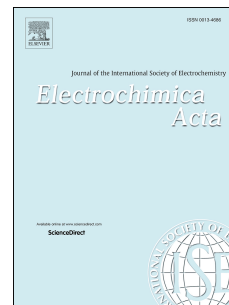# Accepted Manuscript

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Abstract

The creation of defects on the surface of Pt(111) and Pt(100) and the dissolution of Pt were used as probes to investigate the oxidation of the surface in the absence and in the presence of methanol, ethanol, glycerol and ethylene glycol. Electrochemical and Graphite Furnace Atomic Absorption Spectrometry showed that in the presence of ethanol, glycerol and ethylene glycol, in the same potential window, the formation of defects is decreased in comparison to the oxidation of platinum in the absence of these alcohols. Since both the oxidation of the alcohols and the oxidation of the surface depend on PtOH formation, the competition for this species can displace the potential at which the oxidation of the surface oxidation to PtO is favored in the presence of ethanol, glycerol and ethylene glycol. On the other hand, the presence of methanol does not influence the oxidation and subsequent disordering of the surface, possibly because this reaction takes place in parallel with platinum oxidation to PtO.

Keywords: Platinum oxidation; Surface disordering; Platinum dissolution; Alcohol electrooxidation.

1. Introduction

The mechanism of electrooxidation of organic molecules, such as alcohols, is of great importance to energy generation in fuel cells and the production of more added value products. Conditions as pH, nature of the electrocatalyst and concentration can influence the reaction mechanism. Platinum is the most studied electrocatalyst for this kind of reaction, presenting different activity depending on the surface structure. The contribution of PtOH species have been reported in many works [1–10]. In fact, PtOH is the species usually considered as responsible for the oxidation of the adsorbed organic molecules. In the case of alcohols, the following reactions can be considered:

$$R - COH + OH^- + Pt \xrightarrow{k_1} R - COPt + H_2O + e^- \qquad (1)$$

$$Pt + H_2O \xrightarrow{k_2} PtOH + H^+ + e^- \qquad (2)$$

$$R - COPt + PtOH \xrightarrow{k_3} R - COOH \qquad (3)$$

On the other hand, the oxidation of Pt surfaces has been the focus of many researches ([11–17] and references therein). Although Jerkiewicz and coworkers have proposed that Pt is directtly oxidized to PtO [18], the oxidation of platinum is usually summarized in two steps:

$$Pt + H_2O \xrightarrow{k_1} PtOH + H^+ + e^- \qquad (1^{st} \text{ step}) \qquad (4)$$

$$PtOH \xrightarrow{k_2} PtO + H^+ + e^- \qquad (2^{nd} \text{ step}) \qquad (5)$$

After the first step, the oxidation of the surface depends on the presence of PtOH species. As a consequence of Pt oxide formation, Pt dissolution is observed in the negative going sweep [13,19–23].

In this respect, it is expected that in the presence of organic molecules a competition for PtOH$_{ads}$ species should appear. Since there is no way of separating the current related to the surface oxidation from the one obtained from the organic molecule oxidation, it is not possible to evaluate if the surface oxidation takes place in the same extension in the presence of organic molecules than in its absence. Analyzing the voltammograms of alcohol oxidation in comparison to those in free electrolyte, previous works were able to associate the beginning of the oxidation (reaction 3) with the appearance of PtOH$_{ads}$ on the surface and the end of the first oxidation step with the formation of PtO [24–29]. These results enabled the scientific

community to consider that the surface oxidation happens in the same way in the presence of organic molecules or in their absence [25,28,30,31] and works with single crystals do not usually explore the oxidation of organic molecules at potentials higher than 0.9 V. However, considering that both reactions depend on the same species, it is reasonable to expect that some competition must take place, causing mechanistic and kinetics changes in PtO formation. The goal of this work is to investigate if Pt surface oxidation is influenced in the presence of different alcohols. The study is focused on two different electrochemical experiments: Pt dissolution and defect formation on platinum single crystals, both dependent on the PtO formation.

2. Experimental

The solutions used in this work were prepared with H_2SO_4 (suprapur, Merck) and ultrapure water (18.2 MΩcm). Methanol, ethanol, glycerol and ethylene glycol with analytical grade were purchased from Sigma Aldrich. All solutions from electrochemical experiments were deoxygenated with Ar (N50 Air Liquide).

