Pb and Bi-modified Pt electrodes towards Glycerol Electrooxidation in Alkaline media. Activity, Selectivity and the importance of the Pt atoms arrangement.

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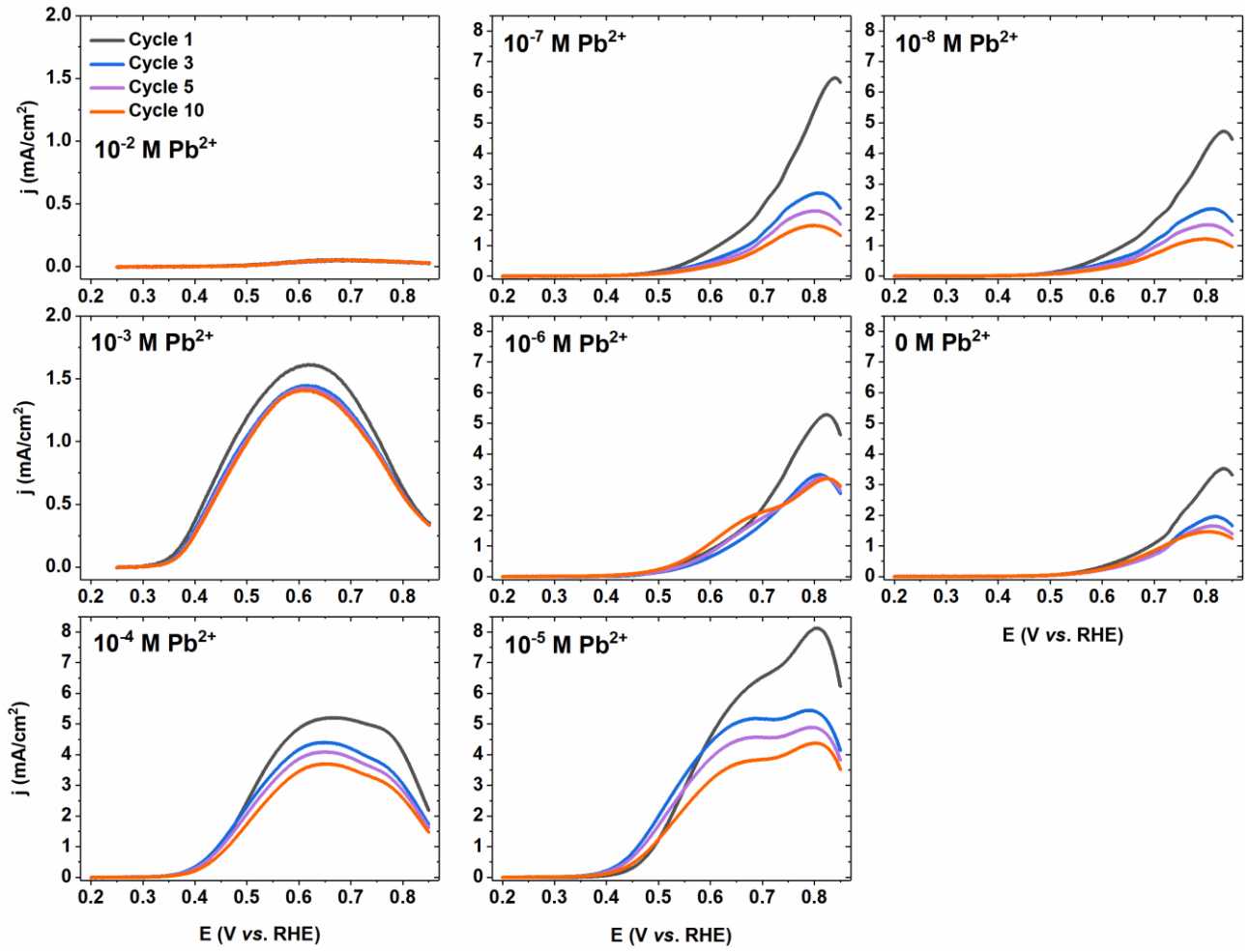

Figure S1: Positive-going scan of several oxidation cycles on polycrystalline platinum (Pt_p) in 0.1 M NaOH + 0.1 M Glycerol (GlOH), using several Pb^{2+} concentrations, as indicated on the inset of each voltammogram. The 10^{th} positive-scan of each concentration was used to make the figure 1 in the manuscript. Scan rate was 10 $mV.s^{-1}$ for all measurements.

