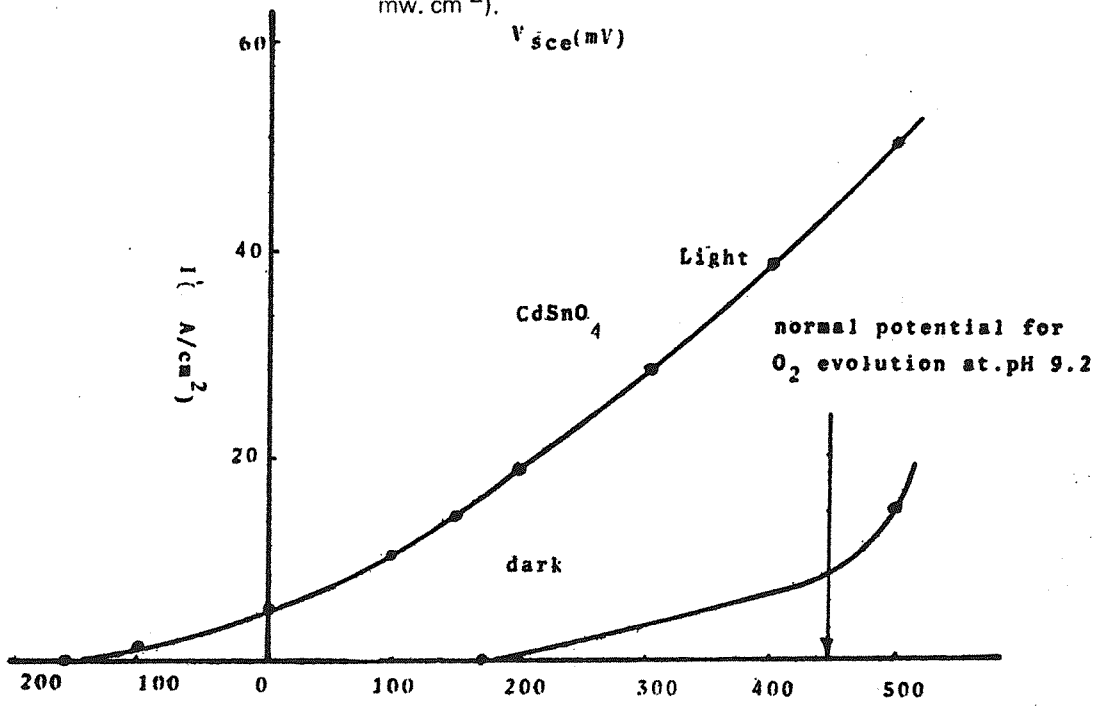
Fig.10- Photoelectrochemical behaviour of sintered Cd_2SnO_4 pellet PH=9.2/Xe illumination (200 mw. cm^{-2}).



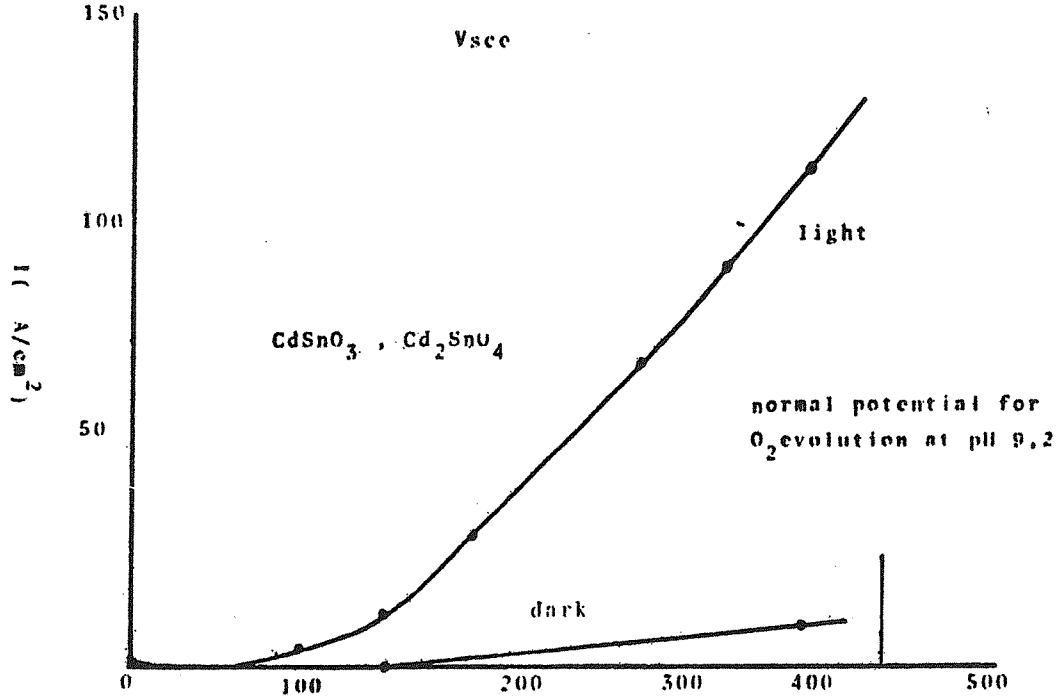
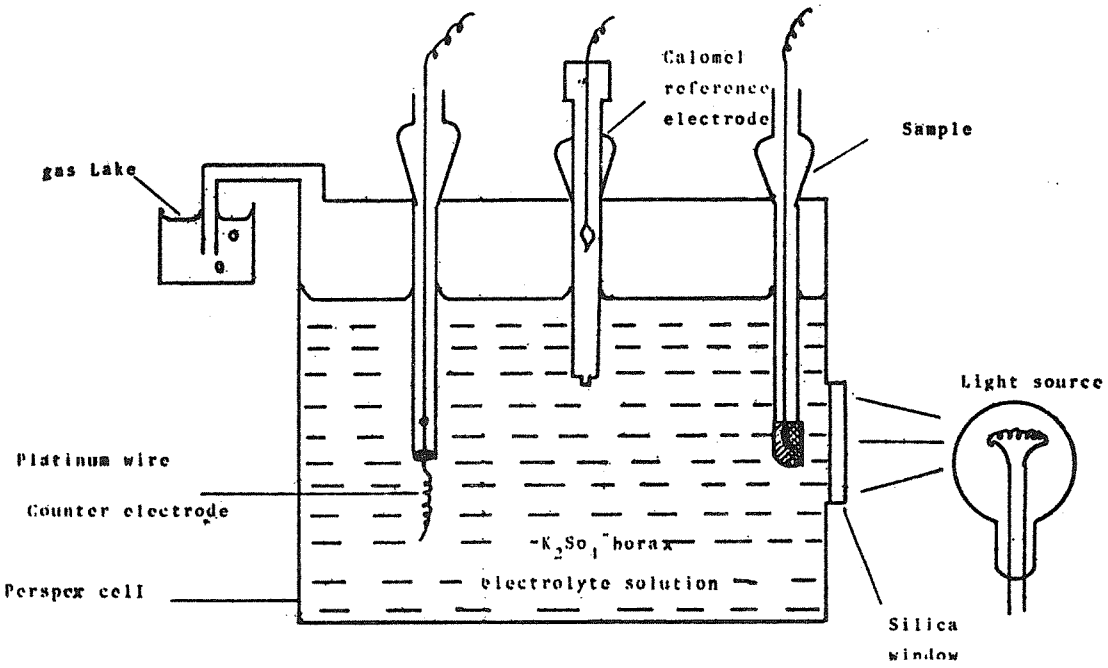


