Kinetics of dissociative adsorption of formic acid on Pt(100), Pt(610), Pt(210) and Pt(110) single-crystal electrodes in perchloric acid solutions

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Abstract

The kinetics of dissociative adsorption of HCOOH on Pt(100), Pt(610), Pt(210) and Pt(110) single-crystal electrodes has been investigated. The oxidation of dissociative adsorbate (DA) derived from the dissociative adsorption of HCOOH was used as a probe reaction together with the potential-step technique of short time windows. The quantity \( Q_{ad} \) of DA produced at a given potential \( E_{ad} \) and in a defined time window \( t_{ad} \) of adsorption has been determined systematically. At fixed \( t_{ad} \), peaked curves of \( Q_{ad} \) versus \( E_{ad} \) in the potential range between -0.25 and 0.25 V/SCE have been obtained on all four electrodes. The maximum rate of dissociative adsorption of HCOOH decreases in the order Pt(110) > Pt(210) > Pt(610) > Pt(100).

1. Introduction

In the study of electrocatalysis of direct fuel cells, it is generally agreed [1-4] that, for most fuels with small organic molecules, anodic oxidation occurs through a dual-path reaction mechanism, i.e.,

\[
\begin{align*}
R & \rightarrow \text{reactive intermediates} \rightarrow \text{CO}_2 \\
\rightarrow \text{dissociative adsorbates}
\end{align*}
\]

where the dissociative adsorbate (DA) originates from the interaction of molecules with the electrode surface (i.e. dissociative adsorption). The DA adsorbs stably in the potential region below the oxygen adsorption potential and consequently poisons the surface of the electrode. This has been denoted the "self-poisoning" phenomenon. A typical example is the electro-oxidation of formic acid on Pt single-crystal electrodes studied by cyclic voltammetry and EMIRS [5], where the surface of the electrode loses its activity almost completely due to self-poisoning in the positive potential sweep. Although the mechanism of formic acid oxidation on different types of Pt electrodes (single-crystal, adatom modified, thin film etc.) has been investigated extensively using in-situ spectroscopic techniques such as EMIRS [5,6], IRRAS [7], FTIRS [8,9], DEMS [9,10] and SERS [11] to determine the nature of reactive intermediates and DA species, the kinetics of the oxidation are still not understood because of the self-poisoning phenomenon which makes it difficult to use transient techniques in kinetic studies. A pioneer study of the kinetics of formic acid oxidation via reactive intermediates was performed by Pletcher and coworkers [12,13] who used the potential-step technique to investigate the oxidation of formic acid on Pt electrodes modified by different metallic adatoms. It was believed that DA formation could be inhibited on such surfaces [14,15]. Nevertheless, the kinetics of the dissociative adsorption of formic acid on Pt electrode have not yet been investigated.

The dissociative adsorption of small organic molecules on an electrocatalyst is an important surface process consisting of stages such as adsorption–desorption equilibrium, cleavage of chemical bonds, formation of new surface compounds, etc. It is obvious that studies of the kinetics of such dissociative adsorption processes will contribute to revealing the details of the interaction between the electrode surface and reagent molecules, developing and enriching theories of electrocatalysis [16]. It is known that the main products derived from the dissociative adsorption of most small-molecule organic fuels, such as formic acid [5–7] and methanol [7,17], on Pt electrodes are carbon...
monoxide species, and that the processes of both the
dissociative adsorption of organic molecules and the
oxidation of the DA depend strongly on the crystallo-
graphic orientation of Pt single-crystal electrodes
[18,19]. In order to understand better the kinetics of
the process of dissociative adsorption of small-mole-
cule organic fuels, it may be very important to be able
to determine the quantity of DA present under given
experimental conditions (adsorption potential, adsorp-
tion time, concentration etc.). In work reported here
the kinetics of the dissociative adsorption of formic
acid on Pt(100), Pt(610), Pt(210) and Pt(110) single-
crystal electrodes was investigated. The oxidation reac-
tion of DA derived from the dissociative adsorption of
formic acid was adopted as a probe reaction, and a
potential-step technique using short time windows con-
trolled by a microcomputer was used to perform the
study. The amount of DA was measured systematically
by analysing \( j-t \) transient curves recorded under dif-
ferent conditions.

