

Photoelectrochemical response of TiO_2 pigmented membranes

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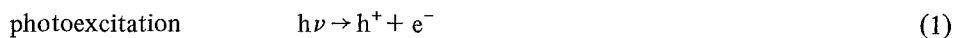
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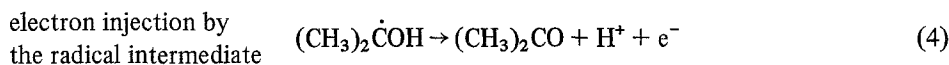
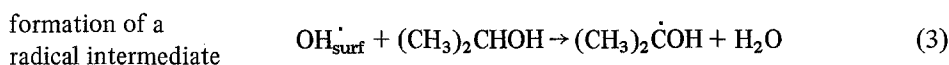
Titanium dioxide pigments have been dispersed in a porous nitrocellulose matrix applied to a vitreous carbon electrode. Illumination of these coated electrodes with monochromatic light in the near UV region gives rise to photocurrents which have been shown to correspond to the oxidation or reduction of hydrogen peroxide produced at the illuminated titanium dioxide particles. Ring-disc and pulsed photocurrent measurements have been used to investigate how the photochemical reaction is coupled by diffusion to the electrochemical detection of hydrogen peroxide. The results of the study suggest that the photocatalytic properties of semi-conductor dispersions may be characterized using similar coated electrodes.

1. Introduction

The photocatalytic properties of titanium dioxide have been investigated widely, and the recent interest in semi-conductor photoelectrochemistry [1] has again focused attention on the ability of TiO_2 to promote oxidation reactions under illumination. Bard [2] has suggested that TiO_2 powders may be useful catalysts for the photo-oxidation of pollutants such as cyanide, and considerable effort is being devoted to the design of disperse systems that can split water under illumination [3, 4]. The ability of illuminated TiO_2 to catalyse oxidation reactions is, however, undesirable when the oxide is incorporated as a pigment in paint resin films, and the 'chalking' of the paint initiated by photo-oxidative attack of the resin at the pigment/polymer boundary is of concern to the paint industry, since it can be an important factor in paint durability [5]. Davidson *et al.* [6-8] have shown that photocurrents can be measured using mesh electrodes coated with semi-conductor powders and, following earlier observations [9, 10] that paint films on metal or carbon substrate electrodes give rise to measurable photocurrents in aqueous solution, we have studied the photoactivity of a number of different TiO_2 powders dispersed in thin ($\sim 15 \mu\text{m}$) nitrocellulose membranes supported on a vitreous carbon electrode. The objectives of the study were to develop, if possible, a sensitive electrochemical method for the rapid assessment of TiO_2 pigment activity and to clarify the mechanism responsible for the photocurrents. The direct weight loss methods [11] that are used to determine the rate of polymer oxidation in paint resins under illumination are time consuming, and a simple, indirect way of screening TiO_2 pigments on the basis of their photocatalytic activity would be useful.

The primary step in the photocatalysed oxidation of organic molecules at illuminated TiO_2 is the photoexcitation of electrons across the band-gap of the oxide (3.2 eV for anatase and 3.0 eV for rutile), and the subsequent reactions of the photogenerated electrons and holes result in the photocatalysed oxidation of organic species by molecular oxygen. For example, the photo-oxidation of isopropyl alcohol is thought to take place via the following route [12-14]:

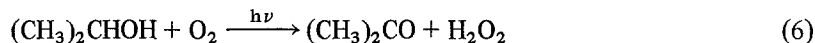




The reaction is balanced by the simultaneous reduction of oxygen to hydrogen peroxide:



so that the overall reaction is the photocatalysed oxidation



Although the chemical and physical changes involved in the chalking of paints are complicated [15] it is reasonable to assume that the primary photochemical steps are similar to those outlined above, and Egerton and King [16] have established that the rate of isopropanol photo-oxidation correlates well with the weathering rate of different paint pigments. Photocatalytic oxidation reactions are usually followed by measuring the rate of formation of oxidation products (acetone in the example discussed above). Since hydrogen peroxide is electroactive, an alternative approach is to detect it at a suitably placed electrode. In practice, rapid and linear detector response is important, so that the path length for diffusion to the detector electrode must be kept as small as possible. With these constraints in mind, we have investigated photocurrents produced at TiO_2 pigmented membranes in thin film and ring-disc electrode configurations. The study has demonstrated that hydrogen peroxide is produced in high yields by the illumination of pigmented membrane electrodes. The hydrogen peroxide can be collected and oxidized or reduced by choosing a suitable potential for the electrode, and the design of an electrochemical method for the assessment of pigment photoactivity therefore appears to be feasible.

