V.J.3 Solid Acid Fuel Cell Stack for APU Applications*

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Objectives

The primary objective of this project is to demonstrate the feasibility of solid acid fuel cells (SAFCs) for auxiliary power units (APUs), capable of operating on low-sulfur diesel fuel and other equivalent reformate.

- Demonstrate the functionality of SAFCs on a variety of reformate including methanol, commercial liquid propane gas, and commercial ultra-low sulfur diesel fuel.
- Scale up and demonstrate the functionality of a 125 cm² SAFC membrane electrode assemblies as the platform for a 300 W SAFC stack.
- Design and model the necessary stack components including bipolar plates, seals, end plates, and hardware.
- Build and characterize the performance of a SAFC stack scalable up to 300 W.
- Generate a conceptual design for a 3 kW diesel SAFC power plant.

Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is directed at the development and demonstration of a SAFC stack as an APU subcomponent for heavy truck usage to reduce idling of the main combustion engine. If successful, the project will address the following DOE technical targets as outlined in the HFCITP Multi-Year RD&D Plan:

TABLE 1. Progress towards Meeting Technical Targets for APU and

 Truck Refrigeration Units

Characteristic	Units	2010/2015 System Targetsª	2009 SAFC Stack Status (20 cm ² cells)
Specific Power	W/kg	100/100	36
Power Density	W/L	100/100	86
Efficiency @ Rated Power ^b	%LHV	35/40	55
Cost ^c	\$/kW	400/400	TBD
Cycle Capability over Operating Lifetime	number of cycles	150/250	20
Durability	hours	20,000/35,000	1,000
Start-up Time	minutes	15-30/15-30	45-60 ^d

^a From Table 3.4.8 (page 3.4-19) of the DOE HFCITP Multi-Year RD&D Plan. ^b Electrical efficiency only – does not include an efficiency aspects of the heating and cooling likely being provided.

^c Cost based on high-volume manufacturing quantities (100,000 units per year). ^d Start-up time based on system modeling and conceptual design. LHV - lower heating value

TBD - to be determined

In this project we are conducting fundamental studies of SAFC tolerances to impurities found in fuel processors used to generate hydrogen-containing fuel gases. Information from these studies can be applied toward the design of stationary and portable fuel processors that meet or exceed the DOE 2011 technical targets found in Table 3.4.6 (page 3.4-18) of the DOE HFCITP Multi-Year RD&D Plan shown in Table 2.

TABLE 2. Progress towards Meeting Technical Targets For Tolerances

 To Impurities Found In Fuel Processors

Characteristic	Units	2005/2011 Targets	Superprotonic 2009 SAFC tolerances to impurities found in fuel
CO content in product stream ^a Steady-state Transient	ppm ppm	10/1 100/25	>200,000 ^b >200,000
H ₂ S content in product stream	ppbv (dry)	<10/<4	>50,000,000°
NH ₃ content in product stream	ppm	<1/<0.1	>100

^a Dependent on stack development (CO tolerance) progress.

^b Superprotonic's SAFC stack is stable running on fuel with >20% CO. ^c Superprotonic's SAFC stack is stable running on fuel with >100 ppmv H₂S.

Accomplishments

- Demonstrated the functionality and stability of the SAFC stack running on synthetic reformate with 10% CO and 100 ppm H_2S .
- Demonstrated the functionality and stability of the SAFC stack running on methanol reformate with 6.8% CO and 10.2% CO₂.
- Demonstrated the functionality and stability of the SAFC stack running on commercial liquid propane gas (LPG) reformate with 10.6% CO, 9.84% CO₂, 0.24% CH₄, 0.005% C₃H₈, and 0.5 ppm H₂S.
- Successfully demonstrated the functionality and stability of the SAFC stack running on diesel reformate with 14% CO, 10% CO₂, 0.3% CH₄ and 1 ppm H₂S.
- Fabricated higher surface area membrane electrode assembly (MEA) and tested several 125 cm² SAFC units to establish a platform for a 300-3,000 W stack.
- Designed and modeled a 300 W SAFC stack based on the 125 cm² MEA platform.



Introduction

SAFCs operate at an intermediate temperature range (230-280°C) and thus offer an attractive compromise between the advantages and disadvantages of low and high temperature fuel cells. Perhaps the most significant advantages of operating a fuel cell at these intermediate temperatures is the effective utilization of a multitude of reformed fuels, including alcohols such as methanol and butanol, and fossil fuels like natural gas and diesel without the complexity of high temperature operation. SAFCs do require humidification but only in the gaseous phase which allow for a simpler water management system. To date, we have demonstrated SAFCs operating on hydrogen/oxygen with peak power densities of over 640 mW/cm² at an operating voltage of 0.6 V and lifetimes greater than 1,000 hours at the cell level. At the stack level, we have operated the SAFC stack on a wide range of reformate including methanol, LPG, diesel, and kerosene.