2.1. Pt(111) and Pt(100) disordering

Single crystal electrodes prepared by Clavilier method, as described in [32], were used as working electrodes, a Pt wire as counter electrode and a reversible hydrogen electrode as reference electrode were used. The single crystal electrodes were flame annealed, cooled in an oxygen free atmosphere (H_2 + Ar) and finally quenched and protected with a drop of water saturated with H_2 and Ar before being transferred to the electrochemical cell. After a cycle in the electrolyte free of alcohol (between 0.06 and 0.9 V or 0.8 V, for Pt(111) and Pt(100), respectively) the electrode was transferred to a cell containing the alcohol. First, two cycles up to 0.8 V or 0.9 V, for Pt(100) and Pt(111) electrodes, respectively, were recorded and then the upper potential (E_{upper}) was selected as desired. After the cycles in the presence of alcohol, the electrode was then rinsed with water and transferred back to the cell free of alcohol and another cycle up to 0.8 V or 0.9 V was taken. The electrochemical cells were kept free from oxygen with Ar, but there was no control of oxygen during the transference of the electrode from one cell to the other.

2.2. Dissolution experiments

The dissolution experiments were carried out using a Pt mesh, an Au mesh and a reversible hydrogen electrode as working, counter and reference electrodes, respectively. 200 cycles were performed between 0.06 and 1.3 V in 20 mL of 0.1 molL^{-1}

H_2SO_4 solution in the absence and in the presence of 0.1M of different alcohols (methanol, ethanol, ethylene glycol, 1,2 propanediol and glycerol).

2.3. GF AAS Instrumentation and Analysis

Graphite Furnace Atomic Absorption Spectrometer (ZEEnit 600, Analytik Jena AG, Jena, Germany) equipped with Platinum hollow cathode lamp (operated at 265.9 nm, 6.0 mA and slit 1.2 nm) was used to perform quantitative analysis of Platinum in aqueous samples. Aliquots of the samples (30 µL) were injected in triplicate (n = 3) by autosampler (MPE 60, Analytik Jena AG, Germany) into a pyrolytically coated transverse-heated graphite tube. Argon 99.998% (v/v) was used as the purge gas. The temperature furnace program used was optimized for aqueous solution containing 100 µg L^{-1} of platinum in 0.1 M sulfuric acid medium. The pyrolysis and atomization temperatures were investigated in the ranges of 1200–1700 ºC and 2000–2700ºC, respectively. All measurements were performed using integrated absorbance (peak area). More information about the experimental conditions are available in the Supplementary Information.

3. Results and discussion

3.1. Pt single crystal disordering experiment

It is known that the surface of single crystal electrodes is extremely sensitive to Pt oxidation. As the surface is oxidized, defects are formed on the surface [19,33,34]. In the case of Pt(111) the decrease of Pt(111) – related terrace peak is followed by the increase of (110) – defect peak and a quantification of the surface disordering can be done. Figure 1(a) shows the increase of defects on the surface of Pt(111) as the electrode is cycled between 0.06 and 1.3 V in 0.1 $molL^{-1}$ H_2SO_4. As described previously [35,36], once the electrode is oxidized, the peak at 0.5 V, characteristic of sulfate adsorption on Pt(111) large domain sites, decreases and a reversible couple appears at 0.12 V, related to hydrogen adsorption/desorption on (110) - defects. Other changes, as the appearance of (100) - defects at 0.27 V and the increase of the Pt oxidation/reduction charge can also be seen. The complete interpretation of the evolution of defects as the electrode is cycled above 0.9 V can be found in references [33] and [35]. In this work, the monitoring of (110) – defects and (111) – terraces will be enough to make the argument.

