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# Preliminary Investigations of Chemical & Morphological Inhomogeneities in $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ Single-Crystalline Perovskite Thin Films by ACTEM and STEM-EELS

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Perovskite-structured materials are employed as cathodes for carrying out the oxygen reduction reaction in solid oxide fuel cells (SOFCs) [1]. Among them, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) exhibits high electronic conductivity and oxygen diffusivity. At the same time, however, LSC suffers from chemical stability issues, particularly the exolution of SrO species from the bulk to the surface, and decomposition to ternary and binary oxides [1,2]. Well-ordered, single-crystalline thin films are ideal model systems to investigate the nanoscale variations in chemistry and microstructure in LSC [3,4].

In this work, dense ~250-nm-thick LSC was deposited using pulsed-laser deposition [5] on a (100)-oriented yttrium-stabilized zirconia (YSZ) single-crystalline substrate, with a 35-nm-thick samarium doped ceria (SDC) buffer layer using KrF laser in 5 mTorr of oxygen. During deposition, the substrate temperature was 700 $^oC$, and fluency was 1.5 $Jcm^{-2}$ keeping the repetition rate as 5 Hz. Substance-to-target distance was kept as 80 mm. After the deposition process, the material system has been annealed at 550$^oC$ in 1 torr of $O_2$ atmosphere for 6 hours and then quenched. We apply aberration-corrected transmission electron microscopy (ACTEM) and electron energy loss spectroscopy in scanning transmission electron microscopy mode (STEM-EELS) in an FEI Titan 80-300 environmental TEM at an accelerating voltage of 300 kV. TEM samples were prepared by tripod polishing followed by Ar ion milling. ACTEM experiments were performed using negative $C_s$ imaging conditions (-11 μm and overfocus), which allows light elements to be visualized with bright contrast [6]. STEM-EELS line spectra were acquired using convergence and collection angles of 9.3 mrad and 18.7 mrad, respectively.

Figure 1a shows a TEM bright field (BF) image of the YSZ/SDC/LSC system. Figure 1b shows a higher magnification image of Figure 1a inset, revealing the single crystalline nature of LSC. Despite the single crystallinity, significant roughness was observed on the surface of LSC (figure 1c). Within these surface features, channel-like domains exist, where the structure deviates from single crystallinity (Figure 1d). Figures 2a to 2c display the annular dark field STEM (ADF-STEM) images of three representative area and the points where the spectra in Figures 2d to 2f were acquired. The EELS spectra are background subtracted by curve fitting. The energy-loss near-edge structures (ELNES) of La-$M_{4,5}$ and Co-$L_{2,3}$ ionization edges vary in intensity going from SDC/LSC layer with either Co or La appear to be deficient toward the surface in Fig. 2d and 2e, respectively. In Figure 2f, EELS spectra seem to reveal that La-L and Co-M edge intensities are approximately constant along the area outside of the channel. Further investigation on 17 different channels revealed similar behavior to Figure 2d and 2e.

In summary, our investigations of LSC reveal the existence of channel-like structures that underlies surface morphological features. The EEL spectra show how the chemical composition likely varies in the channel-like structures. Additional experiments will be performed on plan-view and cross-sectional samples to understand the thermodynamic phenomenon leading to the occurrence of these channels, and the surface properties of the LSC film.

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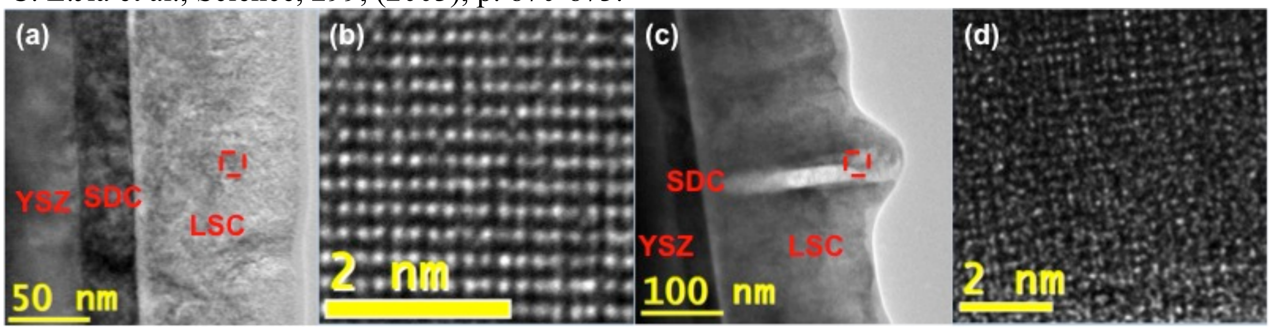


