Report experiment MA 4681

"O-Kedge XRS measurement on $Ba(Zr_{0.88-x}Y_{0.12}Fe_x)O_{3-\delta}$"

We performed XRS measurements on novel material compositions with cubic perovskite structure to be potentially used as cathodes in Protonic Ceramic Fuel Cell (PCFC). These contain barium in the A-site and iron, zirconium and yttrium in the B-site. The amount of yttrium is fixed instead the one of zirconium and iron is variable.

We measured $BaZr_{0.88-x}Y_{0.12}Fe_xO_{3-d}$ samples with Fe content of x = 0.03, 0.06, 0.1, 0.3, 0.7 (with iron in Fe^{3+} oxidation state) and x = 0.06, 0.3, 0.7 (with iron in Fe^{4+} oxidation state). These data will be complemented with the EXAFS experiment to be performed at the beginning of next year (MA 4582).

XRS already prooved to be a useful tool to directly probe the electronic states involving the oxygen and the transition metal **[1]** allowing an understanding of the TM-O bond covalence in similar materials. This quantity is important for the propensity of proton incorporation.

The data are collected at the O *K*-edge (530-565 eV) with an incident energy at 9.7 KeV.

Relevant spectra for the O *K*-edge are reported in **Figure 1**.

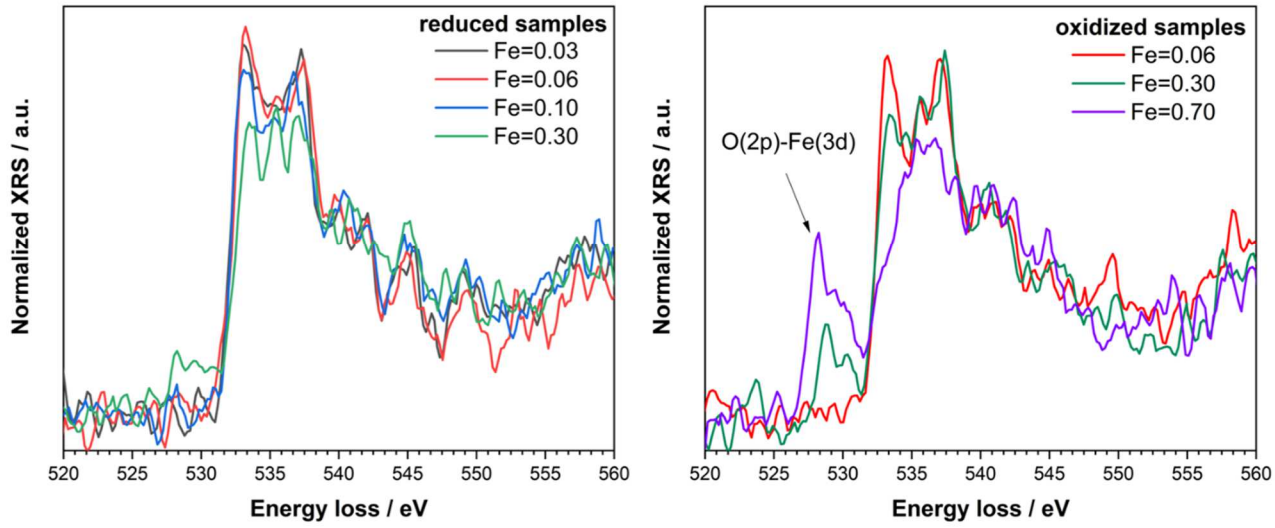

Figure 1. Normalized XRS of the extracted data for reduced samples (left) and oxidized samples (right).

Figure 1 demonstrates how the amount and the formal oxidation state of iron influence the oxygen electronic states. In particular, the pre peak at ≈527 eV (hybridization of oxygen 2p and iron 3d orbitals) is:

(i) Absent for reduced samples independent of the quantity of iron.
(ii) Increasing its magnitude with increasing quantity of iron for oxidized samples.

We plan to perform simulation for these data using the FDMNES package and more details will be provided in the future.

[1] Raimondi, G., Giannici, F., Longo, A., Merkle, R., Chiara, A., Hoedl, M.F., Martorana, A. and Maier, J. X-ray spectroscopy of (Ba,Sr,La)(Fe,Zn,Y)$O_{3-\delta}$ identifies structural and electronic features favoring proton uptake. *Chemistry of Materials*. **(2020)**.