Durable Catalysts for Fuel Cell Protection during Transient Conditions

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DOE/3M Award DE-EE0000456

**2014 DOE Hydrogen and Fuel Cells Program
and
Vehicle Technologies Program Annual Merit Review**

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Project ID: FC006

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Overview

Barriers

Electrode Performance: Catalyst durability under

• **start-up & shut-down** (**SU/SD**) estimated at ~ 4,000 events and

• **cell reversal** (**CR**) estimated at ~ 200 events

Timeline

• Project start date: August 1, 2009

• Project end date: June 30, 2014

• Percent complete: >90% (03/2014)

Budget

Total: $ 5,382,165
- Contractor Share: $ 1,156,433
- DOE Share: $ 4,625,732
        (additional $ 400K to ORNL)

3M (Project lead)

Partners/Collaborators

• **AFCC** (Subcontractor)
  – **Independent evaluation, Short-stack testing, Ex-situ/in-situ characterization, Integration, Fundamental understanding**

• **Dalhousie University** (Subcontractor)
  – **High-throughput catalyst synthesis and basic characterization**

• **Oak Ridge National Lab** (Subcontractor)
  – **STEM Characterization**

• **Argonne National Lab** (Subcontractor)
  – **XAFS, Stability Testing, Selective ORR Inhibitor**

Funds spent (3/2014): $ 5,121,459
(including ORNL cost-share)

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Objectives and Relevance

Objective:

Develop catalysts that will enable PEM fuel cells systems to **weather the damaging conditions** in individual fuel cells during transient periods of **fuel starvation**, thus making it possible to satisfy **2015 DOE targets** for catalyst performance, **PGM loading**, and **durability**.

Relevance:

Fuel starvation could result in high positive voltages at the cathode during **start-up/shut-down (SU/SD)** or, at the anode, during **cell reversal (CR)**. This project will develop a catalyst that **favors the oxidation of water over the dissolution of platinum and carbon** at voltages encountered beyond the range of normal FC operation and beyond the thermodynamic stability of water (> 1.23 V).

Approach:

Materials based, as such, **protection is provided from within** the MEA and is therefore **always "ON"**.

Implementation:

Via **two catalyst material concepts**:

1. **Catalysts with high oxygen evolution reaction (OER) activity**
   i. At the **cathode** for **SU/SD**
   ii. At the **anode** for **cell reversal**

   OER-Cathode-SU/SD
   OER-Anode-CR

2. **Anode** catalysts with **low oxygen reduction reaction (ORR) activity for SU/SD**

   ORR Suppression-Anode

Evaluation:

- Lab-scale for material development (50 cm^2)
- **Scale-up to *full size CCMs*** (>300 cm^2)
- **Short stack integration and *"real life"* testing with AFCC test protocols** (*specifics on next slide*)

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Approach/Milestones

Task 1: OER Active Catalyst	# of Cycles (>)	(<)	PGM (mg/cm^2) (<)	End Voltage (<)	ECSA Loss (%)	Status/Comments
SU/SD (Cathode)						
2011	5,000		0.095	1.60 V	12%	Achieved 09/2011
Go/No Go	5,000		0.090	1.60 V	10%	Achieved 01/2012; End Voltage: 1.48 V
2013	**5,000**		**0.088**	**1.45 V**	**10%**	**Achieved** 11/2012; End Voltage: 1.44 V
Cell Reversal (Anode)						
2011	200		0.050	2.00 V		Achieved 09/2011
Go/No Go	200		0.045	1.80 V		Achieved 01/2012; End Voltage: 1.65 V
2013	**200**		**0.037**	**1.75 V**		**Achieved** 11/2012;End Voltage: 1.62 V

Task 2: Suppression of ORR (Anode)

Go/No Go	A factor of 10 in the kinetic region	Achieved 01/2012; A factor > 100
2013	A **factor of >100** in the kinetic region	**Achieved** 02/2013; A factor > 1,000

Task 3: Scale-up

2012	Scale up to full size cells (> 300 cm^2)	Evaluated in 2012: 10 short stacks
2013	**"Real life"** evaluation – AFCC	**9 x (3 or 15)-cells short stacks**

2013 - 14 Tasks: Mitigating the impact of gas switching on the OER catalyst stability

• **Root cause analysis and working hypothesis**

• OER catalysts modification: **composition and construction parameters**

• **Fundamentals** of modified **OER catalysts activity** and **stability**

Milestone: After 200 Gas Switches(GS) 10 hours at – 0.2 A/cm^2 at < 1.7 V with < 35 mg/cm^2 PGM

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Accomplishments and Progress: 2013 – 2014
AFCC Stack Testing (based on 3M made CCMs)

	Item	Milestone Deliverable	Delivery Date	Planned Tests	Completed tests Sept, 2013
Task #1	a	Performance and reversal testing of NSTF anode with very low and very high OER loading (3 X 15 cell short stacks & 3X3 cell short stacks).	Initial data by Jan 2013	6	3
	b	CO tolerance and SU/SD testing of one of the stacks from "a"	Dec-13	2	1
	Item	Milestone Deliverable	Delivery Date	Total tests	Completed tests as of Sept, 2013
Task #2	a	Performance testing and SU/SD testing of one 15 cell stack with highly selective anode design	Mar-13	2	2
	Item	Milestone Deliverable	Delivery Date	Total tests	Completed tests as of Sept, 2013
Task #3	a	Baseline performance testing of a 15 cell stack with a dispersed anode design	Jan-13	1	1
	b	Testing results data for 4 x 15 short cell stacks. Tests include: Performance (hot operating conditions, normal operating conditions, warm-up operating conditions). Hydrogen concentration sensitivity	Initial data by Jan 2013	4	2
	c	One reversal tolerance test based on a stack from 'b'	Dec-13	1	0
			Subtotal	16	9

Main Findings
➢ Good HOR activity down to **0.02 mg/cm² Pt** (under most conditions)
➢ **>0.015 mg/cm² Ir** required for satisfactory reversal performance
➢ Reversal tolerance loss after **gas switching from air to hydrogen**

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Mitigating the Effects of Hydrogen – Air

1. Root cause hypothesis

1. High electrode potential: - the GS does not provoke a high **anode** potential (~ 1 V under air)
   - OER catalyst is stable up to 1.75 V.
2. Hydrogen-air direct recombination on the *anode catalyst:*
   - On platinum the reaction is vigorous: produces *heat and a variety of radicals*
   - OER-Pt/NSTF construct provides *atomic proximity* of OER catalyst to Pt reaction sites
   - *Admixed* IrRu catalyst with dispersed Pt did not lose much of its performance due to GS

2. Diminishing gas switching impact: The approach

The strategy

1. Slow down the rate of $H_2 + O_2$ reaction by *blocking Pt active sites* to inhibit O_2 adsorption
2. Distance Ir from Pt - place *interlayer between Pt and Ir*

The concept

- material-based as is the OER modified anode
- fits into the philosophy of a protection from within the MEA and as such is always 'on'

Materials requirements

- *stable* when exposed to high potentials during cell reversal
- implementing an amount *sufficient to inhibit* the $H_2 - O_2$ reaction *without compromising HOR*
- manufacturing via processes compatible with the existing OER anode fabrication
- adding little, preferably *not at all*, to the *PGM* loading

Zirconium used as a **model system**

Ir Stabilized   H₂ transport inhibition

Ir separated from heat generation

$H_2 + O_2$
↓
$H_2O + Heat$
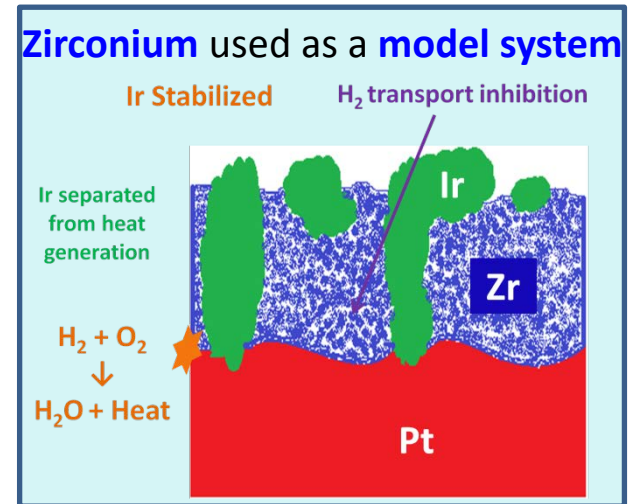
Four 'refractory metals' as stabilizing layer

❑ **Inexpensive** compared to the PGMs
❑ Can be **sputter-deposited** in vacuum

Experimental Protocol

1. Anode Evaluation + Conditioning (14 TC)

2. ORR performance

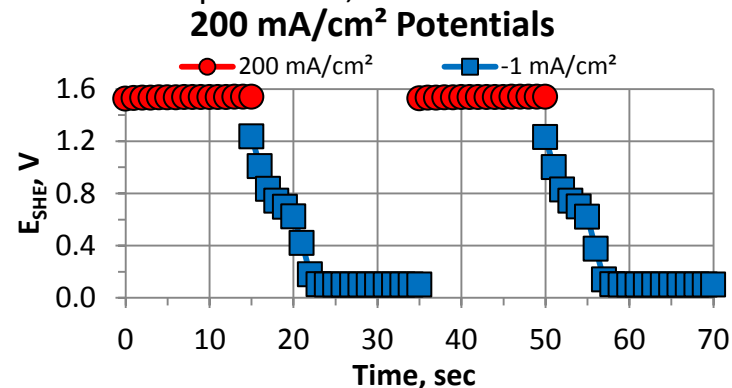3. Low current reversal pulses (12 & 44 mA/cm², 60 & 30 sec, 20 pulses)[1]
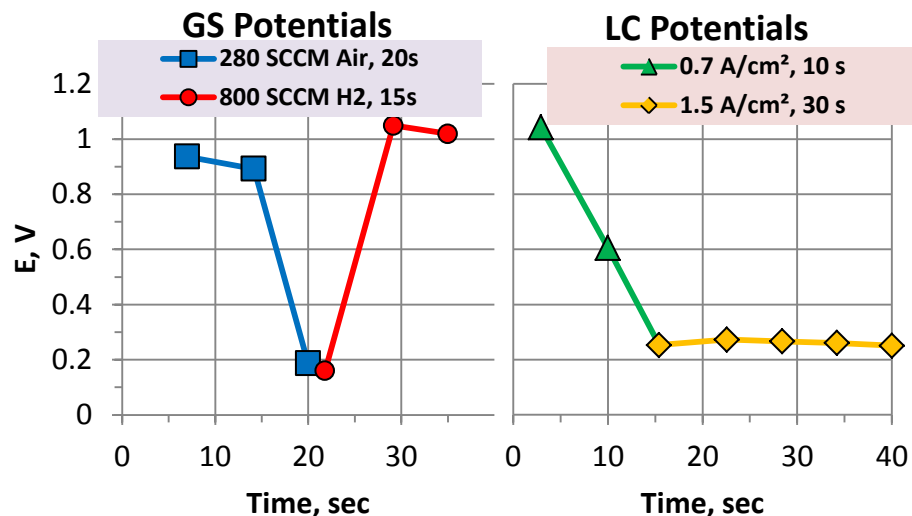
   ❑ 30 sec, -1 mA/cm²

12 and 44 mA/cm² Potentials
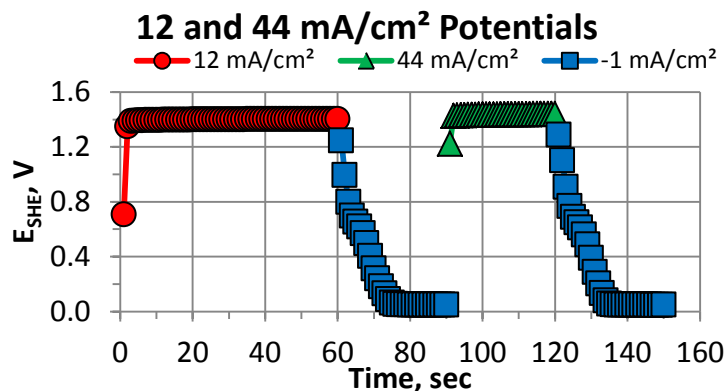
4. High current reversal pulses (200 mA/cm², 15 sec, 200 pulses)[1][2]

   ❑ 20 sec, -1 mA/cm²

   ❑ DOE requirement, 1.7 V

200 mA/cm² Potentials

5. 200 Gas Switch (GS) and Load Cycle (LC)

   ❑ "Real life" degradation experience

GS Potentials / LC Potentials

6. **Most rigorous test: combined/consecutive LC + GS (LCGS)**

7. High current reversal hold (200 mA/cm²)[1]

   ❑ Extended reversal durability (2.2 V, up to 10 hrs)

Extended tests include:

   ❑ 2,000 LCGS

   ❑ Counter Electrode: Air

   ❑ Extended Reversal time >10 hrs

[1]70 C, A/C N$_2$/1% H$_2$@1,000 SCCM, 110% RH

[2]Evaluation of HOR performance and ECSA are made between most step.

