

A comparative study of electrochemical and photoelectrochemical reactions at semiconducting oxidized Ti and TiO₂ single crystal electrodes in view of energy conversion applications

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An experimental investigation was made on the electrode properties of oxidized Ti and of rutile single crystals. Polycrystalline samples were prepared by oxidation in air and partial reduction in H₂ at various temperatures. The current–voltage characteristics in aqueous-indifferent electrolyte solutions in darkness and under illumination demonstrate that it is possible to obtain samples with photoelectrolytic performances at least equivalent to those of monocrystalline TiO₂ samples. Moreover, a pronounced similarity is found between both types of electrodes with regard to the reactivity of the reducing agents added. The influence of different gases (H₂, N₂ or O₂) on the current–voltage behaviour of these electrodes reveals some important aspects concerning their possible use for the conversion of optical energy into chemical or electrical energy.

1. Introduction

It is important from both the fundamental and the practical point of view to establish to what extent the electrochemical and photoelectrochemical properties of single crystals and polycrystalline samples of the same semiconductor material are comparable. Since in a polycrystalline sample different crystal faces are present and a high concentration of lattice defects can be expected in general, the fundamental problem amounts to the question of whether these factors are important in the electrode behaviour of a semiconductor. The practical side of the problem is evidently associated with the applicability of polycrystalline electrodes to electrochemical cells intended to convert solar energy into electrical or chemical energy, where single crystals are too expensive to be used.

Investigations have been made in the past by several workers in order to answer the question

mentioned. Gerischer [1] found that polycrystalline ZnO behaves in a way very similar to that of the single crystal ZnO. Since TiO₂ has been found to be much more stable than ZnO with respect to photocorrosion [2] and has been proposed as a material suitable for the photoelectrolysis of water, several investigations on polycrystalline TiO₂ electrodes have been undertaken [3–8]. Different preparation methods have been tried out. We have chosen to prepare the samples by oxidizing Ti and partially reducing the TiO₂ layer formed in a well-determined gas atmosphere in an electric furnace at a given temperature for a given period of time. The aim was to establish whether preparation under well-determined and reproducible circumstances can lead to polycrystalline semiconductor electrodes with reproducible properties, which can then be evaluated against those of single crystal rutile, the latter having been extensively studied by us in earlier work [9, 10].

2. Experimental

2.1. Preparation of the electrodes

All electrodes used in this work were cut from a commercial titanium plate (99.5% titanium).

Each Ti sample (approximately $0.7 \times 0.7 \times 0.15 \text{ cm}^3$) was polished with emery paper of increasing smoothness until it had a bright appearance. Degreasing of the samples was performed by treatment in boiling 2-propanol. The samples were heated in air for one hour in an electric furnace to a temperature (T_{ox}) between 400 and 1000°C . Afterwards, most of the samples were heated in a hydrogen stream for one hour at a constant temperature (T_{red}) between 550 and 800°C .

One side of the sample was partially ground; there, contact was made with bare titanium metal by means of silver paste. Further details on the procedure for mounting the samples have been given in a previous paper [11].

2.2. Measuring circuit

The apparatus consisted of an electrochemical cell, an electrical measuring circuit and a light source. The cell contained the oxide electrode, a platinum counter electrode, a saturated K_2SO_4 mercurous sulphate reference electrode and an aqueous electrolyte solution, and was equipped with a flat window through which the semiconductor was illuminated.

Two electrical measuring circuits were used. In the first one, the potential difference (source; Knick S13) between the semiconductor and the reference electrode was kept constant (by means of a Keithley 604 Differential Electrometer Amplifier used as a potentiostat) and the current measured by a Vibron Electrometer 33B. In the second one, a constant voltage was applied between the semiconductor and the Pt electrode, the current was measured by means of a General Radio 1807 Nanoammeter, and the voltage between the semiconductor and the reference electrode by means of a Keithley 610A Electrometer.

As a light source, either a microscope lamp (Bausch and Lomb Illuminator type 31-35-38) or a mercury arc (Phillips 93145E) was used. Monochromatic light for the measurement of the

wavelength dependence was obtained by using the monochromator of a Unicam spectrophotometer. Unless otherwise stated, the measurements were performed while bubbling high purity nitrogen through the solution.

3. Results

After heating in air, the Ti samples appeared to be covered by an oxide layer, the colour of which was either white (for $T_{\text{ox}} = 1000^\circ \text{C}$), greyish white (for $T_{\text{ox}} = 800^\circ \text{C}$) or ink blue (for the lower T_{ox}). The X-ray diffraction patterns of the former two showed only peaks of the rutile modification of TiO_2 , while those of the latter could only be attributed to titanium metal. The oxide layer formed at $T_{\text{ox}} > 800^\circ \text{C}$ adhered very badly to the substrate.

