2007 DOE Hydrogen Program

PEM Fuel Cell Freeze Durability and Cold Start Project

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Overview

Timeline
- Project start date: 5/1/2006
- Project end date: 4/30/2007
- Percent complete: 100%

Barriers
- Start-up and shut-down time and energy
- Water transport within the stack
- Durability

Budget
- Total project funding
  - $990K DOE
  - $247K UTC Power

Partners
- United Technologies Research Center (UTRC)
Objectives

• Improve cold-start, or Boot-Strap Start, ("BSS") time by investigating the effects of cell properties and start procedures

• Subject a short stack to freeze/thaw cycling between -40ºC and +20ºC to investigate any possible damage mechanisms

• Subject single cells and/or short stacks to repeated cold starts (BSS), measure performance degradation, and investigate the mechanisms of any performance degradation
Approach

• **Task 1: Cold Start (BSS) Decay Studies**
  – Investigate the effect of freeze and cold start (BSS) procedures on performance decay
  – Alternative cell materials will be evaluated for their resistance to performance loss with repeated cycles.

• **Task 2: Cold Survivability**
  – Conduct freeze/thaw cycling of short stack to -40 °C
  – Conduct teardown analysis to characterize failure modes

• **Task 3: Rapid Cold Start (BSS) Characterization**
  – Investigate the effect of freeze and cold start procedures on BSS capability
  – Investigate effect of alternate cell materials on BSS capability
UTC’s PEM fuel-cell technology

- Traditional, Solid-Plate Cell
  - Water movement is in the channels
  - External water management required
    - Humidification and water recovery
  - Liquid water build-up is unavoidable
    - In the channels and in the GDLs

- UTC’s Microporous-Plate Cell
  - Water movement is through the plate
  - Provides humidification and removal of excess liquid water
  - Single-phase flow in the channels
    - Low pressure drop
    - No local flooding/starvation
Baseline Performance:
30-cell Stack (320-cm$^2$ per cell)

- Poor BSS performance and high frozen resistance on anode end of stack.
- Anode-end resistance is affected by rate of freeze.
Water Movement During Freeze: Frost-Heave Mechanism

\[ P_c = \frac{2\gamma \cos \theta}{r} \]

\[ P_{liq} = P_{gas} - \frac{2\gamma \cos \theta}{r} \]

- As water freezes, effectively, the pore radius decreases, drops the liquid pressure, and induces liquid water movement towards the freezing point.
- In extreme cases, the excess of ice which is formed may push against the porous media, resulting in “frost heave”

Pore cross-section
Proposed Performance-Loss Mechanism (2)

Cathode Side:
Water transport towards cold cathode side
Cathode catalyst layer water content decreases

Anode Side:
Water transport towards cold anode side
Cathode catalyst layer water content increases
Single-Cell Hardware Configuration: Glycol used to create freeze direction

Cathode-Side Freeze

-10°C glycol

Anode-Side Freeze

-10°C glycol
Single-Cell Results: Effect of GDL Permeability

Air Stoichiometry: Initially 5, Decreased to 1.67

- Cell w/ High Permeability GDL performed better after cathode-side freeze
- Cell w/ Low Permeability GDL performed better after anode-side freeze
“Adiabatic” Single-Cell Hardware: Heat used to create freeze direction

- Heating pads on each side mimic stack heat
  - Cell in freezer, no glycol
  - Heating one side during freeze simulates freeze direction
  - Freezing rates more realistic to those experienced in stacks
  - Variable heat on each side during startup, pegged to current density
- Pyropel© insulation between cell and pressure plates and high-density Pyropel© manifolds
- Resistance is very high after anode freeze, due to H₂O movement during freeze (see slides 7 & 8)
“Adiabatic” Single-Cell Results: 0.6 A/cm² BSS from -30°C

- Cell w/ Low Perm GDL maintained positive voltage at 0.6A/cm² after anode freeze to -30°C
- There appears to be an optimum permeability. Results are dependent on rate of freeze.
Effect of GDL on Short-Stack BSS

- When all cells had baseline GDL configuration, anode end performed poorly on 0.3 A/cm² BSS.

- Inserting low permeability GDLs on the anode-end cells greatly improved their BSS performance.
-40°C Freeze/Thaw Survivability

Performance after Freeze-Thaw Cycling -40 and +20 Celsius

Average Cell Voltage (V)

Freeze-Thaw Cycle Number

Scanning Electron Micrographs (SEM) of Unitized Electrode Assemblies (UEA)

After 100 cycles

No changes observed in 20-cell stack after 100 freeze-thaw cycles to -40°C. SEM images same as as-received.
**-40°C Freeze/Thaw Survivability: Second 20-Cell Short Stack**

- Excluding end-cells, negligible performance loss after 111 freeze/thaw cycles.
- Mostly recoverable decay observed on end-cells.
Progress vs. 2010 DOE Targets

• DOE Target: BSS from -40°C
  – Achieved: BSS from -35°C with Short Stack
    • With no air-side purge required on shutdown
    • Short fuel-side purge for system components (e.g., fuel regulator)
  – Achieved: -40°C Freeze/Thaw Survivability

• DOE Target: 50% rated power in 30s from -20°C
  – Baseline Short Stack: 33% r.p.* in 30s from -12°C
  – Single Cell w/ Low Perm GDL:
    • 65% r.p. in 30s from -10°C (anode freeze & cathode freeze)
    • 47% r.p. in 30s from -29°C (anode freeze)
    • 33% r.p. in 30s from -29°C (cathode freeze)

• DOE Target: 50% rated power in 5s from +20°C
  – Achieved: 94% r.p. in 5s from +23°C (single cell)

* UTC’s rated power is 0.65 W/cm²
Future Work

- DOE-funded program completed on 4/30/2007
- Freeze work continues at UTC Power & UTRC
  - Both stack and system-level work ongoing
  - Additional optimization of cell design and materials required to achieve faster cold-start times
  - Further system simplifications to improve robustness
- Results strongly depend on water management:
  - Amount of water present in cell on shutdown
  - Water movement during freeze
  - Water production, movement, and removal on start
Summary

• Excellent BSS and freeze durability results have been achieved with UTC’s microporous-plate cells.

• Freeze-decay mechanism:
  – $H_2O$ moves down thermal gradient across GDL
  – Anode end of stack: More cathode flooding during freeze

• With low permeability GDL:
  – Less $H_2O$ movement during freeze than baseline cells
  – Excellent performance after both anode- and cathode-side freeze

• Notable short-stack results:
  – Cold starts (BSS) successfully conducted down to -35°C
    • No purging of stack on shutdown required
  – 111 freeze/thaw cycles to -40°C with negligible performance loss