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# DEVELOPMENT OF ACCELERATED DURABILITY PROTOCOLS FOR SOLID OXIDE FUEL CELL SYSTEMS

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## ABSTRACT

*Solid oxide fuel cell (SOFC)-based auxiliary power units (APUs) offer a quiet and efficient platform for remote power generation. SOFC systems often utilize a reformer subsystem which converts hydrocarbon fuels into a hydrogen-rich effluent stream utilized by the fuel cell stack for electrical power generation. Rochester Institute of Technology's Center for Sustainable Mobility (RIT / CSM) has conducted research to analyze potential system failures and develop accelerated durability protocols for SOFC systems. Based on this experimental and analytical study, it has been shown that solid carbon formed during fuel reformation is quantifiable, predictable, and affects SOFC system durability.*

*RIT / CSM further developed accelerated durability protocols for SOFC carbon related failure modes, utilizing carbon concentration measurements from SOFC systems combined with post-processing of system operational parameters. Fully integrated SOFC systems were employed to generate a concentration of carbon over various usage profiles, with carbon measured using a real-time photo-acoustic instrument. Additional system parameters, including temperature, pressure, reformer effluent composition, and reactant mass flows were also measured on full SOFC systems to determine the total carbon mass in the effluent stream. This research has demonstrated that application of accelerated thermal cycles significantly accelerates the mass of carbon formed during reformate production relative to nominal SOFC operating conditions.*

## INTRODUCTION

Consideration for sustainable energy conversion and utilization dictate the need for greater efficiency of commercial and military power generation equipment. Energy cost, logistic demands, environmental impact, and mission capability promote the use of advanced fuel cell technologies in theatre as well as in commercial applications. Many of these technologies look increasingly promising as their readiness level matures with each new generation of hardware and control software.

In the military arena, broad agency announcements seek methods to provide power to support engine-off mission scenarios [1]. Integration of fuel cell technology on the Abrams, Bradley or similar vehicle platform allows for greater length reconnaissance missions with lower acoustic and thermal signatures. Other potential military power applications for fuel cell systems include: base power, water purification, communications terminals, battery charging, personal equipment, unmanned vehicles, and sensors.

There are many fuel cell technologies competing for implementation throughout the power level range required for today's high tech military. Leading technologies include proton exchange membrane, direct methanol, and solid oxide, among others. Focusing on auxiliary power units for vehicle power, solid oxide fuel cell (SOFC) systems have several benefits over other technology types.

Using onboard reforming technology, SOFCs can use various military logistics fuel blends to continuously power electronics, thus providing an overall platform efficiency gain. SOFCs do not require ultra-pure hydrogen gas to preserve the cell stacks' longevity and therefore an additional high pressure tank of gaseous fuel or advanced filtration system is not required as with other fuel cell technologies. Conversion of chemical energy to electrical energy without the direct use of combustion provides greater efficiency than most internal combustion engines as well as nearly "silent" operation [2]. SOFC generated power for auxiliary systems utilized during silent watch can increase efficiencies several times over an internal combustion engine at idle [3].

One area of improvement for SOFC systems is control and mitigation of carbon formed during the reformation process as noted by McIntosh and Gorte [4]. There is a variety of potential failure modes associated with carbon deposition within system components. To better understand carbon generation within an SOFC system, experiments were performed to identify the operating states responsible for generating the majority of carbon in the reformate stream. Real-time measurements of carbon concentration were recorded through SOFC thermal cycles and the results are presented below.

## APPROACH

The first step, as shown in Figure 1, was to obtain technical information of the SOFC system selected for testing. Once data were gathered, and hardware and control algorithms reviewed, a reliability centered maintenance (RCM) analysis was conducted on the fuel reformer subsystem. This subsystem was chosen due to the research focus on carbon generation and the function of the reformer being to crack the complex hydrocarbon fuel molecules into hydrogen and carbon monoxide for use in the SOFC stack. During the catalytic reformation of diesel fuel, there is a possibility to generate excess carbon content at various operating conditions. The sub-system tested included the reformer catalyst, combustor, mixer, vaporizers, and thermal enclosure. The objective of this RCM process was to identify key failure modes associated with the components, potential diagnostic features, and opportunities for additional sensors relevant to the investigation of carbon in the system.

