

THE ENERGETIC COEFFICIENT IN LEAD/ACID BATTERY POSITIVE PLATES

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Introduction

Pavlov's model [1] describing the active material in the positive plate of a lead/acid battery has received general acceptance in the literature in recent years. In this model, it is assumed that the active mass comprises a structural part, which supplies the mechanical properties and acts as a pathway for the electrons, and an energetic part able to undergo the oxidation/reduction process. The latter is located on the surface of the structural part and is in contact with the solution mainly in the pores of the plate. The end of the cycle life of a plate commences when the structural part is involved in the oxidation/reduction process since, at this stage, the electronic and mechanical properties start to degrade.

From the above hypothesis, it is possible to define an energetic coefficient (β) as the ratio between the amount of energetic material and the total amount of PbO_2 present in the plate. Obviously, this coefficient will be an important parameter and can be related to the technology used to manufacture the plate. Despite such an advantage, there have been no attempts to measure this parameter, and the usual coefficient reported is the mass utilization coefficient (α) [2].

The main problem to be faced is how to measure, unequivocally, the total amount of energetic material. During a galvanostatic discharge, the measured charge (Q_D), and therefore the amount of material related to it, depends on the discharge conditions, that is: the initial H_2SO_4 concentration and its variation during the discharge; the current density and its distribution over the plate surface; the morphology of the plate pores, etc. From this, the mass utilization coefficient is calculated as Q_D/Q_T where Q_T is the total possible theoretical faradaic charge. The question remains, however, how is the charge related to the total amount of energetic material? This can be termed the 'limiting charge' of discharge (Q_L) since it represents an extreme value of Q_D , giving β as Q_L/Q_T . In the present work, it is proposed that Q_L

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(and therefore β) can be measured using a potentiostatic discharge method. The results obtained, together with the classical Q_D and α , are analysed for automotive types of pasted positive plate.

Positive active-material discharge

Many galvanostatic and potentiodynamic studies on the discharge of different kinds of PbO_2 electrodes have been reported during the past two decades [3 - 8]. These include investigations into both flat and porous PbO_2 deposits on platinum and lead as well as studies on actual battery plates.

In the case of galvanostatic discharges on flat PbO_2 electrodes deposited on platinum, the fundamental work of Asai *et al.* [3] shows that, for a constantly used area (which cannot be the case for a porous electrode), factors that increase the number of nuclei of the product ($PbSO_4$) reduce the charge density (q_D) of the discharge. This is probably due to the fact that a decrease in the size of the $PbSO_4$ crystals will cause an increase in the size of the voids between them and will, in turn, result in lower values of q_D . Such morphological changes were illustrated by scanning electron micrographs [3].

As was proposed previously [4] for a pasted positive plate, the active material of a real plate can be represented by a very simple model, namely, by a continuous system with a cylindrical porous mass normal to the material surface, connecting, or not, the two faces of the plate. The measurements of Asai *et al.* [3] must be related to the utilized part of the internal surface of the porous mass during a galvanostatic discharge. In this respect, studies [5] of the potentiodynamic reduction response of a porous PbO_2 electrode on lead, obtained from lead oxide, gave rise to a similar model, namely, that the reaction can be seen as occurring uni-dimensionally in the porous structure.

Matthews *et al.* [6], using a porous PbO_2 electrode sintered on lead, showed that after potentiodynamic cycling the cathodic peak shifts in the cathodic direction. According to the authors, this is due to a corresponding increase in the ohmic drop. Such behaviour suggests that with cycling, deeper, inner porous surfaces of the active material are used, supporting the idea of 'penetration depth' as advanced by Frumkin [9].

The galvanostatic results of Bode [7] for actual positive plates show that the value of α increases with the H_2SO_4 concentration, with a tendency to level off to a plateau at high values. For thin plates at low current densities, however, a maximum appears at around 3.5 M, followed by a further increase at higher concentrations. The maximum is explained in terms of the specific conductivity maximum of the H_2SO_4 solution (also near 3.5 M), but why there is a further increase in α at higher H_2SO_4 concentrations, or why the maximum appears only at some discharge current densities, is not addressed. There appears to be no other work related to these coefficients in the available literature. The use of impedance measurements

on this kind of electrode has presented interpretation problems [8] related to the appearance of an inductive behaviour at very low frequencies. This behaviour, which is not observed on flat electrodes, has still to be interpreted for a porous structure. On the other hand, the impedance measurements at medium frequencies appear to be related to the porous structure [8]. Finally, the impedance measurements indicate that, under moderate charge/discharge rates, most of the polarization is due to the charge-transfer kinetics, while the ohmic and concentration overvoltages are negligible [8].

Experimental

The working electrodes were positive pasted electrodes from commercial automotive batteries. The electrodes had a geometrical area (both sides) of about 1.5 cm^2 and were received from the factory directly after curing. The formation conditions were 2.5 mA cm^{-2} in H_2SO_4 (sp. gr. 1.050 g cm^{-3}) at 25°C . The soak time was 2 h. After formation, the working electrodes were subjected to five cycles in $4.6 \text{ M H}_2\text{SO}_4$ solution (using a $0.4 \text{ C}/2$ discharge regime) before each measurement. Each measurement represents the data from one electrode. In each case, the reference electrode was an $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode in H_2SO_4 solution of the same concentration as the test. All potentials reported here are referred to this reference electrode. The solution concentration on the surface of the working electrodes was maintained constant during the experiment.