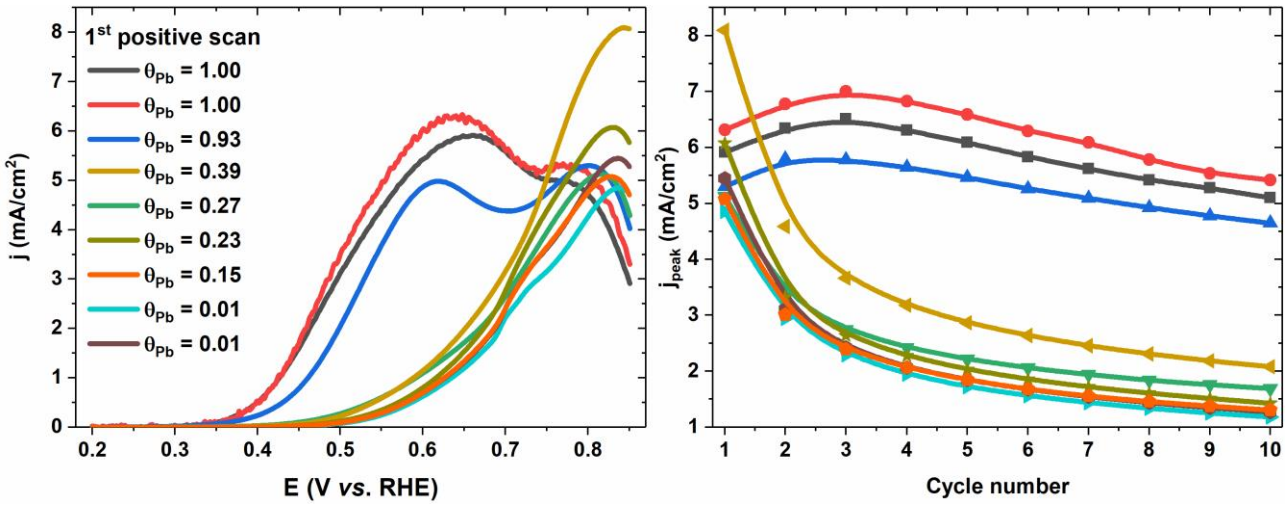

Figure S2: (A) Positive-going scan of the 1st cycle of the electrooxidation of glycerol (EOG) in 0.1 M NaOH + 0.1 M GlOH on Pt_p with varying degrees of lead coverage (θ_{Pb}). Scan rate: 10 $mV.s^{-1}$; (B) Peak current density (j_{peak}) *vs*. cycle number for selected values of θ_{Pb}, using data extracted from figure 1A.