The Pt(100) electrode is even more sensitive to defect formation than Pt(111). The cyclic voltammogram of P1(100) in sulfuric acid is known to have a small peak at ca. 0.28 V and a sharp peak at ca. 0.39 V, related to desorption of hydrogen and adsorption of the anion on the defects and on wide (1x1) surface terraces, respectively [34,37–39]. Figure 1(b) shows the evolution of the voltammetric profile of the Pt(100) electrode submitted to 20 cycles between 0.06 and 1.3 V. It can be seen that in the negative scan, immediately after the first cycle, the peak at ca. 0.39 V (peak i') is almost completely replaced by the peak at 0.28 V (peak ii'), jointly with the increase in the reduction current below 0.2 V. The inversion of the contribution of these two peaks is also seen, in a less pronounced way but growing cycle by cycle, in the positive scan (peaks i and ii), accompanied by changes in the oxygen adsorption region. The reversible processes that takes place at ca. 0.67 V disappears as defects are created on the surface. After 5 cycles there are no more significant changes in the profile, indicating that a stable disordered surface has been reached under voltammetric conditions. To follow more slowly these changes on the Pt(100) surface voltammetry, different upper potentials can be selected. Figure 2a shows the voltammetric changes after one single cycle up to different potentials. The electrode was flame annealed again before recording of each curve and thus correspond to the same initial state. It is possible to realize that as the upper potential increases, and so does the oxide formation, peak i' decreases while an increase can be seen in peak ii'. Both processes are more visible if the potential reaches 1.0 V or higher; at 0.8 V the voltammograms remain stable. Although the inversion in the contribution of peaks i and ii is more visible in the negative scan (i' and ii'), if the electrode is cycled again limiting the upper potential at 0.8 V, peak ii' is partially recovered, achieving a charge comparable to peak i in the positive scan. Figure 2b shows three sequential cycles, the first until 0.8 V, the second until 1.05 V and the third again up to 0.8 V. The behavior of the last is stable as long as the upper potential is kept 0.8 V. This behavior reflects a great mobility of the Pt atoms as consequence of oxygen and hydrogen/anion adsorption on Pt(100) compared to Pt(111) and may indicate that the OH species adsorption in peak i is irreversibly (or through a not completely reversible process) converted to a different species, probably PtO, at more positive potentials. Other possibilities are that this species formed at higher potentials can only be reduced at potentials lower than 0.25 V (peaks iii´and iv´) or that the surface recovers at lower potentials. Figure S1 shows the voltammetric profile after this procedure was repeated five times consecutively. All the cyclic voltammograms of Pt(100) obtained between 0.06 and 0.8 V are stable.

Since the for both Pt(111) and Pt(100) electrodes the appearance of the peaks related to the adsorption of OH on the defects of the surface is dependent on the formation of platinum oxide [33,35,36,38,39], this behavior can be used to measure the extension of the surface oxidation in the presence of alcohol molecules.

The same procedure was repeated in the presence of several alcohols: methanol, ethanol, ethylene glycol and glycerol. The cyclic voltammograms in the presence of alcohols can be seen in the supplementary information (Figures S2 – S8). The results for Pt(111) after the cycles in the presence of two concentrations of ethanol are presented in Figure 3. It is possible to see that in the presence of ethanol the number of defects on the surface formed after 30 cycles up to 1.3 V is significantly lower than in the absence of ethanol. In fact, after being submitted to cycles until 1.3 V in sulfuric acid the electrode presents an electrochemical profile very different from the expected for Pt(111). However, after the same cycling process in the presence of ethanol, the characteristic voltammetric features of Pt(111) can still be seen, with only a few defects, represented by the reversible peak at 0.12 V, and a small decrease of the sulfate adsorption peak on (111) terrace, at 0.5 V. If the concentration of ethanol is increased, the (110) defect peak at 0.12 V even decreases as compared to the previous case, indicating the presence of fewer defects on the surface. These results show that, different from what is usually considered, the oxidation of the electrode surface observed in the absence of ethanol is inhibited in its presence, possibly due to the competition for OH_{ads} species. It seems that in the window potential studied, the rate of ethanol oxidation is higher than platinum oxide formation. The rate of ethanol oxidation increases with ethanol concentration, consuming more OH_{ads} species and thus decreasing the rate of PtO formation. The oxidation of Pt surface to PtO occurs when a precise amount of PtOH is reached on the surface.

The same behavior is observed if ethanol is substituted by ethylene glycol or glycerol (Figure S8), as can be seen in Figure 3b. On the other hand, if the alcohol in solution is methanol, after the 30 cycles up to 1.3 V, it can be seen that the electrode presents as many defects as if it was cycled in the absence of alcohol. The platinum oxide/defects formation does not depend on methanol concentration (Figure 3c), what indicates that in this case, the rate of platinum oxide formation is higher than the alcohol oxidation, and an increase in the alcohol concentration is not enough to prevent the surface oxidation.

Figure 4 shows the voltammetric profile for Pt(100) before and after 15 cycles up to 1.05 V in the absence and in the presence of ethanol, ethylene glycol and

methanol. As for Pt(111), both ethanol and ethylene glycol are able to prevent the oxidation of the platinum surface while methanol allows the formation of PtO and, consequently, the apparition of defects on the Pt(100) surface. Because of the higher sensibility of Pt(100) to oxide formation, the upper potential used in this experiment was considerably lower than for Pt(111) and only 15 cycles were enough to evaluate defect formation [40].

