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# Fuel Cell Systems Analysis

R. K. Ahluwalia, X. Wang and R. Kumar
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**Project ID: FC1**

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

## Barriers

B. Cost

C. Performance

E. System Thermal and Water Management

F. Air Management

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

## Budget

- FY07 funding: $500K
  DOE share: 100%
- FY06 funding: $450K

## Partners

- Honeywell CEM+TWM projects
- IEA Annexes 17 and 20
- FreedomCAR fuel cell tech team
- TIAX, 3M
- $H_2$ Quality Working Group
- Vairex

# Objectives

Develop a validated system model and use it to assess design-point, part-load and dynamic performance of automotive fuel cell systems.

- Support DOE in setting and evaluating R&D goals and research directions
- 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_ENG: Coupled to PSAT (MATLAB/SIMULINK)

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

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

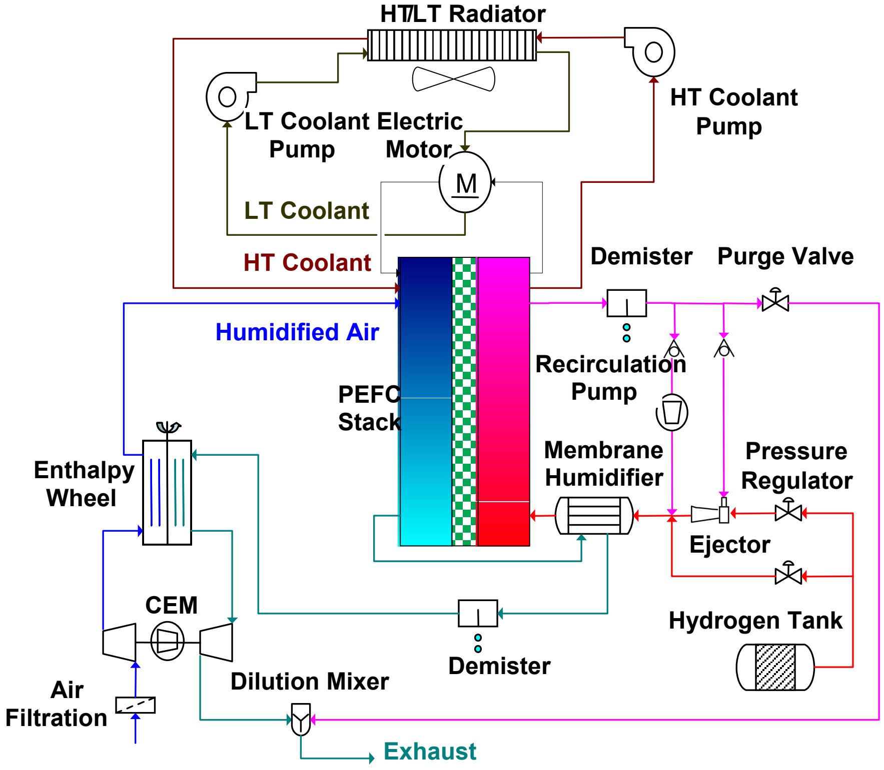
- Formulated correlations for 3M membrane
- Modified MEA model for NSTF catalyst structure
- Validated the stack model against experimental data
- Developed optimum operating maps by integrating the performance of the CEM, stack and humidification device
- Analyzed heat rejection at elevated stack temperature
- Made presentations to DOE and TIAX to convey results
- Supplied performance and component data to TIAX and assisted in the FCS-2007 cost study

2. Impurity effects in support of $H_2$ Quality Working Group

- Developed models for $N_2$, CO, $CO_2$, $H_2S$ & $NH_3$ impurities
- Analyzed effects of anode gas recycle
- Constructed maps for voltage and efficiency degradation

# Argonne 2007 Reference Fuel Cell System

- Modified PFSA membrane for enhanced durability at low humidity
- 3M NSTF ternary-alloy catalyst for low Pt loading, diminished ECSA loss with potential cycling, stability at high potentials
- Higher cell temperature to help with heat rejection



### 2005 Status

- Difficult to meet 50% $\eta_s$ target at acceptable Pt loading
- 1 g-Pt/kW loading for 46% $\eta_s$
- Durability of finely dispersed Pt catalyst and PFSA membrane
- Heat rejection is an issue at 80°C stack temperature

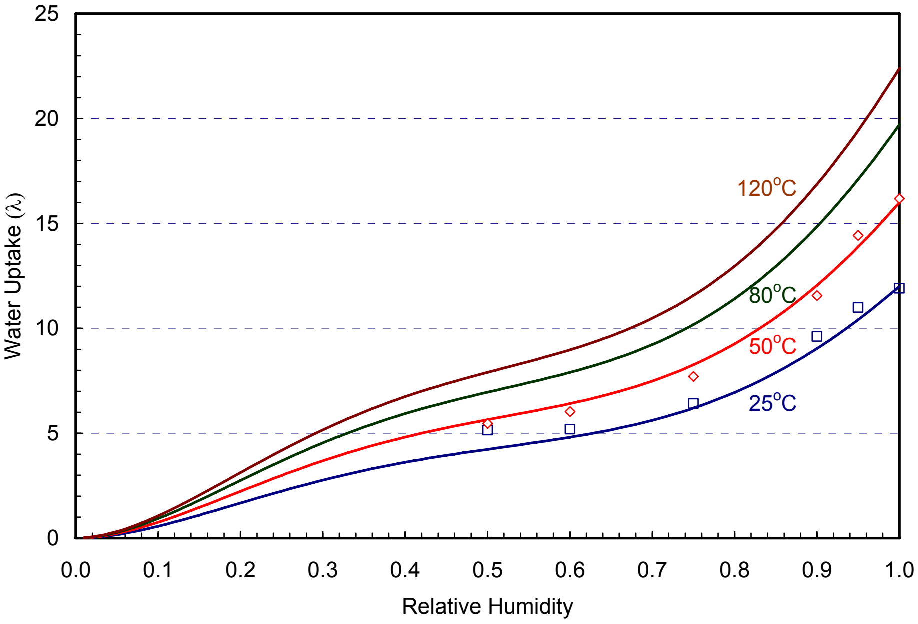
# Correlations for 3M Membrane (EW ~825)

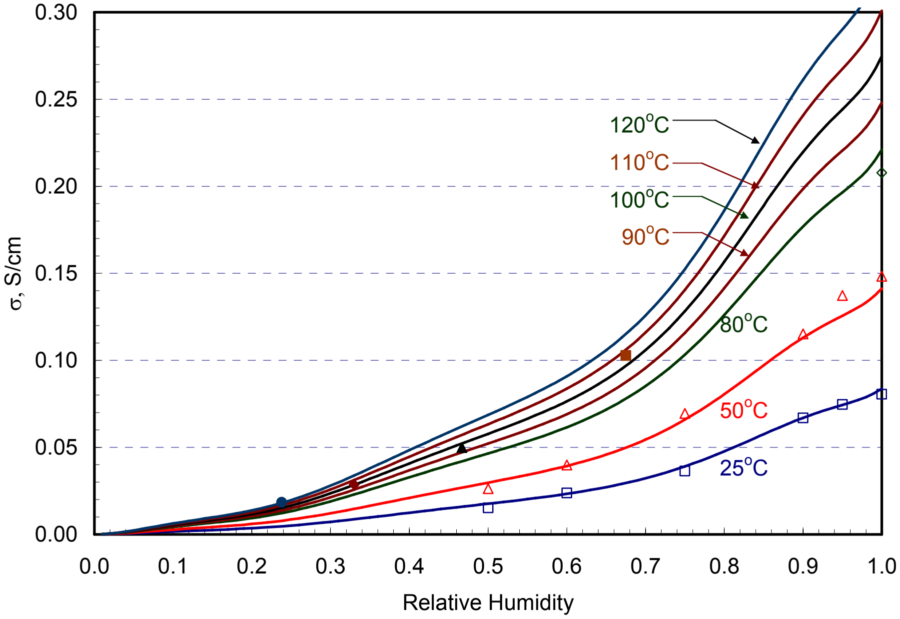
Data Used

- Water uptake (λ) vs. RH at 25°C and 50°C
- Ionic conductivity (σ) vs. λ at 25°C and 50°C
- Ionic conductivity (σ) vs. T at 80°C dew point temperature

