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## Modification of a Pt surface by spontaneous Sn deposition for electrocatalytic applications. 2. Oxidation of CO, formaldehyde, formic acid, and methanol

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**Abstract** The electrocatalytic activity of a spontaneously tin-modified Pt catalyst, fabricated through a simple “dip-coating” method under open-circuit conditions and characterized using surface analysis methods, was studied in electrooxidation reactions of a preadsorbed CO monolayer and continuous oxidation of methanol, formic acid, and formaldehyde in the potentiodynamic and potentiostatic modes. The catalytic activity of the tin-modified Pt surface is compared with that of a polycrystalline Pt electrode. Spontaneously Sn-modified Pt catalyst shows a superior activity toward adsorbed CO oxidation and thus can be promising for PEFC applications. The methanol oxidation rate is not enhanced on the Sn-modified Pt surface, compared to the Pt electrode. Formic acid oxidation is enhanced in the low potential region on the Sn-modified surface, compared to the Pt electrode. The formaldehyde oxidation rate is dramatically increased by modifying tin species at the most negative potentials, where anodic formaldehyde oxidation is completely suppressed on the pure Pt electrode. The results are discussed in terms of poisoning CO intermediate formation resulting from dehydrogenation of organic molecules on Pt sites, and oxidation of poisoning adsorbed CO species via the surface reaction with OH adsorbed on neighboring Sn sites.

**Keywords** Tin-modified Pt · Electrooxidation · CO · Methanol · Formic acid · Formaldehyde

### Introduction

The key problem for low-temperature polymer electrolyte fuel cells (PEFCs), operating on hydrogen (produced by reforming of hydrocarbons) or methanol (in a direct methanol fuel cell, DMFC) feed, is the CO tolerance of the anode catalyst. Pt is one of the best catalysts for H–H or C–H bond dissociation and, therefore, indispensable for PEFC and DMFC applications. However, Pt is also highly sensitive to CO poisoning: the catalyst surface is progressively poisoned by the adsorbed CO, which is present as a trace contaminant in hydrogen feed, or is formed as a result of the stepwise dehydrogenation of methanol [1]. Poisoning CO<sub>ad</sub> species can be oxidatively removed from the Pt surface through a Langmuir–Hinshelwood-type surface reaction with neighboring OH<sub>ad</sub> species electrosorbed from water at more positive potentials [2]. Thus, alloying of Pt with oxophilic metals, such as Ru or Sn, enables electrochemical dissociation of water on nonnoble metal sites at more negative potentials compared to pure Pt and, therefore, allows electrocatalytic oxidation of adsorbed CO at lower anodic overpotentials. The latter model is referred to as a bifunctional mechanism [3, 4] derived to explain a superior catalytic activity of PtRu alloys in the electrooxidation of CO<sub>ad</sub> and methanol [5].

PtSn catalysts demonstrate a superior activity toward electrooxidation of preadsorbed CO and the residues derived upon adsorption of small organic molecules [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18], as well as bulk (continuous) oxidation of CO and hydrogen/CO mixtures [19, 20, 21]. Therefore, these catalysts deserved great attention as promising candidates for possible applications as anode material in low-temperature PEFCs, including DMFCs. Although a superior performance of PtSn catalysts for PEFC applications is widely proved [22, 23, 24], their activity in the electrooxidation of methanol is still under discussion—an enhanced catalytic activity for PtSn catalyst in the methanol oxidation reaction (MOR) [25, 26, 27], in contrast to no/

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negligible enhancement of the MOR rate over PtSn catalysts [17, 18, 19, 20, 21, 23], is reported. On the other hand, some enhancement of the formic acid oxidation rate [26, 27, 28] and significant increase in the formaldehyde oxidation rate by PtSn, compared to pure Pt, is recognized [29, 30]. The latter molecules are known to be intermediates formed in the electrooxidation of methanol [31, 32, 33, 34, 35, 36] and, therefore, their electrooxidation appears to be an important issue related to DMFC operation in terms of both current efficiency and the emission of incomplete methanol oxidation products.

