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# Photovoltaic effects of metal-chlorophyll-a-metal sandwich cells\*

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The microcrystalline chlorophyll-a film prepared by the method of electrodeposition is shown to have strong photovoltaic effects. The photovoltaic cell ( $M_1|Chl|M_2$ ) has lamellar arrangement with the Chl-a film sandwiched between two metal electrodes. With dissimilar electrodes of different work functions,  $\phi_M$ , the cell usually exhibits a dark rectification behavior. A large forward bias current is seen when the metal with a lower  $\phi_M$  is the negative electrode. The rectification is small when the same metal is used as both electrodes. A blocking contact or Schottky barrier is evidently present at the Chl-a/metal junction particularly for the metal having a low  $\phi_M$ . A *p*-type semiconduction in Chl-a is implicated. In the photovoltaic mode, cells such as (Al|Chl|Hg) and (Al|Chl|Au) have an open circuit voltage ranging from 200–500 mV. The power conversion efficiency for these cells is on the order of  $10^{-3}\%$  which is among the highest in photovoltaic cells using organic materials. The direction of the photovoltaic current and the shape of its action spectrum are strongly dependent on the electrode materials. The blocking contact at the Chl-a/metal junction is primarily responsible for the photovoltaic activity of the cell. When this blocking contact is established at the directly illuminated electrode the action spectrum closely matches the absorption spectrum of the Chl-a film. An inverse type response is found when the blocking contact is at the indirectly illuminated electrode with the Chl-a layer essentially acting as an inner filter. The photocurrent is shown to increase when the cell is reverse biased. A minimum quantum yield for charge generation of about 0.03 is found in (Al|Chl|Hg) and (Al|Chl|Au) cells.

## I. INTRODUCTION

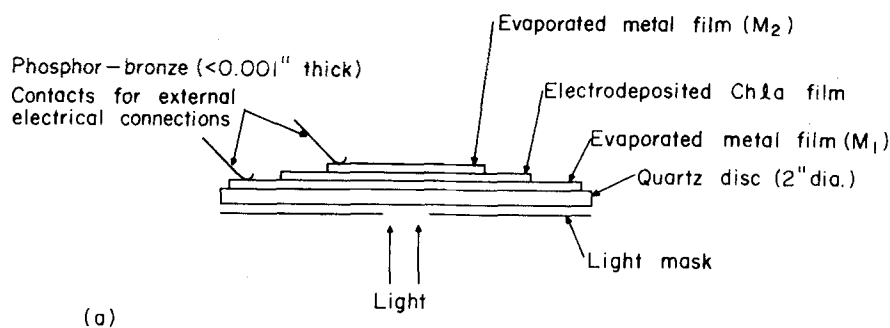
Investigations of photoelectric effects in chlorophyll-a (Chl-a) are important for understanding its semiconducting properties and ought to have a bearing on the primary processes in photosynthesis. However, most studies have dealt with analogues of Chl-a such as phthalocyanines and porphyrins as well as their metallic complexes.<sup>1,2</sup> It appears that it has been relatively more difficult to prepare Chl-a samples, usually in the form of films, suitable for photoelectric experiments. The results obtained with the model substances are often used to impute similar mechanisms for the Chl-a system and ultimately in photosynthesis. The early studies<sup>3,4</sup> of photoconductivity and photovoltaic effects in Chl-a itself have generally found that Chl-a is a rather poor photoconductor. However, it is not clear whether the low quantum efficiency of photoconductivity was due to the low efficiency of charge generation or due to the trapping of charges by the medium. It has been shown more recently that Chl-a under certain specific experimental conditions can have a high quantum efficiency for photoeffects. For example, Akimov,<sup>5</sup> Tributsch and Calvin<sup>6</sup> have found that Chl-a in contact with a semiconductor such as ZnO is rather efficient in sensitizing energy or electron transfer processes. Meilanov *et al.*<sup>7</sup> have measured a quantum yield of about 0.1 for the photoconductivity of Chl-a film sandwiched between two aluminum electrodes. Interestingly, the action spectrum for the photoconductivity was roughly the inverse of the absorption spectrum in this case. Yevstigneyev<sup>8</sup> and co-workers in a series of studies on the photovoltage of Chl-a in solution have shown that the sign and magnitude of the photo potential depends significantly on the pH of the medium and the presence of electron donors or acceptors. Photochemical reactions are implicated. Similar results are reported by Simpson, Freeman, and Reucroft.<sup>9</sup> Reucroft and Simp-

son<sup>10</sup> have observed the photovoltaic effects in Chl-a-Chloranil lamellar systems. They measured the efficiency of power conversion for such a cell and found it to be only on the order of  $10^{-13}$ . Furthermore, with only Chl-a monolayer film, negligible photovoltage was seen.

Extensive work by Soviet investigators has shown that photoconductivity of Chl-a is enhanced in the presence of water vapor.<sup>2,3</sup> The photoconductivity action spectrum shows a red shift when the Chl-a is activated by water. This corresponds to the formation of a new species of Chl-a which has a strong absorption band with a peak at 740–745 nm. More recent work by Katz and co-workers<sup>11</sup> has established that the new species is possibly a Chl-a-H<sub>2</sub>O adduct which has an ordered structure in the aggregated state. This form of Chl-a has been loosely called microcrystalline Chl-a.

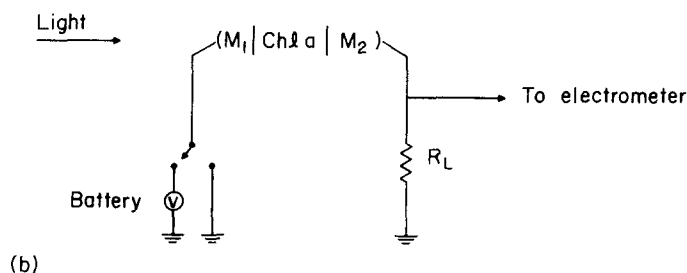
In a previous paper<sup>12</sup> a simple technique has been reported in preparing a film of microcrystalline Chl-a on a metal electrode surface by electrodeposition. The film prepared by this method is very uniform and particularly suitable for photoconductivity and photovoltaic studies. Such a film has been found to give an extremely fast photoconductivity signal with a response time shorter than nanoseconds.<sup>13</sup> The quantum yield for charge generation in such a film is estimated to be greater than 0.05.

The present report is concerned with the photovoltaic effects of microcrystalline Chl-a film prepared by electrodeposition. The photovoltaic system consists of the Chl-a film sandwiched between two metals. It will be shown that this photovoltaic cell has a power conversion efficiency comparable to that reported for the most efficient photovoltaic systems using organic materials. A power conversion efficiency on the order of  $\sim 10^{-4}\%$



(a)

FIG. 1. (a) Photovoltaic cell; (b) symbol for the cell and electrical arrangement.



(b)

has been reported for tetracene film<sup>14,15</sup> sandwiched between aluminum and gold electrodes. A recent report has shown that (Al|Mg-phthalocyanine|Ag) has attained an efficiency of  $10^{-2}\%$ .<sup>16</sup> Other organic systems usually have much lower efficiencies,  $<10^{-6}\%$ .

## II. EXPERIMENTAL

The fabrication of the metal-Chl-a-metal sandwich cell was done in the following sequence. A quartz disc (2 in. diam) used as a base plate was first etched in *aqua regia*, then washed thoroughly with distilled water and then dried in an oven. A semitransparent metal coating (10%–50% transmittance) was vapor deposited on the quartz disc in a vacuum ( $\sim 10^{-5}$  Torr). The heating element was a tungsten spiral. The metal coated quartz disc was removed from the vacuum (and thereby exposed to the atmosphere) before electrodepositing the microcrystalline Chl-a on its surface. No precaution has been taken to avoid oxidation of the metal coating on the quartz surface.

