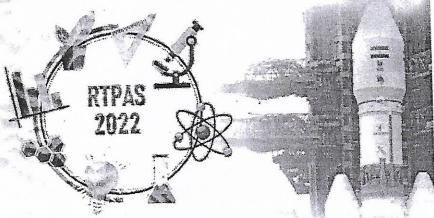


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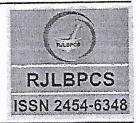
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Studies on use of yttrium sulphide as the storage electrode in photoelectrochemical (pec) storage cell

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Abstract: The study of yttrium sulphide as storage electrode was carried out by designing a special three electrode storage cell system. It consists of three electrodes, namely, storage electrode, photoelectrode and counter electrode. Electrodeposited yttrium sulphide film and CdSe film on to a stainlesssteel substrate has been used as a storage electrode and photoelectrode respectively. The graphite rod was used as a counterelectrode. These three electrodes were immersed in two rectangular transparent plastic boxes containing suitable electrolytes. Boxes were bridged together by agar-agar gel. The cell was illuminated by a high intensity lamp. The electrical characteristics in the mode of charging and discharging were studied.

Keywords: Storage cell, storage electrode, photoelectrode, counterelectrode and agar-agar gel.

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1. introduction:

Now a day, for a sustainable society, energy is unquestionably one of the grand challenges [1, 2]. In this modern world, the social prosperity and economic development depend on the sustainable energy conversion and storage [2]. Since from 19th century, due to vast consumption of non-renewable fossil fuels resulted in a severe anxiety for energy deficiency and the corresponding carbon emissions, creates new environmental issues. There is urgent need of clean, affordable and reliable energy that can substitute fossil fuels and limits the carbon emission issue. Therefore, the interest of researchers focused towards the development of technology to make availability of clean and renewable energy, especially the intermittent energy, energy conversion and storage [3, 4]. Now a day, there is vast demand for electrochemical energy conversion and storage devices, especially portable devices, consumer electronics, and electric vehicles [5–7]. Derek P Gregory has been reported use of rare earth hydrides for storing hydrogen in both stationary and mobile applications [8]. Therefore, it should require rapid development of new materials with high performance in energy conversion and storage devices. In our opinion, scientists underestimated this field

and started working with material having low cast and easy availability. The best materials, for examples, so far reported with relatively with high efficiency and stability for long time are CdSe, WSe₂, CuIn Se₂[9-12].

Photo electrochemical cell can be converted into rechargeable electrochemical storage cell, when storage electrode, capable of undergoing a reversible chemical change is used in it [13]. A reversible chemical reaction occurs at the storage electrode of the type,

$$AX + ne^- \leftrightarrow A + X^{n-}$$

Where A is storage electrode, X is solute present in the electrolyte. Construction of such a cell requires stable low resistance separator which minimizes direct chemical reaction of the electro active redox species, and the selected redox couples suitable to semiconductor photoelectrode. The PEC cells employing third electrode as a storage electrode have been reported in the literature [14-19].

2. Materials and methods:

Preparation of electrode films and electrolytes:

Yttrium-sulphide films have been electrodeposited from the non-aqueous formaldehyde bath $[0.05 \mathrm{M~Y~(NO_3)_3}$ - $0.05 \mathrm{M~CH_3CSNH_2}$ - $0.05 \mathrm{M~CH_3COONa}]$ onto a stainless-steel substrate at room temperature. The CdSe films are electrodeposited from the aqueous bath $[0.1 \mathrm{M~CdCl_2}$ -0.05 M SeO₂] onto stainless steel substrates. The PEC properties of the film were tested with the electrolyte 0.1 M (Na₂S - S - NaOH) s an electrolyte and graphite as a counterelectrode. In order to increase the photo effect, the films were annealed at $200^{\circ}\mathrm{C}$.

The electrolytes are prepared by using analytical grade chemicals in doubly distilled water. The stable electrolyte for the photoanode (CdSe) is polysulphide [20]. It was prepared by taking A.R. Grade Sodium hydroxide and sulphur from. B.D.H., India, and A. R. Grade sodium sulphide, from the Fluka. Appropriate amount of NaOH and Na₂S were dissolved in double distilled water at room temperature. In this solution, sulphur powder was added and mixture warmed up to 55°C with constant stirring. The mixture was maintained at this temperature till all sulphur powder dissolves. The solution was cooled to room temperature, filtered and preserved in the glass stopper air tight bottle. The colour of the the solution was yellowish pink. The yttrium sulphide films are stable in the ferri-ferrocyanide electrolyte. This electrolyte was prepared by taking appropriate amount of potassium ferricyanide and potassium ferrocyanide of analytical grade, dissolved in double distilled water and preserved in the glass stopper air tight bottle.

