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STUDY OF THE EFFECT OF CARBON ADDITIVES IN LEAD-ACID BATTERIES TO IMPROVE THE EFFICIENCY OF MINING EQUIPMENT

Abstract. The mining industry is undergoing a period of radical technological change aimed at improving the efficiency, safety, and sustainability of production processes. One of the key areas of digital and technological transformation in the industry is the electrification of mining equipment and the introduction of advanced battery technologies. It has been noted that lead-acid batteries remain one of the most reliable and durable chemical power sources to date, but they have a number of significant drawbacks. And with the expansion of battery applications in new technologies, battery performance requirements are constantly increasing and the shortcomings of these batteries are becoming increasingly critical. The solution to the problem may be the introduction of electrically conductive carbon additives into the paste, which will increase the strength of the electrode mass by forming a skeletal structure. The purpose of this work is to study the effect of carbon materials of different nature on the characteristics of lead-acid batteries. Determination of ways to improve the characteristics of lead-acid battery electrodes based on the use of nanodispersed carbon-containing additives. Carbon additives such as graphite, carbon black, thermally expanded graphite, fullerenes, graphene, and carbon nanotubes are considered. The effect of nanodispersed carbon-containing additives of various nature on the properties of lead-acid battery electrodes is analyzed. Ways to improve the characteristics of lead-acid battery electrodes based on the use of nanodispersed carbon-containing additives have been identified. The results of this study have made it possible to determine the fundamental applied results, namely, the possibility of flexibly adjusting the macrostructure (porosity and density) and conductivity of the positive and negative electrodes of lead batteries with a very small amount of nanostructured carbon additives (1%). Modifying the composition of the electrode paste by introducing a nanodispersed carbon-containing additive determines ways to optimize the performance characteristics of lead-acid battery electrodes as a whole. Lead-carbon batteries, thanks to their improved performance, economic efficiency, and environmental advantages, can occupy an important niche in the transformation, offering an optimal solution to many of the current challenges in the transformation of the mining industry.

Keywords: lead-acid batteries, nanodispersed carbon-containing additives, conductivity of carbon materials, positive and negative electrodes

1. Introduction

The modern world is undergoing a large-scale energy transformation aimed at reducing carbon footprints and achieving climate neutrality:

- the transition to renewable energy sources (solar, wind, hydroelectric) requires effective storage systems to compensate for their intermittent nature.

- the implementation of strategies to decarbonize the economy in many countries requires reliable energy storage systems;

- the development of distributed generation creates a need for local battery systems;

- the electrification of transport is one of the key areas for reducing CO_2 emissions.

The mining industry is undergoing a period of radical technological change aimed at improving the efficiency, safety, and sustainability of production processes. One of the key areas of digital and technological transformation in the industry is the electrification of mining equipment and the introduction of advanced battery technologies.

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Traditional diesel equipment, which has dominated underground and open-pit mining for decades, is gradually giving way to battery-powered electric counterparts. This transition is driven not only by environmental considerations, but also by the significant economic and operational advantages of electric equipment.

Environmental benefits:

– No local emissions of harmful substances;

– Significant noise reduction (up to 15 dB);

– Possibility of using renewable energy sources.

Economic advantages:

– 30–50% reduction in ventilation costs;

– lower operating costs due to simpler design;

– increased energy efficiency (90% compared to 35% for diesel engines).

Operational advantages:

– instant torque of electric motors;

– precise speed and power control;

– possibility of energy recovery during braking.

Improved safety and working conditions:

– The absence of exhaust gases significantly improves air quality in underground workings.

– Lower noise and vibration levels create more comfortable conditions for workers.

– Reduced risk of explosions due to the absence of flammable fuel materials.

One of the main areas of scientific activity at the M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM NAS of Ukraine) is energy, which focuses on the development and research of obtaining, accumulating, and rationally using electrical energy and the reliability of mining operations.