The electrodeposition of microcrystalline Chl-a on the semitransparent quartz disc was done by a method which has been previously described.<sup>12</sup> The semitransparent quartz disc forms the cathode in the electrodeposition cell. The anode is of polished aluminum. The spacing between the cathode and the anode can be varied between 0.25 to 5 mm by using teflon spacers of different thickness. To electrodeposit the microcrystalline Chl-a on the cathode, a suspension/solution of Chl-a in isoctane was introduced into the cell and a positive voltage was applied to the anode to give a field strength of about 1 kV/cm. Microcrystalline Chl-a (as distinct from the

monomers in solutions) was selectively electrodeposited on the cathode to form a fairly uniform film. The thickness of the film was varied by either using spacers of different thickness or suspension/solution of different concentration (typically  $5 \times 10^{-4}$  M).

To complete the metal-Chl-a-metal sandwich cell, a metal coating was vapor deposited upon the Chl-a layer, to form the back electrode. The Chl-a layer was first masked to expose only its center portion so that the second metal coating did not overlap the first metal coating on the quartz surface. When liquid metals such as mercury were used instead of the vapor deposited metal coating, such metal was simply placed on top of the Chl-a layer to form the back electrode.

The sandwich cell is shown in Fig. 1(a). The contact between the metal film on the Chl-a layer and the external electrical lead was made by means of a thin phosphor bronze metal ( $<0.001$  in. thick). In some cases, a better contact was made by placing a small drop of gallium or Hg/In at the junction. The contact point was located away from the light beam except in the cases when liquid metals were used directly as the electrode.

The metals used as electrodes for the photovoltaic cells are Al, Cr, Au, Cu, Ni, Ag, and the liquid metals used are Hg, Ga, Hg/In (60%–40%). The purity of these metals is better than 99.99%.

The thickness of the microcrystalline Chl-a film was measured by a Michaelson interferometer (Reichert, Austria). The accuracy of the interference measurement was about 30% for the Chl-a film thickness ranging from 1000 to 5000 Å. The optical density of the film

was measured in a Cary 14 spectrometer. Monochromatic light was used in all experiments. The light source is a 1000 W Sylvania tungsten halogen lamp, together with the "High Intensity" Bausch and Lomb monochromator (with a grating blazed for the visible region, catalog number 33-86-02). A photocell (EGG, SFD-160) was used to monitor the relative light intensities. The absolute light intensity was measured by a calibrated Eppley thermopile. The area of the Chl-a film exposed to the incident light was about  $7\text{ mm} \times 10\text{ mm}$ . The absolute flux of the light (745 nm) incident on this area was about 0.05 to 0.5 mW (after correction for the optical density of the metal coating on the quartz disc).

Electrical measurements were made with a Keithley 602 electrometer. The cell was carefully shielded by a brass jacket to minimize stray electrical noises. The sample was normally exposed to the atmosphere. In discussing the various photoelectric effects we shall speak of "open circuit" and "short circuit" modes of measurement. These terms refer to cases where, respectively, the external resistance,  $R_L$ , is much greater than the internal photoresistance of the cell or it is much less than this resistance.

### III. RESULTS

The notation:  $(M_1|\text{Chl}|M_2)$ , will be used for the sandwich cell, similar to that used by Lyons and Newman<sup>14</sup> in the tetracene work. Here  $M_1$  represents the front electrode facing the incident light beam.  $M_2$  represents the back electrode. The electrical arrangement is shown in Fig. 1b. In the photovoltaic mode,  $M_1$  is connected directly to ground. The dark characteristics and photocharacteristics of a typical cell,  $(\text{Al}|\text{Chl}|\text{Hg})$ , will be discussed in detail below. The measurements performed on this cell are representative and are carried out for most of the other cells having different electrode materials.

#### A. Dark $I$ - $V$ characteristic

Figure 2 shows the  $I$ - $V$  characteristics of this typical  $(\text{Al}|\text{Chl}|\text{Hg})$  cell. The Chl-a layer is about  $2500\text{ \AA}$  thick. The optical density (O.D.) of the Chl-a film is about 2.5 at 745 nm. The cell shows a strong rectifying effect. The forward bias corresponds to the Al electrode being negative. Current saturation in the forward direction has not been observed in this type of cell. Application of voltage higher than a few volts ( $\sim 2$ - $4\text{ V}$ ) often results in permanent destruction of the cell by shorting the electrodes. A semilogarithmic plot (Fig. 3) of the forward current versus applied voltage reveals that the forward current increases exponentially at low applied voltage. At higher voltage, the current varies as  $I \propto V^{2-4}$ . The lower exponent applies to the higher voltage range.

The  $(\text{Al}|\text{Chl}|\text{Hg})$  cell invariably exhibits a dark voltage. The open circuit dark voltage has a magnitude in the range from 50 to 150 mV. (The short circuit dark current is usually negligible compared to the photovoltaic current). It varies among different cells, and to a certain extent, depends on the contact area at the Al|Chl and Chl|Hg junctions. The sign of this dark voltage is always the same as that of the photovoltage with the Al electrode being negative. It is understood that in the photoeffects to be described below, the dark component has been subtracted.

#### B. Photoeffects

##### 1. Time behavior of the $(\text{Al}|\text{Chl}|\text{Hg})$ cell

The photovoltaic signal of the  $(\text{Al}|\text{Chl}|\text{Hg})$  cell often exhibits a fast transient spike which decreases gradually to a steady state (Fig. 4). This transient is particularly revealing in the short circuit current signal,  $I_{sc}$ , which has a fast response. In the open circuit mode, (with a

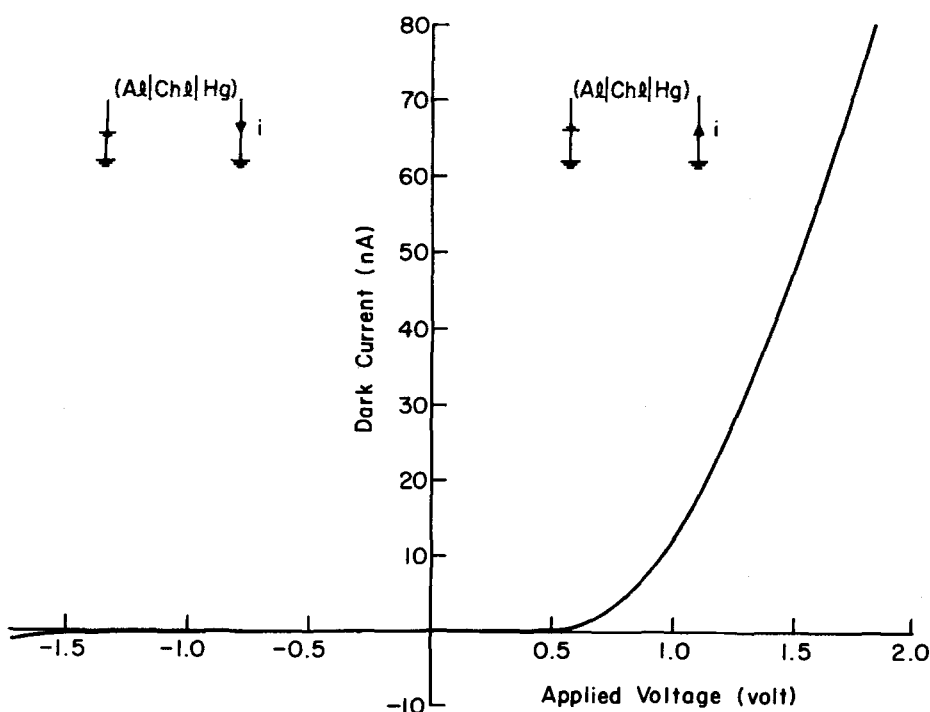


FIG. 2. Dark current-voltage characteristics.

