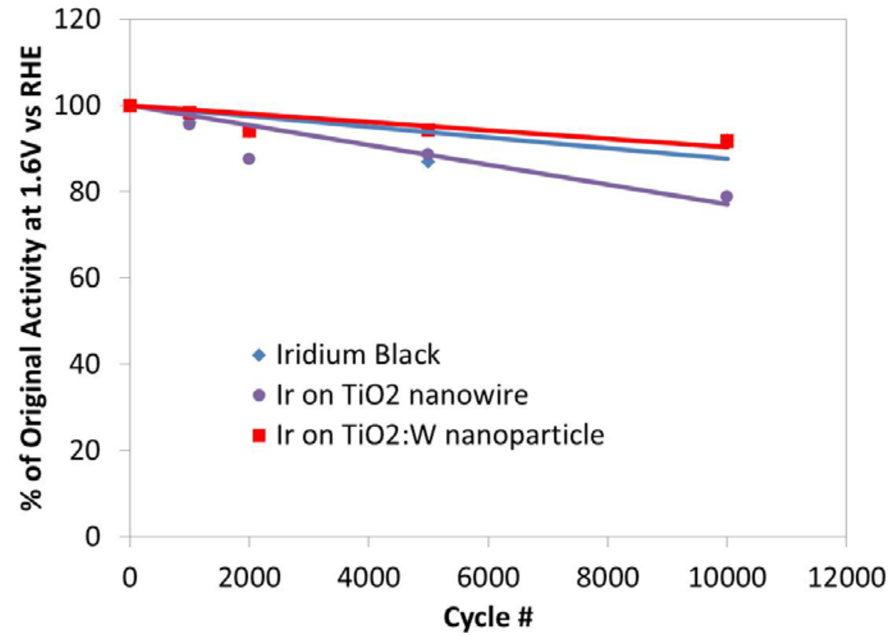
Nano-sized Ir on various supports have been synthesized via chemical deposition

Catalyst OER Activity and Stability from RDE

Initial OER Activity



Voltage cycling from 1.4 to 1.8V

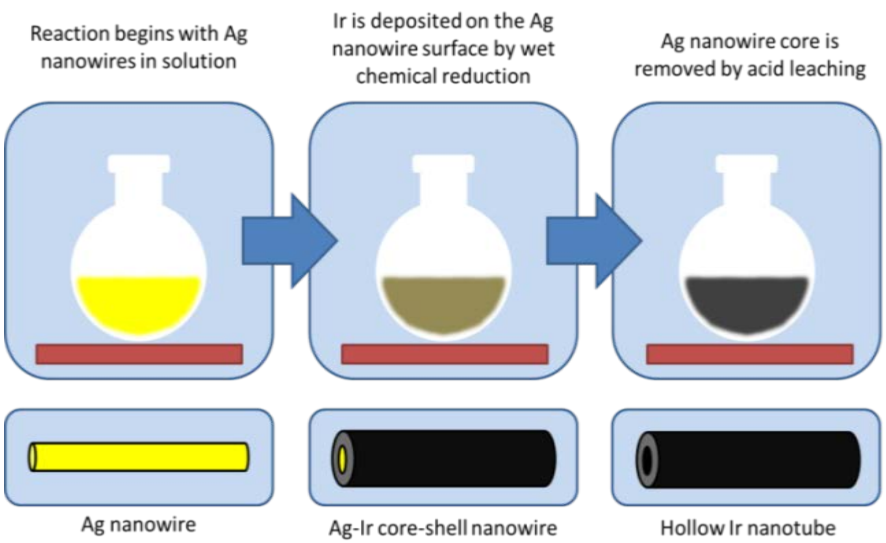


Scan rate: 50 mV/s; **RPM:** 1960 rpm; **Ir loading**:40-80 $\mu g/cm^2$; **Solution:** 0.5M H_2SO_4

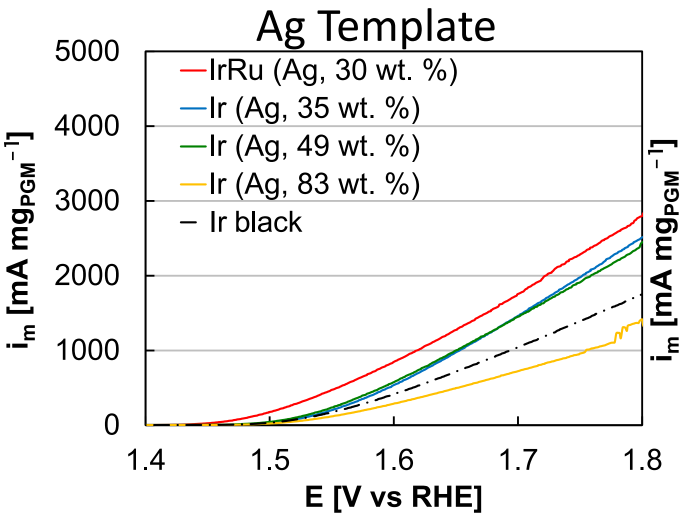
- $Ir/Ti_{0.9}W_{0.1}O_2$ (TiO_2: W) two times higher activity than baseline Ir black (at 1.8V)
- $Ir/Ti_{0.9}W_{0.1}O_2$ also demonstrates good stability during voltage cycling

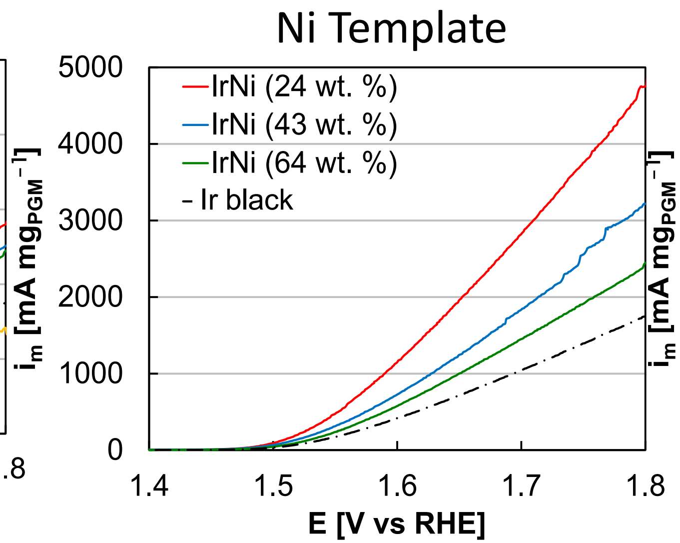
Achievement 2: Ir/Metal Nanowires (NREL)

