

Influence of Electroconductive Additives in the Positive Electrode Material on Morphology, Structure and Characteristics of the Lead-acid Batteries

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The influence of carbon black, red lead and polyaniline additives on the structure and functional characteristics of automotive lead-acid batteries has been studied. The mechanisms contributing to the formation both of lead dioxide by the introduction of these additives and of additional conductive nanostructured cross-linking channels in the case of polyaniline are described.

Keywords: Carbon black, Polyaniline, Red lead, Lead-acid batteries, X-ray phase analysis, Scanning electron microscopy, Nanostructuring of active material.

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1. INTRODUCTION

In operation of lead-acid storage cells (LASCs) compounds with dielectric properties can form. For example, at discharge the active material of electrodes is transformed into lead sulphate, which complicates current collection from active material and charging of a lead-acid battery (LAB) [1].

To remove undesirable effects related to the presence of compounds with dielectric properties and also to improve the electric characteristics of LABs in operation at partial-state-of-charge various electroconducting additives (EAs) [1, 2] are introduced into electrode material (EM).

The present work is devoted to studying behaviour of EAs of various chemical nature in the positive EM and their influence on the structure of formed active material (AM) and electrical parameters of LABs.

In experiments LAB with the following EAs in positive active material were investigated:

1. Low-active carbon black of P803 grade, which was obtained at thermal oxidation of liquid carbohydrate material;
2. Red lead of grade M-4 (92.8 % of lead orthoplumbate (Pb₃O₄) by weight) obtained by thermooxidation of lead oxide;
3. Polyaniline (PANI) of a needle shape of PA-N35 grade obtained from aniline and ammonium persulphate.

2. EXPERIMENTAL SECTION

EM was prepared according to conventional technology from highly-oxidized lead powder (76-78 % PbO) obtained by milling technique and aqueous solution of sulfuric acid with density of 1.4 g/cm³. Formation of LAB was done with pulsed modes of charge in water baths. To make comparable analysis EM was prepared without any additives that made it possible to establish the mechanisms responsible for the structural changes of electrodes and changes of LAB electrical parameters.

3. RESULTS AND DISCUSSION

Fig. 1 presents a structure of various electroconductive additives used in the experiments.

Fig. 2 shows influence of the electroconductive additives on nanostructuring of the positive electrode active material. The difference in the active material structure may be related to various mechanisms of the additives action.

When carbon black was added to positive paste the morphological composition of samples was not distinct in general from sample composition without additives and had tribasic lead sulfate 3PbO·PbSO₄·H₂O and lead oxide α-PbO as major components [2, 3]. During soaking of lead paste in H₂SO₄ solution before formation when there were no additives a reduction in lead paste porosity and a change in medium pH were observed [1]. Carbon black added to the positive lead paste had a critical effect on the AM formation only at LABs formation after soaking.

Carbon black agglomerates consisting of nanoparticles (Fig. 1a) at LASC formation causes the following physical, chemical, and electric processes [1]:

1. Adsorption of H₂SO₄ at the soaking stage in buffer regime [5];
2. Increase in electroconductivity in spite of the crystals of lead sulfate presence, which were formed at the soaking stage (Fig. 3, b-II), and also acceleration of positive electrode formation;

3. Both increase in electroconductivity at the initial stages and its reduction beginning from the second stage of formation (Fig. 3, b-III) due to the increase in porosity of AM because of oxidation of basic amounts of carbon black nanoparticles. It is this mechanism of carbon black effect that may be associated with an increase in the cycle life of LASC that was reported before in [2, 3].

Red lead represents a lead compound capable to interact with H₂SO₄ during paste preparation



However, the X-ray phase analysis (XPA) revealed that the amount of red lead Pb₃O₄ in the paste after curing was virtually equal to its initial content in the reactive mixture, i.e. the component practically did not interact with H₂SO₄.

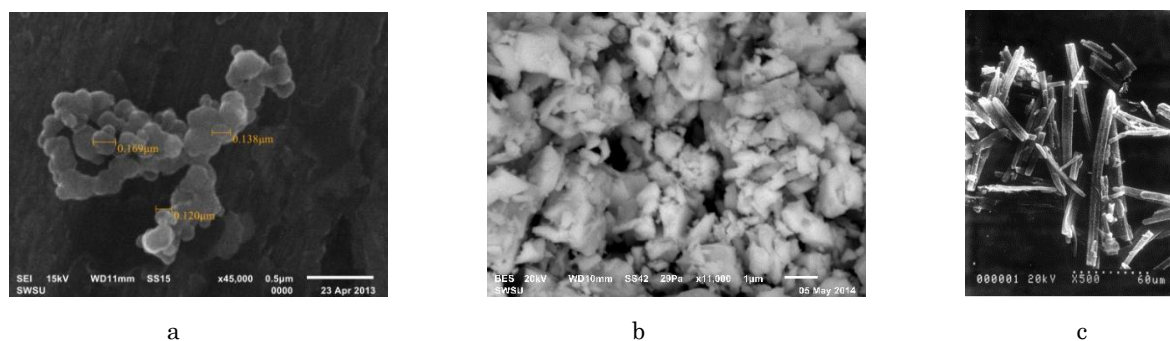


Fig. 1 – Structure of electroconducting additives: a – carbon black agglomerate consisting of nanoparticles, b – red lead, c – polyaniline

