Durable Catalysts for Fuel Cell Protection during Transient Conditions

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3M

DOE/3M Award DE-EE0000456

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Project ID: FC006

Overview

Barriers

Electrode Performance:
Catalyst durability under
30,000+ start-up&shut-down events

Timeline

- Project start date: August 1, 2009
- Project end date: July 31, 2013
- Percent complete: ~ 15% (03/31/2010)

Partners

- **Dalhousie University** (subcontractor)
  - Dr. David Stevens; **High-throughput catalyst synthesis and basic characterization**
- **Oak Ridge National Lab** (subcontractor)
  - Dr. Karren More; **TEM characterization**
- **3M**:
  - George Vernstrom
  - Greg Haugen
  - Theresa Watchke
  - Radoslav Atanasoski

Budget

Total:	$5,782,165		
- DOE Share:	$4,625,732	Funding Received in FY09:	$ 900,000
- Contractor Share:	$1,156,433	Funding for FY10:	$1,260,000

Objectives and Relevance

Develop catalysts that will enable PEM fuel cells systems to **weather the damaging conditions** in the fuel cell **at voltages beyond the thermodynamic stability of water (> 1.2 V)** during the transient periods of start-up/shut-down and fuel starvation by favoring the oxidation of water over the dissolution of platinum and carbon.

Such catalysts are required to make it possible for the fuel stacks to satisfy the current 2010 and 2015 DOE targets for performance and durability.

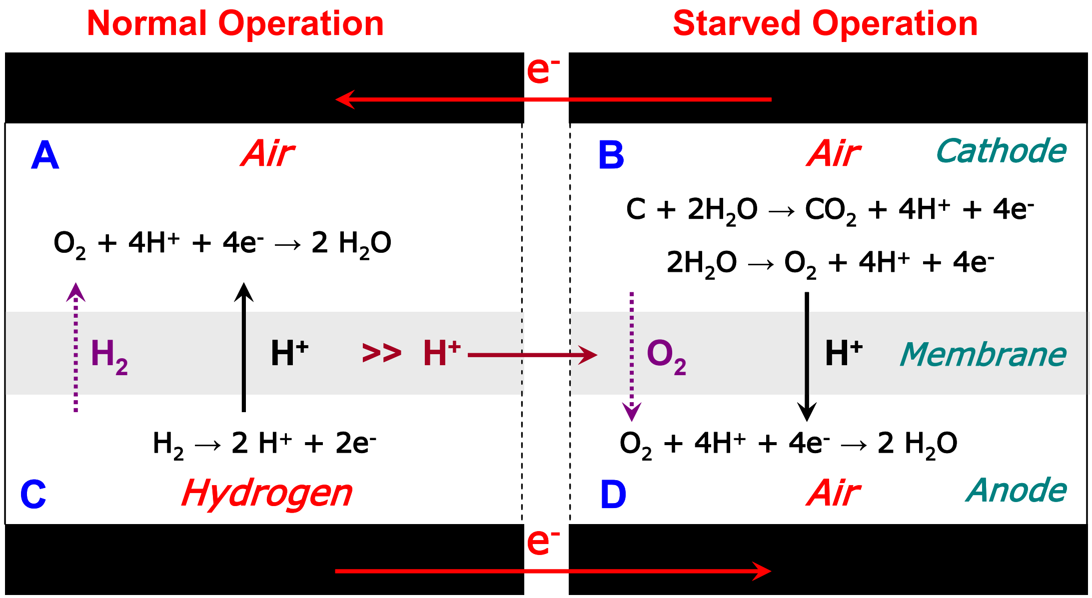
More than 30,000 start-up/shut-downs have been estimated to take place during stack lifetime.

Recent HONDA and GM presentations singled out start-ups and the shut-downs as being the most damaging for the durability of the catalysts (ECS Fall Meeting, 2009)

Approach: Problem Statement

PEMFC with fuel starved region

Electrochemical reactions leading to carbon corrosion and Pt dissolution



*) Modified after Gu et al, ECS Transactions, **11** (1) 963, 2007

Absence of hydrogen and simultaneous **presence of oxygen** in **separate** regions of the anode is necessary to provoke and maintain **cathode potential > 1.23 V.**

While important for durability, Pt partial dissolution current is negligible in comparison.

A, C; *normal FC operation*; **B, D**; ***operation in fuel starved region.***

As presented, region AC acts as a **power source** imposing the same voltage in region BD. Thermodynamically favored reaction in the AIR area (D) is ORR. Protons required in ORR have to come from carbon and/or water oxidation at cathode.

Abnormal operation lasts until **at the anode**

- during shut-down: hydrogen is exhausted;
- during start-up: H_2/H^+ prevails to bring the anode potential negative enough for normal FC state.

Approach: Proposed Solutions

Alleviate the damaging effects **from within the fuel cells** by
- **modifying both the anode and the cathode catalysts** to favor the oxidation of water over carbon corrosion.
- maintaining the **potentials close to the thermodynamic for water oxidation.**

The two catalyst material concepts:

1. Catalysts with high oxygen evolution reaction (OER) activity

2. Anode catalysts with low oxygen reduction reaction (ORR) activity

1. Presence of **highly active OER catalyst** on the **cathode reduces the overpotential** for a given current demand (*region B*).

- Key requirements: Implement the OER catalyst with negligible inhibition **of the ORR** on existing cathode catalyst and with **minimal additional PGM**.
- Approach: Deposit the OER catalyst as a **separate phase - as nanoparticles**.

2. **Inhibition of the ORR on the anode** side lowers the ORR current (*region D*). Through **reduced proton demand** this then decreases the OER current on the cathode (*region B*) resulting in reduced **cathode** potential.

- Key requirement: Implement the ORR inhibiting component with **negligible inhibition of the HOR, either as a mixed or a separate phase.**

Approach: Proposed Solutions

Most active, cost effective, and stable OER catalysts

Activity: **RuO_2** High exchange c.d.; 40 mV/decade Tafel slope; good charge capacity

Activity and **stability**: **RuO_2 + IrO_2: Good** stability; Activity with up to 75% surface IrO_2 is acceptable

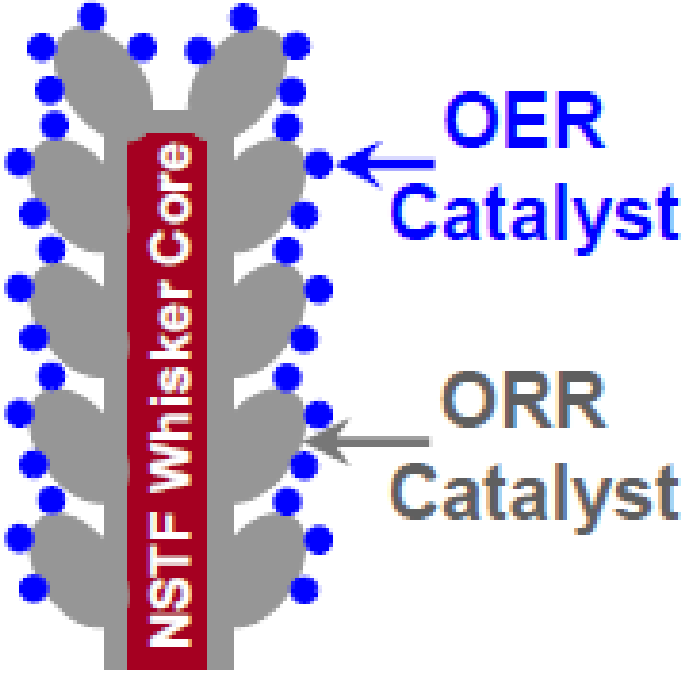
Stability and **cost**: **TiO_2**, *MnO_2, etc.* **RuO_2 - TiO_2** interfacial stability improves from 400 °C to 600+ °C

All the components are isostructural, rutile.

Morphological considerations:

Discrete nanoparticles in order to **minimize blocking** of the base ORR catalysts.

Schematic illustration ORR/OER catalyst



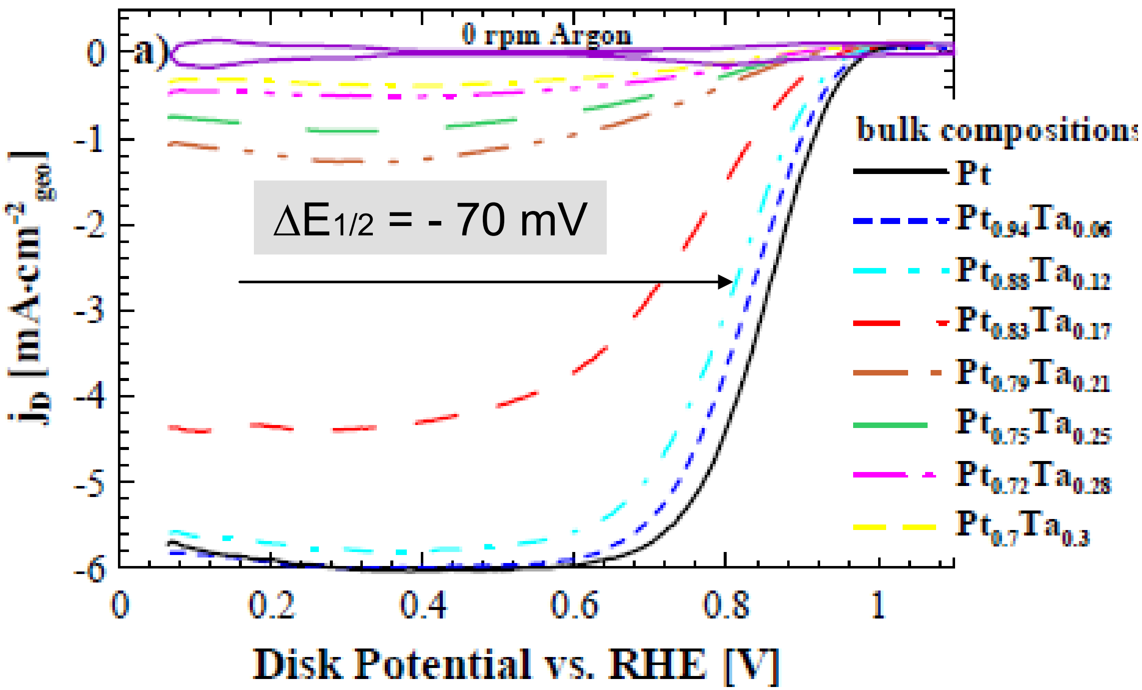
The Model:

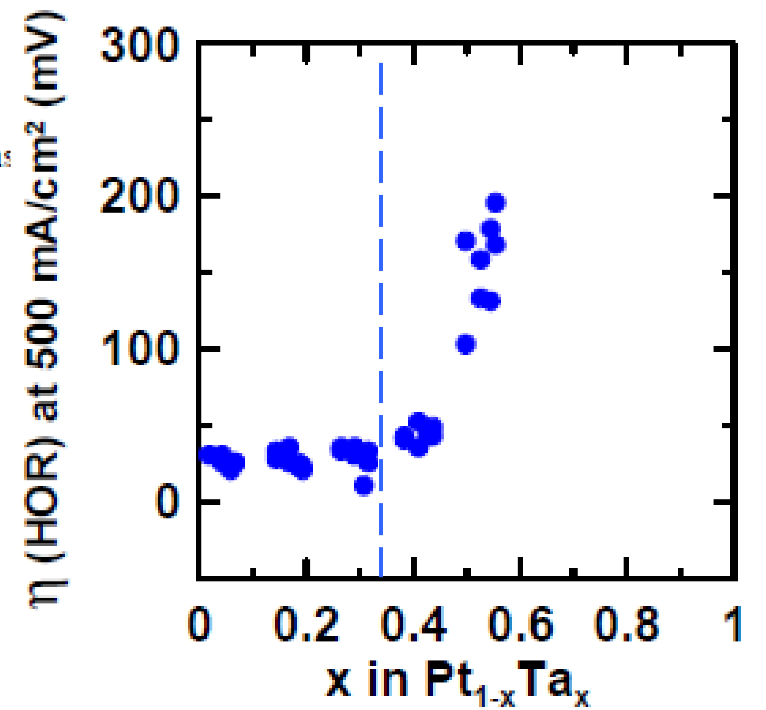
- Achieve **$1 cm^2$ of OER** catalyst on 1 cm^2geo with **OER nano-cubes** of **3 nm** sides to withstand **1 mA/cm^2 OER** at **<1.4 V**.
- Number of catalyst **particles** needed: **2.2×10^{12}**.
- **Ru content**: 0.41 $\mu g/cm^2$ RuO_2 or **0.31 $\mu g/cm^2$** Ru.
- ORR catalyst **surface area blocked**: 0.2 cm^2 or **0.5%** of NSTF entitlement.
- With TiO_2 as support the blocked ORR catalyst area is ~1%.

(further background info in slides 29&30)

Approach: Proposed Solutions

ORR suppression on the anode





ORR curves for $Pt_{1-x}Ta_x$ sputter-deposited *onto glassy carbon measured at 1600 rpm, 30 C in 0.1 M $HClO_4$.*

Bonakdarpour et al.J. Electrochem. Soc., 153,A2304,2006.

Hydrogen oxidation Overpotentials*: 500 mA/cm^2 ; 80 C; 64-electrode cell*

Stevens et al,J. Electrochem. Soc., 154, B566, 2007.

