V.A.11 PEM Fuel Cell Freeze Durability and Cold Start Project

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Objectives

- Characterize proton exchange membrane (PEM) fuel cell durability and performance under freezing conditions.
- Determine effect of start procedures, materials, and cell design on cold start performance and durability.
- Perform freeze-thaw cycling to determine survivability of PEM fuel cells to -40ºC.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Start-up and Shut-down Time and Energy

(D) Water Transport within the Stack

(A) Durability

Technical Targets

UTC is committed to achieving and surpassing key low temperature targets set by DOE and the major automotive original equipment manufacturers (OEMs). The results of this work suggest that further optimization can be performed on gas diffusion layer (GDL) permeability, start procedures, stack and system design, and other aspects to further improve cold-start performance. UTC has every expectation of exceeding the relevant targets (see below) at both the single-cell and short stack level, as well as demonstrating these improvements in complete fuel-cell systems.

The achievements of this project, as measured against the 2010 DOE targets, are as follows:

DOE Target: Unassisted start from -40°C

- Achieved: Unassisted start 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 30 seconds from -20°C (UTC's rated power is 0.65 W/cm^2)

- With baseline cell design, demonstrated 33% rated power in 30 seconds from -10ºC at short stack level
- With improved cell design, demonstrated:
  - 47% rated power in 30 seconds from -30ºC at single cell level after an "anode side" freeze[1]
  - 34% rated power in 30 seconds from -30ºC after "cathode-side" freeze

DOE Target: 50% rated power in 5 seconds from +20°C

- Single-cell with improved design achieved 94% in 5 seconds from +23°C

Accomplishments

- Demonstrated unassisted start from -35°C with 30-cell short stack.
- Observed freeze-related recoverable performance loss on the anode side of the stack, and linked it to frost-heave-driven cathode flooding.
- Designed and built sub-scale and single-cell hardware which successfully captured the freeze

[1] For an "anode side" freeze, a very small amount of heat is applied during freeze on the cathode side of the cell to impose a small temperature gradient across the cell. This simulates a cell within a stack where the anode faces the end of the stack (cold side) and the cathode faces the middle (warm side) of the stack.

performance of the anode and cathode ends of the stack, respectively.
- Evaluated alternative cell materials for their freeze performance.
- Solved the anode-end freeze problem using alternative membrane electrode assemblies (MEA), GDLs, and cell configuration.
- Demonstrated over 100 freeze-thaw cycles to -40°C on a 20-cell stack with negligible performance decay and no structural damage observed in the active area.

Introduction

Traditionally, PEM fuel cells (PEMFCs) use solid bipolar plates as an electronic interconnect and gas-tight seal between adjacent cells. Bipolar plates also contain flow-fields for air, fuel (hydrogen), and coolant. Since water generated at the cathode must be removed in the air stream, liquid water tends to accumulate in the air flow-field and cathode GDLs. Moreover, the fuel must be humidified to prevent anode dry-out due to electro-osmotic drag. UTC has largely overcome these barriers by using micro-porous bipolar plates, which are permeable to liquid water but have a high bubble pressure. These water-transport plates (WTP) humidify the anode and remove excess liquid water from the cathode. The reactant gases need not be humidified, and the cells may be operated at atmospheric pressure.

This work is concerned with the performance of micro-porous plate PEMFCs under freezing conditions. For use in the automotive industry, PEMFCs must be able to start from below-freezing temperatures within a reasonable amount of time. A typical automotive industry requirement is 50% rated power in 30 seconds from -30ºC. To minimize start-up and shut-down time and energy, a cold start should be unassisted - the PEMFC stack should be thawed using waste heat from the fuel cell reaction, without any external heating. An unassisted cold start is referred to as a "boot-strap start" (BSS).

Approach

The cold start performance and durability was evaluated by experimental methods. Short stack cold start fuel cell testing was used to evaluate baseline cell performance and durability, as well as the effect of procedural variables. Single cell cold start fuel cell testing was used to evaluate the effect of material selection and cell design. Analysis of experimental data was used to guide material and cell development.

