

## V.E.6 Durable Catalysts for Fuel Cell Protection during Transient Conditions

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### 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 start-up/shut-down and fuel starvation.
- Demonstrate that these catalysts will not substantially interfere with the performance of nor add much to the cost of the existing catalysts.

### Technical Barriers

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

- (A) Durability
- (G) Start-up and Shut-down Time and Energy/Transient Operation

### Technical Targets

While the number of start-up and shut-down cycles for an automotive fuel cell has been estimated to be over 30,000, the number of these events when the cathode electrochemical potential exceeds 1.23 V has not been assessed. In agreement with DOE, the technical targets for the first year of the project have been defined as follows:

- Develop cathode catalyst that can withstand currents of 1 mA/cm<sup>2</sup> at potential of <1.45 V and 10 mA/cm<sup>2</sup> at potential of <1.50 V with added oxygen evolution reaction (OER) catalyst of no more than 2 µg/cm<sup>2</sup> of platinum group metals (PGM).

### Accomplishments

- Produced OER catalysts with 2 µg/cm<sup>2</sup> PGM that achieved the first year milestone for OER activity of 1 mA/cm<sup>2</sup> at 1.45 V.
- Developed integrated OER/oxygen reduction reaction (ORR) catalysts with only 2 µg/cm<sup>2</sup> (Ru + Ir) showing no loss of ORR activity relative to the baseline ORR catalyst.
- Canvassed the space around the components (Ru, Ir, Ti) of the model OER durable catalyst in the real PEM fuel cell environment.
- Established that Ru is the most active OER catalyst, Ir is the most stable and that combinations of Ru + Ir retain some of the properties of the two.
- Modified the anode catalyst to inhibit ORR while preserving the same activity towards hydrogen oxidation reaction (HOR).



### Introduction

The project addresses a key issue of importance for successful transition of PEM fuel cell technology from development to pre-commercial phase (2010 - 2015). This issue is the failure of the catalyst and the

other thermodynamically unstable membrane electrode assembly (MEA) components during start-up/shut-down and local fuel starvation at the anode, commonly referred to as transient conditions. During these periods the electrodes can reach potentials up to 1.5 V. One way to minimize the damage from such transient events is to minimize the potential seen by the electrodes. At lower positive potentials, increased stability of the catalysts themselves and reduced degradation of the other MEA components is expected. This project aims to develop catalysts that will reduce the potentials experienced during transient conditions. In order to achieve the above goal we are working on two major concepts:

- Cathode catalysts with high activity towards oxygen evolution from water
- Anode catalysts with low oxygen reduction reaction activity.

## Approach

This project will try to alleviate the damaging effects during transient conditions from within the fuel cells, via improvements to the existing catalyst materials. We will modify both the anode and the cathode catalysts to favor the oxidation of water over carbon corrosion by maintaining the cathode potential close to the thermodynamic potential for water oxidation. The absence of hydrogen and simultaneous presence of oxygen in separate regions of the anode is necessary to provoke and maintain cathode potential  $>1.23$  V. Oxygen in these regions of the anode gets reduced. The protons for the reduction of oxygen are supplied from the cathode side via either carbon or 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 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.

Key requirements for both concepts are:

- On the cathode: implement the OER catalyst with negligible inhibition of the ORR on the existing cathode catalyst and with minimal addition of PGM, i.e. to deposit the OER catalyst as a separate, discontinuous phase - as nanoparticles.
- On the anode: implement the ORR inhibiting component with negligible inhibition of the HOR, either as a mixed or a separate phase.

## Results

### Task 1. Efficient Oxygen Evolution Reaction Catalysts

Most of the activity during the first year of the project was related to this task. The catalysts prepared were based around the model catalyst containing ruthenium, iridium, and titanium [1]. Since the oxides of ruthenium and iridium are known to have the best catalytic properties for OER in aqueous solutions, some of the catalyst syntheses were performed in the presence of oxygen [2,3].

