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Competitive Redox Reactions at the ZnO Semiconductor Photoelectrode

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The study of the photoanodic reaction at the ZnO electrode in an electrolyte solution containing redox agents was carried out by means of the rotating ring-disk electrode technique. The competition reactions between the photocorrosion of ZnO and the oxidation of reducing agents were discussed focusing on the potentials of the electroactive species at the semiconductor-solution interface. The ZnO photoelectrode was stabilized in the course of the oxidation of a strong reducing agent dissolved in a solution.

Photo-induced redox reaction at the semiconductor-liquid junction have been extensively investigated with photoelectrolytic synthesis or solar energy conversion in mind.[1–6] The most recent interest in the electrochemical photocells has been the suppression of the photocorrosion of the semiconductor electrode itself during the operation.[7] The stabilization of the photocorrosive semiconductor electrode has been much investigated from several experimental approaches[7–18] and also discussed from the point of view of thermodynamic points.[19,20] However, the charge-transfer kinetics of a photogenerated hole-electron pair is not well understood, so the investigation of photoelectrochemical competitive oxidations at the ZnO electrode by means of the rotating ring-disk electrode (RRDE) is the subject of this work.

The photoanodic reaction of the ZnO electrode in the supporting electrolyte solution is known to consist of the photocorrosion[21–23] of the electrode *per se* by photoholes (p^+):

$$\mathrm{ZnO} + 2\,p^+ \longrightarrow \mathrm{Zn}^{2+} + 1/2\mathrm{O}_2 \qquad (1)$$

Though ZnO has a demerit as the photoelectrode in an electrochemical photocell because of its large bandgap (*ca.* 3.2 eV), the stabilization of ZnO under operation in a solution is necessary for it to be used as a semiconductor-solution photodiode. When we introduce a certain reducing agent into an electrolyte solution, the oxidation (2) of a reducing agent can occur in competition with Process 1:

$$\underset{\text{form}}{\text{reduced}} + n\,p^+ \longrightarrow \underset{\text{form}}{\text{oxidized}} \qquad (2)$$

By using the rotating ring-disk electrode with a semiconductor disk and a metal ring, one can instantaneously ascertain the competition efficiencies of Processes 1 and 2 under illumination by comparing the collection ring currents caused by the reduction of the oxidized products with the geometrical collection current.[10,17,22]

Experimental

The semiconductor electrode used in this experiment was sintered polycrystal ZnO which had been prepared by pressing the reagent-grade ZnO powder at 1.0 t/cm^2 and then heated at 1300 °C for 3 h in the air. The sintered polycrystal was shaped into a disk 6.0 mm in diameter and 1.0 mm in thickness. Indium–gallium alloy was painted onto one face of the polycrystal in order to insure an ohmic contact with the copper conducting wire. Then, the ZnO disk was mounted on a Teflon rod using epoxy resin, together with a Au ring 7.0 mm in inner diameter and 9.0 mm in outer diameter, thus producing a ring-disk electrode system. Sometimes a Au-ring electrode was also amalgamated. The polycrystal face of ZnO was polished with alumina powder, etched in 6 M (M=mol dm^{-3}) HCl for 10 s, and washed with water. The ring-disk electrode thus prepared was connected into an RRDE measurement system (Nikko Keisoku), which has been described elsewhere.[7,10,11,22,24] The light source was a 500 W high pressure mercury arc lamp, while the illuminating wavelengths was selected with a glass filter from 300 to 400 nm. The supporting electrolyte was 0.2 M Na_2SO_4, and all the redox agents used were reagent-grade.

Results

The curves of the ring current, I_R, *vs.* the ring potential, E_R, where the disk photocurrents are constant at the disk potential of 1.0 V *vs.* SCE, are shown in Fig. 1.

