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Photoelectric conversion studies on zinc selenide

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The photoelectroactivity of polycrystalline zinc selenide films prepared by electrochemical co-deposition in zinc sulphate solutions of different concentrations containing the I^-/I_2 redox couple has been investigated. Measured photopotentials, photocurrents and the initial rate of build-up of photopotentials indicate a significant enhancement in photoelectro-convertibility with increase in concentration, in spite of practically no change in the flat band potentials. The photoelectroactivity of a p–n heterojunction photoelectrochemical cell using cadmium selenide along with zinc selenide has also been studied.

1. Introduction

In our earlier work it was demonstrated that polycrystalline zinc selenide thin films endowed with p-type semiconductivity can be obtained by electrochemical co-deposition using a limiting current [1, 2]. The photoresponsiveness of these preparations is, however, not attractive. In the present investigation an attempt has been made to ascertain the possibilities of its enhancement using zinc sulphate solutions of different composition containing the I^-/I_2 redox couple. Zinc selenide has a band gap [3] of 2.7 eV. It is, therefore, of some interest to combine it with some suitable n-type semiconducting electrode to form a heterojunction photoelectrochemical cell [4]. Such a cell using CdSe has been fabricated and its photoresponse studied to adjudge its suitability for photoelectric conversions.

2. Experimental procedure

The experimental procedure already reported [2] was used for the preparation of zinc selenide electrodes. A titanium plate (1.69 cm^2) was cleaned with emery paper, polished with diamond paste (Madras Metallurgical Service Ltd) and washed successively with acetone and deionized water. It was then kept in a solution of zinc sulphate and SeO_2 of known composition for about one hour for soaking. The limiting current needed for electrochemical co-deposition of zinc selenide was determined in the usual manner [5, 6] by varying the potential of the titanium electrode with respect to a saturated calomel electrode using an electronically operated power supply (Hindustan Power Tronix Inc.) and measuring the current between the titanium electrode and a platinum electrode. Deposition was carried out for about four hours. The zinc selenide film thickness was of the order of 5×10^{-4} cm.

A simple experimental arrangement [7] was used for testing the photoelectroactivity of the zinc selenide perparations. Zinc sulphate solution containing KI and I_2 was used to combine the zinc selenide electrode with a platinum counter-electrode to form the photoelectrochemical cell. A thousand-watt tungsten lamp was used for illumination and the photopotential generated thereby was measured with the help of a digital multimeter (HIL 2142, Delhi) having a least count of 0.1 mV. Photopotential build-up and decay were recorded with the help of an Anika recorder A-4. Current–voltage characteristics in the dark and under illumination were studied using a Standard Potentiostate (DB Electronics Model 1078, Pune). For capacitance measurements a Digital LCR Meter (VLCR 7, Vasavi Electronics, Secunderabad) was used.

3. Results and discussion

Photoelectroactivity data, obtained using zinc selenide prepared by electrochemical co-deposition in conjunction with a platinum counterelectrode when zinc sulphate solutions of different concentrations containing the I^-/I_2 redox couple are used, are summarized in Table I. A significant improvement in activity with increase in concentration is observed. The variations of photopotential E_p, and photocurrent I_p with relative light intensity are shown in Figs 1 and 2, respectively.

While I_p varies linearly with light intensity, E_p

TABLE I Photoelectroactivity of zinc selenide in different solutions; each zinc sulphate solution contains 0.1 M KI and 50 mM I_2

Electrolyte solution	E_D (mV)	E_L (mV)	E_P (mV)	I_D (μA)	I_L (μA)	I_P (μA)
1M $ZnSO_4$	−154	+171	325	−0.4	30.5	30.9
2M $ZnSO_4$	−300	+186	486	−0.6	52.9	53.5
4M $ZnSO_4$	−310	+250	560	−2.5	69.8	72.3

TABLE II Photopotential build-up and half-time decay characteristics of zinc selenide in solutions of different composition

