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The Stability of Photoelectrodes

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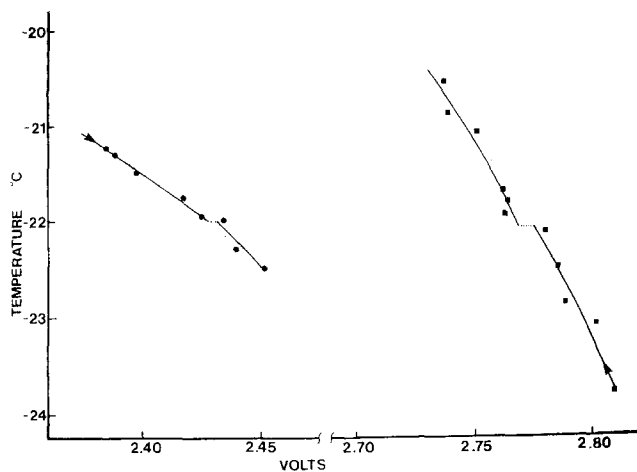|	
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Fig. 3. A plot of the potential required to charge the cell at 10.00 mA cm^{-2} at temperatures between —20° and —24°C.

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. Valeriote (4) has suggested this is freezing of the liquid in the pores of the heterogeneous $PbSO_4$-PbO_2 layer at the anode.

Acknowledgments

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

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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 $\Omega \cdot$ cm.

A p-type GaP was etched in HNO_3-HCl (2:1) mixture (6) and an ohmic contact was made by means of Zn-In alloy (3). The specific resistance was 1.3 $\Omega \cdot$ 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 (Oriel 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.

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
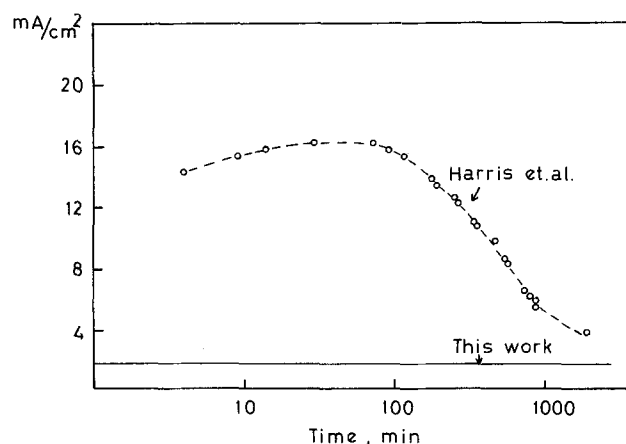

Fig. 1. The photocurrents as a function of time on TiO_2 for the work of Harris et al. compared with that of the present work. Potential used by Harris et al. at pH = 0 was 2.24V (NHE). Potential used by us at pH = 14 was 1.2V (NHE).
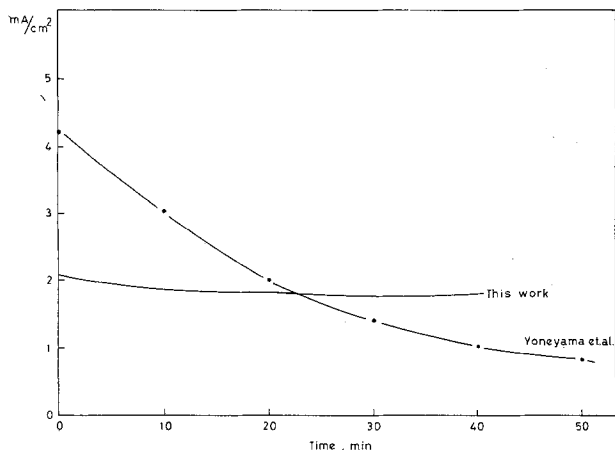
Fig. 2. The photocurrent as a function of time on Zn-doped GaP from the work of Yoneyama *et al.* and that of the present work. Potential used by Yoneyama *et al.* in 1*N* H$_2$SO$_4$ was $+0.19$V (NHE) and the potential used by us in 1*N* NaOH was -0.76V (NHE).

and also solution and illumination conditions. Thus, for the TiO$_2$ 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 TiO$_2$ at 700°C for 4 hr.

The main difference both for the TiO$_2$ and the GaP crystals seems to be the illumination condition. The intensity of light was 0.08 W/cm^2 in this work, 1.4 W/cm^2 in the experiment of Harris *et al.* (1), and 8 $\times$

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