

CHAPTER IV - HYDROGEN PRODUCTION WITH
SEMICONDUCTOR SEPTUM SOLAR CELLS

4.1	Introduction	83
4.2	Energy Storage In The Form of Hydrogen	85
4.3	Experimental	87
4.3.1	Preparation of electrolytes for hydrogen production	87
4.3.2	Hydrogen production with semiconductor septum solar cell	88
4.4	Results and Discussions	91
4.4.1	Hydrogen production at static electrolytic condition	91
4.4.2	Effect of intensity of light on hydrogen production	99
4.4.3	Effect of SC-SEP area on hydrogen production	105
4.4.4	Hydrogen production at two different volumes of electrolyte	112
4.4.5	Hydrogen production at electrolytic dynamic conditions	114
4.4.6	Charging and discharging characteristics of SC-SEP cell	118
4.5	Conclusions	124
	References	

4.1 INTRODUCTION

The exhaustion of oil reserves, now is more than before. The fast growing problem of fuel becomes day by day very critical which demands the need of renewable energy sources whose reaction products will be in the form of a fuel. The increase of energy prices since 1973, first for crude oil and other fossil energy carriers more heightened awareness of energy supply limits.

Hydrogen offers special advantages over existing energy technologies. Included are storability. Its excellent compatibility to different energy systems and it's low in some cases disappearing pollutant emissions are the main argument, for its future energy engineering applications [1]. It is common knowledge that hydrogen produced electrolytically from non fossil sources contain no carbon, no sulfur, no dust particles. Its uses does not produce any carbon monoxide or carbondioxide.

The conversion of sunlight into chemical fuel or electricity in photoelectrochemical cells (PEC) equipped with semiconductor electrodes is of great current interest [2-5]. Hydrogen gas is one of the products of photodecomposition of water, which can be used as a fuel. Hydrogen is an easily manageable and which can be used as a fuel. Exceptionally clean fuel since H_2 is produced from

water and water is available every where. Kallmann and Pope [6-7] have first demonstrated the use of inorganic semiconductors for the same in 1972. The above development have sparked off interest on the possibility of converting solar energy in to chemical energy.

There has been much progress in understanding semiconductor|solution interface and developing new photoelectrochemical solar cells for conversion of solar energy to useful chemicals or electricity [8-12]. Most of research on PEC cells has been conducted in a single compartment of cell where the semiconductor electrode is dipped in an electrolyte coupled with a counter electrode. Recent publications indicate that pigmented bilayer lipid membranes are also of interest in the field of solar energy conversion [13-18]. Further in recent years there has been a great deal of concerted effort towards mimicking the natural process. This has come to be known as artificial photosynthesis; One of its chief aims is the hydrogen production via photolysis and/or generation of electricity [19-22]. Thus in developing system, recently pigmented BLM has been replaced with inorganic semiconductor such as CdS and CdSe in a novel type of photoelectrochemical cell [23-24]. Tien et al have developed a new type of solar cell, termed as semiconductor septum electrochemical photovoltaic (SC-SEP) cell. It has been demonstrated by Tien [25] to generate

hydrogen from sea water, without externally applied voltage and only by using visible light of solar spectrum.

In present investigation attempt has been made to describe and discuss the production of hydrogen from artificial sea water with semiconductor septum cell. Effects of various parameters viz. SC-SEP area, electrolyte, volume of electrolyte and intensity of illumination on hydrogen production have been studied. Hydrogen production at electrolytic dynamic conditions also has been studied. The charging and discharging characteristics of SC-SEP cell were carried out for redox couples.

4.2 ENERGY STORAGE IN THE FORM OF HYDROGEN

Storage of solar energy offers a challenge even today, particularly when desired end product is transportable fuel. Photoelectrochemical solar cells offers two possible approaches for solar energy storage.

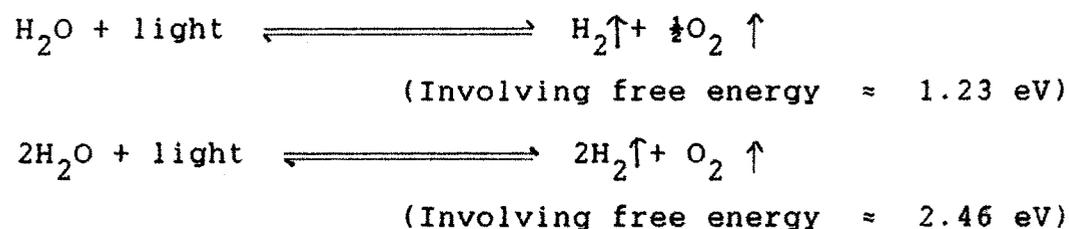
- i) Solar energy can be stored in the form of chemical energy such as secondary batteries.
- ii) Solar energy can be stored in the form of a transportable fuel, such as H₂ hydrogen produced by photoelectrolysis. The hydrogen can later be burnt in fuel cells to generate electrical power.

The renewability, high quality and non-polluting character of hydrogen fuel combined with the abundance of

sea water make photoelectrolysis cell very attractive [26-27]. Recently great advances have been made in the methods of storing hydrogen. This has made hydrogen as an excellent transportable form of energy. Hydrogen can be used to give energy either by direct burning or by using H_2/O_2 fuel cells [28-29].

Photoelectrochemical water splitting is based on the absorption of photons and the generation of electron-hole pairs in a semiconductor, in contact with an aqueous electrolyte. The potential energy of photogenerated minority charge carriers in a semiconductor permit the transition of electron to electrolyte in which these electron transfers can cause chemical reactions, such as splitting of water molecules. Cyclic process of oxidation and reduction of species of electrolyte can bring about release of molecular hydrogen (at cathode electrode) and oxygen (at the anode electrode).

The photoelectrolysis of water can be written as,



The energy of 2.46 approximately corresponds to a

wavelength of 500 nm, a wavelength available in solar radiation. There exist threshold energy of about 6.5 eV, ($\lambda = 190$ nm) only beyond which direct photodecomposition is possible. Such high energy radiation does not reach the earth's surface from the sun. So, the strategy adopted for splitting of water by photons has been to carry out the photodecomposition. Study on photoelectrochemical cells and PEC storage cells have been appeared in the literature [30-35]. The solar energy storage with help of semiconductor septum cells is most promising due to its inherent properties. In this cell, under illumination, on one side of the membrane solution interface reduction occurs and on the other side oxidation takes place. SC-SEP cell may be used for inexpensive photolysis of sea water to hydrogen using solar energy.

4.3 EXPERIMENTAL

4.3.1 PREPARATION OF ELECTROLYTES FOR H₂ PRODUCTION

(a) Preparation of Polysulphide

Appropriate amount of NaOH and Na₂S were dissolved in double distilled water at room temperature. To this solution sulphur powder was added and mixture was warmed upto 55° with constant stirring. This mixture was maintained at temperature till sulphur dissolves completely. This solution was cooled to room temperature, filtered and preserved in the glass stoppered bottle. The colour of the

solution was yellowish pink. This polysulphide solution was filled in light facing compartment of SC-SEP cell.

b) Ferro-Ferri Cyanide in 1 M KOH

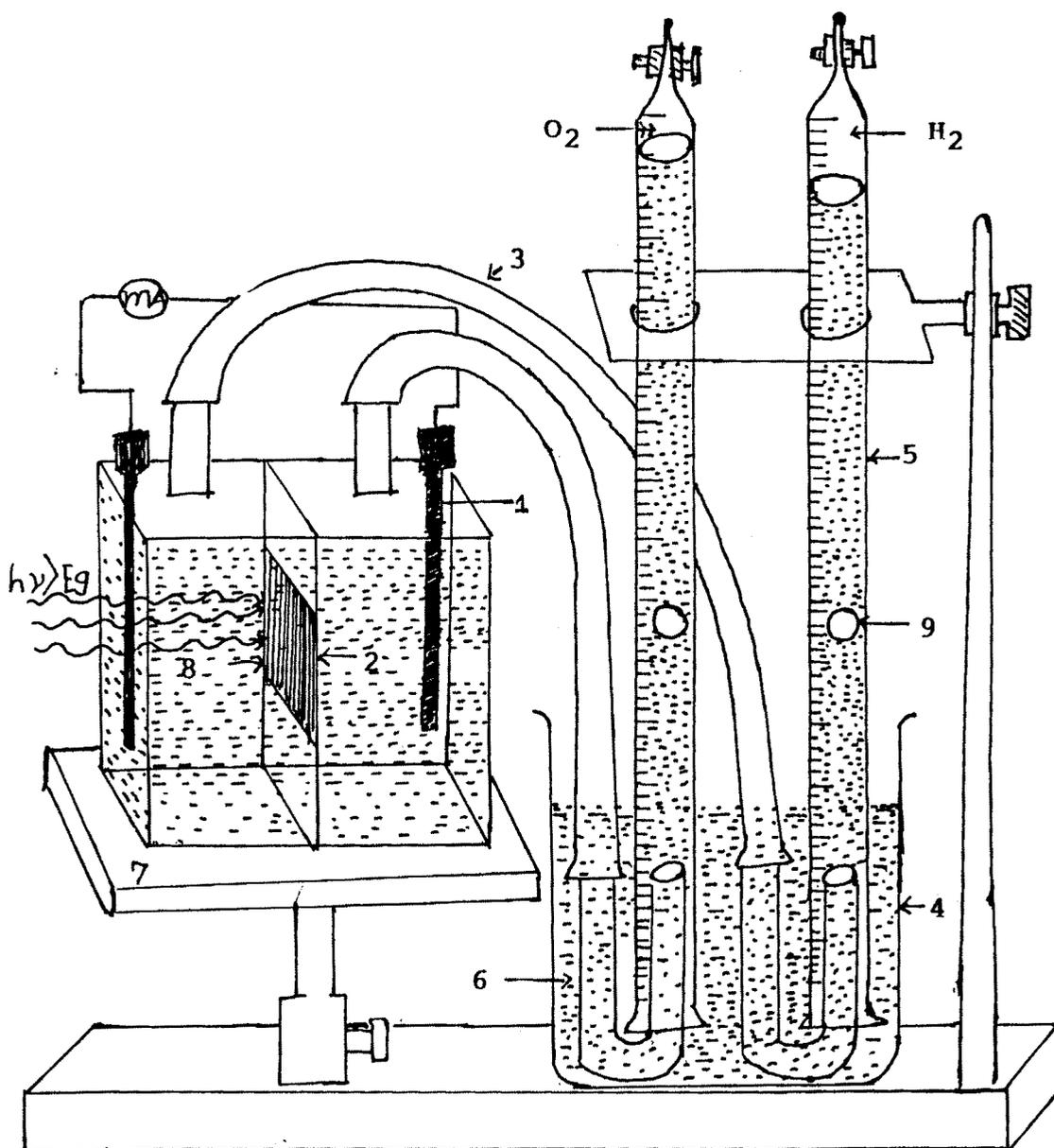
Appropriate amount of $K_4Fe(CN)_6$, $K_3Fe(CN)_6$ were dissolved in doubled distilled water and 1 M KOH at room temperature. This electrolyte was filled in light facing compartment of SC-SEP cell.

c) Artificial Sea Water

Appropriate amount of NaCl was dissolved in doubled distilled water at room temperature. This artificial sea water was filled in dark compartment of SC-SEP cell for H_2 production.

