

A practical method to follow the evolution of electrochemically active areas during plate formation processes in lead acid batteries

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Abstract

A new method to follow the evolution of the plates of a battery during the formation processes is proposed and developed. The developed methodology can be used not only in research but also in the factory laboratories due to its simplicity. To exemplify the methodology, results for formation processes of tubular plates are presented using as precursor PbO or Pb₃O₄. The methodology gives access to the evolution, during its formation process, of the portions of the active material available for the discharge processes, the so called electrochemically active area. At the same time, the proposed technique permits the determination of the whole amount of PbO₂ during formation. Through the results it is pointed out what experimental conditions must be used during the application of the method and examples are given of the kinds of interpretation that can be made. Finally, information is presented which was deduced from the results presented. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

One of the most important processes in the manufacturing of lead acid battery plates is the formation process. The following of a formation process by Hg porosimeter, SEM or BET [1], or even by chemical analysis, presents theoretical and/or practical limitations. Practically, because they allow the analysis only with the use of special equipment. As a consequence, these are methods which present serious difficulties for use in a factory. Theoretically, because of the use of Hg porosimeter, SEM or BET, the analysis always represents an observation of a small portion of the active material which cannot be necessarily representative of all the plate.

If it would be possible to develop a practical method to evaluate the whole of the plate during the formation process, with the possibility to be applied in the factory, a very important aspect of the technology will become easily accessible to manufacturers and even, to researchers. This is the fundamental objective of the present paper. As an example, the formation processes of tubular positive plates were studied.

2. Experimental and method

The tubular plates used for the development of the method were made from PbO and/or Pb₃O₄ powder precursors. The powders had 4.0 and 2.2 μm as average diameters, respectively. The amounts of precursor in the plates were carefully controlled. Formation current densities (i_f), discharge current density (i_d) and specific discharge capacity (C) are given per unit mass of original precursor. Here, there is a complicated problem because, during formation, part of the material continues to be present as precursor while part has been transformed into intermediates and PbO₂. Especially in relation to formation and discharge current densities, the problem is even more complex. This is because an electrode during formation or discharge processes must be considered as a multiple electrode with current going fundamentally to the reaction region [2].

The electrochemical cell used as well as the dimensions of the tubular electrodes used are presented in Fig. 1. The precursor and/or the active materials were confined within a tube of 8 mm inner radius and a spine of 3 mm, with a height for the material volume of 40 mm. The reference electrode was a Hg/Hg₂SO₄, H₂SO₄ of the same concentration as the working solution.

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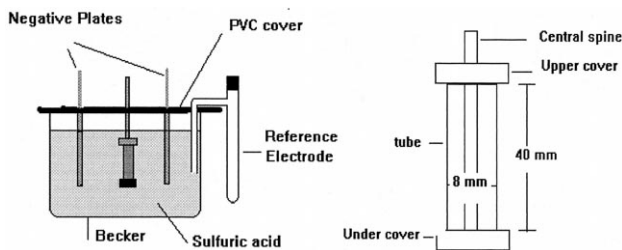


Fig. 1. Electrochemical cell and dimensions of the tubular plate electrodes.

The concentrations of the H_2SO_4 to be used must be carefully chosen. It is important to develop a method so that the end of any discharge becomes controlled by a solid state reaction mechanism and not by the depletion of the sulfuric acid inside the pores of the plate. From this point of view, it is fundamental to have a high H_2SO_4 concentration during the discharge. On the other hand, the formation, in general, is accomplished under a low H_2SO_4 concentration. This means that it is a necessity, if we like to make discharges under solid state control during the formation process, to change from the formation solution with low concentration to a high concentrated solution for the discharge experiments. In the present paper, for simplicity, 4.6 M H_2SO_4 was always used, for formation and discharge, without needing to change the H_2SO_4 solution when the partially formed plates were discharged. On the other hand, taking into account that the discharge must become controlled by a solid state reaction at its end, discharge was made at a slow a rate as possible. The reason for this will be analyzed more deeply later.

To follow the evolution of the whole amount of PbO_2 formed during the formation process, a simple chemical analysis method was developed. For a given stage during formation, the analysis was made by dissolution of the plate material in a HCl solution. The PbO_2 was then reduced with an excess of As_2O_3 present in this same solution. The excess of As_2O_3 was then titrated with KMnO_4 using KI as indicator. The PbO_2 content of these results is given as a percentage of the maximum attainable amount of PbO_2 , considering the case of all the precursor having been transformed.

