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Short Communication

Nanostructured Lead Compounds in Electrode Materials of a Lead-Acid Battery

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The nanostructure and phase composition of the electrode material of lead-acid batteries, formed by chemical transformations with involvement of sulfuric acid solutions of various concentrations, water and carbon dioxide have been studied.

Keywords: Nano-sized, Lead sulfates, Lead-acid batteries, Scanning electron microscopy, Energy-dispersive analysis.

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1. INTRODUCTION

In the last years, interest in the use of nanodimensional materials at the production of lead-acid accumulators (LAAs) has increased. This is due to the fact that the particles size of the initial materials in many respects predetermines electrochemical activity of electrodes [1, 2]. However, as a rule, to make the electrode materials (EMs) of LAAs nanostructured special conditions or introduction of nanodispersed additives are required. For example, the production of nanodispersed composition with the help of lead oxide and carbon by pyrolysis of $Pb(NO_3)_2$ in starched gel [3], nanodimensional crystals of lead dioxide by anode oxidation of lead in melts [4] or solutions [5], nanostructuring of EM by introduction of nano-sized carbon additives [7] or polyaniline [8].

Nevertheless, often in practice at various stages of LAAs production both the natural and scarcely-studied formations of nanodimensional particles of lead compounds are known. This work considers conditions for the formation of those nanoparticles and their identification in the structure of EM.

2. PREPARATION OF MATERIALS AND INVESTIGATION TECHNIQUES

EMs were investigated on the basis of the electrode paste (EP) prepared from the highly-oxidized lead powder (77-79 % of PbO) and aqueous solution of H_2SO_4 (1,4 g/cm^3) with the following additives: carbon black, barium sulfate and an organic expander – for negative paste and red lead – for positive paste. These EMs were used for the production of electrode plates. Plates curing was carried out in a chamber at a relative humidity of air of more than 90 % and a temperature of 40 ± 2 °C, and drying – at a temperature of 70 ± 2 °C and a relative humidity of air of 10-15 %. After batteries formation and testing they were cut, active materials (AMs) were washed by water and dried up in the following atmosphere: O_2 – 0,5 %; CO – less than 0,5 %; CO_2 – 12,5 % at temperatures of 90 ± 5 °C. The EMs were studied with scanning electron microscopy (SEM), energy dispersive analysis (EDA) and X-ray phase analysis (XRFA).

3. RESULTS AND DISCUSSION

As a rule, the main components of EP prepared at temperatures below 60 °C are tribasic lead sulfate $3PbO \cdot PbSO_4 \cdot H_2O$ (3BS), lead oxide PbO and unoxidized metallic lead. Crystals of 3BS are characterized by layered structure, length of 1-5 μm and the cross section size from 0,1 to 1,0 μm [1, 7-9]. Depending on the manufacure method lead oxide can be identified as particles of a spherical or flaked shape from 0,2 to 80 μm in size [1, 9]. However, in some cases both in positive and negative EMs thin needle-like particles (Fig. 1) are found. Length of such particles which are chaotically located on 3BS crystals surface amounts to 1-1,5 μm, and thickness – from 20 to 95 nm.

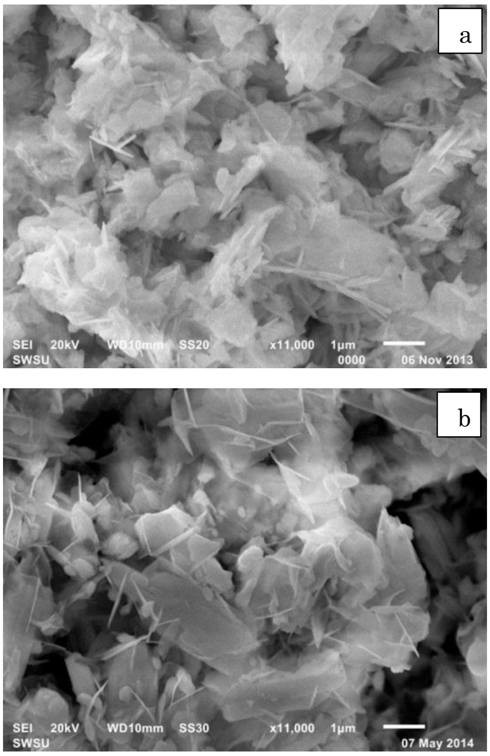

Fig. 1 – SEM-images of EPs after curing: a – positive paste with an additive of Pb_3O_4 (17 %); b – negative paste with an additive of carbon black (0,6 %), $BaSO_4$ (0,6 %) and an organic expander (0,2 %)

The reasons for the formation of needle-like nanocrystals are poorly understood, but the results of XRFA of EMs allow to identify them with hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$, which, at large contents, has an adverse effect on LAAs performance [1]. It is shown [10] that the formation of $2PbCO_3 \cdot Pb(OH)_2$ in positive paste during curing is facilitated by an additive of red lead.

Another compound having sizes of nanoscale region is monobasic lead sulfate $PbO \cdot PbSO_4$ (1BS), which is formed under certain thermodynamic conditions when EP is prepared and also at soaking of electrode plates before formation [1]. Research revealed that the linear sizes of 1BS crystals formed at soaking in sulfuric acid solutions during 180-200 min practically did not change. The intensive growth of the crystals occurred in the first 15-30 min of soaking when their length reached 10 μm and the sizes in cross section – from 0,2 to 2,7 μm (Fig. 2) and then practically did not change. It is reported [1] that the formation of 1BS crystals with a cross size of less than 1 μm is also typical at preparation of lead paste with a high ratio of sulfuric acid to lead oxide (H_2SO_4/PbO from 8 to 15 %).

