

Fuel Cells Systems Analysis

R. K. Ahluwalia and X. Wang

2013 DOE Hydrogen and Fuel Cells Program Review Arlington, VA May 13-16, 2013

Project ID: FC017

This presentation does not contain any proprietary, confidential, or otherwise restricted information.



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

- FY13 funding: \$400K
- DOE share: 100%
- FY12 funding: \$600K

Partners/Interactions

- Eaton, Gore, Ford, dPoint
- SA
- 3M, Nuvera
- ISO-TC192 WG12, JARI, LANL
- IEA Annexes 22 and 26
- Transport Modeling 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 Develop a validated system model and use it to assess design-point, part-load and dynamic performance of automotive and stationary fuel cell systems.

- 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

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

Summary: Technical Accomplishments

Validate and document models for pressurized (S1, 2.5-3.0 atm at rated power) and low-pressure (S2, 1.5 atm at rated power) configurations

- **Stack:** Collaborated with 3M in taking cell data to validate the model for NSTFC MEAs and stacks at pressures up to 3 atm
- Air Management: Collaborating with Eaton to develop and model Roots compressors, expanders and other components for fuel cells
- Water Management: Collaborated with Gore, dPoint and Ford to validate the model for a cross-flow humidifier using Gore's sandwich membrane structure
- Fuel Management: Collaborated with 3M and Ford to validate the model for anode subsystem, including impurity buildup and H_2 ejectors
- System Analysis: Updated and optimized system performance at rated power and part loads (FCS with Honeywell air system)



Stack Model Validation and Documentation

Collaboration with 3M to obtain reference performance data on 50-cm² cells with 3M MEAs and ternary NSTF catalyst: 0.05(a)/0.1(c) mg-Pt/cm²

- Cathode Pt loadings, L_{Pt}(c): 0.054, 0.103, 0.146 and 0.186 mg/cm²
- Pressures: 1.5, 2.5, 3.0, 1-2.5 atm
- Temperatures: 35 -90°C
- RH: 35-100%
- Anode stoichiometry (SR_a): 1.2-5
- Cathode stoichiometry (SR_c): 1.5-10
- H₂ pump tests for HOR kinetics: 0.7-2.5 atm P_{H2}, 45-90°C



- Dynamic response to step changes in cell current density
- ORR kinetics on NSTF catalyst
- Cathode mass transfer overpotentials
 - Model validation and calibration



ORR Kinetics on PtCoMn/NSTF

Determined kinetic parameters for P_{O2}, T and RH (Φ) dependence (γ, E_{O2} and β) of ORR on NSTF catalyst ,and validated against the measured mass activities for eight cells with 0.054-0.186 mg/cm² Pt loading*

Cell Designation	19574	19577	19453	19478	19504	19524	19530	19531
Pt Loading, mg.cm ⁻²	0.054	0.054	0.103	0.103	0.146	0.146	0.186	0.186
ECSA, m_{Pt}^2 .g ⁻¹	12.4	12.6	9.8	9.8	9.2	8.4	7.2	7.0
SEF, $\operatorname{cm}_{\operatorname{Pt}}^{2} \operatorname{cm}^{-2}$	6.7	6.8	10.1	10.1	13.4	12.2	13.4	13
Catalyst Layer Thickness, mm	0.16 ± 0.018		0.32 ± 0.034		0.47 ± 0.048		0.61 ± 0.061	
H_2 Crossover, mA.cm ⁻²	3.2	3.1	2.8	2.9	3.0	2.4	3.5	3.1
Short Resistance, $\Omega \cdot cm^2$	588	267	933	664	182	216	340	379
Absolute Activity, mA.cm ⁻²	11.3	13.5	17.6	18.8	23.5	23.3	25.5	24.1
Mass Activity, A.mg _{Pt} ⁻¹	0.21	0.25	0.17	0.18	0.16	0.16	0.14	0.13
Specific Activity, mA.cm _{Pt} ⁻²	1.69	1.99	1.74	1.86	1.75	1.91	1.90	1.85



7

HOR/HER Kinetics on PtCoMn/NSTF

Specific exchange current density for HOR/HER on NSTF catalyst with 0.05(a)/0.1(c) mg.cm⁻² Pt loading, measured in 50-cm² cell in H₂ pump mode, at 80°C is 60-110% higher than on Pt/C (NFAL conditioning). Four-fold increase in activity if anode conditioned more completely (RFAL)*.