4.3.2 HYDROGEN PRODUCTION WITH SEMICONDUCTOR SEPTUM SOLAR CELLS

The semiconductor septum cells for hydrogen production were constructed as described in chapter III. The experimental set up for study of hydrogen production in SC-SEP cells at static electrolytic condition is as shown in Fig.4.1. The photograph of experimental set up is also as in Fig.4.2. In order to collect O_2 and H_2 gases two burattes of capacity 25 ml were used. Initially these burattes were filled and kept vertically in beaker containing water by using retort stand. SC-SEP solar cell filled with electrolytes was kept on platform so that it remained



- 1) Lead Electrode, 2) Semiconductor Septum, 3) Rubber tube
 4) Beaker filled with water, 5) Burettes, 6) U-shaped glass tube
 7) Platform for SC-SEP cell, 8) n-CdSe film 9) H₂ bubble

Fig.4.1. Experimental set up for hydrogen production at static electrolytic condition



Fig.4.2. Photograph of experimental set up for hydrogen production at static electrolytic condition.

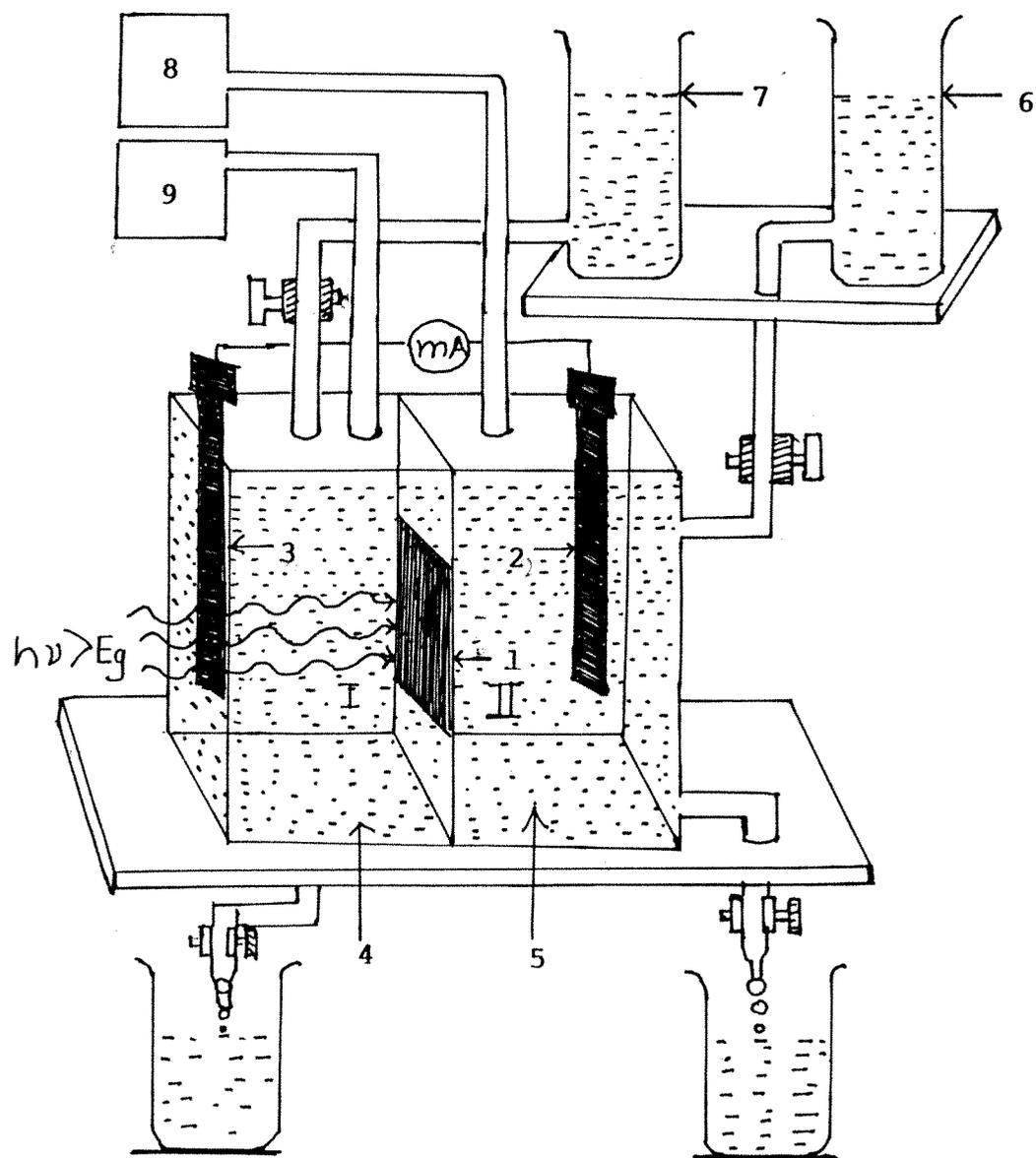
exactly in front of filament of the 500 watt bulb. Outlets for H_2 and O_2 in the two compartments were glass tubes. Rubber tubes were connected to these glass tubes and other ends of rubber tubes were connected to one arm of each U, shaped tube. Other arm of each U, tube was inserted in buratte. Hydrogen and oxygen gases were collected in burattes. In order to avoid excess heating and damaging of SC-SEP cell water filter was kept between 500 watt lamp and cell. Seven SC-SEP cells were constructed and used for study of hydrogen production. Dark compartment of each cell was filled with artificial sea water. Experimental set up to study hydrogen production at electrolytic dynamic conditions is as shown in Fig.4.3. Charging and discharging of SC-SEP cell was also studied by using 1 M $FeCl_3$. The photograph of experimental set up for hydrogen production at electrolytic dynamic conditions is as shown in Fig.4.4. The study of hydrogen production by using different cells was done and it is discussed in following sections.

4.4 RESULTS AND DISCUSSIONS

4.4.1 HYDROGEN PRODUCTION AT STATIC ELECTROLYTIC CONDITION

a) Response of photocurrent with time (Comp. I)

In order to study photoresponse only first compartment of cell was filled with electrolyte (0.2 M ferrocynide ~~to~~ 0.01 M ferricynide in 1 M KOH) and the second compartment of cell was kept empty.



- 1) Semiconductor septum, 2) Lead electrode, 3) Graphite electrode, 4) Compartment I filled with polysulphide,
- 5) Compartment II filled with artificial sea water,
- 6) Artificial sea water container, 7) Polysulphide solution container, 8) H_2 gas collector,
- 9) O_2 gas collector,

Fig.4.3. Experimental set up for hydrogen production at electrolytic dynamic condition

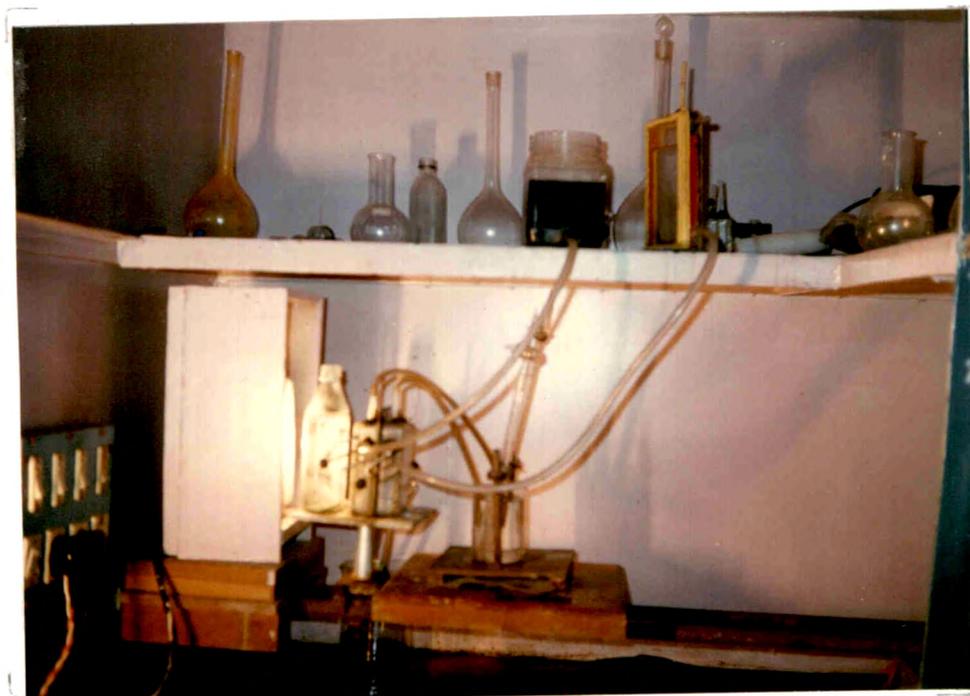


Fig.4.4. Photograph of experimental set up for H_2 production at electrolytic dynamic condition.

It was observed that,

$$V_{\text{dark}} = 0.152 \text{ V} \quad I_{\text{dark}} = 0.13 \text{ mA}$$

The variation of photocurrent with time at constant intensity (100 mw/cm^2) was studied and is as shown in Fig.4.5.

b) Hydrogen Production

The SC-SEP cell with septum area 45 cm^2 was irradiated using 500 watt tungston filament lamp. The intensity of light at the septum electrode was of the order of 100 mW/cm^2 . Both the compartments of the cell were filled and configuration of the cell was,

Graphite Electrode	0.2 M $\text{K}_4\text{Fe}(\text{CN})_6$ 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ 1 M KOH	n-CdSe film	st. steel	Artificial sea water	Pb
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SC-SEP cell was operated under short circuit conditions.

Under illumination, the gas releasing from dark, compartment of SC-SEP cell was collected and measured volumetrically by using graduated buratte and identified to be hydrogen in usual manner (i.e. ignition by lighting a match). The O_2 gas releasing from first compartment of SC-SEP cell was also measured. The mechanism of H_2 production is understood as follows.

When SC-SEP cell was irradiated, electron-hole

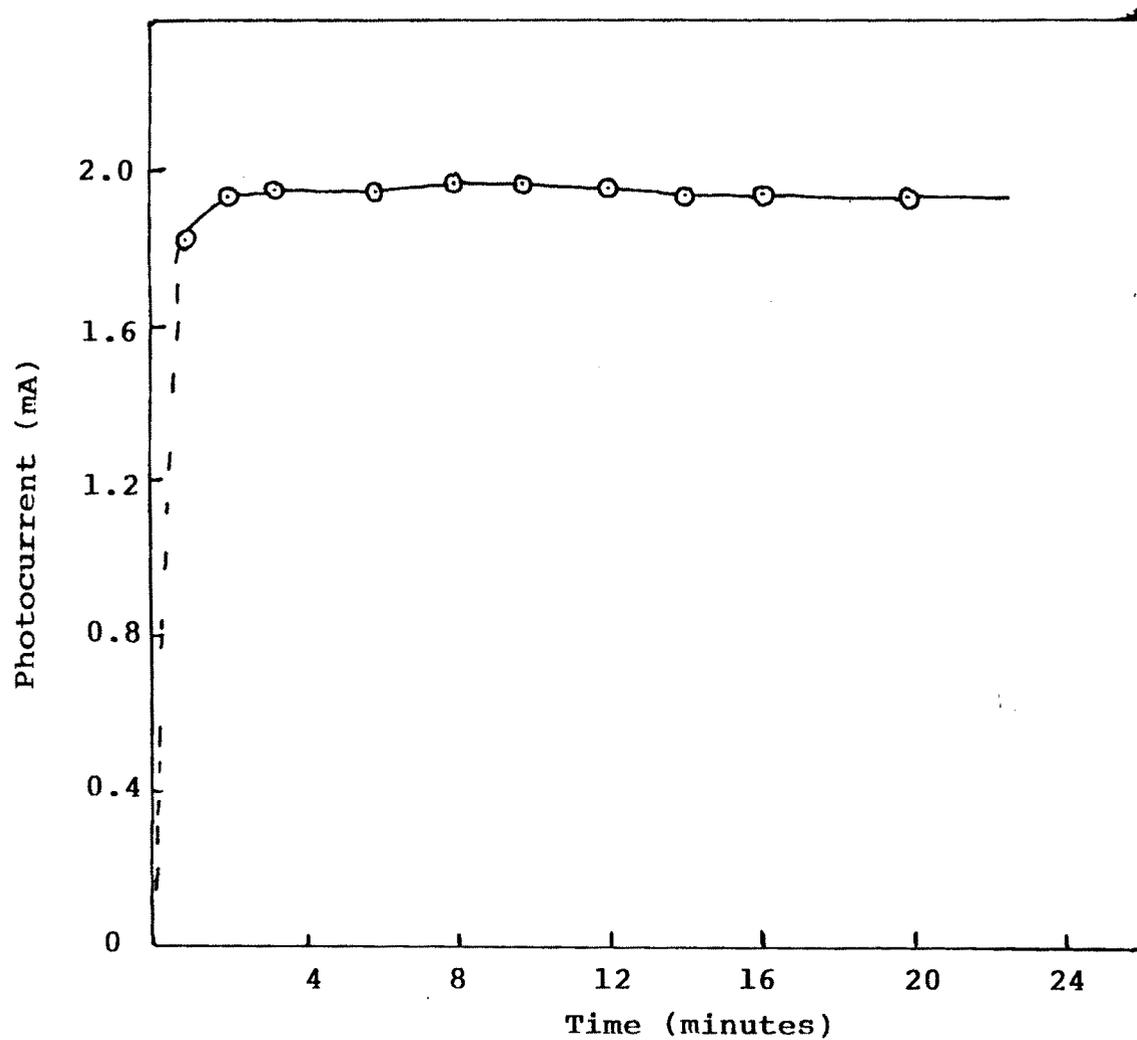
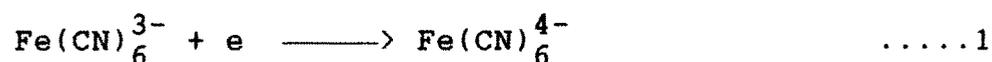


