

## SHORT COMMUNICATION

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**Study of photoelectrochemical corrosion of lead oxide in alkaline solution by the rotating ring-disk electrode technique**

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**Abstract** Photoelectrochemical corrosion of n-type  $\alpha$ -PbO electrodes in aqueous  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{I}^-/\text{I}_3^-$  electrolytes using the rotating ring-disk electrode technique has been investigated. The  $\alpha$ -PbO thin film is found to be more stable in  $\text{I}^-/\text{I}_3^-$  (48%) than in  $\text{Fe}(\text{CN})_6^{3-/4-}$  electrolyte (10%). Preferential adsorption of iodide ions decreases the photocorrosion reaction of holes with  $\alpha$ -PbO. Addition of CsI (0.4 mM) to the  $\text{I}^-/\text{I}_3^-$  electrolyte decreases the photocorrosion from 48% to less than 10%.  $\text{Cs}^+$  ions perhaps nullify the effect of negatively charged surface states of  $\alpha$ -PbO, thus minimizing the trapping of holes at the surface of  $\alpha$ -PbO and hence decrease the possibility of photocorrosion of lead oxide with holes.

**Key words** Photoelectrochemistry · Lead oxide photocorrosion · Rotating ring-disk electrode · Supporting electrolyte · Cesium iodide

**Introduction**

Sharon and co-workers [1–11] and Veluchamy and Minoura [12] have suggested that  $\alpha$ -PbO (band gap 1.92 eV) is a good semiconductor for developing a photoelectrochemical (PEC) solar cell. However, Sharon and Ghosh [13] have recently observed that the nature of the inert metallic counter electrode in such a PEC cell plays an important role in improving the cell current and hence the efficiency of the cell. Furthermore, based on the observation that CsI improves the photocurrent [14, 15] by facilitating the electron transfer reaction at the semiconductor|electrolyte interface, they also studied the effect on the counter electrode of the PEC cell ( $\alpha$ -PbO-redox electrolyte-metal) [13]. It was observed that CsI neither im-

proved nor reduced the performance of the inert metallic counter electrode, but, interestingly enough, the photoelectrochemical stability of  $\alpha$ -PbO in  $\text{Fe}(\text{CN})_6^{3-/4-}$  was found to improve considerably. In view of this behaviour of CsI, the photocorrosion of  $\alpha$ -PbO in  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{I}^-/\text{I}_3^-$  electrolytes with and without CsI was carried out by the rotating ring-disk electrode (RRDE) technique. In this paper, the results of these studies are presented.

**Experimental**

$\alpha$ -PbO semiconductor electrodes were prepared by anodic oxidation of a lead disk (99.9%, diameter 0.6 cm) in an alkaline solution at 80 °C in a potential range of  $-0.2$  V to  $+0.2$  V vs. Hg/HgO (sweep rate  $100 \text{ mV s}^{-1}$ ) [6, 9, 11]. A bi-potentiostat (Pine AFRDE-4) was used for the RRDE study. A platinum electrode with a removable disk (diameter 0.6 cm) and a ring electrode (inner and outer diameters 0.74 cm and 0.84 cm, respectively) were used to calculate the collection efficiency of the RRDE system in 2 mM  $\text{I}^-/\text{I}_3^-$  electrolyte. The rotation speed of the RRDE was kept at 1600 rpm. The  $\alpha$ -PbO disk electrode was mounted on the Teflon holder of the RRDE system using an epoxy resin with a Pt ring having dimensions as mentioned above. For studying the photocorrosion of  $\alpha$ -PbO, two types of redox electrolytes, (1) iodide/iodine (2 mM KI + 1 mM  $\text{I}_2$ ) and (2) 2 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$ , were used. The current-voltage characteristics of the  $\alpha$ -PbO disk as well as the platinum ring electrode in these electrolytes (pH 9.2) were measured under manually chopped light (250 W tungsten-halogen lamp). The potential of the platinum ring electrode was fixed to a value slightly lower than that required to reduce the oxidized species of the redox electrolyte (e.g. 0.0 V vs. SCE for the iodine/iodide system). The chopped currents for both the  $\alpha$ -PbO disk and the platinum ring electrodes were recorded by Houston model 2000 X-Y recorder. All potentials are referred with respect to SCE and all chemicals used were of analytical grade. These experiments were carried out with and without addition of CsI (0.4 mM).

