

CHAPTER - 8

Effect of concentration of the electrolytes on the output performances of PEC cells of both n-WSe₂ and p-WSe₂ photoelectrodes

	Sub Contents	Pages
8.1	Introduction	123
8.2	Experimental	124
8.3	PEC solar cell fabrication	124
8.4	Conclusions	128
	References	132
	Captions of the figures	134

8.1. INTRODUCTION :

During the last decade, a number of photoelectrochemical (PEC), photovoltaic or regenerative cells and their characterization based on semiconductor electrodes in aqueous and non-aqueous media have been put forth by various authors (1-15). There have been several discussions in recent years on 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 (16-20) on the PEC behaviour of TMDC's 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 conversion 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 n-WSe₂ photoelectrodes. Also the concentration of ferri/ferro cyanide electrolyte has been optimised in the case of p-WSe₂ photoelectrodes for better conversion efficiency.

8.2. EXPERIMENTAL :

(a) n-WSe₂ :

Single crystals grown by chemical vapour transport technique using Br₂, TeCl₄ and SeCl₄ + Se as the transporters, have been used in the present work. From Hall coefficient and Mott-Schottky measurements it was ascertained that they were n-type semiconductors.

(b) p-WSe₂

Single crystals grown by chemical vapour transport method using SeCl₄ as a transporter, have also used in the present investigations. Their p-type nature was determined from the Hall co-efficient measurements which was then confirmed from Mott-Schottky plots.

8.3. PEC SOLAR CELL FABRICATION :

The preparation of PEC solar cells have already been described in chapter 6. The n-type and p-type semiconductor electrodes were immersed in an aqueous iodine/iodide and ferri/ferro cyanide electrolyte respectively and platinum grid was used as counter electrode. All the chemicals used

were of AR grade. The PEC cell was so designed that the electrolyte could be changed without disturbing the electrodes configurations. Different type of electrolytes were tried and checked by altering the individual concentrations. Finally those electrolytes giving better photovoltage and photocurrent were selected. Using these electrolytes the open circuit voltage, short circuit current density, fill factor and efficiency were measured. The results are given in Tables 1 and 2.

From Tables 1 and 2 the following conclusions can be drawn.

Amongst the four different electrolytes, the ferri/ferrocyanide electrolyte gives better results with p-WSe₂ electrodes and iodine/iodide electrolyte with n-type WSe₂ electrodes. | X

In order to observe the effect of iodine concentration, electrolytes were prepared by adding different amounts of I₂ to a fixed quantity of NaI. Variations of open circuit voltage $V_{o.c.}$ and short circuit current, $I_{s.c.}$ with iodine concentration are shown in Figs. 8.1 (a), 8.2(a) and 8.3(a) for the n-type crystals of WSe₂ grown by using Br₂, TeCl₄ and SeCl₄+Se transporters respectively. While Figs. 8.1(b), 8.2.(b) and 8.3 (b) show a similar variation of fill-factor

(F.F.) and efficiency ($\eta\%$) with iodine concentration for these photoelectrodes. It is seen that $V_{o.c.}$, $I_{s.c.}$ and efficiency increases with iodine concentration and after reaching a certain maximum decreases with further increase in the concentration. The fill factor shows only an increasing trend Figs. 8.1(b), 8.2(b) and 8.3(b) show a decrease in efficiency at higher concentration of iodine. This decrease arises due to absorption of light in electrolyte which results into lower short circuit currents. The decrease in efficiency can be attributed to the presence of large amounts of elemental iodine which can interact with the surface and generate surface states capable of trapping 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 absorption, which affects the band bending in the semiconductor can also be considered as a factor affecting efficiency (19).

In the case of p-WSe₂ photoelectrodes also the effect of change of concentration of the electrolyte $\left\{ K_3[Fe(CN)_6] + K_4[Fe(CN)_6] \right\}$ has been studied in detail and the results are shown in Fig.8.4(a) and 8.4(b). The figure 8.4 (a) clearly depicts the effect of concentration on open circuit Voltage ($V_{o.c.}$), short circuit current ($I_{s.c.}$), while figure 8.4(b) shows a similar variation of efficiency ($\eta\%$) and fill factor (F.F.)

