V.D.3 Durable Catalysts for Fuel Cell Protection During Transient Conditions

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Contract Number: DE-EE0000456

Subcontractors and Federally Funded Research
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• Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: August 1, 2009
Projected End Date: July 31, 2013

Fiscal Year (FY) 2011 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 (SU/SD) 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 SU/SD 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 been estimated at ~5,000. The number of complete fuel starvation events when a cell experiences a voltage reversal has been estimated at ~200 [1].

In agreement with DOE, the technical targets for the second year of the project have been defined as follows:

- For SU/SD, develop a cathode catalyst that can survive 5,000 excursions (<5 s each) to potentials <1.45 V, with current densities >1 mA/cm^2. Oxygen evolution reaction (OER) catalyst loading to be kept <2 μg/cm^2 of platinum group metals (PGMs)
- For cell reversal, develop anode catalyst that can withstand 200 pulses of -200 mA/cm^2 while maintaining cell voltage <2 V.

FY 2011 Accomplishments

- Both of the technical targets for the second year have been met.
- Generic electrochemical tests for SU/SD and cell reversal were developed and implemented.
- 10,000 SU/SD cycles were achieved with addition of only 2 μg/cm^2 PGM.
- 200 high current densities pulses of -200 mA/cm^2 for cell reversal were achieved with 60 μg/cm^2 of total PGM with cell voltage <1.7 V.
- Platinum dissolution is satisfactorily prevented when the potential is maintained below 1.7 V.
- Advantage of OER-modified Pt/nano-structured thin-film (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 X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis) show indications of interaction of the OER catalysts with the substrate, potentially favorable from a durability point of view.

- High resolution transmission electron microscopy depicting the nanoparticles of Ir and Ru on NSTF provided insight into the observed fuel cell performance and oxygen reduction reaction (ORR) activity.

- Chemically modified Pt/NSTF anode exhibited very low ORR without inhibiting hydrogen oxidation reaction (HOR).

- Independent original equipment manufacturer testing confirmed the 3M lab results.

- OER catalyst scale-up: large size catalyst-coated membranes were fabricated at the 3M pilot plant.

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Introduction

The project addresses a key issue of importance for successful transition of PEM fuel cell technology from the 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 SU/SD and local fuel starvation at the anode, commonly referred to as transient conditions. During these periods, the electrodes can reach potentials up to 1.8 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 is expected.

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 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 thermodynamic 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 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 to implement the added catalyst with negligible inhibition of the fuel cell performance and with minimal increment of PGM.

Results

Task 1. Efficient Oxygen Evolution Reaction Catalysts

The activity during the second year of the project related to this task and revolved around the model catalyst containing ruthenium and iridium [2]. We have shown that the oxides of ruthenium, known to have the best catalytic properties for OER in aqueous solutions, and iridium, known to be the more stable of the two, exhibit the same properties as tested in an MEA [2,3]. To get the advantage of both Ru and Ir, the OER catalysts tested during this reporting period were nominally 90% Ir and 10% Ru. This composition seemed to exhibit the best stability and to provide enhanced OER activity relative to Ir only. All the catalysts were tested in a 50-cm^2 PEM fuel cell, with the working electrode under nitrogen and the reference/counter under either 1% or 100% hydrogen.

SU/SD Test

The first subtask during the second year of the project was the development of a generic, electrochemical test mimicking the real SU/SD events. The principles of the test were based on:

- The amount of air present in the anode compartment during the startup of the fuel cell stack.

- The equivalent amount of charge required for a substantial portion of the oxygen fraction in the air to be reduced.

- Requirement that the voltage does not go over 1.45 V (project milestone).

- Requirement that the OER current does not fall bellow 1 mA/cm^2 (project milestone).

- Constraint that the time for the required charge to be delivered to is <10 seconds.

- The catalyst should withstand 10,000 high voltage excursions (pulses/cycles).