**Results and discussion**

The current-voltage behaviour (Fig. 1) of the platinum disk ( $I_D$ ) and the ring ( $I_R$ ) electrode in 2 mM  $\text{I}^- + 1 \text{ mM } \text{I}_3^-$  at pH 9.2 were recorded for calculating

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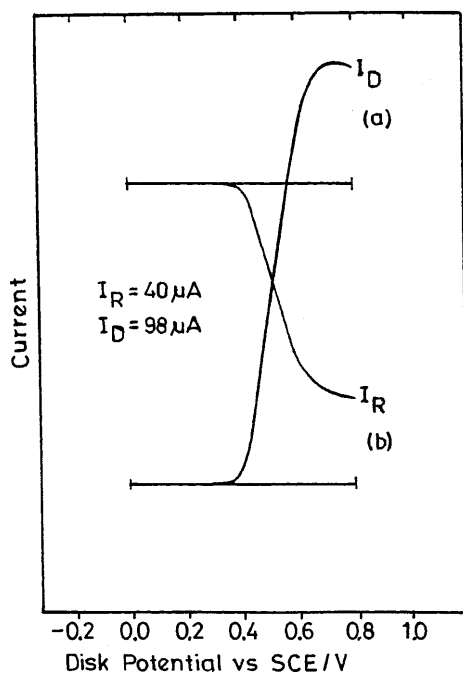


Fig. 1 Current-potential curve at the *a* Pt disk electrode in 2 mM KI and 1 mM  $I_2$  electrolyte at pH 9.2 and *b* collection current at the ring electrode kept at 0.0 V vs. SCE, 1600 rpm

the collection efficiency of the RRDE system. The ring potential was fixed at 0.0 V vs. SCE, as it was found suitable for mass transport-limited reduction of  $I_2$ . The collection efficiency was determined from the ratio of the magnitude of the ring ( $I_{red}$ ) and disk ( $I_{ox}$ ) currents. For this purpose, at some applied potential to the disk electrode, the currents of the disk and ring electrodes were measured [16]. The collection efficiency was found to be 0.195 at various potentials applied to the disk electrode. This value was in agreement with the value supplied (which is based on the geometrical sizes of the two electrodes) by the manufacturer of the RRDE.

For photocorrosion studies, the platinum disk electrode was replaced with the  $\alpha$ -PbO disk electrode and the experiment as discussed above was repeated by maintaining the ring potential at  $-0.3$  V vs. SCE [at this potential, reduction of  $Fe(CN)_6^{3-}$  at the ring electrode was found to occur]. The current-voltage curves for both disk (i.e.,  $I_{ph}$  at  $\alpha$ -PbO) and ring ( $I_{red}$  at Pt ring) electrodes were plotted (Fig. 2). Using the collection efficiency ( $\gamma$ ) of 0.195, the part of the photocurrent produced by the  $\alpha$ -PbO disk electrode owing to the reaction of photogenerated holes with the redox electrolyte was calculated by using the equation:

$$\frac{I_{ox}}{I_{ph}} = \frac{I_{red}}{\gamma I_{ph}} \quad (1)$$

where  $I_{ox}$  = photooxidation current due to the reaction of the photogenerated holes with the redox electrolyte at the  $\alpha$ -PbO disk electrode at a potential  $E_x$ ,  $I_{ph}$  = total photocurrent recorded at the disk electrode (Fig. 2a) at potential  $E_x$  ( $-0.4$  to  $+0.4$  V vs. SCE),  $I_{red}$  = photore-

