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)

Partners/Collaborators

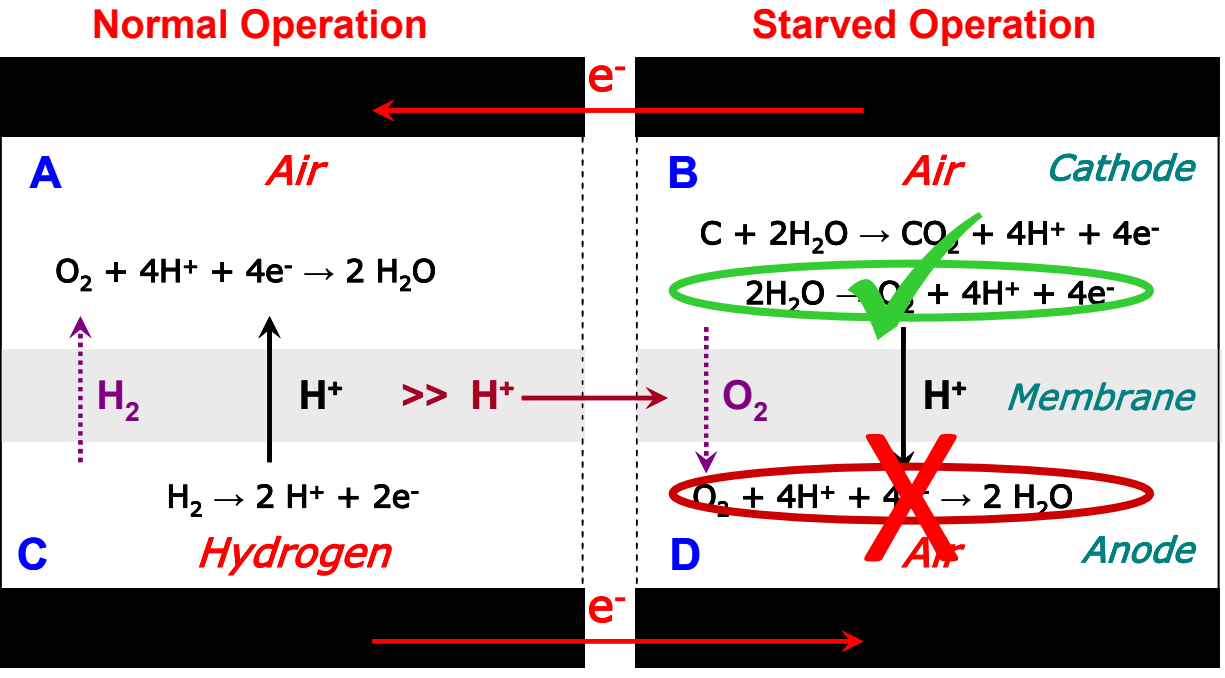
- **Dalhousie University** (subcontractor)
  - **High-throughput catalyst synthesis and basic characterization**
- **Oak Ridge National Lab** (subcontractor)
  - **TEM Characterization**
- **Argonne National Lab** (Collaborator)
  - **Stability Testing, XAFS, Selective ORR Inhibitor**
- **AFCC** (OEM Collaborator)
  - **Independent evaluation, Short-stack testing**
- **3M** (Project lead)

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

PEMFC with fuel starved region

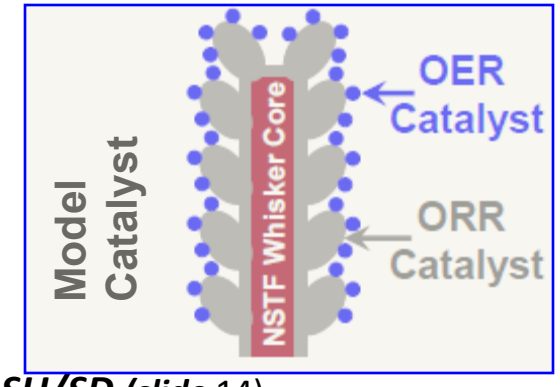
How to minimize damage



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

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.**



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***

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

2011 Project milestones (under consideration) are defined with the new 2015 DOE PGM total loading target (0.125 mg/cm^2) and the new, durability oriented, more realistic testing procedure developed during this reporting period:

- **200 cycles of -200-mA/cm^2** for **cell reversal** with **0.05** mg/cm^2 **total** PGM on the anode **with 2 V upper limit.**
- **5,000 startup cycles** under the existing protocol with **0.095** mg/cm^2 **total** PGM on the cathode **with Pt ECSA loss of <12%**;

Approach: 2011 Specifics

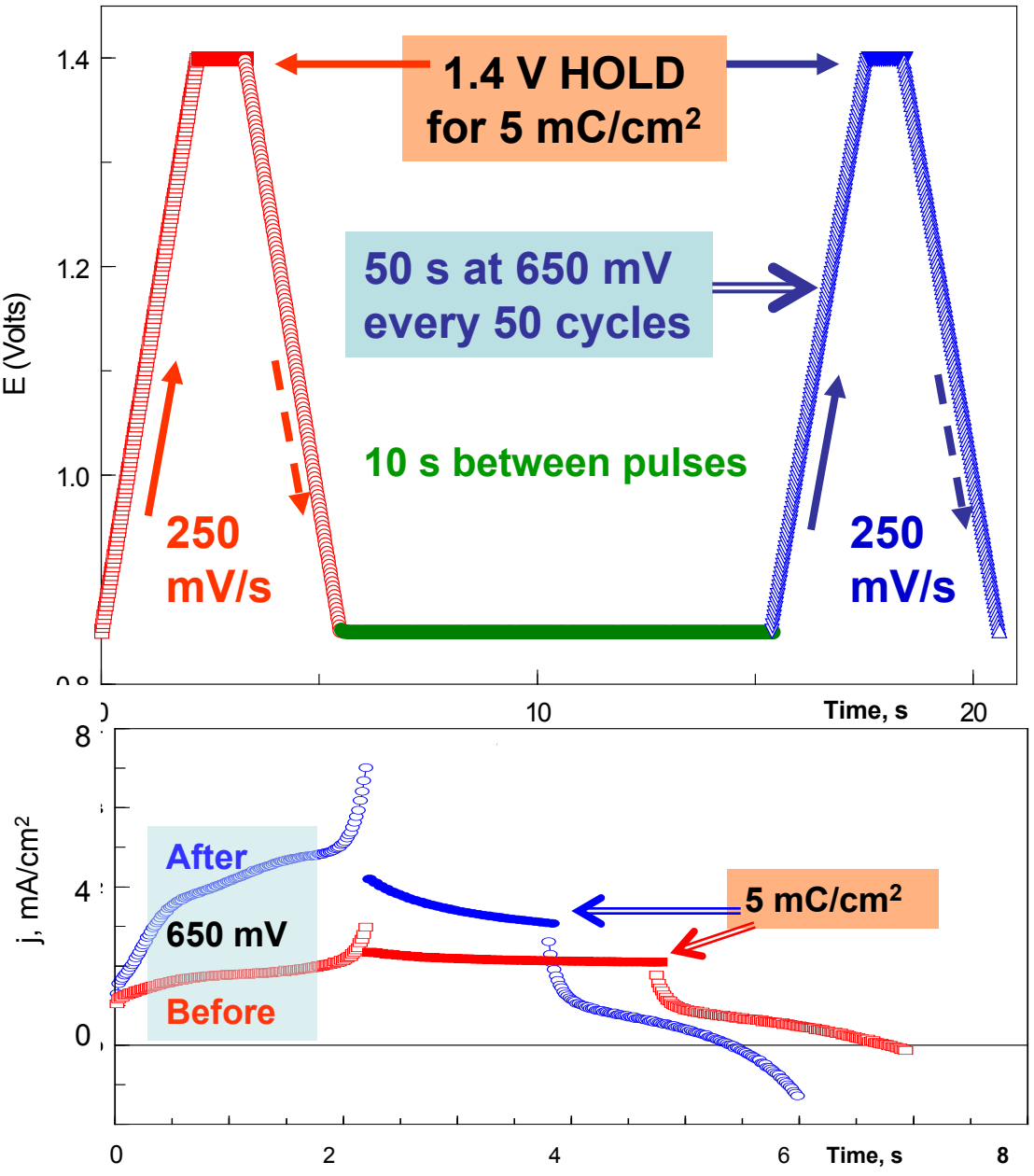
From May **2010** status:

- **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**

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**.

