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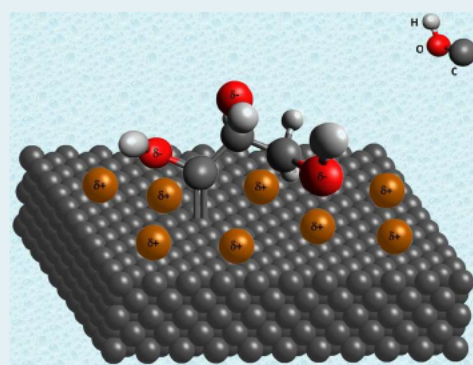
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Pb- and Bi-Modified Pt Electrodes toward Glycerol Electrooxidation in Alkaline Media. Activity, Selectivity, and the Importance of the Pt Atoms Arrangement

Matheus B. C. de Souza, Victor Y. Yukuhiro, Rafael A. Vicente, Cléã. G. Vilela Menegaz Teixeira Pires, José L. Bott-Neto, and Pablo S. Fernández*

ABSTRACT: Herein we investigated the effect of the adsorption of Bi and Pb on polycrystalline platinum (Pt_p) on the electrooxidation of glycerol (EOG) in alkaline media by combining electrochemical, spectroscopic (in situ FTIR), and analytical (online HPLC) techniques. Besides, we used single crystal Pt electrodes to understand the effect of the modification of Pt_p in terms of the atomic arrangements on its surface. We found that the activity of Pt_p increases in the presence of Pb (Pt_p -Pb), which acts by suppressing the pathways with complete C—C bond breaking (to produce carbonate) and enhancing the production of glycerate, formate, tartronate, and glycolate. We also found that Pt(100) and Pt(111) are affected by the adsorption of both adatoms. However, the modification of Pt(110) explains the results obtained with Pt_p . This basal plane is highly activated by Bi and Pb and its behavior is similar to those of Pt_p -Bi and Pt_p -Pb, respectively. These results permit the conclusion that the adatoms acts mainly by activating Pt atoms with low coordination, which generally binds the adsorbates more strongly and, in consequence, suffers more from poisoning. The adatoms act by preventing the formation of multiple bonded intermediates, likely through a combination of a third body effect and also to a change in the electronic configuration at the surface of the catalyst. We propose in this work that the higher promotion of the EOG by the adatoms in alkaline media is due to a stabilization of the negatively charged intermediates by the Coulombic interaction with the positively charged adatoms.

KEYWORDS: Glycerol Electro-oxidation Reaction, Platinum, Lead, Bismuth, in situ FTIR, Online HPLC, Single Crystal Electrodes



INTRODUCTION

The electrochemical conversion of biomass-derived molecules arises as a valuable opportunity toward a green production of fine chemicals and/or electrical energy. In particular, the abundance of glycerol (GLOH) and its several possible value-added oxidation products makes it an interesting molecule to be used in fuel cells and electrolyzers.^{1–6}

The electrooxidation of glycerol (EOG) has been extensively studied on noble metal electrodes both in acid and alkaline media.^{6,7} However, due to the much higher reactivity of the conjugated base (the reaction is sped up when the pH surpasses the pK_a of the alcohol that is being oxidized⁸), the number of studies in alkaline media have increased in the last few years. Thus, despite the complicated solution chemistry,⁹ the use of GLOH in alkaline media in the anode of electrolyzers or fuel cells can contribute with the development of a more sustainable energy use and conversion.^{1–6} In this context, the development of new technologies, for instance, microfluidic electrochemical systems,^{10,11} gives new opportunities for the application of the electrooxidation of alcohols for the

production of energy, value-added oxidized derivatives, and high purity hydrogen.

We recently showed that the adsorption of Bi on polycrystalline Pt electrodes (Pt_p) highly increases the surface activity and the selectivity toward the production of glycerate.¹² Besides, we also showed that the current densities reached with this system were an order of magnitude higher than for similar electrodes in acid media.^{13–15} It has been shown that Pb does not behave very differently than Bi when adsorbed on Pt, especially when it comes to the oxidation of small organic molecules.^{16–18} Thus, in this work we study the EOG in alkaline media on Pb-modified Pt_p . Besides, with the aim of understanding the relation between the Pt atom arrangements at the surface of the catalyst and the effect of the

modifications by adatoms, we study the EOG on single crystal Pt electrodes modified by Bi and Pb.

