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ARTIGO

BEHAVIOR OF n-BaTiO₃ SINGLE CRYSTAL ELECTRODES IN A PHOTOELECTROCHEMICAL CELL

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ABSTRACT

We have observed that BaTiO₃ semiconductor electrodes can photoelectrolyse water without any applied potential for incident radiation greater than the band gap energy ($E_G = 3.15\text{eV}$). By photocurrent measurements the flatband potential was determined as being -1.3V vs SCE in an aqueous solution of NaOH 1M. A conversion efficiency of 2.5% and 1.0% was obtained for the cell operating under UV monochromatic irradiation in the photoelectrolytic and photovoltaic modes respectively. Under solar irradiation of 77 mW/cm^2 the conversion efficiency for the photovoltaic mode was 0.16%.

1. INTRODUCTION

Photoelectrochemical effects on n-BaTiO₃ electrodes have been studied in the last few years by several researchers [1-7]. It presents a relative interest as a chemically stable material during the photoelectrolysis process as well as by its photoelectrochemical capability for different uses as has been done for SrTiO₃, another member from the perovskite family.

However, a comparative study of the efficiencies of photoelectrochemical cells (PEC's) based on BaTiO₃, working with photoelectrolytic and photovoltaic modes, is lacking.

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A complete disagreement has also been noted between the experimental condition of the decomposition of water without any external polarization [4] and the flatband potential determinations, for single and polycrystalline electrodes [3, 5, 6].

In this paper we discuss the BaTiO₃ behavior, using it as a semiconductor electrode in a photoelectrochemical cell, operating both in the photoelectrolytic and photovoltaic mode in basic solution. The flatband potential is determined from photocurrents measurements and its value compared with those reported in the literature. We also have determined characteristic parameters of the cell operating under sun and UV-monochromatic light.

2. EXPERIMENTAL PROCEDURE

2.1 Sample anode preparation

The sample of BaTiO₃ were kindly donated by Dr. J.P. Remeika (Bell Tel. Labs). They were flux grown which yields thin single crystal plates of self-polished surfaces, the *C* axis being perpendicular to them. The large crystal faces were used as electrode surfaces. The dielectric starting materials were submitted to heat treatments at 800°C from 5 to 15 minutes in a reducing atmosphere (8% H₂, 92% N₂) and then rapidly cooled to room temperature. This resulted in dark coloured samples with resistivities varying from 2.4×10^2 to $5.0\ \Omega\text{-cm}$. Ohmic contact was provided by rubbing a Ga-In (10% Ga, 90% In) alloy on the back crystal surface prior to attaching a Cu wire by means of Ag paste.

The electrode sample was then incorporated into a polyester capsule, leaving a front surface of 0.10 cm² free for contact with the electrolyte.

2.2 Electrochemical cell and measurements

The electrochemical measurements were performed in 1M NaOH electrolyte under potentiostatic conditions, using a three compartment cell, provided with a flat quartz window on the BaTiO₃ side for the experiments with light, in which the working electrode (n-BaTiO₃) and counter-electrode (10 cm² Pt foil) were separated by a glass frit. The potential was controlled with reference to a saturated calomel reference electrode (SCE). Thus, all voltages cited in this paper are referenced to the SCE unless stated otherwise.

The photocurrents were measured at 10 mW/cm² UV radiation of 3650 Å, using a 100W pressure lamp with the beam focussed on the semiconductor electrode through an ORIEL bandpass filter (Mod. n° G-522-3650; $\lambda = 3650 \pm \pm 100$ Å). The light intensity was measured by a Laser Precision Radiometer (RK 5100) connected to a pyroelectric sensor (RKP 541) with flat response between 0.3 and 1.2 μ m. A digital electrometer (Keithley 616) was used to measure the potential vs SCE of the counter-electrode.

When necessary the electrolyte in the counter-electrode compartment was purged with ultrapure N₂ gas (White Martins Co.) as delivered. The solutions were prepared from commercially available reagents, p.a. grade. Before each experiment the samples were rinsed with methanol (CH₃OH) and distilled water.

