

... for a brighter future



UChicago ► Argonne<sub>uc</sub>

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

# **Fuel Cell Systems Analysis**

R. K. Ahluwalia, X. Wang, K. Tajiri and R. Kumar 2009 DOE Hydrogen Program Review Arlington, VA May 18-22, 2009

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

### Project ID: FC\_29\_Ahluwalia

# **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

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

### **Partners**

- Honeywell CEM+TWM projects
- Emprise, PermaPure, PNNL
- 3M, Nuvera, Princeton, TIAX
- H<sub>2</sub> 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



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<sub>2</sub>S 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<sup>2</sup> 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**



Scalable compressor map from Honeywell data: pressure ratio (PR) and efficiency (η) as functions of corrected rpm (N<sub>c</sub>) & mass flow rate

- Expander maps from Honeywell data for different nozzle areas as functions of flow (F<sub>f</sub>) and velocity (F<sub>v</sub>) factors: PR(F<sub>f</sub>, N<sub>c</sub>) and η(F<sub>v</sub>, PR)
- Motor efficiency  $(\eta_M)$  as function of motor power  $(P_M)$  and rpm (N)
- Controller efficiency ( $\eta_{MC}$ ) 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 ( $\Delta P$ ) & 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,  $\Delta$ P=3 psi, 100% RH exit





### **CEM Parasitic Power**

- At rated power, the CEM module consumes ~9 kWe at 300 K ambient temperature, 50% O<sub>2</sub> 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<sub>2</sub>/air cell at 0.9 V





# **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</li>
  - 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<sub>ref</sub>=0.25 m<sup>2</sup>
  - 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<sub>ref</sub>=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</p>
- Startup as a function of initial membrane water content: dispersed Pt/C catalysts, N111 membrane, 1770 W/kg stack specific power
  - $-\lambda_i > 10$ , self start not possible from -20°C at V<sub>cell</sub> = 0.6 V
  - $\lambda_i$  = 7.5, self start with ice formation
  - $\lambda_i = 5$ , self start without ice formation
  - $\lambda_i = 2$ , 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:  $T_c = T_c(V_{cell}, \lambda_i)$ 
  - $T_i < -30^{\circ}$ 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  $\lambda$  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  $\lambda$ 
  - 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**





# 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 <sup>2</sup>	0.25	0.25	0.25
Stack power density	mW/cm <sup>2</sup>	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<sub>2</sub>/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 nonuniformities and bulginess alone.





### Water Uptake in Membrane

- Transient model for water transport in membrane and catalyst layers
  - Water uptake is a function of  $\lambda_i$ ,  $\beta$  and current density





# Ambient Pressure FCS with NSTFC Type MEA

Assumptions: NSTFC type MEA, 3 psi  $\Delta P$  between blower & humidifier

	Fuel Cell		Dry Inlet		Wet Inlet			Humidified Air		Cooler	
Case	P	H	Р	H	Р	H	T <sub>DP</sub>	Р	T <sub>DP</sub>	Q	Blower
	bar	°C	bar	°	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 precooled to 46°C which may be difficult





# Pressurized FCS with NSTFC Type MEA

#### Assumptions: NSTFC type MEA, 3 psi $\Delta P$ between compressor & expander

	Fuel Cell		Dry	Inlet	Wet Inlet		Humidified Air		Cooler	Parasitic Power		wer	
Case	£	Т	Р	Т	Р	H	T <sub>DP</sub>	Р	T <sub>DP</sub>	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 precooled to 58°C which may be difficult





# **Argonne Reference 2009 FCS Parameters**

#### **PEFC Stack**

- 2.5 atm at rated power
- 50% O<sub>2</sub> utilization
- 70% H<sub>2</sub> 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<sup>2</sup> 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<sub>2</sub>, 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<sub>2</sub> 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," 212<sup>th</sup> 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<sub>2</sub> 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," 212<sup>th</sup> ECS Meeting, Washington DC, Oct. 7-12, 2007.