Electrolyte solution	R_b^i (mV sec^{-1})	$t_{1/2}^d$ (sec)
1M $ZnSO_4$ + 0.1 M KI + 50 mM I_2	725	2.4
2M $ZnSO_4$ + 0.1 M KI + 50 mM I_2	2250	4.2
4M $ZnSO_4$ + 0.1 M KI + 50 mM I_2	2350	6.6

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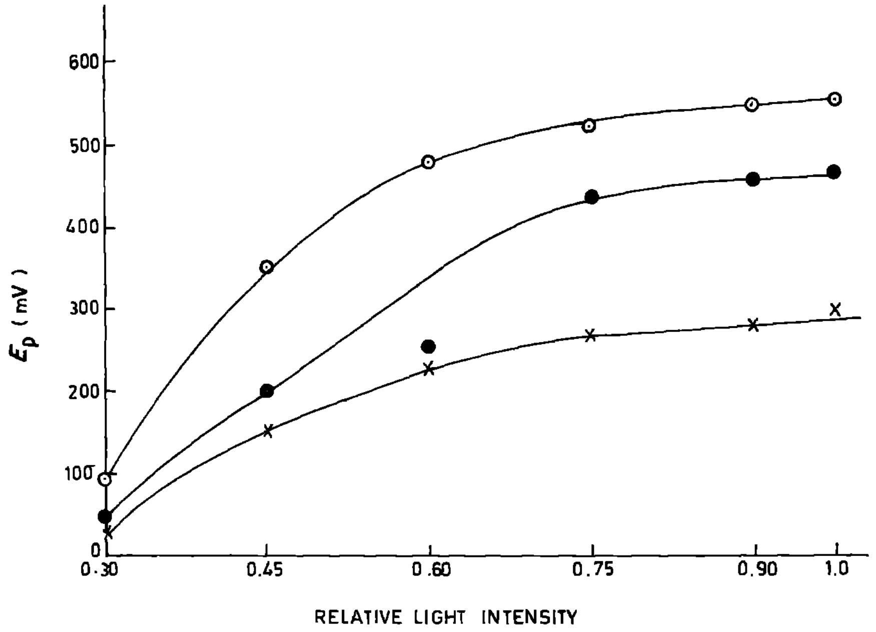

Figure 1 Variation of photopotential with relative light intensity. (×) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (●) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (⊙) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

exhibits a tendency towards saturation at higher light intensities. E_p against log (light intensity) plots are straight lines in all cases, demonstrating the semiconducting nature [8] of zince selenide (Fig. 3). The initial rates of build-up of photopotentials summarized in Table II also indicate enhanced photoresponsiveness when zinc sulphate solutions having higher concentration are used. Current–voltage data given in Fig. 4 are also in agreement with the preceding observations. It therefore appears that charge separation and transfer in the semiconductor electrolyte interfacial region occurs more efficiently with increase in concentration of zinc sulphate. This may arise on account of a modification of the electrical character of the semiconductor electrolyte interface because of preferential accumulation of ionic species present in the solution. The electrical potentials of the electrode E_D, measured in the dark w.r.t. a saturated calomel electrode (Table I) clearly show that the interfacial region acquires enhanced negative charge at higher zinc sulphate concentrations. This alteration in the electrical character of the interfacial region may modify the kinetics of the optically driven electroreduction reaction

$$\tfrac{1}{2}I_2 + e^- \rightarrow I^- \qquad (1)$$

The enhanced negative character of the interface not only facilitates removal of the product species, I^- ions, but may also result in easier accessibility of iodine molecules for electroreduction. It may also be noted at this stage that an increase in the concentration of potassium iodide does not affect the observed photoelectroactivity. In view of the small magnitudes of the photocurrents, the possibility of polarization of the platinum counterelectrode does not exist.

