The role of surface sites on the oscillatory oxidation of methanol on Stepped Pt[n(111) x (110)] electrodes

V. Del Colle,[1,2] P. B. Perroni,[1] J. M. Feliu,[3] G. Tremiliosi-Filho,[1] H. Varela[1,4,*]

[1]*Institute of Chemistry of São Carlos, University of São Paulo*
POBox 780, 13560-970, São Carlos, SP, Brazil.
[2]*Universidade Federal de Alagoas - Campus Arapiraca, Av. Manoel Severino Barbosa*
57309-005, Arapiraca, AL, Brazil.
[3]*Instituto de Electroquímica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain.*
[4] *Max-Planck Institute for the Physics of Complex Systems, Nöthnitzer Str. 38*
01187 Dresden, Germany.

Abstract

Reaction rates and mechanisms of most electrocatalytic reactions are known to critically depend on the structure of the electrode surface. Examples of structure sensitive electrocatalytic systems include the reduction of oxygen and the oxidation of small organic molecules on platinum, for instance. Even more intricate is the effect of the interfacial structure on the oscillatory dynamics commonly observed in some systems. This is somewhat expected because several adsorption and reaction steps are simultaneously active during self-organized potential or current oscillations. Herein we present results of the effect of surface structure on the oscillatory electro-oxidation of methanol in acidic media on Pt(111), Pt(110), and on stepped surfaces Pt(776), Pt(554), Pt(775), and Pt(332). The system was investigated at two methanol concentrations and under voltammetric and galvanostatic regimes. The voltammetric activity towards the electro-oxidation of methanol on stepped surfaces followed this sequence: Pt(776) < Pt(554) < Pt(775) < Pt(332), at high methanol concentration. The reaction rates increase with the density of (110) sites, but small (111) terraces was also found to contribute to the overall process. In terms of potential oscillations, we found specificities that were unambiguously assigned to the surface structure. In particular, the following features were found according to the specific surface studied: period-adding sequences of mixed-mode oscillations; a new type of mixed-mode oscillation; and a particular separation between two types of sequential oscillations. The understanding of the relationship between the surface structure and the underlying dynamics of the surface chemistry during oscillations is a key challenge and our findings in this direction are discussed.

Keywords: methanol, oscillations, electrocatalysis, platinum single crystals, stepped surfaces.

* corresponding author (H.V.): hamiltonvarela@usp.br.

1. Introduction

The electro-oxidation of methanol is an extensively studied reaction because of its importance to the interconversion between chemical and electric energies, as in the direct methanol fuel cell.[1–4] Many efforts have been devoted to understand how reaction rates and mechanism depends on experimental parameters such as the surface structure and composition of the electrode. The complete oxidation of methanol releases $6e^-$ per molecule, and the goal is to obtain CO_2 as the final product at the lowest potential and the highest current density possible. The mechanism on platinum and platinum-based catalysts comprises the occurrence of parallel pathways and involves adsorbed carbonaceous residues (CO_{ad}, HCO_{ad}, $HCOO_{ad}$, and COH_{ad}) and soluble intermediates (HCOOH and HCHO).[1-4]

The electro-oxidation of methanol on smooth platinum is known to strongly depend on the surface structure.[6] Wang *et al.*[7] compared the electroactivity on polycrystalline platinum, Pt_{poly}, Pt(111), and Pt(332) surfaces and observed the increase of reaction rates with increasing step sites without an appreciable increase of the CO_2 production, and concluded that the defect sites enhance both parallel pathways of methanol oxidation. Shin and Korzeniewski[8] stated that an increase in the step density favors the methanol decomposition and the CO formation is inhibited on Pt(111) in the hydrogen adsorption potential region.

Housmans and Koper[9] through cyclic voltammetry and chronoamperometry studied the influence of stepped surfaces having (111) terraces and (110) step sites toward methanol oxidation. The authors reported that the overall oxidation rate increases with an increasing step density and that the products generated, or even methanol, can be adsorbed preferentially on step sites. Also, CO_{ad} formation is favored on step sites and its depletion is high at potentials above 0.55 V *vs.* RHE, while methanol decomposition occurs faster than CO_{ad} oxidation at low potentials.

Grozovski *et al.*[10] reported that using (111) and (100) steps sites with (100) and (111) terraces respectively, there is no increase in the current, whereas (110) steps contribute to a higher electroactivity of methanol reaction. Also, the authors suggest that for the first step occurs a dehydrogenation, which is considered a rate-determining step because of the slowest rate in the process. Also, the effect of the anions in the oxidation process is studied. Kamyabi *et al.*[11] provided a detailed study on the interfacial structure on the electro-oxidation of methanol Pt single crystals.

Nonlinearities in electrochemical systems in the form of multi-stability and oscillating

reaction rates occur in many fuel cell relevant systems.[12] As in the case of small organic molecules[12–16] the electro-oxidation of methanol on platinum and platinum-based surfaces, is known for a long time to display oscillatory behavior under potentiostatic and galvanostatic regimes.[17–28] In general terms, electrocatalytic oscillations result from the self-organized changes in the coverage of different adsorbates, such as carbon monoxide, electrosorbing anions, and oxygenated species, for instance. The understanding of the effect of the surface structure on the kinetic instabilities is very intricate and it is still in its infancy, see ref. [29] and references therein.

We have recently investigated the effect of very tiny random surface defects on the potential oscillations along the electro-oxidation of formic on platinum.[30] We worked with Pt(100) electrodes disturbed by very delicate surface oxidation to different extents. As the main conclusion, it was observed that self-organized potential oscillations are much more sensitive to the surface fine structure than conventional electrochemical signatures. In particular, we proved that evolving oscillatory patterns can be employed to probe the surface fine structure *in situ* and in a non-invasive manner.[30] This study opened some interesting perspectives and called for further systematic investigation. The study of oscillatory reaction rates on stepped surfaces is a palpable choice in this direction.

In the present work, we studied the electro-oxidation of methanol in acidic media on six well-defined surfaces: the basal planes Pt(111) and Pt(110) and the stepped surfaces combining these limiting orientations Pt(776), Pt(554), Pt(775), Pt(332), with focus on the oscillatory behavior under galvanostatic control. The electrodes were initially characterized and evaluated towards the electro-oxidation of methanol by means of cyclic voltammetry at two concentrations of methanol. After that, the dynamics were studied for each surface. A general discussion was provided and them the main aspects summarized.

2. Experimental

All platinum electrodes, low and high Miller index, used in this work were cut and polished from small single crystal platinum beads following the procedure described by Clavilier and co-workers.[31] The stepped surfaces, Pt(776), Pt(554), Pt(775) and Pt(332), belong to the series of Pt(S)[*n*(111)x(111)] having Miller indices Pt(*n*,*n*,*n* - 2). As usual, *n* represents the number of terrace atoms, which implies that these surfaces have 14, 10, 7 and 6 and atom-wide terraces. Since the intersection of a (111) terrace and a (111) step also defines a (110) site these electrodes can be also described as a combination of (*n* - 1) atom-wide (111) terraces and (110) monoatomic steps.

Figure 1 illustrates the one-dimension representation of stepped surfaces in the sequence along the Pt(111) to Pt(110) side of the stereographic triangle. This sequence is characterized by an increase in the amount of the (110) sites and a decrease in the size of the (111) terraces.

