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Study of Water Oxidation and Oxygen Reduction Reactions by Prussian blue and Analogues Compounds

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Abstract
Electrocatalytic processes of water oxidation and oxygen reduction reactions are getting highlighted due to its importance in the development of electrochemical systems to convert and store energy. Oxygen reduction reaction (ORR) in acid and alkaline aqueous solutions demonstrate kinetics and thermodynamic complexity. In sight of that, electrocatalytic analysis of the $Fe^{II}_3[Fe^{III}(CN)_6]_2$ (**PB**) and $Co^{II}_3[Fe^{III/II}(CN)_6]_2$ (**Co-PBA**) thin films (prepared by electrodeposition) for water oxidation reaction (WOR) and oxygen reduction reaction (ORR) were evaluated in acid aqueous solution and in KCl (0.1M) and KNO_3 (0.5M) electrolytes. The PBAs catalysts thin films are highly stable and capable of keeping its catalytic activities during several cycles.

Keywords:
Oxygen reduction reaction (ORR), water oxidation reaction (WOR), 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), 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. Prussian blue isostructural compounds ($Fe^{II}_3[Fe^{III}(CN)_6]_2$ (**PB**) and $Co^{II}_3[Fe^{III/II}(CN)_6]_2$ (**Co-PBA**)) have been prepared and theirs electrocatalytic properties analyzed by cyclic and linear voltammetry in KCl (0.1M) and KNO_3 (0.5M) electrolytes respectively.

Results and Discussion

The electrodes modified electrochemically were obtained from the metallic salt $K_3[Fe^{III}(CN)_6]$ and $K_4[Fe^{II}(CN)_6]$, Fe^{2+} and Co^{2+}, forming the prussian blue $Fe^{II}_3[Fe^{III}(CN)_6]$ (**PB**) and its cobalt analogues $K_2Co^{II}_3[Fe^{II}(CN)_6]_2$ (**Co-Fe^{II}PBA**) and $Co^{II}_3[Fe^{III}(CN)_6]_2$ (**Co-Fe^{III}PBA)**. 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, 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. For the Co-$Fe^{II/III}$PBA films firstly was deposited a Co^0 metallic film from a solution of 0,1 M $CoSO_4$ pH 3 by chronoamperometry applying a potential of -1.6 V over 60 s, then the modified electrode with Co^0 metallic film were treated with solutions of $K_3[Fe^{III}(CN)_6]$ and $K_4[Fe^{II}(CN)_6]$, through a potential of 0.5 V for 300 s forming thin films of **Co-Fe^{II}PBA** and **Co-Fe^{III}PBA** respectively.

Electrocatalytic analysis were taken from the modified electrodes in O_2 solutions for oxygen reduction reaction (ORR) and in absence of O_2 for water oxidation reaction (WOR). The prussian blue $Fe^{II}Fe^{III}$ analysis performed in a 0.1 M KCl solution. For Co-PBA $Co^{II}Fe^{III}$ and $Co^{II}Fe^{II}$ the electrocatalytic analysis were taken in 0.5 M KNO_3 solution.

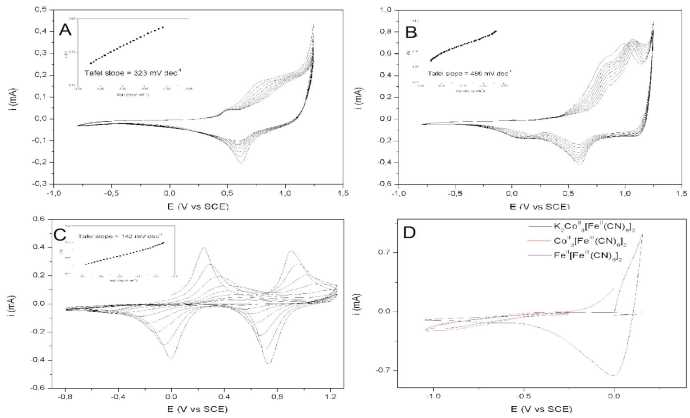

Figura 1. WOR electrocatalytic activities of A) **Co-Fe^{III}PBA**, B) **Co-Fe^{II}PBA** and C) **PB** and D) RRO of Co-$Fe^{II/III}$PBA and PB.

Conclusions

After the prussian blue and analogues electrocatalytic analysis can highlight the **PB** ($Fe^{II}_3[Fe^{III}(CN)_6]_2$) result as it is the catalyst with the lowest degradation among those studied in WOR, also the one with the best yield, presenting a tafel slope value of 142 mV dec^{-1}. Furthermore this catalyst have obtained the lowest overpotential value for water oxidation compared to the others in this study.

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