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# Capacitance characteristics of mixed monolayers of chlorophyll *a* and carotenoid canthaxanthin

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Capacitance measurements of the cells, obtained by sandwiching mixed monolayers of chlorophyll *a* and canthaxanthin between Al and Ag electrodes, have been carried out at various frequencies in the dark and under illumination. The results show that at frequencies of ~ 100 Hz, one observes the voltage-independent geometric capacitance; however, as the frequency of applied bias decreases, a voltage-dependent capacitance, characteristic of a Schottky barrier, appears; this is evidenced by the linear plots of reciprocal capacitance square ($1/C^2$) versus applied voltage, $V_a$. This is explained as due to the depletion layer consisting mainly of trapped charges that are not able to follow the rapid variations in applied voltage at higher frequencies of ~ 100 Hz. Similar observations have also been made with illuminated cells. Light is believed to detrap and mobilize the trapped charges. From linear plot of $1/C^2$ versus $V_a$, the depletion layer parameters, e.g., built-in potential, width at zero bias and space charge density have been determined, and are, respectively, ~ 0.7 V, 290 Å and $2.5 \times 10^{23}/m^3$ in the dark.

## 1. Introduction

With an aim to improve the power conversion efficiencies of Al/chlorophyll *a* monolayers/Ag solar cells, carotenoid canthaxanthin (Cantha), an accessory pigment in green plant photosynthesis, was added to chlorophyll *a* (Chl *a*), and photovoltaic studies of mixed monolayers of Chl *a* and Cantha sandwiched between Al and Ag were recently reported by us [1]. It was observed that the cells Al/mixed monolayers of Chl *a* and cantha (0.5 : 0.5)/Ag showed a small photocurrent, however, the cells of the type Al/Chl *a* monolayers/mixed monolayers of Chl *a* and Cantha (0.7 : 0.3)/Chl *a* monolayers/Ag showed both photocurrent and photovoltage. The power conversion efficiencies of these cells calculated at 680 nm, the maximum of red absorption band of Chl *a*, for incident light power of ~ 13 $\mu W/cm^2$ are ~ 0.05% and are comparable to those of Chl *a* cells [1]. Although the efficiencies of the cells did not show any improvement over Chl *a* cells, a large photocurrent at 500 nm (absent in Chl *a* cells) was observed. This was explained as due to the spectral sensitization of Chl *a* by Cantha. Further, the similarity of the action spectrum, when the cells were illuminated through Al electrode, with the absorption spectrum of the pigment suggested the presence of a Schottky barrier at the Al/pigment interface.

In order to characterize this barrier in terms of its width, built-in potential and charge density, we have carried out capacitance measurements of these cells at various frequencies in the dark and under illumination. It will be seen that due to the presence of a large number of trapped charges, it is only at very low frequencies ~ 0.01 Hz or under illumination that a capacitance characteristic of a Schottky barrier, as evidenced by a linear plot of reciprocal capacitance square against applied voltage, is observed. From such a linear plot the above-mentioned parameters of the barrier have been calculated, and the results are presented here in this paper.

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## 2. Experimental

### 2.1. Materials

Chl *a* was extracted from spinach leaves following the method of Omata and Murata [2]. Canthaxanthin was a generous gift from Hoffman La Roche, Switzerland, and was used without further purification.

### 2.2. Methods

#### 2.2.1. Monolayer deposition and fabrication of photovoltaic cells

For details, please refer to our earlier paper [1]. The cells are of the type Al/20 monolayers of Chl *a*/14 monolayers of mixture of Chl *a* and Cantha (0.7 : 0.3)/10 monolayers of Chl *a* /Ag. These cells, hereafter, will be referred to as Cantha cells.