In a previous communication we explored a simple method for spontaneous modification of a Pt surface by tin species via “dip-coating” in  $\text{SnCl}_2/\text{HCl}$  solution under open-circuit conditions, and subsequent extensive washing of the surface by pure water [37]. This leads to formation of a thin and quite uniform modifying layer of both metallic tin and tin oxide/hydroxide species, as evidenced by characterization of the Sn-modified Pt surfaces using atomic force microscopy, X-ray photoelectron spectroscopy, and cyclic voltammetry [37]. In the present communication we describe and discuss the results of a comparative study on the electrocatalytic activity of spontaneously Sn-modified Pt vs. a clean Pt electrode tested in electrooxidation reactions of preadsorbed CO, and continuous oxidation of formaldehyde, formic acid, and methanol on both surfaces.

## Materials and methods

The solution for spontaneous Pt modification by tin was freshly prepared by dissolving  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in concentrated HCl to avoid the hydrolysis of tin chloride. A spontaneous modification of the clean polycrystalline Pt foil surface was carried out by immersing the sample in  $\text{SnCl}_2/\text{HCl}$  solution under open-circuit conditions at room temperature for 2 min, and subsequent extensive rinsing of the sample by pure water. After drying the surface in a stream of Ar gas (from Elmemesser, 99.999%) the sample was used for electrochemical measurements, as described elsewhere [37].

Electrochemical measurements were performed in 0.5 M  $\text{H}_2\text{SO}_4$  supporting electrolyte containing 1 M of methanol, formic acid, or formaldehyde. A CO (from Elmemesser, 99.997%) adlayer was preadsorbed at a constant electrode potential, purging CO gas through the electrolyte for 10 min followed by purging Ar gas for 40–50 min to completely remove CO from the solution. To avoid disproportionation of formaldehyde in the Cannizzaro reaction, the solution was freshly prepared from paraformaldehyde. Analytical grade chemicals and triply distilled water were used to prepare the solutions.

The cyclic voltammograms were recorded using a computerized potentiostat PI-50-1 and a function generator PR-8 (Russia) in a standard three-electrode electrochemical cell in 0.5 M  $\text{H}_2\text{SO}_4$  solution purged by Ar. The working electrode was Pt foil of  $2 \text{ cm}^2$  ( $1 \times 1 \text{ cm}$ )

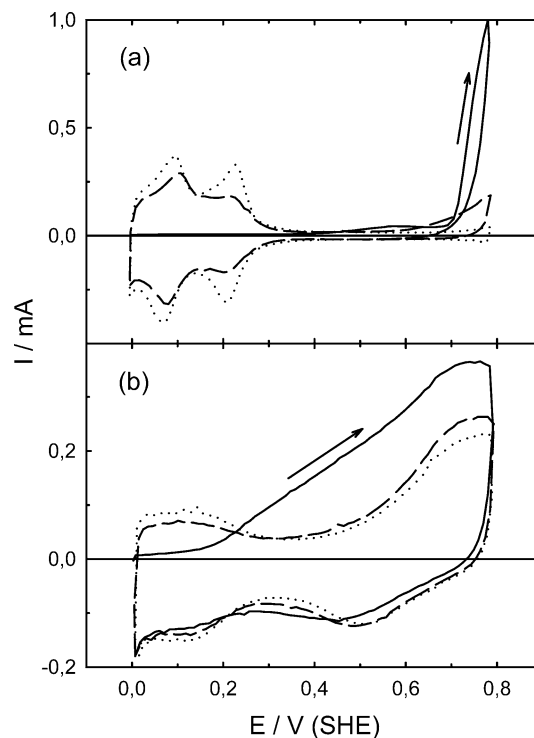
geometric area (real surface area, determined from hydrogen-uptake charge [38, 39],  $6.8 \text{ cm}^2$ ); counter electrode: Pt sheet of ca.  $2 \text{ cm}^2$  area ( $1 \times 1 \text{ cm}$ ), reference electrode:  $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$ . (all potentials are quoted vs. a standard hydrogen electrode, SHE).

## Results and discussion

### Electrooxidation of preadsorbed CO

#### Oxidation of CO on a Pt electrode

The electrooxidation of the preadsorbed CO monolayer (“CO stripping”) on a polycrystalline Pt electrode in the potential range 0 to 0.8 V is shown in Fig. 1a (solid and dashed lines for the first and second positive-going scans, respectively). For the CO-blocked Pt electrode the hydrogen-uptake features, characteristic for a clean polycrystalline Pt electrode [39, 40] within 0 to 0.3 V (Fig. 1a, dotted line), are thoroughly suppressed. A small increase in current (typically, ca. 5% of the total CO stripping charge) occurs in the so-called prepeak region (0.5–0.7 V). This is usually interpreted as the onset of OH adsorption on Pt and oxidation of “weakly” bonded (due to repulsive interactions between adsorbed CO molecules within the adlayer) saturated



