Time-resolved Infrared Studies of Potential Oscillations during Galvanostatic Oxidation of Formic Acid on Pt

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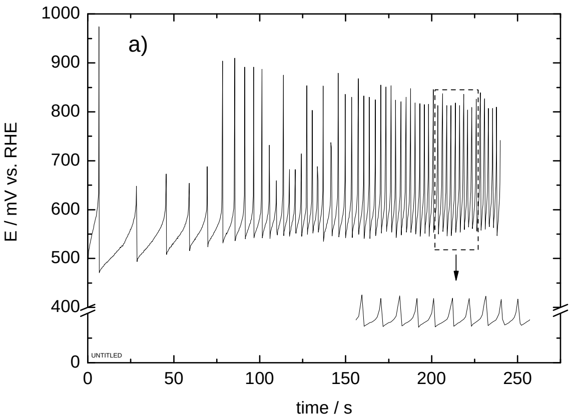
Introduction- Oscillating chemical reactions have attracted a great deal of interest in the past decades. During the electrochemical oxidation of small organic molecules like methanol, formaldehyde, and formic acid oscillations of potential (under galvanostatic conditions) or current (under potentiostatic conditions) have been observed for a long time. It is widely accepted that the oxidation of these molecules follows a so-called “dual-path” mechanism.[1] The indirect path goes via the adsorption of CO, a poisonous intermediate, whereas the direct path describes the direct oxidation of these molecules. At low potentials, the Pt sites are blocked by CO and the direct path is consequently inhibited. At higher potentials, CO is oxidized and only the direct path contributes to the reaction. In a certain mid-range potential region, both reaction paths are possible but interfere with each other. The amplitude of the potential oscillations lies within this potential region. Using time-resolved, surface enhanced infrared absorption spectroscopy (SEIRAS), we were able to monitor the nature and coverage of the adsorbates during the oscillations. The main advantage of SEIRAS compared to conventional IRAS lies in the high sensitivity, which enables time-resolved spectral acquisition.

Experimental- The conventional 3 electrode setup contained a hemicylindrical Si prism having an electroless deposited Pt layer on its flat plane as the working electrode.[2] Potentials were monitored by a reversible hydrogen electrode (RHE) electrode. An EG&G 263A potentiostat/galvanostat and a BIORAD FTS-60A/896 FT-IR spectrometer equipped with a MCT detector, set to an optical resolution of 4 cm^{-1}, were used for the experiments. The electrolyte was a 0.5 M H_2SO_4 solution.

Results and discussion- After verifying the quality of the Pt film by recording a cycling voltammogram the electrochemical oxidation of a monolayer of adsorbed CO was monitored by IR spectroscopy. Thus, a reference for the coverage by CO was obtained. Following this, an appropriate amount of formic acid was added to obtain a 1 M HCOOH containing electrolyte. After switching to the galvanostatic mode, stable oscillations were obtained for various applied currents and monitored by time resolved IR spectroscopy, as can be seen for an applied current of 10 mA from Figure 1. The pattern of the potential oscillations is characterized by sharp spikes separated by regions in which the potential slowly rises. The IR spectra show bands for adsorbed CO (linear bonded at 2069 and bridge bonded at 1830 cm^{-1}) and a band at 1320 cm^{-1} that is ascribed to adsorbed formate.[3] The intensity for the formate band increases with increasing potential whereas the bands for CO show an opposite behavior. As can be seen from the IR spectra, both species are adsorbed at the electrode during the oscillations. These findings show that both reaction paths are followed simultaneously during the oscillations but the ratio of these varies periodically with time. In the low potential state, more Pt sites are blocked by CO and the indirect path is favored to maintain the overall reaction rate. The mechanism of the potential oscillation will be discussed based on a detailed analysis of the spectral data.



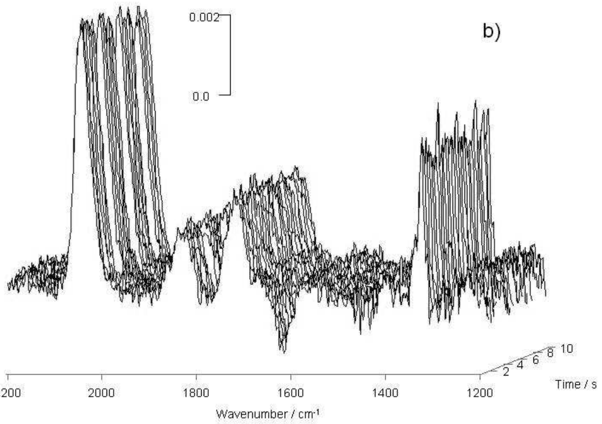


Figure 1: (a) Galvanostatic oscillations, applied current 10 mA, (b) in situ recorded series of IR spectra, time resolution 80 ms

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