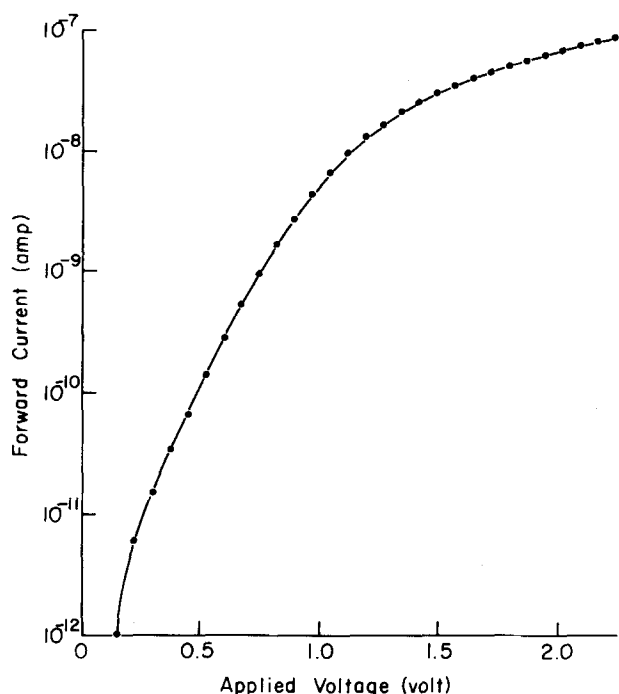


FIG. 3. Semilogarithmic plot of the dark current-voltage characteristics.

measuring resistance  $\sim 10^{14} \Omega$ ), the transient is seen in the open circuit photovoltage,  $V_{oc}$ , as a small initial rise above the steady state level which is reached in about 5 min. The response of the signal in this case is limited by the large time constant of the measuring circuit. The strength of the transient signal is dependent on the history of the sample and the dark wait period between consecutive exposures of the sample to the light.

The time behavior of the cell is rather complicated. In general a freshly prepared cell often shows larger

photovoltaic effects ( $\sim$  by a factor of 2) than one that has been used repeatedly in both dark and photo measurements. The photovoltaic cell is more stable when operating at a low light intensity ( $\sim 0.05 \text{ mW/cm}^2$ ). At this low light level, a typical cell can generate a photocurrent on the order of nanoamperes for a period of an hour without any significant decrease. However, at higher light intensities ( $\sim 10 \text{ mW/cm}^2$ ) the lifetime of the cell is much shortened probably due to deterioration caused by the larger photocurrents. For this reason, all measurements of the photovoltaic effects are carried out at low light levels ( $\sim 0.1 \text{ mW-cm}^{-2}$ ) and only the steady-state values of the signals are reported in this work.

## 2. Photo I-V characteristics

The sign of the photovoltage of the (Al|Chl|Hg) cell is such that the Al electrode is always negative. Figure 5 shows the photo I-V characteristics of a (Al|Chl|Hg) cell operating in the photovoltaic mode. The curve is obtained by varying the load resistance at a constant light intensity ( $\lambda = 745 \text{ nm}$ ). The photo  $V_{oc}$  of the (Al|Chl|Hg) varies between 200 to 500 mV and the photo  $I_{sc}$  ranges from 4 to 10 nA. The maximum power output from this cell through a matching resistor,  $\sim 10^7\text{--}10^8 \Omega$ , is about  $4 \times 10^{-10} \text{ W}$ . The incident light power on the active cell area ( $0.25 \text{ cm}^2$ ) is about  $6 \times 10^{-6} \text{ W}$  (after correction for the O.D. of the Al film). The power conversion efficiency at this light level is on the order of  $10^{-3}\%$ .

The light intensity dependence of  $V_{oc}$  and  $I_{sc}$  is shown in Fig. 6.  $V_{oc}$  is seen to vary only slightly with incident light intensities. Saturation is reached at a light intensity of about  $5 \times 10^{-5} \text{ W-cm}^{-2}$  at 745 nm.  $I_{sc}$  shows a much stronger light dependence with a light exponent in the range 0.8 to 1.0.

When the cell is operated with a reverse bias, i.e. with a positive dc voltage applied to the Al electrode,

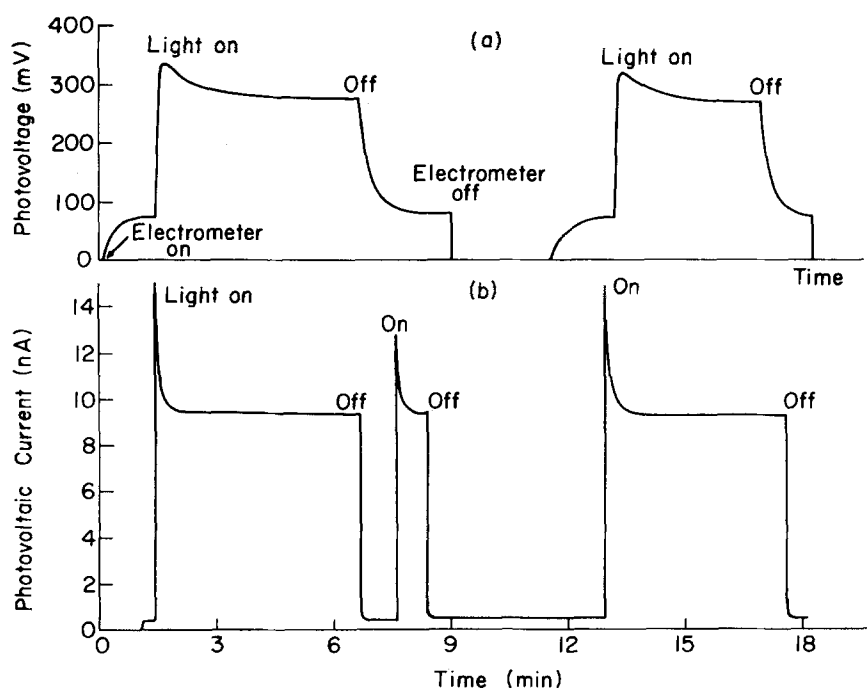


FIG. 4. Time behavior of the photovoltaic signals: (a) open circuit voltage; (b) shorted circuit current.

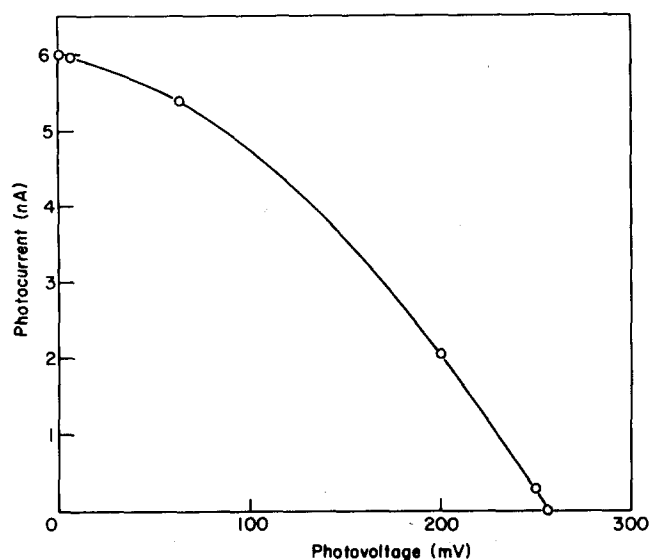


FIG. 5. Photovoltage-photocurrent characteristics.

the photocurrent is seen to increase with the bias voltage (Fig. 7). The photovoltaic current is seen as the intercept at the photocurrent axis. Saturation of photocurrent has not yet been reached with an applied voltage that would result in shorting the electrodes. When the cell is operated with a forward bias, negligible photocurrent is observed (a large dark current is present in this case). Figure 8 shows the light intensity dependence of the photocurrent at different reverse bias voltages. The light exponent increases slightly from 0.83 to 0.89 as the bias voltage increases.

