

V.F.1 CIRRUS: Cell Ice Regulation & Removal Upon Start-Up

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Subcontractors:

- W.L. Gore & Associates, Elkton, MD
- SGL Carbon, Meitingen, Germany
- University of Delaware, Newark, DE

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Project End Date: June 30, 2010

Objectives

The objective of the CIRRUS project is to advance the state-of-the-art in fuel cell operability under subfreezing conditions, consistent with requirements for applications involving such conditions (e.g. automotive, forklifts, backup power systems, and auxiliary power units) and DOE targets, specifically to:

- Demonstrate repeatable achievement of 50% rated power in less than 30 seconds from a -20°C start condition, using less than 5 MJ auxiliary energy.
- Demonstrate unassisted start capability from an initial temperature of -40°C.

Technical Barriers

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

(D) Water Transport within the Stack

(G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Nuvera is demonstrating the ability to meet DOE's 2010 targets in a full format, subscale stack assembly operating in a simulated but fully realistic ambient environment, using system-compatible operating protocols. The hardware platform initially used in this work was Nuvera's Andromeda™ fuel cell, designed in 2005, with an active area of 360 cm² and a rating current density of 1.0 A/cm². In the previous reporting period it was shown that Andromeda is capable of starting from -20°C in 30 sec to 50% of its rated power respecting an energy budget of 5 MJ. This report presents the progress obtained in proving the reliability of the startup procedure identified and the durability of a stack subjected to such protocol.

Though the work on Andromeda has been successful at -20°C, the intrinsically high thermal mass of the stack limits the ability to lower even further the starting temperature and it imposes the removal of the coolant during freeze operation even at -20°C.

Thus a stack redesign was required to study startability from extreme temperatures (-40°C) and allow operations at -20°C with resident coolant that dramatically simplify the fuel cell balance of plant.

This new stack, Orion™ (active area 250 cm², rating current density 2 A/cm²), became available last year, and it has been used as the stack platform for this project since the third quarter of 2009.

Accomplishments

- The reliability of the selected startup procedure (from -20°C) was proven through 200 freeze starts performed on Andromeda.
- The diagnostic run on samples subjected to 200 freeze starts did not show significant degradation of fuel cell materials.
- Orion prototypes demonstrated performance (0.6 V @ 2 A/cm²) matching design expectations.
- The Orion stack was successfully started from -20°C with resident coolant, achieving the DOE targets of time to 50% power within the energy budget.



Introduction

For fuel cells to be commercially viable as powerplants in automotive applications, the ability to survive and start reliably in cold climates (as low as -40°C) is a must. Since fuel cells are water-based energy systems, this requirement is a significant technical challenge.

Water transport studies are imperative for achieving DOE targets for fuel cell startup time from subfreezing conditions. Stack components must be selected that endure thermal and humidity cycling over the operating range, and operating strategies must be devised that enable the fuel cell to start, i.e. generate power and heat up sufficiently before ice extinguishes the galvanic reactions, and afford evacuation of a sufficient amount of water, using a limited amount of auxiliary power, at shutdown.

Approach

Nuvera has structured the project into four different phases: investigation, selection, qualification and validation. In the Investigation phase (third and fourth quarters of 2007, completed) Nuvera surveyed the status of the art on the topic and set up the enabling tools (test infrastructure and modeling capabilities). In the Selection phase (2008, completed) Nuvera used these tools to select a proper freeze start strategy to meet the DOE requirements and a set of materials to enable the successful execution of the test. In the Qualification phase (2009, completed) Nuvera assessed performance stability of the combined material set and operating methods in a durability test campaign. The results of this campaign, supported by the interaction with the partners of the project (W.L Gore, SGL and University of Delaware) drove the identification of improvements of materials, strategy and stack architecture. Finally, the effectiveness of these actions is being verified in the Validation phase (first and second quarters of 2010) in which the most advanced configuration is tested to quantify the improvements achieved.

Results

In 2009 Nuvera set up a test campaign that consisted of repeating the same startup protocol 200 times on an Andromeda stack. As stated before, the objectives were to prove the reliability of the procedure and measure the degradation of the materials to understand the main area of improvement and development. The

test was made possible through the automation of a test stand with integrated climatic chamber (performed in 2008) that allowed five startups per day, significantly accelerating the testing process. The results proved the robustness of the protocol as it can be seen in Figure 1. In fact, all the startups were successful and even though in some cases the stack didn't reach exactly the 50% of rated power after 30 sec (50% of 0.664 W/cm^2), overall the performance was above the 50% target with no decreasing trend over time. Some voltage degradation was noticed along the course of the test but the measurement of the stack resistance proved the decrease in voltage over time can be almost entirely attributed to a progressive loss of compressive load. This issue has been addressed in the Orion stack by implementing a compression system that provides a better control of the compressive load.

