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RECHARGEABLE SOLAR BATTERY (SAUR VIDDYUT KOSH - IV)
Pb_3O_4 SEMICONDUCTOR ELECTRODE

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ABSTRACT

A rechargeable photoelectrochemical solar battery (SAUR VIDDYUT KOSH) based on the n-type Pb_3O_4 / $Fe^{3+},Fe^{2+}//IO_3^-,I^-/Pt$ system has been made. The battery is charged at the rate of 50 $\mu A/cm^2$ (photocurrent). The battery can be charged to a maximum value of 0.41 mA/cm^2 of current and potential of 0.84 V. Other redox electrolyte systems such as I_2/I^-, Cu^{2+}/Cu, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ have also been tried in the second compartment, but the above battery is found to give the best response. V_{fb} of Pb_3O_4 in Fe^{3+}/Fe^{2+} (pH-4) is determined to be equal to -0.32 V with respect to SCE. Effect of hydrogen sintering on the photocurrent and photovoltage is studied. I-V characteristics of n-type Pb_3O_4 electrode are studied, from which power efficiency and fill factor are calculated. The above cell is fully chargeable in solar radiation and charging efficiency is found to be $\sim 72\%$.

1. INTRODUCTION

Currently scientists have been carrying out research to develop photoelectrochemical solar cell utilising stable photoanodes and photocathodes (1,2,3,4). But the main drawback of the PEC cell is that it does not have storage capacity. Our group has been concentrating to make a storage type of rechargeable PEC solar battery (SAUR VIDDYUT KOSH) (5,6). The basic principle of such battery is similar to PEC cell except that the photoanode and the cathode are separated by a membrane (7,8,9,4). The two half

cells contain two types of redox systems, such that the redox potential of the cell is of the reasonable value. In present work, A SAUR VIDDYUT KOSH of the following type is made

$$Pb_3O_4,\ Pt/Fe^{3+},Fe^{2+}//IO_3^-,I^- \ /\ Pt.$$

Pb_3O_4 is selected because it is stable in acidic solutions and has a band gap of 2.1 eV. (10).

In the present work, we report the preparation, characterisation of the n-type Pb_3O_4 electrode, design and fabrication of a SAUR VIDDYUT KOSH.

2. EXPERIMENTAL

The total experimental work is divided in three parts.

a) Preparation of semiconductor material and the n-type doped Pb_3O_4 electrode.

b) Characterisation of semiconductor electrode

c) The use of electrode in rechargeable photoelectrochemical cell

2.1 Preparation

An inexpensive zone melting furnace was used to purify lead. (11). The zone purified lead was refluxed with proportional amount of pure citric acid A.R. Grade, at 100°C for 72 hours. It was then filtered and the filtrate was mixed thoroughly with 99% ethyl alcohol. White crystalline lead citrate was filtered and dried. The decomposition of this citrate at 350°C in air, gave fine orange red crystals which were identified as Pb_3O_4 by X-ray diffraction study.

The pellets of Pb_3O_4 sample of thickness 2mm and diameter 1 cm were prepared with a hydraulic press by applying a pressure of 8 atmospheres/inch^2. The pellets had very high resistance (10^{12} ohm). The pellets were sintered at 300°C in hydrogen atmosphere to increase the n-type conductivity and to remove the binder. Pellets reduced in hydrogen atmosphere under various conditions were used to measure the photoresponse and the resistance (Table 1). The photoresponse was obtained by exposing the

electrode in H_2SO_4(pH-1) and corresponding photocurrent and photovoltage were measured. Halogen/quartz lamp(250 w) was used as source of light.

TABLE 1

No.	Temperature (°C)	Time (hrs)	Resistance (ohm)	I_{ph} (uA/cm^2)	V_{ph} (V)
1	200	2	10^5	62.5	0.06
2	250	2	10^4	75	0.12
3	300	2	0.5-1	500	0.26
4	350	2	1-2	37.5	0.03
5	400	1	2-3	31.25	0.02

2.2 Characterisation

The photocurrent (I_{ph}) and photovoltage (V_{ph}) of semiconductor were measured in different electrolyte systems using Platinum counter electrode. The plot of photocurrent and photovoltage vs time for each of the redox electrolyte system are shown in Fig. 1 and 2 respectively.

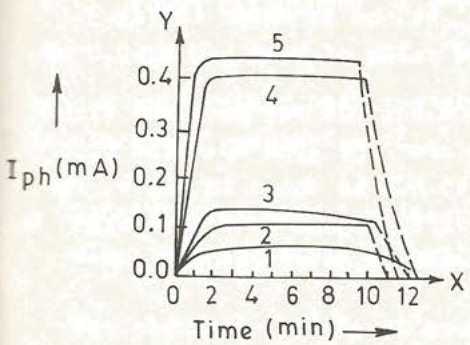


Fig.1: Photocurrent I_{ph} vs time of illumination.

