**Microkinetic Modeling of the Methanol Electro-oxidation Reaction on Platinum**

Enrique A. Paredes-Salazar,1 Alfredo Calderón-Cárdenas,1,2,* Hamilton Varela1,*

1 São Carlos Institute of Chemistry, University of São Paulo, P. O. Box 780, CEP 13560-970 São Carlos, SP, Brazil
2 GIFBA, Universidad de Nariño, 520002 San Juan de Pasto, Nariño, Colombia

*corresponding authors: hamiltonvarela@usp.br (HV), alfredocalderon@udenar.edu.co (ACC)

**ABSTRACT**

The development of electrocatalysts with high activity at low overpotentials for methanol electro-oxidation reaction is one of the challenges to overcome towards the wider applicability of this alcohol in energy conversion systems. Many works in the last decades have contributed with mechanistic studies on this reaction. Nevertheless, the reaction scheme is entangled which makes difficult to correlate it with the kinetic response in electrochemical experiments. In this paper we propose a microkinetic model for the methanol electro-oxidation reaction on polycrystalline platinum. The model was built on relevant mechanistic aspects available in the literature and formulated based on the mean-field approach. The kinetic parameters were determined by optimization and the validation was performed through the comparison with distinct sets of experimental data, namely cyclic voltammetry, chronoamperometry, and also oscillatory time-series recorded under galvanostatic conditions. The resulting model was able to simulate successfully the nonlinear dynamics observed in galvanostatic experiments, including chaotic behavior, as well as a reasonable voltammetric profile with the same set of electrokinetic parameters. The sensitivity analysis of the kinetic parameters showed that the electro-oxidation pathway through the formic acid intermediate is not significant under these experimental conditions and that the OH$_{ad}$ and CO$_{ad}$ species are mainly involved in the origin of the oscillations, while species that affect the rate of formation/consumption of the latter causes the mixed-mode oscillations. The electrokinetic parameters were discussed with the data available for the electrooxidation reaction of formic acid, where the connection between the values highlights the applicability of this approach to other electrocatalytic reactions.

**Keywords:** methanol electro-oxidation, microkinetic modeling, oscillations, numerical simulations, platinum.

**Highlights:**
- A microkinetic model for the methanol electro-oxidation reaction on platinum was developed.
- Simulated results fairly agree with the experimental ones.
- Transitions from simple to chaotic oscillations were observed under galvanostatic conditions.
- The oxidation pathway through the formic acid intermediate is not significant under oscillatory regime.
- The first model of electro-oxidation of low-molecular-mass organic molecules that simulates chaotic behavior
1. Introduction

The methanol electro-oxidation reaction (MEOR) has been extensively studied for applications as fuel in energy conversion systems because methanol has high energy capacities per unit volume and per unit weight.\(^1\)\(^-\)\(^4\) Platinum based materials are the most conventional catalysts for electrodes in low temperature fuel cells, since platinum has a high stability and electrocatalytic activity towards the dissociative adsorption of low-molecular-mass organic molecules.\(^5\) However, one of the disadvantages of platinum as catalyst is that its surface is poisoned by strongly adsorbed intermediate species, mainly carbon monoxide\(^6\) which requires high overpotential to its oxidative desorption.\(^5\) The MEOR on platinum proceeds through many sequential and parallel pathways, involving a number of adsorbed intermediates, and also some soluble by-products which decrease the conversion efficiency. Thus, the challenges are to enhance the kinetics of the electrocatalytic reaction at low overpotentials by suppressing the poisoning processes and to modify the reaction pathway in order to privilege the CO\(_2\) production.\(^7\) Strategies to accomplish these challenges must be based on the available information about the reaction scheme and the rates of single reaction steps, including how they are affected by changes in the experimental conditions. In recent decades, some studies have provided key information on the reaction pathways and intermediates of the MEOR, which allowed proposing some reaction mechanisms with formaldehyde, formic acid, and CO\(_2\) as the main oxidation products.\(^2,3,7\)\(^-\)\(^12\) However, despite a large number of studies since 1960, the mechanism of MEOR is still a matter of debate.\(^7,8,13,14\)

Conventional kinetic studies based on mathematical modeling, that allows the description of overall reaction rates, are essential to obtain information or to support a given mechanistic proposal.\(^15\) Nevertheless, for intricate reaction mechanisms such as the one of the MEOR, these models provide limited fundamental insights on the reaction mechanism and their predictions are valid for a limited range of reaction conditions, since they are typically based on approximations such as the steady-state and the most abundant intermediate, excluding the contribution of important reaction steps under different experimental conditions. Therefore, approaches based on microkinetic modeling are more suitable to obtain mechanistic information since the reaction kinetics is understood from the contribution of the different steps of the reaction mechanism and their interactions.\(^15\)\(^-\)\(^18\)

A microkinetic description is initially built by collecting the available information about the system, which enables building up a reaction mechanism and then the formulation of a
set of ordinary differential equations (ODEs) that involves electrokinetic parameters directly related to the rate coefficients of each reaction step.\textsuperscript{19–21} These kinetic parameters could be obtained from \textit{ab initio} studies, but the currently existing theoretical methodologies require further development in order to improve the accuracy when applied for electrochemical systems. An alternative to determine the electrokinetic parameters is by fitting processes, comparing the simulated and experimental responses in electrochemical experiments.\textsuperscript{19,21} However, the type and number of experiments with which the results of microkinetic modeling are compared plays an important role in the reliability of these values. Among the most traditional experiments used in electrocatalysis, we found the chronoamperometric and voltammetric experiments for evaluating the dynamic behavior of a system after a perturbation from a specific initial state. Still, different microkinetic models associated with distinct reaction schemes can generate similar electrochemical responses,\textsuperscript{17} so that, those conventional experiments seem not enough to select and validate a given model. Therefore, electrochemical experiments whose responses show more specific features of each reaction system are needed.

Kinetic instabilities manifested, for instance, in the oscillations of the electrode potential under galvanostatic conditions are ubiquitous in electrocatalysis\textsuperscript{22,23} and often caused by the overlap between different potential-dependent adsorption isotherms of reaction intermediates can be very useful in this respect. Indeed, this type of electrochemical experiments provides unique insights in the research of mechanistic aspects rather than the conventional ones\textsuperscript{24,25} because the oscillatory patterns are strongly determined by the rate of each reaction step and, therefore they are also sensitive to the electrokinetic parameters associated.\textsuperscript{23,26} In this sense, an important premise of our analysis is that if the microkinetic model can simulate the main characteristics of the system under different experimental conditions, including those where self-organized potential oscillations emerge, with the same set of kinetic parameters, the model is likely to represent the actual reaction mechanism.\textsuperscript{19,27}

Herein we present a microkinetic study of the MEOR on polycrystalline platinum in acidic media, the resulting model was able to simulate the experimental voltammetric profile, as well as the nonlinear dynamics observed in galvanostatic experiments under different conditions, including, for the first time, to the best of our knowledge, the chaotic dynamics found in experiments, with the same set of electrokinetic parameters. Therefore, the microkinetic model results suggest that the reaction mechanism proposed here is a rather
plausible possibility of the actual reaction mechanism. Furthermore, a sensitivity analysis showed that the oxidation pathway by the formic acid intermediate does not contribute significantly to the electrochemical response and can be neglected under oscillatory regime.

