May, 1981] *Bull. Chem. Soc. Jpn.*, **54**, *1305—1307 (1981)* 1305

A Sandwich Photocell Using Chlorophyll Electrodes

Fujio Takahashi* and Tetuo Komori
Faculty of Engineering, Utsunomiya University, Utsunomiya 321

(Received August 22, 1980)

A sandwich-type photocell was made by placing an electrolyte between two electrodes. A transparent electrode, a glass plate coated with In_2O_3, was used for one electrode. A mixture of chlorophyll and 2-(*cis*-10-heptadecenyl)-6-methoxy-*p*-benzoquinone was spread onto this transparent electrode. A Pt plate covered by chlorophyll or a mixture of chlorophyll and riboflavin tetrabutyrate was used as the other electrode. The electrolyte contained flavin mononucleotide in a phosphate buffer. The potential difference between the two electrodes was 314 mV and the maximum photovoltage under illumination was 176 mV. The photocell is compact and can produce a photocurrent for more than 90 h.

Recently there have been many papers concerning the energy conversion from light to electricity by photocells using a chlorophyll-coated electrode.[1,2] We reported already that the photovoltage and the photocurrent were obtainable by light irradiation on a system of a chlorophyll-quinone electrode immersed into an electrolyte.[3] This system consisted of two chambers separated by a porcelain diaphragm; each chamber contained a different electrolyte. The composition of electrolyte in each chamber was changed when the photoelectrolytic reaction was carried out. It was thought that such a photocell had to be made of two electrodes immersed into one electrolyte.

A sandwich-type photocell in which chlorophyll was placed between two different species of metals was found to generate a photovoltage caused by the difference of contact potential barrier on the two interfaces of chlorophyll and metal.[4] If we modeled on this system, a photocell using the electrolyte could be made in a compact shape.

This paper will present the results concerning a sandwich type photocell in which the electrolyte was placed between two different chlorophyll electrodes. This should be more compact than the two-chamber-type photocell, and could be expected to keep the composition of electrolyte constant during a cycle in which the redox compound in the electrolyte was reduced at the cathode and in turn the equivalent amount of reduced compound was oxidized at the anode to recover the original form.

Experimental

Materials. Chlorophyll and 2-(*cis*-10-heptadecenyl)-6-methoxy-*p*-benzoquinone (IQ) were obtained as described in the previous paper.[5] Riboflavin tetrabutyrate (RTB) was made by Wakamoto Pharmaceutical Co. Glutathione (abbreviated GSH or GSSG as the reduced or the oxidized form), flavin mononucleotide (FMN) and the other chemicals were of reagent grade or the best commercially available.

Photocell. A glass plate coated by In_2O_3 containing 5% SnO_2, or a silver or platinum plate (2 cm × 4 cm each) was used as the electrode. One electrode was prepared by covering a layer of a mixture of chlorophyll and IQ (molar ratio 1:5). The layer contained 0.03 μmol/cm^2 of chlorophyll. The other electrode was covered by chlorophyll alone or by a mixture of chlorophyll and RTB. A sheet of parafilm (American Can Co.; 2 cm × 2 cm × 0.013 cm) hollowed out in one part (1 cm × 1 cm) was placed on the electrode and the hollow was filled by the electrolyte. Then another electrode was placed on top of it to set up a sandwich-type photocell.

Measurements. The potential was measured by a Kikusui Denshi volt-ammeter model 116 connected to a recorder. A projector lamp (100 V, 150 W) was used for the source of light. The light of shorter wavelength than 460 nm was cut off by a color filter, V-Y46, and the heat wave band was cut off by a water filter.

Results and Discussion

Various Combination of Electrodes. It was observed that the photovoltage was generated by photocells made up by various combinations of two electrodes under illumination. The electrolyte used was composed of 0.1 M KCl solution containing 1 mM GSH and 1/2 mM GSSG. Glutathione was used because it gave the highest photovoltage among several redox compounds in the electrolyte as reported in the previous paper.[5] The results are summarized in Table 1.