**Fig. 1a,b** Potentiodynamic electrooxidation of a preadsorbed saturated CO adlayer (“CO stripping”) on Pt (a) and Sn-modified Pt (b) electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  solution. Room temperature, adsorption potential 0 V, potential scan rate 50 mV/s. Solid lines, first positive-going scan; dashed lines, second cycle; dotted lines, base cyclovoltammograms in the supporting electrolyte

adlayer, which is further transformed to a “strongly bonded” state at some lower coverage (due to diminished repulsion between  $\text{CO}_{\text{ad}}$  dipoles) [2]. The latter inhibits OH adsorption, and thus  $\text{CO}_{\text{ad}}$  oxidation can occur only at potentials more positive than 0.7 V (Fig. 1a, solid line). Overall in the whole potential range, electrooxidation of adsorbed CO on the Pt electrode occurs via the surface reaction between electroadsorbed OH and  $\text{CO}_{\text{ad}}$  according to the Langmuir–Hinshelwood mechanism [2].

After the first positive-going scan to 0.8 V the hydrogen-upd features occur in the subsequent scan in the potential region 0 to 0.3 V (Fig. 1a, dashed line), indicating a freeing of the Pt surface due to oxidative removal of adsorbed CO. However, the hydrogen-upd peaks are still lower compared to those for the pure polycrystalline Pt electrode (Fig. 1a, dotted line), indicating an incomplete oxidation of the CO adlayer within the first positive-going scan. A quantitative evaluation of the residual  $\text{CO}_{\text{ad}}$  coverage from the ratio of hydrogen-upd charge after the first positive-going scan and that for pure Pt, and from the CO stripping charge in the first positive-going scan to the total CO stripping charge, suggests that ca. 75% of the CO adlayer is oxidized within the first positive-going scan up to 0.8 V. Correspondingly, ca. 15% of the CO adlayer is oxidized in the subsequent scan. The residual 10% of the adlayer can be completely removed in an additional 2–3 cycles in the same potential window (not shown). Note that the CO adlayer can be completely oxidized within one cycle when scanning the electrode potential up to 1.0 V. However, we used the positive potential limit not exceeding 0.8 V to compare the electrooxidation of  $\text{CO}_{\text{ad}}$  on pure Pt with CO stripping on a Sn-modified Pt electrode (Fig. 1b) (the modifying layer is stable only at potentials more negative than 0.8 V [37]).

#### *Oxidation of CO on a Sn-modified Pt electrode*

CO stripping on a Sn-modified Pt electrode is shown in Fig. 1b (solid and dashed lines for the first and second positive-going scan, respectively). The base CV on the Sn-modified Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  solution, included for comparison (Fig. 1b, dotted lines), is in agreement with those reported for a tin-upd-modified Pt electrode in the same potential window [6, 7, 17, 19, 20]. The CO stripping trace on Sn-modified Pt shows an early onset in anodic current (more positive 0.2 V) followed by a broad feature of ill-resolved peaks within the whole potential region, in agreement with literature data for  $\text{CO}_{\text{ad}}$  stripping on Sn-upd-modified Pt surfaces [18, 20]. An initial current increase at the most negative potentials might be due to both onset of CO oxidation and double-layer charging—note the larger pseudo-capacitive contributions in the base CV of Sn-modified Pt (a double-layer charging contribution to the preadsorbed CO stripping charge on PtRu was discussed in detail elsewhere [41, 42, 43]). Nevertheless, differential