2. Methods

2.1 Electrochemical experiments

All electrochemical measurements were carried out in a conventional three-electrode cell, with a Pt sheet as a counter electrode, and a reversible hydrogen electrode (RHE) as reference electrode, prepared in the same supporting electrolyte, versus which all potentials are quoted. A polycrystalline Pt disk with a geometric area of 0.32 cm² was used as working electrode. For the measurements, an Autolab potentiostat/galvanostat PGSTAT 128N was used, and the temperature of the system was controlled with a Cole-Parmer thermostat and kept at 25.0 °C during all experiments. Aqueous solutions used were 0.5 mol L⁻¹ HClO₄ and 0.5 mol L⁻¹ methanol which were prepared using perchloric acid (70%, Sigma-Aldrich), methanol (99.97%, J.T Baker), and Milli-Q-water (18.2 MΩ cm). Before each experiment, the solution was purged with nitrogen (99.996%, White Martins) for at least 15 minutes and kept under this same atmosphere during all experiments to avoid the presence of dissolved oxygen.

Initially, at least 1000 voltammetric cycles were performed in the supporting electrolyte from 0.04 V to 1.60 V vs. RHE at a scan rate of 0.50 V s⁻¹ to standardize the platinum surface. Then, cyclic voltammetry (CV) at 0.10 V s⁻¹ was carried out in the same potential window, and the resulting profile was checked to ensure the cleanliness of the system. Then methanol was added to the supporting electrolyte and the solution was left for 10 minutes to reach thermal equilibrium at 25.0 °C. After that, a cyclic voltammogram was acquired between 0.04 and 1.10 V vs. RHE at a scan rate of 0.01 V s⁻¹. For the chronoamperometry (CA), a potential of 0.85 V vs. RHE for 180 s followed by a potential step to 0.60 V vs. RHE for 300 s were applied. For the galvanostatic experiments, a current value to ensure that the electrode potential does not exceed 0.05 V vs. RHE was applied, then the current step was applied to the value of interest in each experiment. For all measurements, the electrolyte was renewed before each experiment.
2.2 Determination of electrokinetic parameters

In general, the construction and validation of microkinetic models consists of at least four stages: (i) gathering experimental and theoretical information and mechanism statement, (ii) model establishment, (iii) numerical simulations, and (iv) comparison with experiments. Therefore, following these steps, a reaction mechanism was proposed based on the information available in the literature. This allows a rate law to be formulated for each reaction step, which depends on the electrokinetic parameters, $\kappa_m$, and a function of the reactants concentration, surface coverage, the fraction of free catalytic sites, and the reaction order. The core of the resulting model was defined by 13 ordinary differential equations (ODEs) corresponding to the mass balance equations of the 12 reaction intermediates and the charge balance equation at the electrode surface (these stages are further detailed in section 3). Since the simulated response depends on the $\kappa_m$ values, the equations were initially solved with a set of test values that were then determined as an optimization problem, i.e., by determining the parameter values that minimize the sum of mean square error function, $\xi$:

$$\xi = \frac{1}{n} \sum_{i}^{n} (y_{exp,i} - y_{sim,i})^2$$  \hspace{1cm} Eq.1

where $y_{exp,i}$ is the i-th point of a set of n experimental data and $y_{sim,i}$ is the value of the response variable, i.e., the simulated value under identical experimental conditions. The $\kappa_m$ values were found using a semi-automated method, in which a new set of parameters is obtained through a combination of manual changes and algorithms for the non-linear global minimization of the $\xi$ function. The stages were repeated several times in a cycle of formulation, reorganization, and restructuring of the mechanism, considering alternative pathways according to previously published data, until the same set of parameters allowed to simulate different experiments.

All simulations and optimization processes described here were carried out using the software Wolfram Research, Inc., Mathematica, Version 12.3.1, Champaign, IL (2021). The initial conditions for the potential and the coverages of all the intermediates were zero for galvanostatic experiments and in voltammetric experiments, except for CO coverage, $\theta_{CO}$, in CV, which was 0.65 since this species starts to adsorb at the surface at rather low potentials.
In the case of CA, the initial coverage for the OH\ad species, $\theta_{OH}$, was 1.0, since a potential of 0.85 V vs. RHE was applied before the potential step of the experiment.

### 2.3 Sensitivities analysis

To determine how much the simulated oscillatory profile changes with variations in $\kappa_m$, initially, the value of the $\xi$ function was calculated by comparison between the experimental and simulated sets. Then, parameters $\kappa_m$ were slightly modified one at a time and the change generated in the $\xi$ function, $\Delta \xi_m$, caused by the variations $\Delta \kappa_m$ was calculated. In all cases, before determining the value for $\xi$, the simulated oscillatory profile must be shifted in time in order to superimpose one oscillatory period with another experimental. For this purpose, a previous maximization of cross-correlation between these data was used. Thus, the minimum value of $\Delta \kappa_m$ that causes a difference of 10% in the $\xi$ function was defined as the uncertainty of the kinetic parameter and its sensitivity was defined as:

$$ s_{\kappa_m} \equiv \frac{0.1 \kappa_m}{\Delta \kappa_m} \quad \text{Eq.2} $$

It should be noted that the 10% percentage difference was arbitrarily chosen and can be specified with a different value depending on the tolerance level specified by the experimenter. For more details see reference 29.

### 3. Micro-kinetic modeling

#### 3.1. Mechanism

The MEOR is one of the most studied reactions in electrocatalysis, so that an extensive bibliography about the kinetic behavior of the MEOR on platinum and other materials can be found nowadays. In fact, many reaction scheme hypotheses have been proposed and updated when new experimental evidence appears. One of us has suggested a fairly complete mechanism taking into account the adsorbed and soluble intermediates. Nevertheless, some reaction steps that have been experimentally demonstrated were not incorporated. This proposal can be complemented by the experimental and theoretical information reported by Abd-El-Latif and Calderón-Cárdenas et al. In the former, evidence of chemical equilibrium between formic acid and methyl formate is reported. Further reaction steps after the formation of formic acid can be proposed in the same way as the formic acid
electro-oxidation reaction (FAEOR), reported in the latter. This complement is important because it was demonstrated that, along the MEOR, formic acid can be adsorbed back to the electrode surface to continue the oxidation process. The updated and comprehensive mechanism proposed here is presented in Figure 1, it incorporates all details mentioned.