1. KI(pH 4) 2. Ce^{+3}/Ce^{+4}(1M HCl)
3. $Fe(CN)_6^{3-}/Fe(CN)_6^{-4}$ (pH9)
4. Fe^{++}/Fe^{+++}(pH7) 5. Fe^{++}/Fe^{+++}(pH 4)

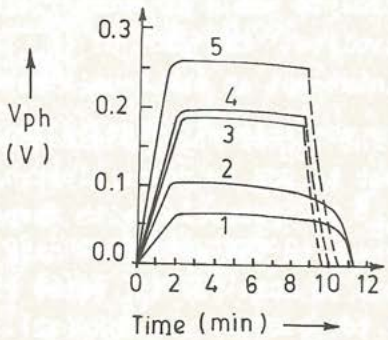


Fig.2:Photovoltage vs time of illumination.

1. Ce^{3+}/Ce^{4++} (1M HCl)
2. KI (pH 4)
3. Fe^{++}/Fe^{+++} (pH 4)
4. Fe^{++}/Fe^{+++}(pH 7)
5. $Fe(CN)_6/Fe(CN)_6$ (pH 9)

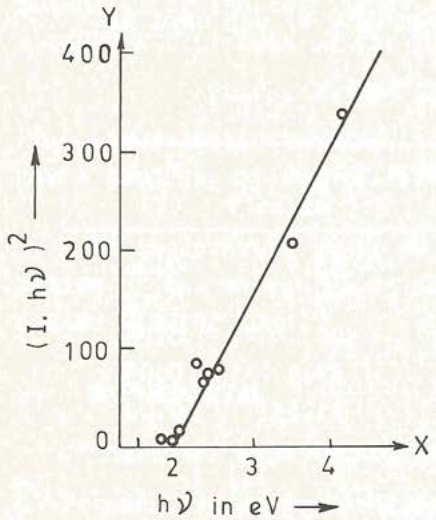


Fig.3:$(I.h\nu)^2$ vs $h\nu$ Band Gap Measurement

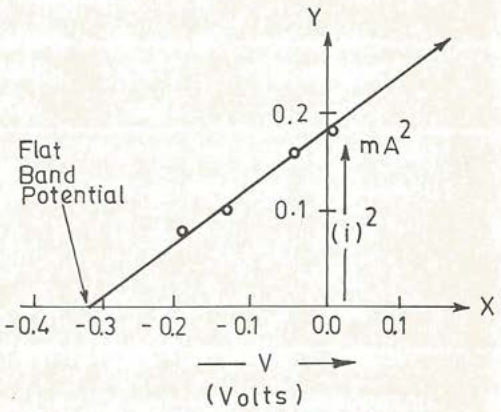


Fig.4: Flat Band Potential Measurement

The band gap was found from the plot of $(I_{ph}.h\nu)^2$ vs $h\nu$ (12). The experimental set up consisted of a Tungsten halogen lamp, monochromater, electrode dipped in Fe^{3+}/Fe^{2+} redox electrolyte and a Pt counter electrode dipped in the same electrolyte. The plot of $(I_{ph}.h\nu)^2$ vs. $h\nu$ is shown in Fig.3. The intercept at the x-axis gave the value of band gap Eg=2.0 eV.

The V_{fb} of Pb_3O_4 semiconductor electrode was measured with respect to SCE in redox electrolyte aFe^{3+}/Fe^{2+}(pH 4). The plot of I_{ph}^2 vs. potential with respect to SCE is shown in Fig.4. The intercept on the potential axis gives V_{fb} equal to -0.31 V with respect to SCE. The V_{fb} value gives the value of E_c for Pb_3O_4 equal to -0.076 V vs. SHE (12).

Maximum power efficiency and fill factor were calculated from the I-V characteristics of the cell. The semiconductor electrode was anodically biased; and photocurrent and photovoltage were measured at different applied potentials. The plot of I_{ph} vs. V_{ph} is shown in Fig.5.

