Performance and Durability of Advanced Automotive Fuel Cell Stacks and Systems with State-of-the-Art d-PtCo/C Cathode Catalyst in Membrane Electrode Assemblies

Rajesh K. Ahluwalia (Primary Contact),
Xiaohua Wang, and J-K Peng
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: 630-252-5979
Email: walia@anl.gov

DOE Manager:
Nancy L. Garland
Phone: 202-586-5673
Email: Nancy.Garland@ee.doe.gov

Project Start Date: October 1, 2003
Project End Date: Project continuation and direction determined annually by DOE

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 research and development (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) 2019 Objectives

- Modify the reference fuel cell system (FCS) configuration to include controls for extended stack durability on operational and start-up and shut-down transients.

- Quantify the impact of low-platinum group metal (PGM) alloy catalysts on the performance and durability of automotive stacks and fuel cell systems.

- Collaborate with the Electrocatalysis Consortium (ElectroCat) to project improvements needed for adoption of PGM-free catalysts in automotive fuel cells.

- Provide modeling support to Strategic Analysis, Inc., in its annual update of progress toward meeting technical targets, including FCS cost.

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[1]:

- (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: 65% at 25% of rated power

- $Q/\Delta T$: 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.

FY 2019 Accomplishments

FCS for light-duty vehicles with PGM-free cathode catalyst:

- Collaborated with ElectroCat in obtaining data to develop and validate model for performance and durability.

- Selected atomically dispersed (AD)Fe-N-C cathode catalyst for initial study.

- Projected improvements needed in catalyst activity and electrode structure to reach 1,000 mW/cm^2 power density in a 90-kW_e stack while meeting $Q/\Delta T = 1.45$ kW/°C target at 2.5 atm inlet pressure, 95°C coolant exit temperature, and 1.5 cathode stoichiometry.

Durability of light-duty vehicle FCS with state-of-the-art (SOA), low-PGM Pt alloy cathode catalyst:

- Collaborated with the Fuel Cell Performance and Durability Consortium and General Motors Corporation (GM) in obtaining data to develop the durability model.

- Modeled SOA dispersed d-PtCo/C (de-alloyed) catalyst system.

- Determined performance degradation and acceptable electrochemical surface area (ECSA) loss to limit derating in FCS power to 10% over lifetime.

FCS for heavy-duty vehicles:

- Demonstrated the benefits of hybridization in meeting $Q/\Delta T$ limits for heat rejection in Class 8, line-haul heavy-duty trucks.

- Obtained initial results for achievable stack power density as function of Pt loading in d-PtCo/C and a-Pt/C (annealed) cathode catalyst systems.

- Obtained initial results for durability of d-PtCo/C and a-Pt/C cathode catalyst systems.

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

The approach for this project includes the following.

- Develop, document, and make available versatile system design and analysis tools:
  - GCtool: Stand-alone code on PC platform
  - GCtool-Autonomie: Drive-cycle analysis of hybrid fuel cell systems.

- Validate the models against data obtained in laboratories and test facilities inside and outside Argonne through collaboration with external organizations.

- Apply models to issues of current interest:
  - Work with U.S. DRIVE Technical Teams
  - Work with DOE contractors as requested by DOE.

RESULTS

We collaborated with GM to determine the performance and durability of membrane electrode assemblies (MEAs) with a SOA d-PtCo cathode catalyst relative to the target of 8,000-h lifetime. As listed in Table 1, the MEA has de-alloyed Pt_3Co catalyst supported on a high surface area carbon (HSAC-a)[1] in cathode, Pt catalyst supported on Vulcan carbon in anode, thin 12-μm reinforced perfluorosulfonic acid membrane, and 200-μm thick diffusion media with microporous layers. The Pt loadings are 0.1 mg/cm^2 in the cathode catalyst and 0.025 mg/cm^2 in the anode catalyst.

Table 1. MEA specifications [1, 2]

Representative State-of-the-Art Low-PGM MEA		
	Cathode	Anode
Catalyst	d-Pt$_3$Co/C	Pt/C
Catalyst Support	HSAC-a	Vulcan
Ionomer Equivalent Weight	825	950
Pt Loading	0.1 mg/cm^2	0.025 mg/cm^2
ECSA	45 m^2/g	60 m^2/g
Electrode Thickness	7 μm	5 μm
Diffusion Medium Thickness	200 μm	200 μm
Membrane	12 μm Reinforced	

We formulated a degradation model for oxygen reduction reaction (ORR) kinetics and O$_2$ transport resistance using the approach outlined in Figure 1 and briefly highlighted below.

