CHAPTER – VIII

Sb_2S_3 based Semiconductor Septum Storage cells

8.1 INTRODUCTION

Photoelectrochemical (PEC) devices are attracting much interest in solar energy research [1]. The PEC devices are very similar to the Schottky type solid state junction solar cells and have many advantages [2,3]. PEC devices are classified into five groups : 1) photoelectrolytic cells, 2) electrochemical photovoltaic cells 3) rechargeable photoelectrochemical cells 4) photogalvanic cells and 5) photoelectrocatalysis cells.

In recent years, much efforts have been directed towards developing new and better energy conversion/ storage devices. However one of the challenging problems in solar energy research is solar energy storage. An alternative strategy has been suggested in which a PEC cell has been used which offers possibility of both solar energy conversion and storage. A number of review articles on PEC storage have been appeared in the literature [4–6]. The solar energy storage cells can be classified as follows 1) Redox storage electrode 2) Redox storage electrolyte and 3) Semiconductor septum storage cell. PEC cells have been used in rechargeable electrochemical storage, septum cells and redox couple storage devices. In the rechargeable electrochemical storage cells, the storage electrode capable of undergoing reversible chemical change is used. PEC cells using a third electrode as a storage electrode have been reported in the literature [7–9]. The solar energy storage with the help of semiconductor septum (SC– SEP) cells is most promising due to its inherent properties. The concept of using semiconductor septum in an energy storage device is based on modeling of natural photosynthetic system with pigmented bilayer lipid membrane [10–11]. In this cell, under illumination, on one side of the membrane – solution interface, reduction occurs while on the other side oxidation takes place. Thus the basic concept in all the systems is light – induced charge separation in the form of electrons and holes which causes reduction on one side and oxidation on the other side. Two different redox couples having standard potentials sufficiency wide apart from each other should be used in order to achieve large photovoltages. Under illumination, these chemical species can be charged and then electrochemical discharged for the production of electricity.

Tien et al. [12] have reported on the septum cell for photoelectrolysis of sea water. This cell consists of CdSe deposited over Ni foil and a Pb counter electrode. The CdSe side contains Ferro/ Ferri cyanide and the Ni side of the electrode contains seawater. Jackowaska and Tien [13] have developed a septum cell in which the PEC cell consists of two chambers with the configuration CdS | Polysulphide | Pt || $CuNO_3$ | Cu. CdSe (pellets) semiconductor septum PEC cells with configuration M_1 | 1 M Na_2S, 1 M NaOH || CdSe || 0.5 M $AgNO_3$ | M_2, where M_1 = SCE, Cu_2S and Pt and M_2 = Pt, Pb and Ag, have been constructed by Xiao and Tien [14] and their PEC characteristics studied using cyclic voltametry. Murali et al. [15] have reported on an electrodeposited CdSe septum of 25 cm^2 area. Chemically deposited CdSe films have been used as a septum by Dumure and Lokhande [9]. Variety of semiconductors viz. CdS, CdSe, CdTe, Fe_2O_3 etc. are used as a semiconductor septum with different electrolyte combinations. These materials are prepared by using various techniques such as electrodeposition [16], chemical bath deposition [9], spray pyrolysis [17], mechanical pressing [13–14] etc.

This chapter reports the spray deposition of *n*– Sb_2S_3 onto stainless steel (S.S.) and titanium (Ti) substrates and their use as septum electrode in redox storage cells. Sb_2S_3 films on metallic substrates are used as a separator of the two redox electrolytes in the two compartments. The redox electrolyte in the first compartment is kept fixed while those in second compartment; being in dark, are changed. The charging of SC–SEP redox storage cells upon illumination and their subsequent electrochemical discharge are discussed.