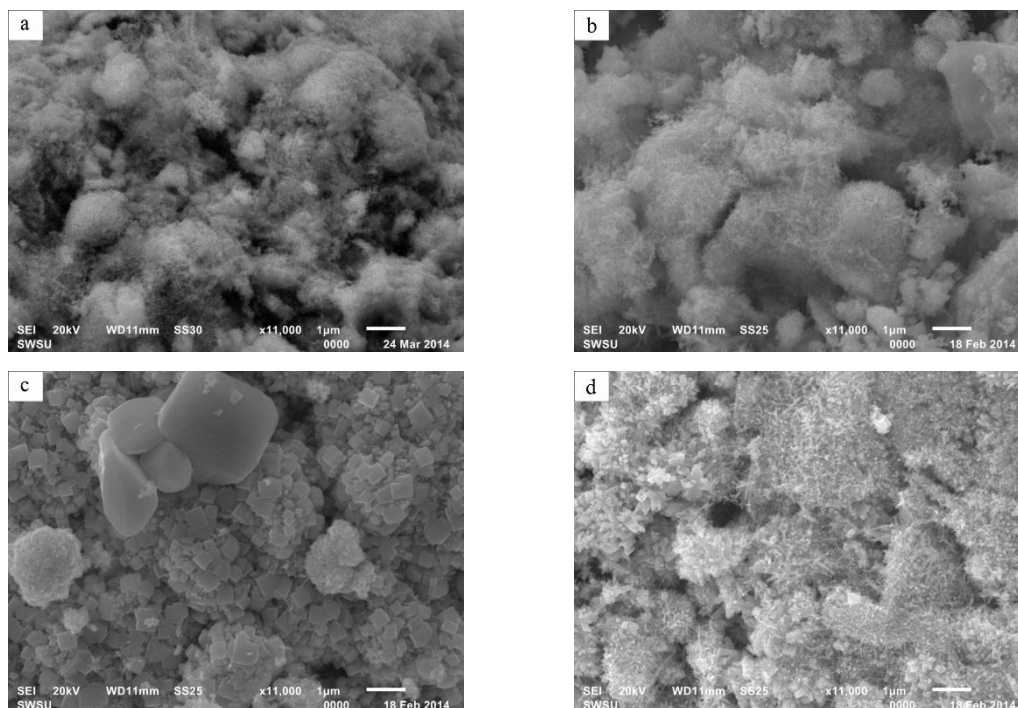


Fig. 2 – Nanostructure of positive active material containing various electroconducting additives: a – without additives, b – carbon black, c – red lead, d – polyaniline

In the case of lead paste with additive of Pb_3O_4 in reaction (1) two molecules of lead sulfate and one molecule of lead dioxide with molar volumes of 48.2 and 24.86 g/cm^3 , respectively, are formed [1]. Therefore, red lead with a molar volume of 75.3 g/cm^3 , in our view, was decomposed under the influence of electrolyte with an increase in volume and compaction of neighboring electrode materials. Such compaction was accompanied by the reduction of porosity in areas where particles of Pb_3O_4 were situated and, as a consequence, diffusion of electrolyte into the inner paste layers was slow (Fig. 4, b-II).

Lead dioxide is a semiconductor of *n*-type with specific conductivity of 11000 $\Omega^{-1} \cdot cm^{-1}$ [1]. Penetrating between the lead sulfate crystals like carbon does it favors the band formation with increased electric conductivity (Fig. 4, b-II). Accumulation of lead dioxide molecules that are the crystallization centers speeds up the AM formation process.

Another case is with PANI, which is a polymer with semiconducting properties and depending on medium may exist in various forms and has different properties (Fig. 5) [4]. For the experiment the most stable

protonated emeraldine form of PANI was used as needle-shape particles with an average diameter of 8 μm and a length of 60-80 μm whose specific conductivity, according to manufacturer, was up to 2.7 S/cm, and surface resistance – 4 Ω/cm^2 . Since amount of the lead powder was several times that of H_2SO_4 introduced into the reactor the reactive medium in general was slightly alkaline [1]. Under such conditions deprotonation of PANI may occur and its transition to the form with a reduced specific electroconductivity [4]. XPA of the lead paste with presence of PANI revealed that the major components of such paste were tribasic lead sulfate $3PbO \cdot PbSO_4 \cdot H_2O$ and lead oxide α -PbO.

