Relation between energetic and utilization coefficients in the positive plates of automotive lead/acid batteries

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Abstract

A new experimental method to distinguish between energetic and structural materials and to characterize the manufacturing technology for positive plates in lead/acid batteries is discussed. This new method proposes the evaluation of the energetic β-coefficient from plots of capacity versus very low current densities under galvanostatic conditions and using real-size positive plates in 2.3–6.9 M H_2SO_4 solutions. The results are identical to those obtained previously from potentiostatic measurements, and they fit a new equation as opposed to Peukert's equation. The independence of the β-coefficient with H_2SO_4 concentration indicates that the discharge of PbO_2 to its products proceeds via a solid-state reaction mechanism.

Keywords: Lead/acid batteries; Energetic coefficient; Automotive batteries; Positive plates; Utilization coefficient

1. Introduction

Due to its technological importance, the lead/acid battery has been the subject of a great number of publications (e.g., Refs. [1,2]). Moreover, a reasonable amount of these studies have attempted to understand the positive-plate charge/discharge mechanism as a chemical reaction. In spite of this, it appears that more work is required to achieve a clear picture.

Two fundamental descriptions have been proposed for the positive-plate charge/discharge mechanism [3]. One of them advances a dissolution–precipitation mechanism, and the other a solid-state mechanism with formation of an intermediate between PbO_2 and $PbSO_4$. The understanding of these reactions is complicated by the fact that, even now, there are discussions about what is the structure that best describes the morphology of the PbO_2 positive active mass (PAM). Views of the positive active mass range from a structure that consists of both agglomerates formed by crystals (α- or β-PbO_2) and gel zones of hydrated polymer-oxide chains (with proton and electron conductivity) [4] through to an electro-crystalline network as described by the agglomerate-of-spheres model [5,6]. On the other hand, the possible mechanism is complicated because the processes may be different for different discharge conditions (current density, sulfuric acid concentration, temperature, ratio of electrolyte/active mass, etc.).

It is interesting to note that the situation is even worse when attempts are made to analyze positive-plate capacity as a function of the discharge conditions and/or the production technology. General facts about the active-material utilization are known. For example, at high discharge current densities, the inner parts of the plates are not used. Further, at the end of a galvanostatic discharge, the process has to be controlled by a mass-transport mechanism but, even in this case, it appears to happen only at what has been called the crystal level, i.e., in the micropores (0.01 μm radius) and not in the macropores of the agglomerate level (0.1–0.6 μm radius) [7].

Nevertheless, there is a way by which these problems can be clarified if it is considered that, on the walls of the microporous structure, the process occurs via a solid-state reaction that gives rise to a transformation of the PbO_2 surface to the product of discharge. Then, the phenomenon becomes clear and the ideas developed for the kinetics of the passivating film [8] may possibly be applied to such porous electrodes, given a quantitative interpretation of the phenomenon. Of course, this hypothesis will create some problems in the way of its applications. One such problem, is the fact that it is becoming more and more clear that, during the discharge processes, the $PbSO_4$ is formed via an intermediate [9], e.g., hydrate PbO or $Pb(OH)_2$. A second problem will be to show that the film growth follows a field-

assisted mechanism. The high resistivity of the film at the end of a discharge causes the porous electrode to resemble a planar electrode. This is due to the fact that the radius of curvature of the PbO_2 surface in the micropores is higher than the film thickness (Å).

Such ideas have given rise to the proposition [10] of a method to distinguish, electrochemically, between so-called 'energetic' material (which can be used in discharges without affecting the cycle life) and 'structural' material (which imparts mechanical and electronic conductivity characteristics to the PAM). It is the structural material that, when it participates in the charge/discharge process, determines the final life of the PAM, provided the system goes to the end of the cycle life. As a result of this proposition [10], it has been possible to determine an energetic coefficient (β-coefficient) by conducting potentiostatic discharge measurements of the active mass. The corresponding limiting charge (Q_L) of a potentiostatic discharge is taken to define the energetic coefficient, namely $\beta = Q_L/Q_T$, where Q_T is the theoretical charge of the same electrode, if all the PbO_2 is discharged to $PbSO_4$. This coefficient is different from the normal mass utilization coefficient, $\alpha = Q_D/Q_T$, where Q_D is the charge of a galvanostatic discharge. Unlike the α-coefficient, the β-coefficient does not depend on the H_2SO_4 concentration [10].

To perform potentiostatic discharges in real battery systems presents some difficulties. Thus, in the work presented here, the same type of positive plates are used as in the previous work [10], and results, while equivalent to potentiostatic discharges, are obtained galvanostatically. This makes it possible to apply the β-coefficient concept practically to characterize a given battery technology. The basic idea is to conduct the galvanostatic discharges at very low rates and to extrapolate the results to zero current density of discharge. Such a method provides the equivalent charge (Q_L) of a potentiostatic discharge and does not depend on the H_2SO_4 concentration, as will be shown later.