It is seen that $V_{o.c.}$ and $I_{s.c.}$ gradually increases with increase in the concentration of the electrolyte acquiring a maximum at $0.05 \text{ M } K_3 [Fe(CN)_6] + 0.05 \text{ M } K_4 [Fe(CN)_6]$ and there after show a decreasing trend, with further increase in the concentration of the electrolyte.

Altering the composition of the electrolyte $K_3 [Fe(CN)_6] + K_4 [Fe(CN)_6]$ will therefore change its redox potential. Since the open circuit voltage and photocurrent change with the redox potential of the electrolyte, the observed change in their values can be attributed to this effect (21). The maximum power will of course be obtained at a particular concentration of the redox couple. Similar to (Kline et al (19) IX) the fill factor in the present case also increases with the increase in the concentration of the electrolyte. The variation of efficiency with concentration Fig. 8.4(b) shows that the maximum efficiency 9.05% is obtained at a concentration of $0.05 \text{ M } K_3 [Fe(CN)_6] + 0.05 \text{ M } K_4 [Fe(CN)_6] + 1 \text{ M } KCL$.

This value of conversion efficiency appears to be much higher than the values reported earlier with p-WSe₂ electrodes by different investigators (15,22,23). The investigations on layer type electrode materials prepared by different techniques have shown that the perfection in the growth parameters and transporting agents play an important role in

role in the quality of their photoelectrochemical perfection (24,25).

During the course of the present work, detailed experiments (Chap-3) were carried out to grow WSe_2 crystals using different transporters. It has been observed that use of $SeCl_4$ as a transporter improves the perfection of the grown $p-WSe_2$ crystals considerably. A possible factor which is likely to contribute to the enhancement of conversion efficiency with these crystals as photoelectrodes, may come about from the growth parameters adopted in their growth. When $SeCl_4$ is used as a transporter, Se atoms are involved which are native to WSe_2 crystals, the incorporation of selenium in the growing crystal does not result in the creation of additional recombination type energy states (gap states), in the band gap. This reduction in the energy states might be responsible for the improved efficiency values obtained in the present work.

8.4. CONCLUSIONS :

1. In all the different electrolytes the iodine/iodide electrolyte gives better results with $n-WSe_2$ electrodes and the ferri/ferro cyanide electrolyte gives better results with $p-WSe_2$ electrodes.

2. Ferri/Ferro cyanide electrolyte with concentration $0.05M K_3 [Fe(CN)_6] + 0.05M K_4 [Fe(CN)_6] + 1M KCl$ gives an efficiency of 9.05% and iodine/iodide electrolyte with concentration $1M NaI + 0.05MI_2$ gives an efficiency of 8.26% with p-WSe₂ and n-WSe₂ electrodes respectively.
3. Effect of concentration of iodine/iodide and ferri/ferro cyanide electrolytes gives a systematic variation in the results which is found to be similar to the reported data in the literature.

TABLE - 8.1

OPEN CIRCUIT VOLTAGE, SHORT CIRCUIT CURRENT DENSITY, FILL FACTOR AND EFFICIENCY OF n- WSe_2 PHOTOELECTRODE IN VARIOUS ELECTROLYTES

$V_{o.c.}$ (mv)	$J_{s.c.}$ (mA/cm^2)	Fill Factor (F.F.)	Efficiency (%)	Electrolyte
80	8.869	0.375	0.26	1M TiCl_3 + 1M TiCl_4
120	1.565	0.421	0.79	0.2M FeCl_3 + 0.1M FeCl_4 + 1M H_2SO_4
300	3.652	0.476	5.21	0.5 M I_2 + 1 M KI
200	2.608	0.458	2.39	0.1M $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.1M $\text{K}_4[\text{Fe}(\text{CN})_6]$ + 1M KCl.

TABLE 8.2.

OPEN CIRCUIT VOLTAGE, SHORT CIRCUIT CURRENT DENSITY, FILL FACTOR AND EFFICIENCY OF p- WSe_2 ELECTRODES IN DIFFERENT ELECTROLYTES.