Fig.11- Photoelectrochemical behaviour of mixed $CdSnO_3$ – Cd_2SnO_4 pellet, PH=9.2/Xe illumination (200 mw.cm^{-2}).

Fig.8- Photoelectrochemical cell arrangement.



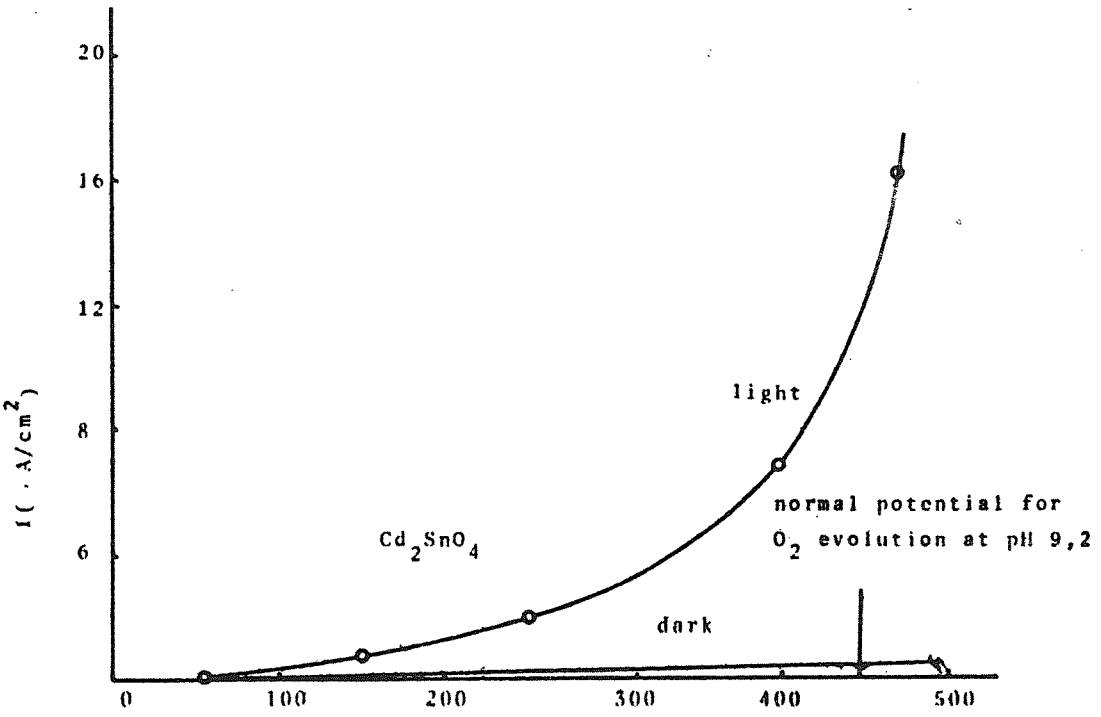
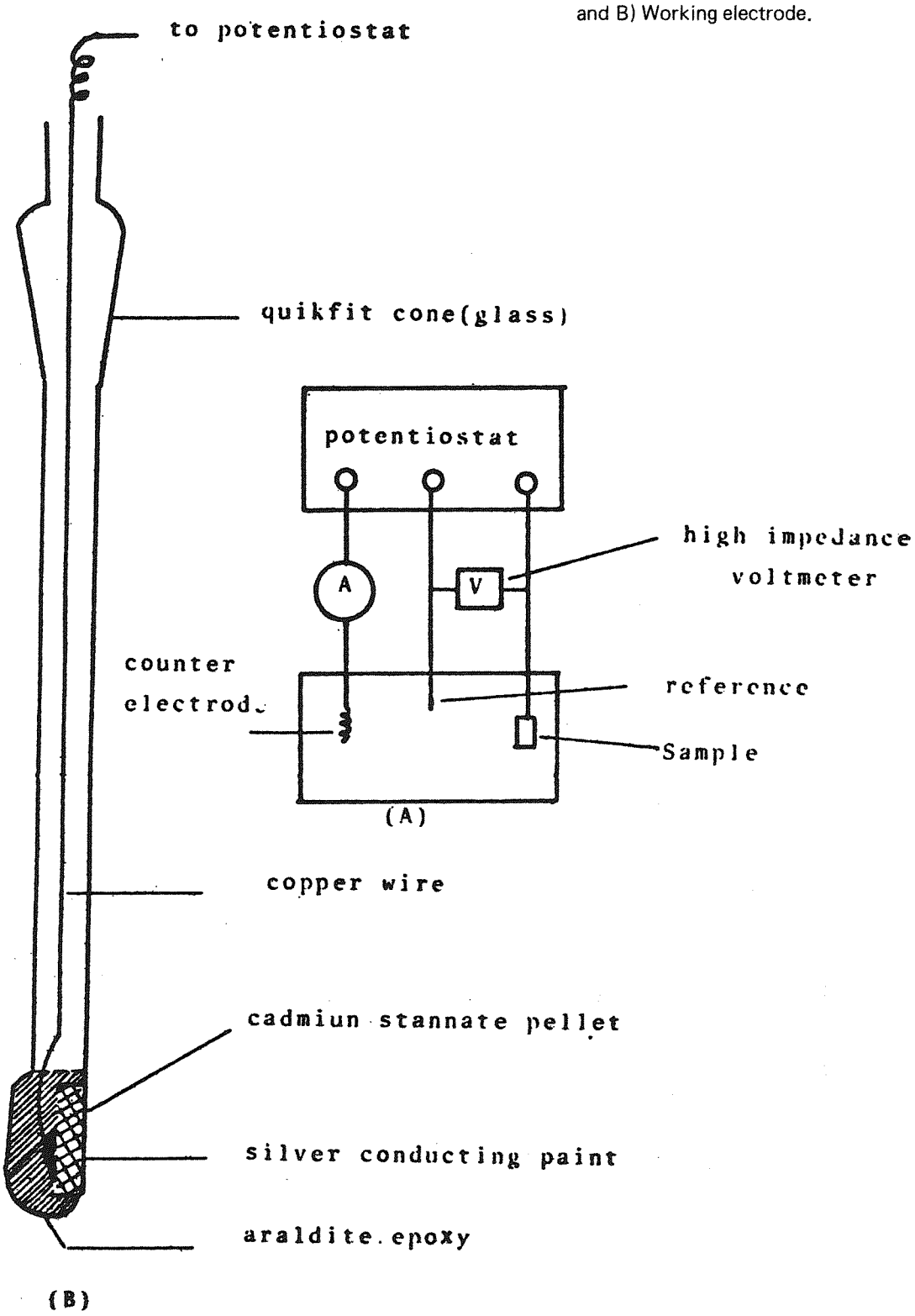


