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Formic acid electrooxidation on noble metal electrodes: The role of pH, surface structure and anion adsorption, and their mechanistic implication

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We have investigated the influence of the electrolyte pH on formic acid (HCOOH) electro-oxidation on both polycrystalline Pt and Au electrodes, and on single-crystalline Au electrodes in perchloric and sulphuric acid based electrolytes. On Au electrodes, the potentiodynamic oxidation currents are found to depend in a non-linear way on the electrolyte pH, in a bell-shaped relation with a maximum of the catalytic activity at the pK_a of HCOOH. On polycrystalline Pt electrodes, this feature is not observed and the catalytic activity increases steadily with increasing pH up to $pH \approx 5$ followed by a plateau until $pH 10$, in contrast with recent observations [T. Joo *et al.*, J. Amer. Chem. Soc., 135 (2013) 9991]. In addition, for Au surfaces, the reaction is only weakly influenced by the electrode surface structure, while for Pt structural effects are

known to be considerable. Anion effects, in contrast, are much stronger for reaction on Au than for Pt electrodes. Also, it is shown that Pt group metal free Au electrodes do not oxidize molecular hydrogen under reaction conditions. The results are discussed in relation to findings in previous mechanistic studies. Most important, the activity is on both electrodes closely correlated with the concentration of $HCOO^-$ anions, for Au with both $HCOO^-$ and HCOOH concentrations. Based on these results, a number of mechanistic proposals put forward in earlier studies must be discarded, examples for mechanisms compatible with these results are discussed.

Introduction

Since many years, the mechanism of formic acid (HCOOH) electro-oxidation has been subject of intensive investigations for two main interests: on the one side as a model reaction of a two electron transfer process and on the other side with regard to practical applications, *i.e.*, the improvement of the electrocatalysts for Direct Formic Acid Fuel Cells. Forty years ago, Capon and Parsons ^[1] summarized the results of earlier studies in the dual-path mechanism for HCOOH electro-oxidation at noble metal electrodes, which has been widely accepted by the community. Nonetheless, the nature of the reactive intermediate for the direct pathway is still strongly debated in the literature, especially since adsorbed formate ($HCOO_{ads}$) has been detected by Osawa's group employing *in situ* Infrared (IR) spectro-electrochemistry ^[2]. This latter species has been proposed as candidate for the reactive intermediate species in numerous contributions ^[3-8], while, oppositely, it has been considered as a site-blocking spectator species in other ones ^[9-12]. It should be noted that the conclusions were based on essentially equivalent experimental observations. Furthermore, the controversy about the role played by

$HCOO_{ads}$ is also present in theoretical studies of the reaction mechanism ^[13;14]. More recently, two new reaction mechanisms have been proposed by Osawa and co-workers. In the first one ^[3;4], these authors argued based on their *in situ* IR data that the reaction involves i) a dimerisation step of aqueous HCOOH, followed by the formation of two $HCOO_{ads}$, and ii) the subsequent electro-oxidation of molecular hydrogen (H_2) formed after the disproportionation of $HCOO_{ads}$ into CO_2 . This latter disproportionation step, which is of purely chemical nature, was considered as the rate determining step (r.d.s.). In this mechanism, the formation of the adsorbed (bridge-bonded) formate species, which is formed by adsorption and deprotonation of HCOOH, was considered by the authors as an irreversible step and as the bifurcation point for the direct oxidation path and the indirect path, *i.e.*, $HCOO_{ads}$ acts also as precursor for the reductive formation of adsorbed CO (CO_{ads}) species, which poison the Pt electrode. In a second recent proposal ^[15], the same authors contributed to a proposal which suggested a reaction scheme where formic acid oxidation proceeds via direct oxidation of formate ions, which are present even in strongly acidic electrolyte, as the main reaction route for the oxidation of formic acid. This process was supposed to occur via a weakly adsorbed formate precursor, which is different from the bridge bonded adsorbed formate formed by adsorption of HCOOH.

The purpose of this communication is to report and discuss the influence of numerous experimental parameters (electrolyte pH, electrode surface structure, nature of the counter-anions, and presence of more strongly adsorbed species (Cl^-)) on the oxidation of HCOOH on different Pt and

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Au electrodes, which may help to better define and/or to discard some mechanistic models proposed previously. Finally, we outline two possible reaction schemes for HCOOH electro-oxidation on Au electrodes, which are compatible with these and earlier data, while for reaction on Pt electrodes the situation is more complex, so that only basic elements of the reaction mechanism and their (in)compatibility with previous proposals can be discussed.

Results and Discussion

Effect of electrolyte pH on HCOOH electro-oxidation

We first concentrate on formic acid oxidation on a polycrystalline (pc) Au crystal. It should explicitly be noted that we are using a pc Au bead crystal which was carefully cleaned from platinum group metals (PGM), employing a method which had been introduced by Clavilier and co-workers.^[16] These authors had shown that such kind of trace impurities can be found even on ultra pure Au samples, and may significantly modify the electrochemical properties of these surface (see also ref. ^[16]). Fig. 1a compares the voltammetric profiles of a PGM decontaminated polycrystalline Au bead obtained in Ar and H₂ saturated 0.5 M H₂SO₄ solutions^[16]. The CV clearly indicates the absence of any oxidation process in the entire potential region relevant for formic acid oxidation. This also means that a PGM decontaminated Au electrode is not active for H₂ oxidation in this potential range, which is not only in contradiction with previous reports^[17], but is in disagreement also with one of the mechanisms recently proposed by Osawa and co-workers^[3,4] for HCOOH electro-oxidation, since their proposal for the reaction mechanism includes a final step of H₂ electrooxidation.

