

Fuel Cells Systems Analysis

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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

- FY13 DOE Funding: \$450K
- Planned DOE FY14 Funding: \$450 K
- Total DOE Project Value: \$450K

Partners/Interactions

- Eaton, Gore, Ford, dPoint
- SA
- 3M, Ballard, Johnson-Matthey (JM), UTRC, Ballard
- 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

Objectives and Relevance

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

Impact of FY2014 work

- FCS needs to operate hotter (>90°C coolant exit temperature), drier (exit RH <100%) and at higher pressures (>2 atm) in order to meet the stack heat rejection target.
- Established the FY2014 baseline cost (\$57.50/kW) of automotive fuel cell systems
- Independently determined the optimum swept volumes and gear ratio for Roots air management system

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:** Collaboration with 3M, Johnson-Matthey/UTRC and Ballard in obtaining data to develop validated models for pressures up to 3 atm

- Ternary PtCoMn/NSTF catalyst system
- De-alloyed PtNi/NSTF catalyst system
- Dispersed Pt/C and de-alloyed PtNi/C catalyst systems

Air Management: Collaborating with Eaton to develop and model Roots compressors and expanders and integrated air management system

Water Management: Collaboration with Gore, dPoint and Ford (cross-flow humidifiers)

Fuel Management: Collaboration with 3M and Ford (impurity buildup, ejectors) **System Analysis:** Collaboration with SA to optimize system performance and cost subject to $Q/\Delta T$ constraint



PtCoMn/NSTF Stack Model Development & Validation

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
- Data over wide range of operating conditions: 1-3 atm, 35-90°C, 35-100% RH, 1.2-5 SR_a, 1.5-10 SR_c, 0-75% N₂ in H₂
- H₂ pump tests for HOR kinetics on ternary catalyst with 0.02 and 0.05 mg/cm² Pt loading in anode: 0.7-2.5 atm P_{H2}, 45-90°C

Model Validation and Documentation

- ORR and HOR kinetics on PtCoMn/NSTF: J. Power Sources, 215(1) 77-88 (2012); JECS, 160(3) F251-F261 (2013)
- Artificial neural network (ANN) and rational models of cathode mass transfer overpotentials
- Nitrogen buildup and anode mass transfer overpotentials



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Q/\Delta T Study – Allowable Operating Temperatures

Previous experience from tests and model suggests that independent of cell voltage, for cell temperatures below 85°C, the power density is close to maximum when the relative humidity (RH) of spent air at stack exit is $\geq 100\%$ (balance between membrane dry-out/catalyst flooding and Nernst potential/ORR kinetics).

- Minimum dew point approach T in humidifier restricted to 5°C
- Allowable cathode gas exit temperature decreases if the operating pressure is lowered or the cathode SR is raised or the exit RH approaches 100%.



Assumptions

 No net water transport to the recirculating H₂ stream (only for the purpose of establishing allowable T limits)



Dew point (dp) approach T: T_{dp} (wet in) – T_{dp} (dry out)

Q/ Δ **T** Study – Optimum Operating Temperatures

Parametric study to investigate the effect of coolant exit temperature on system cost: $Q/\Delta T = 1.45 \text{ kW/}^{\circ}C$, 2.5 atm, $SR_c = 2$, $T_{amb} = 40^{\circ}C$

- For fixed Q/ Δ T, raising the coolant temperature (T, Δ T) results in higher Q, and, therefore, lower cell voltage (V) and higher power density.
- Nearly ten-fold increase in humidifier membrane area (<0.6 to >5 m²) for 100% exit RH as the coolant exit T raised from 85 to 95°C
- Optimum RH is 100% for coolant exit T below 88°C and decreases at higher coolant exit temperatures



Optimization Study

Two-variable optimization study to determine the combination of coolant exit T and cell voltage for minimum system cost, subject to 1.45 kW/°C Q/ Δ T constraint*, for specified Pt loading in anode/cathode catalyst (L_{Pt}), 100% exit RH, and 40°C ambient temperature