The dissociative adsorption of HCOOH on a Pt
electrode surface can be written as follows [5–9,16]:

\[
\begin{align*}
\text{HCOOH} + \text{Pt} & \leftrightarrow \text{PtHCOOH} \quad (2) \\
\text{PtHCOOH} & \rightarrow \text{PtCO}_2 + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

The oxidation reaction of the DA (\( \text{PtCO}_2 \)) is given by

\[
\text{PtCO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- + \text{Pt} \quad (4)
\]

Reaction (4) enables the quantity of DA formed at
different potentials and during different adsorption
times to be detected electrochemically, i.e. it can be
used as a probe reaction in the present investigation.
Systematic studies of the dependence of the amount of
DA produced on the adsorption time and the adsorp-
tion potential enabled the kinetic aspects of the disso-
ciative adsorption of formic acid on Pt single-crystal
electrodes to be elucidated.

2. Experimental

The Pt(100), Pt(610), Pt(210) and Pt(110) single-
crystal electrodes were made in our laboratory as de-
scribed elsewhere [20]. Before each measurement the
electrode was pre-treated as recommended by Clavilier
et al. [21], i.e. it was heated in a hydrogen + oxygen
flame and transferred into an electrochemical cell un-
der the protection of a droplet of pure water. The
solution was prepared from super-pure perchloric acid,
analytical grade formic acid and triple-distilled water.
The solution was bubbled with pure nitrogen gas be-
fore the experiment to remove oxygen, and pure nitro-
gen gas was passed over the solution throughout the
experiment. The reference electrode was a saturated
calomel electrode (SCE). All experiments were carried
out at temperatures of about 22°C.

The transient experiments were performed using a
home-made potentiostat (XDH-II, Department of
Chemistry, Xiamen University) controlled by an AT-286
microcomputer (Dongnan Co. Inc., Xiamen) interfaced
with a processing board (SC-11020, Square-Circle Co.
Inc., Beijing). The software developed in our group
allowed us to control all operational states of the
potentiostat, to acquire data at a rate as fast as 66 µs
per point and to analyse experimental results automatic-
ically. The performance of the experimental set-up can
be characterized by the responses of both potential and
current to polarization of the voltage step generated by
a digital–analogue converter (Fig. 1). It can be seen
that the potential response followed the polarization
input signal well and that the current response showed
only the double-layer charging. This result demon-
strates that our system (including the electrochemical
cell design) is suitable for performing electrochemical
transient studies in short time windows.

3. Results and discussions

3.1. Characterization of cyclic voltammetric studies

Figure 2 shows cyclic voltammograms obtained with
Pt(100), Pt(610), Pt(210) and (110) electrodes in a 5 ×
10^{-4} M HCOOH + 0.1 M HClO_4 solution. When the
electrode was flame treated, transferred to the solution
at 0.0 V and kept at this potential for 2 min, a sharp
oxidation current peak was observed for each electrode
in the positive potential sweep. Comparing this result
with the small oxidation current observed in the nega-
tive potential sweep immediately after the current peak
or in the stable voltammogram recorded after 10 suc-
cessive potential cycles, it is evident that the sharp
peak is due mainly to oxidation of DA produced and accumulated at 0.0 V. However, when electrodes of different orientation are used, the features of the oxidation of the DA, which can be characterized by the potential \( E_p \), the current \( I_p \), and the peak width at half-height \( W_h \), are very different. The three parameters for the four electrodes are as follows: \( E_p, \) Pt(110) (0.405 V) < Pt(210) (0.435 V) < Pt(610) (0.470 V) < Pt(100) (0.475 V); \( I_p, \) Pt(100) (0.795 mA cm\(^{-2}\)) > Pt(110) (0.574 mA cm\(^{-2}\)) > Pt(610) (0.532 mA cm\(^{-2}\)) > Pt(210) (0.417 mA cm\(^{-2}\)); \( W_h, \) Pt(100) (20 mV) < Pt(110) (30 mV) < Pt(210) (75 mV). The smallest value of \( W_h \) obtained with the Pt(100) electrode may indicate the homogeneity of both the surface structure and the adsorbates (mainly linearly bonded CO). The larger values of \( W_h \) for the other three electrodes signifies the existence of bridge-bonded CO species in the DA, and the complexity of the surface structure [18,19]. It may be useful to note from Fig. 2 that the oxidation potential of the DA is greater than 0.3 V for all four electrodes, which is in good agreement with EMIRS results [5-7], and that since \( E_p < 0.48 \text{ V} \) the DA can be oxidized completely at potentials above 0.5 V under potentiostatic conditions.

