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PHOTOELECTROLYSIS USING CHLOROPHYLL ELECTRODES

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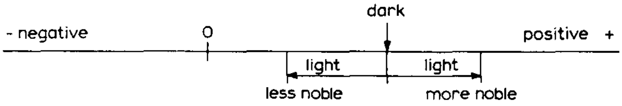
SUMMARY

By the conversion of sunlight to chemical energy, photoelectrolysis was carried out using two different chlorophyll-redox compound lining electrodes. These electrodes were prepared by covering platinum plates with chlorophyll and naphthoquinone or anthrahydroquinone and a conducting adhesive. These electrodes exhibit a photoexciting property. The potential was found to shift to a less noble state when the system of the chlorophyll-naphthoquinone electrode was inserted into NAD solution with illumination. On the other hand, the photoexcitation of the system of the chlorophyll-anthrahydroquinone electrode inserted into ferrocyanide solution made the potential more noble. (If the potential in the dark is in the positive region of the scheme and the potential moves in the positive direction when the light is turned on, it can be said to be more positive or more noble. But if the potential moves in the negative direction in the light, but remains in the positive region, it can be said to become less noble, but it is not suitable to say that it becomes more negative.) To make the potential difference between two electrodes as big as possible, various factors such as intensity of illumination, molar ratio of chlorophyll to naphthoquinone or anthrahydroquinone and concentration of redox compound in electrolyte were examined.



A cell was set up by combining the system of the chlorophyll-naphthoquinone electrode in NAD solution with that of the chlorophyll-anthrahydroquinone electrode in ferrocyanide solution, and photoelectrolysis was carried out by closing the external circuit with illumination. The photovoltage between the two electrodes was 0.25 V and the current density was 8 $\mu A/cm^2$. It was found that NAD was reduced to form NADH at the chlorophyll-naphthoquinone electrode and ferrocyanide was oxidized to form ferricyanide at the chlorophyll-anthrahydroquinone electrode.

INTRODUCTION

It is hoped ultimately that the energy carried by chemical compounds that are obtained as a result of energy conversion can be utilized by using the compounds as depolarizers for storage batteries. If Photosystems I and II in chloroplasts are regarded as a cathode and an anode, respectively, and sunlight as a source of electric power, then the photochemical reaction in the photosystems can be regarded as an electrochemical reaction [1].

Chlorophyll acts as an electron donor to form charge transfer complexes with quinone [2]. Chlorophyll produces a positive hole and a free electron during light exposure, by which one electron transfer occurs in the solution containing chlorophyll and quinone [3, 4]. Photoexcited chlorophyll is able to react with redox compounds pertaining to Photosystems I and II of chloroplasts. It is well known that the reduction potentials of Photosystems I and II are different [5]. This potential difference between two photosystems is thought to produce the driving force for the electron transfer, which provides a reduction of NADP at one side and an oxidation of hydroxide ion at the other. A light excitation of black lipid membranes of chloroplast extract is reported to give rise to the photovoltaic effect [6, 7]. The electrode that chlorophyll was deposited on was found to produce a photocurrent with illumination [8].

It is possible to obtain different photoelectromotive forces during light exposure using electrodes covered by thin layers containing different redox compounds with chlorophyll. A potential difference between two electrodes, which may produce photoelectrolysis during illumination, can therefore be expected. This is visualized as a model in Fig. 1. This chlorophyll-redox compound lining the electrode is characterized as a catalyst in the photoexcited state. (The expression "chlorophyll-redox compound electrode" is used for an electrode lined with chlorophyll/redox compound mixture. Similar expressions are used where the redox compound is specified.) According to Fig. 1 a redox compound, A, gains an electron from chlorophyll, which is excited by illumination. In turn the reduced A reacts with a redox compound, B, in an electrolyte to transfer an electron. The excited chlorophyll falls back to the ground state by gaining an electron from the counter electrode. The redox reaction on the counter electrode proceeds in the same manner as the former electrode except that the electron transfer is in the opposite direction. Therefore this photoelectrolysis using two electrodes which drive an electron transfer by photoexcitation can essentially be distinguished from a solar battery made from semiconductors [9–11], or the electrochemical photolysis, by using a metal oxide electrode [12].