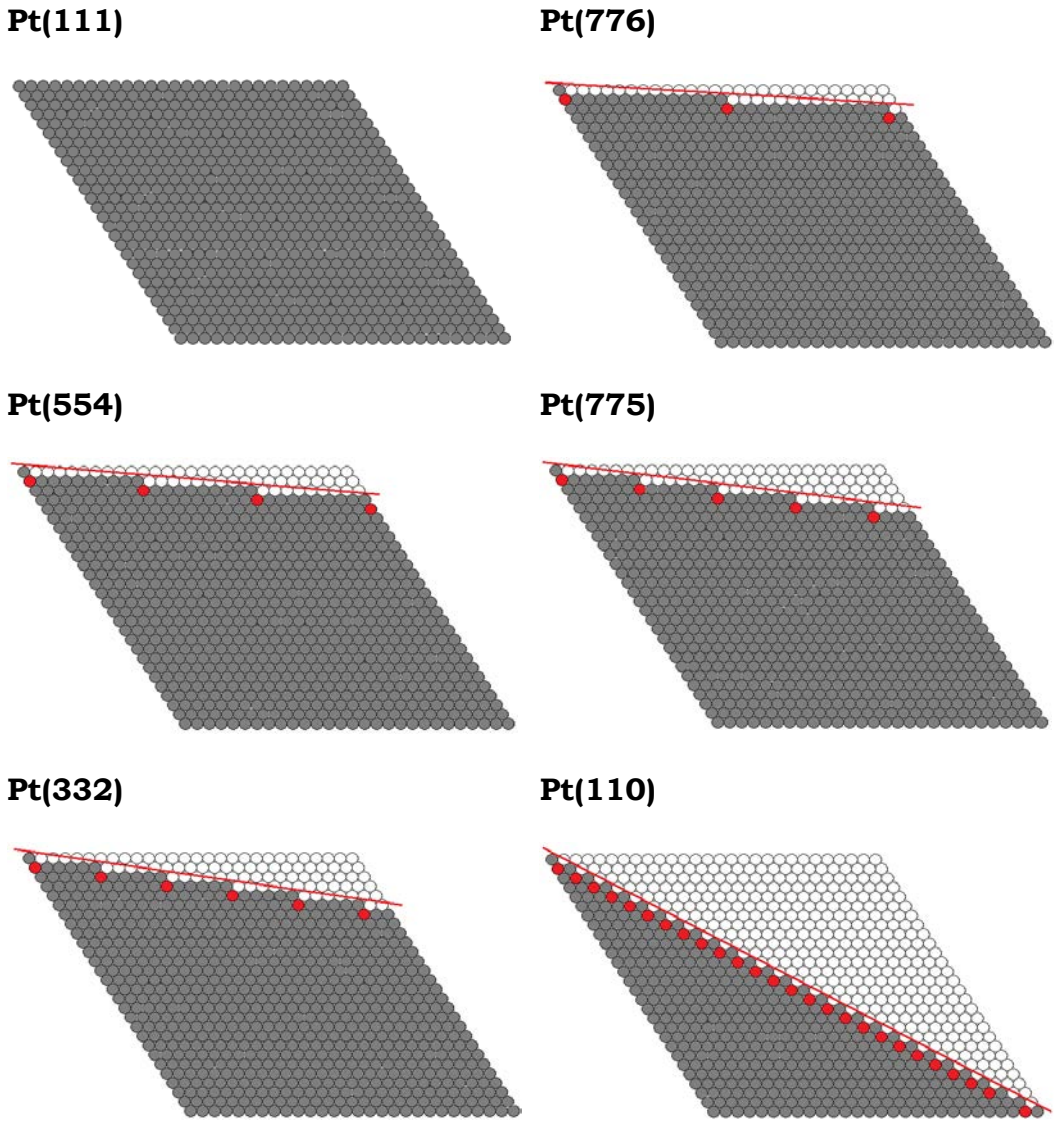


Fig. 1. Two-dimensional representation of the Pt(111), Pt(776), Pt(554), Pt(775), Pt(332), and Pt(110) surfaces. Stepped surfaces Pt(776), Pt(554), Pt(775), and Pt(332) have (111) terraces of different widths and monoatomic (110) steps, and can be also

represented as[32] Pt(s)[13(111) × (110)], Pt(s)[9(111) × (110)], Pt(s)[6(111) × (110)], and Pt(s)[5(111) × (110)], respectively, see text for details.

In the nomenclature introduced by Somorjai and co-workers,[32] stepped surfaces of Miller indexes Pt(776), Pt(554), Pt(775), and Pt(332), can be denoted as Pt[13(111) × (110)], Pt[9(111) × (110)], Pt[6(111) × (110)], and Pt(s)[5(111) × (110)], respectively. In this notation,[32] *n*(111) means a terrace of (111) orientation, with *n* atomic rows in width, and monoatomic (110) steps. In other words, the stepped surface we studied, Pt(776), Pt(554), Pt(775), and Pt(332), have 13, 9, 6, 5 atoms-wide (111) terraces, respectively.

Hydrogen (99.99%) was used for flame-annealing treatment and argon (99.998%) to deoxygenate the solution. Prior to each experiment, the electrodes were flame-annealed in a hydrogen flame and cooled in a reductive $Ar:H_2$ atmosphere (3: 1), after that they were transferred to the electrochemical cell under protection of a drop of deoxygenated ultra-pure water.[33]

All experiments were performed at 25 ^{o}C in a conventional three-electrode electrochemical cell. The chemicals used for solution preparations were sulfuric acid (Panreac, 98%), Methanol (Sigma Aldrich, 99.9%), and ultrapure water from the Millipore system. The counter electrode was a 1 cm × 1 cm platinized Pt foil. The reference electrode was a reversible hydrogen electrode (RHE) and all potentials in this work are referred to it. The electrochemical measurements were performed with a Metrohm PGSTAT302N Potentiostat.

The platinum surface orientation and cleanliness of the electrolyte solution were checked by the stability of the characteristic cyclic voltammograms (CVs), between 0.05 and 0.80 V *vs.* RHE in a 0.5 mol L^{-1} H_2SO_4 aqueous solution. After that, the electrode was transferred, protected by a solution droplet, to another electrochemical cell containing a 0.5 mol L^{-1} H_2SO_4 and 0.2 or 10.0 mol L^{-1} MeOH solution previously deaerated with Argon (White Martins, 99.999%). Thus, to avoid changes in the electrode surface, the surfaces were always polarized at a controlled potential of 0.05 V *vs.* RHE, and the limit potential measured respecting the range between 0.05 and 0.80 V *vs.* RHE. Before galvanostatic/dynamic experiments the electrodes were submitted to one voltammetric cycle in aqueous methanol solution (0.2/10 mol L^{-1}).

3. Results and Discussion

3.1 Voltammetric characterization

Figure 2 shows the voltammetric profiles for all surfaces studied in this work in sulfuric acid aqueous electrolyte. These results are very similar to previously published data[34,35] and the

main characteristics observed along the sequence: Pt(111), Pt(776), Pt(554), Pt(775), Pt(332), and Pt(110), is the decrease in the (111) domains, i.e. the featureless structure between ~0.05 and 0.30 V, and the increase of the peak at (110) sites near terrace borders at 0.13 V. Within the hydrogen adsorption region, that is between 0.06 and 0.35 V, the sharp peak at 0.13 V corresponds to hydrogen adsorption on the 110 step sites, whereas adsorption on the terrace sites gives a broad and featureless signal between 0.06 and 0.35 V. In the (bi)sulfate region, between 0.35 and 0.8 V, the signal reflects the adsorption of the anion on the terrace sites.[34] Also, a small {100} defects formation cannot be discarded for stepped surfaces, once a contribution at 0.28 V assigned to this face is clearly seen, it is more pronounced for Pt(776) surfaces, while for the others ones are practically unobserved.[36]

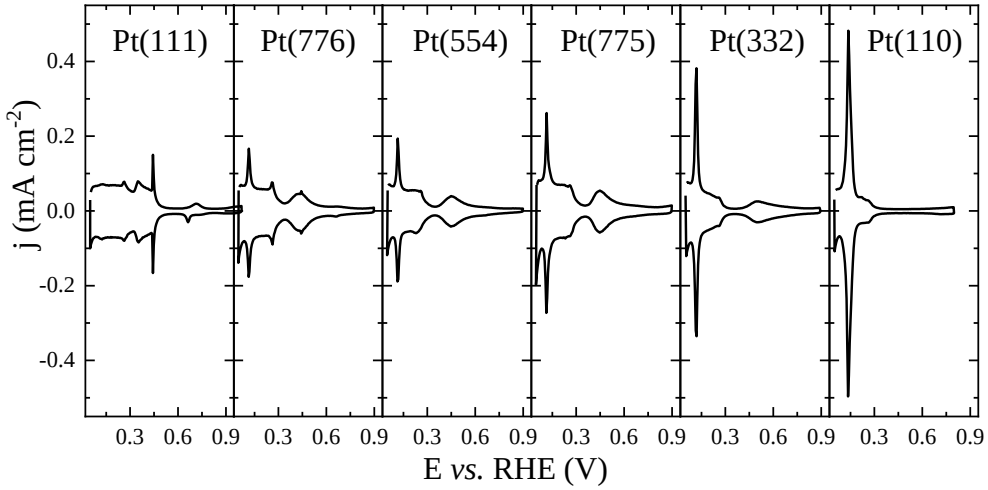


Figure 2: Cyclic voltammetry (ν = 100 mV s^{-1}) of Pt(111), Pt(776), Pt(554), Pt(775), Pt(332), and Pt(110) electrodes. Electrolyte: aqueous solution containing [H_2SO_4] = 0.5 mol L^{-1}.

3.2 Electro-oxidation of methanol at 0.20 mol L^{-1}

The electro-oxidation of methanol on Pt stepped surfaces were investigated and the first voltammetric cycle in each case are given in Figure 3. (FIRST SWEEP? IF SO, MAYBE IT WOULD BE CONVENIENT TO REPORT A STATIONARY-LIKE VOLTAMMOGRAM?) – Vinícius: after the first CV we proceed with the galvanostatic experiments, so that we do not have subsequent cvs. The activity inferred through the voltammetric current increases in the sequence: Pt(111) < Pt(776) ~ Pt(554) ~ Pt(775) ~ Pt(110) < Pt(332). Qualitatively, the main oxidation wave along the positive-going sweep is split into two for the stepped surfaces, whereas a single wave is found for Pt(111) and Pt(110). The reaction rates of the electro-oxidation of methanol

increase with the density of (110) sites, but small (111) terraces also contribute to the overall process.

