

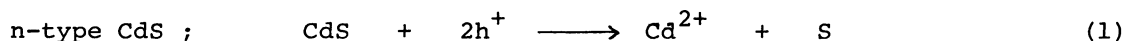
STABILIZATION OF PHOTOANODES IN ELECTROCHEMICAL PHOTOCELLS  
FOR SOLAR ENERGY CONVERSION

Akira FUJISHIMA, Tooru INOUE, Tadashi WATANABE, and Kenichi HONDA

Department of Synthetic Chemistry, Faculty of Engineering,  
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The stabilization of the semiconductor photoanodes by redox agents have been studied in the semiconductor/electrolyte system. A general interpretation of the experimental results is possible referring to the standard redox potentials ( $E_{\text{redox}}$ ) of the reducing agents and to the electrochemical decomposition potentials ( $E_D$ ) of the semiconductors.

There has been much recent interest in the application of n-type semiconductor electrodes to electrochemical photocells (EPC) for the solar energy conversion.<sup>1)</sup> For the construction of an EPC capable of efficient solar energy conversion, several important criteria must be met. First, the semiconductor material should have a band gap energy ( $E_g$ ) small enough to utilize the solar spectrum sufficiently. According to a model calculation,<sup>2)</sup> the ideal  $E_g$  values are 1.4 eV for solar to electrical energy conversion and 2.0 eV for photoelectrolysis of water. Second, semiconductor electrodes must be sufficiently stable against photoanodic reactions. Stable semiconductor photoanodes such as  $\text{TiO}_2$  have a wider band gap ( $\sim 3.0$  eV) resulting in a smaller fraction of the solar spectrum utilized. However, many semiconductors with small band gaps decompose through the photoanodic dissolution, for example,



where  $\text{h}^+$  denotes the positive hole.

We have previously reported the competitive photoanodic oxidation at  $\text{CdS}$ <sup>3)</sup> and  $\text{TiO}_2$ <sup>4)</sup> electrodes in the electrolyte containing various reducing agents. The CdS photoanode can be stabilized through the competitive oxidation (2) of reducing agents against the dissolution of the CdS photoanode.

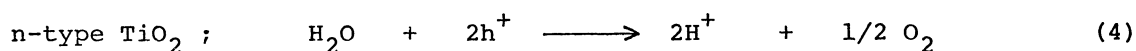
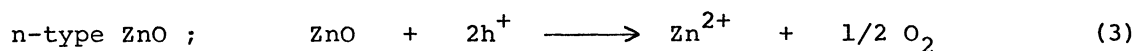


Wrighton et al.<sup>5)</sup> and Minoura et al.<sup>6)</sup> have also reported the stabilization of the CdS photoanode by the calcogenide/polycalcogenide ion system.

In this paper, we investigated the competitive photoanodic oxidation at three n-type semiconductor electrodes (CdS, ZnO and TiO<sub>2</sub>) by means of the rotating ring-disk electrode (RRDE) technique facilitating an *in situ* determination of the competitive oxidation ratio between process (1) and (2). The energetics of the stabilization of photoanodes in the semiconductor/electrolyte system are generally discussed.

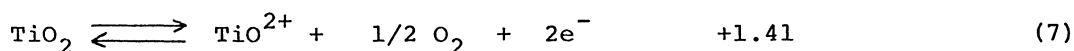
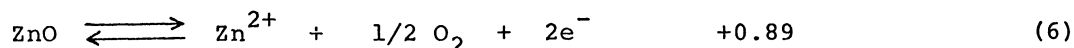
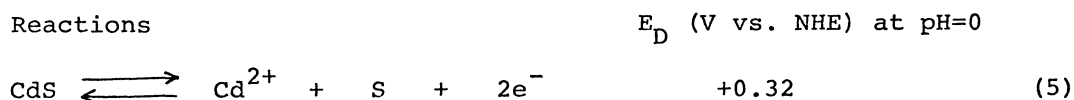
Semiconductors employed in the present study were an n-type CdS single crystal, an n-type TiO<sub>2</sub> single crystal and an n-type ZnO polycrystal. The semiconductor crystals were shaped into disks 6.0 mm in diameter and 1.0 mm in thickness. Ring electrodes were Pt, Au, Cu(Hg) and Au(Hg) 7.0 mm in inner diameter and 9.0 mm in outer diameter. The method of ring-disk electrode preparation and of establishment of an ohmic contact, and the RRDE measurement apparatus were the same as those used in the previous study.<sup>3)</sup> The light source was a 500 W high pressure mercury arc lamp and the wavelength range from 300 to 410 nm was used for illumination. All reducing agents used in this experiments were of a reagent grade. The rotation speed of the RRDE was set at 1000 rpm. The solutions were deaerated with highly purified nitrogen in all experiments.

