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N. Alonso V., M. Beley, Philippe Chartier, V. Ern. Dye sensitization of ceramic semiconducting electrodes for photoelectrochemical conversion. *Revue de Physique Appliquée*, 1981, 16 (1), pp.5-10. 10.1051/rphysap:019810016010500 . jpa-00244894

HAL Id: jpa-00244894

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Submitted on 4 Feb 2008

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Classification
Physics Abstracts
33.20K — 73.40M — 86.30K

Dye sensitization of ceramic semiconducting electrodes for photoelectrochemical conversion

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(Reçu le 28 juillet 1980, accepté le 13 octobre 1980)

Résumé. — Des électrodes céramiques semi-conductrices de ZnO ont été sensibilisées par des colorants Rhodamine B et complexes de Ru (II). Ainsi, la photoréponse des cellules photoélectrochimiques, stabilisées en utilisant l'hydroquinone comme régénérateur, peut être étendue au domaine visible (400-600 nm). Une tension en circuit ouvert de 0,4 eV et des courants de court-circuit jusqu'à 0,2 mA peuvent être obtenus en utilisant des photons dont $h\nu < E_{\text{gap}}$ du semiconducteur.

Abstract. — Semiconducting ZnO ceramic electrodes have been sensitized by Rhodamine B and Ru (II) complex dyes. The photoresponse of the stable electrochemical cells can thus be extended into the visible region (400-600 nm) using hydroquinone as supersensitizer. Open circuit voltage of 0.4 V and short circuit currents up to 0.2 mA can be obtained with photons of $h\nu < E_{\text{gap}}$ of semiconductor.

1. **Introduction.** — Photovoltaic conversion of solar energy with solid state p-n or metalsemiconductor Schottky barrier junctions has found already extensive application in low power installations. Efficiencies near the theoretical values have been obtained, but the cost of fabrication of reasonably good junctions remains high, and considerable research and development effort, notably with amorphous materials is still actively pursued to bring down the cost of the device. Recently several laboratories throughout the world have started parallel research on the feasibility of using electrochemical cells. An electrochemical cell consists simply of a p- or n-type semiconductor, an electrolyte, and a counter-electrode to collect the charge carriers. In such a system the cost of fabrication of the junction is eliminated, since the simple immersion of the semiconductor in the electrolyte creates the depletion layer which is necessary to obtain the

photovoltaic effect. Moreover, with transparent electrolytes, reflection and absorption losses due to the metallic contact on the solid state device are eliminated. Besides, scientific interest is accrued by the fact that, under suitable conditions, it could also work as a solar energy-assisted photochemical or photoelectrochemical device which splits water for the purpose of generating chemical energy in the form of a storable fuel.

An obvious problem with photoelectrochemical cells is their long range stability since, in general, and more like so with low band-gap materials, anodic dissolution of the electrode competes with the redox reaction, and a corrosion of the electrode takes place. The stability problem has been object of intensive studies and several stable electrode-redox couples have been claimed. Recent reviews can be found in references [1, 2, 3]. Other approach is the use of stable high band-gap semiconductor oxide electrodes, e.g. $E_{\text{gap}} > 3$ eV, like TiO₂, ZnO, SrTiO₃, SnO₂, and to extend the useful spectral response range down into the visible region by sensitization with organic dye molecules. Photosensitization with organic dyes has been studied for some time in conjunction with photographic and electrographic processes. More recently,

(*) This work was supported by grant PIRDES ATP 3866 of the Centre National de la Recherche Scientifique in conjunction with the Laboratoire de Spectroscopie and the Laboratoire d'Applications Electroniques.

