	Structure-catalytic activity relationship of Co,Zn - ZIF-derived bamboo-like Fe containing carbons in the oxygen reduction reaction by combined in situ XRD and XAS	Experiment number: MA-4299
Beamline: BM23	Date of experiment: from: 31/10/2018 (08:00) to: 05/11/2018 (24:00)	Date of report: 01/12/2019
Shifts: 17	Local contact(s): PASCARELLI Sakura	<i>Received at ESRF:</i> 13/09/2022
Names and affiliations of applicants (* indicates experimentalists): T. Lastovina *, A. Budnyk *, A. Bugaev *, and Y. Pimonova Southern Federal University, Rostov-on-Don, Russia		

Report:

In this experiment a combined XRD and XAS study was performed on electrochemical catalysts made of porous carbons supporting iron and cobalt nanoparticles (NPs) to determine the origin of their enhanced catalytic activity in the oxygen reduction reaction (ORR). This report describes a part of the obtained results, which were published in a peer-reviewed international journal.

Introduction:

In modern low-temperature air-hydrogen fuel cells, carbon-supported Pt-containing materials are employed as catalysts for the ORR. Due to scarcity and the high cost of Pt, some Pt-free alternatives have been proposed, combining transition metals like Fe and Co and non-metals like N, P, S on a carbonaceous support. Both Fe and Co are known participating in the ORR, but their roles in heterogeneous system remain debated. This experiment was seeking to determine the origin of enhanced catalytic activity by monitoring Fe and Co sites behavior by means of XAS during cycling in a model electrochemical cell.

The catalyst was obtained in a two-step process. At the first, a zeolitic imidazolate framework (ZIF) with a desired cobalt content was synthesized and then enriched with an iron salt. This complex precursor was pyrolyzed at the second step, resulting in a porous N-doped carbon (made of amorphous carbon and bamboo-like CNT), containing Co and Fe nanoparticles. This material expressed an enhanced catalytic activity in the ORR, as it was found in previous studies. The enhanced catalytic activity was supposed to be originating from the ongoing parallel reactions or several metals participating in the ORR.

Experimental details

In situ and *operando* XANES and EXAFS spectra were collected simultaneously at Fe and Co K-edges at the BM23 beamline of ESRF. X-ray absorption spectra were processed in a standard way by using Demeter software for normalization, background subtraction and Fourier-analysis. Principle component analysis of normalized XANES spectra with rotation of basis vectors was performed in FitIt 3.0.

For *in situ* experiment (see Fig. 1), the 1 mm quartz glass capillary were filled with the samples and blocked by a quartz wool from both sides. The capillaries were fixed in the metal holder, which was situated inside the microreactor (a resistive heater) allowing for measurements in the transmission mode. The constant flow of Ar (12 ml/min) was allowed through the capillary limited by a Bronkhorst mass flow controller. The Fe and Co *K*-edge spectra were collected in the 7.0 – 7.6 keV and 7.6 – 8.3 keV ranges, respectively. The energy step in the pre-edge and XANES regions was set to 5 and 0.5 eV, respectively, with 2 s acquisition per point. In EXAFS region, the constant step in *k*-space of 0.05 Å⁻¹ was chosen with acquisition time increasing quadratically from 2 to 4 s. The measurements were performed on sample at room temperature (RT) and heated at 100, 200, 300, 400, and 500 °C.

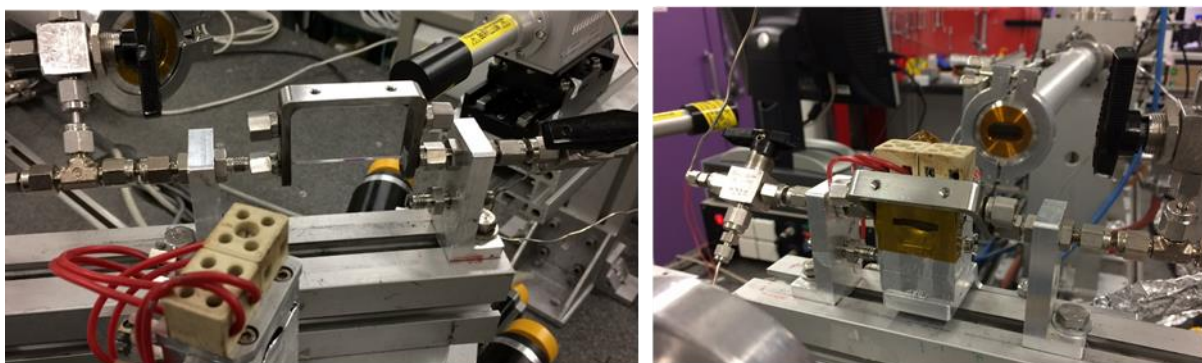


Figure 1. Photographs of the experimental setup for *in situ* XANES and EXAFS at BM23 beamline of ESRF: (1) sample is loaded in a quartz capillary connected to a gas line (*left image*) and (2) the capillary inside a heater is positioned for the measurement in transmission mode under heating (*right image*).