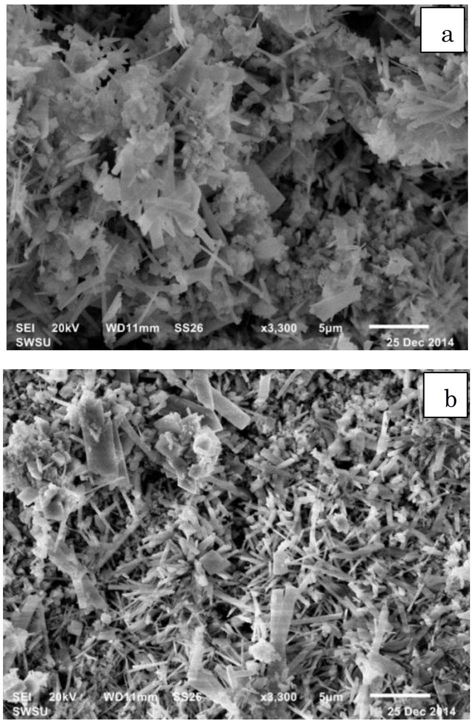

Fig. 2 – SEM-images of electrode pastes after 30 min soaking in H_2SO_4 electrolyte: a – 1,23 g/cm^3; b – 1,40 g/cm^3

Interesting, but so far poorly understood phenomenon of needle-like nanocrystals formation in the structure of spongy lead both after batteries formation and after their operation in various modes is observed. Such crystals have a small length (0,8-1,5 μm) and their size in cross section amounts to 80-100 nm (Fig. 3). Individual crystal formations contain small branches. With consideration for EDA evidence (Fig. 4) it is possible to believe that these nanodimensional crystals have the oxide-hydroxide chemical nature and their formation results from washing of negative electrodes in water and a subsequent drying at the elevated temperatures before SEM-analysis. However, it has not been established so far why the formation of nanodimensional lead compounds does not occur in all samples of negative active material analyzed. Probably it is connected with duration of washing of electrodes in water and their contact with air before drying.

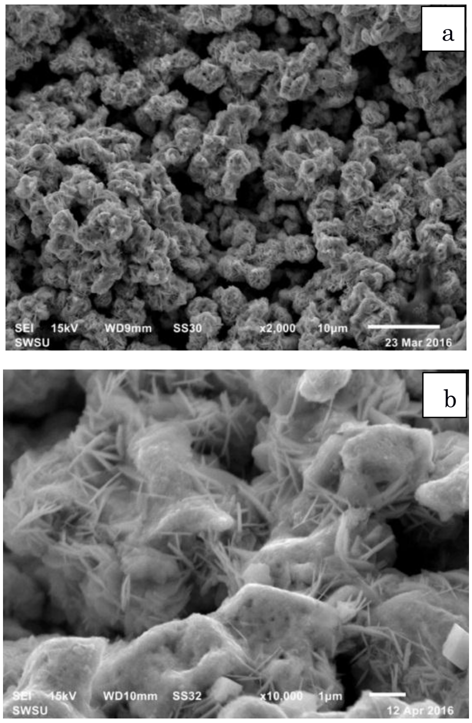

Fig. 3 – Negative active material after a battery testing in the cycling mode at various magnifications

Similar crystals weaved into a net structure were observed on separate sites of EM when cured at a temperature of 90 °C and processed by steam [11]. The authors explain the origin of that nanodimensional crystal structure with interaction of lead compounds with carbon dioxide and the formation of plumbonacrite $Pb_5O(CO_3)_3(OH)_2$ and hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$.

4. CONCLUSION

Considering the chemical nature it is possible to highlight two groups of lead compounds that appear in EM in the form of nanocrystals when conventional technologies without application of special methods of processing and introduction of nano-sized additives are used:

1) those that are formed in chemical processes with involvement of H_2SO_4, for example, $PbO \cdot PbSO_4$, at paste preparation at high acid content (H_2SO_4/PbO from 8 to 15%) or at soaking of electrode plates in solutions of H_2SO_4;

2) those that results from chemical reactions with involvement of water, oxygen, oxygen and carbon dioxide.

The crystal formations of the second group are, as a rule, characterized by the lower aspect ratio, and the reasons and regularities of their appearance and properties are poorly understood up to the present.

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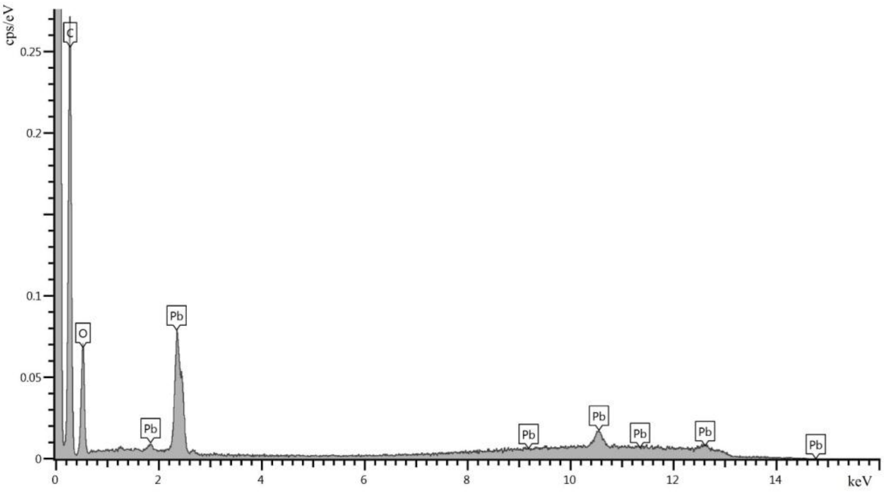

Fig. 4 – Distribution of chemical elements in negative active material

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