The Mott–Schottky plots [9] included in Fig. 5

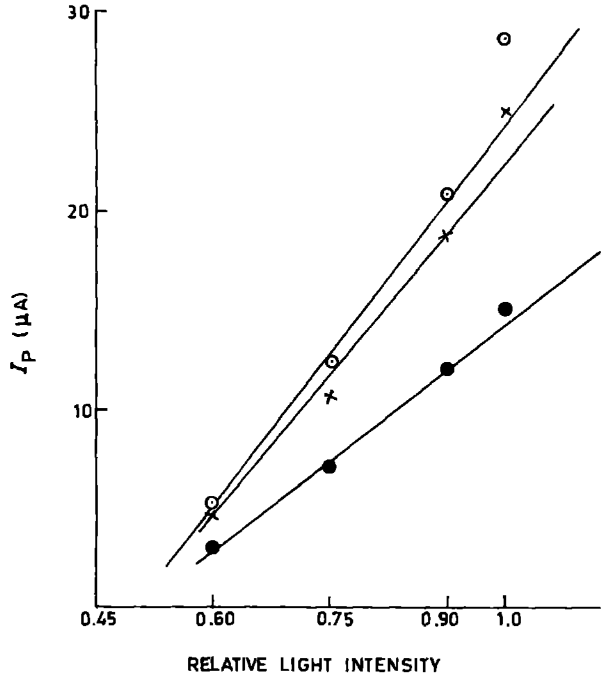

Figure 2 Dependence of photocurrent on relative light intensity. (●) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (×) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (⊙) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

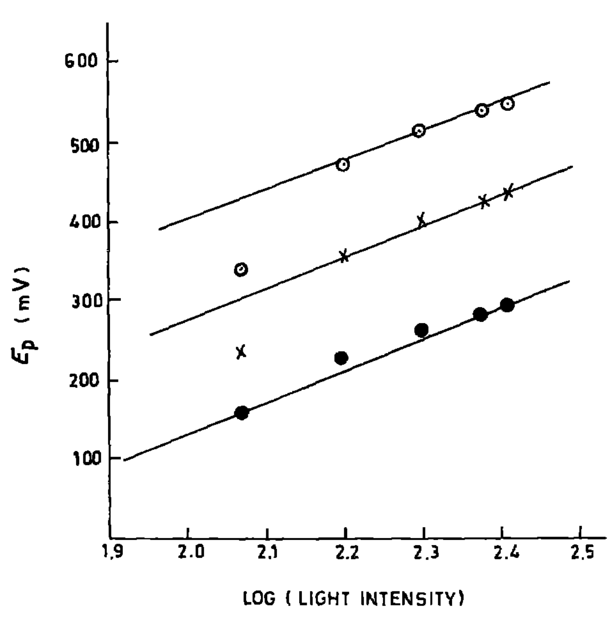

Figure 3 E_p against log (light intensity) curves. (●) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (×) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (⊙) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

