J. Membrane Biol. 41, 377–388 (1978)

Effect of Quinones on the Photoelectric Properties of Chlorophyll *a*-Containing Lipid Bilayers

Barry R. Masters* and David Mauzerall**

The Rockefeller University, New York, New York 10021

Received 12 December 1977

Summary. A Mueller-Rudin lipid bilayer formed from egg lecithin, cholesterol *n*-decane, and chlorophyll *a* when separating asymmetric solutions of oxidant and reductant is capable of developing both a photoconductance and a photovoltage when exposed to continuous light focused on the bilayer region. The incorporation of plastoquinones (PQ-5 or PQ-9) increases the dark and photoconductances up to twenty times. Other quinones and hydroquinones also increased the conductance. The role of pH gradients on the electrical conductivity is discussed in terms of proton and electron transfer across the membrane solution interfaces.

Since Kofler isolated plastoquinone from lucerne in 1946, there has been an accumulation of evidence which supports its putative role in photosynthetic reactions. Crane and Lester (1958) rediscovered this substituted quinone and suggested that it may play a role in the electron transport of higher plants. Plastoquinones play a role analogous to ubiquinone in mitochondria by acting as a redox carrier in the photosynthetic electron system (Amesz, 1973). Plastoquinone is a trisubstituted *p*-benzoquinone: 2,3 dimethyl-5-(3′methyl-2′-butenyl-octakis (3′-methyl-2′-butenylene)- 1,4 benzoquine (Trenner *et al.*, 1959; Kofler *et al.*, 1959). Plastoquinone homologues are designated as PQ-*n*, where *n* indicates the number of isoprenoid units in the side chain.

Plastoquinones are found only in the photosynthetic systems that utilize water as a source of reducing power and evolve oxygen; all other photosynthetic systems contain ubiquinone. In spinach chloroplasts the concentration of PQ-9 is 1.1 moles per 10 moles of chlorophyll (Crane, Ehrlich & Kegel, 1960). Bishop (1959) showed that plastoquinone may function as a redox carrier in photosynthetic electron transport. A detailed review of the role of plastoquinones in photosynthetic electron transport is available (Amesz, 1973).

* *Present Address:* Department of Ophthalmology, Boston University School of Medicine, Boston, Massachusetts 02118.

** To whom reprint requests should be made.

0022-2631/78/0041-0377 $02.40

This investigation is an attempt to study the role of plastoquinones in the photosynthetic system by means of a model system in which the plastoquinone and the chlorophyll are contained in a thin Mueller-Rudin lipid bilayer which separates an oxidizing and a reducing solution. Tien (1968) was the first to observe photoeffects in chlorophyll containing lipid bilayers. He has written a comprehensive monograph on bilayer lipid membranes (Tien, 1974). Photoeffects in pigmented bilayer model systems have been investigated by several authors using various chromophores. A recent symposium summarizes this material very well (Tien, 1976).

Our model system uses purified components, in contrast to some of the previous systems which employed chloroplast extracts, and is a continuation of the investigation of photoeffects in porphyrin-containing bilayer lipid membranes investigated by Hong and Mauzerall (1972*a–b*, 1976). The system that we used consisted of purified chlorophyll *a* (Chl-*a*) and pure synthetic plastoquinone or other quinones which were dissolved in the lecithin-decane spreading solution. Previous studies indicate that the amphiphilic chlorophyll molecule is oriented at the membrane solution interface with the phytyl chain anchored in the hydrocarbon layer of the membrane and the polar porphyrin group situated at the interface (Steinemann *et al.*, 1971). It is found that up to 3×10^{13} chlorophyll molecules per cm^2 can be incorporated into the membrane (Steinemann *et al.*, 1971). The lipophilic plastoquinone molecules are presumed to be dissolved in the fluid hydrocarbon interior of the membrane. In order to introduce asymmetry into the model, and thus make a membrane more related to biological membranes, we place the membrane between oxidizing and reducing solutions. Exposure of this asymmetric system to continuous light absorbed by Chl-*a* results in a photoeffect which has two components: a photoconductance and a photovoltage which in general differ from the corresponding parameters in the dark.

