

Fuel Cell System Modeling and Analysis

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Project ID: FC017

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Overview

Timeline

- Start date: Oct 2003
- End date: Open
- Percent complete: NA

Barriers

- B. Cost
- C. Performance
- E. System Thermal and Water Management
- F. Air Management
- J. Startup and Shut-down Time, Energy/Transient Operation

Budget

- FY17 DOE Funding: \$500 K
- Planned DOE FY18 Funding: \$250 K
- Total DOE Project Value: \$250 K

Partners/Interactions

- Eaton, Ford, Honeywell, UDEL/Sonijector
- SA, Aalto University (Finland)
- 3M, Ballard, Johnson-Matthey Fuel Cells (JMFC), UTRC, FC-PAD, GM
- IEA Annex 34
- Transport Modeling Working Group
- Durability Working Group
- U.S. DRIVE fuel cell tech team
- This project addresses system, stack and air management targets for efficiency, power density, specific power, transient response time, cold start-up time, start up and shut down energy

Objectives and Relevance

Develop a validated system model and use it to assess design-point, part-load and dynamic performance of automotive (primary objective) and stationary (secondary objective) fuel cell systems (FCS)

- Support DOE in setting technical targets and directing component development
- Establish metrics for gauging progress of R&D projects
- Provide data and specifications to DOE projects on high-volume manufacturing cost estimation

Impact of FY2018 work

- Projected 46.0* ± 0.7 kW_e FCS cost at 500,000 units/year and 8.5 ± 0.4 kW_e/g_{Pt} FCS Pt utilization with SOA d-PtCo/C cathode catalyst, reinforced 14µm 850 EW membrane, and Q/ Δ T = 1.45 kW/°C constraint
- Verified that the SOA catalyst system can achieve 1180 ± 55 mW/cm² stack power density exceeding the target at low Pt loading (0.125 mg-Pt/cm² total)
- Projected <5% penalty in power density if the cathode humidifier is removed, and ~15% penalty if stack inlet pressure is lowered to 2 atm from 2.5 atm
- Showed that parasitic power approaches 25 kW_e if the compressor discharge pressure is raised to 4 atm
- Modified the reference system configuration to include valves and controls for protected shutdown, safe startup from sub-freezing temperatures, and limiting cell voltage to 0.85-0.875 V during idle

Approach

Develop, document & 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

Collaborate 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

1	Evaluate the advantages of operating PEMFC stack at elevated pressures up to 4 atm using 2-stage centrifugal compressors.	12/17
2	Determine the comparative performance of PEMFC stacks with and without cathode humidifier.	03/18
3	Evaluate the performance and durability of MEAs with de-alloyed PtCo cathode catalyst on high surface area carbon with tailored pore size distribution relative to the targets of 0.44 A/mg-PGM mass activity, 1000 mW/cm ² at rated power, 300 mA/cm ² at 800 mV, and 5000 h lifetime.	06/18
4	Update the performance and cost of an automotive fuel cell system with an advanced low-PGM catalyst relative to 2020 targets of 65% peak efficiency, $Q/\Delta T$ of 1.45 kW/K, and \$40/kW cost.	09/18

Technical Accomplishments: Summary

Stack: Collaboration with FC-PAD and GM in obtaining data to develop and validate model for pressures up to 3 atm

- State-of-the-art (SOA) dispersed de-alloyed PtCo/C catalyst systems
- De-alloyed PtCo/C catalyst system: durability on drive cycles

Air Management: Investigating integrated air management system with high speed centrifugal compressors and expanders including cooling requirements of motor and airfoil bearings (AFB) and two-stage compressors (Honeywell patent)

Water Management: Optimizing cost of integrated PEFC stack and cross-flow humidifier

 Investigating FCS performance without cathode humidifier (dispersed catalyst electrodes)

Fuel Management: Evaluating the performance of anode system with a pulse injector in lieu of H_2 recirculation blower (collaboration with Ford & UDEL)

Thermal Management: Optimizing system performance and cost subject to $Q/\Delta T$ constraint

System startup and shutdown: Modified reference system to incorporate controls for protected shutdown, safe startup from sub-freeze temperatures, and limiting cell voltage at idle



Argonne 2018 FCS Configuration

Model Framework and Single Cell Hardware

US-EU Differential Cell Hardware*

- P: 1-3 atm; T: 45-95°C,
- RH: 30-150%; X(O₂): 1-21%
- Random Tests: Semi-statistical randomized with multiple variables, forward scans, 3-min hold at each cell voltage
- Controlled Tests: Model guided single-variable with some twovariable tests, forward scans, 3-min hold at each cell voltage





