

## **Efeito de cátions, ânions e do pH em eletrocatalise estudado por meio de instabilidades dinâmicas**

### **Cation, Anion and pH effect in electrocatalysis studied by means of dynamics instabilities.**

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**Resumo:** Dynamic instabilities in electrochemical systems have been studied in the last decades focusing on both to obtain experimental data to build models that explain complex phenomena such as chaos and pattern formation and to reveal the mechanism of catalytic surface reactions.<sup>(1)</sup> Herein we show some contribution provided by our group to understand the effect of experimental parameters on electrochemical oscillations. Firstly, the methanol electro-oxidation reaction (MER) was studied in a wide pH range under voltammetric and oscillatory regimes, employing buffered hydrogen phosphates solutions.<sup>(2)</sup> Potential oscillations during MER are restricted to the pH < 3.5, with slight changes in oscillations frequency and shape, however poisoning rate decreases with the pH in this region. When MER is performed in non-adsorbing anions buffered solution (NaF/HClO<sub>4</sub>) with pH 5.6 the oscillations are present, indicating a phosphate adsorption role in MER mechanism which should be considered in wide pH range experiments. Maintaining the pH = 1.0 and adding anions such as Cl<sup>-</sup> and Br<sup>-</sup> in 1.5 to 6.0 μmol L<sup>-1</sup> range, the poisoning effect was studied by means of poisoning rate and apparent activation energy, the behavior being comparable with the observed with pH increase. The electrolyte cations also play a role on electrocatalytic reaction and influence the dynamics instabilities. Controlling the Pt(111)-OH<sub>ad</sub> stability by means of non-covalent interactions with hydrated cation it was possible to modify natural changes on galvanostat time-series collected during ethylene glycol (EG) electro-oxidation reaction studied in 5 to 20 °C temperature range. These modifications include time-series length, oscillations patterns and frequency changes. While more stable OH<sub>ad</sub> layer in Li<sup>+</sup> presence maintains both EG electro-oxidation and oscillations for longer times, Na<sup>+</sup> and K<sup>+</sup> allow the formation of surface oxides, which results in shorter time-series with fast change of maximum potential and oscillation frequencies for Na<sup>+</sup>-electrolyte. In the presence of K<sup>+</sup> besides short time-series length, oscillations were not observed. The cations also slight influence the Pt-H formation, but these modifications are sufficient to change the oscillation frequency and amplitude during H<sub>2</sub>O<sub>2</sub> electroreduction in alkaline media.<sup>(3)</sup>

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#### **Referências:**

- [1] E. G. Machado, H. Varela *in Encyclopedia of Interfacial Chemistry* 5 (2018) 701-718
- [2] G. B. Melle, *et al. J Electroanal Chem* 826 (2018) 164-169
- [3] K. N. Silva, R. Nagao, E. Sitta *ChemistrySelect* 2 (2017) 11713-11716