Photogenerated carriers (holes) produced by the illumination of the absorbable light, whose energy is greater than a bandgap (3.2 eV) of ZnO, are forced to the surface by the electric field in a space charge layer and then oxidize the electroactive species at the interface. The collection current at the ring electrode caused by the discharge of the oxidized product which flows from the disk electrode gives information about the photoassisted oxidation, the photocorrosion of ZnO, and the oxidation of reducing agents. Cathodic currents which appear at the Au ring electrode in the solution without reducing agents indicate the reduction of the oxygen produced by the photocorrosion process (1). In the presence of a reducing agent in an electrolyte solution, a two-step cathodic current appears at the Au ring electrode, where the first wave of the cathodic current depends on the reduction of an oxidized redox agent produced by Process 2, while the second wave depends on the reduction of the oxygen produced by Process 1. Therefore, we can calculate the competition ratios[6,24] between Processes 1 and 2 from the height of the reduction current at the Au ring electrode.

Figure 2 shows the relation curves of the competitive oxidation ratios of various reducing agents *versus* their concentrations. The competition ratio increases in general with an increase in the concentration of a redox agent, while its value is different for different kinds of reducing agents. When a redox agent is present in a high concentration (*ca.* 1.0 M) in the solution, it is nearly 100%, oxidized by photogenerated holes, while the ZnO photoelectrode is stabilized against

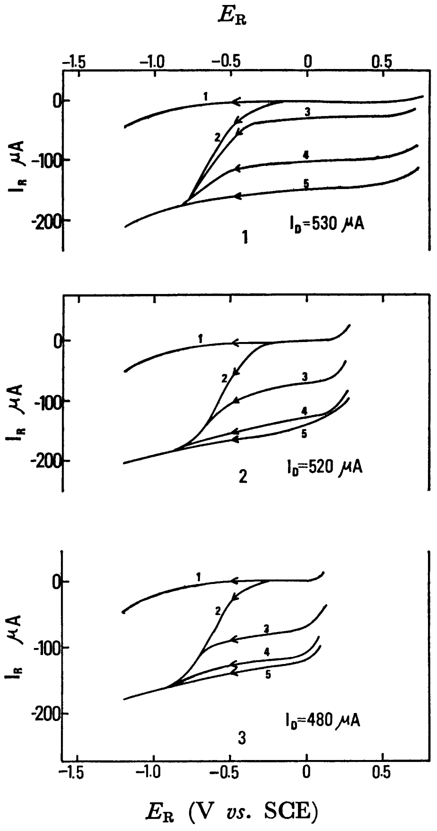


Fig. 1. Current-potential (I_R-E_R) curves at the Au ring electrode at the rotational speed of 1000 rpm with reducing agents in the electrolyte solution. Potential of the ZnO disk electrode was 1.0 V *vs.* SCE. (1) In addition of Br^-, (2) in addition of I^-, (3) in addition of $Fe(CN)_6^{4-}$: 1, in dark with and without reducing agents (red.); 2, in a supporting electrolyte solution; 3, in addition of 10^{-3} M red.; 4, in addition of 10^{-2} M red.; 5, in addition of 10^{-1} M red.; 2—5, under illumination.

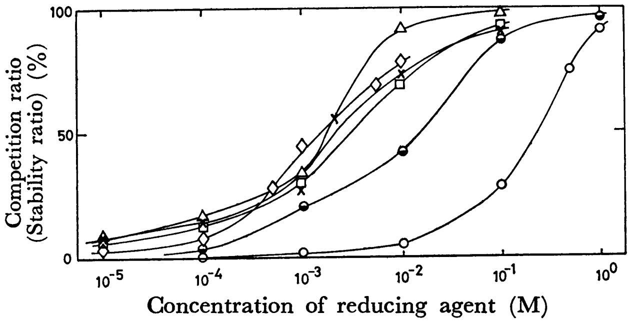


Fig. 2. Concentration dependences of competition ratios for various reducing agents.
×, $S_2O_3^{2-}$; □, SO_3^{2-}; ◇, $Fe(CN)_6^{4-}$; △, I^-; ◒, Br^-; ○, Cl^-.