3. RESULTS AND DISCUSSION

The voltametric behavior for both n-BaTiO₃ and Pt electrodes in a 1M sodium hydroxide (NaOH) solution are given in Figs. 1a and 1b for the case where the electrolyte in the Pt compartment was deoxygenated by bubbling N₂ through the solution (Fig. 1a) and with the electrolyte in the Pt compartment open to air and dissolved oxygen present in the solution (Fig. 1b). Both configurations are recorded at a scan rate of 5 mV/s, with slowly chopped light that permits to obtain at the same time I-V vs SCE curves in the dark and under illumination for the semiconductor electrode. It was observed that the results do not depend on the oxygen dissolved in the BaTiO₃ compartment.

In the first case (Fig. 1a) the n-BaTiO₃ and Pt I-V vs SCE curves intercept at a potential around -1.07 V that is above the potential for hydrogen generation (-1.04 V vs SCE at pH = 13.3) at the dark Pt counter-electrode. At the interception point that indicates a short circuit condition between BaTiO₃ and Pt electrodes, a small anodic photocurrent density of 0.11 mA/cm² was maintained with generation of hydrogen and oxygen in the Pt and BaTiO₃ electrodes, respectively. This results shows that the BaTiO₃ cell can photoelectrolyze water without any applied potential while operating in the photoelectrolytic mode (optical to chemical conversion). In the second case (Fig. 1b) the

n-BaTiO₃ and Pt I-V vs SCE curves intercept at a potential around -0.25 V with a short circuit photocurrent density of 0.24 mA/cm².

In this case there is no photoelectrolysis of water. The optical energy is converted directly in electric energy and the cell is operating in the photovoltaic mode.

In both figures, the I-V vs SCE curves of the n-BaTiO₃ electrode show an anodic photocurrent commencing at -1.30 V. This onset photopotential, V_{on} , can be identified as the flatband potential, V_{FB} , of the n-BaTiO₃ electrode, since the semiconductor was under intense illumination. Thus, the V_{FB} must be at least -1.30 V vs SCE for n-BaTiO₃ in a solution of 1 M NaOH (pH = 13.3). This result disagrees with those reported by Nasby and Quin /3/ and by Frese and Kennedy /5/ that have been determined by capacitance measurements a value of $V_{FB} = -0.80$ V vs SCE in a solution of 2 M NaOH (pH = 13.6) for the single crystal and polycrystalline n-BaTiO₃ electrodes, respectively. However, it is consistent with the fact that in order for a cell to operate spontaneously in the photoelectrolytic mode without any applied potential, it is necessary that under illumination, the flatband potential becomes more negative than the potential for the evolution of hydrogen. We believe that the disagreement between the flatband potential of the n-BaTiO₃ determined in this work and those reported in the literature /3,5,6/ is due to the fundamental differences in the used techniques. More detailed investigations on this matter are being carried out in our laboratory and will be reported in the near future. It is observed still, in both figures, a negligible dark current with anodic polarization. This behavior was observed up to 3.0 V, indicating a blocking of the depletion layer formation.

From a device viewpoint the important characteristic is the current-voltage data where the voltage is measured between the n-BaTiO₃ and Pt electrodes. These data are shown in Fig. 2a and Fig. 2b for the cell operating in the photoelectrolytic and photovoltaic mode, respectively, and were obtained from the curves of Fig. 1a and 1b.

The description of the conversion efficiency of a photovoltaic cell applies also to the photoelectrochemical variety (photovoltaic mode, Fig. 2b) and the maximum power point is determined as $P_{max} = I_{sc} \times V_{oc} \times FF$, where I_{sc} is the short-circuit current, V_{oc} the open circuit voltage and FF the fill factor (a measure of the squareness of the curve). The conversion efficiency ϕ_c , is given then by

$$\phi_c = P_{max}/P_{inc} \quad (1)$$

where P_{inc} is the incident light power.