Only 12% Ta inhibits ORR by a factor of 10. HOR has practically no voltage losses even with 30+ % Ta.

Ta or similar elements built into or on the surface of the anode (HOR) catalyst are going to be produced.

Approach: Catalysts Synthesis and Characterization

Catalysts Synthesis

- Use **Pt - NSTF as an ideal real catalyst** substrate: no carbon interference
- Implement **vacuum deposition processes** fully compatible to the existing NSTF fabrication.
- Use **high throughput approach** for broad material synthesis and initial evaluation (RDE).
- Produce enough catalysts for evaluation of 3 - 4 cells with **50-cm^2 MEAs**, eliminating the need for the first scale-up requirement.
- Use direct particle deposition for proof of concept.

Instrumental Characterization

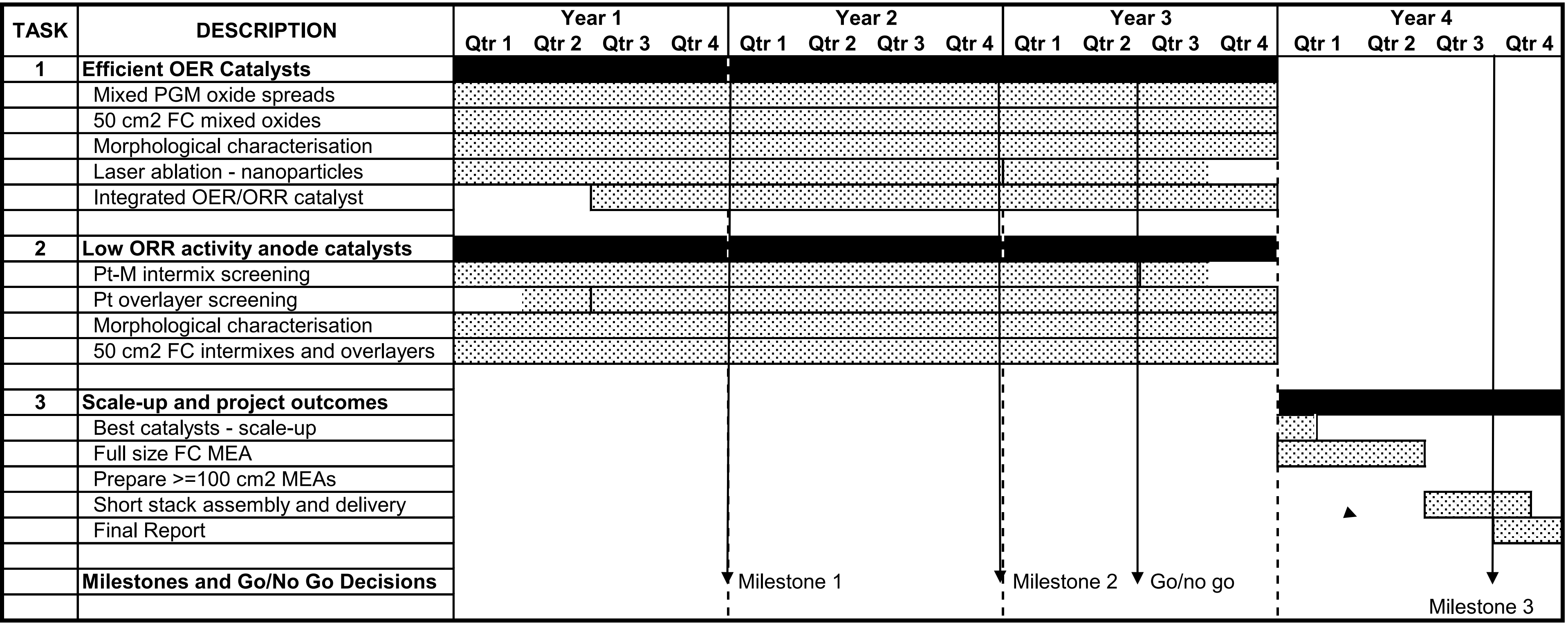
- Extensive in-depth XPS for surface compositional characterization, oxidation state in particular
- XRF for total elements content
- TEM for particle identification and composition and structure characterization.

Functional Characterization **(FC and electrochemical test details: slide #31)**

- Comprehensive testing to ensure the catalyst performs well for intended use (OER on cathode, ORR inhibition on anode) and the level of obstruction of the basic catalyst layer performance (ORR or HOR)

- Start-stop testing under real life conditions (*to be defined with the Tech Team*)

Timeline and Participant Roles



3M – All tasks. Lead, determine, scale-up, and fabricate quantities of the standard (stock) starting and new catalysts. MEA assembly and testing.

Dalhousie – Task 1 and 2. Composition spreads via sputter deposition; *ex situ* characterization; 64-electrode fuel cell testing; RRDE on NSTF grown on GC.

ORNL – All tasks. Structural and compositional TEM characterization, before and after testing.

MILESTONES AND GO/NO-GO DECISION

Until DOE targets for this topic are established, the milestones have been defined by the following project goals (*Year 1 highlighted*):

Milestone #1: **OER** of **1 mA/cm^2** at **1.45 V**; **10 mA/cm^2** at **1.5 V**; PGM: **2 µg/cm^2**.

Milestone #2: **OER** of **1 mA/cm^2** at **1.42 V**; **20 mA/cm^2** at **1.5 V**; PGM: **1.5 µg/cm^2**.

Anode ORR current **reduced** by a factor of **2**.

Demonstrated ORR and HOR performance with integrated catalyst will be substantially the same as the base-line NSTF catalyst.

Go/No-Go: **OER** of **1 mA/cm^2** at **1.40 V**; **100 mA/cm^2** at **1.5** V; PGM: **1 µg/cm^2**.

Anode ORR current **reduced** by a factor of **5**.

Integrated catalyst system meets DOE metrics for durability, performance and PGM loading demonstrated by 50-cm^2 FC testing.

Milestone #3: Short stack for delivery to DOE designated site for testing.

Year One Goal: Explore the space (Ru, Ir, Ti) around the OER model catalyst.

Accomplishments: The model-based OER catalysts

Combination:	Element (ug/cm^2) Pt	Ti	Ru	Ir	O_2
Pt:Pt	150	-	-	-	-
Pt:Ti	150	2	-	-	-
Pt:Ti	150	10	-	-	-
Pt:Ru	150	-	2	-	-
Pt:Ru	150	-	10	-	-
Pt:Ir	150	-	-	2	-
Pt:Ir	150	-	-	10	-
Pt:Ti,Ir	150	1	-	2	-
Pt:Ti,Ir	150	2	-	3	-
Pt:Ti,Ir	150	2	-	4	-
Pt:Ti,Ir,O_2	150	1	-	2	1 sccm
Pt:Ti,Ir,Ru	150	1	2	2	-
Pt:Ti,Ru,Ir,O_2	150	1	2	2	1 sccm
Pt:Ru,Ir,Ti,O_2	150	1	2	2	2 sccm
Pt:Ti,Ir,Ru,O_2	150	1	2	2	7 sccm
Pt:Ir,Ru,O_2	150	-	2	2	7 sccm
Pt:Ru,Ir	150	-	0.5	1.5	-
Pt:Ru,Ir	150	-	1.0	1.0	-
Pt:Ru,Ir	150	-	1.5	0.5	-
Pt:Ru,Ir,O_2	150	-	0.5	1.5	2 sccm
Pt:Ru,Ir,O_2	150	-	1.0	1.0	2 sccm
Pt:Ru,Ir,O_2	150	-	1.5	0.5	2 sccm

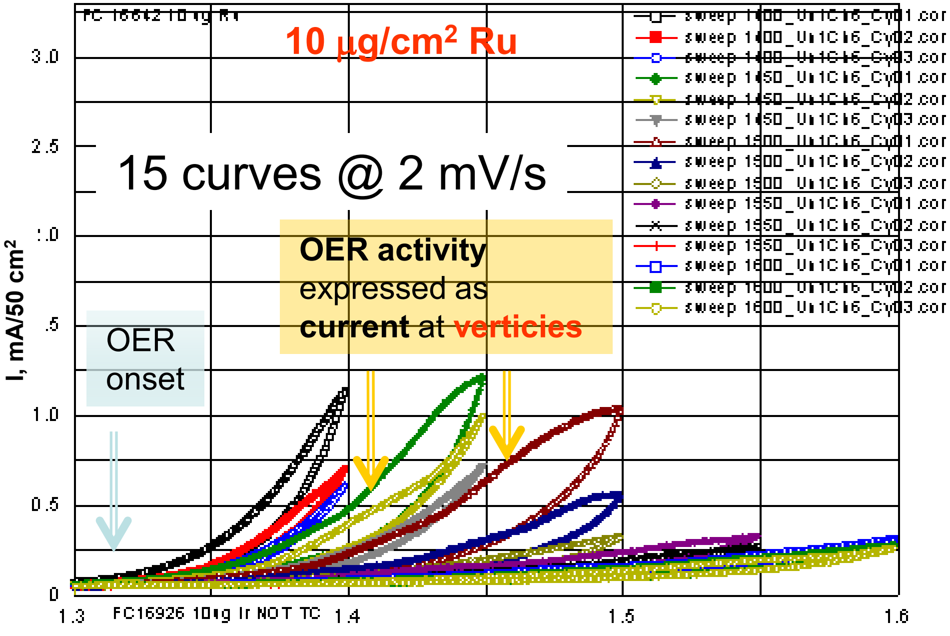
Baseline performance

Individual components:
To enhance the OER effect,
10 μg/cm^2 of PGM were used

Effect of PGM and Ti:
2; 3; 4 μg/cm^2 of Ir
1; 2 μg/cm^2 of Ir
(data in Supplemental #32-35)

The four elements:
2 + 2 μg/cm^2 of Ir +Ru with Ti and Oxygen

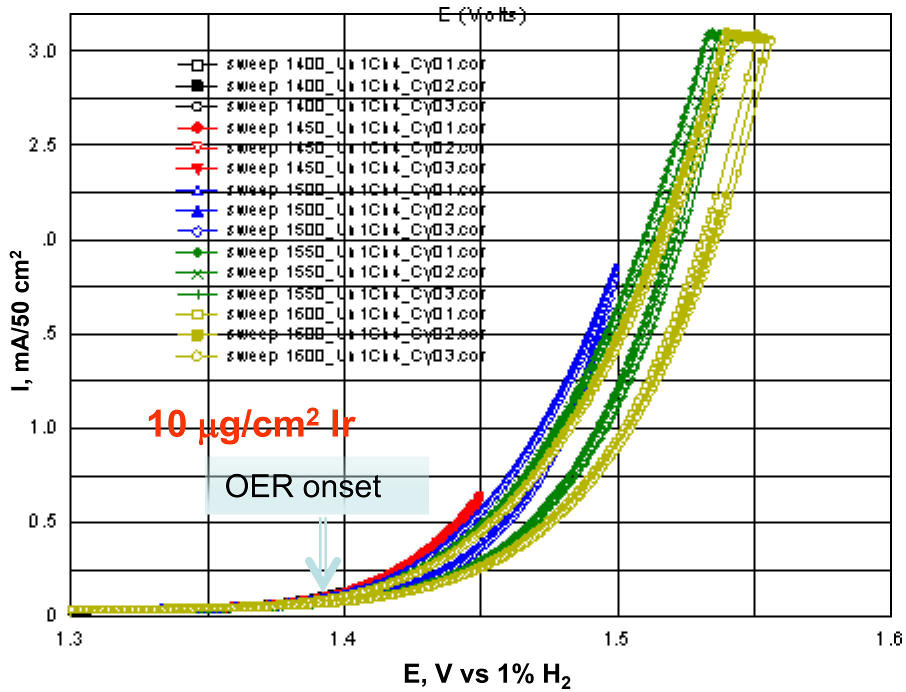
Year One milestone PGM:
1 + 1 μg/cm^2 of Ir +Ru with Oxygen



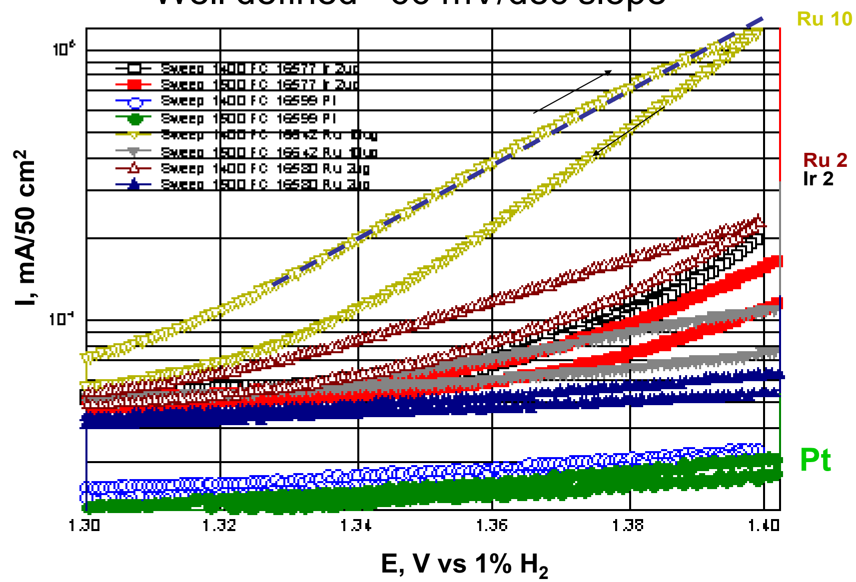
OER of single components

The major findings:

- Ru the most active
- Ir less active but much more stable
- Ti is inactive; same as Pt substrate

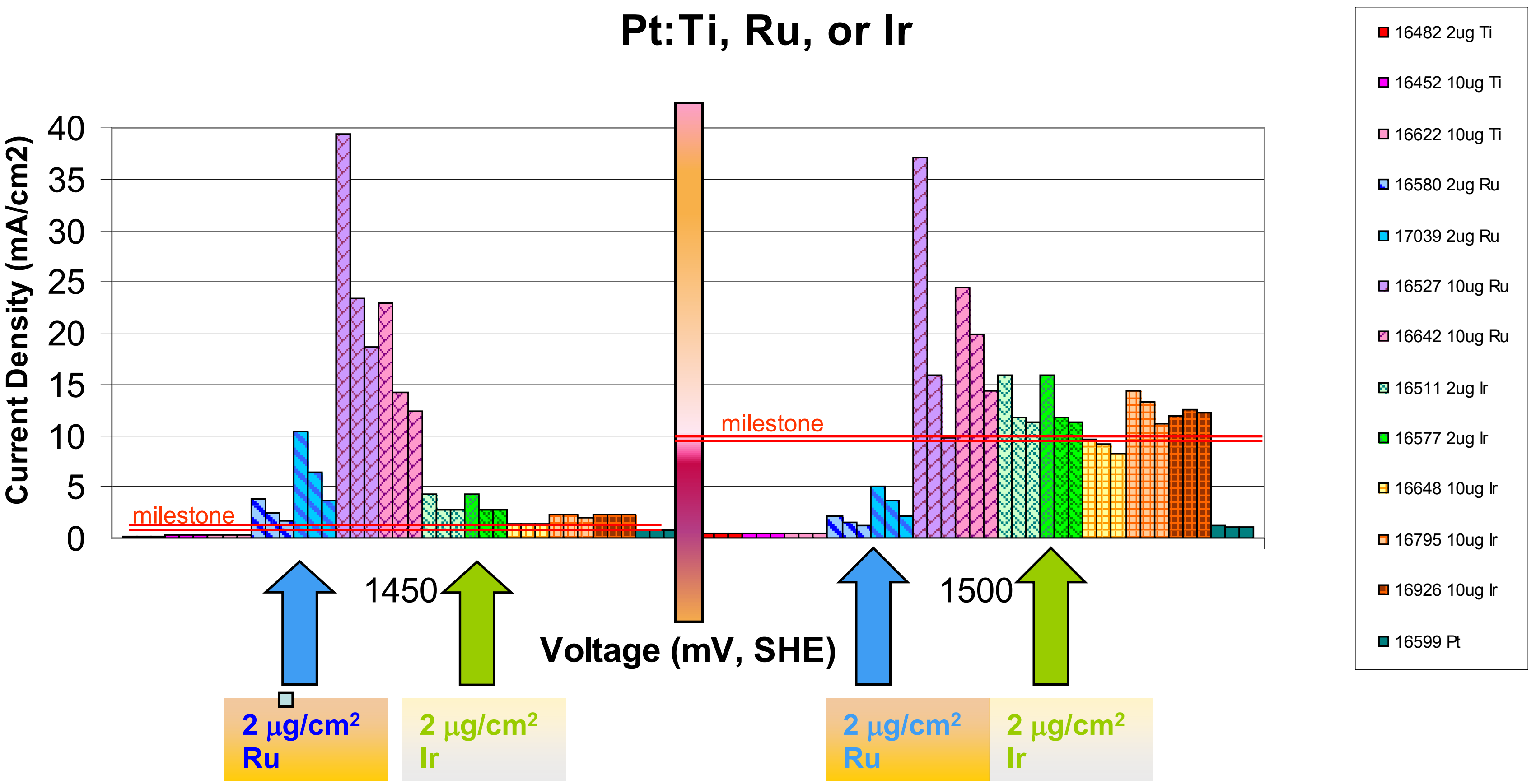


Tafel plot of *Initial* Ru scan (2 mV/s):
Well defined ~66 mV/dec slope



Accomplishments: OER Summary of Single Components

Vertices currents of 3 consecutive sweeps at milestones potentials of 1.45 V and 1.50 V



With exception of Ti and bare Pt, all other catalysts are **above the milestone activity at 1.45 V**: 1 mA/cm².

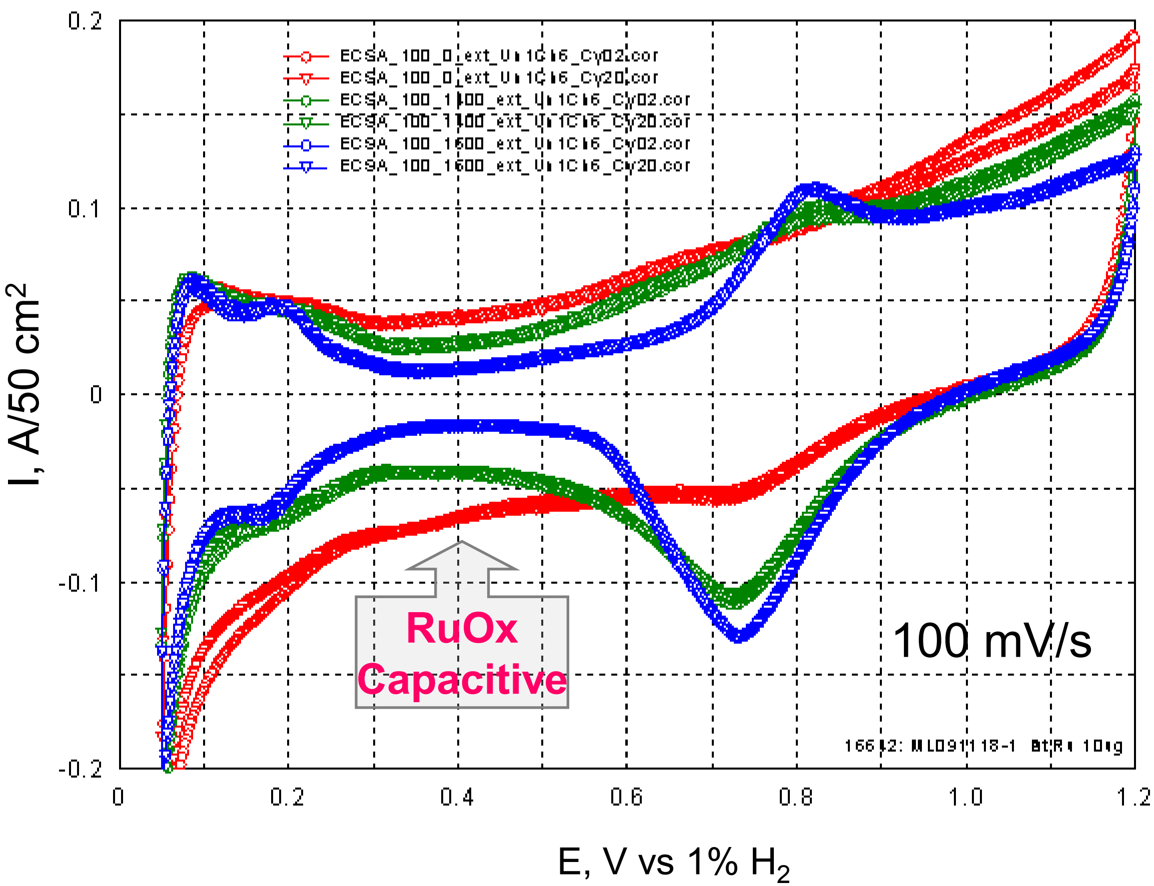
Only **Ir catalysts** exhibit activity **above the milestone** (2 µg/cm² PGM) line at **1.5 V**: 10 mA/cm².

Accomplishments: Ru OER explained

Electrochemical surface properties changes during OER testing

Cyclic voltammograms **before OER**, **after exposure to 1.45 V and 1.65 V**

(Catalyst with 10 μg/cm² Ru; Voltammograms #2 and #20 presented)



CVs dominated by Ru initially 1.25 V:

Large capacitive current in Pt double layer region;

Pt Hupd and Pt oxide suppression

Small change in CVs cycled to 1.25 V

Exposure to 1.45 V:

Features due to Ru are substantially but not completely diminished

Exposure to 1.65 V:

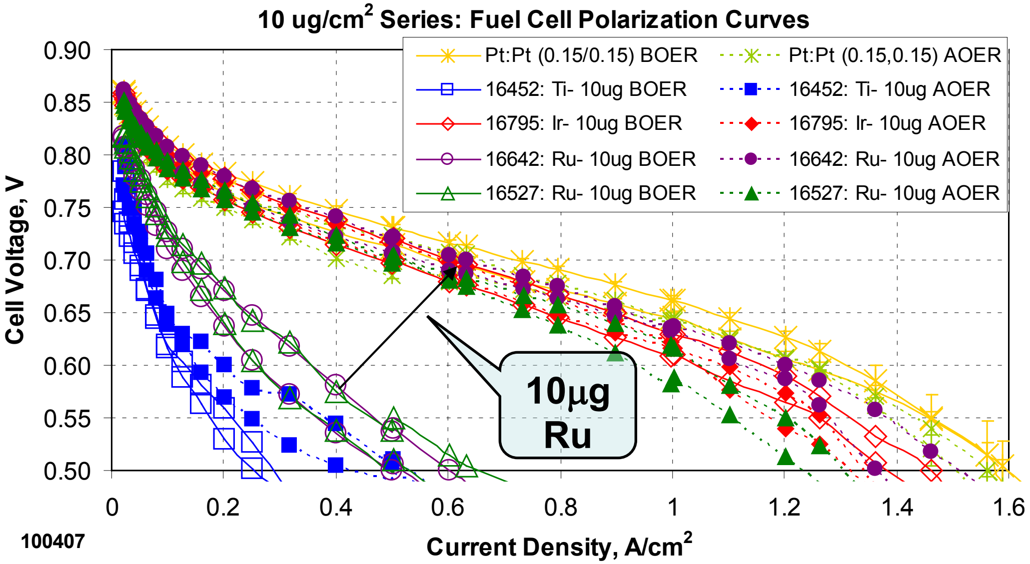
CVs resemble Pt as if Ru were completely removed;

Well pronounced Hupd peaks, double layer and Pt oxidation appropriate for Pt.

Disappearance of Ru from the catalysts explains fully the change in the OER behavior

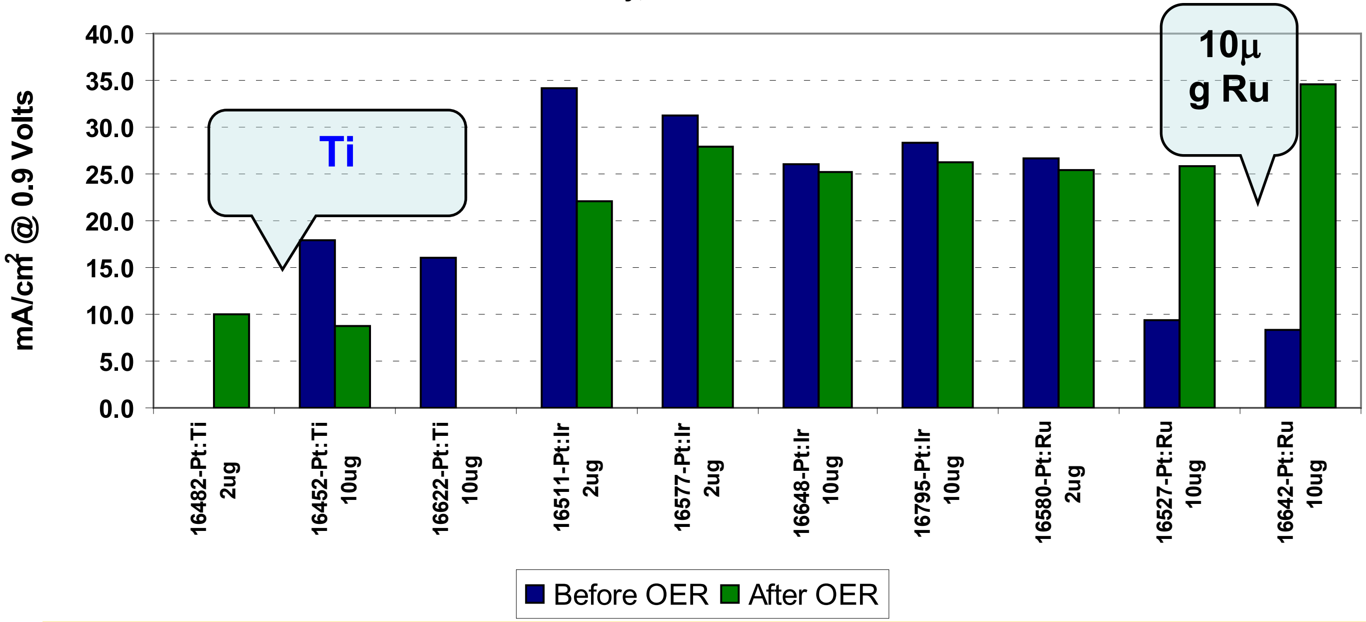
Accomplishments: Impact of OER catalyst on the FC performance

FC polarization curves (Air) and ORR activity at 900 mV (Oxygen; lower graph)



Within the reproducibility of the FC testing, OER added catalysts fall in two groups:

- **No interference** with ORR (all Ir and Ru with 2 μg/cm²)
- **High impact**: **Ti** and high content Ru (10 μg/cm²) before OER test.
- Due to losses, **Ru** (**10** μg/cm²) is the **only** catalyst that moves to low impact group after OER testing.

