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Fuel Cell Systems Analysis

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2009 DOE Hydrogen Program Review

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Project ID: FC_29_Ahluwalia

U.S. Department of Energy

UChicago Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

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

Budget

- FY09 funding: $550K
  DOE share: 100%
- FY08 funding: $500K

Barriers

B. Cost

C. Performance

E. System Thermal and Water Management

F. Air Management

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

Partners

- Honeywell CEM+TWM projects
- Emprise, PermaPure, PNNL
- 3M, Nuvera, Princeton, TIAX
- H_2 Quality Working Group, HNEI, LANL, ISO-TC192 WG12
- IEA Annexes 17 and 20
- FreedomCAR 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

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

Approach

Develop, document & make available versatile system design and analysis tools.

- GCtool: Stand-alone code on PC platform
- GCtool-PSAT: Drive-cycle analysis of hybrid fuel cell vehicles

Validate the models against data obtained in laboratory and at Argonne's Fuel Cell Test Facility.

- Collaborate with external organizations

Apply models to issues of current interest.

- Work with FreedomCAR Technical Teams
- Work with DOE contractors as requested by DOE

Technical Accomplishments

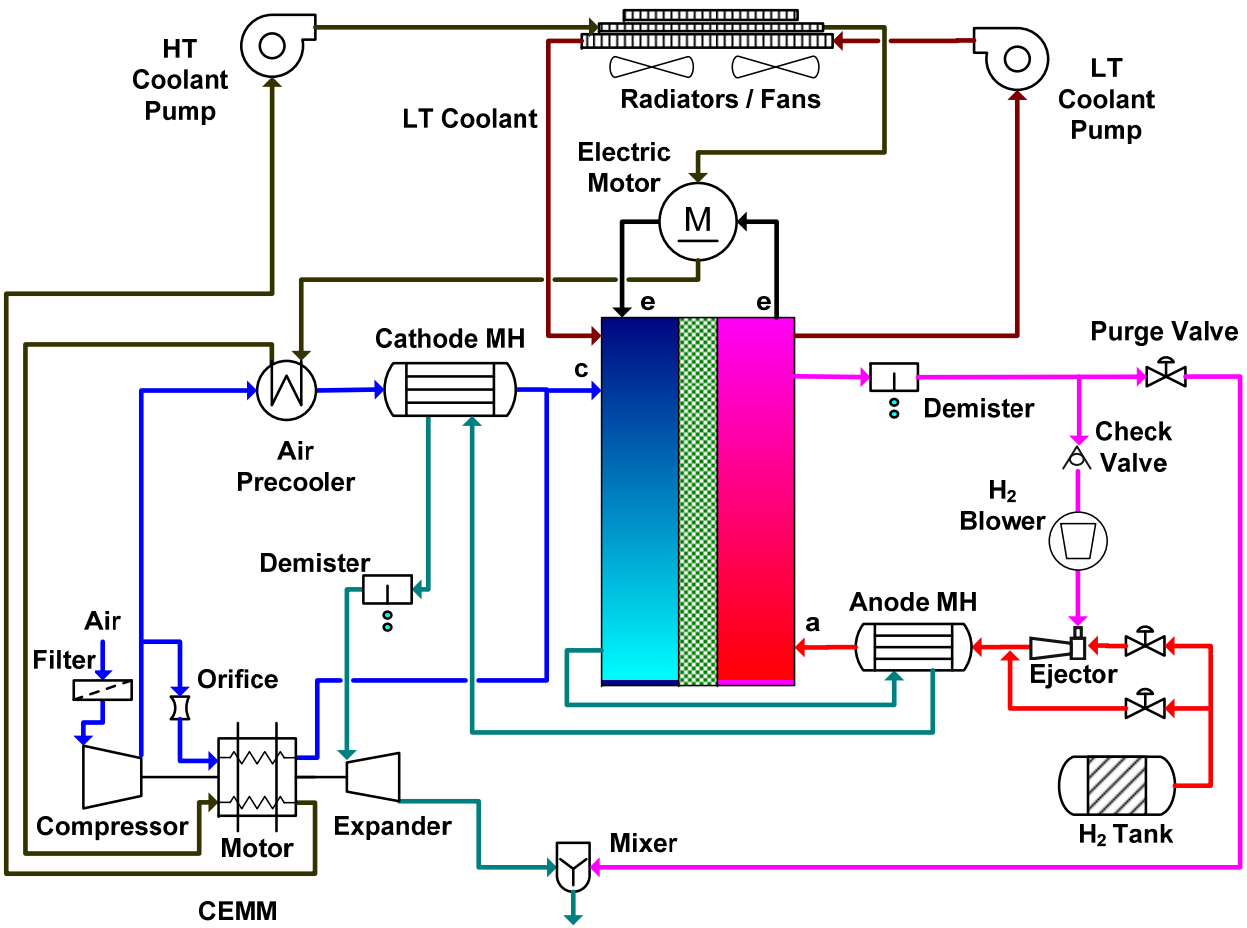
1. System analysis to update the status of technology

- **Stack:** Working with 3M to analyze performance of NSTFC stacks with reduced Pt loading at elevated T
- **Air Management:** Worked with Honeywell to build and validate component maps and analyzed performance
- **Thermal Management:** Working with Honeywell to evaluate performance of advanced automotive radiators
- **Water Management:** Assisting Honeywell to determine performance of full-scale enthalpy wheel and membrane humidifiers
- **Startup and Shutdown:** Determining time and energy for startup and shutdown
- **Drive Cycle Simulations:** GCtool-PSAT for fuel economy of hybrid FCEVs
- **Cost:** Assisted TIAX in projecting cost of Argonne FCS-2009 at high volume manufacturing

2. Impurity effects to support H_2 Quality Working Group (Backup Slides)

- Validated CO and H_2S impurity effect models against LANL/UH data
- Providing modeling support to ISO-TC192 WG-12 efforts

Argonne 2009 Fuel Cell System Configuration



2009 FCS

MEA
- 3M NSTFC MEA
- 0.1(a)/0.15(c) mg/cm^2 Pt
- 90°C at rated power

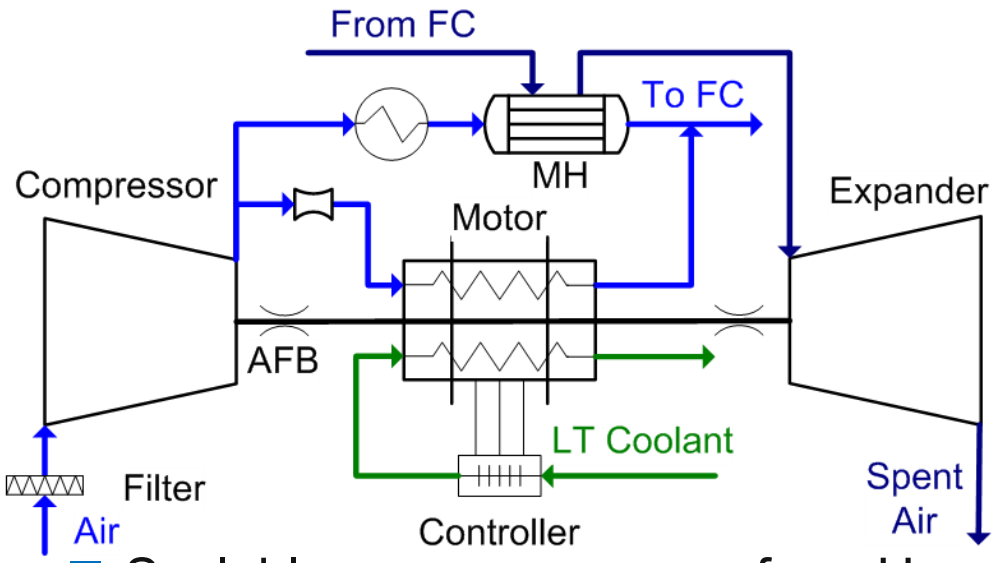
Air Management
- Honeywell CEMM
- Air-cooled motor/AFB

Water Management
- Cathode MH with precooler
- Anode MH w/o precooler

Thermal Management
- Advanced 24-fpi louver fins

Fuel Management
- Series ejector-pump hybrid

Reference Compressor-Expander-Motor Module

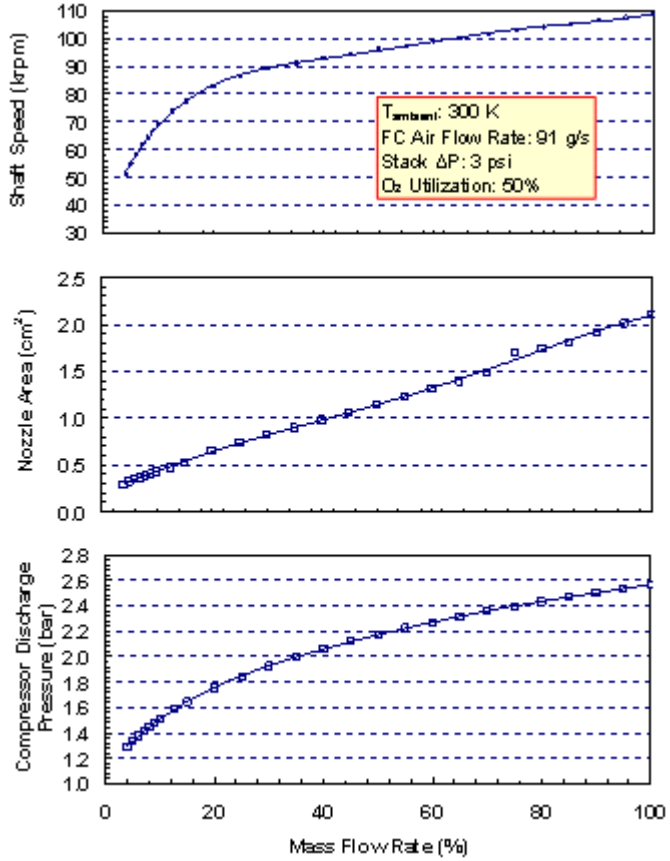


- Mixed axial flow compressor
- Variable nozzle turbine
- 3-phase brushless DC motor, liquid and air cooled
- Motor controller, liquid cooled
- Air foil bearing (AFB)

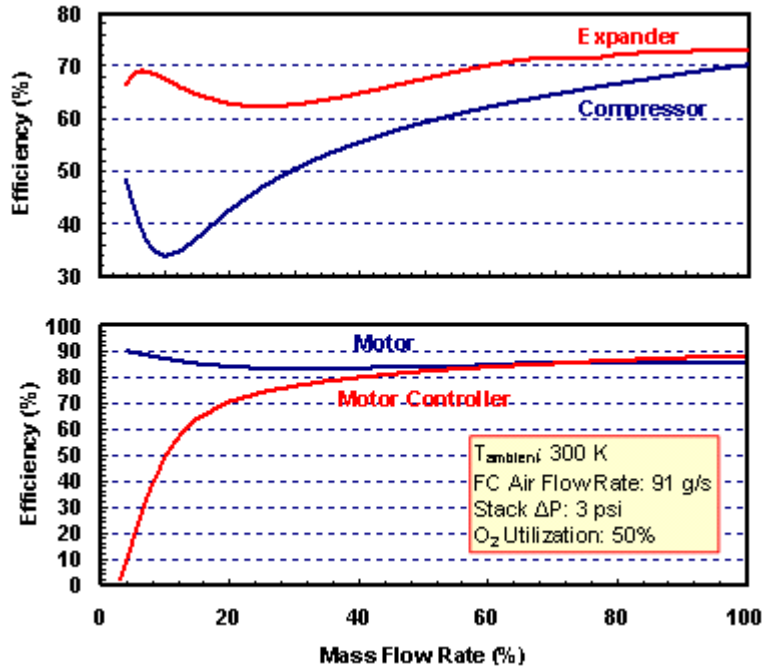
- Scalable compressor map from Honeywell data: pressure ratio (PR) and efficiency (η) as functions of corrected rpm (N_c) & mass flow rate
- Expander maps from Honeywell data for different nozzle areas as functions of flow (F_f) and velocity (F_v) factors: PR(F_f, N_c) and η(F_v, PR)
- Motor efficiency (η_M) as function of motor power (P_M) and rpm (N)
- Controller efficiency (η_{MC}) as function of MC power (P_{MC}) and rpm (N)
- Filter pressure drop as function of air flow rate
- Motor/AFB cooling air flow rate as function of pressure drop (ΔP) & N

Performance of Integrated CEM Module

- Model for matched compressor and expander on common shaft
  - VNT nozzle area and shaft rpm determined to control the stack inlet RH with a membrane humidifier
  - Stack operating at 2.5 bar, 90°C, 91 g/s, ΔP=3 psi, 100% RH exit

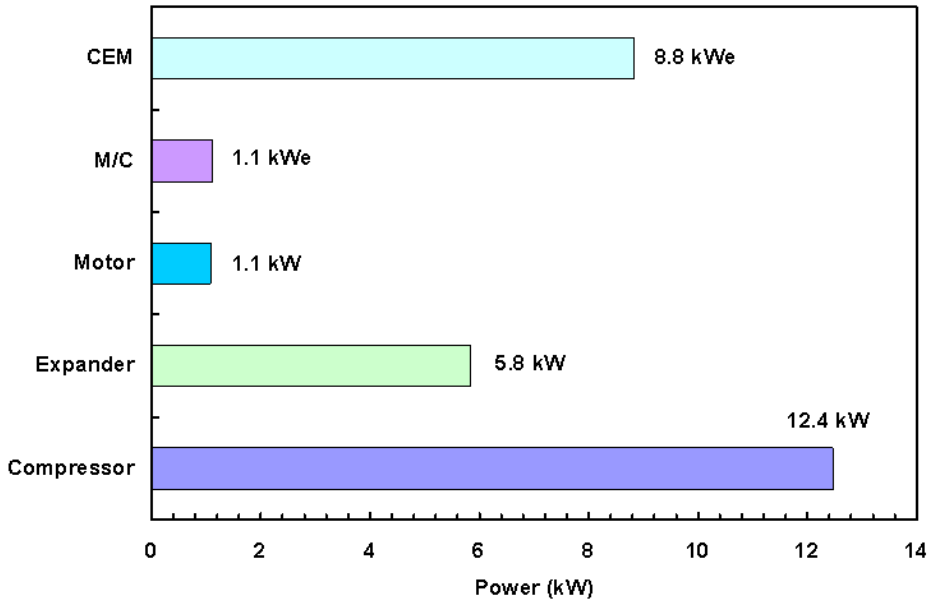


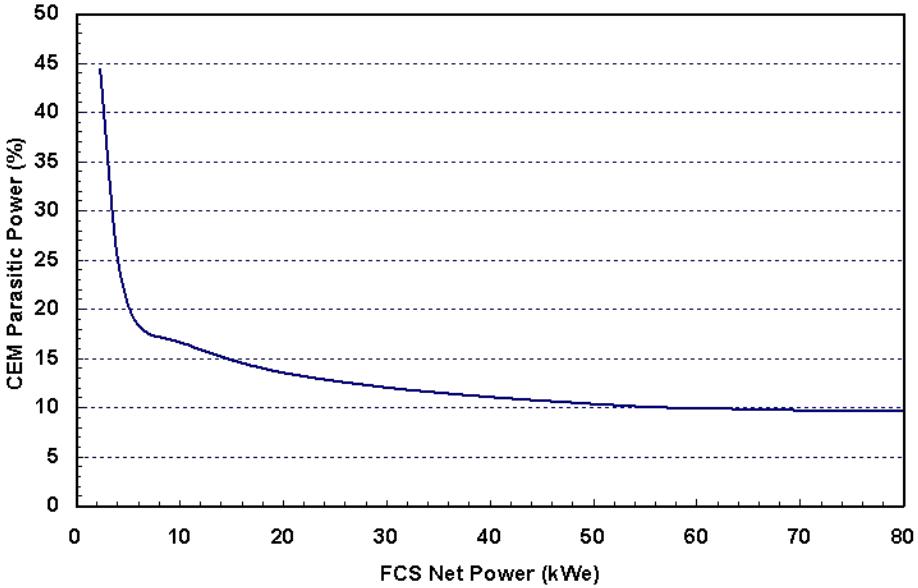
Efficiency	Compressor	Expander	Motor	M/C
Actual	70.3%	73.2%	86.0%	87.3%
Target	80.0%	80.0%	92.0%	92.0%