- Oversaturated H₂: 45-80°C, 0.7-2.5 atm P_{H2}, 1750 sccm H₂
- Anode outlet stream fed to cathode inlet, concurrent flow



*X. Wang, R.K. Ahluwalia, and A.J. Steinbach, Journal of the Electrochemical Society, 160 (3) F251-F261 (2013).

8

Cathode Mass Transfer in NSTF

- Artificial Neural Network (ANN) model for cathode mass transfer overpotential (η_{mc}) and high-frequency resistance (HFR)
- Multilayer Perceptron (MLP) Feed-Forward Network with one hidden layer and 20 neurons, hyperbolic tangent activation function
- Separate sets of weights and biases for 1.5, 2.5 and 3 atm data and for part-load performance



Anode Mass Transfer in NSTF

- Determined mass transfer overpotentials (η_{ma}) from tests: 0-75% N₂ in H₂, variable anode stoichiometry and cathode dew points, 70-85°C, 1.5-2.5 atm.
- Derived and correlated anode mass transfer coefficient as a function of Reynolds number, P, T and H₂ fraction.
- Identified performance losses due to HOR kinetics, anode mass transfer, and decrease in Nernst potential.



Pt Content and System Cost – Interim 2013 FCS

Two-variable optimization study to determine stack T (exit coolant T) and inlet RH_c for lowest system cost* for specified SR_c and system efficiency, 27°C ambient temperature

- Optimum stack T depends on the operating P and SR_c
- Optimum SR_c: 2.5 for P < 1.8 atm, 2 for 1.8 < P < 2.2 atm, 1.5 for P >2.2 atm
- Assumed CEM performance: 71% compressor, 73% expander, 80% combined motor & motor-controller



*Cost estimates from SA correlations for high volume manufacturing

Optimum Pt Loading in NSTF Cathode Catalyst

Three-variable optimization study to determine the combination of stack T, inlet RH_c and SR_c for lowest system cost for specified Pt loading in cathode catalyst ($L_{Pt}(c)$) and system efficiency, 27°C ambient temperature

- Lowest Pt content with 0.05 mg/cm² Pt loading in cathode catalyst
- Lowest system cost with 0.1 mg/cm² Pt loading in cathode catalyst
- Stack and BOP contribute almost equally to the system cost. Raising pressure increases power density even though higher cell V required for specified system efficiency.



Heat Rejection – Q/∆T

Multi-variable optimization study for lowest system cost

 Raising stack T to 95°C to meet Q/∆T constraint results in higher costs (2.5 atm inlet pressure, 40°C ambient temperature)



Air Management System: Roots Compressor and Expander

Collaborating with and providing modeling and system analysis support to Eaton's project. Eaton is still designing the components for fuel cells, but has provided data to help ANL in preparing models.

- Formulated thermodynamic models for Roots blowers and expanders
- Developed performance maps for off-the-shelf Roots compressors: isentropic efficiency, volumetric efficiency, and mechanical efficiency
- Developed performance maps for the first-generation Roots expander: isentropic efficiency, volumetric efficiency, and mechanical efficiency
- Developed performance map for a commercial motor and motorcontroller



Air Management System – Preliminary Performance

Preliminary assessment of a compressor-expander module* using model and available maps of components, all mounted on a single shaft

- ANL Configuration ADT: As tested Roots compressor, expander, and motor and motor-controller
- ANL Configuration PCV: PCV upstream of expander
- ANL Configuration SCE: Scaled compressor and expander

	Parasitic Power (kW)		
Flow Rate	100%	25%	Idle
Status: Centrifugal	11.0	2.3	0.6
Status: Modeled Roots	11.4	2.0	
DOE Target	8.0	1.0	0.2



Water Management System

Collaboration with Gore, Ford and dPoint to develop and validate a model for a cross-flow (or counter-flow) humidifier with Gore 311.05 membrane