Correlations Produced

- Water uptake (λ) vs. RH and T
- Ionic conductivity (σ) vs. λ and T





# Stack Model for 3M’s NSTF Ternary-Alloy Catalyst

Derived correlations for ORR exchange current density & ECSA vs. Pt loading

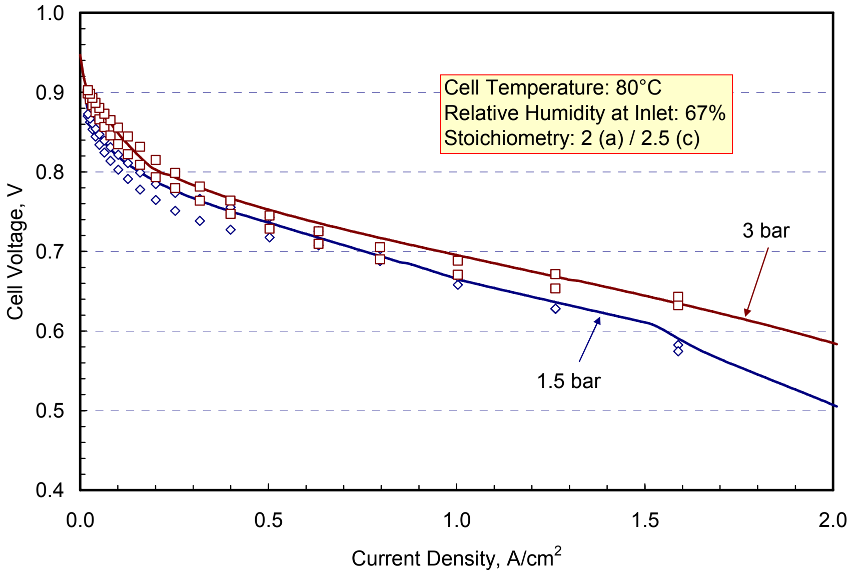
- Specific activity vs. Pt loading for 683-C whiskers
- Mass activity vs. Pt loading for 683-C whiskers

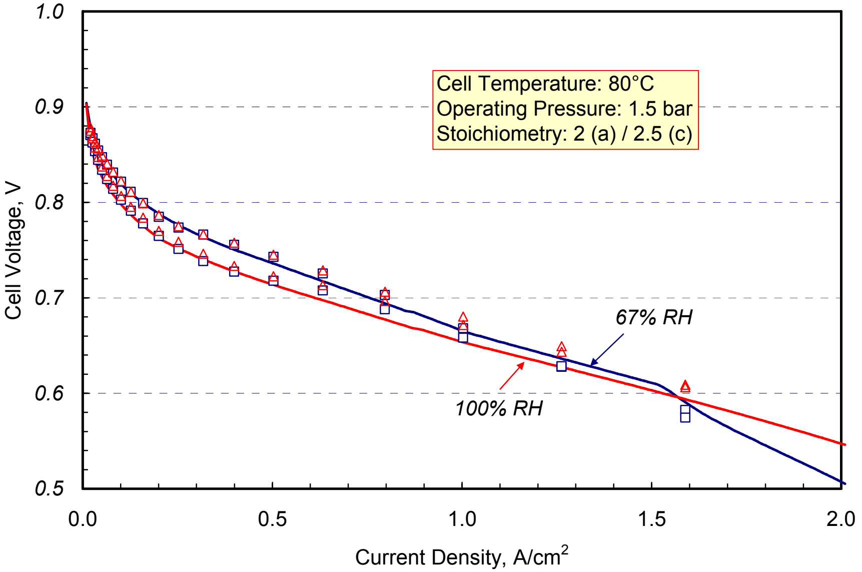
Formulated model for water transport in 3M membrane

- IR drop vs. RH at 1.5 bar
- IR drop vs. P at 67% RH

Formulated semi-empirical model for flooding of NSTF catalysts

- 3M experience with optimum dew point temperatures at different P & T

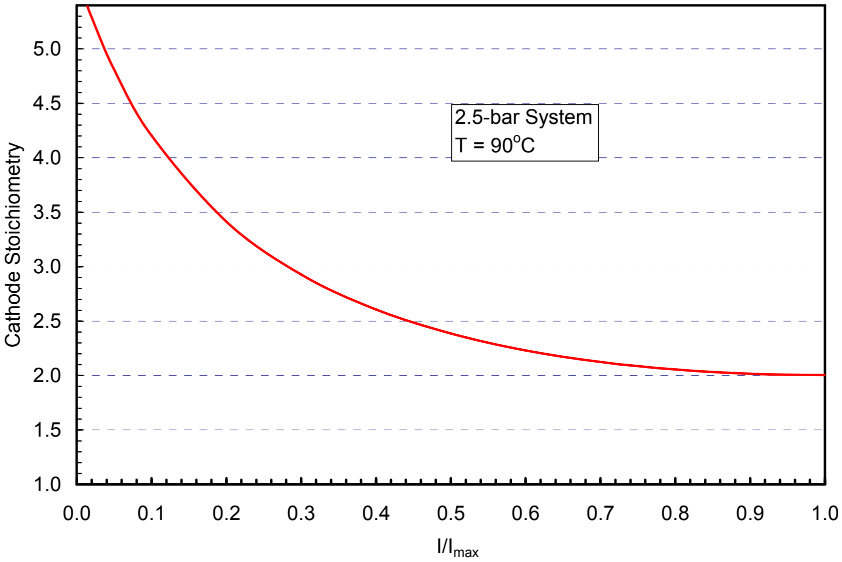


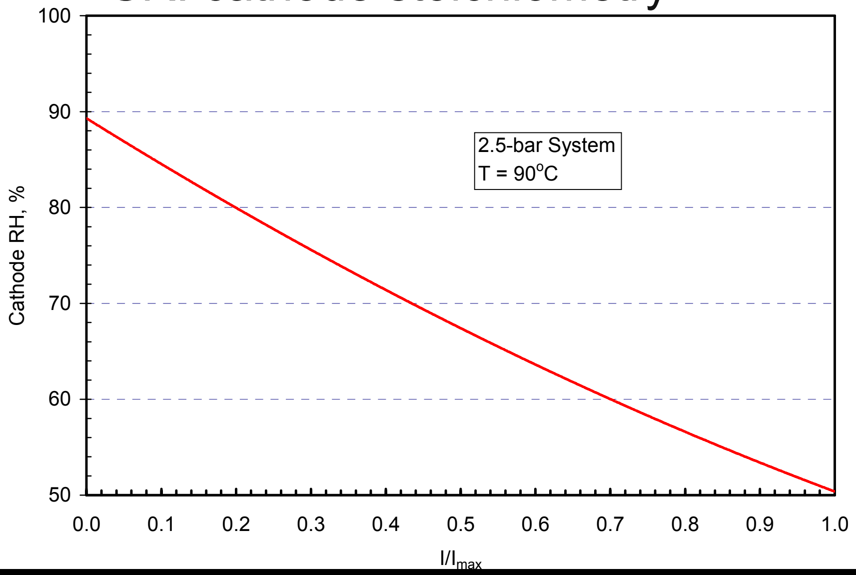


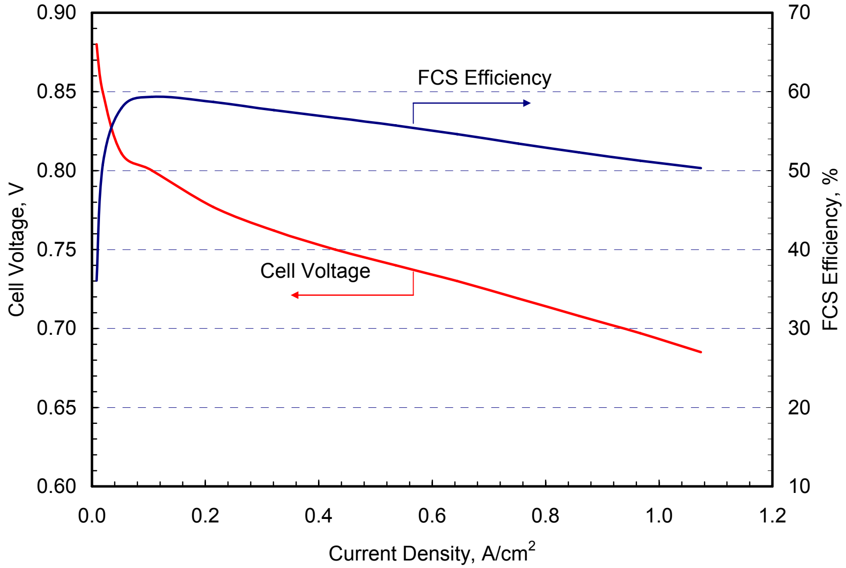
# System Operating Map with 3M Membrane & Catalysts

