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.


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