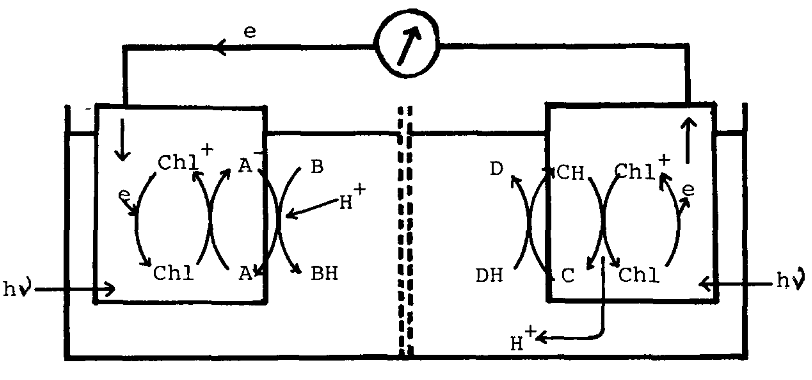


Fig. 1. Schematic diagram of photoelectrolysis.

This paper presents the results on the preparation of the chlorophyll-redox compound electrode and on photoelectrolysis using two different electrodes.

MATERIALS AND METHODS

Chlorophyll and reagents. Chlorophyll was prepared from spinach leaves by Jacobs' method [13] and preserved by dissolving in light petroleum in the dark. Chlorophyll obtained was a mixture of chlorophylls *a* and *b*. Naphthoquinone and anthraquinone were purified by sublimation. Naphthohydroquinone and anthrahydroquinone were obtained by the reduction of naphthoquinone and anthraquinone with sodium dithionite. All the other chemicals were of reagent grade or the best commercially availabel grade.

Ferricyanide, NADH and chlorophyll were determined by the measurements of absorbance at 420, 340, and 645 and 603 nm [14], respectively. NADH was identified using xanthine oxidase with methylene blue.

The conducting adhesive used was Fujikura-Kasei made Dotite D-362.

Preparation of electrodes. Chlorophyll, which was obtained from the stock solution after evacuation of light petroleum, was dissolved in 5 ml of benzene with requisite amounts of redox compounds, and then 1.0 g of conducting adhesive was added to the mixture. On the two faces of the platinum plate (2 cm × 4 cm), 0.5 ml of the mixture was spread and then dried to produce a homogeneous layer.

Measurements of potential. The chlorophyll-redox compound electrode was immersed into phosphate buffer solution (M/30, pH 6.9) that contained a different redox compound as a component electrolyte. The potential against the calomel electrode, which was connected to the system of the chlorophyll-redox compound electrode in the redox compound solution via a salt bridge, was measured before and after photoexcitation. The experiments were carried out in the dark room. The whole electric cell including calomel electrode was placed in the thermostat and controlled at 20 °C. Nitrogen gas was passed into the electrolyte during experiments.

The potential and current were measured by using a Kikusui millivolt-amperometer model 113 and a Toa Electronics Co. recorder EPR-2T. A photoreflector lamp (100 V, 500 W) was used for the illumination. The intensity of illumination was measured by Tokyo Koden illumination meter ANA-300.

Methods of photoelectrolysis. A U-shaped vessel separated into two chambers by a porcelain diaphragm was used for the photoelectrolysis to reduce NAD and to oxidize ferrocyanide in electrolyte using a source of illumination. 60 ml of 5 mM NAD solution were poured into one chamber and the chlorophyll-naphthoquinone electrode was inserted. 60 ml of 5 mM potassium ferrocyanide and the chlorophyll-anthrahydroquinone electrode were placed in the other chamber. The electrodes used were prepared by covering them with 2.5 μmol of chlorophyll and 2.5 μmol of naphthoquinone or anthrahydroquinone with 0.1 g of conducting adhesive. The photoelectrolysis was carried out with illumination at 10 000 lux after closing an external circuit.