The evolution of the plate specific capacity was followed during the formation process, for different stages of formation. This plate capacity will be called specific capacity under formation (C_{uf}) and, in general, for low discharge rates, it will be a function of the formation time. The determination of this capacity for the used tubular plates must be done, for each time of formation, at a very low discharge rate (that means low discharge current density). This is necessary in order to be out of the control of H_2SO_4 diffusion, at the end of each discharge process. The idea is that under this condition the specific capacity under formation will be related to the electrochemically active area of the formed material because the discharge

will occur on all of the PbO_2 surface. Here there is a compromise between the discharge rate and the times needed for the discharge. The best will be to use times of discharge as long as possible (40 h or more) but they can become non practical. In each factory and for each kind of plate production it will be interesting to do a study to determine the convenient discharge current and then, the most convenient discharge rate. Nevertheless, it is always possible to use the data from a comparative point of view. Taking into account these facts, in the present paper a rate of discharges higher than 20 h was used. Comparisons were always possible because the plate geometry, as well as the discharge currents (I_d), were always the same, except when they are explicitly pointed out as different.

It can be seen in Fig. 2 the typical potential (E)/charge passed in discharge (Q_d) = $I_d \times t$ (time of discharge) curves at practically the end of the formation process for the two precursor materials used. For the case of PbO , experiments are presented for two different amounts of precursor, but always for the same tubular plate geometry (seen in Fig. 1). It is important to point out that the interpretations which will be developed for this figure are in agreement with those obtained from all the analyzed E/Q_d experiments during the present work. The results of Fig. 2 are only given as examples.

The curves of Fig. 2 related to PbO as precursor have been obtained always with the same I_d and the differences can be analyzed comparatively as follows. Curves 1 and 2 must be explained on the basis of the different amounts of original PbO used (5.33 g for curve 1 and 4.33 g for curve 2). This difference produces different degrees of polarization, gives rise to different electrochemically active areas (proportional to 3050 C and 2500 C, respectively) and, at the same time, to practically the same capacities per unit mass of precursor (159 and 160 mA h/g, respectively). This increase of charge passed in discharge shows that for the rate of discharge used, at the end of the discharge, the

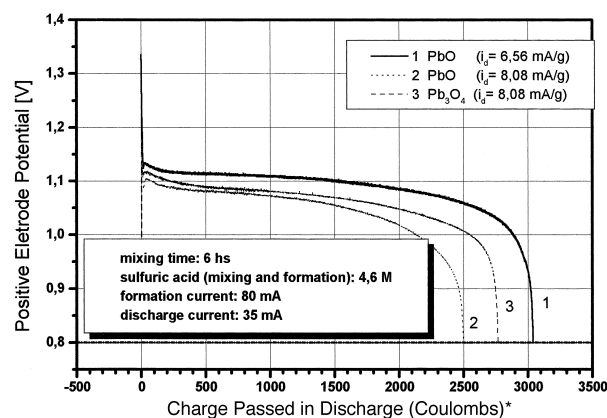


Fig. 2. Typical curves of potential versus charge passed in discharge ($Q_d = I_d \times t$, time of discharge) for tubular plates at the end of the formation process. Low discharge rate ($I_d = 35$ mA). Dimensions of the tubular plate: see Fig. 1. Other data have been given directly or indirectly in the figure. Reference electrode: $\text{Hg}/\text{Hg}_2\text{SO}_4$, 4.6 M H_2SO_4 .

Table 1
Collection of relevant data from Fig. 2

Precursor	Curve number	Plate geometry	Precursor mass, g	Q_d , C	I_d , mA	C, mA h/g
100% PbO	1	see Fig. 1	5.33	3050	35	572
100% PbO	2	see Fig. 1	4.33	2500	35	577
100% Pb ₃ O ₄	3	see Fig. 1	4.33	2780	35	642

process is controlled by a solid state reaction mechanism and not by a H₂SO₄ mass transfer because the porosity, for the case of curve 1, must be smaller.

