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Studies on *n*-CdSe/Ti Semiconductor Septum Based Photoelectrochemical Solar Cell in Regard to the Influence of Structural and Compositional Characteristics of the Semiconductor Electrode

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A new type of photoelectrochemical (PEC) solar cell based on semiconductor septum (SC-SEP) photoelectrode has been shown to yield higher electrical power output than the conventional PEC solar cell. In the present study, photoelectrochemical, structural and compositional characteristics of the semiconductor component in *n*-CdSe/Ti septum, based SC-SEP, PEC solar cell, employing some reversible electrolyte systems under prolonged PEC operation (100 h), revealed that the CdSe photoelectrode undergoes deterioration through 'Cd' loss. For example, in the case of the cell Pt, 1 M 3S//*n*-CdSe/Ti//0.1 M $AgNO_3$ (1 M=1 mol dm^{-3}), Pt; CdSe showed loss of 'Cd'. This resulted in decrease of the cell power output (from V_{ph} and I_{sc} of 1.42 V and 20 mA cm^{-2} to 1.3 V and 13 mA cm^{-2} respectively). It has been shown in the present investigation that the best way to arrest semiconductor deterioration was by adding 0.1 M Se to polysulfide electrolyte thereby stabilizing this efficient SC-SEP, PEC cell.

The current energy crisis has rekindled the interest in renewable energy sources aimed at generating electricity and/or fuel. In this respect, active use of solar energy is unique in that it is inexhaustible and does not contribute to global warming. Solar technology includes semiconductor/liquid junction photoelectrochemical (PEC), and solid state photovoltaic solar cell devices and artificial photosynthetic devices etc., in which photoelectrochemical (PEC) solar cell (i.e. the conversion of solar energy to electrical energy or chemical forms) has several advantages over solid state photovoltaic conversion. A new type of PEC solar cell termed as semiconductor-septum based PEC (SC-SEP,PEC) cell shows promise not only for generating electricity but also for producing chemicals. This device suggested and developed by Tien et al.,[1)] works on the process reminiscent of photosynthesis. The idea for the construction of PEC solar cell based on a semiconductor septum is modelled from natural photosynthetic systems with a pigmented bilayer lipid membrane (BLM).[2–6)] In principle, a pigmented BLM which acts as semiconductor (SC) separates two compartments each containing different redox electrolytes. The difference in standard potentials of these redox electrolyte solutions across the membrane electrode in addition to the usual electrolyte/semiconductor, additional band bending at the semiconductor/metal interface in the septum electrode is the driving force for separating and transferring charge carriers under illumination. These carriers collected at two different BLM/electrolyte interfaces can take part in the redox reactions resulting in a significant photocurrent increase. Similarly, in a SC-SEP, PEC cell, electrons and holes are generated in the depletion layer of semiconductor under illumination. The holes migrate to photoexposed surface and oxidize the electrolyte in light compartment, while electrons travel in the bulk of semiconductor to the other electrolyte interface and reduce other redox couple in the dark compartment, thereby giving high output photovoltage than conventional PEC cell.

In spite of their importance, microstructural aspects and stability of SC-SEP, PEC cell have not been reported so far by the earlier workers. The present communication embodies the results of photoelectrochemical and microstructural studies of SC-SEP electrode i.e., the polycrystalline film of *n*-CdSe on Ti (*n*-CdSe/Ti) in contact with sulfide–polysulfide redox electrolyte conforming to the configuration Pt,S^{2-}–S_n^{2-}// *n*-CdSe/Ti// Redox electrolyte, Ag or Pt. The functioning of the SC-SEP electrode under continuous PEC operation with time has been monitored. Investigations on arresting the deterioration of SC-SEP electrode (loss of cadmium) by modifying the electrolyte have been described and discussed.

