Chapter 3

Preparation of nanostructured PbO$_x$ thin films

*Surface of PbO$_x$: can’t get better than this*
3.1 Introduction

PbO$_x$ is an interesting material due to its applications in photoelectrochemical cells and batteries [17–23]. This non-stoichiometric oxide can be developed with band-gap energies in the range of 1.2 to 2.9 eV by varying $x$ from 1 to 2 for its use in various applications [24–26]. Historically acidic medium is being used to study the photo-effects of the anodized lead electrodes by many groups [27–36]. Although both the $\alpha$-PbO and $\beta$-PbO are photoactive phases of anodized lead, $\alpha$-PbO is found to show better photoactivity. The corrosion of PbO electrodes due to acidic environment was the main drawback of the PEC cell constructed from acidic medium as an active electrolyte. To overcome this problem, alkaline sodium sulfate solutions have been adopted by many researchers [23, 33, 37, 38]. Different electrochemical anodization techniques have been tried to make photoactive phases of PbO out of lead metal [20–22, 39]. Among all the techniques, potentiodynamic anodization is mostly used and hence understood thoroughly [19, 22, 23, 39]. Many groups have explored different approaches for anodization, like pulse coupled potentiodynamic [20], potentiostatic [21] and modified window potentiodynamic [22, 39]. Effect of bath temperature and anodization time is also studied by few groups [23, 40]. The $\alpha$-PbO has got more attraction and studied well because of its major contribution to photoactivity compared to $\beta$-PbO [41]. Many groups have concluded that (110) plane of the $\alpha$-PbO leads to a better photoactive film [21]. In spite of many efforts, the photocurrent density more than 4-5 mA/cm$^2$ and an open circuit photopotential of 800 mV is still a challenging task. The photoelectrochemical properties of anodized PbO in both acidic and alkaline media have been studied by several researchers. Most of these studies were done in aqueous electrolytes.
3.2 Experimental

3.2.1 Electrochemical anodization of Pb electrode

The electrochemical cell used for this study is a well-known three electrode arrangement consisting of working, counter and reference electrodes. The chemicals NaOH, Na$_2$SO$_4$, K$_4$Fe(CN)$_6$ and K$_3$Fe(CN)$_6$, and double distilled water (Milli-Q) were used to carry out all the experiments. A lead metal having an effective geometric area 0.25 cm$^2$ cut from a lead foil was used as a working electrode (WE). The lead electrodes were prepared as discussed in Chapter-2, leaving only the front surface free for the anodization. A platinum foil of area 2 cm$^2$ and Hg/HgO electrodes were used as a counter (CE) and reference electrode (RE), respectively. Prior to anodization, the lead electrode surface was polished with paper of grit designation P800 (surface of particle size 21.8 $\mu$m) and washed with double distilled water. A 0.1 M NaOH (Prepared in 0.1 M Na$_2$SO$_4$) solution was used as an active electrolyte for the anodization. Electrochemical polishing of lead electrode was done just before anodization to remove any organic and inorganic impurities from the surface. Potential pulse anodization was carried out by applying the potential pulse between 0.6 to 0.1 V with 50% duty cycle at 80 $^\circ$C by using a potentiostat/galvanostat. Duty cycle (in %) is defined as $\left(\frac{t_{E1}}{t_{E1}+t_{E2}} \times 100\right)$, with e.g. E1 = 0.6 V (vs. Hg/HgO) and E2 = 0.1 V (vs. Hg/HgO). This potential pulse was selected after number of experiments for optimizing the step from a wide potential window. After anodization, the electrodes were washed thoroughly with double distilled water and sintered at 130 $^\circ$C for 30 min in drying oven.

3.2.2 Photoelectrochemical measurements

Phototelectrochemical measurements were done by using three electrode arrangement utilizing anodized lead as working, Hg/HgO reference and platinum counter electrodes. Solution of 0.1 M K$_4$Fe(CN)$_6$ and 0.01 M K$_3$Fe(CN)$_6$ at 9.2 pH was
used as an active electrolyte for the photoelectrochemical measurements. The photocurrent measurements were done as per the description given in Chapter-2.

