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Structure Analysis of Adsorbed Layers Formed from Methanol on Platinum Electrodes with an Electrochemical Quartz Crystal Microbalance

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The adsorbed species formed from methanol on platinum electrodes have been examined with an electrochemical quartz crystal microbalance (EQCM). The mass of the adsorbed species per surface platinum site was determined from the frequency response of the EQCM, together with number of electrons per Pt site required to oxidize the adsorbed species and coverage from the current response of the EQCM. These values were used to calculate the molar mass of the adsorbed species and the number of adsorption sites. The average composition of the adsorbed species was similar both in 0.1 M $HClO_4$ and 0.01 M NaOH, and was $COH_{2.0-2.4}$. The composition was independent of the adsorption time and the adsorption potential unless the coverage was below 0.2, where accurate determination of the composition was not possible. The average number of adsorption sites was 3.0 in 0.1 M $HClO_4$ and 2.6 in 0.01M NaOH.

A number of studies have been conducted to elucidate the structure of the adsorbed species formed from methanol on a platinum electrode.[1—3] The formation of linear and bridged CO species was clearly shown by in-situ infrared reflection techniques.[4—7] These findings seemed to end the dispute which has continued for more than twenty years. However, mass spectroscopic analysis, such as differential electrochemical mass spectroscopy (DEMS)[8—10] and electrochemical thermal desorption mass spectroscopy (ECTDMS),[11] led to the conclusion that the structure of the adsorbed species was COH, which agrees with that determined by the conventional electrochemical methods.[12,13] Parsons and VanderNoot discussed this discrepancy in their critical review.[1] Among the differences in the experimental conditions that they pointed out, the surface roughness is an essential difference between both techniques. IR techniques always use smooth electrodes, while DEMS uses porous electrodes. Except for a time-resolved measurement, in addition, IR methods are considered essentially to be steady state techniques. On the other hand, DEMS is a transient technique. They finally concluded that IR techniques detect stable species, while DEMS detects weekly adsorbed species.

In order to understand the above-mentioned discrepancy between the two different techniques, and to determine the real structure, it is important to examine the adsorbed species using different techniques. An electrochemical quartz crystal microbalance (EQCM) has recently recognized to be a useful technique for the quantitative analysis of the mass transport at electrode/electrolyte solution interfaces.[14—16] The sensitivity of EQCM is sufficiently high to detect monolayer phenomena. Since EQCM is a gravimetric technique, the quality of EQCM data is similar to that of DEMS, although only the net mass change can be detected and identification of the species can be performed only under a rational assumption. However, we can use a smooth electrode and treat the strongly adsorbed species in EQCM measurements. These experimental conditions resemble those of the IR techniques.

In our previous communication[17] we proposed the possibility that EQCM can be used to determine the structure of the adsorbed species formed from formic acid. In this study, detailed examination of the adsorbed layer formed from methanol on a platinum electrode was examined using a highly sensitive EQCM. The results will not only give useful informtion concerning the adsorbed layer, but also prove the usefulness of EQCM in determining the average structure of the layer.

Experimental

The platinum-coated quartz crystals (AT-cut, 5 MHz) used throughout in this study were obtained from Maxtek (Torrane, CA). Prior to use, each crystal was immersed in a freshly prepared mixture of 50:50 (by volume) concentrated nitric and sulfuric acids for 10 min, followed by a sufficient rinse with water. The crystal was then mounted in an EQCM sensor (Maxtek TPS550), into which an electrochemical cell was screwed. The cell was made of Kel-F and had three ports. Two of them were connected to solution reservoirs and a drain and the other was for a Ag/AgCl/KCl-(sat) reference electrode. A platinized platinum auxiliary electrode was placed in a solution cavity of the cell, and its lead wire was sealed in the cell body. Therefore, the solution cavity was completely closed and was not exposed to the laboratory atmosphere throughout the experiments.

The electrolyte solutions were 0.1 M (1 M=1 $\mathrm{mol\,dm^{-3}}$) $HClO_4$ and 0.01 M NaOH. The cleanness of the platinum surface was first confirmed by taking a cyclic voltammogram in a deoxygenated electrolyte solution. Then, a solution containing 0.1 M CH_3OH and 0.1 M $HClO_4$ (or 0.01 M NaOH) was injected into the cell to initiate the adsorption of methanol. The solution was replaced with the electrolyte solution (0.1 M $HClO_4$ or 0.01 M NaOH) after a certain period of time. Through these adsorption procedures, the electrode potential was kept constant. Finally, a cyclic voltammogram and simultaneous frequency response were taken for the oxidative desorption of the adsorbed species.