For *in operando* XAS measurements of the sample under cyclic voltammetry (CV) using BioLogic SP-50 potentiostat. The electrochemical cell provided by ESRF was employed, and the measurements were arranged in the fluorescence mode (see Fig. 2). The E_{WE} vs E_{RHE} values were acquired continuously from 1.000 to -0.170 V with the scan rate 0.120 mV/s. Fe and Co *K*-edge spectra were collected in fluorescence mode in 7.0 – 7.6 keV and 7.6 – 8.1 keV ranges, respectively. The energy step of 5 and 0.5 eV was used in the pre-edge and XANES regions, respectively, and 0.05 Å⁻¹ step was used in EXAFS region, with 2 s per point acquisition time.

A 28 µl of the catalytic ink were casted onto a glassy carbon plate of 1 cm² and left to dry for 1 h. This plate served as a working electrode in a three-electrode electrochemical cell filled with 0.1 M HClO₄ solution. The cell had a Kapton film window allowing the passage of X-rays. A counter electrode was the Pt wire and the Ag/AgCl (sat. KCl solution) electrode was employed as a reference. The plane of the working electrode was positioned to have the 45° angle against both incoming X-ray light beam and the X-ray fluorescence detector (see Fig. 2 *right*). The distance between the working electrode and the Kapton window was minimized to reduce the absorption of X-ray photons in the electrolyte.

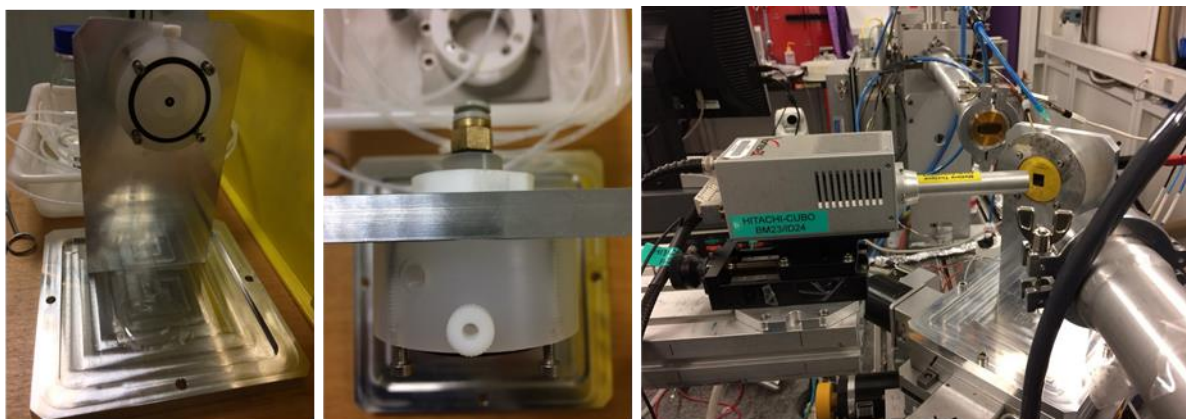


Figure 2. Photographs of two views on the three-electrode electrochemical X-ray scattering cell (*two images on the left*) and the experimental setup (*right image*) for *in operando* XANES and EXAFS acquisition in the fluorescence mode by running cyclic voltammetry of the catalyst in an electrochemical cell.

Selected experimental results

1. Study of Co behavior under *in operando* CV

Operando XAS data at the Co *K*-edge collected during CV were analyzed by MCR-ALS method and two main components were extracted (see Fig. 3). Small changes in the XANES region were observed (Fig. 3a) while the EXAFS part was found to be identical for both components (Fig. 3b). All maxima in the FT analysis of EXAFS of the two components are occurring at the same *R*-values as in the Co foil (green dashed line in **Figure b**) including higher *R*-region, but their intensities are slightly lower. This indicates that metallic Co NPs with *fcc* structure are present in the sample. The first-shell FT-analysis of EXAFS data provides with the following values of the characteristic parameters:

- 1) the first shell interatomic distance, $R_{\text{Co-Co}} = 2.50 \pm 0.01 \text{ \AA}$,
- 2) the Debye-Waller parameter, $\sigma^2_{\text{Co-Co}} = 0.006 \pm 0.001 \text{ \AA}^2$,
- 3) the coordination number, $N_{\text{Co-Co}} = 9.8 \pm 1.1$.