The hydrogen treatment resulted in a darkening of the grey samples and a striking colour change to grey of the ones which were blue. Attempts to make larger samples ($\approx 40 \text{ cm}^2$) failed; the hydrogen treatment ($T_{\text{red}} = 700^\circ \text{C}$) caused a bending of the sample resulting in the oxide layer scaling off. This effect was also observed on some of the smaller samples, making them unsuitable for electrochemical measurements. A slow heating and cooling in hydrogen could not remedy this and made the material entirely brittle. Weighing of the oxide pellets enabled us to estimate the layer thickness which was approximately $5 \mu\text{m}$ at $T_{\text{ox}} = 800^\circ \text{C}$ and $T_{\text{red}} = 700^\circ \text{C}$.

Current-voltage measurements were performed on approximately forty samples, mostly in a 0.01 M HClO_4 solution. Representative $j-V$ curves are given in Fig. 1; for comparison, a $j-V$ curve for a TiO_2 single crystal is also presented. In all experiments, the geometric arrangement was kept rigorously the same.

On applying positive potentials to the TiO_2 electrode ($V > +0.5 \text{ V}$ versus SHE), small anodic dark current densities (of the order $10^{-7} \text{ A cm}^{-2}$) were observed for all electrodes; illumination of the electrode surface always resulted in an increase of the anodic current density, the magnitude of which depended, at fixed light intensity, on the electrode preparation. A first general observation was that higher oxidation temperatures led to higher photocurrent densities

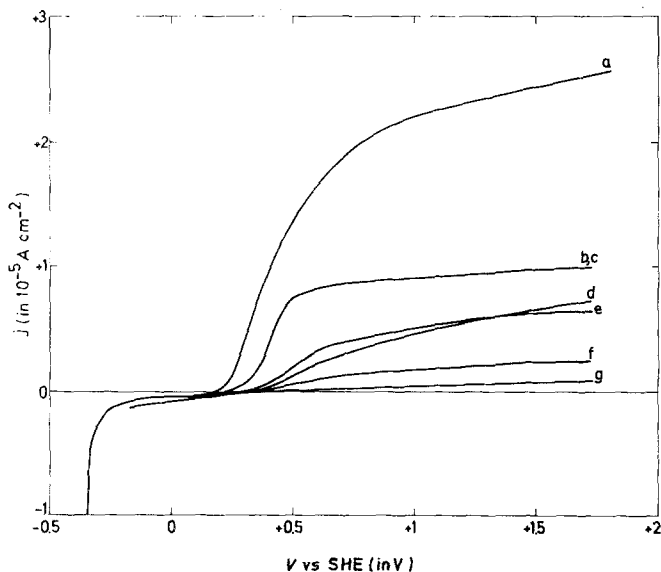


Fig. 1. Photocurrent density versus applied voltage. Electrolyte, 0.01 M HClO_4 . Curve a; $T_{\text{ox}} = 800^\circ\text{C}$, $T_{\text{red}} = 700^\circ\text{C}$; Curve b; $T_{\text{ox}} = 800^\circ\text{C}$, $T_{\text{red}} = 650^\circ\text{C}$; Curve c; TiO_2 single crystal, $T_{\text{red}} = 600^\circ\text{C}$ (15 min); Curve d; $T_{\text{ox}} = 800^\circ\text{C}$, $T_{\text{red}} = 600^\circ\text{C}$; Curve e; $T_{\text{ox}} = 500^\circ\text{C}$, $T_{\text{red}} = 700^\circ\text{C}$; Curve f; $T_{\text{ox}} = 600^\circ\text{C}$, $T_{\text{red}} = 700^\circ\text{C}$; Curve g; $T_{\text{ox}} = 500^\circ\text{C}$.

(for example Fig. 1 Curves e and a). For all oxidation temperatures, a hydrogen treatment considerably enhanced the magnitude of the photoeffect (for example Fig. 1, Curves g and e).

This effect was more pronounced at higher T_{red} (for example Fig. 1, Curves a, b and d). However, 700°C seems to be the upper limit of T_{red} since a treatment at $T_{\text{ox}} = 500^\circ\text{C}$ and $T_{\text{red}} = 800^\circ\text{C}$ did not lead to any photoresponse and resulted in a linear j - V relationship. Practically no photoeffect and very small dark current densities were observed for $T_{\text{red}} < 500^\circ\text{C}$.

