JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 379–382

# *Photoelectrolysis*

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Received 15 October 1976

The photoelectrochemical behavior of *n*-type $TiO_2$ in aqueous solutions was investigated. Current–potential characteristics of polycrystalline $TiO_2$ and single crystals of $TiO_2$ of two different surface orientations (perpendicular and parallel to the 'C' axis) were measured in the dark and under irradiation of a 150 W Xenon lamp with an intensity of 20% of one Sun. The rate of photo-induced oxygen evolution on $TiO_2$ anodes increased in the following order: polycrystal $TiO_2$ < single crystal $TiO_2$ ($\perp$) < single crystal $TiO_2$ ($\parallel$). Photo-induced hydrogen evolution on *p*-type single crystal GaAs was obtained with photocurrents associated with hydrogen evolution over an order of magnitude larger than those obtained for oxygen evolution on illuminated $TiO_2$. The wavelengths at the maxima in the spectral photoresponse of $TiO_2$ were as follows: polycrystal $TiO_2$, 3100 A: single crystal $TiO_2$ ($\perp$), 3250 A; single crystal $TiO_2$ ($\parallel$), 3450 A. The maximum in the spectral photoresponse of GaAs was at 6650 A. A photoelectrolysis cell which consisted of an illuminated polycrystal $TiO_2$ anode and a Pt cathode developed photocurrents equivalent to about 0·1 mA $cm^{-2}$ for an incident radiant power of one Sun.

## 1. Introduction

In 1972 a novel way of electrolysing water was reported in a brief communication by Fujishima and Honda [1]. The cell consisted of an illuminated *n*-type $TiO_2$ single crystal anode and a platinum cathode. Electrolysis was achieved without an external power source by photo-induced oxygen evolution at the $TiO_2$ electrode and hydrogen evolution at the platinum electrode.

Corrosion resistance at the operating conditions of the electrolysis cell is a required characteristic of suitable electrodes for photo-induced oxygen evolution at *n*-type semiconductors and photo-induced hydrogen evolution at *p*-type semiconductors.

In this study, the photo-induced oxygen evolution on *n*-type $TiO_2$ observed by Fujishima and Honda [1] is examined in more detail. Experimental data for two different orientations of single crystal $TiO_2$ and anodically-formed polycrystalline $TiO_2$ were obtained. In addition, photo-induced hydrogen evolution on *p*-type GaAs has been investigated. In each case, current–potential characteristics of the electrolytes have been measured. The spectral photoresponses of both photoelectrochemical reactions were also determined. Since the completion of this experimental work (1974), a number of papers have been published on other similar studies [2–5].

## 2. Experimental

### 2.1 *Apparatus*

Photoelectrolysis experiments were conducted in a 1 l Pyrex cell equipped with a water-cooled jacket for temperature control. A 19 mm diameter port, with a quartz window, extended from the cell through the jacket. Ground-glass joints for cell access were glued to a PVC cover with epoxy cement. The joints provided for the test, counter (platinized Pt) and reference electrodes (saturated calomel electrode), a nitrogen bubbler and a thermometer. An Anotrol 4100 potentiostat was used to polarize the electrodes.

An Osram xenon lamp (150 W) served as the light source. The intensity of the incident radiation on the test electrode was determined as 0·215 Sun with a calibrated NASA secondary standard solar cell SIN 189.

The spectral response of the photocurrents of each electrode was determined with the Xenon lamp and a Leiss single-prism (quartz) monochro-

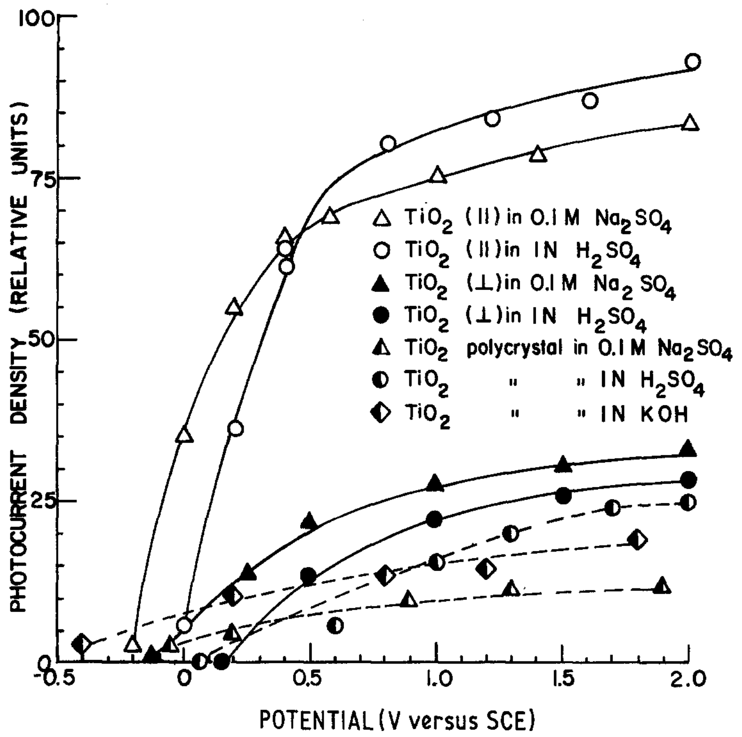

Fig. 1. Photocurrent densities of $TiO_2$ versus potential.

meter. The spectral output of the monochrometer was determined with either an Eppley thermopile or a Photovolt photometer.