In order to further mimic the real fuel cell operating conditions, after every 50 pulses to 1.45 V, the catalyst was periodically exposed to ~0.7 V. Further, in order to mimic the incoming hydrogen front during the startup, a potential ramp of 250 mV/s from the open-circuit voltage, 0.9 V, was imposed. Schematic presentation of the test protocol along with the actual cell response is presented in Figure 1. There is a difference in the current response depending on whether the potential ramp is imposed immediately after the cell has been exposed to 0.7 V or later on during the consecutive cycles (Figure 1A). This difference is due to the oxidation current going towards formation of the PtOx on freshly reduced catalyst. The OER, however, starts at ~1.3V regardless of the state of the platinum. The change of the Pt surface area was adopted as a metric of the successful protection of the platinum. The electrochemically active surface area (ECSA) was measured after every

(A)

(B)
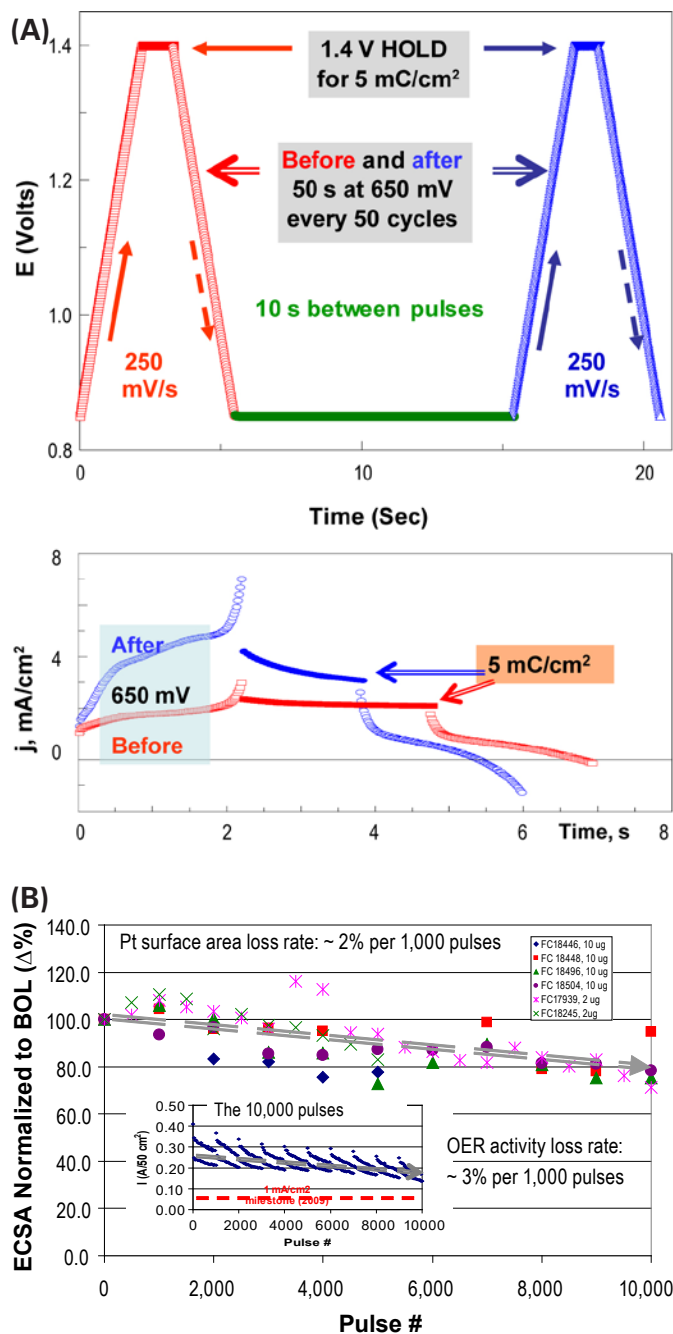
BOL - beginning of life

FIGURE 1. (A) Schematic presentation of the electrochemical test protocol (upper) along with the actual cell response (lower). Steps description: 250 mV/s potential sweep up; 1.4 V HOLD to 5 mC/cm^2; 250 mV/s potential sweep down; 10 s at 850 mV; 650 mV every 50 cycles/pulses; ECSA every 1,000 cycles. 50-cm^2 MEA under nitrogen/1% hydrogen, 70°C, fully saturated. *Note*: Current responses during the potential sweep up, mostly reversible, depend dramatically on OER catalyst state. (B) Pt ECSA changes during SU/SD test and OER catalyst activity decay (inset) during 10,000 cycles. Four 0.15 mg Pt/NSTF catalysts with 10 μg/cm^2 and two with 2 μg/cm^2 additional OER catalyst are presented.

