Durable Catalysts for Fuel Cell Protection during Transient Conditions

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3M

DOE/3M Award DE-EE0000456

2013 DOE Hydrogen and Fuel Cells Program
and
Vehicle Technologies Program Annual Merit Review

Washington DC, May 16, 2013

Project ID: FC006

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: December 31, 2013
- Percent complete: ~ 80% (03/2013)

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** (Collaborator)
  - **Stability Testing, XAFS, Selective ORR Inhibitor**

Budget

Total:	$ 5,782,165
- Contractor Share:	$ 1,156,433
- DOE Share:	$ 4,625,732
	(includes $ 400K to ORNL)

Funding Received in FY12:	$ 1,294,162
Planned Funding for FY13:	$ 950,000

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 therefore **always "ON"**.

Implementation:

Via **two catalyst material concepts**:

1. **Catalysts with high oxygen evolution reaction (OER) activity**
   1. **At the cathode for SU/SD**
   2. **At the anode for cell reversal**
2. **Anode catalysts with low oxygen reduction reaction (ORR) activity for SU/SD**

Evaluation:

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

Approach/2013 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: 1.48V
2013	**5,000**	**0.088**	**1.45 V**	**10%**	**Achieved** 11/2012; End Voltage: 1.44V
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: 1.65V
2013	**200**	**0.037**	**1.75 V**		**Achieved** 11/2012;End Voltage: 1.62V

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 > 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	**3 x 15-cells short stacks** (03/2013)

Additional 2013 Tasks

- **SU/SD test procedure** upon AFCC, Tech Team and Durability Work Group recommendations
- Fundamentals of **Ru-Ir OER activity** and **stability**

Accomplishments and **Progress: 2012/2013**

1. SU/SD: 5,000 cycles/pulses
*New procedure developed; Low PGM loading tested (**90 µg/cm² PGM total** on the cathode) with* **< 5 µg/cm² IrRu**

2013: Low PGM loading tested (88 µg/cm² PGM total on the cathode) with 1.45V upper limit.

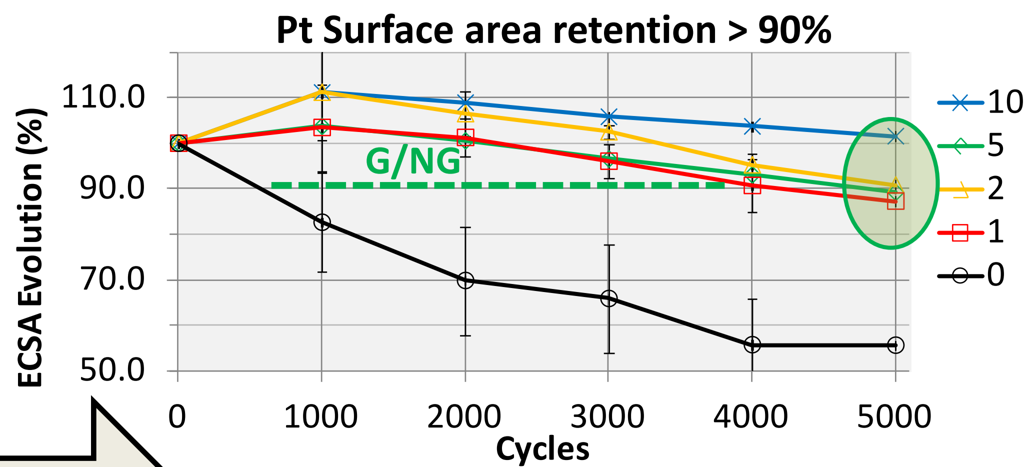
2. Cell Reversal: 200 high current density pulses of 200 mA/cm² mimicking **cell reversal** achieved with **45 µg/cm² of total PGM.**

2013: More rigorous test applied on lower PGM loading (37 µg/cm² total on the anode); Upper Voltage < 1.7 V

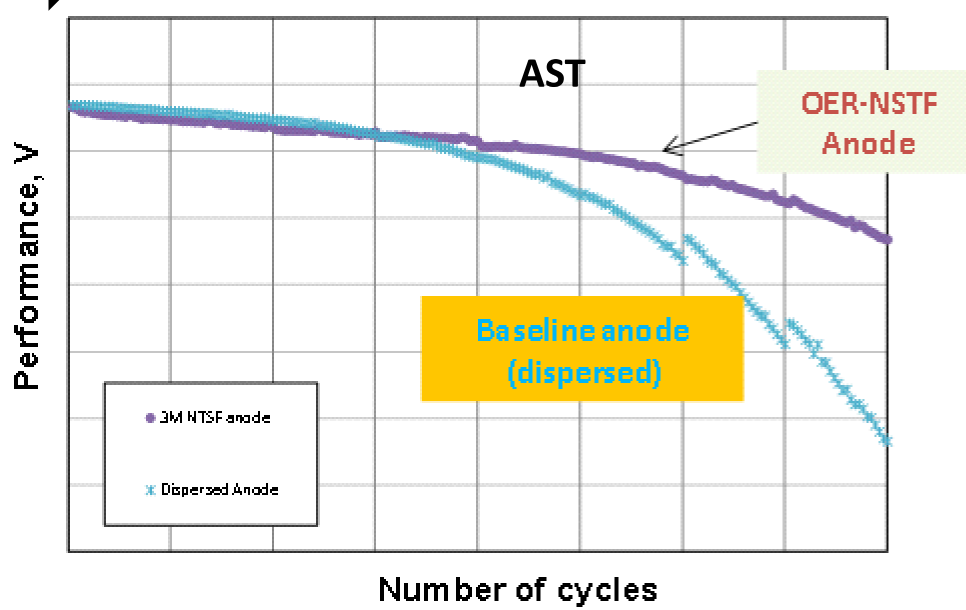
3. ORR inhibition: Effect verified in stack testing at AFCC
2013: More effective catalyst developed.

4. **OER catalyst scaled-up**: Full scale short stacks tested.
2013: Second OEM tested and confirmed the 3M lab results.

2012 highlights

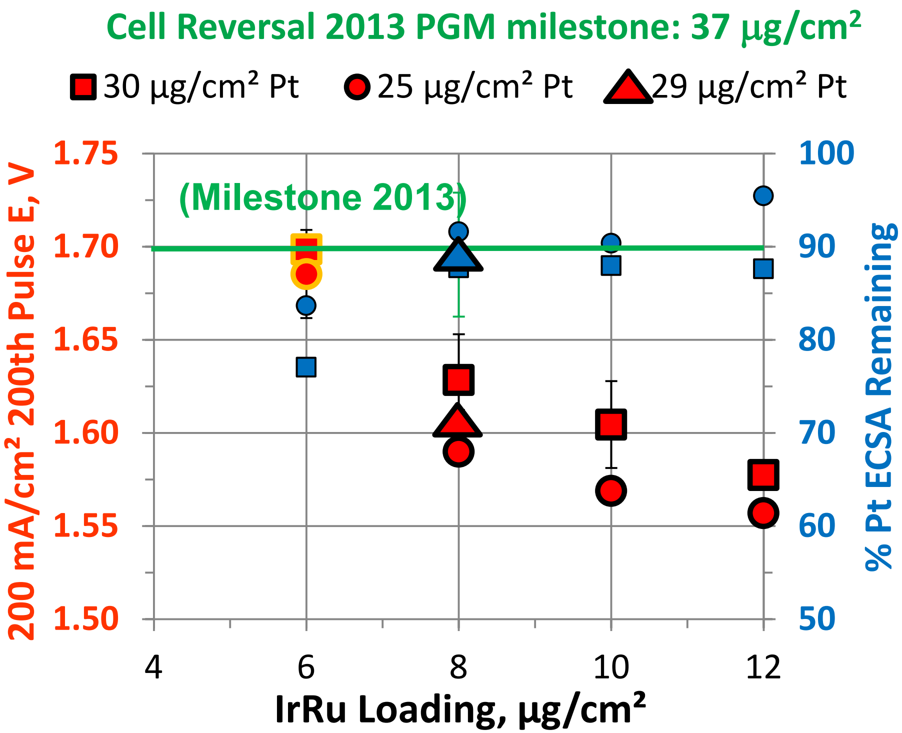


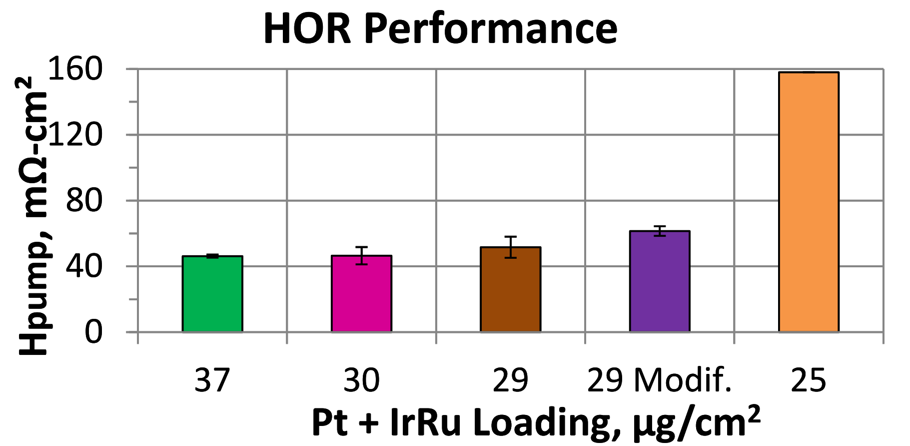
AFCC: NSTF anode has a positive impact on SU/SD durability in a gas switching SU/SD

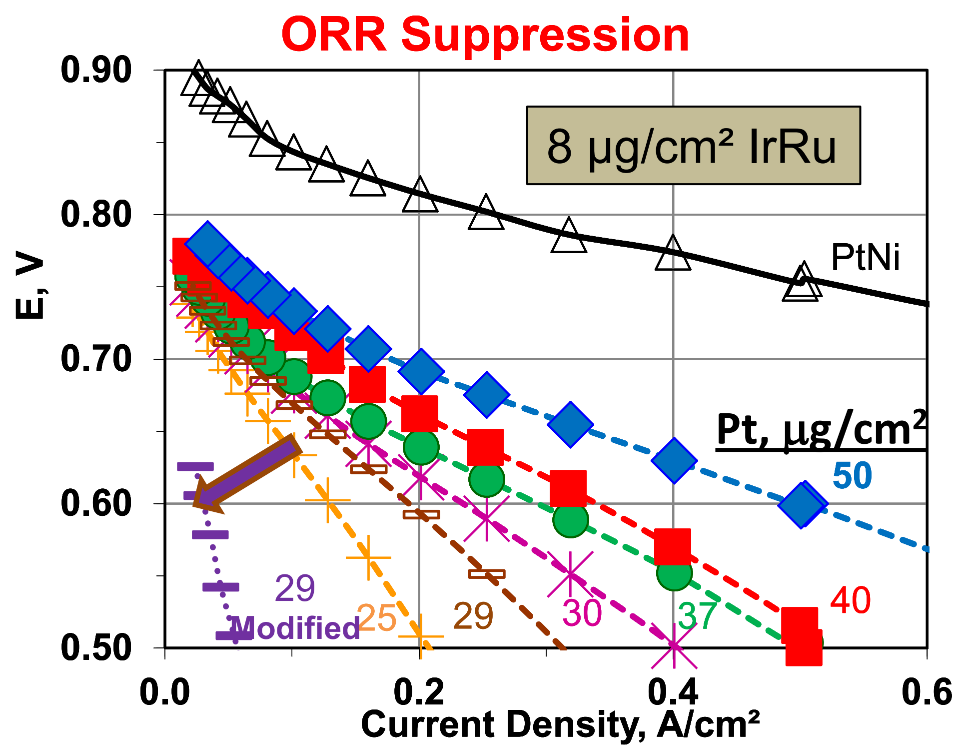


Cell Reversal: 2013 Milestones, HOR activity and ORR Suppression

RuIr loading 6 – 12 μg/cm² on 25 and 30 μg/cm² Pt/NSTF (**3M** Menomonie pilot plant, 300 ft lineal)