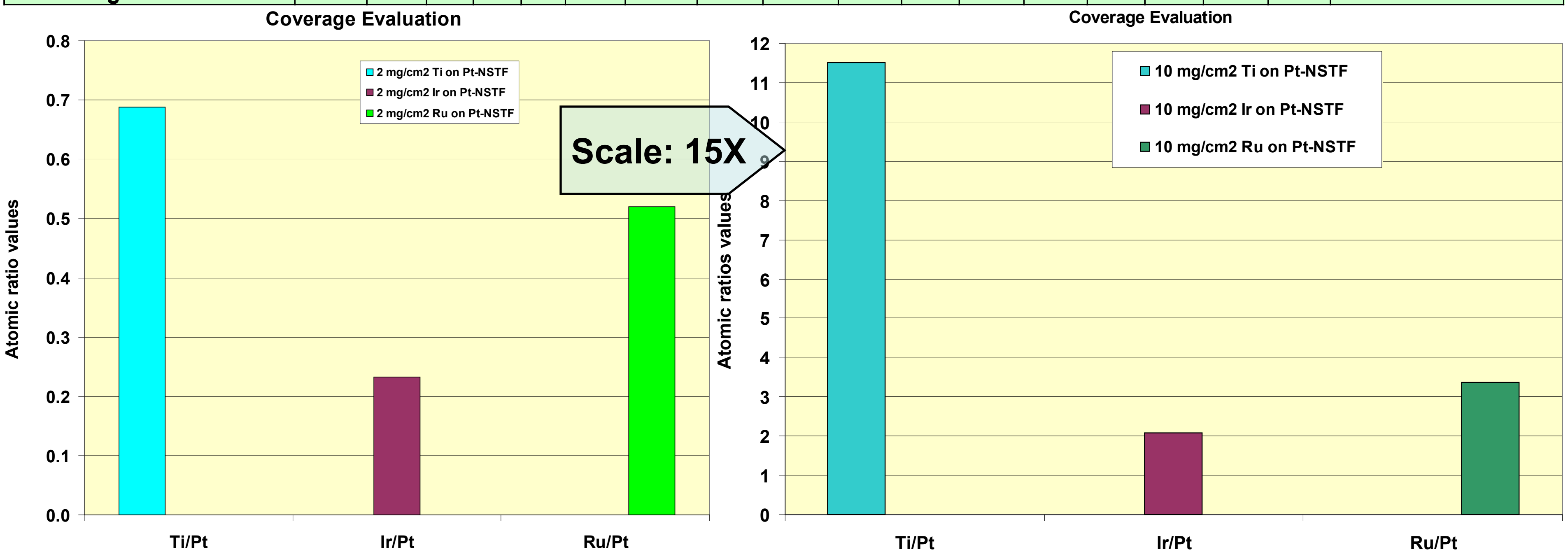


ORR activities at 0.9 V follow the same pattern as the FC polarization curves.
With exception of 10 μg/cm² Ru, the catalysts activities are slightly lower after the OER test.

Accomplishments: Oxidation state and coverage of OER catalyst on Pt-NSTF

XPS Atomic Concentrations and Atomic Ratios of Ti, Ir and Ru Coatings vs. Pt

Sample ID	C	O	Ti	Ir	Ru	Pt	Ti/Pt	Ir/Pt	Ru/Pt	O/Ti	O/Ir	O/Ru	O/Pt	C/Ti	C/Ir	C/Ru	C/Pt	Comment
2 $\mu g/cm^2$ Ti on Pt-NSTF	37	36	11			16	0.7			3.3				3.4				15 % at of O bound to C
2 $\mu g/cm^2$ Ir on Pt-NSTF	22	24		10		43		0.2			2.4				2.2			~ 6 % at of O bound to C
2 $\mu g/cm^2$ Ru on Pt-NSTF	39	23			13	25			0.5			1.8				3		20 % of O bound to C
10 $\mu g/cm^2$ Ti on Pt-NSTF	19	55	23			2	11.5			2.39				0.8				~ 6% at of O bound to C
10 $\mu g/cm^2$ Ir on Pt-NSTF	15	16		46		22		2.1			0.3				0.3			no data
10 $\mu g/cm^2$ Ru on Pt-NSTF	46	20			27	8			3.4			0.7				1.7		~20 % of O bound to C
0.15 mg/cm^2 Pt-NSTF	22	4				74							0.05				0.3	~5 % at of O bound to C



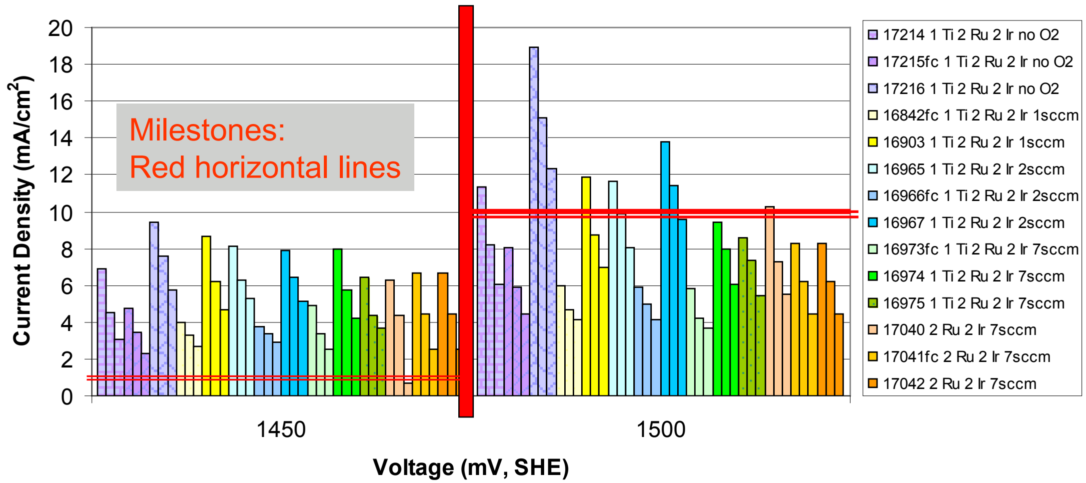
O/Ti ratios indicate that Ti is present as TiO_2. Ir is as IrO_2 only in 2 $\mu g/cm^2$.

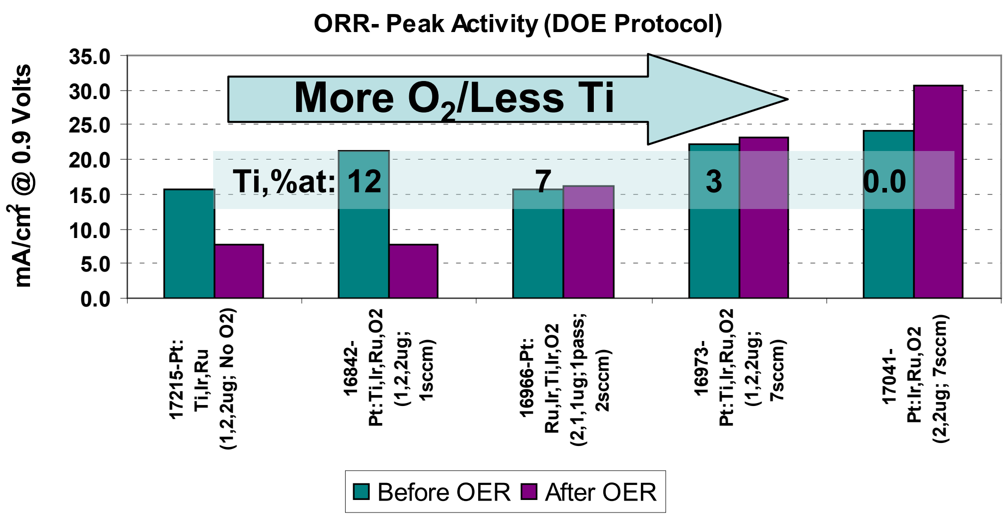
Atomic concentrations of oxidized C, O and Ru indicate that Ru may be present as organo-metallic compound through Ru-O-C bonds for both 2 and 10 $\mu g/cm^2$ on Pt-NSTF (details in #36)

Accomplishments: Ru – Ir – Ti – Ox OER catalyst

Vertices currents of 3 consecutive sweeps at:

1.45 V and 1.50 V





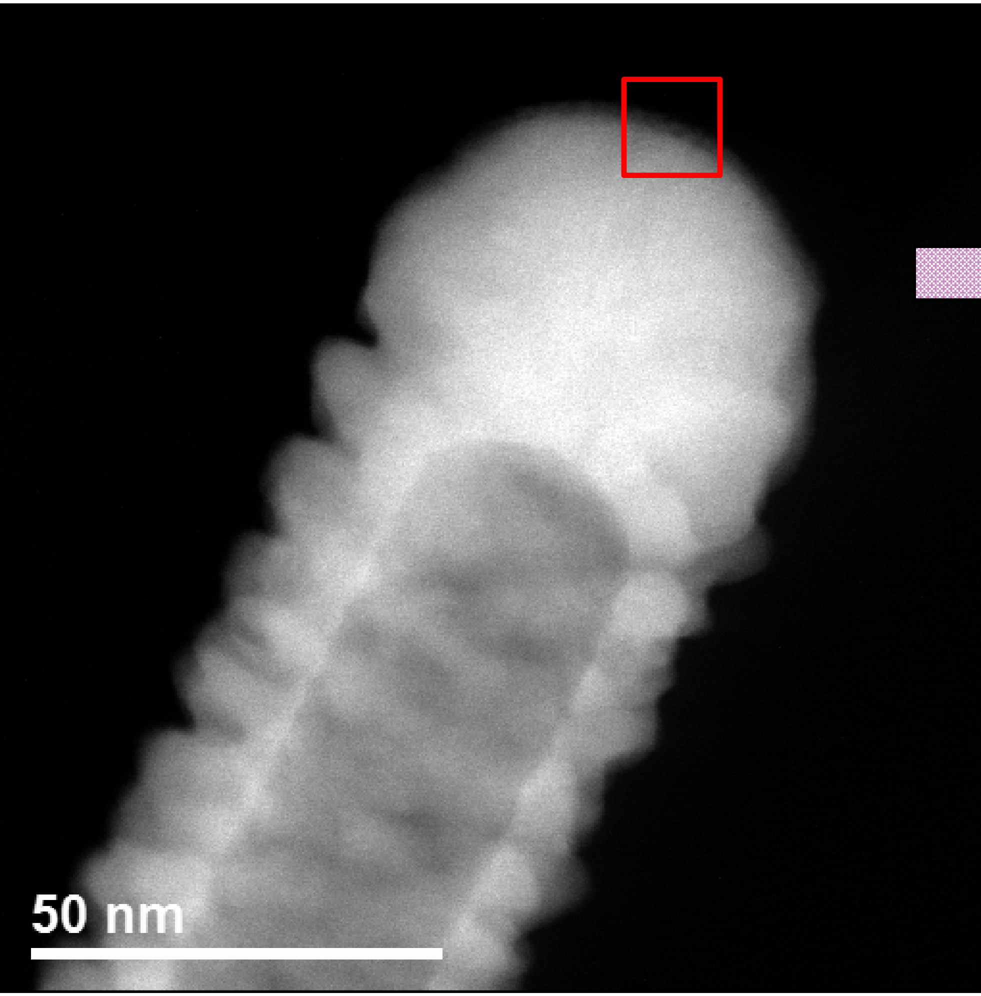
Nominal composition:
2 + 2 + 1 μg/cm² of Ir +Ru + Ti;
Sputter deposition with oxygen flow: 1; 2; 7 sccm

The **presence of oxygen** during the deposition conditions correlates with changes in **FC performance** rather than on the OER activity or stability.

