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## Reformate Fuel Cell System Durability

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### Introduction

The goal of this research is to identify the factors limiting the durability of fuel cells and fuel processors. This includes identifying PEM fuel cell durability issues for operating on pure hydrogen, and those that arise from the fuel processing of liquid hydrocarbons (e.g., gasoline) as a function of fuel composition and impurity content. Benchmark comparisons with the durability of fuel cells operating on pure hydrogen are used to identify limiting factors unique to fuel processing. We describe the design, operation and operational results of the durability system, including the operating conditions for the system, fuel processor sub-section operation over 1000 hours, post-mortem characterization of the catalysts in the fuel processor, and single cell operation.

### Approach: Durability Gasoline Reformate Production and Single Cell Fuel Cells

Our approach to identify the limiting factors on fuel cell system durability is, first, to develop and operate a modular fuel processor system to examine the fuel composition and impurity effects on fuel processor durability and to generate reformate for testing the durability of fuel cell components. Second, we examine the effects of the reformate on the fuel cell components, primarily the membrane electrode assembly (MEA), by testing MEA's in single-cell fuel cells operating on both reformate and pure hydrogen. Third, we use a combination of fuel processor gas analysis, fuel processor catalyst characterization, and MEA characterization during and after operation to quantify performance losses and to identify limiting factors on durability such as poisons. The modular fuel processor subsystem, shown in Figure 1, was designed and constructed to simulate conventional methods of hydrogen generation for PEM fuel cell stacks. The fuel processor consists of a sequence of reactors, a Partial Oxidation/Steam Reformer (POx/SR) or Autothermal Reformer (ATR), Sulfur removal, High-Temperature Shift (HTS), Low-Temperature Shift (LTS), and Preferential Oxidation Reactor (PrOx). Typical commercial



Figure 1. Fuel processor system showing the stages for Partial Oxidation (POx)/Steam reforming, High Temperature Shift (HTS), Low Temperature Shift (LTS) and Preferential Oxidation (PrOx).



and semi-commercial noble metal oxidation catalysts, and noble metal or non-noble metal steam reforming catalysts are used in the ATR. Conventional commercial catalysts also are used in the HTS, LTS, and PrOx to allow full characterization of the catalysts without violating proprietary concerns. The ATR atomic O/C (oxygen/carbon - O from air only) is 0.8 to 0.85, while typical S/C (steam/carbon) is from 1.0 to 1.25. Additional downstream liquid water injection increases the overall S/C ratio to a typical S/C of 2.5 to 3.0. A slipstream of the reformat flow from the fuel processor is routed to the fuel cell test station.

The fuel cell test station can operate 3 single-cell fuel cells with either pure hydrogen or with the gasoline reformat. The direct comparison of pure hydrogen and reformat feeds to the single cells is used to identify the effects that fuel processing reformat has on the fuel cell durability. Currently, 50 cm<sup>2</sup> single cell components are being tested. Performance during the durability test is measured with continual monitoring of the voltage/current performance along with periodic polarization curve, AC Impedance, and Hydrogen Adsorption/Desorption (HAD) measurements to monitor the anode catalyst surface area. Following the durability testing, MEA's will be characterized to evaluate degradation mechanisms.

### Results: Fuel Processor Operation

The fuel processor sub-section was operated with pure iso-octane to verify its performance. Figure 2 shows 800 hours of the fuel processor operation on iso-octane, showing the temperatures in the different stages, and the CO outlet concentration. The temperature in the partial oxidation stage temperature is about 800 – 825 °C and the outlet of the steam reforming section is 775 °C. The average residence time for the ATR section is about 0.5 seconds, which is typically sufficient for complete hydrocarbon conversion.

The HTS temperature is operated at 400 °C, the LTS at 250 °C, the PrOx is controlled to a temperature of 125 °C. The outlet CO concentration from the ATR was typically about 10%, the outlet LTS CO concentration was < 1%, and the outlet CO concentration of the PrOx varied initially from 0 to 150 ppm, with improved controls keeping the CO concentration below 100 ppm and typically below 40 ppm.

