ESRF	**Experiment title:** Investigation of the degradation of solid oxide fuel cells operated in the high temperature electrolysis mode using X-ray fluorescence and XANES	**Experiment number**: MA-3257
Beamline: ID16B	**Date of experiment**: from: 27-01-2017 to: 31-01-2017	**Date of report**: 23/02/2017
Shifts:	**Local contact(s)**: Dr. Julie Villanova	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Julie Villanova, ESRF

Dr. Aline Léon, Karlsruhe Institute of Technology

Dr. Sabine Schlabach, Karlsruhe Institute of Technology

Report:

1. Overview

X-ray fluorescence mapping and Ni K-edge spectroscopy at the nanoscale were carried out for the first time on two types of solid oxide cells. Type 1 was an electrode supported cell, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3/Ce_{0.8}Gd_{0.2}O_{1.9}$/8YSZ/Ni(8YSZ) and type 2 was an electrolyte supported cell, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}$ $O_3/Ce_{0.8}Gd_{0.2}O_{1.9}$/6Sc1CeSZ/Ni($Ce_{0.8}Gd_{0.2}O_{1.9}$). The cells have been operated under real conditions during different time by the European Institute For Energy Research (EIFER).

Five samples were obtained by FIB-cut to have thin transverse slices (1.5-2 µm thickness) and mounted on ID16B sample holder at KIT: (i) three cells after operation time of 6100 h and 9000 h (type 1) and 23000 h (type 2) (ii) for comparison one non-operated cell of both types were analyzed as reference samples. .

2. Measurement/data

Initally, 18 shifts have been asked in order to perform X-ray fluorescence mapping and nano-XANES measurements at Ni, Co and Fe K-edge. Since 12 shifts have been allocated for the measurement we decided to focus the experiment on fluorescence mapping and Ni K-edge spectroscopy. The beamline was settled in the monochromatic mode at an energy of 9.5 keV to localize and study the chemical state of Ni at the interface of the hydrogen electrode/electrolyte and far from the interface. A nickel foil, the initial NiO powder to prepare the cell and $Ni(OH)_2$ were measured as reference. For each sample, 2D fluorescence maps have been performed in the hydrogen electrode until the electrolyte in order to localize the nickel particles. Then, XANES spectra have been recorded on different points on these fluorescence maps. The full data set consists of 1063 spectra at the Ni K-edge using a nanobeam (spot size on the sample 80x80 nm^2). Moreover, a full particle from the type 1 cell operated for 6100 h, has been XAS mapped using a step size of 50 nm and a resolution of 0.5 eV in energy.

We also checked that the high intense beam did not damage the sample by recording small maps of the same sample at the same position after several minutes and hours of acquisition.

3. Status and progress of evaluation

For each sample, region which includes the hydrogen electrode and the interface was defined and element maps with higher lateral resolution were collected, Figure 1. The beam was focused with the Kirkpatrick-Baez mirror system to the sample position to a size of approximately 80×80 nm^2. The XAFS spectra were recorded from 8320 eV to 8400 eV with a dwell time of 0.5 s in the fluorescence mode using silicon drift detector. Data were processed using the IFEFFIT package for background correction and normalization of the experimental data. The spectra were normalized to the transmitted flux and the corresponding current measured out of the sample. Figure 2 displays the spectra obtained at a point close and away from the interface; they are labelled in Figure 1 as point 1 and 2. For comparison, spectra of metallic Ni is shown.

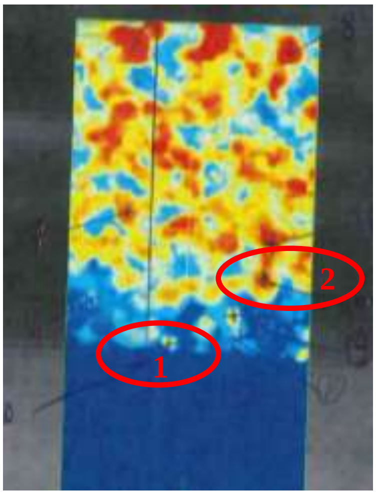

Fig. 1. Elemental map of Ni for a cell which had operated for 6100 h

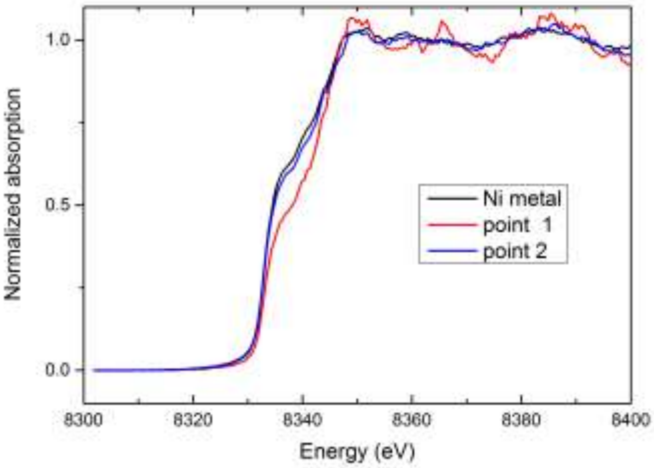

Fig. 2. NanoXAS spectra obtained at a point at the interface (1) and far from the interface (2). Point (1) and (2) are indicated in Figure 1.

Figure 2 indicates that point 2 is in the metallic state and point 1 differs from the pure Ni. Therefore, changes are clearly visible close and away from the interface. For a detail understanding, point scans and line scans were performed on all the samples to study the evolution of the chemical state of Ni at the interface and at the electrode. The data are currently processed.

4. Conclusion

In summary, a comprehensive XANES analysis of the chemical state of Ni was carried out at the interface of the H_2 electrode and electrolyte on sample operated at different time. The preliminary results higlight the presence of Ni in oxidized state specially at the interface. These results are expected to be of high interest and suitable for publication in scientific journals. These first data set need to be completed in the next beamtime:

- To improve the statistics by doing point scans on more particles
- To improve the signal to noise ratio of the acquired spectra by increasing the number of scans
- To perform the NanoXAS at the Fe and Co K-edge to understand the evolution of the oxidation state of these elements with the cell degradation.