Anodic photocurrents appear by the action of photo-generated holes at the n-type semiconductor electrodes under the polarization more positive than the flat-band potential ( $E_{f.b.}$ ). It was verified through quantitative measurements of the products of photoanode reactions that anodic photocurrents at CdS, ZnO and TiO<sub>2</sub> photoanodes originated from the process (1) and the following processes, respectively;



Ratios of competitive oxidations between (1) and (2), (3) and (2), and (4) and (2) were determined by the procedure established in previous studies.<sup>3,4)</sup>

Figures 1 to 3 show the dependence of the competitive oxidation ratios of the reducing agents on their redox potentials ( $E_{\text{redox}}$ ), in comparison with the energy diagrams of semiconductor electrodes. Here,  $E_D$  shows the decomposition potential of the semiconductor derived from thermodynamic data based on the following electrochemical decomposition processes.<sup>8)</sup>



In the cases of CdS (Fig. 1) and ZnO (Fig. 2) photoanodes, one can see that the competition ratio of a reducing agent becomes greater for a reducing agent with a more negative redox potential. The competition ratio is nearly saturated at a potential above the decomposition potential,  $E_D$ , of each semiconductor. This may reflect the fact that the main reaction of the photoanodic process in the supporting electrolyte solution is the dissolution of the electrode itself for these two semiconductors. The present results clearly suggest that the efficiency of dissolution suppression by a reducing agent is mainly controlled by the correlation between  $E_D$  for the electrode and  $E_{\text{redox}}$  for the reducing agent. Such a conclusion has been recently reported by Gerischer<sup>9)</sup> and Bard and Wrighton<sup>8)</sup> based on a thermodynamic reasoning.

In the case of the  $\text{TiO}_2$  photoanode, the result of the competitive oxidation differs from those obtained in the cases of CdS and ZnO photoanodes, because  $\text{TiO}_2$  is a so-called stable electrode. Figure 3 shows the energetics of the competitive oxidation between processes (2) and (4). In an aqueous solution (pH=1.0), the oxidation potential (ca. 1.17 V vs. NHE; indicated by a dashed line) of water is

