V.F.5 Performance and Durability of Advanced Automotive Fuel Cell Stacks and Systems with Nanostructured Thin Film Catalyst Based Membrane Electrode Assemblies

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Overall Objectives

• Develop a validated model for automotive fuel cell systems, and use it to assess the status of the technology.
• Conduct studies to improve performance and packaging, to reduce cost, and to identify key R&D issues.
• Compare and assess alternative configurations and systems for transportation and stationary applications.
• Support DOE U.S. DRIVE automotive fuel cell development efforts.

Fiscal Year (FY) 2016 Objectives

• Quantify the impact of thinner membranes, lower anode Pt loadings, and high-activity de-alloyed nanostructure thin film (NSTF) PtNi cathode on the performance of automotive stacks and fuel cell systems.
• Understand the durability of NSTF electrode under long potentiostatic holds.
• Extend system analysis to alternate non-NSTF membrane electrode assemblies (MEAs) with conventional Pt/C and advanced Pt alloy/C cathode catalysts.
• Incorporate durability considerations in system analysis.
• Provide modeling support to Eaton’s development of Roots air supply system.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:
(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is conducting system level analyses to address the following DOE 2020 technical targets for automotive fuel cell power systems operating on direct hydrogen.

- Energy efficiency: 60% at 25% of rated power
- Q/DT: 1.45 kW/°C
- Power density: 850 W/L for system, 2,500 W/L for stack
- Specific power: 850 W/kg for system, 2,000 W/kg for stack
- Transient response: 1 s from 10% to 90% of maximum flow
- Start-up time: 30 s from –20°C and 5 s from +20°C ambient temperature
- Precious metal content: 0.125 g/kW e rated gross power

Accomplishments

- Quantified the sources of 14–20% decrease in power density and $2.20/kW e increase in cost due to the heat rejection (Q/DT) constraint.
- Identified the dominant NSTF catalyst degradation mode and determined that the cumulative fluoride release (CFR) must be limited to 0.7 mg.cm⁻² for 10% performance degradation over 5,000 h.
- Projected 25% increase in power density and 16.8% reduction in stack cost by reducing anode Pt loading to 0.02 mg/cm², and replacing Pt₆₈(CoMn)₃₂/NSTF with Pt₃Ni/NSTF cathode catalyst and 20-mm 835 equivalent weight (EW) membrane with supported 14-mm 725 EW membrane.
- Demonstrated that, compared to a baseline unit, the V250 module (without expander) reduces parasitic
power by 6.4% at full flow (92 g/s) and by 35% at quarter flow (25 g/s).

INTRODUCTION

While different developers are addressing improvements in individual components and subsystems in automotive fuel cell propulsion systems (i.e., cells, stacks, balance-of-plant components), we are using modeling and analysis to address issues of thermal and water management, design-point and part-load operation, and component-, system-, and vehicle-level efficiencies and fuel economies. Such analyses are essential for effective system integration.

APPROACH

Two sets of models are being developed. The GCtool software is a stand-alone code with capabilities for design, off-design, steady state, transient, and constrained optimization analyses of fuel cell systems (FCS). A companion code, GCtool-ENG, has an alternative set of models with a built-in procedure for translation to the MATLAB Simulink platform commonly used in vehicle simulation codes, such as Autonomie.

RESULTS

We collaborated with 3M in designing tests on 5-cm² active-area differential cells and analyzing the data to model the performance of full-area (>250 cm²) cells with 3M’s state-of-the-art binary dealloyed NSTF catalyst with Pt/C cathode interlayer [1]. The following are the details of the MEAs selected for this study.

