Halide adsorption effect on methanol electro-oxidation reaction studied by dynamic instabilities

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A B S T R A C T

The effect of halide anion adsorption on methanol electro-oxidation reaction in acid media was studied by means of thermal effects on both cyclic voltammograms (CV) and oscillations in galvanostatic time series (GTS). While increasing the chloride concentration we observed a monotonically current decrease followed by an increase of apparent activation energy (E_a) in CV, GTS increases the maximum potential (E_{max}) and decreases both the oscillation frequency (w) and E_a. Poisoning/Freeing rates (dE/dt) increase for a very small Cl^- amount but decreases for higher concentrations. Changing Cl^- by Br^-, albeit observing similar behaviors for currents on CV and w, E_{max} and E_a changes suggest that Br^- probably plays a dual role, i.e. poisoning the surface by its adsorption but also interacting with adsorbed methanol residues. Finally, increasing the pH to 5.6 in a nonadsorbing electrolyte ($HClO_4/NaF$) several oscillations patterns were mapped with a lesser Cl^- influence on both CV and GTS.

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1. Introduction

The methanol electro-oxidation reaction (MER) is widely studied due to its possible use in fuel cell anodes [1]. Besides its practical purposes, the reaction is very interesting for providing understanding of the interactions between organic molecules and catalytic surfaces, displaying several reaction pathways and yielding partial oxidation products [2]. The competition between these pathways can also provide dynamic instabilities during MER, which can be observed as bistability and oscillations [3]. When catalyzed by Pt and acidic media, MER is classified as an HN-NDR oscillator, as it possesses an *N-shaped Negative Differential Resistance* (N-NDR) in potential-current domain partially *Hidden* (H) by reaction residues [3]. Experimentally, oscillations in these systems are observed under both current and potential control, the last form being possible in highly resistive systems.

Recently, our group studied the effect of solution pH on MER focusing on the oscillation regions [4]. Remarkably, the MER activity, inferred by cyclic voltammetry, can be related to oscillatory behavior, i.e. the currents observed in cyclic voltammograms (CV) have a minimum value in pH around 5 and the oscillations are only observed in pH below this turning point. This minimum activity pH also coincides with changes in CO_{ad} [5] and formic acid [6,7] electro-oxidation reactions, two important intermediates in MER. Unfortunately, experiments in a wide pH range are accompanied by electrolyte anion changes, e.g. the main

species in buffered hydrogen phosphate solutions are H_3PO_4 and $H_2PO_4^-$ for pH < 1 and around 5, respectively. The distinct adsorption strength of these anions can also play some role in MER.

According to Markovic et al. [8] anions may affect electrochemical processes by blocking of active sites; modifying the adsorption energy for sites adjacent to adsorbed anions; changing the potential distribution across the interface; and inducing surface restructuring. Specifically, small concentrations of Cl^- (10^{-6}–10^{-5} M) are sufficient to affect the methanol adsorption/reaction on the Pt surface [9–12]. Besides the effects described above, anions, such as those as bromide, can also react with adsorbed methanol intermediates and the reaction products remain strongly adsorbed [9]. Similarly, (bi)sulfate also disturbs methanol adsorption, but its effect on product distribution is not a consensus. By means of High Performance Liquid Chromatograph (HPLC) the electrolysis products of MER were compared in $HClO_4$ and H_2SO_4 solutions revealing similar production of formic acid and formaldehyde in both electrolytes [13]. The current decrease when ClO_4^- is replaced by SO_4^{2-} can be explained in terms of decrease in CO_2 production. These results are in line with the conjecture that at least three contiguous Pt sites are necessary to produce CO_{ad} from methanol adsorption, [14] thus inhibiting the CO_2 production in electrolytes with strong adsorbing anions. On the other hand, Differential Electrochemical Mass Spectrometry (DEMS) in a dual thin-layer flow cell, did not confirm the significant changes in CO_2 efficiency expected when $HClO_4$ is replaced by H_2SO_4 [15].

Few works investigated the anion effect on oscillations of MER. Varela et al. [16] mapped the MER potential oscillations under current control in function of trifluoromethanesulfonate (TFMS) anion

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amounts. While the oscillation time and mean potential evolution in time are strongly influenced by TFMS in a 0 to 0.5 M concentration range, the oscillation frequency and amplitude are less affected. Mukouyama et al. [17] observed high E_{max} oscillation cycles during MER at high Cl^- concentration (10 mM), the phenomena being related to CO_{ad} oxidation at $E > 1$ V [18]. Finally, Varela et al. [19] compared the oscillation dynamics in $HClO_4$ and H_2SO_4 electrolytes following the volatile products distribution by DEMS and performing numerical simulation that allowed the authors to decouple the parallel routes to CO_2 production, namely, the indirect pathway (via CO_{ad} oxidation), and the direct pathway (via oxidation of formaldehyde and formic acid). Interestingly, in the oscillatory regime, the CO_2 production from direct (non-CO) pathway is relatively more affected by the anion adsorption ((bi)sulfate) than the indirect pathway, probably by the competition for active sites.

Oscillations in electrochemical systems have been shown to be a useful tool to reveal the evolution of processes occurring on surfaces. For example, the above cited decoupling direct and indirect methanol pathways, [19] temperature compensation in formic acid [20] and ethylene glycol [21,22] electro-oxidation reactions and the cation effect during H_2O_2 electro-reduction on Pt [23] or ethanol electro-oxidation on Au [24]. Taking advantage of oscillation sensitivity to the experimental conditions, the present work studies the MER in the presence of small amount of chloride and bromide anions focusing on the changes in oscillation parameters, such as frequency, maximum potential and poisoning rate, as well as on the apparent activation energy to better understand the effect of anions on electrochemical systems.

2. Experimental procedures

The experiments were performed in a three-electrode glass cell with temperature control provided by a thermostatic bath (Solab SL 152). A Pt flag with 0.64 cm^2 (electrochemically measured by hydrogen desorption charge, considering 210 μC cm^{-2}) served as the working electrode. A high area Pt mesh and a reversible hydrogen electrode (RHE), prepared with same electrolyte solution, were employed as counter and reference electrodes, respectively. All the solutions were prepared with high pure water (18.2 $M\Omega$ cm, provided by a Milli-Q system) and $HClO_4$ (ACS reagent, 70%), methanol (anhydrous, 99,8%), NaCl and KBr (>99% FT-IR grade) were provided by Sigma-Aldrich. Blank experiments were performed with $HClO_4$ (0.1 M) + methanol (0.6 M) electrolyte with M = mol L^{-1}. The pH 5.6 electrolyte was prepared with $HClO_4$/NaF mixtures following ref. [25] and in this solution a Ag/AgCl/KClsat electrode was employed as reference electrode. Electrochemical data were obtained with an AutoLab potentiostat/galvanostat PGSTAT128N equipped with Scan250 modulus. Pt cyclic voltammogram at 0.1 V s^{-1} from 0.05 to 1.50 V (vs RHE) in a N_2 purged supporting electrolyte was used to attest the cleanness of the systems. A cyclic voltammogram of a considered clean $Pt/H_2O,HClO_4$ system is shown in supplementary files (Fig. S1). All the experiments were done at least three times.

