Fuel Cell System Modeling and Analysis

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Overview

Timeline

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

Budget

- FY18 DOE Funding: $250 K
- Planned DOE FY19 Funding: $300 K
- Total DOE Project Value: $300 K

Barriers

B. Cost

C. Performance

E. System Thermal and Water Management

F. Air Management

J. Startup and Shut-down Time, Energy/Transient Operation

Partners/Interactions

- Eaton, Ford, Honeywell, UDEL/Sonijector
- SA, Aalto University (Finland)
- 3M, Ballard, Johnson-Matthey Fuel Cells (JMFC), UTRC, FC-PAD, GM, ElectroCat
- IEA Annex 34
- ANL-Autonomie, 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 FY2019 work

- In collaboration with ElectroCat, demonstrated that (AD)Fe-N-C PGM-free catalyst has 7.3 ± 0.5 mA/cm^2 initial catalyst activity, and is stable losing <50% activity after 30k 0.6-0.95 V potential cycles.
- Projected that 12X improvement in catalyst activity, doubling of active sites and engineered cathode structure are needed for the above PGM-free catalyst to approach the 1000 mW/cm^2 power density target.
- Demonstrated that 40% of the loss in mass activity of a SOA d-PtCo/C cathode catalyst after 30k potential cycles is due to Co dissolution and 60% due to growth in particle size.
- Verified that the SOA alloy catalyst can achieve >1100 mW/cm^2 power density and >8.25 kW_e/g_{Pt} FCS Pt utilization, and it can meet the durability target if the ECSA loss is limited to 35%.
- Proposed initial heat rejection constraint for 400-kW stacks for Class-8 long-haul trucks: $Q/\Delta T$ = 4.5 kW/^{o}C on 6% grade. Showed that high Pt loading (0.4 mg/cm^2), 675 mV cell potential at rated power, and battery hybridization may be needed to meet the heat rejection and durability requirements.

Q: Stack heat load; ΔT: Stack coolant exit T – Ambient T

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	In collaboration with ElectroCat, establish the baseline performance of SOA PGM-free catalysts for use in automotive PEMFC systems.	12/18
2	In collaboration with GM/FC-PAD, determine the performance of MEAs with SOA d-PtCo/C cathode catalyst relative to the targets of 0.44 A/mg-PGM mass activity, 1000 mW/cm^2 at rated power, and 300 mA/cm^2 at 800 mV.	03/19
3	In collaboration with GM/FC-PAD, determine the durability of MEAs with SOA d-PtCo/C cathode catalyst relative to the target of 8000 h lifetime.	06/19
4	In collaboration with Strategic Analysis, 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, $Q/\Delta T$ = 1.45 kW/^{o}C, and $40/kW cost.	09/19

Technical Accomplishments: Summary

1. Fuel Cell Systems (FCS) for Light Duty Vehicles (LDV) with PGM-Free Cathode Catalyst

- Collaboration 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 1000 mW/cm^2 power density in a 90-kW_e stack while meeting $Q/\Delta T$ = 1.45 kW/^oC target at 2.5 atm inlet pressure, 95^oC coolant exit temperature, and 1.5 cathode stoichiometry

2. Durability of LDV Fuel Cell Systems with State-of-the-Art (SOA), Low-PGM Pt Alloy Cathode Catalyst

- Collaboration with FC-PAD and GM in obtaining data to develop and durability model
- State-of-the-art (SOA) dispersed d-PtCo/C[1] catalyst system
- Determined performance degradation and acceptable ECSA loss to limit derating in FCS power to 10% over lifetime

3. Fuel Cell Systems for Heavy-Duty Vehicles

- Demonstrated the benefits of hybridization in meeting $Q/\Delta T$ limits for heat rejection in Class 8, Linehaul heavy-duty trucks
- Obtained initial results for achievable stack power density as function of Pt loading in d-PtCo/C and a-Pt/C[2] cathode catalyst systems
- Obtained initial results for durability of d-PtCo/C and a-Pt/C cathode catalyst systems

[1]d-PtCo/C: de-alloyed PtCo catalyst on high surface area carbon (HSAC) support
[2]a-Pt/C: annealed Pt catalyst on surface area carbon support

1.0 Fuel Cell Systems with (AD)Fe-N-C Cathode Catalyst

Exploratory study to baseline PGM-free catalyst performance and durability in automotive FCS

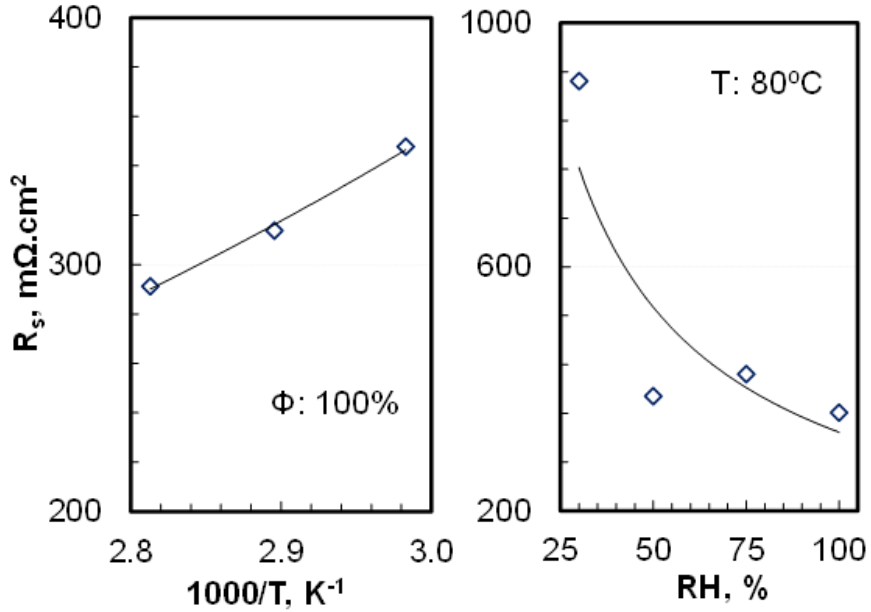
- Protocols for testing performance and durability
- Develop modeling framework for characterizing voltage breakdown and electrode degradation
- Select a catalyst as a compromise between initial activity and stability

MEA composition and fabrication

- Cathode catalyst formulated at LANL (Chung): (AD)Fe-N-C, ~3.8 - 4 $mg_{catalyst}/cm^2$
- CCMs fabricated and tested in differential cell hardware at NREL (Osmieri and Neyerlin): Hand-painted, no hot pressing
- Anode catalyst: 0.2 mg_{Pt}/cm^2, commercial Pt/C

Ionomer resistance determined from ZView analysis of H_2/N_2 impedance at 0.425 V

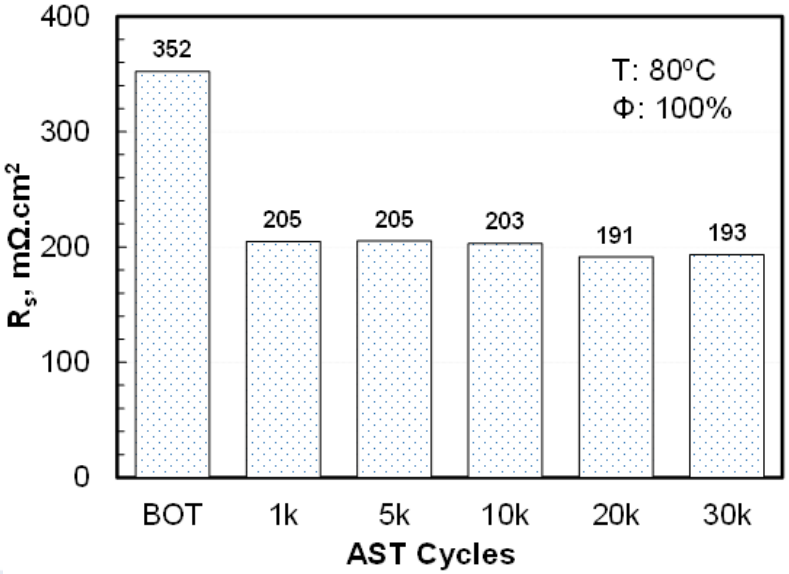
- Thick electrode (cell 1), large ionic resistance, $R_s >> R_\Omega^m$, must be considered in all modeling and analyses



Solid lines are least-square fits

Ionomer stability during catalyst AST

- Conditioning of cell 3 over 1k potential cycles causes >40% decrease in sheet resistance (R_s)
- No ionomer degradation during AST in spite of ~50% decrease in catalyst sites suggesting iron dissolution



***Catalyst formulated at LANL (H. Chung). MEA fabricated and tested at NREL (Osmieri & Neyerlin).**

Kinetics of ORR on (AD)Fe-N-C Catalyst in H_2/O_2

Distributed ORR kinetic model, 100% active sites (θ)

- For Tafel kinetics, η_s^c and iR_Ω^c are separable

$$\eta_c = E_N - E - iR_\Omega^m - \eta_s^a$$

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

$$i = i_0 e^{\frac{\alpha nF}{RT}\eta_s^c}$$

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

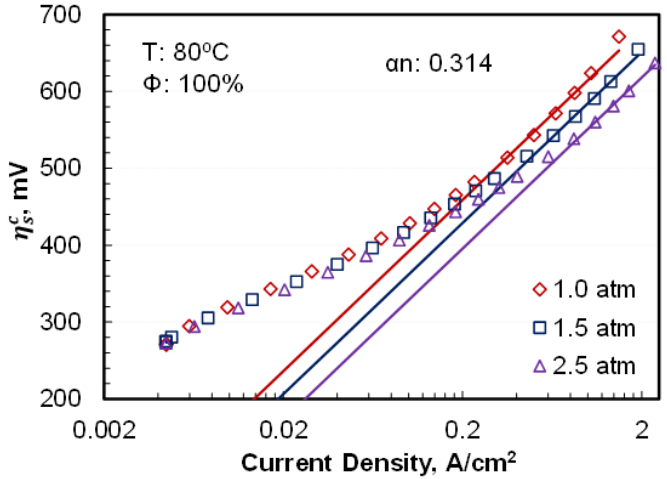
η_c: Cathode overpotential

η_s^c: ORR kinetic overpotential

δ_c: Electrode thickness

σ_c: Ionomer conductivity

- Double Tafel slope, kinetic constants determined from η_s^c at low potentials



ORR Catalyst Activity

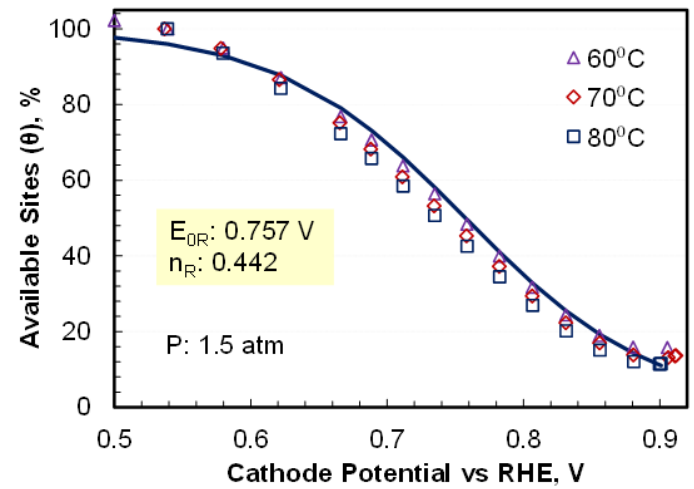
- 7.3 ± 0.5 mA/cm² areal current density (i_0^s) at 0.9 V IR-corrected cell voltage in H_2/O_2, 1.5 atm, 80°C, 100% RH
- Cell performance at 0.8 V H_2/air, 1.5 atm, 80°C, 100% RH: 26.6-29.8 mA/cm² measured, 31.5-

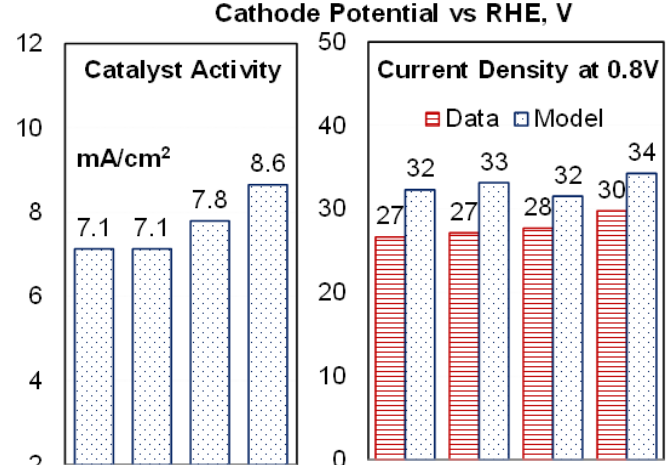
Potential dependence of available active sites

$$i + i_s = i_0\theta e^{\frac{\alpha nF}{RT}\eta_s^c} \qquad 1/\theta = 1 + e^{\frac{n_R F}{RT}(E_c - E_{0R})}$$

