In situ Optical Second Harmonic Generation Study of Electrochemical Oxidation of Formaldehyde on a Polycrystalline Platinum Electrode

Ichizo Yagi, Seiichiro Nakabayashi,# and Kohei Uosaki*
Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060

(Received March 18, 1996)

In situ optical second harmonic generation(SHG) technique was employed to investigate the electrochemical oxidation of formaldehyde on a polycrystalline Pt electrode. At 532 nm excitation, the SH signal generated at a Pt surface seems to be enhanced by the existence of adsorbed CO and can be related to the surface coverage of CO(a) which cannot be determined by the electrochemical methods. Thus, the potential dependence of the SH signal provides useful information to understand the mechanism of this reaction.

The mechanism of electrooxidation of small organic compounds is an important issue in electrocatalysis.[1] This is interesting not only for the development of the fuel cell but also for the understanding of multielectron transfer reaction which is one of the most important chemical reactions. Formaldehyde is one of the most studied molecules in this aspect because of its simple structure. In the proposed mechanism for the oxidation of formaldehyde,[2-4] the dissociated intermediate adsorbed on the electrode (CO(a)) plays important roles. This intermediate is inert and behaves as a poison for the direct oxidation of formaldehyde. Although the existence of CO(a) has been confirmed by the in situ infrared reflection absorption spectroscopy (IRRAS)[2-4] and the role of CO(a) is well established, the kinetics of the adsorption and the oxidation of this species is not well understood because of the lack of the in situ technique with ability to determine the transient surface concentration of CO(a) in real time.

The optical second harmonic generation (SHG) is one of the second order nonlinear optical effects and involves the conversion of two photons of frequency ω into a single photon of frequency 2ω.[5] In the electric dipole approximation, this phenomenon requires a noncentrosymmetric medium. Consequently, the SH signal is sensitive to the nature of the interface and, therefore, is considered to be useful to probe various interfacial phenomena. This technique has been applied to various electrochemical systems such as adsorption of molecules, ions and metal atoms on metal and semiconductor electrodes.[6-8]

In the present study we adopted this technique as an in situ tool for probing the existence of CO(a) on Pt (poly.) during the anodic oxidation of formaldehyde. At 532 nm excitation, SHG on a platinum surface increased with CO(a) chemisorption and can be related to the surface coverage of CO(a) which cannot be detectable with conventional electrochemical measurements.[9]

A 10 mm diameter polycrystalline platinum disk that was held in a Kel-F holder was used as a working electrode (the apparent electrode diameter : 8 mm). The optically flat Pt electrode was electrochemically cleaned in 0.1 M (1 M = 1 mol•dm^{-3}) H_2SO_4 solution before each experiment. A standard three electrode configuration was constructed with an Ag/AgCl (sat'd NaCl) reference electrode and a Pt counter electrode. The electrochemical SHG measurements were carried out in 0.1 M $HClO_4$ solution with or without 0.1 M HCHO at room temperature. The 10 ns pulses of 532 nm light generated by a 10 Hz Q-switched Nd:YAG laser (LEXEL, HY-200S) were employed as a excitation light for the SHG measurements. The fundamental beam was slightly focused onto the surface of a platinum electrode in a spectroelectrochemical cell at 60° angle of incidence. The SH light (266 nm) was separated from the fundamental laser beam with filters and a spectrometer (Ritu, MC-10N) and detected by a photomultiplier tube (PMT: Hamamatsu, R636). The SH signal was averaged with a boxcar averager (Stanford Research, SR250) and was normalized with the SH signal generated in a separate reference channel at each laser shot. The polarizations of the fundamental and SH beam were set with polarization optics.

