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Electrooxidation of formic acid on a polycrystalline Au film electrode–A comparison with mass transport limited bulk CO oxidation and kinetically limited oxalic acid oxidation

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ABSTRACT

We have investigated in a comparative spectro-electrochemical study the oxidation of formic acid on a polycrystalline Au film electrode on the one hand and the transport limited bulk CO oxidation as well as the kinetically limited oxalic acid oxidation on the other hand. Employing in situ FTIR spectroscopy in an attenuated total reflection configuration (ATR-FTIRS) as well as online differential electrochemical mass spectrometry (DEMS), potentiodynamic and potentiostatic measurements were performed under enforced mass transport conditions in a dual thin-layer flow cell. The simultaneous information on the dynamic evolution of Faradaic current, adsorbed species and volatile reaction products, in combination with information gained from isotope labelling experiments, utilizing kinetic isotope effects, and comparison with CO bulk oxidation and oxalic acid oxidation, leads to new insights on the formic acid oxidation reaction on Au and the contributing reaction pathways. The data demonstrate, e.g., that in the low potential regime (0.2–0.4 V_{RHE}) in potentiodynamic measurements the Faradaic current results mainly from formate adsorption rather than from complete oxidation to CO_2, and that in the high potential regime (>1.2 V_{RHE}) dimerization, most likely of adsorbed formate species, results in adsorbed bioxalate formation, which can subsequently either desorb or decompose to CO_2.

1. Introduction

The electrooxidation of formic acid on noble metal electrodes, in particular on Pt electrodes, has often been considered as a particularly simple example for the oxidation of organic molecules, since it results in a single product, CO_2, only. It has been proposed already >40 years ago that formic acid oxidation to CO_2 on a Pt electrode proceeds via two different pathways, an 'indirect pathway' involving formation and oxidation of adsorbed CO, and a 'direct' pathway, where CO_2 is formed directly, without formation/oxidation of CO_{ad} [1,2]. Adsorbed CO was soon identified as a poisoning intermediate in the indirect pathway during formic acid oxidation on Pt electrodes in early spectro-electrochemical studies [3–5], while details of the direct pathway remained unclear and subject to speculation. The mechanistic discussion was re-started after Osawa and coworkers identified the formation of a bridge-bonded adsorbed formate during formic acid oxidation [6], but also during oxidation of methanol [7] and formaldehyde [8]. They proposed that the direct pathway proceeds via the adsorption of formic acid to formate in a one-electron reaction, followed by decomposition of adsorbed formate to CO_2 with the release of a second electron [9]. In an alternative mechanistic model, the adsorbed bridge-bonded formate species were considered to represent spectator species rather than reaction intermediates, leaving the exact nature of the active intermediate in the direct pathway open [10–13]. Despite numerous studies on the reaction kinetics [6,9,11–24], and, more recently, also on the influence of the pH on the reaction kinetics [25–28], the discussion on the mechanism governing the direct pathway for formic acid oxidation is still going on. Theoretical studies, mainly based on density functional calculations with different extents of considering the electrochemical environment also led to contradictory conclusions on the role of adsorbed formate in formic acid oxidation to CO_2 [29–35].

Because of the intense debate on the role of the bridge-bonded adsorbed formate species in the reaction, which was typically limited to "either–or" conclusions, other aspects of the reaction process, in particular the potential dependence of the reaction kinetics and reaction pathways or temporal variations in the reaction rate obtained much less attention. This is topic of the present work, where we explore the electrooxidation of formic acid oxidation on a polycrystalline gold film electrode by in situ infrared FTIRS in an attenuated total reflection configuration (ATR-FTIRS) and by online differential electrochemical mass spectrometry (DEMS) under enforced electrolyte flow. The Au electrode was chosen since on Au the reaction is known to proceed without detectable formation of CO_{ad} [21,36,37], which reduces the complexity of