We found that Bi and Pb promote the EOG and that the electrode activity depends on the adatom coverage. We also found that both adatoms speed up the production of glycerate, formate, glycolate, and tartronate. Finally, by using single crystal electrodes, we conclude that the adatoms act by preventing the adsorption of strongly adsorbed intermediates in low-coordinated Pt atoms, avoiding the poisoning of the most reactive sites of the catalyst.

EXPERIMENTAL SECTION

Electrochemical System and Surface Preparation. A three-electrode cell was used with a potentiostat/galvanostat (μ Autolab type III, Methrom). The working electrode (WE) consisted of a platinum wire with a spherical end, while the counter electrode was a Pt foil. Both electrodes were cleaned by immersion in aqua regia for 30 s, rinsed with ultrapure water, and annealed in a butane flame, followed by quenching with ultrapure water. The reference electrode used was a reversible hydrogen electrode (RHE), and all potentials in this work are with respect to it.

Irreversible adsorption of Pb on Pt was performed by submerging the WE in a $\text{Pb}(\text{NO}_3)_2$ solution for a fixed amount of time with concentrations ranging from 10^{-5} to 10^{-3} M without potential control.¹⁹ After rinsing with ultrapure water, in order to calculate the electrode coverage it was transferred to an electrochemical cell containing only 0.1 M NaOH, and a voltammogram from 0.50 to 0.05 V was recorded. The electrode coverage (θ_{Pb}) was calculated from the hydrogen desorption peaks in this region, by comparing the charge associated with this process before and after the Pb deposition. The Pb-modified electrode (called $\text{Pt}_p\text{-Pb}$ from now on) was then removed from the cell while polarized at 0.5 V, rinsed with ultrapure water, and transferred to a cell containing 0.1 M NaOH + 0.1 M GIOH.

Single Crystal Experiments. Besides Pt_p , Pt single crystal electrodes with (111), (110), and (100) facets, purchased from icryst, were used. Prior to each experiment, to avoid contamination by the adatoms, the surface was cleaned by forming a meniscus with an aqua regia solution for 5 s, followed by rinsing with ultrapure water. Then, the electrode was flame annealed in a butane-oxygen flame for 30 s, followed by cooling in a reductive atmosphere composed by Ar/ H_2 (~2:1) for 40 s. The electrode surface was protected by a droplet of ultrapure water saturated with the Ar/ H_2 mixture to prevent contamination during the transfer to the electrochemical cell.

Blank voltammograms were acquired in 0.5 M H_2SO_4 for each facet before the EOG, to check the system cleanliness and the surface orientation. Then, the electrode was transferred to an electrochemical cell containing 0.1 M NaOH + 0.1 M GIOH + the adatom source (10^{-5} M Bi_2O_3 , 10^{-5} M or 10^{-4} M Pb^{2+}). The meniscus was formed after polarization at 0.3 V and held at this potential for 180 s, followed by the cyclic voltammetry experiment at 10 mV s^{-1} .

In Situ FTIR. In situ Fourier transform infrared (FTIR) experiments were carried out using a Shimadzu IR Prestige-21 spectrometer with MCT detector. A spectroelectrochemical cell equipped with a CaF_2 window, placed on top of a specular reflection accessory (Veemax II, Pike Technologies), was used. The Pt-based electrodes were prepared as described in the electrochemical system and surface preparation section. In situ

FTIR spectra were obtained during linear sweep voltammetry in 0.1 M NaOH + 0.1 M GIOH from 0.2 to 0.85 V at 1 mV s^{-1} . All spectra were collected with an average of 164 interferograms and 4 cm^{-1} resolution. The spectra were plotted as the ratio R/R_0 , where R_0 is the reference spectrum collected at 0.2 V and R is the sample spectrum as a function of potential.

