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## The effect of poisoning species on the oscillatory dynamics of a surface catalyzed reaction

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### INTRODUCTION

Electrochemistry has emerged as a powerful field for observing and controlling dynamic processes due to the rather simple way in which the flux of one of the reactants, e.g. the electric current, can be managed [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]. Methanol oscillatory oxidation can be cited as a model system, displaying simple harmonic potential oscillations whose frequency is decreased when temperature is lowered [3,4]. That system was recently modeled and numerically explored by Sauerbrei et. al [5]. We present here a study of the dynamic behavior for a system slightly modified from Sauerbrei's, in which it incorporates anion adsorption among the possible chemical steps. As this effect is easily reproduced experimentally we also compare our simulations with experimental data.

### METHODOLOGY

Equations from 1 to 4 represented below describe the temporal evolution of the most relevant species reacting during methanol oxidation. They can be attributed to oxide ( $x_2$ ), the adsorbed intermediary HCO ( $x_4$ ) and adsorbed CO ( $x_5$ ). This set also incorporates the potential dependence ( $v$ ) on applied current ( $k_7$ ) and associated electrochemical steps. The set was originally proposed by Sauerbrei et. al. [5] and modified to account for poisoning effects.

$$x_2' [t] = k_3 * (F) * e^{k_6 * v[t]} - k_4 * x_2[t] * x_5[t] - k_5 * x_2[t] * e^{-k_6 * v[t]} \quad (1)$$

$$x_4' [t] = k_1 * (F)^2 * e^{k_6 * v[t]} - k_2 * x_4[t] \quad (2)$$

$$x_5' [t] = k_2 * x_4[t] - k_4 * x_2[t] * x_5[t] \quad (3)$$

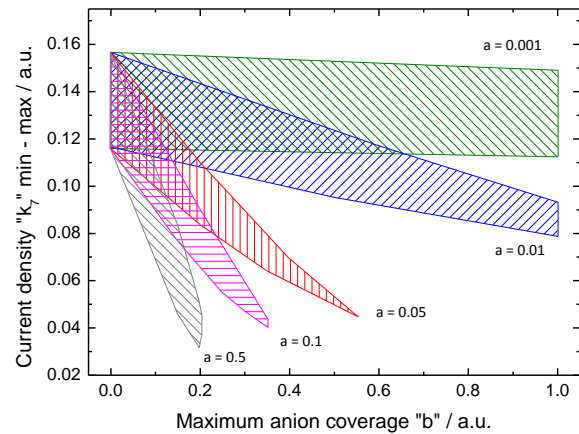
$$v' [t] = k_7 - k_1 * (F)^2 * e^{k_6 * v[t]} \quad (4)$$

$$\text{With: } F = 1 - x_2[t] - x_5[t] - 3x_4[t] - \frac{b * a * e^{k_6 * v[t]}}{1 + a * e^{k_6 * v[t]}}$$

Since electrochemical reactions occur at a surface there must be a term representing the quantity of it that is available for catalysis. Parameter “ $F$ ” accounts for it and is a function of the surface blocking adsorbed species. It also incorporates in its last term the effect of anion adsorption as a function of potential. In this term, “ $a$ ” represents the anion concentration whereas “ $b$ ” refers to the maximum amount that can block the surface. The anion adsorption step basically lowers the number of catalyst sites available for reaction. Anion inhibition was not present in the original model and its consequences will be further explored in the following analysis.

### RESULTS AND DISCUSSION

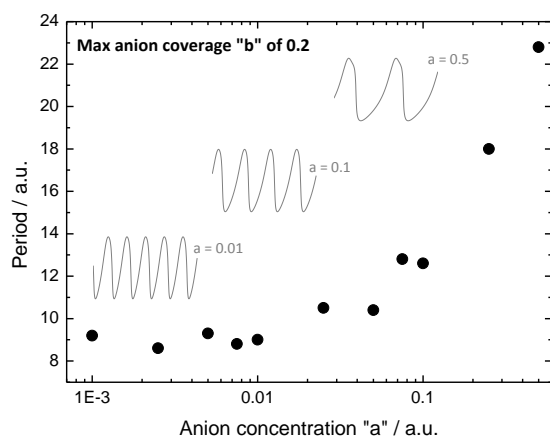
Figure 1 presents a bifurcation diagram for applied current ( $k_7$ ) as a function of maximum anion coverage for three different anion concentrations. Potential oscillations were found for parameters ranging inside the shaded areas.