### 3.2.3 I-V measurements

The I-V measurements were performed by using two electrode arrangement. Photocell consisting of anodized electrode and platinum counter electrode in 0.1 M K₄Fe(CN)₆/0.01 K₃Fe(CN)₆ (9.2 pH) was exposed to a continuous illumination intensity of 100 mW/cm² for recording the I-V spectrum.

### 3.2.4 Stability studies

The stability of prepared photoanode in the solution of 0.1 M K₄Fe(CN)₆/0.01 K₃Fe(CN)₆ (9.2 pH) was checked by measuring short circuit current under constant illumination of 100 W/m². Lower illumination intensity was chosen to avoid radiative heating of the cell. To ensure the effect of only illumination, temperature of the cell was maintained at 40 °C by using hot plate. The short circuit current was recorded after each minute till 270 minutes.

### 3.3 Results and Discussion

#### 3.3.1 Cyclic voltammetric study

A cyclic voltammogram of the Pb electrode in 0.1 M NaOH (prepared in 0.1 M Na₂SO₄) at 80 °C recorded at a sweep rate of 200 mV/s is shown in Fig.3.1. In the positive sweep, two anodic peaks A₁ and A₂ were observed, indicating the step-wise oxidation of Pb to PbO and PbO to PbO₂, respectively. In the negative sweep, a single cathodic peak, C₁ was observed, which can be attributed to the reduction of PbO₂ to PbO. The occurrence of a very small current at the extreme negative end (C₂) is due to partial reduction of PbO to elemental Pb[23]. The
selected window is chosen for two reasons, (1) To control the oxygen content in the film during positive sweep via restricting the applied potential just after the anodic peak A2 (1.25 V) and (2) To prevent reduction of PbO to elemental Pb by restricting the negative sweep at -0.65 V. At the end of cyclic voltammetric study, one can chose potential window as well as suitable potentials where the anodization of Pb metal can be achieved with the required Pb:O stoichiometry. In this study, we have explored a new technique of potential pulse anodization for Pb metal.

3.3.2 Chronoamperometry

In the technique of potential pulse anodization, potential is swept from initial to final value with constant duty cycle for predefined length of time. A typical potential pulse is shown in Fig.3.2. In this study, potentials E1 and E2, % duty cycle \( \left( \frac{t_{E1}}{t_{E1} + t_{E2}} \times 100 \right) \) and total anodization time (t) were varied to optimize the anodization procedure for the realization of best working PbO\textsubscript{x} photoanode. To
Figure 3.2: A schematic of potential pulse applied for anodization of lead electrode.

Figure 3.3: A potential pulse under different duty cycle (a) 33%, (b) 50% and (c) 67%.
start with the optimization, the potential pulse anodization with different combinations of step potentials in the range of anodic peaks were applied for different time at 80 °C. At first instance, potential pulses of 50 % duty cycle in the range of -0.4 to 0.7 V were applied for 800 s. After that, the duty cycles were varied as 33, 50 and 67% for the potential pulse of 0.6-0.1 V for 800 s as shown in Fig.3.3. There after, total anodization time was varied from 400 to 1200 s for the potential pulse between 0.6-0.1 V with 50% duty cycle. All the optimizations were done by analyzing structural, optical and photoelectrochemical properties of the prepared PbO₂ electrodes.

### 3.3.3 XRD analysis

![XRD spectra](image)

**Figure 3.4**: XRD spectra of the films synthesized under bias (a) E₁ = 0.6 V, E₂ = 0.1 V, (b) E₁ = 0.6 V, E₂ = 0 V and (c) E₁ = 0.5 V, E₂ = 0.1 V with 50% duty cycle for 800 s.