2. Experimental details

The measurement of photocurrents with pigmented polymer films presents a number of experimental problems. Early work [9] was performed with alkyd resin films on platinum substrates, but the photocurrent response was found to be sluggish. Bare platinum and gold substrates were found to give significant photocurrents under UV illumination, and attempts to use doped tin oxide films on glass failed for the same reason [9]. A vitreous carbon sheet (Hoechst UK) was finally selected for the substrate electrode since it gave insignificant photocurrents. Cellulose acetate and nitrocellulose films were prepared by evaporating acetone solutions to dryness, and the most satisfactory response was obtained by pipetting an acetone solution of nitrocellulose containing a suspension (0.15% w/v) of TiO_2 onto the surface of the polished vitreous carbon electrode (area: 1 cm^2). Four drops of the suspension were applied to produce a thin film, which subsequent examination by scanning electron microscopy showed to be $15 \pm 5 \mu\text{m}$ thick with a sponge-like structure. About 60% of the surface was covered with the TiO_2 pigment (which tended to agglomerate).

The electrode was immersed in the electrolyte solution and illuminated with monochromatic light (provided by a 250 W xenon lamp and a grating monochromator) via a quartz window in the base of a conventional three electrode electrochemical cell (Fig. 1). The potential of the electrode was controlled with respect to a saturated calomel electrode by a simple operational amplifier potentiostat that incorporated a calibrated zero suppression facility to offset the dark currents. The photocurrents were recorded as the change in current produced by illuminating the electrode for a period of several seconds. The incident photon flux was measured with a calibrated photodiode (traceable to NBS standard).

A vitreous carbon (disc)/gold (ring) electrode was also used in the study, and the ring was masked with adhesive tape during application of the suspension to the disc so that the nitrocellulose membrane was restricted to the disc area. The potentials of the ring and disc electrodes were controlled indepen-

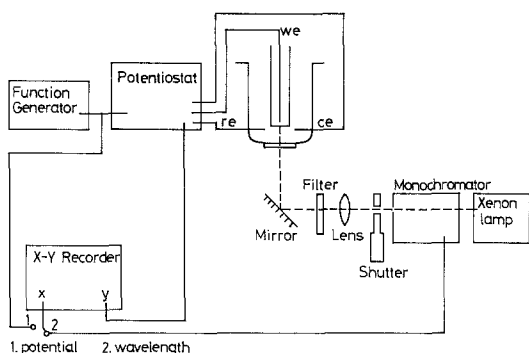


Fig. 1. Experimental arrangement for photocurrent measurements (iV curves and spectra), at TiO₂ pigmented membrane electrodes. For transient photocurrent measurements, the xenon lamp and monochromator were replaced by a xenon flash source.

dently with a four electrode potentiostat, although in most measurements the coated disc electrode was left at open circuit. Some measurements were also made without nitrocellulose by using a thin layer cell in which a quartz window trapped a suspension of TiO₂ against a vitreous carbon electrode.

Transient photocurrent measurements were made by replacing the monochromatic light source with a xenon flash tube ($\tau < 1$ ms). The photocurrent transients were displayed on a digital storage oscilloscope and transferred to an X-Y recorder for analysis. The output of the flash tube was monitored simultaneously by a photomultiplier and displayed on the second channel of the oscilloscope.

3. Results and discussion

3.1. The membrane coated electrode

Photocurrents of several microamperes were observed when pigmented membrane electrodes were illuminated with monochromatic light in air-saturated electrolyte solutions. The magnitude of the

