

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

(Topic 1c)

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

Kickoff meeting for new DOE Fuel Cell projects  
from solicitation DE-PS36-08GO98009 and lab call DE-PS36-08GO98010

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# Project Overview

## Barriers

C. Electrode Performance  
(Technical targets: See milestones)

## Timeline

- Project start date: August 1, 2009
- Project end date: July 31, 2013
- Percent complete: ~ 5%

## Collaborations

- **Dalhousie University** (subcontractor)
  - Dr. David Stevens; **High-throughput catalyst synthesis and basic characterization**
- **Oak Ridge National Lab** (subcontractor)
  - Dr. Karren More; **TEM Characterization**

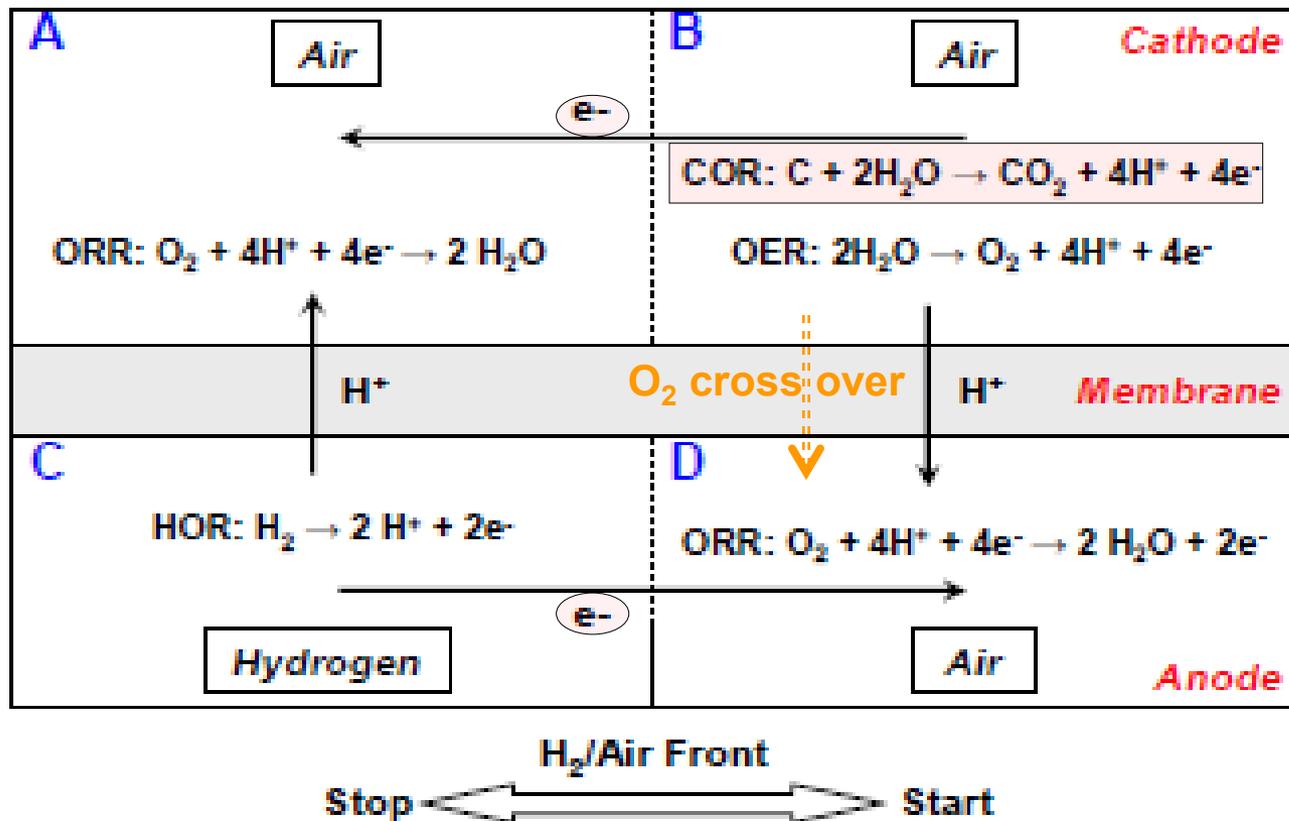
- **3M Team**:

George Vernstrom  
Greg Haugen  
Mark Debe  
Radoslav Atanasoski

BUDGET	FY10	FY11	FY12	FY13	Total
3M Cost Share	352,805	315,128	294,465	194,035	1,156,433
DOE Funding	1,411,222	1,260,511	1,177,861	776,139	4,625,732
Total	1,764,027	1,575,638	1,472,326	970,174	5,782,165

# PEMFC with fuel starved region

## Electrochemical reactions leading to carbon corrosion and Pt dissolution



The **absence of hydrogen** at the anode is necessary but not sufficient to provoke and maintain cathode potential  $> 1.23$  V.