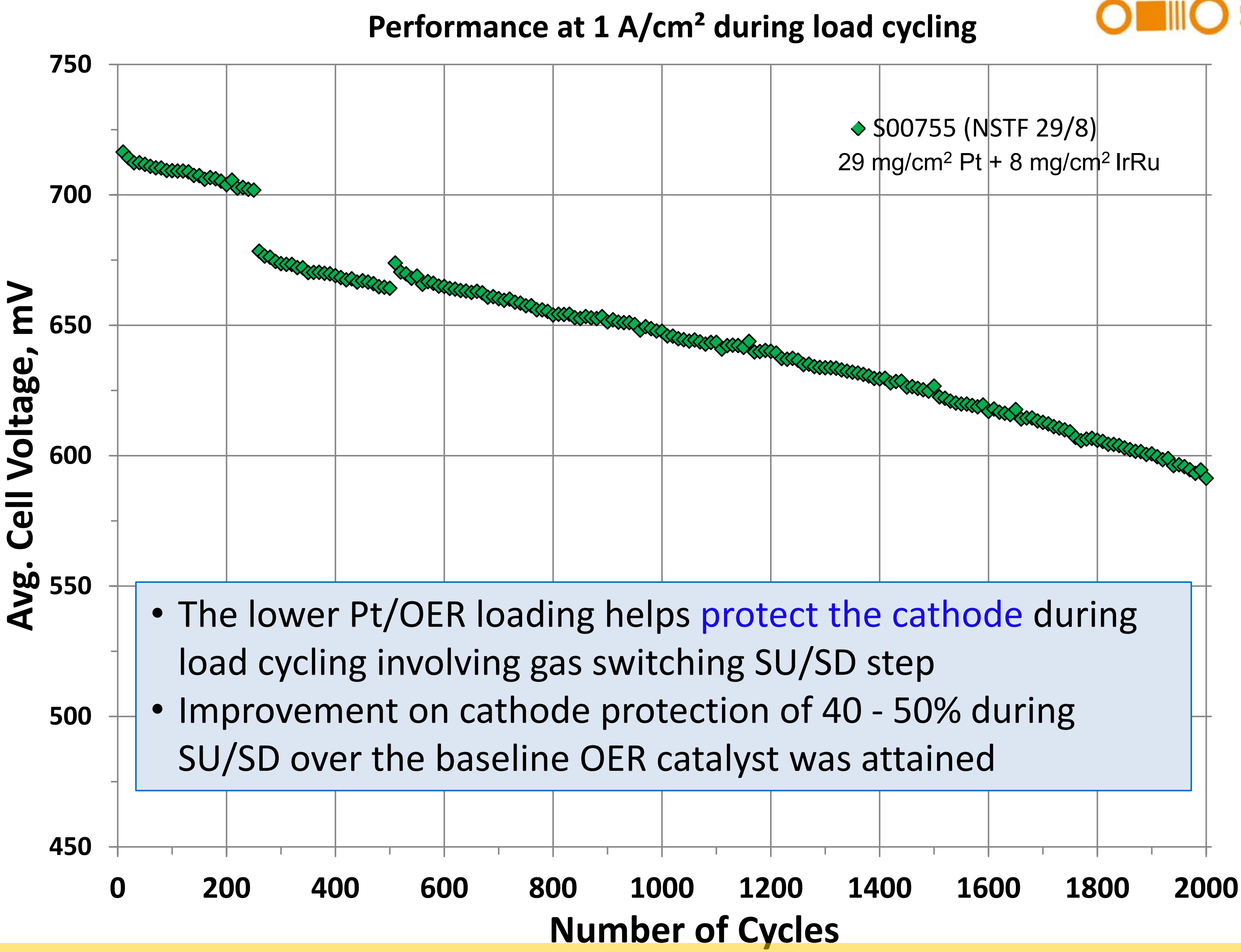
Both Pt/NSTF series with > 8 μg/cm² RuIr fulfill 2013 milestone

The 25 μg/cm² Pt/NSTF will impact the HOR

The 29 μg/cm² Pt/NSTF with 8 μg/cm² RuIr satisfies fully 2013 milestone

Modified 29 μg/cm² Pt/NSTF with 8 μg/cm² RuIr **inhibits ORR over 3 orders of magnitude**

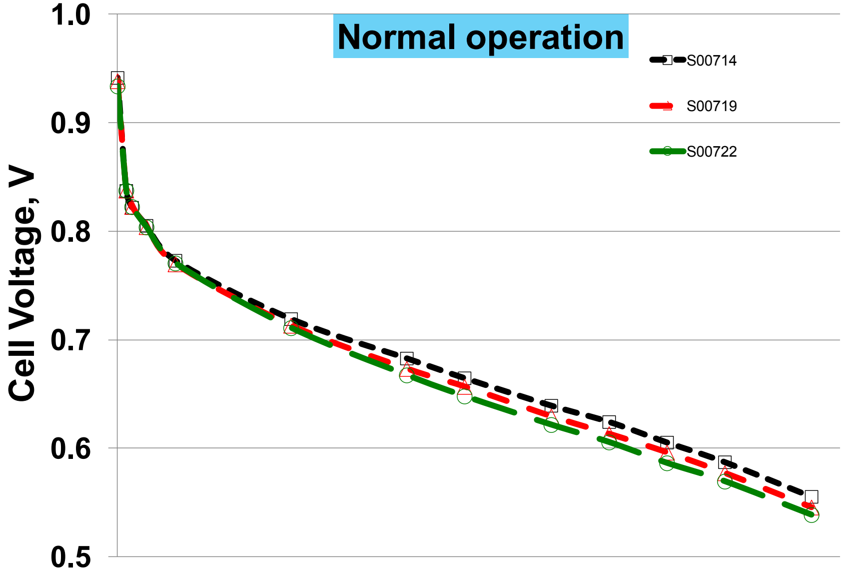
SU/SD Short stacks evaluation: 2013 Milestone OER catalyst

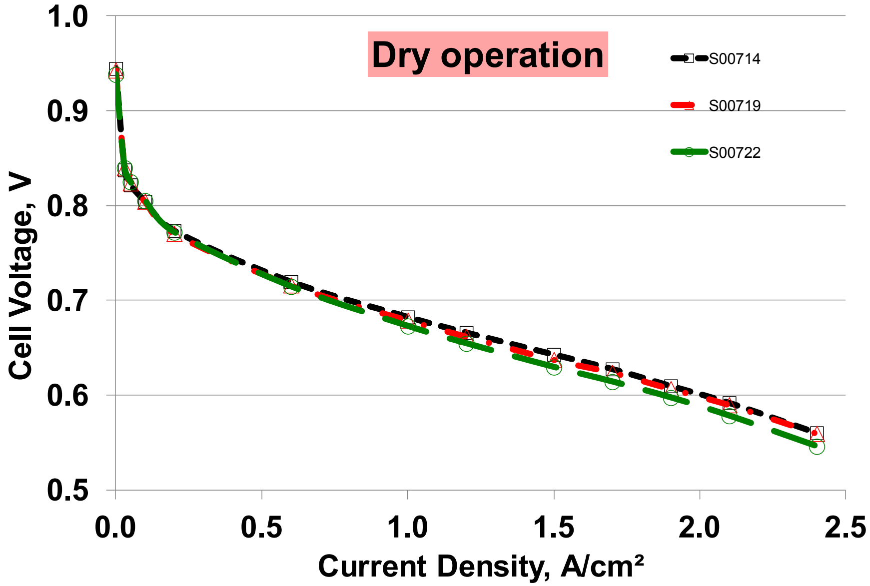


- The lower Pt/OER loading helps protect the cathode during load cycling involving gas switching SU/SD step
- Improvement on cathode protection of 40 - 50% during SU/SD over the baseline OER catalyst was attained

Short stacks evaluation

AUTOMOTIVE FUEL CELL COOPERATION





Milestone: 3 Stacks by 03/2013

Anodes:

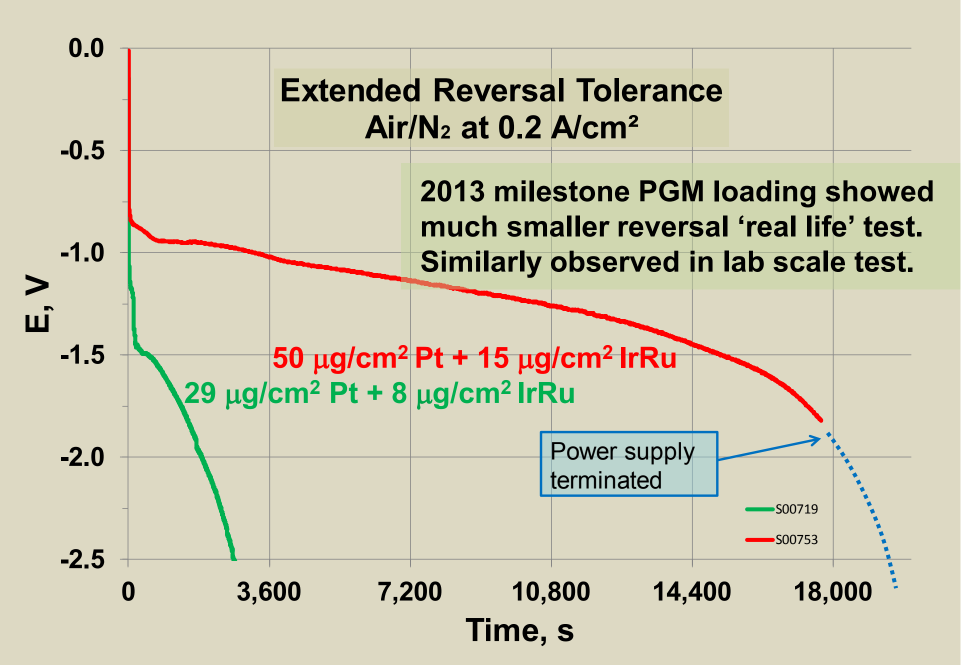
1. Dispersed: 50 μg/cm^2 Pt (commercial catalyst; 3M produced)

2. NSTF: 50 μg/cm^2 Pt + 15 μg/cm^2 IrRu (NSTF base-line; historical)

3. NSTF: 29 μg/cm^2 Pt + 8 μg/cm^2 IrRu (NSTF 2013 milestone)

CCM made by 3M: SA > 300 cm^2

- 3M coated dispersed cathode (0.4 mg/cm^2 Pt)
- 3M 12 μm reinforced, membrane, 725 EW

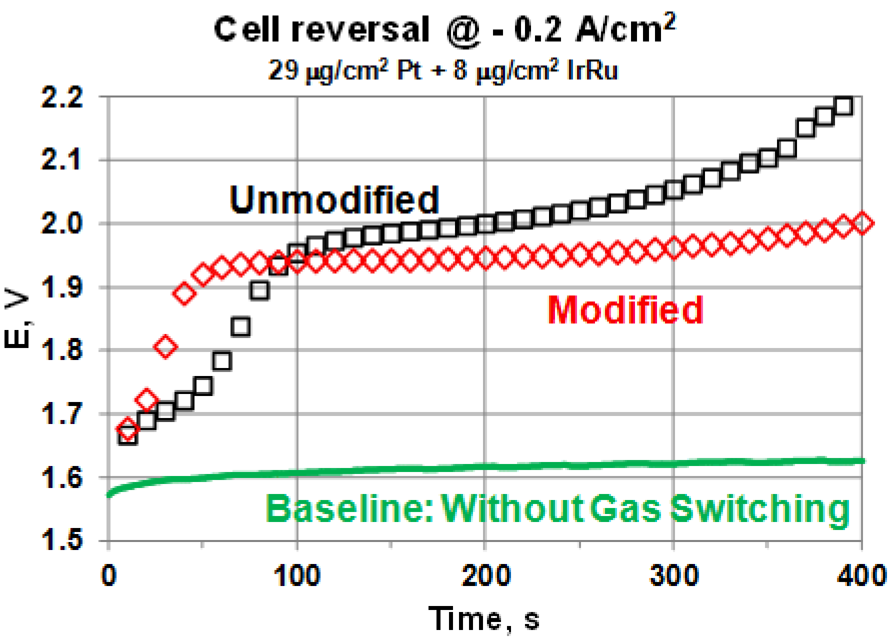


2013 milestone NSTF with 29 μg/cm^2 Pt (58% of base line) did not impact the fuel cell performance