![Figure 1: Proposed reaction scheme for the methanol electro-oxidation reaction on polycrystalline platinum in aqueous acidic medium.](image)

The proposed scheme denotes a complex architecture with several sequential and parallel reaction pathways. The indirect pathway for CO₂ production via adsorbed carbon monoxide (COₐd) involves the dehydrogenation steps 1a, 2a, 3a, and 4c with species strongly adsorbed at neighboring Pt sites, followed by COₐd oxidation through oxygenated species (OHₐd) on the Pt surface to produce CO₂ (step 6c). An alternative pathway can be given after the first dehydrogenation step to produce formaldehyde (HCHO) which can diffuse away from the electrode surface or adsorb again producing HCOₐd (steps 2b and 3b, respectively) to continue the reaction. The HCOₐd species can react with water and methanol molecules to produce formic acid (HCOOH) or methylformate (CH₃OCHO), respectively (steps 4a, 5a, and 4d, 5d, respectively). The two species can be converted to each other through step 6d. Finally, the oxidation of formic acid soluble-intermediate occurs by dehydrogenation and dehydration steps (steps 6a, 7a, 8a, and 8e), with adsorbed formate species as common intermediate. The single reaction steps from \( r_{1a} \) to \( r_{8e} \) are listed below, where species in solution are shown in blue and the adsorbed atom on each adsorbate is shown in red.
CH$_3$OH adsorption:

\[ \text{CH}_3\text{OH} + * \rightarrow \text{CH}_2\text{OH}_{\text{ad}} + \text{H}^+ + e^- \]

HCO$_{\text{ad}}$ formation – Dehydrogenation pathway:

\[ \text{CH}_2\text{OH}_{\text{ad}} + * \rightarrow \text{CHOH}_{\text{ad}} + \text{H}^+ + e^- \]
\[ \text{CHOH}_{\text{ad}} + * \rightarrow \text{CHO}_{\text{ad}} + \text{H}^+ + e^- + 2 * \]

HCO$_{\text{ad}}$ formation – Formaldehyde pathway:

\[ \text{CH}_2\text{OH}_{\text{ad}} \rightarrow \text{HCHO} + \text{H}^+ + e^- + * \]

CO$_2$ formation - Carbon monoxide pathway:

\[ \text{CHO}_{\text{ad}} + * \rightarrow \text{CO}_{\text{ad}} + \text{H}^+ + e^- + * \]
\[ \text{H}_2\text{O} + * \rightleftharpoons \text{OH}_{\text{ad}} + \text{H}^+ + e^- \]
\[ \text{CO}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- + 2 * \]

HCOOH formation - Dehydrogenation pathway:

\[ \text{CHO}_{\text{ad}} + \text{H}_2\text{O} \rightarrow \text{CH(OH)}\text{OH}_{\text{ad}} \]
\[ \text{CH(OH)}\text{OH}_{\text{ad}} \rightarrow \text{HCOOH} + \text{H}^+ + e^- + * \]

HCOOH formation – Methylformate pathway:

\[ \text{CHO}_{\text{ad}} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCHOH} \]
\[ \text{CH}_3\text{OCHOH} \rightarrow \text{CH}_3\text{OCHO} + \text{H}^+ + e^- + * \]
\[ \text{CH}_3\text{OCHO} + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{CH}_3\text{OH} \]

CO$_2$ formation – Formic acid oxidation pathway:

\[ \text{HCOOH} + 2 * \rightleftharpoons \text{HCOO}_b + \text{H}^+ + e^- \]
\[ \text{HCOO}_b + 2 * \rightarrow \text{HCOO}_m + 3 * \]
\[ \text{HCOO}_m + * \rightarrow \text{CO}_2 + \text{H}^+ + e^- + 2 * \]
\[ \text{HCOO}_m + \text{H}^+ + e^- + 2 * \rightarrow \text{CO}_{\text{ad}} + \text{H}_2\text{O} + 2 * \]

For each reaction step described we can write a kinetic equation where the rate coefficients of the electrochemical steps depend on the potential difference at the electrode-electrolyte interface, $\phi(t)$, according to Butler-Volmer formulation. For the sake of simplicity, the surface concentrations of methanol, water, or hydronium ions are considered constant and are grouped, where applicable, into a pre-exponential factor $\kappa_m$ along with the standard kinetic coefficient and the standard potential (for details see section 1 in supporting information). Thus, the kinetic equations for each $m$-th step are:
\[ v_{1a} = \kappa_{1a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{vac}}(t) \]  
\text{Eq. 3}

\[ v_{2a} = \kappa_{2a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CH}_2\text{OH}}(t) \theta_{\text{vac}}(t) \]  
\text{Eq. 4}

\[ v_{3a} = \kappa_{3a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CHO}}(t) \theta_{\text{vac}}(t) \]  
\text{Eq. 5}

\[ v_{2b} = \kappa_{2b} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CH}_2\text{OH}}(t) \]  
\text{Eq. 6}

\[ v_{3b} = \kappa_{3b} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) n_{\text{HCHO}}(t) \theta_{\text{vac}}(t) \]  
\text{Eq. 7}

\[ v_{4c} = \kappa_{4c} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CHO}}(t) \theta_{\text{vac}}(t)^{0.2} \]  
\text{Eq. 8}

\[ v_{5c} = \kappa_{5c} \exp \left( \frac{0.37 F}{RT} \phi(t) \right) \theta_{\text{vac}}(t) \]  
\text{Eq. 9}

\[ v_{-5c} = \kappa_{-5c} \exp \left[ -\left( 1 - 0.60 \right) \frac{F}{RT} \phi(t) \right] \theta_{\text{OH}}(t) \]  
\text{Eq. 10}

\[ v_{6c} = \kappa_{6c} \exp \left( \frac{0.506 F}{RT} \phi(t) \right) \theta_{\text{CO}}(t) \theta_{\text{OH}}(t) \]  
\text{Eq. 11}

\[ v_{4a} = \kappa_{4a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CHO}}(t) \]  
\text{Eq. 12}

\[ v_{5a} = \kappa_{5a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CH(OH)OH}}(t) \]  
\text{Eq. 13}

\[ v_{4d} = \kappa_{4d} \theta_{\text{CHO}}(t) \]  
\text{Eq. 14}

\[ v_{5d} = \kappa_{5d} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) \theta_{\text{CH}_3\text{OCHO}}(t) \]  
\text{Eq. 15}

\[ v_{6d} = \kappa_{6d} \frac{n_{\text{CH}_3\text{OCHO}}(t)}{N_{\text{tot}}} \]  
\text{Eq. 16}

\[ v_{-6d} = \kappa_{-6d} \frac{n_{\text{HCOOH}}(t)}{N_{\text{tot}}} \]  
\text{Eq. 17}

\[ v_{6a} = \kappa_{6a} \exp \left( \frac{0.50 F}{RT} \phi(t) \right) n_{\text{HCOOH}}(t) \theta_{\text{vac}}(t)^2 \]  
\text{Eq. 18}

\[ v_{-6a} = \kappa_{-6a} \exp \left[ -(1 - 0.50) \frac{F}{RT} \phi(t) \right] \theta_{\text{HCOO}}(t) \]  
\text{Eq. 19}

\[ v_{7a} = \kappa_{7a} \theta_{\text{HCOO}}(t) \theta_{\text{vac}}(t)^2 \]  
\text{Eq. 20}
\[
v_{8a} = \kappa_{8a} \exp \left[ \frac{0.50F}{RT} \phi(t) \right] \theta_{HCOO_m}(t) \theta_{vac}(t) \quad \text{Eq. 21}
\]
\[
v_{8e} = \kappa_{8e} \exp \left[ -\frac{(1 - 0.50)F}{RT} \phi(t) \right] \theta_{HCOO_m}(t) \theta_{vac}(t)^2 \quad \text{Eq. 22}
\]