RESULTS AND DISCUSSION

The system of the chlorophyll-redox compound electrode in the redox compound solution

The redox compounds shown in Table I were studied. The redox compound,

TABLE I

POTENTIALS OF THE SYSTEM OF THE CHLOROPHYLL-REDOX COMPOUND ELECTRODE IN REDOX COMPOUND SOLUTION

Results obtained in M/30 phosphate buffer (pH 6.9) at 20 °C, using 6000 lux for 1 min.

Redox compound (1 mM)	Potential (mV vs. standard calomel electrode)			
	Control electrode	Chlorophyll electrode	Chlorophyll-naphthoquinone electrode	Chlorophyll-anthrahydroquinone electrode
Ascorbic acid	− 35 (0)	−91 (−2)	−134 (0)	− 93 (+3)
Cysteine	− 36 (0)	−81 (+3)	−135 (0)	− 85 (+5)
Hydroquinone	+ 50 (0)	+ 7 (−3)	— —	+ 17 (−8)
Glutathione (reduced)	+ 81 (0)	+39 (−2)	+ 15 (−3)	+ 36 (+3)
NADH	+120 (0)	+60 (−4)	− 78 (0)	+ 86 (+7)
$K_4Fe(CN)_6$	— —	— —	+ 26 (0)	+ 60 (+9)
NAD	+ 92 (0)	+27 (+3)	+ 45 (−3)	+115 (0)
2,6-Dichlorophenolindophenol ($3.5 \cdot 10^{-2}$ mM)	+ 99 (0)	+62 (+3)	+ 6 (0)	+ 80 (0)
FAD	+ 88 (0)	+68 (+5)	+ 30 (−3)	+155 (0)
Benzoquinone	+126 (0)	+67 (+3)	— —	+130 (−7)
Lipoic acid (oxidized) (pH 7.8)	+ 97 (0)	+71 (+5)	+ 14 (−4)	+108 (0)
$K_3Fe(CN)_6$	— —	— —	+280 (−4)	+230 (0)
None	+ 76 (0)	+30 (0)	+ 45 (−2)	+100 (0)

which is spread with chlorophyll over platinum electrode, should be insoluble in water and able to form a charge transfer complex with chlorophyll and to react with both photoexcited chlorophyll and the redox compound in the electrolyte. The two electrodes prepared have to give a different potential with illumination. From the above considerations naphthoquinone and anthrahydroquinone were used as redox compounds in the electrode. The conducting adhesive was used in the role of binder to make the electric resistance lower. The layer on the platinum plate consisted of 0.1 g of conducting adhesive, 5 μmol of chlorophyll and 50 μmol of naphthoquinone or anthrahydroquinone.

As depolarizers in the electrolyte, 6 pairs of reducing and oxidizing compounds were chosen and a 1 mM solution of each compound was prepared in 0.03 M phosphate buffer.

The system was set up by putting the chlorophyll-redox compound electrode into each electrolyte, and measuring the potential against the calomel electrode before and after illumination at 6000 lux.

Some typical results of photoresponse are shown in Fig. 2. The potential was found to change rapidly within 1 min when the illumination was applied or removed. Table I summarizes the results in the cases of the chlorophyll-naphthoquinone electrode, the chlorophyll-anthrahydroquinone electrode, the chlorophyll electrode (without redox compound) and the control, which was an electrode covered by conducting adhesive only. The values of potential shift were determined 1 min after the illumination as shown in Fig. 2.

