Improved Electrochemical Route to Synthesis Distinctive Nonstoichiometric Lead Oxide Films for Efficient Photoelectrochemical Cell

Dipal B. Patel*

School of Chemical Engineering & Physical Sciences, Lovely Professional University, Phagwara, Punjab, India

Abstract

Linear sweep voltammetry recipe was modified in the form of square wave pulses of applied electrochemical potentials to synthesize nanostructured nonstoichiometric metal oxide films. Resultant film showed improved structural, optical and photoelectrochemical properties compared to films developed via preexisting and widely used potentiodynamic method. Qualitative photoelectrochemical analysis was performed to scrutinize the effect of potential pulse structure on overall photon conversion efficiency. One of a kind, such nanostructured film possess superior candidature for their application in functional photo-opto-electronic devices.

Keywords: Potentiodynamic, Potential pulse, Duty cycle, Nonstoichiometric, Metal oxide, Nano walls

1. Introduction

Over the years, the applications of nanostructured materials as efficient catalysts [1, 2], in high efficiency energy conversion devices [3, 4] and storage devices [4, 5] have been demonstrated. More specifically, they have shown a tremendous potential in the field of photoelectrochemical cells [6, 7] third generation dye sensitized [8] and quantum dot solar cells [9, 10]. Nanostructures offer versatile benefits over traditional materials as the structure-electrical properties [11, 12] can be greatly tailored. Many researchers have found out new range of materials [13] and novel configurations of the devices [11] for the optimum solar energy conversion into the electric power. Moreover, in the field of DSSCs core-shell type photo electrodes have shown their candidature to be of great importance [14, 15]. On the other hand, oxide nanostructures like TiO$_2$, ZnO, NiO, MoO$_x$, PbO$_x$ are becoming very popular due to their ease of synthesis and extraordinary optoelectrical properties. In this list, PbO$_x$ is an important material for solid/liquid interface devices such as batteries and solar cells. However, for PbO$_x$ photoelectrochemical cells, to achieve photocurrent densities more than 4 to 5 mA/cm$^2$ is still a challenging task. In our study, we showed that this is due to a totally unique charge transport mechanisms of such cells [16]. On the other hand, PbO$_x$ photoanodes are also suitable to make a non-linear junction with ionic liquids (ILs) which is an important aspect to increase the overall stability of the cells [17-18]. Nonetheless, a very first solid state solar cell out of PbO$_x$ has been demonstrated for its possible use in portable devices [19]. Looking at the importance of low dimensional materials, we have made efforts to establish a technique for the fabrication of nanostructured PbO$_x$ thin films. Till date, there are no reports on the development of such films by any means due to its natural tendency to grow as a three dimensional material. However, by using pulsed stimulus, one can restrict the growth of material in a particular direction and can find a way to deposit nanostructures. In the present manuscript we have made efforts to find out the resultant effect of potential pulse parameters like anodization time, duty cycle and applied electrochemical potential. Based on structural, optical and photoelectrochemical studies we have achieved an optimum parametric structure of electrochemical potential pulse for its utilization as photoanode in photoelectrochemical solar cells.

2. Experimental

2.1. Preparation of photoanode

A well-known three electrode arrangement consisting of lead metal foil (0.25 cm$^2$, 99.999 % pure, Alfa Aesar), platinum foil (2 cm$^2$) and Hg/HgO (3 M KOH, +0.098 V vs. NHE) was used for controlled oxidation of lead metal. Aqueous solution of 0.1 M NaOH (in 0.1 M Na$_2$SO$_4$) was kept at 80 °C and used as an active electrolyte for the anodization process. Anodization potentials were applied in the form of customized square wave pulses with the help of Potentiostat/Galvanostat (PGSTAT302N, Autolab) controlled by NOVA-1.9 software.
Figure 1 shows a typical potential pulse structure with step potentials $E_1$ and $E_2$ possessing 50% duty cycle. In built chronoamperometry (~1.33 $\mu$s interval time) was utilized for the realization of desired potential structure of varying step potential, duty cycle and time. After anodization, the electrodes were thoroughly washed with deionized water (Milli-Q, Millipore) and sintered for 30 min at 130 $^\circ$C in a hot air oven. This technique is believed to be capable of synthesizing required phases (e.g., $\alpha$-PbO and/or $\beta$-PbO$_2$ in the case of Pb) and bandgap of variety of metal oxides.

