Electrochemical Oscillations in the HCHO Oxidation on a Pt Electrode

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Abstract: We first report that current oscillations with in-situ mass oscillations in the electrocatalytic oxidation of formaldehyde were observed on a Pt electrode. In the linear sweep voltammogram, quantitative analysis of in-situ mass change on the Pt surface by electrochemical quartz crystal microbalance gave a clue that CO might be the reaction intermediate species, which covered the active area of Pt surface. It results in the lowest current and the highest mass in a period of oscillations. On the other hand, the lowest value of mass arises from the recover of Pt vacant site due to the CO₂ evolution. The periodicity of current oscillations is in excellent agreement with the mass oscillations.

Keywords: formaldehyde, electro-oxidation, hopf instability, current and mass oscillations, in-situ electrochemical quartz crystal microbalance

Introduction

The electrocatalytic oxidation of small organic molecules such as formic acid (HCOOH), formaldehyde (HCHO), and methanol (CH₃OH) on novel metals in acidic solution has been investigated since 19C [1,2]. Since small organic molecules could be used as a fuel for direct C₁ fuel cells, the understanding of the electro-oxidation mechanism of C₁ fuel is needed in order to develop advanced electrode material and to get higher power output.

Of late, Nakabayashi and coworkers [3] has presented that the anodic oxidation of formaldehyde on a Pt electrode is accompanied by the appearance of poisoning intermediate species (i.e., CO). The overall course of reaction with four-electron oxidation process can accordingly be formulated as follows.

\[
\begin{align*}
HCHO + Pt + * & \rightarrow PtCO_{ad} + 2H^+ + 2e \\
H₂O + Pt + * & \rightarrow PtOH_{ad} + H^+ + e \\
PtCO_{ad} + PtOH_{ad} & \rightarrow Pt + CO₂ + H^+ + e + 2 * \\
HCHO + H₂O & \rightarrow CO₂ + 4H^+ + 4e
\end{align*}
\]

where * represents a vacant site on the platinum electrode surface.

Electrochemical oscillation is not an unknown phenomenon and has been observed in a large number of experimental systems such as oxidation of cations, reduction of anions and electocrystallisation [4,5]. The great variety of electrochemical oscillation systems indicate that oscillations are not specific but are a general phenomenon. In the electrocatalytic oxidation of small organic molecules, oscillatory behaviours of current and potential were observed in the previous studies [6-14].

However, current oscillations by combination of quantitative and qualitative analysis in order to classify the mechanistic origin of HCHO electro-oxidation on platinized Pt have not been presented yet. Thus, we analysed the electrochemical impedance spectroscopy (EIS) and in-situ mass change on the electrode surface by electrochemical quartz crystal microbalance (EQCM) to get the better understanding of oxidation mechanism.

Experimental

We used conventional experimental apparatus with three electrodes. Working electrode (WE) was AT-cut P
quartz crystal. Reference electrode (RE) was saturated calomel electrode (SCE) and counter electrode (CE) was Pt wire (99.999%).

All solutions (1M HCHO/0.1M H₂SO₄, 0.5M H₂SO₄) were prepared with ultrawater (Millipore Milli-Q water, 18 MΩ cm) and kept at room temperature. Prior to all experiments, a preliminary cyclic voltammetric (CV) curve between -0.25V and +1.25V (vs. SCE) was recorded in 0.5 M H₂SO₄ in order to confirm the absence of any residuals of impurities. All solutions were deaerated by bubbling high purity N₂ (99.999%) before each measurement. All measurements are performed at room temperature of 25°C.

Potentiostat/galvanostat (EG&G PAR 273A) was used for the linear sweep voltammetry and cyclic voltammetry and in-situ measurement of mass changes were performed by electrochemical quartz crystal microbalance (SEIKO EG&G QCA 917). Impedance spectra were measured at different constant outer potentials using a potentiostat and galvanostat/log-in amplifier (ZAHNER Elektrik IM6). The frequency range investigated reached from 1 kHz to 30 mHz with 25 points per decade.

Results and discussion

Figure 1 shows typical current-potential profile of the polycrystalline Pt electrode in 1M H₂SO₄ with scan rate of 50 mV/s. In cyclic voltamogram, the oxidation of Pt and reduction of Pt oxide in the potential range between +0.20 V and +1.10 V (vs. SCE) have been achieved. In addition, the hydrogen adsorption/desorption in potential range between +0.10V and -0.30 V are also distinctly observed. Thus, it represents the clean polycrystalline Pt surface without any impurities.

In the EQCM, the equation of the resonant frequency change for mass change has been presented by Sauerbrey equation [15],

\[ \Delta f = -C_f \Delta m \]  \hspace{1cm} (5)

in which \( C_f \) (935.7 μHz/g) is a constant which is solely determined by the properties of the quartz crystal.