Developed a method to integrate CEM, EWH, MH and stack for optimum performance

- As P↑, V↑, but $P_{cp}$↑
- As SR↑, V may ↑, but $P_{cp}$↑
- If $T_{dp}$ too high, V↓ due to flooding
- If $T_{dp}$ too low, V↓ due to membrane dry out
- $P_{cp}$: compressor power
  SR: cathode stoichiometry

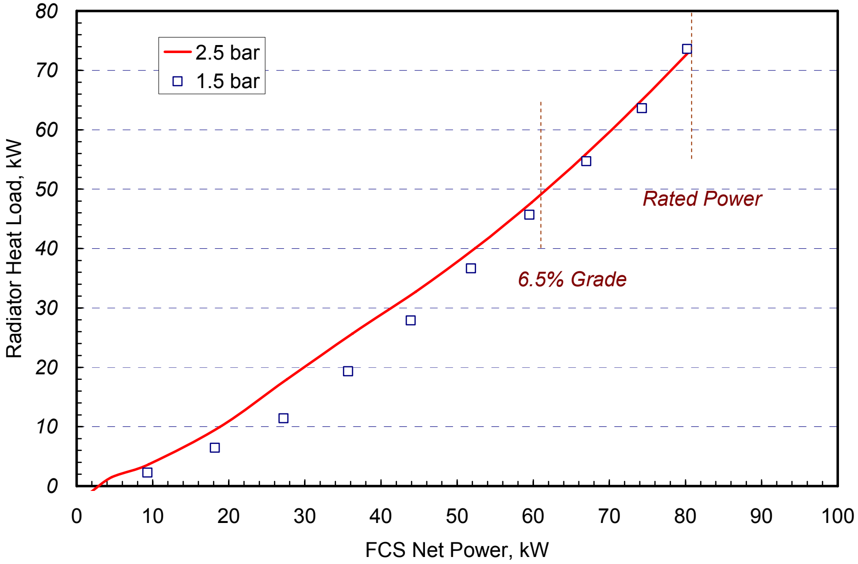


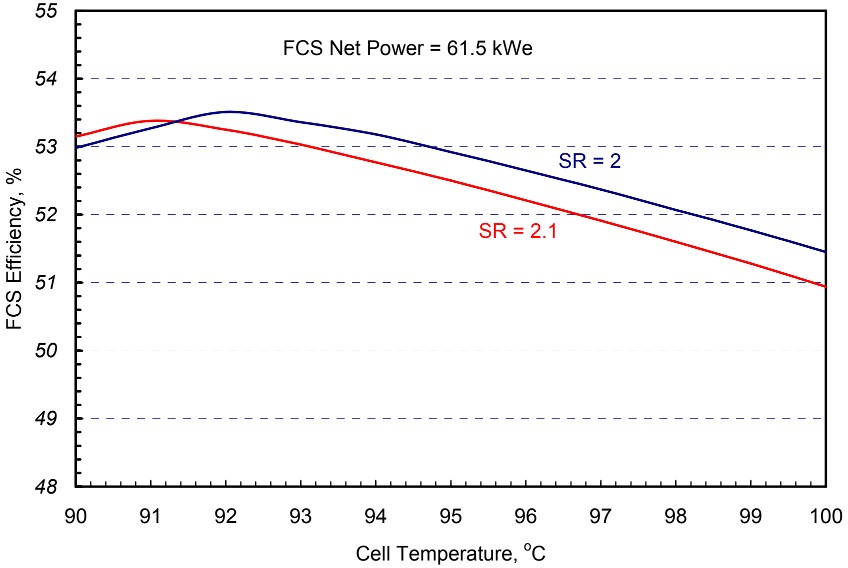


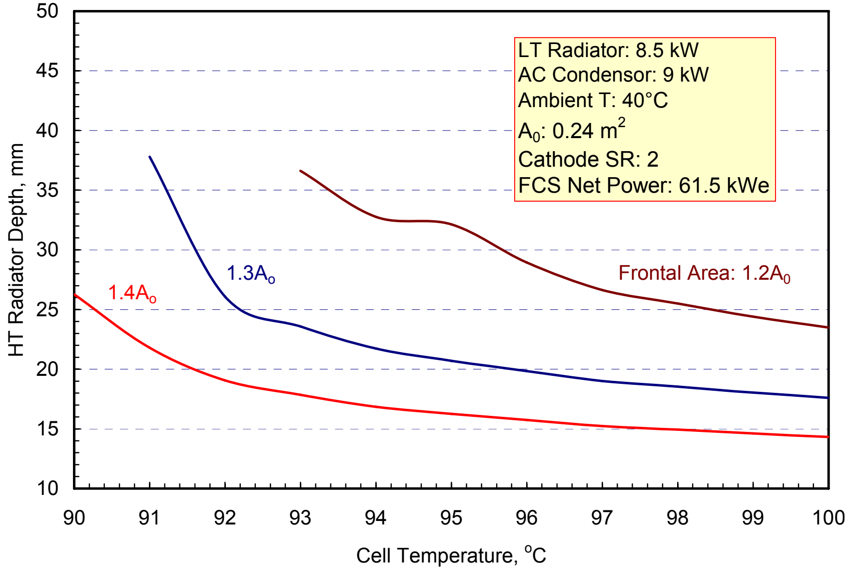


# FCS Heat Rejection

- Heat rejection most challenging at 55 mph on 6.5% grade
- Frontal area reduced by allowing the stack temperature to rise
- Cathode SR must decrease for stack temperature to rise (otherwise membrane dries out)
- Need 94°C for 1.3 x ICE frontal area ($A_0$) and 25 mm depth







# Summary of System Analysis Results

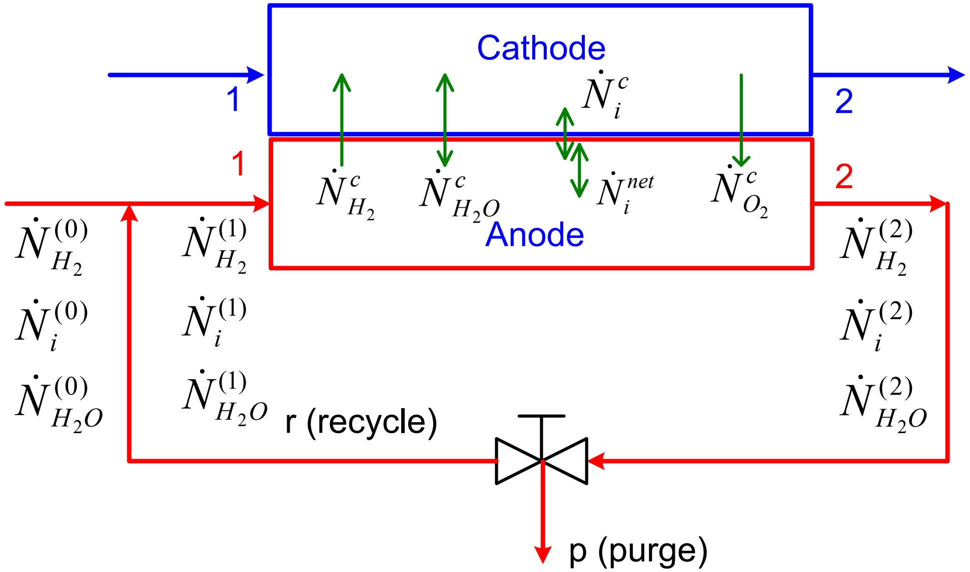
- PGM target met but durability remains to be demonstrated
- Simplification of BOP and CEM bottom-up costing may be needed

