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Pt
CO

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(FTIR)   (differential electrochemical mass spectrometer, DEMS)   Pt   .   Pt

.

(n_e)   . n_e= 2 2   CO   COH   ,

CO   COH.   ,   1 262 cm⁻¹   2 048 cm⁻¹

Pt   CO   COH   .

,   DEMS   -13   CO   .

CO,   CO   75%

.

,   ,   Pt,   ,

Study of the Natu re of Form ic Acid Adsorba tes on Rough Pt and its Interaction with CO

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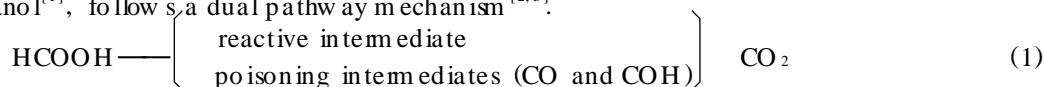
Abstract   The nature of formic acid adsorbates formed on porous platinum electrode has been studied by in-situ infrared reflectance spectroscopic (FT IR) and differential electrochemical mass spectroscopic (DEM S) techniques. By carefully avoiding the contamination of the environment(*i e* , air) voltammetric experiments show that the oxidation of formic acid adsorbates depends on both adsorption potential and adsorption time. The online DEM S results show furthemore that the number of electrons necessary for the formation of one molecule of CO_2 from adsorbed formic acid is independent of the adsorption potential. Its value of 2.2 demonstrates that the composition of formic acid adsorbates is a mixture of CO and COH, but not CO or COH alone. The existence of these two species has been clearly proved by in situ FT IR experiments on electrodeposited platinum with a roughness factor of 11. The bands at 1 262 cm^{-1}, 1 840 cm^{-1}, and in the frequency range of 2 048 to 2 060 cm^{-1} are due to the surface adsorbed COH, bridge and linearly bound CO_{ad}, respectively.

In addition, the interaction between formic acid adsorbates and CO has been investigated by using DEM S via isotopic labelled ^{13}C-formic acid as a probe as well. These experiments show that the surface species previously fromed from CO and formic acid cannot be exchanged by formic acid in solution. whereas about 75 percent of the firstly formed formic acid adsorbates can be replaced by bulk CO.

Key words   Formic acid, Adsorbates, Interaction, Porous Pt, In situ FT IR, DEM S

1   Introduction

The oxidation of formic acid at platinum electrode in acidic medium, as in the case of methanol[1], follows a dual pathway mechanism[2, 3].

$$HCOOH \longrightarrow \begin{bmatrix} \text{reactive intermediate} \\ \text{poisoning intermediates (CO and COH)} \end{bmatrix} CO_2 \qquad (1)$$

In this mechanism, parallel to the oxidatin of formic acid to final product CO_2 via a reactive intermediate, there is a pathway for the formation of poisoning intermediate. Because

of the formation of poisoning intermediate, which can be oxidized only at higher overpotentials, the direct reaction pathway is heavily inhibited. Obviously, the identification of the nature of the poisoning intermediate would contribute to a better understanding of the electrocatalysis of small organic molecules, and to a development of effective catalysts for the practical performance of fuel cells as well.

In the discussion of the nature of formic acid adsorbates, two species are usually assumed: either CO_{ad} as proposed by Lamy[4], COH (or HCO) as postulated by Capon and Parsons[2], Bagotzky et al[5], Breiter[6] and Willsau and Heitbuaum[7]. But mixtures of CO and COOH radical[8] have also been suggested. Besides, some other possibilities have been also proposed, such as HCOO[9], C_2O_3[10].

Early work on the identification of the nature of formic acid adsorbates was carried out by using either coulometry or cyclic voltammetry. These conventional methods offer, however, only indirect information. The knowledge of the nature of the intermediates under the molecular level can by obtained by using recently developed techniques: on line electrochemical mass spectrometer and in situ infrared reflectance spectroscopy.

By using DEMS technique, Willsau and Heitbaum[7] studied the natures of the strongly bound intermediates derived from formic acid, methanol and also reduced CO_2 on porous platinum surface in 0.5 mol/L H_2SO_4, while isotope labelled chemicals were used as mass spectrocscopic probes. It was found that these adsorbates cannot be identical with adsorbed CO. Instead, HCO_{ad} is postulated to be the strongly bound intermediate of formic acid, methanol and reduced CO_2.

On the other hand, Lamy and co-workers[4,11] studied the oxidation of formic acid on Pt, Rh and Pd. The nature of the poisoning intermediate was identified by using in-situ IR reflectance spectroscopy. EMIRS has shown quite convincingly that there are two species on the electrode surfaces: linearly and bridge bound CO regardless of which organic fuel was used, with the exception of formic acid on Pd. For the latter electrochemical measurements have shown that no strong poisoning occurs. The poisoning intermediate derived from formic acid on a series of low index crystal surfaces, namely, Pt(111), Pt(110) and Pt(100), was identified as CO_{ad}[3] as well. It is obvious that the formation of the adsorbate of formic acid shows no sensitivity to the surface structure of the electrodes used.

