ELECTRODES FOR ENERGY STORAGE THROUGH PHOTO-ELECTROCHEMICAL CELLS

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Based on a three-electrode system, conversion and storage *in situ* of solar energy through photoelectrochemical cells are described. Thin films of n-CdS and n-CdSe were used as the photoanode. The possibility of the use of Sb/SbO_2^- and $Co/Co(OH)_2$ as storage electrodes is presented. Principle of storage and factors controlling storage efficiency are discussed.

Great strides have been made in developing solid-state photovoltaic cells for energy conversion, but these devices suffer from the inherent disadvantage of not having any built-in storage capacity. The use of storage batteries along with the photovoltaic cells is not likely to make the system economically viable. The photoelectrochemical cells (PEC), on the other hand, possess the distinct possibility of having a built-in storage mode [1,2]. The possibility of energy storage in situ through the use of Sb/SbO_2^- and $Co/Co(OH)_2$ couples as storage electrodes in conjunction with the conventional photoelectrochemical cells has been explored in the present investigations.

EXPERIMENTAL

The photoelectrochemical storage cell (PESC) was a H-shaped vessel as depicted in Fig. 1. The storage compartment was separated from the PEC containing the photoanode and counter-electrode by using agar-agar gel saturated with KCl.

Thin films of n-CdS and n-CdSe were used as the photoelectrode. n-CdS films were prepared by electrodeposition of cadmium onto titanium sheet (99.99% pure) followed by anodisation of the cadmium in a bath containing 1 M Na_2S in NaOH [3,4]. The films were annealed in nitrogen at 100 ^{o} C for one hour and then etched in 1 M HCl at 60 ^{o} C for ten seconds. Films of n-CdSe were prepared by electrodeposition of cadmium and selenium onto titanium substrate from a solution containing a mixture of cadmium sulphate and selenious acid [5]. The CdSe films were annealed in nitrogen at 550 ^{o} C for one hour. The annealed films were then etched at 60 ^{o} C for ten seconds in a dilute (1:1) acid mixture containing HCl, HNO_3, H_2SO_4 and CH_3COOH in the ratio of 4:1:0.2:0.1 (by volume). Electrical contact to the titanium substrate was made through indium; the electrode, except the semiconductor surface, was covered by epoxy.

Pure platinum wire 9 cm long and 1 mm in diameter, attached to a piece of platinised platinum foil of area 4 cm^2 was used as the counterelectrode.

The electrolyte in the compartment containing the photoanode and counterelectrode was a solution containing Na_2S, S and NaOH (1M each) and that in the storage compartment was a solution containing 1 M NaOH.

Sb/SbO_2^- storage electrode was prepared by partially melting antimony in presence of air followed by casting in the form of a stick. A wire was attached to one end of the antimony

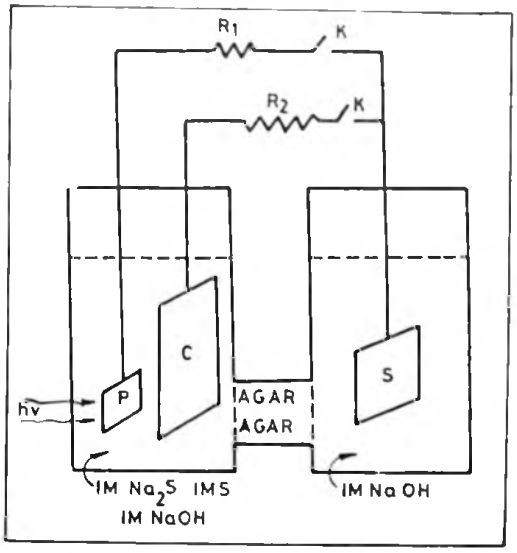


Fig. 1 Photoelectrochemical storage cell.
P-photoanode : either n-CdS or n-CdSe
S-Storage electrode : either Sb/SbO_2^- or $Co/Co(OH)_2$;
C-Counter elelectrode.

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rod. Cobalt, electrodeposited onto a 2 cm^2 platinum foil from a bath containing 0.2 gm cobalt sulphate and 4-5 gms ammonium sulphate in 150 ml dilute ammonium hydroxide (about 4 M), when dipped in alkali resulted in Co/$Co(OH)_2$ electrode.

The light source was a 1000 W tungsten lamp. The polychromatic light intensity measured by a standard silicon solar cell (Suryamapi, supplied by Central Electronics Ltd., India) was maintained at 100 mW/cm^2 . No correction for reflection and adsorption losses were made.

Photocurrent measurements and photoelectrode potentials vs. SCE were carried out by means of a Philips electronic multimeter (PM-2503). All measurements were carried out under constant nitrogen purge.

RESULTS AND DISCUSSION

In a photoelectrochemical cell with n-CdS or n-CdSe photoanode and Pt-counterelectrode both immersed in an electrolyte containing S^{2-}/S_n^{2-} redox couple; the reactions occuring at the electrodes under illumination are :

$$\text{at the anode} : S^{2-} - 2e \longrightarrow S$$

$$\text{at the cathode} : S + 2e \longrightarrow S^{2-}$$

forming, at least in principle, a regenerative system, the net result being flow of electrons from the photoanode to the counterelectrode through the external circuit. The open-circuit photopotentials for cells with n-CdS and n-CdSe were -1.29 V and -1.19 V vs.SCE respectively. The potential of the S^{2-}/S_n^{2-} couple registered by the Pt-counterelectrode was found to be -0.72 V vs. SCE.