In the case that two In_2O_3 electrodes were used for the photocell, the potential of the chlorophyll electrode was found to shift to a positive state with respect to the chlorophyll-IQ electrode when the light was turned on. This is in accord with the result in the previous paper.[5] The In_2O_3 electrode acted as an anode in the system of In_2O_3 and Ag electrodes, but as a cathode in the system of In_2O_3 and Pt electrodes. On the system of Ag|Chl|electrolyte|Chl, IQ|In_2O_3, and the system of In_2O_3|Chl|electrolyte|Chl,IQ|Pt, the potential differences between two electrodes became lower after the light was turned on, because the photopotential of chlorophyll electrode against chlorophyll-IQ electrode was always positive.

Table 1. The potentials of the photocells of

$$\mathrm{M_1|Chl}\left|\begin{array}{l}\text{1 mM GSH}\\ \text{0.5 mM GSSG}\\ \text{0.1 M KCl}\end{array}\right|\mathrm{Chl,\ IQ\ (1:5)|M_2}$$

M_1	M_2	Potential (mV *vs.* M_2)		
		Dark (d)	Light (l)	Photovoltage (l) − (d)
In_2O_3	In_2O_3	15	84	69
In_2O_3	Ag	134	225	91
Ag	In_2O_3	−172	−149	23
In_2O_3	Pt	−98	−88	10
Pt	In_2O_3	175	228	53

3 × 10^4 lx, 20—24 °C.

The highest photovoltage was obtained with the system of In_2O_3|Chl|electrolyte|Chl,IQ|Ag. However this system was unstable. The photovoltage reduced with the lapse of time. Therefore the system of Pt|Chl|electrolyte|Chl,IQ|In_2O_3 was chosen for this work. This system produced a 0.05 μA/cm^2 photocurrent. It was thought that same other redox compound should be used instead of glutathione in order to obtain higher photovoltage and higher photocurrent.

The Photocells with FMN in Electrolyte. It is known that FMN can photoexcite and oxidize NADH, EDTA, or catecholamine easily.[6,7] Therefore, FMN rather than GSSG in the electrolyte might take the electron away from the chlorophyll electrode under illumination. The photoresponse-time curves of the photocell using FMN in the electrolyte were obtained and are shown in Fig. 1. Chlorophyll was coated on the In_2O_3 electrode. Another In_2O_3 electrode without coating was used as a counter electrode. The electrolyte contained 0.1 M KCl and 5 mM FMN in all cases.

The potential-time curve at the top in Fig. 1 shows that the potential shifted to a positive state at the beginning of light irradiation. Then the potential turned over into a negative state. It was assumed that photoexcited FMN might decompose to produce some substance whose isoalloxazine ring was reduced to form a hydroquinone type.[8] If so, the potential of the system containing EDTA, which reduced FMN under illumination,[6] should shift to a negative state more rapidly. It seems that the second curve in Fig. 1 sustains the above assumption. In order to keep the potential positive, the decomposition of FMN had to be avoided. Tryptophan is known to be effective for the suppression of FMN decomposition.[6] As seen at the bottom in Fig. 1, the potential of the system containing an equimolar mixture of FMN and tryptophan remained in the positive state during light irradiation.

A plate of Ag, Pt, or In_2O_3 covered by chlorophyll was used for one electrode. The other one was lined with a mixture of chlorophyll and IQ on In_2O_3 electrode. The electrolyte contained FMN and tryptophan. The results are summarized in Table 2. The potential difference between Ag and In_2O_3 electrodes was 40 mV under illumination. This value was the smallest. The potential difference of the Pt–In_2O_3 system was twice as great as that of the In_2O_3–In_2O_3 system.

It was found that the magnitude of the photovoltage was influenced by the pH of electrolyte. The pH-photovoltage curves obtained from the system of Pt|Chl|electrolyte|Chl,IQ|In_2O_3 are shown in Fig. 2. The maximum photovoltage appeared around pH 7 for the FMN-tryptophan electrolyte. The glutathione result is also shown in Fig. 2.

