

Positive tubular plates of the lead–acid battery General analysis of the discharge process

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Abstract

A general analysis of the discharge process in stationary positive tubular plates of lead–acid batteries is described. In the experimental part, the influence of the rate of discharge and the sulfuric acid concentration on the potential/time (E/t) discharge curves, the variation of specific capacity and the plate resistance during the discharge transient was studied. The potential/time curves show the general pattern. The capacity is related to the complete discharge process and the plate resistance to the conditions in the transient plateau region of the potential/time curves. On this basis, it is shown that the tubular positive discharge behavior can be interpreted with a zone reaction model involving three steps. The first corresponds to the solid-state reaction from PbO_2 to PbO , with passage of current; the second, when the current effectively moved to a deeper surface zone of the pore in the plate, to the chemical reaction between the PbO and H_2SO_4 giving fundamentally disrupted $PbSO_4$, and the third, to a recrystallization of the disrupted $PbSO_4$. With the help of this model, the effect of the depletion of H_2SO_4 in the macropores is also analyzed. All the results are interpreted on the basis of the model.

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1. Introduction

Most studies on the charge/discharge cycle of active material in lead–acid batteries have been based on pasted positive plates or flat electrodes. Publications on the mechanisms in tubular positive plates are rarer, even when, perhaps, they are equivalent to those in pasted electrodes. However, this is unreasonable, considering the well-known fact that tubular positive plates have longer life. The reasons for this longer life are not clearly established on an experimental basis and fundamental research is needed before an explanatory model can be attempted. The given explanation that the pressure exerted by the tubes on the active material is responsible, has not been scientifically demonstrated, although it is reasonably possible. Is this pressure enough to resolve problems like volume variation during discharge, material shedding and other phenomena affecting the cycle life, in this kind of plate? These problems have not been the object of specific published experimental studies of tubular plates. On the other hand,

research on tubular positive plates can contribute to the general understanding of charging/discharging phenomena and their cycle life. Hence, this paper is part of an effort to understand and built models of the behavior of positive and negative lead–acid battery plates, in general. To do this, it is necessary to have a model of the discharge process.

With the above considerations in mind, an overview of the discharge phenomenon is presented in this paper, using measurements of potential/time (E/t) curves, capacities and plate resistances, at various discharge rates and sulfuric acid concentrations. It is shown that the results can be interpreted on the basis of a zone reaction model with three successive steps. This model is a development of a previous one, based on experimental results which showed that the discharge must be considered as a zone reaction process [1].

In this new formulation of the model, the reaction zone moves from the surface of the plate active material in the direction of the spine. The three steps of the process consist of, a solid-state reaction under high fields and passage of current, followed by a solid-state reaction without passage of current and, finally, a recrystallization involving a dissolution/precipitation mechanism. These three successive steps happen at the surface of the pores and micropores of charged

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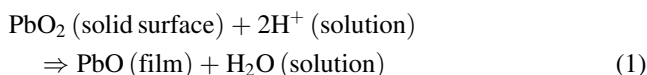
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active material, in the reaction zone. Of course, this qualitative model could be extended to pasted plates.

2. The model

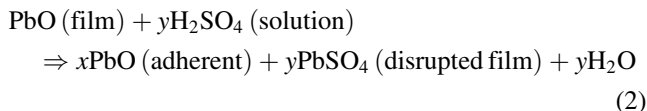
A zone reaction is a solid-state reaction that occurs in a zone of a given material and advances through it. Behind the reaction zone is the transformed region, while in front of it, there is untransformed material. It follows that in the reaction zone the reaction velocity passes through a maximum, and the position of this peak advances in the direction of unreacted material. Mechanism must exist that explains in physicochemical terms this maximum.

In the case of a tubular plate in a lead–acid battery (the idea can be extended to pasted plates), in the proposed model, the reaction zone advances on the surface of the pores into the inner part of the plate, from the plate surface to the spine. The mechanisms responsible for the reaction zone, and its advance toward the spine, are related to solid-state reactions happening on the surface of the pores and to the high conductivity of the PbO₂. First, the current arrives at a region of the pore surface where, owing to the passage of current through the PbO₂/solution interface, a PbO solid-state film grows on the PbO₂ surface, by the following reaction:



This is a solid-state reaction occurring under high fields, with the passage of ionic current through the PbO film. It is the produced film that obliges the current to move toward the spine (going more deeply within the pores in the active material), because the growth of the PbO passivates the PbO₂ surface. On the other hand, the field through the PbO, during its growth, causes the excess of O²⁻ in the PbO₂ to migrate to the solution and prevents ions like SO₄²⁻ from entering inside the growing PbO film, as this would be against the field.

