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Kinetic Coupling of Formaldehyde Oxidation and Oxide Formation on a Platinum Electrode

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(Received April 10, 1997)

The reflectivity of a p-polarized laser beam on a polycrystalline platinum electrode is sensitive to the formation and reduction of the surface oxide. The derivative of this reflectivity is proportional to the current for the oxide formation and reduction. The reflectivity indicates the partial current for the oxide formation and reduction, which is hidden in the total current, including the 4-electron oxidation of formaldehyde. The time course of the reflectivity by a potential-step perturbation shows that formaldehyde makes the rate of the oxide formation and the reduction drastically asymmetric due to dissociative adsorption on the oxide-free platinum-electrode surface.

The electrochemical oxidation of small organic molecules, such as formate formaldehyde and lower alcohols on a platinum surface, has complicated reaction pathways.[1—4] These reactions sometimes have electrochemical bistability, which induces oscillation of the electrochemical parameters, such as the current or the potential, while the reactions proceed.[5—10] Because the electrochemical behavior of these reactions is strongly dependent on the electrode material,[1] the reaction might proceed along with a strong interaction between the reaction intermediates and the electrode surface. These kinds of reactions are called electrocatalytic reactions.[11,12] The self-sustained electrochemical oscillation shows that multiple elementary reactions are involved to accomplish multi-electron oxidation reactions. Some of them are coupled with each other to complete the reaction. In this article, we report on the reaction coupling between the electrooxidation of formaldehyde and the oxide formation and reduction on the platinum electrode.

Experimental

The working electrode was a polycrystalline platinum disk of 10 mm in the diameter. The surface of the electrode was mirror-polished on a polishing disk of Marto ML-150P. It was rinsed with distilled water and sonicated for 300 s before each experiment. The reference and a counter electrode were a Ag|AgCl electrode and a 10 cm platinum wire, respectively.

The electrochemical condition was controlled by a potentiostat (Nikko-keisoku DPGS-1). The electrode potential was scanned by a potential scanner (Nikko-keisoku NPS-2). In the case of a potential-step perturbation, a pulse generator (Hewlett Packard HP8112A) was connected to the potentiostat. The surface of the electrode was irradiated by a 6.1 mW, 670 nm laser beam from a semiconductor laser (Audio Techinica SU-31CG-A10). p-Polarized light from the laser was shone on the electrode surface at an incident angle of 55±5 deg. The position of the laser spot on the electrode surface was close to the center of the disk. The reflectivity of the incident laser beam was detected by the combination of a photo-detector (Hamamatu Photonics S2044) and a signal processor (C7674). Originally, the combination of S2044 and C7674 is a position-sensitive detector by measuring the surface resistance of a photodiode. In this experiment, the system was slightly modified to measure the reflectivity change by subtracting a large amount of the background signal.

The signals of the current, the potential and the reflectivity were fed into an analog-to-digital converter (Stanford Research System SR245) and stored in a computer (Hewlett Packard HP9816). For storage of the fast response, a digital-storage oscilloscope (Hewlett Packard HP54510B) was used. The data were plotted using an ink jet printer (HP2225AJ).

Results

Oxide Formation without Formaldehyde. The intensity of the reflected light (ΔR) and the current were measured simultaneously under cyclic potential-sweep conditions. Typical results in a 2 M ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) sulfuric acid aqueous solution are shown in Figs. 1(a) and 1(c), respectively. The potential-sweep rate was $200\ \mathrm{mV\,s^{-1}}$. The differential shape of the time course of the reflected light intensity ($-\mathrm{d}(\Delta R)/\mathrm{d}t$) is shown in Fig. 1(b), which is called here "the derivative". In a positive-potential scan, the derivative started to increase at 0.71 V, which coincided well with the potential for the beginning of oxide formation in Fig. 1(c). In the negative-potential scan, the potential at the dip of the derivative was 0.56 V, where the cathodic current for the reduction of the surface oxide had a negative peak. Thus, the derivative was qualitatively similar to the current response for the oxide formation and the reduction in Fig. 1(c). Therefore, in this article the derivative is called the laser reflection voltammogram, which is sensitive to the surface oxide on the platinum electrode.

