

Examining Defect Creation at Interfaces in Electrocatalytically Cycled LaFeO₃-SrTiO₃ Thin Films

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Precise control of defects is paramount for control and manipulation of quantum phenomena. Understanding defect formation and evolution at interfaces predicated our ability to understand and control properties in thin films and devices. In complex oxides, atomic scale interfacial defects can be caused by extreme environments such those encountered in catalytic cycling. To gain precise property control, it is important to understand the structural and chemical signatures associated with different defect types. LaFeO₃ (LFO) is a novel perovskite system with strongly defect-regulated catalytic properties, making it a rich system for exploring defect manipulation. Here we examine cation and oxygen defect populations near interfaces in single-crystal LFO grown on (001)-oriented SrTiO₃ substrates and how they change after electrocatalytic cycling.

Scanning transmission electron microscopy (STEM) analyses are conducted using multiple modes of high-angle annular dark field, bright field, and annular bright field imaging to visualize the material microstructure. To complement imaging, local chemical and composition mapping is performed using electron energy loss spectroscopy (STEM-EELS). Our STEM-EELS measurements focus primarily on the O K edge, which is highly sensitive to local bonding and oxygen coordination environment, but we also examine the Fe-L edges to discover how cation states evolved. Imaging revealed no significant microstructural changes. In both cycled and uncycled films, we observed clear differences in EELS in LFO between the surface, middle, and near the film interfaces as well as differences between the cycled and uncycled films. In the uncycled sample, we observed a shift to higher energy loss of the O-K edge near the substrate interface and a shift to lower loss in the Fe-L edges indicating a reduction of cations near the substrate. A similar shift in the Fe-L edges were seen in the cycled sample, but the shifts in the O edges were to lower loss as well as there was distinct change in line shape.

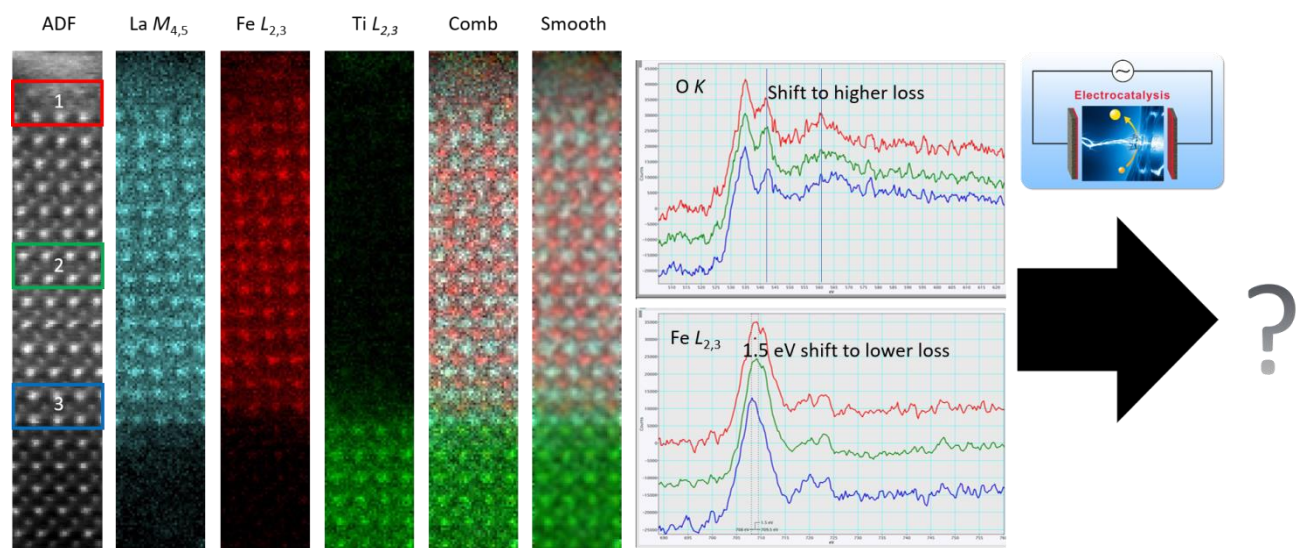


Figure 1. EELS spectra for the uncycled LFO film comparing the surface, middle, and film/substrate interface. The samples were then electrocatalytically cycled to determine how cycling affected defects in the film.

References

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