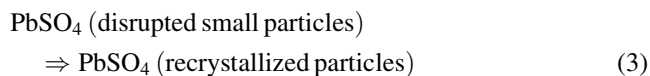
When the current moves to an inner pore surface, the disappearance of the field through the formed PbO means that a new solid-state reaction becomes possible at the initial pore surface region. The new reaction is the partial transformation of the PbO to PbSO₄. It occurs because now, without an electrical field, SO₄²⁻ can enter the PbO film, substituting the O²⁻ in a complex process. This reaction can be described by



with $x + y$ equal to one. The PbO adherent film is maintained because there is always a high field at any interface [2] and, thus, there is an electrostriction force stabilizing a very thin portion of the PbO film in contact with the PbO₂ phase

surface, inhibiting the reaction with the H₂SO₄. The disrupted PbSO₄ formed film is a result of the transformation of part of the PbO to PbSO₄; the latter has a higher partial volume than the former and has a low field through it, which means, a reduced electrostriction force. As a consequence, the disruptive forces become dominant.

Finally, PbSO₄ disrupted particles, due to their very small size, undergo dissolution and precipitation resulting in large particles. This reaction can be represented by



It is these disrupted recrystallized PbSO₄ particles which are normally seen in SEM measurements.

These three reactions occurs in succession at each region of the pore surface, constituting a zone reaction going from the plate surface to the spine, through all the pores, creating together a macroscopic reaction front.

3. Experimental

The galvanostatic discharges were performed on two kinds of tubular positive plate, obtained from stationary 6 V batteries (nominal capacity 25 Ah), with two negative and one positive plate per vessel and coming from two different manufacturers (plates E and F). From the original tubular plates of these batteries were cut seven-tube plates, withdrawing some of the tubes. The resulting plates had geometrical areas (both sides) of 150 and 160 cm² for plates E and F, respectively. The seven-tube plates had a tube inner diameters of 8.2 mm for plates E and 8.5 mm for plates F, with a spine diameter of 3.5 mm for both manufacturers, but with a tube height of 11 cm in plates E and 12 cm in plates F. The average amount of total positive active material in plates E was 157 g and in plates F, 167 g. The spine alloy compositions were, for plates E, 10.3 wt.% Sb, no Sn, < 0.01 wt.% Ca and 0.003 wt.% Ag and, for plates F, 8.9 wt.% Sb, 0.08 wt.% Sn, < 0.01 wt.% Ca and 0.001 wt.% Ag, corresponding in both cases to high-Sb lead alloys with Ag.

Both kinds of original plate, before being disassembled from the battery and cut, were submitted inside the original battery to five deep (C/20) cycles of discharge up to the cut-off voltage (1.75 V per cell). In all cases they were recharged first at 1.0 A for 30 h, followed by a floating period of at least 48 h, so as to be able to come to a minimum of 2.3 V per cell as the initial voltage of the open circuit. At this point a fresh discharge of the battery was started. These five cycles of charge/discharge were done to achieve stabilization.

The positive seven-tube plates were assembled tightly with 1 cm separation between two negative plates, in order to keep the H₂SO₄ concentration constant during the discharge experiments. The sulfuric acid concentration was varied from 2.0 to 6.0 M and the temperature was always maintained at 25 °C. The discharge current was varied from 0.25 to 1.8 A for each seven-tube plate, corresponding

approximately to a variation from $C/80$ to $C/5$. Each plate received a number to allow it to be identified through the experiments. Some of the measurements were repeated with the same plates after they had been working in other concentrations, to estimate the reproducibility of the measurements.

After each galvanostatic discharge at a given H_2SO_4 concentration, each positive seven-tube plate, in the same solution, was recharged at a constant current density of 1.0 A per plate during for about 80 h minimum, and then kept at 2.4 V per cell for 48 h minimum. This recharge corresponds approximately to the maximum amount of charge of discharge obtained at the lowest discharge rate (about $C/80$), multiplied by 1.5, for both kinds of plate. Only after completing this recharge was the H_2SO_4 solution changed and another recharge performed. This consists of about 1 day of stabilizing under a current of 1.0 A per seven-tube plate, followed by a period of floating at 2.4 V per cell up to the moment at which the anodic current was reduced to 0.150 A per seven-tube plate. During this procedure the new H_2SO_4 concentration was analytically monitored and corrected, as necessary. At this point, the new discharge experiment at the new concentration could be started, but before doing so, the instantaneous initial potentials of the cells were always measured to check that these values were higher than the reversible values, showing that the systems were overcharged. During the charge/discharge experiments no bending of positive tubular plates, nor any shedding of their active material, was ever observed.