2.2. Modification of potential pulse structure

Step potentials $E_1$ and $E_2$ were varied in the range of -0.1 to 0.7 V based on the observed anodic and cathodic peaks in cyclic voltammogram. Duty cycle was separately adjusted to 33, 50 and/or 67% by applying selected potentials $E_1$ and $E_2$ as described in Table-1. For any applied square wave potential, duty cycle can be calculated as $T_{on}/(T_{on}+T_{off})$.

Table 1. Potential Pulse Parameters Used for the Optimization of Photoelectrochemical Properties of Synthesized Lead Oxide Films

<table>
<thead>
<tr>
<th>$E_2$ (V)</th>
<th>$E_1$ (V)</th>
<th>$T_{on}$ (s)</th>
<th>$T_{off}$ (s)</th>
<th>Duty cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 to 0.7</td>
<td>-0.1 to 0.3</td>
<td>1</td>
<td>2</td>
<td>33</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>
Figure 2 Potential pulse structure showing different duty cycles (33%, 50% and 67%)

Figure 2 shows a schematic representation of potential pulses having different duty cycles of square wave potential with $E_2=0.6$ and $E_1=0$ V. as it can be seen from above figure that though duty cycle is defined in time domain, it affects the film formation with the help of variation in applied electrochemical potential. In the present case, 0.6 V was applied to the Pb metal for either 1 s (duty cycle 33 and 50 %) or 2 s (duty cycle 66 %). Same way, 0.1 V was in the action for 1 s (duty cycle 66 %) and 2 s (duty cycle 33 and 50 %). Thus in addition to the selected potential for typical electrochemical run, time for individual potential that gets applied also controlled by this novel electrochemical route. At the end total anodization time was also tuned for a period of 200 to 1200 s.

2.3. Characterizations

Electrochemically synthesized anodized PbO$_x$ photoanodes were then characterized for the structural, optical, morphological and photoelectrochemical properties. Structural information was acquired by using X’Pert Pro PANanalytical X-ray diffractometer in the form of X-ray diffraction patterns. The diffused reflectance spectroscopy (DRS) of the anodized films was carried out by using Shimadzu-2600 spectrophotometer equipped with integrated sphere compartment. Moreover, photoresponse spectra of different samples are presented which were recorded by using Potentiostat/Galvanostat (PGSTAT 302N, Autolab).

3. Results and discussion

3.1. X-ray diffraction

Identification of structure and phases of the prepared samples were carried out with the help of X-ray diffractometer (X’Pert Pro) supplied by PANanalytical. XRD spectrum of each sample was recorded in between 20-70° 2θ values at a step size of 0.05°. Machine was operated at 45 kV/40 mA in the thin film mode to acquire information about a very thin layer of anodized lead film. Figure-3 demonstrates base corrected XRD spectra of samples synthesized by varying duty cycle as tabulated in Table-1.
One can observe that the intensity of most prominent peak i.e. (110) plane greatly depends on the adopted duty cycle. Moreover, the intensity of (110) plane for the sample-a is maximum with smallest peak of β-PbO (Figure 3a). On the other hand, there is a noticeable contribution of β-PbO phase in sample-b and α-PbO₂ in sample-c. This observation certainly claims that the duty cycle of the potential pulse plays an important role in deciding the overall crystallinity of the film. It is well-known that pure α-PbO is highly photoactive phase and any contribution from other phases (β-PbO or α-PbO₂) can hinder the performance of PbOₓ films as photoanodes. Therefore it is highly desirable to deposit PbOₓ films with maximum contribution from α-PbO phase. However, it is impossible to totally avoid any other phases in the film.

