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Intra-fuel cell stack measurements of transient concentration distributions

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Abstract

Intra-fuel-cell measurements are required to understand detailed fuel-cell chemistry and physics, validate models, optimize system design and control, and realize enhanced efficiency regimes; in comparison, conventional integrated fuel-cell supply and effluent measurements are fundamentally limited in value. Intra-reactor measurements are needed for all fuel cell types. This paper demonstrates the ability of a capillary-inlet mass spectrometer to resolve transient species distributions within operating polymer-electrolyte-membrane (PEM) fuel cells and at temperatures typical of solid-oxide fuel cells (SOFC). This is the first such demonstration of a diagnostic that is sufficiently minimally invasive as to allow measurements throughout an operating fuel cell stack. Measurements of transient water, hydrogen, oxygen and diluent concentration dynamics associated with fuel-cell load switching suggest oxygen-limited chemistry. Intra-PEM fuel cell measurements of oxygen distribution at various fuel-cell loads are used to demonstrate concentration gradients, non-uniformities, and anomalous fuel cell operation.

Keywords: In situ measurements; In-operando measurements; Intra-fuel-cell measurements; PEMFC; SOFC; Humidity

1. Introduction

Improved fuel cell efficiencies can be realized through detailed understanding of device chemistry and physics provided by in situ intra-reactor measurements that resolve transient species concentration distributions across and within the cells. Such species variations reflect changes in the manifold sub-processes involved in fuel cell operation; e.g., reactants and products distribution and transport, localized and possibly dynamic active-site blocking, membrane degradation, etc. In turn, such species measurements can be used to better understand and optimize the component processes. With integrated or reactor-in and -out (i.e., supply and effluent) measurements, the process can only be optimized on average. In contrast, intra-reactor measurements allow higher-order optimization throughout the fuel cell.

The need for and potential of such advanced-measurement-driven insights is recognized by the broad fuel cell community as demonstrated by the diversity of approaches for resolving various intra-reactor distributions. Nishikawa et al. used a segmented polymer electrolyte fuel cell (PEMFC) and commercially available humidity and temperature sensors to study the distribution of water transport across the membrane [1]. This transport was correlated with current density distributions, humidity, polymer membrane water content and cathode oxygen concentration. The observations allowed a better understanding of the dynamic efficiency distributions along the fuel cell flow path. Hakenjos et al. applied infrared (IR) and visible imaging techniques to a segmented PEMFC with an IR window over the anode flow path to study intra-reactor current, temperature and water distributions [2]. Through this work they associated intra-PEMFC areas of low current density with specific loss mechanisms, and suggested that through this improved knowledge optimized flow-field designs could be realized. Barreras et al. modified a commercial PEMFC to gain optical access throughout one flow path and used laser-induced fluorescence imaging to study reactant flow distributions [3]. The results were used to val-

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Abbreviations: BPR, back pressure regulator; DMFC, direct methanol fuel cell; GDL, gas diffusion layer; i.d., internal diameter; IR, infrared; LHS, left-hand side; MEA, membrane electrode assembly; MFC, mass flow controller; MS, mass spectrometer; o.d., outside diameter; PEM, proton exchange membrane; PEMFC, proton exchange membrane fuel cell; RGA, residual gas analyser; RHS, right-hand side; sccm, standard cubic centimeters per minute; SOFC, solid oxide fuel cell; SpaciMS, spatially resolved capillary inlet mass spectrometer; T_{10-90}, time between the 10% and 90% response points; UHP, ultra-high purity; XAFS, X-ray absorption fine-structure spectroscopy

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idate flow models, identify the source of non-uniform flow, and better understand the sources of inefficiencies. Mench et al. used gas chromatography to measure species distributions, including water, O_2 and N_2, on the anode and cathode sides of a PEMFC's 22-pass serpentine flow path. Measurements were made with 2 min temporal resolution and used to better understand the distributed nature of water transport and chemistry, and its relation to local PEMFC output [4]. Roth et al. used in situ X-ray absorption fine-structure spectroscopy (XAFS) to actively monitor the catalyst oxidation states at a select location within an operating PEMFC, and stated the importance of the technique for studying aging and deactivation processes [5]. Kramer et al. applied neutron imaging to a direct methanol fuel cell (DMFC) to study two phase flow in various flow-path geometries [6]. This work demonstrated the transient and distributed nature of mass-transport limitations, and corresponding distributions in the intra-DMFC electrochemistry efficiency. Of the works cited above, that of Kramer et al. was the least invasive and the only one that did not require direct flow-path access or invasive modifications. This diverse group of efforts not only demonstrates the need for intra-fuel cell diagnostics, but highlights the range of component processes/issues that can have distributed performance and impact the local and integrated fuel cell efficiency. All of the cited works demonstrate significant progress to better understand some component process critical to fuel cell efficiency. A common limitation of this diverse group of diagnostics for resolving intra-fuel-cell distributions is that they require end-plate access and are all limited to single cell applications; i.e., they cannot be applied to resolve inter-cell distributions. Moreover, other than the neutron imaging work [6], the cited diagnostics are of varying degrees of invasiveness. This is generally representative of fuel cell diagnostics; they are invasive and have limited ability for full-stack analysis. Improved diagnostics that are minimally invasive and allow full-stack analysis are needed to realize optimum efficiencies through better understanding of the detailed fuel cell component processes.