- Degrade cells using catalyst accelerated stress test (AST) protocol for 15k, 30k, and 50k cycles.

- Vary upper potential limit (UPL): 0.95, 0.90, and 0.85 V (data for 0.90 and 0.85 V UPLs pending).

- Measure cell performance and H$_2$/N$_2$ electrochemical impedance spectroscopy (EIS) at beginning of test (BOT) and end of test (EOT) for 12 operating conditions spanning 1–2.5 atm, 60°–95°C, 30%–100% relative humidity (RH), and 5–21% X(O$_2$).

- Characterize changes in catalyst and electrode structure using transmission electron microscopy, small angle X-ray scattering, and nano-computed tomography (pending).

- Measure and model Pt and Co dissolution using online inductively coupled plasma mass spectrometry (pending).
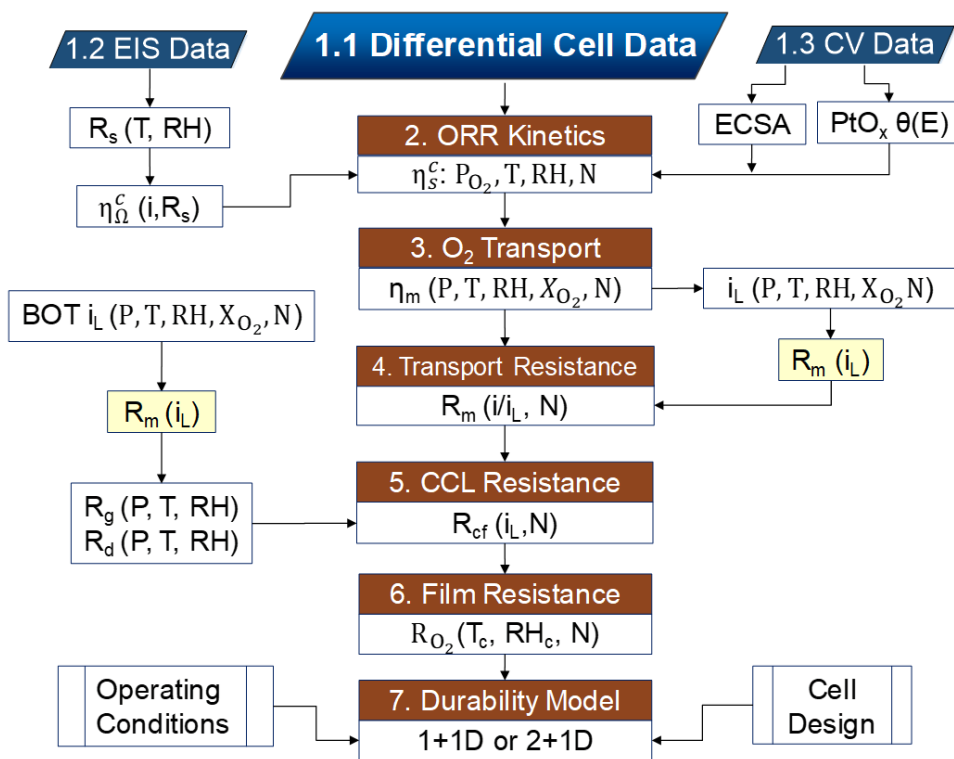

Figure 1. Fuel cell durability model framework using differential cell hardware

To date, we have collected data for catalyst ASTs with 100% and 40% exposure RH [1]. The measured degradation after 30k cycles was smaller at 40% RH (30k-1) than at 100% RH (30k-2): 7.5% vs. 33% ECSA loss, 30% vs. ~50% mass activity loss, and ~20% vs. >25% specific activity loss. We used the polarization data at low current densities to model and investigate the ORR kinetics on degraded d-PtCo/C catalyst. As indicated in Figure 2a, there are negligible changes in the kinetic parameters denoting reaction order (γ), activation energy (ΔH_s^c), and RH dependence (β) in the distributed ORR kinetic model.

$$\eta_c = \eta_s^c + iR_\Omega^c \left(\frac{iR_s}{b}\right)$$

$$i + i_x = i_0 S_{Pt}(1 - \theta)e^{-\frac{\omega\theta}{RT}}e^{\frac{\alpha nF}{RT}\eta_s^c}$$

$$i_0 = i_{0r}e^{-\frac{\Delta H_s^C}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)}P_{O_2}^\gamma \Phi^\beta$$