E_c: Cathode potential; E_{oR}: Redox potential;
n_R: Effective no. of electrons transferred during change in oxidation state

- Near OCV, <10% of sites are available





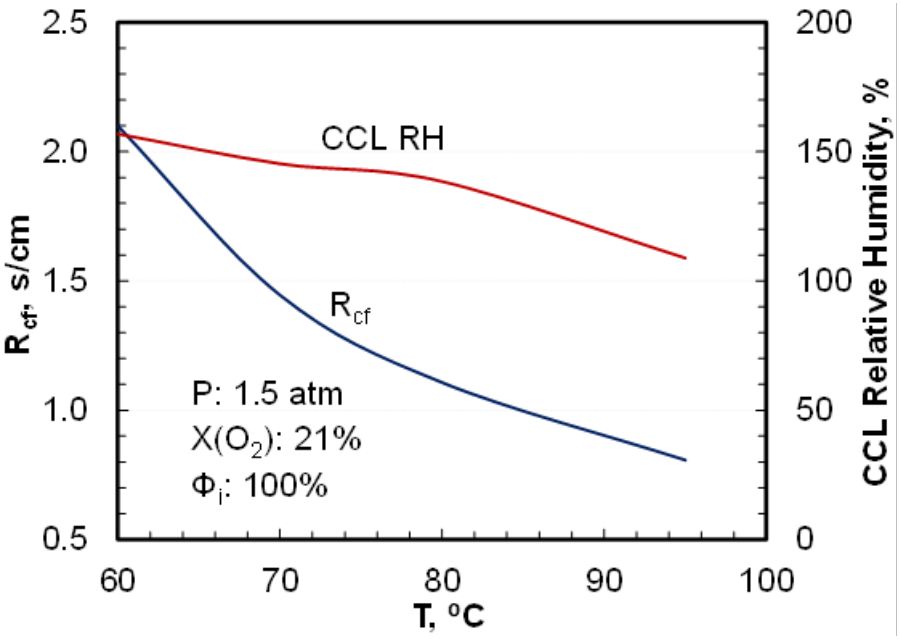
Oxygen Transport in Electrode

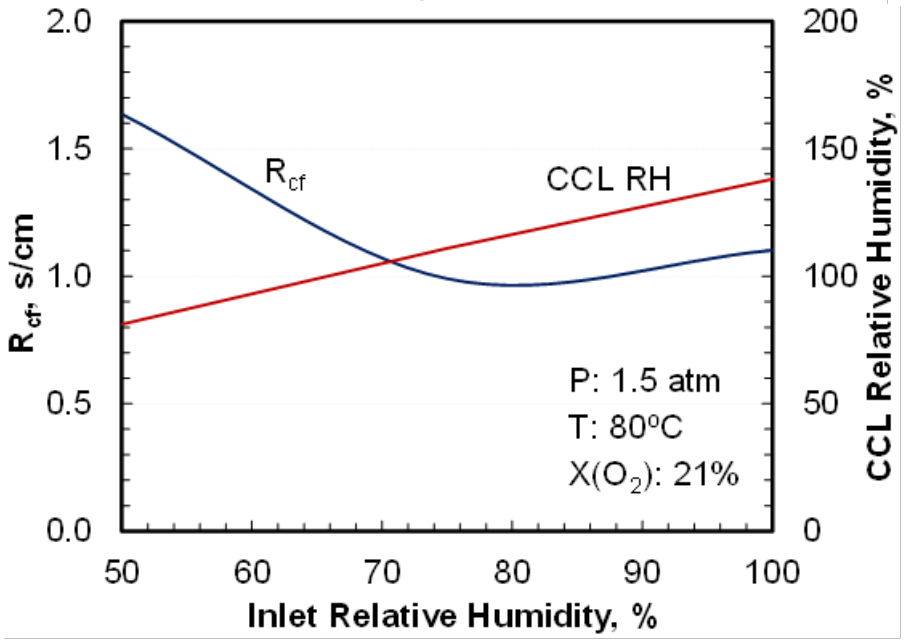
O_2 Transport Resistance (R_{cf}) in Cathode Catalyst Layer (CCL)

- $R_m = R_g + R_d + R_{Kn} + R_{cf}$
- $R_g = R_{gr}(T_r/T)^{1.75}(P/P_r)$
- $R_d = R_{dr}(T_r/T)^{0.5}(P/P_r)$
- $R_{cf} = R_{cfr} f_1(T) f_2(\varphi)$
- R_{cf} modeled as function of CCL temperature and RH

R_{cf} in ~100-µm thick PGM-free electrode is 2-3 times higher than in <10-µm thick low-PGM electrodes

- Comparable value of R_{cf} for 0.1 mg/cm^2 Pt loading, HSAC support, I/C=1.0, 80°C, 100% RH: 0.5 s/cm

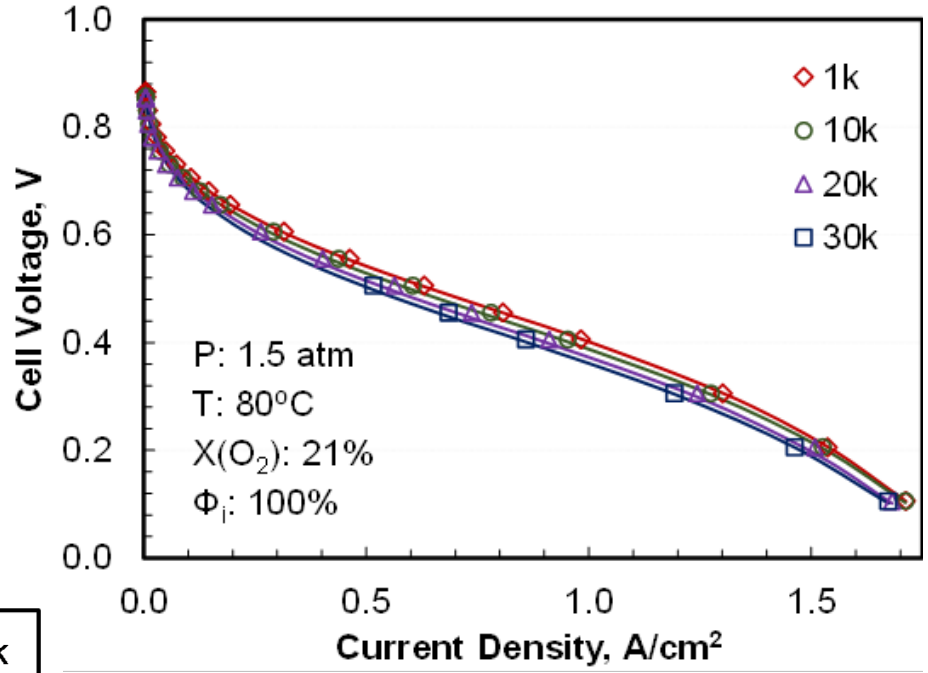


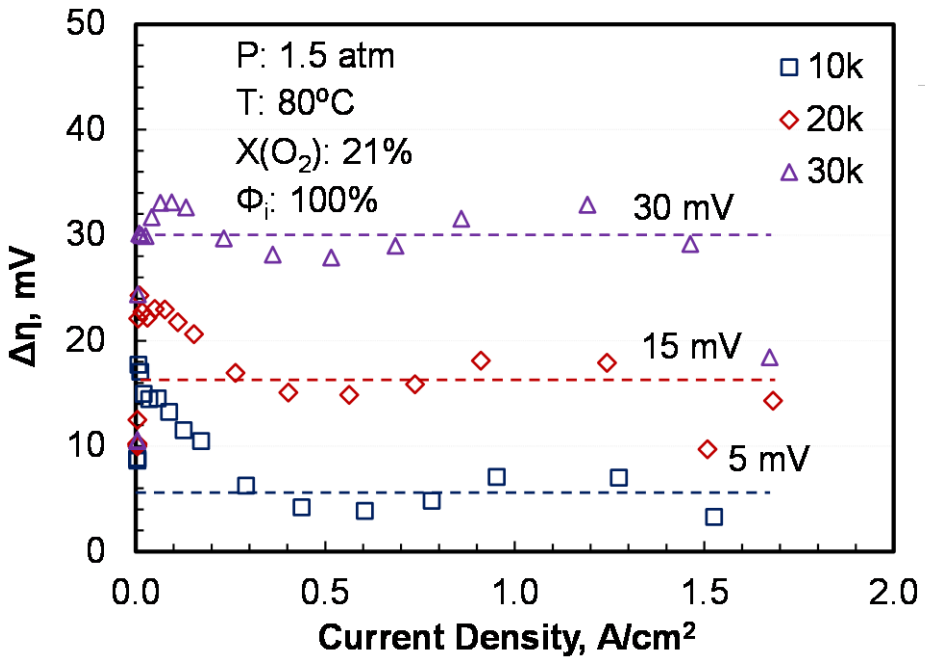


Catalyst Durability

Degradation after 30k AST potential cycles (0.6 - 0.95 V trapezoid) with limited intra-test characterization*

- Voltage loss: 5 mV after 10k cycles, 15 mV after 20k cycles, and 30 mV after 30k cycles
- **Performance degradation mainly due to loss in catalyst activity**





No increase in mass transfer overpotentials – transport resistance is unaffected by AST potential cycles

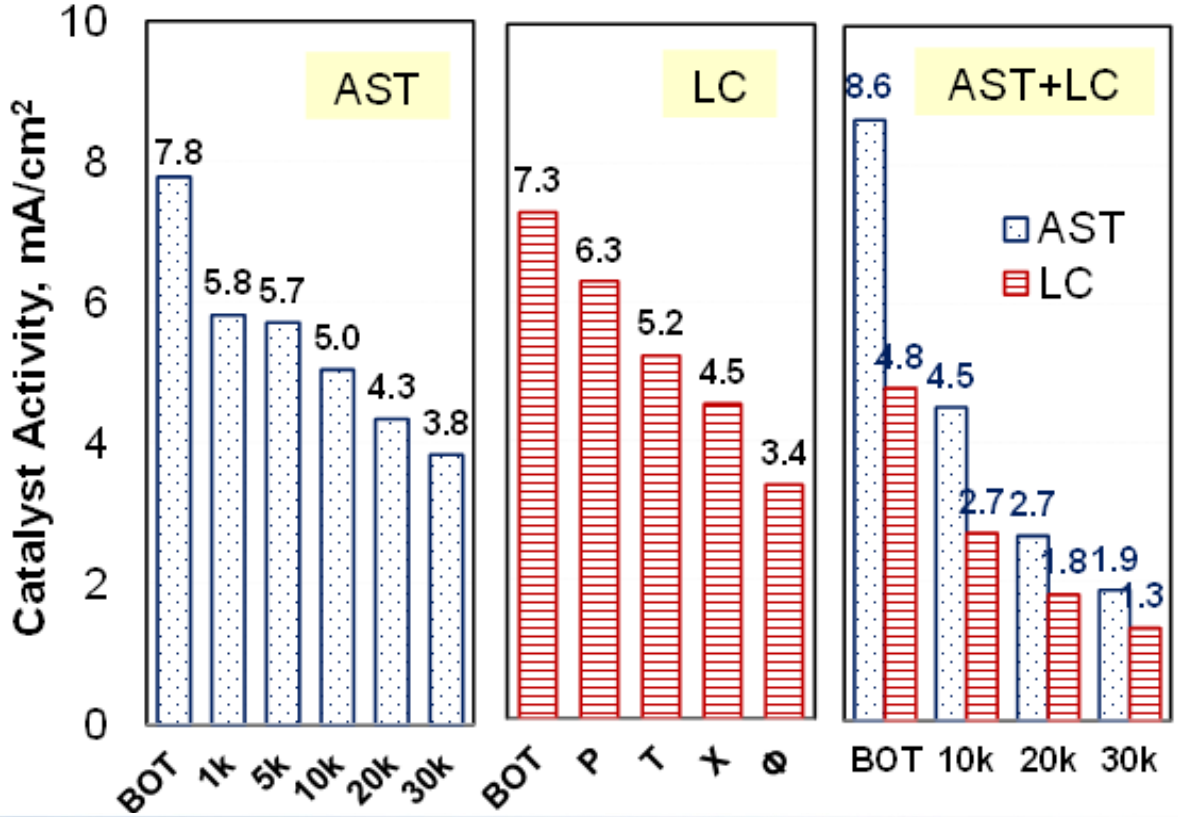
- $\eta = \eta_m + \eta_s^c = E_N - (E + iR_\Omega^m + iR_\Omega^c)$
- $\Delta\eta = \Delta\eta_m + \Delta\eta_s^c = \eta - \eta(1k)$
- $\Delta\eta_s^c$ is independent of current density for $i > 0.4$ A/cm²