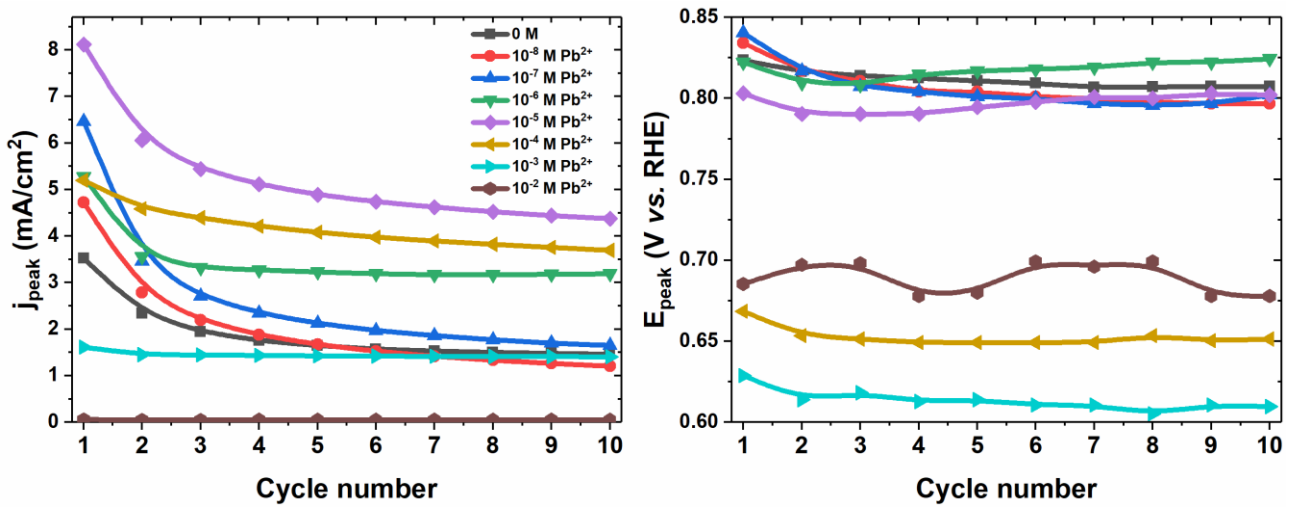

Figure S3: Plots of j_{peak} (left) and peak current potential (right) *vs*. cycle number for the EOG on Pt_p in 0.1 M NaOH + 0.1 M GlOH with varying Pb^{2+} concentrations, as shown. Data extracted from figure 1 in the manuscript.