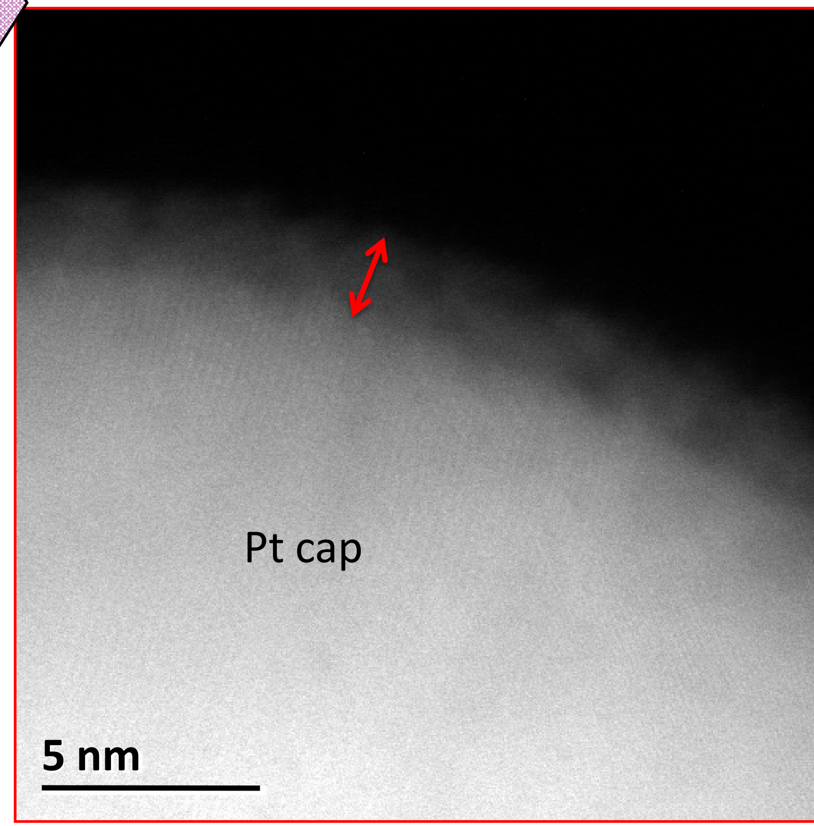
- The polarization curves as well as **ORR activity are affected by the presence of Ti** on the OER catalysts.
- Based on XPS, the **presence of oxygen** during the **catalyst deposition decreases the amount of Ti** **(XPS Ti % at. on Si wafer indicated on lower graph)**.
- As a result, better ORR activity and FC polarization performance is attained where more oxygen is present in the deposition system.

Accomplishments: TEM of Ru – Ir – Ti – Ox OER catalyst

NSTF-Pt withTi/Ru/Ir_7 sccm O_2: Sample prepared by scraping NSTF off substrate



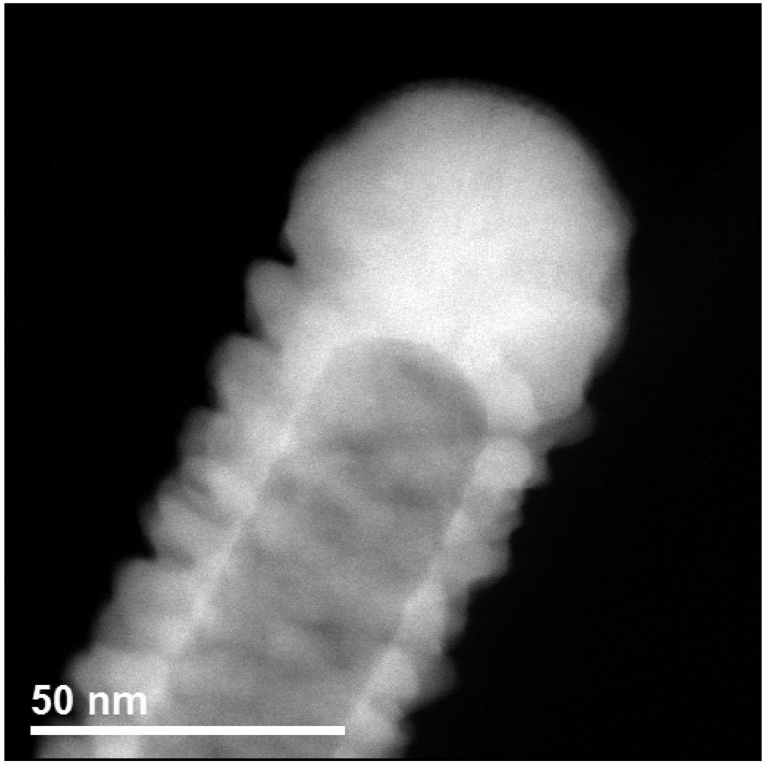
- On a **closer examination**, a **thin, continuous layer** is observed on the surface of the Pt "cap"
- The ~2 nm thick layer is **crystalline**, contains Ti, Ir, and Ru and is primarily on the "cap" surface

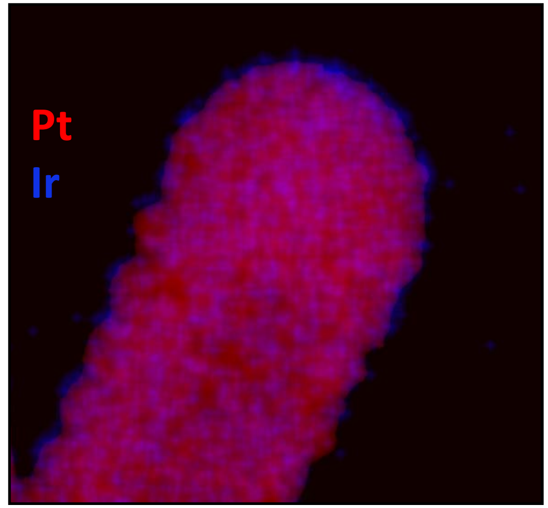


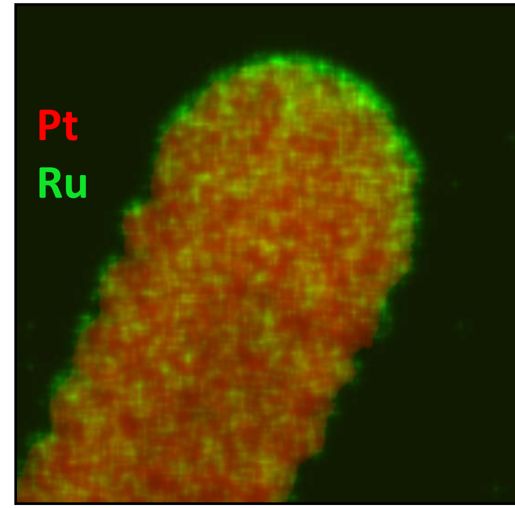
- Pt "cap" is ~40nm thick whereas thickness of Pt along sides of NSTF ~10nm
- **NO individual particles** containing Ti/Ru/Ir were identified on the surface of Pt coating along the sides

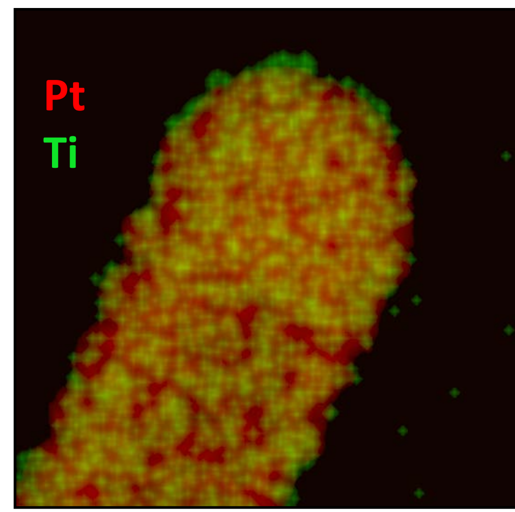
Accomplishments: TEM of Ru – Ir – Ti – Ox OER catalyst

Distribution of individual elements









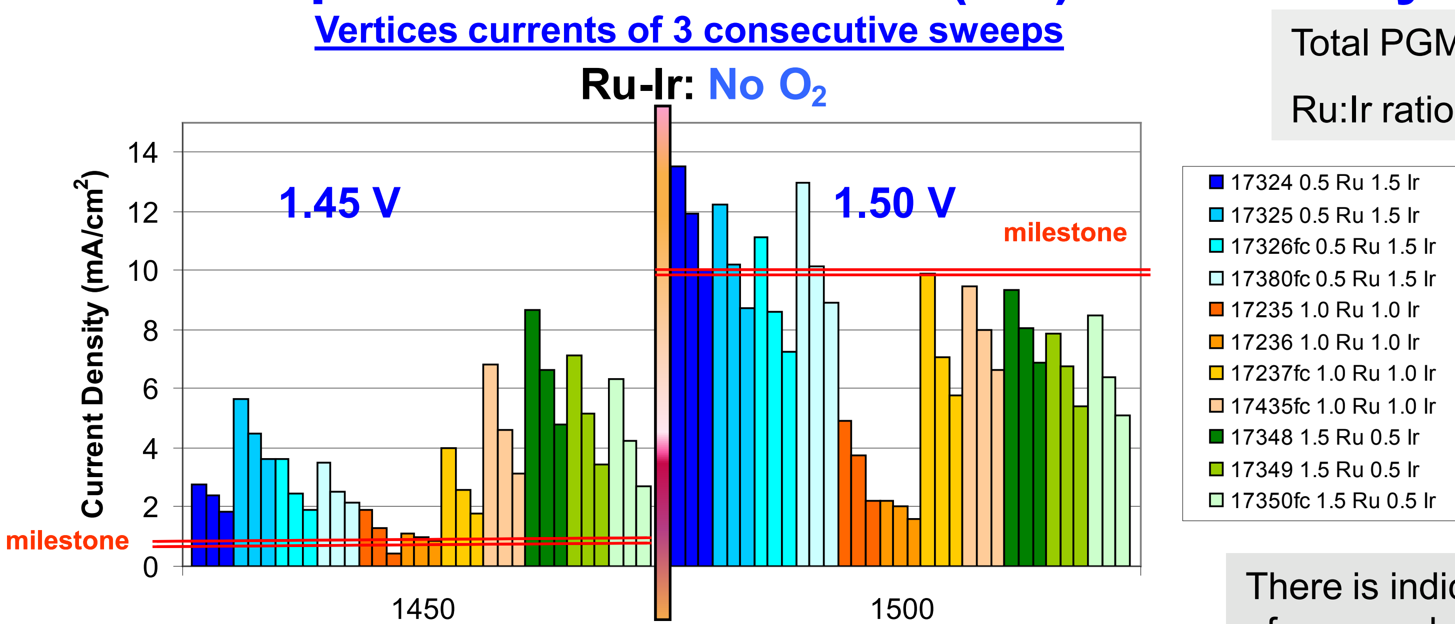
Amount of Ru in the surface layer is greater than either Ti or Ir, in agreement with XPS findings. Oxygen also detected, indicating possible presence of oxides.

Some lattice/ordering but not completely crystalline phase exhibited.