***Solid lines are from model, symbols are data**

Degradation of Catalyst Activity

(AD)Fe-N-C catalyst* has low initial activity but is quite stable under cyclic potentials

- ~50% loss in activity after 30k AST cycles, approaching target; Faster loss over first 1k cycles
- >50% loss in activity after 15 polarization curves (7.5 h) at different pressures (1, 1.5, 2.5 atm), temperatures (60, 70, 80, 95°C), O_2 mole fractions (2, 5, 10, 21%), and RH (30, 50, 75, 100%)
- In combined AST with load cycles, majority of the activity losses occur during polarization measurements, 8.5 h on AST, 8 h on load cycles (LC)

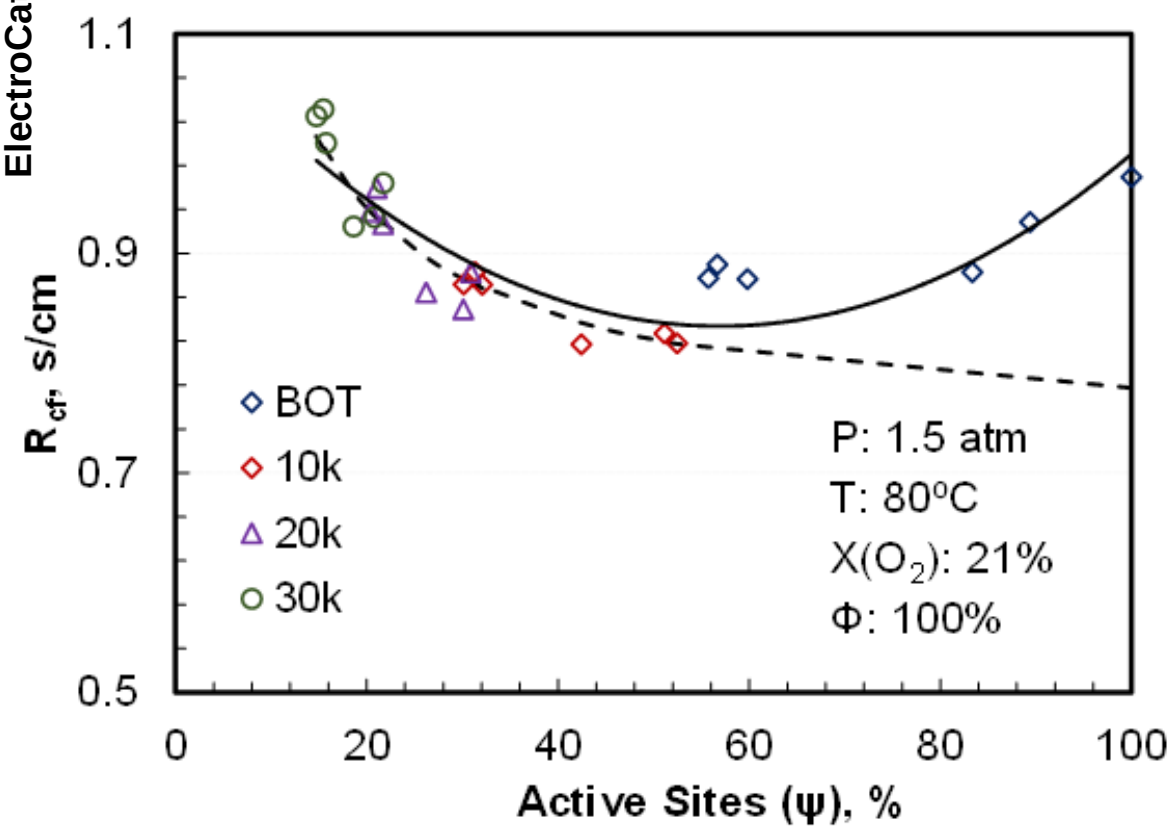


*Data from three different cells

O_2 Transport Resistance in Aged PGM-Free Electrode

>75% loss in active sites* causes <20% increase in O_2 transport resistance (R_{cf}) in the atomically-dispersed catalyst layer

- Low PGM catalyst: 75% loss in ECSA quadruples R_{cf}



R_c: Pore resistance

R_f: Film resistance

δ_c: CCL thickness

L_c: Catalyst loading

A_c: BET area

R_{cf} at Limiting Current Condition

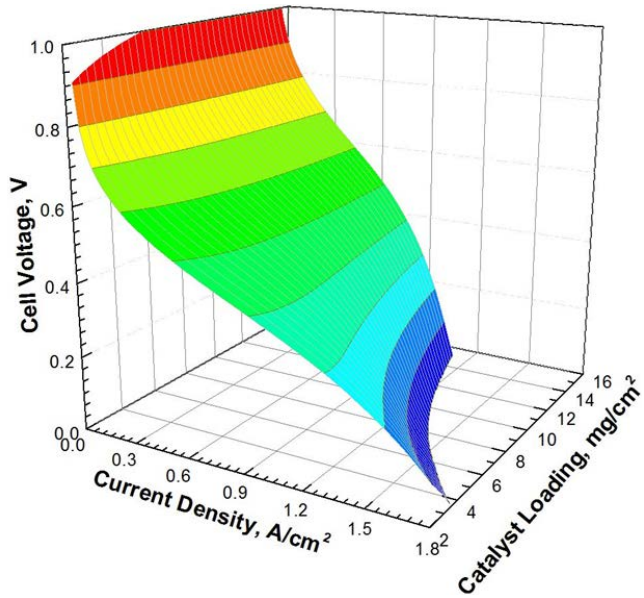
- $R_{cf} = \frac{R_c}{\beta}\coth(\beta)$
- $\beta^2 = \frac{R_c}{R_f}$
- $R_c = \frac{\delta_c}{D_{O_2}}$
- $R_f = R_{f1} + \frac{R_{f2}}{\psi L_c A_c}$

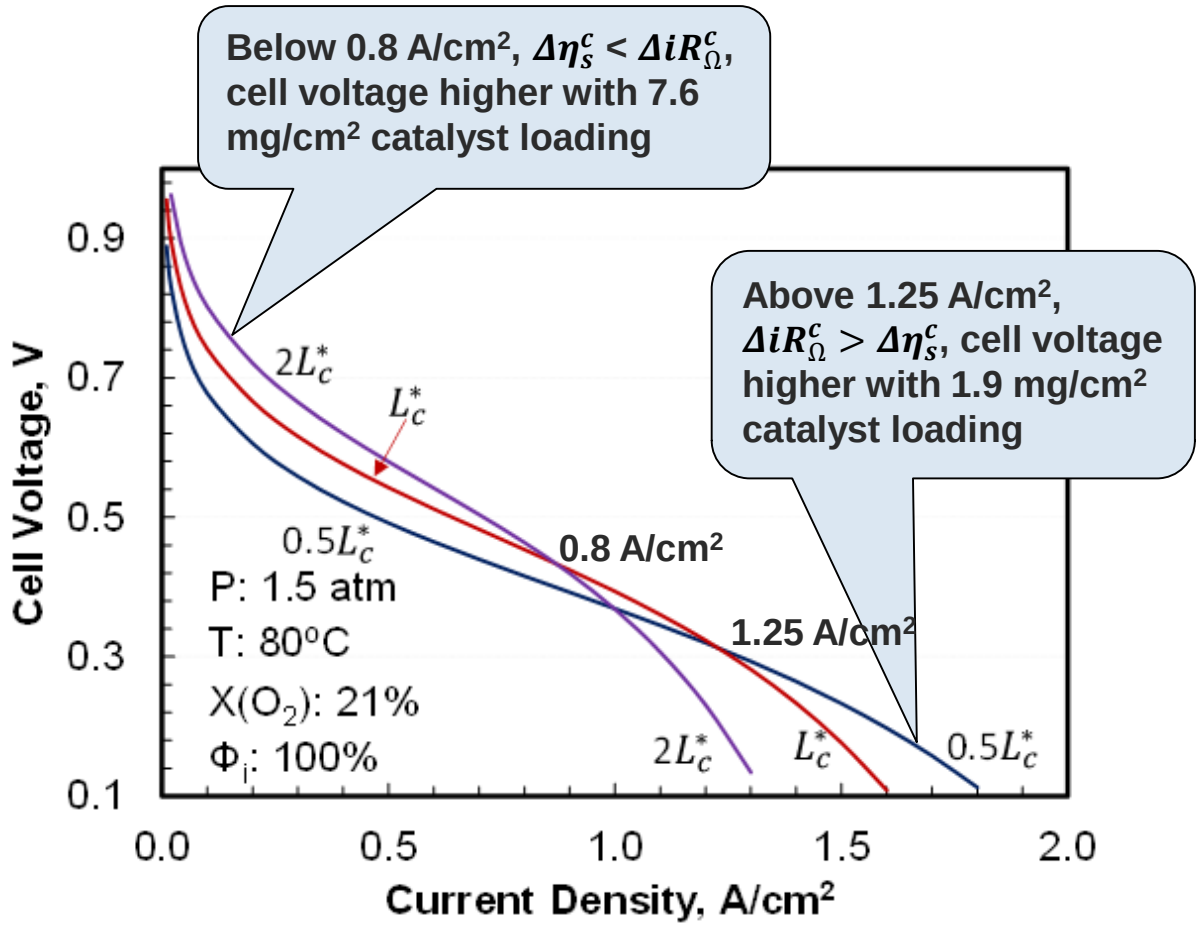
$R_c > R_f$ for the 100-μm thick PGM-free electrode

- $R_c = 8.7$ s/cm
- $R_{f1} = 0.061$ s/cm
- $\frac{R_{f2}}{L_c A_c} = 0.008$ s/cm

Optimization of Catalyst Loading

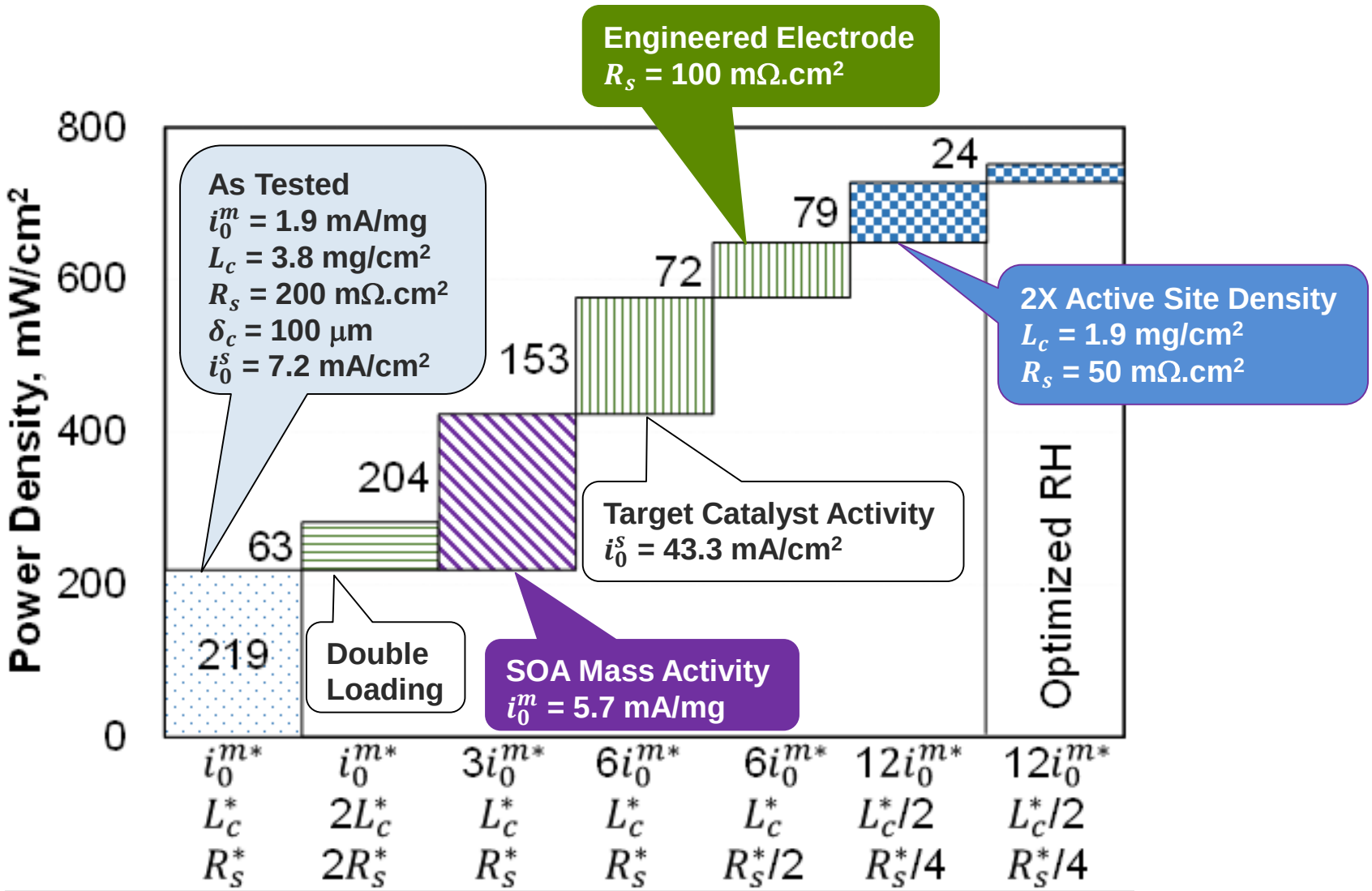
For a catalyst with given mass activity, 1.9 mA/mg for (AD)Fe-N-C, optimum catalyst loading for higher performance depends on current density