In two different situations (after 100 and 200 cycles) the stack was opened and material samples were extracted for analysis at Gore and SGL labs. The investigation was focused on detecting the typical freeze related decay mechanisms identified during the Freeze Workshop held at Nuvera in early 2009. Even though some evidence of degradation occurred, none of these could be related directly to freezing. This finding indicates that the combination of the procedures applied and the materials used did not experience accelerated degradation with respect normal operation of the fuel cell, at least after 200 repetitions. A summary table describing the decay modes investigated, the diagnostic techniques used and the results found is reported in Figure 2 with some pictures illustrating the findings.

Over the course of the year several prototypes of the Orion stack have been assembled to stabilize the hardware and achieve the performance targets. The

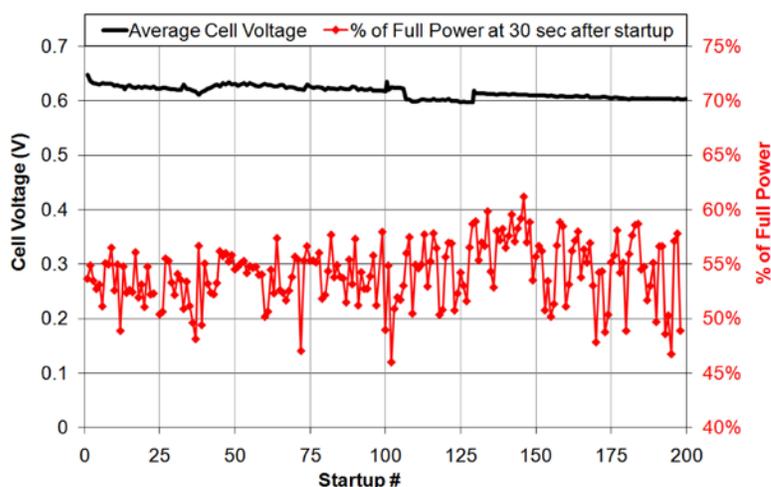


FIGURE 1. Andromeda Stack Started from -20°C , % of Power after 30 Seconds over 200 Repetitions

Aging mode	Analysis performed	Learning
Membrane degradation •RH cycles •T cycles	SEM of MEA	No evidence of damage due to RH cycling. Evidence for localized high compression leading to extrusion of ionomer into electrode cracks.
Interface damage •Catalyst delamination	SEM of MEA	No evident sign. Some delamination observed is compatible with initial status of MEA
Gas compartment blockage •Electrode damage •Corrosion •Pt dissolution	SEM of MEA Backscatter imaging TEM EDS	No strong trends found for Pt particle size in anode or cathode. Some signs of a Pt precipitation band found in the membrane. Slight signs of anode thinning detected in some instances.
GDL damage •Cracking	SEM of GDL (SGL)	Some cracks detected but no significant increase in number or extension of the cracks noticed on samples analyzed after 100 and 200 cycles.

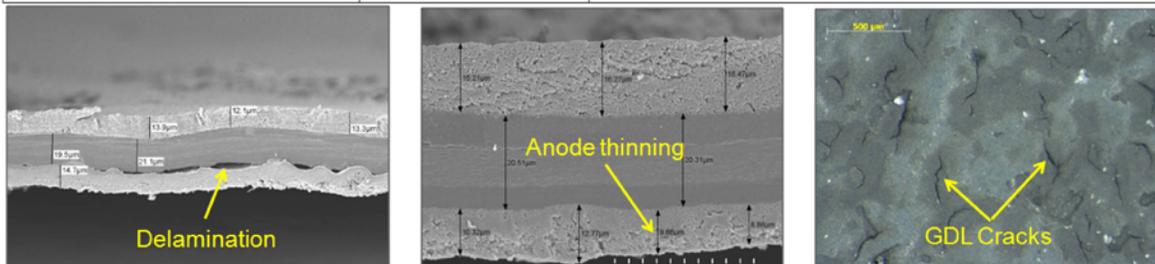


FIGURE 2. Summary Table of Diagnostics Performed on Andromeda Materials Subjected to 200 Freeze Starts from -20°C

stack was designed in 2008 to offer a reduction in thermal mass and fully exploit the Nuvera proprietary flowfield technology that enables operation at high current densities. In this regard the stack was designed to deliver 0.6 V @ 2 A/cm² with a cathode inlet pressure not higher than 800 mbar that is achieved through back-pressurization of the compartment. This way of operating is compatible with the specifics of the compressor used in the HDL-82 system (Nuvera and FIAT development) and it provides a performance advantage at system level with respect to operating the stack at open valve. The performance target was met on multiple stacks and the polarization curve in Figure 3 illustrates the achievement of the goal on a 2-cell Orion stack.