On the other hand, comparing the curves with PbO and Pb₃O₄ as precursors (curves 2 and 3, respectively) with the same amount of original precursor (4.33 g) and, as a consequence, with little difference in the amount of PbO₂ at the end of the formation processes (4.63 g for the PbO and 4.54 g for the Pb₃O₄), the curves also show different electrode polarizations during the discharge, lower electrochemical active area for the plate produced from the PbO than that produced from Pb₃O₄ (proportional to 2500 and 2780 C, respectively) and lower capacity per unit of mass precursors for the PbO precursor (160 mA h/g for the original PbO plate and 178 mA h/g for the Pb₃O₄). This increase of specific capacity for the plate from the Pb₃O₄ precursor is related with its lower original particle diameter giving rise to a higher area. It is important to call attention to this because from a theoretical point of view, the PbO₂ formed directly from the Pb₃O₄ must have a lower specific area than that of the PbO. This is because in the latter case, it can pass through a PbSO₄ intermediate.

Finally, it is also important to point out that the higher capacity obtained for the Pb₃O₄ than for the PbO is maintained when the specific capacity is expressed as mA h per gram of the final obtained PbO₂ (170 and 150 mA h/g, respectively). For the proposed method, the important point is the idea that, under the same discharge current (I_d) and the same plate geometry, the specific capacity per unit mass and the electrochemically active area seems to be proportional and the capacity per gram under these conditions represents the electrochemically active surface area. On the other hand, the high specific capacities per gram of PbO₂ obtained in the present work for all the plates, at the end of the formation process, are due to the fact that the formation was made under a high H₂SO₄ concentration condition. As a consequence, there was a high level of sulfation and then, a high amount of PbO₂ coming from the precursor through the PbSO₄ intermediate. This is another theoretically important aspect of the results.

Perhaps the most realistic way for the analysis of the evolution of the electrochemically active area during formation to proceed, is to use the charge passed in discharge for a given discharge current and plate geometry. Nevertheless, the use of the specific capacity per unit mass to analyze the electrode electrochemically active area makes possible some kind of comparison of the data from a

practical point of view. To show this, it given in Table 1 all the important data related with the curves of Fig. 2 in a comparative way.

3. Results and discussions

It can be seen in Fig. 3 the evolution of the PbO₂ content as a function of time of formation (t) for two different formation current densities and 100% PbO precursor. For one of the cases, the mixing time has been changed. In this figure, the corresponding line for the cases in which the current efficiency would be 100% have also been plotted.

Three points must be emphasized from this figure. Firstly, the efficiency of the process is very low even at the beginning of the formation process, due to the oxygen evolution as a parallel reaction. Secondly, at the end of the formation process, as the result of the fact that in several parts of the plate surface PbO₂ appears, the formation process becomes even slower. This is because the lines of current density, at this formation stage, go directly to these patches of PbO₂ and not to the remainder of precursor, which continues to need to be transformed. This is the reason why at the end of every formation process, some unformed amount of precursor always remain, if the formation time is maintained within its normal value. Finally, the increase of the formation current density does not mean any increase in the formation velocity. This is because after the beginning of formation, the whole current is expended on the oxygen evolution.

Now, when the PbO₂ content is determined for different times of formation, Fig. 4 is obtained for the case of 100% PbO precursor. It is clear that even after 400 h under the formation condition used, the plates are formed up to only 90%. In this sense it will be interesting to compare this

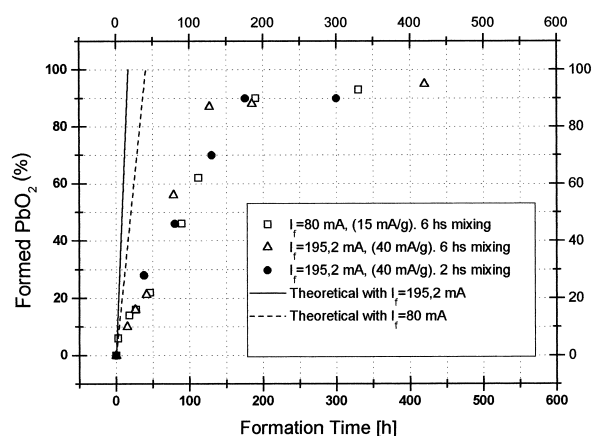


Fig. 3. PbO₂ content versus formation for two different formation current densities. Precursor 100% of PbO. Mixing time 6 and 2 h. H₂SO₄ forming solution used: 4.6 M. Formation currents pointed out in the figure. The theoretical results, for 100% current efficiencies, have also been plotted as continuous and dashed curves.