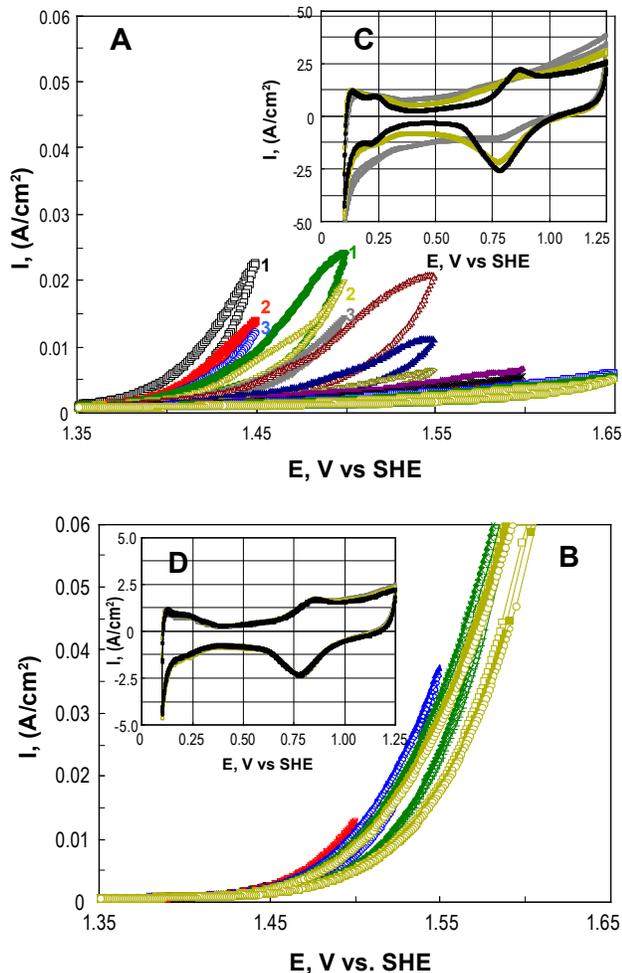
In order to be able to properly examine the inherent activity of the OER catalyst, one needs a substrate with minimal interference from the underlying ORR catalyst. The unique features of 3M's nanostructured thin film (NSTF) catalyst such as the lack of carbon that can corrode and the durability at high potential made it a logical choice as a support for the added OER catalyst. In addition, the NSTF fabrication process of physical vapor deposition via sputtering in vacuum allows for a wide range of materials in variety of compositions to be synthesized [4,5].

The OER catalysts synthesized and characterized can be grouped in four major categories, ranging from single elements up to a quaternary system.

#### 1. The Single Elements

To our knowledge, the most comprehensive study to date of the behavior of Ru, Ir and Ti in the real PEM fuel cell environment was completed during the first year of this project. In addition to testing samples with only  $2 \mu\text{g}/\text{cm}^2$  PGM, as required by the year one milestone, we have produced and tested samples with  $10 \mu\text{g}/\text{cm}^2$  PGM to enhance the impact of the presence of ruthenium and iridium on the cathode ORR catalysts. The OER activity was assessed by quasi-steady state measurements where polarization curves for oxygen evolution were recorded at 2 mV/s. Three consecutive potential sweeps were performed up to each of the voltages set for the year one milestones, 1.45 V and 1.5 V, as well as 1.55 V, 1.6 V and 1.65 V. The first sweep allowed us to assess the intrinsic activity. The second and the third sweep provided insights into the stability of the OER catalysts. The impact of the added OER catalyst on ORR activity was assessed through standard fuel cell performance testing before and after the OER test.

In Figure 1 the OER polarization curves with  $10 \mu\text{g}/\text{cm}^2$  of either Ru (1A) or  $10 \mu\text{g}/\text{cm}^2$  of Ir (1B) over  $0.15 \text{ mg}/\text{cm}^2$  Pt on NSTF are presented. The difference between the two OER catalysts is that Ru is initially more active than Ir, however, Ir preserves its activity even after excursions to very high potentials whereas Ru loses activity. It is worth noting that the OER activity of the platinum itself as well as Pt coated with  $10 \mu\text{g}/\text{cm}^2$



**FIGURE 1.** Polarization curves for oxygen evolution on 10  $\mu\text{g}/\text{cm}^2$  Ru (A) and 10  $\mu\text{g}/\text{cm}^2$  Ir (B) sputter-deposited on 0.15  $\text{mg}/\text{cm}^2$  Pt NSTF. Three consecutive polarization curves for each end voltage at 2 mV/s, 50-cm<sup>2</sup> MEA under nitrogen/1% hydrogen, 70 °C, fully saturated. Current densities in (B) limited by the output of the potentiostat. (C)&(D): Cyclic voltammograms for 10  $\mu\text{g}/\text{cm}^2$  Ru (C) and 10  $\mu\text{g}/\text{cm}^2$  Ir (D) at beginning of test (gray), after exposure to 1.45 V (light grey), and after exposure to 1.65 V (olive).