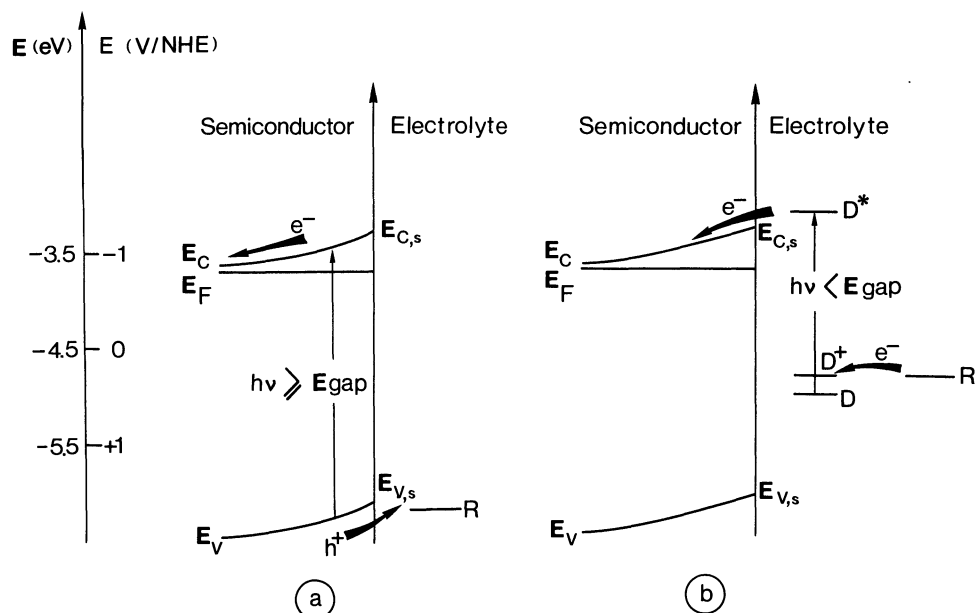
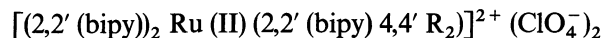


Fig. 1. — Schematic energy diagram of the photovoltaic effect for a n-type semiconductor in an electrolyte : a) without sensitization, b) sensitized with an organic molecule having energy levels D, D*, D⁺ corresponding to the ground, excited (triplet or singlet) and oxidized states. The excitation D → D* is obtained with photons with $h\nu < E_{\text{gap}}$ of semiconductor. The level R symbolizes the energy of a regenerating species in the electrolyte which assures reduction of the molecule back to its ground state. The correspondence of energy scales as customarily used in solid state physics (zero at vacuum level) and in electrochemistry, where the normal hydrogen electrode (NHE) is used as reference is shown on the left. In the present work saturated calomel electrode (SCE) is used as reference, the scale transformation being $E(\text{V/SCE}) = E(\text{V/NHE}) - 0.24 \text{ V}$.

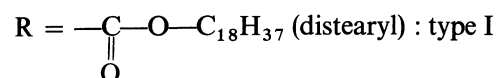
an extensive research program has been started all over the world to investigate, both from a theoretical and a practical point of views, the sensitization by organic dyes of the interface of semiconductor-electrolyte systems as potential candidates for solar energy conversion by stable, wet photoelectrochemical cells. A schematic energy diagram of the principle of operation is shown in figure 1. A review up to 1976 has been given by Gerischer and Willig [4]. Later work can be found in references [5-21]. Most of the work has been done on single crystals, with exception of SnO₂ films [18-20] and ZnO [6, 7] ceramic electrodes. With single crystals the cost of the cell would not likely be competitive with a solid state device, so that the most promising aspect of photoelectrochemical conversion is that using polycrystalline semiconducting electrodes, e.g. thin films or ceramics. Sensitization of ZnO ceramic electrodes has been performed [6, 7] by using rose bengal dye which requires the I₃⁻/I⁻ redox couple as regenerator. Unfortunately, such an electrolyte absorbs in the visible region. It is interesting thus to investigate others systems in which dyes in conjunction with a transparent electrolyte can be used.