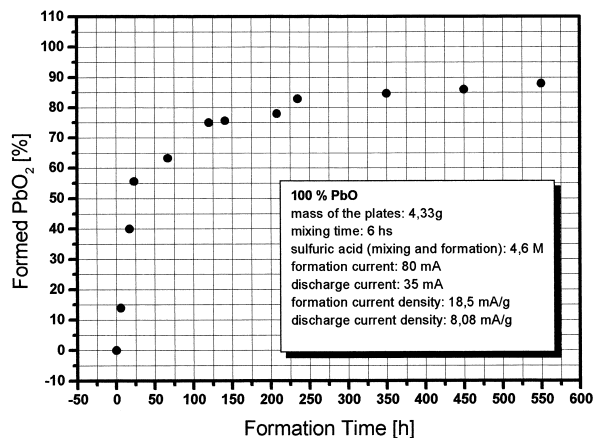


Fig. 4. PbO_2 content versus formation time for 100% PbO precursor. All the other data are given in the figure.

result with those obtained from a precursor formed by 100% Pb_3O_4 (Fig. 8). The important point of Fig. 4 is that, even to arrive to only 90% of formation, the PbO needs longer times than for the case of Pb_3O_4 . The time value obtained for this process will depend on the formation conditions but, the Pb_3O_4 will be always faster (compare Fig. 4 with Fig. 8).

In Fig. 5, for the same plates as Fig. 4, the measured specific capacities are presented as a function of the formation time. It is seen that this kind of representation does not permit to detect clearly any special aspect of the evolution of the electrochemically active area.

In Fig. 6, finally the joint results of Figs. 4 and 5 are presented. This figure constitutes the proposed method for the analysis of the evolution of the electrochemically active area during the formation process. The idea is that the evolution of the specific capacity as a function of the produced PbO_2 , for each given formation time, is a representation of the evolution of the electrochemically active area versus the evolution of the whole amount of formed PbO_2 . This representation permits us to follow when the transformation to PbO_2 is going through the precursor

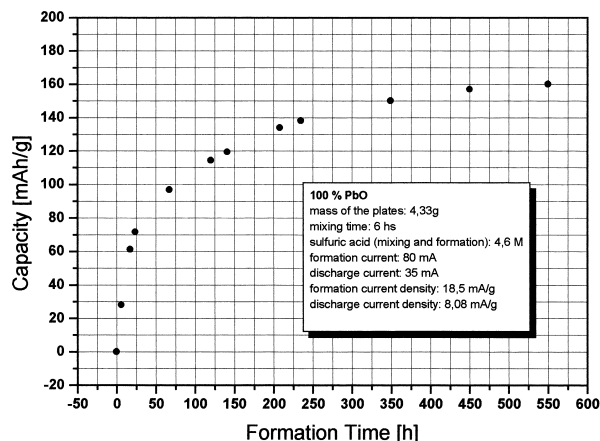


Fig. 5. Capacity versus formation time for 100% PbO precursor. Data from the same plates of Fig. 4. Other data given in the figure.

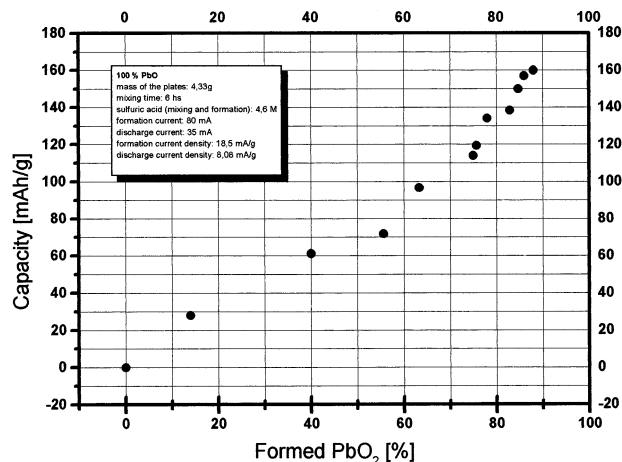


Fig. 6. Capacity versus PbO_2 content for different formation times for 100% PbO precursor. Data obtained from Figs. 4 and 5.

particle surfaces or when it is going through its bulk, considering the material in transformation some kind of “kugelhafen model” [3]. For the present case it is clear that at the beginning there is an increase of both kinds of transformation but after some time (when the PbO_2 content arrives on about 30% to 40%), the transformation to PbO_2 continues to grow through the bulk of the material but not through the surface. The increase of surface electrochemically active area stops. At about 60% of formed PbO_2 , the electrochemically active area begins to increase again. It seems that the last fast increase is clearly pointing out the transformation of materials which have suffered a high level of sulfation. As will be seen, all these aspects are always present in the other cases analyzed. The plateau obtained for the specific capacity under formation (a plateau in the electrochemical active area) is perhaps related to the fact that the oxidation of PbSO_4 to PbO_2 always happens at higher potentials than the other precursors or intermediates and that there is an evolution of the sulfuric concentration inside the reaction zone. This is why it is necessary