Ti is extremely small,  $\sim 0.5$  mA/cm<sup>2</sup> at 1.65 V. The likely cause for the loss of OER activity of the ruthenium catalyst during OER testing can be determined from the cyclic voltammograms before OER, and after exposure to 1.45 V and 1.65 V (Figure 1C). Initially, the cyclic voltammograms are dominated by the presence of ruthenium which is manifested in large capacitive current in the platinum double layer region and by the suppression of the characteristic peaks for hydrogen underpotential deposition (Hupd) and Pt oxide formation and reduction. After exposure to 1.45 V the features from the presence of ruthenium are substantially, but not completely diminished. The cyclic voltammograms only become platinum-like (as if ruthenium were completely removed) after reaching 1.65 V: well pronounced Hupd

peaks, proper double layer and Pt-oxide formation/reduction. Thus, loss of Ru from the Pt ORR catalyst causes the loss of OER activity. In contrast, the cyclic voltammograms for Ir over Pt on NSTF are practically unchanged even after the exposure to 1.65 V.

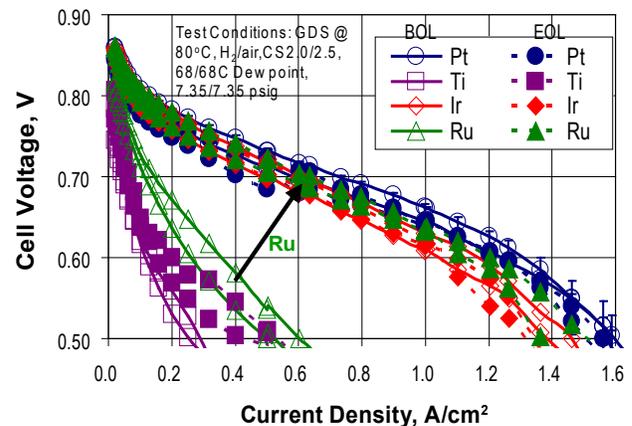
The behavior of catalysts with only 2  $\mu\text{g}/\text{cm}^2$  additional PGM followed the same pattern as samples with 10  $\mu\text{g}/\text{cm}^2$  additional PGM. At the year one milestone potentials for both Ir and Ru catalysts are above the milestone OER activity of 1 mA/cm<sup>2</sup> at 1.45 V. However, only Ir catalysts exhibit activity above the milestone of 10 mA/cm<sup>2</sup> for 2  $\mu\text{g}/\text{cm}^2$  additional PGM at 1.5 V.

As indicated already, integration of the OER catalysts with the existing cathode catalyst, Pt in this study, was examined via 50-cm<sup>2</sup> MEAs (Figure 2). Within the reproducibility of the fuel cell testing, the integrated catalysts fall in two groups:

- No impact – no loss of ORR activity: Ir with 2 and 10  $\mu\text{g}/\text{cm}^2$  and Ru with 2  $\mu\text{g}/\text{cm}^2$ .
- Negative impact – significant loss of ORR activity: high Ru content (10  $\mu\text{g}/\text{cm}^2$ ) before OER testing and Ti.

Loss of Ru during OER testing allowed the 10  $\mu\text{g}/\text{cm}^2$  Ru cells to move from the negative impact group to the no impact group after OER testing. ORR activities measured at 0.9 V according to the DOE protocol follow the same pattern as the fuel cell polarization curves.

In order to get insights into the composition of the OER catalysts, X-ray photoemission spectroscopy (XPS) and electrochemical surface area measurements (via Hupd) were completed on all samples. For all samples assessed, the OER catalysts were deposited over 0.15



**FIGURE 2.** Fuel cell polarization curves before (beginning of life, BOL) and after (end of life, EOL) OER testing for Pt only and 10  $\mu\text{g}/\text{cm}^2$  of Ti or Ir or Ru over 0.15  $\text{mg}/\text{cm}^2$  Pt deposited on NSTF.

mg/cm<sup>2</sup> Pt on NSTF. The atomic concentrations and ratios of Ti, Ir and Ru coatings vs. Pt reveal that Ti covers more of the Pt surface than the other elements. The fraction of the platinum surface covered by the deposited elements is higher than would be expected for pure elements because of the oxidation state of the deposits. Even though no deliberate oxygen was introduced in the vacuum deposition chamber, O/Ti ratios indicate that Ti is present as TiO<sub>2</sub>. Ir is also present as IrO<sub>2</sub> in the thinner coating, 2 μg/cm<sup>2</sup>, while metallic Ir dominates in the 10 μg/cm<sup>2</sup> samples. Because of overlapping of binding energies for carbon and ruthenium, deconvolution of the Ru high resolution spectra is very complex. Nonetheless, because of the key role that ruthenium plays as an OER catalyst component, a rigorous in-depth methodology was developed to determine the real surface concentration of ruthenium and its valence state. Based on the atomic concentrations of Ru, O, and oxidized C, we believe that Ru may be present as organo-metallic compounds through Ru-O-C bonds for both 2 and 10 μg/cm<sup>2</sup> on Pt-NSTF.

