CHAPTER- 5

STABILITY OF MoSe$_2$ / I$_2$ / I$^-$ / Pt

PEC SOLAR CELLS
PART: I

5.1 INTRODUCTION:

The Stability of liquid junction solar cells / photoelectrochemical solar cells is always a big question because of the intense electrochemical kinetics which governs the overall charge transfer mechanism at the rectifying interface. Therefore, even if the viable level of photoelectrochemical conversion process is achieved, it is always an important aspect to see the period of time over which this characteristic remains stable. Even in the presence of the atmosphere, the semiconducting materials are found to decompose though the rates of decomposition are very slow. But, the case becomes a little complicated when the semiconducting material is brought in contact with either acidic or basic electrolytic solution. Hence this chapter deals with the stability aspects of photoelectrochemical solar cells.

5.2 DECOMPOSITION OF SEMICONDUCTOR WITHOUT BIAS:

In presence of the oxidizing agents in electrolyte, a semiconductor is sharply attacked like metals. If this process takes place in an electrolytic conductive environment, the probability is very high that this attack proceeds according to an electrochemical mechanism; that means an anodic and a cathodic process go on at equal rates on the surface thereby compensating the net electrical current which becomes zero. The theory of such independent, superimposed, partial currents, which are coupled only by the electrical field at the surface has been worked out in detail by C. Wagner (1938) [310] long way back in 1938. But the application of this treatment without modifications to semiconductors leads to some difficulties, which are carried by the differentiation of the potential currents into electron and the hole currents. This leads to a new type of coupling.
Besides this electrochemical type of attack, a direct chemical oxidation has been observed by Gerischer and Mindt (1968) [311] in which the rate does not depend on the change in the surface. This attack is found only for oxidizing agents which can form two new chemical bonds simultaneously with the two partners of chemical bond on the surface. The most important of such reagents are chlorine, bromine, iodine and H$_2$O$_2$. The mechanism of these direct attack is represented in Fig. 5.1.

\[ X_2 = \text{I}_2, \text{Br}_2, \text{Cl}_2, \text{H}_2\text{O}_2 \]

Fig. 5.1. Chemical oxidative attack on surface bonds.

5.3 THEORY OF ELECTROCHEMICAL CORROSION FOR SEMICONDUCTORS:

The general condition for a steady state in corrosion is the balance of anodic and cathodic currents: $j^+ = j^-$. In metals, the partial currents depend not only on the composition of the surface and of the electrolyte adjacent to the surface, but also on the electrical field strength in the interface. This electrical field influences these two processes oppositely and the electrode potential adjusts itself to fulfill this balancing condition. The field strength varies little at a semiconductor surface. The governing factors for the rate of charge transfer reactions are the concentrations of electrons and holes in the surface, but only an anodic reaction in the valence band and a cathodic reaction in the
conduction band is influenced by any change of hole or of electron concentration, while the reverse processes go on at practically constant rate. The balancing condition for the net current does not necessarily mean the balancing of the partial currents in each of the bands. It only means

\[ j_c^+ + j_v^+ = j_c^- + j_v^- \]  

(5.1)

the net currents in each of the energy bands must not be zero, but will have opposite sign:

\[ j_c^+ - j_c^- = j_c^- - j_v^+ = j_v^- - j_v^+ \]  

(5.2)

where \( j_c \) is the electron injection current and \( -j_v \) is the hole injection current, which must be equal under corrosion conditions. We see from Eq. (5.2) that corrosion can lead to simultaneous injection of electron and holes. Though formally \( j_c \) could be negative, and corrosion would then mean electron-hole pair extraction, this seems rather unlikely. The reason is that the cathodic process is usually overwhelmingly a hole-injection reaction, because oxidants, which can pick up electrons only from the conduction band are not able to oxidize the semiconductor crystal. But electron-hole pair injection is a rather common possibility in the steady state for the corrosion of semiconductors.

