



Short communication

PbSO₄ as a precursor for positive active material electrodes[☆]M. Foudia^a, M. Matrakova^b, L. Zerroual^{a,*}^a Laboratoire d'Energétique et Electrochimie du solide (LEES), Université Ferhat ABBAS, Sétif 19000, Algeria^b Institute of Electrochemistry and Energy Systems (CLEPS), Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

ARTICLE INFO

Article history:

Received 3 September 2011

Received in revised form 10 January 2012

Accepted 12 January 2012

Available online 21 January 2012

Keywords:

Lead sulphate

Precursor

Positive active material

Lead–acid batteries

Capacity

ABSTRACT

The present work investigates the use of PbSO₄ as a precursor for positive active material (PAM) electrodes. Lead sulphate was prepared by the chemical precipitation of a lead nitrate solution in the presence of sodium sulphate. Tubular electrodes were filled with PbSO₄ and oxidized in solutions with different pH. The study is based on X-ray diffraction analysis (XRD), Thermogravimetry (TG), Differential scanning calorimetry (DSC) and Scanning electronic microscopy (SEM). The capacity of the different PAM electrodes was also determined. The results show that the pH of the electrolyte affects significantly the average crystallite size, phase composition and PAM capacity.

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1. Introduction

The paste is generally prepared by mixing leady oxide with water and a sulphuric acid solution. This leads to the formation of basic lead sulphates. The nature of basic sulphates obtained depends on the conditions of paste preparation. The amount of H₂SO₄ with respect to that of leady oxide determines the phase composition during mixing. The processes during soaking of 3BS and 4BS plates have been investigated by some authors [1–7]. It has been established that the sulphation of the plates is mainly influenced by the phase composition of the cured plate, H₂SO₄ concentration and soaking time.

In our previous work [8], it was shown that during soaking, the proportion of 3BS in the paste decreases and converts to anhydrous lead components. The thermal decomposition of the paste showed a decrease in the quantity of structural water and dehydration energy. At high concentration of H₂SO₄, the plate sulphation process is accelerated. Upon forming, the different phases present in the paste convert to PbO₂ with different proportions of β and α-PbO₂. The former is a result of PbSO₄ conversion whereas the later originates from the oxidation of 3BS crystals.

The phase composition and PAM capacity performance are mainly dependent of the phase composition of the cured plate and soaking conditions. Consequently, many formulations in the paste

mixing process were tested [9] seeking better discharge performance of PAM and many lead compounds were tried as precursors instead of lead powder [10].

The use of lead sulphate in the production of positive active materials has many advantages. For instance, the starting material in the traditional lead–acid battery production is a leady oxide which contains up to 30% of free metallic lead. During paste mixing, free lead reacts with sulphuric acid and undergoes lead sulphate via an exothermic reaction. The temperature rises and a cooling system is necessary to obtain the desirable phase composition of the unformed paste. On the other hand curing is an important step in lead–acid battery production and one of its principal goals is reducing the content of free lead to a level nearer to 1%. To achieve this goal, appropriate and specific equipment is needed. In addition, these steps are time consuming and costly. When lead sulphate is adopted, all these problems are avoided because there is no free lead involved. Consequently, time, electrical energy, human resources and machinery can be saved in the processes of paste mixing and curing.

The densities of some lead compounds are listed in Table 1. It can be seen that lead sulphate has the smallest density of all lead compounds. Higher paste porosity can be obtained when lead sulphate is used as a precursor. As a result, the lead sulphate based pastes give a positive active material with a greater porosity. Increasing the porosity facilitates the diffusion of the electrolyte inside the plate and thus improves its discharge capacity.

The theoretical quantity of electricity required to oxidize 1 kg of lead compounds to PbO₂ is given in Table 2. It can be seen that lead sulphate presents the lowest value. Consequently, electric energy can be saved when lead sulphate is used as the starting material for

[☆] The paper arose from a presentation at Labat Conference 2011, held in Albena (Bulgaria).