3. Results and discussion

Fig. 1 shows the halide Cl^- and Br^- effect on MER under potential (a) and current (b) controls. The blank curves represent the halide free electrolyte, i.e. in 0.1 M $HClO_4$. During positive going scan in the cyclic voltammetry (CV) experiments, the anions apparently do not affect the CV profile at potentials lower than 0.6 V since, in this potential range, the surface is covered by CO_{ad} [2]. After the CO_{ad} oxidation, the current observed in the main peak decreases with the anion adsorption strength ($Br^- > Cl^- \gg ClO_4^-$) following the same trend during the so-called reactivation peak in negative going scan. Minor anion effects are observed in $1.0 < E < 1.4$ V region, where, regardless the halide anion, the currents decrease but follow the same blank trend. At potentials higher than 1.5 V, the onset of halide oxidation yields Cl_2 and Br_2. Under current control, potential oscillations are observed when the
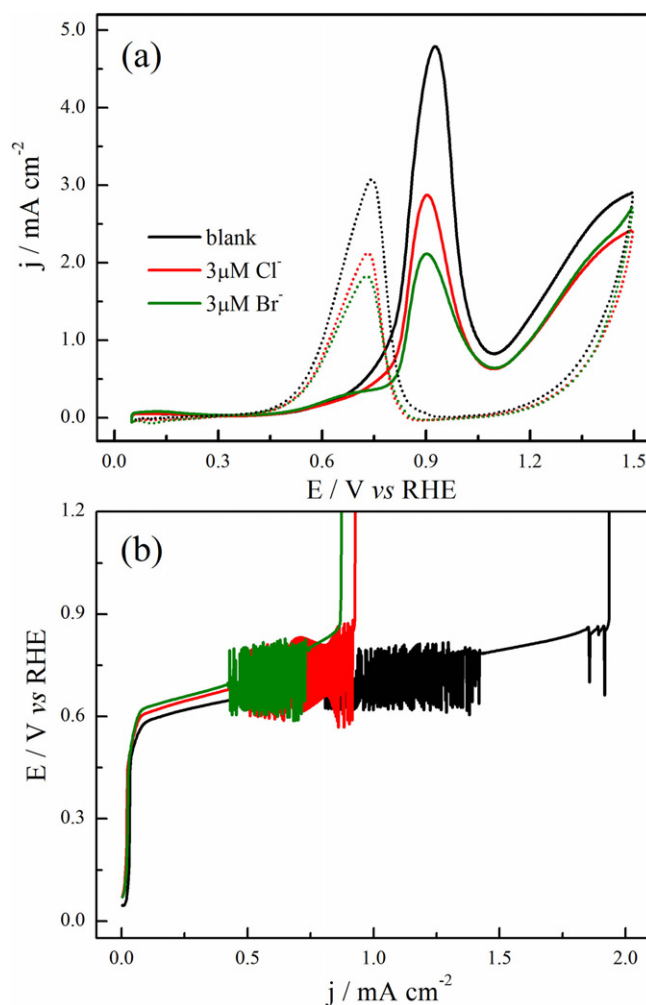

Fig. 1. Anion effect on 0.05 V s^{-1} cyclic voltammograms (a) and 4.7 μA s^{-1} cm^{-2} galvanodynamics curves (b) during methanol electro-oxidation reaction on Pt and 0.1 M $HClO_4$ + 0.6 M methanol. $T = 21$ °C. Solid and dotted lines represent the positive and negative going scans, respectively.

current exceed a given value – onset of oscillations. This onset is negatively shifted by the anion adsorption, with the values 0.80, 0.50 and 0.42 mA cm^{-2} to the blank, 3 μM Cl^- and 3 μM Br^-, respectively. Finally, increasing the current, the oscillations are extinguished and the potential fast jumps to values higher than 1.2 V. The blank CV profiles as well as oscillatory behavior for MER, fully agree with those in the literature [26,27].

The oscillations are also observed along the time at fixed currents (galvanostatic time series, GTS), and to normalize the current values in distinct electrolytes we employed the protocol described in ref. [20] and widely used elsewhere. Under this condition, the system provides several oscillation patterns that spontaneously change along the time [26]. Herein, we focused on the period 1 pattern and Fig. 2(a) presents a 10 s GTS slice, comparing the effect of Cl^- (at 3 and 6 μM) and Br^- (at 3 μM) anions. The demanded time to oscillatory behavior starts after the current is set (induction period) depends on the anion nature, concentration, temperature etc. Herein, the comparison between the distinct experiments is possible because the time was normalized by the oscillation onset i.e. the timescale was shifted in order to the birth of oscillations be placed in $t = 0$ (Hopf bifurcation). Regardless of the anion present, the first stages of oscillations behavior have the same pattern (period 1).