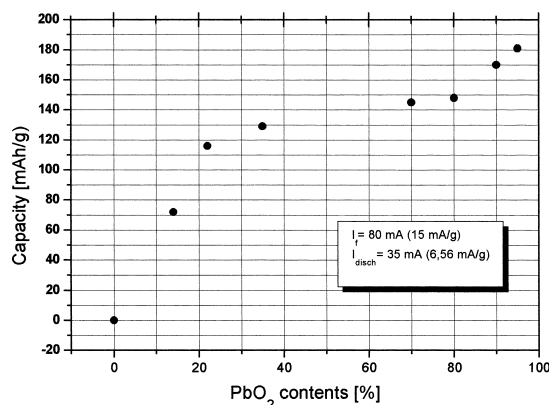


Fig. 7. Capacity versus PbO_2 content for different formation times for 100% PbO precursor. Amount of original PbO : 5.33 g. The amount of original PbO for plates of Fig. 6 was 4.33 g for the same plate geometry.

not to forget that all these processes are related with a reaction zone in order to understand this kind of hypothesis.

To show that the data for the foregoing analysis is representative, equivalent results to those of Fig. 6 has been plotted in Fig. 7, only a 5.33 g PbO was used, instead of 4.33 g, as original precursor. It is seen that the arrest of the increase of the electrochemically active area at about 30–40% occur at a different time. The fact that the arrest in the increase of the capacity gives a higher value (about 140 mA h/g for Fig. 7 against about 70 mA h/g for Fig. 6) is consistent with the argument previously pointed that the increase in the amount of material for the same plate geometry, and the same volume, means an increase of material per unit volume and then, an increase of electrochemically active area per unit volume. This happens even when the quantities found are showing also another kind of phenomenon due to the passage from 70 to 140 mA h/g, when the mass increases only by about 25%. This data also shows that there is no mass transfer control at the end of the discharge process.

Finally, to show the possibilities of the proposed method, in Figs. 8–10 are plotted the equivalent results to those of 100% PbO previously analyzed, when the precursor is 100% Pb₃O₄. The data presented is also for the same amount of precursor original mass (4.33 g) and plate geometry. These figures can then be compared with Figs. 4–6. It is then clearly seen that the problem of the residual precursor at the end of the normal formation times (Fig. 8) is not related to the kind of precursor because it is always present. This is a demonstration that it is related with the patches of PbO₂ which appear at the end of the formation process on the surface of the plates and which concentrate practically all the formation current. This is also the reason why when the plate is submitted to several discharge/charge cycles, the completion of formation process is more easily obtained.

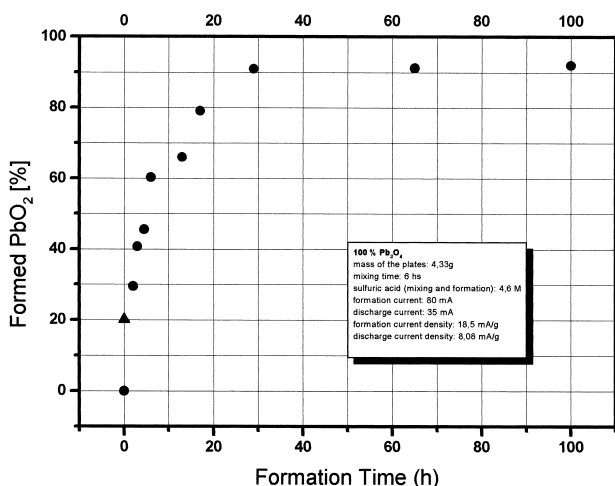


Fig. 8. PbO₂ content versus formation time plot for 100% PbO precursor. All the other data are given in the figure.

