CHEMISTRY LETTERS, pp. 1877-1880, 1987.

Study of Electrochromic Reactions of WO_3/H^+ System by *In Situ* Electrogravimetry

Hideki MASUDA* and Nobuyoshi BABA
Department of Applied Chemistry, Faculty of Technology, Tokyo
Metropolitan University, Fukasawa, Setagaya-ku, Tokyo 158

The reactions of electrochromic display devices were studied *in situ* by measuring the small weight change of the electrode with the liquid phase quartz crystal microbalance. Time response of the weight change during the bleaching and coloring process was in good accordance with those of charge and optical density. Based on the results of weight measurements, the mechanism of the coloring reaction in WO_3/H^+ was discussed.

Electrochromic (EC) property of WO_3 is currently of interest for display devices.[1-6] The EC process in the WO_3 is believed to occur according to the insertion-extraction mechanism of a cation to the host lattice. It is important to investigate the mechanism of the coloring or bleaching process to improve the performance of the display devices. Though many analytical methods have been used to clarify the mechanism of the WO_3 reactions, only limited techniques, such as electrochemical and optical measurements, have been applicable to examine the reaction under the condition of actual electrolytic environment. In the present study, we applied the liquid phase quartz crystal microbalance (QCM) to the *in situ* examination of the EC reaction of the WO_3 thin films.

Measuring the weight change of the electrode accompanying the EC reactions is useful to determine the amount of the cations inserted to the host materials quantitatively, and it can give information concerning the mechanism of EC reactions. However, the earlier effort reported on the weight measurements in EC reactions was carried out under the *ex situ* condition.[6] The *ex situ* method is troublesome, where there may be some limitations in accuracy and reproducibility, because the electrodes have to be rinsed in an appropriate solvent and dried before the each measurement. Adopting the *in situ* method for the weight measurement, one can expect to measure it more precisely and to pursue the kinetics of the EC reactions from the continuous observation of the weight change.

The liquid phase QCM method has recently been applied to several analyses in the liquid environment[7,8] and also in electrochemical systems.[9-12] In this method, the change of mass is detected by measuring the resonant frequency of an oscillating quartz crystal consisting of one face in contact with a liquid, and it has been reported that this method can detect the change of mass less than 10^{-8} g.

We describe here the direct and continuous weight measurement of the coloring/ bleaching reactions of WO_3/H^+ in an aqueous electrolytic solution and discuss the mechanism of the EC reactions in the WO_3.

AT-cut piezoelectric quartz crystals were used for the liquid phase microbalance. Nominal resonant frequency of the crystal was 10 MHz. Au electrodes with thickness about 1000 Å were sputtered onto both sides of the crystal for an electrical oscillator circuit. The WO_3 film was prepared by thermal evaporation of WO_3 powder (Kanto Chemicals) onto one surface of the Au electrodes in a vacuum chamber (5x 10^{-5} Torr). The thickness of the WO_3 film, estimated from the density reported for evaporated WO_3 films (5.2 g/cm^3),2) was usually 2000-3000 Å. The surface area of the WO_3 electrode was 2.0 cm^2. After the evaporation, the quartz crystal was mounted in an electrochemical cell using silicone rubber sealant.

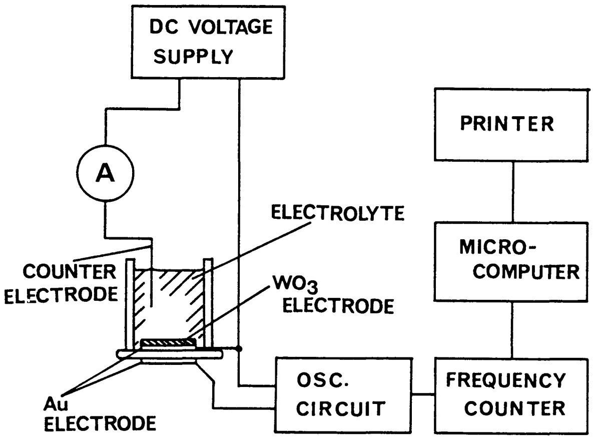

Fig. 1. Experimental set up for weight measurement and electrolysis.

The experimental set up is shown in Fig.1 schematically. The quartz microbalance mounted on the electrochemical cell was connected to the oscillating circuit made up from the integrated circuit (SN741320), which was driven by DC voltage supply(3.0-5.0 V). The frequency of the oscillating circuit was monitored with a frequency counter (Iwasaki Tushin SC-7101) and processed by a microcomputer system (NEC PC-9801F). This experimental instrument can take in the data at sampling time of 1s within an error limit in the frequency of 1 Hz.