Accomplishments: Ru – Ir – (Ox) OER catalyst

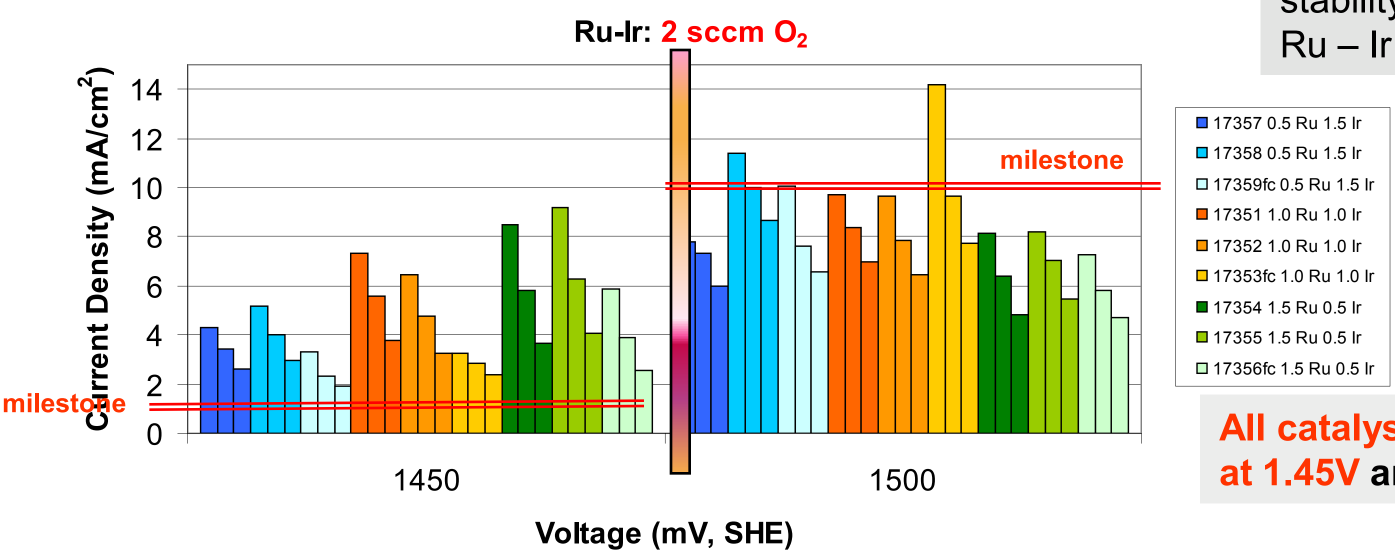
Total PGM loading of 2 $\mu g/cm^2$

Ru:Ir ratio from 3:1 to 1:3 w/w



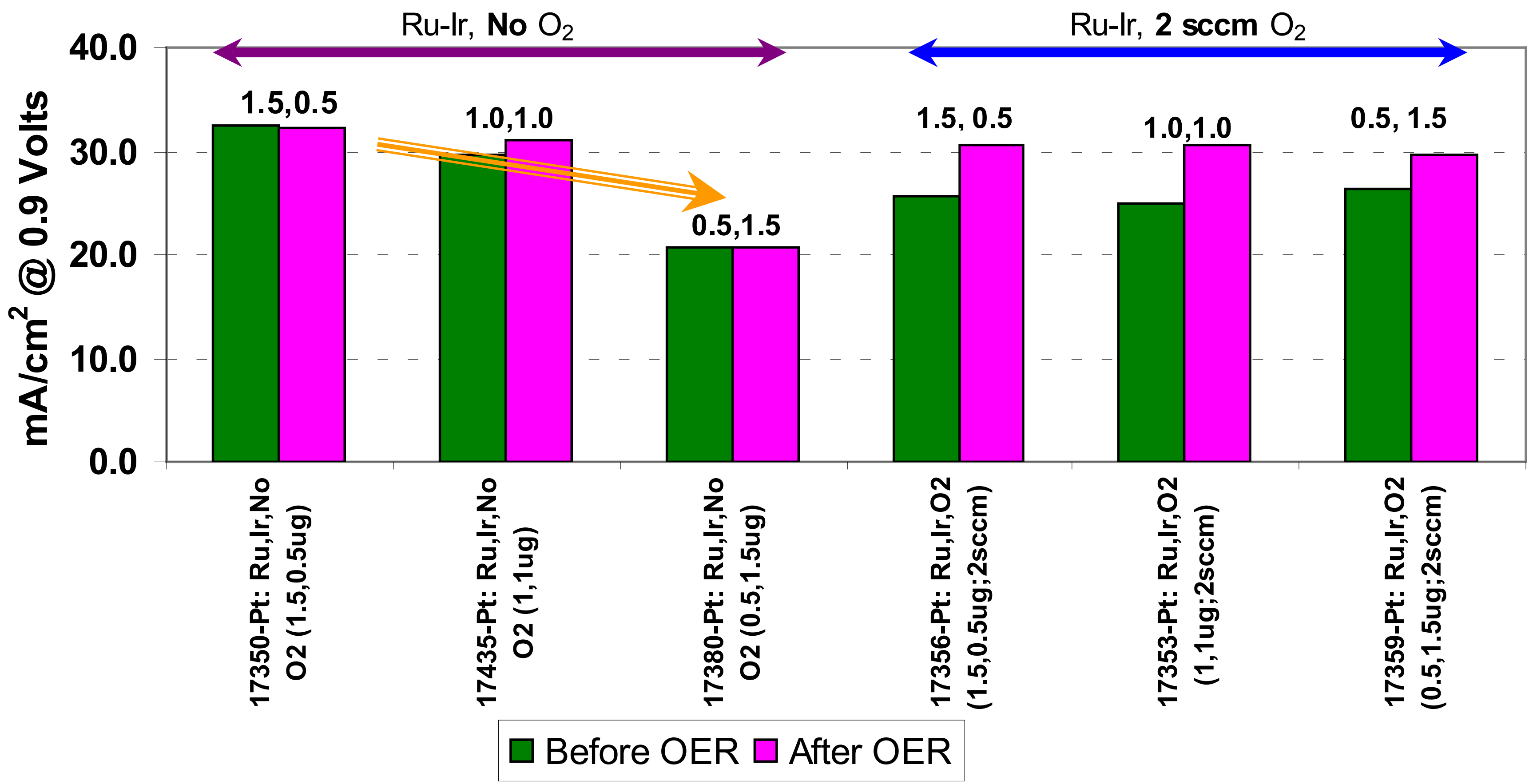
Ru (% at.): 85 67 38 85 67 38

There is indication that the presence of oxygen during the deposition process might be beneficial to the stability of some of the compositions Ru – Ir (1:1 by weight).



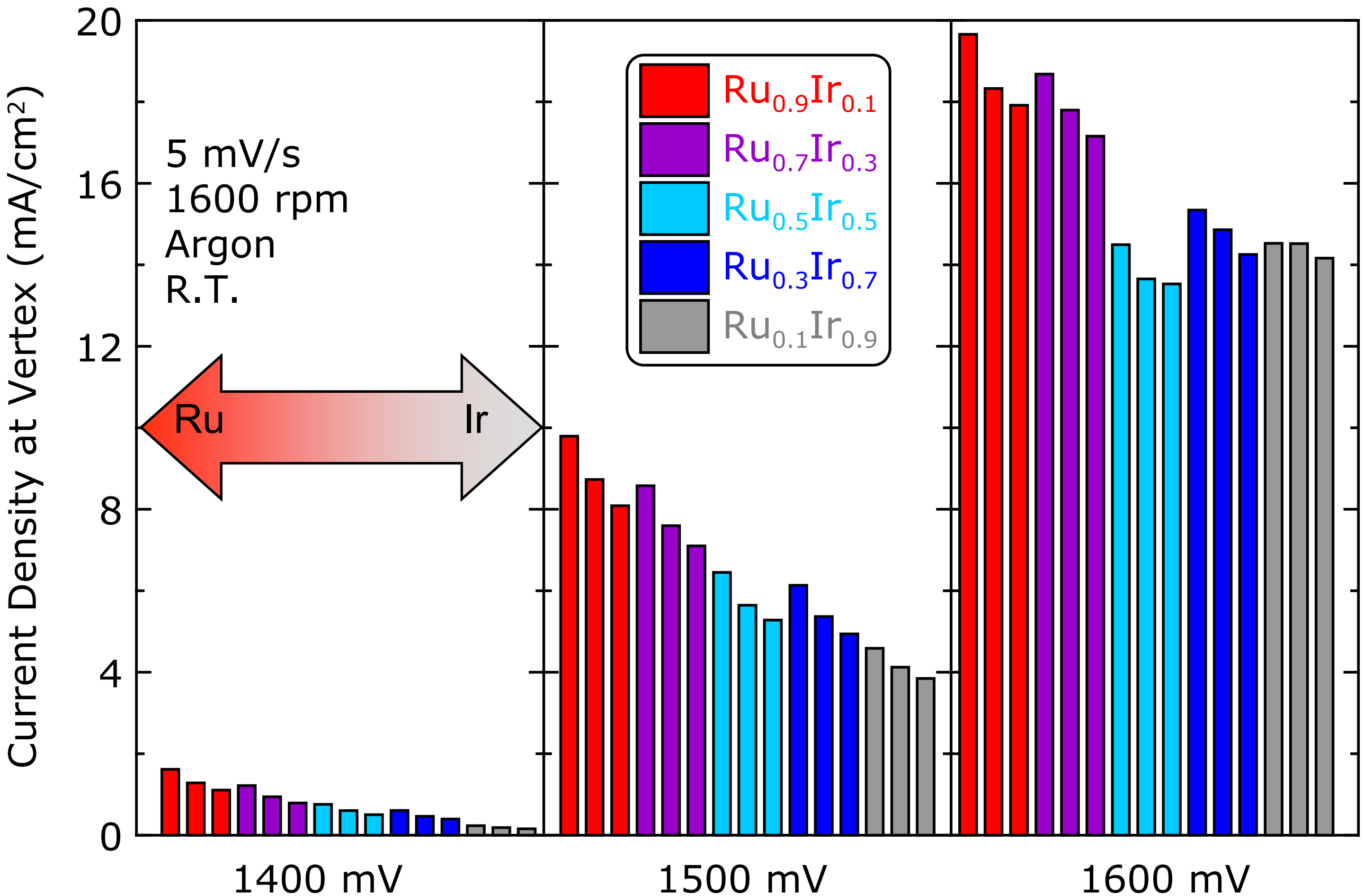
All catalysts achieved the milestone at 1.45V and some at 1.5 V.

Accomplishments: Ru-Ir Series - No O_2 vs. O_2 ORR- Peak Activitv (DOE Protocol)



Samples prepared with oxygen during the deposition process behave the same way. Obvious dependence on the Ru to Ir ratio exists in the absence of oxygen.

RDE OER Assessment of $Ru_{1-x}Ir_x$ on Pt-coated NSTF disks



50 nm/cm^2 deposit of **$Ru_{1-x}Ir_x$** on 0.15 mg/cm^2 Pt (i.e. **5 μg/cm^2 Ru** to **10 μg/cm^2 Ir**)
Peak current density decreases as Ru:Ir ratio decreases
Most noticeable at high potential, increasing Ir content increases stability.
RDE has produced very similar results and trends as did FC testing.

Collaboration and Coordination

Partners

- **Dalhousie University** (subcontractor)
  - Dr. David Stevens; **High-throughput catalyst synthesis and basic characterization**
- **Oak Ridge National Lab** (subcontractor)
  - Dr. Karren More; **TEM Characterization**

- **The project has been fully integrated since its inception, during the proposal phase.**
- **It continues to be run as one single program.**
- **Participants influence project directions based on their own data as well as experimental results obtained by all.**
- **Results are reviewed during weekly scheduled teleconferences and many more unscheduled contacts between participants.**

Future Work

Immediate/remaining of Year 1

- Improve the reproducibility of the FC testing for both FC performance and OER activity
- Modify/simplify test procedure to reflect “real life”, taking into account the Freedom Car Tech Team inputs
- Start the high throughput anode work
- Explore further the model system space by changing deposition conditions
- Attempt catalyst post-processing
- Initial attempts to produce the catalysts in discrete rather than continuous form

Year 2/ Long Term

- Reaching the Project milestones as stated (slide # 10) or modified according to new DOE performance targets in this area.

Summary

• OER catalysts with 2 mg/cm^2 PGM **achieved First Year milestone** for OER activity of **1 mA/cm^2 at 1.45 V**; Several catalysts initially met the milestone of 10 mA/cm^2 at 1.5 V.

• Integrated OER catalysts with up to **2 mg/cm^2 Ru + Ir do not interfere with the ORR.**

• Canvassed the space around the components for the model OER durable catalyst in **real PEM FC** environment.

• Produced and characterized > **40 OER coatings** and > 100 MEAs of Ir, Ru and Ti as **individual elements, binaries and ternaries, with and without oxygen**.

• **Ru** coatings are **most active**, while **Ir** are more **stable**.

• **Combinations** of **Ru + Ir retain** some of the **properties of the two**.

• Catalyst **deposition under oxygen improves** some of the **properties of Ru + Ir**.

• Presence of **Ti inhibits the FC performance** the most.

• Fully characterized coatings with **XPS** (ESCA) show indications of interaction of the OER catalysts with the substrate, potentially favorable from a durability point of view.

• High resolution **TEM** depicting the distribution of Ru, Ir, Ti on NSTF (ORNL) provides insight into the observed fuel cell performance and ORR activity.

Supplemental slides

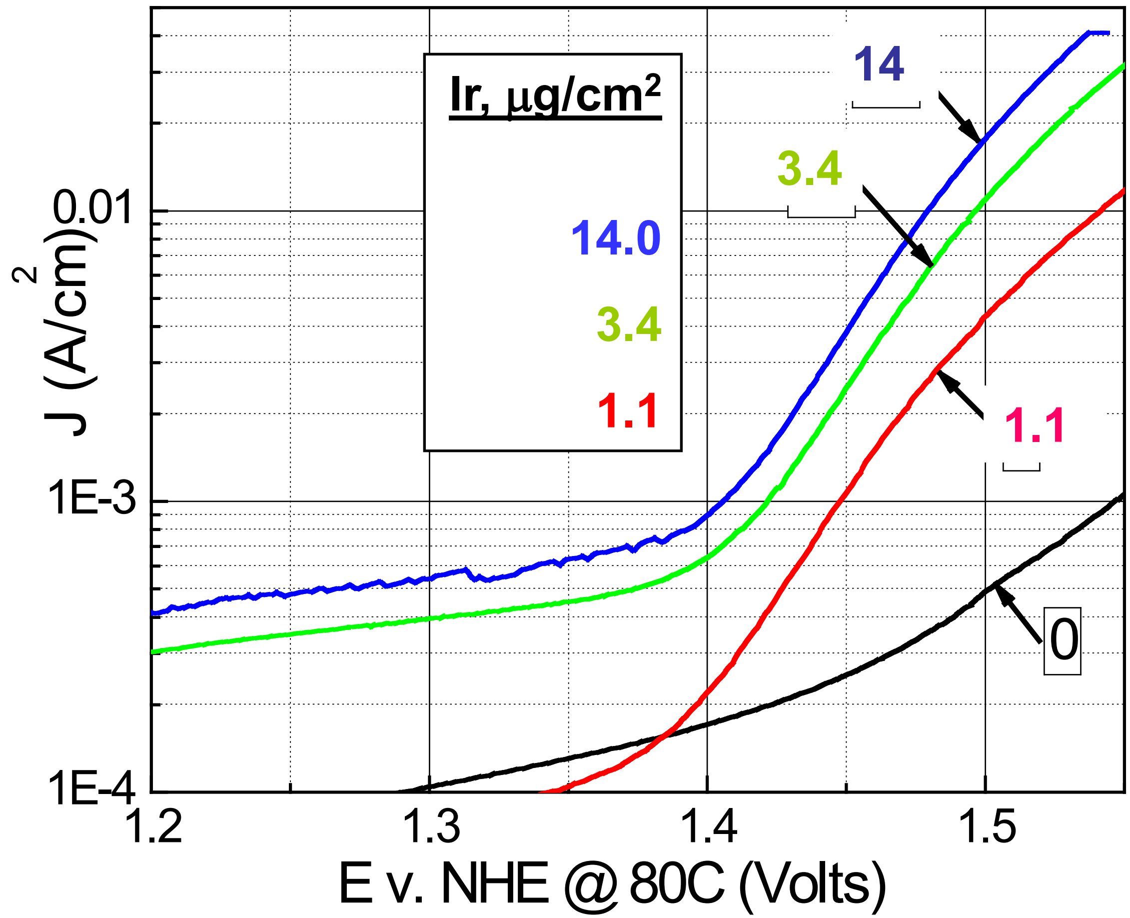
Background for OER Catalyst: Ir

As presented at DOE Annual review 2008

*OER polarization curves on NSTF PtCoMn (0.1mg/cm² Pt) catalyst over-coated with **1, 3, and 12 nm/cm² geo Ir**.*