# Preliminary Analysis of HNEI Cell Data Dependence of $\Delta V$ on CO concentration and T

Modeled steady-state O<sub>2</sub> selectivity for CO and oxidative conversion of CO





### Preliminary Analysis of HNEI Cell Data Dependence of ∆V on J and RH

- Data for 60% RH suggests that the assumption of J<sub>CO</sub> being first order in P<sub>H2O</sub> needs to be revisited
- Apparent disparity between model and ∆V data in H<sub>2</sub>/O<sub>2</sub> mode







#### **Buildup of Impurities with Anode Gas Recycle**

No buildup of CO for inlet CO < 1 ppm, 70%  $\Phi_{H2}$ , 80°C

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

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

Initial increase in ∆V is due to CO adsorption (no purge), subsequent increase due to accumulation of CO<sub>2</sub> and N<sub>2</sub>





### **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<sub>2</sub>S**

- Loss in cell performance due to H<sub>2</sub>S 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<sub>2</sub>S is strongly sorbed on the electrocatalyst (Uribe 2001, Mohtadi 2003).
- Sorbed H<sub>2</sub>S 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<sub>2</sub>S on Pt
  1. nM + H<sub>2</sub>S ↔ M<sub>n</sub>-H<sub>2</sub>S
  2. M<sub>n</sub>-H<sub>2</sub>S ↔ M<sub>n</sub>S + 2H<sup>+</sup> + 2e<sup>-</sup>
  3. M<sub>n</sub>S + 3H<sub>2</sub>O → nM + SO<sub>3</sub> + 6H<sup>+</sup> + 6e<sup>-</sup>
  (Electrochemical oxidation)
- Multi-site sorption of  $H_2S$ , n is a function of total sulfur coverage ( $\theta_S$ )
  - $n \rightarrow 1 \text{ as } \theta_S \rightarrow 1, n \rightarrow N \text{ as } \theta_S \rightarrow 0$
- Near OC,  $M_n$ S can re-convert to  $M_n$ -H<sub>2</sub>S (E<sub>2</sub> = 0.14 V), and H<sub>2</sub>S can desorb for partial recovery
- At a high anode overpotential (E<sub>3</sub> = 0.89 V), M<sub>n</sub>S can oxidize to SO<sub>3</sub>, SO<sub>3</sub> 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  $\theta_S$  corresponding to peak  $\Delta V$  and  $\theta_{H2S}$ , 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





# **Effect of Temperature on H<sub>2</sub>S Poisoning**

- Data from T. Rockward, LANL, 2007
- If Higher the temperature, higher the  $\Delta V$  and higher the V recovery
- Plateau in  $\Delta V$  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,  $\Delta H_d$  = 25 kJ/mol
  - Revised rate constants for R1 and R2
  - Complications due to cell to cell variation in 80°C data





# Effect of Relative Humidity on H<sub>2</sub>S Poisoning

- Data from T. Rockward, LANL, 2007
- The more the amount of local water, the slower the decay in current density due to H<sub>2</sub>S poisoning at constant cell voltage
- Determined the dependence of k<sub>a</sub> on the activity of H<sub>2</sub>O for R1





# Effect of OCV on H<sub>2</sub>S Poisoning

- Data from T. Rockward, LANL, 2007
- Partial recovery in cell voltage after holding the cell at OCV for 3 h with neat H<sub>2</sub>
- Determined k<sub>b</sub> for the electrochemical reaction R2
  - Small change in  $\theta_{\text{S}}$  produces the observed recovery in cell voltage





# **Buildup of H<sub>2</sub>S in Anode Gas Channels**

- At constant current density, steady-state buildup of H<sub>2</sub>S depends on its concentration in fuel H<sub>2</sub> 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<sub>3</sub> 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<sub>out</sub> and C<sub>in</sub> increase with time to reach a maximum





# **Effect of H<sub>2</sub>S Buildup on Cell Voltage**

- At steady-state,  $\Delta V$  is a function of H<sub>2</sub>S concentration in fuel H<sub>2</sub> rather than R.
- The lower the H<sub>2</sub>S concentration and R, the longer the time to reach steady state ( $\tau_{ss}$ ).
- For exposure times less than  $\tau_{ss}$ ,  $\Delta V$  is more sensitive to R at lower H<sub>2</sub>S concentrations in fuel H<sub>2</sub>.





# Limits for H<sub>2</sub>S in Fuel H<sub>2</sub>

- H<sub>2</sub>S concentration needs to be <2 ppb to limit decrease in cell voltage at 0.5 A/cm<sup>2</sup> 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  $\Delta V$  on Pt loading remains to be determined