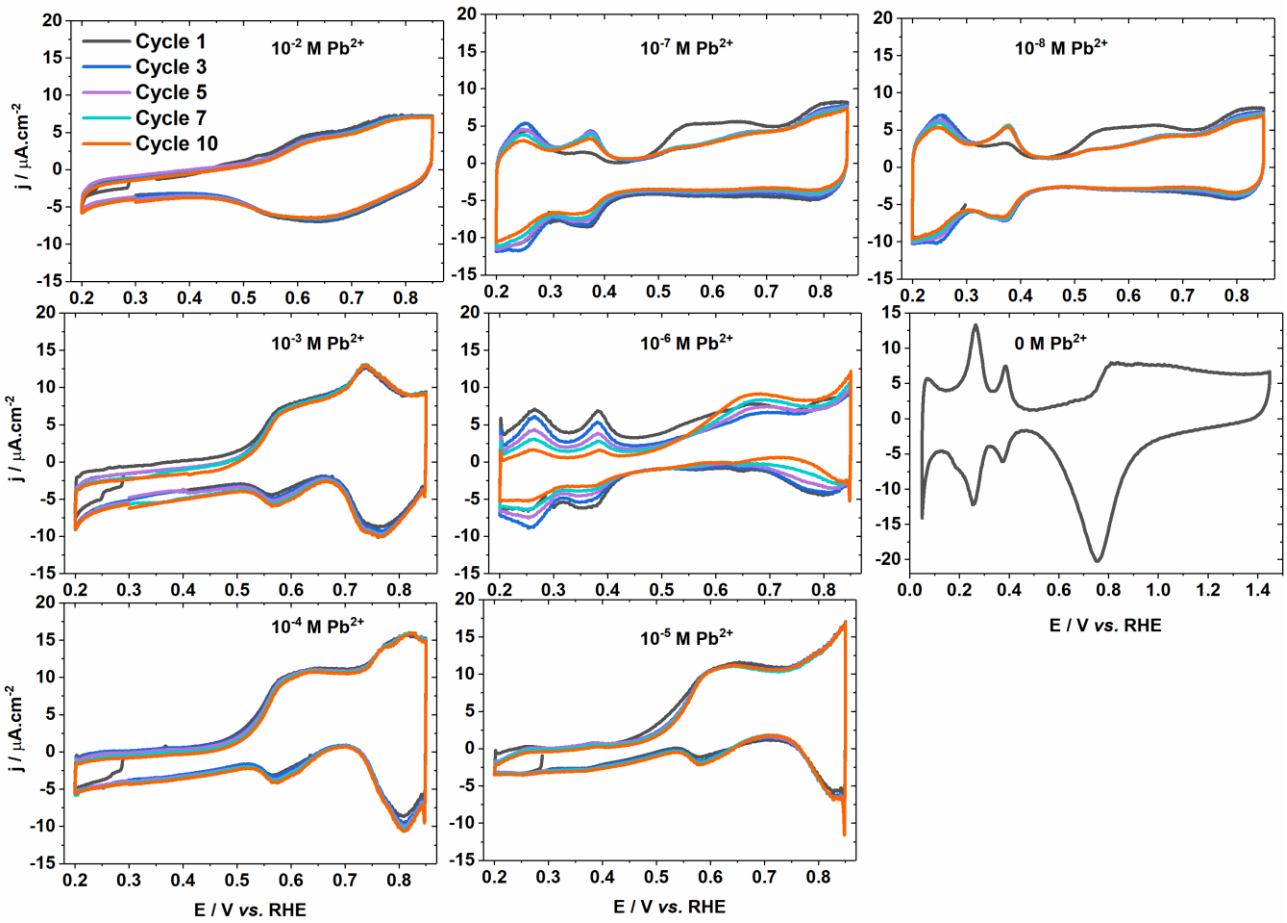

Figure S4: Effect of cycling the Pt_p electrode in 0.1 M NaOH with varying concentrations of Pb^{2+} ions, with the same concentrations used in figure 1 of the manuscript. Scan rate: 10 $mV.s^{-1}$.

