CHAPTER - IV

HYDROGEN PRODUCTION WITH LINE SEMICONDUCTOR SEPTUM CELL

4.1 INTRODUCTION

Another interesting feature of the PEC cell is their capability, at least in principle of chemical conversion of light energy. PEC cells contains reactions of the redox species in the solution to produce compounds, or ions, of chemical interest or materials having energy higher than the original ones. In the regenerative PEC cells, the photogenerated holes or electrons either oxidize or reduce redox species in the solution, and the chemical change is reversed at the counter electrode, keeping the chemical composition of the solution constant. When we short circuit the two electrodes, and separate the reaction products at both the anode and the cathode by use of a membrane, then the products formed at both electrodes may have higher energy than before in certain cases.

A typical example is the decomposition of water in a PEC cells. The photoelectrolysis reaction of water can be written as:

$$H_2O + \text{light} \longrightarrow H_2 \uparrow + \tfrac{1}{2}O_2 \uparrow \quad \text{(involving a free energy = 1.23 eV)}$$

$$2H_2O + \text{light} \xrightarrow{\text{or}} 2H_2 \uparrow + O_2 \uparrow \quad \text{(involving a free energy = 2.46 eV)}$$

The energy of 2.46 eV approximately corresponds to a wavelength of 500 nm, a wavelength available in solar radiation. Unfortunately, water does not have a strong absorption efficient in this region. So, the chemical entities H_2 and O_2 are not formed. There exists a threshold energy of about 6.5 eV ($\lambda \approx 190$ 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 photon has been to carry out the photodecomposition sequentially. The agents employed for the purpose are known as photocatalysts.

The principle of charge transfer reaction and photo-processes resulting in a photoelectrolysis cell is similar to that of a electrochemical photovoltaic cell, the only difference is that now we have two active redox systems H_2O/H_2 and H_2O/O_2.

The convertion of sunlight into electricity and chemical fuel in PEC cells equipped with semiconductor electrodes are of great current interest [1-4]. The SC-SEP solar cell shows promise not only for generating electricity but also for producing chemicals. Tien reported the production of hydrogen in an inexpensive way using seawater and a cheap polycrystalline semiconductor material[5].

In this chapter, new type of cell structure suitable for high intensity by using line concentrator for the production of H_2 has been designed and constructed. The idea for construction of septum cell was taken from the work of Pawar et. al. [6, 7]. Electrodeposition for cylindrical geometry, electrolytic static and dynamic conditions and variation of current has been reported. Interrupted flow method was adopted for H_2 production.

4.2 ENERGY STORAGE IN THE FORM OF HYDROGEN (H_2):

Storage of solar energy offers a challenge even today, particularly when the desired end product is electricity. Solar energy can be stored in the form of transportable form a fuel, such as H_2 by photoelectrolysis. The H_2 can later be burnt in fuel cells etc. to generate electrical power.

The renewability, high quality and non-polluting character of hydrogen fuel combined with the abundance of seawater make photoelectrolysis cells very attractive [8, 9]. Recently great advances have been made in the methods of storing hydrogen in metals/alloys as hydrides [10, 11]. This has made hydrogen 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 [12].

An interesting suggestion is first to obtain

solar electricity through a more efficient electrochemical photovoltaic cell which can subsequently be used for electrolysis of water [13]. This would produce H_2 at higher pressure than obtained in the direct photoelectrolysis cells.

Murphy has proposed model systems for photoelectrolysis [14]. His two-compartment water photoelectrolysis cell given in figure 4.1 is similar to that suggested by Nozik [15] in which both n- and p-electrodes are used. Murphy suggest that if stable photocathodes and photoanodes with wide spectral response can be found, the electrolysis can be carried out in the two-compartment cell of figure 4.1 where a cation-selective membrane keeps the hydrogen and oxygen gases separated. An anion-selective membrane could be used if one or both the electrode reactions involve OH^- rather than H^+ ion. This arrangement has a low efficiency.

In 1970, Fujishima and Honda [16] reported that water could be decomposed in a cell having titanium oxide and platinum electrodes (under small bias). This finding caused much interest among chemists because of the expectation that it would open up a new way of converting solar energy into stable chemical energy.

