

Solar Cell with Chlorophyll Sensitized Cuprous Iodide Electrode.

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Introduction

Electrolytic photovoltaic cells with semiconductor electrodes have attracted much attention as promising devices for the conversion of solar energy.¹⁻²³ In addition to the generation of electricity, such cells, in principle, could produce energy rich compounds (fuels) as the sources of storable energy.^{10,14} If the electrolytic photovoltaic cells are to be of any practical importance in the utilization of solar energy, the semiconductor material in the electrolytic medium must be photostable and sensitive to light in the visible region. The photovoltaic cells with n-Titanium dioxide are photochemically stable and decompose water into hydrogen and oxygen.¹⁰⁻¹⁵ However, they have low efficiencies and their spectral response is mainly in the ultra-violet region. Other semiconductor materials, such as cadmium sulphide and gallium phosphide with higher conversion rates are unstable. They deteriorate rapidly on the exposure to light.¹⁶⁻¹⁹ There are two possible methods of improving the performance of photovoltaic cells. Passivating agents can stabilize the semiconductor electrodes against chemical corrosion. Some success has been achieved by stabilizing the photovoltaic cells with cadmium sulphide and selenide in polychalcogenide solutions.²⁰ An even more promising method would be the sensitization of stable cells to give higher spectral response in the visible region by addition of dyes.²¹⁻²⁴ Apart from practical applications, the spectral sensitization is interesting from a purely theoretical point of view, green plant photosynthesis, the most successful method of solar energy conversion is a sensitization process involving Chlorophyll.²⁵ A study of the sensitization techniques can contribute towards the understanding of the mechanism of green plant photosynthesis. Again the artificial sensitization techniques imitating the green plant photosynthesis could be the most suitable method for harnessing solar power.

Several authors have discussed the performances of photovoltaic cell sensitized with organic dyes. The n-type Zinc oxide photovoltaic cell sensitized with dyes such as Rose Bengal and Rodamine B is reported to have a high quantum conversion efficiency.²¹ The characteristics of a dye sensitized photovoltaic cell depends on the solid state properties of the semiconductor electrode, the electronic excitation levels of the dye and the reducing agent (supersensitizer), often added to the electrolytic medium as stabilizer.²³ No other pigment is so well studied with respect to the photoexcitable electronic energy levels as Chlorophyll.²⁶⁻²⁸ Hence studies on semiconductor-electrolytic photovoltaic devices using Chlorophyll could be expected to give much insight into the mechanism of spectral sensitization. Concepts of solid state physics has gone into the theories of photosynthesis and studies on photovoltaic cells using Chlorophyll can lead to a clarification of numerous puzzling problems connected with photosynthesis.²⁹ Several authors have discussed photovoltaic devices using Chlorophyll as an electron transferring agent. The photoelectrolysis of water at a Chlorophyll—a coated platinum electrode has been

studied by Fong³⁰ et al, Tien³¹ et al, have simulated the photoinduced electron transfer across lipid membranes containing Chlorophyll -a. Miyasaka³² et al. have reported a device using Chlorophyll -a coated SnO₂ photoanode. They have also discussed Chlorophyll -a / lecithin systems with high quantum conversion efficiencies. In this paper we describe a photovoltaic cell with Chlorophyll coated cuprous iodide electrode.

Method of Preparation

The cell we have devised consists of a photocathode of cuprous iodide coated with Chlorophyll -a. The cuprous iodide electrode is prepared by warming a clean sheet of copper in a 1% solution of hydroiodic acid containing 5% of dissolved iodine. A white polycrystalline layer of cuprous iodide is deposited on copper when the copper sheet is left in the warm solution for several hours. Chlorophyll is coated by spraying the electrode with a solution of Chlorophyll -a in methyl alcohol. For the anode we use a copper grid coated with cuprous iodide so that when the electrodes are not illuminated the cell e.m.f. is negligible. As the photovoltage of the cell is higher when the front wall of the cell is illuminated (Fig. 1), a copper grid is used as the anode.