CEM Parasitic Power

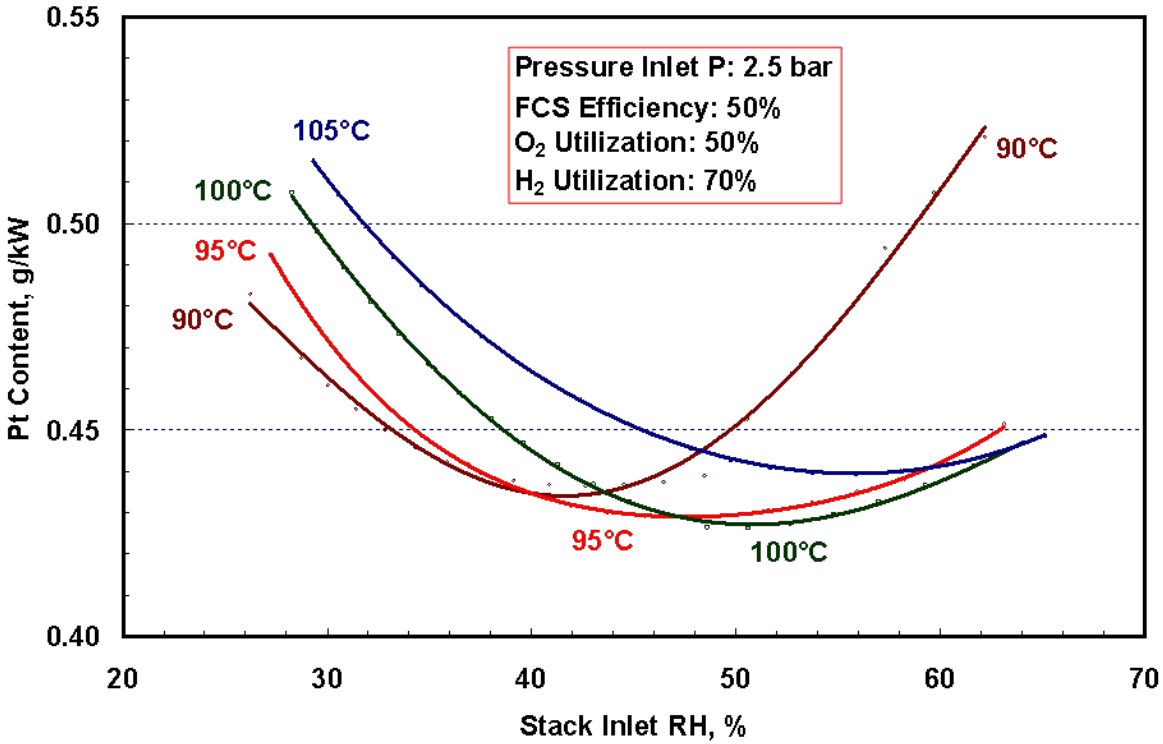
- At rated power, the CEM module consumes ~9 kWe at 300 K ambient temperature, 50% O_2 utilization, 91 g/s air flow rate, 80 kW FCS (net)
  - The DOE target is 4.4 kWe (293 K ambient temperature)
  - Component efficiencies lower than targets
  - At rated power, compressor and expander do not operate at peak efficiency points
  - Additional losses due to filtration and pressure drop





Reference Stack with 3M's NSTF Catalysts

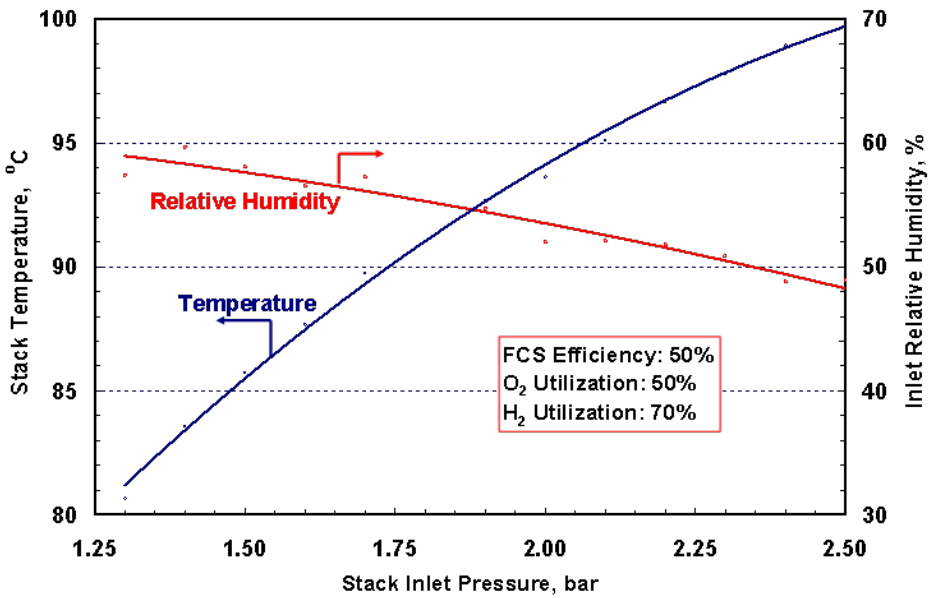
- ORR kinetics at high T (80-120°C) and low RH (20-100%)
  - 3M's single cell data with 0.1(a)/0.15(c) Pt in PtCoMn catalysts and 30-μm 850 EW membrane
  - ECSA, specific activity, short and crossover currents and HFR data from CV, EIS and H_2/air cell at 0.9 V

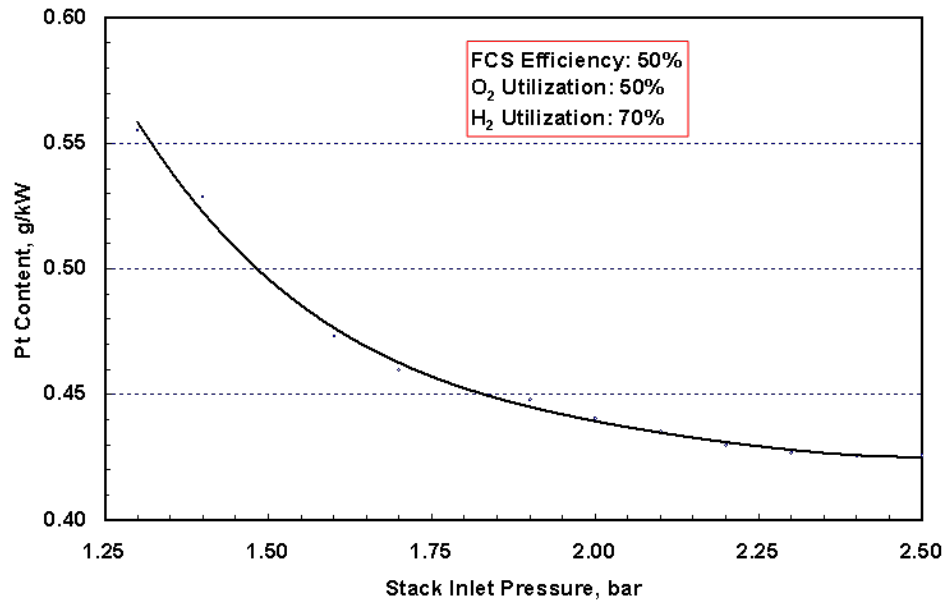


- Parametric study of FCS for specified η_{sys}, stack P_{in}, humidifier approach T_{dp} limit, radiator power, and pressure drops
  - Given P, there is an optimum RH which is a function of T_{stack}
  - Given P, there is an optimum combination of T_{stack} and RH

Effect of Stack Operating Pressure

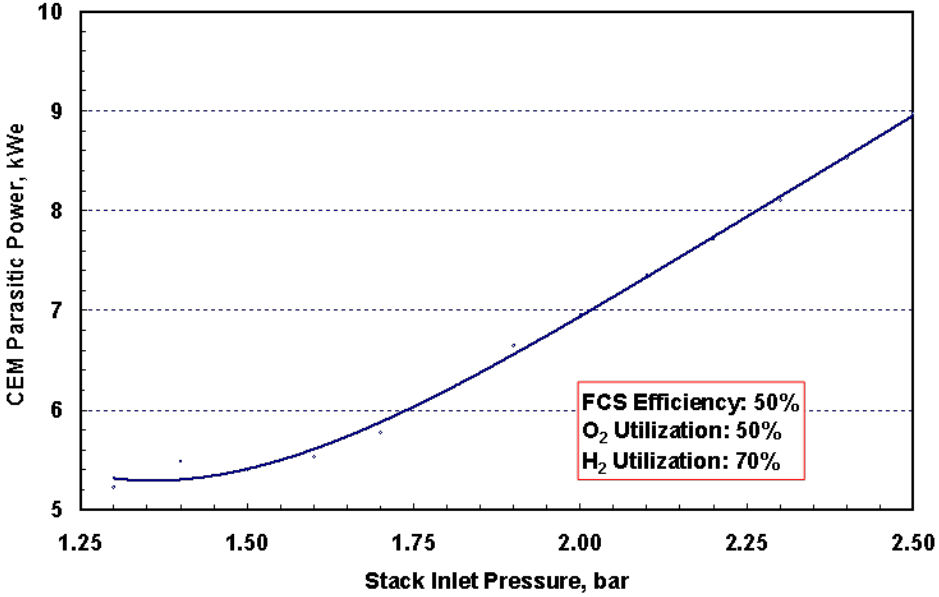
- For specified system efficiency, the optimum stack T increases and the inlet RH decreases with increase in operating pressure
  - The maximum stack temperature may be limited by the membrane and catalyst durability
- At optimum conditions, the overall Pt content decreases with increase in inlet pressure in spite of the larger parasitic losses
  - Pt content <0.3 g/kW for 45% system efficiency
  - Pt content further reduced with 0.1(c)/0.1(a) Pt loading as in recent 3M tests

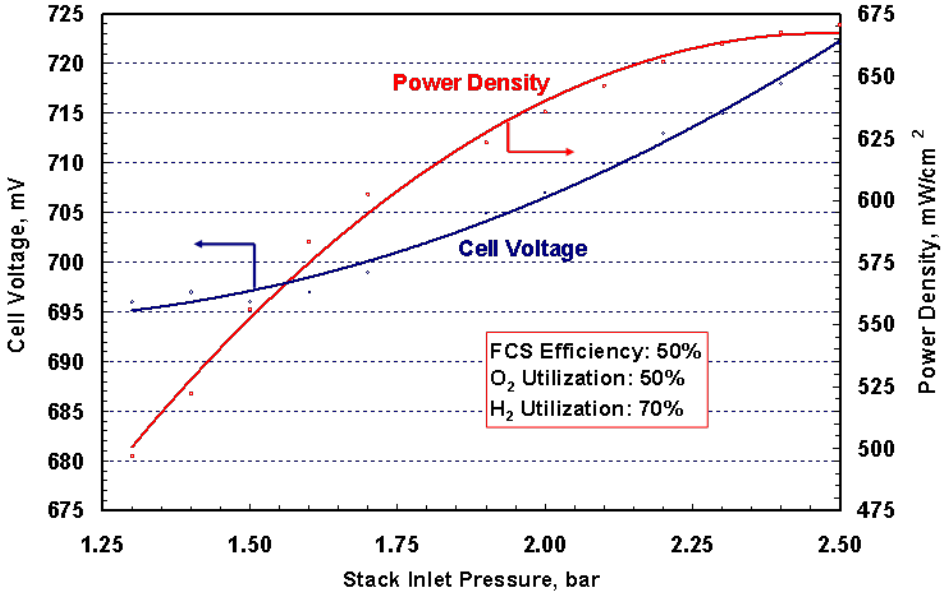




Stack Performance

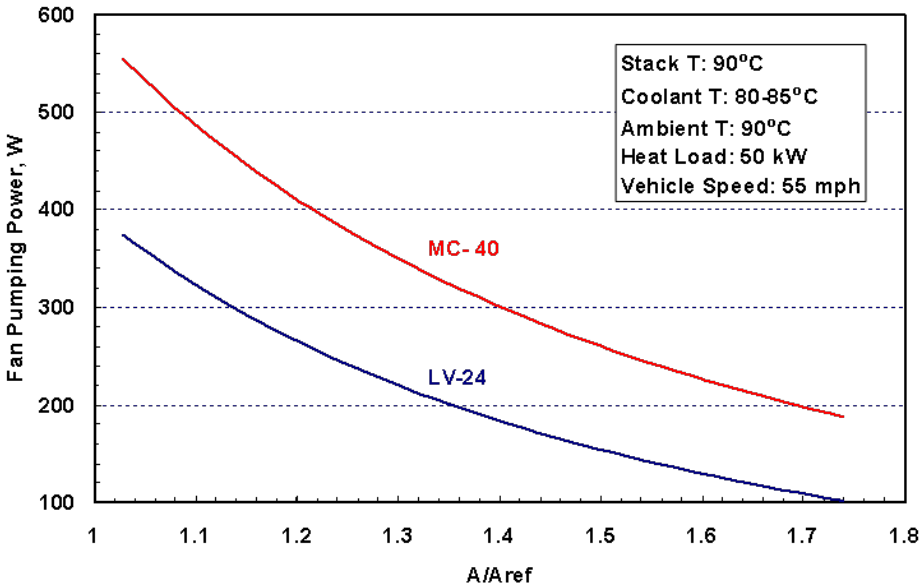
- For constant efficiency at rated power, the cell voltage has to be ~30 mV higher for 2.5-bar stack inlet pressure than for 1.3 bar.
  - 40% larger CEM parasitic power
  - 35% higher power density
  - 30% lower Pt content
  - Although the CEM is designed for 2.5 bar delivery pressure (~110 krpm) at rated flow rate, the compressor efficiency is actually higher at 1.5 bar (75 krpm).

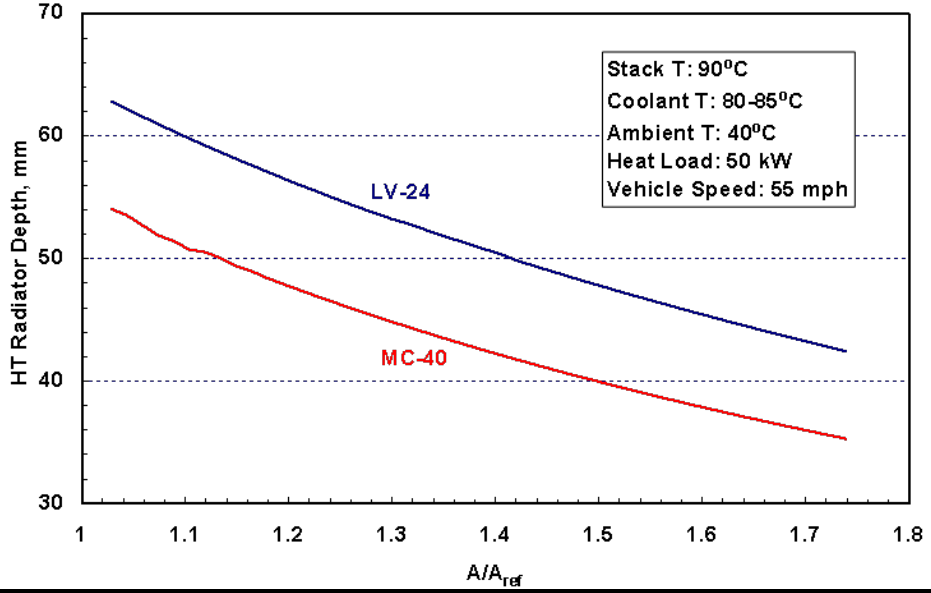




Thermal Management System

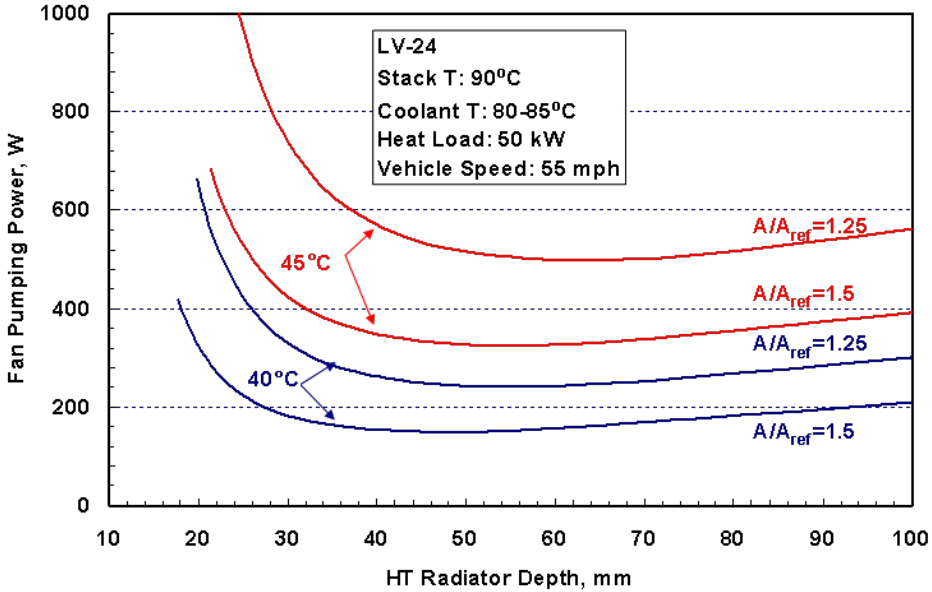
- Heat rejection for FCS radiator is most challenging while driving on 6.5% grade at 55 mph: 50 kW heat load for 80-kW FCS
  - Stacked A/C condenser (8.5 kW) and LT (9 kW) and HT radiators
- Derived f and j factors from Honeywell data with 9”x9” subscale radiators with 18 and 24 fpi louver and 40 and 50 fpi microchannel fins.
- Comparison of 24-fpi louver & 40-fpi microchannel options, A_{ref}=0.25 m^2
  - Reference grill and under-hood fluid mechanics parameters
  - 24-fpi louver requires lower fan power but 40-fpi MC more compact

