V.D.2 Durability of Low-Platinum Fuel Cells Operating at High Power Density

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Subcontractors:
- Los Alamos National Laboratory (LANL) Los Alamos, NM
- Argonne National Laboratory (ANL), Argonne, IL

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Project End Date: August 31, 2013

Overall 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-Pt 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.

Fiscal Year (FY) 2013 Objectives

- Complete comparative study of voltage degradation in single cells with the different flowfield architecture under load cycle protocols.
- Complete durability model of the cathode with the focus on Pt ageing and the cathode electrode performance variations under designed operating conditions.
- Validate the durability model against load cycle tests in short stacks.

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

(B) Cost

Technical Targets

The technical targets for this project are listed in Table 1.

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

Characteristics	Units	2010/2017 Stack Targets	Nuvera 2013 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	1,250[4] and 1,375[5]

[1] Cost assessment of Nuvera's architecture by Directed Technologies Inc. based on their DOE-sponsored Design for Manufacturing and Assembly model [1].
[2] Demonstrated under power profile specific to fork truck applications in material handling market at total Pt loading of 0.5 mg/cm^2.
[3] Demonstrated in 20-cell stack of 360-cm^2 cell active area by Nuvera customer in automotive load profile, total loading 0.5 mg/cm^2.
[4] Demonstrated in 250-cm^2 Orion stack by Nuvera at Pt loading of 0.096 mg/cm^2.
[5] Demonstrated in 50-cm^2 single cell with open flowfield (SCOF) at 2.5 A/cm^2 by Nuvera at Pt loading 0.2 mg/cm^2.

FY 2013 Accomplishments

- ANL completed development of Pt dissolution and catalyst performance degradation models, representing the building blocks of the full cathode durability model and establishing relations between changes in overpotentials, electrocatalyst surface area (ECSA), and oxygen mass transport, calibrating coefficients against the experimental values obtained in single-cell durability tests.
- The project milestone #4, completed on schedule, validated the durability model against load cycle tests in short stacks with membrane electrode assemblies (MEAs) of 250-cm^2 active area.
- Benchmarking of Rochester Institute of Technology land-channel cell architecture against Nuvera **s**ingle cell with open flowfield (RIT vs. SCOF) under the new stress test (NST) N1A concluded independence of the

ECSA loss of the cell architecture and resulted in higher degradation of the RIT cell due to the larger increase in mass transport overpotentials. Results were reported on the MEAs with 0.4- and 0.15-mg_{Pt}/cm^2 cathode loadings.

- Performance loss of 0.002%/hour at the rated current density (RCD) of 1.5 A/cm^2 (0.9 W/cm^2 at the beginning of life), demonstrated on the low-Pt MEAs (total loading 0.2 mg/cm^2) in the open flowfield architecture under the accelerated load cycle test, was related to the 0.0018%/hour performance loss of normal Pt-loaded MEAs (total loading 0.45 mg/cm^2) in Nuvera short stack over 5,500-hr simulated drive cycle test; therefore, proving the feasibility of low-Pt MEAs to achieve 5,000-hr lifetime target at the moderate RCD.
- Dissemination of the cathode durability model was started with the first publication of the Pt dissolution block and will continue in the next months for the catalyst performance degradation.

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 Pt 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 Pt loading as it heads for the DOE target point of 0.2 mg/cm^2 Pt 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-platinum-group metal material costs as well as Pt. Understanding the largely unstudied factors affecting stack durability under these high power conditions is the focus of the present project. Of specific interest is the impact of combining low Pt 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

Development of the durability model by ANL was completed, finalizing the catalyst performance degradation model in addition to the earlier-developed Pt dissolution part of the model, therefore, completing the full cathode durability model and establishing relations between changes in overpotentials, ECSA, and oxygen mass transport. The model, independent of the cell architecture, utilized inputs from the single-cell accelerated stress tests (ASTs) and NSTs, beginning-of-life 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.

