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

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Contract Number: DE-EE0000456

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

Fiscal Year (FY) 2012 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.

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

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].

Upon the Tech Team and the Durability Working Group recommendations, DOE approved the third year and the Go/No-Go technical targets of the project. In Table 1 these targets are listed along with the dates when they were accomplished. Also included are the 2013 targets.

Details of the evaluation procedures will be presented under the Results section.

FY 2012 Accomplishments

• Efficient oxygen evolution reaction (OER) catalysts were developed and successfully tested for SU/SD and cell reversal with a total precious group metal (PGM) content of 0.132 mg/cm²: 0.122 mg/cm² Pt + 0.009 mg/cm² IrRu.

• 5,000 startup/shutdown cycles were achieved with the addition of only 2 µg/cm² PGM on the cathode: 0.085 mg/cm² Pt + 0.002 mg/cm² IrRu.

• 200 high current density pulses of 200 mA/cm² for cell reversal were achieved while maintaining cell voltage <1.8 V with the addition of only 8 µg/cm² PGM on the anode: 0.037 mg/cm² Pt + 0.008 mg/cm² IrRu.
The added OER catalyst satisfactorily maintained platinum stability and performance at both the anode and the cathode; Pt dissolution rate was constrained to <10%.

The fundamentals of the added OER catalysts were revisited; Ru and Ir mass activity of 4 A/mg at 1.45 V and 3.9 A/mg at 1.55 V respectively were reached [2].

High resolution scanning transmission electron microscopy combined with core level X-ray photoelectron spectroscopy data analysis provided insight into the observed OER catalyst activity and durability [2].

Chemically and physically modified Pt/nano-structured thin-film (NSTF) anode exhibited very low ORR without inhibiting the hydrogen oxidation reaction (HOR), thus diminishing the impact of SU/SD.

Scale-up and independent evaluation further confirmed the 3M lab results: In over 10 short stacks and over 80 MEAs utilizing 3M anodes tested in full-scale architecture by AFCC, the OER-Pt/NSTF anode consistently outperformed dispersed baselines with higher loadings.

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 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 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 additional PGM.

Results

Efficient Oxygen Evolution Reaction Catalysts

The activity during the third year of the project continued to revolve around making a more efficient and
durable model catalyst containing ruthenium and iridium [3]. At the same time, the effort was focused on decreasing the total PGM content towards the 2017 DOE target of 0.125 mg/cm². 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-cm² PEM fuel cell, with the working electrode under nitrogen and the reference/counter electrode under either 1% or 100% hydrogen.

SU/SD Test

During the third year of the project, the generic electrochemical test mimicking the real SU/SD events was modified upon the recommendation the Tech Team and the Durability Working Group [4]. The test consisted of the following main steps (the modifications from the previous year are in italics):

- 100 mV/s ramp from 0.9 V mimicking the H₂ front
- 1.6 V upper limit or 5 mC/cm², mimicking the equivalent amount of O₂ to be reacted off for the H₂/H⁺ electrode potential to be established
- 650 mV every 10 cycles/pulses mimicking the cell voltage during normal operation
- ECSA evaluation every 1,000 cycles

A schematic representation of the 2011 test protocol along with the 2012 modifications can be found in [4].

To fulfill the targets/milestones in Table 1, a systematic study was performed on a series of samples with 0.085 mg/cm² of Pt/NSTF. The added OER catalyst was varied from 1–10 µg/cm² of IrRu. The results of this study are presented in Figures 1 and 2. In Figure 1 a comparison between the Pt/NSTF substrate and OER-added catalyst is presented. In the upper panels the voltage cycles and the current responses of unmodified Pt/NSTF and Pt/NSTF with 2 µg/cm² of IrRu are presented. The voltage was allowed to reach 1.6 V unless sufficient current to react all of the remaining oxygen in the cathode compartment was reached (in this test 20 mA/cm²). As expected, bare platinum is not able to produce the required current and therefore it always reaches the 1.6 V test limit. On the other hand, only 2 µg/cm² of IrRu is needed to reach the OER current of 20 mA/cm² at 1.48 V. The logical consequence of the lower voltage should be a reduced Pt dissolution. In the middle panel, the current responses for characteristic cycles of the test procedure are presented: the cycle before the potential is lowered to 0.65 V (cycle n10) and the two cycles following the 0.65 V step (cycles n1 and n2). First of all, the figure illustrates the effectiveness of the IrRu catalyst as demonstrated by the much higher OER current at lower voltage. Secondly, the drop to 0.65 V regenerates the current response on the following voltage sweep for both Pt and for IrRu. As was presented last year [5], in the case of Pt, this is due to the oxide formation on the reduced surface of Pt after being exposed to 0.65 V, while in the case of IrRu, it is due to the regeneration of the OER catalyst itself. The lower panel in Figure 1 presents the change in the OER activity during the 5,000 SU/SD cycles by following the voltage at the end of positive going step from 0.9 V until the current surpasses the 20 mA/cm² or until the upper voltage limit of 1.6 V is reached. As we already pointed out, unmodified Pt always reaches the upper voltage limit of 1.6 V since its activity towards OER is very small. The activity of the three samples with 1, 2, and 10 µg/cm² of IrRu follow the anticipated trend, with the 10 µg/cm² of IrRu having the lowest peak voltage. During the first 2,000 cycles, the three IrRu loadings follow each other very closely, indicating that no noticeable changes/dissolution in the OER catalysts take place. However, with further cycling the differences between the three samples becomes more obvious, indicating clearly the superior stability of the highest IrRu sample.

