

Carbon materials used as additives to active mass of semi-traction lead-acid batteries

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The continuous increase of power consumption, together with the pressure to reduce greenhouse gas emissions, requires the generation of more and more electricity from renewable energy sources (RES). However, this implies other consequences. The electrical grid is an example. In this case, there are not only fluctuations in daily and seasonal levels of power consumption, but also fluctuations in power production. This is particularly related to energy obtained from photovoltaic panels and wind turbines. Energy storage systems (ESS) are a method to temporarily store energy as a buffer for sudden changes of electricity consumption or production. Energy storage methods are based on various technologies. One of the most important, especially for small systems, is based on chemical power sources. In this field, one of the most popular chemical power sources is the Pb/PbO₂ cells system, and especially its variants known as semi-traction and stationary batteries. Despite their disadvantages, lead-acid batteries are inexpensive, easily recycled and offer acceptable performance. Extensive research is being conducted to improve their electrical properties. The present research focuses on the effect of additives of different carbon materials to the electroactive mass on the properties of semi-traction lead-acid batteries such as formation process, capacitance, charge acceptance and cycle life.

Keywords: Semi-traction lead-acid battery, carbon additives, energy storage

INTRODUCTION

In the small system of renewable energy source (RES) installations, wind and solar energy are the most popular, while electrochemical batteries, such as lead-acid batteries [LAB], metal hydride [Ni-MH] batteries, or lithium-ion [Li-ion] batteries, are the most often used for energy storage. Lithium-ion batteries have the highest specific power, but their big disadvantage is their price and difficulty in recycling [1-3]. Lead-acid batteries are characterized by lower specific energy (~25-50 Wh kg⁻¹), energy density (~60-70 Wh dm⁻³), but the low production cost (~50-600 \$ kWh⁻¹) [4, 5] and the possibility of full recycling make them an interesting alternative, especially in small renewable energy installations. Semi-traction and stationary LAB are the most commonly ones used for this type of application [6-8]. The average new LAB contains about 80% of recycled material [9, 10]. The global production volume of lead-acid batteries is reported to have quadrupled between 1990 and 2020. Currently, more than 50% of the market share in terms of power demand is met by the lead-acid battery industry [11]. Although effective recycling programs for LAB have been developed, the main disadvantages

include low energy-to-weight ratio and low endurance under high-rate partial state of charge (HRPSoC) [12-15]. Therefore, research is constantly being conducted to improve the performance of LAB cells. This research involves many elements, such as grid alloy, active mass additives, electrolyte additives, etc. [13-17].

One of the most common undesirable processes occurring in Pb/PbO₂ cells, resulting in their faster failure, is sulfation. The growth of the coarse-grained crystalline layer may occur on both electrodes, and in particular on the negative electrode during the high-rate partial state of charge (HRPSoC) operation. Slowly over time, sulfation becomes permanent as some crystals expand and resist dissolution [18, 19]. Conversion of PbSO₄ to Pb or PbO₂ is inefficient with standard charging methods. To increase the use of negative active mass (NAM), mixtures of lignin, barium sulfate and carbon, known as expanders, are added to the production of negative plates [20]. Lignosulfonate is incorporated into the NAM to increase cycle life, prevent passivation and improve active mass utilization [21-23]. Barium sulfate (BaSO₄) is a nucleating agent (nucleant) for the formation and

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growth of small PbSO_4 crystals. In addition, it facilitates the distribution of these crystals on the surface of the pores of the active mass. This property of BaSO_4 is based on the isomorphism between lead and barium sulfate crystals [24]. Carbon materials are added to the paste mainly to improve the electrical conductivity of the active mass at the end of the discharge, when the content of PbSO_4 crystals in NAM significantly increases [25-27]. The addition of carbon improves strength, and increases the surface area, which can contribute to an increase in energy density [28]. It also facilitates the crystallization of fine PbSO_4 crystals over the entire plate surface by promoting electrochemical reactions [29].

The present research focuses on the effect of carbon material additives to the negative electroactive mass (NAM) on the electrochemical properties of semi-traction lead-acid batteries. Two types of graphite, one type of carbon black (commercially available) and carbon material obtained from flax fibers after carbonization were used in the study.

