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Measurement of Species Distributions in Operating Fuel Cells

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Abstract

Measurement and understanding of transient species distributions across and within fuel cells is a critical need for advancing fuel cell technology. The Spatially Resolved Capillary Inlet Mass Spectrometer (SpaciMS) instrument has been applied for in-situ measurement of transient species distributions within operating reactors; including diesel catalyst, air-exhaust mixing systems, and non-thermal plasma reactors. The work described here demonstrates the applicability of this tool to proton exchange membrane (PEM) and solid oxide fuel cells (SOFC) research. Specifically, we have demonstrated SpaciMS measurements of 1) transient species dynamics across a PEM fuel cell (FC) associated with load switching, 2) intra-PEM species distributions, and transient species dynamics at SOFC temperatures associated with FC load switching.

Introduction

Modeling efforts have suggested spatial non-uniformities in both species and temperature within operating fuel cells. Such distributions have significant impact on fuel cell performance including mechanical integrity, reactants and products management, and efficiency. However, little in-situ spatially resolved measurements are available to assess model predictions. In addition to spatial non-uniformities, temporal non-uniformities may exist as concentration and thermal waves within operating devices. ORNL's expertise in the development and application of minimally invasive diagnostics for species and temperature measurement are believed applicable to elucidate these phenomena. If this can be established and briefly demonstrated in a seed money project, the opportunities for Department of Energy (DOE) and industry sponsorship will be significant.

The Fuels, Engines, and Emissions Research Center (FEERC) at Oak Ridge National Laboratory (ORNL) has been developing diagnostic techniques primarily for the advancement of diesel-engine catalysis both in terms of operating efficiency and emissions reduction. Two tools that could be very beneficial to fuel-cell diagnostics are the SpaciMS and the Phosphor Thermography (PhosphorT) instruments. Both of these tools are based on non-reactive and non-conducting, minimally invasive physical probes uniquely applicable for probing intra-fuel-cell chemistry.

The SpaciMS capillary inlet system is minimally invasive both in terms of its size, ca. 200-µm OD, and sampling rate, ca. 10 µL/min. The glass capillaries are both non-reactive and non-conducting, and can be inserted into small reactor channels and around corners. The capillaries transport the extracted sample from the sample location to a mass spectrometer (MS), where standard electron ionization mass-specific detection is performed. This allows for broad species analysis including O_2, CO_2, H_2S, SO_2 and various hydrocarbons, as well as H_2, which is critical to fuel cell technology. Temporal resolution is largely dictated by capillary length; we have achieved ca. 30Hz and 1Hz temporal resolution using 1 and 2.5-m long capillaries, respectively. The ability of this instrument to accurately quantify hydrogen concentration distributions is unique and attributable to the specific MS type. Our experience with applications of the SpaciMS is also unique and broad, including first measurements of in-cylinder H_2 generation from diesel engines, and intra-catalyst species distribution measurements. Species distributions throughout a fuel-cell stack could be resolved by translation of the SpaciMS probe, or sampling via separate capillaries positioned throughout the stack. This could provide data critical to understanding fundamental device chemistry, improving performance and validating models; for instance,

monitoring of fuel conversion and consumption throughout the stack, and identifying the most effective areas as well as local effect on flow conditions.

Despite its success for elucidating automotive catalyst chemistry, fuel cell applications offer additional challenges. Automotive catalyst environments are typically 300-450 C, non-condensing, with at most typically percent levels of hydrogen. There are many different types of fuel cells, and many different fuel cell issues in need of SpaciMS measurements as generally discussed above. For instance, some fuel cells operate at relatively low temperatures while others operate at high temperatures; some fuel cell environments are condensing while others are not; some fuel cells use pure H_2, others use mixtures, and others incorporate the reforming function into the stack, e.g., to convert methane to H_2. For fuel cells that use pure H_2, there may be challenges to measuring small concentration changes on such a large baseline. Solid oxide fuel cells operate at high temperatures, 800-1000 C; this will affect both the mechanical nature of the capillary physical probe, as well as the sample density and thus signal level. Proton exchange membrane, PEM, fuel cells have condensing environments, which increases the probability of blocking the capillary sample probe. The SpaciMS is applicable to both a broad range of fuel cell types and issues. The proof of principle defined in this proposal is not limited to a single fuel cell type. But rather establishes a foundation upon which we plan to build a broad fuel cell R&D program.

This seed money proposal addresses (1) measuring concentration gradients across fuel cells and (2) measurements at high temperatures indicative of SOFCs. Methods to mitigate water clogging of sample capillaries are not investigated in this proposal. Nevertheless, the proposal will establish the ability of the SpaciMS to make measurements critical to fuel cell research for a broad range of fuel cell types. There is currently no sponsor support to demonstrate the tasks described in this proposal. Individuals closely associated with the DOE mobile and stationary fuel cell programs need demonstrations described here to fully support pursuing DOE funding.