Fig. 2(b) and (c) show the maximum potential (E_{max}) and oscillation frequency (ω) extracted from each cycle during 300 s. E_{max} increases fast near Hoft bifurcation and the Cl^- presence shifts the E_{max} to higher
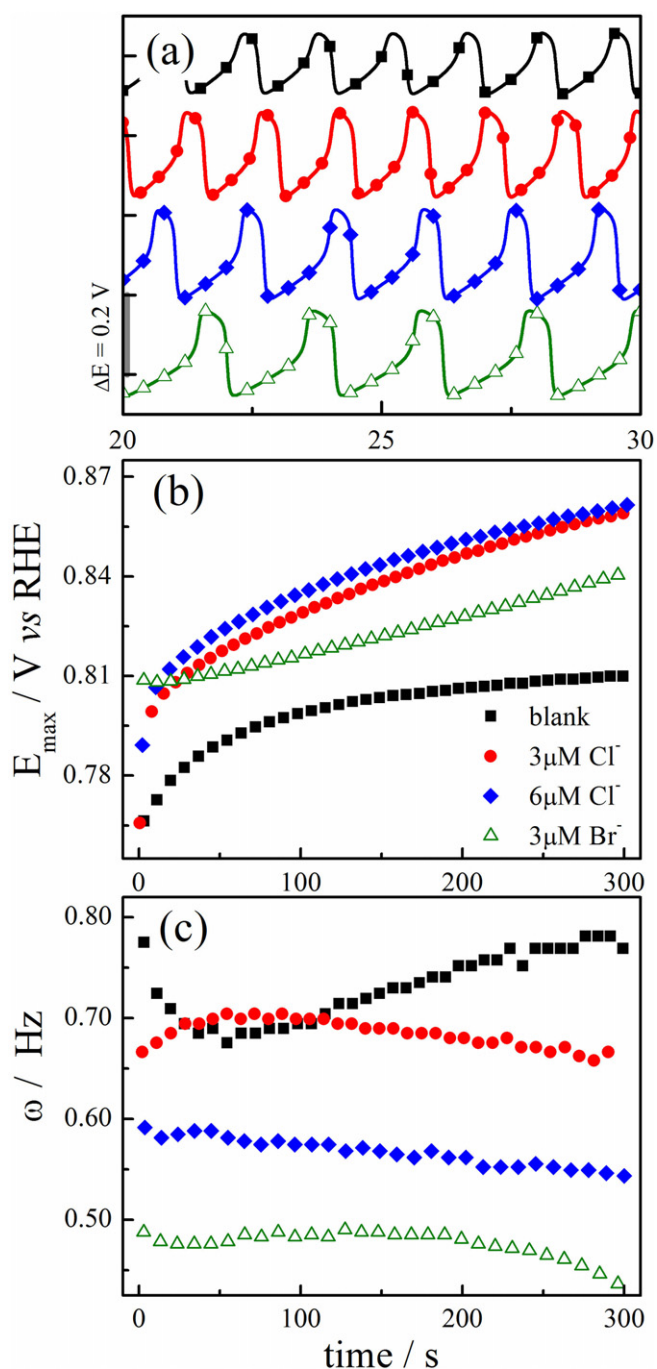
Fig. 2. – (a) Oscillation samples extracted from galvanostat time series with j = 1.11 mA cm^{-2} (blank), 0.72 mA cm^{-2} (3 μM Cl$^-$), 0.61 mA cm^{-2} (6 μM Cl$^-$), and 0.58 mA cm^{-2} (3 μM Br$^-$). (b) and (c) represents the maximum potential (E$_{max}$) reached in each cycle of oscillations and oscillations frequency (ω) along time, respectively.

values, however the curve shape (E$_{max}$ time dependence) seems to be kept in the presence of this anion, regardless the concentration. Contrary, 3 μM of Br$^-$ shifts E$_{max}$ to lower values when compared with Cl$^-$ in the same concentration, moreover, the time dependence seems to be more linear in the presence of Br$^-$. At high potential, the formation of oxygenate species are the responsible to remove the surface poisons and the potential drops, starting a new cycle. Along the time-series there is a drift caused by some slow process that is the responsible to modify the frequency, period, amplitude and to extinguish the oscillatory behavior, it means that several oscillation cycles occur, but the initial conditions of each one are not exactly the same. This slow process is

claimed to be the formation of Pt oxides that, in contrast to hydroxides and adsorbed water, involves subsurface oxygen [26,28]. The subsurface oxygen formation is triggered by the repulsion between the oxygen atoms on surface, so on, it can be influenced by adsorbing anions. Strong adsorbing anions act as surface poisons, therefore, both the onset of PtOH$_x$ (x = 0, 1 or 2) and the subsurface oxygen happen at higher potential [29,30]. Fig. S1(a) (SI files) shows that Cl$^-$ presence modifies the first stages of surface oxidation that occur in the same oscillation potential windows, as well as the hydrogen adsorption/desorption region being squeezed to lower potentials. Similarly, in the presence of Br$^-$ (Fig. S1(b)) both the oxide onset and hydrogen regions are shifted to higher and lower potentials respectively, however, in the presence of methanol (Fig. 2) the oscillation dynamics do not follow the same tendency observed with the Cl$^-$ addition, the behavior being associated with changes on the MER mechanism, as discussed below. The higher Br$^-$ adsorption strength, compared with Cl$^-$, is confirmed comparing the CV in 3 μM of Cl$^-$ and Br$^-$ (Fig. S1(c)).

Oscillation frequency (ω) decreases in the presence of halides, a small inversion is observed for the lower Cl$^-$ concentration, but it seems to relate to the changes in ω evolution in time. Mean oscillation frequency (ω$_{mean}$) over 300 s are: 0.73 ± 0.03, 0.69 ± 0.02, 0.57 ± 0.02 and 0.48 ± 0.02 Hz for the blank, 3 μM Cl$^-$, 6 μM Cl$^-$ and 3 μM Br$^-$, respectively. This trend was also observed by Varela et al. [19] comparing HClO$_4$ and H$_2$SO$_4$ as supporting electrolytes for MER. The authors found that ω$_{mean}$ decreases by 25%, which is comparable with the changes observed after 6 μM Cl$^-$ addition. The advantage of halide addition is to maintain the ionic strength and electrolyte conductivity near the conditions of a blank experiment.

We also extracted the dE/dt parameter from the GTS analysis as well as its potential dependence (Fig. 3). dE/dt at fixed current can be interpreted as poisoning/cleaning surface rate and it allows the comparison of the same pattern potential oscillations [4,22,31–33]. In short, the higher the values in positive or negative directions, the higher the poisoning or cleaning rate, respectively. Thus, the presence of 3 μM Cl$^-$ increases dE/dt when compared to the blank, but increasing the concentration or replacing Cl$^-$ by Br$^-$ causes the decrease of dE/dt. Comparing this trend with the E$_{max}$ and ω shown in Fig. 2, we concluded that small amounts of Cl$^-$ slightly change ω$_{mean}$, (from 0.73 ± 0.03 to 0.69 ± 0.02 Hz) but considerably increase E$_{max}$ as discussed above. Furthermore, when the surface poisons are removed, there is a competition between the anions and methanol adsorption, this last yielding soluble or adsorbed species. The potential drop means that the net processes are providing sufficient electrons to maintain the set current – this occurs by the partial charge transfer during anion adsorption (non-faradaic processes) and faradaic currents from methanol oxidation. However, at low potential, methanol adsorption tends to form CO$_{ad}$ and the surface becomes saturated by these species and anions. At this point, the potential starts to increase again to keep the set current. The anions compete with methanol for free sites and their adsorption causes not only partial charge transfer, but they also change the CO$_{ad}$ formation from methanol adsorption, therefore in the presence of 3 μM Cl$^-$ the dE/dt becomes higher because, although the frequency is the same, the potential windows (E$_{max}$ − E$_{min}$) visited in a cycle is larger.