### 3. Photovoltaic action spectrum

The action spectrum of the photovoltaic current of (Al|Chl|Hg) is shown in Fig. 9. The photovoltaic cur-

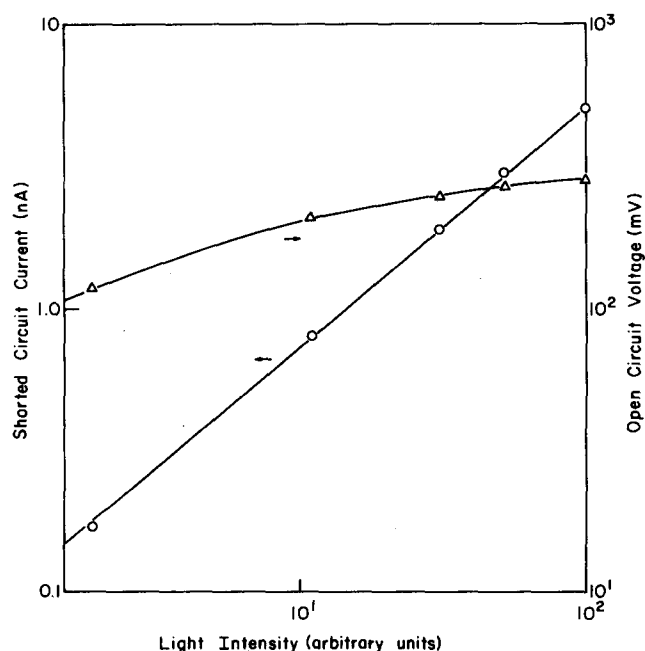


FIG. 6. Light intensity dependence of (I) open circuit voltage; (II) short-circuit current.

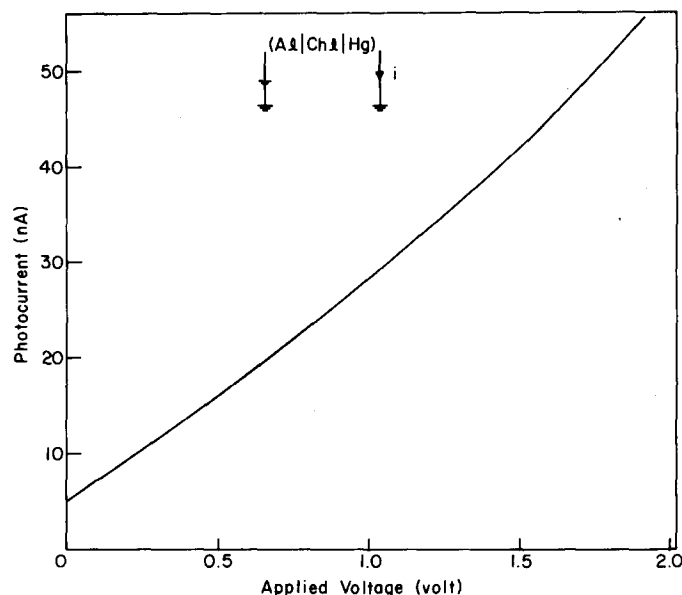


FIG. 7. Photocurrent from a (Al|Chl|Hg) cell with reverse biasing voltage. Al electrode is positive.

rent has been corrected to constant photon flux at each wavelength. In making the measurement of the action spectrum, the slit of the monochromator was set at 1 mm giving a resolution of about 100 Å. The dependence of the photocurrent on the incident light intensity is nearly linear at different wavelengths. The light exponent varies in the range between 0.85 to unity. In making correction for the incident light intensity, a light exponent of unity is assumed. It can be seen that the photovoltaic action spectrum of the (Al|Chl|Hg) cell closely matches the absorption spectrum of the microcrystalline Chl-a film. On heating the microcrystalline Chl-a to about 70 °C for a few minutes, the ordered microcrystalline Chl-a irreversibly changes into a disordered aggregated form of Chl-a possibly by losing its water component.<sup>12</sup> The absorption peak is blue shifted to 675 nm. The absorption spectrum of this new form of Chl-a film is very similar to that of Chl-a in monolayer form. The corresponding photovoltaic current action spectrum for this heat treated film is also blue shifted to match the new absorption bands. The photovoltaic current is about an order of magnitude smaller than that of the microcrystalline Chl-a film.

### C. Electrode effects

Interesting electrode effects on the photovoltaic current action spectrum are seen in cells with Cr as the front electrode. The cell (Cr|Chl|Hg) exhibits a normal action spectrum of the photovoltaic current as seen in (Al|Chl|Hg) cells, which closely matches the absorption spectrum of the Chl-a film (Fig. 10). The sign of the photovoltage is such that the Cr electrode is negative with respect to the Hg electrode. However, if the Hg back electrode is replaced by Hg/In or Ga, the sign of the photovoltage reverses, with the Cr electrode being positive. Furthermore, the action spectrum of the photovoltaic current is now almost the inverse of the Chl-a film absorption spectrum, with the maximum photovoltaic response lying outside the main Chl-a film absorp-

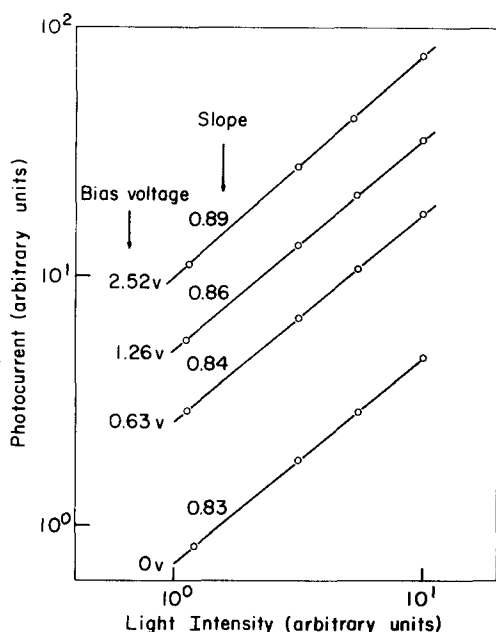


FIG. 8. Light intensity dependence of the photocurrent from a (Al|Chl|Hg) cell with reverse biasing voltage.

tion bands. Figure 10 shows the action spectra of the photovoltaic current in three (Cr|Chl|Hg/In) cells. The Chl-a films of these cells are of different thickness varying between 800 to 3000 Å. The action spectra are corrected to equal photon density at each wavelength and the peak in the near ir region in each spectrum is normalized to unity in order to show the spectral shift of the maximum response. It can be seen that in the cell with thick Chl-a film (~3000 Å), the peaks of the photovoltaic current are at 764 nm and 474 nm. The current is greatly reduced in the region where the Chl-a film absorbs strongly. With the thick Chl-a film, there is also a significant response in the spectral region between 500 nm and 700 nm, where the Chl-a film only absorbs slightly. With thinner Chl-a film in the cell, the photovoltaic current action spectrum is seen to match more closely the absorption spectrum of Chl-a. This is clearly shown in Fig. 10, as a progressive shift of peak photocurrent towards the Chl-a absorption bands and a decrease in the relative magnitude of the current in the 500–700 nm region.