Comparing the results of on-line electrochemical mass spectroscopy and those derived with in situ IR reflectance spectroscopy, obvious discrepancy exists. Some possible causes were suggested by Heitbaum et al[7]. They thought that first, oxygen impurities change the adsorbate in a way that only two electrons are needed for obtaining CO_2, which means that HCO_{ad} could be oxidized to give CO when oxygen or its reduction intermediate is present near the electrode surface. Second, they thought that HCO_{ad} might undergo photodissociation of the H atom upon the absorption of a photon in the C=O double bond and dissipation of the vibration energy. This at least could be imagined if multi-photon absorption occurs during the life time of an excited molecule and if the H-C bond is weakened due to a back donation bonding between C and Pt. From the standpoint of IR reflectance spectroscopy, on the other hand, it was suggested[12] that there are parallel reaction pathways for the forma-

tion of poisoning and reaction intermediate, and that the situation is complicated owing to the coadsorption of many surface species.

In order to verify the difference between the results obtained from on-line electrochemical mass spectrometry and in-situ IR spectroscopy, Heitbaum et al [13] studied the effect of oxygen on the nature of the adsorbate. It was found that the number of electron to form one molecule CO_2 out of strongly adsorbed intermediate decreased to 2-2.5 if traces of oxygen were present. However, during the investigation of the time dependent potential oscillations occurring during galvanostatic formic acid oxidation[14], the obtained data gave no evidence for an adsorbate such as HCO within the limits of error. Instead only two-electron oxidation processes take place which has to be taken as an experimental hint that under the condition of continuous HCOOH oxidation CO must be the main adsorbate. This result turns out to be a great different to that obtained in ref. [7], which may originate from the different conditions of the formation of adsorbates.

It should be bored in mind that smooth and rough surface electrodes were used in IR and DEMS experiments, respectively. The nature of the adsorbates derived from organic fuels may depend upon the electrode surface rather than electrode bulk. Christensen et al [15] noted that the CO_{ad} species is absent in the electrooxidation of methanol on platinised glassy carbon electrodes. It is obvious that a better solution of these discrepancy in the case of formic acid can only be settled by further experiments.

In this paper, the adsorption isotherm of formic acid on sputtered platinum electrode was investigated by using voltammetry, and the identification of the nature of the formic acid adsorbates on electrochemically deposited Pt was carried out by using in situ FTIR and on line DEMS techniques. Finally, the interaction between formic acid and CO was also studied.

2 Experimental

2.1 Chemicals

All solutions were prepared with Milli-Pore water (> 18M Ω). In order to avoid the anion specific adsorption, 0.1 mol/L $HClO_4$ (prepaved from $HClO_4$, > 70%, R. G., Riedel de Haen) was used as supporting electrolyte. Normal formic acid (^{12}C, chemical purity 98% 99%, R. G., Riedel de Haen) and isotope labelled ^{13}C-formic acid (^{13}C 99%, chemical purity 94.5%, Cambridge isotope laboratories) were used without further purification. CO 4.7 (99.997%, Messer Griesheim) was used as received. Argon 4.8 (99.998%, Messer Griesheim) was used to deaerate the solution and eliminate the dissolved CO as well.

2.2 Instrumentations

For the determination of volatile products, electrochemical mass spectrometry (DEMS)[16, 17] was used. This system is controlled by a personal computer (Epson PC20) via 12-bit AD/DA convertor described elsewhere[17]. A special flow cell (total volume is about 8 ml) is constructed in such a way that allows the performance of the replacement of solutions strictly under controlled potential. The working electrode was a layer of platinum sputtered on a microporous ethylene-tetrafluoroethylen copolymer membrance (SCMAT 200/40/60,

mean thickness: 60 μm, porosity: 50% and mean pore size: 0. 17 μm) which is connected directly to the inlet of the ion source of the quadruple mass spectrometer QMG 112 A (Balzers). The counter electrode was a platinum wire (diameter 0. 5mm).

A reversible hydrogen electrode (RHE) was used as reference electrode in all experiments. The potentials reported here refer to this electrode in the same solution.

2. 3 Determination of coverages of surface species

It is generally known that evolution of hydrogen at electrode surface is strongly inhibited by the presence of organic adsorbates. Therefore, the coverages of surface species (Θ_{sp}) are determined from the decreased charge (Q_H) required for the desorption of hydrogen as follow:

$$\Theta_{sp}= (Q_H^0 - Q_H)/Q_H^0 \tag{2}$$

where Q_H^0 and Q_H represent the charges of hydrogen desorption in the absence and presence of surface species, respectively.

3 Results and Discussions

3. 1 Determination of the nature of formic acid adsorbates

1) Voltammetric characteristics of the oxidation of formic acid adsorbates at different coverages