For the promotion of electron transfer at the surface of the chlorophyll electrode, RTB was mixed with chlorophyll on a Pt electrode. RTB was expected to relay the electron from chlorophyll on the electrode to FMN in the electrolyte. The photovoltages on the system of Pt|Chl,RTB|FMN,Trp|Chl,IQ|In_2O_3 are shown in Fig. 3. The results show 176 mV as the maximum photovoltage and 314 mV as the potential difference between the two electrodes.

At the optimum condition of the above photocell, the current shown in Fig. 4 was produced. The current began to reduce gradually with the lapse of time and finally reached an almost constant value.

TABLE 2. THE POTENTIALS OF THE PHOTOCELLS OF

M_1|Chl|5 mM FMN, 5 mM Tryptophan, 0.1 M KCl|Chl, IQ (1 : 5)|M_2

M_1	M_2	Potential (mV *vs.* M_2) Dark (d)	Light (l)	Photovoltage (l) − (d)
In_2O_3	In_2O_3	45	141	96
Ag	In_2O_3	−23	40	63
Pt	In_2O_3	146	289	143

3×10^4 lx, 20—26 °C

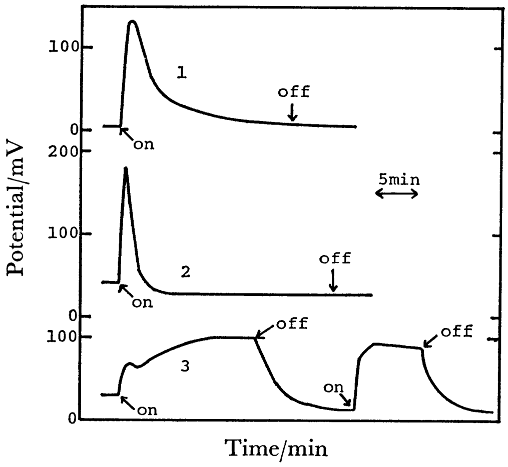


Fig. 1. The potential-time curves of the photocell using FMN in electrolyte.
In_2O_3|Chl|0.1 M KCl, 5 mM FMN, X|In_2O_3.
X: 1; none, 2; 2.5 mM EDTA, 3; Tryptophan.
Chl: 0.03 μmol/cm^2, 20—23 °C, 3×10^4 lx,

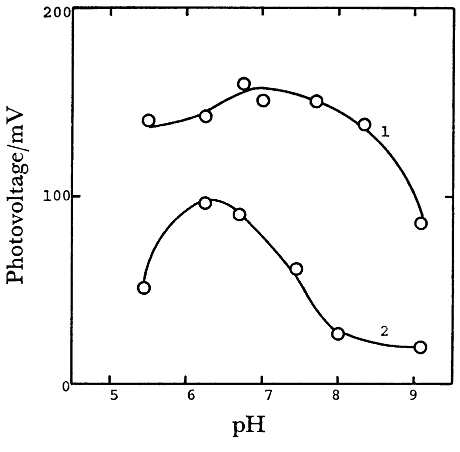


Fig. 2. The influence of pH to the photovoltage.
1: Pt|Chl|5 mM FMN, 5 mM Trp|Chl, IQ|In_2O_3,
2: Pt|Chl|1 mM GSH, 1/2 mM GSSG|Chl, IQ|In_2O_3, Chl: 0.03 μmol/cm^2, Chl:IQ=1:5, 19—24 °C, 3×10^4 lx.

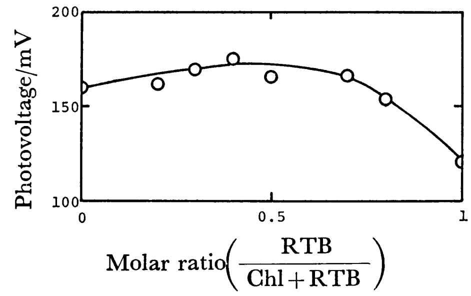


Fig. 3. The influence of molar ratio to the photovoltage.
Pt|Chl, RTB|5 mM FMN, 5 mM Trp (pH 6.7)|Chl, IQ|In_2O_3. Chl: 0.03 μmol/cm^2, Chl:IQ=1:5, 25—31 °C, 3×10^4 lx.