In order that an electrode may function as a storage electrode, its potential should be intermediate between the potential of the photoelectrode under illumination and that of the redox couple in the electrolyte. The electrode potentials [6] of Sb/SbO_2^- and Co/$Co(OH)_2$ couples satisfy this requirement in the present case and, therefore, these couples may be used as storage electrodes according to the reactions :

$$SbO_2^- + 2H_2O + 3e \rightleftharpoons Sb + 4\ OH^-$$

$$E_{Sb/SbO_2^-} = -0.88 \text{ V vs. SCE in 1 M NaOH medium}$$

and

$$Co(OH)_2 + 2e \rightleftharpoons Co + 2\ OH^- ,$$

$$E_{Co/Co(OH)_2} = -0.94 \text{ V vs. SCE in 1 M NaOH medium}$$

The values of electrode potentials reported here were experimental values measured against SCE at 30 °C.

In the three-electrode cell, the third electrode, viz., the Sb/SbO_2^- or $Co/Co(OH)_2$ electrode in the present case, when connected to the photoelectrode under illumination, will act as a cathode and current will flow from the photoelectrode to the third electrode through the external circuit. Next, in the dark the same addditional electrode when connected to the Pt-counterelectrode of the PEC, will act as an anode and current will flow in the reverse direction. Thus it is possible to store current under illumination and derive the same in the dark through the use of the Sb/SbO_2^- or $Co/Co(OH)_2$ as storage electrode.

The current-voltage characteristics of the two PEC's employed here are shown in Fig. 2. Also the potentials of the storage electrodes are shown along the vertical axis. All electrode potentials were measured with respect to SCE.

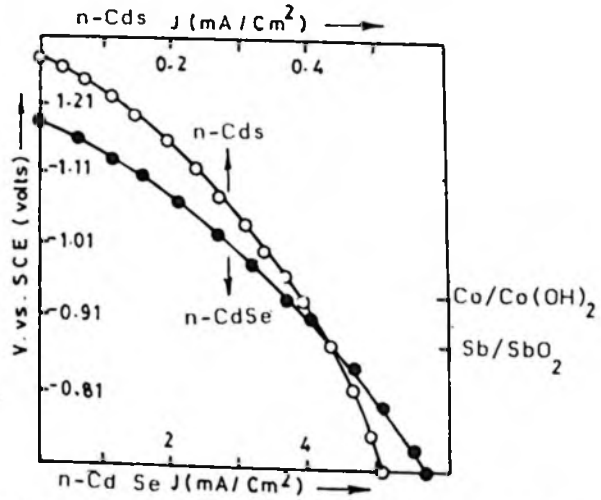


Fig.2 Current potential characteristics of the cells with O n-Cds, n-CdSe light intensity 100 mW/cm^2. Potentials of the storage electrodes are shown on the vertical axis to the right. Pt-counter electrode was at a constant potential of -0.71 V vs. SCE.

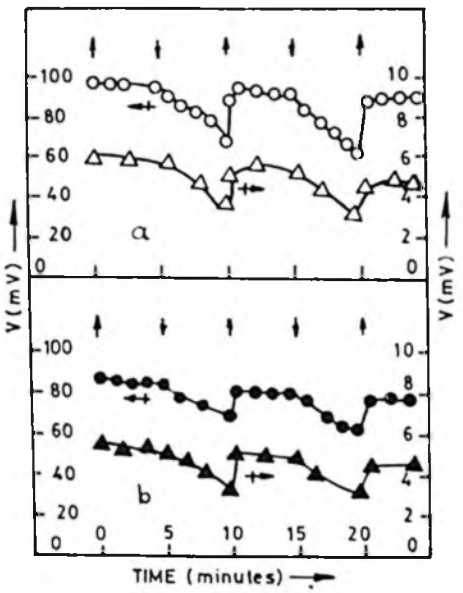


Fig.3 Plot of voltage against time for the photoelectrochemical storage cell under load.
a Storage electrode : Sb/SbO_2^-
photoanode :Δ n-CdS, O n-CdSe
b Storage electrode : $Co/Co(OH)_2$
photoanode : ▲ n-Cds, ● n-CdSe.
Light on; ↑, Light off ↓

A plot of voltage vs. time for the three-electrode photoelectrochemical storage cell is shown in Fig. 3 which clearly demonstrates the storage capability of the system.

The device as such, however, suffers from lack of stability of the storage system. This is presumably due to diffusion of S^{2-}/S_n^{2-} through the agar-agar gel which visibly changes to a yellowish tinge in about half-an-hour time. This diffusion of S^{2-}/S_n^{2-} into the storage compartment lowers the negative potential of the storage electrode resulting in a decrease in storage efficiency which may be improved by separating the two compartments by an ion specific membrane impermeable to sulfide ion.

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