* Corresponding author. Tel.: +213 36 92 51 21; fax: +213 36 92 51 33.

E-mail address: zerroual@yahoo.fr (L. Zerroual).

Table 1
Densities of lead compounds.

Compound	Density (g cm ⁻³)
Pb	11.34
Pb ₂ O	8.34
α-PbO	9.32
β-PbO	9.67
Pb ₃ O ₄	9.10
PbO ₂	9.37
PbOSO ₄	6.32
PbO·PbSO ₄	7.02
3 PbO·PbSO ₄ ·H ₂ O	6.50
4 PbO·PbSO ₄	8.15
PbO·Pb(OH) ₂	7.59

lead–acid battery production. In the present work we investigate the use of chemical lead sulphate as a precursor for PAM electrodes. The effects of the electrolyte pH on the phase composition of PAM, average crystallite size and electrical performance were studied.

2. Experimental

2.1. Preparation of the electrodes

Chemical lead sulphate was prepared by the precipitation of a solution of Pb(NO₃)₂ with Na₂SO₄. The oxidation of PbSO₄ in electrolytes with different pH varying from 0 to 14 was achieved using tubular electrodes. The different solutions were prepared using H₂SO₄, Na₂SO₄ and NaOH. Before each experiment, the Pb–Sb spine was previously subjected to a polarization in 1.28 s.g. H₂SO₄ solution at 1.3 V/Hg/Hg₂SO₄/saturated K₂SO₄ so that a conductive anodic layer of PbO₂ is obtained. This layer ensures the contact between the spine and PbSO₄ precursor and initiates its conversion to PbO₂. Each electrode was filled with PbSO₄ in a powder form then electroformed at a constant current of 50 mA until the complete mass of PbSO₄ was totally converted to a brownish-black PbO₂ powder. The samples were washed several times in distilled water and dried overnight at 105 °C.

2.2. Chemical analysis

The concentrations of PbO₂ and PbSO₄ in PAM for each electrode were, respectively, determined by volumetric titration with a KMnO₄ solution and gravimetric precipitation with 5% BaCl₂. Analytical grade reagents and bidistilled water were used for all solutions.

2.3. X-ray diffraction analysis

The powder X-ray diffraction patterns were taken at ambient temperature using a Bruker D8 advance diffractometer operating at 40 kV and 30 mA with CuK_α radiation ($k = 0.15406$ nm). Radial scans were recorded in the reflection scanning mode with 2θ being changed from 10 to 90°. Bragg's law, defined as $n\lambda = 2d \sin \theta$, was used to compute the crystallographic distance (d) for the examined PAM samples.

Table 2
Quantity of electricity required to oxidize lead compounds.

Compound	Quantity of electricity (Ah kg ⁻¹)
Pb	514
Pb ₂ O	375
PbSO ₄	176
PbCl ₂	193
PbO	240

Table 3
Results from chemical analysis of PAM samples formed at different pH.

PAM prepared at pH	PbO ₂ (%)	PbSO ₄ (%)
0	92.7	2.2
3	92.4	2.4
6	92.1	3.2
9	93.6	1.9
12	89.7	4.6
13	87.6	3.2

The relative intensity of the X-ray characteristic diffraction lines was adopted as a measure of the phase changes in the positive active material. It is defined as the ratio of the "i" phase characteristic reflection intensity to the sum of the intensities of the characteristic diffraction lines of all phases present. The average crystallite size of the different powders was calculated from the full width at the half maximum (FWHM) of [1 1 0] diffraction lines using Sherrer equation. Then samples of the PAM were subjected to SEM observations.

2.4. Thermal analysis

Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) tests were performed using instruments supplied by Metler Toledo: TGA/SDTA 851e and DSC 822e, respectively. All measurements were carried out in a Nitrogen atmosphere at a gas flow-rate of 80 cm³ min⁻¹ for DSC and 50 cm³ min⁻¹ for TGA at a constant heating rate of 10 K min⁻¹. The samples were dried at 60 °C to evaporate the surface absorbed water.

