Elucidation of Reaction Mechanisms Far from Thermodynamic Equilibrium

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Spontaneous formation of self-organized spatiotemporal patterns far from thermodynamic equilibrium is a typical behavior found in reaction–transport systems. During the electrochemical reactions, patterns can emerge because of the interaction between the nonlinear local dynamics of the faradaic processes and the electrical spatial coupling along the interface. In fact, oscillatory dynamics is a prevailing example of complex temporal patterns associated to this spatial structuring. Because of a large number of independent variables and the intrinsic complexity of chemical reaction steps, the study of temporal patterns in electrochemical systems has been limited to monitor only global variables, such as potential and current.

Nevertheless, as observed in the history of the field of nonlinear chemical dynamics, knowledge of the reaction mechanisms is fundamental for the proper understanding and the rational design of chemical patterns. For instance, in the 1970s, Field, Körös, and Noyes (FKN) combined a physico-chemical approach to propose a detailed mechanism for the Belousov–Zhabotinsky (BZ) reaction. Along with the advances in nonequilibrium thermodynamics, the FKN mechanism provided more realistic evidence that chemical oscillations were, indeed, a true event. Since then, the theoretical model known as Oregonator, based on the FKN mechanism, has been systematically used in the study of spatiotemporal patterns in the BZ reaction. This mechanistic approach has been widely developed by Epstein and co-workers at Brandeis in the creation of a taxonomy of homogeneous chemical oscillators. The set, composed of reactive intermediates, catalysts and organic substrates, is divided by families of oscillators, which are interconnected with each other, generating a network of molecular species. This combination is able to identify and classify possible variants of the core oscillators and to provide a reference in designing novel chemical oscillators.

Despite a well-defined categorization of the oscillators and essential variables, the electrooxidation of small organic molecules proceeds with a disparate dynamics, described in terms of period, amplitude, and shape of the oscillations. Examples might include the electrooxidation of formic acid, formaldehyde, methanol, ethanol, ethylene glycol, glycerol, etc. Unlike the classification in the chemical taxonomy for homogeneous oscillators, there is still no such evident scenario for electrocatalytic oscillators. Overall, potential and current measurements have been used to characterize the system as a whole, and a detailed interpretation of the molecular mechanism linked with the dynamic behavior has been rarely proposed. This doctoral thesis aims to contribute in this direction, providing a better understanding of the electrooxidation of methanol on polycrystalline platinum in oscillatory regime. Two work fronts are presented in the extraction of kinetic information based on the reaction mechanism analysis when the system is far from thermodynamic equilibrium.

The first part deals with the elucidation of the chemical nature and its respective effect on the dynamics of the spontaneous drift commonly found in electrochemical time series. Figure 1 shows a

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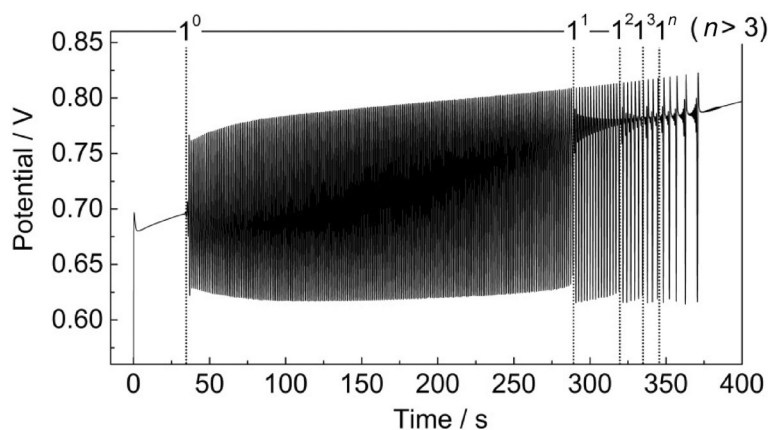*E-mail: nagaodesousar@slu.edu*

Figure 1. Potential time series in the electrooxidation of MeOH at a constant applied current of 1.00 mA cm^{-2}. Initially quasi-harmonic oscillations (1^0) emerge, switching to mixed mode oscillations ($1^1 \rightarrow 1^2 \rightarrow 1^3 \rightarrow 1^n$, with $n > 3$) and to oscillations suppression domain, spontaneously. Reproduced with permission from R. Nagao, E. Sitta, H. Varela, *J. Phys. Chem. C* **2010**, *114*, 22262–22268. Copyright 2010, American Chemical Society.

