Chapter 4

Studies on PbO$_x$/aqueous electrolyte interface

\[ C / \text{F/cm}^2 \]

\[ \text{Potential / V (vs. Hg/HgO)} \]

\[ \text{1 mA/cm}^2 \]

\[ \text{Illuminated} \quad \text{I}_{\text{dark}} \]

Causa Latet, Vis Est Notissima!
4.1 Introduction

The charge transfer mechanisms at solid/liquid interfaces are governing factors for the performance of any PEC cell. The careful investigations of interfaces, materials and junctions require a solid base of theory and efficient experimental tools. A solid-liquid interface is being studied with interest since the pioneering work by Brattain and Garrett [49]. The impedance spectroscopy is being used as an intensive tool to explain the electrical characteristics of solid-solid or solid-liquid junctions [50–69]. Researchers have employed this tool to electrically model the interfaces, study the effect of various parameters on the device, find the loss mechanisms in the device, etc. The impedance spectroscopy is widely used for the investigations of charge transfer properties in DSSCs [50, 70–76]. Though the impedance spectra contain many useful information, they are very difficult to analyse. Researchers[56, 57, 77–79] have made efforts to accurately collect the information from the analysis of impedance spectra. However, in almost all the cases, final conclusions greatly reside on the adopted equivalent circuit.

The conduction mechanism in any of the device out of PbO$_2$/electrolyte interface is of great interest and needs a rigorous analysis. However very few efforts are made in this direction and no claim has been made yet regarding the dominant transport mechanism [80]. The current mechanisms in semiconductor/electrolyte interface can be qualitatively studied by impedance, conductance and capacitance measurements in general, are based on the theories developed for an ideal Schottky junction. Generally the studies are limited to a narrow working region of the device [55, 81](a typical depletion region), but to understand the device as a whole, in fact, in depth analysis of the interface working in different regimes is necessary. For any device, to do so, a well-defined set of experiments explaining and correlating each region of the cell has to be designed. Herein in this chapter, a photoelectrochemical cell (PEC) of the configuration PbO$_2$ (0.25 cm$^2$) film | 0.1 M K$_4$Fe(CN)$_6$ / 0.01 M K$_3$Fe(CN)$_6$ (9.2 pH) | Pt (2 cm$^2$) is perturbed by small A.C. signal to study the properties of the PbO$_2$/electrolyte interface.
4.2 Experimental

All the nanostructured PbO$_x$ electrodes used in this study were synthesized by potential pulse anodization technique as discussed in Chapter-3. To study the interface properties, a PEC cell of the configuration PbO$_x$(0.25 cm$^2$) film | 0.1 M K$_4$Fe(CN)$_6$ / 0.01 K$_3$Fe(CN)$_6$ (9.2 pH) | Pt (2 cm$^2$) was constructed. The reference electrode used for all the measurements was Hg/HgO (3 M KOH). The photocurrent spectra were recorded under white light chopping illumination condition using tungsten halogen lamp. All the electrochemical impedance measurements were done using potentiostat/galvanostat. The impedance and conductance spectra were recorded in the frequency range of 100 kHz to 0.1 Hz by applying a small (10 mV) A.C. stimulus with the D.C. potentials from 1.4 to -0.6 V. A cool white SMD LED matrix operated by regulated power supply (L3205, Aplab) was used as light source for the EIS measurements.