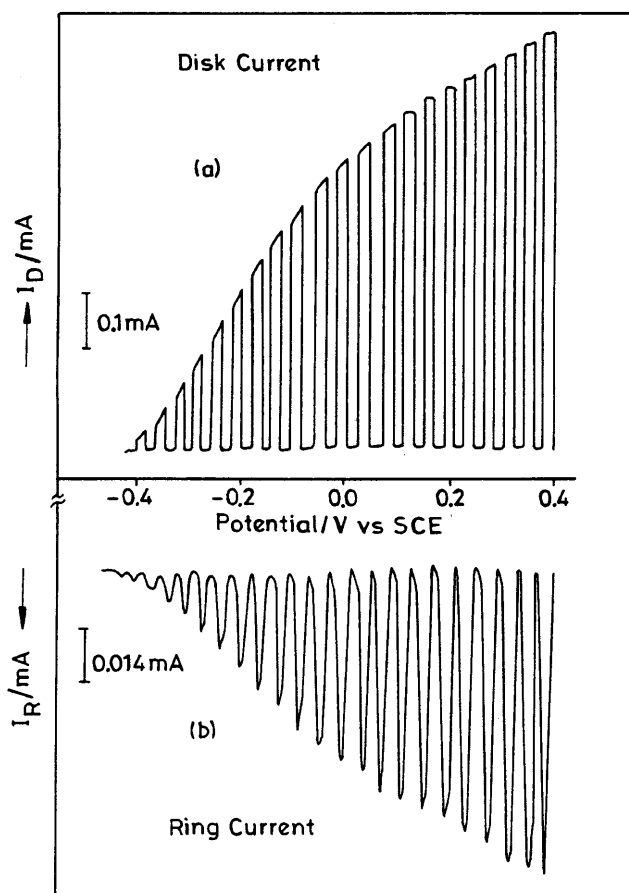


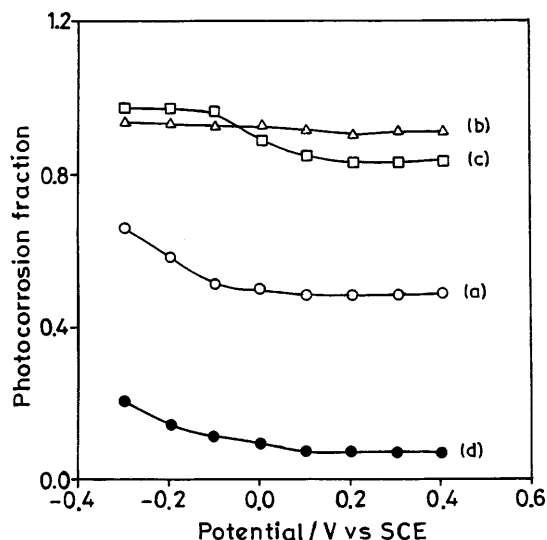
Fig. 2 Current-potential curve at the *a*  $\alpha$ -PbO disk and *b* Pt ring at 0 V vs. SCE in 2 mM KI and 1 mM  $I_2$  electrolyte at pH 9.2 under a chopped light illumination. The rotation rate was 1600 rpm

duction current at the ring electrode (Fig. 2b) owing to the reduction of the redox electrolyte (e.g., reduction of  $I_3^-$  which was produced owing to oxidation of  $I^-$  at the  $\alpha$ -PbO disk electrode at potential  $E_x$ ; Fig. 2a).

The photocorrosion current at a potential  $E_x$ , for example in the  $I^-/I_3^-$  system, was calculated by subtracting  $I_{ox}$  from  $I_{ph}$ . This calculation was carried out for various values of biasing potential and the results for  $I^-/I_3^-$  and  $Fe(CN)_6^{3-/4-}$  are plotted in Fig. 3. The graph (Fig. 3a) suggests that, with the  $I^-/I_3^-$  system, 48% of the total photocurrent is due to photocorrosion. Unlike with  $I^-/I_3^-$ , photocorrosion of  $\alpha$ -PbO in  $Fe(CN)_6^{3-/4-}$  is of the order of 90% (Fig. 3b).

It is interesting to note that there was no effect of these redox electrolytes on the magnitude of the photopotentials obtained by illuminating  $\alpha$ -PbO of the PEC cell using either  $Fe(CN)_6^{3-/4-}$  or  $I^-/I_3^-$  electrolytes. Both electrolytes gave almost the same photopotential of 800 mV.

