# Durable Catalysts for Fuel Cell Protection
## during
# Transient Conditions

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**3M**

**DOE/3M Award DE-EE0000456**

**2011 DOE Hydrogen and Fuel Cells Program**
and
**Vehicle Technologies Program Annual Merit Review**

Washington DC, May 10, 2011

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:   July 30, 2013
- Percent complete: ~ 35%
  (03/11/2011)

## Budget

Total:                        $5,782,165
- DOE Share:           $4,625,732       Funding Received in FY10:   $ 600,000
- Contractor Share:  $1,156,433       Funding for FY11:                $1,200,000
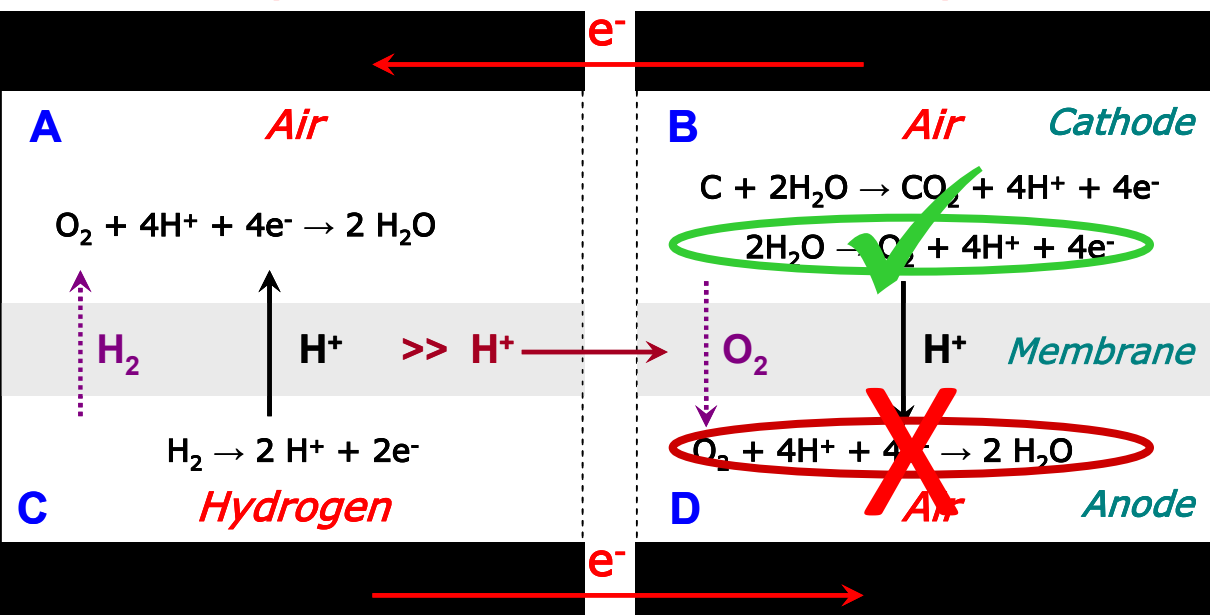
## Partners/Collaborators

- **Dalhousie University** (subcontractor)
  - **High-throughput catalyst synthesis and basic characterization**
- **Oak Ridge National Lab** (subcontractor)
  - **TEM Characterization**

- **Argonne National Lab** (Collaborator)
  - **Stability Testing, XAFS, Selective ORR Inhibitor**
- **AFCC** (OEM Collaborator)
  - **Independent evaluation, Short-stack testing**

- **3M** (Project lead)
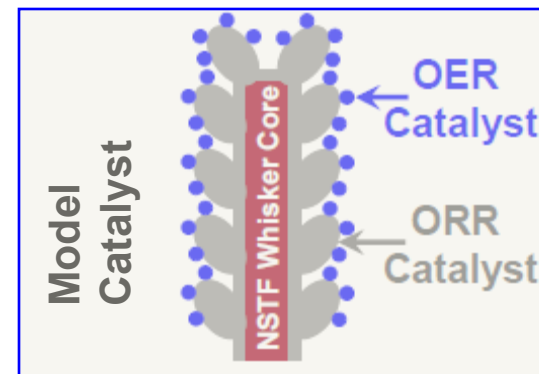
# PEMFC with fuel starved region
## How to minimize damage

**Normal Operation**  **Starved Operation**



**A** — Air — Cathode

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

$H_2$  $H^+$  >> $H^+$

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

**C** — *Hydrogen*

**B** — Air — Cathode

$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$

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

$O_2$  $H^+$  Membrane

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

**D** — *Air* — Anode

After Gu et al, ECS Transactions 11 (1) 963, 2007

$H_2$/Air Front

Stop ⟺ Start

Alleviate 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,**
- **using 3M NSTF as an ideal substrate for fully integrated catalyst development under extreme conditions with no direct carbon interference.**



Model Catalyst — NSTF Whisker Core — OER Catalyst — ORR Catalyst

**The two catalyst material concepts:**

1. *Catalysts with high oxygen evolution reaction (OER) activity*
   i. *At cathode for SU/SD (slides 6 – 9)*
   ii. *At anode for cell reversal (slides 10 – 13)*

2. *Anode catalysts with low oxygen reduction reaction (ORR) activity for SU/SD (slide 14)*

3. *Scale-up to full size CCMs*

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# Objectives and Relevance

The **ultimate objective** of the Project is to 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.**

A **specific objective** of this Project is to develop a catalyst that will **favor 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).**

**The 2010 Project milestones** were based on the Oxygen Evolution Reaction (OER) activity of the catalyst:

**1 mA/cm² at 1.45 V**; **10 mA/cm² at 1.5 V**; Additional PGM: **2 µg/cm²** (achieved)

**2011 Project milestones** (under consideration) are defined with the new 2015 DOE PGM total loading target (0.125 mg/cm²) and the new, durability oriented, more realistic testing procedure developed during this reporting period:

➢ **200 cycles of -200-mA/cm² for cell reversal** with **0.05** mg/cm² **total** PGM on the anode **with 2 V upper limit.**

➢ **5,000 startup cycles** under the existing protocol with **0.095** mg/cm² **total** PGM on the cathode **with Pt ECSA loss of <12%;**

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# Approach: 2011 Specifics

From May **2010** status:
- **Canvassed** the space around the **components** for the model OER durable catalyst in **real PEM FC** environment
- **Ru** coatings are **most active**, **Ir** are more **stable** while **Ru + Ir retain** some **properties of the two**.
- Initial characterization by **XPS** (ESCA) indicated possible interaction of the OER catalysts with the NSTF substrate, potentially favorable from a durability point of view.
- High resolution **TEM** depicted the distribution of Ru, Ir, Ti on NSTF (ORNL)

## 2011

- Develop durable **OER catalyst based on Ir and Ru**

- Establish the **extent of the OER catalyst protective action**

- Develop more **realistic, generic SU/SD** test around the milestones voltage of 1.45 V

- **Expand the OER catalyst testing to higher current densities to encompass cell reversal and accelerate the OER catalyst durability testing**

- Elucidate the **roles of Pt/NSTF** substrate and the **OER catalyst** on the durability

- Understand the **fundamentals of the OER catalyst by non-electrochemical means**

