Chemical and Electrochemical Properties of La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ (LSCF) Thin Films upon Oxygen Reduction and Evolution Reactions

The Oxygen Evolution and Oxygen Reduction Reactions (OER/ORR), occurring at the oxygen electrode of Solid Oxide Cells (SOCs) in the two possible ways of operation, require substantial overpotentials, therefore lowering the operating efficiency of the cells. The reaction mechanisms occurring at these electrodes are still not completely understood due to their complexity and localized character at the interfaces between different materials or between the gas atmosphere and the electrocatalyst, and need in situ techniques with very high chemical sensitivity, with the additional difficulty of probing the materials as close as possible to their realistic operating conditions. In addition, the properties of LSCF are, despite numerous studies, still unclear in many aspects, despite LSCF being one of the state-of-the-art electrocatalysts used for SOCs. It is understood that the surface chemical composition deviates from the nominal bulk composition, and that secondary phases can segregate at the surfaces and interfaces during operation. Furthermore, the electrochemical properties such as Area Specific Resistance (ASR), oxygen exchange coefficient ($k_{ex}$), ASR activation energy ($E_a$) and $pO_2$ exponents for LSCF reported in the literature vary considerably. This study aims to better understand the properties of LSCF, by combining the results of Electrochemical Impedance Spectroscopy (EIS) and Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) on model electrodes, both in polarized and unpolarized conditions. In particular, NAP-XPS studies of the surface chemistry evolution under operation, as well as the correlation between surface potential changes in relation to the applied overpotential are addressed, in an attempt to determine the real driving force for the oxygen reactions. For this purpose, thin films of LSCF are deposited by Pulsed Laser Deposition (PLD) through shadow masks, in order to obtain well-defined electrode geometries with low risk of contamination, and subsequently tested both in highly clean EIS measuring setups and at the synchrotron beamline. The results of both kinds of experiments are correlated, the goal being a better understanding of the material's properties under operation, as well as possible degradation phenomena.