- Ternary Anode: Ptₓ₆(CoMn)₇ₓ, 0.019 mg/cm²
- Binary Cathode: PtₓNiₓ/NSTF, dealloyed (Johns Hopkins University chemistry), 0.096 mg/cm²
- Membrane: 3M-S (supported) 725 EW) perfluorosulfonic acid stabilized with chemical additive, 14 mm
- Anode Gas Diffusion Layer (GDL): 3M “X3” (experimental backing, 3M hydrophobization)
- Cathode GDL: 3M 2979
- Cathode Interlayer: 3M Type “B”, 0.016 mg/cm²

For reproducibility of data, the test campaign included three thermal conditioning cycles (TCs) in normal and reverse flow before each test series and 1 TC before each polarization curve. Test series were designed to obtain performance data over a wide range of pressure (P: 1–3 bar), temperature (T: 45–90°C), O₂ mole fraction (X(O₂): 1–21%, 100%), anode relative humidity (RH(a): 30–100%) and cathode relative humidity (RH(c): 30–150%), all at constant hydrogen (Q(H₂): 1 slpm) and air (Q(air): 3 slpm) flow rates. Changes in high frequency resistance, H₂ crossover, mass activity, electrochemical surface area (ECSA), and short resistance were monitored. Over ~735 h actual test time, the ECSA decreased by ~25% from 22.9 to 17.2 m²/g.

Figure 1a shows the variability in polarization curve at the reference conditions that were visited multiple times during the course of the campaign. We did not observe any significant systematic degradation and have classified the polarization curves in two groups, high performance (HIP) and representative performance (REP).

We estimated the oxygen reduction reaction (ORR) kinetic parameters from internal resistance and crossover corrected cell voltages at low current densities in H₂/O₂ and H₂/air (see Figures 1b, 1c, and 1d). The modeled mass activity of binary PtₓNiₓ/NSTF with cathode interlayer was compared with the data for two other NSTF catalysts analyzed in earlier works [2,3]. In general, the modeled mass activities of all three catalyst systems are consistent with the data obtained using the 3M standard protocol. Compared to the baseline ternary Ptₓ₆(CoMn)₇ₓ/NSTF catalyst, the mass activity of binary d-PtₓNiₓ/NSTF catalyst with cathode interlayer is 78–144% higher.

We determined the limiting current density (iₗ) and correlated mass transfer overpotential (hₘ) with reduced the current density (i/iₗ). For convenience, we defined iₗ as the current density at which hₘ = 300 mV. In our terminology, hₘ includes any internal resistance drop in the electrode. We also determined relationships between hₘ (and iₗ) and all operating variables: P, T, X(O₂), RH(a), RH(c), i/iₗ. Figures 1e and 1f are illustrative examples of this relationship for one variable, i.e., pressure.

Work is underway to calibrate the performance model developed using differential cell data with 50-cm² cell data for finite cathode/anode stoichiometries and operating temperatures needed to satisfy the Q/DT constraint. The preliminary results indicate that 3M’s best-of-class (BOC) 50-cm² cell data are closer to the modeled results without mass transfer overpotentials. There is a parallel ongoing effort to replicate 3M’s BOC performance with identical cells and conditioning procedures. In the future, we also hope to validate our model with data from full-area short stack being built.

We integrated the cell model in our FCS analysis code and conducted a study to project the beginning of life performance of FCS with d-PtₓNiₓ/NSTF catalyst and cathode interlayer, subject to Q/DT constraint [3]. The MEAs in this study have 0.131 mg/cm² total Pt loading and 725 EW, 14 mm 3M-S membrane. At optimal conditions, the optimal power density is determined by high frequency resistance and ORR activity rather than mass transfer overpotentials. The projected cost ($1,500/tr-oz Pt price) and Pt content are
$48.4–48.7/kW e$ at 2.2–2.5 atm, and $0.152–0.155$ g-Pt/kW e at 2.5–3.0 atm stack inlet pressure, see Figures 2a and 2b.