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CCM Evaluation

- **Catalysts Depositions** (Andy, Armstrong, 3M)
  (>60, 5 ft each)
- **CCM Testing** (Jimmy Wong, Theresa Watschke, 3M)
  (>200, 50-cm^2 FC)

Impact of Layer Thickness: Zr

Layer thicknesses are per geometric surface area; Actual thicknesses on NSTF are smaller

200 mA/cm² Reversal
20 µg/cm² Pt + 15 µg/cm² Ir

Legend:
- Baseline
- 50 Å Zr
- 75 Å Zr
- 100 Å Zr
- 150 Å Zr
- 200 Å Zr
- 250 Å Zr
- 300 Å Zr
- 350 Å Zr

After Cond | After 12&44 mA/cm² | After 200 mA/cm² | After GS 200
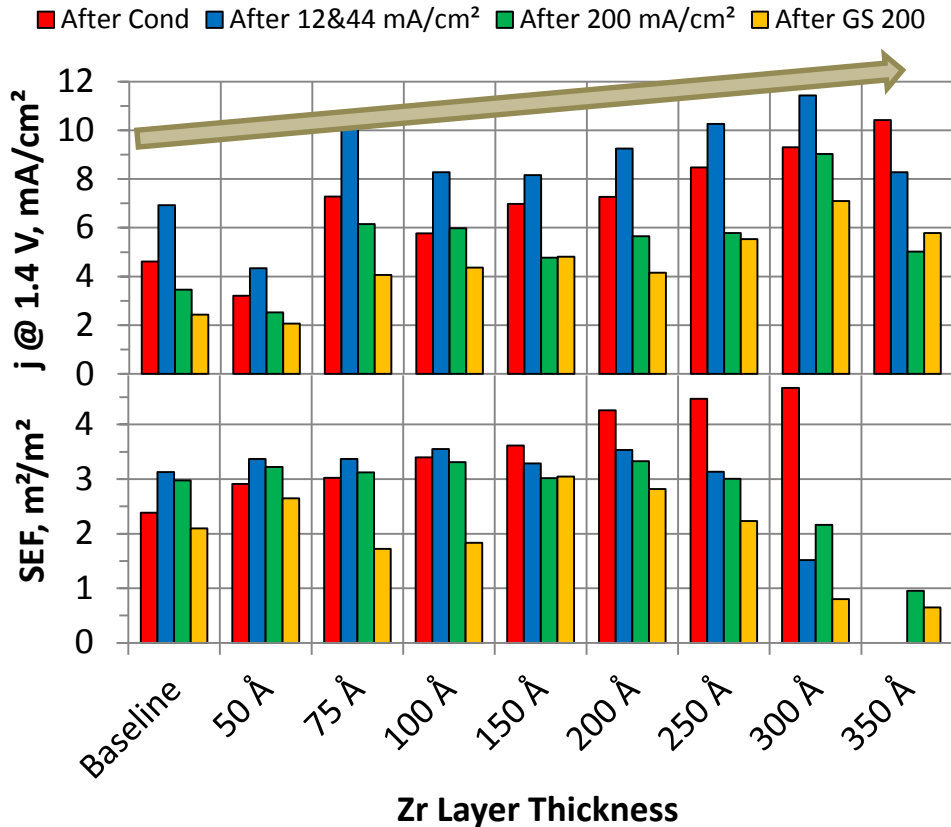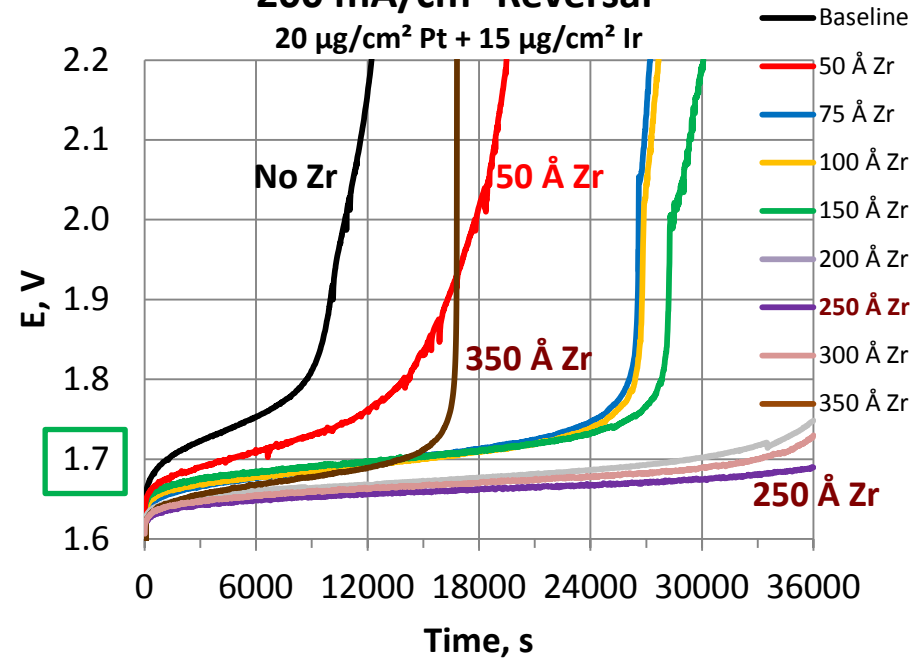
Addition of only 50 Å Zr already benefits cell reversal

Best reversal durability is around 250 Å Zr, 10 hours under the 1.7 V target

Durability starts to suffer at >300 Å Zr
Note: Graphs presented are representative of multiple CCMs

OER Activity increases with thicker Zr layer (up to 300 Å Zr)

Pt surface area follows similar trend

The Impact of Zr Layer Location

Reversal durability after GS of 20 µg/cm² Pt + 15 µg/cm² Ir

- Zr placed on same anode substrate in **3 different positions**: **T**op (PtIrZr), **S**andwich (PtZrIr), **M**ixed (PtZr(150 Å) IrZr Mixed(100 Å))
- Zr Thickness layer: 250 Å (100 Å and 150 Å for comparison)

200 mA/cm² Reversal
20 µg/cm² Pt + 15 µg/cm² Ir

Legend:
- 250 Å Zr T
- 100 Å Zr S
- 150 Å Zr S
- 250 Å Zr S
- 150 Å S + 100 Å M Zr

Zr on top | No Zr | Zr interlayer

E, V (y-axis: 1.6 to 2.2)
Time, s (x-axis: 0 to 36000)
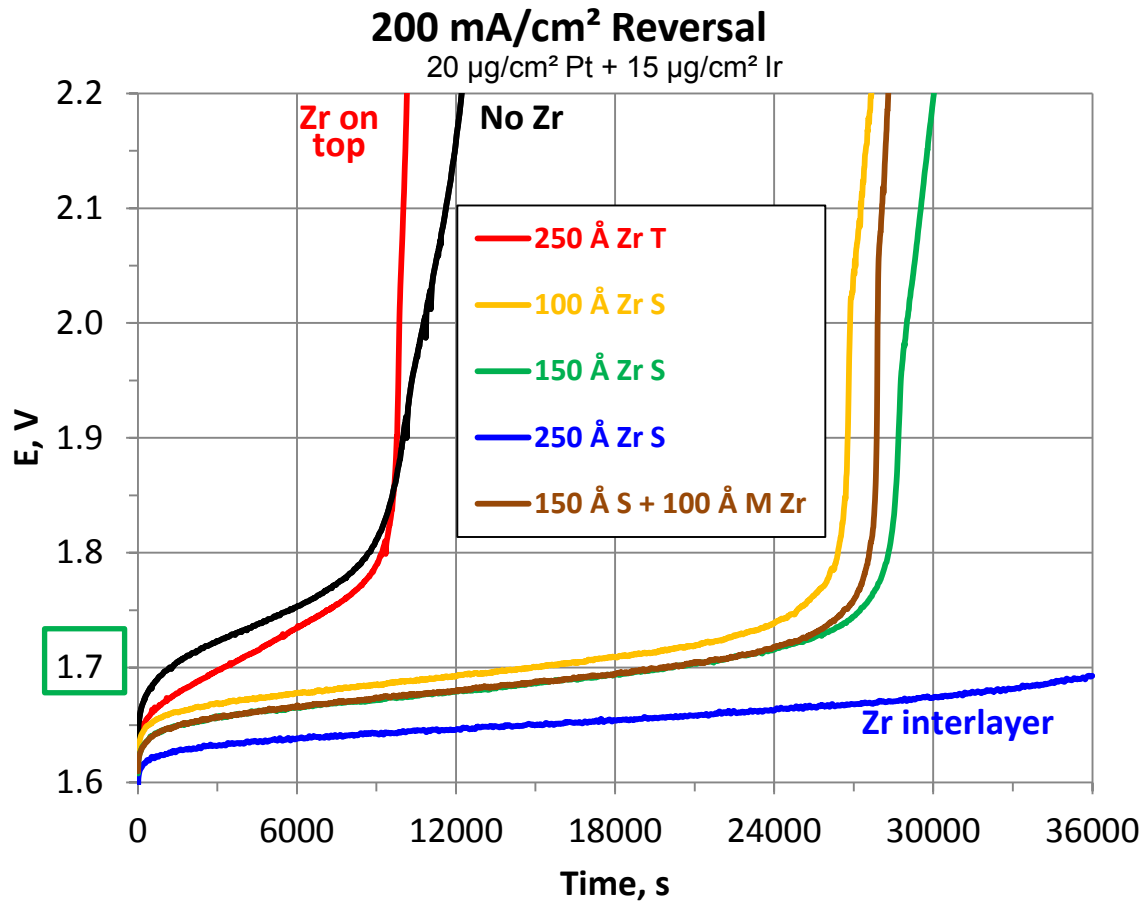
- The **placement of Zr** in the Pt, Ir, Zr catalyst is crucial

- Zr is most effective as interlayer between Pt and Ir, the **'S'** construction

- Zr had very little effect as a top layer , **'T'** construction

- '**M**ixed' Zr + Ir layer construct did not add any benefits

- **Separating Pt from Ir mitigates substantially the gas switch impact.**

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Comparison of Zr, Hf, Ti, Ta as Additives
- best of each class is displayed -

CR Durability after GS
20 µg/cm² Pt + M + 15 µg/cm² Ir

OER Activity

Pt Surface Area

HOR
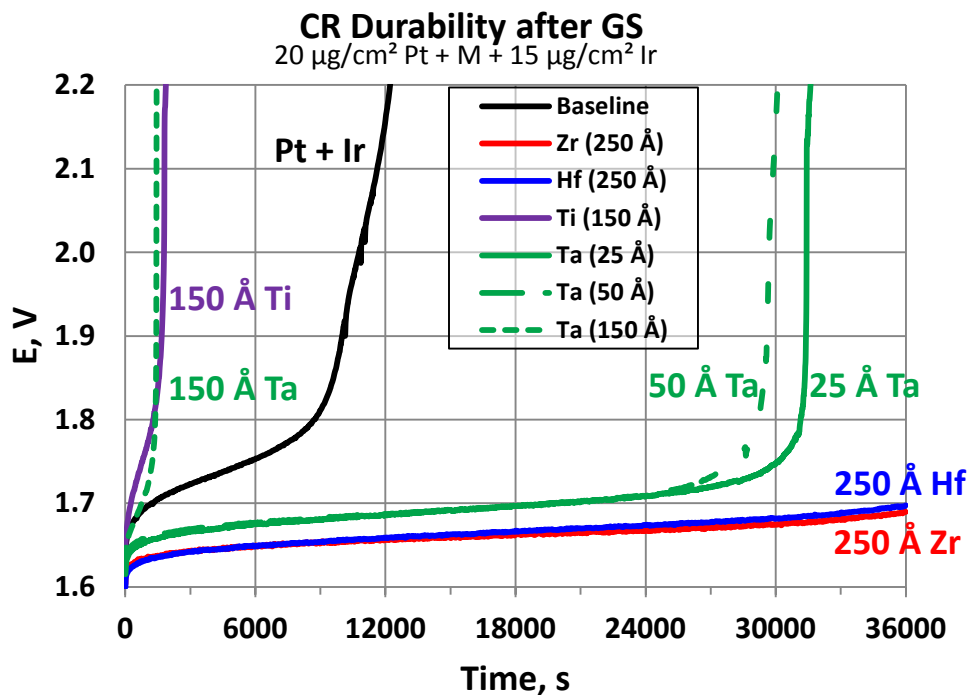
- **Zr** and **Hf** produce **superior** reversal durability and OER activity (within the DOE target).

