

V.A.1 Durable Catalysts for Fuel Cell Protection during Transient Conditions

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Contract Number: DE-EE0000456

Subcontractors and Federally Funded Research and
Development Centers:

- Dalhousie University, Halifax, Nova Scotia, Canada
- Oak Ridge National Laboratory, Oak Ridge, TN
- AFCC Corporation, Burnaby, BC, Canada
- Argonne National Laboratory, Argonne, IL

Project Start Date: August 1, 2009

Projected End Date: December 31, 2013

Overall Objectives

- Develop catalysts that will enable proton exchange membrane (PEM) fuel cell systems to weather the damaging conditions in the fuel cell at voltages beyond the thermodynamic stability of water during the transient periods of fuel starvation.
- Demonstrate that these catalysts will not substantially interfere with the performance of nor add much to the cost of the existing catalysts.

Fiscal Year (FY) 2014 Objectives

- Expand the catalyst evaluation towards 'real life' application with emphasis on hydrogen – air gas switching.
- Perform root cause analysis and develop working hypothesis of the impact of gas switching.
- Mitigate the impact of gas switching on the oxygen evolution reaction (OER) catalyst stability.
- Synthesize modified OER catalysts and narrow composition and construction parameters.
- Establish fundamentals of the activity and stability of the modified OER catalysts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

The DOE-approved technical target for the final year had the following milestone:

- 2014 Milestone: After 200 gas switches, achieve cell reversal of 10 hours at -0.2 A/cm^2 at $<1.7 \text{ V}$ with $<0.035 \text{ mg/cm}^2$ platinum group metal (PGM).

Accomplishments

The final-year project milestone has been achieved:

- Constructs with additional refractory metals have fulfilled the cell reversal requirement after gas switching

within the 2014 program milestone voltage limit, <1.7 V, and PGM loading, <0.035 mg/cm².

In addition:

- The hypothesis that separating the OER catalyst from atomic proximity of Pt may alleviate the impact of gas switching was proven.
- As an added benefit of the separating layer, improved OER activity was achieved.
- Fundamental materials studies aimed at understanding the extraordinary durability of the new OER-Pt/nano-structured thin-film (NSTF) constructs have converged to conclude that stabilizing the Pt and Ir oxides is paramount to increasing reversal endurance.



INTRODUCTION

The project addresses a key issue of importance for successful transition of PEM fuel cell technology from development to the pre-commercial phase (2010-2015). This issue is the failure of the catalyst and the other thermodynamically unstable membrane electrode assembly (MEA) components at the anode during start-up/shut-down (SU/SD) and local fuel starvation, commonly referred to as transient conditions. During these periods, the electrodes can reach potentials up to 2 V. One way to minimize the damage from such transient events is to lower the potential seen by the electrodes. At lower positive potentials, increased stability of the catalysts themselves and reduced degradation of the other MEA components are expected.

APPROACH

This project tries to alleviate the damaging effects during transient conditions from within the fuel cells via improvements to the existing catalyst materials. We are modifying both the anode and the cathode catalysts to favor the oxidation of water over carbon corrosion by maintaining the cathode potential close to the onset potential for water oxidation. The presence of a highly active OER catalyst on the cathode reduces the overpotential for a given current demand, thus reducing the driving force for carbon and platinum dissolution. In addition, inhibition of the oxygen reduction reaction (ORR) on the anode side lowers the ORR current through reduced proton demand, which in turn decreases the OER current on the cathode, resulting in reduced cathode potential.

A key requirement for both concepts is to implement the added catalyst with negligible inhibition of the fuel cell performance and with minimal increment of PGM.