As is well known, lead-acid batteries (LAB) are widely used in the mining industry due to their reliability, relative cheapness, and resistance to harsh operating conditions. Currently, they are used in electric transport in mines, including battery-powered electric locomotives for transporting cargo and personnel, mine electric locomotives and draisines, loading and delivery machines, and underground self-propelled trolleys; in auxiliary equipment – emergency lighting in underground workings, portable lamps for miners (mining lamps), alarm and communication systems, control and measuring instruments, and in safety systems – backup power for ventilation systems, emergency drainage systems, automatic atmosphere control systems, evacuation equipment, etc.

However, traditional lead-acid batteries have a number of significant drawbacks. These include a limited number of charge-discharge cycles (usually 300–500), sensitivity to partial state of charge (PSoC), high sulfation rate during deep discharges, relatively low charge acceptance, and degradation at high discharge currents. These disadvantages are becoming increasingly critical as batteries are used in new technologies that require higher performance.

Meanwhile, battery performance requirements are constantly increasing:

– increased specific energy capacity – to reduce device size and weight;

– increased specific power – to ensure high peak loads;

– increased service life and number of cycles – to reduce the cost of ownership;

– expanded temperature range – for operation in extreme conditions;

– increased safety – especially for large energy storage systems;

– reduced charging time – for increased ease of use.

In recent years, scientific and practical interest has been aroused by the reduction of destruction and erosion of the negative electrode through the introduction of carbon additives, which increase the strength of the mass itself by forming a skeletal structure [1–4].

These same studies note that adding electrically conductive fibrous materials, such as carbon nanotubes, to the paste not only contributes to greater depth of active mass processing and electrolyte access to its inner layers, but also reduces the battery formation and charging time.

It has been established [5, 6] that the introduction of technical carbon into negative active material significantly improves charge acceptance and slows down the sulfation of negative plates during simulation of cyclic charge-discharge at high rate partial state of charge (HRPSoC) of batteries. Hollenkamp et al. [7] studied the formation of lead sulfate on negative plates with increased carbon content by exposing batteries to simulated hybrid electric vehicle cycles at a rate of 2C for three to four consecutive cycles and observed an improvement in battery life.

Dynamic characteristics are also improved. Batteries with carbon additives demonstrate better power output at low temperatures, which is important for operation in cold mines. The charging speed can be increased by 30–50% without compromising service life.

The type of carbon additive is also important. Graphite improves electrical conductivity, activated carbon creates an additional surface for electrochemical reactions, and graphene combines both advantages but is more expensive. The optimal concentration is usually 0.5–2% of the mass of the active substance of the negative electrode.

It is important to note that excessive amounts of carbon can cause undesirable side effects, such as increased hydrogen evolution during charging. Therefore, it is necessary to balance the composition of the active mass taking into account specific operating conditions.

For mining companies, the use of batteries with carbon additives means the possibility of reducing equipment downtime for charging, increasing intervals between repairs, and reducing the total cost of ownership of electric transport. This makes this technology promising for the modernization of the existing battery fleet.

Therefore, for a more detailed understanding of the mechanism of influence of carbon additives on LAB parameters, the IGTM NAS of Ukraine, under contract No. 01/01-20/42/202223, conducted experimental studies at the Ukrainian State

University of Chemical Technology [10] on lead-acid battery electrodes based on nanodispersed carbon- containing additives, which were used in writing this paper.

The purpose of this work is to study the influence of carbon materials of different nature on the characteristics of LAB. Determination of ways to improve the characteristics of lead-acid battery electrodes based on the use of nanodispersed carbon-containing additives.

2. Methods

To investigate the effect of nanodispersed carbon-containing additives on the electrophysical characteristics of lead-acid battery electrodes, a complex of experimental methods was applied.

Research Objects

The following materials were used as research subjects:

- natural graphite EUZ-M from Zavalievske deposit (GOST 10274-79);
- acetylene black (TU 14-7-24-80);
- fullerene (provided by M.S. Poliakov Institute of Geotechnical Mechanics of NAS of Ukraine);
- thermally expanded graphite (TEG and TEG CNK, developed by Enerize Corporation, USA);
- graphene (provided by Soheil Davaryar company, Australia).

Electrical Conductivity Determination Method

The main research method was the technique for determining powder conductivity using the electromagnetic non-contact method proposed by Enerize Corporation (USA) [10]. The method allows non-destructive determination of specific electrical conductivity (σ, S/m) of powder materials on a 20 MHz inductance coil.

