

Electrosynthesis and photoelectroactivity of polycrystalline *p*-zinc selenide

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Abstract. The photoelectroactivity of polycrystalline zinc selenide films prepared by electrochemical codeposition 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.

Keywords. Photoelectrochemical cell; electrochemical codeposition; semiconductor photoelectrochemistry; energy conversion.

1. Introduction

Cadmium chalcogenides are among the most studied materials for photoelectrodes in photoelectrochemical cells (Ellis *et al* 1976; Heller *et al* 1977; Cahen and Hodes 1978). These electrodes exhibit reasonable conversion efficiencies and successfully resist the impairment in functional activity when illuminated in aqueous polysulphide solutions. The photoelectroactivity of zinc selenide has also been studied to some extent (Lemasson and Gautson 1981; Lemasson *et al* 1982; Russak 1982). Zinc selenide usually exhibits *n*-type semiconductivity. For solar energy conversion *p*-type semiconductors with acceptable stability and compatibility are important so that enhanced photoresponsiveness when illuminated may become possible. We have prepared zinc selenide electrodes by electrochemical codeposition using limiting currents to study their photoelectroactivity in aqueous zinc sulphate solution containing the I^-/I_2 redox couple. All preparations exhibit *p*-type semiconductivity. Capacitance was measured for characterization in terms of flat band potential. The current-voltage behaviour in dark and under illumination along with the capacitance data were used to establish their *p*-type semiconductivity. The observed photopotentials vary with light intensity and exhibit a tendency towards saturation at higher light intensities.

2. Experimental

The procedure as reported earlier (Singh and Rai 1985; Singh *et al* 1986) was used for preparing zinc selenide electrodes. A titanium plate (1.69 cm²) was cleaned with emery paper, polished with diamond paste (Madras Metallurgical Service Limited) and washed successively with acetone and deionized water. It was then soaked for about an hour using zinc sulphate and SeO₂ of known composition. The limiting current needed for electrochemical codeposition of zinc selenide was determined in the usual manner (Glasston 1971; Vagramyan and Solov'eva 1961) by varying the potential of the titanium electrode with respect to a saturated calomel electrode

using an electronically operated power supply (Hindustan Power Tronic Inc) and measuring the current between the titanium electrode and a platinum electrode. Deposition was carried out for about 4 h. The thickness of the zinc selenide film was 5×10^{-4} cm.

A simple experimental arrangement (Ellis *et al* 1976) was used for testing the photoelectroactivity of the zinc selenide preparations. Zinc sulphate solution containing KI and I_2 was used to combine the zinc selenide electrode with a platinum counterelectrode to form the photoelectrochemical cell. A tungsten lamp (1000 W) was used for illumination and the photopotential thus generated was measured using a digital multimeter (HIL 2142, Delhi) with a least count of 0.1 mV. The photopotential build-up and decay were recorded (Anika recorder A-4) and the current-voltage characteristics both in dark and under illumination were studied using a standard potentiostat (DB Electronics, Pune model 1078). 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 codeposition in conjunction with a platinum counterelectrode are summarized in table 1. Zinc sulphate solutions of different concentrations containing the I/I_2 redox couple were used. The variations of photopotential E_p , and photocurrent I_p with relative light intensity are shown in figures 1 and 2 respectively.

Table 1. 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_I (mV)	E_P (mV)	I_D (μ A)	I_L (μ A)	I_P (μ A)
1 M $ZnSO_4$	-154	+171	325	-0.4	30.5	30.9
2 M $ZnSO_4$	-300	+186	486	-0.6	52.9	53.5
4 M $ZnSO_4$	-310	+250	560	-2.5	69.8	72.3

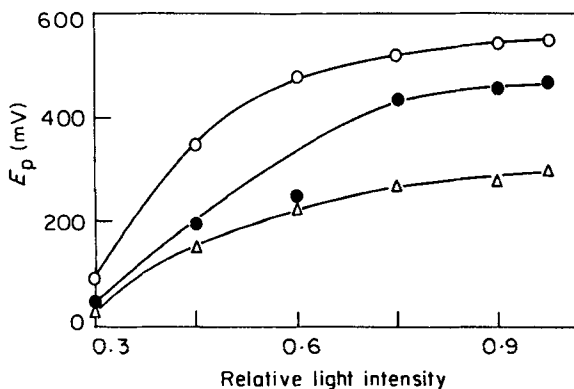


Figure 1. Variation of photopotential with relative light intensity. (Δ) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 ; (\bullet) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 ; (\circ) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 .

