

Microstructural Barrier-locking Formation Mechanism of Dispersed Current-forming Components of Current Power SupplyA.P. Kuzmenko¹, E.A. Grechushnikov¹, V.A. Kharseev¹, M.B. Dobromyslov²¹ South-West State University, 94, 50 let Oktyabrya Str., 305040 Kursk, Russia² Pacific National University, 136, Tikhookeanskaya Str., Khabarovsk, Russia

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The influences of carbon additive on the structure and phase composition of the positive electrode material as well as technical and operational characteristics of starter lead-acid batteries have been studied. The mechanism of interaction of carbon additives with lead powder is proposed. It is established that the presence of carbon in the positive electrode material increases the lifetime of lead-acid starter batteries, as confirmed by tests.

Keywords: Current power source, Lead-acid batteries, Carbon additives, Positive electrode material, Negative electrode material, Dispersed current-forming components.

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1. INTRODUCTION

In electrical industry, for many years various additives are used that make electric parameters of batteries higher and also influence on the structure and phase composition of the electrode active material. One of such additives is carbon in various forms. A lot of studies [1-4] are devoted to the use of carbon-bearing additives for positive material. It is reported that addition of carbon to electrode material serves to increase its electroconductivity and as a result to accelerate the process of positive electrode formation. Carbon is unstable during a positive electrode formation and after formation (battery charging) more than a half of the additive is oxidized to form carbon dioxide.

The goal of the work was investigation of structural and phase changes occurring during preparation of positive electrode material containing carbon black additive and without the one and influence of these changes on electric parameters of batteries.

2. EXPERIMENTAL SECTION

Samples of positive electrode material were studied for which highly-oxidized lead oxide powder (77-79 % PbO) was used. The powder was prepared by milling technique. For paste preparation aqueous solution of sulfuric acid (1.4 g/cm³) was used. Sulfuric acid and lead oxide powder were used in ratio of 4.9 % (weight). As a carbon additive carbon black of grade P803 was used, which was obtained by thermo-oxidative decomposition of liquid hydrocarbon material. The ratio of the additive to the lead oxide powder weight was equal to 1 %. For comparative analysis the positive electrode material was prepared without carbon black additive.

Structural peculiarities and the changes in the surface properties of electrode materials were investigated by using scanning electron microscope (SEM) JEOL JSM-6610LV (SEM, 20 kV, up to 10000 \times). Phase analysis (XPA) of samples was carry out with the use of powder diffractometer EMMA (60 kV, 80 mA, Cu K α , 1.54 Å).

3. RESULTS AND DISCUSSION

It was established in analyzing the prepared paste composition that carbon black made it less plastic and the reduction in density from 4.00-4.02 g/cm³ to 3.91-3.95 g/cm³ was observed.

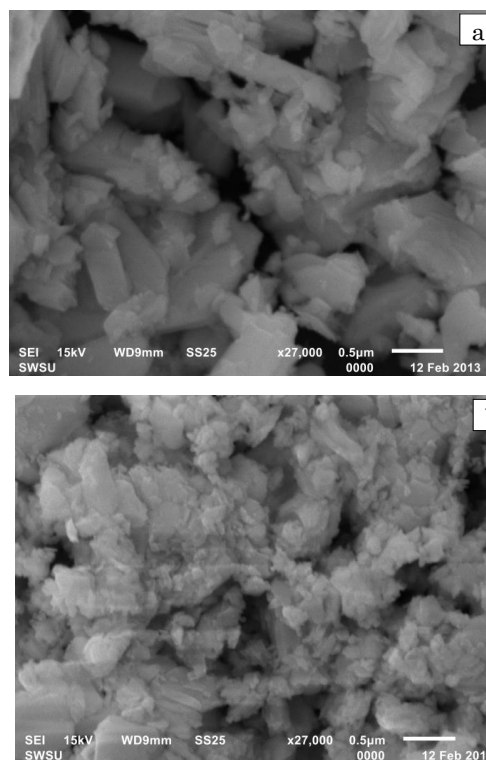


Fig. 1 – Structure of dried paste positive after curing: a – with the addition of carbon black, b – without adding carbon black

Fig. 1 shows SEM images of dried pasta after curing. On these Fig is not to see particles of carbon black. This is probably due to the fact that during the formation of lead sulfate crystals separated carbon agglomerates into smaller particles. Also it should be noted that paste containing carbon additive consists of planar crystals with a clearly pronounced form oblong

up to 2 microns. The crystals $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, surrounded by lots of smaller particles round, which is likely to include lead oxide. In this crystal structure there is a large number of pores. The pasta which did not contain an additive of carbon after maturation has turned into a structure consisting of a smaller flake particles of indefinite shape, which are formed in dense layers.

Data of X-ray phase analysis (XPA) indicates that irrespective of identical preparation conditions of the electrode material with carbon black additive had higher content of tribasic lead sulfate $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ and lower content of lead oxide $\alpha\text{-PbO}$ (Fig. 2). Irrespective of carbon availability lead oxide in the form $\beta\text{-PbO}$ was also observed. The increase in $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ content in the positive paste with carbon black probably have a bearing on features in interaction of carbon aggregates with lead oxide powder.

