Mass transfer phenomena induced by surface gas flow rate in the hanging meniscus configuration: A case study of the methanol electro-oxidation reaction on Pt(100)

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ABSTRACT

The study of electrochemical systems using single-crystal electrodes under conditions that allow the occurrence of an oscillatory response can be a valuable tool to obtain a proper correlation between structure, composition, and electrocatalytic activity. Measurements with single-crystal electrodes are usually performed in the hanging meniscus configuration, so, it is essential to understand the impact of different experimental parameters on the electrochemical response, mainly under oscillatory regime, which are very sensitive to the electrochemical environment. In this study, we investigated the influence of surface gas flow rate, commonly used to avoid the contribution of the oxygen reduction reaction to the electrochemical response, on the methanol electro-oxidation reaction on Pt(100) electrodes. Controlled experiments were conducted to analyze the effect of this parameter on the electrochemical behavior in the chronoamperometric, voltammetric, and oscillatory responses. The results show that while chronoamperometric and voltammetric profiles remain relatively unaffected by varying gas flow rates, the oscillatory response undergoes significant changes. The induction period, the existence region of potential oscillations, and the transition between oscillatory patterns are notably influenced. The observed effects suggest that the subtle agitation caused by increased gas flow rate enhances mass transfer phenomena near the electrode surface, impacting the presence of soluble species and their role in the oscillatory behavior. In addition, the occurrence of mixed-mode oscillations is attributed to the periodic re-establishment of methanol concentration in the double layer. The findings highlight the importance of controlling the surface gas flow rate to ensure reliable and reproducible results in electrochemical experiments performed in the hanging meniscus configuration.

1. Introduction

Most electrochemical reactions involve species adsorbed on the electrode surface during their transformation from reactants to products. The adsorption energies of these intermediates, governed by the interaction force between the adsorbed molecules and the surface, play a crucial role in establishing the energy changes along the reaction pathway and consequently impact the overall reaction rate [1]. For this reason, it is imperative to study the correlation between the structure, composition, and electrocatalytic activity of the electrode surface toward a certain electrocatalytic reaction. This knowledge enables the design of catalytic materials with optimized properties, aimed at increasing the reaction rate and selectivity of electrochemical reactions.

In this context, interfacial electrochemistry using single-crystal electrodes has emerged as a powerful tool because these electrodes possess a controlled surface distribution of atoms and specific active sites [1,2], making them well-suited to correlate electrocatalytic properties with electrode surface properties.

On the other hand, depending on the presence of properly operating feedback loops in the reaction mechanism and the experimental conditions under which the reactions are studied, non-linear phenomena can spontaneously arise, resulting in bistability and oscillatory response, for instance [3,4]. This behavior is closely associated with the reaction mechanism and the potential-dependent interaction between the intermediates and the surface. Thus, the characteristics of the oscillatory patterns, such as the frequency, amplitude, and waveform are

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determined by the combination of the rates of each reaction step [5]. As a result, electrochemical experiments in the oscillatory regime might provide unique insights into the study of surface phenomena [6]. In this regard, the combination of the two previously mentioned approaches can yield a highly sensitive response, enabling a more accurate correlation between the electrochemical behavior and microscopic properties.

An experimental approach commonly employed for working with single-crystal electrodes is the well-known hanging meniscus configuration [7–10]. In this setup, a hemispherical working electrode with a specific arrangement of atoms on its flat face is brought into contact with the solution. It is then positioned slightly above the electrolyte level, forming the hanging meniscus, which ensures that only the ordered surface is in contact with the electrolyte [1,2,8]. Some studies have highlighted that the geometry of the meniscus, which depends on factors such as the electrode material, electrolyte surface tension, and the height of the electrode above the electrolyte level [8,11], can influence the electrochemical response. This is particularly relevant when one of the reactants is present in the gas phase, as it can affect mass transport phenomena. Therefore, this experimental parameter should be carefully considered in kinetic studies [7,8].

In studies where it is necessary to avoid the current contribution associated with the oxygen reduction reaction (ORR), the electrolyte is initially purged with an inert gas, typically Ar, and a surface gas flow is maintained throughout the experiment [12]. In this context, small pressure changes around the meniscus, caused by the gas flow, can affect its shape and, consequently, affect the electrochemical response, particularly in the oscillatory regime, since these experiments exhibit higher sensitivity to the characteristics of electrode surface compared to conventional techniques such as cyclic voltammetry (CV) and chronoamperometry (CA) [13]. Since the influence of surface gas flow rate on the electrochemical response has not been previously described, we emphasize the importance of controlling this experimental parameter to improve the reliability of electrochemical studies. This is crucial to obtain representative results of the system and to ensure reproducibility across different laboratories.