- **Ta** best reversal is with only **25 Å** layer

- **Ti** inhibits the OER

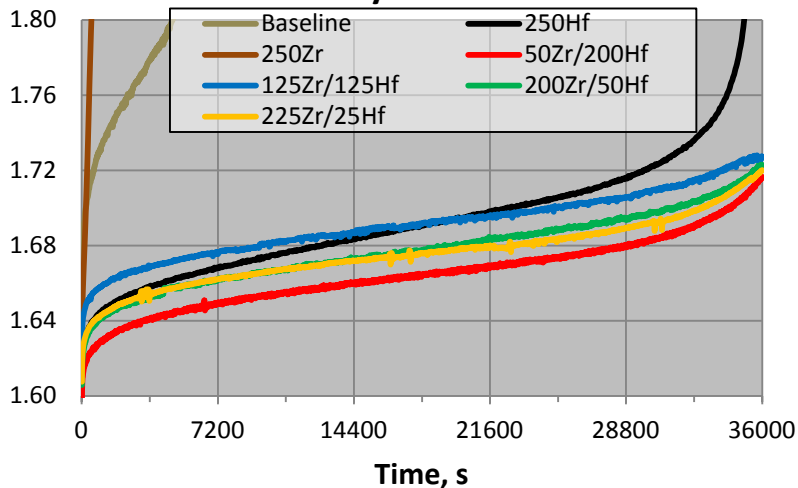- Hydrogen Oxidation Reaction (HOR) is within the margin of error

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11
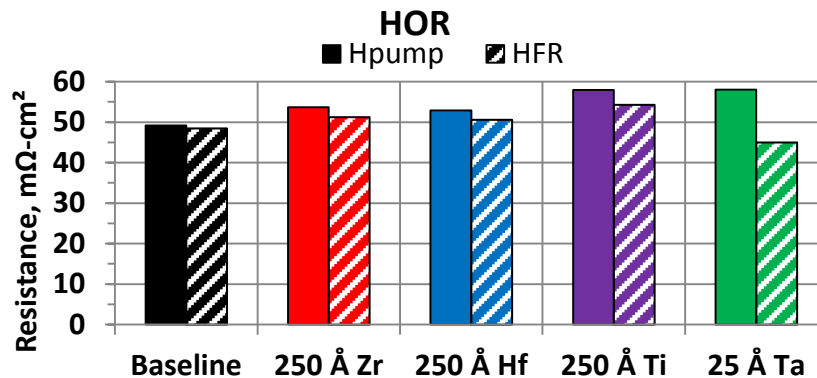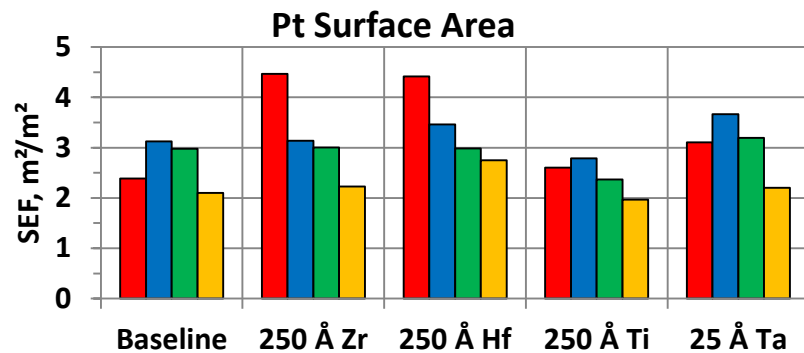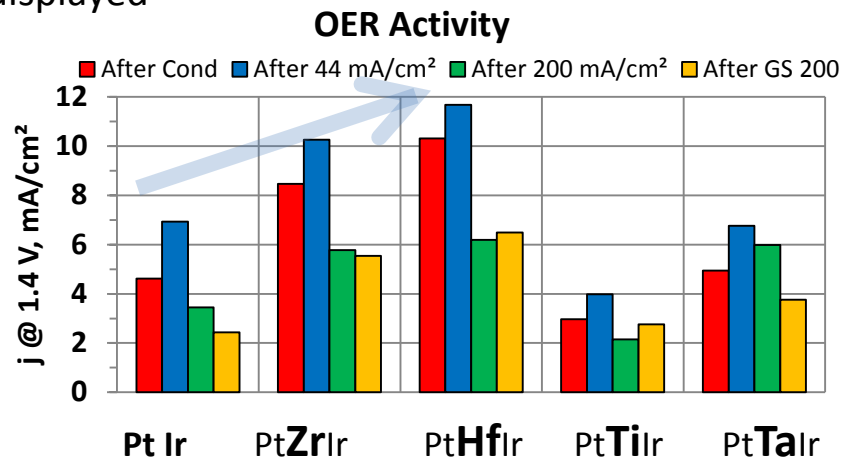
Impact of Combined Zr and Hf Interlayer
- tested under combine consecutive Load Cycle and Gas Switching (LCGS) -

CR Durability: Place of Zr & Hf

Legend: Baseline, 250Hf, 250Zr, 125Hf + 125Zr, 125Zr + 125Hf, 125Zr/125Hf, 125Hf/125Zr
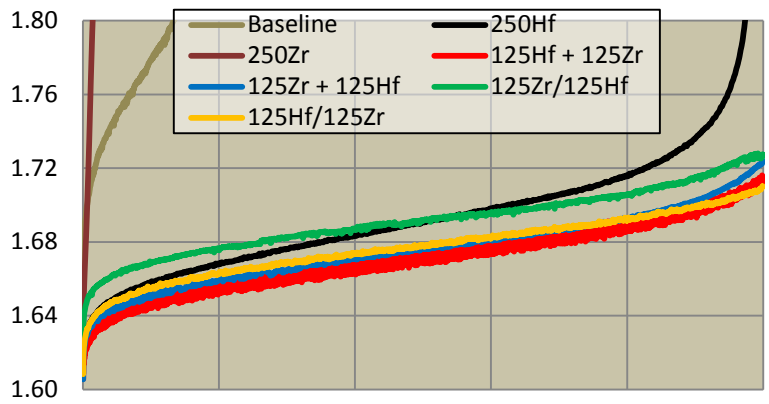
CR Durability: Ratio of Zr & Hf

Legend: Baseline, 250Hf, 250Zr, 50Zr/200Hf, 125Zr/125Hf, 200Zr/50Hf, 225Zr/25Hf

- Combined Zr and Hf, **Reversal tolerance after 200 LCGS cycles** increases above single additives.
- Effect of **Placement of Zr and Hf** in respect to each other within the interlayer is **minor**
- Wide range of **Zr/Hf ratios - 90/10 to 10/90** produces acceptable reversal tolerance.
- Pt surface area as well as OER activity are enhanced by Zr & Hf over baseline.

Legend: After Conditioning, After 44mA, After 200mA, After GS, After CR
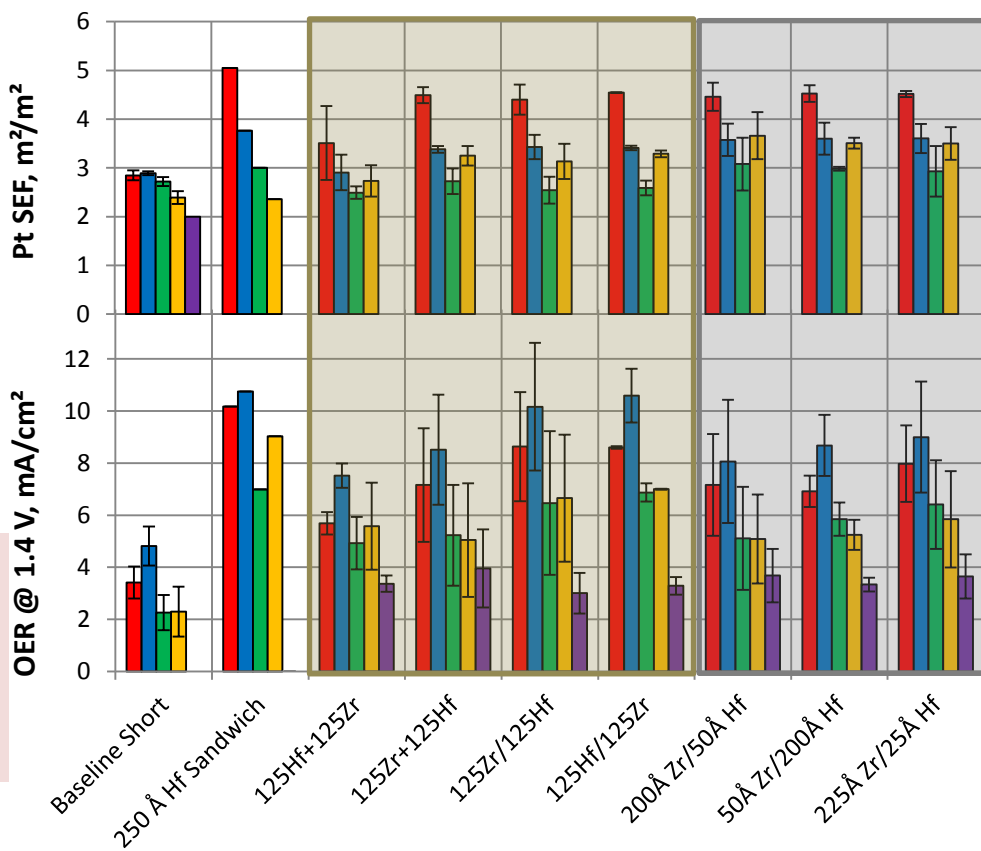
The wide range of Zr/Hf ratios and constructs within the **separating layer**:
- **Eliminates** the needs for use of **ultrapure** Zr and Hf in respect to each other
- Allows a wide **processing window**

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'Real Life' Application:

Testing with Cathode under AIR
Testing extended beyond 10 h milestone
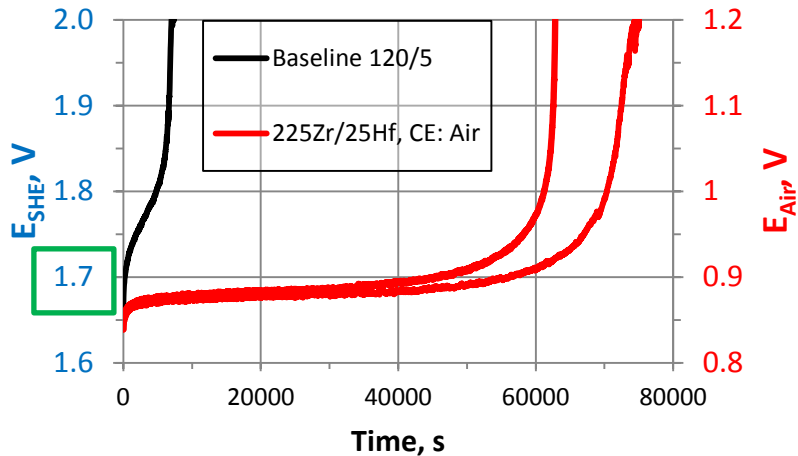
Impact of extended LCGS cycling
CR Durability after 2000 LCGS
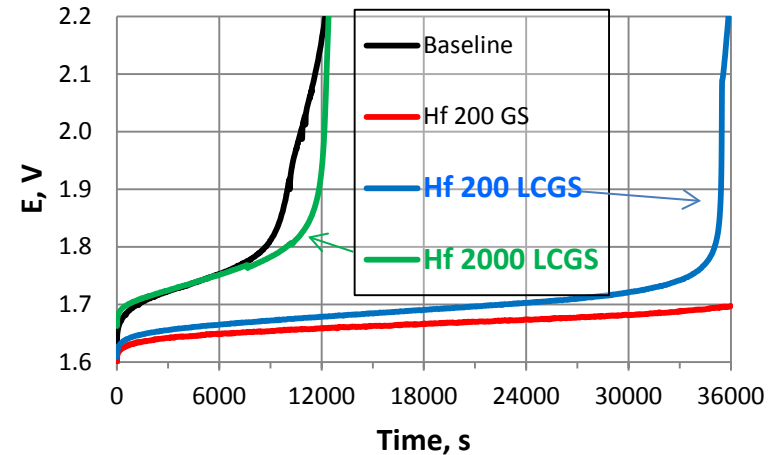
During reversal the cathode is under air rather than hydrogen (used in most of our evaluation on the counter electrode).

