Measurement of Oxygen Diffusivity of SOFC Cathode Materials Using FTIR Emission Spectroscopy

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Mixed conducting ceramics are considered viable candidates for solid oxide fuel cell (SOFC) cathodes due to their greater catalytic activity for oxygen reduction. Strictly electronic conducting cathodes are only active along and near the triple phase boundary between the electrolyte, cathode, and gas (region 1 in Figure 1). With a mixed ionic-electronic conductor (MIEC) cathode, oxygen reduction can occur at the triple phase boundary as well as along the interface between the gas and the cathode (region 2 in Figure 1). This increase in catalytically active surface area allows the SOFC to be operated at lower temperatures, which would permit the use of cheaper materials for cell components such as interconnect and sealant.

When oxygen reduction occurs away from the triple phase boundary (TPB), the oxygen vacancies (or oxygen anion) must be transported through the cathode to (or away from) the active reaction sites. In fact, the degree of extension of the active reaction zone from the TPB to MIEC surface is determined critically by the rate of oxygen transport through the MIEC cathode. When attempting to model the performance of a SOFC with a MIEC cathode, one must thus need the diffusivity of the oxygen ion through the cathode. Preliminary studies indicate that both surface reaction kinetics and bulk transport properties may be deduced from the time dependence of FTIR spectra collected during transition from one equilibrium state to another.[2] In this study, we have further explored the use of FTIR emission spectroscopy to obtain information about oxygen diffusion in SOFC cathode materials.

Dense pellets of Sm$_{0.2}$Sr$_{0.8}$CoO$_3$ (SSC), La$_{1-x}$Sr$_x$Co$_2$O$_{2.5}$ (LSF), La$_{1-x}$Sr$_x$CoO$_3$ (LSC) and La$_{1-x}$Sr$_x$MnO$_3$ (LSM) were pressed and sintered for use in a diffuse reflectance sample chamber modified for IR emission spectroscopy. A Bruker Equinox 55 spectrometer with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector was used for the FTIRES measurements. A background single-beam emission was collected with the cathode material in equilibrium with pure argon gas. Emission spectra were then collected continuously as the gas flowing through the cell was switched from argon to different oxygen partial pressures (1% to 100% O$_2$) and then back to argon.

Figure 2 shows a series of spectra for an SSC pellet at 600ºC as the atmosphere changes from argon to air. The emissivity of SSC changed as the defect structure of the bulk adapted to the change in oxygen partial pressure. The speed at which the equilibrium structure was obtained depends upon the diffusion rate of oxygen ions through the lattice. By considering the amount of oxygen entering (or exiting) the lattice and the time it took to do so, a rough estimate of the oxygen diffusivity was obtained.

Further, by taking measurements at multiple temperatures, the activation energy for the diffusivity could be obtained.

![Current collector](image1.png)

**Figure 1** Detail of the catalytically active regions of a mixed conducting SOFC cathode

![FTIR emission spectra of SSC pellet at 600ºC as the atmosphere changed from argon to air](image2.png)

**Figure 2** FTIR emission spectra of SSC pellet at 600ºC as the atmosphere changed from argon to air

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Reference