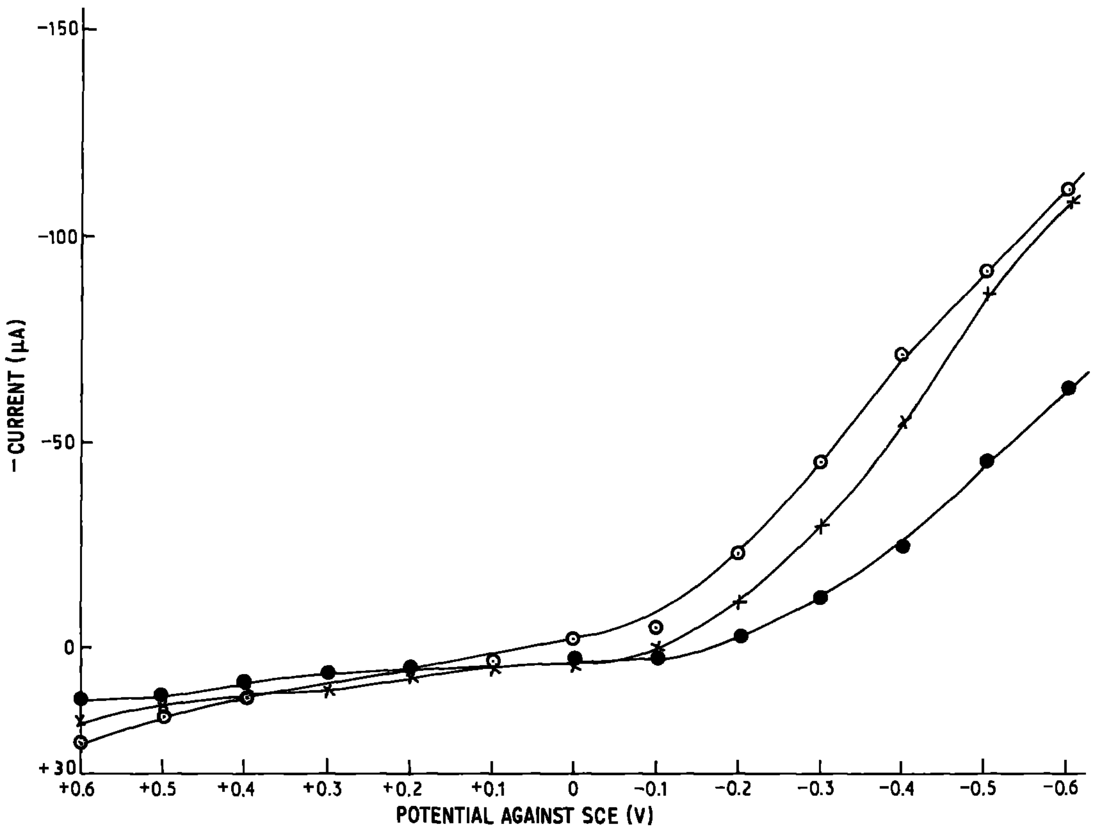

Figure 4 Photocurrent voltage characteristics. (●) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (⊙) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (×) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

do not show a significant change in flat band potentials with concentration. The charge carrier densities derived from the slopes of these plots are included in Table III. The charge carrier density is related to the slope of the M–S plot by

$$n_D = \frac{2}{\varepsilon\varepsilon_0 q(\text{slope})} \qquad (2)$$

where n_D = charge carrier density, ε and ε_0 = dielectric constants of the vacuum and semiconductor, respectively, and q = electronic charge.

The applicability of the first-order rate law for photopotential build-up is verified in Fig. 6, wherein log $[(E_P)^0 - (E_P)_t]$ against t plots are seen to be linear. $(E_P)^0$ is the steady state value of the photopotential. Rate constant values derived from the slopes of these plots are included in Table III. Photopotential decay occurs relatively slowly, as indicated by the half-time decay $t^{d}_{1/2}$ values given in Table II.

TABLE III Values of charge carrier density, n_D, and the rate constant, K

Electrolyte solution	n_D (cm^{-3})	K (sec^{-1})
1M $ZnSO_4$ + 0.1M KI + 50 mM I_2	0.79×10^{15}	2.24
2M $ZnSO_4$ + 0.1M KI + 50 mM I_2	1.29×10^{15}	3.68
4M $ZnSO_4$ + 0.1M KI + 50 mM I_2	1.23×10^{15}	3.89

Zinc selenide prepared by electrochemical codeposition exhibits p-type semiconductivity. Its band gap is 2.7 eV and in combination with a suitable n-type semiconductor it may be used to form a heterojunction photoelectrochemical cell. It has already been shown that n-type polycrystalline cadmium selenide exhibits reasonable activity in cadmium acetate solution containing the I^-/I_2 redox couple [10]. In the present investigation we have studied the photoelectroactivity of the cell formed by a combination of zinc selenide and cadmium selenide. The cell may be represented as

$$\begin{gathered}\text{CdSe}\,|1\text{M}\ Cd(CH_3COO)_2 + 0.1\text{M KI} + 50\,\text{mM}\ I_2 \\ \|2\text{M}\ ZnSO_4 + 0.1\text{M KI} + 50\,\text{mM}\ I_2|\ \text{ZnSe}\end{gathered} \qquad (3)$$

Cadmium acetate and zinc sulphate solutions were connected through a salt bridge. The two electrodes were first illuminated separately and their photopotentials measured with respect to a platinum counter-

