In situ Optical Studies of Solid Oxide Fuel Cells

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There is a continuing interest in understanding the physical processes and chemical reactions responsible for the performance and degradation of solid oxide fuel cells (SOFCs). While these devices have traditionally been characterized using electrochemical measurements, such as voltammetry and impedance spectroscopy, recent methods have been developed using *in situ* optical techniques which provide new information on physical, material and chemical changes that occur in functioning cells. These techniques, which have been used primarily to characterize anodes, permit detailed and real-time studies to identify how various fuels and operating conditions affect important SOFC processes, such as the propensity for detrimental carbon formation.[1,2] Following initial studies using Raman spectroscopy to monitor Ni oxidation and carbon deposition,[3] subsequent work combined this method with near infrared thermal imaging. Results from these studies indicate that coking while operating on methanol depends on the temperature – methanol forms less carbon than methane at 800 ºC, but more than methane at 700 ºC[4] – and that ethanol effectively reforms with steam at 800 °C to operate more cleanly than at lower temperatures or than methanol.[5]

In this study we describe results using Fourier transform infrared emission spectroscopy (FTIRES) that has only recently been applied to the study of SOFC anodes.[6] In our initial report using this method,[6] we described the first direct detection and assignment of a molecular intermediate on an SOFC anode, adsorbed CO_2 ($CO_{2(ad)}$), which was observed during and subsequent to operating an anode-supported SOFC on methane. In addition to the adsorbed species, gas phase products – CO and CO_2 – as well as the methane fuel were observed and recognized by their rotational structure. Electrochemical control and supporting studies in which CO_2 was introduced into the cell provided critical evidence to confirm the assignment of the IR emission band near 2350 cm^{-1} to $CO_{2(ad)}$. We have expanded this work using FTIRES as well as Raman spectroscopy and thermal imaging to investigate SOFCs operating on methanol and biogas (CO_2 and CH_4) under various conditions.

FTIRES studies of Ni/YSZ anode-supported SOFCs using methanol at 800 ºC yield results similar to those obtained with methane and agree with the observations from our previous Raman and thermal imaging studies comparing methane and methanol operation in SOFCs.[4] Figure 1 shows FTIRES spectra observed from SOFC anodes while operating on methane and methanol. As evident from the rotationally resolved methane signature observed for the C-H stretching band near 3000 cm^{-1}, there is a much a higher fraction of the gas phase methane preserved in the fuel stream compared to the very small amount, if any, observed for methanol. Previous observations based on FTIR studies of the fuel streams showed that methanol reforms to a greater extent than methane. Also, more extensive oxidation for methanol is indicated in the FTIRES spectra by the stronger bands observed for the oxidation products, which includes not only $CO_{2(ad)}$ near 2350 cm^{-1} but also gas phase CO centered near 2100 cm^{-1}. In addition to measurements while the cells were operating on the fuels, electrochemical oxidation measurements were carried out in which the fuel feed is terminated and FTIRES is performed as current is being drawn from the cell to oxidize carbon that was deposited on the anode during the cell operation. Stronger FTIRES bands were observed after running with methane, corroborating our previous result that methane has a higher propensity to produce carbon on the anode at 800 ºC.

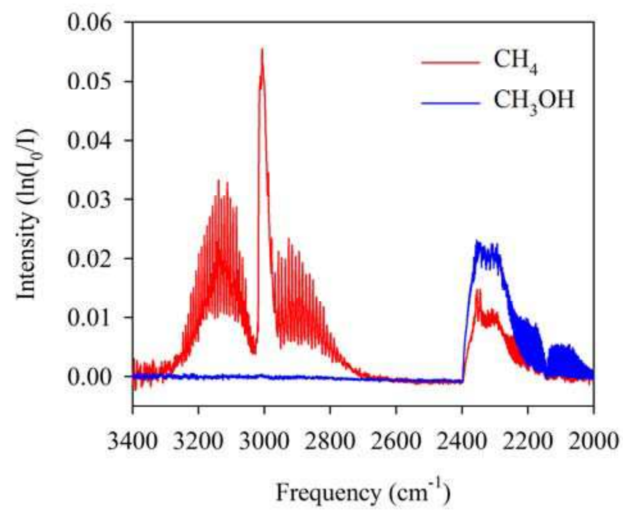

Figure 1. FTIRES spectra of Ni/YSZ SOFC anodes operating on methane and methanol at 330 mA.

Combined FTIRES, Raman and thermal imaging studies were performed on a model biogas mixture (1:1 CO_2:CH_4). The thermal imaging results indicate substantially larger temperature decreases (~ 10 ºC) for the introduction of biogas to the SOFC anode compared to methane (< 2 ºC) which demonstrates CO_2-mediated anode activity for methane reforming with CO_2. In addition, both Raman and FTIRES spectra indicate more carbon deposition occurred with methane than operating SOFCs with biogas. These results provide a detailed characterization from several methods that biogas is less detrimental to the anodes with respect to carbon deposition than simply running with methane.

These results demonstrate that FTIRES complements the capabilities of other *in situ* optical methods – such as Raman and thermal imaging – to provide a comprehensive, real time perspective for characterizing SOFC performance and degradation mechanisms.

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