By measuring the mass of portions of charged active material, both dry and wet, the average macroporosity of the active mass of each studied systems was determined. The active material of plates E had a macroporosity of 0.61 ± 0.02 and that of plates F, 0.52 ± 0.02 .

The reference electrode was in all cases $Hg/Hg_2SO_4/H_2SO_4$ (3.0 M) at all the H_2SO_4 concentrations used. All potentials are referred to this electrode.

4. Results and discussions

4.1. The potential/time curves

Typical galvanostatic discharge plots for the two kinds of positive seven-tube plates are shown in Fig. 1 for several i_g (galvanostatic discharge current densities, in mA/g of active material) and the same H_2SO_4 concentration (4.0 M). Comparing the set of curves, it is clear that the two plates are nearly equivalent.

An interesting point arising from these general E/t results is that all the transients show the “coup de fouet” at the start, which can be seen by enlarging the initial region of the transient. The analysis of these enlarged results shows that the coup de fouet is reduced with decreasing i_g . On the other hand, it disappears if the plate is not fully charged (for example, if it is kept at the free potential for some time). This points to a mechanism involving nucleation and coalescence of the nuclei. Nevertheless, any conclusion in this respect needs to be carefully thought out because, in this region, the charging currents are very important, due to the fact that the potential is changing drastically. This is perhaps the reason that, in this region, the transient does not follow a pattern which can be explained merely in terms of a nucleation and growth mechanism. Actually in this region, the experiments are not strictly galvanostatic, even if they are in the rest of the transient. This last remark relates to the fact that, in a zone reaction model, the distribution of current in the reaction zone is also not constant.

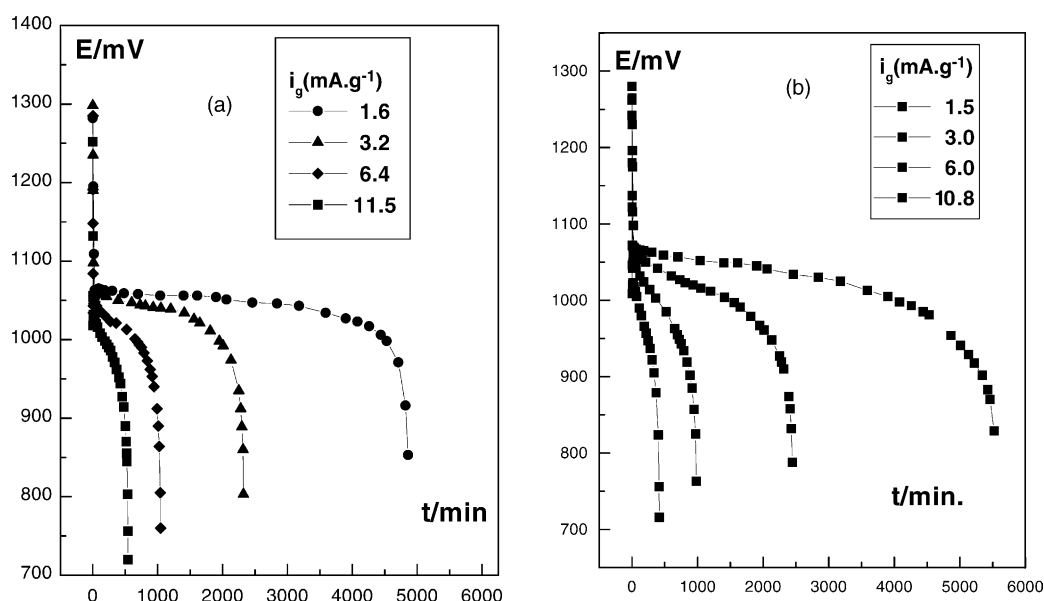


Fig. 1. Typical discharge plots for positive seven-tube plates at several current densities of discharge, in 4.0 M H_2SO_4 at 25 °C: (a) plates E, (b) plates F. Discharge current densities in mA/g of active mass are shown in each figure.

It is clear from the foregoing analysis that the initial transient region of the discharge needs to be more deeply analyzed from a theoretical and experimental point of view. However, this is a very complicated region, owing to the charging currents.