SU/SD test procedure via Gas Switching between Hydrogen and AIR

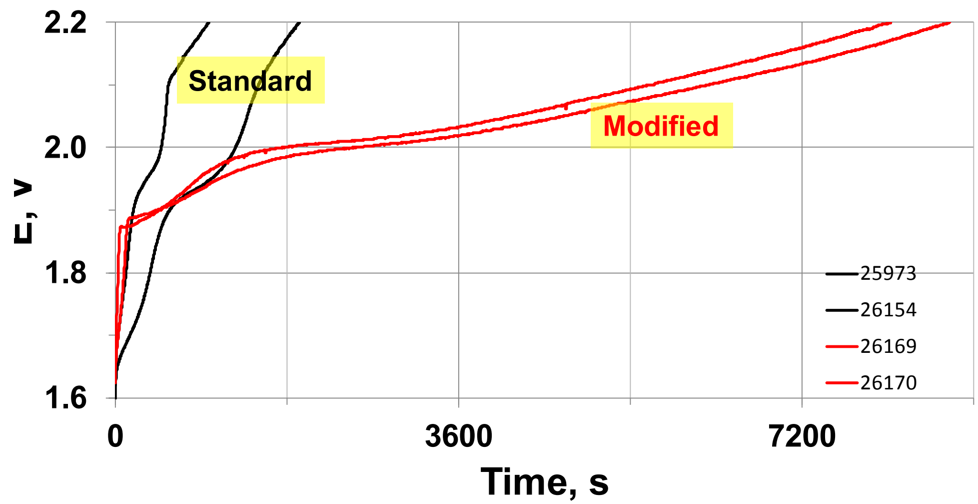
Baseline: Without Gas Switching

as shown below



Reversal durability after **400** mimicked **'life cycles' including Gas Switching** steps

Standard 50 µg/cm² Pt + 15 µg/cm² IrRu and
Modified OER catalyst shown (3M lab test)

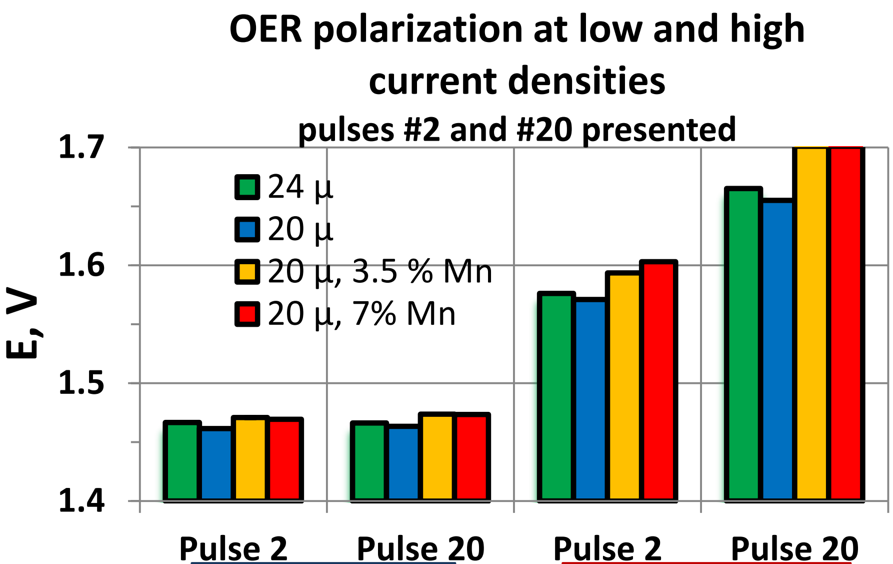


Modified OER catalyst shows
improved durability by a factor > 5

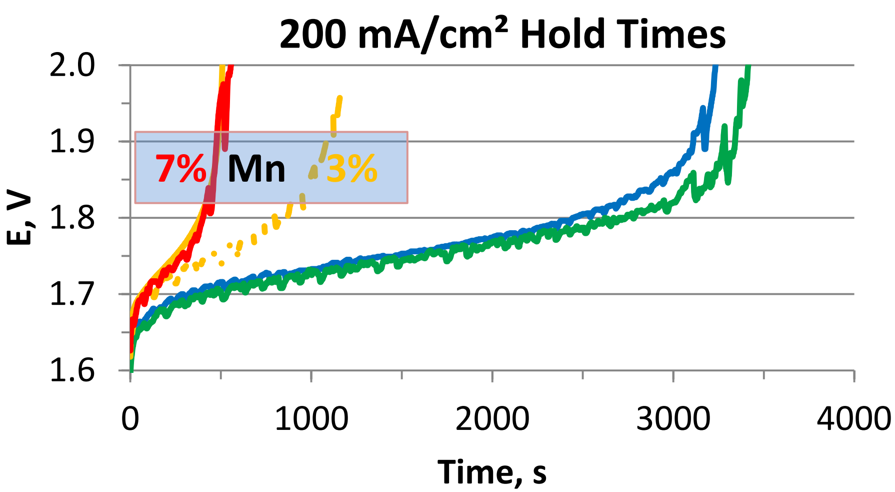
Gas Switching impacts significantly the inherent OER activity of IrRu.
Modification of the OER catalyst for **improved durability is underway.**

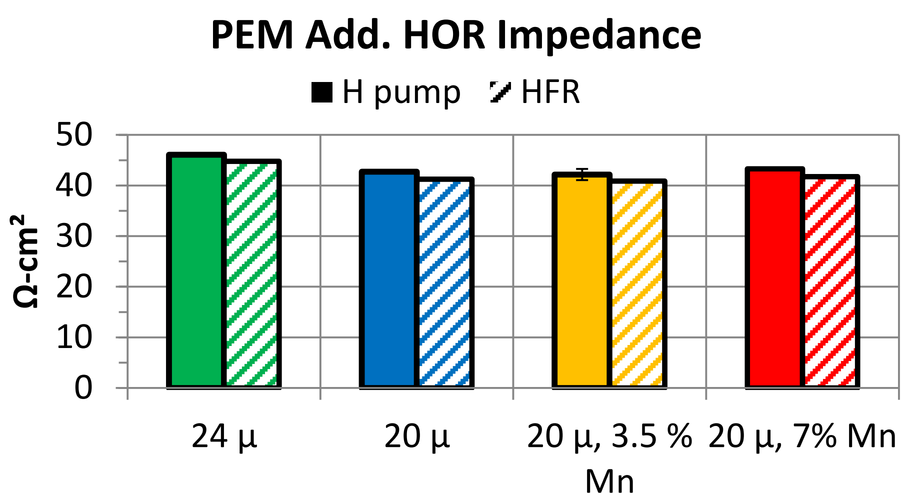
OER with Membrane Additive

"Real Life" membranes contain additives



Mn as an additive inhibits OER at higher current densities! This is reflected on the overall reversal durability.



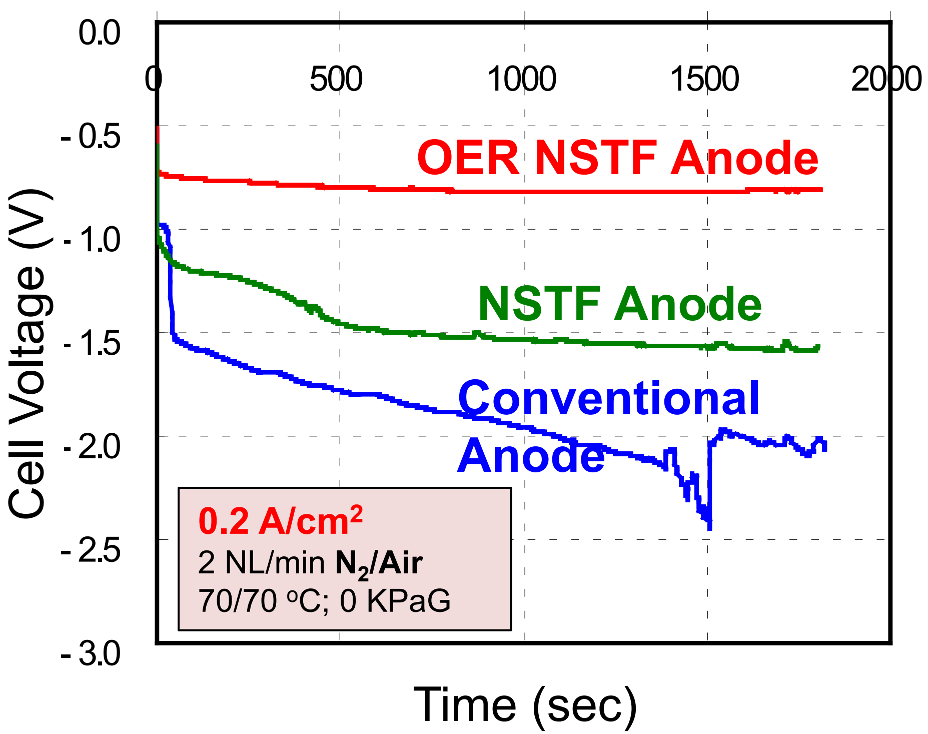


HOR is not impacted by the additive

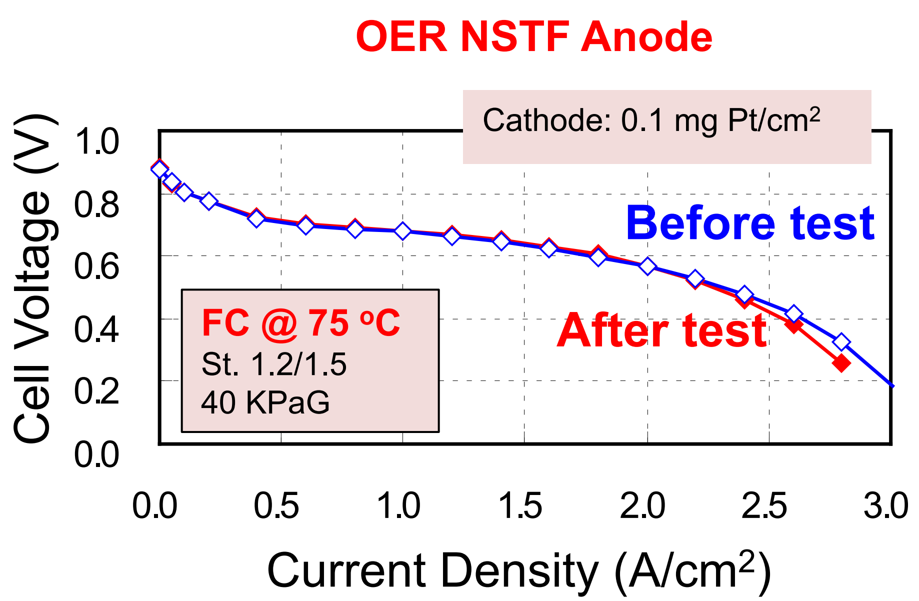
OEM Evaluation

OEM "A" Test Results of 3M OER Modified Pt/NSTF Anode Catalyst

Hydrogen Starved Operation



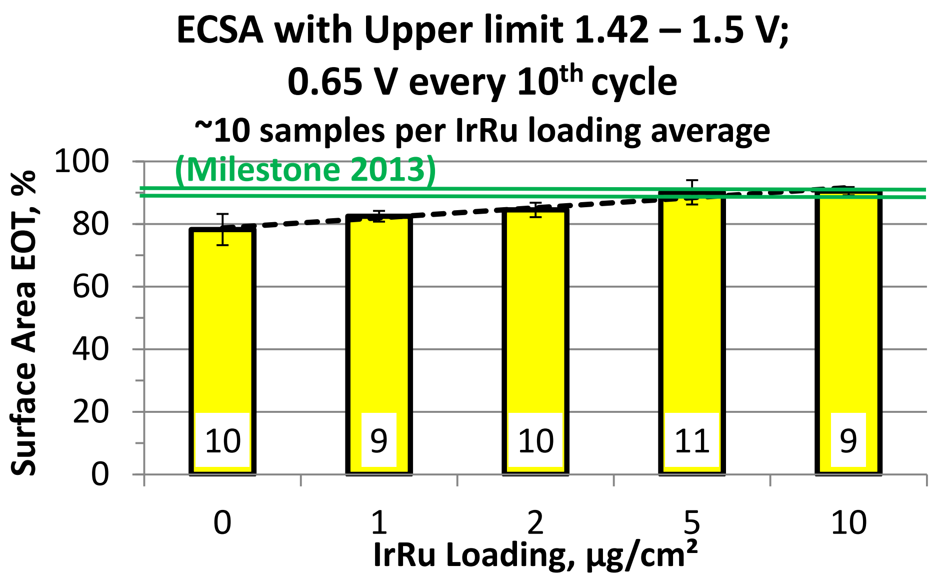
Normal Fuel Cell Operation

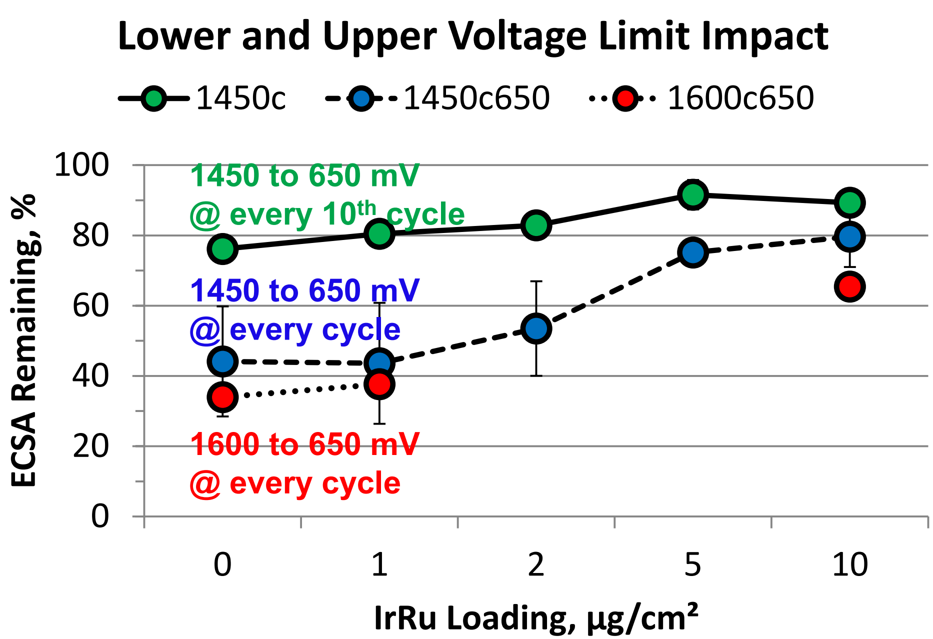


<u>FC Components:</u>
Anode: 3M IrRu on Pt/NSTF
Membrane, cathode, GDLs, etc: OEM proprietary

