



CHAPTER

IV

CHAPTER IV
THE SnS THIN FILMS : PHOTOELECTROCHEMICAL
(PEC) STUDIES

4.1	Introduction	66
4.2	The Photoelectrochemical (PEC) Effect and Requirements of a PEC cell	67
4.2.1	The photoelectrochemical (PEC) Effect	67
4.2.2	The requirements of a PEC cell	68
4.3	Experimental Techniques	70
4.3.1	Preparation of the photoelectrode material	70
4.3.2	Fabrication of a PEC cell	71
4.3.3	Characterization of a PEC cell	71
	a) Electrical properties	71
	i) The I-V and C-V characteristics in dark	73
	ii) The built-in-potential determination	73
	iii) The power output curve	73
	b) The optical properties	74
	i) Photo response	74
	ii) Spectral response	74
	iii) Speed response	74
4.4	Results and Discussion	74
4.4.1	The electrical properties	75
	a) The I-V and C-V characteristics in dark	75
	b) The built-in-potential determination	80
	c) The power output characteristics in light	80

4.4.2	The optical properties	83
	a) The photo response	83
	b) The spectral response	85
	c) The speed response	85
4.5	Conclusions	89
	References	90

4.1 Introduction

Twenty first century is the century of the global demands: the need for nonconventional energy resources is considered as a potential driving force for the power requirements. The harnessing of one of the most abundant, inexhaustible and pollution free sources of energy, the solar energy in the form of an electrical energy still leaves much to be achieved. It is this, that has attracted researchers to investigate the potential materials for device applications in solar / electrical conversion systems; thus the technology of photovoltaics has gained immense momentum in recent years. Prospective semiconductor materials for the possible electrochemical application include tin chalcogenides which satisfy most of the requirements of an efficient solar to electrical energy conversion.

The semiconductors which possess appropriate band gaps (1.1 to 1.5 eV) that respond to the maximum span of the electromagnetic spectrum, high absorbance in the visible region and a band to band type of transitions are more effective in photoelectrochemical conversion

/1-4/. Thus, tin sulphide seems to be a promising candidate in this respect since it shows a strong absorption of light of wavelengths shorter than 800 nm. Therefore, we thought it to be interesting to investigate the electrochemical photovoltaic properties of this material. The crystallographic, microscopic, optical spectroscopic and electronic transport properties, those decide its use as a photoelectrochemical converter, are discussed in chapter III.

With its cheap and nonexpensive synthesis in a simplest way (by a chemical growth process /4-9/), it has, when brought in the near vicinity

of an electrolyte redox couple, additional overriding advantages over the conventional solid state devices /1,2,4-10 /.

Therefore an electrochemical converter (PEC cell), employing tin sulphide as its one of the active components, has the following potential advantages as : i) easy method of fabrication, ii) no problem of lattice mismatch, iii) no need for antireflective coating, iv) with a proper choice of an electrolyte redox couple, the Fermi energy could be adjusted to a desired level etc.

Considering the materialistic aspects of SnS into account and development of the low cost high efficiency electrochemical device, we planned for the synthesis of the tin sulphide in thin film form and to employ it in the electrochemical conversion. Section 4.2.1 gives preparation of the material under controlled conditions whereas fabrication of an electrochemical device (PEC cell) is cited in the section 4.2.2. The various experimental techniques for the measurements and the methods to characterize the PEC cell are outlined in the sections (4.2.2.) and (4.2.3). The results of the measurements and their adequate explanation are given in the section 4.3.

4.2 The Photoelectrochemical (PEC) Effect and Requirements of a PEC Cell

4.2.1 The photoelectrochemical (PEC) Effect

The photoelectrochemical (PEC) system is one by which one can trap the solar radiation and convert it into useful chemical or an electrical energy. The system works on the principle of photovoltaic effect. Thus a PEC effect is one in which the irradiation of an electrode / electrolyte system produces a net change in the electrode potential when

the circuit is open or a change in the current if the circuit is closed /1-3/. Thus the PEC cells employing the above effect are classified as :

a) The electrochemical photovoltaic cells

In PEC cells, the photo produced electron – hole pair is used to generate the electricity in the same way as that of the solid state solar cells. The photoassisted reaction that takes place at the counter electrode is simply reversed at the semiconductor electrode. Ideally the cell operates on the principle of conversion of light into electricity with no change in the electrolyte or the electrode composition.

b) The photoelectrolytic cells

In these cells, optical energy is converted into chemical energy. The photogenerated hole is used to oxidize one species while the electron is used to reduce it.

c) The rechargeable cells

The current interest is to develop a solar rechargeable photoelectrochemical cells /1,3/. In this system two redox electrolytes are used and are separated by an ion selective membrane.

d) The photogalvanic cells

In these cells optical energy is converted into an electrical energy /1-3/ at the cost of photo absorption by the molecular species in the solution. The charge transfer from an excited molecule to an electrode with light absorbing system generates the electrical power.

4.2.2 The requirements of a PEC cell

The electrochemical photovoltaic cells have the following advantages over the conventional p-n junction Schottky barrier cells /1,2/.

1. The PEC cells are easy and simple to fabricate.
2. Many complicated processing steps in the fabrication of the p-n junction are simplified or eliminated.
3. Growth of large area single crystal is not required.
4. Since the junction formation is a spontaneous process, randomly oriented crystallites can be used.
5. The complicated and costlier doping and diffusion steps are eliminated.
6. Since the current is carried by the redox species and the counter electrode, the need for front metallisation is eliminated.
7. The need for AR coatings can be avoided by building a nonreflective structure into the surface of a semiconductor by a simple etching process.
8. One of the most important advantages is that the PEC cells have a facility for chemical storage.

Several reviews on this issues are appear in the literature. In addition to the above advantages, the following are the requirements

a) A semiconductor photoelectrode

The active photoelectrode material should satisfy the following conditions

- i) The photoelectrode material should be of the direct band gap type with a high optical absorption coefficient ($10^4 - 10^5 \text{ cm}^{-1}$).
- ii) The bandgap should be such that the maximum span of the solar spectrum should be utilized ($E_g = 1.2 - 1.5 \text{ eV}$).
- iii) The donor concentration should be optimum ($10^{16} - 10^{19} \text{ cm}^{-3}$).

