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Physicochemical and electrochemical study of lead acid battery positive active mass (PAM) modified by the addition of bismuth

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This study attempts to discuss the influence of Bi alone and its combination with Sb and Sn on the electrochemical performance of the PAM of lead acid batteries. The different additives were added in the electrolyte as cations. PAMs were prepared by electro formation of cured battery plates in the presence and absence of a dopant (non-doped sample ND). The results from different analyses showed that bismuth alone gives a remarkable improvement of the capacity. The highest performance of PAM is obtained when bismuth is mixed with tin together as dopants.
The incorporation of bismuth and tin cations leads to an increase of the quantity of structural water in PAM. This increases the hydrated and amorphous zones within the PbO_2 particles and leads to an improvement of the electrochemical capacity.

Key words: Lead acid battery, Positive active mass, Bismuth, Tin, Antimony, Capacity.

INTRODUCTION

The active mass of the positive plate of the lead-acid battery is a gel-crystal system that conducts electricity by electrons and protons in hydrated areas of the gel zones [1]. The properties of the active material were modified by the introduction of dopants, but few reports in the literature deal with these investigations [2-7]. The effect of the addition of ions of the elements of group V (Arsenic, Antimony and Bismuth) introduced in the spin alloy or in the solution during the rebuilding process of the active material structure and the PbO_2 powder density were investigated. The results showed that these dopants decrease the value of the critical density [8]. H.Y. Chen *et al.* [9] found that bismuth improves the capacity and cycle life. In our previous works, we studied the effect of the doping of lead dioxide with some metallic ions on the composition of PAM gel zones and its relationship to battery performance. The results showed that the quantity of water present in the gel zones and PAM discharge capacity are mainly dependent on the nature of the dopant [10, 11].

The aim of this work is the study of the physicochemical properties of the lead acid battery positive active mass, modified by adding Bi alone and combined with Sb and Sn at different concentrations and their electrochemical performances. The study was based on chemical analysis, X-ray diffraction (XRD), thermogravimetry (TG) and scanning electronic microscopy (SEM). The capacity of the different PAMs is determined by galvanostatic discharge.

EXPERIMENTAL

Plate preparation

In order to investigate the effect of bismuth on the positive active mass, four kinds of positive electrodes were prepared. Lead dioxide was prepared by electroformation of industrial cured battery plates (with grids cast from a Pb-5wt. % Sb alloy) in acidic solution according to the method described by Voss and Freundlich [12]. The cured plates were soaked in 1.40s.g. H_2SO_4 solution for 18h and then formed in 1.05s.g. H_2SO_4 solution. The dopants were dissolved in the electrolyte as Bi_2O_3, Sb_2O_3 and $SnCl_2$. Table 1 shows the concentrations of dopants.

Table 1. Concentrations of the different dopants added to the PAM.

Dopant	Concentration, ppm
Bi	25
Bi-Sb	25-50
Bi-Sn	25-100

The formed plates were washed in running water for several hours to remove the excess of sulfuric acid. Then they were dried overnight at 110°C. Part of the active mass was removed from the grids,

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washed with a hot saturated acetate ammonium solution to remove the $PbSO_4$ traces, dried and ground to a powder.

The positive active materials were characterized by XRD analysis using an APD-15 Philips 2134 diffractometer. The changes in relative intensity of the X-ray characteristic diffraction lines for the different phases in PAM were adopted as a measure of the phase changes in the PAM with the effect of additives.

The thermal analysis tests were performed using an instrument supplied by MettlerToledo: TGA/SDTA 851e. All measurements were carried out in a nitrogen atmosphere at a gas flow-rate of $50cm^3min^{-1}$ and at a constant heating rate of $10Kmin^{-1}$.

The SEM observations were performed by a scanning and transmission electron microscope JEOL 200 CX (Japan).

Electrochemical tests were performed with a classical three electrode cell. The working electrode is a PAM powder hand pressed on a conductive graphite collector. A platinum sheet was used as a counter-electrode. The non-doped and doped electrodes were discharged at a constant cathodic current of 1mA and the potential versus capacity curves were recorded using a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode. All the experiments were carried out at room temperature in 1.28 s.g. H_2SO_4 solution.