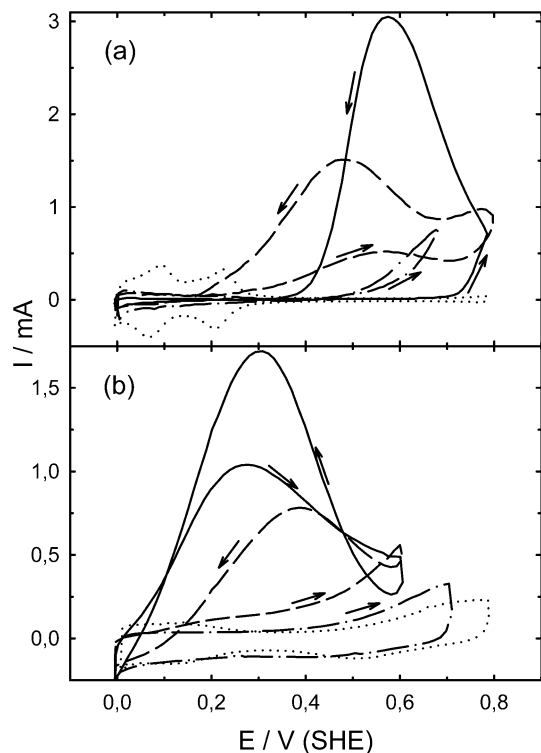
electrochemical mass spectrometry [11, 12, 13, 14] and infrared spectroscopy measurements [15, 44] reveal an onset of  $\text{CO}_2$  formation on Pt/Sn surfaces at potentials as negative as 0.2 V. Such an early  $\text{CO}_{\text{ad}}$  oxidation, compared to the Pt electrode, is usually explained by both the ability of tin to adsorb OH at more negative potentials, compared to Pt, and the reaction with neighboring CO species adsorbed on Pt sites (bifunctional mechanism), or modification of the d-band electronic structure of Pt by tin and weakening CO bonding to Pt, especially, for the case of PtSn alloys [45, 46], and oxidation of the weakly bonded  $\text{CO}_{\text{ad}}$  fraction at lower overpotentials.

A quantitative evaluation of the adsorbed CO coverage on the Sn-modified Pt surface can be done by integrating the current in the first positive-going scan after subtracting the base CV current in the potential range 0.22 to 0.78 V. This gives ca. 0.55 monolayer (ML) coverage vs. the saturated CO adlayer on Pt in the first positive-going scan, and about 0.05 ML in the subsequent positive-going scan (more positive 0.3 V), i.e., a total  $\text{CO}_{\text{ad}}$  coverage of ca. 0.6 on the Sn-modified Pt surface. Alternatively, subtracting the charge in the subsequent negative-going scan after adsorbed CO stripping results in the total  $\text{CO}_{\text{ad}}$  coverage ca. 0.66. Assuming that CO is adsorbing selectively and exclusively on Sn-free Pt sites but not on Sn species, the resulting Sn species relative coverage, evaluated from the CO stripping charge, is 0.4–0.34. The latter value is ca. 2.5 times lower than that (about 0.9) found from the H-upd charge for the same Sn-modified Pt surface [37]. This discrepancy can be due to mobility and contraction of the tin adlayer induced by CO, strongly adsorbing on Pt sites, as evidenced recently using in situ STM for CO adsorbed on a Sn-upd-modified Pt(111) electrode [47].

Electrooxidation of methanol, formaldehyde, and formic acid

#### *Potentiodynamic measurements*

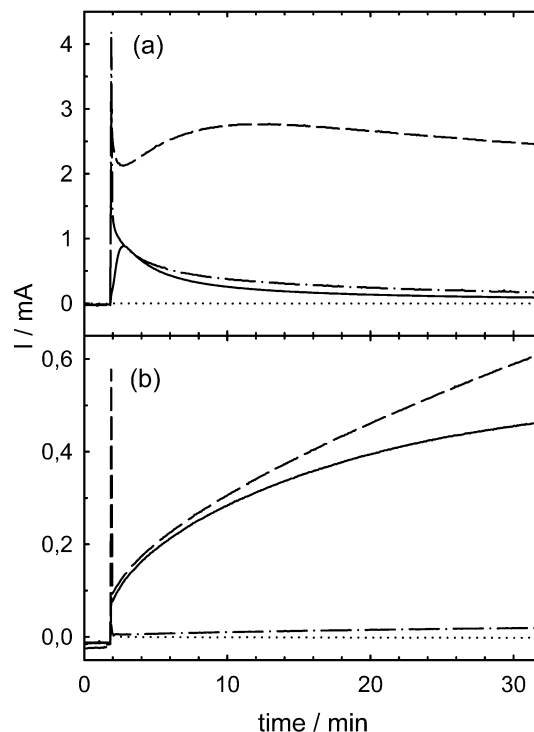
*Oxidation of C-1 organic molecules on a Pt electrode* Methanol oxidation on a Pt electrode in 1 M  $\text{CH}_3\text{OH} + 0.5 \text{ M } \text{H}_2\text{SO}_4$  solution (Fig. 2a, dash-dotted line) at potentials negative of 0.4 V is blocked by poisoning adsorbed CO species, formed as a result of catalytic dehydrogenation of methanol, as well documented by in situ IR spectroscopy measurements [48, 49, 50, 51, 52, 53, 54]. However, hydrogen adsorption/desorption features on the Pt electrode are not completely suppressed in methanol solution as in the case of the saturated CO adlayer (Fig. 1a, solid line). This suggests a lower coverage of poisoning species in the hydrogen-upd region due to hindering of methanol dehydrogenation by adsorbed hydrogen [35]. However, at more positive potentials (in the double-layer region) the  $\text{CO}_{\text{ad}}$  coverage increases to ca. 0.5 of the saturated CO adlayer as shown by recent DEMS measurements [35]. This suggests that