2.5. Electrochemical investigations

Electrochemical tests were performed with a classical three-electrode cell. The working electrode is a PAM powder hand-pressed on a conductive carbon collector. A large platinum foil was used as a counter-electrode. The electrodes were discharged at a constant cathodic current of –1 mA and the potential versus capacity curves were recorded using an Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode. All experiments were carried out at room temperature in 1.28 s.g. H₂SO₄ solution.

3. Results and discussion

Table 3 summarizes the results obtained for the chemical composition of the PAM samples formed in solutions with different pH. The data show that the quantity of unconverted lead sulphate is less than 5% which means that the oxidation was completed although the paste is non conductive. Positive active materials formed in solutions with pH higher than 9 contain less PbO₂ predicting the amorphous character of these powders compared to the other samples with high content of PbO₂ which means that they are more crystalline.

XRD patterns of the samples prepared with different pH are presented in Figs. 1 and 2, respectively. The following characteristic reflections were used: $d = 3.50$ Å for tetragonal PbO₂ and $d = 3.12$ Å for orthorhombic PbO₂. When the pH value increases, broadness and intensity losses of the (1 1 0), (1 0 1) and (2 0 0) reflections are observed. From Fig. 3 it appears that small particles with an amorphous character are obtained in alkaline solutions and a decrease in the particle size is observed as the pH increases. Fig. 4 shows the variation of the different powders phase composition with pH solutions. In solutions with pH value lower than 13, only β-PbO₂ is detected. When the pH of the solution reaches 13.5 small amount of α-PbO₂ is formed. It represents 20% of the total mass. At a pH of 14, a proportion of 80% of the positive active material is α-PbO₂.

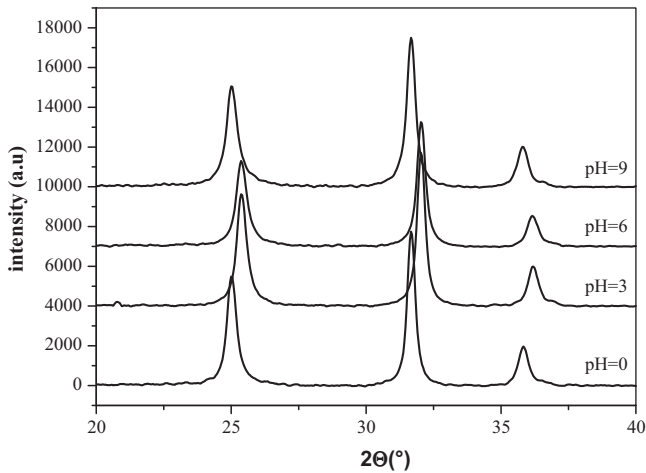


Fig. 1. XRD patterns of PAM formed in solutions with pH varying from 0 to 9.

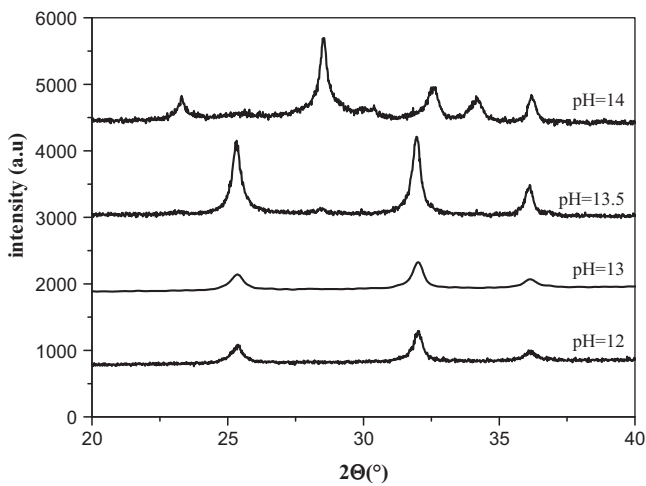


Fig. 2. XRD patterns of PAM formed in solutions with pH varying from 12 to 14.

