

## Experiment Report Form



	<b>Experiment title:</b> Monitoring water splitting mechanisms in metal chalcogenides and phosphides by operando X-ray absorption spectroscopy	<b>Experiment number:</b> 31-01-115
<b>Beamline:</b> BM31	<b>Date of experiment:</b> from: 10 March 2021 at 08:00 to: 17 March 2021 at 08:00	<b>Date of report:</b> 21.06.2021
<b>Shifts:</b> 21	<b>Local contact(s):</b> STOIAN Dragos Constantin Tel: Email: dragos.stoian@esrf.fr	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Prof. Dr. Greta R. Patzke Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland Dr. Carlos. A. Triana* Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland Yonggui Zhao* Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland Chong Huang* Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland		

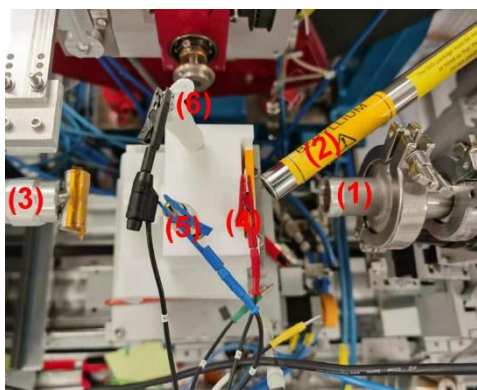
### Report:

#### Background

Transition metal phosphides (TMPs) have been reported as efficient electrocatalysts for water splitting due to their high catalytic activities.<sup>[1-2]</sup> However, their reaction mechanisms, in particular, the surface reconstruction and structural stability during electrocatalytic reactions, have not been fully understood yet. Consequently, the optimal design of high-performance electrocatalysts requires extended knowledge of their reaction mechanisms. Therefore, *operando* insights into TMPs during water splitting are urgently needed. Our experiments aimed to understand the reaction mechanisms and tracking the structural reconstruction of TMPs during the hydrogen and oxygen evolution reactions (HER and OER).

#### *Operando* and *ex situ* X-ray absorption spectroscopy (XAS) tests.

The *operando* and *ex situ* XAS tests were performed at the beamline BM31. *Ex situ* measurements were carried out on powder samples dispersed in cellulose. For *operando* measurements, the samples were loaded on carbon paper with a loading mass of 2.0~3.0 mg/cm<sup>2</sup>. All the *operando* electrochemical measurements were carried out using in-house developed electrochemical cell at room temperature in 1.0 M KOH (**Figure 1**). For the HER test, the chronoamperometric method with a cathodic polarization from 50-100 mV vs. RHE was applied for the working electrode, and an anodic polarization from 0.8 V to 1.55 V vs. RHE



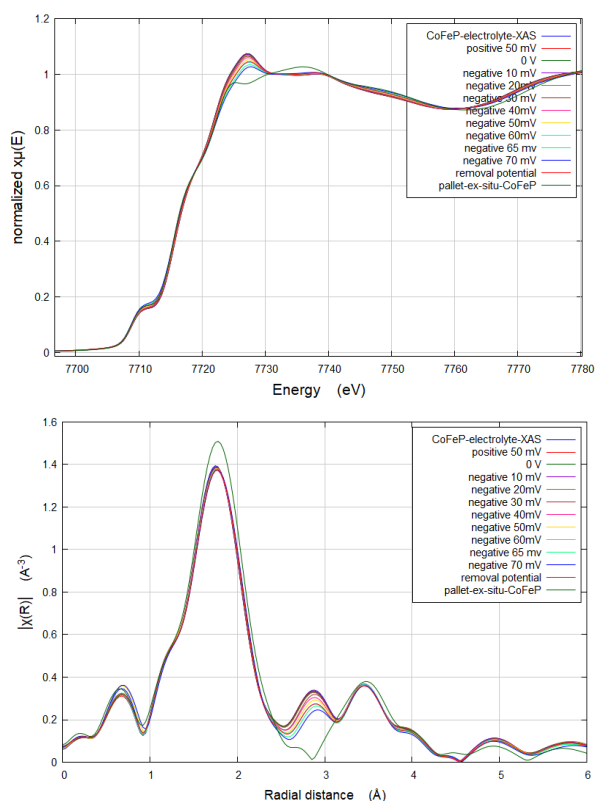
**Figure 1.** The *operando* XAS setup. 1) X-ray beam; 2) Vortex® one-element silicon drift detector; 3) Flight tube for transmission signal; 4) Working; 5) Reference and (6) Counter electrode.

Fe substituted Co phosphides (denoted CoFeP). Because the XAS data was dramatically affected by the generated gas bubbles ( $H_2$ ) when the potentials were lower than negative 70 mV vs. RHE, here, we only present the XAS data before the mentioned potential. Based on the *operando* XANES results (**Figure 2 top**), when our catalysts were submerged into the electrolyte, an obvious white line peak feature was observed at around 7727 eV. Then, with the cathodic polarization, the intensity of this peak shows a decreasing tendency. After removed the potentials, it can slightly be recovered to a higher intensity. For the EXAFS data, the *ex situ* CoFeP only shows one prominent backscattering peak at around 1.77 Å (**Figure 2 bottom**), which is mainly arising from the first shell Co-P.<sup>[3-5]</sup> After immersing CoFeP into the electrolyte and upon application of cathodic polarization a second scattering shell appeared at 2.85 Å and afterward it showed structural relaxation. Based on previous studies,<sup>[6-7]</sup> we assigned this second scattering peak to the formation of P-Co-O-Fe-P units. Analogous results were also detected from Fe *K*-edge XAS data. Therefore, we concluded that our CoFeP sample would suffer structural reconstruction to in situ generated P-Co-O-Fe-P configurations, which could act as the real catalytic active species during the HER process.