Online Sample Collection and High-Performance Liquid Chromatography (HPLC). A platinum disk with 1.0 cm diameter was used as the WE during online sample collection. Samples were collected using a Shimadzu sample collector FRC-10A by placing a PEEK capillary close to the WE (in the hanging meniscus configuration). Prior to sample collection, nine cycles were performed at 10 mV s^{-1} , so that the HPLC results can be correlated to the stable voltammogram. Samples were collected at $60 \mu\text{L min}^{-1}$, while the potential was swept at 1 mV s^{-1} , therefore each sample corresponds to a 60 mV potential interval in the corresponding potential sweep. Samples travel for 7 min through the PEEK capillary tube until reaching 0.5 mL eppendorf tubes, containing $10 \mu\text{L}$ of a 0.3034 M H_2SO_4 solution, used to reduce the sample's pH to 3.30 so that undesired side reactions are avoided⁹ and to match the mobile phase's pH.

HPLC measurements were performed in a Shimadzu LC-6AD chromatograph with a quaternary pump, a thermostatic column compartment, an UV-vis, and a refractory index detector, both kept at $35 \text{ }^\circ\text{C}$. Three columns (Aminex HPX87-H + two Shodex Sugar SH1011) were used in series with a Bio-Rad 1250131 precolumn, kept at $84 \text{ }^\circ\text{C}$. The mobile phase was 0.5 mM H_2SO_4 with a flow rate of 0.6 mL min^{-1} , and the injection volume was $20 \mu\text{L}$. This methodology of analyzing the samples collected online during the cyclic voltammetry will be called online HPLC from now on.

Chemicals. Solutions were made with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, $25 \text{ }^\circ\text{C}$, Millipore), and the chemicals were used without prior purification. The chemicals employed were sulfuric acid (ISO grade, Merck Emsure), nitric acid (p. a. ACS, LS Chemicals), hydrochloric acid (p. a. ACS, Vetec Chemistry), glycerol (ACS grade, Sigma-Aldrich), sodium hydroxide (semiconductor grade, 99.999% trace metal basis, Sigma-Aldrich), lead(II) nitrate (99.999% trace metals basis, Sigma-Aldrich), and bismuth(III) oxide (ReagentPlus, Sigma-Aldrich). Chemicals used for the HPLC and FTIR standards were dihydroxyacetone (Pharmaceutical Secondary Standard, Sigma-Aldrich), D-glyceric acid calcium salt dihydrate (99%, Sigma-Aldrich), DL-glyceraldehyde ($\geq 90\%$, Sigma-Aldrich), glycolic acid (99% ReagentPlus, Sigma-Aldrich), sodium mesoxalate monohydrate ($\geq 98.0\%$, Sigma-Aldrich), glyoxylic acid monohydrate (98%, Sigma-Aldrich), tartronic acid (97%, Sigma-Aldrich), oxalic acid (99%, anhydrous, Sigma-Aldrich), formic acid ($\geq 95\%$, Sigma-Aldrich), sodium β -hydroxypropionate hydrate ($\geq 97\%$, Sigma-Aldrich), and deuterium oxide (99.9% atom% D, Sigma-Aldrich).

RESULTS

Electrochemical Results. Figure 1 shows the 10th positive-going scan of the EOG in Pt_p for solutions containing different Pb^{2+} concentration. Figure S1 shows the changes in the positive potential sweep along cycling. Irreversible adsorption of the adatoms also shows a similar trend (Figure S2). Different to Bi,¹² where we found an optimum concentration of 10^{-5} M, in this case the highest activities were observed in a wider range of concentrations, that is, 10^{-5}