The project aims to demonstrate the commercial viability of SAFC technology and addresses many of the key DOE technical barriers and targets for enabling fuel cells as an attractive power source. The primary focus is on APU applications in the range of 300-3,000 W peak for truck idling reduction. The fuel of interest is diesel with low sulfur content.

Approach

To achieve the project objective of developing a SAFC stack capable of running on diesel reformate with the necessary performance, stability, and durability as set by the DOE for APU applications, we need to thoroughly evaluate the SAFC using air as the oxidant and a variety of reformates as the fuel. This includes synthetic reformate as well as reformed commercial fuels with high level of impurities, such as CO, CO₂, and H₂S, typically found in fuel processors used to generate hydrogen-containing fuel gases. Accordingly, initial efforts were focused on extensive physicochemical characterization of the SAFC stack on air along with synthetic, methanol, LPG, and low sulfur diesel reformates.

Once sufficient understanding was gained from the characterization, the effort was expanded to scaling up the MEA fabrication to higher surface areas for commercial applications. Two parallel approaches are being used for the scale-up: 1) electrolyte densification via cold-pressing techniques based on a modified version of the current method and 2) a completely new MEA fabrication process with densification of the electrolyte based on roller compaction techniques. Design and modeling of a 300 W stack will also take place along with the MEA scale-up activities. In addition, a conceptual design for a 3 kW SAFC power plant will be generated based on information learned from the MEA scale-up and 300 W stack design.

Results

In the past year Superprotonic has focused on characterization of SAFC stack performance on synthetic reformate and reformed fuels such as methanol, LPG, and diesel. These evaluations are very important for addressing the durability barriers and technical targets for tolerances to impurities found in fuel processors. The tests were performed using 20 cm² MEAs in 10-cell and 20-cell stack configurations.

For the first evaluation, we used a synthetic reformate with 50% H₂, 40% N₂, 10% CO, and 100 part-per-million H₂S. The fuel and oxidant gas humidity was set at about 0.3 bar water vapor pressure using two separate PermaPure[™] humidifiers. We ran the stack for approximately 16 hours to test its stability under exposure to carbon monoxide and hydrogen sulfide. At the beginning of the evaluation, we obtained polarization curves with pure hydrogen as well as the synthetic reformate for comparative purposes. At the end of the 16-hour experiment, we repeated the polarization curve sequence to evaluate the stack performance after exposure to CO and H_aS. As shown in Figure 1, there is an approximately 17% drop in the fuel cell stack performance when we switched from pure hydrogen to synthetic reformate. This drop may be the result of dilution and/or slight differences in the hydrogen content of the synthetic reformate. In other words, the equivalent amount of hydrogen in the synthetic reformate may be lower than the pure hydrogen. However, more importantly, there is essentially no difference in fuel cell stack performance before and after exposure to CO and H₂S, based on the polarization curves and power density data. Results for the reformed methanol fuel evaluation are shown in Figure 2. The reformate flow rate was 2.8 standard liter per minute (SLPM) to provide an equivalent flow rate of 1.0 SLPM hydrogen. The composition of the methanol reformate was 74.2% H₂, 6.8% CO, and 18.2% CO₂. Owing to the higher hydrogen content, the effect of hydrogen dilution is not as strong as the case with the synthetic reformate.



FIGURE 1. Polarization curves for pure hydrogen fuel (pink square) and synthetic reformate fuel (blue cross) before and after 16 hours of exposure to CO and H_2S (hydrogen - navy blue dash, reformate – brown circle). The power density data also suggest there is no adverse effect due to CO and H_2S .

