



Experiment title:

In operando study of electrochemical gas purification:
Application of HERFDXANES/
XES to monitor the effect of electrical polarisation on Mn in

Experiment number:
CH-4053

<p>Beamline: ID26</p>	<p>Date of experiment: from: 30/4-2014 to:4/5-2014 and from: 14/6-2014 to: 16/6-14</p>	<p>Date of report: <i>Received at ESRF:</i></p>
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Report:

1. Background and motivation

Solid oxide electrodes based on the perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) are under investigation for application in electrochemical gas conversion, a novel technology for cleaning of diesel engine exhaust. During electrochemical gas purification NO_x contaminants will be electrochemically reduced to N_2 and O^{2-} on the LSM electrode, when the electrode is electrically polarized. The Mn, and especially the ability of Mn to change oxidation states, has been suggested to be crucial for the electrochemical reduction of NO_x . Despite of this, direct, *in operando* experimental investigations of the interplay between electrical polarization and the Mn oxidation state/electronic structure in LSM electrodes have until now been missing, despite of intensive theoretical work on the subject. During the experiments described herein the aim was to conduct an *in operando* study of how the application of electrical polarisation affects Mn oxidation state/electronic structure in LSM electrodes using a combination of XAS/XES experiments at ID26. The findings from these experiments may support the further development of electrodes for electrochemical gas

purifications, and may furthermore be relevant to the solid oxide fuel cell (SOFC)/solid oxide electrolysis cell (SOEC), community, which also applies LSM based perovskite electrodes.

2. Experimental

The samples investigated were $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3\pm\beta}$ (LSM50) model electrodes subjected to the *in operando* investigation, and powder reference samples of $\text{MnO}(\text{Mn}^{2+})$, $\text{Mn}_2\text{O}_3(\text{Mn}^{3+})$ and $\text{MnO}_4^{(4+)}$ which were investigated ex situ. For the *in operando* investigation a custom-build test-cell was used, in which the sample was heated by a small heat-stage and electrically polarized using a Gamry Ref600 potentiostat. During the *in operando* investigation the sample temperature was 500 °C and the cell was kept in stagnant air, while electrical polarisations in the range -850 mV to +800mV were applied on the electrodes, with the majority of the polarisations conducted in the cathodic regime from 0 mV (OCV) to -850 mV.

At OCV and with the various electrical polarisations on the cells the following techniques were applied: HERFD-XANES on the Mn K edge, non-resonant $\text{K}\beta$ XES on the Mn $\text{K}\beta$ main emission lines and RIXS on the Mn K-pre-edge.

3. Results

HERFD-XANES: While positive (anodic) polarisation of the electrode did not affect the XANES, the application of a negative (cathodic) polarisation in the range -600 mV to -850 mV caused a reversible shift in the Mn K edge towards lower energies (Figure 1 a), due to a decrease in Mn oxidation state and the associated change in Mn-O bond distances. The Mn K edge energy as function of the applied cathodic potential is shown in Figure 1 b.

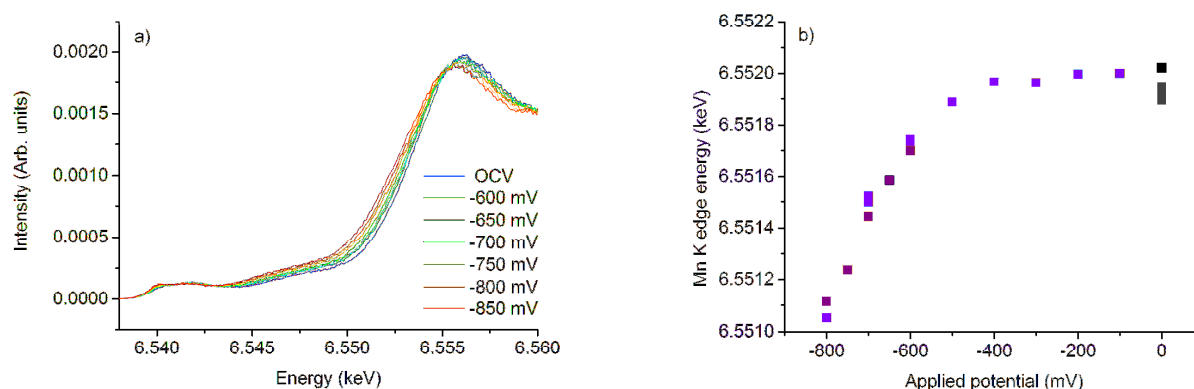


Figure 1. a) HERFD-XANES at the Mn K-edge recorded at OCV and with potentials applied on the electrode; b) the Mn K-edge energy (determined as the value mid-way between the pre-edge and post-edge) as function of the applied potential.