- **Evaluate and adopt inputs from OEMs**

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# Generic SU/SD test: Electrochemical Equivalent
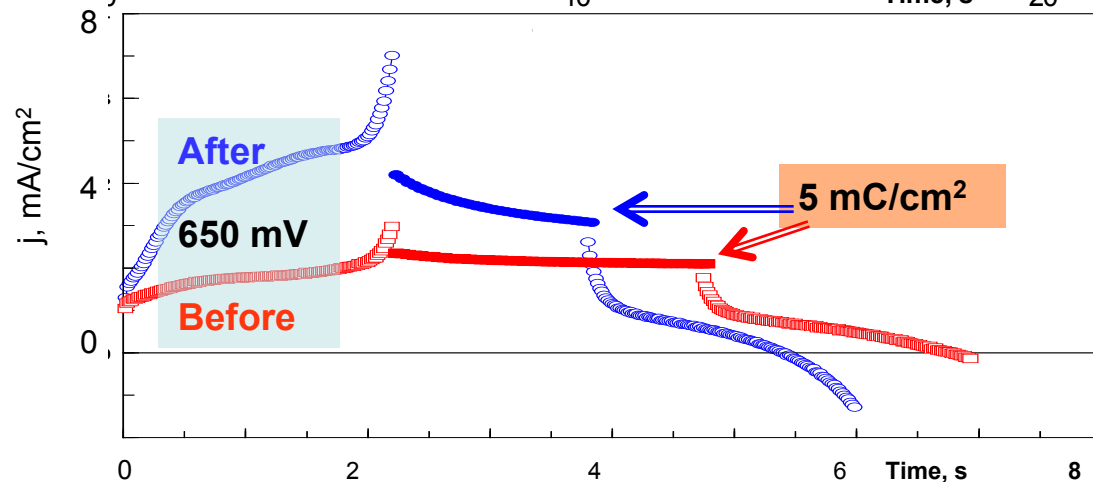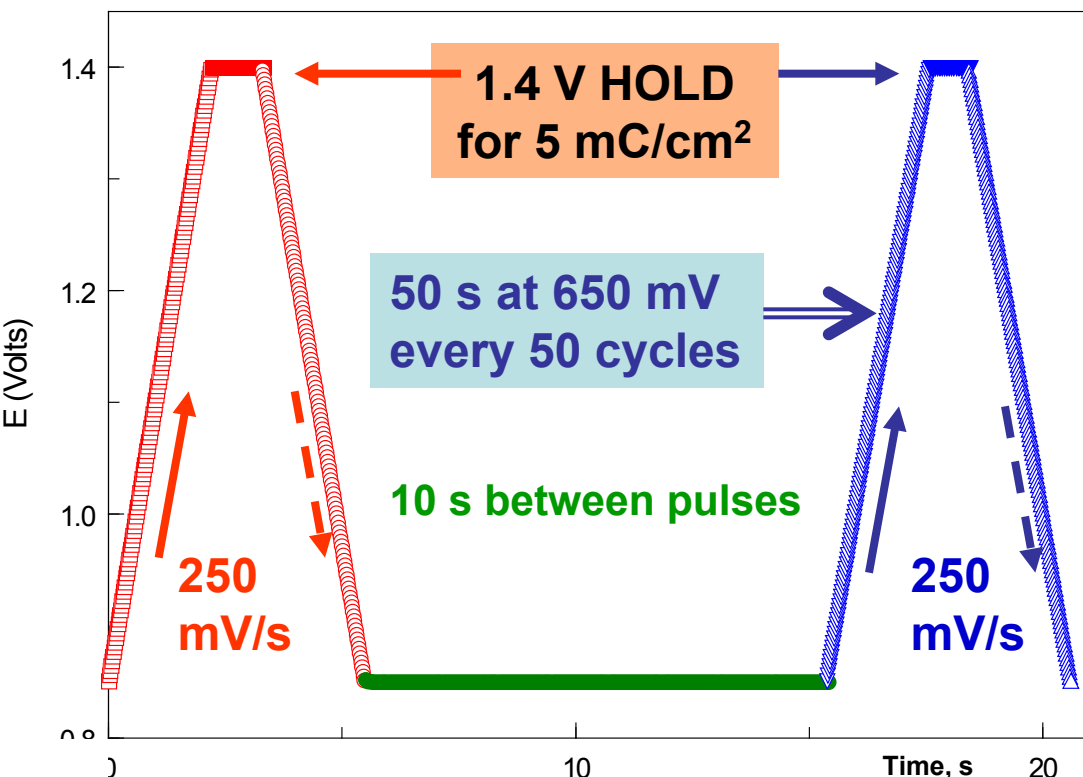


- **250 mV/s** ramp: mimics $H_2$ front.

- **1.4 V HOLD to 5 mC/cm²**: mimics the equivalent amount of $O_2$ to be reacted off for **$H_2$/$H^+$ electrode potential to be established**.

- **10 s at 850 mV** (*vs.* 1% $H_2$) assumed anode OCV under AIR.

- **650 mV every 50 cycles/pulses:** mimics cell voltage during normal operation.

- **E-Chem. SA** every **1,000 cycles**

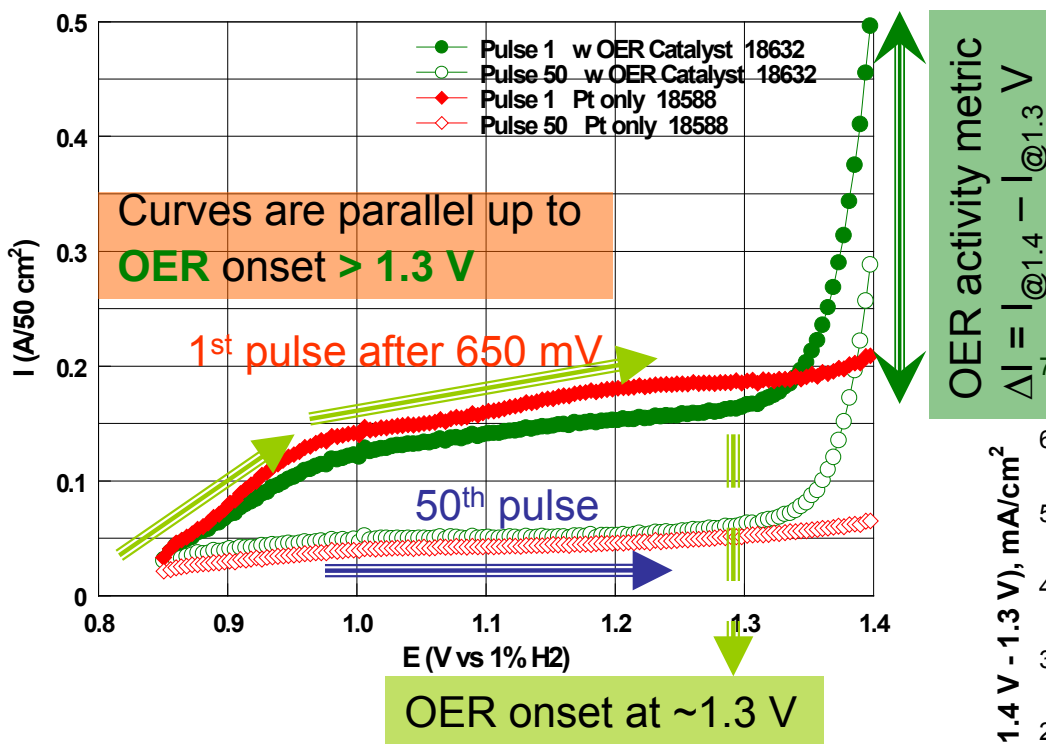- **Initial goal (arbitrary): 10,000 cycles** with current during HOLD **> 1 mA/cm²**.

The actual response

**Note: Features, mostly reversible, depend dramatically on OER catalyst state.**

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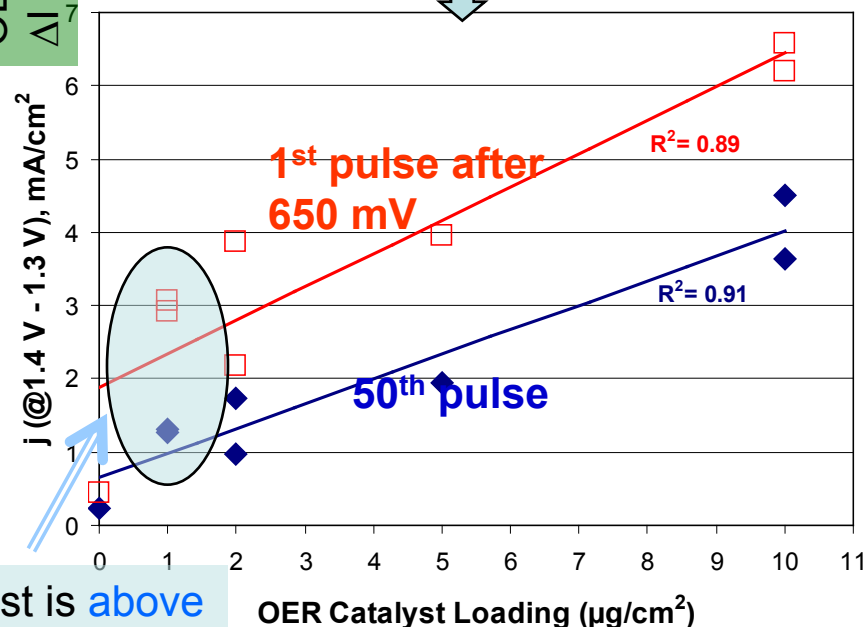# Electrochemical Evaluation: Characteristic pulses
## OER catalysts and Pt behavior during Start-up:
The response during 250 mV/s ramp to 1.4 V **before** and **after** regeneration at 0.65 V
Only fully reduced Pt plays a role during Start-up



Curves are parallel up to **OER** onset > 1.3 V

1st pulse after 650 mV

50th pulse

OER activity metric $\Delta I = I_{@1.4} - I_{@1.3}$ V

OER onset at ~1.3 V

**Note: Pt surface not regenerated at 0.85 V; OER catalyst also passivates during pulsing.**

OER catalyst activity is linear with loading.