- There is no significant difference in the reversal durability, other than potential shifts, whether there was hydrogen or air on the counter electrode.
- The anode can endure an **additional 2 – 4 hours beyond the milestone 10 hours** at 1.7 V voltage limit and up to an additional 10 hours to the "real life" 2.2 V limit.

- With ten times more LCGS pulses, **2000**, the reversal tolerance is decreased by a factor of 3, yet to a respectable **3.3 hours**.

Fundamental Evaluation

- **XPS** (Liliana Atanasoska, 3M)
- **Cyclic Voltammetry** (Dennis van der Vliet, 3M)
- **EXAFS** (Debbie Myers, A. Jeremy Kropf, ANL)
- **STEM** (David Cullen, ORNL)

XPS: Ir, Zr, and Pt Concentrations and Oxide level as a Function of Zr Thickness

- As received samples -

Atomic Concentrations as a Function of Zr Thickness
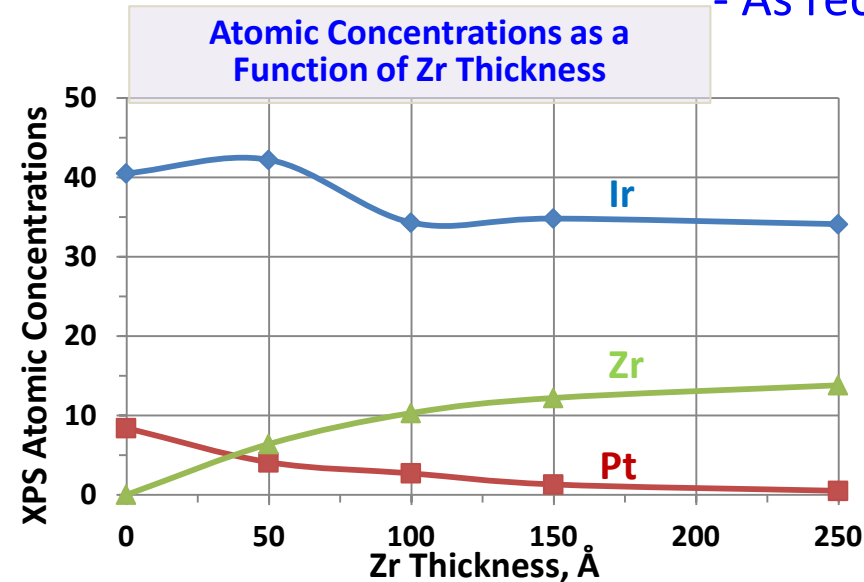
- **XPS** data are in agreement with **having Zr between Pt and Ir**

- **Ir level is constant** consistent with its position on the surface

- **Pt signal attenuates** with the increase of Zr layer thickness

- Zr 3d: Zr metal (~80%), Zr sub-oxide and ZrO_2
- O 1s: Growth of oxide oxygen
- No significant change in Pt 4f and Ir 4f core level spectra

Zr 3d and O 1s Core level spectra
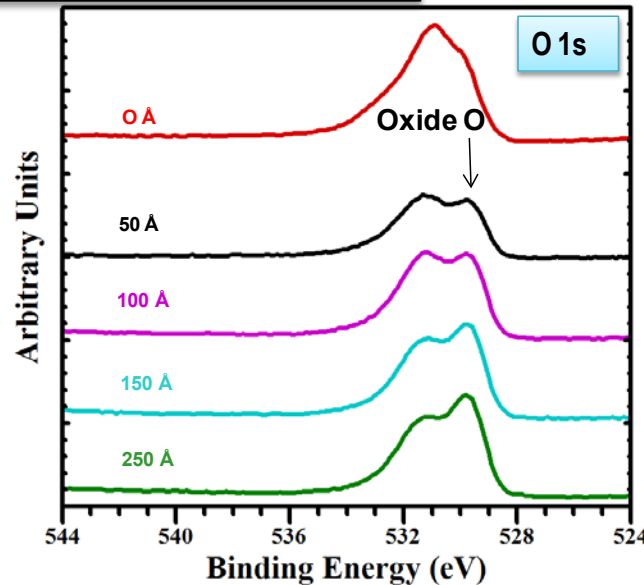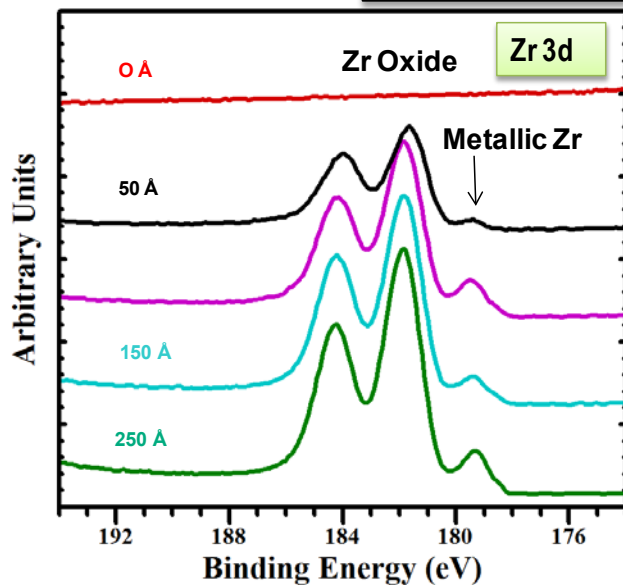
Hf deposit contains 3% at. of Zr
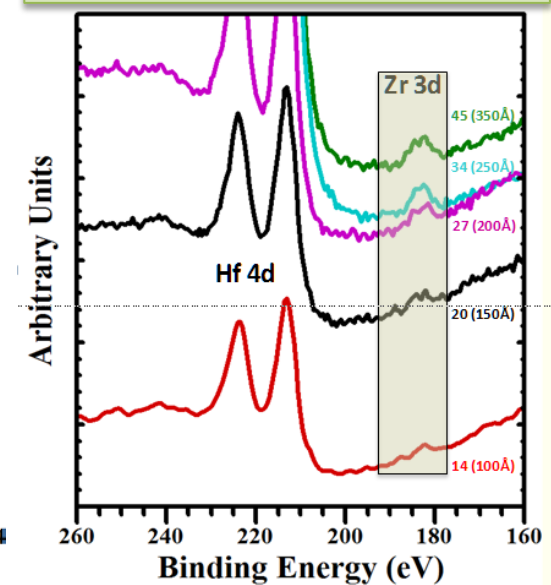
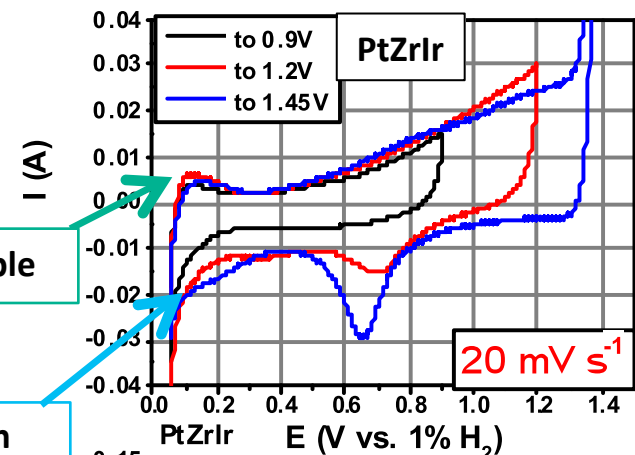# Stability of PtZrIr: Blank Cyclic Voltammetry
- Evaluated as CCMs -

o Larger PtOx reduction peak with Zr
  - Indicates **more Pt oxide is formed**
o IrOx reduction at slightly lower potential
  - **Stabilization of iridium oxide**
  - **H_{upd} is blocked** by the oxide.
  - Blockage is **reversible**
o Extensive scanning to 1.45 V **irreversibly** blocks the H_{upd}
  - this causes anode performance loss

Hf exhibits irreversible H_{upd} blockage, different than Zr
  - Stable in GS, but performance loss

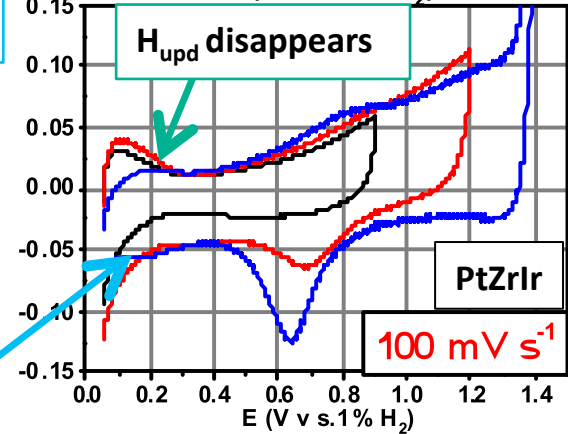**Stabilizing the Pt and Ir oxides is paramount in increasing OER catalyst durability.**
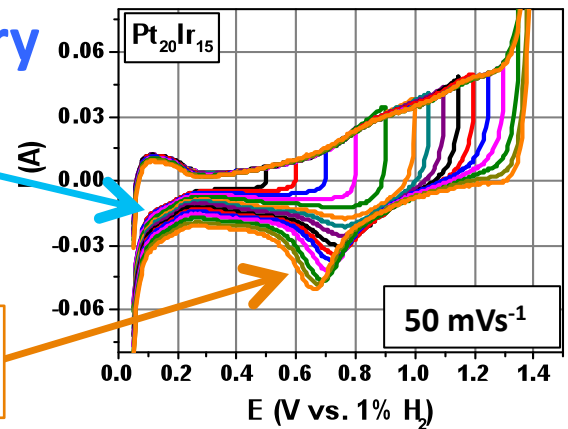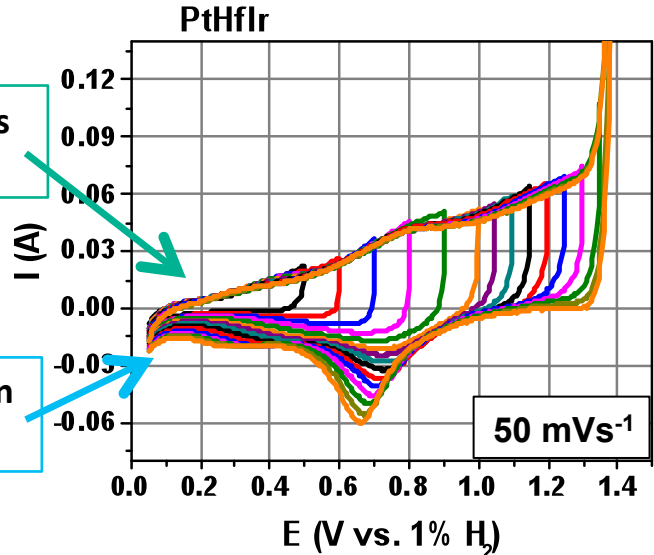