Representative State-of-the-Art Low-PGM MEA				
	Cathode	Anode		
Catalyst	d-Pt ₃ Co/C	Pt/C		
Catalyst Support	HSAC	Vulcan		
onomer Equivalent Weight	950	950		
Pt Loading	0.1 mg/cm ²	0.025 mg/cm ²		
ECSA	45 m²/g	60 m²/g		
Electrode Thickness	7 μm	5 μm		
Diffusion Medium Thickness	200 µm	200 µm		
Vembrane	18 μm R	einforced		

*All tests conducted at GM (S. Arisetty Lead), FCPAD-FC156 collaboration (S. Kumaraguru PI)

Kinetics of ORR on d-PtCo/C Catalyst



[1] Arisetty et. al. (2015), ECS Transactions, 69, 273-289

Calibration of ORR Kinetic Model*

$$\begin{split} &i_0 \text{ calibration: 1 data point per pol curve} \\ & \text{ Data: } i+i_x=i_0S_{Pt}(1-\theta)e^{-\frac{\omega\theta}{RT}}e^{\frac{\alpha nF}{RT}\eta_S^c} \\ & \text{ Model: } i_0=i_{0r}e^{-\frac{\Delta H_S^c}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)}P_{O_2}^{\gamma}\Phi^{\beta} \end{split}$$

 η_s^c calibration: all data in kinetic region

• Data:
$$\eta_s^c = E_N - E - iR_{\Omega}^m - iR_{\Omega}^c$$

• Model:
$$\eta_s^c = b \left[\ln \left(\frac{i + i_x}{i_0 S_{Pt}} \right) - \ln(1 - \theta) + \frac{\omega \theta}{RT} \right]$$



Mass Activity for ORR on d-PtCo/C Catalysts

- d-PtCo/C has 2X modeled mass activity of a-Pt/C that has nearly the same particle size
- d-PtCo/C and d-PtNi/C alloy have comparable mass activities
- Both low-PGM alloy catalysts (d-PtNi/C and d-PtCo/C) meet the mass activity targets of 440 A/g_{Pt}



Oxygen Mass Transfer: Limiting Current Density



T: Bipolar plate temperature; T_c: CCL temperature Φ : Gas channel RH; Φ_c : CCL RH

water transport across membrane

Limiting Current Density: Effect of Pressure

At constant $P(O_2)$, i_L decreases with increase in P because of the inverse dependence of O_2 gas phase diffusivity on P.

 The decrease in *i_L* is less than proportional to 1/P, implying that non-Fickian diffusion controls mass transport resistance At constant $X(O_2)$, i_L increases with increase in P because of higher $P(O_2)$.

• The increase in i_L is somewhat less than proportional to $P(O_2)$, implying that mass transport resistance also increases with $P(O_2)$.



Limiting Current Density: Effect of Temperature and RH

Dependence of i_L on $T_c >> T^{3/2}$, confirming that processes other than Fickian diffusion are rate controlling.

 O₂ permeability through the ionomer film on the catalyst particles For given T_c , i_L is highest at an intermediate RH in CCL (ϕ_c^*).

- CCL flooding for $\phi_c > \phi_c^*$
- ϕ_c^* Increases at higher T_c



The plot includes all the experimental data for i_L at different T, P=1.6 atm, X(O_2)=10%, and Φ =100%. For comparison, the model was used to rescale the i_L data to P(O_2)=0.12 atm, and ϕ_c =100%.

The plot includes all the experimental data for i_L at different Φ , T=45, 70 and 95°C, P=1.6 atm and X(O_2)=10%. For comparison, the model was used to rescale the i_L data to P(O_2)=0.12 atm and different T_c=45, 70 and 95°C.

Performance of Automotive FCS with SOA d-PtCo/C Cathode Catalyst

Modeled optimal beginning of life (BOL) performance of automotive FCS subject to Q/ Δ T=1.45 kW/°C constraint: 0.125 mg/cm² total Pt loading; 850 EW, 14- μ m chemically-stabilized, reinforced membrane

FY2018 model based on differential cell data supports FY2017 landmark result

- 46.0 ± 0.7 \$/kW_e projected cost* at 2.5 atm stack inlet pressure and 95°C stack coolant outlet temperature for high volume manufacturing
- Removing membrane humidifier slightly lowers the system cost at 2.5 atm stack inlet pressure

Results are preliminary pending model validation using data from 50-cm² integral cell

 Error bars reflect variance of kinetic data in random and controlled tests and include degradation between the two series of tests

Effect of manufacturing volume on projected cost (SA)

- 500,000 units/year: 46 \$/kW_e
- 100,000 units/year: 51 \$/kW_e
- 10,000 units/year: 88 \$/kW_e



*Using 2018 cost correlations from Strategic Analysis (SA), 500,000 units/year, no H₂ blower. Includes \$2.01 cost increase in 2018 for manufacturing bipolar plates and MEAs, added controls, and CEMM price inflation.

