V.E.3 Durability of Low Platinum Fuel Cells Operating at High Power Density

Scott Blanchet (Primary Contact), Olga Polevaya, May Tan
Nuvera Fuel Cells Inc.
Building 1, 129 Concord Rd.
Billerica, MA 01821
Phone: (617) 245-7667
Email: blanchet.s@nuvera.com

DOE Managers
HQ: Kathi Epping Martin
Phone: (202) 586-7425
Email: Kathi.Epping@ee.doe.gov
GO: Gregory Kleen
Phone: (720) 356-1672
Email: Gregory.Kleen@go.doe.gov

Technical Advisor
Thomas G. Benjamin
Phone: (630) 252-1632
Email: Benjamin@anl.gov

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- Los Alamos National Laboratory, Los Alamos, NM
- Argonne National Laboratory, Argonne, IL

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Fiscal Year (FY) 2012 Objectives

- The objective of this project is to study and identify strategies to assure durability of fuel cells designed to meet DOE 2015 cost targets.
- Develop a practical understanding of the degradation mechanisms impacting durability of fuel cells with low platinum loading ($\leq$0.2 mg/cm^2) operating at high power density ($\geq$1.0 W/cm^2)
- Develop approaches for improving the durability of low-loaded, high-power stack designs.

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
(B) Cost

Technical Targets

TABLE 1. Progress toward Meeting Technical Targets for Transportation Fuel Cell Stacks Operating on Direct Hydrogen for the Transportation Applications

Characteristics	Units	2010/2015 Stack Targets	Nuvera 2012 Status
Cost	\$/kWe	25/15	~22 estimated[1]
Durability with cycling	Hours	5,000	12,000 hrs[2] 5,500 hrs in automotive cycle conditions[3]
Performance at rated power	mW/cm^2	1,000	1,145[4] and 1,200[5]

[1] Cost assessment of Nuvera's architecture by Directed Technologies Inc. based on their DOE-sponsored Design for Manufacturing and Assembly model [1]. 0.572 V/cell @ 2.0 A/cm^2 was obtained at 0.2 mg/cm^2 platinum loading on Orion stack by Nuvera.
[2] Demonstrated under power profile specific-to-fork truck applications in material handling market at total platinum loading of 0.5 mg/cm^2.
[3] Demonstrated in 20-cell stack of 360-cm^2 cell active area by Nuvera customer under automotive load profile ,at the total platinum loading of 0.50 mg/cm^2.
[4] Demonstrated in 250-cm^2 Orion stack by Nuvera at platinum loading of 0.2 mg/cm^2.
[5] Demonstrated in 50-cm^2 single cell with open flowfield (SCOF) by Nuvera at platinum loading of 0.2 mg/cm^2.

FY 2012 Accomplishments

- The third project milestone, completed on schedule, benchmarked the serpentine land-channel cell with the open flowfield cell (SCOF) developed by Nuvera and validated at Los Alamos National Laboratory (LANL). Results were reported under selected accelerated stress test (AST) protocols on the MEAs with 0.4 mg_{Pt}/cm^2 and 0.15 mg_{Pt}/cm^2 cathode loadings. The data analysis indicated ohmic, diffusion, and pressure drop benefits of SCOF over the land-channel architecture at the beginning of life (BOL) at low pressure conditions. Similar voltage degradation was observed at the current densities below 1 A/cm^2 in both cell architectures.
- Go/No-Go project review by the DOE resulted in a Go decision to continue with the project as scheduled. Durability testing of MEAs with 0.4 mg_{Pt}/cm^2 and 0.15 mg_{Pt}/cm^2 cathode loadings in both SCOF and stack cells concluded that subscale SCOF adequately represents full-area Orion stack for performance and durability under automotive load protocols.
- Argonne National Laboratory (ANL) completed development of platinum dissolution and cell performance models, representing the building blocks of the fuel cell durability model and establishing relations between changes in overpotentials, electrocatalyst surface area (ECSA) and oxygen mass transport, and moved to modeling of the platinum transport.