Reaching Performance and Cost Targets

Systematic improvements* needed in catalyst activity and electrode structure to reach 1000 mW/cm^2 power density in a 90-kW$_e$ stack while meeting Q/ΔT = 1.45 kW/^{o}C target at 2.5 atm inlet pressure, 95°C coolant exit temperature, and 1.5 cathode stoichiometry



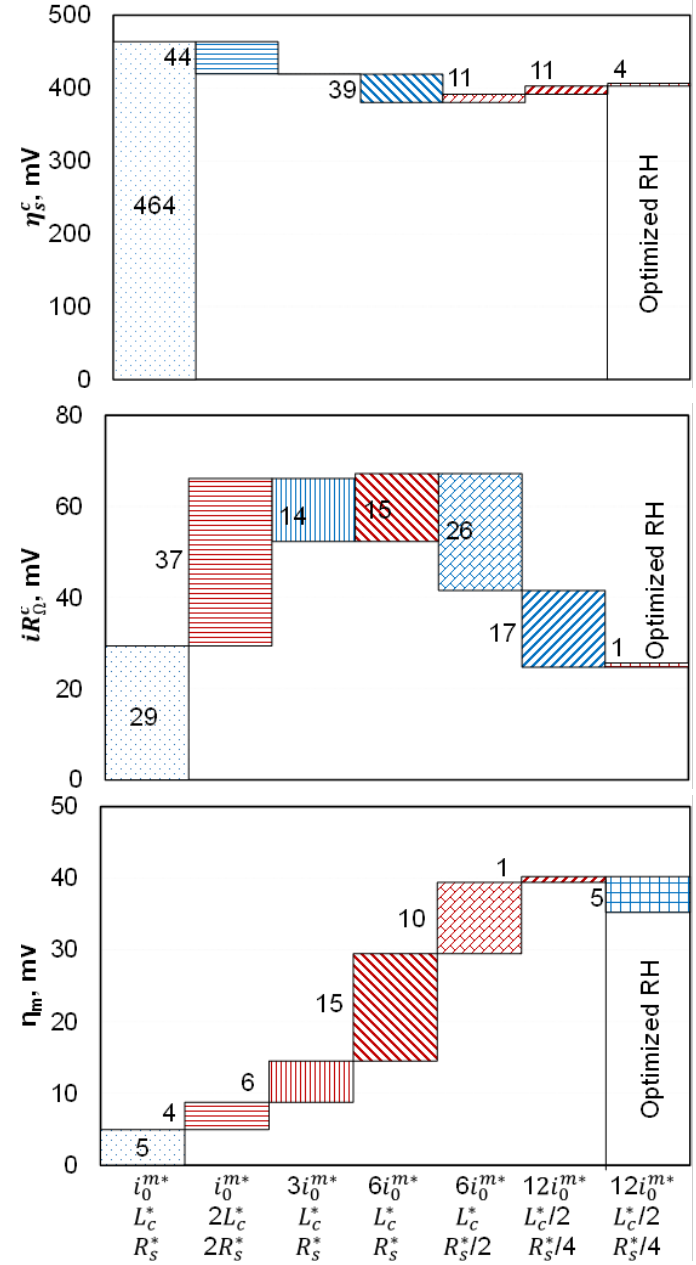
*Improvement in power density comes from higher current density at constant cell voltage (656 mV)

Mechanism of Power Density Improvement

Advances Needed

- Reduce kinetic losses with 12X mass activity
- Reduce iR_{Ω}^{c} overpotential with 2X active site density and engineered electrode structure for 50% lower sheet resistance
- Manage mass transfer losses with 0.5X electrode thickness

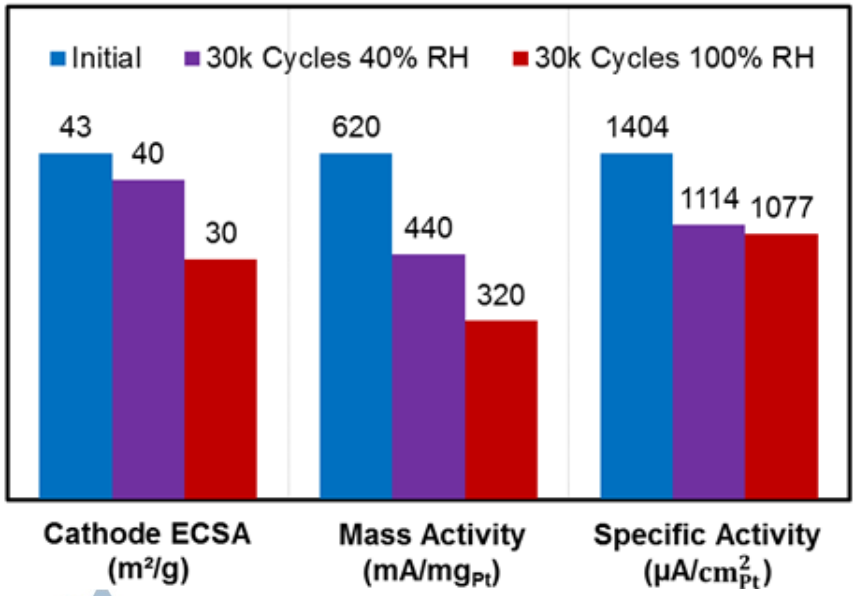
	(AD)Fe-N-C Catalyst	Advanced Catalyst
Mass Activity	1.9 mA/mg	22.6 mA/mg
Catalyst Loading	3.8 mg/cm^2	1.9 mg/cm^2
Specific Activity	7.2 mA/cm^2	43.3mA/cm^2
Electrode Thickness	100 μm	50 μm
Sheet Resistance	200 mΩ.cm^2	50 mΩ.cm^2
Current Density	330 mA/cm^2	1150 mA/cm^2
Kinetic Loss	465 mV	405 mV
Ohmic Loss	40 mV	70 mV
Mass Transfer Loss	12 mV	35 mV

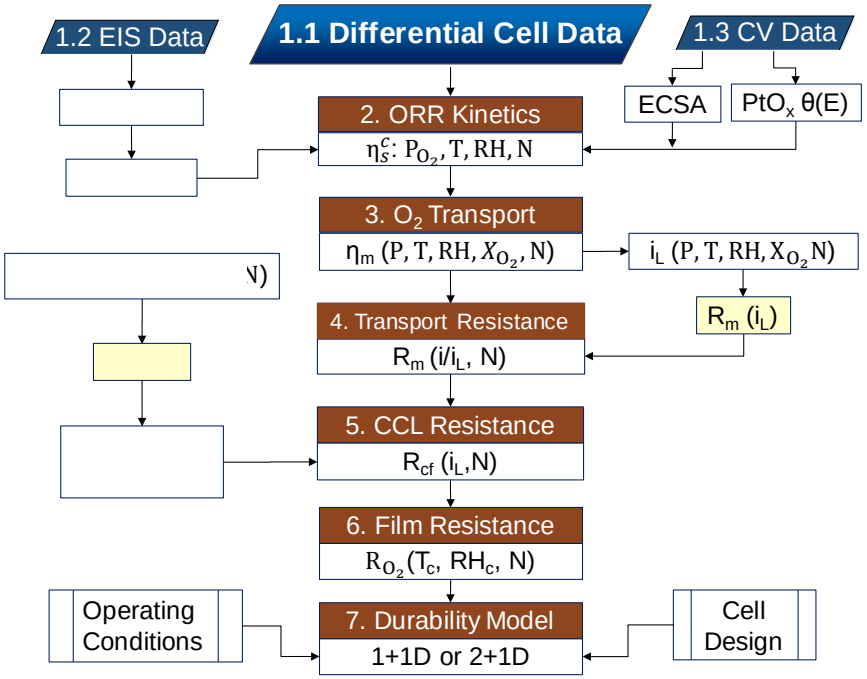


2.0 Fuel Cell Durability Model Framework using Single Cell Hardware

Degradation Model for ORR Kinetics and O_2 Transport Resistance*

- Degrade cells using catalyst AST protocol for 15k, 30k and 50k cycles
- Vary upper potential limit: 0.95, 0.90, 0.85 V
- Measure cell performance and H_2/N_2 EIS at BOT and EOT for 12 operating conditions; 1-2.5 atm; 60-95°C; 30-100% RH; 5-21% $X(O_2)$
- Characterize changes in catalyst and electrode structure using TEM, SAXS and nano-CT (pending)
- Measure and model Pt and Co dissolution using online ICP-MS (pending)





GCtool Model

Representative State-of-the-Art Low-PGM MEA		
	Cathode	Anode
Catalyst	d-Pt_3Co/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	

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

ORR Kinetics on Degraded d-PtCo/C Catalyst

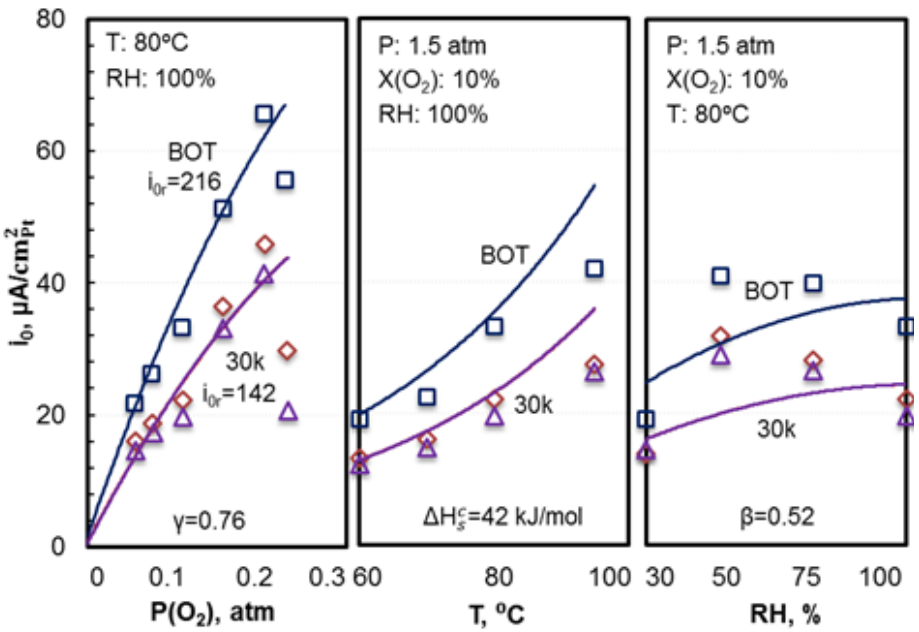
- Negligible changes in kinetic parameters denoting reaction order (γ), activation energy (ΔH_S^c), and RH dependence (β)
- Majority of the 33% drop in i_{0r} (proportional to specific activity, $\mu A/cm_{Pt}^2$), occurs in AST at 40% RH (30k-1) during which time ECSA drops by 7.5%
- Beyond 7.5% ECSA loss, degradation in mass activity in AST at 100% RH (30k-2) is due to decrease in roughness (S_{Pt})