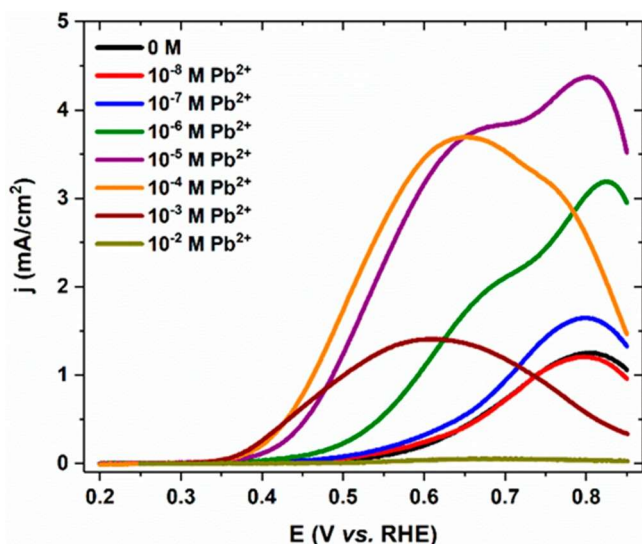


Figure 1. Tenth positive-going scan of the EOG on Pt_p in 0.1 M NaOH + 0.1 M GIOH with varying concentrations of Pb^{2+} in solution. Scan rate: 10 mV s^{-1} .

and $10^{-4} \text{ M Pb}^{2+}$ (Figure S3). Very interestingly, cycling the Pt_p in 0.1 M NaOH + $10^{-x} \text{ M Pb}^{2+}$ (without GIOH) we found that the higher activities match the concentrations where the hydrogen adsorption–desorption region was completely suppressed, as was already found for $\text{Pt}_p\text{–Bi}^{12}$ (Figure S4).

In Situ FTIR and Online HPLC. In order to understand the electrochemical results in terms of the products and/or intermediates formed during the positive potential sweep, we combine in situ FTIR and online HPLC.

Figure 2 shows spectra obtained at different electrochemical potentials for Pt_p and $\text{Pt}_p\text{–Pb}$. A careful discussion about the

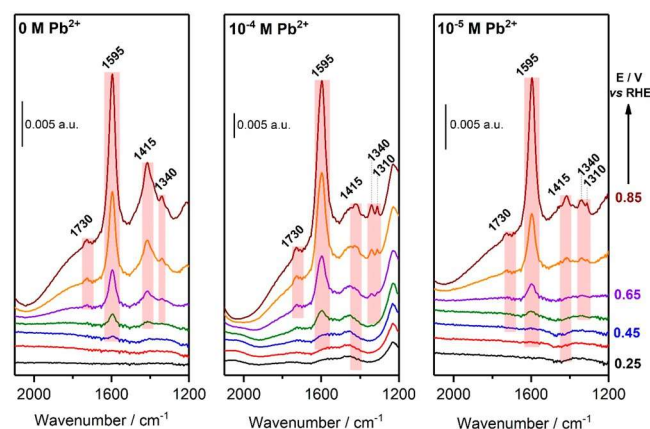


Figure 2. In situ FTIR spectra obtained for the EOG on Pt_p in 0.1 M NaOH + 0.1 M GIOH with 0 M (left), 10^{-4} M (center), and 10^{-5} M (right) Pb^{2+} ions in solution. Scan rate: 1 mV s^{-1} .

band assignment was made in our previous paper.¹² However, in this work we took spectra for several possible products at lower concentrations (Figure S5), that is, with values similar to those determined by using HPLC (shown in Figure 3), and we found important differences for some products. For all the systems studied, we observe an intense and broad band centered at 1595 cm^{-1} (that could be due to the presence of many molecules), other broad feature at 1415 cm^{-1} likely due to the generation of carbonate (even if it is not possible to

discard contributions from other molecules, for instance, formate), and two relatively small bands at 1340 and 1310 cm^{-1} . The latter are probably due to the generation of oxalate, and the former could have contributions from mesoxalate and/or tartronate. Similar bands were observed in recent contributions^{20,21} using single crystals electrodes for the EOG in alkaline media.

These sets of spectra show that for $\text{Pt}_p\text{–Bi}$, the introduction of Pb significantly reduces the band assigned to carbonate (1400 cm^{-1}), indicating a suppression of the EOG pathway in which the two C—C bonds are broken. However, our previous analysis and comparison between the in situ results and the spectra for the standards showed that it is really hard to arrive at definitive conclusions solely using this technique.