The project objectives were fully realized. Intra-PEM SpaciMS measurements were demonstrated in addition to the original project objective list.

Technical Approach

The SpaciMS was applied to measure transient species concentration distributions associated with fuel cell operation. A 3-stack, 34-W commercial PEM fuel cell was used to create the PEM test environment. A resistive load bank was used to create load variations. The anode reactant conditions were 100sccm, 35% H2, 35% Ar, 30% H2O, 22psig. The cathode reactant conditions were 100sccm, 14% O2, 56% Ar, 30% H2O, 25psig. For intra-PEM SpaciMS measurements, 4 capillaries were installed along both the anode and cathode flow paths; small grooves to house the sample capillaries were milled into both sides of a single bipolar plate, and the capillaries were sealed in place with silicone. Capillaries were installed in the inlet manifold and at ca. 0.15, 0.46 and 0.78 along the serpentine flow paths.

To demonstrate SpaciMS measurements at SOFC temperatures, the PEM exhaust streams were heated to 900C. To effect sample heating, each exhaust stream was passed through a 4.25-ft length of 1-mm ID tubing contained in a tube furnace at 900C. SpaciMS sampling capillaries were inserted into the heated tubes, and positioned to sample ca. 8-in prior to the heated tube's exit from the furnace; i.e., the sample location was within the 900C furnace.

Results and Discussion

Measurements were made of PEM exhaust species concentration as the FC load was switched. Fuel cell output was varied from 0.02 to 0.95W. Distinct step changes in H2, O2, H2O and Ar concentrations were observed to accompany load step changes. In general increasing load resulted in greater H2 and O2 depletion. Argon diluent concentrations increased with H2 and O2 consumption on both the anode and

cathode sides, respectively. High water loading conditions could challenge the capillary sampling system resulting in partial transient capillary occlusion or in the worst case capillary clogging; transient occlusion events resulted in high frequency dynamics on the pressure and non-water species traces, and a longer-term water concentration dynamic as the excess water was removed from the capillary. Water blocking of the capillary stopped sample flow and caused the SpaciMS to go to high vacuum; this type of water clogging can often be reversed by reverse flow of N2 through the sample capillary. Water-induced dynamics were most prevalent on the cathode (O2) side at high load conditions. This is as expected since cathode-side water concentration should be highest at high-load conditions. Low-frequency variations in both species concentrations and FC output were observed even at a steady-load condition. These are apparently due to transient local reactant depletion or passivation; e.g., local water condensation.

Measurements of dynamic species concentrations at SOFC temperatures posed little additional challenges. The higher temperature environment results in fewer molecules in the MS due to decreased sample density, and increased capillary resistance; because of the greater sample temperature and correspondingly small mean free path. These effects posed no great measurement challenge, as evidenced by the signal-to-noise ratio of the high-temperature measurements relative to the lower-temperature (PEM-out) measurements. Certainly at SOFC-typical temperatures quartz sample capillaries become fragile because the polyimide coating burns off at temperatures above ca. 400C. This is not a problem as long as sufficient care is taken; e.g., minimize vibrations and rough surfaces contacting the capillaries. In fact, we demonstrated that bent sample capillaries and even those bent against a sharp metal edge do not break when the polyimide is removed. We had intended to investigate stainless-steel, SS, capillaries and/or crimped SS large-bore capillaries, and their comparison to quartz capillaries. We were unable to perform this work.

Intra-PEM species measurements have always been perceived as the most challenging SpaciMS application due to the condensing nature of the environment; specifically, due to the expected high probability for capillary clogging by liquid water. We initially planned to mitigate water clogging by housing the sample capillary in a heated and insulated SS sleeve. However, due to time and funding limitations, bare quartz (185-um OD, polyimide coated) capillaries were used. The method of capillary-probe installation via milled grooves with silicone sealing resulted in leak-free probe access. Despite our expected difficulties, we experienced no water-clogging problems with any of the intra-PEM capillaries. This is notable particularly because realistic water concentrations were used. In fact, the water-associated sampling challenges were strictly confined to the capillaries outside the PEM. The intra-PEM SpaciMS measurements resolved O2 depletion and maldistribution as shown in Fig. 1. Figure 1 shows the oxygen concentration at five locations through the PEM, with the FC operating at five different load conditions. The measurements made at 0L, 0.15L, 0.46L and 0.78L, where L is the serpentine pathlength, used capillaries installed in the PEM. The measurement at 1L used a capillary positioned outside the PEM in the FC exhaust stream. Figure 1 indicates monotonically increasing oxygen consumption along the PEM cathode flow path within the PEM. For all loads investigated, the PEM out oxygen concentration is greater than that at the 0.78L intra-PEM location. It is important to realize that these measurements were taken on one cell of a three-parallel-cell PEM. Since separate measurements indicated no air leaks, the behavior of Fig.1 indicates that other parallel (not instrumented/measured) MEAs are less efficient than the instrumented MEA; because those other MEAs are less efficient, they use less oxygen than the instrumented cell and increase the exhaust concentration. For instance at 980mW, the instrumented cell is exhausting ca. 0% oxygen, but the two parallel cells are exhausting some combination of oxygen concentration that averages to ca. 8%. This further demonstrates the need for measurement of intra-PEM FC species distributions. Figure 1 also shows significant oxygen consumption at the 980mW case, with the oxygen being depleted somewhere between the 0.15L and 0.46L locations; i.e., in this case the back 54 to 85% of the flow path is inactive due to an oxygen limited condition. At all locations the oxygen consumption increases with increasing FC output.