$V_{o.c.}$ (mv)	$J_{s.c.}$ (mA/cm ²)	Fill Factor (F.F.)	Efficiency (%)	Electrolyte
65	1.25	0.307	0.25	0.2M FeCl ₂ + 0.1M FeCl ₃ + 1M H ₂ SO ₄
110	2.08	0.381	0.87	2M NaI + 0.5M Na ₂ SO ₄ + 0.5M H ₂ SO ₄
134	2.70	0.341	1.23	0.2M K ₄ [Fe(CN) ₆] ⁺ 0.01M K ₃ [Fe(CN) ₆] ⁺ + 0.05M KCl
150	5.41	0.487	3.95	0.1M K ₃ [Fe(CN) ₆] ⁺ + 0.1M K ₄ [Fe(CN) ₆] ⁺ + 1M KCl

R E F E R E N C E S

1. Ellis. A.B., Kaiser S.W. and Wrighton M.S., 1976,
J. Am. Chem., Soc., 98, 1635.
2. Manassen J.M, Hodes G and Cohen D., 1977,
J.Electrochem. Soc., 124, 532.
3. Miller B and Heller A., 1977,
J.Electrochem. Soc., 124, 697.
4. Gerrard W.A. and Owen. J.R., 1977,
Mater Res. Bull., 12, 677.
5. Fujishima A, Kohayakawa K and Honda K, 1975,
J.Electrochem. Soc., 122, 1487.
6. Wrighton M, 1979,
Acta Chem. Res., 12, 303.
7. Tributsch. H, 1978,
J.Electrochem. Soc., 125, 1086.
8. Ahmed. S.M. and Gerischer H, 1979,
Electrochimica Acta., 24, 705.
9. Kautek W, Gerischer H. and Tributsch H, 1979,
Ber. Bunsenges. Phys. Chem., 83, 1000.
10. Scheenmeyer L.F. and Wrighton M, 1979,
J. Am. Chem. Soc., 101, 6496.
11. Fan F.R. and Bard. A.J, 1981,
J.Electrochem Soc., 128, 945.
12. Lewerenz H.S., Heller. A and Disalvo F.J, 1980,
J.Am. Chem. Soc., 102, 1877.
13. Kline G, Kam. K.K., Ziegler R and Parkinson.
B.A., 1982.
Solar Energy Mater., 6, 537.
14. Nozik A.J. 1978,
Am. Rev. Phys. Chem., 29, 189.

15. Gobrecht. J, Gerischer. H and Tributsch. H, 1978,
Ber. Bunsenges Phys., Chem., 82, 1331.
16. Agarwal M.K, patil V.R. and Patel P.D, 1982,
J.Electrochem. Soc., India, 31,3.
17. Audas R and Irwin J.C, 1981,
J. Appl. Phys., 52, 11, 6954.
18. White H.S., Abruna H.D. and Bard A.J., 1982,
J.Electrochem Soc., 129,265.
19. Kline G. kam. K.K., canfield D and parkinson B.A.,
1981.
Sol. Energy Mater, 4, 301.
20. Offo. H., Muller N and Gerischer. H, 1982,
Electrochimica Acta., 27, 707.
21. Butler M.A., 1980,
J.Mater Sci., 15, 1.
22. Kautek W, Gobrecht. J. and Gerischer H, 1980,
Ber. Bunsenges Phys., Chem., 84, 1034.
23. Nagasubramanian G. and Bard A.J., 1981,
J.Electrochem. Soc., 128, 1055.
24. Azaiez C, Levy. F, Campet G. and Claverie, 1986,
D-53, 6th Int. Conf. PEC conversion and storage of
solar energy (paris.).
25. Prasad G. and Srivastava O.N., 1988,
J. Phys. D. Appl. Phys., 21, 1028.

