

The New Direction for Development of Production of Lead Acid Accumulators

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Abstract: The brief description of the well-known paste technology of production of positive and negative electrodes of Lead Acid Accumulators (LAA) is presented, the shortcomings thereof were specified. It was suggested to use in the production of lead-acid accumulators the new technology of manufacturing the positive and negative electrodes allowing to significantly reduce the accumulator manufacturing cycle to simplify the technology, significantly reduce the capital and production costs, solve the main production ecological issues related to pollution of the process environment. The results of the comparative analysis of the positive surface electrodes samples and electrodes produced using the paste technology were presented. The study is meant for engineers and technical specialists working in the area of design and production of lead-acid accumulators.

Key words: Accumulator, electrode, surface electrode, paste, paste technology, environmental issues

INTRODUCTION

By selection of electrochemical systems for industrial production of accumulators of various application except for the electrical parameters one should also take into account a number of criteria that also determine the practicality and possibility of the production design: the value of the capital and production costs, degree of safety when in operation, the scope of the scheduled works on maintenance of Accumulator Batteries (AB), environmental compatibility of production, possibility and cost of disposal of the waste AB, degree of the industry readiness for the new production, experience in operating the new electrochemical system, etc.

The integrated analysis of the main consumer-oriented characteristics of different electrochemical systems showed that the Lead-Acid Accumulators (LAA) remain rather competitive. This is confirmed by the fact that they still cover 70-80% of the market for electrochemical power sources (Kamenev, 2005).

The paste technology used in the production of lead-acid accumulators includes such operations as: preparation of lead alloys for terminals, grid casting, preparation of the oxidized plumbum dust, paste, pasting of grids, drying, etc., that significantly complicate the production, require employment of substantial capital and production costs as well as create intractable environmental issues. That is why an integrated solution

of the problem is needed to be found that will be related to the design of the new technology of electrode production that would exclude the manufacturing processes that can be hazardous to a human and would allow producing accumulators featuring the improved specific energy characteristics. The new technology shall ensure the corrosion resistance of electrodes (Misra, 2012; Kamenev *et al.*, 2014; Wagramyan and Solovyeva, 1960; Razina, 1982).

The existing technology of production of surface electrodes (of plate type) where the positive electrode paste is produced by electrochemical oxidation of the lead terminal surface allows to significantly simplify production of positive electrodes however, they come short of their specific electrical specifications as compared to the paste electrodes since the sufficient thickness of the paste layer cannot be achieved.

TEST PERFORMANCE PROCEDURE

In order to get the desired thickness of electrode paste layer the authors conducted studies allowing to produce the surface electrodes by the electrochemical oxidation of the lead terminal base ensuring the desired thickness of the paste layer (KNOW-HOW). The analysis of the existing surface electrodes (of the plate type) showed that the most significant shortcomings of such positive electrodes are determined by inception during the paste electrochemical oxidation process of the subsurface

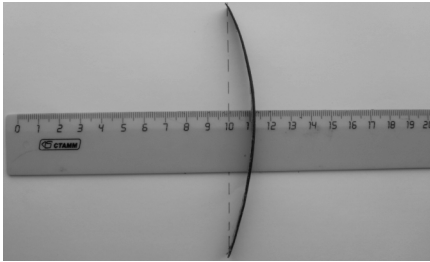


Fig. 1: Dependence of the subsurface stress force acting in the Paste (P) on the thickness of the coating layer (d_M)

stresses the value of which increases along with the increase in the paste thickness. The specified effect was proved experimentally.

Figure 1 presents the lead sample shaped from one side (the paste thickness makes about 0.9 mm), the active coating appears on the convex side of the sample which demonstrates the action of the forces stretching the deposit.

The value of the subsurface stress force may be approximately calculated according to the Stoney's formula (Wagramyan and Solovyeva, 1960):

$$p = \frac{4}{3} \cdot \frac{E' \cdot d_T^2 \cdot z^2}{d_{oc} \cdot l^2} \quad (1)$$

Where:

- p = The subsurface stress force (N/cm²)
- E' = Module of the base elasticity (N/cm²)
- d_T = Thickness of the electrode base (cm)
- d_{oc} = Deposit thickness (cm)
- z = Electrode deflection (cm)
- l = Electrode length (cm)

Table 1 shows how sample deflection changes during the process of electrochemical formation depending on the paste thickness.

According to the experimental data as to deflection of the 10 cm long sample (Table 1) the diagram of dependence of the subsurface stress force operating in the paste on the average thickness of the paste layer obtained by means of electrochemical oxidation of the lead terminal was made (Fig. 2).

