CHAPTER 8

EFFECT OF IODINE CONCENTRATIONS AND TEMPERATURE ON THE PERFORMANCE OF PEC CELLS BASED ON MoS_xSe_{2-x} ELECTRODES

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8.1 Introduction

There have been several discussions in recent years on photoelectrochemical (PEC) methods of solar energy conversion. An important factor affecting the conversion efficiency is the electrolyte. The detailed studies have been carried out by various workers[1-19] on the photoelectrochemical behaviour of MoS_2 and $MoSe_2$ in contact with different aqueous and non-aqueous redox electrolytes. Their results have indicated the iodide/iodine, I^-/I_2 system to be optimal redox couple for the best performance and stability. Since the light conversion efficiency of the cell based on I^-/I_2 depends upon iodine content of the redox couple, the iodine concentration has been optimised in the present work for better conversion efficiencies of MoS_xSe_{2-x} photoelectrodes.

Further a key element of PEC devices is the semiconductor-electrolyte interface. The degree of effectiveness of minority carrier charge transfer across this interface will have direct bearing on the ultimate energy conversion efficiency of the system. The strategy of enhancing this charge exchange by elevating the temperature has the added advantage of utilizing the near IR region of solar spectrum, which otherwise would be wasted. Temperature also has beneficial effects on the optical properties of the semiconductor. An effort has therefore been made to critically evaluate the effect of temperature on the photovoltaic performance of MoS_xSe_{2-x} photoelectrodes.

8.2 Results and Discussions

Iodine concentration effect

The grown single crystals of molybdenum sulphoselenides as photoelectrodes and platinum grid as counter electrode have been used for fabrication of PEC cells. The photoelectrochemical glass cell (Fig. 8.1) has been so designed that the electrolyte can be changed without disturbing the electrode position. Electrolytes of different concentrations of iodine are prepared by addition of 2 M NaI, 0.5 M Na_2SO_4 and 0.5 M H_2SO_4 in double distilled water. All the chemicals are of A.R. grade. The effect of iodine concentration on open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor and efficiency (n %) for MoS_xSe_{2-x}, $0 \leq x \leq 2$ are shown in Figs. 8.2, 8.3, 8.4 and 8.5 respectively. Fig. 8.2 indicates that the open circuit voltage increases initially and then either decreases or remains constant as iodine concentration increases. The fill factor shows an increasing trend (Fig. 8.4), while the short circuit current I_{sc} decreases (Fig. 8.3). The net result is

Fig. 8.1	Experimental set up of PEC cell for study of iodine concentrations.
Fig. 8.2	Plots of open circuit voltages (V_{OC}) versus iodine concentrations I_2 (M) for PEC cells with molybdenum sulphoselenides photoelectrodes. $I_L = 100$ mw/cm^2.
Fig. 8.3	Plots of short circuit currents (I_{SC}) versus iodine concentrations I_2(M), for PEC cells with molybdenum sulphoselenides photoelectrodes. $I_L = 100$ mw/cm^2