To improve the quality of the data, all *operando* XAS signals collected at constant potential were measured 10 times, and then merged to a total XAS signal for analyses. The  $k^3$ -weighted Fourier transform (FT) for all the *operando* EXAFS data was conducted in the  $k$ -ranges of 0 to 12 Å<sup>-1</sup>. For the investigation of *operando* Co *K*-edge EXAFS data, the  $k$ -ranges were limited to 3 to 11 Å<sup>-1</sup>. Due to the extremely low amounts of Fe ions in our sample (the atomic ratio of Co/Fe is around 3.5), it was challenging to acquire the high quality of EXAFS data on the Fe *K*-edge. Therefore, the investigations of Fe *K*-edge EXAFS data were only limited to  $k$  ranges from 3 to 9 Å<sup>-1</sup>.

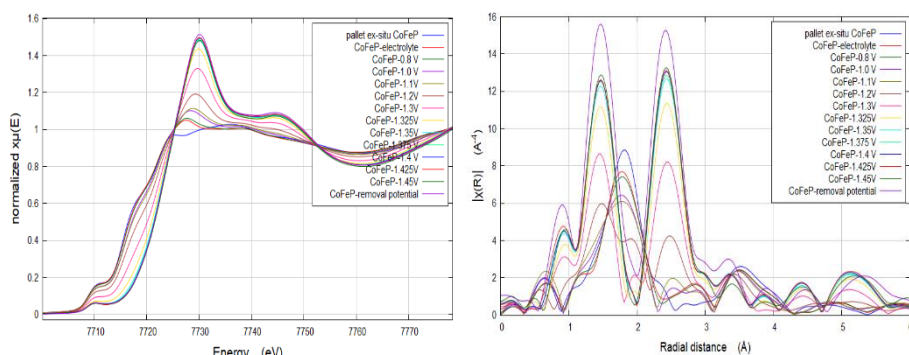
## Results

As shown in **Figure 2**, we first measured the *operando* XAS data for



**Figure 2.** *Operando* XAS results for CoFeP during HER process.

The *operando* Co *K*-edge XAS data of CoFeP during the OER process were also collected to investigate dynamics and reaction mechanisms. As shown in **Figure 3 (left)**, with the anodic polarization, an obvious positive energy shift was observed for the Co *K*-edge XANES spectra, which is ascribed to the formation of higher Co valence states.



**Figure 3.** *Operando* XAS results for CoFeP during OER process.

Moreover, the overall line shape of the XANES spectra of CoFeP during the OER test was mismatched with the *ex situ* spectrum, suggesting that the as-prepared CoFeP underwent a structural transformation during the OER process. The *operando* EXAFS spectra (**Figure 3 right**) indicated two main scattering peaks at around 1.46 Å for the Co<sup>III</sup>-O path and 2.42 Å for the Co<sup>III</sup>-Co<sup>III</sup>/Fe<sup>III</sup> paths,<sup>[6-7]</sup> respectively, when the potential is higher than 1.3 V vs. RHE. Similar conclusions were also demonstrated by the Fe *K*-edge XAS data, suggesting that the as-prepared CoFeP would be transformed into (Co, Fe)OOH during the OER test.

## Conclusions

In summary, we successfully performed *operando* XAS experiments for CoFeP during the HER and OER tests. Based on our *operando* XAS data, we found that as-prepared CoFeP samples undergo a structural reconstruction both in the HER and OER processes. For the HER process, CoFeP would *in situ* reconstruct a configuration of P-Co-O-Fe-P, which likely serves as the real HER catalytic active species. By comparison, the *operando* XAS spectra of CoFeP demonstrated the formation of (Co, Fe)OOH during the OER test. These results are also consistent with our initial expectations in our beamline proposal.

## References

- [1] Shi, Y. M., Zhang, B., *Chem. Soc. Rev.* **2016**, *45*, 1529.
- [2] Y. Zhu, H.-C. Chen, C.-S. Hsu, T.-S. Lin, C.-J. Chang, S.-C. Chang, L.-D. Tsai, H. M. Chen, *ACS Energy Lett.*, **2019**, *4*, 987.
- [3] S. Sun, X. Zhou, B. Cong, W. Hong, G. Chen, *ACS Catal.*, **2020**, *10*, 9086.
- [4] H. Zhang, W. Zhou, J. Dong, X. F. Lu, X. W. Lou, *Energy Environ. Sci.*, **2019**, *12*, 3348.
- [5] Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W.-C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.*, **2018**, *140*, 2610.
- [6] B.-J. Kim, E. Fabbri, D. F. Abbott, X. Cheng, A. H. Clark, M. Nachttegaal, M. Borlaf, I. E. Castelli, T. Graule, T. J. Schmidt, *J. Am. Chem. Soc.*, **2019**, *141*, 5231.
- [7] B. Pattengale, Y. Huang, X. Yan, S. Yang, S. Younan, W. Hu, Z. Li, S. Lee, X. Pan, J. Gu, J. Huang, *Nat. Commun.*, **2020**, *11*, 4114.