RESULTS AND DISCUSSION:

Chemical analysis

Table 2 summarizes the chemical composition of the PAM samples formed in solutions with different additives. The data show that traces of bismuth, tin and antimony are present in the active mass. The highest percentage of Bi is obtained for the solution containing Bi and Sn. Small quantities of unconverted $PbSO_4$ were found in the majority of the samples.

Table 2. Results from chemical and ICP-AES analyses of doped and non-doped PAMs.

Samples	PbO_2 %	$PbSO_4$	PbO	$Sn.10^3$ %	$Bi.10^3$ %	$Sb10^3$ %
ND	89.50	3.24	5.19	0	0	0
Bi	86.07	1.25	5.89	0	4.0	0
Bi-Sb	86.37	2.58	6.55	0	5.6	5.0
Bi-Sn	85.90	1.87	8.80	4.0	9.7	0

XRD analysis

All detected peaks in Fig.1 were identified to be β-PbO_2. No differences in the spectra were observed, but changes in peak intensity were clearly detected between the modified PAMs and unmodified one.

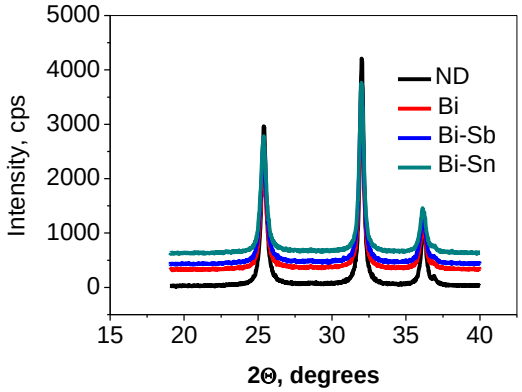

Fig 1. XRD patterns of doped and non-doped PAMs.

The average crystallite size was calculated from the full width at the half maximum (FWHM) of [110] diffraction lines using the Sherrer equation. The crystallite size values showed that more amorphous particles of PbO_2 were obtained in solutions containing the different additives. As a consequence we can deduce that Bi, Sn and Sb tend to diminish the crystallinity of the PAM particles. The crystallite sizes calculated for the different PAMs are reported in Table 3**.**

Table 3. Average crystallite sizes calculated for doped and non-doped PAMs.

Samples	Size (nm)
ND	21.9
Bi	18.2
Bi-Sb	18.2
Bi-Sn	18.4

Thermal analysis

The changes in water content in the PAMs are measured by thermal analysis. The thermo gravimetric (TG) curves are shown in Fig. 2. The values for the structural water are reported in Table 4. It is clear that the additives increase the water content in the PAMs. The highest amount of structural water is obtained for sample containing Bi-Sn mixture.

Table 4. Values of structural water in PAMs.

Samples	Structural water (%)
ND	0.58
Bi	1.39
Bi-Sb	2.13
Bi-Sn	2.41

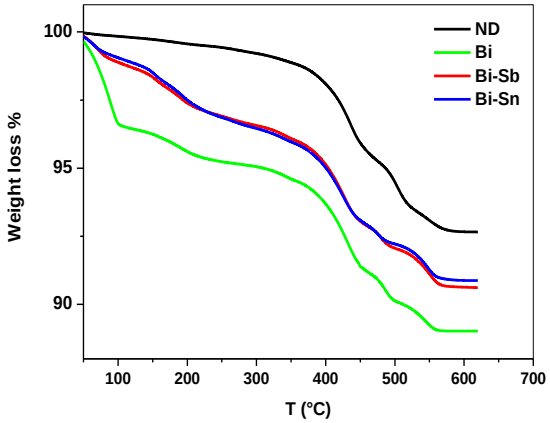

Fig 2. TG curves of doped and non-doped PAMs.