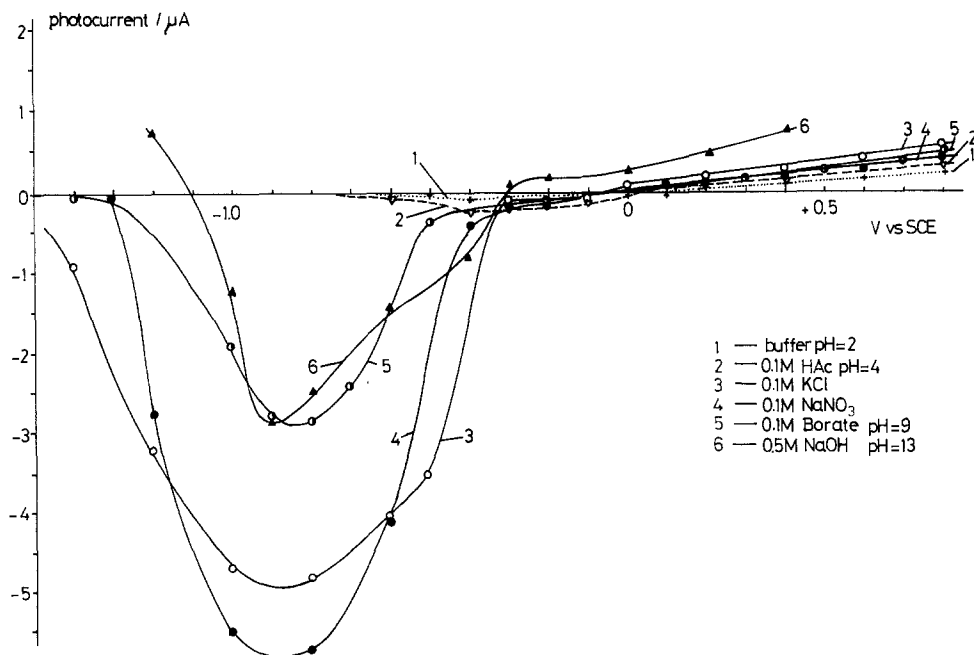


Fig. 2. Photocurrents (difference between currents under illumination and in the dark) for electrodes coated with anatase pigment in the electrolytes shown in the figure (air-saturated solutions).

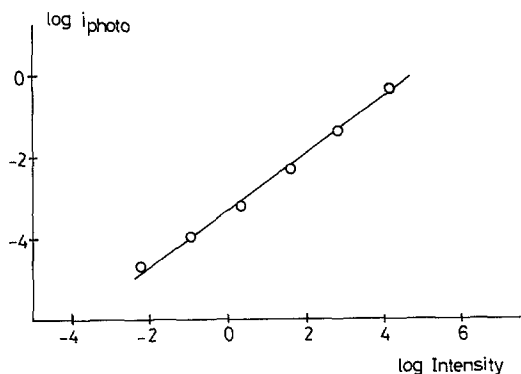


Fig. 3. Intensity dependence of the photocurrent for the TiO_2 -coated electrode measured in air-saturated 0.1M KCl at -0.9 V vs SCE (wavelength = 390 nm).

photocurrent at any particular wavelength and potential was found to be reproducible to better than 10% for a series of membrane coatings prepared with the same type of pigment. The shape of the photocurrent–time response varied with electrode potential and with the pH of the solution, and both anodic and cathodic photocurrents were observed depending on the potential region. Fig. 2 presents a set of results, obtained in different electrolyte solutions, which show that the cathodic photoresponse is largest in neutral and alkaline solutions. An interesting feature of the photocurrent response is that it falls at potentials more negative than -1.0 V vs SCE and in one case even appears to change sign. Under these conditions a cathodic photocurrent spike was observed when the light was switched on, and the photocurrent then appeared to become anodic. This effect was most pronounced at high illumination levels.

The photocurrent response was measured as a function of the illumination intensity and, as Fig. 3 shows, a square root relationship was observed. This result suggests that the efficiency of the photocurrent-generating process is controlled by second order charge–carrier recombination, a conclusion which is supported by the work of Egerton and King [16] who have reported that the rate of photo-oxidation of isopropanol in TiO_2 suspensions also depends on the square root of the illumination intensity.