The SEM micrographs of the different samples are illustrated in Fig. 5. Spherical lead dioxide particles are assembled in small agglomerates which are closely interconnected and form aggregates. Positive active materials formed in alkaline solutions exhibit nano-sized particles compared to those obtained in acidic solutions. These results confirm the data of the XRD analysis.

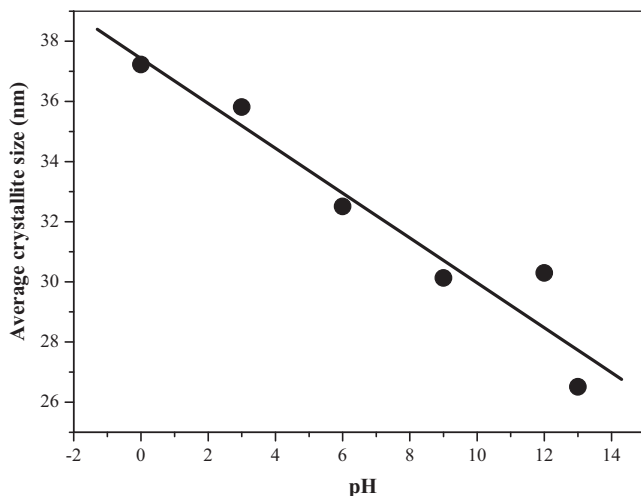


Fig. 3. Average crystallite size of PAM formed in solutions with different pH.

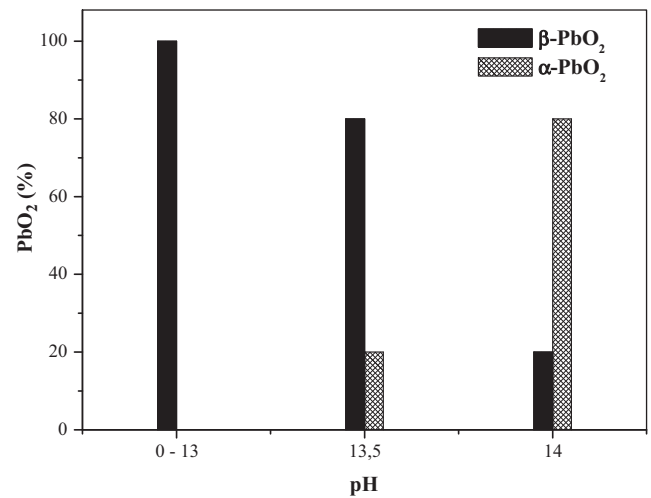


Fig. 4. Phase composition of PAM formed in solutions with different pH.

Fig. 6 presents the weight loss of the different positive active materials as a function of temperature. The curves show two domains: the first of which in the temperature range of 25–300 °C corresponding to the decomposition of the gel zones of PAM. The second one appears at a temperature higher than 300 °C which is relative to the degradation of the crystalline part of PAM to PbO_x (with $1 < x < 1.9$). As shown in Fig. 7, the DTG curves feature a characteristic peak at 60 °C which corresponds to the evaporation of surface water and two other peaks, respectively, at 170 and 230 °C which are relative to two types of structural water chemically bonded as hydroxyl groups in PbO(OH)₂ the amorphous component of PAM. In Fig. 8 are reported the water content of the gel zones of the different samples against the pH of the solutions. It is clearly evidenced that the pH of the electrolyte influences significantly both the surface and the structural water of the amorphous PAM. The DSC curves are presented in Fig. 9. Upon heating, amorphous parts in PAM are decomposed to PbO_x with water and oxygen evolution. A first endothermic peak appears at 60 °C and corresponds to the presence of physisorbed water in the gel zone of the PAM. When increasing the temperature two exothermic peaks are recorded, respectively, at 170 and 230 °C. They are associated with the presence of structural water as hydroxyl groups. In the temperature range of 300–600 °C, three shape endothermic peaks were observed. They correspond to the well-known intermediate oxides, pseudo-cubic α -PbO_x, pseudo-cubic β -PbO_x, and pseudo-tetragonal Pb₃O₄. The average dehydration and dehydroxylation energies were calculated, respectively, by integrating the surface areas of the endothermic and exothermic peaks in the temperature range of 25–300 °C. The values obtained for the solutions with different pH are reported in Table 4. It is evident that both the surface and the structural water of the amorphous part of PAM are affected by the pH of the electrolyte. In addition, the hydroxyl groups are strongly bonded and require more energy to decompose than those of the weakly bonded water.