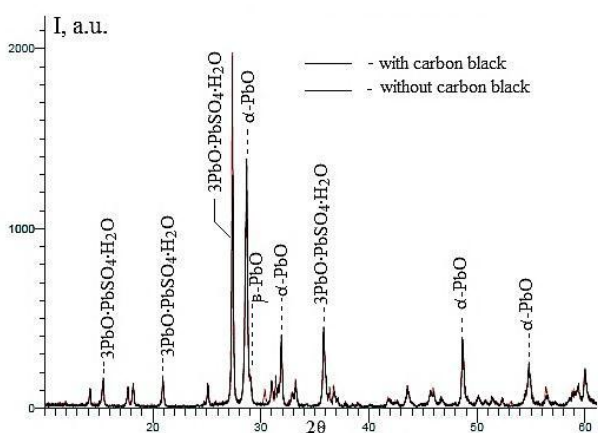


Fig. 2 – XRD positive paste phase composition 1 hour after preparation

It is well known that diffusion of sulfate-ion SO_4^{2-} to the surface of lead oxide particles [4] is a limiting stage in creation of lead sulfate from lead powder. This is explained by the fact that solubility of lead oxide under conditions of paste preparation in a weakly alkaline medium is very low; therefore, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ is produced only at the surface of lead oxide particles. Thus, free active surface of lead oxide is blocked by strong sediments of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ that is not able to be removed in paste mixing conditions.

Nevertheless, the carbon particles present a barrier for blocking the lead oxide surface. Due to features in carbon black production its surface has various functional groups and in contact with water or aqueous solutions of mineral acids specific physico-chemical processes may occur, particularly, adsorption and chemisorption of oxygen, water, acid, Fig. 3a-c. In this way formation of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ crystals will take place, which have a reasonably large molar volume, over three-times larger than that of lead oxide [4].

Formation and growth of such crystals under the surface of a carbon particle cause eventually its detachment. Together with carbon from the lead oxide powder particle surface crystals of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ will also be detached. As a result of these complex physico-chemical transformations the surface of lead

powder becomes free from blocking sediments of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (Fig. 3c). Thus the surface of the lead oxide powder particle is capable to react with sulfate ions and form an extra mass of tribasic lead sulfate $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$.

Also, XPA of electrode materials without carbon additive revealed that after curing and drying some amount of hydrocerussite $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and monobasic lead sulfate $\text{PbO} \cdot \text{PbSO}_4$ was formed.

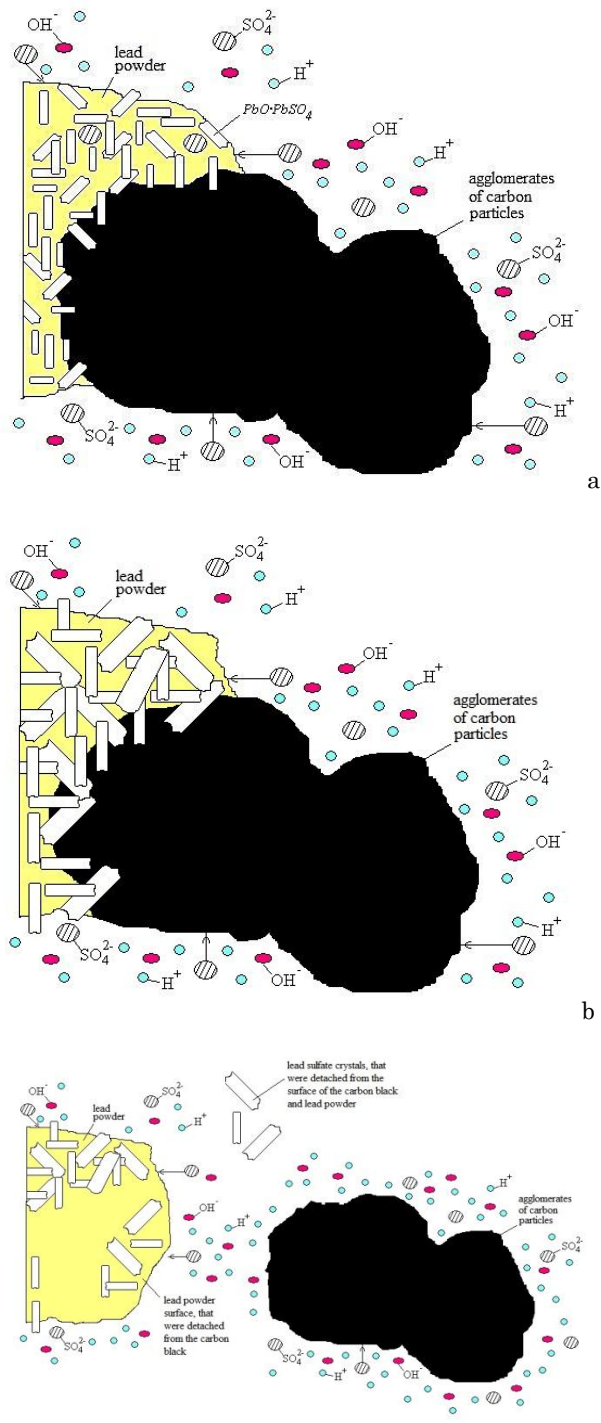


Fig. 3 – The interaction mechanism of carbon black with lead powder

4. CONCLUSIONS

Observed increase in content of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ in a positive material due to additions of carbon black may be related to the feature in interaction of carbon aggregates with lead oxide powder dictated by barrier-blocking mechanism characteristic of carbon compounds.

Longer cyclelife of lead-acid batteries may be due to the fact that in dried positive plates without carbon additive undesirable compounds such as $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and $\text{PbO} \cdot \text{PbSO}_4$ are formed. Their availability may cause shedding of the positive active mass during batteries manufacturing and operation.

REFERENCES

1. Petr Baca, Karel Micka, Petr Krivik, Karel Tonar, Pavel Toser, *J. Pow. Sour.* **196**, 3988 (2011).
2. D. Pavlov, P. Nikolov, T. Rogachev, *J. Pow. Sour.* **196**, 5155 (2011).
3. D.A.J. Rand, *Valve-regulated Lead-acid Batteries. First Ed.* (Elsevier: 2004).
4. D. Pavlov, *Lead-acid Batteries: Science and Technology. First Ed.* (Elsevier science: 2011).