Increasing the Cl$^-$ amounts, both ω and E$_{max}$ follow the same trend observed after the first Cl$^-$ addition, (this is also true for ω in presence of Br$^-$) but now the poisoning rates monotonically decrease.

Indeed, the presence of small amount of halide anions affects the MER, however, while under voltammetry conditions the changes are observed as a monotonical decrease of current, parameters extracted from oscillations change in a complex manner. The presence of Cl$^-$ blocks Pt sites hindering methanol adsorption but, the decrease of active site can also change the oxidation mechanism, favoring the non-CO pathway. This statement is in line with the T. Iwasita [13] and A. Cuesta [14] works in which they concluded that the decrease of contiguous sites on Pt modifies the methanol electro-oxidation pathways, disfavoring processes that involve several sites as the CO$_2$ formation
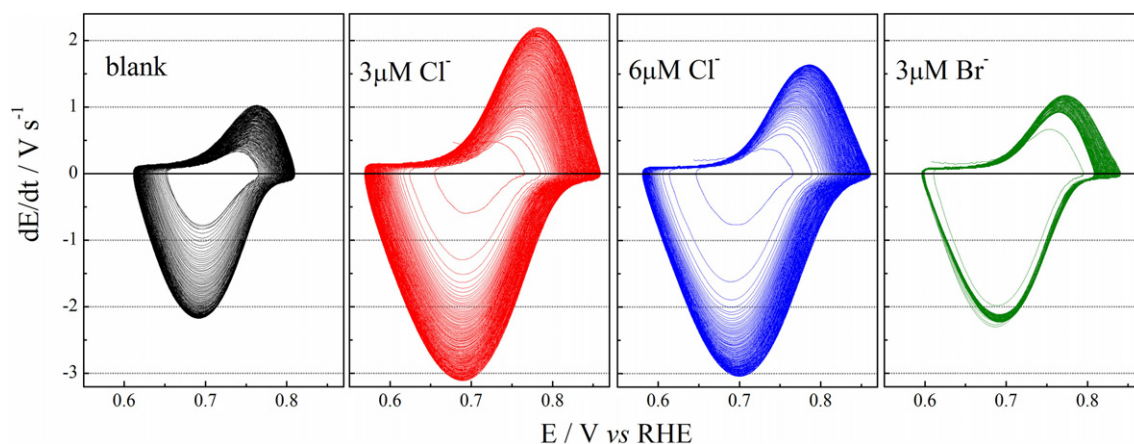
Fig. 3. – dE/dt profiles for the galvanostatic time series of Fig. 2.

through the CO_{ad}. Since oscillation parameters are strongly dependent on system conditions (CO_{ad} covering, for example), increasing the Cl^- amount induces a poisoning effect caused by anions adsorption, but could also avoid the formation of an intrinsic reaction poison, i.e. CO_{ad}, therefore dE/dt decreases. The changes of dE/dt with Cl^- concentration can be compared to the change caused by the increase of pH reported in ref. [4]. Thus, the oscillation dependence with pH can also be connected to the distinct anion adsorption. Finally, maintaining the temperature and methanol concentration, the oscillations are inhibited at higher halide concentrations, so we did not observe the high potential excursions described in ref. [17].

3.1. The temperature effect

The changes in the MER mechanism are reflected in apparent activation energy (E_a), so, to study the effect of halide anions in this system we performed experiments in a 7 to 35 °C temperature range and analyzed several kinetic descriptors by means of Arrhenius Equation. The simplest way to obtain the E_a in an electrochemical system is to use the current as proportional to the reaction constant (k_r). Representative experiments can be found in SI files in both absence and presence of halides. Herein, we adopted the current at the main peak in CV positive going scan and the E_a was estimated by the slope of $\ln j_{peak}$ versus $1/T$ plots. The obtained E_a's (E_a (j_{peak})) are shown as black squares in Fig. 4 and the error bar represent the standard deviation of three experiments performed on different days (All these values are shown in Table S1 in SI files section). E_a values increase with Cl^- concentration, from 45 to 55 kJ mol^{-1}. The value in absence of Cl^- agrees with ref. [34] and it is lower than the values reported in ref. [35], probably due to the higher methanol concentration and the presence of SO_4^{2-} instead ClO_4^- ions in the electrolyte. The relationship between the current peak decrease and E_a increase is not straightforward since on increasing the amount of Br^-, the Ea seems to be constant (considering the error bar).

The mean oscillation frequency (ω_{mean}) also has been used as proportional to k_r in the Arrhenius equation [20–22,33,35]. In this case, a galvanodynamic sweep is performed for each temperature and the oscillation window is employed as the parameter to normalize the current in which the oscillations frequency will be estimated in a GTS. SI file detailed shows the process to obtain E_a by oscillations frequency (E_a (ω_{osc})) and the obtained values are shown as red circles in Fig. 4. Interestingly, E_a in the halide-free electrolyte ($[Cl^-] = 0$) is slightly higher than the obtained value employing the current peak. However, increasing the Cl^- concentration, E_a decreases to values below 45 kJ mol^{-1}. This dependence indicates the Cl^- does not act as a mere surface blocker but possibly exerts some role on the MER mechanism that is reveled under the oscillatory regime as discussed above. When Cl^- is replaced by Br^- (Fig. 4(b)), the opposite trend is lost, i.e. a small amount

of Br^- shift the E_a to slight higher values but when $[Br^-] = 3$ μM, decrease for values near to the blank. This change agrees with the maximum potential along the GTS described in Fig. 2(b), confirming that