Table 4
Dehydration and dehydroxylation energies of PAM samples formed at different pH.

PAM prepared at pH	Dehydration energy (J g ⁻¹)	Dehydroxylation energy (J g ⁻¹)
0	-5.49	-
3	-2.49	13.84
6	-4.46	14.99
9	-8.93	-
12	-	19.59
13	-2.71	16.02

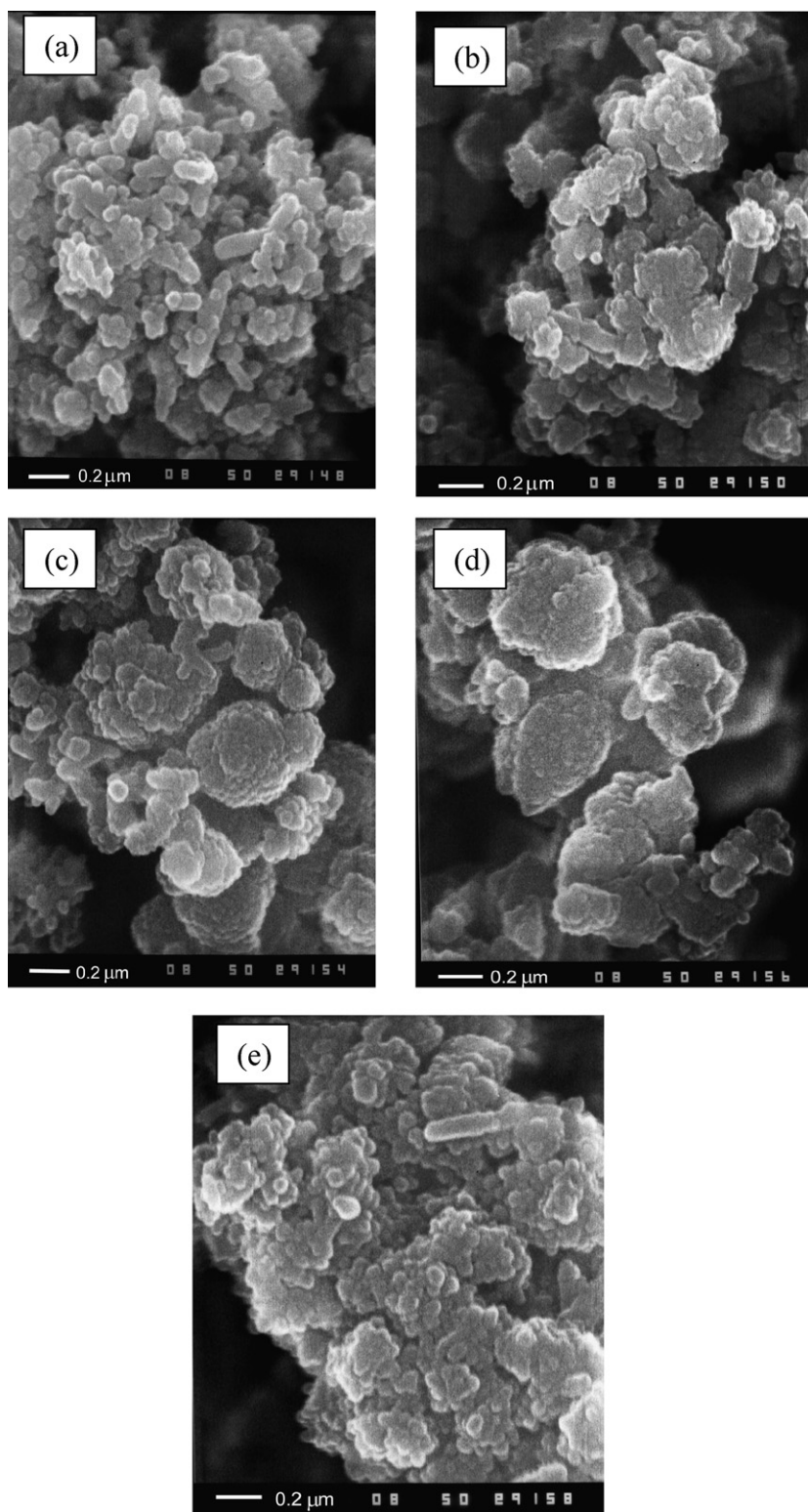


Fig. 5. SEM micrographs of PAM formed in solutions with different pH: (a) 3, (b) 6, (c) 9, (d) 12 and (e) 13.

Fig. 10 presents the changes in PAM capacity versus pH. It can be seen that the pH of the solution influenced significantly the PAM capacity. The higher the pH of the solution, the higher is the capacity of the PAM. Thus, the specific capacity of the positive active mass formed at pH=0 is 63 mAh g^{-1} , whereas at pH>10, the specific capacity of the positive active