The counter electrodes comprised negative automotive-battery plates, with an area twice that of the positive plate. A plastic structure was used to maintain the electrodes in a rigid assembly. The discharge measurements were carried out using either galvanostatic or potentiostatic control, while the recharging was always conducted in the galvanostatic mode.

Results and discussion

Two types of discharge were carried out at different H_2SO_4 concentrations. The first was the normal galvanostatic discharge, using a current density of 15 mA cm^{-2} and a cut-off potential of 120 mV cathodic to the potential plateau of the discharge. This was considered to be the Q_D value for these conditions. As it is very difficult to normalize the Q_D values from electrode to electrode, since the values are related to the morphology of the plates, Fig. 1 presents the quantities measured directly.

The second discharge method was a potentiostatic procedure at a potential that was equal to the cut-off potential adopted above in the galvanostatic experiments. The total potentiostatic charge recorded to a constant value was taken as a measurement of Q_L and is given in Fig. 2. These results, which have not been normalized for the real area of each electrode, give virtually a constant value. This finding strongly supports the

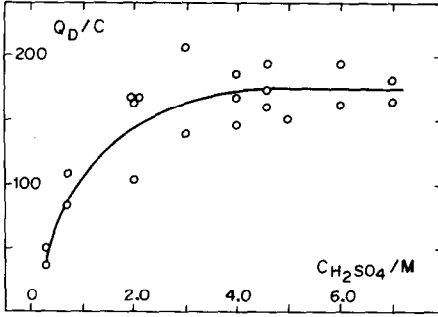


Fig. 1. Q_D values for pasted positive plates as a function of H_2SO_4 concentration. Discharge current density, 15 mA cm^{-2} . Each point corresponds to a different electrode.

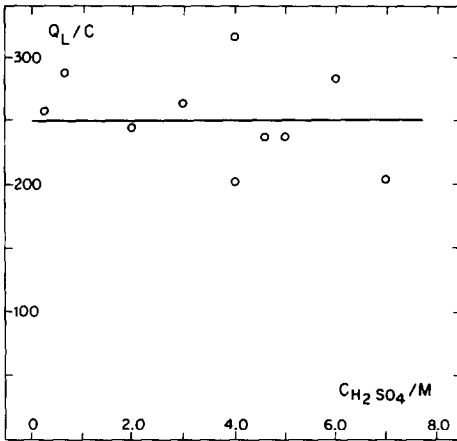


Fig. 2. Q_L values for pasted positive plates as a function of the H_2SO_4 concentration. Each point corresponds to a different electrode.

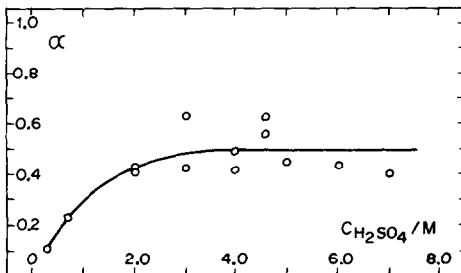


Fig. 3. α vs. H_2SO_4 concentration for a pasted positive plate.

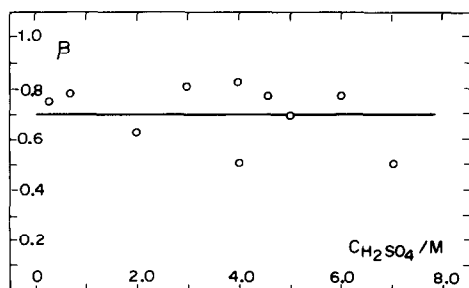


Fig. 4. β vs. H_2SO_4 concentration for a pasted positive plate.

idea of the proposed method, but at the same time it displays behaviour that is different from that reported by Asai *et al.* [3]. A possible interpretation must be that the results correspond to two different electrochemical methods (galvanostatic experiments were conducted by Asai *et al.*). It appears that the amount of $PbSO_4$ formed under potentiostatic conditions does not depend on the H_2SO_4 concentration.

Using Faraday's laws to determine the total possible amount of charge for each plate (Q_T), it was possible to calculate α and β (see Figs. 3 and 4). The values of α neither exhibit a maximum nor an increase at high concentrations. The absence of a maximum, due to the ionic specific resistivity minimum or to the reduction in the charge surface density in a galvanostatic discharge [3], must be associated with an area factor. In this respect, mercury porosimeter measurements on these plates show a porous structure with a lower radius at the surface than in the bulk. On the other hand, the value of β suggests that, in this type of automotive pasted positive plate, the structural part of the total amount of PbO_2 is only 30%. The important fact of this determination is that it is intimately related to the technology employed.

Conclusions

An electrochemical potentiostatic method has been proposed to measure the energetic material and, thereby, the energetic coefficient. The results obtained for an automotive pasted positive plate reveal that the energetic material constitutes practically 70% of the total PbO_2 . This is to be expected for batteries designed fundamentally to provide high power.

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