The onset of the j - V curves of all samples coincided within a voltage range of approximately 0.15 V. In some cases (for example Fig. 1 Curves b and c) the path of the curve was very similar to that of a TiO_2 single crystal electrode; in other cases, even higher photocurrent densities could be obtained (Curve a).

A measurement of the wavelength dependence of the photocurrent density revealed a close parallelism between rutile single crystal and oxidized titanium electrodes (the normalized curves had a completely identical shape and were shifted over no more than 5 nm against each other).

The determination of the donor density by impedance measurements failed because of a high dissipation and a considerable frequency dependence of the capacitance which characterized the polycrystalline samples.

In another series of experiments, the electrochemical behaviour of reducing agents was investigated. In the dark, it was found that only those reducing agents which showed electron injection at rutile single crystals [9] caused the same effect at polycrystalline TiO_2 electrodes. The magnitudes of the injection current densities and the shapes of the j - V curves were very similar for both kinds of electrodes. This is illustrated in Fig. 2 for Ti^{3+} and V^{2+} as injection agents.

On illumination, the occurrence of the well-known current multiplication effect [10] was checked on oxidized Ti samples with a limited number of reducing agents. An increase of the anodic photocurrent was observed on adding the following agents; formic acid, oxalic acid, tartaric acid (as the Na, K salt), citric acid (as the tri-Na salt) and methanol. None of these species was found to cause an increase of the dark anodic current density. Typical current-voltage curves are presented in Fig. 3. The multiplication current was lowered on adding KBr , Na_2SO_3 or MnCl_2 . For comparable concentrations of these reducing agents, the lowering was the greatest for MnCl_2 and the smallest for KBr . Also these results are similar to those obtained on single crystal rutile [10].

In order to get more insight into the possibility of the photoelectrolysis of water, we performed photocurrent-voltage measurements in which not only the potential difference between the semi-

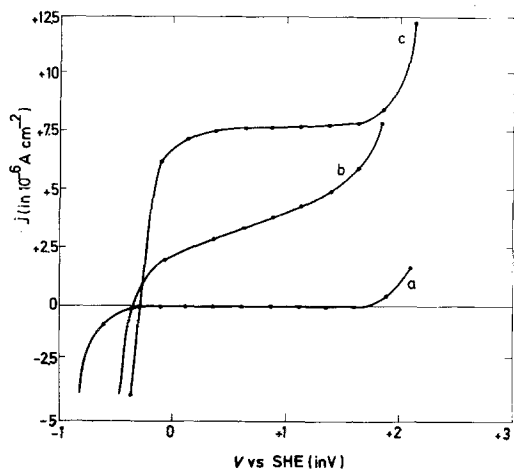


Fig. 2. Anodic dark current-voltage curves. Sample preparation, $T_{\text{ox}} = 500^\circ \text{C}$. Curve a, $0.25 \text{ M K}_2\text{SO}_4 + 0.01 \text{ M H}_2\text{SO}_4$; Curve b, $0.25 \text{ M K}_2\text{SO}_4 + 0.01 \text{ M H}_2\text{SO}_4 + \approx 0.01 \text{ M VSO}_4$; Curve c, $0.25 \text{ M K}_2\text{SO}_4 + 0.01 \text{ M H}_2\text{SO}_4 + \approx 0.01 \text{ M TiCl}_3$.

conductor and reference electrodes (V_{sr}), but also that between the semiconductor and platinum electrodes (V_{sp}) was registered. This also allowed us to plot the current through the cell as a function of the potential difference between the Pt and the reference electrodes (V_{pr}) which is given by

$$V_{\text{pr}} = V_{\text{sr}} - V_{\text{sp}} \quad (1)$$

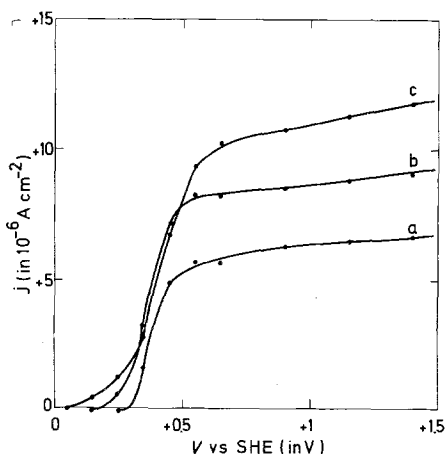


Fig. 3. Photocurrent density versus applied voltage. Sample preparation; $T_{\text{ox}} = 800^\circ \text{C}$, $T_{\text{red}} = 650^\circ \text{C}$. Curve a, 0.01 M HClO_4 ; Curve b, $0.01 \text{ M HClO}_4 + 0.74 \text{ M HCOOH}$; Curve c, $0.01 \text{ M HClO}_4 + 0.14 \text{ M (COOH)}_2$.

