

## DESIGN OF ADDITIVES TO ENHANCE THE PERFORMANCE OF THE LEAD ANODE IN SULPHURIC ACID

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### Introduction

This paper gives an outline of recent research into the mechanism of electrocrystallization of lead sulphate on lead and the search for improved expanders for the negative plate of lead/acid batteries. The main objective is to develop a model for the formation of  $\text{PbSO}_4$  in terms of the electrochemical reactions that take place on the lead anode, and to use this model to study the action of organic additives containing the sulphonate group [1, 2].

The broad features of the action of expanders have been reviewed by Pavlov [3], and much empirical knowledge has been acquired over a long period [4]. It is clear that expanders of the lignosulphonate type are strongly adsorbed on the lead surface and dissolving  $\text{Pb}^{2+}$  ions must migrate through this adsorbed layer [5]. The presence of adsorbed molecules of expander has been observed to affect the anodic oxidation of lead [6], the cathodic reduction of lead sulphate [7], the morphology of lead sulphate crystals [3], and the porosity and surface area of the negative plate material [8, 9]. The active mass of porous lead in the negative plate has been shown to consist of two types of structure: a primary skeleton that serves as a mechanical support and a current collector, and a secondary structure of fine crystallites of lead that is consumed during discharge and is rebuilt upon re-charging [10]. The morphology of the secondary structure is affected by the presence of expanders; the latter favour the growth of smaller crystallites with greater surface area.

The morphology and specific surface area of the negative plate material must depend ultimately on the various electrochemical reactions that contribute to the overall charge and discharge processes. An attempt is made here to dissect the overall anodic process into separate reactions using transient kinetics methods.

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## Mechanism of anodic formation of lead sulphate

Previous kinetic investigations using linear-sweep voltammetry [3, 11, 12] and potential-step transients [7, 13, 14] have established that initial dissolution of  $Pb^{2+}$  ions is followed by formation of a solid phase on the surface. In the work reported here, potential-sweep and potential-step experiments have been conducted over a range of potentials and temperatures ( $-18$  to  $30^\circ C$ ) and the results have been fitted quantitatively to a mechanism consisting of the following separate reactions [1, 2].

### (a) Growth of a conductive surface film of $PbSO_4$

The thickness of the film increases with the potential in the range 10-100 molecules of  $PbSO_4$ . The kinetics of formation of this film are governed by instantaneous nucleation followed by lateral growth at a rate ( $i_g$ ) proportional to the expanding perimeter, with allowance for overlap, in accordance with the established theory of Bewick, Fleischmann and Thirsk [15], *i.e.*,

$$i_g = at \exp(-bt^2) = q_g d\theta/dt \quad (1)$$

where  $\theta$  is the fractional coverage. The theory is modified slightly here to correct for the edge profile of the expanding centres; these will not be perfect cylinders but will be likely to have bevelled edges.

### (b) Dissolution of $Pb^{2+}(aq)$ from the bare lead surface

The dissolution rate ( $i_d$ ) is proportional to the fraction of the surface uncovered by the film, *viz.*,

$$i_d = i_d^0(1 - \theta) \quad (2)$$

### (c) Transmission of $Pb^{2+}$ through the conductive film

Since the above two processes are not sufficient to account for the observed current transients, it is proposed that the film transmits cations by electromigration in the solid state. These  $Pb^{2+}$  cations will enter the electrolyte solution at the outer surface of the film and contribute to the build-up of dissolved  $Pb^{2+}$  adjacent to the electrode. The anodic current due to the film transmission ( $i_f$ ) is proportional to the film coverage, diminished by the fractional coverage,  $\Psi$ , of the passivation layer of  $PbSO_4$  that precipitates on top of the conductive film, *i.e.*,

$$i_f = 2Fk_f(\theta - \Psi) \quad (3)$$

### (d) Precipitation of the passivating layer

Once the concentration of dissolved  $Pb^{2+}$  (created by reactions (b) and (c) above) has increased above the critical supersaturation limit, precipitation of polycrystalline  $PbSO_4$  takes place on the outer surface of the conductive film:

$$d\Psi/dt = k_p(\theta - \Psi) \quad (4)$$

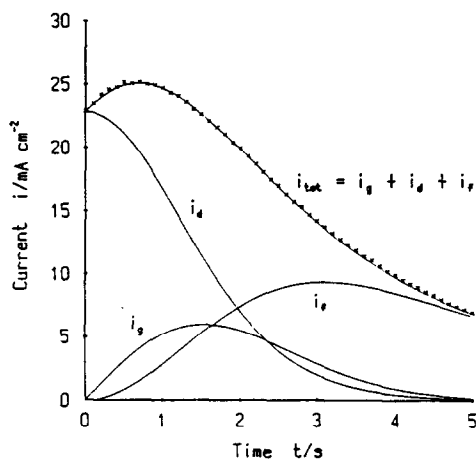


Fig. 1. Potential step transient for  $\text{PbSO}_4$  formation. Lead anode in 35% sulphuric acid at  $18^\circ\text{C}$ . Pretreatment at  $-756\text{ mV}(\text{she})$  for 10 s, then potential stepped from  $-456$  to  $-266\text{ mV}(\text{she})$ . Experimental data points,  $\times$ , compared with the simulated curves for the charge transfer processes of the model.

This passive film does not transmit ions and, hence, is different in nature from the conductive film.

This mechanism has been fitted to the experimental data by computer simulation and satisfactory agreement has been obtained [1, 2]. An example of a potential-step transient is shown in Fig. 1 where the total current for reactions (a), (b) and (c) is compared with experiment. The novel feature of the proposed mechanism is the ionically conductive film that transmits lead cations under the applied electric field. The other features of the mechanism are similar to those of previous authors [7, 12, 14].

### Action of methyl orange and other sulphonates

Many commercial expanders contain the sulphonate group, which is negatively charged even in the presence of sulphuric acid. It is possible that the adsorption of anionic substances is favoured by the fact that the potential of zero charge of lead is  $-0.62\text{ V}(\text{she})$  and, hence, the lead electrode carries a positive charge at the potential of the negative plate (around  $-0.35\text{ V}(\text{she})$ ). A number of sulphonic acids have been tested by the potential-sweep method at a lead anode in 35% sulphuric acid with the following results:

No effect:

- benzenesulphonic acid
- p*-aminobenzenesulphonic acid
- p*-toluenesulphonic acid
- sulphamic acid

No potential shift, but 10 - 30% decrease of anodic charge:

methanesulphonic acid

trichloromethanesulphonic acid

Shift of potential by +50 mV and 20% decrease in anodic charge:

xylene orange

The only *favourable case* was methyl orange. This gave no change in potential but there is an increase in anodic charge of 20% at  $-18^{\circ}\text{C}$  (see Fig. 2) and 50% at room temperature (in the latter case after continuous potential cycling for over 1 h). This encouraging result was followed by a test in a 6 V/2 A h battery to which methyl orange was added to give a 0.1% solution. Under fast discharge, at constant current and low temperature, the overpotential at the negative plate was 300 mV lower and the capacity was increased by 20% compared with the control. During recharge, however, the red colour was converted to yellow (due to oxidation of methyl orange at the positive plate) and the resulting solution had no effect on the discharge characteristics compared with the control. It appears that methyl orange has a significant effect on performance of the negative plate, but its solubility in sulphuric acid makes it unsuitable for use in a practical battery.

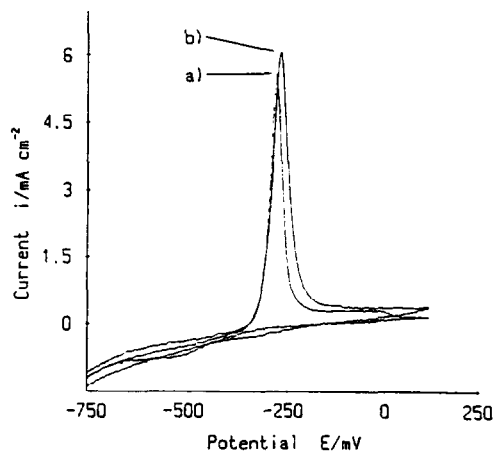
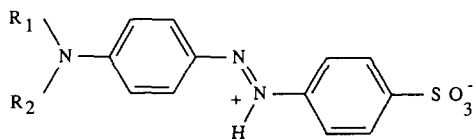


Fig. 2. Action of methyl orange on the anodic reaction. Voltammograms at  $-18^{\circ}\text{C}$  in 35% sulphuric acid: (a) before, (b) after addition of  $0.2\text{ g ml}^{-3}$  methyl orange; sweep  $20\text{ mV s}^{-1}$ .