Fig. 8.1

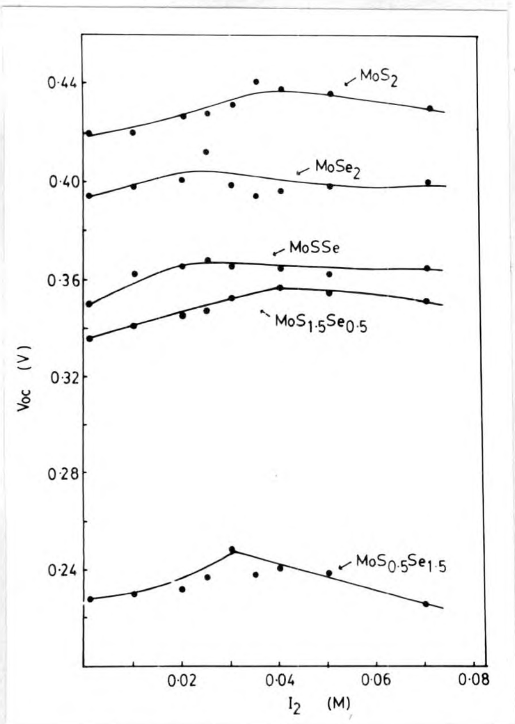

Fig. 8.2

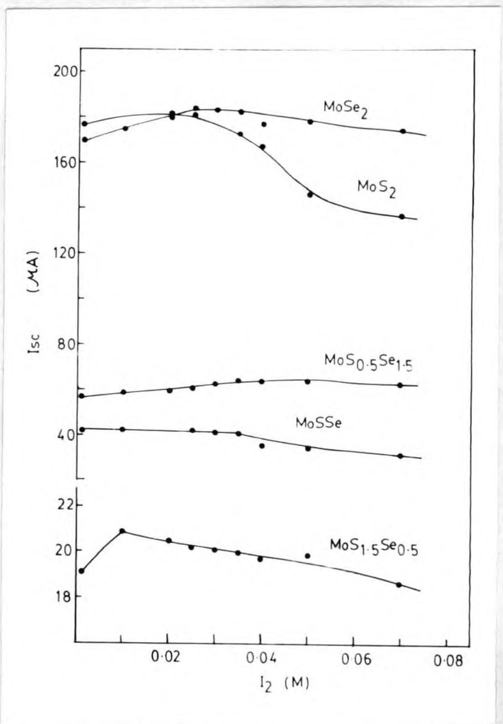

Fig. 8.3

that the energy conversion efficiencies of PEC cells based on molybdenum sulphoselenides photoelectrodes are affected by changing the iodine concentration from 0.001 to 0.07 M I_2. The decrease in efficiency at higher concentration of iodine is due to absorption of light in electrolyte which result into lower short circuit currents. The decrease in efficiencies can also be attributed to the presence of large amounts of elemental iodine which can interact with the surface and generate surface states which can trap charges of either sign. This causes large changes of potential drop in Helmholtz double layer as well as shifts in the energy position on band edges. The amount of iodine adsorption, which affects the band bending in the semiconductor can also be considered as a factor affecting efficiency11).

Temperature effect

The photoelectrochemical cell assembly described in chapter 7 has been used for studying the effect of temperature. A fresh electrolyte (prepared by mixing A.R. grade 0.025 M I_2, 2 M NaI, 0.5 M Na_2SO_4, 0.5 M H_2SO_4 in double distilled water) has been used. The temperature of the electrolyte has been measured with the help of a mercury thermometer. Photocurrent-voltage measurements have been made at the different temperatures, keeping the intensity of

Fig. 8.4	Plots of fill factors versus iodine concentration I_2 (M), for PEC cells with molybdenum sulphoselenides photoelectrodes. $I_L = 100$ mw/cm^2.
Fig. 8.5	Plots of efficiencies versus iodine concentrations I_2 (M) for PEC cells with molybdenum sulphoselenides photoelectrodes. $I_L = 100$ mw/cm^2.
Fig. 8.6(a)	Plots of variations of short circuit current, I_{SC}, and open circuit voltage V_{OC} of $MoSe_2$, $MoS_{0.5}Se_{1.5}$ and MoSSe based PEC cells, with the temperatures.
Fig. 8.6(b)	Plots of variations of short circuit current, I_{SC} and open circuit voltage V_{OC} of $MoS_{1.5}Se_{0.5}$ and MoS_2 based PEC cells, with the temperatures.