IrOx-reduction

PtOx-reduction

$Pt_{20}Ir_{15}$

50 mVs^{-1}

I (A)

E (V vs. 1% H$_2$)

PtZrIr

to 0.9V
to 1.2V
to 1.45V

Hupd stable

20 mV s^{-1}

I (A)

E (V vs. 1% H$_2$)

IrOx-reduction stable

PtHfIr

H_{upd} disappears irreversibly

IrOx-reduction still visible

50 mVs^{-1}

I (A)

E (V vs. 1% H$_2$)

PtZrIr

H_{upd} disappears

IrOx-reduction smaller

100 mV s^{-1}

I (A)

E (V v s.1% H$_2$)

Synchrotron Comparative Analysis Pt – Ir and Pt-Zr-Ir Catalyst
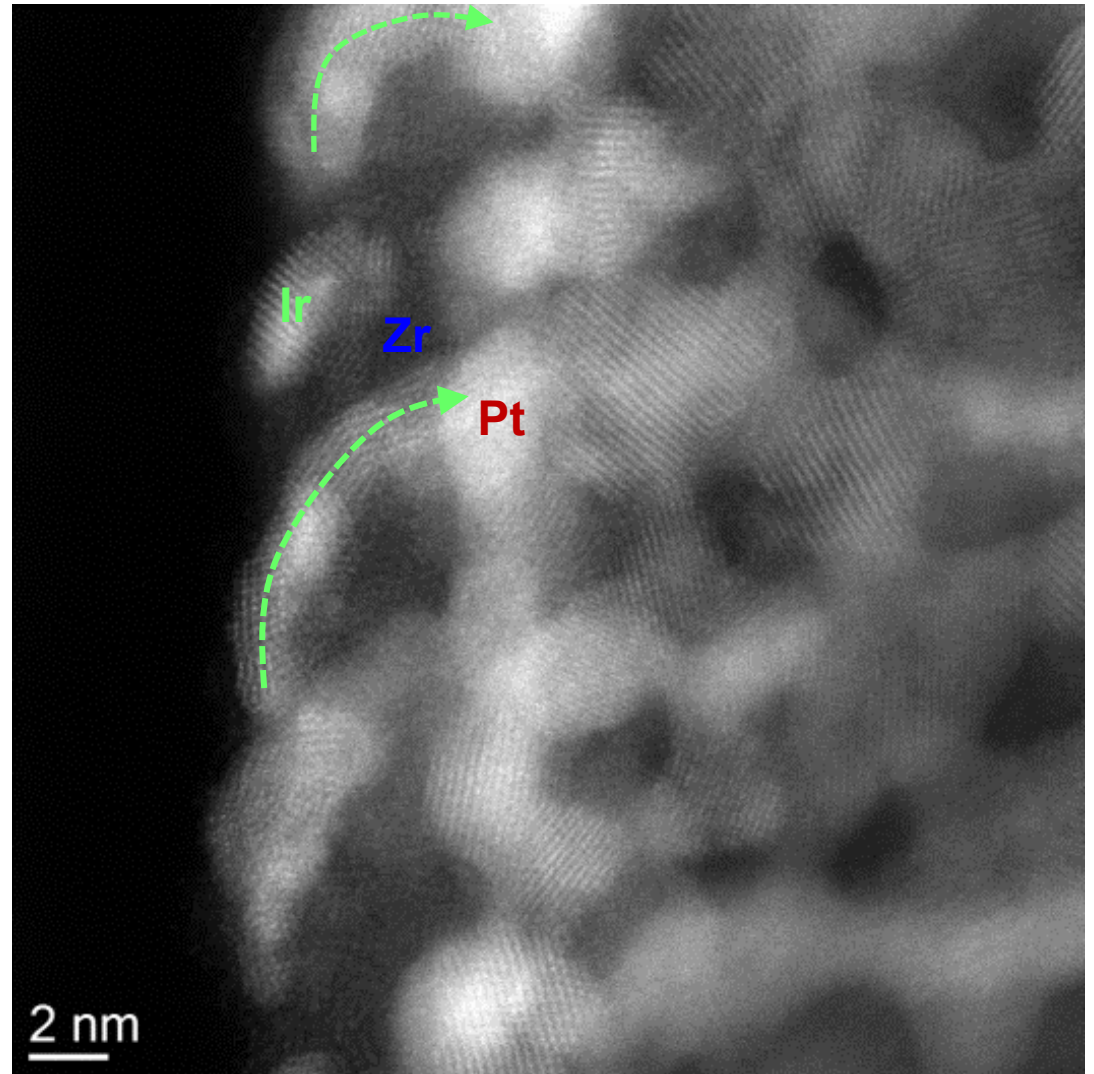## - Ir to Pt ratio at different stages of CCM testing -

- More Pt than Ir is lost from anode during conditioning of Pt-Ir and Pt-Zr-Ir

- Ir was lost from anode without Zr interlayer

- With Zr interlayer, anode retained Ir

- Supports hypothesis that Zr interlayer is maintaining anode activity by preventing loss of Ir

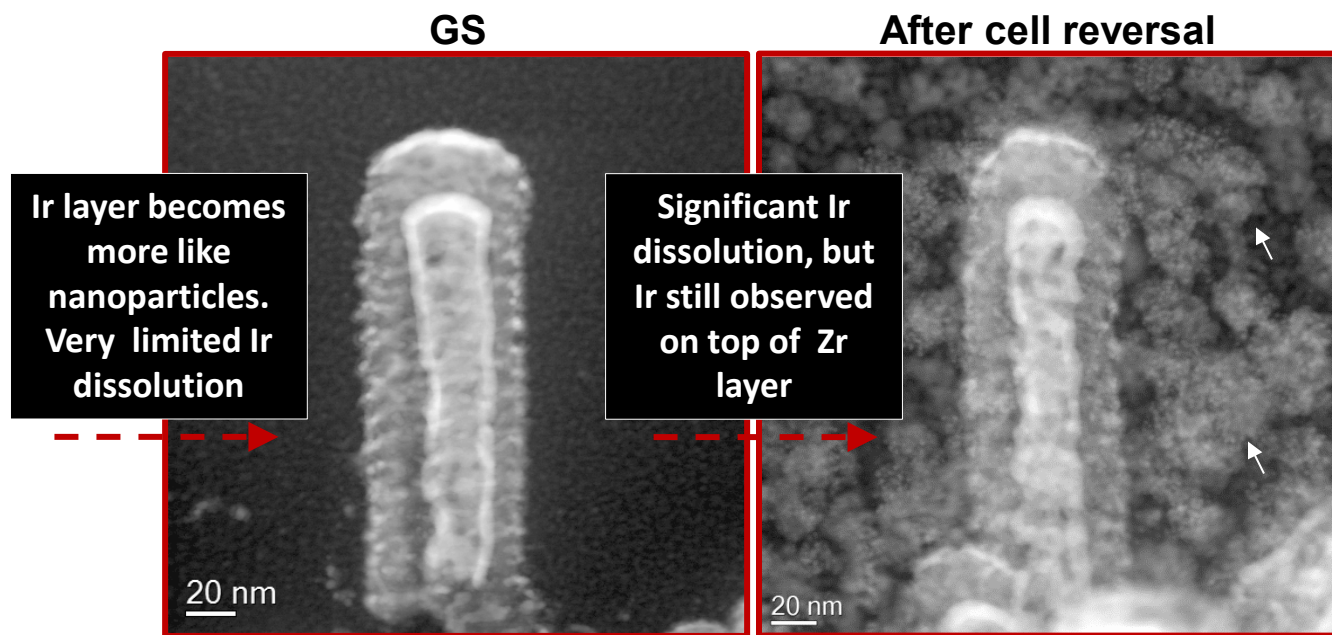Ir and Pt fluorescence acquired at 15 spots on anode

Argonne National Laboratory
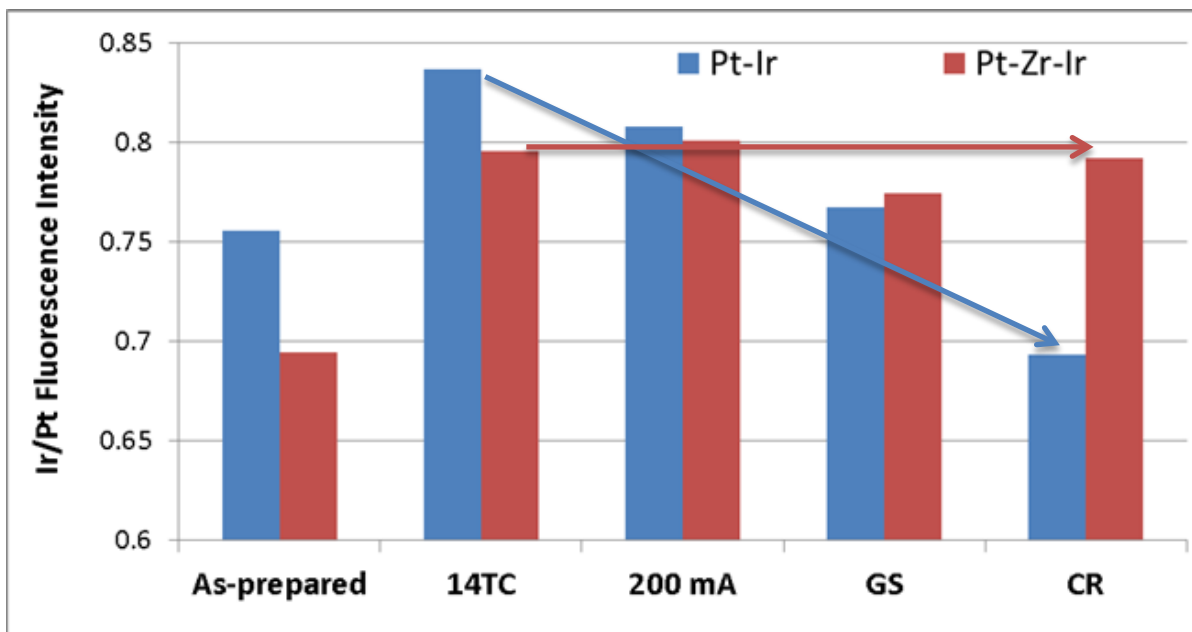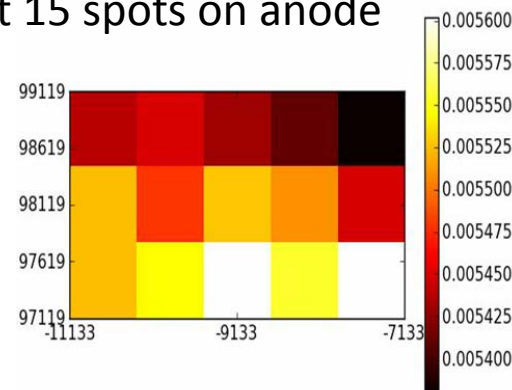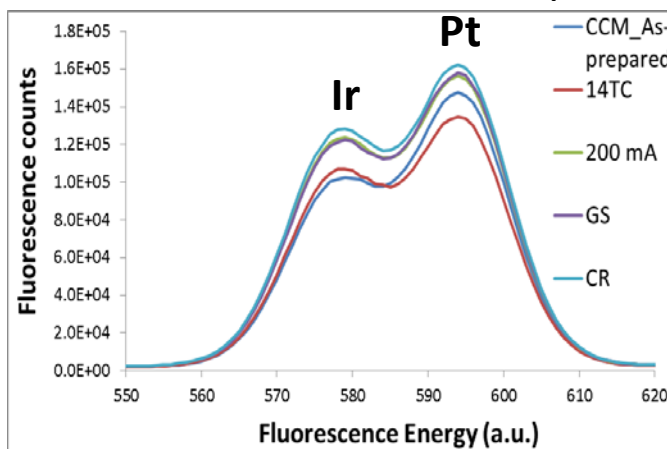
- Z-contrast STEM image of PtZrIr whisker surface in CCM before testing

- Ir, Zr(oxide), and Pt regions are labeled.
    - Interconnected network of Pt particles with regions of bare perylene-red
    - **Darker Zr(oxide) layer between Pt and Ir**
    - Bright **Ir "islands" on top of Zr layer**.