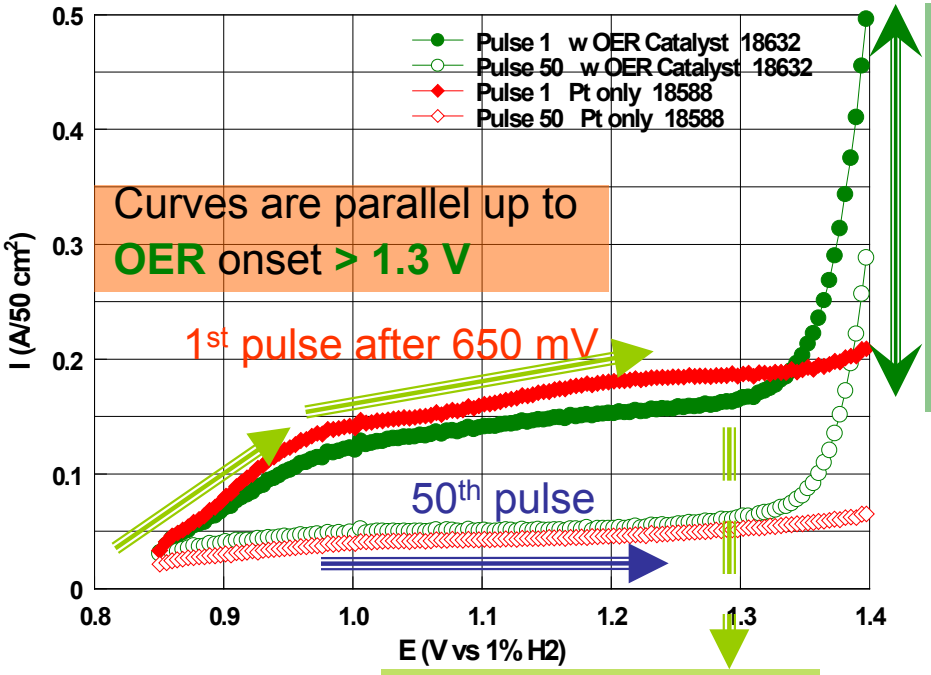
The actual response

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

Electrochemical Evaluation: Characteristic pulses

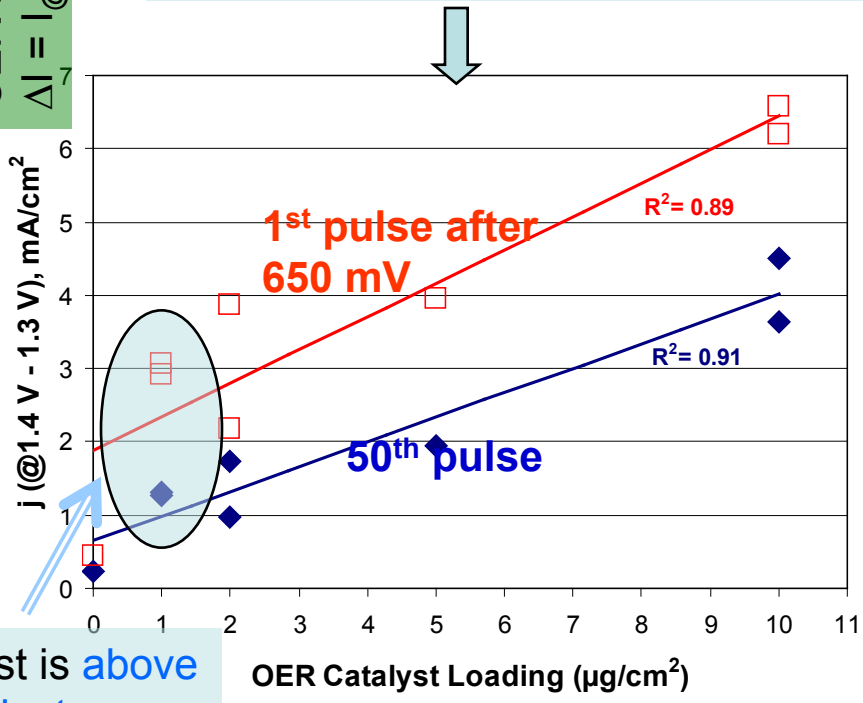
OER catalysts and Pt behavior during Start-up:

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



OER catalyst activity is linear with loading.

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

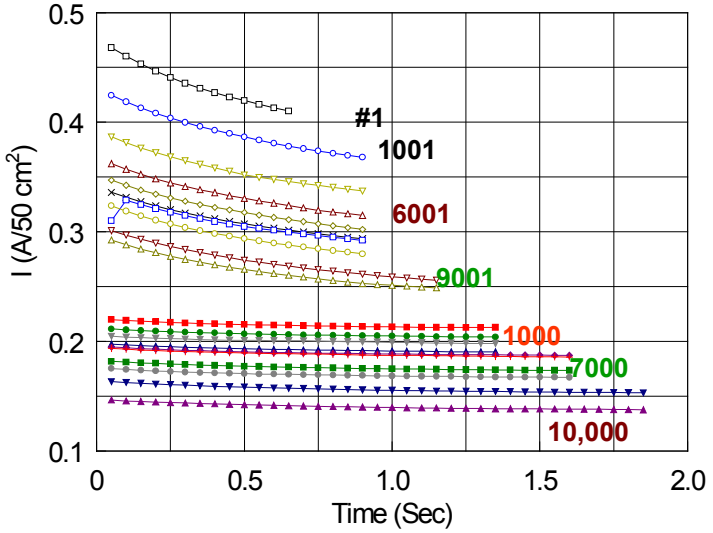


Note: Pt surface not regenerated at 0.85 V; OER catalyst also passivates during pulsing.

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

SU/SD Electrochemical Evaluation: Characteristic responses

Current change **during** and **at end of** **1.4 V HOLD** until 5 mC/cm^2 charge is reached