10-fold loading increase improves **OER activity by a factor of ~3.5**



1st pulse after 650 mV    $R^2 = 0.89$

50th pulse    $R^2 = 0.91$

**1 μg/cm² OER catalyst is above the original Project milestones.**

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# SU/SD Electrochemical Evaluation: Characteristic responses

Current change **during** and **at end of** 1.4 V HOLD until 5 mC/cm² charge is reached



Current change **during** HOLD at 1.4 V until total charge of 5 mC reached

Upper tier: pulse# 1, 1001, …., 9001
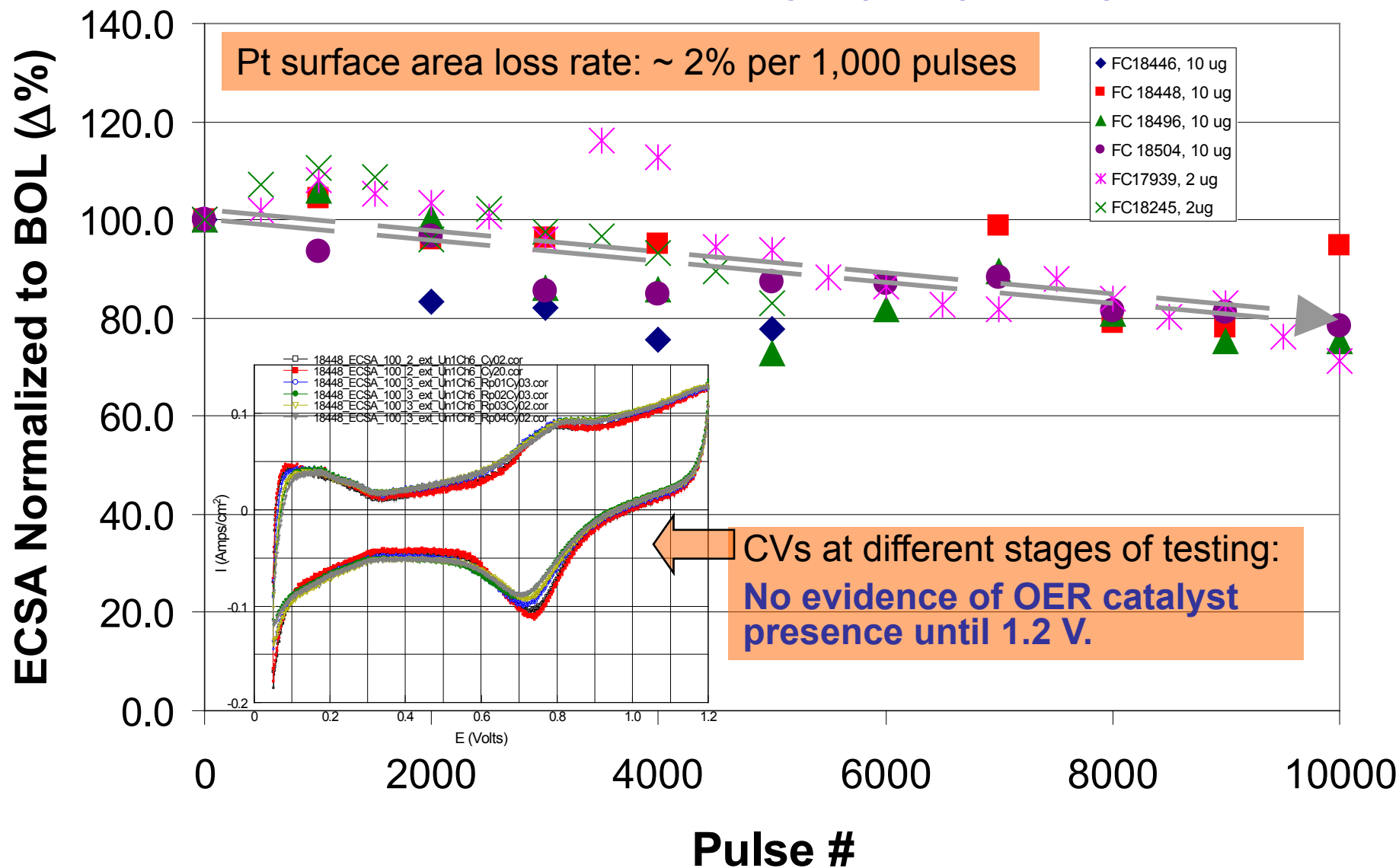
Lower tier: pulse# 1000, 2000, …, 10,000

Note: current decay results in longer time

**OER current depends on "regeneration" voltage: lower voltage such as during ECSA assessment produces most active catalyst.**

**Almost no decay if starting pulse voltage is 650 mV.**

Inside the 10,000 pulses

Upper: Pulses #: 1; 1001; 2001; 3001

Middle: Pulses #: 51 - 951; …; 3051-3951

Bottom: Pulses #: 50 - 100; …;3050-4000

The 10,000 pulses

1 mA/cm2 milestone (2009)

**Overall OER activity decay: ~30%**

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# Electrochemical Evaluation: Pt ECSA Loss during Start-up
## - A metric for the base cathode catalyst (ORR) activity losses -

Pt surface area loss rate: ~ 2% per 1,000 pulses

Legend:
- ◆ FC18446, 10 ug
- ■ FC 18448, 10 ug
- ▲ FC 18496, 10 ug
- ● FC 18504, 10 ug
- ✳ FC17939, 2 ug
- ✕ FC18245, 2ug

**ECSA Normalized to BOL (Δ%)** (y-axis: 0.0 to 140.0)

**Pulse #** (x-axis: 0 to 10000)

Inset plot legend:
- 18448_ECSA_100_2_ext_Un1Ch6_Cy02.cor
- 18448_ECSA_100_2_ext_Un1Ch6_Cy20.cor
- 18448_ECSA_100_3_ext_Un1Ch6_Rp01Cy03.cor
- 18448_ECSA_100_3_ext_Un1Ch6_Rp02Cy03.cor
- 18448_ECSA_100_3_ext_Un1Ch6_Rp03Cy02.cor
- 18448_ECSA_100_3_ext_Un1Ch6_Rp04Cy02.cor

Inset axes: I (Amps/cm²) vs E (Volts)

CVs at different stages of testing:
**No evidence of OER catalyst presence until 1.2 V.**

# Cell reversal: testing protocol
## OER at High Current Densities

**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
- 6. 100 pulses @ **200 mA/cm²**; 15 s
  2 V upper limit
- 7. 10 min at close to 0 V
- 8. 100 pulses @ **200 mA/cm²**; 15 s
  2 V upper limit
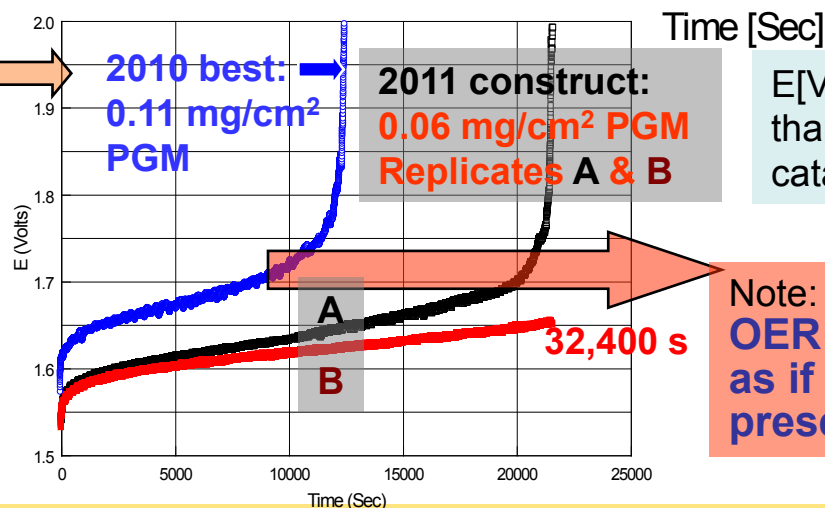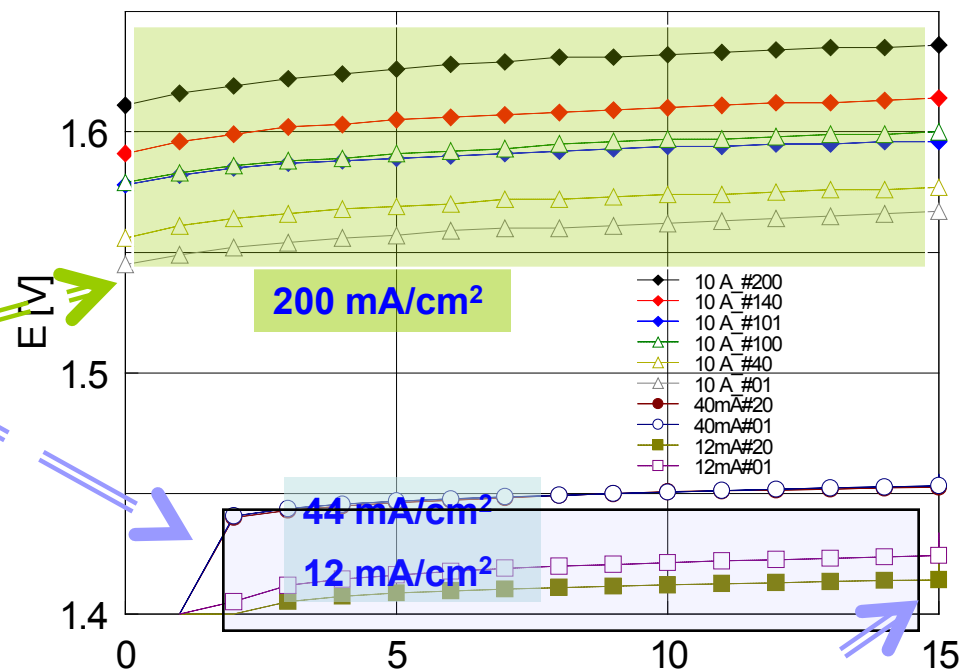- 9. ECSA

Additional durability:

- 10a. **Continuous polarization** @ 200 mA/cm²; 2 V upper limit
- 10b. High current density pulsing – up to **400 mA/cm²**

**\*) All pulses square wave followed by −1 mA/cm² for 1 min.**

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



**200 mA/cm²**

Legend:
- 10 A_#200
- 10 A_#140
- 10 A_#101
- 10 A_#100
- 10 A_#40
- 10 A_#01
- 40mA#20
- 40mA#01
- 12mA#20
- 12mA#01

**44 mA/cm²**

**12 mA/cm²**

Time [Sec]

E[V] @Pulse # 20 lower than pulse #1; initial OER catalyst activation.