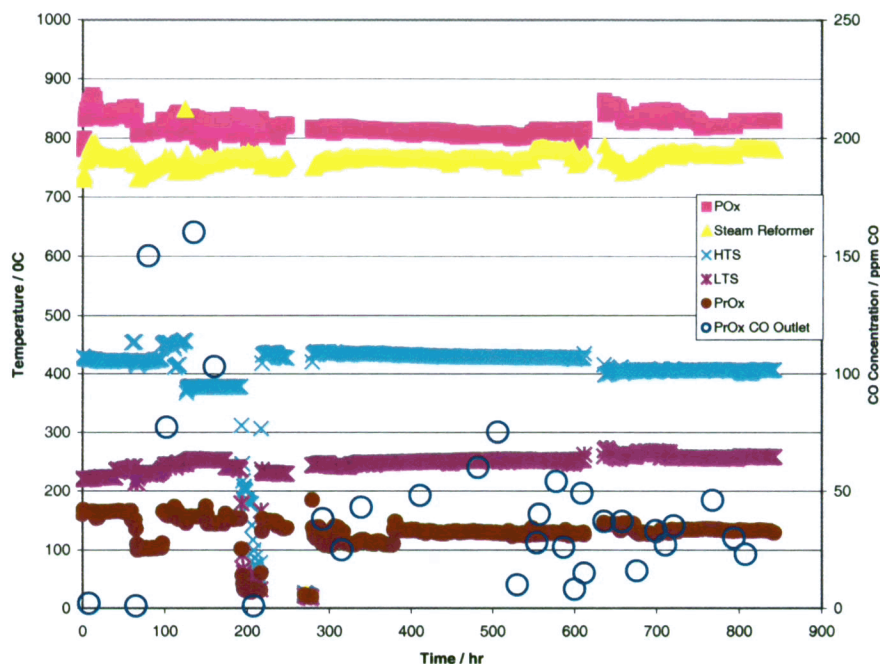


Figure 2. Temperature and PrOx Outlet CO concentration of fuel processor system during ~ 800 hrs operation.

Figure 3 shows operation of the fuel processor sub-section on iso-octane for 11 days, after which the fuel was switched to a simulated gasoline of 74% iso-octane, 20% xylene, 5 % methylcyclohexane and 1% 1-pentene. After only two days of operation on this simulated gasoline, the pressure drop between the ATR and HTS increased due to carbon formation. Post characterization of the carbon formed showed that a high concentration of solidified hydrocarbons were present in the carbon (30% by weight). To prevent carbon formation

between these reactor sections, the HTS water injection was moved from the inlet to the outlet of the steam reformer section.

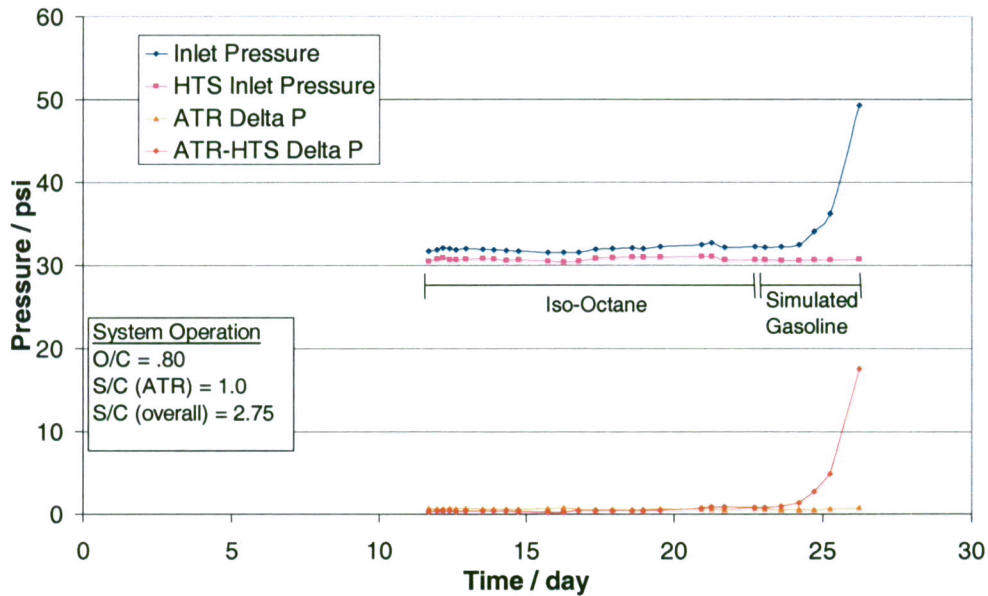


Figure 3. Operation of fuel processor with iso-octane / simulate fuel. Inlet pressures and pressure drops are shown demonstrating the buildup of carbon in between the ATR and HTS.

After extended operation, the catalysts present in the fuel processor were characterized to observe any potential degradation of the catalysts. The relative catalyst surface areas of the ATR, HTS, LTS and PrOx catalysts all show decreases after extended operation. The initial portion of the ATR catalyst, where the fuel oxidation occurs shows a large decrease in surface area, over an order of magnitude decrease from about  $3 \text{ m}^2/\text{g}$  to  $< 0.2 \text{ m}^2/\text{g}$  (note that the surface area is low because the support material is included in the measurement). Other portions of the ATR catalyst did not show as big a decrease in surface area. The LTS catalyst surface area decreases about 50 % which appears to be independent of the catalyst location in the LTS section. The measured PrOx catalyst surface area shown in Figure 4, decreased as a function of the axial location in the reactor catalyst volume. The measured PrOx catalyst surface area shows a high decrease in the upstream section, while in downstream sections of the PrOx, approximately 75% of the original surface area is maintained.