Fig 1b displays results on the potentiodynamic oxidation of 0.1 M HCOOH on a polycrystalline Au bead at two different pH values: 0.2 and 3.6, where the latter essentially corresponds to the pK_a of HCOOH. In the strongly acidic electrolyte, the Au electrode exhibits a very low catalytic activity for formic acid oxidation, with an onset of oxidation at ca. 0.80 V, in agreement with previously reported data^[1]. The maximum activity is obtained for a partially oxide-covered surface, at ~1.48 V, and subsequently the Faradaic current decays rapidly to negligible values. At pH 3.6, the onset of oxidation is shifted by ca. 500 mV to lower potentials, leading to currents in the onset regime comparable to those of Pt electrodes in strongly acidic electrolytes^[18]. The maximum oxidation current density, 300 $\mu\text{A cm}^{-2}$, is obtained at 1.15 V, prior to the formation of surface oxides (see Fig. 1a). The absence of a hysteresis for positive- and negative-going scans between 0.30 V and 1.00 V indicates an almost negligible surface poisoning at these lower potential values, while at higher potentials the competing oxide formation leads to a pronounced hysteresis. The absence of a CO_{ad} induced poisoning on Au electrodes agrees well with findings in *in situ* IR measurements, which did not detect any CO_{ad} on the surface^[4]. For completeness it should be noted, however, that this experimental finding does not rule out the formation and instantaneous desorption of CO during HCOOH oxidation, since CO_{ad} is not irreversibly adsorbed on Au^[19-21].

Figure 1. a) Base cyclic voltammograms (0.5 M H₂SO₄, $\nu = 50 \text{ mV s}^{-1}$) on a PGM decontaminated polycrystalline Au bead in Ar saturated electrolyte (grey trace) and in H₂ saturated electrolyte (dotted black trace); b) potentiodynamic oxidation of 0.1 M HCOOH on the same sample at 10 mV s^{-1} in 0.5 M (b) sulphate with the electrolyte pH fixed at 0.2 (black trace) and 3.6 (grey trace).

Similar measurements were performed for various pH values below and above the pK_a of HCOOH on a polycrystalline Au bead (Fig. 2) and, for the sake of comparison, also on a polycrystalline Pt bead (Fig. 3). The onset of the oxidation current in the anodic scan on the polycrystalline Au bead is illustrated in Fig. 2a. Clearly, there is a non-linear relation between the catalytic activity and the electrolyte pH, with the highest current densities obtained for a pH value equal to the pK_a of HCOOH. This result confirms similar findings obtained earlier by Crépy *et al.*^[22] at 60°C. In Fig. 2b, we illustrate the influence of the electrolyte pH on the apparent exchange current densities^[23] (j_0 , green triangles) and Tafel slopes (red squares) in the potential region of the current onset determined in the anodic scan. The exchange current densities j_0 vary considerably, with a maximum for an electrolyte pH at the value of the pK_a of HCOOH. The values for the Tafel slopes range between ca. 220 – 260 mV dec^{-1} . Very high Tafel slopes have been reported earlier for HCOOH electro-oxidation on Au electrodes^[3,4,22,24]. A plot of the current densities vs pH at 1.0 V is displayed in Fig 2c. It also shows an optimum of the catalytic activity of polycrystalline Au electrodes when half of the formic acid in the bulk of the solution is dissociated into formate ions (at $\text{pH} = \text{pK}_a$).

Figure 2. Potentiodynamic oxidation of 0.1 M HCOOH on a PGM decontaminated polycrystalline Au bead at 10 mV s⁻¹. a) Onset of oxidation at various electrolyte pH as indicated in the figure. b) Influence of the electrolyte pH on the Tafel slope (open squares) and on the exchange current density j_0 (triangles) as obtained from Tafel plots of the onset regime in the positive-going scan. c) Plot of the current densities at 1.0 V versus the electrolyte pH. All experiments were conducted at constant (b)sulphate concentration (0.5 M).

The above data clearly indicate that a plausible mechanism for the electro-oxidation of formic acid at gold electrodes should include a distinct pH effect, as proposed earlier based upon results of (radio)electrochemical studies and on kinetic isotope effects [25]. The pH-dependence observed here for reaction at a Au electrode is essentially similar to that reported recently by Joo et al. [15] for formic acid oxidation at polycrystalline Pt, using a rotating disk Pt electrode in phosphate buffer solutions. Those authors proposed that the dominant reaction pathway for formic acid oxidation involves the direct oxidation of formate ions via a weakly adsorbed formate precursor, whereas the bridge-bonded adsorbed formate, which in their interpretation is formed by dissociative adsorption of formic acid, is little active for further oxidation. It should be noted that this latter statement is in complete contrast to earlier proposals of these authors, where the bridge-bonded adsorbed formate was claimed to be the reaction intermediate in the dominant pathway [3-6]. The decrease of the HCOOH oxidation current above pH $\approx$ pK_a was explained by an increasing site blocking of the surface due to adsorption of hydroxyl species (OH_{ads}) and / or surface oxide formation, while the decrease at lower pH values was attributed to the decreasing concentration of HCOO⁻ anions [15].

