The effect of poisoning species on the oscillatory dynamics of an electrochemical reaction

B C Batista, G C A Ferreira, H Varela
1 Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, CEP 13560-970, São Carlos, SP, Brazil, and 2 Ertl Center for Electrochemistry and Catalysis, GIST, Cheomdan-gwagiro 261, Buk-gu, Gwangju 500-712, South Korea.

E-mail: varela@iqsc.usp.br

Abstract. Electrochemistry is a prone field for observing complex behavior such as simple and mixed-mode oscillations, chaos and spatiotemporal pattern formation. Although modeling and numerical analysis of those systems is relatively common, analysis of the inner structure of the oscillatory region is a rather unexplored issue. We describe in this paper a numerical study of a surface catalyzed reaction that is being poisoned by a foreign adsorbing species. The effect of the poison coverage on the oscillatory period and amplitude is discussed with the help of parameter plane diagrams and mechanistic analysis. A coherent picture explaining the effect of the poison adsorption on the dynamic features is then constructed based on the obtained data.

1. Introduction
Electrochemistry has emerged as a powerful field for observing and controlling dynamic processes mainly due to the rather simple way in which the flux of one of the reactants, viz. the electric current, can be controlled [1]. Particularly in electrocatalysis, several systems present complex behavior expressed in the form of multi-stability, periodic and complex oscillations, chaos, and spatiotemporal pattern formation [2,3].

The oscillatory electro-oxidation of methanol on platinum surfaces can be cited as a model system, displaying simple harmonic potential oscillations and conventional Arrhenius-like temperature dependence [4-6], unlike other parent systems [3,7]. This system was recently modeled and numerically explored by Sauerbrei et al. [8] focusing on stability and bifurcation analysis. We present here the study of the dynamic behavior for a slightly modified version of this model, in which it incorporates anion adsorption among the possible chemical steps. The investigation was carried out by means of an in-depth investigation of the inner structure of the bifurcation diagrams, similarly to the two-dimensional analysis previously reported for other systems [9-11]. Although very demanding from computational point-of-view, such analysis provides a non-comparable detailed view of the dynamic structure of the model.
2. Model and preliminary analysis

The model utilized was based on that proposed by Sauerbrei et al. [8] described by equations 1 to 4, which represent, respectively, the time evolution of adsorbed oxides ($\theta_O$), adsorbed HCO ($\theta_{HCO}$), adsorbed carbon monoxide ($\theta_{CO}$) and the electrode potential ($\phi$). Other terms are introduced in Table 1.

\[
\begin{align*}
\theta_O(t) &= k_1Fe^{\theta(t)} - k_2\theta_O(t)\theta_{CO}(t) - k_3\theta_O(t)e^{-k_4\theta(t)} \\
\theta_{HCO}(t) &= k_1F^2e^{k_5\phi(t)} - k_2\theta_{HCO}(t) \\
\theta_{CO}(t) &= k_2\theta_{HCO}(t) - k_4\theta_O(t)\theta_{CO}(t) \\
\phi(t) &= I - k_1F^2e^{k_5\phi(t)}
\end{align*}
\]

We introduced a modification on the parameter $F$, which represents the amount of free surface sites, by adding an adsorption term for a blocking species ($\theta_P$),

\[
F = 1 - \theta_O(t) - \theta_{CO}(t) - 3\theta_{HCO}(t) - \theta_P(t) \\
\theta_P(t) = \frac{b_ae^{k_5\phi(t)}}{1 + a e^{k_5\phi(t)}}
\]

This modification accounts for the anion adsorption as a function of the potential and can be easily deduced from thermodynamic and electrochemical assumptions [12]. The dependence is given in terms of parameters $b$ and $a$, which stand for the maximum amount of poison coverage that can be achieved and the concentration of the anion in solution, respectively. Increasing either $b$ or $a$ leads to an increase in the amount of anion adsorbed for a given potential.