Representative results are given in Fig. 4. It should be remarked that currents and not current densities must be plotted since the surface areas of the semiconductor and Pt electrodes are different. The influence of the hydrogen and oxygen eventually evolved on the current-potential behaviour was studied by bubbling these gases through the solution. It is seen that the behaviour of especially the platinum electrode is determined by the surrounding gas atmosphere. Moreover, the dependence of the anodic photocurrent on the potential of the semiconductor (versus the reference electrode) does not differ substantially for these three gases. The cathodic part of the $I-V_{\text{sr}}$ curve is the same for H_2 and N_2 bubbling; oxygen strongly enhances the cathodic current.

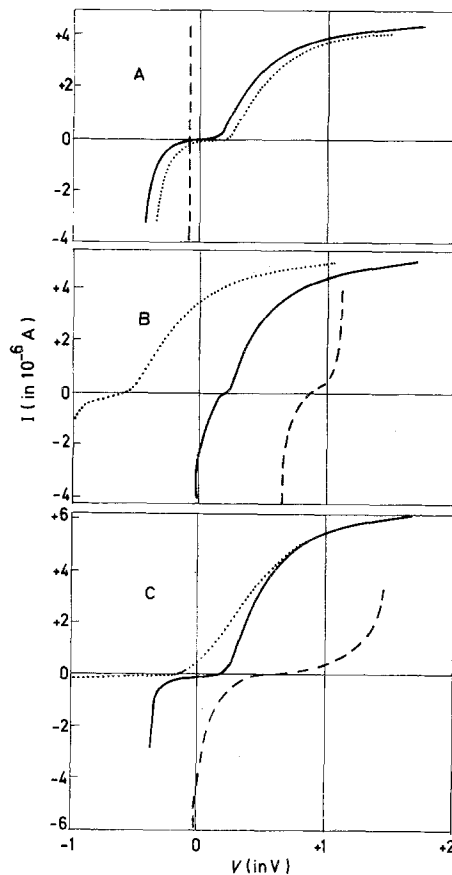


Fig. 4. Photocurrent-voltage curves under gas bubbling. Sample preparation; $T_{\text{ox}} = 800^\circ \text{C}$, $T_{\text{red}} = 700^\circ \text{C}$. Surface area of TiO_2 electrode, 0.25 cm^2 . Surface area of Pt electrode; 8 cm^2 . Part A; in hydrogen. Part B; in oxygen. Part C; in nitrogen.

..... $I-V_{\text{sp}}$
 ——— $I-V_{\text{sr}}$
 - - - $I-V_{\text{pr}}$

4. Discussion

Thin TiO₂ layers on metallic titanium can be obtained by various methods, such as:

- (a) Anodic oxidation of Ti in aqueous solution;
- (b) Thermal oxidation by electrical heating in a furnace;
- (c) Thermal oxidation by heating in a gas flame;
- (d) Spraying TiO₂ powder on Ti using the plasma jet method.

Up to now, the first three methods were investigated by Fujishima [3]. Houlihan [7] confined his work to the third preparation method (using a natural gas flame), whereas Gissler [8] used both the thermal oxidation and the plasma jet method. Cléchet [5] reports measurements, performed on one sample only, prepared by thermal oxidation in a furnace.

According to Fujishima [3], samples prepared by heating in a gas flame show anodic photocurrents nearly as large as those obtained with rutile single crystal electrodes. However, the experimental conditions of the gas flame method cannot be reproduced as well as those of the other methods. Fujishima [3] also reports that for samples prepared by the first two methods the magnitude of the photocurrents is about the same and one order of magnitude lower than that of the single crystal. Gissler [8] on the other hand has found that the preparations (b) and (d) resulted in no substantial differences. Hence we confined our work to a systematic investigation on the second preparation method, which is quite reproducible and economically very feasible. As temperature changes affect the degree of oxidation and reduction more profoundly than treatment duration does, the temperature was chosen as the only variable in preparation.

Our results demonstrate that it is possible to obtain a photocurrent density exceeding the corresponding one at single crystal TiO₂. The best results were obtained after oxidation at 800° C followed by hydrogen treatment at 700° C. Since the donor density in this sample could not be determined, the thickness of the space charge layer can only be estimated. Assuming a donor density of the order of 10²⁵ m⁻³ (as found in single crystals with equal reduction pretreatment [9]) the space charge layer thickness at a band bending of

1 eV is calculated to be approximately 3×10^{-8} m, which is small compared to the oxide layer thickness (see results).