\( F, R, \) and \( T \) are the Faraday constant, the universal constant of gases, and the temperature, respectively. The values for charge transfer coefficients were established at 0.5, except for the steps \( r_{5c}, r_{-5c}, \) and \( r_{6c} \) which are involved in the formation and consumption of \( \text{OH}_{\text{ad}} \) species and strongly change the simulated oscillatory response. Therefore, these charge transfer coefficients were optimized to values between 0.3 and 0.7 as expected for elementary reactions. \( \theta_x(t) \) is the fraction of the catalytic surface covered by the species \( x \), and \( \theta_{vac}(t) \) is the fraction of free catalytic sites:

\[
\theta_{vac}(t) = 1 - 2 \theta_{CH_{2}OH}(t) - 2 \theta_{CHOH}(t) - \theta_{CHO}(t) - \theta_{OH}(t) - 1.516 \theta_{CO}(t) - \theta_{CH(OH)OH}(t) - \theta_{CH\text{OCHOH}}(t) - 2 \theta_{HCOO_b}(t) - \theta_{HCOO_m}(t)
\]

Here \( \theta_{CO}(t) \) is multiplied by 1.516 because CO can be adsorbed in two forms, CO-bidentate (CO-B) and CO-lineal (CO-L), which require one and two Pt surface atoms, respectively.\(^{30}\) It was shown that for a CO coverage equal to 1, close to equilibrium there is the relationship \( \theta_{CO-B} \approx 0.258 \theta_{CO-L}. \) \(^{35}\) Thus,

\[
\theta_{CO} = \theta_{CO-L} + 2\theta_{CO-B} = \theta_{CO-L} + 2(0.258 \theta_{CO-L}) = 1.516 \theta_{CO-L}
\]

This means that, on average, one CO molecule is adsorbed at 1.516 platinum site. On the other hand, \( \theta_{CH_{2}OH}(t) \) is multiplied by 2 because, although the molecule is adsorbed at one Pt atom, the molecule could cause a steric hindrance at the neighboring platinum site due to its size, acting as it was adsorbed on two vacant sites. This behavior was reported by Cuesta,\(^{36}\) who showed that methanol requires more than one Pt site to be converted to CO. In all cases, the rates of the elementary reactions were defined as:

\[
v_m \equiv \frac{1}{\vartheta_m} \frac{d}{dt} \left( \frac{n_x(t)}{N_{tot}} \right) \quad \text{Eq. 23}
\]

where \( \vartheta_m \) is the stoichiometric coefficient of each elementary reaction step, \( n_x(t) \) the number of moles of species \( x \) in the vicinity of the catalytic surface, and \( N_{tot} \) the number of moles of electrocatalytic sites on the platinum surface, in this way, \( v_m \) has units of \( \text{s}^{-1} \). Note that for the case of the species adsorbed on the catalyst \( \theta_x(t) = \frac{n_x(t)}{N_{tot}} \).
3.2. Modeling

We have considered that sites at the surface are, by all means, equivalent, and that the adsorbed species are randomly distributed and without interaction among them. These simplifications are known as the mean-field approximation (MFA),\(^{37}\) where the dynamics of the system is described by the coverage of intermediate species at the electrode surface and the variation in the concentration of species over time, that is, the mass balance for each species. Thus, after formulating the possible pathways for MEOR and determining the kinetic equations for each step, it is possible to establish a mass balance for each chemical species on the electrode surface (equations 24 – 35).

\[
\frac{d\theta_{CH_2OH}(t)}{dt} = v_{1a} - v_{2a} - v_{2b} \quad \text{Eq.24}
\]

\[
\frac{d\theta_{CHO}(t)}{dt} = v_{2a} - v_{3a} \quad \text{Eq.25}
\]

\[
\frac{d\theta_{CHO}(t)}{dt} = v_{3a} + v_{3b} - v_{4c} - v_{4a} - v_{4d} \quad \text{Eq.26}
\]

\[
\frac{d\theta_{OH}(t)}{dt} = v_{5c} - v_{-5c} - v_{6c} \quad \text{Eq.27}
\]

\[
\frac{d\theta_{CO}(t)}{dt} = v_{4c} + v_{8e} - v_{6c} \quad \text{Eq.28}
\]

\[
\frac{d\theta_{CHOH}(t)}{dt} = v_{4a} - v_{5a} \quad \text{Eq.29}
\]

\[
\frac{d\theta_{CH_3OCHOH}(t)}{dt} = v_{4d} - v_{5d} \quad \text{Eq.30}
\]

\[
\frac{d\theta_{HCOO}(t)}{dt} = v_{6a} - v_{-6a} - v_{7a} \quad \text{Eq.31}
\]

\[
\frac{d\theta_{HCOO}(t)}{dt} = v_{8a} - v_{8b} - v_{8e} \quad \text{Eq.32}
\]

\[
\frac{1}{N_{tot}} \frac{dn_{HCHO}(t)}{dt} = v_{2b} - v_{3b} \quad \text{Eq.33}
\]

\[
\frac{1}{N_{tot}} \frac{dn_{CH_3OCHO}(t)}{dt} = v_{5d} + v_{-6a} - v_{6d} \quad \text{Eq.34}
\]

\[
\frac{1}{N_{tot}} \frac{dn_{HCOO}(t)}{dt} = v_{5a} + v_{6a} + v_{-6a} - v_{-6d} - v_{6a} \quad \text{Eq.35}
\]
\[
\frac{d\phi(t)}{dt} = \frac{i_{tot}}{A} - F \frac{N_{tot}}{A C_d} \left( v_1 + v_2 + v_3 + v_4 + v_5 - v_{-5} \right) = \frac{i_{BCB}}{A} C_d^2 - F N_{BCB} A C_d^2 (v + \sum v_i / 2 + v_8 - v_4 + v_9 / 2 - v_4 / 2)
\]

Eq.36

An equation corresponding to the electric charge balance at the electrode interface (equation 36) must be included in the system of ODEs to complete the core of the electrokinetic model. The charge balance can be visualized as the sum of the faradaic current and the capacitive current that determines the total current flowing through the system, \(i_{tot}\). In the experiments, it is reported the current density, \(j_{tot}\), equivalent to electric current per unit cross-section, i.e., \(i_{tot} / A\). Here, \(C_d\) is the capacitance associated with the electric double layer per area, and \(A\) is the electrode area. Typical values, equivalent to the experimental conditions, for the factors considered as constants are reported in Table 1. The kinetic parameters of our model, \(\kappa_m\), were phenomenologically determined by fitting the experimental data as described.

**Table 1:** Constants used in the numerical simulations.

<table>
<thead>
<tr>
<th></th>
<th>(F) / C mol(^{-1})</th>
<th>(R) / J mol(^{-1}) K(^{-1})</th>
<th>(T) / K</th>
<th>(A) / cm(^2)</th>
<th>(C_d) / C V(^{-1}) cm(^{-2})</th>
<th>(N_{tot}) / mol cm(^{-2})</th>
<th>(R_s) / Ω</th>
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<td>298.15</td>
<td>0.32</td>
<td>2.4x10(^{-5})</td>
<td>2.18x10(^{-9})</td>
<td>8.00</td>
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4. Results and Discussion

The comparison between simulated and experimental results under steady-state conditions is an important starting point given the complexity of the MEOR mechanism, since it allows the identification of key intermediates. However, this type of response does not provide information on the time-dependent properties of the system and, furthermore, throughout our work we have observed how different models, associated with different reaction schemes, can reproduce similar steady electrochemical responses. Therefore, for the kinetic evidence to support a mechanistic proposal, it is convenient to simulate the behavior of the system variables over time and far from steady-state, to consider the transient response involving most of the possible reaction steps.