**Fig. 2a,b** Potentiodynamic electrooxidation of methanol (*dash-dotted lines*), formic acid (*dashed lines*), and formaldehyde (*solid lines*) on Pt (**a**) and Sn-modified Pt (**b**) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1 M CH<sub>3</sub>OH. Room temperature, potential scan rate 50 mV/s. *Dotted lines*: base cyclovoltammograms in the supporting electrolyte

the onset of the methanol oxidation reaction (MOR) occurs in concert with oxidation of the CO<sub>ad</sub> species [55, 56], though adsorbed formate was also identified in a recent SEIRAS study of the MOR and assigned as a possible reactive intermediate [54]. Moreover, recent DEMS studies show that incomplete oxidation of methanol to formaldehyde and formic acid prevails over complete oxidation to CO<sub>2</sub> on smooth Pt or at low catalyst loading [34, 36]. However, due to the 3-fold difference in the number of electrons in these reactions (two electrons for methanol oxidation to formaldehyde and six electrons for complete oxidation to CO<sub>2</sub>) they constitute, to about the same extent, to the measured Faradaic current at a low (ca. 10%) contribution of methanol oxidation to formic acid (four-electron reaction), according to DEMS data [36].

The onset of formic acid oxidation on a Pt electrode in 1 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution occurs more positive than 0.2 V (SHE) (Fig. 2a, dashed line). Recent electrochemical studies combined with surface-enhanced infrared spectroscopy (SEIRAS) in the attenuated total reflection (ATR) configuration show that electrooxidation of formic acid occurs through both poisoning CO<sub>ad</sub> species and a parallel path reactive intermediate identified as adsorbed formate anion [57]. Notably, the only possible reaction product of formic acid electrooxidation (regardless of adsorbed CO or reactive intermediate) is



**Fig. 3a,b** Potentiostatic electrooxidation of methanol (*dash-dotted lines*), formic acid (*dashed lines*), and formaldehyde (*solid lines*) on Pt (**a**) and Sn-modified Pt (**b**) electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1 M CH<sub>3</sub>OH, HCOOH, or H<sub>2</sub>CO, respectively. Room temperature, electrode potential step from 0 to 0.6 V (SHE). *Dotted lines*: potential step in the supporting electrolyte

CO<sub>2</sub>. Electrooxidation of the adsorbed poisoning CO intermediate on the Pt electrode occurs at potentials more positive than 0.7 V (Fig. 1a), resulting in a decrease in poisoning CO<sub>ad</sub> coverage, as evidenced by in situ IR spectroscopy [48, 49, 50, 51, 52, 53, 54], and a corresponding increase in oxidation current in the negative-going scan (Fig. 3a). Electrooxidation of formic acid in the low potential region (below 0.6 V) occurs predominantly through a parallel “reactive intermediate” path, apparently via adsorbed formate [57], on a partly CO-blocked Pt surface. Electrooxidation of formic acid to CO<sub>2</sub> at such negative potentials is possible, since it does not require oxygen addition in contrast to oxidation of the poisoning CO intermediate.

Formaldehyde oxidation on a Pt electrode in 1 M H<sub>2</sub>CO + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the positive-going scan is fully blocked by poisoning adsorbed CO species formed as a result of catalytic dehydrogenation of formaldehyde [58, 59] (Fig. 2a, solid line). The onset of formaldehyde oxidation occurs more positive than 0.7 V (SHE), corresponding to electrooxidation of poisoning CO<sub>ad</sub> species (Fig. 1a) and freeing of the Pt sites for formaldehyde oxidation, as evidenced from the current increase in the negative-going scan. However, the oxidation current decreases soon due to a fast re-poisoning of the catalyst surface by adsorbed CO as a result of formaldehyde dehydrogenation. Recent DEMS studies show that incomplete formaldehyde oxidation to formic

acid prevails over complete oxidation to  $\text{CO}_2$  on Pt/Vulcan catalyst [60].

