Electrochemical investigation of an illuminated TiO_2-electrode

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Received 9 October 1974

The electrochemical behaviour of a TiO_2-film electrode has been investigated with and without illumination. An anodic photo current has been observed in agreement with the results of Fujishima and Honda [5]. This current can be described by an oxide type electrode reaction evolving O_2. The potential of this electrode reaction depends on the logarithm of the light intensity and can only become sufficiently cathodic to allow for a water splitting process if very high light intensities are available. At lower light intensities a system consisting of a TiO_2-film electrode and a reversible oxygen electrode works as a fully regenerative photocell, oxygen being evolved at the illuminated TiO_2 electrode and consumed at the counter electrode.

1. Introduction

TiO_2 is a semiconductor with a band gap energy of $3 \cdot 06$ eV corresponding to a light absorption edge of $0 \cdot 45 \, \mu m$ [1]. It becomes n-type conducting by a slight reduction in hydrogen or water/hydrogen mixtures, or simply by heating in vacuum [2].

Photo-electrochemical effects at semiconductor-electrolyte interfaces have been known for a long time. They arise from changes in the charge distribution in the double layer by electron-hole pairs generated by illumination with light of wavelengths below the absorption edge [3, 4]. So far, only a small number of semiconductor electrodes have been investigated under illumination. The experiments showed in most cases that during anodic polarization a decomposition of the semiconductor occurs under illumination, making the electrode less suitable for photoelectric energy conversion. An exception however is rutile, where even at a relatively high anodic polarization and intense illumination no traces of decomposition products could be found [5].

Photochemical investigations on rutile [6] have shown that illumination with light of wavelengths below the absorption edge causes oxygen liberation and the formation of a lower oxide according to the reaction: $2\,TiO_2 \xrightarrow{h\nu} Ti_2O_3 + \frac{1}{2}O_2$. Such a reaction is very likely because TiO_2 is known to have a tendency toward crystallographic shear and to exhibit a number of Magneli-phases of the type Ti_nO_{2n-1} [7] in which oxygen is either very mobile or easily exchanged with another phase. These properties could explain also the stability of TiO_2-electrodes, considering that Ti_2O_3 can react with water according to the reaction

$$Ti_2O_3 + H_2O \longrightarrow 2TiO_2 + 2H^+ + 2e^- \text{ [8]}.$$
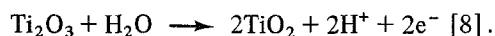
In photo-electrochemical measurements, so far* only potentiostatic experiments on n-type TiO_2- single crystals at pH $4 \cdot 7$ have been performed [5]. From these measurements it has been concluded that water decomposition takes place in an electrochemical cell simply by illumination with visible light.

The purpose of this work is to investigate the TiO_2-electrode behaviour in more detail. In view of eventual applications of TiO_2-electrodes, we have used for our investigation TiO_2-film electrodes.

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* Note added in proof: After submission of the manuscript a detailed investigation [10] on the photocatalytic deposition of noble metals on TiO_2 appeared in which a large part has been devoted to the electrochemical behaviour of TiO_2-electrodes.

2. Experimental

Two different kinds of electrodes have been prepared, one by thermal oxidation of titanium and the other by spraying TiO_2 powder on titanium sheets using the plasma jet spraying method. Both kinds of TiO_2 films have been slightly reduced in vacuum to improve the electrical conductivity [9]. Commercial 99·9% titanium has been used. The TiO_2 films have been investigated by X-ray powder analysis; they showed patterns typical of the rutile structure. The film thickness was of the order of $50 \mu m$.

We found that TiO_2-films prepared by the thermal oxidation method tend to spall from the Ti substrate. Films prepared by the plasma jet spraying method are however mechanically stable and do not spall even under strong anodic polarization. In most of our experiments we used electrodes prepared by the latter procedure. After a corrosion test of 60 h under anodic polarization at 600 μA and with illumination, no titanium ions could be found in the solution (about 150 cm^3) within the sensitivity 0·6 $\mu g\, cm^{-3}$ of the analysing method.