Fig.3 presents the obtained DTG curves - the first derivative of the TG curves normalized toward the mass of the samples. The DTG curves for all samples have characteristic peaks in the range from 50 to 300°C that are related to the evaporation of water in different parts of the PAM. The peaks at a temperature higher than 300°C are related to the degradation of PbO_2 to PbO. The DTG curve for the non-doped sample features two characteristic peaks in the range from 50 to 300°C. The first one at 100°C is related to the evaporation of the physisorbed water and the second one is related to the evaporation of the structural water from the gel zone of the positive active mass. In the temperature range from 100 to 300°C the two additional peaks appear for doped PAMs. These peaks are indicative of different types of bounded water in the PAMs gel zones and confirm that the dehydration of PAMs occurs in three stages. We can deduce from the thermal analysis that the addition of Sn increases the quantity of the structural water as described earlier [11].

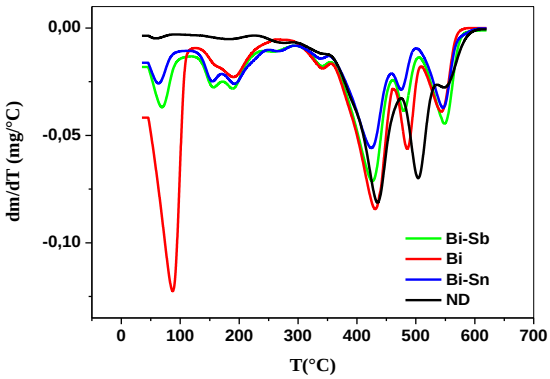

Fig 3. DTG curves of doped and non-doped PAMs.

SEM morphology

Fig.4 presents the scanning electron micrographs of different PAMs. The micrographs show that the morphology of the positive active material is not affected by the bismuth incorporation.

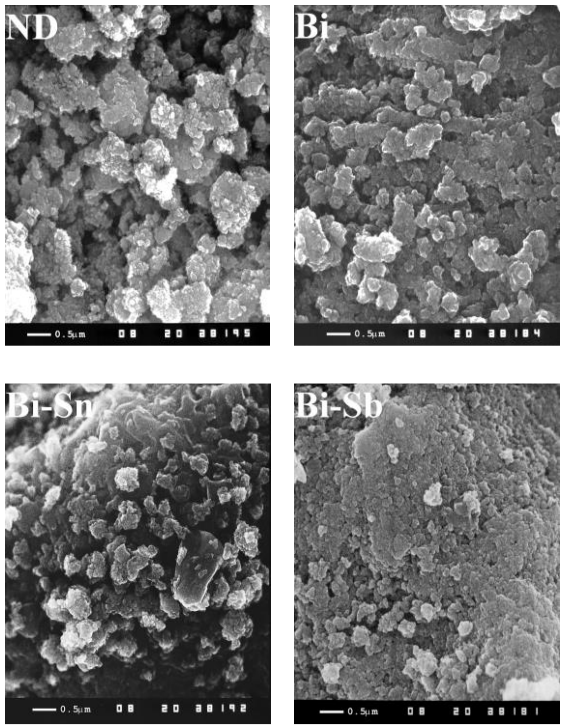

Fig 4. SEM micrographs of the PAMs with dopants.

Electrochemical properties

Fig.5 shows the discharge curves of modified PAMs compared to the positive active mass without additives (ND). Bismuth incorporated in the PbO_2 gel zones improves its electrochemical activity. It is clear that the capacity of PAM with bismuth alone is considerably better than a non-doped one. In order to see the effect of the synergy of bismuth, tin and antimony which have proved their positive influence on PAM in earlier studies, we have introduced mixtures of Bi-Sb and Bi-Sn in the PAM. The best capacity is obtained for PAM formed in H_2SO_4 containing the mixture of Bi-Sn(100-25 ppm). Fig.6 presents the variation of the PAM's capacity versus the amount of structural water in the samples. The data show that the highest capacity is obtained for the PAM doped by a Bi-Sn mixture, which contains the greatest amount of structural water and the higher percentage of Pb^{IV}.