Returning to Fig. 1, it is necessary to understand in more detail the zone reaction region and the influence it has on the whole transient region. The idea of a reaction zone cannot be ignored, even if the model proposed in the present paper is not accepted. This follows from two observations. Firstly, in a previous paper [1], in which the current was arrested in two different ways during the discharge, in one case directly cutting the current and in the other, cutting it only after exchanging the H_2SO_4 solution for water, the amount of PbSO_4 formed was measured in each case, demonstrating unequivocally the existence of the reaction zone. Secondly, it is a well-known fact that, when the discharge rates are increased sufficiently, only the active material regions near the plate surface are discharged. Of course, this is explained traditionally by the depletion of the H_2SO_4 concentration under these high rate of discharge conditions. Nevertheless, if the reaction were happening through the whole plate, the reaction products would be found in all parts of the plate, even in these circumstances, and this is not the case. Thus, it must be accepted that in some sense the discharge reaction begins at the plate surface and then goes in the direction of the spine, in a manner that depends on discharge rate and H_2SO_4 concentration.

Finally, in relation with the end of the reaction zone, alternative conduction paths through the electrolyte solution (the H_2SO_4 solution) and through a high porosity conducting media (the PbO_2), with the solution in its pores, must be considered. It is to be expected that the current will seek a path through the high conducting media rather than through the solution in the pores. This will happen when there is no obstruction to the passage of the current from the solution to the solid phase, that means, as long as the PbO film has not grown too thick. This preference for the conduction through

the PbO_2 introduces the mechanisms that result in the end of the reaction zone giving rise to the PbO film.

In Figs. 2 and 3, there are typical plots of the discharge for each kind of positive tubular plate at various acid concentrations at very low and high current densities, respectively. In the case of very low rates of discharge (Fig. 2), it is observed that the capacity is practically independent of the H_2SO_4 concentration. The differences are within the experimental error (less than 10%) for both kinds of plate. This points to a solid-state reaction, in principle, without the participation of the H_2SO_4 . The controlling step is then the formation of the PbO film on the surface of the PbO_2 . On the other hand, at high rates of discharge (Fig. 3), the capacity (C) diminishes with decreasing H_2SO_4 concentration. This dependence of C on H_2SO_4 , at a high rate of discharge, demonstrates the importance of the H_2SO_4 depletion in the pores at high discharge rates, which is well known. However, this is not the only factor, as will be seen in the following. All these results can be better understood by representing C (in mAh/g of active material) as a function of i_g at different H_2SO_4 concentrations or, differently, by plotting C as a function of H_2SO_4 concentration at different i_g , as will be discussed in the next section.

4.2. The results seen at the end of the discharge processes

In Fig. 4, all the C values seem to tend to a single value for zero i_g . This is in agreement with a previously found result for pasted positive plates [3]. This shows that in the limit, at zero i_g , there is a maximum value for discharge which seems not to depend on the H_2SO_4 concentration. This value is 150 mAh/g for plates E and 170 mAh/g for plates F and corresponds to the maximum obtainable value without destroying the structure of the active material. These values are related to what can be called the energetic coefficient. On the other hand, it is clear in Fig. 4 that the effects of varying i_g are higher for plates F than for plates E (see that the fall of

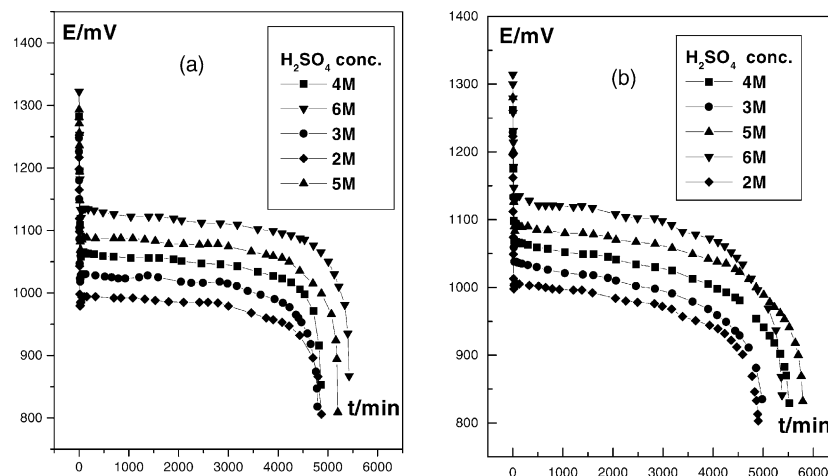


Fig. 2. Typical very low rate of discharge plots in different H_2SO_4 concentrations for the two kinds of positive tubular plates at 25 °C: (a) plates E, (b) plates F. Discharge current density in mA/g of active material (1.56 mA/g for plates E (a) and 1.5 mA/g for plates F (b)).