For PEC's operating in the photoelectrolytic mode (which have two redox couples) producing, therefore, a chemical product, it is possible to apply the model for solid state devices (Eq. 1) since we define an effective power, P_{eff} , produced by the cell and given by /8/

$$P_{eff} = IV_{eff} = I(\Delta V_{redox} - V_{appl}) \quad (2)$$

or

$$P_{\text{eff}} = I(V_{\text{electrolysis}} - V_{\text{appl}})$$

where I is the current flow, $\Delta V_{\text{redox}} (= V_{\text{electrolysis}})$ is the voltage difference between the redox couples, and V_{appl} is an external voltage, that usually must be applied

to drive the cell, depending on how large is the electron affinity of the semiconductor. Ed. (2) is a general power expression valid for a cell which not only drives the chemical production process but may, in addition, produce electrical power by connecting a load between anode and

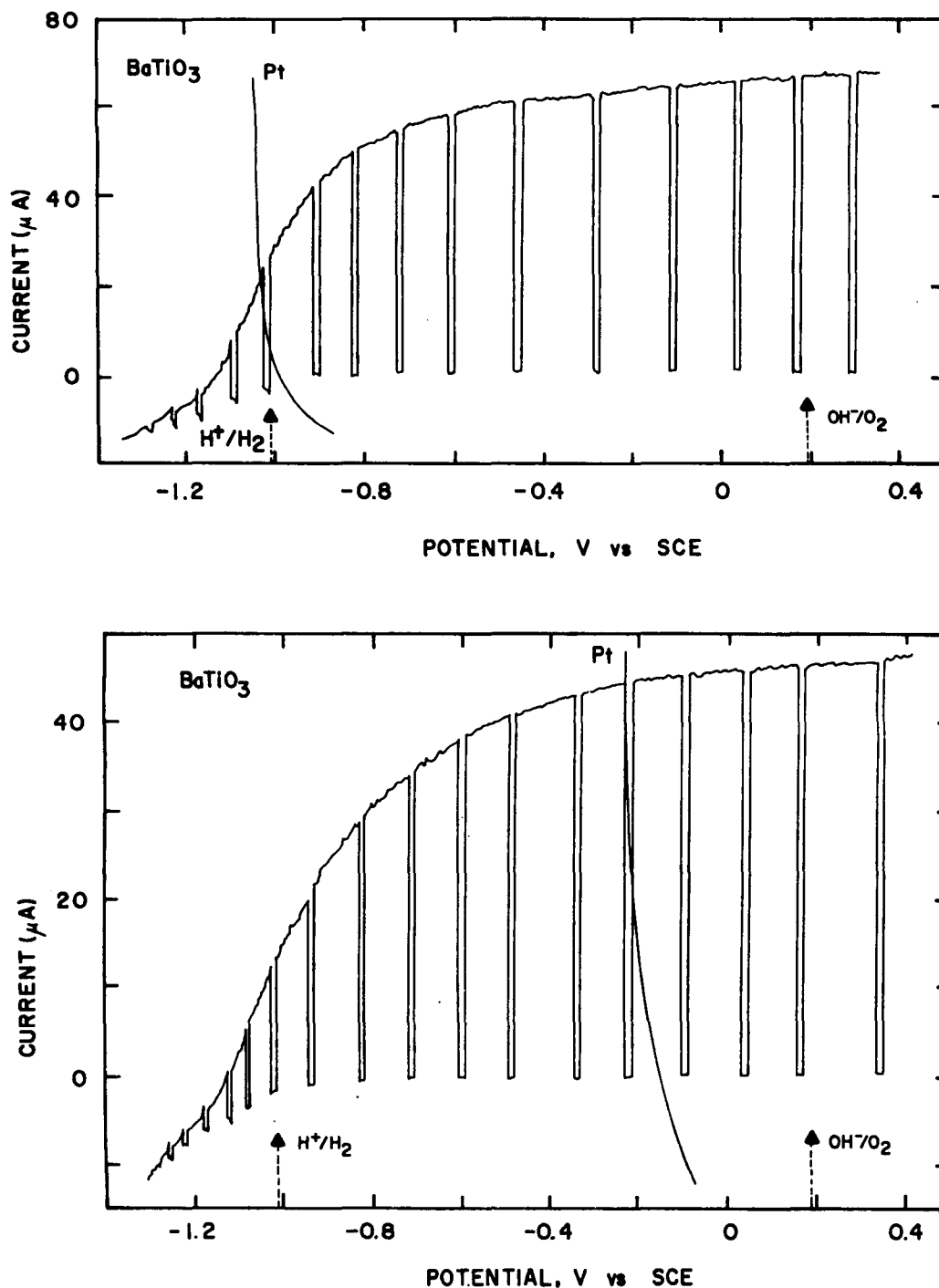