Distributed ORR Kinetic Model

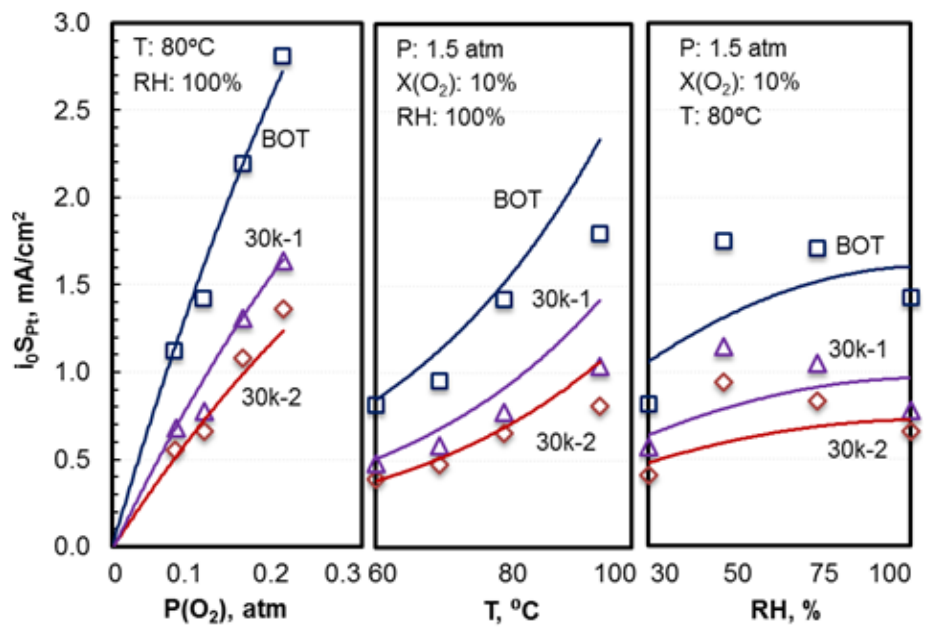
- $\eta_c = \eta_s^c + iR_\Omega^c\left(\frac{iR_s}{b}\right)$

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

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



Effect of Co dissolution on ORR kinetics



Combined effects of Co dissolution and

Effect of Ageing on O_2 Transport Resistance (d-PtCo/C Catalyst)

After 30k cycles, R_{cf} has increased by >50% at 40% RH exposure and >125% at 100% RH exposure

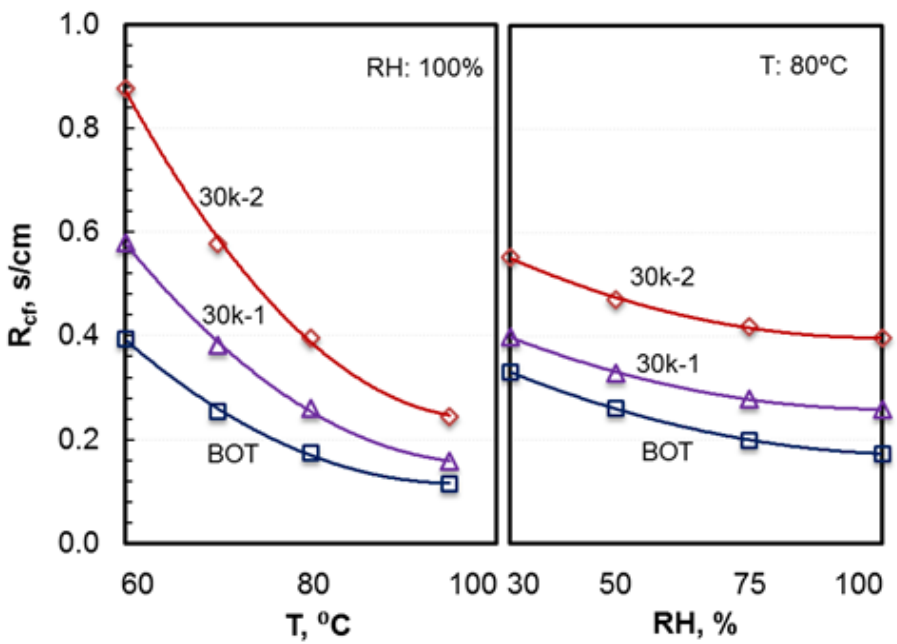
- Lower S_{Pt} accounts for 8% of the increase in R_{cf} at 40% exposure and 45% increase at 100% exposure
- 48-60% of the increase in R_{cf} is associated with reduced permeability of O_2 through the ionomer

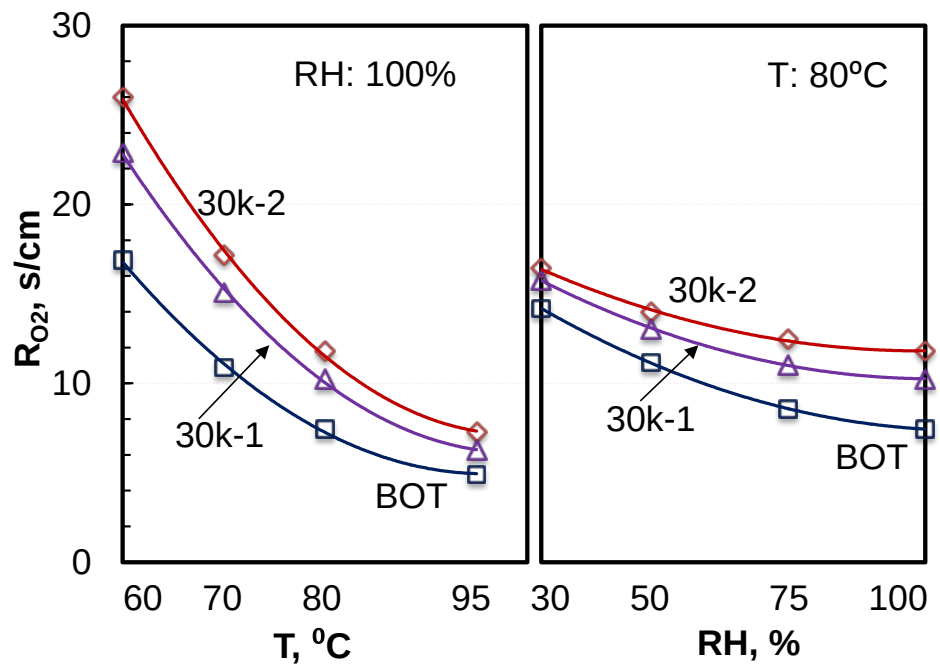
O_2 Transport Model

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

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

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



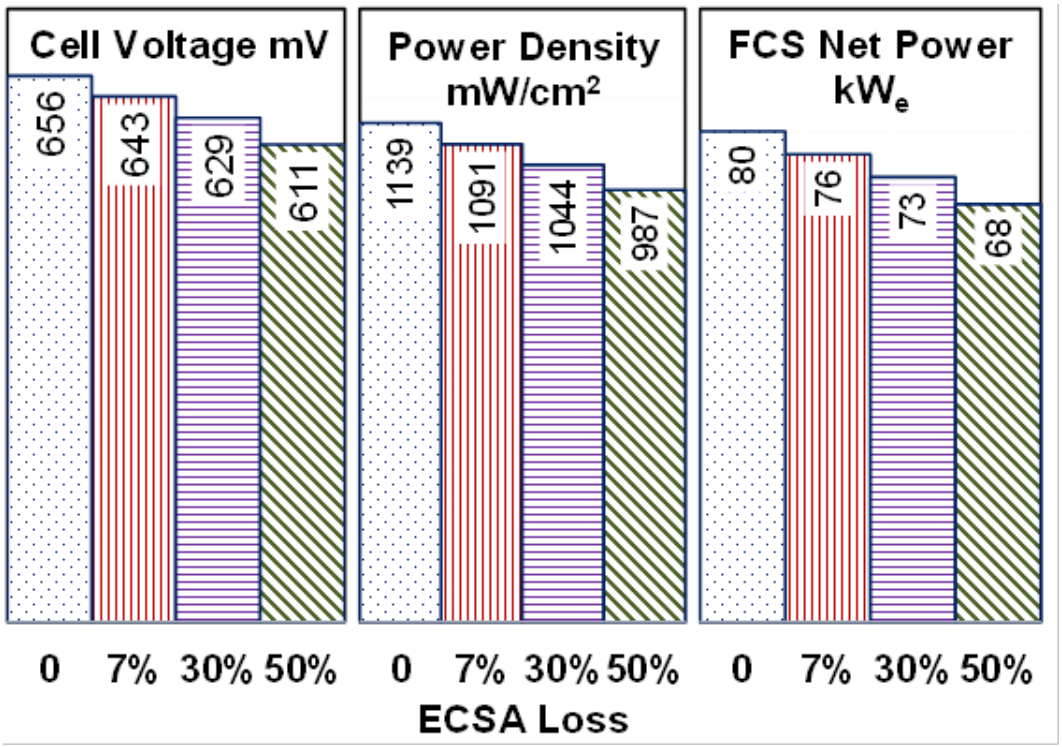


Projected FCS Performance Degradation (d-PtCo/C Catalyst)

Simulations at constant air flow rate (variable cathode stoichiometry) and heat rejection

- To meet the target of 10% derating in FCS power over lifetime, the acceptable ECSA loss (ΔA_{Pt}) is limited to ~35%

	ECSA	Mass Activity	Specific Activity	Cell Voltage	Power Density	Current Density	FCS Power
	m^2/g	mA/mg_{Pt}	$mA/cm^2{}_{Pt}$	mV	mW/cm^2	A/cm^2	kW_e
BOL	43	650	1450	656	1139	1.736	80
EOL	28	320	1090	627	1038	1.654	72

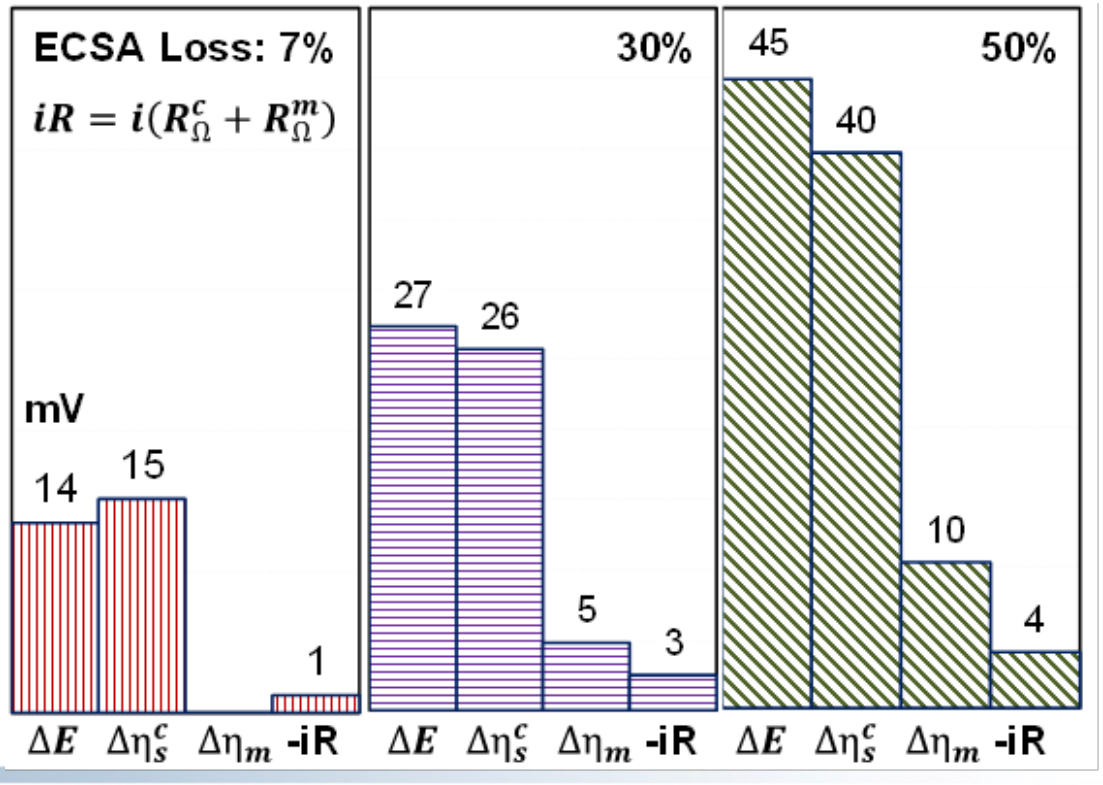


Mechanism of Performance Degradation (d-PtCo/C Catalyst)

Simulations at constant air flow rate (variable cathode stoichiometry) and heat rejection

- Cell voltage loss at rated power mainly due to increase in kinetic overpotential

	Cell Voltage	Kinetic Loss	Ohmic Loss	Mass Transfer Loss
	mV	mV	mV	mV
BOL	656	392	71	55
EOL	611	431	67	65
ΔV	45	40	-4	10