**2010 best: 0.11 mg/cm² PGM**

**2011 construct: 0.06 mg/cm² PGM Replicates A & B**

A

B

**32,400 s**

Note: **Sharp increase of OER voltage at ~1.7 V, as if no OER catalyst present**

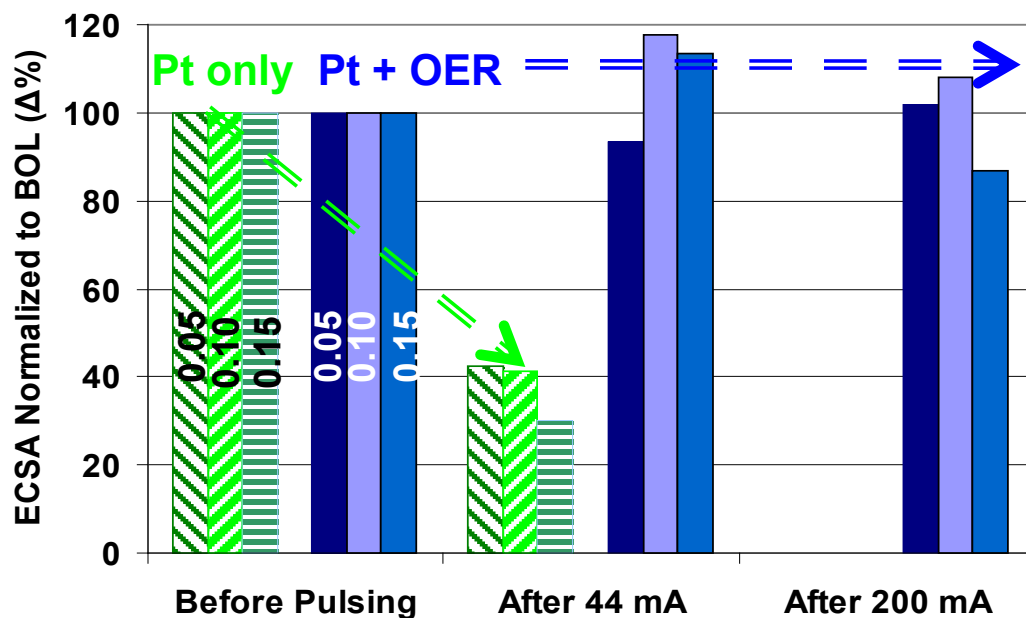# High Current Density Behavior:
# Pt loading effect on OER

10 μg/cm$^2$ OER catalyst

**Effect of Pt loading on OER activity**
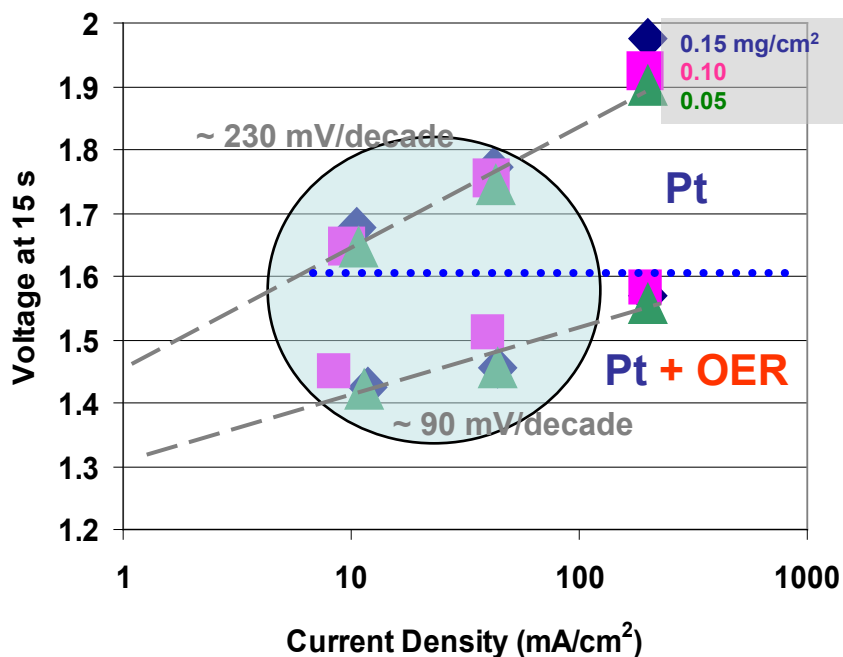


It appears that the OER activity is independent of the Pt loading

**Effect of OER on Pt Stability**
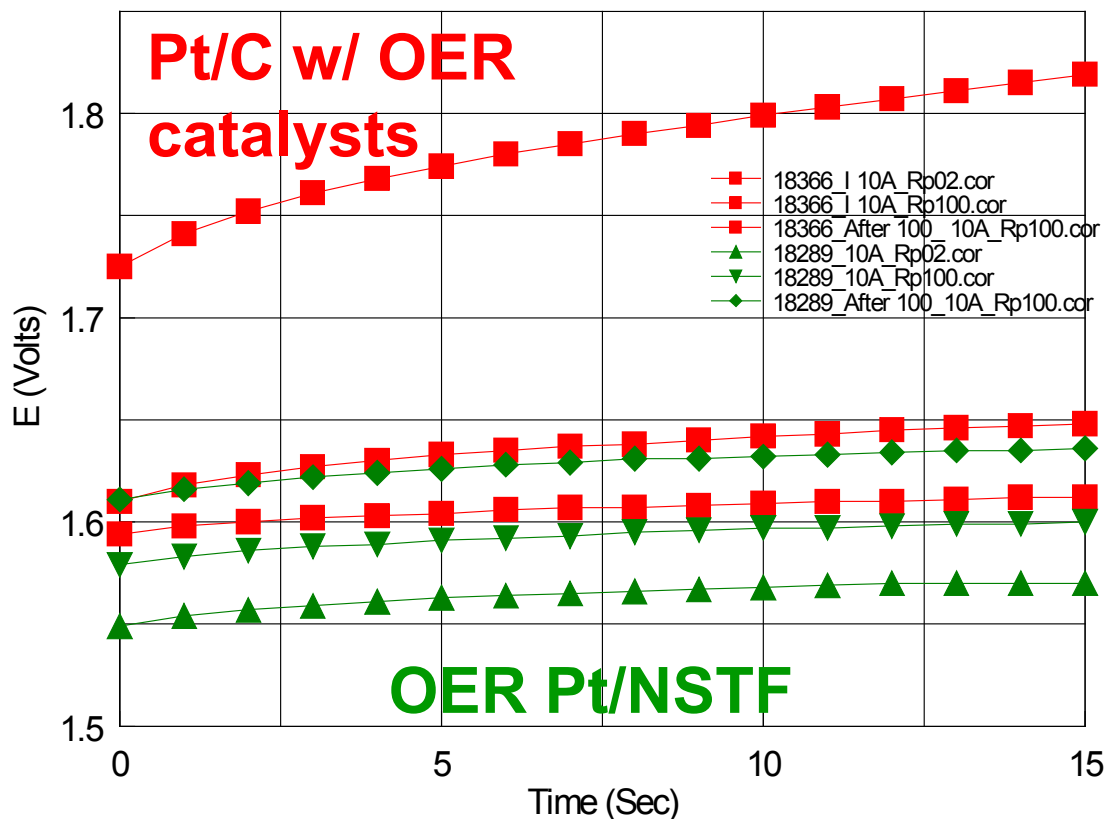


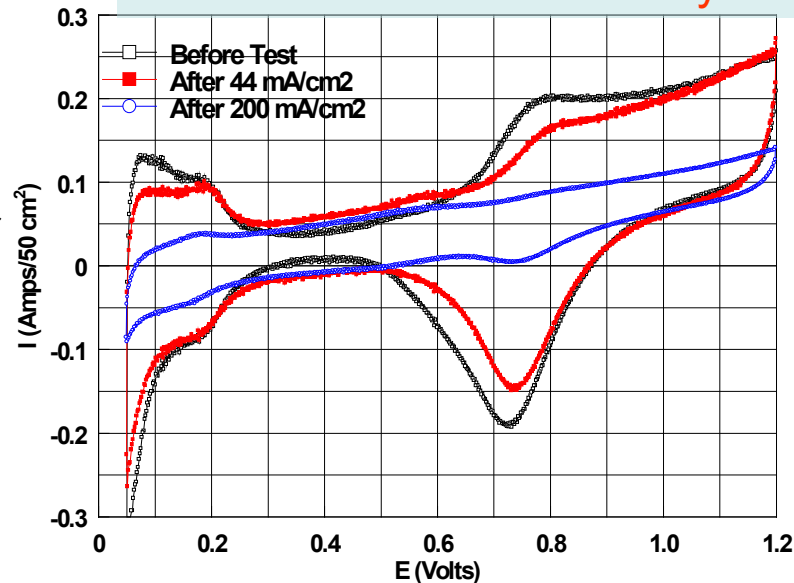Surface area of Pt without OER decreases as if >1.6 V is the Pt stability limit