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

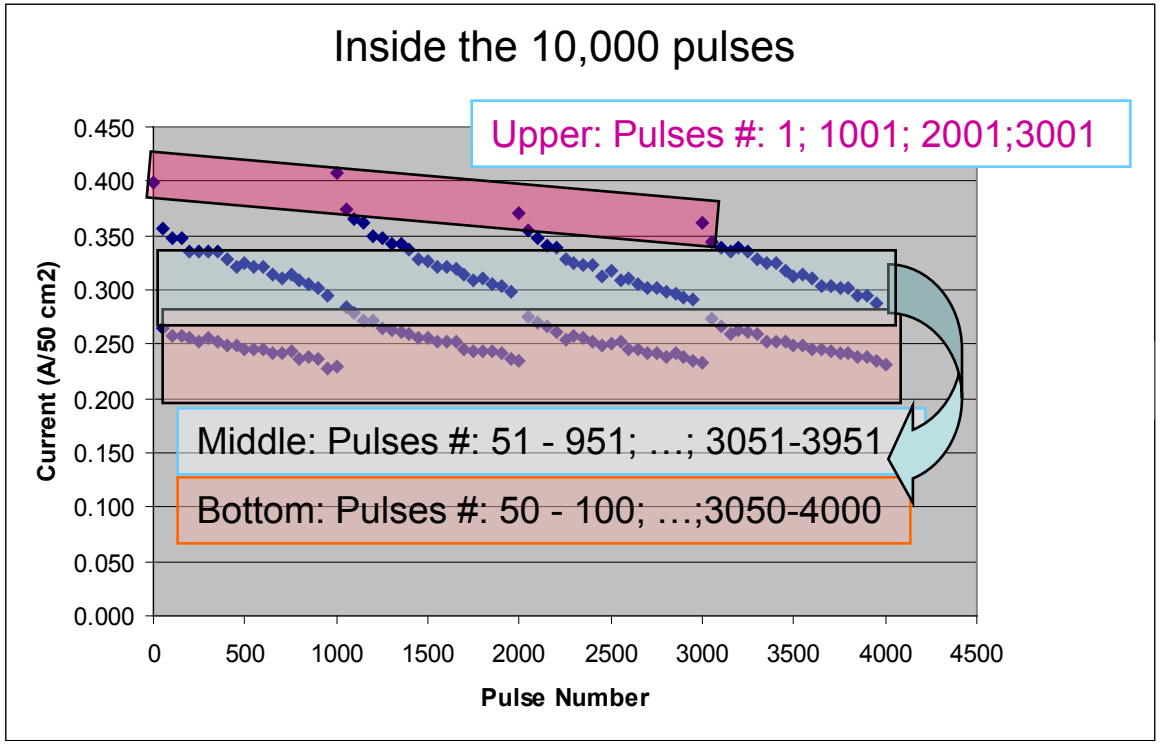
Upper tier: pulse# 1, 1001, …., 9001

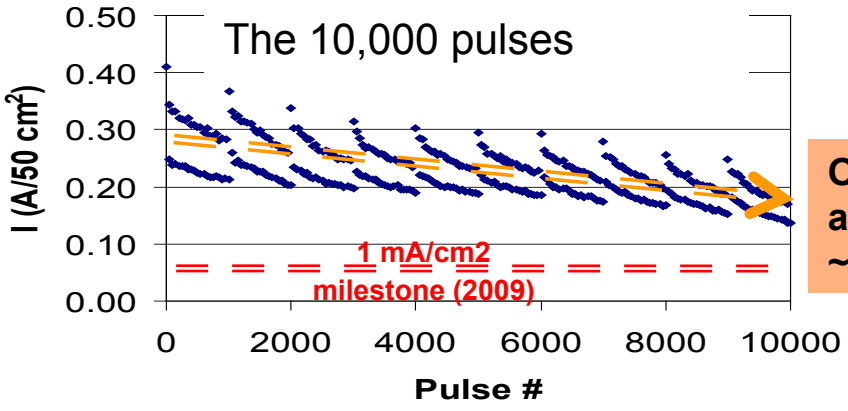
Lower tier: pulse# 1000, 2000, …, 10,000

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.