In principle, this mechanism could also act as dominant reaction pathway on Au electrodes. In that case, however, one would expect a distinct difference in the pH of the maximum activity between gold and platinum electrodes due to the different potential regimes where OH adsorption takes place on the two electrodes. To better understand this fact, we performed additional experiments over a pH range (0-7) on a (flame-annealed) polycrystalline Pt bead electrode (Fig. 3a). As

expected and opposite to the behavior of the Au electrode, pronounced CO_{ad} poisoning of the Pt electrode occurs, which is evidenced by the large hysteresis between the anodic and cathodic scan [1]. We also observe a clear effect of the electrolyte pH on the potentiodynamic traces during HCOOH electro-oxidation. The CO stripping in the positive scan is clearly less pH sensitive than formic acid oxidation (see also refs [26;27]), although the currents in the negative scan systematically increase with the pH. In Fig. 3b, we show a plot of the maximum current densities in the negative scan. It indicates a distinctly different effect of the electrolyte pH on the catalytic activity than obtained for the polycrystalline Au electrode (see Fig. 2). Most important for the comparison of the formic acid oxidation behavior with that on a Au electrode is the observation that the oxidation currents do not show a maximum activity at a pH close to the pK_a, but increase continuously up to pH $\approx$ 7. These results agree with data reported earlier on the electrolyte pH effect in the electro-oxidation of HCOOH on Pt electrodes [28;29], but differ significantly from the recent results in ref. [15], where a maximum activity was observed at pH $\approx$ pK_a.

Figure 3. Potentiodynamic oxidation of 0.1 M HCOOH at 50 mV s⁻¹ on a polycrystalline Pt bead electrode at various electrolyte pH as indicated in the figure. a) Cyclic voltammogram, b) plot of the maximum current density recorded during the backward potential scan versus the electrolyte pH. All experiments were conducted at constant (b)sulfate concentration (0.5 M). Full and dashed traces give the molar fraction of HCOOH and HCOO⁻ in solution, respectively, as function of the pH.

It is important to note that the order of magnitude of the oxidation currents is significantly higher for Pt (2-11 mA cm⁻²) than for Au (max. 0.3 mA cm⁻²) electrodes. Also the oxidation peaks are shifted positively as the pH increases. In that case,

the protons released during the oxidation reaction may cause a modification of the local pH in the vicinity of the electrode, lowering this compared to the pH of the bulk solution. This may alter the relationship between electrode activity and pH. In order to exclude or identify possible contributions arising from local pH modifications, we performed additional experiments with a polycrystalline Pt rotating disk electrode (RDE) at 1000 rpm in order to lower the local pH decrease. The results are shown in Fig. 4. As in case of the polycrystalline Pt bead electrode, the oxidation current does not show a maximum at a pH close to the pK_a , and the activity increases continuously until a current plateau is reached at pH 5 - 6. Finally the maximum currents drops dramatically for an electrolyte pH higher than 11. One should note that the current densities are ca. 50% higher at 1000 rpm than in quiescent electrolyte. Higher rotation rates induce only a minor additional increase in the current density (less than 6% at 4000 rpm and at pH 6.7 compared to 1000 rpm, not shown). Therefore, the data presented in Fig. 4b are a proper representation of the pH dependence of the Faradaic current, additional effects on the Faradaic currents due to local pH modifications would be in the percent range. In this context it should be noted that local modifications of the pH in the vicinity of the electrode would simply lower the extent of the current increase with increasing pH, but not transform this into a bell-shaped curve with a maximum at the $pH = pK_a$.

Smaller differences in the current traces are explained by the different pre-treatment of the working electrode, which leads to rougher surfaces for the RD electrode, and to Ohmic drop effects in case of the RDE measurements. Finally, it is worth noting that in our potentiodynamic traces for HCOOH oxidation on Pt electrodes, two oxidation peaks are clearly distinguished during the cathodic scan, while the potentiodynamic traces presented by Osawa and co-workers differ in that point (see Fig. 1a in ref.^[15]).

Figure 4. Potentiodynamic oxidation of 0.1 M HCOOH at 50 mV s⁻¹ on a polycrystalline Pt rotating disk electrode ($\Omega = 1000$ rpm) at various electrolyte pH as indicated in the figure. a) Cyclic voltammogram, b) plot of the maximum current density recorded during the backward potential scan versus the electrolyte pH. All experiments were conducted at constant (b) sulfate concentration (0.5 M). Full and dashed traces give the molar fraction of HCOOH and HCOO⁻ in solution, respectively, as function of the pH.