- Durability testing under the new stress test (NST) representing combined power cycle protocols has been completed on Orion short stacks and will continue in SCOF at Nuvera and in the General Motors/Rochester Institute of Technology 50-cm^2 cell at LANL.

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Introduction

Understanding and improving the durability of cost-competitive fuel cell stacks is imperative to successful deployment of the technology. Stacks will need to operate well beyond today's state-of-the-art rated power density with very low platinum loading in order to achieve the cost targets set forth by DOE ($15/kW) and ultimately be competitive with incumbent technologies. Little to no study of durability factors has been carried out in this area of design and operation. The industry today is focusing mostly on reduced platinum loading as it heads for the DOE target point of 0.2 mg/cm^2 platinum and 1.0 W/cm^2 power density. As demonstrated through DOE-sponsored cost modeling, this point falls short of the corresponding $15/kW stack cost target for 2015.

Approach

Nuvera proposes an accelerated cost-reduction path focused on substantially increasing power density to address non-PGM material costs as well as platinum. Understanding the largely unstudied factors affecting stack durability under these high power conditions is the focus of the present program. Of specific interest is the impact of combining low platinum loading with high power density operation, as this offers the best chance of achieving long-term cost targets. The team effort is divided into two activities: modeling and experimentation.

Results

Durability testing in 50-cm^2 SCOF cells and 250-cm^2 Orion stacks was conducted in order to prove consistency in the degradation mechanisms between the two test articles in support of the Go/No-Go project milestone. Testing was conducted under load cycling NST protocol N1A, at two levels of temperature and cathode humidification on 0.45 mg$_{Pt}$/cm^2 and 0.2 mg$_{Pt}$/cm^2 MEAs. N1A test was designed to mimic catalyst cycling AST B1 protocol, defined by the DOE, with the addition of the current draw, cycled between 0.025 and 2 A/cm^2. The upper potential in N1A is lower than in the B1 AST, and consistent with the simulated driving cycle N3 previously tested on Orion short stacks. Aggregated assessment of the performance metrics for N1A durability testing concluded qualitative and quantitative similarity in the degradation patterns and mechanisms between both test articles. Voltage degradation as a function of tested current densities under N1A protocols is shown in Figure 1. Low platinum MEAs exhibited increasing decay as current increased while decay for the higher-loaded MEAs remained relatively constant with change in current. This result was reproduced at different test conditions. The differences between SCOF and Orion were small, thereby proving results from SCOF to be representative for durability model development at ANL – the final deliverable of this project.

Over the past year, SCOF, developed by Nuvera under DOE funding, was validated at LANL under AST catalyst cycling protocols, by comparison to the serpentine land-channel cell, previously tested with the same platinum loading MEAs. Low resistivity and pressure drop of the open flow fields resulted in measurable performance benefits of lower Pt loading MEAs at the BOL over the quad serpentine cell at low pressure conditions as shown in Figure 2. In both cell architectures cathode ECSA and mass activity decreased similarly during 30,000 potential cycles and resulted in similar cathode thinning and Pt particle growth, confirmed by scanning electron microscopy and X-ray diffraction measurements. The analysis of cell impedance showed equal increase in charge transport resistance with ageing at low current density. At current densities higher than 1 A/cm^2 the voltage decays in SCOF were higher than the land-channel cell. This is attributed to the lower pressure drop and, therefore, lower average cathode operating pressure in SCOF, given the same value of the back pressure was maintained in both tests.

