
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

BRUNO MARCANDALLI, IGNAZIO RENATO BELLOBONO

Influence of wavelength on the photoeffects at polycrystalline semiconductors. Energy conversion efficiencies of photo-electrochemical cells employing a titanium dioxide film anode and a hydrogen or oxygen cathode

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. 65 (1978), n.1-2, p. 87-92.
Accademia Nazionale dei Lincei

[<http://www.bdim.eu/item?id=RLINA_1978_8_65_1-2_87_0>](http://www.bdim.eu/item?id=RLINA_1978_8_65_1-2_87_0)

L'utilizzo e la stampa di questo documento digitale è consentito liberamente per motivi di ricerca e studio. Non è consentito l'utilizzo dello stesso per motivi commerciali. Tutte le copie di questo documento devono riportare questo avvertimento.

*Articolo digitalizzato nel quadro del programma
bdim (Biblioteca Digitale Italiana di Matematica)
SIMAI & UMI*

<http://www.bdim.eu/>

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica fisica. — *Influence of wavelength on the photoeffects at polycrystalline semiconductors. Energy conversion efficiencies of photoelectrochemical cells employing a titanium dioxide film anode and a hydrogen or oxygen cathode.* Nota (*) di BRUNO MARCANDALLI e IGNAZIO RENATO BELLOBONO (**), presentata dal Socio G. SARTORI.

RIASSUNTO. — È stata sperimentata una pila fotoelettrochimica a due compartimenti (anolita e catolita costituiti rispettivamente da NaOH 1 N e da H₂SO₄ 1 N), con anodo di biossido di titanio policristallino e catodo di nero di platino. In funzione della lunghezza d'onda, tra 250 e 450 nm, sono state misurate e determinate la densità di corrente di corto circuito, la tensione elettrica a circuito aperto, la resa quantica, e la resa globale di conversione energetica. I dati sperimentali indicano che la conversione di energia fotoassistita si produce con rese, sia quantiche che globali, più basse di quelle di una pila autorigenerativa, dotata degli stessi elettrodi ma ad elettrolita unico (NaOH 1 N), anche nella regione di completo assorbimento della radiazione incidente. Per quest'ultimo tipo di pila, infatti, le rese quantiche, al massimo di assorbimento, risultano assai elevate (80% circa) ed abbastanza soddisfacente (circa 5%) la resa energetica di conversione alle lunghezze d'onda di assorbimento.

Although the photovoltaic effect has been known for a long time [1, 2], it was not until the fifties of the present century [3] that a real interest was shown in energy sources making use of this effect. Many investigators observed photocurrents at various electrode materials, such as CdS [4], Hg [5-7], Ge [8], ZnO [9, 10], GaAs [11], GaP [12], CuO [13], TiO₂ [14-18], and SnO₂ [19]. In most of the semiconductor studies single crystals were used and only more recently [17-19] has the behaviour and the application of thin-film polycrystalline electrodes been examined, particularly in photoelectrochemical investigations. It was generally found that the bandgap energy illumination produced electron hole pairs which took part in the electrochemical processes; more specifically, electrons for the cathodic photocurrent in *p*-type materials, and holes for the anodic reaction in *n*-type electrodes.

One of the most important advantages of the use of semiconductor electrodes is that the charge transfer processes occur only through the energy bands. As a consequence, in the presence of sensitizers, charge transfer processes involving the excited states can be studied by observing

(*) Pervenuta all'Accademia il 28 giugno 1978.

(**) To whom correspondence should be addressed: Cattedra di Chimica, Facoltà di Scienze, University of Milan; 20133 Milano, Via C. Saldini, 50.

the sensitized photocurrents [19-22]. Furthermore, attention has been drawn to the use of polycrystalline materials in place of single crystals [17] since, from the practical standpoint of realizing large scale electrochemical photocells, this kind of semiconductor electrode is highly preferable. As in energy conversion processes, one of the major factors to be considered is the energy conversion efficiency, which markedly depends on wavelength. We deemed it useful to undertake a study on this argument which so far has not been investigated in detail. In the present paper energy conversion efficiencies as a function of wavelength were measured in an electrochemical photocell similar to that described by Fujishima, Kohayakawa, and Honda [17], employing anodes coated with a titanium dioxide film and platinum black cathodes.