The XRD spectra of PbO₂ electrodes prepared by applying pulses of different potentials as (a) (0.6-0.1 V), (b) (0.6-0 V) and (c) (0.5-0.1 V) are shown in
Fig.3.4. As it can be seen from the Fig.3.4 that the films consist of pure $\alpha$-PbO [20, 21, 24, 42] phases with small trace of $\beta$-PbO. However, intensity of most prominent peak i.e. (110) plane greatly depends on E2. It was observed that the intensity of (110) plane for the potential pulse 0.6-0.1 V is maximum with smallest peak of $\beta$-PbO phase (Fig.3.4.a). On the other hand the difference of ±0.1 V in either E1 or E2 changes the phase a lot. For the potential pulse 0.6-0 V (Fig.3.4.b), the intensity of $\beta$-PbO phase is more and the contribution from $\alpha$-PbO phases is minimum compared to other two cases (Fig.3.4.a and c). It was interesting to note that the effect of E2 on the crystallinity of PbO$_x$ film is much more than E1. Hence, from this study the potential pulse of 0.6-0.1 V was identified as a suitable step function for the preparation of highly crystalline PbO$_x$ films. The effect of duty cycle on the crystallinity of PbO$_x$ film is shown in the

![XRD spectra of the films synthesized for E1 = 0.6 V and E2 = 0.1 V for 800 s with duty cycle (a) 50%, (b) 33% and (c) 67%.

Fig.3.5: XRD spectra of the films synthesized for E1 = 0.6 V and E2 = 0.1 V for 800 s with duty cycle (a) 50%, (b) 33% and (c) 67%.](image)

Fig.3.5. It was observed that $t_{E2}$ (duration for E2) has a dominant effect on the relative intensity of $\alpha$ and $\beta$-PbO. It can be seen that by increasing the hold time at E2, intensity of (110) plane decreases and $\beta$-PbO increases (Fig.3.5.b). Hence,
from this study the potential pulse 0.6-0.1 V with 50% duty cycle was found to be appropriate for the further optimization. After optimizing the potential pulse we opt for determining total anodization time required for preparing highly crystalline PbO\textsubscript{x} films. The XRD spectra of the films prepared for different time (a). 800 s, (b). 700 s and (c). 900 s are shown in Fig.3.6. Interestingly it was found that the total anodization time of 800 s result into the films with pure α-PbO phase having minimal contribution from β-PbO or any other mix phases (Fig.3.6.a). It was also noticed that other mix phases occur by increasing total anodization time beyond 800 s (Fig.3.6.c). However, the potential pulse technique allows to synthesis the PbO\textsubscript{x} films with minimum/no contribution from mixed phases which is difficult to achieve by potentiodynamic anodization method[20]. Table-3.1 summarizes the optimization of potential pulse structure through normalized peak intensities obtained by XRD studies. At the end of all the optimizations, we found suitable potential pulse with pulse parameters E\textsubscript{1} = 0.6 V, E\textsubscript{2} = 0.1 V, t\textsubscript{E1} = 1 s, t\textsubscript{E2} = 1 s and t = 800 s. The slow scan (1°/min) XRD spectrum of the film prepared

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{xrd_spectra.png}
\caption{XRD spectra of the films synthesized for E\textsubscript{1} = 0.6 V, E\textsubscript{2} = 0.1 V with 50% duty cycle for (a) 800 s, (b) 700 s and (c) 900 s.}
\end{figure}
Figure 3.7: The XRD pattern of the oxide film synthesized by potential pulse anodization under optimized pulse conditions i.e. E1 = 0.6 V, E2 = 0.1 V, 50% duty cycle for 800 s anodization time.

Table 3.1: Parameters obtained from XRD analysis of potential pulse optimization conditions.

<table>
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<tr>
<th>Potential pulse parameters</th>
<th>Normalized intensity (%)</th>
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<tr>
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<tr>
<td>E1</td>
<td>E2</td>
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<tr>
<td>0.6</td>
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<tr>
<td>0.6</td>
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<td>0.6</td>
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</table>

by applying optimum potential pulse is shown in Fig.3.7. The most intense line of α-PbO (110) was used to calculate the d-spacing of tetragonal PbO by using the Eq.2.2. The calculated d-spacing for (110) plane comes out to be 2.804 Å, which matches very well with the standard value of α-PbO phase[24]. The crystallite size (D) was derived from the FWHM of the XRD peak by using Scherrer formula[43] as in Eq.2.1. All the structural parameters extracted from the XRD spectra of
potential pulse and potentiodynamically prepared PbO$_x$ films are listed in Table 3.2.