Fig.9- Photoelectrochemical behaviour of sintered $CdSnO_3$ pellet, PH=2, Xe illumination (200 Mw. cm $^{-2}$).

Fig.7- Schematic illustration of =A) Cell arrangement and B) Working electrode.



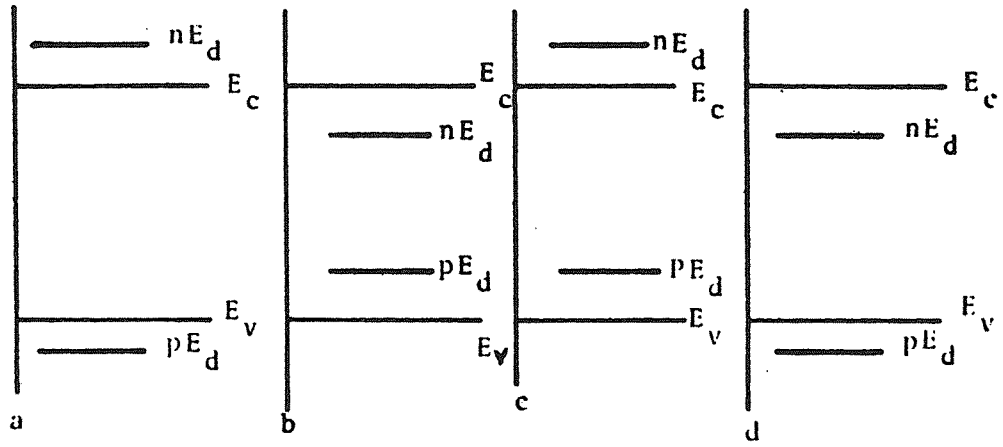


Fig.5- The relative positions of semiconducting electrode conduction E_c and Valance E_v band edges and decomposition potentials for anodic pEd cathodic nEd decomposition.

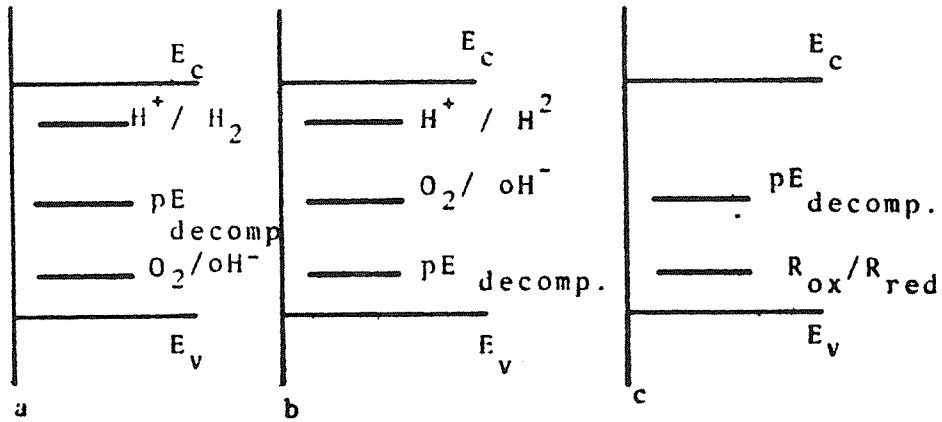


Fig. 6- Relative positions of decomposition potentials and desired redox potentials for photo-electro-lysis and wet photovoltaic cells using n-type semiconductor.