Although the bandgap of rutile is fairly large (3.05 eV) [23], allowing it to usefully capture only a small fraction of the solar radiation on the surface of the earth (only about 3 % occurs in the 315-400 nm range [24]), it is one of the very few semiconducting materials considered sufficiently stable when used as an illuminated anode in an aqueous electrochemical cell [25] [14, 16], even if some instabilities caused by aging effects in single crystal reduced rutile anodes have been recently reported [26]. In any case the illuminated TiO_2 electrode is very attractive, both because oxygen is evolved at potentials more than one volt lower than the thermodynamic oxygen evolution potential [27] and because hydrogen evolution has been proven at a suitable counterelectrode by giving a cathodic bias [17, 28] and/or by having catholyte and anolyte of different composition [17, 29] (photoassisted energy conversion [30]).

In order to compare this type of conversion with that of a photoelectrochemical cell employing a titanium dioxide film anode and an oxygen counterelectrode in such a way as to have oxygen evolution as a forward reaction and oxygen reduction at the cathode, energy conversion measurements have also been made with this latter kind of cell. No overall chemical change occurs in this system and the absorption of light results in the generation of electrical power [18].

EXPERIMENTAL

The titanium dioxide-film electrodes were prepared by the thermal oxidation of commercial 99.9 % titanium plates at 1300-1350 °C. These films, examined by X-ray powder analysis, showed patterns typical of the rutile structure. A slight reduction in vacuum improved electrical conductivity [31]. The film thickness was of the order of 10 μm , so that absorption of incident radiation was virtually complete at all investigated wavelengths.

Quantum yield studies were carried out with a 1000 W xenon arc lamp which was placed in the housing of a spectrophotometer assembly mounted on an optical bench and using a high intensity grating monochromator.

By means of quartz condensing lenses the irradiating beam was focused into a spectrophotometric quartz cell in the center of which the titanium dioxide-film electrode (1.45 cm^2) immersed in a 1 N NaOH solution was placed. This anolyte was separated from the catholyte ($0.5 \text{ M H}_2\text{SO}_4$ for the Fujishima cell or 1 N NaOH for the self-regenerative cell) by means of an agar-agar salt bridge. Platinum black was employed as the cathode (9.5 cm^2). The catholyte of the Fujishima cell was carefully deoxygenated, while that of the self-regenerative cell was oxygenated by bubbling oxygen through solution. The volume of gas evolving at the cathode of the Fujishima cell was measured by a suitably calibrated microburette. Voltage, current and power of the cell were obtained as a function of the load resistance during illumination at various wavelengths. Potassium ferrioxalate was used for actinometry, according to the method of Hatchard and Parker [32]. Energies as a function of wavelength were measured with a passing band of 6 nm which was also used for quantum yields measurements: in these experimental conditions energy values per unit time and surface ranged from 40 to $600 \mu\text{W cm}^{-2}$.

RESULTS AND DISCUSSION

Energy conversion in an electrochemical photocell, which consists of titanium dioxide as an anode, and platinum as a cathode, employing catholyte and anolyte of different composition as in the present paper—that is adding chemical energy to the system—occurs with the assistance of light. The short circuit current density and the open circuit voltage of the cell at various wavelengths are reported in Figure 1 a, in which the quantum efficiency and the energy conversion efficiency values are also shown. The quantum efficiency, defined as the current density at the titanium dioxide electrode divided by the flux of radiation (that is the electrons flowing per impinging photon) was determined under potentiostatic conditions for the saturation current. The values obtained by this method were only $20\text{--}35\%$ higher than those obtained from hydrogen evolution measurements. The energy conversion efficiency was evaluated as the ratio between the maximum power per unit surface of the titanium dioxide electrode and the radiation flux. In this way, a value not corrected for the added energy is obtained. In order to compare in Figure 1 a all values of current density and power, these were referred to a standard illumination of $300 \mu\text{W cm}^{-2}$.

As expected, all the curves show a sharp decrease near the bandgap energy. The figures agree fairly well with some recent values reported in the literature [29], even if they should be regarded only as representative, since different titanium dioxide films differ in their photoresponse depending on its preparation and physical characteristics [34]. The mechanism of this kind of energy conversion, which has been thoroughly discussed [14, 17, 27, 28, 29, 30, 33], justifies the relatively low quantum efficiency ($0.06\text{--}0.09$) obtained by this system, even in conditions of virtually complete absorption