OEM Conclusion: **OER catalyst** presence on NSTF is **necessary** for H_2 starved operation

Su/Sd: The Impact of the Lower and the Upper Voltage Limit





- Up to **1.5 V** the ECSA retention is as expected (Test procedure on slide # 25).
- Excursions to **650 mV at every cycle** shows a much larger surface area loss than with any of the previous test procedures.
- **100 mV increase in the upper voltage** limit, to **1.6 V**, results in **26% additional** Pt surface area loss.
- By the end of the **5,000 cycles**, the OER activities of **1 μg/cm²** have fallen into the range of Pt samples. However, **10 μg/cm²** has more than enough OER catalyst to **still protect Pt**.

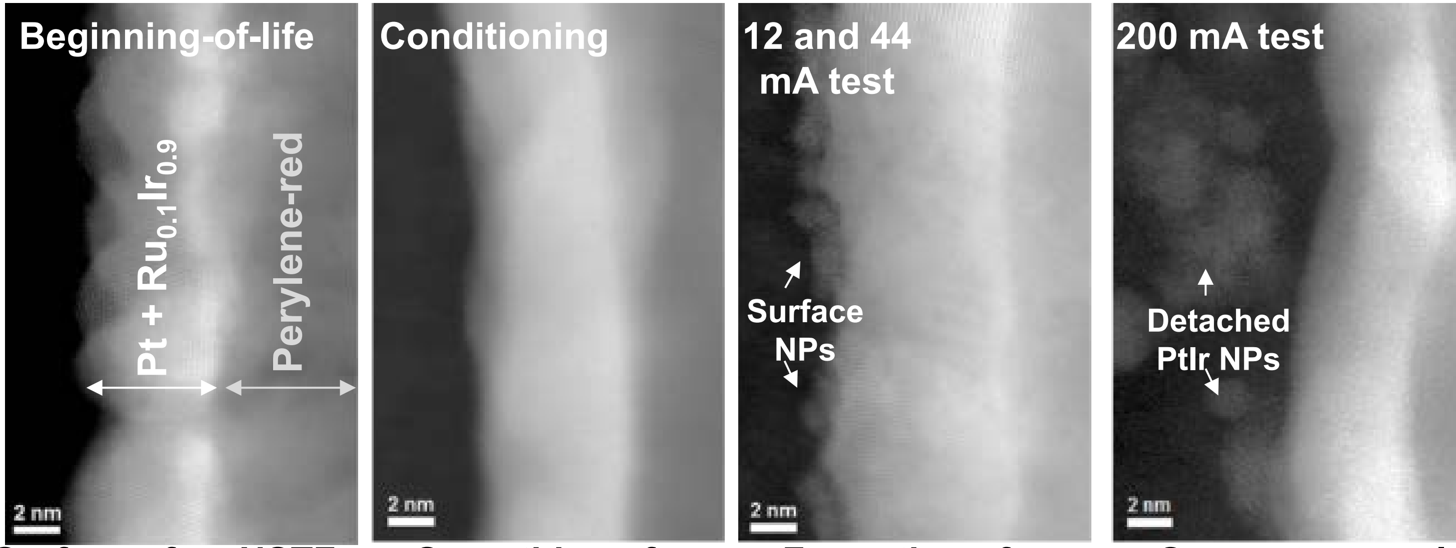
Pt dissolution is strongly determined by
- the frequency of the lower voltage limit
- the upper voltage limits

The question: Why Pt exposed to the same potential regime dissolves less when OER catalyst is present?

Fundamentals: Effect of Cell Reversal on OER NSTF catalysts.

Z-contrast STEM images of NSTF whisker surfaces observed at four different stages of CR tests

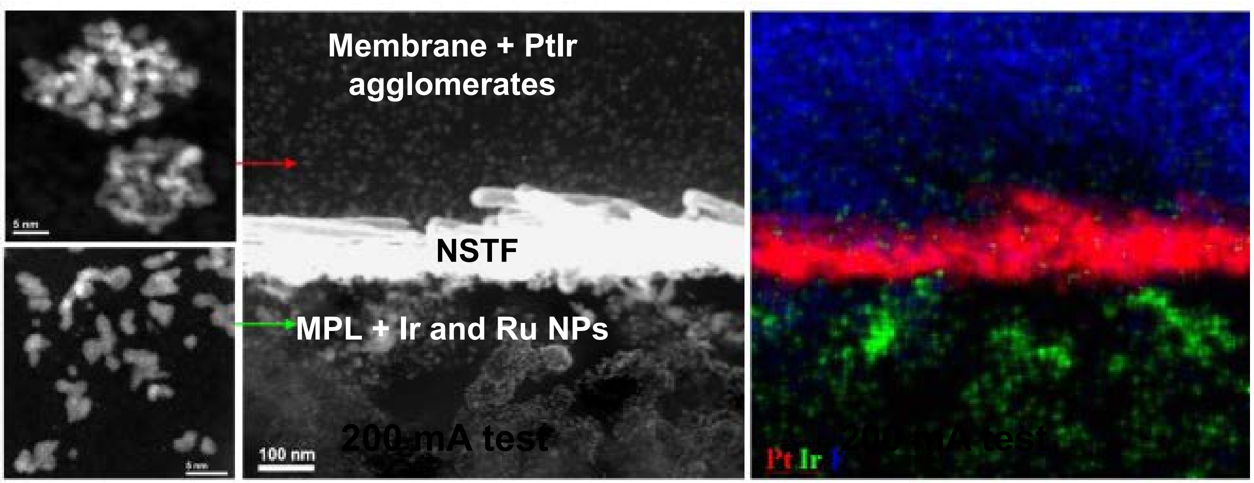
IrRu loading: 10 µg/cm²



Surface of an NSTF whisker showing structured Pt layer coated with IrRu	Smoothing of whisker surfaces, some Ru loss observed	Formation of nanoparticles (NPs) on surface, some Ir loss observed	Severe to complete IrRu losses, formation of PtIr NPs in membrane, Ir and Ru NPs in MPL

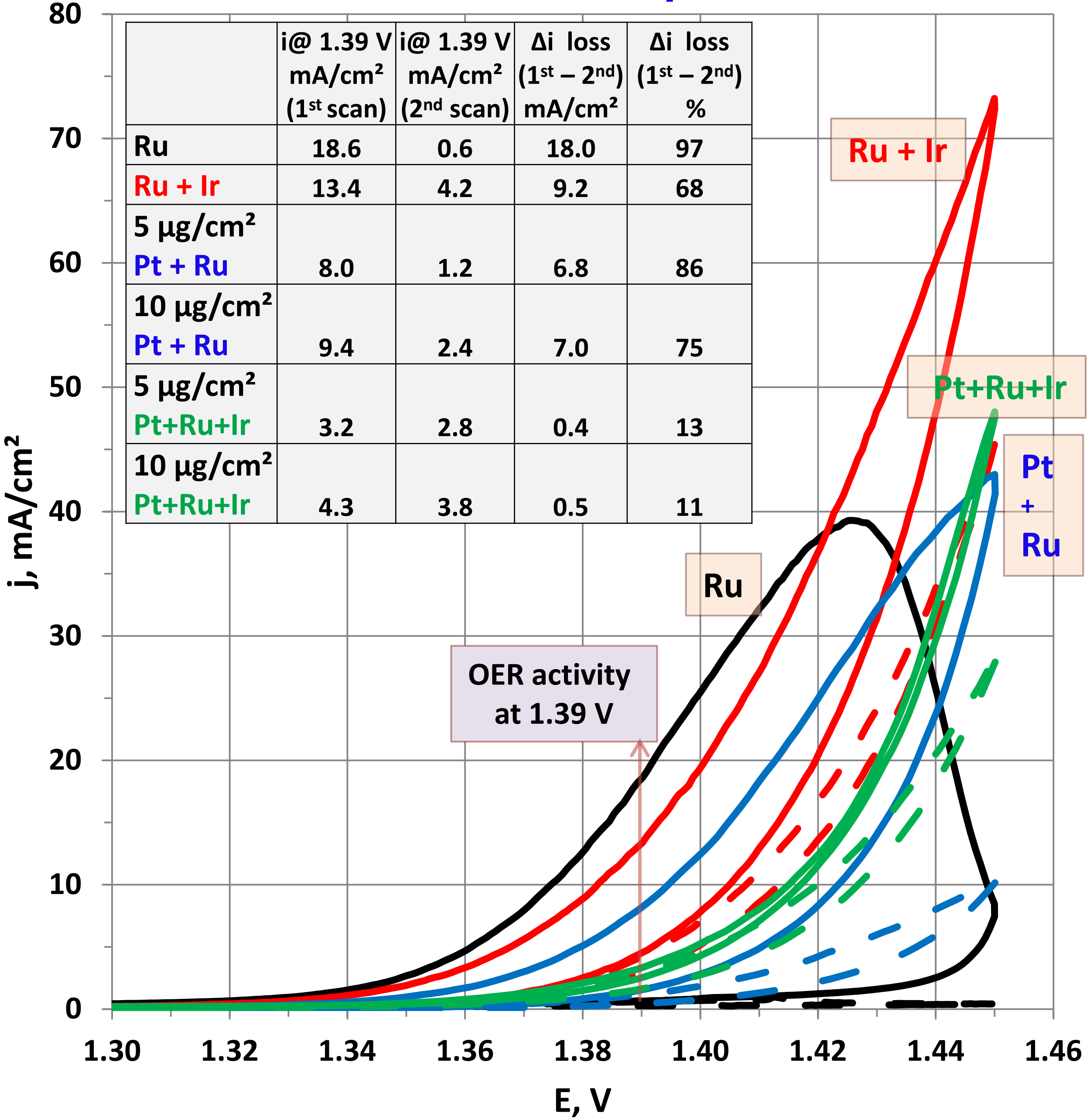
PtIr agglomerates formed in membrane near NSTF

Most of the Ir NPs are found in MPL layer



NSTF anode after complete CR test. Elemental maps for Pt, Ir and Ru (overlaid). Most of the Ru and Ir migrates to the MPL layer, where it forms metallic nanoparticles.