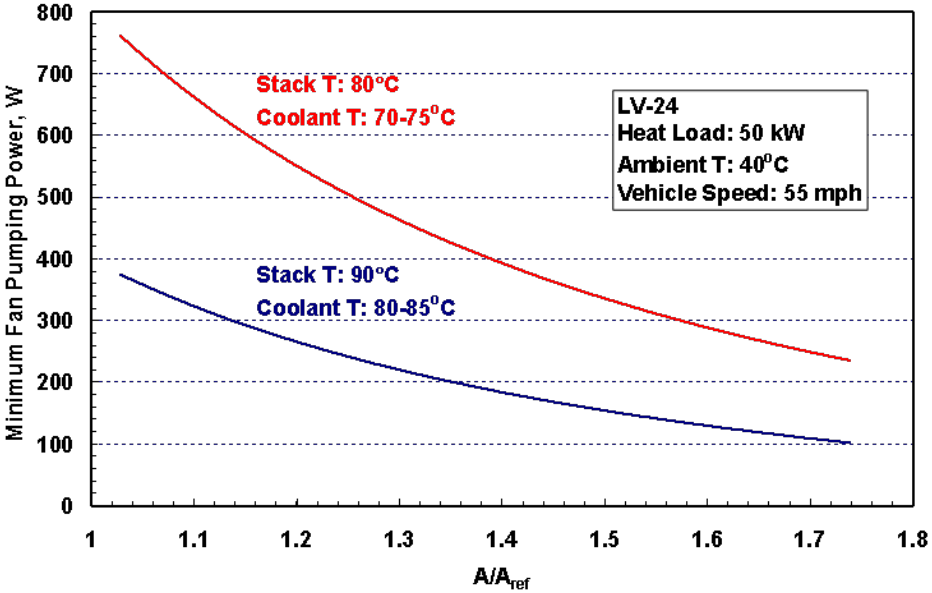




Heat Rejection vs. Ambient/Stack Temperature

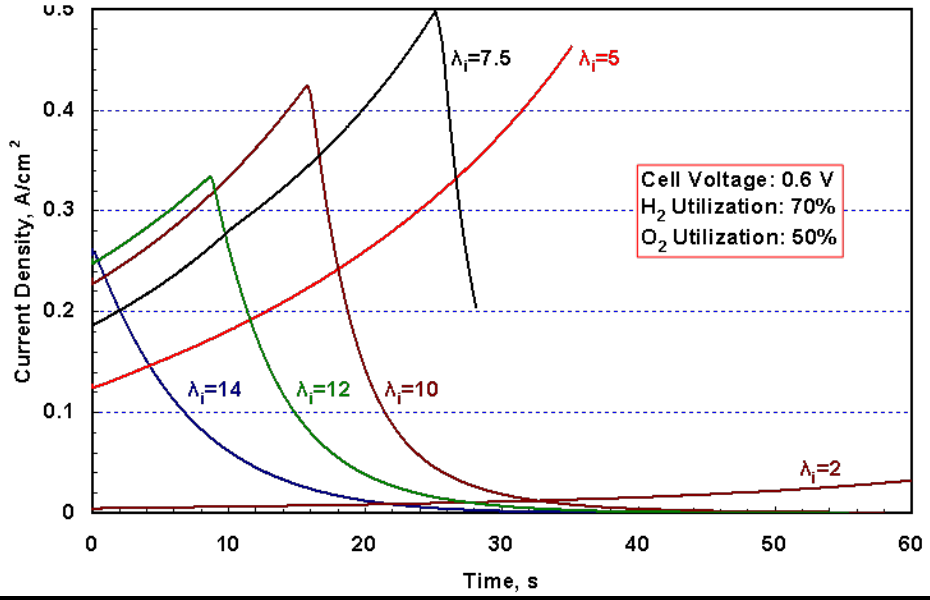
- For given frontal area, there is an optimum radiator depth that leads to minimum pumping power
  - Larger the frontal area, the smaller the pumping power,
  - Higher the ambient temperature, the larger the pumping power
  - Large frontal area and pumping power needed for 50°C T_{amb}
- For the same pumping power (300 W), 80°C stack requires 40% larger frontal area than the 90°C stack
- For the same frontal area (A/A_{ref}=1.25), the pumping power more than doubles if the stack operates at 80°C rather than 90°C

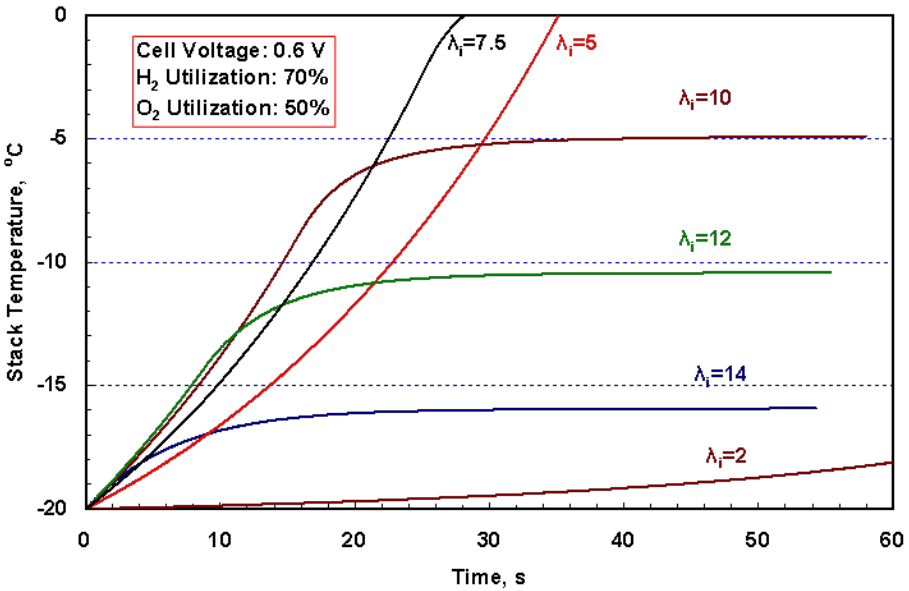




Startup from Subfreezing Temperatures

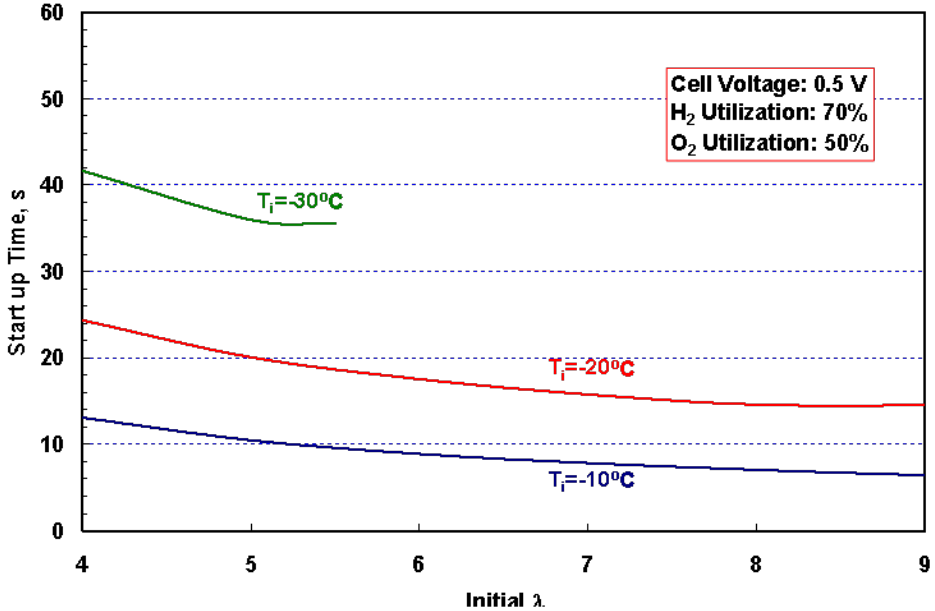
- DOE 2010 target: unassisted start from below −20°C, 50% of rated power within 30 s, <5 MJ energy for startup and shut down
- Startup as a function of initial membrane water content: dispersed Pt/C catalysts, N111 membrane, 1770 W/kg stack specific power
  - λ_i > 10, self start not possible from −20°C at V_{cell} = 0.6 V
  - λ_i = 7.5, self start with ice formation
  - λ_i = 5, self start without ice formation
  - λ_i = 2, inordinately long start-up time

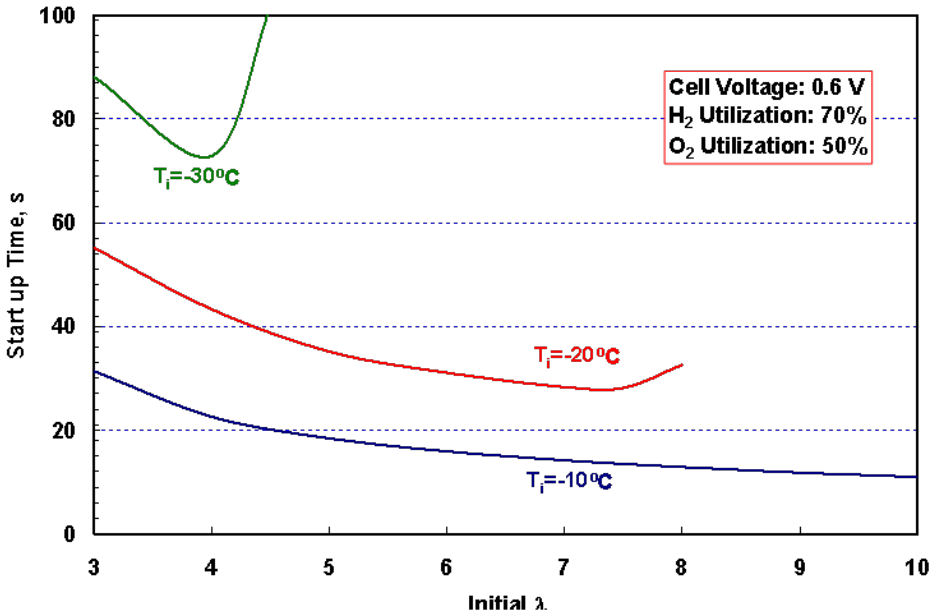




Self-Start of PEFC Stacks

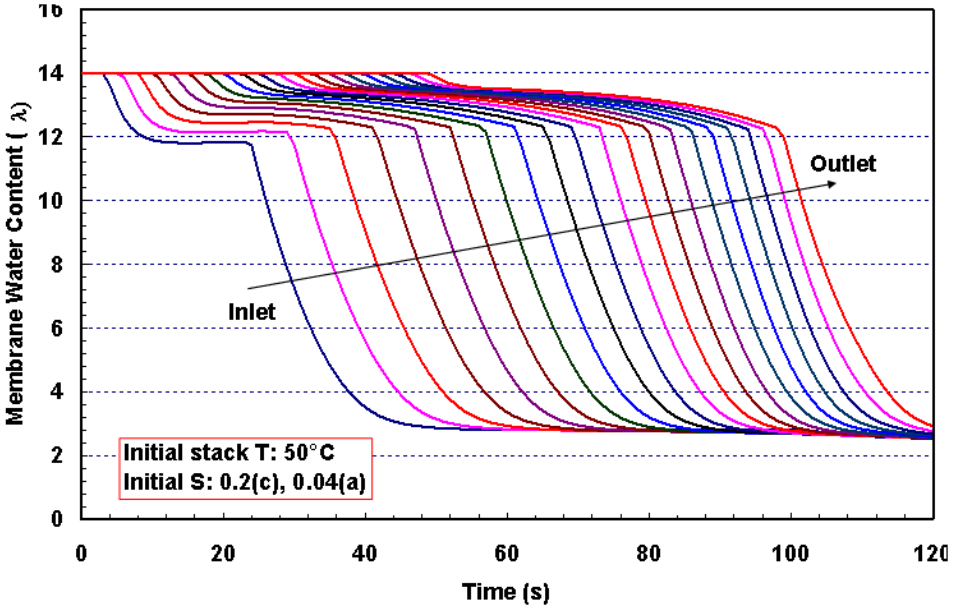
- Critical cell voltage for self start: $V_c = V_c(T_i, \lambda_i)$
  - $V_{cell} > 0.6$ V, self start not possible from −20°C with $\lambda_i = 8$
- Critical temperature for self start: $T_c = T_c(V_{cell}, \lambda_i)$
  - $T_i < -30$°C, self start not possible at 0.6 V, $\lambda_i = 5.5$
- Results given for warm up to 0°C
  - Minimum time generally corresponds to startup at the lowest cell voltage and $\lambda_i = \lambda_c$

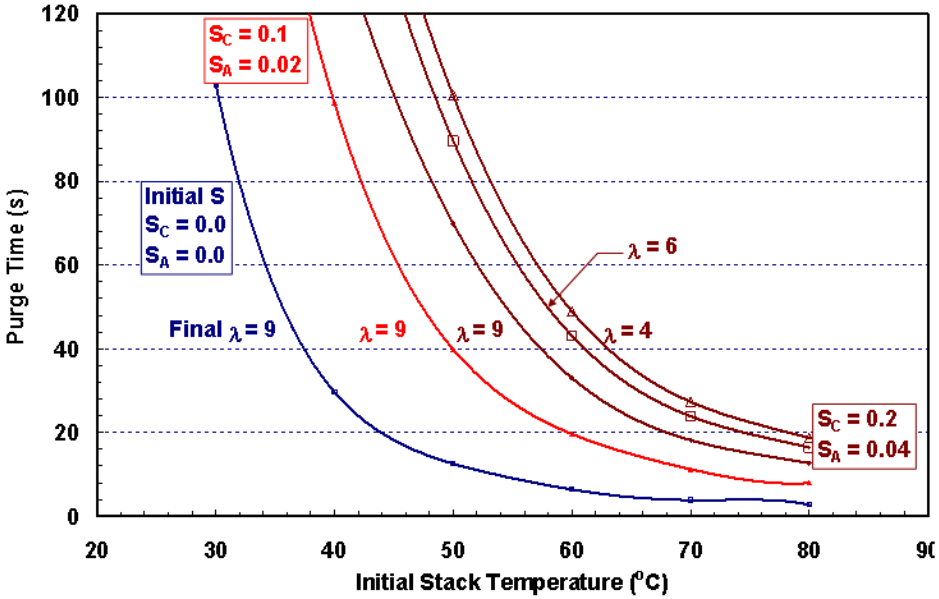




Stack Shutdown

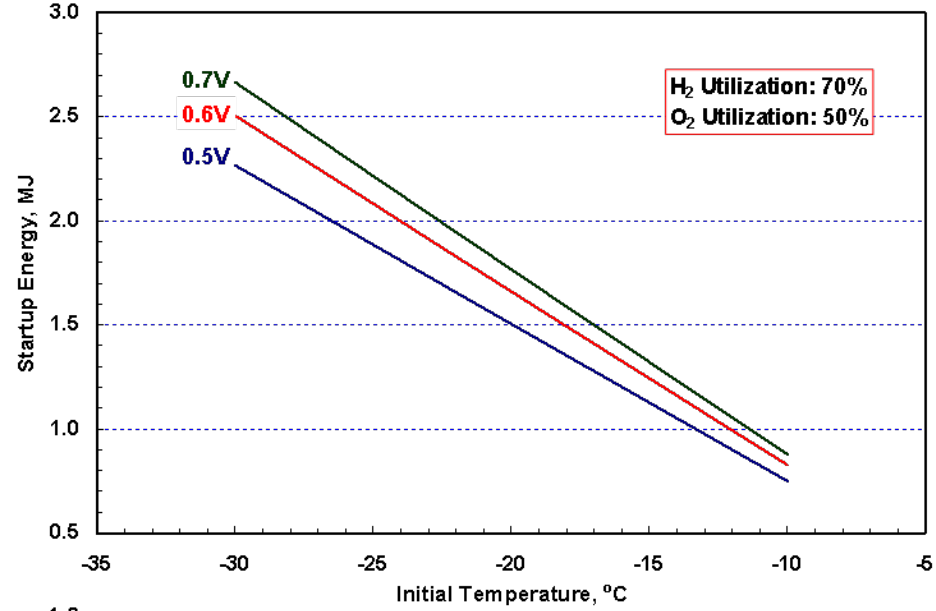
- Time and energy to dry the membrane, using cathode purge, to λ at which self start possible
  - Drying of cathode gas diffusion layer and catalyst layer
  - Drying of anode gas diffusion layer and catalyst layer
  - Drying of membrane
- Shutdown time depends on initial stack T, saturation (S), and target λ
  - Long shutdown time if initial stack T < 40°C, cathode S > 0.1
  - Air flow rate selected for 30% exit RH, >27 g/s, nozzle wide open