In this study, we focus on the methanol electro-oxidation reaction (MEOR) on a Pt(100) electrode and in acidic media. This reaction is of significance due to the applicability of this alcohol in direct methanol fuel cells (DMFC) and its role in transitioning the current energy sector toward a sustainable and clean scenario [14,15]. The single-crystal Pt (100) plane was used because, among the low-index single-crystal platinum electrodes, it exhibits the highest activity in the high-potential region, which is crucial as the electrode is mainly maintained in this region during potential oscillations [16]. Furthermore, the Pt(111) electrode has been reported to display oscillatory behavior only at high methanol concentrations [17], leading to rapid poisoning of the electrode surface by CO_{ad} species. The Pt(110) surface is highly sensitive to undergoing different reconstructions during cooling after flame annealing, resulting in significant differences in the electrochemical response [18], making it challenging to establish a meaningful correlation with the electrode surface. Here, we show the effect of surface gas flow rate in both voltammetric and chronoamperometric experiments, followed by its influence on oscillatory experiments performed under applied current control, specifically under galvanodynamic and galvanostatic conditions.

2. Methods

2.1. Electrochemical measurements

The electrochemical measurements were carried out in a conventional three-electrode cell consisting of a cylindrical main body with dimensions of approximately 4.5 cm in diameter and 6.0 cm in height. The cell, including the junctions for the placement of the electrodes and gas inlet and outlet connections, has a total height of *ca.* 9.5 cm. A large

Pt wire was used as a counter electrode and a reversible hydrogen electrode (RHE) as a reference electrode, prepared in the same supporting electrolyte, *versus* which all the potentials are quoted. The Pt (100) electrode was prepared from a single-crystal bead (*ca.* 2.5 mm diameter) which was oriented, cut, and polished according to the procedure described by Clavilier [19]. Immediately before each electrochemical measurement, the electrode was cleaned using the flame annealing technique, cooled in an atmosphere containing a mixture of H_2/Ar and the surface was protected with water saturated with this gas mixture to prevent contamination before immersion in the electrochemical cell [19]. The electrode was then transferred to the cell and placed in the hanging meniscus configuration maintaining a controlled potential of 0.10 V.

For the measurements, an Autolab potentiostat/galvanostat PGSTAT 128 N was used, and the temperature of the system was controlled with a thermostat (Haake FK) and kept at 25 °C during all experiments. 0.5 mol L^{-1} $HClO_4$ and 0.5 mol L^{-1} $HClO_4$ + 0.5 mol L^{-1} methanol aqueous solutions were prepared using perchloric acid (70%, Merck suprapure), methanol (Merck suprapure), and ultrapure water (Milli-Q, 18.2 MΩ cm). Prior to each experiment, the solution was purged with argon (99.998%), and then the gas was placed as surface gas flow, which was maintained throughout the experiment to avoid the presence of dissolved oxygen and varied to study its influence on the electrochemical response. For all experiments, the cleanliness of the electrode surface and the solutions were checked by the quality and stability of the characteristic voltammetric features of well-defined single-crystal electrodes in the absence of methanol. The cyclic voltammetry was performed from 0.05 V to 0.80 V at a scan rate of 0.050 V s^{-1} in the supporting electrolyte and at 0.010 V s^{-1} for the solution containing methanol. For the chronoamperometric experiments, the electrode potential was initially set at 0.80 V for 2 s, followed by a potential step to 0.10 V for 1 s from which the potential was shifted to 0.60 for 150 s. For the galvanostatic experiments, a potential value of 0.80 V for 2 s, followed by a potential step to 0.10 V for 1 s was applied, then the current step was applied to the value of interest in each experiment.

3. Results and discussion

To assess the impact of argon surface flow rate on the electrochemical response, we initially established the minimum flow rate required to prevent the ORR from influencing the measured current density. The 10th cycle of the voltammetric profile of the Pt(100) electrode in $HClO_4$ 0.5 mol L^{-1}, using a gas flow rate of 0.3 mL s^{-1}, is depicted as the black line in the inset of Fig. 1. This profile exhibits the characteristic features expected for this system, confirming the cleanliness and quality of the electrode surface [1,2]. Importantly, the CV profile is centered around zero on the *y*-axis (current density), indicating the absence of any significant ORR contribution to the electrochemical response. However, when the gas flow rate was decreased to 0.2 mL s^{-1}, a slight shift towards negative values in the current density was observed, as shown by the blue line in the same figure. This shift suggests the presence of an ORR contribution when the flow rate drops below 0.3 mL s^{-1}. Therefore, we established 0.3 mL s^{-1} as the minimum gas flow rate value to be maintained during all subsequent measurements.