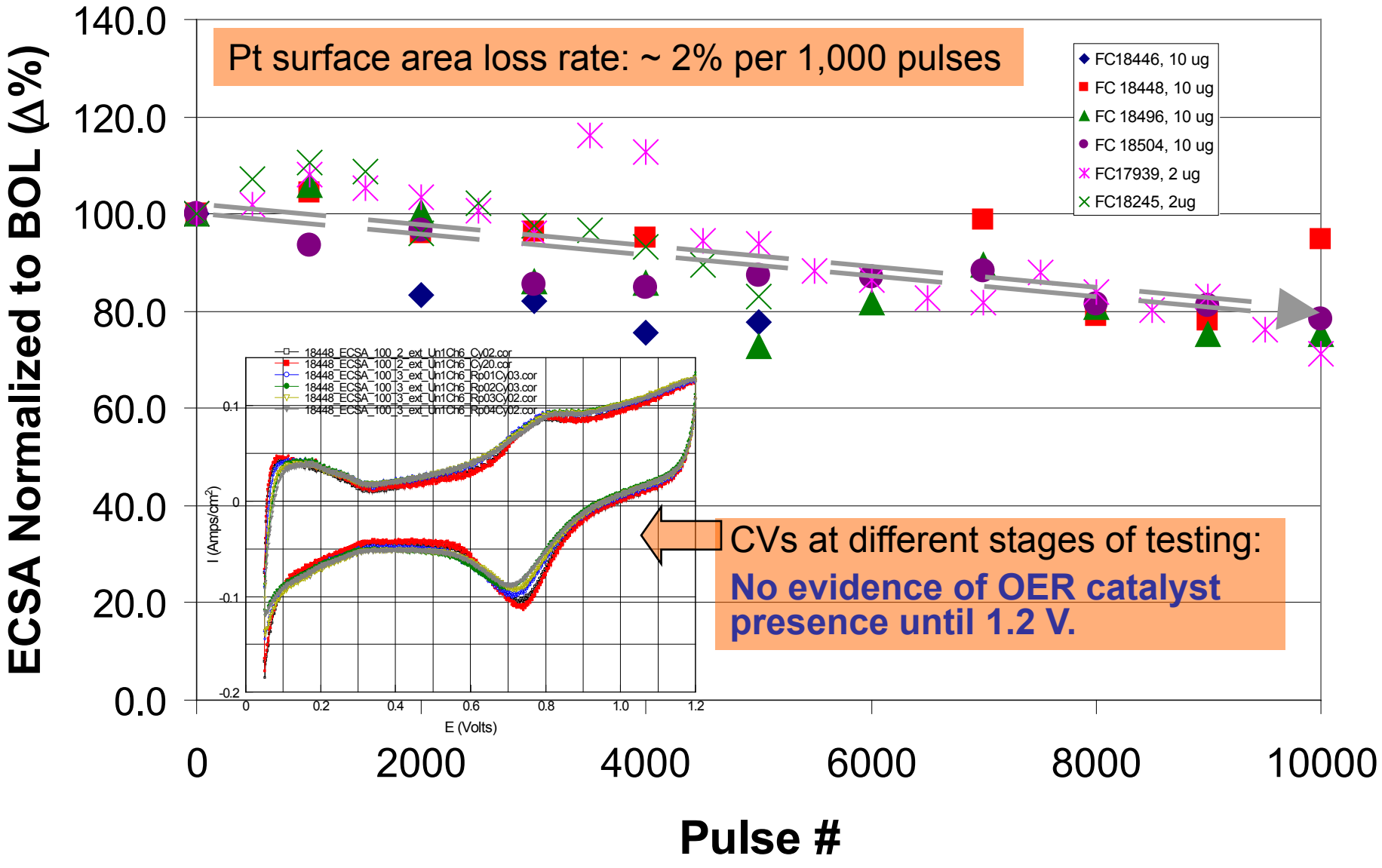




Overall OER activity decay: ~30%

Electrochemical Evaluation: Pt ECSA Loss during Start-up

- A metric for the base cathode catalyst (ORR) activity losses -

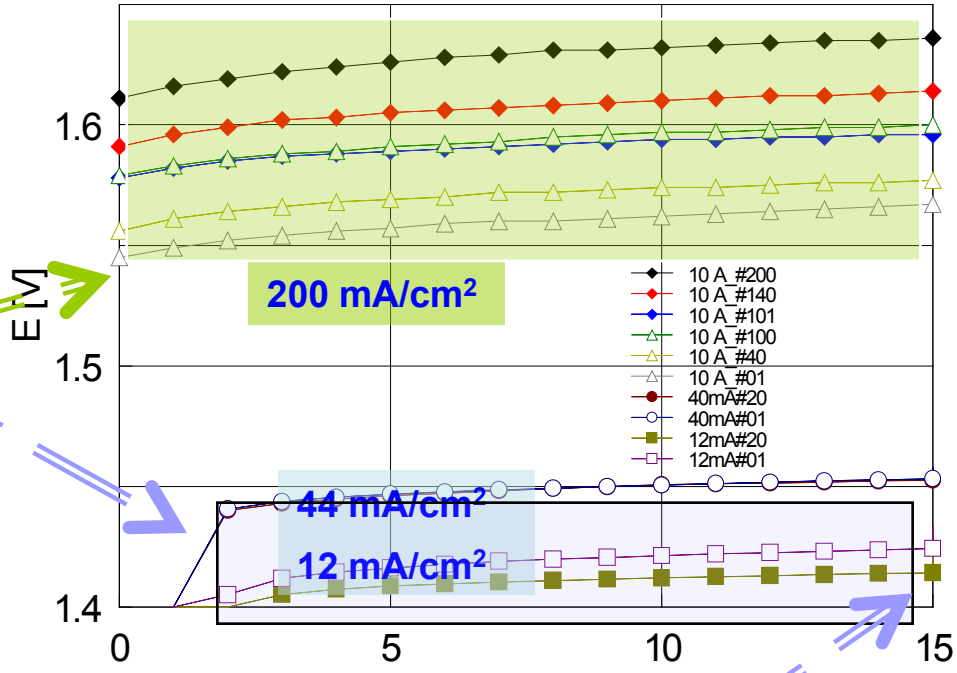


Cell reversal: testing protocol

OER at High Current Densities

Test protocol:

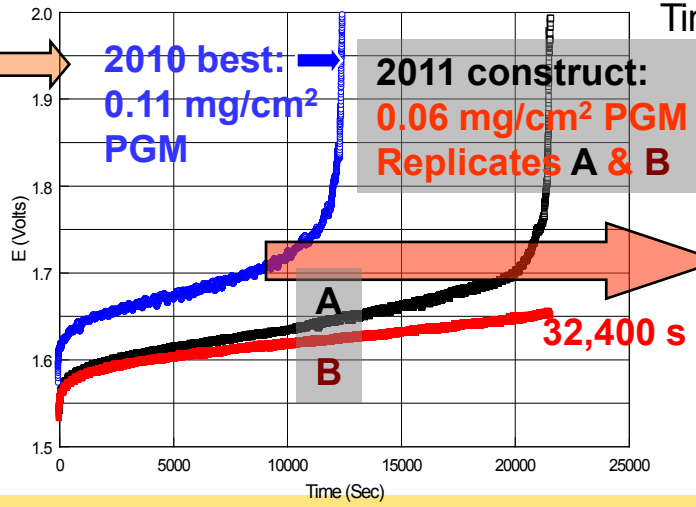
- 1. MEA Conditioning
- 2. ECSA
- 3. 20 pulses* @ **12 mA/cm²**; 60 s
- 4. 20 pulses @ **44 mA/cm²**; 30 s
- 5. ECSA
- 6. 100 pulses @ **200 mA/cm²**; 15 s
  2 V upper limit
- 7. 10 min at close to 0 V
- 8. 100 pulses @ **200 mA/cm²**; 15 s
  2 V upper limit
- 9. ECSA



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

Additional durability:

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



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

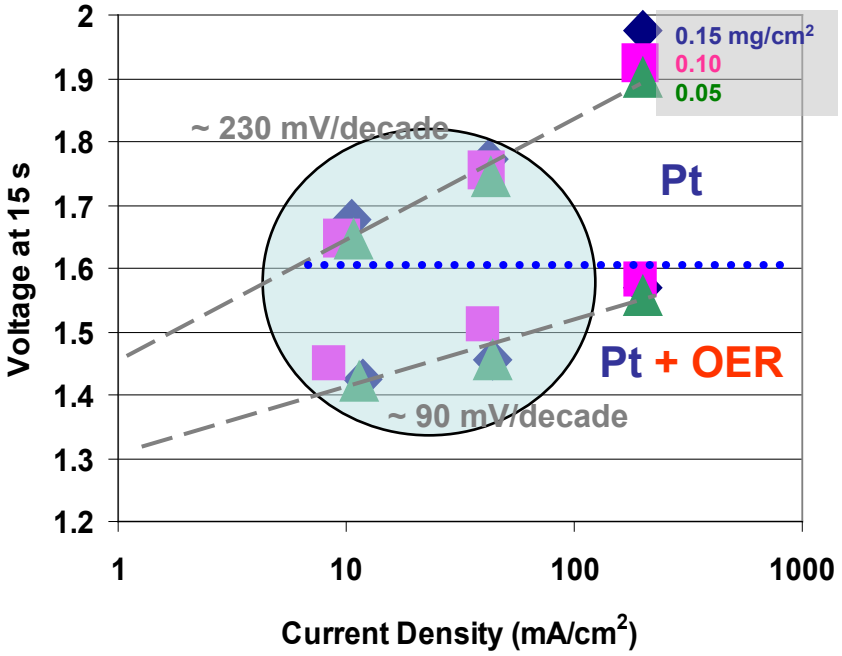
***) All pulses square wave followed by –1 mA/cm² for 1 min.**

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

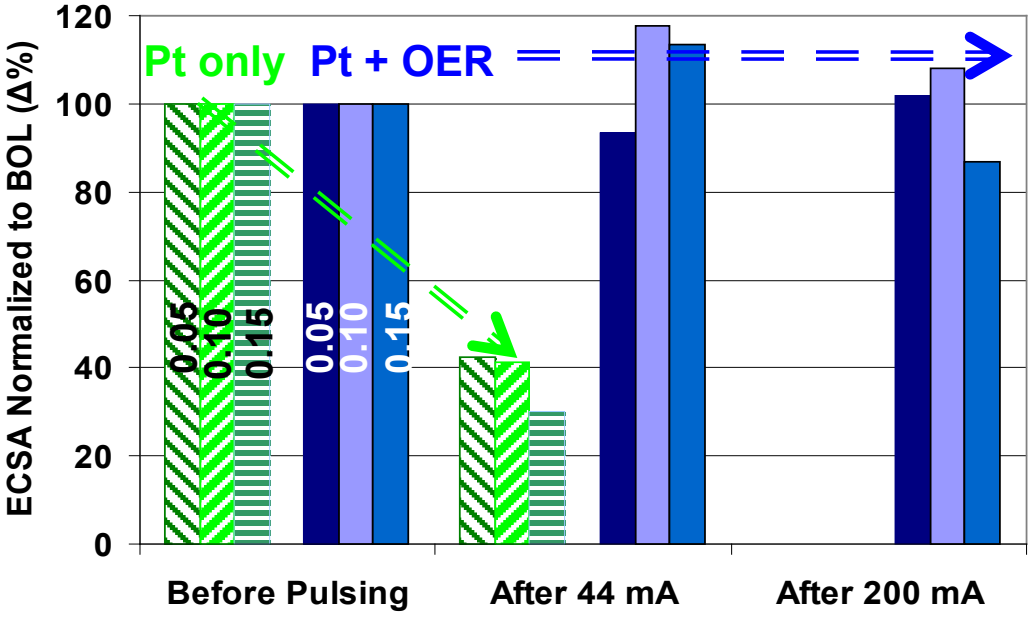
High Current Density Behavior:
Pt loading effect on OER