It has been shown (Hong & Mauzerall, 1972*a*) that the photoconductance is due to the porphyrin or chlorophyll cation which is the charge carrier in the membrane, and whose conductance is dependent on the structure and hence the mobility of the molecule in the lipid bilayer (Hong & Mauzerall, 1976).

The origin of the present work was the postulate that plastoquinones incorporated into the chlorophyll BLM could function as an intramembrane carrier for electrons and protons and couple the interfacial electron transfer reactions between the chlorophyll molecules and the oxidizing and reducing agents in the two aqueous phases. Considerable evidence

exists for such a function in photosynthetic systems (Witt, 1971). Since the previous work on pigmented lipid bilayers (Hong & Mauzerall, 1976) had shown that the mobility of the porphyrin cation was the rate limiting step in the transmembrane conductance, it seemed reasonable that the smaller plastoquinone molecules could move across the bilayer more readily and couple the redox reactions at the interfaces resulting in an enhanced conductance. At a sufficient concentration of quinone, direct inter-quinone electron transfer might lead to even greater conductance. Protons would be expected to accompany the electron flow. We found some evidence for increased conductance, but still limited by another reaction, possibly that of proton transport across the interface.

Materials and Methods

Mueller-Rudin bilayer lipid membranes (BLM) were formed from 2% egg lecithin (Sylvana, Millburn, New Jersey) and 1% cholesterol (Applied Science Laboratories, State College, Pennsylvania) in *n*-decane, di-*n*-amyl ether (10:1, v/v). The lecithin was stored in sealed evacuated ampules in liquid nitrogen. The *n*-decane (Eastman Organic Chemicals, New York) was purified by shaking with concentrated sulfuric acid to remove unsaturated hydrocarbons, washed with sodium bicarbonate then with distilled water, dried with molecular sieves, and vacuum distilled. The di-*n*-amyl ether (Aldrich Chemical Co, Milwaukee, Wisconsin) was stirred with acidified ferrous sulfate to remove peroxides, washed with distilled water, dried, and vacuum distilled. Chl-*a* was extracted from fresh spinach and purified by column chromatography over polyethylene and sugar (Strain & Svec, 1966). The purity and concentration of Chl-*a* was determined on a Cary 15 recording spectrophotometer. The *p*-benzoquinone, *p*-benzohydroquinone, and duroquinone were gifts from Dr. S. Granick (The Rockefeller University). Ubiquinone 50 (Co-enzyme Q_{10}), were obtained from Sigma Chemical Co., St. Louis, Missouri. The plastoquinones PQ-5 (2,3, dimethyl-5-geronylbenzoquine) and PQ-9 were a gift of Dr. O. Isler, Hoffman-La Roche, Basel, Switzerland, and were used without further purification. The UV spectra of both PQ-5 and PQ-9 were measured and the compounds were in the oxidized form as determined from their absorption spectra. All of the inorganic salts were of analytical reagent grade (Mallinckrodt, St. Louis, Missouri) and were used without further purification. Measurements of photoeffects in membranes requires that several constraints be applied to insure the validity of the experimental measurements. It is important to insure that there is no effect of illumination on the BLM in the absence of Chl-*a*, thus excluding electrode artefacts. In the absence of Chl-*a* there was no effect of incorporating the quinones either in the dark or during illumination. The photoeffects required the presence of Chl-*a* and were solely determined by the asymmetric redox systems in the aqueous solutions and independent of the direction of illumination. We also stress the importance of using pure compounds in attempting to reconstruct the photosynthetic system. The plastoquinones were synthetized and analyzed for purity and chemical structure. Samples of Chl-*a* were purified by chromatography in order to separate them from Chl-*b* and other plant pigments. Lecithin in vials was stored in liquid nitrogen and formed membranes that were very stable and gave reproducible resistances.