The Pt dissolution model included generic dissolution and oxide growth thermodynamics and kinetics, accounting for the ECSA loss and particle growth dependence on the cycle, determined primarily by the coalescence mechanism. Predictability of the Pt dissolution model specific to the ECSA under load cycling is shown in Figure 1 for the serpentine cell and the open flowfields architecture (SCOF and short stacks). Modeled ECSA loss was similar for both

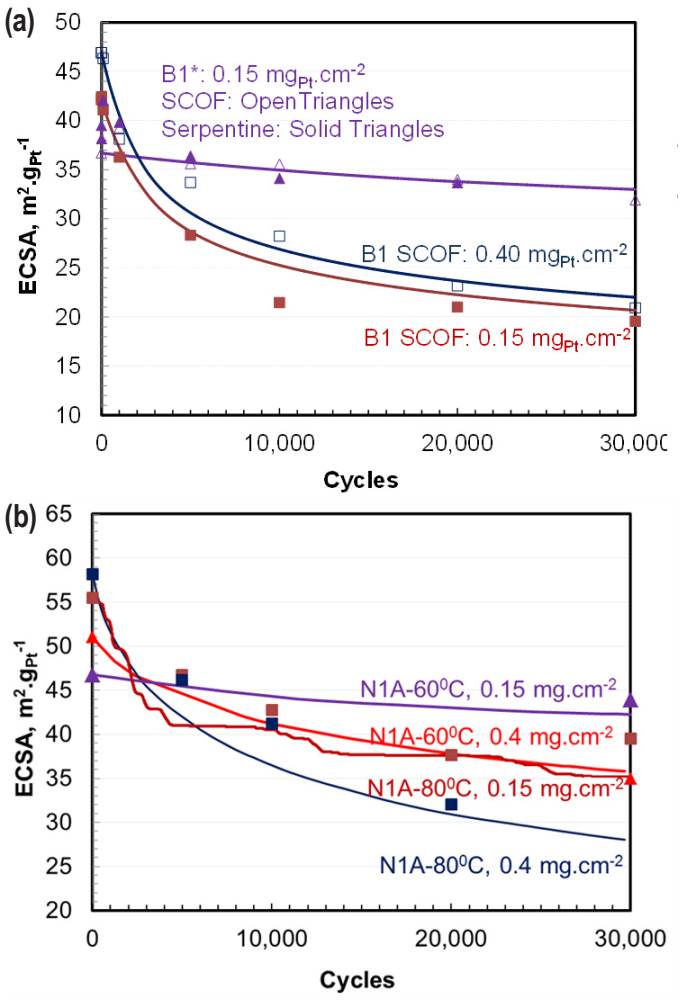
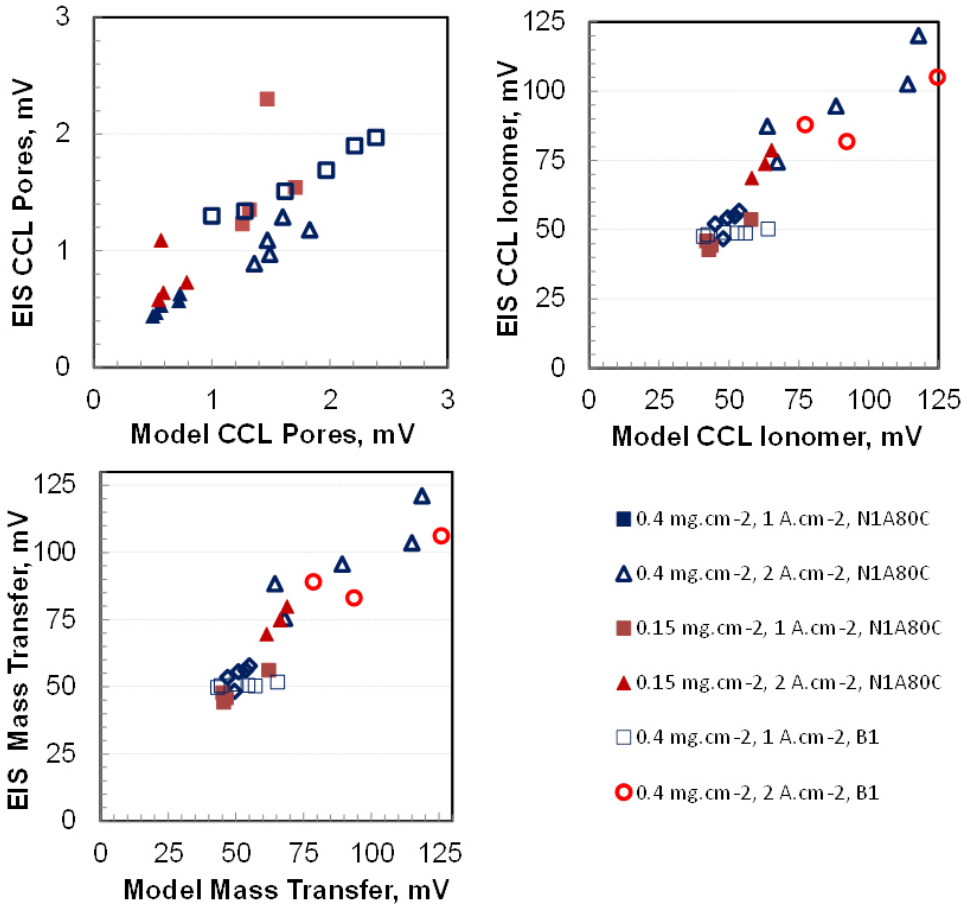