| | Units | 2005 Status | 2007 Status | 2010 Target | Comments |
|---|---|---|---|---|---|
| System Cost | $\$/kW_e$ | 108 | 67 | 45 | |
| System Efficiency at 25% Rated Power | % | 57 | 60 | 60 | Peak efficiency |
| System Efficiency at Rated Power | % | 46 | 50 | 50 | |
| System Specific Power | W/kg | 710 | 790 | 650 | |
| System Power Density | W/L | 590 | 640 | 650 | |
| Stack Cost | $\$/kW_e$ | 62 | 30 | 30 | per $kW_e$ stack |
| Stack Efficiency at 25% Rated Power | % | 59 | 62 | 65 | |
| Stack Efficiency at Rated Power | % | 52 | 55 | 55 | |
| Stack Specific Power | W/kg | 1860 | 1900 | 2000 | |
| Stack Power Density | W/L | 1730 | 2070 | 2000 | |
| MEA Cost | $\$/kW_e$ | 55 | 21 | 15 | |
| MEA Performance at Rated Power | $mW/cm^2$ | 670 | 740 | 1280 | |
| MEA Degradation Over Lifetime | % | >90% | TBD | 10 | |
| PGM Cost | $\$/kW_e$ | 44 | 16 | 8 | Pt Cost<br>2005: $29/g<br>2007: $35/g |
| PGM Content (peak) | $g/kW_e$ | 1.1 | 0.4 | 0.5 | |
| PGM Loading (both electrodes) | $mg/cm^2$ | 0.75 | 0.3 | 0.3 | |
| Membrane Cost | $\$/m^2$ | 24 | 16 | 40 | |
| Bipolar Plate Cost | $\$/kW_e$ | 3 | 3 | 6 | |
| CEM System Cost | $ | 1080 | 1080 | 400 | |

- Cost numbers are from TIAX with slightly different assumptions

# *Modeling of Impurity Effects*

- What are the mechanisms by which impurities in fuel $H_2$ ($N_2$, CO, $CO_2$, $H_2S$ and $NH_3$) affect the performance of fuel cells?
- What is the effect of anode gas recycle on buildup of impurities?
- What is the effect of buildup of impurities on cell voltage?
- What are the impacts of purge and impurity buildup on stack efficiency?



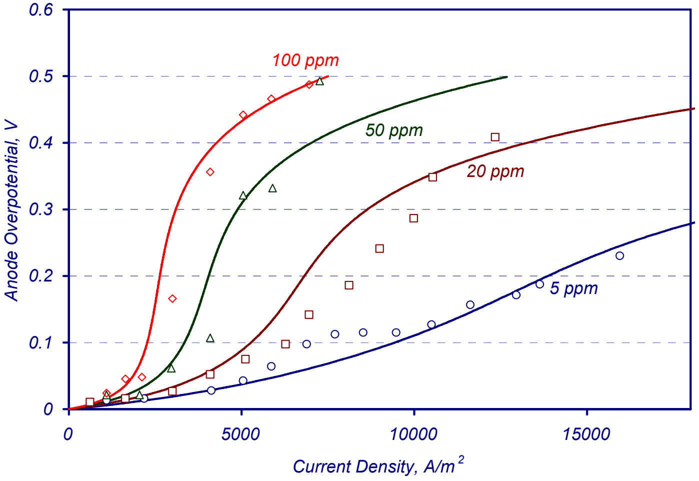
- Once-through cathode stream
- Anode gas recirculation
- Crossovers of $H_2$, $O_2$, $N_2$ and $H_2O$ included

$$R = \dot{N}_r / \dot{N}_p$$

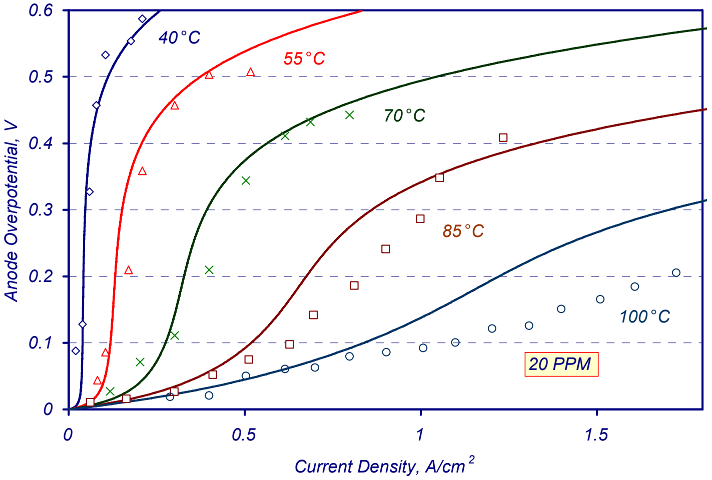
# Pt Poisoning Model

- Hydrogen Oxidation Reaction
  - $H_2 + 2M \Leftrightarrow 2M\text{-}H$ (Dissociative Adsorption)
  - $M\text{-}H \Rightarrow M + H^+ + e^-$ (Electrochemical Oxidation)
- CO Poisoning of Pt
  - $CO + 2M \Leftrightarrow M_2\text{-}CO$ (Associative Adsorption on Bridge Sites)
  - $CO_2 + 2M\text{-}H \Rightarrow M_2\text{-}CO + H_2O$ (Reverse Water-Gas Shift)
  - $M_2\text{-}CO + H_2O \Rightarrow 2M + CO_2 + 2H^+ + 2e^-$ (Electrochemical Oxidation)
- Reactions with Oxygen
  - $M_2\text{-}CO + \frac{1}{2} O_2 \Rightarrow 2M + CO_2$ (CO Oxidation)
  - $2M\text{-}H + \frac{1}{2} O_2 \Rightarrow 2M + H_2O$ ($H_2$ Oxidation)
- $H_2S$ Poisoning of Pt
  - $M + H_2S \Leftrightarrow M\text{-}H_2S$ (Reversible Associative Adsorption)
  - $M\text{-}H_2S + M\text{-}H \Rightarrow M_2S + 3/2H_2$ (Irreversible Dissociation)
  - $M_2S + 2H_2O \Rightarrow 2M + SO_2 + 4H^+ + 4e^-$ (Electrochemical Oxidation)