CAPTIONS OF THE FIGURES :

- Fig.8.1.(a) plots of variations of open circuit voltage ($V_{o.c.}$), and short circuit current ($I_{s.c.}$) of n-WSe₂ electrode (grown by Br₂) with concentration of iodine.
- Fig.8.1.(b) plots of variations of fill factor (F.F.) and efficiency (η %) of n-WSe₂ electrode (grown by Br₂) with concentration of iodine.
- Fig.8.2.(a) plots of variation of open circuit voltage ($V_{o.c.}$) and short circuit current ($I_{s.c.}$) of n-WSe₂ electrode (grown by TeCl₄) with concentration of iodine.
- Fig.8.2.(b) plots of variation of fill factor (F.F.) and efficiency (η %) of n-WSe₂ electrode (grown by TeCl₄) with concentration of iodine.
- Fig.8.3.(a) plots of variations of open circuit voltage ($V_{o.c.}$) short circuit current ($I_{s.c.}$) of n-WSe₂ electrode (grown by SeCl₄ + Se) with concentration of iodine.
- Fig.8.3.(b) plots of variations of fill factor (F.F.) and efficiency (η %) of n-WSe₂ electrode (grown by SeCl₄ + Se) with concentration of iodine.
- Fig.8.4.(a) plots of variations of open circuit voltage ($V_{o.c.}$) and short circuit current ($I_{s.c.}$) of p-WSe₂ electrode (grown by SeCl₄) with concentration of K₃ [Fe(FN)₆] + K₄ [Fe(CN)₆] .
- Fig.8.4.(b) plots of variations of fill factor (F.F.) and efficiency (η %) of p-WSe₂ electrode (grown by SeCl₄) with concentration of K₃ [Fe (CN)₆] + K₄ [Fe(CN)₆] .

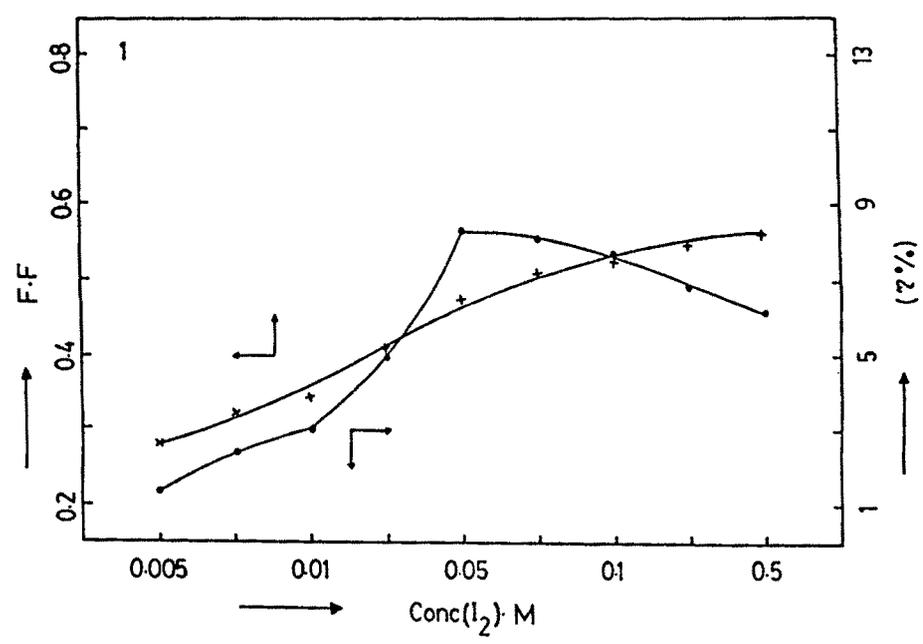
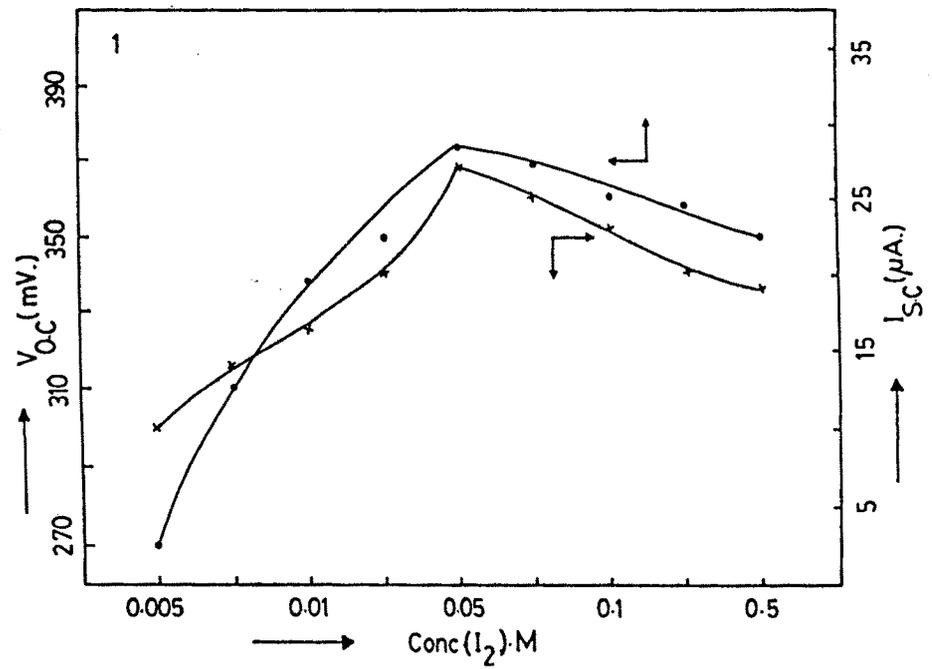