- iv) The minority carrier diffusion length (L_D) and the depletion layer width (W) should be large.
- v) It should be stable against photo-dissolution and electrochemical corrosion when placed in a redox couple.
- vi) Charge carriers should have high mobility and life time.
- vii) The material should be thick enough so as to absorb all the incident light.
- viii) The cost of the basic materials and the manufacturing processes and the quantum efficiency should be acceptable.

b) An electrolyte

A proper choice of an electrolyte coupled with its composition is also a crucial parameter. An electrolyte should be such that :

- i) It should be transparent with a high conducting supporting electrolyte.
- ii) The redox reactions should be diffusion limited and stable under the illumination for a longer duration.
- iii) It should be cheap and non-toxic.

c) A counter electrode

A counter electrode is also equally important. It should have :

- i) Low overpotential for redox reactions to occur.
- ii) Large area to reduce the concentration polarization.
- iii) Chemical inertness with an electrolyte.

4.3 Experimental Techniques

4.3.1 Preparation of the photoelectrode material

Tin sulphide photoelectrode (thin film, $t=0.3\mu\text{m}$) was obtained onto the well processed stainless steel substrates / 9-11/. For deposition, AR purity stannous chloride and thioacetamide were mixed in a definite proportion. Triethanolamine was used as a complexing agent and pH of

the reaction mixture was maintained about 10.5 ± 0.2 . The detailed procedure is given in the sections (2.2.2) and (2.2.3).

4.3.2 Fabrication of a PEC cell

An electrochemical conversion cell (PEC) was fabricated in our laboratory, the schematic of which is shown in fig. 4.1. It consists of two test tubes, one hard glass test tube of the inner diameter 2.7 cm and length 7 cm and other an ordinary test tube of inner diameter 1.5 cm and length 12 cm. The two test tubes were connected by a small glass tube of diameter 0.3 cm. This H-shaped assembly is fitted in a copper pot of a suitable size. A window of the dimension 2 cm x 0.5 cm was made for illumination of the photoelectrode.

A PEC cell of the configuration p-SnS / 0.5M, $K_3 Fe (CN)_6$ - $K_4 Fe (CN)_6$ / C was devised in this H-shaped assembly using an electrolyte and a graphite carbon counter electrode. The graphite carbon rod was sensitized in a medium concentrated CoS solution for 24 hours. The distance between a photoelectrode and a counter electrode was of the order of 0.3 cm. A rubber cork was used to air tighten the cell and to give mechanical support to both counter electrode and the photoelectrode. The active area of the photoelectrode to be exposed to the light was defined by a common epoxy resin.

4.3.3 Characterization of a PEC cell

a) The electrical properties

The electrical properties of a PEC cell can tell us much more about the nature of the junction formed and the charge transfer process across the electrode / electrolyte interface. These properties have been studied through the current-voltage and capacitance-voltage characteristics in dark, barrier height determination and power output curve.

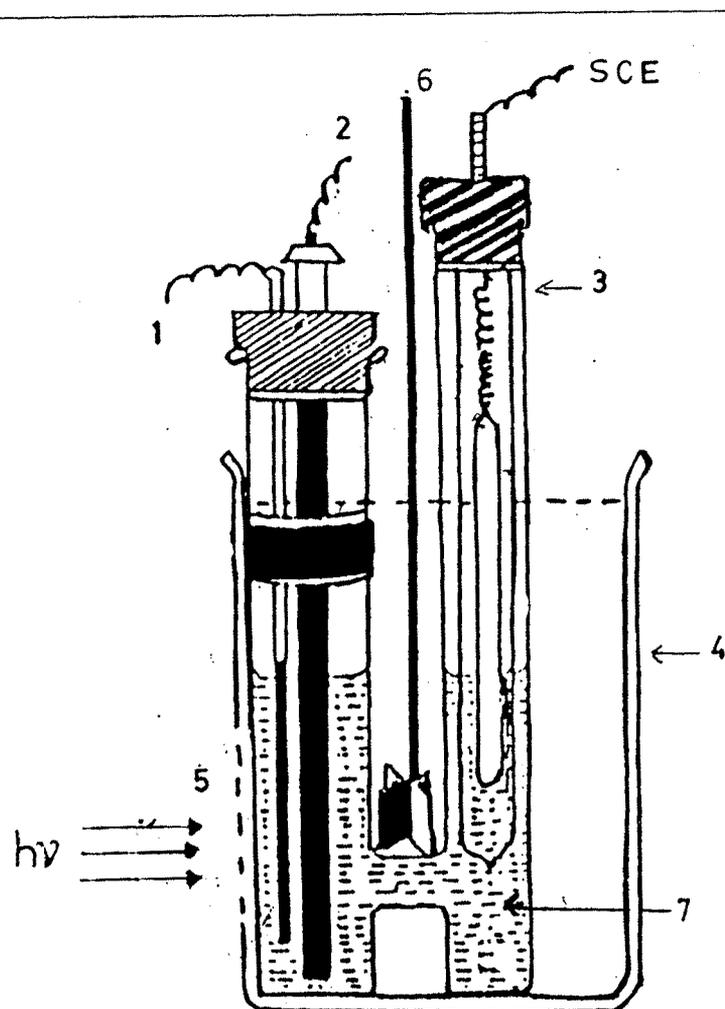


Fig. 4.1 Design and fabrication of a PEC cell showing:

1. Photoelectrode,
2. Counter electrode,
3. Glass cell,
4. Copper pot,
5. Slit,
6. Stirrer,
7. Liquid electrolyte.

i) The current –voltage and capacitance –voltage characteristics in dark

For the I-V characteristic of a cell in dark, a conventional two electrode cell geometry, as constructed above, was used. The applied voltage to the junction was varied with a helical potentiometer (10 turn, 1 K Ω) and was recorded with an Agronic – 113, 4 ½ digit voltmeter. The current flowing through the junction was measured by a Hewlett-Packard, 34401, 6 ½ digit multimeter.

