Structural Characterization of Transition-Metal Carboxyethanephosphonates as Precursors of Electrocatalysts

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Phosphorus-containing coordination polymers (CPs) are considered as one of the most promising precursors of materials alternative to the highly expensive commercial catalysts (Pt, Ru and Ir) used in polymeric fuel cells and electrolysers.[1] Among them, metal phosphonates, a subtype of coordination polymers, are attractive precursors due to their great chemical and structural diversity. Indeed, the possibility of containing in their compositions electrocatalytically active transition metals in combination with other elements (N, C, P, S, etc…) may enhance the electrochemical properties of the resulting materials after pyrolytic treatments.[2]

In this work, we report the synthesis and crystal structures of several transition-metal phosphonates derived from the ligand phosphonopropionic acid (PPA). Solids with compositions $A_xB_{1-x}[O_3PCH_2CH_2COOH]_2{\cdot}nH_2O$ (A^{2+} and B^{2+}= Mn, Fe, Co, and Ni; 0≤ x≤ 2 and n= 0, 2) were prepared by thermal-drying or mechano-assisted synthesis and, depending on the metal cation and water content, different layered frameworks were obtained, which have been solved from laboratory powder X-ray diffraction data. All obtained solids were pyrolyzed under 5%H_2-Ar atmosphere, at different temperatures, in order to obtain transition-metal phosphides (M_xP) which have been studied as possible electrocatalysts toward Oxygen Evolution Reaction (OER), Oxygen Reduction Reaction (ORR) and Hydrogen Evolution Reaction (HER). Correlations between the crystalline structures of the precursor phases with the electrocatalytic activity of the pyrolyzed derivatives will be discussed.

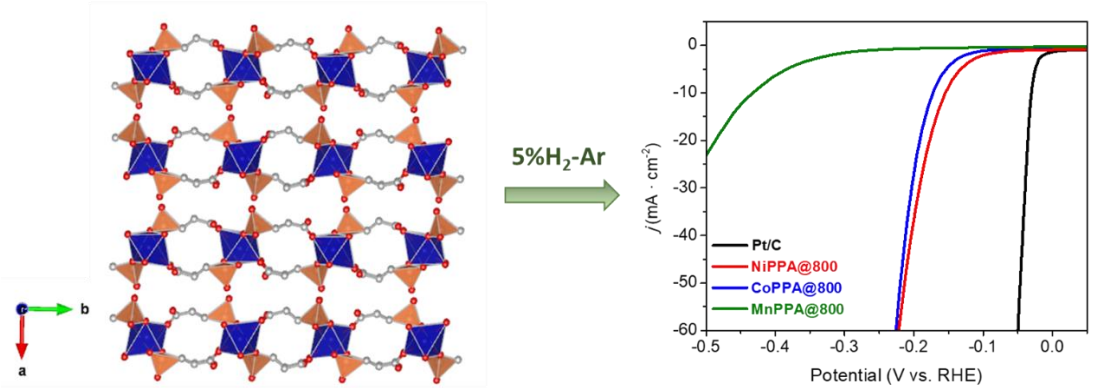

Figure 1. Packing of the layers in $Co[O_3PCH_2CH_2COOH]_2$ (**CoPPA**) and linear sweep voltammetry curves of selected electrocatalysts, obtained at 800 ºC, toward the HER.

References

[1] X. Lin, *et al*. *Adv. Mater. Interfaces* **2020**, *7*, 2000676.

[2] Zhu, Y.-P., *et al*. *ACS Materials Lett.* **2020**, *2*, 582−594.