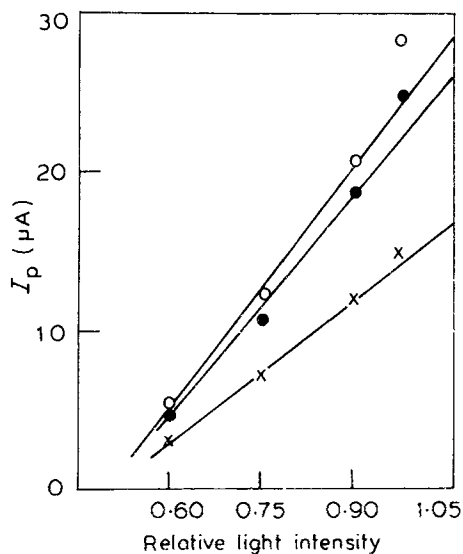


Figure 2. Dependence of photocurrent on relative light intensity. (○) 4 M ZnSO_4 + 0.1 M KI + 50 mM I_2 ; (●) 2 M ZnSO_4 + 0.1 M KI + 50 mM I_2 ; (x) 1 M ZnSO_4 + 0.1 M KI + 50 mM I_2 .

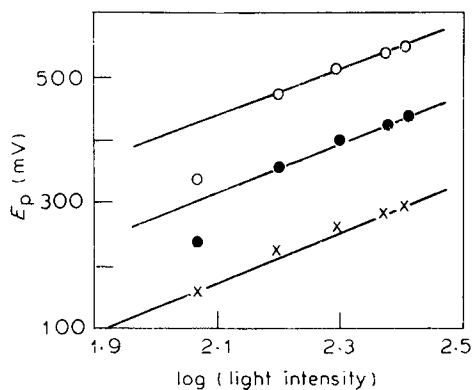


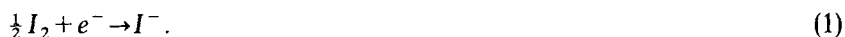
Figure 3. E_p against log (light intensity) curves. (○) 4 M ZnSO_4 + 0.1 M KI + 50 mM I_2 ; (●) 2 M ZnSO_4 + 0.1 M KI + 50 mM I_2 ; (x) 1 M ZnSO_4 + 0.1 M KI + 50 mM I_2 .

Table 2. Photopotential build-up and half-time decay characteristics of zinc selenide in solutions of different composition.

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

While I_p varies linearly with light intensity, E_p 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 (Davidson *et al* 1979) of zinc selenide (figure 3). The initial rates of build-up of photopotentials (table 2) also indicate enhanced photoresponsiveness when zinc sulphate solutions with higher concentration are used. Current-voltage data (figure 4) agree with the above 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 dark about a saturated calomel electrode (table 1) 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



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 arise.

The Mott-Schottky plots (Fu-Ren and Bard 1981) included in figure 5 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 3. The charge carrier density is related to the slope of the M-S plot by

$$n_D = 2/[\varepsilon \varepsilon_0 q (\text{slope})], \quad (2)$$

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

The applicability of the first-order rate law for photopotential build-up can be verified in figure 6, wherein $\log [(E_p)^0 - (E_p)_t]$ against t plots are 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 3. Photopotential decay occurs relatively slowly, as indicated by the half-time decay $t_{1/2}^d$ values given in table 2.