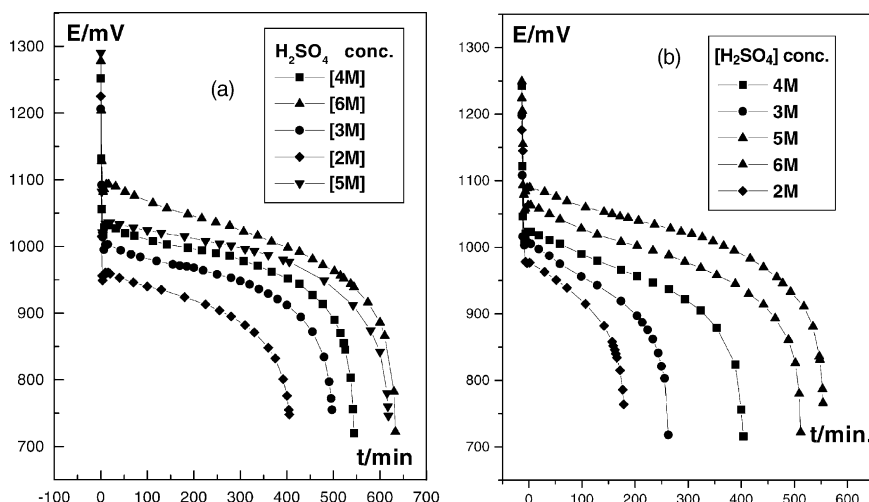


Fig. 3. Typical high rate of discharge plots in different H_2SO_4 concentrations for the two kinds of positive tubular plates at $25\text{ }^\circ\text{C}$: (a) plates E, (b) plates F. Discharge current density in mA/g of active material (11.5 mA/g (a) and 10.8 mA/g (b)).

C is higher for plates F than for plates E, comparatively). This is in agreement with the found porosities (0.52 for plates F and 0.61 for plates E), perhaps pointing to H_2SO_4 depletion problems but at the same time suggesting the need to take into account the kinetic characteristics of Eq. (1), from the point of view of the present model.

At low discharge rates, which allow time for H_2SO_4 diffusion up to the reaction zone, as explained in a previous paper [1], the decrease of the thickness of the PbO layer with the increase of i_g can be related to the increase of the number of nuclei of PbO . This is because PbO formation on PbO_2 implies the formation of a new phase and, therefore, a nucleation and growth mechanism. This has been proved experimentally in unpublished results [4] on flat PbO_2 deposited electrodes on Pt. On the other hand, even at low growth rates, it is known that in passivation transients [2], when i_g is increased, there is a reduction in the amount of

film needed for passivation. This is because a rise in i_g implies an increased rate of injection of point defects in the growing film under transient conditions and, therefore, an increase of the rate at which the point defects recombine. As a consequence, the thickness of the film required for passivation to occur is less because the film aging (the defect recombination) arrives early.

At high rate of discharge, in addition to these phenomena, the reduction of C with rising i_g becomes influenced, and even controlled, by the depletion of H_2SO_4 inside the pores, when the diffusion of H_2SO_4 from the external solution cannot maintain the necessary concentrations in the reaction zone. This phenomenon produces a reduction of the discharge reaction depth measured from the plate surface of the used active material.

As a consequence, the decrease of C with i_g in Fig. 4 can be influenced by several factors, sometimes hard to separate.

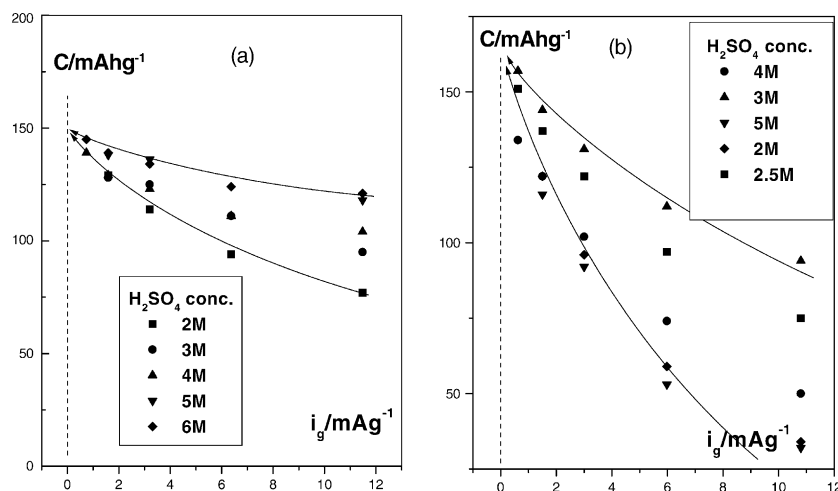


Fig. 4. Capacity (in mAh/g of active material) vs. discharge current density (in mA/g of active material), at $25\text{ }^\circ\text{C}$ and at different H_2SO_4 concentrations: (a) plates E, (b) plates F.