Figure 3 shows the potential sweep at 1 mV s^{-1} for Pt_p and $\text{Pt}_p\text{–Pb}$ and the concentration of products close to the electrode as a function of the electrochemical potential. These data were extracted from the chromatograms in Figure S6, the peak assignment was done based on the retention times of several EOG products (Figure S7), and the concentration was calculated using the calibration curves shown in Figure S8 (for more details see S1).

The electrochemical results (Figure 3) show again the impact of the adatom and its concentration on the electrode activity. For all the systems, there is a steady increase in the concentration of glycerate, glycolate, and formate from 0.45–0.50 V. Besides, for $\text{Pt}_p\text{–Pb}$ we also observe the production of tartronate and other minor products, possibly hydroxypyruvate and glyoxylate. These results are similar to those already reported for $\text{Pt}_p\text{–Bi}^{12}$ and complemented in this work (Figure S9).

Single Crystal Electrodes. In order to understand the electrochemical activation of Pt_p in terms of the Pt atoms arrangement, we performed the EOG on Pt(111), Pt(100), and Pt(110) in the presence and absence of Bi and Pb. Figure 4 shows results obtained with Pt_p and the single crystal in the presence and absence of adatoms. The electrochemical result for the unmodified electrodes reminds others recently reported in similar experimental conditions.^{20,21} Bi and Pb highly improve the electrocatalytic behavior of Pt(110). In contrast, Pt(111) and Pt(100) are relatively poorly activated by both adatoms, at least in these experimental conditions. In general, the adatoms improve the reaction onset but they do not have an important effect in the current densities, except for Pt(111)–Bi that doubles the currents shown by Pt(111).

DISCUSSION

Electrochemical results show that the modification of Pt_p with Pb strongly impacts both the activity and selectivity for the EOG. As observed for $\text{Pt}_p\text{–Bi}$, the adatom coverage changes the cyclic voltammogram shape (Figures 1 and S1), which means that the current densities are modified in different ways for different electrochemical potentials. This complex relation between the adatoms coverage and the electrochemical response, also observed for other adatoms in other systems,²² rules out the possibility of having a third body effect as the only response for the activation of Pt_p . The complexity of the modified electrodes is not surprising as it is well-known that the adatoms change the structure and the electric charge during a potential sweep in the potential window used in this paper.^{19,22–24} Heterogeneous surfaces inevitably contain a broad distribution of catalytic sites, that is, microscopic regions with different projected density of states that bind the