RESULTS

Durable Oxygen Evolution Reaction Catalysts. During the previous four years, we have developed and integrated Ir and IrRu OER components with Pt catalyst on 3M NSTF support [1-4]. The catalyst was tested via the electrochemical equivalent to start-up conditions, sustaining up to 5,000 pulses to <1.5 V. However, the *same catalyst, when applied on the anode side for cell reversal mitigation, lost its OER activity when exposed to real gas switching (GS) from hydrogen to air*. In Figure 1, the difference in the cell reversal durability is illustrated by comparing the baseline OER-Pt/NSTF (20 μg/cm² Pt + 15 μg/cm² Ir) after the 200 GS cycles with the same catalyst after the electrochemical equivalent of 200 pulses. It is obvious that the gas switches are detrimental to the OER. The initial hold potential of the GS-cycled catalyst is about 50 mV higher than without the GS, and the decay to MEA failure happens 2.5 hours sooner. Clearly, gas switches are damaging the MEA in a way that the electrochemical equivalent of 200 pulses (designed to simulate SU/SD cycles) did not predict.

Root Cause Hypothesis. *High electrode potential* is usually the first cause to be associated with the catalyst failure during SU/SD. However, the *GS does not provoke a high anode potential*; the maximum potential that can be reached under air is about 1 V (Figure 2A). Numerous tests performed during the past three years have proven that the OER catalyst is stable up to 1.75 V, with simulated pulses (Figure 2B) integrated into the testing to confirm the catalyst stability during SU/SD events. This precludes high potential during GS as the cause of the OER catalyst degradation.

The only other plausible explanation involves the *hydrogen-air direct recombination on the anode catalyst*.

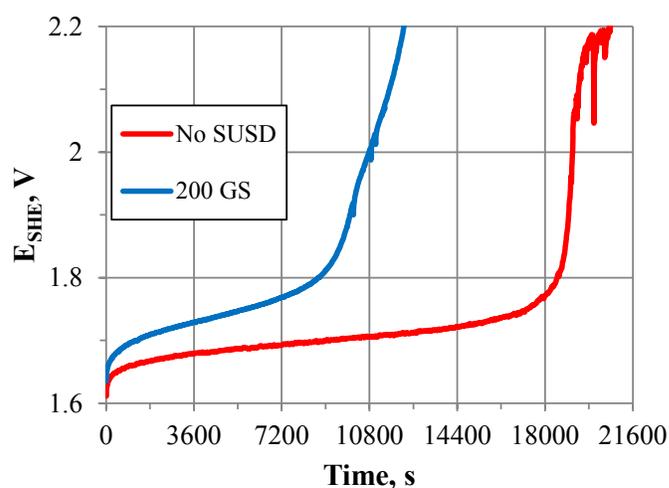


FIGURE 1. Effect of GS on reversal durability: potential as a function of time at 200 mA/cm² galvanostatic hold. The blue line represents reversal durability after 200 gas switches on IrPt/NSTF (20 μg/cm² Pt + 15 μg/cm² Ir); 50-cm² MEA under nitrogen/1% hydrogen, 70°C, fully saturated.

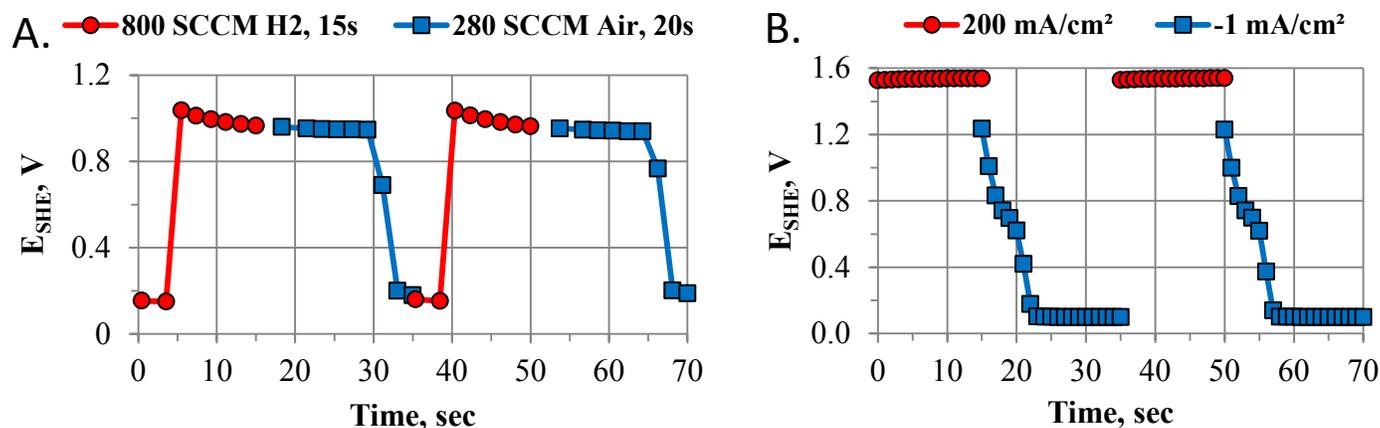


FIGURE 2. Potential Profiles of the Anode During Gas Switching (A) and During Electrochemically Simulated Pulses (B)