Organometallic dyes such as Ru(bipy)₃²⁺, i.e. tris(2,2' bipyridine) ruthenium (II), and related complexes have been increasingly attracting attention since the first report [22] of their ability to induce electron transfer reaction of the excited state, and the work by Creutz and Sutin [23] who pointed out the possibility of decomposition of water induced by visible

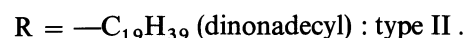
light. Recent research development in this field can be found in references [24] to [26]. The ground state complex absorbs visible light to form a d to π* charge transfer excited state which is relatively long lived (lifetime 0.6 μs in water) [22] as compared to conventional organic dyes (lifetime about 10⁻⁹ s). It seems that this excited state is a triplet charge transfer state. TiO₂ single crystals have been already sensitized with the Ru(bipy)₃²⁺ dye by Clark and Sutin [13] and later by Hammet *et al.* [14]. Also, sensitization has been obtained on the same electrode by chemical attachment of the dye on the crystal [12]. Chemically stable electrode was then obtained, but the photocurrent excitation spectrum did not show the characteristic absorption peak of the dye at ~ 450 nm. Memming and coworkers [18-20] have sensitized SnO₂ films, one of their techniques [19] consisted of applying monolayers by the Langmuir-Blodgett method of the Ru(II) complexes of the type :



where :



or



Also, recently, Mackor and Schonmann [15] have reported sensitization of pure and doped SrTiO₃

single crystals with the type II dinonadecyl complex of Ru (II) although the, simpler, complex Ru (bipy)₃²⁺ seems not sensitize SrTiO₃ single crystals [13].

In this work we wish to report studies of sensitization of semiconducting ZnO ceramic electrodes with Ru (II) dye molecules of type II. As this dye absorbs at ~ 450 nm, we have also investigated the feasibility of extending the spectral response towards longer wavelengths by using a mixture of Ru (II) and Rhodamine B (RhB) dyes adsorbed on the electrode.

2. Experimental. — Ceramics of ZnO (1.2 cm in diameter) were prepared from commercial high grade zinc oxide powder (Merck pro analysi) by sintering in two steps. The pellets were first moulded by compression (10 ton.) before firing in air at 1 000 °C for 3 h, and quenched. It were then ground into fine powder, pressed again into disks and heated at 1 300 °C for 3 h, and quenched. The samples obtained by this method were semiconducting with a resistivity ~ 10³ Ω.cm at room temperature. Contacts on the back surface were made by attaching a fine copper wire with silver paste (Degussa 2000) which makes an ohmic contact with the ceramic. The samples were then mounted in glass tubes and moulded with an epoxy resin. Prior to use, the front surface of the electrode was etched for 3 min. in 5 N HCl solution which attacked the surface exposing grain (typically 20 μ) boundaries as observed by microscopy.

All electrolytes were made with distilled water. The base electrolyte was 1.5 M KCl with 5 × 10⁻³ M hydroquinone (H₂Q) which served as dye reducing agent. Before each experiment the electrolyte was purged with nitrogen. Prior to the application of the dye each electrode was tested for a correct *I-V* Schottky barrier rectifying characteristics. The electrodes were coated with the dye as follows. The electrode was immersed in a 10⁻³ M acetonitrile solution of the Ru (II) complex, type II, for 30 min, then washed with distilled water in which the dye is insoluble, and dried. On several electrodes prepared in this way RhB was deposited by dipping for few seconds in 10⁻³ M Rhodamine B in acetonitrile solution. After drying the electrode were washed with distilled water to eliminate excess RhB deposited on the sample. Tests to sensitize simultaneously with both dyes by immersion in a 10⁻³ M Ru (II) complex + 10⁻³ M RhB acetonitrile solution gave only electrodes sensitized by the Ru (II) complex indicating preferential adsorption of the organometallic dye on the ZnO ceramic surface.

The experimental setup is shown in figure 2. The semiconductor electrode and a platinum wire counter-electrode were placed in close proximity to each other. A saturated calomel reference electrode (SCE) was used to control the working electrode potential. A 150 W xenon arc lamp served as a light source, which was passed through a water filter followed by a monochromator (Jobin Yvon H25). In some experiments the monochromator was replaced by a C.S.