Measurements were conducted for two material states:

- non-compacted state (natural bulk density);
- compacted state (after mechanical pressing).

For each sample, the following were determined:

- specific density (ρ, g/cm^3);
- specific electrical conductivity (σ, S/m).

Electrode Mass Research

To evaluate the effect of carbon additives on electrode properties, electrical conductivity measurements were performed for:

- positive paste mixture with various additives (concentration ~1% by mass);
- negative paste mixture with various additives (concentration ~1% by mass).

This allowed establishing a correlation between the properties of individual carbon materials and their impact on the characteristics of electrode masses as a whole.

3. Theoretical part

Lead-carbon batteries retain the basic operating principle of lead-acid batteries, based on electrochemical reactions between lead, lead dioxide, and sulfuric acid. The main reaction during discharge:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2Pb\ SO_4 + 2H_2O.$$

During charging, the reaction proceeds in the opposite direction. The introduction of carbon materials does not change the basic chemistry, but significantly affects the physical processes in the electrodes.

The effect of carbon depends on the amount and type of carbon, its activation, surface area and porosity, purity, and the ratio of paste components [8]. Some types of carbon can improve the performance of the electrode, while others will “poison” it. This difference is explained by various mechanisms [9], none of which can accurately propose a universal model of carbon action. That is why, in order to ensure reliable and stable operation of any current source, electrodes, as well as their active components, must have stable physical and chemical characteristics. With this in mind, it is necessary to select high-quality raw materials with a clear understanding of the structure, properties, and type of carbon additive.

Carbon additives perform several important functions:

- improving the electronic conductivity of the active mass of electrodes;
- forming a stable porous structure that prevents the active material from compacting;
- creating conditions for reversible reactions at the electrode-electrolyte interface;
- encapsulation and stabilization of active lead particles to prevent their agglomeration;
- reduction of internal resistance and associated energy losses;
- improvement of charge acceptance due to a more uniform distribution of the charging current.

The research was conducted using a method for determining the electrical conductivity of powders by electromagnetic non-contact means, proposed by Enerize Corporation (USA) [10].

One of the most important parameters of electrode materials is conductivity, since this parameter largely determines the rate of electrochemical processes. To determine the quality of materials at the initial stage of electrode paste preparation and electrode manufacturing from raw components, the conductivity values of powder materials added as additives to the electrode paste of positive and negative electrodes were established.

The following materials were used in the study: natural graphite EUZ-M from the Zavalevskyi deposit (GOST 10274-79); acetylene soot, TU 14-7-24-80; fullerene, provided by the IGTM NAS of Ukraine; thermally expanded graphite, developed and provided by Enerize Corporation; graphene, provided by Soheil Davaryar (Australia).

Among the nanodispersed carbon-containing additives studied, high conductivity values are observed for fullerene and graphene ($3.32 \cdot 10^{-3}$ and $1.24 \cdot 10^{-3}$ S/m, respectively) in an uncompacted state. For non-compacted materials such as thermally expanded graphite and carbon black, the conductivity is 10^{-4} S/m. After compaction, the conductivity of fullerene remains almost unchanged, but the conductivity of thermally expanded graphite and carbon black increases by an order of magnitude (Table 1, Fig. 1).

The conductivity of fullerene on a 20 MHz inductance coil is twice as high as that of thermally expanded graphite RGO CNK ($3.35 \cdot 10^{-3}$ and $1.27 \cdot 10^{-3}$ S/m, respectively). In this case, higher conductivity values should have been expected for electrode pastes containing fullerene. However, the conductivity of the positive paste mixture with fullerene is $<10^{-5}$, and the conductivity of the negative paste mixture with fullerene is $6.80 \cdot 10^{-5}$ S/m.