If the upper potential is increased, more defects can be seen, as represented in Figure 5 a and b for ethylene glycol and ethanol, respectively. However, the same oxide formation obtained in the absence of alcohol can only be achieved in the presence of these alcohols if the chosen upper potential is 1.3 V (remark that in Figure 5a the voltammetric curves, after 15 cycles up to 1.3 V, in the absence and in the presence of 0.1 molL^{-1} ethylene glycol are superimposed). If the upper potential is 1.05 V, almost no changes on the electrode surface can be observed after the cycling treatment in the presence of ethanol or ethylene glycol. This potential almost coincides with the end of the first alcohol oxidation peak at (Figure S10), which is 1.08 V. In the presence of methanol, if the upper potential is kept as low as 0.95 V, a stable oxidation profile can be seen (Figure S11) and less defects are formed, compared to the surface cycled in the absence of alcohol (Figure 5c).

Analyzing the ethylene glycol oxidation curves up to different upper potentials, presented in the supplementary information (Figures S10 and S11), if the upper potential is higher than 1.05 V, it is possible to see changes in the peak potential and/or peak current cycle after cycle. However, if E_{upper} is maintained at 1.05 V, the electrode shows a stable activity for the alcohol oxidation, with no changes in current or peak potential from one cycle to the next. This behavior is probably related to the changes observed on the electrode surface (defects) if it is oxidized, what seems to happen in the presence of ethylene glycol only if the potential reaches values higher than 1.05 V. This potential is very close to the end of the peak (1.08 V), being not high enough that the oxidation process has ended, nor low enough so the majority of the alcohol oxidation is still taking place. In this way, the eventual changes observed cycle by cycle for the oxidation of different alcohols, such as increase or decrease in current, can be a consequence of the changes on the surface [40,41], besides the blockage by adsorbed intermediates [42].

3.2. GF AAS Results

Since the oxidation of Pt surface is directly related to the dissolution of Pt, the second experiment carried out to support the results obtained by using single crystal platinum electrodes disordering was the quantification of Pt in solution after 200 cycles between 0.06 and 1.3 V in the presence and the absence of alcohols. Because of the low metal concentration obtained, Graphite Furnace Atomic Absorption Spectrometry (GFAAS) was chosen as the analytical method. Table 1 shows the average ($n = 3$) concentrations of the platinum found in the samples analyzed. It is possible to see that the results are very similar to those obtained from the electrochemical experiments. After 200 cycles, the higher concentration of Pt in solution was obtained in the absence of alcohol and in the presence of methanol. After 200 cycles in the presence of ethylene glycol and ethanol, the Pt concentration level was a little bit lower than in absence of alcohol, while a very small concentration was detected after the 200 cycles in glycerol and 1,2 propanediol. These results are in agreement with the electrochemical results on model platinum single crystal electrodes, indicating that the presence of alcohol molecules, different than methanol, influence the oxidation of the surface, and so, the diffusion of Pt atoms to the solution.

Table 1: Pt concentration ($\mu g\ L^{-1}$) and experimental standard deviation, n = 3, determined in solution aqueous after 200 cycles between 0.06 and 1.3V in H_2SO_4 0.1 molL^{-1}.

	Concentration ($\mu g\ L^{-1}$)
Samples	200 cycles
H_2SO_4	17.22 ± 1.97
Methanol	17.21 ± 0.29
Ethanol	14.11 ± 1.63
Ethylene glycol	16.87 ± 2,45
1,2 propanediol	3.83 ± 1.53
Glycerol	5.86 ± 1.03

3.3. Discussion

The nature of the alcohol as much as the surface structure have important roles in the observed oxidation changes. In this way, it is not yet possible to correlate these variables with the extension of the surface oxidation. However, it is clear from the results presented here that in the presence of organic molecules the oxidation current cannot be easily separated among platinum oxidation and organic molecule oxidation.