In this case, the situation is very similar to that under illumination and electron-hole pair injection causes a change in the distribution of carriers in space-charge layer. A detectable effect can be expected only if the space-charge layer is very sensitive to any change in the equilibrium distribution, that is, for a depletion or an inversion layer. As it is seen, the anodic oxidation of semiconductors consumes holes and occurs only if the surface is p-type. Therefore, this electron-hole-pair injection can be noticed only in n-type specimens, and especially when an inversion layer is formed underneath the surface.
The resulting effect is a deviation of corrosion potential in the negative direction from that value which one would expect from simple superposition of anodic and cathodic current voltage curves. This can be treated [Gerischer and Beck (1960a)] [312] like the origin of a photovoltage in a p-n junction, which reduces the potential drop over this junction according to the well-known relationship [Ryvkin (1965), Bube (1960)] [313,314]

\[ \Delta U = \frac{kT}{e_0} \ln \left[ 1 + \left( \frac{j_c}{j_{\text{sat}}} \right) \right] \]  

(5.3)

where, \( j_{\text{sat}} \) represents the saturation current of the minority carrier (holes in this case) to the surface. Since the change of the measured electrode potential is opposite in sign to that of \( \Delta \phi_s \), such a deviation in corrosion potential must have the negative sign for an n-type specimen.

### 5.4 DIFFERENT METHODS FOR CORROSION STUDIES:

As already mentioned, stability of a photoelectrode is determined by its corrosion characteristics which is usually measured in terms of corrosion rates. In a simple way, corrosion rate may be determined from the effects of corrosion. The materials may become unstable due to corrosion in various ways. They may develop cracks and break upon strain. They may suffer fatigue and thereby lose mechanical properties to become brittle. The material on the surface may be transformed into oxides, which in turn may peel off or dissolve away, causing a weight loss. The electrical resistivity has also been found to increase due to the cross-sectional shrinking of substances. Microscopic changes on the surface, e.g. tarnishing, de-colouration, formation and widening of the etch pits etc. may also result from corrosion [315]. The byproducts of corrosion may also change the PH of the electrolyte in contact [316]. Thus, by
accessing and gauging any of these effects before and after a known time, corrosion rate can be estimated. Various methods, used, in general, for its estimation are briefly described in subsequent sections.

5.4.1 Weight Loss Method

If mass is removed from the specimen by corrosion, the amount of mass can be determined by careful weighing of the specimen before and after the corrosion rate is determined as [317]

\[
\text{Corrosion rate} = \frac{\text{Weight loss} \times 534}{\text{Area} \times \text{Time} \times \text{Density}}
\] (5.4)

Usually corrosion rate is measured in milli inches per year (MPY)

This method is valid only if corrosion is largely uniform over the surface and considerably faster. To find the mass of the material which do not undergo corrosion, the corrosive products must be removed carefully without removing the uncorroded material. This is very difficult to achieve [318]. The reproducibility of results is very poor as it involves measurement of small weight differences between initial and final weights. This method is usually employed for a specimen showing spontaneous dissolution in the environment.

5.4.2 Pit Depth Measurements:

When the effects of corrosive attack on the specimen are localized on surface, etch pits are formed. Using a microscope of high magnification and resolution, etch pit dimensions can be measured. Knowing the area and the depth, corrosion rate can be found out by estimating the weight loss.
5.4.3 *Galvanic Corrosion Method:*

Since corrosion involves charge transfer reaction at the interface, monitoring of galvanic current can also be used for estimating the corrosion rate. This method can be successfully employed if the current generated due to charge transfer reactions is sufficiently large. This is usually used to estimate the corrosion rate of dissimilar metals.

5.4.4 *Electrochemical Method*

There are two different approaches, which are usually followed for the estimation of corrosion rate by this method.

1. Varying the current and measuring the resulting potential. This is called galvanodynamic method.

2. Varying the potential and measuring the resulting current. This is called potentiodynamic method.

Both these techniques are based on the polarization phenomena and center around probing the shift in the original equilibrium on application of external driving force at the interface. Since these methods can be used for low corrosion rate specimens and are more informative, they are advantageous and reliable. As one of these methods i.e. potentiodynamic method, has been used in the present studies, it is discussed here a bit in detail.

5.5 THEORY OF ELECTROCHEMICAL METHOD OF CORROSION STUDIES:

Under original equilibrium condition, the electrochemical reactions (oxidation and reduction) give rise to a current called corrosion current ($I_{\text{CORR}}$)
and the corresponding potential is called corrosion potential ($E_{\text{corr}}$). The applied charge or potential results in an over potential. If the over potential is positive with respect to $E_{\text{corr}}$, anodic reaction is accelerated and the resulting current is called anodic current. If over potential is negative the cathodic reaction is accelerated and the current is called cathodic current [319]. Both these currents are called polarization currents.