FIGURE 1. Validation of Pt dissolution model specific to cathode ECSA in a) SCOF and serpentine single cells under catalyst cycling ASTs, and b) SCOF and stack cells under N1A load cycle tests. Symbols are experimental data, lines show results of the modeling.

flowfields and not affected by the loading but, rather, upper cycle potential. Rapid fluctuations of the upper potential limits during one of the tests in Figure 1b are well simulated by the irregular shape of the modeling curve. As resulted from the aqueous studies, the dissolution rates at 80°C were higher than at 60°C, explaining higher ECSA decrease in the higher temperature N1A tests.

Platinum migration out of the cathode and re-deposition in the membrane, occurring with MEA ageing under load cycling, were studied by transmission electron microscope imaging and quantified by the direct particle counting methods developed at Oak Ridge National Laboratory [2]. Although an insignificant loss of Pt mass from the cathode to the membrane was concluded and, therefore, omitted from the model, imaging of the cathode-membrane interface showed great differences in Pt propagation into the membrane in the MEAs after NSTs. After the ASTs with no current draw from the cell, Pt particles grew to the larger sizes and remained at the interface without moving into the membrane.

The innovative multi-nodal reaction-diffusion model of the proton exchange membrane fuel cell cathode developed in the past year targeted characterizing mass transport overpotentials specific to the gas diffusion layer, catalyst, and ionomer in the electrode interface. The transport coefficients of the model were derived from the comprehensive analysis of the alternating current impedance spectra, using resistances of the equivalent transmission circuits. Variations in the transport coefficients with ageing under potential cycling were studied to formulate the correlations of the transport overpotentials as a function of current density and time. The transport coefficients were correlated to the cathode ECSA, Pt particle size, catalyst layer thickness, and operating conditions. The parity plots in Figure 2 show good fit between modeling and experiments as well as the dominating role of oxygen transport through the electrode ionomer in total overpotentials under studied conditions. Validation of the cathode performance degradation model applied to the MEAs with 0.4- and 0.15-mg_{Pt}/cm^2 cathode loadings is shown in Figure 3 under load cycle N1A and



CCL – cathode catalyst layer; EIS - electrochemical impedance spectroscopy

FIGURE 2. Parity plots of mass transport overpotentials (through the cathode catalyst layer, ionomer, and overall) derived from the model against experimental electrochemical impedance spectroscopy data in N1A and B1 tests.