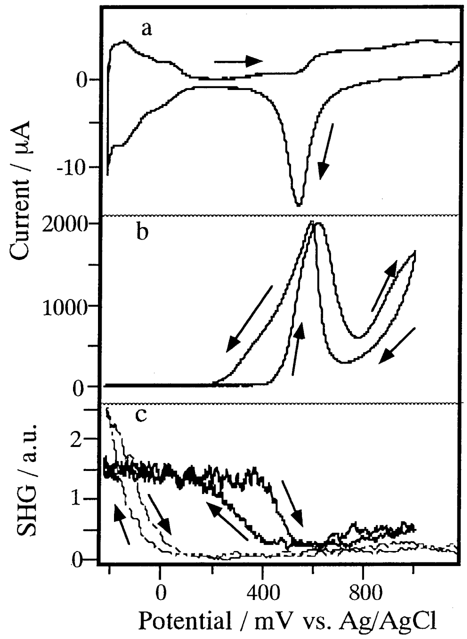

Figure 1. Cyclic voltammograms of a Pt electrode in 0.1 M $HClO_4$ (a) without and (b) with HCHO and (c) simultaneously recorded potential dependence of the p-in/p-out SH intensity (dashed line: without HCHO, solid line: with HCHO). Sweep rate was 5 mV•sec^{-1}.

Figure 1(a) shows the cyclic voltammograms (CVs) of the Pt electrode in 0.1 M $HClO_4$ solution (a) and in 0.1 M $HClO_4$ solution containing 0.1 M HCHO (b) and the simultaneously recorded potential dependence of the p-polarized SH intensity (c) obtained in 0.1 M $HClO_4$ solution with (solid line) and without (broken line) 0.1 M HCHO with the p-polarized light excitation. The CVs in Figure 1(a) and (b) were typical for Pt electrodes in $HClO_4$ solution with and without high concentration HCHO, respectively. The hydrogen waves completely disappeared in the solution with HCHO at the sufficiently slow scan rate, showing the existence of CO(a) on Pt. The SH intensity in 0.1 M $HClO_4$ solution was almost constant in fairly wide potential region except in hydrogen adsorption region where the SH intensity increased

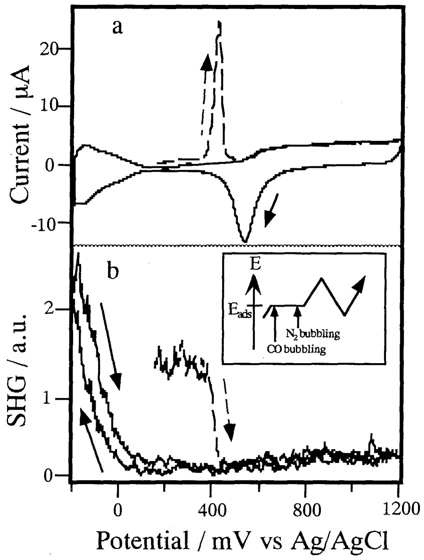

Figure 2. The potential dependence of (a) current and (b) p-in/p-out SH intensity at a Pt electrode with pre-adsorbed CO during the first 2 cycles of potential scan (the broken lines represent the 1st scan). Sweep rate was 5mV•sec^{-1}. The inset is the potential scheme employed.

as potential became negative (Figure 1(c), broken line).[10] In the solution with HCHO, the SH intensity was high and constant in negative potential region up to +0.4 V. It is clear that the high level of SH intensity in this case was not due to the adsorbed hydrogen. The SH intensity decreased as the anodic current started to flow around +0.4 V in the anodic scan. In the reverse (cathodic) scan, the SH intensity started to increase with the decline of the anodic current around +0.4 V and returned to its initial value around +0.15 V where the anodic current ceased to flow. These results suggest that the intensity of SH light was enhanced by the existence of CO(a), and the decrease and increase of the SH intensity reflected the oxidative desorption and the dissociative adsorption of CO(a), respectively. Although the surface oxidation of Pt occurred at sufficiently anodic potential region, the SH intensity was almost constant in this potential region as was the case in $HClO_4$ solution without HCHO, indicating that the SH signal was not affected by the oxygen species in this wavelength. In addition, the potential dependent variation of SH intensity was not detectable for other optical polarization conditions.