FCS with SOA d-PtCo/C Cathode Catalyst: Pt Utilization

Modeled optimal beginning of life (BOL) performance of automotive FCS subject to Q/ Δ T=1.45 kW/°C constraint: 0.125 mg/cm² total Pt loading; 850 EW, 14- μ m chemically-stabilized, reinforced membrane

FY2018 model based on differential cell data supports FY2017 landmark result

- Modeled stack Pt utilization (9.5 \pm 0.5 kW_e/g_{Pt}) exceeds the target (8.0 kW_e/g_{Pt})
- Modeled FCS Pt utilization (8.5 \pm 0.4 kW_e/g_{Pt}) also exceeds the target
- Stack inlet pressure ≥ 2.0 atm needed to meet the Pt utilization target



FCS with SOA d-PtCo/C Cathode Catalyst: Power Density

Modeled optimal beginning of life (BOL) performance of automotive FCS subject to Q/ Δ T=1.45 kW/°C constraint: 0.125 mg/cm² total Pt loading; 850 EW, 14- μ m chemically-stabilized, reinforced membrane

FY2018 model based on differential cell data supports FY2017 landmark result

- Modeled gross stack power density (1180 ± 55 mW/cm²) exceeds the target (1000 mW/cm²) at low Pt loading (0.125 mg-Pt/cm² total)
- Stack inlet pressure ≥ 2.0 atm needed to meet the power density target



Air Management System



Simulation results: 73 g/s air flow rate, and 2.5 atm compressor discharge P; 2.3 atm expander inlet P, 85°C inlet T, fully saturated; 40°C ambient T

Expander

Spent

Air

10.4 kW

12

10

8

Performance of Two-Stage Centrifugal Compressor

Mixed axial and radial flow compressors on a common shaft with AFBs and 3phase brushless DC motor; Honeywell US Patent 2015/0308456

- AFB*/motor cooling air extracted downstream of the pre-cooler and is not recovered
- Compressor power ~25 kW_e at 4-atm discharge pressure
- Results for existing compressor but resized motor and motor controller





Proposed Argonne 2018 FCS Configuration with Controls

- Stack idling: Limit cell voltage by operating at low SR(c) and low O₂ concentration
- Stack shutdown: Avoid H₂-air front during subsequent start-up by depleting oxygen
- Sub-freeze start: Prevent icing by maximizing in-stack heat production*



*M. Toida, Y. Naganuma, and T. Ogawa, "Fuel Cell System and Method for Discharging the System," US 2016/0141672 A1, May 19, 2016.

Mitigation of High Cell Voltages

SOA stack limits cell voltage to 0.85 V during idle



Lowering stack temperature may also be inadequate and has thermal inertia



Reducing cathode stoichiometry may not provide adequate control of cell voltage



Reducing O₂ concentration by recycling spent air provides most control



M. Sato, "Fuel cell System and method of Controlling the Same," US 2017/0047602 A1, Feb. 16, 2017. S. Kawahara, K. Suematsu, M. Toida, and R. Akaboshi, "Fuel Cell System and Control Method Thereof," US 9,531,022 B2, Dec. 27, 2016.

Controlling O₂ Concentration at Stack Inlet

Controlling O₂ concentration at stack inlet by recycling cathode spent air and bypassing stack*



Air inlet and recycle valves not included in Argonne 2018 FCS configuration

Model for mixed cathode potential at low cathode stoichiometry



Recycle and bypass depend on desired reduction in O_2 concentration at stack inlet and SR(c)



Increase in compressor flow rate to reduce inlet O₂ concentration below 21%

M. P. Wilson, V. Yadha and C. A. Reiser, "Low Power Control of Fuel Cell Open Circuit Voltage," US 8,808,934 B2, Aug. 19, 2014.