The junction capacitance was measured under reverse bias condition for various applied voltages / 9-10 /. The three electrode system was used for this purpose viz. a photoelectrode, a counter electrode and a saturated calomel electrode (SCE) as reference. The potential applied across the junction was measured versus SCE and was varied with a 10 turn 1 K Ω helical potentiometer. It was measured by an Agronic- 113, 4 ½ digit voltmeter. The junction capacitance was measured using an Aplab-4910, 4 ½ capacitance meter at a superimposed frequency of 1KHz and 1V_{pp} ac voltage.

ii) The built-in-potential determination

The built-in-potential of the above cell was determined by noting the temperature dependent reverse saturation current of a cell. The reverse saturation current was noted at various temperatures from 90⁰ C down to the room temperature. A FET input nanoammeter, DNM - 121, 4 ½ digit, was used for this purpose.

iii) The power output curve

The power output curve that determines the maximum power output from a cell, was obtained for the cell under a constant illumination intensity of 22.4 mW/cm². A 250 W tungsten filament lamp was

employed to illuminate the cell. A water filter was interposed between a lamp and a cell to avoid heating of the cell. The illumination intensity was measured using a LX-101 (Lutron, Taiwan) lux meter. The voltage and current were measured as usual.

b) The optical properties

i) Photo response

The photo response of a cell formed with a good quality SnS photoelectrode was obtained by measuring the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) at different illumination intensities. The illumination intensity was measured with a LX-101 (Lutron, Taiwan) lux meter and I_{sc} and V_{oc} were measured as above.

ii) Spectral response

This gives spectral sensitivity of the photoelectrode material. The variation of the short circuit current (I_{sc}) with the incident wavelength (λ) was measured using a Digispectronic 20-D, Milton and Roy, (USA), spectrophotometer. The range of wavelengths used was from 450 nm to 1000 nm. The short circuit current was recorded with a Hewlett-Packard, 6 ½ digit multimeter.

iii) Speed response

This is the time variation of I_{sc} or V_{oc} of a cell into two different modes : first, when cell is illuminated for a particular time and second when light is removed from the cell. In our case we have measured V_{oc} of a cell when cell was illuminated and noted the decay when light was cut off.

4.4 Results and Discussion

The characterization of an electrochemical conversion cell through the electrical and optical properties is an unique tool in identifying the

suitability of the semiconductor material (electrode) for photovoltaic applications. When a semiconductor electrode is dipped into an electrolyte redox couple, an equilibrium is established between the semiconductor and an electrolyte solution by redistribution of the charges. This rearrangement of the charges results in a strong local field at the junction. When such a junction is illuminated by a light of energy greater than the optical band gap of the semiconductor, the electron-hole pairs are generated in the depletion region /1-4/. The charge separation takes place due to the local field at the interface and the probability of annihilation of a hole with an electron is reduced. Under the optimum condition, the light penetration depth becomes equal to the depletion layer width and almost all the incident light is absorbed in the depletion layer. This process results in a counter field which is maximum at the open circuit condition called as “open circuit photovoltage” /5-8/. When a counter electrode is connected externally to the semiconductor electrode, the holes move to the surface of the semiconductor and oxidize the electrolyte species while electrons move deep into the bulk of the semiconductor and reduce the oxidized species at the counter electrode, thus allowing two way traffic redox reactions to occur /1-4/.

4.4.1 The electrical properties

a) The I-V and C-V characteristics in dark

The I-V characteristic, in dark, of a cell formed with a good quality SnS electrode was studied at room temperature. It was observed that a small dark voltage, V_D and a dark current, I_D were noticed. The polarity of this dark voltage was positive towards the SnS electrode. The origin of this dark voltage lies in the difference between the two half cell potentials of a cell and could be expressed as /1,3/

$$V_D = E_{\text{SnS}} - E_{\text{carbon}} \quad \dots(4.1)$$

where, E_{SnS} and E_{carbon} are respectively, the half-cell potentials developed when the SnS and carbon electrodes are immersed in the electrolyte. From the observed polarity it is seen that

$$E_{\text{SnS}} > E_{\text{carbon}} \quad \dots(4.2)$$

The presence of small dark current (I_D) suggests that there is some deterioration of the electrode material in the electrolyte /1-3/. The electrochemistry and photoelectrochemistry of a semiconductor / electrolyte interface are much complicated compared to a semiconductor / metal interface, however, certain assumptions have been imposed on the semiconductor / electrolyte interface to interpret the charge transfer mechanism across it. Thus assuming a semiconductor / electrolyte interface as the analogue of a Schottky barrier cell, the current transport through the interface is defined by a well known Butler-Volmer relation /1,2,12/

$$I = I_0 \{ \exp [(1 - \beta) VF / RT] - \exp (- \beta VF / RT) \} \quad \dots(4.3)$$

where, I_0 is the equilibrium exchange current density, β is a symmetry factor, V is the over voltage, R is a universal gas constant and F is a Faraday constant. A symmetry factor of 0.5 corresponding to a symmetrical barrier yields a symmetrical I vs V curve. This means that an interface cannot rectify a periodically varying potential. If $\beta > 0.5$, then I vs V curve would not be symmetrical and the interface has rectifying property called " Faradaic rectification" / 2,5-7,11/. The dynamic current-voltage characteristic for this cell was therefore, studied in dark and is shown in fig. 4.2. The I - V characteristic is non-symmetric. Thus a rectifying type of the junction has been formed in our case /1,2,12/. The characteristic was further analyzed to determine the magnitude of a symmetry factor β and the observed value of β is greater

