

# Experimental study of the alkalization model for the $\text{PbSO}_4$ anodic layer on lead/acid positive-plate grids

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## Abstract

A lead electrode has been prepolarized anodically in sulfuric acid solution and then subjected to a cathodic potential sweep with simultaneous illumination. The photocurrents produced by  $\text{PbO}$  change from anodic to cathodic values pass through zero as the potential sweep continues. Under the present conditions, the potential at zero photocurrent is a fixed value, viz.,  $-0.65$  V, (versus  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ), and is equal to the flat-band potential of  $\text{PbO}$ . From this, the pH in the  $\text{PbO}$  layer is calculated to be 9. This finding provides strong support for the alkalization model of the  $\text{PbSO}_4$  anodic layer.

## Introduction

The corrosion mechanism of lead/acid battery positive grids has been a subject of great interest to scientists for many years. As a consequence, considerable research has been directed towards understanding the anodic polarization process of lead electrode in  $\text{H}_2\text{SO}_4$  solution, and towards identifying the corresponding changes in the phase composition of the corrosion layer formed on the electrode. Pavlov [1–4] was the first to elucidate the mechanism of alkalization of the lead electrode during anodic oxidation. This mechanism is based on a hindrance to the diffusion of sulfate species in the intercrystalline pores of the  $\text{PbSO}_4$  layer which acts as a semipermeable membrane.

Ruetschi [5] artificially prepared a precipitated membrane of  $\text{PbSO}_4$  and demonstrated that this membrane is highly selective; it was nonpermeable for  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$  and  $\text{Pb}^{2+}$  but permeable for  $\text{H}^+$  and  $\text{OH}^-$ . It was shown that the pH at the interface of  $\text{Pb}/\text{PbO}$  can be expected to reach a value of 9.34, for equal activities of  $\text{Pb}^{2+}$  and  $\text{HPbO}_2^-$ . In further studies, Pavlov [6, 7] comprehensively elaborated the mechanism and presented an alkalization model for the  $\text{PbSO}_4$  anodic layer [8].

It is instructive to detect the actual pH of the  $\text{Pb}/\text{PbO}$  interface on lead electrode after prepolarization. Among the *in situ* studying approaches, the photoelectrochemical method based on the semiconducting properties of lead oxides is one of the most useful techniques for investigating the  $\text{PbSO}_4$  anodic layer. Pavlov [6–9], Barradas [10–12] and other workers [13–15] have studied the photoelectrochemical properties of the  $\text{Pb}/\text{PbO}/\text{PbSO}_4/\text{H}_2\text{SO}_4$  electrode. The results showed that the lead oxides forming beneath the  $\text{PbSO}_4$  layer are photoactive in the visible band of the spectrum and that the photoactivation takes place when the potential of the electrode is within the range of 0 to 1.0 V (versus  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ). Because both  $\text{H}_2\text{SO}_4$  and  $\text{PbSO}_4$  are transparent, a photocurrent is produced in the layer of lead oxides when an anodically prepolarized lead electrode is irradiated with visible light.

The work reported here aims to probe the actual pH conditions (by means of the photoelectrochemical method) under which PbO is stabilized in the anodic layer, and, thereby, to provide further experimental evidence for the alkalization model.

## Experimental

A lead electrode (99.997% pure) was anodically oxidized in H<sub>2</sub>SO<sub>4</sub> solution in the dark at a certain potential for a certain duration. This was immediately followed by illumination with monochromatic (435 nm) chopped (75 Hz) light of about 10 mW cm<sup>-2</sup> intensity and by reduction with cathodic linear sweep voltammetry (LSV).

The anodic oxidation was carried out under potentiostatic conditions in a 30% solution of H<sub>2</sub>SO<sub>4</sub> in triple-distilled water. The working electrode was covered with resin tape so that a lead surface of 0.04 cm<sup>2</sup> area was exposed to the electrolyte. Experiments were performed in a three-electrode glass cell, with a separate counter-electrode compartment and an optically flat glass window. Platinum was used as the counter electrode and Hg/Hg<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>SO<sub>4</sub> as the reference electrode. All potentials are reported with respect to this reference electrode. Experiments were conducted at ambient temperature, namely, 22 ± 0.5 °C.