The CV profiles in the presence of 0.5 mol L^{-1} methanol (Fig. 1(a)) show that the current density begins to increase around a potential of *ca.* 0.40 V, which coincides with the onset potential of OH adsorption on the electrode surface [14,20], and reaches the maximum at about 0.77 V. An important observation is the difference in peak characteristics between the forward and backward scans in the CV profiles. Specifically, the backward scan exhibits a broader peak compared to the forward scan. This phenomenon can be attributed to the fact that, during the forward scan, the electrode surface is initially blocked by adsorbed CO species, which are formed as soon as OH is adsorbed on the surface ($E > 0.35$ V) [14,21]. Above 0.70 V, adsorbed OH in the free sites reacts with CO,
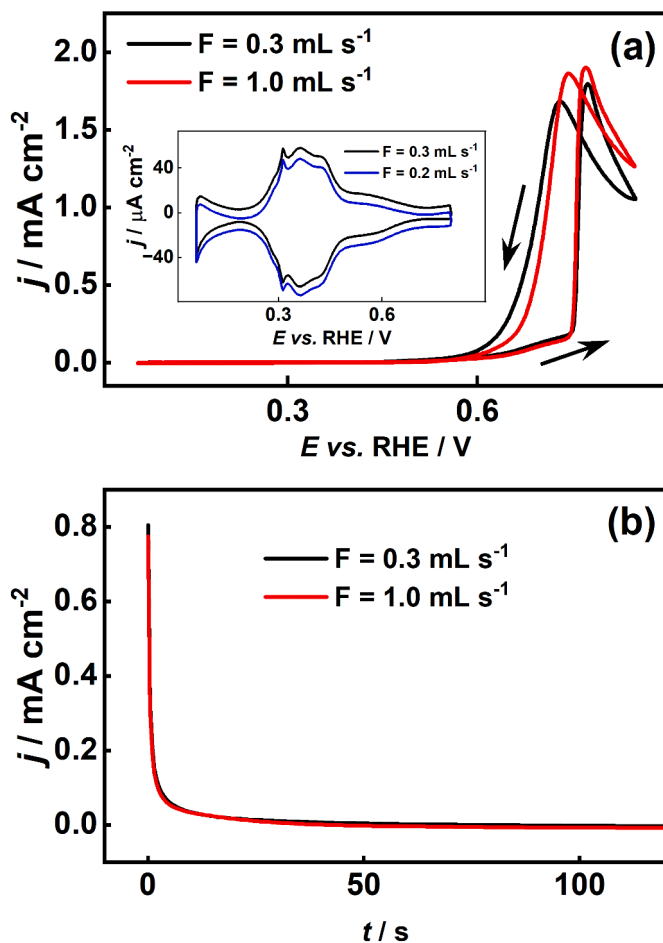
Fig. 1. (a) First cycle in the voltammetric profiles of Pt(100) in 0.5 mol L^{-1} HClO$_4$ + 0.5 mol L^{-1} CH$_3$OH, scan rate: 10 mV s^{-1}. Inset figure corresponds to the 10th cycle in the voltammetric profile of the Pt(100) electrode in the absence of CH$_3$OH, scan rate: 50 mV s^{-1}. (b) Chronoamperometric curves at 0.60 V on Pt(100) in 0.5 mol L^{-1} HClO$_4$ + 0.5 mol L^{-1} CH$_3$OH. Red, black, and blue lines correspond to surface gas flow rates of 1.0 mL s^{-1}, 0.3 mL s^{-1}, and 0.2 mL s^{-1}, respectively.

releasing surface sites with the subsequent sharp increase in the current density [14,20–22]. On the other hand, during the start of the backward scan, a significant number of active sites are available on the electrode surface since the CO adsorbed during the forward scan has been oxidized. Consequently, any methanol molecule reaching the surface can be readily oxidized to CO$_2$ at potentials above 0.60 V. This increased availability of active sites contributes to the broader peak observed in the backward scan. It is consistent with previous reports in the literature and characterizes the specific electrochemical system under investigation [14,20–22].

When the gas flow rate was increased from 0.3 mL s^{-1} (minimum flow rate without ORR contribution) to 1.0 mL s^{-1}, the CV profiles in Fig. 1(a) only show minor changes. Above *ca.* 0.77 V during the forward scan, the current density is slightly higher, and, during the backward scan, the current peak shifts *ca.* 10 mV toward a more positive potential. Additionally, this peak exhibits slightly higher peak current density values, accompanied by a steeper drop as the potential decreases. The observed differences in the CV profiles at different gas flow rates can be attributed, mainly, to the influence of the flow rate in the diffusion. The increment in the gas flow rate can cause small pressure changes around the hanging meniscus, leading to subtle movements that agitate the solution. These vibrations can enhance mass transport phenomena, allowing for increased mobility of species near the electrode surface. During the forward scan, since the electrode surface is initially covered

by CO species, the increased mass transport induced by the vibrations in the hanging meniscus does not significantly impact the system behavior. This is because the CO$_{ad}$ prevents direct interaction with the electrode surface, limiting the impact of enhanced mass transport. At potentials above *ca.* 0.77 V, the CO$_{ad}$ oxidation occurs releasing active sites on the electrode surface. As the gas flow rate increases, the enhanced methanol diffusion results in higher oxidation currents. This explains the observed shift in the peak current towards more positive potentials and the slightly higher current density observed above approximately 0.77 V in the CV. In the backward scan, the increased mass transport of methanol molecules contributes to a faster poisoning of the electrode surface resulting in a steeper drop in the total current.