SpaciMS measurements of transient species concentration were demonstrated

a) across a PEM FC
b) at SOFC-typical temperatures
c) within a PEM FC

Benefits

The research is consistent with DOE missions to increase energy efficiency, reduce dependence on foreign oil, and improve environmental quality. The DOE Hydrogen programs promote broad fuel cell deployment for both stationary and mobile power generation and promise to have positive impacts on all of these DOE mission areas. This project has demonstrated a tool capable of providing measurements that are critical for fuel cell technology development, and hence applicable to forwarding the DOE mission. This diagnostic capability is beneficial to multiple other federal agencies (DOD, DOT, etc) that are investigating fuel cells.

References

None

Figure:

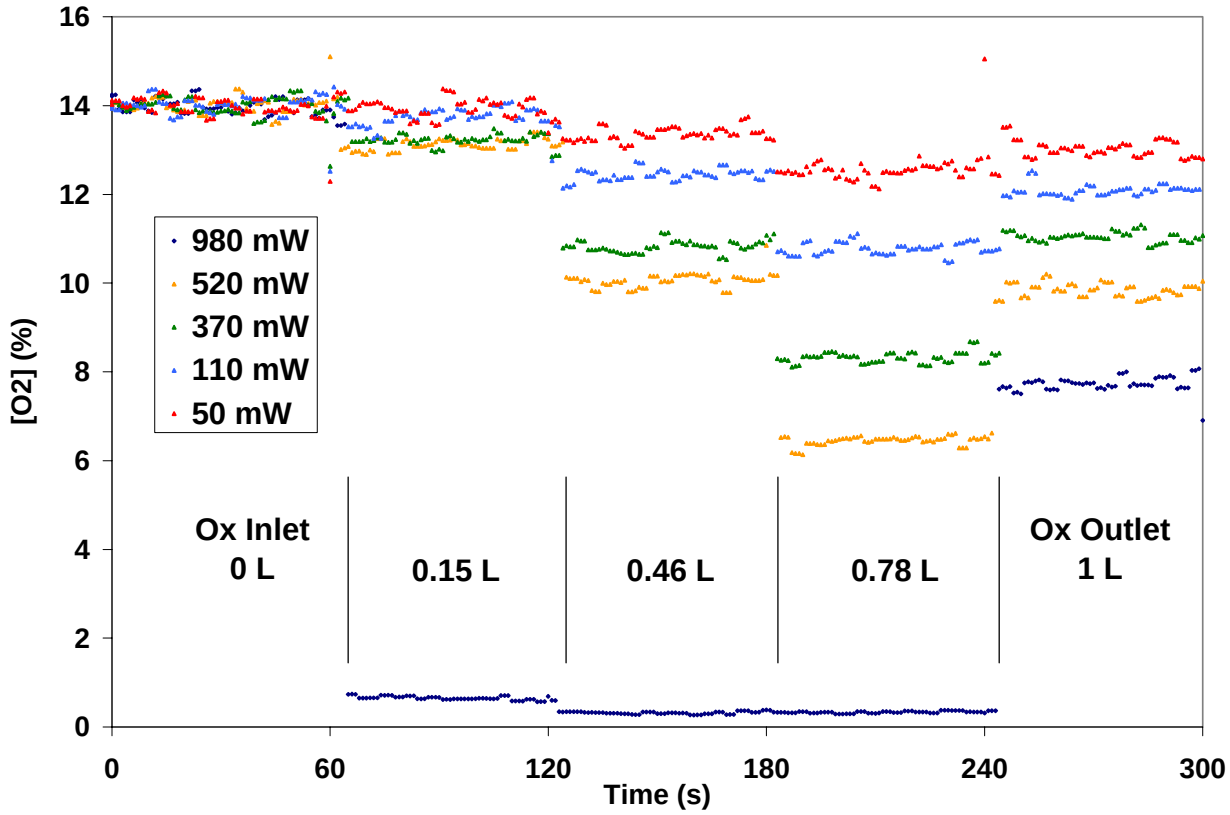

Fig. 1. Intra-PEM SpaciMS measurements of O2 consumption and maldistribution