2. Experimental

The galvanostatic discharges were performed on single and real positive plates (9 Ah each plate for $C/20$ discharge conditions, area = 280 cm^2/two sides, 1.9 mm thickness, average PAM weights = 73 ± 1 g, grid rod diameter 1.7 mm). Each plate was taken from an automotive 36 Ah battery/14 PLI AJAX made in the same production line as in Ref. [10]. The grid alloy composition was 3.2wt.%Sb–0.13wt.%Sn–0.10wt.%As and Cu < 0.01 wt.%.

A tribasic lead sulfate paste (density = 4.2 g cm^{-3}) was produced starting from a PbO powder with 27 wt.% Pb produced in a Shimadzu mill. To the powder was added 28 wt.% of water and 7.5 wt.% free H_2SO_4;

all weights and compositions are given with respect to the net PbO content in the original powder. These pastes were applied to the grids and placed in a flash-drying oven at a temperature of 240 °C for 15 s, as employed during the regular process of battery manufacturing. Soon after, the plates were cured for 72 h in a closed chamber that was maintained at a temperature of 40 °C and a humidity of 55%. The batteries were assembled and submitted to one-step container formation at a current density of 5 mA cm^{-2} (19 mA g^{-1}) in 1.05 g cm^{-3} H_2SO_4. Then, the formation solution was changed to a 1.31 g cm^{-3} H_2SO_4 to achieve the regular 1.26 g cm^{-3} H_2SO_4 electrolyte. Finally, the batteries were submitted to five deep ($C/10$) cycles of discharge (3.2 mA cm^{-2}; 12 mA g^{-1}) and charge (1.6 mA cm^{-2}; 6.2 mA g^{-1}, 30 h) to achieve stabilization.

Single positive plates were disconnected from the automotive batteries and assembled with a 0.7 mm separation between two negative plates, in order to keep the H_2SO_4 concentration constant during the experiments. The sulfuric acid concentration was changed from 2.3 to 6.9 M and the temperature was maintained at 25 °C. After each galvanostatic discharge, the positive plates, in different H_2SO_4 concentrations, were recharged at a constant current density of 1.6 mA cm^{-2} (6.2 mA g^{-1}) for 24 h. After that, they were kept at 2.3–2.33 V/cell for 48 h until starting the next discharging experiment.

The reference electrode was an $Hg/HgSO_4/H_2SO_4$ (4.6 M) to which all the potentials are referred.

3. Results and discussion

Typical galvanostatic discharge plots are shown in Figs. 1 and 2. (Note, in the literature, these kinds of results are usually shown for higher discharge conditions.) The data indicate a nucleation process at the beginning of discharge (which is well known for flat electrodes [11]), the normal plateau and, finally, the fast potential decay at the end of the discharge. This
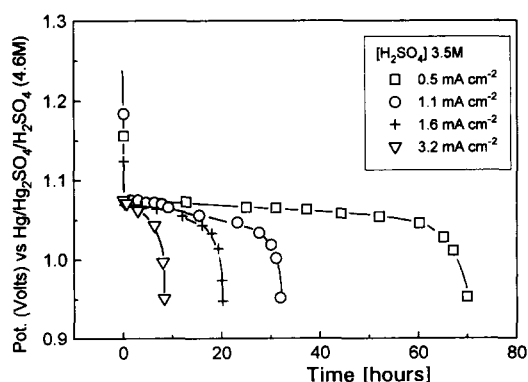

Fig. 1. Typical discharge plots for different low current densities in 3.5 M H_2SO_4 at 25 °C.
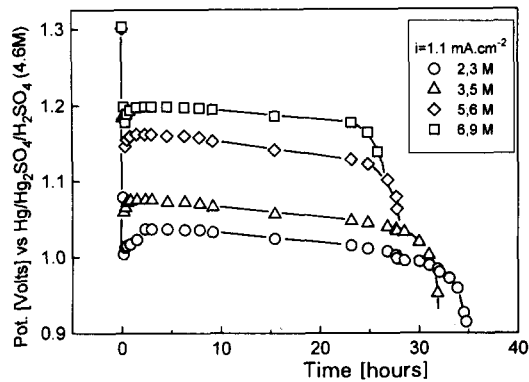
Fig. 2. Typical discharge plots for different H_2SO_4 concentrations at 25 °C. Discharge current density = 1.1 mA cm^{-2} (4.1 mA g^{-1}).
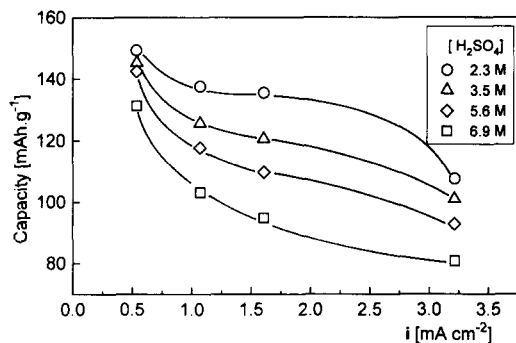

Fig. 3. Typical plots of capacity vs. discharge current density for different H_2SO_4 concentrations, from a very low to a low discharge condition.

decay is due to the fact that the electrode is looking for a new reaction as a result of the ageing of the first product of the PbO_2 discharge.

