

The influence of anion adsorption on the parallel reaction pathways during the oscillatory electro-oxidation of methanol

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Introduction

The electro-oxidation of small organic molecules (e.g. formic acid, methanol, ethanol, etc.) is known to follow the dual pathway mechanism [1]. The direct pathway proceeds *via* reactive intermediates, which are quickly oxidized to carbon dioxide. On the other hand, the indirect pathway occurs in parallel and proceeds through the formation of adsorbed carbon monoxide (CO_{ad}), which reacts with adsorbed oxygenated species at high potentials *via* a Langmuir-Hinshelwood mechanism. Recently, we have reported the experimental decoupling of the parallel pathways during the electro-oxidation of methanol, under far from equilibrium conditions [2]. In the present contribution we profounder those investigations and report the influence that the supporting electrolyte exerts on the parallel pathways during the oscillatory electro-oxidation of methanol on platinum.

Experimental

The working electrode (real area of 3.9 cm²) was prepared by platinum sputtering deposition on a Teflon membrane (Gore-Tex, PTFE) with thickness of around 50 nm. A platinized electrode was used as a counter electrode while a reversible hydrogen electrode as a reference electrode. All electrochemical experiments were performed in solutions prepared with high purity water (Milli-Q, 18.2 MΩ cm), HClO₄ (Sigma-Aldrich, 71%), H₂SO₄ (Sigma-Aldrich, 98%), H₃COH (J.T. Baker, 99.9%) and controlled by the potentio/galvanostat (Autolab, PGSTAT 30). The cell temperature was kept constant at 20.0 ± 0.1 °C using a Cole-Parmer Polystat temperature controller. DEMS device was adapted to an electrochemical cell through two chambers system (Pfeiffer, Vacuum) in order to obtain an *on line* temporal resolution of around 0.1 s. A quadrupole (Pfeiffer, QMA 200) was utilized as analyzer with the mass/charge ratio (m/z) predetermined. The faradaic and mass currents were normalized by CO stripping charge and [CO₂]⁺ signal, respectively.

Results and Discussion

Figure 1 shows the potential time-series at $j = 0.35 \text{ mA cm}^{-2}$ followed by $m/z = 44$ (i.e. CO₂) and $m/z = 60$ (i.e. H₃COOH) in different electrolytes (plate a-c, HClO₄ and plate d-f, H₂SO₄). For each potential cycle there are at least three peaks of CO₂ associated for different process [2] in contrast to harmonic and out-of-phase oscillations of H₃COOH. Peak *i* (and *i'*) correspond to the CO₂ formation from the indirect pathway while peaks *ii*, *iii* (and *ii'*, *iii'*) from the direct pathway. The presence of (bi)sulfate in comparison of perchlorate anions results an increase in the oscillation period around 25% and a higher definition of the peaks for CO₂ time-series appeared.

Galvanostatic experiments were carried out from 0.20 to 0.40 mA cm⁻² and different profiles for the CO₂ peaks were observed. The contribution of the direct and indirect pathway was evaluated by deconvolution of the CO₂ peaks.

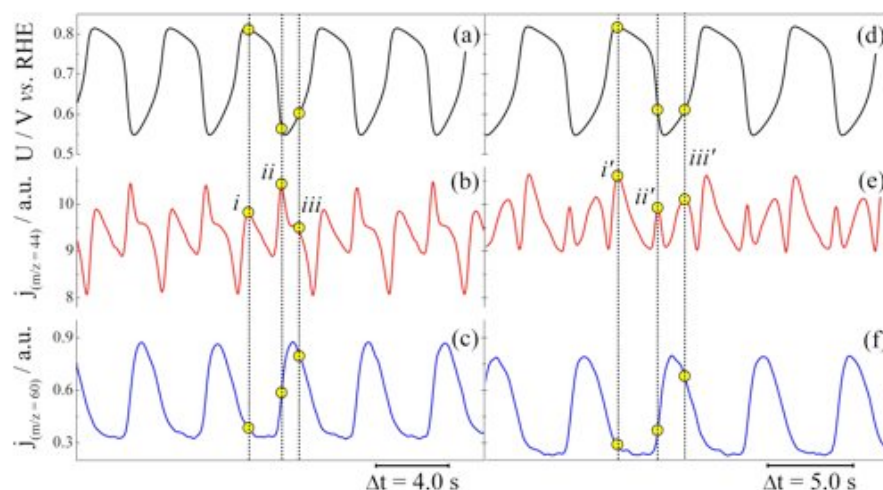


Figure 1: *Period-1* potential time-series during methanol electro-oxidation in perchloric (a-c) and sulfuric (d-f) acidic medias at $j = 0.35 \text{ mA cm}^{-2}$ accompanied by the mass fragments of $m/z = 44$ (b and e) and 60 (c and f). $[\text{H}_3\text{COH}] = 2.0 \text{ mol L}^{-1}$, $[\text{HClO}_4] = [\text{H}_2\text{SO}_4] = 0.5 \text{ mol L}^{-1}$ and $T = 20^\circ\text{C}$.

The overall CO_2 production increased with the applied current. The direct pathway seems to be predominant over the indirect pathway, contributing to about of 63 to 72% of the total CO_2 production. As oscillations evolve in time, there is an increase in the CO_2 production from the indirect pathway, whereas a decrease is observed along the direct route, this effect is less pronounced at higher applied currents, where a slight increase in the CO_2 contribution from the direct pathway is discernible at considerably long times. Similar dynamic behavior was observed also as function of the applied current.

Anion adsorption plays, if any, a minor role on the relative weight of parallel pathways. Besides H_3COOH , the overall production of CO_2 kept the same order of magnitude for both electrolytes, considering the same applied current.

Conclusions

Carbon dioxide produced from the direct and indirect pathways was measured separately under oscillatory regime during the electro-oxidation of methanol by means of *on line* DEMS. The overall production of H_3COOH and CO_2 is rather insensitive for nature of the electrolyte and the direct pathway is the majority chemical route for the conversion to CO_2 .

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References

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