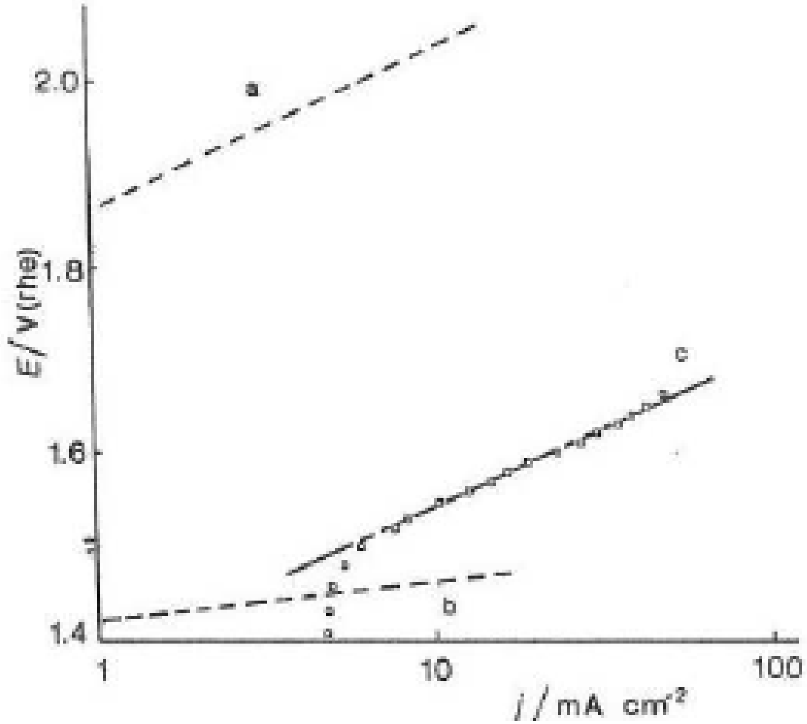
50-cm² FC

Counter electrode: same as working without Ir.
Test conditions: FC 80 °C, Working: N_2; counter/reference: 1% H_2 in N_2; 1000 sccm, 0 psig, 100% RH; Potential scan rate: 1 mV/s.



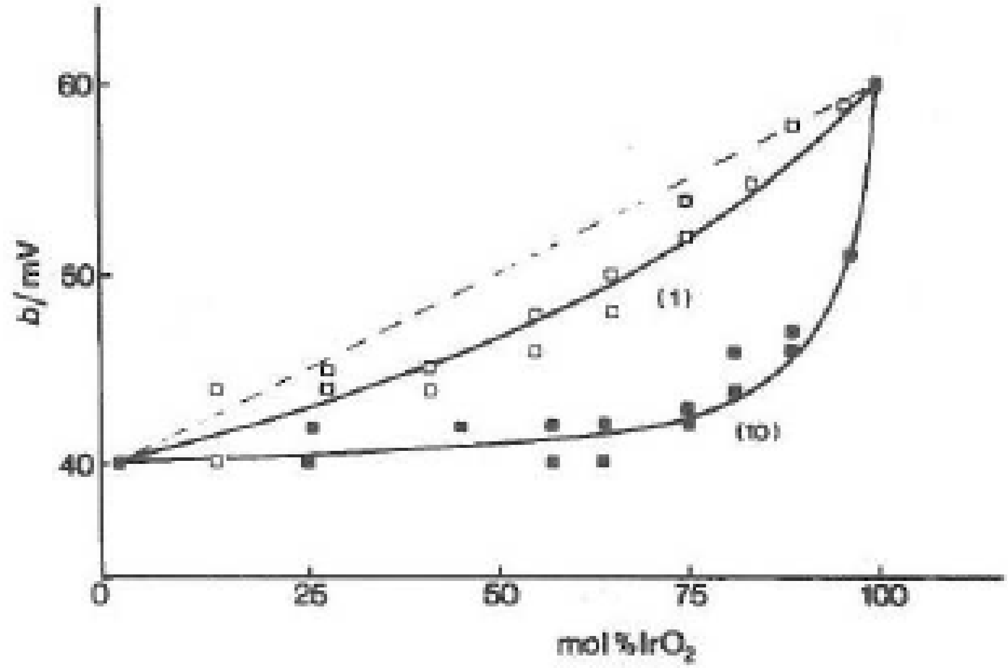
At 1 mA/cm² only 1.1 µg/cm² Ir depolarizes OER by 100 mV!

Fundamentals – most active OER catalysts



Polarization curves for oxygen evolution on (a) Pt, (b) RuO_2 single crystal, and (c) RuO_2 film. 1M $HClO_4$ at 25 °C

Trasatti, Electrochim. Acta **36**, 225, 1992



Dependence of Tafel slopes for OER on surface composition of RuO_2 + IrO_2. PGM precursors dissolved in aqueous (open symbols) and non-aqueous solvents (closed symbols). PGM content determined by XPS.

Atanasoska et al, Vacuum, **40**, 91, 1990.

Approach: Electrochemical Characterization (OER Catalyst)

1. Fuel cell performance *before* and *after* OER testing
2. OER testing (under nitrogen) via quasi-steady state (2 mV/s or 1 mV/s) polarization measurements
3. Surface area measurements and characterization via cyclic voltammetry
4. Durability assessment at end of testing via constant voltage polarization

Fuel cell configuration: OER catalysts are deposited on 0.15 mg/cm2 Pt Thick, 35 μm 3M membrane, no additive. Counter/reference electrode: 0.15 μg/cm^2 Pt under **diluted** hydrogen. Gas flows: 1,000 sccm 110% rh; cell: 70 ^{o}C.

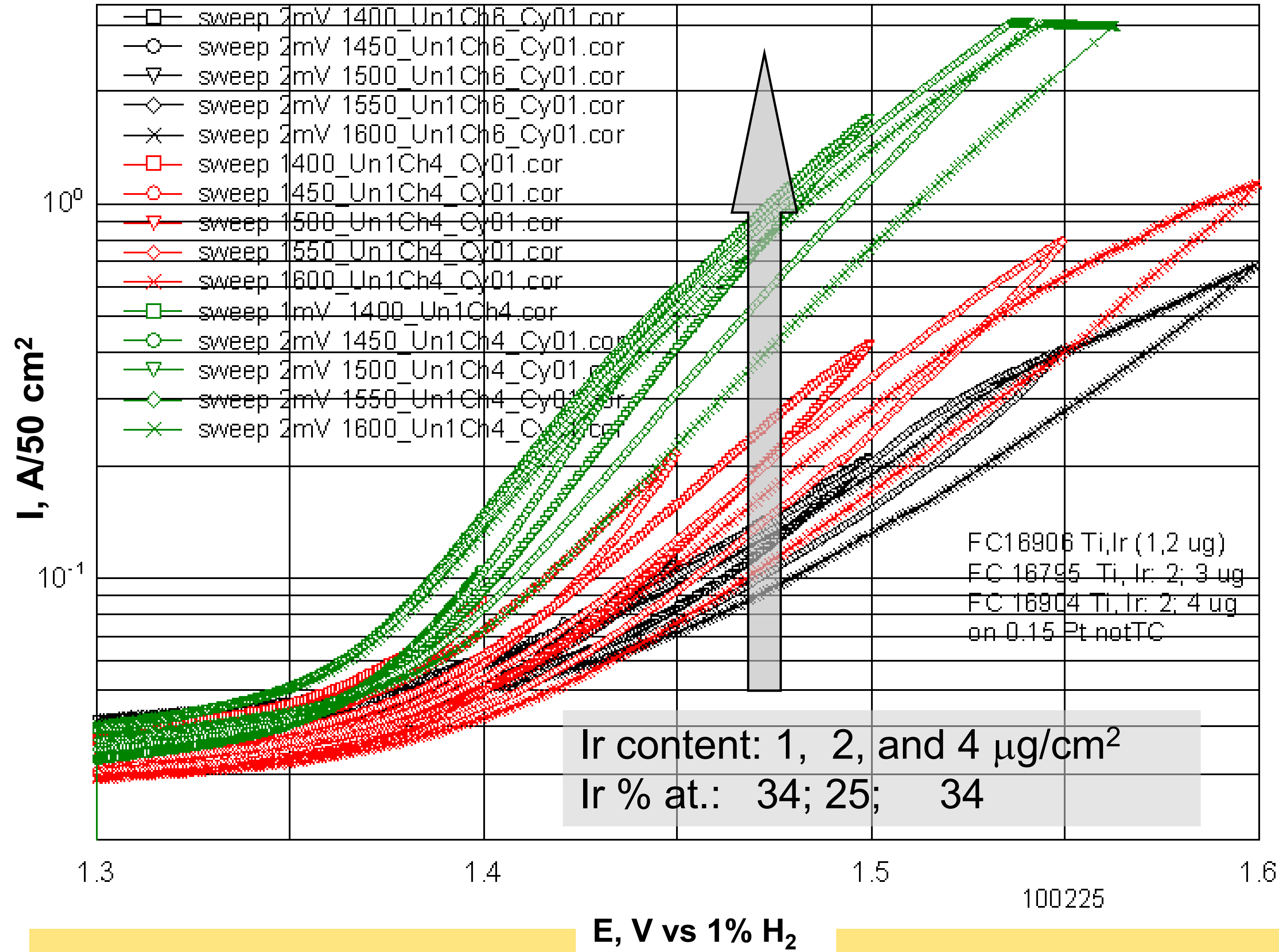
OER Test Protocol

1. Initial 20 CVs, 100 mV/s, from 1.25 V – 0.05 V, after 50 s at 1.25 V before the first CV
2. ECSA determination
3. 2 Polarization curves at 2 mV/s and 1 at 1 mV/s, from 0.6 V – 1.45V
4. Repeat steps 1 – 3 to positive end point of 1.5, 1.55, 1.60, and 1.65 V
5. 300 s constant voltage at every 50 mV form 1.45 to 1.65 V
6. Repeat step 2

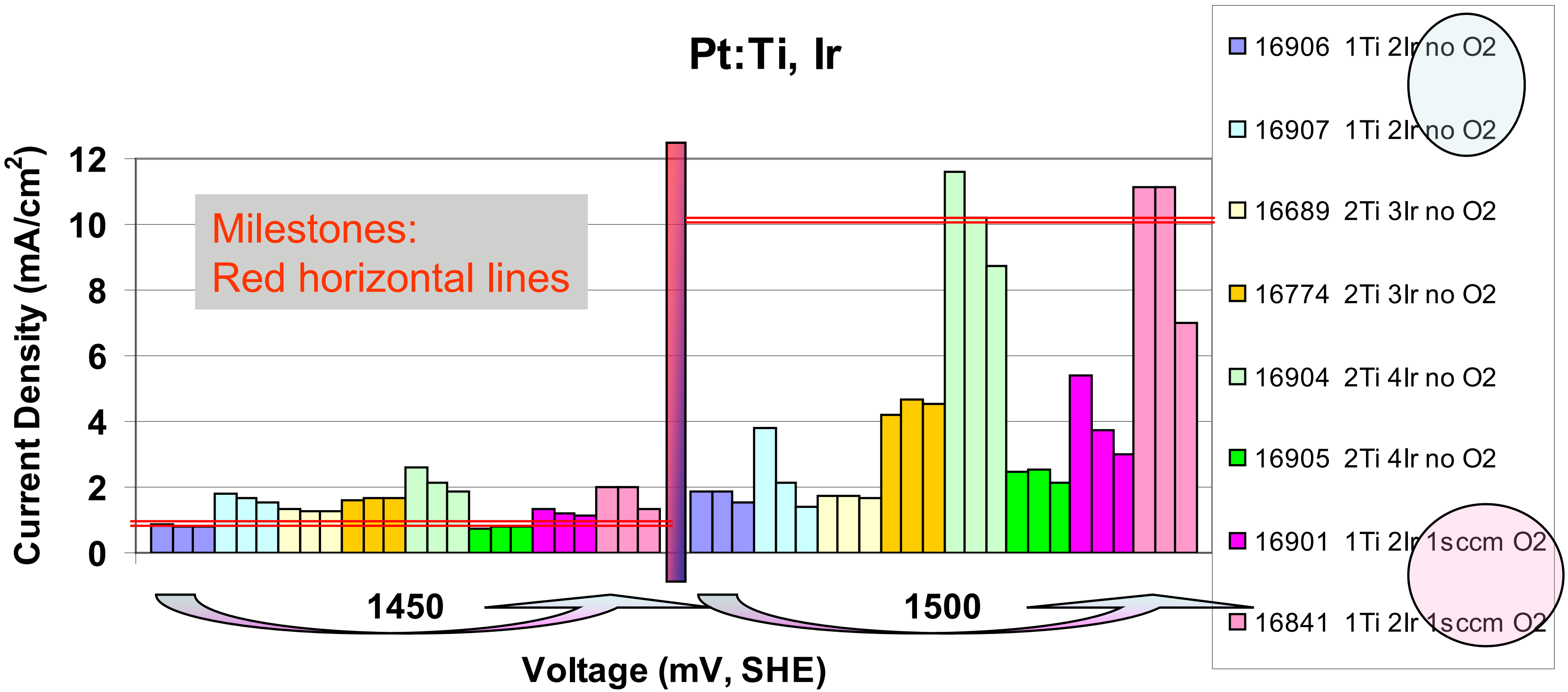
Time the cathode is over 1.25 V: ~ 6,000 s.