## 2. Ti - Ir OER Catalyst

The purpose of this series was to explore the influence of the combination of one OER-active (Ir, 1 - 2 μg/cm<sup>2</sup>) and one supportive, OER-inactive component (Ti, 2 - 4 μg/cm<sup>2</sup>). The results obtained suggested that the properties of these two elements are additive. OER activity improves with the Ir content. The OER activity improves further when the catalyst is made in the presence of oxygen. This improvement is more prominent at higher potentials. However, both the polarization curves as well as the intrinsic ORR activity are lower due to the Ti coverage of the ORR catalyst (Pt).

Transmission electron microscopy (TEM) results from Oak Ridge National Laboratory reveals that both

Ti and Ir are clearly observed on the Pt surface as a thin layer. A Ti/Ir “nanocrystalline” layer is observed on the surface of Pt “cap” and ~50 nm down the sides of the Pt/NSTF ORR catalyst. The Ti/Ir layer is ~4-5 nm thick. In high resolution XPS, these samples show an unusual Ir spectral feature that appears only when Ti and Ir are deposited on the same catalyst. This feature will be a subject of further investigation.

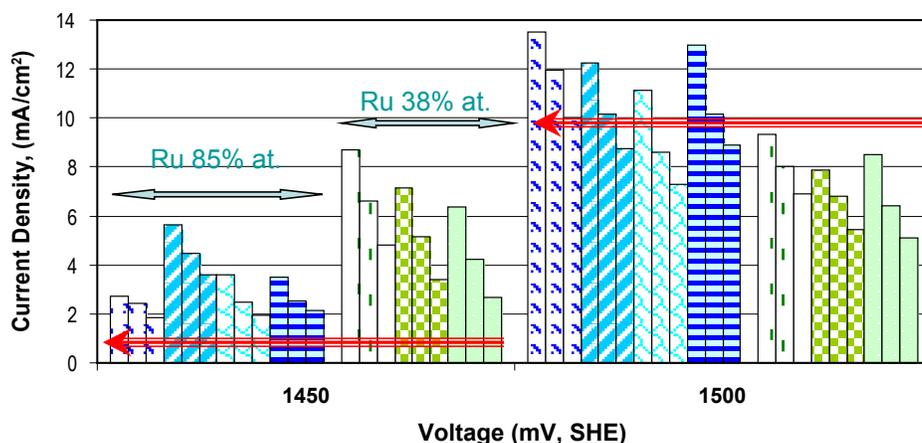
## 3. Ti - Ir - Ru - Ox OER Catalyst

The purpose of this series was to explore the combination of the model catalysts where all the components are present. The primary variable here was the flux of oxygen during the sputter deposition. The most interesting finding in this series was that the presence of oxygen during deposition correlates with changes in fuel cell performance rather than with the OER activity or stability. Based on XPS, the presence of oxygen during the catalyst deposition decreases the amount of sputtered Ti, most probably due to the oxide buildup on the surface of the Ti target.

TEM imaging showed a thin, continuous layer of Ti, Ru and Ir was present on the surface of the Pt/NSTF “cap” and on the surface of the Pt coating along the sides of the coated NSTF whiskers. However, no individual particles were seen. The ~2 nm thick layer is crystalline, contains Ti, Ir, and Ru and is primarily on the “cap” surface. The amount of Ru in the surface layer is greater than either Ti or Ir, in agreement with XPS data for the same samples. Oxygen was also detected, indicating the possible presence of oxides.

## 4. Ir - Ru - Ox OER Catalyst

Based on the evaluation of the single component OER catalysts as well as the negative impact of Ti on the fuel cell performance, further effort on the project



**FIGURE 3.** OER current densities at 1.45 V and 1.5 V for binary Ru and Ir catalysts. Data extracted from three consecutive polarization curves (see Figure 1). Multiple MEAs per catalyst composition presented (each with different fill pattern). Arrow indicates the year one milestone activities at 1.45 V and 1.5 V.