A general cycle of potential oscillations under galvanostatic control, i.e. constant applied current ($I$), may be described as follows: while the electrode potential is low the catalyst is said to be active. Gradually it becomes poisoned with adsorbed HCO and CO; as a consequence, the electrode potential rises in order to keep the overall current $I$ constant. The increase in the electrode potential however leads to an increase of the oxide production which in turn enhances the oxidation of adsorbed carbon monoxide, cleaning thus the electrode surface. Accompanying the recovering of the high activity, the electrode potential starts decreasing again to keep the current, the amount of oxides decrease, and the whole cycle starts anew.

All these steps are related to the specific reactions taking place and that were incorporated in equations 1-5 by the kinetic law of mass action. Parameters used are listed in Table 1.

| Rate | Meaning | Value |
|------|---------|-------|
| $k_1$ | Methanol adsorption | 4 |
| $k_2$ | CO production | 10 |
| $k_3$ | Oxide production | 1 |
| $k_4$ | CO and oxides reaction | 2 |
| $k_5$ | Oxide reduction | 6 |
| $k_6$ | Faradaic term | 15 |
| $I$ | Applied current | variable |

Figure 1 brings at its left side a collection of potential time series obtained for poison concentrations ranging from 0 to 0.5 and maximum coverage set at 0.2. The curves were normalized so as to display the same amplitude. On the right side the behavior of carbon monoxide coverage is presented for those extreme concentration conditions. It is seen that the eye striking feature of the anion presence is to decrease the oscillation period. It is interesting to note however that only the rising part of the curves seems to be affected, leading to the observed loss of harmonicity. For galvanostatic experiments, the rising part of the curve is mechanistically associated with the blockage.
of active catalyst sites, particularly by carbon monoxide (CO). The right-side picture shows that this may also be the case for the system under investigation. It can be seen that the amount of carbon monoxide produced at the surface is greatly reduced when the anion effect is incorporated. This particular issue will be discussed in connection with experiments in a forthcoming paper [13]. In the next we explore different facets of the bifurcation diagrams.

![Figure 1](image)

**Figure 1.** Left: potential time series obtained with equations 1-5 and parameters as given in Table 1 with \( b = 0.2 \) and (a) \( a = 0, I = 0.14 \); (b) \( a = 0.01, I = 0.11 \); (c) \( a = 0.05, I = 0.09 \); (d) \( a = 0.1, I = 0.07 \); (e) \( a = 0.5, I = 0.05 \). Right: CO coverage time series obtained for (a) \( a = 0, I = 0.14 \); and (e) \( a = 0.5, I = 0.05 \).

3. **Parameter plane diagrams**

The study of individual temporal series led to the recognition of an effect of the poisoning species on the oscillation period. Since oscillations are found to happen for differing values of parameters when different amounts of poison are present, which could cause misleading conclusions, we endeavored on a large scale analysis by constructing parameter plane diagrams and thus gaining a more representative picture of this system. Figure 2 display two-dimensional regular diagrams discriminating oscillatory (light coded) and non-oscillatory (dark-blue coded) domains for five distinct concentrations of blocking species. Diagrams were constructed by collecting a potential time series for a given set of \( I \) and \( b \), and color was attributed in such a way that light ones accounted for the presence of oscillations. Only simple periodic oscillations were found for the whole spectra of parameters studied.

Two main aspects accompanying the increase of the poison concentration are clearly discernible in Figure 2. First, the values of current for which oscillations are found decrease with increasing poison influence, which is to say higher values of parameters \( a \) and \( b \). Second, the region of parameters where the phenomenon is observed also shrinks for the same kind of perturbation. As the poison adsorbs on the surface inhibiting all surface catalyzed reactions their velocity should be reduced. As a consequence higher values of applied current cannot be sustained by the poisoned system explaining thus the shift of the oscillatory region towards the lower values of applied current \( I \) needed to support oscillations.
Deeper understanding of the underlying processes can be achieved if information of the inner structure of the parameter diagrams is available. Figure 3 brings such a study: each diagram contains 400x400 points accounting for the oscillation period obtained from numerically calculated stationary time series of the electrode potential. Each point was colored according to the oscillation period, non-oscillatory solutions were denoted in white. It is important to note that the white regions correspond to presence of stable steady states.