Effect of Au surface structure, electrolyte counter-ions and presence of strongly adsorbed species (Cl⁻) on HCOOH electro-oxidation

The effect of the surface structure on the electrooxidation of HCOOH has been established earlier for platinum; both the intrinsic catalytic activity and the poisoning rate are higher for Pt(100) than for Pt(111) (see for example ref.^[18]). Studies on Au single crystalline electrodes are scarce, and the data are not consistent with respect to possible structural effects^[30;31]. Measurements using Au(100) and Au(111) electrodes revealed that the formic acid electrooxidation reaction is little structure sensitive on Au, at least with respect to the general characteristics of the reaction, which are rather similar for the single crystal electrodes and the polycrystalline bead electrode (Fig. 5). We find a strong effect of the electrolyte pH also for the Au single crystal electrodes, with a maximum catalytic

activity towards HCOOH electrooxidation at an electrolyte pH of 3.7, at the pK_a of formic acid, independently of the Au surface structure. In strongly acidic electrolyte, the surface structure has very little effect on both the onset of oxidation and the maximum current density. In contrast, at $pH \approx pK_a$, HCOOH oxidation is favoured following the sequence $Au(111) > Au(poly) > Au(100)$. Here the current density at 1.0 V (both in the positive and negative scan) is about twofold higher for Au(111) than for Au(100).

Figure 5. Potentiodynamic oxidation of 0.1 M HCOOH at 10 mV s^{-1} on polycrystalline Au, Au(111) and Au(100), from top to bottom, showing the influence of the electrolyte counter-ion: ClO_4^- (grey traces) and SO_4^{2-} (black traces) and the influence of the electrolyte pH (0.2 (dotted lines) and 3.7 (solid lines)). Only the anodic scans are presented. All experiments were conducted at constant perchlorate or (bi)sulphate concentration (0.5 M).

The nature of the electrolyte anion, weakly adsorbing (ClO_4^-) or more strongly adsorbing (SO_4^{2-}), also influences the oxidation of HCOOH. At an electrolyte pH of 0.2, all Au electrodes are inactive below 0.80 V in 0.5 M H_2SO_4 , and show a very low current up to 1.2 V. In contrast, in 0.5 M HClO_4 , at the same pH of 0.2, there is a clear oxidation current at potentials $>0.3 \text{ V}$, in agreement with findings of Beltramo *et al.* [24]. Furthermore, the onset for oxidation in HClO_4 solution is similar (around 0.30 V) to that observed at $pH = pK_a$. Finally, at this latter pH, the onset potential is identical for both anions. These findings in total point to a competition for the adsorption sites between the adsorbed reactive intermediate for HCOOH electro-oxidation and strongly adsorbing anions at low pH values. The effect of this competition seems to decrease with increasing pH and to vanish at $pH \approx pK_a$. Fast scan voltammetry had shown that the adsorbed species from HCOOH solutions exhibit an adsorption behaviour very similar to that of adsorbed anions [32]. Because of the significant upshift in the onset of oxidation in the presence of (bi)sulphate anions at low pH values, the adsorbed reactive species should be more weakly adsorbed than (bi)sulphate anions. Finally, it should be noted that for the Au electrode there was no

noticeable influence of the electrode surface structure and of the electrolyte counter-ions on the Tafel slopes (not shown).

In a third set of experiments we performed additional potentiodynamic HCOOH oxidation measurements at $pH = 3.8$ ($\approx pK_a$), with about 5 mM of NaCl intentionally added to the electrolyte (0.5 M SO_4^{2-}) to strongly increase the anion adsorption (see Fig. 6). The addition of NaCl resulted in a dramatic decrease of the catalytic activity of both polycrystalline Au and Pt electrodes, clearly denoting that the oxidation reaction is strongly affected by site-blocking adsorbed species. The decrease is much larger for the Au electrode than for the Pt electrode (Fig. 6a), which can be explained by a stronger adsorption of the reactive intermediate on Pt than on Au, assuming that Cl^- adsorption is strong on both surfaces. In total, the result clearly illustrates that even trace amounts of Cl^- in the electrolyte have pronounced effects on the formic acid oxidation reaction and on the voltammetric profile, in particular on Au electrodes. Interestingly, the current profile for HCOOH electro-oxidation in the presence of NaCl on a polycrystalline Pt electrode (number of oxidation peaks and their relative intensities) closely resembles the one recently published by Osawa and co-workers for HCOOH oxidation in a phosphate buffered electrolyte.

Figure 6. Effect of Cl^- addition on the potentiodynamic oxidation of 0.1 M HCOOH on a) a polycrystalline Au electrode and b) a polycrystalline Pt electrode. Chloride-free electrolyte (dotted line) and 5 mM Cl^- containing electrolyte (plain line) were used, all experiments were conducted at $pH = 3.8$ and in 0.5 M SO_4^{2-} at 10 mV s^{-1} .

Reaction mechanism for HCOOH oxidation

The kinetic results described and discussed above provide new insight into the mechanism of the formic acid oxidation reaction at Pt and Au electrodes. Although kinetic data alone are generally not sufficient to unambiguously identify the mechanism of a catalytic reaction and the nature of the important reaction intermediates – despite of numerous more or less successful attempts to do so – the present data allow to exclude specific mechanistic proposals and to define

borderlines for future proposals. This shall be discussed in the following.