The color/bleach cycle was performed by using a DC voltage supply. The electrolyte was a 5 wt% H_2SO_4 aqueous solution and the counter electrode was a platinum wire. The current accompanying the coloring/bleaching process was monitored with a digital ammeter (ADVANTEST TR8652) and the charge passed was obtained by integrating the current.

The change of the frequency of the AT-cut quartz crystals due to the weight gain or loss on the surface has been quantified by Saurbray as follows:13)

$$\Delta f= (-2.3 \times 10^{-6}) \times f^2 \times \Delta W/S, \quad (1)$$

where Δf is the change in frequency (Hz), f is the resonant frequency of the crystal (Hz), ΔW is the change in weight (g), and S is the area of the electrode (cm^2) for oscillation. Eq.1 has been used to describe the effect of the weight gain or loss on the quartz crystal in the vapor phase. It has been reported that this relationship also holds in liquid environment. Experimental confirmation of this relationship was carried out also in our instrument by using galvanostatic electrodeposition of Ag on Au electrodes.

Figure 2-a shows the typical change in frequency of the QCM for the 2300 Å WO_3 electrode during the coloring/bleaching reactions in the H_2SO_4 aqueous solution. The current response simultaneously measured is also shown in Fig.2-a. When the WO_3 electrode is cathodically polarized (at -2.0 V), the frequency begins to decrease with time and attains to saturated value after about 30 s electrolysis.

The decrease in frequency indicates the increase of the weight of the WO_3 electrode, and the time dependence of the frequency change is in good accordance with the cathodic current behavior. When the polarity of the applied voltage is reversed from -2.0 to +2.0 V, the frequency increases with bleaching process. The change of the weight of the electrode evaluated from the Eq.1 was ca. 300 ng at the saturated point in the Fig.2-a and was corresponding to 1.2% of total weight of the WO_3.

The time response of the weight change evaluated in Fig.2-a is qualitatively in good accordance with those of charge passed (Fig.2-b), and of the change in optical density measured at 600 nm (Fig.2-c). In the evaluation of the charge, the background current in Fig.2-a was excluded. The change of the optical density in Fig. 2-c was measured separately by using a WO_3 film evaporated on an optically transparent electrode in a cell configuration similar to that in the weight measurement.

Figure 3 shows the maximal weight change (-2.0 → 2.0 V) plotted against the thickness of WO_3 films. The change of the weight is found to be in linear relationship with the film thickness. This result implies that protons penetrate into the almost entire thickness, when the WO_3 film thickness is as small as 3000 Å.

From the result in Fig. 3, we can estimate the effect of change in liquid phase on the weight measurement. For the liquid phase QCM, the thin liquid layer in the vicinity of the electrode surface vibrates together with the quartz crystal.[9] For this reason, there is a possibility that the change in the liquid phase due to the potential change affect the weight measurements. However, the weight change at zero thickness obtained from the extrapolation of the line plotted using a least square method was extremely small and, therefore,

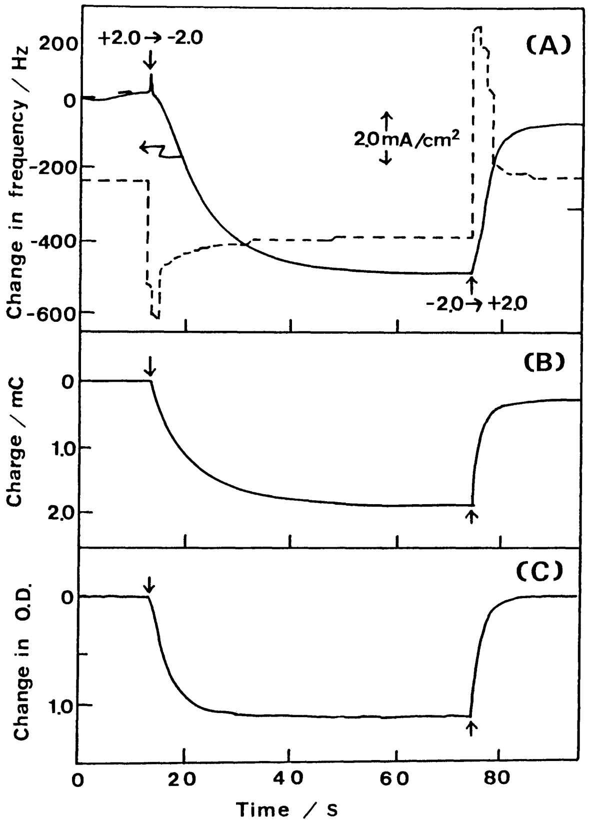

Fig. 2. Change in frequency (——) and current density (---)(A), charge (B), and change in optical density (C) vs. time curves for WO_3 electrode; 5 wt% H_2SO_4.