EXPERIMENTAL

Commercially available graphites included: expanded natural graphite (Superior Graphite abbreviation - SG), synthetic graphite (Cybrid 1 Imerys - CG), carbon black (SuperP Imerys - CB). Carbon material (CF) was obtained during carbonization of natural flax fibers. Conditions for carbonization of plant material were: time: 2h, $T = 700^\circ\text{C}$, gas: N_2 . Capacitance measurements of the selected carbon materials were carried out on electrode material which contained 85% tested carbons, 10% binder polytetrafluoroethylene (Sigma–Aldrich) and 5% acetylene carbon black (Super C65, Imerys). Electrodes were prepared in the form of pellets (12 mm in diameter). The carbon composite electrodes were used to prepare symmetric electrochemical capacitors (ECs) in Swagelok[®] cell systems with 316 L stainless steel current collectors. The electrolyte was 1 M H_2SO_4 , potential range 0.000-0.800 V in a two-electrode system, scan rate 5 mV/s. Tests were carried out at ambient temperature with a VMP3 potentiostat/galvanostat (Biologic, France) and results were analysed using EC-Lab[®] software. The specific conductivity of carbon materials was measured at a pressure of 40 bar, on a Carlo De Giorgi S.R.L. hand press in a cylindrical vessel. NAM was based on lead powder produced in a ball mill with a composition of about 75% PbO and 25% Pb . This powder was mixed with a standard expander used for SLI batteries (standard sample), which contains 0.3 wt%

carbon black, 0.3 wt% sodium lignosulfonates and 1.0 wt% BaSO_4 . The modified masses were enriched in carbon materials in the amount of 0.5 wt% (or 0.2% of CF). The smaller addition of CF was due to the observed viscosity difficulties during pasting. In addition, a mixture of graphite CG and carbon black CB in a mass ratio of 4:1 was also used. The addition of the mixture to the active mass was also 0.5 wt%. Other technological operations (including the process of curing and formation) were carried out in accordance with the technology of the Jenox company. 2V cells and 12V batteries were produced. The 2V cells were thermostated at 45°C during the formation process. The cells contained standard positive electrodes. Negative electrodes for 2V cells were handmade pasted. The open circuit voltages (OCV) and internal resistance (IR) of the cells were measured using a HIOKI BT-3554 (Japan) battery tester. Electrical tests of model cells were performed using a Digatron UBT - 50-18-10 tester (Germany). Electrochemical tests of Pb/PbO_2 systems were carried out with the use of VMP-III BioLogic potentiostat/galvanostat (BioLogic, France) with current booster and EC-Lab v. 11.10 software. SEM images were obtained using the scanning electron microscope Quanta 250 FEG, FEI ThermoFisher scientific device with energy dispersive spectroscopy module.

RESULTS

Research of pure carbon materials

The morphology and microstructure of carbon graphite are shown in Figs. 1 and 2.

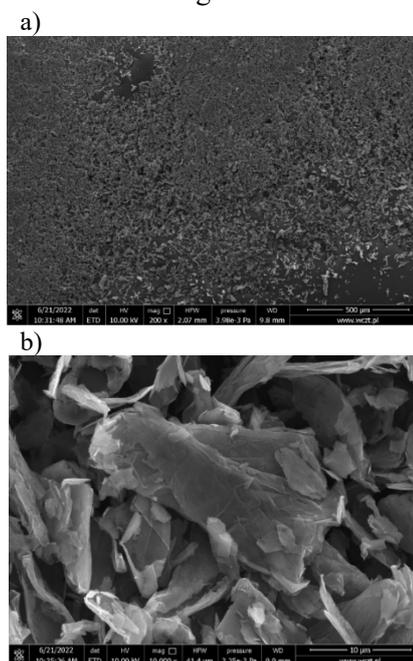


Fig. 1. Morphology (a) and microstructure (b) of graphite SG.

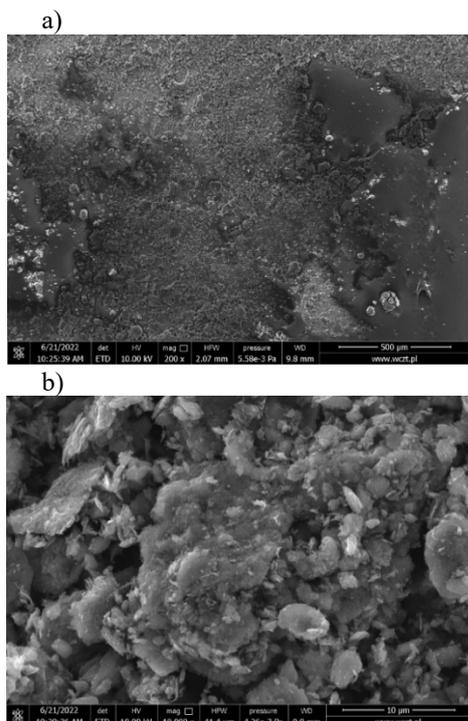


Fig. 2. Morphology (a) and microstructure (b) of graphite CG.