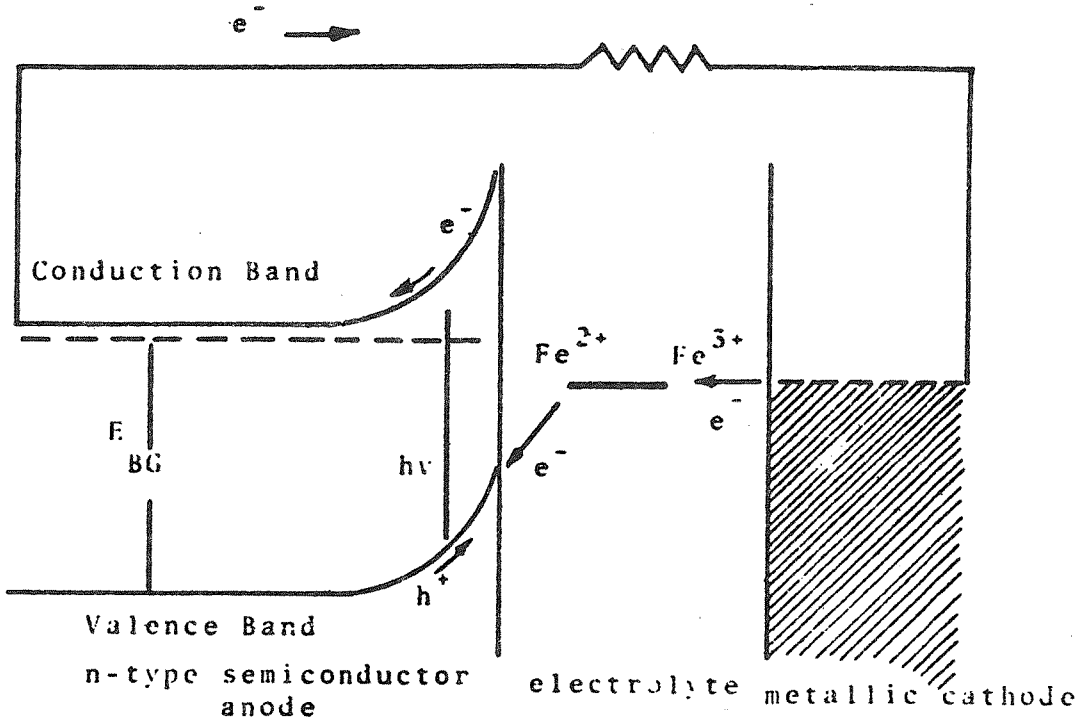


Fig.3- Energy level diagram for electrochemical device which produces electricity but no chemical products.

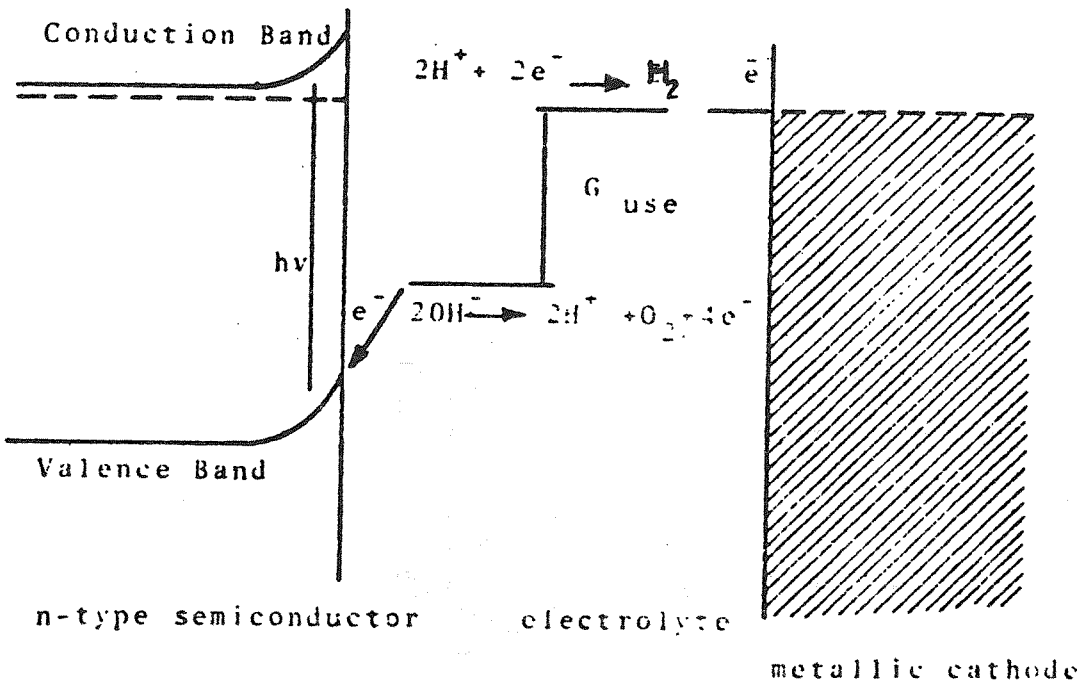


Fig. 4- Energy level diagram for an electrochemical device which produces a chemical products.

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Figures Captions:

Fig.1- Typical photoelectrochemical cell.