Photoassisted decomposition of water in PEC cells

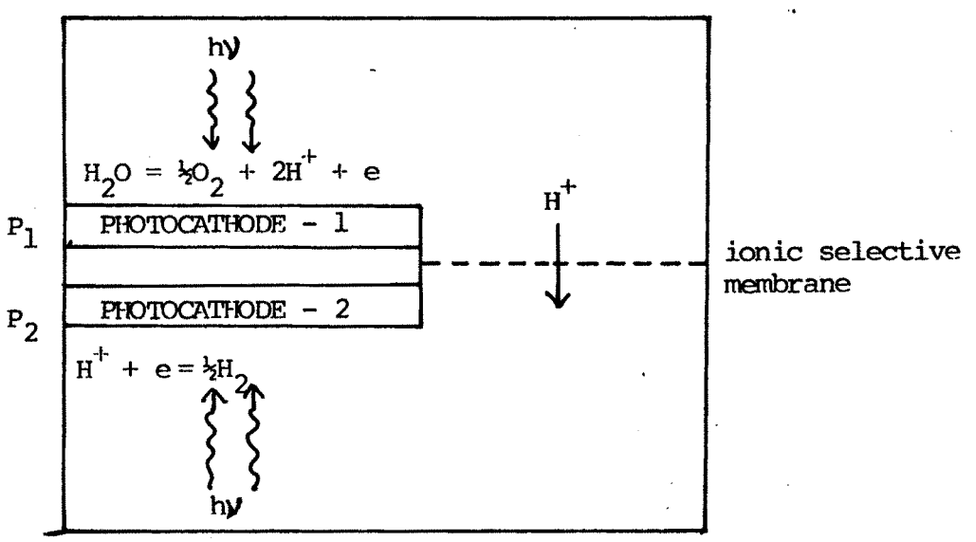


Fig.4.1. Schematic representation of two-compartment photoelectrolysis cell (After Murphy, 1978).

is now a well known phenomenon to all electrochemists. It requires wide band gap semiconductors e.g. TiO_2, $SrTiO_3$, etc. The chemical reactions, when TiO_2 is used for the production of hydrogen are as follows:

At anode : $TiO_2 + 2h\nu \longrightarrow 2e^- + 2h^+$

$2h^+ + H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+$

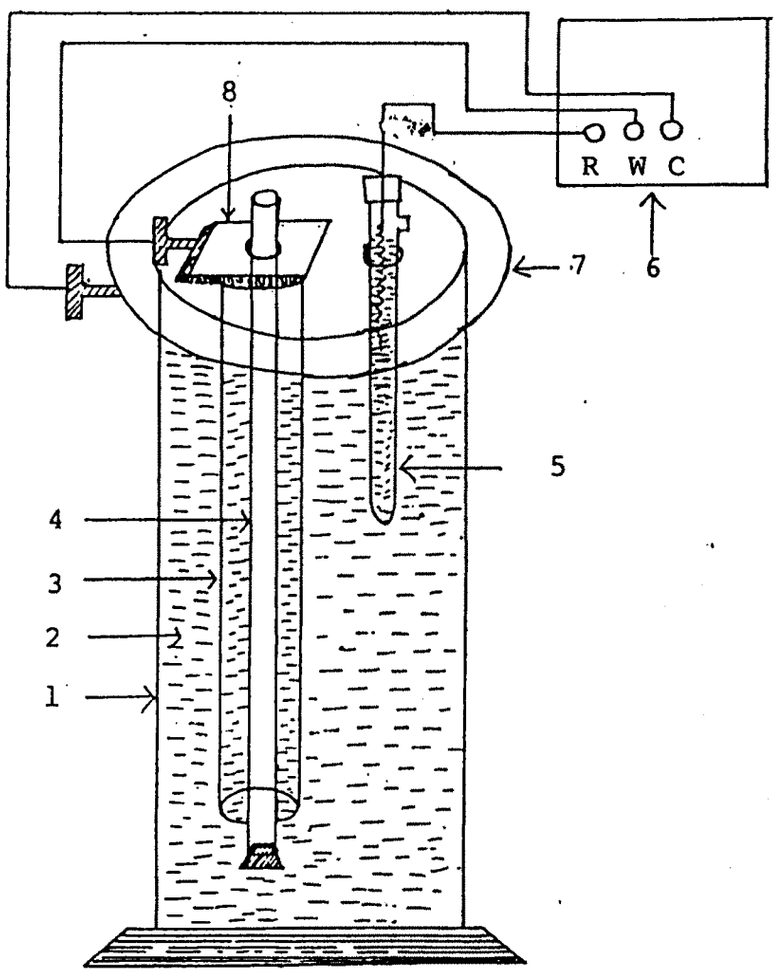
At Cathode : $2e^- + 2H^+ \longrightarrow H_2$