The wavelength dependence of the photocurrent was measured in the range 250–450 nm, and the data were normalized to constant incident photon flux by taking the square root intensity dependence into account. Examples of the spectra obtained in this way are given in Fig. 4. The spectral response for rutile and anatase pigment samples is clearly different and, as Fig. 4 demonstrates, the photocurrent threshold corresponds closely in each case to the band gap of the material. The monochromatic conversion efficiency for most of the pigments was found to lie in the range 10–40%, although, of course,

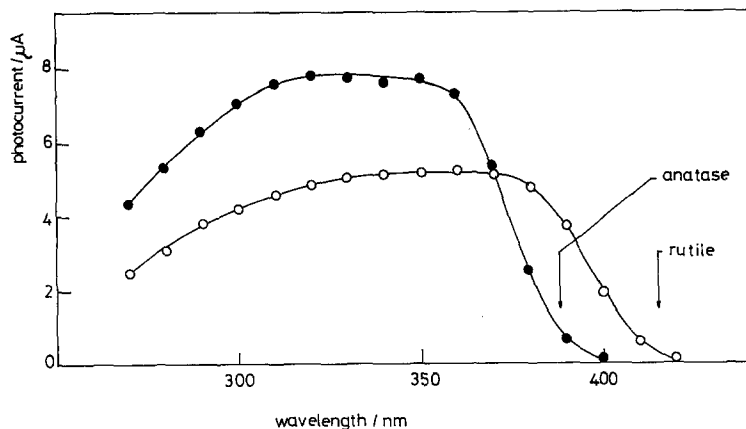


Fig. 4. Corrected photocurrent spectra for rutile and anatase pigment samples measured at -0.8 V vs SCE in air-saturated 0.5M NaOH. The absorption thresholds corresponding to the band gaps of the two modifications of TiO_2 are shown in the figure.

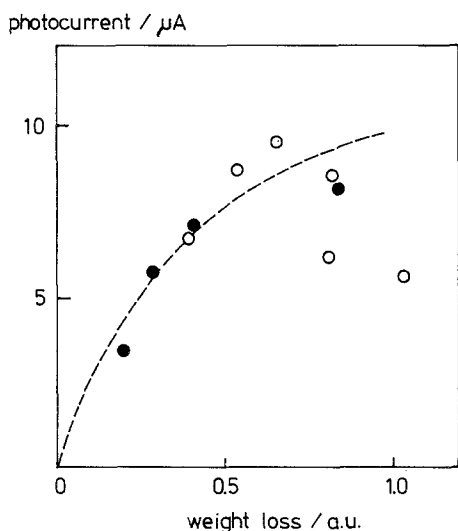


Fig. 5. Correlation between photocurrent (measured at -0.8 V vs SCE in air-saturated 0.5 M NaOH) and the relative rates of weight loss for alkyd resin films containing the pigment (data provided by BTP Tiioxide Ltd).
 ● sulphate pigments, ○ chloride pigments.

the square root intensity dependence implies that the conversion efficiency is intensity dependent. Nevertheless, the very high value of conversion efficiency suggest that the materials used in the study have considerably photocatalytic activity.

The durability of pigmented alkyd resins can be obtained from the relative rate of weight loss under illumination in Marr accelerated weathering equipment [11], and data for the pigments were made available by BTP Tiioxide Ltd. Fig. 5 shows that a reasonable correlation between photocurrent and relative weight loss was obtained for a series of pigments prepared by the sulphate process, whereas the correlation for a series of pigments prepared by the chloride process was less satisfactory. Although these early results look promising, further work would be needed in order to develop the method as a reliable empirical way of assessing the photoactivity of pigments.

3.2. Ring-disc measurements

The spectra shown in Fig. 4 show that the photocurrents are closely related to photoexcitation of the TiO₂ dispersion, but the steady-state photocurrent measurements do not allow us to distinguish readily between a direct electronic mechanism for the photocurrent (involving electrical contact to the substrate electrode) and an indirect mechanism involving hydrogen peroxide as an intermediate. The electrochemical behaviour of hydrogen peroxide at vitreous carbon was therefore examined by adding controlled amounts of it to the electrolyte solution [17]. The current-voltage curves measured in this way resembled the photocurrent-voltage curves so closely that it was clear that hydrogen peroxide was indeed produced by illumination of the TiO₂ pigmented electrode. Since, however, Dunn *et al.* [18] have attributed the photocurrents observed when a suspension of TiO₂ is illuminated, to direct electron transfer from TiO₂ particles to the substrate electrode, a series of measurements was carried out with a vitreous carbon (disc)/gold (ring) electrode in order to make an unambiguous distinction between the two possible mechanisms. The disc was coated with a suspension of TiO₂ in nitrocellulose and illuminated at open circuit, and the current at the ring was monitored in order to detect hydrogen peroxide. As Fig. 6a shows, illumination of the coated disc gives rise to a ring current which can be attributed to the oxidation of photogenerated hydrogen peroxide, and the magnitude of this current, after correction for the collection efficiency of the ring, was of the same magnitude as the disc photocurrent measured when the disc was held at the same potential.