The morphology and microstructure of the carbon black and carbon material obtained from the flax fibers are shown in Figs. 3 and 4, respectively.

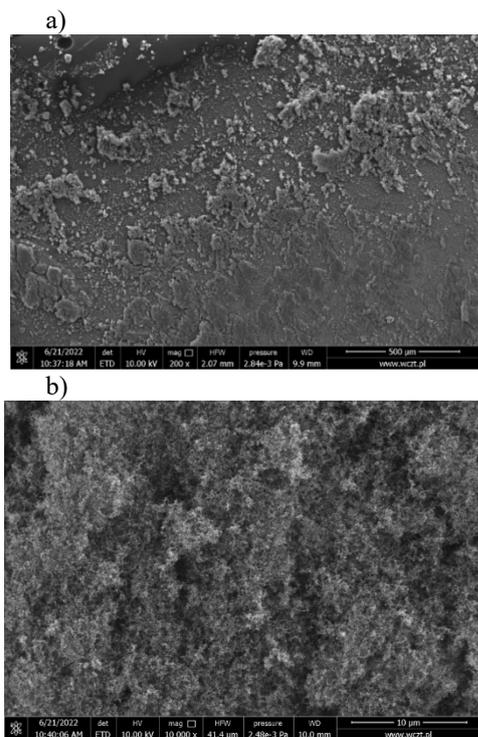


Fig. 3. Morphology (a) and microstructure (b) of carbon black CB.

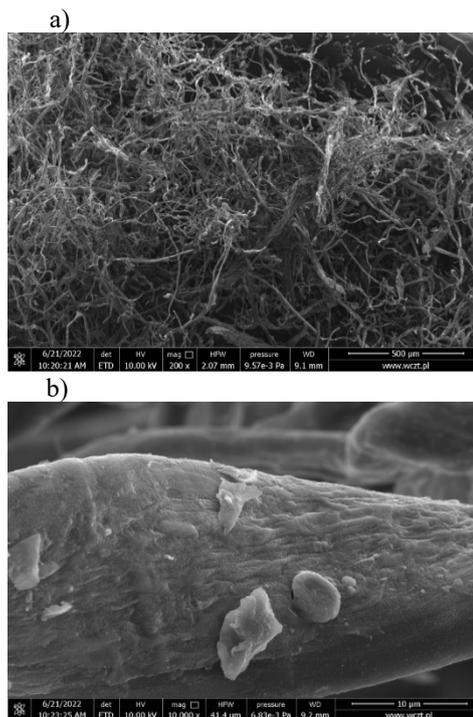


Fig. 4. Morphology (a) and microstructure (b) of carbon materials CF.

From Figs. 1-4, it can be noted that there are significant differences in the morphology and microstructure of the analysed carbon materials. These differences are observed even for both types of graphite used in the research. The specific conductivity (under pressure of 40 bar) and capacitance of the double layer of the tested carbon materials are shown in Fig. 5 and Table 1.

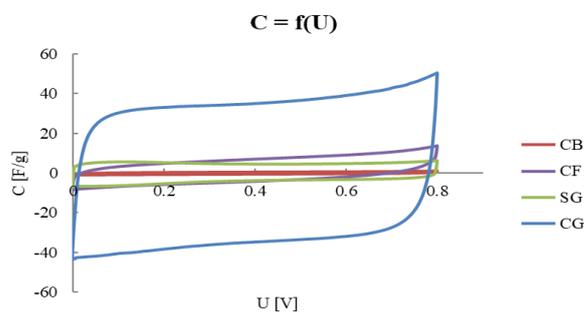


Fig. 5. Cyclic voltammety of tested carbon materials.

Table 1. Capacitance and specific conductivity of carbon materials.

	Capacitance	Conductivity
	F/g	S/cm
SG	4.5	4.1
CG	33.8	3.3
CB	<1.0	3.5
CF	5.2	0.2

As expected, each of the carbon materials exhibited significantly different electrochemical properties. The capacitance of the double layer of CF material was unexpectedly high. For CB material, on the other hand, it was very low. It should be also noted that the conductivity of the CF material was very poor.

2V cell testing

The 2V cells were assembled from two positive plates and one negative plate. The intended capacitance of the cell was 8 Ah. The soaking time with sulfuric acid was 30 min. The formation program is shown in Table 2.