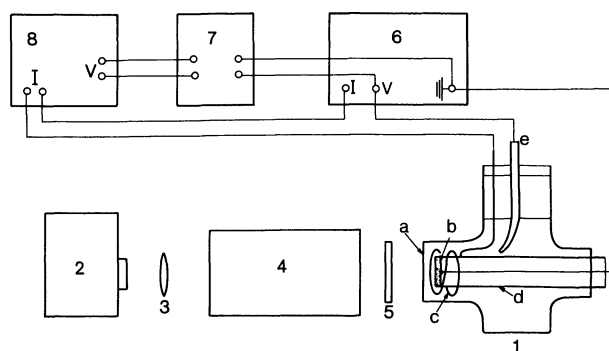


Fig. 2. — Experimental setup : 1 Cell (a, flat window ; b, semiconducting electrode ; c, platinum counter-electrode ; d, glass tube ; e, saturated calomel electrode (SCE)); 2 a 150 W XBO xenon arc lamp ; 3 Lens ; 4 Monochromator ; 5 Filter ; 6 Potentiostat ; 7 Digital voltmeter with analog output ; 8 XY recorder.

3-72 Corning filter with which a broad band excitation in the visible range (400-700 nm) is obtained. The potentiostatic measurements were done in a standard manner with a potentiostat (Tacussel type P.R.T. 2000) with which the current-voltage characteristics were recorded on a X-Y recorder. The exciting light intensity was determined by means of a thermopile (Kipp-Zonen) together with a microvoltmeter. An electrolyte layer with thickness corresponding to the experimental distance between the cell window and the photoelectrode was inserted into the light beam to correct for any absorbance or reflection so that the actual intensity falling on the sample could be estimated. All data were normalized to a constant, independent of λ , incident light power.

3. Results and discussion. — In the dark the rest potential of the ZnO electrode in the 1.5 M KCl electrolyte (pH \approx 6.5) was reproducibly found in the ~ + 50 mV/SCE region. The value was the same both with the uncoated and with the dye-covered electrodes. Furthermore, this dark rest potential is insensitive to the presence of hydroquinone (H₂Q) or even of quinhydrone (QH₂Q) in the electrolyte, that is, the semiconductor electrode doesn't pick up the redox potential of the Q/H₂Q couple. The dark current was found to be sensitive to the presence of O₂ in the electrolyte. It increases by a factor of 2-3 when O₂ is bubbled through a previously outgassed solution. In the photoexcited experiments the platinum counter-electrode potential was typically + 0.140 V/SCE. This potential is not well thermodynamically defined because of the absence of quinone in the hydroquinone containing solution. Thus, all experiments were performed under potentiostatic conditions (*vs.* SCE). The solutions were always outgassed and photocurrent action spectra obtained with the ZnO electrode polarized at + 50 mV/SCE so that the dark current could be considered as negligible in the experiment.

Figure 3 shows the photocurrent response as a function of wavelength for a ceramic ZnO electrode sensitized with the Ru (II), type II complex. For

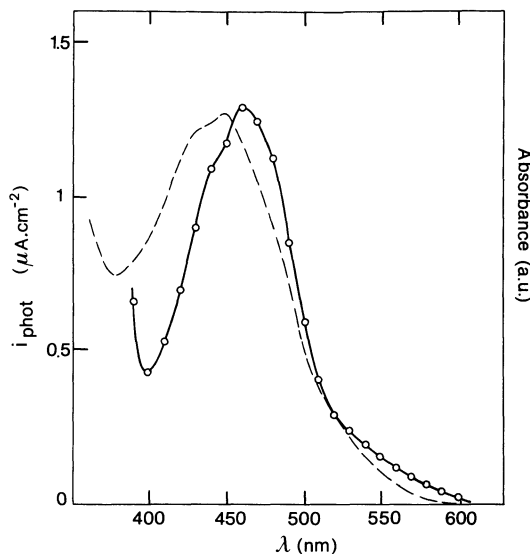


Fig. 3. — Photocurrent action spectrum of a ZnO ceramic electrode sensitized with the dinonadecyl Ru (II) complex dye (type II shown in text). The electrode is held at + 50 mV/SCE and excited at a constant light power of $0.28 \text{ mW} \cdot \text{cm}^{-2}$ throughout the spectrum. The dashed curve shows for comparison the absorption spectrum (in a.u.) of a 10^{-3} M acetonitrile solution of the dye.