In solutions purged with nitrogen the residual ring current due to oxygen reduction was sufficiently small that changes in the ring current could also be monitored at potentials more negative than -0.2 V.

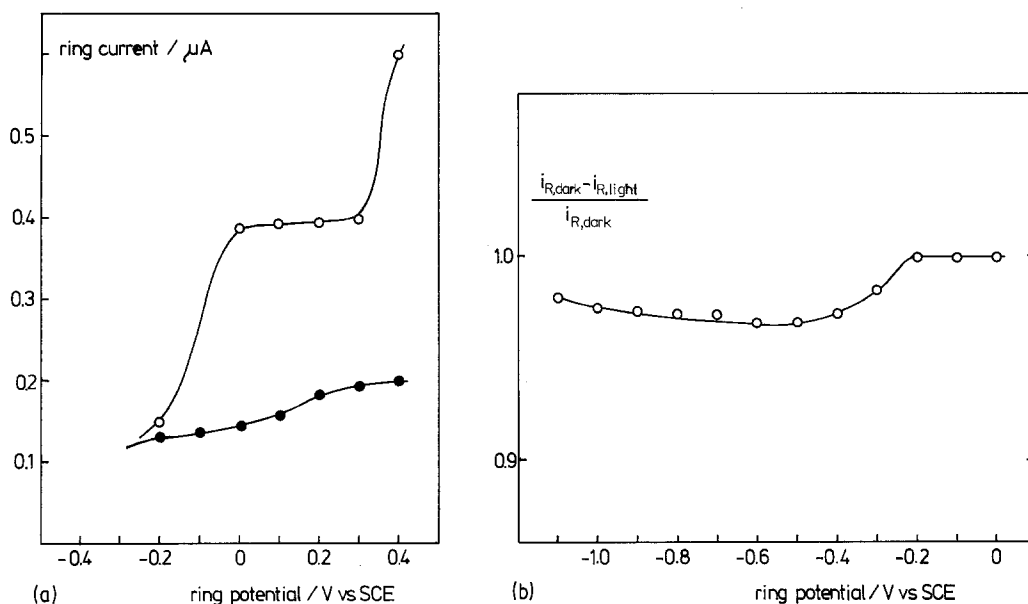


Fig. 6. (a) Ring current measured with anatase pigmented membrane disc at open circuit. \circ air-saturated 0.5M NaOH; \bullet 0.5M NaOH purged with nitrogen. The ring current corresponds to the oxidation of H_2O_2 produced at the illuminated membrane disc. $W = 9$ Hz, $\lambda = 350$ nm, ring collection efficiency 0.17. (b) Shielding effect on oxygen reduction at the ring produced by illuminating the pigment-coated disc at open circuit in 0.5M NaOH. (Residual oxygen concentration 7×10^{-5} mol dm^{-3} .) $W = 9$ Hz, $\lambda = 350$ nm.

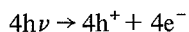
When the disc was illuminated at open circuit, the cathodic ring current was immediately reduced, as shown in Fig. 6b. This shielding effect provides direct proof that oxygen is consumed by the illuminated TiO_2 pigmented membrane. In fact, it might be expected that the shielding of oxygen reduction would be compensated by the additional reduction current due to hydrogen peroxide, but the reduction of hydrogen peroxide on gold is sufficiently slow that the shielding of oxygen reduction is predominant [17]. The shielding of oxygen reduction is probably also responsible for the apparently 'anodic' photocurrents measured in some cases at extreme negative potentials (see Fig. 2).

3.3. The photo-oxidation mechanism

Although the results discussed above demonstrated that oxygen is converted to hydrogen peroxide at the pigmented membrane electrode, it was not clear whether the nitrocellulose polymer was involved in a reaction analogous to Equations 1–6. A thin layer cell was therefore constructed in which a TiO_2 suspension free of nitrocellulose was trapped by a quartz optical window pressed close to a vitreous carbon electrode. The photocurrents measured with this arrangement were of a similar magnitude to those obtained with polymer-coated electrodes, and it is therefore apparent that the nitrocellulose simply acts as an inert matrix which maintains the TiO_2 dispersion in close contact with the substrate electrode.