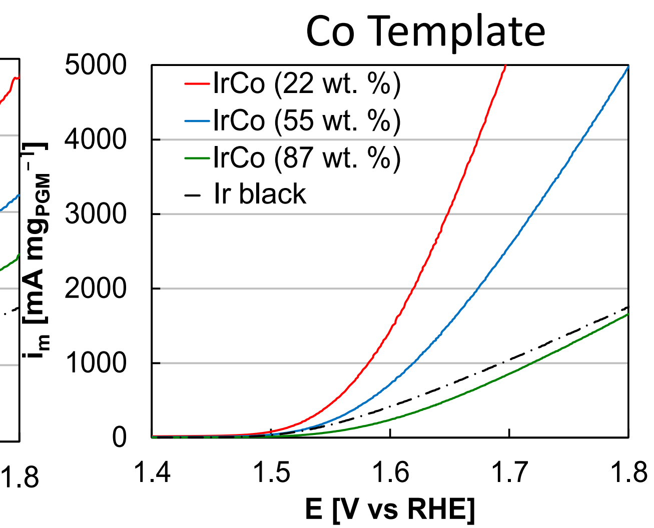
- Extended Continuous Nano-Structured Catalysts
- Partial Galvanic Displacement
  - "Thrifting" of the iridium layer
  - Various metal templates (Ag, Ni or Co)
- Ir Loading can be further controlled by acid leaching

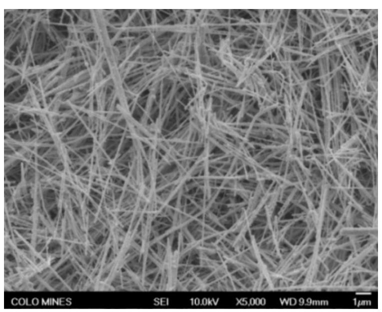


Ir/Metal Nanowires Based on Various Templates

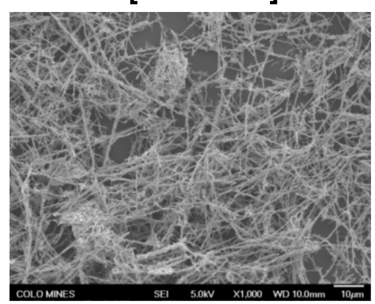




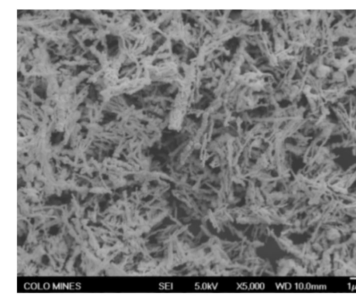




Ir/Ag (35 wt.%)



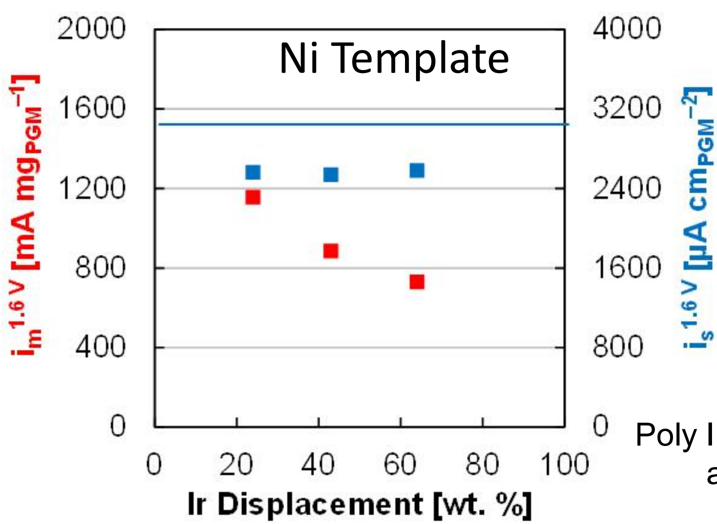
Ir/Ni (24 wt.%)



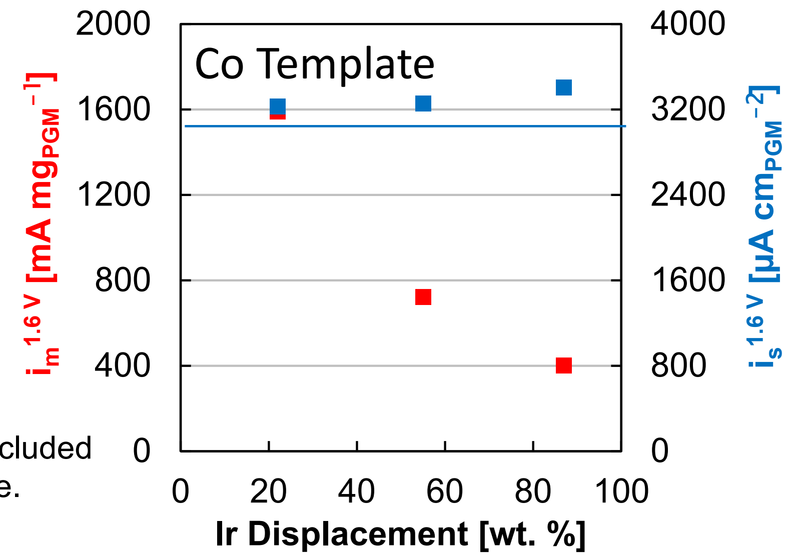
Ir/Co (22 wt.%)

- Ir/Co nanowires demonstrates highest activity
- Addition of Ru dramatically improves activity at OER onset

Mass and Specific OER activities of Ir/Metal NWs



Poly Ir specific activity included as the solid blue line.