10 μg/cm² OER catalyst

Effect of Pt loading on OER activity



Effect of OER on Pt Stability



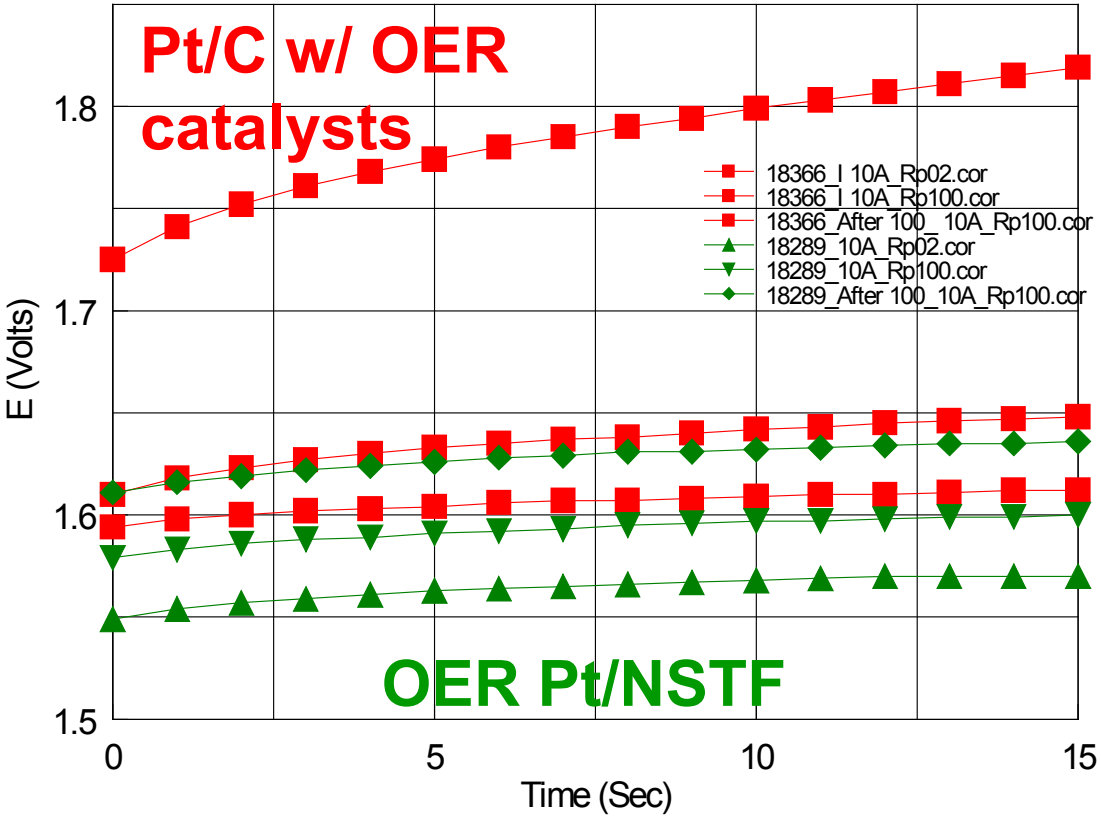
It appears that the OER activity is independent of the Pt loading

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

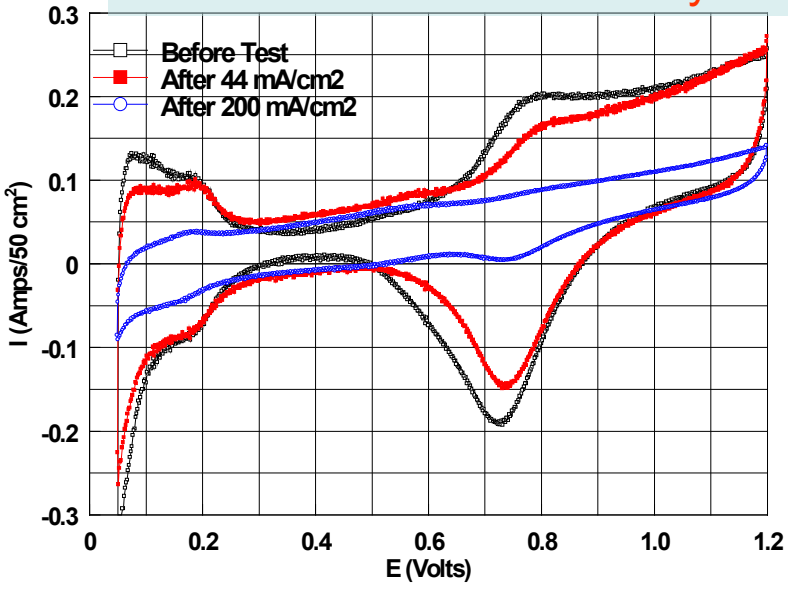
Cell reversal: Comparison of commercial OER added Pt/C (3M prepared) catalyst with OER modified Pt/NSTF

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

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



CVs for Pt/C w/ OER catalysts



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.

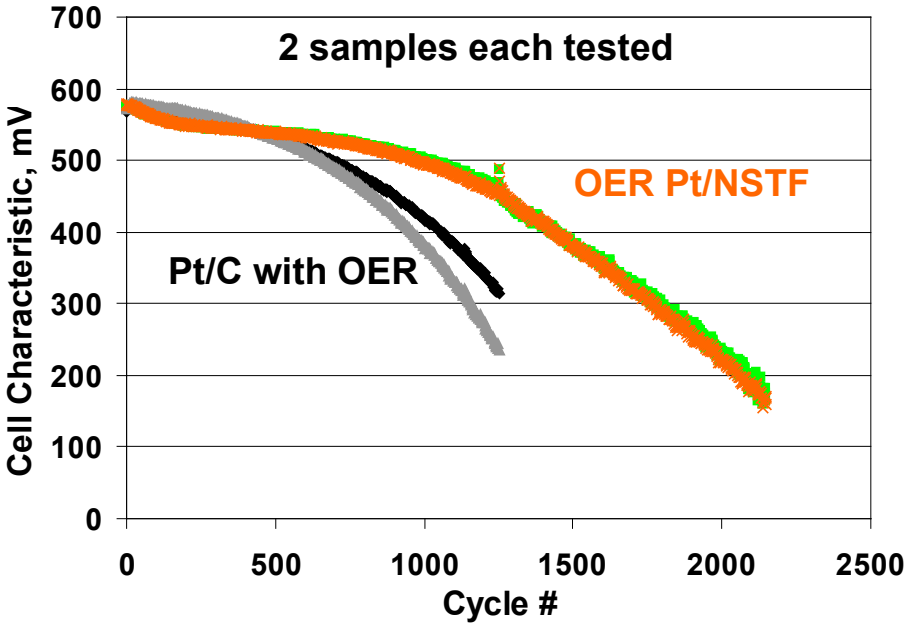
2. Pt/C ECSA lost 86% of original.

3. Pt/NSTF ECSA is practically unchanged.

AFCC Evaluation of 3M OER Modified Anode 0.06 mg/cm^2 PGM/NSTF

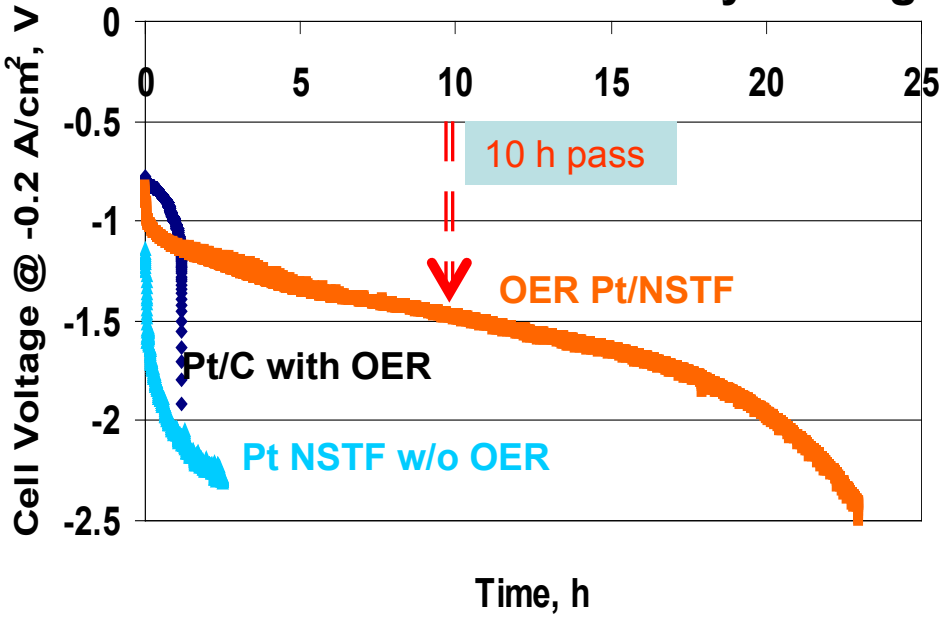
3M coated commercial 0.05 mg/cm^2 Pt/C with OER catalyst and
3M 0.05 mg/cm^2 Pt/NSTF anodes tested for comparison