The general features discussed for Figure 2 are also found in Figure 3. More important is the period behavior that now arises. For any individual graph it can be seen that the increase of the maximum amount of poison that can be adsorbed leads to an increase of the oscillation period. Comparison between pictures for rising values of anion concentration reveals that large areas of the diagrams are covered with blue and pink which also indicate that period is large.

**Figure 2.** Bifurcation diagrams in the $b$ versus $I$ plane for five distinct values of anion concentration, $a$. 

---

**Figure 3.** Each diagram contains 400x400 points accounting for the oscillation period obtained from numerically calculated stationary time series of the electrode potential. Each point is colored according to the oscillation period, non-oscillatory solutions are denoted in white. It is important to note that the white regions correspond to presence of stable steady states.

The general features discussed for Figure 2 are also found in Figure 3. More important is the period behavior that now arises. For any individual graph it can be seen that the increase of the maximum amount of poison that can be adsorbed leads to an increase of the oscillation period. Comparison between pictures for rising values of anion concentration reveals that large areas of the diagrams are covered with blue and pink which also indicate that period is large.
Figure 3. 400x400 parameter plane diagrams obtained varying parameters $b$ and $I$ for six distinct values of anion concentration as specified in the graph. The colorscale represents the temporal period associated with the oscillations found for each set of parameters.

A comprehensive summary of the data contained in the structured bifurcation diagrams is given in Figure 4. It displays the mean value of the period for five anion concentrations as function of the maximum amount of blocking species and its computation was done by summing up all values of period for a given value of $b$ and dividing the result by the total of constituents in the sum.
4. Numerical analysis

Altogether, the obtained data reveals a coherent scenario for the anion effect: there is a general decrease in the period of oscillations when the poisoning species influence is increased. In order to take advantage of that large amount of information we shall now take a grander view at the system under consideration looking for an explanation of the period effect. In a complex oscillatory network, reactions can be classified according to their contribution to the oscillation period, some has a positive contribution, and some a negative contribution to the oscillation period [14]. In a recent article Kiss et al. [15] derived an analytical expression for the oscillatory frequency of a generic electrochemical model. As the system under consideration is quite more complicated and specific we now shall take a numerical approach to this analysis by studying how the individual reaction rates influence the oscillation period. Figure 5 displays such an examination. An individual constant was varied while the others were kept at their original values (see Table 1).

Figure 4. Mean temporal period of oscillations as function of the maximum anion coverage. The graph was constructed with data displayed in Figure 3.

Figure 5. Dependence of the logarithm of the individual rate constants on the oscillation period. $k_1$ is rate of methanol adsorption; $k_2$ is the carbon monoxide production; $k_3$ is the oxide production; $k_4$ is the reaction between CO and oxides; and $k_5$ is the rate of oxide reduction.
Figure 5 shows that the formation of adsorbed carbon monoxide, the surface oxidation and the reaction between those species led to a decrease in the period of oscillations while methanol adsorption and oxide reduction caused a period increase. Particularly the rate of carbon monoxide oxidation displayed the highest effect on the oscillation period. Table 2 shows a summary of the information contained in Figure 5.

| Constant  | Significance         | Rate of change of period |
|-----------|----------------------|--------------------------|
| ↑\(\kappa_1\) | Methanol adsorption | + 2.4                    |
| ↑\(\kappa_2\) | CO production       | - 1.3                    |
| ↑\(\kappa_3\) | Oxide production    | - 2                      |
| ↑\(\kappa_4\) | CO and oxides reaction | - 40                   |
| ↑\(\kappa_5\) | Oxide reduction     | + 0.7                    |

It is noteworthy that the overall trend in Figure 5 and Table 2 is the decrease of the period as the rates of reaction are increased given that the period reducing steps possess a higher weight. One way of altering the individual rates all at once is, for example, to increase the temperature of the system. Electrochemical experiments aiming at understanding this effect have revealed that the oscillations do indeed follow an Arrhenius type behavior for which an increase in temperature leads to an increase in the oscillation frequency [5]. The results presented in Table 2 thus provide a mechanistic basis to understand these experimental results.