### The search for a new expander — lauryl orange

In order to make an additive of negligible solubility, but still containing the zwitter ion structure of methyl orange in acidic solution, the new compound lauryl orange was synthesized:



Methyl orange:

 $R_1 = \text{CH}_3$  $R_2 = \text{CH}_3$ 

Lauryl orange:

 $R_1 = \text{C}_{12}\text{H}_{25}$  $R_2 = \text{H}$ 

The dodecyl substituent on the amino group resulted in complete insolubility in sulphuric acid, but the substance showed very strong adsorption on leady oxide and on a clean lead surface. By pretreating a lead electrode with lauryl orange in dichloromethane, an adsorbed layer could be prepared. This gave a relatively low anodic charge, as seen in Fig. 3, which should be compared with Fig. 2(a).

Battery tests were conducted by treating leady oxide with lauryl orange in dichloromethane before preparing the paste for the negative plate. It was found that lauryl orange was strongly adsorbed and prevented oxidation of the free lead in the leady oxide during the curing process. The battery test is shown in Fig. 4: the capacity of the negative plate containing lauryl orange is lower than the control and the overpotential is increased. A similar result was obtained when lauryl orange was directly adsorbed onto the porous lead of a formed negative plate. The conclusion is that alkyl derivatives of *p*-aminoazobenzene-*p'*-sulphonic acid show promise as expanders for the negative plate, provided a balance can be obtained between selective adsorption, which stimulates the anodic reaction, and excessive adsorption which stifles the overall anode performance.

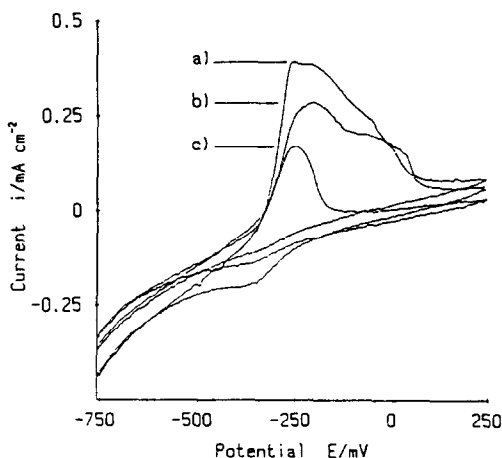


Fig. 3. Action of adsorbed lauryl orange. Voltammograms at  $-18^\circ\text{C}$  in 35% sulphuric acid: (a) immediately after adsorption; (b) after 2 h; (c) after 12 h; sweep  $20\text{ mV s}^{-1}$ .

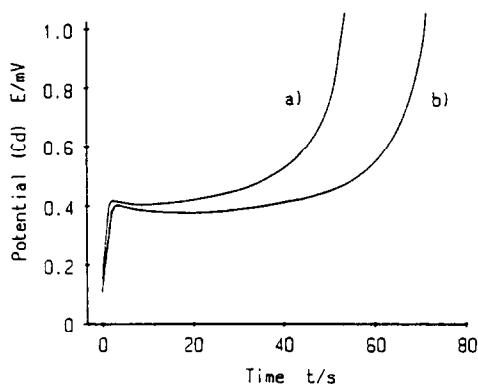


Fig. 4. Constant-current discharge of a negative plate. Potential vs. the cadmium electrode as a function of time for a current of 18.5 A at  $-18^{\circ}\text{C}$  in 35% sulphuric acid: (a) 10 mg lauryl orange per 100 g leady oxide used to prepare plate; (b) no lauryl orange.

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