



## Implementing Pair Distribution Function analysis to rationalize the water-splitting activity of Co-phosphonate-derived electrocatalysts.

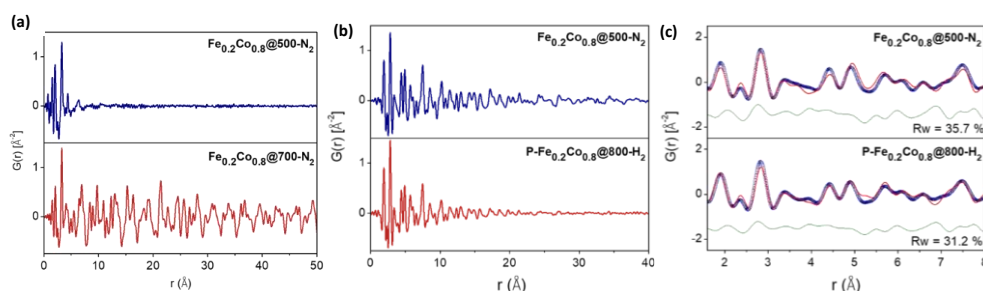
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Pair Distribution Function analysis (PDF) is a total X-ray scattering technique, including the diffuse scattering and the Bragg diffraction. Thus, PDF can be used to characterize structural domains of amorphous solids to investigate local order/properties correlations [1].

Herein, a follow-up of the chemical evolution of pyrophosphate- or phosphide-based Fe/Co electrocatalysts is carried out by synchrotron PDF analysis. The catalysts were prepared from the metal (*R,S*) 2-hydroxyphosphonoacetates by pyrolysis in N<sub>2</sub> (500 °C and 700 °C) or 5%-H<sub>2</sub>/Ar (800 °C) and studied toward the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Comparison of PDF patterns of the amorphous (500 °C) and the semicrystalline Fe/Co pyrophosphates (700 °C) showed that the local order of the amorphous solid is composed of nanoclusters of ~ 7 Å (Figure 1). In contrast, the PDF pattern of the Fe/Co phosphide (800 °C) is formed by a mixed of the crystalline phases *o*-Co<sub>2</sub>P and *o*-CoP. Differential PDF (d-PDF) analysis of the spent catalysts revealed that, irrespectively of the amorphous or crystalline nature, all pyrolyzed solids transformed under OER operation into biphasic CoO(OH), composed of discrete clusters with size ≤ 20 Å (Figure 1) [2].



**Figure 1.** (a) PDF patterns of cobalt pyrophosphates. (b) Post-OER d-PDF patterns of two Fe/Co electrocatalysts. (c) d-PDF fits to *R*-3*m* and *P*6<sub>3</sub>/*m*mc CoO(OH) polymorphs.

### References

[1] Farrow, C.L.; Bediako, D.K.; Surendranath, Y.; Nocera, D.G.; Billinge, S.J.L. *J. Am. Chem. Soc.* **2013**, *135*, 6403–6406.

[2] Vílchez-Cózar, A.; Colodrero, R.M.P.; Bazaga-García, M.; Marrero-López, D.; El-refaei, S.M.; Russo, P.A.; Pinna, N.; Olivera-Pastor, P.; Cabeza, A. *Appl. Catal. B: Environmental* **2023**, *337*, 122963.