*Oxidation of C-1 organic molecules on a Sn-modified Pt electrode* The Sn-modified Pt electrode shows negligible enhancement of the MOR rate (Fig. 2b, dash-dotted line) compared to the Pt electrode at potentials below 0.6 V (Fig. 2a, dash-dotted line), in agreement with previously reported data for Sn-upd-modified Pt [17, 18, 19, 20] and alloyed PtSn [22, 23, 24] electrodes. This can be rationalized by taking into account that methanol oxidation is a complex reaction involving several subsequent dehydrogenation steps [1, 2]. As a result several neighboring Pt sites are required for dehydrogenation of methanol to CO [61, 62]. Apparently, tin species (which are inactive for methanol dehydrogenation) partly block the Pt surface and hinder methanol dehydrogenation/oxidation. As a result, although spontaneously Sn-modified Pt exhibits a superior catalytic activity toward adsorbed CO oxidation, the overall MOR rate is kinetically hindered by modifying tin species blocking active Pt sites for methanol dehydrogenation.

The Sn-modified Pt catalyst shows some increase in formic acid oxidation rate (Fig. 2b, dashed line) during the positive-going potential scan, compared to Pt (Fig. 2a, dashed line) at potentials more positive than 0.1 V (SHE), i.e., in the low potential region. Apparently, oxidized tin species help to remove poisoning adsorbed CO intermediates, formed as a result of the dehydration of formic acid, at lower potentials compared to Pt (see Fig. 1a)—this causes an increase in formic acid oxidation current during the negative-going potential scan. However, modifying tin species simultaneously block the active Pt sites required for HCOOH dehydrogenation/oxidation as discussed for the case of methanol oxidation.

The formaldehyde oxidation rate on a Sn-modified Pt surface (Fig. 2b, solid line) is increased dramatically compared to that on a Pt electrode (Fig. 2a, solid line) even at potentials as low as 0.1 V (SHE), resulting in an anodic peak centered at ca. 0.3 V (SHE), in agreement with previously reported data for electrodeposited PtSn alloy [29] and microfabricated tin island arrays performed on a Pt surface [30]. Apparently, Sn species at a submonolayer coverage on a Pt surface do not interfere significantly with dehydrogenation of formaldehyde which requires only a limited number of free Pt sites, and the surface reaction between adsorbed CO and OH species can occur at the Pt/Sn boundary [30]. Alternatively, due to the strong reducing ability of formaldehyde, electrocatalytic reaction in this potential region may involve reduction of tin oxy-species by formaldehyde and electrochemical reoxidation of tin.

#### Potentiostatic measurements

*Potentiostatic oxidation of C-1 organic molecules on a Pt electrode* Notably, the Faradaic current in potentiodynamic measurements for the electrooxidation of C-1

organic molecules (Fig. 2) depends on the scan direction and the potential window, especially for formic acid (Fig. 2, dashed lines) and formaldehyde (Fig. 2, solid lines). As discussed previously, this can be explained by the onset of electrooxidation of poisoning  $\text{CO}_{\text{ad}}$  species at the positive potential limit (depending on the potential of OH electroadsorption on the Pt and Pt/Sn surfaces), causing an increase in oxidation current during the negative-going scan. Evidently, the slow oxidation kinetics of poisoning  $\text{CO}_{\text{ad}}$  species at low potentials via surface reaction with neighboring  $\text{OH}_{\text{ad}}$  in a Langmuir–Hinshelwood-type reaction on the Pt electrode, or through a bifunctional mechanism on the Sn-modified Pt surface, cause Faradaic current hysteresis in cyclic voltammetry measurements (Fig. 2). Due to this reason a comparison of electrocatalytic activity toward the oxidation of methanol, formic acid, and formaldehyde on Pt and Sn-modified electrodes is complicated in potentiodynamic measurements. Moreover, constant potential (or current) measurements, rather than potentiodynamic ones, are more representative of realistic fuel cell operating conditions. Therefore we performed constant potential measurements on Pt and Sn-modified Pt electrodes at 0.6 V in 0.5 M sulfuric acid solution containing 1 M of methanol, formic acid, or formaldehyde (Fig. 3).