Any plausible mechanistic proposal for the reaction has to be able to explain the influence of the electrolyte pH, the nature of the anion and the difference between the reaction characteristics on Pt and Au electrodes according to the experimental observations presented above. For the first point, we refer also to a recent study ^[15]. The main findings of the present work can be summarized as follows:

1. Both for Au and Pt electrodes, the reaction rate increases with increasing pH in the range of low pH values. At higher pH values, the rate increases steadily up to a pH of 5 – 6, and then remains constant at higher pH values for Pt, in agreement with a previous report ^[28], while it exhibits a distinct maximum at $\text{pH} \approx \text{pK}_a$ on a Au electrode. Note that the finding for Pt is distinctly different from that in ref. ^[15], but in agreement with earlier reports ^[28;29]. The current increase with increasing pH is significantly more pronounced for Au, by more than one order of magnitude, than for Pt.
2. The characteristic bell-shape of the current – pH plot on Au electrodes is independent of the nature of the anion (ClO_4^- , SO_4^{2-}), and also the position of the maximum of the reaction rate on the Au electrode appears at the same pH value, which is equivalent to the pK_a of formic acid ($\text{pK}_a = 3.8$).
3. On Au electrodes, more strongly adsorbing anions (SO_4^{2-}) shift the onset of the reaction to significantly higher potential in strongly acidic solution compared to weakly adsorbing anions (ClO_4^-), while at the pK_a there is little difference in the onset potential.
4. More strongly adsorbing anions (Cl^- , SO_4^{2-} vs. ClO_4^-) lead to a significant reduction of the reaction current in the range of low reaction potentials (< 0.9 V) for Au, while for Pt it remains unchanged for potentials below < 0.5 V (compare Fig. 5 and Fig. 6 and see also ^[33]).
5. Finally, Au electrodes are inactive for H_2 oxidation in the potential range up to the onset of OH adsorption / surface oxide formation.

We will begin with considering the simpler case of Au electrodes, where the absence of CO_{ad} poisoning and OH adsorption in the potential range of interest provides a much simpler scenario than for Pt electrodes. In this case, we can rule out any mechanism which is solely based on the amount of adsorbed bridge bonded formate species (see, e.g., the mechanisms proposed in refs. ^[5;6] for reaction on Pt), since this would not properly reproduce the bell-shaped pH dependence of the activity. We can also discard the mechanism proposed by Cuesta et al. ^[3;4] for reaction on Au electrodes, which involved the chemical reaction of a HCOO_{ad} dimer as rate limiting step and the subsequent electrooxidation of the released H_2 as essential reaction steps, because of the negligible H_2 oxidation activity of Au electrodes under reaction conditions.

As already discussed by Joo et al. ^[15], a distinct pH effect in the reaction rate requires that at least on reaction step is pH dependent. Those authors proposed for formic acid oxidation on Pt that the initial activity increase with increasing pH, in the range of low pH values ($\text{pH} < \text{pK}_a$ of formic acid), results from the increasing concentration of HCOO^- anions in the electrolyte, indicating that this rather than HCOOH is the reactive species,

despite of the very low concentration of HCOO^- at low pH values (3 % at $\text{pH} = 2.3$). This would fit also to our data, both for Pt and Au. Assuming that the reactive intermediate resulting from HCOO^- interaction with the electrode surface interacts weaker with Au than with Pt, this can explain also the much lower reaction rate observed on Au than on Pt by the lower steady-state coverage of the reactive intermediate.

The subsequent decrease of the activity at higher pH values, which is required for the formation of a bell-shaped current – pH correlation, can generally be explained by two effects, either by an increasing coverage of a site blocking species with increasing pH or by the necessity of a second (adsorbed) reaction partner, whose concentration / coverage decreases with increasing pH. If this occurs in the same pH range as the coverage / concentration increase of the first reactant, a more or less symmetric, bell-shaped current – pH correlation will result. Joo et al. had proposed that for reaction on Pt the decreasing activity at higher pH values ($\text{pH} > \text{pK}_a$) results from an increasing adsorption of OH^- species, whose concentration increases with increasing pH. This leads to increasing site blocking and thus to a decreasing reactivity at higher pH values ^[15]. While the general effect of a reduced activity with increasing site blocking or with decreasing concentration / coverage of a second reaction partner is straightforward and obvious, it depends strongly on the nature of the respective reactants and on their interaction with the electrode whether this leads to a bell-shaped activity curve or whether it results in a curve with an extended, plateau-like maximum. Even more stringent are the requirements for a bell-shaped activity curve with its maximum at a specific point, in this case at the pK_a of formic acid. By chance, this may be achieved for an electrode – adsorbate / reactant system with an appropriate adsorbate formation / adsorption behavior, in this case the formation / removal of OH_{ad} , but there is no intrinsic correlation which would enforce a maximum activity at the pK_a ^[34]. In such case, however, one would expect a distinct change in the activity – pH correlation when changing from Pt to Au, since in the latter case OH adsorption is much weaker and OH_{ad} formation occurs only at much higher potentials than on Pt, e.g., at > 1.2 V in 0.5 M H_2SO_4 (see Fig. 1a). Experimentally, however, we find exactly the behavior which was predicted by Joo et al. for formic acid oxidation on Pt, with a bell-shaped activity curve that has its maximum at the pK_a of formic acid for formic acid oxidation on Au. Obviously, in that case, for reaction on Au, the decrease in activity for $\text{pH} > \text{pK}_a$ can not result from an increasing OH_{ad} formation, but must be due to another effect.

