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Emissions Sensors for High Temperature Fuel Cell Applications

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***Abstract*—High temperature fuel cells such as solid oxide fuel cells offer a high efficiency, fuel flexible, low emission strategy for distributed generation. In order to validate emissions performance of pollutants such as NOx and CO, analyzers that provide accurate measurements of low single digit values of these species are needed. Analyzer requirements are described along with respresentative results for low emission practical devices. The results demonstrate reliable analyzer performance and confirm low emission levels.**

I. INTRODUCTION

High temperature fuel cells such as solid oxide (SOFC) offer some significant advantages compared to fossil fueled heat engines in terms of system efficiency and pollutant emissions. In particular, the ability to internally reform legacy fuels makes these SOFC systems flexible for use with arbitrary fuels. Furthermore, the pollutant emissions levels from these systems are "negligible." In regions where air quality is poor, very aggressive regulation has resulted in a need for power generation technologies that produce low single digit levels of pollutants such as oxides of nitrogen (NOx). Because of the levels required by these regulations, even the inherently low emission of pollutants from technologies like the SOFC must be quantified and compared to the regulation limits. require confirmation. Because of the inherently low emissions levels and the high moisture content of the exhaust stream, the accurate monitoring and determination of emissions performance requires careful consideration in terms of gas sensors. In response to this, emissions analyzer systems directed specifically at the challenges presented by fuel cell systems have been developed. In the present study, the approach to overcoming the challenges presented by the SOFC fuel cell exhaust emissions is described and example results are shown from a 25kW system operating on natural gas.

In this paper, the requirements for an analyzer that is used to monitor exhaust gas concentrations are outlined based on the operational characteristics of a prototype SOFC system. Of particular interest are the emissions of oxides of nitrogen and carbon monoxide. The details of the analyzers assembled to evaluate the emissions are then described. The performance of the analyzers are evaluated and examples of results for the prototype SOFC are presented.

II. ANALYZER REQUIREMENTS

A. *Fuel Cell Operation*

Siemens Westinghouse 25 kW Tubular Solid Oxide Fuel Cell is the first SOFC pre-commercial prototype and research platform. The SOFC is a tubular design configured as a single cell per tube. The system includes 576 tubular cells, with 3 in parallel and 192 in sires [1, 2]. In the system, fuel cells sit vertically with the holes upwards. As shown in Figure 1, air is fed into inside (cathode) of the tubular cells, and fuel from reformer flows through the outer surface (anode) of the tubes. Oxygen ion is generated at cathode side and migrates though electrolyte to anode side. At anode side, the oxygen ion reacts with fuel and electron is produced. The electron travels through an external circuit to cathode side and reacts with oxygen to complete the cycle. Products from fuel cell stack with a temperature about 700°C are used to preheated air in the recuperator (not showed in the picture), and the exhaust temperature is about 140°C (based on natural gas fuel). More details about system configuration can be seen in references [1, 3]

Exhaust gases from natural gas based SOFC systems mainly contain N_2, O_2, H_2O and CO_2 with trace amounts of CO, hydrocarbons, NO_x and SO_x based on the former observation [1, 4]. Typical exhaust concentrations at full load are summarized in Table 1. Major components were predicted from former simulation work [3], which is consistent with the observed data. The information about trace gases is provided by Siemens Westinghouse [4]. When system starts up, shuts down or operates at part-load, the exhaust concentrations may change based on the former observation [1].