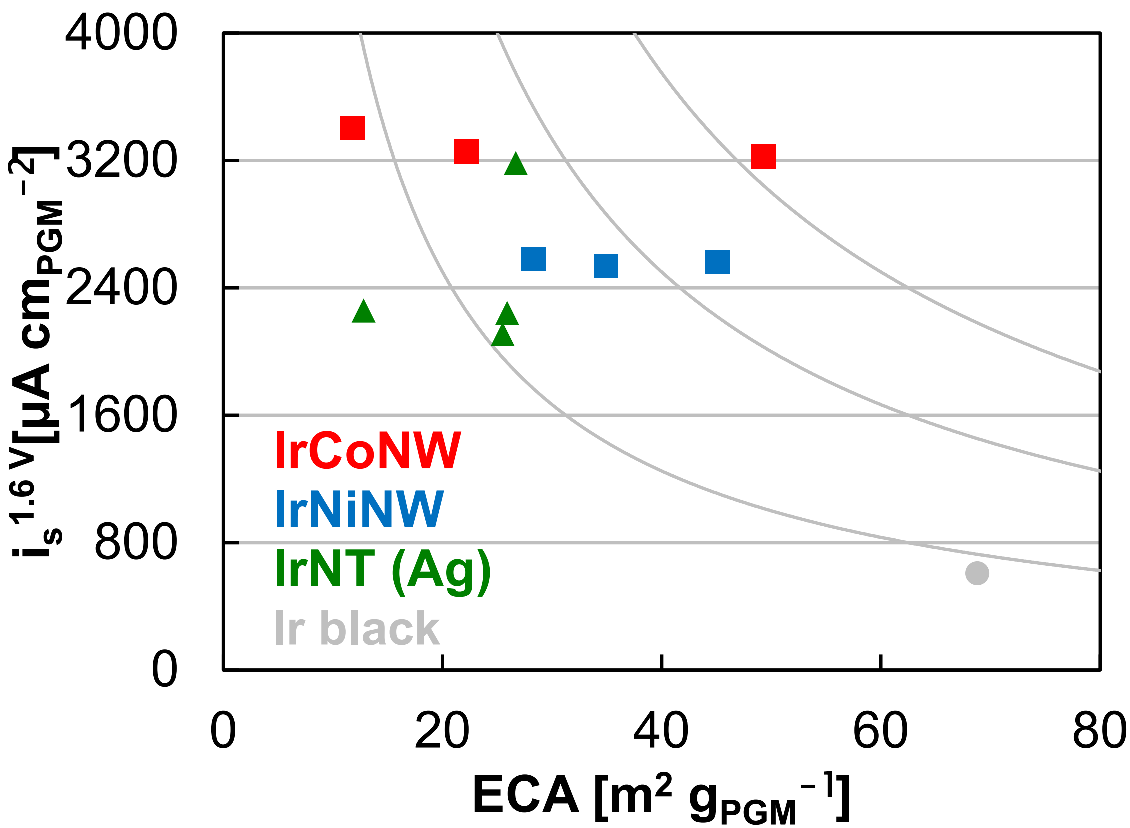


ECAs and OER activities (at 1.6 V vs. RHE) of Ir black and Poly Ir.

	ECA $[m^2\,g_{Ir}^{-1}]$	$i_m^{1.6\,V}$ $[mA\,mg_{Ir}^{-1}]$	$i_s^{1.6V}$ $[\mu g\,cm_{Ir}^{-2}]$
Ir black	68.8	417.9	607.4
Poly Ir	–	–	3021.3

- Specific activity of Ir/Co and Ir/Ni NTs essentially independent of displacement level
- Mass activity changes reflective of changes in ECAs (measured by Hg underpotential deposition)