The general behaviour of the capacity as a function of the discharge current density for different sulfuric acid concentrations is given in Fig. 3. These results are given for very low discharge current densities, to show that the behaviour presents some differences when compared with the normal one. The time of discharge goes from approximately 10 to 60 h for the applied discharge current densities.

The first observation that must be emphasized is the fact that all the results appear to converge to the same value as the current density tends towards zero. This is important, because it points out a structural characteristic of the PAM that is independent of the discharge condition. This will be discussed later.

The second observation that must be emphasized is the fact that, at lower H_2SO_4 concentrations, the capacity curve (Fig. 3) changes its curvature as current densities are increased to higher values. This behaviour is evidently related to the diffusion of the H_2SO_4 inside of the pores and its influence can appear in different conditions for different battery-plate technologies. Since the aim is to find an intrinsic property of the PAM that depends only on its morphology, and then on its

production technology, this last region of the experimental results (namely, high current densities and low concentration) will not be considered in the following analysis.

Returning to the problem of the extrapolation: how to do it and, at the same time, how to understand the idea that only one capacity is obtained at zero current? To do this, several analyses of the data were attempted in order to find a linear behaviour. Typical straight lines were obtained for the representations of the logarithm of the capacity (log C) versus the current density (i). These are presented in Fig. 4.

From Fig. 4, it is clearly seen that Peukert's equation [12] is not applicable at very low discharge current densities. The following equation is valid:

$$\log C = mi + \log C_0 \qquad (1)$$

In this equation, m is a function of the sulfuric acid concentration. The constant C_0 is the capacity at zero discharge current density. This is independent of the sulfuric acid concentration and it characterizes the positive-plate manufacturing technology. The data of Fig. 4 also show that the different concentrations, taking into account the experimental errors, give a unique value of C_0. If it is considered that this value of C_0 corresponds to the maximum possible discharge without affecting the structure, this will be the Q_L charge. Then, given the theoretical total possible charge (Q_T) (i.e., that of the energetic material plus that obtained from the structural material), the energetic coefficient $\beta = Q_L/Q_T$ can be calculated. The dependence of this coefficient on the sulfuric acid concentration is presented in Fig. 5. The important point in Fig. 5 is not only that β is independent of H_2SO_4 concentration but the fact that this value of β corresponds to that obtained in a previous work by applying the potentiostatic discharge method [10]. All of this suggests that an intrinsic property of the positive plate is being examined.

Returning to Eq. (1), even if it is actually empirical, it must be related to the basic solid-state mechanism
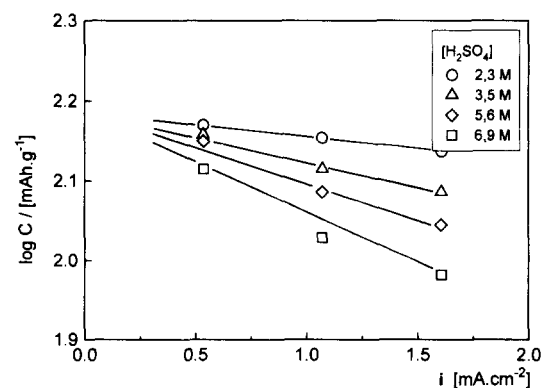

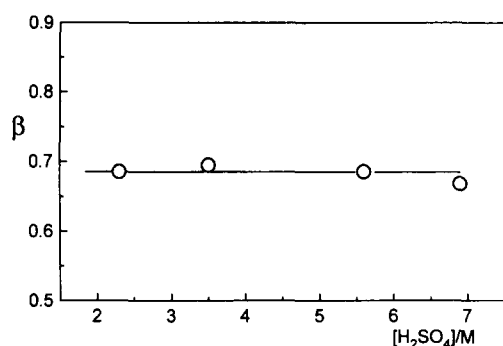Fig. 4. Typical results showing the linearity of log C vs. i for different H_2SO_4 concentrations.

Fig. 5. Energetic β-coefficient plotted vs. H_2SO_4 concentration for automotive-battery positive plates.

of discharge. In future theoretical work, an attempt will be made to understand this behaviour from a basic point of view. Surely, the deduction of such behaviour will contribute to a deeper understanding of the system. The first result from this work is to emphasize that the capacity at zero discharge current (C_0) could be representative of the real active surface of a positive plate. This, in turn, is one of the most important parameters of any manufacturing technology for positive plates.

4. Conclusions

Previous work has demonstrated the use of potentiostatic discharges to determine the amount of energetic material in the PbO_2 of a positive plate. Of course, this amount is dependent on the plate manufacturing technology. The impracticability of experiments by potentiostatic discharges in real-size plates has prompted the development of a galvanostatic method which gives the same results as those obtained from potentiostatic measurements. This is considered important because it is now possible to evaluate the energetic material in a normal factory laboratory and for real battery systems.

Also the research findings have shown that Peukert's equation is not effective for very low discharge conditions. For the latter, a new equation is proposed in which the logarithm of the capacity is a linear function of the discharge current density. This linear function allows determination of the energetic material in a real-size positive plate.

The new equation presented is expected, when deduced from theoretical work, to increase the understanding of the behaviour of positive plates.

Acknowledgement

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