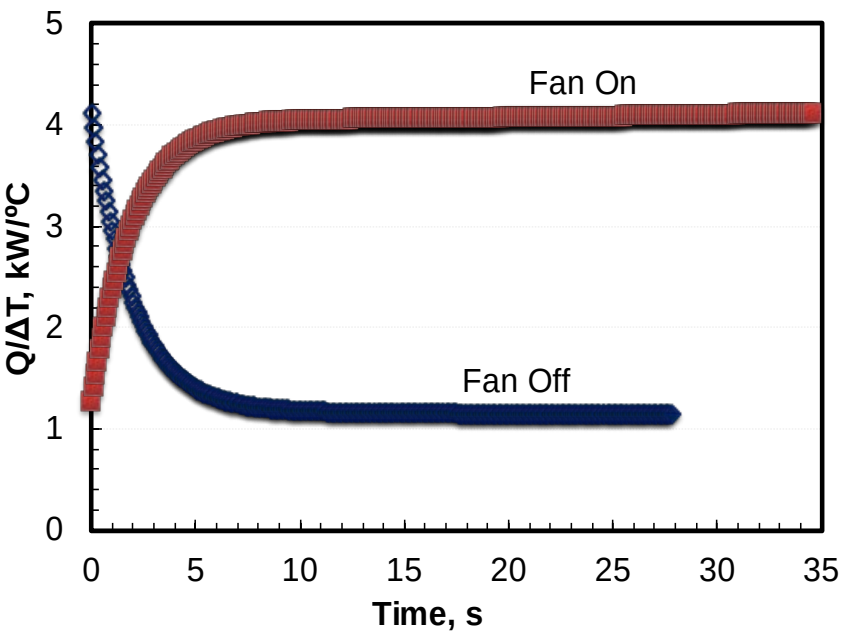
3. Fuel Cell Systems for Heavy-Duty Vehicles: Heat Rejection in Class 8, Linehaul Trucks

Continuous duty cycles that are critical in determining heat rejection requirement*

- For traffic safety, must maintain 30 mph on 6% grade (infrequent occurrence)
- For >1,000,000 mile durability, limit stack temperature on 60-mph cruising speed
- To facilitate adoption of new technology, minimal changes to heat rejection equipment

Autonomie simulation of radiator heat transfer on 6% grade, 330-kW baseline power

- Single speed, 30-kW radiator fan turned on when coolant temperature >105°C
- Radiator fan turned off when coolant temperature < 95°C



Q/ΔT Limits for Diesel Trucks

- Hill climbing: Q/ΔT = 4.5 kW/°C, 25°C ambient temperature, radiator fan on
- Highway cruising: Q/ΔT = 2.6 kW/°C, radiator fan off
- Highway cruising: Q/ΔT = 5.4 kW/°C, radiator fan on

Heat Rejection Metrics for Diesel Engines in Class-8 Long Haul Trucks		
	Climb at 6% grade	**Highway Cruising**
Speed	30 mph	60 mph
Maximum/desired coolant temperature	105°C	95°C
Ambient temperature	25°C	50°C
Fan	On	Off
Propulsion Power	330 kW	150 kW

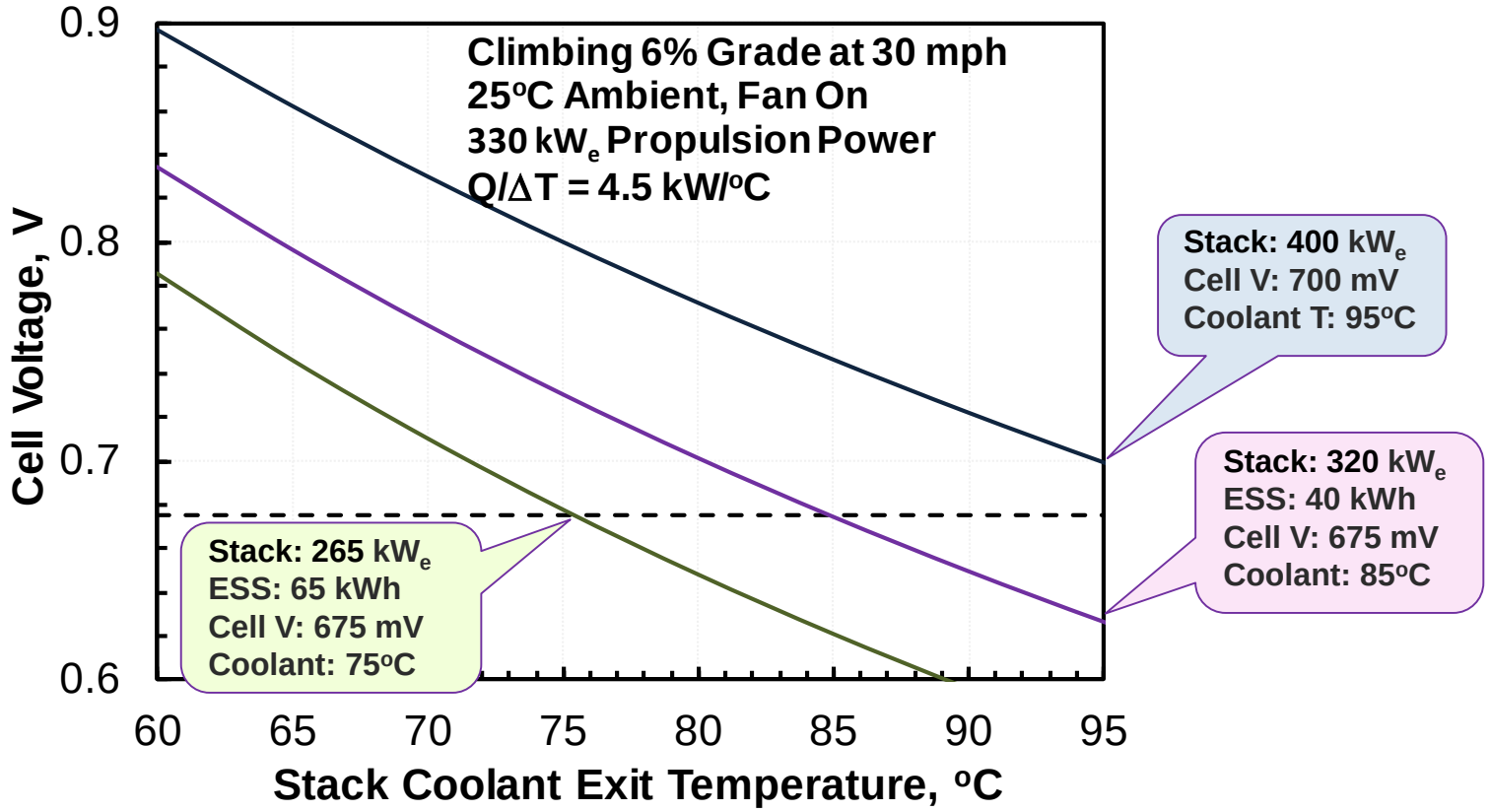
*K. Sim, R. Vijaygopal, A. Rousseau, and J. Marcinkoski, H2@Scale-End Use Applications, Fuel Cell Truck Powertrain R&D Activities and Target Review, July 30 -31, 2018, Argonne National Laboratory

Fuel Cells for Linehaul Heavy-Duty Trucks
Envelope of Operating Potentials and Temperatures

Stand-alone stack needs to operate at 700 mV cell voltage and 95°C coolant exit temperature at rated power to meet the Q/ΔT constraint.

Benefits of hybrid fuel-cell dominant propulsion system with energy storage battery (ESS)

- Smaller stack (320-265 kW_e) with higher power density (lower cell voltage, 675 mV)
- Improved durability because of lower operating temperature (75-85°C coolant exit T)
- Possible trade-off between power density (cell voltage) and durability (temperature)

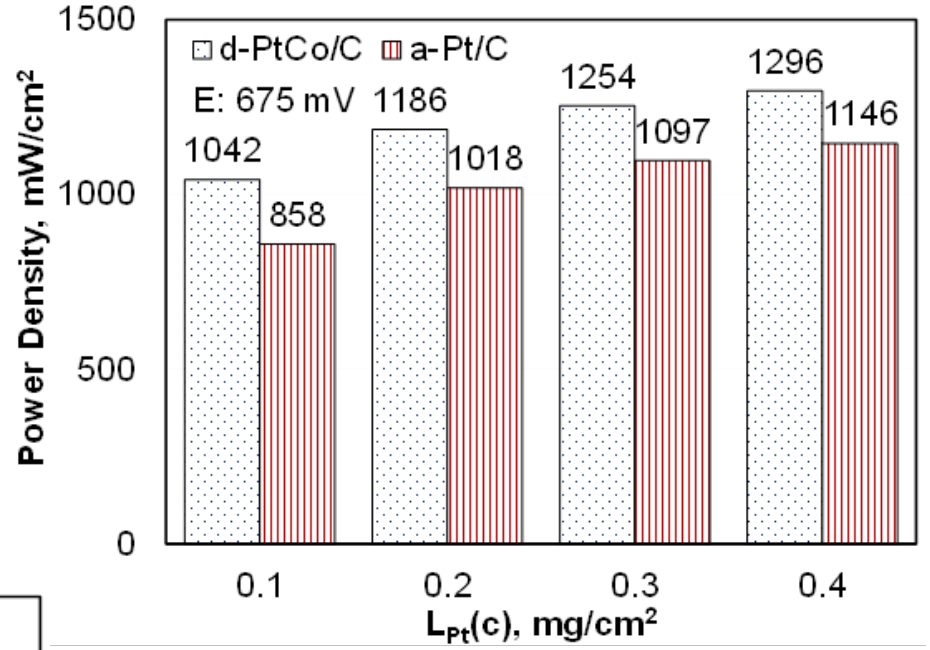


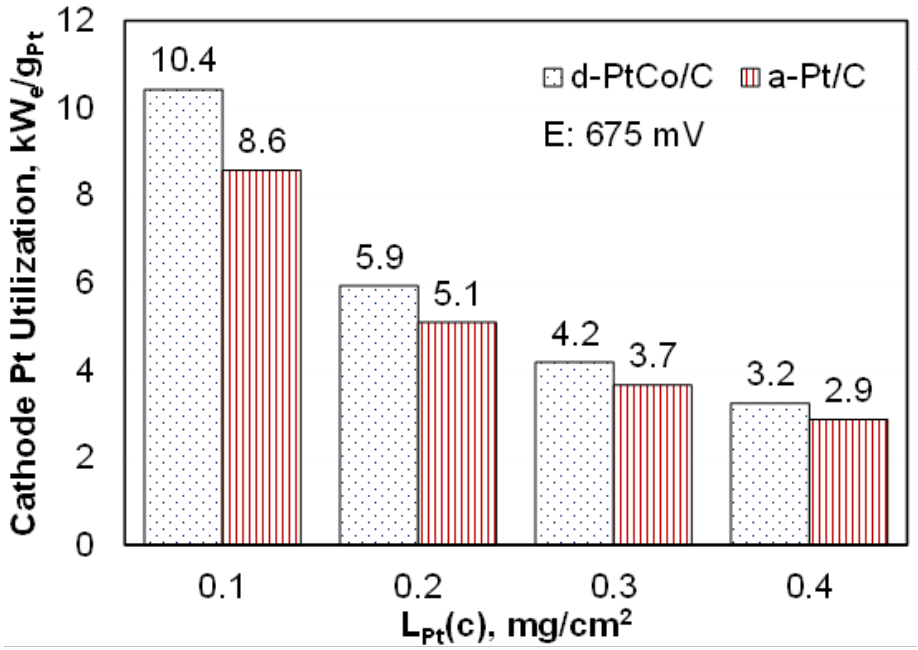
FCS Power = 0.9 x Stack Power; Propulsion Power = (FCS Power – Fan Power) + Battery Power

Performance of Fuel Cell Systems for HDVs

Preliminary Results

- Pt/C: 0.3 for 0.1 - 0.2 mg/cm^2 loading, 0.5 for 0.3 - 0.4 mg/cm^2 loading
- d-PtCo/C catalyst: 650 mA/mg mass activity (i_0^m) and 43 m^2/g ECSA for 0.3 Pt/C, 10% smaller for 0.5 Pt/C
- a-Pt/C catalyst: 330 mA/mg mass activity and 30 m^2/g ECSA for 0.3 Pt/C; 10% smaller for 0.5 Pt/C





