Durable Catalysts for Fuel Cell Protection during Transient Conditions

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3M

DOE/3M Award DE-EE0000456

2012 DOE Hydrogen and Fuel Cells Program
and
Vehicle Technologies Program Annual Merit Review

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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 31, 2013
- Percent complete: ~ 65% (03/2012)

3M (Project lead)

Partners/Collaborators

- **AFCC** (Subcontractor – *under consideration)
  - **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 FY11: $ 1,258,190
Planned Funding for FY12: $ 550,000

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 is therefore **always "ON"**.

Implementation:

Background info: #22

Via **two catalyst material concepts**:

1. **Catalysts with high oxygen evolution reaction (OER) activity**
   1. **At the cathode for SU/SD** (slides 6 – 9) **OER-Cathode-SU/SD**
   2. **At the anode for cell reversal** (slides 10, 11) **OER-Anode-CR**
2. **Anode catalysts with low oxygen reduction reaction (ORR) activity for SU/SD** (slide 12, 13) **ORR Suppression-Anode**

Evaluation:

- Lab-scale for material development
- ***Scale-up to full size CCMs***
- ***Short stack integration and testing with AFCC test protocols*** (slide 14, 15)

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: 1.48V
2013	5,000	0.088*	1.45 V	10%	*Under consideration
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		*Under consideration

Task 2: Suppression of ORR (Anode)		Status/Comments
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	*Under consideration

Task 3: Scale-up		Status/Comments
2013	Scale up to full size cells; Independent evaluation	Evaluated in 2012: > 10 full scale/short stacks

Additional 2012 Tasks

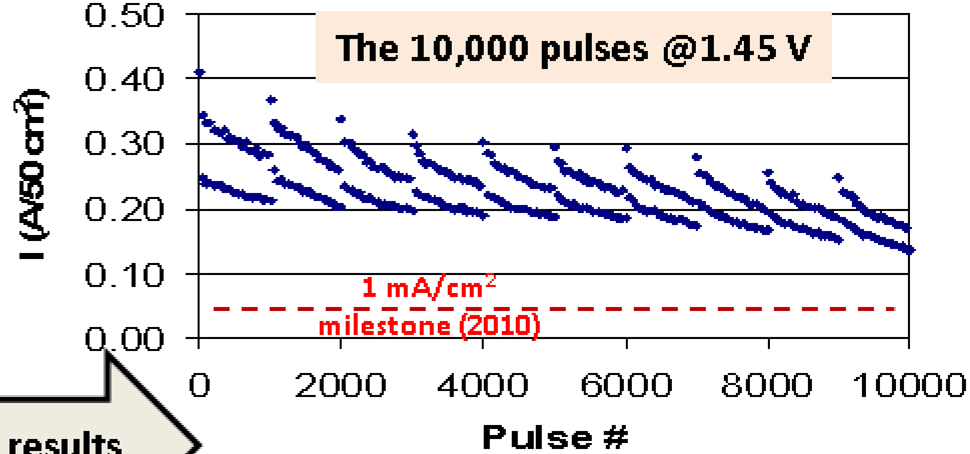
- **New SU/SD test procedure** upon Tech Team and Durability Work Group recommendations
- Fundamentals of **Ru** and **Ir OER activity** and **stability**

Accomplishments and Progress: 2011/2012

1. SU/SD: 10,000 cycles/pulses of electrochemical equivalent to gas switching were achieved with the addition of only **2 µg/cm² IrRu** on 0.15 mg/cm² Pt **cathode**.

2012: New procedure developed; Low PGM loading tested (90 µg/cm² PGM total on the cathode)

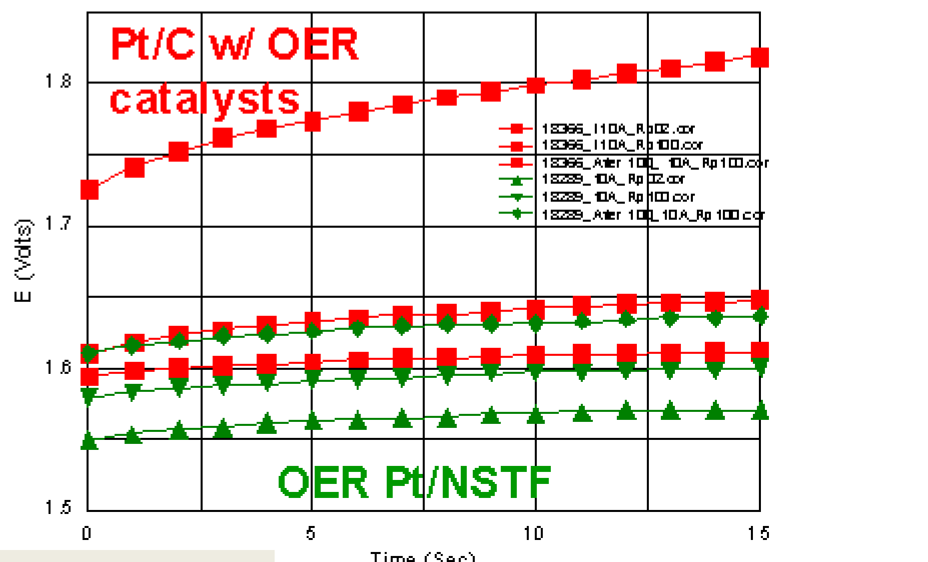
2011 results



2. Cell Reversal: 200 high current density pulses of 200 mA/cm² mimicking **cell reversal** achieved with **60 µg/cm² of total PGM.** **Advantage** of **OER modified Pt/NSTF** over **OER added Pt/C** catalyst clearly **established.**

2012: More rigorous test applied on lower PGM loading (45 µg/cm² total on the anode)

Cell Voltage at 200 mA/cm²: Pulse # 2; 100; 200



3. ORR inhibition: Initial effect obtained at ANL

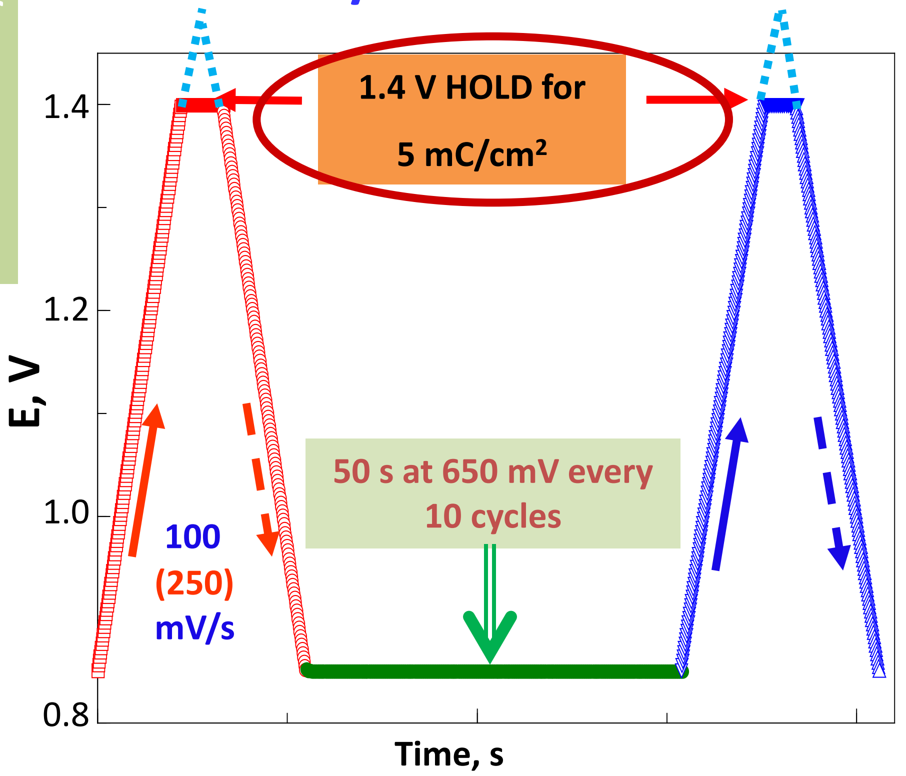
2012: Variety of approaches tested.

4. Independent OEM testing confirmed the 3M lab results.

2012: OER catalyst scaled-up: Full scale short stacks tested.

2012 Pt/C Tests: #23

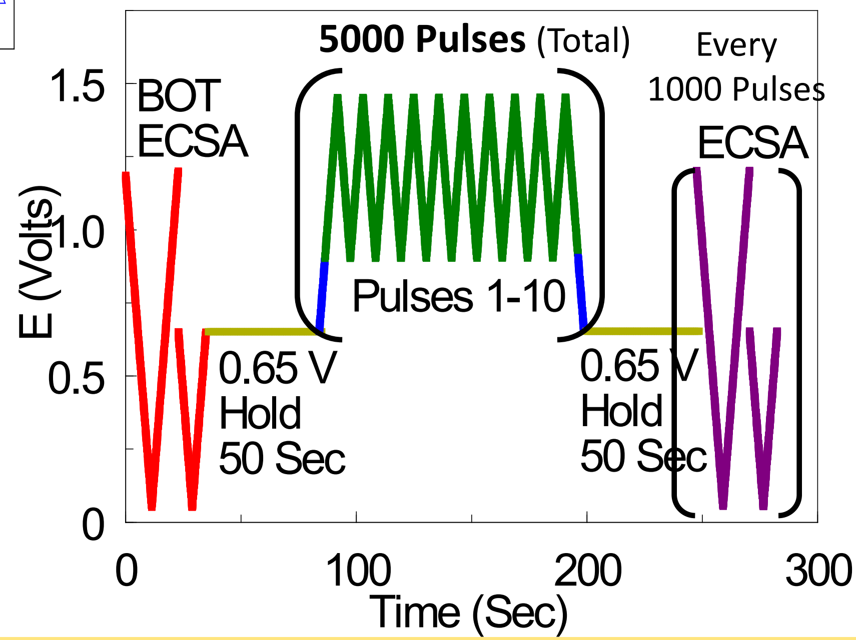
Task 1: SU/SD Generic Electrochemical Equivalent Test