Specific OER Activity Vs. OER Activities

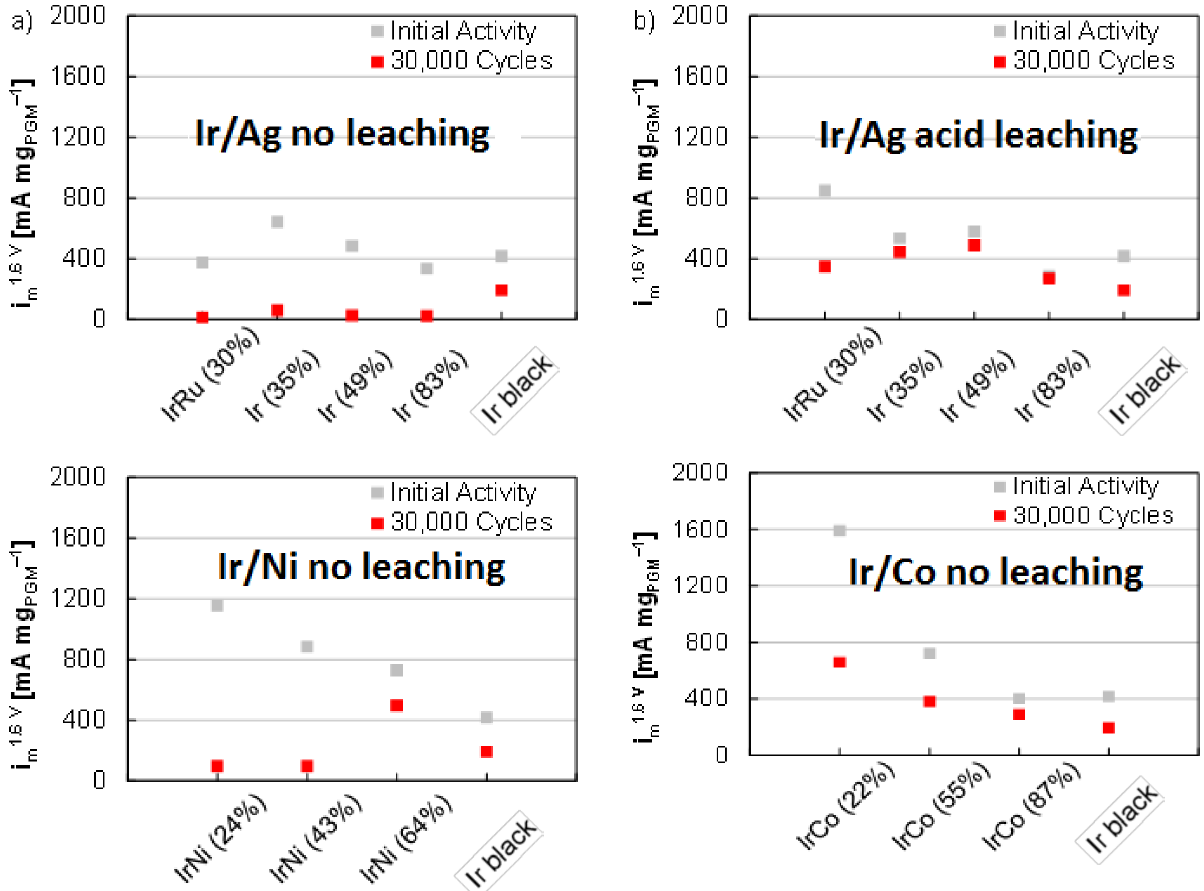


Contour lines are of constant mass OER activity (500, 1000, 1500 mA mg_{PGM}^{-1}).

- Ir/Co best activity compared to Ir black
- 3.8 times specificity greater than Ir black
- 3 times mass activity greater than Ir black

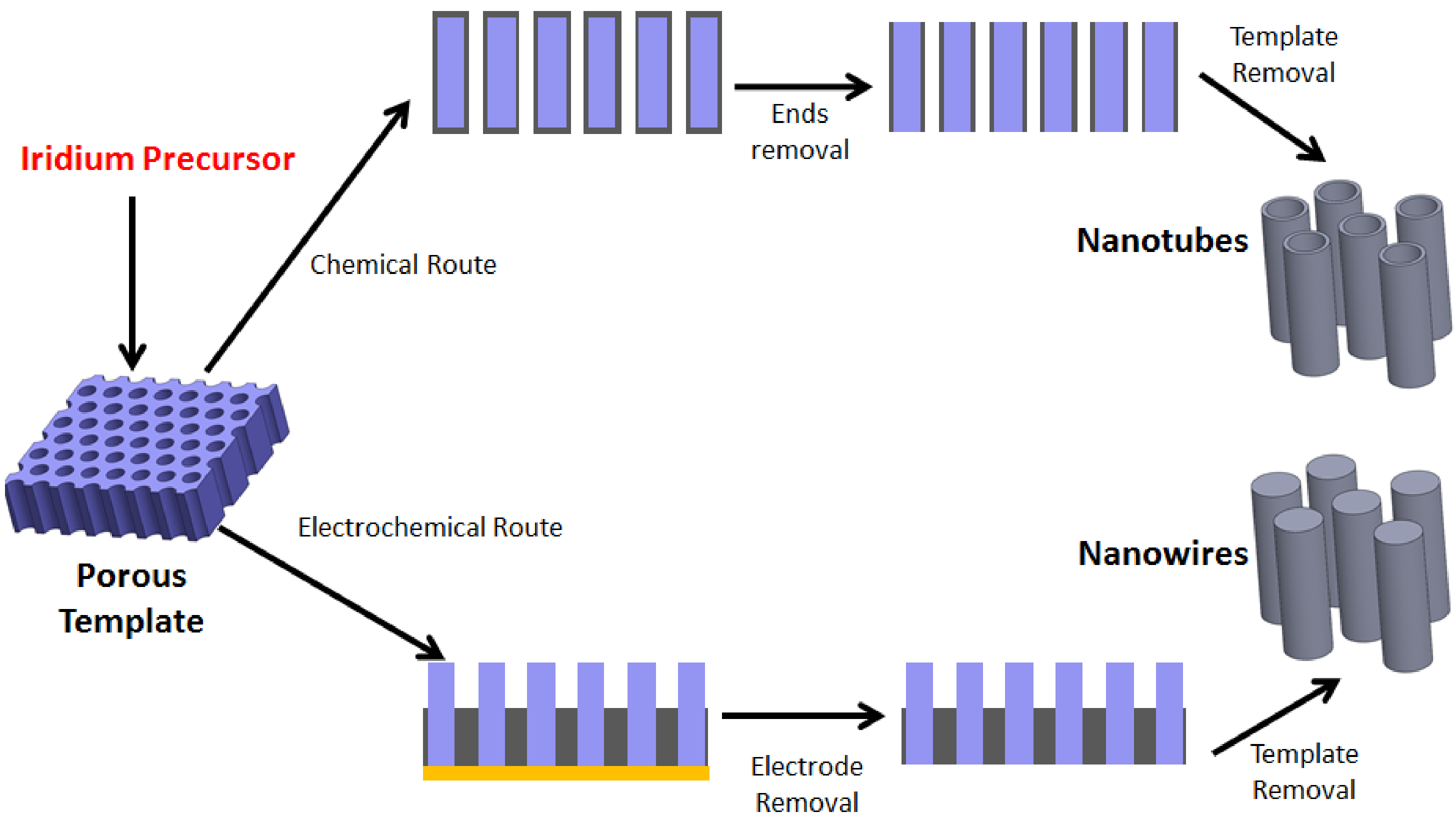
GINER NREL NATIONAL RENEWABLE ENERGY LABORATORY 3M

Ir/Metal Stability after Voltage Cycling



- Voltage cycling from 1.4 V to 1.8V 30,000 cycles, 100mV/sec.
- The lower Ir loading, the higher initial activity, the faster activity decay
- Acid leaching stabilizes the catalyst activity