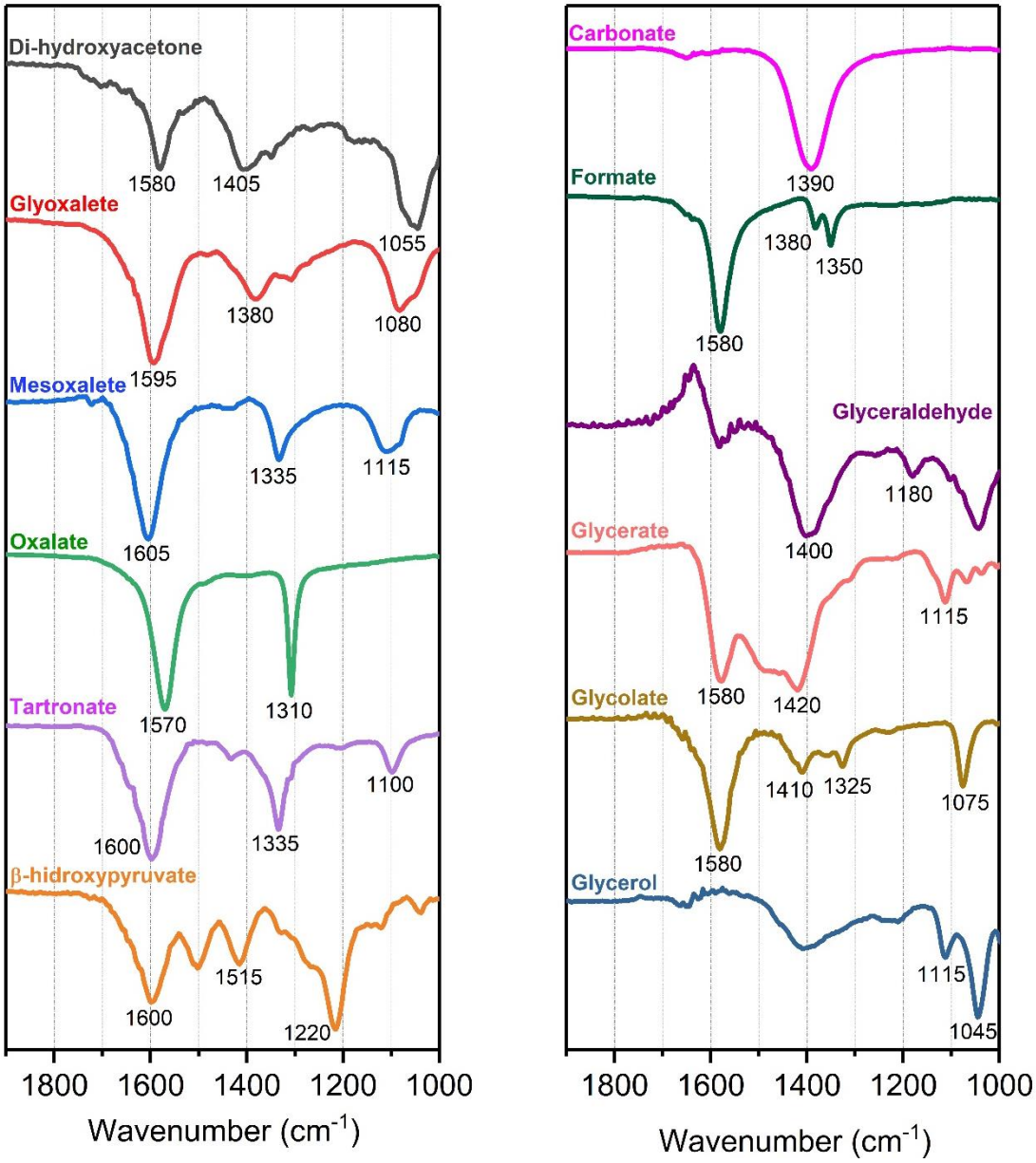

Figure S5: ATR-FTIR spectra of possible glycerol electrooxidation products in 0.1 M NaOH solution + 20 mM product.

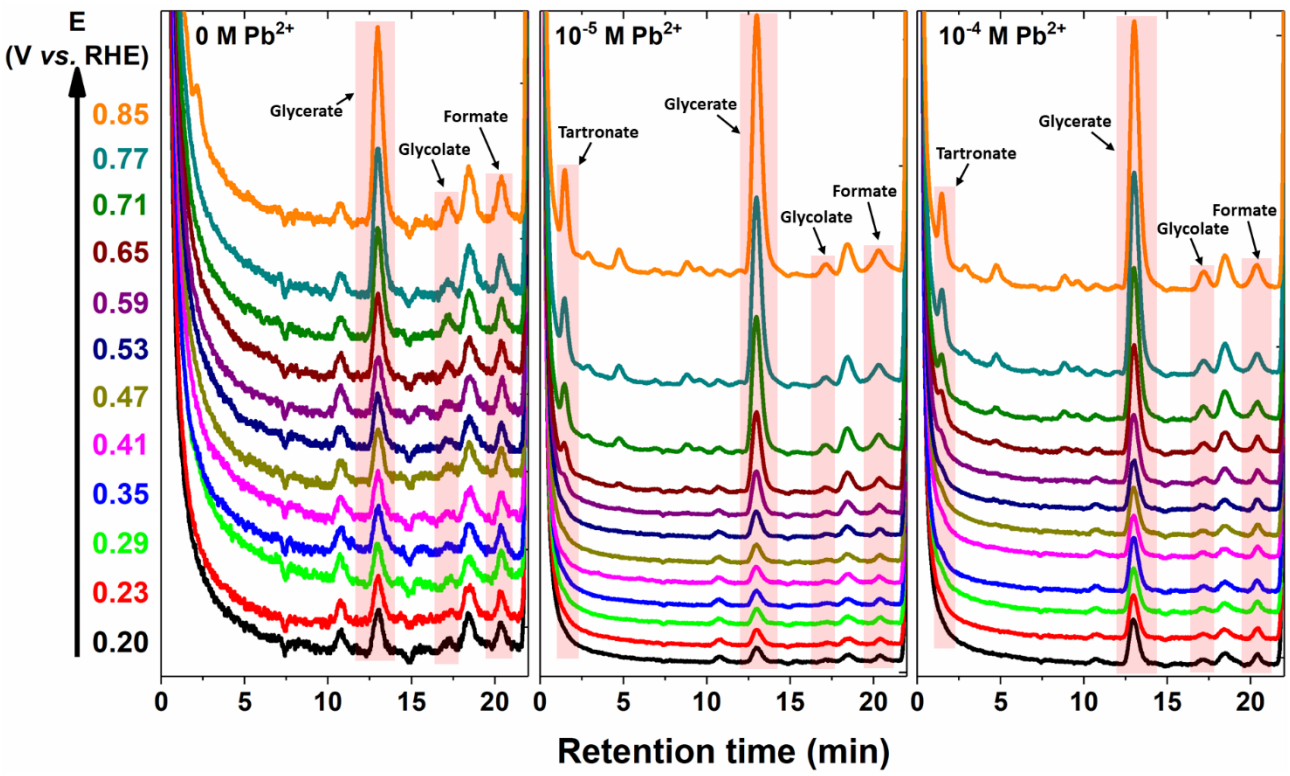

Figure S6: Chromatograms obtained from the samples collected during the EOG on Pt_p in 0.1 M NaOH + 0.1 M GlOH with varying concentrations of Pb^{2+}, as indicated. Scan rate: 10 mVs^{-1}. Samples collected at 60 $\mu L.min^{-1}$. Each chromatogram represents the electrolyte sampled during a 60 mV potential interval, and the scale on the left side indicates the average potential of each intervals.