Experimental

The *n*-type CdSe/Ti septum electrode was prepared following the slurry mixture painting method.[7,8)] The electrode material was etched with dilute HCl for 20 s and washed in freshly prepared sodium sulfide solution. The electrolyte for illuminated compartment was prepared by dissolving 1 M of NaOH, Na_2S, and S (1 M 3S) in double distilled water (1 M=1 mol dm^{-3}). The electrolytes (0.1 M) for the dark compartment were prepared with analytical grade $AgNO_3$, $FeCl_3$/$FeCl_2$, $Ce(SO_4)_2$/$Ce_2(SO_4)_3$, $K_3[Fe(CN)_6]$/$K_4[Fe(CN)_6]$, KI/I_2, in double distilled water. The contacting electrodes used in illuminated and dark compartments were Pt and Ag. The photoelectrochemical (PEC) measurements were carried out in three electrode assembly with Pt (counter) and saturated calomel (reference) electrode placed in light compartment and the other metal (working) electrode in dark compartment. The Lucite SC-SEP cell had a glass window for illumination and Lucite separator with hole, over which the semiconductor septum electrode was glued. The electrochemical measurements were performed using Princeton Applied Research

(PAR) 173 Potentiostat/Galvanostat, PAR 179 I/E Converter, PAR 175 Universal Programmer and Houston 2000 X-Y-t recorder. Illumination was provided by a tungsten lamp of 100 W (Intensity 100 mW cm^{-2}). Impedance measurements of n-CdSe/Ti in contact with polysulfide electrolyte were performed employing PAR 273 Potentiostat and Lock-in Amplifier for Flat-band potential determination. The semiconductor septum electrode n-CdSe/Ti, was structurally characterized through X-ray diffractometry (XRD) using Philips PW-1710 X-ray diffractometer. The changes in surface morphology and elemental composition of CdSe of septum electrode with time were studied using Philips CM-12 Electron Microscope embodying STEM and PV-9900 EDAX (Energy Dispersive Analysis of X-rays) analyzer.

Results and Discussion

Figure 1 shows the current–voltage (I–V) characteristics of conventional single compartment cell Pt, 1 M 3S// n-CdSe/Ti PEC cell. Its photovoltage V_{Ph} (V_{oc}(light)$-V_{\mathrm{oc(dark)}}$) and short-circuit photocurrent I_{sc} (I_{sc}(light)$-I_{\mathrm{sc(dark)}}$) were 0.64 V and 6 mA cm^{-2}. In order to understand the influence of dark compartment with various redox couples on SC-SEP cells, the power output of SC-SEP cell having redox couples like Sn^{4+}/Sn^{2+}, Fe^{3+}/Fe^{2+}, $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, I_3^-/I^-, Ag^+/Ag, and Ce^{4+}/Ce^{3+} in dark compartment were recorded, keeping the constituents of the light compartment (Pt,S^{2-}/S_n^{2-}) unchanged. The theoretical photovoltages expected from these SC-SEP, PEC cells containing various redox electrolytes in dark compartment has been thought to be due to the potential drop between flat-band potential of n-CdSe/S^{2-}–S_n^{2-} interface and E_{redox} of the electrolyte in dark compartment. In order to establish this, we measured the redox potential (E_{redox}) of electrolyte in dark compartment and flat-band potential of n-CdSe. The E_{redox} of various electrolytes in dark compartment was computed against SCE reference electrode, from their standard redox potential (E°) values[9] using Nernst

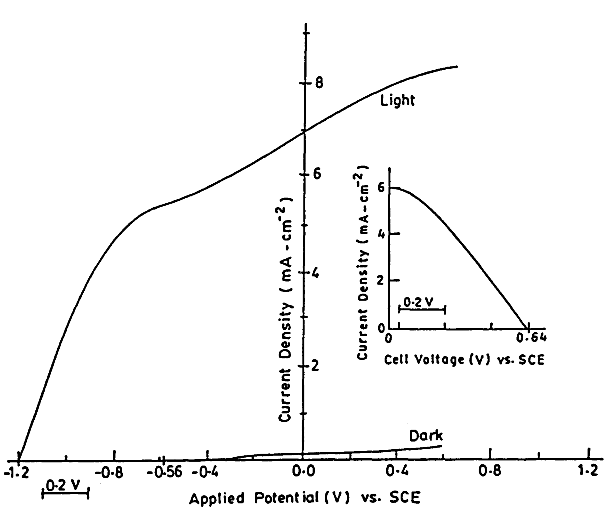


Fig. 1. Current-voltage (I–V) characteristics of photoelectrochemical cell Pt, 1 M 3S//CdSe/Ti (Inset showing short-circuit power characteristics).