It can be understood that there must be an optimal oxidation and a corresponding reduction temperature. Higher oxidation temperatures produce thicker oxide layers which were found to scale off. On the other hand, the oxide layer has to be thick enough to absorb as much incident light as possible. As the hydrogen treatment determines the semiconducting behaviour, T_{red} has to be high enough to accomplish the partial reduction over the whole depth of the oxide layer; otherwise, a nearly stoichiometric insulating layer would remain between the semiconducting oxide and the metal substrate. A too high T_{red} may result in a high donor concentration and hence in a very thin space charge layer, so that a large fraction of the photoproduced electron-hole pairs would be lost by recombination in the bulk of the oxide. A too high T_{red} could also lead to the formation of insulating lower titanium oxides. In the latter case no appreciable photocurrent can be expected. The linear j - V relationship, without any photoeffect, observed for $T_{\text{ox}} = 500^\circ \text{C}$ and $T_{\text{red}} = 800^\circ \text{C}$ has apparently to be attributed to the presence of such a layer. Furthermore, when hydrogen has penetrated throughout the oxide layer, it may dissolve in the underlying metal substrate causing brittleness, as was observed in some of our experiments.

The comparison of the various literature results on polycrystalline TiO₂ is complicated by the great diversity of experimental conditions such as light intensity, spectral distribution of light and solution composition. The most obvious standard for comparing different results is the behaviour of the TiO₂ single crystal in identical conditions: this has been done in Fig. 1 with regard to the photoelectrochemical behaviour in an indifferent electrolyte solution. A clear similarity between both kinds of electrodes emerges from this figure, also apparent in the initial shape of the slope of the photocurrent-voltage curves. Our results establish moreover that the behaviour of both kinds of electrodes in the presence of reducing agents is precisely the same in darkness as under illumination. In the latter circumstances this result could be anticipated because no noticeable effect

of crystal orientation on the current multiplication phenomenon was detected [10].

The present results lead to certain considerations concerning the use of polycrystalline TiO₂ electrodes in semiconductor/electrolyte solar cells. As pointed out in Section 1, the study of the latter systems has recently attracted much interest, especially in view of their possible practical application for hydrogen production. Most of the considerations found in the literature in this context, are based upon measurements of the current as a function of the potential difference between the semiconductor and reference electrodes in a three-electrode cell. However, practical solar cells contain two electrodes only; the semiconductor and a counter electrode. Therefore, we thought it would be interesting to consider the connection between the current-voltage characteristics in the two- and the three-electrode cell in order to separate the effects associated with the individual electrodes involved. This can be done on the basis of graphical representations such as Fig. 4. A given point $+I$, V_{sp} corresponds to a point $+I$, V_{sr} and a point $-I$, V_{pr} , the three potentials being connected by Equation 1. The full line in Fig. 4c corresponds to Curve a in Fig. 1. From the voltage dependence of the cathodic part of the dashed line it can be presumed that the corresponding current is due to the reduction of H⁺. The low anodic short circuit current (the dotted line at $V = 0$) has to be ascribed to a slow oxidation at the illuminated TiO₂ electrode and a corresponding reduction at the Pt electrode. If no nitrogen were bubbled through the solution, the H₂ formed at the Pt electrode would shift the cathodic branch of the dashed line to more negative potentials, thus lowering and eventually stopping the H₂ formation. This is confirmed by the curves in Fig. 4a; no hydrogen evolution at the Pt electrode at 1 atm can be expected, since the short circuit would be cathodic. It should be remarked that the potential of the Pt electrode corresponds with the theoretical value of the hydrogen electrode, calculated from the Nernst equation.

It can be concluded that continuous photoelectrolysis of water is not possible in the circumstances studied. However, an applied electro-

motive force allows a 'photoassisted electrolysis' to occur, as was demonstrated by some investigators [12, 13]. This e.m.f. may come either from an external voltage source [12] or from a pH difference between the TiO₂ and the Pt compartment [13]. In the presence of oxygen, a considerable anodic short circuit current is seen to flow through the cell (dotted line at $V = 0$ in Fig. 4b). Since the reaction at the Pt electrode can here be expected to be the electroreduction of O₂, this implies that the cell considered can be used as a photoelectrochemical cell operating under regenerative conditions. This point has been stressed before by other authors [14].

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