**Figure 1-** Bifurcation diagram  $k_7 - b$  obtained employing three values of anion concentration “ $a$ ” and equations from 1 – 6. Other parameter values were:  $k_1=4$ ,  $k_2=10$ ,  $k_3=1$ ,  $k_4=2$ ,  $k_5=6$ ,  $k_6=15$ .

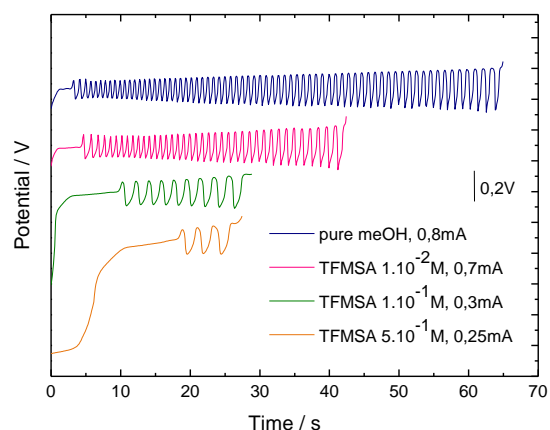
The effect of augmenting anion concentration is that oscillations occur at relatively lower values of applied current density and the window of parameters for which they can be found is reduced. This is chemically reasonable as the diminishment of the available area must have its counterpart on decreased values of current density for the applied current to have the same approximate values.

Keeping the maximum anion coverage “ $b$ ” at 0.2 and analyzing the effect of anion concentration “ $a$ ” on the potential oscillatory behavior it was constructed a curve representing the period’s dependence on anion concentration. The curve is shown at Figure 2 along with three temporal series collected for selected values of  $a$ .



**Figure 2 – The effect of anion concentration on the oscillatory period, along with some selected snapshots of potential time series. Period was calculated for time series at the upper  $k_f$  limit value for oscillation observation.**

Figure 2 shows a steady increase in the oscillation period (time difference between two consecutive potential peaks) for increasing anion concentration. It is noteworthy that the same behavior was observed experimentally for a system containing the anion TFMSA as can be seen at Figure 3.



**Figure 3 – Experimental potential oscillations during methanol oxidation on a polycrystalline platinum electrode for several anion concentrations. Base electrolyte was  $\text{HClO}_4$   $0.1\text{molL}^{-1}$ . Temperature was at  $25^\circ\text{C}$ .**

Experimental data shown in Figure 3 was obtained during oscillatory methanol oxidation on a polycrystalline platinum electrode under galvanostatic control. It can be observed that the oscillation period increases as the amount of anion increases. The general morphology of the observed oscillations also becomes less harmonic when the inhibiting condition is increased. Those features are qualitatively observed by the modified set of differential equations (see Figure 2).

## CONCLUSIONS

The modification proposed in the set of ODEs is very general. It only introduces a potential dependent blocking coverage on the calculation of the available catalyst sites. However, as intuited from the simulated behavior, control over the frequency of the kind of electrochemical oscillator presented here can be achieved just by this simple addition and correspondent adjustment of the applied current density. No specific adsorption or lateral interaction effects were necessary to reproduce experimental behavior.

From an electrochemical perspective the increased values of period should be observed for several different anions since their adsorption is raised for increasing values of potential, although particular specificities should be observed on the blockage function.

## REFERENCES

- [1] K. Krischer, “Principles of temporal and spatial pattern formation in electrochemical systems” Modern Aspects of Electrochemistry Vol. 32, B.E. Conway, J.O’M. Bockris, R.E. White eds., Kluwer Academic Publishers, New York, pp. 1-138, 2002.
- [2] K. Krischer, H. Varela, “Oscillations and other dynamic instabilities” Handbook of Fuel Cells: Fundamentals Technology and Applications Vol. 2, W. Vielstich, A. Lamm, H.A. Gasteiger eds., Wiley, Chichester, pp. 679-701, 2003.
- [3] M. Krausa, W. Vielstich, “Potential oscillations during methanol oxidation at Pt-electrodes. Part 1: experimental conditions” Journal of Electroanalytical Chemistry Vol. 399, pp. 7-12, 1995.
- [4] E.A. Carbonio, R. Nagao, E.R. Gonzalez, H. Varela, “Temperature effects on the oscillatory electro-oxidation of methanol on platinum”, Physical Chemistry Chemical Physics Vol. 11, pp. 665-670, 2009.
- [5] S. Sauerbrei, M. Nascimento, M. Eiswirth, H. Varela, “Mechanism and model of the oscillatory electro-oxidation of methanol” Journal of Chemical Physics, Vol. 132, pp. (154901-1)-(154901-10)