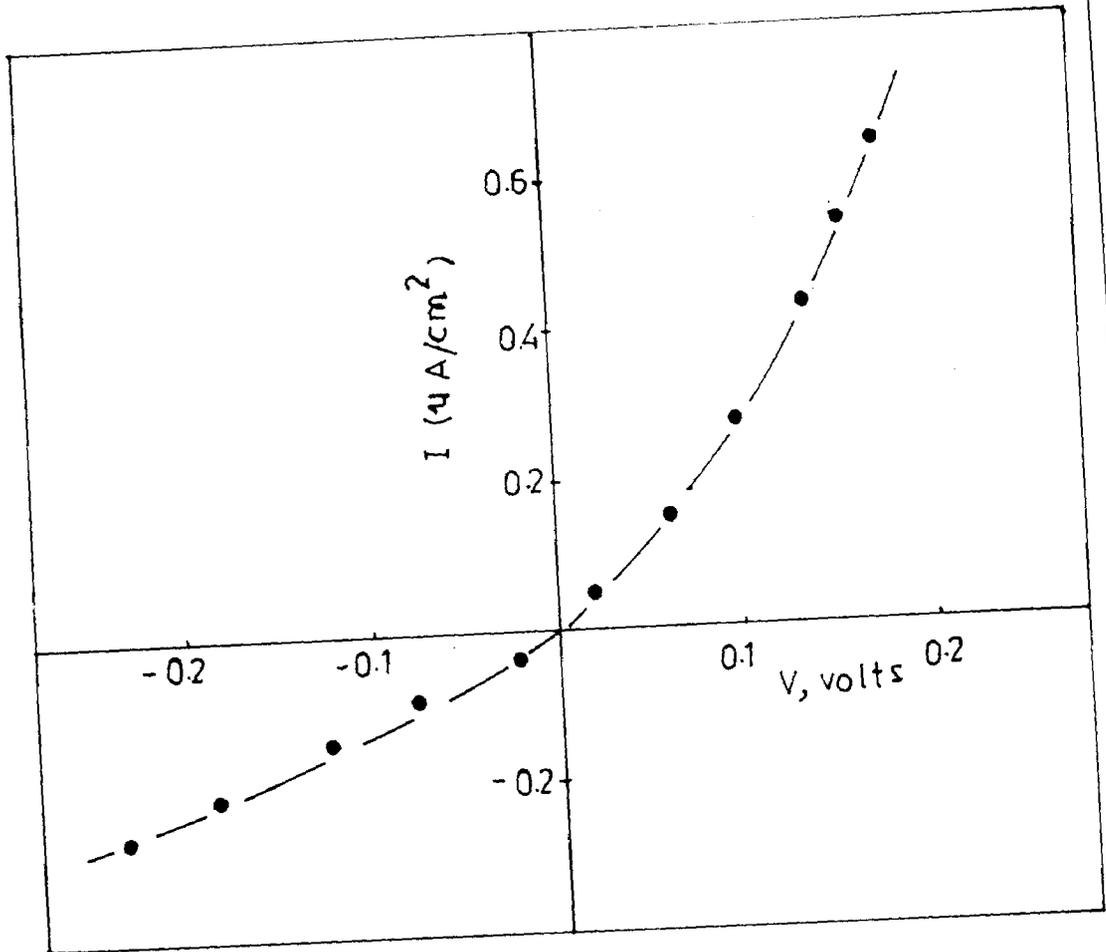


Fig. 4.2 Current voltage relation for a cell formed with SnS photoelectrode under forward and reverse bias.

than 0.5 . This confirms rectifying nature of the junction. The reverse bias current was expected to saturate however, it increased as the reverse voltage is increased. In electrochemical cells, this kind of behaviour is generally observed and is attributed normally to the /1,2,6/ : 1) generation of the electron hole-pairs in the depletion layer under high applied reverse bias and 2) onset of the electron injection from the electrolyte into the semiconductor due to the tunneling process. The junction ideality factor (n_d), which is a measure of the quality of the junction, was determined from the linear region of the $\log I$ vs V plot as shown in fig. 4.3. The calculated magnitude of n_d (4.63) is higher than its ideal value which is generally the case for semiconductor / liquid junction cells. The deviation from the ideal behaviour, obviously, represents the recombination mechanism prevailing at the interface /1,2,5-8 /.

The capacitance–voltage measurements were done on the cell to evaluate the flat band potential (V_{fb}) which determines the relative positions of the Fermi levels of a semiconductor and an electrolyte and therefore the amount of band bending at the interface /1,2/ . The intrinsic band bending at the interface is a measure of the depletion layer width inside the semiconductor and hence determines the ability of an electrode to operate at the short circuit condition. This is also equivalent to a measure of the maximum open circuit voltage (V_{oc}) that can be attained from a cell. For a semiconductor / electrolyte interface, the observed capacitance is mainly due to the semiconductor space charge region. The capacitances due to the Helmholtz and Gouy diffused layers are assumed negligible due to the high ionic concentration of the

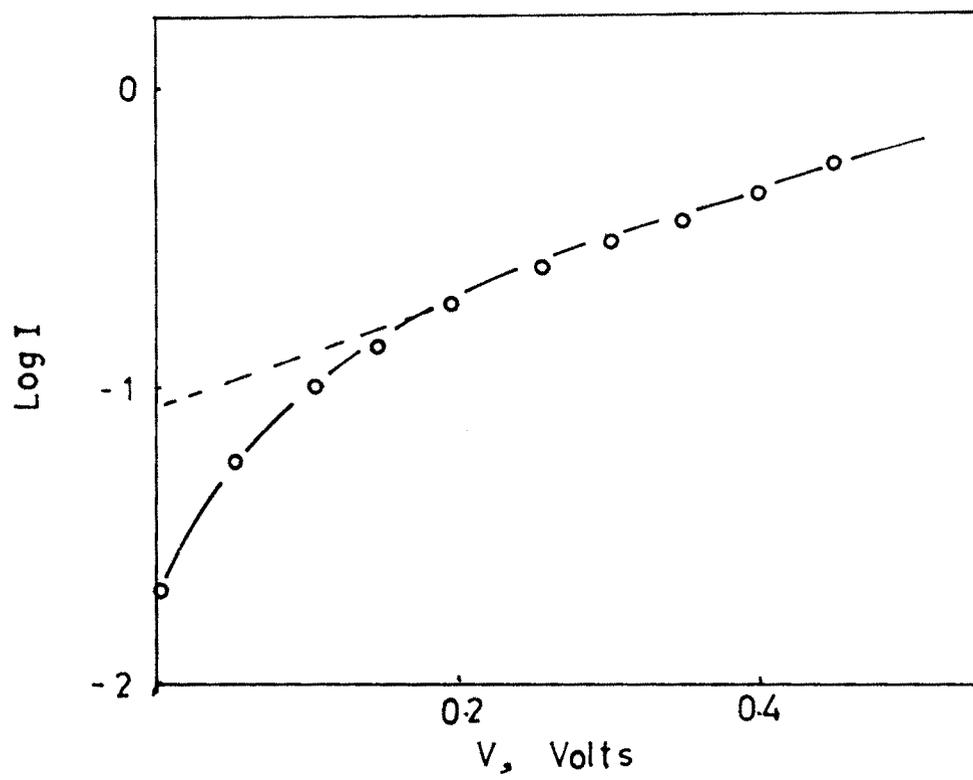


Fig. 4.3 Variation of $\log(I)$ vs V for a cell.

electrolyte [1,12]. The space charge capacitance C_{sc} is related to the applied reverse voltage, V as

$$C^{-2} = [2 / (q \epsilon \epsilon_0 N_D)] [V - V_{fb} - kT / q] \quad \dots(4.4)$$

where, C is the space charge layer capacitance per unit area, q is an electronic charge, ϵ is the semiconductor dielectric constant, ϵ_0 is the permittivity of the free space (8.86×10^{-14} F / cm), V_{fb} is the flat band potential, N_D is the donor density, k is a Boltzman's constant and T is the absolute temperature. The Mott-Schottky plot was then constructed from the C - V measurements to determine the flat band potential and is shown in fig. 4.4. The flat band potential was obtained by extrapolating the linear region of C^{-2} vs V variation on the voltage axis and is +560 mV.