Non-resonant $\text{K}\beta$ XES

Non-resonant $\text{K}\beta$ XES were recorded and IAD values calculated according to the procedure described by Vanko et al.¹, the MnO spectrum was used as reference. A close to linear dependency was observed between the oxidation states of the MnO_x references and the IAD values (Figure 2).

From the IAD a decrease in average oxidation state for Mn in LSM electrodes from 3.4 to 3.2 was found when the cathodic polarisation was increased from 0 mV to -800 mV (Figure 2).

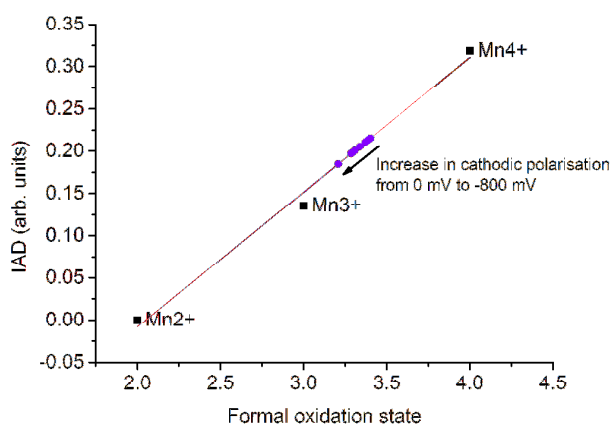


Figure 2. Integrals of the absolute values of the difference spectra (IAD) for the MnO_x powder references (black squares) and for the LSM electrodes at OCV and during cathodic polarisation (purple circles). The reference for calculating the IAD was in all cases the MnO (Mn^{2+}) spectrum.

RIXS

The RIXS planes recorded on the LSM electrode at OCV and during cathodic polarisation showed a weakening of a feature located at Energy Transfer ≈ 65 eV. This weakening is assigned to cathodic polarisation filling the e_g orbitals of the Mn, thus decreasing the possibility of spin up transitions.

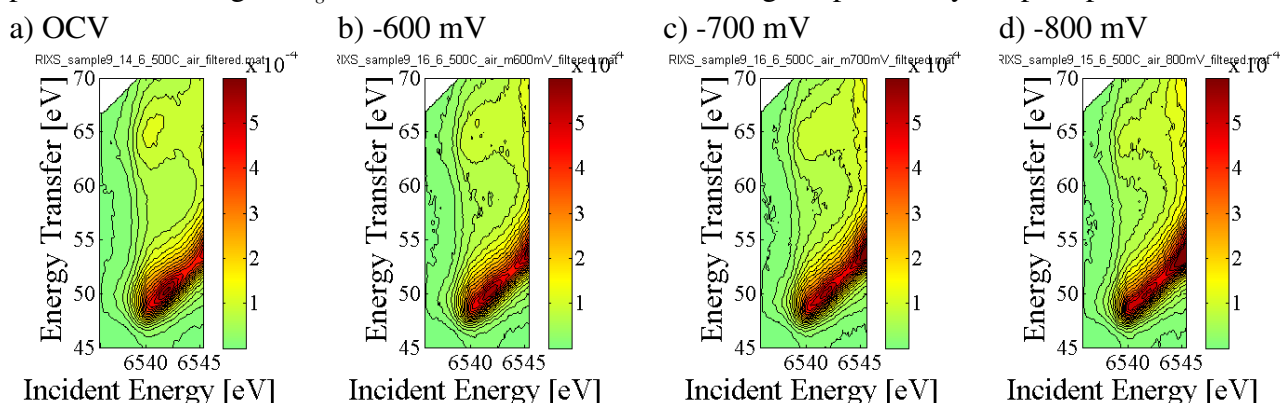


Figure 3. RIXS planes recorded at the Mn K pre-edge on LSM electrodes at a) OCV and subjected to b) -600 mV, c) -700 mV and d) -800 mV.

4. Conclusions

The combination of XAS and XES conducted *in operando* at ID26 has for the first time established extensive, experimental evidence of reversible changes in the oxidation states/electronic structure around Mn in LSM electrodes upon electrical polarization, as predicted by theory. These findings allow for coupling changes in the electronic structure in an operating solid oxide electrocatalyst to the electrochemical performance of the electrodes.

¹ G. Vanko, T. neisius, G. Molnár, F. Renz, S. Kárpáti, A. Shukla and F. M. F. de Groot, *J. Phys. Chem. B.*, **110**, (2006) 11647