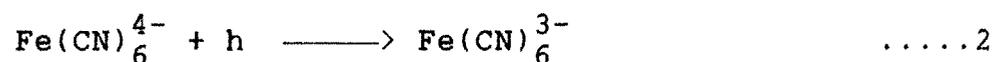
Fig.4.5. Variation of photocurrent with time (Comp. I).

pairs are generated. These holes and electrons are separated under the influence of electric field in the space charge region. At the left hand side of SC-septum, the electrons migrate through the bulk of the SC-to the metal|electrolyte interface. There are four solid|liquid junctions (from right to left : C.E.|Electrolyte, Electrolyte|M, SC|Electrolyte, Electrolyte|C.E.).

The following redox reactions take place at these respective junctions. At the left carbon electrode|Electrolyte junction.



The photogenerated holes at the SC-septum|electrolyte interface oxidize and following reaction takes place in first compartment.



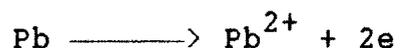
As such the pH of its concentration remains constant as observed experimentally and thus in the first compartment no net chemical change takes place in the bathing solution.

However, in the second compartment the electrode was lead (Pb) and following reaction takes place, in case of artificial sea water.



The photogenerated electrons at the stainless steel surface reduce adsorbed H^+ ions from aqueous solution to hydrogen, which upon combination are released from surface as molecular hydrogen. The pH of the solution in the dark compartment of SC-SEP cell was measured before and after hydrogen gas collection. The change in the pH was found from 7.1 to 9.4

This finding is similar with equation 3. The electrons for the reaction (equation 1) originate from right contacting electrode (pH).



The Pb^{2+} from the Pb electrode thus produced may exist either as PbSO_4 , PbO , PbO_2 or as $\text{Pb}(\text{OH})_2$ in equilibrium with their dissociated ions.

Thus over all reactions are as follows,

In left chamber no net chemical change should take place in the bathing solution, where as in the right chamber containing Pb electrode H_2O is decomposed into H_2 and OH^- ions.

The variation of hydrogen production with time is as shown in Fig.4.6. It seen that initial rate of hydrogen

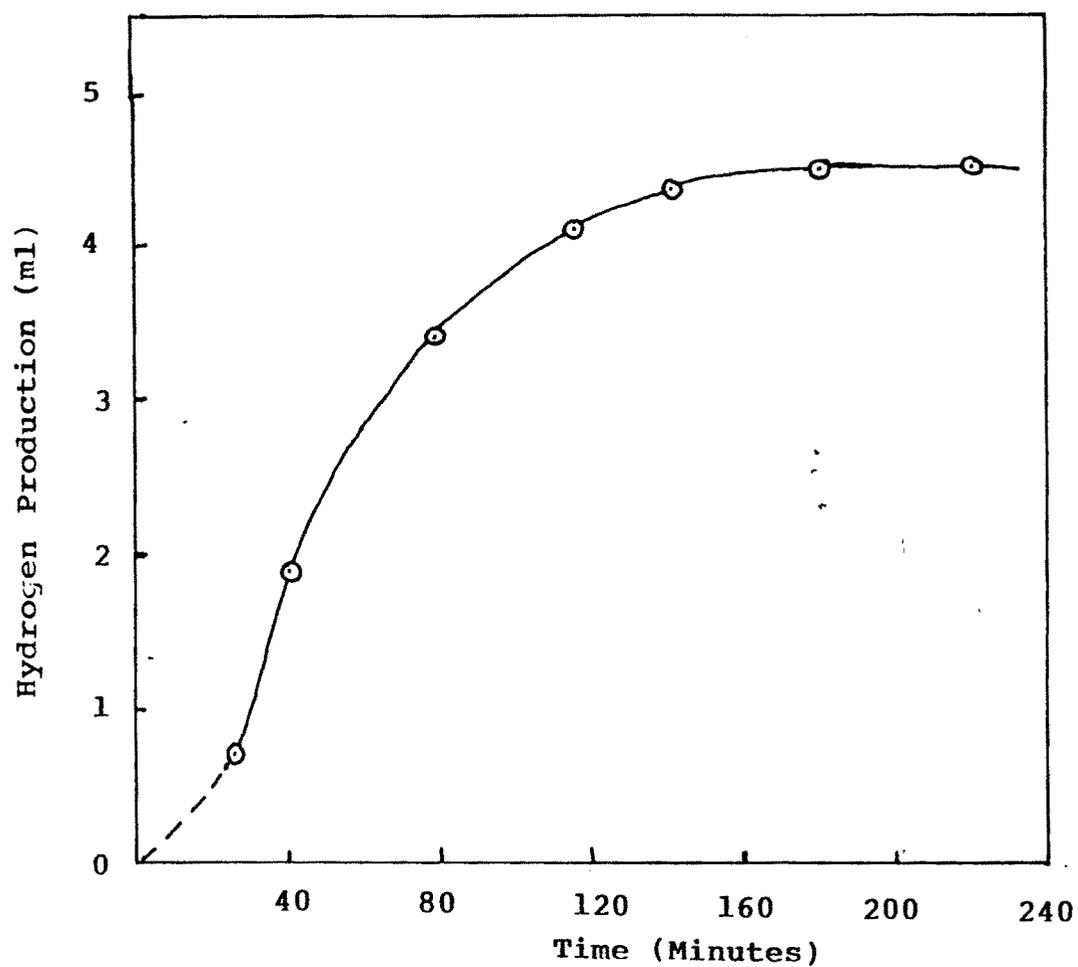


Fig.4.6. Hydrogen production with time at static electrolytic condition for following configuration of SC-SEP cell.

Graphite Electrode	0.2M, $K_4Fe(CN)_6$ 0.01M, $K_3Fe(CN)_6$ 1M KOH	n-CdSe film	St. steel	Art. sea water	Pb
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production was high but it decreases as time increases and attains a saturation after 3 Hrs. This is because of increase of OH ions concentration. This resulted to stop H₂ production. When cell was irradiated under open circuit condition, no bubbles were observed at stainless steel surface.

c) Short circuit current (I_{sc}) variation studies

In order to understand the process of H₂ production, short circuit current across two electrodes was measured by using multimeter.

The variation of short circuit current with time was studied and is as shown in Fig.4.7.

Initially short circuit current suddenly decreases and then slightly gets increased. Afterwards, during hydrogen production short circuit current (I_{sc}) decreases with time. This decrease in current may be due to fact that hydrogen bubbles resulted to stop flow of electrons.

4.4.2 EFFECT OF INTENSITY OF LIGHT ON HYDROGEN PRODUCTION

(a) (i) Photocurrent and photovoltage (Compartment I)

First compartment of SC-SEP cell was filled with polysulphide. Dark current and voltage were measured across semiconductor electrode and counter electrode. It was observed that dark and photovoltage and current are as shown in table 4.1.

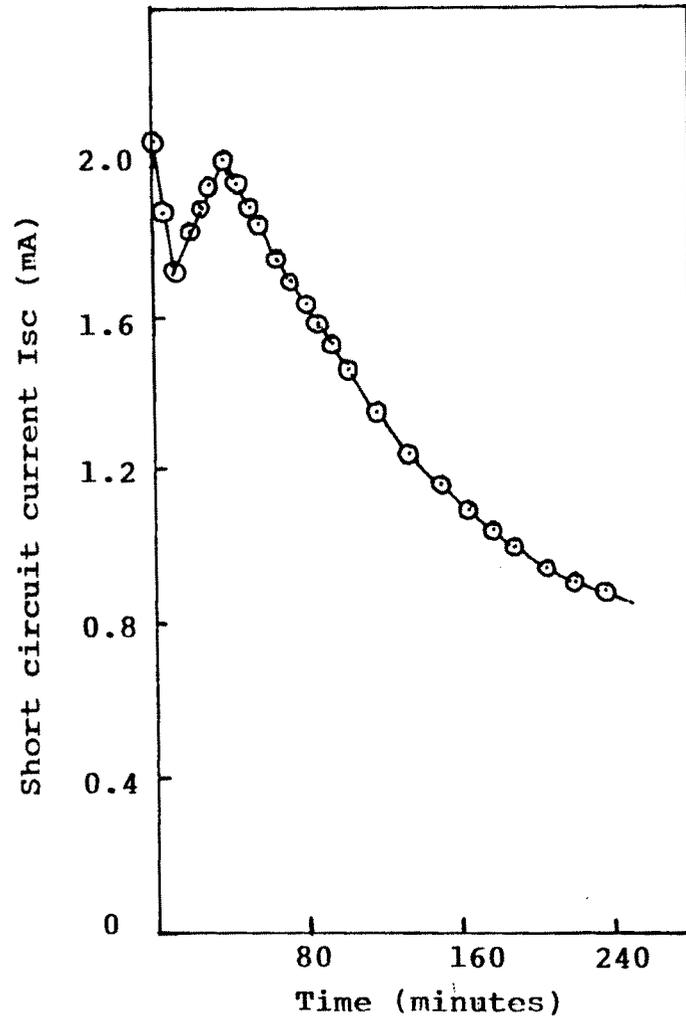


Fig.4.7. Variation of short circuit current with time for static electrolytic condition

Table 4.1

Dark current	Dark voltage	Photocurrent	Photovoltage
0.195 μ A	0.273 V	3.4 mA	0.465 V

Table 4.2

Cell	Septum area	Dark current
1	30.5 cm ²	0.09 mA
2	45.0 cm ²	0.16 mA

Table 4.3

Before charging		After charging	
Open circuit voltage	Short circuit current	Open circuit voltage	Short circuit current
2.3 Volt	35 mA	0.87 Volt	145 mA

ii) Photoresponse for different intensities (Compartment I)

First compartment of SC-SEP cell was filled with polysulphide and irradiated at different intensities. Variation of photocurrent at different intensities was studied and is as shown in Fig.4.8. It is observed that photocurrent increases with intensity of light.

b) Hydrogen Production At Three Different Intensities

The SC-SEP cell with septum area 30.5 cm^2 was irradiated using 500 watt tungstan filament lamp. Both the compartments of the cell were filled and configuration of the cell was,

Graphite Electrode	Polysulphide 1M NaOH+1M Na ₂ S + 1 MS	n-CdSe film	Stainless steel	Artificial sea water	Pb
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Variation of hydrogen production with time for three different intensities is as shown in Fig.4.9. The quantity of hydrogen production was measured at three different intensities and is observed as following,

I) Intensity 85 mW/cm^2

At this intensity hydrogen production was observed from 50 minutes and attains saturation value at about 190 minutes. The quantity of hydrogen collected was 4.2 cc.

