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EFFECT OF ILLUMINATION INTENSITY ON STABILIZATION OF ZnO PHOTOANODES IN HALIDE SOLUTIONS

Tetsuhiko KOBAYASHI, Hiroshi YONEYAMA, and Hideo TAMURA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadakami, Suita, Osaka 565

The ratio of the photoanodic oxidation of halide ions in competition with the photoanodic dissolution of ZnO was investigated as a function of illumination intensity and concentration of halide ions. A relatively low illumination intensity was found to be desirable for stabilizing the photoanode in iodide solutions, while a high illumination intensity was favorable in bromide solutions. The energetic position of the quasi-Fermi level of positive holes relative to the decomposition potential of ZnO and to the redox potentials of halide ions seems to govern the phenomena.

The stabilization of semiconductor electrodes in aqueous solutions has been one of the main subjects in studies on photoelectrochemical cells. Up to date, several efforts have made successes in stabilizing n-type semiconductors by adding appropriate reducing agents into electrolyte solutions.[1-4] A guideline to predict the stabilization was also presented[5,6] and found to fit fairly well with the experimental results.[7] Although fairly intensive studies have been conducted on the stabilization, no report has been published on effects of the illumination intensity on the stabilization. The present study was conducted, therefore, to get information on this point in ZnO/halide ion systems. It is well established that illuminated ZnO dissolves anodically;[8,9]

$$ZnO + 2p^+ \longrightarrow Zn^{2+} + 1/2O_2 \qquad (1)$$

If halide ions X^- are present in the electrolyte, these will be competitively oxidized[7]

$$2X^- + 2p^+ \longrightarrow X_2 \qquad (2)$$

The percentage of the competitive oxidation of halide ions can be evaluated by means of the rotating ring-disk electrode (RRDE) technique.[10,11]

A single crystal (2 mm thick) and a non-porous sinter (5 mm thick) of ZnO were used in the present study. These were machined to 5.8 mm diameter to mount in a Teflon rod as the disk electrode. The face perpendicular to the C-axis was used as the electrode surface of the single crystal. The dimension of a platinum ring electrode was 7.0 and 9.0 mm in the inner and outer diameter. The ring-disk electrodes were consecutively soaked in conc.HCl for 10 sec and in conc.H_3PO_4 for 5 min before use. A 500 W super high pressure mercury arc lamp was employed as a light source. The electrolytes were of doubly distilled water and reagent grade chemicals. All the measurements were conducted under nitrogen atmosphere. A sce was used as a reference electrode, and the potentials cited in this paper are referred to this electrode. In the present study, the potential of the ZnO disk electrode was fixed at 1.0 V where the saturated photocurrent was observed. The potentials of the ring electrode chosen were 0 V for I_2, 0.05 V for Br_2 and 0.2 V for Cl_2. At the potentials selected, the preferential reduction of the halogen molecules occured under a diffusion controlled process. The rotation rate of the ring-disk electrode was set at 1000 rpm.

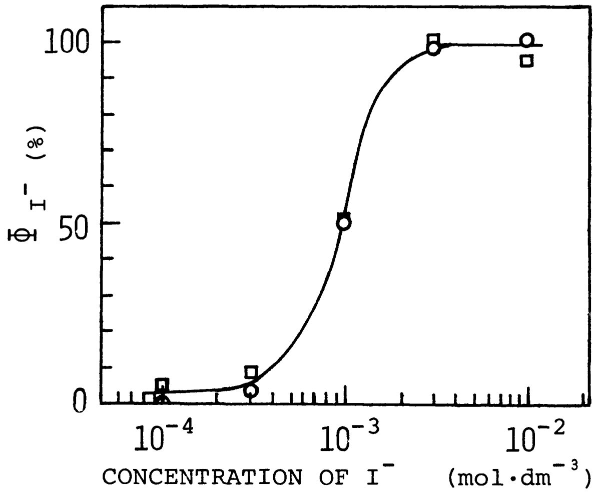

Fig. 1 The percentage of the competitive oxidation of I^- on ZnO electrodes as a function of its concentration. —○— : single crystal, —□—: sinter.