Measurements were then carried out with the pigmented membrane electrode in the presence of isopropanol in order to test whether the photo-oxidation followed Equations 1–6 in this case. Fig. 7 demonstrates that the photocurrent is increased by a factor of two when isopropanol is added to the solution, and this 'current doubling' effect [12] is consistent with the mechanism of photo-oxidation summarized in Equations 1–6. Since hydrogen peroxide is still formed in the absence of an organic substrate, it was concluded that the following reaction sequence must occur:

photoexcitation



(7)

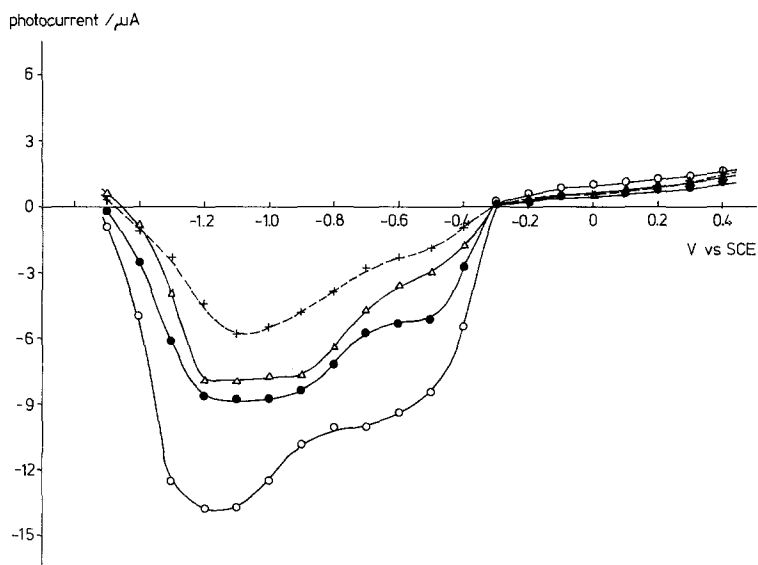
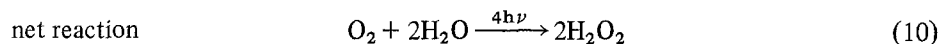
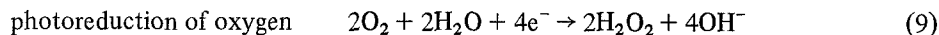
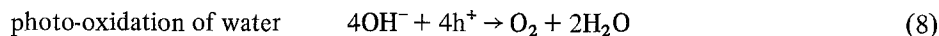
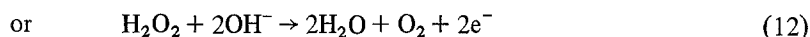


Fig. 7. Photocurrent-voltage curves for pigmented membrane electrode showing the effect of adding isopropanol. + 0.5M NaOH (no isopropanol); Δ 20% isopropanol; \bullet 50% isopropanol; \circ 80% isopropanol.



The important feature of this scheme is that it requires two photons to produce a molecule of hydrogen peroxide, whereas the current doubling scheme only requires one photon (Equation 6).

The subsequent reactions of photogenerated H₂O₂ depend on the potential of the detector electrode:



It can be seen that the sum of the photogeneration and detection reactions corresponds either to the photo-assisted reduction of oxygen or to the photo-assisted evolution of oxygen, giving an apparent quantum efficiency of 1 in the absence of an organic substrate such as isopropanol.

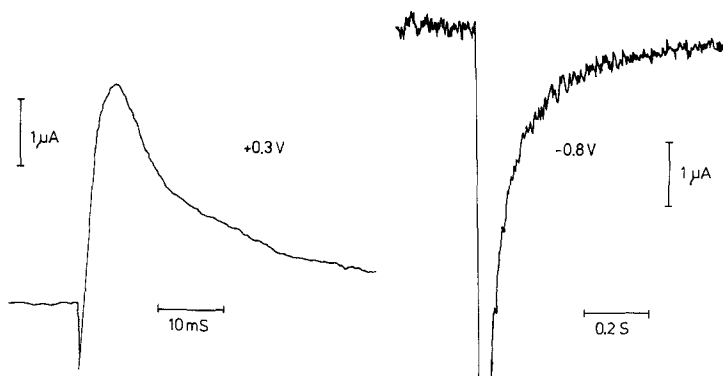


Fig. 8. Transient photocurrent response of pigmented membrane electrode in air-saturated 0.5M NaOH at the potentials shown. Flash duration < 1 ms.