Overall : $H_2O + 2h\nu \longrightarrow \frac{1}{2}O_2 \uparrow + H_2 \uparrow$

4.3 EXPERIMENTAL

4.3.1 Electrodeposition of CdSe Thin Films for Cylindrical Geometry:

Figure 4.2 shows the experimental arrangement for electrodeposition of CdSe thin films from aqueous solution on steel pipe substrates. The deposition bath was prepared with 10 mM $CdSO_4$ and 10 mM SeO_2. The electrochemical cell was of a conventional three electrode configuration with saturated Calomel electrode (SCE) as reference and steel pipe of 10 cm in length and 2.5 cm in diameter serving as counter electrode. Another steel pipe of 12 cm in length and 1 cm in diameter was inserted inside the counter electrode. A rubber seal was used at the lower end of working electrode to avoid deposition inside the pipe. The EG and G potentiostat was used for electrodeposition. The time for



1. Cylinder
2. 10mM $CdSO_4$ + 10mM SeO_2 Solution
3. Steel pipe as counter electrode
4. Steel pipe as working electrode
5. Saturated Calomal electrode as referance electrode
6. EG and G Potentiostat

7.&8. Backelite holders

Fig.4.2. Experimental arrangement for electrodepositon on steel pipe substrates.

electrodeposition was 1 hour. The cylindrical film was deposited and annealed at 270°C temperature in air for 30 min.

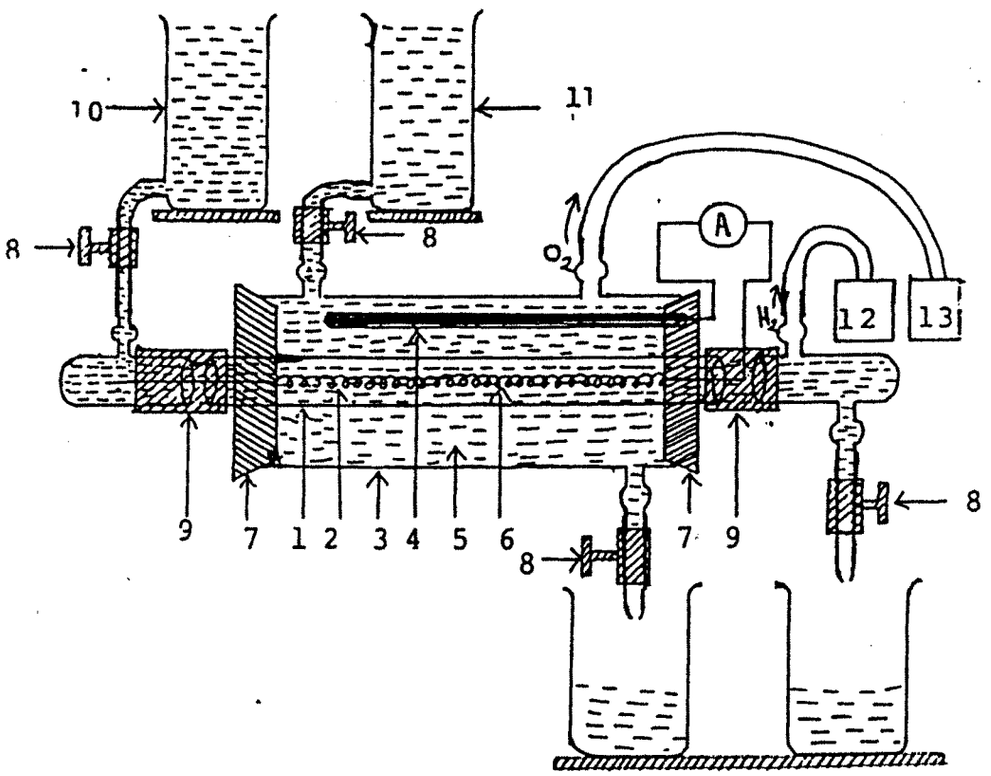
4.3.2 Geometry of Line Semiconductor Septum Solar Cell :

Figure 4.3 shows the geometry of H_2 production line semiconductor septum solar cell. It consists of a glass tube of 10 cm in length and 3 cm in diameter with three side tubes, one for O_2 outlet, second and third for redox solution in and out. The cylindrical semiconducting film formed on steel pipe is centrosymmetrically fitted into the glass tube with rubber sealing without disturbing the deposited film. Graphite rod electrode was fitted in glass tube through rubber seal. Then the T shaped glass tubes are connected to the deposited steel pipe through rubber tube. Lead (Pb) electrode in the spiral form was used in steel pipe.