8.2 EXPERIMENTAL

8.2.1 Construction of semiconductor – septum (SC–SEP) storage cell

When a semiconductor electrode is taken as a separator of two compartments containing aqueous electrolytes in PEC cells, it is called a Semiconductor Septum (SC–SEP) solar cell. In the present work, the spray pyrolysis technique was used to deposit the antimony chalcogenide thin films. In case of films deposited on FTO coated glass, it is not possible to bring the second electrolyte in contact with rare side of the semiconductor. Therefore, it was thus necessary to use to films on metallic substrates for their use as a SC–

SEP. As has been seen from the Chapter VII that only Sb_2S_3 films deposited using non– aqueous medium (NA– Sb_2S_3) show acceptable performance in the PEC cells. These films deposited on Ti and S.S. substrates were further used for construction of SC–SEP storage cells.

8.2.1.1 Semiconductor septum

Preparation and characterization of spray deposited *n*– Sb_2S_3 have already been published elsewhere [18–19]. Sb_2S_3 films were prepared onto stainless steel and titanium substrates by keeping the preparative parameters at their optimized values [18], except substrate temperature. In [18] films were formed on the amorphous glass substrates at 250 ^{o}C, while in the present case the optimized substrate temperature for stainless steel and titanium substrates is 175 ^{o}C. For an optimization of substrate temperature, films were deposited at 150, 175 and 200 ^{o}C respectively and tested for their photoactivity by using them in PEC cell formed with 0.5M polyiodide electrolyte. The films prepared at 175 ^{o}C showed relatively higher values of open circuit voltage and short circuit current. At 200 ^{o}C, due to decrease in film thickness, there is decrease in photoactivity. Comparatively lower decomposition temperature for Sb_2S_3 on metallic substrates than that on amorphous glass substrates is due to higher thermal conductivity of former than the latter.

8.2.1.2 Redox electrolytes

In a PEC cell, the electrolyte provides a medium for scavenge of photogenerated holes from photoelectrodes. Inorganic or organic solvents along with supporting electrolytes may be used as electrolytes in PEC cells. In the present work, various electrolytes e.g. polysulphide, Ferro– Ferri cyanide, etc. were used in a second compartment in addition to polyiodide electrolyte in the first compartment containing SC–SEP electrode.

8.2.1.3 Counter electrode

In a PEC cell, the electrolyte species are reduced at counter electrode and again are oxidized at the n– type photoelectrode giving no net change in the composition of electrolyte. For fabrication of SC–SEP solar cell, graphite was used as a counter electrode in both the compartments.

8.2.1.4 Cell construction

Thin films of Sb_2S_3 of (2.2 cm X 2.2 cm) ≈ 4.84 cm^2 area deposited on stainless steel substrate was inserted in a rectangular box of glass (2.2 cm X 2.2 cm X 7.5 cm) to form two compartments. All edges of the rectangular cell and thin film electrode were fixed with epoxy resin (Araldite made in India). The photoelectrode compartment was filled with polyiodide [0.5M (KCl + KI) + 0.01M I_2]. The another redox electrolyte in second compartment (stainless steel side) was 1M polysulphide (NaOH + Na_2S + S).

Another cell consisted of two separate rectangular compartments (2.2 cm X 2.2 cm X 2.2 cm) made of backellite with 1 cm diameter holes drilled on their sides facing towards each other. The Sb_2S_3 film deposited on titanium substrate was then fixed between two compartments, drilled walls being in contact with the film and titanium respectively, with epoxy resin. A quartz glass window was made to illuminate the Sb_2S_3 from other side of compartment. The tungsten halogen lamp (500 Watt) was used to illuminate the septum electrode. The compartment adjacent to the lamp was filled with 0.5M polyiodide solution. Other compartment was filled with 0.1M Ferro–Ferri cyanide [$K_4Fe(CN)_6$ / $K_3Fe(CN)_6$] redox electrolyte. A water filter was interposed between the cell and light source to avoid heating of an electrolyte. The cells were discharged across two separate load resistances as 1K and 10 K respectively.