Figure 2(a) and 2(b) show the current-potential profile and mass change on the platinized Pt electrode in the HCHO oxidation, respectively. At the low outer potential ranging between -0.2V and +0.3 V, the dissociation of HCHO (i.e., dehydrogenation and CO adsorption) induces small anodic current resulting in constant mass change. At ca. +0.45 V, the onset of HCHO oxidation (i.e., CO oxidation) is observed and it is caused by the reaction with OH adsorbed resulting from the oxidation of surface water. Interestingly, from the anodic potential of ca. +0.75 V, we clearly observe current oscillations on the positive current-potential slope. In parallel, mass oscillates on the anodic scan and the average value of mass change is ca. 125 ng.

Initial burst of anodic current at +0.75V is due to the reaction (3), i.e., CO₂ evolution and it presents the clean Pt surface. Then, the anodic current abruptly decreases, which could be owing to the adsorption of intermediate specie (CO) on the surface. Between current decrease and second burst of current, current slightly increase and it might be OH adsorption. In Figure 2(b), current increase induces the mass decrease and vice versa. In early 1980s, Jackman and coworkers [16] experimentally observed that the saturation adsorption coverage of CO molecules was about \( 1.0 \times 10^{13} \) atoms/Pt cm² and it is in excellent agreement with theoretical value of \( 1.31 \times 10^{13} \) atoms/cm². If all mass change of 125 ng measured by in-situ EQCM (see Figure 2(b)) represents the CO adsorption on Pt surface, we conclude that the active surface area of polycrystalline Pt crystal for the CO
adsorption is ca. 2.0 cm$^2$.

The onset potential of current oscillations on the anodic scan (see Figure 2(a)) is about +0.75 V. In general, Hopf bifurcation usually exists in front of the onset of current oscillation. According to previous studies [17-19], we assume that the mechanistic origin of current oscillations in the HCHO oxidation belong to hidden negative differential resistance (HNDR).

In order to prove the above assumption, impedance spectra are measured for various potentiostatic operation points in the front of the onset of periodic instabilities.

**Figure 3.** Electrochemical impedance behaviour of formaldehyde oxidation at a platinized Pt electrode measured at three outer potentials of (a) +0.65 V, (b) +0.70 V, and (c) +0.73 V.

**Figure 4.** The Bode plot at +0.70 V shows the phase shift as a function of frequency. Experimental condition is same as in Figure 2. (a) Phase angle and (b) log $|Z|$.

EIS (Electrochemical Impedance Spectra) has the usefulness of the studying oscillatory electrochemical systems. If the influence of the ohmic loss is less than a simple radial shift in the impedance plane, the possibility of bifurcation can test graphically from the impedance spectra measured potentiostatically. By the use of these points, we predict to probe the dynamical instabilities of the electrochemical system.

According to previous classification of mechanistic origin of electrochemical oscillations, HNDR oscillator crosses the real impedance at a finite frequency but at zero frequency. As anodic potential, i.e., closed to the Hopf bifurcation, increases, the value of the negative real impedance approached the zero value.

Figure 3 shows the Nyquist plots at three different potentials in the front of current oscillations on the anodic scan as shown in Figure 2(a). At the potential of +0.65 V (Figure 3(a)), the impedance plot $Z(\omega)$ exhibits a clockwise capacitive-inductive loop indicating dynamically stable stationary operating points. However, Figure 3(b) shows that the impedance profile is changed as anti-clockwise loop at the potential of +0.70 V. The intersection of the negative real axis is obtained at a finite frequency, $\omega_0 \approx 0.2$ Hz. Then, $Z(\omega)$ again exhibits positive real resistances at very low frequencies. In other words, either in very fast variation of potentials or at very slow reaction rate, the impedance shows constant value or positive value. The detailed shape of the Nyquist plot bears information on the mechanistic origin of the oscillatory behaviour, which can be used to predict the dynamical stability of oscillatory systems, i.e., Hopf instability.

Figure 4 shows the Bode plot at the potential of +0.70 V. This profile adequately reveals that phase angle drastically changes from -180 to +180 at the frequency of about $\omega_0 \approx 0.2$ Hz (see dotted circle). This drastic phase change results in an anti-clockwise profile, which
negative real axis was intersected in the Nyquist plot (see Figure 3(b)).

Conclusions

We investigated the electrochemical oscillations of formaldehyde (HCHO) on Pt electrode by using EQCM and EIS techniques. Experimental observations exhibit HCHO oxidation on Pt belongs to HNDR oscillator, i.e., class IV mechanistic classification according to previous works [18], as did HCOOH and CH₃OH oxidation [8, 13]. Further study with appropriate analyzing methods will be carried out in order to get more clear mechanistic origin of HCHO oxidation and it will contribute the development of higher power output fuel cells by applying an external pulse with correct frequency obtained by EIS technique.

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References