mass is higher than 90 mAh g^{-1} . For comparison, tubular electrodes produced with leady oxide and red lead (~40 wt.%) as starting material and formed at pH close to 0 (standard technology) have PAM specific capacity of about 72 mAh g^{-1} [11]. This means that tubular electrodes prepared with PbSO_4 as PAM precursor and formed in electrolytes with pH higher than 10 have better specific

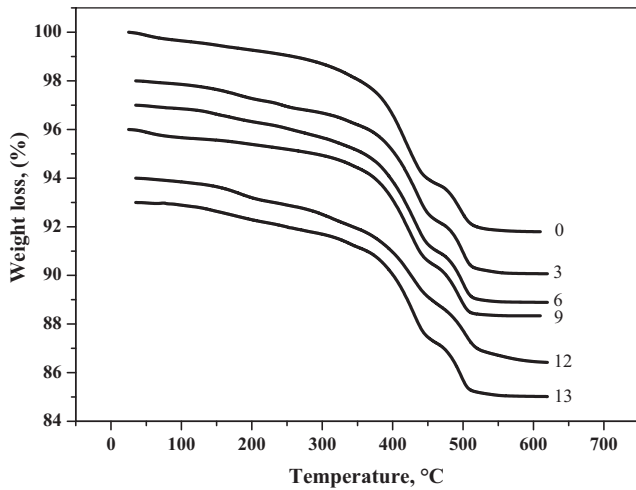


Fig. 6. Weight losses of PAM formed in solutions with different pH versus temperature.

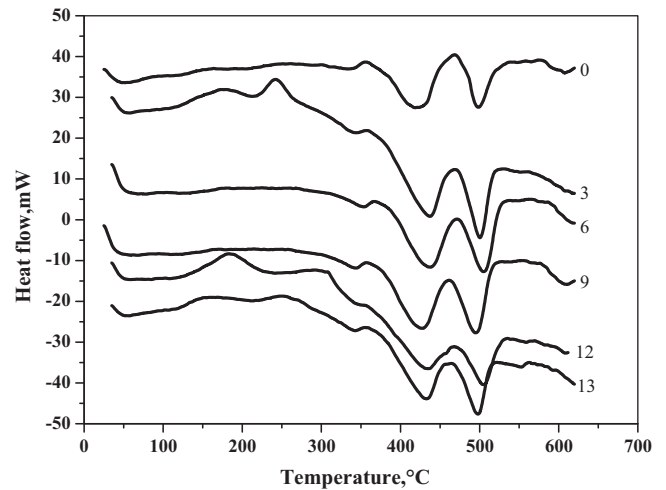


Fig. 9. DSC curves of PAM formed in solutions with different pH versus temperature.