The **presence of oxygen** at the anode is required for the transient phenomena to happen.

\*) Modified after Gu et al, ECS Transactions, 11 (1) 963, 2007

**A, C; normal FC operation; B, D; operation in fuel starved region.**



**3M approach:** Alleviate the damaging effects **from within the fuel cells**, by **modifying both the anode and the cathode catalysts** that will enable PEM fuel cell systems to weather the conditions in the fuel cell at **voltages beyond the thermodynamic stability of water** during the transient periods.

To achieve the above goal 3M will work on **two major concepts**:

- 1. Catalysts with high oxygen evolution reaction (OER) activity**
- 2. Anode catalysts with low oxygen reduction (ORR) reaction activity**

1. Presence of **highly active OER catalyst** on the **cathode** will **reduce the overpotential** for a given current demand (*region B*).
  - Key requirements: Implement the OER catalyst with **negligible inhibition of the ORR** on the existing cathode catalyst and **minimally added PGM**.
  - Deposit the OER catalyst as a **separate phase - as nanoparticles**.
2. **Inhibition of the ORR on the anode** side will lower the ORR current (*region D*). Through **reduced proton demand** this then lowers the OER current on the cathode (*region B*) resulting in reduced **cathode** potential.
  - Key requirement: Implement the ORR inhibiting component with **negligible inhibition of the HOR, either as a mixed or a separate phase**.

## The Proposal: What is New and Why 3M

The two-part catalyst approach makes good electrochemical sense. The two concepts proposed combined with the NSTF support demonstrated stability is an extremely compelling aspect the prior art (by the applicants and others) is well documented.