Another constraint for the formation of a useful asymmetric membrane system is that the redox compounds be limited to the aqueous phases and do not diffuse across

the membrane. The use of potassium ferrocyanide and potassium ferricyanide as redox agents in the aqueous phases confines them to the hydrophilic phase. Their high charge density prevents them from partitioning into the hydrophobic lipid membrane phase. Both of these compounds undergo reversible one-electron transfer reactions, and cause no change in the membrane resistance, either in the dark or during illumination in the absence of Chl-*a* incorporation into the BLM. Membranes were formed by the brush technique over a 1.95 mm^2 hole in a Teflon septum, which separates two 5-ml compartments. The standard conditions were: 10 mM solutions of potassium ferricyanide (oxidizing side) and 10 mM potassium ferrocyanide (reducing side) in 0.1 M potassium chloride, 10 mM potassium phosphate buffer pH 7.0. A battery powered motor rotated two magnetic fleas which continuously stirred the two solution compartments. The temperature was maintained at 25 ± 1 °C. The Chl-*a* lecithin membranes thinned uniformly in less than 1 min and had resistances greater than $10^9\ \Omega\ cm^2$. They were stable for many hours and capable of withstanding potential differences of 180–200 mV. Water used to prepare the solutions was doubly distilled from potassium permanganate. The pH gradients were formed across the membranes by adding small aliquots of concentrated potassium hydroxide or hydrochloric acid.

A pair of calomel (frit junction) electrodes (Beckman Instruments, Fullerton, California) with a saturated potassium chloride bridge provided electrical contact with the solutions. The voltage clamp apparatus has been previously described (Hong & Mauzerall, 1972*a*, 1976). The apparatus was set to a 1-sec time constant. The measured parameter is the current flowing across an external resistor in the feedback loop which keeps the voltage drop across the membrane constant at the preset clamping voltage, V_c.

Since the pigmented membrane separating redox solutions has a conductance at least ten times that of the control membrane, we are concerned only with the pigment channel conductance (Hong & Mauzerall, 1972*a*). If the conductances and voltages are independent of the clamping voltage, a plot of change in feedback current with light off and on should be linear *vs.* clamping voltage. Since this is so, we shall make that assumption. If the conductances and voltages were linear functions of V_c, the same observation would hold, but the "conductances" and "voltages" would contain the slope parameters. We believe the present data do not justify this elaboration, nor the more probable nonlinear dependences on V_c. The following method was thus used to separate dark and photoconductances and voltages. The slope of the plot of feedback current in the dark (I_D) or light (I_L) *vs.* Clamping voltage (V_c) is defined as the dark (G_D) or light (G_L) conductance. The dark (V_D) or light (V_L) voltages are defined by the value of I_D or I_L at $V_c=0$ divided by G_D or G_L or, equivalently, as the negative of the intercept on the V_c axis at I_D or $I_L=0$. The photo conductance (G_p) and photo voltage (V_p) are defined as $G_p=G_L-G_D$ and $V_p=V_L-V_D$. Since the photoconductance, G_p, was usually only 10–30% of G_D a more accurate evaluation was obtained by plotting the change in feedback current on illumination, $\Delta I=I_L-I_D$, versus V_c. The value of ΔI could be obtained more accurately by using electrical offsets in the measurement. Steady-state illumination was provided by a Helium-Neon laser (Metrologic Instruments, Bellmawr, New Jersey, 632.8 nm, 5 mW) which was focused to illuminate the bilayer portion of the membrane. An aluminum shutter was used to control the illumination. The feedback current increased linearly with light intensity over the range of illumination used.

Results

1) Photoresponse in Chl-a-Containing BLM

When a lecithin, cholesterol BLM, separating 10 mM ferricyanide and 10 mM ferrocyanide in 0.1 N KCL is doped with Chl-*a*, voltage clamped

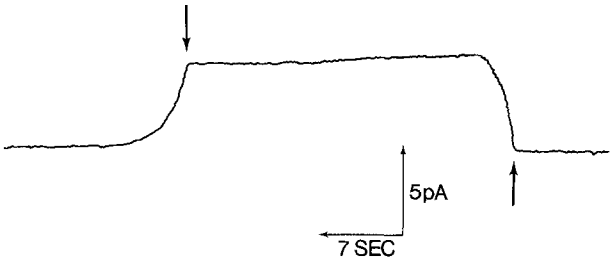

Fig. 1. The steady-state photoresponse from BLM containing Chl-*a* (5.14 mM) separating 5-mM solutions of ferricyanide and ferrocyanide in 0.1 N KCL (standard conditions). The BLM was voltage clamped at +100 mV. The small arrows indicate light on (↑) on the right side and light off (↓) on the left side. The rise time and the decay time are dependent on light intensity