#### 2.2.2. Capacitance measurements

These measurements have been made by low frequency oscillographic technique as described by Twarowski and Albrecht [3]. A periodic triangular voltage is applied to the cell, and the current flowing through the cell is recorded as a function of applied bias. The capacitance, $C$, of the cell is then calculated from the following formula [3]

$$C = (J_+ - J_-)/8V_0 f, \tag{1}$$

where $J_+$ and $J_-$ are the two values of current at the applied voltage; $V_0$ is the amplitude and $f$ is the frequency of applied voltage. If the capacitance of the system is dominated by that of the high-resistance Schottky barrier, its dependence on applied bias follows the relation expressed in eq. (2) [4]

$$\frac{1}{C^2} = \frac{2}{A^2 e \epsilon \epsilon_0 N}(V_b + V_a), \tag{2}$$

where $e$, $\epsilon$, $\epsilon_0$, $A$ and $N$ are, respectively, the electronic charge, the dielectric constant of pigment, the permittivity of free space, active area of the cell and charge density of the barrier; $V_b$ and $V_a$ are the built-in potential and applied bias, respectively. The negative $V_a$ refers to the forward bias.

A plot of $1/C^2$ versus $V_a$ should thus give a straight line if the capacitance is attributable to the Schottky barrier. Further, from the slope and the two intercepts with the axes one can determine $N$, $V_b$ and width $W$ of the barrier (at zero bias), if the dielectric constant of the pigment is known.

## 3. Results

The capacitance measurements of the Cantha cells have been carried out at various frequencies

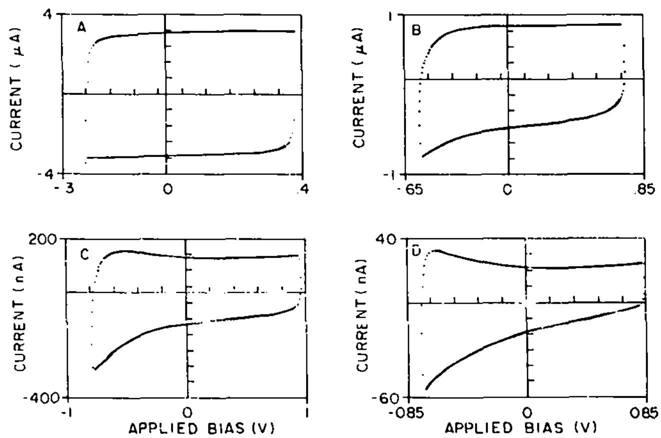


Fig. 1. Current–voltage traces for a Cantha cell in the dark. Triangular bias applied to Al electrode at (A) 100 Hz, (B) 10 Hz, (C) 1 Hz and (D) 0.01 Hz. Negative voltages represent forward bias while the positive voltages the reverse bias.

in the dark and under illumination and are described below.

### 3.1. Dark C–V measurements

Fig. 1 shows the current–voltage oscillograms of the cell recorded at 100, 10, 1 and 0.01 Hz. Inspection of these curves with reference to eq. (1) suggests that the capacitance at 100 Hz is independent of applied voltage. However, as the frequency of applied bias decreases, asymmetry in these curves sets in and the capacitance begins to show voltage dependence. This is seen in fig. 2 where the curves of reciprocal capacitance square ($1/C^2$) versus applied bias, $V_a$, are plotted. An almost linear plot, characteristic of a Schottky barrier can be observed at 0.01 Hz. The voltage-dependent capacitance at low frequencies has also been observed for Chl *a* [5] and other organic semiconductors [3,6–8].

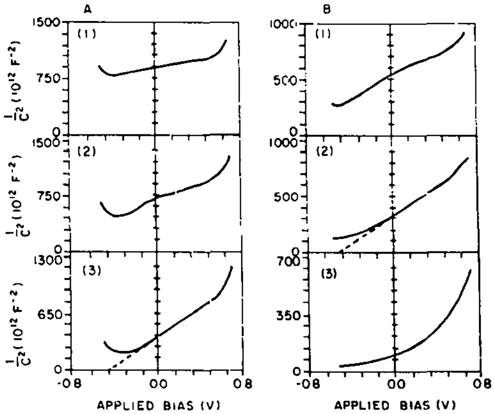


Fig. 3. $1/C^2$ versus $V_a$ plots for a Cantha cell with triangular bias applied to Al at 1 Hz (A) and 0.1 Hz (B) in dark (1) and under illumination with 680 nm wavelength of intensity 4 $\mu W/cm^2$ (2) and 13 $\mu W/cm^2$ (3).