Considering that both the reaction of electrooxidation of alcohols and the oxidation of the Pt surface depend on the same reactant, Pt-OH, Figure 6 shows a diagram representing a possible explanation to the observed results. If these reactions have different rate constants and the rate of each one is considered as a linear function of the potential, in the absence of alcohol the oxidation of the surface takes place at potentials higher than 0.8 V (this can vary, depending on the electrode surface structure). However, if the alcohol is present, at this potential the electrooxidation of the organic molecule predominates and the oxidation of platinum will only take place at higher potentials. The oxidation of platinum surface to PtO occurs when a precise amount of PtOH is reached on the surface. The coverage of PtOH increases with potential, but in the presence of alcohols, because of the competition for OH_{ads} species, the specific amount of PtOH needed to form PtO is only achieved at higher potentials. If the concentration of the alcohol is increased, and so its oxidation rate, it leads to an increase of the potential at which the oxidation of the surface is favored.

The presence of methanol does not influence the creation of defects, nor does the increase in its concentration affect its oxidative behavior. For both Pt(111) and Pt(100) methanol oxidation present a higher offset compared to the other alcohols, with a contribution at ca. 1.0 V, suggesting that both methanol and the surface oxidation reactions may be favored in a potential window between 0.8 and 1.1V (see Figures S7, S8 and S12). For both concentrations of Pt(111), the oxidation current at potentials higher than 1.0 V increase cycle by cycle. This behavior, besides for methanol, is only seen for 0.01 molL^{-1} glycerol, as can be illustrated in Figure S4, which shows the formation of more defects on the surface, compared to a higher concentration of glycerol (see Figure S9) and to ethanol (Figure 3). In these cases, we can conclude that this current at E > 1 V is probably related to the oxidation of the surface.

4. Conclusion

Studies of Pt(111) and Pt(100) disordering and platinum dissolution, all related to Pt oxide formation, were carried out in the presence and absence of different alcohols. The oxidation of the surface was measured by the formation of defects on the surface or the dissolution of platinum. The results showed that in the presence of alcohols different than methanol, the oxidation of the surface is displaced to more positive potentials since the surfaces were less defective in the presence of the alcohols than in its absence. This effect is favored by the increase in alcohol concentration. This behavior indicates that the competition for oxygenated species on platinum surface diminishes the formation of Pt oxides. No changes in defect formation

or platinum dissolution were observed in the presence of methanol, suggesting that the oxidation of this molecule may occur in parallel with platinum oxidation to PtO at potentials higher than 0.95V.

Considering that platinum dissolution is an important issue to the study of fuel cells, the results presented in this works are of great importance to this field [22,43]. More work is in progress, but preliminary results show that the competition for OH_{ads} species is also present for other electrodes. If that is the case, adapting the conditions at which the fuel cell functions can be of great importance to the durability of the catalyst.

5. Acknowledgments

6. References

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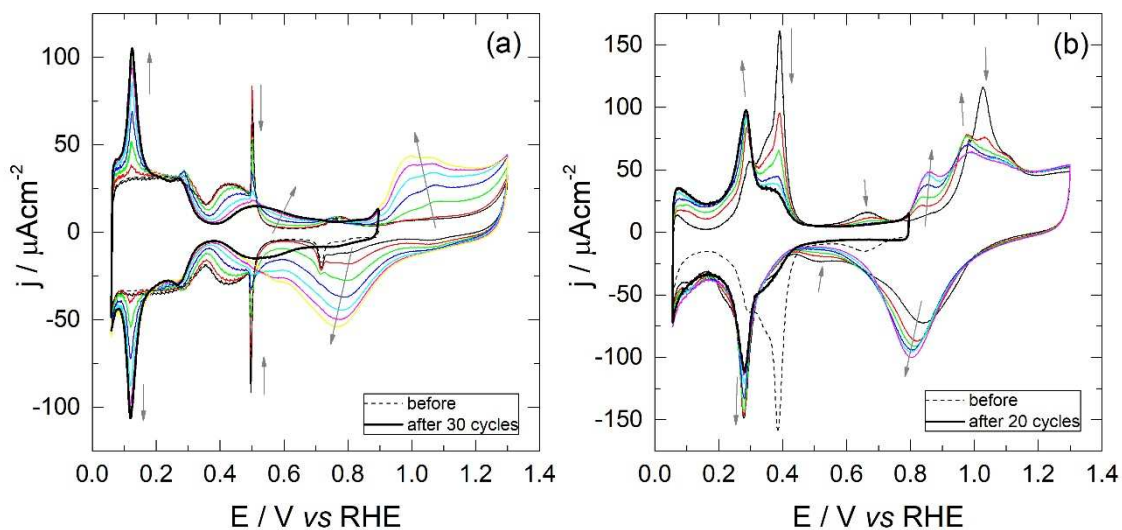
Figure 1