A qualitative investigation of the formic acid adsorbates was carried out by using voltammetry. Fig. 1 shows potential scan curves for the anodic stripping of formic acid adsorbates formed on a sputtered platinum electrode (roughness factor *ca.* 20) at 250 mV from a solution of 0. 01 mol/L HCOOH + 0. 1 mol/L HClO$_4$ for different adsorption time. At short adsorption time (curve 1, Θ_{res}= 0. 13), there appears an asymmetric peak in the stripping voltammetry, its peak potential is located at 675 mV. With the increase of the adsorption time, a small shoulder (curve 2, Θ_{res}= 0. 172) appears at the current increasing side. This undefined feature increases with increase of the adsorption time. At saturation adsorption (3 minutes) it becomes the main peak (curve 5, Θ_{res}= 0. 84) being located at 680 mV, and the former asymmetric one (at Θ_{res}= 0. 13) shows in this case only a small spike (located at 692 mV) at the right side of the main peak. In addition, it is observed that the oxidation peak potential for the main peak increases with the increase of the coverage degree of formic acid adsorbates, which demonstrates that island oxidation
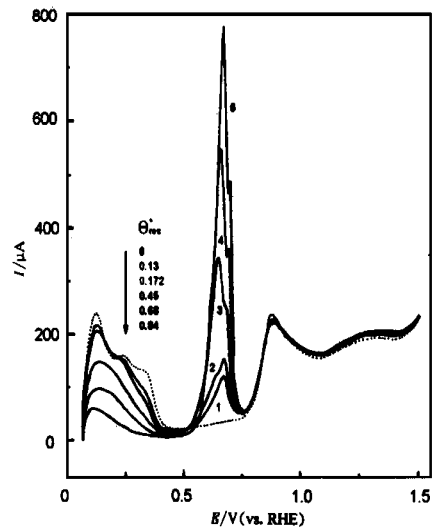

Fig. 1 Anodic voltammograms for the oxidation of formic acid adsorbates at a sputtered platinum electrode in 0. 1 mol/L HClO$_4$ at 10 mV/s. The submonolayers of formic acid adsorbates were formed at 250 mV from a solution of 0. 01 mol/L HCOOH + 0. 1 mol/L HClO$_4$ during different adsorption time

mechanism is operative. Considering the oxidation of formic acid adsorbates formed on smooth single crystal platinum electrodes[18] shows single peak located at different potentials respective to different planes. The appearance of two peaks in our case could be due to the presence of a certain preoriented basals on sputtered platinum surface. Those basal sites are preferentially occupied by formic acid adsorbates whose oxidation results in the asymmetric peak.

Comparison of the hydrogen region suppressed by the deposition of formic acid adsorbates with the case for CO, it can be found that the adsorption of formic acid, unlike that of CO which suppresses simultaneously the weakly and strongly bound hydrogen adatoms, hinders the strongly bound hydrogen adatoms preferentially. This phenomenon becomes much more clear when formic acid adsorption reaches its saturated state (Θ_{res}= 0. 84, curve 5). The adsorption of strongly bound hydrogen adatoms is completely suppressed, but the adsorption of weakly bound hydrogen adatoms can still take place on the rest of the surface sites. A cause of this difference could result from either different adsorption behaviour between CO and formic acid or different composition of surface species being formed.

2) Dependence of the coverage on adsorption potential

The oxidation of formic acid adsorbates formed at different adsorption potential on sputtered platinum electrode for 3 minutes is shown in Fig. 2. It can be seen clearly that the dependence of the anodic stripping voltammetry for the oxidation of formic acid adsorbates on the coverage degree shows a similar behaviour as in Fig. 1. The asymmetric peak appears when the coverage degree of formic acid adsorbates is very low; with the increase of the coverage (Θ_{res}) by changing the adsorption potential, there appears a new peak at the negative side of the asymmetric peak (curves for E_{ad}= 75 mV). This

Fig. 2   Anodic voltammograms for the oxidation of formic acid adsorbates at a sputtered platinum electrode in 0. 1 mol/L HClO₄. After the surface species were formed from a solution of 0. 01 mol/L HCOOH+ 0. 1 mol/L HClO₄ at the potential of E_{ad} during 3 minutes, the solution was then exchanged by 0. 1 mol/L HClO₄ for 3 minutes. For comparison the results of blank experiment is also shown (dotted curves). Scan rate 10 mV/s. (a) Current/Potential curves (CV), and (b) MSCV for CO_2, m/e = 44

new one, increasing abruptly with Θ_{res}, becomes the main component on the surface at E_{ad}= 215 mV. The dependence of the coverage of formic acid adsorbates at a sputtered platinum electrode on the adsorption potential is shown in Fig. 3. As expected this relationship be-
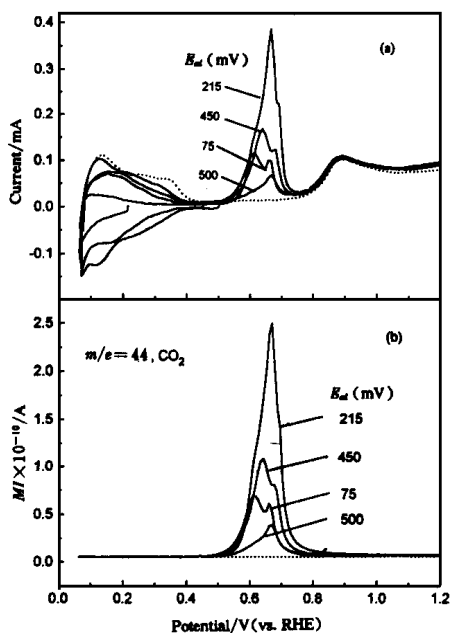
tween Θ_{res} and E_{ad}, being similar to that observed on smooth one, shows an asymmetric bell shape. Three different regions can be classified: In the first region of 50 to 200 mV, there is an abrupt increase in the coverage of formic acid with the increase of the potential; In the second region of 200 to 300 mV, there is no dependence of Θ_{res} on the potential. This hints that a maximum adsorption of formic acid ($\Theta_{res} = 0.84$) is reached in this potential region. In the third region of 300 to 650 mV, there is an abrupt decrease in coverage with E_{ad}. In addition, it is found that there is almost no adsorption of formic acid taking place at $E_{ad} < 50$ mV and $E_{ad} >$ 650. The former is due to the inhibition of a monolayer of hydrogen adatoms; the latter is due to the formation of the surface oxide.

