



	Experiment title: Interdiffusion and reaction across an annealed electrolyte/cathode interphase for solid-oxide fuel cells	Experiment number: ME-1351
Beamline: ID21	Date of experiment: from: 19/02/2014 to: 25/02/2014	Date of report: 03/03/14
Shifts: 18	Local contact(s): Murielle Salomè	<i>Received at ESRF:</i>
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Report:

Samples were prepared by placing two sintered flat surfaces of electrolyte ($\text{La}_{0.8}\text{Ca}_{0.02}\text{NbO}_4$, LNC) and cathode ($\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ – LSM) in contact, and aging the bilayer at high temperatures (1100-1250 °C) for several hours (12 to 72 h). The bilayer was then cast in resin, cross-cut to expose the interface and polished at < 1 micron roughness.

We measured microXANES spectra at the following edges: Nb L₃, La L₃, Mn K. The fluorescence maps for other elements present in the samples (namely: Sr, Ca) were collected as well, provided that their emission lines were excited at the absorption edge under consideration. On the Nb L₃-edge only a microXANES signal was collected, but the edge features proved extremely sensitive to changes in coordination state (see figure 1). As it is evident from the plot, the spectrum on the LSM part of the bilayer shows the typical double-edge feature of octahedrally-coordinated Nb⁵⁺ as found in the perovskite B-site.

For this reason, we also acquired fluorescence maps at two energies coordination states (2377 and 2450 eV, corresponding to octahedrally-coordinated and total Nb⁵⁺, respectively). These are reported in figure 2: it can be seen that immediately out of the LaNbO_4 parent phase Nb⁵⁺ adopts a coordination that is typical of a perovskite environment.

On the La and Mn edges, we could also collect microEXAFS signals up to about 8 Å⁻¹. In some cases, they proved much more valuable than the edge features alone to discriminate between two different coordination states (see figure 3).

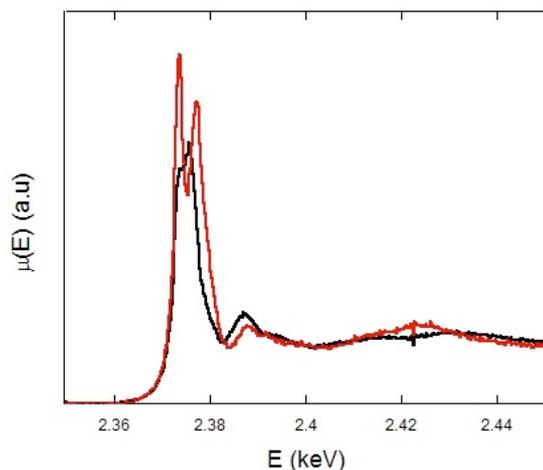


Figure 1 – Normalized microXANES spectra at the Nb L_3 -edge: in the LNC side (black line), and in the LSM side (red line).

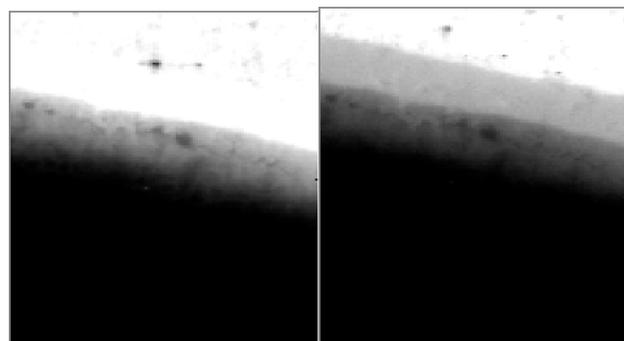


Figure 2 – Fluorescence maps at the Nb L_3 -edge: on the left, the map at 2377 eV; on the right, the map at 2450 eV.

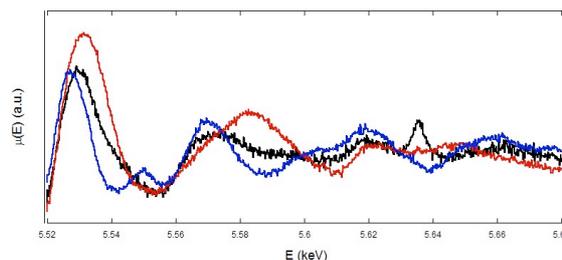


Figure 3 – microEXAFS on the La L_3 -edge in different points of an LSM/LNC sample.

The experiment was successful in the following points: 1) we applied microXANES and microEXAFS to the problem of electrode-electrolyte compatibility for the first time: this is a key point in materials research and development for energy applications; 2) a complete mapping of concentrations and coordination state was obtained for all cations and all samples, confirming that Mn^{3+} is not incorporated in LNC, while Nb^{5+} shows changes in its local structure and diffuses to great lengths towards the cathode. The Mn microXANES data also showed changes that will be analyzed quantitatively through comparison with literature data to assess the oxidation state and the number of oxygen vacancies in its first coordination shell.

The present results represent the first application of microfocus X-ray absorption spectroscopy to the study of cathode-electrolyte compatibility in solid-oxide fuel cells. The beam size available on ID21 (less than $0.5 \mu m^2$) and the s/n ratio proved well suited to this study, and allowed us to extract information at an unprecedented detail as what concerns the spatial distribution and coordination state of different cations in an interface modeling a working device: a first brief communication containing the main results of this experiment was published on *Chemistry of Materials*. [1]

We plan to extend the present study to other kinds of electrode materials, including ceramic anodes, cermets, and oxide-ion conductors, reproducing different working conditions of real devices: this will provide unprecedented insight on the mechanisms governing electrolyte-electrode compatibility and electrochemical performance in solid oxide fuel cells.

A future extension of the beamline energy range up to the end of the first transition metal series (Co, Ni, Cu) would open tremendously the possibility to study materials of high technological interest for energy applications (e.g. composite anodes containing Ni/NiO or Cu/CuO, cathodes based on La_2NiO_4 and $LaCoO_3$, etc.).