Figure 1. Current-voltage curves for n-BaTiO₃ and Pt electrodes of a photoelectrochemical cell into a 1 M NaOH electrolyte, PH = 13.3 under 10 mW/cm² light intensity of wavelength $\lambda = 3650 \text{ \AA}$. Scan rate: 5 mV/s. The light was chopped to obtain the I-V behavior under dark and illuminated conditions. The arrows indicate the standard potentials of the redox couples, H⁺/H₂ and OH⁻/O₂. Semi-

conductor electrode area: 0.20 cm².

- Photoelectrolytic mode: the electrolyte in the Pt compartment of the cell was deoxygenated by bubbling N₂ through the solution.
- Photovoltaic mode: the electrolyte in the Pt compartment is open to air, and having dissolved oxygen in the solution.

cathode. Thus the general equation for conversion efficiency of PEC's operating in the photoelectrolytic mode can be written as

$$\phi_c = P_{\text{eff(max)}}/P_{\text{inc}} \quad (3)$$

Then, in the Figs. 2a and 2b the description and determination of the maximum power point is the same as for conventional photovoltaic cells.

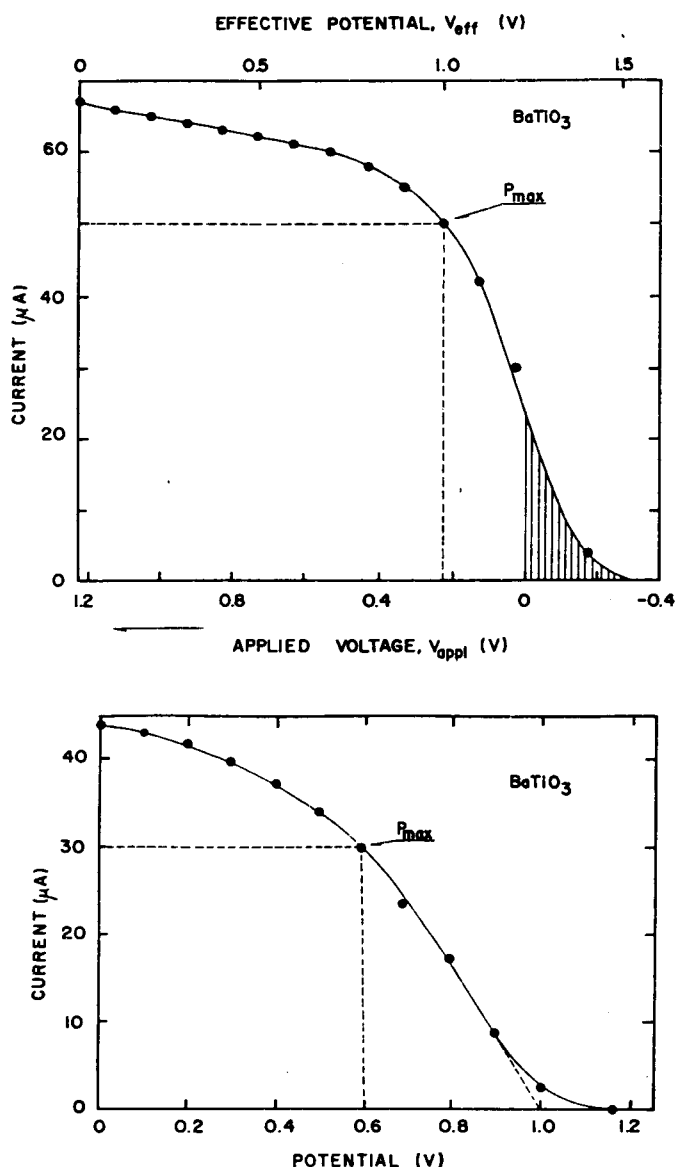
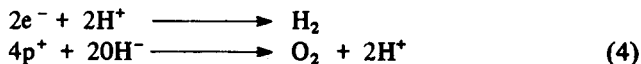