There are some minor contributions not identified in the figure, for both Pt_p-Pb systems. The 2.5 min peak is likely due to hydroxypyruvate, and the one at 9 min is probably due to glyoxylate. We were unable to identify the peak at 5 min, as it did not match to any of the peaks shown in figure S7.

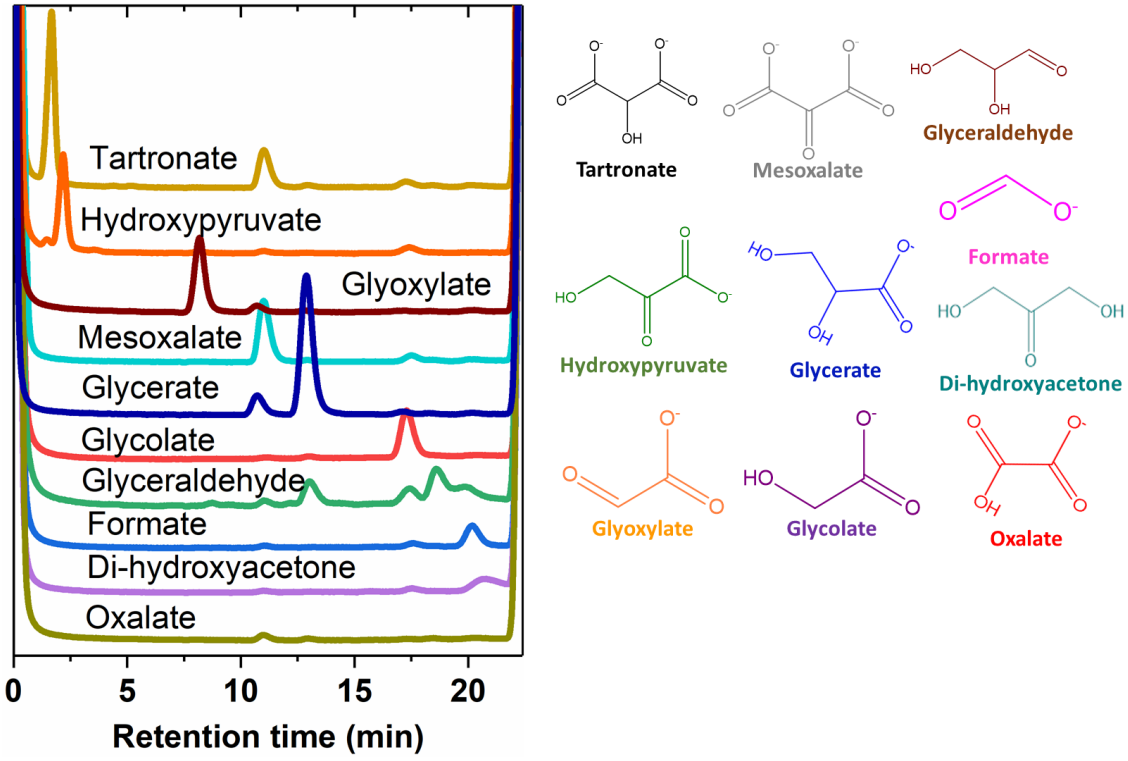

Figure S7: Chromatograms used to identify the oxidation products of the EOG. Each sample contains the acidified electrolyte solution (0.1 M NaOH + 0.1 M GlOH + 0.11 M H_2SO_4) with 1 mM of the analyte.

The calibration curves for the 4 oxidation products (formate, glycolate, glycerate and tartronate) were obtained by making 7 different standard samples, with a volume of 5 mL, each sample with different concentrations of the oxidation products (table S1).