### 2.2. *Electrodes*

Polycrystalline $TiO_2$ was formed by anodizing titanium metal electrodes in $H_2SO_4$ at potentials from 1–3 V versus SCE for 1–20 h. The electrodes were cylindrical pieces cut from pure titanium rod (1·27 cm diameter and 1 cm long) which were degreased in hot benzene for 2 h. The cylindrical surface was covered with shrinkable teflon tubing. One of the cross-sectional surfaces was exposed to the solution. This surface was polished with 400 and 600 grit silicon carbide paper followed by treatment in 1 N HF for 1 min.

The two *p*-type $TiO_2$ single crystals were supplied by the Jet Propulsion Laboratory. Both were about 1 mm thick with doped Al. One crystal (⊥) was cut with the working surface perpendicular to the *c*-axis. The other crystal (‖) was cut parallel to the *c*-axis. The (⊥) crystal was converted to *n*-type by heating in a vacuum (approximately $10^{-5}$ Torr) for 4 h at 700° C. The (‖) crystal was converted to *n*-type by reduction in flowing hydrogen in a Vycor tube at 800° C for about 3 h. Ohmic contacts were made by electroplating copper (1 μm thickness) to the back of the electrode and soldering a copper wire to the deposited copper layer with indium.

An electrode was constructed from a single crystal of GaAs. The material was *p*-type (carrier concentration — $1 \cdot 4 \times 10^{-6} \text{cm}^{-3}$; resistivity 1·5 Ω cm) doped with cadmium. Ohmic contact was made by soldering copper wires directly on the crystal with indium. The contacts of all the single crystals were found to be ohmic with a transistor diode curve tracer. The single crystal electrodes were masked with Apiezon wax except for the surfaces exposed to the electrolyte.

## 3. Results

Polycrystalline $TiO_2$ (anodized Ti) in 1 N $H_2SO_4$, 0·1 M $Na_2SO_4$ and 1 N KOH exhibited positive photocurrents as shown in Fig. 1. The dark currents were negligible between — 0·5 to + 2·0 V. Fig. 1 also shows current–potential characteristics of both *n*-$TiO_2$ crystals in 1 N $H_2SO_4$ and $Na_2SO_4$. The rates of photo-induced oxygen evolution (photocurrents) on $TiO_2$ (‖) were substantially larger than that on $TiO_2$ (⊥) in both solutions. The latter were slightly higher than the photocurrents of the polycrystalline materials in all three electro-

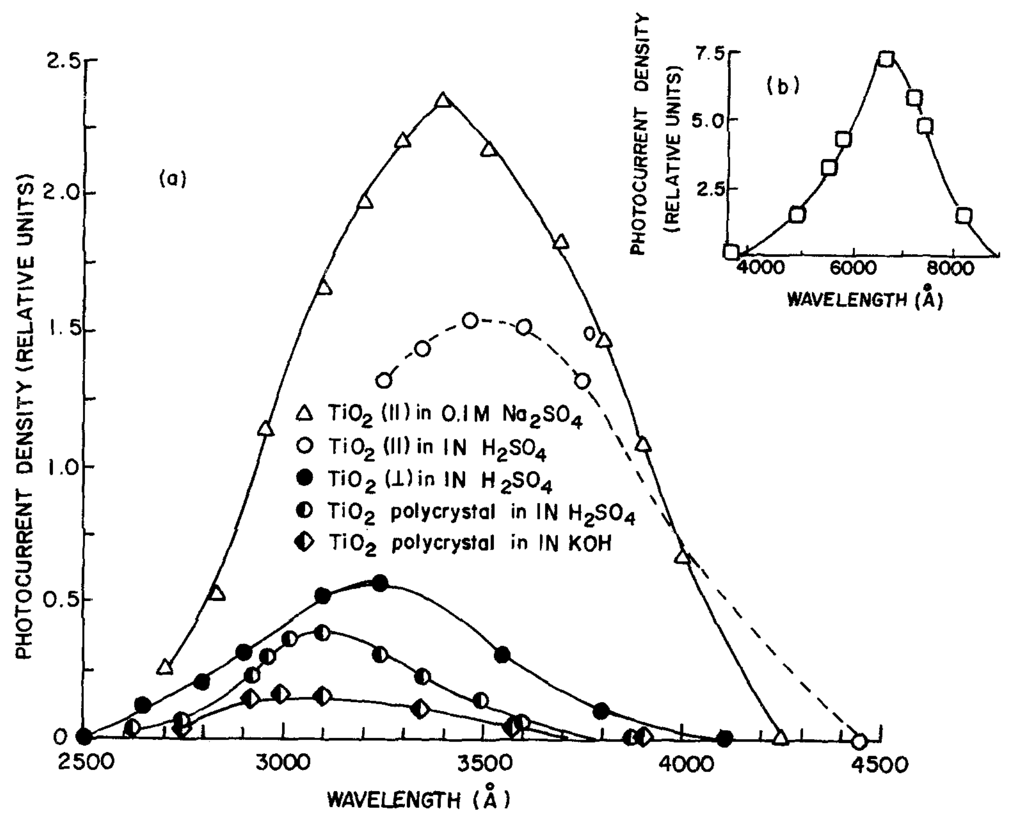

Fig. 2. Spectral photoresponse of (a) $TiO_2$ and (b) GaAs.