- Green arrows indicate regions where **Ir** and **Pt** layers appear to be in **physical contact** with each other.

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STEM: Catalyst Modifications during Testing

GS   **After cell reversal**

PtZrIr

Ir layer becomes more like nanoparticles. Very limited Ir dissolution

Significant Ir dissolution, but Ir still observed on top of Zr layer

PtIr

Additional Ir dissolution observed

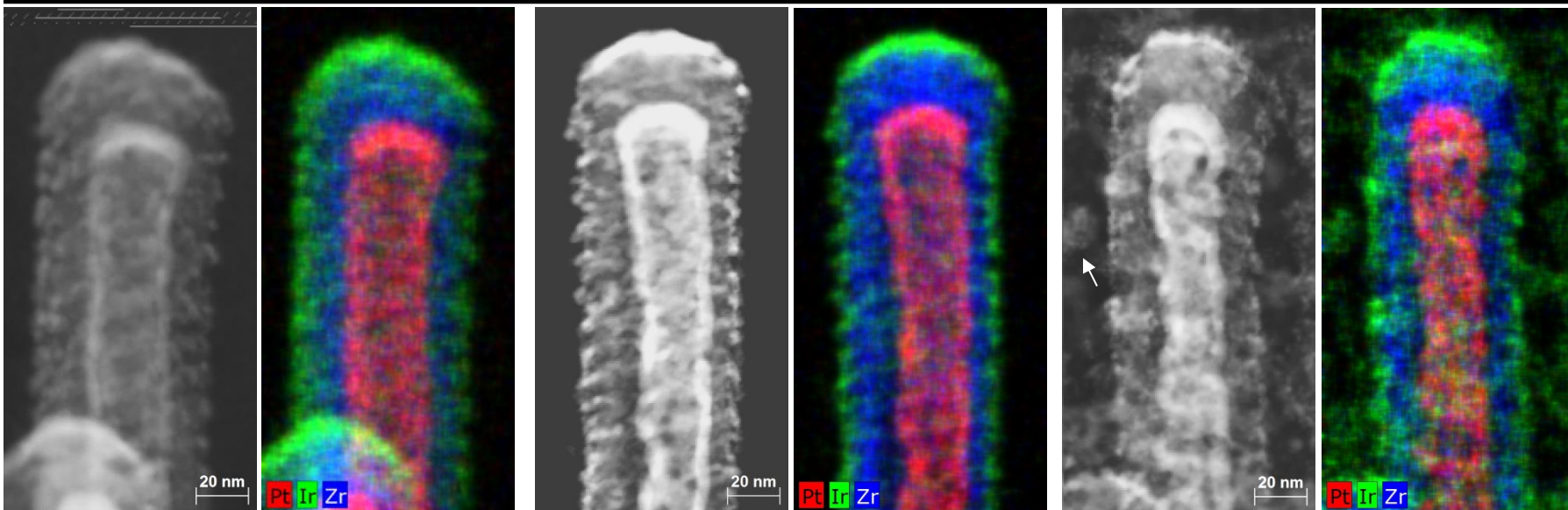Complete or nearly complete Ir dissolution

20 nm

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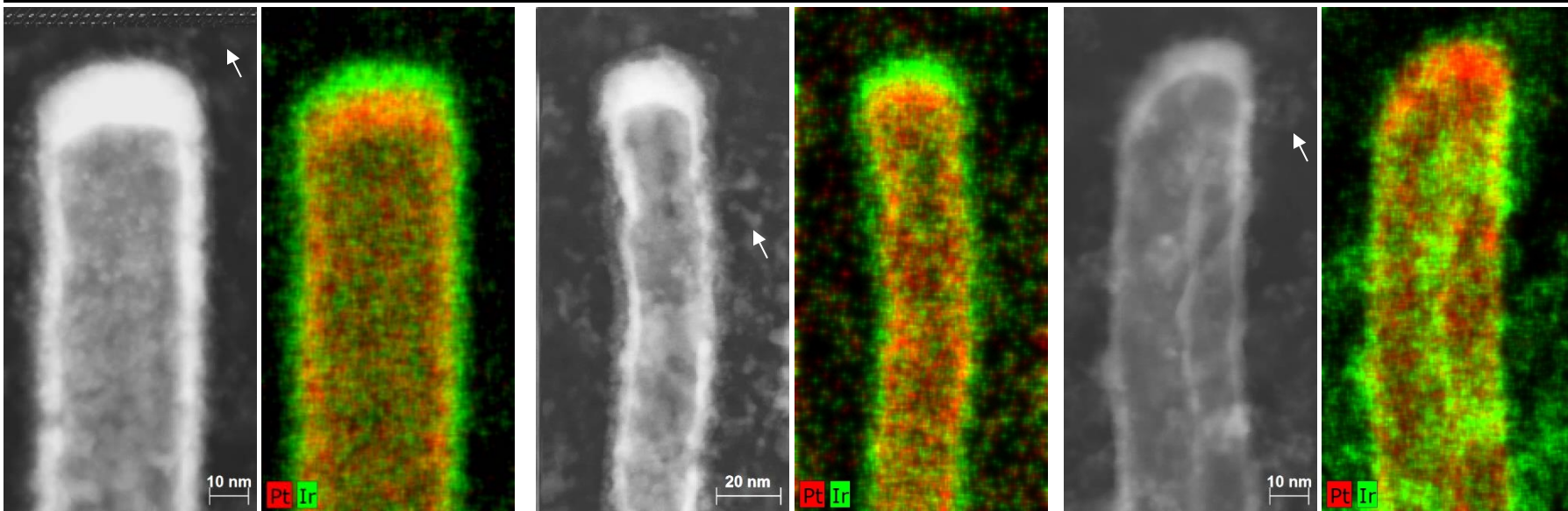**200 mA/cm²** **GS** **After cell reversal**

Ir on surface throughout test, significant loss only observed after cell reversal, still see some Ir on surface
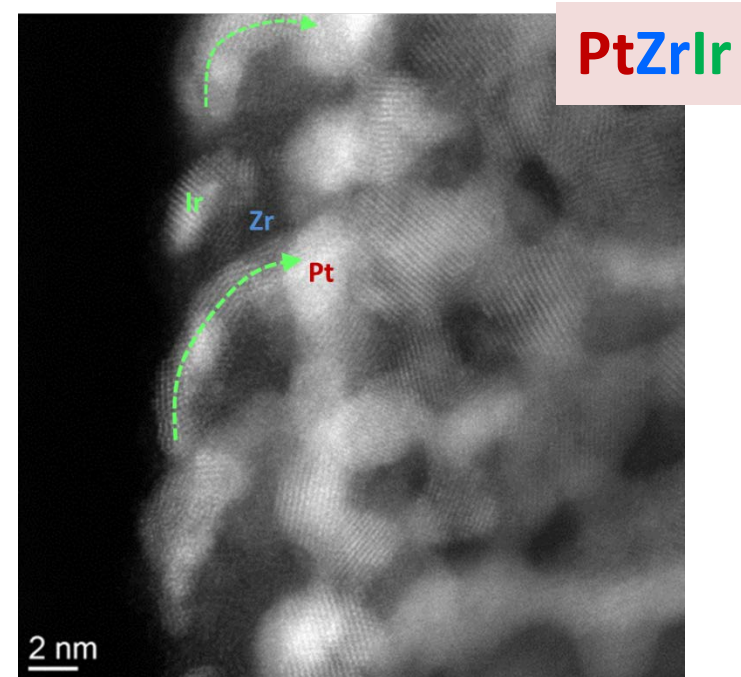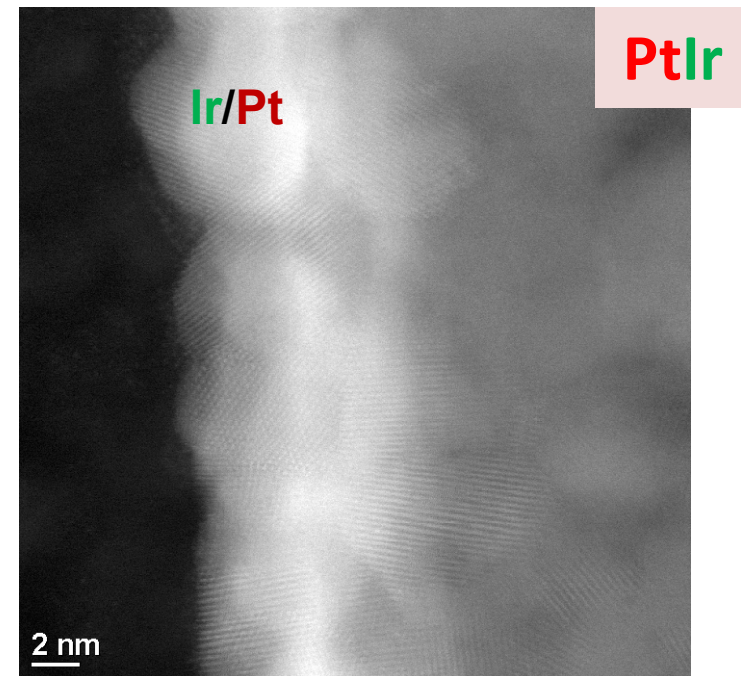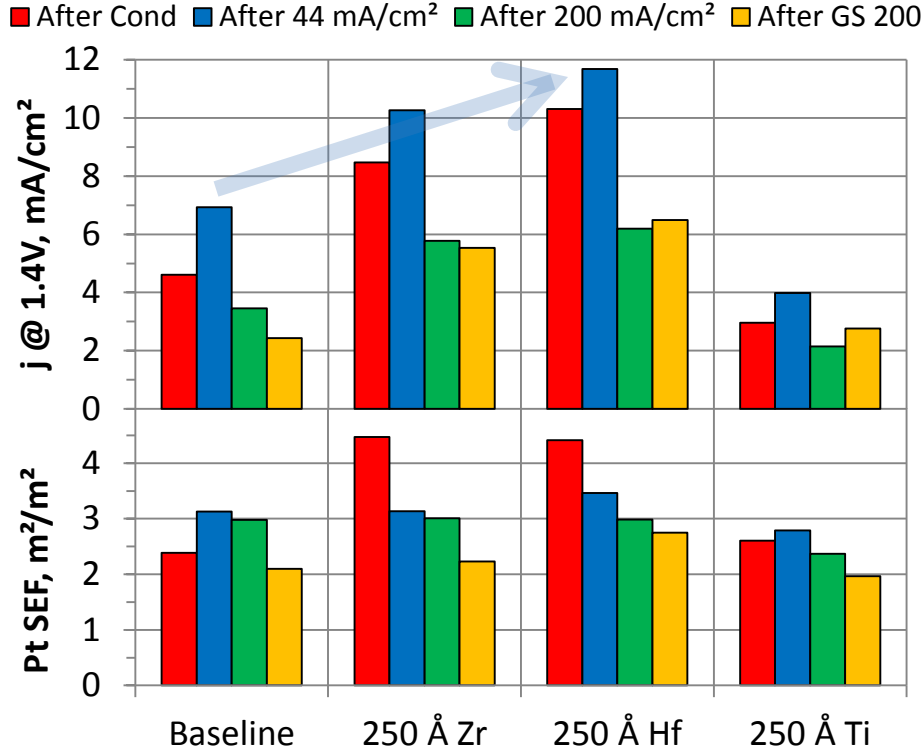
PtZrIr

Ir losses begin at 200 mA, continue during GS and Cell Reversal, complete or nearly complete loss observed

PtIr

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Structure-Performance Relationships

- As received samples -

Legend: ■ After Cond ■ After 44 mA/cm² ■ After 200 mA/cm² ■ After GS 200

y-axis (top): j @ 1.4V, mA/cm²
y-axis (bottom): Pt SEF, m²/m²
x-axis: Baseline, 250 Å Zr, 250 Å Hf, 250 Å Ti

PtIr — Ir/Pt — 2 nm

PtZrIr — Ir, Zr, Pt — 2 nm

Differences in **Ir morphology may relate to improved surface area and OER performance of PtZrIr**

- PtIr: **Ir grows epitaxially on Pt**, the two catalyst are indistinguishable in Z-contrast images.
- PtZrIr: **Ir grows in crystalline "islands" over ZrOx**

Collaboration

Partners

- **AFCC** (Subcontractor):
  - **Independent evaluation, Short-stack testing, Ex-situ/in-situ characterization, Component integration, Fundamental understanding**

- **Dalhousie University** (Subcontractor)**:**
  - **High-throughput catalyst synthesis and basic characterization**
  - **Fully integrated since its inception, during the proposal phase**
  - **It runs as one single program**
  - **Results reviewed during weekly scheduled teleconferences and many more unscheduled contacts between participants.**

- **Oak Ridge National Lab** (Subcontractor)**:**
  - **Fully integrated, provides invaluable feedback and insight into the OER catalyst**
  - **STEM and EDS analysis fully synchronized with catalyst development**

- **Argonne National Lab** (Subcontractor)**:**
  - **EXAFS characterization and OER catalyst stability**
  - **ORR suppression on anode**

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Reviewers' Comments

Reviewer: Utilizing **AFCC** to provide gas switching under real-world conditions **allowed for discovery of issues** at low OER catalyst loadings that were not observable under simulated conditions
PI: In the lack of firm DOESUSD targets, OEMs inputs, **AFCCs in particular**, played a **crucial role in orienting** this project towards the 'real world' application.