# Cell reversal: Comparison of commercial OER added Pt/C (3M prepared) catalyst with OER modified Pt/NSTF

**Same Pt loading; 2X OER catalyst on Pt/C**

Cell Voltage at 200 mA/cm$^2$: Pulse # 2; 100; 200



**Pt/C w/ OER catalysts**

**OER Pt/NSTF**

Legend:
- 18366_I 10A_Rp02.cor
- 18366_I 10A_Rp100.cor
- 18366_After 100_ 10A_Rp100.cor
- 18289_10A_Rp02.cor
- 18289_10A_Rp100.cor
- 18289_After 100_10A_Rp100.cor

CVs for Pt/C w/ OER catalysts



Legend:
- Before Test
- After 44 mA/cm2
- After 200 mA/cm2

| ECSA changes: | Pt/C | Pt/NSTF |
|---|---|---|
| **Before Pulsing:** | 13.4 | 4.1 |
| **AFTER 44 mA/cm$^2$** | 9.2 | 4.6! |
| **AFTER 200 mA/cm$^2$** | 1.9! | 4.4 |

Continuous 200 mA/cm$^2$ end test

|  | 60 s | 4,800 s |
|---|---|---|

1. OER/NSTF activity remains within 0.07 V in spite of lower ECSA.

2. Pt/C ECSA lost 86% of original.

3. Pt/NSTF ECSA is practically unchanged.

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# AFCC Evaluation of 3M OER Modified Anode
# 0.06 mg/cm² PGM/NSTF

3M coated commercial 0.05 mg/cm² Pt/C with OER catalyst and
3M 0.05 mg/cm² Pt/NSTF anodes tested for comparison

## SU/SD Durability testing



**2 samples each tested**

OER Pt/NSTF
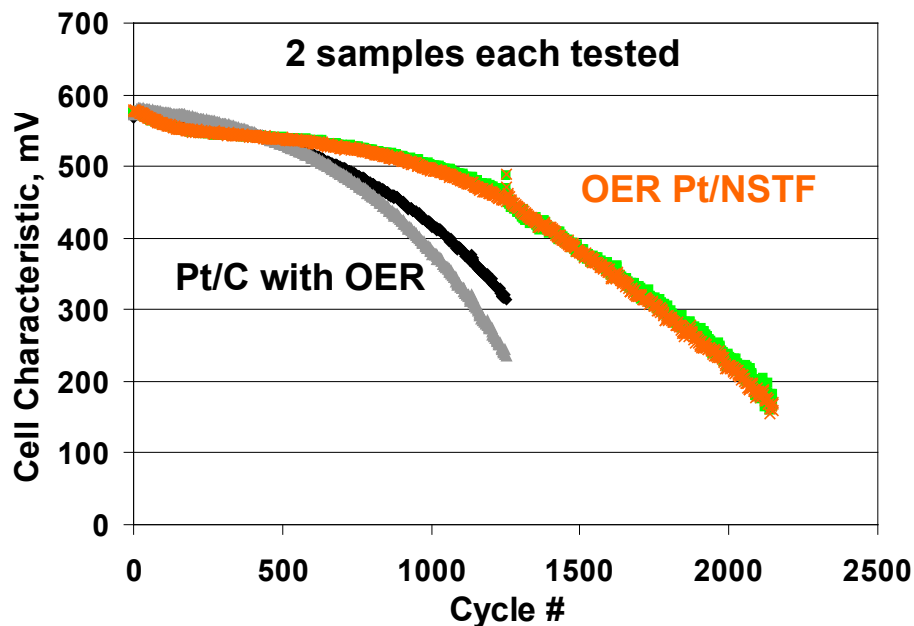
Pt/C with OER

Anode **gasses switched**
between AIR and HYDROGEN

## Cell Reversal Durability testing



10 h pass

OER Pt/NSTF

Pt/C with OER

Pt NSTF w/o OER
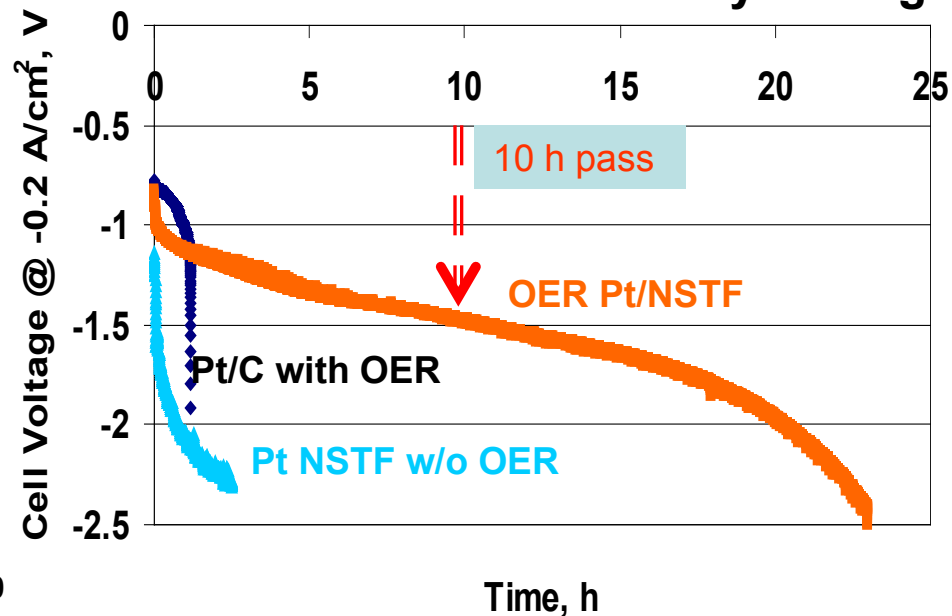
**Negative current** (-0.2 A/cm²) imposed
Anode: Nitrogen; Cathode: Air

**Note: OER Pt/NSTF outperforms Pt/C with OER in both tests**

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**SELECTIVITY OF REAL CATALYSTS**

Pt/NSTF

$a_2$ The Model

a₁

40 nm
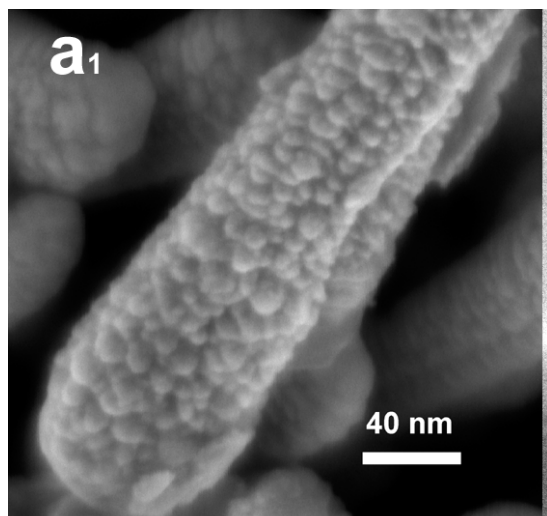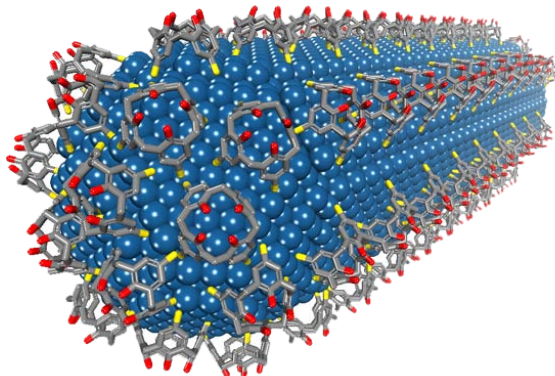
**Selectivity from single crystals can be completely transferred to real fuel cells catalyst (!!!)**

uninhibited

HOR

suppressed

ORR

— 3M NSTF catalyst
— CME NSTF w/ calix
···· CME NSTF w/calix @ 60° C

Based on: "Selective catalysts for the hydrogen oxidation and oxygen reduction reactions by patterning of platinum with calix[4]arene molecules"
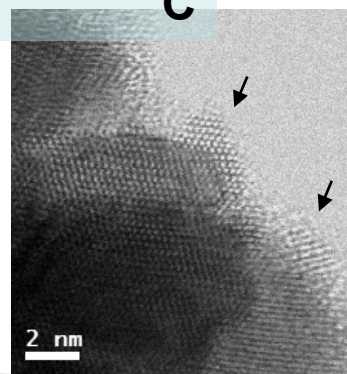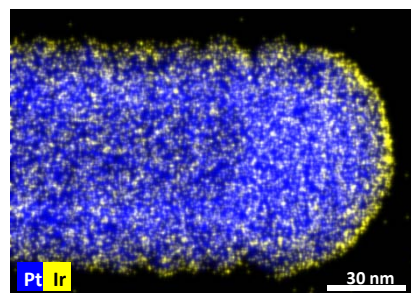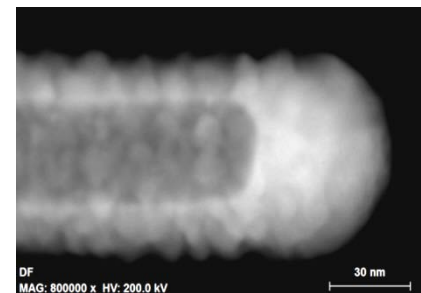B. Genorio et al., *Nature Materials*, Oct., 2010