For the electrochemical investigations we used a two-compartment cell separated by a porous glass diaphram. An optically flat quartz window is sealed in the compartment of the TiO_2 electrode. The solution was stirred by circulating it through a mixing vessel with a pump. This procedure is particularly useful, in order to keep constant the pH in a unbuffered solution*, because as a consequence of the electrode reactions, the pH in both cell compartments is changing in an opposite direction. Saturated calomel electrodes with Luggin-type calillaries have been used as reference electrodes. 0·1 M Na_2SO_4 solutions were used throughout; the pH was adjusted by adding NaOH and H_2SO_4 respectively.

As light source a 60 W medium pressure mercury lamp stabilized to about ± 2% was used. Its spectrum contains some u.v. contributions, (mainly the 0·254 μm line), however, qualitatively, the same results were obtained after filtering out the u.v. components. It could also be shown that direct solar irradiation caused about the same photo

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* It has been observed that the phthalic acid/phthalate buffer is unstable under radiation in the presence of the TiO_2 electrode due to photo-oxidation of the organic molecules.
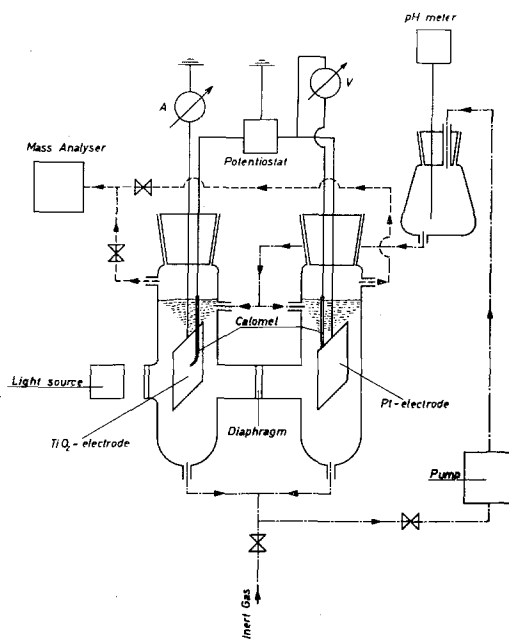

Fig. 1. Experimental arrangement and electrochemical cell.

current. The analysis of the gas atmosphere in the two cell compartments has been performed with a quadrupole mass spectrometer (Balzers QMG 111A). The electrode area was 5 cm^2. A schematic view of the experimental arrangement is shown in Fig. 1.

3. Results and discussion

The results of potentiostatic measurements obtained at different pH, with and without illumination of the TiO_2-electrode, are shown in Fig. 2 where the current density I is plotted against the electrode voltage E. The curves show qualitatively the known characteristic behaviour of n-type semiconductor electrodes; namely that an anodic current is flowing only with illumination and reaches a saturation value at moderate anodic polarization. The curve for pH 5 is in good agreement with that of the measurements [5] of pH 4·7, apart from the fact that in the present work an additional current increase at $E = 1·7$ V (SCE) was observed. This has been observed also at the other pH-values, and is due to O_2-evolution as it is observed also on Pt-electrodes.