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the reaction. Based on careful comparison of the Faradaic current, the CO_2 formation rate and the formation/removal of adsorbed species we want to elucidate whether there are additional processes contributing to the measured Faradaic current under specific reaction conditions. Further information shall be gained by identifying kinetic isotope effects (KIEs) in the formic acid oxidation reaction, by comparing the reaction kinetics and the rates of formic acid oxidation/CO_2 formation on HCOOH and on the deuterated analogon DCOOH. Here we assume that if the ratio of the respective rates is close to one, the C—H bond remains intact or C—H bond breaking is not involved in the rate limiting step, while for significantly higher values the latter is the case. For comparison and as reference for the formic acid oxidation reaction, we also investigated the bulk oxidation of CO to CO_2 [38] and oxalic acid oxidation to CO_2 [39] under similar reaction conditions, focusing on aspects relevant for formic acid oxidation such as the role of mass transport in bulk CO oxidation, the correlation between Faradaic current and CO_2 formation (in both reactions) or the identification/exclusion of reaction intermediates in the formic acid oxidation reaction which had not been considered so far.

In the following, we will after a brief description of the experimental details first present and discuss the combined ATR-FTIRS/DEMS results obtained for bulk CO (Section 3.1) and oxalic acid oxidation (Section 3.2) on a polycrystalline gold electrode under well-defined mass transport conditions. This is followed by analogous measurements for HCOOH oxidation (Section 3.3) and for DCOOH oxidation (Section 3.4). The latter section includes a detailed discussion of kinetic isotope effects in different reaction pathways and their correlation with CO_2 current efficiencies. Finally we use these data to calculate the different contributions to the Faradaic current in potentiodynamic formic acid oxidation on a Au film electrode (Section 3.5). The main findings and conclusions from these results are discussed in a comprehensive picture in Section 4 and finally summarized in the Conclusions.

2. Experimental

A thin (~50 nm thickness) Au film was prepared by electroless deposition [40] onto the planar face of a hemi-cylindrical Si prism, followed by careful annealing in a butane flame under a continuous flow of nitrogen [41]. This should improve the film adhesion to the Si substrate and thus the stability against the continuous electrolyte flow in a thin layer flow cell. The roughness factor of the resulting film of around 3.5 was determined from the Au oxide reduction charge (Supporting Information-SI, Fig. S1) and the exposed geometric area (ca. 0.8 cm^{-2}). A Au film thickness of 55 ± 5 nm was derived from atomic force microscopy imaging (Nanosurf Flex AFM 5) (SI, Fig. S2). For the measurements, the Au film covered planar face of the Si prism was pressed against the flow cell body fabricated from Kel-F. A circular gasket of ~1 cm inner diameter (thickness ca. 50 μm) between prism and cell body resulted in a thin layer cell with a volume of about 10 μl. The electrolyte entered the cell via an inlet capillary opening in the center of the cell, which was surrounded by six outlet capillary openings close to the gasket. These led to a second thin-layer compartment, which was closed off to the outside by a porous Teflon membrane (Scimat, 60 μm thick, 50% porosity, 0.2 μm pore size) supported on a stainless steel frit. Online detection of the gaseous products formed at the Au film electrode was facilitated by a mass spectrometer (Pfeiffer Vacuum, QMS 422) in an ultrahigh vacuum (UHV) chamber, where the latter was connected to the cell by a bellow, with the membrane separating it from the electrolyte [42,43]. A time delay of ca. 1 s between Faradaic and mass spectrometric currents, reflecting the time required for transporting the reaction products from the electrode to the second compartment in the flowing electrolyte, was estimated from potential-step experiments and corrected accordingly.