Figure 3a shows the current transients during the potentiostatic oxidation of methanol (dash-dotted line), formic acid (dashed line), and formaldehyde (solid line), and a corresponding transient in the supporting electrolyte (dotted line) at a Pt electrode after stepping the potential from 0 to 0.6 V. The current for the case of methanol oxidation after stepping the potential initially sharply increases (Fig. 3a, dash-dotted line) due to oxidation of upd-adsorbed hydrogen, pseudo-capacitive charging of the double-layer due to adsorption of bisulfate anions, and oxidation of both adsorbed poisoning CO and methanol. Although it is not possible to discriminate between these contributions from the Faradaic current alone, it is known that the coverage of  $\text{CO}_{\text{ad}}$  derived from methanol adsorption is low on the hydrogen-upd-blocked surface [35]; the latter prevents methanol adsorption and dehydrogenation to CO. This causes an initially high methanol oxidation current as confirmed by simultaneous mass spectrometric measurements of  $\text{CO}_2$  formation [36]. However, poisoning intermediate  $\text{CO}_{\text{ad}}$  species are also derived at 0.6 V during methanol oxidation. Since  $\text{CO}_{\text{ad}}$  electrooxidation on the Pt electrode occurs only at a low rate at this potential (see Fig. 1a) the electrode is gradually poisoned by adsorbed CO, resulting in the current decrease (Fig. 3a, dotted line). The methanol oxidation products for constant potential electrolysis at 0.6 V, as shown by DEMS for a smooth Pt electrode [34] and a carbon-supported Pt catalyst [36] at low loading, are formaldehyde, formic acid, and  $\text{CO}_2$  at a corresponding ratio of ca. 0.6:0.3:0.1.

Oxidation of formic acid occurs on the Pt electrode at a high and relatively constant rate within 30 min after

the potential step from 0 to 0.6 V (Fig. 3a, dashed line). A higher formic acid oxidation rate, compared to methanol (Fig. 3a, dash-dotted line), can be interpreted as comparatively greater oxidation of formic acid through a reactive non-CO intermediate route, e.g., adsorbed formate [57], on a partly  $\text{CO}_{\text{ad}}$ -blocked electrode surface. The variation in formic acid oxidation current with time can be attributed to the changes of the  $\text{CO}_{\text{ad}}$  poisoning intermediate steady-state coverage during electrooxidation.

The formaldehyde oxidation current after stepping the Pt electrode potential from 0 to 0.6 V is initially suppressed (Fig. 3a, solid line), indicating a complete poisoning of the Pt surface by adsorbed CO species, derived upon adsorption of formaldehyde already in the hydrogen-upd region, in agreement with the FTIR [58, 59] and DEMS data [60]. The increase in formaldehyde oxidation current within the first minute after potential stepping is due to the onset of electrooxidation of poisoning  $\text{CO}_{\text{ad}}$  species and the freeing of Pt sites, required for formaldehyde oxidation. However, the formaldehyde oxidation current decays further with time (Fig. 3a, solid line) due to re-poisoning of the catalyst surface by adsorbed CO, similar to methanol electrooxidation (Fig. 3a, dash-dotted line). As found recently using DEMS [60], formaldehyde oxidation on a Pt catalyst at 0.6 V gives mainly formic acid at a current efficiency of ca. 85% (and  $\text{CO}_2$  formation current efficiency 15%). Taking into account the two-electron oxidation of formaldehyde to formic acid and the four-electron oxidation to  $\text{CO}_2$ , a ratio of formic acid to  $\text{CO}_2$  of ca. 10:1 can be estimated for formaldehyde oxidation at 0.6 V based on the DEMS data [60].

*Potentiostatic oxidation of C-1 organic molecules on a Sn-modified Pt electrode* Comparative current transients for the potential step from 0 to 0.6 V on a Sn-modified Pt electrode are shown in Fig. 3b for methanol (dash-dotted line), formic acid (dashed line), and formaldehyde (solid line) oxidation, and for a corresponding transient in the supporting electrolyte (dotted lines). The methanol oxidation current on the Sn-modified surface (Fig. 3b, dash-dotted line) is considerably lower, compared to that on the Pt electrode (Fig. 3a, dash-dotted line)—initially, the Sn-modified surface has a rather low activity toward methanol electrooxidation, in contrast to the highest activity of the Pt surface immediately after the potential step. Although the current transient for methanol oxidation on the Pt electrode shows an exponential decay (Fig. 3a, dash-dotted line), methanol oxidation on a Sn-modified Pt surface is slightly increased with time (Fig. 3b, dash-dotted line). Nevertheless, the methanol oxidation current on the Sn-modified Pt electrode attained after electrolysis for 30 min at 0.6 V is ca. 10-fold lower compared to that on the Pt electrode. This suggests that the Pt/Sn surface is a poor catalyst for methanol oxidation, despite its superior activity toward adsorbed CO oxidation, in agreement with literature data [17, 18,

19, 20, 21, 23]. As discussed previously, this can be interpreted in terms of blocking of the Pt surface sites, required for dehydrogenation of methanol, by modifying tin species.