Fundamentals: The impact of individual OER components



	i@ 1.39 V mA/cm² (1st scan)	i@ 1.39 V mA/cm² (2nd scan)	Δi loss (1st – 2nd) mA/cm²	Δi loss (1st – 2nd) %
Ru	18.6	0.6	18.0	97
Ru + Ir	13.4	4.2	9.2	68
5 µg/cm² Pt + Ru	8.0	1.2	6.8	86
10 µg/cm² Pt + Ru	9.4	2.4	7.0	75
5 µg/cm² Pt+Ru+Ir	3.2	2.8	0.4	13
10 µg/cm² Pt+Ru+Ir	4.3	3.8	0.5	11

OER activity and stability of

Ru; Ru +Ir; Pt + Ru; and Pt+Ru+Ir

Compositions: Perylene Red/Pt/Ru/Ir

Ru: *20 µg/cm² in all*

Ru + Ir: 5 µg/cm² Ir

Pt + Ru: 5 µg/cm² Pt

Pt + Ru + Ir: 5 µg/cm² Pt; 5 µg/cm² Ir

(CVs not presented)

Pt + Ru: 10 µg/cm² Pt

Pt + Ru + Ir: 10 µg/cm² Pt; 5 µg/cm² Ir

Testing:

Two consecutive scans CV s @ 2 mV/s

1st scan: solid lines

2nd scan: dotted lines

OER activity: (assessed at 1.39 V, before significant Ru dissolution occurs)

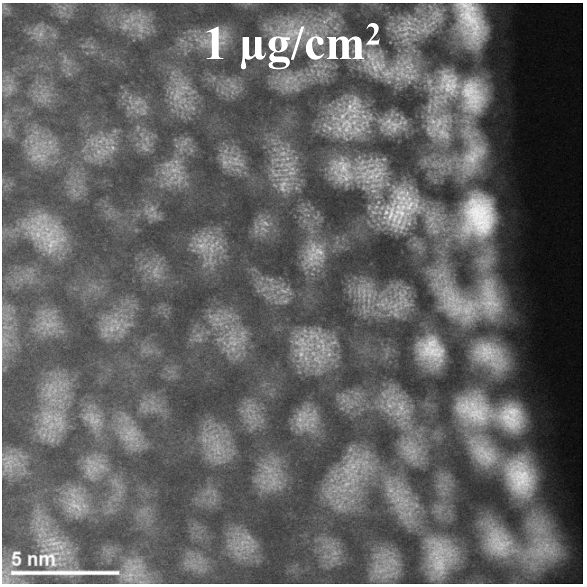
Ru has the best activity and the worst stability

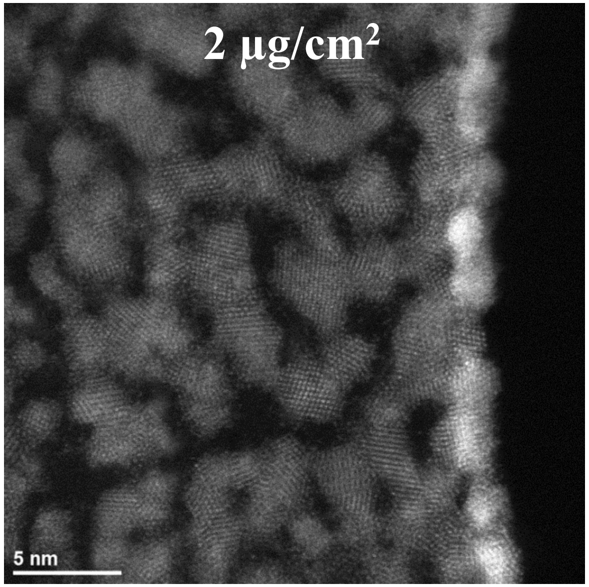
Ir retains most of Ru activity and provides some stability

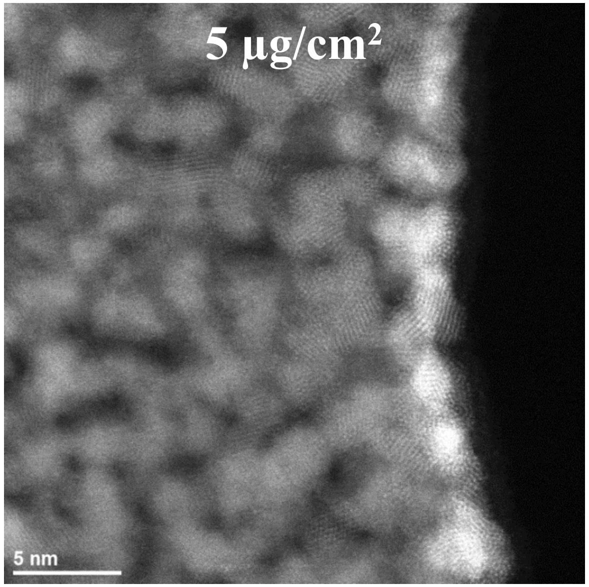
Pt decreases Ru activity without providing sufficient stability

Pt + Ir decrease the activity further but provide much better stability as shown at higher potentials

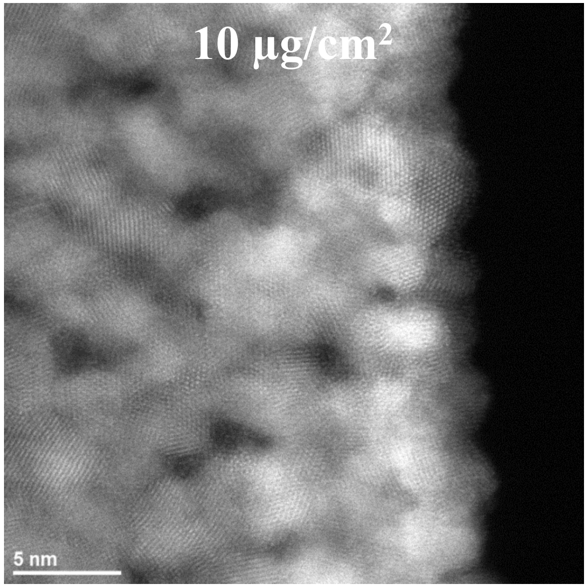
Fundamentals: Ru disposition on bare perylene

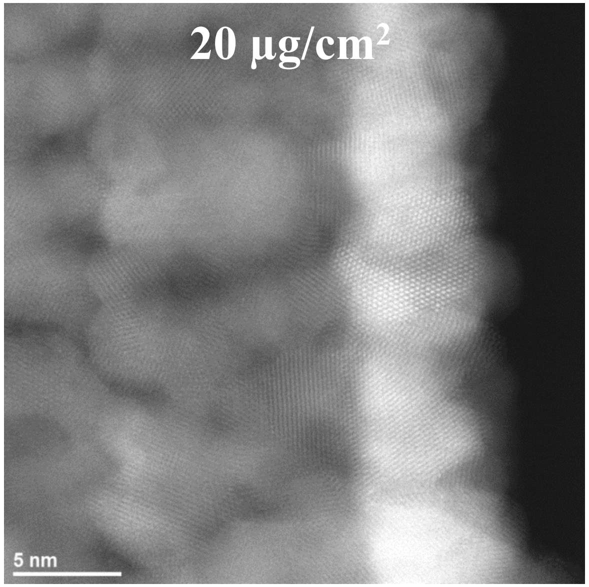






1 – 2 nm Ru particles

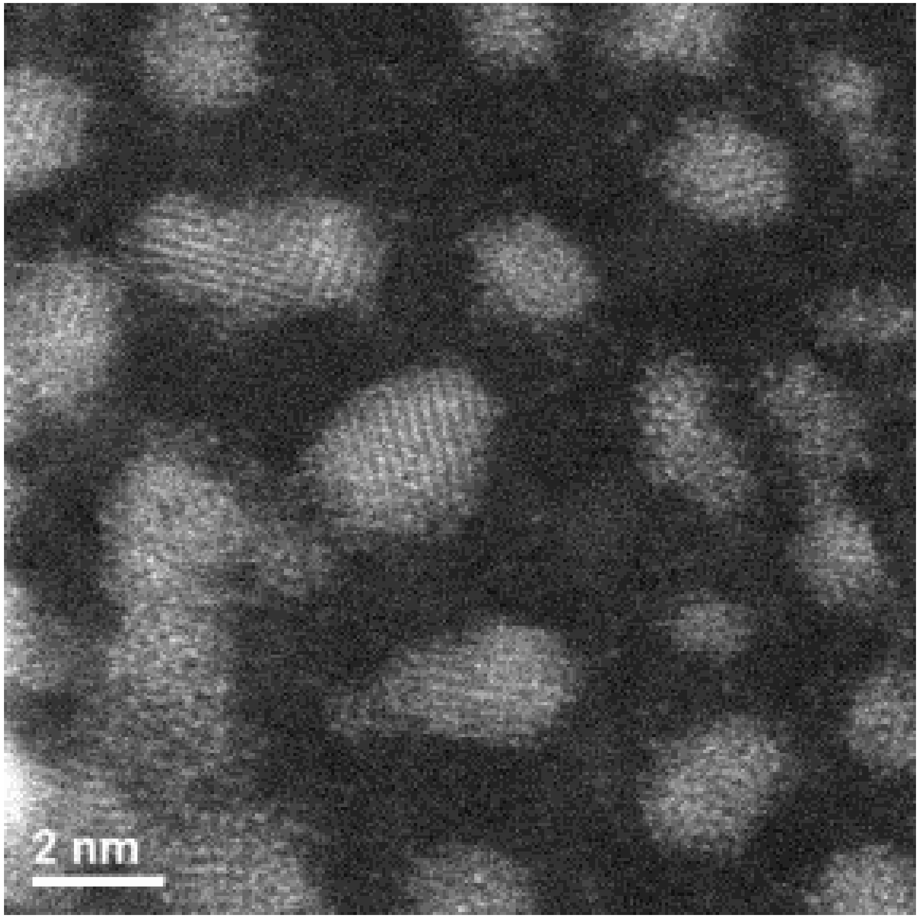




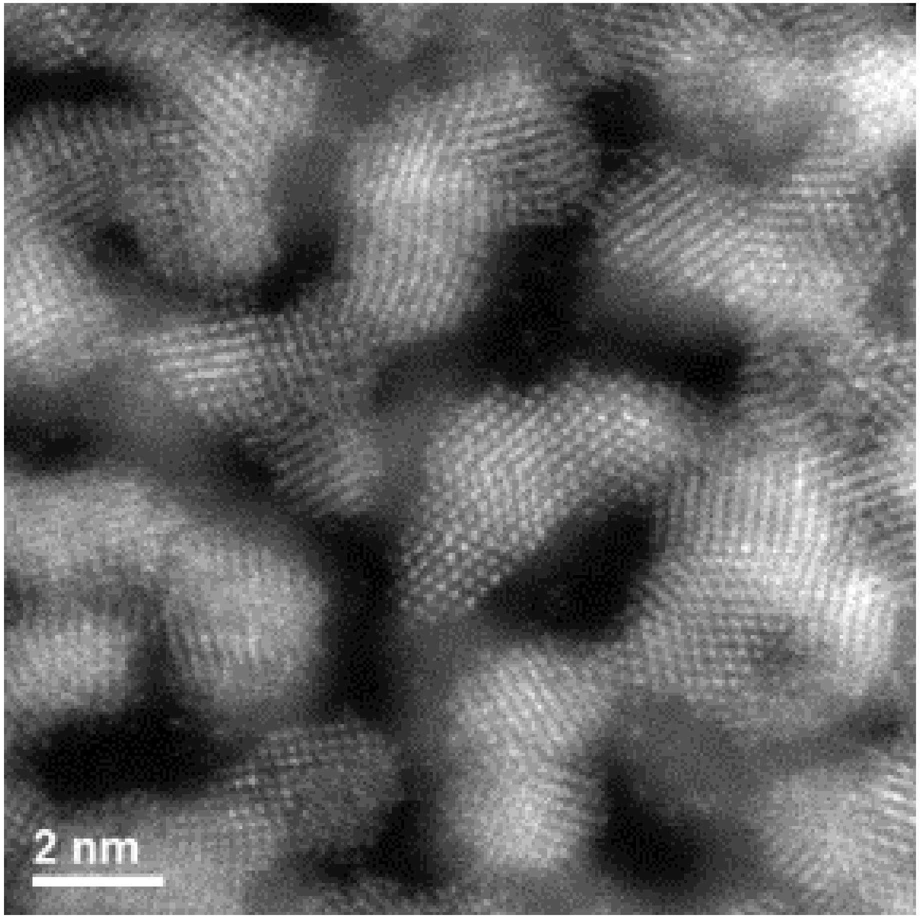
Visible coating discontinuities at lower loadings