Fig. 3 Dependence of the coverage of formic acid adsorbates on adsorption potential. The data were obtained from CVs in Fig. 2

It should be also emphasized that the saturated coverage ($\Theta_{res} = 0.84$) of formic acid adsorbates at a sputtered platinum is somewhat higher than the value of 0.75 for smooth electrodes reported previously. This phenomenon can be probably attributed to the surfaces with different roughness factors.

3) In-situ FTIR results

In order to get a common knowledge over the results between anodic stripping voltammetry of formic acid adsorbates and DEMS experiments (will be presented in the next section 1.4), in situ FTIR spectroscopy was used to characterize the nature of adsorbed formic acid at an electrodeposited platinum electrode (roughness factor ca. 11) in 0.1 mol/L HClO$_4$. Use of such a porous electrode was aimed to confirm a similar surface properties between the sputtered platinum electrode and the electrochemically deposited one, so that the experimental results of in situ FTIR can be regarded as a direct reflection of those in DEMS measurements.

After adsorption and electrolyte replacement as described in Fig. 2, a reference spectrum (R_0) was measured at 0.1 V. Then the potential was stepped forward to 1.40 V at which a sample spectrum (R) was measured. The calculated reflectance spectrum (R/R_0) is shown in Fig. 4. Three positive bands can be defined because of the anodic stripping of the previously formed formic acid adsorbates. The positive-going bands at 2 048 cm^{-1} and 1 840 cm^{-1} (see the insert) can be assigned to the C–O stretching vibrations of linearly- and bridge bound CO, respectively. Parallel to these two features, another positive-going band located at 1 261 cm^{-1} (see the insert) can be assigned to COH surface species as discussed in literature[19]. From the relative intensities of the bands, it can be concluded that linearly bound CO is the main component from formic acid adsorption, multibound CO and COH only account for small percentages. Other bands are due to the increase or decrease in concentra-
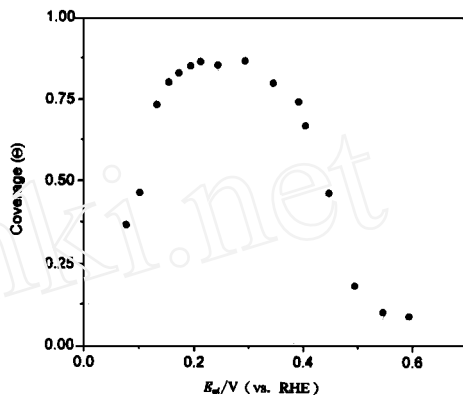
tions of solution species in the cavity of the thin layer between working electrode and CaF$_2$ optical window accompanying the electrochemical processes. The negative-going band at 2 342 cm^{-1} is due to the formation of $^{12}CO_2$ from the oxidation of adsorbates at 1. 40 V , and the negative-going band at 2 276 cm^{-1} is due to $^{13}CO_2$ (which results from the small amount impurity of isotope H^{13}COOH). The bands at 1 645 cm^{-1} and 1 100 cm^{-1} due to respectively uncompensated water and ClO$_4^{-1}$ anion.

The spectra for formic acid adsorbates formed at different potential are shown in Fig. 5. In Fig. 5 a, the amount of linearly bound CO (see the positive-going band at wavenumber between 2 048 cm^{-1} and 2 060 cm^{-1}) increases up to a adsorption potential E_{ad}= 250 mV , then shows decrease. The bridge bound CO (at 1 840 cm^{-1}) appears only at lower adsorption potential (E_{ad} = 100 mV). However, it is interesting to find that the change of the intensity of the band at 1 262 cm^{-1} for COH (see Fig. 5 b) is almost potential independent between 0. 10 V and 0. 50 V.

Based upon the results described above, it can be concluded that on a porous surface platinum (roughness factor *ca.* 11), linearly bound CO and multibound COH can be formed at any adsorption potential (in the range of 50 mV to 600 mV).
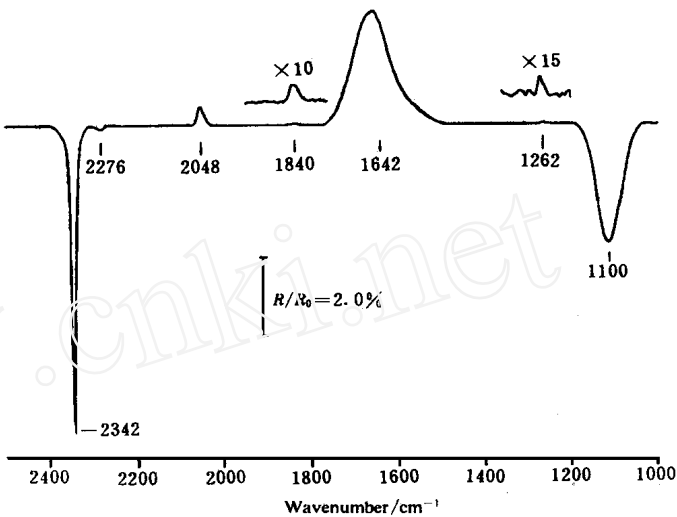

