

Study of the mechanism of reduction of the electrode (α and β - PbO_2) material retrieved from the battery waste, using all solid electrolyte. (Preservation of the nature of lead and sulfuric acid).

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Abstract:

Actually, lead-acid Batteries use sulfuric acid as electrolyte either for the formation of plates or for the charge-discharge service in its cycle life unfortunately, sulfuric acid is nefaste for environment once the batteries are deteriorate.

The present work contributes in the replacement of this electrolyte by a solid state one based on $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$.

The cycle life of lead-acid battery depends on the nature and quantity of hydrogen species. Lead dioxide could be prepared either by chemical or electrochemical route.

We studied the effect of the departure of the water of structure by heating on the electrochemical capacity of α - PbO_2 and β - PbO_2 . The study was carried out by using a solid electrolyte: $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$. The results show that the departure of the water of structure causes a considerable reduction in the capacity that it is for α - PbO_2 or β - PbO_2 .

The lead dioxide is an oxide non-stœchiometric containing in its structure of the hydrogenated species (Hook-freezing system) [1]. The lifespan of the lead battery depends on nature and the quantity on these hydrogenated species. Lead dioxides can be prepared either by chemical way, or by electrochemical way. It is known that PbO_2 prepared by chemical way is inactive, on the other hand that prepared by electrochemical process is very active. The kinetics of the process of formation of PbO_2 plays an important part in the distribution of the protons in the structure obtained electrochemically [2,3,4] Boher [5] located the ion H^+ in the structure of PbO_2 on the edge common to the octahedral neighbours, thus creating a connection of the type $\text{O}-\text{H}\cdots\text{O}$, where two oxygen considered form an edge common to two octahedral [PbO_6]. The proton being preferentially related to one of oxygen, but likely to jump easily on close oxygen.

Keywords: lead-acid Batteries, sulfuric acid, $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$, α - PbO_2 and β - PbO_2 , water of structure

I) Summary:

We studied the effect of the departure of the water of structure by heating on the electrochemical capacity of α - PbO_2 and β - PbO_2 . The study was carried out by using a solid electrolyte: $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$. The results show that the departure of the water of structure causes a considerable reduction in the capacity that it is for α - PbO_2 or β - PbO_2 .

II) Introduction:

The lead dioxide is an oxide non-stœchiometric containing in its structure of the hydrogenated species (Hook-freezing system) [1]. The lifespan of the lead battery depends on nature and the quantity on these hydrogenated species. Lead dioxides can be prepared either by chemical way, or by electrochemical way. It is known that PbO_2 prepared by chemical way is inactive, on the other hand that prepared by electrochemical process is very active. The kinetics of the process of formation of PbO_2 plays an important part in the distribution of the protons in the structure obtained electrochemically [2,3,4] Boher [5] located the ion H^+ in the structure of PbO_2 on the edge common to the octahedral neighbours, thus creating a connection of the type $\text{O}-\text{H}\cdots\text{O}$, where two oxygen considered form an edge common to two octahedral [PbO_6]. The proton being preferentially related to one of oxygen, but likely to jump easily on close oxygen.

III) Experimental:

III-1) Preparation of the pastille.

III-1-1 Problems involved in the realization of the positive electrode.

For any kinetic study of the electrode, it initially was necessary to obtain a stable and reproducible system. Its development in its most powerful form required a very long optimisation of the parameters such as the composition of the electrode and working. The practical realization of this study ran up against several obstacles related to the following requirements:

- 1) Proportion of the acetylene black and graphite in the mixture.
- 2) The proportion of $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$ in the positive electrode: if this content is too weak, the composite electrode is detached from the purely electrolytic part and is exhausted after release from the mould.
- 3) The quantity of $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$ playing the part of electrolyte between the negative and positive electrodes.
- 4) Pressure to be applied to the whole and duration of pressing.
- 5) The reproducibility of the electrode.

III-1-2 Préparation du mélange constitutif de la masse positive.

After a test of several series of association of the various products, the composition of the composite electrode which seems to us to be the best is :

- 100 mg of PbO_2 .
- 20 mg of electronic binder (a mixture of 1/3 of acetylene black and 2/3 of graphite).
- 80 mg of $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$.

The homogenisation of the mixture was carried out using an electric mixer during thirty minutes.

III-1-3 Preparation of the pastille.

The unit masses composite-electrolyte consists of two layers carried out in only one operation per pressing in a Perkin-Elmer mould. The powder of $\text{HSbO}_3 \cdot 0,55\text{H}_2\text{O}$ is initially introduced into the mould, with a piston, one slightly packs with the hand this powder in order to make

homogeneous its surface. The composite mixture is then introduced into the mould. The unit is subjected to a pressure of 7t/cm^2 during a quarter of hour. After release from the mould, one obtains a pastille 13 mm in diameter and 2 mm thickness as figure 1 shows it.