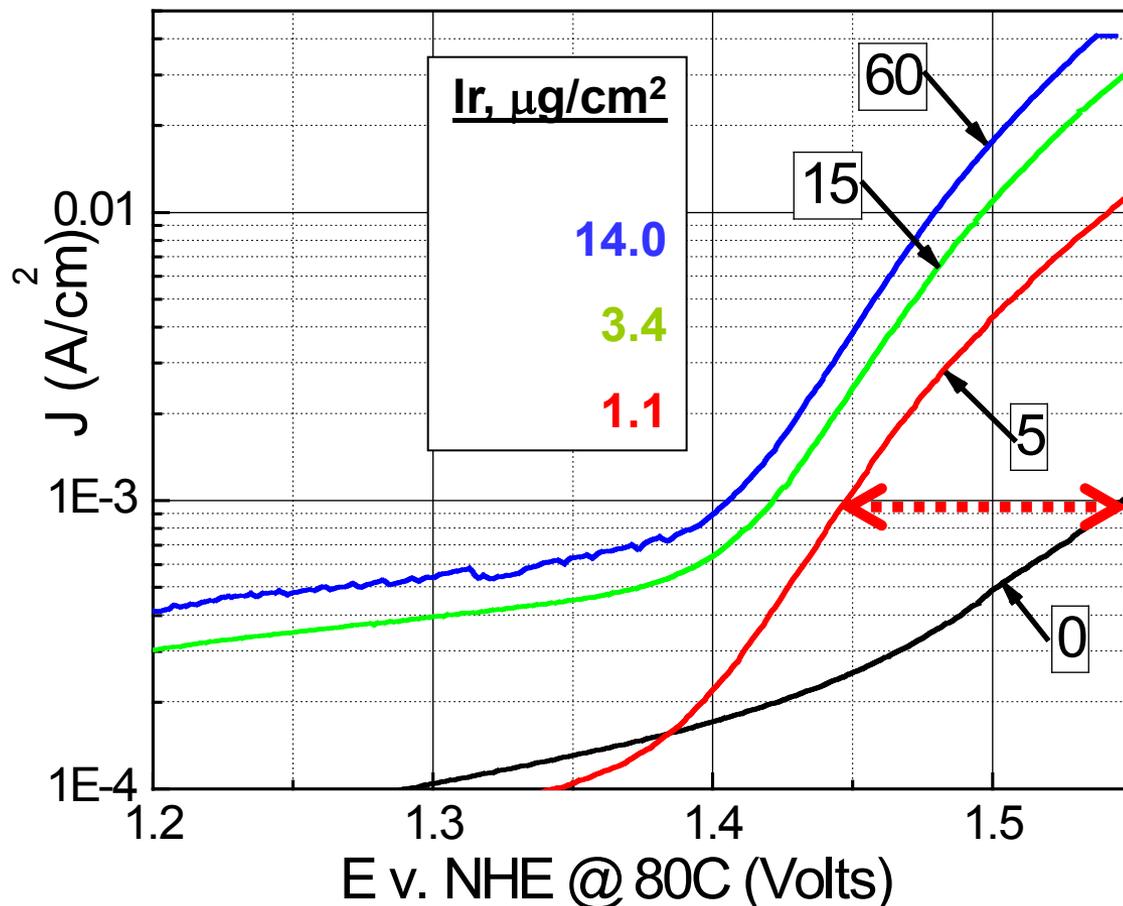
**A****B****C**

.....

*Comparison of FC characteristics of Pt/C and Pt/NSTF MEAs before and after exposure at 1.5 V. Pt/NSTF catalyst exposed for 180 minutes; Pt/C catalyst exposed for 30 minutes. **A**: ECSA (NSTF-Pt, top; Pt/C, bottom); **B**: AC impedance; **C**: Polarization curves.*

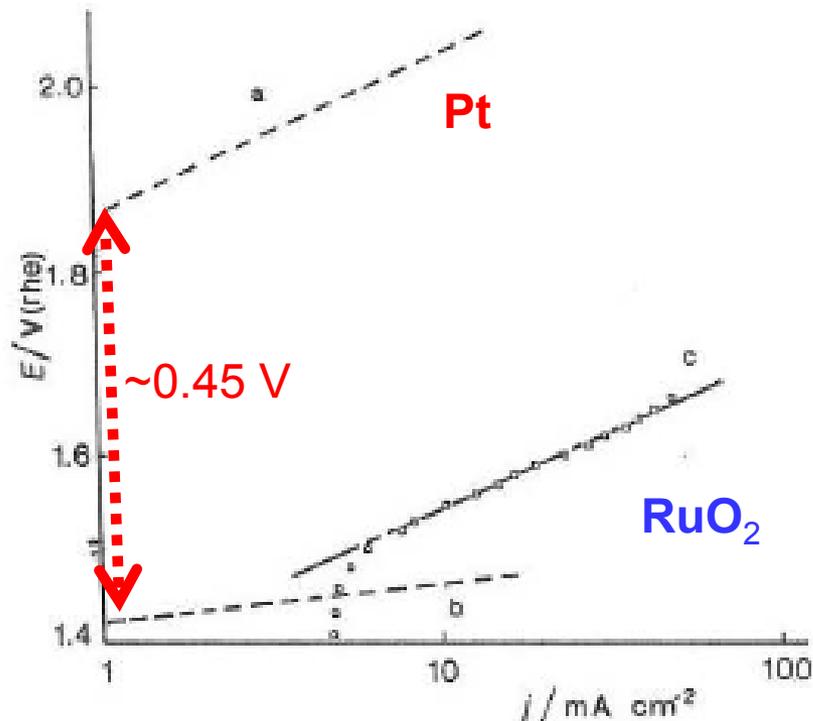
## Concept 1 – OER: Ir Catalyst

OER polarization curves on NSTF PtCoMn ( $0.1 \text{ mg/cm}^2$  Pt) catalyst over-coated with 5, 15 and  $60 \text{ nm/cm}^2$  geo Ir.  
 $50\text{-cm}^2$  FC  
 Counter electrode: same as working without Ir.  
 Test conditions: FC  $80^\circ\text{C}$ ,  
 Working:  $\text{N}_2$ ; counter/reference:  
 $1\% \text{ H}_2$  in  $\text{N}_2$ ;  
 $1000 \text{ sccm}$ ,  $0 \text{ psig}$ ,  $100\% \text{ RH}$ ;  
 Potential scan rate:  $1 \text{ mV/s}$ .