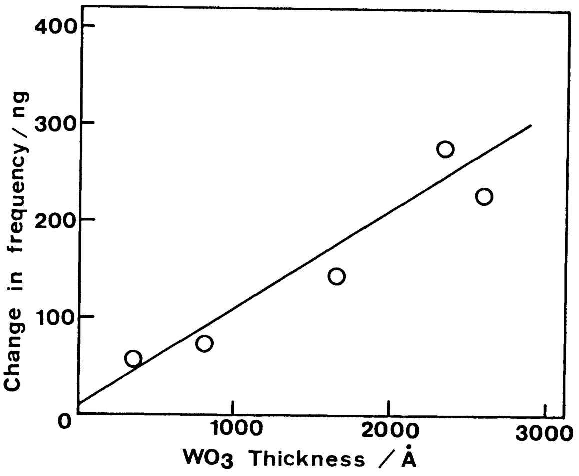

Fig. 3. Change in weight vs. film thickness of WO_3 electrode; 5 wt% H_2SO_4, -2.0→+2.0 V.

it can be concluded that the contribution of the change in liquid layer to the weight measurement is negligibly small compared with that in WO_3 electrode.

Table 1. Ratio of weight change to specific charge for WO_3 samples

Sample NO.	d/Å	dW/ng	Q/mC	(dW/Q)/ng mC^{-1}	dW/e$^{a)}$
1	2360	277	1.87	148	14.4
2	1427	162	1.03	157	15.3
3	1307	142	1.26	113	11.0
4	2610	398	2.70	147	14.3
5	1642	147	1.57	100	9.7
6	2592	232	1.90	122	11.9
7	1936	301	1.74	173	16.8
8	1916	349	1.86	188	16.1
9	1123	157	0.88	180	17.5

a) Atomic mass unit/number of electrons
5 wt% H_2SO_4, -2.0→+2.0 V.

In Table 1 are summarized the ratios of the weight change to the charge passed for the several independent samples. The data of the thin films less than 1000 Å were excluded from this table because of the poor reliability of the charge measurement for EC reactions. The comparative experiments by the *ex situ* weight measurements for the same samples could not be made, because coloring state of the WO_3 films is not stable in the atmospheric condition due to the rapid oxidative bleaching with oxygen. The atomic mass unit (1.66×10^{-24} g) per single electron, dW/e, which was calculated from the dW and Q was found to be in the range of 10-18, and the averaged value of these measurements was 14.1. This result implies that the proton penetrates into the WO_3 accompanied by some amount of H_2O. The recent reports based on IR [5,6]and ex situ weight measurements[6] have suggested the participation of the water in the coloration/bleaching reaction of the WO_3 electrode. The results in the Tab.1 are qualitatively in agreement with this mechanism.

We could also examine some other properties of EC reactions in the WO_3/H^+ systems, e.g., aging effects of the WO_3 films in initial several color/bleach cycles and memory characteristics in the open circuit condition. These properties could be observed reproducibly on repeated experiments.

In conclusion, it was confirmed that the EC reaction could be examine clearly by the *in situ* electrogravimetry. Since this technique is extremely sensitive and can measure the mass change of the electrodes continuously in the electrolytic environment, further experiments will show the detailed information concerning the mechanism of EC reactions.

References

1) B. W. Faughnan, R. S. Crandall, and P. M. Heyman, RCA Rev., 36,177 (1975).
2) J. P. Randine, J. Electron. Mater., 7, 47 (1978).
3) I. Shimizu, M. Shizukuishi, and E. Inoue, J. Appl. Phys., 50, 4027 (1979).
4) H. Morita and H. Washida, Jpn. J. Appl. Phys., 19, L228 (1980).
5) B. Reichman, A. J. Bard, and D. Laser, J. Electrochem. Soc., 127, 647 (1980).
6) N. Yoshiike and S. Kondo, Denki Kagaku, 54, 423 (1986).
7) T. Nomura and O. Hattori, Anal. Chim. Acta, 115, 323 (1980).
8) M. Thompson, C. L. Arthur, and G. K. Dhaliwal, Anal. Chem., 58, 1206 (1986).
9) S. Bruckenstein and S. S. Swathirajan, Electrochim. Acta, 30, 851 (1985).
10) S. Bruckenstein and M. Shay, J. Electroanal. Chem., 188, 131 (1985).
11) J. K. Kaufman, K. K. Kanazawa, and G. B. Steet, Phys. Rev. Lett., 53, 2461 (1984).
12) D. Orata and D. A. Buttry, J. Am. Chem. Soc., 109, 3574 (1987).
13) G. Sauerbrey, Z. Phys., 155, 206 (1955).

(Received June 20, 1987)