This mechanism came into consideration based on the key observation that the otherwise inferior conventional, dispersed OER-added catalyst—*admixed* IrRu catalyst with dispersed Pt—did not lose much of its performance due to GS. As is well known, hydrogen and oxygen (in the air) can directly react, and the reaction can be vigorous in the presence of platinum. This reaction produces *heat and a variety of radicals*. The OER-Pt/NSTF construct is such that the OER catalyst is in *atomic proximity* of the Pt reaction sites. Therefore, both the heat and the reactive radicals can directly impact the thin-film OER catalyst before the heat is dissipated and the radicals recombined. This is in contrast to the dispersed catalyst, where the two catalyst components, Pt/C for hydrogen oxidation reaction (HOR) and IrRu for OER, are well separated on the atomic scale. Therefore, the OER catalyst within the dispersed anode suffers very little from the SU/SD event, while the durability of the OER-Pt/NSTF is quickly compromised. Based on this hypothesis, the concept and the strategy for diminishing the damaging effect of the gas switching were based on two principles:

- *Slowing down the rate of the chemical reaction between hydrogen and oxygen*, while leaving the electrocatalytic HOR unaffected. This will decrease the rate of both the release of heat and the creation of radicals. Whereas the reaction is chemical in nature, the fact that the recombination of the two elements needs catalytic sites to proceed provides a theoretical background upon which the approach of this proposal can be justified. Specifically, we would block a sufficient number of the platinum active sites in a fashion similar to the inhibition of the ORR [4]. Since the incoming hydrogen molecules during startup will react with the adsorbed oxygen, a substantial reduction in the number of the sites where oxygen can be adsorbed and subsequently radicals formed will effectively reduce the rate of the HOR.
- *Inducing a physical separation of Pt from the OER*, which will reduce both the number of radicals and the

extent of heat transfer from the Pt sites where they are generated to the OER where they cause degradation.

This concept is material-based, just like the OER-modified anode. The concept fits into the philosophy of a protection from within the MEA and as such is always ‘on.’ The success of the concept would depend on

- finding a material that is stable when exposed to high potentials during cell reversal
- implementing an amount sufficient to inhibit the undesired H₂-O₂ reaction without compromising the anode performance
- manufacturing via processes compatible with the existing Pt/NSTF anode fabrication
- adding little, preferably not at all, to the PGM loading.

Materials with the required stability were found in the *group of transition elements known as refractory metals*. Due to the high affinity for oxygen, these metals form extremely inert oxide films on their surfaces, which is the source of their high stability. These elements are inexpensive compared to the PGMs and can be sputter-deposited in a vacuum while their compounds can be generated via reactive sputtering or by using a sputtering target of the desired composition. Most of these elements and their oxides are known inhibitors for the ORR; therefore, their application will not only inhibit the HOR but will also enhance the protection of the cathode during SU/SD. As we have shown in this project [4], using the deposition of tantalum (Ta) on Pt, a relatively small coverage of Ta reduces the ORR substantially without any noticeable adverse effect on the HOR.

Four metals from the group of refractory metals were selected for rather rigorous evaluation: Zr, Hf, Ti, and Ta. The catalyst fabrication and evaluation were intended to

- Determine the range of added elements
- Ascertain the stability of the added element in PEMs

- Establish testing procedures and protocols
- Evaluate the performance for cell reversal
- Understand the fundamentals of the impact of the added elements.