The proven high power density of the stack helps to reduce its thermal mass because it decreases the number of cells that are needed to obtain the rated power. Furthermore, the stack hardware is lighter, which leads to a lower intrinsic thermal mass, and the cooling compartment is smaller, which results in lower overall mass of coolant that is resident during the startup phase. The tests run on Orion highlighted the effectiveness of the design actions described above. A dedicated coolant loop was built to supply an Orion stack with an anti-freezing cooling fluid (mixture of water and ethylene glycol) and such loop was installed on a portable rack that allowed freezing the stack and the coolant system as a whole. The startup performed on this setup was successful as shown in Figure 4 where

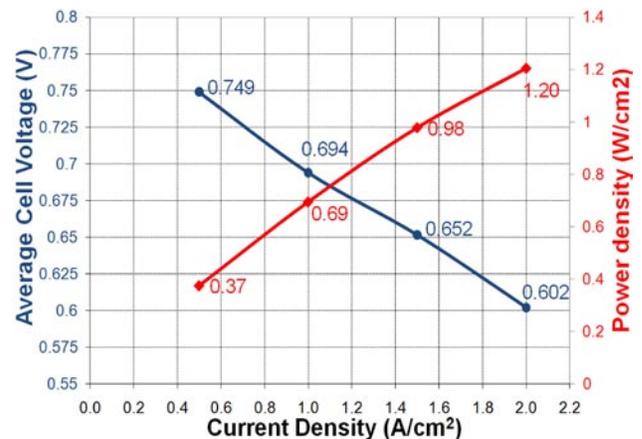


FIGURE 3. Polarization Curve of Orion Meeting Desired Performances (0.6 V @ 2 A/cm²)

the Orion stack was able to start from -20°C and in 28 seconds it reached the 50% of rated power (50% of 1.2 W/cm²). The total energy spent to purge the stack during the shutdown phase and the subsequent startup was calculated at 2.937 MJ, which is less than the DOE target of 5 MJ.

Conclusions and Future Directions

Nuvera will focus the remaining months of the project on exploring the capability of Orion to start from

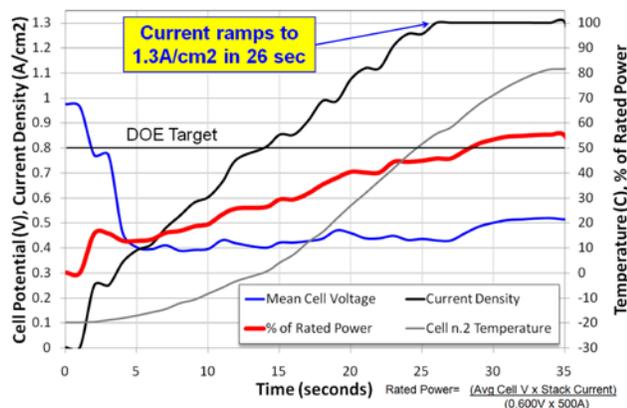


FIGURE 4. Startup from -20°C, Orion Stack with Resident Coolant

extreme temperatures approaching -40°C. Preliminary tests conducted at -30°C seem to confirm the advantage of a reduced thermal mass but more investigation is needed.

For the future Nuvera recognizes the need to study the impact of different pre-conditions on the ability to start from sub-freezing temperature. For this purpose Nuvera implemented a technique to monitor the high frequency resistance of the stack during operation, which is recognized by the fuel cell community as a good indicator of the state of hydration of the membrane, the effectiveness of the purging procedure applied, and the likelihood of a successful startup.

Finally the work done in CIRRU has proven that the temperature over the surface of the membrane electrode assembly is far from being uniform during the startup and the knowledge of the temperature gradients as a function of time might be an interesting area of study to drive the optimization of materials and procedures.

FY 2010 Publications/Presentations

1. September 2009 - Billerica, MA, Detroit, MI (via conference call) - FreedomCar Review.
2. June 2010 - Washington D.C. - 2010 DOE Hydrogen Program Merit Review (FC55).