- Low stack inlet pressures (1.5 atm) may not be acceptable because the coolant exit temperature is restricted to <82°C, ΔT < 42°C, Q < 61 kW, cell V >740 mV
- SR_c < 2 needed to keep cell voltages below 700 mV at 2.5 atm stack inlet pressure; no such restriction at 3 atm inlet pressure



System Cost and Pt Content

- Large differential in cost and Pt content between saturated and superheated cathode exits at low operating pressures
- Lowest system cost is at 3-atm operating pressure, although the cost saving is small compared to 2.5-atm operating pressure
- Dependence of system cost on operating P and SR_c is completely different for specified Q/∆T than for specified system efficiency (earlier results)
- Optimum stack exit RH >95% for stack inlet pressure higher than 2.5 atm, <83% at 1.5 atm.



Cell Voltage and Power Density

- For specified Q/∆T constraint, the required cell voltage is 65 mV lower at 1.5 atm stack inlet pressure if the stack is operated hotter (95°C vs. 90°C coolant exit temperature) and drier (83% RH rather than 100% RH).
- Power density is <500 mW/cm² at stack operating pressures below 1.8 to 2 atm
- Small differences in power densities for saturated and superheated (RH < 100%) cathode outlets at stack inlet pressures higher than 2.5 atm as the optimum RH approaches100%.



System Efficiency and Stack Heat Loads

- Imposing Q/AT constraint makes the system efficiency at rated power a function of the operating pressure. The required efficiency is higher at lower stack inlet pressures.
- Required system efficiencies are lower (desired result) if the cathode outlet is superheated than if it is saturated (although there are durability implications)
- The anode outlet may contain condensed water; the stack heat load includes this latent heat and the sensible heats due to rise in gas temperatures.



Optimum Pt Loading

Parametric optimization to determine Pt loading for minimum cost, $SR_c = 1.5$

- Cathode with the lowest Pt loading (0.05 mg/cm²) has the smallest Pt content (mg/kW_e) but also the lowest power density
- Optimum Pt loading in cathode for lowest system cost is between 0.05 and 0.125 mg/cm² if Pt price is \$1500/tr-oz, slightly higher if Pt price is \$1100/tr-oz



Impact of Q/AT Constraint

 Raising stack temperature and cell voltage to meet Q/AT constraint results in higher costs and may require operating pressures >2 atm

Minimum cost subject to Q/ Δ T=1.45 constraint, 100% exit RH, 40°C ambient temperature (T _{amb})				Minimum cost, 47.5% system efficiency, 100% exit RH, T _{amb} = 40°C			
Stack Inlet P	System Eff.	Cell V	Pt Content Cost		Cell V	Pt Content	Cost
atm	%	mV	g/kW _e	\$/kW _e	mV	g/kW _e	\$/kW _e
1.5	55.7	739	0.67	92.6	635	0.26	55.4
2.0	51.8	701	0.35	63.7	649	0.25	54.8
2.5	48.8	676	0.27	57.9	664	0.24	55.3
3.0	46.7	661	0.24	56.2	678	0.25	57.3



HOR/HER on PtCoMn/NSTF Catalysts

- Investigated HOR/HER kinetics on ternary NSTF catalyst with ultra low Pt loading (0.02 mg.cm⁻²) in H₂ pump mode
- 50-cm² cell operated in H₂ pump mode with oversaturated H₂ at constant H₂ flow rate (1750 sccm), same Pt loading in anode & cathode
- On completely conditioned electrodes, HER on cathode catalyst is slower than HOR on anode catalyst with the same Pt loading ($\alpha > 0.5$)
- Significantly higher HOR overpotentials on partially conditioned anodes
- Comparable exchange current densities for HOR on Pt/C and NSTF catalysts but much lower ECSA
- Reducing anode Pt loading from 0.05 to 0.02 mg.cm⁻² incurs ~25 mV HOR overpotential at 1.5 A.cm⁻²



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Kinetics of ORR on De-alloyed Pt₃Ni₇/NSTF Catalysts