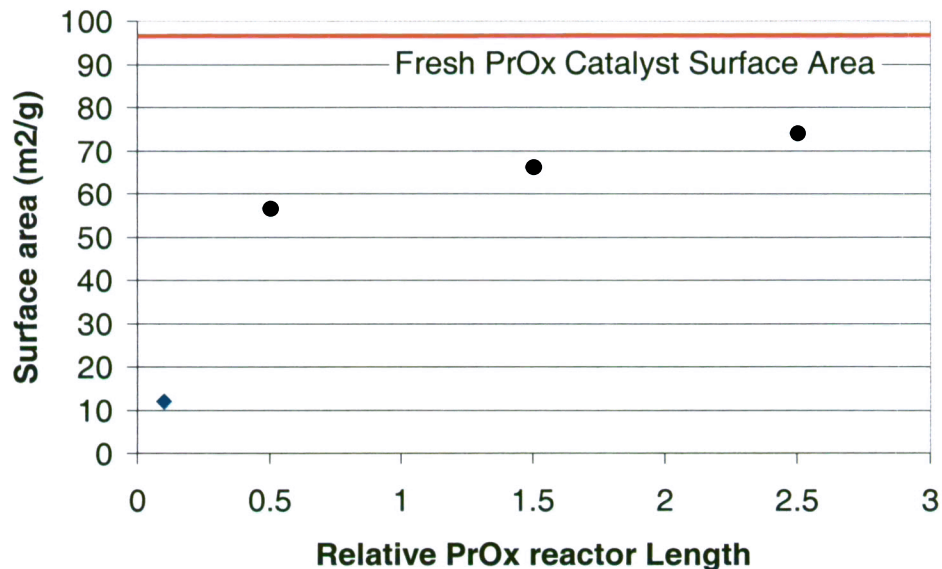


Figure 4. PrOx Catalyst surface area after ~ 1000 hrs of operation.

## Results: Single Cell Operation

Figure 5 shows a single cell with N112 MEAs operating on pure hydrogen, and on reformat produced from the fuel processor. The steady state performance of the MEA on pure hydrogen was about  $0.9 \text{ A/cm}^2$  at  $0.62 \text{ V}$ . At hour 48, the pure hydrogen feed was switched to the gasoline reformat. Even though the CO content of the fuel processor was below 50 ppm, and air injection was used for the anode of the fuel cell, the performance of the fuel cell was poor, as shown by the rapidly dropping current density of the MEA. As the reformat was switched back to pure hydrogen, the performance recovered quickly, within a few minutes.

Analysis of the fuel processor condensate showed that hydrocarbons were present. The hydrocarbons found in the condensate include hydrocarbons with molecular weights higher than those present in the original fuel, over MW (molecular weight) of 150. This potentially means that some polyaromatic hydrocarbons are formed. Changes to the catalyst used in the fuel processor ATR section have been made to reduce the hydrocarbon output of the fuel processor section to improve performance of the fuel cells.

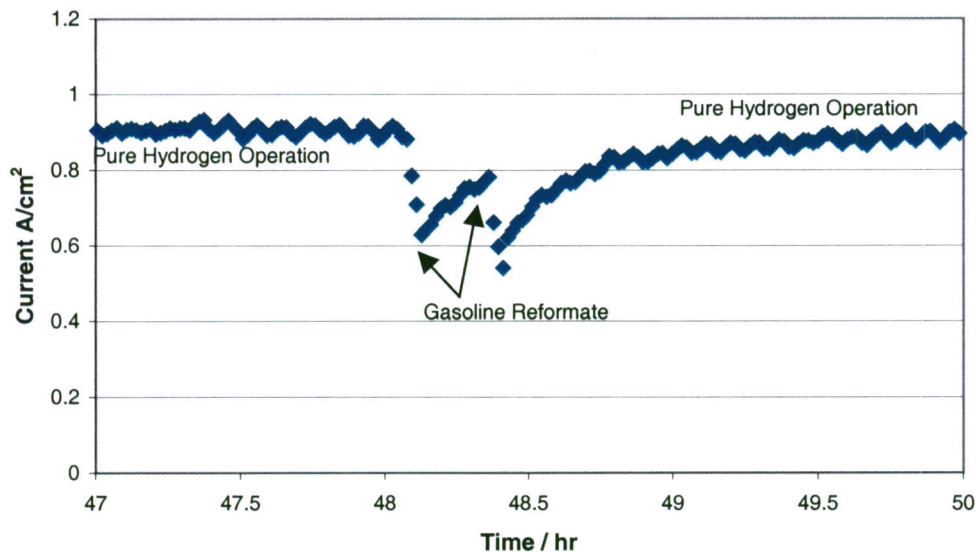


Figure 5: Single Cell operation on H<sub>2</sub>, followed by operation on gasoline reformat.

## Conclusions

Fuel processor operation producing hydrogen with low carbon monoxide content has been demonstrated for over 1000 operational hours. The catalyst surface decreased in all the stages of the fuel processor with the amount of decrease depending on the catalyst and its axial location in the catalyst volume. Although the carbon monoxide concentration in the outlet of the fuel processor is low, the performance of the single cells is poor, apparently due to small amounts of hydrocarbons present in the reformat stream. Carbon formation over relatively long periods of time was also an issue between the ATR and HTS stage when fuels containing aromatics were used.

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