

High Resolution Electron Microscopy Characterization of $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoC}_4$ Thin Film Cathode Materials

F. Yang¹, Y. Chen², Z. Cai², N. Tsvetkov², M. Burriel³, H. Tellez⁴, B. Yildiz², J. A. Kilner³, D.B. Williams¹, D.W. McComb¹

¹. Department of Materials Science and Engineering, The Ohio State University, Columbus, USA

². Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Boston, USA

³. Department of Materials, Imperial College, London, UK

⁴. International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, Japan

Solid-oxide fuel cells are developed as a clean energy conversion technology for electric production. Recent research has focused on finding affordable cathode materials with high reactivity to oxygen reduction reaction. Pulse laser deposited $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ (LCS214) thin film is investigated as a candidate for such cathode material [1, 2].

Thin film LSC214 was grown by pulse laser deposition (PLD) on SrTiO_3 (STO) (001) or LaSrAlO_4 (SLAO) (100) substrate. Due to the lattice parameter constraint of the substrate, the deposited thin film will grow in different orientations. High-resolution high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) is used to characterize both samples with a focus on the surface of the films. The S/TEM samples were lifted out by dual beam focused ion beam (FIB) method. To protect the film surface from ion beam damage, samples were coated with gold before FIB lift-out.

Most common feature is that all LSC214 films exhibit a darker contrast region of a few nanometers immediately underneath the gold layer. Energy dispersive spectroscopy (EDS) analysis suggests that right under the gold layer is a Sr enriched region. This feature was observed in all LSC214 films on two different substrates. The following two features were observed sporadically on the film surface.

The first feature observed in all samples is the dome shaped regions about 10 nm in diameter, shown in figure 1. These dome shaped regions have a complex structure. At the bottom of the dome is a distinct layer that usually exhibits a hexagonal atomic lattice. Part of this layer can extend to the dome shaped Au cap, with other parts of the dome region having a very low intensity. EDS analysis verified that this layer of hexagonal lattice is Sr and O rich. The region with very low intensity has very few X-ray counts, suggest little material in this region. Small particles of the same atomic structure were observed at fault boundaries on film surface. The nature of the Sr/O rich material is not known. Using the stoichiometry of LSC214 as an internal standard, the composition of this layer is close to SrO. However, the interatomic spacing of known SrO structure is not consistent with observations in the STEM images.

The second feature was only observed on the top surface of LSC214 on the STO (001) substrate, not on the surface of LSC214 on SLAO (100). The feature consists of Perovskite type atomic structures at the very top of the film surface, located immediately underneath the gold layer, shown in figure 2. The bulk of the film material has the Ruddlesden-Popper (R-P) structure ($n=1$) with and stoichiometry of $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$. Analogous Perovskite structure would have a stoichiometry of $(\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$. The Co/(La+Sr) ratio is higher for Perovskite structure than that for the R-P structure. This has been confirmed by EDS analysis.

Future work will be carried out on characterization on LSC214 films of different compositions and how possible different structural and compositional features will affect oxygen transport properties.

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References:

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 [2] A Kushima, D Parfitt, A Chroneos, B Yildiz, JA Kilner, RW Grimes, *Physical Chemistry Chemical Physics* **13** (2011), p.2242.