4.3 Results and discussion

4.3.1 Photoresponse of PbO$_x$ electrode

The photoresponse of the PbO$_x$ electrode under white light chopping illumination is shown in Fig.4.1. The onset potential ($V_{on}$) of the cell is -0.52 V with the maximum current density of 4.03 mA/cm$^2$. It was interesting to observe that the photoresponse persists a unique nature. For any semiconductor/electrolyte junction, operating region of PbO$_x$ electrode is divided into four conditions i.e. accumulation, depletion, inversion and deep-depletion. The five distinct regions mentioned in Fig.4.1 are based on the direction of photocurrent and the nature of the current spikes. The region below the flat band is assigned to the accumulation of the majority carriers on the electrolyte side and hence cathodic photocurrent is obtained from n-type semiconductor. The region just above the flat band is depletion as band starts aligning according to applied potential. A logarithmic
increase in photocurrent is found up to 0.4 V achieving the highest rate of increase in photocurrent. Furthermore increase in potential up to 0.7 V shows a linear increase in the photo and dark current due to depletion. This region can be assigned to the inversion region of the cell. The potentials above 0.8 V shows an exponential increase in photo and dark current, a typical nature of the deep-depletion layer. We believe that such kind of distinct nature might be due to one or more governing charge transfer/transport phenomena occurring in a typical PEC cell. It is known that A.C. stimulus can retrieve the information of semiconductor, electrolyte and interface. Hence, these regions are rigorously studied after various measurements like impedance, conductance and capacitance to gain insights to the charge transport mechanism.
4.3.2 Impedance Spectroscopic Study

The impedance spectra of the constructed PbO$_x$ electrode were recorded from 1.4 to -0.6 V, i.e. from deep-depletion to accumulation region by applying a small (10 mV) A.C. signal in the frequency range of 100 kHz to 0.1 Hz. As it can be seen from the Fig.4.2 that the Nyquist plots at each potential comprise of two distinct semicircles. To assign these semicircles to appropriate physical phenomena occurring at either solid/liquid or solid/solid interface, we carried out two different set of experiments. In first, porosity of PbO$_x$ films was varied by preparing the films by potentiodynamic and potential pulse technique. The FE-SEM images of the films prepared by two different techniques are shown in Fig.4.3. The Nyquist plots of the PbO$_x$ electrode prepared by different techniques are shown in Fig.4.4. As it can be seen from the figure that by varying the porosity diameter of first semicircle changes greatly. Hence, first semicircle can be assigned to the charge transfer resistance or the pore resistance. In second set of experiments, illumination intensity was varied. The effect of illumination intensity on the diameter of second semicircle is shown in the Fig.4.5. It was observed that the diameter of second semicircle decreases by increasing illumination intensity. Hence, the second semicircle must be due to the bulk electrolyte interface comprising of a resistance
Figure 4.3: FE-SEM images showing the surface morphology of the anodized lead oxide films prepared by (a) potentiodynamic and (b) potential pulse methods at magnifications of X 10000.

Figure 4.4: Impedance measurements of lead oxide films with different porosity to assign the first semi circle.

for the recombination in the bulk and the capacitance due to bulk electrolyte interface.
Figure 4.5: Nyquist plots of the PbO$_x$ electrode under different illumination conditions.

4.3.2.1 Qualitative Interpretation

The recorded and fitted impedance spectra of PbO$_x$ electrode under different bias conditions are shown in the Fig.4.6. As discussed, the regions namely accumulation, flat band, depletion, inversion and deep-depletion have different nature of current spikes. To identify these regions itself from the nature of the Nyquist plots, the impedance spectra of these four regions are compared. For doing so, an equivalent circuit as shown in Fig.4.7 was fitted to the data. Though the transmission line models are appropriate to understand the solid/liquid junction properties as it takes into account all the interfaces actively participate in the system, researchers are motivated to use the lumped element circuit model [57, 82–84] for more complicated systems like porous oxide semiconductors where the contribution from well-known components such as space charge region is often taken in the cumulative contribution with the chemical capacitance of the material. This
Figure 4.6: A comparison of Nyquist plots of the PbO$_x$ electrode under (a) Accumulation (-0.6 V) (b) Flatband (-0.5 V) (c) Depletion (0.3 V) and (d) Inversion (0.8 V). Experimental (c) and fitted (+) data.

Figure 4.7: The equivalent circuit used for relating the rate of increase in photocurrent spectrum to various components of the PEC cell in which $R_s$ is a series resistance of the cell. $R_{ct}$ and CPE1 are the charge transfer resistance and chemical capacitance occur at the interface of PbO/PbO$_x$ and electrolyte medium. $R_{rec}$ represents the bulk or recombination resistance of the photoanode and CPE2 is the total contact capacitance of the bulk material.