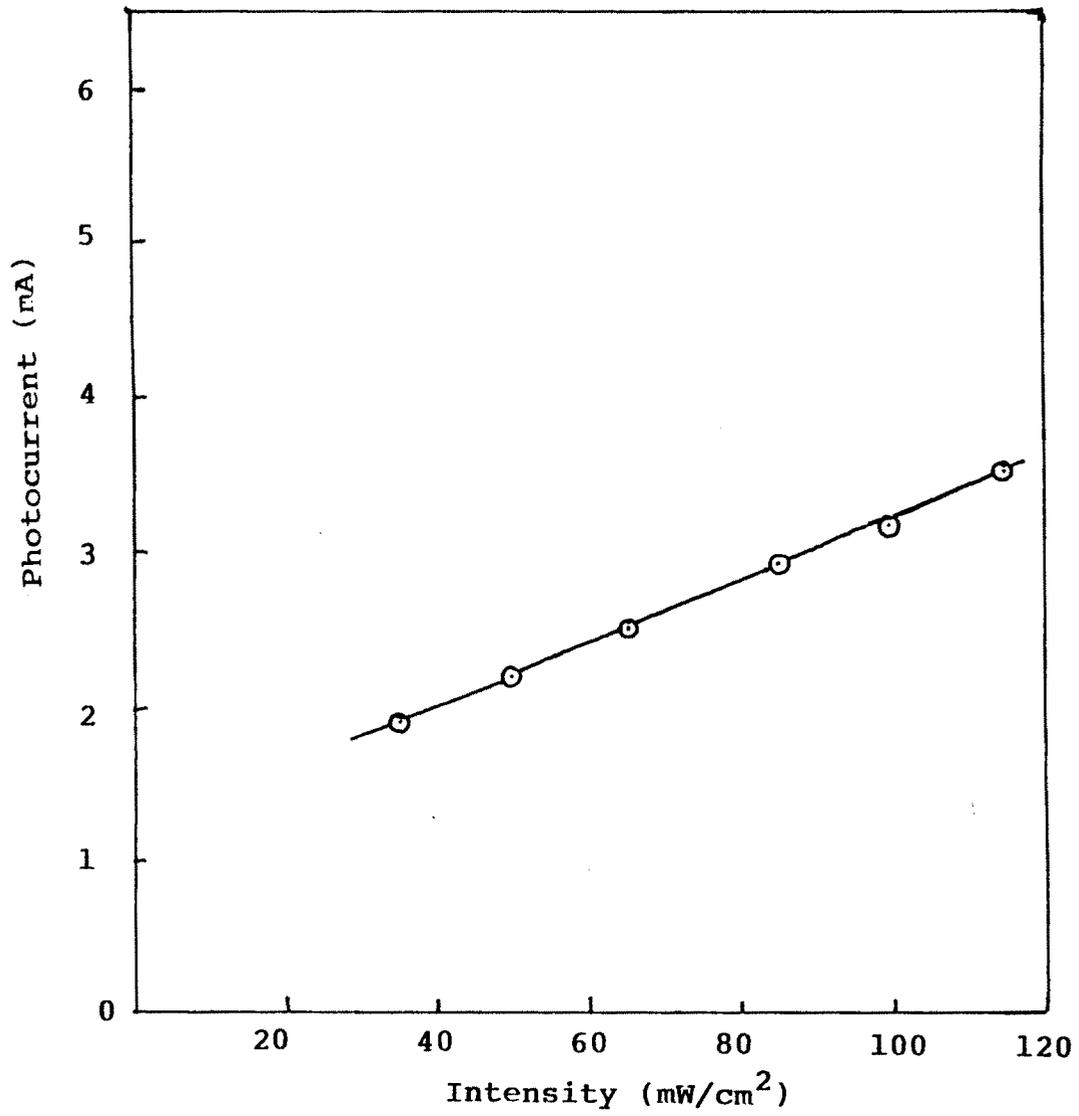


Fig.4.8. Response of photocurrent at different intensities (Comp. I)

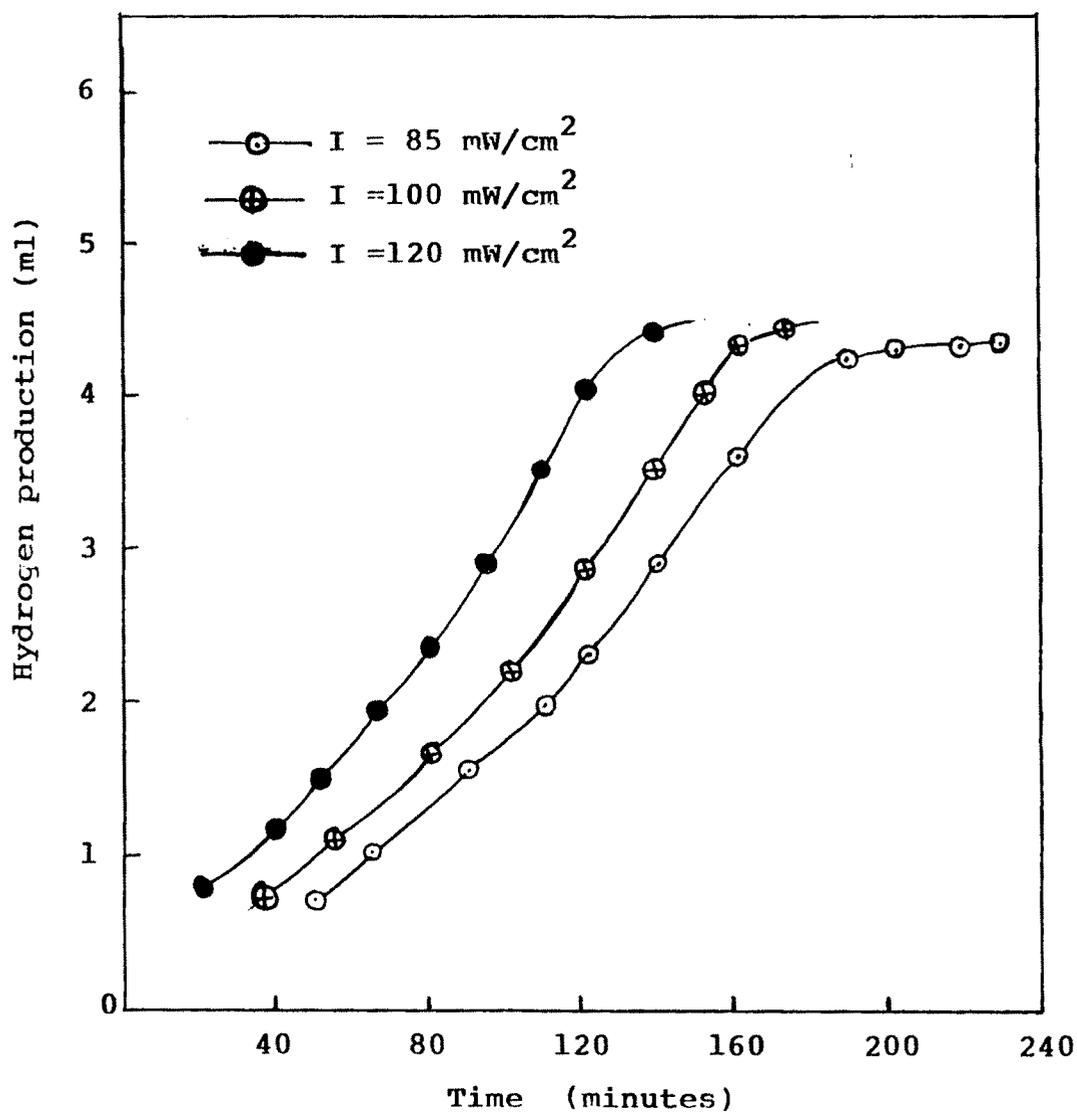


Fig.4.9. Hydrogen production in SC-SEP cell at different intensities of light for following SC-SEP cell arrangement.

Graphite electrode	1M 3 S	n-CdSe	St. steel	Art. sea water	Pb
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II) Intensity 100 mW/cm^2

At this intensity hydrogen production was observed from 32 minutes and attains saturation value after time 175 minutes. The quantity of hydrogen collected was 4.4 cc.

III) Intensity 120 mW/cm^2

At this intensity hydrogen production was observed from time 20 minutes and attains saturation stage at time 160 minutes. The quantity of hydrogen collected was 4.5 cc.

It was found that the quantity of hydrogen collected is almost same for three different intensities but rate of hydrogen production is different.

4.4.3 EFFECT OF SC-SEP AREA ON HYDROGEN PRODUCTION

Two SC-SEP cells of septum area $A = 30.5 \text{ cm}^2$ and $B = 45 \text{ cm}^2$ were used to study hydrogen production.

a) Response of photocurrent with time (Compartment I)

First compartment of each cell was filled with polysulphide and both cells were tested for same intensity 100 mW/cm^2 . Two cells were of same electrolyte capacity. Dark currents for two cells with area 30.5 cm^2 and 45 cm^2 were measured as in table 4.2

Variation of photocurrent with time for these two cells of different septum area was studied and is as shown in Fig.4.10.