Durability testing in short stacks under simulated combined city and highway driving cycle NST N3 protocol continued at the rated current density (RCD) of 2 and

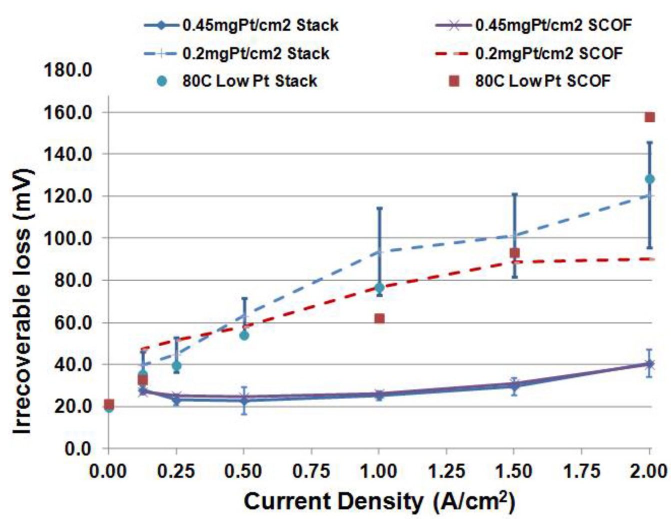

FIGURE 1. Cell voltage decay in SCOF and Orion stack cells past 30,000 load cycles, data from 60°C and 80°C N1A NSTs. Total MEAs loading 0.45 and 0.2 mg$_{Pt}$/cm^2.

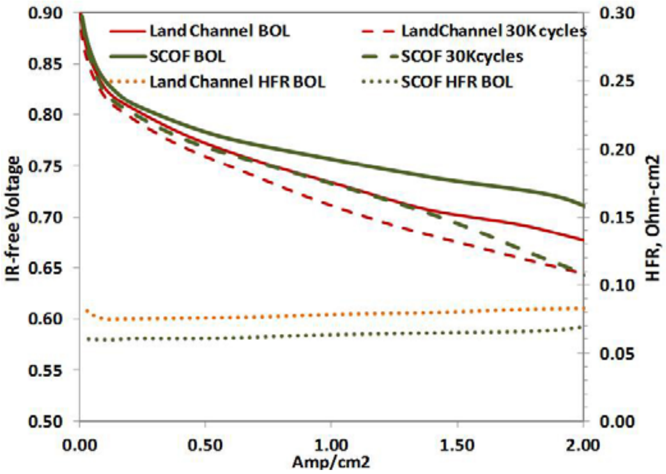

FIGURE 2. BOL and end-of-test polarization curves of 0.2 mg_{Pt}/cm^2 MEAs in SCOF and quad-serpentine land-channel cell, aged under catalyst cycling AST (30,000 triangle potential cycles 0.582-0.883 V). 100% relative humidity inlets, 80°C cell, 3.4 ata.

3 A/cm^2 on 0.2- and 0.45 mg_{Pt}/cm^2 MEAs respectively. In this NST the cathode pressure and flow conditions vary with the current density, following the operating map of the air compressor in the automotive system. Both activation and mass transfer overpotentials and their increase with aging were affected by the decreased Pt loading as shown in the upper graphs in Figure 3.

The cell voltage degradation of the low loaded Pt MEAs was two times higher at 2 A/cm^2 than at 1 A/cm^2, attributed to the near zero oxygen partial pressure at the electrode with the increased operating current. At current densities lower than 1 A/cm^2, the cell voltage degradation was not influenced by the current density, which was in agreement with the levels of oxygen partial pressure and consistent with the AST results reported last year.

In 0.45 mg_{Pt}/cm^2 MEAs the irrecoverable voltage losses in the representative stack cells during NST N3 have been estimated by subtracting the measured voltage recovery, following test restarts and concluding that operation at the RCD of 3 A/cm^2 did not accelerate degradation compared with operation at the rated current density RCD of 2 A/cm^2 as shown in the lower graphs in Figure 3.