Figure 2 at the paste thickness of about 0.5 mm the subsurface stress forces reach the value over 100 N/cm² which is apparently sufficient for the detachment of the coating from the terminal surface. The loss of the mechanical and electric contact is observed already at the paste thickness exceeding 0.3-0.4 mm. As the result of this by further increase of the paste thickness the peeling thereof takes place. Therefore, it does not seem to be

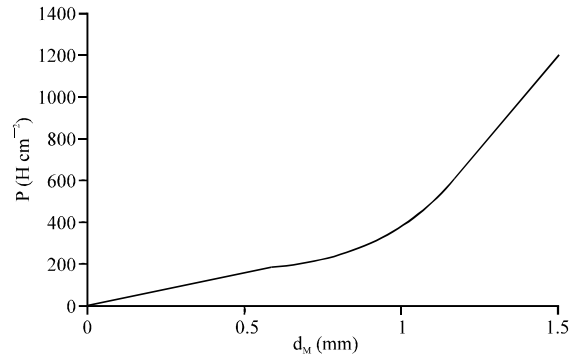


Fig. 2: The effect of the subsurface stress forces by electrochemical paste formation

Table 1: Dependence of the sample deflection on the thickness of coating during the electrochemical formation process

Duration of the formation process (h)	Paste thickness (mm)	Sample deflection Z (mm)	Nature of the subsurface stress forces
0	0.00	0.0	Initial condition
5	0.37	0.7	Low effect
15	0.50	4.7	Stretching
20	0.70	7.1	Stretching
24	0.90	10.0	Stretching

possible to get a thicker paste layer. The ratio between the coating weight and the electrode weight is low and consequently, such electrodes feature low specific characteristics.

According to Wagramyan and Solovyeva (1960), increase in the formation current density results in increased density of deposits obtained electrochemically. Rise of the temperature of electrochemical deposition process usually reduces the deposit strain however, the analysis of the temperature impact on the subsurface stress forces in the deposited coating makes no sense in the case with LAA since at the temperature over +30°C the process of the electrode formation is low-efficient because of the increased intensity of the competing processes.

The effect of different additives introduced to the electrolyte on the subsurface stress force is of theoretical and practical interest to us. As was shown by Razina (1982), in order to improve the quality of the PbO₂ deposit the surface-active agents were used: p-toluene sulfonamide, hexa-ethylene-oxylaurine ether, gelatin, OP-7, etc. However, this regards the lead dioxide deposits obtained by means of electrochemical deposition from the salt solutions (for example, Pb(NO₃)₂ on the different bases. By making of the positive electrode for LAA such solution will be rather low-efficient since formation of the active material from the surface layer of the lead terminal takes place at the high oxidizing potentials at which most of the surface active agents will be destructed at the very beginning of the formation process.

The rate of corrosion of the positive electrode terminal during the LAA depends heavily on the screening effect, i.e., on the thickness of the active material layer covering the terminal (Feliu *et al.*, 1972). Thus, in the existing surface electrodes with the thin layer of active material the rate of the terminal corrosion will be remarkably higher. As the result, the desired service life of the LAA using the positive surface electrodes is attained by means of increasing the initial thickness of the lead terminals to 10-12 mm which does not allow achieving high specific electric characteristics.

It should be noted that in the LAA with the positive surface electrodes of the plate type the technology of designing of the negative surface electrodes has not been implemented and consequently, the issue of the complete exclusion of use of the oxidized lead powder by LAA production has not been solved.

Taking into account the experimental results described earlier, researchers have designed the method of production of the surface electrodes of new type that are equal to the modern paste electrodes in their specific characteristics and at the same time significantly simplify the technology and reduce the capital and production costs. This technology allows to concurrently solve the environmental issues of LAA production.

In the surface electrodes of the new kind the weight of the active material may make not <50-70% of the electrode weight which is typical for the paste electrodes. At the same time, the rate of the terminal corrosion is reduced and it is not necessary to increase its thickness in order to achieve the desired service life. To get the desired thickness of the active material by means of electrochemical oxidation of the lead terminal surface it is necessary to neutralize the effect of the subsurface stress forces in the material breaking the mechanical and electric contact thereof with the terminal. In order to compensate the effect of the subsurface stress forces it was suggested to perform the process of the electrochemical electrode formation under the pressure directed perpendicularly to the surface of the active material formed (Konovalov *et al.*, 1994). In the experiments performed the pressure on the active material formed was applied with the use of the elastically stretching porous shield made from the corrosion-resistant material in which the shaped lead terminal was placed. The test terminals were made from the C1 lead in the shape of a flat sheet (plate) and in the shape of a round rod. Shaping was carried out in sulfuric acid electrolyte according to the procedure specified by Ovari and Karbasov. The cyclic charging-discharging was carried out in the sulfuric acid solution with the density of 1.28 g/cm³ at the temperature 20-22°C. The specific electric performance was calculated on the basis of the results of measurements performed during the 5th charging-discharging cycle at the current

of the 20 h mode of charging to the final potential of the positive electrode 1.95 V against the reference cadmium electrode. Electrodes were charged by the current equal to 0.1 capacity of the 10 h mode of charging to the electrode potential stability. Long-term cycling was performed for accumulators the capacity of which was limited by the positive electrode.

RESULTS

Certain characteristics of the test positive surface and existing electrodes are represented in Table 2. As it appears from the data of Table 2 the positive electrodes obtained according to the new technology are vastly superior to the existing surface electrodes in the specific capacity and have smaller specific lead consumption.