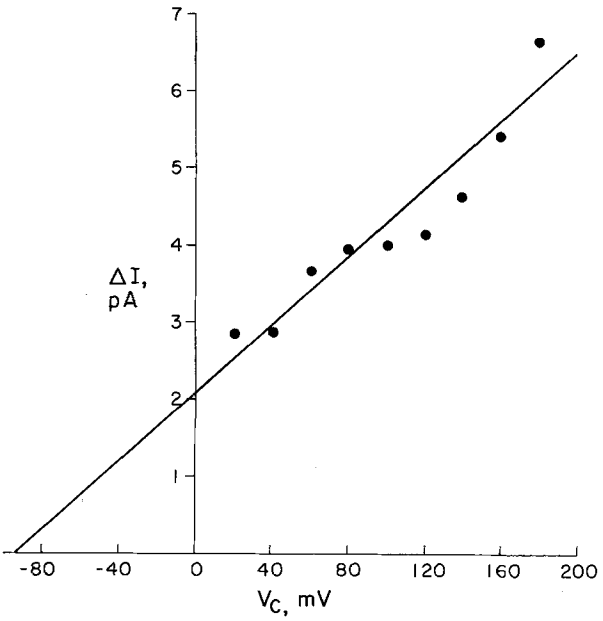

Fig. 2. The photoeffects of Chl-*a* (3.82 mM) BLM under the standard conditions. The abscissa, V_c, is the voltage at which the BLM is clamped, and the ordinate is ΔI, the difference in feedback current in the light minus that in the dark. The dark emf was 17 mV and the dark conductance was 0.1 nS

at +100 mV, and illuminated with steady-state light of 633 nm, a steady-state photoresponse developed which is shown in Fig. 1. The following procedures were performed as controls: (i) a lecithin, cholesterol BLM, separating a solution of potassium ferricyanide and potassium ferrocyanide yielded no detectable photoresponse upon illumination with 633 nm light, (ii) the same system described above but doped with Chl-*a* elicits a photoresponse that is independent of the direction of the incident light. Figure 2 shows a representative graph of the photoresponse of

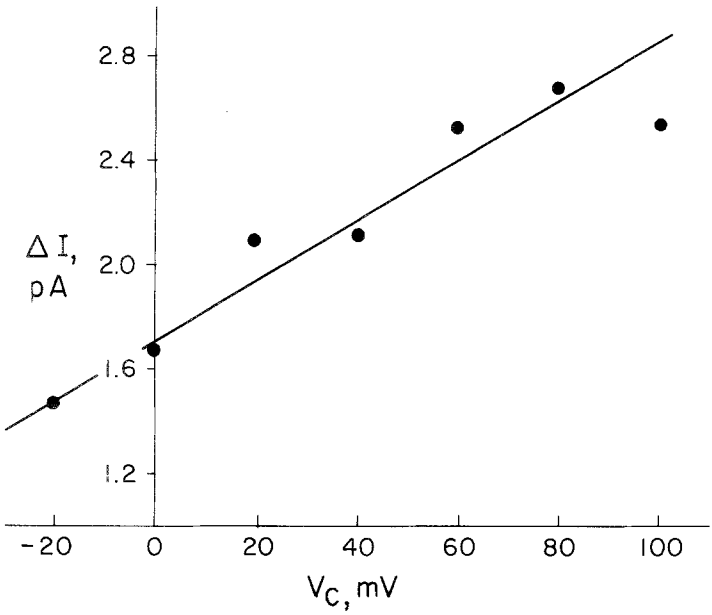

Fig. 3. The effect of 9.15 mM PQ-9 on the photoeffects of Chl-*a* BLM under the standard conditions. The dark Emf was 6 mV and the dark conductance 0.7 nS

a Chl-*a* BLM. The change in the current in the feedback circuit is a linear, increasing function of the clamping voltage. These bilayers were stable for 2 hr at clamping voltages of 200 mV. Since the conductance in the dark of the Chl-*a*-containing membrane was at least ten times that of the unpigmented membrane, we can neglect the lipid bilayer conductance and concern ourselves only with the pigment channel conductance (Hong & Mauzerall, 1972*a*).