SU/SD Durability testing



Anode **gasses switched**
between AIR and HYDROGEN

Cell Reversal Durability testing



Negative current (-0.2 A/cm^2) imposed
Anode: Nitrogen; Cathode: Air

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

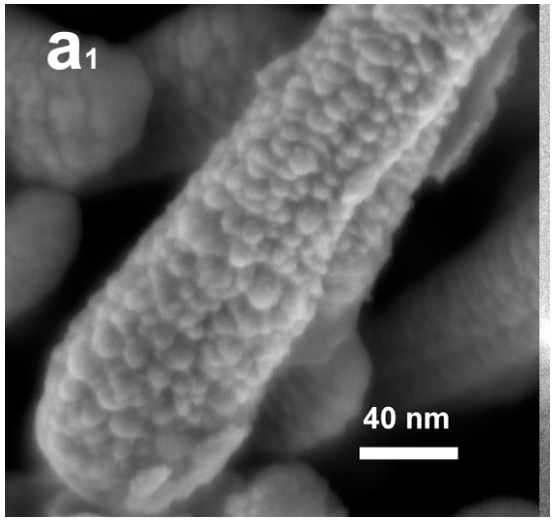
Anode catalysts with low ORR activity for SU/SD

and uninhibited HOR

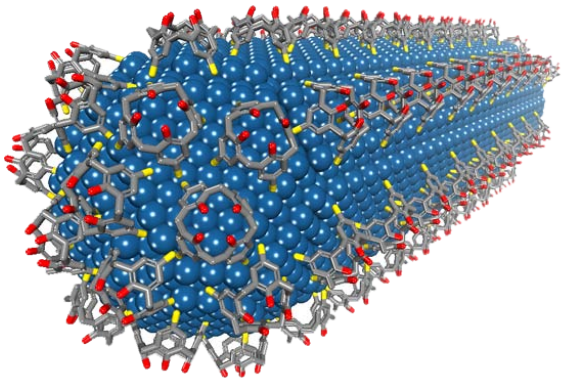
Argonne NATIONAL LABORATORY

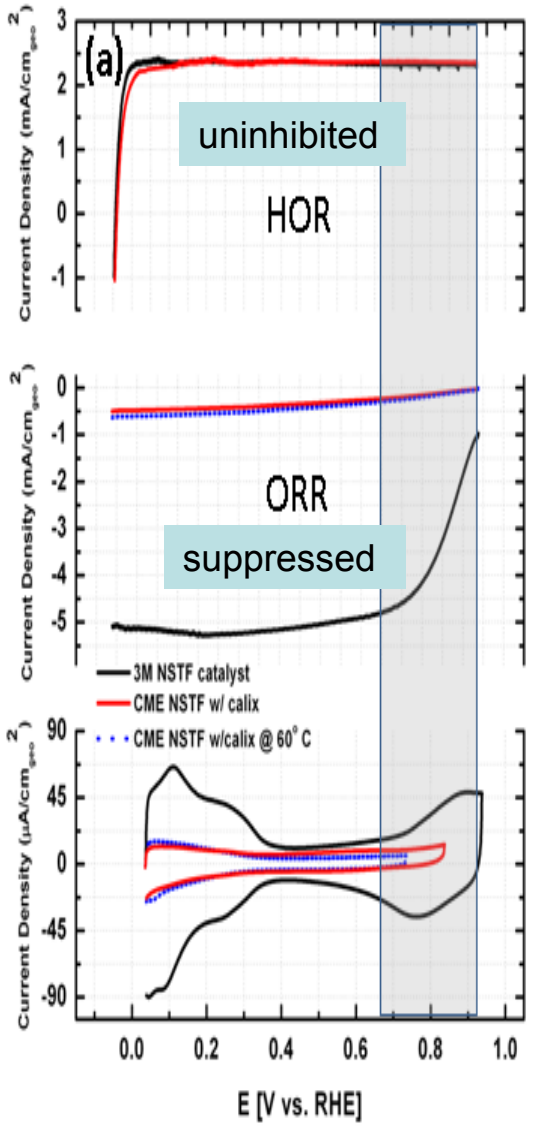
SELECTIVITY OF REAL CATALYSTS

Pt/NSTF



a2 The Model

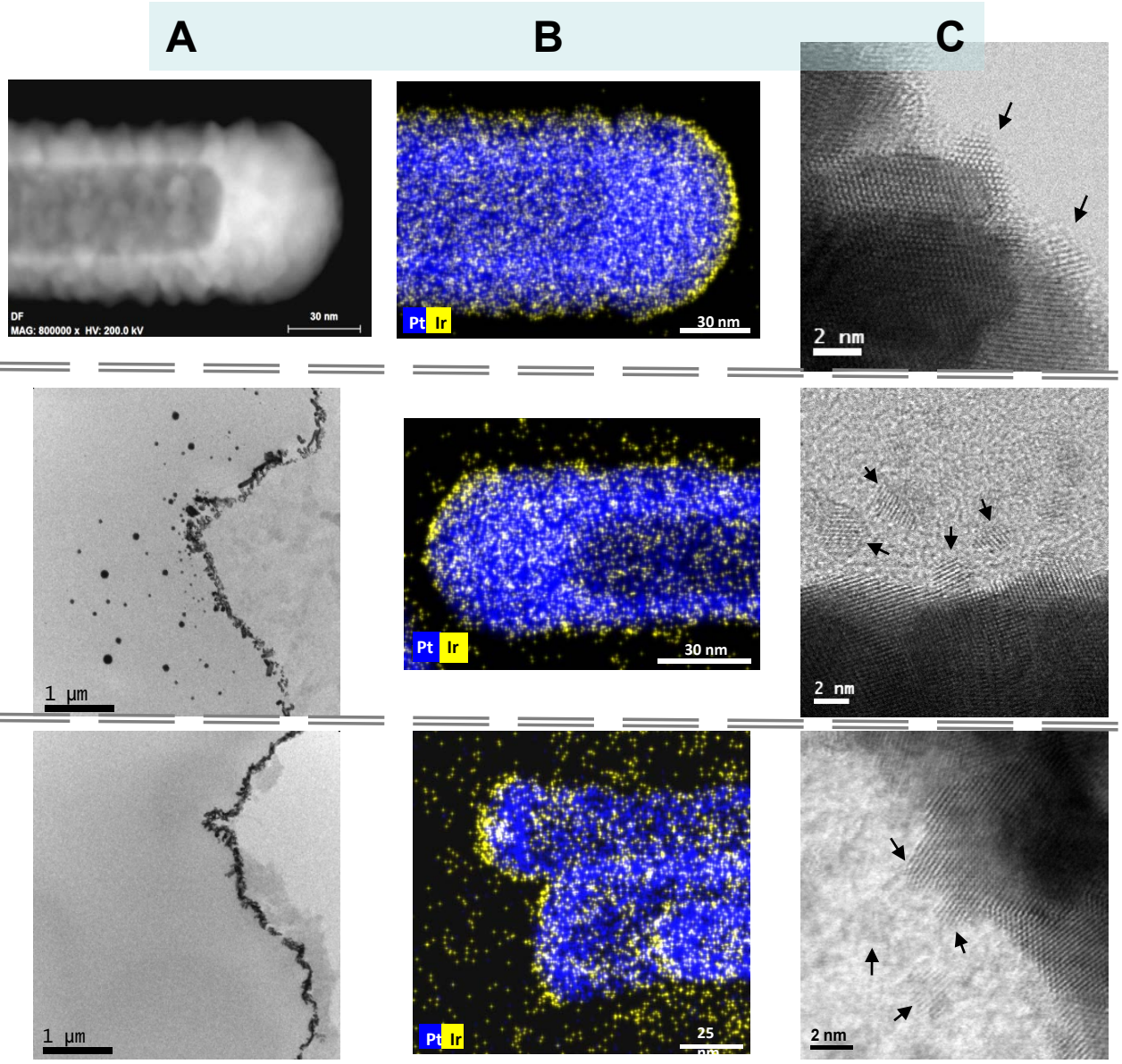




Selectivity from single crystals can be completely transferred to real fuel cells catalyst (!!!)