In the case of the chronoamperometric experiments conducted at 0.60 V, Fig. 1(b) demonstrates that there is no discernible difference in the electrochemical responses between the two different flow rates. In both cases, the current density values rapidly approach zero, indicating that at this potential, the CO$_{ad}$ species poison the electrode surface and that higher potentials are required to achieve complete oxidation of the methanol molecule [20–22]. These results suggest that the increased gas flow rate influences the electrochemical reactions occurring at higher potentials, potentially affecting the kinetics and mass transport processes. It is important to note that, while differences are observed in the CV profile, they are relatively small and may not significantly impact the overall behavior of the system.

The influence of the argon gas flow rate on the oscillatory electrochemical response of the MEOR was investigated under current control. Typical experiments to determine the range of applied current density in which potential oscillations can be observed are galvanodynamic experiments, in which the applied current is varied linearly while measuring changes in the cell potential [3]. Fig. 2(a) shows the galvanodynamic profile of the MEOR at the lowest argon gas flow rate without contribution from the ORR to the current density. In this case, at a current density of 0.11 mA cm^{-2}, the electrochemical response loses its stability, and spontaneous oscillatory dynamics emerge. These oscillations extend up to a current density of 1.38 mA cm^{-2}, beyond which potential abruptly rises above 1.10 V to maintain the applied current density. During the current scan, an interesting observation is that the minimum potential value reached during the oscillations decreases as the applied current increases, whereas the maximum potential value reached by the oscillations is almost constant. Consequently, the amplitude of the oscillations increases. This is a characteristic behavior of the MEOR where transitions from simple oscillations to a mixed-mode oscillatory regime are observed, resulting in complex patterns, small amplitude, and high-frequency oscillations alternating with large amplitude and low-frequency oscillations. Large amplitude oscillations have been correlated with the presence of soluble species [23], indicating their significant influence on the oscillatory kinetic behavior of the Pt(100) surface, particularly at higher current densities. It is noteworthy that the potential changes during the oscillations are related to the total coverage of species that block the electrode surface [3,24]. Consequently, the decrease in the minimum potential observed at higher current densities means a temporary reduction in surface coverage, leading to a delay in the surface inactivation caused by adsorbed poisons, particularly CO$_{ad}$. This behavior has been demonstrated to be advantageous, as it promotes enhanced long-term performance and increased power density during the electro-oxidation of other organic molecules [25].

When the gas flow rate is increased to higher values (Fig. 2(b–e)), it becomes evident that the galvanodynamic profile is perturbed. At lower gas flow rates, a larger range of current values exhibits oscillatory behavior, while at higher gas flow rates, the potential response during the experiment displays an increasing window of non-oscillatory behavior. This window separates a small group of simple oscillations occurring at *ca.* 0.12 mA cm^{-2} from the region encompassing mixed-mode oscillations. This implies that at low applied currents, the influence of small movements in the hanging meniscus is less significant, as
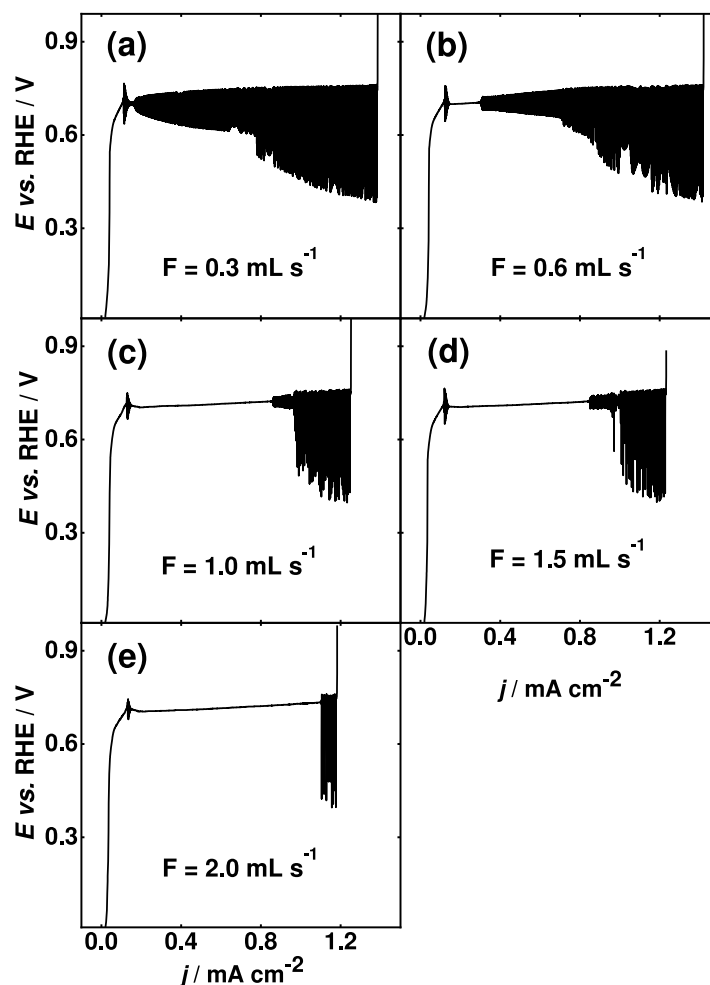
Fig. 2. Galvanodynamic scan profiles of Pt(100) in 0.5 mol L^{-1} HClO$_4$ + 0.5 mol L^{-1} CH$_3$OH, scan rate: 2.0 μA s^{-1} cm^{-2}, at different surface flow rates (a) 0.3 mL s^{-1}, (b) 0.6 mL s^{-1}, (c) 1.0 mL s^{-1}, (d) 1.5 mL s^{-1}, and (e) 2.0 mL s^{-1}.