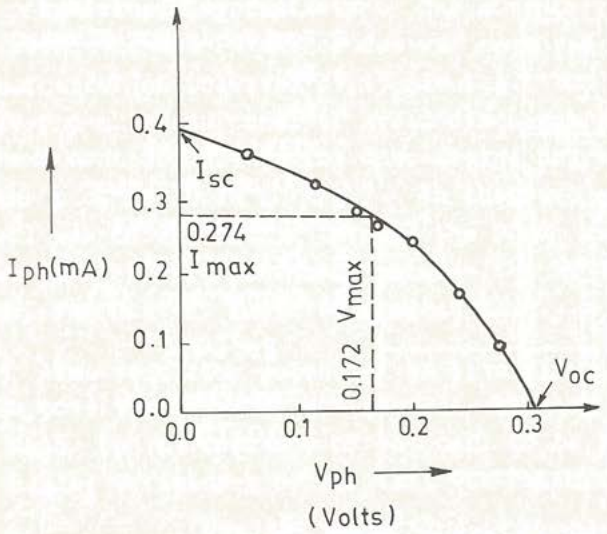


Fig.5: Determination of Power efficiency and Fill Factor. Photocurrent vs photovoltage

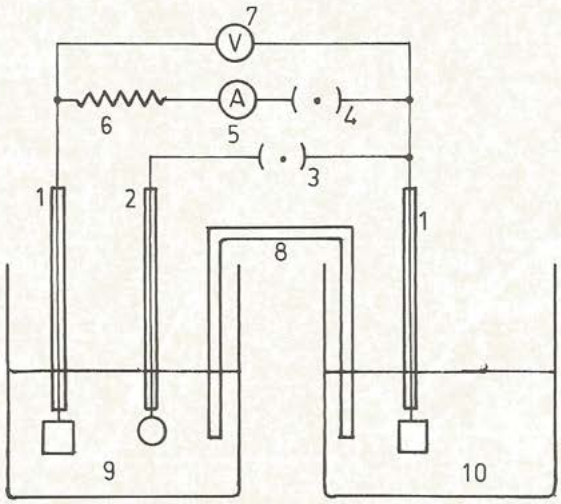
$$\text{Fill factor} = \frac{V_{max} \cdot I_{max}}{V_{oc} \cdot I_{sc}} = 0.38$$

$$\text{Power efficiency} = \frac{V_{max} \cdot I_{max}}{\text{Power input } (60\ mW/cm^2)} \times 100 = 0.09\%$$

which shows a rather poor conversion efficiency of solar energy into electrical energy.

2.3 SAUR VIDDYUT KOSH (Application of the semiconductor electrode to make a rechargeable solar battery)

The electrode was first mechanically polished with SiC paper No.400, then ohmic contact was made with colloidal silver paste. Copper wire was soldered on the silver surface. The electrode was then mounted in a glass tube and sealed with epoxy resin. All other sides of the pellet except the front one were insulated by applying epoxy resin. The electrode surface was washed with double distilled water prior of dipping into the electrolyte. The diagram of the experimental set up is shown in fg.6.



1.Platinum Electrodes
2.Semiconductor Electrod
3.Key
4.Key
5.Milliammeter
6.100 ohm Resistor
7.Millivoltmeter
8. Salt-bridge
9. Compartment (1)
Fe^{3+}/Fe^{2+}
10.Compartment(2).
IO_3^-/I^-

Fig.6: SAUR VIDDYUT KOSH (Rechargeable Solar Battery).

The compartment 1 contained $FeSO_4/Fe_2(SO_4)_3$ (0.1 M each) redox electrolyte. Compartment 2 contained one of the following redox electrolytes: I_2/I^-, Cu/Cu, IO_3^-/I^-, $Fe(CN)_6/Fe(CN)_6$. The current and voltage output of the rechargeable cell with different electrolytes is given in the table 2.

TABLE 2

Redox Electrolyte in compartment 1	Redox electrolyte in compartment 2	pH	I $\mu A/cm^2$	V mV	Time min.
Fe^{3+}/Fe^{2+}	I_2/I^-	4	50	26	60
Fe^{3+}/Fe^{2+}	$Fe(CN)_6^{3-/4-}$	9	158.5	29	60
Fe^{3+}/Fe^{2+}	IO_3^-/I^-	8	408.0	93	60
Fe^{3+}/Fe^{2+}	Cu^{2+}/Cu	4	332.5	20	60

The cell was charged between Pb_3O_4 electrode and Pt electrode of compartment 2, whereas the discharging process took place between the two Pt electrodes of the respective compartments.

Since the IO_3^-/I^- system gave the best current and voltage

output in the radiation of halogen lamp, the same experiment was repeated in solar radiation. The momentary discharge current between the two Pt electrodes was measured through 100 ohm resistor after an interval of 15 minutes. The circuit was disconnected after each measurement to avoid discharging. The current was drawn continuously during discharging process. The current vs. time plot is shown in Fig.7. In the next experiment, while the cell was being charged through the Pb_3O_4 electrode and Pt.electrode the open circuit potential between the Pt electrodes of the two compartments was measured against time.