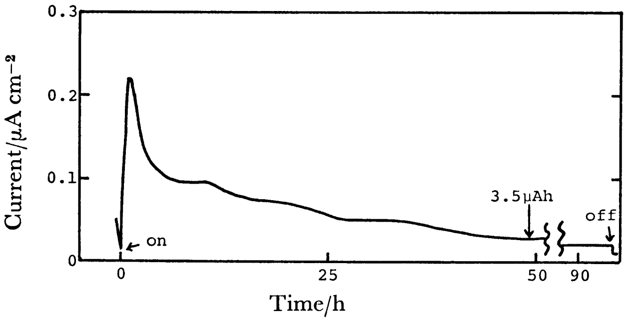
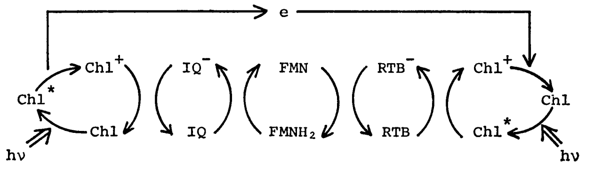


Fig. 4. The photocurrent.
Pt|Chl, RTB|5 mM FMN, 5 mM Trp (pH 6.7)|Chl, IQ|In_2O_3. Chl: 0.03 μmol/cm^2, Chl:RTB=1:1, Chl:IQ=1:5, 31—32 °C, 3×10^4 lx.

A steady state was found to exist after the current which had been passed reached the theoretical amount for the reduction of FMN in the electrolyte (3.5 μA h).

It is plausible from Fig. 1 that FMN in the electrolyte is reduced at the chlorophyll-RTB electrode and the photopotential shifts to a negative state, and thus the photocurrent becomes smaller. The reduced FMN, which is a strong reducing agent,[9] is susceptible to being oxidized to reproduce FMN at the chlorophyll-IQ electrode. Therefore it is very possible that a steady state was obtained during the photoelectrochemical reaction.

As a conclusion, the electron transfer process of the photocell may be the following:



References

1) H. Tributsch and M. Calvin, *Photochem. Photobiol.*, **14**, 95 (1971); V. B. Evstigneev *et al.*, *Biofizika*, **19**, 810, 820, 997 (1974); F. K. Fong and N. Winograd, *J. Am. Chem. Soc.*, **98**, 2287 (1976); T. Miyasaka, T. Watanabe, A. Fujishima, and K. Honda, *J. Am. Chem. Soc.*, **100**, 6657 (1978).

2) A. F. Janzen and J. R. Bolton, *J. Am. Chem. Soc.*, **101**, 6342 (1979).

3) F. Takahashi and R. Kikuchi, *Biochim. Biophys. Acta*, **430**, 490 (1976); F. Takahashi and R. Kikuchi, *Bull. Chem. Soc. Jpn.*, **49**, 3394 (1976); F. Takahashi, M. Aizawa, R. Kikuchi, and S. Suzuki, *Electrochim. Acta*, **22**, 289 (1977).

4) C. W. Tang and A. C. Albrecht, *J. Chem. Phys.*, **62**, 2139 (1975); **63**, 953 (1975).

5) F. Takahashi, K. Seki, R. Kaneko, S. Sato, and Y. Kusumoto, *Bull. Chem. Soc. Jpn.*, **54**, 387 (1981).

6) G. K. Radda and M. Calvin, *Biochemistry*, **3**, 184 (1964); G. K. Radda, *Biochim. Biophys. Acta*, **112**, 448 (1966).

7) F. Takahashi, M. B. Rahman, and H. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 716 (1976).

8) "Riboflavin," ed by R. S. Rivlin, Plenum Press, New York and London (1975), p. 12.

9) "Progress in Bioorganic Chemistry," ed by E. T. Kaiser and F. J. Kézdy, John Wiley & Sons, New York (1976), Vol. 4, p. 44.