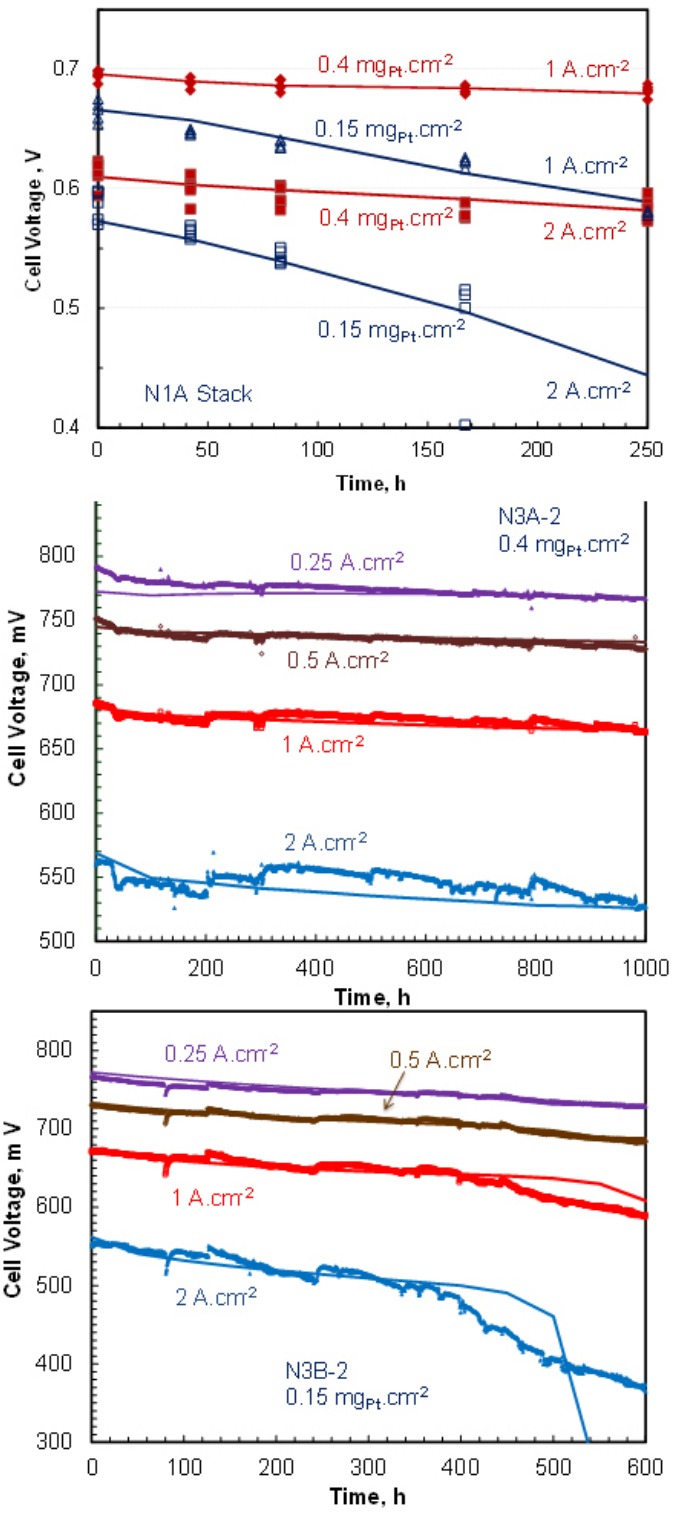


FIGURE 3. Validation of performance degradation model in stacks at the RCD = 2.0 A/cm^2 under N1A load cycle test (upper chart); N3 simulated drive cycle test, total loading 0.45 mg$_{Pt}$/cm^2 (middle chart); N3 test, total loading 0.2 mg$_{Pt}$/cm^2 (lower chart).

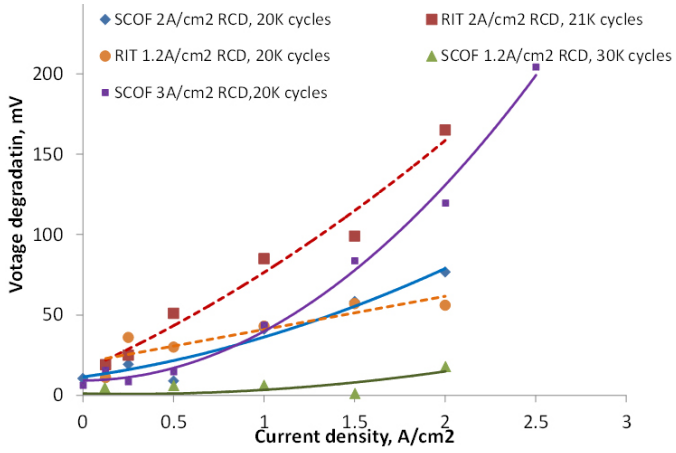


FIGURE 4. Voltage degradation in SCOF and RIT cells under N1A load cycle tests. RCD varied from 1.2 to 3.0 A/cm^2. Total loading is 0.2 mg$_{Pt}$/cm^2.

simulated drive cycle N3—both tested in short Orion stacks. Validation of the degradation model in full active area stack cells concluded the fourth milestone of this project.

