

Solid Oxide Fuel Cell Cathodes: Unraveling the Relationship between Structure, Surface Chemistry and Oxygen Reduction.

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In the pursuit of a complete understanding of solid oxide fuel cell (SOFC) operation, the complex nature of the oxygen reduction reaction has emerged as both an important, and as yet, intractable problem. To fully understand the dynamic nature of this reaction, an understanding of the dominant rate-limiting step(s) that appear(s) to occur at the gas exposed cathode surface, it is of fundamental importance to exploit its role during operating conditions. This can only be accomplished by taking a multi-disciplinary approach – examining the problem from both an electrochemical (i.e. device performance) and surface science (i.e. structural) perspectives. Towards this end the following questions are posed: What changes occur to the surface chemical composition and the oxidation states of cations in a SOFC cathode as a result of the oxygen reduction reaction (ORR)? Similarly, what changes to the surface crystal structure occur and how are they related to the ORR?

The presented work displays results of our preliminary experiments to answer the above questions. Heteroepitaxial thin-film samples of 20% Sr-doped LaMnO₃ have been grown on both LaAlO₃ (001) and 9mol% yttria-stabilized zirconia (YSZ (111)) single crystals using pulsed laser deposition. The quality of these films has been confirmed using x-ray diffraction (XRD) and transmission electron microscopy (TEM). Compositional inhomogeneities between the surface and bulk as a result of heating to 800°C have been investigated using in-situ total reflection X-ray fluorescence (TXRF) at the National Synchrotron Radiation Light Source (NSLS). Using soft x-ray techniques, we have begun to investigate the role of cations in the ORR. Using x-ray emission and absorption spectroscopy (XES and XAS respectively) combined with resonant photon emission spectroscopy (RPES) on samples that have been heated or heated and subjected to a DC bias before being rapidly quenched, clear differences in the Mn charge states were observed. This correlates with a large reduction in the total polarization resistance monitored by electrochemical impedance spectroscopy. Further, we have also obtained oxygen surface exchange coefficients using electrical conductivity relaxation (ECR) and diffusivities using O-18 annealing experiments. These results will eventually be correlated with the oxygen reduction reaction occurring at the cathode surface.