A typical experiment to study the transient behavior of an electrochemical system is chronoamperometry, in which a potential step is applied while the current is measured over
time. Thus, to simulate the total current of the system, equation 37 must be used to relate its dependence on the potential supplied by the potentiostat, $U_{app}$.\textsuperscript{23,38}

$$i_{tot} = \frac{U_{app} - \phi(t) - \phi_{ref}}{R_s}$$

Eq.37

where $\phi_{ref}$ is the potential of the reference electrode and, in our case, it is equal to zero since we used the RHE in the same supporting electrolyte. The comparison of the dynamic response was evaluated at $U_{app} = 0.60$ V vs. RHE, preceded by a potential step of 0.85 V vs. RHE to control the initial conditions of the electrode surface, since it is well established that at this potential the electrode surface is fully covered by OH\textsubscript{ad} species. In this case, after solve the optimization problem by comparison between the simulated and experimental responses (c.f. section 2.2), different sets of parameters were obtained that generate a very similar kinetic response (see section 2 in supporting information), which is not convenient for our purpose. As a consequence, the value of the parameters predicted by the fit between the simulated current and the experimental one has a large uncertainty, making chronoamperometry alone not a suitable technique for our purpose.

Voltammetric experiments, in which a linear potential perturbation is applied to the working electrode while measuring the current flowing through the electrochemical cell, were also evaluated. The experimental and simulated anodic scans in Figure 2(a) show that the current density starts to increase at ca. 0.55 V vs. RHE (onset potential) until reaching its maximum at ca. 0.85 V vs. RHE, values that agree with those reported in the literature for the MEOR under similar conditions. The onset potential of methanol oxidation coincides with the start of the formation of OH\textsubscript{ad} species (Figure 2(b)), which react with the CO\textsubscript{ad} species already present on the electrode surface form potentials below of 0.55 V vs. RHE,\textsuperscript{39} causing the current to increase. After 0.85 V vs. RHE, experimentally, the current density decreases because the Pt surface undergoes rearrangements with the conversion of Pt-OH\textsubscript{ad} into Pt oxides that cover the surface and precludes the adsorption and subsequent oxidation of methanol.\textsuperscript{39} On the other hand, in the model, we are only considering the formation of OH\textsubscript{ad} species from water without transformations to Pt oxides at higher potentials, so the OH\textsubscript{ad} species reaches the maximum coverage at 0.85 V vs. RHE and oxidize CO\textsubscript{ad} species to CO\textsubscript{2}. After this potential in the model, the surface starts to be blocked again by CO\textsubscript{ad} species instead of Pt oxides (experimental behavior) and the current density decreases. Therefore, the simulated
coverages after 0.85 V vs. RHE (shaded area in Figure 2(b)) do not represent the actual behavior at the electrode surface. However, this does not affect our next analyses, since the comparisons between the experimental and numerical results are made at potentials lower than those of oxide formation on the electrode surface. In addition, the simulated coverages of the CO\textsubscript{ad}, and CH\textsubscript{2}OH\textsubscript{ad} species in Figure 2(b) are qualitatively similar to changes with the potential in the spectral band intensities observed during potentiodynamic experiments\textsuperscript{39–41}.

The difference in width between the simulated and experimental profiles is due to the fact that the model predicts an exponential increase in current density when the applied potential increases to higher values (according to the Buttler-Volmer theory), however, experimentally there is a great influence of the mass transport of soluble electroactive species on the current density\textsuperscript{42}, which is not included in the model, and makes the experimental current increase slower than that predicted by the model, causing experimental voltammetric profiles wider than simulated ones. We tried to include diffusion effects, which define the concentration of the soluble species in the vicinity of the electrode, but the numerical complexity increases greatly when dealing with a system of many partial differential equations. Thus, we assume the same concentration of soluble species at any distance from the electrode surface.
Figure 2: (a) Experimental and simulated positive-going potential sweep for the electro-oxidation of methanol on platinum; (b) corresponding coverages for the CO\textsubscript{ad}, OH\textsubscript{ad}, and CH\textsubscript{2}OH\textsubscript{ad} species obtained from the model. Electrolyte: aqueous solution containing [HClO\textsubscript{4}] = 0.5 mol L\textsuperscript{-1} and [CH\textsubscript{3}OH] = 0.5 mol L\textsuperscript{-1}. Scan rate: 10 mV s\textsuperscript{-1}. Remaining parameters as in Table 2.

As mentioned above, the greater the number of experiments that the model is capable of simulating, the greater the reliability of the proposed model, so that, after simulating an acceptable global kinetic response, \textit{i.e.}, experimental and simulated voltammetric profiles that agreed on the onset and peak current potentials, we can proceed to the next stage and evaluate the electrochemical responses that show more specific characteristics of the system. We then explore galvanostatic experiments under conditions that allow the emergence of temporal oscillations of some of the system variables, including the potential at the interface, \(\phi(t)\), which, in general terms, reflect the self-organized changes in the coverages of intermediate species.\textsuperscript{24,43}
4.1. The role of self-organized phenomena

According to the parametric conditions in which the dynamic of the experiment is carried out, some of the non-linear phenomena that can be observed are the appearance of multiple steady-states (multi-stability), simple oscillations of the variables involved in the system dynamics, complex oscillations, and even chaotic behavior. Non-linear phenomena in many electrochemical systems are due to the presence of an N-type negative differential resistance (N-NDR), which arises when the increase in the potential difference across interface causes a decrease in the available electrode area, a decrease in the rate coefficient, or a decrease the concentration of the reacting species at the electrode. If this situation leads to a further increase in the potential difference, this process is referred to a positive feedback loop. However, in the absence of other feedback loops, the N-NDR only causes bi-stability. Since our system shows periodic and complex oscillations, additionally, it must have at least one negative feedback loop that responds with a certain delay to changes in potential and current. For the case of the MEOR specifically, the N-NDR is a hidden N-type negative differential resistance (HN-NDR), as proved in impedance experiments, and the system oscillates under both potential and current control modes.

The oscillatory features during the dynamics of the electrocatalytic system depend on the coupling of the feedback loops in the system, which are closely related to the reaction scheme and the interaction between the variables. Consequently, the frequency, amplitude, and waveform of the oscillations are determined by the rates of each reaction steps. Furthermore, as the oscillatory dynamics of the MEOR is associated with the HN-NDR that mainly involves the adsorbed chemical species, the diffusion effects not included in the model are not decisive to predict the main characteristics of the galvanostatic response. These details are suitable for evaluating the reliability of the proposed reaction mechanism and for estimating the value of the model parameters.

For the electro-oxidation of many small organic molecules is it generally stated that the HN-NDR is caused by the formation of OH_{ad} species from water. When the potential increases, more OH_{ad} species are formed, causing the blockage of the electroactive surface, inhibiting the reaction to proceed. In this case, an increase in the potential causes a further increase in the potential in an autocatalytic process, in order to maintain the applied current. On the other hand, the most important negative feedback loop starts with the increase in potential, which induces the reaction between OH_{ad} and CO_{ad} on the electrode surface. This
process releases sites on the surface and thus reduces the potential needed to maintain the applied current.\textsuperscript{23}

Figures 3(a-b) and 3(c-d) show the cell potential during galvanostatic experiments and simulations, respectively, under similar conditions. The proposed model was able, with the same set of parameters (reported in Table 2), to reproduce important characteristics of the oscillatory dynamics, such as the frequency, waveform, and potential range of the oscillations. Additionally, our model can reproduce the increase in the complexity of the oscillations when the current is increased (Figures 3(c-d) and 5), behavior that was observed experimentally and, as far as we know, has not yet being captured by previous models.\textsuperscript{45,48–50} Altogether, these observations strongly support the reliability of the proposed model.