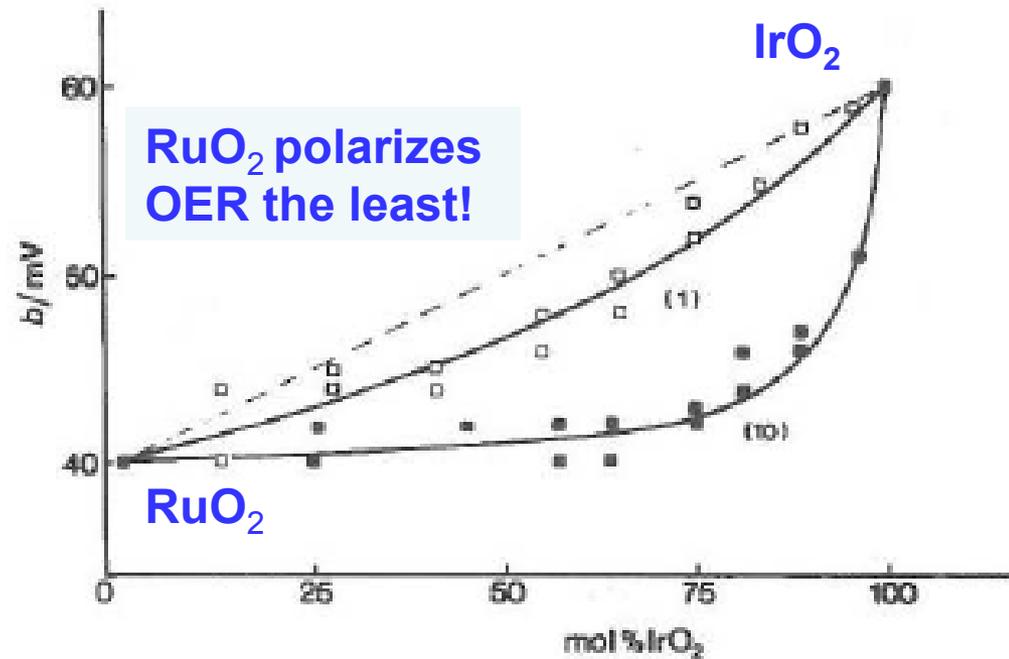


**At  $1 \text{ mA/cm}^2$  only  $1.1 \mu\text{g/cm}^2$  Ir depolarizes OER by  $100 \text{ mV}$ !**

# Concept 1 – OER: Most active catalysts



*Polarization curves for oxygen evolution on (a) Pt, (b) RuO<sub>2</sub> single crystal, and (c) RuO<sub>2</sub> film. 1M HClO<sub>4</sub> at 25 °C*



*Dependence of Tafel slopes for OER on surface composition of two RuO<sub>2</sub> + IrO<sub>2</sub> electrodes. PGM precursors dissolved in aqueous (open symbols) and non-aqueous solvents (closed symbols). PGM content determined by XPS.*

# Concept 1 – OER: Most active and stable catalysts

## Target composition

**Activity:**  $\text{RuO}_2$

High exchange c.d.; 40 mV/decade Tafel slope; good charge capacity

**Activity and stability:**  $\text{RuO}_2 + \text{IrO}_2$

Good stability and activity; up to 75% surface  $\text{IrO}_2$  is OK

**Stability and cost:**  $\text{TiO}_2$ ,  $\text{MnO}_2$

Interfacial stability improves from 400 °C to 600+ °C

Stable interfacing with the ORR catalyst

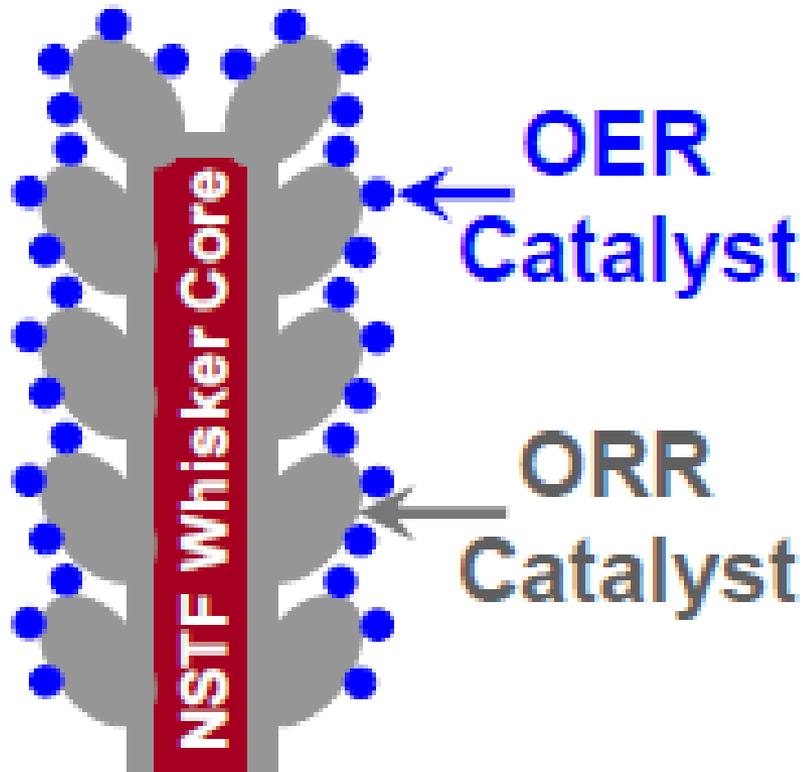
All the components are isomorphous, rutile.