Table S1: Analyte concentrations of the samples used in the calibration curve

	Analyte concentration (µM)			
Sample	Formate	Glycolate	Glycerate	Tartronate
1	5.0	1.0	10.0	10.0
2	20.8	17.5	175.0	91.7
3	36.7	34.0	340.0	173.3
4	52.5	50.5	505.0	255.0
5	68.3	67.0	670.0	336.7
6	84.2	83.5	835.0	418.3
7	100.0	100.0	1000.0	500.0

Each sample consists of a 5 mL solution of the acidified electrolyte (0.1 M NaOH + 0.1 M GlOH + 0.11 M H_2SO_4) with different concentrations of the 4 main oxidation products. The calibration curves obtained are shown in figure S8. Glycolate and formate have a 6-point curve because we were unable to detect them at the concentrations specified for sample #1 in table S1.

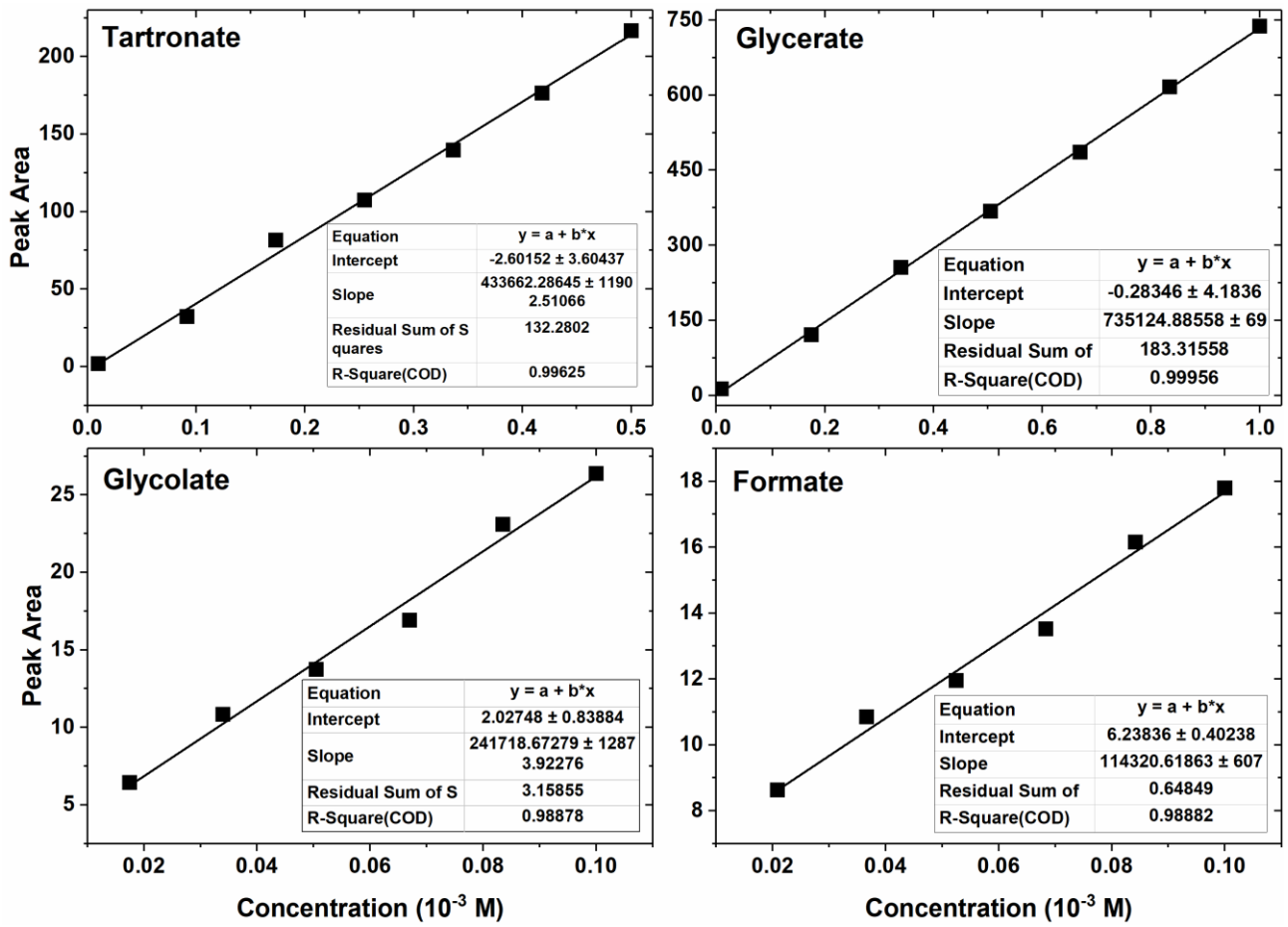

Figure S8: Calibration curves used to quantify formate, tartronate, glycerate and glycolate. Each point was obtained from the samples indicated in table S1.

