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Study of Charge Compensation Mechanism in IrOx Electrochromic Reactions by *In Situ* Electrogravimetry

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The mechanism of the charge compensation in the coloring/bleaching reactions in IrOx films was studied by *in situ* electrogravimetry. The weight change measured with a liquid phase quartz crystal microbalance indicated that the cations were ejected from the IrOx film to a bulk electrolyte during anodic coloration.

Iridium oxide (IrOx) films are a promising material for the application to electrochromic (EC) display devices.[1-4] In EC reactions of IrOx, it is generally accepted that anodic coloration is accompanied by the ejection of electrons from the IrOx to a substrate electrode. However, the mechanism of charge compensation for coloration/bleaching reactions has not been sufficiently clear yet. Two mechanisms have been proposed to interpret the compensation of the local electroneutrality of the IrOx films: the cation ejection,[2,3] and the anion injection mechanisms[4] for the anodic coloration reactions.

In the present study, the weight change of the IrOx thin film electrodes during coloration and bleaching reactions was analyzed *in situ* by a liquid phase quartz crystal microbalance (LP-QCM) method, and the charge compensation mechanism of IrOx EC reactions was discussed.

The LP-QCM and the other instruments for electrochemical and optical measurements are similar to those reported previously.[5,6] IrOx EC films were prepared by the periodic reverse current electrodeposition from sulfatoiridate solutions.[7] The periodic reverse current iridium oxide film (PRIROF)[8] was applied to Au sputtered electrodes (0.5 cm in diameter), which were formed on an piezoelectric quartz crystal with characteristic frequency of 10 MHz for oscillator circuitry. Then, a glass tube was mounted with a silicone rubber sealant on the quartz plate to construct the electrochemical cells with the LP-QCM. A 0.1 M H_2SO_4 aqueous solution was used as an electrolyte, and a platinum wire was used as a counter electrode.

Figures 1-a and -b show the changes in weight and optical density measured at 632.8 nm during the coloring/bleaching reactions of the IrOx film in the 0.1 M H_2SO_4 aqueous solution. When the IrOx film was anodically polarized (+1.0 V), coloration took place [colorless --> blue black]. At the same time, the weight of the IrOx film began to decrease and attained to a constant value. The change of the weight at the saturated point was ca. 500 ng for the electrolysis at +1.0 V. This decrease in weight accompanying the coloration indicates that the charge compensation in the IrOx films is achieved by ejection of cations from the IrOx film to the bulk electrolyte. At the reverse cathodic polarization (-1.0 V), the weight of the electrode increased with time accompanying the bleaching of the film and returned to almost the initial value. These weight changes during the coloring/bleaching cycles showed good reproducibility.

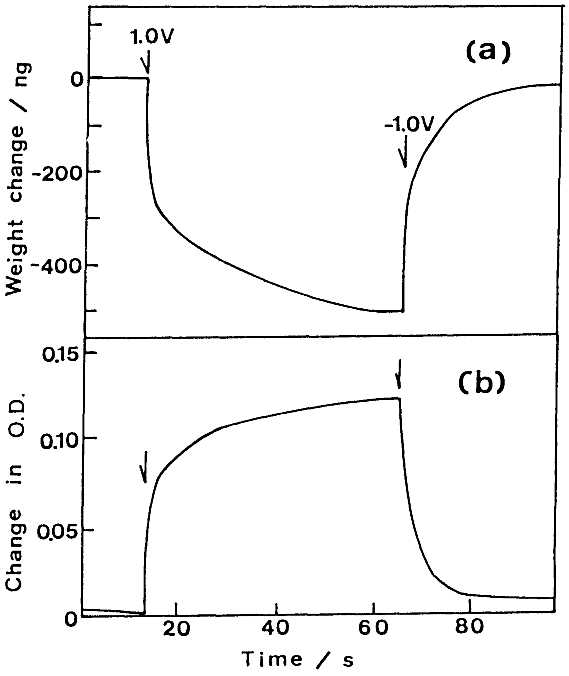

Fig. 1. Change in weight (a) and optical density (b) versus time curves for IrOx electrode; 0.5 M H_2SO_4, ± 1.0 V, $S = 0.2\ cm^2$, $\lambda = 632.8$ nm.

The response time in weight change of the present IrOx film measured with the *in situ* electrogravimetry during coloring /bleaching reactions is shorter than that of WO_3/H^+ electrochromic systems.$^{5,6)}$ This indicates that the highly porous structure of the IrOx film$^{2)}$ permits the rapid migration of the ions to the film.

The ratio of the weight change to the charge passed was measured to identify the migrating species. Although the values of weight change/charge ratio showed some scatter in measured IrOx samples in the range of 36-14$^{9)}$ at the present stage, it is suggested that the coloration/bleaching reactions in IrOx films occur with accompanying the migration of the hydrated protons (H_3O^+) rather than free protons (H^+).

The measurements of the weight change were also carried out in neutral (0.1 M Na_2SO_4) and alkaline (0.1 M NaOH) solutions. Similarly to the acidic condition, decrease of the weight was observed also under the neutral and alkaline conditions accompanying the anodic coloration. These results are in conflict with anion (OH^-) injection mechanisms for coloration in neutral and alkaline solutions,$^{4)}$ and implies that the cation mechanism, Na^+ or hydrated proton migration, dominants also in neutral and alkaline conditions.

References

1)S. Gottesfeld, J. D. E. McIntyre, G. Beni, and J. L. Shay, Appl. Phys. Lett., 33, 208(1978).

2)S. Gottesfeld and J. D. E. McIntyre, J. Electrochem. Soc,, 126, 742(1979).

3)J. D. E. McIntyre, S. Basu, W. F. Peck, Jr., W. L. Brown, and W. M. Augustyniak, Phys. Rev. B, 25, 7242(1982).

4)G. Beni, C. E. Rice, and J. L. Shay, J. Electrochem. Soc., 127, 1342(1980).

5)H. Masuda and N. Baba, Chem. Lett., 1987, 1877.

6)H. Masuda, H. Tanaka, and N. Baba, Bull. Chem. Soc. Jpn., in preparation.

7)T. Yoshino, N. Baba, and K. Arai, Jpn. J. Appl. Phys., 26, 1547 (1987).

8)Conditions for IrOx preparation were as follow; $Ir_2(SO_4)(H_2O)_x$: 0.2 wt%, voltage:+1.4, -0.7 V/SCE, 1/12 Hz, temperature: 35 C, electrolysis time: 15 min.

9)weight changes expressed as an atomic mass unit($1.7x10^{-24}$g) per single electron.

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