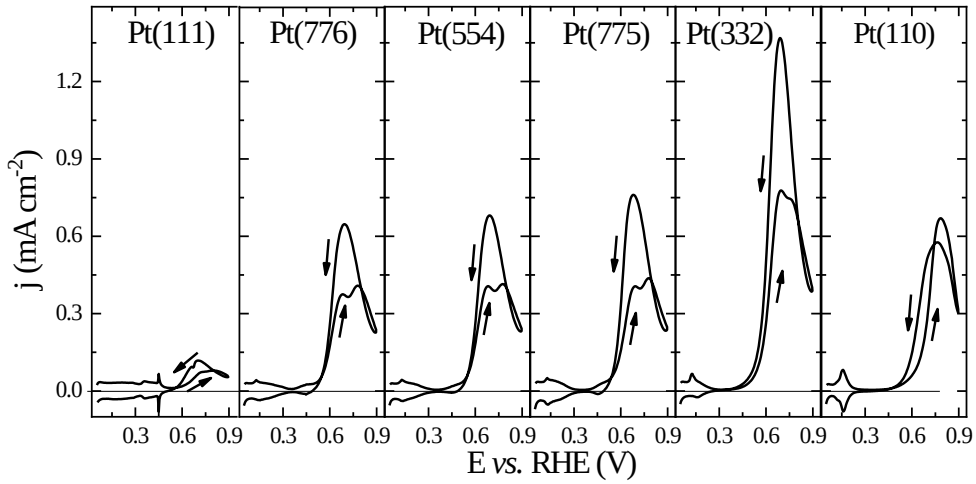


Figure 3: Voltammetry (at 50 mV s^{-1}) of the electro-oxidation of methanol on Pt(111), Pt(776), Pt(554), Pt(775), Pt(332), and Pt(110) electrodes. Electrolyte: aqueous solution containing $[H_3COH]$ = 0.20 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}.

On the Pt(111) electrode, anion adsorption strongly blocks the surface and the resulting oxidation currents are very low. The hydrogen and anion adsorption processes are discernible between 0.05 – 0.50 V; at 0.45 V the *butterfly* peak assigned to disorder-order phase transition due to the formation of the adsorbed sulfate layer is seen. The onset potential of the electro-oxidation of methanol starts at c.a. 0.54 V, the reverse scan showed a small hysteresis and, thereafter, the currents fall due to the strong adsorption of sulfate anion on this surface.[9]

The hysteresis has been associated with the formation of strongly adsorbed species, mainly CO, that are formed on the electrode surface at low potentials, during the positive-going scan, and as the potential is scanned to high values, close to the reverse potential, these species are oxidized. Consequently, the active sites released for further reaction show a current increase along the negative-going sweep although shifted towards lower potentials.[37] This hysteresis is observed for subsequent cycles for the oxidation of several small organic molecules.[36]

With respect to the results on the Pt(110) surface, the current peak in the hydrogen regions is noticeable and indicates its strong adsorption, while for the stepped surfaces a small contribution for this process is observed. The reaction currents in the positive-going scan for this surface are relatively higher than that on most stepped surfaces, but the onset potential is

displaced to more positive potentials by about 100 mV. The negative-going scan is quite different with respect to other surfaces, the peak potential is smaller than that observed in the positive sweep.

Another important point to be highlighted is the influence of interfacial charge over many electrochemical reactions, in our case, organic methanol oxidation reaction. For Pt electrodes where several adsorption reactions occur at the same time withinvolving charge transference, then the potential of zero total charge (E_{pztc}) can be calculated measured by electrochemical meansurements and then potential of zero free charge (pzfc) was identified in different approaches. The charge properties on the electrode surface may affect the electrocatalysis of organic oxidation reactions, once the strongly adsorbed intermediates maybe are formed at low potentials that maybe coincide with the PZTCzero charge potentials. CITE V. Briega-Martos, E. Herrero, J.M. Feliu Current Opinion in Electrochemistry 2019, 17:97-105.[38]

According to Gómez *et al.*[39] the potential of zero total charge in aqueous sulfuric acid shifts by 0.15 V when {110} step sites are added on (111) terraces. It appears that the pzfc of the terrace sites shifts from the Pt(111) basal plane (0.53 V) towards positive values when the terrace size decrease (50 and 60 mV for Pt(775) and Pt(332), respectively), while the local pzfc of the step sites remains constant at 0.16 V, irrespectively of the terrace length. CITE R. Martinez-Hincapie, V. Climent, J.M. Feliu, Electrochimica Acta 307 (2019) 553-563; R. Martinez-Hincapie, V. Climent, J.M. Feliu, Current Opinion Electrochemistry 2019, 14:16-22. The authors found[39] that a surface having 7 terrace-atoms, Pt(775), showed a E_{pzc} displacement of ca. 0.15 V when compared to Pt(111) in sulfuric acid. As the conditions reported by authors were identical to that used here, tTheseis potentials coincides with hydrogen desorption on the terraces, while the hydrogen desorption peak assigned to {110} monoatomic steps occurs at 0.13 V. A comparison between Pt(111) and Pt(775) surfaces can bring us highlights about the influence of potential of zero total charge over methanol electrocatalytic reaction.It becomes clear that methanol oxidation takes place at potentials positive to that of zero charge.

In a kinetic study in pefrchloric acid invonving the series of stepped surfaces used here, it was found that the intrinsic activity increases as the step density increases. Also, the beginning of methanol oxidation shifted towards slightly more negative values. The surfaces were not extremely poisoned on the {111} terraces, even in presence of {110} steps, the poison process taking place around the pzfc of the terraces. This points out that methanol adsorbs as a neutral molecule around the pzfc. Moreover, methanol oxidation is sensitive to anion adsorption, pointing to a weak interaction with the electrode surface. T CITE V. Grozovski, V. Climent, E. Herrero, J.M. Feliu, J. Electroanal. Chem. 662 (2011) 43-51aking into account the Pt(111) and

Con formato: Inglés (Reino Unido)

Con formato: Inglés (Reino Unido)

Pt(775), as already was studied in the literature,[39] the values of E_{pzc} were 0.33 and 0.23 V, respectively. In this respect, methanol oxidation is influenced by anion and poisoning at potentials positive to the zero free charge. It is important to remark that sulphate anion adsorption is particularly important on the Pt(111) basal planes, the presence of steps breaking the required long range order to develop the widely reported ($\sqrt{3}$ x $\sqrt{7}$) sulphate adlayer.

CITE Grozovski and reference 9 from Marc Koper.According to Fig. 2 is possible to compare the CVs of methanol electrooxidation, an analysis of Pt(111) reveals that the E_{pzc} occurs close to hydrogen region, therefore no relevant contribution to form intermediates like CO is observed for this surface at this potential, once the surface charge is composed mostly by anions. [xx] In addition, the low rate methanol reaction lies in the strong anion adsorption, which below of 0.45 V, (bi)sulfate starts to desorb from the Pt(111), consequently, the active sites are unavailable to further methanol adsorption.[9]

Now, considering a Pt(332), that it was the most active surface in our study, and comparing it with the stepped surface studied by Gómez and co-workers,[39] the addition of step sites shifts the E_{pzc} to more negative potentials compared to Pt(111). Differently to the latter surface, the potential of zero total charge is ca. at 0.23 V,[39] where the anion is present on the terrace. Thereafter this potential the currents registered in the CV increases significantly, this implies that methanol oxidation is strongly catalyzed by the presence of step sites that further contribute to diminishing the anion adsorption. However, the interfacial surface charge for stepped surface seems to be formed by species highly active, this assumption is supported by Koper *et al.*[9] where (111) terraces lead to an improvement over the reaction rate, probably as a result of disruption of the anion adlayer. SummarizingIn summary, the electro-oxidation of methanol strongly depends on the surface arrangement, we have observed thatand {110} steps sites influences positively the electro-oxidation of methanol. However,, once these stepped surfaces are more susceptible in forming CO at low potentials due to different adsorption of water and electrolyte anions, that play an important rule role over the electroactivity for MEO.[9,10]

The system was investigated under galvanostatic regime and the potential oscillations were nearly unaffected by the electrode surface at $[H_3COH]$ = 0.20 mol L^{-1}. This is somehow surprising given the differences observed in the voltammetric profiles. Figure 4 illustrates representative oscillations for the Pt(554) surface. The effect of the applied current is given in panel 4(a); harmonic oscillations observed near the onset and slightly higher amplitude are presented in Figure 4(b) and (c), respectively. The oscillatory frequencies near the bifurcation point generally increase with the applied current for a given surface and range from 0.10 to 0.50 Hz in all cases, c.f. Figure S1 in Supplementary File. These small amplitude oscillations are

Código de campo cambiado

Con formato: Sangría: Primera línea: 0 cm, No ajustar espacio entre texto latino y asiático

slower than those found on Pt_{poly}.[22,23] As already reported,[29] no oscillations were observed on the as-prepared Pt(111) surface.