The EQCM system was basically the same as that described previously.[18] Briefly, the oscillation frequency was recorded simultaneously with the electrode potential and current by a personal computer interfaced to a high resolution frequency counter (Philips, PM6654C) and a potentiostat (Toho Tech. Res., 2001) through a general-purpose interface bus (GP-IB) and an A/D board, respectively. A triangular potential wave was generated by a function generator (Toho Tech. Res., FG-02). The noise level of this EQCM system was ±0.05 Hz in frequency without any signal averaging for a sampling interval of 0.06 s, so that a frequency change well below the monolayer level could be accurately measured.

All solutions were prepared using chemicals of reagent grade (Wako Chem.) and high-purity water (Milli-Q water).

Results

A typical cyclic voltammogram taken in 0.1 M $HClO_4$ after the adsorption of methanol at 0 V for 5 min is shown in Fig. 1a. The electrode potential was first scanned in the negative direction and then reversed in the positive direction at −0.2 V. A large peak at 0.425 V on a positive-going potential scan is due to the oxidation of adsorbed species formed from methanol (adsorbed C_1 species). The following current response was completely the same as that of a clean platinum electrode. This indicates that the adsorbed C_1 species was completely oxidized during the first positive-going potential scan, and that there did not remain a trace of methanol in the solution cavity of the cell.

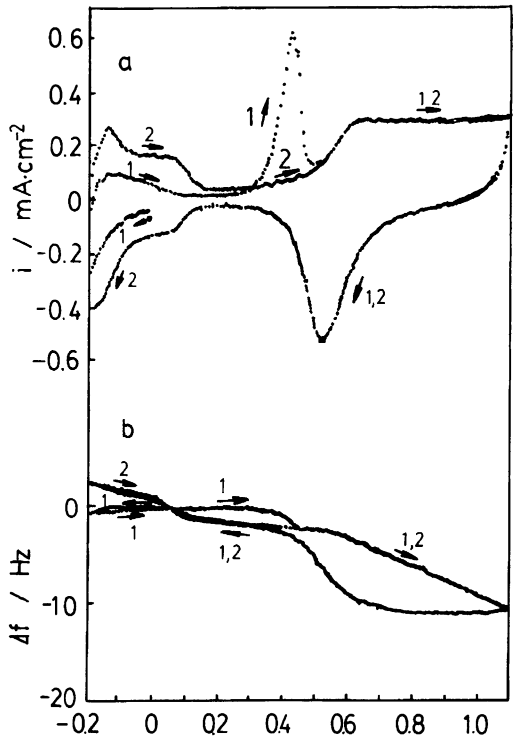


Fig. 1. Current (a) and frequency (b) responses during the oxidation of adsorbed C_1 species formed from methanol on a Pt electrode. An electrolyte solution was 0.1 M $HClO_4$. Adsorption was conducted at 0 V for 5 min. Sweep rate was 50 mV s^{-1}. 1: first scan, 2: second scan.

The surface coverage of the adsorbed C_1 species (θ) and the electron per site (eps), defined below, were calculated from these data:

$$\theta = (Q_H^{\circ} - Q_H)/Q_H^{\circ} \qquad (1)$$

$$\mathrm{eps} = Q_{ox}/(Q_H^{\circ} - Q_H) \qquad (2)$$

where Q_H° and the Q_H are charges required for the oxidation of the adsorbed hydrogen in the absence and presence of the adsorbed C_1 species on a platinum surface, respectively. Q_{ox} presents the charge passed during the oxidation of the adsorbed C_1 species. Thus, eps gives the number of electrons per surface Pt site necessary for oxidizing the adsorbed C_1 species. For four separate experiments conducted under the same conditions as shown in Fig. 1a, θ and eps were calculated to be 0.69 and 1.52 as average values, respectively.