Within the experimental error, the identical values of *R* and σ^2 were obtained for both components and for the reference Co foil.

The coordination number of 9.8, which corresponds to the particle size of ca. 2 nm (assuming an ideal spherical shape).

Given the EXAFS data do not change during the ORR, the small changes in XANES region may be indicative for some alteration in the electronic state of surface atoms. In particular, the growth of the first near-edge peak at $E = 7725 \text{ eV}$ (Fig. 3) can be a signature of surface oxidation (Co–O bonds). This feature was observed evolve under changing potential of the working electrode: it appears at around 0.5 V and gradually disappears with decreasing potential. It restores when the potential reaches 0.2 V.

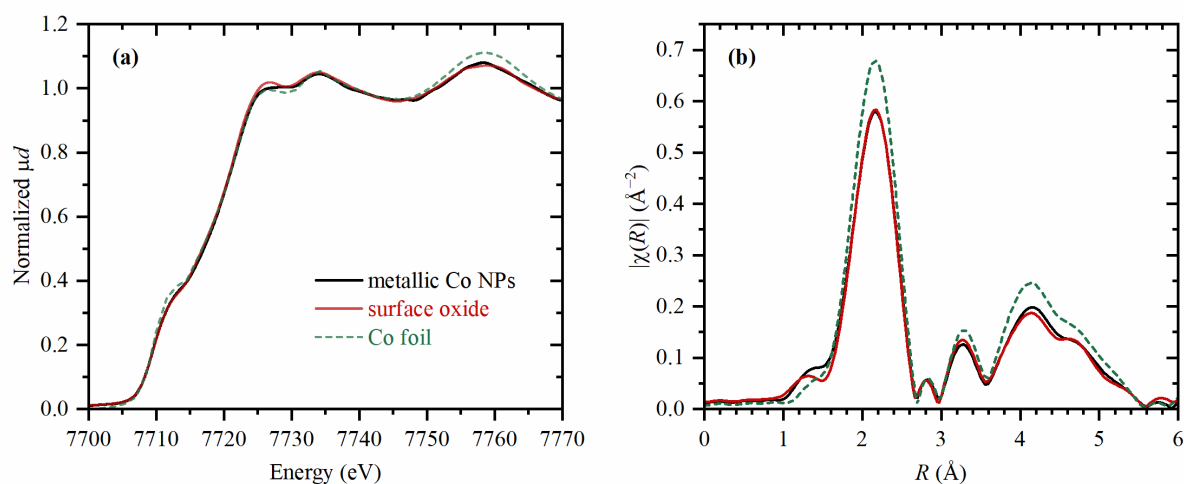


Figure 3. XANES part (a) and FT EXAFS (b) of the two components (black and red solid lines) derived by MCR-ALS. The reference Co foil data is shown by a dashed green line.

2. Study of Fe behavior under *in operando* CV

The Fe content in the samples is considerably lower than that of Co. In particular, for the catalyst with Co:Zn = 2:1 nominal composition, which was found the most active and stable in the ORR, the ratio of remaining (after pyrolysis) Co:Fe = 15:1 wt% as found by the XRF measurements. A poor quality of Fe *K*-edge XAS does not allow to analyze the time-evolution of Fe species.

Therefore, all 12 spectra collected during one cycle (solid lines in Fig. 4) were averaged. The position of the edge (Fig. 4a) is close to that of the reference iron foil; therefore, iron is expected to be in the Fe⁰-state. At the same time strong EXAFS oscillation in the $\chi(k)$ representation (Fig. 4b) implies the presence of a metallic neighbor (either Fe or Co). This is because the non-metal neighbors such as O, N, or C would not cause strong oscillations at high k (above $\sim 6 \text{ \AA}^{-1}$).