- 2-D finite-difference model for heat and mass transfer with ΔP
- Literature data for water uptake and water diffusivity in the ionomer
- Gas phase, interfacial and ePTFE resistances derived from static and dynamic permeation tests (W.B. Johnson, FC067)
- Validated against Ford data for a full-scale unit, 10-100% flow rates, 1.2-2.3 atm, 30-70°C temperature range, 40-90% RH



Assessment of Humidifier Performance

- The cross-flow humidifier with M311.05 membrane meets the DOE target of 4.2 g.m⁻².s⁻¹ at stipulated conditions (including 11°C approach dew point temperature) if the inlet dry air is cooled below 65°C.
 - Additional targets for cost, weight, volume, maximum operating T and pressure differential, pressure drop, air leakage and durability
- Depending on approach T_{dp}, water flux can be 10-30% higher with counter-flow than cross-flow
- With dry air pre-cooled to < 73^oC, water flux exceeds 5 g.m⁻².s⁻¹ at 2.5 atm and 15^oC approach dew-point temperature



Fuel Management

Collaborated with Ford to develop and validate a model for H_2 ejectors with converging-diverging and subsonic nozzles

- Flow choked at nozzle throat, supersonic flow at nozzle exit; oblique shock at inlet to mixing section
- Flow choked at nozzle throat, normal shock inside nozzle
- Subsonic flow in nozzle

Modeled Suction Flow Rate, g·s⁻¹

2

0



Suction

Chamber

Secondary

Flow

Mixina

Chamber

Diffuser

Pipe

Performance of Fuel Management System

- 1. Hybrid ejector-blower system
- Variable inlet pressure with bypass valve to admit additional hydrogen during anode purge
- 2. Anode system without a blower

т RH

2.25

2.00

Ynode SR 1.75

1.50

1.25

1.00

0

ŕ

Increasing

N₂ Content

20

Variable pulse frequency and pulse width* 2.50





Collaborations

Air Management	Eaton
Stack	3M, Nuvera
Water Management	Gore, Ford, dPoint
Thermal Management	Honeywell Thermal Systems
Fuel Management	3M, Ford
Fuel Economy	ANL (Autonomie)
H ₂ Impurities	3M, ISO-TC-192 WG
System Cost	SA
Dissemination	IEA Annex 22 and 26, Transport Modeling 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
- Conducting joint life-cycle cost studies with SA

Future Work

- 1. Support DOE development effort at system, component, and phenomenological levels
- 2. Support SA in high-volume manufacturing cost projections, collaborate in life-cycle cost studies
- 3. Alternate MEAs with advanced alloy catalysts
- De-alloyed PtNi on NSTF (3M collaboration)
- De-alloyed PtNi on corrosion-resistant carbon support (ANL catalyst project with JM and UTRC as partners)
- 4. Balance-of-plant components
- Air management system with Roots compressors and expanders (Eaton collaboration)
- Elevated temperature operation for heat rejection, Q/AT target (collaboration with OEM)
- Simplified anode system, pulsed ejectors/purge (OEM collaboration)
- 5. Incorporate durability considerations in system analysis
- 6. System optimization for cost, performance, and durability
 - Drive cycle simulations for durability enhancement

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:	Extended the NSFC stack model to 3 atm; validated the earlier conclusion that Pt content and FCS cost can be reduced to less than 0.2 g/kW and \$50/kW
	Modeled Roots compressors and expanders; established base- line performance of integrated unit with different configurations
	Validated the humidifier model against data for a full-size unit to show that Gore M311.05 membrane can achieve >4.2 g/m ² /s water flux with pre-cooling
	Obtained initial results on the effect of $Q/\Delta T$ on Pt content and system cost
	Extended and validated the model for hydrogen ejectors
Collaborations:	3M, dPoint, Eaton, Ford, Gore, SA, ANL (Autonomie)
Future Work:	Fuel cell systems with emerging de-alloyed catalysts
	Alternate balance-of-plant components
	System analysis with durability considerations on drive cycles