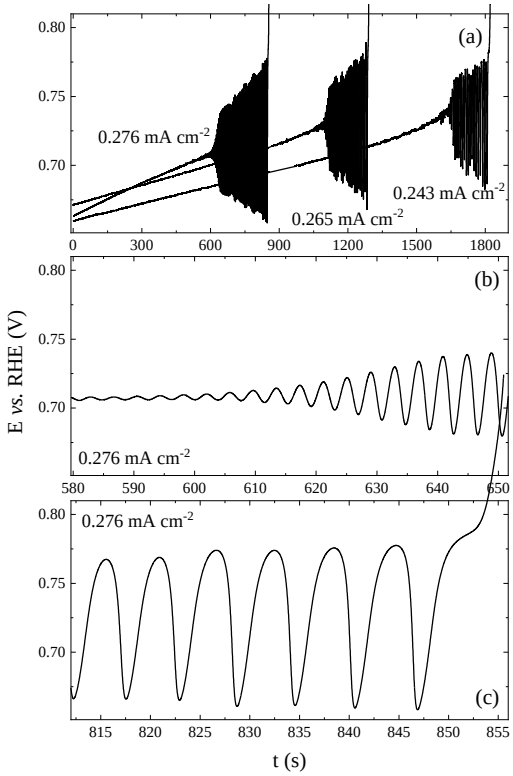


Figure 4: Oscillatory electro-oxidation of methanol on Pt(554) (a) at three applied currents. Details of oscillations at 0.276 mA cm^{-2}, are given in (b) and (c). Electrolyte: aqueous solution containing $[H_3COH]$ = 0.20 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}.

After this initial assessment, we looked for parameter regions where the effect of surface sites becomes more pronounced. It is already known that potential oscillations along the electro-oxidation of methanol on platinum are mainly encountered in two modes:[17,18,21–23,25–27] small amplitude and high frequency, type *S*, and large amplitude and low frequency, type *L*. Oscillations of type *L* are often associated to mixed-mode oscillations with the superposition of small modulations at high potentials.[25] The occurrence of both types *S* and *L* and also the number of potential modulations present in the later have been used to characterize very tiny surface structures.[30]

Okamoto and co-workers[40] reported a detailed study of the experimental parameters where oscillations of type *S* and *L* are found. Overall, the occurrence of both oscillations separated by a quiescent period is favored at high methanol concentration. Based on this work, we decided to carry out experiments with [H_3COH] = 10 mol L^{-1}, where separated *S* and *L* windows, and thus mixed-mode oscillations, are expected to occur abundantly.[40]

3.3 Electro-oxidation of methanol at 10 mol L^{-1}

Figure 5 depicts the voltammetric profiles for the electro-oxidation of methanol at 10 mol L^{-1}. The two limiting surfaces, corresponding to the basal planes, show the lower activities, with Pt(110) being considerably more active than Pt(111). The voltammetric signatures of the electro-oxidation of methanol on stepped electrodes reinforce the pivotal role of surface structure. The two current peaks are again found here, at about 0.60 and 0.80 V and more pronounced than that for [H_2SO_4] = 0.20 mol L^{-1}. The first peak is somewhat suppressed on Pt(332), the 6-atoms terrace surface.

The activities of the stepped surfaces follow the trend observed for [H_3COH] = 0.20 mol L^{-1} but with more pronounced differences in the voltammetric currents: Pt(776) < Pt(554) < Pt(775) < Pt(332). Again, the increase in the density of (110) sites clearly increases the reaction rates for the electro-oxidation of methanol, but small (111) terraces also contribute to the overall process. For the sake of comparison, the activity on polycrystalline platinum at this high concentration, as inferred from the current maximum in the cyclic voltammogram, is slightly smaller (Figure S2) than that found for the Pt(332) electrode, yet larger than that for Pt(775), Figure 5.

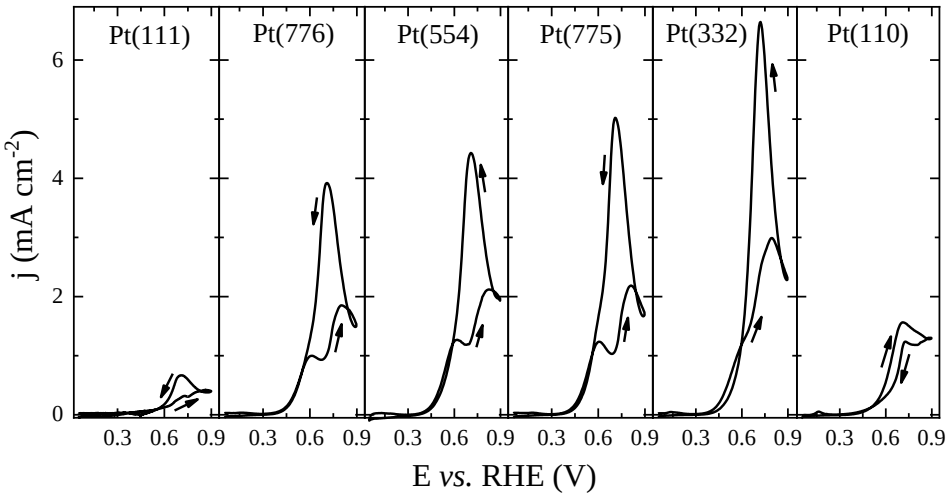


Figure 5: Voltammetry (at 50 mV s^{-1}) of the electro-oxidation of methanol on Pt(111), Pt(776), Pt(554), Pt(775), Pt(332), and Pt(110) electrodes. Electrolyte: aqueous solution containing [H_3COH] = 10 mol L^{-1} and [H_2SO_4] = 0.5 mol L^{-1}.

Another interesting point is concerning to the hysteresis effect observed for all stepped surfaces, the same behavior is not observed for Pt(110), the currents in the negative-going scan were lower than those presented in the anodic profile and a peak at 0.73 V appears. Herein the species strongly adsorbed formed during the positive-going scan, specially at high potentials, seems to keep on the surface without being oxidized, once no free Pt sites are available to proceed with the reaction and, thus, the hysteresis is inhibited.

After the voltammetric characterization, we proceeded with a detailed study of the electro-oxidation of methanol under galvanostatic conditions and no oscillations were found on Pt(111) and Pt(110), the less active surfaces according to Figure 5. In contrast to that observed for [H_3COH] = 0.20 mol L^{-1}, the surface structure of the stepped surfaces clearly influences the resulting dynamics. In the following, we discuss the peculiarities in the potential oscillations according to the stepped surface.

Dynamics on Pt(776), Pt(s)[13(111) × (110)], electrode.

Potential oscillations along the electro-oxidation of methanol on Pt(776) were studied at different applied currents (from 0.492 to 1.60 mA cm^{-2}), results are given in Figure S3 in the Supplementary File. Overall, the duration of the oscillations decreases with the increase of the applied current.[25,41,42] Typical oscillations are illustrated in Figure 6 for an applied current of 0.738 mA cm^{-2} and in terms of the (a) overall time-series, (b) initial, and (c) final cycles.

Generally speaking, the oscillatory features given in Figure 6 resemble those observed in polycrystalline platinum, even at different temperatures,[23] but interesting dissimilarities are also present. For comparison, Figure S4 in the Supplementary File shows typical potential oscillations for the electro-oxidation of methanol at this unusual high concentration (10 mol L^{-1}) on Pt_{poly}.

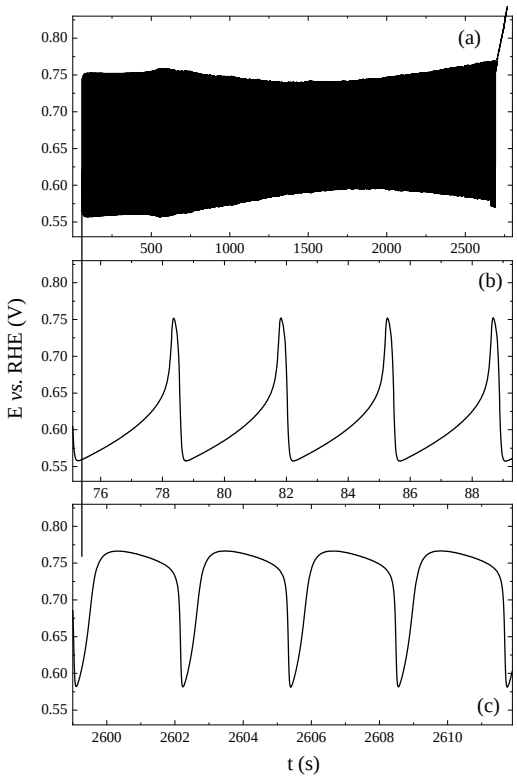


Figure 6: Oscillations in the electro-oxidation of methanol on a Pt(776) electrode, at 0.738 mA cm^{-2}. Electrolyte: aqueous solution containing $[H_3COH]$ = 10 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}.

Figure 7 exhibits the contrast of the initial, relaxation-like, oscillations on (a) Pt(776) and (b) Pt_{poly}, in terms of time-series and their time-derivative. Oscillations on Pt(776) have an amplitude of ~ 200 mV (0.55 – 0.75 V), and a period of 3.5 s; on Pt_{poly} oscillations occur between 0.60 and 0.78 V, and are faster, with a period of 1.2 s. In terms of the oscillations' waveform, less round, steeper oscillations characterize the dynamics on Pt(776), when compared to that on Pt_{poly}. The dE/dt profiles[43] given in panels (a) and (b) further evidence that the oscillations on Pt(776)

surface have a more well-defined two poisoning processes; in contrast, the dE/dt evolution on Pt_{poly} is clearly smoother.

