



	Experiment title: Metal-Support Interactions on Iridium-based Catalysts for electrochemical Water Electrolysis probed by operando QuickXAS	Experiment number: CH-6512
Beamline: BM23	Date of experiment: from: 31.01.2023 to: 03.02.2023	Date of report:
Shifts: 9	Local contact(s): Cesare Atzori (email: cesare.atzori@esrf.fr)	<i>Received at ESRF:</i>
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Report:

Goal of the experiment

This set of experiments was planned to provide fundamental insights into the metal-support-interactions (MSI) of Iridium nanoparticles (Ir NPs) deposited on three different support materials such as carbon (C), titanium dioxide (TiO₂), and antimony doped tin oxide (ATO) for oxygen evolution reaction (OER) in acidic media. Operando electrochemical XAS studies enable us to identify the dynamic behavior of the nature of IrO_x species and its electronic and geometric interactions (oxidation state, local environment) on different support materials as a function of the applied potential before and during OER. In a two-step synthetic route, colloidal Ir NPs were prepared first and then immobilized on either the carbon, TiO₂, or ATO support material [1, 2]. As an alternative to Ir, few operando XAS investigations on Ru-based electrocatalysts as function of the potential for OER were also performed. From XAS data, principal component analysis (PCA), linear combination fit (LCF) and EXAFS analysis were carried out to understand the potential-dependent behavior of the chemical state of Ir for ~2 nm NPs and the nature of catalytically active Ir oxide species during OER.

Experiment details

During our beamtime, we performed operando electrochemical XAS experiments of different OER catalysts using carbon and TiO₂ as support material. Depending on the concentration, XAS spectra were collected in transmission or fluorescence mode to obtain a good signal to noise ratio. A spectro-electrochemical home-made flow cell equipped with our samples deposited on a gas diffusion layer (GDL), a graphite (counter electrode), and an Ag/AgCl (reference electrode) in 0.05 M H₂SO₄ was used. A chronoamperometry method was applied for all measurements starting from OCP to 1.6 V_{RHE}, while holding each potential for at least 10 min in order to obtain sufficient data quality.

Results

Due to some technical problems with the monochromator at the beamline, analyses of the Ir L_{III}-edge XAS data of the samples are very difficult. The monochromator was not stable over a series of XAS measurements. Measurements had to be repeated and therefore not all Ir-based samples could be investigated. XAS data that can be analyzed are shown below in an exemplary manner. Very interestingly, the Ir L_{III}-edge XANES spectra of the 20 wt.% Ir/C and Ir/TiO₂ show higher white line intensity compared to the Ir reference foil, signifying a strong oxidation behavior of the Ir NPs. This observation is in excellent agreement with our previous work on particle proximity effect for oxygen reduction reaction (ORR) [3]. The particle proximity effect is based on the interparticle distance, which can be controlled by the metal loading. The metallic character of the NPs increases with higher loading and therefore with smaller interparticle distance. Moreover, the chemical state of Ir is also influenced by the support material. More precisely, the white line intensity for 20 wt.% Ir/C is higher than for

20 wt.% Ir/TiO₂, see **Fig. 1a**. The high oxidation state of Ir species supported on carbon is very likely related to the larger interparticle size distance, because the BET surface area of the carbon support is around 10 times larger than that for TiO₂. Due to its high initial oxidation state, the series of potential-dependent XANES data shows no further changes in chemical state of Ir before and during OER, as shown in **Fig. 1b**.