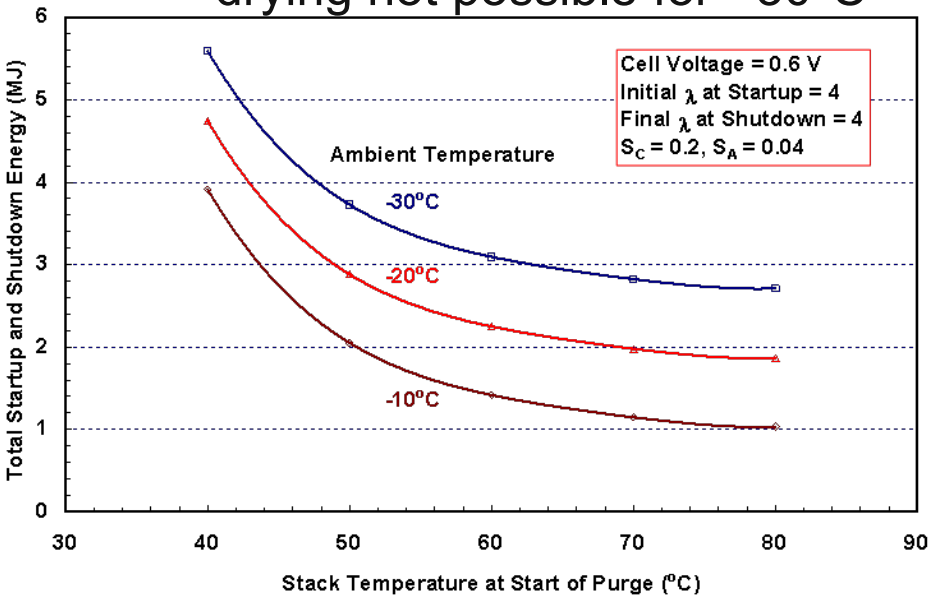


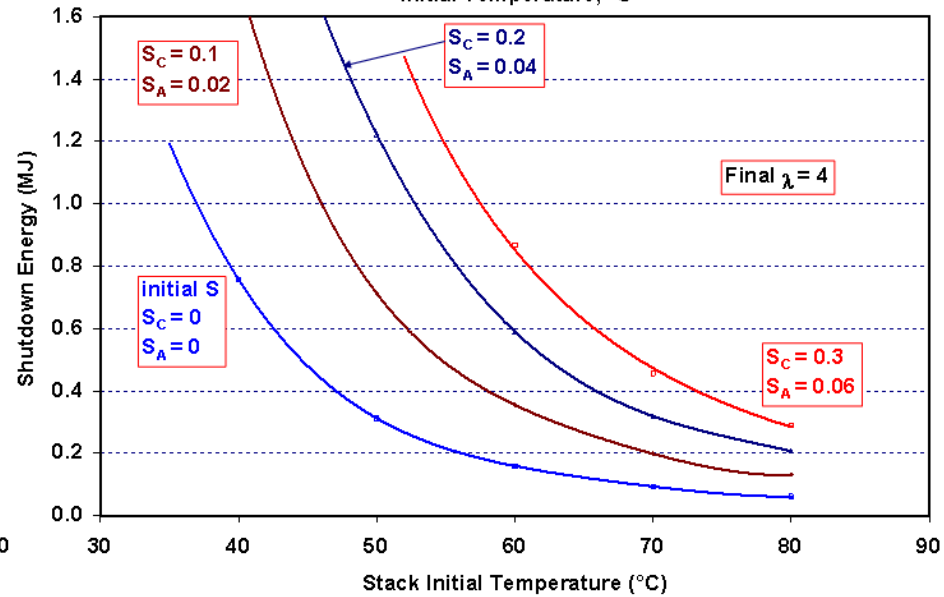


Startup/Shutdown Energy

- Startup/shutdown energy (Q): LHV of H_2
- Startup Q depends on T_{amb}, V_{cell}
  - Startup t>30s at −20°C, λ_i=4
  - Startup t<30s at −20°C, λ_i=6, but no self-start at −30°C
- Shutdown Q depends on initial stack T, S, final λ
  - Shutdown t>4min at T=40°C, drying not possible for <30°C

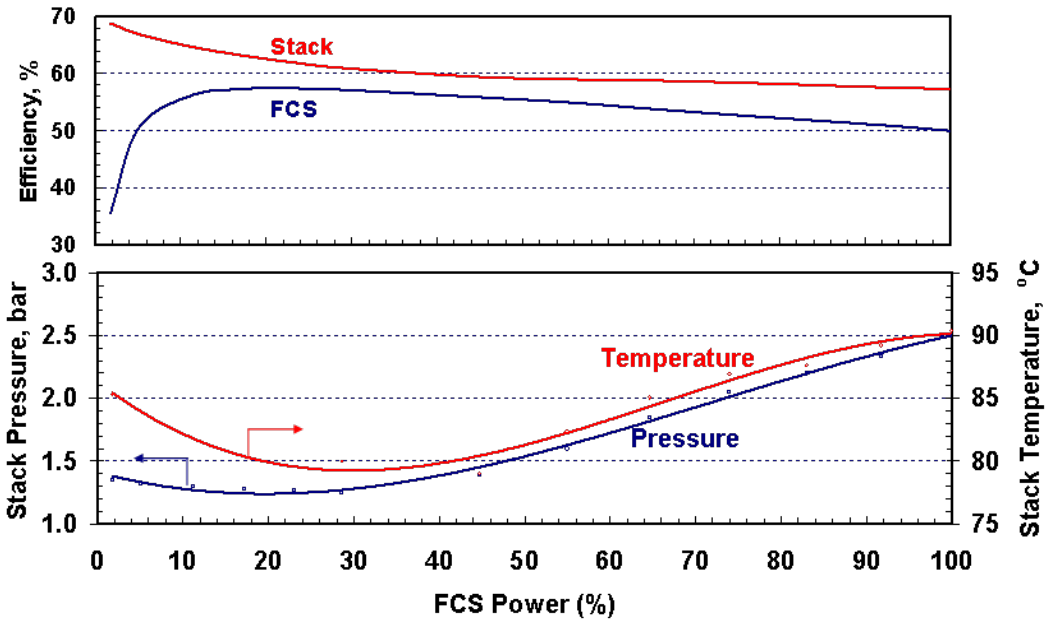






FC Systems Analysis: Status and Summary

- System performance
  - At rated power, operating points selected to minimize Pt content for specified system efficiency
  - At part load, operating points determined to maximize system efficiency (fixed components)
- Drive cycle simulations underway to understand the relationship between FCS performance, fuel economy and rated power efficiency (Pt content)



		S50	S47	S45
FCS efficiency at rated power	% LHV	50	47	45
FCS peak efficiency	% LHV	57		
Cell voltage at rated power	mV	721	685	655
Pt loading	mg/cm^2	0.25	0.25	0.25
Stack power density	mW/cm^2	640	840	970
Pt content	g/kW	0.45	0.34	0.30
FCS specific power	W/kg	674		
FCS power density	W/L	559		

Future Work

1. Systems Analysis

- Support DOE/FreedomCAR development effort at system, component, and phenomenological levels
- Collaborate with 3M on durability, reduced Pt loading (0.1(c)/0.05(a)), elevated T, and low RH operation of stacks
- Continue cooperation with Honeywell to validate air, thermal, and water management models
- System optimization for cost, performance, and durability
- Drive cycle simulations
- Alternate membrane, catalyst structures, and system configurations

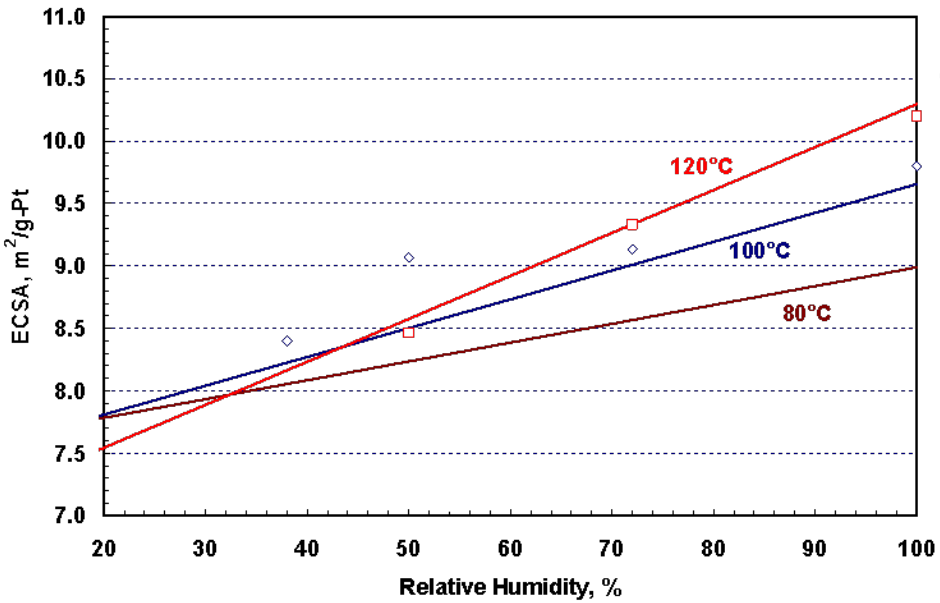
2. Hydrogen Quality

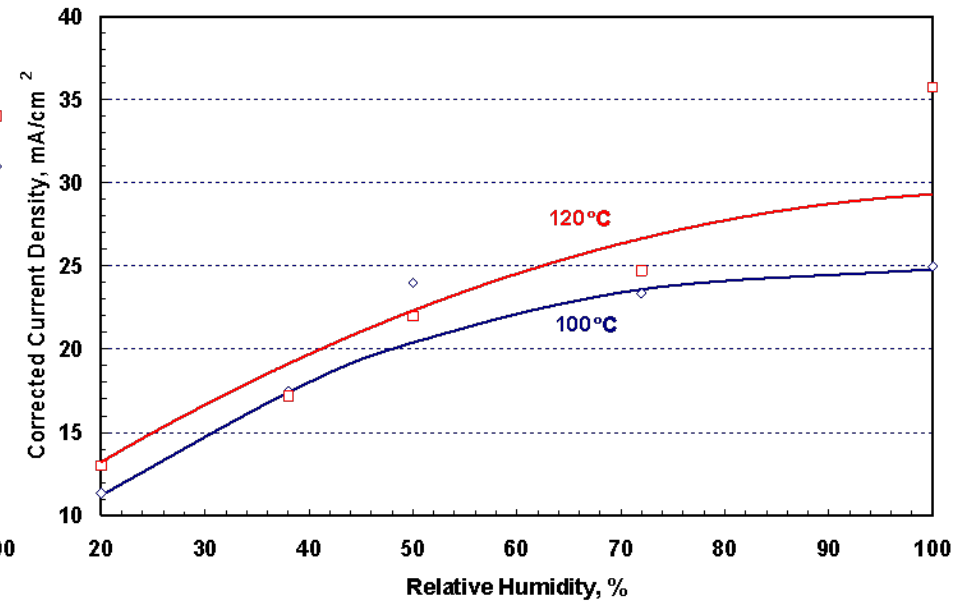
- Validate impurity models against U.S. and JARI data
- Project effects of proposed standards on stack performance
- Support the Hydrogen Quality Working Group and the Codes and Standards Technical Team

Additional Slides

NSTFC ORR Kinetics at High T and Low RH

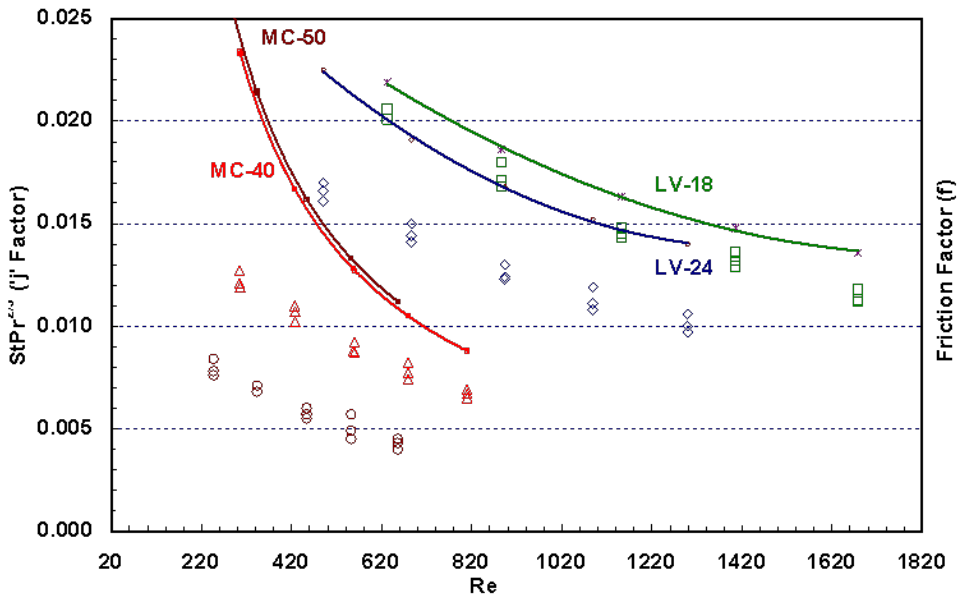
- 3M's single cell data with 0.1(a)/0.15(c) Pt in PtCoMn catalysts and 30-μm 850 EW membrane
- ECSA, specific activity, short and crossover currents and HFR data from CV, EIS and H_2/air cell at 0.9 V
  - 80°C data: initial, after 100°C exposure and after 120°C exposure
  - 100°C and 120°C data: 20, 35, 50, 72 and 100% RH, constant 1-bar O_2 partial pressure

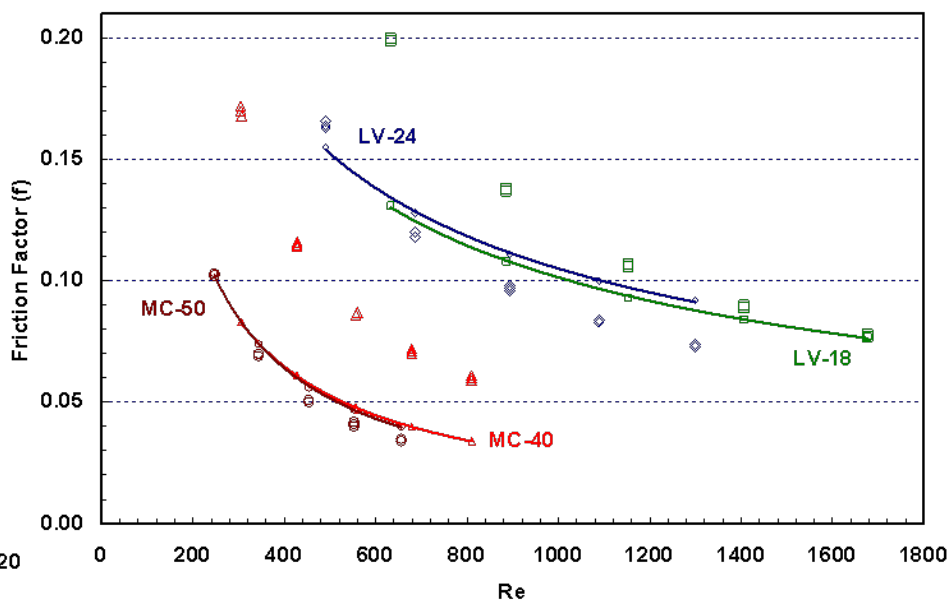




Advanced Radiator: f and j factors

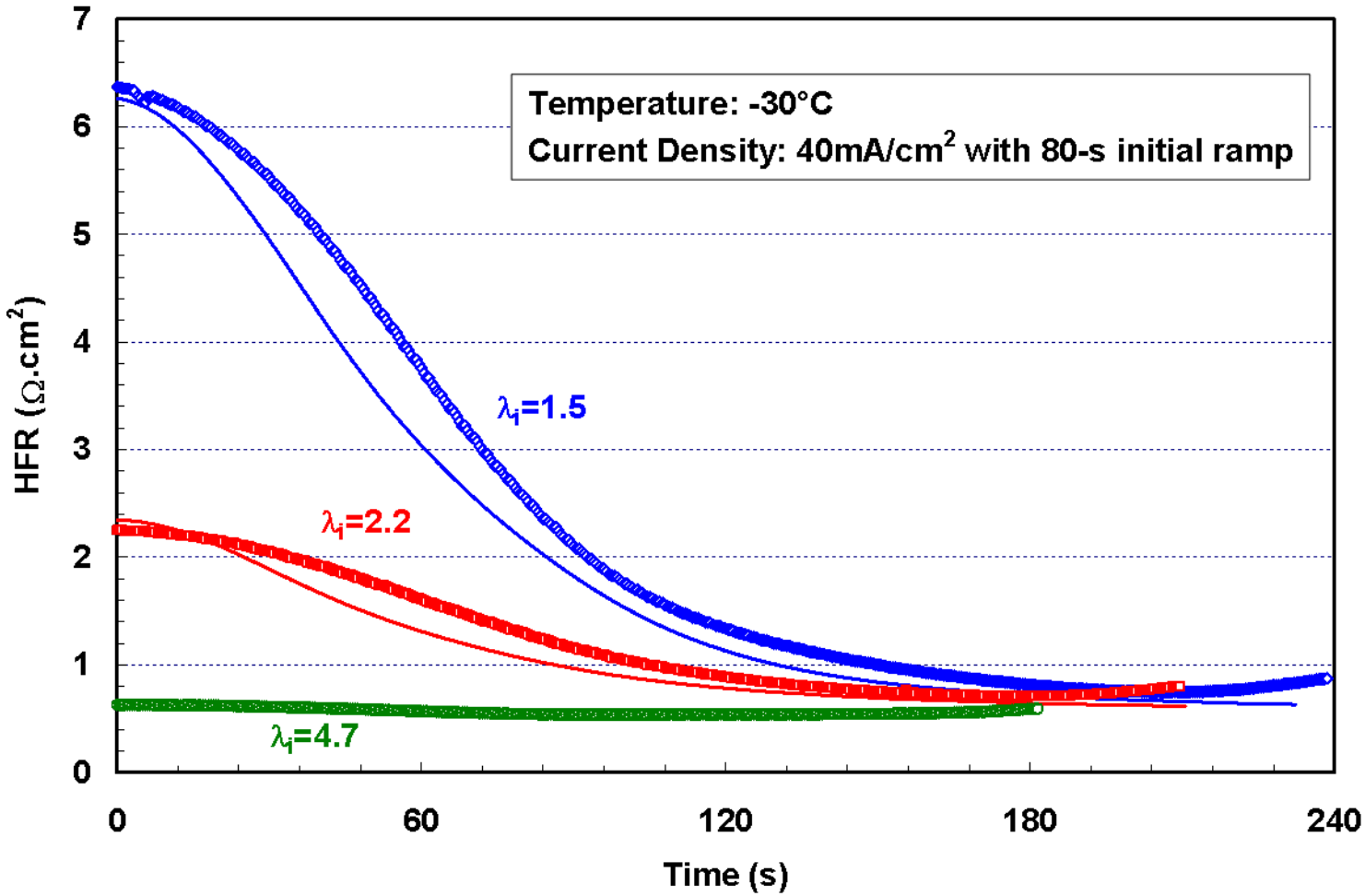
- Derived f and j factors from Honeywell data with 9”x9” subscale radiators with 18 and 24 fpi louver and 40 and 50 fpi microchannel fins.
- The literature correlation for louver fins does not adequately reflect the dependence of f and j on fin pitch.
- Significant deviation of data from literature correlations for plain microchannel fins that cannot be explained by channel non-uniformities and bulginess alone.