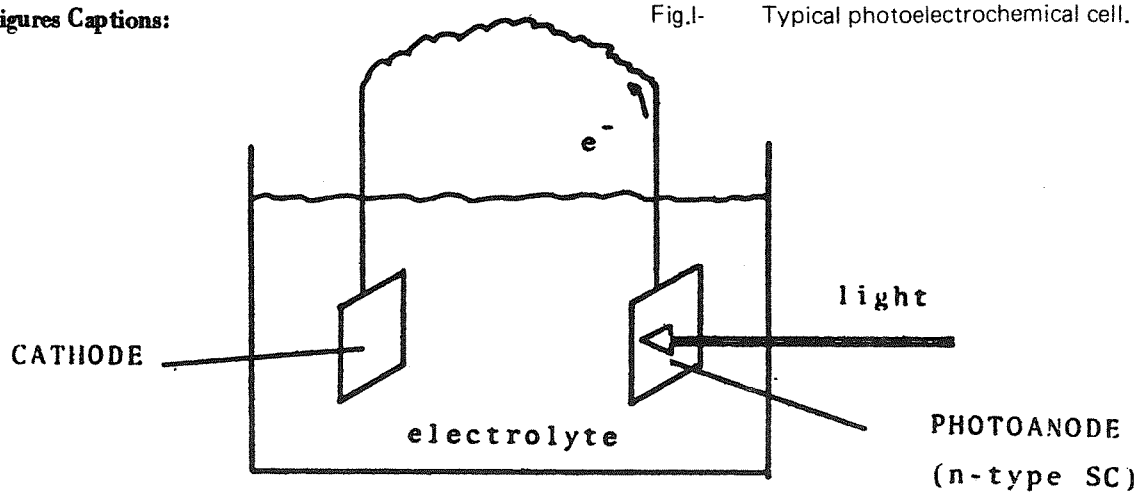
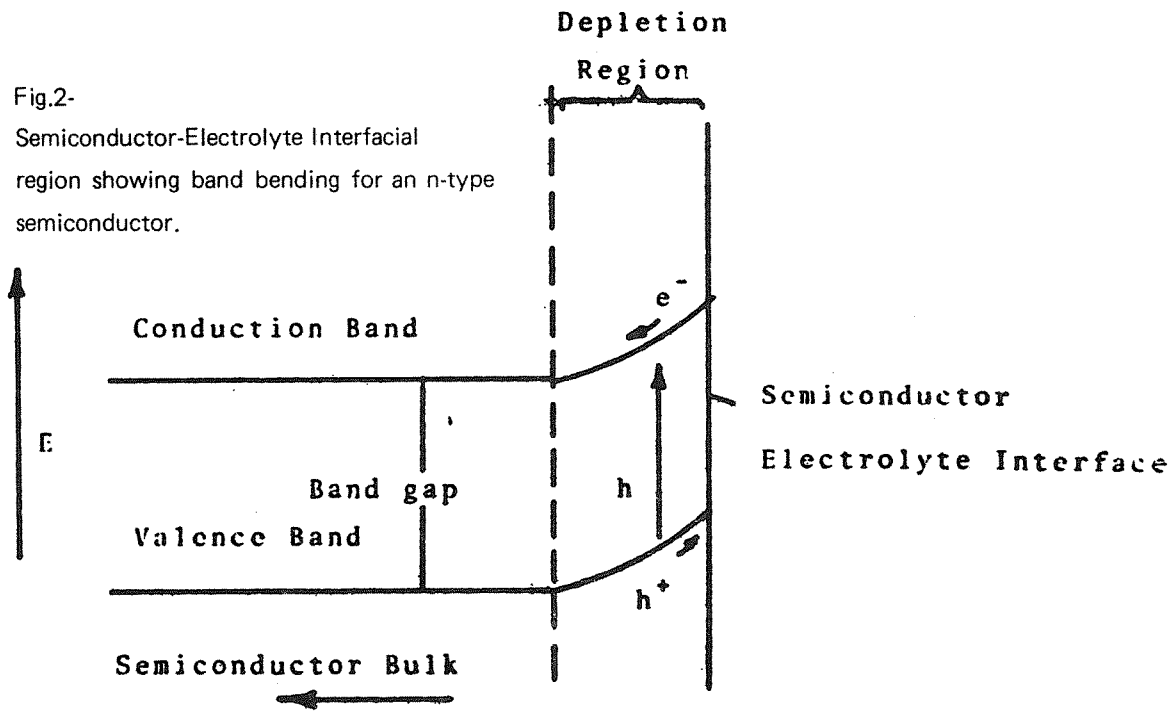


Fig.2-
Semiconductor-Electrolyte Interfacial region showing band bending for an n-type semiconductor.



pected from the larger bandgap in SnO_2 (3.5. eV) the onset of photoconductivity occurs at about 350 nm, with Voc of about -400 mV referred to a saturated calomel electrode at PH=9 photoconversion in SnO_2 below 350 nm is considerably more efficient than in the stannate samples. The lack of similarity between the photoelectrochemical behaviour of SnO_2 and the cadmiun stanates confirms that the results for the stannates reflect their intrinsic behaviour, and are not simply due to traces of unreacted SnO_2 remaining in the sample.

In order to see whether the photoelectrochemical properties of the cadmium stannates might be impaired by the polycrystalline nature of the samples, single crystals of Cd2 SnO4 in the form of long needle-like whiskers of about Imm x Imm cross-section were also tested. Although these crystals clearly showed n-type behaviour, the photocurrents were extremely small even at high potentials and light intensities. These single crystals were too small to permit conductance measurements to be made, but if they possessed similar insultating properties to the Cd_2SnO_4 monocrystals gown by shannon et al (I7) their poor photoelectrochemical is under standable. Thus it appears that the photoelectrochemical properties reported here for polyrystalline samples may depend on their oxygen vacancy concentration, which in turn is a function of the method of their preparation.

5. CONCLUSIONS

I. A small but significant photoelectrochemical effect is shown by polycrystalline pellets of both cadmium stannates, the photocurrent (and background current) of $CdSnO_3$ being greater than that of Cd_2SnO_4. Both stannates are stable in water and alkaline electrolytes for periods of up to several weeks.

2. It has been shown that the electrochemical methods are useful for determining the majority carrier type and the optical band gap. Both stannates show n - type semiconductivity, with a bandgap of about 2.3. ev, estimated from the wavelength dependence of the photocurrent.

3. The low guantum efficiency achieved with the candmium stannate samples suggest that these materials probably will not be able to compete with some recently reported photoanodes (11) unless their properties are improved.