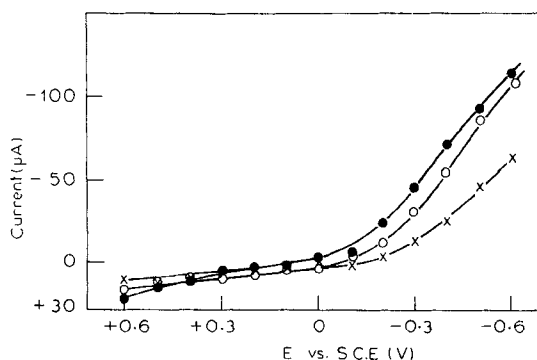


Figure 4. Photocurrent voltage characteristics. (●) 4 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 ; (○) 2 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 ; (x) 1 M $ZnSO_4$ + 0.1 M KI + 50 mM I_2 .

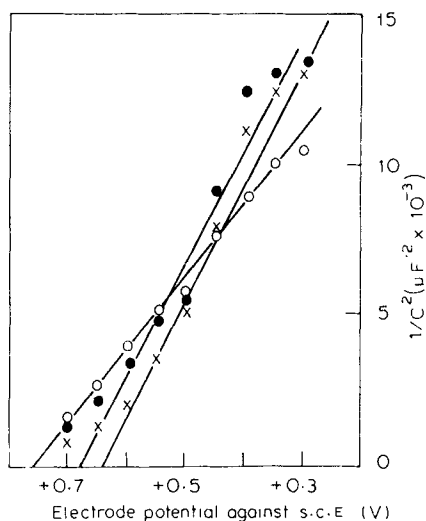


Figure 5. Mott-Schottky plots. (○) 4 M ZnSO₄ + 0.1 M KI + 50 mM I₂; (●) 2 M ZnSO₄ + 0.1 M KI + 50 mM I₂; (x) 1 M ZnSO₄ + 0.1 M KI + 50 mM I₂.

Table 3. Values of charge carrier density n_D and the rate constant K .

Electrolyte solution	n_D (cm ⁻³)	K (s ⁻¹)
1 M ZnSO ₄ + 0.1 M KI + 50 mM I ₂	0.79×10^{15}	2.24
2 M ZnSO ₄ + 0.1 M KI + 50 mM I ₂	1.29×10^{15}	3.68
4 M ZnSO ₄ + 0.1 M KI + 50 mM I ₂	1.23×10^{15}	3.89

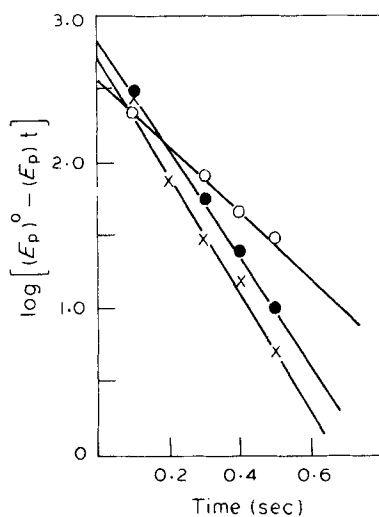
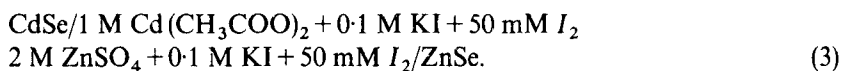


Figure 6. Test of the validity of the equation $E_p = E_p^0 \exp(-kt)$.

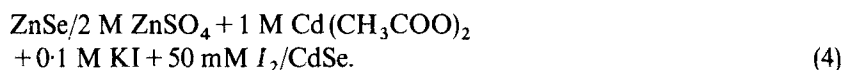
Zinc selenide prepared by electrochemical codeposition exhibits *p*-type semi-conductivity. Its band gap is 2.7 eV and in combination with a suitable *n*-type

semiconductor it may be used to form a heterojunction photoelectrochemical cell. It was shown that *n*-type polycrystalline cadmium selenide exhibits reasonable activity in cadmium acetate solution containing the I^-/I_2 redox couple (Singh *et al* 1986). We have studied the photoelectroactivity of the cell formed by a combination of zinc selenide and cadmium selenide. The cell may be represented as



Cadmium acetate and zinc sulphate solutions were connected through a salt bridge. The two electrodes were illuminated separately and their photopotentials measured about a platinum counterelectrode. Photopotentials were also measured when both the semiconductor electrodes were illuminated together. Experimental results summarized in table 4 clearly show enhanced photoresponsiveness when both the electrodes were simultaneously illuminated. Photopotential build-up and decay plots are shown in figure 7. The initial build-up rates derived from these plots are also shown in table 4.

