ESRF	**Experiment title:** Where does the unique CO2 senistivity of La2O2CO3-based sensors come from? – spectroscopic and electrical investigations	**Experiment number**: MA1777
Beamline: ID26	**Date of experiment**: from: 21.07.2013 to: 31.07.2013	**Date of report**: Updated on 27.08.2014
Shifts: 18	**Local contact(s)**: Pieter Glatzel	*Received at ESRF:*

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Report:

This is an updated report pointing out the progress in analysis and dissimination of the results obtained at the beamtime.

We studied the mechanism of CO_2 interaction with lanthanum oxycarbonate based sensors. We carried out in-situ HERFD-XAS and valence band RIXS at the La L_3 edge. The Lα1 transition and absorption were recorded by monitoring the Lα1 intensity. All the in-situ experiments were performed at 250°C operating temperature and in 50% humid air and different CO_2 concentration.

1. **The results obtained during the beamtime were presented at MRS Symposium "Applications of In-Situ Synchrotron Radiation Techniques in Nanomaterials Research", USA April 2014**
   Paper AAA3.04 O. Hirsch, L.Liu, K.Kvashnina, P. Glatzel, M. Niederberger, D. Koziej
   "In-situ X-ray absorption and emission spectroscopic studies of the interaction between CO_2 and lanthanum-oxycarbonates nanoparticles"

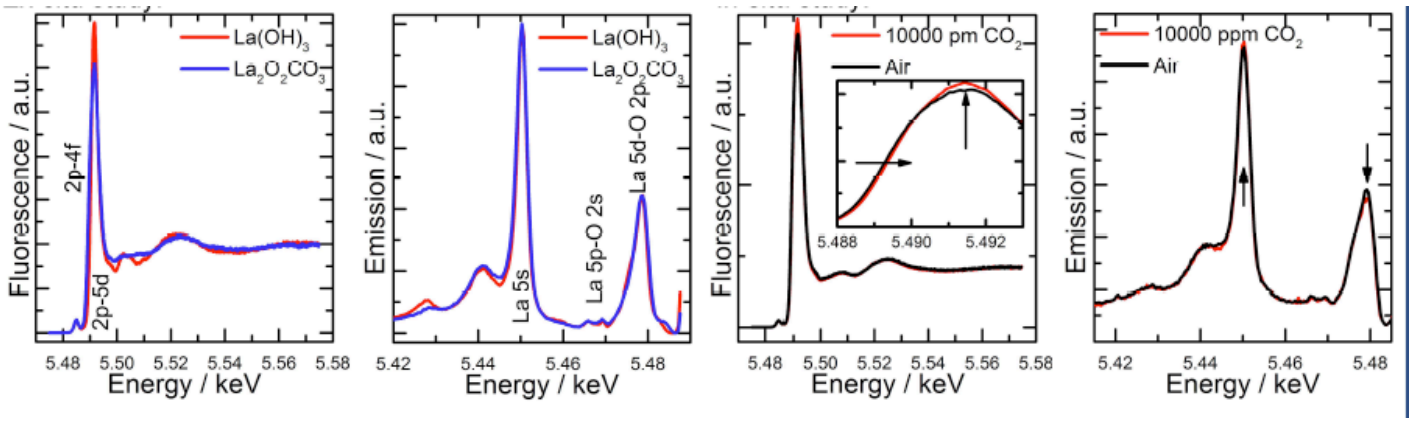

Figure 1. HERFD XAS and XES measurements (left) ex-situ (right) in-situ during CO_2 sensing at 250C.

2. **The initial analysis** of XAS and XES data showed strong discripencies between the FEFF simulation and measured data. We found out that unlike commonly anticipated, the $La_2O_2CO_3$ nanoparticles crystalized not in the monoclinic but in the hexagonal crystal structure. Therefore we Rietevled-refinded the crystal structure of $La_2O_2CO_3$ nanoparticles and used these results as an input parameters for FEFF simulation.
3. **So far accomplieshed analysis (See Figure 1 above).** We determined the main features in the XAS and XES spectra by using FEFF9 program package:
   - HERFD XAS: The pre-edge feature arises from a 2p to 4f quadrupole transition and the main feature is a 2p-5d transition. Both features can be reproduced with FEFF calculations for both compounds, $La(OH)_3$ and $La_2O_2CO_3$.
   -Valence-to-core (vtc) XES: In the XES spectra we can determine from FEFF calculations a mixing from La 5d states with O 2p states at energies around 5.48 keV. The features at 5.47 keV arise from a mixing of oxygen 2s states and lanthanum 5p states. The large feature at 5.45 keV represents La 5s states. The two features at 5.43 and 5.44 keV cannot be reproduced with the FEFF program package.
   - In-situ HERFD XAS: Upon CO_2 exposure we detect an increase in the white line intensity and a shift towards higher energies of the white line position, both of which correspond to an oxidation. The electron density on the lanthanum atoms is therefore smaller.
   - In-situ vtc XES: The changes in the in-situ XES spectra upon CO_2 exposure show a decreased intensity of the feature at 5.48 keV and an increased intensity of the feature at 5.45 keV. Taking into account that XES features represent the occupied electronic states, the feature at the higher energy represents the electrons from the valance band and the density of those states decreases during CO_2 rich atmosphere.
   - The in-situ results of both spectroscopic methods (HERFD XAS and vtc XES) corresponds well with the sensor experiment itself. In the sensor experiment we measure the electrical resistance over time and varying CO_2 concentrations. By increasing the CO_2 concentration in the atmosphere the resistance increases drastically. The spectra analysis revealed a lower electron density during a CO_2 rich atmosphere, i.e. less electrons can contribute to the conductivity, thus the resistance increases.
4. **In progress:** Understanding the mechanism of CO_2-particle interaction
   - FEFF calculations in order to understand the effects of different adsorption types on the XAS/XES spectra of $La_2O_2CO_3$
5. **The dissemination** of the resulst in the form of manuscript is planned for the November 2014.