Spatial Mapping of Co valence bias dependence in LSCF Cathodes

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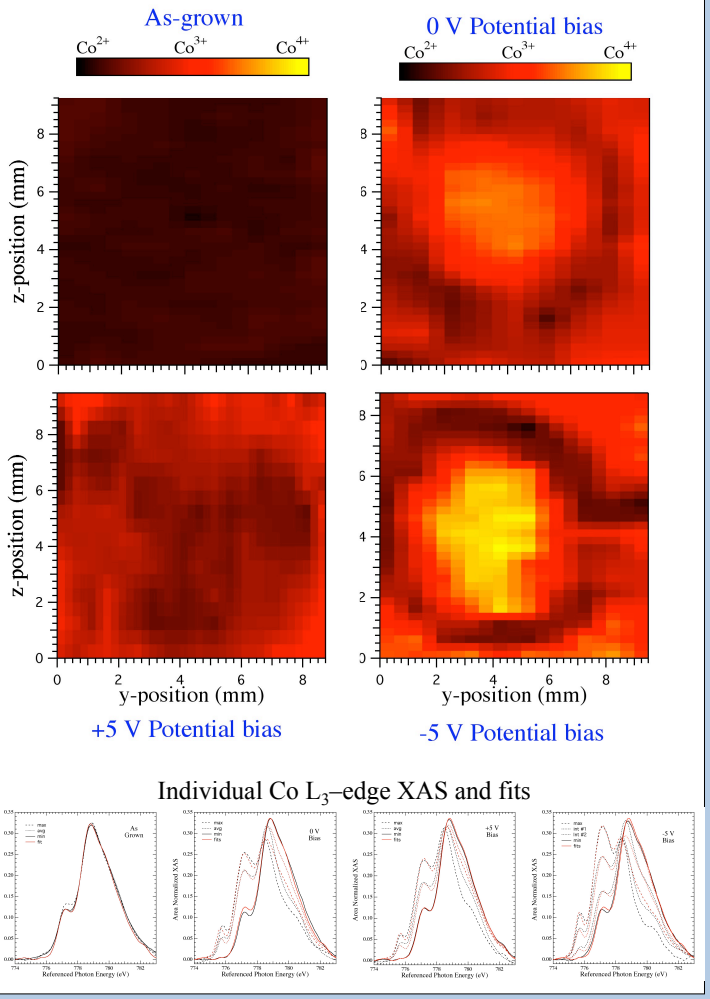
The Co valence of PLD deposited $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ films on GDC has been mapped with 250 μm resolution under different bias conditions (in the as-grown state, after 50 hours at 850 °C and 0 V bias, and after 50 hours at 850 °C and 500 mV bias). These large area (1 cm^2) valence mappings can be conducted in a few hours with the unique configuration of BL 6.3.1 at the the Advanced Light Source.

XAS Results

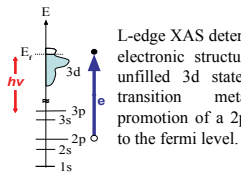


Conclusions

1. As-grown films are oxygen deficient, Co uniformly Co^{2+}
2. Annealing at 850 °C for 50 hrs with 0 V bias, Co valence changes to Co^{3+}, but varies substantially.
3. Operation for 50 hours at 850 °C and 500 mV bias, Sr segregation larger on the oxygen dissociation side with Co valence observed to be nearer to Co^{2+} while on the oxygen recombination the valence is nearer to Co^{4+}.
4. **Spatial variation attributed to oxygen availability**.

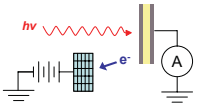
X-ray absorption process

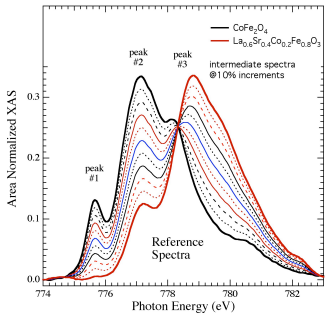
X-ray Absorption Spectroscopy (XAS) provides for element specific electronic structure determination. Decomposition of the Co valence in a multi-valence system can be accomplished by comparison with measured or calculated reference standards and fitting. Below is shown measured XAS spectra for fully stoichiometric LSCF (6428) and $CoFe_2O_4$ and mixed compositions. These two reference spectra are used to fit the measured Co L_3-edge spectra at different applied potentials.



L-edge XAS determines the electronic structure of the unfilled 3d states of the transition metals by promotion of a 2p electron to the fermi level.

Total Electron Yield (TEY) detection.





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