EMPIRICAL STABILIZATION OF TRANSIENT TIME-SERIES IN AN ELECTROCHEMICAL SYSTEM

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Abstract: Experimentally obtained time-series in oscillatory electrochemical systems are often found to vary slowly in time, even when all controllable parameters are kept constant. This slow drift normally makes the long term analysis a complex task. Herein we introduce an empirical method to stabilize transient time-series and it has been tested for the electro-oxidation of methanol on a platinum surface. Typical stabilization in the oscillatory period amounts about 5 to 20 times with respect to the non-stabilized system has been achieved.

keywords: complex dynamics in chemical systems, electrochemistry, time-series stabilization, oscillations.

1. INTRODUCTION

Electrochemical oscillators are probably the most paradigmatic example of oscillatory dynamics in chemical systems. The vast majority are known to display oscillatory kinetics in either the electrode potential of the reaction current, according to the parameter that is kept constant. Resulting time-series are usually very reproducible and stable, when compared to other chemical systems. In spite of such advantages, some experimental time-series obtained in electrochemical systems are associated to spontaneous transitions among different patterns, although the fact that all controllable parameters are kept constant [1]. Those transitions are in principle connected to surface processes rather than transport or bulk effects.

Herein we present a simple empirical method to stabilize the experimental time-series. The method consists of slowing decrease the applied current in order to account for the continuous surface population change and was tested for the oscillatory electro-oxidation of methanol on platinum.

2. EXPERIMENTAL

The working electrode (WE) was a smooth polycrystalline platinum with real area 0.3 cm^2 and roughness factor of about 1.0, calculated with respect to the charge of one hydrogen monolayer. A high area mesh of platinized platinum was utilized as counter electrode (CE). A reversible hydrogen electrode (RHE) prepared with the same concentration of supporting electrolyte was used as reference electrode (RE). All the solutions were prepared with high purity water (system Millipore Milli-Q, 18 MΩ cm), perchloric acid (Merck, suprapur 70-72%) and methanol (J.T. Baker, chromatography grade 99.9%). All electrochemical measurements were carried out at 25.2 °C with a potentiostat/galvanostat (Autolab/Eco-Chemie, PGSTST30).

3. RESULTS

Galvanostatic experiments during the electro-oxidation of methanol under polycrystalline platinum were conducted in a wide range of applied currents, j. Oscillations replace a stable stationary state by a subcritical Hopf bifurcation. They become less harmonic and with larger amplitude, presenting after some time the spontaneous transition to mixed mode oscillations. Following the increase of j, the limit cycle collides with the focus saddle-point referent to oxygen evolution in the phase space by a homoclinic bifurcation which promotes the destruction of the oscillations. For a wide range of applied currents, the non-stabilized base system presents spontaneous transitions from *quasi*-harmonic to mixed mode oscillations in the sequence: $1^0 \rightarrow 1^1 \rightarrow 1^2 \rightarrow 1^3 \rightarrow 1^n$; $n > 3$ (L^S: L large and S small amplitude oscillations).

The nature of the transient time-series is probably connected to an unknown time-dependent bifurcation parameter that varies independently on the fact that all controllable parameters are kept constant. A measure of this drift can be made through the drift of the mean electrode potential, U_m, calculated for each oscillation period. The rate of change of the mean potential, dU_m/dt, amounts to $+ 0.519$ mV s^{-1}, for the induction period; $+ 0.041$ mV s^{-1} for the period one, 1^0 state; $+ 0.452$ mV s^{-1} for 1^1; $+ 0.595$ mV s^{-1} for 1^2; and $+ 1.980$ mV s^{-1} for 1^3 state. In order to compensate the natural drift of U_m found in the galvanostatic experiments, we applied a *negative galvanodynamic sweep* (NGS) at different rates, $-dj/dt$. Figure 1 exhibits the oscillatory time-series under NGS control.
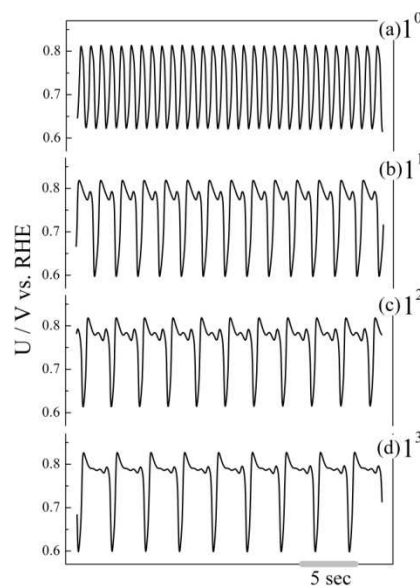
Figure 1 – Periodic *quasi*-harmonic and mixed mode oscillations under negative galvanodynamic sweep (NGS) at j = 0.99 mA cm^{-2}.