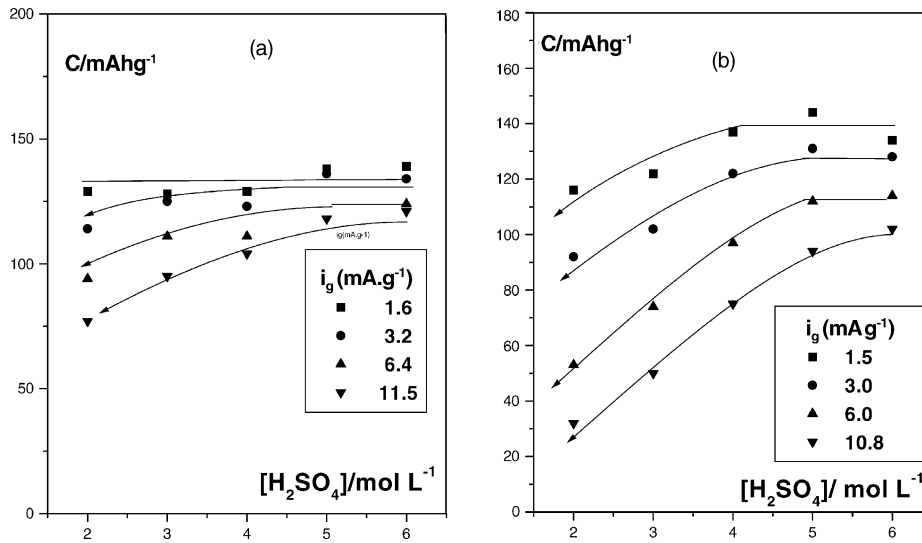


Fig. 5. Capacity (in mA.h/g of active material) vs. sulfuric acid concentration, at 25 °C, at different discharge current densities (in mA/g of active material): (a) plates E, (b) plates F.

First, the nucleation and growth of PbO; second, the characteristics of passivity transients regarding the growth of PbO layers on PbO₂ and third the H₂SO₄ depletion phenomenon. It is seen then that the decrease of C with increasing i_g is not a simple process and results from two different mechanisms at low rates of discharge and three at high ones. This makes it interesting to look at these same results from another point of view.

In Fig. 5, the results of Fig. 4 are presented from this other point of view. Here, it is possible to see clearly that, at high H₂SO₄ concentrations, the C values are practically independent of the H₂SO₄ concentrations, indicating a solid-state reaction without participation of the H₂SO₄ (Eq. (1)). Nevertheless, these constant C values, independent of H₂SO₄ concentration in this region, do depend on the corresponding i_g value. This dependence on i_g is related, as shown in the analysis above, not only to the nucleation and growth of the PbO layer, the first step of the reaction process given by Eq. (1) [1], but also to the general phenomenon of passivity related with the growth of continuous passivating films, in this case of PbO.

On the other hand, in Fig. 5, at low H₂SO₄ concentrations, C is seen to be independent of the H₂SO₄ concentration only at very low i_g , a condition that allows enough time for the diffusion of the H₂SO₄, inhibiting the reduction of the reaction area.

Finally, in Fig. 5 at low concentrations and relatively high i_g , the C values are dependent on the three mechanisms, the nucleation and coalescence of the PbO nuclei, the general passivity behavior of the growing PbO film and the depletion of H₂SO₄.

All these facts seem to agree with the proposed reaction model for the discharge, described in Eq. (1). The problem is that, once the amount of PbO formed on a given surface region of a pore is defined, so is the amount of PbO available

to participate in the reactions corresponding to Eq. (2) and the amount of PbSO₄ that can participate in Eq. (3), though these last two also depend on the ratio x/y , which is in general very small. This is because the remaining PbO passivating film cannot be thick, to be submitted to the interfacial high field. It only needed to inhibit the ionic passage of current and this can happen through a high ionic resistivity of the film, which may have only some mono-layers of thickness.

4.3. The results seen during the discharge transient, at the plateau

As pointed out earlier, it is important not only to study the capacity, that is, the results at the end of the discharge, but also to try to found out whether the model of a reaction zone moving from the surface of the plate to its interior, can explain the results at the plateau of the discharge. In a previous paper, this was achieved in a study of negative plates [5] by determining the resistance of the plates (R_p) at a given quantity of discharge. The resistance of a plate for this purpose must be defined as

$$R_p = \left(\frac{\partial E}{\partial i_g} \right)_{Q_d} \quad (4)$$

where E is the electrode potential of the plate with respect to the reference electrode and Q_d is a given quantity of discharge, both in the plateau region of the discharge. In the zone reaction model a given Q_d is equivalent to looking at a particular zone of the plate. If i_g is given in mA/g then the R_p will be obtained in Ω g.