The approximation is equally valid below the frequency of $10^7$ Hz [84]. In the equivalent circuit $R_s$ is the total series resistance of the cell, $R_{ct}$ is the charge transfer resistance at the pore electrolyte interface, CPE1 is due to all the capacitances from pore electrolyte interface, $R_{rec}$ is the recombination resistance and CPE2 is the constant phase element related to the PbO$_x$/electrolyte interface including
double layer and chemical capacitance of the film. The CPE is defined as,

\[ Z_{CPE} = \frac{1}{(i\omega)^nY_0} \]  

(4.1)

where, \( Y_0 \) is the capacitance & the exponent \( n \) is 1 for an ideal capacitor. The chemical capacitance is expected to occur at the interfaces where the density of states on each side differs in a great amount. For the \( \text{PbO}_x \) electrode under investigation, aqueous electrolyte has an infinite density of states relative to the oxide semiconductor which leads to a chemical capacitance in aid to the double layer capacitance. Fitting the equivalent circuit to all the experimentally obtained impedance spectra at different applied potentials lead to the estimation of \( R_s, R_{ct}, R_{rec}, \) CPE1 and CPE2.

As shown in Fig.4.6a, the accumulation region has a closed first semicircle and negative values in the second semicircle at lower frequencies. The source of this kind of nature in the impedance spectra is believed to be an adsorption process at the semiconductor/electrolyte interface. Many researchers have studied the adsorption process by impedance spectroscopy [85, 86]. One can notice that the resistances offered in this region are negligible for any charge transfer process to take place and hence one can expect current in this region if the accumulated majority carriers find empty carrier states in the electrolyte following the isoenergetic charge transfer process [87]. We, in our system, have also observed a noticeable cathodic current. This certainly claims that majority charge carriers are accumulated on the electrode/electrolyte interface and cannot travel through the bulk of the semiconductor to take part in anodic conduction. However the redox couple with the formal potentials negative of \( V_{on} \) readily exchange electrons in both directions leading to a cathodic current. When the flat band situation is achieved, the impedance spectra start taking its expected shape comprising of two semicircles as shown in Fig.4.6b. However the relatively high value of \( R_{ct} \) limits the current in this region and the high \( R_{rec} \) allows the carriers to be extracted without recombination. The dependence of \( R_{ct} \) and \( R_{rec} \) on the potential is shown in the Fig.4.8 and Fig.4.9, respectively. When the potential is swept from -0.4 to 0.4 V the \( R_{ct} \)
FIGURE 4.8: Variation of charge transfer resistance with bias under dark and illumination conditions.

FIGURE 4.9: Variation of bulk recombination resistance with bias under dark and illumination conditions.

increases exponentially with increase in potential making it difficult for the charge carriers to travel through the semiconductor. However, the $R_{\text{rec}}$ increases linearly; allowing the carriers to have enough life time to travel through the bulk and extracted by the electrode. Hence the logarithmic increase in current is observed till
0.4 V achieving the maximum depletion width of 0.250 μm. Variation in depletion width with illumination intensity is shown in Fig.4.10. We also observed that at a maximum depletion, the impedance curve has a single RC component with CPE2 nearly as an ideal capacitor. This is the potential where maximum rate of increase in current is achieved. As the potential is further swept from 0.4 to 0.8 V (Fig.4.6c) we observed that $R_{ct}$ decreases linearly and $R_{rec}$ decreases exponentially and hence the resultant photo and dark current increase linearly. We have found that for the cell under present investigation the maximum photocurrent (at 0.7 V) is extracted from this inversion region where generation and recombination rates are optimum. Further increase in potential from 0.9 to 1.4 V leads to an exponential increase in dark current and compressed semicircle is obtained as shown in Fig.4.6d. For this region, $R_{ct}$ decrease linearly and $R_{rec}$ increases exponentially with potential. This is a characteristic of inversion layer where the minority carrier density is more than the majority carrier density on the interface facilitating the recombination. A table of parameters used to obtain the simulated spectra shown in Fig.4.6 is shown in Table-refeistable. The effect of irradiance on the various circuit elements is shown in Fig.4.8, 4.9 and 4.11. An obvious decrease in the
resistances with illumination is obtained. However, a Gaussian behavior of both 
$R_{ct}$ and $R_{rec}$ with change in potential was found. This behavior of $R_{ct}$ and $R_{rec}$
can be explained by assuming that charge transfer and recombination occurs via
exponential distribution of traps on the semiconductor nanowalls to the Gaussian
distribution of states in the electrolyte [50]. In addition, the probability of the
trap state to capture the electron also varies with the potential and hence going
from accumulation to deep-depletion region; it was interesting to observe two dis-