3.2. UV-vis spectroscopy

Optical properties in the form of diffused reflectance spectroscopy were performed between wavelengths 900-300 nm in the step size of 1 nm. Non-specular reflectance from anodized lead surface was allowed to get confined within integrated sphere attachment of UV-visible spectrometer (Shimadzu-2600) to better understand the material properties. First derivative of spectral diffused reflectance (dR/dλ) as shown in Figure-4 was calculated to accurately find out the optical bandgap of the films.
Figure 4 First derivative of diffused reflectance spectra of anodized PbOx films synthesized by potential pulse anodization with the implication of varying potential pulse structure

From above figure dual bandgap nature of synthesized photoanodes was confirmed having optical bandgap energies 2.71 and 1.95 eV corresponding to orthorhombic (β) and tetragonal (α) phases of PbOx, respectively. It was further qualitatively found out that the α-PbO and β-PbO both have contributed almost equally only in the films prepared for duty cycle other than 50%. Whereas for the sample-a, the absorption peak of α-PbO almost merged with the β-PbO characteristic showing that the contribution from α-PbO is minimal in this film. Hence, the optical study complemented very well the XRD analysis and showed that sample-a possesses better photo activity compared to other samples.

3.3. Photoelectrochemical performance

To demonstrate the significance of the technique and hence the nanostructured films, photoresponse measurements were carried out for each film. Potentiostat/Galvanostat (PGSTAT 302N, Autolab) was operated with the help of NOVA-1.9 to record photoresponse at scanning interval as low as 2.44 mV. Figure-5 represents typical photoresponse spectra recorded under chopped white light illumination conditions.

Figure 5 Photoresponse spectra recorded under chopped white light illumination condition

Firstly, the stable dark current characteristics for all the samples in the measurement potential window indicate the formation of ideal Schottky junction at PbOx/electrolyte interface. However, the dark current characteristic of the sample-a was found to be superior to the other samples. This feature indicates that the accumulated holes are
promptly being swept away from the photoanode and hence the stability of the electrode can be maintained for a longer time. This in turn increases the photoelectrochemical window of a particular PEC cell. In fact, the photoelectrochemical window for samples-b and c was around 0.8 V compared to more than 1V of sample-a. Table-2 shows a complete data set of the varied pulse parameters and the photocurrent density of each film while used as a photoanode of a PEC cell.

Table 2. Comparison of Photocurrent Density of Anodized Films (Synthesized by Varying Potential Pulse Structure) Utilized in Photoelectrochemical Cell (PECs).

<table>
<thead>
<tr>
<th>Anodization conditions</th>
<th>PEC performance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step potentials (V)</strong></td>
<td><strong>Duty cycle</strong></td>
</tr>
<tr>
<td>E₂</td>
<td>E₁</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.2</td>
</tr>
<tr>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Potentiodynamic (0-0.5 V)</td>
<td></td>
</tr>
</tbody>
</table>

One can notice from the table that, a maximum photocurrent density (2.46 mA/cm²) can be extracted at certain potential pulse conditions (E₂=0.6 V, E₁=0.1, Duty cycle 50%, t=800 s). Hence at the end of this study, it was clear that the electrodes prepared through this unique potential pulse anodization offer superior structural, optical and photoelectrochemical properties.

4. Conclusion

The presented structural data of anodized PbOₓ films are of high impact for those who require specific phase formation (e.g., α-PbO and/or β-PbO₂) while synthesizing non-stoichiometric metal oxides with the help of electrochemical routes. Optical data in the form of UV-visible diffused reflectance spectra can be readily shadowed to understand presence of dual bandgap in metal oxide films. Photoanode instability can be addressed by perceiving dark current characteristic of existing photoresponse spectra. The potential pulse method allowed the synthesis of PbOₓ films with most pure photoactive PbO phase which was previously very challenging to achieve through potentiodynamic anodization technique.

Acknowledgments

Author acknowledges the technical support from his parent institute, Pandit Deendayal Petroleum University, Gandhinagar. Author also acknowledges his current institute, Lovely Professional University, Phagwara for providing the financial and administrative support.