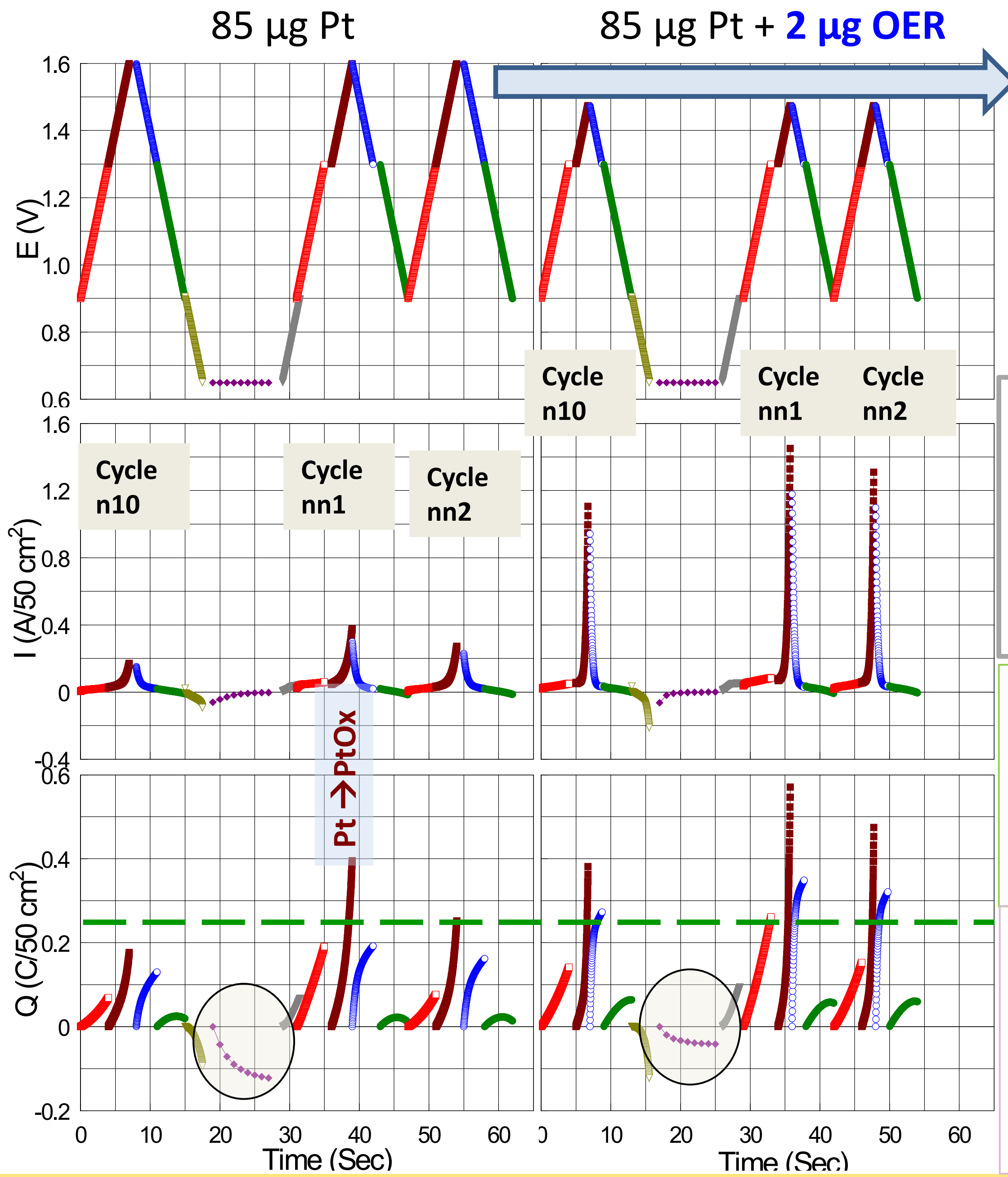
- 100 mV/s ramp: mimics H_2 front.
- 1.6 V upper limit or to 5 mC/cm^2: mimics the equivalent amount of O_2 to be reacted off for H_2/H^+ **electrode potential to be established**.
- 650 mV every 10 cycles/pulses: mimics cell voltage during normal operation.
- ECSA every 1,000 cycles
- **Durability criteria:**
  > 5,000 cycles; > 5 mC/cm^2; < 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.



Go/No go SU/SD: 90 μg/cm² PGM total; New Protocol @ 100 mV/s, up to 1.6 V



120 mV lower end V with IrRu

Note: Test done with 1A/50 cm² (nominally) current limit, sufficient for achieving required **5 mC/cm²**

At cycle ***nn1*** current w/IrRu is 3 times higher than substrate Pt. **Most critical**: At cycle ***n10*** current with IrRu is > 5 times higher, **sufficient for G/NG**

Only at cycle ***nn1*** Pt produces charge over required 5 mC/cm²

With OER catalyst, the charge at cycle 5,000 is > 5 mC/cm²

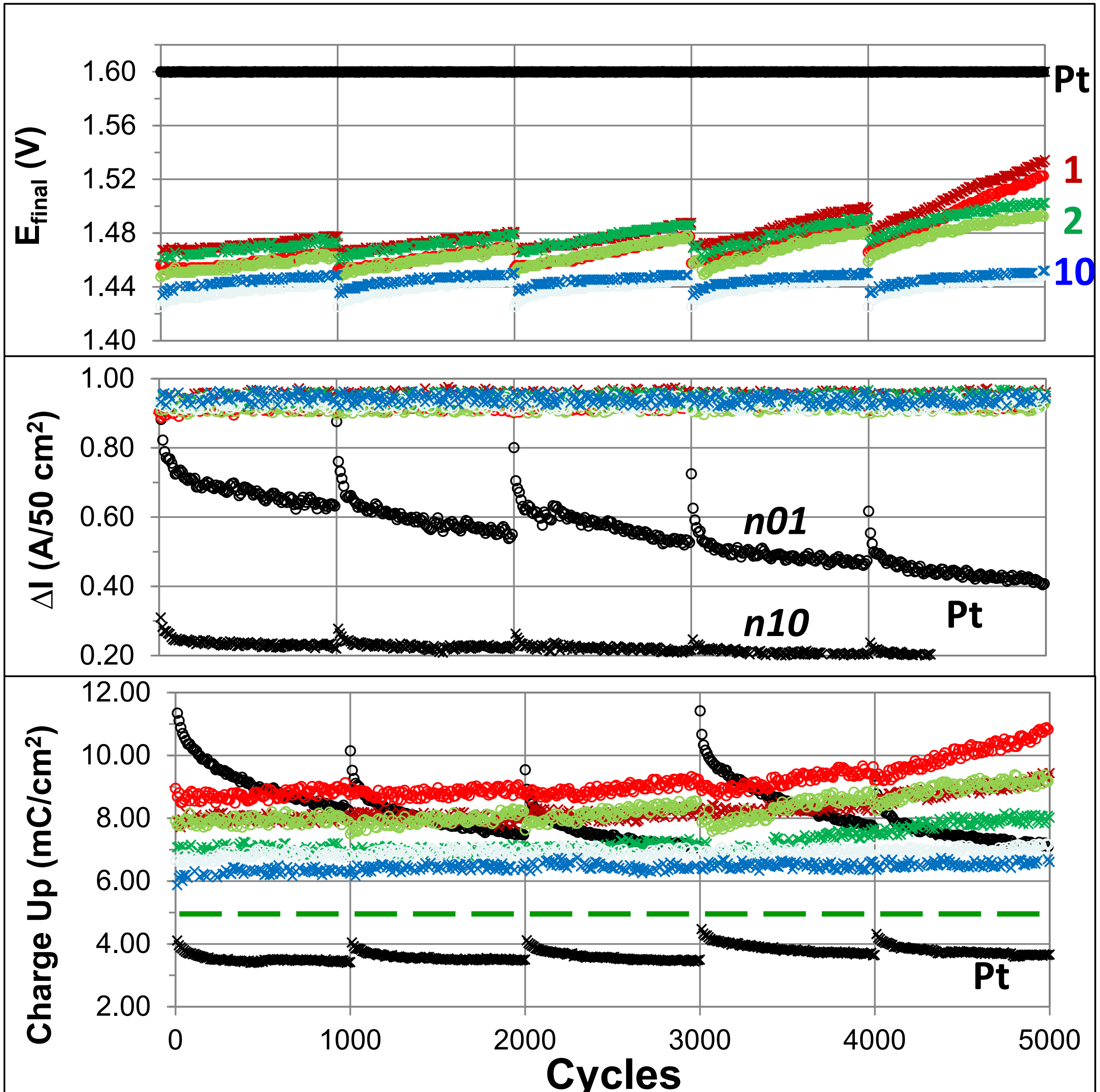
Oxide reduction charge at 0.65 V HOLD is much higher for Pt:

OER catalyst restrains Pt voltage to less oxidative values!