From a practical viewpoint a *p-n* heterojunction cell with a common electrolyte is desirable. To explore this possibility the performance of the cell was studied.



The results summarized in table 5 show that the PEC cell (4) exhibits improved

Table 4. Photoelectroactivity of *p-n* photoelectrochemical cell 3.

Electrode system*	E_D (mV)	E_L (mV)	E_P (mV)	R_b^i (mV s^{-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 1 M ZnSO₄ + 0.1 M KI + 50 mM I₂; CdSe was tested in 1 M (CH₃COO)₂ Cd + 0.1 M KI + 50 mM I₂; for testing ZnSe/CdSe, the two solutions were connected by a salt bridge.

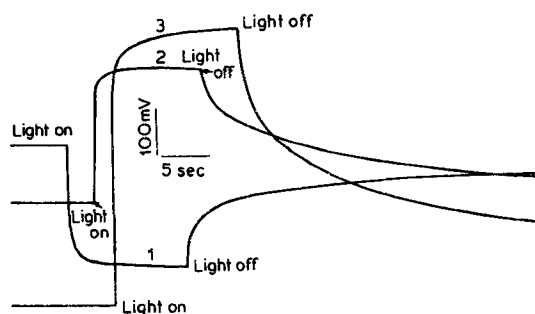
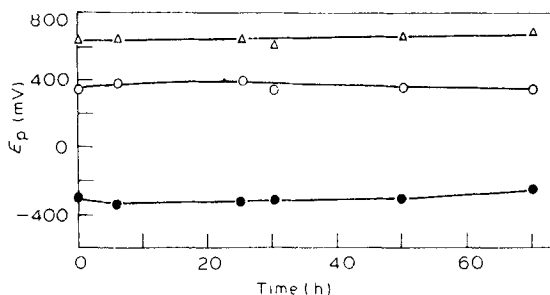


Figure 7. Photopotential build-up and decay curves for *p-n* PEC cell. 1. *n*-CdSe 1 M Cd(CH₃COO)₂ + 0.1 M KI + 50 mM I₂ Pt; 2. *n*-ZnSe 2 M ZnSO₄ + 0.1 M KI + 50 mM I₂ Pt; 3. *n*-CdSe 1 M Cd(CH₃COO)₂ + 0.1 M KI + 50 mM I₂ 2 M ZnSO₄ + 0.1 M KI + 50 mM I₂ *p*-ZnSe.

Table 5. Photoelectroactivity of ZnSe, CdSe and ZnSe/CdSe electrodes in mixed electrolyte, 2 M ZnSO₄ + 1 M Cd(CH₃COO)₂ + 0.1 M KI + 50 mM I₂.

Electrode system	E_D (mV)	E_L (mV)	E_P (mV)	R_b^i (mV s ⁻¹)	I_D (μA)	I_L (μA)	I_P (μA)
ZnSe/Pt	-256	-1129	385	1700	-6	+21	27
CdSe/Pt	-330	-645	-315	1750	+3	+304	307
ZnSe/CdSe	+110	-780	670	3250	+1	+98	97

**Figure 8.** Function stability in mixed electrolyte containing 2 M ZnSO₄ + 1 M Cd(CH₃COO)₂ + 0.1 M KI + 50 mM I₂ for p-n photoelectrochemical cell. (○) ZnSe/Pt, (●) CdSe/Pt, (△) ZnSe/CdSe.

photoelectroactivity. No significant impairment in functional activity of the system was observed during this study (figure 8).

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

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