

***In Situ* spectroscopic insights into methane fuel oxidation in Ni/YSZ solid oxide fuel cells**

John D. Kirtley,^a Michael B. Pomfret,^c Daniel A. Steinhurst,^b Jeffrey C. Owrutsky,^c and Robert A. Walker^a

^aDep't of Chemistry and Biochemistry, Montana State University, PO Box 173400, Bozeman, MT 59717

^bNova Research, Inc., Alexandria, VA 22308

^cChemistry Division, Naval Research Laboratory, Washington, D.C. 20375

Solid oxide fuel cells (SOFCs) have recently attracted considerable attention as sources of efficient DC electrical power. While the overall description of SOFC operation is straightforward, detailed and validated mechanisms describing fuel oxidation are few. High operational temperatures are required for sufficient oxide diffusion through the electrolyte, and this restriction poses significant experimental challenges for studying SOFC chemistry *in situ* and in real time. Nevertheless, direct identification of molecular intermediates and material changes is crucial in order to fully understand the chemical processes involved in SOFC operations, including the origins of SOFC degradation.

Recent advancements of *in situ* optical techniques, have begun providing direct insight into fuel oxidative processes occurring at Ni/YSZ anodes of SOFCs under varying operational conditions. (1-4) Raman spectroscopy coupled with chronopotentiometry can quantify carbon growth on SOFC anodes with <2 s resolution, 1 μm spatial resolution. NIR thermal imaging reveals thermodynamics associated with changes in surface chemistry on a component level with 0.1°C temperature resolution, and with high temporal and spatial resolution (<0.25 s and <10 μm , respectively). Newly developed FTIR emission spectroscopy has identified gas phase species and transient, steady-state CO₂ adsorbed on Ni, with 0.5cm⁻¹ resolution and 100 s temporal resolution.

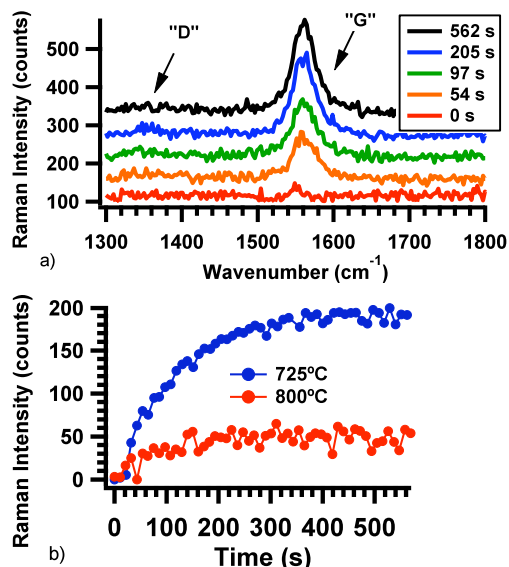


Figure 1. (a) Growth of the Raman "G" peak at 1556cm⁻¹, observed *in situ* from a cell operating at OCV under methane fuel near 725°C. (b) Comparison of graphite growth at two temperatures.

In this work, we present new insights into methane oxidative processes occurring on Ni/YSZ SOFC anodes by combining observations from these three *in situ* optical techniques. At temperatures ranging from 700-800°C, the relative rates of carbon formation reactions are measured using Raman spectroscopy. (Fig. 1) Deeper insights into the mechanisms responsible for methane oxidation result from coupling Raman data with time-dependent

temperature gradients observed in NIR thermal data. (Fig. 2) Methane cracking is an endothermic process; electrochemical oxidation is an exothermic process; carbon formation reduces surface emissivity and also appears to be exothermic. These claims are supported by general observations that link increased spectroscopically observable carbon formation with less anode cooling. At the lowest temperatures sampled (700°C), carbon forms more rapidly and extensively while the system cools less, compared to operation at higher temperatures.

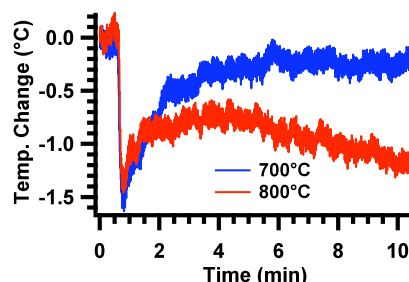


Figure 2. Comparison of temperature changes at the Ni/YSZ anode of two SOFCs operating at OCV and at 700°C and 800°C with methane fuel.

FTIR emission measurements provide further clues into these processes by comparing CO₂, CO_{2(ads)}, CO, and CH₄ species observed *in situ* (Fig. 3). Quantitative comparisons of the kinetics of each of these species under changing operational conditions provide direct mechanistic clues into carbon deposition pathways and their impact on overall MEA performance. During carbon formation from methane, little CO₂ and CO is observed at OCV. These species first appear when the MEA is polarized. Subsequent electrochemical removal of graphite indicates that more carbon species are removed in the form of CO₂ and CO following exposure at OCV relative to exposure under polarization. We anticipate that the correlation of each of these three optical techniques will ultimately lead to insights undergirding effective SOFC operation with hydrocarbon fuels.

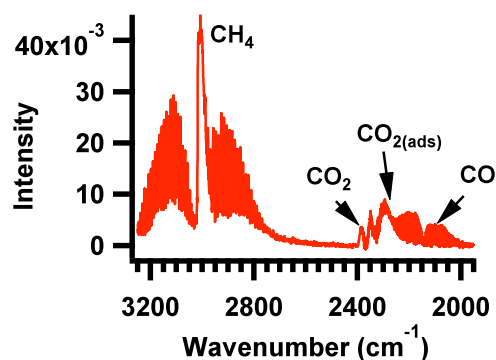


Figure 3. FTIR emission spectrum acquired from a cell operating under methane under 360mA at 800°C.

References

1. E. Brightman, R. Maher, G. J. Offer, V. Duboviks, C. Heck, L. F. Cohen and N. P. Brandon, Review of Scientific Instruments, 83 (2012).
2. M.B. Pomfret, D.A. Steinhurst and J.C. Owrutsky, J. Phys. Chem. Lett., **1310**, 4 (2013).
3. J.D. Kirtley, D.M. Halat, M.D. McIntyre, B.C. Eigenbrodt and R.A. Walker, Analytical Chemistry, **9745**, 84 (2012).
4. M. B. Pomfret, D. A. Steinhurst and J. C. Owrutsky, Energy & Fuels, **2633**, 25 (2011).