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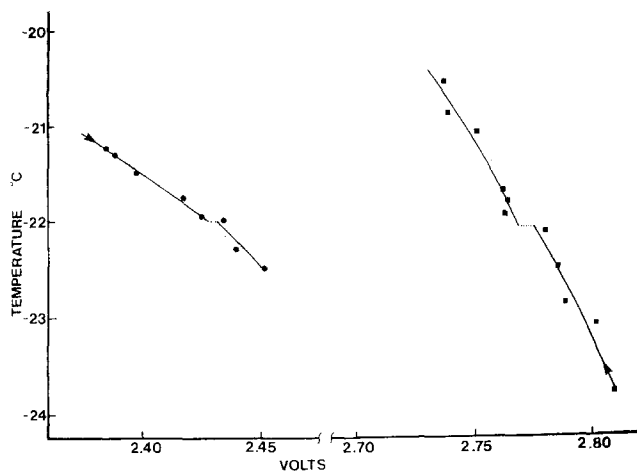


Fig. 3. A plot of the potential required to charge the cell at 10.00 mA cm^{-2} at temperatures between -20° and -24°C .

of electrode surface that tended to behave differently (with and without gas evolution and with and without concentration gradients) were smaller tending to have linear dimensions less than 1 mm.

The electrodes from the automotive battery showed a distinct change in impressed voltage required to

charge at a constant current density of 10.00 mA cm^{-2} at -22°C as the temperature was raised or lowered. Figure 3 shows that the slope of the cooling run ($\partial V/\partial T$) is greater than the warming run, but each shows an abrupt change of about 10 mV at -22°C . Valeriotte (4) has suggested this is freezing of the liquid in the pores of the heterogeneous $\text{PbSO}_4\text{-PbO}_2$ layer at the anode.

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The Stability of Photoelectrodes

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The stability of a semiconductor electrode under illumination is one of the key points in the prospect for the photoelectrochemical production of hydrogen.

Recently, Harris *et al.* (1) reported that TiO_2 single crystals were not stable and the photocurrents decreased with time in all cases they examined. Similar results were reported by Wrighton *et al.*, although they found no sign of decomposition of TiO_2 (2). Also, Yoneyama *et al.* (3) found that p-GaP was not stable under illumination, although they mentioned that there could be a possibility of obtaining a stable condition by choosing a suitable electrolyte, etc.

The stability of a TiO_2 single crystal cut perpendicularly to the c axis [(001) face] obtained from Nakazumi Crystal Corporation and of a p-type GaP wafer [Zn doped, (111) face] donated by Dr. K. Akita of the Fujitsu Laboratory Limited was examined in 1N NaOH solution.

The TiO_2 single crystal was reduced in a hydrogen atmosphere at 800°C for 5 hr (4). An ohmic contact to TiO_2 was obtained by means of indium (5) and a copper wire was soldered onto the indium. The specific resistance of the crystal was $2.0 \Omega \cdot \text{cm}$.

A p-type GaP was etched in $\text{HNO}_3\text{-HCl}$ (2:1) mixture (6) and an ohmic contact was made by means of Zn-In alloy (3). The specific resistance was $1.3 \Omega \cdot \text{cm}$.

The semiconductor electrodes were mounted in a Teflon electrode holder with an epoxy resin so that only the faces to be examined were exposed to the solution. The electrode area was 0.125 cm^2 . A 900W Xe lamp (Canrad-Hanovia 538 C1) was used as a light source and an infrared absorbing filter (Oriol G-776-7100) was placed between the light source and the electrochemical cell. A PAR 173 potentiostat was employed to maintain the electrodes at given potential.

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Key words: photoelectrode, titanium dioxide, gallium phosphide, semiconductor electrode.

The results are shown in Fig. 1 for TiO_2 and in Fig. 2 for p-GaP.

Although Harris *et al.* (1) mentioned that the photocurrent of TiO_2 decreased in all cases studied by them and Wrighton *et al.* (2) reported the fall of the photocurrents with time but without details, the photocurrents in our work did not change detectably over 1000 min (Fig. 1).

