Atomic Resolution Transmission Electron Microscopy of Perovskite Nanoparticle Surfaces Exposed to Gas Environments at Elevated Temperatures.

Barnaby D.A Levin[1], Armando Cardenas[1], J. Mark Weller[1], Andrew Dopilka[1] and Peter A. Crozier[1]

[1.] School for the Engineering of Matter, Transport, and Energy, Arizona State University, USA.

Doped lanthanum cobalt oxide perovskites such as $La_xSr_{1-x}CoO_3$ (LSC) are among the most promising materials for intermediate temperature solid oxide fuel cell (SOFC) cathodes [1]. However, segregation of strontium to the surface of LSC perovskites has been observed to occur during synthesis, and at exposure to elevated temperatures [2-3]. Surface strontium segregation degrades the ability of the perovskite to exchange oxygen at the perovskite-gas interface, reducing the activity for oxygen electrocatalysis [4-5]. Aberration-corrected scanning/transmission electron microscopy (S/TEM) may provide an atomic level understanding of the chemical, crystallographic, and morphological changes that occur at different surfaces of perovskites upon exposure to oxidizing and reducing atmospheres at elevated temperatures, which will help to guide the design of improved SOFC cathodes.

Using a molten-salt based synthesis [6], we have developed a novel method for preparing LSC using mixtures of alkali-metal nitrates, nitrites, and hydroxides as solvents. The resulting nanoparticles may be characterized at high resolution in TEM. Figure 1 shows high angle annular dark-field (HAADF) and bright-field (BF) STEM images of an as-synthesized cubic LSC nanoparticle exhibiting (100) and (110) facets. In the BF-STEM image, a thin (< 1 nm) layer of material is visible on both the (100) and (110) surfaces of the nanoparticle. X-ray energy dispersive spectroscopy (XEDS) line profiles across the both (100) and (110) surfaces indicate that this surface layer is rich in strontium. Electron energy-loss spectroscopy (EELS), acquired from a second nanoparticle, shows a shift of the cobalt L-edge to lower energies at both the (100) and (110) surfaces (Figure 2). This shift suggests a reduction in the oxidation state of cobalt at the surfaces of the LSC particles [7], which may correspond to an increased concentration of oxygen vacancies at the surfaces.

Our goal is to examine chemical and structural changes to the surfaces of LSC particles under different conditions. Identical location *ex-situ* STEM and EELS will allow us to track changes in the composition of the surfaces of LSC nanoparticles after exposure to oxidising and reducing atmospheres at elevated temperatures. Furthermore, *in-situ* TEM will allow us to observe changes in atomic structure that occur on the surfaces of these particles *during* exposure to different atmospheres at elevated temperatures. Our results will provide important feedback to help guide the design of more durable perovskite cathodes for SOFCs [8].

References:

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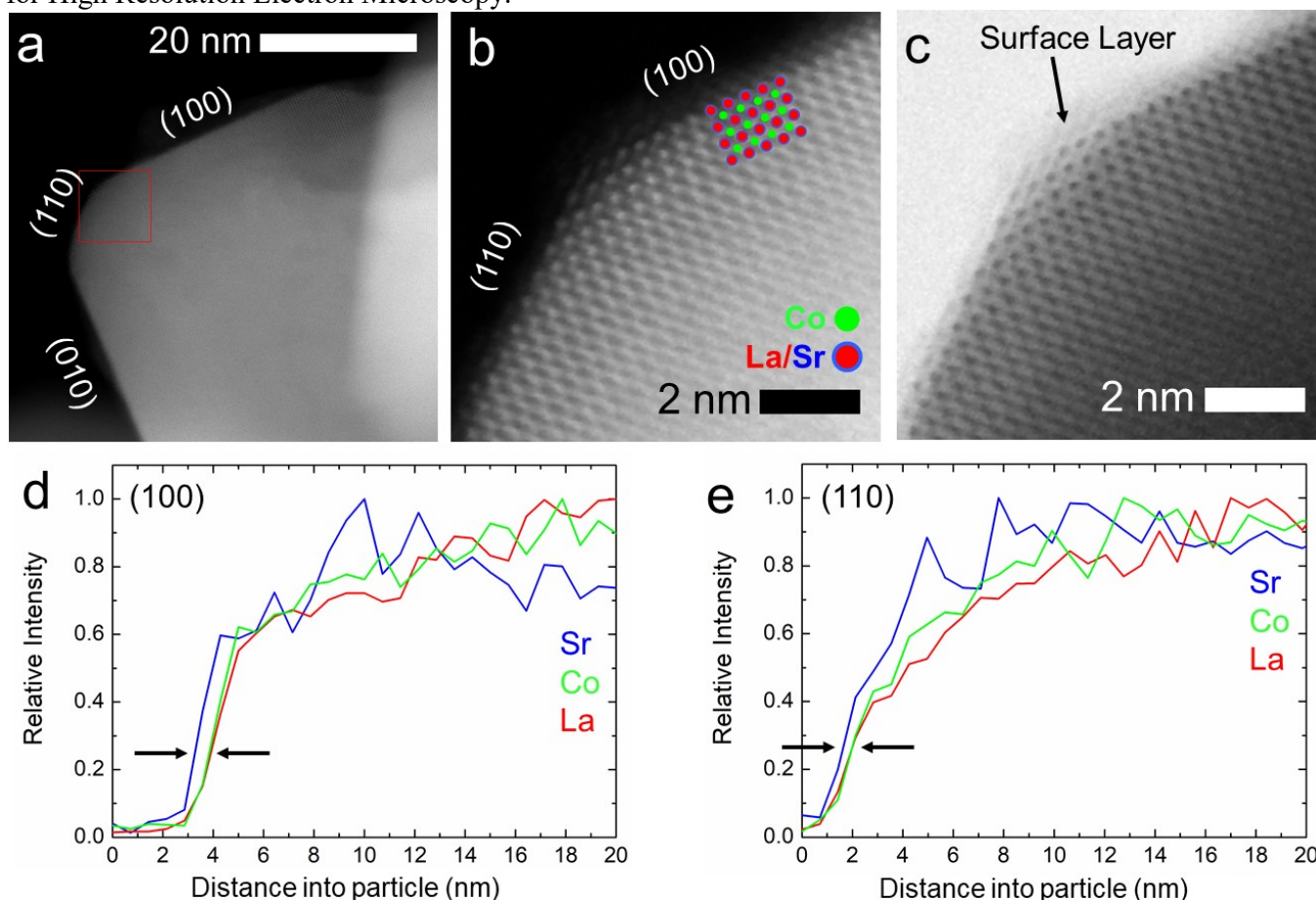
for High Resolution Electron Microscopy.