The electrode offers a resistance to oxidation or reduction when the over potential is applied. This resistance is known as polarization resistance. At corrosion potential, both reaction rates are equal in magnitude, resulting in no current through the circuit. These cathodic or anodic currents ($I_{\text{corr}}$) are directly related to the polarization resistance $R_P$. Hence, $I_{\text{corr}}$ is a measure of this corrosion rates. Since there is no direct method to measure $I_{\text{corr}}$, polarization technique provides a powerful tool to evaluate the corrosion rate and polarization resistance of the electrode [319,320].

When a charge $\Delta q$ is given to the electrical double layer of the electrode, the equilibrium shifts and so the potential jumps to another value $E_m$ from $E_{\text{corr}}$. Neglecting the leakage by corrosion reactions, the over voltage ($E$) can be written as

$$E = E_m - E_{\text{corr}}$$  \hspace{1cm} (5.5)

The double layer acts as a capacitor and the differential capacity ($C_d$) per unit area is assumed to be constant. The incremental charge induced on the electrode is progressively consumed by corrosion reaction and the potential drifts back to $E_{\text{corr}}$. The amount of charge consumed during an interval $t$ is given by

$$\Delta q_t = C_d (E - E_t)$$  \hspace{1cm} (5.6)

where $E_t$ is the over potential at an instant $t$. 
The resulting current at that instant is given by Butler Volmer equation [10]

\[ I_t = I_{CORR} [\exp (\alpha_+ n_+ F E_t / RT) - \exp (\alpha_ - n_ - F E_t / RT)] \]  \hspace{1cm} (5.7)

where \( \alpha_+ \) and \( \alpha_- \) are the transfer coefficients

\( n_+ \) and \( n_- \) are the number of charge carriers that take part in anodic and cathodic reactions,

\( F \) is Faraday's constant,

\( R \) is gas constant and

\( T \) is the absolute temperature.

By applying small field approximation, equation (5.7) reduces to

\[ I_t = 2.3 I_{CORR} \left( \frac{1}{\beta_a} + \frac{1}{\beta_c} \right) E_t \]  \hspace{1cm} (5.8)

where

\( \beta_a = 2.3 \alpha_+ n_+ F / RT \)

\( \beta_c = 2.3 \alpha_- n_- F / RT \)

are called Tafel constants. From above equation, polarization resistance \( R_p \) can be given as

\[ \left( \frac{1}{R_p} \right) = 2.3 I_{CORR} \left( \frac{\beta_a + \beta_c}{\beta_a \beta_c} \right) \]  \hspace{1cm} (5.9)

Thus, the plot of \( E_t \) against \( I_t \) is a linear curve whose slope directly gives polarization resistance \( R_p \).

From equation (5.7) the reduced Butler Volmer equations for anodic and cathodic reactions can be given by [322]
\[ E_t = A + \log I \] (anodic) \hspace{1cm} (5.10a)

\[ E_t = B + \log I \] (cathodic) \hspace{1cm} (5.10b)

here \( A \) and \( B \) are constants.

Above equations are known as Tafel equations. From here, it can be seen that a plot of \( E_t \) against \( \log I \) is linear for large values of \( E_t \), whose slopes give the Tafel constants. These can be used to find out \( I_{\text{CORR}} \) using equation (5.9).

Since the mass of the material corroded is given by Faraday's law the mass removed at \( E_{\text{CORR}} \) can be given as

\[ M = \rho A d = M_{\text{CORR}} \frac{t}{ZF} \] \hspace{1cm} (5.11)

From here, the corrosion rate can be given as

\[ \frac{d}{t} = \frac{M_{\text{CORR}}}{\rho Z FA} \] \hspace{1cm} (5.12)

Substituting \( F \)

\[ \text{Corrosion rate} = 0.13 \text{ E.W.} \frac{I_{\text{CORR}}}{A \rho} \] \hspace{1cm} (5.13)

where, E.W. is equivalent weight,

\( M \) is molecular mass,

\( Z \) is number of electrons involved in one act of reaction,

\( \rho \) is the density and

\( d \) is depth through which corrosion take place,
Thus using the evaluated $I_{\text{CORR}}$ value, corrosion rate can be determined using equation (5.13).