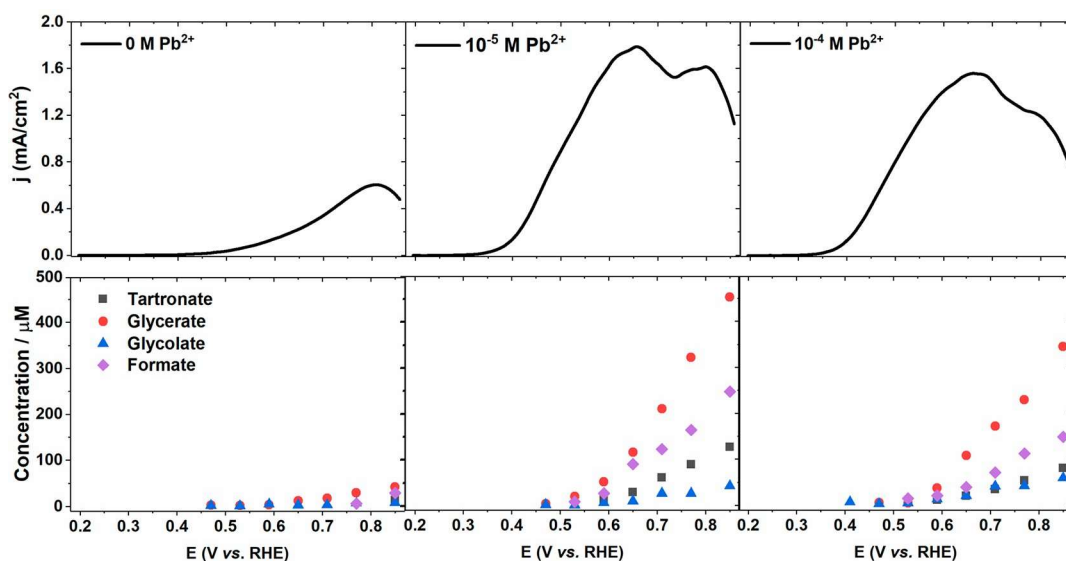


Figure 3. Current densities (above) and distribution of the EOG oxidation products (below) with electrode potential for the Pt_p (left), Pt_p in 10⁻⁵ M Pb²⁺ (center), and Pt_p in 10⁻⁴ M Pb²⁺ (right). The base electrolyte composition was 0.1 M NaOH + 0.1 M GIOH. Scan rate: 1 mV s⁻¹.

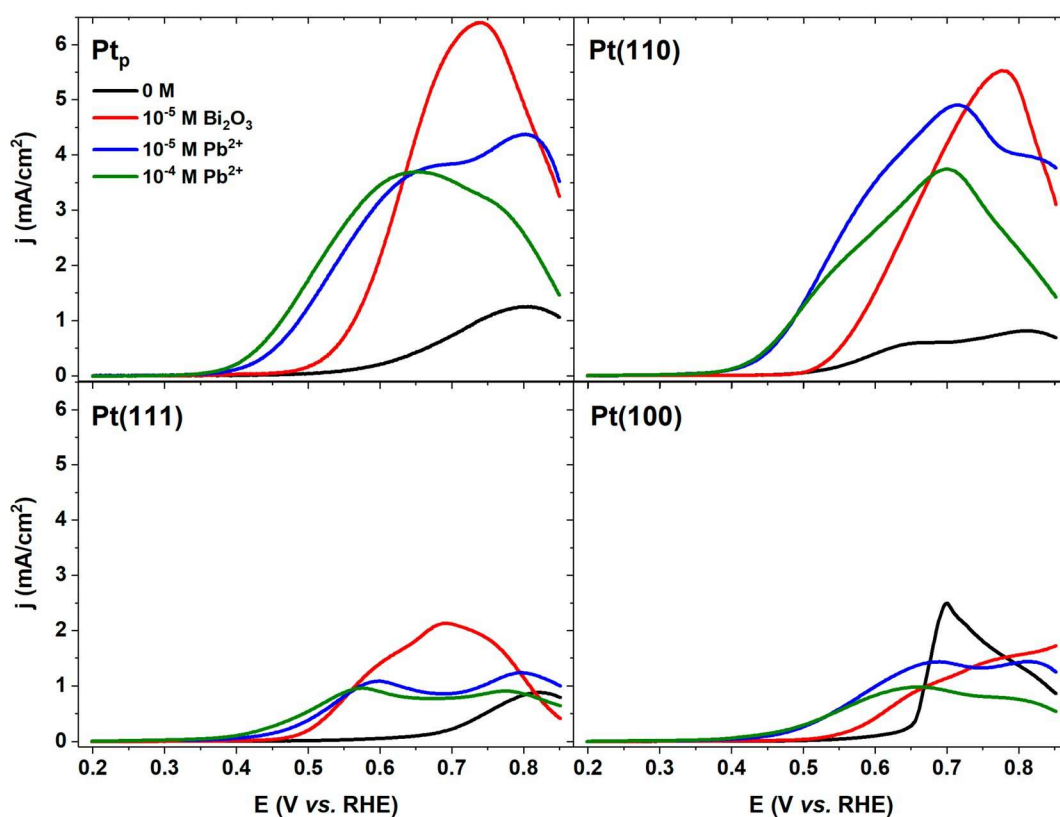


Figure 4. Comparison of the 10th positive-going scan of the EOG on the Pt_p electrode with the Pt_p-Bi and Pt_p-Pb systems (top, left) with the same results obtained using the Pt(110) systems (top, right). The same experiment but using the Pt(110) (top, right), Pt(111) (bottom, left), and Pt(100) (bottom, right) single crystal electrodes. Base electrolyte composition was 0.1 M NaOH + 0.1 M GIOH for all experiments with a scan rate of 1 mV s⁻¹.