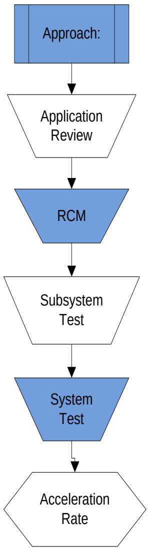

**Figure 1:** Project process approach

Based on the results of the RCM analysis two additional high value laboratory instruments were utilized: a scanning mass spectrometer and a photo-acoustic soot meter (Figure 2). These laboratory instruments enabled in-situ reformer effluent characterization.

**Figure 2:** Laboratory analysis equipment

To store and process the multitude of system sensor signals recorded during extended durability cycling, a SQL server database was setup using RIT/CSM processes for diagnostic and prognostic asset health management. Data were input to the database using proprietary consolidation and population software. Viewing and processing of the data post-test required in-house developed Java™ and Matlab® based visualization tools to interrogate and compare data acquired in different runs, and on different systems.

Based on earlier reformer subsystem research at RIT/CSM on the relationship among oxygen/carbon ratio (O/C), system thermal profiles and the resulting carbon generated during fuel reformation, accelerated durability test protocols were developed for the full SOFC system. In these subsystem experiments the soot meter had been applied to correlate carbon to reformer temperature (Figure 3). The experiment consisted of a single catalyst tube heated within an electrically controlled furnace. Vaporized diesel and water were added to a stream of blended synthetic anode recycle gas before entering the heated catalyst. A mass spectrometer and soot meter were utilized to sample the effluent downstream, with results recorded relative to furnace temperature set point.

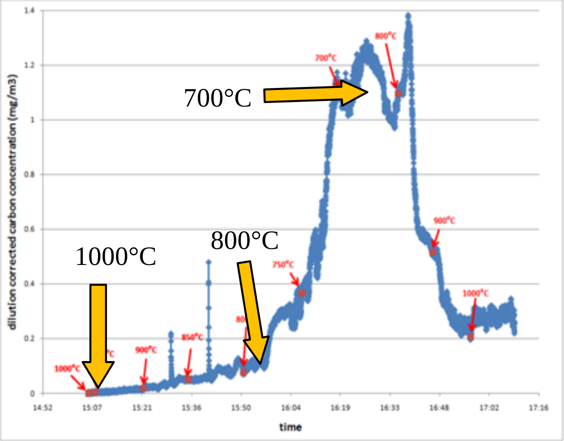

**Figure 3:** Carbon concentration (mg/m3) downstream of a reformer at varying furnace temperatures

Thermal profiles for the full SOFC system test results presented herein were based on a standard thermal ramp rate to prevent extraneous failures. The ratio of the cumulative mass of carbon in the warm-up state with respect to the cumulative mass of carbon in the system electrical state was used to quantify the acceleration rate of the test.

## EXPERIMENT

The SOFC system was started cold using a battery, power supply, and certified ultra low sulfur diesel (ULSD) fuel. The system sequenced through five different operating states for a single thermal cycle. The first system state was initiated by heating the diesel fuel and then igniting it to warm the system in order to prevent undesired side reactions. Operation continued with the creation of reformate until the stack was heated to its nominal operating temperature. Once the desired stack temperature was reached, the system was enabled to provide electrical power to the internal and external loads. During shutdown, the system load was disconnected with the fuel and air continually reduced until the stack no longer actively transported oxygen ions.

The accelerated test profile is shown by the dashed line in Figure 4, accelerating the frequency of warm-up and cool-down states while truncating the electrical load state. This accelerated profile allowed for five complete thermal cycles in the course of one work week. The non-accelerated test profile was defined assuming the system was heated up and remained hot for an entire week, as is expected to be typical for future mobile SOFC applications, shown by the solid line in Figure 4.