5.6 CORROSION IN PEC SOLAR CELLS:

The process of corrosion in case of PEC solar cells leads to the degradation of the photoconversion characteristics which is never desirable for a practical viability. As discussed earlier, the electrons and holes take part in the process of corrosion along with the oxidizing and reducing species of the liquid electrolytes. The generation of electron hole pairs or the availability of these pairs is different under illumination compared to the dark condition of the semiconducting electrode. Therefore in the following section, the corrosion mechanism of the semiconductor has been discussed for both cases; i.e. the dark condition and illumination condition.

5.6.1 Corrosion In PEC Solar Cells In Dark :

Corrosion can be controlled effectively only if the mechanism involved is well understood. The dissolution of semiconductor photoelectrode is due to the weakening of the bonding between the constituent atoms. This arises due to participation of bonding electrons / holes in the interfacial reactions [323].

Considering the decomposition of a semiconductor $AB$ ($A^{2-}$ $B^{2+}$), the two decomposition reactions are written as [324]

**Cathodic decomposition**

$$AB + 2e^- \leftrightarrow A + B^{2-}$$

or

$$AB \leftrightarrow A + B^{2+} + 2e^-$$
Anodic decomposition

\[ \text{AB} + 2h^+ \leftrightarrow \text{A}^{2+} + \text{B}^{+} + 2e^- \]

\[ \text{AB} \leftrightarrow \text{A}^{2+} + \text{B} + 2e^- \]

The relative positions of the energy level involved in cathodic reaction \( nE_D \) and anodic reaction \( pE_D \) are the main governing factors allowing or forbidding the decomposition reaction [325,326]. Consequently, the semiconductor electrode in a particular electrolyte will be stable if the energy levels are located as shown in Fig. 5.2(a) for an n-type semiconductor electrode. This shows that the electrode is less prone to corrosion if the reductive decomposition potential lies above the conduction band edge and the oxidative decomposition potential lies below the valance band edge [326]. Other possibilities are as given in Fig. 5.2.(b,c). In practice, the stability criteria in a PEC solar cell is laid down as

\[ pE_D < E_{\text{redox}} < nE_D \]

The decomposition potential depends on the composition of the electrolyte, the redox potential, the Fermi energy level and the charge carrier concentration [327]. Thus, the doping concentration also has an influence on the stability of the electrode. The surface defects, dislocation, inclusions, stacking faults, grain boundaries etc. are the other factors which sometime play an important role in the corrosion mechanism [328].

If the charge transfer to a fast redox couple is more probable than that to the decomposition reaction, the electrode may be more stable. If such species are not available, the decomposition reactions may predominate. Hence, corrosion of the semiconductor electrode is both thermodynamically as well as kinetically controlled process.
Fig. 5.2 Relative positions of redox and band energies in n-type semiconductor PESC indicating its stability.
(a) Stable.
(b) Stable against anodic decomposition.
(c) Unstable.
5.6.2 Corrosion In PEC Solar Cells Under Illumination:

A semiconductor electrode, stable in dark may not be stable under illumination. The Fermi levels splits into two quasi Fermi levels under illumination [328], as shown in Fig.5.3, due to the photogenerated charge carriers. The shift in the quasi Fermi levels are given by

\[ nE^*_f - nE_f = kT \ln (1 + \frac{\Delta n^*}{n_0}) \]  
\[ \text{Eq. 5.14} \]

\[ pE^*_f - pE_f = kT \ln (1 + \frac{\Delta p^*}{p_0}) \]  
\[ \text{Eq. 5.15} \]

where * represents the parameters under illumination.

These shifts in the Fermi levels or redox energy levels may make the semiconductor more prone to corrosion. The shifts increase with the illumination intensity as the photogenerated minority carrier concentration increases and so under certain illumination condition, quasi Fermi energy level may coincide with the anodic decomposition or cathodic decomposition energy level. Thus, enhancement of intensity may accelerate the decomposition reaction when the favourable conditions [329] are established (Fig5.4). These conditions are

\[ E_f^* \geq nE_D \] for cathodic decomposition

\[ E_f^* \leq pE_D \] for anodic decomposition

Hence, the stability of the electrode depends both on the intensity and also on the rate of charge transfer in redox reaction. Faster the charge
Fig. 5.3 Quasi fermi levels under illumination.
(a) p-type semiconductor.
(b) n-type semiconductor.
Fig. 5.4 Energy levels under illumination.
(a) in dark.
(b) under high illumination.
unstable due to cathodic decomposition.
(c) under low illumination less stable than (a) but more than (b),
transfer to the redox species, lesser is the decomposition of electrode. Therefore, in photocorrosion also kinetics plays an important role.