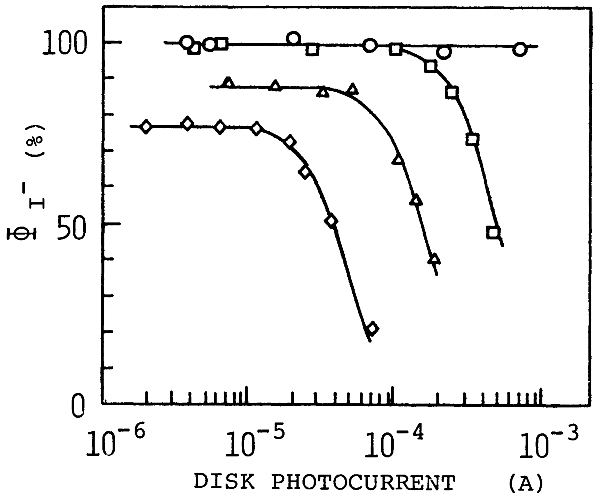

Fig. 2 The percentage of the competitive oxidation of I^- on the sinter electrode as a function of the disk photocurrent. The electrolyte concentration (mol·dm^{-3}); —○—: 10^{-2}, —□— : 10^{-3}, —△— : 3.16×10^{-4}, —◇— : 10^{-4}.

The ratio of the ring current i_R due to the reduction of I_2 to I^- to the total photoanodic current of the ZnO disk i_D, obtained under an illumination condition to give the saturated photocurrent of 4.5×10^{-4} A, was constant in the concentrations larger than 3.16×10^{-3} mol·dm^{-3}, and accorded roughly with the collection efficiency derived theoretically for a simple charge transfer reaction.[12)] The percentage of the competitive oxidation of the iodide ions Φ_{I^-} was then assumed to be 100 % in these concentrations. The same assumption was applied on evaluation of Φ in other halide solutions. Figure 1 shows Φ_{I^-} as a function of the concentration of iodide ions. The results similar to Fig. 1 were already presented for the case of Br^- solutions.[13)]

Figure 2 shows effects of the illumination intensity on Φ_{I^-}. The disk photocurrent in the abscissa is a measure of the illumination intensity. It is noted from this figure that Φ_{I^-} was constant in a region of small i_D, but decreased with an increase in the illumination intensity beyond a certain critical i_D which depended on the I^- concentration.

In the case of the oxidation of Br^-, however, a quite different behavior was observed. Figure 3 shows Φ_{Br^-} as a function of i_D for several concentrations of bromide ions. With an increase in i_D, Φ_{Br^-} increased to reach a maximum, followed by a decreasing tendency. Judging from these results, a different behavior may be expected also for the oxidation of Cl^-. According to the experimental results obtained, however, Φ_{Cl^-} was quite low even when the concentration as high as

0.1 mol·dm^{-3} was used, although there seemed to be a faint tendency of increase in Φ_{Cl^-} with i_D (see Fig. 3).

The present study revealed that the complete suppression of the anodic dissolution could be achieved in a high concentration of I^- and Br^- under certain illumination conditions, namely, under a relatively low illumination intensity for I^- and a high illumination intensity for Br^-. An other important finding obtained in this study was that there was no appreciable difference in the reactivity of halide ions Φ_{X^-} between the single crystal and the sinter electrode.

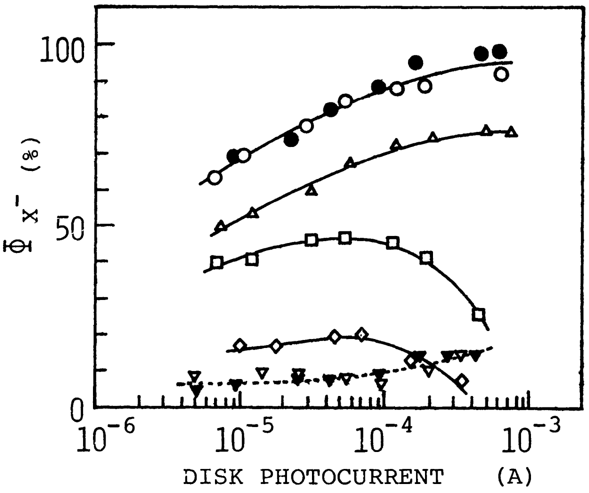

Fig. 3 The percentage of the competitive oxidation of halide ions on ZnO electrodes as a function of the disk photocurrent. Solid line: Br^-, dotted line: Cl^-. Open symbol: single crystal, closed symbol: sinter. The electrolyte concentration (mol·dm^{-3}); —○●—: 10^{-1}, —△—: 10^{-2}, —□—: 3.16×10^{-4}, —◇—: 10^{-4}, --▽--▼--: 10^{-1}.

