Air Cooled Stack Freeze Tolerance

Project ID: FC025
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20120515

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Overview

Timeline
- Start: June 1, 2009
- Finish: November 15, 2011
- Progress: Complete

Budget
- Total Project Funding: $3.679M
  - DOE Share: $2.423M
  - Plug Power Share: $1.256M (34%)
- FY 2009 Funding: $0.900M
- FY 2010 Funding: $0.975M
- FY 2011 Funding: $0.548M

Barriers
- (A) Durability (with respect to start-up, freezing and low relative humidity operation)
- (B) Cost (with respect to stack and balance of plant trade-off)
- (C) Performance (with respect to voltage degradation, low relative humidity and sub-zero performance)

Partners
- Plug Power
- Ballard Power Systems
  - Cara Startek
Project Objectives / Relevance

• This project addresses critical barriers to fuel cell commercialization by developing a low cost fuel cell stack and system with 5000 hour durability and -30°C capable performance for the near term material handling market
  • Stack and system developed together to meet cost, durability, and freeze tolerance performance requirements
  • No specific DOE technical targets established for material handling application at the time of this project
  • The primary technical target established for this project is based on the cost Go / No Go metric
  • Inherent to the cost metric requirement are minimum performance and durability requirements
  • 2011 project activities focused on validating the 5000 hour durability on next generation MEA designs and validating design mitigation strategies to improve freeze tolerance performance at -30°C ambient temperature
  • Specific project targets and results are presented on the following slide as related to DOE barriers
<table>
<thead>
<tr>
<th>Characteristic (DOE Barrier)</th>
<th>Project Target</th>
<th>Project Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>≥ 25% cost reduction compared to liquid cooled stack solution [while simultaneously meeting the durability and performance targets]</td>
<td>Projected 57% initial product cost reduction and projected 32% product life cycle cost reduction</td>
</tr>
<tr>
<td>Durability</td>
<td>5000 hour stack life with &gt;0.54 volts/cell at 51.7 amps</td>
<td>Validated 5000 hour durability on 6 air cooled fuel cell stacks [average durability 5700 hours]</td>
</tr>
<tr>
<td>Performance</td>
<td>Sustained operation in -30°C ambient temperature with stack inlet air temperature &gt;0°C and stack temperature gradient &lt;10°C</td>
<td>Designed and validated sustained operation at -30°C ambient temperature; stack inlet temperature &gt;2°C and stack temperature gradient &lt;6°C</td>
</tr>
</tbody>
</table>
Approach

- Use understanding of market needs, system requirements, stack-system limitations, historical data, models and small scale testing to develop stack/system operating strategies to achieve required freeze function and durability.
- Build stacks/system with mitigation strategies.
- Test stack/system for against requirements and perform failure analysis.

**Phase 1**
- Baseline Stack Freeze Testing
- Baseline Stack Durability Testing
- Baseline Stack Freeze Failure Analysis
- Baseline Durability Failure Analysis

**Phase 2**
- Generate Hypothesis for Freeze Function
- Generate Hypothesis for Durability
- MEA Concept Performance Screening
- MEA Accelerated Stress Screening
- Stack System Modeling for Freeze
- Stack System Modeling for Durability
- Stack System for System Input

**Phase 3**
- New Concept Freeze Testing
- Stack Level Durability Testing
- Advanced Systems, Baseline Stack
- System Level Freeze Durability Testing

**Go / No Go**
Technical Accomplishments and Progress

Air Cooled Stack Durability Test - Average Cell Voltage @ 51.7A versus Time

Verification of 5000 hour stack durability

5000 hour target is from Life Cycle Cost Analysis presented in 2010
Technical Accomplishments and Progress

Air Cooled Stack Durability Test - Transfer Leak Rate versus Time

Normal Leak initiation at ~4500 hours

No leak initiation at >5000 hours with 2 techniques
1) System strategy to mitigate stress via reduced time at OCV
2) Advanced MEA concept with improved membrane durability

Verification of 1 system level strategy and 1 stack level strategy to mitigate MEA membrane stress
Technical Accomplishments and Progress

Air Cooled Stack Durability Test - Number of Air-Air Starts versus Time

- **2010 Results**
  - SN8134_AirAir
  - SN8135_AirAir
  - SN13077_AirAir
  - SN13078_AirAir
  - SN13086_AirAir