### 3.2. Illuminated cells

In figs. 3A and 3B are shown the $1/C^2$ versus $V_a$ curves for illuminated cells for two frequencies, i.e., 1 and 0.1 Hz. It can be seen that while the capacitance in the dark (curves 1) is voltage-dependent, the ideal linear relation between $1/C^2$ versus $V_a$ is not seen. However, with illumination of adequate light intensity, a linear plot characteristic of a Schottky depletion layer is obtained (fig. 3A, curve 3 and fig. 3B, curve 2). It should be remarked that when the frequency of the applied voltage is low the intensity of light required for a linear $1/C^2$ versus $V_a$ plot is also low. The illumination has been carried out with 680 and 500 nm wavelengths; 680 nm wavelength is strongly absorbed by Chl *a* while 500 nm is weakly absorbed by Chl *a* but is strongly absorbed by

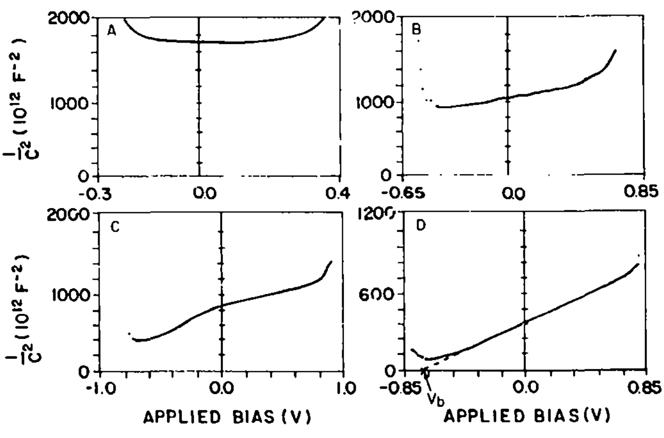


Fig. 2. $1/C^2$ versus $V_a$ plots for the Cantha cell of fig. 1.

Cantha. The results obtained with both illumination wavelengths are identical.

### 3.3. Depletion layer parameters

These parameters, namely, the built-in potential, $V_b$, the width, $W$, and space charge density, N, have been obtained from the linear $1/C^2$ versus $V_a$ plots. A value of 3.2 for the dielectric constant of pigments has been used. This has been evaluated from the capacitance measurements of the cells at 100 Hz where only the geometric capacitance (with pigments behaving as dielectric) is observed. The values of the depletion parameters obtained in the dark are $V_b \approx 0.7$ V, $W \approx 290$ Å and $N \approx 2.5 \times 10^{23}/m^3$. For illuminated cells they are, respectively, 0.5 V, 250 Å and $3.6 \times 10^{23}/m^3$. These values of $V_b$ are in agreement with those obtained in photovoltaic studies [1]. The decrease in $V_b$ and $W$ for illuminated cells is most probably due to light acting as a source of forward bias that opposes the built-in field. The increase in space charge density is a result of detrapping and photogeneration of charge carriers by light.

## 4. Discussion

### 4.1. Effect of frequency

The voltage-dependent capacitance, characteristic of a Schottky barrier, at low frequencies is due to the depletion layer consisting mainly of trapped charges. It should be recalled that in fabrication of the cells, Chl $a$ and Cantha deposited on Al electrode are in the form of Langmuir–Blodgett films which are amorphous and possibly possess a large number of structural imperfections and inhomogeneities that can act as traps immobilizing the charges temporarily or permanently. As a result, the trapped charges in these type of samples are far more numerous than the free charges; thus, it is the trapped charges that determine the width and other properties of the space charge region.