Fig. 4   In situ FT IR spectrum (1 024 scans with resolution of 8 cm^{-1}) for formic acid adsorbates on an electrochemically deposited platinum electrode (R_f = 11) in 0. 1 mol/L HClO$_4$. The formic acid adsorbates were formed at 0. 10 V during 3 minutes from a solution of 0. 01 mol/L HCOOH+ 0. 1 mol/L HClO$_4$. Reference and sample spectra were collected at 0. 10 V and 1. 40 V , respectively
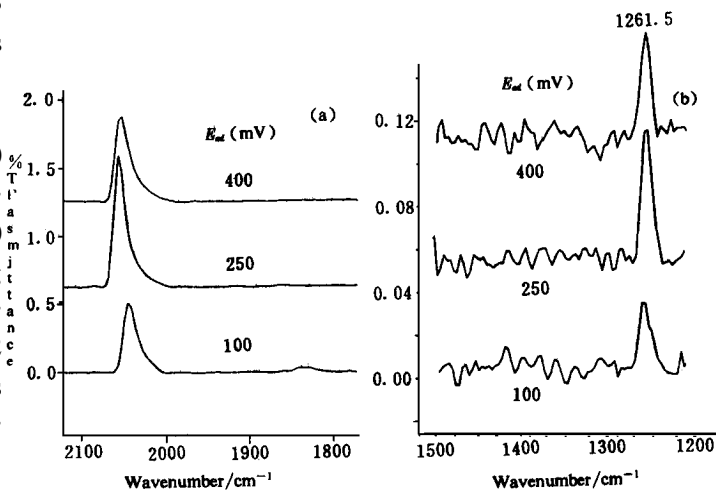

Fig. 5   In situ FT IR spectra (1 024 scans with a resolution of 8 cm^{-1}) for formic acid adsorbates formed as in Fig. 4 but at different adsorption potentials (E_{ad}= 0. 10, 0. 25 and 0. 40 V) on the electrochemically deposited platinum electrode (R_f = 11) in 0. 1 mol/L HClO$_4$. Reference spectrum and sample spectra were collected at E_{ad} and 1. 40 V , respectively. (a) Spectra of linearly and bridge bound CO, (b) spectra of surface species COH

However, the formation of multibound CO is limited by experimental conditions. It can be formed only either at lower adsorption potential (i.e., $E_{ad}= 100\,mV$) or at low surface coverage of organic residues. In the latter case, with the increase of the surface coverage the bridge bound CO must be interconverted into stronger bound CO (linearly bound CO). This suggestion has been proved by the in situ FTIR results on single crystal platinum[3].

4) DEMS results

The DEMS technique is an useful tool for qualitative on-line detection of volatile products electrochemically generated. Besides, it offers a possibility for quantitative analysis of the volatile products formed in electrochemical reactions as well, because there is a direct proportional relationship between electric current and simultaneously registered mass intensity for a certain faradaic reaction. Therefore, in terms of equation (3), the numbers of electron (n_e) for the formation of one molecule of CO_2 out of formic acid adsorbates can be easily determined.

$$n_e = K^* \mathbf{Q}/\mathbf{Q} \tag{3}$$

where $\mathbf{Q}/\mathbf{Q}$ represent the faradaic charge for the electrooxidation of organic adsorbates and the integration under the corresponding mass ion current-potential curve for CO_2. K^* is a constant including all parameters of mass spectrometer, which are not specific for a given electrochemical process. This constant can be calibrated in terms of the method previously advocated[17] by using CO as a probe. In our case, this constant was determined a few times repeatedly under same conditions at the beginning of a series of experiments. An average value of this constant $K^* = 1.73 \pm 0.02 \times 10^{-6}$ was obtained.

Fig. 2 b shows the simultaneously registered mass signal for CO_2 ($m/e= 44$), during the anodic stripping of formic acid adsorbates at sputtered platinum in acid solution (see Fig. 2 a). The mass signal follows the current well. This demonstrates clearly that the current signal obtained in CV comes out of the oxidation of formic acid adsorbates. By substituting the average value of the parameter K^* ($= 1.73 \pm 0.02 \times 10^{-6}$) into equation (3) the electron numbers necessary for the formation of one molecule CO_2 out of formic acid adsorbates are calculated. The results for formic acid adsorbates formed at the potentials between 75 mV and 500 mV are listed in Table 1. The electron number n_e shows an independence in the adsorption potential, except for $E_{ad}= 500\,mV$. Since the in situ FTIR experiments have shown that out of the formic acid adsorbates CO and COH can be formed on the electrode surface. Thus an average value of $n_e= 2.2$ demonstrates unambiguously that the surface species, derived from a solution of $0.1\,mol/L\ HCOOH + 0.1\,mol/L\ HClO_4$ on porous platinum at different adsorption potential, should not consist of CO or COH alone, but of a mixture of them, because the surface species in form of CO or COH alone need respectively two or three electrons to form one CO_2 molecule. Based upon this concludsion a ratio of CO COH= 4 1 can be obtained.

