# Photosensitized Electrolytic Oxidation of Iodide Ions on Cadmium Sulfide Single Crystal Electrode[1]

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The semiconductor electrode reactions have been studied by a number of research workers[2]; they exhibit interesting behavior different from that of metal electrodes. The present authors[3] have studied mainly the effect of the irradiation with light on the semiconductor electrode reactions and have learned that the oxidation reactions, such as oxygen evolution from water or the oxidation of halogen ions, occur at more negative potentials than the standard oxidation potential on a $TiO_2$ or ZnO single crystal electrode.[4]

The behavior of the CdS semiconductor electrode, which has a band gap of 2.4 eV, has been reported only by Williams,[5] who especially studied the mechanism of its photo-voltaic effect.

In the present paper, it is concluded that the photosensitized electrolytic oxidation does occur on the CdS electrode in the same way as on the $TiO_2$ and ZnO electrodes. It will also be reported that the mechanism of this photosensitized electrolytic reaction can be determined by using the method of a rotating ring-disk electrode, in which the disk electrode consists of a cadmium sulfide single crystal and the ring electrode gold or amalgamated gold.

The anodic current of the CdS electrode does not flow in the dark, but under irradiation it flows in proportion to the intensity of light at potentials more positive than $-0.68$ V (*vs.* SCE) and depends on the wavelength of light (the greatest anodic current is found to flow at 520 m$\mu$, *i. e.*, 2.4 eV). The anodic reaction is related to the holes formed by the irradiation in the valence band and is rate-controlled by the supply of the holes to the surface of the electrode.

When the anodic reaction occurs on the CdS disk electrode, the reduction current on the ring amalgamated electrode is found to begin to flow from $-0.6$ V towards the negative potential and then to appear in the limiting reduction current region. The half-wave potential of this reduction corresponds to the reduction of $Cd^{2+}$ to Cd. The ratio of the disk electrode current to the ring electrode current nearly agrees with the calculated collection efficiency. After the anodic disk current flows for several minutes, the surface of CdS is observed to become white-yellow because of some adhered substance, which is found to be sulfur from its high solubility into $CS_2$. These facts indicate that the anodic reaction of the CdS electrode under irradiation is the anodic dissolution of the electrode, as expressed by the following reaction (1):

$$CdS + 2p^+ \rightarrow Cd^{2+} + S. \qquad (1)$$

When the electrolyte solution contains iodide ions, the apparent anodic behavior is similar to that in the electrolyte not containing iodide ions from the viewpoint of the current-voltage curves of the CdS electrode. However, the anodic current can be attributed to the oxidation of iodide ions:

$$2I^- + 2p^+ \rightarrow I_2 \qquad (2)$$

as revealed from the behavior of the ring electrode, which shows an increase of the reduction current at a more negative potential than 0.3 V, indicating the formation of iodine on the CdS surface. In this case, the change of the CdS surface can scarcely be detected after the anodic oxidation.

The fact that the starting potential of the oxidation of iodide ions is $-0.68$ V, which is much more negative than its reversible potential, indicates that photosensitized electrolytic oxidation occurs even on CdS.

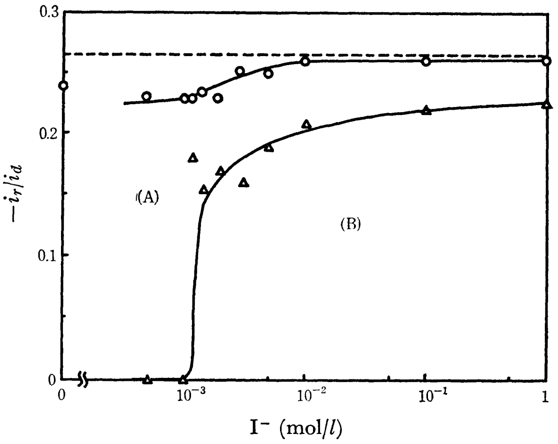

Fig. 1. Competition between dissolution of CdS and oxidation of iodide ions against the concentration of iodide ions.

Potential of the disk electrode ($V_d$): 1.0 V

△: Potential of the ring electrode, $-0.40$ V, at which iodine can be detected.

○: Potential of the ring electrode, $-1.00$ V, at which both iodine and cadmium ions can be detected.

In Fig. 1, the ratio of the current of the amalgamated ring electrode to the disk current against the concentration of iodide ions is shown. The collection efficiency of this electrode is calculated to be 0.265 from the geometric dimensions of the electrode. When the concentration of iodide ions is lower than $10^{-3}$ mol/$l$, the dissolution of CdS occurs ((A) in Fig.1); on the other hand, when it is higher than $10^{-3}$ mol/$l$, the oxidation of iodide ions occurs in competition with the dissolution of CdS ((B)). The degree of the competition between the reaction (1) and (2) may depend on the amount of iodide ions adsorbed on the CdS surface.

The results will be reported in detail in due course.

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[1] Studies on Photosensitive Electrode Reactions. IV.

[2] For example, H. Gerischer, *J. Electrochem. Soc.*, **113**, 1174 (1966).

[3] A. Fujishima, K. Honda, and S. Kikuchi, *Kogyo Kagaku Zasshi*, **72**, 108 (1969).

[4] This behavior has previously been termed "photosensitized electrolytic oxidation" by the present authors.[3]

[5] R. Williams, *J. Chem. Phys.*, **32**, 1505 (1960).