For all different pH's a cathodic current can be observed with illumination at voltages which are more positive than the reversible hydrogen electrode
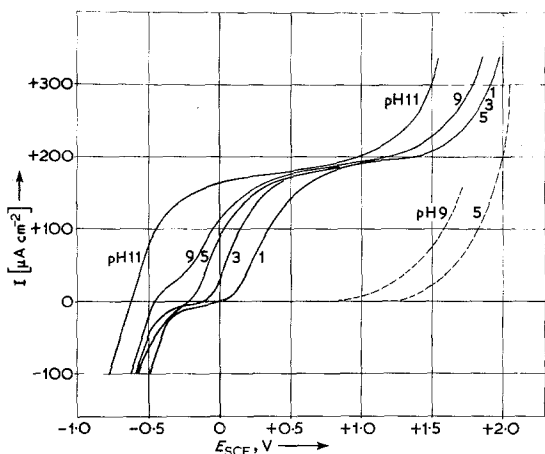
Fig. 2. Current density I against the potential E of a TiO$_2$-electrode for different pH's with (full line) and without illumination (dotted line).
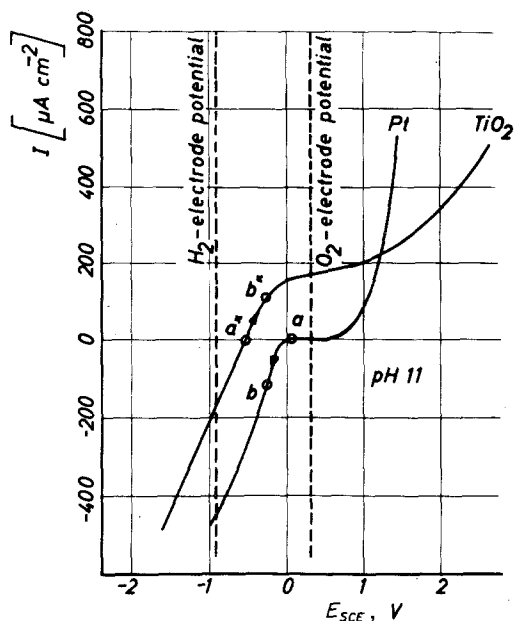

Fig. 3. Current density I against the potential E of an illuminated TiO$_2$-electrode and the corresponding bright counter Pt-electrode. The open circuit voltage of the cell TiO$_2$/0·1 M Na$_2$SO$_4$/Pt is indicated by the potential difference between the points a and a*. At short circuit conditions given by b and b* the cell voltage is zero.

potential. Therefore this cathodic current cannot be caused by a hydrogen evolution, suggesting that another cathodic reaction is occurring. This is also supported by the fact that the curves are not only shifted parallel as a function of pH, but also change

their shape remarkably. The curves without illumination differ only slightly from those with illumination (except for $I < 20\,\mu A\,cm^{-2}$) and have therefore not been drawn.

In Fig. 3, the I/E-curve for TiO$_2$ and that of the bright Pt-counter electrode, at pH 11, have been plotted together. This shows clearly that at the Pt electrode no hydrogen evolution but oxygen reduction takes place*, as long as the anodic photo current does not exceed its saturation value. In an acid solution similar measurements showed the same result.

No hydrogen could be detected by a gas analysis of the atmosphere in the Pt-cell compartment after several runs at pH 5 and 11 of 24 h at about $600\,\mu A$ anodic photo current. During these runs the potential of the illuminated TiO$_2$ electrode was maintained potentiostatically at 0·6 V (SCE). The cell voltage was smaller than the water decomposition voltage. In the TiO$_2$ cell compartment, however, an oxygen evolution was observed in agreement with other [5] reported measurements.
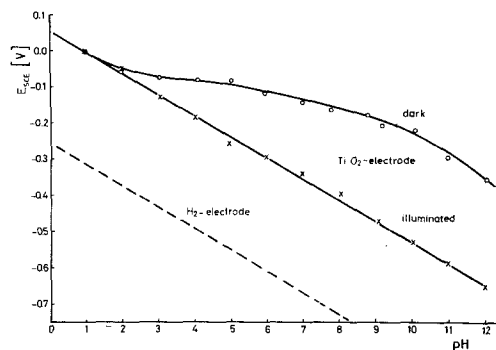

Fig. 4. Potential E of an illuminated TiO$_2$-electrode as a function of the pH of the solution.

