

Photoelectrochemical studies on thin film Pb_3O_4 photoelectrodes

Sudhir Kumar & Maheshwar Sharon*

Department of Chemistry, Indian Institute of Technology, Bombay 400 076

and

S R Jawalekar

Department of Electrical Engineering, IIT, Bombay

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Photoelectrochemical properties of thin film of Pb_3O_4 prepared by thermal annealing of electro-deposited thin film of PbO_2 have been studied. Energy levels of band diagram of Pb_3O_4 are experimentally found to be 4.26 eV and 6.40 eV for conduction and valence bands respectively. It is observed that $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ electrolyte gives the maximum photo-current with this material. Effect of thickness of thin film of Pb_3O_4 on the photoconversion efficiency has been calculated. A maximum efficiency of 0.21 % with a fill factor 0.4 has been observed with 0.6 micron thick film. Prolonged illumination of the electrode results in decrease of photo-current suggesting the unstability of film over a long period.

Sharon *et al.*¹ have reported the solar energy conversion efficiency of Pb_3O_4 photoelectrode as 0.09%. They used this material in a pellet form which could have large number of grain boundaries and other centres for trapping photogenerated carrier produced at the Pb_3O_4 -electrolyte interface. Theoretical efficiency for this material is expected to be around 10-15 % (because its band gap is 2.14 eV). It is therefore, appropriate to study the photoelectrochemical properties of Pb_3O_4 -electrolyte interface using a thin film of this material².

Materials and Methods

Analar grade chemicals and doubly distilled water were used. Thin films of Pb_3O_4 (2 cm $\times$ 1.0 cm $\times$ 0.02 cm) over nickel substrate were prepared by annealing various films of PbO_2 (prepared by method described elsewhere²) at 450°C in air for 24 hr. Electrical back contact to films was taken from the nickel substrate. All sides of film except the surface were coated with water resistant insulating paint (Favibond) to avoid short circuiting of substrate with electrolyte. The photoelectrochemical (PEC) cell was constructed by dipping the photoelectrode and counter electrode (platinum foil) in suitably selected electrolyte, kept in a vessel with quartz window. The photoelectrode was illuminated through a quartz window by tungsten halogen lamp [Thorn UK 24V, 250 watt] to give 60 mW/cm² intensity at the surface of the electrode.

The band-edge positions of Pb_3O_4 were obtained by UV-photoelectron spectroscopy (UVPS) with He-I as the sources. Onset of the spectrum gives valence band edge positions³. The fermi level position (i.e. flat band potential) of Pb_3O_4 film was obtained by measuring photo-current under biasing condition. The biasing potential at which photo-current became zero was taken as the flat band potential. The potentials were measured with respect to a standard calomel electrode.

Cyclic voltammetry was used to study the electrochemical behaviour of redox couple and the current-voltage characteristics of the semiconductor-electrolyte junction. Cyclic voltammograms were obtained both under dark and illuminated conditions. The programmed potentials obtained from voltage programmer (PAR model 175) were applied on the working electrode of the electrochemical cell through potentiostat (PAR model 173) to get current-voltage characteristics on x-y-t recorder (Huston 2000). The standard calomel electrode and small platinum foil (2 mm $\times$ 4 mm) were used as a reference and an auxiliary electrode, respectively. The presence of dark anodic and cathodic currents suggest a poor schottky junction. This experiment was also repeated under chopped light condition where the photo-current (versus applied sweep potential) was measured with light falling on the electrode intermittently. The effect of chopped light with $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ electrolyte was studied. Iodate/iodide system though gives a better photoresponse¹, was

discarded because the cyclic voltammogram of this electrolyte with inert platinum electrodes showed the presence of more than one type of anodic reactions as compared to the reactions occurring with ferro/ferric cyanide system.

Atomic absorption spectroscopy (AAS) was used to detect the lead ions (if any) present in the electrolyte of the PEC cell due to electrochemical or photoelectrochemical corrosion of Pb_3O_4 electrode. For this experiment the PEC cell was kept under illuminated condition for 2 hr every day for 15 days and then the electrolyte was analysed for the presence of lead ions. There was no detectable amount of lead ions present in the solution of the cell.

The effect of thickness of film on the photocurrent was studied using a cell of type :

Pb_3O_4 ferro/ferric cyanide, pH 9.0 Pt.

Photo-current photo-voltage characteristics were studied using the above cell with film thickness 0.6 micron. I_{max} and V_{max} were calculated graphically.