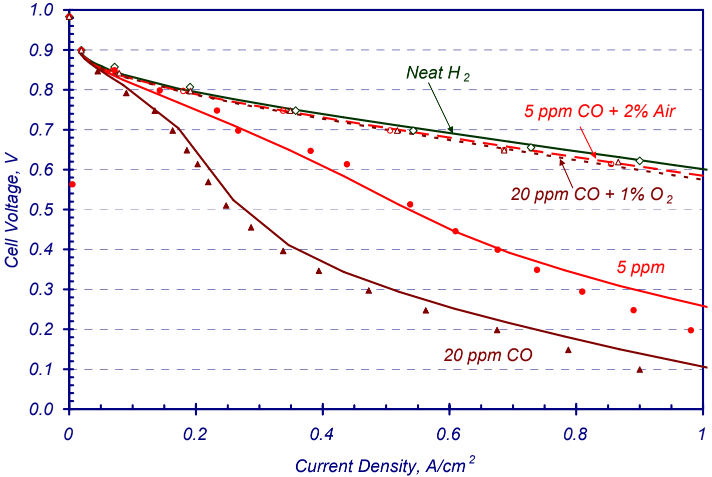
# $CO/CO_2$ Poisoning Model Validation



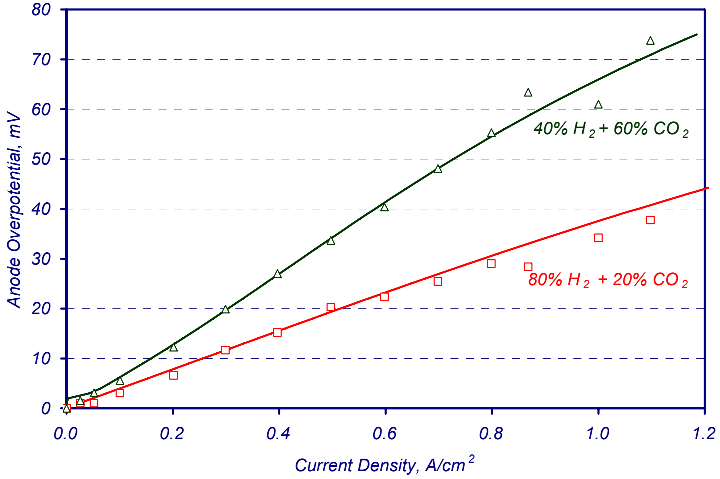
- Data from Lee et. al., Electrochemica Acta, 44, 3283-3293, 1999
- Nafion 115 membrane, 0.4 mg/cm$^2$ Pt on anode and cathode
- Data with $H_2/O_2$ & $H_2$-$CO/O_2$, $P(H_2)=P(O_2)=1$ atm in humidified streams



- Data from Uribe et. al., Electrochemical and Solid State Letters, 7, A376-A379, 2004
- Nafion 105 membrane, 0.2 mg/cm$^2$ Pt on anode and cathode, 80ºC, 5-cm$^2$ cell area



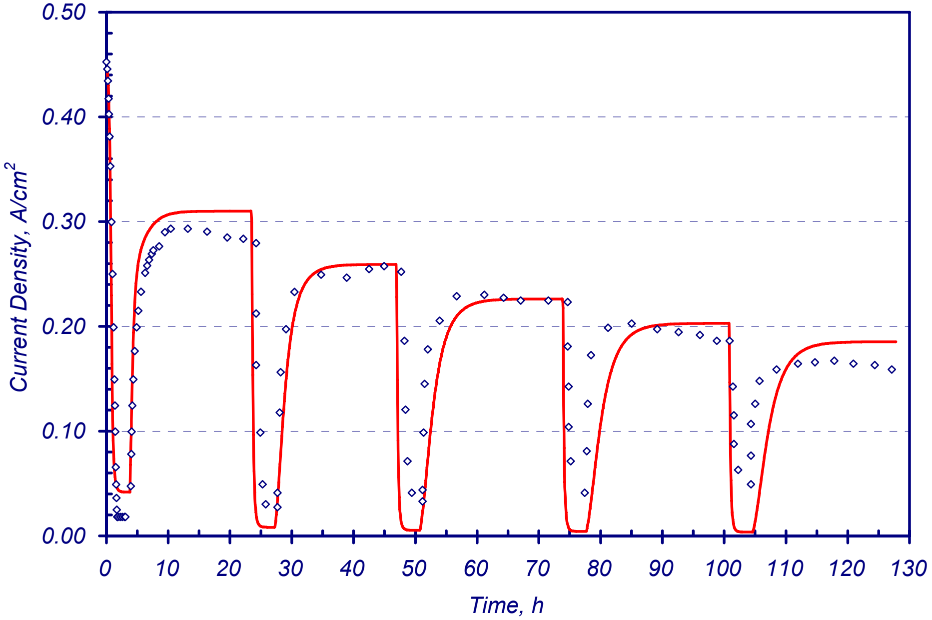
- Data from Gu et. al., J. Electrochemical Society, 151 (12), A2100-A2105, 2004
- 25-µm Gore-Select membrane, 0.4 mg/cm$^2$ Pt on anode and cathode, 80ºC, 20-cm$^2$ cell, SR = 1.2/2.0 anode/cathode

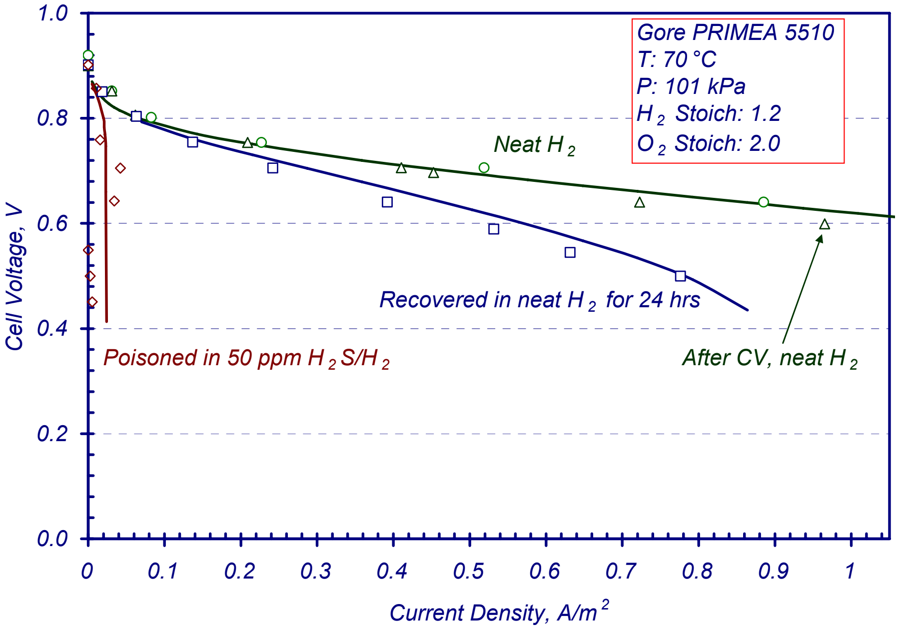


# $H_2S$ Poisoning Model Validation

- Mohatdi, PhD thesis, USC, 2004
- Gore PRIMEA MEA Series 5510
- 25 μm membrane
- 0.4 mg/cm$^2$ Pt on anode & cathode
- Poisoned by 50-ppm $H_2S$ for 3.8 h
- Recovery in neat $H_2$ for 24 h
- Constant $V_c$ (0.69 V), 70°C, 101 kPa

- Data from Mohtadi et. al., Electrochemical and Solid-State Letters, 6 (12) A272-A274, 2003
- Partial recovery after exposing poisoned catalyst to neat $H_2$ for 24 h
- More complete recovery after cyclic voltammetry, 0.9 V max voltage





# $NH_3$ Effect on Cell Performance

Transient stack model with steady-state option

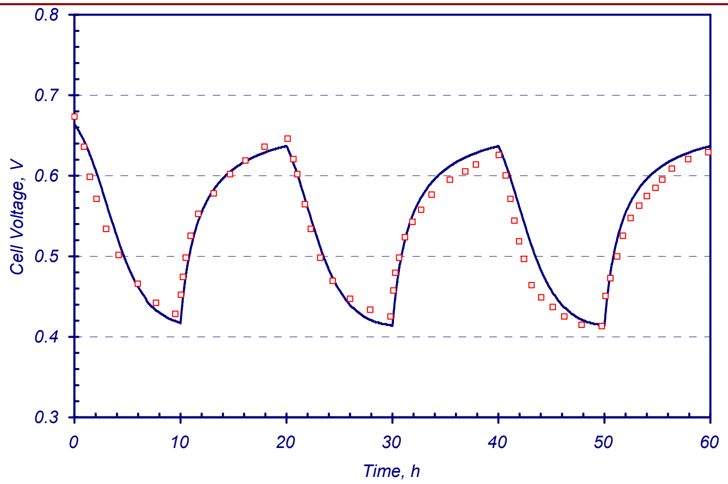
- $NH_3$ uptake in ionomer modeled as reversible absorption-desorption
- Reversible $NH_3$ uptake in membrane, exposed to anode & cathode gases
- Effect of $NH_4^+$ on conductivity empirically derived