Figure 2. Current-voltage characteristics of an n-BaTiO₃/1M NaOH/Pt photoelectrochemical cell.

- Photoelectrolytic mode showing the I - V_{eff} and I - V_{appl} characteristics obtained from curves of Fig. 1a.
- Photovoltaic mode showing the I - V characteristics obtained from curves of Fig. 1b.

We can observe in the Fig. 2a that the BaTiO₃ can photoelectrolyse water without any applied potential but its maximum conversion efficiency is obtained only when

an external voltage of 0.23 V is applied. Using Eq. (3) we have determined for monochromatic light intensity of 10mW/cm² ($\lambda = 3.650 \pm 100 \text{ \AA}$) a conversion efficiency $\phi_c = 2.5\%$. The fill factor was 0.45. From the Eq. (2) note that $I \times V_{\text{electrolysis}}$ is equal to stored power as H₂ and $I \times V_{\text{appl}}$ represents the power supplied by the external source. Then, if the applied voltage is negative both chemical and electrical energy can be obtained /9/. Thus in the Fig. 2a (optical to chemical conversion) photocurrent at $V_{\text{appl}} > V_{\text{electrolysis}} (= 1.23 \text{ V})$ represents chemical storage, and photocurrent at $V_{\text{appl}} < 0$ signifies chemical and electrical storage (dashed area). In this cell we have noted H₂ and O₂ evolution in the Pt and BaTiO₃ electrodes respectively, the decomposition reaction being given, as in the TiO₂ and SrTiO₃ electrodes /10,11/ by



where e^- and p^+ represent electrons and holes that react with the acceptors (H^+/H_2) and donors (OH^-/O_2) species in the electrolyte (see Fig. 3a).

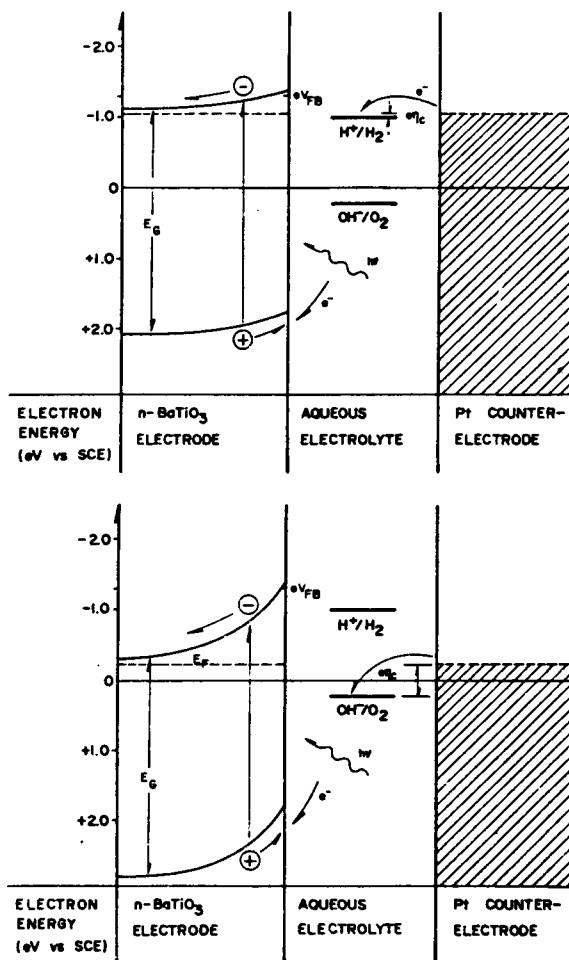
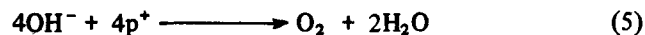