tinct Gaussian (i) from -0.6 to 0 V and (ii) 0.1 to 1.2 V. The capacitance CPE2
increases significantly when going from dark to illumination. This certainly claims
that this capacitance is not only associated with the chemical capacitance between
bulk PbO$_2$ and electrolyte interface but also with the surface trap states. Hence
the increase in current is due to the conduction via trap states under illumination
condition. To address this observation and study the charge transfer processes in
mentioned PEC cell, a detailed C-V study under illumination is carried out and
discussed.
4.3.3 Capacitance-Voltage Study

4.3.3.1 Quasistatic Characteristic

![C-V plot](image)

Figure 4.12: The C-V plots for the determination of density of trap states at lower frequencies.

It is known that the minority carriers are not affected by the high frequency measurements as they are generated by thermal excitation. To have information about their contribution in the current mechanism, the C-V measurements were done at low frequency as shown in Fig.4.12. The contribution in the accumulation and deep-depletion regions can be seen where sudden increase in capacitance is noticed. This observation at low frequency is possible when the traps are actively involved in the conduction [53]. As the potential is swept negative of $V_{on}$, the capacitance increases indicating enhanced recombination in the space charge region due to available minority carriers. The same situation can be seen at inversion side; however the value of capacitance is less due to large recombination as the number of minority carriers is more in this region. This data in conjunction with high frequency data were used to calculate the interface trap density [88] from the
Eq. 4.2,

$$D_u = \frac{C_d^{LF} - C_d^{HF}}{q^2}$$

(4.2)

In order to see the effect of illumination on the trap density, the measurements were done under varied illumination and it is found that the trap density has a linear dependency (Fig. 4.13) on the illumination intensity. Furthermore, the plot

**Figure 4.13**: Variation in trap state density as a function of illumination.

**Figure 4.14**: Differential capacitance plot for the PbO$_2$ electrode under dark and illumination condition showing (i) Schottky junction characteristic frequency ($\omega_1$) and (ii) Trap states characteristic frequency ($\omega_2$).
of $\omega \frac{dC}{d\omega}$ vs. $\omega$ is shown in Fig.4.14. The two maxima can be directly seen from the plot which unambiguously can be assigned to the ideal Schottky junction ($\omega_1$) and trap states ($\omega_2$) contribution. We observed that even under dark condition, the contribution from trap states is visible and under illumination the peak intensity of $\omega_2$ is increased significantly confirming the conduction through light generated traps. This gives information about very low activation energy of the traps. This is revealed for the first time for PbO$_2$ system.

4.3.3.2 Dynamic Performance of the Cell

![Mott-Schottky and C-V plots](image)

**Figure 4.15:** Mott-Schottky and C-V plots at frequency of 100 kHz and illumination intensity of 100 mW/cm$^2$ for the determination of donor densities and trap density, respectively.