5.7 BRIEF REVIEW OF CORROSION IN TMDCs BASED PEC SOLAR CELLS:

The photocorrosion decomposition proceeds in several stages and corresponding potentials of each reaction may not coincide with that for the decomposition [119]. Moreover, the kinetics of photocorrosion also depends on the features of electronic configuration and bonding mechanism. The rate of charge transfer at the interface depends on the overlapping of electron orbits of the atoms, which decides energy band structure and the bond strength between atoms. The small overlapping leads to reduction in the probability of charge transfer. So the photogenerated charge carriers are available for the decomposition reaction. This is the case in semiconductors like CdS, CdSe, ZnO etc. in which the covalent bonds are formed by the orbitals of electro positive and electro negative atoms. Under illumination, the holes are generated due to inter band transition between valence band (the band of p-electrons) and the conduction band (the band of s-electrons). In this case the localization of the holes at the inter atomic bonds weaken the bonding between the constituent atoms and initiates anodic dissolution of the electrode under illumination [326,328,329,330].

In general, the dissolution of a compound semiconductor AB involves electronic orbitals and occurs in a number of steps [102,331]. If in the semiconductor AB the valance band corresponds to the electronic orbitals of B atoms (like II-VI and III-V compounds), then the presence of photogenerated holes in the valance band will weaken the A-B bonds and increase their tendency to interact with electron donor species in the electrolyte. An A atom may thus go into solution as an A⁺ ion. Following the above arguments, Garischer(1978)[102] has suggested that the semiconductor electrodes in
which phototransitions do not involve bonding orbitals would be more corrosion resistive.

In this respect, transition metal dichalcogenides have emerged as very promising materials. The above point can be well illustrated by taking the example of the comparison of MoS$_2$ / MoSe$_2$ and CdS. In CdS, the photocorrosion is relatively easy because the phototransition of carriers corresponds to 3p orbitals of S and 5s orbitals of Cd. These are also the bonding orbitals for CdS. Hence a phototransition would weaken the bonds and initiate a corrosion reaction. For MoS$_2$ or MoSe$_2$, the case is different. Electron energy bands of MoS$_2$ or MoSe$_2$ with respect to the redox energy levels of aqueous electrolytes are shown in Fig.5.5. The relative positions of the redox level and the band energies in PEC solar cells constructed using n-type semiconductor has been shown in Fig.5.2. A comparison of Figures 5.5 and 5.2 shows that MoSe$_2$ or MoS$_2$ are not completely unamenable to dissolution from purely thermodynamic consideration. However, they have been found as fairly stable electrodes in PEC solar cells. This can be attributed to the fact that the phototransitions in these materials involve non bonding d-d orbitals of Mo atoms. The usefulness of Molybdenum and Tungsten chalcogenides has been amply demonstrated by Tributsch (1977,1978)[331,90,91] Tributsch et.al. (1979) and Gobrescht et. al. 1978a,b. Several reports can be seen in literatures regarding the stability of TMDC PEC solar cells [325,327,119,332,333,277,270].

However, TMDCs show photoanodic decomposition due to the photogenerated holes [334]. The photogenerated holes in these electrodes oxidize water to OH radical, which in turn react chemically with the electro negative atom such as S or Se on the surface of the electrode. Thereby oxidizing them to sulphates or selinates. So, the proper choice of redox couple is the only solution for the stabilization of TMDC electrodes. It has been found that I'/I$_2$ redox couple is more stable system, due to the passivation of Van der
Fig. 5.5 Position of electron energy bands of MoS$_2$ and MoSe$_2$ *vis-à-vis* redox energy levels of aqueous electrolytes.
Waals edges in contact with the electrode [334]. Organic electrolytes are also found to stabilize the electrodes [330]. Other factors which influence photocorrosion of TMDC based semiconductor electrodes are the presence of steps, dislocations etc. on its surface, formed during the growth of the crystals.
PART -II