Two possible mechanisms, which at least in a first order approximation would be compatible with our findings for reaction at Au and with previously reported data, are briefly described in the following. In both cases, the experimentally observed pH dependence is introduced by the fact that both HCOOH and HCOO^- are required as reaction partners for the reaction to proceed, which fixes the maximum activity at the pK_a in a straightforward way.

In the first mechanism, the reaction is assumed to proceed via the adsorption of $[\text{HCOOH-HCOO}]$ dimers, which then react to CO_2 via a short lived adsorbed reaction intermediate, according to eqs. (1) and (2):

In this reaction mechanism, the electrolyte pH plays a major role in the reaction kinetics by controlling the amount of formic acid - formate dimers in solution. Thus, the bell-shaped catalytic activity as a function of the electrolyte pH (Fig. 2c) can be easily explained. However, while the chemical bonding between formic acid molecule and formate ion in solution is most likely via hydrogen bonding, the nature (structure) of the adsorbed reactive intermediate resulting from the adsorption of such dimer precursor is unknown. In any case, however, the reactive intermediate must be different from the bridge-bonded adsorbed formate, in contrast to previous proposals^[3-6]. This proposal for the reaction resembles partly the mechanism recently proposed by Cuesta et al.^[3,4] who postulated that HCOOH dimers play a key role in the reaction to explain the observed effect of the HCOOH concentration. On the other hand, other important aspects of the reaction scheme proposed by these authors are not compatible with our observations. As mentioned previously, the reactive decomposition of two adjacent adsorbed bridge-bonded formates in a purely chemical bimolecular reaction step can be excluded, since that mechanism would not take into account the effect of the electrolyte pH and since it would also require the oxidation of molecular hydrogen, which is not possible under reaction conditions on Au electrodes (Fig. 1a). In this mechanism, the adsorbed bridge bonded formate detected by IR spectroscopy would act as site blocking species, as proposed earlier by Behm and co-workers^[9-11]. We would like to note that in a more sophisticated picture one would also need to include the pH dependence of the coverage of these adsorbed bridge-bonded formate species, which would cause a deviation from the ideal bell-shaped form of the activity plot (see also the discussion in the supporting information in ref.^[15]).

A second plausible reaction mechanism, which would also account for the key role played by the electrolyte pH on the HCOOH oxidation rate, would involve a possible reaction/interaction between bridge-bonded adsorbed formate species and formate anions. This mechanism assumes that the adsorbed bridge-bonded formate species are mainly formed via adsorption of HCOOH molecules (eq. (3)) (see also ref.^[15]):

This mechanism differs from the first one described in eqs. (1) and (2) in that in this second case adsorbed bridge bonded formate species act as reaction partner rather than formic acid itself. In this case, the formate anions will facilitate the irreversible oxidation of bridge-bonded adsorbed formate to CO₂ (Eq. 4) by accommodating the released protons. As long as the coverage of the adsorbed bridge bonded formate species follows the concentration of formic acid, which is mainly true in the range of lower coverages, this would also lead to a bell-shaped activity behavior. Also in this case, the nature of the actual reaction intermediate is not known.

In this mechanism, the electrolyte pH plays a major role in the reaction kinetics, by controlling the amount of formic acid

and formate molecules / anions in solution, from which the oxidation reaction proceeds. In the limits of a linear relation between formic acid concentration and adsorbed bridge bonded formate coverage (see ref.^[3,4]), both mechanisms would lead to a quadratic relation between oxidation current and adsorbed formate coverage (at constant potential) as it was observed experimentally^[3,4]. Here, it is important to point out that based on a coulometric analysis Xu et al.^[12] recently derived that the oxidation current on a Pt(111) electrode is not linearly proportional to the square of the adsorbed formate coverage. Nevertheless, also the mechanism proposed by these authors^[12], which involves the formation of adsorbed carboxyl species as r.d.s., followed by their oxidative deprotonation, would not match the pH effects observed in the present work.

These two different mechanistic proposals for reaction on Au electrodes would both be compatible with the anion adsorption effects discussed above. Overall, the adsorbed anions act as site blocking species, competing with the adsorbed reactive intermediates. The competitive adsorption will mainly be determined by the specific adsorption strength of the species present (reactive intermediate and site blocking species) and by the concentration of the respective dissolved precursor species at each particular pH. Thus, in strongly acidic solution (low concentration of formate anions), one would expect that more strongly adsorbing anions (SO₄²⁻) shift the onset of the reaction to higher potential compared to weakly adsorbing anions (ClO₄⁻), as observed experimentally (Fig. 5). Adsorbed (bi)sulphate species act as site blocking species, either hindering the adsorption of the reactive intermediate (pathway via [HCOOH-HCOO]⁻ adsorption) or decreasing the adsorbed bridge bonded formate coverage (pathway via HCOO_{ad} - HCOO⁻ reaction). Because of the much higher concentration of formate anions in solution, these differences are much less pronounced and obviously negligible at the pK_a where the onset potential and the maximum oxidation current are essentially similar in sulphuric and perchloric solution. This and the experiments performed in the presence of strongly adsorbed species (Cl⁻) suggest that the adsorption strength of the reactive intermediate must be moderate.