The control electrode exhibited no response to the illumination. The illumina-

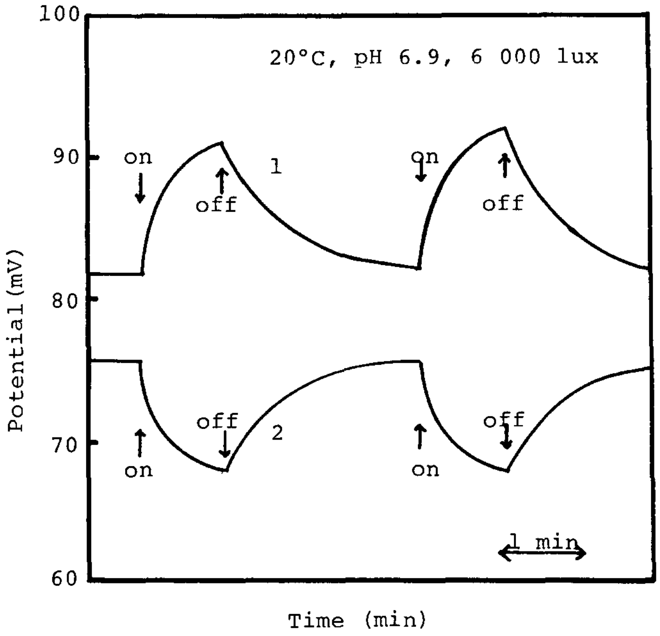


Fig. 2. Photoresponse of the electrodes. (1) The system of the chlorophyll-anthrahydroquinone electrode in 3 mM ferrocyanide solution. (2) The system of the chlorophyll-naphthoquinone electrode in 3 mM NAD solution. The molar ratio of chlorophyll and naphthoquinone or anthrahydroquinone was 1:1. Each system was connected with the calomel electrode via a salt bridge and was placed in the dark room. Potential shifts occurred when the light (6000 lux) was turned on (arrow) and potentials returned to their original values when the light was turned off. Potentials are given relative to the standard calomel electrode.

tion on the system of the chlorophyll electrode in the reducing compound solution made the potential less noble and that on the system of the chlorophyll electrode in the oxidizing compound solution made it more noble. It was found that the potential of each system in the dark was influenced by the redox compound. The results suggested that the illumination on the system of the chlorophyll electrode in the reducing compound solution might result in a transfer of an electron from the electrolyte to the electrode. With the system of the chlorophyll electrode in the oxidizing compound solution the electron transfer might be directed in the reverse way. Therefore the chlorophyll-naphthoquinone electrode might gain an electron from the counter electrode during the illumination. On the other hand photoexcited chlorophyll-anthrahydroquinone electrode might release an electron to the counter electrode. In turn the chlorophyll-naphthoquinone electrode might reduce and the chlorophyll-anthrahydroquinone electrode might oxidize the redox compound in electrolyte. It is desirable to obtain a higher potential difference between two electrodes for the photoelectrolysis. The potential on the system of the chlorophyll-naphthoquinone electrode in the oxidizing compound solution should be as noble as possible, and that on the system of the chlorophyll-anthrahydroquinone electrode in the reducing compound solution as little noble as possible.