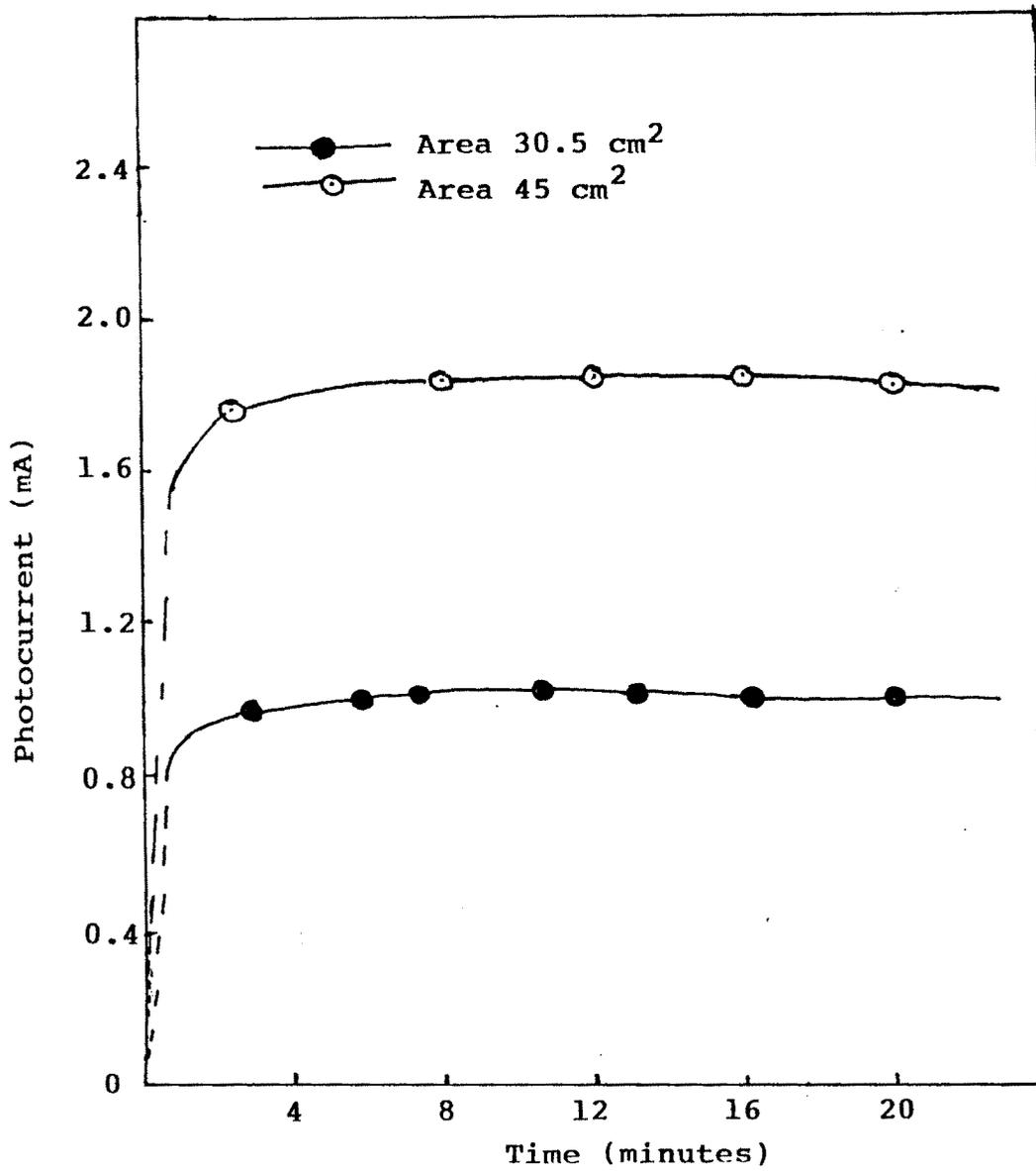


Fig.4.10. Variation of photocurrent with time for two different SC-SEP area of n-CdSe films. (Comp.I)

b) Hydrogen Production

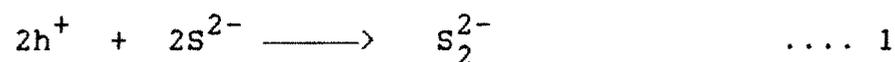
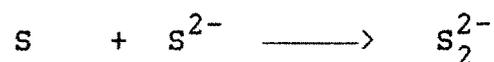
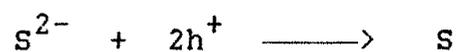
Two SC-SEP cells of different septum area were filled with electrolytes. The configuration of each cell was as follows.

Graphite Electrode	Polysulphide	n-CdSe film	Stainless steel	Artificial sea water	Pb
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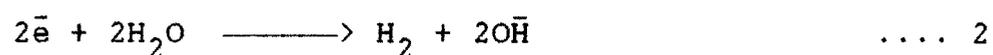
The intensity of light was 105 mW/cm^2 . The hydrogen production in a cell with polysulphide ($1\text{M Na}_2\text{S} + 1\text{M NaOH} + 1 \text{ MS}$) can be understood as follows. There are four solid|liquid junctions :

electrode | Electrolyte, Electrolyte|Metal, Semiconductor|electrolyte, and Electrolyte|Counter electrode

At the left electrolyte|semiconductor interface.



The photogenerated electrons at the stainless substrate reduce adsorbed H^+ ions from aqueous solution to hydrogen atoms, which upon combination are released from the surface as molecular hydrogen. In the case of artificial sea water.



In the first compartment at the Graphite electrode|Electrolyte junction.



Reactions 1 and 3 indicate that the redox species present in photoexposed compartment goes through chemical change i.e. conversion of S^{2-} to S_2^{2-} .

pH of the polysulphide in 1st compartment remains constant. Thus in the first compartment no net chemical change takes place.

The pH of artificial sea water in the second compartment was found to change from 7.2 to 9.5.

Variation in hydrogen production with time for two cells with different semiconductor septum area are as shown in Fig.4.11.

1) Cell With SC-SEP Area 30.5 cm^2

For this cell hydrogen production was observed after 52 minutes and it was continued upto 210 minutes. The variation of H_2 production with time is as shown in Fig.4.11. It is seen that initially rate of H_2 production was high and then decreases as time increases and attains saturation value. The quantity of hydrogen collected in time 210 min was 4.3 cc.

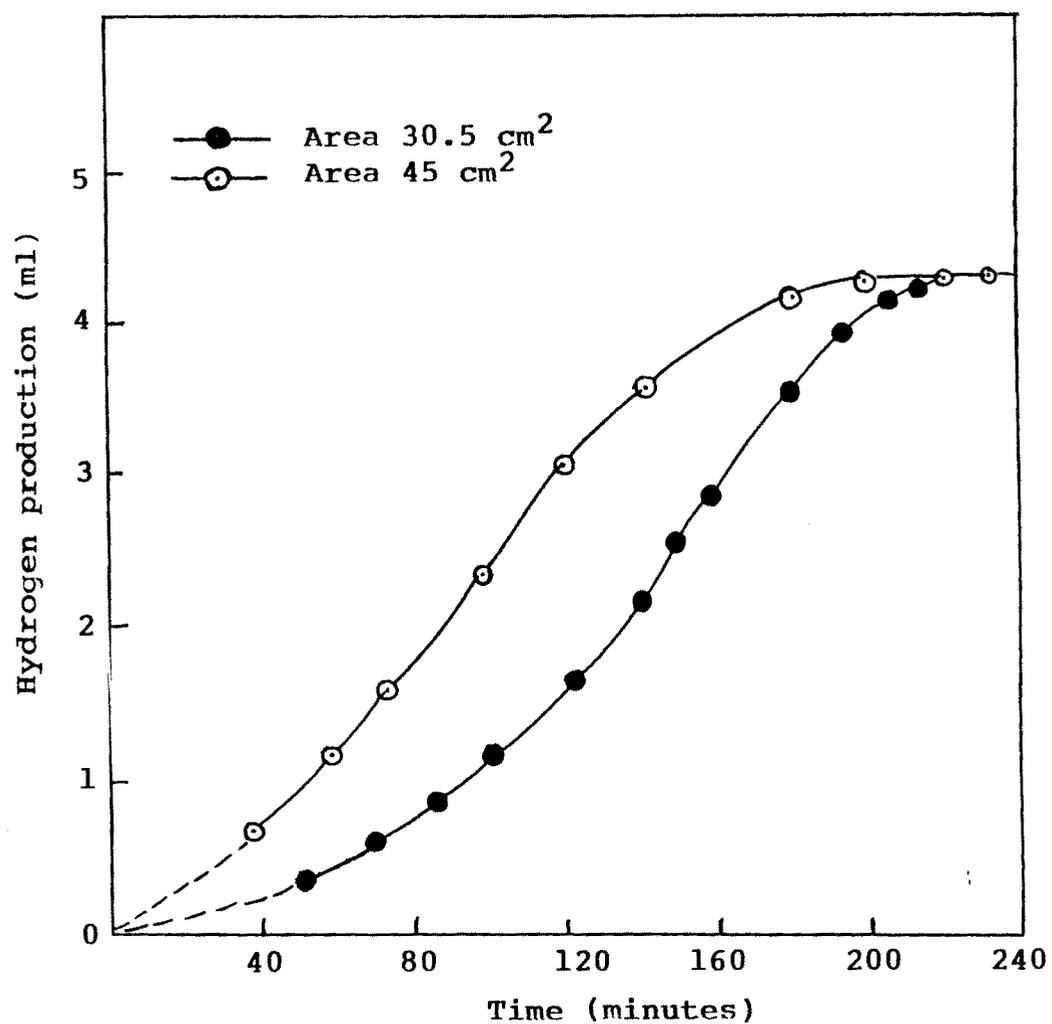


Fig.4.11. Hydrogen productin in two cells of different SC-SEP area of films for following configuration.

Graphite electrode	1M 3 S	n-CdSe	st. steel	Art. sea water	Pb
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2) Cell With SC-SEP Area 45 cm^2

In this cell hydrogen production was observed after 38 minutes and it was continued upto 200 minutes. The variation of H_2 production with time is as shown in Fig.4.11. The quantity of hydrogen collected in time 210 min was 4.3 cc.

From the fig it is observed that the rate of H_2 production depends upon semiconductor septum areas but quantities of hydrogen produced in two cells of different semiconductor septum areas were found to be same.

c) Variation of Short Circuit Current

Variation of short circuit current during H_2 production was studied and is as shown in Fig.4.12.

1) For cell with SC-SEP area $A = 30.5 \text{ cm}^2$

Initially short circuit current decreases suddenly and again increases to value 0.9 mA and after that decreases.

2) For cell with SC-SEP area $B = 45 \text{ cm}^2$

In this case current decreases from magnitude 1.42 mA during hydrogen production.

In both cases initially current slightly decreases and then tends to increase and after that decreases. The

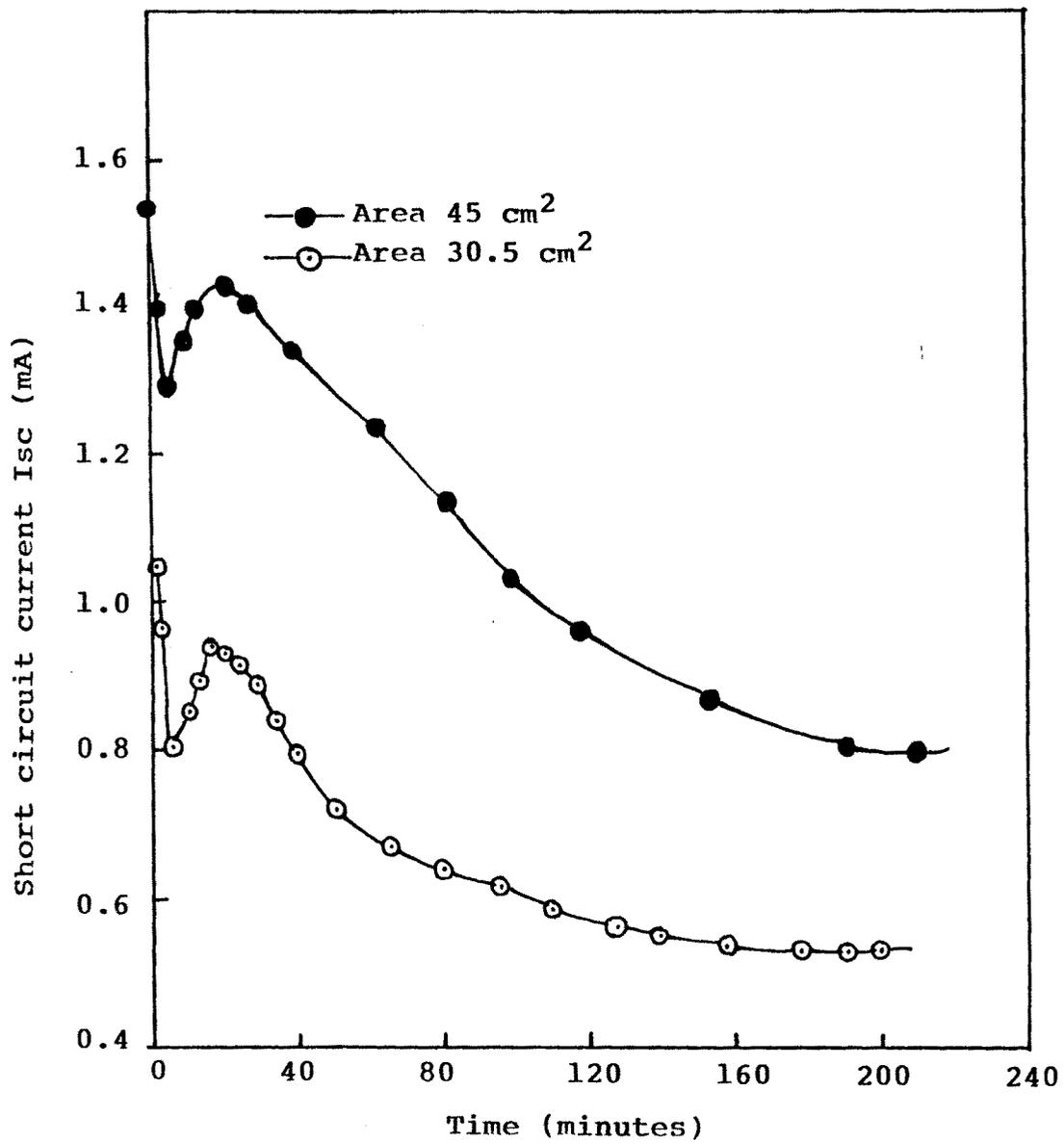


Fig.4.12. Variation of short circuit current with time for two different SC-SEP area of films.

decrease in current may be due to the fact that hydrogen bubbles resulted to stop flow of electrons.