The electrolyte (150 cm<sup>3</sup>) was deoxygenated with purified nitrogen. The working electrode was subjected to a standard pretreatment before each experiment. This involved reducing the working electrode at -1.2 V until the current was less than 0.5 μA. A Stonehart potentiostat (model BC 1200) and a Fisher recorder (series 500) were used for polarization and current measurements, respectively. An E.G.&G. PARC (model 175) Universal Programmer and a Hewlett-Packard (model 7035) x-y recorder were used for the respective programming and recording LSVs.

A 1 kW xenon-mercury lamp served as the source of illumination. The light beam was passed, successively, through an IR filter (2% aqueous CuSO<sub>4</sub> solution), a monochromator and a focusing lens. Experiments were performed by using an E.G.&G. PARC (model 194A) light chopper and an E.G.&G. PARC (model 128A) lock-in amplifier. A second Hewlett-Packard (model 7035) x-y recorder was used to record the photocurrents.

## Results and discussion

### *Photoelectric response of the PbSO<sub>4</sub> anodic layer*

Immediately following potentiostatic prepolarization for 20 min, the lead electrode was subjected to illumination and a cathodic LSV at a scan rate of 2 mV s<sup>-1</sup>. The voltammograms and the corresponding photocurrent curves were recorded simultaneously. A part of the curve obtained after prepolarization at 0.4 and 0.8 V is shown in Fig. 1. The two cathodic peaks are attributed to the reduction of PbO and PbSO<sub>4</sub>, respectively [11, 16]. The positions of both the photocurrent peak and the PbO reduction peak are coincident and the two kinds of currents tend to change in the same manner.

The following fact should be noted. When the cathodic photocurrent declines and almost approaches the base (-0.9 V or so), the PbO peak is overlapped by a very small peak (*x* in B and D, Fig. 1) with a value about 1 nA. Even when the prepolarization potential is so negative (e.g., -0.4 V) that the reduction peak for PbO and the corresponding photocurrent peak both disappear, the unknown small peak *x* is still present. The origin of this peak is unknown. Its existence does not, however, affect the photocurrent of the lead oxides.

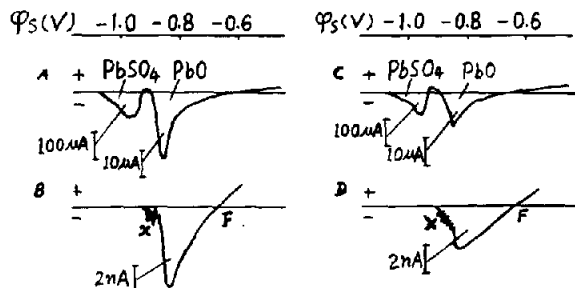


Fig. 1. Voltammograms (A, C) and corresponding photocurrent curves (B, D) for lead in 30%  $\text{H}_2\text{SO}_4$  at a scan rate of  $2 \text{ mV s}^{-1}$ . Prepolarization potentials: 0.8 V (A, B); 0.4 V (C, D).  $\phi_s$  = sweep potential.

TABLE 1

$\phi_s(\text{F})$  values at different  $\phi_p$

$\phi_p(\text{V})$	0	0.2	0.4	0.6	0.8
$-\phi_s(\text{F}), (\text{V})$	$0.65 \pm 0.02$	$0.67 \pm 0.02$	$0.62 \pm 0.01$	$0.65 \pm 0.01$	$0.67 \pm 0.02$

#### Determination of the flat-band potential from the change in photocurrent

Figure 1 shows that the anodic photocurrent gradually becomes smaller as the negative-going sweep proceeds. After passing a certain point, F, on the voltammogram, the photocurrent becomes cathodic. The photocurrent at point F equals zero. The corresponding sweep potential, denoted by  $\phi_s(\text{F})$ , does not change (within a reasonable error range) when the electrode is prepolarized at different potentials,  $\phi_p$ . Thus  $\phi_s(\text{F})$  is considered to be a fixed value in the present work. The values for  $\phi_s(\text{F})$  given in Table 1 are the arithmetic mean of three measured values for each  $\phi_p$ . The average of all measured values of  $\phi_s(\text{F})$  was  $-0.65 \pm 0.03 \text{ V}$ .