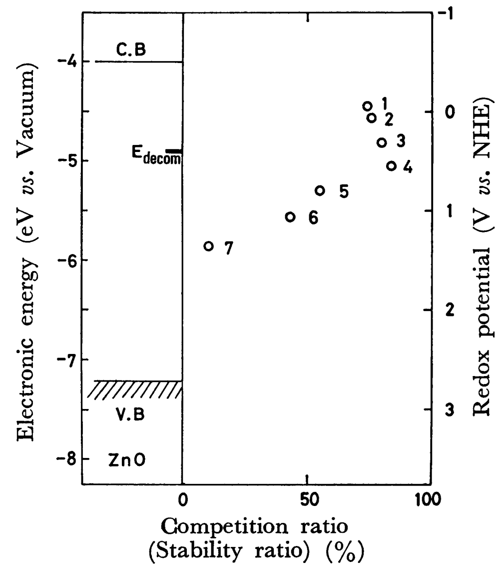


Fig. 3. Competition ratios (stability ratios) of various reducing agents (0.01 M) as a function of their redox potentials. E_{decom} denotes the oxidative decomposing potential of ZnO, C. B. the conduction band, V. B. the valence band of ZnO, respectively.
1, $S_2O_3^{2-}$; 2, SO_3^{2-}; 3, $Fe(CN)_6^{4-}$; 4, I^-; 5, Fe^{2+}; 6, Br^-; 7, Cl^-.

the photocorrosion process (1).

Figure 3 shows the competitive oxidation ratios (stability ratios) of a variety of reducing agents (10^{-2} M) as a function of their redox potentials. The results indicate that the reducing agent with a more negative redox potential has a larger competition ratio and can better stabilize the photoelectrocorrosive ZnO electrode.[9]

Discussion

For charge transfer across the semiconductor-solution junction, the statistical equations have been established by several investigators.[26] The photocurrent at the illuminated n-type semiconductor electrode is determined by the overlap of the relative distributions of states in the valence band holes and of the reducing agents in the electrolyte solution; that is,

$$I_{ox} = k^\circ [\mathrm{Red}] \int_{-\infty}^{0} K^\circ(\mathrm{E}) D_+(\mathrm{E}) W_R(\mathrm{E}) \mathrm{d}E \qquad (3)$$

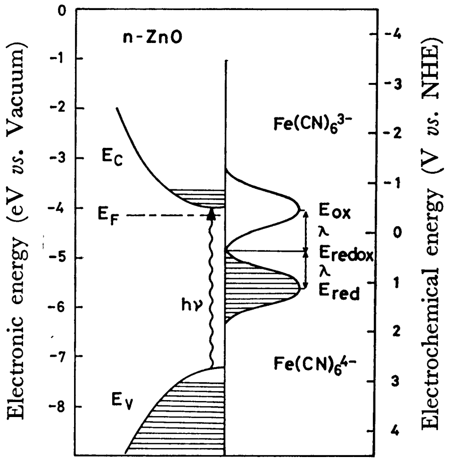
where I_{ox} is the anodic photocurrent, [Red] is the concentration of a reducing agent in a solution, $D_+(\mathrm{E})$ is the density of photogenerated holes in a semiconductor, and $W_R(\mathrm{E})$ is the distribution function of a reducing agent. Figure 4 shows the schematic distributions between the states of the ZnO electrode and a redox agent ($Fe(CN)_6^{3-/4-}$) in the solution. The distribution functions (W_{ox}, W_{red}) of this redox couple are given by;