comparison, the absorption profile (a.u.) of the dye in a 10^{-3} M acetonitrile solution is also shown. Both curves show similar, well defined, structure but the photocurrent peak is shifted towards the longer wavelengths. Such red shift is usually observed in semiconductor sensitization responses and has been attributed by Gerischer [27] to a stronger polarization interaction of the molecular excited state with the semiconductor as compared to that of the ground state. This observation agrees with the results on SnO_2 films by Memming *et al.* [19], but contrasts with the results of Anderson *et al.* [12] who obtained a featureless photocurrent action spectrum with derivatives of $\text{Ru}(\text{bipy})_3^{2+}$ chemically attached to TiO_2 crystals. Figure 4 shows the photocurrent response of the same electrode which has been subsequently sensitized with Rhodamine B dye as described previously. The photoresponse extends now into the yellow region showing the characteristic peak of RhB sensitization at $\sim 560 \text{ nm}$. The insert gives, for comparison, the response of a ceramic ZnO electrode coated just with RhB. This RhB excitation spectrum is analogous to that observed by Gerischer *et al.* for ZnO single crystals [4]. The overall maximum monochromatic quantum efficiency ($\approx 1.5\%$) is obtained at the Ru(II) complex peak and is the same whether or not the electrode has been also sensitized with RhB. This seems to indicate that partial coverage by Ru(II) complex dye takes place at selective sites of the ceramic surface and that the RhB molecules adsorb at different sites. This may explain the relatively small quantum efficiency although other effects like a high charge carrier-recombination rate at the ZnO-electrolyte interface or a small dye-semiconductor charge transfer rate, as compared to the direct to the ground state,

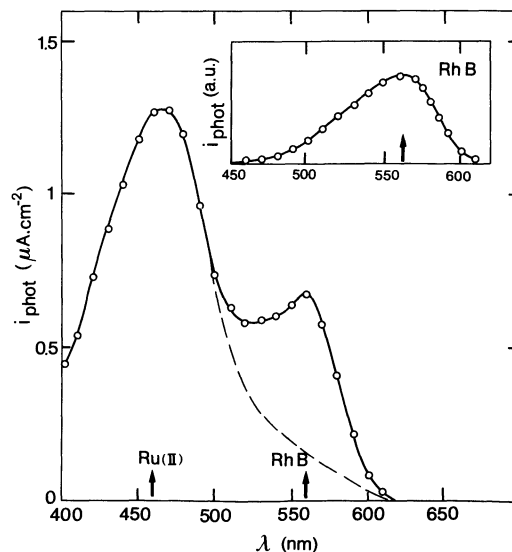


Fig. 4. — Photocurrent action spectrum performed under the same conditions as in figure 3 but with the ZnO electrode subsequently sensitized with Rhodamine B dye as described in text. The dashed extension of the Ru (II) complex peak corresponds to data as obtained prior to Rhodamine B sensitization (Fig. 3). The insert illustrates the photoresponse of a ZnO ceramic electrode when sensitized just with the Rhodamine B dye.

fluorescent or non-radiative, deactivation rate of the molecular excited state, cannot be yet ruled out.