### 3.3.4 Proposed growth mechanism of PbO$_x$ nanostructured film

![Layered crystal structure of PbO](image)

\(\alpha\)-PbO is arranged in a layered structure as shown in Fig.3.8. Photoactive phase of \(\alpha\)-PbO (tetragonal) with cell parameters \(a=3.97\) Å and \(c=5.03\) Å can be obtained through electrochemical anodization technique. Layered crystal structure of \(\alpha\)-PbO thermodynamically facilitates the layered growth if proper anodization conditions are provided. Unit cell structure of \(\alpha\)-PbO and \(\alpha\)-PbO$_2$ are given in Fig.3.9.a and b, respectively.
The mechanism for the anodization process, as presented by group of researchers[44–46], is discussed below:

In alkaline medium (at pH 13 to 14) a thin layer of Pb(OH)$_2$ first forms, which further reacts with excess of OH$^-$ to give Pb(OH)$_3^-$ species:

\[
Pb + OH^- \rightleftharpoons Pb(OH)_{ads} + e^- \tag{3.1}
\]

\[
Pb(OH)_{ads} + OH^- \rightleftharpoons Pb(OH)_2 + e^- \tag{3.2}
\]

\[
Pb(OH)_2 + OH^- \rightleftharpoons Pb(OH)_3^- \tag{3.3}
\]

Ph(OH)$_2$ can also decompose to give PbO as given in,

\[
Pb(OH)_2 \rightleftharpoons PbO + H_2O \tag{3.4}
\]

When the applied potential is more positive than 0.3 V (vs. RHE), PbO formation takes place via a three dimensional nucleation and growth mechanism. The chemical and electrochemical reactions are as follows:

\[
Pb(OH)_{ads} + OH^- \rightleftharpoons Pb(OH)_2 + e^- \tag{3.5}
\]

\[
Pb(OH)_{ads} + OH^- \rightleftharpoons PbO^-_{ads} + H_2O \tag{3.6}
\]

\[
PbO^-_{ads} \rightleftharpoons PbO + e^- \tag{3.7}
\]
Thus, it can be concluded that PbO film of desire thickness can be synthesized by electrochemical anodization of Pb electrode in NaOH solution.

The potential pulse anodization technique was utilized for the first time for the preparation of PbO$_x$ photoanodes. To thoroughly understand the growth of nanostructured thin films, the films were prepared by applying optimized pulse condition for different time of anodization. The FE-SEM images of substrate coverage after

![FE-SEM images](image)

**Figure 3.10:** FE-SEM images of substrate coverage after the anodization time of (a) 2, (b) 6, (c) 20, (d) 100, (e) 300 and (f) 600 second at magnification of X 50000.

the anodization time of 2, 6, 20, 100, 300 and 600 second are shown in Fig.3.10. The formation of the nano walls by the application of potential pulse clearly indicated two stage growth process of the oxide film. In the very beginning stage of anodization, the substrate i.e., metallic lead undergoes electrochemical etching and a uniform layer of oxide film is formed all over the substrate (Fig.3.10 a, b and c).

However, in due course of time the second stage growth induces where a potential pulse imposes a localized field gradient that results in variation of charge transfer at specified localized sites. Hence it favors the formation of vertically aligned nano walls structures(Fig.3.10 d and e). It was observed from Fig.3.10 that the whole substrate covers with aligned nanowalls after 600 s of anodization time. To have gross idea about the composition of underneath as well as wall structure, EDX analysis was carried out in small domains on overall film as shown in Fig.3.11. It was observed that the underneath layer is of stoichiometric PbO compound and
the nanowall assemblies were oxygen reach. Hence, the overall film was found to be nonstoichiometric in nature i.e. PbO$_x$. Spectrum wise compositional data are listed in Table 3.3. It is interesting to note that the conventional route of potentiodynamic anodization[23] never lead to the formation of nanostructured films. A comparison between the surface morphologies obtained by both the techniques is shown in the Fig.3.12. As it can be seen from the figure that in the absence of any potential pulse the formation of oxide film takes place by the collision of irregular clusters in non-uniform manner Whereas, in the case of potential pulse technique the nanowalls of typical thickness of 60-80 nm were observed.