The (Cr|Chl|Hg/In) cell is slightly rectifying, the forward bias is with the Cr electrode being positive. When the cell is operating with the reverse bias the photocurrent is seen to increase, and the action spectrum is similar to that seen in the photovoltaic mode, (i.e., the inverse of the absorption spectrum). However, when the cell is operating with a forward bias (i.e., with positive applied voltage on the Cr electrode) there is a large dark forward current and a small photocurrent is seen to superimpose on this dark current. An interesting spectral response is observed here. When incident light falls within the absorption bands of the Chl-a film, the photocurrent is in the same direction as the dark current. As the incident light moves out of the absorption band of Chl-a, and the Chl|Hg/In junction receives more illumination, the photocurrent is in a

direction opposite to that of the dark current.

Photovoltaic effects have also been observed in Chl-a cells with evaporated metal films as both the front ( $M_1$ ) and the back ( $M_2$ ) electrodes. When  $M_1$  and  $M_2$  are of similar metals such as (Au|Chl|Au), (Cr|Chl|Cr), the photovoltaic effects are either small or not observed at all. Rectification is not seen, and the cells usually have very low internal resistance ( $<10^5\Omega$ ). When Al is used as both electrodes, the cell usually exhibits a large dark voltage (~300 mV). The open circuit photovoltage is rather small (~100 mV). The front Al electrode is always positive relative to the back Al electrode. The action spectrum of the photovoltaic current is almost the inverse of the absorption spectrum. The cell has little rectification effect. A reverse of spectral response of the photovoltaic effect is observed in this cell when operated under external bias condition. When a negative voltage is applied to the Al front electrode, the action spectrum of the photocurrent is similar to that seen in the photovoltaic mode, being inverse to the Chl-a absorption spectrum. When the polarity of the applied voltage is reversed (front Al is now positive), the photocurrent also reverses sign, and interestingly, the action spectrum of the photocurrent now matches more closely the shape of the absorption spectrum of the Chl-a film (Fig. 11).

Large photovoltaic effects are seen in (Al|Chl|Au), (Al|Chl|Ni), (Al|Chl|Cu) cells. Use of noble metals for both front and back electrodes usually results in cells with low photovoltaic effects. The photo  $V_{oc}$  of the

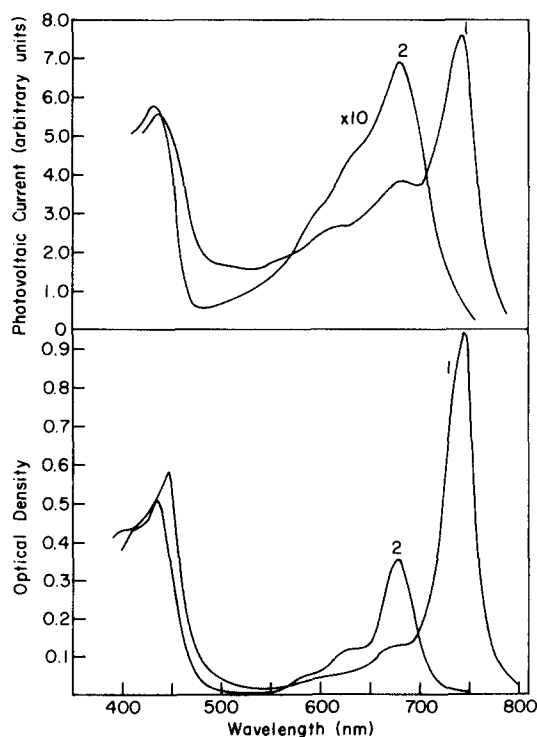


FIG. 9. Upper curves—Action spectra of photovoltaic current of (Al|Chl|Hg) cells: (1) microcrystalline Chl-a film; (2) Chl-a film obtained from (1) after heat treatment. Lower curves—Absorption spectra of microcrystalline Chl-a film (1) heat-treated Chl film (2).

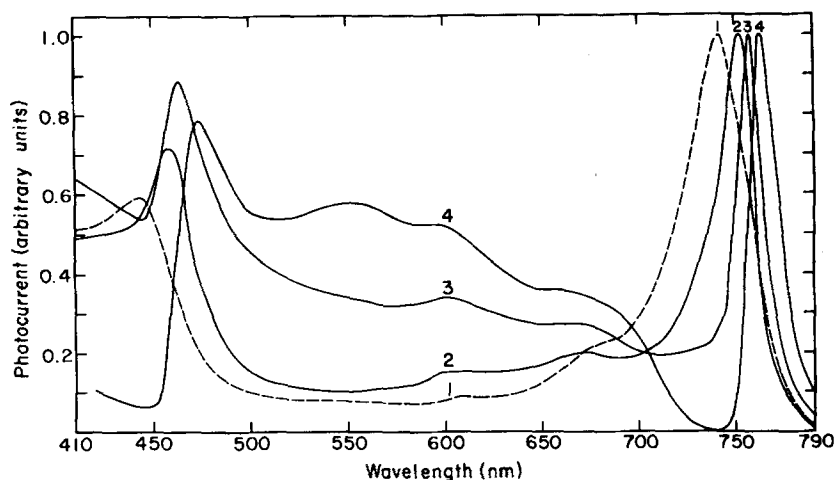


FIG. 10. Action spectra of the photovoltaic current. (1) (Cr|Chl|Hg) cell, O.D. of the Chl film at 745 nm is 2.5. (2), (3) and (4), are the action spectra for the (Cr|Chl|Hg/In) cells, the O.D. of the Chl films is respectively, 0.8, 1.3, and 3.0. The peak photocurrent in the near ir is normalized to unity in each curve. Note the sign of the photocurrent in (Cr|Chl|Hg) cell is opposite to that in the (Cr|Chl|Hg/In) cells (see text).

(Al|Chl|Au) is about 250 mV (average of measurements from ten cells). The average power output from (Al|Chl|Au) cells is about  $2 \times 10^{-10}$  W from an active area of  $0.5 \text{ cm}^2$  where the light power ( $\lambda = 745$ ) is about  $2 \times 10^{-5}$  W. The power conversion efficiency is on the order of  $10^{-3}\%$ , similar to that seen in (Al|Chl|Hg) cells. The (Al|Chl|Au) cell also shows strong rectification phenomena, the forward direction is with the Al electrode being negative. The action spectrum of the photovoltaic current and the absorption spectrum of the Chl-a film are well matched. When Al is made the back electrode, as in (Au|Chl|Al) cells, the photovoltaic activity is generally small, and the action spectrum is invariably inversely related to the absorption spectrum. It must be emphasized that this simple reversal of electrode materials in fact involves a different sequence of fabrication and that this may play some role in changing the photoelectric behavior.

#### IV. DISCUSSION

It is shown that microcrystalline Chl-a film prepared by method of electrodeposition has remarkable photovoltaic properties when it is sandwiched between two dissimilar metals. The photovoltaic effects of the ( $M_1$ |Chl| $M_2$ ) cells are generally characterized by (i) the existence of the dark voltage, particularly in cells with Al as one of the electrodes or both, (ii) the rectifying effects, (iii) the dependence of the photovoltaic activities on the electrode materials, and (iv) the variation of the spectral response. In these respects the photovoltaic activities in the Chl-a system are very similar to those seen in tetracene<sup>14,15</sup> and Mg-phthalocyanine films<sup>16</sup> in sandwich cells. The resemblance to the latter system is perhaps not coincidental, considering the structural similarity between the two. Power conversion efficiency on the order of  $10^{-20}\%$  is reported for the (Al|Mg-phthalocyanine|Ag) cell,<sup>16</sup> which is the highest among photovoltaic cells using organic materials. The Chl-a systems, (Al|Chl|Au), (Al|Chl|Hg) studied in the present work have a power conversion efficiency about  $10^{-30}\%$ .