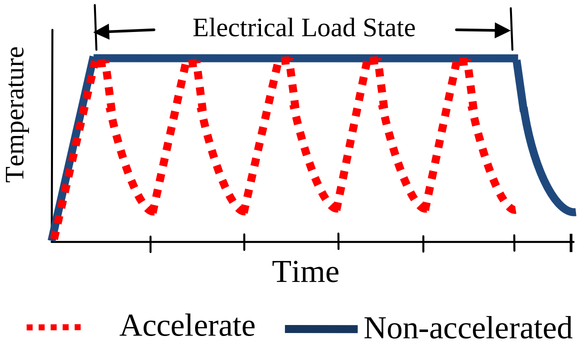

**Figure 4:** Accelerated and non-accelerated temperature test profiles

Soot meter samples were extracted from the system downstream of the reformer, before the effluent entered the desulfurizer bed. This location in the system had produced the highest measurements of carbon concentration during earlier tests. Figure 5 shows the sample locations of the mass spectrometer and soot meter in relation to the reformer, heat exchanger, and desulfulrizer.

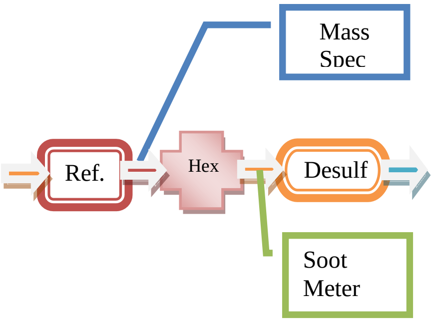

**Figure 5**: Simplified flow schematic and sampling points

The SOFC system operation was primarily automated with minimal, if any, operator intervention. Electrical power from the fuel cell stacks was drawn for approximately 20 minutes during each accelerated test profile. This test sequence allowed the system to cool to 50°C before the start of testing the next morning. Electrical loading of the system was performed using a load bank and stepped from idle to rated power in the test data shown herein.

## CALCULATION

Carbon formation internal to the reformer can contaminate the catalyst active area, thereby decreasing the reformer efficiency. Likewise, carbon buildup within the stacks can interrupt flow balancing to the cells and weaken the electrolyte. To determine the approximate acceleration factor for catalyst/stack degradation resulting from thermal cycle tests on the SOFC system, the mass of carbon in the effluent stream was determined for warm-up, electrical load, and cool-down states. To determine the acceleration factor, two primary calculation steps were required. The first step was to calculate the total mass of carbon measured in each of the individual system states; see Equation (1). The second step was to calculate the acceleration rate using the total mass of carbon produced during the accelerated and the non-accelerated test profiles, as defined by Equation (2).

$$M_{carbon} = \frac{m * F_{std} * F_{density} * [C_{carbon} + c_{offset}] * S}{\rho_{effluent}} \tag{1}$$

where: $M_{carbon}$ = *Mass of carbon per sample period*, *m* = *Effluent mass flow rate*, $\rho_{density}$ = *Effluent density*, $F_{std}$ = *Standard state conversion factor*, $F_{density}$ = *Density conversion factor*, $C_{carbon}$ = *Carbon concentration from the soot meter*, $c_{offset}$ = *zero signal offset, and S = Sample period*

The formula used for the acceleration rate calculation was:

$$Acceleration\ Rate = \frac{(M_{acc})}{(M_{non})} \tag{2}$$

where: $M_{acc}$ = *cumulative mass of carbon measured during an accelerated test*, $M_{non}$ = *theoretical cumulative mass of carbon measurable during a non-accelerated test profile.*

The assumptions used to calculate the carbon acceleration rate were:

- The carbon measured in the reformer effluent stream is proportional to the carbon formed in the system (i.e., no upstream carbon deposition).
- The soot meter signal offset is zero mg/m$^3$, implying that only measurements above this value signify significant levels of carbon.

## RESULTS AND DISCUSSION

Figure 6 illustrates the concentration of carbon measured throughout an accelerated system test. A potential cause of increased carbon generation during the warm-up state, before reformer fuel is injected, is separation of carbon from the catalyst side of the reformer deposited during the previous test cycle. As the outlet of the reformer heated beyond 600°C before fueling, the soot meter detected carbon in the effluent stream. Simultaneously the $CO_2$ and $H_2O$ concentrations increased by two orders of magnitude. Previous thermal gravimetric analyses performed by RIT/CSM showed a rapid increase in carbon oxidation from 500 to 600°C. Boldyreva *et al.* [5] also showed $CO_2$ formation from carbon oxidation being predominant above 550°C. This indicates that carbon and hydrocarbons may separate from the reformer catalyst with some of the deposits oxidizing to form water and carbon dioxide. In the warm-up state, the thermal energy in the reformer may not yet be sufficient to completely reform the diesel fuel [6] and therefore generates increased levels of carbon.