(Cycle 1499-1501)

SU/SD: Comparison of Pt *only* with Pt w/ 1, 2, 10 µg/cm² IrRu

Points for cycles *n01* (upper lines) and *n10* (lower lines) presented



Note: Test done with current limit of 1 A/50 cm²

Cell voltage **with 10 µg/cm²** IrRu unaffected after 5,000 cycles

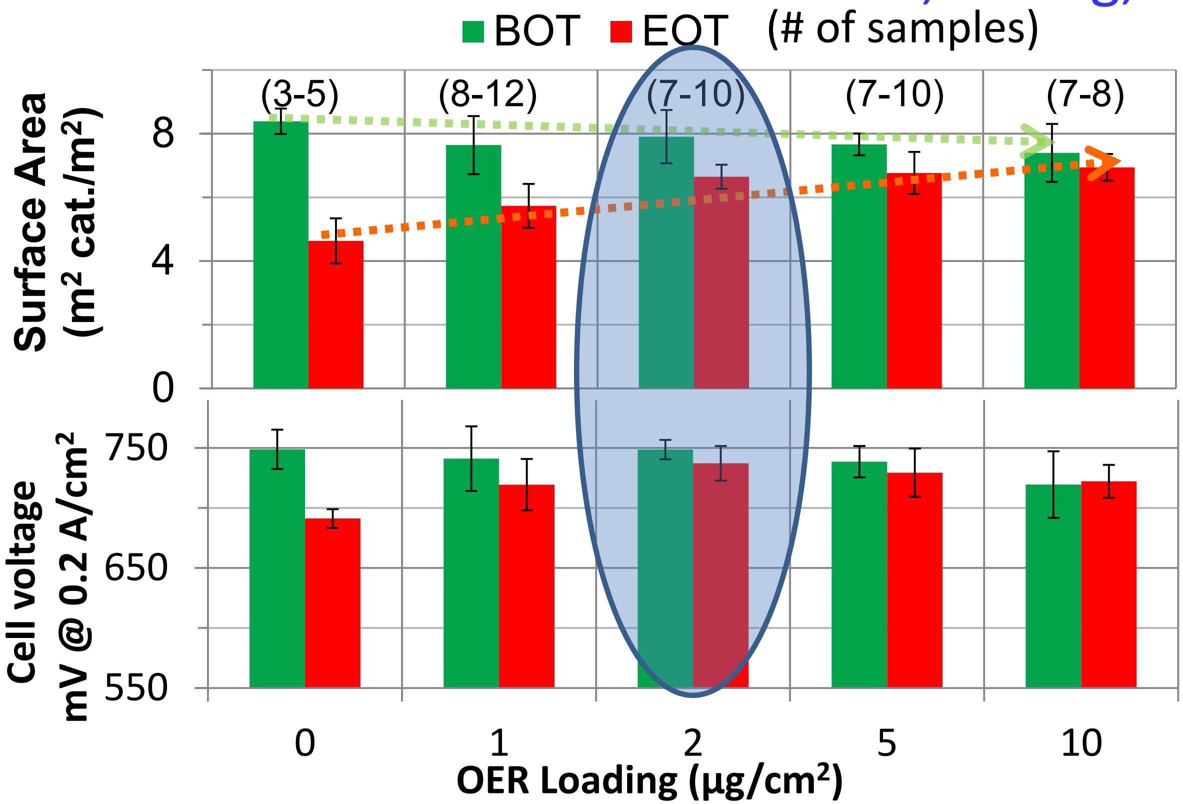
Polarization curves: #24

For Pt current @ 1.6 V presented. Note the spread between the current before (***n10***) and after (***n01***) "regeneration" at 650 mV.

Charge with IrRu is above required 5 mC/cm² during all 5,000 cycles.

Charge on Pt is above only during ***n01*** cycles and is due to PtOx formation rather than water oxidation.

ECSA and FC Performance before, during, and after 5,000 SU/SD



45 samples tested

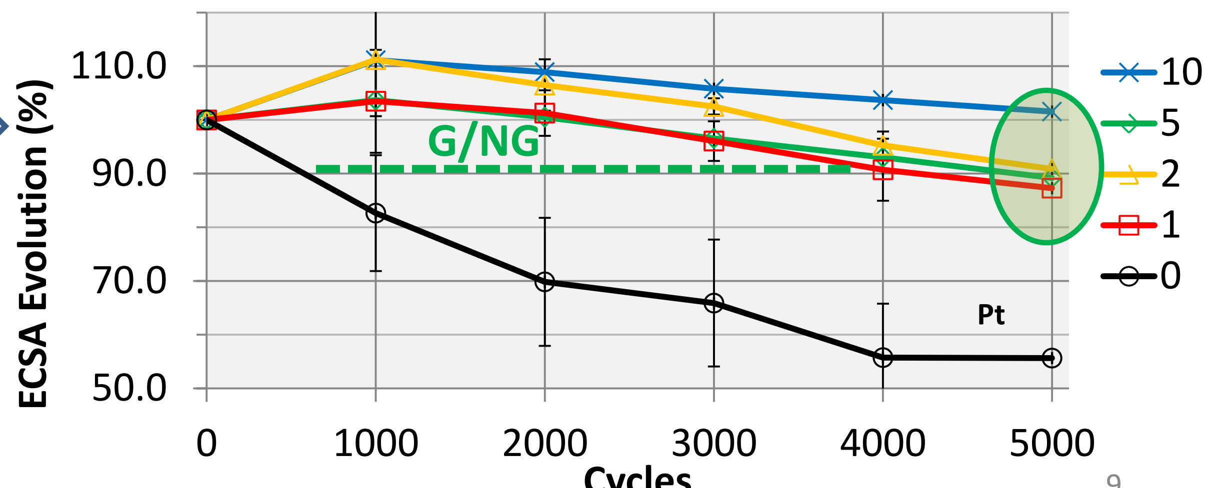
For **many samples at 2, 5,** and 10 µg/cm² ECSA loss after 5,000 SU/SD cycles is **less than G/NG goal of 10%.**

Considering both **performance** and ECSA, it appears that **optimum OER loading is around 2 µg/cm².**

Samples have achieved the **Go/No Go requirement:** **2 µg/cm² OER catalyst** have **87 µg/cm² total PGM** loading (nominal) and **~ 10% ECSA loss.**

Surface Area Evolution during 5,000 SU/SD

Within the spread of ECSA estimates, IrRu-Pt/NSTF with **1, 2, and 5 µg/cm²** are at the **G/NG milestone of 90% SA retention.**



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

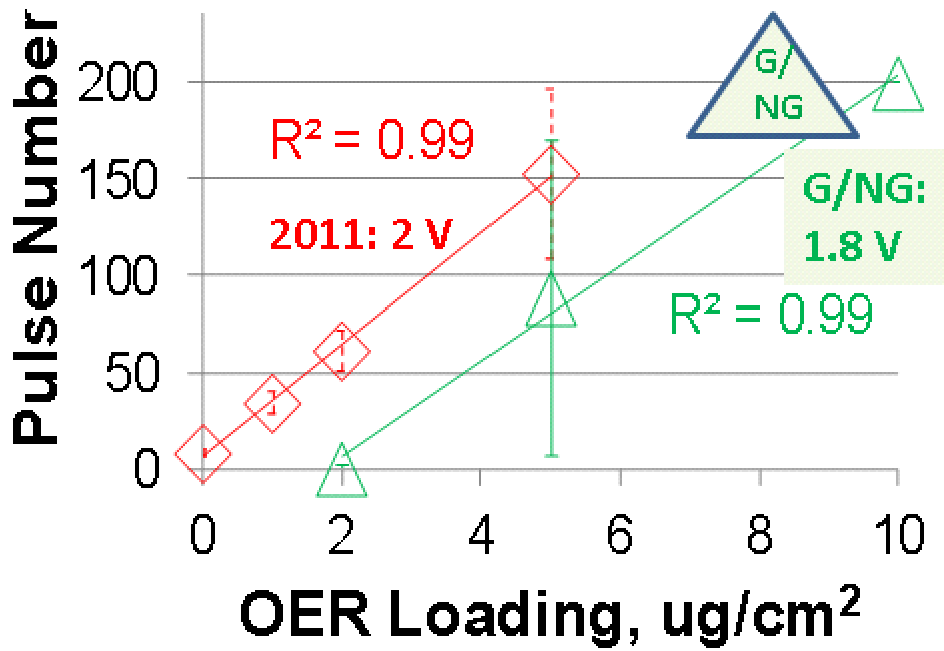
Additional durability:

- **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

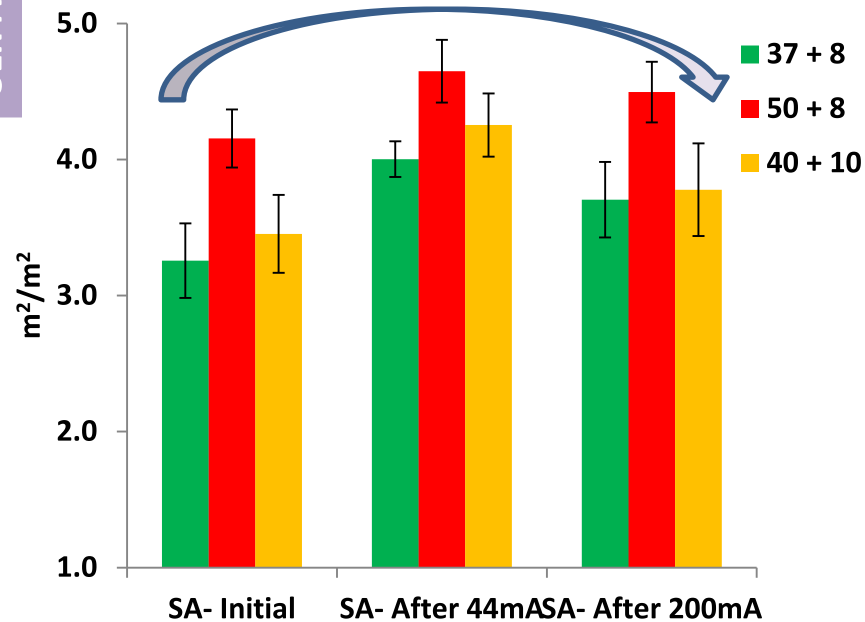
Number of cycles to **upper limit** of **2 V** and **1.8 V**



