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Effect of Bi modification on Pt single crystals towards the glycerol electrooxidation in alkaline media

Victor Y. Yukuhiro*, Matheus B. C. de Souza, Rafael A. Vicente, Cléo T. G. V. M. T. Pires, Pablo S. Fernández

Abstract
The high demand for the biodiesel has increased the glycerol (GlOH) generation, since it is a co-product of biodiesel production, surpassing the industrial demand. In this context, the glycerol electrooxidation reaction (GER) is an interesting option for its chemical valorization, generating high value-added products. In the present work, we studied the GER on different surfaces of Pt single crystals modified with bismuth to understand the effect of the catalyst structure on the activity and reaction pathways.

Key words:
Electrocatalisys, Glycerol, Single Crystal

Introduction

The increasing demand for biodiesel has increased the glycerol (GlOH) generation, since it is a co-product of its synthesis. This increasing in the availability of GlOH surpassed the industrial demand. Due to this, many research groups started to investigate alternative uses for this excess GlOH[1].

This work intends to study the GER in alkaline media using Pt single crystals of the main crystallographic orientations modified with bismuth. We aim to understand the effects of catalyst structure towards the activity of Pt for this reaction, and the effects of Bi modification.

Results and Discussion

Image 1 shows the positive potential sweep for the GER on Pt electrodes. We observed that Pt(100) shows the highest current densities and Pt(110) the lowest onset potential without the Bi modification.

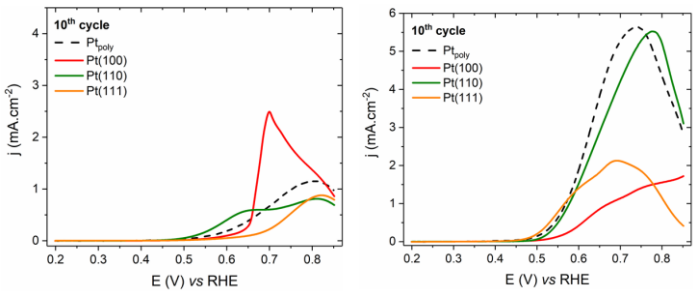

Image 1. 10th positive going scan of the GER in absence (left) and presence (right) of Bi^{3+} ions in solution. Base electrolyte is 0,1 M NaOH + 0,1 M GlOH, with 10^{-5} M Bi_2O_3 in the Bi-modification, with scan rate 10 $mV.s^{-1}$.

After adding Bi^{3+} ions to the electrolyte with GlOH, the (110) facet increases the current density by more than fivefold. The (111) facet had an increase in its current density, but more interestingly, lower the onset of the reaction for about 0,2V. Finally, the (100) neither improve the onset nor the current density.

Our results explain the higher current densities observed on the polycrystalline Pt electrode after the bismuth modification. A polycrystalline electrode is a combination of several crystallographic orientations. We showed that (110) facet has the highest activity among the different crystallographic orientations examined, after the Bi modification. Therefore, the (110) facet is the main contributor to the GER in alkaline media on a polycrystalline Pt electrode.

Conclusions

The electrode modification with Bi showed an increase in activity for some surfaces. We observed that Pt(110) shows the highest current density and is the major contributor to the behavior shown for a polycrystalline Pt electrode. For the (111), a lower onset and higher current densities were observed, when comparing to the unmodified electrode. In the following, we will characterize the oxidation products using a combination of *in-situ* FTIR and HPLC.

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[1] Ciriminna, R. et. al. *Eur. J. Lipid. Sci. Technol*. **2014**, 116(10), 1432.