

Short Communication

Kinetic Characteristics, Phase and Structural Changes in Electrical Materials and Devices

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Electron-microscopic and X-ray studies have revealed that the ability of lead-acid storage batteries to adopt charge due to physico-chemical processes occurring in the lead paste and on the border of the “shunt-paste” depends dramatically on both the initial moisture content in the lead paste and keeping enhanced humidity in the exposure chamber for plates.

Keywords: Scanning electron microscopy, X-ray diffraction, Lead-acid batteries

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1. INTRODUCTION

Chemical composition, phase structure of both electrode composition and active material influence greatly service properties of lead-acid storage battery along with operating practice of formation [1]. Despite a long history of using these power sources the consistent analysis of the interrelation of the triad “composition-structure-properties” has not been made. In the paper, in development of earlier investigations on this problem [2], structural and phase changes that accompany the surface formation and charge formation on electrode plates and their influence on functional and electric characteristics of storage batteries have been studied by electron microscopic (SEM) (JEOL JSM6610LV) and X-ray techniques (X-ray study) (GBC EMMA, CuK α).

2. EXPERIMENTAL SECTION

Samples of lead mass were prepared according to the standard procedure from highly-oxidized lead powder – PbO (76 \pm 1 %) and sulfuric acid solution of 1.4 g/cm³ with mass ratio of compositions: 4.9 for positive and 4.5 % for negative sample. The negative active mass included 1 % carbon, barium sulphate and stretcher Vanisperse HT-1. Dried electrode plates were used to assemble storage batteries of rated capacity 60 A·h. The electrodes were manufactured by stamping and stretching method from Pb-Ca-Sn melt. Studied were three groups of electrode plates produced in several stages in a soaking chamber with humidity that was prepared by various ways:

- by steam generator – immediately after manufacturing with exposure during 22 h at a temperature of 45 \pm 5 °C and a relative humidity of 95-65 % and with consecutive drying during 14 h at a temperature of 65 \pm 5 °C and a relative humidity of 5-10 %;
- by wetting the floor with water before loading plates and spraying water with injectors – at analogous modes.

Studied were also electrode plates exposed during 2 h at a temperature of 25 \pm 1°C and a relative humidity of 80 \pm 2 %.

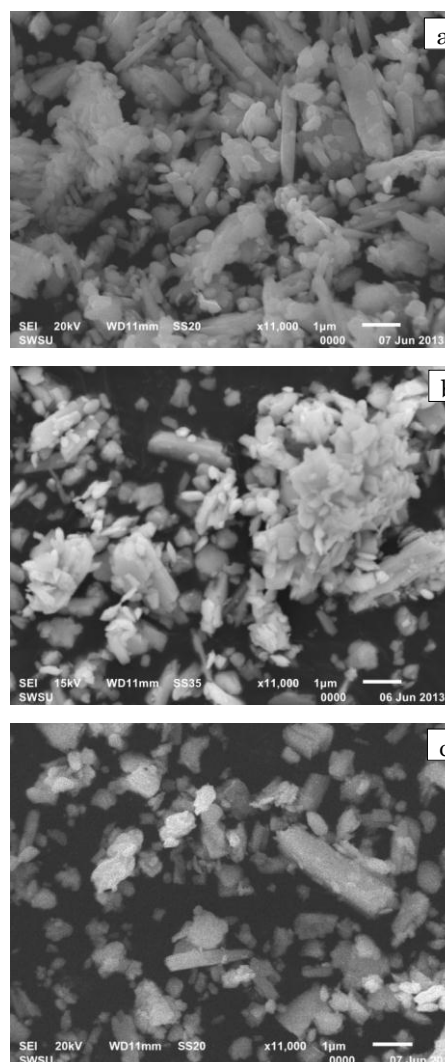


Fig. 1 – Paste structure of negative electrode plates after exposure and drying: a – the first group, b – the second group, c – the third group

3. RESULTS AND DISCUSSION

Investigations conducted by SE and X-ray techniques made it possible to establish structural differences in compositions of electrode pastes depending on the method and conditions of their exposures in a chamber. The paste of plates of the first group (Fig. 1a) presents a well-formed skeleton that consisted of oblong crystal particles up to 3 μm in length – according to X-ray technique tri-basic lead sulfate (3PbO·PbSO₄·H₂O) (Fig. 2) and smaller-sized particles of a rounded shape - lead oxide (μ-PbO) (Fig. 2). The composition of the second group plates (Fig. 1b) is of similar structure. However, there were unreacted free particles and aggregates the size smaller than 1 μm. The third group (Fig. 1c) is characterized by a chaotic location and a different size and shape of unstructured particles. In all samples studied low content of lead oxide in the form β-PbO was found (Fig. 2).