3.2. \( j-t \) transient features of the potential-step experiments

In order to investigate the kinetics of dissociative adsorption of formic acid on the surfaces of Pt single-crystal electrodes, the experimental procedure shown in the inset to Fig. 3 was carried out. After flame treatment of the electrode, the potential was set to 0.700 V and held at this value for 2 min to oxidize and desorb all adsorbates. It was then switched to the adsorption potential \( E_{ad} \) and kept at this value for a given adsorption time \( t_{ad} \). Finally, the potential was stepped to the oxidation potential \( E_{ox} \) and the \( j-t \) transient was recorded immediately.

The \( j-t \) transient curves recorded for a Pt(100) electrode in a \( 5 \times 10^{-4} \text{ M HCOOH} + 0.1 \text{ M HClO}_4 \) solution with \( E_{ad} = -0.030 \text{ V} \), \( E_{ox} = 0.550 \text{ V} \) and various values of \( t_{ad} \) are shown in Fig. 3. When \( t_{ad} = 0.0 \text{ s} \) (Fig. 3(c)) the transient current may consist of double-layer charging, oxygen adsorption (0.55 V is above the onset potential for oxygen adsorption) and the oxidation of HCOOH in solution. As the HCOOH concentration was so low that the oxidation current quickly reached its limiting values, the transient current decayed to zero within a time window less than 30 ms. As \( t_{ad} \) was increased, the transient current developed a
more pronounced peak with features similar to those of the oxidation of carbon monoxide adsorbed on a Pt(100) electrode [22]. At $t_{ad} = 10.0 \text{ s}$ (Fig. 3(a)) only a transient current shoulder around 8.52 ms is observed. At $t_{ad}$ values of 50.0 s, 100.0 s and 400.0 s (Figs. 3(b), 3(c) and 3(d) respectively), a well-defined current peak is observed with peak intensities $j_{tp}$ of 7.854 mA cm$^{-2}$ at $t_{tp} = 14.90 \text{ ms}$, 7.114 mA cm$^{-2}$ at $t_{tp} = 18.20 \text{ ms}$ and 5.190 mA cm$^{-2}$ at $t_{tp} = 29.20 \text{ ms}$ respectively. As $t_{ad}$ increases, $t_{tp}$ also increases. Nevertheless, even with $t_{ad} = 400.0 \text{ s}$ the current decayed to zero in a time window of less than 110 ms, showing that the oxidation of the DA was completed quickly. The time for double-layer charging, which can be measured from the time corresponding to the fast dropping part of the current immediately after the potential has been stepped to $E_{ox}$, decreases with increasing $t_{ad}$ confirming that the DA is a neutral species (CO) whose presence in the double layer decreases the differential capacity.

The charge $Q_{ad}$ corresponding to DA oxidation is obtained by subtracting the charge under Fig. 3(e) ($t_{ad} = 0.0 \text{ s}$) from the charge under the curves at a given $t_{ad} > 0.0 \text{ s}$. Obviously, $Q_{ad}$ represents the quantity of DA derived from HCOOH dissociative adsorption on the Pt(100) electrode surface at given potential $E_{ad}$ within the time window $t_{ad}$.