FIGURE 1. Development of performance model using differential cell data for MEA with d-Pt,Ni NSTF catalyst with cathode interlayer. Equation for ORR kinetics: $i + i_c = i_{ORR} P_{O_2}^{a} \phi^{b} e^{-\frac{E_{O_2}}{RT} \gamma}$. Reproducibility of test data for standard conditions: (b) ORR kinetics: $P(O_2)$ dependence; (c) ORR kinetics: RH dependence; (d) ORR kinetics: T dependence; (e) Limiting current density correlation; (f) Mass transfer overpotential correlation. Solid lines are model results.

Figures 2c, 2d, and Table 1 compare the cost and performance of fuel cell systems with different NSTF catalysts and membranes. The 2015 reference FCS includes ternary catalyst MEA and 20 mm, 835 EW membrane without mechanical reinforcement [4]. The 2016 reference FCS includes binary NSTF catalyst with Pt/C cathode.
interlayer and mechanically reinforced 14 mm, 725 EW membrane. For better understanding of results, we included an FCS with binary NSTF catalyst and Pt/C cathode interlayer but 20 mm, 835 EW membrane as in 2015 FCS. Compared to the 2015 reference FCS, the 2016 FCS has 25% higher stack power density: 12.3% due to higher ORR activity and 12.7% due to thinner membrane. It also has 16.8% lower stack cost: 10% due to higher ORR activity and 6.8% due to thinner membrane. The projected performance and cost of 2016 FCS are 973 mW/cm$^2$ stack power density,
0.152 g/kW$_e$ Pt content, and 48.40 $$/kW_e$ system cost at high volume manufacturing.

**Durability of MEAs with NSTF Catalysts**

We have been collaborating with 3M to develop a test protocol for determining the stability of the baseline ternary NSTF catalyst under potentiostatic conditions [5]. The protocol consists of repeatedly degrading the cell for 10 h at constant potential with periodic $F^-$ collection and partial reconditioning with 1 TC cycle. Every 20 h of degradation, polarization curves are taken in $H_2$/air. Every 40–80 h of degradation, the cell is reconditioned more fully with 3 TC cycles and data are obtained to measure the cathode ORR activity, cathode ECSA, $H_2$ crossover, shorting resistance, and cell polarization in $H_2$/air. The tests were run on 50-cm$^2$ cells with quad serpentine flow fields and ternary catalysts with 0.05 mg/cm$^2$ Pt loading on anode and 0.15 mg/cm$^2$ Pt loading on cathode. The cells used 3M, 825 EW, membrane that was 20 mm thick. The membrane was chemically stabilized with an anti-oxidant additive but was not mechanically supported.

Figures 3a and 3b present voltage degradation determined from the polarization curves for three current densities representing near open-circuit condition (0.032 A/cm$^2$), kinetic region (0.32 A/cm$^2$), and the region where the mass transfer overpotentials may become important (1 A/cm$^2$). The voltage degradation rates are comparable at 0.032 A/cm$^2$ and 0.32 A/cm$^2$ indicating that the underlying mechanism may be related to the slowdown of ORR kinetics at low current densities. The voltage degradation rates are much larger at 1 A/cm$^2$ suggesting that mass transfer in the MEA is also impeded with exposure time. The data quantitatively confirms that the voltage degradation rates are accelerated at lower hold potentials and higher exposure temperatures.

Figures 3c and 3d present the fluoride emission rate (FER) measured by ion chromatography of the collected water samples. $F^-$ concentrations in the water samples were