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

Advanced Instrumental Analysis: TEM of as received, SU/SD tested , and CV tested OER Catalysts



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

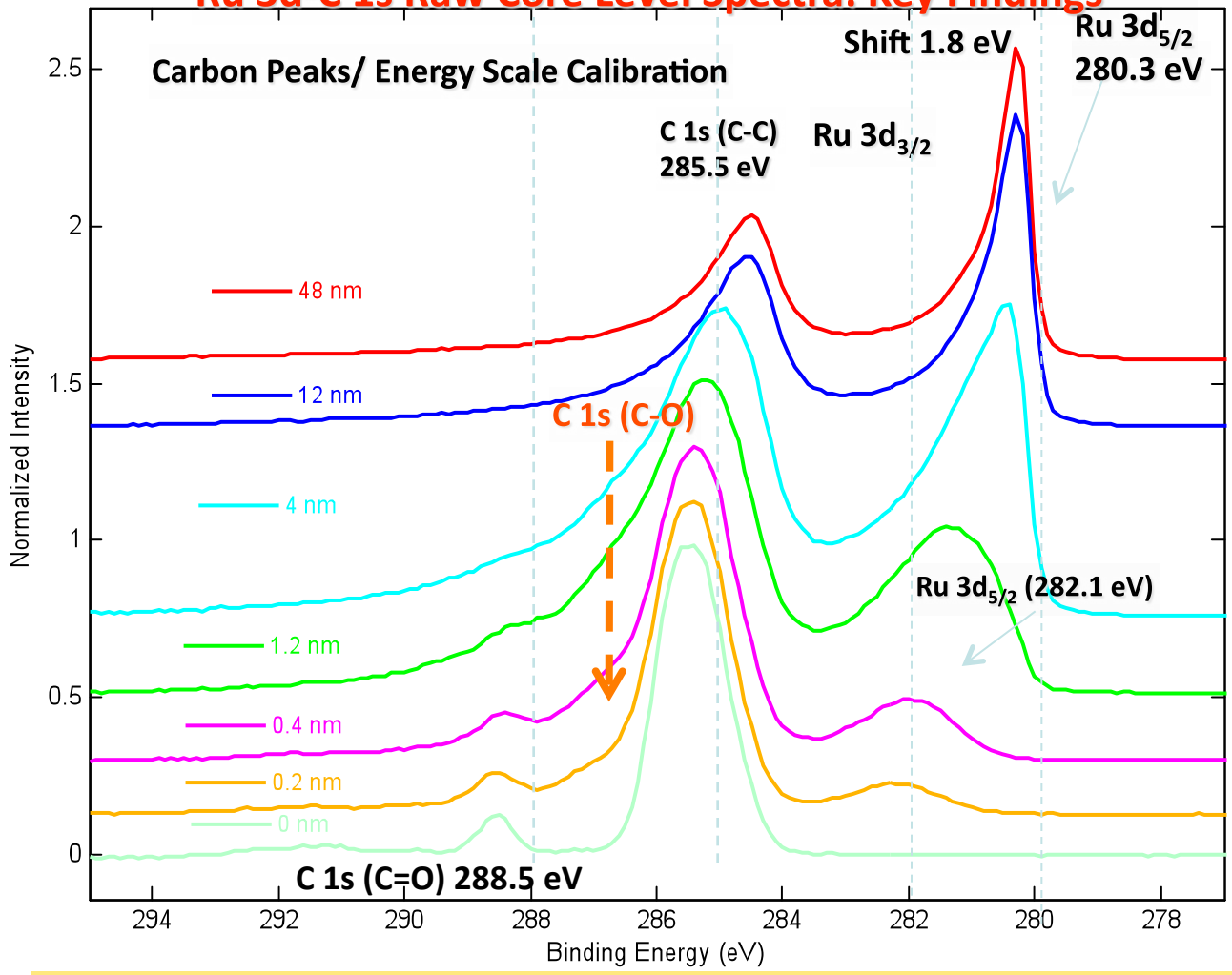
C) Arrows indicate **remaining** Nanoparticles of Ir

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



Appearance of C 1s peak at ~ 287 eV indicating formation of Ru-O-C bonds

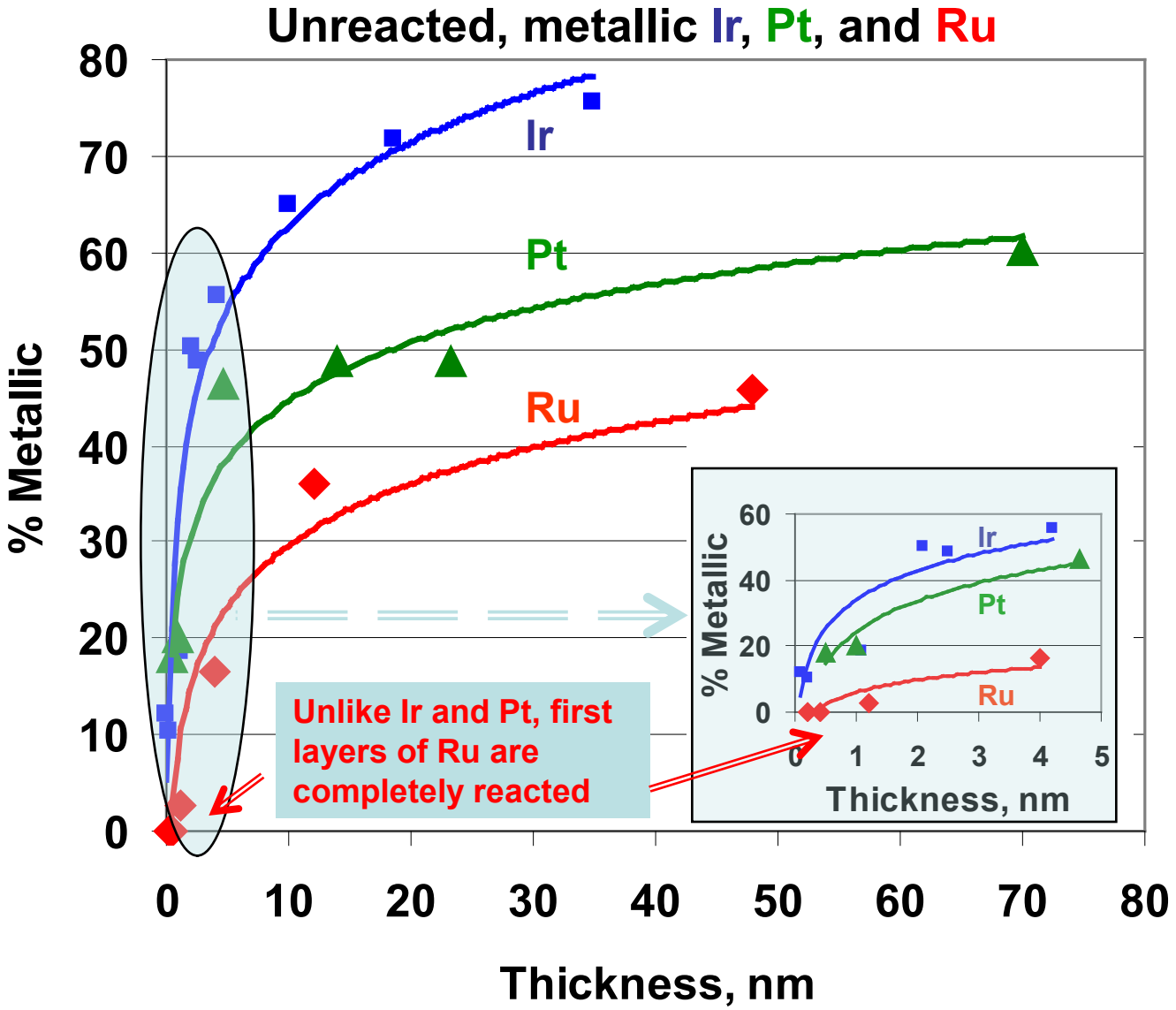
There is no C 1s peak at ~ 287 eV for Perylene Red Substrate

