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PHOTOELECTROCHEMICAL BEHAVIOR OF CHROMATOPHORES AT SOME NOBLE METAL ELECTRODES

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When the photosynthetic organs, chromatophores, were electrolyzed under light by using some noble metal electrodes, the observed photocurrent depended both on electrode potential and on the concentration of chromatophores. The photocurrent was enhanced by addition of PMS, Methoxy PMS or DCPI to the chromatophore suspension. The mechanism of the photocurrent is also discussed briefly.

It has been expected that new energy without any pollution might be obtained in large amount in stead of petroleum. An utilization of inexhaustible solar energy is, therefore, desired as fulfilling the above mentioned condition. In this viewpoint, Fujishima and Honda[1], and Yoneyama et al.[2] developed photolytic systems of water using semiconductor electrodes and confirmed generation of hydrogen. However, it seems to be somewhat practice because the optimum wavelength for the photolysis lies in the ultraviolet region. Then, Matsumura et al.[3] studied the photogalvanic cell with a dye and observed the electron transfer from the dye molecule excited by visible light to the semiconductor electrode. This method is, however, disadvantageous because of the necessity to add a dye reductant for the observation of the continual photocurrent.

On the other hand, plant or photosynthetic bacterium possesses chloroplast or chromatophore as a photosynthetic organ, and efficiently converts solar energy to chrmical energy[4]. This photosynthetic organ possesses a large amount of light-harvesting pigments (chlorophyll analogs and carotenoid) and a sequence of electron transport system[5], which is driven over a wide wavelength[6]. As a model of the photosynthetic system, Takahashi and Kikuchi[7] devised chlorophyll electrodes and investigated conversion of solar energy to electrical energy. Moreover, Benemann et al.[8], Rao et al.[9], Ochiai[10] and Yagi[11] carried out photolysis of water to obtain hydrogen using chloroplast with hydrogenase. However, hydrogen could not be continually produced because of lowering the enzyme activity in the chloroplast.

On the other hand, chromatophore possesses a simpler structure than chloroplast, and its activity can be maintained for a relatively long time. We investigated the polarographic behavior of redox components bound to chromatophores under light, and found that the chromatophore possesses redox components whose current-potential curves were influenced by irradiation[12].

The present paper deals with the photoelectrochemical behavior of chromatophores by means of the constant potential electrolysis.

Chromatophores were prepared by the ordinary method[6] from the wild strain of Rhodospirillum rubrum. The chromatophores were suspended in 0.1 M Tris buffer (pH 8.0) and stored at 4°C in the dark. The concentration of chromatophores is expressed in terms of absorbance of bound bacteriochlorophyll at 880

nm (A_{880}). The most suitable electrolytic cell was devised in order to measure the resulting photocurrent when light was irradiated to the chromatophores. Dissolved oxygen was removed from the solution by bubbling oxygen-free nitrogen for 30 min. The irradiation was carried out with a tungsten lamp (60 W). A platinum plate (3X4 cm^2) or mercury pool electrode (3X4 cm^2) was used as a working electrode, a platinum wire as a counter electrode, and a saturated calomel as a reference electrode.

A typical current-time curve at a platinum electrode is shown in Fig. 1. The photocurrent was observed as soon as the light from a tungsten lamp was put on in the midst of an electrode at the constant potential, and when light was put off, the photocurrent decayed within a few seconds, finally to the background current. The increase of a current immediately after lighting was taken as the value of photocurrent. Light was put on when the background current was equal to 1/3, 1/5 or 1/10 of the initial current, or two minutes after beginning of electrolysis in the dark. The values of the photocurrent were almost the same for each condition (Fig. 2). Ther fore, the photocurrent was hereafter measured two minutes after beginning of electrolysis. Since the value of photocurrent became maximum at 6000 lx. as shown in Fig. 2, lighting was carried out at this illuminance.

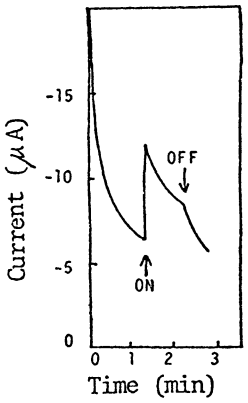


Fig. 1. A typical current-time curve on Pt electrode at -400 mV vs. NHE.

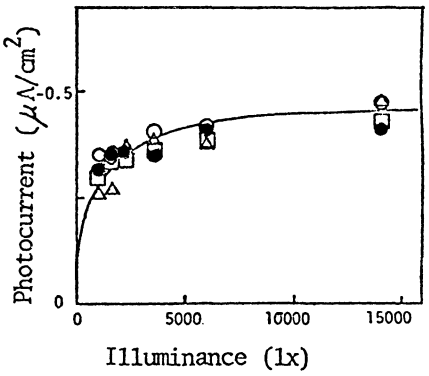


Fig. 2. Relationship of the photocurrent to illuminance. △,□, ○ and ● represent the values of 1/3,1/5, and 1/10 of the initial current, and 2 min. after beginning of electrolysis, respectively, obtained on Pt electrode at -400 mV vs. NHE.