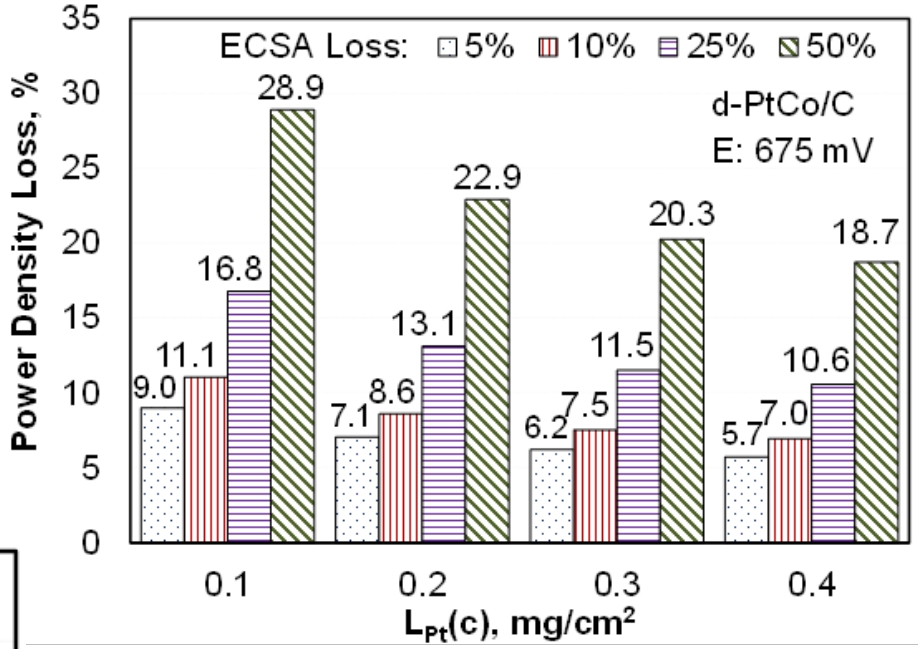
Performance of d-PtCo/C vs. a-Pt/C Catalysts: Preliminary Results

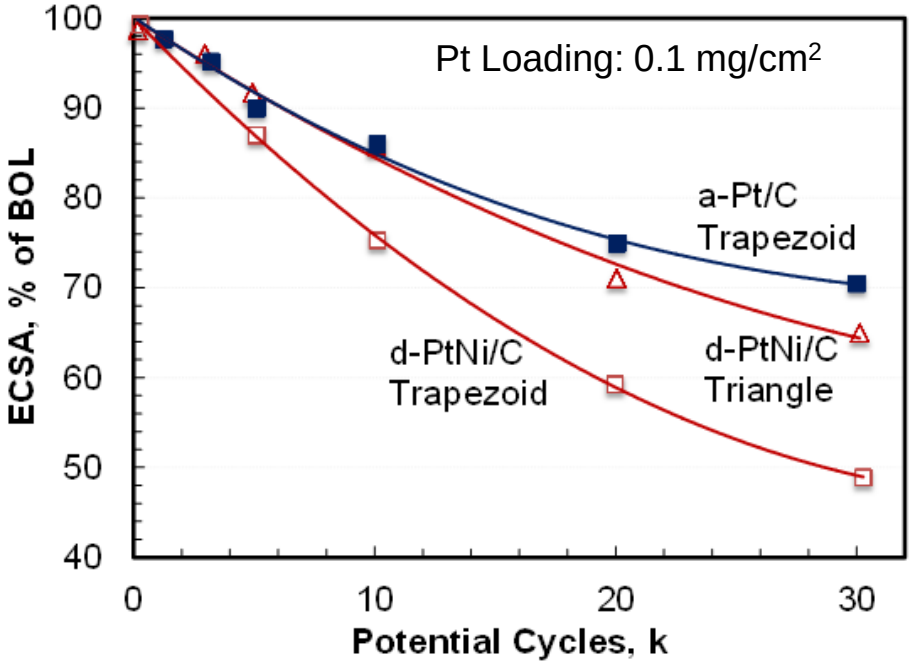
- 2.5 atm stack inlet pressure, 85°C coolant exit T, 1.5 SR(c), 675 mV cell voltage
- Power density at 0.4 vs. 0.1 mg/cm^2 Pt loading: 24% higher for d-PtCo/C catalyst, 34% higher for a-Pt/C catalyst
- d-PtCo/C catalyst provides 21% higher power density at low Pt loading, 13% higher at high Pt loading
- Pt utilization always substantially smaller at higher Pt loadings

Durability of Fuel Cell Systems for HDVs

Preliminary Results

- d-PtCo/C catalyst: Specific activity (i_0^S) decreases and R_{O_2} increases as Co dissolves (see slides 16 and 17)
- a-Pt/C catalyst: Constant specific activity and R_{O_2} during the duty cycle
- $\Delta i_0^m = \Delta(i_0^S S_{Pt})$
- $\Delta R_{cf} = \Delta(\frac{R_{O_2}}{S_{Pt}})$





Durability of d-PtCo/C vs. a-Pt/C Catalysts: Preliminary Results

- Smaller performance degradation at higher Pt loadings
- a-Pt/C catalyst more stable than alloy catalyst on potential cycles
- Tighter system controls needed to retain the intrinsic higher activity of d-PtCo/C catalyst

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)
	ElectroCat: Electrocatalysis Consortium (FC156)
Water Management	Gore, Ford, dPoint: Materials and Modules for Low-Cost, High-Performance Fuel Cell Humidifiers (FC067)
Thermal Management	ANL-Autonomie, 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, identifies and sizes components, and provides this information to SA for high-volume manufacturing cost estimation

Shaded rows indicate main collaborations in FY19

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 life-cycle 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 and PGM-free catalysts for light-duty vehicles
   - 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)
   - Emerging PGM-free catalysts and electrode structures (ElectroCat collaboration)
4. Fuel cell systems for medium and heavy-duty vehicles and locomotives
   - Heat rejection considerations and impact
   - Low and high-PGM catalysts and MEAs for >1,000,000 mile durability
   - Bipolar plates and flow fields for large stacks (300 kW)
   - Configuring systems with multiple stacks
   - Fuel cell systems as range extenders
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:	▪ In collaboration with ElectroCat, demonstrated that (AD)Fe-N-C PGM-free catalyst has 7.3 $\pm$ 0.5 mA/cm^2 initial catalyst activity, and is stable losing <50% activity after 30k 0.6-0.95 V potential cycles. ▪ Projected that 12X improvement in catalyst activity, doubling of active sites and engineered cathode structure are needed for the above PGM-free catalyst to approach the 1000 mW/cm^2 power density target. ▪ Demonstrated that 40% of the loss in mass activity of a SOA d-PtCo/C cathode catalyst after 30k potential cycles is due to Co dissolution and 60% due to growth in particle size. ▪ Verified that the SOA alloy catalyst can achieve >1100 mW/cm^2 power density and >8.25 kW_e/g_{Pt} FCS Pt utilization, and it can meet the durability target if the ECSA loss is limited to 40%. ▪ Proposed initial heat rejection constraint for 400-kW stacks for Class-8 long-haul trucks: $Q/\Delta T$ = 4.5 kW/^{o}C on 6% grade. Showed that high Pt loading (0.4 mg/cm^2), 675 mV cell potential at rated power, and battery hybridization may be needed to meet the heat rejection and durability requirements.
Collaborations:	ElectroCat, FC-PAD, GM, Garrett – Advancing Motion Corp., SA
Future Work:	Fuel cell systems with PGM-free catalysts Fuel cell systems for heavy-duty vehicles and locomotives System analysis with durability considerations on drive cycles

Reviewers' Comments

Sample comments and feedback

- This work is highly relevant to the DOE technical targets
- The modeling methodology and procedures are highly developed
- The approach of the project is technically sound
- The project showed nice accomplishments this year, in particular regarding the idle state, shut down strategies
- Very good progress made.
- Collaboration with FC-PAD and ElectroCat should be enhanced
- The project is relevant in its role of integrating evolutions of component and sub component performances. A valuable impact is also to help SA to better estimate the cost status. It might be higher if the model could be validated at a stack and/or system level and not only at single cell level
- The use of longer durability testing data (as 100h is very short and 95°C is not representative of real-life) coming either from FC-PAD or from ANL testing using current automotive durability testing protocols
- I would recommend a similar analysis to that performed here for non-PGM (and perhaps an AEM) systems. Increased emphasis on Pt dissolution/impact on ECSA would be beneficial.

Work scope consistent with above recommendations

√ On-going work on performance and durability of PtCo/C catalysts in collaboration with FC-PAD and an industrial partner.

√ Initiated new activity on activity and stability of PGM-free catalyst in collaboration with ElectroCat partners

√ Projected advancements needed in PGM-free catalysts to meet performance targets for light-duty vehicles

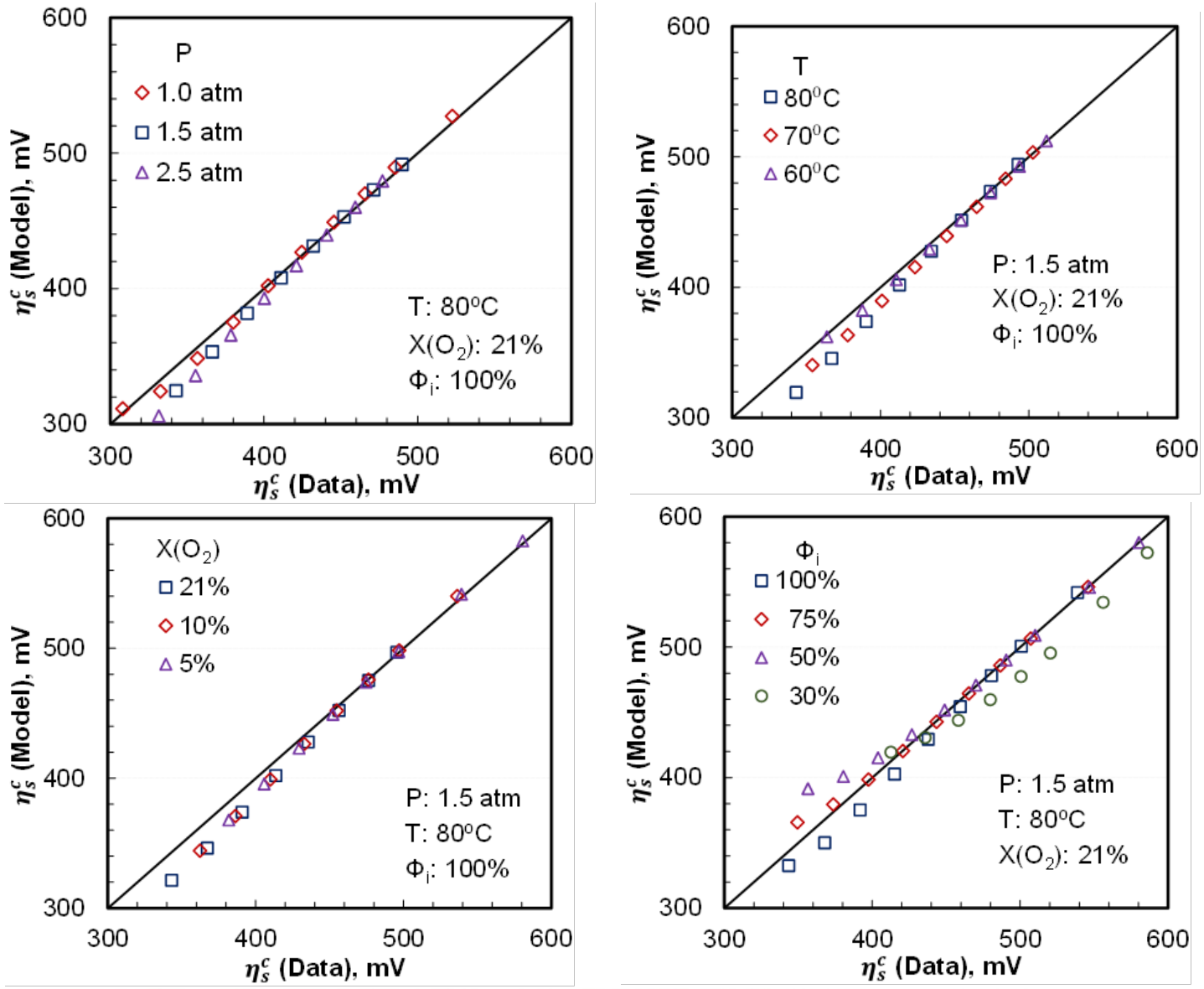
√ Added a task on dissolution of Pt and transition metals. Published a related paper on measuring and modeling of dissolution on potential cycles.

√ Analyzing data on a SOA stack and fuel cell system.