Imaging Ru and Ru + Ir OER Layers on Perylene

Ru: 1 µg/cm²

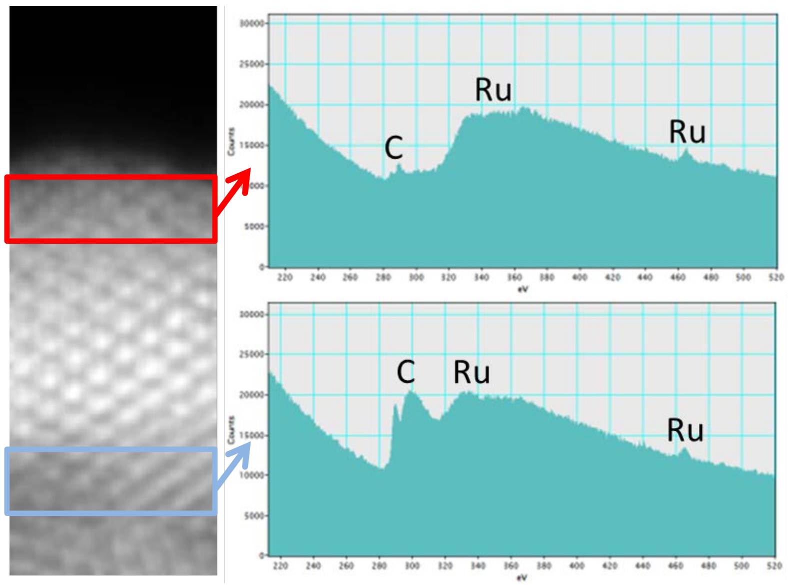


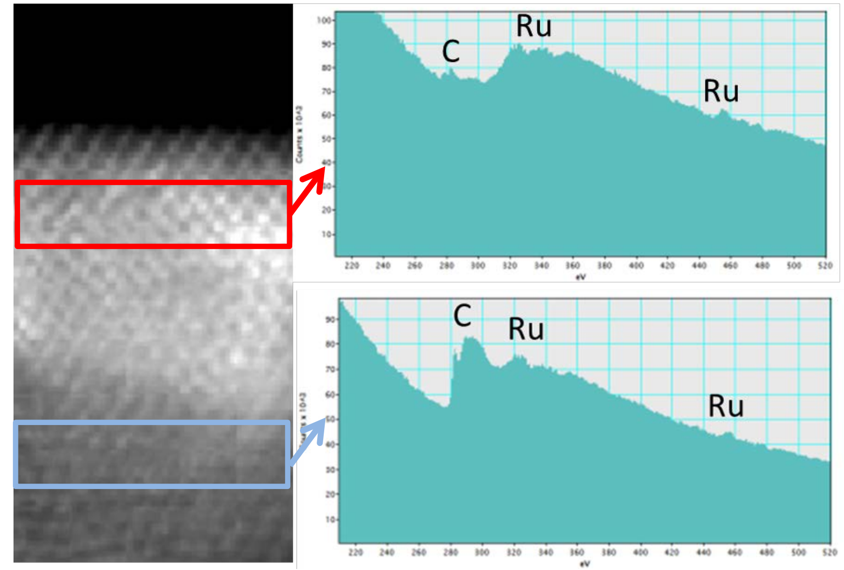
Ru: 1 µg/cm² + 5 µg/cm² Ir



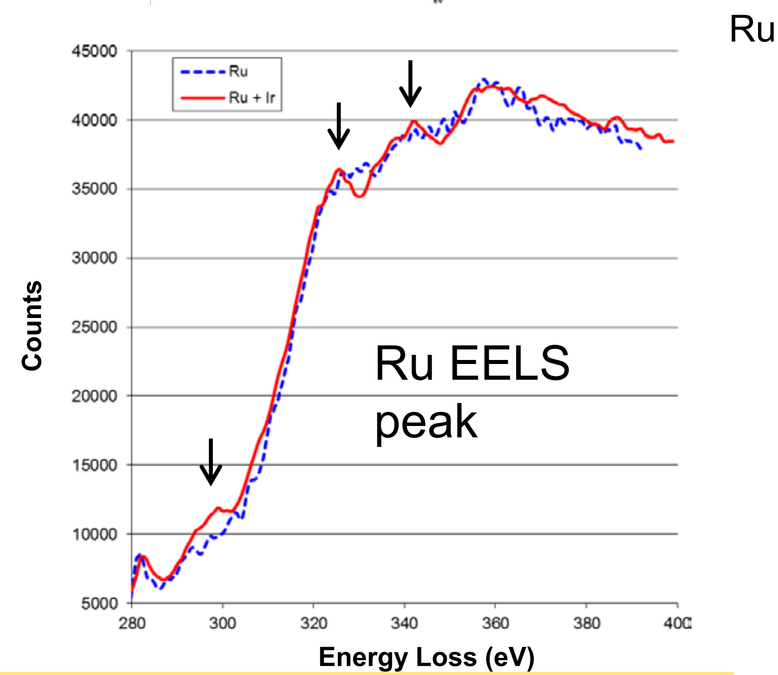
Ru particles covered by Ir

EELS Mapping of Ru and Ru+Ir OER Layers on Perylene

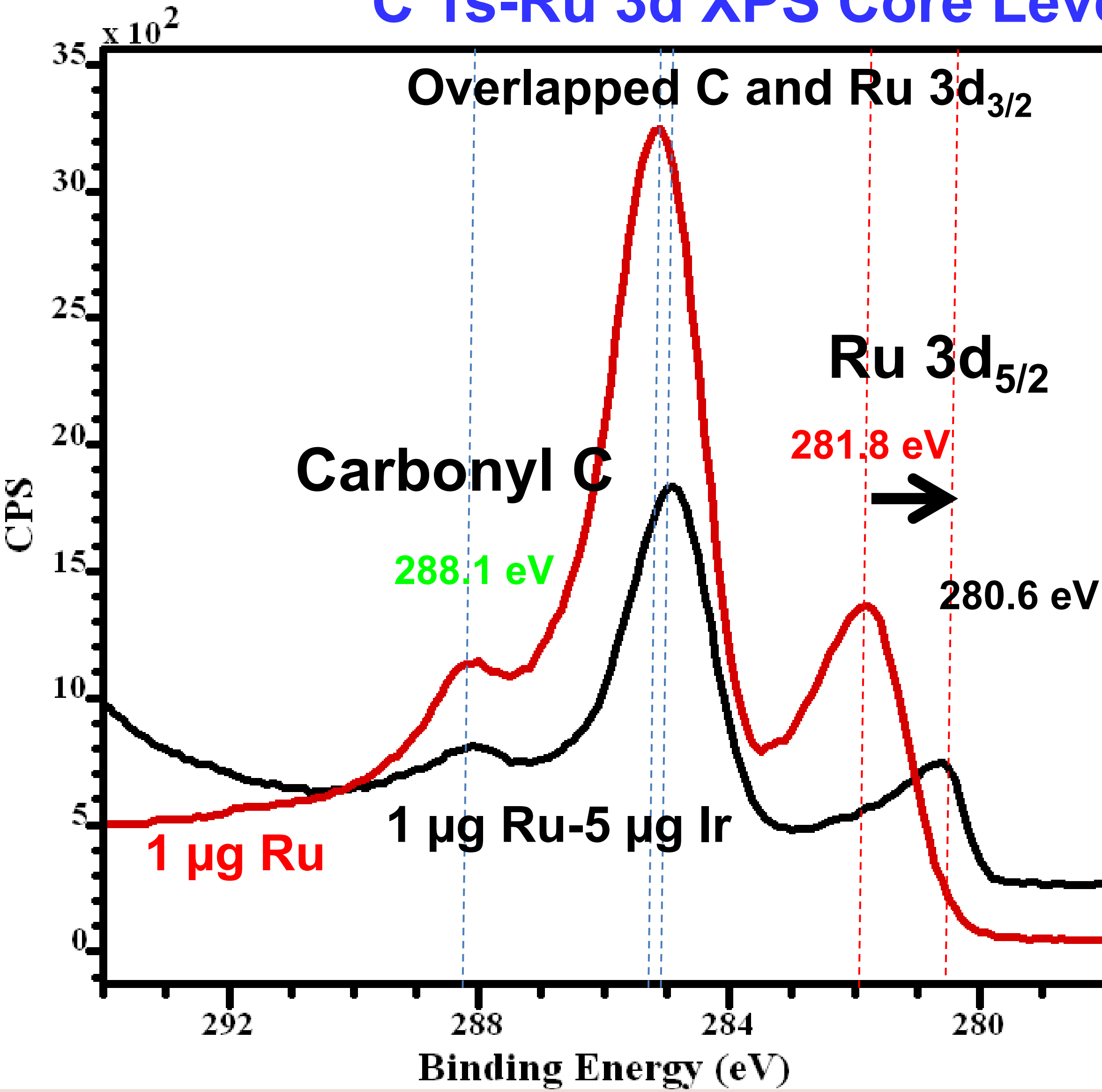




- Electron energy loss spectroscopy (EELS) can be used to detect low loadings of Ru.
- Peak **overlap between C and Ru** does complicate analysis.
- Peaks in EELS near edge fine structure appear in Ru edge with the addition of Ir.
- We will try to understand the origin of these peaks and correlate to improved stability.



C 1s-Ru 3d XPS Core Level Spectra



R.T. Atanasoski, L.L. Atanasoska, D.A. Cullen, G.M. Haugen, K.L. More, G.D. Vernstrom: *"Fuel Cells Catalyst for SuSD: Electrochemical, XPS, and TEM Evaluation of Sputter-Deposited Ru, Ir, and Ti on Pt-Nano-Structured Thin Film (NSTF) Support"*, ***Electrocatalysis* 3**, 284–297, 2012.

1 µg/cm² Ru and 1 µg Ru + 5 µg/cm² Ir plotted together clearly show:

(a) Without Ir there is a significant shift of Ru $3d_{5/2}$-Ru $3d_{3/2}$ doublet to high BE of ~ 282 eV which **indicates Ru interaction with perylene red**

(b) **Addition of Ir shifts** the Ru $3d_{5/2}$-Ru $3d_{3/2}$ doublet to lower BE, **characteristic of Ru metallic state**

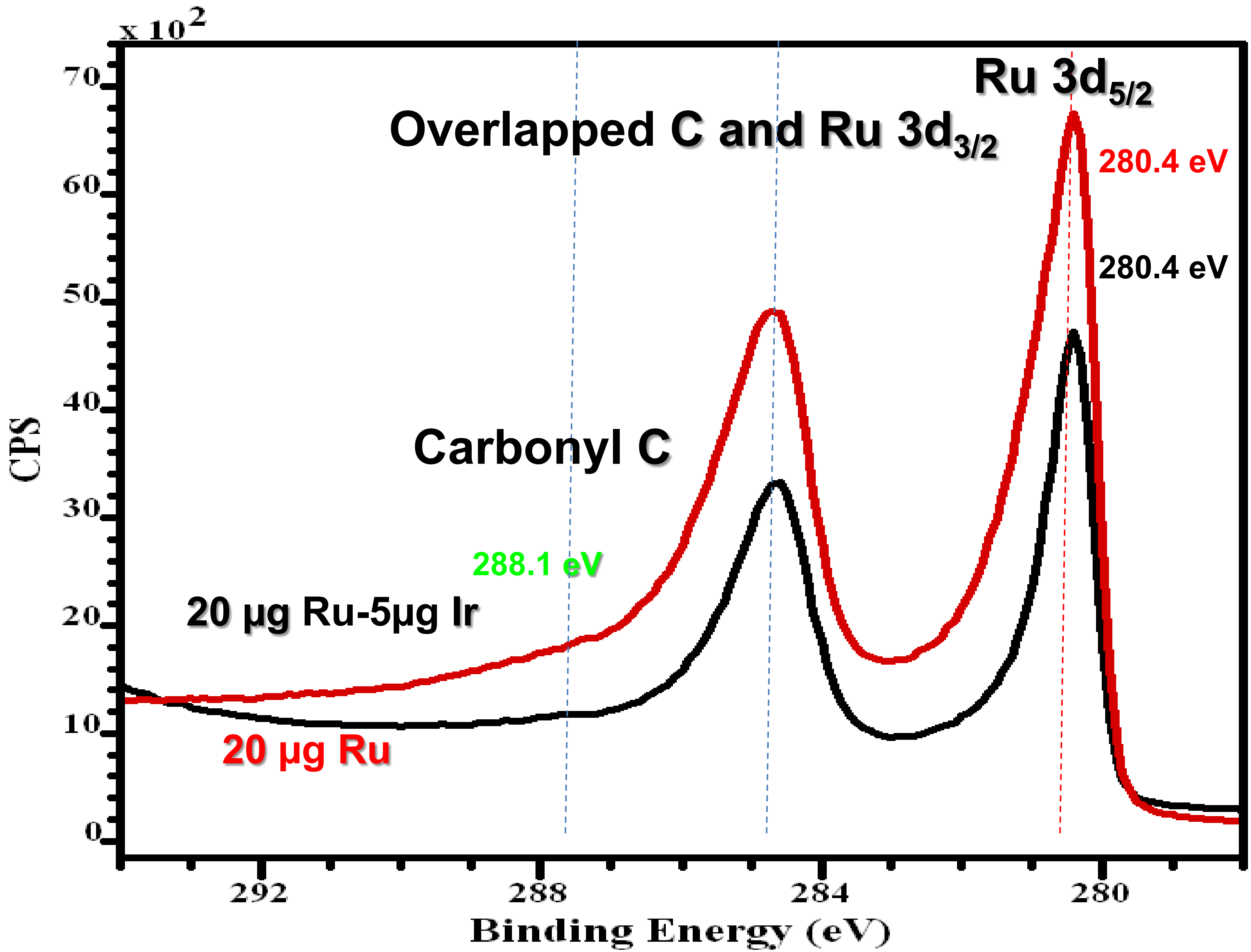
(c) The shift of Ru $3d_{5/2}$ peak is obvious