The experimental electrode samples are equal to the industrial paste electrode in the specified characteristics. The XRD-analysis of the active material of the experimental electrodes after performance of 5 and 300 charging-discharging cycles showed that in general the phase composition of the material corresponds to the β -modification of the lead dioxide. The active material porosity made 50-51% and the specific surface area 1.9-2.5 m²/g.

The efficiency of the experimental electrode weight is confirmed by the relatively high material utilization ratio. At the average material thickness of 2.6 mm it makes (%):

- The 20 h mode -56
- The 5 h mode -49
- The 1 h -37
- The 5 min mode -19

The results of the study show that by increasing the thickness of the active coating it is possible even at the rather thin terminal to get the desired electrode service life and significantly improve its specific electric characteristics. At the same time the coating weight makes 50-70% of the electrode weight.

Researchers have investigated the possibility of production of the negative electrode using the powderless technology. For this purpose the surface positive electrode (active material thickness 2.4-2.6 mm) was formed as a negative electrode to the potential minus 0.2 V as compared to the reference cadmium electrode. The specific electric characteristics of negative electrodes were close to the relevant values of the surface positive electrodes. By long-term cycling their capacity and therefore, the internal resistance determining the self-discharge remained almost the same. This is why the question about the total life of the negative surface electrode remains open. The methods of increasing the

Table 2: Technical specifications of the test positive surface and existing electrodes

Electrode specification	Average thickness (mm)		Specific capacity (Ah kg ⁻¹)	Specific lead consumption (g Ah ⁻¹)
	Active material	Terminal		
Terminal-flat sheet, formation under pressure	2.8	1.1	62	14.6
Terminal-round rod, formation under pressure	2.6	Diameter 1.2	83	11.2
Existing surface electrode (I-1)	0.5	11.5	13	60.0
Paste electrode (ACC 6MTS-9)	1.8	1.8	56	16.2

Table 3: Technical specifications of the accumulator within R20 dimension

Parameters	Values
Voltage (V)	2.0
Rated capacity of the 20 h discharging mode (Ah)	2.0
Life time, charging-discharging cycles	Over 200
Specific energy (Wh kg ⁻¹)	32
Daily self-discharge (%)	0.1-0.2
Weight (g)	125
Dimensions (mm):	
Height	61
Diameter	32

Table 4: Technical parameters of the test and commercial sample of the accumulator ABN-72

Parameters	Parameter value		
	Test sample	ABN-72	Remark
Voltage (V)	2	2.0	-
Rated capacity of the 10 h discharging mode (Wh kg ⁻¹)	83	72.0	The 5th cycle
Daily self-discharge (%)	0.2	0.7	-
Life time	Corresponds to the life time of ironclads	400.0	The test samples were tested using the accelerated procedure*

*Accelerated testing procedure: number of the charging-discharging cycles at the temperature +60°C during 38 h -11; number of the regular charging-discharging cycles according to the standard procedure (Gost, 1999) for fixed accumulators -100

LAA performance by means of the grid configuration were investigated for the purpose of reduction of accumulator internal resistance and dependence of the accumulator internal resistance on the state of discharge (Nakhaie *et al.*, 2014; D'Alkaine *et al.*, 2009). It is researchers opinion that these techniques do not allow to fundamentally increase the specific energy characteristics of accumulators.

The studies performed by the authors allowed designing, producing and testing a few test LAA samples with the surface positive and negative electrodes their main characteristics are presented in Table 3 and 4.

Comparison of the technical specifications of this accumulator with the foreign compatibles confirms that the specified sample corresponds to the international performance standards. The undeniable technical advantage of this accumulator is the low lead fill (17 g Wh⁻¹) and relatively high specific energy (32 Wh kg⁻¹).

Table 4 represents some comparative technical specifications of the test accumulator against the surface electrodes produced within dimensions of the commercial accumulator ABN-72. During the tests the capacity remained almost the same.

The capacity of the test sample was also confirmed during testing at the factory test station. Taking into account that the ironclad surface electrodes were used we may hope that their life time will make not <1000-1500 charging-discharging cycles. Such power sources may become widely used as fixed and exide accumulators. The use of pure lead (C0, C1) for production of surface electrodes makes designing of the sealed (maintenance-free) accumulators significantly easier which allows to substantially reduce the labor intensity in the course of operation thereof.

CONCLUSION

The designed technology of the surface positive and negative electrodes of the new kind allows significantly optimizing the production costs and solving the main environmental issues determined by the led-caused pollution of the working and adjacent areas.

The new technology of production of positive and negative surface electrodes allows to substantially reduce the lead filling, excludes the use of additives by production of terminals and allows to reduce the manufacturing cycle and accumulator cost by 40-60%.

LAA with electrodes made with the use of the new technology may find application in the fixed, oxide and other current sources of various purposes

The new technology of production of LAA with surface electrodes may be easily mastered by any accumulator plant.

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