The existence of photovoltaic activities in a cell requires (i) an asymmetry in the cell either in the dark or when illuminated and (ii) photogeneration of free charge carriers. In the Chl-a system using dissimilar metal

electrodes the asymmetry condition in the dark is presupposed. This asymmetry is possibly due to the presence of the contact potential (or Schottky type) barriers between the Chl-a and the metal electrodes. There is evidence from earlier work<sup>3</sup> that Chl-a is a *p* type semiconductor with the majority charge carriers being positive holes. The contact between the Chl-a and a metal is thus relatively more ohmic for the metal having a high work function such as Au, and more blocking for the metal with lower work function such as Al. The results of this work can be qualitatively explained in terms of a *p* type semiconduction in Chl-a with the active photovoltaic region at the blocking contact between Chl-a and the metal with the lower work function.

Figure 12a shows a hypothetical energy scheme for the ( $M_1$ |Chl| $M_2$ ) system, in which both  $M_1$ |Chl and Chl| $M_2$  contacts are taken to be blocking. Electronic energy barriers are present in both junctions. In the idealized limit where one junction is ohmic, the energy barrier is absent at that junction. Figure 12(b) shows such an

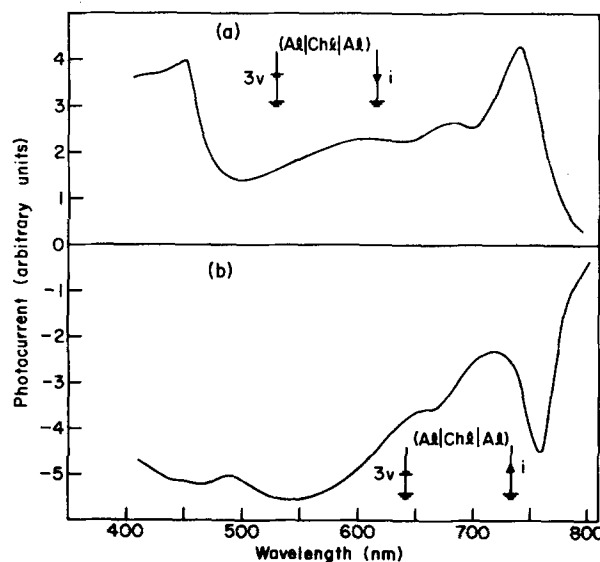


FIG. 11. Action spectra of the photovoltaic current of (Al|Chl|Al) cell: (a) The front electrode is positive; (b) the back electrode is positive.



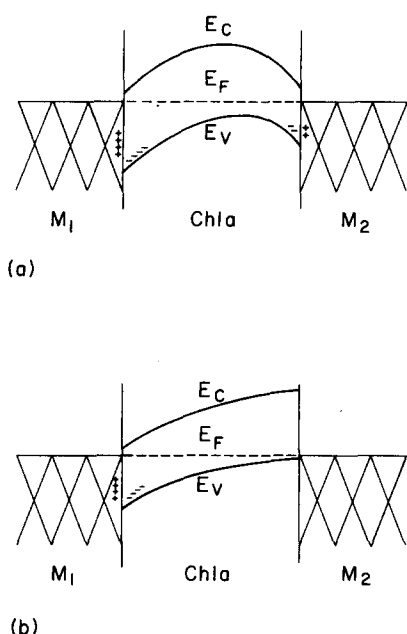


FIG. 12. Energy scheme of one ( $M_1 | \text{Chl} | M_2$ ) system: (a) Both  $M_1 | \text{Chl}$ ,  $\text{Chl} | M_2$  contacts are blocking. (b)  $\text{Chl} | M_2$  contact is ohmic,  $M_1 | \text{Chl}$  contact is blocking.  $E_C$  = conduction band of Chl.  $E_V$  = valence band of Chl.  $E_F$  = Fermi energy level.

ohmic contact between  $\text{Chl} | M_2$ .

The strong rectification phenomena seen in the Chl-a system such as ( $\text{Al} | \text{Chl} | \text{Hg}$ ), ( $\text{Al} | \text{Chl} | \text{Au}$ ) can be attributed to the existence of a large blocking contact at the  $\text{Al} | \text{Chl}$  junction. These systems may be represented as in Fig. 12(b). The cell is reverse biased when the positive voltage is applied to the Al electrode thus increasing the barrier potential at the  $\text{Al} | \text{Chl}$  junctions and decreasing the hole current from Chl to the Al electrode. For a forward bias the current is seen to increase exponentially with the bias voltage at the low voltage range. The bias voltage has in effect lowered the barrier potential. Such behavior is indicative of the presence of the Schottky type barrier.<sup>17</sup> An effort to analyze this behavior using an ideal Shockley equation<sup>17</sup> is compromised by the fact that our system very likely involves two barriers and carrier recombination within the barrier regions.

Rectification is usually not seen in cells with the same electrode materials. In cases where both electrode Chl contacts are equally blocking such as in ( $\text{Al} | \text{Chl} | \text{Al}$ ) cell [Fig. 12(a)] the rectification effect is either small or not seen at all, since the biasing voltage necessarily increases the barrier height at one junction and decreases that in the other. The slight rectification seen in some ( $\text{Al} | \text{Chl} | \text{Al}$ ) cells may be due to some asymmetry present in the cell as a result of the preparation sequence.

In Table I are listed the photovoltaic cells studied in this work. In the photovoltaic mode (no biasing voltage) the sign of photovoltage and the difference in the work function of the electrode metals seem to have a direct correspondence. The photovoltage at the front electrode,  $M_1$ , is negative relative to the back electrode,  $M_2$ , when  $\phi_{M_1} < \phi_{M_2}$  and positive when  $\phi_{M_1} > \phi_{M_2}$ . Furthermore,

in the former case, where  $\phi_{M_1} < \phi_{M_2}$ , the action spectrum of the photovoltaic current bears close resemblance to the absorption spectrum of the Chl film. A reciprocal relation between the action spectrum and the absorption spectrum is seen in cells where  $\phi_{M_1} > \phi_{M_2}$ . In both cases, the light enters the cell through  $M_1$ . It is clear that the photoactive region is at the electrode having the lower work function. The behavior of the sign of the photovoltage, as well as the location of the photoactive region, tells us that the photoactive region is at the electrode having the dominant Schottky barrier and that the Chl is a  $p$  type semiconductor.

With Cr as the front electrode, the blocking contacts can be made at the  $\text{Cr} | \text{Chl}$  junction when metal with higher work function such as Hg is used as the back electrode. In this arrangement the action and absorption spectrum are well matched. In ( $\text{Cr} | \text{Chl} | \text{Ga}$ ) and ( $\text{Cr} | \text{Chl} | \text{Hg/In}$ ) cells, however, the blocking contact is now at the back electrode since  $\phi_{\text{Cr}} > \phi_{\text{Ga}}$ ,  $\phi_{\text{In}}$ ; a reversal of the sign of photovoltage is observed and the action spectrum is seen as the inverse of the Chl-a absorption spectrum. This inverse relationship between the action and the absorption spectrum indicates that the light absorbed at the front surface of these cells is not effective in creating free charge carriers. In effect, the Chl-a layer is acting as an inner filter which screens the blocking contact from the incident light, and only charge carriers generated within this contact barrier width or close to it have a finite probability of transiting this junction to be registered as carriers in the external circuit. Most charges generated in the bulk of the Chl-a away from the blocking junction simply are not long-lived enough to diffuse into the junction.