Table 1. Photoelectrochemical Characteristics of CdSe/Ti Based SC-SEP, PEC Cell: Pt, 1 M 3S//CdSe/Ti//Redox Electrolyte, Contacting Electrode

S. No.	Electrolyte in light compartment (1 M)	Electrode in light compartment	Electrolyte in dark compartment (0.1 M)	Electrode in dark compartment	Flatband potential V_{Fb}(V) vs. SCE	E_{redox} of electrolyte in dark compartment (V) vs. SCE	Theoretical photovoltage V_{ph} (Theor.) /V	Experimental photovoltage V_{ph}/V	Short-circuit photocurrent I_{sc}/mA cm^{-2}
1.	$NaOH+Na_2S+S$	Pt	NIL	NIL	−1.0	—	—	0.64	6
2.	$NaOH+Na_2S+S$	Pt	$SnCl_4/SnCl_2$	Pt	−1.0	−0.17	0.83	0.82	2
3.	$NaOH+Na_2S+S$	Pt	$K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$	Pt	−1.0	0.22	1.22	1.0	3.5
4.	$NaOH+Na_2S+S$	Pt	KI/I_2 in 1 M Na_2SO_4	Pt	−1.0	0.29	1.29	1.20	2.5
5.	$NaOH+Na_2S+S$	Pt	$FeCl_3/FeCl_2$	Pt	−1.0	0.53	1.53	1.14	6
6.	$NaOH+Na_2S+S$	Pt	$AgNO_3/Ag$	Pt	−1.0	0.50	1.50	1.42	20
7.	$NaOH+Na_2S+S$	Pt	$Ce(SO_4)_2/Ce_2(SO_4)_3$	Pt	−1.0	1.19	2.19	1.22	2

equation. The flat-band potential of CdSe/Ti in polysulfide was measured from $1/C^2$ vs. V (Mott-Schottky) plot. The capacitance values measured at low frequencies showed distortion, due to non-uniformities on the electrode surface. Therefore, the flat-band potential of the SC-SEP electrode was measured at a high frequency of 50 kHz. As shown in Fig. 2, the flat-band potential of the SC-SEP electrode was −1.0 V vs. SCE at 50 kHz. The results of the present study have been presented in Table 1. By computing the theoretical photovoltage from the values of V_{Fb} of SC-SEP and E_{redox} of electrolytes in dark compartment, it is clear that most of our experimental results are in good agreement with the theoretically expected values. The photovoltage (V_{ph}) of the SC-SEP, PEC cell has been observed to increase as redox couples of more positive redox potential were added into the dark compartment. However, some redox couples exhibited slight deviation from the theoretical values. This deviation has been thought to be due to surface reaction between septum electrode and the redox systems and due to unfavorable charge transfer in these redox couples. The current-voltage characteristics of Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt have been shown in Fig. 3. This corresponds to the optimum system investigated by us among the different SC-SEP, PEC cells studied, having various redox electrolyte combination in the dark compartment. The observed photovoltage (V_{ph}) and short-circuit photocurrent (I_{sc}) for this cell were 1.42 V and 20 mA cm^{-2}. It has recently been reported that by the application of small external bias to a PEC and SC-SEP, PEC cell, it is possible to obtain an overall gain in the output photovoltage of these cells.[8,10] With this in view, when we applied an external bias of +0.1 V between SC-SEP and contact electrode in dark compartment, the output power characteristics of the Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt cell have changed to V_{ph} and I_{sc} of 1.9 V and 8 mA cm^{-2} (Fig. 4). It appears that negatively charged ions (S^{2-} and $S_n{}^{2-}$) of the light compartment electrolyte get adsorbed over CdSe surface under the influence of positive bias (0.1 V). The excess negative charge on the surface of CdSe is associated with a negative shift of flat band potential which is realized as enhancement in photovoltage (from 1.42 to 1.9 V). At the same time decrease in photocurrent (from 20 to 8 mA cm^{-2}) shows that some recombination centers (surface states) become active which suppress the short circuit photocurrent of the PEC septum solar cell.

