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Adsorption and electrooxidation of ethylene glycol and its C_2 oxidation products on a carbon-supported Pt catalyst: A quantitative DEMS study

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ABSTRACT

Aiming at a better understanding of ethylene glycol oxidation, the adsorption and oxidation of ethylene glycol and its incomplete C_2 oxidation products glycol aldehyde, glyoxal, glycolic acid, glyoxylic acid and oxalic acid on carbon supported Pt catalysts were investigated by on-line differential electrochemical mass spectrometry (DEMS) under continuous electrolyte flow. This includes adsorption transients at different, constant potentials, oxidative removal ('stripping') of the resulting adsorbates, and potentiodynamic bulk oxidation/reduction of the respective molecules. The data show a pronounced influence of the different functional groups on the adsorption and oxidation characteristics, with hydroxyl and carboxylic functions resulting in lower adsorption rates and pronounced potential effects, while aldehyde functions lead to high adsorption rates at all potentials. The potential effects in the adsorption rate are mainly ascribed to surface blocking by H_{upd} species. For aldehydes and acids, CO_2 formation occurs already at potentials below the onset of OH_{ad} formation, which is ascribed to the decomposition of the carboxylic group or of the diol groups of hydrated aldehydes. The contributions of different reaction pathways, including: (i) 'direct' oxidation to CO_2, (ii) indirect oxidation to CO_2 *via* formation and further oxidation of CO_{ad}, and (iii) incomplete oxidation to more highly oxidized C_2 species, with the possibility of their further reaction *via* re-adsorption and reaction along (i)–(iii), are discussed.

1. Introduction

In the last decades, the electrooxidation of ethylene glycol (EG) has attracted considerable attention due to its potential application in fuel cells and as a model C_2 compound in electrocatalysis [1–7]. The observation of a large variety of incomplete oxidation products (glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid and oxalic acid), which were detected by in situ infrared spectroscopy [1,5,8–17] or by chromatographic product analysis [1,12,16,18–21] on the one hand and of strongly adsorbed or soluble C_1 species such as CO_{ad} [1,5,8–11,13,15–17] formic acid, and formaldehyde [21], respectively, led to the conclusion that EG oxidation can proceed *via* two different pathways (see Fig. 1). The first pathway involves C–C bond breaking and subsequent oxidation of the C_1 fragments; in the other pathway, the reaction proceeds *via* sequential oxidation of the functional groups without attacking the C–C bond. This results in the various C_2 molecules listed above. Following the 'desorption–re-adsorption–further reaction' reaction scheme proposed recently for the oxidation of methanol and formaldehyde [22–25], we assume that the incomplete oxidation products can re-adsorb on the electrode or catalyst surface and undergo either dissociative adsorption to produce $C_{1,ad}$ species or further oxidation of the functional groups, as described above for the adsorption/oxidation of EG. For reaction in acid electrolyte at room temperatures and potentials below 0.9 V, this reaction sequence stops at the stage of oxalic acid formation, which cannot be oxidized under these conditions [26].

In such kind of consecutive reaction, the formation and subsequent re-adsorption—further reaction of the desorbed incomplete oxidation products will play an important role, and, therefore, a detailed knowledge of the adsorption/oxidation behavior of these C_2 molecules is a key element for the mechanistic understanding of the EG oxidation reaction and its characteristics in Direct Alcohol Fuel Cells. Furthermore, the strongly bound 'poisoning' species may both affect the catalytic activity and modify the selectivity during the ongoing reaction, e.g., *via* a reduced number of free Pt sites or a decreased number of free pairs of Pt sites (reaction ensembles), which were proposed to be required for dissociative adsorption of the respective molecules [18,19]. The tendency for dissociative adsorption, on the other hand, depends on the functional groups (alcohol, aldehyde and carboxylic function) present in the oxidation intermediates. For instance, the different functional groups present in the incomplete EG oxidation products (glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid and oxalic acid) were found to affect

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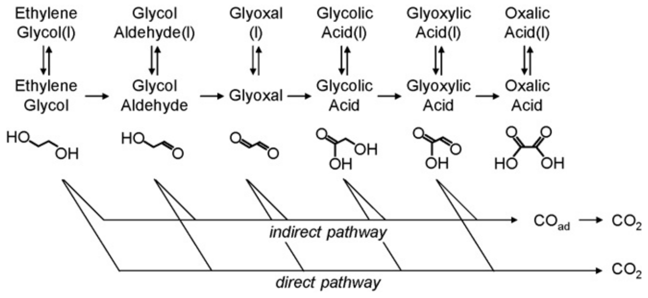

Fig. 1. Reaction scheme for the electrooxidation of ethylene glycol. For reaction in acidic electrolyte at room temperatures and potentials below 0.9 V, the reaction stops at the stage of oxalic acid, which cannot be oxidized under these conditions. Desorption, re-adsorption and further oxidation of the reactive C_2 intermediates increase the formation of higher oxidized reaction products with increasing space velocity. (l) denotes the dissolved species, no index stands for the molecularly adsorbed species ('adsorption precursor').

the adsorption kinetics of these C_2 molecules and the composition of the adlayer [18]. This behavior closely resembles our previous observation of pronounced differences in the adsorption/oxidation behavior of ethanol [27–29] and acetaldehyde [27,30] on a Pt/C catalyst. Also from a practical point of view, C–C bond splitting plays an important role in the oxidation of C_2 molecules. First of all, complete oxidation to CO_2 ensures an efficient utilization of the fuel. Moreover, the emission of incomplete oxidation products is highly undesirable due to their high toxicity. Finally, because of the contribution of re-adsorption—further reaction effects at each stage of the reaction, it is mandatory to perform experimental studies under continuous electrolyte exchange in order to minimize the above mentioned effects, rather than adsorbing from ill-defined mixtures which are produced *via* accumulation of by-products in the electrolyte in the absence of continuous electrolyte exchange.