### 3.3.5 UV-Vis spectroscopy

The optical studies of prepared lead oxide electrodes can only be carried out by UV-Vis Diffuse reflectance spectroscopy due to opaque backside of the electrodes.
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Figure 3.12: FE-SEM images showing the surface morphology of the anodized lead oxide films prepared by potentiodynamic (a, b, c) and potential pulse (d, e, f) methods at magnifications of X 5000 (a, d), X 10000 (b, e) and X 25000 (c, f).

Figure 3.13: Diffuse reflectance spectra of the oxide film synthesized under different potential pulse anodization conditions; (a) E$_1$ = 0.6 V, E$_2$ = 0.1 V, 50% duty cycle for 800 s, (b) E$_1$ = 0.6 V, E$_2$ = 0 V, 50% duty cycle for 800 s, (c) E$_1$ = 0.5 V, E$_2$ = 0.1 V, 50% duty cycle for 800 s, (d) E$_1$ = 0.6 V, E$_2$ = 0.1 V, 33% duty cycle for 800 s, (e) E$_1$ = 0.6 V, E$_2$ = 0.1 V, 67% duty cycle for 800 s, (h) E$_1$ = 0.6 V, E$_2$ = 0.1 V, 50% duty cycle for 700 s and (i) E$_1$ = 0.6 V, E$_2$ = 0.1 V, 50% duty cycle for 900 s.
The reflectance spectra of all the varied potential pulse and time of anodization conditions are shown in Fig.3.13. One can notice dual absorption signature at energy values 1.95 and 2.71 eV corresponding to tetragonal (α) and orthorhombic (β) phases, respectively. It is interesting to note that the β-PbO phase absorbs strongly than the α-PbO in all the films. Although XRD pattern does not show any characteristic peak of β-PbO except the peak at $2\theta = 54.79^\circ$, which is attributed to both α-PbO and β-PbO. This anomaly can be explained on the basis of either low crystallinity of β-PbO phase or its minimum content in resulting films. Hence, the UV study indicates that the anodized film contains photo active α-PbO phase with β-PbO as an impurity. It was further observed that the contribution of α-PbO band is comparable with that of β-PbO only in the films prepared by applying potential pulse of 0.6-0.1 V, 50% duty cycle for 700 and 800 s.

As the diffuse reflectance measurements gave gross idea about the band gaps

![Figure 3.14](image)

**Figure 3.14:** Tauc plot for the determination of (a) direct and (b) indirect bandgap of anodized PbO$_x$ film.

(direct and indirect, both) present in the film, Tauc plots were derived to estimate the band gap values. The direct band gap of PbO$_x$ films was determined by Eq.3.8,

$$(\alpha \nu)^2 \propto (\nu - E_g)$$

and the indirect band gap was calculated by using the Eq.3.9

$$(\alpha \nu)^{1/2} \propto (\nu - E_g)$$
The obtained bandgap values from the Tauc plots (Fig. 3.14a) for direct (2.15 eV and 2.71 eV) and (Fig. 3.14b) indirect bandgap (1.93 eV) calculations are in well agreement with available literature [20]. Hence, according to XRD and UV studies the most suitable anodization conditions by potential pulse method were found to be the same. The photocurrent measurements were performed to accurately identify the suitable pulse conditions based on photoactivity of the films.

3.3.6 Photoelectrochemical measurements

photocurrent characteristic of the anodized lead electrode prepared by applying different potential pulse conditions were recorded in the active electrolyte of Fe(CN)$_6^{4/-3}$ in aqueous (9.2 pH) medium[20]. Obtained photoresponse charac-

![Graph](image)