3.4. Transient photocurrents

The detection of hydrogen peroxide by Reaction 11 and 12 relies on effective diffusion of the material through the porous nitrocellulose membrane. The large photocurrents obtained with thin nitrocellulose films are a consequence of their open sponge-like structure; thicker alkyd resin films are more compact preventing efficient collection of hydrogen peroxide, and the photocurrents are correspondingly smaller [9]. The response time for diffusion in a thin film structure is expected to be of the order of l^2/D , where l is the diffusion path and D the effective diffusion coefficient of H_2O_2 , and for $l = 10^{-3}$ cm and $D = 10^{-5}$ cm² s⁻¹, the calculated response time of 0.1 s agrees well with the experimental values for the nitrocellulose films. The characterization of diffusion processes is best carried out by non-stationary techniques, and the diffusional coupling to the detector electrode was therefore investigated by illuminating the electrode with a short (< 1 ms) flash of light so that the photogeneration of H_2O_2 was restricted to a time interval much smaller than the characteristic time constant l^2/D . Fig. 8 shows examples of the transient photocurrents which are obtained. A quantitative treatment of the transient photocurrent behaviour was based on the simplified model of the pigmented membrane shown in Fig. 9a. Clearly, the diffusion problem is complicated by the distribution of pigment in the membrane and by the absorption profile for thin films containing a uniform dispersion of TiO_2 , it seems reasonable to assume that the hydrogen peroxide concentration profile is initially flat as shown in Fig. 9b. If the reaction of hydrogen peroxide at the detector electrode occurs under diffusion control, the concentration profile will develop with time as shown in the figure. The ring-disc measurements show that a significant fraction of the photo-generated H_2O_2 escapes into solution, and we have therefore chosen to assume the boundary condition $C_{\text{H}_2\text{O}_2} = 0$ at $x = l$. The system is then exactly analogous to a thin layer cell, and the solution of the diffusion problem given by Hubbard and Anson [19] can be used in a modified form which takes into account the boundary condition at $x = l$:

$$i(t) = \frac{2nFADC^*}{l} \sum_{m=1}^{\infty} \exp\left(\frac{-(2m-1)^2\pi^2Dt}{l^2}\right) \quad (13)$$

At short times, Equation 13 reduces to the Cottrell equation for semi-infinite linear diffusion, whereas at long times it predicts an exponential decay of the photocurrent. The l^2 term in the denominator of Equation 13 implies that the decay time constant is extremely sensitive to the film thickness. Fig. 10a compares the experimental results with a set of curves calculated numerically from Equation 13. Clearly, a satisfactory fit is obtained for a film thickness very close to the real value ($\sim 15 \mu\text{m}$). The initial concentration of hydrogen peroxide immediately after the flash was calculated to be 10^{-8} mol cm⁻³. Fig. 10b shows a plot of photocurrent vs charge which has been extrapolated in order to obtain an independent estimate of the initial concentration. The value of C^* calculated from the intercept is about half of the value used to fit the decay curve in Fig. 9a, suggesting that half of the H_2O_2 escapes into solution as predicted by the simple model illustrated in Fig. 9.

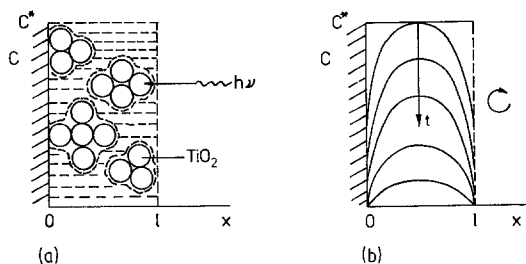


Fig. 9. (a) Schematic representation of TiO_2 pigmented membrane showing H_2O_2 profiles around the particles immediately after the flash. (b) Simplified concentration profiles developing as H_2O_2 is lost by diffusion into solution and reaction at the electrode surface.