Durability testing in 50-cm^2 SCOFs and land-channel (RIT) architecture supported modeling and allowed comparing cell architectures for voltage degradation under load cycling. Testing was conducted under N1A protocol at two levels of cathode Pt loading (0.40- and 0.15-mg$_{Pt}$/cm^2) and RCD (1.2 and 2.0 A/cm^2). N1A test in SCOF was also conducted at 3 A/cm^2 RCD, expectedly resulting in higher voltage degradation at the RCD and lower degradation at the upper cycle potential. N1A test was designed to mimic catalyst cycling AST B1 protocol, defined by the DOE, with the addition of the current draw, cycled between two levels of the current density. The upper potential in N1A is lower than in the B1 AST, and consistent with the simulated drive cycle N3 previously tested on Orion short stacks. Aggregated assessment of the performance metrics for N1A durability testing concluded similar ageing of Pt in both cell architectures and higher voltage degradation in the RIT cell as a function of the current density, shown in Figure 4 and attributed to the larger increase in mass transport overpotentials in the RIT architecture.

Low-Pt MEAs exhibited increasing decay as the current increased, while the decay for the higher loaded MEAs remained relatively constant. This result was reproduced at the different test conditions, both in single cells and in short stacks. The voltage degradation of low-Pt MEAs in the open flowfield single cells remained low at 0.002%/hour at the RCD, not exceeding 1.2 A/cm^2, therefore promising to achieve automotive lifetime target of 5,000 hours with 10% performance loss.

Durability testing in short stacks under simulated combined city and highway driving cycle NST N3 protocol continued at the RCD of 2.5 A/cm^2 on 0.45 mg$_{Pt}$/cm^2 MEAs.

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.

CONCLUSIONS AND FUTURE DIRECTION

- A complete durability model of the cathode was developed at ANL with the focus on Pt ageing and the cathode electrode performance variations under designed operating conditions.
- The model was calibrated using inputs from the ASTs and NSTs in single cells and then validated against durability tests in short stacks with 250-cm^2 active area cells.
- Durability testing under NST protocols has been completed on all studied single cells at LANL and Nuvera and on short stacks at Nuvera, yielding valuable data inputs to the durability model.
- The feasibility of low-Pt MEAs to achieve the 5,000-hr lifetime target at the moderate RCD below 1.2 A/cm^2 was demonstrated by relating the degradation rate under the accelerated load-cycle test to the degradation rate in the 5,500-hr drive-cycle test completed on Nuvera short stack (360-cm^2 active cell area, 0.45 mg_{Pt}/cm^2 loading).
- Dissemination of the cathode durability model was started with the first publication of the Pt dissolution block and will continue in the next months for the catalyst performance degradation, concluding the final program milestone.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Poster presentation at the Fuel Cell Seminar 2012, November 5–8, Mohegan Sun, CT was awarded the 2nd prize.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. O. Polevaya, Durability of Low Pt Fuel Cells Operating at High Power Density, 2013 DOE Annual Merit Review, Washington, DC, May 14, 2013.

2. R.K. Ahluwalia et al., Thermodynamics and Kinetics of Platinum Dissolution from Carbon-Supported Electrocatalysts in Aqueous Media under Potentiostatic and Potentiodynamic Conditions Fuel Cells, Electrolyzers, and Energy Conversion, J. Electrochem. Soc. 2013 160(4): F447-F455.

3. O. Polevaya, Presentation at the Durability Working Group Meeting 2013, February 28, Washington, DC.

4. O. Polevaya, Presentation at the USCAR Fuel Cell Technical Team Meeting, January 16, Detroit, MI.

5. O. Polevaya et al., Fuel Cell Durability at High Power Density from Subscale Single Cells to the Full Area Stacks, Poster presentation at the Fuel Cell Seminar 2012, November 5–8, Mohegan Sun, CT.

6. R.K. Ahluwalia, Modeling Durability of ORR Catalysts in Polymer Electrolyte Fuel Cells, Fuel Cell Tech Team Meeting, Southfield, MI, September 12, 2012.

REFERENCES

1. B. James et al., Mass Production Cost Estimation for Direct H_2 PEM Fuel Cell Systems for Automotive Applications, 2012 Update, October 18, 2012.

2. K.L. More, Characterization of fuel cell materials, 2012 DOE Annual Merit Review, Washington, DC, May 14–18, 2012.