

ABSTRACT

Quantification of Point Defects in Mixed Conducting Oxides with Photon and Electron Spectroscopies

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In mixed conducting, nonstoichiometric oxides the identification and quantification of ionic and electronic charge carriers and their evolution during electrochemical processes have become a routine application for *in situ* and *operando* X-Ray based spectrosopcies.[1]. Unfurtunately, direct quantification is not straight forward, and comparing results from conventional electrochemical methods to those obtained from X Ray absorption (XAS) or photoelectron spectroscopy (XPS) can seemingly show discrepancies.[2] In this contribution, we will use $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) as an example how to derive a quantitative defect model of the near suface region from XAS and XPS. We will show that the electron hole concentration, which plays a major part in the oxygen exchange reaction, is in accordance with the bulk defect chemistry, a surprising result since the discontinuity at the gas-solid interface would suggest differently. We propose that the ability of LSF to maintain the bulk defect chemistry at the near surface region stems from the A-site sublattice at the surface dynamically reacting to changes in oxygen partial pressure and temperature, namely the Sr to La ratio and precipitation of Sr rich phases creating A-site vacancies, which in turn can "buffer" the electron hole concentration. In addition, we were able to track these A-site surface rearrangements with time resolved in situ XPS, showing that these reactions take place at the same time scale as the oxygen exchange itself.

[1] D. N. Mueller, in Applications of X-ray Photoelectron Spectroscopy to Catalytic Studies, Catalytic Science Series Vol. 21, p. 457, S. Zafeiratos, Ed. (World Scientific, Singapore, 2023)
[2] R. A. De Souza, D. N. Mueller, Nat. Mater. 20, 443–446 (2020).