Post-NST diagnostics of the MEAs included evaluation of platinum loss to the membrane, using transmission electron microscopy imaging and direct particle counting methods developed at the Oak Ridge National Laboratory. Platinum migration out of the cathode and re-deposition in the membrane, occurring with ageing MEAs under load cycle protocols, was quantified for particle size and mass distribution. Results are summarized in Figure 4 for the

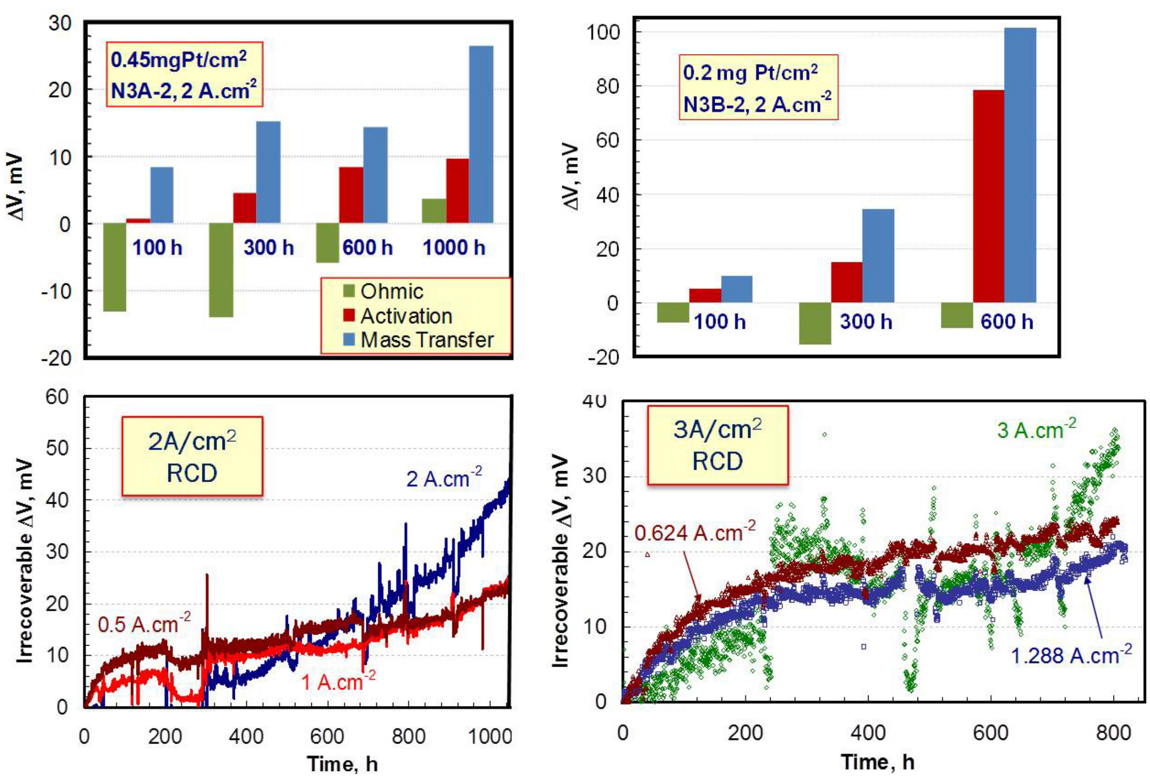

FIGURE 3. Effect of Platinum cathode loading (upper graphs) and RCD (lower graphs, MEAs with the total loading 0.45 mg_{Pt}/cm^2) on durability of stack cells in the simulated drive cycle tests N3.

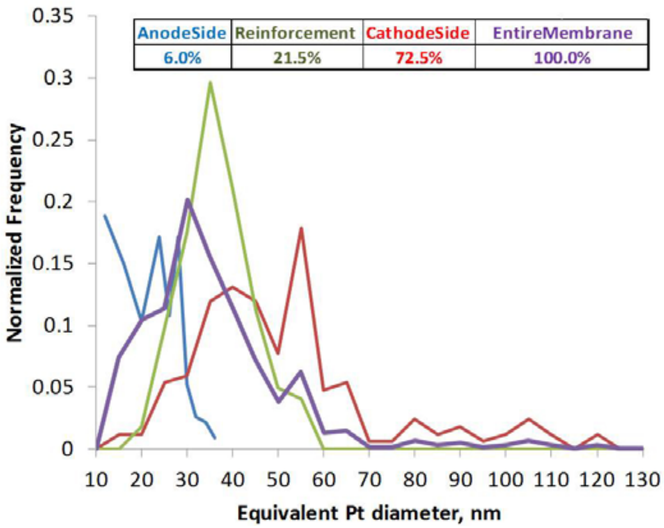

FIGURE 4. Platinum particle size and platinum mass distribution in the membrane after N3 NST at 3 A/cm^2 RCD.