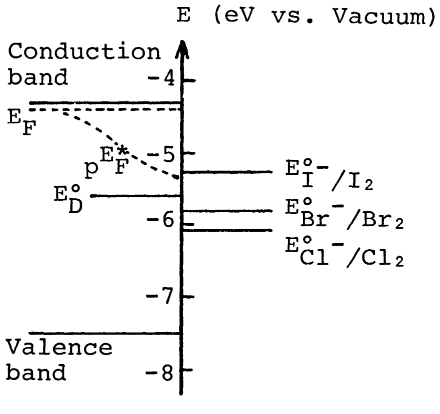

Fig. 4 Energetic correlation between ZnO electrode and redox electrolytes. E_D° and $E^\circ_{X^-/X_2}$ denote the energy levels corresponding to the decomposition potential of ZnO and the redox potentials of halide ions, respectively. -4.75 eV for the sce vs. the vacuum level.[14)]

Figure 4 shows the energy correlation of the electrode relative to the reactants in solution. On construction of the diagram, the reported value of the flat-band potential of ZnO was employed.[8)] According to the thermodynamic argument on the stability of semiconductor electrodes[5,6)] the suppression of the anodic dissolution of ZnO may be expected for I^-, but would not be so for Br^- and Cl^-, if the illumination intensity effects were not taken into consideration.

With an increase in the illumination intensity I_{photo}, the energetic position of the quasi-Fermi level of positive holes $_pE_F^*$ is lowered. The position of $_pE_F^*$ is theoretically given by eq.(3),[5)]

$$_pE_F^* = E_V - kT\ln[(p_0 + \Delta p^*)/N_V] \qquad (3)$$

where p_0 and Δp^* denote the concentration of positive holes in the dark and the increment of positive holes by illumination, respectively. E_V is the energetic position of the valence band edge, and N_V is the effective density of states in the valence band. In the case of iodide solutions, $|_pE_F^*| > |E^\circ_{I^-/I_2}|$ will be achieved at I_{photo} smaller than that required to establish $|_pE_F^*| > |E_D^\circ|$. The situation quite reverse to this holds in the bromide case. $|_pE_F^*| > |E_D^\circ|$ is achieved firstly, and at much higher i_D $|_pE_F^*| > |E^\circ_{Br^-/Br_2}|$ is established.
If an assumption is made that $|_pE_F^*| \geqq |E^\circ_{X^-/X_2}|$ is desirable for halide ions X^- to be oxidized preferentially,[5,15)] the

stabilization will be observed at a relatively small i_D or low I_{photo} in the iodide solution, but a high I_{photo} will be required in the bromide case. In the latter case, however, a possibility for the anodic decomposition of ZnO cannot be ruled out, since $|{}_pE_F^*| > |E_D^\circ|$ is also satisfied under such a condition.

Referring to the experimental results obtained in 0.1 mol·dm^{-3} Br^-, apparent stabilization was achieved at such a high I_{photo} as to give i_D larger than 2.0×10^{-4} A. In the lower concentration of Br^-, Φ_{Br^-} increased to its maximum with increasing i_D, followed by a decrease. Beyond i_D giving the maximum Φ_{Br^-}, the surface concentration of Br^- seems not enough to sustain i_D, and then Φ_{Br^-} decreases. In the ascending portion of Φ_{Br^-}, the surface concentration of Br^-, which seems to be controlled by the adsorption equilibrium as in the case at SnO_2 electrodes,$^{16)}$ must be enough, and Φ_{Br^-} is entirely controlled by the energetic relation of ${}_pE_F^*$ to $E^\circ_{Br^-/Br_2}$. In the iodide case, the adsorption equilibrium seems to govern the phenomena, too. In the region giving the constant Φ_{I^-}, the competition ratio seems to be entirely controlled by the coverage of iodide. When i_D is very small, $|{}_pE_F^*| > |E^\circ_{I^-/I_2}|$ may not be established. However, if any reaction takes place under such an illumination condition, the oxidation of iodide ions not the decomposition will occur preferentially, because $E^\circ_{I^-/I_2}$ is higher than E_D°. Beyond the critical i_D which depends on the concentration of I^-, Φ_{I^-} decreases in a manner similar to that discussed above for the bromide case.

The present results showed that 100 % inhibition of the anodic dissolution was possible in the electrolytes of I^- and Br^- under certain conditions, but this does not necessarily imply that there is no decomposition of ZnO under such conditions. There is a possibility for the oxidation products of I^- and Br^-, namely I_2 and Br_2 to decompose chemically ZnO. This problem is currently being investigated in our laboratory and will be published in an other paper.

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