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!**

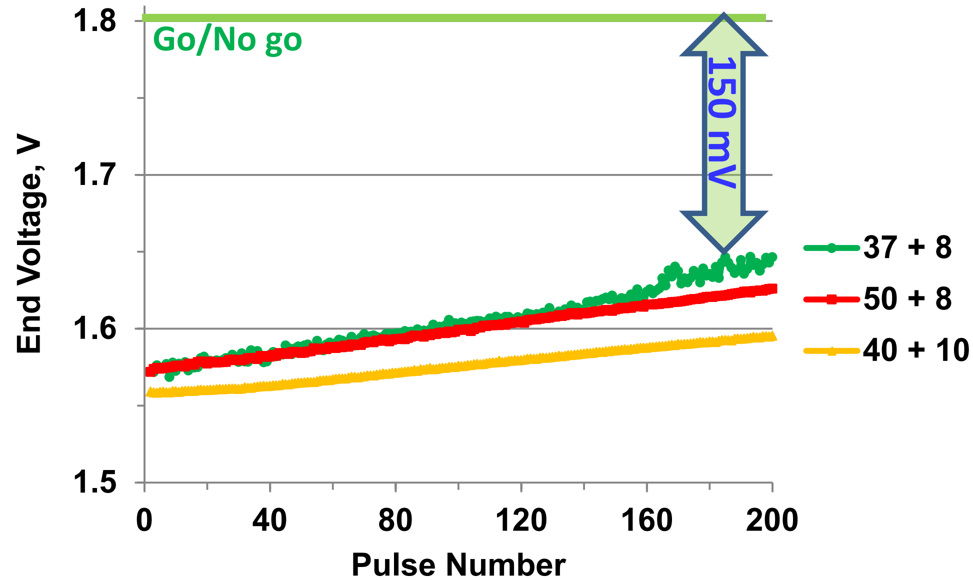
ECSA Changes during CR Testing

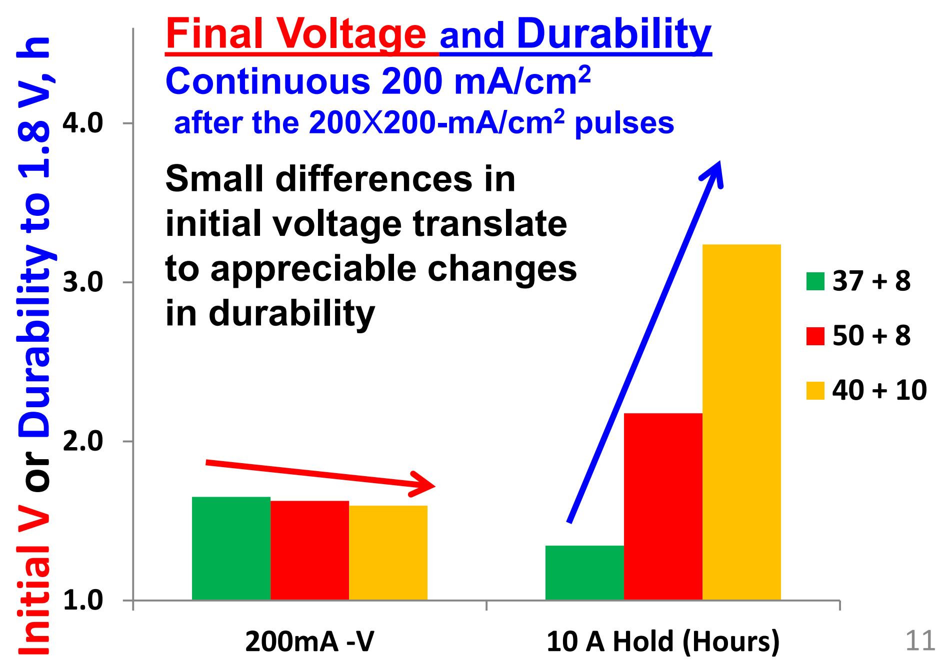


Pt loading determines ECSA:
50 > 40 > 37 μg/cm² Pt

- OER loading and Pt loading enhance OER activity.
- Durability follows the same loading pattern
- The **G/NG** loading, **37 Pt + 8 RuIr μg/cm² is 150 mV lower than the G/NG voltage target (1.8 V)**

OER Activity Retention

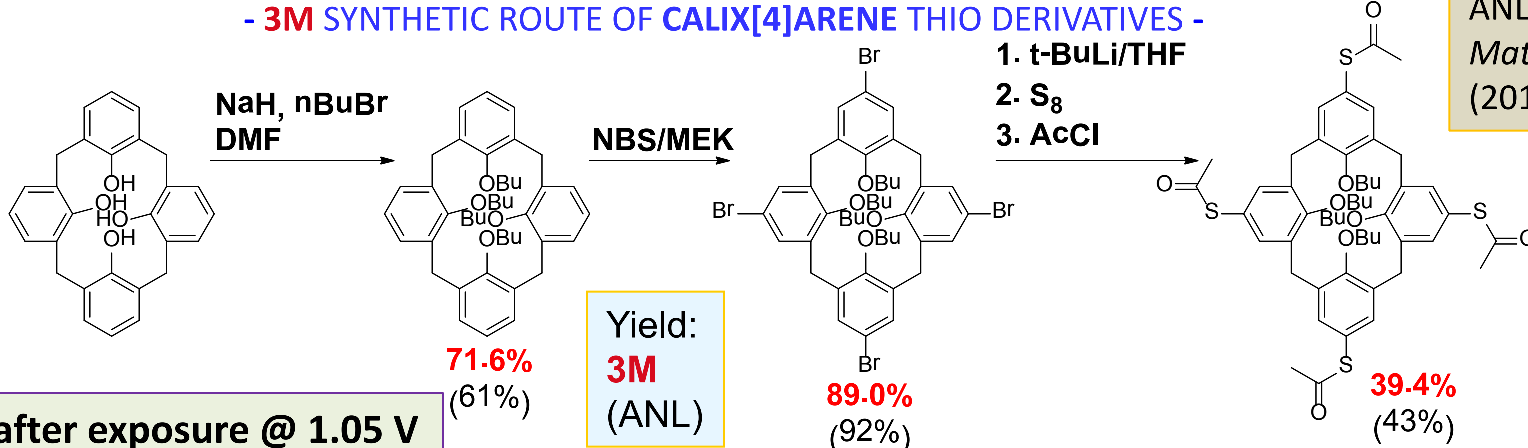




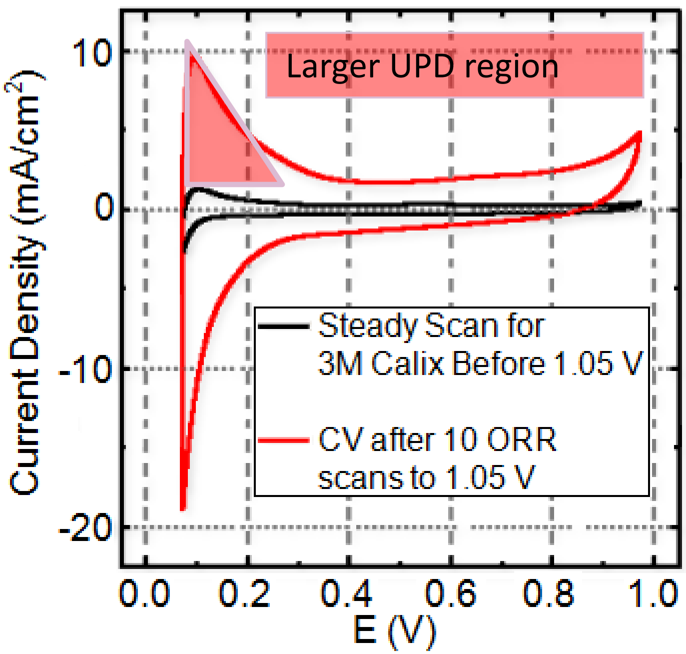
Task 2: 3M vs. ANL calix[4]arene ORR suppression on Pt(111)

Based on ANL, *Nature Materials*, (2010)