Figure 1: Evolution of Pt(111) (a) and Pt(100) (b) voltammetric profiles as the electrodes are cycled between 0.06 and 1.3 V versus RHE in 0.1 molL^{-1} H$_2$SO$_4$ at 50 mVs^{-1}. Arrows indicate the evolution of peaks. Dotted and bold lines are the cycles before and after 30 (a) or 20 (b) cycles until 1.3 V, respectively. (a) 1st, 5th, 10th, 15th, 20th, 25th and 30th cycles represented; (b) 1st, 2nd, 3rd, 5th, 10th and 20th cycles represented.

Figure 2
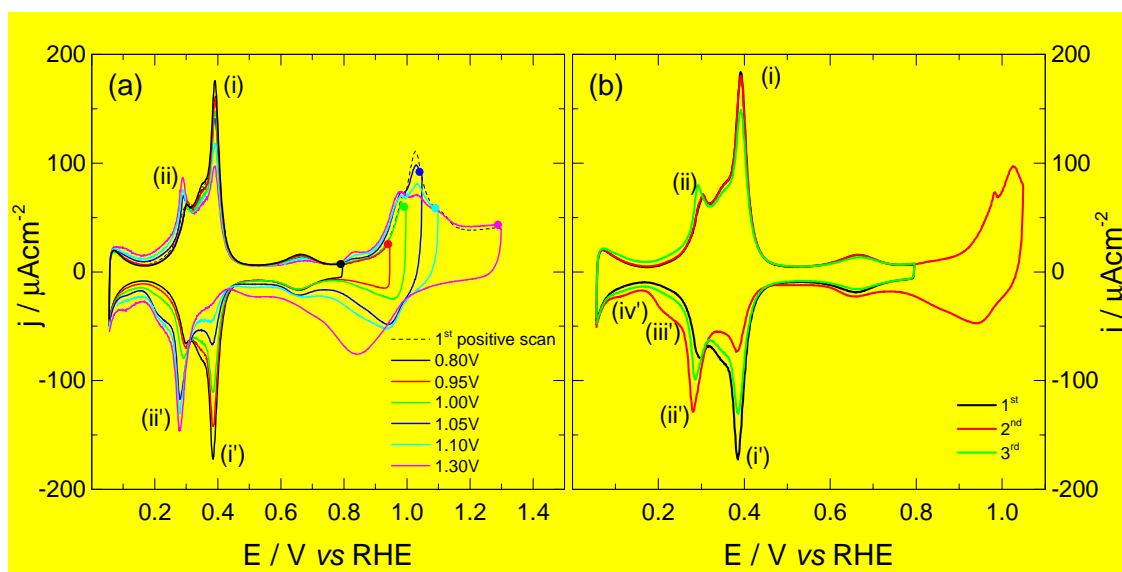
Figure 2: (a) Voltammetric profiles of Pt(100) between different upper potentials and 0.06 V; dashed line represents the first positive scan and dots the end of data acquisition. (b) Three sequential cycles: 1st until 0.8 V, 2nd until 1.05 V and 3rd until 0.8 V. Scan rate 50 mVs^{-1} in 0.1 molL^{-1} H$_2$SO$_4$.
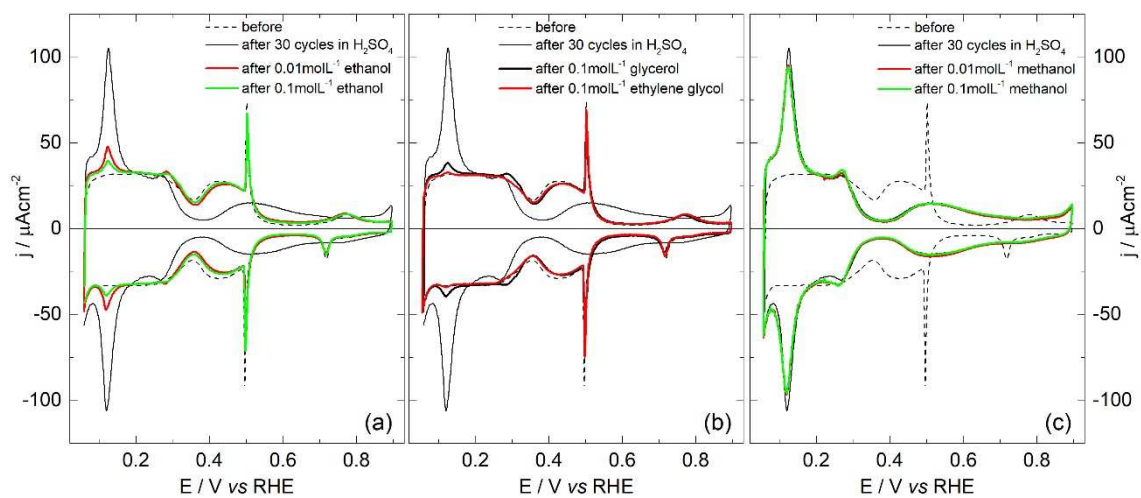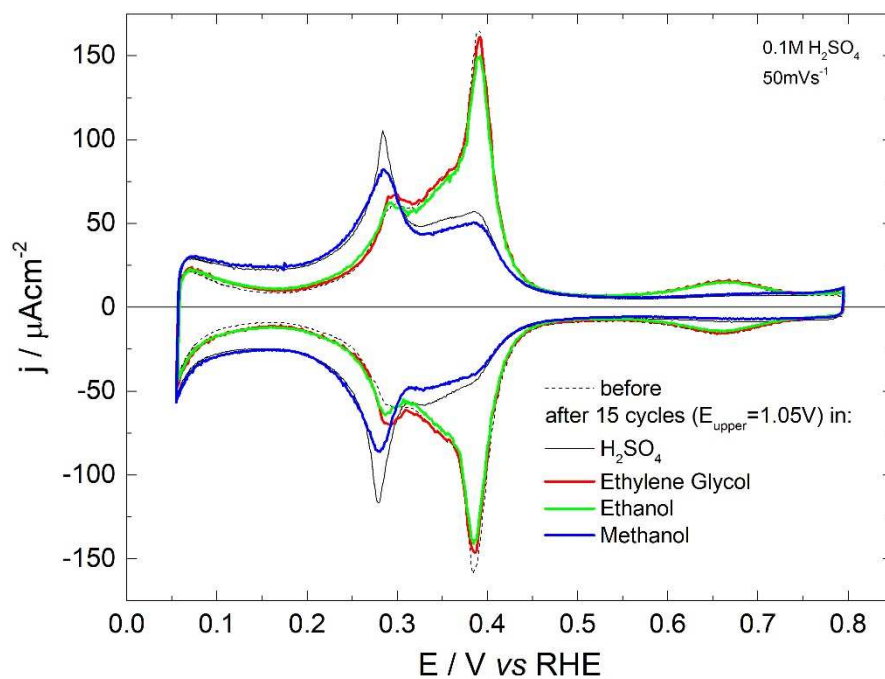
Figure 3

