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

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• Oak Ridge National Laboratory, Oak Ridge, TN

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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/cm². Oxygen evolution reaction (OER) catalyst loading to be kept <2 μg/cm² of platinum group metals (PGMs)
• For cell reversal, develop anode catalyst that can withstand 200 pulses of -200 mA/cm² 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/cm² PGM.
• 200 high current densities pulses of -200 mA/cm² for cell reversal were achieved with 60 μg/cm² 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.
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-cm² 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/cm² (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
As presented in Figure 1B, platinum with as little as 2 $\mu g/cm^2$ additional OER catalyst was able 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. 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.

**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.

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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/cm², 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. Same Pt loading; 2X OER catalyst on Pt/C. (A) Cell voltage during 15 seconds pulses at 200 mA/cm²: Pulse # 2; 100; 200 presented. (B) AFCC cell reversal test under nitrogen/air: Continuous -200 mA/cm². 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, SiO₂, polytetrafluoroethylene (PTFE), etc. over the top of Pt (“overlayer” spreads) and co-depositions from Pt and targets such as Ta, Nb, Ti, Hf, TiO₂, 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/cm² for cell reversal with 0.045 mg/cm² total PGM on the anode with 1.8 V upper limit.
  - 5,000 startup cycles under the existing protocol with 0.09 mg/cm² 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


Invited Presentations


Presentations


Presentations to DOE


References

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