**Figure 1.** (a) TEM Bright field image showing yttrium stabilized zirconia (YSZ), samarium doped ceria (SDC) and $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) layers. (b) ACTEM image of the Figure 1a inset showing the single crystalline nature of LSC in a [110] projection. (c) BF image of another region containing the channel-like regions. (d) ACTEM image acquired from the region marked in figure 1c where the atomic structure becomes disordered.

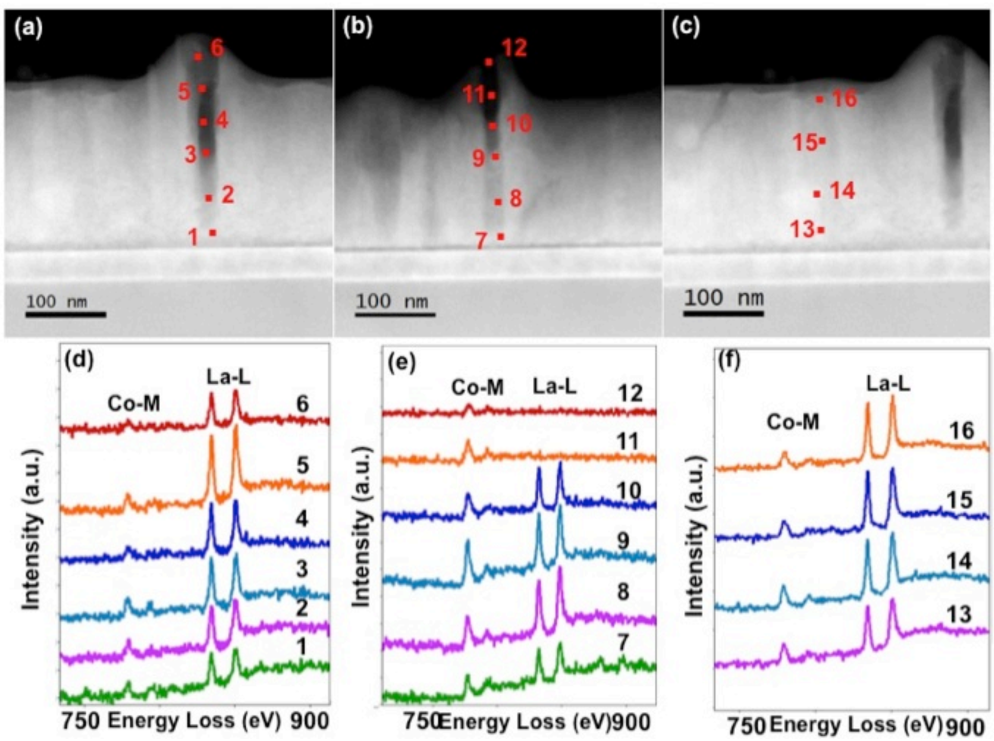


**Figure 2.** (a to c) Annular dark field STEM (ADF-STEM) images of the YSZ/SDC/LSC material system and the marked points where corresponding STEM-EELS spectra in figure 2d to 2f were acquired. (d to f) STEM-EELS spectra acquired from the points marked from 1 to 16 (figure a to c) showing the intensities of Co-$M_{4,5}$, and La-$L_{2,3}$ ionization edges for comparison (d,e) inside and (f) outside the channels.