2) The Effect of Quinones on the Photoresponse of the Chl-BLM-Redox System

In general, the addition of quinones to the pigmented BLM-redox system caused the dark and photo-conductances to increase and the dark and photo emf's to decrease. Figure 3 shows a representative photo response for the system containing PQ-9 and Fig. 4, one for the system containing PQ-5. The increase in feedback current is approximately linear with clamping voltage, implying a constant photoconductance. The data of many such experiments are summarized in Table 1. With PQ-9, the effects were small, except at the very highest concentration. With PQ-5,

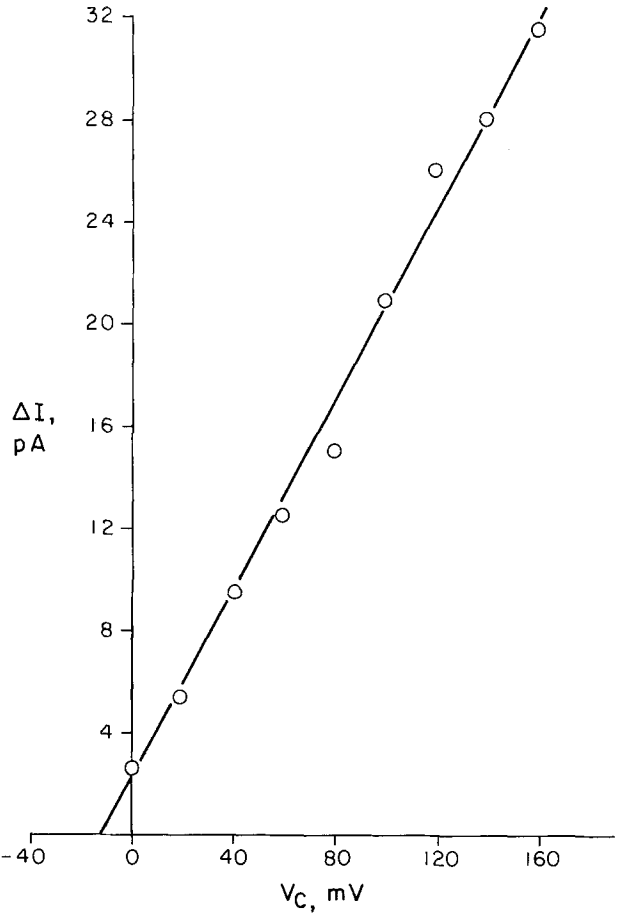

Fig. 4. The effect of 20 mM PQ-5 on the photoeffects of a Chl-*a* BLM under the standard conditions. The dark emf was 4 mV and the dark conductance 1.6 nS

the effects were larger, the conductance increasing 5–10 times and the photovoltage decreasing by a similar factor. The variation from experiment to experiment was large, but these figures are representative of the data. Table 2 lists the effects of various quinones and their redox forms on the system. Most of the quinones increased the conductance in the light, but only PQ-5 and *p*-benzohydroquinone increased it by large factors (10 and 20 times) in the dark. The oxidized and reduced forms of duro and benzoquinones had differing effects, showing that an equilibrium redox situation was not reached during the experimental time. The large increase in dark conductance with *p*-benzohydroquinone required Chl, since in the absence of the pigment the dark conductance was 0.01 nS (nano Siemens), about the same as that of the BLM alone.