On the other hand, the surface structure of the Au electrodes seems to play a minor role in the general characteristics of the reaction. For low pH values the surface structure effect is almost negligible both in terms of the onset of oxidation and the maximum current density; at pH ≈ pK_a, the HCOOH oxidation current density at 1.0 V is about twofold higher for Au(111) than for Au(100), but with a similar onset potential (about 0.6 V). On Pt electrodes, in contrast, structural effects were shown to be much more pronounced^[18]. In a simple picture this can be understood by a rather small structural variation in the weak interaction of Au with adsorbed species, while for their much stronger interaction with Pt the surface structure plays a more important role.

Overall, we could show that the bell-shaped pH dependence of the formic acid oxidation activity on Au electrodes can only be reproduced if both formate anions on the one hand and formic acid or adsorbed bridge bonded formate species participate in the reaction. Different from a recent proposal for reaction on Pt^[15], OH adsorption is too weak to facilitate the decrease at pH values > 3.8 (pK_a of formic acid). This rules out any mechanism which is solely

based on the adsorbed bridge bonded formate species detected by IR spectroscopy as reactive intermediate.

The situation is distinctly different for reaction at a Pt electrode. First of all, the reaction rate is heavily affected by surface poisoning by adsorbed CO, which is formed as a side product in the indirect (CO_{ad} formation/oxidation) pathway^[1]. Following the procedure used by Joo et al.^[15], we essentially avoided this problem by using the (initial) activity in the negative-going scan, where the CO_{ad} coverage is very low.

The different pH - dependence for the catalytic activity of the polycrystalline Pt electrode (see Fig. 3), with a continuous increase of the activity up to $\text{pH} \approx 5 - 6$ and, in agreement with earlier studies^[28;29], a constant activity at higher pH values until pH 10, seems to indicate that in this case, i.e., for polycrystalline Pt with a fixed structure, the reaction rate is solely determined by the concentration of HCOO^- in the electrolyte. This is not only different from the basic mechanism derived above for reaction at Au electrodes (see also eqs. (1-2) and (3-4)), but also in contrast to the recent proposal by Joo et al.^[15]. The latter discrepancy is easily explained by the difference in experimental data, where we do not find the bell-shaped activity behavior observed by the latter authors. It could also mean, however, that the reaction proceeds in a similar way as discussed for Au, but that the decrease in activity due to adsorption of site blocking species or due to an increasing lack of second reaction partner occurs only at higher pH values and not in the pH regime of the pK_a . In that case one would expect the formation of a plateau in the activity and a decrease only at higher pH values. Hence, while it is clear that the increase in activity up to $\text{pH} \approx 5 - 6$ follows the concentration of HCOO^- anions in the electrolyte, indicating that these anions rather than the HCOOH molecules are the decisive precursor for the reaction, we can rule out from the present data whether another species is involved either as site blocking species, which would cause the activity to decrease at higher pH values.

In this context it is important to realize that the pH effect is much less pronounced for Pt than for Au, while on the other hand Pt is much more active for formic acid oxidation. While on the latter electrode the reaction rate increases by a factor of 150 with increasing pH, up to the maximum rate at $\text{pH} = 3.8$, the difference is only a factor of ~ 6 for Pt (see Figs. 2c and 3b). This would be in agreement with the suggestion by Joo et al.^[15] and also in earlier work by Behm and co-workers^[10;11;35], who mentioned that the formate pathway may contribute to the overall reaction rate, but is not the dominant reaction pathway.

Distinct differences in the reaction behavior on Pt and Au electrodes are observed also in the structural sensitivity and in the anion effects. While for Pt electrodes, the influence of the surface structure on the oxidation rate is large^[18], it is relatively weak for Au electrodes (see Fig. 4). The effect of chloride traces on the catalytic activity is also much more pronounced for Au than for Pt (see Fig. 6). These observations in combination may suggest that the reaction mechanism for HCOOH oxidation is different for both metal electrodes, unlike previous proposals^[3;4]. Nevertheless, a final decision on the reaction mechanism and on the nature of the reaction intermediate is not possible in the moment, neither for reaction on Au, and much less for reaction on Pt. Open questions are, e.g., why the adsorbed bridge bonded formate is mainly formed from HCOOH and not from (dissolved) HCOO^- anions, the physical origin for the different pH dependence for Au and

Pt, or the origin for the much more pronounced pH effect for Au than for Pt. More work to clarify these points and to define more precisely the effect of the electrolyte pH on the electro-oxidation of HCOOH , e.g., on low-index Pt single crystalline electrodes, is in progress.