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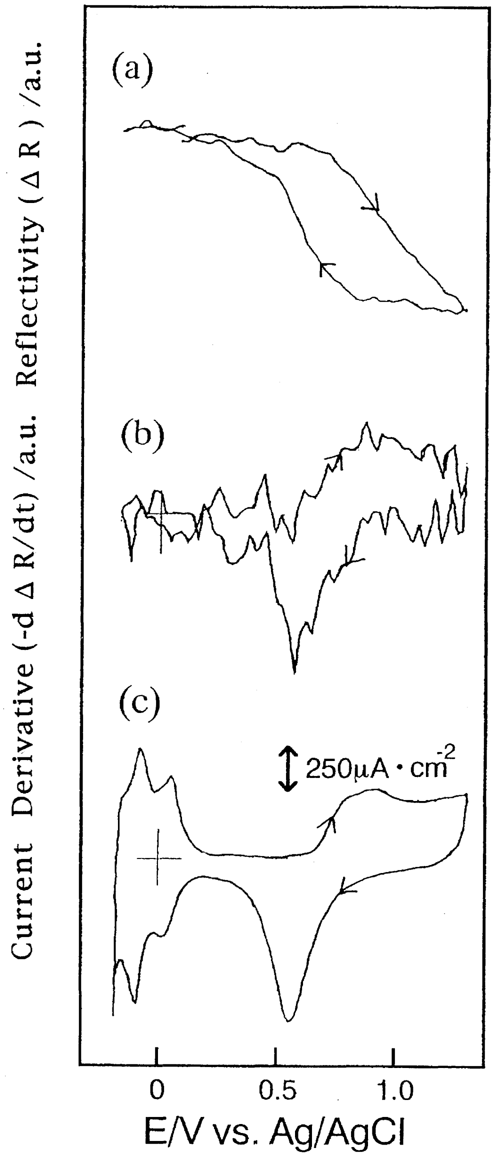

Fig. 1. The intensity of the reflected laser beam (a), the laser reflection voltammogram (b), and the cyclic voltammogram (c) of platinum electrode in 2 M sulfuric acid aqueous solution.

In order to clarify the relationship between the change in the reflectivity and the electrochemical charge of the oxide formation, the reflectivity was measured as a function of the charge. The oxide layer had been formed in advance by keeping the electrode potential at 0.9 V. The potential was then stepped to 0 V. The change in the reflectivity is defined schematically in the inset of Fig. 2. The charge for the oxide was estimated by integrating the current decay for the reducing the oxide in the negative-potential step. As shown in Fig. 2, the reflectivity varies proportionally as a function of the charge up to 500 μC cm^{-2}, where the deviation from a linear relation starts. Within the region of the linear relationship, the time course of the reflectivity informs the kinetics of the oxide formation and the reduction.

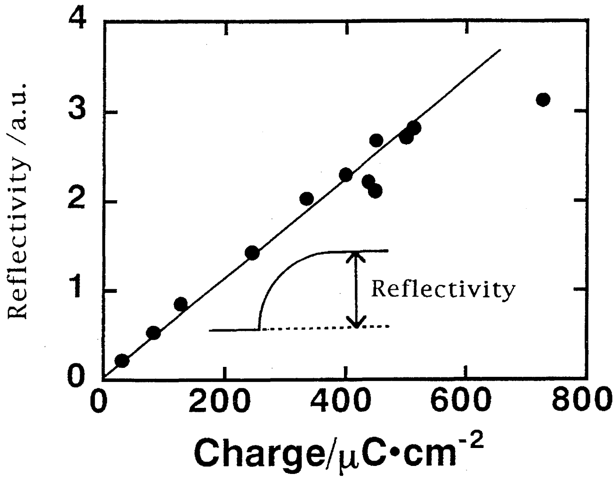

Fig. 2. The relationship between the reflectivity charge by the reduction of the surface oxide and the charge of the reaction in 2 M sulfuric acid aqueous solution. The inset at lower right is the definition of the reflectivity change.