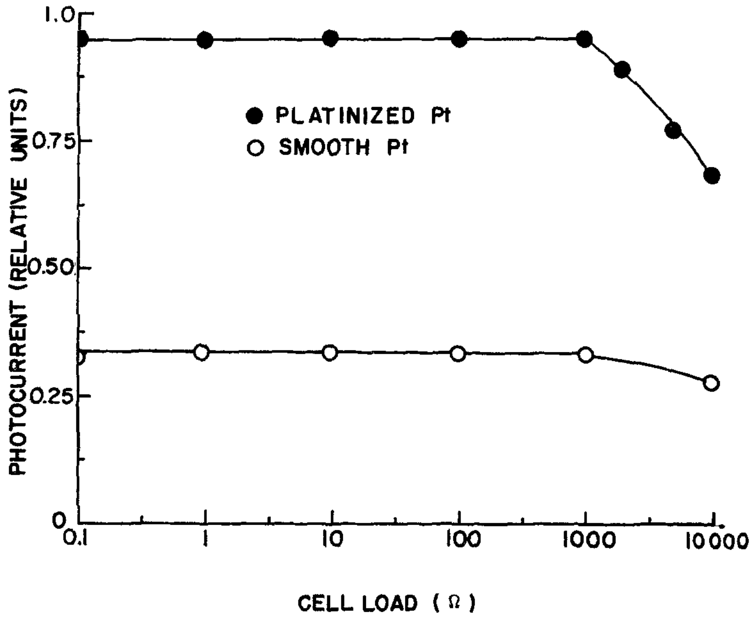

Fig. 3. Photocurrent versus load of a polycrystalline $TiO_2$-Pt photoelectrolysis cell.

lytes. The photocurrents of both single crystals increased much more sharply below about 0·5 V. Above this potential, photocurrents tended to saturation currents.

Photo-induced hydrogen evolution on *p*-type GaAs was obtained. Saturation photocurrents were observed below about − 1·0 V. The magnitude of these photocurrents were over an order of magnitude larger than that observed for $TiO_2$. Considerable fluctuation in the saturation photocurrents was observed with current spikes occurring at the same time as large hydrogen bubbles were swept away from the electrode surface. The lower bounds in the fluctuatiing saturation photocurrents were due to the large resistance overpotentials caused by the presence of large hydrogen bubbles at the electrode surface.

Titanium dioxide has a band gap energy of 3·03 eV which indicates that photoeffects may be obtained at wavelengths shorter than 4045 A. Fig. 2(a) shows the spectral photoresponse of polycrystalline and single crystal $TiO_2$. Maxima in the photocurrents of polycrystal $TiO_2$ in 1 N $H_2SO_4$ and 1 N KOH were obtained at about 3100 A. On the other hand, maxima in the photocurrents of the single crystals [at 3250 A for $TiO_2$ ($\perp$) and at 3450 A for $TiO_2$ ($\parallel$)] were shifted to longer wavelengths. The magnitude of the spectral photoresponse of $TiO_2$ ($\perp$) was slightly larger than that observed for the polycrystals; however, it was substantially larger for $TiO_2$ ($\parallel$).

The band gap of GaAs is 1.35 eV which corresponds to a wavelength of 9080 A. Fig. 2b shows that photocurrents were observed at wavelengths shorter than 9000 A. The maximum in the photocurrent occurred at 6650 A.

Although a photoelectrolysis cell was constructed by Fujishima and Honda [1] actual performance characteristics were not presented. We have constructed photoelectrolysis cells which consisted of an illuminated polycrystalline $TiO_2$ anode and either a smooth platinum or platinized Pt cathode. During operation of the photocells, oxygen was evolved at the illuminated polycrystalline $TiO_2$ and hydrogen was evolved at the Pt cathode. Fig. 3 shows that the photocurrents of the $TiO_2$-platinized Pt cell were about a factor of four larger than the $TiO_2$-smooth Pt cell. The photocell appears to be a constant current source consistent with electron tunneling as the rate determining step in the oxygen evolution reaction on $TiO_2$ [6], and photocurrent as only a function of the intensity and wave length of the incident radiation.

The photocurrent developed by the polycrystal $TiO_2$-platinized Pt cell was equivalent to approximately 0·1 mA $cm^{-2}$ for a radiant power of one Sun. Since only about 9% of the incident radiation from the Xenon lamp has radiation energy greater than the band gap of $TiO_2$, 3·03 eV, a power efficiency of about 8%, based on the effective incident radiation energy, was obtained.

## Acknowledgement

This work was supported by the President's Fund, California Institute of Technology, grant number PF-064 (1973–4).

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