In Figure 2 the surface area changes during the SU/SD testing is presented along with the impact of the presence of the IrRu on the fuel cell performance. A large number of MEAs (45) were tested in order to compensate for the inevitable glitches during these very long procedures. The upper panel presents the Pt surface area changes before

FIGURE 1. Comparison between the Pt/NSTF substrate and OER added catalyst loading under 2012 SU/SD test protocol (see text): 0.085 mg/cm² of Pt/NSTF; OER catalyst loading 1–10 µg/cm² of IrRu. 50-cm² MEA under nitrogen/1% hydrogen, 70°C, fully saturated. (upper) Voltage response for characteristic cycles for Pt/NSTF (left) and 2 µg/cm² of IrRu on Pt/NSTF (right). Voltage allowed to reach 1.6 V unless current surpasses 20 mA/cm². (middle) Current responses for the same cycles as in (upper), (lower) The end voltage at the upper going potential sweep until current reaches 20 mA/cm² during the 5,000 SU/SD cycles; IrRu loading indicated on the graph.
and after the 5,000 cycles measured via Hupd (ECSA). The loss of Pt ECSA is clearly correlated with the OER catalyst loading, since the Pt is exposed to lower cell voltages with higher IrRu loading. The lower panel follows the relative changes of Pt ECSA during the 5,000 SU/SD cycles. Here again the difference between bare Pt/NSTF and IrRu modified samples is quite obvious. From the point of view of the project targets, change in Pt ECSA of <10%, the samples with 2 and 5 µg/cm² of IrRu are both within the target range and are within the total Go/No-Go PGM requirement of 90 µg/cm².

For completeness, in the middle panel the fuel cell performance of the samples is presented. Looking at the fuel cell performance before and after the SU/SD test, it seems that the samples with 2 µg/cm² of IrRu show the optimal performance, which means that the project target can be fulfilled with a total of only 87 µg/cm² of total PGM, 85 µg/cm² of Pt with only 2 µg/cm² of IrRu.

Cell Reversal Test

In electrochemical terms, the cell reversal test procedure remained the same as in the previous year [5]. However, the total PGM loading target was decreased to 45 µg/cm². The upper voltage limit requirements were 2 V for the 2011 FY and was lowered by 0.2 V, to 1.8 V for the Go/No-Go decision. In Figure 3 the number of 15 sec. 200 mA/cm² cycles up to the two voltage limits, 2 V and 1.8 V, are presented for catalysts with 40 µg/cm² Pt/NSTF as a substrate, with 1–10 µg/cm² added IrRu. There is a linear relationship between the OER catalyst loading and the number of cycles to ‘failure’, i.e. until the voltage limit was reached. Only some of the 5 µg/cm² IrRu samples fulfilled the 2 V required and none achieved the Go/No-Go 1.8 V. Only the samples with 10 µg/cm² IrRu completed the 200 pulses without surpassing the 2 V limit (not presented) and 1.8 V limit. Therefore, additional samples were made with the Go/No-Go target total PGM loading of 45 µg/cm²; 37 µg/cm² Pt/NSTF with 8 µg/cm² IrRu. As presented in Figure 3, these samples reached the 200th 200 mA/cm² pulse without going over the limit of 1.8 V. As a matter of fact, the voltage at the end of the test was more than 0.15 V lower than the Go/No-Go target. In the lower panel of Figure 3, the evolution of the end voltages of all 200 pulses for three different combinations of Pt and IrRu loadings are presented. An interesting observation from this figure is that both the IrRu loading and the Pt loading influence durability and OER activity. This could be important in designing the future catalyst, where an obvious optimization between the amount of Pt, a necessary component for the HOR activity, and the added IrRu, the key to the cell reversal performance, has to be attained.