The oscillation frequency recorded simultaneously during the potential cycling is also shown in Fig. 1b. The frequency remained approximately constant in the potential range of −0.2—0.3 V of the first scan. The frequency started decreasing upon oxidation of the adsorbed C_1 species, and finally merged into that for a clean platinum electrode. The frequency response during potential cycling on a clean platinum electrode has been examined by us;[18] it is concluded that the frequency changes observed in so-called hydrogen and double-layer regions are due to the adsorption/desorption of water molecules. The drift of oscillation frequency was negligibly small on the time-scale of these experiments, as shown by the fact that the frequency response in the second and subsequent several scans were completely the same as each other.

The frequency data were analyzed using the frequency difference at −0.2 V between the first and second scans ($\Delta f_{-0.2\mathrm{V}}$). This difference is clearly caused by oxidative desorption of the adsorbed C_1 species. At −0.2 V in the first scan, a part of the surface was covered by the adsorbed C_1 species, and the rest by the adsorbed hydrogen. In the second scan, on the other hand, the whole platinum surface was covered only by the adsorbed hydrogen. Denoting the molar mass of the adsorbed C_1 species per surface platinum site as mps (mass per site), therefore, the following equation holds:

$$\Delta f_{-0.2\mathrm{V}} \cdot S = (Q_H^{\circ}/F) \cdot [\{\theta \cdot \mathrm{mps} + (1-\theta) \cdot 1\} - 1 \cdot 1] \qquad (3)$$

where S is the EQCM sensitivity of 17.7 ng cm^{-2} Hz^{-1}. Q_H°/F gives the number of moles of surface platinum atoms. Substitution of θ of Eq. 1 into Eq. 3 gives

$$\mathrm{mps} = \Delta f_{-0.2\mathrm{V}} \cdot S/\{(Q_H^{\circ} - Q_H)/F\} + 1 \qquad (4)$$

The average mps was 10.3 for adsorption at 0 V for 5 min.

The experiments were repeated under various adsorption conditions different in the adsorption time and potential. The current and frequency responses during the potential cycling were similar to those shown in Fig. 1, except that magnitude of these responses was dependent on the adsorption conditions. Figure 2 shows the dependence of θ, eps, and mps on the adsorption time at 0 V. The coverage increased with the adsorption time, and reached the maximum value of ca. 0.72 at 10 min. Both eps and mps are larger at a short adsorption time of $\leqq 1$ min, and become constant at $\geqq 5$ min. These results indicate that the structure of the adsorbed layer is identical when the adsorption time is longer than 5 min.

The potential dependence of the coverage, eps and mps is shown in Fig. 3, where the adsorption time is fixed at 5 min. The coverage-potential curve is bell-shaped and agrees with that reported previously.[12,13] Eps and mps are approximately independent of the adsorption potential in the range of 0—0.225 V, and are 1.50 and 10.3, respectively.

Similar measurements and analysis have also been conducted in a 0.01 M NaOH solution. A cyclic voltammogram taken after the adsorption of methanol at −0.65 V for 5 min is shown in Fig. 4. An anodic peak due to oxidation of the adsorbed C_1 species appeared at −0.18 V. Complete coincidence between the current response after the oxidation and that of a clean Pt electrode shows, as the case in 0.1 M $HClO_4$, that the species was completely oxidized, and that the replacement of a methanol solution with a pure NaOH solution was achieved excellently. The corresponding frequency response is also similar to that in 0.1 M $HClO_4$. However, there exists a difference in the frequency decrease upon oxidation of the C_1 species, which is not so clear in a NaOH solution as in a $HClO_4$ solution. This will be discussed in a latter section. The difference in the frequency response during the potential cycling on a clean platinum electrode between NaOH and $HClO_4$ solutions has been discussed previously.[18]

At the negative end of the potential scan, the frequency decreased slightly both in the first and second scans. When the potential of a clean Pt electrode was scanned to more negative, the frequency kept decreasing and reached a constant value at ca. −1.4 V.[19] The magnitude of the frequency decrease was dependent on the cation used. It is reported that the point of zero charge of Pt in alkaline solutions is in the double-layer region.[20] Therefore, the frequency decrease at ca. −0.85 V and the more negative potentials seems to be