Table 1 – Results of conductivity measurements of thermally expanded graphite and other carbon materials

Material type	Non-compacted		Compacted	
	density ρ, g/cm³	conductivity σ, S/m	density ρ, g/cm³	conductivity σ, S/m
Fullerene	0.116	$3.32 \cdot 10^{-3}$	0.157	$3.35 \cdot 10^{-3}$
Graphene	0.099	$1.24 \cdot 10^{-3}$	0.108	$5.15 \cdot 10^{-3}$
RGO CNK	0.042	$3.38 \cdot 10^{-4}$	0.055	$1.27 \cdot 10^{-3}$
RGO	0.011	$4.26 \cdot 10^{-4}$	0.014	$1.34 \cdot 10^{-3}$
Carbon black	0.182	$6.77 \cdot 10^{-4}$	0.223	$1.37 \cdot 10^{-3}$

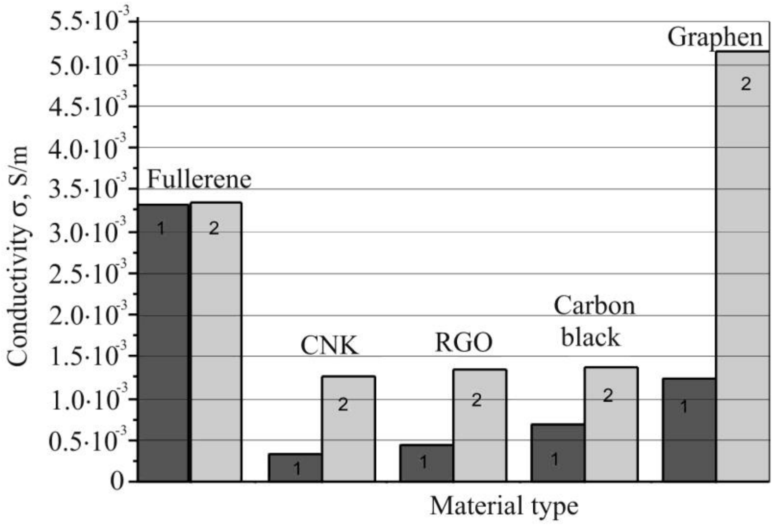

Figure 1 – Conductivity measurement data for carbon additives (non-compacted (1) and compacted (2)) using an electromagnetic non-destructive non-contact method

That is, the conductivity of the mixture of paste for positive electrodes and the mixture of paste for negative electrodes with the addition of graphite RGO CNK is higher than the conductivity of the mixture of paste for positive electrodes and the mixture of paste for negative electrodes with the addition of fullerene.

The authors suggest that there is a combined effect of two factors: conductivity and density of carbon material. Thermally expanded graphite RGO CNK is lighter (0.055 g/cm^3) than fullerene (0.157 g/cm^3). Due to its greater volume in the same mass of the mixture, thermally expanded graphite is better distributed in the electrode structure, thereby ensuring satisfactory electrical contact between the particles of the mass components.

4. Results and discussion

The data presented illustrate the synergistic effect of the conductivity and macrostructure of a nanodispersed carbon-containing additive on the conductivity of the mixture of masses for positive and negative electrodes.

The results of this study determine the fundamental applied results: the possibility of flexibly adjusting the macrostructure (porosity and density) and conductivity of the positive and negative electrodes of lead-acid batteries with a very small amount of nanostructured carbon additives (1%). Modifying the composition of the electrode paste by introducing a nanodispersed carbon-containing additive determines ways to optimize the performance characteristics of lead-acid battery electrodes as a whole.

It can be concluded that carbon additives perform several important functions:

– improving the electronic conductivity of the active mass of electrodes;

– forming a stable porous structure that prevents the active material from compacting;

– creating conditions for reversible reactions at the electrode-electrolyte interface;

– encapsulating and stabilizing active lead particles to prevent their agglomeration;

– reducing internal resistance and associated energy losses;

– improving charge acceptance through a more uniform distribution of charging current.

In addition, current trends in the development of lead-carbon technologies take into account the principles of sustainable development:

– use of bio-carbon materials from renewable raw materials;

– development of recycling technologies with the extraction and reuse of carbon components;

– increasing battery life, which reduces the overall environmental footprint;

– creating a closed production cycle with minimal waste.

5. Conclusions

Carbon-based additives have a significant impact on the performance of lead-acid batteries, especially in partial charge modes, which are typical for many applications, including mining equipment and energy storage systems.