small amplitude oscillations are mainly driven by species adsorbed on the electrode surface [13]. However, these oscillations are not sustained due to the system is very sensitive to perturbations near the Hopf bifurcation, the point where the steady state transitions to the oscillatory regime [26]. The sensitivity arises from the coexistence of two attractors: a limit cycle that generates the oscillatory behavior and a fixed point that causes the steady state [26]. Thus, fluctuations in experimental variables can induce transitions between these attractors, leading to the collapse of the limit cycle and the loss of oscillatory behavior. Nonetheless, at higher applied currents, the oscillations reappear as the system moves further away from the Hopf bifurcation, enhancing the stability of the limit cycle. In these cases, despite their re-emergence, higher surface flows result in fewer harmonic simple oscillations. The mixed-mode oscillations, on the other hand, appear to be more stable, as higher surface fluxes do not lead to the collapse of the limit cycle. In this case, even at the highest flow rate of 2.0 mL s^{-1} used in this study (Fig. 2 (e)), mixed-mode oscillations are observed. However, as the perturbation of the hanging meniscus increases, the range of oscillations decreases, potentially explaining the absence of oscillatory behavior during the MEOR on a rotating disk electrode under these conditions. Mixed-mode oscillations and amplitude changes are discussed in detail below, along with galvanostatic experiments.

It is important to emphasize that the changes in the galvanodynamic profile caused by uncontrolled parameters can have significant implications. These changes can potentially result in the omission of critical processes occurring at certain current densities during analysis, leading to erroneous conclusions regarding the reaction mechanism. This is of

particular concern because the waveform of the observed oscillations often provides valuable insights into the processes taking place at the electrode surface [6,27–29]. Furthermore, this effect can give rise to misunderstandings, especially when employing an empirical approach commonly used to compare the oscillatory response under different experimental conditions (*e.g.*, temperature, concentration, and pH). This approach involves normalizing the applied current relative to the window of the oscillatory region, thus excluding the influence of the applied current. However, when uncontrolled parameters, such as gas flow rate, impact the extent of the oscillatory region, this normalization method may lead to misinterpretations or misjudgments [30].

The influence of the surface argon flow rate on the oscillatory response of the MEOR under current control was further studied at a constant applied current. Fig. 3 shows the temporal series obtained at an applied current of 0.700 mA cm^{-2}, corresponding to a value in the middle of the oscillatory window in Fig. 2(a), using an argon flow rate of 0.3 mL s^{-1}. Fig. 3(a) displays the complete temporal series, revealing an induction period of *ca.* 40 s, *i.e.*, the time required for the system to approach the attractor and initiate sustained oscillations [5]. Overall, the amplitude of the oscillations progressively increases over time until the potential rises to values above 0.90 V. To gain a more detailed understanding, Figs. 3(b-d) show expanded regions of the complete time series. In Fig. 3(b), the oscillatory behavior is observed to start with small amplitude and periodic oscillations. As time progress, the oscillations become less harmonic, as depicted in Fig. 3(c). Ultimately, the dynamic behavior evolves to mixed-mode oscillations (Fig. 3(d)), characterized by small modulations around 0.76 V, which exhibit a
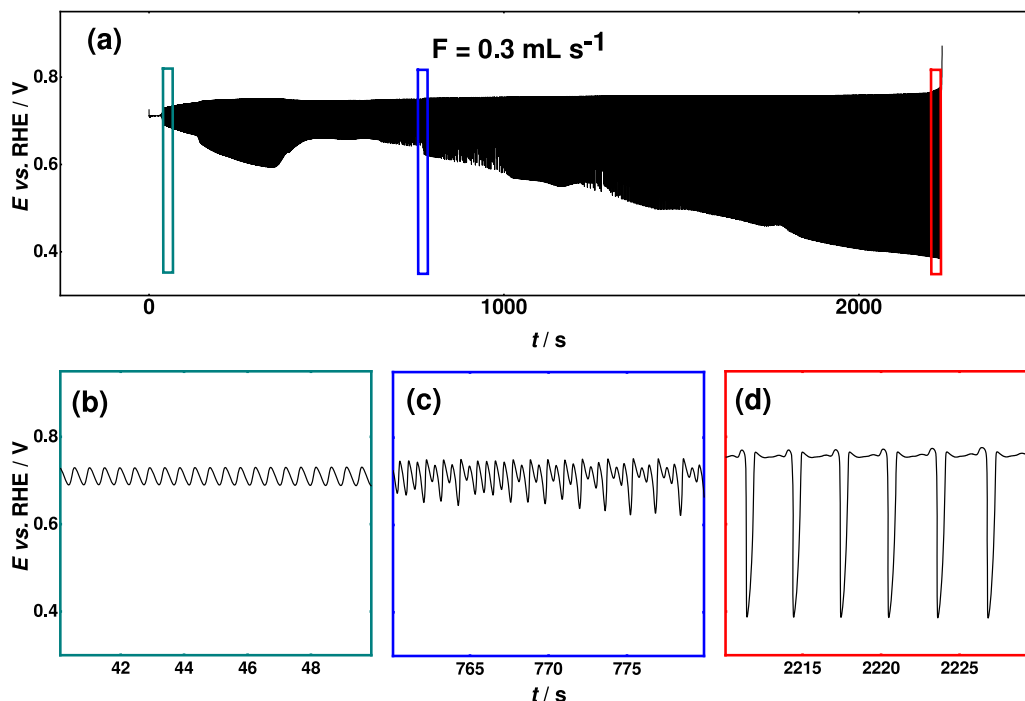
Fig. 3. Oscillatory dynamics of the cell potential during the electro-oxidation of methanol on Pt(100) electrode at $j_{app} = 0.700$ mA cm^{-2} and surface flow rate of 0.3 mL s^{-1}. (a) complete time series, and (b, c, d) details of the complete time series. Remaining experimental conditions as in Fig. 2.

