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## ENERGETICS OF TETRAPHENYLPORPHYRIN ELECTRODE/ELECTROLYTE INTERFACE

By

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### Abstract

This paper deals with the energetics at the interface between the tetraphenylporphyrin (TPP) electrode and the electrolyte with a redox couple of *p*-benzoquinone and hydroquinone. The redox potential ( $E_{\text{redox}}$ ) in the electrolyte and the flatband potential ( $E_{\text{fb}}$ ) of the TPP electrode were defined, and their pH-dependence as well as that of the photovoltage ( $V_p$ ) was measured. It was found that  $E_{\text{fb}}$  changed with 0.059 V per pH unit at acidic region, and the ratio of  $V_p$  to ( $E_{\text{fb}} - E_{\text{redox}}$ ) which corresponded to the upper limit of the photovoltage was nearly constant (0.8~0.9) over the whole range of pH studied. Furthermore, using a rotating ring-disk electrode, hydroquinone photoproducted at the TPP disk electrode could be detected at the ring electrode.

### Introduction

Much attention has recently been paid to the elucidation of the photoelectrode process at an interface between organic dye film (such as porphyrins<sup>1-4</sup>), phthalocyanines<sup>5-7</sup>), or others<sup>8</sup>) and electrolyte. At present the results have generally been interpreted in terms of the semiconductive properties of these dyes.<sup>6</sup>

We have studied the photoelectrochemical properties of tetraphenylporphyrin (TPP) film which was sublimed onto a platinum plate (being abbreviated as TPP electrode hereafter), and have recently found that the oxidation potential of porphyrins is important for the appearance of the photovoltage.<sup>4</sup> However, in order to discuss the energetics in further detail, it has been desired to correlate the photovoltage ( $V_p$ ) with the flatband potential ( $E_{\text{fb}}$ ) of the TPP electrode and the redox potential ( $E_{\text{redox}}$ ) in the electrolyte, because the difference between  $E_{\text{fb}}$  and  $E_{\text{redox}}$  will afford the upper limit of the photovoltage.<sup>8</sup>

In the present study, we attempted to define the energy levels of  $E_{\text{redox}}$  and  $E_{\text{fb}}$  at first. The  $E_{\text{redox}}$  level in the electrolyte was defined by the use

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of a *p*-benzoquinone and hydroquinone couple. The flatband potential was determined from the measurement of the photocurrent response under chopped illumination.<sup>9,10</sup> As described later, the reproducibility of  $E_{fb}$  was highly improved when the TPP electrode was rotated. Subsequently, the pH-dependence of  $E_{redox}$  and  $E_{fb}$ , as well as that of  $V_p$  was systematically measured. These experiments indicated that  $E_{fb}$  changed with 0.059 V per pH unit at acidic region, and the ratio of  $V_p$  to  $(E_{fb} - E_{redox})$  was nearly constant (0.8~0.9) over the whole range of pH studied. Furthermore, using a ring-disk electrode, we could detect hydroquinone at the ring electrode during the observation of the cathodic photocurrent at the TPP disk electrode. The results will briefly be reported in this paper.

### Experimental

Tetraphenylporphyrin was synthesized and purified as described previously.<sup>4</sup> A rotating electrode, which consisted of a platinum ring and disk separated by a Teflon insulator, was purchased from Hokuto Denko Ltd. The dimensions of the disk and ring were:  $r_1=4.0$  mm=radius of the disk,  $r_2=5.0$  mm=inner radius of the ring,  $r_3=6.0$  mm=outer radius of the ring. Tetraphenylporphyrin was vacuum sublimed onto the platinum disk plate. As the edge of the disk was not completely covered by TPP, its surroundings were thinly coated with Apiezon grease in order to avoid direct contact with the electrolyte. The thickness of the TPP layer was about 100 nm. The schematic illustration of the measuring assembly is shown in Fig. 1.

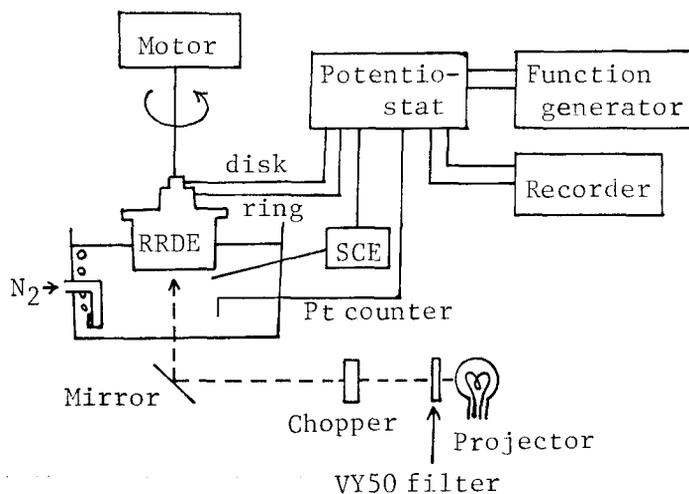


Fig. 1. Measuring assembly.