FIG-81(a,b)

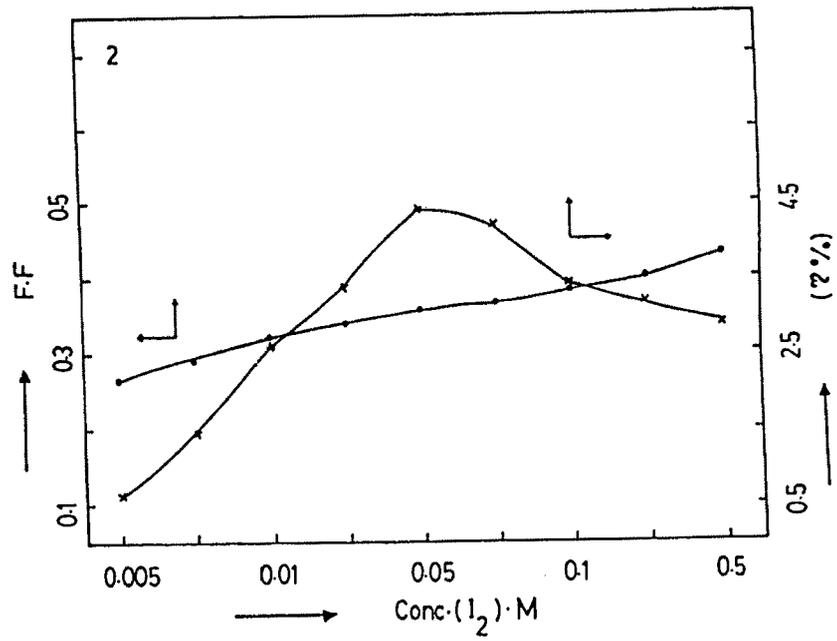
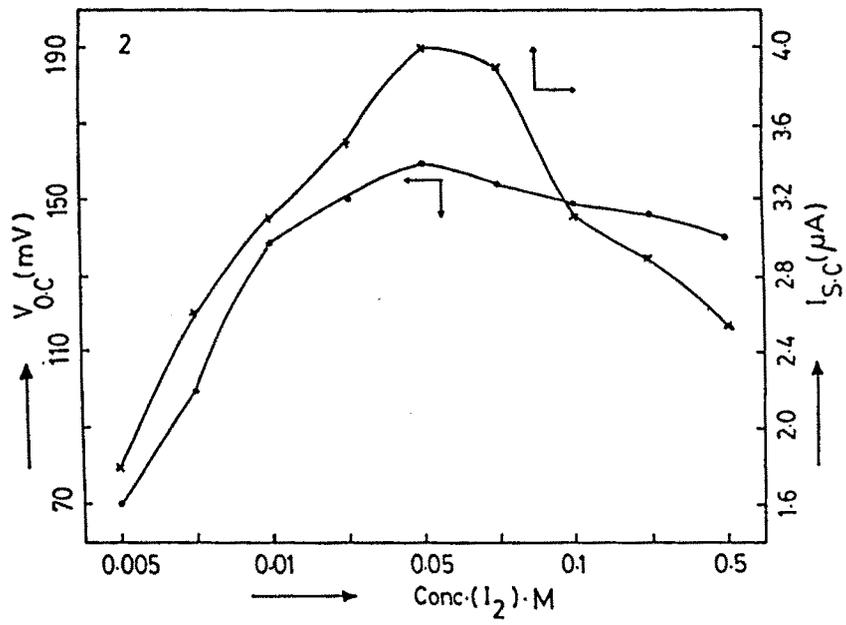