For the reformed propane fuel evaluation, we also used a 20-cell stack made up of 20 cm² SAFCs. The fuel and oxidant gas humidity was set at about 0.3 bar water vapor pressure using two separate PermaPure[™] humidifiers. The reformed fuel was obtained with a propane steam reformer running at approximately 650°C. The reformate fuel flow rate was 5.8 SLPM to best approximate an equivalent flow of 1.0 SLPM H₂. We evaluated both "pure" LPG as well as commercial LPG available at vendors such as The Home Depot. The composition of the pure propane reformate was 40.4% H₂, 34.4% N₂, 10.8% CO, 9.5% CO₂, and <1% of other byproducts such as CH_4 and C_3H_8 . The composition of the commercial propane reformate was 41.1% H₂, 34.6% N₂, 10.6% CO, 9.84% CO₂, <1%other byproducts such as CH_4 and C_3H_8 , and 0.5 ppm H_aS. There are four time points of interest in the experiment. At time points 1, 2, 3, and 4 we ran the SAFC stack on 1.0 SLPM H₂, 5.8 SLPM pure LPG reformate, 1.0 SLPM H₂, and 5.8 SLPM commercial LPG reformate, respectively. At all time points, we obtained polarization curves after switching the fuel at the anode. After the fourth polarization scan, we ran the stack steady-state on a 1 ampere direct current load for approximately 4 hours. After the steady-state run, we acquired another polarization scan for comparative purpose. Figure 3 summarizes all polarization scans from the propane reformate evaluation. The purpose of the polarization scans at time points 1 and 3 on pure hydrogen is to establish baselines for evaluating the SAFC stack performance on the two LPG reformates. The results from the evaluation suggest a very slight drop in performance when we switched from pure hydrogen to reformed LPG fuels. Based on the composition of the reformate, we believe most of the reduction in power density and stack voltage is the result of hydrogen dilution. These results suggest that the SAFC possesses



FIGURE 2. Polarization curve from a 20-cell SAFC stack running with pure humidified hydrogen (blue data) and reformed methanol fuel (red data). There is a slight reduction in performance possibly due to dilution.



Current density, *i* / A cm⁻²

FIGURE 3. Polarization curves from the evaluation of SAFC stack on liquid propane gas reformate. The solid data points are power densities and the unfilled data points are electric potentials.

excellent fuel compatibility with commercial liquid propane gas reformates.

The fuel of choice for APUs in the trucking industry is low-sulfur diesel. Accordingly, for the final portion of the flex-fuel evaluation, we ran a SAFC stack on hydrogen fuel processed from a bench-top diesel auto-thermal reformer. The exit of the reformer was connected to the inlet manifold of the stack anode with a tubular, air cooled heat exchanger in between. The stack anode inlet manifold allowed the operation of the stack on either a H₂ gas or the reformate gas stream. Diesel fuel was purchased from a local gas station with a total sulfur content of 400 ppm by weight. The tests were conducted first by using pure H_2 as the fuel for the stack to obtain stack baseline polarization (IV) curves. We then switched to the reformate at flow rates approximately equivalent to the corresponding pure H₂ flows. The reformate composition was analyzed using a gas chromatograph (GC) to confirm its product distribution. Based on the GC measurement, the diesel reformate contained 41% N₂, 35% H₂, 14% CO, 10% CO_2 , 0.3% CH_4 , and 1 ppm H_2S by volume. The oxygen-to-carbon (O₂:C) and water-to-carbon (H₂O:C) ratios were 1:2 and 2:1, respectively. After running the stack on diesel reformate for a few minutes for stability purpose, we collected the stack IV curves to compare with the data to the pure H₂ runs. Figure 4 illustrates a polarization curve comparison between hydrogen and low-sulfur reformate. It is important to note that the hydrogen content for the diesel reformate was only 35% and the pure hydrogen fuel used for comparison purpose in Figure 4 was not diluted down to these percentages. In addition, the CO and CO₂ contents at 14% and 10%, respectively, for the diesel reformate were higher than expected.



Current density, (A/cm⁻²)

FIGURE 4. Polarization curves for a SAFC stack running on diesel fuel reformate (pink lines) compared to pure hydrogen (blue lines).

Overall, our evaluation of the SAFC stack on reformed fuels yielded positive results. These results suggest that byproducts, such as CO, CO_2 , CH_4 , and H_2S , from reformed fuels such as methanol, LPG, and diesel had minimal adverse effect on the SAFC stack performance with hydrogen dilution being the dominant mechanism for reduction in power output.

In order to demonstrate the commercial viability of the SAFC, we also need to increase the MEA surface area to a size that will allow us to achieve the targeted specific power and power density shown in Table 1. For this project, this equates to fabricating an MEA with surface area greater than 100 cm^2 to establish a platform for the 300 W stack. In the past year, we demonstrated the ability to fabricate a functional 125 cm² SAFC MEA using existing equipments. However, at approximately 47 mW/cm², the power density of these MEAs is not as high as the 20 cm² MEA version but we expect to be able to markedly improve the performance with better equipment and optimized electrolyte.

Complementary to the 125 cm² MEA fabrication, we also designed and modeled the 300 W stack. Using a conservative value of 120 mW/cm² for the cell power density, we expect to operate 20 125 cm² cells at a cell operating voltage of 0.7 V. The stack weight and volume are 10 kg and 2.8 liter, respectively. The exaggerated weight of the stack is due to the fact that we used machined stack components. We expect the stack weight will reduce greatly as we transfer to high-volume manufacturing processes.