(d) The shift in Ru $3d_{3/2}$ peak cannot be seen clearly without curve fitting analysis because of its overlapping with aromatic/aliphatic C 1s peak

(e) The shift of Ru $3d_{3/2}$ peak can only be seen via a very small shift of the most intense peak of overlapped C-C and Ru $3d_{3/2}$

(f) The very visible carbonyl carbon peak of perylene red is convenient for a calibration because it shows that the Ru shift is real and not some artifact of charging

(g) The following slides show that the shift of **Ru 3d doublet by Ir addition decreases proportionally with increased Ru loading**



x 10^2
70
60
50
40
30
20
10
0
CPS
Overlapped C and Ru 3d3/2
Ru 3d5/2
280.4 eV
280.4 eV
Carbonyl C
288.1 eV
20 µg Ru-5µg Ir
20 µg Ru
292
288
284
280
Binding Energy (eV)

Collaboration

Partners

- **AFCC** (Subcontractor):
  - **Independent evaluation, Short-stack testing, Ex-situ/in-situ characterization, Component integration, Fundamental understanding**
- **Dalhousie University** (Subcontractor; ended 12/31/2012)**: 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)**: STEM Characterization**
  - **Fully integrated, provides invaluable feedback and insight into the OER catalyst**
  - **STEM and EDS analysis fully synchronized with catalyst development**
- **Argonne National Lab** (Collaborator; no activity during the final year)**:**
  - **EXAFS characterization and OER catalyst stability**
  - **ORR suppression on anode**

Future Work

The remainder of the final year will be focused on 3 major areas:

- OER-Pt NSTF catalysts evaluation **readiness for “real life”** automotive applications
  - Continue the short stack evaluation with AFCC with new/modified OER catalysts
  - Assess the boundaries of the OER – Pt/NSTF application
  - Assess the lowest Pt loading limit in respect to performance
- **R&D of the OER catalyst with respect to durability** in ‘real life’
  - Fundamental **materials studies** to further the understanding and the paths to improvement of the stability of the OER-Pt NSTF catalysts
- Fundamental **engineering studies** of the OER-Pt NSTF catalysts
  - Understand the impact of processing, integration and interaction with other MEA components

Summary

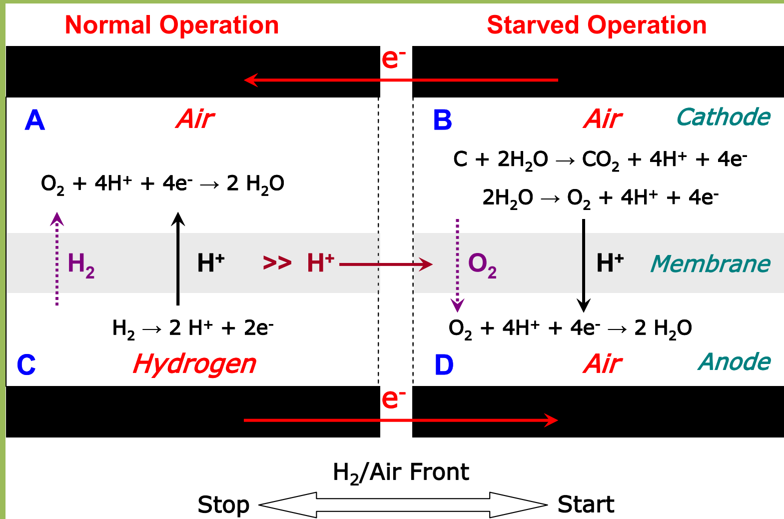
The final year project milestones have been achieved:

- **200 cycles of 200 mA/cm^2** for **cell reversal** with **0.037** mg/cm^2 **total** PGM on the anode **with 1.7 V upper limit**
- **5,000 startup cycles** with **upper voltage limit of 1.45 V** and with **0.088** mg/cm^2 **total** PGM on the cathode **with ECSA loss of < 10%**;
- **Reduced ORR** current on the **anode** by a **factor > 1000;**
- **Fundamentals of the high specific and mass OER activity of RuIr-Pt/NSTF were explored and potential explanations elaborated;**
- **Full size MEAs for three short stacks were produced at 3M and were evaluated by AFCC;**
- **FC performance of low loading Pt on OER-able anode was the same as on higher Pt loading anodes, for both NSTF and dispersed based catalysts;**
- **Shortcomings identified during the stack testing were addressed and preliminary solutions were successfully assessed;**
- **Second OEM tested and confirmed the 3M lab results**.

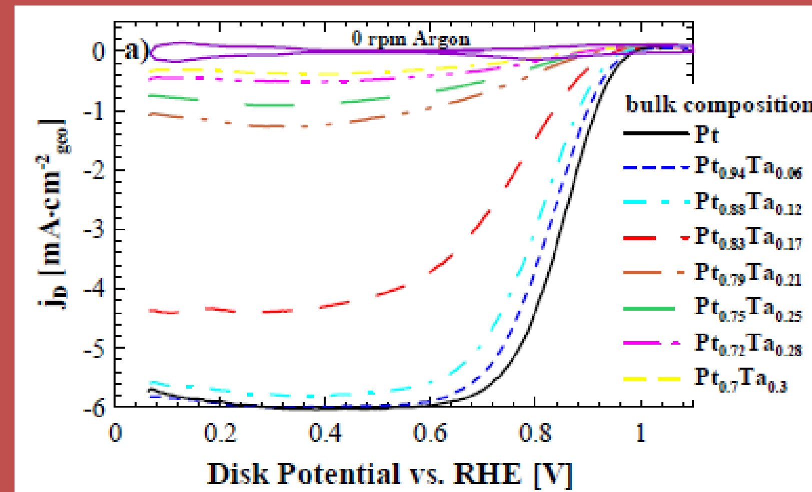
Technical Back-Up Slides

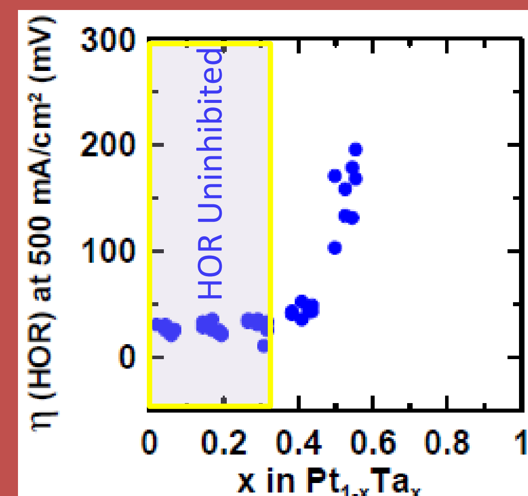
SU/SD and OER Catalysts Development Fundamentals

SU/SD Explained

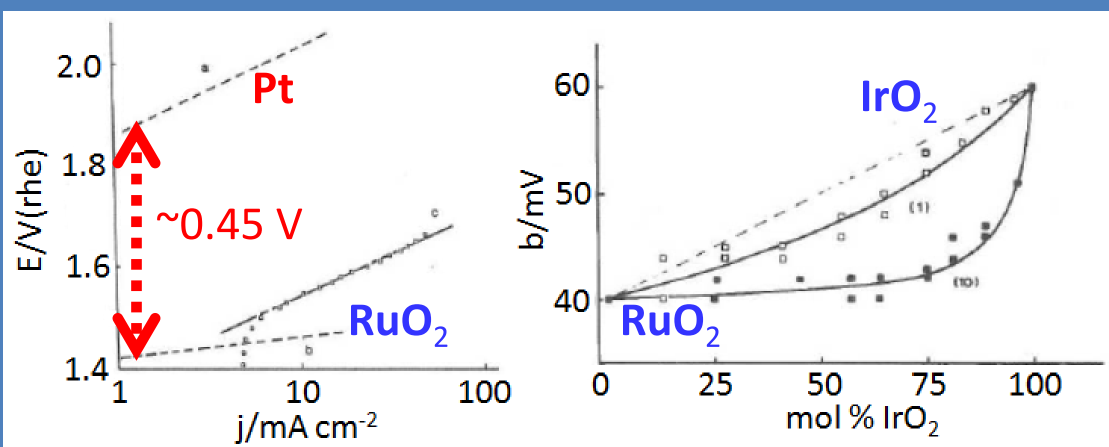


Basis for Task 2: ORR Inhibition

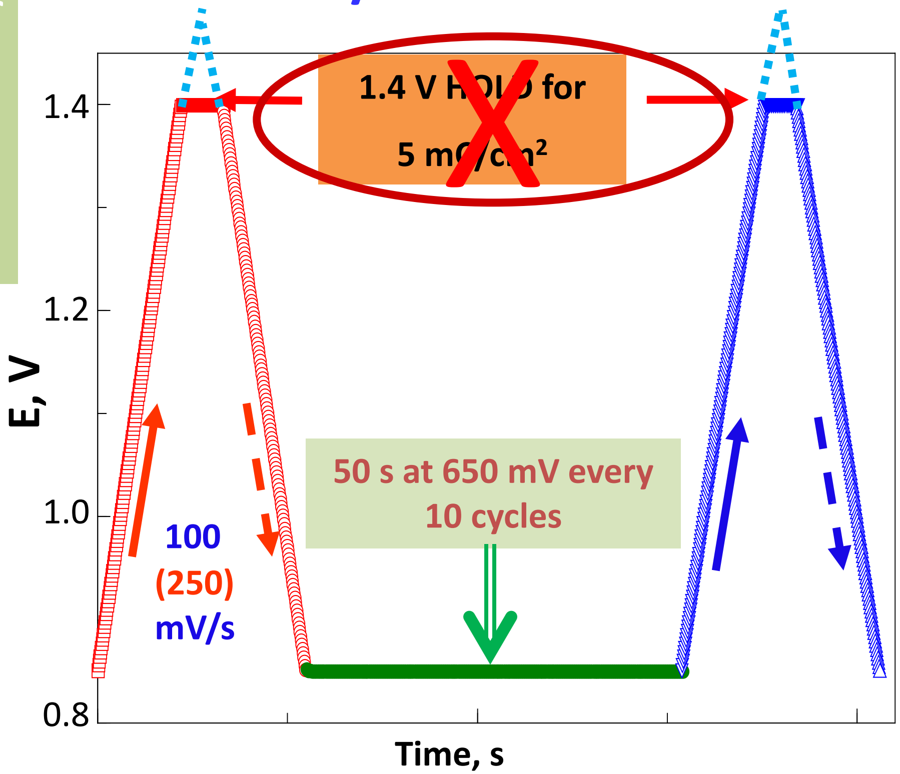




Basis for Task 1: OER Catalyst



Task 1: SU/SD Generic Electrochemical Equivalent Test

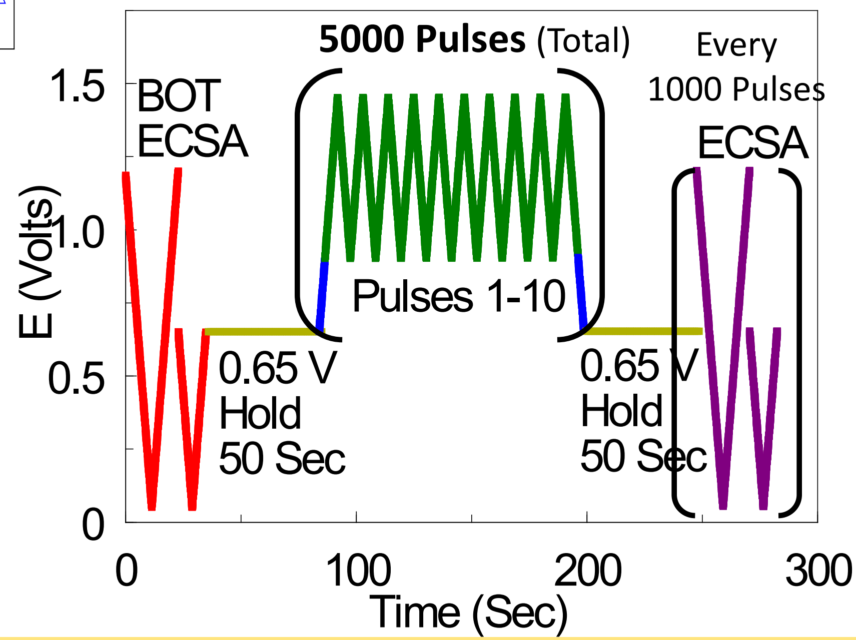


- **100 mV/s** ramp: mimics H_2 front.
- **1.6 V upper limit or to 5 mC/cm²**: mimics the **equivalent amount of O_2 to be reacted off** for **H_2/H^+ electrode potential to be established**.
- **650 mV every 10 cycles/pulses:** mimics cell voltage during normal operation.
- **ECSA** every **1,000 cycles**
- **Durability criteria:**
> 5,000 cycles; **> 5 mC/cm²**; **< 1.6 V** ; **Δ ECSA < 10%**

Note: Current responses, mostly reversible, depend dramatically on OER catalyst state:

Current immediately after the 650 mV step is the highest due to the contribution of the PtOx formation and the OER component regeneration.