On the basis of above discussion NAD and ferrocyanide were taken up for

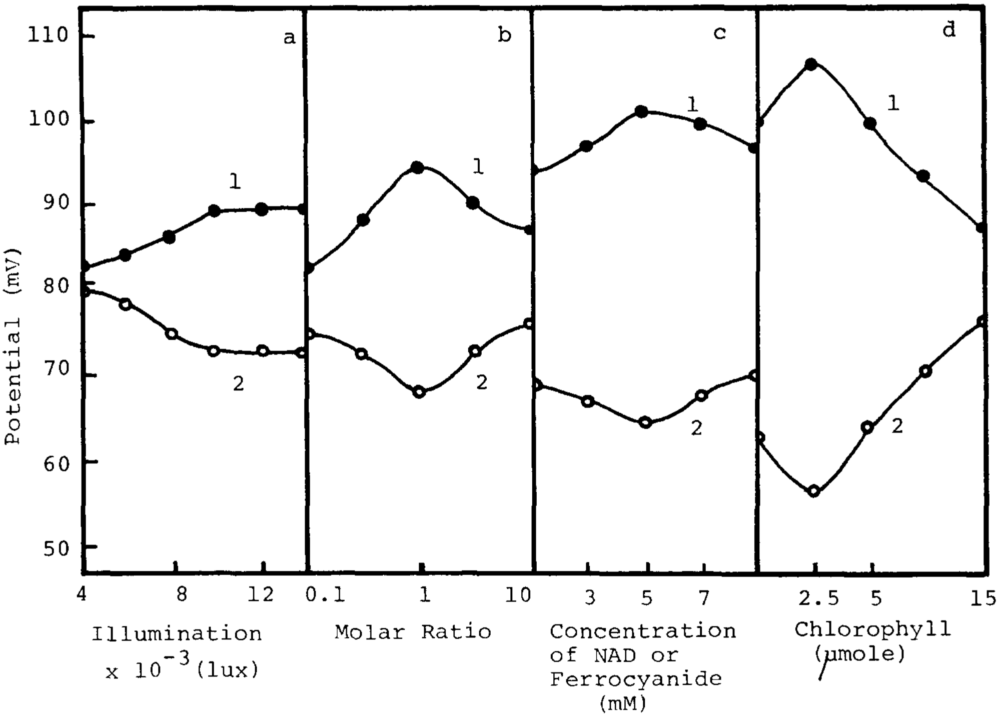


Fig. 3. The influence of various conditions to the potential. (1) The system of the chlorophyll-anthrahydroquinone electrode in ferrocyanide solution. (2) The system of the chlorophyll-naphthoquinone electrode in NAD solution. (a) 5 μmol of chlorophyll and 50 μmol of naphthoquinone or anthrahydroquinone were spread on the platinum plate, and the concentration of NAD or ferrocyanide was 1 mM in the electrolyte. The photoresponse of each system was determined with various strengths of illumination. (b) The potential shift of each system was measured with various molar ratio of naphthoquinone or anthrahydroquinone to chlorophyll on the platinum plate. The total number of mol of two components on the electrode was kept constant. The concentration of NAD or ferrocyanide was 1 mM. The intensity of illumination was fixed to 10 000 lux. (c) The optimal concentration of NAD or ferrocyanide in the electrolyte was surveyed with the illumination at 10 000 lux. On the platinum plate 5 μmol of chlorophyll and 5 μmol of naphthoquinone or anthrahydroquinone were spread. (d) Finally the optimal amounts of chlorophyll and naphthoquinone or anthrahydroquinone on the platinum plate were determined with the illumination at 10 000 lux. The molar ratio of two components was kept at 1:1. The concentration of NAD or ferrocyanide in the electrolyte was 5 mM. Potentials are given in mV relative to the standard calomel electrode.

redox compounds in electrolyte coming in contact with the chlorophyll-naphthoquinone electrode and the chlorophyll-anthrahydroquinone electrode, respectively.

Various conditions that might influence the potential were examined to obtain the conditions necessary for maximum potential difference. The results are summarized in Fig. 3. At first the value of potential shift from the potential in the dark to that in the light was measured with a different intensity of illumination. Each electrode used for the above measurement consisted of 5 μmol of chlorophyll and 50 μmol of naphthoquinone or anthrahydroquinone. The molar ratio of chlorophyll to naphthoquinone or anthrahydroquinone was 1 : 10. Each electrolyte contained 1 mM NAD or 1 mM potassium ferrocyanide in M/30 phosphate buffer (pH 6.9). The potential shift was found to reach a plateau in the region above 10 000 lux on illumination, so that the intensity of illumination was set up to 10 000 lux on the subsequent experiments (Fig. 3a). The effect of molar ratio on potential difference was also examined. The molar ratio of chlorophyll to naphthoquinone or anthrahydroquinone was varied, keeping the total number of mol constant. The concentrations of electrolyte were kept at 1 mM. The optimal ratio for both the electrodes was found to be 1 : 1 (Fig. 3b). At optimal conditions, 10 000 lux and the molar ratio of electrodes of 1 : 1, the optimal concentration of NAD or ferrocyanide in the electrolyte was found to be 5 mM (Fig. 3c). Finally, the optimal total number of mol of chlorophyll and naphthoquinone or anthrahydroquinone with 0.1 g conducting adhesive was to be 5 μmol (Fig. 3d). Under these optimal conditions, the potential of the chlorophyll-naphthoquinone electrode in NAD solution and that of the chlorophyll-anthrahydroquinone electrode in the ferrocyanide solution were found to become 25 mV less noble and 28 mV more noble, respectively, under illumination than in the dark.