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The electrode was rotated at 200 to 2000 rpm by the use of a rotating apparatus (Hokuto Denko Ltd., HR-101 A). The current-voltage curves were obtained with a dual potentiostat (Hokuto Denko Ltd., HR-101 B) and a function generator constructed at this laboratory. A digital tester (Sanwa Electric Instrument Co., Ltd., 7200 ES) was used for monitoring the voltage. Light from a 1 kW projector lamp (Kondo Sylvania Ltd., JCP) was filtered through a Toshiba VY 50 Glass Filter ( $\lambda > 500$  nm) to avoid the direct excitation of the redox compound. The light was mechanically and periodically chopped with the aid of a rotary solenoid. By adding *p*-benzoquinone (Q) and hydroquinone (H<sub>2</sub>Q) into the electrolyte solution, the redox potential of the solution was kept constant. *p*-Benzoquinone was purified by a vacuum sublimation prior to use. The redox potential due to the reaction equilibrium ( $Q + 2H^+ + 2e \rightleftharpoons H_2Q$ ) obeyed following Nernst's equation over the entire range of concentration.

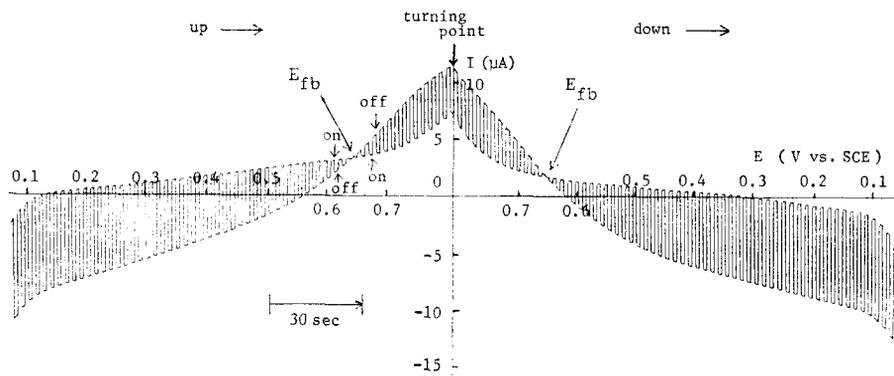
$$E_{Q/H_2Q} = E_{Q/H_2Q}^{\circ} - \frac{RT}{2F} \ln \frac{[H_2Q]}{[Q][H^+]^2}$$

The concentration of *p*-benzoquinone was usually in the order of  $10^{-3}$  M. The pH of the solution was varied with the use of the Britton and Robinson buffer which was prepared by mixing an acid solution (H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH, H<sub>3</sub>BO<sub>3</sub> mixture) with a base solution (NaOH). The pH measurement was carried out with a digital pH meter (Toa Electronics Ltd., HM-10 B). Sulphuric acid solution (1 N) was used at pH 0.30. The solutions were deaerated with highly purified nitrogen. All experiments were carried out in a room of temperature controlled at 26°C.