E [V vs. RHE]
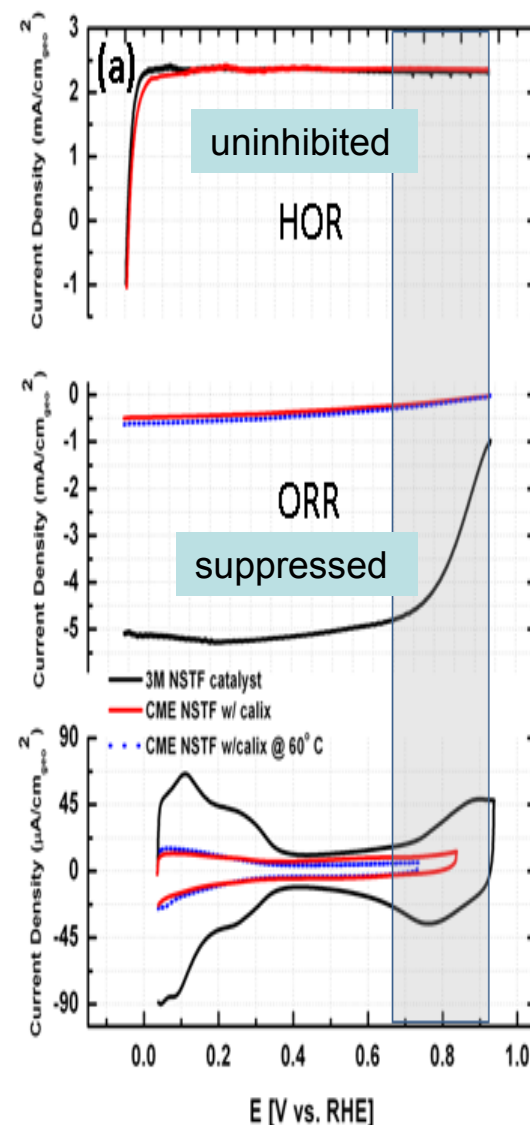
# Advanced Instrumental Analysis: TEM of as received, SU/SD tested , and CV tested OER Catalysts

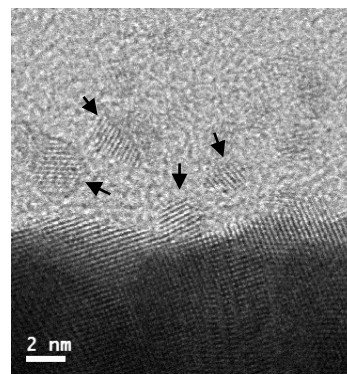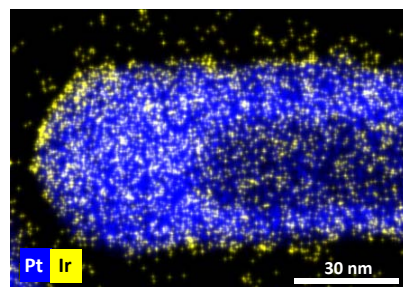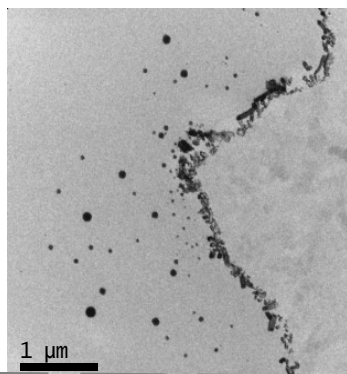| **A** | **B** | **C** |
|---|---|---|



**As received**

IrRu modified Pt NSTF whisker:
A) DF image
B) EDS map
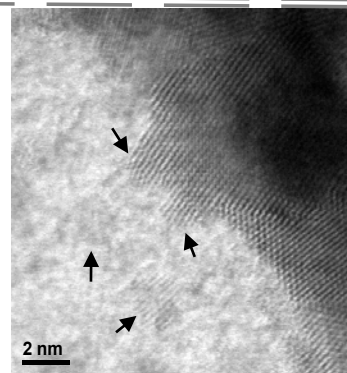C) Arrows indicate **Nanoparticles** of **Ir + Ru,** as **intended**

**SU/SD tested: 10,000 + cycles**
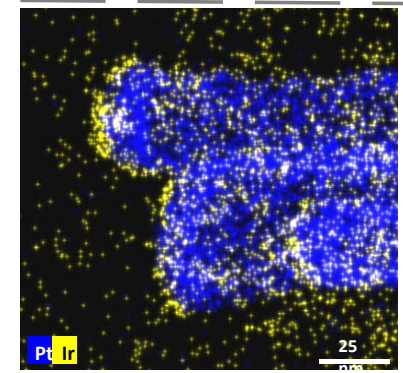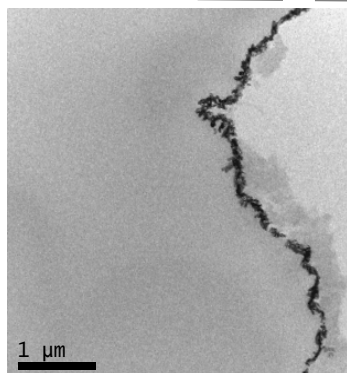A) BF image of cathode; large **particles in membrane identified as Pt**
B) EDS map indicates Ir in membrane in NSTF proximity
C) Arrows indicate **remaining** Nanoparticles of Ir on NSTF

**CR tested: 200 cycles + HOLD**
A) BF image of anode;
**No Pt particles in membrane**
B) EDS map indicates presence of Ir in the vicinity of NSTF
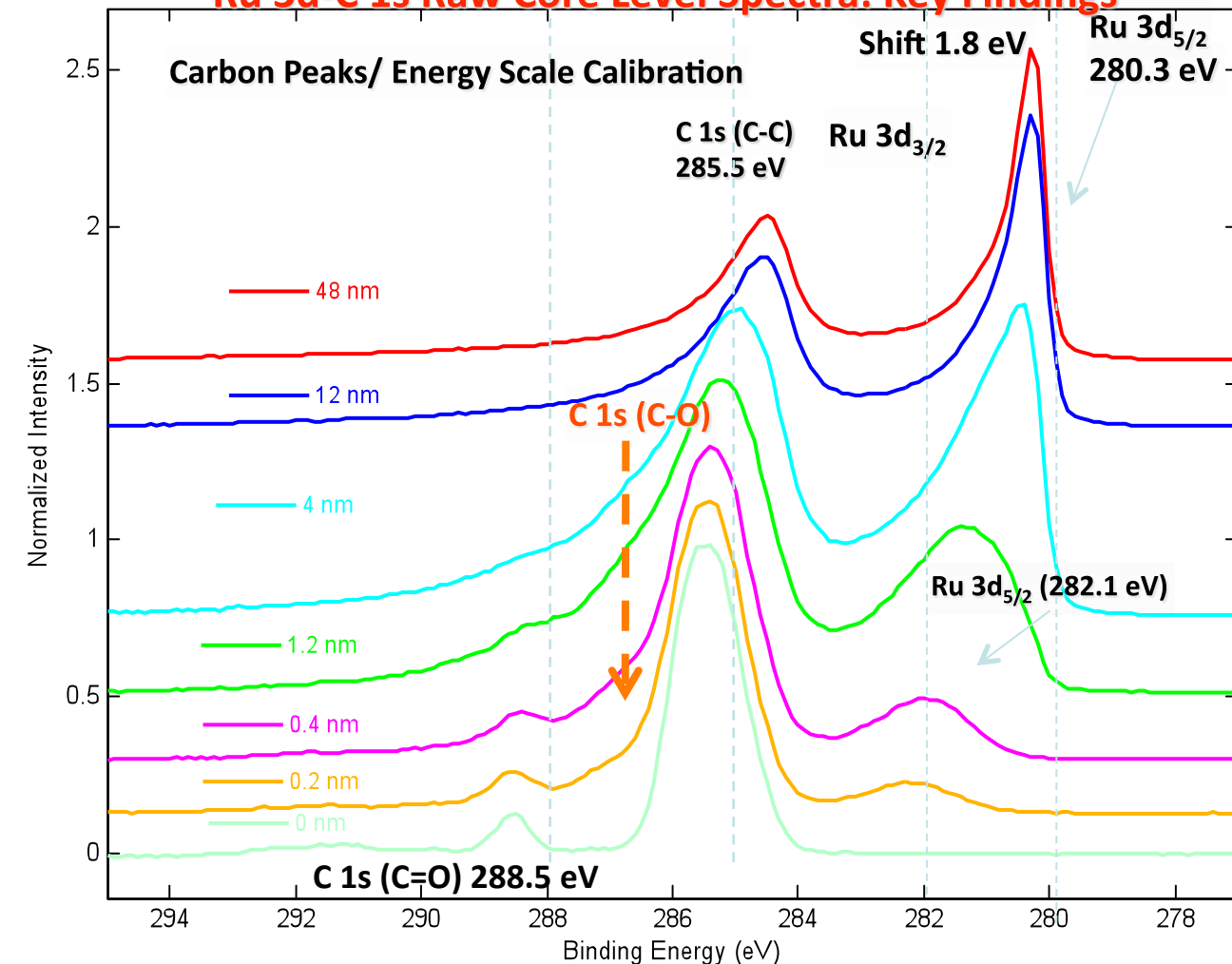C) Arrows indicate **remaining** Nanoparticles of Ir