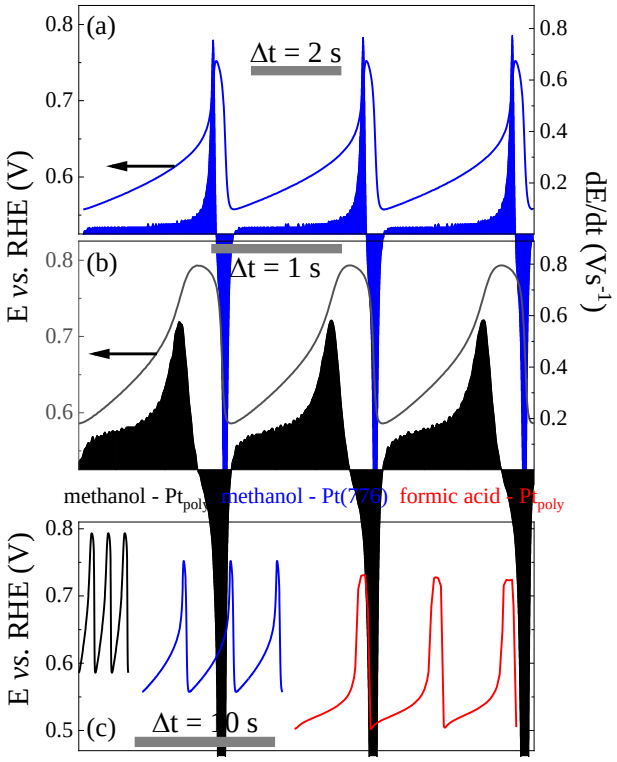
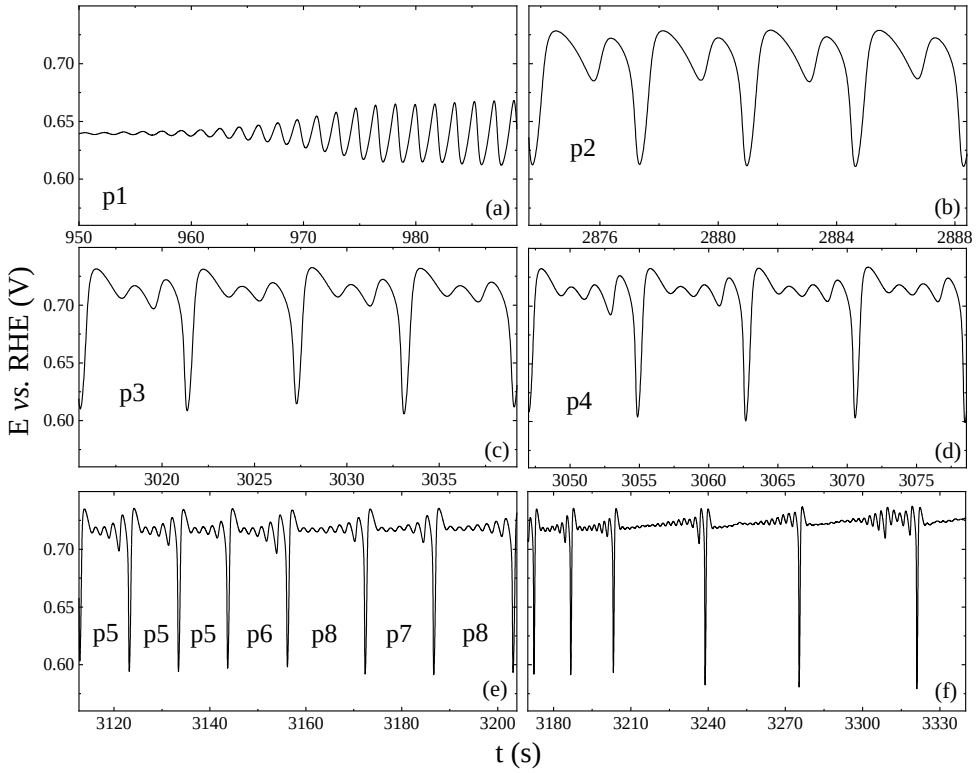


Figure 7: Time-series (and their time-derivative) of the oscillatory electro-oxidation of methanol on (a) Pt(776), at 0.738 $mAcm^{-2}$, and (b) on Pt_{poly}, at 1.445 $mAcm^{-2}$. Electrolyte: aqueous solution containing $[H_3COH]$ = 10 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}. (c) the same time-series as in (a) and (b), and also for the electro-oxidation of formic acid on Pt_{poly}, for sake of comparison, taken from Figure 2(b) at 0.88 mA cm^{-2} in reference [43].

Figure 7(c) also includes typical oscillations recorded for the oscillatory electro-oxidation of formic acid on Pt_{poly} [43] in addition to the comparison between methanol on Pt(776) and Pt_{poly}. From left to right, in the sequence: methanol on Pt(776) – methanol on Pt_{poly} – formic acid on Pt_{poly}, it becomes apparent that the active state, i.e. the lower potential limit, decreases; the frequency decreases; and the oscillations get steeper; besides the features already mentioned. Therefore, it becomes clear that oscillations during the electro-oxidation of methanol on Pt(776) somewhat resemble those found for the electro-oxidation of formic acid on Pt_{poly}.[43] In terms of

reaction mechanism, a remarkable difference between potential oscillations found in the electro-oxidation of methanol and formic acid on Pt_{poly} is the larger variation in the coverage of adsorbed CO, θ_{CO}, in the case of the later.[26] In fact, the amplitude of oscillations in θ_{CO} has been investigated by means of *in situ* infrared (IR) spectroscopy in the attenuated total reflection (ATR) configuration using a platinum film, and it was found to range from 0.24 to 0.37 ML,[26] and from 0.20 to 0.40 ML,[44] for the electro-oxidation of methanol and formic acid on Pt_{poly}, respectively. Therefore, the features described for the oscillations on Pt(776) can be thought of a result of the larger amplitude of the oscillating coverage of adsorbed CO, and thus of the higher activity of the surface. A decisive proof of this argument is in principle unfeasible because of the impossibility of doing experiments with stepped surfaces using the ATR configuration. Nevertheless, this inference is fully supported by experiments with stepped surfaces, where the amount of adsorbed CO increases with the increase of density of step sites.[9] This is an intrinsic feature, and the steeper waveforms with a more discernible definition of two regions of poisoning, c.f. Figure 7(a), characterize the potential oscillations found in all stepped surfaces investigated here.

Figure 8 shows the time evolution of the oscillatory electro-oxidation of methanol on Pt(776) at 0.492 mA cm^{-2}. As in the case found on Pt_{poly},[22] oscillations set in via a supercritical Hopf bifurcation with sinusoidal waveform and develop in time, analogously to that observed when the applied current is increased,[25,41] to chaotic behavior. Mixed-mode oscillations are usually registered in between,[25] with the intercalation of *one* large and *n* small amplitude oscillations, LS^n. The total period (n+1) computed for the time evolution in Figure 8 clearly denotes a period-adding sequence from 1 to 6, with periods 7 and 8 being also detected. The accumulation of small modulations at high potentials become hard to distinguish and eventually gives rise to chaos; nevertheless, periods 7 and 8 are also observed after period 6.



398

399 **Figure 8:** Time evolution of the oscillatory electro-oxidation of methanol on a
400 Pt(776) electrode at 0.492 mA cm^{-2}. Electrolyte: aqueous solution containing
401 $[H_3COH]$ = 10 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}.

402

403 The emergence of these mixed-mode states obviously depends on parameters such as
404 applied current, but since all surfaces were investigated under comparable conditions, it is clear
405 that the observed systematized period-adding sequence is favored on Pt(776) surfaces. It is thus
406 plausible to infer that this specific configuration stabilizes the modulation around high potentials.
407 This observation is in line with the presence of this type of mixed-mode oscillations on Pt_{poly},
408 which contains a considerable amount of (111) terraces. Indeed, comparable period-adding
409 sequences for the electro-oxidation of methanol have been also observed on Pt_{poly}.[18,22,25,40] For
410 instance, Okamoto and co-workers described similar oscillations with transitions from 1 to 3,[40]
411 and from 1 to 5,[18] but with some irregularities in between. Furthermore, if the (111) promotes the
412 development of those small modulations, additional sites are also needed for oscillations, as they
413 are apparently absent on Pt(111) electrodes.[29]

414

Dynamics on Pt(554), Pt(s)[9(111) × (110)], electrode.

Oscillatory behavior on this surface was rather similar to that on Pt(776), but with less complete sequence of period-adding patterns. Oscillations were found from 0.5 to 0.72 mA cm^{-2} and typical data are presented in Figure S5 in the Supplementary File for intermediate applied current. Again, oscillations presented in Figure S5(b) clearly show the steep transition to high potentials discussed above, c.f. Figure 6(b).

Dynamics on Pt(775), Pt(s)[6(111) × (110)], electrode.

Typical oscillations on this surface are given in the Supplementary File, Figure S6. Most features discussed above are also preserved here. The prevalence of steeper oscillations also occurs on this surface, Figure S6(b), reinforcing thus the observation that this specific feature of stepped surfaces. As illustrated in Figure S6 (a1) and in detail in (a2), there is a *quiescent period between small amplitude oscillations*. The appearance of such a quiescent period, previously unreported, is somewhat common in the potential oscillations along the electro-oxidation of methanol, but it seems that only slower and larger amplitude oscillations have been observed after this dormant interval.[17] This is confirmed in the systematic work performed by Mukouyama *et al.*[40] The occurrence of this quiescent interval between small amplitude oscillations depends on the applied current and at slightly higher currents on, oscillations change to high amplitude ones quickly, c.f. Figure S6(b).

