

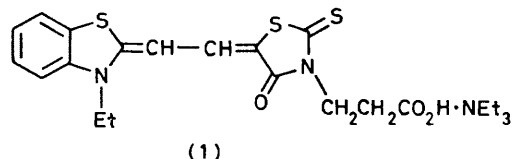
## Photoassociated Electrolytic Reduction of Water at an $\text{In}_2\text{O}_3$ Optically Transparent Electrode coated with Merocyanine Dye

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**Summary** The electrochemical photolysis of water at an  $\text{In}_2\text{O}_3$  electrode coated with merocyanine dye was found to require an applied voltage; at  $<1.23$  V hydrogen was evolved.

THE light-induced evolution of  $\text{H}_2$  at a pigmented semiconductor electrode is currently one of the most active research topics in electrochemistry; the results may be of practical importance in utilizing visible light as a photofuel. Recently, merocyanine solar cells (or photodiodes) with high sunlight efficiencies have been developed.<sup>1,2</sup> We report here the attempted photoelectrochemical reduction of water by visible light at an  $\text{In}_2\text{O}_3$  optically transparent electrode (o.t.e.) covered with a thin-layer of the merocyanine dye (1).



The dye solution in  $\text{CHCl}_3$  (2 ml; 1 mM) was sprayed on the o.t.e. ( $3.3 \times 5.0 \text{ cm}^2$ ) to produce a homogeneous layer which contained  $0.12 \mu\text{mol cm}^{-2}$  of the dye. The freshly prepared electrode was then mounted as a window of the photoelectrochemical cell (volume 100 ml) to give  $4 \text{ cm}^2$  as the available area for electrolysis. A platinum plate ( $4 \times 4 \text{ cm}^2$ ) was used as the anode and an aqueous solution of 0.1 M  $\text{HNO}_3$  and 0.4 M  $\text{KNO}_3$  was used as the electrolyte. Oxygen

was expelled from the solution by bubbling argon through it, and the temperature was kept at  $25 \pm 1^\circ \text{C}$ . A 500 W xenon arc lamp with a Y-48 filter was employed as the light source on the cathode from the o.t.e. side. Measurements were made using a method similar to that used by Miyasaka *et al.*<sup>3</sup>

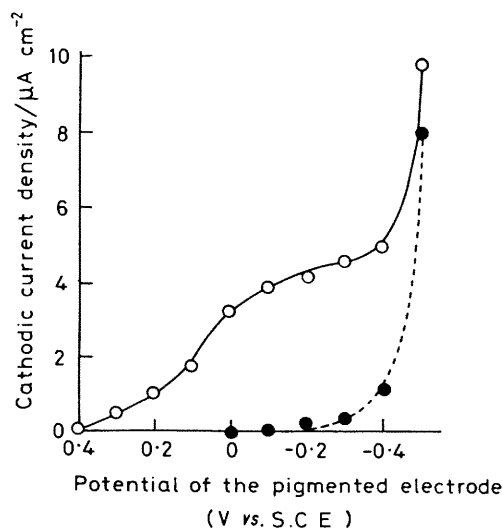


FIGURE. Cathodic current densities at the  $\text{In}_2\text{O}_3$  optically transparent electrode coated with merocyanine dye at various potentials in the dark (dashed line) and under irradiation (solid line).

The onset potential for hydrogen generation in the dark was *ca.*  $-0.35$  V [*vs.* S.C.E. (saturated calomel electrode)] as estimated from the current-potential curve shown in the Figure. Irradiation on the cathode induced a marked shift of the onset potential in a more positive direction and an apparent increment in the cathodic current (Figure). In addition, the cell voltage for the electrolysis of water under galvanostatic conditions drastically decreased with irradiation. By exposing the cathode to light, the cell voltage for

the electrolysis of water could be lowered from the thermodynamic value ( $1.23$  V) to  $0.77$  V at a current density of  $1 \mu\text{A}/\text{cm}^2$  (see the Table). The electrolysis was maintained for 7 h at a constant current density of  $2 \mu\text{A}/\text{cm}^2$ . The liberation of small bubbles of gas at the pigmented electrode could be seen during the electrolysis.  $0.02$  ml of this gas was collected and g.l.c. analysis† showed that it was hydrogen. During the 7 h of the electrolysis, the cell voltage did not change from the initial value ( $0.98$  V). It was found that the photocurrent spectrum at the pigmented electrode under potentiostatic conditions ( $0$  mV *vs.* S.C.E.) coincided fairly well with the absorption spectrum of the electrode. In addition, after the photoelectrochemical experiments, the chemical stability of the dye was examined by t.l.c.<sup>4</sup> and it was confirmed that it had not formed any degradation products.

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TABLE. Cell voltages for the electrolysis of water at various current densities

| Current density/<br>$\mu\text{A cm}^{-2}$ | Cell voltage/V |             |
|---|----------------|-------------|
|   | Dark           | Irradiation |
| 1   | 1.26           | 0.77        |
| 2   | 1.48           | 0.98        |
| 3   | 1.50           | 1.04        |
| 4   | 1.53           | 1.24        |

† G.l.c. conditions: Molecular sieves, 13X; column length, 150 cm; carrier gas, argon; temperature  $40^\circ\text{C}$ ; flow rate of carrier gas  $80 \text{ ml min}^{-1}$ ; retention time of hydrogen as a reference, 20 s.

<sup>1</sup> A. K. Ghosh and T. Feng, *J. Appl. Phys.*, 1978, **49**, 5982.

<sup>2</sup> K. Iriyama, M. Shiraki, K. Tsuda, A. Okada, M. Sugi, S. Iizima, K. Kudo, S. Shiokawa, T. Moriizumi, and T. Yasuda, *Suppl. Jap. J. Appl. Phys.*, in the press.

<sup>3</sup> T. Miyasaka, T. Watanabe, A. Fujishima, and K. Honda, *J. Am. Chem. Soc.*, 1978, **100**, 6657.

<sup>4</sup> M. Yoshiura and K. Iriyama, manuscript in preparation.