FIG-8.2(a,b)

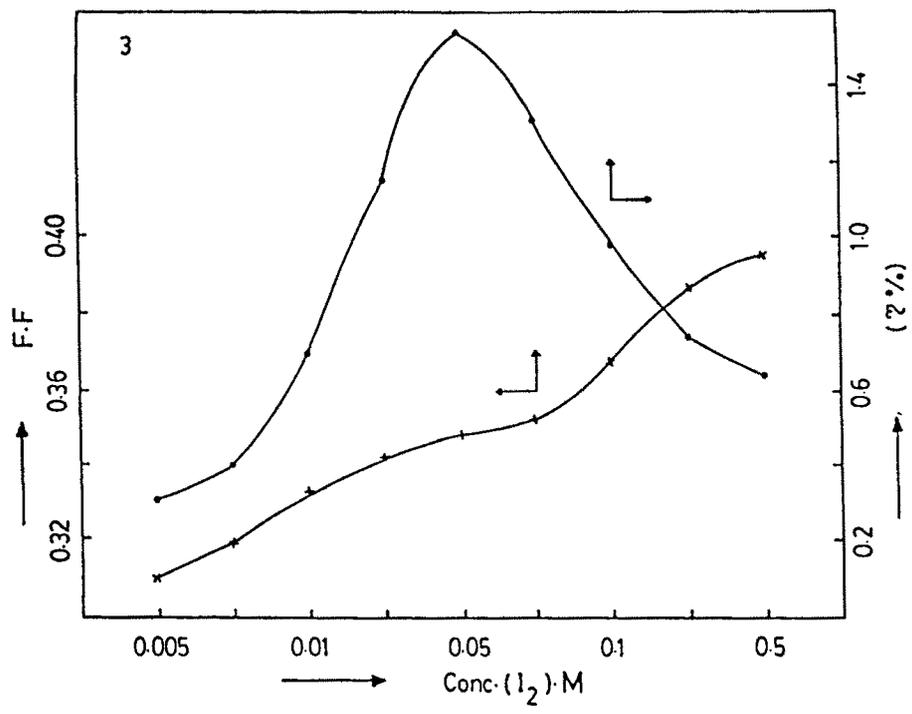
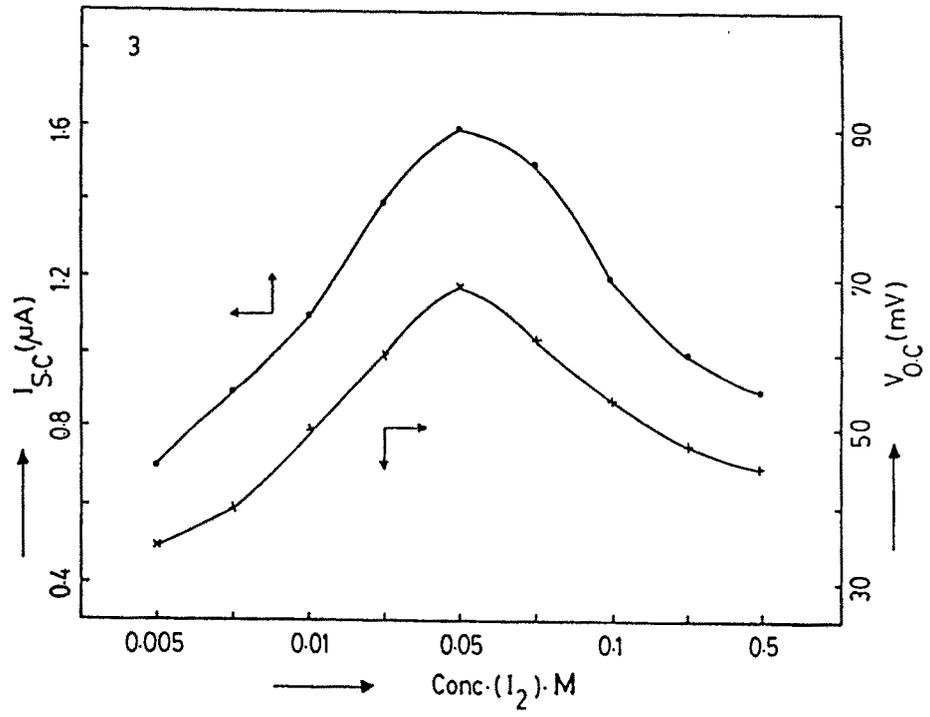