Figure 3: Voltammetric profile of Pt(111) before (dashed) and after 30 cycles in the absence (black) and in the presence of (a) ethanol 0.01 molL^{-1} (red) or 0.1 molL^{-1} (green), (b) glycerol (black) and ethylene glycol (red) 0.1 molL^{-1} and (c) methanol 0.01 molL^{-1} (red) or 0.1 molL^{-1} (green). Scan rate: 50 mVs^{-1} in 0.1 molL^{-1} H$_2$SO$_4$.

Figure 4

Figure 4: Voltammetric profile of Pt(100) before (dashed) and after 15 cycles until 1.05 V in the absence (black) and in the presence of 0.1 molL^{-1} ethanol (green), 0.1 molL^{-1} methanol (blue) and 0.1 molL^{-1} ethylene glycol (red). Scan rate: 50 mVs^{-1} in 0.1 molL^{-1} H$_2$SO$_4$.
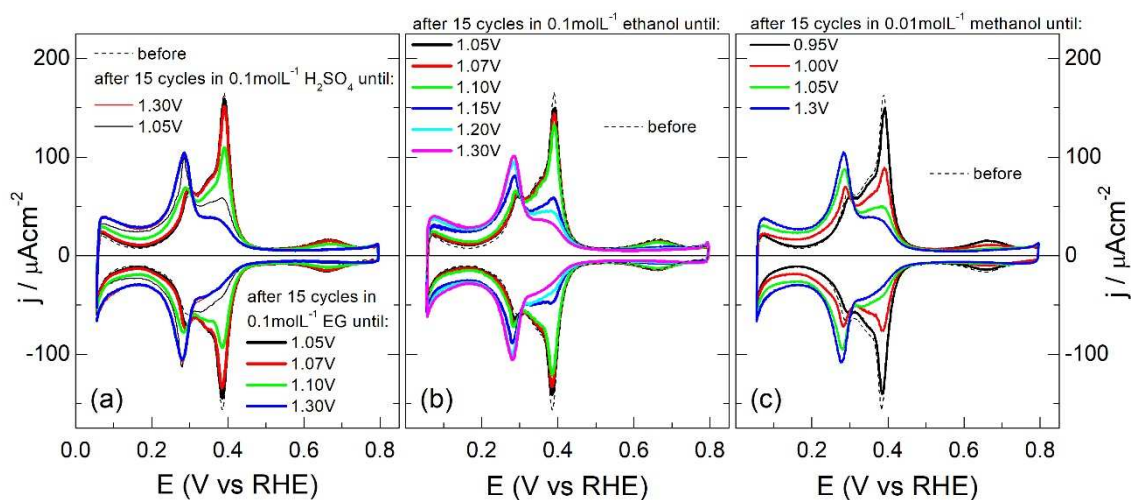
Figure 5

Figure 5: (a) Voltammetric profile of Pt(100) before (dashed) and after 15 cycles in the absence (solid) and in the presence (bold) of 0.1 molL^{-1} ethylene glycol (a), ethanol (b) or methanol (c) with different upper potentials. Scan rate: 50 mVs^{-1} in 0.1 molL^{-1} H$_2$SO$_4$.
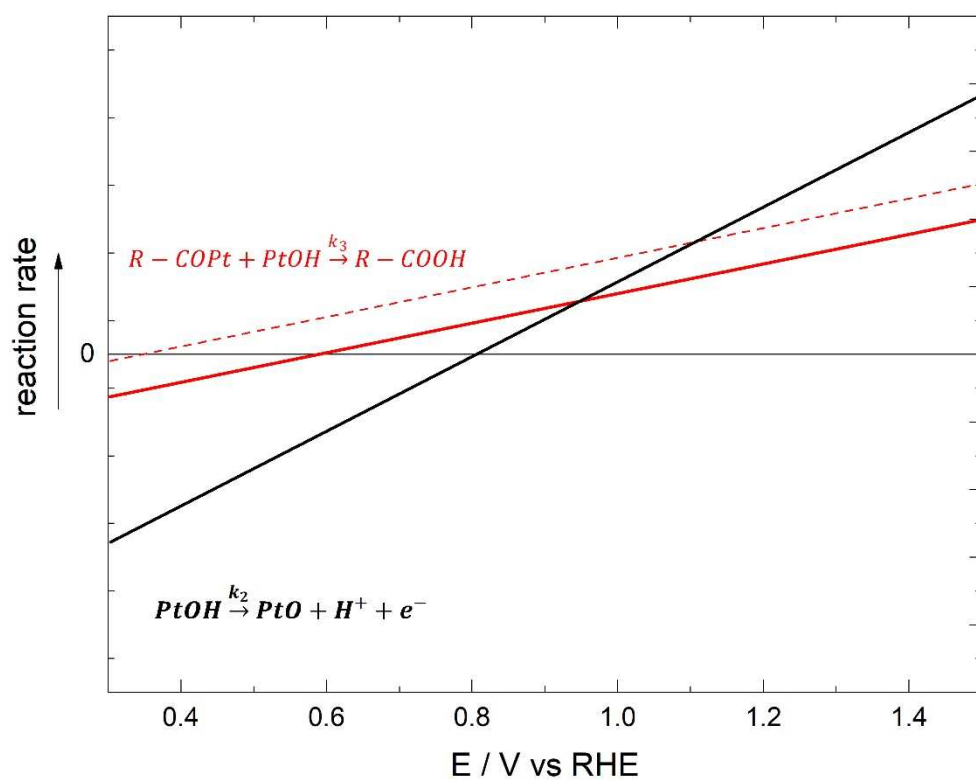
Figure 6

Figure 6: Schematic representation of the reaction rate evolution as a function of potential.

Highlights

- The oxidation of Pt surface in the presence and absence of alcohols was studied.

- The oxidation of Pt surface was measured by the amount of defects created and platinum dissolution analysis.

- The oxidation of Pt surface is prevented in the presence of alcohols different than methanol due to the competition for OH_{ads} species.