In general, the effect of the traps is to diminish the mobility and increase the response time of the charge carriers. Thus when the frequency of the applied voltage in capacitance measurements is large, the carriers responsible for the depletion layer are not able to respond to the rapid variations in the applied voltage. Consequently, only the voltage-independent geometric capacitance (Chl $a$ and Cantha behaving as dielectrics) is observed. However, as the frequency of the applied bias decreases and falls within the response time of the trapped charges, voltage-dependent capacitance characteristic of a Schottky depletion layer begins to appear. The presence of traps in organic semiconductors is a common phenomenon, and their influence on capacitance characteristics of the cells have been observed by other researchers also [3,5–7].

### 4.2. Effect of light

Besides the use of low frequencies, light also can bring the electrical response time of trapped charge carriers within the time variations of applied voltage by mobilizing them. Although the exact mechanism by which mobilization of trapped charge by light takes place is not well understood at present, it is possible that light supplies the necessary energy equivalent to the trap depth and sends the trapped electrons or holes into conduction and valence bands, respectively. The free charges are then able to follow the variations in applied bias, and the capacitance measured is that of the Schottky barrier.

The effect of light intensity is rather quite interesting. In general, if the period $(1/f)$ of applied bias is close to the electric response time of the trapped charges, a large number of charges are already able to follow the changes in applied field and one needs only a small amount of light to detrap and mobilize the remaining carriers. However, if the frequency of the applied signal is higher, i.e., the time period is smaller compared to the response time of the charges, most of the carriers fail to respond and relatively more intense light is needed to mobilize the greater number of trapped charges. This may explain the results presented in fig. 3A (curve 3) and fig. 3B (curve 2) where we see that when the frequency of oscillating probe voltage is 1 Hz the intensity of light necessary to obtain a linear relation between $1/C^2$

versus $V_a$ is $\sim 13$ μW/cm$^2$. However, when the frequency is decreased to 0.1 Hz, many of the carriers already respond to the external voltage, and consequently, less intense light of $\sim 4$ μW/cm$^2$ is enough to mobilize the trapped charges.

From the point of view of the space charge density, $N$, the role of light intensity seems to change its distribution. In the beginning before illumination, when the curves $1/C^2$ versus $V_a$ are not linear, for example fig. 3B (curve 1), the charge density calculated from tangents (slopes) at various points in the depletion layer is non-uniform, irregular and varies between $2.3 \times 10^{23}/m^3$ and $7 \times 10^{23}/m^3$. However, when the cell is illuminated and if light intensity is right, the distribution of charges becomes uniform ($N = 3.5 \times 10^{23}/m^3$) throughout the depletion layer and the curve $1/C^2$ versus $V_a$ is linear (fig. 3B, curve 2). Now if the light intensity is further increased, the linear $1/C^2$ versus $V_a$ curve is distorted (fig. 3B, curve 3) and the charge density once again becomes non-uniform and decreases from $\sim 11 \times 10^{23}$ to $2.5 \times 10^{23}/m^3$ as one goes away from the blocking contact towards the bulk of the pigment. While the uniformization of charge density, i.e., the observation of a linear $1/C^2$ versus $V_a$ curve by light as a result of mobilization of trapped charge carriers is understandable, the curved $1/C^2$ versus $V_a$ plots and non-uniformization of charge density with higher light intensity is rather difficult to explain, although light-induced increase of p-type semiconductive character of Chl *a* and Cantha may be a possibility.

## 5. Conclusion

The capacitance measurements of the cells at low frequencies in the dark and under illumination show that the depletion layer of Schottky barrier present at the Al/pigment interface is mainly due to the low mobility trapped charges that fail to respond to the applied voltage variations at high frequencies, thus resulting into voltage-independent geometric capacitance. The measurements at low frequencies ($\sim 0.01$ Hz) and under illumination do show a voltage-dependent capacitance of a Schottky barrier. At low frequencies, the trapped charges are able to follow the applied voltage while light is thought to detrap and mobilize the charges. From linear plots of $1/C^2$ versus $V_a$, various depletion layer parameters in the dark and under illumination have been determined. To get a better insight into the trapping and detrapping phenomenon, capacitance experiments as a function of temperature would be very helpful.

## Acknowledgements

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