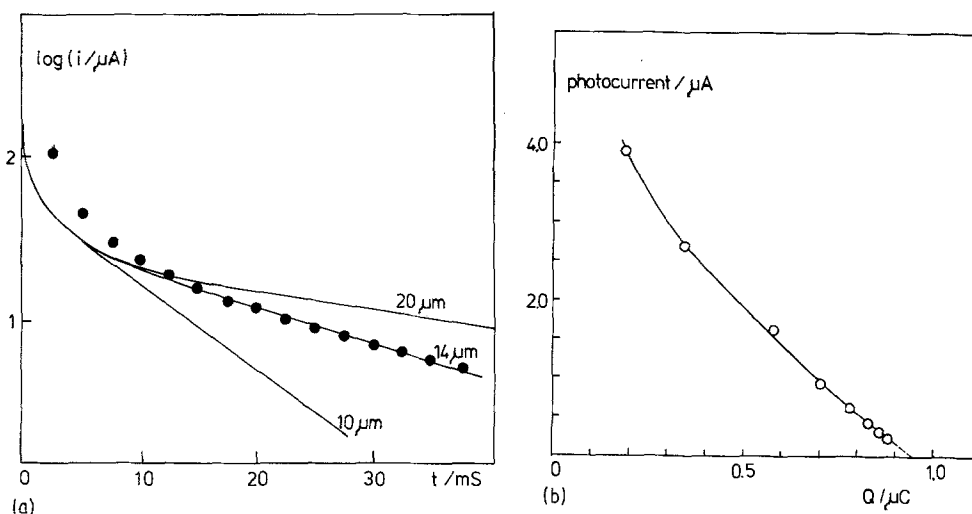


Fig. 10. (a) Comparison of photocurrent decay with the shape predicted by Equation 13 for an initial concentration of H_2O_2 (immediately after the flash) of $10^{-8} \text{ mol cm}^{-3}$. The sensitivity of the theoretical curves to film thickness is evident in the figure. (b) Photocurrent vs charge plot used to calculate the total amount of H_2O_2 collected by the detector electrode. The result shows that about half of the H_2O_2 escapes into solution.

4. Conclusions

Illumination of TiO_2 pigmented nitrocellulose membrane electrodes in the presence of oxygen gives hydrogen peroxide in high yields, and the photocurrents observed with membrane-coated electrodes are due to the subsequent oxidation or reduction of photogenerated hydrogen peroxide. The membrane-coated electrodes behave as thin layer cells, and about half of the photogenerated H_2O_2 is collected by the substrate electrode; the remainder escapes into solution and can be detected at a ring electrode. The processes involved in the generation of photocurrents in TiO_2 pigmented membranes are summarized in Fig. 11 which illustrates how hydrogen peroxide links the heterogeneous photochemistry occurring at the TiO_2 particles to the electrochemical detection process at the substrate electrode. The efficiency of the process appears to be limited by charge-carrier recombination in the TiO_2 particles, but at the low monochromatic intensities used here, the quantum efficiency for H_2O_2 exceeds 10% in most cases. The porous membrane electrodes developed in this work may also find application in the study of reactions at other dispersed semi-conductor systems, since they allow rapid and sensitive detection of electroactive photoproducts.

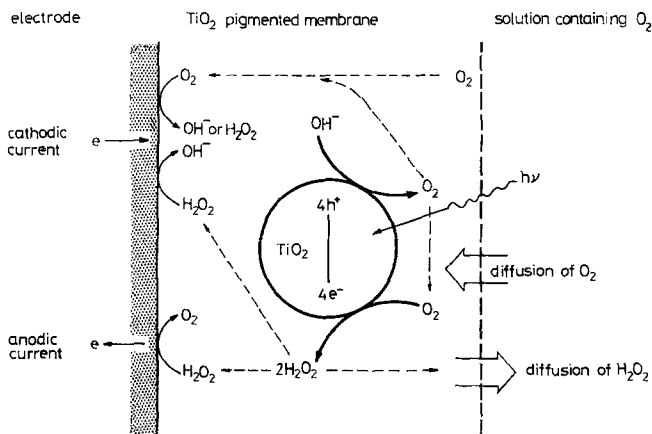


Fig. 11. Summary of the photogeneration reactions and subsequent electrode reactions which are responsible for the photocurrents at TiO_2 -pigmented membrane electrodes.

Acknowledgements

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