Figure 3. Energy level diagram for an n-BaTiO₃/1M NaOH/Pt photoelectrochemical cell at short circuit conditions.

- Photoelectrolytic mode illustrating the decomposition of water into H₂ and O₂.
- Photovoltaic mode producing electricity no chemical products.

When operating in the photovoltaic mode (Fig. 2b) this cell shows a conversion efficiency $\phi_c = 1.0\%$. The short-circuit photocurrent density was $J_{sc} = 0.22 \text{ mA/cm}^2$, the open circuit photovoltage $V_{oc} = 1.15 \text{ V}$ and the fill factor $FF = 0.41$. In this instance, in the illuminated n-BaTiO₃ anode, there is a reaction with oxygen evolution that has been studied with both single crystal [12,13] and thin film [14] materials, represented by



The reaction in the Pt is the well-known reduction of oxygen



that is just the reverse of the anodic reactions, except that electrons participate in it instead of holes. Here, OH^-/O_2 is the reversible redox couple as is shown in Fig. 3b. In this operating mode the conversion efficiency of the cell is smaller than in the photoelectrolytic one. It should be pointed out that the Pt counter-electrode has a large over-potential η_c relative to the redox couple (OH^-/O_2) level. A counter-electrode, as an oxygen cathode used by Bard [15], with a potential levelling with the couple OH^-/O_2 , would improve its efficiency.

The voltages and currents of the cell in were photovoltaic mode for different load resistances R_L , were measured in bright sunlight, (77 mW/cm^2). From these data the I vs V characteristic was built and the conversion efficiency

($\phi_c = 0.16\%$) determined. Under the optimum load conditions the fill factor was $FF = 0.45$, the short circuit photocurrent density $J_{sc} = 0.24 \text{ mA/cm}^2$ and the open circuit photovoltage $V_{oc} = 1.00 \text{ V}$. The internal resistance of the cell was estimated to be $10^3 \Omega$ from the power versus load resistance curves. Of course, the efficiency for solar energy conversion is much lower than for monochromatic light ($\lambda = 3650 \text{ \AA}$) because only 3% of the photons of the solar spectrum ($\lambda = < 3936 \text{ \AA}$) would be absorbed at a BaTiO₃ electrode [16]. In this region of the spectrum the quantum efficiency is variable as shown in Fig. 4. The high value of the internal resistance was attributed to an inadequate geometrical disposition of the cell electrodes.

4. CONCLUSIONS

In the present work BaTiO₃ single crystal electrodes have been used as photosensitive elements in photoelectrochemical cells operating in both photoelectrolytic and photovoltaic modes.

The results show that the BaTiO₃ electrodes in basic solutions can photoelectrolyse water without any applied potential when exposed to sunlight and this is consistent with a flatband potential value of -1.3 V vs SCE that we have determined by photocurrent measurements in 1M NaOH solution.

