

Far from equilibrium electro-oxidation of small organic molecules: the use of *on line* Differential Electrochemical Mass Spectrometry (DEMS)

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The electro-oxidation of many small organic molecules on platinum and on platinum-based surfaces is known to display oscillatory kinetics under some circumstances. Examples include the spontaneous occurrence of current and/or potential oscillations. [1] More than mere curiosity, oscillations might reveal some mechanistic aspects that remain hidden under non-oscillatory regime.

We have recently reported the experimental investigation of the oscillatory electro-oxidation of methanol on platinum using *on line* Differential Electrochemical Mass Spectrometry (DEMS).[2] Concomitantly to the potential oscillations we followed the evolution of production of carbon dioxide and methylformate under oscillatory regime. We employed an integrated approach consisting of experiments, modeling and simulations, and were able to decouple the CO₂ production from direct and indirect pathways. Besides quantifying the contributions of parallel pathways, we have also investigated the impact of anion adsorption. [3] Our recent work using *on line* DEMS to study the oscillatory electro-oxidation of small organic molecules opens some interesting perspectives. In the present contribution we explore some possibilities in this direction for other systems.

Following the conservation of charge in the equivalent electrochemical circuit, we can compare the first time-derivative of the electrode potential with the faradaic contributions from the gaseous products detected by DEMS. Figure 1 shows results for the experimentally obtained time-traces of electrode potential and of carbon dioxide production. The first time-derivative of the electrode potential is also included.

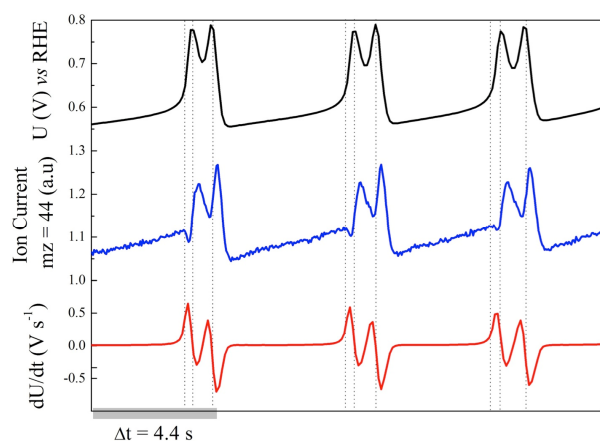


Figure 1: Time evolution of the electrode potential (top), the ion current for the production of carbon dioxide (middle), and dU/dt (bottom), for the galvanostatic electro-oxidation of formic acid on platinum.

As clearly seen in Figure 1 the time-series for the production of carbon dioxide is nicely mirrored by the dU/dt evolution. This fact reveals that the reaction current

registered during the oscillatory electro-oxidation of formic acid is fully represented by the complete oxidation to carbon dioxide, a rather simple process, which involves the transfer of only two electrons. For the case of methanol, we compared the dU/dt with the first derivative of the electrode potential with the faradaic contributions for the CO₂ and methylformate evolution. The results show that, in contrast to that for formic acid, the production of partially oxidized soluble products plays a significant role during the oscillatory electro-oxidation of methanol. The quantitative analysis shows that information obtained by means of this approach seems unique to the oscillatory regime and, thus, are not evident under regular regime. We are currently applying this approach to the electro-oxidation of ethanol, a complex molecule whose electro-oxidation involves more possibilities than the C1 species studied so far.

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