Table 1. The effect of plastoquinone on the Chl-BLM-redox system

Quinone	Conc. (mM)	Conductance (nS)		Voltage (mV)	
		Dark	Photo	Dark	Photo
None	–	0.2±0.1	0.03±0.015	9±3	9±2
PQ-9	1.7	0.2	0.02	5	6
	9	0.7	0.01	6	2
	13	0.4	0.02	14	4
	17	0.4	0.01	3	3
	33	0.7	0.03	1	4
	230	3.0	0.09	1	3
PQ-5	20	1.7	0.17	6	1
	50	1.2	0.10	8	3

The concentration of Chl-*a* in the BLM spreading solution varied from 3.3 to 5.1 mM with no discernable effect. Other conditions were standared (*see* experimental section). Root mean square errors of the control experiments are given

Table 2. The effect of various quinones and hydroquinones on the Chl-BLM-redox system

Quinone (Q)	Conc. (mM)	Conductance (nS)		Voltage (mM)	
		Dark	Photo	Dark	Photo
None	–	0.2±0.1	0.03±0.015	9±3	9±2
Plasto Q-9	17	0.4	0.01	3	3
Plasto Q-5	20	1.7	0.17	6	1
UBIQ-50	23	0.2	0.03	13	10
DUROQ	4.5	0.3	0.07	6	5
DUROHYDROQ	4.5	0.2	0.33	6	−1
p-benzo Q	17	0.4	0.015	15	5
p-benzhydro Q	18	4.7	0.04	3	0

The Chl-a concentration varied from 3.3 to 5.1 mM. Other conditions were standard (*see* experimental section). Root mean square errors of the control experiment are given.

3) Proton Gradients and the Conductivity of the Quinone-Chl-BLM-Redox System

The possible proton movement is expected to be in the same direction as the electron flow (*see Discussion*). This flow of protons carried by the hydro or semi-quinone would cause decreased conductance to be measured. Since only a small change or a large increase in conductance was seen in the previous experiments at neutral pH, attempts were made to change the probability of proton flow by forming a pH gradient

across the membrane. We were restricted to pH$\geqq$7 on the oxidizing side because of the instability of ferricyanide ion in acid. The pH gradients will be given as oxidant side/reducing side. A gradient of 7/11 had little effect on the dark and photo conductance of the Chl-BLM-redox system, but a gradient of 11/7 increased the photo conductance six times and doubled the dark conductance. When PQ-9 was present, essentially the same effect on the photo conductance was obtained, but the dark conductance decreased seven (gradient 7/11) and three (gradient 11/7) times from the already high conductance (0.7 nS) with no gradient. The presence of PQ-5 caused a large increase in dark conductance for the 7/11 gradient and no change in the photo conductance. In general, the dark voltages increased in the presence of the gradients, and the only exception to the general rule of decreasing voltage with increasing conductance occurred with PQ-5 and the 7/11 gradient in the dark.

Discussion

We begin by describing our interpretation of the photoeffects in the chlorophyll lipid bilayer-aqueous redox system, which is based both on the present work and on previous work with very similar systems (Hong & Mauzerall, 1972*a–b*; 1976). The pigment is confined to the lipid bilayer, and the redox reactants are confined to the two aqueous phases (Fig. 5). Those chlorophyll molecules close to the interface can transfer an electron to ferricyanide ion, forming Chl cation and ferrocyanide. The reaction goes to a slight extent in the dark, but is complete with the excited state of Chl because of, respectively, disfavorable and favorable free energies. The cation can react with ferrocyanide at the same interface, regenerating Chl and ferricyanide, at a rate dependent on the concentration of ferrocyanide at the interface. This is kept very low in the present experiments. The cation can also diffuse down its concentration gradient to the reducing side of the bilayer, where rapid electron transfer occurs (Hong & Mauzerall, 1976). The steady-state conductance will be determined by the number of charge carriers and thus the light intensity, and inversely by the time required for a Chl molecule to undergo a complete cycle of diffusion and electron transfer at both interfaces. The steady-state photovoltage is a more complicated phenomena which involves concentration polarizations in the lipid and at the interfaces. In support of this view, we have noted that the rate of stirring affects the voltage, which is a direct proof of gradients in the aqueous layer.