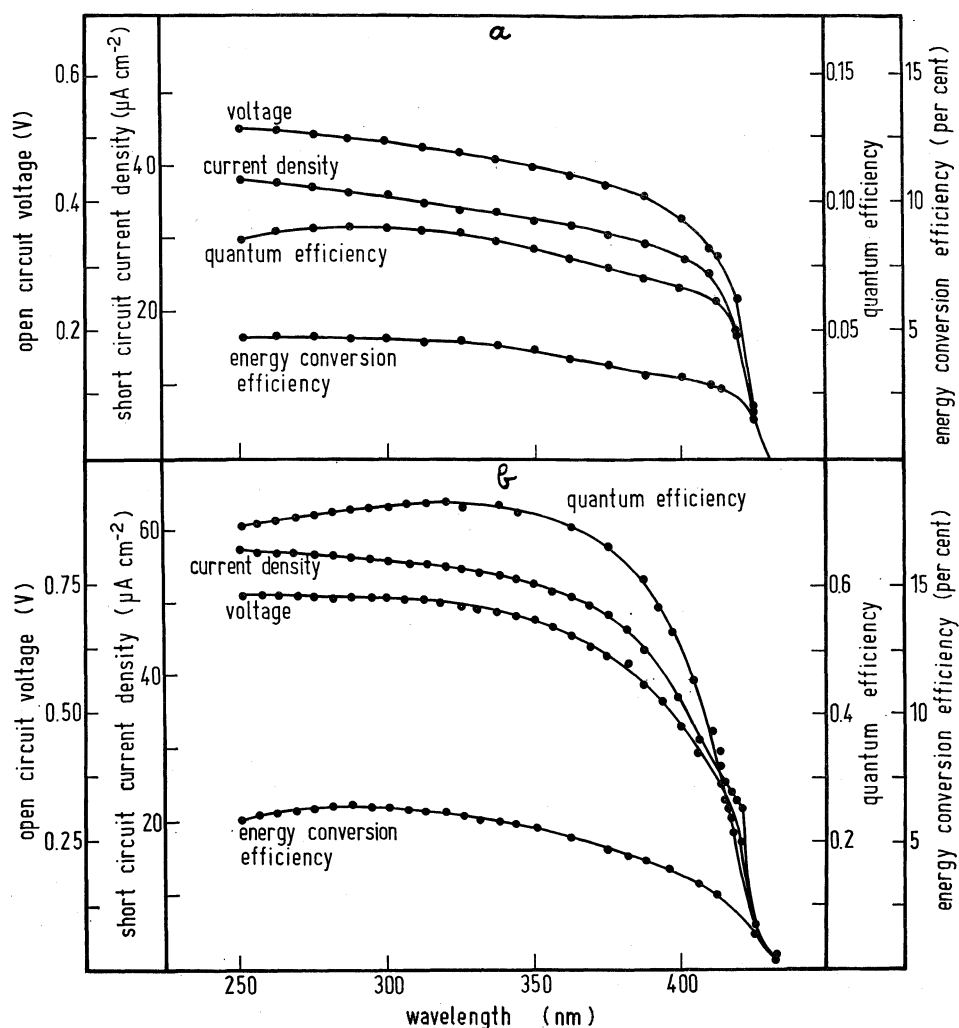


Fig. 1 a (above) - Short-circuit current density, open-circuit voltage, quantum efficiency and energy conversion efficiency for a two-compartment photoelectrochemical cell employing a titanium dioxide-film anode (1 N NaOH as anolyte) and a platinum black cathode (1 N N_2SO_4 as catholyte).

Fig. 1 b (below) - Short-circuit current density, open circuit voltage, quantum efficiency and energy conversion efficiency for a photoelectrochemical cell employing a titanium dioxide film anode, an oxygen counter-electrode (Pt black) and 1 N NaOH as electrolyte.

of radiation, and the comparable values of the energy conversion efficiency as well. Apparent values of 3-5 % were measured, but when these latter are corrected to account for the different anolyte and catholyte compositions, in terms of hydrogen ion activity, values lower by about one order of magnitude result. Consequently, the photoassisted electrolysis of water in the cell devised by Fujishima and Honda [14, 16], although attractive,

does not seem very promising when the technological and economic aspects are considered. The effect of wavelength on the cell characteristics quantitatively confirms the low efficiency as a solar cell, despite the necessity of employing an electrical or an electrochemical bias (difference of pH between anolyte and catholyte) to reach the equilibrium potential of the H^+/H_2 couple.

A more favourable situation, from the energetic point of view, is found in the electrochemical photocell when both anolyte and catholyte are formed by 1 N NaOH solution and the cell is working self-regeneratively. The short circuit current density, the open circuit voltage, the quantum efficiency and the energy conversion efficiency values for this cell are reported in Figure 1 b (referred to a standard illumination of $300 \mu W cm^{-2}$). The observed behaviour clearly indicates that this type of cell is able to very closely satisfy the ideal requirements, that is:

- 1) the photocurrent, in the current/potential curves, rises as rapidly as possible to its saturation value;
- 2) the saturation current, for a given radiation flux, is as large as possible;
- 3) the overpotential of the oxygen electrode, with the platinum black cathode in alkaline solution, is as small as possible.