Conclusions

Based on a careful and detailed comparative study of the pH dependence in formic acid oxidation on different Au and Pt electrodes and of the effect of strongly adsorbing anions and of the electrode surface structure in this reaction, we could unravel a number of important mechanistic details of that reaction, which contribute significantly to the mechanistic understanding of this apparently simple, but nevertheless mechanistically non-understood reaction. Specifically, we arrived at the following observations and conclusions on the mechanism of formic acid oxidation:

1. For the oxidation of HCOOH on bulk Au electrodes, the observation of i) a bell-shaped correlation between activity (in the potential regime of the reaction onset) and pH, with a maximum for a pH value identical to the pK_a of formic acid, and ii) the relatively weak adsorption of OH points to a reaction mechanism where both HCOOH and HCOO^- are involved in the reaction. This may be either directly, by formation and subsequent adsorption and reaction of $[\text{HCOOH} - \text{HCOO}]$ dimers, or indirectly, by formation of HCOO_{ad} from HCOOH and reaction of that species with HCOO^- to form CO_2 . In both cases the nature of the reaction intermediate is unclear, but it is definitely not the adsorbed bridge bonded formate species detected by IR spectroscopy.
2. The pH dependence of the reaction in combination with the absence of molecular H_2 oxidation on PGM decontaminated Au electrodes in acidic solutions rule out a mechanism proposed previously for formic acid oxidation on a Au electrode, which involves the chemical reaction of two (adjacent) adsorbed bridge bonded formate species, followed by electrooxidation of the H_2 resulting in the first step.
3. The pH dependence is independent of the nature of the anion in the supporting electrolyte (ClO_4^- vs. SO_4^{2-}), ruling out a site blocking by adsorbed anions as origin for the decay of the activity at $\text{pH} > \text{pK}_a$. This further supports the above conclusion that the bell-shaped activity – pH correlation is due to reaction between HCOOH (or HCOO_{ad} resulting from HCOOH) and HCOO^- anions.
4. Two reaction mechanisms which agree with the experimental observations and previous reports for formic acid oxidation on Au electrodes were formulated. It should be noted however, that other reaction mechanisms fulfilling these kinetic conditions cannot be ruled out from the present data.
5. For reaction on Pt surfaces we observed a distinctly different pH dependence of the activity, with a steady increase of the catalytic activity up to $\text{pH} \approx 5 - 6$. The correlation between increasing concentration of HCOO^- anions in the electrolyte and catalytic activity indicates that similar to Au these anions act as precursor for the reaction.

Site blocking by adsorbed OH (or surface oxide) does not seem to play a role under these reaction conditions, at least not in the pH regime up to $\text{pH} \approx 5 - 6$, in contrast to a previous proposal^[15].

6. This together with other marked differences in the reaction characteristics, such as the much more pronounced pH effect on Au or the much stronger structural sensitivity of Pt, may suggest that different reaction mechanisms operate for HCOOH oxidation on Pt and Au electrodes, but can be explained also by the different adsorption strengths of the adsorbed species involved in the reaction. The much weaker pH effect on Pt compared to Au may also indicate contributions from a second pathway, e.g., from the formate pathway, in that case.

In summary, this study demonstrated the potential but also the limitations of kinetic studies varying a number of parameters. Further work is needed for an unambiguous decision on the mechanism and in particular for the identification of the reaction intermediate(s) in this apparently simple reaction.

Experimental Section

The experiments were conducted in a three-electrode beaker glass cell, using a gold wire as counter electrode. The potentials were measured against a reversible hydrogen electrode (RHE) or mercury/mercurous sulphate electrode connected to the cell via a Luggin capillary. All potentials refer to the RHE scale after correction of the thermodynamic effect of the pH on the electrode potentials. Appropriate amounts of H_2SO_4 or HClO_4 (suprapure Merck), Na_2SO_4 or NaClO_4 (HiPerSolv, Prolabo), and NaOH (99.99%, Sigma-Aldrich) were added to MilliQ® water (Millipore, 18 M Ω cm) in order to prepare electrolytes at various pH values, maintaining a constant (bi)sulphate or perchlorate concentration (0.5 M). For all experiments, the initial concentration of HCOOH was fixed at 0.1 M. Thus, depending on the electrolyte pH, formic acid will be more or less dissociated, but the overall concentration of formic acid + formate ions was constant for all experiments. The electrolytes were purged by Ar bubbling (Westphalen 6.0 N). Particular attention was paid to the cleanness of the experimental set-up. Polycrystalline gold and platinum beads prepared from metal wires (99.999% purity, Alfa Aesar) as well as Au single crystals were used as working electrodes. For the polycrystalline gold electrode, traces of residual platinum group metals (PGM) contaminations were removed by aqua regia / flame annealing treatment, following a procedure recently developed by the Alicante group^[16]. Au single crystalline electrodes were prepared according to a modification of the Clavilier's method^[36]. An EDI-101 rotating disk electrode (2 mm Pt tip, Radiometer) was also used. The rotation rate was controlled by a Radiometer CTV 101 apparatus. Prior to the use of the Pt RDE, this was electrochemically cleaned (cycles between surface oxidation and hydrogen adsorption-desorption regions) in 0.5 M H_2SO_4 until a stable voltammetric response was obtained. All experiments were conducted at room temperature.

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Keywords: formic acid oxidation • gold • platinum • pH effect • reaction mechanism

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ARTICLES

An unsolved reaction mechanism.

None of the mechanistic proposals reported previously can rationalize the activity of noble metal electrodes towards formic acid oxidation. Does a systematic investigation under various experimental conditions can provide new ideas?

S. Brimaud, J. Solla-Gullón, I. Weber, J.M. Feliu and R.J. Behm*

Page No. – Page No.

Formic acid electrooxidation on noble metal electrodes: The role of pH, surface structure and anion adsorption, and their mechanistic implication