

TITLE: In situ Synchrotron X-ray Characterization of Potential-dependent Cation Segregation and B-site Surface Oxidation State in Model Thin-film Perovskite Cathodes

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ABSTRACT:

We used pulsed laser deposited films of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSCF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) on single crystal yttria-stabilized zirconia (YSZ) substrates as model cathodes to better understand the surface processes under solid oxide fuel cell operating conditions. We designed a new electrochemical half cell for in situ X-ray scattering, fluorescence and spectroscopy. This cell is specifically designed to perform X-ray measurements with the cathode currents flowing out-of-plane or in-plane directions of the PLD film. The new cell enables us to better delineate the surface processes of the air-film interface vs. bulk processes normal to the film under solid oxide fuel cell operating conditions. To avoid transient effects, we applied -1V of applied potential in the in-plane direction for ~72 hours at 700°C on our samples before the in situ experiments. Ex situ characterization of these samples showed B-site (Mn in LSM and Co in LSCF) surface segregation with a change in surface B-site oxidation state compared with the bulk. These trends were verified with further in situ LSCF experiments where we were able to observe the segregation/desegregation of the Co compared with Fe and the accompanying Co oxidation state changes under cathodic/anodic potential. We also observed changes in the lattice parameter of the LSM and LSCF due to applied potential which showed different in-plane and out-of-plane effects.