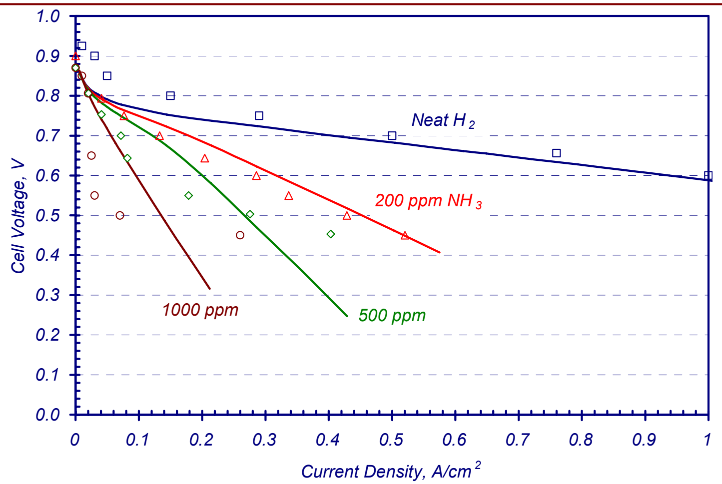
Data from Electrochem. & Solid-State Letters, A133-A135, 2003

- Gore PRIMEA Series 5621, 35 μm membrane, 0.45 mg/cm$^2$ Pt-Ru on anode, 0.6 mg/cm$^2$ Pt on cathode, 70°C, 101 kPa

- Poisoned by 200-ppm $NH_3$ for 10 h
- Recovery with neat $H_2$ for 10 h
- Constant current density: 0.6 A/cm$^2$

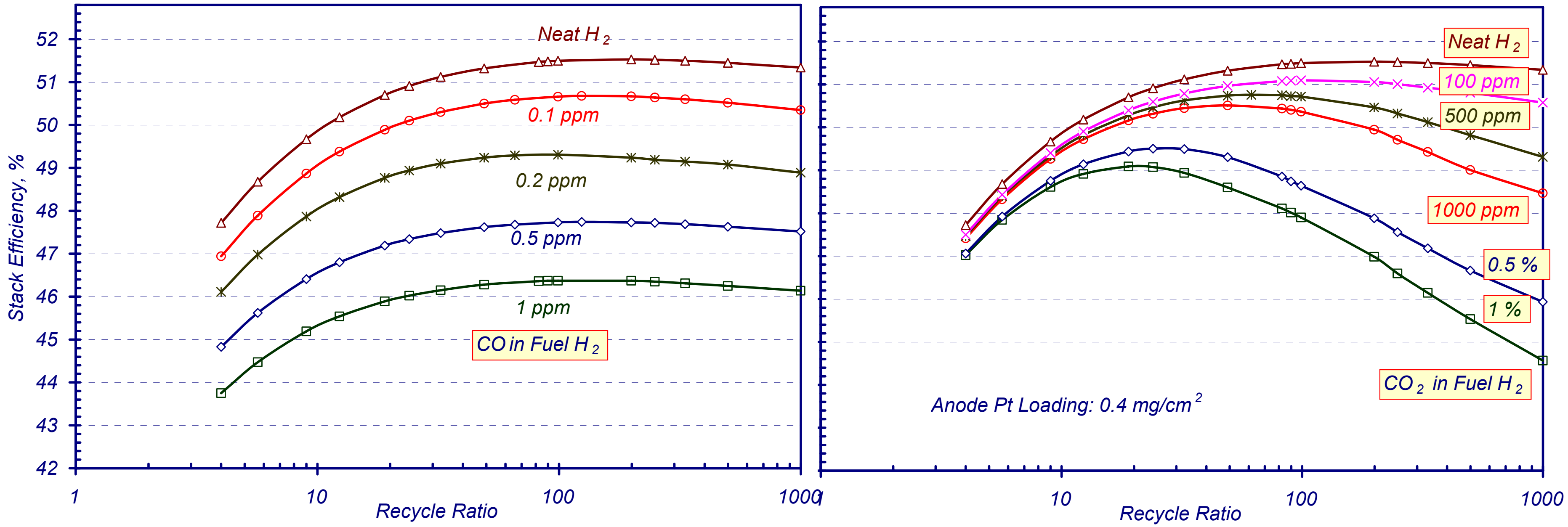
- Exposure to 200-ppm $NH_3$ for 10 h
- Equal dose at other impurity levels
- Stoich: 1.2 for $H_2$, 2 for $O_2$





# Optimum Recycle Ratio with CO/$CO_2$ in Fuel $H_2$

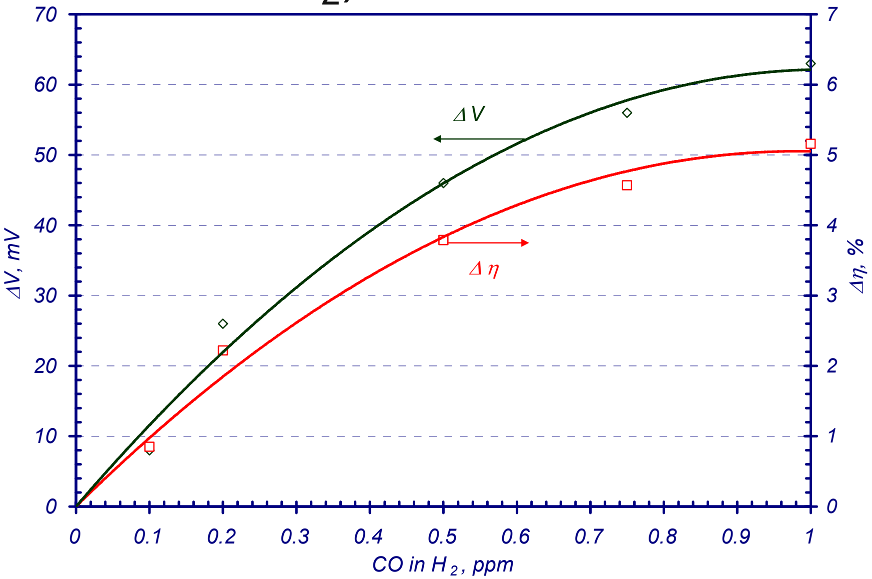
- Stack efficiency defined as DC power generated divided by LHV of $H_2$ utilized, reacted or purged
- Optimum recycle ratio decreases with CO or $CO_2$ concentration in fuel $H_2$
  - Optimum R: 125 with neat $H_2$
  - Optimum R: 80 with 1-ppm CO in fuel $H_2$
  - Optimum R: 20 with 1% $CO_2$ in fuel $H_2$

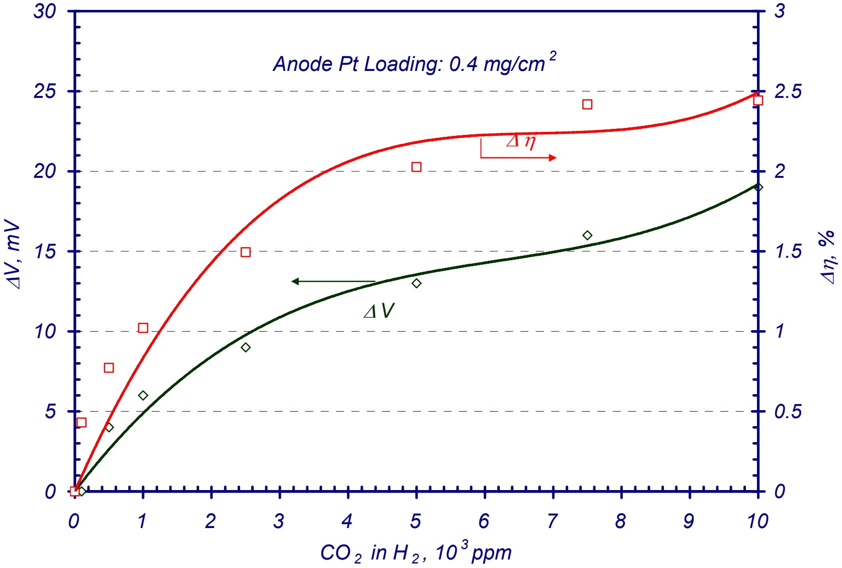


# Summary: Limits for CO and $CO_2$ in Fuel $H_2$

Pressurized stack, 0.4 $mg/cm^2$ Pt loading, 50 μm Nafion membrane, 50% $H_2$ utilization, 70% per-pass $H_2$ utilization