1,000 cycles. As presented in Figure 1B, platinum with as little as 2 μg/cm^2 additional OER catalyst was able
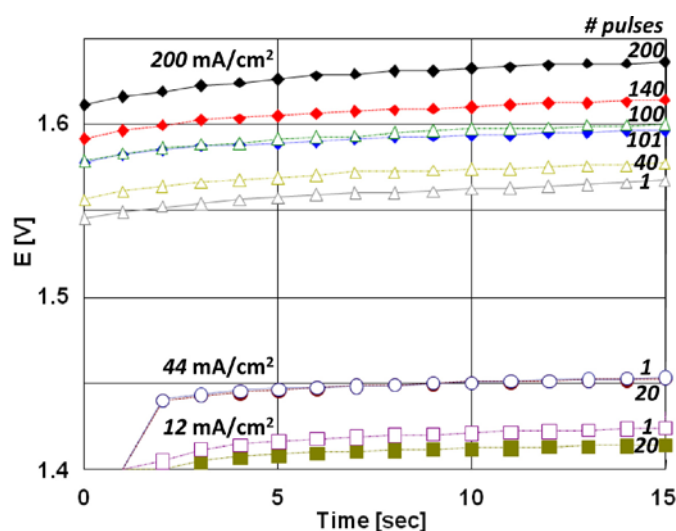
Cell Reversal Test Protocol

MEA Conditioning

ECSA

20 pulses* @ 12 mA/cm^2, 60 s

20 pulses @ 44 mA/cm^2, 30 s

ECSA

100 pulses+ @ 200 mA/cm^2, 15 s

10 min @ 0V

100 pulses+ @ 200 mA/cm^2, 15 s

ECSA

* square waves pulses followed
  by 1 mA/cm^2 for 1 min
+ 2 V upper limit

FIGURE 2. Cell reversal test procedure and the typical outcome; cell voltage responses during first 15 seconds are presented. Note the "reverse" order of the pulse #1 and #20 for 20 mA/cm^2 and 44 mA/cm^2 due to activation of the OER catalyst and between #100 and #101 at 200 mA/cm^2 due to regeneration for 10 minutes at ~0.0 V.

to achieve 10,000 pulses with approximately 2% loss of ECSA/1,000 cycles. At the same time the OER catalyst itself lost 30% of its original activity (see inset in Figure 1B).

Cell Reversal Test

In electrochemical terms, the cell reversal requirements are equivalent to testing the OER activity at high current densities. In Figure 2 the test procedure and the typical outcome is presented. Essentially, the test protocol is based on the fact that during cell reversal the anode is exposed to very positive voltages, 2 V and higher. Usually, such highly damaging conditions do not last for a very long period of time. Consequently, the core of our test consists of 200 pulses at 200 mA/cm^2 followed by 1 minute at potential close to 0 V [1]. As depicted in Figure 2, the potential with every consecutive 200-mA/cm^2 is more positive. However, the presence of a good OER catalyst does keep the
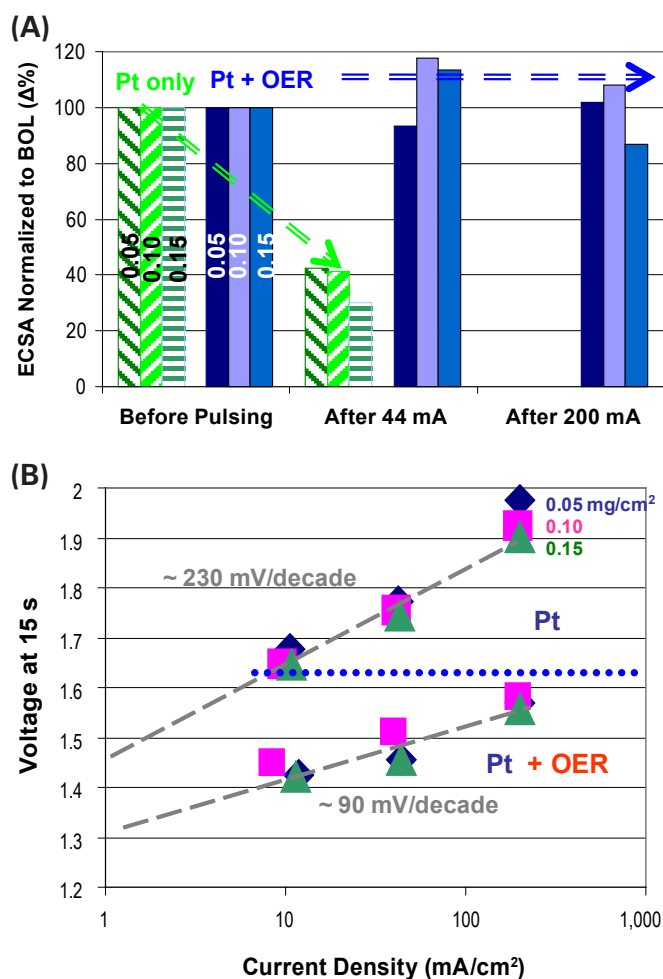
(A)