period and amplitude approximately 7 and 9 times higher, respectively, compared to the initial stages of the oscillatory response.

When the experiment was conducted under similar conditions but with a higher gas flow rate (1.0 mL s^{-1}), the oscillatory region is indeed found to decrease significantly compared to the experiment with a lower flow rate. Fig. 4(a), depicted in the same scale as Fig. 3(a), illustrates this change, showing that the oscillatory response is lost at *ca.* 1370 s, where the potential reaches values higher than 0.90 V. In contrast, when the

gas flow rate is 0.3 mL s^{-1}, the oscillatory behavior is sustained until *ca.* 2230 s. Additionally, Fig. 4(b) shows that the induction period is significantly increased to *ca.* 820 s when using a higher gas flow rate, which may be due to the sensitivity of the system near the Hopf bifurcation as discussed above. In this case, although the amplitude of the oscillations at the beginning of the oscillatory response is slightly lower compared to the previous case, the waveform and the period remain similar. This indicates that the higher gas flow rate has an impact on the
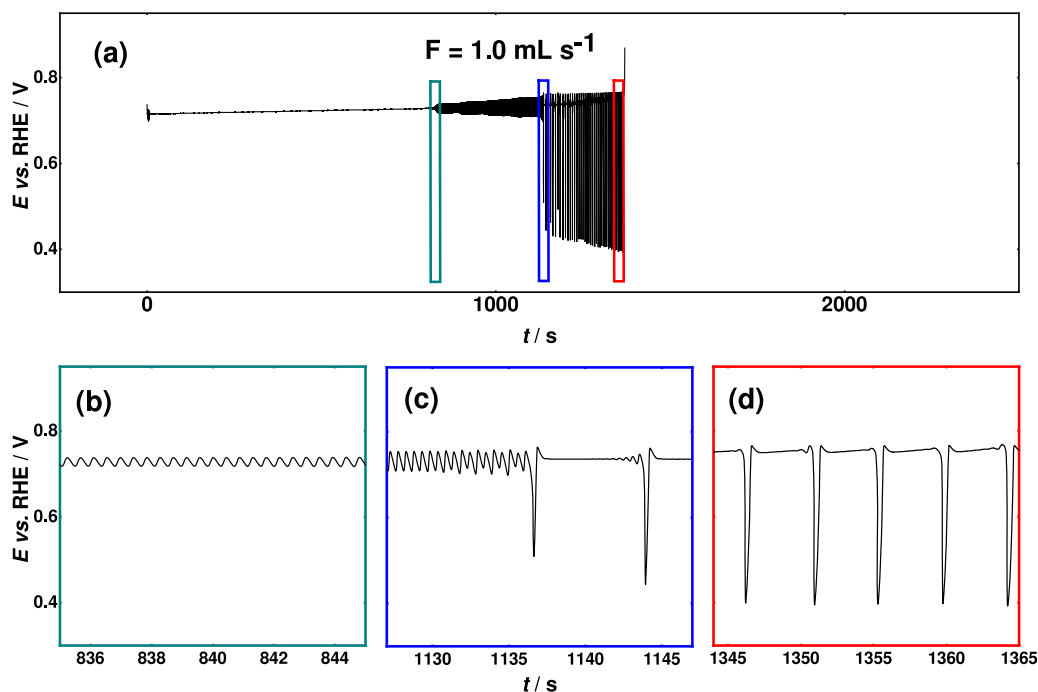

Fig. 4. Oscillatory dynamics of the cell potential during the electro-oxidation of methanol on Pt(100) electrode at $j_{app} = 0.700$ mA cm^{-2} and gas flow rate of 1.0 mL s^{-1}. (a) complete time series, and (b, c, d) details of the complete time series. Remaining experimental conditions as in Fig. 2.

stability of the hanging meniscus and, consequently, on the oscillatory response. However, once the oscillatory behavior is initiated the system exhibits similar oscillatory dynamics in terms of waveform and period since the origin of this type of oscillations is mainly caused by adsorbed species [3,24,29,31].