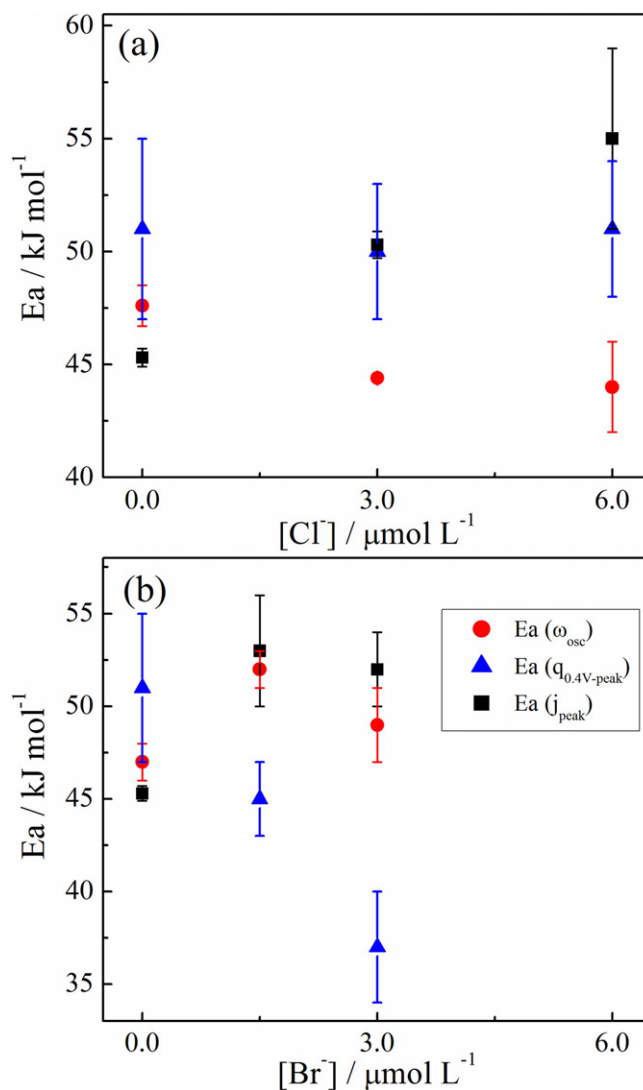**Fig. 4.** Activation energy obtained with three methods during MER on Pt in the presence of distinct amount of Cl^- (a) and Br^- (b). Electrolyte composition is the same as Fig. 1.
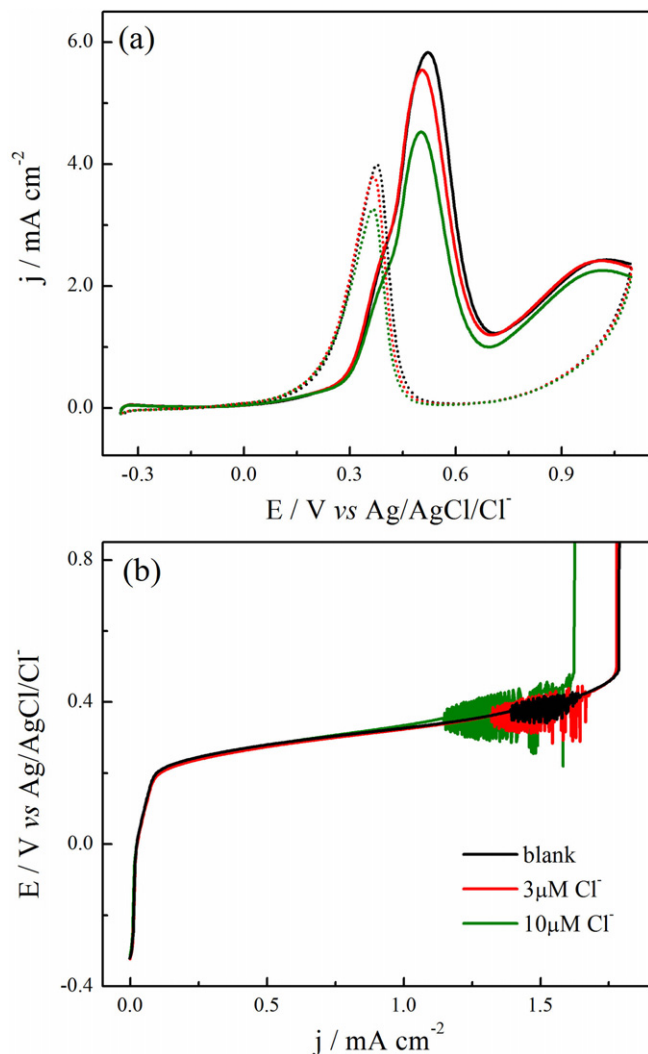
Fig. 5. Anion effect on 0.05 V s^{-1} cyclic voltammograms (a) and 4.7 µA s^{-1} cm^{-2} galvanodynamics curves (b) during methanol electro-oxidation reaction on Pt and 0.5 M methanol +0.1 M HClO$_4$ + 0.5 M NaF (pH 5.6). $T = 25$ °C. Solid and dotted lines represent the positive and negative going scans, respectively.

the inhibition caused by Br$^-$ in the MER is different from the inhibition caused by Cl$^-$.

The E$_a$ values obtained in the oscillatory regime in the presence of halide anions differ from the values obtained with j$_{peak}$ probably because the potential region is distinct (E$_{peak}$ is ca 0.9 V and during oscillations E$_{max}$ does not reach these values). Moreover, during oscillations the potential is swept along a window in which distinct adsorption processes occur. To compute these processes, we estimated the E$_a$ using the charge produced in the region between 0.4 V and the peak potential as parameter to replace k_r in the Arrhenius equation. This potential window is slightly larger than the potential swept during oscillations for all conditions. The E$_a$ values obtained in this way (E$_a$(q$_{0.4V - peak}$)) are shown as blue triangles in Fig. 4 and interestingly, their values are close to those obtained in a haline-free solution, regardless of the method employed. They also follow the same tendency of E$_a$(j$_{peak}$) in the presence of Cl$^-$. In the presence of Br$^-$ the E$_a$(q$_{0.4V - peak}$) values decrease reaching 37 $\pm$ 3 kJ mol^{-1} for 3 µM of Br$^-$. Again, the behavior of MER in the presence of Br$^-$ is distinct of that one in presence of Cl$^-$. Br$^-$ seems to play an important role in the low potential regions, decreasing the charge temperature-dependence (Ea(q$_{0.4V - peak}$)) but maintaining the temperature-dependence of current (Ea(j$_{peak}$)) and slight increasing to the frequency (Ea(ω_{osc})).

In principle, the higher Br$^-$ adsorption strength compared to Cl$^-$ should be compensate in the experiment with lower Br$^-$ concentration, for example, the inhibition caused by 6 µM of Cl$^-$ on cyclic voltammograms is similar to the inhibition caused by 3 µM of Br$^-$, however, E$_{max}$, oscillation frequency and E$_a$ do not agree with this tendency. One possible explanation comes from a 1973 Sobkowski and Wieckowski paper [9] that estimated the surface concentration of methanol (actually, methanol residues) by means of radiometric techniques concluding that "The adsorbed intermediates react with bromide and iodine ions and the products of the reaction remain strongly bound to the surface, being only partially oxidized at +1.2 V". Br$^-$ is a more reactive halide than Cl$^-$ in acid catalyzed nucleophilic substitution reactions, which could explain the difference between these anions on the MER.