We are currently working on a fairly general approach to the double barrier problem based on the single barrier theory presented by Tsarenkov.<sup>18</sup> For the present, however, let us employ a very simple model to interpret our results. We assume that there exists a photoactive slab of finite thickness either at the front metal-Chl-a junction or at the back Chl-a metal junction, and that only light absorbed by this slab is effective in creating

TABLE I. List of photovoltaic cells. The cell is illuminated through the semitransparent electrode  $M_1$ . Note the correspondence between the sign of the electrode  $M_1$  and the sign of the difference in work functions of  $M_1$  and  $M_2$ .

Cell type ( $M_1   \text{Chl}   M_2$ )	Sign of electrode in photovoltaic mode $M_1$	Difference in work functions <sup>a</sup> $\phi_{M_1} - \phi_{M_2}$
(Al   Chl   Hg)	—	—0.45
(Cr   Chl   Hg)	—	—0.16
(Cr   Chl   Hg/In)	+	+0.73
(Cr   Chl   Ga)	+	+0.41
(Al   Chl   Al)	+	0
(Al   Chl   Au)	—	—0.74
(Al   Chl   Ni)	—	—0.93
(Al   Chl   Cu)	—	—0.52
(Au   Chl   Al)	+	+0.74

<sup>a</sup>The work function data are taken from the *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, 1970), 51st edition.

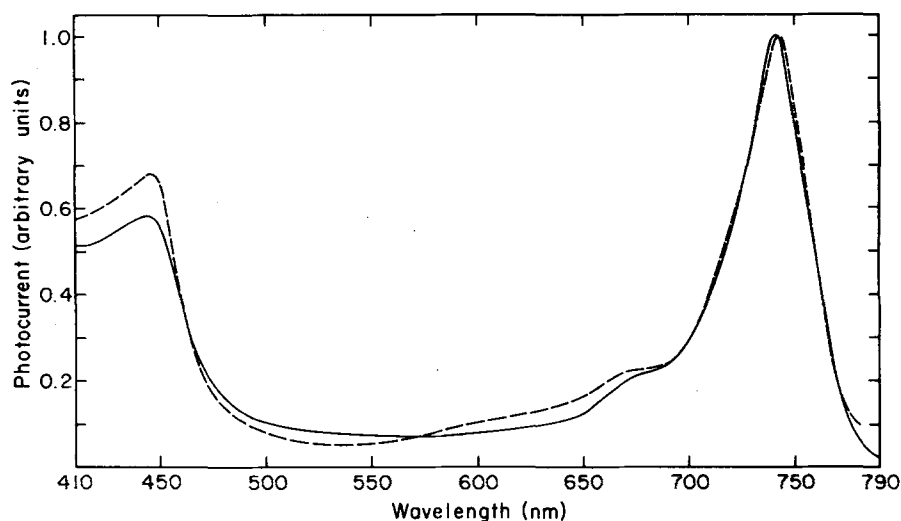


FIG. 13. Experimental (—) and calculated (---) action spectra of the short circuit photovoltaic current of (Cr|Chl|Hg) cell. Thickness of Chl film = 2000 Å, O.D. (745 nm) = 2.0.

free charges. Light absorbed by the Chl-a layer outside this slab is considered ineffective in the charge production. This photoactive slab is presumed to be at least the width of where the electrostatic field due to the presence of the electrical double layers can effect the electron-hole separation.

The rate of charge generation at a distance  $x$  from the front surface within the barrier width  $\delta$  is proportional to  $k \exp(-kx)$ , where  $k$  is the absorption coefficient of the Chl-a film. In the case that the barrier is present at the front junction, such as in the (Cr|Chl|Hg) cell, the total charge produced per unit time within the barrier width  $\delta_f$  is given by the integral:

$$N = \phi I_0 \int_0^{\delta_f} k \exp(-kx) dx = \phi I_0 [1 - \exp(-k\delta_f)] \quad (1)$$

where  $\phi$  is the quantum efficiency of charge generation by light and  $I_0$  is the incident light intensity. The photovoltaic current is simply proportional to  $N$ , assuming constant charge mobility. In Fig. 13, the experimental and the calculated photovoltaic current action spectra for a (Cr|Chl|Hg) cell are shown. Both curves are normalized to unity at 745 nm. In calculating the action

spectrum the  $k$  values are obtained from the optical density data and the thickness of the Chl-a film. The value  $\delta_f = 200$  Å is chosen to give the best fit between the experimental and the calculated action spectra. It can be seen that the agreement between the two curves is very good. (The slight discrepancy at the shorter wavelength region may be due to some error in the correction for the incident light intensity).

In the case where the barrier is present at the back junction such as in (Cr|Chl|Hg/In) cell, the total charge produced in the barrier width  $\delta_b$  is given by integrating Eq. (1) from  $l - \delta_b$  to  $l$ , where  $l$  is the thickness of the Chl-a film:

$$N = \phi I_0 \exp(-kl) [\exp(k\delta_b) - 1] \quad (2)$$

Figures 14 and 15 show the experimental and the calculated photovoltaic action spectra for two (Cr|Chl|Hg/In) cells with Chl-a films of thickness about 800 Å and 2000 Å. The experimental and the calculated curves are normalized at 600 nm. In both plots,  $\delta_b$  is chosen to be 400 Å. It can be seen that the agreement between the experimental and the calculated curves is very approximate in this case. The locations of the maximum and

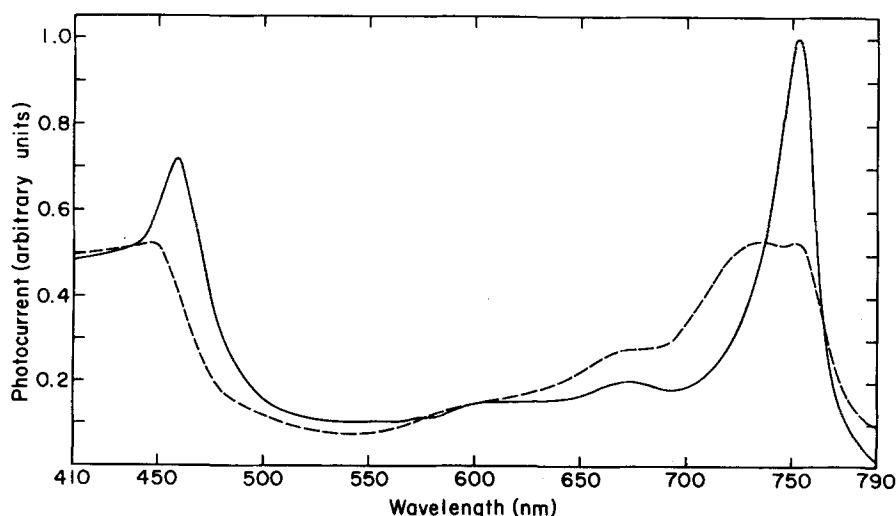


FIG. 14. Experimental (—) and calculated (---) action spectra of the short circuit photovoltaic current of a (Cr|Chl|Hg/In) cell. Thickness of Chl film = 800 Å, O.D. (745 nm) = .75.