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# Advanced Instrumental Analysis: XPS of sputter-deposited ultra-thin layers of Ru on Perylene Red NSTF

**Motivation:** Ru 3d5/2 peak shift of ~0.4 eV, found for sputter-coated 2 μg/cm² Ru *with respect to* 10 μg/cm² Ru onto Pt/NSTF, interpreted as chemical interaction Perylene Red with Ru and formation of Ru-O-C bonds.

**Proof of Ru-O-C bond existence points to the cause of Ru containing OER catalyst stability.**

## Ru 3d-C 1s Raw Core Level Spectra: Key Findings



Carbon Peaks/ Energy Scale Calibration

Shift 1.8 eV

Ru 3d$_{5/2}$ 280.3 eV

C 1s (C-C) 285.5 eV

Ru 3d$_{3/2}$

C 1s (C-O)

48 nm
12 nm
4 nm
1.2 nm
0.4 nm
0.2 nm
0 nm

Ru 3d$_{5/2}$ (282.1 eV)

C 1s (C=O) 288.5 eV

Normalized Intensity

Binding Energy (eV)

**Appearance of C 1s peak at ~ 287 eV indicating formation of Ru-O-C bonds**
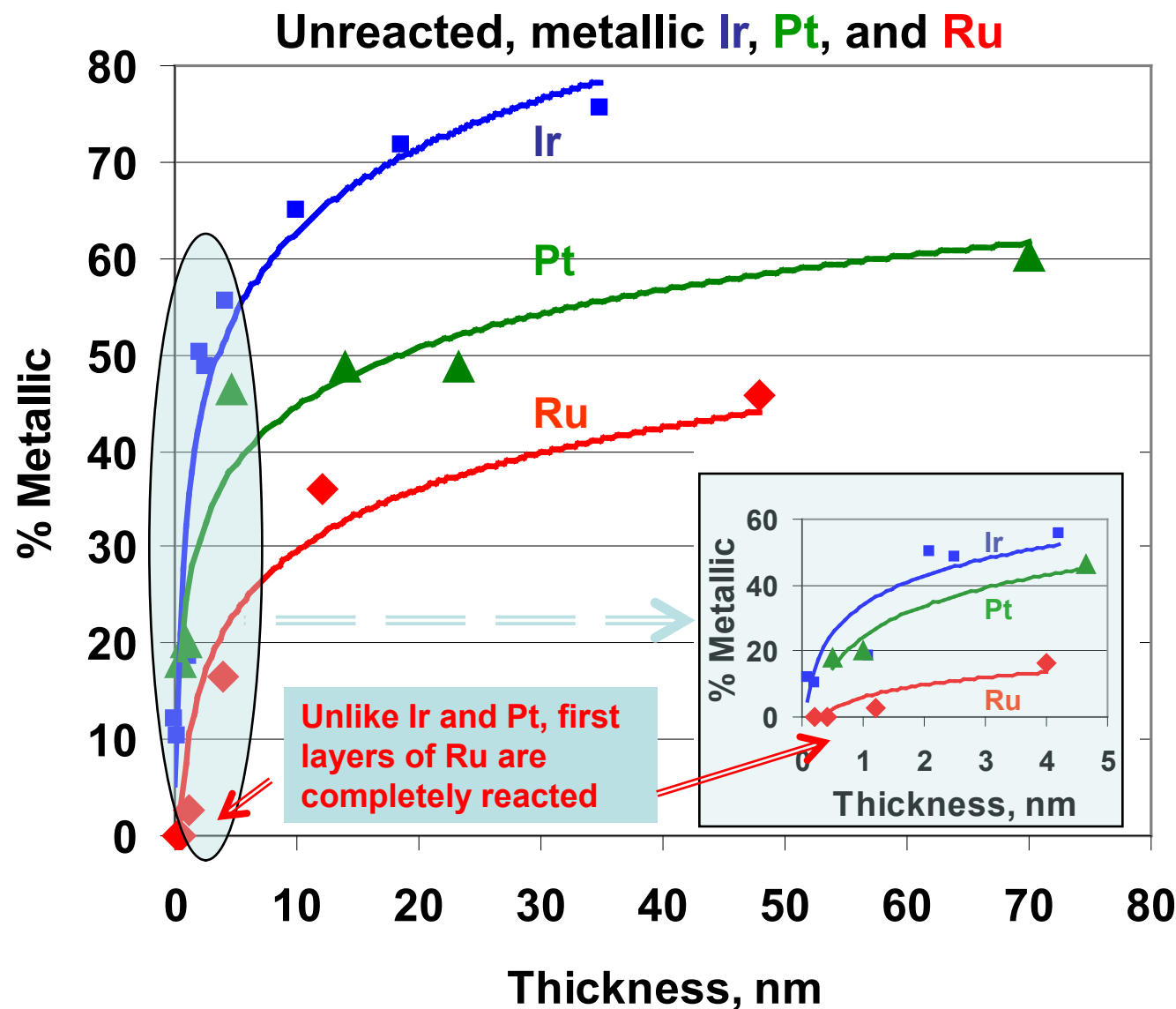
There is no C 1s peak at ~ 287 eV for Perylene Red Substrate

**Ru 3d BE Peak Broadening at Low Coverage**
*(indicates contribution of multiple oxidation states)*

**Ru 3d BE Shift of ~ 1.3 eV**
*(charging effect of ~0.5 eV subtracted)*

**C 1s peaks of Perylene Red and low Ru coverage are shifted by 0.5 eV** *(C 1s BE location used for calibration is 285 eV)*

# Advanced Instrumental Analysis: XPS of sputter-deposited ultra-thin layers of Ru on Perylene Red NSTF



**Unreacted, metallic Ir, Pt, and Ru**

Chart axes: % Metallic (y-axis) vs Thickness, nm (x-axis). Curves labeled Ir, Pt, Ru.

Inset chart: % Metallic vs Thickness, nm with curves Ir, Pt, Ru.

**Unlike Ir and Pt, first layers of Ru are completely reacted**

**OER catalyst explained** (tentative)

**TEM:**
**Nanoparticles** of **Ir + Ru**, as **intended**, were **produced** and **survived** even the most rigorous of tests.

**XPS:**
Existence **Ru-O-C** bond points to the **root cause** of Ru containing OER **catalyst stability**: strong bonding of Ru with perylene that **prevents coalescence** of the deposited OER catalyst nanoparticles.

# Collaboration

## Partners

- **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)**: TEM Characterization**
    - **Samples analyzed provide invaluable insight into the OER catalyst**

- **Argonne National Lab** (Collaborator; Partnership with two groups)**:**
    - **EXAFS characterization and OER catalyst stability**
    - **ORR suppression on anode**

- **AFCC** (OEM Collaborator):
    - **Independent evaluation; "real life" input**

# Future Work

## Immediate/remaining of FY 11

• Determine the **lowest PGM** loading with acceptable HOR and OER: Comparative study of 0.01 – 0.04 mg/cm$^2$ Pt NSTF with and without OER catalyst.

• Modify/simplify test procedure to reflect "real life", taking into account the Freedom Car Tech Team and DOE Durability Work Group inputs.

• Explore further the Ir/Ru/Pt model system space by implementing new Pt + OER **catalysts architectures.**

• Explore the practicality of sputter-deposited and/or chemically (ANL) modified anode for low ORR.

• Further understanding of the protective domain and the role of the OER catalyst by relying on state-of-the-art instrumental techniques available at the National Labs (ORNL, ANL).