Technical Backup Slides

Cell Averaged PtCoMn/NSTF ORR Kinetics

- Series A data for low current densities, < 0.5 A.cm⁻², small mass transfer effects
 - Challenges: more than 1 parameter varying at a time, finite utilization, variability in data
 - Two step approach for determining Tafel equation parameters: cellaveraged kinetics, local kinetics

$$i + i_{x} = i_{0}A_{Pt}L_{Pt}P_{O_{2}}^{\gamma}\Phi^{\beta}\exp(\frac{\alpha nF}{RT}\eta) \qquad i_{0} = i_{or}\exp[-\frac{E_{O_{2}}}{R}(\frac{1}{T}-\frac{1}{T_{r}})]$$

- Stepwise procedure for determining cell-averaged kinetic parameters
 - Dependence on average P_{O_2} from series 2 data at 80°C, 50% O_2 utilization, 100% RH at cell exit (γ = 0.36)
 - Dependence on T from Series 1 (and 2) data at 75-90°C, 50% O_2 utilization, 100% RH at cell exit (E_{O_2} = 57.7 kJ/mol)
 - Dependence on RH from Series 3 (and 1) data for different exit RH (β = 1.3), $\alpha = 0.4665/(1+0.0926\Phi)$

Local PtCoMn/NSTF ORR Kinetics

- Formulated 1-D model for local values of *i*, P_{O2}, P_{H2} and Φ from the measured polarization curves, JPS 215 (2012) 77-88
- Optimizer to determine i_0 , E_{O_2} and β
 - Unable to improve γ because overpotentials not as sensitive to P
 - Unable to change α because of convergence issues (too sensitive)

$$i_{0r} = 6.8 \times 10^{-7} \text{ A.cm}_{\text{Pt}}^{-2}, \quad \text{E}_{O_2} = 39.5 \text{ kJ.mol}^{-1}$$
$$\beta = \begin{cases} 0.9 + 1.5(0.65 - \Phi) & \Phi < 0.65\\ 0.9 & \Phi \ge 0.65 \end{cases}$$



Pt Content and System Cost

0.30

bt Content, g/kW 0.20 60

55

50

Cost, \$/kW

S₃: 3 atm; η_s: 47.5%

Pt Content

 ΔT_c : 10°C

SR: 2(c) / 2(a)

L_{Pt}: 0.15(c) / 0.05(a) mg/cm²

- Optimum stack T (exit coolant exit T) and inlet RH_c at which the Pt content and the system cost* are lowest depend on the operating P
- At optimum stack T, Pt content and system cost are lower at 2.5 and 3 atm operating P



Optimum Cathode Stoichiometry

Optimum stoichiometry and is smaller at higher operating pressures: 1.5 at 2.5-3 atm and 2.5 at 1.5 atm



System Cost vs. System Efficiency Trade-Off

Four-variable optimization study to determine stack T, inlet RH_c , SR_c and $L_{Pt}(c)$ for lowest system cost for specified system efficiency*

System	L _{Pt} (c)	Cell V	Power Density	Pt Content	C	Cost (\$/kW	/)
Efficiency, %	mg/cm ²	mV	mW/cm ²	g/kW	Pt	Stack	System
Stack Inlet P = 2	2.5 atm; SRo	= 1.5-1.6					
40.0	0.112	579	1134	0.16	5.7	20.7	47.0
45.0	0.108	634	971	0.18	6.4	22.9	48.0
47.5	0.110	661	882	0.20	7.0	27.8	49.4
50.0	0.111	695	753	0.23	8.3	28.2	52.5
Stack Inlet P = 1.5 atm; SR _c = $2.4-2.5$							
40.0	0.074	569	860	0.16	5.7	23.7	50.9
45.0	0.086	633	849	0.18	6.3	24.4	50.4
47.5	0.093	665	817	0.19	6.8	25.5	50.9
50.0	0.104	696	755	0.22	7.9	27.8	52.7



32

Nitrogen Buildup and Performance Losses

Dynamic simulations (system S1, variable P, 85°C); ISO H₂ quality

- Single purge, additional H₂ at rated flow rate, 2x anode system volume
- Smaller purge losses, but larger decrease in cell voltage, at higher power or greater allowable N₂ buildup
- For optimum efficiency, allowable N₂ buildup is a compromise between purge loss and decrease in cell voltage



Optimum Purge Schedule

Conducted dynamic simulations at constant power to determine the optimum purge schedule and the allowable N_2 buildup