Design of the Three Electrodes Storage Cell:

The design of three electrode battery was reported by many researchers in various journals [21-25]. Here, cell consists of three electrodes, namely, CdSe as a photoelectrode, graphite as counterelectrode and yttrium sulphide as storage electrode. Two rectangular transparent plastic boxes were fixed with M-seal by conducting bridge of 3 cm in length formed with Agar-Agar gel. The size of each rectangular box is $4.0 \times 1.5 \times 7.5 cm^3$. One compartment of cell consists of CdSe as a photoanode ($5cm^2$ area) and graphite rod ($6.2cm^2$ area) as the counterelectrode. The volumes of the electrolytes were 35 cc in each compartment of the cell. The electrolyte 0.1 M (Na₂S-NaOH) was used in first compartment. The other compartment consists of 0.1 M [K₃Fe(CN)₆] – K₄Fe(CN)₆] electrolyte with yttrium sulphide storage electrode which is kept in dark.

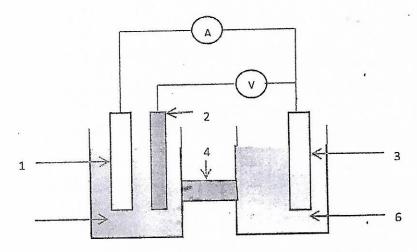


Fig.1: Schematicdiagram of the redox storage cell during charging

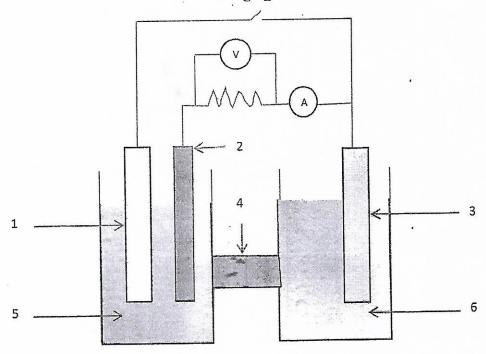


Fig.2: Schematicdiagram of the redox storage cell during discharging

The cell was illuminated by using 500 Watt tungsten filament lamp. The light intensity was $200mW/cm^3$. The electrical characteristics in the mode of charging were studied with the circuit diagram shown in fig.1 and fig.2 respectively. In fig. 1)- CdSe photoanode, 2)-counterelectrode, 3) Y-S storage electrode, 4) Agar-Agar gel, 5) 0.1 M (Na₂S - S - NaOH) and 6) K₃Fe(CN)₆] - K₄Fe(CN)₆. The current and voltages were recorded using the digital current and volt meters respectively.

3. Result and discussion:

The Configuration of the Cell and Charge Transfer Mechanism:

The configuration of the cell was as follows:

 $K_4Fe(CN)_6$]/Y-S.

During charging the photoreaction occurring at the two electrodes can be described as follows:

$$n - CdSe + hv \rightarrow e^- + h^+$$
 $(hv > E_g)$

Due to localized electric field at junction,

$$e^- + h^+ \rightarrow e^-_{bulk} + h^+_{surf}$$

(i.e. near the interface of the semiconductor electrolyte)

$$2h^+ + S^{2-} \rightarrow S$$
 (at the CdSe)

i.e. oxidation of electrolyte would occur, which is present near interface.

$$e^-_{bulk} \rightarrow e^-$$
 Storage electrode

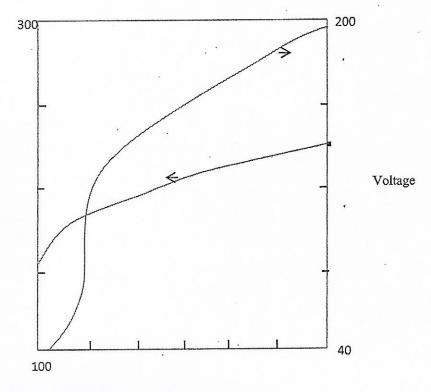
(Transfer to through back of semiconductor to the storage electrode)

$$2e^{-} + Y-S \rightarrow Y + S^{2-}$$

when Y-S was the storage electrode.

Charging and Discharging Studies of the CdSe/ 0.1M (Na₂S - S – NaOH) / C / 0.1M - $[K_3Fe(CN)_6] - K_4Fe(CN)_6]$ /Y – S.

During the period of charging, photocurrent raised from 0.15 to $0.225mA/cm^2$, while cell voltage rose from 30 to 200 mV as shown in fig.3 within the period of 120 minutes.



Discharging of the cell using 6 KO load across the storage electrode and counterelectrode results in an initial current of 25 $\mu A/cm^2$ and after the period of two hours current drops to $6 \,\mu A/cm^2$. The cell voltage also decreased from 600 to 300mV as shown in fig.4. It can be seen that the potential drops rather severely under load. This is attributed to resistance losses in the systems such as those in the photoactive layer and electrolyte, polarization losses at the counterelectrode and semiconductor metal contact.

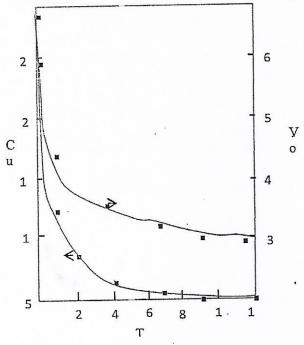


Fig.4: Discharging

Conclusion:

From above studies of charging and discharging characteristics, it is concluded that yttrium sulphide film may be used as a storage electrode.

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