Dynamics on Pt(332), Pt(s)[5(111) × (110)], electrode.

Figure 9 shows snapshots of two time-series, @1.445 and 1.735 mA cm^{-2}, recorded on Pt(332), the surface with the smallest (111) terraces studied (n = 5). Intricate high frequency, low amplitude, stiff oscillations are observed around the bifurcation point in (a). At higher currents, c.f. panel (b1), these oscillations are clearly discernible. Qualitatively, the small modulations that co-exist with the higher amplitude oscillations occur in a potential region placed *around the mean value of the high amplitude oscillations*. In contrast, mixed-mode and chaotic potential oscillations along the electro-oxidation of methanol on platinum[18] are mainly characterized by the presence of small amplitude modulations *around the upper potential limit*. The irregular/chaotic oscillations found on Pt(332) are somewhat faster than those on Pt_{poly}. The estimated frequencies for the large amplitude oscillations in Figure 9(b1) vary from about 0.1 to 0.5 Hz, whereas the ones on Pt_{poly} fall into the range 0.025 – 0.05 Hz, as illustrated in Figure 8(f). The conventional modulations at high potentials, c.f. Figure 8(f), occurs after the decrease of the electrode potential after reaching this maximum. In contrast, small amplitude modulations on the Pt(332) electrode

emerge after the increase of the potential from its lower limit, i.e. the most active state. The potentials visited in the course of the self-organized oscillations reflect the nature and coverage of adsorbed species so that the peculiar oscillations found on Pt(332) are certainly associated with different surface chemistry reactivity than that on Pt_{poly}.

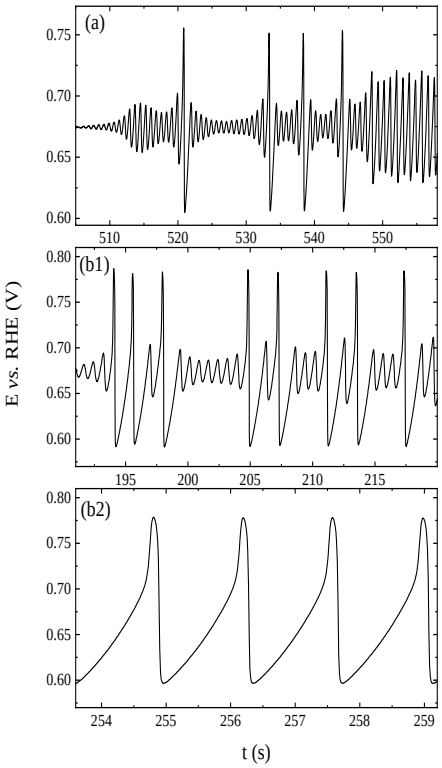


Figure 9: Oscillatory electro-oxidation of methanol on Pt(332) surface, at different applied currents: (a) 1.445 mA cm^{-2}, and (b) 1.735 mA cm^{-2}. Electrolyte: aqueous solution containing $[H_3COH]$ = 10 mol L^{-1} and $[H_2SO_4]$ = 0.5 mol L^{-1}.

Oscillations illustrated in Figure 9(b1) have apparently no parallel in the electro-oxidation of methanol on platinum under comparable conditions. Sitta and co-workers[45] reported the presence of small modulations around the mean value for this system but at pH 2.15. The general waveforms of these oscillations are unlike those reported here and are probably due to the relatively higher pH used. This specific type of chaotic dynamics exemplified in Figure 9(b1) was observed here only on Pt(332), the surface with the smallest (111) terraces studied. This observation on this limiting stepped surface can be though as an evolution of the stiffer oscillations present in stepped surfaces. HAVE WE DATA WITH SURFACES WITH SHORTEST TERRACES? – unfortunately we don't.

467

468 **3.4 General discussion**

469 Comparing the oscillatory electro-oxidation of methanol on polycrystalline and on single
470 crystal and stepped surfaces can be very illustrative. Dynamics on Pt(111), Pt(100), and Pt(100)
471 surfaces have been reported.[29] In the present work we present and discuss the experimental
472 investigation of the oscillatory electro-oxidation of methanol on stepped platinum electrodes,
473 namely surfaces with (111) terraces of different sizes and monoatomic (110) steps: Pt(776),
474 Pt(554), Pt(775), and Pt(332), besides Pt(111) and Pt(110). The voltammetric activity on stepped
475 surfaces was generally higher than that on Pt(111) and Pt(110). Importantly, more than simply a
476 matter of activity, the spontaneous emergence of potential oscillations revealed peculiar,
477 previously unsees, aspects of the stepped surfaces.

478 Oscillations at lower methanol concentrations (0.20 mol L^{-1}) were nearly independent on
479 the surface structure and only small amplitude oscillations were recorded. Previous studies[30]
480 indicated that the concomitant presence of oscillations of small, *S*, and large, *L*, amplitudes can be
481 useful to distinguish very small differences in surface structure. Okamoto and co-workers[40] found
482 that higher methanol concentrations promote the appearance of *S* and *L* oscillations. Therefore,
483 we performed experiments at [H_3COH] = 10 mol L^{-1}, and, indeed, very interesting behavior was
484 registered. Alternatively to the enhancement of the mass transport conditions, using, for instance,
485 a rotating disk electrode, increasing the bulk concentration of methanol enhances its
486 concentration in the neighborhood of the electrode, but do not promote the removal of partially
487 oxidized species from the electrode vicinity.[7,46–48] In fact, we have shown that oscillations of type
488 *L* are suppressed when the solution is stirred.[30] Possible candidates of partially oxidized species
489 that could play a role in the generation of *L* oscillations are dissolved $HCOOCH_3$, HCOOH, and
490 HCHO species.

491 The main characteristics of the galvanostatic oscillations recorded on the stepped surfaces
492 are the steep transition to high potentials, higher amplitudes, lower frequencies and also the lower
493 potentials reached, c.f. Figure 7(c). These features prevail in all stepped surfaces studied and
494 reflect the simultaneous presence of (111) terraces separated by monoatomic (110) steps.
495 Mechanistically speaking, the comparison among the potential oscillations in the electro-
496 oxidation of methanol on Pt_{poly} and on stepped Pt surfaces, and in the electro-oxidation of formic
497 acid on Pt_{poly} suggests that the oscillatory behavior and the correspondingly higher voltammetric
498 activities on stepped surfaces are probably also related to the higher amplitude in the CO
499 coverage along the process. In addition, the shape of the potential increase depicted in Figure 7
500 indicates a more complex, two-step, poisoning process. On disordered polycrystalline surfaces,

the poisoning process is usually smoother and more subtle and delicate processes are apparently hidden, likely because the lack of surface structure control.

Further analysis of the oscillatory dynamics on stepped surfaces reinforces the peculiarities associated with the specific sizes of the (111) terraces. In contrast to the trivial trends in the voltammetric signatures, very reproducible and specific features were found under oscillatory regime. Large (111) domains, on Pt[13(111) × (110)], Pt(776) electrode, were found to stabilize the small amplitude modulations found around the upper potential limit in *L*-type oscillations, resulting in an unparallel complete period-adding sequence of mixed-mode oscillations. On Pt(775), the 6 atoms-wide (111) terraces surfaces, a peculiar separation between oscillations of *S*-type was observed at low applied currents. Finally, a new type of potential oscillations for the electro-oxidation of methanol was found for the limiting surface studied: the stepped surface with smaller, only five atoms wide, (111) terraces studied, the Pt(s)[5(111) × (110)] ≡ Pt(332) surface. These oscillations resemble the steep features mentioned for the stepped surfaces but develop into mixed-mode oscillations completely distinct from that previously observed for this system. Whereas modulations around high potentials values usually found in conventional mixed-mode oscillations in this system are due to the difficulty to completely oxidize the adsorbed carbon monoxide, modulations around intermediate values found here on Pt(332), certainly reflect a different mechanistic origin.