![FIGURE 3. Durability of NSTF catalyst and MEA under long potentiostatic holds at 0.3–0.9 V. (a) Voltage degradation at different hold potentials; (b) Voltage degradation at different temperatures; (c) FER at different hold potentials; (d) FER at different temperatures.](image-url)
very low, 20 ppb or less. Although the concentrations were similar, F− generation rate increases with decreasing hold potential (i.e., increasing current density) due to higher effluent water flow rate (production + supplied). The measured FERs are similar but higher on cathode than on anode for all hold potentials, suggesting that FER measured in cathode effluent was produced locally in cathode. The trend of measured cathode FER increasing with decreasing cell voltage is consistent with the observed dependence of \( \text{H}_2\text{O}_2 \) production on potential in rotating ring disk electrode tests [6]. The measured anode FER correlates with the cell voltage rather than the anode potential. Rotating ring disk electrode experiments in a hydrogen environment have shown that \( \text{H}_2\text{O}_2 \) generation decreases as the anode potential is raised. For these reasons, it is unlikely that the measured F− in anode effluent water was due to \( \text{H}_2\text{O}_2 \) produced locally in the anode by the reaction of \( \text{O}_2 \) crossing over from the cathode \( (2\text{H}^+ + \text{O}_2 + 2e^- = \text{H}_2\text{O}_2) \). Further work is needed to determine whether FER on cathode and anode are related and if F− detected in anode water was actually produced in the cathode and permeated through the membrane.

We used the data for F− concentration in effluent cathode water samples obtained during V-series and T-series to develop the following empirical correlation for cathode FER \( (N_{\text{F}}, \text{mg/cm}^2\cdot\text{h}) \) as a function of cell potential \( (E, \text{V}) \) and exposure temperature \( (T, \text{K}) \).

Figure 4a presents the measured loss in surface enhancement factor (SEF, \text{cm}^2-Pt/cm^2-planar), that is the product of the ECSA (\text{cm}^2-Pt/mg-Pt) and the Pt loading \( (L_{\text{Pt}}, \text{mg-Pt/cm}^2) \). It indicates that the higher the exposure temperature the greater is the rate of loss of SEF at 600 mV hold potential, but the maximum loss is limited to about 30% to 40% at 60 A/cm² 90°C. SEF loss appears to be self-limiting and ceases when the whiskerettes dissolve and disappear. Previous studies showed similar SEF loss when the NSTF catalyst was subjected to 30,000 triangle potential cycles in \( \text{H}_2/\text{N}_2 \) (cyclic voltammetry) and \( \text{H}_2/\text{air} \).
We determined the kinetic parameters from the measured polarization curves at low current densities where the mass transfer overpotentials are negligible. Figure 4b presents the estimated kinetic overpotentials as a function of current density and CFR for the six tests. The solid linear lines in Figure 4b, representing the least-square fit of the data, are nearly parallel, implying that there are only small changes in the Tafel slope with potential and the exposure temperature since and . Implicitly, is also a function of the hold potential and the exposure temperature since and depend on these variables.

CONCLUSIONS AND FUTURE DIRECTIONS

We determined the ORR kinetic parameters from IR and crossover corrected cell voltages at low current densities in H2/O2 and H2/air. Compared to the baseline ternary PtCoMn/N/NSTF catalyst, the mass activity of binary d-PtNi/N/NSTF catalyst with cathode interlayer is 78–144% higher.

We determined the performance and cost of a reference 2016 automotive FCS that includes a stack with binary NSTF catalyst with Pt/C cathode interlayer and mechanically reinforced 14 mm, 725 EW, reinforced membrane. Compared to the 2015 reference FCS that includes a ternary catalyst and 20 mm, 835 EW, unsupported membrane, the 2016 FCS has 25% higher stack power density: 12.3% due to higher ORR activity and 12.7% due to thinner membrane. It also has 16.8% lower stack cost: 10% due to higher ORR activity and 6.8% due to thinner membrane. The projected performance
and cost of 2016 FCS are 973 mW/cm² stack power density, 0.152 g/kWₚ Pt content, and $48.40/kWₑ system cost at high volume manufacturing.

We have conducted tests (3M collaboration) and developed a model for NSTF catalyst durability under long potentiostatic hold. The model and data show the mechanisms of degradation of ECSA, kinetic activity and O₂ mass transfer and their relationship with fluoride release from membrane. We project that the target of less than 10% lifetime performance degradation can be achieved by restricting CFR to 0.7 mg/cm².

**FY 2016 PUBLICATIONS/PRESENTATIONS**


**REFERENCES**