(A)

(B)

FIGURE 3. The effect of OER catalysts on platinum stability; Pt loading: 0.05, 0.10, and 0.15 mg/cm^2; OER catalyst loading: 10 μg/cm^2. (A) Platinum ECSA loses after 44 mA/cm^2 pulses without (solid blue) and with the OER catalyst (shaded green). (B) Cell voltage dependence on Pt loading. *Note* the Tafel like dependence for both catalysts on Pt loading.

(B)

FIGURE 4. Comparison of cell reversal behavior between OER-modified Pt/NSTF substrate and dispersed Pt/C with admixed IrRu catalyst. Same Pt loading; 2X OER catalyst on Pt/C. (A) Cell voltage during 15 seconds pulses at 200 mA/cm^2: Pulse # 2; 100; 200 presented. (B) AFCC cell reversal test under nitrogen/air: Continuous -200 mA/cm^2.

potentials below 1.7 V. In Figure 3 the effect of the presence of the OER catalysts and the effect of the platinum loading are presented. As is clear from the figure, regardless of the loading, platinum without the OER catalyst loses over 50% of the original surface area even after the initial low current densities pulses (Figure 3A). The most obvious reason for this loss is the fact that, at 44 mA/cm^2, the OER on Pt proceeds at potentials almost 0.3 V higher than the same Pt catalyst with addition of the Ir + Ru (Figure 3B).

In Figure 4, a comparison between the cell reversal behavior of OER-modified Pt/NSTF substrate and dispersed Pt/C with admixed IrRu catalyst is presented. In spite of the fact that the dispersed catalyst has twice as much OER catalyst, the performance and therefore the stability of NSTF-based catalyst is far superior (Figure 4A). It is worth pointing out that the Pt ECSA for Pt/C dropped 86% during the test while Pt/NSTF remained practically the same. The superior durability of the Pt/NSTF with OER catalyst was
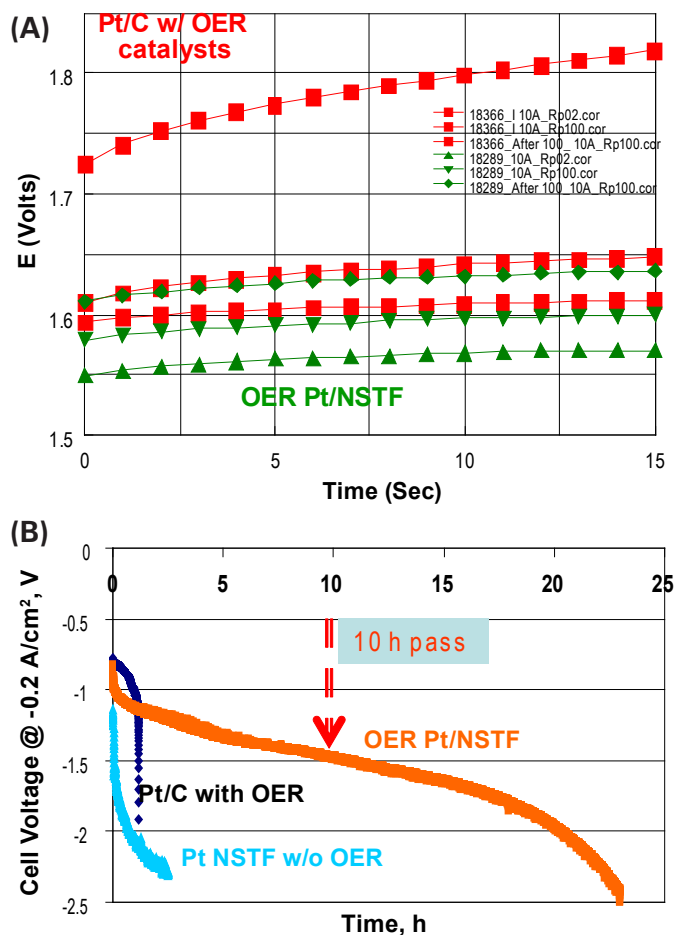
confirmed by an independent testing completed by the stack manufacturer AFCC (Figure 4B). Moreover, the OER-modified Pt/NSTF is the only catalyst that achieved the AFCC required 10 hours "pass" point.