4.4.4 EFFECT OF VOLUME OF ELECTROLYTE ON HYDROGEN PRODUCTION

The effect of volume of electrolyte on hydrogen production in two cells with same SC-SEP area was studied. Both SC-SEP cells were irradiated to light of intensity 115 mW/cm^2 . Volumes of electrolytes (Artificial sea water) in dark compartment of two cell were,

i) $V_1 = 210 \text{ cc}$ and ii) $V_2 = 285 \text{ cc}$

The variation of hydrogen production w.r. to time for two volumes of electrolytes is as shown in Fig.4.13.

a) SC-SEP cell with volume $V_1 = 210 \text{ cc}$

For this volume of electrolyte hydrogen production was observed from 42 minutes. From Fig.13. It is seen that initially rate of hydrogen production was high but decreases as time increases and attains a saturation stage after time 180 minutes. The quantity of hydrogen collected in time 180 minutes was found to be 4.1 cc.

b) SC-SEP cell with volume $V_2 = 285 \text{ cc}$

For this SC-SEP cell hydrogen production was observed from 32 minutes and attains a saturation stage after time 210 minutes. The quantity of hydrogen collected in time 210 minutes was 5.4 cc.

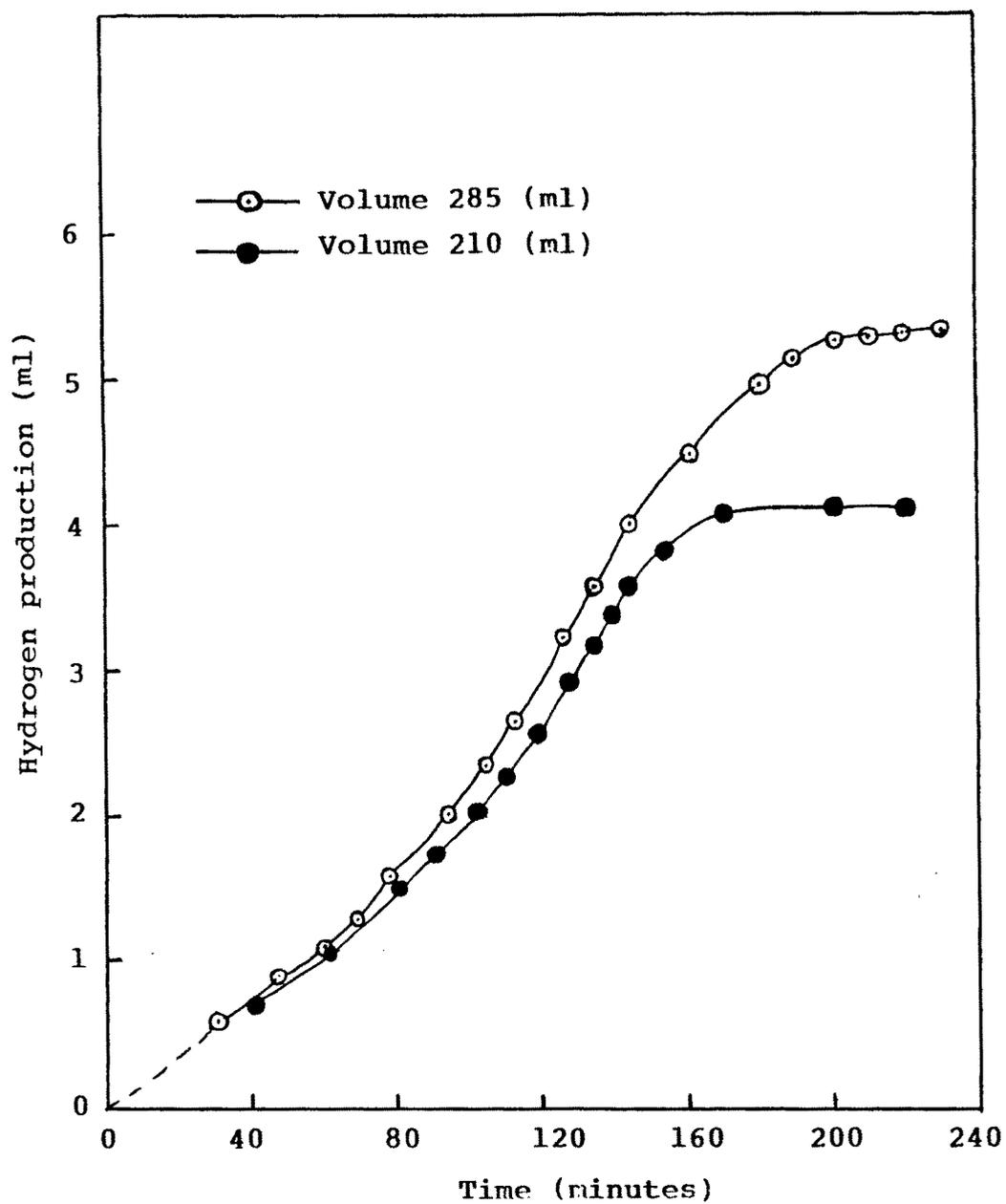


Fig.4.13. Hydrogen production with time for two different volumes of electrolyte.

From the Fig.4.13 it is observed that quantity of H_2 production depends on volume of electrolytes filled in SC-septum cells.

For large volume H_2 production was large. It may be due to the fact that more number of water molecules are available for decomposition in a SC-septum cell of large volume.

4.4.5 HYDROGEN PRODUCTION IN ELECTROLYTIC DYNAMIC CONDITIONS

a) Hydrogen Production

In static electrolytic condition hydrogen production was stopped after time 3 hrs. The pH of the solution in the IInd compartment (i.e. artificial sea water) was measured before and after hydrogen gas collection. The increase in the pH of solution was due to increase of OH^- ion concentration.

For continuous hydrogen production one can make arrangement of continuous flow of electrolytes as shown in Fig.4.3.

In order to study H_2 production for continuous flow, slight modification was made in fabrication of semiconductor septum solar cell. SC-septum cell was constructed in such a way that there were inlets and outlets for electrolytes in both the compartments. These

inlets and outlets were glass tubes fixed to cell by using m-seal and Araldite. Electrolytes were introduced into SC-SEP cell through inlets by using rubber tubes from electrolyte container and electrolyte flow was adjusted by using pinch cocks.

For continuous flow method variation of hydrogen production with time is as shown in Fig.4.14. The rate of hydrogen production was found to be very slow as compared with hydrogen production at static electrolytic condition. This may be due to the fact that some of the ions and part of hydrogen produced flows with electrolytes from outlets of SC-SEP cell. Thus continuous flow method is not suitable for hydrogen production.

For continuous production of hydrogen, it is necessary to stabilize pH of the solution in the IInd compartment of SC-septum cell. This was done by changing the electrolyte solution. The variation of hydrogen production with time for interrupted flow of electrolytes in both compartments is as shown in Fig.4.15. In first stage the H_2 production was observed from 42 minutes. Initially rate of hydrogen production was high and decreases with increase in time. After time about 180 minutes, it attains a saturation stage and hydrogen production was stopped due to excess of OH^- ions in IInd compartment. The quantity of hydrogen collected in time 180 minutes was 4.5cc.

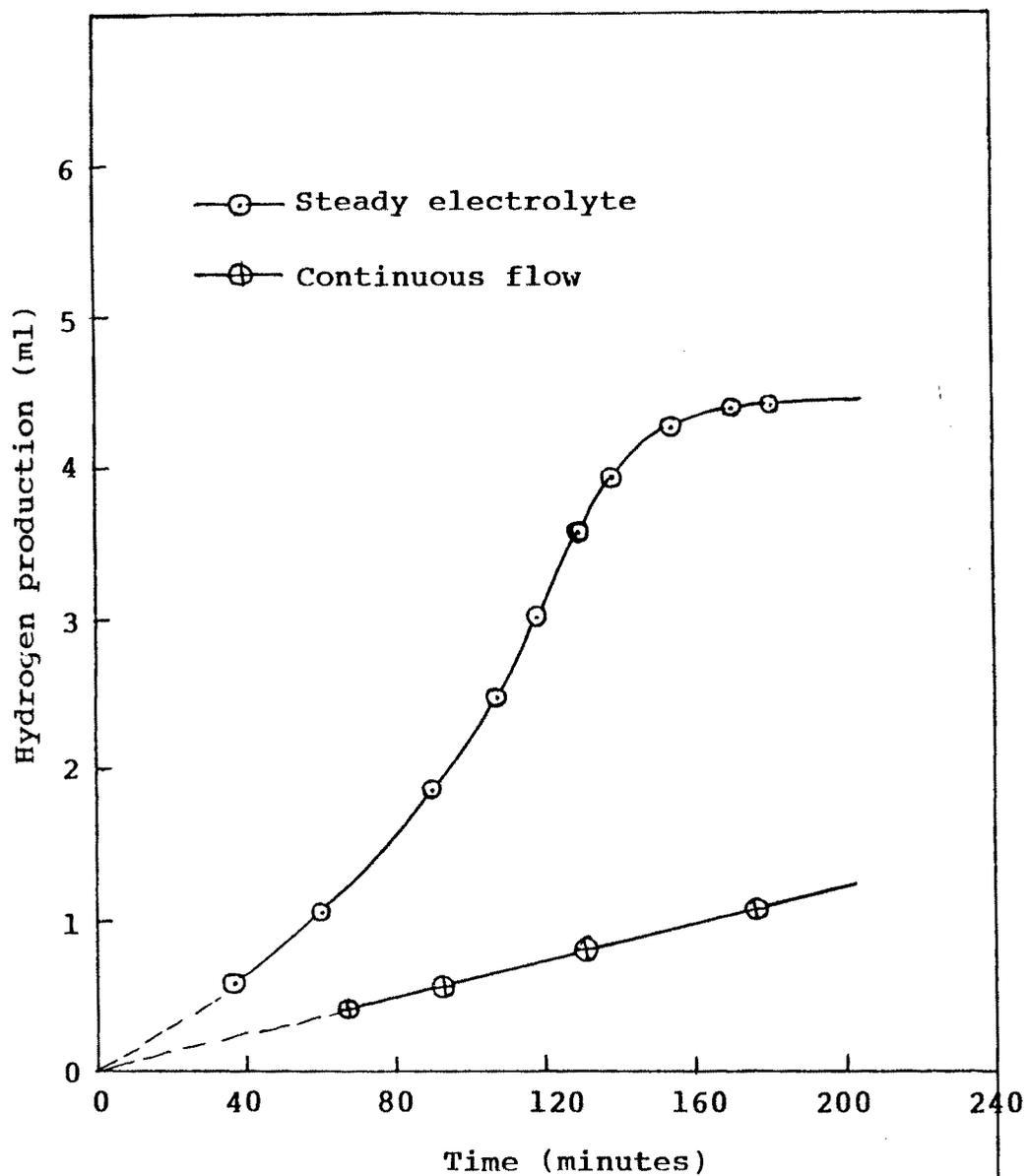


Fig.4.14. Hydrogen production for continuous flow of electrolyte with flowing configuration of SC-SEP cell.