3.2. The solution pH effect

To analyze the effect of pH without the hydrogen phosphate anions influence the pH was set to 5.6 in HClO$_4$/NaF buffered solutions in which the anions absorption (ClO$_4^-$ and F$^-$) are negligible. Fig. 5(a) shows the
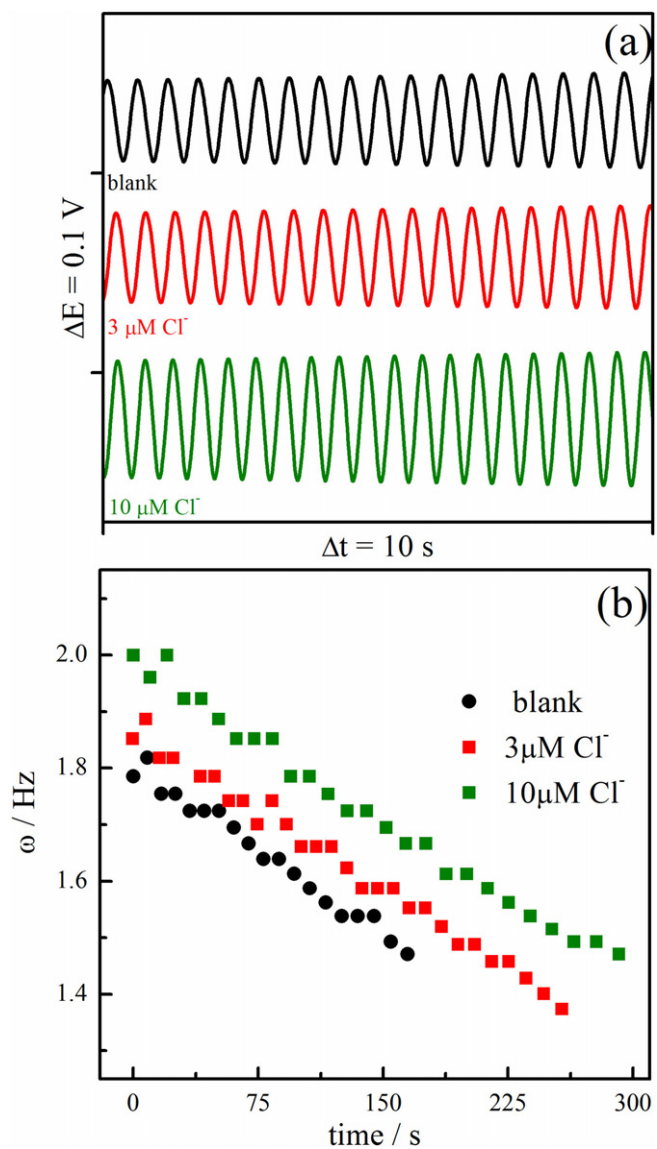

Fig. 6. – (a) Oscillation samples extracted from galvanostatic time series with j = 1.9 mA cm^{-2} (blank), 1.48 mA cm^{-2} (3 µM Cl$^-$) and 1.42 mA cm^{-2} (10 µM Cl$^-$) performed in HClO$_4$/NaF electrolyte (pH 5.6) + 0.5 M methanol. (b) Represents oscillations frequency (ω) along period 1.
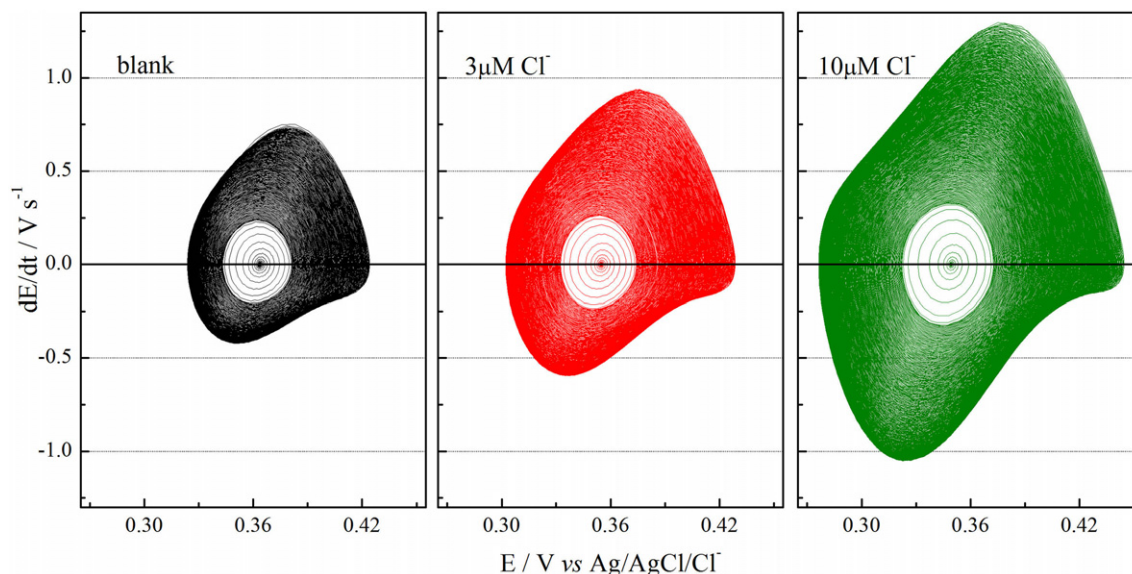
Fig. 7. dE/dt profiles for galvanostatic time series of Fig. 6.

CV during the MER at pH 5.6 in absence (black lines) and presence of 3 (red) and 10 μM (green) of Cl^-. Remarkably, the shape and current magnitude is maintained when compared with the CV of Fig. 1. This shape is lost is the presence of hydrogen phosphates and a current decrease is also observed from pH 1.3 to 5.0. Moreover, the current inhibition caused by the presence of Cl^- in pH 5.6 is lower than at pH ~ 1.0, i.e. while the presence of 3 μM of Cl^- inhibits 40% of current peak at pH ~ 1.0, a decrease of only 8% is observed for the same amount of Cl^- in pH 5.6. Galvanodynamic curves (Fig. 5(b)) reveal low amplitude oscillations at this pH and the presence of Cl^- increases the amplitude and shifts the current oscillation region to lower values. Fig. 6 shows some oscillation features extracted from GTS. The whole period 1 time-series can be found in Fig. S5 in SI files. When compared to oscillations observed during the MER at pH ~ 1.0, the amplitude decreases by ca 50% and the oscillation frequency is doubled. ω_{mean} over the first 150 s are: 1.66 ± 0.09, 1.73 ± 0.08, and 1.85 ± 0.09 for the blank, 3 μM Cl^-, and 10 μM Cl^-, respectively. The increase of ω_{mean} in pH 5.6 also contrasts with the decrease of these parameters at pH ~ 1.0. The GTS evolves to more complex patterns with period 2 and 3 as already observed in pH ~ 1.0, However, remarkably, at pH 5.6 the mixed-mode oscillations, also known as period 1^n with $n > 0$, are very stable along the GTS. Moreover, the oscillations are extinguished for some seconds and then return with another oscillation pattern. This behavior is also observed during the formic acid electro-oxidation reaction in the presence of 5 μM Cl^- [36]. Samples of MER oscillations at pH 5.6 can be found in Fig. S6 in SI files.