The DEMS setup was calibrated using CO_2 formation in the CO bulk oxidation reaction by calculating the calibration constant $K^* = (n \cdot I_{MS}) / I_F$ [44], where n stands for the number of electrons per CO_2 molecule formation ($n = 2$ for oxidation of CO and formic acid to CO_2, and $n = 1$ for oxidation of oxalic acid to CO_2), and I_{MS} and I_F are the ion current for $m/z = 44$ and the Faradaic current, respectively. Using the K^* value determined this way, the mass spectrometric ion currents can be converted into partial Faradaic currents for CO_2 formation in CO bulk oxidation and formic acid oxidation. The current efficiency for CO_2 formation (CCE) was calculated as the ratio of the partial current for CO_2 formation and the measured Faradaic current. The kinetic H/D isotope effect was calculated either as the ratio of the Faradaic currents or of the mass spectrometric currents, respectively, during HCOOH and DCOOH oxidation over the Au film electrode.

The Si prism together with a homemade mirror accessory formed a single beam attenuated total reflection configuration (incident beam angle ca. 60°), which was located in the sample chamber of a Cary 680 FTIR spectrometer (Agilent Technologies). The latter was equipped with a p-polarizer and a liquid nitrogen cooled mercury cadmium telluride detector. The infrared spectroscopy measurements were performed at a spectral resolution of 4 cm^{-1} and a temporal resolution of one second *per* spectrum (by co-adding 5 interferograms), using p-polarized light. The reference spectra were sampled at the potentials indicated in N_2-saturated supporting electrolyte. The spectra are presented in the absorbance mode, i.e., as $\log(R_0/R)$, where R_0 and R are the reflectances at the reference potential in supporting electrolyte, and at the sample potential in CO-saturated or 0.1 M formic acid/0.5 mM oxalic acid containing solution, respectively. Such data processing results in spectra with peaks pointing up for an increased absorption in R with respect to R_0, and peaks pointing down for a loss of absorption in R compared to R_0.

Two Pt counter electrodes were used, located in separate compartments at the inlet and outlet of the thin layer cell, respectively. A reversible hydrogen electrode, which was connected to the outlet of the cell via a Teflon capillary, served as reference electrode. All potentials are quoted, however, against that of the reversible hydrogen electrode (RHE). The potential of the working electrode was controlled by a Pine Instruments potentiostat (model AFRDE5), the current-voltage characteristics were acquired by a computerized data acquisition.

1.0 M solution of perchloric acid (Merck, suprapur) and Millipore MilliQ water (18.2 MΩ cm) were used as a supporting electrolyte. Electrolytes were prepared by adding oxalic acid (Merck, analytical grade) to obtain 0.5 mM oxalic acid solution, or by adding formic acid (Merck, analytical grade)/D1-formic acid (95 D%, Sigma-Aldrich) to obtain 0.1 M (deuterated) formic acid solution. CO saturated electrolyte was prepared by bubbling CO (Messer-Griesheim, N4.7) through the electrolyte, which results in a saturation concentration of ca. 1 mM at ambient temperature. Otherwise all electrolytes in the supply bottles were continuously purged with high purity N_2 (Westfalen Gas, N4.8) before and during the experiment. The electrolyte flow rate of ca. 50 μL s^{-1} was driven by the hydrostatic pressure; maintaining a constant electrolyte height in the supply bottles ensured a constant flow rate and also a constant collection efficiency of the membrane inlet system to the mass spectrometer.

3. Results

3.1. CO bulk oxidation on a Au film electrode

CO bulk oxidation was studied for comparison since it also involves formation of CO_2 as only product, in a two electron process, and to address effects arising from mass transport limitation and from Au surface oxidation. Furthermore, this reaction was used to calibrate the ion current for CO_2 formation. Fig. 1 shows simultaneously recorded Faradaic currents (as measured: full line) and as derived from mass the spectrometric current (circles) (a), the $m/z = 44$ ion current (b), the integrated band intensities of linearly bonded adsorbed CO (CO_L) (c), and a sequence of ATR-FTIR spectra (each 5th displayed, reference spectra acquired at 0.0 V in N_2-purged supporting electrolyte) recorded during