Graphite electrode	IM. 3 S	n-CdSe	St. steel	Art. sea water	Pb
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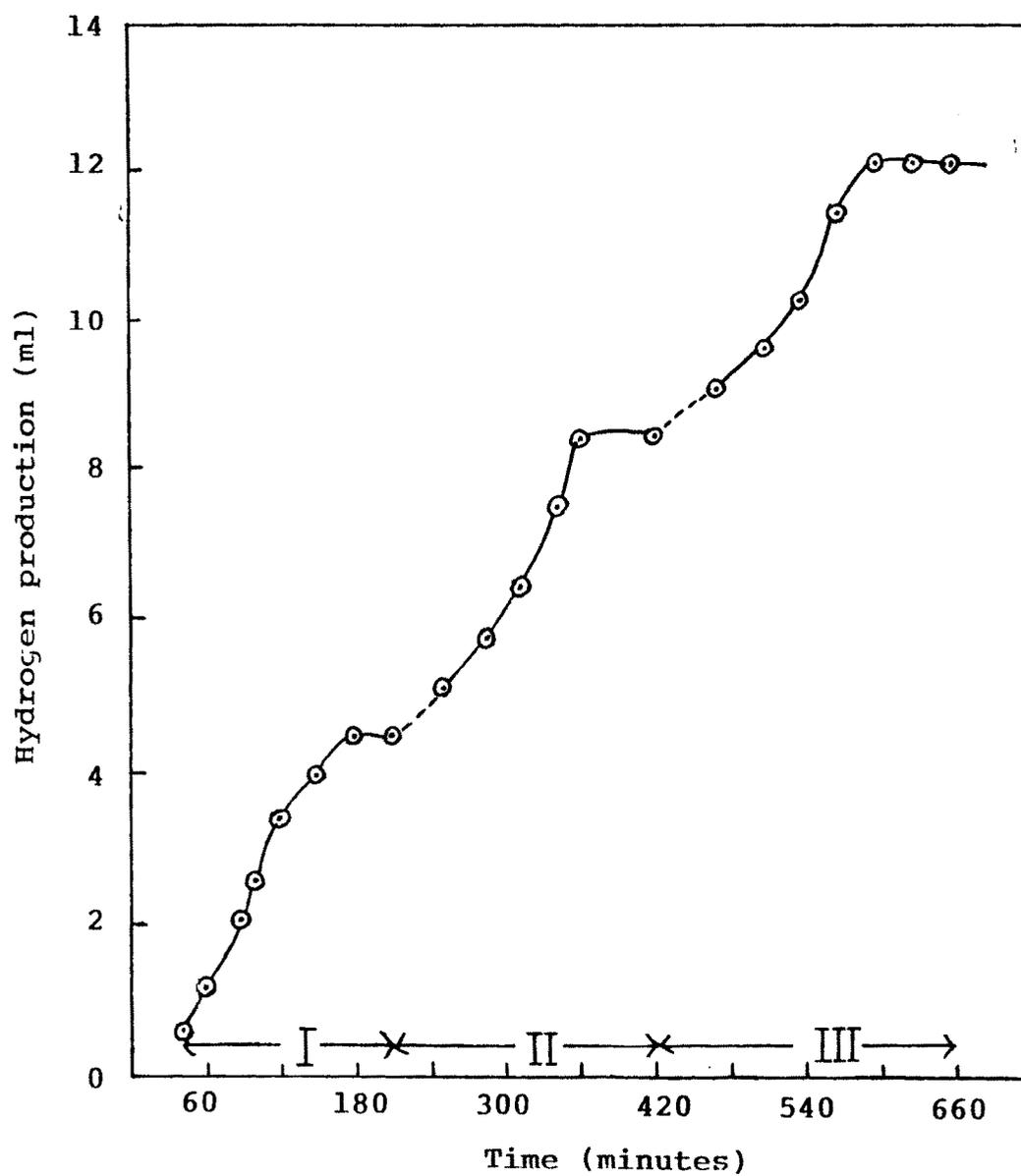


Fig.4.15. Hydrogen production at interrupted flow of electrolytes with following configuration of SC-SEP cell.

Graphite electrode	1M 3S	n-CdSe	St. steel	Art. sea water	Pb
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By adjusting screws of pinchcocks, electrolytes in both compartment were changed and again process of H_2 production was started. In IInd stage hydrogen production process was observed after 45 minutes. It attains saturation after time 180 minutes due to increase of OH ions. The quantity of hydrogen collected in time 180 was 4.1 cc.

Similarly in the third stage hydrogen production was observed after 48 minutes. The quantity of hydrogen collected in this stage was 3.9 cc. In this way making arrangement of interrupted flow the continuous hydrogen production was observed.

b) Current variation studies

In order to understand the process of H_2 production, the variation of current verses time was studied and is as shown in the Fig.4.16. It is observed that at the begining of every stage short circuit current suddenly decreases then slightly increases. Afterwards, short circuit current decreases with time during hydrogen production. This may be due to the fact that the hydrogen bubbles resulted to stopped flow of electrons.

4.4.6 CHARGING AND DISCHARGING CHARACTERISTICS

The semiconductor septum solar cell shows promise not only for hydrogen production but also for generating

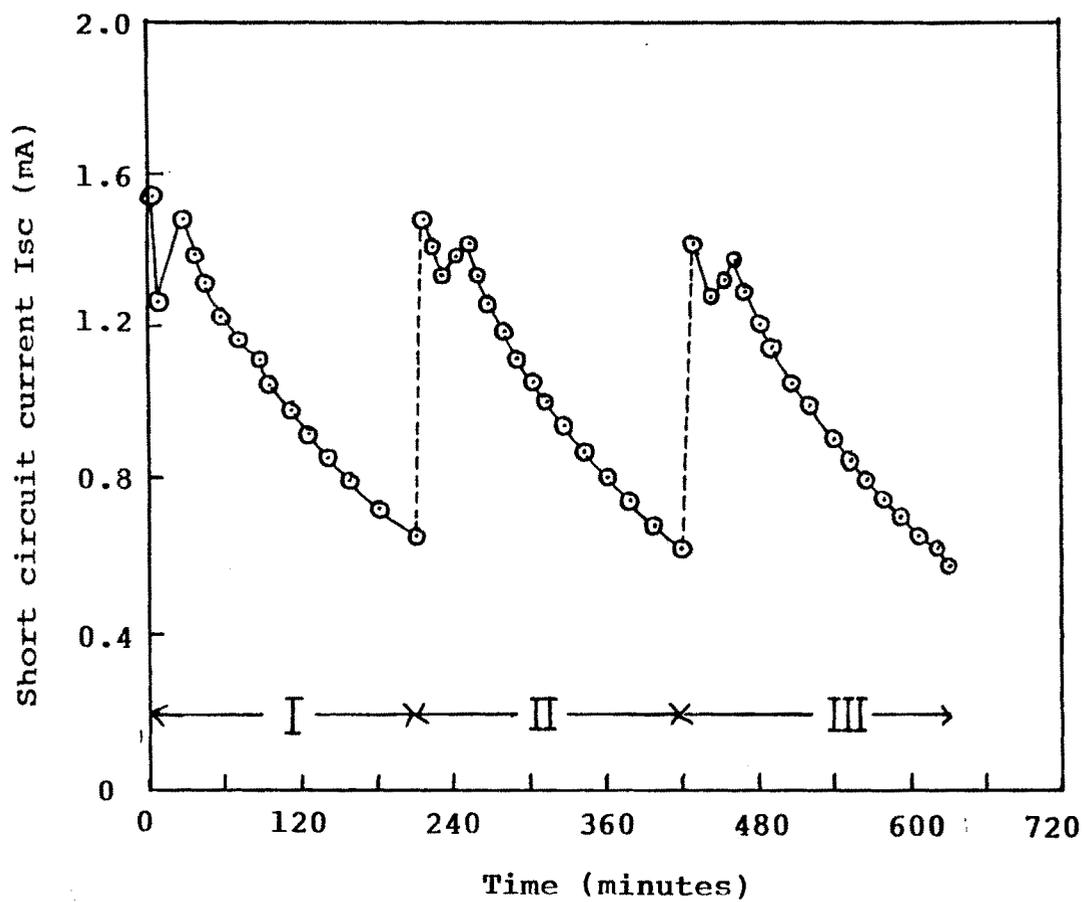
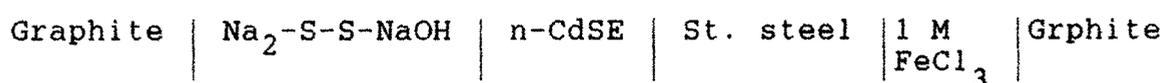


Fig.4.16. Variation of short circuit current with time for interrupted flow of electrolytes.

electricity. In present investigation attempt has also been made to study charging and discharging characteristics of semiconductor septum solar cell.

a) Charging characteristics

The construction of SC-SEP cell for this study is discussed in chapter III. The compartment facing to lamp was filled with polysulphide solution in contact with n-CdSe film. Other dark compartment was filled with a redox couple like 1 M FeCl_3 (500 ml). The septum exposure area of SC-SEP cell was 80 cm^2 . The counter electrode in both compartments were graphite plates. The configuration of cell was,



The magnitude of open circuit voltage depends on following factor.

- 1) Difference in fermi level.
- 2) Adaptability of electrode|electrolyte interface.
- 3) Total number of charges stored in compartments.

1) Difference in fermi level

The cell voltage depends on electrolytes present in two compartments. Electrolytes in two compartments are such that their chemical potentials Fredox_1 and Fredox_2 do not coincide.

2) Adaptability of electrode|electrolyte interface.

The nature of electrode|electrolyte interface is dependent on particles present on the surface of the electrode and forces between the particles and the ions in an electrolyte. As per nature of the forces solid electrolyte interfaces can be classified into the three types [36-37], i) electronically and chemically inert interfaces, ii) chemically inert but electronically active interfaces and iii) corrosive interfaces.

3) Total number of charges stored in compartments.

The short circuit current of the cell depends upon total number of charges stored in compartments.

In order to study the mechanism of charging we have studied variation of cell voltage with time during excitation of cell. The variation of open circuit voltage with time is as shown in Fig.4.17. It is observed that open circuit voltage increases exponentially with time and attains a saturation value. Open circuit voltage before and after charging SC-SEP cell for 1 Hr. was as in table 4.3

b) Discharging characteristics of SC-SEP cell

When the circuit is made through an external load, the reaction proceeds in opposite direction and cell gives up the stored energy as electrical energy.