As shown in Figure 2b, the majority of the 33% drop in i_{0r} (proportional to the specific activity, $\mu A/cm_{Pt}^2$) occurs in AST at 40% RH (30k-1) during which time ECSA drops by 7.5%. Beyond 7.5% ECSA loss, degradation in mass activity in AST at 100% RH (30k-2) is due to decrease in roughness (S_{Pt}).
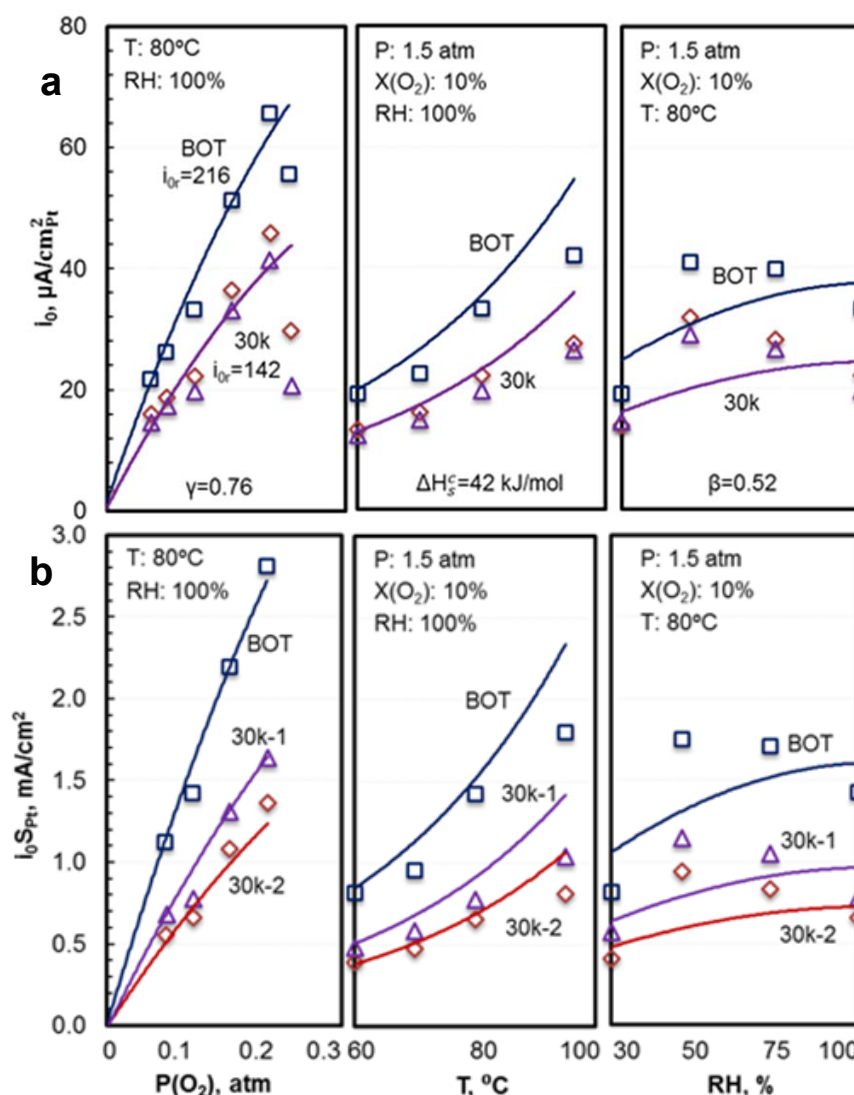

Figure 2. ORR kinetics on degraded d-PtCo/C catalyst: (a) effect of Co dissolution on ORR kinetic parameters; and (b) combined effects of Co dissolution and growth in catalyst size on ORR kinetic parameters

We used the polarization data at high current densities to model and investigate the effect of aging on O_2 transport resistance in d-PtCo/C catalyst. As outlined in Figure 1, we extracted the limiting currents (i_L) from the mass transfer overpotentials (η_m), determined the O_2 transport resistance (R_m), and represented R_m in terms of pressure-dependent resistances in the gas channel (R_g) and diffusion media (R_d) and pressure-independent resistances for Knudsen diffusion (R_{Kn}) and electrode (R_{cf}).