An important parameter, useful to compare the performance of the ceramic semiconductor with that of a single crystal, is the flat band potential E_{fb} which gives a measure of the band bending obtained in the depletion layer at the semiconductor surface in contact with the electrolyte. As pointed out by Gerischer *et al.* [4] the flat band potential can be obtained from the $I-V$ characteristics of the sensitized cell, since the potential (e.g. *vs.* SCE) for the onset of the photocurrent is a measure of E_{fb} because, for dyes whose excited state lies above the surface edge of the valence band, as shown in figure 1, injected electron flow will start with the onset of the bending of the band. Figure 5

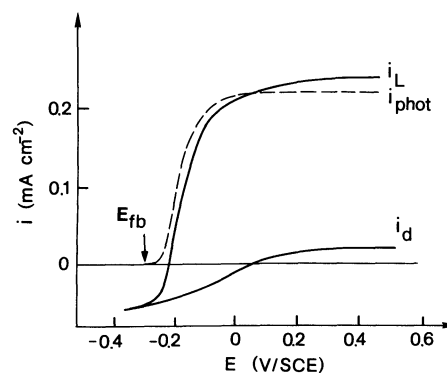
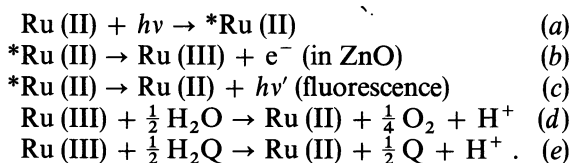


Fig. 5. — Extended current-voltage characteristics of a doubly sensitized ZnO ceramic in the dark (curve i_d) and under broad band (400-700 nm) excitation in the absorption region of the dyes (curve i_L). Subtraction of the dark current yields the characteristics i_{phot} (dashed curve). The onset of the photocurrent occurs at a flat band potential of $E_{fb} = -0.3 \text{ V/SCE}$.

shows the I - V characteristics of a doubly sensitized ZnO electrode. The dark current (i_d) is shown together with the characteristics (i_L) obtained with a broad band (400-700 nm) visible light excitation of the dyes. After subtraction of the dark current the characteristic i_{phot} (dashed curve) is obtained with an onset at the flat band potential $E_{\text{fb}} \simeq -0.3$ V/SCE. This value is close to the value predicted for single crystals of ZnO with the law [28] $E_{\text{fb}} = E_{\text{fb}}^0 - 0.060 \text{ pH}$ and using the value of $E_{\text{fb}}^0 = -0.38$ V/SCE given by Dewald [29] at pH 8.5. It seems thus that the photovoltaic effect observed here occurs mainly at grains whose surfaces have electrochemical properties similar to that of single crystals of ZnO.

It is worthwhile to analyse the role of hydroquinone (H_2Q) as supersensitizer of the Ru (II) complex dye in the regenerative cell. It has been shown by several authors [12-15, 18, 19] that the product of oxidation of the excited $^*\text{Ru}$ (II) state, that is, the corresponding Ru (III) oxidized form can oxidize H_2O molecules without the need of any other reducible species in the electrolyte. This is due to the fact that the respective standard redox potentials for the different Ru (II) complexes lie in the ranges $E_{\text{Ru(III)/Ru(II)}}^0 = 0.85$ to 1.25 and $E_{\text{Ru(III)/}^*\text{Ru(II)}}^0 = -1.25$ to -1.01 V/SCE [30]. Assuming the redox potentials of the dye used here to lie in the same region, the following reaction mechanisms can be considered to take place :



Process (a) is the excitation of the dye by the external photon flux, (b) and (c) are competitive processes for the decay of the excited state either by an electron transfer to the semiconductor or by radiative decay to the molecular ground state, respectively. Processes (d) and (e) are the regenerative processes leading to the reduction of the oxidized state left after process (b). Both processes (d) and (e) are energetically possible since at pH 6.5 the redox potentials

$$E_{\text{Q/H}_2\text{Q}}^0 = 0.07 \text{ V/SCE}$$

and $E_{\text{O}_2/\text{H}_2\text{O}}^0 = 0.60$ V/SCE are both smaller than $E_{\text{Ru(III)/Ru(II)}}^0$ and should compete with each other. The fact that process (d) is also operative is verified by the observation that without H_2Q in the electrolyte a small photocurrent can be sustained though the cell with a slow evolution of oxygen gas at the sensitized semiconductor surface. Supersensitization by a factor of about 4 when hydroquinone is present in the system indicates that H_2Q is oxidized at a faster rate than H_2O and process (e) is predominant.