- Shorter purge schedule and smaller allowable N₂ concentration at higher power
- Developed criterion for purging anode without relying on a H₂ sensor
- Running drive-cycle simulations to verify and improve dynamic optimum purge criterion



CEM Operating Conditions Part Load

Optimum operating conditions for maximum FCS efficiency at part load*

- CEM variables: expander nozzle area and CEM shaft speed, as a function of FCS net power (fixed SR(c))
- Simulations to map range of stack inlet P and coolant exit T for FCS efficiency within 0.25 percentage points of the optimum



Scaled CEM maps

- 71 60% compressor efficiency, 20 maximum turndown
- 73 50% expander efficiency with variable nozzle inlet area
- 87 92% motor efficiency
- Poor controller efficiency at low loads



FCS Performance at Part Load

- 6 kW_e CEM parasitic power at SR(c) = 1.5, 27°C ambient T; system power derated at 40°C ambient T
- 210 W_e CEM parasitic power at idling: turndown of 20, 30% minimum controller efficiency
- 60% peak efficiency target reached at ~10% power



Peak Efficiency Sensitivity Study

	FCS Efficiency ¹ %	System Cost ² \$/kW	Comments
2012 ANL Status ³	57.7	45.2	3M ternary NSTF catalyst with 0.185 mg/cm ² Pt loading, Honeywell CEM, 1.5 cathode stoichiometry, 47.5% system efficiency at rated power
Thinner Membrane	57.9	43.1	Reinforced membrane; thickness reduced from 24 to 12 mm
Improved Air Management System	59.0	42.9	New Eaton project to develop efficient Roots blowers and expanders
Passive Anode System	59.3	42.8	Hybrid hydrogen blower-ejector replaced with a pulse ejector
2X Catalyst Activity 5X Catalyst Activity	61.0 63.4	41.8 40.7	New 3M project to develop dealloyed Pt ₃ Ni ₇ /NSTF catalyst

¹FCS efficiency refers to system efficiency at 25% power. System efficiency can be higher at lower loads.

²Cost of 80-kW_e fuel cell systems estimated using SA correlations for high-volume manufacturing (500,000 units/year). All systems have 47.5% efficiency at rated power.
³RK Ahluwalia, X Wang, R Kumar, "Fuel Cells Systems Analysis," Fuel Cell Tech Team Meeting, Southfield MI, July 18, 2012

38

Sources of Inefficiencies

	Cell Voltage	Stack Efficiency	Parasitic Power ¹	FCS Efficiency ²	Comments
	mV	%	%	%	Metrics at 25% power
2012 ANL Status ³	767	60.9	5.3	57.7	3M ternary NSTF catalyst with 0.185 mg/cm ² Pt loading, Honeywell CEM, 1.5 cathode stoichiometry, 47.5% system efficiency at rated power
Thinner Membrane	769	61.0	5.3	57.9	HFR affects system cost more than it affects efficiency at 25% power.
Improved Air Management System	769	61.1	3.6	59.0	Parasitic power is small since the compressor discharge pressure is only 1.25 atm at 25% power.
Passive Anode System	769	61.1	3.1	59.3	Hybrid hydrogen blower-ejector replaced with a pulse ejector
2X Catalyst Activity	790	62.8	2.9	61.0	Peak efficiency is most sensitive to catalyst activity for ORR or Pt loading
5X Catalyst Activity	820	65.1	2.7	63.4	for dispersed catalysts.

¹Parasitic power as percent of power produced by stack

²FCS efficiency refers to system efficiency at 25% power

³RK Ahluwalia, X Wang, R Kumar, "Fuel Cells Systems Analysis," Fuel Cell Tech Team Meeting, Southfield MI, July 18, 2012

dPoint Humidifier with Gore M311.05 Membrane

- Single channel, steady or transient, counter-flow or cross-flow with heat and mass transfer
- 2-D finite-difference model, variable number of nodes
- Literature data for water uptake and water diffusivity in the ionomer
- Gas phase, interfacial and ePTFE resistances derived from static and dynamic permeation tests (W.B. Johnson, FC067)
- Pressure drop correlation from the unit experimental data
- Cross-over of N₂ and O₂



40