![Figure 3: Oscillatory dynamics of the cell potential during the electro-oxidation of methanol on platinum at different applied currents densities. (a) experimental and (c) simulated potential profiles at $j_{app} = 0.900 \text{ mA cm}^{-2}$; and (b) experimental and (d) simulated potential profiles at $j_{app} = 1.000 \text{ mA cm}^{-2}$. Electrolyte: aqueous solution containing $[\text{HClO}_4] = 0.5 \text{ mol L}^{-1}$ and $[\text{CH}_3\text{OH}] = 0.5 \text{ mol L}^{-1}$. Remaining parameters as in Table 2.](image)

The period-one oscillations (@ $j_{app} = 0.900 \text{ mA cm}^{-2}$) in Figure 3(c) are mainly related to the total coverage of species on the electrode surface, which depends dominantly on the coverages by $\text{OH}_{\text{ad}}$ and $\text{CO}_{\text{ad}}$ species. In this case, the minimum and maximum values of the
potential oscillations correspond with the minimum value of $\theta_{OH}$ and the maximum value of $\theta_{CO}$, respectively, as shown in Figure 4(a). Since CO$_{ad}$ species are already present on the electrode surface from lower potentials, when water adsorbs to form OH$_{ad}$ species ($\tau_{5c}$), the surface is further blocked. Thus, the electrode potential increases to keep the applied current until reaching a maximum value of 0.83 V vs. RHE. At this point, CO coverage is maximal and the reaction between CO$_{ad}$ and OH$_{ad}$ proceeds at high rates releasing active sites.$^{23}$ With free sites available on the surface, the coverages of species such as CH$_2$OH$_{ad}$ and CH$_3$OCHOH$_{ad}$ increase, however, these processes are not significant to increase the total coverage (see Figure 4(a)). During these processes, electrons are produced by the oxidation reactions and the potential needed to keep the applied current decreases. With the fall of the potential and the consumption of OH$_{ad}$ species by the reaction, $\theta_{OH}$ also decreases rapidly, therefore $\theta_{CO}$ starts to increase again. When this happens, there are no longer enough OH$_{ad}$ species on the surface to oxidize the CO species, and the potential increases to accelerate the reactions and in order to keep up the applied current.$^{8,23}$ Thus, the whole process begins anew.
Figure 4: Surface coverages of CO$_{ad}$, OH$_{ad}$, CH$_2$OH$_{ad}$, CH$_3$OCHOH$_{ad}$ species, and total coverage plotted with the potential for simulated galvanostatic experiments during the methanol electro-oxidation reaction at a) $j_{app} = 0.900$ mA cm$^{-2}$, and b) $j_{app} = 1.000$ mA cm$^{-2}$. Methanol concentration 0.5 mol L$^{-1}$. Remaining parameters as in Table 2.

Experimentally, the MEOR shows other non-linear phenomena than the simple oscillations just discussed. As can be seen in Figure 3(b), period-two oscillations emerge as the applied current density increases.$^{8,25,51}$ The model proposed in this work also allowed simulating this dynamic behavior (Figure 3(d)) with the same set of parameters, $\kappa_m$, shown in Table 2. The coverages given in Figure 4(b) show that the main feedback processes involved in the period-two oscillations are related to OH$_{ad}$ and CO$_{ad}$ species at the electrode surface as in the period-one oscillations. This is because these coverages change with the potential synchronized in the same way as discussed above. However, the existence of more complex...
behaviors, *i.e.*, the emergence of period-two oscillations, suggests additional feedback loops acting simultaneously, in which CH$_2$OH$_{ad}$ species also seem to be involved. In this case, when OH$_{ad}$ species react with CO$_{ad}$ and release active sites, the coverage by CH$_2$OH$_{ad}$ species increases. This process leads to increase $\theta_{CO}$ (with some delay), which increases the total coverage on the surface and causes a slight increase in the electrode potential before falling to the low potential region, *cf.* Figure 4(b), which gives rise to complex oscillations.

### 4.2. Other predictions of the MEOR electrokinetic model

The results of the model proposed here show how the increase in the applied current density leads to more complex oscillations, which was discussed in terms of period-one and period-two oscillations. In addition, when the applied current is kept constant, as time increases, spontaneous transitions to more complex oscillations until an aperiodic behavior are observed (Figure 5(a-b)), which is also in agreement with experimental observations.\cite{25,44,52,53} Experimentally, the spontaneous transitions have been attributed to slight changes in the surface composition over time, such that the composition of the different absorbates does not return to its initial state after a single cycle in the oscillatory response. These changes, which are not perceptible in a single cycle, cause a small accumulation or depletion of species on the surface as the dynamics of the system evolve.\cite{25} As a consequence, the oscillations spontaneously evolve towards other waveforms (Figure 5(a)) where the changes in the mean potential compensate for these variations in the surface coverage. In the model, the change in the waveform patterns is caused by the variations in the total mean coverage, which is described by the time evolution of the coverage of all intermediates on the electrode surface.
Figure 5: Other complex dynamics of cell potential during the methanol electro-oxidation reaction at different applied currents densities. a) $j_{app} = 1.05 \text{ mA cm}^{-2}$ and b) $j_{app} = 1.06 \text{ mA cm}^{-2}$ (blue curve $\theta_{CO} = 0.000$, red curve $\theta_{CO} = 0.001$. All other initial conditions were zero c.f. section 2.2), c) two-dimensional projection of the chaotic attractor, and d) next-minimum return map for the time series in (b).

Figure 5(b) shows the time series for the cell potential at an applied current density of 1.06 mA cm$^{-2}$ in which an aperiodic behavior can be observed. For the system to be considered chaotic, in addition to aperiodic behavior, it must also show deterministic dynamics and sensitivity to initial conditions. Since the dynamics of the system is governed by equation 24 to equation 36, which are not subjected to random influences, the aperiodic response is the result of the architecture and the interaction of the variables involved. In this case, a small difference in the initial conditions, say $\theta_{CO} = 0.001$ instead $\theta_{CO} = 0.000$, leads to different time series (red and blue curves in Figure 5(b), respectively), which illustrates the strong sensitivity of the system to the initial conditions. It is also useful to plot the trajectories in phase space which reflects the existence of a so-called strange attractor, which has a clear structure for deterministic chaos instead of successive points randomly distributed without a coherent structure for stochastic data. Figure 5(c) shows the trajectory generated by the coverages by CO$_{ad}$ and OH$_{ad}$ species corresponding to the time series in Figure 5(a), which
shows a closed curve that stays in a roughly circular volume of phase space but does not cross the same path more than once.