The oxidation current for formic acid on the Sn-modified Pt electrode at 0.6 V (Fig. 3b, dashed line) initially is significantly (ca. 20 times) lower, compared to that on the Pt electrode (Fig. 3a, dashed line). However, the formic acid oxidation rate on the Sn-modified Pt surface continuously increases within 30 min (Fig. 3b, dashed line), in contrast to a slow decay in the formic acid oxidation rate on the Pt electrode (Fig. 3a, dashed line). As a result, the formic acid oxidation rate on the Sn-modified electrode after electrolysis for 30 min at 0.6 V is ca. 4-fold lower compared to that on the Pt electrode, with a tendency to become comparable on both surfaces at a steady state.

The formaldehyde oxidation current transient on the Sn-modified Pt electrode (Fig. 3b, solid line) shows an increase with time similar to that for formic acid (Fig. 3b, dashed line), in contrast to a decrease in formaldehyde oxidation current on the Pt electrode, after passing the maximum at ca. 1 min after stepping the potential (Fig. 3a, solid line). The formaldehyde oxidation current on the Sn-modified Pt surface after 30 min electrolysis at 0.6 V is ca. 5-fold larger, compared to that on the Pt electrode, suggesting that Sn-modified Pt is a good catalyst for formaldehyde oxidation in agreement with potentiodynamic measurements (see Fig. 2) and literature data [29, 30].

In general, for all three C-1 compounds studied (methanol, formic acid, and formaldehyde), the potentiostatic current transients at 0.6 V show an increase with time on the Sn-modified Pt surface (Fig. 3b). Although Sn species demonstrate a satisfactory stability at this potential, as found from electrochemical measurements described in the previous part of this paper [37], partial losses of tin during long-term oxidation experiments cannot be excluded. This could explain an increase in the oxidation current with time, assuming greater blocking of the Pt surface at initially higher Sn coverage. The variations in both coverage and composition of tin species for differently prepared Pt/Sn catalysts most likely result in differences of their electrocatalytic performance, as reported in the literature. On the other hand, tin species at the Pt surface can be contracted by strongly adsorbed CO, as discussed previously, derived from dehydrogenation of organic molecules. The results for the influence of electrode potential, coverage of modifying tin species, and temperature on the electrooxidation rate of C-1 molecules will be presented in a forthcoming publication [63].

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## Conclusions

The electrocatalytic activity of spontaneously Sn-modified Pt was compared to that of a polycrystalline Pt electrode in the electrooxidation of preadsorbed CO and

simple C-1 organic molecules, i.e., methanol, formic acid, and formaldehyde, related to direct methanol fuel cell applications. The spontaneously Sn-modified Pt catalyst shows a superior activity toward adsorbed CO oxidation and thus can be promising for PEFC applications operating on CO-contaminated hydrogen oxidation. The methanol oxidation rate is hardly enhanced on the Sn-modified Pt surface, compared to the Pt electrode. Formic acid oxidation is enhanced in the low potential region on the Sn-modified surface, compared to the Pt electrode. The formaldehyde oxidation rate is dramatically increased by modifying tin species at the most negative potentials where anodic formaldehyde oxidation is completely suppressed on the pure Pt electrode.

These results suggest that submonolayer amounts of tin on Pt surfaces facilitate oxidation of formaldehyde, known as a by-product of methanol electrooxidation, and thus increase the current efficiency of the overall methanol oxidation reaction and decrease toxic formaldehyde emissions. However, the coverage of tin species must be optimized to prevent significant blocking of Pt sites required for the initial catalytic dehydrogenation of methanol. Overall, the catalytic effect of tin oxy-species can be explained in terms of oxidation of poisoning adsorbed CO species, either preadsorbed from CO saturated solution or derived during dehydrogenation of organic molecules.

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