The I - V characteristics of a doubly sensitized cell under a broad (400-700 nm) visible light excitation in the dyes absorption region is shown in figure 6.

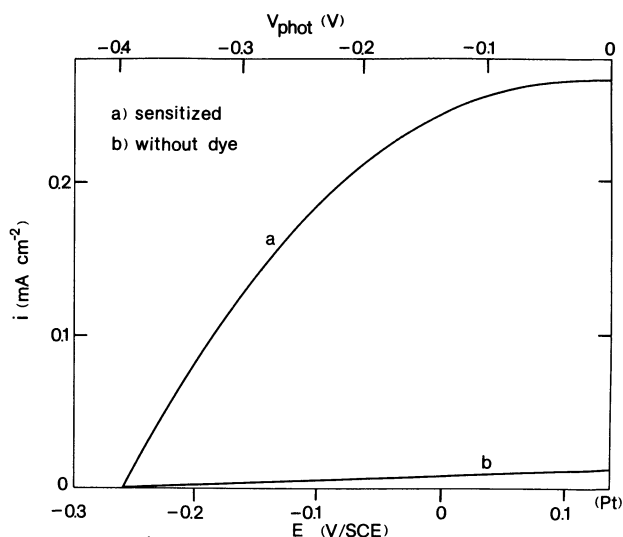


Fig. 6. — Fourth quadrant (positive power) current-voltage characteristics of the doubly sensitized ZnO ceramic electrode cell under 0.4 W.cm^{-2} broad band (400-700 nm) excitation in the absorption region of the dyes and under potentiostatic SCE conditions. The open circuit voltage of the cell, with respect to the metallic (Pt) electrode, is 0.4 V as indicated by the upper scale. The response under the same conditions of a non sensitized ZnO ceramic (curve b) is also shown.

For comparison the response of the same electrode but without dye coating (curve b) is also shown. Under potentiostatic conditions and with a power of incident light of $\sim 0.4 \text{ W.cm}^{-2}$ the maximum short circuit current densities obtained so far lie in the 0.22 - 0.24 mA.cm^{-2} range. The open circuit voltage of the cell is $V_{\text{OC}} = 0.4$ V as shown by the upper scale of figure 6, referred to the platinum counter-electrode.

4. Conclusion. — It is shown that stable photoelectrochemical cells with broad response in the visible region can be obtained by sensitizing with dye mixtures, including an organometallic dye, ceramic semiconducting oxide electrodes and using transparent electrolytes containing hydroquinone as a supersensitizer. Although it is premature to speculate on any future technological application of such device, it is worthwhile to emphasize that cheap, large scale, production of ceramic oxides is already a well known art in electro-acoustic transducer technology. Moreover, ceramics have the advantage of increasing the effective electrode area and a better use of diffuse light. Clearly, many problems remain to be solved, namely the reduction of the series resistances without degradation of charge carrier recombination rates at the surface, improvement of dye adsorption techniques, and systematic studies of dye-electrode systems in which the radiative and non-radiative decay rates of the molecular excited state become negligible as compared to the rate of oxidation of the dye by the electron transfer to the electrode. Such work retains

also a purely scientific interest since it is expected that many ceramic electrodes will behave in a not much very different way from single crystals and the electrochemistry as well as the mechanisms responsible for the deactivation of excited states of organic molecules in the proximity of a semiconducting surface

could be studied in systems where single crystals are difficult to obtain.

Acknowledgements. — We are grateful to Dr. J. P. Sauvage of the Laboratoire de Chimie Physique Organique for supplying the dinonadecyl Ru (II) dye.

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