- 3M SYNTHETIC ROUTE OF CALIX[4]ARENE THIO DERIVATIVES -

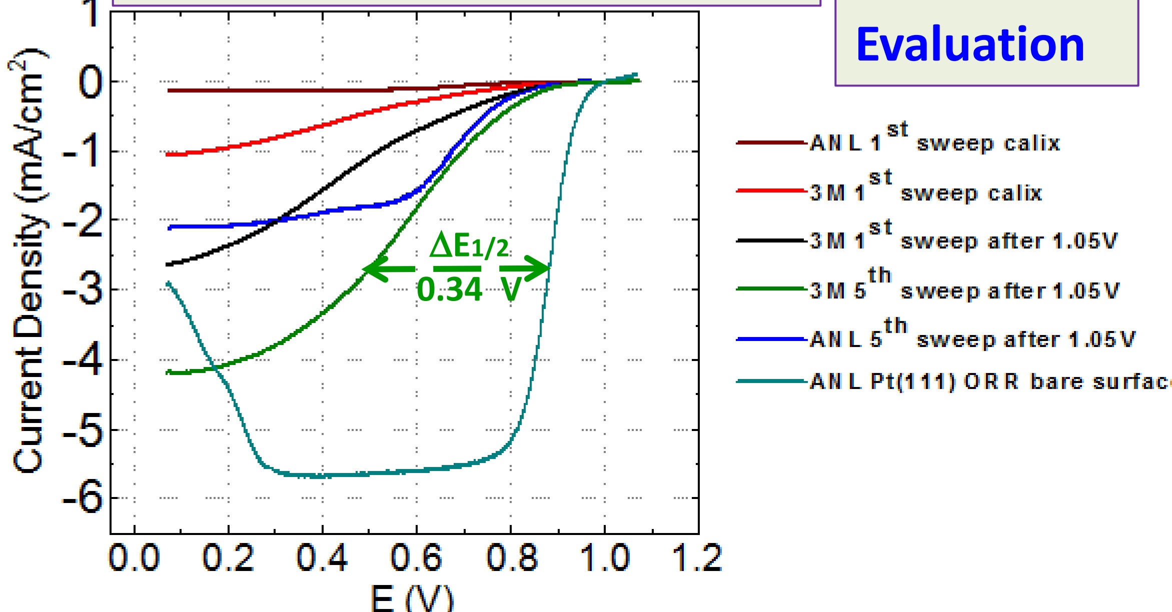


CVs after exposure @ 1.05 V



ORR activity after exposure @ 1.05 V

RDE Evaluation

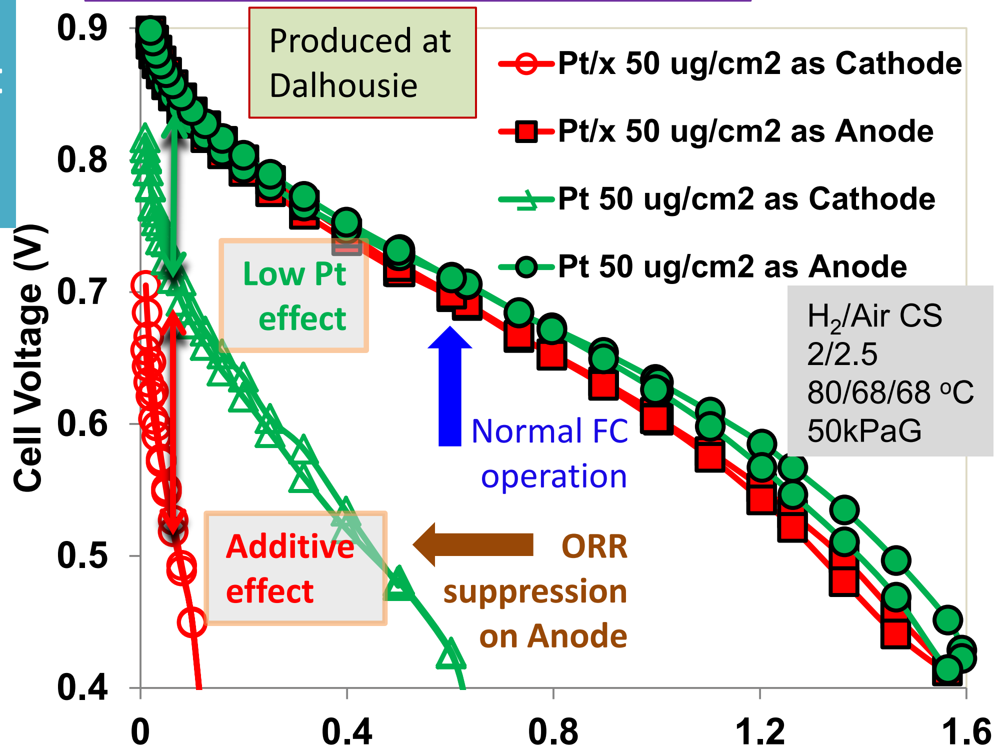


- Both samples **relatively stable up to 0.95 V** (i.e. the scans reached a steady state).
- At **1.05 V, 3M calix changes more than the ANL** suggesting somewhat **lower stability.**

- **ORR Suppression of > 0.3 V warrants further synthetic effort**
- **Stability to be examined in the CR region of high anode potentials, > 1.4 V**

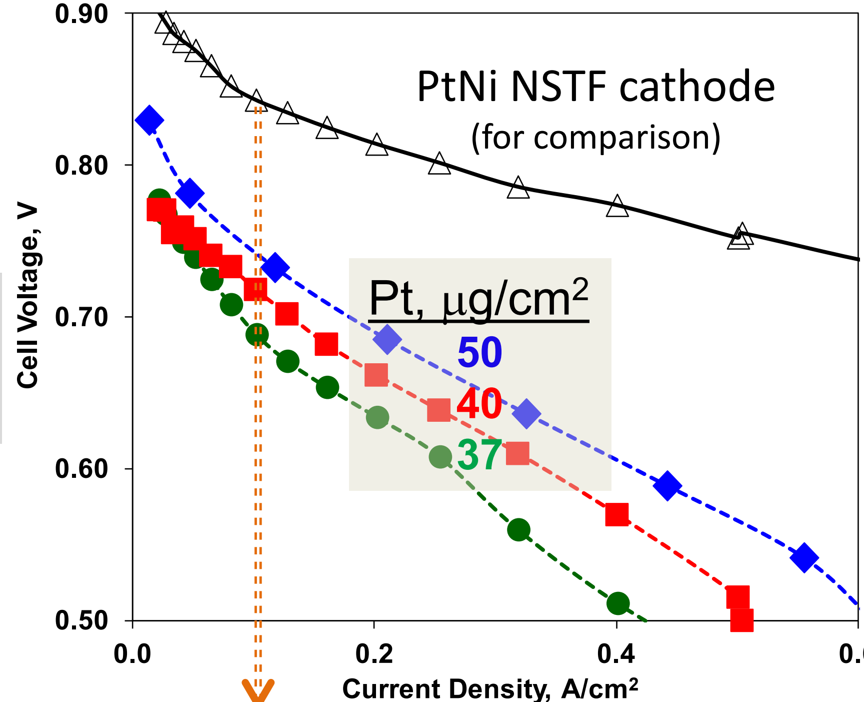
ORR Suppression: "Mixed" Anode Catalyst and Low Pt Loading Effect

Mixed Pt binary with "Additive"



> **300 mV** translate to >**1,000 times slower ORR**

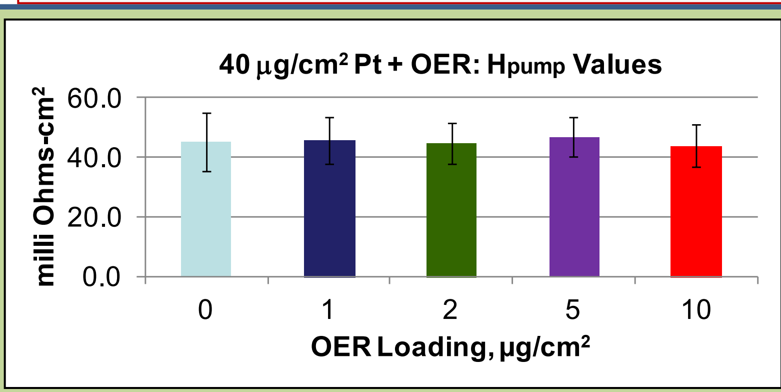
Low Pt Loading Effect on Suppression



Pt loading plays a prominent role in **ORR suppression**:

At 0.1 A/cm²: **160** > **120** > **100** mV

Pt, µg/cm²: 37 40 50



The OER added catalyst did not interfere with the normal HOR anode operation!

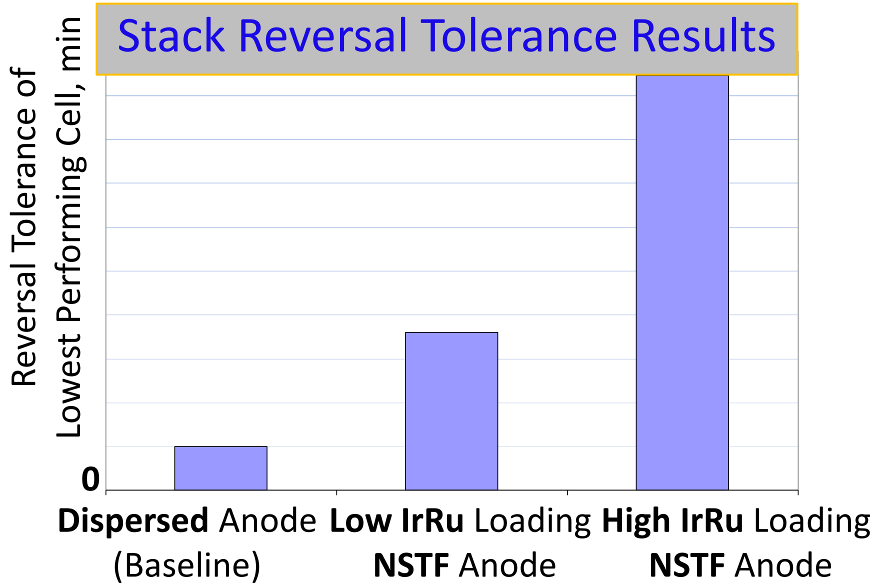
Task 3: Scale up and Independent Evaluation

AUTOMOTIVE FUEL CELL COOPERATION®

- Produced: **Hundreds of lineal meters** of fully integrated OER catalyst on Pt/NSTF
- Converted: OER-Pt/NSTF **in full size CCMs**
- Evaluated: **Short Stacks** by **AFCC for Cell Reversal** and **SU/SD**

Overview of AFCC OER/NSTF Evaluation

- The NSTF anode + OER concept has been evaluated at AFCC during the last two years.
- Significant effort using both subscale and **full scale testing** has been done following **AFCC's demanding technology** development process using anodes tailored for AFCC requirements
- *In 2011, **over 10 short stacks*** and over ***80 MEAs*** using OER-Pt/NSTF anode have been tested ***in full scale*** architecture
- Promising results demonstrating **performance, CO tolerance, freeze tolerance, SU/SD benefits, and reversal tolerance**
- **Overall results**: the ***OER modified NSTF anode is a promising MEA vehicle component***.



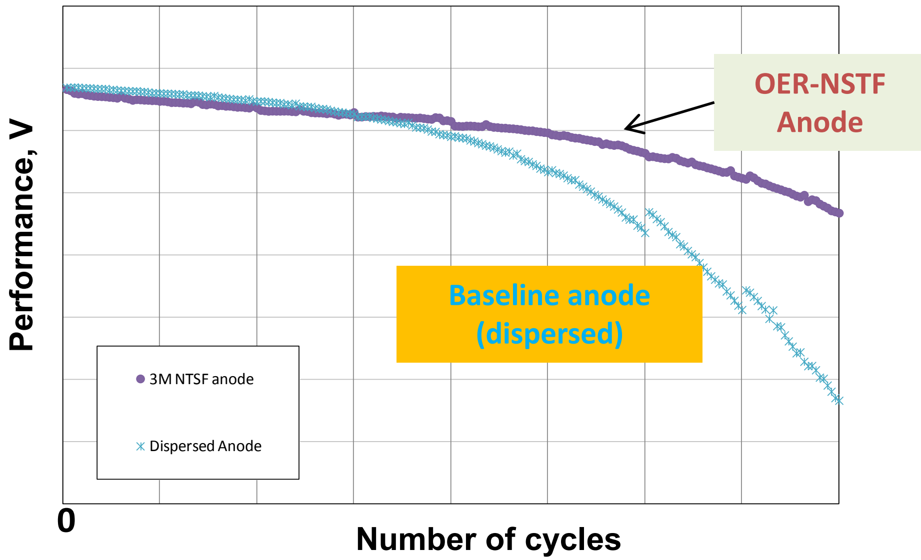
In stacks, as in AFCC's subscale configuration (reported in 2011 AMR) the **OER-Pt/NSTF anode consistently outperformed** dispersed baselines with higher loadings