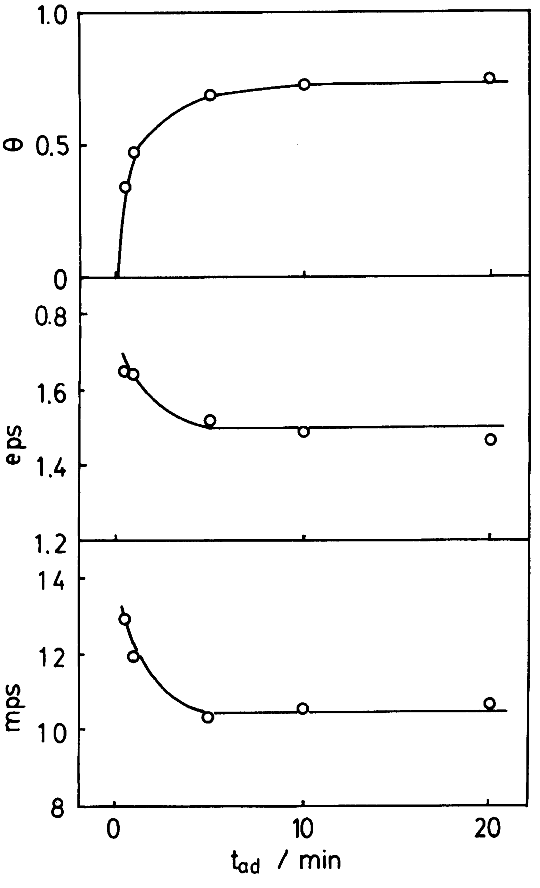


Fig. 2. Dependence of coverage, eps and mps on adsorption time. Adsorption was conducted at 0 V in 0.1 M $HClO_4$.

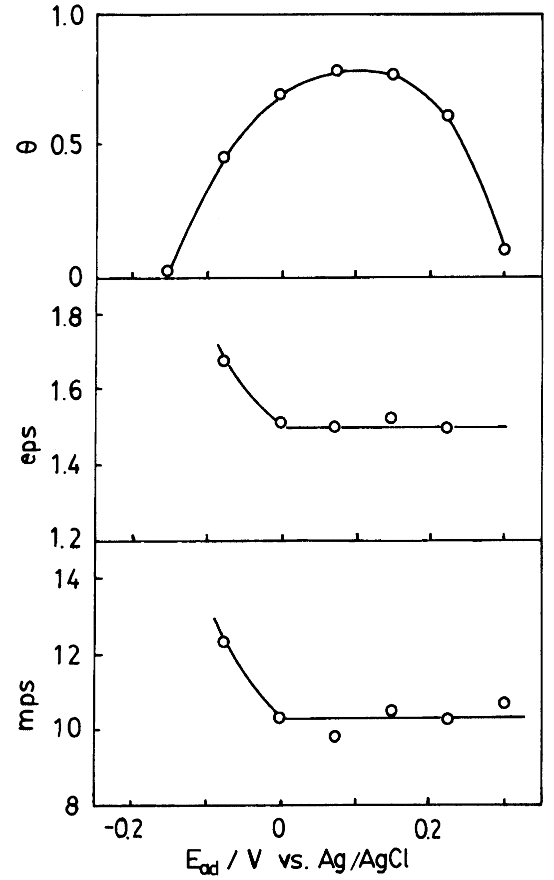


Fig. 3. Dependence of coverage, eps and mps on adsorption potential. Adsorption time: 5 min. Solution: 0.1 M $HClO_4$.