Hodes [14] and Licht et al. [15] have reported that, among many halides, CsI plays an important role in enhancing the photocurrent of a PEC cell. Therefore, RRDE studies, on similar lines as stated earlier, were carried out with  $Fe(CN)_6^{3-/4-}$  as well as  $I^-/I_3^-$  redox



**Fig. 3** Effect of the applied potential on the photoinduced corrosion for a n-type  $\alpha$ -PbO electrode. The solutions were *a* 2 mM KI and 1 mM  $I_2$ , *b* 2 mM  $Fe(CN)_6^{3-/4-}$ , *c* 0.4 mM CsI in 2 mM  $Fe(CN)_6^{3-/4-}$  and *d* 0.4 mM CsI in 2 mM KI and 1 mM  $I_2$  at pH 9.2

electrolytes containing CsI (0.4 mM). The results of the photocorrosion are plotted in Fig. 3c and d. It appears that photocorrosion has decreased a little with  $Fe(CN)_6^{3-/4-}$  (Fig. 3c), but much less than with the  $I^-/I_3^-$  (Fig. 3d) system, showing a decrease of the photocorrosion of  $\alpha$ -PbO from 48% to 10%.

The extent of stabilization of  $\alpha$ -PbO (photoanode) perhaps depends upon the competition between two reactions involving photogenerated holes at the surface of  $\alpha$ -PbO: (1) oxidation of the redox electrolyte at the semiconductor/electrolyte interface, leading to oxidation of the redox couple, and (2) rupture of bonds at the surface of  $\alpha$ -PbO, giving the photocorrosion current. The photogenerated holes at the surface of  $\alpha$ -PbO are expected to possess a high rate constant for the oxidation of the redox electrolyte, provided they are freely available for the oxidation of the redox electrolyte. If holes are trapped at the surface of  $\alpha$ -PbO owing to the presence of negatively charged surface states, then there is a greater possibility for holes to oxidize  $\alpha$ -PbO. The effect of surface states can be minimized by two processes: (1) covering the surface of  $\alpha$ -PbO with a layer of some ions which prevents the holes being trapped at the negatively charged surface states present at the surface of  $\alpha$ -PbO or/and (2) neutralizing the negatively charged surface states with some specific unhydrated cations. If the redox electrolyte is preferentially adsorbed at the surface, it will prevent the photogenerated holes coming in contact with negatively charged surface states before they have the chance to oxidize the redox electrolyte. If this is so, the photogenerated holes will prefer to oxidize of the redox electrolyte instead of  $\alpha$ -PbO. Octahedral  $Fe(CN)_6^{4-}$  is likely to be less efficiently adsorbed at the  $\alpha$ -PbO surface than the linearly shaped  $I_3^-$  complex. As a result of this, the  $Fe(CN)_6^{3-/4-}$  electrolyte would not be

able to protect the  $\alpha$ -PbO surface from trapping photogenerated holes by the negatively charged surface states as effectively as the iodide/iodine system, thus favouring the photogenerated holes to oxidize the redox electrolyte more effectively than oxidizing  $\alpha$ -PbO, in turn making it more stable in  $I^-/I_3^-$ .

$Cs^+$  is known to exist as an unhydrated cation [15] and can therefore easily be adsorbed at negatively charged surface states present at the surface of  $\alpha$ -PbO. In this way, if there were some negatively charged surface states not neutralized by the  $I^-/I_3^-$  electrolyte, CsI may neutralize the negatively charged surface states of  $\alpha$ -PbO further to prevent the oxidation of  $\alpha$ -PbO by photogenerated holes. As a result of this, corrosion of  $\alpha$ -PbO (48%) is further reduced to 10% by the addition of CsI.

## Conclusions

Photocorrosion of  $\alpha$ -PbO is observed to be 90% and 48% in a PEC cell with  $Fe(CN)_6^{3-/4-}$  and  $I^-/I_3^-$  electrolytes, respectively. Addition of CsI (0.4 mM) further decreases the photocorrosion of  $\alpha$ -PbO in  $I^-/I_3^-$  electrolyte to 10%. Preferential adsorption of iodine/iodide and CsI electrolytes on the  $\alpha$ -PbO minimizes the effect of negatively charged surface states present at the surface of  $\alpha$ -PbO, thus making  $\alpha$ -PbO photoelectrochemically stable.

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