The resulting potential vs time plot is shown in Fig.8. It was possible to carry out several charging and discharging cycles showing the performance of the cell to be reproducible. The charging efficiency of the cell was calculated as

$$\text{Charging Efficiency} = \frac{(I_{max} \cdot V_{max})\ \text{Battery}}{(I_{max} \cdot V_{max})\text{PEC}} \times 100 = 72\%$$

3. RESULTS AND DISCUSSION

In order to get maximum photocurrent and photopotential the system should have low resistance and large space charge layer. Hydrogen reduction increases the oxygen deficiency as well as

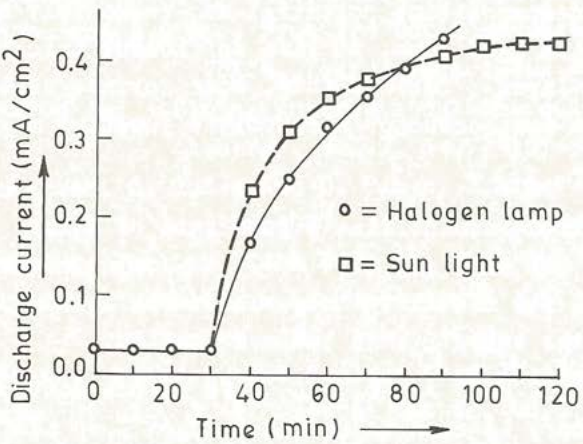


Fig.7: Current vs time plot of rechargeable battery.

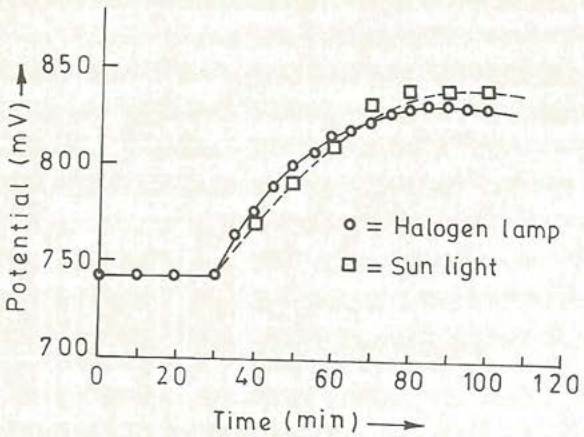


Fig.8: Potential vs time plot of the rechargeable battery.

decreases the space charge region (13). Since both are opposing each other, one would get a best condition when resistance is lowest and photocurrent is maximum. The table (1) suggests that the pellet reduced at 300°C for 2 hours gives the best photo-response. Hence for all subsequent studies these pellets were used.

As seen from Fig.1 Pb_3O_4 pellets gave the best photocurrent with Fe^{3+}/Fe^{2+} redox system. This behaviour may be ascribed to the fact that the redox potential of this couple is just above that of the anodic decomposition potential and reasonably below that of the conduction hand edge, to give sufficient thickness of the space charge layer. Besides this, some surface state modifications at the semiconductor electrolyte junction might be playing a role (14).

The Pb_3O_4 electrode can utilise a good part of solar spectrum due to its low band gap (2.1 eV). The major advantage in using Pb_3O_4 is in its stability in aqueous media at low pH. As it is evident from the table 2 that the combination:

Pb_3O_4, Pt/Fe^{3+}, Fe^{2+} // IO_3^-, I^- / Pt is the most promising. When this battery is charged in the halogen lamp the current was found to increase continuously for about one hour. But when the same experiment was performed in solar radiation, the momentary discharge current saturated after about 80 minutes (Fig.7).

The dark current was constant at about 0.03 mA. for half an hour. In both the cases the variation of current and potential with time was found to be almost similar upto 50 minutes.

The increase of potential with time shows also the same behaviour for both the conditions (Fig.8).

4. CONCLUSIONS

It is possible to make solar chargeable battery (SAUR VIDDYUT KOSH) with Pb_3O_4 as photoanode. The efficiency of conversion from solar energy to electrical energy is rather low (0.09%). But the efficiency of charging of the Saur Viddyut Kosh is 72%. However, the power is not retained by the cell for the long period, because the amount of the chemical conversion is controlled by 0.09% of the cell. Hence, unless the photoconversion efficiency is increased to a reasonable value (15%), the life of the SAUR VIDDYUT KOSH would be short. We are presently carrying out research in this direction.

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