Finally, the dE/dt curves for period 1 oscillations are shown in Fig. 7. The poisoning/freeing rate is lower in pH 5.6 than in pH ~ 1.0. The increase of Cl^- is accompanied by the increase of dE/dt which could represent the same processes occurring after the first Cl^- addition (from 0 to 3 μM) in pH ~ 1.0. Thus, it can be concluded from this set of data that the MER is also affected by adsorbing anions at pH 5.6. The effect is less pronounced in CV profiles and oscillation frequencies; however, the amplitude of oscillations considerably increases mainly due to the decrease of minimum potential reached in each cycle.

4. Conclusion

The influence of halide anions on the methanol electro-oxidation reaction was studied on distinct experimental conditions under both potential and current control. The oscillations present under galvanostat control allowed us to analyze parameters such as the oscillations frequency (ω), maximum potential visited on each oscillation cycle (E_{max}), poisoning/freeing surface rates (dE/dt) and the activation energy (E_a). The influence of distinct amounts of bromide and chloride was tested in 0.1 M $HClO_4$ and HClO4/NaF buffered solutions with pH 5.6. In contrast with the monotonical current decrease observed in cyclic voltammograms, the presence of Cl^- and Br^- modifies the oscillations in a complex manner as observed by the changes in E_{max}, E_a and dE/dt in 0.1 M $HClO_4$. E_{max}, ω and dE/dt changes with Cl^- concentration were explained in terms of surface site inhibition, probably leading the reaction to distinct pathways. The decrease of E_a estimated by ω supports the reaction pathway changes in the presence of Cl^-, likewise, the increase of E_a estimated by j_{peak} indicates that Cl^- influence depends on the way in which the methanol electro-oxidation is performed. The conclusions addressed for the presence of Cl^- on the system cannot be straightforwardly applied to Br^-, since, despite Br^- having a higher adsorption strength on the surface than Cl^- the reactive of Br_{ad} could be playing some role on MER. Finally, it was observed oscillations during MER in pH = 5.6, with small influence of Cl^- under both cyclic voltammetry and oscillatory conditions. The presence of oscillations in this pH shed some light on the effect caused by other anions such as hydrogen phosphates that completely inhibit the oscillatory behavior in pH > 4.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2019.113657.

References

[1] F. Samimi, M.R. Rahimpour, Direct methanol fuel cell, Methanol, Elsevier 2018, pp. 381–397, https://doi.org/10.1016/B978-0-444-63903-5.00014-5.

[2] M.T.M. Koper, S.C.S. Lai, E. Herrero, Mechanisms of the oxidation of carbon monoxide and small organic molecules at metal electrodes, Fuel Cell Catal, John Wiley & Sons, Inc, Hoboken, NJ, USA 2008, pp. 159–207, https://doi.org/10.1002/9780470463772.ch6.

[3] E.G. Machado, H. Varela, Kinetic instabilities in electrocatalysis, Encycl. Interfacial Chem, Elsevier 2018, pp. 701–718, https://doi.org/10.1016/B978-0-12-409547-2.13369-4.

[4] G.B. Melle, F.W. Hartl, H. Varela, E. Sitta, The effect of solution pH on the oscillatory electro-oxidation of methanol, J. Electroanal. Chem. 826 (2018) 164–169, https://doi.org/10.1016/j.jelechem.2018.08.033.

[5] R. Gisbert, G. García, M.T.M. Koper, Oxidation of carbon monoxide on poly-oriented and single-crystalline platinum electrodes over a wide range of pH, Electrochim. Acta 56 (2011) 2443–2449, https://doi.org/10.1016/j.electacta.2010.11.032.

[6] J. Joo, T. Uchida, A. Cuesta, M.T.M. Koper, M. Osawa, Importance of acid–base equilibrium in electrocatalytic oxidation of formic acid on platinum, J. Am. Chem. Soc. 135 (2013) 9991–9994, https://doi.org/10.1021/ja403578s.

[7] J.V. Perales-Rondón, E. Herrero, J.M. Feliu, Effects of the anion adsorption and pH on the formic acid oxidation reaction on Pt(111) electrodes, Electrochim. Acta 140 (2014) 511–517, https://doi.org/10.1016/j.electacta.2014.06.057.

[8] D.V. Tripkovic, D. Strmcnik, D. van der Vliet, V. Stamenkovic, N.M. Markovic, The role of anions in surface electrochemistry, Faraday Discuss. 140 (2009) 25–40, https://doi.org/10.1039/B803714K.

[9] J. Sobkowski, A. Wieckowski, The influence of halide ions on methanol adsorption and oxidation on a platinized electrode, J. Electroanal. Chem. Interfacial Electrochem. 41 (1973) 373–379, https://doi.org/10.1016/S0022-0728(73)80416-4.

[10] N. Markovic, P.N. Ross, The effect of specific adsorption of ions and underpotential deposition of copper on the electro-oxidation of methanol on platinum single-crystal surfaces, J. Electroanal. Chem. 330 (1992) 499–520, https://doi.org/10.1016/0022-0728(92)80327-Z.

[11] J. Sobkowski, K. Franaszczuk, K. Dobrowolska, Effect of anions and pH on the adsorption and oxidation of methanol on a platinum electrode, J. Electroanal. Chem. 330 (1992) 529–540, https://doi.org/10.1016/0022-0728(92)80329-3.

[12] E. Sitta, H. Varela, On the open-circuit interaction between methanol and oxidized platinum electrodes, J. Solid State Electrochem. 12 (2008) 559–567, https://doi.org/10.1007/s10008-007-0349-6.