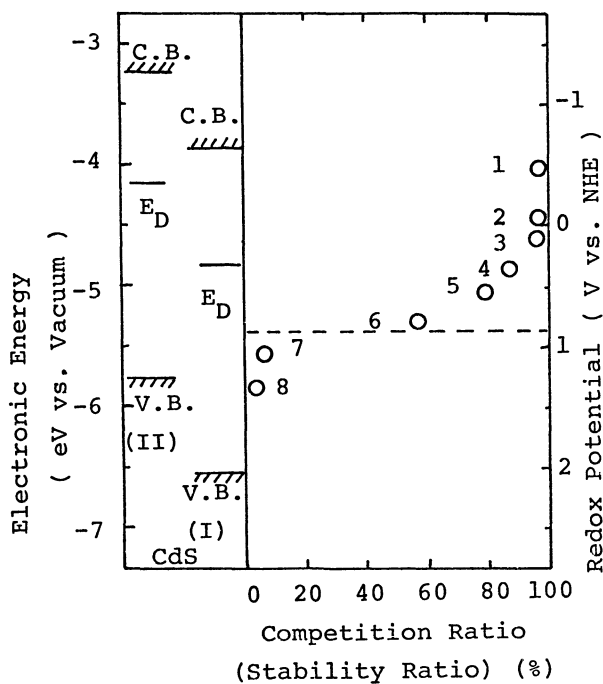


Fig. 1 Correlation between the energy diagram of CdS and dependence of competition ratio on redox potentials of reducing agents (0.01 M) at pH=6.0. (I); without  $\text{S}^{2-}$  (II); with 0.01 M  $\text{S}^{2-}$ . 1;  $\text{S}^{2-}/\text{S}$ , 2;  $\text{S}_2\text{O}_3^{2-}/\text{S}_4\text{O}_6^{2-}$ , 3;  $\text{SO}_3^{2-}/\text{S}_2\text{O}_6^{2-}$ , 4;  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ , 5;  $\text{I}^-/\text{I}_2$ , 6;  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , 7;  $\text{Br}^-/\text{Br}_2$ , 8;  $\text{Cl}^-/\text{Cl}_2$ . ----- ; oxidation potential of water

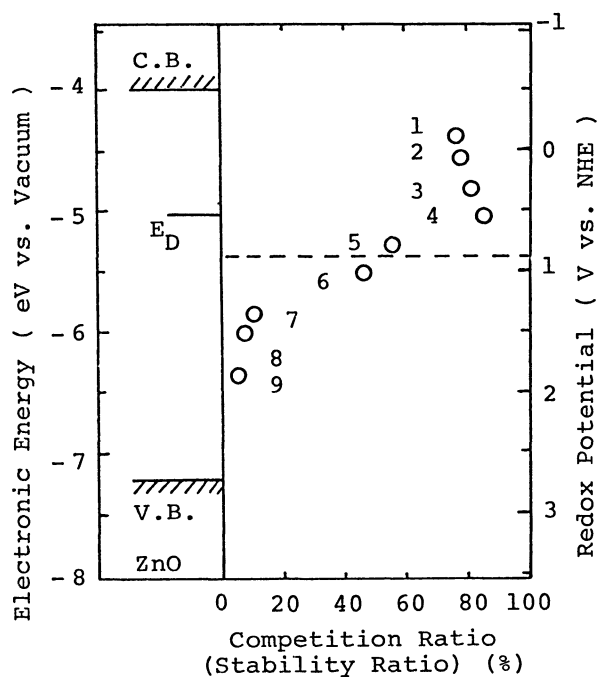


Fig. 2 Correlation between the energy diagram of ZnO and the dependence of competition ratio on redox potentials of reducing agents (0.01 M) at pH=6.0. 1;  $\text{S}_2\text{O}_3^{2-}/\text{S}_4\text{O}_6^{2-}$ , 2;  $\text{SO}_3^{2-}/\text{S}_2\text{O}_6^{2-}$ , 3;  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ , 4;  $\text{I}^-/\text{I}_2$ , 5;  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , 6;  $\text{Br}^-/\text{Br}_2$ , 7;  $\text{Cl}^-/\text{Cl}_2$ , 8;  $\text{Mn}^{2+}/\text{Mn}^{3+}$ , 9;  $\text{Co}^{2+}/\text{Co}^{3+}$ . ----- ; oxidation potential of water