We have discussed some mechanistic aspects of the oscillatory electro-oxidation of methanol on polycrystalline platinum.[24,30] Herein we summarize some critical aspects relevant to the present discussion. Site-demanding steps, including for instance methanol dehydrogenation,

$$H_3COH + 3 * \rightarrow CO_{ad} + 3H^+ + 3e^- + 2 * \quad \text{(r1)},$$

are likely to require terraces and are thus influenced by the size of (111) domains. Herein * accounts for a free platinum site. On the other hand, monoatomic (110) steps, as well as defect sites, are expected to favor the formation of adsorbed carbon monoxide,[9] either from HCO_{ad}:

$$HCO_{ad} \rightarrow CO_{ad} + H^+ + e^- \quad \text{(r2)},$$

or via the re-adsorption of the mentioned partially oxidized species:

$$\text{Partially oxidized species} \rightarrow CO_{ad} + H_2O \quad \text{(r3)},$$

and,

$$\text{Partially oxidized species} \rightarrow CO_{ad} + 2H^+ + 2e^- \quad \text{(r4)}.$$

Partially oxidized species, viz. $HCOOCH_3$, HCOOH, and HCHO, are expected to play a role in the oscillations observed here.[30]

In addition, the formation of oxygenated species from water,[49,50] is also privileged on step sites. The presence of such species is critical to the Langmuir-Hinshelwood step:

$$CO_{ad} + OH_{ad} \rightarrow CO_2 + H^+ + e^- + 2\,* \qquad \text{(r5)}.$$

Steps r1-5 include clearly non-elementary, cf. (r1), and, presumably, elementary steps, (r2) for instance. Besides the simplified picture discussed along with these steps, all possible steps depend on the surface structure. The voltammetry responses illustrated in Figures 3 and 5, indicates that the presence of (110) steps clearly enhances the oxidation rates, but the activity decreases on Pt(110) electrode, unambiguously attesting that terraces of (111) orientation are also needed to reach high rates. The oscillatory dynamics found here clearly points to a more intricate dependence on the surface structure. Solving the whole puzzle, however, is an ongoing task, and further studies, preferentially combining experiments, modeling, and simulations, are in progress. Importantly, this study further reinforces the importance of electrochemical oscillations in electrocatalysis,[12,16] mainly by revealing relevant features that are hidden under regular, non-oscillatory conditions.

4. Conclusions

We reported in this paper results of the electro-oxidation of methanol on stepped Pt[n(111) x (110)] surfaces under voltammetric and galvanostatic regime, where potential oscillations emerge. The study was carried out in acidic media (aqueous sulfuric acid electrolyte) and on Pt(111), Pt(110), and on stepped surfaces Pt(776), Pt(554), Pt(775), and Pt(332). It was found that the reaction rates of the electro-oxidation of methanol increase with the density of (110) sites, but small (111) terraces also contribute to the overall process, as the Pt(332) surface is considerably more active than Pt(110). In particular, the electrocatalytic activity, as inferred in the voltammetric current, was found to increase in the sequence: Pt(111) < Pt(776) ~ Pt(554) ~ Pt(775) ~ Pt(110) < Pt(332), when $[H_3COH] = 0.20$ mol L^{-1}; and: Pt(111) < Pt(110) << Pt(776) < Pt(554) < Pt(775) < Pt(332), for $[H_3COH] = 10$ mol L^{-1}.

Under oscillatory regime, the effect of the interfacial structure can get even more complicated than the changes in the trends of the overall activity, as several adsorption and reaction steps are simultaneously active during self-organized potential or current oscillations. Indeed, the potential oscillations observed under galvanostatic control, display specificities unambiguously assigned to the surface structure.

At $[H_3COH] = 0.20$ mol L^{-1} no oscillations were found on Pt(111), and only small amplitude (S-type) oscillations were observed for other surfaces, with oscillatory frequencies

between 0.10 and 0.50 Hz. At [H_3COH] = 10 mol L^{-1} no oscillations were observed on the limiting surfaces, i.e. Pt(111) and Pt(110). For the stepped surfaces, the size of the (111) terraces and density of step sites were found to clearly affect the oscillatory dynamics. First of all, the large amplitude, relaxation-like oscillations found on stepped surfaces are clearly different than those found on polycrystalline platinum, Pt_{poly}. Taking the Pt(776) as a representative example, potential oscillations have an amplitude of ~ 200 mV (0.55 – 0.75 V), and a period of 3.5 s; on Pt_{poly} oscillations under identical conditions occur between 0.60 and 0.78 V and have a period of 1.2 s. Interestingly, the oscillations' waveform and less round and steeper on stepped surfaces, when compared to Pt_{poly}. The comparison of the potential oscillations in the electro-oxidation of methanol on stepped and polycrystalline surfaces with previously published data[26,43,44] suggested that the amplitude of the oscillating coverage of CO_{ad} is larger on stepped surfaces. This is in agreement with previous reports that attest that the amount of adsorbed CO increases with the increase of density of step sites.[9] This feature is present in all stepped surfaces studied and thus results of the presence of (111) terraces separated by monoatomic (110) steps. In fact, the larger amplitude of the oscillating coverage of CO_{ad} is likely to be the main mechanistic aspect underlying the dynamic features assigned to the stepped surfaces.

The specific features assigned to the surface structure are summarized as follows: (a) 13 atoms-wide (111) domains, on Pt[13(111) × (110)] ≡ Pt(776) electrode, stabilized the small amplitude modulations found around the upper potential limit in *L*-type oscillations, resulting in an unparallel complete period-adding sequence of mixed-mode oscillations; On the 6 atoms-wide (111) terraces, Pt(775), surfaces, a peculiar separation between oscillations of *S*-type was observed at low applied currents; A new type of potential oscillations was found on the stepped surface with smaller, only five atoms wide, (111) terraces surface studied here, i.e. Pt(s)[5(111) × (110)] ≡ Pt(332).

We have pursued modeling and numerical simulations of oscillatory behavior in electrocatalytic systems as a way of obtaining reliable reaction rate constants.[51,52] This approach uses experimental data to provide a micro-kinetic description of the whole system, rather than fitting chronoamperometric data, for instance. Experimental results using well-ordered single crystal surfaces like the ones reported here are certainly of help in the investigation of how a given surface site influences specific reaction steps.

Acknowledgments

GTF and HV (Grant No. 2013/16930-7) acknowledge São Paulo Research Foundation (FAPESP) for financial support. HV (Grant No. 306060/2017-5) acknowledges Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. This study was partially financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001. Authors thank Dr. B. A. F. Previdello for experimental assistance.

References

1 R. Parsons and T. VanderNoot, *J. Electroanal. Chem.*, 1988, 257, 9–45.
2 S. Wasmus and A. Küver, Methanol oxidation and direct methanol fuel cells: a selective review, *J. Electroanal. Chem.*, 1999, **461**, 14–31.
3 T. Iwasita, Electrocatalysis of methanol oxidation, *Electrochim. Acta*, 2002, **47**, 3663–3674.
4 N. M. Markovic and P. N. Ross Jr., Surface science studies of model fuel cell electrocatalysts, *Surf. Sci. Rep.*, 2002, **45**, 117–229.
5 S. Sriramulu, T. D. Jarvi and E. M. Stuve, A kinetic analysis of distinct reaction pathways in methanol electrocatalysis on Pt(111), *Electrochim. Acta*, 1998, **44**, 1127–1134.
6 E. Herrero, K. Franaszczuk and A. Wieckowski, Electrochemistry of methanol at low index crystal planes of platinum. An integrated voltammetric and chronoamperometric study, *J. Phys. Chem.*, 1994, **98**, 5074–5083.
7 H. Wang and H. Baltruschat, DEMS study on methanol oxidation at poly- and monocrystalline platinum electrodes: The effect of anion, temperature, surface structure, Ru adatom, and potential, *J. Phys. Chem. C*, 2007, **111**, 7038–7048.
8 J. Shin and C. Korzeniewski, Infrared spectroscopic detection of CO formed at step and terrace sites on a corrugated electrode surface plane during methanol oxidation, *J. Phys. Chem.*, 1995, **99**, 3419–3422.
9 T. H. M. Housmans and M. T. M. Koper, Methanol Oxidation on Stepped Pt[n (111) × (110)] Electrodes: A Chronoamperometric Study, *J. Phys. Chem. B*, 2003, **107**, 8557–8567.
10 V. Grozovski, V. Climent, E. Herrero and J. M. Feliu, The role of the surface structure in the oxidation mechanism of methanol, *J. Electroanal. Chem.*, 2011, **662**, 43–51.
11 A. Testolin, S. Cattaneo, W. Wang, D. Wang, V. Pifferi, L. Prati, L. Falciola and A. Villa, Cyclic Voltammetry Characterization of Au, Pd, and AuPd Nanoparticles Supported on Different Carbon Nanofibers, *Surfaces*, 2019, **2**, 205–215.
12 H. Varela, M. V. F. Delmonde and A. A. Zülke, in *Electrocatalysts for Low Temperature Fuel Cells: Fundamentals and Recent Advancements*, eds. T. Maiyalagan and V. S. Sagi, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2017, pp. 145–163.
13 M. Hachkar, B. Beden and C. Lamy, Oscillating electrocatalytic systems. Part I. Survey of systems involving the oxidation of organics and detailed electrochemical investigation of formaldehyde oxidation on rhodium electrodes, *J. Electroanal. Chem.*, 1990, **287**, 81–98.
14 K. Krischer and H. Varela, in *Handbook of Fuel Cells*, eds. W. Vielstich, A. Lamm and H. A. Gasteiger, John Wiley & Sons, Ltd, Chichester, UK, 2010, vol. 2, pp. 679–701.
15 U. Krewer, T. Vidakovic-Koch and L. Rihko-Struckmann, Electrochemical oxidation of carbon-containing fuels and their dynamics in low-temperature fuel cells, *ChemPhysChem*, 2011, **12**, 2518–2544.
16 E. G. Machado and H. Varela, in *Encyclopedia of Interfacial Chemistry*, Elsevier, 2018, pp. 701–718.