The Mott-Schottky and C-V plots at 100 kHz for the PbO$_2$ electrode are given in Fig.4.15. The two distinct slopes were identified and used to calculate two distinct level densities in the semiconductor. The typical values of $3.88 \times 10^{16}$ cm$^{-3}$ and $1.35 \times 10^{17}$ cm$^{-3}$ are calculated for deep level and shallow level donor density, respectively, as expected for PbO$_2$ system [20, 21, 42, 89, 90]. As it can be readily seen from the plot that the contribution from shallow level impurities is dominant till -0.4 V, whereas at potentials greater than -0.3 V, the deep level contribution is also accounted for. This observation can also be supported from
the band bending theory; as more positive bending occurs, the deep level impurities actively participate in the transport process [91, 92]. The C-V plot shows a minimum capacitance $C_{\text{min}}$ at 0.4 V confirming the maximum depletion width in the semiconductor. This result exactly matches with the observation from the photoresponse spectra. The sharp decrease in capacitance in the depletion region is the reason for a logarithmic increase in the photocurrent (Fig.4.1, region b) and further increase (Fig.4.1, region c) is limited due to increase in the capacitance. The Mott Schottky measurements at different temperature were carried out to find the shift in flat band potential of the cell. As the potential is swept from accumulation to depletion, the deep trap states are filled with the carriers and as the potential is swept from depletion to deep-depletion these states move above the Fermi level facilitating detrapping of these carriers via working electrode [50, 53]. As the detrapping process is thermally activated, the detrapping is diminished as temperature decreases. This phenomenon causes change in flat band potential with temperature and the activation energy of the trap states can be calculated from such measurement using Arrhenius Eq.4.3,

$$ln(\Delta V_{fb}) = ln(A) - \frac{E_a}{kT}$$  

(4.3)

Where, $\Delta V_{fb}$ is change in flatband potential, $k$ is Boltzmann constant and $T$ is a temperature in kelvin.

The Arrhenius plot for the determination of the activation energy of the trap states from the flat band potential shift is shown in Fig.4.16. As it can be clearly seen from the plot, two activation energies (0.2 and 0.8 meV) were determined for the traps. Such low activation energy of the traps suggests that the conduction in the PbO$_2$ system is inherently trap assisted even under dark condition at room temperature which is already observed in Fig.4.14. Due to the practical limitations involved for the measurement at high temperature, the temperature range of 30 to 85 °C was selected for the activation energy calculation. To justify the accuracy of the calculated activation energies, the complementary Arrhenius plot of D.C. conductivity is shown in the Fig.4.17. As it is shown that the number density of
Figure 4.16: Arrhenius plot for the flatband potential.

Figure 4.17: Arrhenius plot for the D.C. conductivity.

trap states is of the order of $10^{14}$ cm$^{-3}$, one can assign the charge carrier involved in the trapping process by temperature dependent C-V measurements [53, 88]. We observed that as temperature is swept from 70 to 40 °C, the C-V plot shifts to the left as shown in Fig.4.18. This certainly claims that holes are involved in the trapping process. To illustrate the contribution of holes from trap states in the current mechanism; either via hopping or tunneling phenomenon, a detailed study
on the A.C. conductivity of the cell is carried out.

### 4.3.4 A.C. conductivity of the cell

![Diagram](image)

**Figure 4.19:** Variation of AC conductivity with bias under (a) dark and (b) illumination condition for the determination of hopping rate.

A plot of A.C. conductivity of the cell calculated from the parallel conductance measurement under dark and illumination conditions are shown in Fig.4.19(a) and (b), respectively. As the D.C. conductivity of the cell can be directly measured
from the plateau region, the more accurate measurement can be done from the Nyquist plot of the conductivity Fig.4.20. As well known, at high frequencies the dispersive nature of the cell can be seen and at low frequencies the polarization effects were noticed. The dispersion at high frequencies can be attributed to the high probability of hopping of ions or charges. However in the PEC cell
of mentioned configuration, the ion hopping and conduction probability is very small and thus dispersive nature of the cell can directly be attributed to the trap assisted hopping of charge carriers. To correctly assign only hopping [93–96] and not tunneling mechanism associated with trap assisted conduction, a plot of frequency exponent S of universal power law (4.4) against temperature is shown in Fig.4.21. The negative slope of such plot confirms hopping phenomenon in the system.

