



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Bimetallic electrocatalysts for Solid Oxide Electrolysis Cells - intermetallic synergy and structural alterations	Experiment number: 20222122
Beamline: LISA	Date of experiment: from: 21.02.2023 to: 24.02.2023	Date of report: 15.05.2023
Shifts: 9	Local contact(s): Alessandro Puri	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): <ol style="list-style-type: none">*Patryk Błaszczak, Advanced Materials Center, Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland*Agata Ducka, Advanced Materials Center, Institute of Nanotechnology and Materials Engineering, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland		

Report:

During the measurements at the LISA beamline at the ESRF, materials consisting of the nickel cermet infiltrated with different transition metals were studied. Samples were provided in both oxidized state (marked as OX) and reduced in pure hydrogen at 800°C (marked as RED). Additionally, some reference materials, such as manganese oxides or Co-containing spinels, were measured as well. Materials were measured in the transmission mode at room temperature. As the amount of infiltrated metals was low (~3 wt.%) when compared to the nickel (~50 wt.%), the absorption signal from the Ni K-edge overwhelmed other materials. In case of the K-edge of elements with atomic number lower than Ni ($Z < 28$), this problem was solved by the cutting off the Ni K-edge energy range, however the signal remained noisier. Unfortunately, for Cu-impregnated cells, the EXAFS signal of Ni K-edge was significantly overlapping with Cu K-edge, which made it impossible to measure Cu edge in transmission mode and because of this reason, for Cu-modified samples, fluorescence mode was applied. Collected data was analysed using the Athena software. Because the Ni spectra were of perfect quality, the Fourier transform was performed to analyse the EXAFS region and to determine the changes in the local surrounding of Ni atoms with respect to different infiltrated metals. FT was not implemented for Cu/Ni-YSZ samples, as in this case, the Cu K-edge was disturbing the EXAFS spectra of Ni.

The XAS spectra for Ni-edge in both oxidized and reduced states are presented in the Fig.1 (left). For the reduced infiltrated cells, the signal can be contributed totally to the nickel in the metallic state. Additionally, no significant differences can be found after reduction between various infiltrated metals: neither in edge position nor intensity nor the EXAFS region. Considering the oxidized materials, the increase of the white lines' intensity can be seen, when compared to the reduced samples. This observation indicates presence of nickel oxide in the cells. On the other hand, signs of metallic nickel can also be found, such as formation of the pre-edge feature (at ~8330 eV), which is characteristic to Ni metal and originates from transition from 1s to 3d orbitals. Another indicator is the EXAFS spectra similar to the reduced ones, which means that the local environment of the nickel atoms is dominated by the metallic surrounding. As all cells were reduced prior to the infiltration process, all the aforementioned observations can be expected. During the firing, nickel could be partially oxidized either to nickel oxide, or the Ni-transition metal compounds. Interestingly, distinct changes in the white line intensity are observed for manganese and iron infiltrated materials. The observed intensity decrease comes from the lower amount of transitions available between 1s and LUMO (lowest unoccupied molecular orbital) orbitals. It can be

possible that such behaviour originates from formation of other Ni-Mn or Ni-Fe compounds or the lower amount of oxidized nickel, as the pre-edge feature is also slightly more intense for those two samples.

The FT EXAFS signal (with phase correction of 0.5 Å included) is presented in Fig.1 (right). The EXAFS analysis has proven that in reduced cells, nickel is present in completely metallic state, as can be seen by the peak formation at about 2.45 Å, which is almost the exact value as Ni-Ni bonds length in metallic nickel (*Fm-3m*) – 2.46 Å. Similar feature is visible for oxidized sample, which is in line with theory that Ni environment is dominated with metallic bonds. However, around 2.79 Å, an additional peak is formed and its intensity differs between different samples. This peak may be originating from the Ni-Ni bonds in NiO (2.9 Å) or other species such as spinel structures. Although, with respect to both the intensity of the main peak and the decrease of the second, especially for Fe and Mn- infiltrated cells, it is more probable that this additional feature originates from NiO formation, rather than other structures.

