



	Experiment title: Structural effects of protons and dopants in mixed-conducting fuel cell cathodes	Experiment number: MA-4015
Beamline: BM26A	Date of experiment: from: 09/07/2018 to: 13/07/2018	Date of report: 25/02/2020
Shifts: 9	Local contact(s): Alessandro LONGO	<i>Received at ESRF:</i>
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Report:

Perovskite materials with cubic structure, to be used as cathodes in Proton Ceramic Fuel Cell (PCFC), were measured in this experiment on the BM26A beamline @ ESRF. These materials contain barium and lanthanum in the A-site and iron and zinc in the B-site.

The samples being measured are: $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ (BL5F), $\text{Ba}_{0.75}\text{La}_{0.25}\text{FeO}_{3-\delta}$ (BL25F), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (BSFZn20), $\text{SrFe}_{0.8}\text{Zn}_{0.2}\text{O}_3$ (SFZn20), $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (BL5FZn20), $\text{BaFe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BFY20).

All the samples were measured in the oxidized (all iron ions in the 4+ oxidation state) and reduced (all iron ions in the 3+ state), instead for BL5FZn20 and BFY20 measured also in hydrated and dry conditions.

It was demonstrated by Zohourian et al. [1] that 5-25% of lanthanum in the A-site of the perovskite prevents the formation of the hexagonal structure known to be detrimental for the proton uptake process, this justifies the presence of this rare earth element in samples BL5F and BL5FZn20, in the BFY20 the Y^{3+} itself can stabilize the cubic structure.

Ref [1] shows that substituting Zn on the B-site of BL5F significantly increases the proton uptake (much strongly than expected from the relative oxygen vacancies increase, since Zn^{2+} acts as an acceptor) thus probably (i) the presence of a redox inactive cation with full d orbitals, (ii) the possible lattice local distortions since Zn^{2+} is larger than Fe^{3+} and (iii) the lower electronegativity of the zinc, affect the proton uptake.

All the samples were measured at the Fe K-edge, using $\text{SrFeO}_{3-\delta}$ (SFO), Fe_2O_3 and FeO as standards for Fe^{4+} , Fe^{3+} and Fe^{2+} . Additionally, Zn- containing and Y-containing samples were also measured at the Zn K-edge and Y K-edge. All the assigned beamtime was used and we were able to measure all compositions with a good signal to noise ratio.

The Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectrum contains information on the average coordination and oxidation state of iron.

In **Figure 1** the Fe K-edge XANES spectra of all the samples are reported, highlighting edge energy changes. The charge transfer changes along the Fe-O bond were investigated independently in the O K-edge measurements at ID20 during the experiment MA-4144.

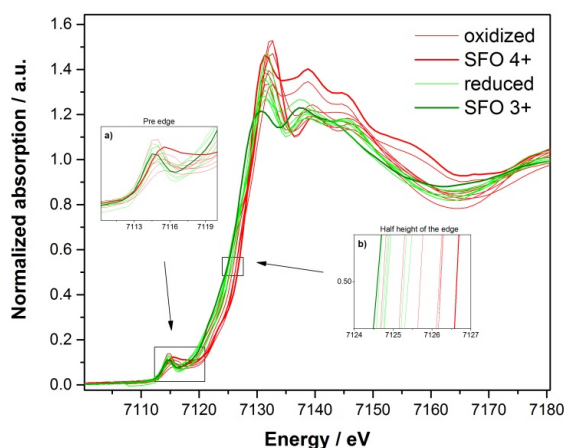


Figure 1. XANES of the iron K-edge of the reduced samples (light green), oxidized samples (red), SFO red (olive, bold) and SFO ox (red, bold). Inset a) is the magnification of the pre edge. Inset b) shows the half height of the edge.

The EXAFS signals of all samples, which contain information on the atomic structure, were fitted up to the third shell (about 4.2 Å) around Fe, Zn, and Y using a cubic perovskite model with the corner sharing octahedra. Multiple scattering along the perovskite colinear paths Fe-O-Fe-O were necessary to achieve satisfactory fitting on the third shells. Representative fits for the different measured edges are shown in **Figure 2**.

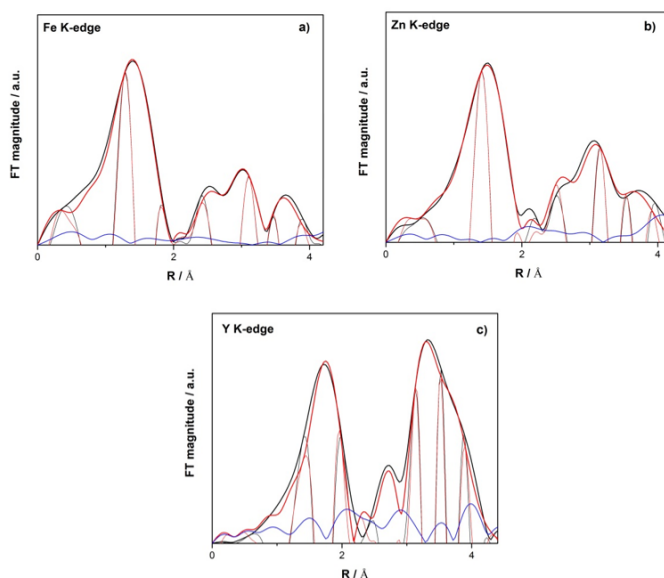


Figure 2. Representative FT EXAFS data and fittings on the Fe, Zn and Y K-edges. Experimental data are reported in black, fitting in red, and residual in blue.

With this experiment we were able to demonstrate that there are local distortion in barium ferrite perovskites when doped with oversized redox inactive cations such as zinc or yttrium. The local distortions influence strongly the proton uptake capability of the material by tuning the oxide ion basicity. More insight on this topic will be given with a paper in preparation which includes also the results at the O K-edge.