If the three-step zone reaction model used in the previous section is consistent with the data, as in the case of the negative plates, plotting E versus i_g must give a straight line with the same slope for all the H₂SO₄ concentrations. To

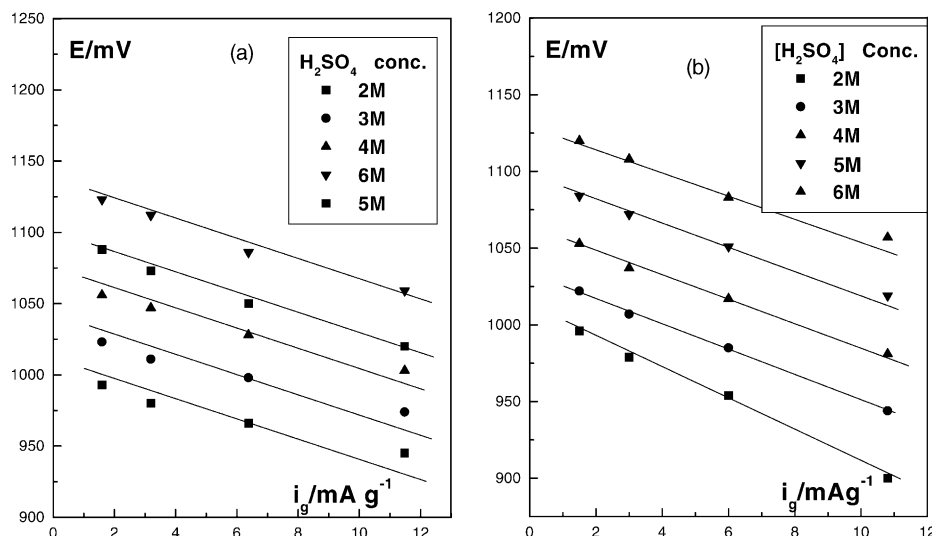


Fig. 6. Potential of the positive tubular plates (vs. the reference electrode) vs. discharge current density (in mA/g of active material) for a quantity of discharge of 15.0 kC at 25 °C, in the plateau region and at the different H_2SO_4 concentrations: (a) plates E, (b) plates F.

obtain these results, E must be taken in the plateau region for a given Q_d . Typical data of this kind can be seen in Fig. 6 for both kinds of plates studied. It is seen that in both systems, the plots are linear, giving a constant R_p of $5.5 \pm 0.5 \Omega g$ for plates E and a higher value of 7.0 ± 0.5 for plates F, at all H_2SO_4 concentrations, excepting 2.0 M, at which the slope gives $10.0 \Omega g$, for these last plates. The difference between 5.5 and $7.0 \Omega g$ is in agreement with the respective porosities of the two kinds of plates (0.61 for E and 0.52 for F). This is because it is the porosity that determines, in some average way, the relation between total current density and the potential inside the pores, in the reaction zone. It is incorrect to explain this through the H_2SO_4 depletion, because this does not exist at the higher concentrations, even at the end of the discharge process, and the E/i_g slopes are the same for

low and high H_2SO_4 concentrations. Instead of that, this shows the importance of the porosity which controls the conditions under which the reactions at the reaction zone happen, perhaps by controlling the surface area of the reaction zone. This question will need to be studied more deeply.

Regarding the result of $10.0 \Omega g$ for the low concentration of 2.0 M in the case of the F plates, it is possible that a large ohmic drop occurs in the pore solution giving rise to this increase of the plate resistance. Once again, it cannot be attributed to H_2SO_4 depletion, as this would vary with i_g , and not give a straight line.