TABLE IV Photoelectroactivity of p–n photoelectrochemical cell [3]

Electrode system*	E_D (mV)	E_L (mV)	E_P (mV)	R^{i}_{b} (mV sec^{-1})	I_D (μA)	I_L (μA)	I_P (μA)
ZnSe/Pt	−188	+102	290	1550	−10.0	+20.9	30.9
CdSe/Pt	+66	−240	−306	1450	−0.3	+15.9	16.2
ZnSe/CdSe	−26	−660	686	3250	+0.1	+38.3	38.2

*ZnSe was tested in 1M $ZnSO_4$ + 0.1M KI + 50 mM I_2; CdSe was tested in 1M $(CH_3COO)_2Cd$ + 0.1M KI + 50 mM I_2; for testing ZnSe/CdSe, the two solutions were connected by a salt bridge.

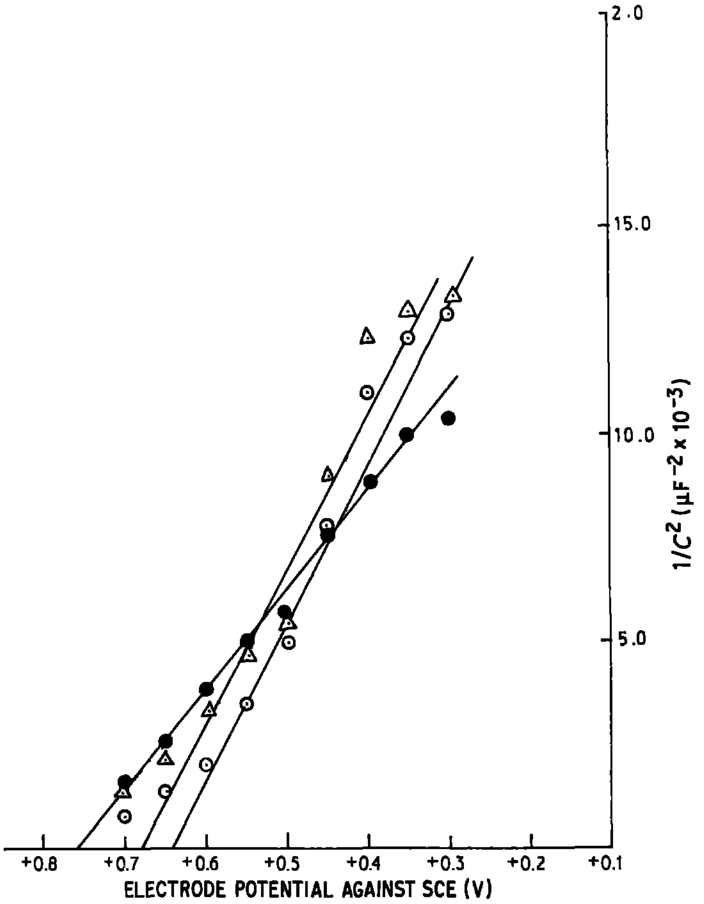

Figure 5 Mott–Schottky plots. (⊙) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (×) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (●) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

TABLE V Photoelectroactivity of ZnSe, CdSe, and ZnSe/CdSe electrodes in mixed electrolyte, 2M $ZnSO_4$ + 1M $Cd(CH_3COO)_2$ + 0.1M KI + 50 mM I_2

Electrode system	E_D (mV)	E_L (mV)	E_P (mV)	R_b^i (mV sec^{-1})	I_D (μA)	I_L (μA)	I_P (μA)
ZnSe/Pt	−256.0	−1129.0	385.0	1700.0	−6.0	+21.2	27.2
CdSe/Pt	−330.0	−645.0	−315.0	1750.0	−3.0	+304.0	307.0
ZnSe/CdSe	+110.0	+780.0	670.0	3250.0	+1.0	+98.0	97.0