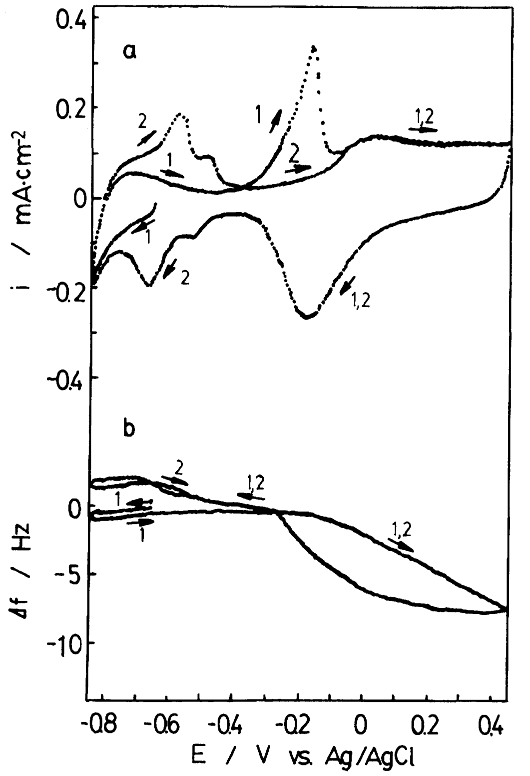


Fig. 4. Current (a) and frequency (b) responses during the oxidation of adsorbed C_1 species formed from methanol on a Pt electrode. An electrolyte solution was 0.01 M NaOH. Adsorption was conducted at −0.65 V for 1 min. Sweep rate was 50 mV s^{-1}. 1: first scan, 2: second scan.

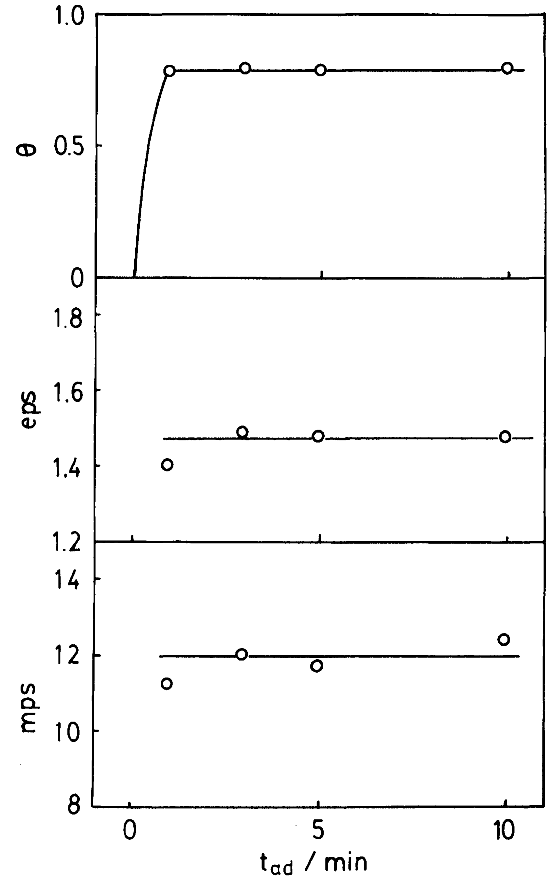


Fig. 5. Dependence of coverage, eps and mps on adsorption time. Adsorption was conducted at −0.65 V in 0.01 M NaOH.

due to the specific adsorption of the sodium ion. To avoid the complexity due to the specific adsorption, the frequency difference at − 0.8 V between the first and second scans was used to calculate the mps.

Figures 5 and 6 show the adsorption time and potential dependence of the coverage, eps and mps, respectively. Each point in the figures presents the average value of three separate experiments. All of θ, eps, and mps are essentially independent of the adsorption time, ranging from 1 min to 10 min. This means that the adsorbed layer was formed immediately after the introduction of methanol, and remained unchanged for at least 10 min. The coverage depends on the adsorption potential in a bell-shaped manner as in the case of $HClO_4$. Both eps and mps show a similar trend; these values slightly decreased as the adsorption potential became positive to −0.55 V, beyond which accurate determination of these values was not possible because of the low coverage. The average values of eps and mps in the range of −0.75—−0.55 V are 1.51 and 11.6, respectively, and are used for further analysis in the following section.

Discussion

Although eps and mps are dependent on the adsorption potential, these are considered to be approximately constant at higher coverages as mentioned above. These constant values and the conditions under which the values were taken are summarized in Table 1. Interestingly, both eps and mps are very similar in $HClO_4$ and NaOH, suggesting that the structure of adsorbed C_1 species is identical in both cases. However, this seems to be curious, since the frequency response upon the oxidation of the C_1 species was different. The frequency decrease (mass increase) upon oxidation of the adsorbed C_1 species is due to the adsorption of a heavier (in mass per site) chemical species on the site becoming vacant after the oxidative desorption of the adsorbed C_1 species. This new chemical species should be water as described above and in our previous paper,[18] and the potential-dependence of water adsorption is different between the cases in $HClO_4$ and in NaOH. This can explain the above-mentioned difference in the frequency response upon oxidation. To simplify the explanation, we denote the potentials where the oxidation current of the adsorbed C_1species starts increasing and terminates as E_i and E_t, respectively. The frequency decrease observed upon the oxidative desorption of the adsorbed C_1 species, $\{f(E_i)-f(E_t)\}$ is 2.1 Hz for $HClO_4$ and is 0.6 Hz for NaOH. The amount of adsorbed water