## Structural considerations

**Discrete nanoparticles** in order to minimize blocking of the base ORR catalysts. (next slide)

# Concept 1 - ORR/OER integrated catalyst

*Schematic illustration of the proposed mixed ORR/OER catalyst concept*



## The Model:

Achieve **1cm<sup>2</sup> of OER** catalyst on 1 cm<sup>2</sup> geo with **OER nano-cubes** of **3 nm** sides to withstand **1 mA/cm<sup>2</sup> OER** at **<1.42 V**.

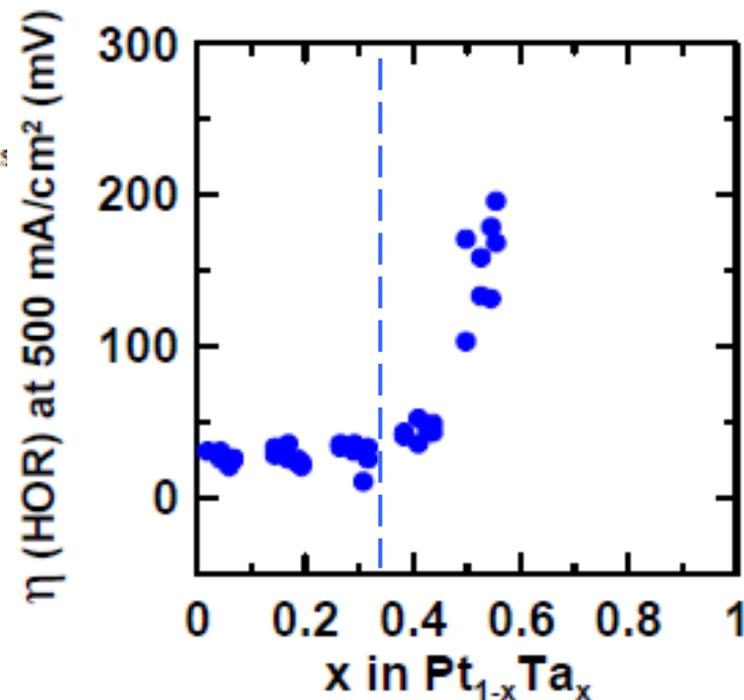
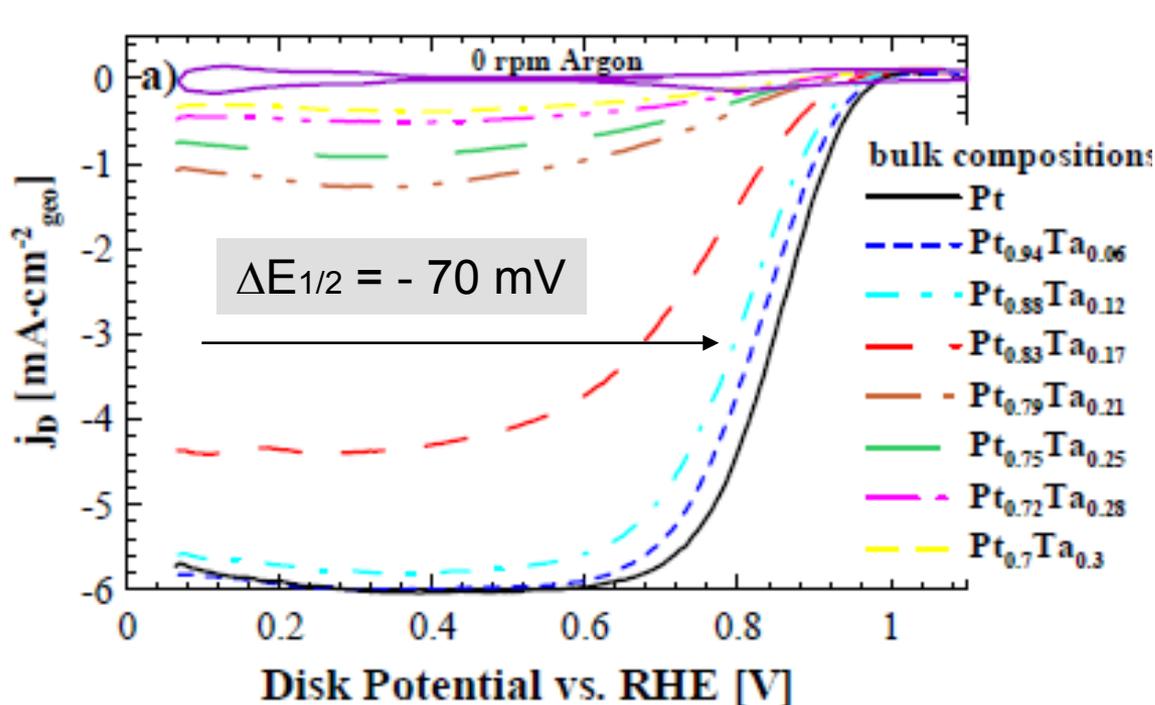
Number of catalyst **particles** needed: **2.2x10<sup>12</sup>**.