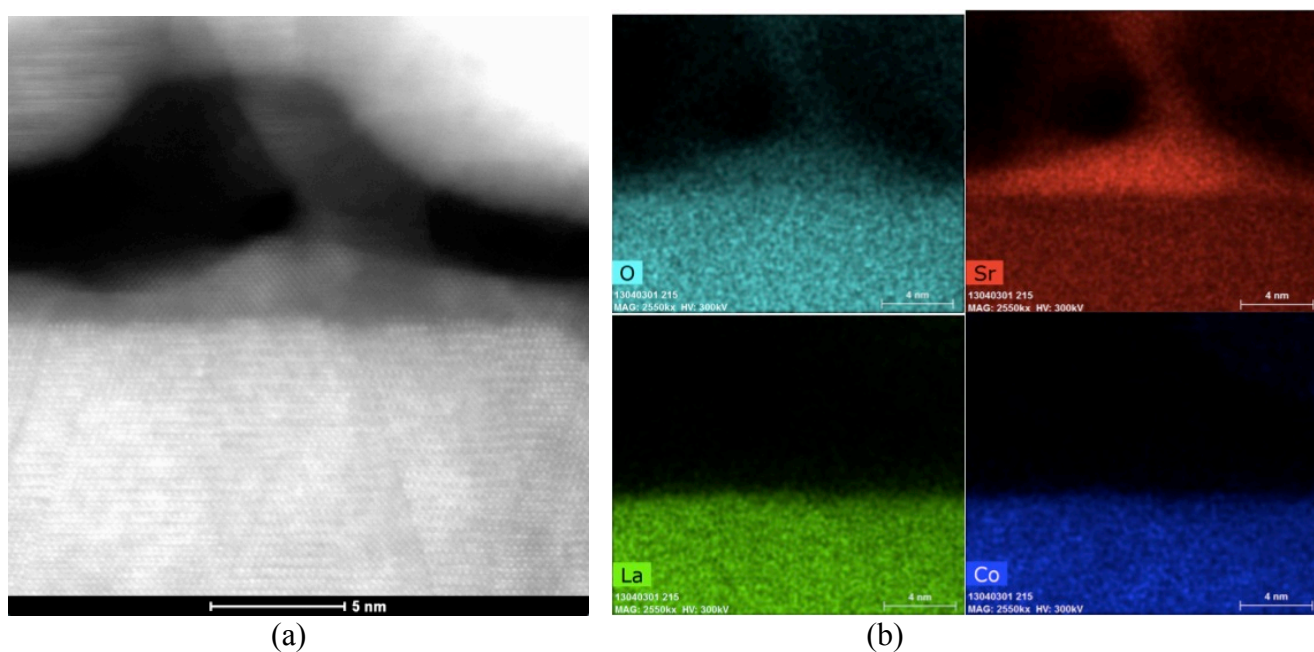


Figure 1. (a) STEM image of a dome-shaped feature with Sr/O rich phase on LSC214 film surface, (b)STEM-EDS analysis.

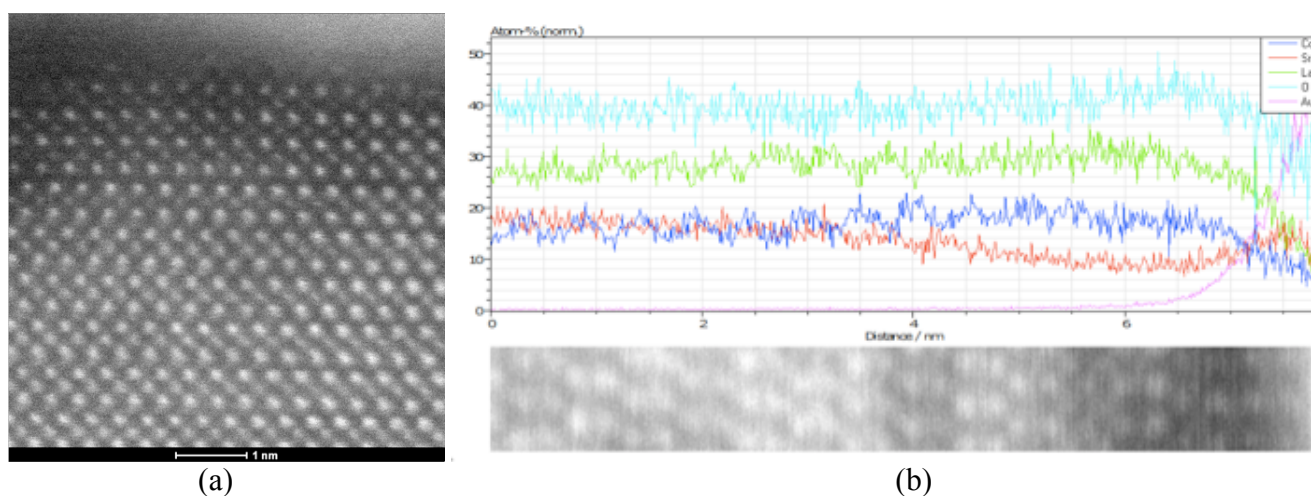


Figure 2. (a) STEM image of Perovskite structure on the surface of LSC214 film on STO substrate; (b) STEM-EDS analysis of the same region.