These issues were topic of recent and ongoing studies in our laboratory, where we investigated the adsorption and oxidation behavior of EG and its incomplete oxidation by-products on different carbon supported noble metal catalysts under realistic flow conditions by differential electrochemical mass spectrometry (DEMS). First results on the interaction of EG with Pt/C, PtRu/C and Pt_3Sn/C catalyst electrodes, which for the Pt/C catalyst also included the influence of reaction parameters such as EG concentration, potential scan rate or catalyst loading, were reported in Refs. [31,32]. In all cases, the current efficiency for CO_2 formation during EG oxidation was found to not exceed a few percent at ambient temperatures. Accordingly, large amounts of incomplete oxidation products are formed under these conditions, which, however, cannot be directly monitored by DEMS due to their low volatility.

In the present paper, we will focus on the adsorption and dissociation of EG and its oxidized C_2 derivatives glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid and oxalic acid upon their interaction with a commercial Vulcan XC-72 carbon supported Pt/C catalyst (E-Tek Inc., 20 wt.% Pt) at different constant potentials at ambient temperatures. The composition and coverage of the resulting adsorbates will be evaluated from quantitative adsorbate electrooxidation in supporting electrolyte ('adsorbate stripping'). Next, we will describe and discuss potentiodynamic DEMS measurements for electrooxidation of the C_2 molecules on the Pt/C catalyst under continuous mass transport to specifically address how the functional groups are affecting the overall electrochemical response and the current efficiency for CO_2 formation. Finally, we will address the implications of the present findings for the understanding of the complex network of adsorption and electrooxidation processes occurring during electrocatalytic EG oxidation under steady-state conditions.

2. Experimental

The DEMS set-up and the preparation of the thin-film electrode were described in detail in previous publications [33,34]. In short, the DEMS set-up consists of a differentially pumped dual-chamber ultrahigh vacuum system equipped with a quadrupole mass spectrometer (Balzers QMS 112), a Pine Instruments potentiostat and a computerized data acquisition system.

The thin-film Pt/Vulcan catalyst (20 wt.%, E-Tek Inc.) electrodes for the DEMS measurements were prepared by pipetting and drying 20 μl of aqueous catalyst suspension (2 mg ml^{-1}), and then 20 μl aqueous Nafion solution in the center of mirror polished glassy carbon disks (Sigradur G from Hochtemperatur Werkstoffe GmbH, 9 mm in diameter). The catalyst thin film has a diameter of ca. 6 mm, a geometric surface area of 0.28 cm^2, and a Pt loading of 28 μg/cm^2.

The thin-film electrode was mounted in a dual thin-layer flow cell [35,36] and pressed against a ca. 100 μm thick spacer. This results in an electrolyte volume of ~5 μl at the working electrode. The electrolyte flow was enforced by the hydrostatic pressure in the supply bottle (flow rate about 35 μl s^{-1}), ensuring a fast transport of the species formed at the electrode to the mass spectrometric compartment (time delay ca. 1 s), where the volatile products were evaporated into the mass spectrometer through a porous membrane (Scimat, 60 μm thick, 50% porosity, 0.2 μm pore diameter). Two Pt wires at the inlet and outlet of the thin-layer cell, connected through an external resistance (1 MΩ), were used as counter electrodes. A saturated calomel electrode (SCE), connected to the outlet of the DEMS cell through the Teflon capillary, served as reference electrode. All potentials, however, are quoted against that of the reversible hydrogen electrode (RHE).

2.1. Electrochemical measurements

The chronoamperometric measurements of the current transients were performed using two electrolyte supply bottles, one with supporting electrolyte and the other one with a solution containing 0.1 M ethylene glycol or its oxidative derivatives. The bottles were connected to the common inlet of the thin-layer flow cell. This set-up ensures a constant and continuous mass transport to the electrode during adsorption, and allows a fast electrolyte exchange, which is necessary for adsorption transients at constant potential. The Faradaic current transients on a clean Pt/Vulcan catalyst and the corresponding mass spectrometric signals of CO_2 (m/z = 44) were measured for about 5–6 min at constant electrode potential, after switching from the pure supporting electrolyte to the solution containing EG or the respective oxidative derivatives. The adsorption time is started (t = 0) upon arrival of the reactant at the electrode detected by the Faradaic current.

The supporting electrolyte (0.5 M H_2SO_4) was prepared from Millipore Milli-Q water and ultrapure sulfuric acid (Merck). Ethylene glycol (p.a.), glyoxal (40% solution in water, for synthesis), glycolic acid (p.a.), glyoxylic acid monohydrate (for synthesis) and oxalic acid dehydrate (p.a.) were obtained from Merck, glycoaldehyde dimer (≥98%) from Fluka (Sigma–Aldrich) and CO from Messer-Griesheim (N4.7). Before the measurements, all solutions were deaerated by high-purity Ar (MIT Gase, N6.0). Adsorption/stripping and bulk oxidation of the various C_2 species were performed at room temperature (23 ± 1 °C).

2.2. Adsorption rate evaluation

The adsorption rates were determined from the Faradaic current transients upon exposure of the working electrode to the electrolyte containing the respective C_2 molecules at a fixed potential ('chronoamperometric transients'). The electrolyte exchange results in an initial current peak, whose maximum current is con-