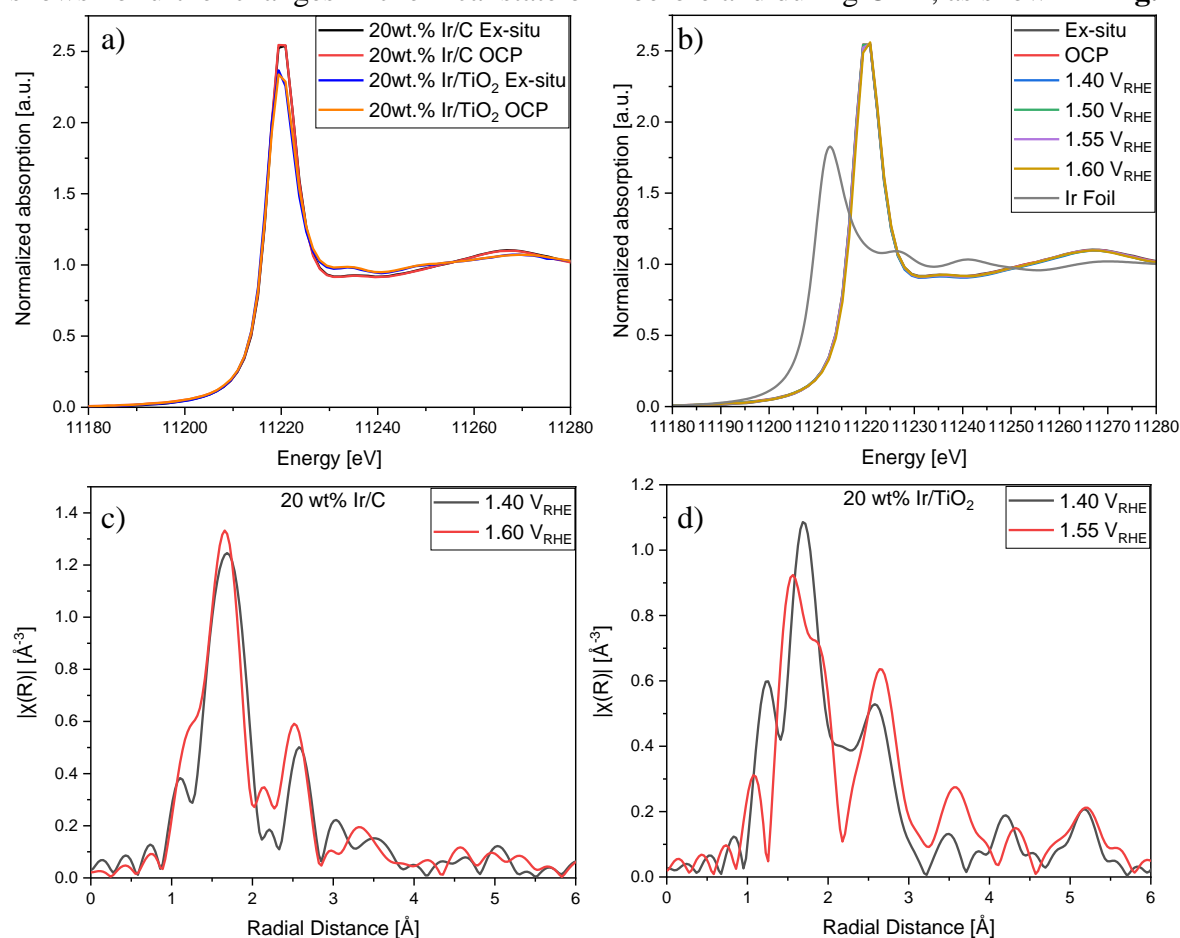


Figure 1: Ir L_{III}-edge XANES data of 20 wt.% Ir/C and Ir/TiO₂. (a) Comparison of the white line intensity for 20 wt.% Ir/C and Ir/TiO₂ as ex-situ pellet and at OCP in 0.05 M H₂SO₄. (b) Series of potential-resolved XANES data of Ir/C before and after OER. (c) Fourier-transformed EXAFS data of 20 wt.% Ir/C at 1.40 and 1.60 V_{RHE}. (d) Fourier-transformed EXAFS data of 20 wt.% Ir/TiO₂ at 1.40 and 1.60 V_{RHE}.

Figure 1c and **1d** show the comparison of the Fourier-transformed Ir L_{III}-edge EXAFS data of 20 wt.% Ir/C and Ir/TiO₂ before and during the OER in 0.05 M H₂SO₄. It is obvious that the coordination number and bond length (R) of Ir-O and Ir-Ir change with the applied potential. The catalytically active Ir species form during the OER. From the EXAFS data, for Ir/C both R(Ir-Ir) and R(Ir-O) increase with higher anodic potential. An opposite trend is pointed out for Ir/TiO₂, where both R(Ir-Ir) and R(Ir-O) decrease during the OER.

Conclusion

Overall, we were able to measure operando electrochemical Ir L_{III}-edge XAS data of Ir NPs supported on C or TiO₂ during this beamtime. Due to the particle proximity effect, the Ir NPs supported on carbon are much more oxidized than on TiO₂. As the XANES data shows a high oxidation state of Ir, no changes in the potential-resolved XANES data is observed. However, EXAFS data shows an opposite trend in the bond length of Ir-Ir and Ir-O for Ir/C and Ir/TiO₂, indicating the different formation of catalytically active Ir species during the OER.

References

- [1] J K. Mathiesen et al., Chemical Insights into the Formation of Colloidal Iridium Nanoparticles from In Situ X-ray Total Scattering: Influence of Precursors and Cations on the Reaction Pathway. *Journal of the American Chemical Society*, 2023, 145, 1769–1782.
- [2] F. Bizzotto et al., Ir nanoparticles with ultrahigh dispersion as oxygen evolution reaction (OER) catalysts: synthesis and activity benchmarking. *Catalysis Science and Technology*, 2019, 9, 6345–6356.
- [3] M. Inaba et al., The Oxygen Reduction Reaction on Pt: Why Particle Size and Interparticle Distance Matter. *ACS Catalysis*, 2021, 11, 7144–7153.

Publications resulting from this work

We are currently working on the publication of the data collected during this beamtime.