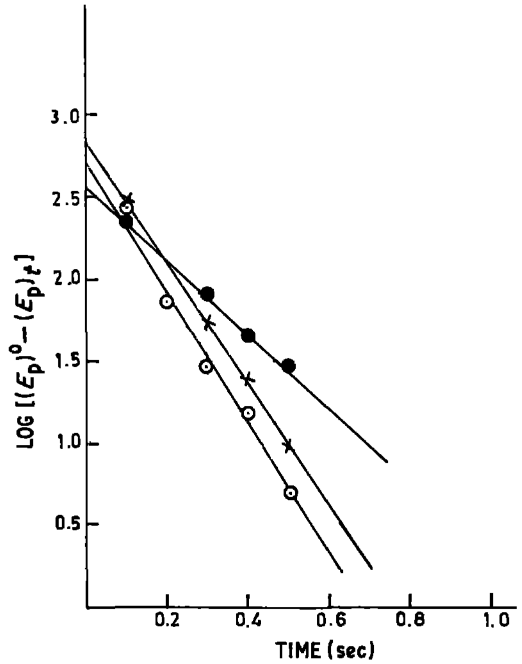

Figure 6 Test of the validity of the equation $E_P = E_P^0 e^{-Kt}$. (⊙) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (×) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2; (⊙) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2.

electrode. Photopotentials were also measured when both the semiconductor electrodes were illuminated together. Experimental results summarized in Table IV clearly show that enhanced photoresponsiveness is obtained upon simultaneous illumination of both the electrodes. Photopotential build-up and decay plots are shown in Fig. 7. The initial rates of build up derived from these plots are also included in Table IV.

From a practical view point a p–n heterojunction cell having a common electrolyte will be more desirable. In order to explore this possibility we investigated the performance of the cell

$$\text{ZnSe}\ |2\text{M ZnSO}_4 + 1\text{M Cd(CH}_3\text{COO)}_2 + 0.1\text{M KI} + 50\text{mM I}_2|\ \text{CdSe} \qquad (4)$$

Essential results are summarized in Table V. It is seen that the set-up of Cell 4 exhibits reasonably improved photoelectroactivity. It is interesting to note that no significant impairment in functional activity of the system is observed for the period of study (Fig. 8).

These results clearly demonstrate that enhanced photoresponsiveness is obtained from the heterojunction photoelectrochemical cell wherein cadmium selenide is combined with zinc selenide.

