Investigating Solid Oxide Fuel Cell Cathode Degradation via Operando X-ray Absorption Spectroscopy

Samson Lai, Mingfei Liu, Meilin Liu, Faisal M. Alamgir
School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA

Email: faisal.alamgir@mse.gatech.edu

Solid oxide fuel cells (SOFCs) show significant promise as highly efficient, fuel flexible, solid-state energy conversion devices (1, 2). However, they are complex materials and systems that require specific conditions for optimal operation. High temperatures, oxidizing and reducing atmospheres, and electrical polarization create significant barriers to studying the materials in their active state. Information from traditional *ex situ* characterization techniques falls short in accurately describing the material state during operation, when the chemical phenomena responsible for SOFC deficiencies occur. *Operando* spectroscopy is a challenging but uniquely rewarding method of investigating SOFC materials under operating conditions. X-ray absorption spectroscopy provides both electronic and structural information with elemental selectivity, providing clues about the mechanisms of interaction between the electrode material and its environment.

A symmetrical cathode cell configuration was chosen to minimize complexity. To increase surface sensitivity and limit signal from the bulk, a 200-nm thick thin film of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\pm\delta}$ (LSCF) was fabricated onto a 10 mm x 10 mm single crystal of YSZ by RF-sputtering and subsequent annealing. The counter electrode was a 50 µm tape cast LSCF pasted over a GDC buffer layer on the reverse side of the substrate and co-fired. The cell was affixed to a stainless steel sample holder using Ag paste.

A custom designed furnace was constructed to enable control over temperature, gas contamination, electrical polarization, and windows for x-ray entry and fluorescent x-ray exit. A schematic of the design is shown in Figure 1. Windows made of Kapton film were incorporated to enable x-rays to enter, fluoresce from the sample, and exit above the sample and through a reference metal foil for energy calibration.

Hard x-ray absorption spectroscopy was performed using Beamline X18B of the National Synchrotron Light Source at Brookhaven National Laboratory. The assembly was slightly angled to achieve a glancing incidence geometry which illuminated the surface of the thin film electrode. Fluorescent x-rays were collected through a large Kapton window from an overhead angled Lydle detector. Near edge (XANES) and extended fine structure (EXAFS) were collected for Fe and Co as a function of electrical polarization (at open circuit and with a -1.0 V bias), temperature (400°C and 750°C), and as a function of H_2O or CO_2 introduced directly over the electrode through a glass pipet inserted through the Kapton film.

As seen in Figure 2, Fe XANES data show how CO_2 and H_2O have oxidative and reductive effects, respectively, at 700°C and under -1.0 V bias. These effects are markedly different from those observed at 400°C and those observed in Co, thereby evidencing the need for an element-specific *operando* technique to understand the combined influence of operating conditions on the material state. Information from these *operando* experiments may provide unique insights into the degradation mechanisms caused by gas contaminants.

We present an *operando* synchrotron x-ray spectroscopy technique for SOFC cathode materials. The separate and combined influences of the cathodic polarization, CO_2, and H_2O can be readily observed in the oxidative and reductive shifts of the absorption edge in Fe and Co. Other influences on the atomistic local structure of Fe and Co as function of the operating parameters will be discussed in further detail.

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Dr. Mingfei Liu's current affiliation and address is Phillips 66 Research Center, Bartlesville, OK 74003 USA.

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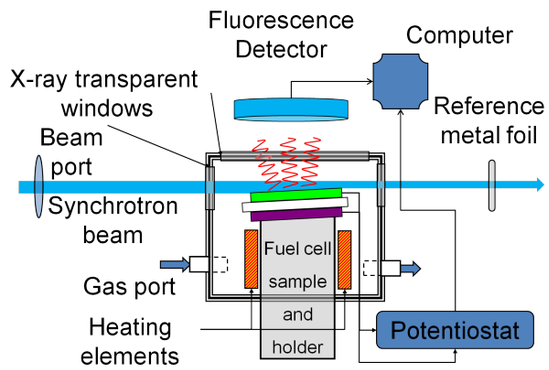

Figure 1. A schematic of the custom-designed furnace for *operando* x-ray absorption spectroscopy.

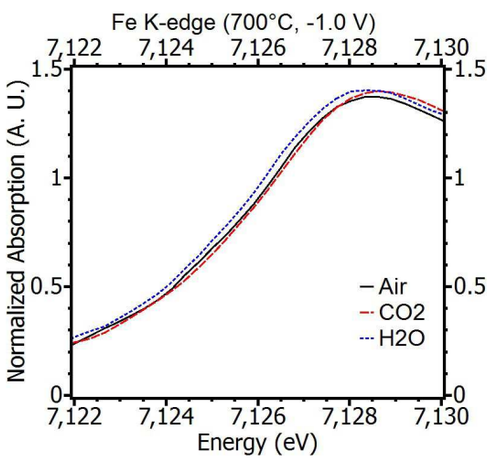

Figure 2. Near edge X-ray absorption spectroscopy shows that different gases can oxidize or reduce the Fe.