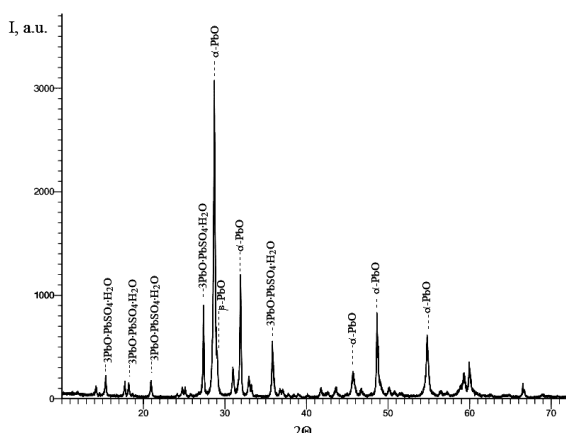


Fig. 2 – X-ray pattern of negative paste after maturation and drying

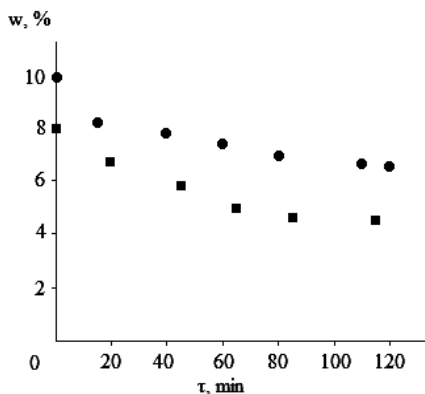


Fig. 3 – Kinetic curves of moisture content changes in positive (●●●) and negative (■ ■ ■) plates at their storage in the open air at a temperature of 25 ± 1 °C and a relative humidity of 80 ± 2 %

Those structural differences in shape, size, and relative position of the particles in the third group were due to changes in moisture content during 2 h, which is corroborated by kinetic curves (Fig. 3) from which the critical value of humidity reducing recrystallization level was determined [1]. The difference in kinetic regularities of moisture evaporation from negative plates is explained by its lower initial content and existence of auxiliary additives in electrode pastes.

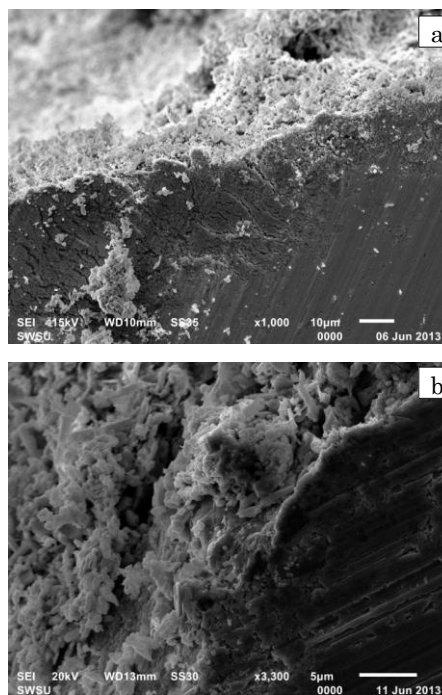


Fig. 4 – Structure of transverse cuts of “shunt – paste” for various ways of exposure of electrode plates: 1 – the first group; 2 – the third group

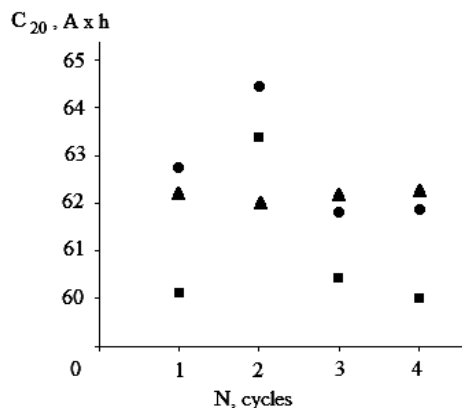


Fig. 5 – Dynamics of nominal capacity changes for storage batteries according to cycles: (●●●) – the first group, (■ ■ ■) – the second group, (▲ ▲ ▲) – the third group

To analyze the state of the transitional layer “shunt – paste” transverse cuts were prepared with SEM. As SEM images show (Fig. 2) there exists an interphase transition in contrast – from light to solid dark, and in structure – from friable, which corresponds to a corrosive layer (to 30 μm), to uniform –lead-calcium alloy of the shunt. In the surface layer of the lead paste of the third group electrode plates many microcracks (on the order of 1 μm) and detachments appeared (Fig. 4b).