The space between glass tube and deposited side of steel pipe is the I^{st} compartment filled with 0.2M $K_4Fe(CN)_6$ + 0.01M $K_3Fe(CN)_6$ + 0.1 M KOH solution. Space inside the steel pipe is the II^{nd} compartment filled with artificial seawater.

4.4 RESULTS AND DISCUSSION

The cylindrical semiconductor septum cell was tested in laboratory by irradiation with light from halogen



1. Deposited Steel Pipe
2. Lead (pb) electrode
3. Glass tube
4. Graphite electrode
5. 0.2M $K_4Fe(CN)_6$ + 0.01M $K_3Fe(CN)_6$ + 0.1M KOH
6. Artificial Sea water
7. Rubber seal
8. screw pinch cocks
9. Rubber tubes connectors
10. Artificial Sea water container
11. Polysulphide solution container
12. H_2 gas collector (measured Volumetrically by using a graduated test tube)
13. O_2 gas collector

Fig.4.3. Geometry of Line Semiconductor Septum Solar cell.

tube of 1000W under different conditions for hydrogen production. Photograph of experimental arrangement is shown in figure 4.4. The generation of H_2 gas is found to depend on various factors as discussed in following sections.

4.4.1 Electrolytic Static Condition:

When the cell is irradiated with light of high intensity, H_2 gas released from II^{nd} compartment and O_2 gas released from I^{st} compartment. This is understood as follows.

When the cell is irradiated, electron-hole pairs are generated at semiconductor-liquid junction. Holes enters into I^{st} compartment and following reaction takes place.

$$Fe(CN)_6^{4-} + h \longrightarrow Fe(CN)_6^{3-}$$

At the same time Pb electrode in II^{nd} compartment gives electron, comes into I^{st} compartment through the external short circuit and following reaction takes place,

$$Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-}$$

As such the pH of its concentration remains constant as observed experimentally and thus in the I^{st} compartment no net chemical change takes place in the bathing solution. However, in the II^{nd} compartment, the electrode was lead (Pb) and following reaction takes place,

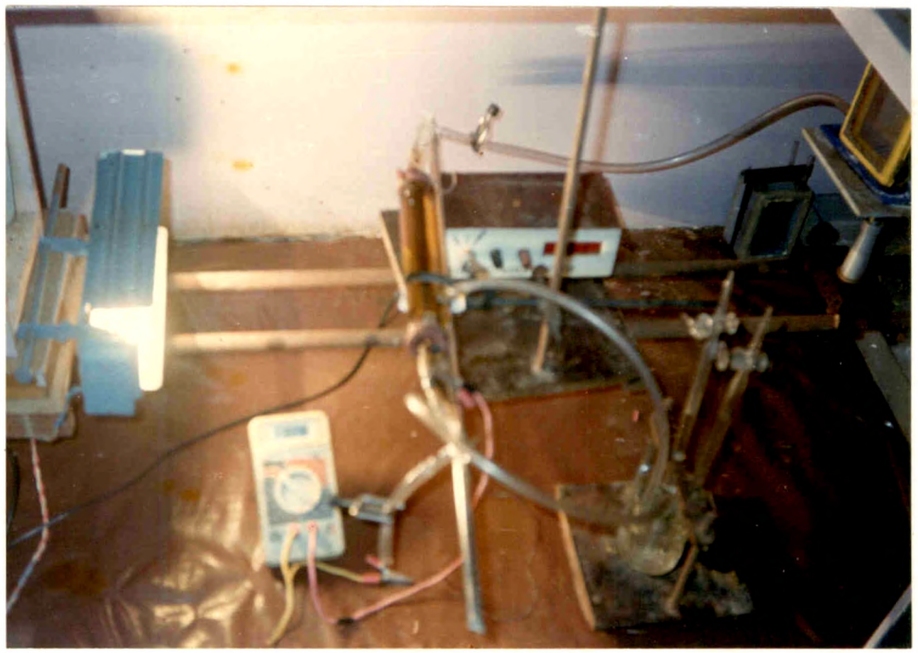


Fig.4.4. Photograph of experimental arrangement of line semiconductor septum cell for H_2 production.