With a view of developing stable and efficient SC-SEP, PEC cell, we have monitored the output power characteristics of the Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt cell after keeping it under PEC operation for ca. 100 h. The output power characteristics showed a decrease of V_{ph} and I_{sc} from 1.42 V and 20 mA cm^{-2} to 1.3 V and 13 mA cm^{-2}, respectively after ca. 100 h (Fig. 5). The fill factor (F.F.) has also decreased from 0.52 to 0.30. In order to further understand the cause of

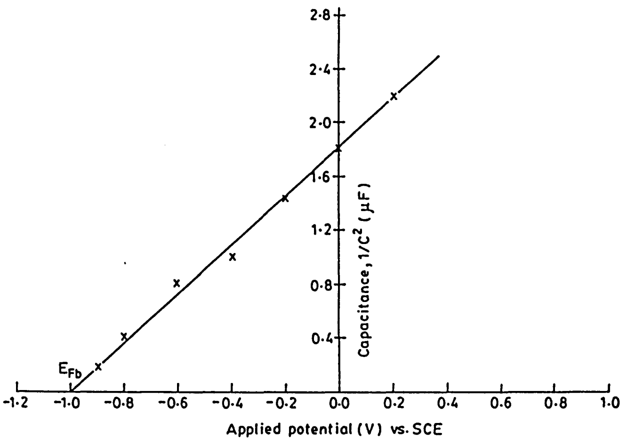


Fig. 2. Mott-Schottky plot of Pt, 1 M 3S//CdSe/Ti cell (Freq.: 50 kHz).

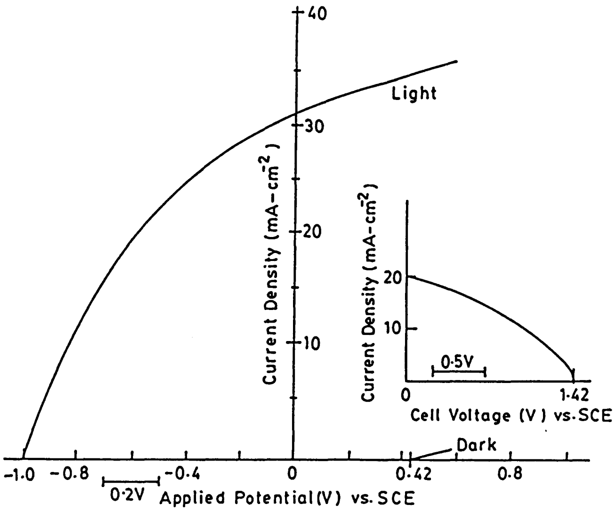


Fig. 3. Current-voltage (I–V) characteristics of semiconductor septum photoelectrochemical cell, Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt (Initial) (Inset showing short-circuit power characteristics).

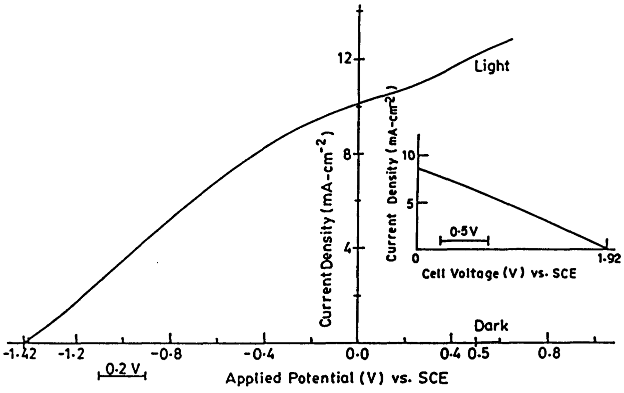


Fig. 4. Current-voltage (I–V) characteristics of semiconductor septum photoelectrochemical cell, Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt (after applying +0.1 V bias for 1/2 h) (Inset showing short-circuit power characteristics).