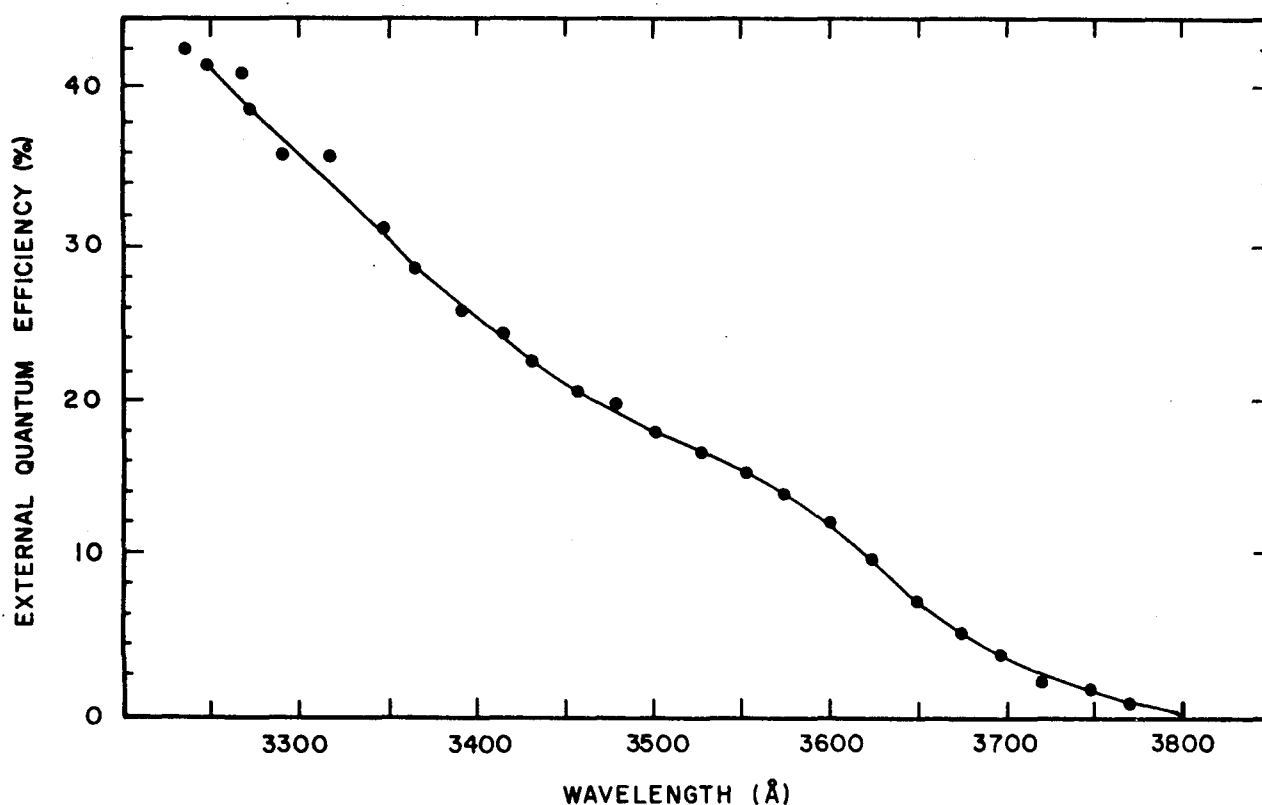


Figure 4. External quantum efficiency vs wavelength of an n-BaTiO₃ electrode into aqueous electrolyte (1M NaOH, pH = 13.3).

The conversion efficiency for the photoelectrolytic mode was larger than for the photovoltaic one. We attribute this difference to the fact that the Pt counter-electrode has a large over-potential relative to the redox couple (OH^-/O_2) level.

ACKNOWLEDGMENTS

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ARTIGO

SYNTHESIS OF WYERONE BENZENE ANALOGUE, ITS EPOXIDE DERIVATIVE AND OTHERS α -ALKYNYLCARBONYL COMPOUNDS

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ABSTRACT

Methyl 3-[4-(hept-4Z-en-2-yn-1-one)-phenyl]-prop-2E-enoate, its epoxide derivative and others α -alkynylcarbonyl compounds were prepared through Grignard's reaction.

INTRODUCTION

Wyerone (1) and wyerone-epoxide (2) are phytoalexins of plants belonging to Papilionaceae family^{1,2,3}. Their tiophenic structural analogues were synthesized by Thaller