Add Insert 1.6V and 0.65 V data



Cell Reversal: 2011 and Go/No Go Milestones

23 samples; 4 + replicates per **RuIr loading 1 – 10 µg/cm²** on **40 µg/cm² Pt/NSTF**
(Fabricated at the **3M** Menomonie pilot plant, 200 ft lineal)

Test protocol:

- 1. MEA Conditioning
- 2. ECSA
- 3. 20 pulses* @ **12 mA/cm²**; 60 s
- 4. 20 pulses @ **44 mA/cm²**; 30 s
- 5. ECSA

200 x 200 mA/cm²
2011: Ecell < 2.0 V; 0.050 mg/cm² PGM
G/NG: Ecell < 1.8 V; 0.045 mg/cm² PGM

- 9. ECSA

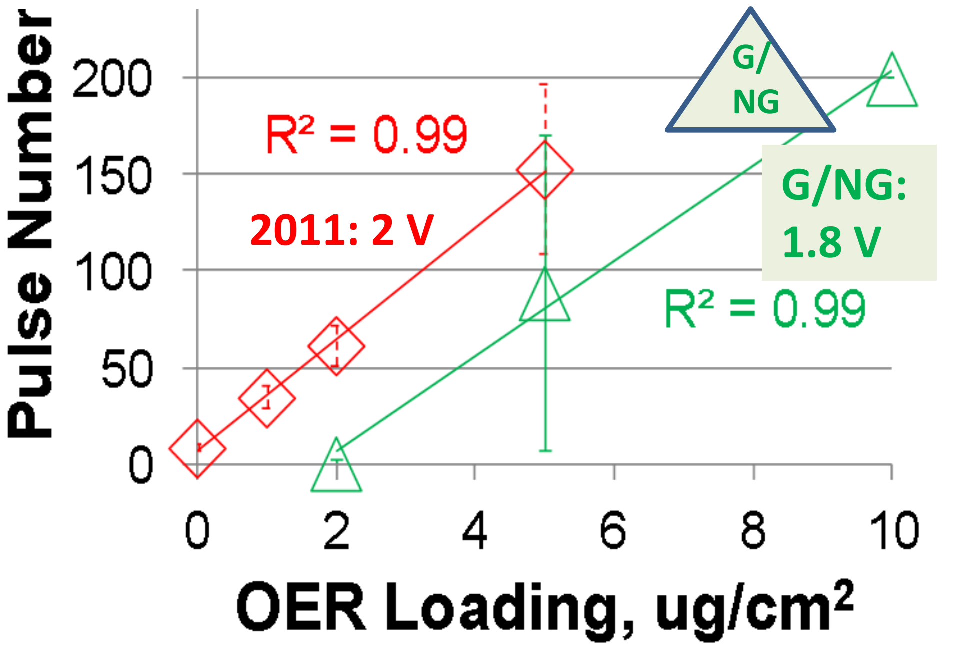
Additional durability:

- **Continuous polarization**
  @ 200 mA/cm²; 2 V upper limit

* All pulses (cycles) square wave followed by –1 mA/cm² for 1 min.

FC conditions:
70/80/80 °C; 1000 sccm
A: N_2; C: H_2

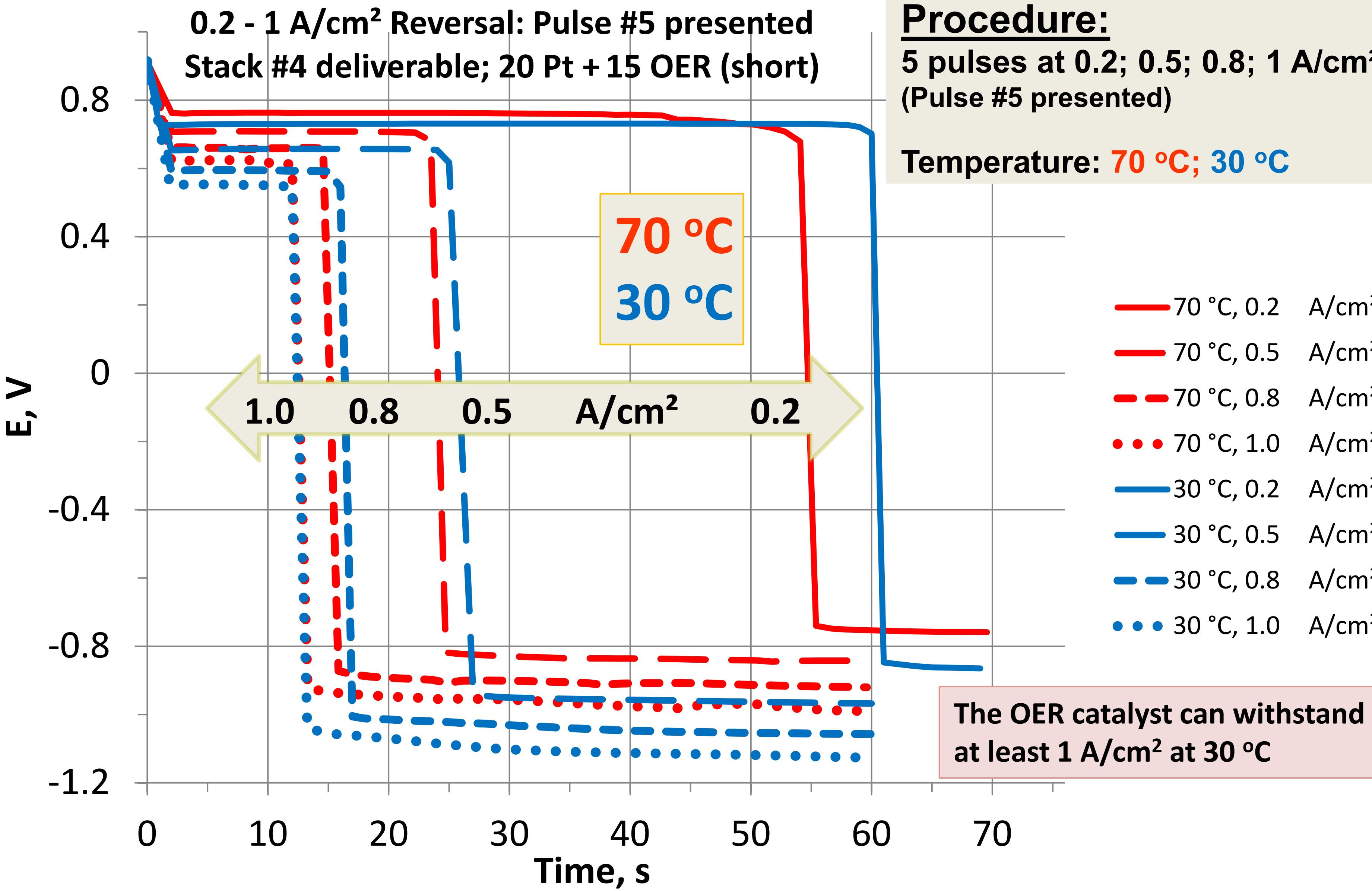
Number of cycles to **upper limit** of **2 V** and **1.8 V**



All 6 samples tested w/ 10 µg OER have passed 200 cycles with a lot of "room" to spare. **These samples fulfilled Year 2 milestone**.

To strictly fulfill the PGM loading requirement NOMINALLY **8 µg/cm² OER on 37 µg/cm² Pt/NSTF** was fabricated. **These samples fulfilled the Go/NG milestone!**

Cell Reversal at high currents



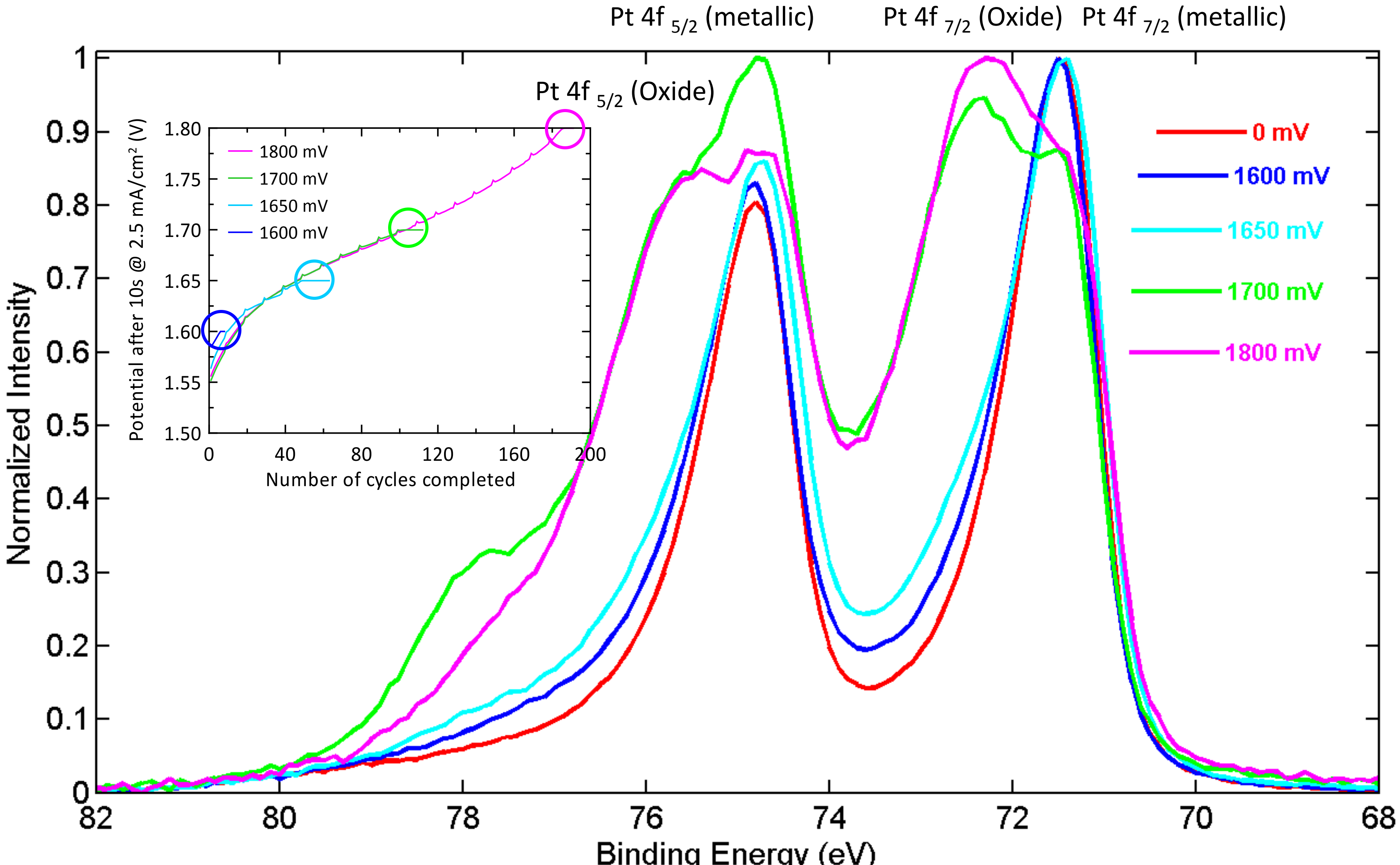
Procedure:

5 pulses at 0.2; 0.5; 0.8; 1 A/cm²
(Pulse #5 presented)

Temperature: 70 °C; 30 °C

The OER catalyst can withstand at least 1 A/cm² at 30 °C

$Pt_{0.8}Ru_{0.2}$ Pt-XPS data



Pt only shows significant oxidation above 1.65 V