FIG. 8.3(a,b)

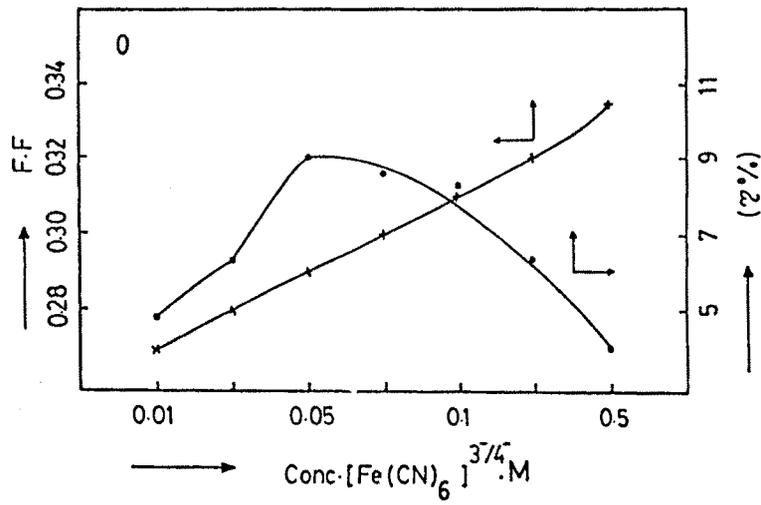
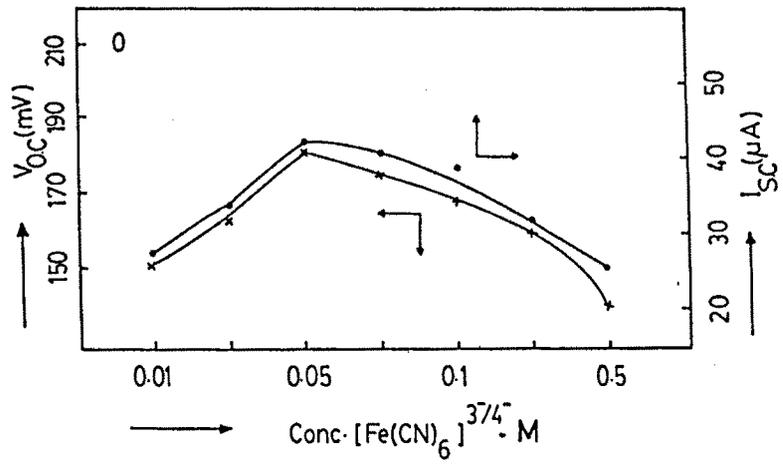


FIG. 8.4 (a, b)