potential time series in the electrooxidation of methanol on polycrystalline platinum at 1.00 mA cm^{-2}. Potential oscillations emerge after an induction period, showing initially a quasiharmonic shape, and then, it slowly evolves to mixed mode oscillations in the sequence: $1^1 \rightarrow 1^2 \rightarrow 1^3 \rightarrow 1^n$ with $n > 3$. In this particular temporal pattern, oscillations are characterized by intercalating large (L) and small (S) amplitude cycles (L^S). Remarkably, these type of transitions can also take place in galvanodynamic control in which applied current is varied in a constant sweep rate. This observation clearly indicates that stationary current experiments may be affected by some change in the overall surface area such that an increase in the current density is achieved along the time series.

Transient oscillations are widely observed in closed reacting systems once irreversible processes act to restore the equilibrium state by increasing entropy. In order to maintain stable chemical oscillations, therefore, fresh reactants have to be pumped into the system, while final products are removed to outside of it, providing a high free energy and elimination of the excess entropy, respectively. This procedure has been successfully applied in the study of homogeneous chemical oscillators with the aid of a continuously stirred tank reactor (CSTR). Indeed, experimental bifurcation diagrams have been built considering the accurate control of chemical flows into the reservoir. As observed, the electrified interface is already connected to inexhaustible reservoirs as well. The system is open to electron flow, based on the operation mode of the potentiostat, and to the bulk solution in which the concentration of the organic reactants remains practically unchanged.

According to the long-term dynamics, the increase of the mean potential might reflect an accumulation of reaction intermediates on the surface in a rather slow time scale. Regarding the charge balance in the equivalent circuit, the increase of mean potential has to be accompanied by a decrease of the overall faradaic current since the system is conducted under galvanostatic control, that is, constant applied current. If this statement were true, the use of a negative galvanodynamic sweep (NGS) would stabilize the time series by the compensation of the spontaneous drift, described as surface area modifications, keeping the same applied current density. This idea was confirmed by a very efficient empirical stabilization of number of cycles from 5 to 20 times, depending on the oscillatory pattern. The control of the uncompensated oscillations by NGS suggests that temporal patterns observed in stationary current experiments are closely related to the current-driven transitions presented in the galvanodynamic experiments due to an accumulation of some reaction intermediates and, consequently, the decrease of the overall active surface area.

Based on spectroscopic evidences of the time evolution of reaction intermediates in long-term dynamics during the electrooxidation of methanol, the uncontrollable drift found in the time series was identified as the accumulation of oxygenated species on the surface. Because of the presence of the place-exchange mechanism, a nonmonotonic increase of the mean potential can be observed, particularly, when carbonaceous species, resulting from the partial oxidation of the organic molecules, reactivate the surface momentarily. Numerical simulations were also carried out by the use of a generic electrochemical oscillator. Overall, the drift was recognized as a purely surface effect. Qualitatively, the

model reproduced the main features observed experimentally which validated the empirical method of stabilization. As the main result, the time-dependent bifurcation parameter acts as irreversibly adsorbed species on the electrode surface, changing the local current density. Therefore, the transient behavior was rationalized as the coupling of two subsystems: the fast one, composed of the feedback loops that are responsible for the oscillations, and the slow one, which is associated with the accumulation of oxygenated species, driving the system for different regions in the bifurcation diagram.

Different from the analysis in long-term dynamics, the second part of this thesis deals with the mechanistic analysis in the fast subsystem. It is a consensus that the electrooxidation of methanol proceeds through a parallel, dual-pathway mechanism. The indirect pathway is related to the reaction between adsorbed carbon monoxide (CO_{ad}) and oxygenated species ($(H)_xO_{ad}$, with $x = 0$, 1, or 2) via a Langmuir–Hinshelwood mechanism when the potential is larger than 0.7 V vs. reversible hydrogen electrode (RHE), approximately. In addition, the direct pathway proceeds via reactive intermediates such as formaldehyde and formic acid, which can diffuse to the solution or readsorb on the surface. Although systematic studies have been carried out in the understanding of the catalytic aspects of the electrooxidation of methanol, the production of carbon dioxide (CO_2), that is, the final product in the oxidation process, has been detected only as a combination of the direct and indirect pathways. The contribution of CO_2 formation in each chemical route has been calculated by indirect means.