adsorbates with different energies (so-called electronic effect).^{22,25} Besides, these kind of structures are mandatory for the possibility of a bifunctional mechanism, which can be present or not in our case.^{22,25}

FTIR shows that the addition of the adatoms decreases the concentration ratio CO₃²⁻/carbonyl-containing compounds, that is, the adatom prevents the total C—C bond breaking of

GIOH. As in our previous paper,¹² we ascribed this effect to a lower probability of finding neighboring platinum atoms, decreasing the available area to form triple- and double-bonded intermediates (Figure 5), which were proposed based on computational experiments performed by Garcia et al.²⁶

Once more, online HPLC shows that it is a powerful technique to study the EOG, clarifying the difficult assignment

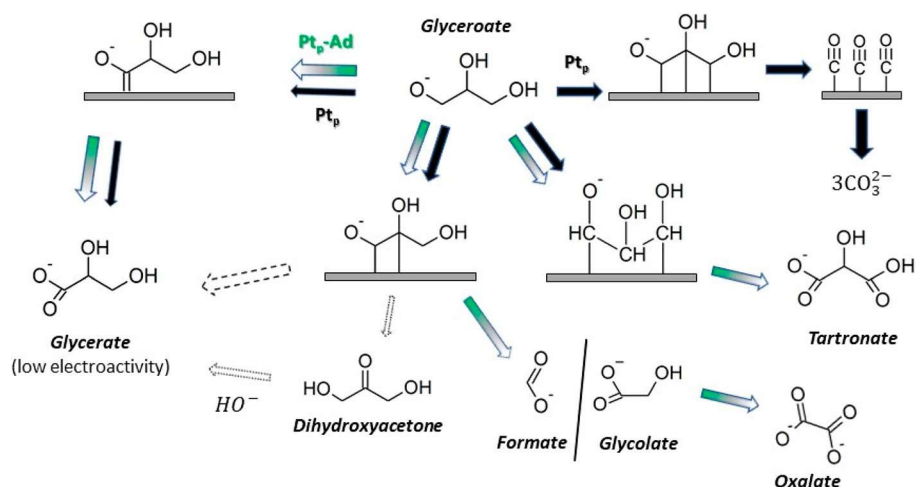


Figure 5. Reaction pathways proposed for the EOG on the bare Pt_p electrode and after modification by Bi and Pb. Black arrows represent the pathway for the clean Pt_p , whereas the green and gray arrows indicate the pathways for the modified electrode. GIOH is not included as a reactant as it is less reactive than its conjugated base.

of the FTIR bands and allowing us to get a more clear picture of the relationship between the adatom modification and the reaction selectivity. The addition of Pb highly increases the production of glycerate, formate, and glycolate, products that were already observed with Pt_p . Interestingly, the presence of Pb and Bi activate a pathway producing tartronate, which is barely observed with Pt_p (Figure S6). We tentatively ascribe this product to a pathway containing an intermediate bonded to the surface through the primary carbons (Figure 5). In principle, tartronate could be generated through the oxidation of glycerate, however, it was shown that it does not react on Pt_p ,²⁷ in Figures S9 and S10, we show that it is also quite unreactive on the modified electrodes.

The addition of the adatom impacts the activity of Pt single crystal electrodes in a different way. Pt(111), Pt(100), and Pt(110) oxidize GIOH at much lower potentials in the presence of the adatoms. However, in terms of current densities, Pt(111) and Pt(100) are barely affected, except when Pt(111) is modified by Bi, which explains the fact that the system Pt_p -Bi has a higher peak current than Pt_p -Pb.

The results obtained with Pt(110) in the presence of adatoms is quite similar to those obtained by Pt_p -Bi and Pt_p -Pb, which permit one to conclude that the main effect of the adatoms is to activate Pt atoms with low coordination and that they are the main contributors to the catalytic effect of Pt_p .

