FLAIR Colloquium

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Room R4/23, Building L6|01

What X-Rays spectroscopy can tell us about point defects (and what not)

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X-Ray spectroscopies such as absorption and photoemission (XAS and XPS, respectively) have long been used to determine the electronic structure of complex materials. In nonstoichiometric oxides, the identification and quantification of ionic charge and its evolution during electrochemical processes have become a routine application of these methods, especially since spectroscopy at elevated temperature and pressures have become possible and more and more readily available. Unfortunately, the results obtained from XPS and XAS sometimes deviate considerably from those obtained from classical electrochemical methods [1] which can be attributed to the simple fact that both techniques probe different things [2]: XAS and XPS cannot probe an isolated atom or ion in a material but rather how it is present in its immediate surrounding. Oxygen K-edge XAS, for example, is highly sensitive to the immediate coordination and symmetry. This leads to the realization that those spectroscopic tools can be used to identify properties and processes that are far beyond the concept of an oxidation state, and thus should be used complimentary to, rather than supportively of electrochemical methods.

In this presentation I will first show how the seemingly straightforward use of XPS and XAS to determine ionic charge or oxidation states can lead to misinterpretations, but then expand on how the origin of these provides insights into peculiar properties of mixed conducting perovskite materials used in electrochemical devices. In the oxygen separation membrane material $Sr(Ti,Co)O_{3-\delta}$, for examples, Oxygen K-edge XAS revealed a percolation mechanism of the electronic conductivity, while in the cathode material $(Pr,Ba)CoO_{3-\delta}$, X-Ray microscopy revealed a nanoscopic decomposition process [3]. I will further show how multivariate statistical analysis methods can assist in extracting significant information from huge datasets collected by these techniques.

[1] A. Walsh, A. A. Sokol., J. Buckeridge, D. O. Scanlon, C. R. Catlow, *Nat. Mater.* **2018**, *17*, 958-964.
[2] R. A. De Souza, D. N. Mueller, *Nat. Mater.* **2020**, *20*, 443–446.
[3] D. N. Mueller *et al.*, J. Phys. Chem. C **2021,** 125, 10043-10050.