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Study of Oxygen Reduction Reaction by Prussian Blue Analogue Compounds

Daniel Salomão Doretto*, Thiago V. de B. Ferraz, Gabriel de O. Aparecido, Juliano Alves Bonacin.

Abstract

Keywords:
Water splitting, Oxygen reduction reaction (ORR), Prussian blue and its analogues.

Introduction

Water splitting is one of the methods for hydrogen gas generation. In this process the anode produce oxygen through oxygen evolution reaction (OER) and the cathode produce hydrogen through hydrogen evolution reaction (HER). These are examples of feasible electrochemical reactions by the use of electroactive catalyst. In this way many studies for the prussian blue analogues (PBAs) modified electrodes electrocatalyst activity has been contrasting. In this study prussian blue isostructural compounds ($Fe^{II}_3[Fe^{III}(CN)_6]_2$ (**PB**), $Co^{II}_3[Fe^{III/II}(CN)_6]_2$ (**Co-PBA**) and $Ni^{II}_3[Fe^{III}(CN)_6]_2$ (**Ni-PBA**)) have been electrodeposited and theirs electrocatalytic properties analyzed by cyclic and linear voltammetry in KCl (0.1M) and in KNO_3 (0.5M).

Results and Discussion

The electrodes modified electrochemically were obtained from the metallic salt $K_3[Fe^{III}(CN)_6]$, Fe^{2+}, Co^{2+} and Ni^{2+}, forming the prussian blue $Fe^{II}_3[Fe^{III}(CN)_6]$ (**PB**) and its cobalt $Co^{II}_3[Fe^{II}(CN)_6]_2$ (**Co-FePBA**) and nickel $Ni^{II}_3[Fe^{III}(CN)_6]_2$ (**Ni-FePBA)** analogues. The PB thin film was obtained through its deposition on the FTO work electrode by cyclic voltammetry between the potentials -0.245 to 0.555 V (SCE), with a scan rate of 10 mVs^{-1}, in a free oxygen electrolytic cell containing 10 mM $FeCl_3$, $K_3[Fe^{III}(CN)_6]$ and 0,1 M KCl/HCl. The Co-FePBA films were obtained through its electrodeposition on a FTO conductive glass electrode by cyclic voltammetry between the potentials 0.0 to 1.1 V (SCE), with a scan rate of 100 mV s^{-1}, in a cell free of oxygen containing 0.5mM $Co(NO_3)_2$, 0.25mM $K_3[Fe(CN)_6]$ and 0.25M KCl. Ni-PBA films were electrodeposited on FTO conductive glass electrode by cyclic voltammetry between the potentials -0.145 e 0.955 V (SCE), with a scan rate of 50 mVs^{-1}, in a cell containing 2 mM $NiNO_3$, 1 mM $K_3[Fe(CN)_6]$ and 0.05 M KNO_3.

Electrocatalytic analysis were taken from the modified electrodes in O_2 saturated solutions for oxygen reduction reaction (ORR), where the cell was bubbled with O_2 gas for 15 minutes in order to saturate the electrolyte with O_2. The prussian blue analysis performed in a 0.1 M KCl solution and for both Co-PBA and Ni-PBA the electrocatalytic analysis were taken in 0.5 M KNO_3 solution. For the analysis were used potentials between -1.0 and 0.0 V (SCE) by cyclic voltammetry with a scan rate of 20 mVs^{-1}.

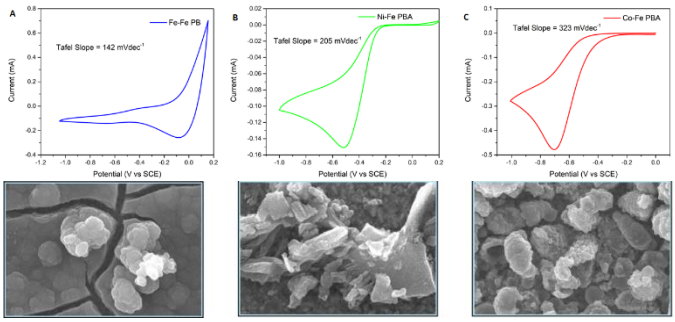

Image 1. ORR for PB (A), Ni-PBA (B) and Co-PBA (C), with their respective values for the tafel slope, with the corresponding SEM images bellow.

Conclusions

After the prussian blue and analogues electrocatalytic analysis can highlight the **PB** ($Fe_3[Fe(CN)6_6]_2$) result as it is the catalyst with the best yield, presenting a tafel slope value of 142 mV dec^{-1}. We can also highlight the great performance of the Ni-PBA catalyst which have a small difference for the tafel slope value of the PB and still have room for improvement.

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