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



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 μg/cm² PGM**.
- 200 high current densities **pulses of -200 mA/cm²** mimicking the **cell reversal** were achieved with **60 μg/cm² 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

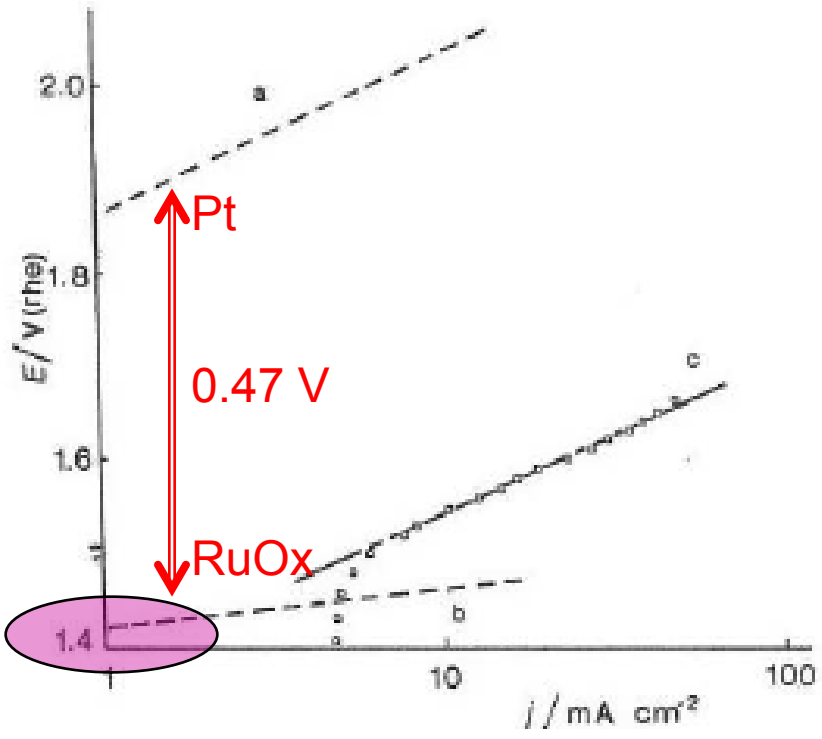
Presented at: **12th UECT**, Ulm, Germany, June 16, 2010

Key Variables for devising generic test procedure

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

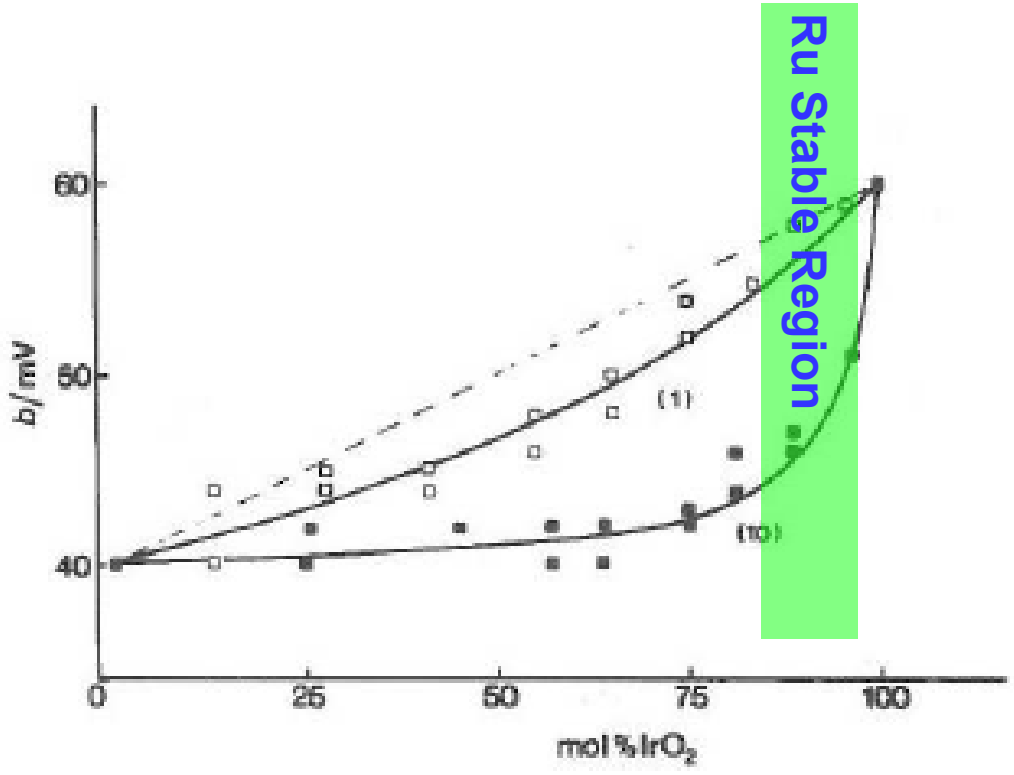
Time (duration) at given voltage levels

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

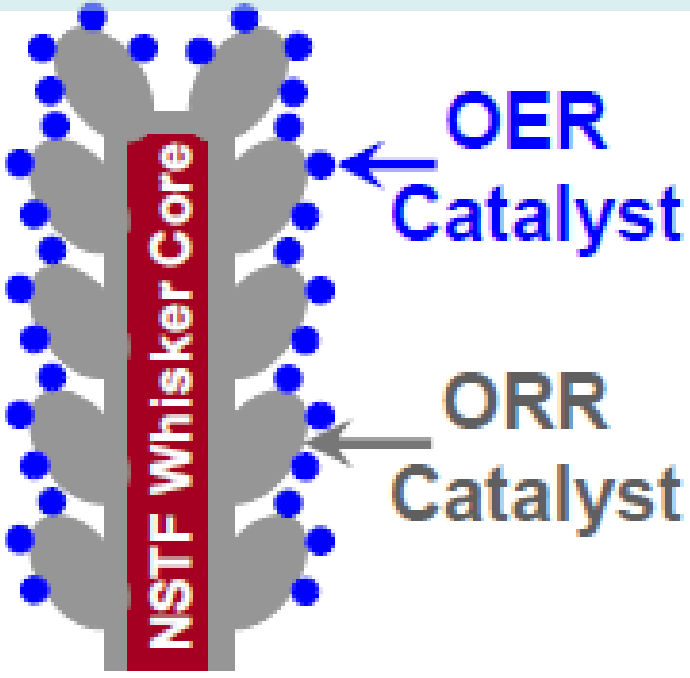
Stability and **cost**: **TiO_2**, *MnO_2, etc.* **RuO_2 - TiO_2** interfacial stability improves from 400 °C to 600+ °C

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: **$2.2x10^{12}$**.
- **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%.