5.8 CHOICE OF THE TECHNIQUE FOR CORROSION INVESTIGATIONS OF MoSe₂ PEC SOLAR CELLS:

As discussed in section 5.4, there are several methods available for the studies of corrosion of the material. The weight loss method is not proper choice for the corrosion investigations in case of PEC solar cells, because it is not possible to find out the change in weight of the semiconductor at every step of the studies. The pit depth measurement technique requires the study of development of etch pits on the surface of the semiconductor which remains in the contact of the electrolyte. These studies can be done using the optical microscope having a high magnification and resolution. The galvanic corrosion method can be successfully used to carry out the corrosion studies provided the current generated due to charge transfer reactions is sufficiently large. This method is usually used in case of the dissimilar metals. The electrochemical method is based on either the measurement of resulting potential on account of varying current or the measurement of resulting potential due to change in applied voltage. This is an easier technique and can be accomplished conveniently and successfully in case of liquid junction solar cells. Therefore in present investigations, the electrochemical method has been employed to investigate the corrosion behaviour of MoSe₂ PEC solar cells.

5.9 EXPERIMENTAL TECHNIQUE FOR CORROSION INVESTIGATIONS OF MoSe₂ PEC SOLAR CELLS:

In the present investigations, the corrosion rates have been determined by measuring the polarization resistance and the Tafel constants through potentiodynamic scanning. These measurements were done using EG & G model 273 potentiostat / Galvenostat. This potentiostat / galvenostat is capable of being operated in the following modes-
i. Potentiostatic
ii. Potentiodynamic
iii. Galvanostatic
iv. Galvanodynamic.

Its operation in these modes is governed by the following capabilities of the potentiostat / Galvanostat.

a) It can impose and display desired potential on the working electrode with respect to a standard reference electrode (usually a saturated Calomel electrode).

b) It can measure and display the total current flowing between the working electrode and the counter electrode.

c) It can enable control and scanning of the applied potential/current in the respective modes.

In fact, push button controls provided on the front panel of this instrument facilitate the choice of the desired scanning rate, scanning range, start and stop commands, etc. to facilitate a real time experiment. A scan status display additionally provides a continuously updated status information about the advance of the experiment. A diagram showing the front panel controls of the model 273 potentiostat / galvanostat along with the experimental arrangement for studying the corrosion characteristics has been given in Fig. 5.6.

For measuring the polarization resistance (defined as the resistance of the working electrode to oxidation during the application of an external potential), potentiodynamic scanning has been limited to \( \pm 20 \text{ mV} \) across the corrosion potential \( E_{\text{CORR}} \). At \( E_{\text{CORR}} \), the anodic and the cathodic currents are equal and hence the net current is zero. The scan rate of measurements was
Fig. 5.6 Front panel controls of the model 273 potentiostat/galvanostat along with the experimental set up for corrosion study.
kept at 0.1 mV/sec. For determining Tafel constants, the data were obtained by potentiodynamic scanning in a range of ± 350 mV across \( E_{\text{CORR}} \). The scan rate during these investigations was also kept at 0.1 mV/sec with the knowledge of \( I_{\text{CORR}} \) and the polarization resistance, corrosion rates were evaluated using the relation.

\[
\text{Corrosion rate (MPY)} = \frac{0.13 \times \beta_a \times \beta_c \times (E. \ W.)}{2.3 \times R_p \left( \beta_a + \beta_c \right) \times \text{Area} \times \text{Density}}
\] (5.16)

where, \( \beta_a \) and \( \beta_c \) are anodic and cathodic Tafel constants respectively, and \( E. \ W. \) is the equivalent weight.