When a higher gas flow rate was employed, the increase in the amplitude of the potential oscillations during the experiment underwent an abrupt change, increasing from 21 mV to 375 mV as shown in Fig. 4 (c). This differs from the previous scenario, where the oscillations evolved gradually from simple to mixed-mode, with a progressive increase in amplitude. As mentioned above, large amplitude and mixed-mode oscillations have been associated with the presence of soluble species during the MEOR [13,23,32]. However, their role in the feedback loops that give rise to the oscillations is still unclear. Assuming that the role of soluble species is mainly attributed to direct interactions with the electrode, it would be anticipated that under enhanced mass transport conditions, the occurrence of such oscillations would be suppressed or that the transition to mixed-mode oscillations would be delayed as the accumulation of species near the electrode is slower due to continuous removal. However, contrary to these expectations, the abrupt change in amplitude observed in Fig. 4(c) suggest a different mechanism, possibly involving a periodic re-establishment of the methanol concentration in the double layer.

The periodic replenishment of methanol helps explain the occurrence of mixed-mode oscillations at higher currents in galvanodynamic experiments and a longer time in galvanostatic experiments. In the former case, higher applied currents accelerate methanol consumption, leading to a deficit of this molecule at the electrode surface. In the latter case, as time progresses, methanol consumption increases, and by-products accumulate in the solution, hindering the approach of methanol to the electrode surface and creating a methanol deficit. This reduced availability of methanol at the surface results in a decrease in total surface coverage of the electrode surface by blocking species and, consequently, a decrease in the potential required to sustain the current, as potential changes are closely related to the total coverage, as mentioned previously [3,24]. In response to the methanol deficit, the

double layer undergoes restructuring, promoting the adsorption of methanol molecules at high rates, which in turn increases the coverage of intermediates, leading to an increase in potential.

At a higher surface flow rate of 1.0 mL s^{-1}, the more efficient arrival of methanol at the surface reduces the frequency of restructuring cycles during mixed-mode oscillations compared to a lower surface flow rate of 0.3 mL s^{-1} (*cf.* Figs. 3(d) and 4(d)). As a consequence, the electrode remains for a longer time in the high-potential regions, where modulations are mainly attributed to changes in the coverage of adsorbed species [29]. Moreover, the enhanced mass transfer at higher flow rates accelerates the restructuring of the double layer resulting in a faster increase in potential from the low to the high potential regions compared to lower surface flow rates. It is noteworthy that previous studies have indicated that the minimum potential value reached during the oscillations coincides with the minimum coverage of OH species [29], which are significantly formed from potentials near 0.40 V at the Pt(100) surface [33]. These observations suggest that the minimum potential during the oscillations may decrease towards the potential at which significant formation of OH species occurs, as their presence on the surface enhances methanol adsorption [14] and consequently increases the coverage of intermediate species.

To better illustrate the influence of mass transfer phenomena on the oscillatory behavior, experiments were conducted at a higher current density of 1.3 mA cm^{-2}. These conditions promote the emergence of mainly large amplitude oscillations [23]. Using a gas flow rate of 0.3 mL s^{-1}, the oscillations with large amplitude are observed at short times during the experiment, as shown in Fig. 5(a). Interestingly, during the same experiment, when the gas flow rate is increased to 1.0 mL s^{-1} (shaded regions in Fig. 5(a)), the delicate balance between mass transport and species adsorption is disrupted, resulting in the loss of the oscillatory behavior. This can be observed in the expanded sections shown in Fig. 5(b), (c), and (d). However, when the flow rate is reduced back to the initial value of 0.3 mL s^{-1}, the system recovers the conditions necessary for the re-emergence of large amplitude oscillations. These findings provide strong evidence of the crucial role played by the mass transfer phenomena of soluble species (which are influenced by the
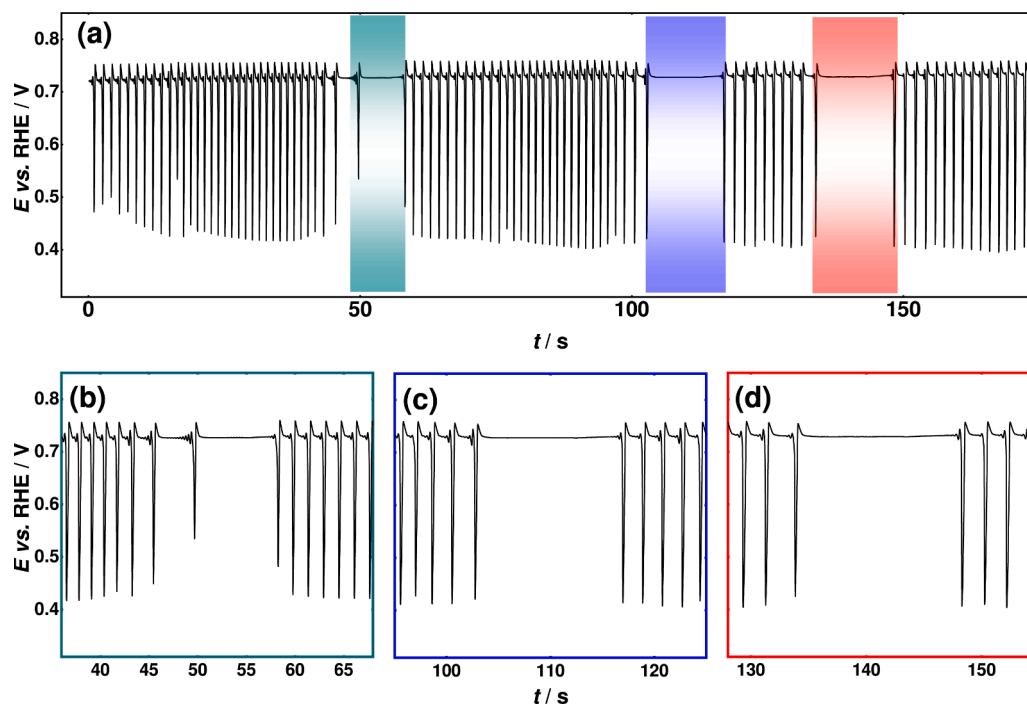