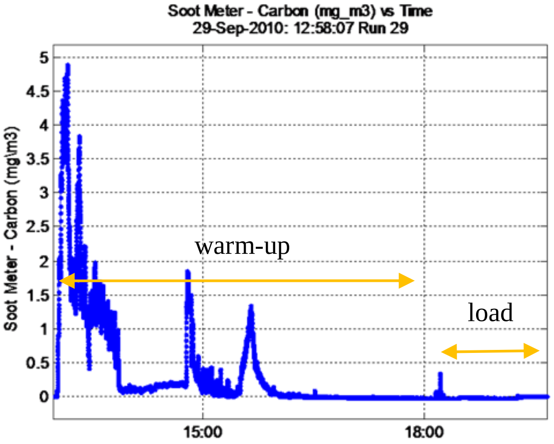

**Figure 6:** Concentration of carbon (mg/m$^3$) for system operating states vs. time (hr:min)

Using the database and Matlab® routines, the mass of carbon was calculated from the system parameters and plotted in Figure 7 over the course of system operation. Reformer operating conditions which produce substantial carbon deposits and known carbon precursors such as ethylene and methane [7, 8] were confirmed by the simultaneous measurements of effluent composition and carbon concentration.

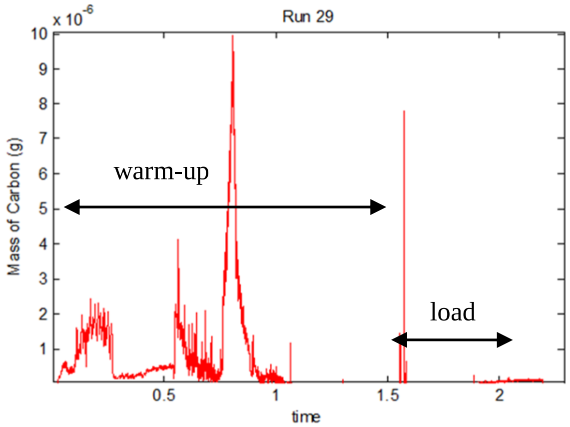

**Figure 7:** Calculated mass of carbon for system operating states vs. time ($10^4$ sec)

Further investigation and sample acquisition will be investigated in future RIT/CSM work. The mass of carbon produced for 5 days of thermal cycles and the mass of carbon produced for a theoretically normal week of non-accelerated testing is provided in Table 1. The ratio of these masses yields the proposed acceleration rate for downstream carbon deposition of 2.7. A mean time to failure analysis was also performed to verify the acceleration rate but is beyond the scope of this paper.

| | |
|---|---|
| Mass of carbon produced: Total Accelerated (grams) | 5 x 0.010 |
| Mass of carbon produced: Non-accelerated (grams) | 0.019 |
| Acceleration Rate: | 2.7 |

**Table 1:** Carbon acceleration rate

## CONCLUSIONS

The use of thermal cycles to accelerate carbon related failure modes has been demonstrated to decrease the operating lifetime of SOFC systems. Using real-time carbon measurement equipment to quantify an acceleration factor, it is estimated that carbon failure modes will occur approximately 2.7 times sooner when operating under accelerated thermal profiles as compared to a "nominal" SOFC operating condition. These results include system warm-up, electrical load, and cool-down sequences. The acceleration factor is based on calculated mass flows of carbon for US07 ultra low sulfur diesel fuel.

Further acceleration may be achieved through modification of the air- or water-to-fuel ratios, but could artificially decrease the life of the system. Likewise, increasing the thermal ramp rate may result in anode-to-cathode cross-over leaks, thus unrealistically shortening the life of the SOFC stacks. Additional durability acceleration may be achieved by controlling the system operating conditions during test to maximize carbon generation at the start of warm-up and applying the thermal cycling profile at this condition.

## ACKNOWLEDGMENT

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