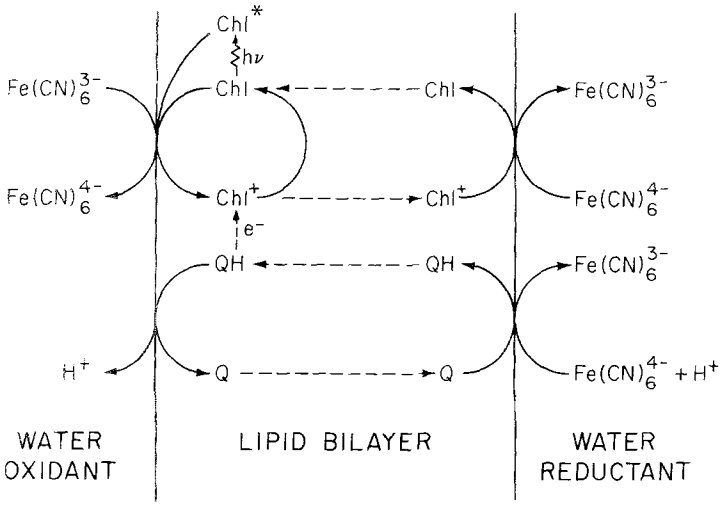

Fig. 5. Scheme to illustrate the coupling between the Chl-*a* molecules and the quinone molecules inside the lipid bilayer. The chlorophyll in the ground state (Chl), in the excited state (Chl*), and the chlorophyll cation (Chl^+) are confined to the lipid membrane, together with the quinone in the oxidized (Q) and reduced (QH) form. The ferricyanide and the ferrocyanide are confined to the aqueous phases. Coupling may occur either through the direct migration of quinones across the membrane or by the multiple shunt mechanism described in the text. Reduction of Q in the lipid bilayer is accompanied by uptake of protons from the water and oxidation by release to the water

The general correlation of lower voltages with increasing conductance is strong evidence for concentration gradients within the membrane. The steady-state photovoltage arises from the photon-formed charge transfer pairs at the interface and decreases with the dissipation of these gradients through diffusion and reaction at the reducing interface. The dependence of the relaxation times on light intensity (Fig. 1, legend) is in agreement with the view. The limiting current arises either from the light-limited number of carriers or from the limiting mobility and interfacial reaction of these carriers. Since we can estimate that the quantum yield for this current would be only 10^{-5} and we have evidence of a much larger yield ($\sim 10^{-1}$) at the interface (Hong & Mauzerall, 1976), the second hypothesis is far more likely and agrees with the conclusion on the photoconductance (*see below*). The relation of the dark voltage and conductance was more variable and may contain several components.

The effects of adding quinones to this system can now be anticipated. As shown in Fig. 5, the reduced form of the quinone is oxidized by Chl^+, generating Chl and the oxidized quinone which, following diffusion

to the reducing interface, is reduced there. Four forms of the reduced quinone can be considered: The semiquinones $Q^{\cdot -}$ and $QH^{\cdot}$ and the hydroquinones QH^- and QH_2. We omit the hydroquinone form Q^{--} as being highly disfavored by the lipid environment. While oxygen in the bilayer can react with the semiquinones, the ions formed, $O^{\cdot}_2^-$ and $HO^{\cdot}_2$ would react similarly to the semiquinones to first approximation, only their mobility would be greater. The reaction of Chl^+ with the anions will carry current of the same sign as Chl^+ migration and thus will increase the conductivity in proportion to the increased mobility of the anions over the chlorophyll cation. However, the neutral forms of the reduced quinones will be favored in the membrane over the anionic forms. The reaction of Chl^+ with the neutral forms is expected to occur by loss of a proton at the oxidant interface, since the cationic protonated quinone forms are strong acids. In this case no electrical current would pass across the membrane, but proton transport would become coupled to electron transport. Finally, if the concentration of quinone in the bilayer were sufficiently large, direct electron (and proton) jumps could occur between quinones causing charge (or proton) migration without physical migration of the quinone. It was, in fact, found that the addition of lipid-quinones PQ-9 and PQ-5 increased the conductance between roughly two- and ten-fold (Table 1). Except for the large increase of conductivity at the highest PQ-9 concentration, which could be the onset of the interesting electron jump conductivity, the increase of conductance seems to be limited. Interfacial photo electron transfer and the reaction of Chl^+ with ferrocyanide are known to be very rapid (< 1 μsec) under these conditions (Hong & Mauzerall, 1976). The electron transfer reactions with quinones may be slow, but use of a more powerful reductant than ferrocyanide, NADH, did not increase the conductance with PQ-9. Therefore, proton flow may be limiting. This possibility was tested by varying the pH of the oxidant and reductant sides of the membranes. With PQ-9 no large difference was seen over that with Chl alone, but with PQ-5 a 15-fold increase conductance was seen with a pH gradient. This gradient opposes the proton flow and and thus would increase the electrical conductivity. This limited evidence, together with the striking fact that by far the largest conductivity changes (about 20-fold) occurred with the most water soluble substance, *p*-hydrobenzoquinone (Table 2), suggests that an interfacial reaction is limiting. The evidence presented here is incomplete, but we believe it offers a promising approach to the study of electron and proton interfacial reactions so important to all of biology.