Fig. 5. (a) Oscillatory dynamics of the cell potential during the electro-oxidation of methanol on Pt(100) electrode at $j_{app} = 1.300$ mA cm^{-2} and gas flow rates of 0.3 mL s^{-1} and 1.0 mL s^{-1}. (b, c, d) expanded sections of the complete time series, corresponding to shaded areas in (a). These regions correspond to the time when the gas flow rate was increased to higher values. Remaining experimental conditions as in Fig. 2.

surface gas flow rate) in the occurrence of the observed oscillatory behavior. This observation clearly highlights the significance of controlling the surface gas flow rate in such systems.

In summary, this study has demonstrated the influence of surface gas flow rate on the electrochemical response during the MEOR. The observed trends highlight the sensitivity of the oscillatory dynamics as a valuable tool to obtain detailed and comprehensive information on the electrochemical system. Therefore, it is very important to account for the influence of uncontrolled experimental parameters, such as surface gas flow rate, in the study of these systems. It should be noted that the impact of the magnitude of the gas flow rate may vary depending on the geometry and size of the cell used in each experiment. However, this study emphasizes the importance of considering this parameter to ensure the accuracy, reproducibility, and comparability of the results. Furthermore, controlling the experimental conditions is crucial to avoid overlooking or over-considering processes, mainly, when correlating reaction mechanisms, including all the individual reaction steps, with the overall kinetic response, as in microkinetic modeling [6,29,34]. Thus, in the case of the oscillatory response, if certain characteristics, such as induction period, amplitude, waveform, and sustainability of the oscillations, are affected by parameters not taken into account, the analysis may lead to erroneous conclusions about the processes at the electrode surface. Therefore, regardless of the specific details of the system studied here, the conclusion of this study can be applied to other electrocatalytic reactions, especially when studying those with oscillatory behavior. For future research, a combination of numerical and experimental approaches could attempt to optimize the cell geometry and identify the most appropriate method of gas distribution to mitigate electrolyte perturbations in the hanging meniscus caused by the surface gas flow.

4. Conclusions

The influence of surface gas flow rate on the electrochemical response during measurements in the hanging meniscus configuration has been demonstrated, particularly on the oscillatory behavior during the MEOR. While no significant differences were observed in chronoamperometric and voltammetric experiments, distinct changes were observed in the oscillatory response under different gas flow rate conditions. The changes in the induction period, amplitude, and existence region of the oscillations indicate that higher gas flow rates can induce subtle movements of the solution in the hanging meniscus, enhancing the mass transport near the electrode surface. Furthermore, the occurrence of mixed-mode oscillations was attributed to the cyclic re-establishment of methanol near the electrode surface, with the minimum potential reached during the oscillations correlating with the potential of significant OH species formation. This emphasizes the importance of carefully controlling the gas flow rate to obtain representative and accurate results, ensuring the proper consideration of processes occurring at the electrode-electrolyte interface. It is crucial for future research to address this experimental parameter during electrochemical experiments in the hanging meniscus configuration to enhance the accuracy, reproducibility, and comparability of data, particularly in the study of oscillatory systems, and to advance our understanding of electrochemical systems as a whole.

CRediT authorship contribution statement

Enrique A. Paredes-Salazar: Investigation, Formal analysis, Writing – original draft. **Enrique Herrero:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **Hamilton Varela:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

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.

Data availability

Data will be made available on request.

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