A more sensitive analysis than the presence of the strange attractor in the phase space is the next-minimum return map or also called the one-dimensional Poincaré map in which the value of the minimum potential at each cycle is plotted along the horizontal axis and the value of the next minimum along the vertical axis. The next-minimum return map in Figure 5(d) shows a curve with some trend indicating that the aperiodic patterns in Figure 5(b) actually corresponds to deterministic chaos, rather than periodic or random behavior, where clusters of points or randomly distributed points, respectively, are expected. This is an important result since, to our knowledge, it is the first time that a model reproduces the chaotic dynamics experimentally found along the MEOR.

So far, we have emphasized the reliability of our model by presenting the multiple non-linear experimentally observed behaviors that the model is capable of reproducing with the same set of electrokinetic parameters, including the chaotic behavior just mentioned. These results, together with consistent experimental and simulated voltammograms, reinforces the reliability of our model of the MEOR.

4.3. Sensitivity analysis of kinetic parameters

In the search for a methodology to estimate the degree of uncertainty of the kinetic parameters and, likewise, to quantify the contribution of each reaction step to the potential oscillations generated by the galvanostatic experiment, we have recently proposed a sensitivity analysis, cf. section 2.3. The values for the estimated uncertainty of $\kappa_m$ values and the sensitivities are shown in Table 2 (For details of uncertainty estimation see supporting information).

Table 2: Parameters used for the microkinetic simulations, with estimated uncertainty and sensitivity.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value / s$^{-1}$</th>
<th>Period-one Oscillations</th>
<th>Period-two Oscillations</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>Uncertainty</td>
<td>Sensitivity</td>
</tr>
<tr>
<td>$\kappa_{1a}$</td>
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<td>1.4 x 10$^{-1}$</td>
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<td>8.13 x 10$^{-3}$</td>
<td>8.3 x 10$^{-1}$</td>
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<td>2.01 x 10$^{-1}$</td>
<td>2.6 x 10$^{-1}$</td>
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<td>$\kappa_{2b}$</td>
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<td>1.54 x 10$^{-5}$</td>
<td>6.5 x 10$^{-1}$</td>
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<tr>
<td>$\kappa_{3b}$</td>
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<td>3.11 x 10$^{-5}$</td>
<td>6.1</td>
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<tr>
<td>$\kappa_{4c}$</td>
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<td>1.7 x 10$^{-1}$</td>
</tr>
<tr>
<td>( \kappa_{5c} )</td>
<td>1.680 \times 10^{-2}</td>
<td>9.19 \times 10^{-5}</td>
<td>1.8 \times 10^{1}</td>
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<tr>
<td>( \kappa_{-5c} )</td>
<td>1.030 \times 10^{6}</td>
<td>1.37 \times 10^{4}</td>
<td>7.5</td>
</tr>
<tr>
<td>( \kappa_{6c} )</td>
<td>4.487 \times 10^{-7}</td>
<td>4.19 \times 10^{-9}</td>
<td>1.1 \times 10^{1}</td>
</tr>
<tr>
<td>( \kappa_{4a} )</td>
<td>2.910 \times 10^{-6}</td>
<td>2.91 \times 10^{-6}</td>
<td>1.0 \times 10^{-1}</td>
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<tr>
<td>( \kappa_{5a} )</td>
<td>1.850 \times 10^{-3}</td>
<td>1.85 \times 10^{-3}</td>
<td>1.0 \times 10^{-1}</td>
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<tr>
<td>( \kappa_{4d} )</td>
<td>8.782 \times 10^{3}</td>
<td>5.22 \times 10^{1}</td>
<td>1.7 \times 10^{1}</td>
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<tr>
<td>( \kappa_{5d} )</td>
<td>7.000 \times 10^{-4}</td>
<td>2.19 \times 10^{-4}</td>
<td>3.2 \times 10^{-1}</td>
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<td>( \kappa_{6d} )</td>
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<td>4.10 \times 10^{-5}</td>
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<td>( \kappa_{-6d} )</td>
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<td>( \kappa_{7a} )</td>
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<td>( \kappa_{8a} )</td>
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<td>( \kappa_{8e} )</td>
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<td>1.98 \times 10^{5}</td>
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</table>

Each electrokinetic parameter defined in this work is directly related to the corresponding single reaction rate. Thus, the sensitivity values can be used to compare the contribution of each reaction step to the obtained oscillatory pattern. The high uncertainty and low sensitivities in some parameters indicate that some reaction steps do not contribute significantly to the oscillatory electrochemical response. Specifically, the values of reaction steps involved in the production and oxidation of formic acid \((r_{4a}, r_{5a}, r_{6d}, r_{-6d}, r_{6a}, r_{-6a}, r_{7a}, r_{8a}, \text{and } r_{8e})\) reveal that these are minimally involved in the feedback loops that give rise to the oscillations. This may be due to the fact that when comparing the values of the electrokinetic coefficients corresponding to the parallel reactions that lead to the production of formic acid, CO\(_{ad}\), and methylformate \((r_{4a}, r_{4c}, \text{and } r_{4d}, \text{respectively})\), the value of \(r_{4a}\) is the lowest and the rate of this step can be negligible, meaning that this entire oxidation pathway can be ruled out as contributing to the oscillatory profile under these conditions. However, this does not mean that the initially proposed model is wrong and that this oxidation pathway should not be considered in the MEOR mechanism, since it is important under other experimental conditions, such as different pH values and temperatures. Either way, the rates of the individual reaction steps should be the output of the model, not initial assumptions.

On the other hand, the steps that contribute the most are \(\kappa_{5c}, \kappa_{4c}, \kappa_{4d}, \text{and } \kappa_{1a}\), namely, the formation of OH\(_{ad}\) species from water, the formation of CO\(_{ad}\) species from CHO\(_{ad}\), the formation of CH\(_3\)OCHOH\(_{ad}\) species from CHO\(_{ad}\), and the first step of methanol dehydrogenation to produce CH\(_2\)OH\(_{ad}\), respectively, so that small variations in their values...
produce rapid changes in the waveform of the oscillatory profile. This is consistent with the results discussed previously, as the \( r_{5c} \) and \( r_{4c} \) reaction steps produce OH\(_{ad}\) and CO\(_{ad}\) species, respectively, which have the highest coverage values and are the species mainly involved in the feedback loops. \( k_{4d} \) affects the rate at which HCO\(_{ad}\) produces CH\(_3\)OCHOH\(_{ad}\) (\( r_{4d} \)), which is the only reaction parallel to the CO\(_{ad}\) formation from HCO\(_{ad}\) species (\( r_{4c} \)) after discarding steps with low sensitivity values. Thus, small changes in \( k_{4d} \) affect the proportion of HCO\(_{ad}\) available to produce CO\(_{ad}\), and therefore affect the interaction between the variables that generate the oscillations. In the case of \( k_{1a} \), this electrokinetic parameter affects the rate of formation of CH\(_2\)OH\(_{ad}\) species, which in turn has an effect on \( \theta_{CO} \) at higher values of current density as discussed above (see Figure 4), also affecting the main feedback loop. This shows that at higher current densities, the oxidation pathway through CO\(_{ad}\) is favored, since, when the pathway through formic acid is neglected, the oxidation of CO\(_{ad}\) to CO\(_2\) generates two electrons (steps \( r_{4c} \) and \( r_{6c} \)) while the formation of methylformate generates only one electron (step \( r_{5d} \)) per molecule of HCO\(_{ad}\). In this way, it is possible to deduce that the species that most affect the oscillatory profile and cause the mixed-mode oscillations are those that somehow affect the relationship between formation and consumption of CO\(_{ad}\) species and therefore affect the global feedback loop.

