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

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Development Centers:
- Dalhousie University, Halifax, Nova Scotia, Canada
- Oak Ridge National Laboratory, Oak Ridge, TN
- AFCC Automotive Fuel Cell Cooperation, Burnaby, BC, Canada

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) 2013 Objectives

- Start-up/shut-down: 5,000 cycles/pulses with loading of 0.088 mg/cm^2 precious-grade metal (PGM) total on the cathode, 1.45 V upper limit and >90% surface area retention.

- Cell Reversal: 200 high current density pulses of 200 mA/cm^2 with loading of 0.037 mg/cm^2 PGM total on the anode and upper voltage limit <1.7 V.

- Oxygen reduction reaction (ORR) inhibition on the anode: factor of >100 in the kinetic region.

- Catalyst scale up: short stacks testing for 'real life' application.

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

Technical Targets

While the number of start-up and shut-down (SU/SD) cycles for an automotive fuel cell has been projected 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 anticipated at ~200 [1].

In Table 1, DOE approved technical targets of the project are listed along with the dates when they were accomplished.

FY 2013 Accomplishments

The final year project milestones have been achieved:

- 200 cycles of 200 mA/cm^2 for cell reversal with 0.037 mg/cm^2 total PGM on the anode with 1.7 V upper limit.

TABLE 1. The Technical Targets

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
	2013	5,000	0.088	1.45 V	10%	Achieved 03/2013
Cell Reversal (Anode)						
	2011	200	0.050	2.00 V	10%	Achieved 09/2011
	Go/No-Go	200	0.045	1.80 V	10%	Achieved 01/2012
	2013	200	0.037	1.70 V	10%	Achieved 03/2013
Task 2: Suppression of ORR (Anode)						
	Go/No-Go	Factor of 10 in the kinetic region				Achieved 01/2012
	2013	Factor of >100 in the kinetic region				Achieved 02/2013
Task 3: Scale-Up						
	2013	'Real life' evaluation readiness				12/2013; ~11 stacks

OER - oxygen evolution reaction; ECSA - electrochemically active surface area

- 5,000 start-up cycles with upper voltage limit of 1.45 V and with 0.088 mg/cm^2 total PGM on the cathode with ECSA loss of <10%.

- Reduced ORR current on the anode by a factor >1,000.

- Fundamentals of the high specific and mass OER activity of RuIr-Pt/nanostructured thin film (NSTF) were explored and potential explanations elaborated.

- Full-size catalyst-coated membranes (CCMs) for three short stacks were produced at 3M and were evaluated by AFCC.

- Fuel cell performance of low-loading Pt on OER-able anode was the same as on higher Pt loading anodes, for both NSTF and dispersed-based catalysts.

- Shortcomings identified during the stack testing were addressed and preliminary solutions were successfully introduced.

- Second fuel cell manufacturer tested and confirmed the 3M lab results.

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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 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 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 is 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 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

Efficient Oxygen Evolution Reaction Catalysts

The activity during the fourth year of the project continued to revolve around making a more efficient and durable OER catalyst while decreasing the total PGM content towards the 2017 DOE target of 0.125 mg/cm^2. Most of the OER catalysts tested during this reporting period were nominally 90% at Ir and 10% at Ru. All the catalysts were tested in a 50-cm^2 PEM fuel cell, with the working electrode under nitrogen and the reference/counter electrode under either 1% or 100% hydrogen.

SU/SD Test

The generic electrochemical test mimicking the real SU/SD events remained the same as in 2012 [1,2]. Two modifications were made to explore the impact of the upper level potential and frequency of potential excursions to the lower level on the Pt surface area loss. The modifications were:

- 1.6 V upper limit at every cycle, rather than to 1.45 V.

- 0.65 V lower limit at every cycle rather than at every 10 cycles.

This study was performed on a series of samples with 0.085 mg/cm^2 of Pt/NSTF. The added OER catalyst was

varied from 1–10 $\mu g/cm^2$ of IrRu. The results for the ECSA retention after 5,000 cycles are presented in Figure 1. In comparison with the usual cycles to 1.45 V with 0.65 V lower limit excursions at every 10 cycles, both cycling modifications have a significant impact on the ECSA losses. Excursions to 650 mV at every cycle show a much larger surface area loss than with any of the previous test procedures. 150 mV increase in the upper voltage limit, to 1.6 V, results in 26% additional Pt surface area loss. By the end of the 5,000 cycles, the OER activities of 1 $\mu g/cm^2$ IrRu have fallen into the range of Pt samples. However, 10 $\mu g/cm^2$ of IrRu has more than enough OER catalyst to still protect the platinum. The two implications for the future work are:

(i)   Pt dissolution is strongly determined by the frequency of the lower voltage limit and by the level of the upper voltage limits.