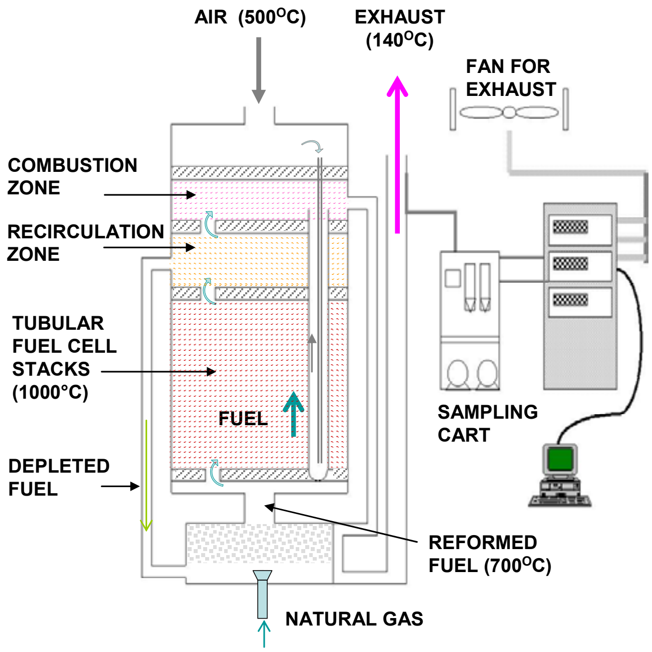

Figure 1. SOFC Gas Path Schematic

Table 1. Typical SOFC Exhaust Composition

Component	**Composition (vol. %)**	
	Inlet PNG, [3]	Exhaust at full load, [3, 4]
CO_2	1.4	2
N_2	0.39	77
O_2		17
H_2O		4
CO		Not measurable
CH_4	96.36	
C_2H_6	1.45	
NOx		< 0.5 ppm
SOx		Not measurable
VOCs		Not measurable
Others	0.4	

B. Species of Interest

Sensors to monitor the performance of SOFCs should address species indicated in Table 1. A principal advantage of high temperature fuel cells is that, unlike low temperature units (e.g., PEM) they can internally reform a wide variety of fuels, including both gaseous and liquid fuels. As a result, their emissions performance vs other devices such as microturbines and reciprocating engines is of interest.

As a result, monitoring "typical" products of combustion such as oxides of nitrogen, carbon monoxide, and unburned hydrocarbons are of particular interest. However, as mentioned concentrations of these species may often be on the ppb levels. Futhermore, the presence of water makes sample treatment a particularly challenging issue since many species of interest (e.g., NO_2) are water soluable and may be "lost" in any process that drops out water.

III. Analyzer Approach

To address the special requirements associated with the monitoring of the fuel cell exhaust species, a package of individual analyzers and sample conditioning is required. Such a pacakge is illustrated in Figure 2. The console consists of three different analyzers: a HORIBA Ltd. Type CMA-647 typically for industrial use to monitor O_2, CO_2, and CO, a HORIBA Ltd. Type APNA-360 typically for ambient air measurement of NO_x, and a HORIBA Ltd. Type APHA-360, also typically for ambient air measurement of total hydrocarbons (THC) and methane (CH4).

Figure 2. AP-360 Fuel Cell Emissions Analyzer

The package illustrated in Figure 2 does not measure hydrogen which a species of particular interest for fuel cell applications. For this specie, a mass spectrometer (HORIBA Ltd. Model MSHA-1000) system is used to continuously measure hydrogen concentrations in the sample gas. This instrument contains a magnetic sector type mass filter, ion source, detector, electronics, and power supply. The analyzer is specifically designed to measure high concentrations of hydrogen up to 100%.

A. NOx

Oxides of nitrogen are a species of primary interest due their role in the degradation of urban air quality and, as a result, their substantial regulation. Fuel cells represent a next generation of technology that can achieve the ultralow NOx emissions needed to provide sustainable power generation for to meet future energy requirements.

The NOx analyzer utilizes a cross-flow chemiluminescence method (EPA Reference Method RFNA-0196-111) to measure NOx [5]. By reacting NO in the exhaust with ozone, some of the NO oxidizes to NO_2* (NO_2

in an electronically excited state). When this excited species returns to the groud state, it radiates light (chemiluminescence) which is proportional to the concentration. The AP-360 is designed for low range detection of NOx—as low as 0.0005 ppm. In the current study, ranges of 0 to 0.4, 0 to 1, 0 to 4, and 0 to 10 ppm were available. The detection scheme used features optical filtering and coatings to minimize interference from water and hydrocarbon species.

B. CO/CO2

The CO and CO_2 measurements are made with a non-dispersive infrared (NDIR) detector [5]. In the NDIR detector, the gas being sampled and an air sample as a base line are alternately introduced to the detector at a constant frequency. The air gas is supplied from atmospheric air that is sent through a catalyst. The output signal is modulated based upon the frequency of the distribution of the gases. The concentration of the component being measured is a function of the amplitude of the output signal.