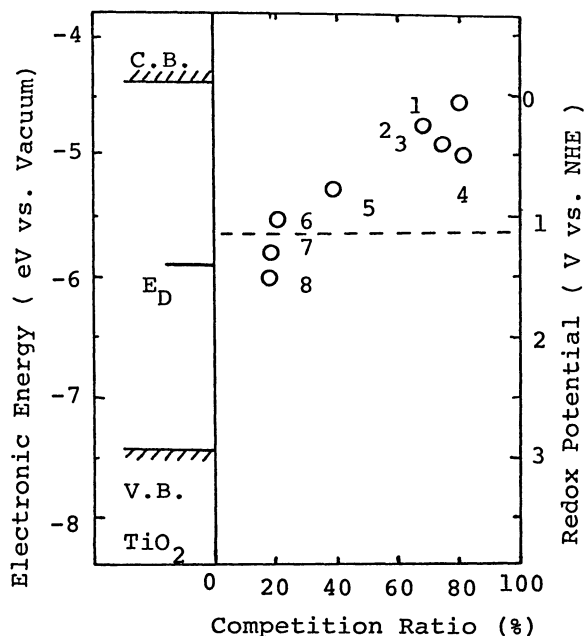


Fig. 3 Correlation between the energy diagram of  $\text{TiO}_2$  and the dependence of competition ratio on redox potentials of reducing agents (0.01 M) at  $\text{pH}=1.0$ . 1;  $\text{SO}_3^{2-}/\text{S}_2\text{O}_6^{2-}$ , 2;  $\text{Fe}(\text{CN})_6^{4-}/3-$ , 3;  $\text{I}^-/\text{I}_2$ , 4;  $\text{H}_2\text{Q}/\text{Q}$ , 5;  $\text{Fe}^{2+}/3+$ , 6;  $\text{Br}^-/\text{Br}_2$ , 7;  $\text{Cl}^-/\text{Cl}_2$ , 8;  $\text{Mn}^{2+}/3+$ . ----- ; oxidation potential of water

more negative than  $E_D$  (ca. 1.35 V vs. NHE) of the  $\text{TiO}_2$  electrode. Therefore, the oxidation of water majority (55 M) in solution precedes the photoanodic decomposition of  $\text{TiO}_2$ , which may be the reason why  $\text{TiO}_2$  is a stable electrode. The most positive redox potential where the competition ratio of reducing agents is saturated in Fig. 3 is rather negative than  $E_D$  of  $\text{TiO}_2$  and the oxidation potential of water, compared with the cases for  $\text{CdS}$  and  $\text{ZnO}$  photoanodes. This discrepancy of the potential can be recognized from the concentration dependence<sup>4,10</sup> of the reducing agent on the competitive oxidation that occurs between the oxidation of water (55M) and that of reducing agents (0.01M).

Consequently, we can conclude that the precedence of the competitive oxidation at a photoanode depends upon the redox potential of the electrochemically active species at the interphase. So, a suitable combination of a semiconductor material and a redox agent can promise the stabilization of the EPC's photoelectrode and the more effective utilization of the solar spectrum.

#### References

- 1) A. Fujishima and K. Honda, *Nature*, **23** (1972).
- 2) H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **80** 1046 (1976).
- 3) T. Inoue, T. Watanabe, A. Fujishima, K. Honda, and K. Kohayakawa, *J. Electrochem. Soc.*, **124** 719 (1977).
- 4) T. Inoue, T. Watanabe, A. Fujishima, and K. Honda, *Chem. Lett.*, 1073 (1977).
- 5) A. B. Ellis, S. W. Kaiser, J. M. Bolts, and M. S. Wrighton, *J. Am. Chem. Soc.*, **99** 2839 (1977).
- 6) H. Minoura, M. Tsuiki, and T. Oki, *Ber. Bunsenges. Phys. Chem.*, **81** 588 (1977).
- 7) A. Fujishima and K. Honda, *Seisan Kenkyu*, **22** 524 (1970).
- 8) A. J. Bard and M. S. Wrighton, *J. Electrochem. Soc.*, **124** 1706 (1977).
- 9) H. Gerischer, *J. Electroanal. Chem.*, **82** 133 (1977).
- 10) T. Inoue, T. Watanabe, A. Fujishima, and K. Honda, in "Semiconductor-Liquid Junction Solar Cells: Proceedings of a Conference on the Electrochemistry and Physics of Semiconductor-Liquid Interfaces under Illumination", 77-3, ed. by A. Heller, *Electrochem. Soc., Princeton* (1977), pp. 210-221.

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