Oxide Formation with Formaldehyde. In a 0.5 M sulfuric acid aqueous solution, formaldehyde was added to a concentration of 50 mM, and identical cyclic potential sweep measurements as those in Fig. 1 were conducted. The shape of the cyclic voltammogram, as shown in Fig. 3(c), is drastically changed from Fig. 1(c). However, the reflectivity and the laser reflection voltammogram, which are shown in Figs. 3(a) and 3(b), respectively, are similar to those of Figs. 1(a) and 1(b), expect that the potential for oxide formation and reduction is shifted to the negative direction by ca. 80 mV. The difference in the pH of the solution is 0.6 between 2 M and 0.5 M H_2SO_4. Assuming that the onset potential of Pt oxide decreases by 60 mV per pH unit, it would be $0.6 \times 60 = 36$ mV. The potential shift obtained by the reflectograms between Fig. 1 and Fig. 3 is not explained only by the pH difference. However, since the identical shape of the oxide formation and reduction is obtained with formaldehyde, the laser-reflection voltammogram reveals the electrochemical formation and reduction of the surface oxide, even in contact with an electrolyte solution containing formaldehyde. In the conventional cyclic voltammogram, the current for platinum oxide formation and the reduction is hidden in the current for the electrooxidation of the formaldehyde.

Time Course of the Oxide Formation and Reduction. The transient of the reflectivity for the oxide formation and reduction was measured in a 2 M sulfuric acid aqueous solution, Figs. 4(a) and 4(b), respectively. The electrode potential was stepped from 0 to 0.9 V (Fig. 4(a)). In the case of the reduction of the oxide, the potential was stepped from 0.9 to 0 V (Fig. 4(b)). The curves shown in Fig. 4 were obtained by averaging 32 measurements. The potential modulation was conducted by a symmetric rectangular wave with a frequency of 0.5 Hz.

Identical measurements were conducted in the presence of 50 mM of formaldehyde in a 2 M sulfuric acid aqueous solution. The results for the oxide formation and reduction are shown in Figs. 5(a) and 5(b), respectively.

Without formaldehyde, the speeds of the rise and decay

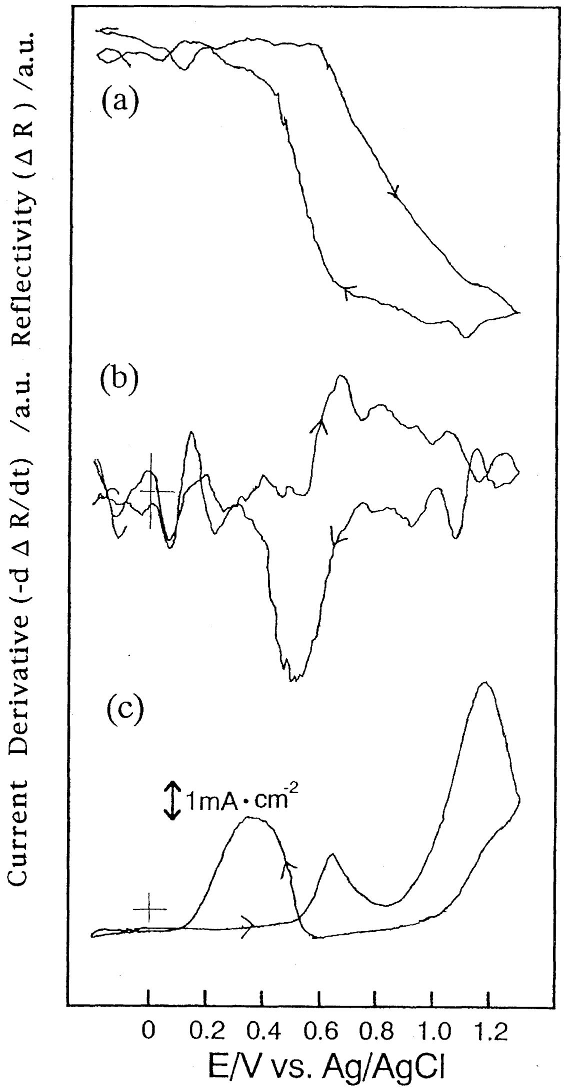

Fig. 3. The intensity of the reflected laser beam (a), the laser reflection voltammogram (b), and cyclic voltammogram (c) of platinum electrode in 0.5 M sulfuric acid aqueous solution containing 50 mM formaldehyde.

of the reflectivity for the oxide formation and reduction are almost the same as shown in Figs. 4(a) and 4(b), respectively. However, with formaldehyde in the solution, the rate of oxide formation was drastically slowed down, as shown by the slow rise time of ca. 20 ms in Fig. 5(a). Since the speed of the transient for the curves in Figs. 4(b) and 5(b) is almost on the same order, the reduction rate of the oxide is not affected by formaldehyde in the solution.