Tab. 1 Dependence of the electron numbers for formation of one molecule of CO_2 out of formic acid adsorbates and the coverage of poisoning species on adsorption potential

E_{ad} (mV)	75	100	135	175	250	300	350	400	500
Θ_{res}	0. 37	0. 46	0. 75	0. 84	0. 85	0. 86	0. 80	0. 75	0. 18
n_e	2. 24	2. 18	2. 19	2. 20	2. 23	2. 14	2. 14	2. 25	2. 51
Average of n_e	2. 20 (excluding E_{ad}= 500 mV)								

3. 2 Interaction between the surface species derived from formic acid and CO by using isotope labelled formic acid as a probe

1) Oxidation of the adsorbates derived from CO and ^{13}C formic acid alone

In this experiment formic acid was adsorbed at 250 mV for 10 minutes from a solution of $5 \times ^{-3}$ mol/L $H^{13}COOH$ + 0. 1 mol/L $HClO_4$, then the bulk formic acid was removed by replacing the solution with base electrolyte during 5 minutes (*ca.* 100 ml) under potential control. The voltammetric characteristics (CV) for the oxidation of formic acid adsorbates on a sputtered platinum in base electrolyte is presented in Fig. 6 (a, dotted curve), the simultaneously registered mass signals for $^{13}CO_2$ (Fig. 6 b, dotted curve, the main component due to an oxidation of isotope labelled formic acid adsorbates) and $^{12}CO_2$ (Fig. 6 c, dotted curve, due to the presence of 1% $H^{12}COOH$ in $H^{13}COOH$ and the resolution of the mass spectrometer). As expected the shapes of mass signals take after the anodic stripping peak in CV again.

In another experiment, CO was adsorbed at 250 mV by bubbling CO gas during 10 minutes. Then dissolved CO was eliminated by Ar bubbling (*ca.* 5 minutes). The CV and simultaneously recorded mass signals of ^{12}CO and ^{13}CO for the oxidation of adsorbed CO on sputtered platinum in 0. 1 mol/L $HClO_4$ are shown in Fig. 7 (dotted curves). A small amount of $^{13}CO_2$ signal (Fig. 7c, dotted curve) results from m/e= 44 signal due to the less resolution of the mass spectrometer.

2) Interaction of surface species with bulk formic acid

In order to study the interaction between adsorbed and bulk formic acid, 5×10^{-3} mol/L $H^{13}COOH$ was adsorbed to saturation at 250 mV (10 min.), then the solution was replaced first by 0. 1 mol/L $HClO_4$ during 5 minutes, and subsequently by 0. 01 mol/L $H^{12}COOH$ + 0. 1 mol/L $HClO_4$. After 10 minutes interaction with bulk formic acid, the solution was exchanged again by $HClO_4$ during 5 minutes in order to remove the ^{12}C formic acid in solution. After that an anodic potential scan at 10 mV/s in base electrolyte was started. The results are shown in Fig. 6 (solid curves). The recorded CV and MSCVs of $^{13}CO_2$ and $^{12}CO_2$ for the oxidation of the surface species in this case coincide well with those without interaction with 0. 01 mol/L $H^{12}COOH$ (see Fig. 6 dotted curves). This fact clearly demonstrates that there is no displacement of adsorbed formic acid by bulk formic acid. This shows a good agreement with the results observed on Rh(111) by using Real-Time FTIR Spectroscopy[20] in which they found that there is essentially no replenishment of the initially adsorbed ^{13}CO with ^{12}CO
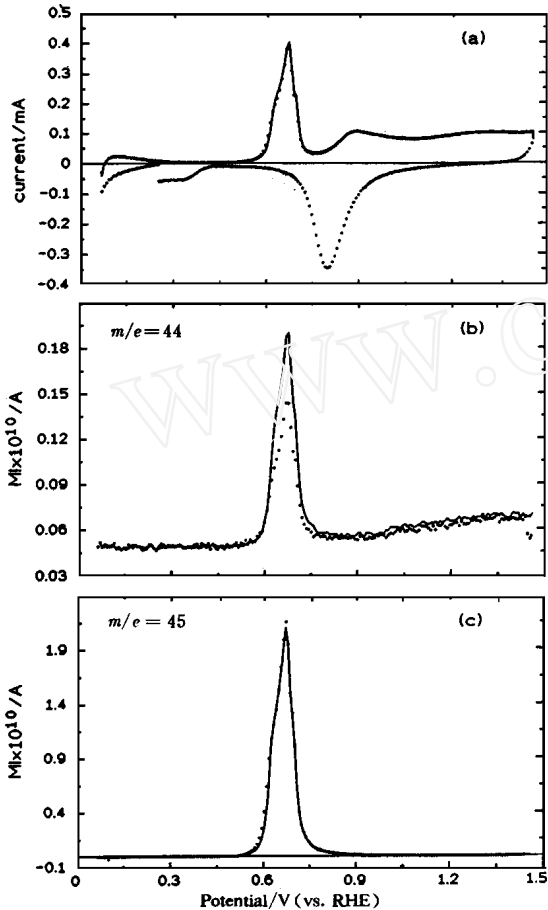
Fig. 6 Oxidation of the formic acid adsorbates formed
from a solution of 5×10^{-3} mol/L $H^{13}COOH+$
0.1 mol/L $HClO_4$ at 0.25 V during 10 minutes
on a sputtered platinum electrode in 0.1 mol/L
$HClO_4$, after 10 minutes interaction with 0.01
mol/L $H^{12}COOH$. For comparison, the result of
the oxidation of formic acid adsorbates alone is
also presented (dotted lines). Scan rate 10 mV/s
(a)CV, (b) MSCV for $^{12}CO_2$ ($m/e=44$), and
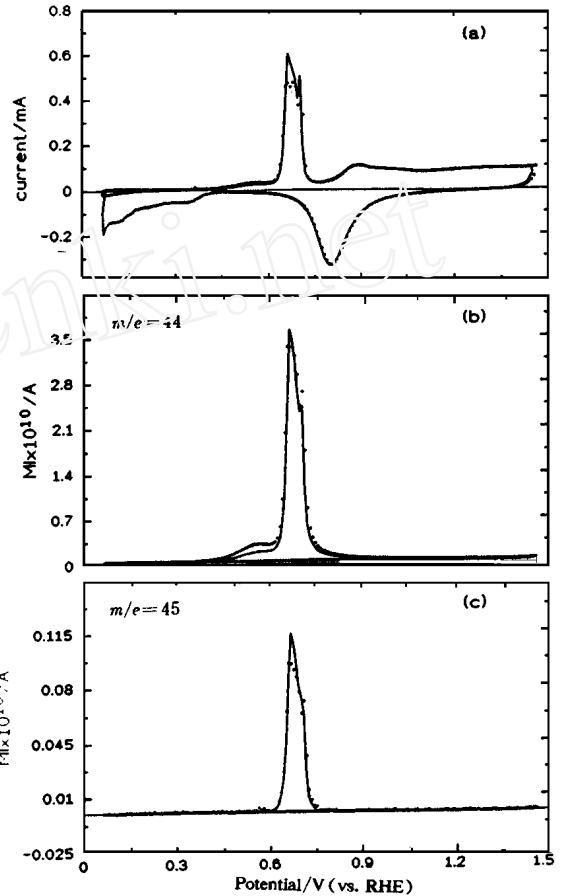(c) MSCV for $^{13}CO_2$ ($m/e=45$)