Ti – Ir OER catalyst: OER Polarization curves

OER activity improves with Ir content

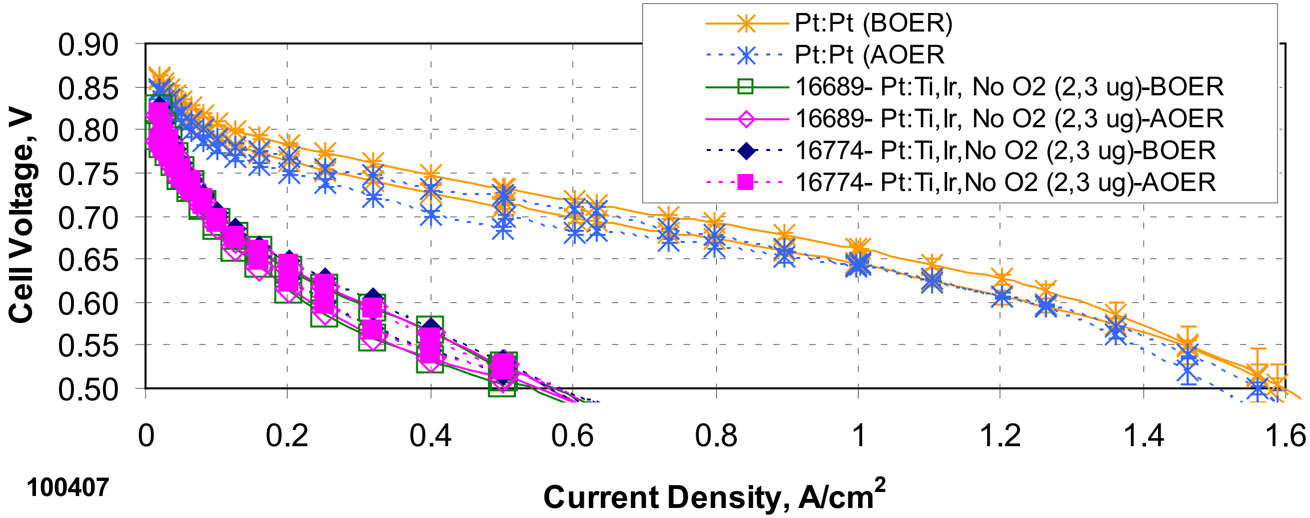


Ti-Ir Series: Current at vertex of 3 consecutive OER Polarization curves

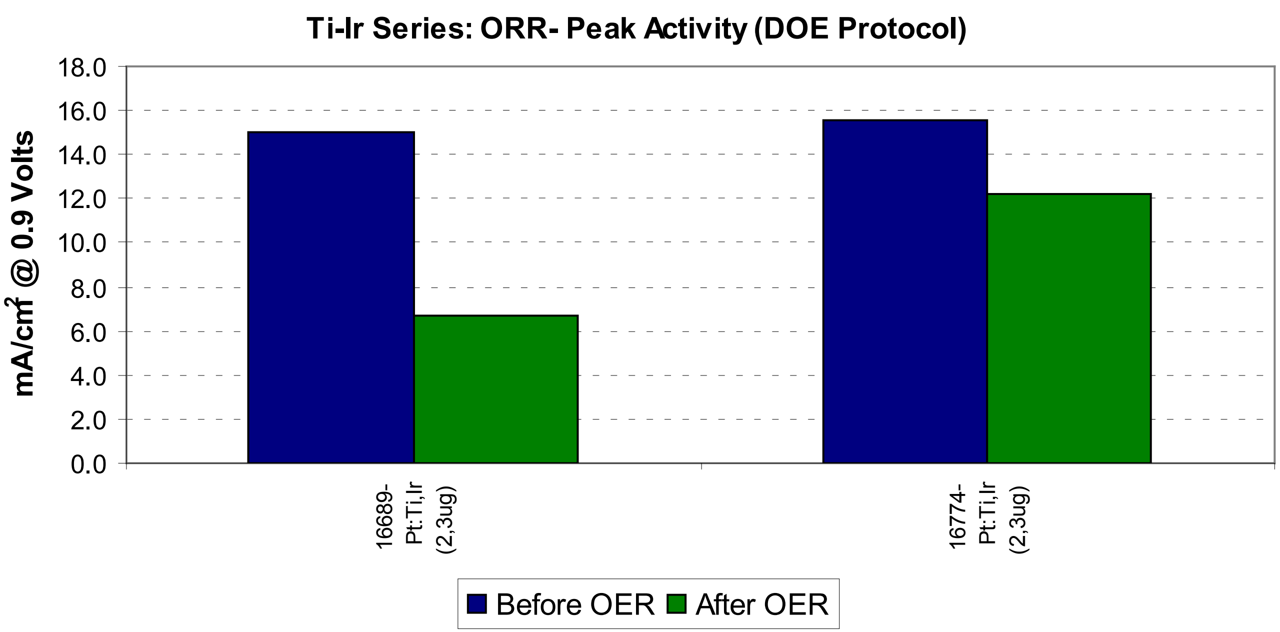


Besides increasing with Ir content, OER activity improves when the catalyst is made in the presence of oxygen. This is more prominent at higher voltages.

Ti-Ir Series: Fuel Cell Polarization Curves

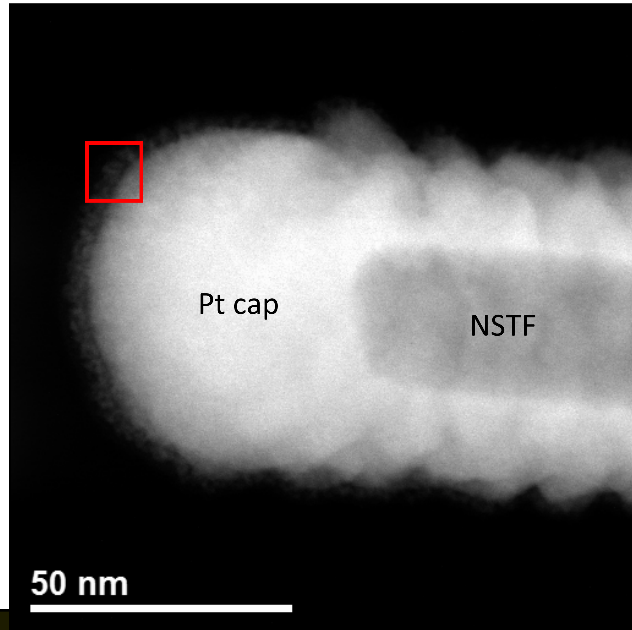


Both the polarization curves as well as the ORR activity are lower due to the Ti coverage of the ORR catalysts (Pt)

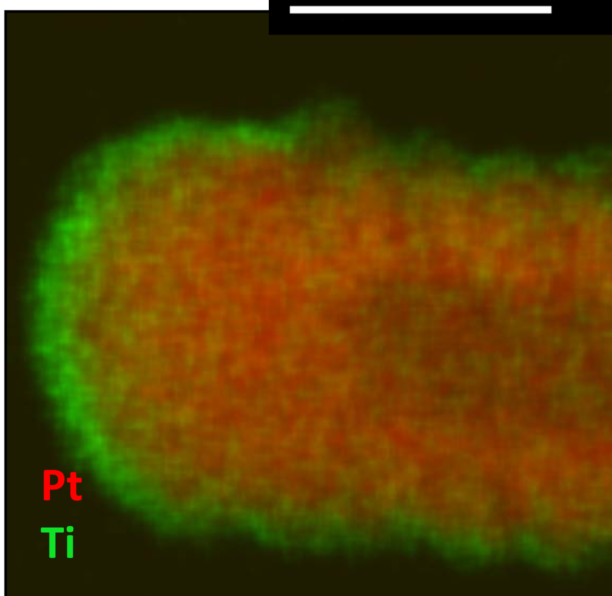


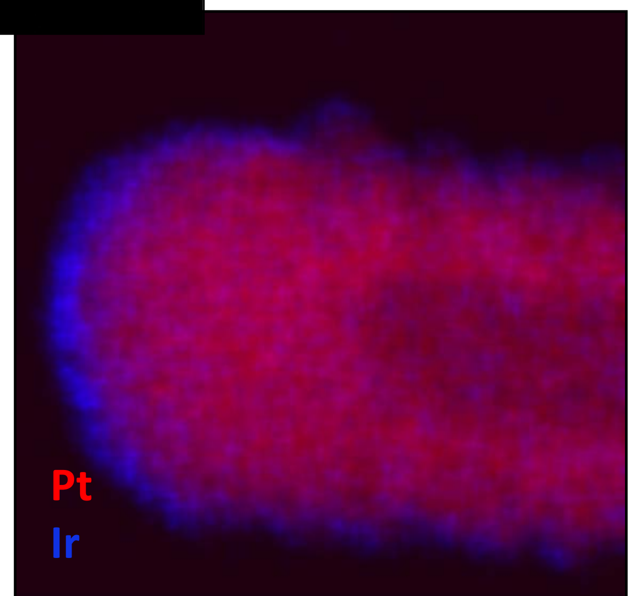
Ti-Ir Series: TEM of NSTF Pt w/ Ti- 2 $\mu g/cm^2$, Ir- 4 $\mu g/cm^2$

Both Ti and Ir are clearly observed on the Pt surface, as a thin layer



- Ti/Ir “nanocrystalline” layer observed on surface of Pt “cap” and ~50nm down sides of Pt/NSTF
- Thickness of Ti/Ir layer ~4-5nm (2X thicker than Ti/Ru/Ir layer; slides 18&19)

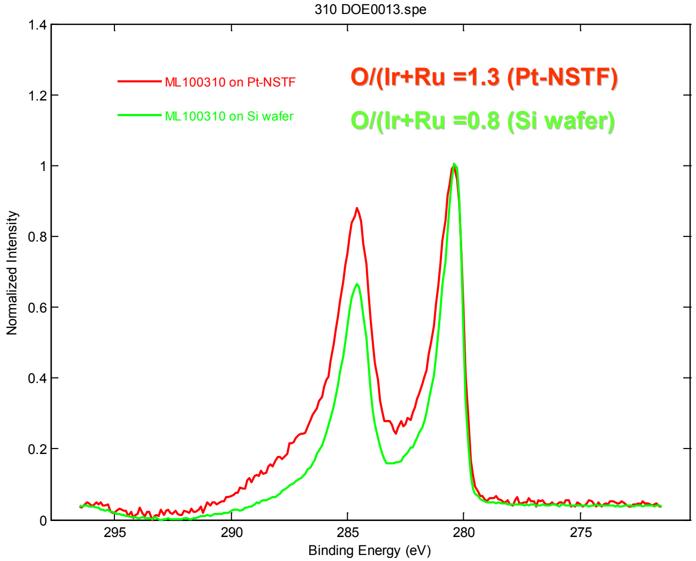




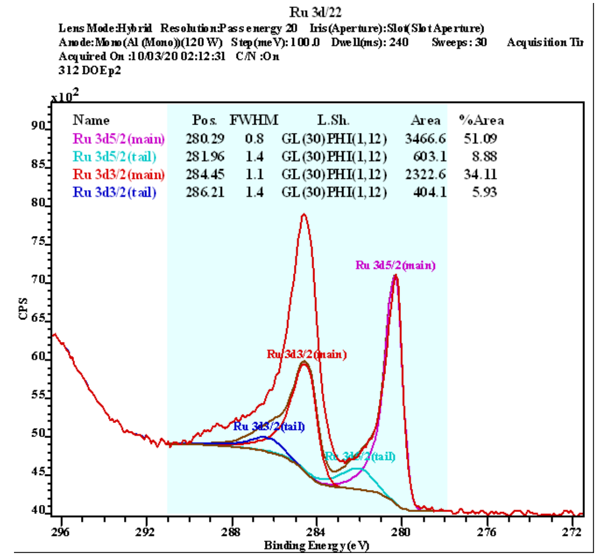
100128Pt-Ti/Ir

XPS: Rigorous curve-fitting procedure for Ru and Carbon

Overlapped Ru 3d-C 1s core level photoemission for Si wafer and Pt-NSTF substrates



Curve fitting analysis step of Ru 3d-C 1s core level photoemission including Ru 3d contribution only



Curve fitting analysis of Ru 3d-C 1s core level photoemission for ML100310-1 on Pt-NSTF and Si wafer