Results and discussion

The valence band position of Pb_3O_4 is found to be 6.4 eV (Fig.1) and the conduction band position is found to be 4.26 eV (considering the band gap of this material as 2.14 eV⁴). Corresponding values on the NHE scale would be -0.24 V and +1.9 V for conduction and valence bands respectively. The fermi level which is equivalent to the electrode potential of a semiconductor when bands are flat, i.e. flat band potential⁵ is found to be -0.3 V versus SCE (Fig.2). This value which corresponds to 4.44 eV on the vacuum scale, is in agreement with results published elsewhere⁴. Considering these values for the band diagram of Pb_3O_4 , the redox electrolytes suitable for this material should have redox potential within the range of 0.0 V (lower than conduction band) to 1.1 V (above the decomposition potential versus NHE), because theoretical anodic decomposition potential of Pb_3O_4 calculated from Eq.(1) comes to +1.18 V⁵⁻⁸.



There are two redox electrolytes, i.e., $\text{Fe}(\text{CN})_6^{3-/4-}$ (0.46 V) and IO_3^-/I^- (+0.3 V) which are stable at high pH and their redox potentials fall within this range. The cyclic voltammograms of both these redox electrolytes show that $\text{Fe}(\text{CN})_6^{3-/4-}$ is a better electrolyte because it has

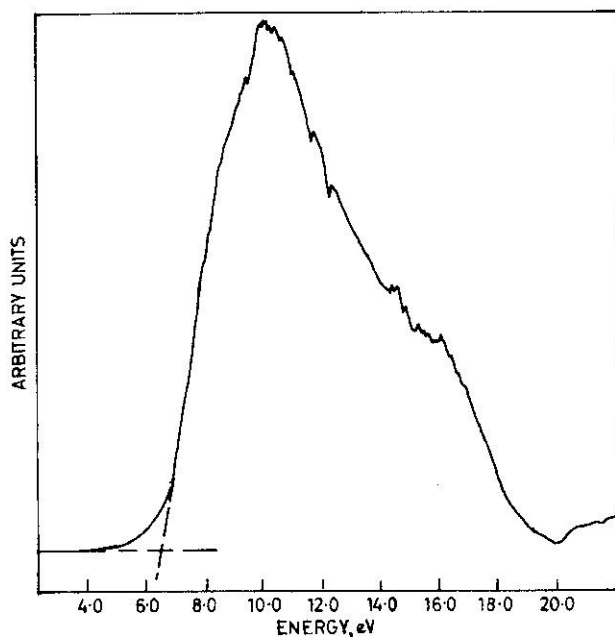


Fig. 1—Ultraviolet photoelectron spectrum of Pb_3O_4

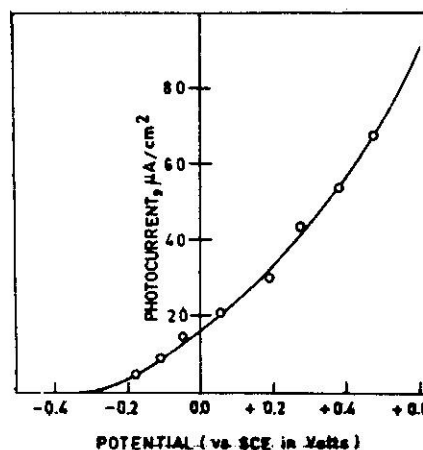


Fig. 2—Photo-current-sweep potential with Pb_3O_4 electrode to determine flat band potential by photo-current onset method

sharp anodic and cathodic peaks (Fig.3). Compared to iodate/iodide system which shows more than one type of anodic reactions. Moreover, ferro-ferric cyanide is also reported to be electrochemically reversible⁶. The redox potential of this electrolyte has been calculated from the average of forward and return peak potential (Fig.3)⁷, and is found to be +0.21 V (versus SCE). This is in agreement with the reported value⁸. Therefore for all other photoelectrochemical studies, ferro-ferric cyanide electrolyte was used.

The photocurrent-potential characteristic of this electrolyte with Pb_3O_4 film electrode suggests the presence of some cathodic dark leakage current (Fig.4), which may be due to some exchange cur-

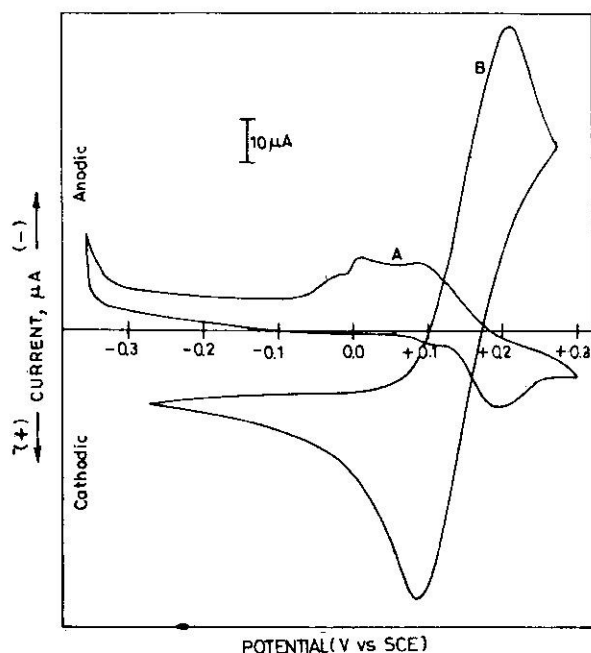


Fig. 3—Cyclic voltammogram of redox couple on platinum electrode. [Scanning rate 50 mV/sec and electrode area 1.0 cm². (A) Iodate/iodide electrolyte at pH 7.0 and (B) Fe(CN)₆^{3-/4-} electrolyte at pH 7.0]