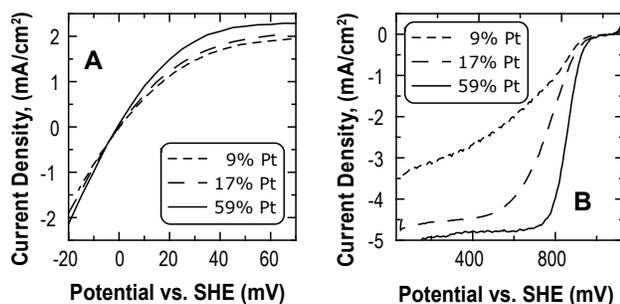
focused on the binary composition of Ir and Ru. The ratio of Ru:Ir was varied from 3:1 to 1:3 w/w (85–38 Ru at%), keeping the total OER added PGM loading at  $2 \mu\text{g}/\text{cm}^2$ , the level defined by the milestone for year one. In addition, the same catalysts were deposited in the presence of oxygen. All catalysts achieved the milestone OER activity at 1.45 V and some at 1.5 V (Figure 3). Samples prepared with oxygen during the deposition process behaved the same way. As such the binary Ru–Ir catalyst composition has been chosen for future studies aimed at achieving different morphologies.

## Task 2: Anode Catalysts with Low Oxygen Reduction Reaction Activity

This task is based on the notion that HOR as a facile reaction can proceed with practically unchanged rate when a Pt catalyst gets passivated by additives such as tantalum [6]. The rate of the ORR, a much more demanding reaction, on the other hand, decreases much more rapidly [7]. The effort in this task is still in the beginning phase. A series of  $\text{Pt}_{1-x}(\text{Ta}_2\text{O}_5)_x$  coatings on NSTF whiskers grown on glassy carbon disks for HOR and ORR assessment were produced. As expected, the presence of significant amounts of  $\text{Ta}_2\text{O}_5$  decreases the ORR by an order of magnitude while the exchange current densities for HOR decrease by only a small amount (Figure 4).

## Conclusions and Future Directions

- Integrated OER/ORR catalyst systems with  $2 \mu\text{g}/\text{cm}^2$  of additional PGM achieved the first year milestone for OER activity of  $1 \text{ mA}/\text{cm}^2$  at 1.45 V, with no impact on the ORR.
- Exploring the space around the components (Ru, Ir, Ti) of the model OER durable catalyst in real PEM fuel cell environment provided a direction for the future synthetic efforts which will be based around combinations of Ru + Ir.



**FIGURE 4.** Hydrogen polarization curves (A) and oxygen polarization curves (B) on a series of  $\text{Pt}_{1-x}(\text{Ta}_2\text{O}_5)_x$  catalysts deposited on NSTF-coated carbon disks. RDE at 900 rpm in 0.1 M  $\text{HClO}_4$  saturated with hydrogen or oxygen at room temperature.

- Having established the inherent activities of the OER catalyst, future catalyst evaluation protocols will focus on more realistic startup–shutdown test conditions, including cell reversal.

## FY 2010 Publications/Presentations

1. Radoslav Atanasoski: “Durable Catalysts for Fuel Cell Protection during Transient Conditions” presented at the DOE Kickoff meeting, Sept. 30, 2009, Washington, D.C.
2. Radoslav Atanasoski: “PEM Fuel Cells: Focus on Durability”, Electrochemical Section of the Chemical Soc., Belgrade, Serbia, Oct.13, 2009, *Invited*.
3. D.A. Stevens, A. Bonakdarpour, R.J. Sanderson, E. Marvel, S. Wang, R.T. Atanasoski, M.K. Debe and J.R. Dahn: “Development of multi-component PEM fuel cell catalysts for enhanced stop-start protection”, 217<sup>th</sup> Electrochemical Soc. Meeting, Vancouver, Canada, April 25 – 29, 2010.
4. R.T. Atanasoski, Project review at the DOE 2010 Vehicle Technologies and Hydrogen Programs Annual Merit Review, June 8, 2010, Washington, D.C., FC# 006.
5. R. Atanasoski: “Fundamental and practical aspects of Nano-structured thin film catalysts for PEM fuel cells: Focus on Durability”, Ulm ElectroChemical Talks 2010: “2015“ Technologies on Batteries and Fuel Cells, Ulm, Germany, 16 June 2010, *Invited*.

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