After discarding the steps with low sensitivities, i.e., those that do not contribute significantly to the oscillatory response, the values of the electrokinetic parameters indicates that the main limitations of the MEOR are the steps involving the formation of the soluble species HCHO, CH\(_3\)OCHOH, and CO\(_2\). A comparison between the resulting reaction mechanism of the MEOR and the reaction mechanism of one of its by-products, in this case, the formic acid, shows that both reactions have in common the steps that involve the main species that originate the feedback loops, i.e., the CO\(_{ad}\) formation step (coming from HCO\(_{ad}\) for the MEOR and from HCOO\(_m\) for the FAEOR) and its consumption by OH\(_{ad}\) species coming from water, usually called the indirect oxidation pathways. In this way, for comparative purposes, the values of the electrokinetic parameters for the reaction steps of the FAEOR mechanism were calculated, in the same units as the \( k_m \) for the MEOR (s\(^{-1}\)), based on data from a previous model\(^{19}\) (for calculation details see section 4 in the supporting information). The \( k_m \) values including the potential-dependent term (\( k_m(\phi) \)) corresponding to the CO\(_{ad}\) formation and to the common reaction steps in both reactions are shown in Figure 6.
Figure 6: Electrokinetic parameters including the potential dependent term corresponding to CO$_{ad}$ formation and to the common reaction steps in the FAEOR (dashed lines) and in the MEOR (straight lines) as function of the electrode potential.

From the set of $k_m$ values for the both reactions (see Table 2 and Table 2S), we can deduce that the CO$_2$ production from CO$_{ad}$ and OH$_{ad}$ ($CO_{ad} + OH_{ad} \rightarrow CO_2 + H^+ + e^- + 2*$) is the slowest step in both reactions, with similar $k_m$ values (4.487x10^-7 s$^{-1}$ for MEOR and 2.554x10^-7 s$^{-1}$ for FAEOR). In the same way, when the potential-dependent term is included, these steps remain the slowest in almost the entire potential window (see Figure 6). This is in agreement with reports in the literature that suggest the poisoning of the platinum surface as one of the major problems in the electrooxidation of small organic molecules since the surface is blocked by CO$_{ad}$ species that are difficult to oxidize.$^4$ It is worth mentioning that the electrolyte used in both reactions was different, i.e., sulfuric acid in the FAEOR$^{19}$ and perchloric acid in the MEOR, however, although the effect of anions is not explicitly considered in the fit of the $k_m$ values, the reaction between CO$_{ad}$ and OH$_{ad}$ species to produce CO$_2$ is less dependent on the adsorbed anions in the MEOR under oscillatory regime,$^8$ which can explain the similarity of the $k_m(\phi)$ plots for these steps in both reactions.

The $k_m(\phi)$ values corresponding to the formation of OH$_{ad}$ species from water ($H_2O + * \rightarrow OH_{ad} + H^+ + e^-$) show that this reaction step is slower in the FAEOR than that in the MEOR at potentials between 0.1 V and 0.6 V vs. RHE, while that at higher potential (> 0.6 V vs. ...
RHE), the values are similar. For the reverse reaction \( OH_{ad} + H^+ + e^- \rightarrow H_2O + * \), the values of \( k_m(\phi) \) are higher for the FAEOR than for the MEOR in the entire potential window. In this case, the different electrolytes lead to different arrangements of double layer and generate different behaviors for the same reaction on the platinum surface.\(^{55}\) Therefore, the formation and desorption of OH\(_{ad}\) species on the electrode surface can be hindered by the strong adsorption of sulfate anions (SO\(_4^{2-}\)), while it is less affected by the presence of perchlorate anions (ClO\(_4^-\)), making the values of \( k_m(\phi) \) smaller in the FAEOR than in MEOR. The effect of the electrolyte on the FAEOR has been observed in previous studies that suggest that chemical species, such as specifically adsorbed anions, can affect the adsorption of both OH\(_{ad}\) and formic acid molecules giving rise to mixed-mode oscillations.\(^{56,57}\) Finally, Figure 6 shows an opposite trend in the \( k_m(\phi) \) values for the CO\(_{ad}\) formation in the FAEOR and in the MEOR. This is because this reaction step corresponds to an electroreduction process in the former, while it corresponds to an electro-oxidation process in the latter. Therefore, the formation of CO\(_{ad}\) from HCOO\(_m\) is favored at lower potentials, while its formation from CHO\(_{ad}\) in the ME is favored at higher potentials.

Once those electrokinetic parameters \( (k_m \text{ values}) \) were obtained independently in a different study,\(^{19}\) the correspondence between the values in both systems is strong evidence of the reliability of this approach to relate information at the mesoscopic scale, such as laboratory experiments, with information at the microscopic scale, such as the reaction mechanism and reliable rate coefficient values, which can be used to model other electrocatalytic systems with common reaction pathways. Furthermore, this microkinetic approach contemplates its applicability in understanding complex surface processes in order to rationally design electrocatalysts and optimize reaction conditions, since it is possible to analyze how experimental parameters (for instance, electrocatalytic material, electrolyte, and temperature, among others) affect the different reaction pathways and, consequently, the efficiency and selectivity of a given reaction.

4. Conclusions

A microkinetic description of the methanol electro-oxidation reaction on polycrystalline platinum electrodes in acidic medium was developed. The comprehensive model was validated by means of the comparison with experimental data obtained under different conditions, the model was optimized, and the data reproduced with the same set of
kinetic parameters. In this sense, by the numerical analysis of the model, we found that voltammetric, chronoamperometric, and steady-state experiments by themselves are not the most suitable to find kinetic parameters for the surface reaction. However, experiments under oscillatory regime proved to be suitable since the oscillations in the electrode potential reflects the changes in the surface coverages of distinct adsorbates.

Overall, an almost quantitative agreement between experiments and simulations was obtained in most cases with the optimized set of kinetic parameters. The obtained model was also capable of reproducing, for the first time, the increase in the complexity of the oscillation waveform due to changes in the applied current, including the chaotic behavior observed in experiments. Therefore, the microkinetic model presented in this work provide important kinetic evidence of the MEOR reaction mechanism. In addition, the sensitivity analysis allowed at identifying the key species in the oscillatory dynamics and showed that, under these conditions, the formic acid pathway does not contribute significantly to the oscillatory profile and can be neglected in the model.

Finally, some of the obtained rate constants were discussed in connection with other comparable ones for the electro-oxidation of formic acid on platinum in an acid medium,\(^{19}\) and the correspondence between the values and their dependence on the electrode potential shows the applicability of this approach to understanding other electrocatalytic processes. The obtained electrokinetic parameters can be used for those elementary reaction. This approach has proven to be relevant to the investigation of reaction mechanism, the basis for the rational design of catalysts and for the optimization of reaction conditions.

**Supporting Information**
Details of the definition for the electrokinetic parameters \((k_m)\); electrokinetic parameters fitted using chronoamperometric experiments; estimation of uncertainty of each electrokinetic parameter; and determination of the electrokinetic parameters for the formic acid electro-oxidation reaction.

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