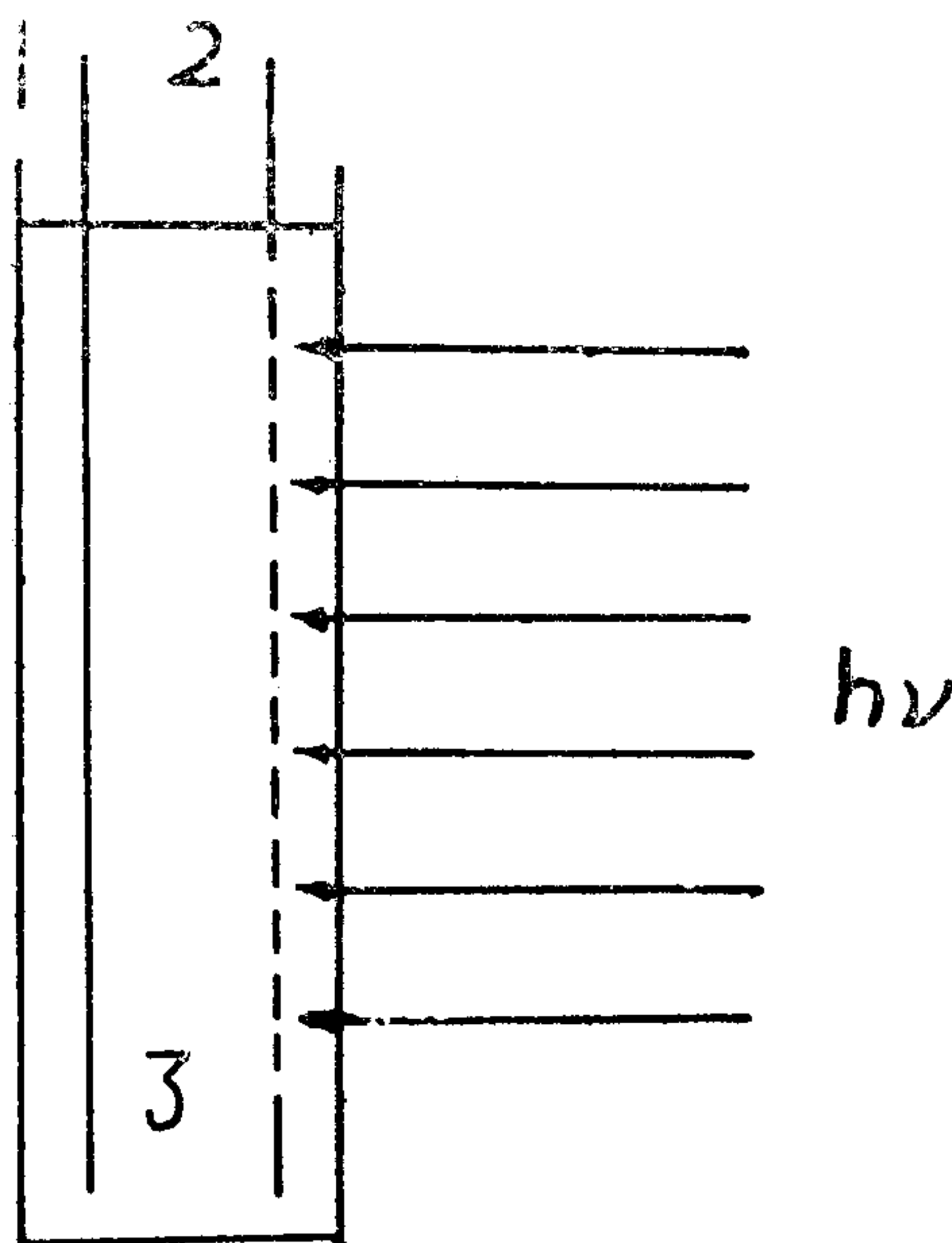


Fig. 1. Schematic diagram of the photovoltaic cell.

1. Cuprous iodide photocathode. 2. Copper grid anode. 3. 0.01 M KI solution.

A 0.01 M solution of potassium iodide is used as the electrolyte. The open-circuit voltage of the cell when the cathode is illuminated (intensity of illumination on the cathode $\sim 1 \text{ W cm}^{-2}$) with a 100 W tungsten filament lamp is about 60 mV. The stable value of the open circuit voltage is found to be independent of the thickness and the way in which the chlorophyll layer is deposited. The time response of the cell, i.e., the plot of open circuit voltage versus time is indicated in Fig. 2. Quantitative measurements of the closed circuit

current-potential characteristics of the cell was not possible because they were dependent upon the thickness and the way in which the Chlorophyll layer is deposited. Thus far we have not succeeded in finding a reproducible method of depositing the Chlorophyll in layers on cuprous iodide.