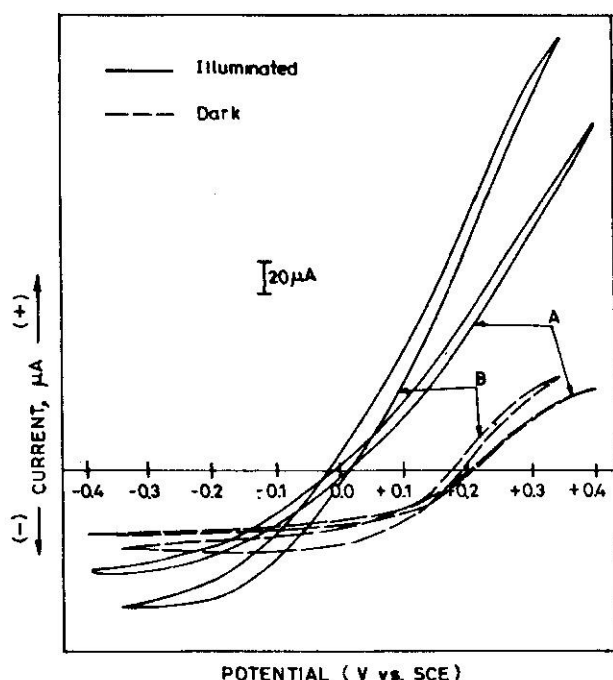


Fig. 4—Cyclic voltammogram of Fe(CN)₆^{3-/4-} redox couple on Pb₃O₄ electrode under dark and illuminated condition. [(A) with freshly prepared electrode and (B) with electrode which was kept under illumination in PEC cell for 15 days]

rent. Under ideal condition this current should be very low. The small anodic current may represent a poor junction formation with this electrolyte. The potential of dark current onset gives redox potential of the electrolyte¹⁰. The average of the

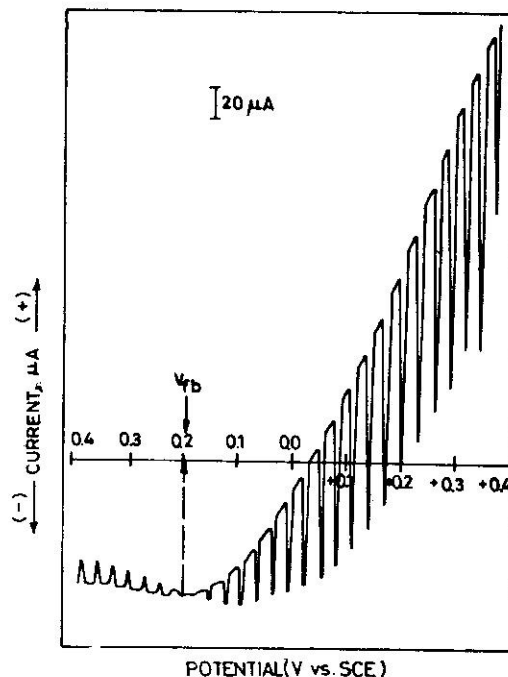


Fig. 5—Photo-current-sweep potential with Pb₃O₄ in ferro-ferric cyanide electrolyte under chopped light illumination. [Scanning rate 50 mV/sec electrode area 1.0 cm²]

two onset potentials during anodic and cathodic sweeps is +0.21 V (versus SCE, Fig. 4) which is the redox potential of the electrolyte. This value is the same as that obtained on platinum working electrode.

Being an n-type material, the cyclic voltammogram under illumination shows an expected large shift in anodic current compared to the cathodic photo-current (Fig. 5). The effect of chopping of light on the voltammogram suggests the photoreponse to be fast (Fig. 5). The potential, when the photo-current is zero gives the flat band potential of Pb₃O₄ in ferro-ferric cyanide electrolyte, i.e. -0.19 V versus SCE. Similar experiment when carried out with pure buffer solution of pH 7.0, the flat band potential is found to be -0.3 V (versus SCE). These two values are different because the flat-band potential also depends upon the nature of the electrolyte¹¹.