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and Cd_2Sno_4 pellets were found to be 3.0×10^{-3} and 1.3×10^{-2} ohm cm respectively. These values compare reasonably with the room-temperature conductance of Cd_2SnO_4, for which values of up to 1.33×10^{3} ohm^{-1} - cm^{-1} have been reported (4), but are rather different from the reported resistivities of single crystal undoped orthorhombic $CdSnO_3$ and Cd_2SnO_4 (17), which were described as insultating and semiconducting Since the conductivity of these materials is thought to be due to oxygen deficiency (4), the higher conductances of the present samples may be due to the introduction of anion defects during the solid state reaction between the oxide powders. The results of the photoelectrochemical experiments on sintered $CdSnO_3$ and Cd_2SnO_4 pellets are shown in Fig. 9. and 10. respectively, from which it is seen that $CdSnO_3$ shows a much larger phtovoltage and photocurrent than that of Cd_2SnO_4.

The dark current from $CdSno_3$ was also significantly greater than in Cd_2SnO_4 in which no background current was observed even at normal oxygen evolution potentials. This increased dark current in $CdSnO_3$ could be due to greater porosity of the sample pellet, which might also explain the lower reproducibility of measurements on that phase. Both $CdSnO_3$ and Cd_2SnO_4 pellets were stable in water and alkaline solutions for periods of several weeks, and showed no apparent tendency to dissolve or disproportionate even at potentials up to those of oxygen evolution.

Tests were also conducted on a Cd_2Sno_4 pellet which had been sintered in an open vessel, losing some Cd from the outer surface, thereby forming an outer layer of $CdSno_3$. This mixed - phase sample gave a smaller photovoltage than pure $CsSnO_3$ but showed a much larger photocurrent (Fig. 11). In all other respects the sample had similar electrical properties to the pure $CdSnO_3$ phases.

Although there was some slight variation in the as-tested densities of the various pellets due to differences in sinterability of the two stannates (the dicadmium-compound sintered more readily than the monocadmuim), the differences in photocurrent densities of the various samples are less likely to be due to this factor than to differences in the oxygen non-stoichiometry of the various phases, which has been shown by Shannon et al (17) to exert a considerable influence on their electrical properties.

In all samples oxygen evolution was observed under intense illumination, even at potentials below the usual threshold for such a reaction. Since this effect was observed only on the anodic side, this result is consistent with n-type semiconducting behaviour. This is in agreement with the previous observation (4) that thin films of amorphous Cd_2SnO_4 exhibit n-type semiconductivity, with oxygen vacanices providing the donor states. The absence of physical degradation of the samples suggests that the oxygen is derived from the electrolyte rather than from the anode materials although some loss of oxygen from the pores may be possible without causing observable disintegration of the pellets.

The experiments with monochromatic radiation showed a photo-response down to approximately $5300A^{o}$, but te cutoff was not sharpt, possibly due to the polycrystalline nature of the samples, and the low intensity level of the available monochromatic radiation. Nevertheless this cutoff wavelength corresponds to about 2.3 eV, in reasonable agreement with the optical bandgap of 2.06 eV reported for $CdSnO_4$ films (4). The present results indicate no significant difference in the bandgap of $CdSnO_3$ and Cd_2SnO_4 within the limitations of the experiment. Comparison of these data for the cadmium stannates with previously published photoelectrochemical data for SnO_2 (18) shows that SnO_2 behaves quite differently. As would be ex-

also be used as protective coatings for unstable small band-gap semiconductors (11).

3. EXPERIMENTAL WORK

Cd_2Sno_4 and $CdSnO_3$ powders were prepared as described in our previous work (5) one cm. diameter pellets of the pure phases were formed by pressing at $3x10^3$ kg. cm^{-2} and sintered at $1050c^o$ for 2 h. in colsed crucibles.

An electrical contact was made to the sample by attaching a copper wire to the back face of the pellet with silver dag. A low resistance ohmic contact was found to be achieved by this method. The sample was attached to a quickfit cone by means of Araldite, ensuring that the whole back face and edges of the pellet were covered by epoxyresin (as shown in Fig. 7.B.).

The mounted sample was inserted in the cell shown in fig. 8. The saturated calomel electrode (S.C.E.) permits an accurate measurement of the sample voltage whilt the potentiostat allows the voltage of the sample to be adjusted while monitoring the current. The platinum counter electrode is used to complete the current-flow circuit. (Any current flowing through the reference electrode ruins its accuracy, and can destroy the electrode). The silica window of the cell ensures good transparency to light at all visible wavelengths. The U.V. - filtered xenon light source was used because it is a reasonable match to the solar spectrum and gives a useful output over the whole visible spectrum. The light source was placed at such a distance that approximately 200 mW/cm^2 of light energy was incident on the sample surface. (A ligh flow greater than this could cause excessive heating of the cell). A 0.5M K_2So_4+ +0.IM Borax solution was chosen because it gives the electrolyte a good conductivity and holds the P^H at 9.2. (Both cadmiun oxide and tin oxide are very insoluble at this ph-hence the cadmium stannates should be also).

The voltage of the electrode was first measured against a S.C.E. with the potentiostat disconnected, and the cell completely blocked-out. This gave a value, $E_{dark\ o.c.,}$ for the open-circuit dark voltage of the sample. The xenon light was then placed at a predetermined distance with the silica window unshielded and the voltage again measured against the S.C.E. after it had stabilized (which usually occurred in five minutes) to give $E_{photo\ o.c.}$ The potentiostat was then connected and the voltage of the sample relative to the S.C.E. raised in 50 mV steps-monitoring the steady-state current at each step. When the voltage corresponding to the theoretical oxygen evolution voltage (0.447 volts versus S.C.E.) was reached, the potentiostat was disconnected and the cell reshielded. When the original $E_{dark\ o\ c.}$ was re-established, a similar procedure was used to obtain the current-voltage characteristics under dark conditions.