We wish to thank Dr. F.T. Hong for helpful discussions. This work was supported by the NIH grant GM-20729.

References

Amesz, J. 1973. The function of plastoquinones in photosynthetic electron transport. *Biochim. Biophys. Acta* **301**:35

Bishop, N.I. 1959. The reactivity of a naturally occurring quinone (Q-255) in photochemical reactions of isolated chloroplasts. *Proc. Nat. Acad. Sci. USA* **45**:1696

Crane, F.L., Ehrlick, B., Kegel, L.P. 1960. Plastoquinone reduction in illustrated chloroplasts. *Biochem. Biophys. Res. Commun.* **3**:37

Crane, F.L., Lester, R.L. 1958. The distribution and function of coenzyme Q. *Plant Physiol.* **33** (Suppl. Vii)

Hong, F., Mauzerall, D. 1972*a*. The separation of voltage-dependent photoemfs and conductances in Rudin-Mueller membranes containing magnesium porphyrins. *Biochim. Biophys. Acta* **275**:479

Hong, F.T., Mauzerall, D. 1972*b*. Photoemf at a single membrane-solution interface specific to lipid bilayers containing magnesium porphyrins, *Nature New Biol.* **240**:154

Hong, F.T., Mauzerall, D. 1976. Tunable voltage clamp method: Application to photoelectric effects in pigmented bilayer lipid membranes. *J. Electrochem. Sci.* **123**:1317

Kofler, M., Langemannm, A., Rüegg, R., Chopard-dit-Jean, L.H., Rayround, A., Isler, O. 1959. Die Struktur eines pflanzlichen chinons mit isoprenoiper seitenkette. *Helv. Chim. Acta* **42**:1283

Steinemann, A., Alamuti, N., Brodmann, W., Marschall, O., Lauger, P. 1971. Optical properties of artificial chlorophyll membranes. *J. Membrane Biol.* **4**: 284

Strain, H.H., Svec, W.A. 1966. Extraction, separation, estimation, and isolation of the chlorophylls. *In*: The Chlorophylls. p. 21. L.P. Vernon and G.R. Seely, editors. *Academic press. New York*

Tien, H.T. 1968. Light-induced phenomena in black lipid membranes constituted from photosynthetic pigments. *Nature (London)* **219**:272

Tien, H.T. 1974. Bilayer-Lipid Membranes. Marcel Dekker, New York

Tien, H.T. 1976. Photoelectric bilayer lipid membranes. *Photochem. Photobiol.* **24**:95

Trenner, N.R., Arison, B.H., Erickson, R.E., Shunk, C.H., Wolf, D.E., Folkers, K. 1959. Coenzyme Q. VIII. Structure studies on a plant quinone. *J. Am. Chem. Soc.* **81**:2026

Witt, H.T. 1971. Coupling of quanta, electrons, fields, ions and photophosphorylation in the functional membrane of photosynthesis. *Q Rev. Biophys.* **4**:365