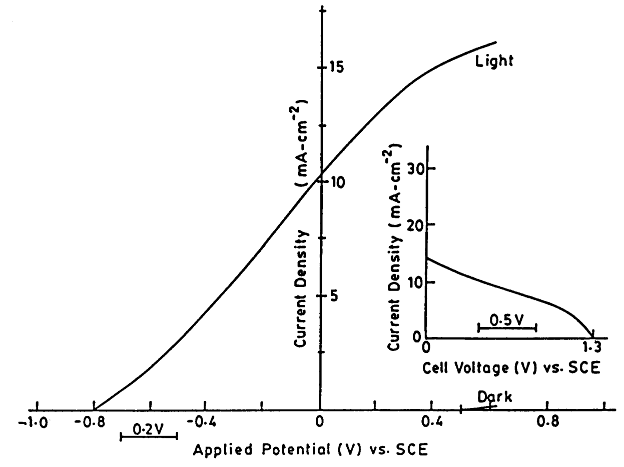
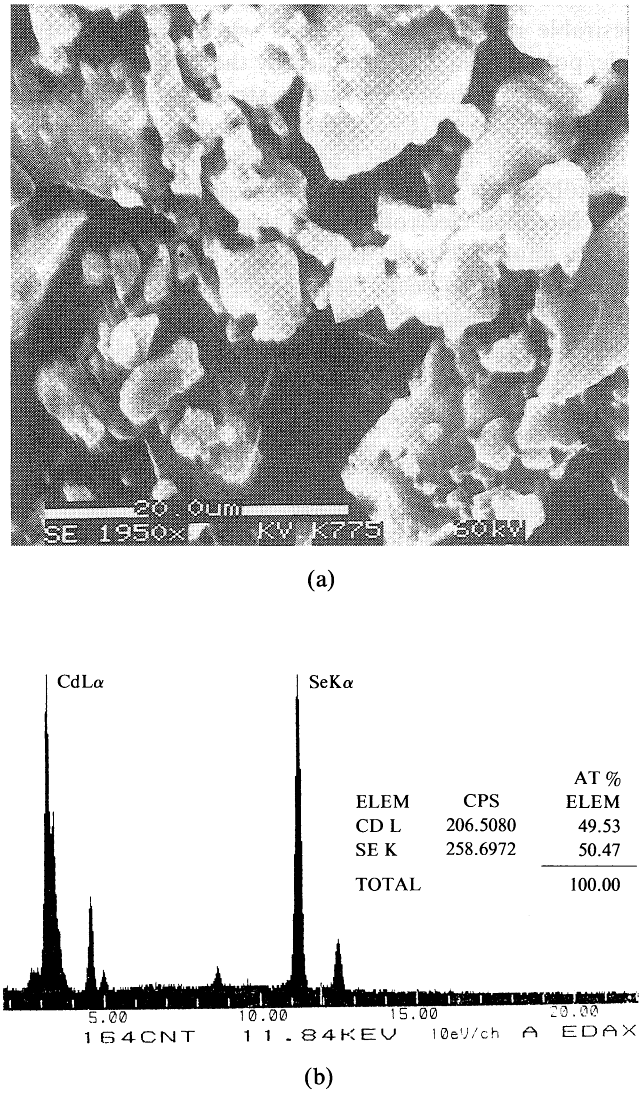


Fig. 5. Current-voltage (*I–V*) characteristics of semiconductor septum photoelectrochemical cell Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$, Pt (after ca. 100 h) (Inset showing short-circuit power characteristics).