5.10 RESULTS AND DISCUSSIONS:

The potentiodynamic scanning using the potentiostat has been used to study the corrosion behaviour of MoSe\(_2\) PEC solar cells, for both p-type and n-type. For n-type MoSe\(_2\), the Tafel plots obtained for MoSe\(_2\)/l\(_2\)/l'/Pt PEC solar cell studied in a range around ± 350 mV across the corrosion potential has been shown in Fig. 5.7 and from this figure it can be seen that the value of corrosion potential \( (E_{\text{CORR}}) \) is found to be -250 mV. From the nature of the graph it can be seen that the anodic dissolution and the cathodic dissolution have different rates i.e. the nature of the deviation of Hall voltage with current assumes different slopes across \( E_{\text{CORR}} \). Using the slope of the straight line fit to the Tafel data, the Tafel constant \( \beta_a \) (known as anodic Tafel constant) and \( \beta_c \) (known as cathodic Tafel constant) have been calculated and their values were found to be 0.056 V/dec and 0.235 V/dec respectively. These values, later on, have been used for the calculation of the corrosion rate observed in present case. The same measurements have also been carried out in a range ± 20 mV across the corrosion potential and the results have been shown in Fig.5.8. The slope of the V-I plot shown in Fig. 5.8 has been calculated and was found to be
Fig. 5.7 Tafel Plots for n- MoSe$_2$/I$_2$/T Pt PEC solar cell.
Fig. 5.8 Polarization resistance plot for n-MoSe$_2$/I$_2$/I/Pt PEC solar cell.
As it is discussed earlier, MoSe$_2$ belongs to a class of transition metal dichalcogenides which are found to be very stable against corrosion and decompositions. This directly indicate that MoSe$_2$ is a highly resistive material for corrosion and hence, the polarization resistance should be high. In present case the polarization resistance has been found to be 4.08 KΩ, which is indeed a somewhat high value indicating the fact that MoSe$_2$ crystals which have been used as photoanodes in PEC solar cells are polarization resistant. If we look at the value of corrosion rate calculated here (7.77 $\times$ 10$^{-4}$ MPY), it can be inferred that this value of corrosion rate is very small indicating that the rate of corrosion is very slow. Thus, from these results it is concluded that MoSe$_2$ crystals are found to be stable against corrosion / decomposition when used with Iodine / Iodide electrolyte to form PEC solar cells.

p-type MoSe$_2$ crystals have also been used in present case for fabrication of PEC solar cells. Therefore, some investigations regarding the corrosion for the photocathodes constructed using p-MoSe$_2$ crystals have also been carried out. The Tafel plots investigated for five different photocathodes constructed using p-type MoSe$_2$ crystals have been shown in figures 5.9, 5.10, 5.11, 5.12 and 5.13. From all these figures, it is clearly seen that the variation of anodic current and the cathodic current with the voltage is different. Using the slopes of both these regions the Tafel constants $\beta_a$ and $\beta_c$ have been calculated for all cases and the values have been given in Table 5.1.

The same Tafel plots have been investigated in a range $\pm$ 20 mV across the corrosion potential for the calculation of polarization resistance in each case which have been graphically represented in Figures 5.14, 5.15, 5.16,
Fig. 5.9 Tafel Plot for p-MoSe$_2$/I$_2$/I'/Pt PEC solar cell.
Fig. 5.10 Tafel Plot for p-MoSe$_2$/I$_2$/I'/Pt PEC solar cell.
Fig. 5.11 Tafel Plot for p-MoSe$_2$/I$_2$ / I / Pt PEC solar cell.
Fig. 5.12 Tafel Plot for p-MoSe$_2$/I$_2$/I$^-$/Pt PEC solar cell.
Fig. 5.13 Tafel Plot for p-MoSe₂ / I₂ / I⁻ / Pt PEC solar cell.
Fig. 5.14 Polarization resistance plot for p-MoSe₂ / I₂ / I⁻ /Pt PEC solar cell.
Fig. 5.15 Polarization resistance plot for p-MoSe₂/I₂/I/Pt PEC solar cell.
Fig. 5.16 Polarization resistance plot for p-MoSe₂/I₂/T/Pt PEC solar cell.
5.17 and 5.18 respectively. The values of $R_p$ for all these electrodes have been given in Table 5.2.

The values of Tafel constants $\beta_a$ and $\beta_c$ and the value of polarization resistance $R_p$ are given in Table 5.1 and 5.2 and they have been used to calculate the corrosion rate. The calculated values of corrosion rate have also been presented in table 5.2. From the careful observation of the data given in Table 5.2, it can be seen that the corrosion rate is very small and the polarization resistance is high. This is obvious because the tendency of corrosion or the decomposition is inversely proportional to the resistance of the material towards polarization. This is nearly seen in present case where the increase of one order in the polarization resistance leads to a decrease of one order in the corrosion rate.

From above investigations, a general conclusion can be drawn as follows,

"MoSe$_2$ material has been observed to be quite stable against corrosion when it is used along with the Iodine / Iodide solution for the fabrication of PEC solar cells".