The cell reversal test protocol as described in [4] was added by

- GS cycling (20 sec air, 15 sec H₂)
- High current reversal hold up to 10 hours (-200 mA/cm², to 2.2 V)

and it was carried out using 50-cm² MEAs at 70°C, A/C N₂/1% H₂ @ 1,000 SCCM, 110% relative humidity.

The *constructs with zirconium* were tested first, and the results were such that eventually zirconium was considered as a *model system*. This material was studied in detail to understand the fundamentals of the mechanism with which the refractory metal oxides can mitigate the degradation through gas switching. It became clear from Zr study that the layer thickness and position within the PtIr anode is of great importance. Fundamental characterization of the PtZrIr model system using advanced analytical techniques, including X-ray photoelectron spectroscopy and scanning transmission electron microscopy (STEM), allowed for better understanding of how to improve durability.

The greatest impact to increasing reversal durability after GS was with *Zr deposited between Pt and Ir* (Figure 3A), forming a M-Ox interlayer ('sandwich') construction, validating our starting hypothesis that a physical separation of Pt from the OER catalyst is key in mitigating GS degradation. The best-of-class interlayer constructs for all four elements is represented in Figure 3B, from which we concluded that planar equivalent of 250 Å Zr and Hf gave the highest reversal durability performance, reaching 10 hours under 1.7 V.

Finally, in Figure 4, comparative STEM images of IrPt/NSTF and IrZrPt/NSTF are presented at different stages of the durability test protocol. These images illustrate well the considerably improved retention of the Ir catalyst when Zr is present between Pt and Ir, as result of which a better cell reversal durability was observed. Along with the other techniques used in this period, the understanding of the extraordinary durability of the new OER-Pt/NSTF constructs has converged to conclude that stabilizing the Pt and Ir oxides is paramount to increasing the reversal endurance.

FY 2014 PUBLICATIONS/PRESENTATIONS

Papers

1. Vincent Lee, Darija Susac, Sumit Kundu, Viatcheslav Berejnov, Radoslav T. Atanasoski, Adam P. Hitchcock, Jürgen Stumper: "STXM Characterization of Nanostructured Thin Film Anode

