High temperature solid oxide fuel cells (SOFCs) are a commercially viable electro-chemical alternative for distributed power applications. The cathode of a SOFC is responsible for electroreduction of dioxygen and subsequent transport of $O^2-$ to the electrolyte [1,2]. Impedance spectroscopy data from epitaxial perovskite thin film cathodes, with composition La$_{0.8}$Sr$_{0.2}$CoO$_3$, showed improved electrocatalytic properties as well as higher oxygen non-stoichiometry when compared to bulk LSC [3]. Pulsed laser deposition (PLD) was used to deposit 40-50nm thick (La,Sr)$_2$CoO$_3$ (noted LSC$_{113}$) films on yttrium stabilized zirconium (YSZ) substrates prepared with a ~5nm Gd doped cerium oxide (GDC) buffer layer. Thin films of LSC$_{113}$ thin films capped with LSC$_{214}$ ((La,Sr)$_2$Co$_3$O$_4$) layers of varying thickness were also synthesized on GDC/YSZ substrates. This study was undertaken to better understand the nano- and pico-scale mechanisms responsible for improved electrocatalytic properties and document the atomic structure and elemental composition of the near surface, bulk, and electrolyte interface regions of complex oxide thin film SOFC cathodes.

Atomic resolution imaging and chemical analysis of the thin film cathode materials was done by scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) imaging, bright field imaging (BF), and electron energy loss (EEL) spectrum imaging. Micrographs and EEL spectra were acquired using a FEI Titan S 80-300 with a CEOS aberration corrector and GIF Quantum with dual EELS, and a Nion UltraSTEM with Gatan Enfina. Energy dispersive X-ray spectroscopy (EDS) experiments were also conducted with a Hitachi HF3300 and a Noran SiLi detector.

The LSC$_{113}$ thin film, ~15nm LSC$_{114}$ surface layer, GDC buffer layer, and YSZ substrate are clearly observed in FIG. 1A. The thin film contains nano-scale domains and domain boundaries that continue from the GDC buffer layer into the epitaxial surface layer (FIG. 1B). The difference in the atomic arrangement of LSC$_{113}$ perovskite unit cells and LSC$_{214}$ layered perovskite unit cells are seen in FIG. 1C. X-ray analysis of the SOFC thin film cathode material (FIG. 2) confirmed the presence of La, Sr, Co and O and an increased Sr signal in the LSC$_{214}$ layer. Structure modulation, parallel to the GDC/YSZ interface, was present throughout the entire thickness of the LSC$_{113}$ thin films (with or without LSC$_{214}$) and was determined to result in a unit cell expansion of ~15% and a unit cell contraction of ~10%, with a small net expansion of the average unit cell volume, attributed to oxygen vacancy ordering [4]. The relationship of electrocatalytic properties of the thin film cathodes, lattice expansion and LSC$_{214}$ layered perovskite surface layer will be discussed. [5]

References:
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FIG. 1. (above) (A) STEM BF micrograph of the SOFC cathode imaged in (100) orientation. The YSZ substrate is located on the left side of the image, the 5nm GDC buffer layer appears as dark contrast to the right of the YSZ substrate. Slight mis-orientation between grains of LSC$_{113}$ produced contrast and the ~15nm LSC$_{214}$ layer is located far right in this field of view. (B) STEM HAADF image of the LSC113 and LSC214 region of the cathode. (C) Atomic resolution STEM HAADF of the interface between the LSC$_{113}$ and LSC$_{214}$ films.

FIG. 2. (right) X-ray line scan, from the substrate, through the buffer, LSC$_{113}$ and LSC$_{214}$ layers as shown by the arrow in the BF image below the spectra. Each of the elements are present throughout the thin film region, but an increased Sr signal was detected in the LSC$_{214}$ region. The intense signal observed from data point position 0-20 is Y from the YSZ substrate.

FIG. 3. (A) STEM HAADF micrograph of a (100) orientated LSC thin film. Unit cell ordering in the ‘bulk’ region of the thin film was observed as indicated by arrows. From this image it was determined that 1pixel = 0.25Å. (B) Map of variations in unit cell dimensions from a 40 x 40 unit cell array chosen from (A). The light contrast pixels in the map indicate a decrease in unit cell dimension and the darker pixels an expanded unit cell. It is proposed that expansion and contraction of the unit cells is due to oxygen vacancy ordering.