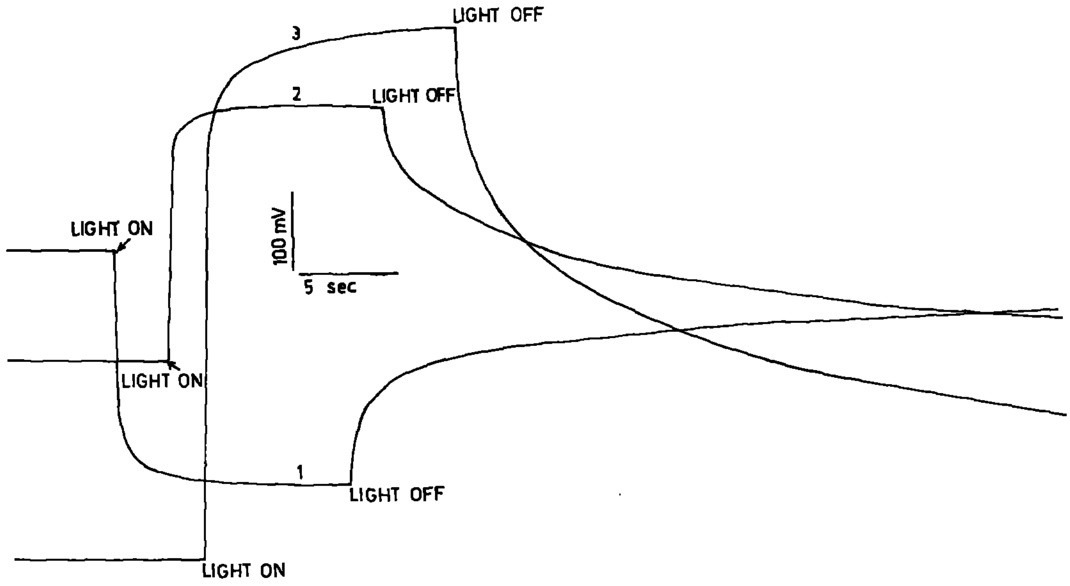

Figure 7 Photopotential build-up and decay curves for p–n PEC cell. (1) n-CdSe|1 M $Cd(CH_3COO)_2$ + 0.1 M KI + 50 mM I_2|Pt; (2) n-ZnSe|2M $ZnSO_4$ + 0.1 M KI + 50 mM I_2|Pt; (3) n-CdSe|1 M $Cd(CH_3COO)_2$ + 0.1 M KI + 50 mM I_2||2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2|p-ZnSe.

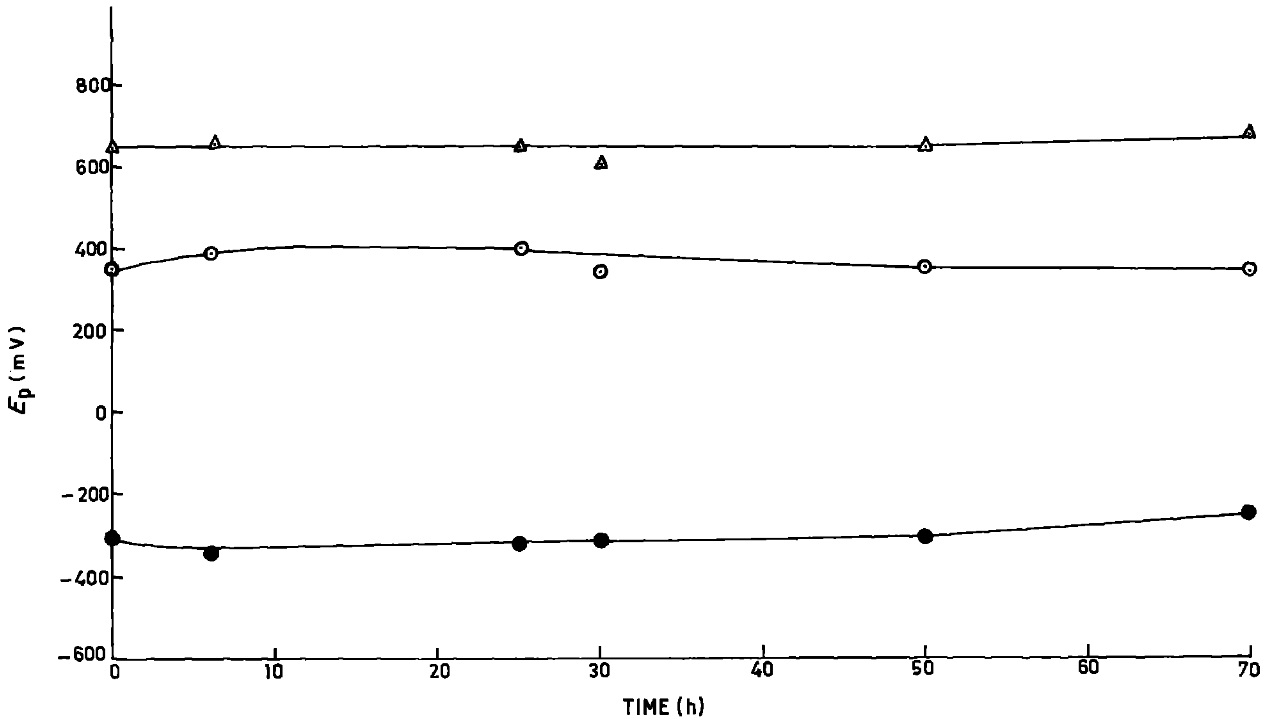

Figure 8 Function stability in mixed electrolyte containing 2 M $ZnSO_4$ + 1M $Cd(CH_3COO)_2$ + 0.1 M KI + 50 mM I_2 for p–n photoelectrochemical cell. (○) ZnSe|Pt, (●) CdSe|Pt, (△) ZnSe|CdSe.

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