Although the previous examples are limited to PEMFC and DMFC devices, intra-fuel-cell and inter-stack diagnostics are needed to improve the understanding and efficiency of all fuel cell types. SOFC gas analysis is generally recognized as particularly difficult [7]. Nevertheless, advanced diagnostics have been applied to study fundamental SOFC chemistry [8–10]. The work of Finnerty et al. is particularly notable in the context of this paper in that an MS was used to resolve transient SOFC reforming and carbon deposits [10]; Finnerty's paper demonstrates the value of real-time in situ diagnostics for understanding detailed reactor chemistry, but on an integrated reactor-effluent basis. Minimally invasive intra-reactor diagnostics could extend these insights to allow the distributions of reactions within the SOFC to be studied.

Spatially resolved capillary-inlet mass spectrometry (SpaciMS) is a candidate species diagnostic for making minimally invasive intra- and inter-stack measurements within fuel cells. The instrument is based on direct capillary sampling to a residual gas analyzer; i.e., capillaries are directly mounted in the bipolar-plate channels, blocking less than 3% of the flow-path and sampling at approximately $10\,\mu L\,min^{-1}$. This sampling methodology is minimally invasive and enables species measurements in both single- and multi-cell configurations. Moreover, the SpaciMS measurement methodology is relatively easy to configure and implement, and thus accessible to the entire fuel-cell community.

This instrument was primarily developed to improve the understanding of the detailed chemistry and species distributions in diesel engine exhaust and catalyst systems, and has been successfully implemented into a wide range of conditions including: catalyst beds on both bench-scale [11,12] and full-engine platforms [13,14], advanced diesel combustion [15], non-reacting gas mixing [16], and electrically active non-thermal plasma reactor chemistry [17]. In these applications the SpaciMS has been configured to provide 104 ms–1 s temporal resolution (based on T_{10-90} response, i.e., time between the 10% and 90% response points), and quantify species concentrations in the 10 ppm to tens of percent ranges. Although these applications have required concentration gradients to be measured only on centimeter scales, the spatial resolution is limited only by the ability to control capillary translation; e.g., 2 mm spatial resolution should be readily feasible. The SpaciMS has provided unique detail regarding the network and sequence of catalyst chemistry, and previously unavailable insights into improving the performance efficiency of diesel-catalyst systems. Similar unique insights into fundamental fuel cell chemistry and physics are expected from SpaciMS applications.

Fuel cell applications offer several additional challenges to SpaciMS measurements compared to the primarily combustion and catalysis examples cited above. Diesel catalyst environments are typically 300–450 °C, non-condensing, with at most typically percent levels of hydrogen. For fuel cells using pure H_2, there may be challenges to measuring small concentration changes on a large baseline. High temperature, 800–1000 °C, SOFC operation will affect both the mechanical nature of the capillary physical probe, as well as the sample density and thus signal level. The condensing PEMFC environment increases the possibility of capillary probe occlusion by liquid water. The effort described here details the investigation of these issues and assesses the feasibility of SpaciMS for the described applications. This paper describes the first application of the SpaciMS for the measurement of fuel cell species transients associated with load switching, and intra-fuel-cell species distributions. Measurements are made at temperatures characteristic of PEMFC and SOFC devices to demonstrate broad instrument applicability.

2. Experimental

2.1. Fuel cell platform

A commercially available (ProFC-3, H_2 Economy) three-cell PEMFC stack, with 7 cm × 7 cm active area per cell, was used for the research described here. The graphitic bipolar plates incorporated 13-pass 918 mm long dual parallel serpentine flow channels, with crossed anode–cathode flow paths. The flow paths