Protected Shutdown

Protected shutdown algorithm

- Step 1: Isolate the cathode circuit by closing the air intake valve and opening the air recycle valve
- Step 2: Deplete oxygen by applying load while supplying hydrogen
- Step 3: Shut the compressor (if on) and isolate H₂ circuit by closing the H₂ main valve
- Step 4: Allow H₂ and N₂ in anode and cathode circuits to equilibrate

Step 4: Equilibration of anode and



Step 2: Depletion of oxygen with cathode air recycled by compressor



Step 4: Equilibration of H₂ partial pressures in anode and cathode circuits

Collaborations

Air Management	Honeywell: Cost and Performance Enhancements for a PEM Fuel Cell Turbocompressor (FC27)
	Eaton: Roots Air Management System with Integrated Expander (FC103)
Stack	3M: High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation (FC104)
	Ballard/Eaton: Roots Air Management System with Integrated Expander (FC103)
	JMFC and UTRC: Rationally Designed Catalyst Layers for PEMFC Performance Optimization (FC106)
	FC-PAD: Fuel Cell Performance and Durability Consortium (FC135, FC136, FC137, FC138, FC139)
	GM: Highly-Accessible Catalysts for Durable High-Power Performance (FC144)
	GM: Durable High-Power Membrane Electrode Assemblies with Low Pt Loadings (FC156)
Water Management	Gore, Ford, dPoint: Materials and Modules for Low-Cost, High-Performance Fuel Cell Humidifiers (FC067)
Thermal Management	3M, Honeywell Thermal Systems
Fuel Management	3M, University of Delaware (Sonijector)
Fuel Economy	ANL-Autonomie (SA044), Aalto University (Fuel Cell Buses)
H ₂ Impurities	3M
System Cost	SA: Manufacturing Cost Analysis of Fuel Cell Systems and Transportation Fuel Cell System Cost Assessment (FC163)
Dissemination	IEA Annex 34, Transport Modeling Working Group, Durability Working Group, Catalysis Working Group
Argonne develops	the fuel cell system configuration determines performance identi-

 Argonne develops the fuel cell system configuration, determines performance, identifies and sizes components, and provides this information to SA for high-volume manufacturing cost estimation

Proposed Future Work

- 1. Continue to support DOE development effort at system, component, and phenomenological levels
- 2. Continue to support SA in high-volume manufacturing cost projections, collaborate in lifecycle cost studies
- Optimize system parameters considering costs at low-volume manufacturing
- Life cycle cost study for medium and heavy duty vehicles (Ballard, Eaton, SA)
- 3. Alternate MEAs with advanced alloy catalysts
- State-of-the-art low PGM Pt and Pt alloys (FC-PAD collaboration)
- Alternate electrode structures (FC-PAD FOA projects collaboration)
- Durability models (FC-PAD and GM collaboration)
- 4. System architecture and balance-of-plant components
- Air management system with centrifugal and Roots compressors and expanders (Honeywell/Eaton collaboration)
- Fuel and water management systems: anode gas recirculation, internal/external humidification
- Bipolar plates and flow fields for low pressure drops and uniform air/fuel distribution, cell to stack performance differentials
- Strategies and controls for stack idling, startup and shutdown, subfreezing temperatures
- 5. Incorporate durability considerations in system analysis
- System optimization for cost, performance, and durability on drive cycles (Advanced alloy catalyst systems)

Any proposed future work is subject to change based on funding levels.

Project Summary

Relevance:	Independent analysis to assess design-point, part-load and dynamic performance of automotive and stationary FCS
Approach:	Develop and validate versatile system design and analysis tools Apply models to issues of current interest Collaborate with other organizations to obtain data and apply models
Progress:	Projected $46.0 \pm 0.7 $ %/kW _e FCS cost at high volume manufacturing and $8.5 \pm 0.4 \text{ kW}_{e}/\text{g}_{Pt}$ FCS Pt utilization with SOA d-PtCo/C cathode catalyst, reinforced 14-µm 850 EW membrane, and Q/ Δ T = 1.45 kW/°C constraint Verified that the stack can achieve 1180 ± 55 mW/cm ² power density exceeding the target at low Pt loading (0.125 mg-Pt/cm ²) Projected <5% penalty in power density if the cathode humidifier is removed, and ~15% penalty if stack inlet pressure is lowered to 2 atm from 2.5 atm Showed that parasitic power approaches 25 kW _e if the compressor discharge pressure is raised to 4 atm Modified the reference system configuration to include valves and controls for protected shutdown, safe startup from sub-freezing temperatures, and limiting cell voltage to 0.85 V during idle
Collaborations:	3M, Eaton, GM, Gore, JMFC, SA, UTRC, UDEL/Sonijector
Future Work:	Fuel cell systems with emerging high activity catalysts Alternate balance-of-plant components System analysis with durability considerations on drive cycles

Reviewers' Comments

Sample comments and feedback

- ANL employs sound approach in forecasting performance but need more validation
- Impressive range of accomplishments, excellent study of catalyst systems, but needs more focus on Ni loss and other degradation mechanisms
- Excellent collaborations, but needs better definition of engagement with FC-PAD.
- Closer collaboration with OEMs to obtain stack and system data
- The project addresses multiple barriers including cost, performance, thermal/water/air subsystems, but more validation needed.
- Future work appears to be appropriate. More emphasis on durability in future.