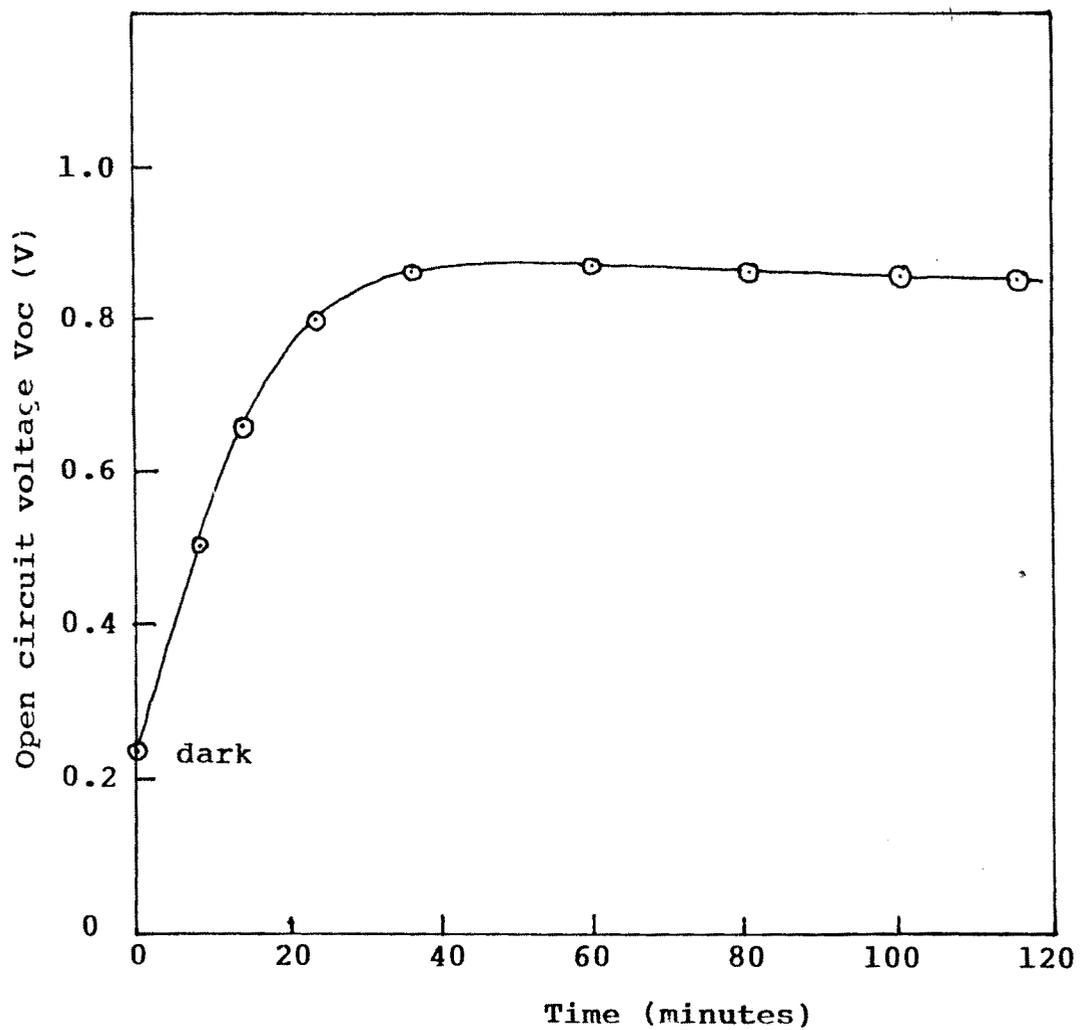


Fig.4.17. Charging curve for SC-SEP cell with following system.

Graphite electrode	1M 3 S	n-CdSe	St. steel	1M FeCl ₃	Graphite electrode
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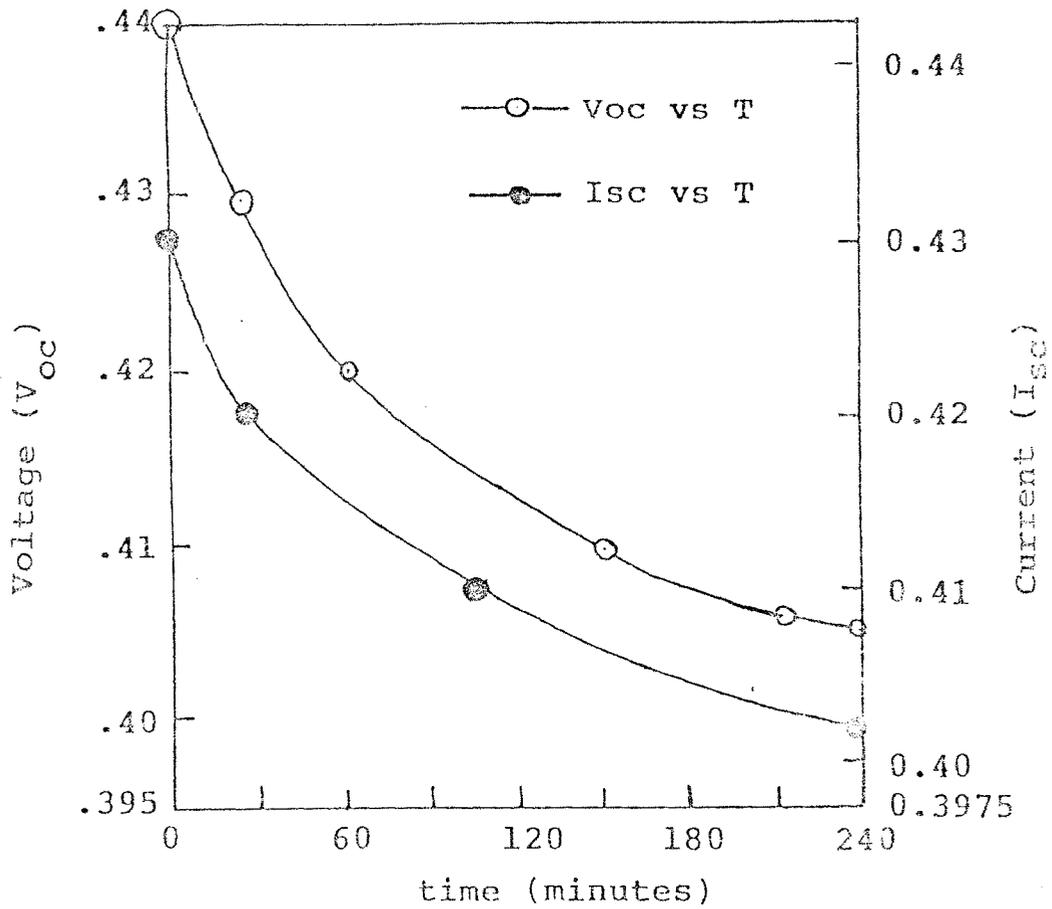


Fig. 4.18(a) Variation of discharging current and voltage with time for SC-SEP cell.

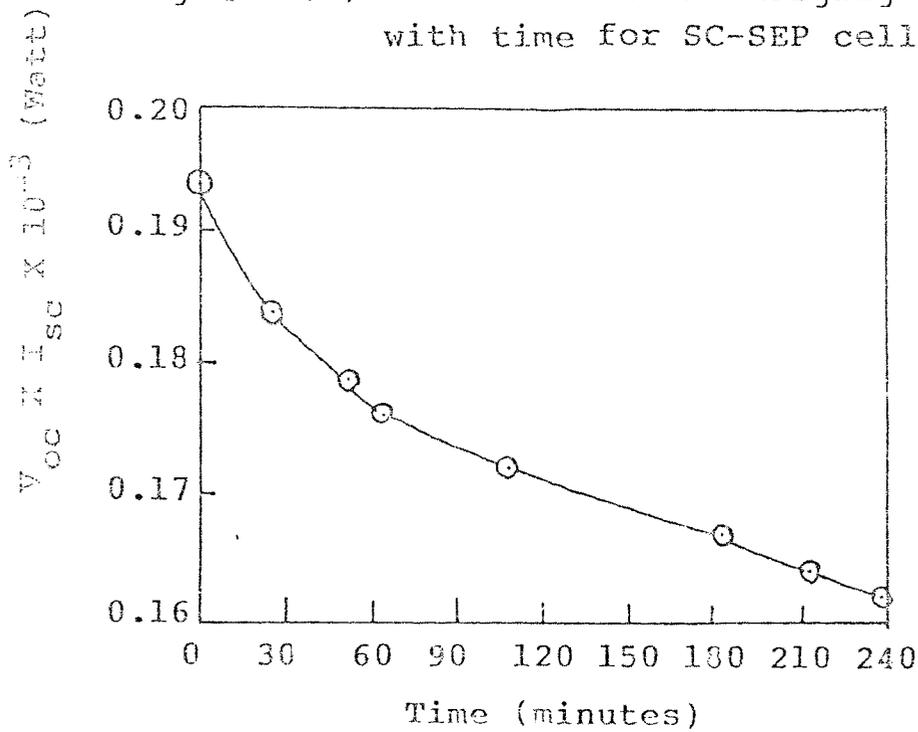


Fig. 4.18(b) Output power with time at 1K-Ohm load.

Discharging mode of SC-SEP cell across load resistance $1\text{ K}\Omega$ is as shown in Fig.4.18(a). In dark condition, the voltage and short circuit currents were measured with time. It was found that initially current and voltage falls rapidly then decreases slowly with time.

The continuous power could be generated through an external load for 3 Hrs. The variation of output power with time of system using load $1\text{ K}\Omega$ across the two electrodes is as shown in Fig.4.18(b).

4.5 CONCLUSIONS

In a semiconductor septum electrochemical photovoltaic cell (SC-SEP) hydrogen production is possible, under short circuit condition by photolysis of sea water using solar energy.

When only first compartment was filled with polysulphide, then photocurrent was found to increase with intensity. The photocurrent also found to depend on area of n-CdSe film.

At static electrolytic condition 4.5 cc hydrogen production was observed in time about 3 hours for following SC-SEP cell arrangement.

Graphite	0.2M K Fe(CN)	n-CdSe	Stainless	Artificial	Pb
Electrode	0.01M $\overset{4}{K}$ Fe(CN) $\overset{6}{}$	film	steel	sea water	
	0.1 M $\overset{3}{KOH}$	$\overset{6}{}$			

when SC-SEP cell was operated under open circuit condition no hydrogen production was observed.

The rate of hydrogen production was found to increase by increasing intensity of illumination. Hydrogen production was also studied for different SC-SEP area of films in two cells. The rate of hydrogen production increases with increasing semiconductor septum area of film. It was also observed that maximum quantity of hydrogen production depends on volume of electrolytes in two compartments of SC-SEP cell.

The pH of the solution in second compartment containing sea water was measured before and after hydrogen gas collection and found to change from 7.1 to 9.4. This change in pH was because of increase of OH^- ions, hydrogen production was studied at electrolytic dynamic condition for following system.

Graphite	1M 3S	n-CdSe film	Stainless steel	Artificial sea water	Pb
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The continuous flow of electrolyte method is not suitable for continuous hydrogen production because of some of the ions and part of H_2 gas produced flows through electrolytes from outlets of SC-SEP cell. The continuous H_2 production was observed by making arrangement of interrupted flow of electrolyte.

The SC-SEP cell can also store electric energy, above some threshold, the highest value of which depends upon difference between the redox potential of system. When 1 M FeCl_3 was filled in second compartment of the cell, the open circuit voltage after charging cell for 1 Hr at intensity 100 mW/cm^2 was 0.87 volt. The discharging of same cell across $1 \text{ K}\Omega$ was also studied. The continuous power could be generated through external load for time more than 3 hours.

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