degradation, we carried out the surface structure and compositional analysis of the semiconductor septum electrode after removing from the cell and washing with double distilled water. The scanning electron micrographs shown in Figs .6 and 7 exhibit a clear change in the surface morphology of the semiconductor electrode surface after ca. 100 h. The compositional analysis of these samples slown in Figs. 6 and 7 invariably showed a gradual departure from the Cd/Se stoichiometry corresponding to a decrease in Cd concentration. The decrease in power output of the SC-SEP cell has been thought to arise due to these structural and compositional variations. In the present study, the change in Cd/Se ratio of the semiconductor septum appears to be due to dissolution of cadmium (as a result of photocorrosion). Under illumination, CdSe is oxidized to Cd^{2+} and Se. The Cd^{2+} ion probably reacts with S^{2-} ion to give rise to CdS within a very short time of its formation (because of high surface concentration of S^{2-} ions) and

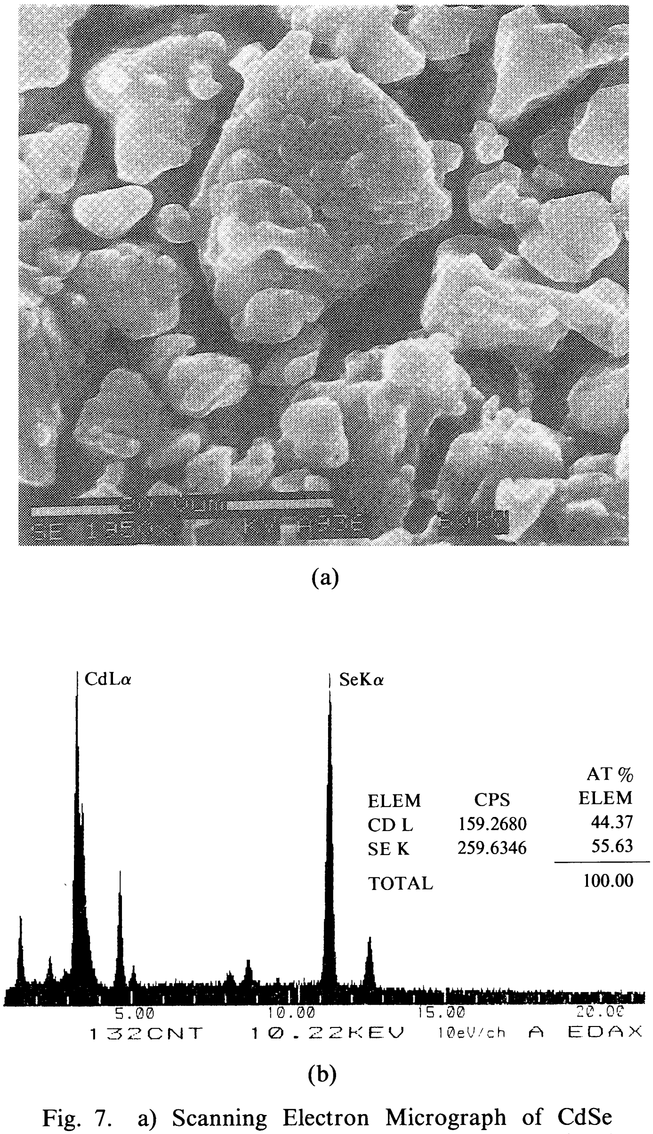


ELEM	CPS	AT % ELEM
CD L	206.5080	49.53
SE K	258.6972	50.47
TOTAL		100.00

(a)

(b)

Fig. 6. a) Scanning Electron Micrograph of CdSe Thin Film (Initial). b) EDAX analysis of CdSe Thin Film (Initial).