The FT of EXAFS contains a strong metal-metal contribution (Fig. 4c) but the positions and the shape of peaks are different from those of the reference Fe-foil. Such discrepancy can take place when the local structure of Fe atoms in the sample is different from the *bcc* arrangement of a bulk iron. Based on such qualitative analysis one may assume that Fe atoms are in zero oxidation state in the mixed Fe-Co NPs. In order to prove the assumption, the first FT-analysis on k -weighted data in k range from 2 to 8.5 \AA^{-1} was performed, and the fitting results are following:

- 1) the first shell interatomic distance, $R_{\text{Fe-Fe}} = 2.52 \pm 0.01 \text{ \AA}$,
- 2) the Debye-Waller parameter, $\sigma_{\text{Fe-Fe}}^2 = 0.002 \pm 0.003 \text{ \AA}^2$,
- 3) the coordination number, $N_{\text{Fe-Fe}} = 5.1 \pm 1.4$.

The R-factor is of 0.023 and the reduced χ^2 is of 3.39.

The fit with Fe-Co contribution gives the following values:

- 1) the first shell interatomic distance, $R_{\text{Fe-Co}} = 2.52 \pm 0.01 \text{ \AA}$,
- 2) the Debye-Waller parameter, $\sigma_{\text{Fe-Co}}^2 = 0.004 \pm 0.003 \text{ \AA}^2$,
- 3) the coordination number, $N_{\text{Fe-Co}} = 6.4 \pm 1.5$.

Accordingly, the R-factor is of 0.017 and the reduced χ^2 is of 2.46.

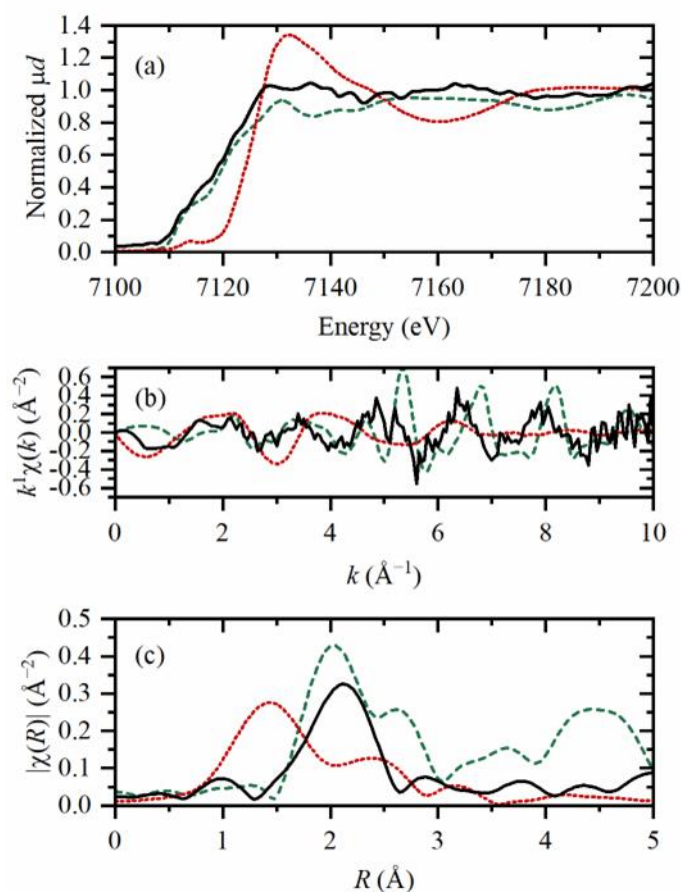


Figure 4. XANES (a), k^1 -weighted $\chi(k)$ signals (b) and their FT (c) for the sample (Co:Zn = 2:1 nominal composition) during the ORR (solid black) as well as for the reference Fe-foil (dashed green) and Fe oxide (dotted red).

By comparing the fitting results within two approaches, the fit with Fe–Co contribution gives a better agreement and reaches a reasonable value of σ^2 . The fit performed using *bcc* structure gave bad agreement with unreasonable results. Although it is usually difficult to distinguish Fe ($Z = 26$) and Co ($Z = 27$) neighbors from EXAFS analysis, the combination of the above-mentioned facts provides a strong indication in favor of conclusion that there are Fe atoms embedded in Co NPs. Considering the low coordination of Fe atoms, one may assume that Fe atoms are preferentially located on the surface of Co NPs.

Communication of the obtained results

T. Lastovina, A. Budnyk, Y. Pimonova, A. Bugaev, V. Dmitriev, Thermally-induced arrangement of cobalt and iron in the ZIF-derived Fe,Co,Zn-N/C catalysts for the oxygen reduction reaction, *International Journal of Hydrogen Energy*, 2019, V. 44 (41), P. 23010-23022; DOI: 10.1016/j.ijhydene.2019.07.022