We are now at a position of explaining the anion effect in the oscillatory electro-oxidation of methanol on platinum surfaces. The general effect of the anion is to block active sites thus reducing the velocity of reactions associated with free catalyst sites. This should greatly reduce the amount of carbon monoxide produced since its production involves the highest number of metal sites. It was shown in Figure 2 that the carbon monoxide poisoning is indeed reduced when the anion influence is incorporated in the set of equations. Since the velocity of CO oxidation is directly dependent on its coverage it will also be reduced by adsorbed anions. Figure 6 brings the velocity of the reaction discussed and shows that there is indeed a decrease in its overall and mean values when the anion is added.

**Figure 6.** Left: temporal evolution of the velocity of CO oxidation for conditions given in Table 1 with \(b = 0.2\) and (a) \(a = 0, I = 0.14\); (e) \(a = 0.5, I = 0.05\).
As given in Table 2, the CO oxidation reaction possesses the highest weight on the period of oscillations. It has been demonstrated that the poison greatly influences the reaction of CO oxidation, reducing its velocity. Therefore, reducing the CO reaction is equivalent to moving towards the left side of Figure 5 which leads to a decrease in the period of oscillations.

5. Conclusion
We investigated in this paper the impact of poisoning anions on the oscillatory electro-oxidation of methanol on platinum. The study was performed in terms of a model consisting of four ordinary differential equations. It has been demonstrated that the inclusion of a competing adsorbing species leads to a decrease in the period of oscillations and reduced rates of individual reactions. The anion effect was reasoned by its influence on the carbon monoxide oxidation reaction which was found to have the most profound weight on the oscillation frequency.

Acknowledgments
The authors acknowledge Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, HV # 09/07629-6) and Conselho Nacional de Desenvolvimento Científico (CNPq, BCB # 141723/2009-2, HV # 302698/2007-8) for financial support.

References

[1] Krischer K 2002 Modern Aspects of Electrochemistry vol 32, ed B E Conway and J O’M Bockris (New York: Kluwer Academic Press) p 1
[2] Krischer K and Varela H 2003 Handbook of Fuel Cells: Fundamentals Technology and Applications vol 2, ed W Vielstich et al. (Chichester: Wiley) p 679
[3] Sitta E, Nascimento M and Varela H 2010 Phys. Chem. Chem. Phys. DOI: 10.1039/c002574g
[4] Krausa M and Vielstich W 1995 J. Electroanal. Chem. 399 7
[5] Carbonio E A, Nagao R, Gonzalez E R and Varela H 2009 Phys. Chem. Chem. Phys. 11 665
[6] Boscheto E, Batista B C, Lima R B and Varela H 2010 J Electroanal. Chem. 642 17
[7] Nagao R, Epstein I R, Gonzalez E R and Varela H 2008 J. Phys. Chem. A 112 4617
[8] Sauerbrei S, Nascimento M, Eiswirth M and Varela H 2010 J. Chem. Phys. 132 154901-1
[9] Bonatto C and Gallas J A C 2008 Phil. Trans. R. Soc. A 366 505
[10] Freire J G, Field R J and Gallas J A 2009 J. Chem. Phys. 131 044105
[11] Nascimento M A, Gallas J A C and Varela H 2011 Phys. Chem. Chem. Phys. 13 441
[12] Gileadi E 1993 Electrode kinetics for chemists, chemical engineers and material scientists (Moskow: VCH Publishing)
[13] Ferreira G C A, Batista B C and Varela, H 2010 in preparation
[14] Ruoff P 1992 J. Interdiscipl. Cycle Res. 23 92.
[15] Kiss I Z, Pelster L N, Wickramasinghe M and Yablonsky G S 2009 Phys. Chem. Chem. Phys. 11 5720