- Collaborated with 3M to Investigate ORR kinetics on de-alloyed Pt₃Ni₇/NSTF catalyst with low 0.125 mg.cm⁻² Pt loading
- 50-cm² cell operated in H₂/O₂ at constant H₂ (1900 sccm) and O₂ (2200 sccm) flow rates corresponding to SR = 2(a)/5(c) at 2.5 A.cm⁻²
 - Anode catalyst: PtCoMn/NSTF with ultra-low 0.02 mg.cm⁻² Pt loading
- De-alloyed Pt₃Ni₇/NSTF has 80% higher mass activity (0.31 A.mg_{Pt}⁻¹) than PtCoMn/NSTF (0.17 A.mg_{Pt}⁻¹) with the same 0.125 mg.cm⁻² Pt loadings

 \circ >50% higher ECSA: 14.5 vs. 9.6 m_{Pt}².g⁻¹

- >20 % higher specific activity: 2.17 vs. 1.80 mA.cm_{Pt}⁻²
- Derived kinetic parameters for ORR on de-alloyed Pt₃Ni₇/NSTF catalyst



Kinetics of ORR on Dispersed Pt/C and De-alloyed PtNi/C



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Mass Transfer in De-alloyed PtNi/C MEAs

Collaborating with UTRC and JM to develop a model for mass transfer in cells with de-alloyed PtNi/C cathode catalysts

- Controlled H₂/air data for 12.5 cm² cells operated at large stoichiometries
- Developed point correlations for limiting current density (i_L) as function of P, T, RH and flow rates
- Developed point correlations for mass transfer overpotentials in terms of P, T, RH, Q and i/i_L

400

300

100

0

0.0

-100

ک<mark>ہ</mark> 200

1.5 atm

2.0 atm

2.5 atm

0.5

Φ: 100%

X(O₂): 21%

Air: 3 slpm

H2: 1 slpm

1.0

1.5

2.0

2.5

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- Deriving mass transfer resistances for O₂ transport through GDL, CCL pores and ionomer
- Validated finite-difference model for locally varying flow conditions and current densities





Roots Air Management System with Integrated Expander

Argonne is collaborating with Eaton-led team to model and analyze Roots air management system and optimize it for use in Ballard fuel cell module

- Developed models for Twin Vortices Series Roots compressor, three-lobe Roots expander, prototype motor and motor-controller
- Developed an integrated model of compressor, expander and motor/motorcontroller
- Analyzed selected configuration with 5 shafts, 10 bearings, 3 gears, and 1 coupling: compressor and motor on the same shaft, and expander on a different shaft
- Determined compressor and expander swept volumes (SCE*), compressor shaft speed and gear ratio for minimum CEM parasitic power at rated power: 92 g/s air to compressor, 40°C ambient T, 2.5 atm discharge pressure; 88 g/s spent air to expander at 2.2 atm, 70°C, 100% RH.
- Optimum compressor shaft speed (22,000 rpm) to push the expander toward max efficiency for 2.5 atm discharge pressure
- Gear ratio 2.2, 10,000 expander shaft rpm
- Compressor swept volume: 0.765X
- Expander swept volume: 0.85X



Projected Performance of Roots Air Management System

Characteristic	Units	2011 Status	2017 Target	Roots - SCE
Input power at full flow (with / without expander)	kW _e	11.0 / 17.3	8 / 14	11.6 / 16.4 ^b
Combined motor/motor-controller efficiency at full flow	%	80	90	90.9
Compressor / expander adiabatic efficiency at full flow	%	71 / 73	75 / 80	64.5/79.6
Compressor / expander isentropic efficiency at full flow	%		67.5 / 80	59.7/61.2
Input power at 25% flow (with / without expander)	kW _e	2.3 / 3.3	1.0 / 2.0	1.8 / 2.4
Combined motor/motor-controller efficiency at 25% flow	%	57	80	70.7
Compressor / expander adiabatic efficiency at 25% flow	%	62 / 64	65 / 70	61.8/88.2
Compressor / expander isentropic efficiency at 25% flow	%		58.5 / 70	53.3/53.5
Turndown ratio (max/min flow rate)		20	20	20
Input power at idle (with / without expander)	W _e	600 / 765	200 / 200	280 ^a / 510
Combined motor/motor-controller efficiency at idle	%	35	70	50.6
Compressor / expander adiabatic efficiency at idle	%	61 / 59	60 / 60	50.5/80.9
Compressor / expander isentropic efficiency at idle	%	61 / 59	54 / 60	33.6/35.1