(ii)   The question why Pt exposed to the same potential regime dissolves less when OER catalyst is present should be addressed.

Cell Reversal Test

In electrochemical terms, the cell reversal test procedure remained the same as in the previous year [2]. However, the total PGM loading target was decreased from 45 $\mu g/cm^2$ to 37 $\mu g/cm^2$. The upper voltage limit requirement of 1.8 V for FY 2012 was lowered to 1.7 V for 2013. In Figure 2 the end voltage of 200th 0.2 A/cm^2 cycle and ECSA estimate are presented for two series of catalysts: 25 $\mu g/cm^2$ and 30 $\mu g/cm^2$ Pt/NSTF as substrates with 6–12 $\mu g/cm^2$ added IrRu. All the catalysts with >8 $\mu g/cm^2$ IrRu samples fulfilled the 1.7 V milestones. However, the H-pump value as an

expression of the hydrogen oxidation reaction activity for the 25 $\mu g/cm^2$ Pt/NSTF with 8 $\mu g/cm^2$ IrRu was by a factor of 3 higher than the 30 $\mu g/cm^2$ Pt/NSTF with the same amount IrRu. Therefore, to fully satisfy the milestone PGM loading of 37 $\mu g/cm^2$, a new series of samples was made with 29 $\mu g/cm^2$ Pt/NSTF with 8 $\mu g/cm^2$ IrRu. The H-pump value for this sample was satisfactory and so were the cell reversal characteristics as presented by the triangles in Figure 2.

Scale-Up and Short-Stack Evaluation

In 2013, the scale-up and the full-size short stack evaluation continued to be the focus of the project. The 2013 milestone for the scale-up called for evaluation of three short stacks. The CCM compositions were as follows:

Anodes:

1.   Dispersed: 50 $\mu g/cm^2$ Pt (commercial catalyst; 3M produced)

2.   NSTF: 50 $\mu g/cm^2$ Pt + 15 $\mu g/cm^2$ IrRu (NSTF baseline; historical)

3.   NSTF: 29 $\mu g/cm^2$ Pt + 8 $\mu g/cm^2$ IrRu (NSTF 2013 milestone)

All the CCMs were made by 3M with the same 3M-coated dispersed cathode (0.4 mg/cm^2 Pt) and 3M 12 μm reinforced membrane, 725 equivalent weight (surface area >300 cm^2). The final MEA and stack assembly and testing was done by AFCC.

As illustrated in Figure 3, performance-wise all three stacks came very close to each other. Actually, the 2013

Lower and Upper Voltage Limit Impact
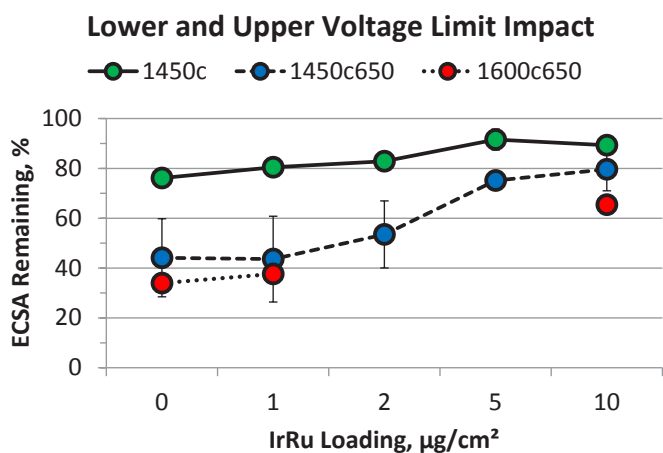
Green (top line): 1.45 V upper limit with lower limit of 0.65 V at every cycle 10th cycle
Blue (middle line): 1.45 V upper limit with lower limit of 0.65 V at every cycle
Red (bottom line):1.6 V upper limit with lower limit of 0.65 V at every cycle.
2012 SU/SD test protocol (see text); 0.085 mg/cm^2 of Pt/NSTF; OER catalyst loading 1–10 $\mu g/cm^2$ of IrRu. 50-cm^2 MEA under nitrogen/1% hydrogen, 70°C, fully saturated. 5,000 SU/SD cycles; IrRu loading indicated on the graph.