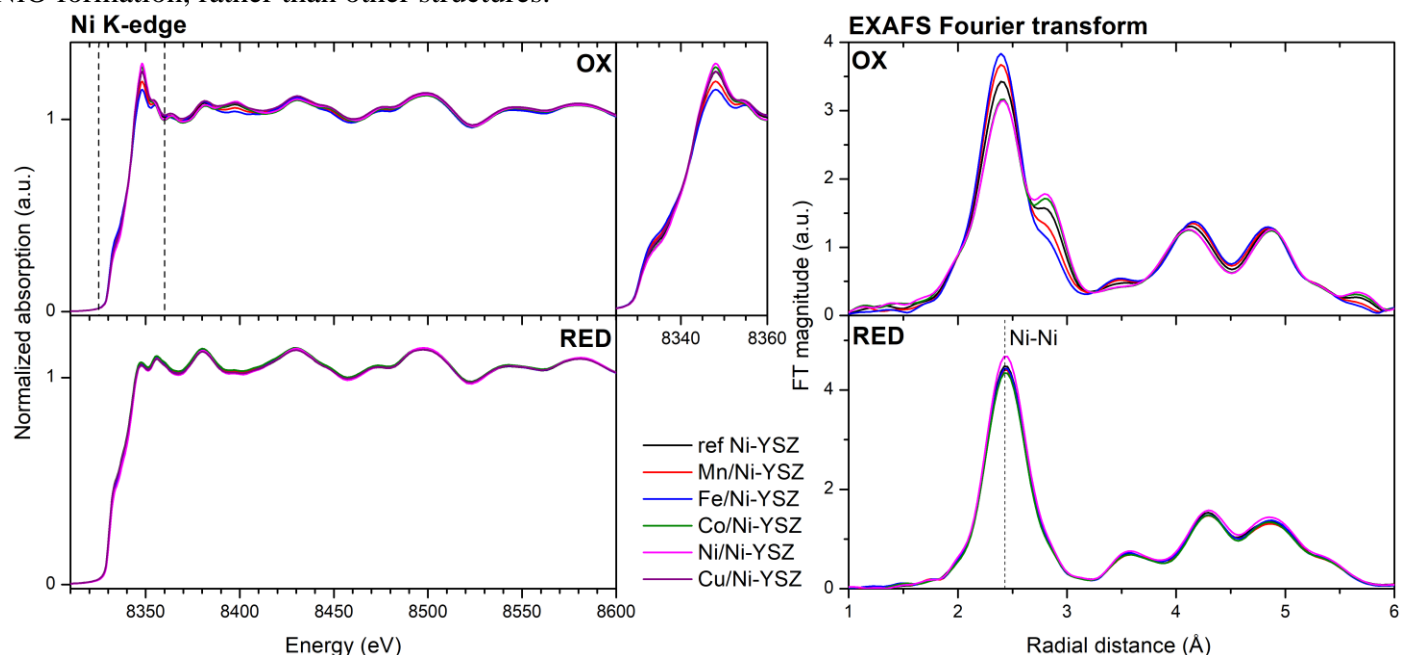


Fig. 1. XANES and EXAFS measured for Ni K-edge for both reduced and oxidized samples (left) and EXAFS FT (right)

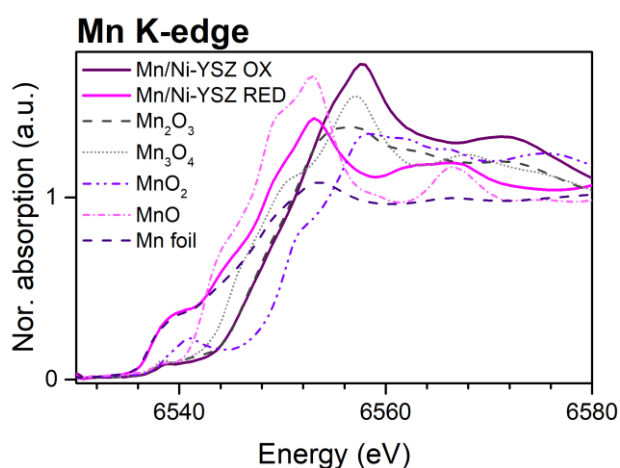


Fig. 2. XANES of the manganese K-edge of infiltrated cells, reference oxides and Mn foil.

Moreover, as stated before, the K-edge spectra of respective metals infiltrated into Ni-YSZ cell were also collected and are presented in Figs. 2 and 3. The XANES region of manganese with all the reference materials is shown in Fig. 2. As Mn is hardly reducible metal, the pure signal from metal itself is rather hardly expected, different from Ni spectra. In the case of oxidized sample, it was found out that the XANES spectrum originates from the presence of Mn_3O_4 and Mn_2O_3 , while after the reduction, the oxides were reduced to MnO. What is more it is probable that a small amount of Mn nanoparticles were formed upon reduction, as the pre-peak feature consistent with this from Mn foil can be found. Another clear evidence for reduction to Mn/MnO is the significant shift of the white line of reduced material to lower energies.

Wide-range XAS spectra of Mn, Fe, and Co are plotted in Fig. 3. For the infiltrated metals, Fourier transform analysis was not implemented, as the signal was strongly disturbed by the Ni K-edge. But one can say a little about changes in the local environment by analysing the EXAFS range in Fig. 3. It's clearly seen that for the Co-impregnated cell, after reduction the Co was present mostly in the metallic neighbourhood, as the EXAFS signal is similar to that of the Co foil. At the same time, small amount of oxidized cobalt remained in the sample, which