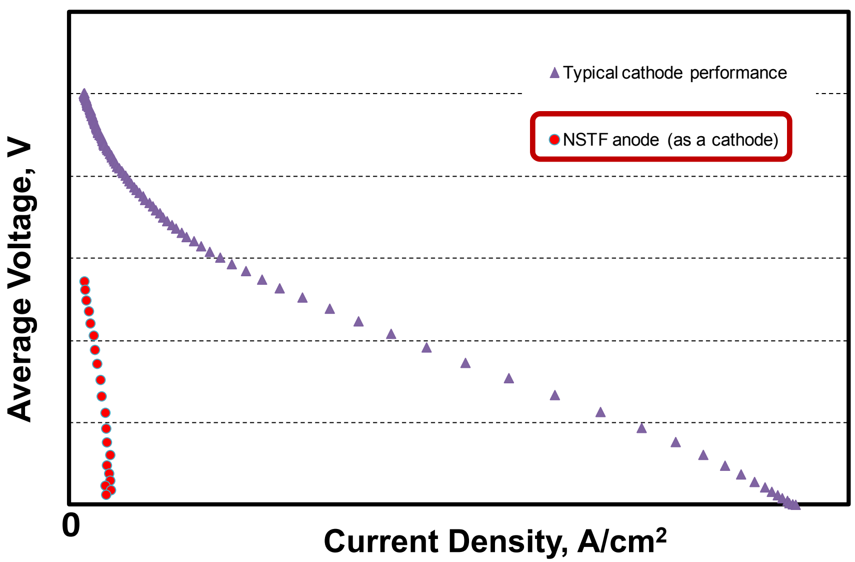
Despite lower tolerance than in subscale hardware, the NSTF anode concept still has a **very good reversal tolerance** for the given loadings

Task 3: Scale up and Independent Evaluation
-Stack SU/SD Tolerance -

AUTOMOTIVE FUEL CELL COOPERATION®

- **NSTF anode has a positive impact on SU/SD durability in a gas switching SU/SD AST**





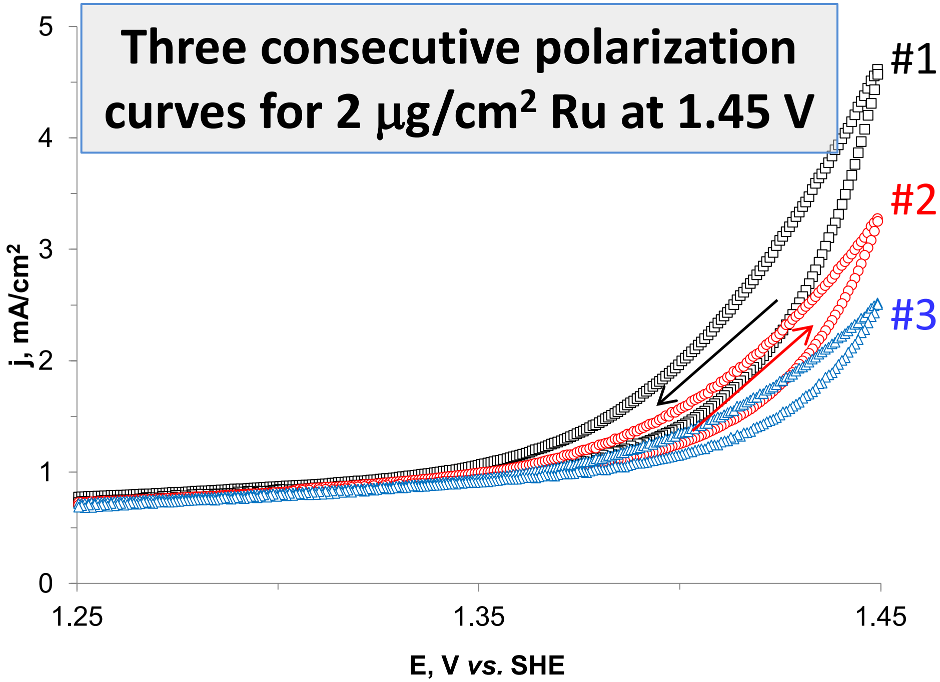
- The NSTF anode + OER catalyst is very **selective**
  - **Inhibits ORR** as shown by polarization results
- Smaller (*secondary*) effects
  - Low Ru content leads to lower Ru crossover related degradation
  - Some Ir may migrate to the cathode and have a OER cathode effect

Future Challenges:

- OER/NSTF performance **should have no negative impact** compared to a conventional dispersed anode
- **Stability** of the OER layer **under extended drive cycles** (2,000 hours) and after SU/SD testing
- Testing for **anode contaminants** (in addition to CO)
- 3M and AFCC driving fundamental understanding of **engineering issues** related to **interfaces and compatibility** of OER/NSTF with other MEA components and anode layer design

OER Fundamentals: Ru Stability and OER Activity

Three consecutive polarization curves for 2 μg/cm² Ru at 1.45 V



Ru stability region: overlapping of **the negative going with the subsequent positive** going scan: **1.40 – 1.42 V**

(Ir mass activity @1.55 V**: 3.9 A/mg**
Published: 1.5 A/mg)

More info: #25

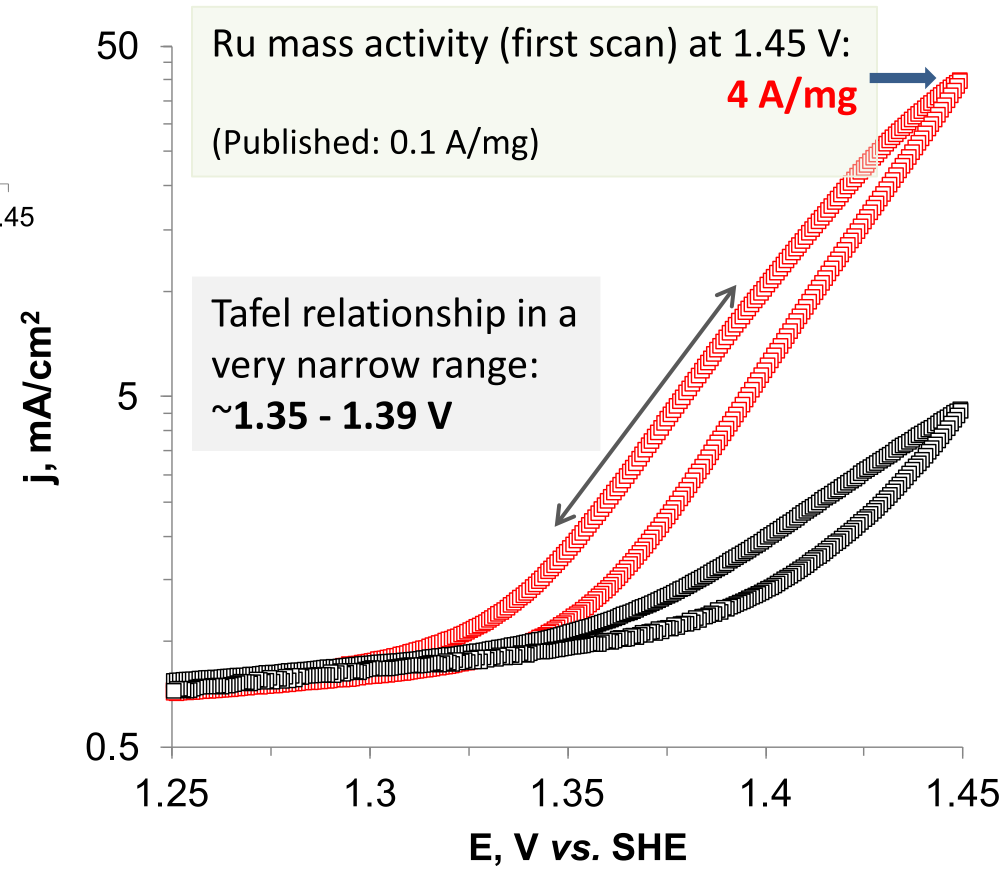
First polarization curves for 10 μg/cm² and 2 μg/cm² Ru

Tafel region on the positive going scans as indicator of Ru stability

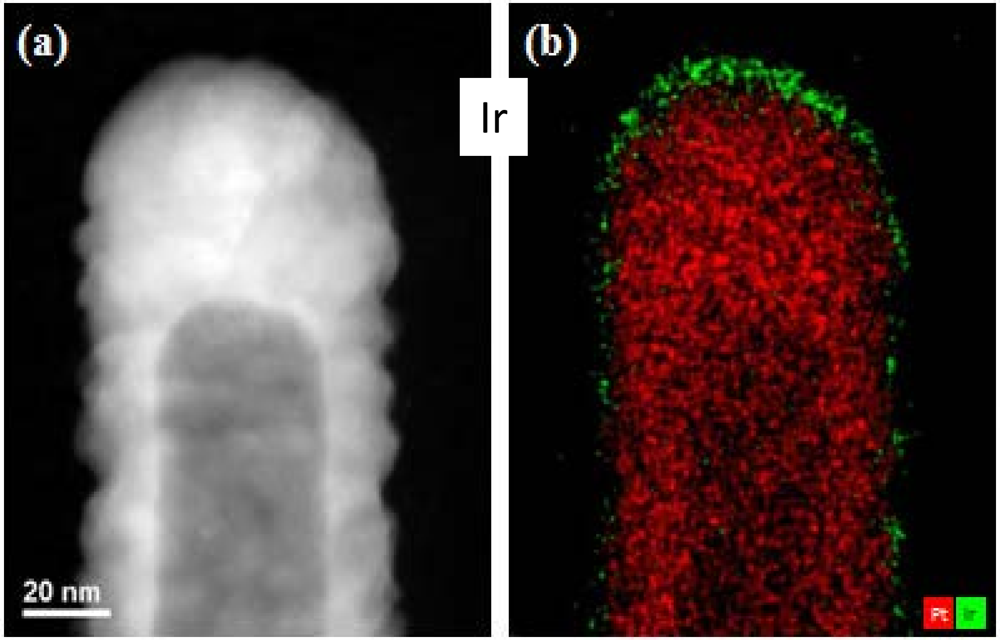
Ru mass activity (first scan) at 1.45 V: **4 A/mg**

(Published: 0.1 A/mg)