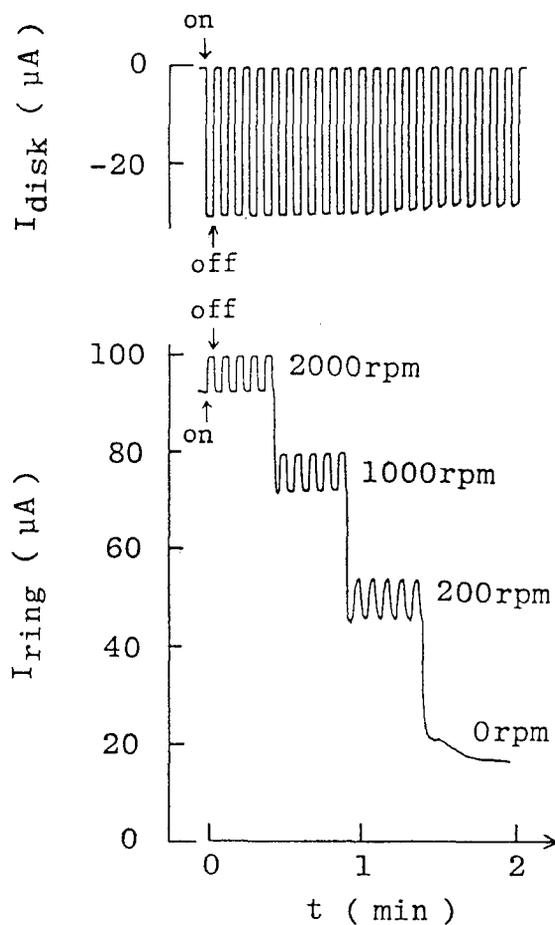
### Results and Discussion

Figure 2 shows a current-voltage curve of the TPP electrode in a buffer solution of pH 5.94. The electrode was rotated at 2000 rpm, and the light was turned on and off at the 2.5 second cycle. Reproducible data were obtained at a rotation speed above about 1000 rpm. Without rotation, reproducibility of the curves was poor probably because of the accumulation of any substances produced in the neighborhood of porphyrin electrode surface. As is seen from Fig. 2, it is possible to evaluate the flatband potential ( $E_{fb}$ ) from the voltage at which the photocurrent disappears. However, when the quantity of hydroquinone was increased, such a point was difficult to be observed as a result of the increase in the dark current. Accordingly, the addition of hydroquinone was restricted to only about 2% of *p*-benzoquinone.

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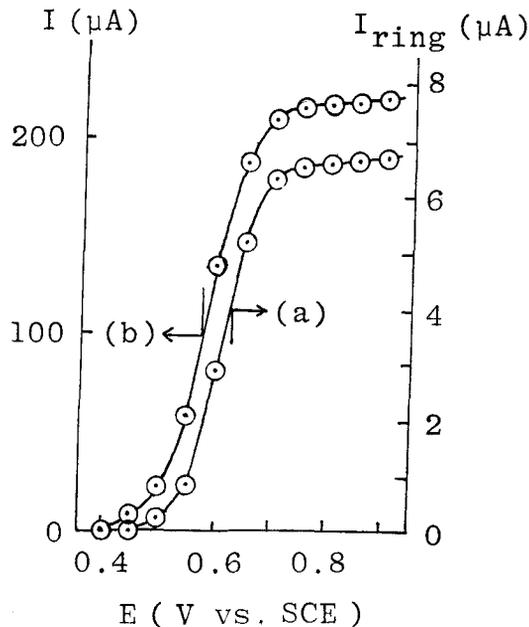
**Fig. 2.** Current-voltage curve for TPP electrode with redox couple of *p*-benzoquinone and hydroquinone under chopped illumination; pH 5.94, *p*-benzoquinone:  $1.4 \times 10^{-3}\text{M}$ , hydroquinone:  $2.8 \times 10^{-5}\text{M}$ .



**Fig. 3.** Detection of hydroquinone; disk electrode: +0.4 V vs. SCE, ring electrode: 0.8 V vs. SCE, pH 0.30.

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On the other hand, we could detect hydroquinone at the ring electrode during the observation of the cathodic photocurrent at the TPP disk electrode. As shown in Fig. 3, the anodic current was obtained at the ring electrode when the cathodic photocurrent was observed at the disk electrode. At the ring electrode, the dark anodic current increased linearly with the square root of the rotation speed, indicating that the dark current at the ring electrode was determined by the mass transport of hydroquinone. At the disk electrode, no appreciable change of the photocurrent was observed against the increase of the rotation rate. This implies that the photoelectrode reaction at the disk is rate-limiting. The current-voltage curve on the ring electrode induced upon illumination of the disk is shown in Fig. 4(a). In order to identify the species undergoing oxidation at the ring electrode, the current-voltage characteristic of the ring electrode was compared with that of the Pt electrode where only hydroquinone was present in the solution, Fig. 4(b). The two current-voltage curves coincide fairly well as depicted in Fig. 4. Consequently, it is concluded that the cathodic photocurrent observed at the TPP disk is attributed to the photoformation of hydroquinone



**Fig. 4.** Identification of hydroquinone; pH 0.30. (a) Current-voltage curve at ring electrode under illumination; *p*-benzoquinone:  $1.4 \times 10^{-3}$  M, hydroquinone:  $2.8 \times 10^{-5}$  M. (b) Current-voltage curve for hydroquinone; hydroquinone:  $2.8 \times 10^{-4}$  M.

