The oscillatory electro-oxidation of small organic molecules: Coupled disparate time-scales and the evolution of surface fine structure

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The electro-oxidation of small organic molecules (formic acid, methanol, ethanol, glycerol, etc.) is often accompanied by kinetic instabilities in the form of oscillations and multi-stability. The importance of studying such reactions is primarily due to their relevance in energy conversion systems and a considerable development in this field has been reached recently. It has been recently shown by our Group at University of Sao Paulo that studying some reactions under oscillatory regime might provide key mechanistic information. It is presented in this talk the latest works developed regarding the oscillatory electro-oxidation of small organic molecules on platinum, platinum-based, and gold surfaces. The results are focused on the dynamics, mechanism and efficiency, including half-cells (poly- and single crystals and modified surfaces), and polymer electrolyte membrane (PEM) reactors, and are discussed in connection with the current literature. An important aspect to be presented in depth is the effect of surface defects on the oscillatory electro-oxidation of methanol. Experiments were carried out on Pt(100) surfaces with different degrees of random surface defects and results discussed in terms of short and long term evolutions of oscillations and surface structure. Finally, some perspectives and directions for future research are also presented.

PeakForce scanning electrochemical microscopy for nanoscale multimodal imaging: Topography, nanomechanics, nanoelectrics and electrochemistry

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Studies of reactivity heterogeneity on the nanoscale require approaches capable of simultaneously capturing correlated multidimensional information. In situ, in vivo, non-invasive methodologies are also inevitable, e.g. for battery and biological research. Scanning electrochemical microscopy (SECM) is the only approach for studying local electrochemistry. Classic SECMs generally face challenges on the distance control between tip and sample (essential for obtaining accurate electrochemical information), low spatial resolving power (typically >µm), and capture either only electrochemical information or only low-quality surface topography. SECM based on atomic force microscopy (AFM-SECM) can potentially overcome these issues. However, high-quality and high-consistency nanoelectrode AFM probes with a characteristic dimension <100 nm are not easily fabricable. Furthermore, classic contact mode is not suited for imaging highly soft and fragile samples (e.g. biological or energy materials). Tapping mode minimizes shear forces, but its mechanical resonance dependence poses difficulties for imaging in liquid or when ambient temperature varies. Recently, we have developed batch-fabricated, high-quality and robust SECM probes (exposed Pt tip with ~200 nm height and ~50 nm end diameter). Their robustness allows >10 h continuous electrochemical testing with an ease-of-use focus. Together with our recently developed PeakForce Tapping (PFT) mode, which features intermittent sample contact without shear forces, directly controlled imaging forces as low as <50 pN, and quantitative mechanical mappings at normal AFM scan rate, in situ, in vivo, non-invasive, stable imaging for challenging fragile and soft samples gets possible. High-quality SECM probes with PFT (PeakForce SECM) access multidimensional information in the electrochemical environment with <100 nm spatial resolution, including topographic, conductivity, mechanical, and electrochemical properties. This presentation showcases a variety of application examples using PeakForce SECM, including catalysis, surface defects on lamellar, patterned nanostructured electrodes, and nanoelectric measurements in liquid, demonstrating the versatility of PeakForce SECM for today's highly-multidisciplinary research.