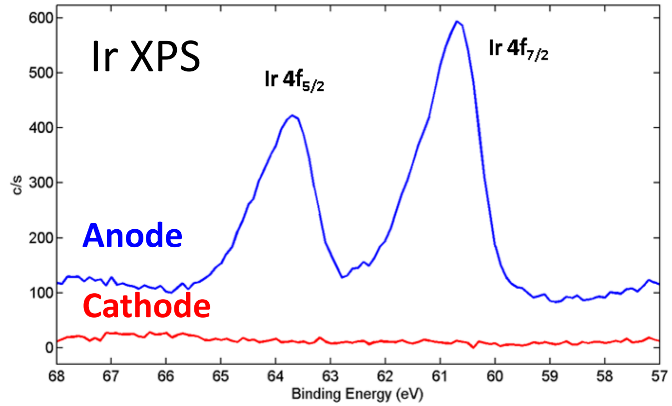
Tafel relationship in a very narrow range: **~1.35 - 1.39 V**



OER Fundamentals : End of test STEM of Ir and High resolution XPS of Ir, Ru and Ti

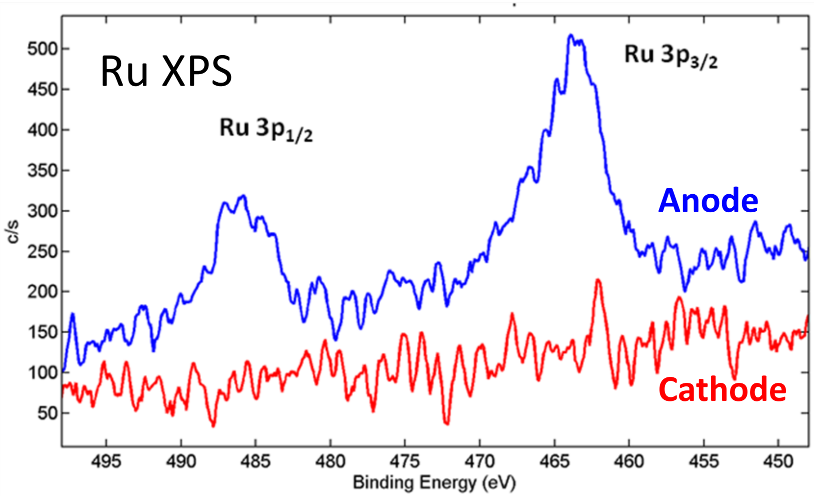


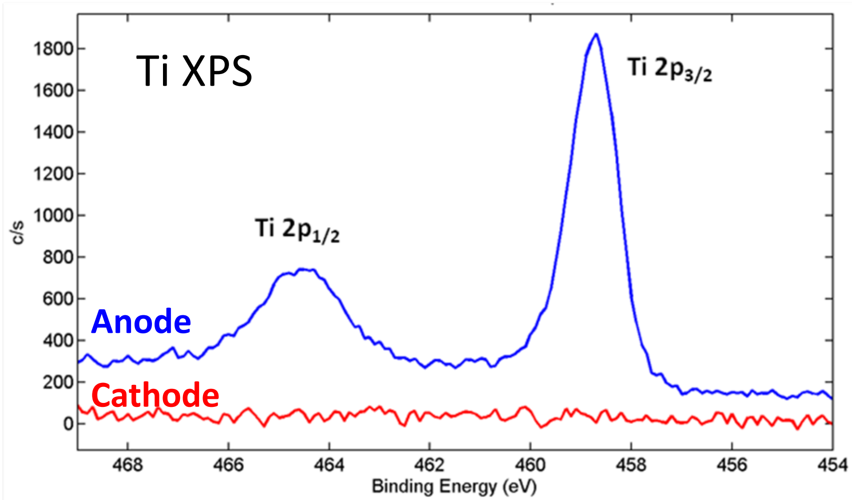
STEM (a) and EDS map (b) of **Ir 10 μg/cm²** on Pt-NSTF **after FC performance** tests. Nearly all the **Ir remains on the whisker** surface indicating **Ir**, **unlike Ti and Ru**, is stable in FC environment.



In tested MEAs, EDS did not detect any Ti or Ru.

XPS Core Level Spectra of tested CCM. Anode side: Ir 4f, Ru 3p and Ti 2p peaks (**blue curves**); **Cathode (counter) side**: **No Ru, Ti and Ir peaks detected** in the same BE region for uncoated Pt-NSTF (**red curves**)





Collaboration

Partners

- **AFCC** (Subcontractor -* under consideration):
  - **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)**: STEM Characterization**
  - **Samples analyzed provide invaluable insight into the OER catalyst**
  - **STEM and EDS analysis fully synchronized with catalyst development**
- **Argonne National Lab** (Collaborator; Partnership with two groups)**:**
  - **EXAFS characterization and OER catalyst stability**
  - **ORR suppression on anode**

Future Work: Phase 2

(Draft: under Consideration by DOE)

The major directions for Phase 2 are condensed **in four work packages**:

- Further R&D of the OER catalyst with respect to PGM loading and durability
  - Attempt to reach New Milestones with total PGM lodgings aligned with the **2015 DOE targets of 0.125 mg/cm^2 total**.
  - Assess the **limits of PGM cathode - anode distribution** while preserving the required cathode (ORR) and anode (HOR) performance.

- Fundamental **materials studies** aimed at understanding the extraordinary activity and stability of the OER-Pt NSTF catalysts;

- Fundamental **engineering studies** of the OER-Pt NSTF catalysts aimed at understanding the processing, integration and interaction with other MEA components;

- OER-Pt NSTF catalysts evaluation **readiness for "real life"** automotive applications.

Summary

All Go/No Go milestones have been achieved:

- **200 cycles of 200 mA/cm²** for **cell reversal** with **0.045** mg/cm² **total** PGM on the anode **with 1.8 V upper limit (Actual: 1.67 V).**
- **5,000 startup cycles** under the newest protocol with **0.09** mg/cm² **total** PGM on the cathode **with ECSA loss of < 10%**;
- **Reduced ORR** current on the **anode** by a **factor of > 10 (Actual > 1000).**

Other major achievements:

- **Achieved unprecedented OER mass activity**
  - **NSTF delivered a new level for OER activity as did for ORR/NSTF**
- **Performance proved in short stacks at AFCC (Task #3)**
- **OER/NSTF brought NSTF very close to "real"/stack application**

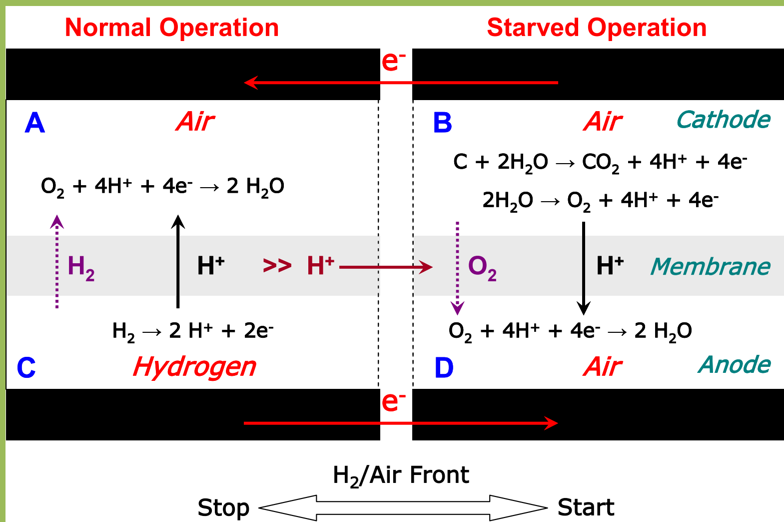
General:

- **Most of the work proposed and outcomes envisaged have been realized and/or accomplished by 3M, AFCC and their partners/collaborators.**

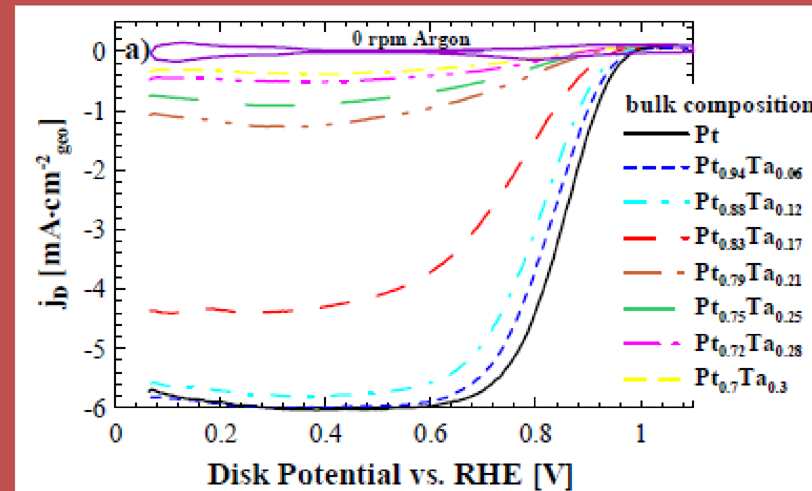
Technical Back-Up Slides

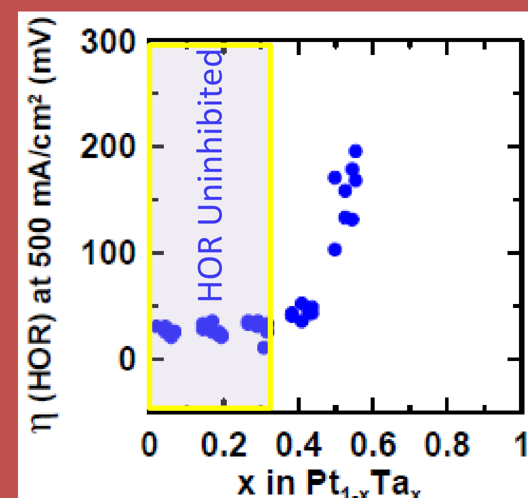
SU/SD and OER Catalysts Development Fundamentals