$$2H_2O + 2e \longrightarrow H_2 \uparrow + 2OH^-$$

H_2O is decomposed to hydrogen (H_2) and OH^- ions. These OH^- ions formed on lead (Pb). Thus Pb^{2+} from Pb electrode produced may exist either as PbO or as $Pb(OH)_2$ in equilibrium with their dissociated ions. pH was changed from 7.1 to 9.4. This is in agreement with the suggested mechanism.

The variation of H_2 production with time is shown in figure 4.5. It is seen that initially rate of production of H_2 was high, but decrease as time increases and attains a saturation after some time. This is because of the increase in OH^- ions concentration. This resulted in stopped of H_2 production.

4.4.2 Effect of Light Intensity on H_2 Production

The variation of H_2 production with time at different intensities is shown in figure 4.5. When distance between source of light and cell was 10 cm, production of H_2 starts from 10 minute and volume of H_2 in 23 minute was 4.4 ml. When distance between source of light and cell was 17 cm, production of H_2 starts from 14 minute and volume of H_2 in 78 minute was 3.8 ml. This indicates that the rate of H_2 production is proportional to the intensity of light.

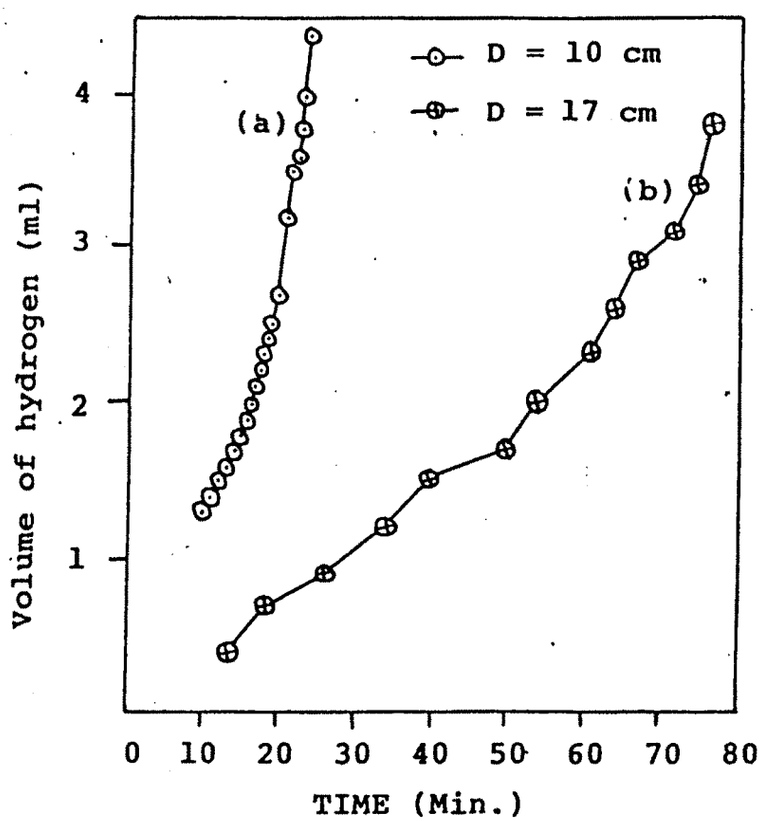


Fig.4.5. The variation of H_2 production with time.
Curve (a) is at D = 10 cm and
Curve (b) is at D = 17 cm
where D = distance between source of light and cell.

4.4.3 Electrolytic Dynamic Condition:

In electrolytic static condition, the production of H_2 was stopped when OH^- ions become excess. For continuous production of H_2, one can made arrangement of continuous flow of the electrolytes. For continuous flow method, the variation of H_2 production with time is shown in figure 4.6, curve (a). The rate of production of H_2 was very slow. This may be due to the fact that, some of the ions and part of H_2 produced flows with electrolyte. Thus continuous flow method is not suitable.