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from *p*-benzoquinone.

In Fig. 5 is shown the pH-dependence of the flatband potential ( $E_{fb}$ ) and the photovoltage ( $V_p$ ) of the TPP electrode, as well as that of the redox potential ( $E_{redox}$ ) of *p*-benzoquinone and hydroquinone couple. The flatband potential changed with 0.059 V per pH unit below pH 2. This means that the primary ion to react with TPP is  $H^+$  at this region, and the TPP surface is in equilibrium with electrolyte according to  $H_2TPP + 2H^+ \rightleftharpoons H_4TPP^{2+}$ , because in this case, a change of  $E_{fb}$  with pH is expressed by the following

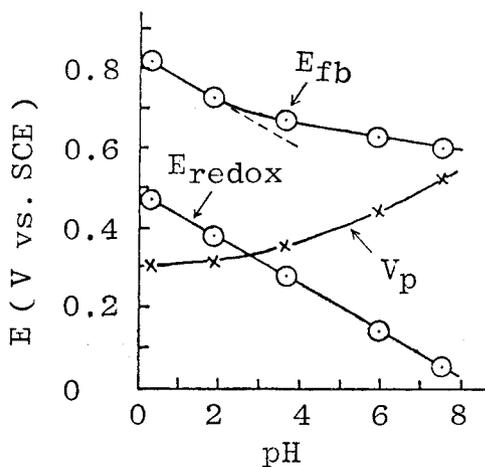


Fig. 5. pH-dependence of  $E_{redox}$ ,  $E_{fb}$ , and  $V_p$ .

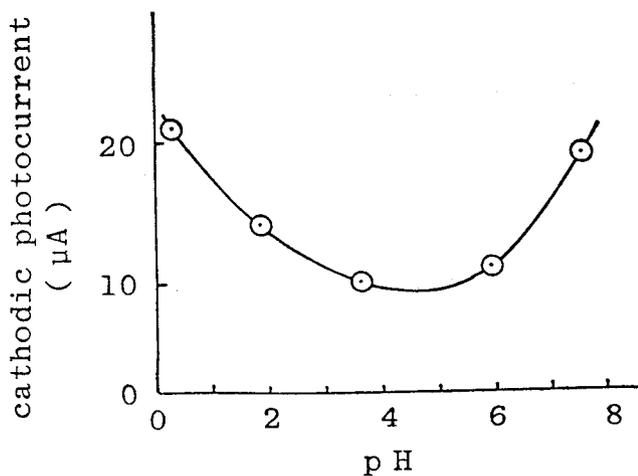


Fig. 6. pH-dependence of cathodic photocurrent.

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relationship at room temperature<sup>9</sup> :

$$E_{fb} = \text{const.} - \frac{RT}{F} \text{pH} = \text{const.} - 0.059 \text{pH (V)}$$

At higher pH's,  $E_{fb}$  deviates significantly from this slope, indicating that  $H^+$  is not the dominant species, but other ions contained in buffer solution may probably be adsorbed on the TPP surface. It is interesting to compare the observed  $V_p$  with  $(E_{fb} - E_{redox})$  which gives the upper limit of the photovoltage. As can be seen from Fig. 5,  $V_p$  and  $(E_{fb} - E_{redox})$  both increase as pH rises; the ratio of  $V_p/(E_{fb} - E_{redox})$  is nearly constant (0.8~0.9) over the whole range of pH studied.

As for the pH-dependence of the cathodic photocurrent, increases in the photocurrent were observed below pH 4 and above pH 6 (Fig. 6). The increase at the neutral side was reasonably correlated to the increase of the photovoltage at this region. The increase at acidic side is probably due to kinetic reason, because the rate of the formation of hydroquinone depends upon the  $H^+$  ion concentration. In spite of such pH-dependence of the photocurrent and the photovoltage, the ratio of  $V_p/(E_{fb} - E_{redox})$  is almost independent of pH, suggesting that the efficiency for the photovoltage is little affected by a change of environment around the neighborhood of the TPP electrode surface, but it reflects the bulk property of TPP itself. Accordingly, the ratio can conveniently be utilized as a parameter which characterizes the photoeffect of the TPP electrode under the applied light intensity. Our attention is now directed toward the measurement of the ratios on various metalloporphyrins showing different life times of the excited state.

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