Photoelectrolysis

The photoelectrolysis was carried out with the system of chlorophyll-naphthoquinone electrode in NAD solution with that of chlorophyll-anthrahydroquinone

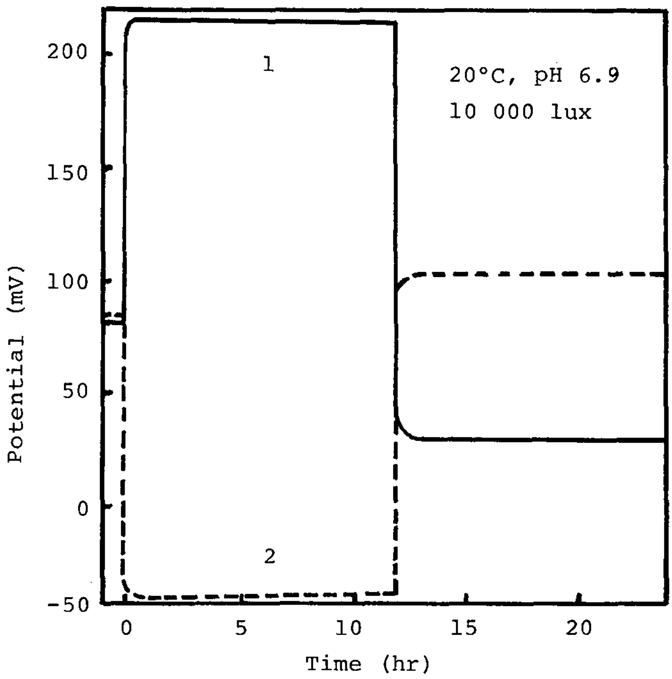


Fig. 4. The potential-time curve during photoelectrolysis on the system of the chlorophyll-naphthoquinone electrode in 60 ml of 5 mM NAD solution with the chlorophyll-anthrahydroquinone electrode in 60 ml of 5 mM ferrocyanide solution with the illumination at 10 000 lux. On the platinum plate 2.5 μmol of chlorophyll and 2.5 μmol of naphthoquinone or anthrahydroquinone were spread. The potentials of both electrodes were measured with the lapse of time. The light was turned off after 12 h, keeping the circuit closed. Potentials are given in mV relative to the standard calomel electrode.

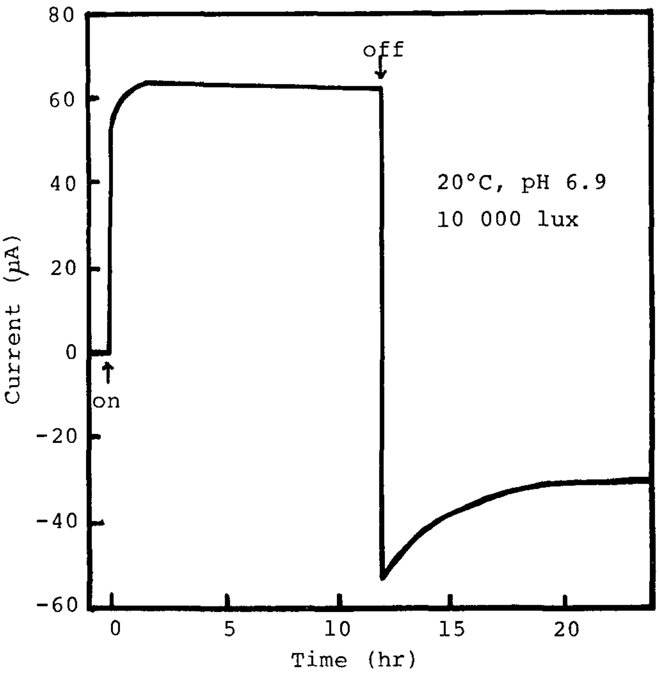


Fig. 5. The current-time curve during photoelectrolysis measured in the same experiment as in Fig. 4.

electrode in ferrocyanide solution. A cathodic and an anodic reaction occurred at the chlorophyll-naphthoquinone electrode and the chlorophyll-anthrahydroquinone electrode, respectively. The photovoltage between two electrodes was 0.25 V. When either of two electrodes was sheltered from light, the cell would not produce current. Both electrodes need to be photoexcited for photoelectrolysis to occur. The conversions of NAD to NADH and of ferrocyanide to ferricyanide were determined with the lapse of time. The current was kept almost constant. Turning the light off and keeping the external circuit closed after 12 h, the cell was found to produce a reverse current caused by a reverse electromotive force (Figs. 4 and 5). The amount of current passed during 12 h was $28 \cdot 10^{-6}$ Faraday. From Fig. 6, 11 μmol of NADH and 21 μmol of ferricyanide were produced. Current efficiency during the 12 h was calculated to be 79 % and 78 % for the NAD/NADH and ferricyanide/ferrocyanide systems, respectively.