Water Uptake in Membrane

- Transient model for water transport in membrane and catalyst layers
  - Water uptake is a function of λ_i, β and current density

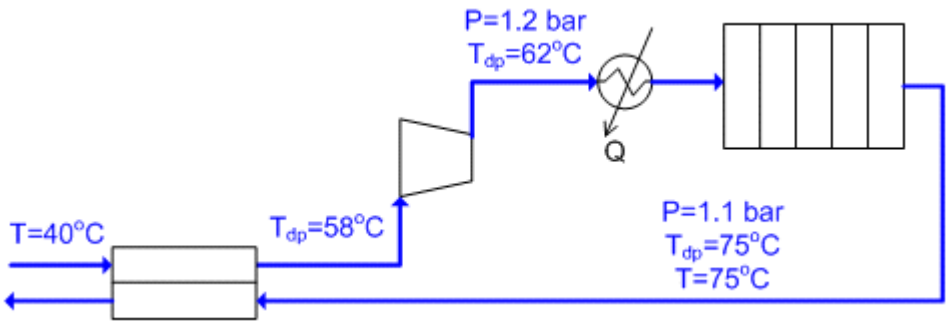


Ambient Pressure FCS with NSTFC Type MEA

Assumptions: NSTFC type MEA, 3 psi ΔP between blower & humidifier

Case	Fuel Cell		Dry Inlet		Wet Inlet			Humidified Air		Cooler	Blower
	P	T	P	T	P	T	T_{DP}	P	T_{DP}	Q	
	bar	°C	bar	°C	bar	°C	°C	bar	°C	kW	kWe
1-1	1.2	75	1	40	1.1	75	75	1	58	2.4	5.1
1-2	1.2	75	1.2	46	1.1	75	75	1.2	62	2.7	3.8

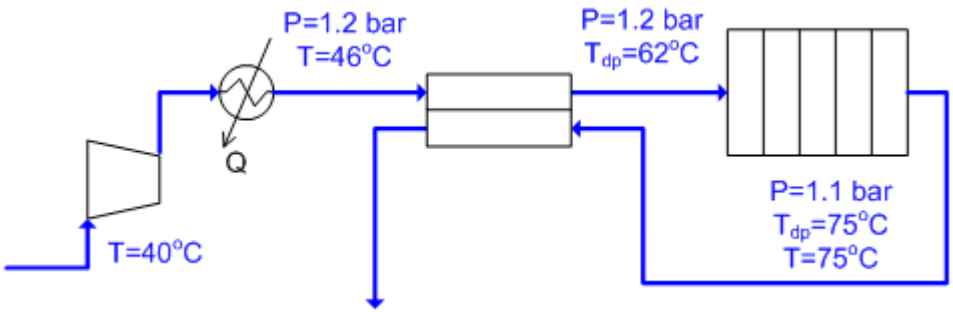
Case 1-1 Ambient Pressure FCS with Pre-humidification



- Humidifier located before blower
  - Higher parasitic power
  - Stack may need pre-cooler

Case 1-2 Ambient Pressure FCS with Post-humidification

- Humidifier located after blower
  - Lower parasitic power
  - Humidifier needs air pre-cooled to 46°C which may be difficult

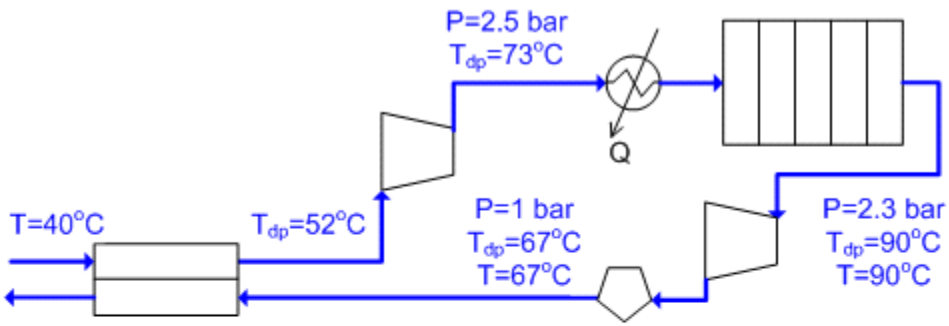


Pressurized FCS with NSTFC Type MEA

Assumptions: NSTFC type MEA, 3 psi ΔP between compressor & expander

Case	Fuel Cell		Dry Inlet		Wet Inlet			Humidified Air		Cooler	Parasitic Power		
	P	T	P	T	P	T	T_{DP}	P	T_{DP}	Q	CP	Exp	Total
	bar	°C	bar	°C	bar	°C	°C	bar	°C	kW	kW	kW	kWe
2-1	2.5	90	1	40	1	67	67	1	52	9.6	13.8	7.6	7.3
2-2	2.5	90	2.5	58	2.3	90	90	2.5	73	9.6	11.3	5.8	6.5

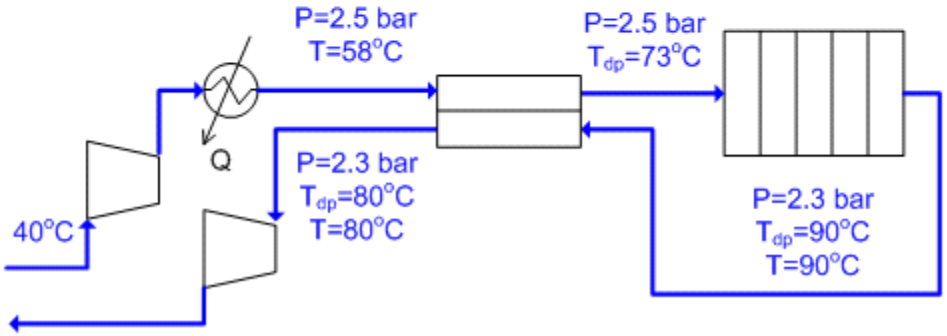
Case 2-1 Pressurized FCS with Pre-humidification



- Humidifier before compressor
  - Higher parasitic power
  - Stack needs pre-cooler
  - Cooling CEM motor potentially problematic

Case 2-2 Pressurized FCS with Post-humidification

- Humidifier after compressor
  - Lower parasitic power
  - Humidifier needs air pre-cooled to 58°C which may be difficult



Argonne Reference 2009 FCS Parameters

PEFC Stack

- 2.5 atm at rated power
- 50% O_2 utilization
- 70% H_2 consumption per pass
- Cell voltage at rated power: 0.721 V
- 30-μm 3M membrane at 90°C
- Pt loading: 0.1/0.15 mg/cm^2 on anode/cathode
- GDL: 275-μm woven carbon fiber
- 2-mm expanded graphite bipolar plates, each with cooling channels
- 10 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: 70% compressor, 73% expander, 86% motor, 87% controller
- Turn-down: >20
- 5 psi pressure drop at rated power

Heat Rejection System

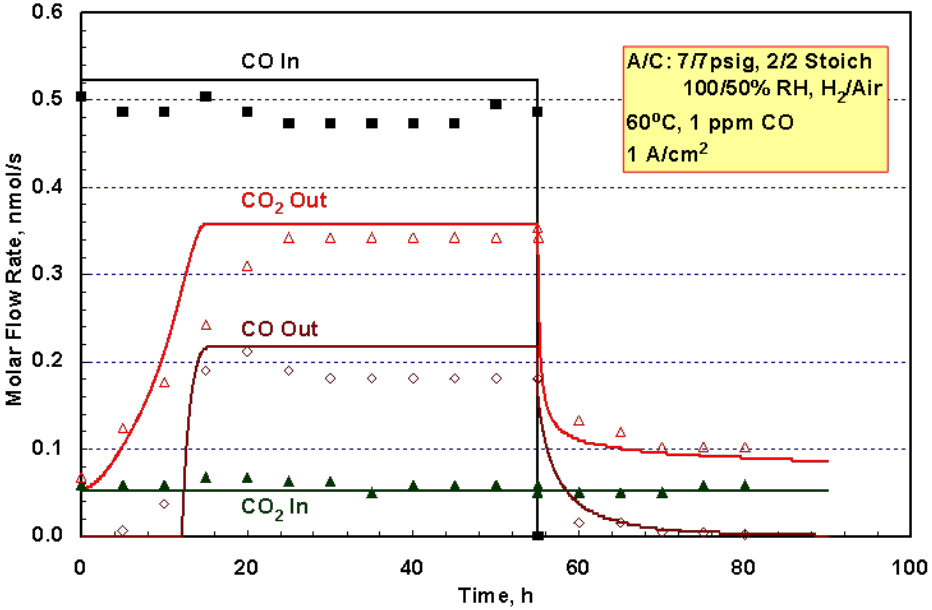
- Two circuits: 85°C HT, 55°C LT coolant
- 55% pump + 92% motor efficiency
- 45% blower + 92% motor efficiency
- 10 psi pressure drop each in stack and radiator

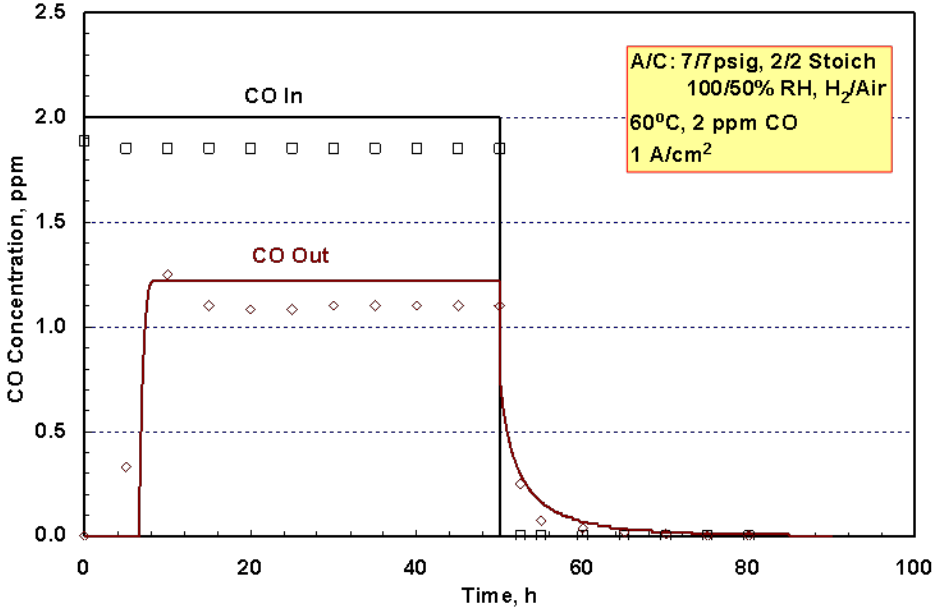
Water Management System

- MH for air, 50% RH at rated power
- MH for H_2, 50% RH at rated power

Preliminary Analysis of HNEI Cell Data
CO Conversion at 60°C

- At 60°C, measured CO conversion increases from 64% with 1-ppm inlet CO to 71% with 2-ppm inlet CO.
- In our simulation, the steady-state O_2 selectivity for CO is 3.1% with 1-ppm inlet CO and 7.5% with 2-ppm inlet CO.
- We calculate that with 1-ppm CO at inlet, O_2 crossover accounts for 35.2% of CO that is converted to CO_2 (33.5% with 2-ppm inlet CO).

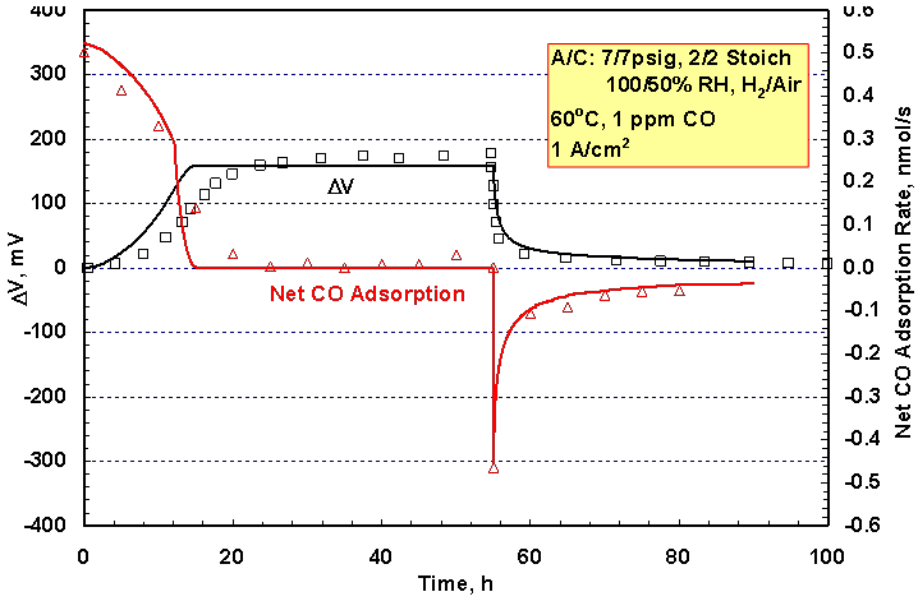


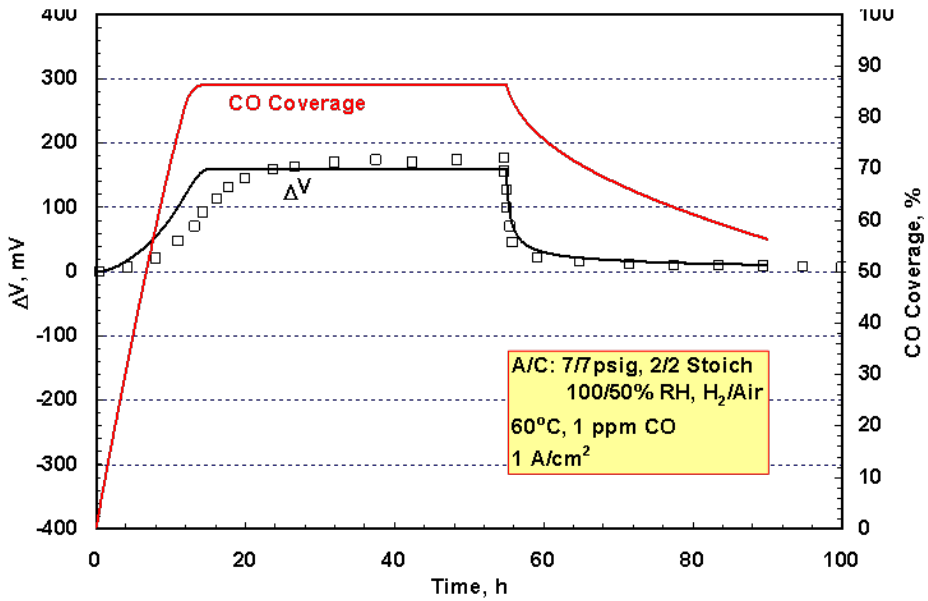


Refs. G. Bender, M. Angelo, K. Bethune, S. Dorn, D. Wheeler, and R. Rocheleau, "The Anode Overpotential Dependence on Oxygen Permeation During PEMFC Operation with CO," 212th ECS Meeting, Washington DC, Oct. 7-12, 2007.