In Fig. 4, the TiO$_2$ electrode potential is plotted against the pH of the solution as measured with and without illumination. It is seen that illumination shifts the electrode potential toward more negative values. A straight line, the slope of which is 0·058 V, is obtained. Under the experimental conditions the potential of the illuminated TiO$_2$ electrode is more positive than that of the hydrogen electrode; therefore no water decomposition is possible in the galvanic cell.

* The oxygen present in the solution comes from the atmosphere and as will be shown later evolves from the TiO$_2$-electrode.
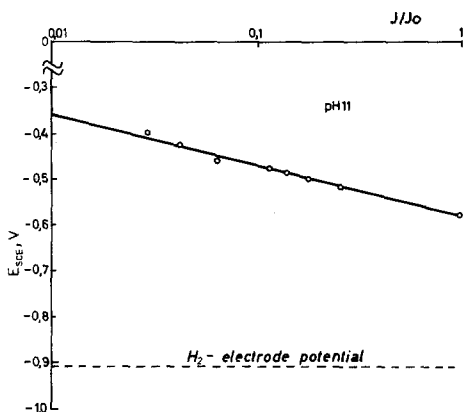
Fig. 5. Potential E of a TiO_2-electrode as a function of the logarithm of the ratio of the light intensity $\mathcal{F}/\mathcal{F}_0$. $\mathcal{F}_0$ is the intensity normally used in the experiments. $\mathcal{F}$ has been varied by changing the distance of the light source to the cell.

Fig. 5 shows the measured TiO_2-electrode potential as a function of the decadic logarithm of the ratio $\mathcal{F}/\mathcal{F}_0$; $\mathcal{F}$ is the light intensity which has been varied by changing the distance of the light source to the electrode, and $\mathcal{F}_0$ is the intensity which was used for the previously described measurements. Here a straight line the slope of which is 0·048 V is also obtained.

Usually it is assumed that the oxygen evolution is caused by a reaction of photo-generated holes p^+ with water according to [5]

$$2h\nu \longrightarrow 2e^- + 2p^+ \qquad (1)$$

$$2p^+ + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+. \qquad (2)$$
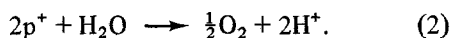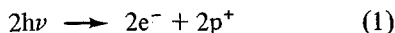
However, to explain the observed cathodic current at voltages more positive than the reversible hydrogen electrode potential (see Fig. 3), either a hole injection (see Equation 2 in the reverse sense) has to be assumed or the problem is formulated by combining the known photochemical reaction [6]:

$$2TiO_2 + 2h\nu \longrightarrow Ti_2O_3 + \tfrac{1}{2}O_2^* \qquad (3)$$
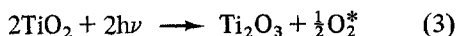
with the electrode reaction [8]

$$Ti_2O_3 + H_2O \rightleftarrows 2TiO_2 + 2H^+ + 2e^-, \qquad (4)$$

where Ti_2O_3 is not necessarily a phase at unit activity as it is in fact not the case in the present

* As well as Ti_2O_3, we can expect that also the constituents of the other Magneli-phases of composition Ti_nO_{2n-1} are products of the photoreaction. It is intended to investigate the photoreaction 3 in a separate work.

circumstances. It is apparent that the overall reaction is the same in both cases. It is also to be expected that the electrode potential dependence on the pH and on the light intensity is equal for both formulations. The pH dependence is evident from Equations 2 and 4. To calculate the potential dependence on the light intensity it was assumed that two holes are necessary for the formation of one molecule of Ti_2O_3. Assuming that the equilibrium concentration of holes is proportional to the light intensity (this is justified as long as the light intensity does not become too high [4], the following expression for the potential of the illuminated electrode is obtained:

$$E = E^\circ - 2\cdot303\,\frac{RT}{F}\cdot pH - \frac{RT}{F}\ln\,(\mathcal{F}/\mathcal{F}_0). \quad (5)$$

E° is a constant, R, T and F are the gas constant, the absolute temperature and the Faraday constant respectively.

