Fuel Cell Systems Analysis

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Project ID: FC1
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
- H₂ 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 H₂ Quality Working Group
   - Developed models for N₂, CO, CO₂, H₂S & NH₃ 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 ($\lambda$) vs. RH at 25°C and 50°C
- Ionic conductivity ($\sigma$) vs. $\lambda$ at 25°C and 50°C
- Ionic conductivity ($\sigma$) vs. T at 80°C dew point temperature

**Correlations Produced**
- Water uptake ($\lambda$) vs. RH and T
- Ionic conductivity ($\sigma$) vs. $\lambda$ 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

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>2005 Status</th>
<th>2007 Status</th>
<th>2010 Target</th>
<th>Comments</th>
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<tbody>
<tr>
<td>System Cost</td>
<td>$/kW_e</td>
<td>108</td>
<td>67</td>
<td>45</td>
<td>[Cost numbers are from TIAAX with slightly different assumptions]</td>
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<tr>
<td>System Efficiency at 25% Rated Power</td>
<td>%</td>
<td>57</td>
<td>60</td>
<td>60</td>
<td>Peak efficiency</td>
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<tr>
<td>System Efficiency at Rated Power</td>
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<td>System Specific Power</td>
<td>W/kg</td>
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<td>790</td>
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<td>System Power Density</td>
<td>W/L</td>
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<td>640</td>
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<tr>
<td>Stack Cost</td>
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<td>30</td>
<td>30</td>
<td>per kW_e stack</td>
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<td>Stack Efficiency at 25% Rated Power</td>
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<td>59</td>
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<td>21</td>
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<td>MEA Performance at Rated Power</td>
<td>mW/cm²</td>
<td>670</td>
<td>740</td>
<td>1280</td>
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<td>MEA Degradation Over Lifetime</td>
<td>%</td>
<td>&gt;90%</td>
<td>TBD</td>
<td>10</td>
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<td>PGM Cost</td>
<td>$/kW_e</td>
<td>44</td>
<td>16</td>
<td>8</td>
<td>Pt Cost</td>
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<td>PGM Content (peak)</td>
<td>g/kW_e</td>
<td>1.1</td>
<td>0.4</td>
<td>0.5</td>
<td>2005: $29/g</td>
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<tr>
<td>PGM Loading (both electrodes)</td>
<td>mg/cm²</td>
<td>0.75</td>
<td>0.3</td>
<td>0.3</td>
<td>2007: $35/g</td>
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<td>Membrane Cost</td>
<td>$/m²</td>
<td>24</td>
<td>16</td>
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<td>Bipolar Plate Cost</td>
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<td>CEM System Cost</td>
<td>$</td>
<td>1080</td>
<td>1080</td>
<td>400</td>
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</table>

- Cost numbers are from TIAAX with slightly different assumptions
Modeling of Impurity Effects

- What are the mechanisms by which impurities in fuel H₂ (N₂, CO, CO₂, H₂S and NH₃) 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 H₂, O₂, N₂ and H₂O included

\[ R = \frac{\dot{N}_r}{\dot{N}_p} \]
Pt Poisoning Model

- Hydrogen Oxidation Reaction
  - $\text{H}_2 + 2\text{M} \rightleftharpoons 2\text{M-H}$ (Dissociative Adsorption)
  - $\text{M-H} \rightarrow \text{M} + \text{H}^+ + e^-$ (Electrochemical Oxidation)

- CO Poisoning of Pt
  - $\text{CO} + 2\text{M} \rightleftharpoons \text{M}_2\text{-CO}$ (Associative Adsorption on Bridge Sites)
  - $\text{CO}_2 + 2\text{M-H} \rightarrow \text{M}_2\text{-CO} + \text{H}_2\text{O}$ (Reverse Water-Gas Shift)
  - $\text{M}_2\text{-CO} + \text{H}_2\text{O} \rightarrow 2\text{M} + \text{CO}_2 + 2\text{H}^+ + 2e^-$ (Electrochemical Oxidation)

- Reactions with Oxygen
  - $\text{M}_2\text{-CO} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{M} + \text{CO}_2$ (CO Oxidation)
  - $2\text{M-H} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{M} + \text{H}_2\text{O}$ (H$_2$ Oxidation)

- H$_2$S Poisoning of Pt
  - $\text{M} + \text{H}_2\text{S} \rightleftharpoons \text{M-H}_2\text{S}$ (Reversible Associative Adsorption)
  - $\text{M-H}_2\text{S} + \text{M-H} \rightarrow \text{M}_2\text{S} + 3/2\text{H}_2$ (Irreversible Dissociation)
  - $\text{M}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{M} + \text{SO}_2 + 4\text{H}^+ + 4e^-$ (Electrochemical Oxidation)
CO/CO₂ Poisoning Model Validation