C. UHC

The methane (CH_4) and THC measurements were made with a flame ionization detector (FID) [5]. The AP-360 uses a selective combustion method which utilizes differences in flame temperature between HC species to identify methane and non-methane hydrocarbons (NMHC) in a single package. Total hydrocarbons (THC) is the sum of the methane and NMHCs.

D. O_2

The O_2 measurements are made with a paramagnetic technique [5].

E. Sample Conditioning

The sample is conveyed to the analyzer through heated sample lines maintained above the dew point of the exhaust gas (~150 C) so that condensation does not occur. The sample stream then splits into two streams. One goes through a NOx converter to convert all N_2O and NO_2 to NO prior to water removal. The other stream goes into the water dropout and cooler directly via a heat exchanger. After the first water dropout, the two sample gas streams are introduced into the thermoelectric cooler (Peltier Cooler). This cooler decreases the temperature of the sample gas down to 20°C and reduces the water vapor pressure. The thermoelectric cooler system is much smaller than a conventional cooler with coolant and also allows continuous sampling over long testing periods due to its virtual maintenance-free operation. The stream of the treated sample gas after the sampling system makes the bypass flow as shown in Figure 34. Eventually the gas stream through the NO_x converter is drawn by the internal pump of the NOx analyzer and analyzed. The other gas stream is drawn by similar pumps to the CO, CO_2, O_2, and hydrocarbon analyzers and analyzed accordingly. Bypass flows of sample gases are included in the design of the system and in several of the individual analyzers to speed response times and increase measurement accuracy. These bypass flows are connected to the exhaust line (accepting the analyzed gas streams from each analyzer) with great care to not pressurize the exhaust. If the pressure in the exhaust line is not kept at one atmosphere, the sample gas pressure fluctuation prior to analyzers will produce extra error. Pictures of the sampling cart are shown in Figure 34.

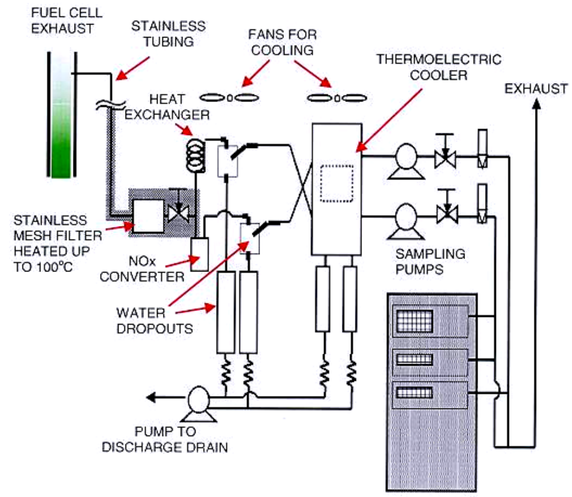

Figure 3. Sample Conditioning.

IV. RESULTS

A. Analyzer Performance

Of particular interest is the ability of any analyzer to provide reliable results of the very low emission levels. As a result, specific performance on NOx emissions is of particular interest. Tests were carried out using 4 different NOx analyzers which are suited for measurement of single digit NOx levels. Figure 4 prseents a summary of the % error of the reading when provide with a 10 ppm NOx sample. The results show that all the analyzers evaluated have less than 0.4% variation of the reading (nominally +/- 0.04 ppm for the gas sampled here).

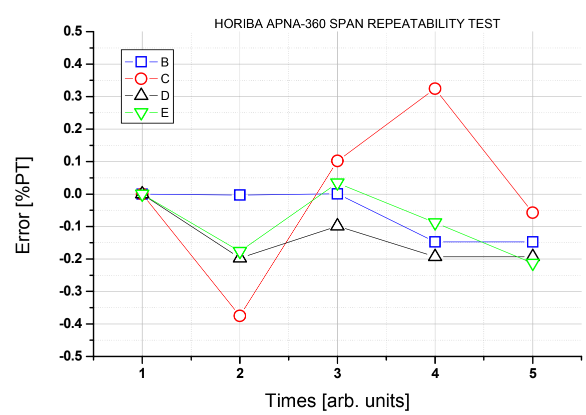

Figure 4. Repeatability on 10ppm NOx span gas.