Also, the photocurrent of p-GaP decreased only slightly with time (Fig. 2). This behavior is different from that reported by Yoneyama *et al.* (3).

These results suggest that the stability of the photocurrent at semiconductors depends upon the preparation, dopant, and pretreatment of the semiconductor

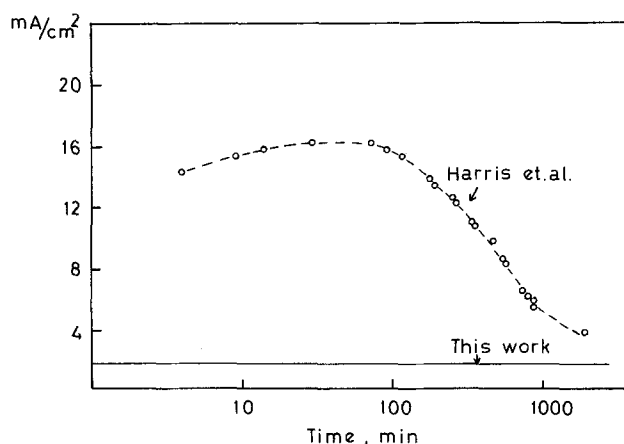


Fig. 1. The photocurrents as a function of time on TiO_2 for the work of Harris *et al.* compared with that of the present work. Potential used by Harris *et al.* at $\text{pH} = 0$ was 2.24V (NHE). Potential used by us at $\text{pH} = 14$ was 1.2V (NHE).

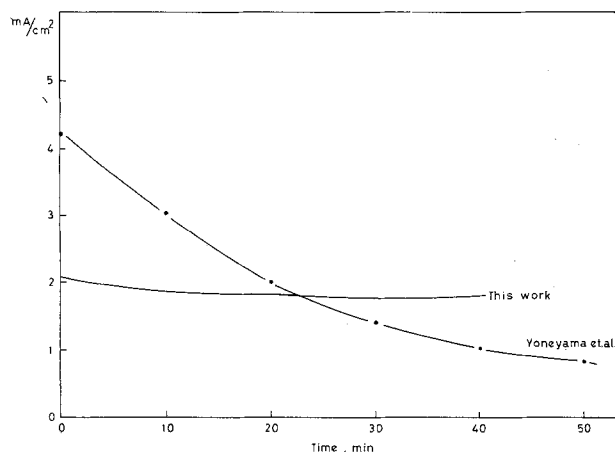


Fig. 2. The photocurrent as a function of time on Zn-doped GaP from the work of Yoneyama *et al.* and that of the present work. Potential used by Yoneyama *et al.* in 1N H₂SO₄ was +0.19V (NHE) and the potential used by us in 1N NaOH was -0.76V (NHE).

and also solution and illumination conditions. Thus, for the TiO₂ electrode, we carried out a hydrogen atmosphere reduction for 5 hr at 800°C, whereas Harris *et al.* (1) used 15 min at 600°C and Wrighton *et al.* (2) reduced TiO₂ at 700°C for 4 hr.

The main difference both for the TiO₂ and the GaP crystals seems to be the illumination condition. The intensity of light was 0.08 W/cm² in this work, 1.4 W/cm² in the experiment of Harris *et al.* (1), and 8 ×

10⁻⁶ einstein/min (1 mm diam spot) (351, 361 nm doublet emission) which is equivalent to about 5 W/cm² in the work of Wrighton *et al.* (2). Accordingly, the current density of this work was 1.7 mA/cm² and that of Harris *et al.* and Wrighton *et al.* were 16 mA/cm² at maximum and 100 mA/cm², respectively.

The intensity of light was not reported by Yoneyama *et al.* (3) but one may hypothesize that it is stronger than that of this work, because the light of a 500W Hg lamp was focused on to the electrode, while collimated light of a 900W Xe lamp was used in this work.

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