Reviewer: The approach would prove **more universally valuable** if also applied on **non-corrosion resistant** electrodes such as **dispersed catalysts on carbon**
PI: Within the stability limit of the support, it **can be done only for SUSD** by suppressing the ORR on the anode. Not for cell reversal where the potential is > 1.7 V.

Reviewer: The gas switching and OEM **cycling protocols** would be especially important **to disclose**
PI: We have **disclosed all the lab procedures in details**. This program would benefit if OEMs do the same.

Reviewer 1:   ….**cost** of the catalyst may be **an issue**.
Reviewer 2:   ….that catalyst durability is improved and the **cost of the catalyst is kept low**
PI: We have been **decreasing the PGM loading throughout the project**. The 2014 additives are non-PGM.

Reviewer: these catalysts cannot be **"ready for real life" until NSTF is ready for real life**
PI: Fully **aware of and agree** with. 2014 additives got the OER anode one more step closer to real life readiness. In general, the many achievements of this **program have brought the NSTF the closest it has been to practical application.**

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Summary: Major Findings

- Constructs with additional refractory metals have fulfilled the cell reversal requirement after gas switching and /or gas switching with load cycling within the **2013 Program milestone voltage limit, < 1.7 V, and PGM loading < 0.037 mg/cm²**.
- **Hypothesis** that **separating the OER catalyst from atomic proximity of Pt may alleviate the impact of gas switching was proven.**
- Added benefit of the separating layer is the **improved OER activity**.
- Fundamental materials studies aimed at **understanding the extraordinary durability of the new OER-Pt/NSTF constructs have converged to concluding that** **stabilizing the Pt and Ir oxides is paramount to increasing reversal endurance**.

Future Work

and Challenges beyond the end of the Program

General:

- While cell reversal functionality can be achieved, the final OEM determination will be made based on HOR performance under **variety of extreme conditions**.
- While preserving all the positive attributes, OER/NSTF performance **should have no negative impact compared to a conventional dispersed anode.**
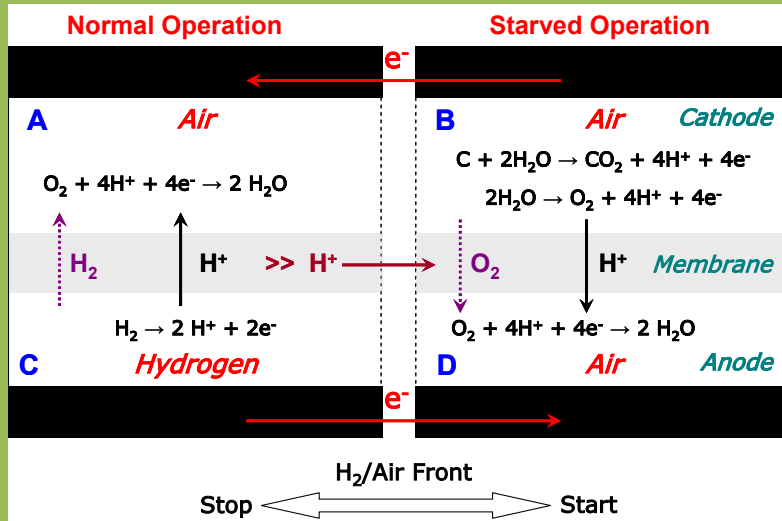
Specific:

- The **constructs** with a **separating layer** open up opportunities for use of **wider array of commercially acceptable materials** to address both the OER performance and the application issues in general:

  - attempt to reproduce the cell reversal data with **commercial grade interlayer materials**

- **Specific OEM requirements** can be more readily addressed by **the flexibility offered by the new constructs including the protection of carbon supported catalysts**.
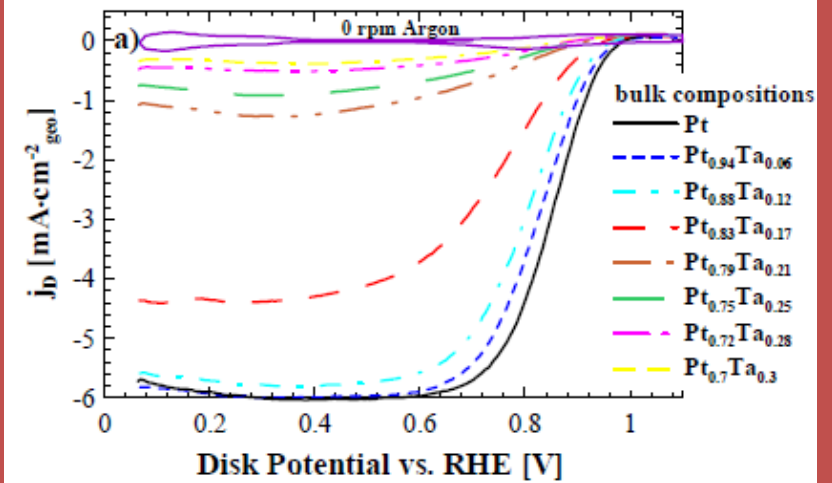
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Technical Back-Up Slides
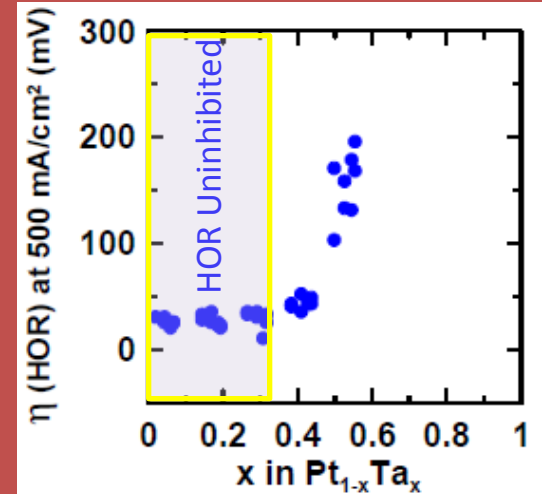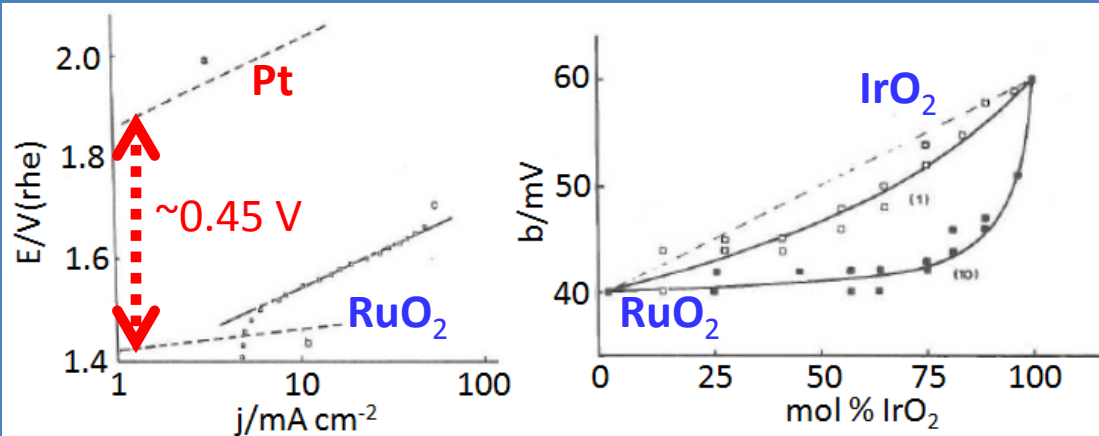
SU/SD and OER Catalysts Development Fundamentals

SU/SD Explained

Normal Operation | Starved Operation

A — Air — Cathode
$O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$

B — Air
$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

H_2 H^+ $>> H^+$ O_2 H^+ Membrane

$H_2 \rightarrow 2 H^+ + 2e^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$

C — Hydrogen
D — Air — Anode

H_2/Air Front
Stop ⟵ ⟶ Start

Basis for Task 2: ORR Inhibition

bulk compositions
Pt
$Pt_{0.94}Ta_{0.06}$
$Pt_{0.88}Ta_{0.12}$
$Pt_{0.83}Ta_{0.17}$
$Pt_{0.79}Ta_{0.21}$
$Pt_{0.75}Ta_{0.25}$
$Pt_{0.72}Ta_{0.28}$
$Pt_{0.7}Ta_{0.3}$

0 rpm Argon

Basis for Task 1: OER Catalyst

Pt

~0.45 V

RuO_2

IrO_2

RuO_2

HOR Uninhibited

Reversal durability after **400** mimicked **'life cycles'** **including Gas Switching** steps
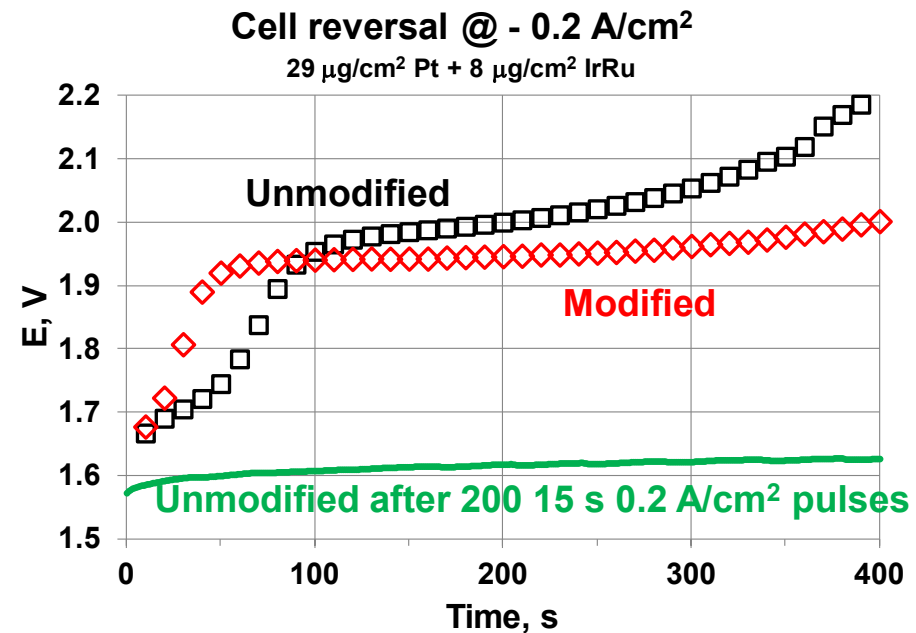
Standard 50 mg/cm² Pt + 15 mg/cm² IrRu and **Modified** OER catalyst show (3M lab test)