- CO in fuel $H_2$ <100 ppb for $\Delta V$ =10 mV at 1 $A/cm^2$
  - ~1%-point $\Delta\eta$
  - Results are for optimum R (~100 at 100 ppb CO in $H_2$)
- $CO_2$ in fuel $H_2$ <2500 ppm for $\Delta V$ =10 mV at 1 $A/cm^2$
  - ~1.5 %-point $\Delta\eta$
  - Results are for optimum R (~40 at 2500 ppm $CO_2$ in $H_2$)



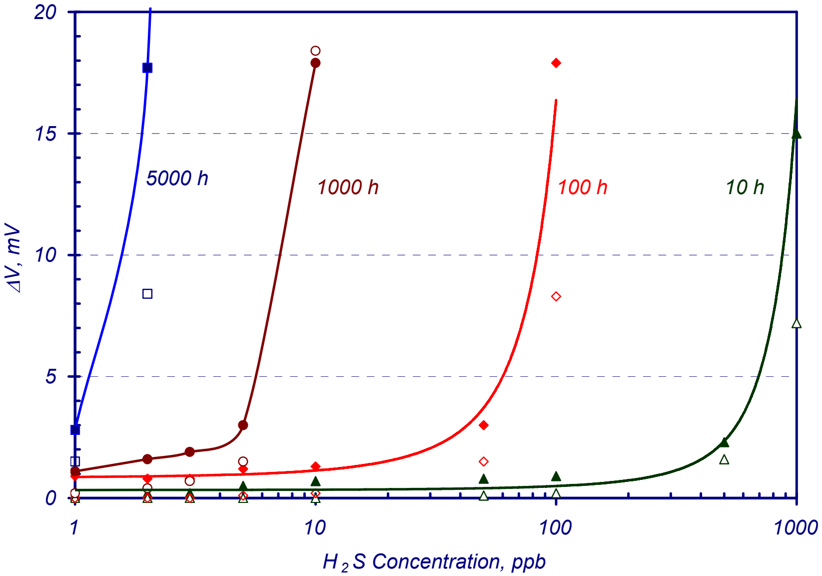


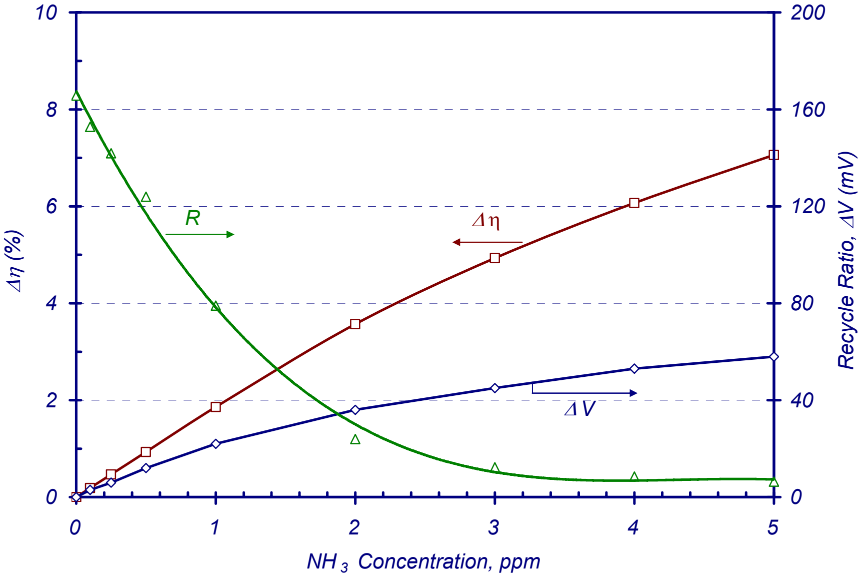
# Summary: Limits for $H_2S$ and $NH_3$ in Fuel $H_2$

Pressurized stack, 0.4 mg/cm$^2$ Pt loading, 50 μm Nafion membrane, 50% $H_2$ utilization, 70% per-pass $H_2$ utilization

- $H_2S$ <2 ppb for ΔV=10 mV at 0.5 A/cm$^2$ after 5000 h
- At low dosage, ΔV weakly depends on R, R=10/100 (open/closed symbols)

- $NH_3$ <200 ppb for ΔV=10 mV at 1 A/cm$^2$
- Optimum R depends on $NH_3$ in fuel $H_2$: 80 for 1-ppm and 12 for 3-ppm $NH_3$





# Future Work

1. System Analysis

- Support DOE/FreedomCAR development effort at system, component and phenomenological levels
- Continue collaboration with Honeywell to validate air, thermal and water management models
- Work with Vairex on blowers for low-pressure FCS options

2. Hydrogen Quality

- Expand work on fuel and air impurity effects
- Support experimental projects on impurity effects
- Support the Hydrogen Quality Working Group and the Codes and Standards Technical Team

3. Durability

- Develop models for End-of-Life performance

# Additional Slides

# Argonne Reference 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: 0.685
- 30-μm 3M membrane at 90°C
- 3M ternary alloy: 0.2/0.1 mg-Pt/cm$^2$ on cathode/anode
- GDL: 275-μm non-woven carbon fiber
- 2-mm expanded graphite bipolar plates, each with cooling channels
- 10 cells/inch

**Fuel Management System**

- Hybrid ejector-recirculation pump
- 40% pump efficiency
- 2 psi pressure drop at rated power

**Air Management System**

- Compressor-expander module
- Liquid-cooled motor
- Efficiencies at rated power: 78% compressor, 82% expander, 92% motor, 92% controller
- Turn-down: 20
- 5 psi pressure drop at rated power

**Heat Rejection System**

- Two circuits: 85°C HT, 55°C LT coolant
- 75% pump + 92% motor efficiency
- 60% blower + 92% motor efficiency
- 10 psi pressure drop each in stack and radiator