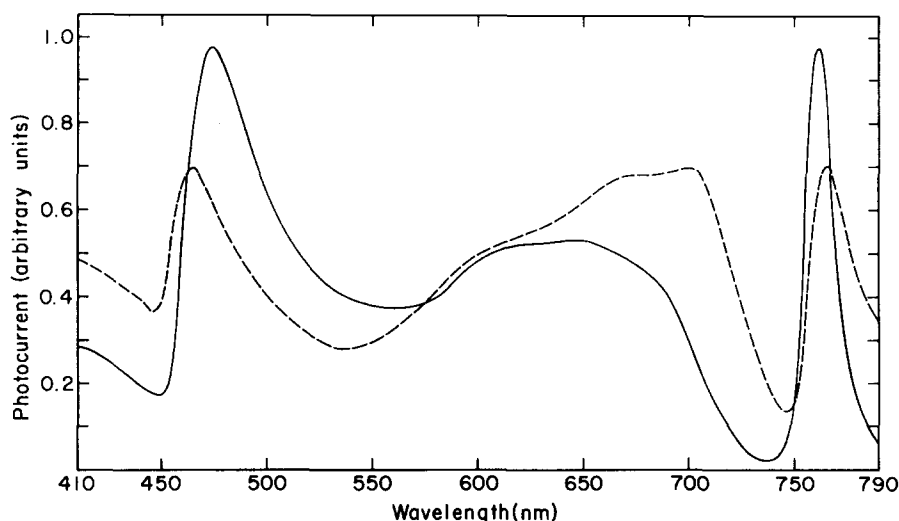


FIG. 15. Experimental (—) and calculated (---) action spectra of the short circuit photovoltaic current of a (Cr|Chl|Hg/In) cell. Thickness of Chl film = 2000 Å,  $O_D(745 \text{ nm}) = 2.0$ .

the minimum agree only fairly well. Difference between the two curves is particularly apparent in the region between 630–710 nm and also in the region above 760 nm. It must be noted that the shape of the calculated action spectrum is rather insensitive to the choice of  $\delta_b$ , whenever  $k\delta_b \ll 1$ . When other values of  $\delta_b$  were chosen to make the plots in Figs. 13 and 14, action spectra of reasonably similar shape were obtained even with  $\delta_b$  as large as 800 Å. Because the agreement between the experimental and the calculated action spectra is so qualitative, it is clearly difficult to assign an accurate value for the slab thickness  $\delta_b$  and use of a more elaborate method<sup>18</sup> is discouraged.

The increase in photocurrent when the cell is reverse biased with an external voltage can be explained in terms of the consequent increase in the energy barrier at the contact with a stronger electric field in the barrier region. We assume that the lifetime of the photogenerated minority charge carriers is limited by recombination in this space charge region, i.e., the diffusion length of the charge carrier is possibly shorter than the barrier width. The fact that the light exponent for the photocurrent is less than one (Fig. 8) could already be a hint of recombination controlled lifetime of the carriers in the space charge region. As the electric field in this region increases, the carrier has a greater chance of transiting the barrier region before being trapped, and to thus provide its maximum current. The small increase of the light exponent of the photocurrent with increasing reverse bias may also be related to this effect. The ratio of steady state photocurrent to incident photon flux, known as photoelectric gain, is about  $1.5 \times 10^{-3}$ . This is increased to about  $3 \times 10^{-2}$  when the cell is operated with a reverse bias voltage of about 2 V. (Further increase in the biasing voltage tends to damage the cell by shorting the electrodes). Since the upper limit of the photoelectric gain only represents the lower limit in the quantum yield of charge generation, it is possible to conclude that the lower limit for the quantum yield of charge generation in the Chl-a film is at least 0.03.

It has been shown that in the (Al|Chl|Al) cell a rever-

sal of the bias voltage can cause a change in sign of the photovoltaic effects and a reversal of the action spectrum (Fig. 11). This can also be readily understood in terms of the photovoltaic activities at the blocking contact. Assuming that the cell is ideally symmetric, i.e., the Al|Chl, Chl|Al contacts are equally blocking, little photovoltaic effect would be seen. In reality, a small asymmetry is always present (the physical nature of the two contacts very likely differ), and a small photovoltaic effect is observed. However, when the cell is strongly biased with the front Al electrode being positive, a stronger blocking contact is established at this region, and the photovoltaic effect is seen with its action spectrum matching the absorption spectrum of the Chl-a film. If the blocking contact is established at the back Chl|Al junction by reversing the biasing voltage, the sign of photovoltage is reversed, and accordingly, the inverse pattern between the action and the absorption spectra is seen.

It is evident from the general qualitative behavior of this Chl-a system that we are dealing with a cell where a barrier potential at a Chl-a metal contact plays a vital role. From the analysis of the action spectra it appears that the effective width  $\delta$  of the photoactive layer may be on the order of a few hundred Angstroms. The question remains whether this represents the actual thickness of the barrier layer or includes a significant region from which photogenerated charge carriers or excitons manage to reach the barrier layer itself, which would then be of considerably lesser thickness. In the study of the tetracene cell<sup>15</sup> the possibility that excitons diffuse into the barrier region and then ionize is suggested. On the other hand in the Mg phthalocyanine system<sup>16</sup> it seems more likely that, to the extent that diffusion is important, it is charge carriers that diffuse, because excitons appear to ionize very easily in that solid. The barrier layer in this latter system is about 250 Å. From our previous flash photoelectric studies on the Chl-a system<sup>13</sup> we have found that a minimum diffusion length for charge carriers in the Chl-a solid is about 130 Å. The carrier lifetime appears to be shorter than  $10^{-9}$  sec. In fact if

a diffusion length of  $130 \text{ \AA}$  were chosen in the analysis of the action spectrum of the (Cr|Chl|Hg|In) cell using the model which includes the contribution of charge carrier diffusion into the barrier, an effective photoactive slab on the order of few hundred Angstroms thick is also obtained.

It has been noted that a transient photocurrent spike is often present in the photovoltaic signals. This transient may be related to the "fast" photoconductivity signal seen previously in the Chl-a 3-methylpentane system,<sup>19</sup> which has been ascribed to the charge separation within a Chl-a microcrystallite. It is also possible that this transient signal is due to the detrapping of previously trapped charges in the microcrystalline Chl-a film. Work just being completed promises to considerably clarify this question.

As mentioned in the introduction, Meilanov *et al.*<sup>7</sup> calculate a quantum yield of 0.1 for charge generation in Chl-a film. In their case the cell was invariably in the presence of strong biasing voltage. That is, their studies were in the photoconductive mode rather than in the photovoltaic mode as in the present work. The effects seen in their case (including the inverse action spectrum) were symmetric in polarity and were interpreted in terms of strong bipolar carrier injection from the electrodes. The high quantum yield calculated for their system led the authors to state that photoinduced charge generation can be a major result of light absorption by Chl-a. Our results as well, tend not to agree with the earlier evidence that Chl-a is not a good photoconductor. In the earlier work Chl-a monolayer films were normally used for photoconductivity studies. It is possible that these monolayer Chl-a films may have excessively high trap density; the recombination or trapping of charges in the bulk of Chl-a film may well limit the photocurrent to an insignificant level.

## V. CONCLUSION

An electrodeposited microcrystalline Chl-a film when sandwiched between two dissimilar metals is shown to have rather strong photovoltaic effects. The active area primarily responsible for the photovoltaic activity is at the metal|Chl-a junction having the metal with the lower work function. A Schottky type barrier is present at this junction and *p*-type conduction is implicated in Chl-a. The action spectrum of the photovoltaic current is strongly and understandably dependent on whether the barrier is at the front electrode or at the back electrode. In the former case, correspondence between the action and the absorption spectrum is seen, and in the latter, the action spectrum reflects an inner filter effect giving an "inverse" type response. The Chl-a cells such as

(Al|Chl|Au), (Al|Chl|Hg) are found to be among the best photovoltaic cells using organic materials in their power conversion efficiency.

*Note added in proof.* We have just completed a more thorough study of (Cr|Chl|Hg) cells. These cells appear to be considerably more efficient, the best of them giving a power conversion efficiency of about  $5 \times 10^{-2}\%$  (based on photons incident upon the Chl-a film).

## ACKNOWLEDGMENT

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