Though the AAS results obtained after the analysis of electrolyte of the PEC cell suggest the absence of any dissolved lead ions due to any electrochemical or photoelectrochemical corrosion of Pb₃O₄ electrode, the photo-current shows a gradual decrease in its magnitude, from 1.0 mA/cm² (Fig. 6). The latter experiment suggests that electrode surface must be changing somehow to show a decrease in photo-current. For this purpose a cyclic voltammogram was taken with the electrode which had been constantly illuminated

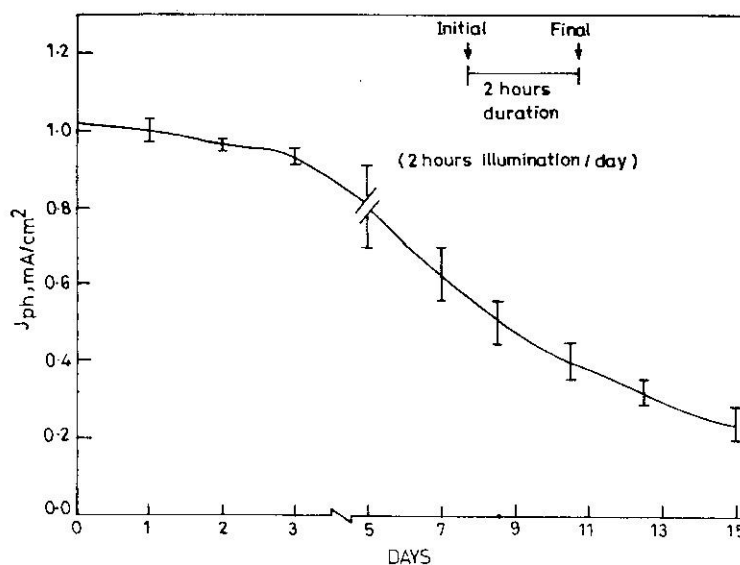


Fig. 6—Reduction in photo-current under constant illumination for 15 days (2 hr of continuous illumination/day)

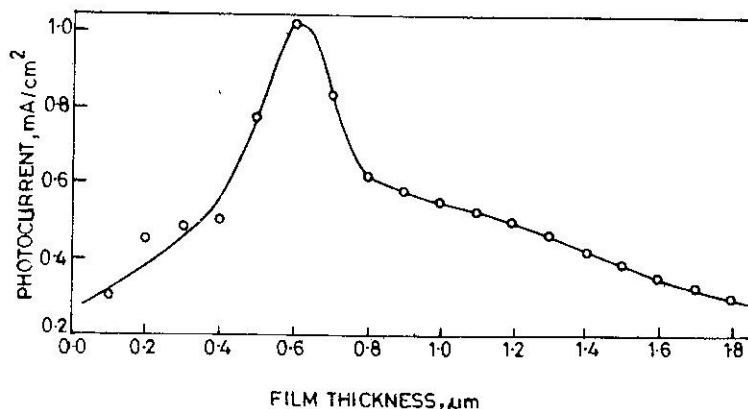


Fig. 7—Photo-current with Pb_3O_4 electrode versus thickness of the film

for 15 days. Results of this experiment does not show (Fig.4) any appreciable change in the photo-current-voltage characteristics of the electrode. This result confirms that Pb_3O_4 does not undergo any photochemical corrosion to such an extent that surface behaviour could change appreciably. However, such a behaviour needs to be investigated further.

The plot of photocurrent versus thickness (Fig.7) of the film gives a maximum value at 0.6 micron. This is perhaps because, film thickness less than surface charge layer width, prevents charge recombination in the bulk and thickness that is equal to more than the penetration depth of light (reciprocal of absorption coefficient) utilises all the photons falling on it for charge generation. The maximum value of absorption length ($1/\alpha$) that a semiconductor can attain is approxi-

mately equal to the wavelength of light at which it exactly matches the band gap¹². This value comes to be 0.585 micron for Pb_3O_4 . Since the space charge layer width of Pb_3O_4 film is 0.78 micron⁴, the optimum thickness (0.6 micron) obtained from Fig.7, lies between these two values and hence produces maximum photocurrent. Considering these experimental results, the maximum efficiency of PEC cell with configurations: $\text{Pb}_3\text{O}_4/\text{Fe}(\text{CN})_6^{-3}, \text{Fe}(\text{CN})_6^{-4}/\text{Pt}$ was calculated and with film thickness of 0.6 micron, electrolyte concentration 0.1 N (both i.e. ferric and ferrous cyanide solutions), and pH 12.0 give the maximum solar energy conversion efficiency of 0.21 %. This value is still far from the theoretical value. The different characteristics of this cell are: $I_{\text{sh}} = 1.2 \text{ mA/cm}^2$; $V_{\text{oc}} = 300 \text{ mV}$; $I_{\text{max}} = 0.7 \text{ mA/cm}^2$; $V_{\text{max}} = 180 \text{ mV}$; fill factor = 0.40; and efficiency = 0.21 %

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