Metal carboxyphosphonates-based electrocatalysts.
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INTRODUCTION
Oxygen evolution reaction (OER) and Hydrogen evolution reaction (HER) are key steps for efficient energy conversion and storage technologies, which rely in the use of the scarce and expensive precious-metal materials. On the other hand, metal phosphonates, a kind of coordination polymers, formed by the combination of appropriate organophosphonate ligands with a wide variety of metal ions1, can be thermally treated2, to generate non-precious electrocatalysts.

In this work, we report the electrocatalytic properties of a family of pyrophosphates and phosphides solid solutions obtained by pyrolysis of Co1-xFexHPAA (HPAA= H3O2P-CH(OH)-COOH) used as precursor.

EXPERIMENTAL/THEORETICAL STUDY
1. Preparation of precursors:
Different stoichiometric solid solutions with composition Co1-xFexHPAA (x= 0, 0.3, 0.7, 1) were prepared by refluxing of CoSO4 and FeSO4 together with the HPAA ligand (1:1) in an aqueous solution for 1 day. The resulting solids were filtered off, washed with ethanol and, finally, dried at 60°C.

2. Pyrolysis of materials.
The materials were pyrolyzed in a tubular furnace at temperatures between 700 and 1000 °C for 1-5 hours under a N2 or Ar-H2 flow.

3. Cyclic Voltammetry
The electrochemist study of the samples focused in OER. All electrochemical measurements were performed with a Bio-Logic VMP3 potentiostat/galvanostat having a built-in EIS analyzer. The electrochemical activity and stability of catalysts were measured in a three-electrode electrochemical cell using a 3 mm diameter glassy carbon rotating disc electrode (RDE).

RESULTS AND DISCUSSION
Under N2, annealing of the cobalt precursor led a mixture of Co2P2O7 and Co3P4O12. Fe(II)-containing samples evolve to a mixture of monoclinic and triclinic Fe3P2O7. However, treatment in H2-Ar at 850 °C yields a cobalt phosphide, Co2P, or a mixed cobalt-iron phosphide, (Co,Fe)2P.

The bimetallic Co-Fe phosphide samples exhibit an improvement in terms of overpotential respect the analogous cobalt phosphide sample, obtaining the best result (304 mV) for the precursor composition Co0.5-Fe0.5 (fig 1.).

However, pyrophosphates have low values in OER compared to phosphides being Fe-Co pyrolized at 900°C that have the best values (279 mV). Fe pyrophosphate have not catalytic properties. In the same way than phosphides Co have less values than mix Fe-Co, so probably iron have an effect that improve the electrochemical properties of the materials.

CONCLUSION
Co1-xFexHPAA metal phosphonates were prepared and pyrolyzed under N2 and H2/Ar flows. The resulting powders were structural and electrochemically characterized by XRD and CV, respectively. The obtained materials possess different structures depending on the temperature and pyrolysis atmosphere. Samples pyrolyzed in N2 at 1000 °C are monophosphates, while phosphides form in H2/Ar at 850 °C.

REFERENCES

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