In a photoelectrochemical study of the anodic oxidation of lead in  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{H}_2\text{SO}_4$  solutions, Buchanan [15] pointed out that the crossover in photocurrent from anodic to cathodic is due to the intrinsic semiconducting properties of the lead oxide, rather than a change from n- to p-type conductivity. The change in the sign of the photocurrent demonstrates that the electric field in the oxide layer reverses at the crossover point, that is, at the point of zero photocurrent. This mechanism is outlined in Fig. 2. The band-gap energy,  $E_g$ , is assumed to be 2.8 eV, a value that is taken from the data of Barradas [10], and Hardee and Bard [17] attributed to  $\beta\text{-PbO}$ . This value of 2.8 eV for PbO in the anodic layer on lead electrode differs from the data of other scientists, viz., 1.9 eV; this discrepancy has been explained by Bullock [13, 14].

On the basis of the above discussion, it is reasonable to take the potential at zero photocurrent of the PbO layer,  $\phi_s(\text{F})$ , as the flat-band potential of the PbO layer,  $V_{\text{fb}}(\text{PbO})$ , under *in situ* conditions. Therefore:

$$V_{\text{fb}}(\text{PbO}) = \phi_s(\text{F}) = -0.65 \text{ V} \quad (1)$$

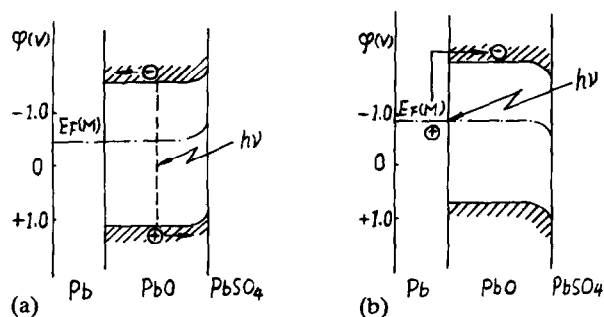


Fig. 2. Schematic of mechanism that produces a photocurrent in the PbO layer. (a) Bulk excitation of PbO layer; (b) photoemission from Pb into PbO layer.  $E_F$ =Fermi level.

### *In situ* evaluation of pH in the PbO layer

In order to evaluate the pH around a semiconductor layer from the known value of the  $V_{fb}$ , the following equation [18] can be used:

$$qV_{fb} = E_{cs}^0 - \mu + B - 2.3kT (\text{pH}) \quad (2)$$

where  $q$  is the charge on the electron;  $E_{cs}^0$  is the standard energy of the conduction band edge of the semiconductor;  $\mu$  is the energy difference between the bulk conduction band edge and the Fermi energy;  $B$  is a constant. For a certain system:

$$E_{cs}^0 - \mu + B = C = \text{Constant} \quad (3)$$

and, when  $T=295$  K, eqn. (2) can be simplified to:

$$v_{fb} = A + 0.0585 \text{ pH} \quad (4)$$

where  $A$  is another constant.

Hardee and Bard [17] reported a value for  $V_{fb}(\text{PbO})$  of  $-0.3$  V (versus saturated calomel electrode) when the  $\text{pH}=9$ . Referring this potential to a  $\text{Hg}/\text{Hg}_2\text{SO}_4/30\%$   $\text{H}_2\text{SO}_4$  reference electrode gives:

$$V_{fb}(\text{PbO}) = -0.3 + 0.242 - 0.626 \approx -0.7 \text{ V} \quad (5)$$

Substitution of  $\text{pH}=9$  and  $V_{fb} = -0.7$  V in eqn. (4) yields a value for  $A$  of  $\sim -1.2$  V. Now, by using the  $V_{fb}$  value of  $-0.65$  V that has been found in this work, again a  $\text{pH}$  of 9 is obtained for the PbO layer. This result is very close the  $\text{pH}$  value of 9.34 that was adopted by Ruetschi [5] and, thus, presents convincing evidence for the alkalization model.

### Conclusions

After a lead electrode in 30%  $\text{H}_2\text{SO}_4$  solution is potentiostatically prepolarized over the range  $0 \sim +0.8$  V for 20 min, the anodic layer on the electrode is photosensitive to monochromatic light of 435 nm. The potential at zero photocurrent is  $-0.65$  V. This value is exactly the flat-band potential of the PbO layer and from which a  $\text{pH}$  value of 9 is found for the PbO layer. This result from *in situ* detection is significant for the alkalization model of the  $\text{PbSO}_4$  anodic layer.

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