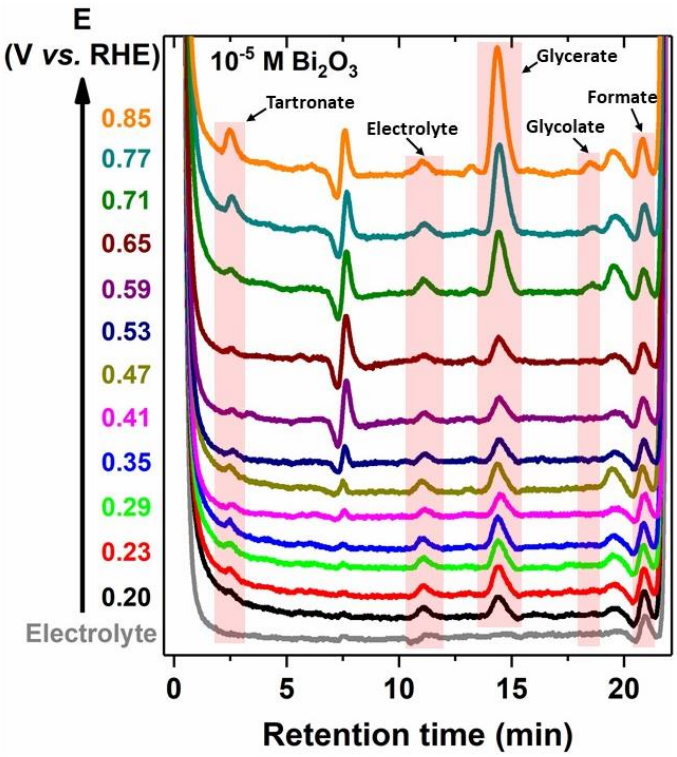

Figure S9: Chromatogram obtained for the EOG on the Pt_p-Bi system, using the same experimental conditions seen in figure S4, with the exception that 10^{-5} m Bi_2O_3 is added to the electrolyte instead of Pb^{2+}. These results were obtained in a similar manner than those of our previous publication, however, the acquisition of a more sensitive detector permit us to improve the signal/noise ratio.

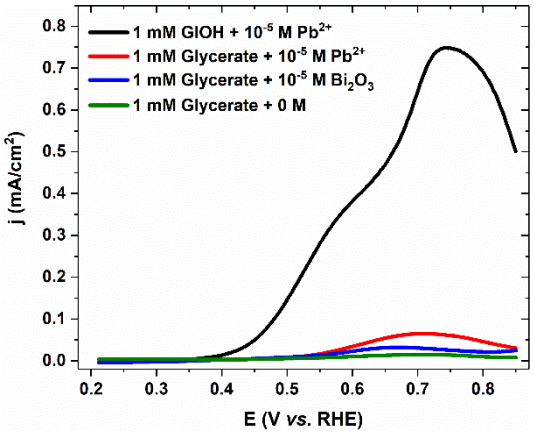

Figure S10: Comparison of the 10^{th} positive-going scan of the EOG with 1 mM GlOH on Pt_p in 0.1 M NaOH + 10^{-5} M Pb^{2+} (black) with the oxidation of 1 mM glycerate in 0.1 M NaOH with 10^{-5} M Pb^{2+} (red), 10^{-5} M Bi_2O_3 (blue) or absence of adatoms (green). Scan rate: 10 $mV.s^{-1}$.