SU/SD Explained

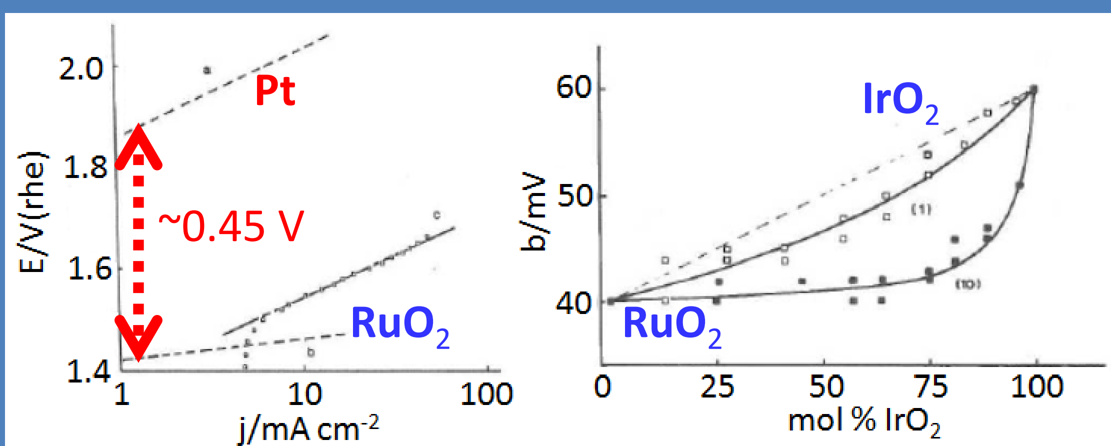


Basis for Task 2: ORR Inhibition



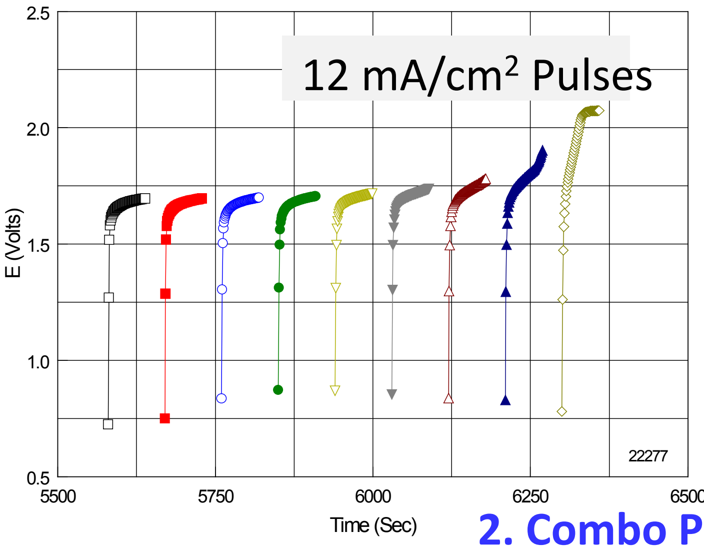


Basis for Task 1: OER Catalyst

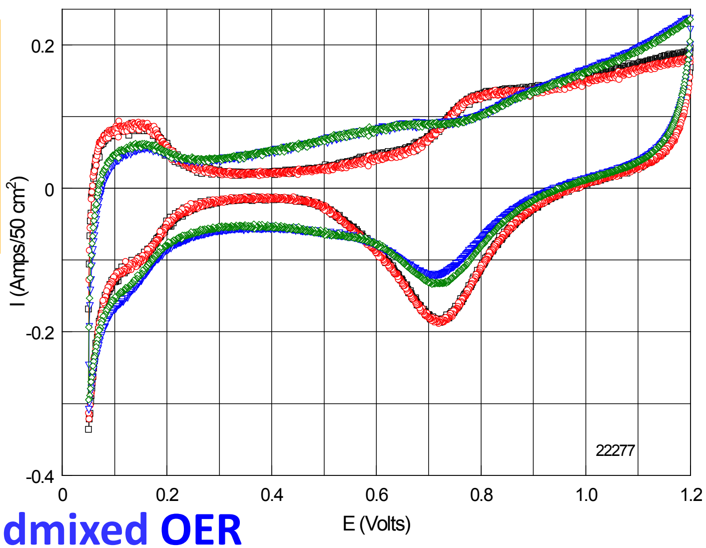


Can OER - Pt/NSTF protect CARBON?

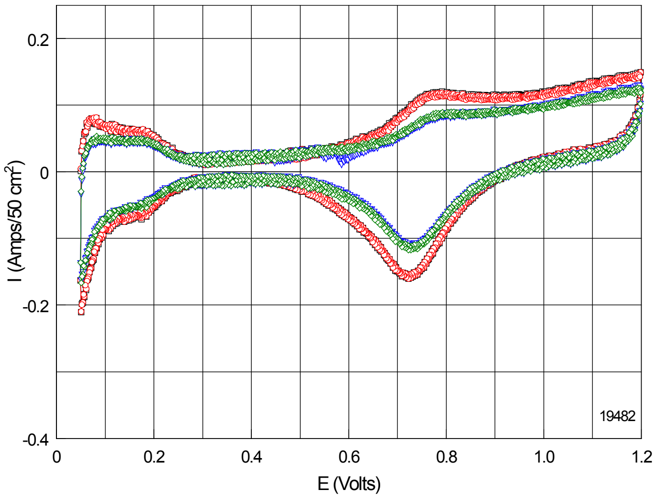
1. Combo Pt/HARD CARBON added/adjacent to OER - Pt/NSTF
- Cell Reversal Test -



- Catalyst failed at pulse #9!
- Carbon deterioration is obvious in the CVs



2. Combo Pt/HARD CARBON with admixed OER
- SU/SD-



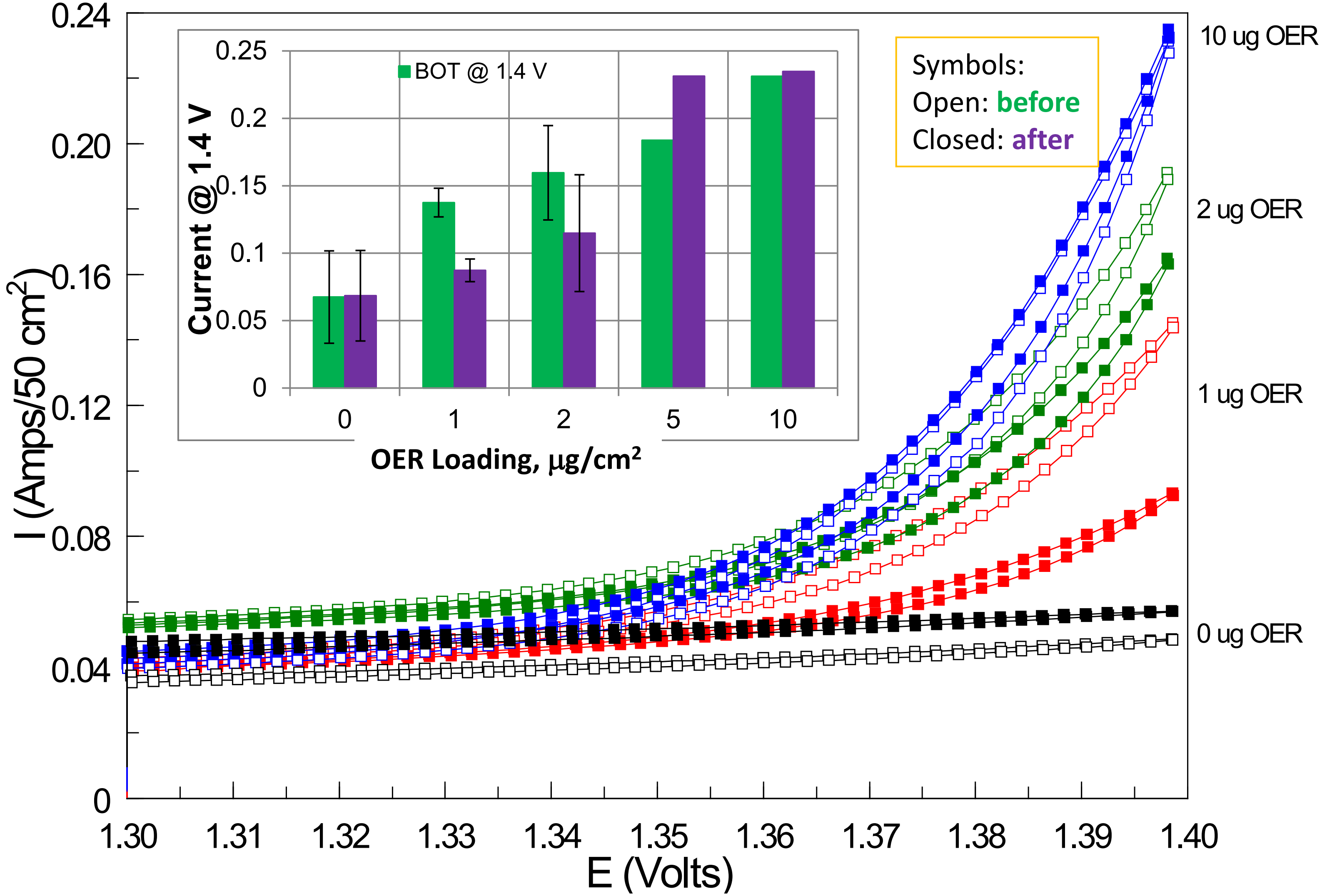
- The catalyst failed at cycle #1060, *vs.* OER – Pt/NSTF, which with ½ of RuIr routinely achieved 5,000+ cycles.
- No carbon deterioration is obvious in the CVs
- Pt Hupd does not seem to decrease a lot

<u>Conclusions</u>

- Different deterioration mechanisms in the two tests are due to the upper voltage: 1.75 V in CR *vs.* 1.45 V in SU/SD.
- Neither of the carbon catalysts are stable enough to withstand any of these voltages

OER Activity: OER Polarization Curves before and after 5,000 SU/SD Cycles

Potential sweep @ 2 mV/s
(Pt loading: 85 μg/cm²)



OER activity is maintained better with OER catalyst loading

Ru, Ir, Ti Initial Characterization: streamlined version

First of the three scans for the upper limit of 1.45 V, 1.55 V, and 1.65 V for 10 mg/cm² of each of the three elements along with the uncoated Pt-NSTF
2 mV/s scans