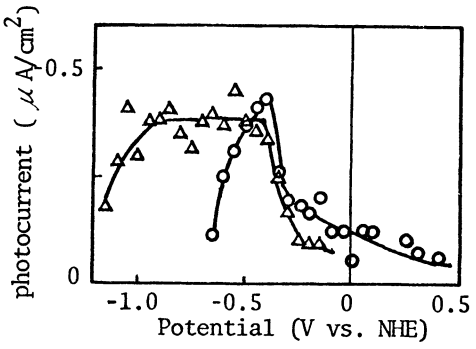


Fig. 3 Dependence of the photocurrent on applied potential. ○ and △ represent the value obtained on Pt and Hg pool electrodes, respectively.

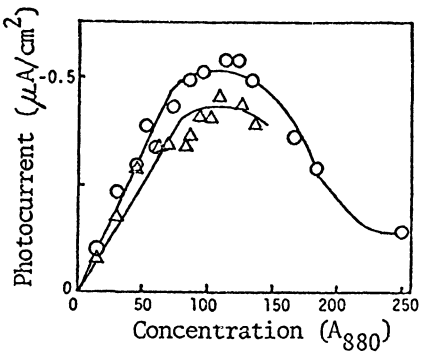


Fig. 4. Dependence of the photocurrent on concentration of chromatophores. The experimental conditions were the same as those in Fig.3, except that the applied potential was kept constant at -400 mV vs. NHE.

The measured photocurrent depended on the applied potential, and its maximum was observed at about -400 mV vs. NHE on both platinum and mercury pool electrodes (Fig. 3). In addition, the photocurrent increased with increasing concentration of chromatophores until A_{880} was equal to about 80 and then it decreased

because of lowering of the permeability of light (Fig. 4). The measurement of photocurrent was, therefore, carried out at A_{880} = 75 unless otherwise noted. It is clear from these experimental results that the reactant on the electrode is chromatophore itself, and the photocurrent results from a photo-excited redox component bound with chromatophores. Furthermore a photocurrent was enhanced by addition of some redox reagents to a suspension of chromatophores (Fig. 5). 5-Methylphenazinum methyl sulfate (PMS), 1-Methoxy-5-methyl phenazinum methyl sulfate (Methoxy PMS) or 2,6-dichlorophenolindophenol (DCPI) had a particular sensitizing effect among various redox additives. The photocurrent sensitized by these redox reagents depended on electrode potential, and its maximum was observed at about -200 mV vs. NHE for each reagent (Fig. 6). The sensitized photocurrent was observed in fairy lower concentration of PMS, Methoxy PMS or DCPI than that of chromatophores, and increased with increasing concentration of each reagent (Fig. 7). At the constant concentration of these reagents, the photocurrent also increased with increasing concentration of chromatophores. It seems possible that the photocurrent is sensitized by some interaction between a reagent and a redox component bound with chromatophores because the sensitizing effect is not always attributed only to their redox potentials.

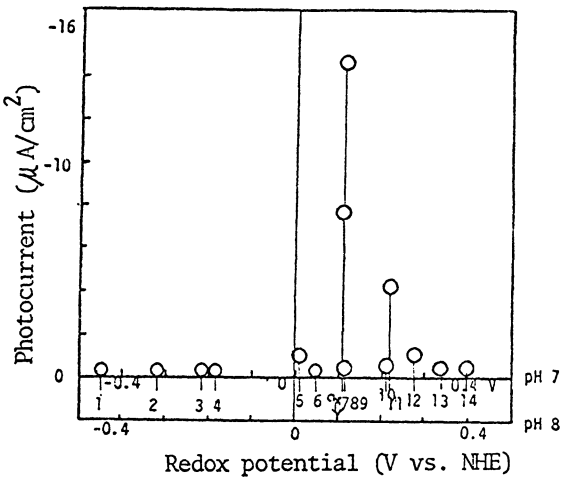


Fig. 5 Effect of redox reagents to the photocurrent. Number in the figure represents the redox reagent as follows; 1 methyl viologen, 2 neutral red, 3 FMN, 4 riboflavin, 5 methylene blue, 6 ascorbate, 7 Methoxy PMS, 8 PMS, 9 toluylene blue, 10 toluidine blue O, 11 DCPI, 12 p-methylaminophenol, 13 ferrocyanide, 14 p-phenylenediamine. The photocurrent for each reagent was measured at optimum condition on Pt electrode.