Results

Figure 1 shows the voltage profile during a cold start from -10ºC at 0.4 A/cm^2. The cells on the cathode end and middle of the stack performed well, but the cells on the anode end of the stack performed poorly. The cathode end is defined as the side of the stack in which the cathode electrode and flow-fields face the end of the stack and the anode faces the middle of the stack, and vice versa for the anode end. The resistance after freezing was also found to be higher for the cells on the anode end of the stack. Figure 2 shows conceptually why the anode end cells perform poorly. There is a temperature gradient during the freezing process as heat is lost from the end of the stacks. During the freezing process, water flows due to a capillary pressure gradient caused by the freezing of water in small, hydrophilic pores. This mechanism has been referred to as "frost-heave", a term which is more commonly used in the field of soil science. On the anode end, water flows towards the anode, and vice versa for the cathode end. For the anode end cells, water flows from the porous bipolar plate, across the cathode GDL, which has high liquid permeability, and into the cathode catalyst layer. Water flow from the cathode catalyst layer across the membrane is slow, due to the relatively low liquid permeability of the membrane. This water movement during freeze results in a higher fill level in the cathode catalyst layer, resulting in higher resistance to oxygen transport into the electrode. On the cathode end, water flows out of the cathode catalyst layer, across the cathode GDL, and into the cathode porous plate. Little water flows from the anode catalyst layer across the

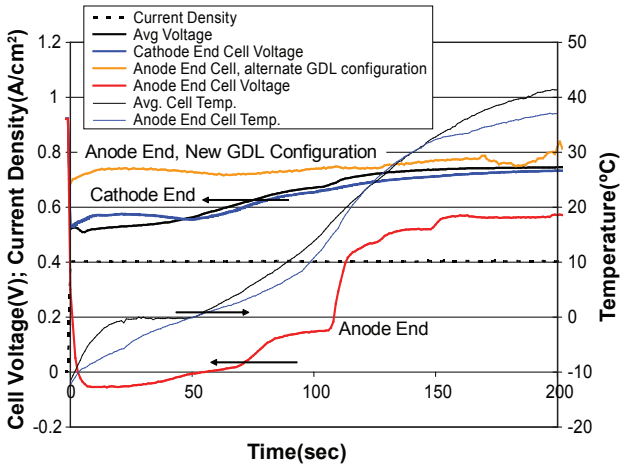

FIGURE 1. Effect of Cell Location on Cold Start Performance of a 30-Cell Short Stack (-10°C, 0.4 A/cm^2)

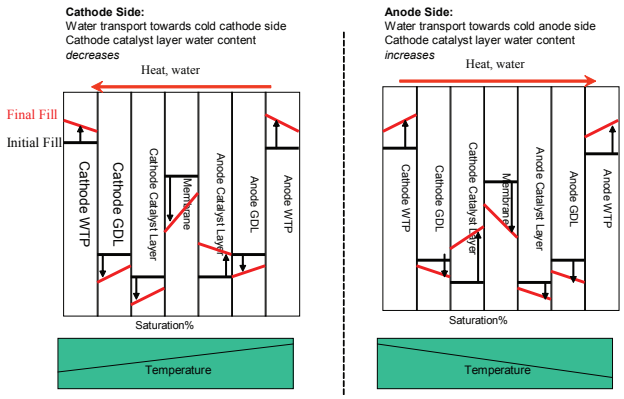

FIGURE 2. Schematic showing proposed effects of the frost-heave mechanism at opposite ends of the stack. Black lines indicate fill level before inducing temperature differential; red lines show fill levels after inducing the indicated temperature differential.