b) The built-in-potential determination

The barrier height of a cell also referred as built-in-potential (ϕ_B) can be determined by measuring the reverse saturation current of a cell at various temperatures. For a Schottky barrier junction, the reverse saturation current (I_0) is related to the temperature T as

$$I_0 = AT^2 \exp (\phi_B / kT) \quad \dots(4.5)$$

where, A is a Richardson's constant, k is a Boltzman's constant and ϕ_B is the barrier height. The reverse saturation current has an exponential dependence on the working temperature. This is shown in fig. 4.5. The built-in-potential was then computed from the linear region of the $\log (I_0 / T^2)$ vs $1/T$ variation. The observed magnitude of ϕ_B , determined from the slope of this graph, is 0.38 eV.

c) The power output curve

When a cell is illuminated by a light of constant illumination intensity ($22.4 \text{ mW} / \text{cm}^2$), the current-voltage characteristic shifts in a fourth

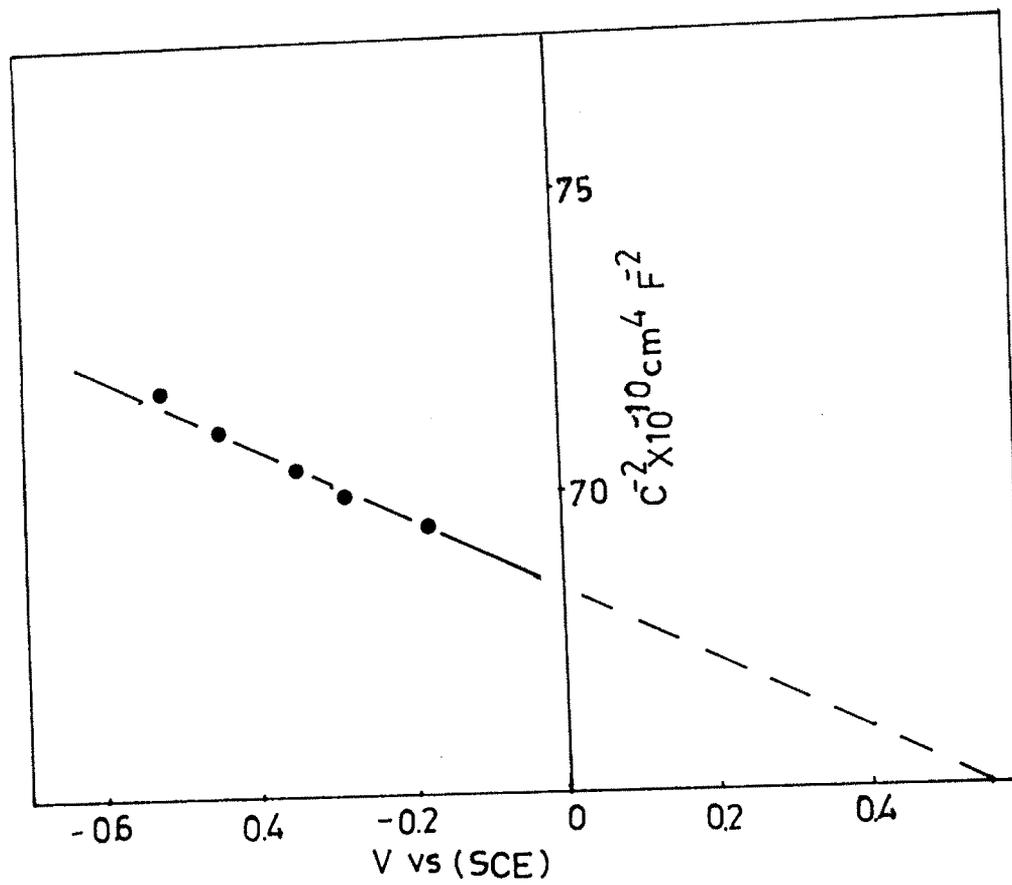


Fig. 4.4 Mott-Schottky plot for a SnS based PEC cell.