To confirm that the enhancement of SHG is due to the existence of CO(a), we carried out a separate experiment using CO gas as the source of adsorbate. At first, CO gas was bubbled through 0.1 M $HClO_4$ solution in the electrochemical cell for 10 minutes, with the electrode potential being held at a certain potential (E_{ads}). The solution was left another 15 minutes and then, dissolved CO was purged by bubbling N_2 gas through the solution and potential was scanned to positive direction. Figure 2 shows (a) CV and (b) the potential dependence of SH intensity during the first two potential scans with E_{ads}=+0.15 V. Inset shows the potential scheme employed. The CO(a) oxidation current was observed at +0.4 V in the 1st anodic scan and no current peak assigned to CO(a) oxidation appeared in the 2nd anodic scan. The SH intensity was high up to +0.4 V where anodic current due to CO(a) oxidation started to flow in the 1st anodic scan. In the 2nd scan, the usual potential dependence of SH intensity observed for bare Pt electrode was obtained. These results indicate that the CO(a) on Pt is responsible for the enhancement of SH intensity.

The solid line in Figure 1(c) is now considered to represent the surface concentration of CO(a) during the oxidation of formaldehyde. In the anodic scan, the coincidence of the decrease of the SH intensity and the increase of the anodic current showed that the oxidative desorption of CO(a) triggered the direct oxidation of formaldehyde. In the cathodic scan, the anodic current flowed as the direct oxidation of HCHO takes place as soon as the Pt oxide is reduced. The SH intensity, i.e., CO(a) coverage, gradually increased after the anodic current peak, showing the dissociative adsorption of CO(a), which inhibits the direct oxidation of HCHO, is a relatively slow process.

Some advantages of SHG measurement to monitor the chemisorption of CO(a) on Pt in comparison with other spectroscopic techniques should be mentioned. The reflectance measurement may provide almost same information due to the electronic transition,[11-13] but the reflectance signal is affected by the surface oxide formation and the separation of the contributions from CO(a) and that from the surface oxide is difficult. On the other hand, the SH signal is not affected by the Pt oxide formation as clearly shown here. Furthermore, the SHG measurement can follow the reactions in real time in contrast to the IRRAS that is the most useful technique to study chemisorption. Thus, it is demonstrated that the SHG measurement is very useful for in situ study of time dependent phenomena.

In conclusion, we have found that the SH intensity in the UV wavelength range was enhanced by the chemisorption of CO molecule on Pt electrode and the change of the SH intensity reflected the surface coverage of CO(a) upon electrochemical oxidation of formaldehyde.

This work was partially supported by the Sumitomo Foundation. IY acknowledges the Japan Society for the Promotion of Science for the JSPS Research Fellowship for Young Scientists.

References and Notes

\# Present address: Department of Chemistry, Faculty of Science, Saitama University, Urawa 338.

1 R. Parsons and T. VanderNoot, *J. Electroanal. Chem.*, **257**, 9 (1988).

2 K. Kunimatsu and H. Kita, *J. Electroanal. Chem.*, **218**, 155 (1987).

3 S. G. Sun, J. Clavilier, and A. Bewick, *J. Electroanal. Chem.*, **240**, 147 (1988).

4 K. Nishimura, R. Ohnishi, K. Kunimatsu, and M. Enyo, *J. Electroanal. Chem.*, **258**, 219 (1989).

5 Y. R. Shen, "The Principle of Nonlinear Optics" Wiley, New York (1984).

6 R. M. Corn and D. A. Higgins, *Chem. Rev.*, **94**, 107 (1994).

7 G. L. Richmond, J. M. Robinson, and V. L. Shannon, *Prog. Surf. Sci.*, **28**, 1 (1988).

8 I. Yagi, J. M. Lantz, S. Nakabayashi, R. M. Corn, and K. Uosaki, *J. Electroanal. Chem.*, **401**, 95 (1996).

9 S. Nakabayashi, N. Sugiyama, I. Yagi, and K. Uosaki, *Chem. Phys.*, in press.

10 D. J. Campbell and R. M. Corn, *J. Phys. Chem.*, **92**, 5796 (1988).

11 J. A. Caram and C. Gutierrez, *J Electroanal. Chem.*, **305**, 259 (1991).

12 A. Cuesta and C. Gurierrez, *J. Electroanal. Chem.*, **383**, 195 (1995).

13 Y. Ikezawa, N. Nagashima, T. Shibata, and T. Takamura, *J. Electroanal. Chem.*, **365**, 261 (1994).