The doping of PAM leads to the incorporation of bismuth, antimony and tin cations which increase the quantity of the structural water in PbO_2. This obviously leads to PAMs with more hydrated and amorphous zones, consequently the capacity increases. The improvement in the percentage of the capacity of PAM is mentioned in Table 5.

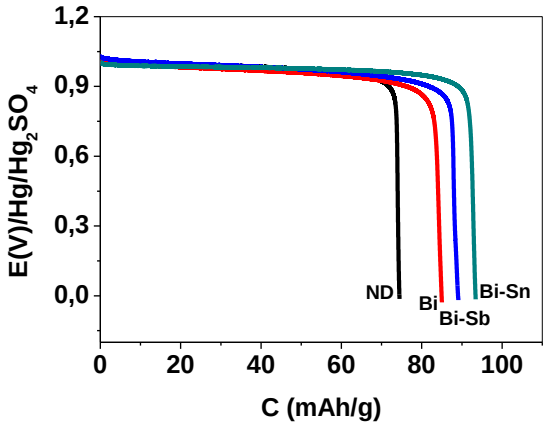

Fig 5. Comparison of the electrochemical behavior of non-doped PAM (ND) and ones with Bi alone and mixtures of Bi-Sb and Bi-Sn.

Table 5. Capacity (%) of different PAMs.

	Bi	Bi - Sb	Bi - Sn
Capacity (%)	14.16	19.46	25.57

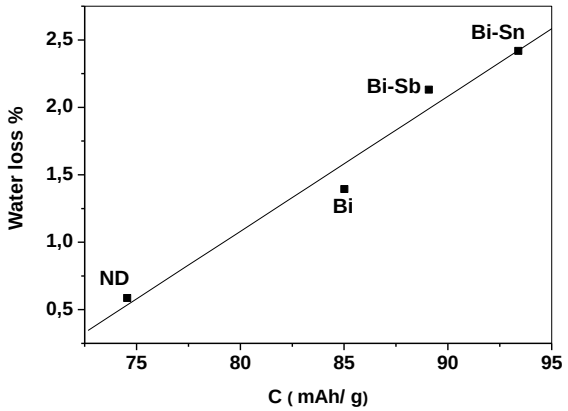

Fig 6. Evolution of the discharge capacity of different PAMs with the loss of structural water.

CONCLUSIONS

The objective of this work was the development of a battery with improved properties. The different results have shown that bismuth yields a remarkable increase in capacity. Better performance for PAM is obtained when Bi and Sn are added together in the electrolyte. This can be explained by the fact that a mixture of Bi and Sn modifies the hydrated and the gel parts of PAM leading to more amorphous and small sized hydrated particles. Hence the capacity increases and a synergy is obtained when the positive active mass is doped by a mixture of Bi and Sn. The incorporation of the different metallic cations leads to an increase in the quantity of a structural water which improves the electrochemical activity of PAM. These results should be applied in the process of lead acid battery technology.

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ФИЗИКОХИМИЧНО И ЕЛЕКТРОХИМИЧНО ИЗСЛЕДВАНЕ НА ПОЛОЖИТЕЛНАТА АКТИВНА МАСА В ОЛОВЕН АКУМУЛАТОР, МОДИФИЦИРАН ЧРЕЗ ДОБАВЯНЕ НА БИСМУТ

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(Резюме)

Изследва се влиянието на бисмут, както и неговите комбинации с антимон и калай, върху електрохимичните свойства на положителната активна маса в оловния акумулатор. Различните добавки са направени в електролита и са под формата на катйони. Положителните активни маси са получени след формиране на зрели плочи в присъствие или отсъствие на добавки. Резултатите от различни анализи показват, че бисмутът като самостоятелна добавка значително увеличава капацитета на клетката. Характеристиките на положителната активна маса са най-добри, когато добавката е комбинация от бисмут и калай.

Присъствието на йоните на Bi и Sn спомага за повишаване количеството на структурна водав положителната активна маса. Така се увеличават зоните с хидратираните аморфни частици PbO_2, което води до увеличаване на капацитета.