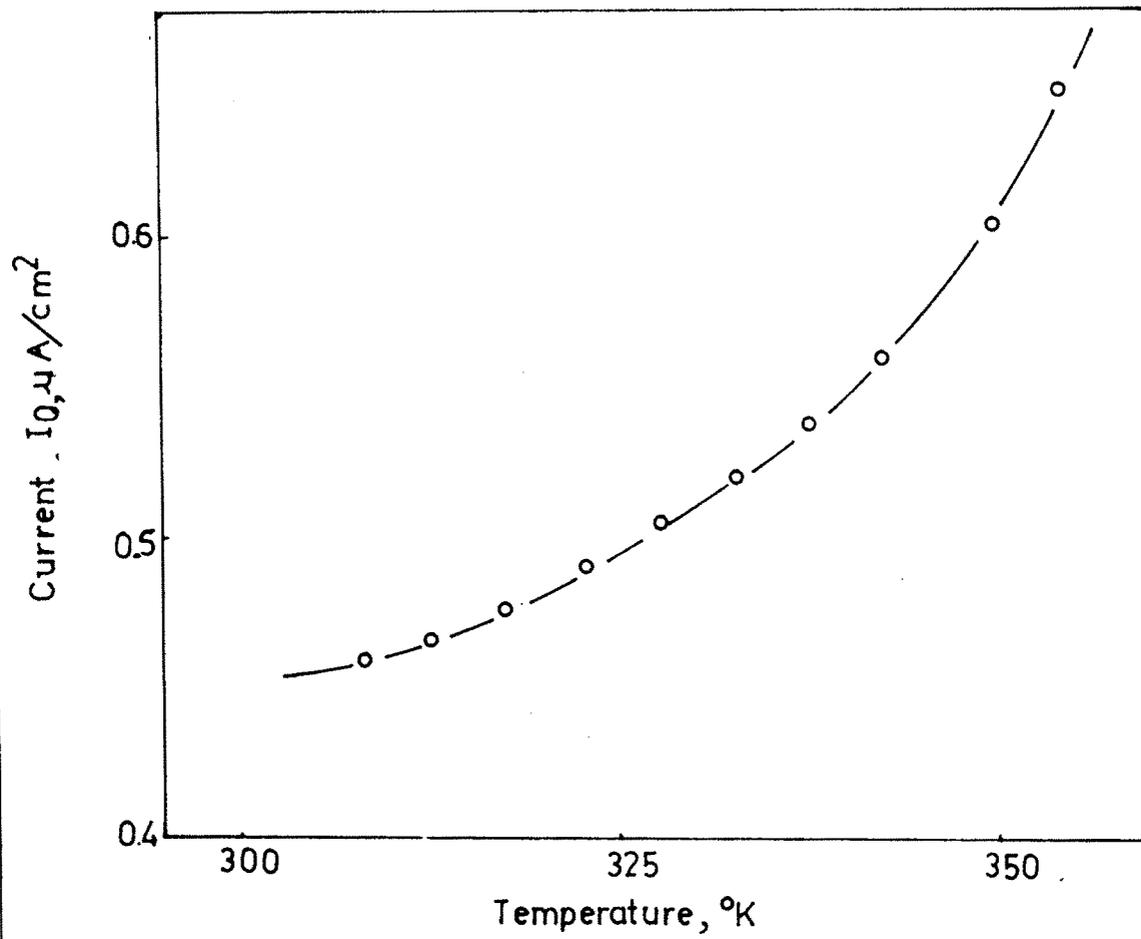


Fig. 4.5 Variation of reverse saturation current (I_0) with working temperature.

quadrant. This is the characteristic feature of a solar cell as an electricity generator [1,5,7]. In the present case power output curve was obtained for the cell under study. Fig 4.6 shows such a current–voltage curve. The cell parameters namely , open circuit voltage (V_{oc}), short circuit current (I_{sc}), efficiency (η %), form factor (ff %) and series resistance (R_s) and shunt resistance (R_{sh}) were computed from this curve. Typical values of the above parameters are :

$$\begin{aligned} V_{oc} &= 0.228 \text{ V}, & \eta \% &= 0.024, & R_s &= 1280 \ \Omega, \\ I_{sc} &= 0.12 \text{ mA/ cm}^2, & \text{ff \%} &= 39.6, & R_{sh} &= 6 \text{ K } \Omega. \end{aligned}$$

4.4.2 The optical properties

a) The photoresponse

The cell was illuminated with a white light source and the open circuit voltage and short-circuit current were noted for various incident illumination intensities. The semiconductor / electrolyte interface can be regarded as a Schottky barrier cell and it is therefore possible to represent the current- voltage characteristic by the relation [1,2]

$$I = I_{ph} - I_d = I_{ph} - I_o [\exp (qV / n_d kT) - 1] \quad \dots (4.6)$$

where, I is the net current density, I_{ph} and I_d are the photo and dark current densities , respectively, I_o is the reverse saturation current density, V is the applied bias voltage and n_d is a junction ideality factor. For bias voltages exceeding $3 \text{ kT} / q$ and at the equilibrium open circuit conditions [6,8]

$$I_d = I_{ph} \text{ and } V = V_{oc} .$$

Thus, equation (4.6) can be rearranged as follows

$$V_{oc} = (n_d kT / q) \ln (I_{sc} / I_o) \quad \dots(4.7)$$

where, V_{oc} is the open circuit photovoltage and I_{sc} is the short circuit current density. Since $I_{sc} \gg I_o$ a plot of V_{oc} vs $\ln I_{sc}$ should yield a

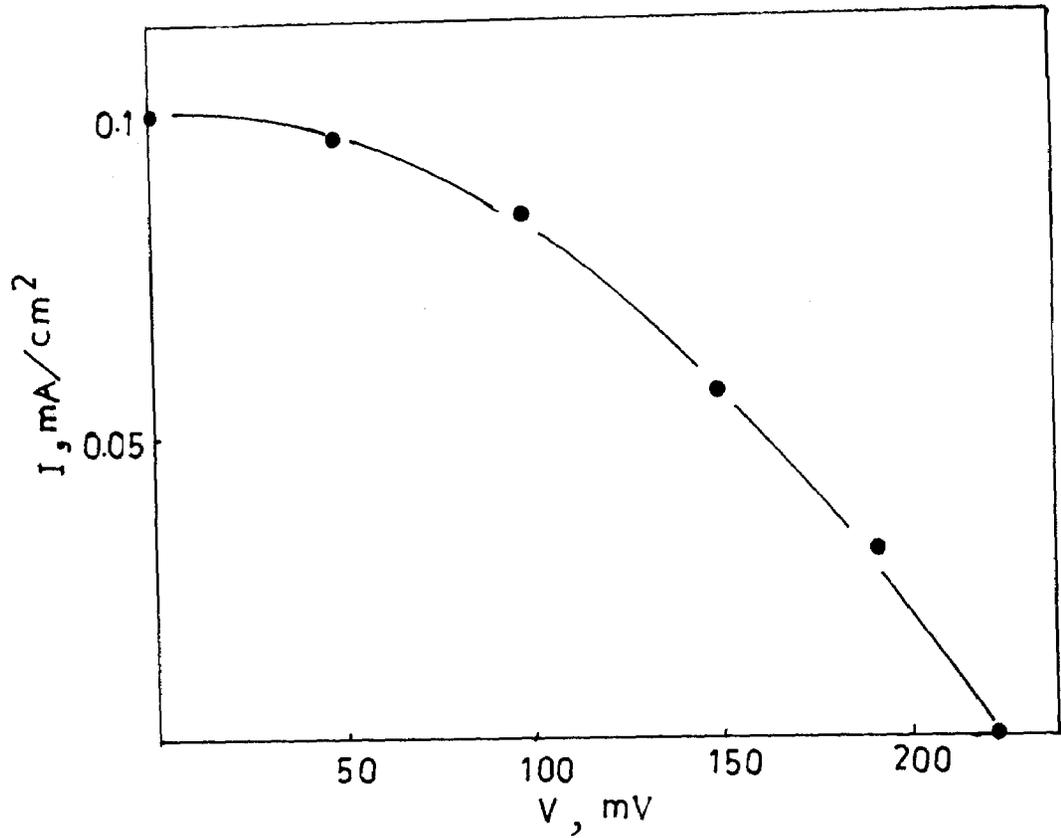


Fig. 4.6 The power output curve for a typical cell formed with SnS electrode.