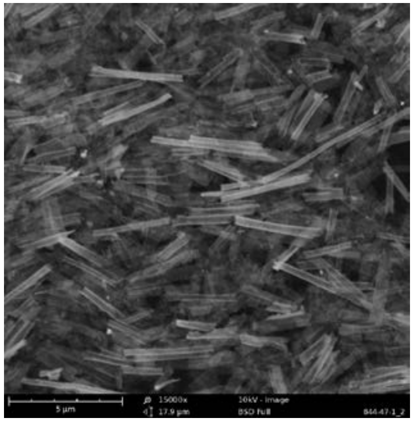
Achievement 3: IrNTs/IrNWs from Template (Giner)

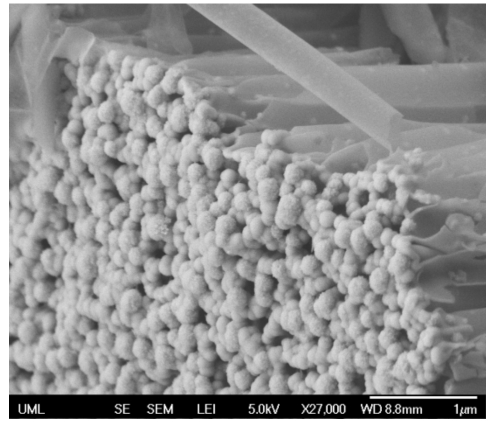


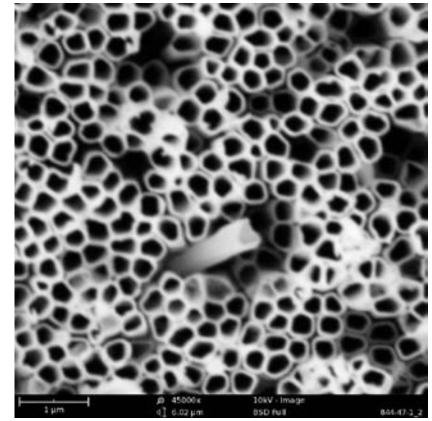
- Template can be alumina or polycarbonate
- Template is removed by sodium hydrogen oxide solution
- Sintering after template removal is performed to modify structure and property