## FY Year 12

Reaching the Project Go/No-Go targets as proposed according to new DOE performance targets for total PGM loading:

➢ **200 cycles of –200-mA/cm$^2$** for **cell reversal** with **0.045** mg/cm$^2$ **total** PGM on the anode **with 1.8 V upper limit.**

➢ **5,000 startup cycles** under the existing protocol with **0.09** mg/cm$^2$ **total** PGM on the cathode **with PT ECSA loss of <10%**;

➢ **Reduce ORR** current on the **anode** by a **factor of 10.**

# Summary

- Up to **10,000 cycles/pulses** mimicking the **startup/shutdown** were achieved with addition of only **2 $\mu$g/cm$^2$ PGM**.

- 200 high current densities **pulses of -200 mA/cm$^2$** mimicking the **cell reversal** were achieved with **60 $\mu$g/cm$^2$ of total PGM** with **cell voltage <2 V**.

- **Platinum dissolution** is satisfactorily **prevented** when the potential is maintained **below 1.7 V.**

- **Generic tests** for SU/SD and Cell reversal were developed and implemented.

- **Advantage** of **OER modified Pt/NSTF** over **OER added Pt/C** catalyst was clearly **established**.

- Progress in **elucidating** the **roles** of **Pt** and the added **OER catalysts** was made.

- 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 nanoparticles of Ir and Ru on NSTF provided insight into the observed fuel cell performance and ORR activity.

- Chemically modified **Pt/NSTF anode** exhibited very **low ORR** without inhibiting HOR.

- **Independent OEM testing confirmed the 3M lab results**.

- OER catalyst **scale-up**: Large size CCMs were fabricated at 3M pilot plant.

# Back-up Slides

# Electrochemical Equivalent/Generic Test:
## Basis for development

**Lifetime requirement: 6000 hrs – of what?**

13600+ startups **4000 air-air starts**
Potential excursions on cathode from **0 to 1.4 V** } **Startup**

**70+ starts** from **-25 °C**
**1000+** starts from **-5 °C** } **Cell reversal**

Standby cycles: On the order of 500,000

Short drive cycles: Average 4 trips per day

Dynamic load cycling

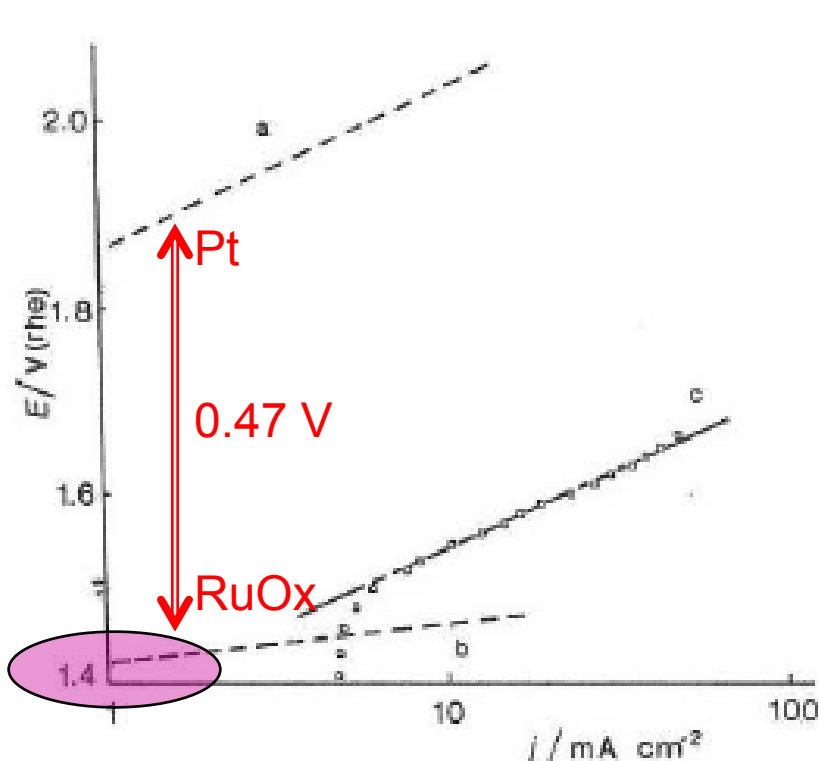Presented at: **12th UECT**, Ulm, Germany, June 16, 2010

**Key Variables** for devising generic test procedure

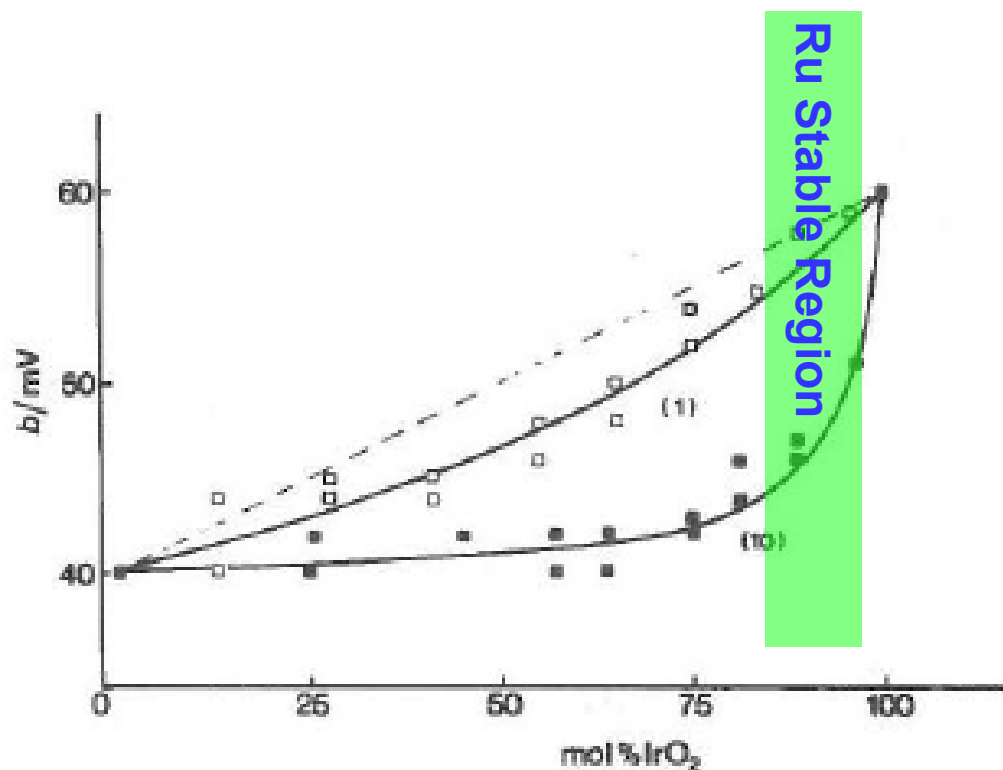**Voltage**: 1. level a cell arrives at; 2. level of anode at start; 3. levels in between

**Time (duration)** at given voltage levels

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# 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.

# OER Modified Cathode (Anode)

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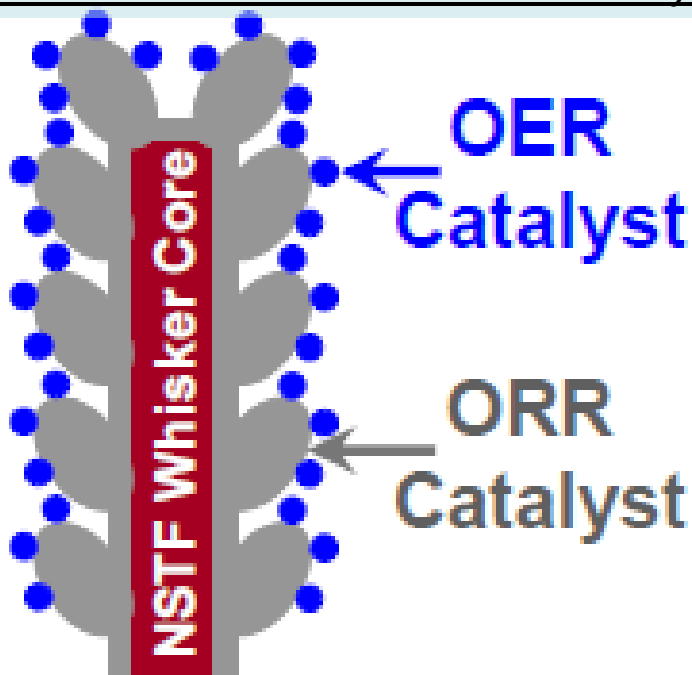
Stability and **cost**: **$TiO_2$**, *$MnO_2$, etc.* **$RuO_2$ - $TiO_2$** interfacial stability improves from 400 °C to 600+ °C

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 **1cm² of OER** catalyst on 1 cm²geo with **OER nano-cubes** of **3 nm** sides to withstand **1 mA/cm² OER** at **<1.4 V**.

• Number of catalyst **particles** needed: **$2.2 \times 10^{12}$**.

• **Ru content**: 0.41 μg/cm² $RuO_2$ or **0.31 μg/cm² Ru**.

• ORR catalyst **surface area blocked**: 0.2 cm² or **0.5%** of NSTF entitlement.

• With $TiO_2$ as support the blocked ORR catalyst area is ~1%.

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