8.3 Results and Discussion

8.3.1 Charging and discharging of SC–SEP storage cell

The semiconductor septum storage electrode separates the two compartments of the storage cell as shown in Fig. 8.1. The semiconductor septum cell under illumination causes generation of electron hole pairs, the electrons jump into the conduction band from valence band. The electron further moves towards the bulk of the semiconductor and via metallic substrate travel into the other compartment where it is received by the oxidized species, and gets reduced. These species can again be deoxidized by transferring an electron to the metal electrode in compartment II, in dark while hole moves

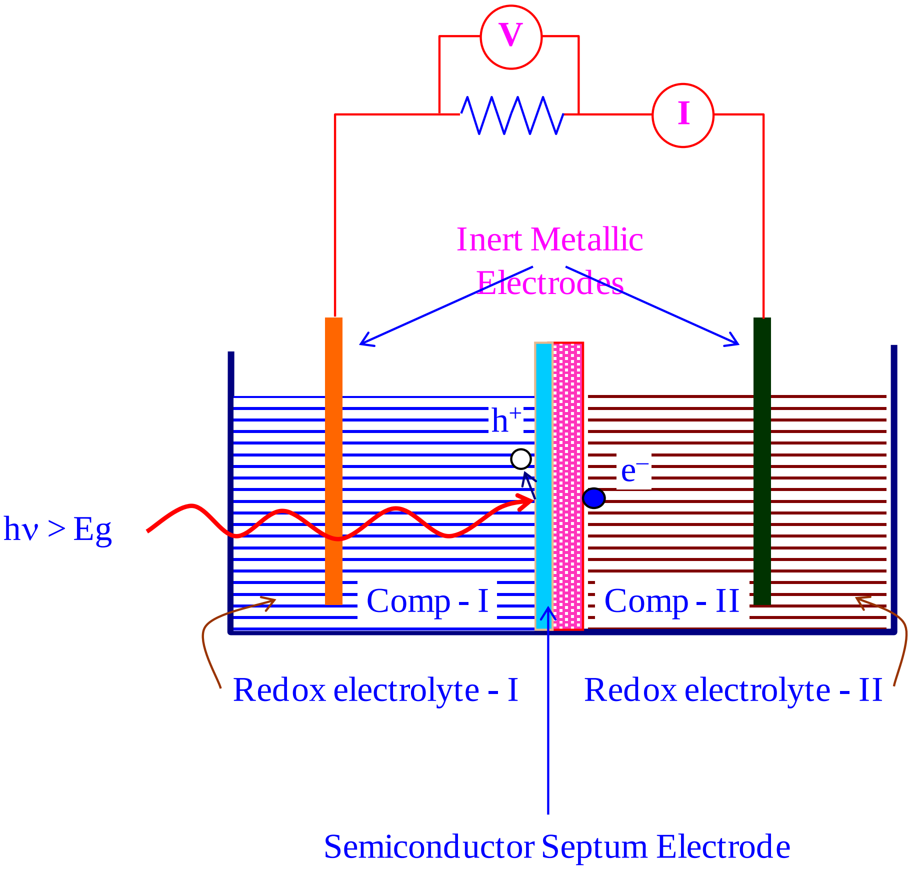

Fig.8.1 Schematic diagram of a Semiconductor septum Storage cell

towards the surface of the semiconductor and accepted by the reduced species present in compartment I, and get oxidized. In dark, these oxidized species accept electrons from compartment II, resulted in the electricity flow through external load.

For I^{2-}/I_2^{2-} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electrolytes in I and II compartments, the following steps occur during charging of the cell

$n\text{–}\ Sb_2S_3 + h\nu \longrightarrow e^- + h^+$ $(h\nu \geq Eg)$

$I^{2-} + 2h^+ \longrightarrow I$

$I + I^{2-} \longrightarrow I_2^{2-}$ (compartment I)

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

When two inert metal electrodes (highly polished graphite) in two compartments are shorted through suitable load resistance, the cell discharges, with following reactions

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

$I^{2-} + 2e^- \longrightarrow I_2^{2-}$ (compartment I)

