

Study on Surface Segregation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ by in situ Total-Reflection X-ray Absorption Spectroscopy

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1. Introduction

Lowering of the cathodic overvoltage is one of the paramount strategies to improve the performance of solid oxide fuel cells (SOFCs). $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) is considered a potential cathode material for SOFCs since it shows the high electrochemical performance. The cathodic reaction contains many elementary reaction processes which are rather complex. Preliminary studies have revealed that the surface reaction is the rate-determining step of LSC electrode reaction [1]. This means the surface reaction kinetics mainly causes the cathodic overvoltage. However, the processes occurring at the electrode surface is still poorly understood. For instance, some researchers indicate that LSC is exposed to Sr segregation under SOFC operating condition [2,3]. The true phenomena of the surface reaction have not yet been clearly understood, because the previous measurement techniques are not enough to detect the surface structure change with nanometer range under SOFC operating conditions. In this study, we applied total-reflection fluorescence XAS (TRF-XAS) method, which integrates the fluorescence yield obtained under total reflection,[4] to investigate the surface reaction of LSC cathode. This method is useful to observe the surface reaction at the nanometer scales [5]. Furthermore, we performed *in-situ* measurement since the surface structure is mainly changed under operating condition. We discuss the electronic structure change at the electrode surface of LSC thin film electrode.

2. Experimental

We prepared $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films by using pulsed laser deposition method. Substrate we use was YSZ (110) single crystal. First we deposited $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ buffer layer about 5 nm. After that $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ was deposited for about 25 nm thickness. *In-situ* TRF-XAS measurements were performed at the beam line BL01B1 at SPring-8, Japan. Co *K*-edge fluorescence XAS spectra were measured by using 19-elements solid state detector. During measurements, the temperature was maintained at 1073 K, oxygen partial pressure was kept at 10^5 Pa and applied voltage was kept in the 0 to -900mV range.

3. Results and Discussion

Co *K*-edge x-ray absorption near edge structure (XANES) spectra at surface LSC thin film measured at 1073 K under 10^5 Pa $p(\text{O}_2)$ and several applied voltage(0 ~ -900mV) are shown in Fig.1(a). The surface XANES spectrum is shifted towards lower energy for the lower applied voltage. However bulk XANES spectra have small change with applied voltage (Fig.1(b)). This result indicates that the surface of LSC thin film electrode has

different electronic structure when applied voltage. The observed spectra change at the surface can be explained by Sr segregation in LSC lattice structure from figure print technique. Figure 2 shows schematic illustration of oxygen chemical potential profiles around dense electrodes. At the open circuit condition, the oxygen chemical potential is constant in gas phase, electrode and electrolyte. In this case, there is not driving force for Sr segregation. Applying voltage causes oxygen potential drop at the surface. The drop at the surface might have a role for driving force for Sr segregation.

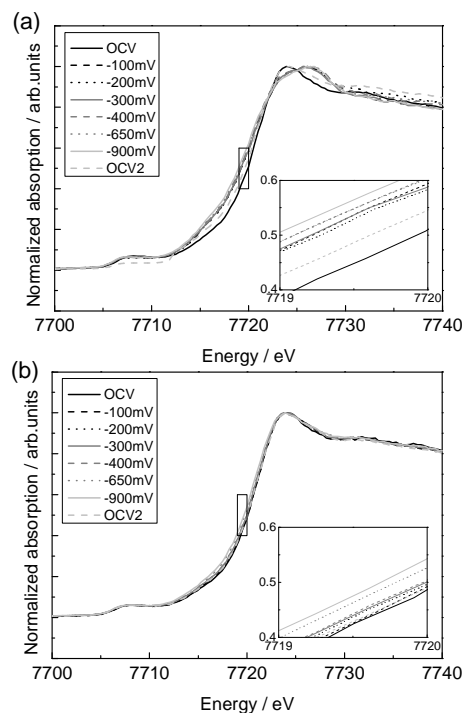


Fig. 1 Total-Reflection X-ray absorption near edge structure at Co *K*-edge of (a) surface and (b) bulk LSC thin film measured at 1073 K under $p(\text{O}_2) = 10^5$ Pa and several .

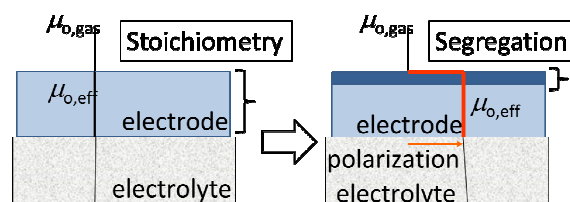


Fig. 2 Schematic illustration of oxygen chemical potential profiles around dense electrodes. When voltage is applied to the electrodes, the oxygen chemical potential at the electrode surface shifts.

References

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