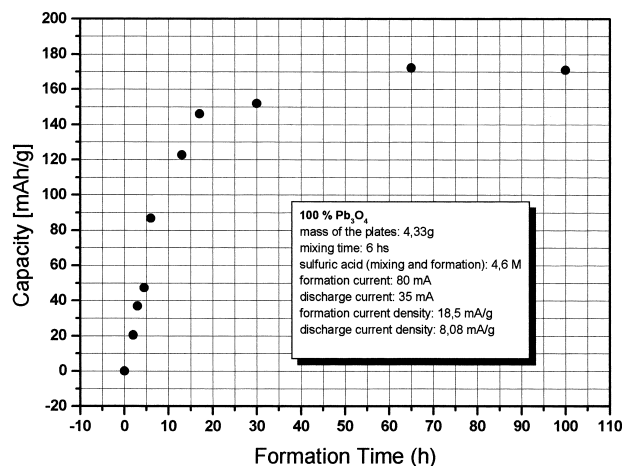


Fig. 9. Capacity versus formation time for 100% Pb₃O₄ precursor.

A second point previously pointed out, but which must be emphasized here, is the clear demonstration of the known fact that the total formation time for a 100% Pb₃O₄ precursor is drastically reduced.

Finally, the most important point for the demonstration of the possibilities of the proposed method comes from the analysis of Fig. 10. This figure is characterized by a rapid increase of the PbO₂ content when there is a small increase of the specific capacity and then, of the electrochemically active area. This is a very important point because at the same time it demonstrates that the reaction from Pb₃O₄ goes first to PbO₂ and PbO, and even more significantly, that the new PbO₂ formed during this first stage presents a lower specific electrochemically active area than that produced from the PbO through the PbSO₄ as intermediate. This data then validates the previous supposition. When the PbO₂ is formed without passing through the PbSO₄, with its high molar volume, the resulting PbO₂ does not present a high microporosity on its surface.

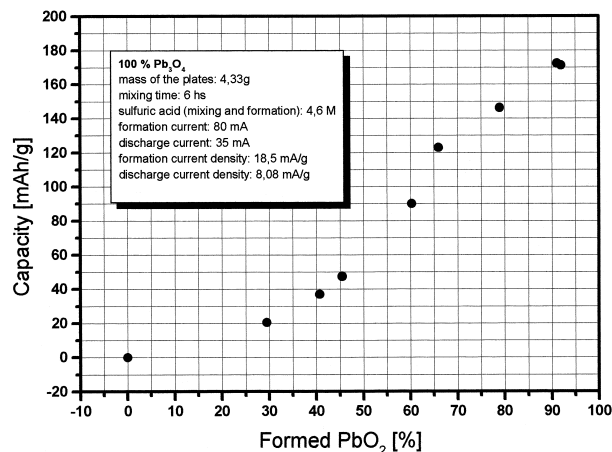


Fig. 10. Capacity versus PbO₂ content for different formation times and for 100% Pb₃O₄ precursor. Data obtained from Figs. 8 and 9.

4. Conclusions

As a conclusion, it is clearly seen that the representation of the capacity under formation, measured for different times of formation versus the corresponding PbO_2 content for these same times, taking into account that both determinations can be made possible in any factory laboratory, can contribute important information about each specific formation process. For this it was pointed out that the rate of discharge must be higher than 20 h.

As a demonstration of which kind of knowledge can be obtained, it has been discussed in the present paper different formation conditions of tubular plates, and through this, it was possible to understand the evolution of the specific capacity under formation or more practically, the capacity per unit mass or the electrochemically active area with formation time. It was shown that through the use of very low rates of discharge, it is possible to be under solid state reaction control instead of under transfer of mass control at the end of a discharge. It was shown that this is fundamental in order to measure comparatively the electrochemically active area. A simple chemical method was proposed to follow the evolution of the PbO_2 content during the formation process. It was demonstrated that the formation process efficiency is very low. It was shown that the interesting representation of the process is that of the

specific capacity versus the formed PbO_2 content for each given formation time. It was demonstrated that not only does the Pb_3O_4 give rise to PbO_2 and PbO in a first reaction step but that the first-formed PbO_2 , coming directly from the Pb_3O_4 , gives rise to a lower specific electrochemically active area on the PbO_2 . An empirical demonstration was presented of the well known fact that the incorporation of Pb_3O_4 as the original precursor reduces the formation time, but that at the same time, it does not affect the problem of residues of precursors at the end of formation. An explanation was given for this fact based on the formation of patches of PbO_2 on the surface of the plate which condense the majority of the current at the end of the formation process. Finally, the ideas developed from the measurements permit to understand the dependence of the obtained capacity on the amounts of precursor used in the plate and the discharge current used.

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