For $S^{2-}/\ S_2^{2-}$ electrolyte in II compartment the reactions are as follows

during charging

$S + 2e^- \longrightarrow S^{2-}$

during discharging

$S_2^{2-} \longrightarrow S^{2-} + e^-$

Voltage and current versus time plot of the charging and discharging behavior of | C | 0.5M Polyiodide | *n*– Sb_2S_3 | S.S. || 1M Polysulphide | C |

septum storage cell are shown in Fig. 8.2. Also Fig. 8.3 depicts charging under 80 mW / cm^2 and discharging cycle of redox system | C | 0.5M Polyiodide | *n*– Sb_2S_3 | Ti || 0.1M $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$ | C |. Various results of changes in photovoltage during charging and photovoltage and photocurrent during discharging are listed in Table 8.1.

The cells were charged continuously for 2 hr. Photovoltage gets saturated in around 1 hr. The discharging of the cells is relatively faster during first 60 minutes, then it is quite slow. Thus the cell works not only as a generator but also the storage of electricity.

Table 8.1 : Changes in photovoltages during charging and photovoltages and photocurrents during discharging for different systems.

Cell Configuration	Charging after 1 hr		Discharging after 2 hr	
	Δ V (mV)	Δ I (μA)	Δ V (mV)	Δ I (μA)
C | 0.5M I^{2-}/I_2^{2-} | *n*– Sb_2S_3 | S.S.|| 1M S^{2-} / S_2^{2-} | C	250	84	11(1K) 99 (10 K)	14.5(1 K) 2.5 (10 K)
C | 0.5M I^{2-}/I_2^{2-} | *n*– Sb_2S_3 | S.S. || 0.1M $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ | C	220	24	9 (1 K)	2 (1 K)
C | 0.5M I^{2-} / I_2^{2-} | *n*– Sb_2S_3 | Ti || 0.1M $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ | C	256	11	42 (10 K)	1.7 (10 K)