Preliminary Analysis of HNEI Cell Data
Net CO Adsorption

- Within the limits of GC accuracy (0.6% error in carbon balance), CO uptake is consistent with adsorption on linear sites at 90% coverage.
- Additional data needs
  - CO conversion at 80°C (T dependence of O_2 selectivity for CO)
  - CO conversion in hydrogen pump mode (electrochemical vs. chemical oxidation of CO, 60 and 80°C)





Refs. G. Bender, M. Angelo, K. Bethune, S. Dorn, D. Wheeler, and R. Rocheleau, "The Anode Overpotential Dependence on Oxygen Permeation During PEMFC Operation with CO," 212th ECS Meeting, Washington DC, Oct. 7-12, 2007.

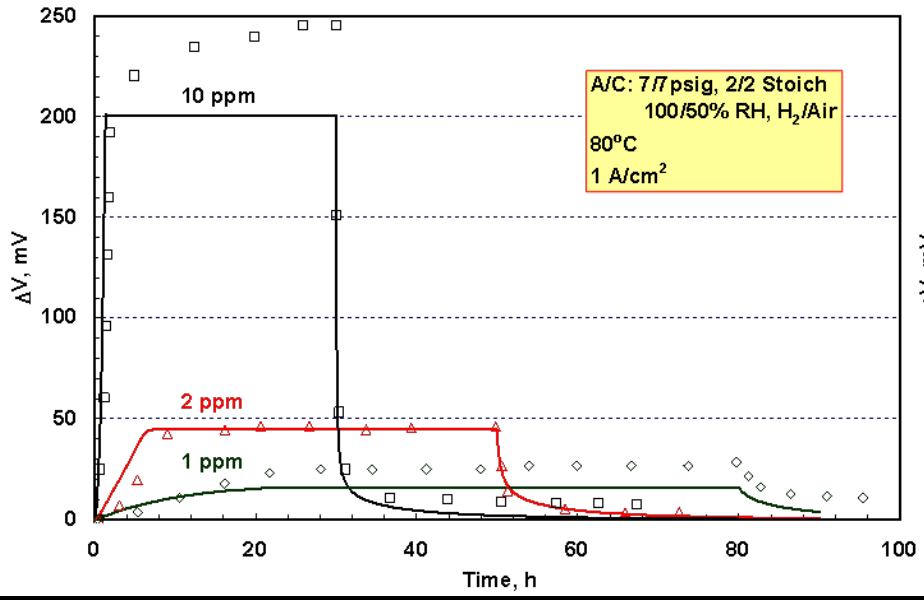
Preliminary Analysis of HNEI Cell Data
Dependence of ΔV on CO concentration and T

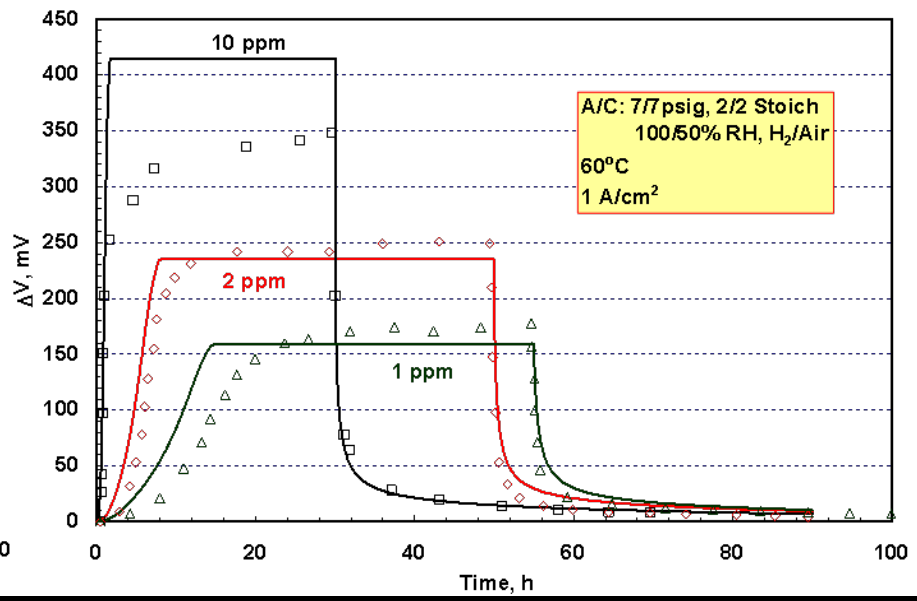
Modeled steady-state O_2 selectivity for CO and oxidative conversion of CO

	T	Inlet CO (ppm)		
	T(°C)	1	2	10
S_{CO}	60	3.1%	7.5%	40.0%
S_{CO}	80	1.8%	4.0%	25.4%
F_{ox}	60	35.2%	33.5%	24.3%
F_{ox}	80	10.0%	23.9%	23.5%

$$S_{CO} = \frac{\dot{N}_{O_2}^{CO}}{\dot{N}_{O_2}^{CO} + \dot{N}_{O_2}^{H_2}}$$

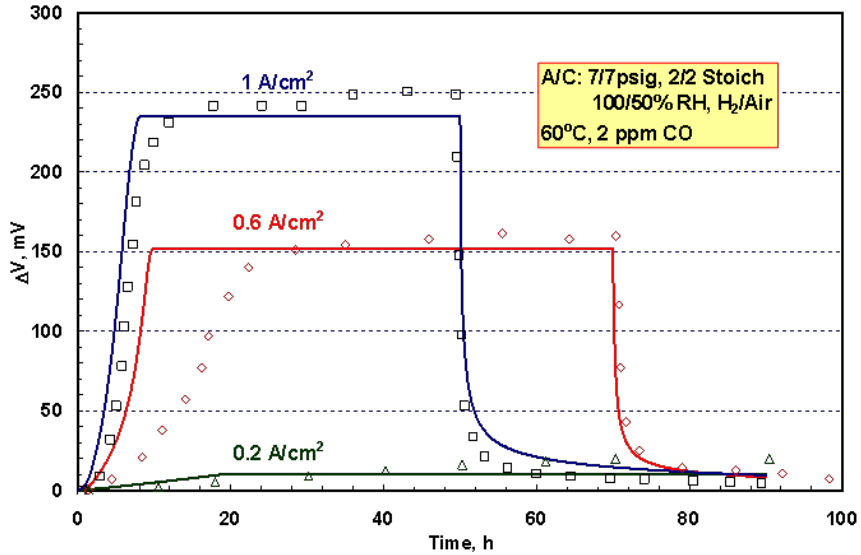
$$F_{ox} = \frac{\dot{N}_{CO}^{O_2}}{\dot{N}_{CO}^{O_2} + \dot{N}_{CO}^{EC}}$$

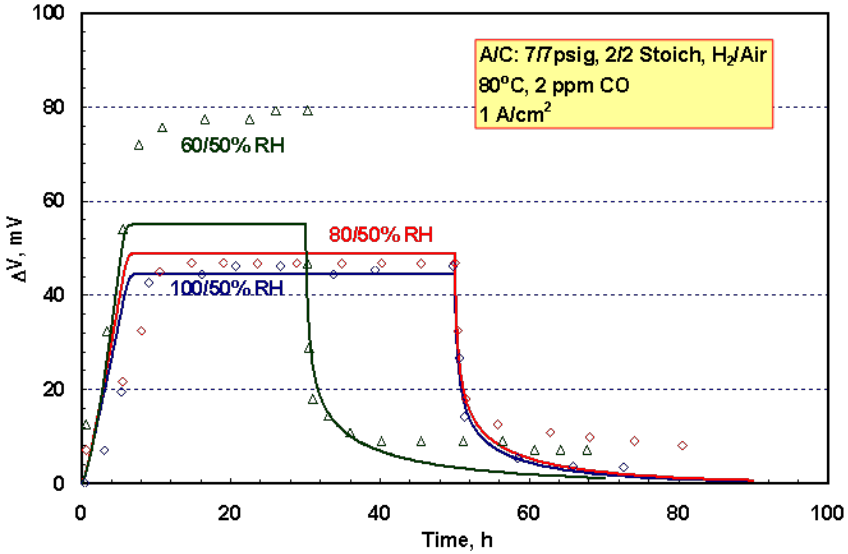


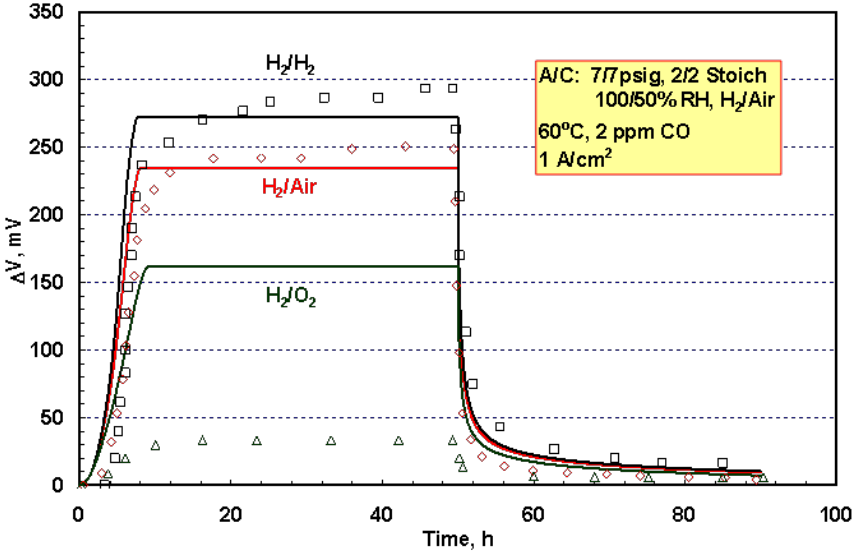


Preliminary Analysis of HNEI Cell Data
Dependence of ΔV on J and RH

- Data for 60% RH suggests that the assumption of J_{CO} being first order in P_{H2O} needs to be revisited
- Apparent disparity between model and ΔV data in H_2/O_2 mode







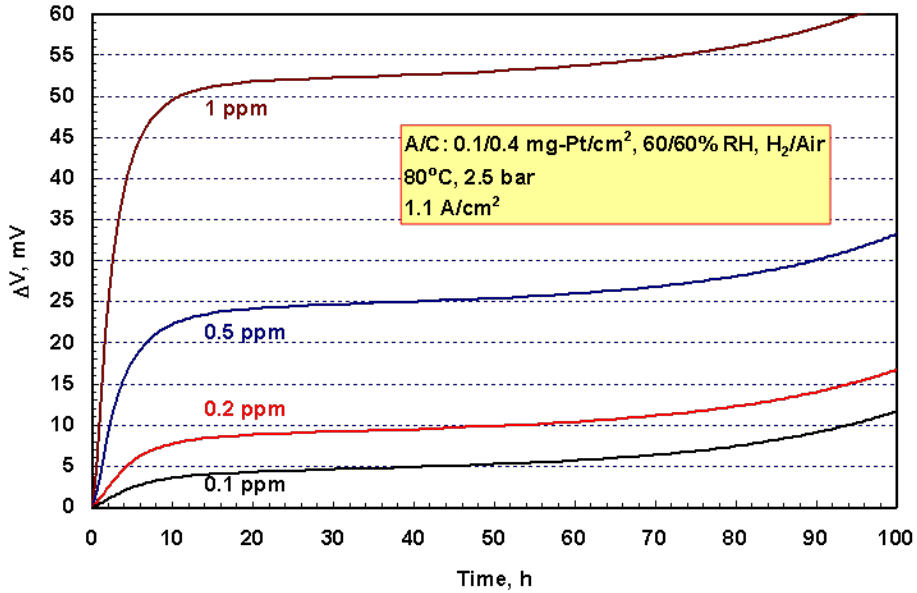
Buildup of Impurities with Anode Gas Recycle

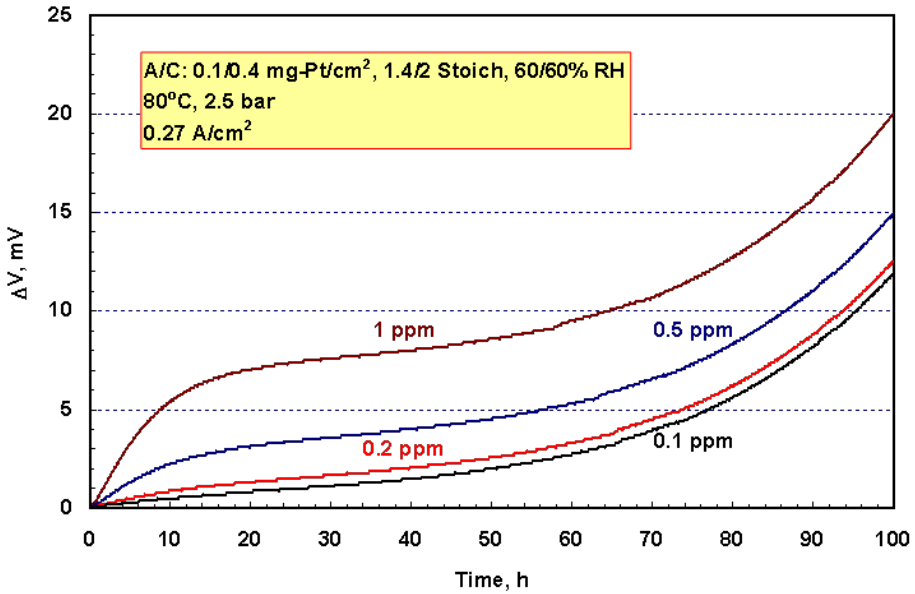
- No buildup of CO for inlet CO < 1 ppm, 70% Φ_{H2}, 80°C

$$\Phi_{CO} = 1 - \dot{N}_{CO}^{out} / \dot{N}_{CO}^{in}$$

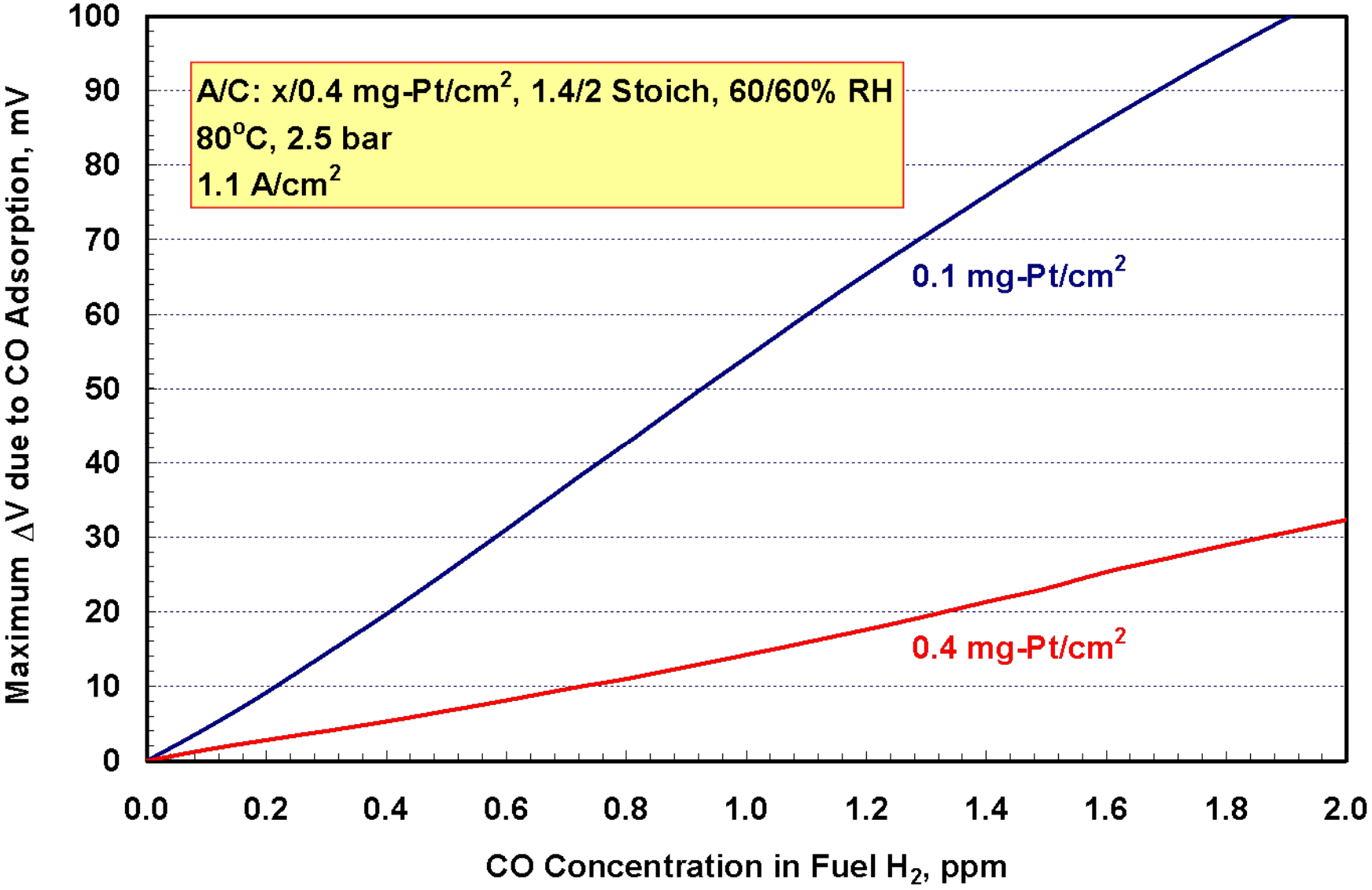
$$R_{CO} = \frac{C_{CO}^{out}}{C_{CO}^{in}} = \frac{1-\Phi_{CO}}{1-\Phi_{H_2}}$$