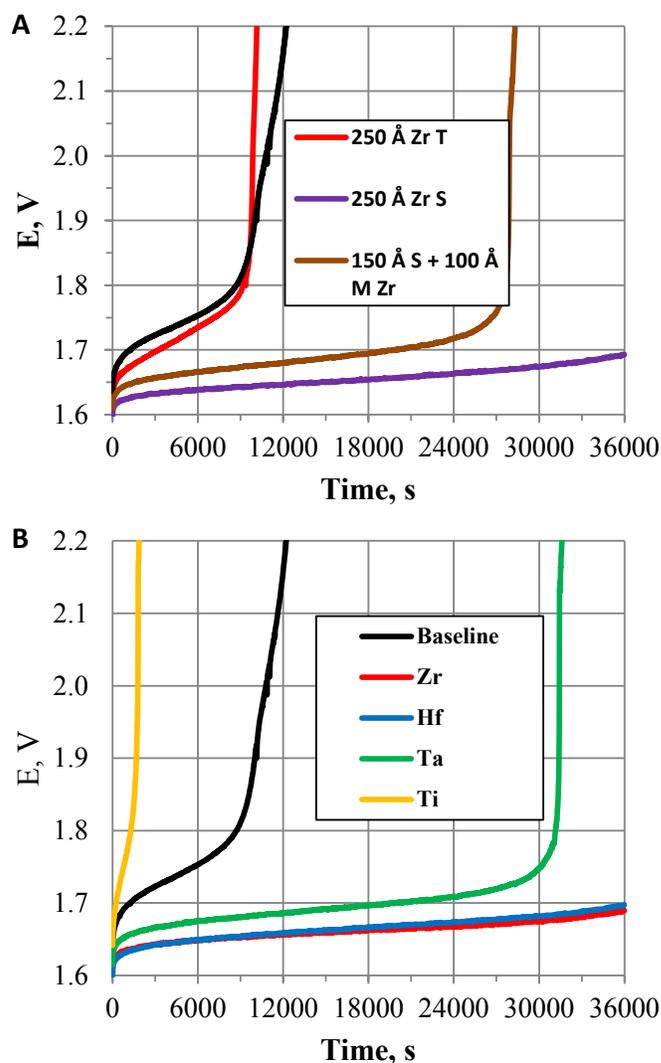


FIGURE 3. Cell reversal durability after 200 gas switches in addition to 200 pulses at 200 mA/cm². (A) Three different constructs of 250-Å Zr added to the Pt/NSTF: atop deposited Zr (T); Zr sandwiched between Pt and Ir (S). 150-Å Zr deposited on top of Pt, followed by 100-Å Zr intermixed with Ir (M); Black line: baseline IrPt/NSTF. (B) Reversal potential of the four refractory metals added as a sandwich between Pt and Ir.

Before and After Start-up Shut-down and Reversal Tests", *Transaction of the Electrochemical Society* 58 (2013) 473-479.

2. LL Atanasoska, DA Cullen, RT Atanasoski: "XPS and STEM of the interface formation between ultra-thin Ru and Ir OER catalyst layers and Perylene Red support whiskers", *J. Serb. Chem. Soc.* 78 (12) 1993-2005 (2013).

3. Vincent Lee, Adam P. Hitchcock, Marcia West, Viatcheslav Berejnov, Sumit Kundu, Darija Susac, Juergen Stumper, Radoslav Atanasoski and Mark Debe: "STXM Investigations of Nano Structured Thin Film Catalysts for Proton-Exchange-Membrane Fuel Cell Applications", *J. Power Sources* 263, 163 - 174 (2014).

4. Timothy Crowtz, David Stevens, Robbie Sanderson, Jessie Harlow, George Vernstrom, Ljiljana Atanasoska, Greg Haugen, and