The transient response is also of interest for the study of high temperature fuel cells in order to develop and confirm dynamic models under development [6, 7]. An example of analyzer response to step changes in emissions is shown in Figure 5 which indicates significant differences for the two analyzers shown.

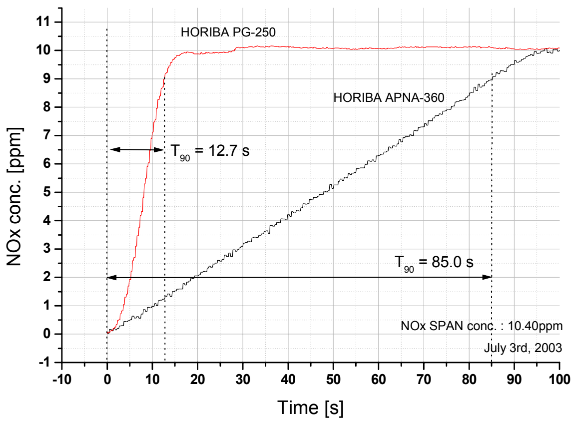

Figure 5. Transient Response of NOx.

B. Example Applications

Measurements were performed on the 25kW S-W SOFC using the APNA-360 during startup. These results are shown in Figure 6 and illustrate some signficant variation in NOx levels. However, it is noted that even at startup, the peak levels of NOx are generally below 1 ppm. At steady state, the levels drop to less than 0.5 ppm which is consistent with manufacturer specification (see Table 1).

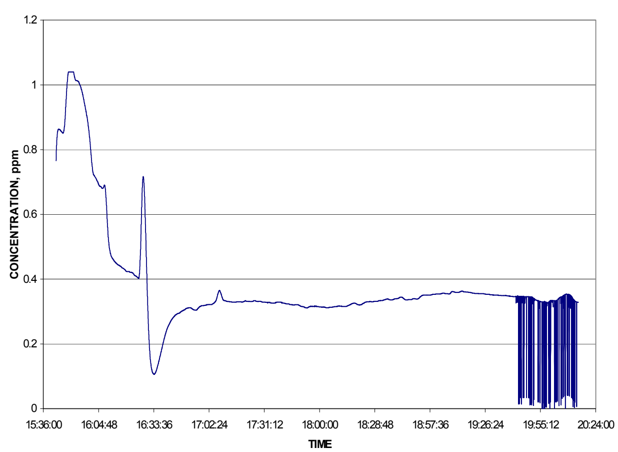

Figure 6. SOFC Startup NOx Emissions.

Results were also obtained for a low emissions microturbine generator (MTG) as shown in Figure 7 for various loads. In this study, the same two analyzers compared in Figure 5 were used in parallel. The results demonstrate the strong influence that load has on the MTG NOx emissions. The results also show that, at full load (60 kW), the NOx levels are below 1 ppm. Careful examination of Figure 7 shows that the APNA-360 exhibits a bit slower response compared to the PG-250.

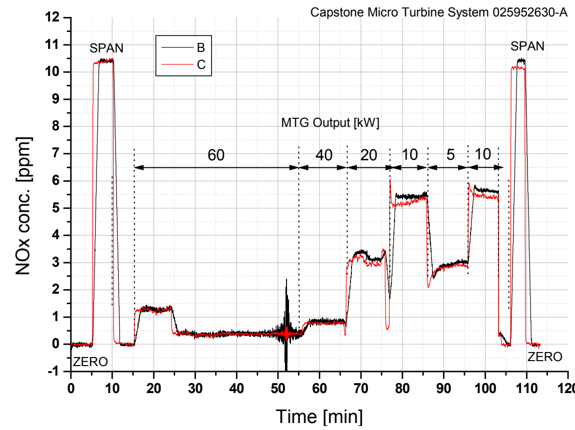

Figure 7. MTG Transient NOx Behavior.

V. Summary

Accurate measurements of low single digit NOx levels measured from high temperature fuel cells can be accomplished using careful sample conditioning and careful measurement methods. The results obtained confirm the ultra low emissions produced by an solid oxide fuel cell.

VI. Acknowledgements

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