By moving the light source close up to the silica window and holding the $CdSn0_3$ sample at +400 mV (S.C.E.), it was possible to cause a current of several milliamps to flow, and a colourless gas was observed to be evolved (Presumably oxygen).

In an effort to determine the band gap of the samples, the cell was placed in front of a monochromator. A 100w unfiltered high pressure mercury lamp was used as the source, and the monochromator was slowly scanned from the U.V. part of the spectrum through to red. The current from the cell was monitored while the output from the monochromator was intermittently blocked off. This was necessary because of the low sensitivity of the samples which resulted in the photocurrent being only of the same magnitude as the background current. When no significant difference between illuminated and dark current was observed, the wavelength at which this occurred was noted (cut-off).

4. RESULTS AND DISCUSSION

The room-temperature resistivity values of $CdSno_3$

the decomposition potential lies above the reaction potential as in (a) then the potential drop for an electron going to the hole at the valence band edge is greater for the decomposition reaction than for the evolution reaction. This potential drop of "effective overpotential" is a measure of the relative driving force available for the two reactions. In case (b) the overpotential available for oxygen production is greater than that for the decomposition reaction and one would expect preferential 0_2 production. In case (c) the stituation in a wet photovoltaic cell is demonstrated.

Here since PE $_{decomposition}$ lies above the R_{ox}/R_{red} edge, again the semiconductor will corrode, but if R_{ox}/ R_{red} could lie above PE decomposition the semiconductor is kinetically more stable.

2.4. Efficiency

Another important aspect of the photoelectrochemical process is the efficient conversion of photons to excited electrons and their efficient utilization. In general, the generation and separation of carriers in the semiconductor is the rate-limiting step rather than the chemical kinetics at the interface(I2). Since only photons of energy larger than band gap of the semiconductor can be used, the band gap must be chosen to optimize the conversion efficiency. There are two competing factors which determine the optimum band E_g. Since only photons of enrgy greater than E_g will be contributed to the photocurrent, E_g must be as small as possible. However every photon absorbed by the semiconductor irrespective of its energy, can contribute at most the energy E_g. Thus to maxi- The maximize the energy conversion efficiency per photon it is necessary to maximize the band gap.

Another factor is the optical absorption depth compared to the depletion layer thickness. Since we need the electric Field in the depletion layer to separate the electron - hole pairs and since most of the charge carriers in semiconductors have short diffusion lengths, it is important to absorb most of the light in the depletion layer region. This region is increased in depth when the material has a low doping level (II) but usually the need for low resistance precludes this approach to maximizing useful photon absorption.

Photons can be lost by reflection from the cell window and from the electrode surface, and it is desirable to use anti-reflection coatings (I5). Coloured electrolytes may also introduce absorption losses and hence the optical path in the electrolyte should be minimized.

2.5. Oxide Semiconductor Electrodes

A number of metal oxides, as well as various mixed and compound oxides like the titanates have semiconducting properties of interest in the photoelectrochemical context. In general these materials are n-type semiconductors made conducting by introducing oxygen vacancies. This is frequently done by the reducing the material in H_2 or in vacuum at elevated temperatures.

Of the oxide semiconductors SnO_2, TiO_2 and $SrTiO_3$ are most studied (2, 16). Most of the n-type oxides are most stable against photoelectrochemical oxidation than non-oxides and a feature that makes them attractive as photoelectrodes is the possibility of making them in large areas by very simple and inexpensive processes.

Since oxide electrodes are mostly n-type semiconductors because of the presence of vacancies, the question of electrode instability due to exidation arises. With oxygen being formed at this electrode under the influence of light, should not the vacancy sites at the surface be re-oxidized? This process may well occur, but it will change the material from an n-type to an intrinsic semiconductor only in a very thin layer at the surface. So long as this layer is thin compared to the depletion region it will have no appreciable effect, except to modify the band bending and to extend the depletion region somewhat. Oxides may

action by the reversible ferric-ferrous couple ($Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq}$). Here the reaction is driven one way at the anode ($Fe^{2+}_{aq} + e^- \rightleftharpoons Fe^{3+}_{aq} + e^-$) and in the opposite direction at the cathode ($Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq}$). Thus in such a system there is no net chemical change and the power produced must be extracted via the electrical load. Such cells are commonly called wet photovoltaic cells by analogy with the corresponding solid state devices (12).

Another type of photoelectrochemical device results in the production of a chemical product. Its energy level diagram is illustrated in Fig. 4. Here two irreversible electrochemical couples are driven, with one reaction taking place at the anode and the other at the cathode. This results in a net chemical change in the electrolyte. At the cathode, the reaction is ($2H^+ + 2e \longrightarrow H_2$) and at the anode the reactions is ($2oH^- \longrightarrow S2H^+ + {}^0_2 + 4e^-$). This reaction is photosynthetic in that external energy must be provided to drive this reaction. The net amount of energy stored is the difference between the redox potentials of the two couples (Δ Guse). In photoelectrochemical cells three basic criteria must be discerned; flat-band potential, stability and efficiency.

2.2. Flat-band Potential

The flat-band potential is the voltage of the semiconductor back contact with respect to some reference electrode in the electrolyte at which there is no band bending (i.e. the conduction band level in the bulk of the Semiconductor is the same as its level at the interface). The flat-band voltage locates the Fermi level relative to electrolyte levels and hereby locates the band edges, since the Fermi level relative to band edges is determined by the doping of the semiconductor. The positions of the band edges relative to the electrolyte levels are the important features in determining whether the desired electron transfer reactions can take place and whether there is sufficient inherentband bending to allow the cell to operate without bias. It should be emphasized that the application of external reverse bias does not change the amount of band bending, the width of the depletion layer and the effectiveness of charge separation within the semiconductor.

The flat-band condition can be found from the intercept on the voltage axis of the so called Mott-Schottky capacitance-voltage plot-i.e., the plot of I/C^2 vs V. (II).