Discussion

Recently, surface-adsorbed CO has been monitored in the cyclic potential sweep condition by a second-harmonic generation (SHG) technique pumped by green light (532 nm) from a 10 Hz pulsed YAG laser.[9] The adsorbed CO enhances the SH light intensity by the optical resonance between the second harmonics (266 nm) and the optical state made by CO adsorption on platinum, whose absorption peak is lo-

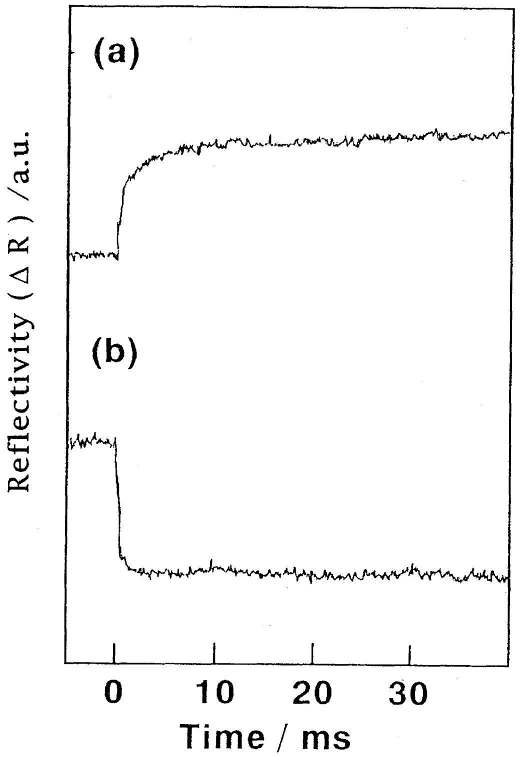

Fig. 4. The time course of the reflectivity by the positive, 0 to 0.9 V (a) and negative, 0.9 to 0 V (b) potential step perturbations on platinum electrode in 2 M sulfuric acid aqueous solution.

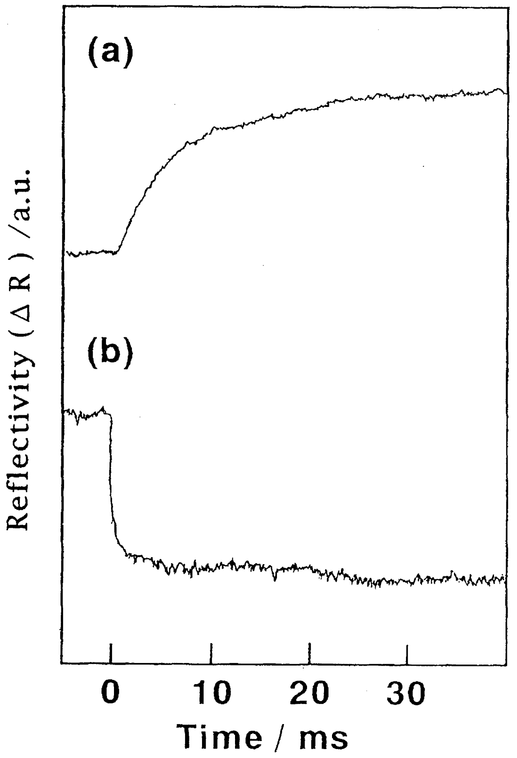

Fig. 5. The time course of the reflectivity by the positive, 0 to 0.9 V (a) and negative, 0.9 to 0 V (b) potential step perturbations on platinum electrode in 2 M sulfuric acid aqueous solution containing 50 mM formaldehyde.