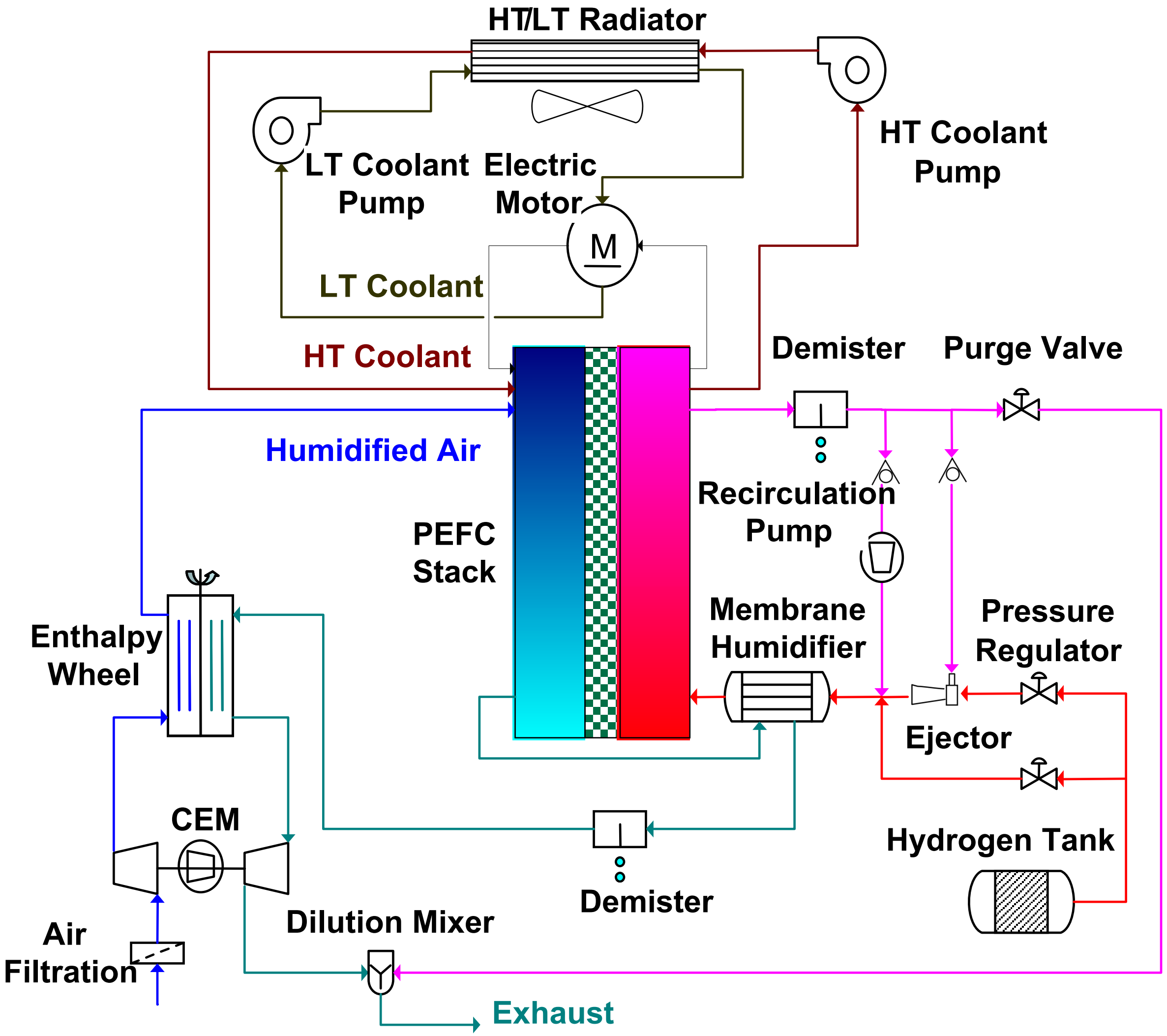
**Water Management System**

- EWH for air, 51% RH at rated power
- MH for $H_2$, 51% RH at rated power

# Reference FCS Configurations

| | Argonne 2005 FCS | Argonne 2010 FCS | Argonne 2015 FCS |
|---|---|---|---|
| **Stack Subsystem** | | | |
| Membrane | PFSA: 50 µm | Modified PFSA:30 µm | High T Membrane |
| Electrocatalyst | Pt/C,<br>0.5/0.25 mg/cm$^2$ Pt (c/a) | Pt Alloy | Pt Alloy or Non PM |
| GDL | 275-µm Woven Carbon Cloth | Non-Woven Carbon + Micro Porous Layer | Non-Woven Carbon + Micro Porous Layer |
| Bipolar Plate | 2-mm Expanded Graphite | Graphite / Metal | Graphite / Metal |
| Cell Power Density | 666 mW/cm$^2$ @ 0.65 V | TBD | TBD |
| Temperature | 80°C | >90°C | <=120°C |
| **Air Management Subsystem** | | | |
| Pressure | Pressurized - 2.5 atm | Pressurized - 2.5 atm | Near Ambient |
| Technology | CEM | CEM | Blower (BMM) |
| **Water Management Subsystem** | | | |
| Humidification | External | External / Internal | None |
| Technology | EWH + MH | EWH + MH<br>Advanced Flow Field | None |
| **Thermal Management Subsystem** | | | |
| Radiator Concept | Standard Automotive, LT + HT Circuits | Advanced Automotive, LT + HT Circuits | Standard Automotive, LT + HT Circuits |
| Stack Coolant | Ethylene Glycol | Ethylene Glycol | Ethylene Glycol |
| **Fuel Management Subsystem** | | | |
| Fuel H2 | High Purity | FC Quality | FC Quality |
| Anode Gas Recirculation | Ejector / Blower | Ejector / Blower | Dead Ended |
| Purge | Periodic | Periodic | Continuous |

# *Argonne 2010 FCS Configuration*



## Changes from FCS 2005

### MEA

- Catalyst: Ternary Pt alloy
- 3M's NSTFC
- Organic whisker support
- 3M PFSA membrane

### AMS

- CEMM: 2.5 bar

### WMS

- No change

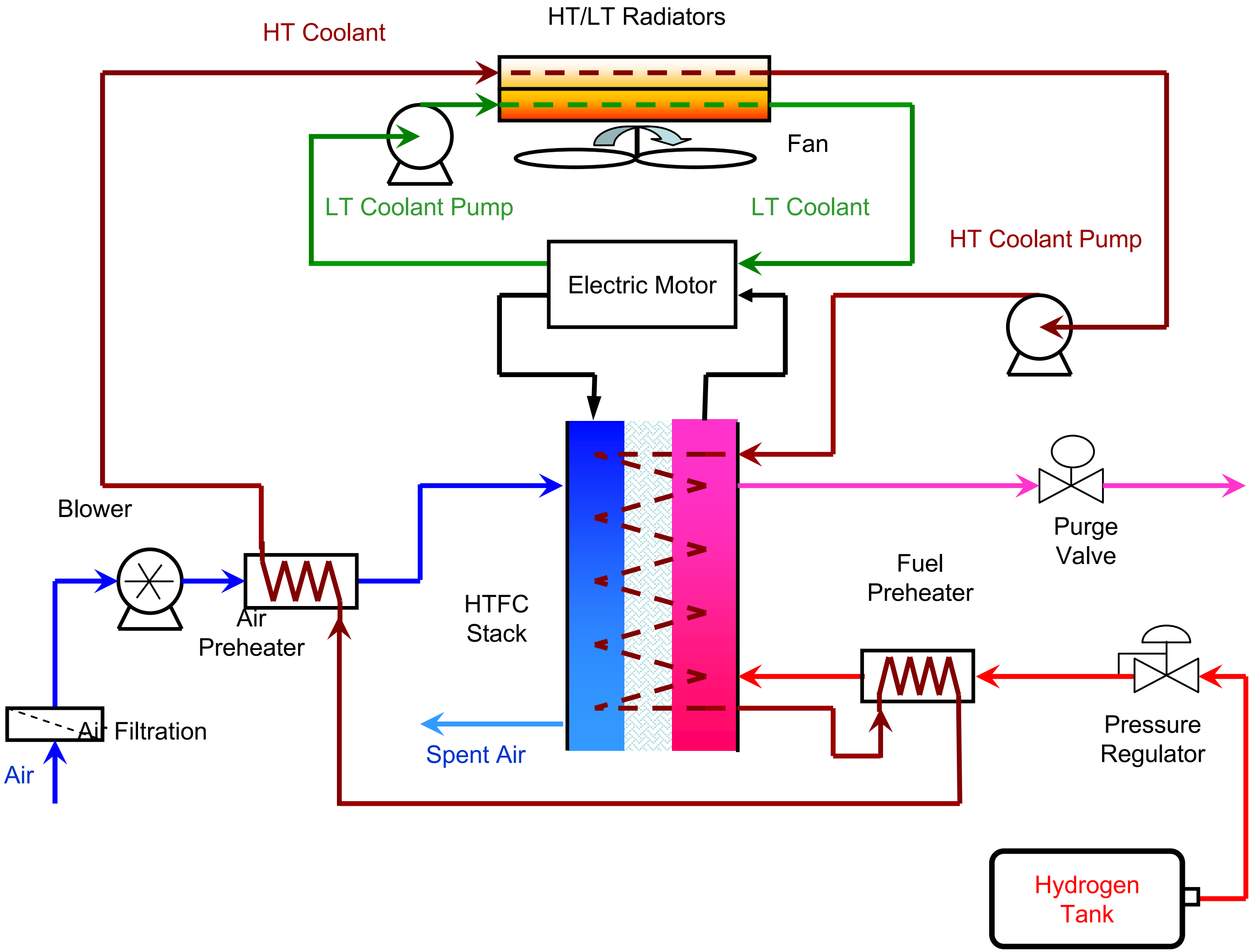
### TMS

- No change

### FMS

- No change

# Argonne 2015 FCS Configuration



## Changes from FCS 2010

MEA
- Non PM catalyst
- HTM

AMS
- BMM

WMS
- None

TMS
- Standard radiator

FMS
- FC quality $H_2$
- Dead-ended