- Initial increase in ΔV is due to CO adsorption (no purge), subsequent increase due to accumulation of CO_2 and N_2

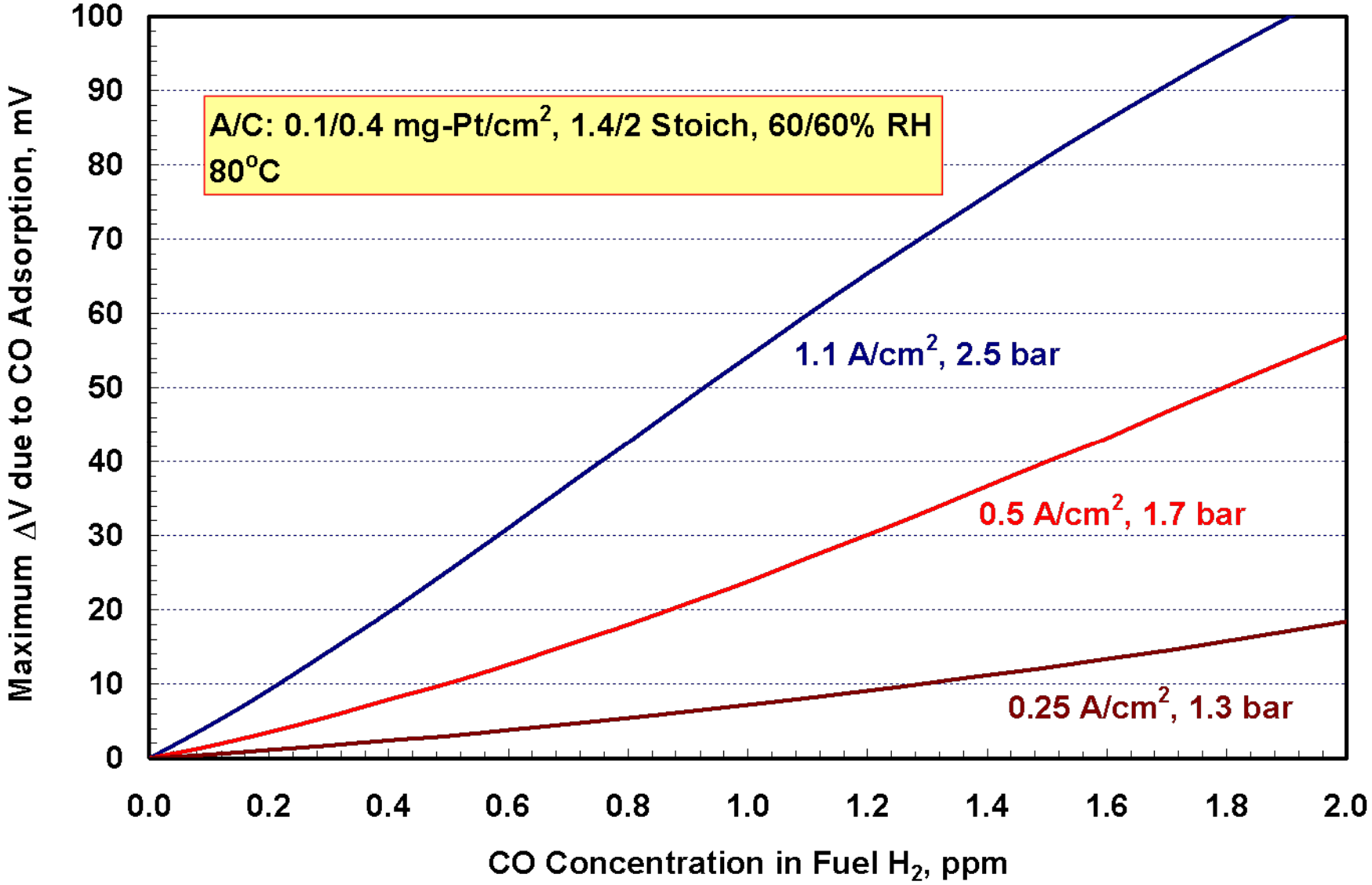




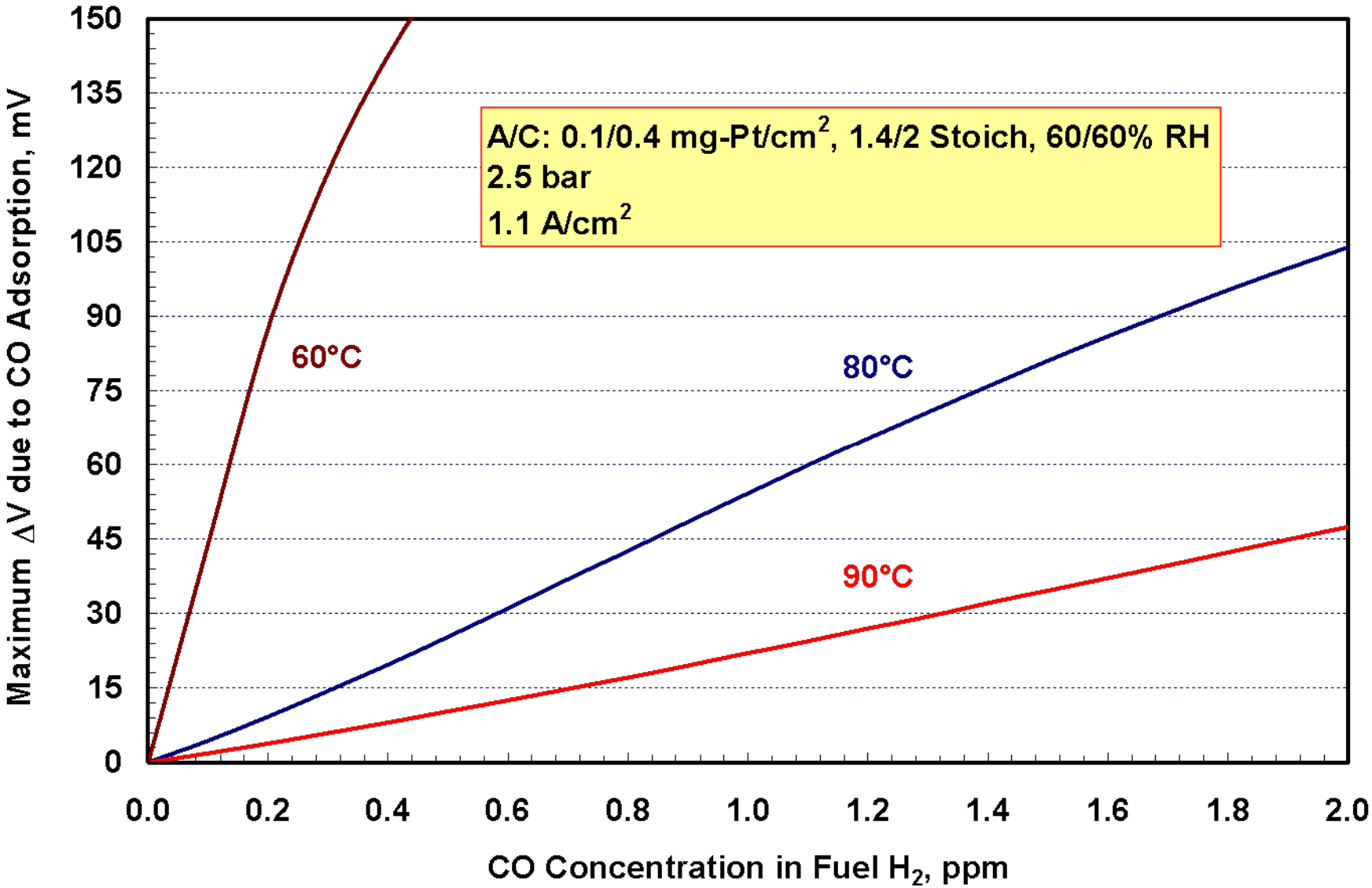
Anode Overpotential: Effect of Pt Loading



Anode Overpotential: Effect of Current Density



Anode Overpotential: Effect of Cell Temperature



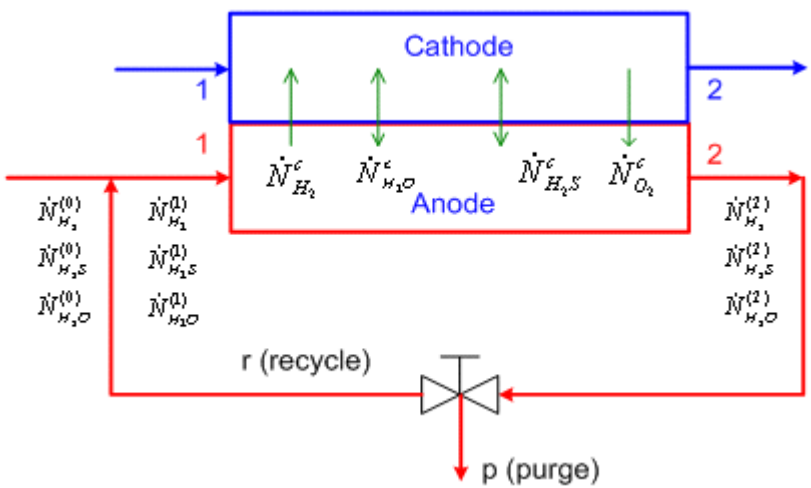
Mechanism of Cell Degradation due to H_2S

- Loss in cell performance due to H_2S exposure is mostly irreversible under normal operating conditions (Uribe 2001, Garzon 2008)
- Partial recovery in performance at open-circuit voltage (Garzon 2008)
- CV data shows that H_2S is strongly sorbed on the electrocatalyst (Uribe 2001, Mohtadi 2003).
- Sorbed H_2S can be oxidized at high cell voltages, >0.85 V vs. DHE. Multiple oxidation cycles are required (Mohtadi 2003, Sethuraman 2006) and the recovery may be less than 100%.
- Sulfur is more strongly sorbed at lower temperatures (Mohtadi, 2005).
- Sulfur tolerance of Pt-Ru alloy is inferior to Pt catalyst (Mohtadi 2003).

Modeling Approach

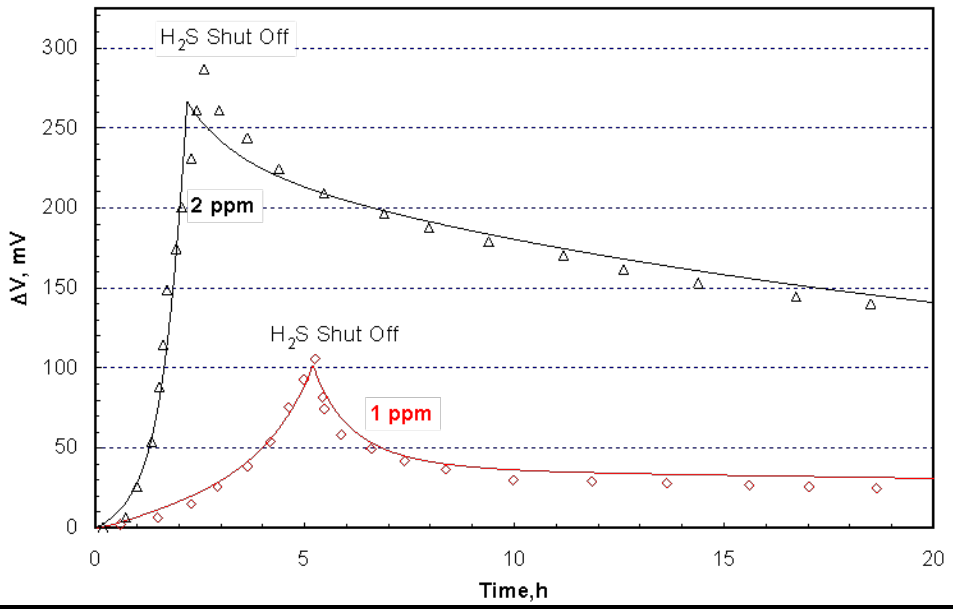
- Sequential Sorption of H_2S on Pt
  1. $nM + H_2S \leftrightarrow M_n\text{-}H_2S$ (Associative chemisorption)
  2. $M_n\text{-}H_2S \leftrightarrow M_nS + 2H^+ + 2e^-$ (Electrochemical reaction)
  3. $M_nS + 3H_2O \rightarrow nM + SO_3 + 6H^+ + 6e^-$ (Electrochemical oxidation)
- Multi-site sorption of H_2S, n is a function of total sulfur coverage (θ_S)
  - $n \rightarrow 1$ as $\theta_S \rightarrow 1$, $n \rightarrow N$ as $\theta_S \rightarrow 0$

- Near OC, M_nS can re-convert to $M_n\text{-}H_2S$ (E_2 = 0.14 V), and H_2S can desorb for partial recovery
- At a high anode overpotential (E_3 = 0.89 V), M_nS can oxidize to SO_3, SO_3 assumed completely soluble in water and removed from the system



Derived rate constants for R1 and R2 from LANL transient poisoning and recovery data

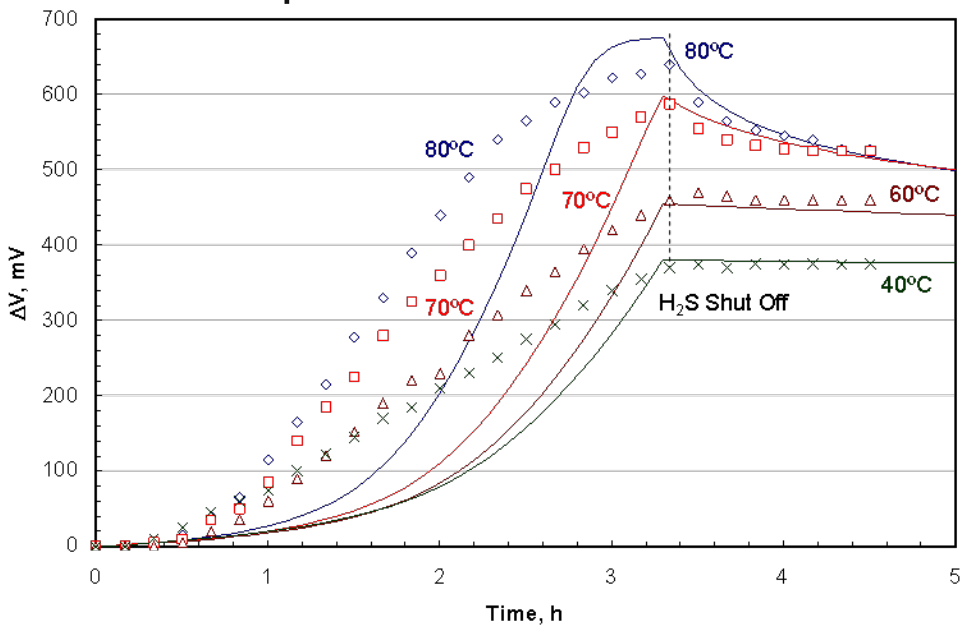
- Data from T. Rockward, LANL, 2007
- Developed rational method of determining rate constants for R1 & R2
  - Calculated max θ_S corresponding to peak ΔV and θ_{H2S}, backward R2 neglected (assumed N)
  - Determined k_d for R1 and $\Delta(\Delta H_d)$ from 1-ppm V recovery data
  - Determined k_a for R1 and k_f for R2
  - Determined N to match 1 & 2-ppm poisoning and recovery data



- Pt Loading: 0.22 mg/cm^2
- Membrane: Nafion® 112
- Membrane Area: 50 cm^2
- Temperature: 80ºC
- Pressure: 30 psig
- Current Density: 0.8 A/cm^2
- Flow Rate: 360 sccm (a)
  2100 sccm (c)