As can be seen from Fig. 4, the potential of the illuminated TiO_2 electrode indeed depends linearly on the pH. The experimental slope is in good agreement with the theoretical value of $2\cdot303\,\dfrac{RT}{F} =$ 0·0591 V. Also, the measured functional dependence on the light intensity (Fig. 5) is in agreement with the expected one. The measured slope is about a factor of two too large, however, a fact for which we have yet no explanation. We see that on increasing the light intensity the potential may become lower than the reversible hydrogen electrode potential, thus allowing for an hydrogen evolution at the counter electrode only by illumination of the TiO_2-electrode. An inspection of Fig. 5 shows however that for this to occur the light intensity must be a factor of 100–1000 greater than that which we used in our experiment and which is comparable with the solar irradiation on the earth.

As long as the TiO_2-electrode potential is more positive than the reversible hydrogen electrode potential, a cell of the type $TiO_2/0\cdot1$ M Na_2SO_4/Pt is working under an external load as indicated in Fig. 3 by the lines from the points a and a* to b and b* respectively. There is not a net change of the electrolyte composition; the cell is working in a regenerative way evolving oxygen at the TiO_2-electrode and reducing the same quantity at the Pt electrode. In Fig. 6 the current-voltage characteristic of such a cell is seen for different pH's. The
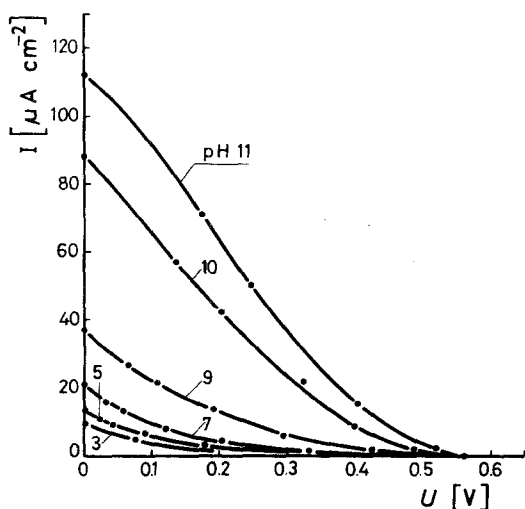
Fig. 6. Current-voltage characteristics of the cell $TiO_2/0\cdot1$ M Na_2SO_4/Pt at different pH's at constant illumination.

more basic the solution becomes, the higher the efficiency of the cell becomes; the efficiency for pH 11 in our arrangement is of the order of $0\cdot5$ %.* If no transfer of oxygen to the Pt cell compartment is possible, the cell current drops slowly to zero.

4. Conclusions

The TiO_2 electrode under illumination shows a complex electrochemical behaviour. We have observed two different anodic processes in both of which O_2 is evolved. One process is the ordinary oxygen evolution as it occurs also at the platinum

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* No attention has been given in this work to improving the efficiency of the cell. This could be done by optimization of the film thickness, by the choice of a more suitable electrolyte and by sensitisation of the TiO_2- and the auxiliary electrode as has been already suggested earlier [5]. Due to the relatively high band gap energy, TiO_2 has an inherent low efficiency without sensitization.

electrode under anodic polarization independent of the illumination. The other process is dependent on the illumination and it can be formulated as an oxide type electrode reaction, the potential of which is a function of the light intensity. Two cathodic processes have been observed. One is the ordinary hydrogen evolution as observed also at platinum electrodes on cathodic polarisation. The other one is the reverse of the above-mentioned oxide type electrode reaction.

A water splitting process caused simply by an illumination of the TiO_2 electrode is possible, but only with very high light intensity of the order of 100 times the solar irradiation on the earth. We have shown, however, that TiO_2 can be used also as a photo-sensitive electrode in a chemically regenerative cell of the type $TiO_2/0\cdot1$ M Na_2SO_4/Pt.

Acknowledgement

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