2.3. Stability

The most crucial condition that the semiconducting electrodes must satisfy is stablity under the rather rigorous conditions, under which they are operated. They must not only be stable against chemical dissolution in the electrolyte but also stable against electrochemical corrosion and photo-corrosion (I5).

In any assessment of electrode stability the main concern must be the intrinsic thermodynamic stability of the electrode. It must be distinguished whether the reaction of interest is thermodynamically more or less favourable than the appropriate oxidative of reductive decomposition reactions for the semiconductor. The completely stable case occurs when the reductive decomposition potential lies above (more negative than) the conduction band and the oxidative decomposition potential lies below (more positive than) the valence band edge (Fig. 5) Under these conditions, the electrode cannot provide electrons or holes with sufficient energy to drive the decomposition reactions. Most of semiconductor/electrolyte combinations show behaviour of the forms b,c and d in fig 5. (12).

Attention must be directed toward the relative positions of the decomposition potentials and the redox potential of interest. Fig. 6. illustrates typical examples for a photoelectrolysis cell and for a wet photovoltaic cell. In the photoelectrolysis case if

cal properties of both cadmium-tin oxides, in order to elucidate their importance and possible applications in solar energy conversion. It also appears to be interesting in a scientific way to find out the photo-anodic properties of two mixed oxides made of a relatively unstable oxide (CdO) and a relatively high energy band gap semiconductor(SnO_2). Due to the novelty of the photoelectrochemistry field, a brief overview of the theory is also presented in this paper.

2. THEORY OF PHOTELECTROCHEMICAL SOLAR ENERGY CONVERSION

Sunlight in the near infrared, visible and near ulrtaviolet regions has considerable energy (about 0.9 to 3 electron volt per photon) and its intensity could provide a significant contribution to our electrical and chemical resources if efficient and inexpensive systems utilizing readily available materials could be devised for the conversion process.

A photoelectrochemical device is one in which a semiconducting electrode is illuminated in a liquid cell and drives elecrochemical reactions as both electrodes. These cells may be of two types; one is directrd primarily towards the production of electricity(Wet photovoltaic Cells) and the other produces chemical products through a chemical change at the electrode or electrolyte.

The major advantage of photoelectrochemical device over, more conventional solare cells, is the ease with whichthe device can be construceted, Another advatage over the silicon solar cells is the ability to store solar energy by the direct production of chemicals(e.g.H_2).

Photoelectrolysis of water by using sunlight is extremely attractive for several reasons. Firstly this type of solar energy conversion helps the energy storage problem, since hydrogen can be stored much more easily than either electricity or heat. Secondly, hydrogen is valuable as a potential fuel and energy carrier,finally, hydrogen is valuable since it is used in large quantities for ammonia synthesis and petroleum refining.

The application of photoelectrochemistry to energy conversion was first shown by fujishima et al in 1969 (10), who demonstrated the photodecomposition of water at a TiO_2 electrode. This made little impression however, until the energy crsis of the early seventies. A number of recent review articles have been written in this field and cover all different aspects of photoelectrochemical process for solar energy conversion (11-14).

2.1. The Semiconductor-Electrolyte System

A typical photoelectrochemical cell is shown in fig. 1. When a semiconductor is immersed in an electrolyte, the chemical potential of the electrons on each side of the interface will be different, so that charge transfer will occur until equilibrium is reached leading to the establishment of a junction field. Figure 2. shows the general model associated with the semiconductor - electrolyte interfacial region showing that the bands in a semiconductor can be bent near the surface in such a way as to inhibit recombination of electron-hole pairs. Thus, when the surface of a semiconductor is illuminated with photon energy greater than the band gap of the semiconductor, an electron is excited into the conduction band and the electron and holes are separated by the electric field in the depletion region before they can recombine.

The easiest way to describe the operation of a photo-electrochemical cell is to examine its energy diagram. The simplest device consists of a semiconducting electrode, a metallic electrode and an electrolyte as shown in fig. 3. The energy in the electrolyte for which electrons must be provided to drive the electrochèmical reaction is known as the redox potential and is usually referred to the staurated calomel electrode. The energy position at which the conduction band for n-type material intercepts the solid electrolyte interface is known as the flatband potential (V_{fL}).

Figure 3. represents the single electrochemical re-

Photoelectrochemical Properties of Cadmium Stannates

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ABSTRACT

Photoelectrochemical devices for conversion of solar energy into chemical energy and electrical energy are discussed with emphasis on how the various materials properties of the photoactive electrodes influence device efficiency and stability. In recent years interest in the use of oxide photoanodes has gorwn dramatically. As an example, our work on photoelectrochemical behaviour of both Cd_2SnO_4 and $CdSnO_3$ n-type semiconductor oxides, when illluminated in alkaline solutions, is discussed in detail.

I. INTRODUCTION

The problem of utilizing solar energy for direct production of electricity and fuels has become a field of great current interest and has encouraged new fundamental investigations of the interactions of light,electron flow and chemical reactions at electron surfaces in electrochemical cells (1).

Oxide materials such as TiO_2 and SnO_2 have been reported to show interesting photoelectochemical properties (2).

Mixed Oxides such as $SrTiO_3$ and $Hg_2Nb_2O_7$ also are reported to be useful photo-anodes(3). The features which make oxide materials attractive as photoelectrodes are their considerably better stability compared to elemental semiconductors and also the possibility of making them in large areas by very simple and inexpensive process.

One of the oxide systems which is of special interest for solar energy conversion is CdO/SnO_2 (4). Two distinct compounds, Cd_2SnO_4 and $CdSnO_3$ exist within this system(5). Dicadmium stannate is reported to have high optical transmission over the visible range as well as high conductivity (4,5). Potential usefulness of this compound in transparent electrode and heat mirror applications has recently indicated (7,8). Monocadmium stannate is reported to have some similar properties as Cd_2SnO_4 (6,9).

The present paper considers the photoelectrochemi-