S.S. – stainless steel
Ti – Titanium

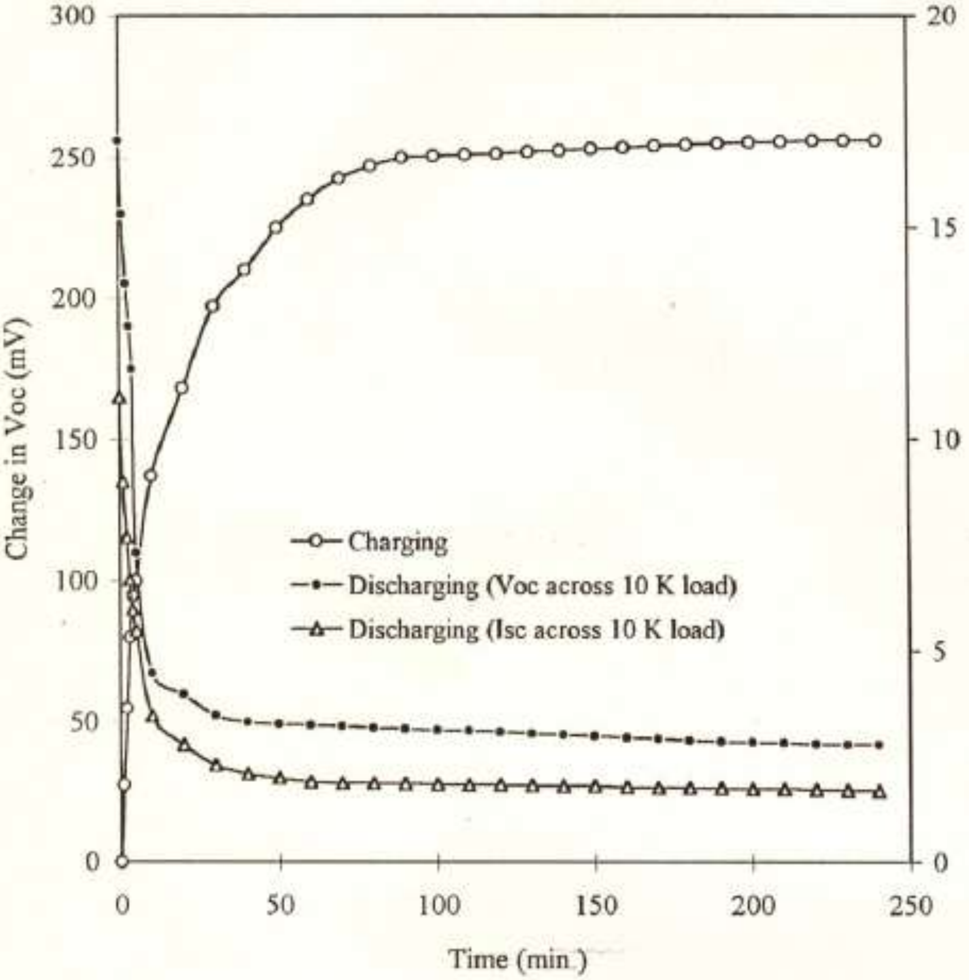

Fig. 8.2 : Voltage and current versus time plot for the charging and discharging behaviour of the C/0.01M KI / Sb_2S_3 / Ti /0.1M Ferri-ferro cyanide / C septum storage cell

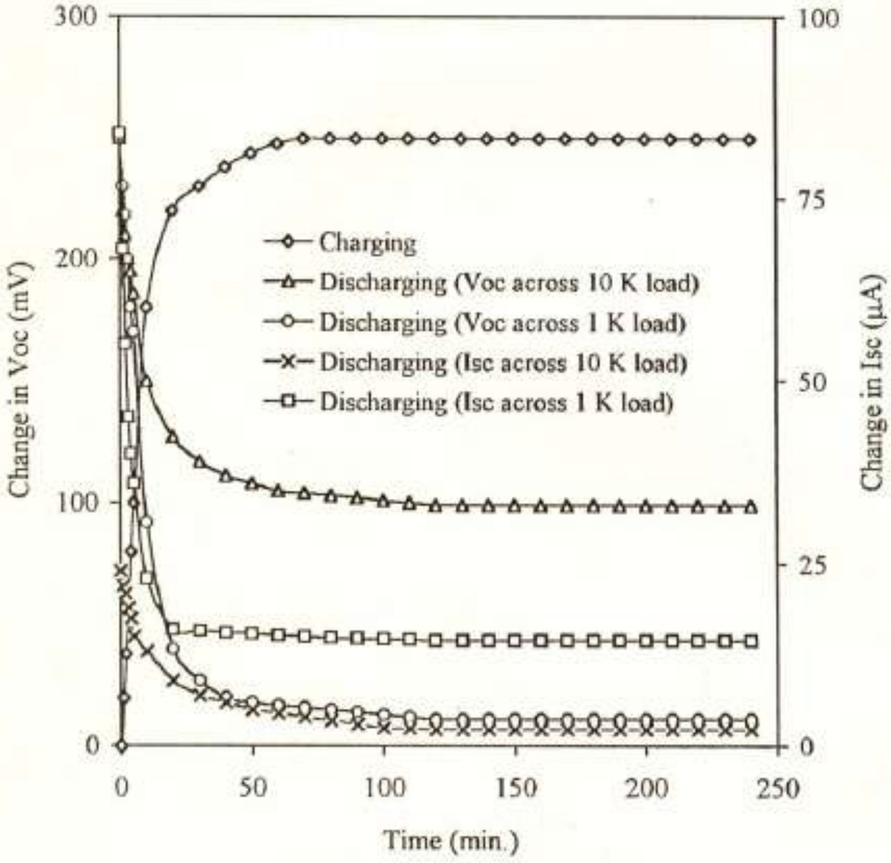

Fig. 8.3 : Voltage and current versus time plot for the charging and discharging behaviour of the C/0.01M KI / Sb_2S_3 / S.S. / 1M Polysulphide / C septum storage cell

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