is suggested by remaining small edge feature at 7725 eV, which can be attributed to Co^{2+} . At the same time, XAS spectrum for oxidized sample got a white line, which position (7727.5 eV) lies between Co_3O_4 (7729 eV) or spinel structure CoNi_2O_4 (7726.7 eV). Generally speaking, both XANES and EXAFS of the oxidized cell infiltrated with Co, may be considered as dominated by Co_3O_4 presence with traces characteristic of CoNi_2O_4 spinel (like small feature at the slope of the white line), which is consistent with our previous studies [1]. A similar case may be considered for the Fe-infiltrated sample, as the oxidized cell is fully characterized by presence of Fe_3O_4 oxide. After the reduction, the intensity of the peak decreases significantly and a shift toward lower energies can be observed, confirming the reduction of Fe ions. However, spectrum of the reduced sample is not equal to collected Fe foil, one should keep in mind that reference foil could have been partially reoxidized which would influence the signal. It cannot be excluded that after the reduction, Fe can be found in both metallic and oxidized state (most probable FeO). Moreover, the additional peak at around 7130 eV can be linked with FeO in the sample [2]. Although, considering the reduction temperature of the iron oxides, the 800 °C should be enough to completely reduce iron oxides to its metallic form. Also, EXAFS spectrum of analysed material differs significantly from metallic characteristics (unlike Co on Ni, described before), which would strongly suggest simultaneous presence of some Fe^{2+} ions. The analysis of the Mn spectra was presented in more detail in the previous paragraph.

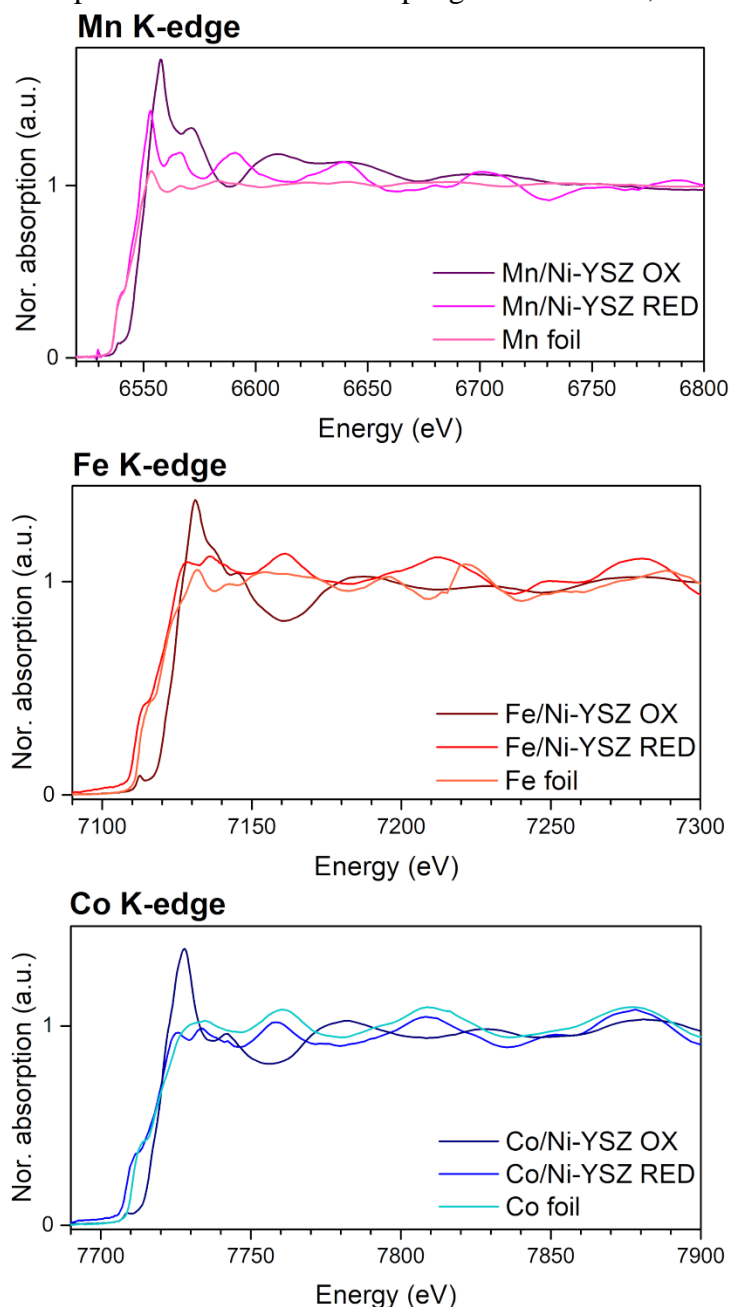


Fig. 3. K-edge spectra of respective metals in infiltrated samples. Spectra for metal foils are plotted for reference.

References:

- [1] Błaszczak P, Zajac M, Ducka A, Matlak K, Wolanin B, Wang S-F, et al. High-temperature Co-electrolysis of $\text{CO}_2/\text{H}_2\text{O}$ and direct methanation over Co-impregnated SOEC. Bimetallic synergy between Co and Ni. *Int J Hydrogen Energy* 2022. <https://doi.org/10.1016/J.IJHYDENE.2022.08.057>.
- [2] Istomin SY, Chernova V V., Antipov E V., Lobanov M V., Bobrikov IA, Yushankhai VY, et al. Wide-Range Tuning of the Mo Oxidation State in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{2/3}\text{Mo}_{1/3}\text{O}_3$ Perovskites. *Eur J Inorg Chem* 2016;2016:2942–51. <https://doi.org/10.1002/ejic.201600020>.