

Synthesis, structural characterization and electrocatalytic properties of cobalt phosphides and pyrophosphates derived from glyphosine.

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Area: chemical crystallography; structure and properties of materials

Metal phosphonates (MPs), a subclass of coordination polymers, result from the bonding of phosphonic acids (RPO_3^{2-}) with metal ions, giving rise to an uniform dispersion of the metal sites at the atomic scale. This characteristic allows the preparation of metal-phosphorous-based nano-carbon composites by a simple one-step pyrolysis, what makes them very attractive precursors of Non-Precious Metal Catalysts (NPMCs) [1, 2].

Herein, we report the synthesis, characterization and electrochemical properties of three cobalt(II) coordination polymers derived from the glycine-N,N-bis(methylenephosphonic acid) (BPMGLY), with formula $[\text{Co}(\text{C}_4\text{H}_9\text{O}_8\text{NP}_2(\text{H}_2\text{O})_2)] \cdot n\text{H}_2\text{O}$ ($n=0, 2$). In contrast with the zero-dimensional structure of $[\text{Co}(\text{C}_4\text{H}_9\text{O}_8\text{NP}_2(\text{H}_2\text{O})_2)] \cdot 2\text{H}_2\text{O}$ (**Co-BPMGLY-I**) [3], the two new polymorphs synthesized, $\text{Co}(\text{C}_4\text{H}_9\text{O}_8\text{NP}_2(\text{H}_2\text{O})_2)$ (**Co-BPMGLY-II** and **Co-BPMGLY-III**), whose structures have been solved from powder diffraction data, show two-dimensional frameworks with different connectivity between the Co^{2+} ions and the ligand within the sheets (Figure 1).

These MPs were used as precursors of NPMCs by pyrolyzing them under 5% H_2/Ar at different temperatures. The electrochemical behavior of the resulting compounds, mainly crystalline cobalt pyrophosphates and/or phosphides, is fully studied regarding to the Oxygen Evolution and Reduction Reactions (OER and ORR, respectively) as well as Hydrogen Evolution Reaction (HER). Cobalt phosphide (CoP) derived from **Co-BPMGLY-I** displayed the best results, showing an overpotential of 156 mV for HER.

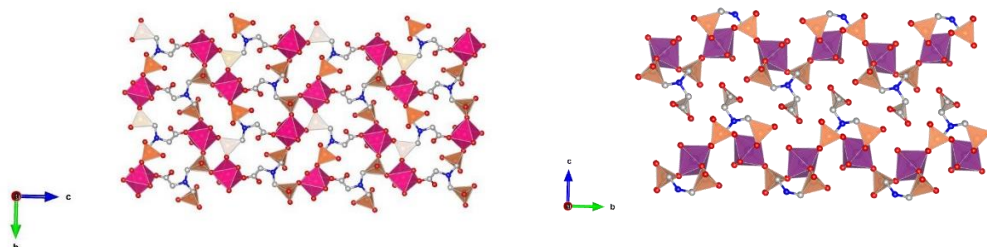


Figure 1. Crystalline structure of Co-BPMGLY-II (left) and Co-BPMGLY-III (right).

References

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