Effect of Temperature on H_2S Poisoning

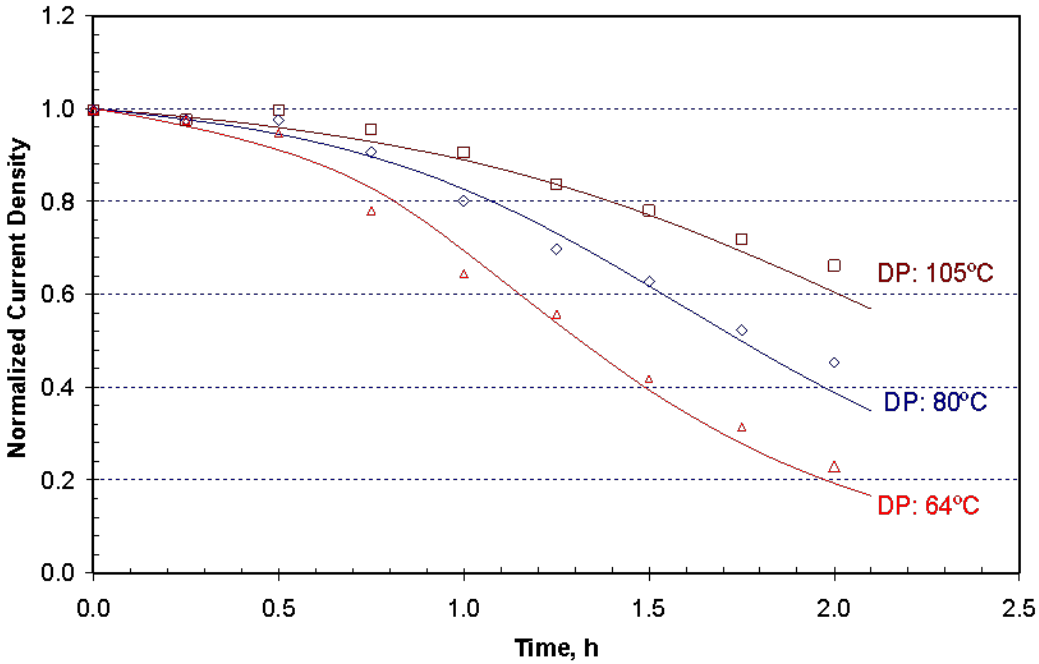
- Data from T. Rockward, LANL, 2007
- Higher the temperature, higher the ΔV and higher the V recovery
- Plateau in ΔV for long-time exposure at 70-80°C: $r_1 = r_2 = r_3$
- Developed rational method for determining rate constants for R2 - R3
  - Determined E_a for R1 and k_e for R3, ΔH_d = 25 kJ/mol
  - Revised rate constants for R1 and R2
  - Complications due to cell to cell variation in 80°C data



- Pt Loading: 0.22 mg/cm^2
- Membrane: Nafion® 112
- Membrane Area: 50 cm^2
- Temperature: 80°C
- Pressure: 30 psig
- Current Density: 0.8 A/cm^2
- Flow Rate: 400 sccm (a)
  2100 sccm (c)
- H_2S Concentration: 2 ppm

Effect of Relative Humidity on H_2S Poisoning

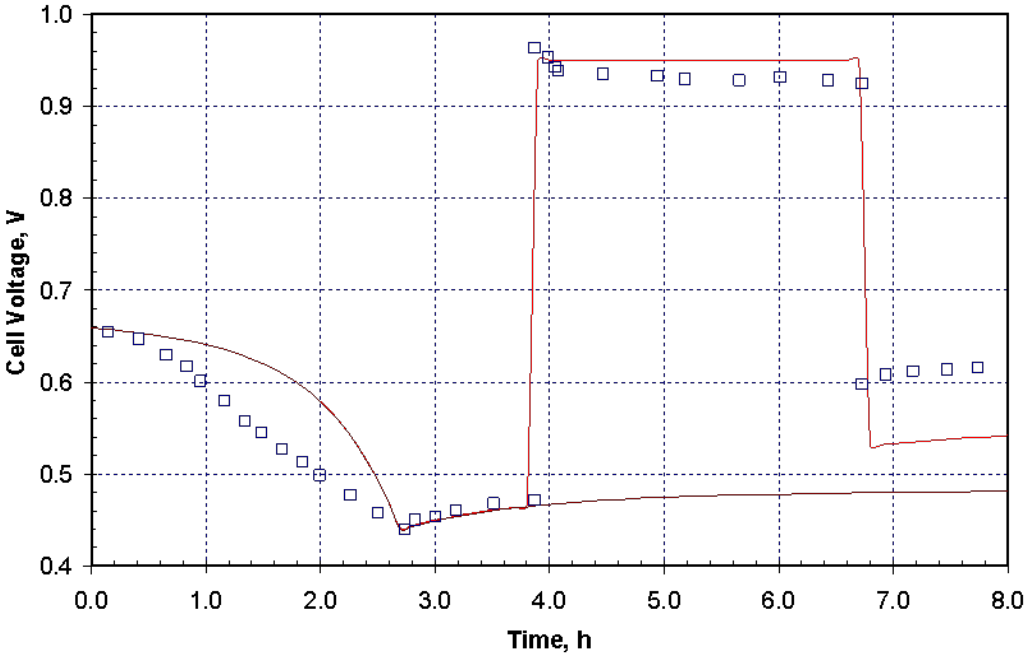
- Data from T. Rockward, LANL, 2007
- The more the amount of local water, the slower the decay in current density due to H_2S poisoning at constant cell voltage
- Determined the dependence of k_a on the activity of H_2O for R1



- Pt Loading: 0.20 mg/cm^2
- Membrane: Nafion® 112
- Membrane Area: 50 cm^2
- Temperature: 80ºC
- Pressure: 30 psig
- Cell Voltage: 0.5 V
- Flow Rate: 400 sccm (a)
  2100 sccm (c)
- H_2S Concentration: 2 ppm

Effect of OCV on H_2S Poisoning

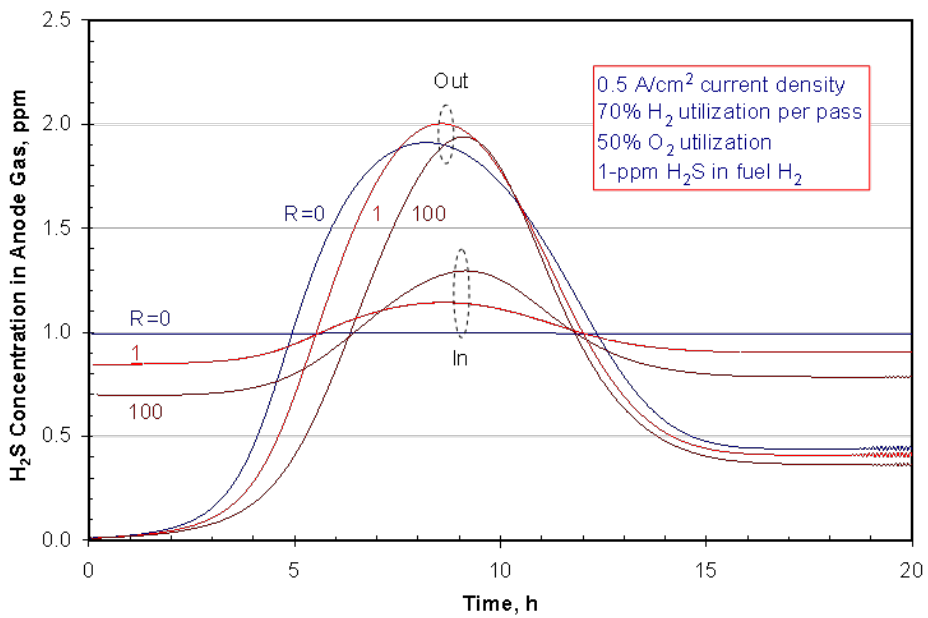
- Data from T. Rockward, LANL, 2007
- Partial recovery in cell voltage after holding the cell at OCV for 3 h with neat H_2
- Determined k_b for the electrochemical reaction R2
  - Small change in θ_S produces the observed recovery in cell voltage

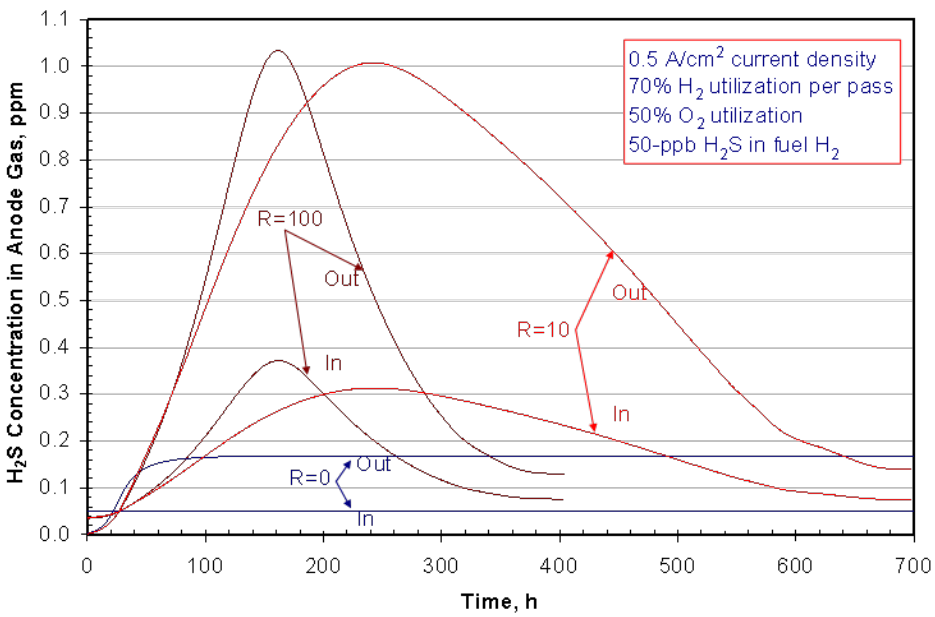


- Pt Loading: 0.2 mg/cm^2 (a)
  0.2 mg/cm^2 (c)
- Membrane: Nafion® 112
- Membrane Area: 50 cm^2
- Temperature: 80ºC
- Pressure: 30 psig
- Flow Rate: 362 sccm (a)
  2100 sccm (c)
- H_2S Concentration: 1.5 ppm

Buildup of H_2S in Anode Gas Channels

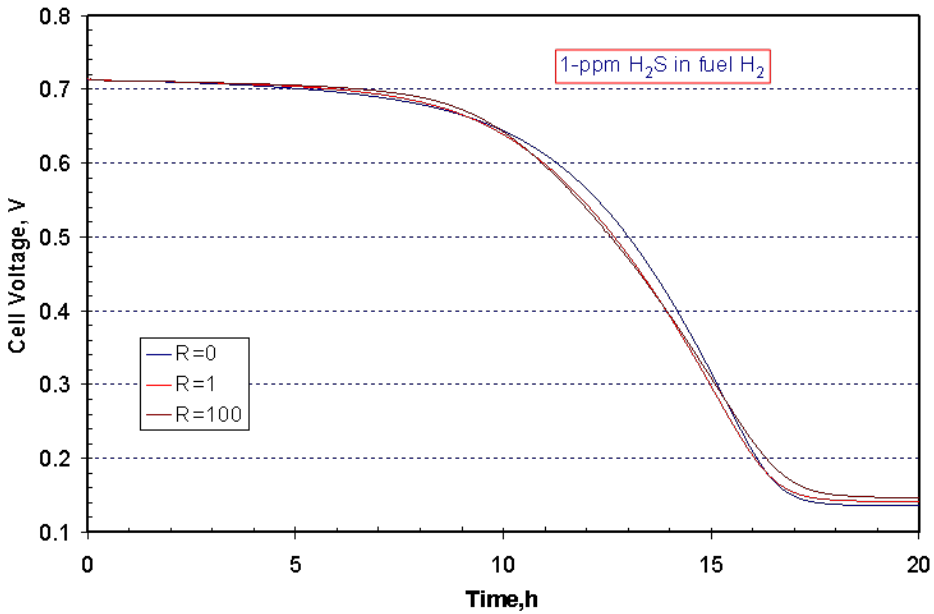
- At constant current density, steady-state buildup of H_2S depends on its concentration in fuel H_2 and R
- No accumulation ($C_{in}/C_f < 1$) for 1-ppm H_2S in fuel H_2 regardless of R
  - $C_{out}/C_{in} < 1$ and $<<1/(1-\phi_{H2})$: significant conversion to SO_3 via R3
  - Result in qualitative agreement with JARI data
- H_2S does accumulate for lower H_2S concentration in fuel H_2 (50 ppb)
- Prior to reaching SS, C_{out} and C_{in} increase with time to reach a maximum

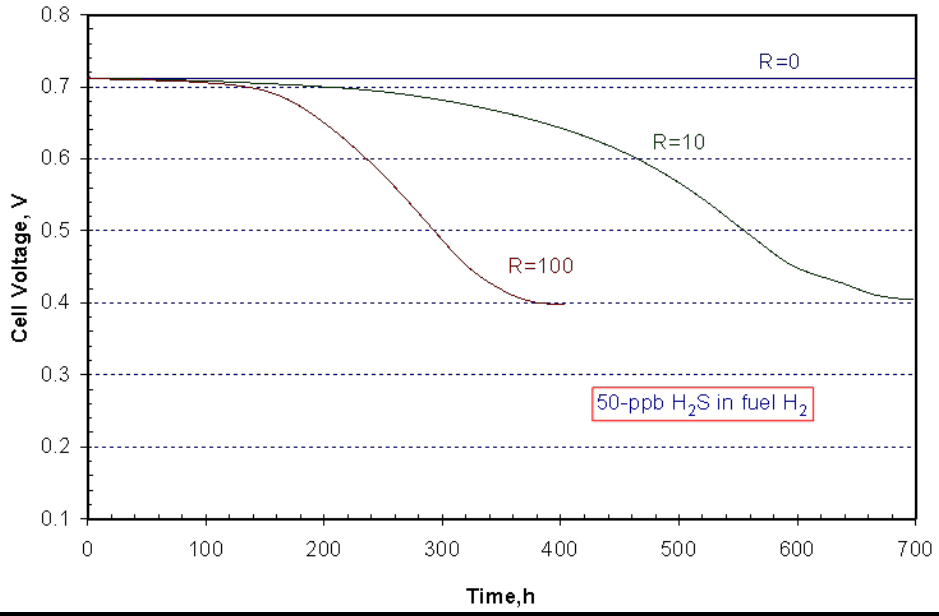




Effect of H_2S Buildup on Cell Voltage

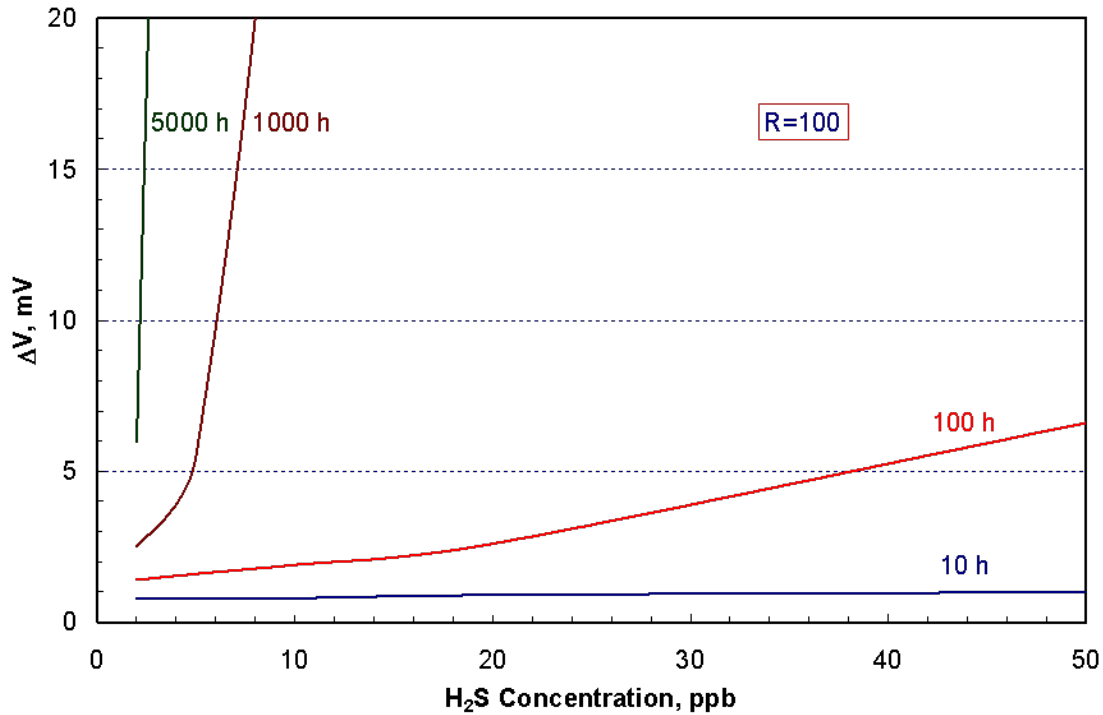
- At steady-state, ΔV is a function of H_2S concentration in fuel H_2 rather than R.
- The lower the H_2S concentration and R, the longer the time to reach steady state (τ_{ss}).
- For exposure times less than τ_{ss}, ΔV is more sensitive to R at lower H_2S concentrations in fuel H_2.





Limits for H_2S in Fuel H_2

- H_2S concentration needs to be <2 ppb to limit decrease in cell voltage at 0.5 A/cm^2 to 10 mV after 5000 h
  - Impurity limit can be relaxed if the exposure time is reduced (periodic tune up)
  - Both dosage and concentration affect the decrease in cell voltage
  - Dependence of ΔV on Pt loading remains to be determined



- 0.5 A/cm^2 current density
- 70% H_2 utilization per pass
- 50% O_2 utilization