SEM and TEM of IrNTs

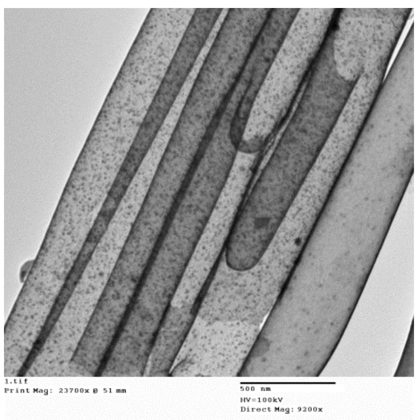
SEM

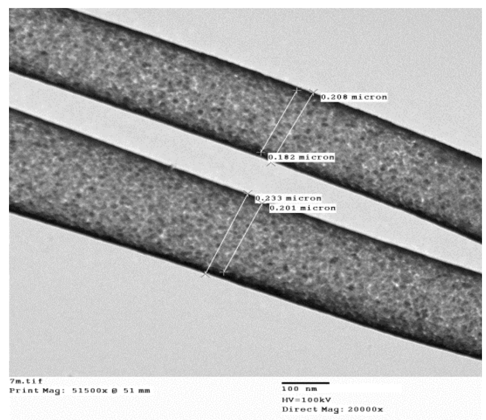


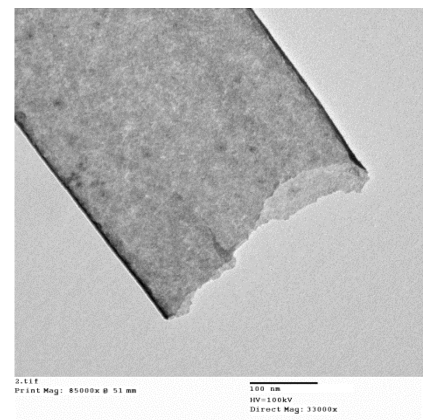




TEM

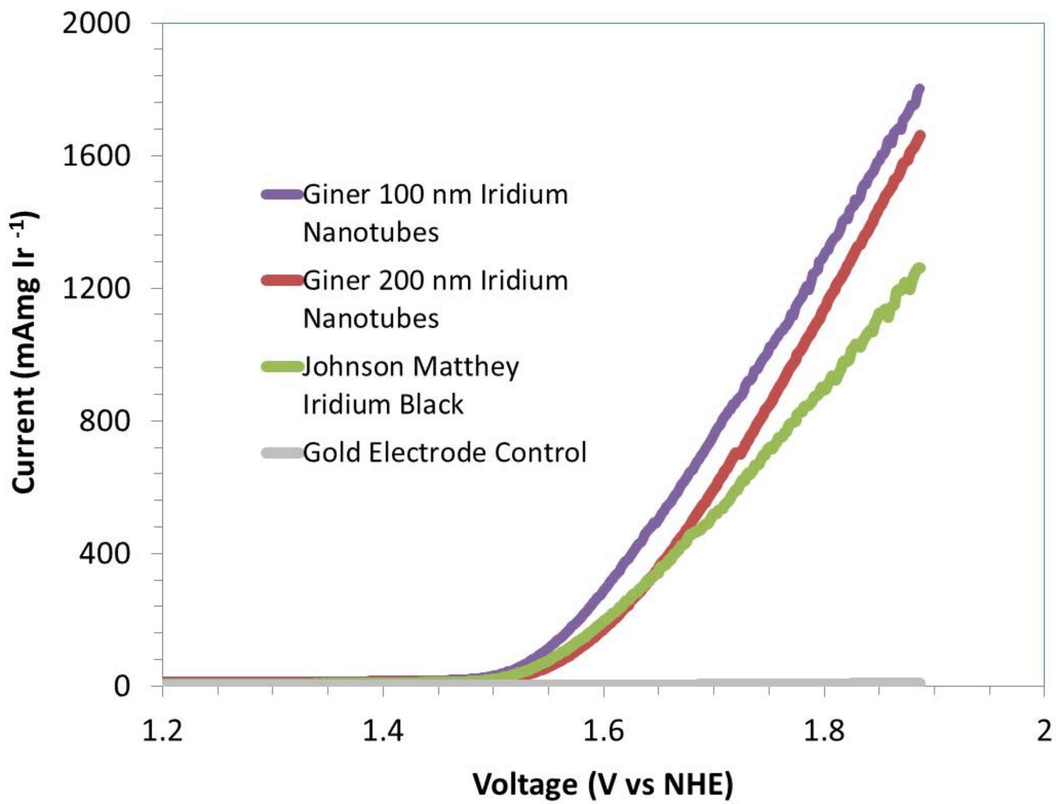






- IrNTs diameter can be 200, 100, 50 or 20nm
  - dependent on alumina pore size
- IrNTs length from 5 to 20 μm

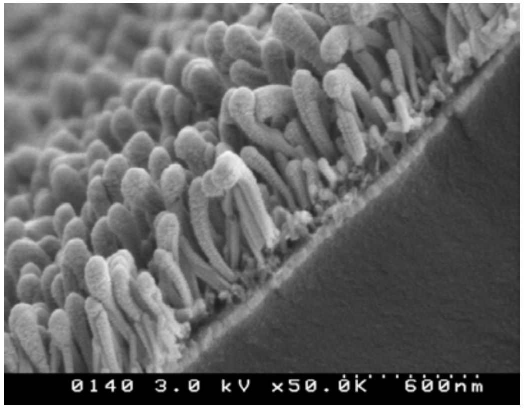
IrNTs OER Activity from RDE

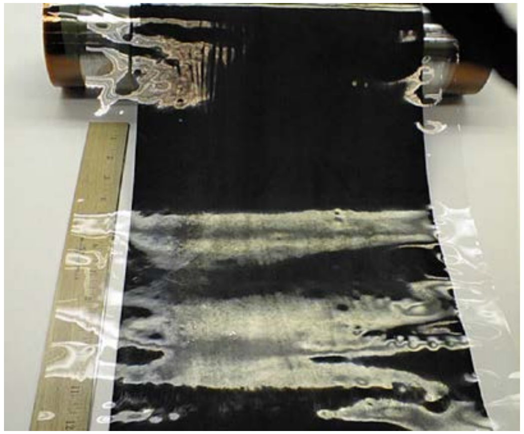


Scan rate: 50 mV/s:
RPM: 1960 rpm
Ir loading:40-80 μg/cm^2
Solution: 0.5M H_2SO_4

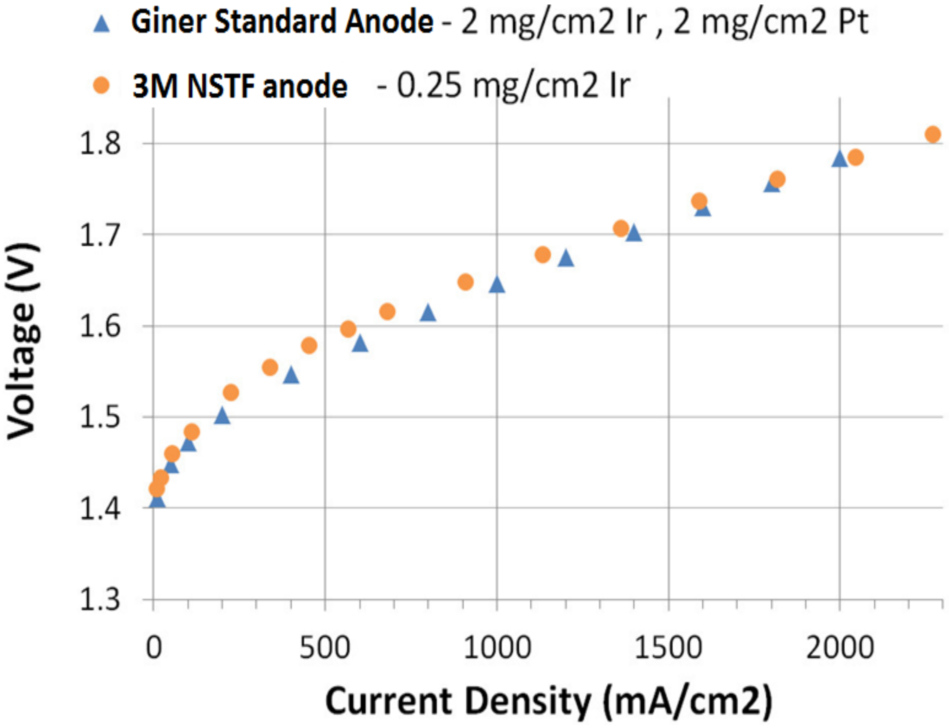
- Ir NTs exhibits 50% higher OER activity than Ir black
- Activity may further improve by altering process conditions (temp., template, precursor)
- Need to compare with NREL Ir/metal nanowires

Achievement 4: Ir Coated Whiskers on Nano-Structured Substrate (3M)



