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An OLEMS investigation of the electro-oxidation of ethanol on Pt and Pt_3Sn catalysts

N. Vilas-Bôas*, G. N. Tessaro, L. Hostert, A. G. S. Oliveira-Filho, J. Perez, H. Varela
São Carlos Institute of Chemistry, University of São Paulo
C.P. 760, 13560-970, São Carlos, SP, Brazil
**e-mail: naiza@usp.br*

The electro-oxidation of ethanol on platinum and platinum-based catalysts in acidic media produces acetic acid, acetaldehyde, and CO_2. Detecting those volatile species is critical for mechanistic analysis and, thus, for catalyst development, as well as applications such as fuel cells and electrolyzers. Herein, we report the experimental investigation of the dynamics of volatile species production during the oscillatory electro-oxidation of ethanol using online electrochemical mass spectrometry (OLEMS).[1] The gas diffusion electrode of Pt_3Sn/C (80% wt.) was synthesized using borohydride and compared to a commercial Pt/C (80% wt.) catalyst. We monitored the production of acetaldehyde (m/z = 25 and 29), carbon dioxide (m/z = 22 and 44), and acetic acid (m/z = 60) for both catalysts. Overall, Pt_3Sn/C decreased the onset potential compared to Pt/C along the voltammetric sweep. We estimated the production through multiple linear regression (MLR) [2] analysis of the ionic currents from carbon dioxide, acetic acid (including an estimated current to account for the suppression of the response from volatile species), and acetaldehyde in relation to the total faradaic current. The MLR allowed us to identify the optimal contribution of each ionic current to match the total faradaic current, providing an estimate of the maximum possible faradaic contribution and clarifying the role of individual species in the overall electrochemical process. This analysis demonstrates that most of the faradaic current arises from acetic acid and acetaldehyde species. Furthermore, the MLR reveals that the adsorption mechanism of the species differs between Pt/C and Pt_3Sn/C catalysts, highlighting a distinct role for the Sn-containing alloy in the ethanol electro-oxidation mechanism. The interplay among the potential-dependent adsorption isotherms of different adsorbates might give rise to oscillations in those systems,[3] and the resulting potential oscillations might impact the activity and the overall conversion. During the galvanostatic experiments, the bimetallic Pt_3Sn/C electrode exhibited oscillations at lower potentials (ca. 0.7 V), while Pt/C oscillated around 1 V. Regarding the products detected during the oscillatory regime, it was possible to observe simultaneous oscillation of the products and different waveforms between the electrocatalysts. Pt/C showed a more pronounced decline in signs product as the potential stabilized, as observed by OLEMS; in contrast, the Pt_3Sn/C electrode displayed a more constant behavior and demonstrated mitigation in the poisoning effect. These findings highlight the importance of precise control over reaction conditions to optimize the selectivity and efficiency of ethanol electro-oxidation, contributing to the development of more efficient and sustainable electrochemical processes. The combination of conventional cyclic voltammetry and potential oscillations provided relevant mechanistic aspects, particularly in terms of the evolution of volatile species.

References

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