The main mechanism of action of carbon-containing additives is to improve the conductivity of the negative active mass and reduce sulfation processes. When carbon materials such as graphite, carbon black, or graphene are added to the negative plates, they create additional conductive paths in the porous structure of the active mass. This is especially important during charging, when it is necessary to ensure an even distribution of current across the entire surface of the electrode.

Carbon additives significantly reduce the internal resistance of the battery. The reduction in resistance can range from 15% to 40% depending on the type and amount of carbon used. This results in better charge acceptance, especially at high currents, which is critical for regenerative braking of electric vehicles or for fast recharging.

One of the biggest problems with lead-acid batteries is the progressive sulfation of negative plates. Lead sulfate crystals gradually increase in size and become difficult for the electrolyte to access, reducing the capacity and service life of the battery. Carbon additives slow down this process by improving current distribution and reducing local areas with high sulfate concentration.

To summarize the above, it can be noted that the use of battery technologies, including lead-carbon batteries, may become a prerequisite for solving many of the challenges of the modern world. From ensuring energy security and implementing decarbonization strategies to supporting digital transformation and adapting to climate change, batteries are becoming a critically important element of technological infrastructure.

Conflict of interest

Authors state no conflict of interest.

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ДОСЛІДЖЕННЯ ВПЛИВУ ВУГЛЕЦЕВМІСНИХ ДОБАВОК В СВИНЦЕВИХ АКУМУЛЯТОРАХ ДЛЯ ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ РОБОТИ ГІРНИЧОГО ОБЛАДНАННЯ

Слободянникова І.Л., Привалов В.М., Усатенко В.В.

Анотація. Гірнича промисловість переживає період кардинальних технологічних змін, спрямованих на підвищення ефективності, безпеки та сталості виробничих процесів. Одним з ключових напрямків цифрової та технологічної трансформації галузі є електрифікація гірничого обладнання та впровадження передових акумуляторних технологій. Відмічено, що свинцево-кислотні акумуляторні батареї дотепер залишаються одними із надійних, довговічних хімічних джерел струму, однак, мають низку істотних недоліків. А з урахуванням розширення сфер застосування акумуляторів у нових технологіях, вимоги до характеристик акумуляторів постійно підвищуються та недоліки даних акумуляторів стають дедалі критичнішими. Вирішенням проблеми може стати введення в пасту електропровідних вуглецевих добавок, що дозволить підвищити міцність маси електрода за рахунок формування скелетної структури. Метою даної роботи є дослідження впливу вуглецевих матеріалів різної природи на характеристики свинцево-кислотні акумуляторні. Визначення шляхів підвищення характеристик електродів свинцево-кислотних акумуляторів на основі використання нанодисперсних вуглецевмісних добавок. Розглянуті такі вуглецеві добавки, як графіт, сажа, терморозширений графіт, фулерени, графен та вуглецеві нанотрубки. Проаналізовано вплив нанодисперсних вуглецевмісних добавок різної природи на властивості електродів свинцево-кислотних акумуляторів. Визначені шляхи підвищення характеристик електродів свинцево-кислотних акумуляторів на основі використання нанодисперсних вуглецевмісних добавок. Результати даного дослідження дозволили визначити принципові прикладні результати, а саме, можливість гнучко регулювати макроструктуру (поруватість та щільність) і провідність позитивного і негативного електродів свинцевих акумуляторів абсолютно невеликою кількістю наноструктурованих вуглецевих добавок (1%). Модифікація складу пасти електродів введенням нанодисперсної вуглецевмісної добавки визначає шляхи оптимізації експлуатаційних характеристик електродів свинцевого акумулятору в цілому. Свинцево-вуглецеві акумулятори, завдяки своїм покращеним характеристикам, економічній ефективності та екологічним перевагам, можуть зайняти важливу нішу в трансформації, пропонуючи оптимальне рішення для багатьох сучасних викликів в трансформації гірничої галузі.

Ключові слова: свинцево-кислотні акумулятори, нанодисперсні вуглецевмісні добавки, провідність вуглецевих матеріалів, позитивний і негативний електроди