



	<b>Experiment title:</b> Microscopic compatibility and cation diffusion between ferrite cathodes and proton-conducting LaNbO <sub>4</sub> for solid oxide fuel cells	<b>Experiment number:</b> ME-1373
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 04/02/2015 to: 10/02/2015	<b>Date of report:</b> 14/02/15
<b>Shifts:</b> 18	<b>Local contact(s):</b> Giulia Veronesi	<i>Received at ESRF:</i>
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## Report:

Samples were prepared by placing two sintered flat surfaces of electrolyte (La<sub>0.8</sub>Ca<sub>0.02</sub>NbO<sub>4</sub>, LNC) and cathode in contact, and aging the bilayer at high temperatures (1100-1250 °C) for several hours (12-144 h). The cathodes under investigation are doped lanthanum ferrites, namely: La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> (LSCF) and La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.9</sub>Cu<sub>0.1</sub>O<sub>3</sub> (LFCu). The bilayer was then cast in resin, cross-cut to expose the interface and polished at < 1 micron roughness.

We measured microXRF maps and microXANES spectra at the K-edges of Ca (4 keV) and Fe (7 keV). At the Fe K-edge, the fluorescence maps for all other elements present in the samples were collected as well, except for Cu, whose K emission lines were not excited at this energy range.

The beam was monochromatized with Si(220) crystals, and focused with KB mirrors down to 0.4 x 0.7 μm<sup>2</sup>. MicroXRF maps were acquired with a minimum 0.25-0.5 μm step. At the Ca<sup>2+</sup> edge, the horizontal beam size increased to about 1.4 μm, which was possibly due to worsening KB performance.

The main observations concerned the diffusion of Ca<sup>2+</sup> and Nb<sup>5+</sup> from LNC towards the cathode, and the diffusion of Sr<sup>2+</sup> and Fe<sup>2+/3+</sup> in the opposite direction. In some cases, the interdiffusion regions extended for more than 50-100 microns, and large microXRF maps (about 300 x 300 μm<sup>2</sup>) were collected. Apart from simple diffusion, the formation of definite secondary structures was also observed in the maps, with clearly layered interfaces. MicroXANES signals collected in different regions confirmed that the coordination states

(and possibly oxidation state, in the case of Fe) are critically affected by the interdiffusion. MicroEXAFS signals were also collected up to about 9-10 Å<sup>-1</sup>.

The experiment was successful in the following points: 1) after applying microXANES and microEXAFS to the problem of electrode-electrolyte compatibility for the first time in our previous experiment (ME-1351), and detecting the unexpected accumulation of the Ca<sup>2+</sup> dopant away from LNC towards LSM, we confirmed that the same effect exists also when LNC is annealed in contact with other perovskite cathodes; 2) sparse data exist in the literature concerning the near-edge and EXAFS analysis of Ca<sup>2+</sup> in ceramic materials: with this experiment, we plan to confirm directly a solid-state mechanism of incorporation of Ca<sup>2+</sup> by perovskite cathodes in contact with LNC, possibly limiting the electrolyte performance.

About 8 samples were analyzed on both Fe and Ca edges, collecting 20 microXRF maps and about 180 microXANES and microEXAFS spectra on selected points.

We also investigated the electrolyte Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2</sub> (SDC) in contact with the cathodes LSCF and LSFCu, on the Fe K-edge and Ce L<sub>3</sub>-edge. The fluorescence maps (Fig. 1) show the formation of islands enriched in Fe and Sm in the SDC area when in contact with LSCF, while LFCu present a large diffusion region.

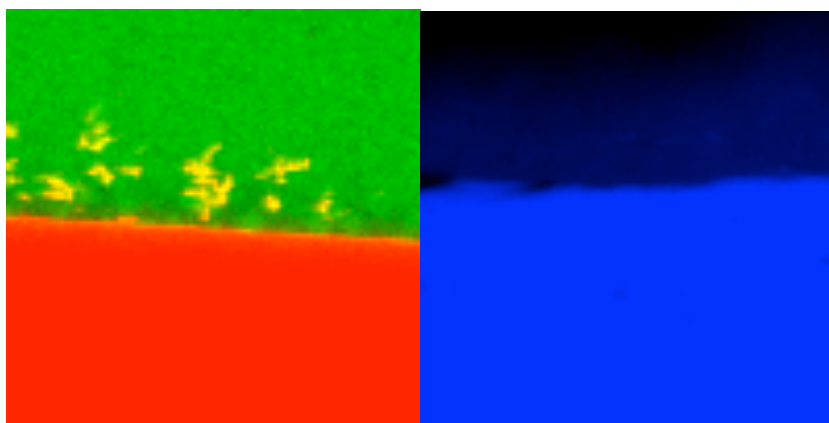


Figure 1 – Left: Fe (red) and Sm (green) cluster together after Fe diffusion in SDC. Right: Fe diffusion in SDC/LSFCu (SDC above, LSFCu below). Maps: 100 x 100 microns.

The microXANES spectra show the transition from Ce<sup>4+</sup> to Ce<sup>3+</sup> on crossing the interface from SDC to the cathodes.

These latter results have been submitted recently to *ACS Applied Materials and Interfaces*. Another manuscript focusing on LNC/LSCF is currently in preparation.