Finally, it is important to point out that, as reported previously for negative plates [5], so in the present case of positive tubular plates, if the data in Fig. 6 are redrawn,

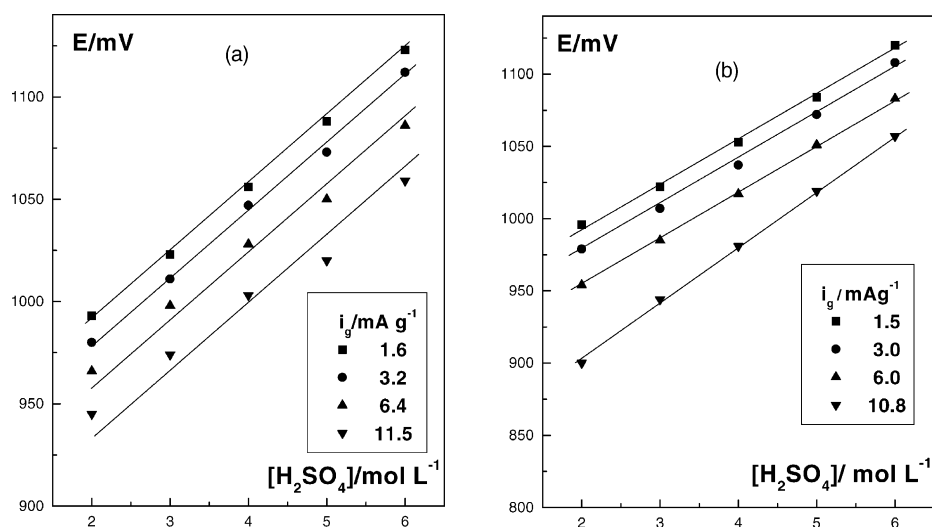


Fig. 7. Potential of the positive tubular plates vs. H_2SO_4 concentration for a quantity of discharge level of 15.0 kC, at 25 °C, in the plateau region and at the different discharge current densities: (a) plates E, (b) plates F.

plotting E versus H_2SO_4 concentration at constant i_g , this also gives straight lines. In this case, the plots give positive slopes (in the negative case [5] they give, of course, negative slopes), as can be seen in Fig. 7. From the point of view of the new model this is due to the fact that at constant Q_d the reaction area seen is always the same and, for a given i_g , the system is at a constant overpotential. Consequently, as the reversible potential changes linearly with the H_2SO_4 concentration [6], the measured potential at Q_d must also change linearly if the reaction is in the linear part of the Tafel region. This observation adds another point to the overall interpretation made so far, showing that for the discharge conditions under study the current densities are very low in comparison with the exchange current density of the processes.

Finally, in the case of Fig. 7b, for the same reasons as in Fig. 6b, the curve at 2.0 M for plates F shows another time differentiated slope maintaining the linearity.

5. Conclusions

A general qualitative zone reaction model with three reaction steps is proposed to describe the whole discharge process in positive plates of lead–acid batteries. Several kinds of results are analyzed, and it is shown that all of them can be interpreted from the point of view of the model.

The analysis points to the presence of a first solid-state reaction, assisted by a field, with the passage of current and without participation of H_2SO_4 . More explicitly, this first reaction with the passage of the current corresponds to the transformation of PbO_2 to PbO on the surface of the PbO_2 , creating a passivating film which forces the current to look for inner pore surfaces.

This reaction is followed by another chemical solid-state reaction of the formed PbO with H_2SO_4 , the other reactant. This second step happens when the current has moved on from the region in question to inner ones, due to the passivating process related to the formation of the PbO . When the field through this PbO has been effectively reduced by the removal of the current, permitting the penetration of SO_4^{2-} ions into the PbO , the reaction of PbO with H_2SO_4 can take place. Given the difference between the partial molar volumes of the PbO and PbSO_4 ,

and taking into account the disappearance of the field that may stabilize the whole PbO formed films in the presence of the H_2SO_4 , it is suggested that the reaction between these two reactants gives rise partially to a thin passivating film of PbO but, at the same time, to a disrupted PbSO_4 film, possibly present in the form of nanometric particles. The thin PbO film of a few monolayers, covering and protecting the rest of the PbO_2 , is stabilized by the presence of the field which always exists at any interface.

Finally, this process is completed by the recrystallization of the disrupted PbSO_4 film, giving rise to the well-known PbSO_4 microscopic particles, under which it is assumed that the thin PbO film continues to exist.

Each one of these steps are occurring successively on the surface of the pores of the active material in the reaction zone which moves from the surface of the plate to the pores and micropores, deeper within the active material.

On the other hand, as in the traditionally held view, it is assumed that when there is a reduction of the H_2SO_4 concentration inside the macropores, due to high rates of discharge and low external H_2SO_4 concentrations, this depletion of sulfuric acid hinders the advance of the reaction zone into the active material. This produces a reduction of the depth of the discharge region and, consequently, a reduction of the plate capacity. The results show that this cannot happen at low discharge current rates, or even at high ones, when the H_2SO_4 concentration is high enough, even when the discharge reaches its end. In this case the end comes when the whole inner surface has been passivated by the thin PbO film covered, of course, by the well-known layers of PbSO_4 crystals.

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