For continuous production of H_2 it is necessary to stabilize the pH of the solution in II^{nd} compartment. This is done by changing the electrolyte solution. The variation of H_2 production with time for interrupted flow of electrolytes in both the compartments is shown in figure 4.6, curve (b).

In the first stage, it was observed that, the production of H_2 was upto 75 minute. After that the production of H_2 was stopped due to excess OH^- ions in the II^{nd} compartment. So changing both the electrolytes by the screw pinch cocks as shown in figure 4.3 and again start the process. Then it was observed that the production of H_2 was started after 15 minute and continue upto 50 minute. Similarly in the 3^{rd} stage the production of H_2 was upto 60 minute.

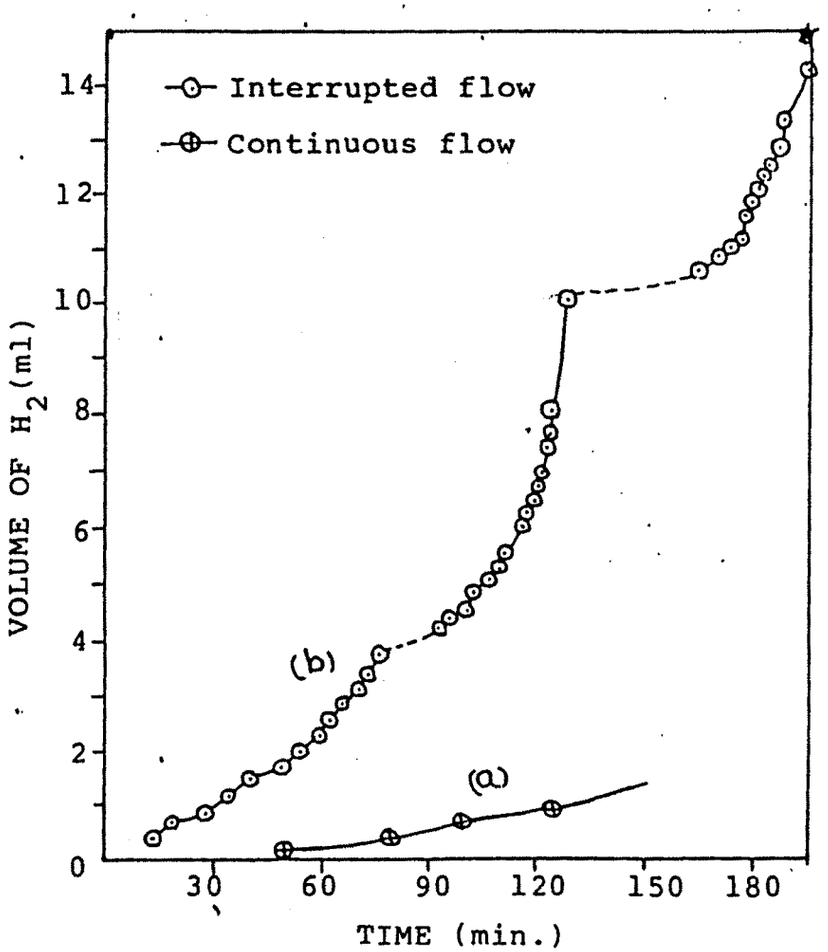


Fig.4.6. Variation of H_2 production with time for interrupted flow of electrolyte (curve b) and curve (a) for continuous flow.

In this way making the arrangement of interrupted flow, the continuous production of H_2 was observed.''

4.4.4 Current Variation Studies:

In order to understand the process of H_2 production, the variation of current versus time was studied and shown in figure 4.7. It was observed that during the production of H_2 current was decreased. This may be due to the fact that when H_2 bubbles are produced which stopped the flow of electrons.

4.5 CONCLUSION

In the present investigation, the new type of line semiconductor septum solar cell has been designed and used for the production of H_2. The production of H_2 mostly depends on intensity of light. The pH of electrolyte was found to change with H_2 production under electrolytic static conditions. However, continuous production of H_2 was observed under electrolytic dynamic conditions.