$$R_m = R_g + R_d + R_{Kn} + R_{cf}$$

$$R_{cf} = \frac{R_{O_2}}{S_{Pt}}$$

$$R_{O_2} = R_{O_2}(T_c, \Phi_c, N)$$

Figure 3a presents the O_2 transport resistance (R_{cf}) in the electrode from which we have derived the roughness-dependent (S_{Pt}) local O_2 transport (R_{O_2}). After 30k cycles (N), R_{cf} has increased by >50% at 40% RH exposure and >125% at 100% RH exposure. Reduction in S_{Pt} after cycling accounts for 8% of the increase in R_{cf} at 40% exposure and for 45% of the increase in R_{cf} at 100% exposure. Nearly 48%–60% of the increase in R_{cf} is associated with the reduced permeability of O_2 through the ionomer (see Figure 3b).
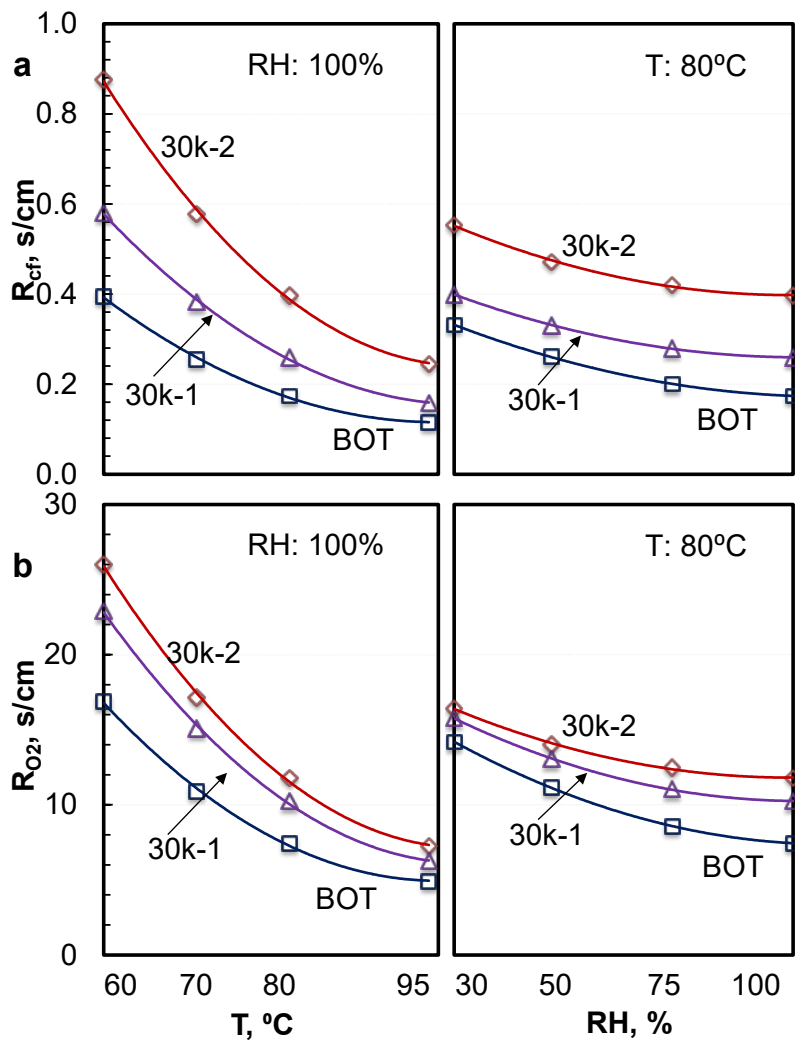

Figure 3. Effect of aging on O₂ transport resistance in d-PtCo/C electrode: (a) O₂ transport resistance in electrode (R_{cf}) and (b) local O₂ transport resistance (R_{O_2})