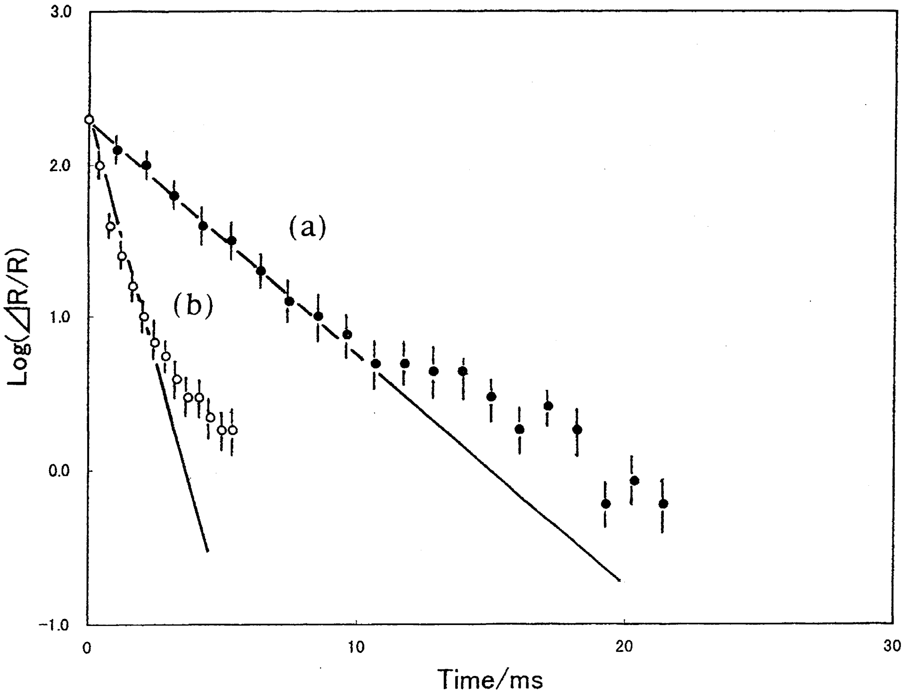

Fig. 6. The time course of the logarithm of the reflectivity change by the positive, 0 to 0.9 V potential perturbations on platinum electrode in 2 M sulfuric acid aqueous solutions with (a) and without (b) 50 mM formaldehyde.

cated at 270 mn.[13] The dynamics of the electrochemical CO reaction monitored by the SHG technique is underway in this laboratory. The SHG experiment simultaneously measured with the cyclic voltammogram has shown that the platinum electrode surface is covered by CO, which is formed by the dissociative adsorption of formaldehyde.[8,9] Then, in a solution containing formaldehyde, the surface is convered by CO at the initial stage of the positive potential step. The oxide formation follows the oxidation of adsorbed CO on the platinum surface. This is the reason why formaldehyde slows down the reflectivity changes, as shown in Fig. 5(a). However, in the negative potential step, the time course of the reflectivity are identical between Figs. 4(b) and 5(b). This shows that the reduction of the surface oxide initially occurs even in a solution containing formaldehyde. The dissociative adsorption of formaldehyde never occurs on the oxide surface.

The rise of the reflectivity shown in Figs. 4(a) and 5(a) are plotted based on first-order kinetics. The closed and open circles in Fig. 6 present the case with and without formaldehyde in the solution, respectively. The plots are normalized to the initial intensities of the reflectivity for the convenience to compare the rates of oxide formation. The plots in Fig. 6 systematically deviate from straight lines in both cases. This suggests that the reaction propagates on the electrode surface inhomogeneously due to 2-dimensional nucleation and growth mechanism.[14] Though the total time evolution of the reaction might not be explained by the first-order kinetics, the initial slope indicates the intrinsic rates of the oxide formation, which is free from the spatially overlapping interference of the growing nuclei. The apparent lifetime of the reaction estimated from the initial slopes are 7 and 2 ms for with and without formaldehyde in the solution, respectively.

The oxidation of formaldehyde can proceed on an adsorption-free platinum surface through another reaction route.[5,8,10] The adsorption-free platinum surface is produced after the oxide is electrochemically reduced. The current by this reaction path is observed as the anodic current peak in the cyclic voltammogram when the potential is scanned toward the negative direction, as shown in Fig. 3(c). Under this route, the oxidation dose not proceed though the dissociative intermediate, i.e., CO. This process is thus called the direct oxidation of formaldehyde. The direct oxidation of formaldehyde occurs on the negative potential step as a secondary process after the reduction of oxide until the surface is covered by CO.

Thus, the most probable mechanism to explain why formaldehyde slows down the rate of the oxide formation is two-step oxide formation in a solution containing formaldehyde. However, the reduction of the oxide occurs as a primary process whether the solution contains formaldehyde or not. Then, the rate of the reduction is not affected by formaldehyde.

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