- **2011 Results**

**Control strategy refinement to reduce the number of air to air starts**

- **2010 Tests**
- **2011 Tests**
## Stack Durability Test Summary

<table>
<thead>
<tr>
<th>Stack</th>
<th>Cells</th>
<th>MEA</th>
<th>Hours</th>
<th>Cycles</th>
<th>Deg Rate at 51.7A (µV/hr)</th>
<th>Deg Rate at 29.0A (µV/hr)</th>
<th>Transfer Leak</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN8134</td>
<td>36</td>
<td>V1</td>
<td>6253</td>
<td>2163</td>
<td>-16.2</td>
<td>-9.8</td>
<td>Yes</td>
<td>Finished 2010</td>
</tr>
<tr>
<td>SN8135</td>
<td>36</td>
<td>V1</td>
<td>6456</td>
<td>3275</td>
<td>-27.1</td>
<td>-15.0</td>
<td>No</td>
<td>Finished 2010</td>
</tr>
<tr>
<td>SN13077</td>
<td>36</td>
<td>V2</td>
<td>5785</td>
<td>1119</td>
<td>-16.8</td>
<td>-12.0</td>
<td>Yes</td>
<td>Finished 2011</td>
</tr>
<tr>
<td>SN13078</td>
<td>36</td>
<td>V2</td>
<td>7054</td>
<td>1354</td>
<td>-15.6</td>
<td>-12.3</td>
<td>Yes</td>
<td>Finished 2011</td>
</tr>
<tr>
<td>SN13086</td>
<td>36</td>
<td>V2-A</td>
<td>5261</td>
<td>1019</td>
<td>-13.3</td>
<td>-6.9</td>
<td>No</td>
<td>Finished 2011</td>
</tr>
</tbody>
</table>

### MEA Version Description

- **V1** – baseline (original) Ballard Air Cooled Stack MEA
- **V2** – baseline MEA with improvements to cathode catalyst to mitigate corrosion
- **V2-A** – V2 MEA with improvement to membrane to mitigate transfer leak
## Mitigation Activities

<table>
<thead>
<tr>
<th>Issue from Phase 3 tests</th>
<th>Proposed Mitigations - 2010 Go / No Go</th>
<th>Actual Mitigation - 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS durability</td>
<td>- Improve control strategy</td>
<td>- Manage system startup controls and stack idle time to minimize AA starts (\rightarrow) 46% reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Perform periodic cathode air starves to minimize catalyst oxide layer growth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Manage mixed potentials in cells on shutdown to minimize carbon corrosion damage</td>
</tr>
</tbody>
</table>
| Stack temperature at +40C ambient | - Larger pleated filter  
- Filtration space claim | Low pressure drop particulate and chemical filter developed for the available space claim; fan is able to maintain target stacks temperatures at +40C ambient temperature |
| Inlet air temperature gradient | - Heater location  
- Air recirculation ducting  
- Ambient air inlet ducting | CFD modeling used to optimize air flow and minimize stack inlet air temperature gradients without the use of a heater – Final systems built with new inlet and air recirculation ducting; see test results |
| Moisture condensing and freezing | - Heater location  
- Air recirculation ducting  
- Ambient air inlet ducting | CFD modeling used to optimize air flow and minimize stack inlet air temperature gradients – No condensing or freezing observed during final low ambient temperature testing |
Original Test Results at -30°C Ambient - 2010

- Stack temperature near optimum
- Stack inlet air temperature below 0°C and non-optimal 35°C gradient
- The following 5 slides demonstrate 2011 design mitigation steps that converge to Stack Inlet Air Temperature >0°C target and Stack Temperature Gradient <10°C target
Air Recirculation CFD Model for -30°C Ambient - initial duct modeling

Technical Accomplishments and Progress

Initial concept had 25% variance in velocity profile and 45°C temperature variation
Technical Accomplishments and Progress

Air Recirculation CFD Model for -30°C Ambient - refined duct modeling

Figure 3: Air Temperature Profile at stack inlet – air duct refinements

Figure 4: Air Velocity Profile at stack inlet – air duct refinements

Refined concept 15% variance in velocity profile and 20°C temperature variation
Technical Accomplishments and Progress

Air Recirculation Test Results at -30°C Ambient Temperature
- Instrumented Stack Module, Medium Power Condition

Inlet Air Temperature above 0°C target and Stack Temperature within 10°C gradient target

10/10/2011 -30°C Amb, 28A, 39 Cell Stack, Type-A Air Recirc Duct

3.5 to 7.5°C inlet air T

33 to 43°C stack T
Technical Accomplishments and Progress

Air Recirculation Test Results at -30°C Ambient Temperature - Instrumented Stack Module, Idle Condition (worst case)

Inlet Air Temperature above 0°C target and Stack Temperature within 10°C gradient target

3 to 4.5°C inlet air T

10/10/2011 –30°C Amb, 11A, 39 Cell Stack, Type-A Air Recirc Duct

18 to 23°C stack T

10/10/2011 –30°C Amb, 11A, 39 Cell Stack, Type-A Air Recirc Duct
16

Ambient temp measured in system, actual ambient temp = -30°C

Low Ambient Temperature System Test Results

System ran for 8-hrs continuous under both high and low load profiles with no performance loss or operational issues
Technical Accomplishments and Progress