It is frequently said in (electro)catalysis that the atoms with low coordination are usually the most reactive.^{25,28} In the case of Pt, we generally see that Pt(110) (which is the basal plane with atoms with lowest coordination) or defected surfaces are usually relatively active for the oxidation of several small organic molecules but they are prone to poisoning.^{14,28–30} FTIR experiments usually show the presence of adsorbed CO (the most well-known poison for Pt surfaces)^{29,30} even if it is clear that it is not the only strongly adsorbed poisoning substance.²⁶ We showed that the adatoms inhibit the formation of multiple bonded intermediates and diminish the electrode poisoning, for example, reducing the CO coverage.¹² Thus, these experiments strongly suggest that, besides an important electronic effect,^{22,31} the adatoms act to prevent the poisoning of Pt atoms with low coordination, which are present in a high percentage in Pt_p , therefore liberating most of the catalyst surface to oxidize GIOH.

Apart from the third body and the electronic effect, we showed that the adatoms modified the electric double layer (Figure S4), and it is well-known that their configuration and oxidation state depends on the electrochemical potential.^{22–24} Computational and electrochemical experiments showed that when Bi and Pb are deposited on Pt, they tend to remain positively charged.^{17,22} Thus, these adatoms can interact with the oxygen atoms of the EOG intermediates (as those shown in Figure 5) stabilizing them. These kinds of species were previously proposed by Garcia et al.³² for an enediol intermediate in acid media (equivalent to our proposed intermediate bonded to the surface through the primary and secondary carbon). In principle, the positively charged adatom can act activating all the intermediates proposed here. Besides, it is reasonable to believe that the adatom-intermediate interaction can be higher than in acid media, since one of the oxygen atoms is negatively charged, enhancing the contribution of the Coulombic attraction. This interaction might be one of the reasons why Bi and Pb promoted the EOG more in alkaline than in acid media.

Regarding the structure of the adsorbates, an intuitive reasonable possibility would be to propose an interaction between the negatively charged oxygen atom of the glycerate and the positively charged adatom. We do not discard this possibility, but we think that the intermediates adsorbed through the carbon are a more direct step toward the necessary dehydrogenation of the carbon chain. As mentioned earlier, similar intermediates to those of Figure 5 were already proposed,³² but more systematic computational experiments are needed in order to get further insights about the EOG in alkaline media in the presence and absence of adatoms.

Finally, using more adatoms (with different electro-negativities) and in situ X-ray absorption experiments in the Pt and adatoms edges, we could get deeper insights about the relationship between the catalyst surface structure and the p-d band electronic structure as a function of the electrochemical potential.³³ These sets of data (coupled to computational chemistry experiments) could potentially permit one to connect the electrodes activity and selectivity with fundamental aspects (structural and electronic) of the modified electrodes and ultimately guide us to a rational design of surfaces with high activity and selectivity for the EOG.

CONCLUSION

Bi and Pb adatoms promotes the EOG on Pt_p. The modification of the surface decreases the available area for the formation of multiple-bonded intermediates, modifies the electronic configuration at the surface of the catalyst, and generates positively charged species that may act to stabilize the intermediates of the reactions.

The adatoms speed up the production of glycerate, glycolate, formate, and tartronate and suppress the complete oxidation of GIOH to carbonate.

Interestingly, both adatoms promote the EOG in acid and alkaline media, however, the difference in activity between the bare and the modified electrode is much bigger in alkaline media. We ascribed it to a higher stabilization of the negatively charged intermediates (in acid media they have no charge) by the positively charged adatoms.

ASSOCIATED CONTENT

*Supporting Information

The Supporting Information is available free of charge at

EOG in 0.1 M NaOH + 0.1 M GIOH with partial electrode coverage; cyclic voltammetry experiments in 0.1 M NaOH + 10^{-x} M Pb²⁺ (from x = 8 to 1); ATR spectra of possible oxidation products in 0.1 M NaOH; chromatograms of possible oxidation products in the acidified electrolyte solution; chromatograms for the EOG in 0.1 M NaOH + 0.1 M GIOH in the absence of Pb²⁺ and presence of 10⁻⁵ M Bi₂O₃, 10⁻⁵ and 10⁻⁴ M Pb²⁺; calibration curves for the quantification of products detected by HPLC; oxidation of glycerate in Pt_p, Pt_p-Bi and Pt_p-Pb (PDF)

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Notes

The authors declare no competing financial interest.

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