[13] E.A. Batista, G.R.P. Malpass, A.J. Motheo, T. Iwasita, New mechanistic aspects of methanol oxidation, J. Electroanal. Chem. 571 (2004) 273–282, https://doi.org/10.1016/j.jelechem.2004.05.016.

[14] A. Cuesta, At least three contiguous atoms are necessary for CO formation during methanol electrooxidation on platinum, J. Am. Chem. Soc. 128 (2006) 13332–13333, https://doi.org/10.1021/ja0644172.

[15] H. Wang, 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 111 (2007) 7038–7048, https://doi.org/10.1021/jp068328n.

[16] G.C.A. Ferreira, B.C. Batista, H. Varela, Experimental assessment of the sensitiveness of an electrochemical oscillator towards chemical perturbations, PLoS One 7 (2012), e50145. https://doi.org/10.1371/journal.pone.0050145.

[17] Y. Mukouyama, S. Yonezawa, R. Taguchi, T. Gojuki, T. Kuge, H. Okamoto, Regeneration oscillation observed during oxidation of methanol, formic acid, and formaldehyde with chloride ions, Electrochemistry 82 (2014) 960–965, https://doi.org/10.5796/electrochemistry.82.960.

[18] B. Peng, Y.-G. Yan, W.-B. Cai, Surface-enhanced IR spectroscopy investigation on the electro-oxidation of CO adlayer at a polycrystalline Pt film electrode in Cl−-containing HClO4, Electrochim. Acta 55 (2010) 8307–8311, https://doi.org/10.1016/j.electacta.2010.04.029.

[19] R. Nagao, D.A. Cantane, F.H.B. Lima, H. Varela, Influence of anion adsorption on the parallel reaction pathways in the oscillatory electro-oxidation of methanol, J. Phys. Chem. C 117 (2013) 15098–15105, https://doi.org/10.1021/jp4028047.

[20] R. Nagao, I.R. Epstein, E.R. Gonzalez, H. Varela, Temperature (over)compensation in an oscillatory surface reaction, J. Phys. Chem. A 112 (2008) 4617–4624, https://doi.org/10.1021/jp801361j.

[21] E. Sitta, M.A. Nascimento, H. Varela, Complex kinetics, high frequency oscillations and temperature compensation in the electro-oxidation of ethylene glycol on platinum, Phys. Chem. Chem. Phys. 12 (2010) 15195–15206, https://doi.org/10.1039/c002574g.

[22] E. Sitta, R. Nagao, H. Varela, The electro-oxidation of ethylene glycol on platinum over a wide pH range: oscillations and temperature effects, PLoS One 8 (2013), e75086. https://doi.org/10.1371/journal.pone.0075086.

[23] K.N. da Silva, R. Nagao, E. Sitta, Alkali cation effect during the oscillatory electroreduction of H 2 O 2 on Pt, ChemistrySelect 2 (2017) 11713–11716, https://doi.org/10.1002/slct.201702276.

[24] K. da Silva, S. Maruyama, E. Sitta, High order cyclic voltammograms during electrooxidation of ethanol catalyzed by gold, J. Braz. Chem. Soc. 28 (2017) 1725–1731, https://doi.org/10.21577/0103-5053.20170020.

[25] V. Briega-Martos, E. Herrero, J.M. Feliu, The inhibition of hydrogen peroxide reduction at low potentials on Pt(111): hydrogen adsorption or interfacial charge? Electrochem. Commun. 85 (2017) 32–35, https://doi.org/10.1016/j.elecom.2017.10.016.

[26] R. Nagao, E. Sitta, H. Varela, Stabilizing nonstationary electrochemical time series, J. Phys. Chem. C 114 (2010) 22262–22268, https://doi.org/10.1021/jp109554r.

[27] A.L. Martins, B.C. Batista, E. Sitta, H. Varela, Oscillatory instabilities during the electrocatalytic oxidation of methanol on platinum, J. Braz. Chem. Soc. 19 (2008) 679–687, https://doi.org/10.1590/S0103-50532008000400011.

[28] M.F. Cabral, R. Nagao, E. Sitta, M. Eiswirth, H. Varela, Mechanistic aspects of the linear stabilization of non-stationary electrochemical oscillations, Phys. Chem. Chem. Phys. (2013) https://doi.org/10.1039/c2cp42890c.

[29] A. Zolfaghari, Elucidation of the effects of competitive adsorption of Cl—and Br— ions on the initial stages of Pt surface oxidation by means of electrochemical nanogravimetry, Electrochim. Acta 47 (2002) 1173–1187, https://doi.org/10.1016/S0013-4686(01)00841-6.

[30] B.E. Conway, A. Zolfaghari, W.G. Pell, G. Jerkiewicz, Voltammetry, nanogravimetry and double-layer capacitance studies on chemisorption of Cl— and Br—, competitive with potential-dependent electrosorption of O species at Pt electrodes, Electrochim. Acta 48 (2003) 3775–3778, https://doi.org/10.1016/S0013-4686(03)00510-3.

[31] N. Perini, E. Sitta, A.C.D. Angelo, H. Varela, Electrocatalytic activity under oscillatory regime: the electro-oxidation of formic acid on ordered Pt3Sn intermetallic phase, Catal. Commun. 30 (2013) 23–26, https://doi.org/10.1016/j.catcom.2012.10.019.

[32] F.W. Hartl, A.A. Zülke, B.J. Fonte, H. Varela, Temperature dependence of the evolving oscillations along the electrocatalytic oxidation of methanol, J. Electroanal. Chem. 800 (2017) 99–105, https://doi.org/10.1016/j.jelechem.2016.11.032.

[33] A.A. Zülke, H. Varela, The effect of temperature on the coupled slow and fast dynamics of an electrochemical oscillator, Sci. Rep. 6 (2016), 24553. https://doi.org/10.1038/srep24553.

[34] J.L. Cohen, D.J. Volpe, H.D. Abruña, Electrochemical determination of activation energies for methanol oxidation on polycrystalline platinum in acidic and alkaline electrolytes, Phys. Chem. Chem. Phys. 9 (2007) 49–77, https://doi.org/10.1039/b612040g.

[35] E.A. Carbonio, R. Nagao, E.R. Gonzalez, H. Varela, Temperature effects on the oscillatory electro-oxidation of methanol on platinum, Phys. Chem. Chem. Phys. 11 (2009) 665–670, https://doi.org/10.1039/b811636a.

[36] S. Chen, T. Noles, M. Schell, Differences in oscillations and sequences of dynamical states caused by anion adsorption in the electrochemical oxidation of formic acid, J. Phys. Chem. A 104 (2000) 6791–6798, https://doi.org/10.1021/jp001066j.