The quantum efficiencies are satisfactorily high in the region where radiation is absorbed effectively, as is the overall energy conversion efficiency, the main losses for this latter being caused by the charge transfer processes at the electrode interfaces, particularly in the cathodic reaction.

Acknowledgement. Financial support from the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged.

REFERENCES

- [1] E. BECQUEREL (1839) - «Compt. Rend.», 9, 561.
- [2] W. G. ADAMS and R. E. DAY (1877) - «Proc. Roy. Soc.», A 25, 113.
- [3] Cfr. P. RAPPAPORT (1954) - «Phys. Rev.», 93, 246.
- [4] W. H. BRATTAIN and C. G. B. GARRETT (1955) - «Bell System Tech. J.», 34, 129.
- [5] R. WILLIAMS (1960) - «J. Chem. Phys.», 32, 1505.
- [6] H. BERG (1960) - «Naturwissenschaften», 47, 320.
- [7] M. HEYROVSKY (1966) - «Nature», 200, 880.
- [8] G. C. BARKER, A. W. GARDNER and D. C. SAMMON (1966) - «J. Electrochem. Soc.», 113, 1182.
- [9] H. GERISCHER (1966) - «J. Electrochem. Soc.», 113, 1174.
- [10] F. LOHMANN (1966) - «Ber. Bunsenges. Phys. Chem.», 70, 87.
- [11] H. GERISCHER (1966) - «Ber. Bunsenges. Phys. Chem.», 69, 578.
- [12] R. MEMMING and H. TRIBUTSCH (1971) - «J. Phys. Chem.», 75, 562.
- [13] H. R. SCHÖPPEL and H. GERISCHER (1971) - «Ber. Bunsenges. Phys. Chem.», 75, 1237.
- [14] A. FUJISHIMA and K. HONDA (1972) - «Nature», 238, 37.

- [15] A. FUJISHIMA, K. HONDA and S. KIKUCHI (1969) - « J. Chem. Soc. Japan », 72, 108.
- [16] A. FUJISHIMA and K. HONDA (1971) - « J. Chem. Soc. Japan », 74, 355.
- [17] A. FUJISHIMA, K. KAHAYAKAWA and K. HONDA (1975) - « J. Electrochem. Soc. », 122, 1487.
- [18] W. GISSLER, P. L. LENSİ and S. PIZZINI (1976) - « J. Appl. Electrochem. », 6, 9.
- [19] H. KIM and H. A. LAITINEN (1975) - « J. Electrochem. Soc. », 122, 53.
- [20] H. GERISCHER and H. TRIBUTSCH (1968) - « Ber. Bunsenges. Phys. Chem. », 72, 437.
- [21] H. GERISCHER and H. TRIBUTSCH (1969) - « Ber. Bunsenges. Phys. Chem. », 73, 850.
- [22] A. FUJISHIMA, E. SUGIYAMA and K. HONDA (1971) - « Bull. Chem. Soc. Japan », 44, 304.
- [23] R. G. BRECKENRIDGE and W. R. HOSLER (1953) - « Phys. Rev. », 91, 793.
- [24] M. D. ARCHER (1975) - « J. Appl. Electrochem. », 5, 17.
- [25] H. GERISCHER (1975) - « J. Electroanal. Chem. Interfacial Electrochem. », 58, 263.
- [26] L. A. HARRIS and R. H. WILSON (1976) - « J. Electrochem. Soc. », 123, 1010.
- [27] J. MANASSEN, D. CAHEN, G. HODES and A. SOFER (1976) - « Nature », 233, 97.
- [28] A. J. NOZIK (1975) - « Nature », 257, 383.
- [29] M. S. WRIGHTON, D. S. GINLEY, P. T. WOLCZANSKI, A. B. ELLIS, D. L. MORSE and A. LINZ (1975) - « Proc. Nat. Acad. Sci. U.S.A. », 72, 1518.
- [30] See Discussion to Reference [17], « J. Electrochem. Soc. ».
- [31] J. YAHIA (1963) - « Phys. Rev. », 130, 1711.
- [32] C. G. HATCHARD and C. A. PARKER (1956) - « Proc. Roy. Soc. », A 235, 518.
- [33] M. D. ARCHER in « Photochemistry », Spec. Period. Repts. (1976) vol. 7, pag. 569.
- [34] D. LASER and A. J. BARD (1976) - « J. Electrochem. Soc. », 123, 1027.