Fig. 7 Oxidation of the surface species derived from
CO at 0.25 V during 10 minutes on a
sputtered platinum electrode in 0.1 mol/L
$HClO_4$, after 10 minutes interaction with $5\times$
10^{-3} mol/L $H^{13}COOH$. For comparison the
result of the oxidation of adsorbed CO alone
is also presented (dotted lines). Scan rate 10
mV/s (a)CV, (b)MSCV for $^{12}CO_2$ ($m/e=$
44), and (c) MSCV for $^{13}CO_2$ ($m/e=45$)

formed from solution formic acid during the voltammetric cycle, prior to its electrooxidative
removal Sililar results were obtained if we used adsorbed CO to interact with bulk formic
acid $H^{13}COOH$. As can be observed in Fig. 7 (solid curves) the CV and the corresponding
MSCVs for $^{13}CO_2$ and $^{12}CO_2$ are the same as those without interaction with $H^{13}COOH$ (com-
paring the dotted curves in Fig. 7), which indicates that CO adsorbate formed on sputtered
platinum cannot be removed by bulk formic acid as well

3) Interaction of formic acid adsorbates with bulk CO

In another experiment, saturated ^{13}C formic acid adsorbates were formed on the same electrode as in Fig. 6 from a solution of 5×10^{-3} mol/L $H^{13}COOH$ + 0.1 mol/L $HClO_4$, at 250 mV during 10 minutes. The solution was then replaced by base electrolyte, subsequently ^{12}CO was bubbled during 5 minutes. After elimination of bulk CO by argon bubbling for 5 minutes, a cyclic potential sweep was resumed (Fig. 8, solid curves). The corresponding carbon dioxide product was followed by simultaneously recording the mass signals for $m/e = 44$ ($^{12}CO_2$, Fig. 8b, solid curve) and $m/e = 45$ ($^{13}CO_2$, Fig. 8c, solid curve). After the interaction of formic acid adsorbates with bulk CO, the intensity for $^{12}CO_2$, $m/e = 44$ (due to the oxidation of CO, Fig. 8 b, solid curve) increased considerably. In contrast, the intensity for $^{13}CO_2$, $m/e = 45$ (due to the oxidation of adsorbed formic acid, Fig. 8c, solid curve) reduced to about 30% of its original value. By integrating the areas for both CO_2 mass intensities, it was found that the total amount of the surface species was increased as compared to that of the oxidation of formic acid adsorbates alone (see Fig. 8 b and c, dotted curves). Obviously, the increased amount of the surface species can be attributed to the adsorption of CO on those sites of the electrode surface (about 16% surface sites of the electrode is still free in the case of the adsorption of formic acid reaching its maximum) which are not accessible to the adsorption of formic acid. In addition, a predesorption peak located at about 550 mV (Fig. 8 b, solid curve), which is a characteristic for the oxidation of adsorbed CO on platinum, is observed. These facts demonstrate clearly that introduction of CO into this system results in an essential exchange between previously adsorbed formic acid and bulk CO.

