DOI: 10.20396/revpibic2720192721

XXVII Congresso de Iniciação Científica Unicamp
16 a 18 de outubro de 2019 - Campinas | Brasil

Modification of conventional and 3D printed electrodes with Co3[Co(CN)6]2 catalyst for oxygen evolution reaction studies.

Rodrigo R. Kogachi*, Amanda T. N. de Moraes, Priscilla J. Zambiazi, Juliano A. Bonacin.

Abstract
The oxygen evolution reaction is one of the barriers to the development of technologies involving water splitting, a process which generates hydrogen gas, an alternative clean source of energy. To determine the catalytic efficiency of cobalt(II) hexacyanocobaltate(III) in this reaction, structural characterizations and electrochemical measurements were made for applications on modified electrodes.

Key words:
cobalt(II) hexacyanocobaltate(III), modified 3D printed electrodes, oxygen evolution reaction.

Introduction

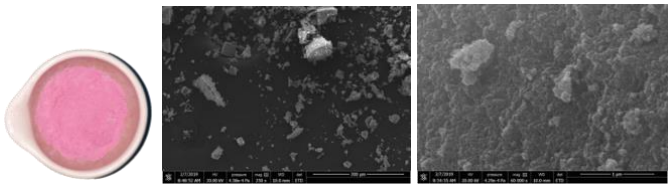
The search for new ways to obtain energy is a global challenge. Hydrogen gas stands out as a clean alternative, whose subproduct of the combustion reaction is only water vapor, in addition to it's high calorific power[1].

$H_2(g)$ can be produced by water electrolysis, composed by the reduction of H^+ ions and the oxygen evolution reaction (OER), which is neither kinetically nor thermodynamically favorable and with a high overpotential associated[1,2]. In this context, the $Co_3[Co(CN)_6]_2$ catalyst, a Prussian Blue analogue (PBA), is studied to optimize the process.

Therefore, structural characterization methods and electrochemical measurements such as scanning electron microscopy (SEM) and linear sweep voltammetry (LSV) were performed on the catalyst and on a 3D printer filament with $Co_3[Co(CN)_6]_2$ incorporated to it, in order to determine the catalytic efficiency of the electrodes in OER.

Results and Discussion

The synthesis of cobalt(II) hexacyanocobaltate (III) generated a crystalline pink solid, as shown in **Image 1(a)**. Its morphology was investigated by SEM, revealing the existence of caracteristic cubic nanoparticles of the PBA, as seen in **Images 1(b)** and **1(c)**.



(a) **(b)** **(c)**

Image 1. (a) Powdered catalyst. **(b)**, **(c)** Scanning electron micrographs of $Co_3[Co(CN)_6]_2$.

The studies related to the process of water oxidation assisted with the catalyst were applied on modified electrodes, produced after the milling of polylactic acid (PLA)/graphene filament and subsequent heating and mixing with the powdered catalyst. Then, the homogeneous mass had its size reduced on a marble surface and was introduced into the laboratory's bench-extruder. **Image 2** shows the scheme of the modified electrode production.

In a pH 7 solution, a LSV was performed on the modified electrode with 20%(m/m) of $Co_3[Co(CN)_6]_2$, generating the graph of **Image 3(a)**. The Tafel plot on **Image 3(b),** considering a 1.59 – 1.79V range, resulted in a Tafel slope (TS) of 422 $mV.dec^{-1}$. Comparing this result with literature, it is possible to see that these high values for TS are a refflection of the nature of the electrodes. For exemple, a fluorine doped tin oxide (FTO) glass is more conductor than a polymer based electrode, considering this 422 $mV.dec^{-1}$ to be an acceptable value for the TS[3].

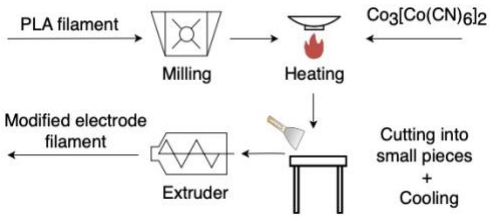


Image 2. Flowchart for incorporation of the catalyst into the PLA/graphene filament.

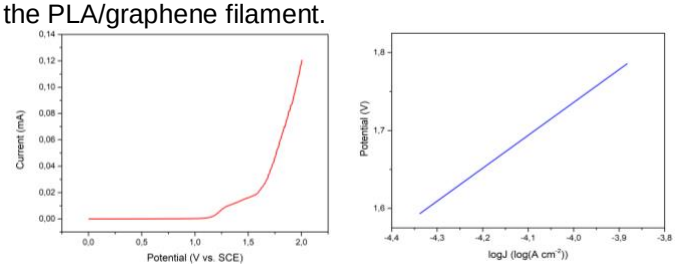


Image 3. (a) Linear voltammogram of modified electrodes (PLA/graphene/catalyst). **(b)** Tafel slop derived from the linear sweep voltammogram from 1.59 to 1.79V.

Conclusions

Through the electrochemical studies performed on the PBA synthetized in this work, it was observed that even though $Co_3[Co(CN)_6]_2$ did not obtain a TS as good as expected, its low cost enables a large scale production, that compensates the small slope achieved. Furthermore, 3D printing technology associated with software modeling increases the number of possibilites for applications in the water splitting field.

Acknowledgement

Acknwoledgemts to CNPq and FAPESP for financial and institutional support (grant#2013/22127-2 and grant#2017/23960-0).

[1] Doyle, R. L.; Lyons, M. E. G. The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design, in: S. Giménez, J. Bisquert (Eds.), *Photoelectrochem. Sol. Fuel Prod.*, Springer International Publishing, Cham, **2016**: pp. 41–110. doi:10.1007/978-3-319-29641-8_2.
[2] Suen, N.-T.; Hung, S.-F.; Quan, Q.; Zhang, N.; Xu, Y.-J.; Chen, H. M. *Chem. Soc. Rev.* **2017**, *46*, 337–365.
[3] Pires, B. M.; dos Santos, P. L.; Katic, V.; Strohauer, S.; Landers, R.; Formiga, A. L. B.; Bonacin, J. A. *Dalton Trans.* **2019**, 48, 4811–4822.