5.11 VARIATION OF EFFICIENCY AND FILL FACTOR OF MoSe$_2$ PEC SOLAR CELLS WITH TIME:

From above results it is now clear that the parameters of the MoSe$_2$ PEC solar cells should not get affected largely over a period of time and hence the photoconversion characteristics should be constantly stable with time. To confirm this inference, the efforts have been made to study the variation of some important parameters (like photoconversion efficiency and fill factor) with time. For these investigations, two photoelectrodes were chosen
Fig. 5.17 Polarization resistance plot for p-MoSe$_2$/I$_2$/I$/$Pt PEC solar cell.
Fig. 5.18 Polarization resistance plot for p-MoSe$_2$/I$_2$/I$^-$/Pt PEC solar cell.
Table 5.1 Values of Tafel Constants for MoSe$_2$ based PEC solar cells.

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Tafel constants</th>
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<tr>
<td></td>
<td>$\beta_a$ (V/Dec.)</td>
<td>$\beta_c$ (V/Dec.)</td>
</tr>
<tr>
<td>1</td>
<td>0.485</td>
<td>0.209</td>
</tr>
<tr>
<td>2</td>
<td>0.135</td>
<td>0.232</td>
</tr>
<tr>
<td>3</td>
<td>0.196</td>
<td>0.265</td>
</tr>
<tr>
<td>4</td>
<td>0.248</td>
<td>0.307</td>
</tr>
<tr>
<td>5</td>
<td>0.138</td>
<td>0.068</td>
</tr>
</tbody>
</table>

Table 5.2 Results of Corrosion behaviour of MoSe$_2$ based PEC solar cells.

<table>
<thead>
<tr>
<th>Electrode No.</th>
<th>Polarization resistance $R_P$ (K$\Omega$)</th>
<th>Corrosion rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.5</td>
<td>$5.23 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>$3.24 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>182.5</td>
<td>$5.15 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>36</td>
<td>$2.06 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>14.23</td>
<td>$1.99 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
having similar photoconversion characteristics. Electrode no. F was investigated for its photoconversion behaviour as per the following cycle.

Step 1 The electrode was dipped in the electrolyte and the photoconversion characteristics were studied.

Step 2 The electrode was taken out of the electrolyte for some time.

Step 3 The electrode was again inserted in the electrolyte for investigating the photoconversion characteristics.

Step 4 The electrode was again taken out from the electrolyte for the same time.

Step 5 The electrode was again dipped in the electrolyte and its photoconversion characteristics have been investigated.

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</tbody>
</table>
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This process was continued for a number of hours and at each time the photocurrent conversion characteristics of MoSe$_2$ / I$_2$ / I$^+$ / Pt PEC solar cells have been investigated. The variation of photoconversion efficiency of PEC solar cell with electrode no. F with time for 20 mW/cm$^2$ and 100 mW/cm$^2$ intensity of incident illumination has been shown in Fig. 5.19 and 5.20 respectively. Similarly the variation of fill factor for the same electrode for the same intensities of incident illumination has been shown in Fig. 5.21 and 5.22 respectively.

One PEC solar cell having electrode no. D was investigated for its photoconversion characteristics over a large period of time in such a way that the electrode was constantly left in the electrolyte without taking out for this time. The variation of photoconversion efficiency of this electrode at two different intensities of incident illumination with time has also been shown in Fig.
Fig. 5.19 Variation of efficiency of MoSe$_2$ PEC solar cell over a period of time (electrode F).
Fig. 5.20 Variation of efficiency of MoSe$_2$ PEC solar cell over a period of time (electrode F).
Fig. 5.21 Variation of fill factor of MoSe$_2$ PEC solar cell over a period of time (electrode F).
Fig. 5.22 Variation of fill factor of MoSe$_2$ PEC solar cell over a period of time (electrode F).
5.23 and 5.24 and the fill factor variation observed in similar way has been represented in Fig. 5.25 and 5.26. From all these figures, it can be seen that the efficiency and fill factor of both the electrodes remain stable over a period of time under investigation, which is as per the expectation drawn from the corrosion studies. Thus, from the corrosion investigations and stability investigations of MoSe$_2$ PEC solar cells presented above it is broadly concluded that MoSe$_2$ PEC solar cells are stable against corrosion as was projected by S.Chandra [301] also.
Fig. 5.23  Variation of efficiency of MoSe₂ PEC solar cell over a period of time (electrode D).
Fig. 5.24 Variation of efficiency of MoSe$_2$ PEC solar cell over a period of time (electrode D).
Fig. 5.25 Variation of fill factor of MoSe$_2$ PEC solar cell over a period of time (electrode D).
Fig. 5.26 Variation of fill factor of MoSe₂ PEC solar cell over a period of time (electrode D).