In work [6] it is reported that 1-2 % PANI additive to the positive AM of LASC increases capacity up to 30 %. According to our data such needle-shape additive of PANI to the positive electrode material did not result in this increase (Fig. 6). These results may be explained by the processes given in Fig. 4a when the initial protonated form of PANI (Fig. 4, a-I) during the paste preparation turns into deprotonated form with dramatically less electroconductivity up to the soaking stage.

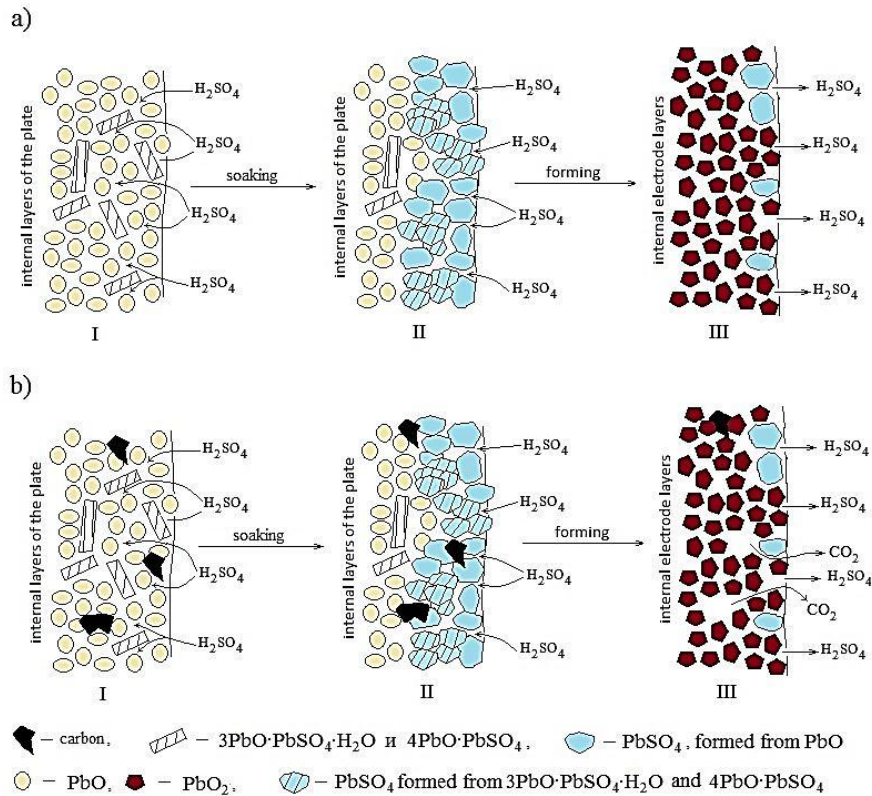


Fig. 3 – Stages of structural changes in forming LASC: a – without additives in the lead paste; b – with 1 % additive of carbon (I – dried lead paste after maturation , II –lead paste after impregnation in a solution of sulfuric acid, III – positive active mass after formation)