Following the procedure in Figure 1, we modified our FCS performance code (GCtool) by incorporating the above aging models for ORR kinetics and O_2 transport resistance. We then used the updated model in a study to project FCS performance degradation as a function of ECSA loss due to aging. We consider an 80-kW$_e$-net FCS with the MEA materials listed in Table 1. At rated power, the stack achieves 1,139 mW/cm^2 power density (1.5 cathode stoichiometry) at BOL under conditions necessary to meet the heat rejection constraint ($Q/\Delta T = 1.45$ kW/°C) [3, 4]: 656-mV cell voltage (and 1.736-A/cm^2 current density), 2.5-atm stack inlet pressure, and 95°C coolant exit temperature. The fresh cathode catalyst has 43-m^2/g ECSA, 650-mA/mg$_{Pt}$ mass activity, and 1,450-µA/cm^2$_{Pt}$ specific activity. Neglecting any small deterioration in air management system and radiators, we hold air flow rate (74 g/s) and heat rejection (~85 kW) constant, thereby allowing SR(c) to increase and cell voltage to decrease as the stack degrades. Characterizing cell degradation in terms of ECSA loss, Figure 4 presents the resulting loss in FCS net power and stack power density taking advantage of the allowance for lower cell voltage. These results suggest that the target of 10% derating in FCS power over lifetime can be met by limiting the acceptable ECSA loss to 35%. At the EOL defined by this criterion, the ECSA has decreased to 28 m^2/g, mass activity to 320 mA/mg$_{Pt}$, specific activity to 1,090 µA/cm^2$_{Pt}$, and power density to 1,038 mW/cm^2 at 627-mV cell voltage and 1.654-A/cm^2 current density.
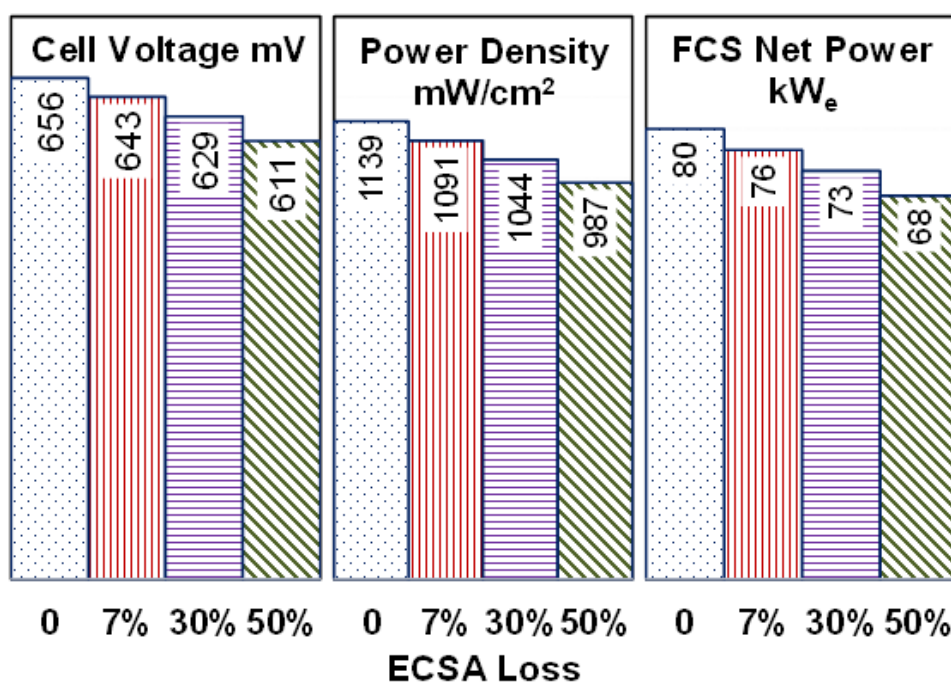

Figure 4. Projected FCS performance degradation with SOA d-PtCo/C cathode electrode at rated power with constant air flow rate and heat rejection

CONCLUSIONS AND UPCOMING ACTIVITIES

- We demonstrated that SOA d-Pt$_3$Co/HSAC cathode catalysts in MEAs can lead to power densities exceeding the 2020 target of 1,000 mW/cm^2 at 0.125 g/kW$_e$ PGM content under operating conditions (95°C, <100% outlet RH, SR(c) = 1.5, 2.5-atm stack inlet pressure) required to meet the heat rejection constraint ($Q/\Delta T = 1.45$ kW/°C). We also showed that stack Pt utilization exceeding the target of 8.0 kW$_e$/g$_{Pt}$ could be achieved with this catalyst system.

- We demonstrated that 40% of the loss in mass activity of the SOA d-PtCo/C cathode catalyst after 30k potential cycles is due to Co dissolution and 60% is due to growth in particle size.

- We showed that the durability target of 10% loss in rated power could be achieved if the ECSA loss is limited to 35%.

- Our future work will focus on methods of mitigating degradation of low-loaded d-PtCo/C catalysts under cyclic potentials and on automotive drive cycles. The future work will also emphasize medium- and heavy-duty vehicles' performance and durability.

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12. R.K. Ahluwalia, X. Wang, and J.-K. Peng, "Performance of Advanced Automotive Fuel Cell Stacks and Systems with State-of-the-Art d-PtCo/C Cathode Catalyst in Membrane Electrode Assemblies," FY 2018 Annual Progress Report, DOE Hydrogen and Fuel Cells Program, 2019.

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