The amount of current passed ($28 \cdot 10^{-6}$ Faraday) was much greater than the theoretical amount of current for the reduction of naphthoquinone and for the oxidation of anthrahydroquinone on the electrodes ($5 \cdot 10^{-6}$ Faraday because of 2 electrochemical equivalents). It seemed that naphthoquinone was not reduced and anthrahydroquinone was not oxidized during photoelectrolysis.

When the chlorophyll-naphthohydroquinone electrode was used as cathode and the chlorophyll-anthraquinone electrode as anode in the cell for photoelectrolysis, under the same conditions as in Fig. 4 except for the electrodes, the potential difference between the two electrodes was 34 mV and the photocurrent was not observed. If naphthoquinone was reduced completely and anthrahydroquinone oxidized complete-

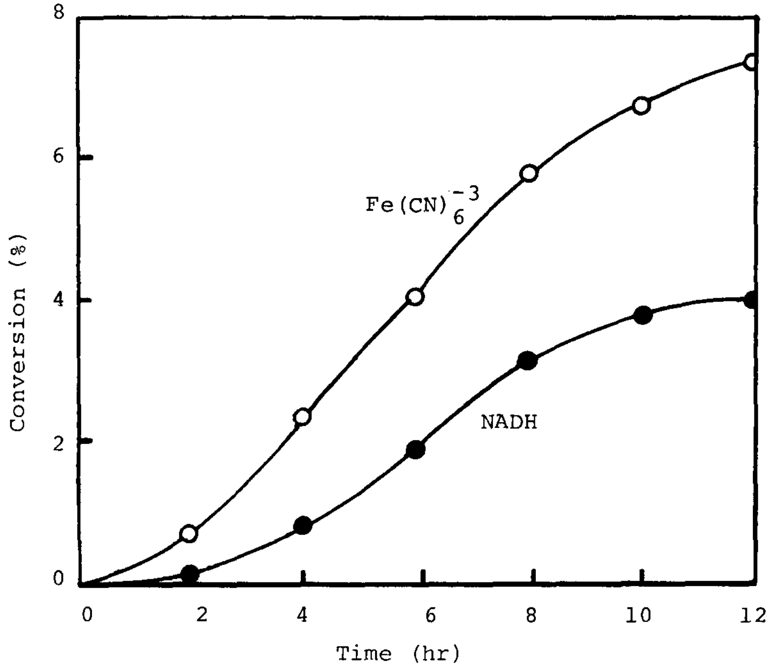


Fig. 6. The reduction of NAD and the oxidation of ferrocyanide during photoelectrolysis determined in the same experiment as in Fig. 4.