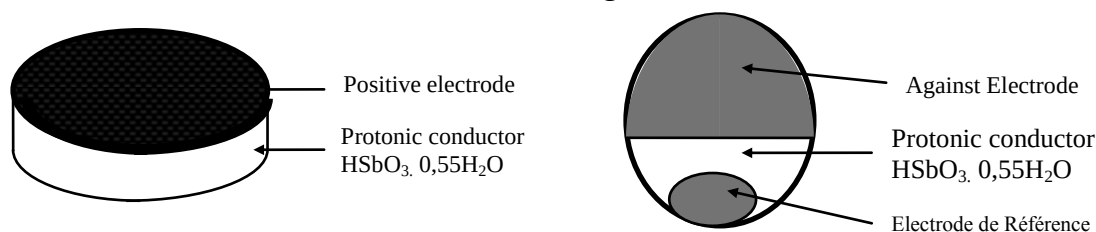


Figure 1: Diagram of the pastille: electrode composite-electrolyte.

The interface electrode composite-electrolyte thus obtained is mechanically very solid. The face of the pastille, opposed to that of the positive electrode will be useful like an electrode of reference and against electrode. These two last are carried out by application of the layers of platinum lacquer. These two electrodes occupy only part of the surface of the disc, which avoids a short-circuit between them. Figure 2 shows the provision of these two electrodes.

III-4) Device of discharge.

The pastille is placed in a device which ensures the electrical contacts and isolates the two atmospheres (air on the side of the electrode of work and H_2 + steam on the side of against electrode and the electrode of reference). The electrochemical cell of measurement is represented on figure 2.

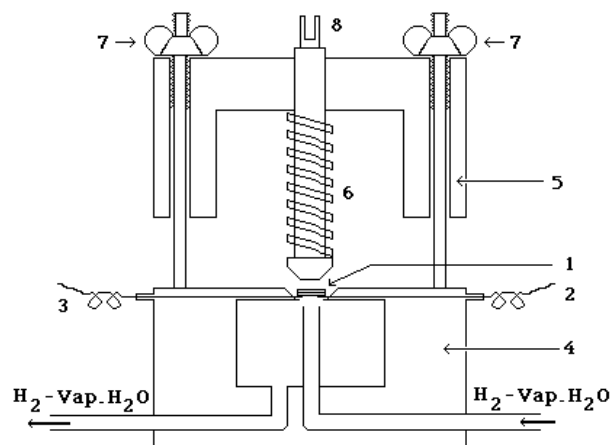
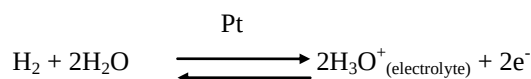


Figure 2: Detailed diagram of the whole of measurement for the electrochemical cell with 3 electrodes.

- (1) - Composite electrode.
- (2) - Contact for electrode of reference.
- (3) - Contact for against electrode.
- (4) - Plexiglass base.
- (5) - Plexiglass lid.
- (6) - Metal spring.
- (7) - Screw for tightening.
- (8) - Metal tube and contact of the electrode of work.

The pastille is represented in (1). This one rests on a metal stainless steel disc, ensuring the exits of current of the electrode of reference (2) and of against electrode (3). On the higher part of the pastille is a stainless steel part (8) which ensures the electrical contact of the electrode of work. The lid (5) is attached to the base by means of nuts (7).

For all the experiments which follow we used this cell with three electrodes. Water in the gas mixture plays an important part in the mechanism of oxydo-reduction of molecular hydrogen H_2 to interface electrolyte-Pt, the assessment corresponds to the following reaction:



The process with the electrode $H_2 + \text{steam } H_2O / Pt / H\text{SbO}_3 \cdot 0,55H_2O$ has a good reversibility and a good stability provided that this electrode is permanently in contact with the gas mixture water hydrogen-steamer necessary to the good course of the reaction in the anodic direction. Figure 3 shows the electrochemical chain of measurement:

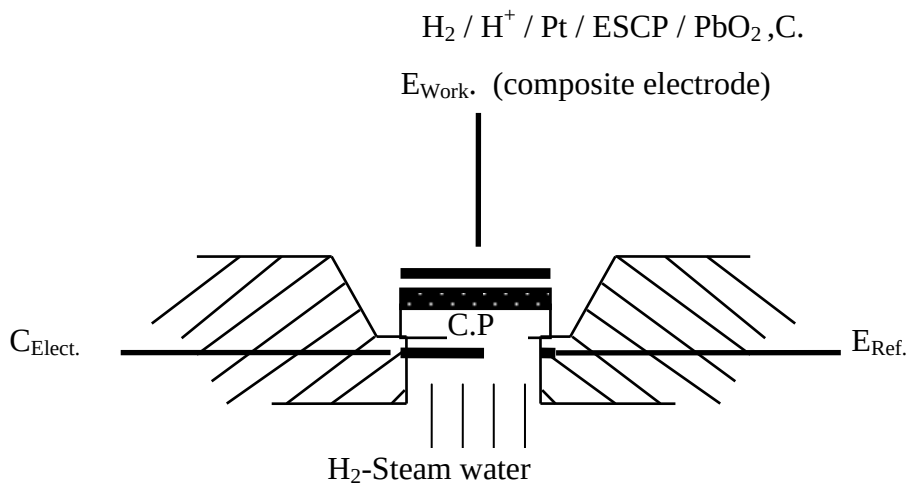


Figure 3: Detail of the pastille inside the cell.

III-5) Intensiostatic study in very solid medium.

III-5-1) Measure of the potential at the abandonment.

After assembly of the pastille in the cell electrochemical and put in circulation of the gas mixture $H_2 +$ steam, we for each electrode measured the tension with the abandonment. For the α - PbO_2 variety the value of the initial tension to the abandonment is included/understood between 1,44 V and 1,47 V, on the other hand for the β - PbO_2 variety it varies between 1,42 V and 1,45 V.

All the values of the tensions are given compared to the electrode of comparison $H_2 / H^+ / Pt$ to a temperature at 25°C.

III-5-2) Study of the capacity of discharge for $i = -300 \mu A$.

The curves of intensiostatic discharge for the two varieties are represented on figures 4 and 5. In very solid medium, we observe the same phenomenon as in study in sulphuric medium, the heating causes an important ohmic fall for the two varieties of PbO_2 . The presence of the stage is related on the existence of water and especially to the water of structure. The departure of this last has an influence much more important on the α - PbO_2 variety than β - PbO_2 .

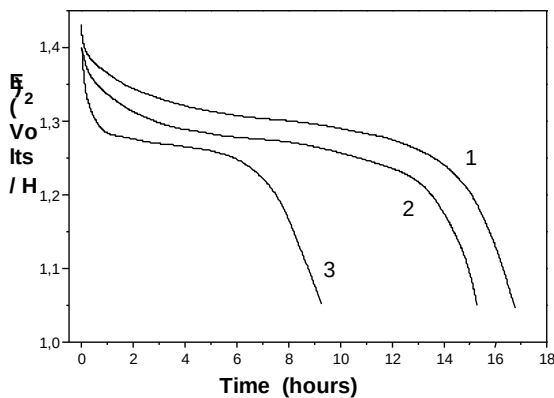


Figure 4: Curve of discharge at $i = -300 \mu A$ of

(1) α - PbO_2 , (2) α - PbO_2 heated at 140°C, (3) α - PbO_2 heated at 230°C.

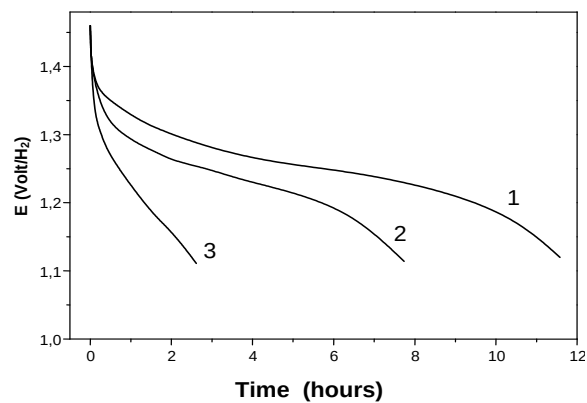


Figure 5: Curve of discharge with $i = -300 \mu A$ of

For better illustrating this phenomenon we gathered on table 1 the values of the capacity of discharge for a tension of cut of 1,1 volt and we calculated the percentage of loss of capacity of discharge.

	α -PbO ₂	α -140	α -230	β -PbO ₂	β -140	β -230
Time (hours) *	11,74	07,89	02,55	16,27	15,01	08,84
Capacity mAh/g	35,22	23,67	07,65	48,81	45,03	26,52
Loss of capacity (%)	-----	32,79	78,27	-----	07,74	45,66

* Tension of cut 1,1 volts

Table 1: Capacities of discharge of the piles containing α et β -PbO₂ for $i = -300 \mu\text{A}$.

IV) Conclusion:

The study shows that the departure of surface water generates losses of capacity of 32,79 and 07,74% respectively for α and β -PbO₂, this shows us that in very solid medium, the surface water east of capital importance in the mechanism of reduction of α -PbO₂. This result is in agreement with that obtained at the time of the study carried out in sulphuric medium and showing the variation of D_{H^+} with the temperature [6]. In the same way the departure of the OH of structure seems to have a considerable influence on the capacity of α -PbO₂ since one records an almost double loss of that obtained in the case of β -PbO₂.

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