One can use line semiconductor septum solar cell for H_2 production by using line concentrator for high intensity as shown in Figure 4.8 (Photograph)

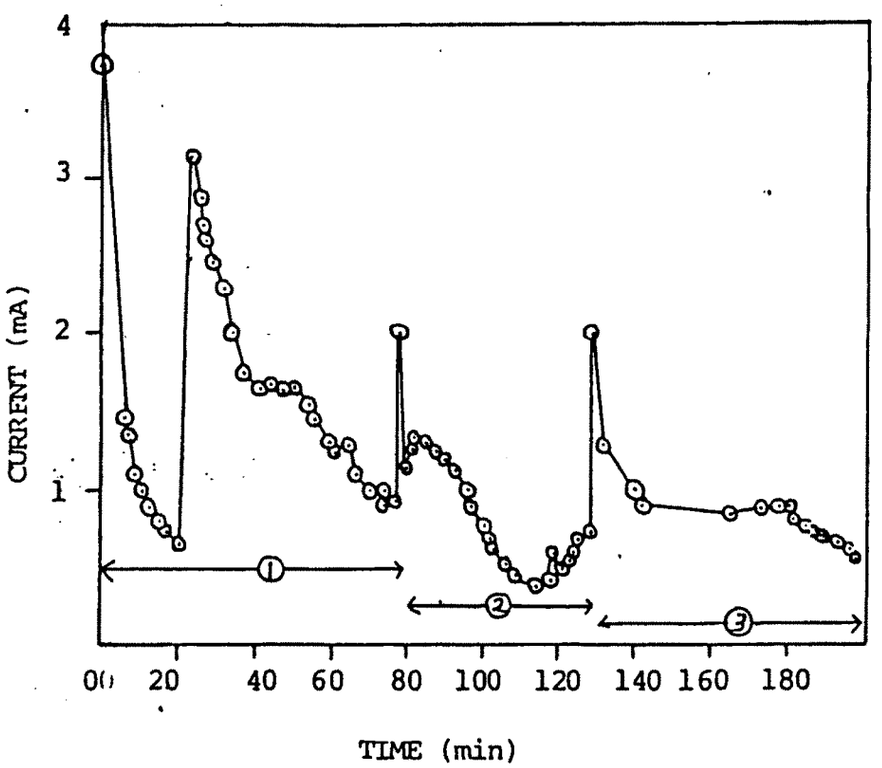


Fig.4.7. Variation of current with time.

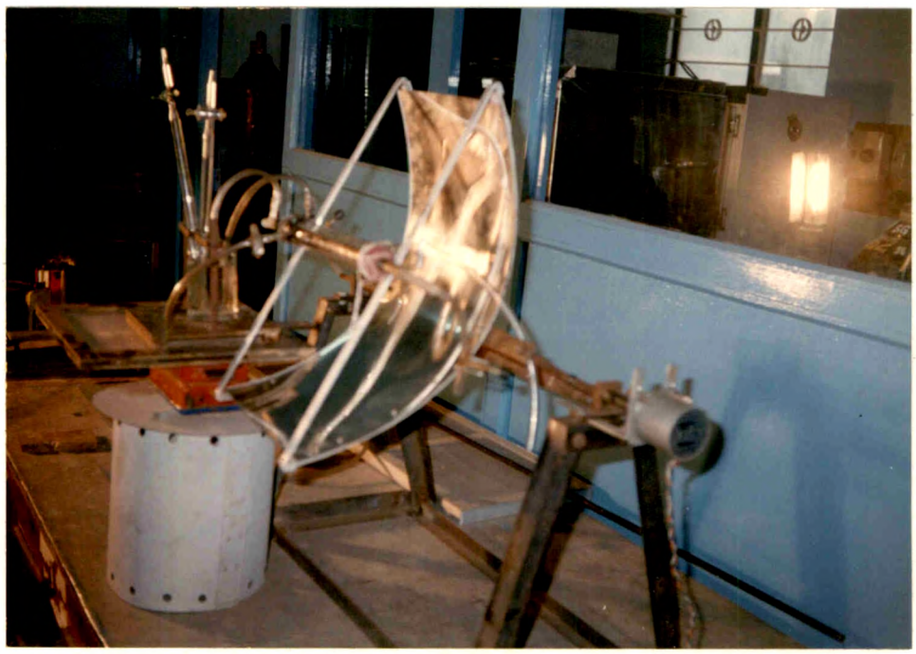


Fig.4.8. Photograph of experimental set-up of line semiconductor septum cell for H_2 production by using line concentrator.

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