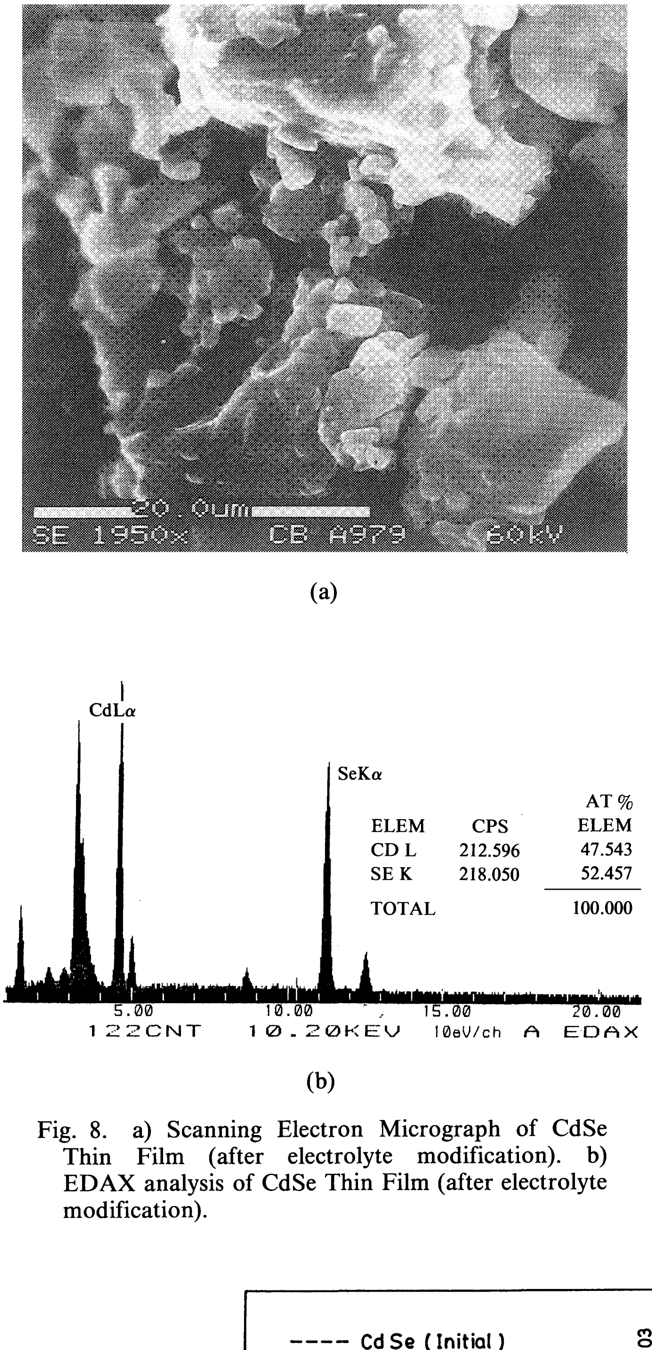
ELEM	CPS	AT % ELEM
CD L	159.2680	44.37
SE K	259.6346	55.63
TOTAL		100.00

(a)

(b)

Fig. 7. a) Scanning Electron Micrograph of CdSe Thin Film (after ca. 100 h). b) EDAX analysis of CdSe Thin Film (after ca. 100 h).

selenium reacts with S^{2-} ion to form SeS^{2-} species in the electrolyte solution. It appears that the rate of formation of CdS (over the slurry painted CdSe film) is higher than the formation of SeS^{2-} species in solution. After prolonged PEC operation (ca. 100 h), the CdS over CdSe peels off in polysulfide solution. This may be the likely cause for the loss of Cd from the electrode as observed in the present investigation. However, the exact reason of Cd loss is not quite intelligible at present. Since SC-SEP cell is much superior to the conventional PEC solar cell in regard to the power output characteristics, if the impediment regarding material dissolution can be checked, the SC-SEP cells can become viable systems. Keeping this in view, efforts were directed towards circumventing the photocorrosion (Cd loss) problem. It was found that the best way to check this problem was through electrolyte modification—a process which has already been reported to be effective in improving the PEC characteristics of $CuInSe_2$, CdSe, and InP.[11,12] Electrolyte modification through several species has been tried and the most desirable results were obtained when electrolyte (sulfide/polysulfide) was modified by the addition of 0.1 M Se. Figure 8 shows the surface structure and compositional analysis of CdSe photoelectrode (on Ti sheet) after ca. 100 h of PEC operation with the modified electrolyte. It has been observed under PEC operation with modified electrolyte, that the normal Cd/Se ratio of the photoelectrode and the cell output parameters (V_{ph} and I_{sc}) have been restored and the effect of photocorrosion minimized.