Figure 1. **(a)** HAADF-STEM image of an as-synthesized cubic LSC nanoparticle. Some of the facets of the particle are labeled. **(b)** Magnified HAADF-STEM of the area from (a) marked by the red box. Atomic structure is visible at both the (100) and (110) surfaces of the particle. The relative positions of La/Sr and Co columns are shown in the overlay. **(c)** BF-STEM image from the same area as (b). In this imaging mode, a layer of material is visible on the surface of the particle. **(d)** and **(e)** XEDS line profiles across the (100) and (110) surfaces. The early onset of the Sr signal suggests that the surface layer is Sr rich.
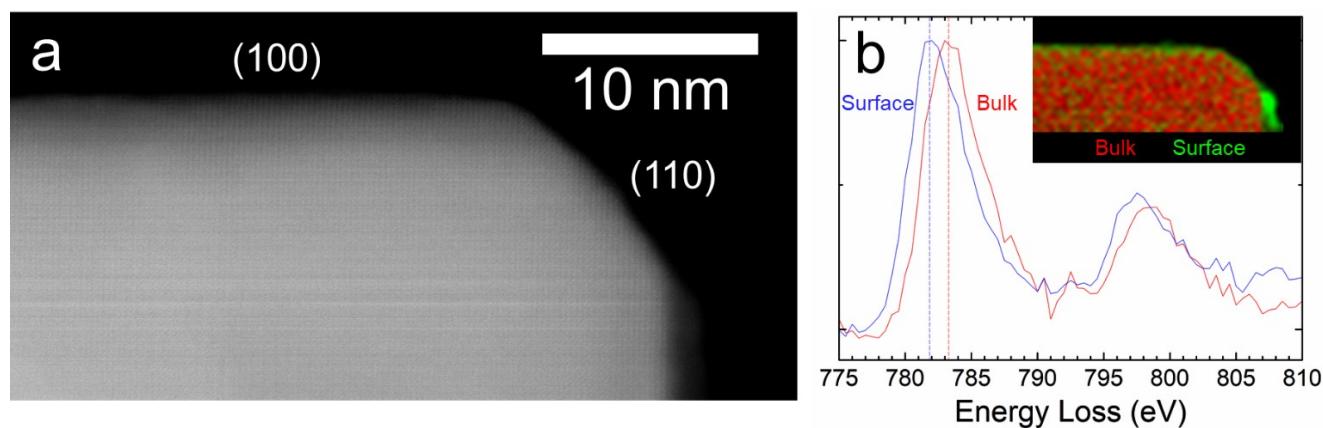

Figure 2. (a) HAADF-STEM image of an LSC nanocube with the (100) and (110) facets labeled. **(b)** Cobalt L-edge electron energy loss spectra showing the different profiles observed on the surface, and in the bulk of the particle. The inset shows a color overlay map of the two profiles.