FIGURE 1. The Impact of the Upper Level Potential and the Frequency of Potential Excursions to the Lower Level on the Pt Surface Area Loss
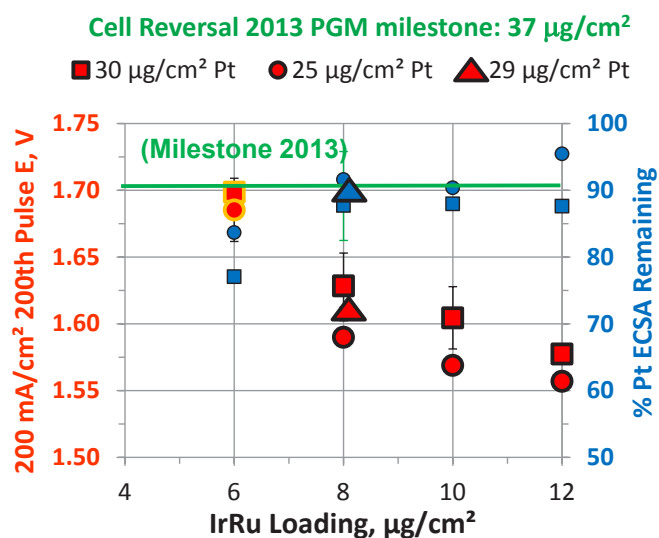
FIGURE 2. Cell reversal testing for two series of OER catalysts: 25 $\mu g/cm^2$ and 30 $\mu g/cm^2$ Pt/NSTF as substrates with 6–12 $\mu g/cm^2$ added IrRu. The end voltage of 200th 15 sec. 200 mA/cm^2 cycle (red) and ECSA estimate (blue) are presented. The big triangle represents the 2013 milestone sample with 8 $\mu g/cm^2$ on 29 $\mu g/cm^2$ Pt/NSTF. Note: Samples with 6 $\mu g/cm^2$ added IrRu did not fulfill the end voltage requirement
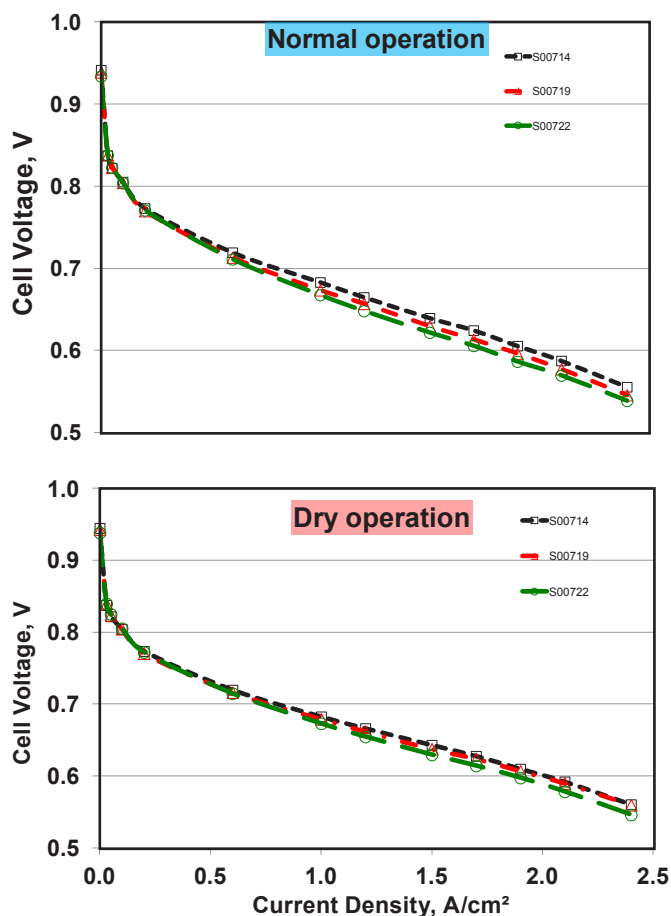
Black: Dispersed: 50 μg/cm² Pt (baseline commercial catalyst)
Green: NSTF: 50 μg/cm² Pt + 15 μg/cm² IrRu (2012 NSTF baseline)
Red: NSTF: 29 μg/cm² Pt + 8 μg/cm² IrRu (NSTF 2013 milestone)
3M-coated dispersed cathode (0.4 mg/cm² Pt) and 3M 12 mm reinforced, membrane, 725 equivalent weight (surface area >300 cm²). Final MEA and stack assembly and testing done by AFCC.