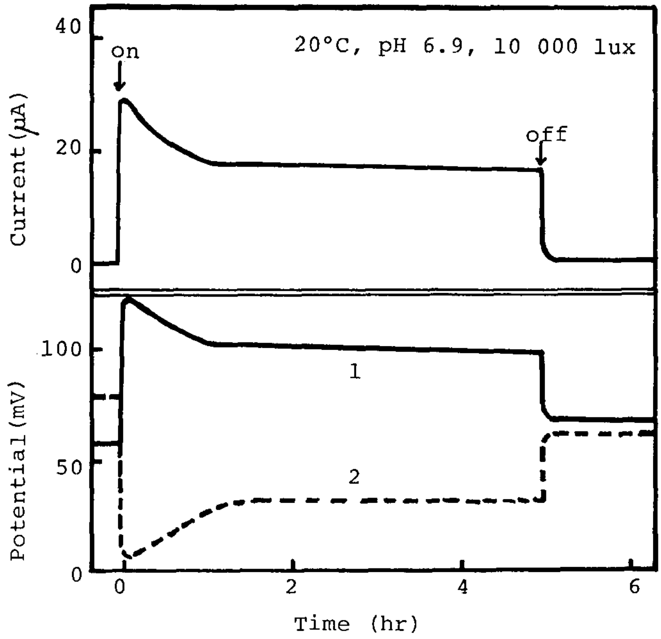


Fig. 7. Photoelectrolysis with the system chlorophyll-naphthoquinone electrode/phosphate buffer solution/chlorophyll-anthrahydroquinone electrode. The same electrodes as in Fig. 4 were used. (1) The chlorophyll-anthrahydroquinone electrode. (2) The chlorophyll-naphthoquinone electrode. Potentials are given in mV relative to the standard calomel electrode.

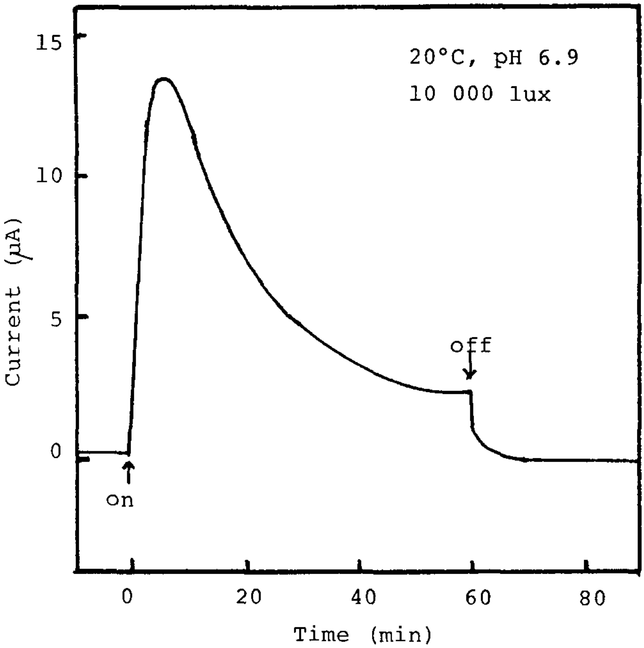


Fig. 8. The photoelectrolysis with the system of the chlorophyll-anthraquinone electrode in 60 ml of 5 mM NAD solution with the chlorophyll-naphthohydroquinone electrode in 60 ml of 5 mM ferrocyanide solution. On the platinum plate 2.5 μmol of chlorophyll and 2.5 μmol of anthraquinone or naphthohydroquinone were spread.

ly, it seemed that the chlorophyll-naphthoquinone electrode and the chlorophyll-anthrahydroquinone electrode were no longer capable of reducing NAD and oxidizing ferrocyanide. As a possible explanation of this result, we would propose that a 1 : 1 complex of chlorophyll and naphthoquinone or anthrahydroquinone was formed on the electrode and that this complex might be photoexcited to transfer an electron.

The photoelectrolysis was carried out using the chlorophyll-naphthoquinone electrode, the chlorophyll-anthrahydroquinone electrode and the electrolyte containing neither NAD nor ferrocyanide. The current and photovoltage produced (Fig. 7) were lower than those in Figs. 4 and 5. The products of electrochemical reaction at both electrodes have not yet been identified, but are probably hydrogen and oxygen.

The photoelectrolysis was carried out by inserting the chlorophyll-anthraquinone electrode in place of the chlorophyll-naphthoquinone into NAD solution and the chlorophyll-naphthohydroquinone electrode in place of the chlorophyll-anthrahydroquinone electrode into ferrocyanide solution. The result obtained is shown in Fig. 8. The photovoltage was 60 mV. As compared with Figs. 4 and 5, it is concluded that the combination of the chlorophyll-naphthoquinone electrode and the chlorophyll-anthrahydroquinone electrode gives a higher photovoltage than that of the chlorophyll-anthraquinone electrode and the chlorophyll-naphthohydroquinone electrode. This follows because the redox potential of naphthoquinone/naphthohydroquinone (0.482 V) is more noble than that of anthraquinone/anthrahydroquinone (0.155 V) [15].

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