Table 1. Average Values of eps and mps, and Calculated Composition of the Adsorbed C_1 Species

Solution	E_{ad} / V	eps	mps	y in COH_y	Molar mass	Number of Ads. Sites
0.1 M $HClO_4$	0—0.225	1.50	10.3	2.4	30.4	3.0
0.01 M NaOH	−0.75—−0.55	1.51	11.6	2.0	30.2	2.6

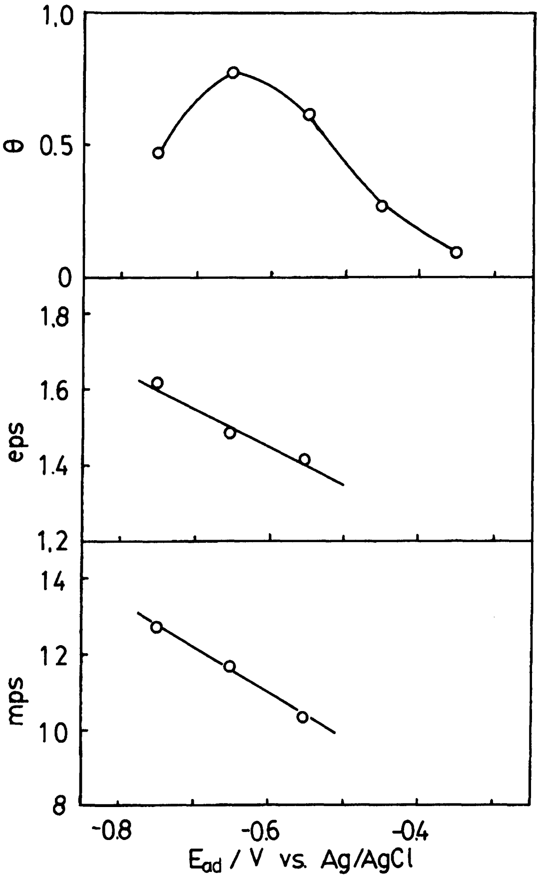


Fig. 6. Dependence of coverage, eps and mps on adsorption time. Adsorption time: 5 min. Solution: 0.01 M NaOH.

molecules can be estimated from the frequency response taken with cyclic voltammograms of clean Pt electrodes, which correspond to the second cycle voltammograms of Figs. 1 and 4. At the potential in the hydrogen region where the frequency maximum is attained, the surface is considered to be completely covered with hydrogen atoms, but not with water.[18] The potential is denoted as $E_{h,m}$. Therefore, $\{f(E_{h,m})-f(E_t)\}$ reflects the coverage by water at E_t, and is 4.7 Hz for $HClO_4$ and 3.1 Hz for NaOH. The difference between them (4.7−3.1=1.6 Hz) agrees well with the difference in $\{f(E_i)-f(E_t)\}$ (2.1−0.6=1.5 Hz). After the desorption of the adsorbed C_1 species, therefore, more water molecules can be adsorbed in $HClO_4$ than in NaOH, so that the frequency decrease becomes larger in $HClO_4$.

As described in the Introduction, several species have been proposed as the species formed from methanol. The eps and mps expected for these species are listed in Table 2. Among them, COH gives an mps of 9.7, closest to the observed value of 10.3—11.6 (Table 1), while larger mps are expected for both linear and bridged CO species. However, the eps expected for COH is 1.0 and definitely disagrees with the observed value of 1.5 in this study. Although the latter value can be explained by an equimolar mixture of linear and bridged CO species, this is not the case, since the mps should be 21 for such a mixed layer. Therefore, the present results indicate that the structure of the adsorbed layer is more complicated than those reported with IR and mass spectroscopic techniques. The presence of hydrogen atom in the adsorbed layer is suggested by the fact that the observed eps and mps can not be explained assuming only the CO species.