^a Compressor discharge pressure less than 1.2 atm at idle

^b CEM power projections for system without expander based on R3 compressor data

Adiabatic efficiency based on inlet and outlet temperatures. Isentropic efficiency based on torque (power)



*Projected performance based on current hardware. Eaton anticipates additional improvements from advances in design.

Collaborations

Air Management	Eaton	
Stack	3M, Ballard, JM, Nuvera, UTRC	
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)
- Joint publication with Gore, Ford and dPoint on validated model for cross-flow module with Gore M311.05 membrane; alternate water transport membrane
- Joint publication with Ford on validated model for H₂ ejectors; Pulsed ejectors/purge (OEM collaboration)
- 5. Incorporate durability considerations in system analysis
 - System optimization for cost, performance, and durability

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:	Developed FCS optimization model subject to $Q/\Delta T$ constraint; Demonstrated that Pt content of 0.27 g/kW and system cost of \$57.90/kW can be achieved at $Q/\Delta T=1.45$.
	Integrated models for Roots compressors and expanders and motor/motor-controller. Determined the optimum displacements and gear ratio for 11.6 kW CEM parasitic power.
	Validated 80% increase in mass activity of 3M's de-alloyed Pt ₃ Ni ₇ /NSTF over PtCoMn/NSTF with same Pt loading
	Determined ORR activity and mass transfer in developmental PtNi/C catalyst systems
Collaborations:	3M, dPoint, Eaton, Ford, Gore, JM, SA, UTRC, 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 Back-Up Slides

Publications and Presentations

Journal Publications

R. K. Ahluwalia, S. Arisetty, J-K Peng, R. Subbaraman, X. Wang, N. Kariuki, D. J. Myers, R. Mukundan, R. Borup, and O. Polevaya, "Dynamics of Particle Growth and Electrochemical Surface Area Loss due to Platinum Dissolution," Journal of the Electrochemical Society, 161 (3) F291-F304 (2013).

S. Ahmed, D. P. Papadias, and R. K. Ahluwalia, "Configuring a Fuel Cell based Residential Combined Heat and Power System," Journal of Power Sources, 242, 884-894 (2013).

D. D. Papadias, R. K. Ahluwalia, J. K. Thomson, H. M. Meyer III, M. P. Brady, H. Wang, R. Mukundan, and R. Borup, "Degradation of SS316L Bipolar Plates in Fuel Cell Environment: Corrosion Rate, Barrier Film Formation Kinetics and Contact Resistance," accepted for publication in Journal of Power Sources, (2014).

T. Q. Hua, R. K. Ahluwalia, L. Eudy, G. Singer, B. Jemer, N. Asselin-Miller and T. Patterson, "Status of Hydrogen Fuel Cell Electric Buses Worldwide," submitted to Journal of Power Sources, (2014).

Conference Presentations

N. Garland and R. K. Ahluwalia, "Report from the Annexes: Annex 26.," IEA AFC ExCo 46th Meeting, Salzburg, Austria, May 22-23, 2013.