ELEM	CPS	AT % ELEM
CD L	212.596	47.543
SE K	218.050	52.457
TOTAL		100.000

(a)

(b)

Fig. 8. a) Scanning Electron Micrograph of CdSe Thin Film (after electrolyte modification). b) EDAX analysis of CdSe Thin Film (after electrolyte modification).

In order to further investigate the structural variation of the CdSe polycrystalline thin film on Ti with time, we recorded the X-ray diffraction (XRD) patterns of the fresh samples and those after operating under PEC conditions for ca. 100 h. The comparative XRD patterns of CdSe as shown in Fig. 9 makes it evident that there is no discernible change in the positioning and

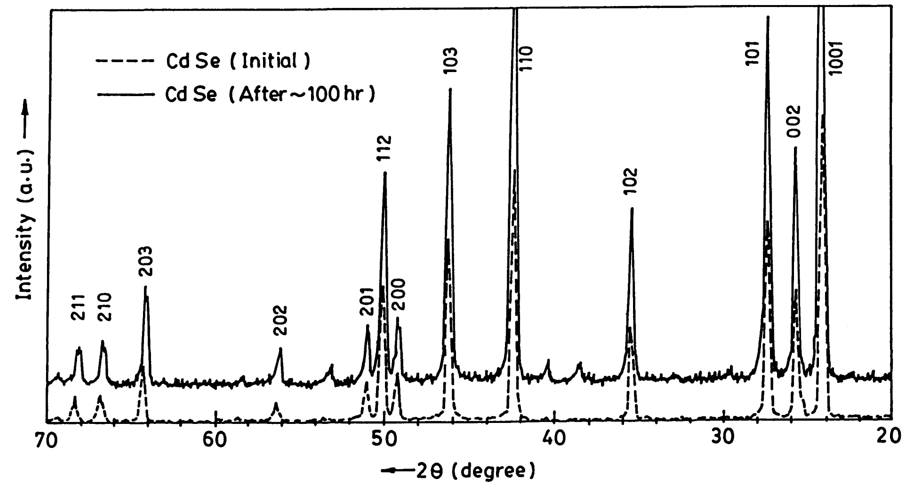


Fig. 9. X-Ray diffraction patterns of polycrystalline thin film of CdSe (---) initial and (——) after ca. 100 h.

intensity of XRD peaks even after the prolonged use of SC-SEP electrode. The lattice parameters of CdSe remained unchanged.

Conclusions

In the present investigation, studies of the newly discovered SC-SEP, PEC solar cell have been carried out with reference to structural and compositional characteristics and their correlation to its PEC characteristics. For the *n*-CdSe/Ti bearing SC-SEP solar cell employing several feasible electrolytes, the configuration corresponding to Pt, 1 M 3S//*n*-CdSe/Ti//0.1 M $AgNO_3$, Pt; SC-SEP solar cell, it has been found that after about 100 h of PEC operation, the SC component of the septum i.e., CdSe undergoes deterioration. Although the gross structure of CdSe remained invariant, loss of Cd has been found to occur at the surface of *n*-CdSe photoelectrode. This is detrimental and leads to lowered PEC power output i.e. V_{ph} and I_{sc} decreased from 1.42 V and 20 mA cm^{-2} to 1.3 V and 13 mA cm^{-2} respectively. It has been found that the semiconductor deterioration can be checked through electrolyte modification by adding 0.1 M Se to the polysulfide electrolyte, thereby yielding stable and efficient SC-SEP, PEC cell. Further studies in regard to understanding the effect of applied bias on SC-SEP cell, development of more suitable redox couples and SC-SEP electrodes are in progress.

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