**Ru content:** 0.41  $\mu\text{g}/\text{cm}^2$  RuO<sub>2</sub> or 0.31  $\mu\text{g}/\text{cm}^2$  Ru.

ORR catalyst **surface area blocked:** 0.2 cm<sup>2</sup> or **0.5%** of NSTF entitlement.

With TiO<sub>2</sub> as support blocked ORR catalyst area is ~1%.

## Concept 2 – ORR suppression on the anode



**ORR curves for  $\text{Pt}_{1-x}\text{Ta}_x$**   
 measured at 1600 rpm, 30 °C in 0.1 M  $\text{HClO}_4$ .  
 Samples **sputter-deposited** onto glassy carbon

**Hydrogen oxidation**  
**Overpotentials:  $500 \text{ mA/cm}^2$**   
 at 80 °C in a 64-electrode cell

**ORR is inhibited by a factor of 10 with only 12% Ta.**

**HOR has practically no voltage losses even with 30+ % Ta.**<sup>10</sup>



## MILESTONES AND GO/NO-GO DECISION

Until DOE targets for this topic are established, the milestones are defined upon the following project goals:

**Milestone #1:** OER of 1 mA/cm<sup>2</sup> at **1.45 V**; **10 mA/cm<sup>2</sup>** at 1.5 V; PGM: **2 μg/cm<sup>2</sup>**.

**Milestone #2:** OER of 1 mA/cm<sup>2</sup> at **1.42 V**; **20 mA/cm<sup>2</sup>** at 1.5 V; PGM: **1.5 μg/cm<sup>2</sup>**.

**Anode ORR current reduced** by a factor of **2**.

Demonstrated ORR and HOR performance with integrated catalyst will be substantially the same as the base-line NSTF catalyst.

**Go/No-Go:** OER of 1 mA/cm<sup>2</sup> at **1.40 V**; **100 mA/cm<sup>2</sup>** at 1.5 V; PGM: **1 μg/cm<sup>2</sup>**.

**Anode ORR current reduced** by a factor of **5**.

Integrated catalyst system meets DOE metrics for durability, performance and PGM loading demonstrated by 50-cm<sup>2</sup> FC testing.

**Milestone #3:** Short stack for delivery to DOE designated site for testing.

## Reviewers' comments

The idea of adding low surface-coverage nanoscale OER catalyst particles to a high specific activity ORR catalyst to enhance OER reactions without compromising the ORR activity (Concept #1) is intriguing. However, retention of separate OER and ORR catalyst functions in such a structure over multiple reaction cycles assumes that the OER catalyst nanoparticles and ORR catalyst layers remain chemically and structurally distinct during cycling. Given the demanding electrochemical reaction conditions, the small size of the OER particles as well as their tendency to migrate and coalesce, and the nature of the contact between the OER particles and the ORR catalyst layer, this assumption seems highly speculative and may be a risk factor underlying the viability of Concept #1.

This comment addresses a potential problem common to many small particle systems. Based on our own and others literature data, the catalysts material itself,  $\text{RuO}_2/\text{TiO}_2$ , lasts for many thousands of hours in industrial environment.  $\text{RuO}_2$  is not soluble in water unless for extended period of time the potential reaches very positive values. Furthermore, unlike the weak van der Waals forces that are holding Pt nanoparticles to carbon, the oxides will be anchored more strongly to the substrate.