**Figure 3.15**: Photocurrent characteristic of the lead oxide films synthesized under bias (a) $E_1 = 0.6 \text{ V}$, $E_2 = 0.1 \text{ V}$, (b) $E_1 = 0.6 \text{ V}$, $E_2 = 0 \text{ V}$ and (c) $E_1 = 0.5 \text{ V}$, $E_2 = 0.1 \text{ V}$ with 50% duty cycle for 800 s.
time are shown in Fig.3.15, 3.16 and 3.17, respectively. One can notice the effect of E1 on the dark current characteristic from Fig.3.15. photocurrent characteristic (Fig.3.15 a and b) for the lead oxide films prepared using E1 = 0.6 V showed stable dark current characteristic compared to 0.5 V (Fig.3.15 c). It was also observed that the electrodes prepared by E1 = 0.6 V, E2 = 0.1 V resulted in maximum photocurrent density of 4.03 mA/cm² (Table-3.4). Change in duty cycle of potential pulse deteriorate both the photo and dark current characteristic of photocurrent characteristic (Fig.3.16.b and c). Significant decrease in the photocurrent density was also observed for the duty cycle other than 50%. From Fig.3.17 one can notice that the photocurrent characteristic of photoanodes prepared by E1 = 0.6 V, E2 = 0.1 V and 50% duty cycle showed improved dark current characteristics with moderate current densities (Table-3.4) compared to other pulse conditions. However, anodization time (t) has a control over the photoelectrochemical window of the cell. One can notice that the optimized anodization time of 800 s results into
the largest photoelectrochemical window with highest photocurrent density for the PbO$_x$ electrode.

Table 3.4 summarizes the observed onset potential ($V_{on}$) and photocurrent density ($J_{sc}$) values for different potential pulse conditions used for the optimization. One can conclude the pulse condition, $E_1 = 0.6$ V, $E_2 = 0.1$ V, 50% duty cycle and 800 s anodization time as most suitable for anodization of lead electrode for optimum photoresponse characteristics. The photocurrent variation at different applied potentials under chopped white light illumination condition for the optimized potential pulse anodized photoanode is shown in Fig. 3.18. The photocurrent attains the maxima at an applied bias of 1 V. An onset potential for anodic photocurrent is observed at -0.52 V with a blocking zone of $\sim$ 1.5 V (-0.52 to 1 V).
Table 3.4: Parameters obtained from PEC measurements

<table>
<thead>
<tr>
<th>E1 (V)</th>
<th>E2 (V)</th>
<th>t_{E1} (s)</th>
<th>t_{E2} (s)</th>
<th>t (s)</th>
<th>V_{on} (V)</th>
<th>J_{sc} (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.1</td>
<td>1</td>
<td>1</td>
<td>800</td>
<td>-0.52</td>
<td>4.03</td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
<td>800</td>
<td>-0.59</td>
<td>3.54</td>
</tr>
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<td>1</td>
<td>800</td>
<td>-0.56</td>
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<td>2</td>
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<td>-0.69</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>900</td>
<td>-0.50</td>
<td>3.01</td>
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</table>

Figure 3.18: The photocurrent characteristic of the PbO_{x} electrode prepared by applying optimized pulse in aqueous active electrolyte of 0.1 M K_{4}Fe(CN)_{6} /0.01 M K_{3}Fe(CN)_{6} (9.2 pH) under chopped white light illumination condition at an incident irradiance of 100 mW/cm²
Figure 3.19: Mott-Schottky plot for the lead oxide film in aqueous active electrolyte of 0.1 M K₄Fe(CN)₆/0.01 M K₃Fe(CN)₆ (9.2 pH).

Figure 3.20: Change in flatband potential with applied frequency for (a) E₁ = 0.6 V, E₂ = 0.1 V, 50% duty cycle for 800 s, (b) E₁ = 0.6 V, E₂ = 0 V, 50% duty cycle for 800 s, (c) E₁ = 0.5 V, E₂ = 0.1 V, 50% duty cycle for 800 s, (d) E₁ = 0.6 V, E₂ = 0.1 V, 33% duty cycle for 800 s, (e) E₁ = 0.6 V, E₂ = 0.1 V, 67% duty cycle for 800 s, (h) E₁ = 0.6 V, E₂ = 0.1 V, 50% duty cycle for 700 s and (i) E₁ = 0.6 V, E₂ = 0.1 V, 50% duty cycle for 900 s.
3.3.7 Capacitance-Voltage measurements

Mott Schottky plots for the electrode prepared by applying optimized pulse conditions are shown in the Fig.3.19. It can be seen from the figure that the prepared photoanodes possess two distinct slopes corresponding to shallow and deep level donor states. The values of doping densities were calculated from the Eq.3.10 as 3.65×10^{15} and 1.67×10^{14} cm^{-3} for shallow and deep levels, respectively.

\[
\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{\varepsilon_0\varepsilon_r q N_D} \left(V - V_{fb} - \frac{kT}{q}\right)
\]

(3.10)

where \(C_{sc}\)=space charge capacitance, \(\varepsilon_0\)=free space permittivity, \(\varepsilon_r\)=relative permittivity, \(q\)=charge of electron, \(N_D\)=Donor state density and \(kT=0.026\) eV.