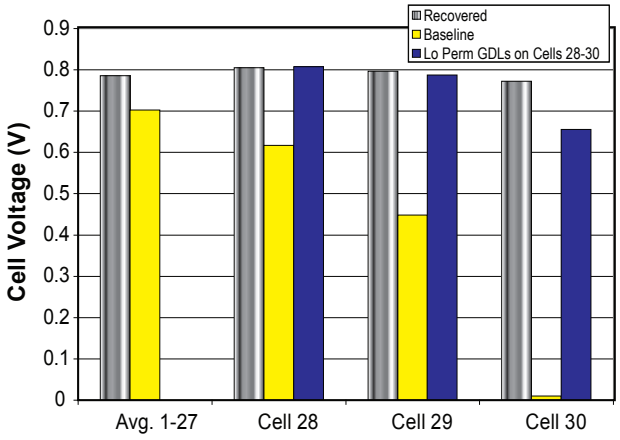

FIGURE 3. Comparison of Anode End Cell Performance for New Cell Configuration within a 30-Cell Short Stack

membrane, so the fill level of the cathode catalyst layer is relatively low for cells on the cathode side of the stack, allowing good oxygen transport during the cold start.

The high liquid permeability of the cathode GDL allows water movement towards the cathode catalyst layer on the anode end. To improve the anode end cell performance, the liquid permeability of the cathode GDL was reduced. Figure 3 shows a cold start from -10ºC to 0.4 A/cm^2 when cathode GDLs with low water permeability were used. The performance was improved substantially.

Figure 4 shows cold start performance data for several cells with various GDL configurations with varying liquid permeability. The best performance to date was obtained for UEA configuration #2 after an anode side freeze. This same cell did not perform well after a cathode size freeze, though. The best cathode side start was with UEA configuration #3, but this cell did not perform well after an anode side freeze. The best cell which started well for both an anode side and cathode side freeze was UEA configuration #1.

A short stack was also subjected to 100 freeze/thaw cycles between room temperature and -40ºC. A small, recoverable performance loss of the end cells was observed, although no loss was observed for the majority of the cells. Delamination between the MEA and the sealant material was observed in the seal region, but no physical damage was seen in the active area.

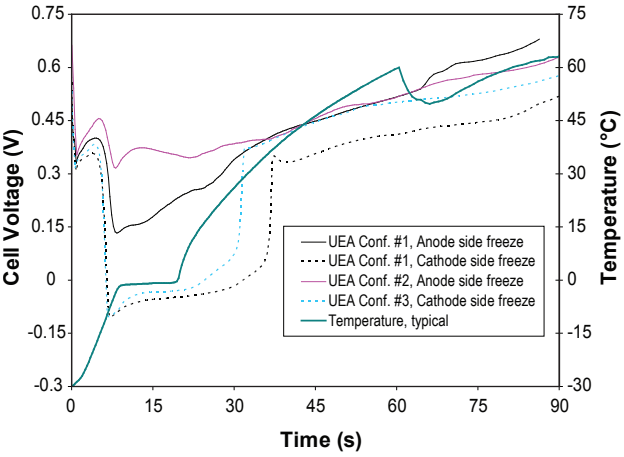

FIGURE 4. BSS Voltage Profiles for Various GDL Configurations during Single Cell Boot-Strap Starts from -30°C and 0.6 A/cm^2

Conclusions and Future Directions

- Cold start performance of anode end cells was very poor at the start of this work; by understanding and controlling water movement during the freezing process, the cold start performance of the anode end cells was greatly improved.
- A PEM fuel cell was freeze/thaw cycled to -40ºC with no significant performance degradation or mechanical damage seen in the active area; some mechanical damage was observed in the seal area where delamination of the MEA from the sealant material was observed.
- Additional optimization of GDL and MEA materials is expected to lead to faster cold start times

FY 2007 Publications/Presentations

1. Q2, 2006 Quarterly Report to DOE.
2. Q3, 2006 Quarterly Report to DOE.
3. Q4, 2006 Quarterly Report to DOE.
4. Q1, 2007 Quarterly Report to DOE.
5. 2006 Final Report to DOE.