FIGURE 3. Short Stacks Full Cell Architecture Evaluation of OER Modified Pt/NSTF Anodes: Performance under Normal and Dry Conditions

milestone NSTF with 29 μg/cm² Pt with 58% of baseline 50 μg/cm² Pt did even slightly better. However, due to the much lower OER catalyst content, 8 μg/cm² IrRu vs. 15 μg/cm² IrRu, the cell reversal durability for the 2013 milestone NSTF did suffer. A proper balance between the Pt and IrRu contents should be able to remedy this drawback while keeping the performance benefits as presented in Figure 3.

FUTURE WORK

The remainder of the final year will be focused on three major areas:

- OER-Pt NSTF catalysts evaluation readiness for "real life" automotive applications:
  - Continue the short stack evaluation with AFCC with new/modified OER catalysts.

  - Assess the boundaries of the OER–Pt/NSTF application.
  - Assess the lowest Pt loading limit with respect to performance.
- Research and development of the OER catalyst with respect to durability in 'real life':
  - Fundamental materials studies to further the understanding and the paths to improvement of the stability of the OER-Pt NSTF catalysts.
- Fundamental engineering studies of the OER-Pt NSTF catalysts:
  - Understand the impact of processing, integration and interaction with other MEA components.

FY 2013 PUBLICATIONS/PRESENTATIONS

Papers

1. 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.

2. RT Atanasoski, DA Cullen, GD Vernstrom, GM Haugen 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.

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. LL Atanasoska, DA Cullen, AE Hester, RT Atanasoski: "XPS and STEM of the interface formation between ultra-thin Ru, Ir and Pt layers and perylene red catalyst support whiskers", *ECS Transactions* (Abs# 3748, PRiME 2012, Honolulu, Hawaii).

Presentations

1. R.T. Atanasoski, L.L. Atanasoska, D.A. Cullen, A. Hester: "*Oxygen Evolution Reaction on Minute Amounts of Ru and Ir Catalyst for Application in Fuel Cell Protection", Symposium I4 - Electrocatalysis 6*, PRiME 2012, Honolulu, Hawaii, Oct. 08, 2012 (Invited, opening talk; # 3737).

2. L.L. Atanasoska, DA Cullen, A. Hester, RT Atanasoski: "*XPS and STEM of the Interface Formation between Ultra-Thin Ru, Ir and Pt Layers and Perylene Red Catalyst Support Whiskers*" (Abstract #3748, Honolulu PRiME 2012).

3. D. Stevens, J. Harlow, R. Sanderson, T. Crowtz, J. Dahn, G. Vernstrom, L. Atanasoska, G. Haugen, and R. Atanasoski: "*Rotating Disk Electrode Techniques Designed to Simulate Fuel Cell Startup/Shut-Down Transient Conditions*" (Abstract #1319, Honolulu PRiME 2012).

4. J. Harlow, D. Stevens, R. Sanderson, T. Crowtz, J. Dahn, G. Haugen, L. Atanasoska, G. Vernstrom, and R. Atanasoski:

"*Durable, OER-Active Compositions of Pt, Ir, and Ru for PEM Fuel Cell Start-Stop Protection*" (Abstract #1365, Honolulu PRiME 2012).

Presentations to DOE

1. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" Project progress Review, presented to DOE (internal), September, 2012, St. Paul, Minnesota.

2. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" Project progress Review, presented to DOE (internal), April, 2012, Vancouver, Canada.

3. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" presented at the FC Tech Team, Detroit, April, 2013.

4. "Durable Catalysts for Fuel Cell Protection during Transient Conditions" presented at the DOE 2013 AMR, May, 2013, Washington, D.C.

REFERENCES

1. RT Atanasoski, DA Cullen, GD Vernstrom, GM Haugen 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. R.T. Atanasoski, Project review at the DOE 2010 Vehicle Technologies and Hydrogen Programs Annual Merit Review, May 2012, Washington, D.C., FC# 003.