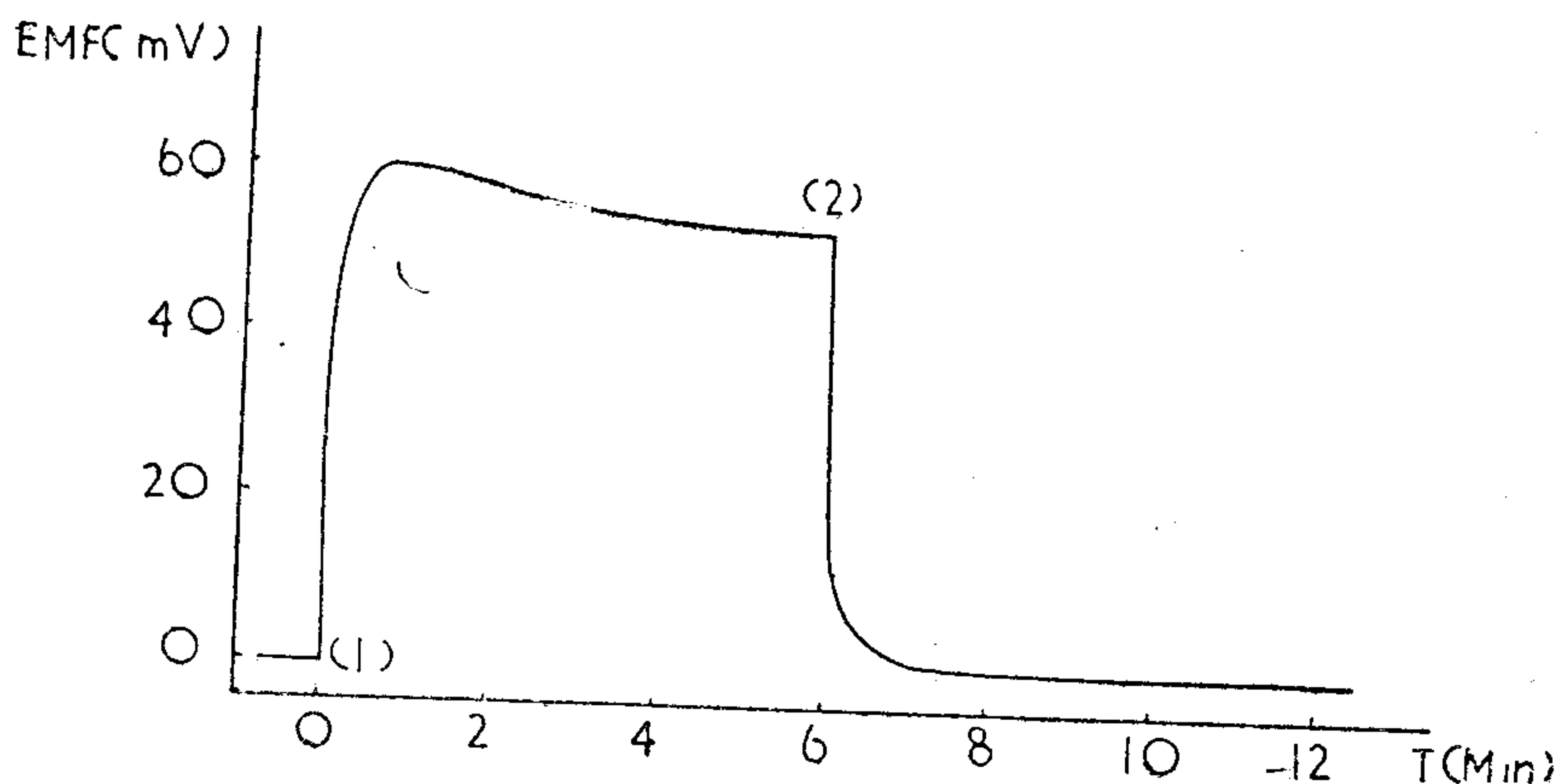


Fig. 2. Plot of open circuit voltage versus time.
(1) Light on (2) Light off

Discussion

An important property of the cell is its stability. Even upon short circuiting, the Chlorophyll layer or the CuI deposit is not destroyed by strong illumination. The cuprous iodide electrode also shows sensitized photoresponses with other dyes such as Rhodamine B, Methylene Blue, Malachite Green and Neutral Red. However, unlike Chlorophyll these dyes get rapidly deteriorated on the exposure to light. Also as Chlorophyll is insoluble in water the pigment is not lost to the electrolyte as in the case of the other dye sensitized photovoltaic cells. The spectral response of the cell is maximum near the absorption peak (675 nm.) of Chlorophyll -a in the red region. However, there is no response of the cell near the other absorption peak of Chlorophyll -a in the blue region. The origin of the dye sensitized photocurrent is supposed to be due to electron transfer between the excited dye and the semiconductor. In a n-type semiconductor, the electrons in the dye are photoexcited from the ground state to the first singlet (or triplet) excited state. The excited electron is then transferred to the conduction band. In a p-type semiconductor, the photocurrent is due to the transfer of holes from the excited dye to the valence band.

Cuprous iodide is a mixed conductor the charge carriers are Cu^+ ions, electrons or holes. However, at temperatures less than 300°C the ionic conduction is insignificant and in the presence of traces of excess iodine³³, the conduction is mainly due to holes. The cuprous iodide layer prepared in the manner we have described, behaves as a p-type semiconductor having a band gap of about 0.31 eV. The photocurrent is due to transfer of holes from the excited dye to the valence band of the semiconductor.

Since the response of the cell is mainly in the red region it is not practically useful as a photovoltaic cell. However, since the cell is stable it could be used as a model for further development of Chlorophyll sensitized cells. Chlorophyll and a large number of natural and organic dyes get easily absorbed in cuprous iodide. We have found that other familiar semiconductor materials such as cadmium sulphide, zinc oxide and cuprous oxide do not absorb Chlorophyll so well as cuprous iodide.

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