We addressed this issue utilizing a combination of experiments, modeling, and simulations. In fact, we were able to separate CO_2 contributions from direct and indirect pathways when the system was kept in the oscillatory regime. Figure 2 depicts simultaneously recorded potential oscillations as black lines and mass fragments of $m/z = 44$ (carbon dioxide) in red and 60 (methylformate) in blue, conducted with the aid of differential electrochemical mass spectrometry (DEMS) coupled with the electrochemical cell in a) perchloric and b) sulfuric acidic media. The production of CO_2 from the indirect pathway occurs mainly in the potential interval above 0.76 V vs. RHE, represented as a gray band in the time series. Bellow this threshold, where the coverage of oxygenated species is vanishingly small, the CO_2 production along the direct pathway can be considered as the major route for methanol oxidation.

Therefore, it was possible to classify the CO_2 peaks $i\,(i')$ and $iv\,(iv')$ as the main contributions from the indirect pathway, and the peaks $ii\,(ii')$ and $iii\,(iii')$ from the direct pathway. Monitoring peaks $i\,(i')$ and $iv\,(iv')$ are very important for testing new catalysts with the aim of CO_{ad} removal from the surface and modeling mixed-mode oscillations in the electrooxidation of small organic molecules, respectively. The peak $ii\,(ii')$ is induced by the autocatalytic increase of the number of active sites in the reactivation process, while peak $iii\,(iii')$, accompanied by the production of $HCOOCH_3$, is associated with readsorption steps of formic acid and formaldehyde, for instance. The CO_2 peaks were deconvoluted, and the individual contributions were analyzed at constant applied currents. Interestingly, the direct pathway was the chemical route more affected by the inhibition caused by anion adsorption.

As demonstrated, important information on the chemical kinetics is not accessible in conditions close to equilibrium. In this situation, the system relaxes quickly to the steady state, and no coherence in time and space is observed. However, when the gradient is large enough to move the system away
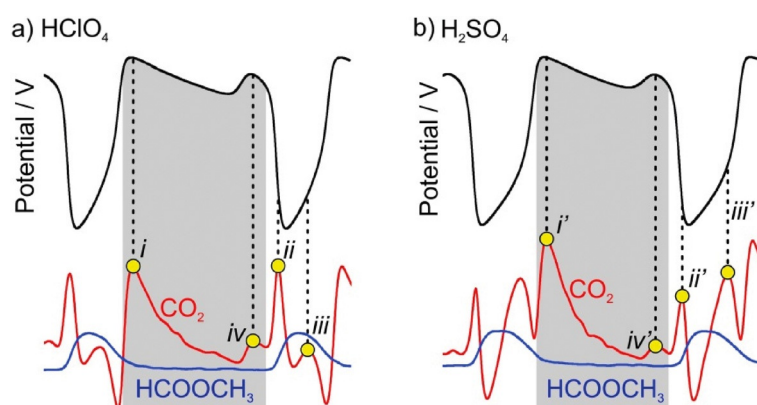

Figure 2. Details for 11 type oscillations for aqueous a) $HClO_4$ and b) H_2SO_4 at $[H_3COH] = 2.0$ M and applied current of 0.40 mA cm^{-2}. Potential oscillations are represented by black lines, while the mass fragments of $m/z = 44$ (CO_2) and 60 ($HCOOCH_3$) are shown in red and blue lines, respectively. Reproduced with permission from R. Nagao, D. A. Cantane, F. H. B. Lima, H. Varela, *J. Phys. Chem. C* **2013**, *117*, 15098–15105. Copyright 2013, American Chemical Society.

from the thermodynamic equilibrium, fluctuations intrinsic to the system are amplified. Accompanied by oscillatory dynamics, some characteristics between the elementary reaction steps are evidenced. This mechanistic interpretation adopted in this doctoral thesis highlights the possibility of being used as an alternative methodology to study the electrocatalysis of coupled chemical reactions.

Publications arising from this work:

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