\[ \sigma_{ac} = A\omega^S \]  

(4.4)

The hopping rate \( \omega_p \) can be found from the same plot by extrapolating the twice of D.C. conductivity value on the curve and then extending on the x-axis. It was found that \( \omega_p \) grows exponentially with applied potential, which is plotted in Fig.4.22. This is because as potential is swept from accumulation to depletion, and than to deep-depletion region, the bands are bending more and more positively giving raise to the hopping mechanism. As we claimed that trap density is light dependent, an increase in hopping rate is observed with illumination. It also can be noted from the fitted data, that the rate of increase is more (4.08 times) in the dark whereas less (2.79 times) under the illumination conditions. Hence under
illumination condition, available holes for the hopping through trap states are less compared to dark condition. This is due to the decrease in minority carrier lifetime and increased recombination rate under illumination. The minority carrier life time was calculated from $R_{rec}CPE2$ time constant and is shown in the Fig.4.23. It can be clearly seen from the plot that under illumination condition the minority carrier life time is an order less than the dark condition. This difference is only visible in the operating region (depletion) of a $\text{PbO}_x$ electrode and the effect of illumination was merely visible elsewhere.

### 4.3.5 Accentuation of effective hopping rate

As per the previous discussions, due to a very low activation energies of the trap states, the hopping mechanism is inherently present in the system and is a dominant charge transfer mechanism. To know the contribution from the light generated traps in the hopping process, we need to have the data for the hopping rate under illumination condition only. Hence it is necessary to plot the absolute difference of the hopping rate under illuminated and dark conditions with the applied
potential. However, some studies show the analysis of hopping rate [97, 98], this exercise of analysing the effective hopping rate is carried out for the first time. The plot of effective hopping rate under illumination condition for the system under investigation is showed in the Fig.4.24. It is interesting to see that the maximum effective hopping rate under illuminated condition is achieved at a potential of 0.7 V, which is the potential where a maximum photocurrent is extracted from the cell (see Fig.4.1). Such kind of complementary plot is presented for the first time in order to understand the dominance of trap assisted hopping mechanism in the operation of PEC cell consisting of porous semiconductor oxide/aqueous electrolyte interface. One can also observe a drastic decrease in the light generated hopping in the deep-depletion regime because of the highest positive bend bending, which leads to the dominant hopping current in the dark also. It has been noticed, the increase of hopping rate is more in the dark compare to illuminated conditions. In the deep-depletion condition, because the contribution from the traps present under dark condition is maximum leading to a great increase in the dark current of the PbO$_2$ electrode. Thus it can be infer from all the experiments that current mechanism in the PbO$_2$/electrolyte system can be understood by Correlated Barrier Hopping (CBH) model. Finally, a pictorial representation of charge transfer process occurring in the mentioned PEC cell is given in Fig.4.25.
4.4 Conclusions

In conclusion, efforts have been made to understand the dominant charge transfer mechanisms in a typical PEC cell of the configuration PbO$_x$ (0.25 cm$^2$) film | 0.1 M K$_4$Fe(CN)$_6$ / 0.01 M K$_3$Fe(CN)$_6$ (9.2 pH) | Pt (2 cm$^2$). It has been shown that the nature of increase in photo and dark currents can be understood by impedance spectroscopy. An in depth analysis of the charge transport mechanism in such interface has been carried out by employing different techniques and complemented appropriately. The interface of porous semiconductor oxide electrode/electrolyte can be best represented by an equivalent circuit having the series combination of each interface offering different time constants. It was found that the major transport mechanism of typical PEC cell is hopping via trap states. The calculated activation energies of trap states were found to be 0.2 and 0.8 meV. Further it was found that the maximum photocurrent is obtained at the inversion region where the rate of carrier generation and recombination are optimum. This result is further complemented by the effective hopping rate of the charge carriers under illumination conditions.