$$W_{red} = \exp\,[-\lambda(E - E^\circ_{F,el} + \lambda)^2/4\mathrm{d}T]$$

$$W_{ox} = \exp\,[-(E - E^\circ_{F,el} - \lambda)^2/4kT\lambda]$$

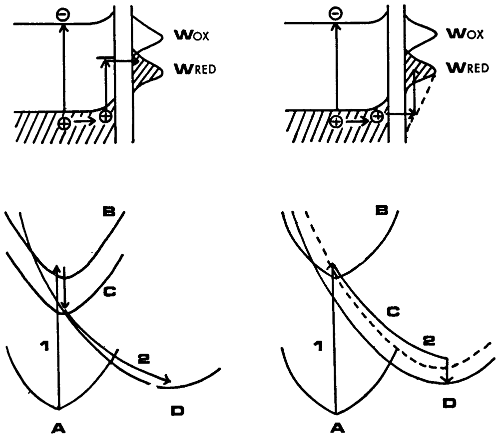
where λ denotes a reorganization energy (*ca.* 0.75 eV[27,28]), $E^\circ_{F,el}$ denotes the Fermi level of the electrolytes, and E denotes the energy level. It can be expected from the mapping between $D_+(\mathrm{E})$ and $W_{red}(\mathrm{E})$ that it will be difficult for $Fe(CN)_6^{4-}$ to be oxidized by the photogenerated holes in the valence band, whereas $Fe(CN)_6^{3-}$ will be reduced by the electrons in the conduction band. However, $Fe(CN)_6^{4-}$ is actually oxidized well by the photogenerated holes at the ZnO photoelectrode, as is shown in Fig. 3.

Therefore, for the elucidation of the photo-hole



Energy distribution

Fig. 4. Schematic illustration of the energy distributions between ZnO and a redox agent ($Fe(CN)_6{}^{3-/4-}$) in the solution.



(A) charge transfer via surface state
(B) direct charge transfer

Fig. 5. Schematic explanation for charge transfer kinetics, upper illustration for hole transfer and lower one for reaction coodinations. (A) Charge transfer via surface state, (B) direct charge transfer. A, initial state; B, photoexcited state; C, intermediate state; D, final state. 1, Photoexciting process; 2, relaxation process.

transfer across the semiconductor-solution interface, the following two schemes are considered to be probable. One process is the charge transfer *via* surface states within a bandgap, when the overlap between distributions of surface states and of reducing species is necessary. For the explanation of this scheme, some investigators have reported that positively charged holes could transfer to reducing species *via* the surface states at the ZnO photoelectrode.[29,30] Another process is the direct transfer of a positively charged hole to the excited states of reducing species, when the distribution of reducing species becomes an unsymmetrical one. Figure 5 presents schematic representations of the above two processes. However, from this experiment it is hard to decide which process is more acceptable.

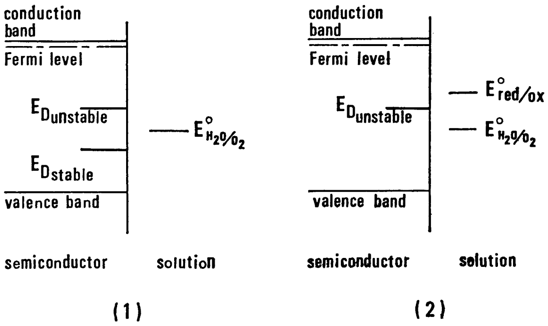


Fig. 6. Enegetic elucidation for stability of photoelectrodes in the course of redox reactions at the interface. E_D denotes the decomposition potential of a semiconductor electrode *per se*.
(1) Stable or unstable case of semiconductor photoelectrodes *versus* photoelectrolytic oxidation of water.
(2) Stabilized case of an unstable photoelectrode in the course of photoelectrolytic oxidation of reducing agents.

As for the stability of the photoelectrodes, the guidance has been presented from the point of view of thermodynamics[19,20] and on the basis of the experimental results,[10,31] focusing upon the redox reactivities of electroactive species at the semiconductor-solution interface. The stability of an n-type semiconductor photoelectrode in a supporting electrolyte solution is determined by the potentials of the competitive oxidations between the photocorrosion of a semiconductor and the oxidation of water, as schematically shown in Fig. 6. From this consideration, while TiO_2 is a stable photoelectrode because this oxidative decomposition potential is more positive than the oxidation potential of water, the ZnO photoelectrode becomes a stable photoanode in the course of the competitive oxidation of dissolved reducing agents whose redox potentials are more negative than the decomposing potential of ZnO.

Conclusion

Many semiconductor electrodes cause photocorrosion by means of an action of photogenerated carriers when they are illuminated in water. However, once a photocorrosive semiconductor electrode is stabilized, a new way of its use may be developed, for example, as photosensitive devices,[32] including the photoelectrode in the electrochemical photocell.

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