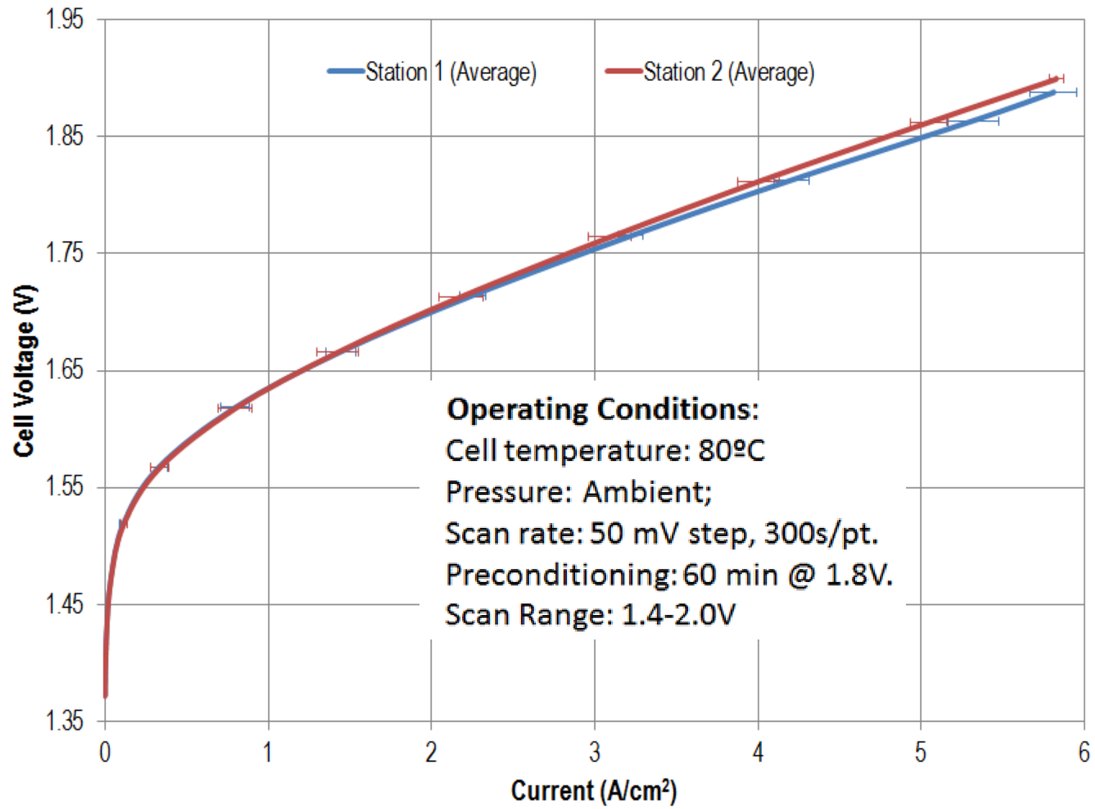


Roll-to-roll web processing



3M IrNSTF anode demonstrates comparable performance to standard anode but at 1/8 Ir loading and 1/16 PGM loading

MEA-to-MEA and Cell-to-Cell Performance Reproducibility of Baseline IrNSTF



Experimental Details

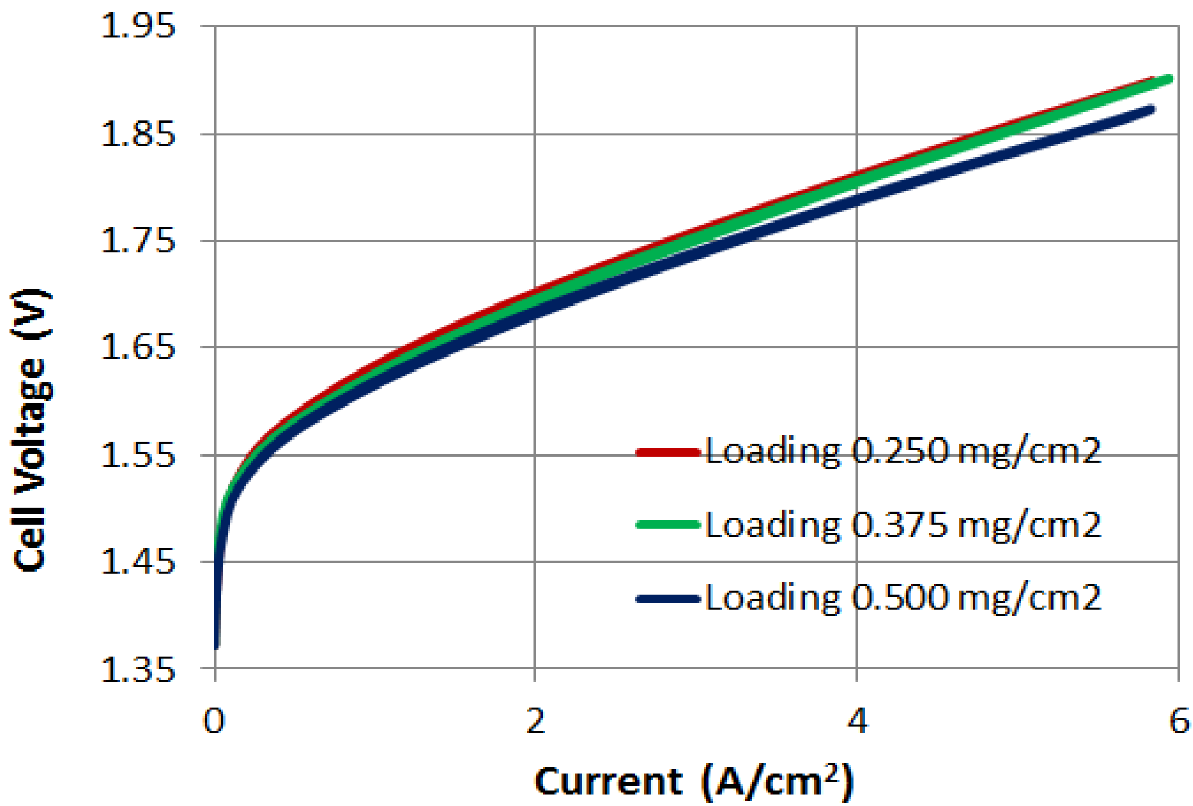
Giner's proprietary anode flow field and GDLs used for the test

Each graph is an composite of 5 individual tests (10 MEAs total)

Two different cells tested on two test stands (cells were swapped around between test stations)