MEA sectioned after completing the N3 driving cycle test at 3 A/cm^2 RCD for 820 hours. While platinum mass balance will provide the direct input to the durability modeling studies, the presence of multiple platinum particles early in cell testing, as well as the consistency of the cathode-membrane interface throughout the test provided innovative insights on the mechanism of platinum loss to the membrane.

Development of the durability model by ANL continued with the completion of thermodynamically independent platinum dissolution studies and material-specific kinetics. The team demonstrated good progress on the analysis of the cell transport properties with ageing and moved to defining the platinum ion transport – the final step in composing the full picture of fuel cell ageing. The model, independent of the cell architecture, will utilize inputs from catalyst cycle ASTs, BOL properties of the studied material set, and prescribed use cycles to output cathode ECSA, particle size distribution, overpotentials and cell voltage as a function of cycle time and the current density.

Conclusions and Future Direction

- Durability study of 0.45 and 0.2 mg_{Pt}/cm^2 MEAs in SCOF and stack cells concluded similarity in the degradation patterns and mechanisms between both test articles. Therefore, the data from SCOF, adequately representing full-area Orion stack for the performance and durability under automotive load protocols, proved the quality inputs to the durability model development at ANL – the final deliverable of the Spire project.
- The NST campaign will be moved from SCOF to General Motors/Rochester Institute of Technology herringbone cell architecture for durability benchmarking at LANL and will continue in SCOF at Nuvera, refocusing efforts towards the next project milestone: validating results of the durability model.
- Development of the durability model will be completed by the addition of the platinum transport block, and the model results will be validated against the fuel cell tests in support of 2013 project milestones #4 and #5. (Milestone #4 - Model correlations to full-area test results; milestone #5 - Validated model and data set published.)
- Post-test analysis of platinum in the membrane using transmission electron microscopy will continue in support of platinum ion transport model development by ANL.
- Operation at high power densities enabled by the open flowfield architecture and proven at the low platinum loading provided the ground work for accelerated cost-reduction path to the cost targets set by the DOE.

FY 2012 Publications/Presentations

1. O. Polevaya, Durability of Low Pt Fuel Cells Operating at High Power Density, 2012 DOE Annual Merit Review, Washington, D.C., May 16, 2012.

2. S. Arisetty et. al., Catalyst Durability in PEM Fuel Cells with Low Platinum Loading, JECS, 159(5) B1-B8 (2012) .

3. S. Arisetty, Effect of platinum loading on catalyst stability under cycling potentials, 220th Meeting of ECS, 2011, Boston, MA.

4. O. Polevaya, Spire Project Review with Freedom Car Technical Team, January 11, 2012, Southfield, MI.

5. F. Gambini et. al., Durability of fuel cells under high power density operation, 220th Meeting of ECS, 2011, Boston, MA.

6. S. Arisetty et. al, Effect of platinum loading on catalyst stability under cycling potentials, ECS Transactions, 41 (1), 797 (2011) .

7. S. Arisetty et al, Effect of load cycles on fuel cell durability, Poster, 5th International conference on polymer batteries and fuel cells, ANL, Argonne, July 2011.

8. R.K. Ahluwalia, Dissolution of Platinum from ORR catalysts in polymer electrolyte fuel cells, 2nd International Workshop on Degradation Issues in Fuel Cells, Thessaloniki, Greece, September 21–23, 2011.

9. R. Subbaraman, Ex-situ Potentiostatic and Potentiodynamic Durability of Low Pt Loading fuel cell MEAs, 220th Meeting of ECS, 2011, Boston, MA.