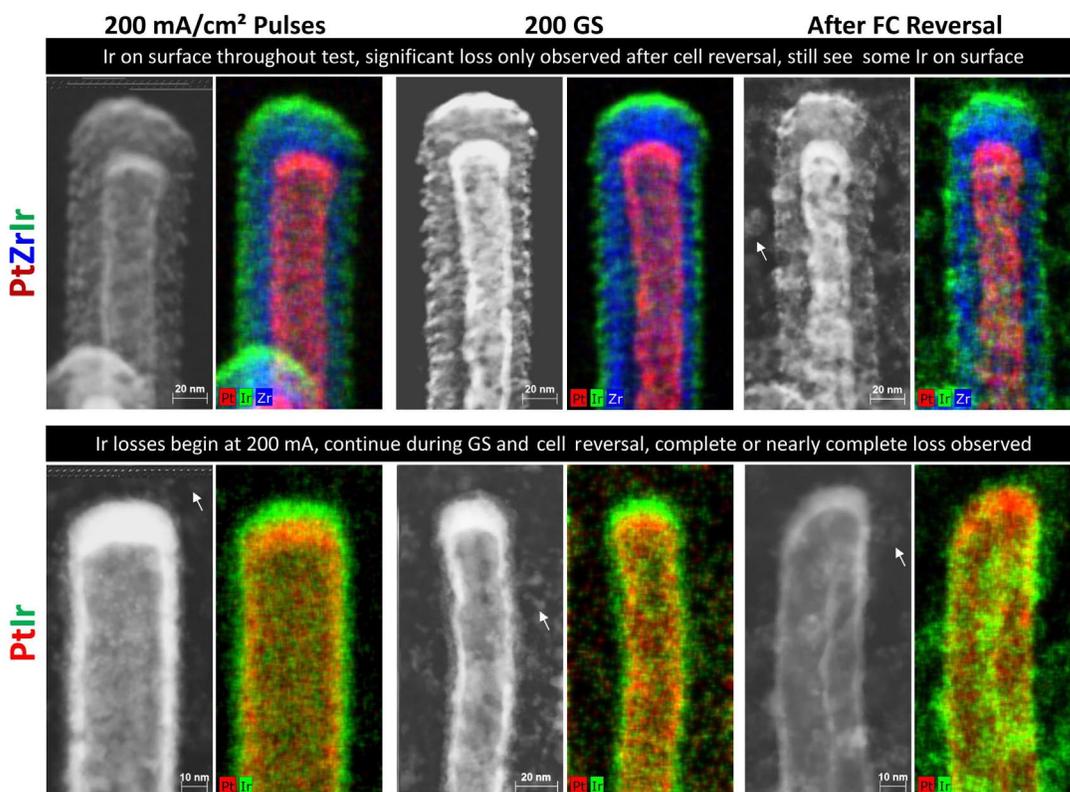


FIGURE 4. Comparative STEM images and elemental maps of IrPt/NSTF and IrZrPt/NSTF at different stages of the durability test protocol. Left panel: after 200 pulses at 200 mA/cm². Middle panel: after 200 gas switches. Right panel: after the cell reversal durability test at 200 mA/cm². Note that IrPt/NSTF endured only 3.3 hours vs. a full 10 hours for IrZrPt/NSTF. Zr catalyst constructs: 250-Å Zr sandwiched between Ir and Pt.

Radoslav Atanasoski, Jeff Dahn: “The effect of Ru or Ir addition on Nano-Structured-Thin-Film supported Pt fuel cell catalysts under rotating disk electrode simulated start-up shut-down”, *J. Electrochem. Soc.* 161 (10) F961-F968 (2014).

5. DA Cullen, KL More, LL Atanasoska, RT Atanasoski: “Impact of IrRu Oxygen Evolution Reaction Catalysts on Pt Nanostructured Thin Films under Start-Up/Shutdown Cycling”, *J. Power Sources* 269, 671-681, 2014.

Presentations

1. GM Haugen, GD Vernstrom, LL Atanasoska, and RT Atanasoski: “SU/SD, a Materials Solution”, Abstract #1279, 224th ECS Meeting (oral presentation).

2. T.C. Crowtz, D.A. Stevens, R.J. Sanderson, C.W. Watson, J.E. Harlow, and J.R. Dahn: “An RDE assessment of sputtered Ir-Ru-Pt overlayer nanostructured thin film catalysts for protection of PEM fuel cell cathodes against start-up and shut-down: The durability of oxygen reduction activity”, Abstract #1552 (oral presentation).

3. Vincent Lee, Darija Susac, Sumit Kundu, Viatcheslav Berejnov, Radoslav T. Atanasoski, Adam P. Hitchcock, Jürgen Stumper: “STXM Characterization of Nanostructured Thin Film Anode Before and After Start-up Shut-down and Reversal Tests”, Abstract #1322, 224th ECS Meeting (oral presentation).

Presentations to DOE

1. “Durable Catalysts for Fuel Cell Protection during Transient Conditions” Project progress Review, presented to DOE (internal), November, 2013, St. Paul, Minnesota.

2. “Durable Catalysts for Fuel Cell Protection during Transient Conditions” Project progress Review, presented to DOE (internal), Web conf., April, 2014.

3. “Durable Catalysts for Fuel Cell Protection during Transient Conditions” presented at the FC Tech Team, Detroit, April, 2014.

4. “Durable Catalysts for Fuel Cell Protection during Transient Conditions” presented at the DOE 2014 AMR, June, 2014, Washington, D.C.

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1. RT Atanasoski, DA Cullen, GD Vernstrom, GM Haugen, and LL Atanasoska: “A Materials-Based Mitigation Strategy for SU/SD in PEM Fuel Cells: Properties and Performance-Specific Testing of IrRu OER Catalysts”, *ECS Electrochem. Lett.*, 2 (3) F25-F28, 2013.

2. RT Atanasoski, LL Atanasoska, DA Cullen: “Efficient Oxygen Evolution Reaction Catalysts for Cell Reversal and Start/Stop Tolerance” in M. Shao ed., “*Electrocatalysis in Fuel Cells: A Non and Low Platinum Approach*”, Chapter 22, Springer, March, 2013.

3. RT Atanasoski, LL Atanasoska, DA Cullen, GM Haugen, KL More, GD Vernstrom: “Fuel Cells Catalyst for Start-up and Shutdown Conditions: 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.

4. R.T. Atanasoski, Project review at the DOE Vehicle Technologies and Hydrogen Programs Annual Merit Review, 2010 - 2014, Washington, D.C., FC# 003.