The flatband potential was found to be -0.55 V (intercept on X-axis of Fig.3.19), which is more negative than the onset potential (-0.52 V) of anodic photocurrent found in PEC studies(Fig.3.18). This can be explain by the Gärtner Butler (GB) model [47, 48], which states that a diffusion of photogenerated minority carriers to the electrode surface in the absence of any electric field leading to a non zero photocurrent at \(V_{fb}\) and hence \(V_{on}\) in PEC measurement will shift towards a positive potential for n-type semiconductor.

The effect of frequency on the flatband potential (\(V_{fb}\)) of PbO_x photoanodes developed by different potential pulse conditions are shown in Fig.3.20. It was observed that the PbO_x photanodes prepared by applying 67% duty cycle pulse has more negative flatband potential compared to all other electrodes. The rate of change of \(V_{fb}\) was found to be different for the electrodes prepared by different pulse conditions. However, 'frequency dispersion' was found to be minimum in the case of photoanodes prepared by optimized pulse conditions (i, a and h of Fig.3.20).

3.3.8 I-V study

The power conversion efficiency curve for a PEC cell of anodized film with an active electrolyte of Fe(CN)_6^{4/-3} in aqueous (9.2 pH) is shown in Fig.3.21. The
open circuit voltage and a short circuit current density were found to be 768 mV and 3.01 mA/cm². The maximum power conversion efficiency was found to be 0.87% with a fill factor of 37%. The highly resistive oxide film resulted in offering high series resistance of 115 Ω, which is mainly attributed for the poor performance of the cell as a power generating device.

### 3.3.9 Stability study

The photoanodic behaviour of anodized electrode under continuous illumination conditions was studied. The stability curve of nanostructured PbOₓ electrode in Fe(CN)₆⁻⁴/⁻³ is presented in Fig. 3.22. It was observed that the short circuit current decreases continuously with illumination time. It can be seen that the photocurrent density decreases to 54.7% of its initial value after 270 min under constant illumination of 100 W/m². This can be considered as moderately stable photoanode, as most of the electrodes in aqueous medium degrades faster than the electrodes used in the present study.
Chapter 3. *Preparation of nanostructured PbO$_x$ thin films*

![Graph showing decay of short circuit photocurrent with time under constant illumination.]

**Figure 3.22:** Decay of short circuit photocurrent with time under constant illumination of 100 W/m$^2$ for PbO$_x$ photoanode in 0.1 M $K_4$Fe(CN)$_6$/0.01 M $K_3$Fe(CN)$_6$ in aqueous (9.2 pH)

### 3.4 Conclusion

In conclusion, the potential pulse technique for the anodization of lead metal was explored for the first time. The effect of different pulse parameters viz. potential, duty cycle and anodization time was studied in detail. After all the measurements an optimized pulse with $E1 = 0.6$ V, $E2 = 0.1$ V, 50% duty cycle and anodization of 800 s was found to be most suitable for the use of PbO$_x$ photoanodes in photoelectrochemical cells. The photo action spectrum of constructed PEC cell showed the $J_{sc}$ of 3.01 mA/cm$^2$, $V_{oc}$ of 768 mV, Fill factor of 37% leading to efficiency of 0.87%. It was found that the application of potential pulse results into the formation of vertically aligned interconnected nano wall assemblies all over the active area. It is believed that such nanostructures either facilitates or prohibit the charge transfer processes in a working device. Hence, in next chapter, a detailed investigation by using impedance spectroscopy is carried out to understand the role of nanostructured PbO$_x$ film in the charge transfer mechanism of typical photoelectrochemical cell.