A comparison of the $j$--$t$ transient features of DA oxidation on Pt(100), Pt(610), Pt(210) and Pt(110) electrodes is shown in Fig. 4. It is known from Fig. 3 that $j$--$t$ transient features depend on the quantity of DA. Figure 4(a) shows a three-dimensional plot of four curves corresponding to the oxidation of similar amounts $Q_{ad}$ of DA on the different electrodes: 178.9 $\mu$C cm$^{-2}$ for Pt(100), 177.5 $\mu$C cm$^{-2}$ for Pt(610), 177.4 $\mu$C cm$^{-2}$ for Pt(210) and 182.8 $\mu$C cm$^{-2}$ for Pt(110). A well-defined current peak is observed on the $j$--$t$ transients of Pt(100) and Pt(610); $j_{tp}$ and $t_{tp}$ are 7.8 mA cm$^{-2}$ and 13.1 ms respectively for Pt(100), and 6.5 mA cm$^{-2}$ and 16.7 ms respectively for Pt(610). However, only a shoulder, around 13.00 ms and 2.00 ms respectively, is observed on the $j$--$t$ transients for the Pt(210) and Pt(110) electrodes. When the $j$--$t$ transients obtained with $t_{ad} = 200.0 \text{ s}$ and $E_{ad} = -0.030 \text{ V}$ (the quantity of charge for DA oxidation is now different for each electrode, and is 191.8 $\mu$C cm$^{-2}$ for Pt(100), 177.5 $\mu$C cm$^{-2}$ for Pt(610), 225.1 $\mu$C cm$^{-2}$ for Pt(210) and 244.5 $\mu$C cm$^{-2}$ for Pt(110)) are compared, a current peak is observed on all four curves (Fig. 4(b)).

There are no significant differences between the curves for Pt(100) and Pt(610) in Fig. 4(b) and those for the same electrodes in Fig. 4(a), except that in the case of Pt(100) $j_{tp}$ decreased to 6.2 mA cm$^{-2}$ and $t_{tp}$ was shifted positively to 22.6 ms. The $j$--$t$ transient obtained with Pt(210) displays, after double-layer charging current, a plateau and a current shoulder around 36.0 ms. The $j$--$t$ transient recorded on the Pt(110) electrode shows a relatively sharp current peak at 3.02 ms with $j_{tp} = 15.4 \text{ mA cm}^{-2}$. It is obvious that the differences in the features of the $j$--$t$ transients for DA oxidation on different Pt single-crystal electrodes are related directly to the surface structure of the electrode and the rate of nucleation and growth of the oxide islands in the DA layer [22].

As has been reported by Leger et al. [23] and by Santos et al. [24], the adsorption of CO in saturated solution on Pt electrodes is a complex process. A
variety of adsorbed CO species (linearly bonded, bridge-bonded and multi-bonded) have been identified by in-situ IR spectroscopy studies [5-9], cyclic voltammetry [23] and potentiostatic [24] experiments. In the present study the $Q_{ad}$ obtained from the $j-t$ transient curves corresponds to the total amount of DA produced at specific values of $E_{ad}$ and $t_{ad}$, and provides a direct indication of the kinetics of dissociative adsorption of formic acid on Pt single-crystal electrodes. Thus the differences between the species (linearly bonded, bridge-bonded and multibonded CO) present in the DA have been ignored in the following discussion.

### 3.3. Potential dependence of the dissociative adsorption of formic acid on Pt single-crystal electrodes

Figure 5 shows the variation of $Q_{ad}$ with $E_{ad}$ at $t_{ad} = 60.0$ s for each Pt single-crystal electrode. For convenience in the data analysis, the hydrogen desorption curve $j_{H-E}$ recorded in pure electrolyte (0.1 M HClO$_4$) and the coverage $\Theta_H$ of hydrogen adatoms on the electrode surface calculated from $j_{H-E}$ are also displayed. It can be seen that the variation of $Q_{ad}$ with $E_{ad}$ for all four electrodes yields a peaked curve with its maximum at about 0.0 V. However, there are some variations in the features of the curves for different electrode orientations. The most significant difference is observed in the peak width at half-height $W_{ad}$ which decreases in the order Pt(110) (263 mV) > Pt(210) (239 mV) > Pt(610) (193 mV) > Pt(100) (162 mV). The variation of $Q_{ad}$ at fixed $t_{ad}$ shown in Fig. 5 implies the variation of the rate of dissociative adsorption of HCOOH on the electrode surface with $E_{ad}$, and the large values of $W_{ad}$ indicate that it may take place at higher rates over a relatively wide range of electrode potential.