It is possible to distinguish the complex patterns and stabilize them individually as 1^n, n = (a) 0, (b) 1, (c) 2, (d) 3 applying different NGS rates, *vide* Figure 1. Incomplete Farey sequence has been found in our experiments, presenting a concatenation of two others states such as $1^0 1^1$ and $2^0 1^1$ between the period transition from 1^1 to 1^0 which are easily predict by the firing numbers [2]. The efficiency of the stabilization procedure can be verified at different NGS rates by means of the oscillatory time, t_{osc} for each temporal pattern, as shown in Table 1.

Table 1: Oscillatory time vs. the negative galvanodynamic sweep.

1^0		1^1		1^2		1^3	
$-\mu A\ s^{-1}\ cm^{-2}$	s	$-\mu A\ s^{-1}\ cm^{-2}$	s	$-\mu A\ s^{-1}\ cm^{-2}$	s	$-\mu A\ s^{-1}\ cm^{-2}$	s
0	20	0	29	0	15	0	24
0.5	116	0.10	37	0.10	17	0.050	27
1.0	183	0.15	45	0.20	26	0.100	89
1.5	440	0.20	54	0.30	45	0.125	93
2.0	335	0.25	106	0.35	55	0.150	114
3.0	210	0.30	188	0.40	158	0.175	127
4.0	153	0.35	76	0.45	70	0.180	60
5.0	99	0.40	23	0.50	16	0.200	34

Overall, the stabilization improvement is small at low NGS rates and only short oscillatory time is achieved. Increasing the NGS rate, the stabilization becomes more efficient. For the optimum NGS rate the stabilization seems to compensate the natural drift of the time-dependent bifurcation parameter and rather long time-series are observed. After reaching the maximum, the stabilization becomes less efficient, which indicates that NGS is faster than the transient response in oscillatory regime, reaching the stationary state before the destruction of the limit cycle by a homoclinic bifurcation. Even though, is still possible to observe further stabilization in high rates of NGS in comparison with the galvanostatic experiment without the stabilization procedure. The optimum NGS values keep the system oscillating, at least, 5 times more for the 1^3 case, and more than 20 times for the 1^0 state.

4. DISCUSSION

A generic equation that describes the time-evolution of the current density J during methanol electro-oxidation at the working electrode can be derived as,

$$\frac{dJ}{dt} = \kappa \left(\frac{d\theta_{CO}}{dt} + 2\frac{d\theta_{HCOO}}{dt} + \frac{d\theta_{(H)_xO}}{dt} \right) \qquad (1)$$

where κ depends on the adsorbed intermediates such as carbon monoxide CO, formate HCOO and $(H)_xO$ for x = 0, 1 or 2 according to the nature of the adsorbed oxygenate specie, respectively.

$$\kappa = \frac{j}{\left(1 - \theta_{CO} - 2\theta_{HCOO} - \theta_{(H)_xO}\right)^2} > 0 \qquad (2)$$

Under NGS control, J is constant, therefore,

$$\left(\frac{d\theta_{CO}}{dt} + 2\frac{d\theta_{HCOO}}{dt} + \frac{d\theta_{(H)_xO}}{dt} \right) = 0 \qquad (3)$$

Based on the experimental observation in long term dynamics [3] this result is valid *if and only if* $d\theta_{(H)_xO}/dt >$ 0, whereas $d\theta_{CO}/dt < 0$ and $d\theta_{HCOO}/dt \to 0$. It indicates that the unknown species that are adsorbed and accumulated on the surface during the oscillatory behavior under galvanostatic experiment are $(H)_xO$. In this sense, NGS compensates the decrease of the effective electrode area by decreasing the imposed current j, keeping a stationary current density, dJ/dt = 0. The time-scale of the coverage of oxygenated species is thus,

$$-\frac{d\theta_{CO}}{dt} \cong +\frac{d\theta_{(H)_xO}}{dt} \qquad (4)$$

Note that the stabilization procedure could work as an analogous to the reagent control in a continuous-flow-stirred-tank-reactor in a homogeneous chemical system. In electrochemical environment, electrons can participate as reactants in the reaction network under galvanostatic regime, which indicates the applied current density j as a parameter of stabilization.

5. CONCLUSIONS

We have presented a method to stabilize experimentally obtained electrochemical time-series. The method was tested for the electro-oxidation of methanol on a platinum surface. Temporal patterns were stabilized by a *negative galvanodynamic sweep* (NGS), at different rates of *-dj/dt*. It was found to be successful for the case studied and stabilizations as high as 20 times in the oscillatory window of the non-stabilized system were observed. The stabilization mechanism has been discussed in terms of the coverage of reaction intermediates and can be applied to other electro-catalytic systems. The application of this approach opens perspectives to the experimental study of complex dynamics transitions by stabilizing, for instance, high order mixed mode states.

References

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