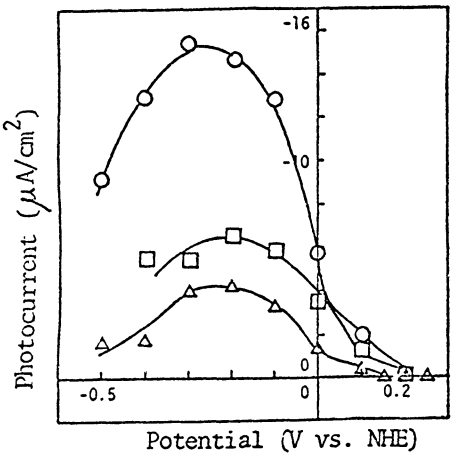


Fig. 6 Effect of redox reagents on photocurrent. (Pt electrode)
concentration; each 100μM
○Methoxy PMS, □PMS, △DCPI

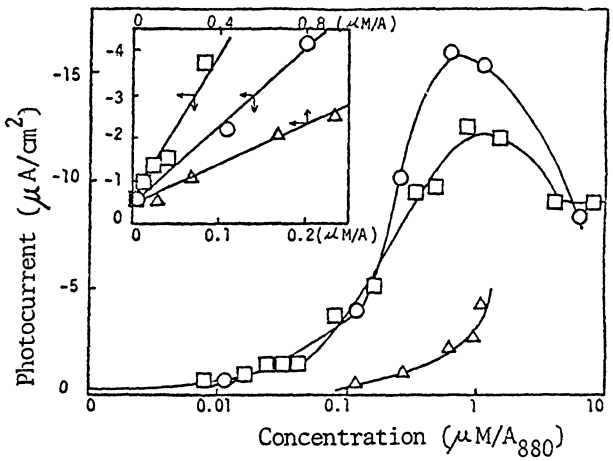


Fig. 7 Dependence of photocurrent on concentration of added reagent. Symbols in the figure are the same as those in Fig. 6. The applied potential was kept constant at -200 mV vs. NHE.

Experiments as mentioned below were carried out to find out a species of reactant with chromatophores. First, electrolysis of chromatophores was carried out for two minutes before lighting, during which PMS, Methoxy PMS or DCPI was added to the solution

at various time intervals. Second, one of these reactants was first electrolyzed and at any intervals later chromatophores were added to this solution, subjected to electrolysis for two minutes. In both experiments photocurrent was measured after lighting. Throughout this manipulation, the ratio of electro-reduced chromatophores to native chromatophores (Chr^-/Chr) was kept constant and only the ratio of electro-reduced redox reagent to unreacted reagent (PMS^-/PMS, Methoxy PMS^-/Methoxy PMS or $DCPI^-/DCPI$) was changed at the same time. The experimental results are shown in Fig. 8. It is clear from these results that the reactant with chromatophores was the reduced form of each redox reagent (PMS^-, Methoxy PMS^- or $DCPI^-$).

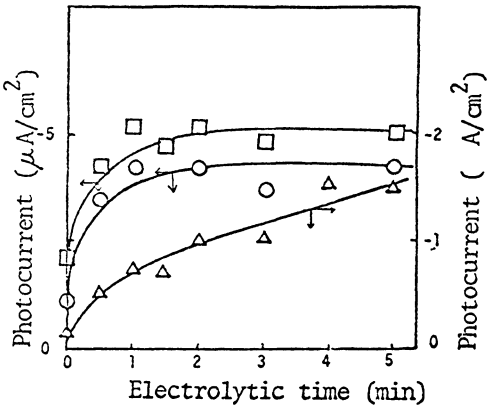


Fig. 8 Dependence of photocurrent on the ratio of electro-reduced reagent to unreacted reagent. (A_{880}=10) Simbols in figure are the same as those in Fig. 6.

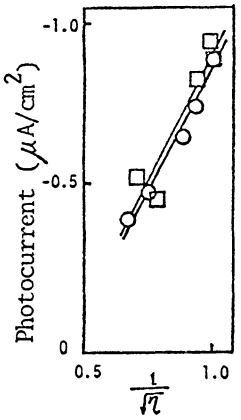
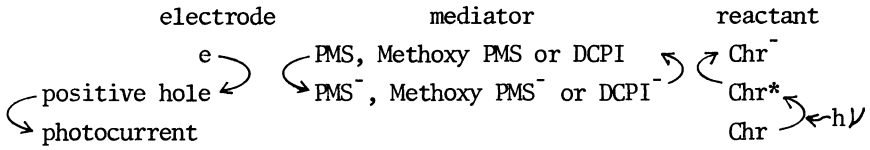


Fig. 9 Dependence of photocurrent on the viscosity of solution. (A_{880}= 5) ○ sucrose, □ glycerin . PMS; 20μM/A_{880} potential; -150 mV vs. NHE.

Next, sucrose or glycerin was added into the electrolytic solution in order to examine the nature of photocurrent. The photocurrent decreased with increasing viscosity of the solution, being proportional to the resiprocal of the square root of viscosity (Fig. 9). Accordingly, it seems probable that the diffusion velocity of chromatophore takes some roles in photocurrent.

The mechanism of photocurrent is considered to be presumably as follows, although a further detailed discussion is impossible at the present stage.



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