17 M. Krausa, W. Vielstich, M. Kraus and W. Vielstich, Potential oscillations during methanol oxidation at Pt-electrodes Part 1: experimental conditions, *J. Electroanal. Chem.*, 1995, **399**, 7–12.

18 H. Okamoto, N. Tanaka and M. Naito, Chaos in the oxidation of formaldehyde and/or methanol, *J. Phys. Chem. A*, 1997, **101**, 8480–8488.

19 M. V. F. Delmonde, M. A. Nascimento, R. Nagao, D. A. Cantane, F. H. B. Lima and H. Varela, Production of volatile species during the oscillatory electro-oxidation of small organic molecules, *J. Phys. Chem. C*, 2014, **118**, 17699–17709.

20 R. Nagao, R. G. Freitas, C. D. Silva, H. Varela and E. C. Pereira, Oscillatory electro-oxidation of methanol on nanoarchitectured Ptpc/Rh/Pt metallic multilayer, *ACS Catal.*, 2015, **5**, 1045–1052.

21 J. Lee, C. Eickes, M. Eiswirth and G. Ertl, Electrochemical oscillations in the methanol oxidation on Pt, *Electrochim. Acta*, 2002, **47**, 2297–2301.

22 A. L. Martins, B. C. Batista, E. Sitta and H. Varela, Oscillatory instabilities during the electrocatalytic oxidation of methanol on platinum, *J. Braz. Chem. Soc.*, 2008, **19**, 679–687.

23 E. A. Carbonio, R. Nagao, E. R. Gonzalez and H. Varela, Temperature effects on the oscillatory electro-oxidation of methanol on platinum, *Phys. Chem. Chem. Phys.*, 2009, **11**, 665–670.

24 S. Sauerbrei, M. A. Nascimento, M. Eiswirth and H. Varela, Mechanism and model of the oscillatory electro-oxidation of methanol, *J. Chem. Phys.*, 2010, **132**, 1–10.

25 R. Nagao, E. Sitta and H. Varela, Stabilizing nonstationary electrochemical time series, *J. Phys. Chem. C*, 2010, **114**, 22262–22268.

26 E. Boscheto, B. C. Batista, R. B. Lima and H. Varela, A surface-enhanced infrared absorption spectroscopic (SEIRAS) study of the oscillatory electro-oxidation of methanol on platinum, *J. Electroanal. Chem.*, 2010, **642**, 5.

27 R. Nagao, D. A. Cantane, F. H. B. Lima and H. Varela, The dual pathway in action: decoupling parallel routes for CO2 production during the oscillatory electro-oxidation of methanol, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5.

28 R. Nagao, D. A. Cantane, F. H. B. Lima and H. Varela, Influence of anion adsorption on the parallel reaction pathways in the oscillatory electro-oxidation of methanol, *J. Phys. Chem. C*, 2013, **117**, 15098–15105.

29 B. A. F. Previdello, P. S. Fernández, G. Tremiliosi-Filho and H. Varela, Oscillatory Electro-oxidation of Methanol on Platinum Single Crystal Electrodes, *Electrocatalysis*, 2016, **7**, 276–279.

30 B. A. F. Previdello, P. S. Fernández, G. Tremiliosi-Filho and H. Varela, Probing the surface fine structure through electrochemical oscillations, *Phys. Chem. Chem. Phys.*, 2018, **20**, 5674–5682.

31 J. Clavilier, D. Armand, S. G. Sun and M. Petit, Electrochemical adsorption behaviour of platinum stepped surfaces in sulphuric acid solutions, *J. Electroanal. Chem.*, 1986, **205**, 267–277.

32 B. Lang, R. W. Joyner and G. A. Somorjai, Low energy electron diffraction studies of high index crystal surfaces of platinum, *Surf. Sci.*, 1972, **30**, 440–453.

33 J. Clavilier, K. E. Actii, M. Petit, A. Rodes and M. A. Zamakhchari, Electrochemical monitoring of the thermal reordering of platinum single-crystal surfaces after metallographic polishing from the early stage to the equilibrium surfaces, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **295**, 333–356.

34 V. Del Colle, A. Berná, G. Tremiliosi-Filho, E. Herrero and J. M. Feliu, Ethanol electrooxidation onto stepped surfaces modified by Ru deposition: Electrochemical and spectroscopic studies, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3766–3773.

35 V. Del Colle, J. Souza-Garcia, G. Tremiliosi-Filho, E. Herrero and J. M. Feliu, Electrochemical and spectroscopic studies of ethanol oxidation on Pt stepped surfaces modified by tin adatoms, *Phys. Chem. Chem. Phys.*, , DOI:10.1039/c1cp20546c.

36 A. F. B. B. Barbosa, V. Del Colle, A. M. Gómez -Marín, C. A. Angelucci, G. Tremilios Filho, A. M. Gómez-Marín, C. A. Angelucci and G. Tremiliosi-Filho, Effect of the Random Defects Generated on the Surface of Pt(111) on the Electro-oxidation of Ethanol: An Electrochemical Study, *ChemPhysChem*, 2019, **20**, 3045–3055.

37 F. Colmati, G. Tremiliosi-Filho, E. R. Gonzalez, A. Berná, E. Herrero and J. M. Feliu, Surface structure effects on the electrochemical oxidation of ethanol on platinum single crystal electrodes, *Faraday Discuss.*, 2008, **140**, 379–397.

38 V. Briega-Martos, E. Herrero and J. M. Feliu, Pt(hkl) surface charge and reactivity, *Curr. Opin. Electrochem.*, 2019, **17**, 97–105.

39 R. Gómez, V. Climent, J. M. Feliu and M. J. Weaver, Dependence of the Potential of Zero Charge of Stepped Platinum (111) Electrodes on the Oriented Step-Edge Density: Electrochemical Implications and Comparison with Work Function Behavior, *J. Phys. Chem. B*, 2000, **104**, 597–605.

40 Y. Mukouyama, O. Furuyama, Y. Bundo and H. Okamoto, Separate Current Range for Appearance of Potential Oscillation during Methanol Oxidation on Platinum, *Electrochemistry*, 2014, **82**, 573–577.

41 M. F. Cabral, R. Nagao, E. Sitta, M. Eiswirth and H. Varela, Mechanistic aspects of the linear stabilization of non-stationary electrochemical oscillations, *Phys. Chem. Chem. Phys.*, 2013, **15**, 1437–1442.

42 N. Perini, B. C. Batista, A. C. D. D. C. Angelo, I. R. Epstein and H. Varela, Long-lasting oscillations in the electro-oxidation of formic acid on PtSn intermetallic surfaces, *ChemPhysChem*, 2014, **15**, 8.

43 N. Perini, E. Sitta, A. C. D. Angelo and H. Varela, Electrocatalytic activity under oscillatory regime: The electro-oxidation of formic acid on ordered Pt3Sn intermetallic phase, *Catal. Commun.*, 2013, **30**, 23–26.

44 G. Samjeské, A. Miki, S. Ye, A. Yamakata, Y. Mukouyama, H. Okamoto and M. Osawa, Potential oscillations in galvanostatic electrooxidation of formic acid on platinum: A time-resolved surface-enhanced infrared study, *J. Phys. Chem. B*, 2005, **109**, 23509–23516.

45 G. B. Melle, F. W. Hartl, H. Varela and E. Sitta, The effect of solution pH on the oscillatory electro-oxidation of methanol, *J. Electroanal. Chem.*, 2018, **826**, 164–169.

46 E. A. Batista, G. R. P. Malpass, A. J. Motheo and T. Iwasita, New insight into the pathways of methanol oxidation, *Electrochem. commun.*, 2003, **5**, 843–846.

47 E. A. Batista, G. R. P. Malpass, A. J. Motheo and T. Iwasita, New mechanistic aspects of methanol oxidation, *J. Electroanal. Chem.*, 2004, **571**, 273–282.

48 H. Wang, T. Löffler and H. Baltruschat, Formation of intermediates during methanol oxidation: A quantitative DEMS study, *J. Appl. Electrochem.*, 2001, **31**, 759–765.

49 M. J. T. C. Van Der Niet, N. Garcia-Araez, J. Hernández, J. M. Feliu and M. T. M. Koper, Water dissociation on well-defined platinum surfaces: The electrochemical perspective, *Catal. Today*, 2013, **202**, 105–113.

50 M. J. S. Farias, G. A. Camara and J. M. Feliu, Understanding the CO Preoxidation and the Intrinsic Catalytic Activity of Step Sites in Stepped Pt Surfaces in Acidic Medium, *J. Phys. Chem. C*, 2015, **119**, 20272–20282.

51 A. Calderón-Cárdenas, F. W. Hartl, J. A. C. Gallas and H. Varela, Modeling the triple-path electro-oxidation of formic acid on platinum: Cyclic voltammetry and oscillations, *Catal. Today*, 2020, in press.

52 J. G. Freire, A. Calderón-Cárdenas, H. Varela and J. A. C. Gallas, Phase diagrams and dynamical evolution of the triple-pathway electro-oxidation of formic acid on platinum,

773 *Phys. Chem. Chem. Phys.*, 2020, **22**, 1078–1091.
774