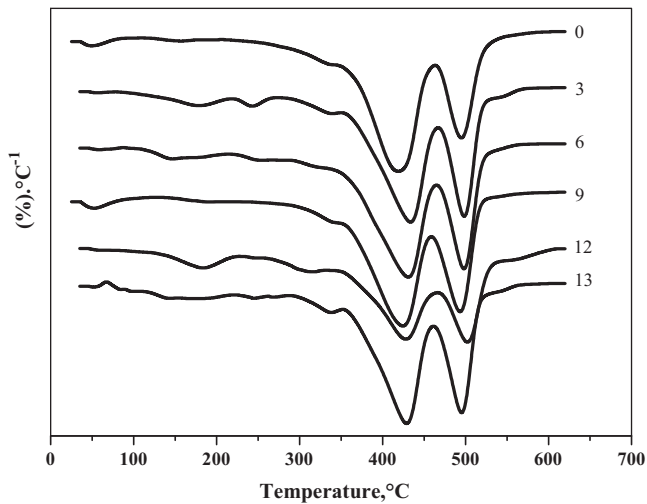


Fig. 7. DTG curves of PAM formed in solutions with different pH versus temperature.

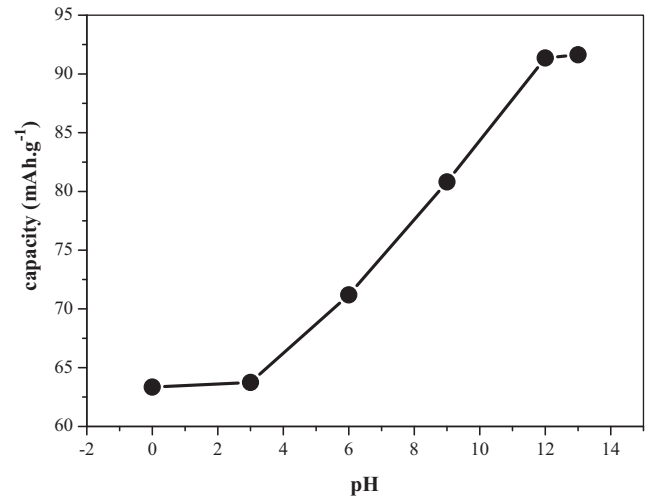


Fig. 10. Capacity of PAM formed in solutions with different pH.

capacity performance than tubular electrodes produced by the classical technology. This could be due to the amorphous character of the small particles of the PAM obtained in the alkaline solution.

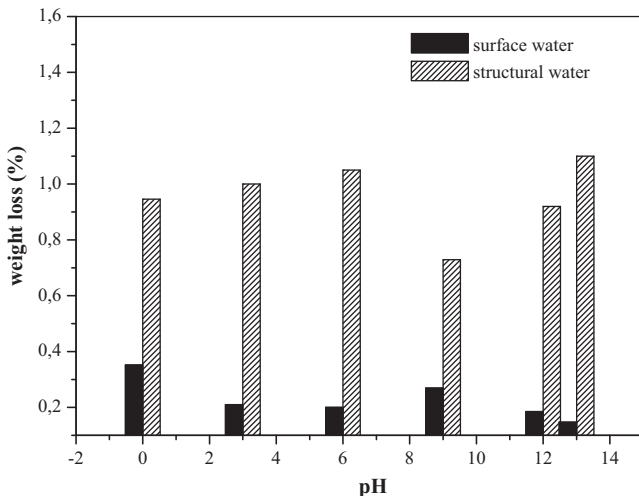


Fig. 8. Water content of PAM formed in solutions with different pH.

4. Conclusion

The preparation of PbSO_4 is an easy process and its use as a precursor for PAM electrodes is possible and could be introduced in the process of manufacturing of lead–acid battery plates. PAM electrodes with a controlled phase composition may be obtained by adjusting the pH of the electrolyte. The results showed that in alkaline solutions small particles of PAM are obtained giving high capacity performance.

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