We find that the average composition of the adsorbed layer can be determined. Denoting the adsorbed C_1 species as CO_xH_y, the following equations hold:

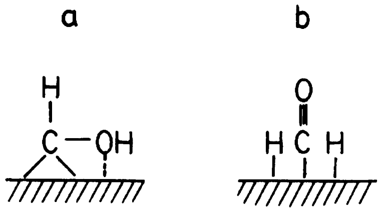
$$\text{mps} = (12 + 16\cdot x + y)/N_s \tag{5}$$

$$\text{eps} = (4 - 2\cdot x + y)/N_s \tag{6}$$

where N_s presents the number of Pt sites occupied by a single adsorbed C_1 species. The value of x should be 1 or 2. In the case of x=2, the adsorbed species ($COOH_y$) is characterized by an mps of (44+y) and an eps of y, since N_s should be 1. This is not the case. It is therefore reasonable to assume x=1. Using Eqs. 5 and 6 and the observed mps and eps values listed in Table 1 we can determine y and N_s. The results are summarized in Table 1 together with the molar mass of the adsorbed species. The composition of the adsorbed C_1 species expressed by $COH_{2.4}$ (3 sites) in $HClO_4$ and by $COH_{2.0}$ (2.6 sites) in NaOH. These are similar to each other, as expected. One of the plausible structures is shown in Scheme 1a. However, it should be mentioned that the above-mentioned composition is not necessarily for a single adsorbed species, but may be an average one of

Table 2. eps and mps Expected for Adsorbed Species Proposed Previously

Adsorbed species		eps	mps
CO	(1 site)	2.0	28
CO	(2 sites)	1.0	14
COH	(3 sites)	1.0	9.7
CHO	(1 site)	3.0	29
COOH	(1 site)	1.0	45



Scheme 1. Possible structures of the adsorbed C_1 species.

the adsorbed species.

In the studies using DEMS and ECTDMS, it is concluded that the adsorbed C_1 species is COH. Although the present results agree with their studies from the point of the existence of hydrogen atoms in the adsorbed layer, the present study presents more hydrogen atoms. In order to examine the possibility that the adsorbed C_1 species initially formed is reduced during the potential scan in the hydrogen region, the electrode potential was scanned to positive from the adsorption potential. The charge required to oxidize the adsorbed C_1 species was exactly the same as that when the potential was first scanned to the negative direction. We therefore conclude that the adsorbed C_1 species was not reduced before the oxidation, and that the hydrogen atoms included in the adsorbed layer came from methanol.

The adsorbed CO species have been clearly demonstrated by in-situ IR measurements, but not by the present EQCM study. However, this does not necessarily mean that both results are not in harmony with each other. The composition of $COH_{2.4}$ or $COH_{2.0}$ determined by EQCM indicates an average one of the adsorbed layer, and therefore the layer may consist of several species. The simplest case is shown in Scheme 1b, where an adsorbed CO and two adsorbed hydrogen atoms constitute a unit of the adsorbed layer. This unit occupies three sites. Since these adsorbed hydrogen atoms are not desorbed oxidatively until the adsorbed C_1 species is oxidized, they should be stabilized in the matrix of adsorbed CO. At this moment, however, we do not have any evidence by which we can rationalize the stabilization of the adsorbed hydrogen. Other combinations of adsorbed species can be considered on the basis of $C_2O_2H_{2y}$ ($2 \cdot N_s$ sites), $C_3O_3H_{3y}$ ($3 \cdot N_s$ sites), etc. For example, $C_3O_3H_6$ ($y=2.0$, 7.8 sites for the species formed in NaOH) gives same composition as that expected for a mixed assembly by an adsorbed CO and two CH_2OH. However, the number of adsorption sites (7.8 sites) are not expected for this assembly. Although we have tested many possibilities, none of them can explain the results well, except for those shown in Scheme 1.

In summary, the average composition of adsorbed C_1 species formed from methanol was determined to be $COH_{2.4}$ in $HClO_4$ and $COH_{2.0}$ in NaOH by a highly sensitive electrochemical quartz crystal microbalance. This species occupies approximately three platinum sites. Examination of the structure of the adsorbed layers in the presence of methanol in solution is now under investigation.

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