Data from Lee et. al., Electrochemica Acta, 44, 3283-3293, 1999
- Nafion 115 membrane, 0.4 mg/cm² Pt on anode and cathode
- Data with H₂/O₂ & H₂⁻/CO/O₂, P(H₂)=P(O₂)=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/cm² Pt on anode and cathode, 80°C, 5-cm² cell area

Data from Gu et. al., J. Electrochemical Society, 151 (12), A2100-A2105, 2004
- 25-μm Gore-Select membrane, 0.4 mg/cm² Pt on anode and cathode, 80°C, 20-cm² cell, SR = 1.2/2.0 anode/cathode
**H₂S Poisoning Model Validation**

- Mohatdi, PhD thesis, USC, 2004
- Gore PRIMEA MEA Series 5510
- 25 μm membrane
- 0.4 mg/cm² Pt on anode & cathode
- Poisoned by 50-ppm H₂S for 3.8 h
- Recovery in neat H₂ 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 H₂ for 24 h
- More complete recovery after cyclic voltammetry, 0.9 V max voltage

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**Graphs:**

- Time, h vs. Current Density, A/cm²
- Cell Voltage, V vs. Current Density, A/m²

- **Gore PRIMEA 5510**
  - T: 70 °C
  - P: 101 kPa
  - H₂ Stoich: 1.2
  - O₂ Stoich: 2.0

- **Recovered in neat H₂ for 24 hrs**

- **Poisoned in 50 ppm H₂S/H₂**

- **After CV, neat H₂**
**NH₃ Effect on Cell Performance**

Transient stack model with steady-state option

- NH₃ uptake in ionomer modeled as reversible absorption-desorption
- Reversible NH₃ uptake in membrane, exposed to anode & cathode gases
- Effect of NH₄⁺ on conductivity empirically derived


- Gore PRIMEA Series 5621, 35 μm membrane, 0.45 mg/cm² Pt-Ru on anode, 0.6 mg/cm² Pt on cathode, 70°C, 101 kPa

- Poisoned by 200-ppm NH₃ for 10 h
- Recovery with neat H₂ for 10 h
- Constant current density: 0.6 A/cm²

- Exposure to 200-ppm NH₃ for 10 h
- Equal dose at other impurity levels
- Stoich: 1.2 for H₂, 2 for O₂
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 CO₂ in Fuel H₂

Pressurized stack, 0.4 mg/cm² Pt loading, 50 μm Nafion membrane, 50% H₂ utilization, 70% per-pass H₂ utilization

- CO in fuel H₂ <100 ppb for $\Delta V = 10 \text{ mV at } 1 \text{ A/cm}^2$
  - ~1%-point $\Delta \eta$
  - Results are for optimum R (~100 at 100 ppb CO in H₂)

- CO₂ in fuel H₂ <2500 ppm for $\Delta V = 10 \text{ mV at } 1 \text{ A/cm}^2$
  - ~1.5 %-point $\Delta \eta$
  - Results are for optimum R (~40 at 2500 ppm CO₂ in H₂)
Summary: Limits for H$_2$S 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$_2$S <2 ppb for $\Delta V=10$ mV at 0.5 A/cm$^2$ after 5000 h
- At low dosage, $\Delta V$ weakly depends on R, R=10/100 (open/closed symbols)

- NH$_3$ <200 ppb for $\Delta V=10$ 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/cm² 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

<table>
<thead>
<tr>
<th>Stack Subsystem</th>
<th>Argonne 2005 FCS</th>
<th>Argonne 2010 FCS</th>
<th>Argonne 2015 FCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>PFSA: 50 μm</td>
<td>Modified PFSA: 30 μm</td>
<td>High T Membrane</td>
</tr>
<tr>
<td>Electro catalyst</td>
<td>Pt/C, 0.5/0.25 mg/cm² Pt (c/a)</td>
<td>Pt Alloy</td>
<td>Pt Alloy or Non PM</td>
</tr>
<tr>
<td>Bipolar plate</td>
<td>2-mm Expanded Graphite</td>
<td>Graphite / Metal</td>
<td>Graphite / Metal</td>
</tr>
<tr>
<td>Cell Power Density</td>
<td>666 mW/cm² @ 0.65 V</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
<td>&gt;90°C</td>
<td>&lt;=120°C</td>
</tr>
</tbody>
</table>

### 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            | None           |
| Advanced Flow Field               |                      |                    |                |

### 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 H₂
  - Dead-ended