As in earlier discussions, the comparison of the maximum $Q_{ad}^{M}$ of $Q_{ad}$ measured from the peaked curves in Fig. 5 effectively represents the relative proportion of the maximum rate of dissociative adsorption of HCOOH which can be attained on the different electrodes. Measured values of $Q_{ad}^{M}$ are 252.1 $\mu$C cm$^{-2}$ for Pt(110), 220.2 $\mu$C cm$^{-2}$ for Pt(210), 186.6 $\mu$C cm$^{-2}$ for Pt(610) and 181.7 $\mu$C cm$^{-2}$ for Pt(100), i.e. they decrease in the order Pt(110) > Pt(210) > Pt(610) > Pt(100). Although there is a small variation in the value of $E_{ad}$ at which $Q_{ad}^{M}$ was measured with different electrodes (−0.030 V for Pt(110) and Pt(210), 0.010 V for Pt(100) and 0.050 V for Pt(610)), the order of $Q_{ad}^{M}$ obtained also represents the order in which the maximum rate of dissociative adsorption of HCOOH is attained on these electrodes, i.e. the order of $Q_{ad}^{M}$ can also be interpreted as the order of activity of the four electrodes towards the dissociative adsorption of HCOOH. It is known that the (100), (610), (210) and (110) single-crystal planes are all located in the [001] crystallographic zone, and the configuration of the two stepped surfaces can be described as

$$(610) \leftrightarrow 6(100)-(110)$$

$$(210) \leftrightarrow 2(100)-(110)$$

i.e. they both contain terraces of (100) symmetry of different width and steps of (110) symmetry of monatomic height. The above results demonstrate that Pt(110) possesses a higher activity than Pt(100) for towards the dissociative adsorption of HCOOH. The activities of the Pt(210) and Pt(610) electrodes, which have different proportions of (110) and (100) sites on their surfaces, fall between those of the Pt(110) and Pt(100) electrodes.

The results shown in Fig. 5 can also be interpreted as follows.

(i) The adsorption of HCOOH is in competition with hydrogen adsorption. It can be seen that when the II adatom coverage is close to a monolayer HCOOH can barely adsorb on the Pt(100) surface, consequently very little DA is produced.

(ii) The values of $\Theta_H$ at which $Q_{ad}^{M}$ is obtained vary with the orientation of the electrode (0.557 for Pt(100), 0.183 for Pt(610), 0.275 for Pt(210) and 0.043 for Pt(110)), which may be an indication of the different requirements for H adatoms in assisting the dissoci-
tion of adsorbed HCOOH on the different electrode surfaces.

The peaked relationship obtained between $Q_{ad}$ and $E_{ad}$ for $t_{ad} = 60.0$ s was not affected when the bulk concentration of HCOOH was varied. For example, the centre of the maximum of $Q_{ad}$ obtained with the Pt(100) electrode (Fig. 6) is close to 0.0 V regardless of the bulk concentration of HCOOH. Nevertheless the $Q_{ad} - E_{ad}$ curve moves up in parallel when the bulk concentration of HCOOH is increased, implying that the adsorption equilibrium of HCOOH on the electrode surface is the first step of the dissociative adsorption. The measured values of $Q_{ad}$ for different bulk concentrations of HCOOH are 153.6 $\mu$C cm$^{-2}$ ($1 \times 10^{-4}$ M HCOOH), 181.7 $\mu$C cm$^{-2}$ ($5 \times 10^{-4}$ M HCOOH) and 223.9 $\mu$C cm$^{-2}$ ($1 \times 10^{-3}$ M HCOOH), corresponding to DA coverages of 0.367, 0.435 and 0.536 respectively. The coverage $\theta_{DA}$ was calculated using

$$\theta_{DA} = \frac{Q_{ad}}{2Q_H}$$

(5)

where $Q_H$ is the charge for hydrogen adsorption for Pt(100) (taking 209 $\mu$C cm$^{-2}$ as the theoretical value) and assuming that the oxidation of each DA species (irrespective of whether it is a linearly bonded or bridge-bonded CO species) will transfer two electrons.