- Excellent performance is also confirmed by tests at 3M facility;
- Super high current densities (5.7A/cm^2) with minimal mass transport limitations

Impact of Ir Loading on Performance of Ir-NSTF MEAs



Experimental Details

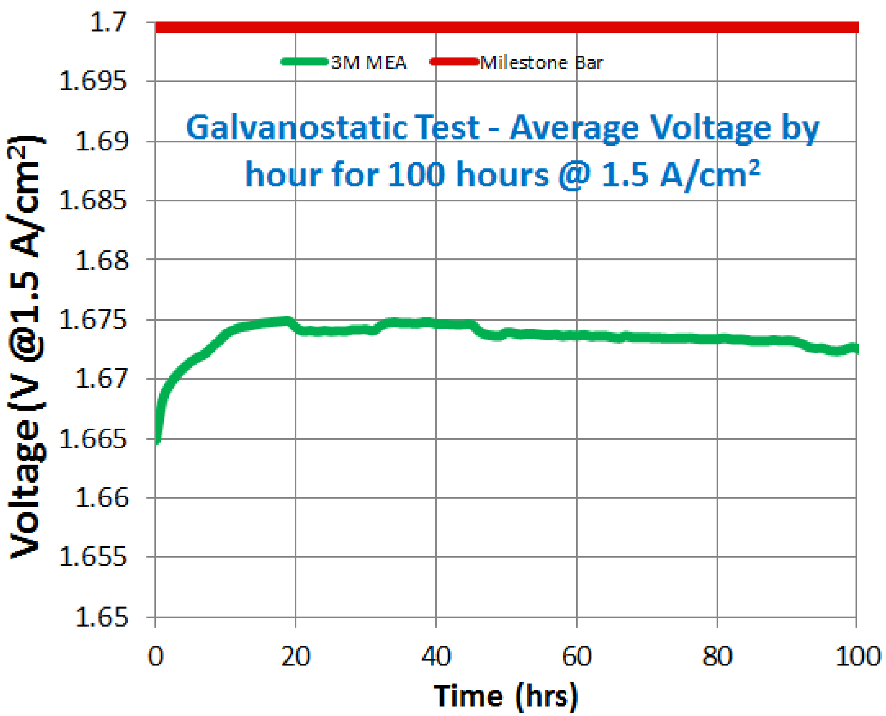
Same baseline membrane used throughout these experiments

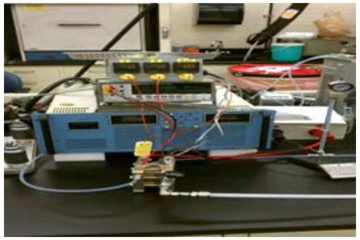
The same catalysts used throughout these experiments (exc. loading)

Electrode catalyst loadings were increased on both anode and cathode at the same levels

- Increasing Ir loading from 0.25 to 0.5mg/cm^2 barely changes the performance, indicating high activity of Ir/NSTF catalyst

Performance Milestone: 100 hours 1.5 A/cm² @ 1.7 V/cell or less





Milestone
(by July 2014)

- PGM < 0.5 mg/cm²
- 1.7 V@ 1A/cm² target
- Reaching 100 hour at 1.5 A/cm²

Milestone has been surpassed 3 months earlier than delivery date

Collaborations

Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Brian Rasimick, Allison Stocks, Tom McCallum	Prime, oversees the project; broad screening of catalyst supports; electrolyzer hardware design and validation; electrolyzer cell tests, cost analysis
National Renewable Energy Laboratory (NREL) Bryan Pivovar, Shaun Alia, K. C. Neyerlin	Sub; iridium/metal nanowires development and screening, iridium surface area characterization
3M Company (3M) Krzysztof Lewinski, Sean Luopa	Sub; NSTF based catalyst development, electrolyzer cell tests, short production, cost analysis

- Participating institutes maintain active interactions via frequent teleconferences and regular visits for exchanging ideas, providing inputs and updating research progress
- NREL provides fundamental insights on iridium mass and specific activity via RDE for initial catalyst screening
- 3M and Giner provide an industry perspective performing benchmarking, durability testing, and large scale MEA fabrication and testing

Future Research

Focus will be given on MEA tests and catalyst cost analysis for the 2nd year:

- 3M: Extend MEA durability to 1000 hours
- NREL and Giner:
  - Design electrode for developed catalysts: Ir nanotubes, Ir nanowires, and Ir supported on W-doped TiO_2
  - Perform In-situ electrolyzer MEA tests to select one best catalyst
  - Compare the selected catalyst with 3M NSTF catalyst
- Develop economical analysis of materials and system
  - Catalyst and MEA cost from short production
  - Electrolyzer system cost and efficiency

Project Summary

- **Ir-based OER catalysts for PEM electrolysis have been successfully synthesized and characterized at NREL, 3M and Giner**:
  - Giner: various supports and Ir nanotubes
  - NREL: Ir/metal nanowires
  - 3M: Ir NTSF
- **3M NSTF catalyst demonstrates superior performance**:
  - Comparable performance to standard Ir black catalyst but at ⅛ Ir loading
  - 1.675 V at 1.5 A/cm^2 for 100 hours, with Ir loading < 0.5mg/cm^2
  - Significantly exceeding the milestone set for July 2014.
- **Giner and NREL: RDE data show promising activity of developed catalysts compared to commercial Ir black:**
  - Ir supported on W-doped TiO_2 mass activity increased by 2 times
  - Ir/Co nanowires mass and specific activity increased by 3 times
  - MEA tests ongoing to select one best catalyst to be compare with 3M catalyst

Acknowledgments

- Financial support from DOE under the contract # DE-SC0007471

- DOE Fuel Cell Technologies Office
  - David Peterson
  - Erika Sutherland

- Giner Personnel
  - Monjid Hamden
  - Tim Norman
  - Corky Mittelsteadt

- UMass Lowell for conducing TEM
  - Prof. Zhiyoung Gu
  - Dr. Gao Fan