Standard

Modified

Legend: 25973, 26154, 26169, 26170
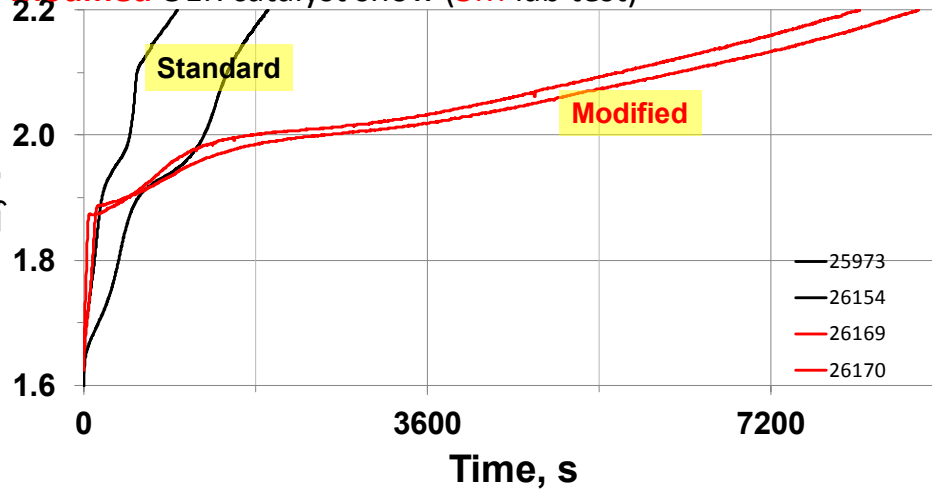
Modified OER catalyst shows **improved durability by a factor > 5**

Reversal durability after **200 Gas Switching** steps on Milestone 2013 PGM Loading

Modified OER catalyst show (3M lab test)

Cell reversal @ - 0.2 A/cm²
29 μg/cm² Pt + 8 μg/cm² IrRu

Unmodified

Modified

Unmodified after 200 15 s 0.2 A/cm² pulses

Gas Switching impacts significantly the inherent OER activity of IrRu. **Modification of the** OER catalyst for **improved durability is underway.**

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Stability correlation to blank cyclic voltammetry

Stability of additives – Zr/Au

- Insight in mechanism of stability increase by additives.
  - Evaluation of additive on Au NSTF elucidates the additive's basic fingerprint and stability in the cyclic voltammogram (CV)
  - Influence on OER stability probed by comparison with base composition of PtIr 20+15 µg/cm^2
- **Stability of oxides (Pt, Ir and additive) are the key in OER activity and stability**
 - Oxides that are too stable, however, will deactivate the HOR

Zr/Au Voltammetry at 70 °C

- Slight apparent increase in Au oxide feature at 1.4 V. No additional features created
- Extensive potential cycling at 2 mVs^{-1}
  - Redox feature at 1.4/1.1 V increases
  - Feature appears at 0.3 V
    - May be evidence of GDL degradation
- Post mortem analysis:
  - Gold has migrated from anode to membrane
  - Increase in oxide feature is likely a result of roughening
- **No Zr dissolution current spotted at any time**

Zr/Au, 20 mV s^{-1}
— Au NSTF
— Zr/Au

Increase with higher upper limit

Zr/Au, 2 mV s^{-1}
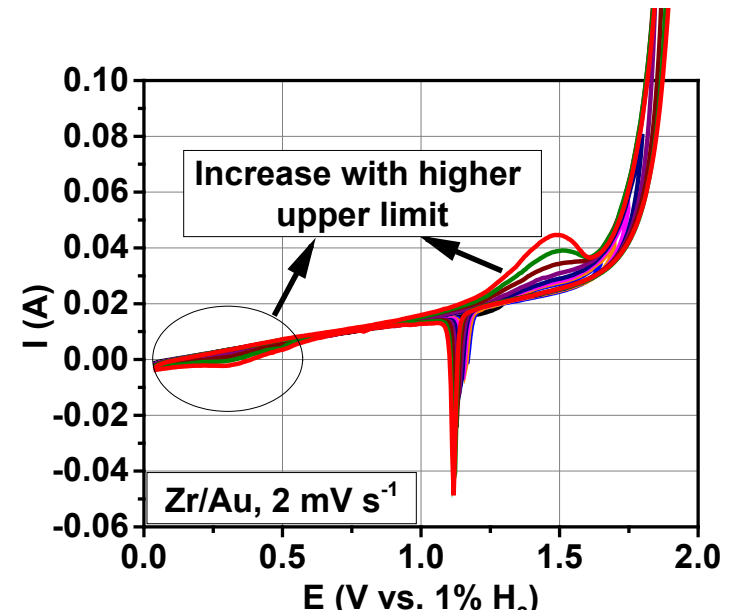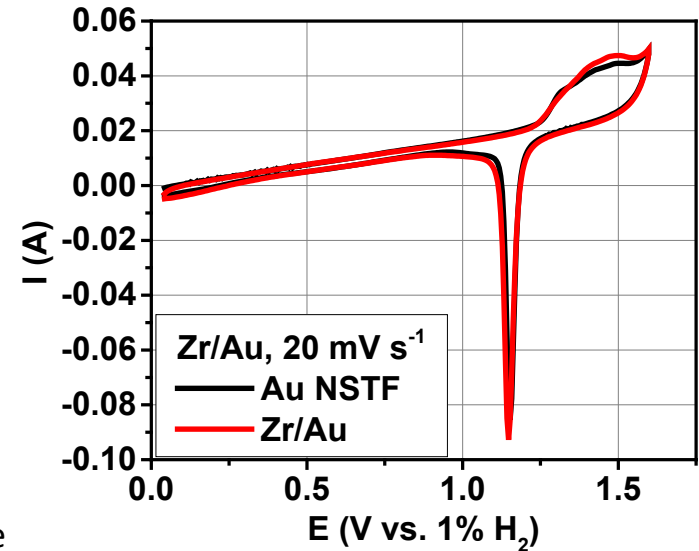
XAFS Analyses at Pt, Ir, and Zr Absorption Edges

- Pt-Zr (250 Å)-Ir catalyst and CCM samples after various treatments (Note: NSTF Pd cathode)

- Fitting of near edge region to metal and oxide standards to determine extent of oxidation of Pt, Zr, and Ir

- Atomic-level fitting of extended absorption region (EXAFS) to determine local coordination and bond distances
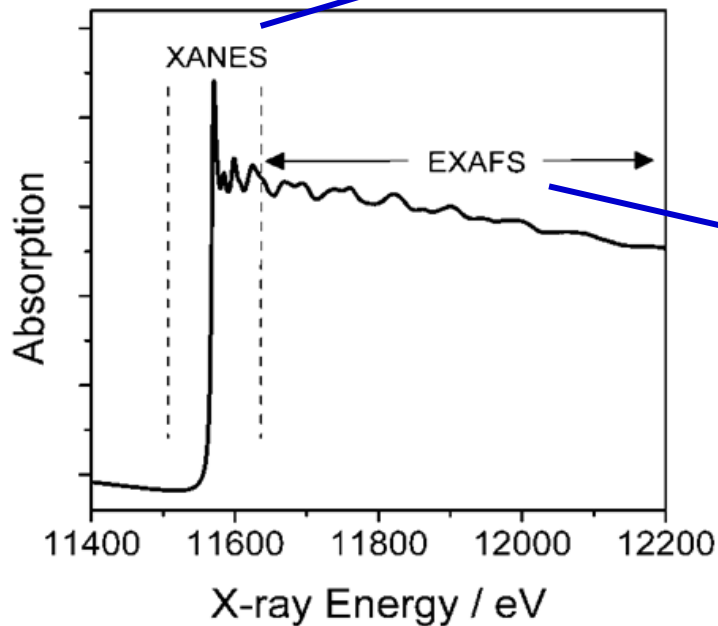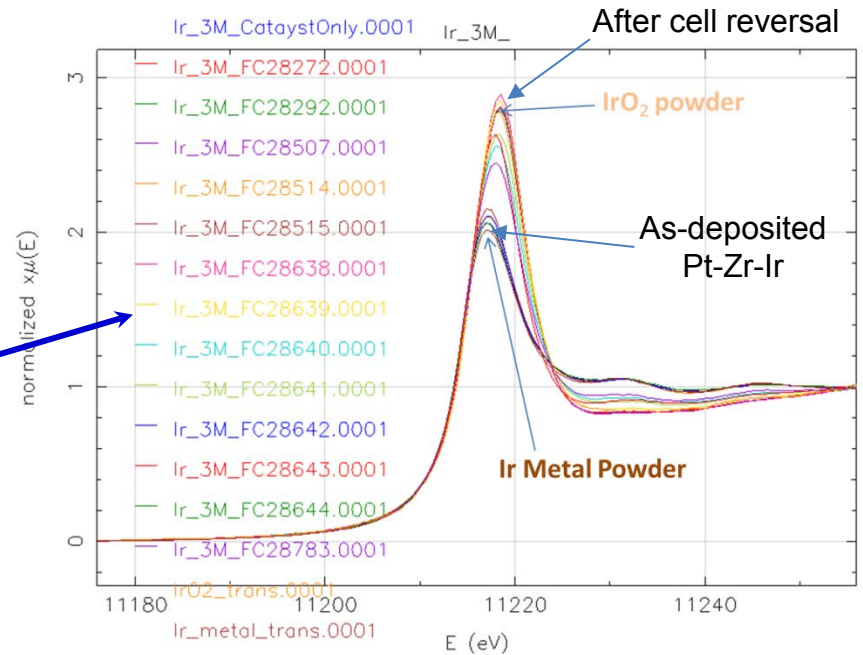
Fourier Transform
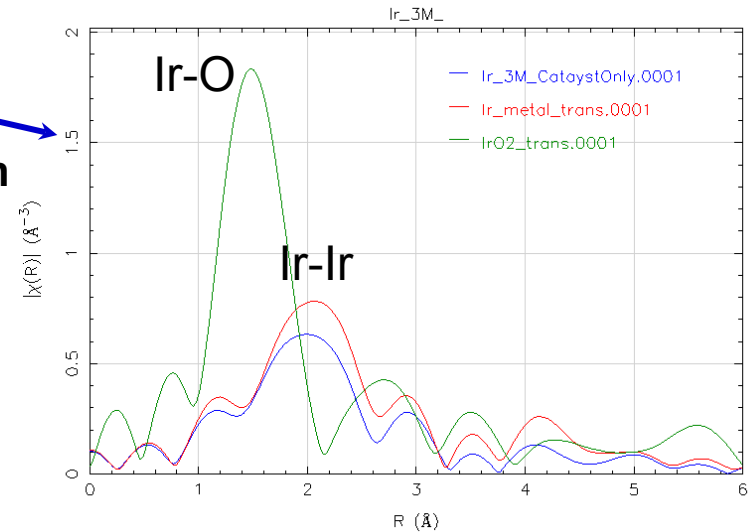
Summary of XANES Analysis: Pt-Zr-Ir catalyst

- **As-prepared**
  - Pt metallic; Zr in Pt particles; Pt-Zr particles coated with ZrO_2; Ir either deposited on ZrO_2 or on perylene red whisker

- **Conditioned**
  - Pt, Ir, and Zr oxidized; Zr shows greatest change in oxidation state; Pt-Zr intermetallic retained

- **200 mA/cm² treatment**
  - Zr almost entirely removed from Pt particles; Zr further oxidized, Ir almost fully oxidized to IrO_2

- **Gas switching**
  - Ir oxide partially reduced (35% metallic); Pt slightly reduced; Zr oxide unchanged

- **Cell reversal**
  - Zr nearly fully oxidized, Ir fully oxidized, Pt reduced, Zr and Ir are found on the cathode

- **Postulated role of Zr interlayer:**
  - allows the oxidation of Ir, inhibiting Ir dissolution and loss
  - formation of Pt-Zr surface alloy during deposition inhibits interaction between Pt and Ir

Argonne National Laboratory