Task 2. Anode Catalysts with Low Oxygen Reduction Reaction Activity

The intent of this work is to find compositions that dramatically reduce the ORR activity of the deposited Pt while still maintaining high HOR activity. Numerous composition spreads were prepared via sputter deposition at Dalhousie University. These spreads included depositions from sputtering targets such as Ti, Ta, ZrO, SiO$_2$, poly-tetrafluoroethylene (PTFE), etc. over the top of Pt ("overlayer" spreads) and co-depositions from Pt and targets such as Ta, Nb, Ti, Hf, TiO$_2$, Ag ("intermix" spreads). However, the best success was achieved by our partners at ANL. They successfully deposited calix[4]arene molecules on 3M Pt/NSTF with properties close to ideal to the goal of this task [4].

Conclusions and Future Directions

- The main conclusion is that platinum dissolution can be satisfactorily slowed down when the OER catalyst maintain the electrode potential below 1.7 V.

Future Work

- Modify/simplify test procedure to reflect "real life", taking into account the U.S. DRIVE 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 modified anode for low ORR (ANL).
- Understand further 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).
- Work toward 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.

FY 2011 Publications/Presentations

Papers

1. *Rapid RDE Evaluation of Catalyst Performance and Durability during Transient Conditions: The Pt-Hf Binary System.* T.D. Hatchard, J.E. Harlow, D.A. Stevens, Gary Chi-Kang Liu, R.J. Sanderson, N. van der Bosch, J.R. Dahn, G.M. Haugen, G.D. Vernstrom and R.T. Atanasoski, *Electrochim. Acta (*doi:10.1016/j.electacta.2011.05.059*)*.

2. *Development of Catalysts with Enhanced Tolerance to Fuel Cell Transient Conditions*, D.A. Stevens, R.J. Sanderson, T.D. Hatchard, T.C. Crowtz, J.R. Dahn, G.D. Vernstrom, G.M. Haugen, T. Watschke, L.L. Atanasoska, and R.T. Atanasoski, *ECS Transactions*, 33 (1) 419 (2010).

Invited Presentations

1. R. Atanasoski: *"Durability of Thin Film Catalysts for PEM Fuel Cells"*, *Key-Note Lecture*, "Electrochemical Energy Conversion and Storage" symposium , 61st Annual Meeting of the International Society of Electrochemistry, September 2010, Nice, France.

2. R. Atanasoski: *Durable Catalysts for Transient Conditions*,, 6th Annual International Conference, FUEL CELLS DURABILITY & PERFORMANCE 2010, Boston, Dec. 09, 2010.

3. R. Atanasoski: *"Role of catalysts durability in PEM Fuel Cells"*, *Key-Note Lecture,* "Role of Catalysis in Fuel Cells" Symposium, 241st Amer. Chem. Soc., Anaheim, CA, 03/29/2011.

Presentations

1. "Development of Catalysts for Enhanced Tolerance to Fuel Cell Transient Conditions" by D. Stevens, G. Vernstrom, R. Sanderson, G. Haugen, T. Hatchard, T. Crowtz, T. Watschke, M. Debe, R. Atanasoski, and J. Dahn, 218th Electrochemical Soc. Meeting, Las Vegas, 2010.

Presentations to DOE

1. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" presented at the FC Tech Team, Detroit, April 27, 2011.

2. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" presented at the DOE 2010 AMR, May 10, 2011, Washington, DC.

3. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" Project Progress Review, presented to DOE, Nov. 08, 2010, St. Paul, Minnesota.

References

1. A. Nelson, Presentation at the *12th Ulm ElectroChemical Talks*, Ulm, Germany, June 15–17, 2010.

2. 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.

3. R.T. Atanasoski et al., FY 2010 DOE Hydrogen Annual Progress Report Review, V.E.6.

4. B. Genorio, R. Subbaraman, D. Strmcnik, D. Tripkovic, V.R. Stamenkovic, and N.M. Markovic, *Angew. Chem. Int. Ed*. 2011, 50, 5468–5472.