

Inpe – National Institute for Space Research, São José dos Campos – SP –Brazil, July 26-30, 2010.

KINETIC INSTABILITIES DURING GLYCEROL ELECTRO-OXIDATION ON PLATINUM

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Keywords: electrochemical systems, glycerol, electrochemical oscillators, mixed mode oscillations

1. Introduction

Instabilities in electrochemical systems can be subdivided into two classes. One class includes purely chemical instabilities, i.e., instabilities which arise from chemical kinetics. The electrode potential is not an essential variable for these kinds of instabilities. The second class of instabilities, however, requires the interaction of chemical and electrical variables. Koper [1] presented a consistent picture to describe why and when electrochemical system oscillates. The basic requirements are a negative differential resistance (NDR) and a finite ohmic resistance. NDR can be originated by the adsorption of a chemical activator/inhibitor, an intermediate or by electrostatic effects between electroactive species and the electrode. Besides slow mass transport processes can lead to oscillatory instabilities in electrochemical systems.

Among the electrochemical systems, oxidation of small organic compounds, mainly C1 molecules, at noble metal (usually Pt) is the most explored reaction in oscillatory conditions [2]. Recently, Sitta *et al.* [3] presented a systematic study about oscillatory instabilities of ethylene glycol (C2 molecule) electro-oxidation on Pt, where it was reported a rich dynamic behavior with robust time-series, different temporal patterns and high oscillation frequencies.

In this communication, we reported a study of the glycerol (G) electro-oxidation on Pt in alkaline media. Galvanodynamic and galvanostatic experiments were performed to delineate the general behavior as a function of glycerol concentration ([G]) and applied current density (*j*). To the best of our knowledge, there is just one paper [4] dealing

with glycerol electro-oxidation in oscillatory conditions.

2. Experimental details

All experiments were performed in a conventional electrochemical cell with three electrodes. A platinum sheet with 0.27 cm² of electroactive area was used as working electrode. As counter electrode was used a platinized platinum mesh and all the potentials were measured versus the reversible hydrogen electrode (RHE), prepared in the same solution used as supporting electrolyte (potassium hydroxide – KOH). Solutions were prepared from Millipore water and chemicals PA grade: KOH (Aldrich) and glycerol (Mallinckrodt). Unless state otherwise, the following conditions hold: temperature: 25°C and [KOH] = 1M.

3. Results

Before studying the system dynamics under galvanostatic mode, were performed galvanodynamic experiments at different glycerol concentrations (0.05 M, 0.1 M and 0.2 M). These experiments were conducted to the sweep rate of 3.85 $\mu\text{Acm}^{-2}\text{s}^{-1}$ from zero current up to that one in which the potentials reaches 1.4 V. The galvanodynamic experiments gave us insight about the current density (*j*) range in which system presents oscillatory behavior.

The galvanostatic experiments reveal a rich variety of oscillatory states at 0.55 mAcm^{-2} for low glycerol concentration. Figure 1 presents typical potential time-series obtained at $j = 0.55 \text{ mAcm}^{-2}$ for [G] = 0.05 M, where we can see that small high-frequency harmonics appear between the large spikes which suggests the presence of mixed mode

oscillations. This phenomenon has frequently been observed in models and experiments of chemical and electrochemical oscillators⁵.

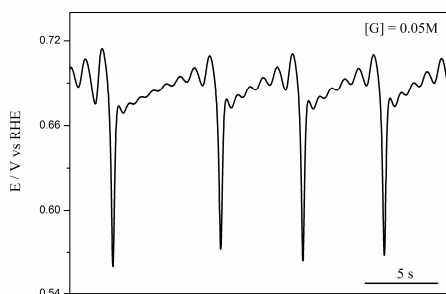


Figure 1. Potential time-series during the glycerol electro-oxidation. Applied current density: 0.55 mAcm^{-2} ; $[G] = 0.05 \text{ M}$.

Interestingly, as $[G]$ increases the system dynamic evolves to a state where the number and amplitude of the small oscillations, between the spikes, are significantly reduced. Figure 2 shows the time-series obtained in $[G] = 0.1 \text{ M}$ and 0.55 mAcm^{-2} . The same one is observed at the end of time-series presented in Figure 1.

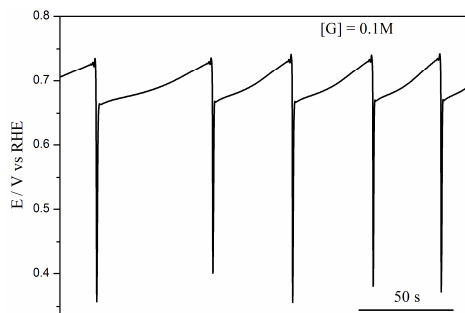


Figure 2. Potential time-series during the glycerol electro-oxidation. Applied current density: 0.55 mAcm^{-2} ; $[G] = 0.1 \text{ M}$.

For higher glycerol concentration, increasing the current density leads the system to oscillatory patterns as complex as that one observed in Figure 1.

Mixed mode oscillations cannot be described from the same mechanistic point of view those simple periodic oscillations. This kind of oscillatory behavior is called by more complex dynamics and their mathematical description requires at least three variables.

Strasser *et al.* [6] reported mixed mode oscillation during formic acid oxidation on Pt (100) under potentiostatic control. When the system was subjected to stirring, the mixed mode oscillations

disappear. So they concluded the set of chemical species essential for the occurrence of the small-amplitude spikes does involve at least one solution species.

More complex oscillations can arise owing to slow transport processes. For NDR oscillators it was shown that diffusion of the electroactive species introduces two distinct feedback modes into the system. Also in HNDR oscillators, the occurrence of more complex oscillations can be coupled to the slow diffusion of electroactive species. In this case, a more elaborated model consists of two subsystems, one of the NDR type and one of the HNDR type, the complex behavior arising from their interactions. This is the main idea of the model proposed by Strasser *et al.* [7] to explain the mixed mode oscillations observed during formic acid oxidation cited early. However, since NDR oscillators do not oscillate under galvanostatic conditions, this mechanism cannot be used for explaining mixed mode oscillations or even other complex behavior observed under galvanostatic control.

From the experimental findings it is not possible to settle the question of what scenario leads to the formation of mixed mode oscillations. Considering the several reactions pathways and intermediates, which might be strongly bounded to the electrode surface, we can certainly propose an additional negative feedback loop to be crucial to the dynamics which, together with the negative and the positive feedbacks involved in the simple oscillations, gives rise to mixed mode oscillations.

Acknowledgements: The authors thank to FAPESP (CPO 09/16449-1, HV 09/07629-6) and CNPq (ES 141455/2008, HV 302698/2007-8) for financial support.

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