To establish functional and electric characteristics of storage batteries tests were conducted the results of which are shown in Fig. 5. It was found that the samples of the first group at the second stage of “charging-discharging” had the maximum nominal capacity, the maximum of which reached 64.4 A·h, whereas for the third group – 61.9 A·h, which is in line with the analysis of phase and structural changes. Lower value of the nominal capacity for the third group’s batteries was

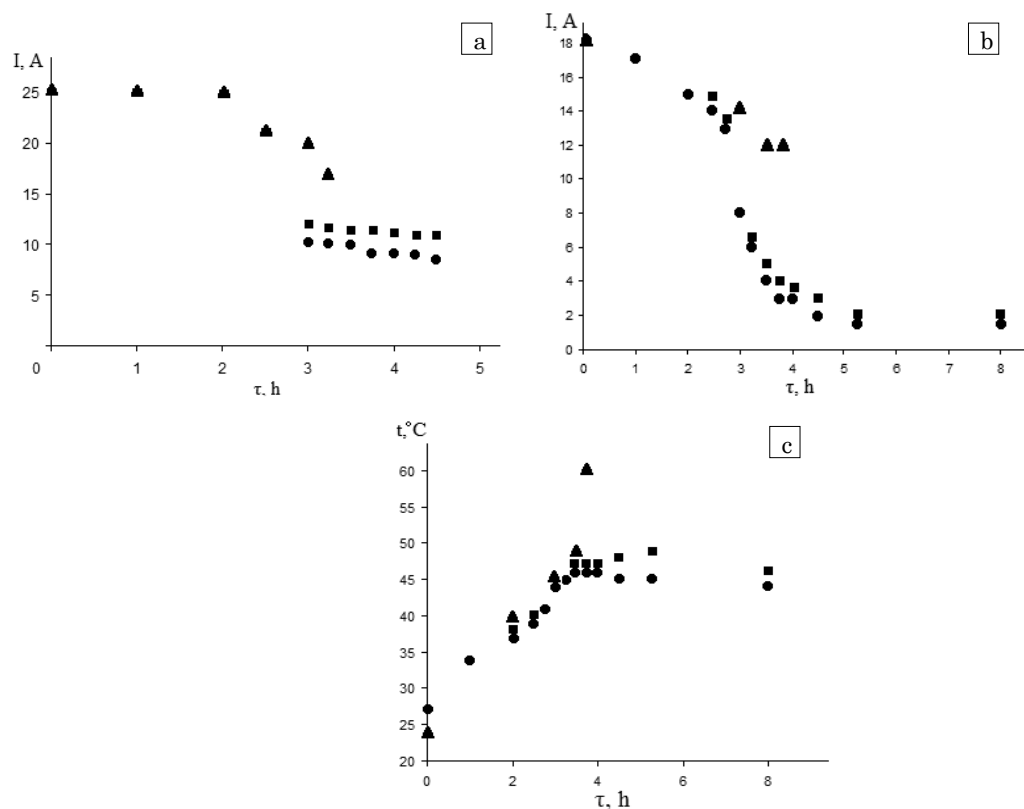


Fig. 6 – Kinetics of current changes in samples of various groups: (●●●) – the first group, (■■■) – the second group, (▲▲▲) – the third group; ($25 \pm 1^\circ\text{C}$ without cooling, 16 V at batteries charging); a – $I_{max} = 25$ A; b – $I_{max} = 18$ A; c – temperature changes as for b-case

obviously due to significant inhomogeneity of the surface structure (Compare Fig. 4a and Fig. 4b).

The fact that the capacity of the third group's batteries was constant is indicative of a low activity of the charge-forming electrode surface.

Charging capacity of batteries was checked when these charged at a constant voltage of 16 V after 20-h discharging. In the samples of the first group the electrodes have the lowest transitional resistance of "shunt-active mass" and hence, electric energy losses to overcome internal resistance were minimal.

The distinction among internal resistances was established by studying the kinetics of decreasing resistance (Fig. 6a, b), which is also supported by an abrupt increase in electrolyte temperature for samples of the third group. Two hours of discharging the current

value remained constant and was equal to 25 A; electrolyte temperature of the samples of the first and second group amounted to 40°C , while of the third group's samples amounted to 45°C , which is obviously due to dramatically higher resistance.

4. CONCLUSIONS

Thus, functional and electric characteristics of storage batteries critically depend on physico-chemical processes occurring within the lead paste and on the border of the "shunt-paste", which are most dependent on both the initial moisture content in the lead paste and keeping enhanced humidity in the exposure chamber for plates.

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