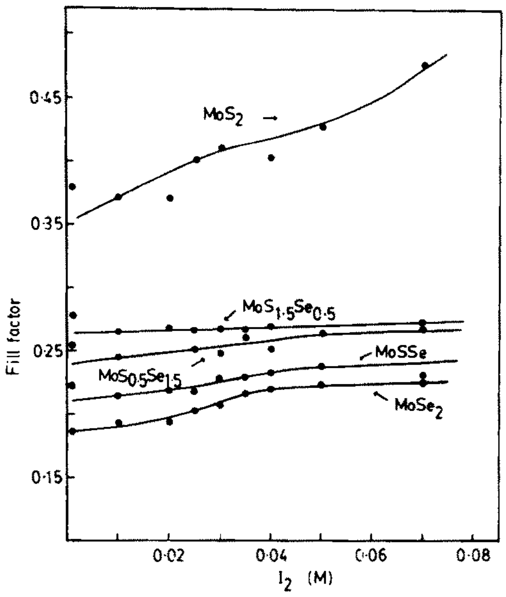

Fig. 8.4

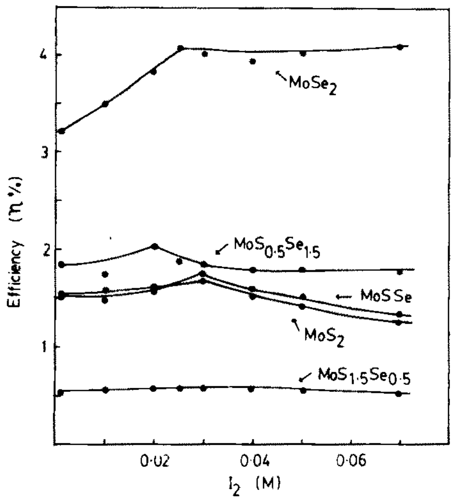

Fig. 8.5

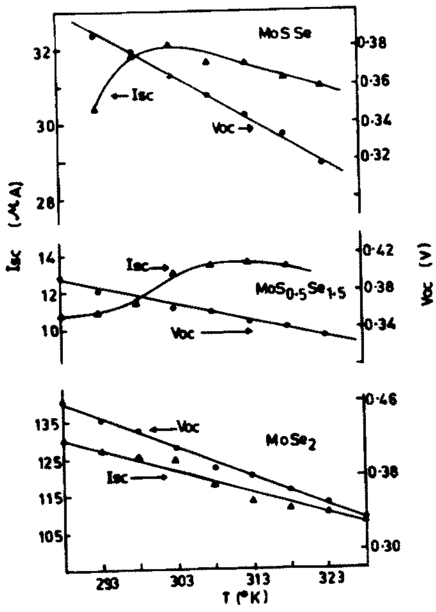

Fig.8.6(a)

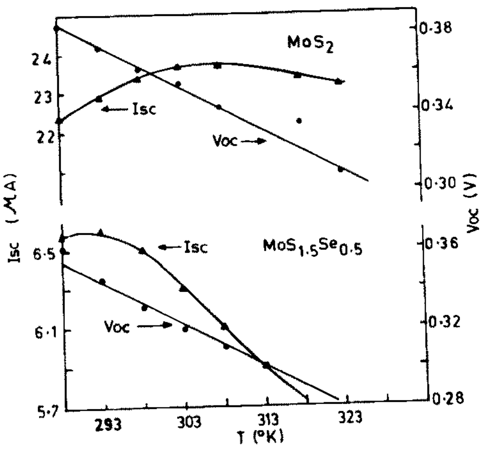

Fig. 8.6(b)

illumination constant (100 mw/cm^2). During heating the electrolyte is continuously stirred with a magnetic stirrer to maintain a uniform temperature.

Curves showing short circuit currents (I_{sc}) and open circuit voltages (V_{oc}), at different temperatures are illustrated in Fig. 8.6(a) and Fig. 8.6(b). The open circuit voltages are found to decrease with increase in temperature. This decreasing trend of open circuit voltage is in confirmation with the observations of Skyllas Kozacos et al[20)] and Djemal et al[21)] for $MoSe_2$ and MoS_2 respectively. This decrease can be explained by applying the Schottky barrier model through the equation[22)],

$$V_{oc} = \frac{nkT}{e} \ln (I_{ph}/I_o) \qquad (8.1)$$

where I_o is the reverse saturation current, I_{ph} is the photocurrent and n is the diode quality factor. The reverse saturation current I_o, in the above equation is found to increase with increase in temperature satisfying the following relation,

$$I_o = A^* T^2 \exp (-\phi_b/kT) \qquad (8.2)$$

Here A^* is Richardson constant and ϕ_b is the barrier height. Therefore according to Schottky barrier model the open circuit voltage V_{oc} depends upon I_o, the reverse saturation current , which in turn depends upon the temperature. The rates of decrease of the open circuit voltage V_{oc} with the temperature are given in Table 8.1 and are compared with the rates reported by other workers.

Fig. 8.6 (a, b) reveals that the peaks in short circuit currents (I_{sc}) are observed for all compounds in the series MoS_xSe_{2-x}, $x \neq 0$ except $MoSe_2$. It may also be noted that the band gap of compound for $x = 0$ (i.e. $MoSe_2$) is found to be smaller than rest of the compounds in the series MoS_xSe_{2-x} for which it is seen to increase with x. At present author is not able to correlate the presence of a peak in I_{sc} for compounds $x \neq 0$ and its absence for compound $x = 0$ i.e. $MoSe_2$ with the band gap. However, nature of I_{sc} for compounds ($x \neq 0$) can be explained as follows.

The initial increase in short circuit current I_{sc} (Fig. 8.6 (a,b)) is attributed to the increase in absorption coefficient of semiconductor[23)]. According to Rajeshwar et al[24)], the increase in short circuit current

Table 8.1

Rate of decrease of open circuit voltage

Compound	This work mV/°C	Reported work mV/°C
$MoSe_2$	3.08	3.2[20)]
$MoS_{0.5}Se_{1.5}$	2.00	
MoSSe	2.5	
$MoS_{1.5}Se_{0.5}$	2.02	
MoS_2	2.02	

I_{sc} has its origin both on temperature induced changes in the optical and electrical properties of semiconductor and corresponding variations in the potential and charge distribution across the semiconductor-electrolyte interface. It is observed by Agarwala et al$^{25)}$ that

(i) the wavelength response shifts toward infrared with increasing temperature because of bandgap narrowing

(ii) the diffusion length of photogenerated carriers increases with increasing temperature, and

(iii) the absorption coefficient at longer wavelength increases with increasing temperature because of bandgap narrowing.