Work scope consistent with above recommendations

- ✓ On-going work on differential cell data for PtCo/C dispersed catalysts in collaboration with FC-PAD and an industrial partner. Initial results on performance and durability are included in FC-PAD presentations. The PI is FC-PAD coordinator for modeling and validation thrust area.
- ✓ Examining durability during idling, startup/shutdown and sub-freeze start. Added valves and controls to mitigate catalyst degradation.
- Analyzing system simplification (compressor air bleed), component elimination (humidifier, H₂ recirculation blower) and alternative operating conditions (higher pressures)
- ✓ Expanded collaboration with an OEM on model validation using 10-50 cm² cells.
 Analyzing data from a SOA automotive stack and fuel cell system.
- ANL is a subcontractor to SA on FC-163 project, responsible for supplying performance and design data. Plans and recent results are discussed in bi-weekly calls.

Technical Back-Up Slides

Electrode Resistance

Electrode (σ_c) and membrane conductivities (σ_m) from Galvanostatic impedance data in H_2/N_2 at 0.4 V with 5 mV perturbation

 ZVIEW transmission line model (100 repeat units)

 H_2/N_2

T:80°C, P:1.5 atm



Relative Humidity, %



3.0

2.5

2.0

1.5

Oxide Formation on d-PtCo/C Catalyst

1.2

Reduction Charge, Q/ГS_{Pt}) 0 3.0 3.0 3.0

0.2

0.0 0.6

1.2

1.0

0.8

0.6

0.4 0.2 0.0

0.6

50°C

0.8

0.7

1 (

0.8

80°C Φ 100%

□ 50%

△ 35%

1.0

0.9

Solid solution model for PtO_x formation developed from measured CV reduction charge after 45-min hold at constant potential¹

$$Pt + H_2 O = PtOH + H^+ + e^-$$

$$PtOH = PtO + H^+ + e^-$$

$$\theta = \theta_{PtOH} + \theta_{PtO}$$

$$K_i = c_{H^+} \left(\frac{\theta_i}{\theta_{i+1}}\right) e^{-\frac{F}{RT}[E - E_{0i}]} = K_{i0} e^{-\frac{\omega_i}{RT}\theta_i^{x_i}}$$



[1] Arisetty et. al. (2015), ECS Transactions, 69, 273-289

Model Validation

Work in Progress

- Validation tests on 50-cm² integral cell with controlled SR(c) and SR(a)
- Differential cell tests with 0.05 and 0.2 mg/cm² Pt loadings in cathode
- Extracting resistances for O₂ transport in GDL, CCL pores and ionomer

Future Work

Catalyst accelerated cell tests to model durability

Differential cell operated in integral mode: Constant SR(c), variable P





Projected Performance of CEMM with Bleed Air Recovery

Compressor

Filter

MMM

From FC

AFB

To FC

LT Coolant

Expander

Spent

MH

Motor

Assumption: CEM cooling air can be recovered and combined with humidified air upstream of the PEFC stack

 Data are for as-built components. Efficiencies and performance can be improved by resizing the components to match the actual operating conditions



Simulation results for 73 g/s air flow rate and 2.5 atm compressor discharge P; 2.3 atm expander inlet P, 85°C inlet T, fully saturated; 40°C ambient T

Comparative Performance of CEMM w/o Bleed Air Recovery

From FC

Motor

MH

Controller

To FC

AFB

Expander

Spent

Air

AFB Cooling Valve

LT Coolant

Precooler

Cooling

Air

Compressor

Filter

Air

 \overline{M}

A control valve used to split predetermined amount of air downstream of the pre-cooler to cool AFB and motor; this cooling air is lost irrecoverably.

 Data are for as-built components. With resizing, the parasitic power can be reduced to 7.0 kW_e with bleed air recovery and 8.1 kW_e w/o bleed air recovery.



Simulation results for 73 g/s air flow rate and 2.5 atm compressor discharge P; 2.3 atm expander inlet P, 85°C inlet T, fully saturated; 40°C ambient T