Fig. 8 Oxidation of the formic acid adsorbates (formed from a solution of 5×10^{-3} mol/L $H^{13}COOH$ + 0.1 mol/L $HClO_4$ at 0.25 V during 10 minutes) on a sputtered platinum electrode in 0.1 mol/L $HClO_4$, after 10 minutes interaction with CO. After the interaction, the dissolved CO was removed by bubbling Ar for 5 minutes, for comparison, the result of the oxidation of the formic acid adsorbates alone is also shown (dotted lines). Scan rate 10 mV/s (a) CV, (b) MSCV for $^{12}CO_2$ ($m/e = 44$), and (c) MSCV for $^{13}CO_2$ ($m/e = 45$)

The exchange between previously adsorbed formic acid adsorbates and bulk CO can be ascribed to two possibilities, one is that the bonding energy between CO and Pt is stronger than that between formic acid adsorbates and Pt, therefore the previously adsorbed formic
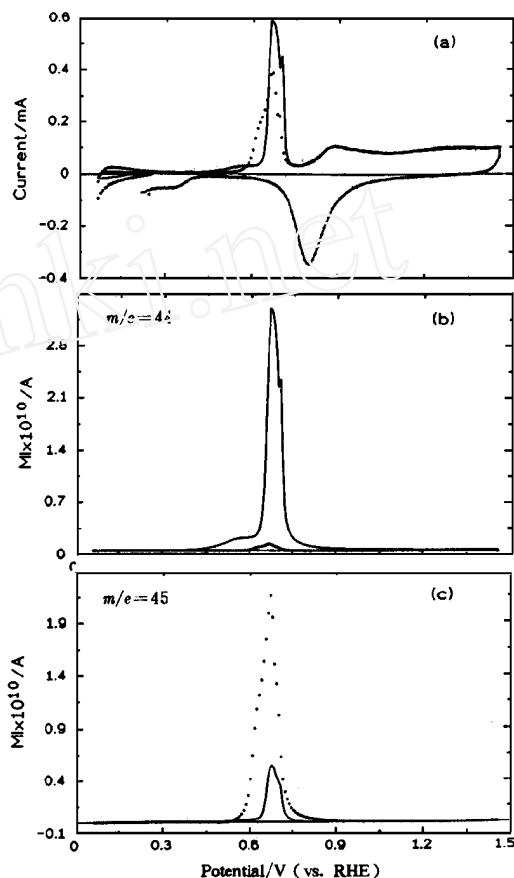
acid adsorbates can be replaced by bulk CO; The other one is as that advocated by Iwasita[21] who suggested that presence of weakly physisorbed CO acts as a precursor for the adsorption-desorption mechanism. The chemisorbed CO on Pt in condensed phase, like that in the case of gas phase, has a high mobility. The diffusing CO molecules may be trapped in the potential well of physisorption state and then desorb, giving rise to the observed isotopic exchange. In the case of formic acid, the adsorbates consist of linearly bound CO and multibound COH in a ratio of 4 1 as determined by DEMS experiments. It is also accepted that COH species bound to Pt surface, in triple form, is stronger than CO_{ad}. Therefore, it is reasonable to suggest that previously adsorbed COH derived from formic acid cannot be replaced by bulk CO in the former mechanism. Therefore, out of the formic acid adsorbates, to a maximum extent, *ca*. 80% of the surface species in the form of linearly bound CO_{ad} surface species, which could act as precursors for the adsorption-desorption mechanism, can be replaced by bulk CO. In the cases of interaction of saturately adsorbed formic acid and CO_{ad} with bulk formic acid, there is essentially no observable isotopic replenishment due to the fact that there is no enough surface sites (at least two sites) next to each other for the dehydrogenation of formic aicd. Therefore, no isotopic exchange is expected.

4 Conclusions

The experimental facts described above can be summarized as follows:

1) The adsorption isotherm for formic acid at porous platinum electrode in acid solution shows a similar behaviour as that on smooth one. A maximum dissociative adsorption ($\Theta_{res}=$ 0. 84) can be observed in the potential region of 0. 20 to 0. 30 V. In addition, at a given adsorption potential(*i. e.*, 0. 25 V), the accumulation of the residue shows a time dependence. After three minutes a maximum adsorption is reached.

2) In situ FTIR spectroscopic results confirm that the formic acid adsorbates formed at porous platinum electrode consist of mainly CO and small amount of COH. The CO /COH ratio at the maximum adsorption of formic acid is 4 1 according to the on line DEMS results.

3) Isotope experiments show that saturated formic acid adsorbates previously formed on a porous platinum electrode cannot be replaced by formic acid in solution. This fact demonstrates that the process for the adsorption of formic acid at platinum electrode is irreversible, in which steric hindrance plays also a decisive role.

4) The interaction between formic acid and CO is also detailed studied with the help of on line DEMS technique. The results show that previously adsorbed monolayer of CO cannot be replaced by formic acid in solution due to the steric effect. In contrast, previously formed monolayer of formic acid adsorbates up to a 80 percent can be exchanged by bulk CO. Obviously, the linearly bound CO derived from formic acid acts as the precursor for the attacking of CO from solution. It can be also further concluded that the adsorbed CO is movable on the electrode surface showing the same as in gas phase. Therefore, once the adsorbed CO molecule is trapped in the potential well allowing for weakly adsorbed CO exchanging with the CO in solution.

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