Storage batteries for submarines (extended abstract)*

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The submarine storage batteries play an important role as the main source of electric power on diesel-electric submarines and as a reserve source on nuclear submarines. From the very beginning of submarines development and up to now lead storage batteries are most widely used there as chemical sources of electric power. For various reasons nickel–cadmium and silver–zinc batteries are not so widely spread.

Lead storage batteries are characterized by high-reliability, cost-efficiency, basic-materials availability, and well-developed production technology. The significant achievements of the recent years in the increase of the energy specific density deprive other more energy-consuming electrochemical systems of their advantages.

The development of lead storage batteries for submarines differs in some respects from the development and manufacture of common starter and traction batteries.

The considerable height, reaching 1000 mm and more, leads to nonuniform vertical current distribution in electrodes, i.e., to substantial reduction of the active material utilization factor in the lower portion of the electrodes, and high ohmic losses in the current taps. The nonuniformity of current distribution along the electrodes height, as well as the gravitational phenomena result in the electrolyte segregation density along the accumulator depth leading to increased self-discharge and electrodes passivation.

Current loads in short-discharge modes reach 10 000 A and more, thus leading to battery heating and the necessity for intensive heat abstraction.

The fact that the volume occupied by storage batteries in submarines greatly determines their displacement and, consequently, their speed makes it necessary to achieve maximal volumetric specific energy. The necessity to utilize (afterburn) hydrogen released from the battery during submerged dieseling requires minimal rates of gassing.

The modern submarine storage batteries are to be highly shock and vibration resistant.

Let us dwell upon the basic methods providing the implementation of the aforementioned requirements.

High-specific electrical characteristics are achieved, in the first place, by increasing the active material utilization factor. In modern designs this factor value reaches 60 to 63% in prolonged modes of the battery's operation. Such high values of active material utilization factor are based upon the use of highly-porous positive electrode pastes possessing prescribed properties. The creation of such a technology of active

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material production was preceded by intensive researches in the physical-chemical properties and structural phase transformations in electrode pastes and active material during different technological operations. The premature shedding of highly porous active material is prevented by the use of binders. Binders are mainly represented by combinations of polymeric fibres and fluoroplastic suspensions, which create a special polymeric frame keeping the active material from shedding.

The increase of the specific energy, especially in the intensive discharge modes, was achieved on the basis of the use of copper negative electrodes grids. Possessing high conductance and being light-weight, the copper grids made it possible to increase the specific electrical characteristics by 20 to 25%. Besides, copper sheets improve the vertical current distribution in electrodes and increase the active material utilization factor. Over thirty years ago Russia was the first to use copper grids in lead storage batteries. At present, the production of copper stretch grids is waste-free and totally mechanized. Copper is thermodynamically insoluble against oxidation. For this reason it is coated with lead and an intermediate sublayer of tin. In short discharge modes, there take place high ohmic losses of voltage in the current-conducting assembly.

The conductance of the current-conducting assembly can be increased on the basis of the use of copper or aluminium inserts in the terminal? For this purpose we have developed new technological processes of thermal-diffusion leading and tinning of aluminium.

The high value of active material utilization factor can also be achieved by the selection of efficient expanders. The most widely used in Russia was the BNF tanner which is in many respects superior to lignins, also used as expanders.

For heat abstraction usually a water cooling system is used. The design of the cooling system depends upon the battery designation, i.e., the operating conditions. Sometimes they represent copper or titanium coils placed in the electrolyte above the upper edge of the electrode block. The coils or loop coolers are protected against intercoil or chemical corrosion on the basis of connecting the copper coolers to negative titanium and positive terminals. In other designs the cooling channels are placed directly in the current-conducting assembly – terminals and taps.

The vertical electrolyte segregation is prevented by stirring with compressed air. It is achieved by either letting the air pass through thin plastic tubes arranged along the side edges of the electrodes, or by means of an airlift system representing an air tube placed in the transport tubes. The airlift stirring of the electrolyte is preferable since it does not lead to stirring-up the sludge accumulated at the bottom of tanks, as well as it does not increase the internal battery resistance due to the presence of air bubbles.

As was stated earlier, the rate of gas release is a very important factor. It is known that the rate of self-discharge and hydrogen release depends, in the first place, upon the type and quantity of antimony and other components doping the anodic alloy being transferred from the positive electrode to the negative one, as well as upon the electrolyte purity. The precipitating additives characterized by low values of hydrogen overvoltage increase the rate of the hydrogen release on the negative electrodes.

Thus, most important for the reduction of self-discharge and gassing is the reduction of antimony content in the lead alloy used for the manufacture of positive grids.

At present, several antimony-free and low-antimony alloys are known. Among the most widely used are: lead–calcium, lead–antimony–selenium–arsenic and lead–antimony–cadmium. The antimony content in the two latter alloys can be reduced to 1.5 to 2.5%. However, for batteries operating in the charge/discharge mode, i.e., used on diesel-electric submarines, it might be difficult to use lead–calcium alloys due to rapid reduction of the battery's capacity resulting from the passivation of the corrosion layer.

In batteries with relatively thick positive electrodes (3 mm and more) also may be used such alloys as lead–antimony, 3 to 3.5 wt.%, or lead–antimony–arsenic–silver.

Besides, two- or three-fold reduction of hydrogen release rate may be achieved by the introduction into the electrolyte of additives inhibiting self-discharge. The most widely used are α-naphthol and new additives manufactured under the "Rus" trademark. The latter also possesses high-desulfating properties. THat is why they are most widely used in all types of lead storage batteries.

The required shock and vibration resistance of batteries is achieved on the basis of the use of tanks made of strong armored plastics, electric microporous separators, and improvements in the design of several parts and units. The improvements are based upon the recently worked out computation methods, software, and general optimization of the battery design.

It was usually believed that the increase of the specific electrical characteristics of batteries inevitably leads to the shortening of their service life. However, usually the increase of the specific energy density was achieved on the basis of the reduction of the thickness. The accumulated experience in the development and practical operation of batteries indicate that the realization of the above-mentioned and other factors may lead not only to battery life shortening, but to increase it as well. It is now confirmed that the life of lead storage batteries with pasted electrodes used as reserve power sources on nuclear submarines is no less inferior to that of batteries with other types of positive electrodes.

It is also known that the operation of batteries with armour-clad electrodes on diesel-electric submarines is characterized by a limited number of prolonged discharges corresponding to the submarine's economical running. The maintenance of such batteries takes a considerable amount of time. The initial actuation of such batteries is a long procedure, too.

With due consideration of the afore-mentioned and other recommendations there have been created and operated for a long time in Russia a number of high-capacity shock-resistant storage batteries with pasted electrodes. Their specific energies are characterized by the following values: 160 W h/l or 55 W h/kg in prolonged operation modes and 60 W h/l or 25 W h/kg in hour-long modes.

The above energy parameters of storage batteries define and limit the tactical and technical parameters of various submarines.

In one design we have mounted the storage battery outside the submarine pressure hull in a watertight enclosure. The hydrostatic pressure compensation and the elimination of the tape and joints contact with sea water are achieved on the basis of the electrolyte separation from the sea water by a special insulating liquid.

Secrecy considerations concerning 'know-how' have made it difficult for the author to give more detailed review of research and development work, as well as to analyse new operation modes (rapid charge, methods of dry batteries' quick actuation). We are ready to share this experience in the process of scientific and technological cooperation with our foreign partners.