

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 $Co_{1-x}Fe_x$ HPAA (HPAA= $H_3O_2P-CH(OH)-COOH$) used as precursor.

EXPERIMENTAL/THEORETICAL STUDY

1. Preparation of precursors:

Different stoichiometric solid solutions with composition $Co_{1-x}Fe_x$ HPAA ($x= 0, 0.3, 0.7, 1$) were prepared by refluxing of $CoSO_4$ and $FeSO_4$ 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 N_2 or $Ar-H_2$ 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 N_2 , annealing of the cobalt precursor led a mixture of $Co_2P_2O_7$ and $Co_2P_4O_{12}$. Fe(II)-containing samples evolve to a mixture of monoclinic and triclinic $Fe_2P_2O_7$. However, treatment in H_2 -Ar at 850 °C yields a cobalt phosphide, Co_2P , 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 $Co_{0.5}Fe_{0.5}$ (fig 1.).

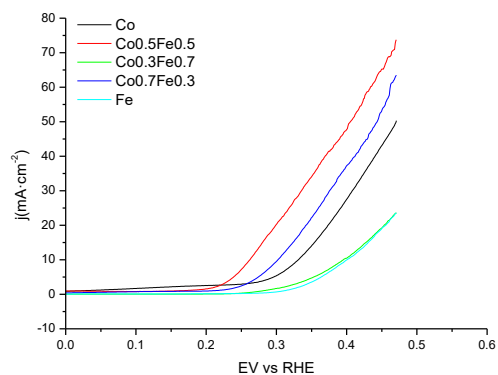


Fig. 1: LSV OER of Co-Fe phosphides, $(Co,Fe)_2P$.

However, pyrophosphates have low values in OER compared to phosphides being Fe-Co pyrolyzed 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

$Co_{1-x}Fe_x$ -HPAA metal phosphonates were prepared and pyrolyzed under N_2 and H_2/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 N_2 at 1000 °C are monophasic diphosphates, while phosphides form in H_2/Ar at 850 °C.

REFERENCES

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2. R. Zhang, et al. ACS Appl. Mater. Interfaces, 9, 14013–14022 (2017).

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