straight line and from the slope of this graph the junction ideality factor (n_L) in light was determined. An ideal device should have n_L equal to unity so that the slope of the above plot should be 60 mV. Fig. 4.7 represents such a plot, which gives the value of n_L equal to 5.91.

b) The spectral response

A study of the spectral response of a PEC cell is important since it is directly related to the solar spectrum and gives informations which are useful in identifying the recombination centres and diagnosing the problems related to the efficiency losses. The photo current action spectra of a cell was therefore examined and is shown in fig. 4.8. It is seen that spectra peaks at about 900 nm. The decreased response on the shorter wavelength side is consistent with the increased absorption by the Ferri / Ferrocynide electrolyte and surface recombination of minority carriers. Whereas the decay of I_{sc} at longer wavelengths can be attributed to the non-optimized thickness and transition between the defect levels/1,2/.

c) The speed response

The speed response characteristic of a PEC cell is the rise and decay of I_{sc} and are V_{oc} with time. Fig. 4.9 demonstrates the rise and decay of V_{oc} with time for a cell. The decay of V_{oc} follows the second order kinetics

$$V_{oc}(t) = V_{oc}(0) t^{-b} \quad \dots (4.8)$$

where $V_{oc}(0)$ and $V_{oc}(t)$ are the open circuit voltages at $t = 0$ and t second respectively after turning of the light source and b is a rate constant. The slow decay in V_{oc} can be ascribed to the presence of surface states and hence the Fermi level pinning /1,2,8 / .

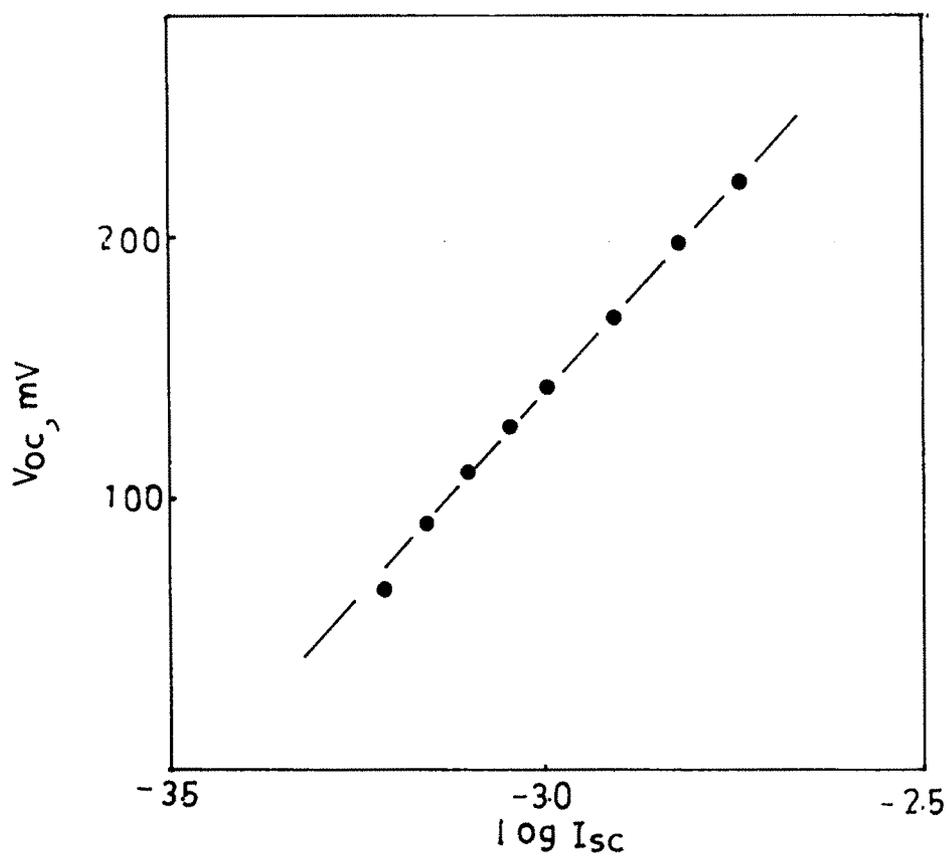


Fig. 4.7 Plot of V_{oc} versus $\log I_{sc}$ for the above cell.

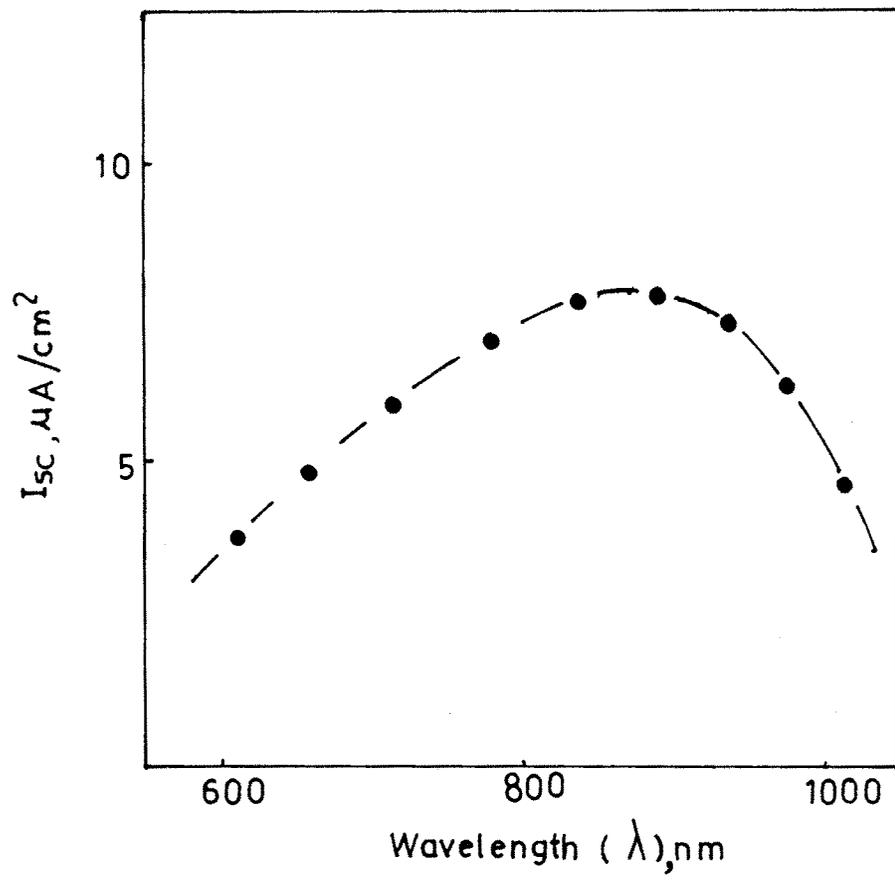


Fig. 4.8 The photo current action spectra for the cell.