Meetings Hosted

R. K. Ahluwalia, "IEA Advanced Fuel Cells Annex 26: Fuel Cells for Transportation," Arlington, VA, May 14, 2013.

Reviewers' Comments

Generally favorable reviews with recommendations to

- Initiate work on non-NSTF catalyst systems
- Expand MEA and stack partners beyond 3M
- Maintain reciprocal collaboration with SA on cost analysis
- Good new collaboration with Eaton on Roots compressors and expanders
- Identify major cost reduction strategies
- Initiate durability studies and consider durability in optimization studies
- Report results on start-up and shut-down time and energy and transient operation
- Collaborate with other projects on cathode over-potential analysis

Work scope consistent with above recommendations

- $\sqrt{}$ Initiated new effort on dispersed Pt/C and de-alloyed PtNi/C catalyst systems
- $\sqrt{}$ New collaborations with Johnson-Matthey, UTRC and Ballard
- $\sqrt{}$ Close coordination with SA on cost analysis and optimization
- $\sqrt{}$ Identified major cost reduction strategies for the Systems Analysis team
- On-going work on durability in a related project to be incorporated in system analysis
- $\sqrt{}$ Published papers in JPS on start-up and shut-down time and energy
 - Member of Transport Modeling Working Group

Critical Assumptions and Issues

PEFC Stack

- 1.5-3 atm at rated power
- 40-67% O₂ utilization (SR_c: 1.5-2.5)
- 50% H₂ consumption per pass
- Cell voltage at rated power: TBD
- 24-µm 3M membrane at TBD temperature
- 3M ternary alloy: 0.1/0.05 mg-Pt/cm² on cathode/anode
- GDL: 235-µm non-woven carbon fiber with MPL
- 1.1-mm metal bipolar plates, each with cooling channels
- 17 cells/inch

Fuel Management System

- Hybrid ejector-recirculation pump
- 35% pump efficiency
- 3 psi pressure drop at rated power

Air Management System

- Compressor-expander module
- Liquid-cooled motor
- Efficiencies at rated power: 71% compressor, 73% expander, 89.5% motor, 89.5% controller
- Turn-down: 20
- 5 psi pressure drop at rated power

Heat Rejection System

- Two circuits: 75-95°C HT, 10°C ΔT
 65°C LT coolant, 5°C ΔT
- 55% pump + 92% motor efficiency
- 45% blower + 92% motor efficiency
- 10 psi pressure drop each in stack and radiator

Water Management System

 Membrane humidifier, TBD dew-point temperature at rated power

Stack T permitted to rise to 95°C for short durations under some driving conditions

PtCoMn/NSTF Stack Model Development and Validation

Single cell data variability

- Reference condition (1.5 atm, 80°C, 100% RH) visited multiple times in five series of tests performed in Cell 19478
- Error bar established as deviation from the measured average voltage as function of current density

Cell to cell data variability

- Same reference condition (2.5 atm, 85°C, 100% RH) visited multiple times in four series of tests performed in Cells 23272 and 23102
- Cell to cell variability established as deviation from the measured average voltage in the two cells as function of current density



Performance Improvement Trajectory

With reduced high-frequency resistance (HFR), improved stack water management and advanced air management system, de-alloyed $Pt_3Ni_7/NSTF$ type cathode catalyst with 2X mass activity (compared to PtCoMn/NSTF) can meet the 60% efficiency target even though there are mass transfer issues at high current densities.

For 65% efficiency, the mass activity has to further increase to 5X

	Power Density	Efficiency @ 25% Power	Peak Efficiency	Comments
	mW/cm ²	%	%	
2014 Status	634	57.5	59.5	25 mΩ.cm ² ASR of bipolar plates. Membrane
				resistance function of T, RH and current density.
High Frequency Resistance	675			15 m Ω .cm ² ASR of Treadstone bipolar plates
Stack Water Management	741			50% reduction of mass transfer overpotentials from
				baseline 3M data for ternary NSTF catalyst
Advanced Air Management	758			DOE targets for efficiencies at rated power,
System				25% power, and idling
2X Catalyst Activity	853	61.4	63.6	3M's de-alloyed Pt ₃ Ni ₇ /NSTF has 400 A/g-Pt mass
				activity compared to 180 A/g-Pt for ternary catalyst
5X Catalyst Activity	962	62.9	65.1	Aggressive projection, Single Crystal PtNi Meso-TF
				Markovic, 2013 AMR
10X Catalyst Activity	1033	64.1	66.3	Theoretical limit for Pt ₃ Ni(111)
				vanderVliet et al, Nature Materials 11 (2012) 1051