In terms of modeling, we simulated the gas flow and pressure distribution for the individual bipolar plate flow field and a simplified model of a 20-cell 300 W SAFC stack. For the bipolar plate, we used FloWorks, finite element analysis plug-in module for Solidworks. In a fuel cell stack, the bipolar plate functions as the support for the MEA, fuel and oxidant supplier, and conductivity medium. The modeled 7075 aluminum bipolar plate, with a thickness of 0.125 inch (0.3 cm), consisted of fuel cell flow field, heat exchange flow field, and manifold. The flow field diameter is 5 inches (12.7 cm) with an area of 19.625 in² (126.6 cm²). The flow pattern of the bipolar plate would affect the flow distribution and fuel mass transport; thus, a good flow field design should have uniform flow distribution at high velocity with low pressure drop. The boundary condition for the bipolar plate simulation is as follows:

- Temperature of humidified air: 20°C was used to study bipolar plate flow field.
- Inlet volume flow: 100 sccm per minute.
- Outlet static pressure: 101,325 Pascal.

Our computational modeling results of the fuel flow field gas flow and pressure distribution suggest that our bipolar plate design should allow for good uniformity of gas flow at high flow velocity throughout the MEA. The pressure drop from the inlet to the outlet is relatively small (<0.2%).

We also modeled the gas flow velocity and pressure distribution in a stack configuration using a commercially available computational fluid dynamics software package called *CFdesign*. The purpose of this simulation was to determine cell-to-cell gas flow uniformity. In our model, the SAFC stack consists of the gas manifolds, two end plates and twenty 125 cm² bipolar plates. The primary function of the manifold is to supply gas for flow field of each fuel cell, which in a stack, plays a very important role in controlling gas flow uniformity. Factors such as area, shape and length of manifold would affect the pressure drop and cell-to-cell flow distribution. Generally, the smaller pressure drop in manifold and bigger pressure drop in flow field would provide a more uniform flow distribution of cell-to-cell. Non-uniform cell-to-cell flow distribution may lead to fuel starvation which would affect stack performance and durability. In the stack model, the flow field consists of four channels, each with a channel depth of 0.035 inch and a width of 0.0425 inch. Owing to computation limits, we had to simplify the flow field and replaced the serpentine channels with shorter straight channels with the same cross section. The channel length varies between 5.5 to 6 inches. The inlet flow to each cell was set at 200 SCCM.

From the stack simulation, we can conclude that the pressure drop is greatest in the gas tube leading into the manifold. Within the manifold, the pressure profile is relatively flat for both the inlet and outlet manifold. Since the pressure profile is flat both at the inlet and outlet manifold, we can also conclude that the pressure drop between inlet and outlet is the same for all cells. This behavior should lead to good uniformity of gas distribution throughout the stack. It is important to note that we expect, in an actual stack with longer flow field channels, the bigger pressure drop due to the longer channel would lead to more uniform flow distribution. In other words, the flow distribution should be better in an actual stack than that of our model. For comparison, we simulated a case with a much higher flow rate at 10 liters per minute. The higher flow rate provide a larger pressure drop from the inlet to the outlet manifold across the flow field channels. As predicted, the cell-tocell velocity distribution is more uniform with high flow rate as compared to low flow rate.

Conclusions and Future Directions

Superprotonic's SAFCs constitute a transformative technology for cost-effective mass adoption of the fuel cell. SAFC MEAs, with a solid-state proton conducting electrolyte layer, operate at an intermediate temperature of approximately 250°C, and are impermeable to gases. These electro-physical properties afford SAFCs a clear advantage over existing fuel cell technologies in term of cost, durability, fuel flexibility, thermal cycling, and simplified system design. In the past year, Superprotonic has completed the following:

- Demonstrated stable stack operation on synthetic reformate with >10% CO, 100 ppm H_2S , and 100 ppm NH_3 .
- Demonstrated stable stack operation on methanol and LPG using a steam reformer.
- Demonstrated stable SAFC stack operation on diesel using an auto-thermal reformer.
- Scaled-up the MEA surface area from 20 cm² to 125 cm^2 .
- Completed the design and modeling of a 300 W SAFC stack.

For the remainder of the project, Superprotonic will continue to optimize the MEA performance to levels of commercial viability, demonstrate the functionality of a SAFC stack at in the 300 W range, and complete a conceptual design of a 3 kW SAFC power plant running on diesel fuel.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting – Washington, DC – May 2009; Presentation FC_45: "Solid Acid Fuel Cell Stack for APU Applications", Presented by Hau H. Duong, Superprotonic, Inc.

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