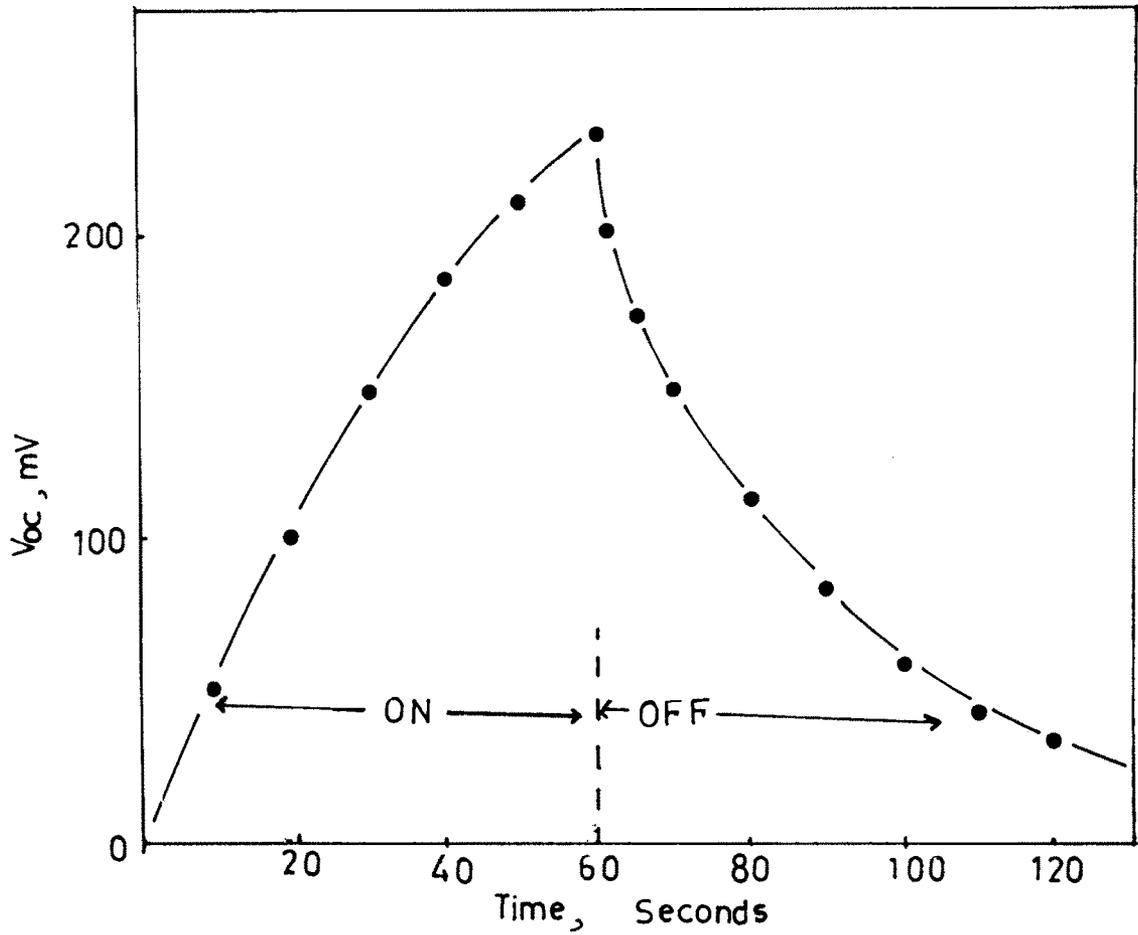


Fig. 4.9 Variation of the open circuit (V_{oc}) with the time.

4.5 Conclusions

Fabrication of a PEC cell using SnS thin film photoelectrode is very simple, cheap and convenient. The PEC cell was formed and the photoelectrochemical behaviour of the cell was examined. The dark I-V and C-V characteristics showed presence of recombination centers and the surface states at the electrode / electrolyte interface. The cell performance is found to be poor.

References

1. S. Chandra, in, "Photoelectrochemical Solar Cells, (ed) D. S. Compbell, Gordon and Breech Science Publishers, N.Y , 1985.
2. Aruchami, G. Aravamudan and G. V. Subba Rao , Bull. Mater.Sci.4 (1 982) 483.
3. J. Nozik, in, "Semiconductor Liquid Junction Solar Cells", Proc. Conf. on Electrochem. and Physics of Semiconductor Liquid Interface under Illumination, (ed) A. Heller, Airlie, Verginia, Vol. 77-3, The Electrochem. Soc., N. J., (1977) 2173.
4. H. Gerischer, in "Topics in Aapplied Physics" Vol. 31, Solar Energy Conversion, Springer, (ed) B. O. Seraphin, Heidelberg, (1979) 115.
5. L.P. Deshmukh and S. G. Holikatti, J. Phys. D : Appl. Phys. 27 (1994)1786.
6. K. Rajeshwar, L. Thompson, P. Singh, R. C. Kainthla and K. L. Chopra, J Electrochem. Soc.128 (1981) 1744.
7. L. P. Deshmukh , B. M. More, C. B. Rotti and G. S. Shahane, Mat. Chem. Phys. 45 (1996)145.
8. L. P. Deshmukh and V. S. Sawant, Solar Cells 31(1991)549.
9. B. T. Raut, V. B. Patil, P. D. More, V. S. Karande and L. P. Deshmukh Ind. J. Pure & Appl. Phys. (Commu.)
10. B. T. Raut, V. B. Patil, E. U. Masumdar and L. P. Deshmukh , Proc. National Conference on Materials and Semiconductor Technologies in Electronic Research, G. B. Pant University of Agriculture and Technology, Pant Nagar(U. P.), India 9-10 Nov.,2000.
11. B. T. Raut, D. S. Sutrave, V. B. Patil and L. P Deshmukh, National Seminar On Recent Trends In Materials Science, S. V. University, Tirupati (A. P.), 25-27 Nov., 1999.

12.J. O. M. Bockris and A. K. N. Reddy, in "Modern Electrochemistry",
Vol. II (eds.) J. O. M. Bockris and A. K. N. Reddy, Plenum Press, N.
Y. , (1973)1173.