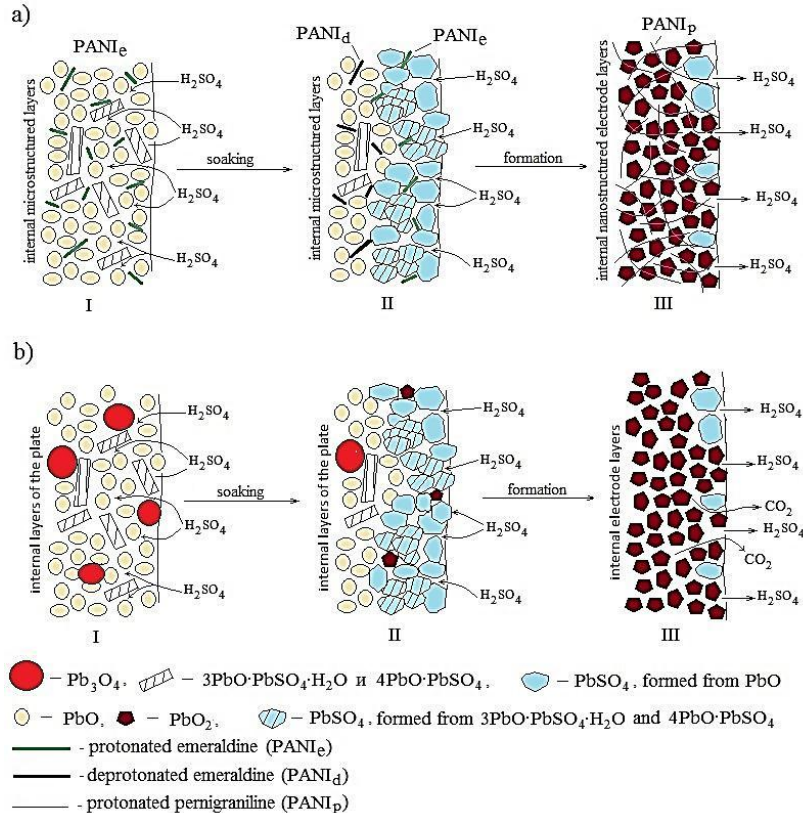


Fig. 4 – Stages of structural changes in forming LASC: a – with 1.1 % additive of polyaniline; b – with 16 % additive of red lead (I – dried lead paste after maturation , II –lead paste after impregnation in a solution of sulfuric acid, III – positive active mass after formation)

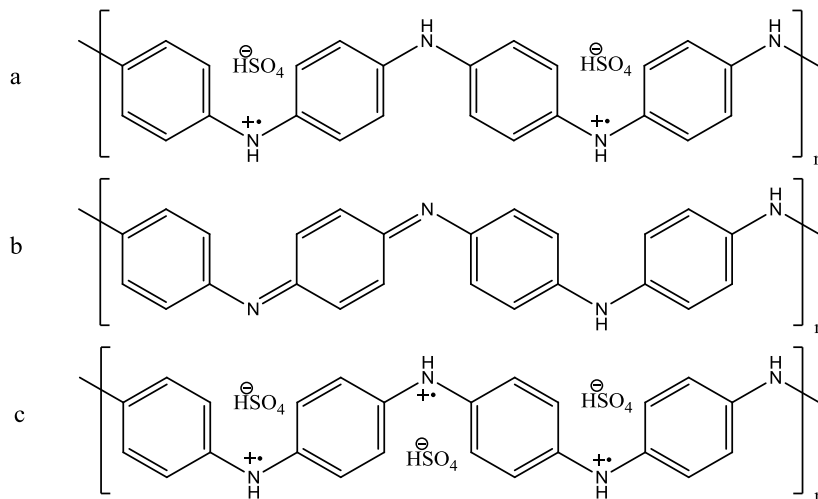


Fig. 5 – Structural formulae of PANI various forms: a – protonated emeraldin (initial), b – deprotonated emeraldin (alkaline), c – protonated pernigraniline (oxidized)

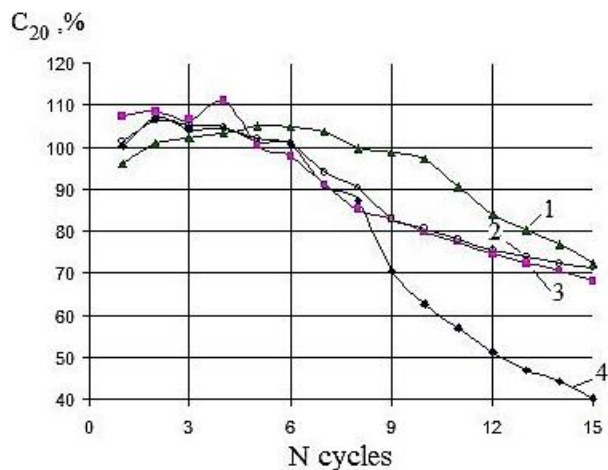


Fig. 6 – Dynamics of changes of AB rated capacitance with various additives at cycling (one cycle corresponds to 20 h and test by dry run current at $-18\text{ }^{\circ}\text{C}$): 1 – PANI (1.1 %), 2 – technical carbon (1 %), 3 – red lead (16 %), 4 – without additive

After that dissociated H_2SO_4 penetrates into the surface and middle layers of the electrode plate making medium acidic. The protonation-deprotonation of PANI

is a reversible process [4]. However, H_2SO_4 ions have no time to reach inner layers of the electrode plate and PANI situated in that layers is left in a deprotonated form with relatively low electroconductivity (Fig 4, a-II). When LAB is charged at first neighboring to the grid layers of the lead paste are formed. As the current flows within layers of positive AM the electrode potential increases gradually. In such conditions PANI is capable to oxidize and turn into pernigraniline form (Fig.4, a-III) with specific electroconductivity between protonated and deprotonated emeraldine [4] but nevertheless by several orders of magnitude less than specific conductivity of PbO_2 . In addition it was found that in the presence of polyaniline electric current promotes formation of plain crystals covered by a net consisting nanofibres of 35-45 nm thick.

4. CONCLUSIONS

Thus the investigations of EAs effect on functional characteristics of LAB have shown that carbon black additive enhances porosity of the positive AM and cycling life of the battery, red lead increases the initial capacity, PANI also increases cycling life of LAB up to two times due to the formation of current-conducting cross-linking nanostructure.

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