Scale Up and Independent Evaluation

The scale up and the full size stack evaluation could be considered as the most important achievement of the project. While within the scope of the statement of project objectives, the whole effort was entirely financed by 3M and AFCC.

3M produced many hundreds of lineal meters of fully integrated OER catalyst on Pt/NSTF that were subsequently converted into full-size CCMs. The CCMs were evaluated in Short Stacks by AFCC for Cell Reversal and SU/SD. The next section is the AFCC report (modified based on AMR presentation slides 14 and 15) [4].

AFCC Overview of OER/NSTF Evaluation

The NSTF anode + OER concept has been evaluated at AFCC during the last two years. Significant effort using both subscale and full-scale testing has been done following AFCC’s demanding technology development process using anodes tailored for AFCC requirements. Over 10 short stacks and over 80 MEAs using OER-Pt/NSTF anodes have been tested in full-scale architecture. Promising results demonstrating performance, CO tolerance, freeze tolerance, SU/SD benefits, and reversal tolerance were obtained.

Overall, the OER-modified NSTF anode is a promising MEA vehicle component. In stacks, as in AFCC’s subscale configuration (reported at the 2011 AMR), the OER-Pt/NSTF anode consistently outperformed dispersed baselines with
higher loadings. As presented in Figure 4 (upper panel), despite lower tolerance than in subscale hardware, the NSTF anode concept still has a very good reversal tolerance for the given loadings.

As presented in Figure 4 (lower panel), OER-Pt/NSTF anode has a positive impact on SU/SD durability in a gas switching SU/SD accelerated stress test. The NSTF anode with OER catalyst is very selective since it inhibits ORR as shown by fuel cell polarization results (see inset: the anode was tested as a cathode, under air). This finding by AFCC is a direct confirmation of the alternative, Task 2 approach in mitigating SU/SD negative impact based on inhibiting the ORR on the anode. Smaller, secondary effects contributing to the OER-Pt/NSTF anode positive impact on SU/SD may be due to some Ir migration to the cathode that could produce an OER-enhancing cathode effect. The low Ru content leads to lower Ru crossover-related degradation.

AFCC listed the following as Future Challenges:

- OER/NSTF performance should have no negative impact compared to a conventional dispersed anode

Conclusions and Future Directions

In conclusion, besides completing all the Go/No-Go milestones, the project has accomplished the following:

- Show stability of the OER layer under extended drive cycles (2,000 hours) and after SU/SD testing
- Tolerance for anode contaminants (in addition to CO)
- 3M and AFCC should drive the fundamental understanding of engineering issues related to interfaces and compatibility of OER/NSTF with other MEA components and anode layer design.

DOE Hydrogen and Fuel Cells Program

FY 2012 Annual Progress Report
• OER/NSTF brought NSTF catalyst concept very close to "real"/stack application
• Most of the work proposed and outcomes envisaged have been realized and/or accomplished by 3M, AFCC and their partners/collaborators

Future Work

Further research and development of the OER catalyst with respect to PGM loading and durability:
• Attempt to reach new milestones with total PGM loadings aligned with the DOE targets of 0.125 mg/cm²
• Assess the limits of PGM cathode – anode distribution while preserving the required cathode (ORR) and anode (HOR) performance
• Proceed with fundamental materials studies aimed at understanding the extraordinary activity and stability of the OER-Pt/NSTF catalysts
• Conduct fundamental engineering studies of the OER-Pt/NSTF catalysts aimed at understanding the processing, integration and interaction with other MEA components
• Evaluate OER-Pt NSTF catalysts’ readiness for “real life” automotive applications.

Special Recognitions

1. 2012 DOE Hydrogen and Fuel Cells Program R&D Award in Recognition of Outstanding Achievements in Low Platinum Group Metal Catalyst Performance and Durability.

FY 2012 Publications/Presentations

Papers


Invited Presentations


Presentations to DOE


References

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