Next Generation Order Picker from Plug Power

- Announced in October 2011 and based on the technology developed over the course of this 2 year project with the DOE
- Shipped over 100 units to at least 4 customers in Q4 2011 and have received positive customer feedback
- Units can operate in a freezer environment; operating range -30°C to +40°C
Collaboration

- Modeling and operating strategy collaboration with Ballard Power Systems (subcontract partner)
- Stack model from Ballard / System model from Plug Power
- Models used with actual load profiles to optimize operating strategies to meet performance, efficiency, and durability requirements
- Test data, including degradation rates and failure analysis results, are fed back to improve the model capability
Summary

- Dominant failure modes related to catalyst and membrane degradation
  - Dissolution and carbon corrosion during air-air starts, membrane degradation during OCV
  - Two MEA designs show reduced degradation in lab testing, new materials mitigate dissolution, corrosion and membrane leaks

- 5000 hour durability target met using operating strategies to reduce stressors
  - 5000 hour durability target: >0.54 volts/cell at 51.7 amps current draw
  - Mitigate failure modes related to air-air starts and OCV time with both MEA improvements and system operating strategies
  - AST’s and models used to define system operating strategies for extended lifetime

- Freeze tolerance designed into the FC system, capable of -30°C operation
  - Freeze capable stack technology more expensive than freeze prevention at system level
  - Minimal degradation seen from freeze start-ups from -10°C, below -10°C the stack had issues with consecutive freeze start-ups
  - Stack thermal model identified inlet heaters and cathode recirculation as design mitigations
  - CFD modeling used to minimize the inlet air temperature gradient and eliminate freezing of recirculation air as observed in the original tests
  - Sustained operation at -30°C possible with system mitigation strategies employed

- Projected initial product cost reduced by 57% and life cycle cost reduced by 32% utilizing ACS technology for material handling order picker applications by compared to the incumbent liquid cooled stack solution
Technical Back-Up Slides
Air-Cooled Stack Freeze Test Results

- ACS has functional limitations in environments below -10°C
  - Excessive stack cooling and low ambient RH are main causes
  - Below -10°C start-up resulted in variability and catalyst damage
  - Due to membrane resistance and ice accumulation in the catalyst layer
- Freeze durability cycling @ -5°C shows no change in degradation rate compared to ambient cycling
  - Recommendation: explore system modifications to keep stack temperature above -10°C

Air Polarization at -10°C

Not Possible to Run at Low Current Densities

Freeze Start Cycling at -5°C & Ambient

Baseline A1M1C1
- Upper and lower bounds
- Target Stack Temperature
- Target Stack A1M1C1
- Stack Temperature A2M3C3

Baseline A1M1C1 -5C
Baseline A1M1C1 Ambient
A2M3C3 -5C
A2M3C3 Ambient

Cumulative Air-Air Starts
Define Baseline Stack Degradation Modes

Failure analysis identified membrane leaks causing corrosion and platinum dissolution to be the dominant failure modes.
Screening with ASTs & Stack Durability Models

- Guided by failure analysis results, seek components that offer improved resistance to leaks, corrosion and platinum dissolution
- Membrane AST and time to leak initiation during stack durability testing follow linear trend
- Semi-empirical voltage degradation model exhibits a linear trend with stack level durability testing
  - Model based on corrosion/dissolution ASTs and steady state degradation rates

Stack Vs. Membrane Accelerated Stress Test

Stack Vs. Catalyst Voltage Degradation Model

- $R^2 = 0.999$
- Some advanced concepts have very low degradation rates
System Operating Strategy Development

- Development of an analytical system model to evaluate performance and durability of a Fuel Cell / Battery Hybrid System
- Collaboration with Ballard to understand stack stressors and failure modes then develop system operating strategies to mitigate stressors
  - Air-Air Starts degrade the catalyst and cause voltage degradation
  - Time at OCV degrades the membrane and causes transfer leaks
  - High currents and stack temperatures stress the membrane
  - Mixed potentials (at start-up and shutdown) degrade the catalyst
- Baseline stack testing with customer load profiles; system model used to generate the stack operation, durability data w/o expense of a system
System Bench Test Results

ACS System Bench, 38 Cell Stack S/N 13085
Includes all system components

Verification of 5000 hour durability in a system

Linear degrade rate over first 4800 hrs = -4.9 µV/cell-hr

Linear degrade rate over last 700 hrs = -82 µV/cell-hr

# A-A Starts

Load Profile Changed

Test Stopped at 5520 hrs