All these collectively cause increase in I_{sc} with increasing temperature.

The increase in short circuit current (Fig. 8.6 (a,b)) is however limited at higher temperatures. The decrease in short circuit current I_{sc} at higher temperatures is explained by Skyllas Kazacos et al$^{20)}$ as follows. The short circuit current $I_{sc}(\lambda, T)$ can be approximated by Gartner's expression$^{26)}$ as

$$I_{sc}(\lambda, T) \simeq e\phi_o(\lambda) \left\{ 1 - \frac{e^{-\alpha(\lambda, T)[\phi_b(T)]^{1/2} W_o}}{1 + \alpha(\lambda, T)L_p} \right\} \qquad (8.3)$$

where $\phi_o(\lambda)$ is the photon flux, W_o is the width of the space charge layer for a potential drop of 1 V, L_p is the hole diffusion length and $\phi_b(T)$ is the barrier height. Thus $I_{sc}(\lambda, T)$ can either increase or decrease with increasing temperature depending on relative changes of $\alpha(\lambda, T)$ and $\phi_b(\lambda, T)$ with temperature. In the present study the short circuit currents decrease at higher temperatures. Hence, for these cells the decrease in the barrier height dominates the increase in the absorption coefficients with increasing temperature.

Fig. 8.7 illustrates the variation of the efficiency (η %) and fill factor of PEC cells based on molybdenum sulphoselenides, at different temperatures. The efficiency of the PEC cells except $MoS_{1.5}Se_{0.5}$ in the other compounds of the grown series pass through a peak at about 303 °K as the temperature increases. Fig. 8.7 also shows an increasing trend in fill factor for $MoSe_2$, $MoS_{1.5}Se_{0.5}$ and MoS_2, while a peak behaviour for $MoS_{0.5}Se_{1.5}$ and MoSSe photoelectrodes. The peak in efficiency or power is the resultant effect of changes in electrical and optical properties of semiconductor electrolyte junction[24].

8.3 Conclusions

1. The efficiency, fill factor, open circuit voltage

Fig. 8.7 Plots of variations of conversion efficiencies (η %) and fill factors of molybdenum sulphoselenides based PEC cells, with the temperatures.

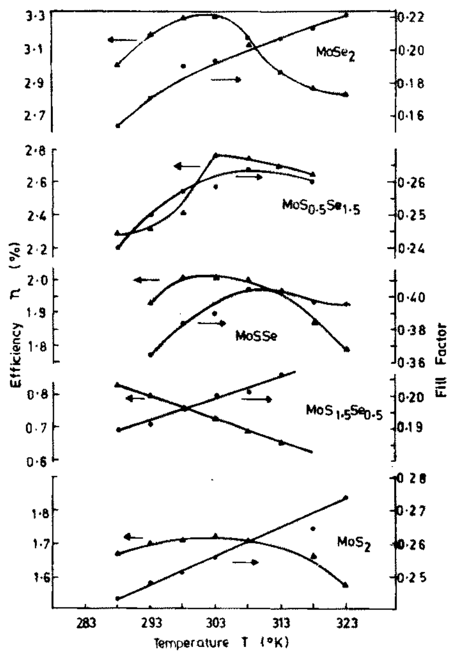
MoSe$_2$
MoS$_{0.5}$Se$_{1.5}$
MoSSe
MoS$_{1.5}$Se$_{0.5}$
MoS$_2$
Efficiency η (%)
Fill Factor
Temperature T (°K)
283
293
303
313
323
3·3
3·1
2·9
2·7
2·8
2·6
2·4
2·2
2·0
1·9
1·8
0·8
0·7
0·6
1·8
1·7
1·6
0·22
0·20
0·18
0·16
0·26
0·25
0·24
0·40
0·38
0·36
0·20
0·19
0 28
0·27
0·26
0·25

Fig. 8.7

and short circuit current of PEC cell is found to depend upon the electrolyte content concentration (Iodine) and operating temperature of cell.

2. The use of more iodine content in electrolyte suggests a decrease in efficiency and short circuit current.

3. The open circuit voltages show a decreasing trend in their values with the increase in temperature.

4. Peak in efficiency is found at about 303°K for all the compounds (MoS_xSe_{2-x}) except $MoS_{1.5}Se_{0.5}$.

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