3.4. Determination of the initial rate of dissociative adsorption of formic acid on Pt single-crystal electrodes under specific conditions

Analysis of the variation of $Q_{ad}$, obtained at constant $E_{ad}$, with $t_{ad}$ can provide further information on the kinetics of the dissociative adsorption of formic acid on Pt single crystal electrodes. The results obtained with the Pt(100) electrode (Fig. 7) show that when $E_{ad}$ was fixed at $-0.030$ V, $Q_{ad}$ first increased rapidly yielding a linear relationship, which is shown schematically by the asymptotic straight line. It reached a value of 170.1 $\mu$C cm$^{-2}$ at $t_{ad} = 40.0$ s, and then slowly increased in the $t_{ad}$ range between 40.0 s and 400.0 s. It is evident that the slope $S_i$ of the linear relationship in the initial part of $Q_{ad}$ vs. $t_{ad}$ curve may represent the initial rate $v_i$ of dissociative adsorption, i.e. the rate of dissociative adsorption of formic acid at a clean Pt(100) surface on which no species except H adatoms are present under the given conditions ($E_{ad}$, HCOOH concentration etc.). $S_i$ has been measured as 24.0 $\mu$C cm$^{-2}$ s$^{-1}$. It is known that the oxidation of each DA molecule (CO species) will transfer two electrons to the electrode. Thus $v_i$ can be calculated from $S_i$ using the relation

$$v_i = 10^{-6} \frac{S_i}{2F}$$

(6)

where $F$ is the Faraday constant ($9.648 \times 10^4$ C mol$^{-1}$). Then the value of $v_i$ for $E_{ad} = -0.030$ V is calculated as $1.24 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$. It has been shown in Fig. 4 that $E_{ad} = -0.030$ V is close to the peak of the curve of $Q_{ad}$ vs. $E_{ad}$, and that the rate of the dissociative adsorption depends on $E_{ad}$. The variation of $Q_{ad}$ with $t_{ad}$ at $E_{ad} = -0.100$ V is also displayed in Fig. 7. In this case, $Q_{ad}$ increases slowly with increasing $t_{ad}$, finally approaching its maximum value. Despite the slow variation of $Q_{ad}$ with $t_{ad}$ it was possible to calculate a value of $S_i = 2.93 \mu$C cm$^{-2}$ s$^{-1}$ from the initial part of the curve, which yields $v_i = 1.52$
The results reported in the present paper demonstrate that the kinetics of dissociative adsorption of HCOOH on Pt single-crystal electrodes can be studied successfully by using the oxidation of DA as a probe reaction together with potential-step technique of short time windows. At fixed adsorption time ($t_{ad} = 60.0$ s) the amount $Q_{ad}$ of DA derived from the dissociative adsorption of HCOOH on Pt(100), Pt(610), Pt(210) and Pt(110) electrodes varies with the adsorption potential $E_{ad}$, yielding peaked curves for $E_{ad}$ in the range between $-0.25$ V and $0.25$ V, with the maximum at about $0.0$ V. This relationship effectively represents the variation of the rate of dissociative adsorption of HCOOH with $E_{ad}$. Comparison of the maximum value of $Q_{ad}$ for each peak obtained with different Pt single-crystal electrodes generated a decreasing order of Pt(110) > Pt(210) > Pt(610) > Pt(100), which also denotes the order of the maximum rate of dissociative adsorption of HCOOH that can be attained on these electrodes. The different activities of the four Pt single-crystal electrodes towards dissociative adsorption of HCOOH is attributed to the different surface structures of the electrodes. From the variation of $Q_{ad}$ with $t_{ad}$ at $E_{ad} = -0.030$ V the initial rate $u_i$ of dissociative adsorption of HCOOH on each Pt single-crystal electrode has been evaluated: $1.24 \times 10^{-11}$ mol cm$^{-2}$ s$^{-1}$ for Pt(100), $1.01 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$ for Pt(610), $1.40 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$ for Pt(210) and at $1.65 \times 10^{-10}$ mol cm$^{-2}$ s$^{-1}$ for Pt(110). The present results confirm that the adsorption–desorption equilibrium of HCOOH is the first step in the dissociative adsorption, and that a different requirement for hydrogen adatoms in the dissociative process of adsorbed HCOOH occurs with different orientations of the Pt single-crystal electrodes.

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References