Technical Back-Up Slides

Kinetics of ORR on (AD)Fe-N-C Catalyst in H_2/Air

Kinetic model developed using H_2-O_2 data, 0.5–2 atm $P(O_2)$, applicable to H_2-air data, 0.02–0.25 atm $P(O_2)$, at current densities < 0.3 A/cm^2



Aqueous Stability of PtCo Alloys: Time-Resolved On-Line ICP-MS Measurements

Objectives

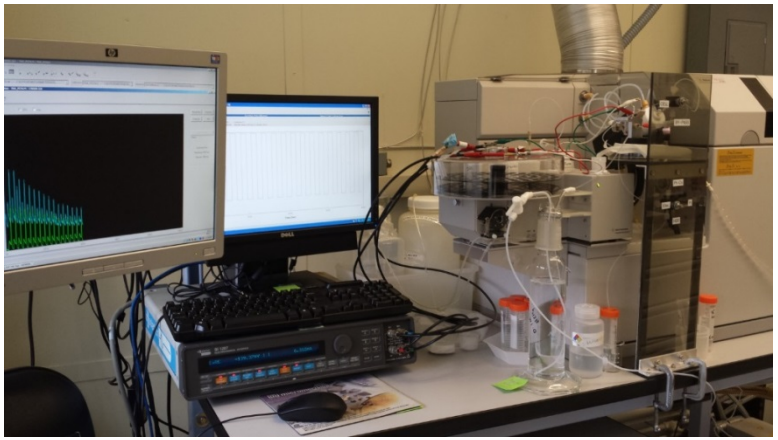
- ✓ Real time measurements of Pt and Co dissolution under cyclic potentials
- ✓ Resolve anodic vs. cathodic dissolution of Pt and Co

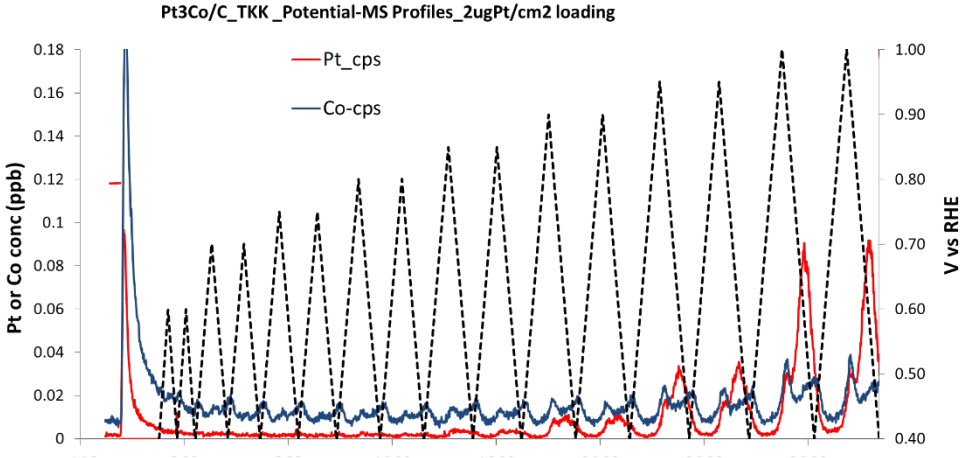
Catalysts

- ✓ TEC36E52, Pt_3Co/HSC, 46.5 wt% Pt, 4.7 wt% Co, 5.7 nm TEM
- ✓ Umicore Elyst P30 0670, 27.5 wt% Pt, 3 wt% Co, 4.4 nm TEM
- ✓ Catalyst-ionomer ink deposited on GC at 2 µg-Pt/cm²

ICP-MS: Agilent 7500ce
Octopole; Cell: BASi

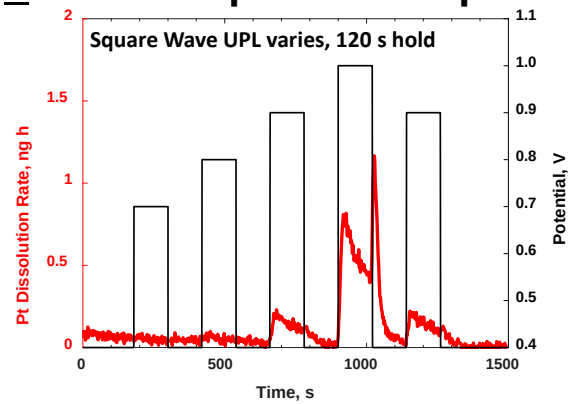
- ✓ Co dissolution observed at all potentials
- ✓ Distinct peaks in anodic and cathodic dissolution of Pt above 0.9 V
- ✓ Potential dependent dissolution rates of Pt and Co



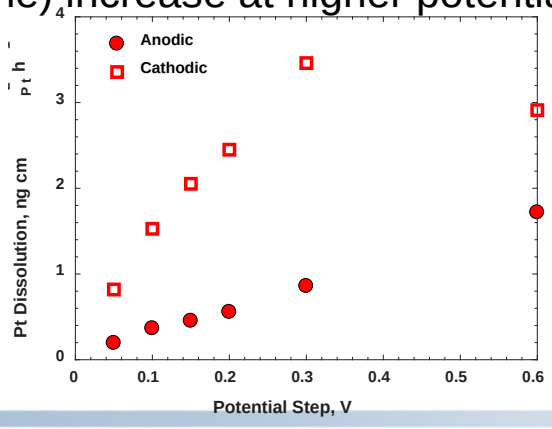


Dissolution of Pt from Umicore Pt_7Co_3/C Cathode Catalyst on Stair-Case Potentials, 180-s Potential Hold

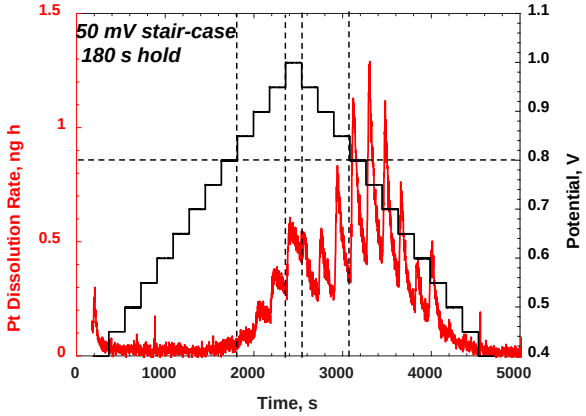
- ✓ **Cathodic dissolution not significant for UPL ≤0.9 V in square wave potentials**



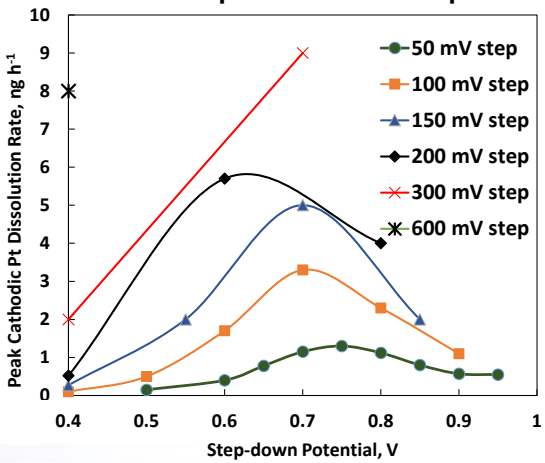
- ✓ **~3-time higher Pt dissolution during cathodic than anodic steps, stair-case potential, 1 V UPL**
- ✓ Both anodic and cathodic Pt dissolution rates (amount dissolved divided by cycle time) increase at higher potential steps



- ✓ Distinct anodic and cathodic peaks
- ✓ Anodic peaks higher at higher potentials
- ✓ Highest cathodic peak on potential step from 0.8 to 0.75 V

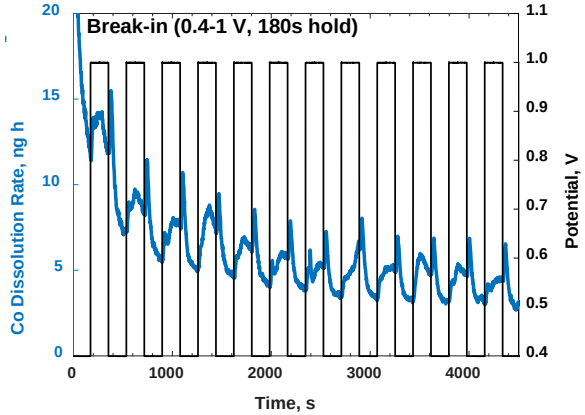


- ✓ Peak cathodic dissolution rate depends on the initial potential and the potential step
- ✓ **Peak cathodic rate reaches a maximum at 0.65-0.75 V step down potential**

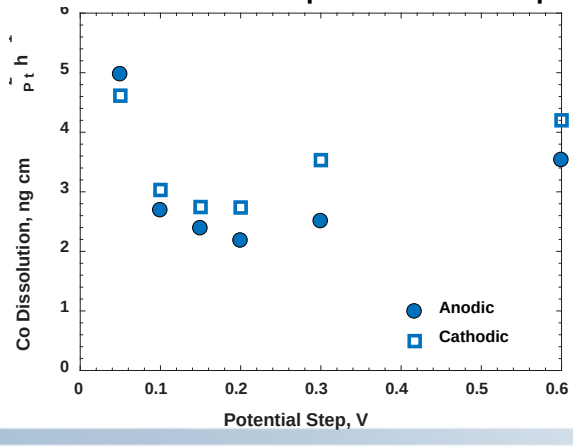


Dissolution of Co from Umicore Pt_7Co_3/C Cathode Catalyst on Stair-Case Potentials, 180-s Potential Hold

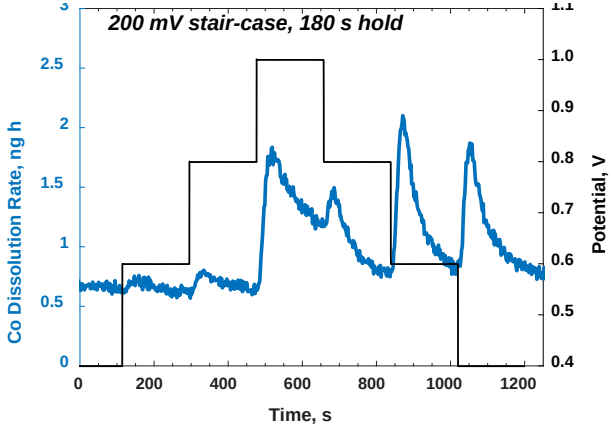
- ✓ Break-in protocol requires >1-h conditioning on 0.4-1.0 V square wave potentials



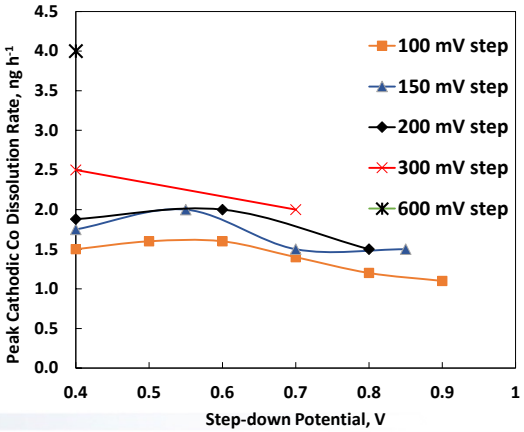
- ✓ **Comparable Co dissolution during anodic and cathodic steps**
- ✓ Anodic and cathodic Co dissolution rates (amount dissolved divided by cycle time) lowest for 200 mV potential step



- ✓ **Anodic Co dissolution rate nearly constant for potentials up to 0.8 V**
- ✓ Anodic peaks observed at potentials >0.8 V
- ✓ Highest cathodic peak on potential step from 0.8 to 0.6 V



- ✓ Peak cathodic dissolution rate depends on the initial potential and the potential step



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JES Focus Issue on Proton Exchange Membrane Fuel Cell (PEMFC) Durability

Potential Dependence of Pt and Co Dissolution from Platinum-Cobalt Alloy PEFC Catalysts Using Time-Resolved Measurements

Rajesh K. Ahluwalia,[1] Dionissios D. Papadias,[1] Nancy N. Kariuki,[2] Jui-Kun Peng,[1] Xiaoping Wang,[2] Yifen Tsai,[1] Donald G. Graczyk,[1] and Deborah J. Myers[2,*,z]

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An electrochemical flow cell system with catalyst-ionomer ink deposited on glassy carbon is used to investigate the aqueous stability of commercial PtCo alloys under cyclic potentials. An on-line inductively coupled plasma-mass spectrometer, capable of real-time measurements, is used to resolve the anodic and cathodic dissolution of Pt and Co during square-wave and triangle-wave potential cycles. We observe Co dissolution at all potentials, distinct peaks in anodic and cathodic Pt dissolution rates above 0.9 V, and potential-dependent Pt and Co dissolution rates. The amount of Pt that dissolves cathodically is smaller than the amount that dissolves anodically if the upper potential limit (UPL) is lower than 0.9 V. At the highest UPL investigated, 1.0 V, the cathodic dissolution greatly exceeds the anodic dissolution. A non-ideal solid solution model indicates that the anodic dissolution can be associated with the electrochemical oxidation of Pt and PtOH to Pt^{2+}, and the cathodic dissolution to electrochemical reduction of a higher Pt oxide, PtO_x ($x > 1$), to Pt^{2+}. Pt also dissolves oxidatively during the cathodic scans but in smaller amounts than due to the reductive dissolution of PtO_x. The relative amounts Pt dissolving oxidatively as Pt and PtOH depend on the potential cycle and UPL.

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