Table 2. 2 V cell formation program

Step	Time	Current
	h	A
1	0.5	0.2
2	0.5	1.0
3	0.5	2.2
4	6.0	3.5
5	1.5	2.8
6	2.0	2.2
7	2.0	1.5

The overall time of the formation process was 13 h, and the total charge delivered to the cells was equal to 34.3 Ah. After the formation process, the plates containing only CB additive exhibited degradation of the active mass (Fig. 6) and therefore subsequent tests were carried out on active masses containing CG+CB additive in the ratio of 4:1.



Fig. 6. Negative plate with CB additive after formation process.

Table 3 presents the first three C₂₀ capacities of the tested cells. It can be noted that the NAM with CF material required 3 charge/discharge cycles to achieve a capacitance similar to the other cells. The highest C₂₀ capacities were obtained for cells containing NAM with the addition of CG and CG+CB.

Table 3. C₂₀ capacities for 2V cells (three charge/discharge cycles)

Additive	Electrical capacitance C ₂₀		
	I	II	III
	Ah	Ah	Ah
Standard	7.94	7.73	7.83
SG	7.62	7.48	7.60
CG	7.88	7.95	7.95
CG+CB	7.99	7.91	7.83
CF	3.43	5.99	7.80

Fig. 7 presents the relative values of the cells' internal resistance obtained in the charged condition (cell containing NAM without additives=100%).

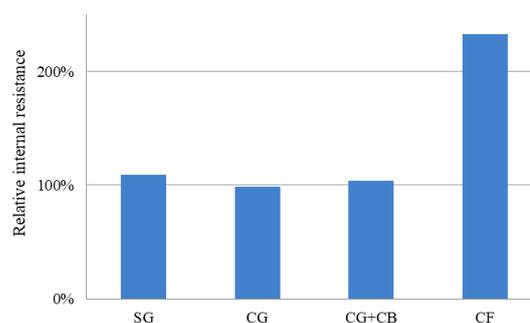


Fig. 7. Relative internal resistance of the cells (100%-cell containing NAM without additives)

The internal resistance of the cells containing carbon compounds was similar to that of the reference sample. The significantly higher resistance of the electrode with added CF material may be indicative of decrease of active mass cohesion or resistance at the grid/active mass interface. The higher resistance can also be explained by the fact that the negative active mass consists of pure lead, and any addition to the electrode can be considered as an element that increases resistance. The conductivity of pure carbon CF-type material was about 5-6% of that of SG and CG graphites. Graphite-based carbon materials, on the other hand, exhibited relatively good conductivity for a non-metallic material and as an additive to NAM did not affect the internal resistance of the negative electrodes.

Based on the experimental data from stages one and two, it was decided to focus on SG, CG and CG+CB material additives in further studies.

12V battery tests

The last stage of the research was to make 6-cell batteries with a theoretical capacitance of 45 Ah. At this stage, the tests included the determination of the discharge capacitance with currents from C₂₀

($I=2.25A$) to 3C ($I=135A$) (Fig. 8) and the endurance in cycle test according to EN 50342-1:2015 standard.

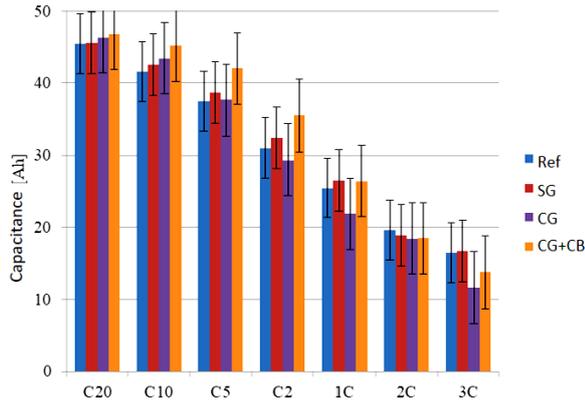


Fig. 8. Battery capacities for different discharge currents.

Based on the discharge times of the different currents, all the batteries exhibited similar electrical characteristics. However, LAB with modified NAM demonstrated modestly better properties up to a value of 1C (45A). Among them, only plates with CG had lower discharge characteristics over a wide range of currents.

The dependence of the discharge times for different currents (Equation 1) allowed to determine the Peukert coefficient (Table 4). Peukert coefficient (k) expresses the approximate change in capacitance of LAB at different discharge rates:

$$C = I^k t \quad (1)$$

where:

- C - capacitance, Ah;
- I - discharge current, A;
- t - discharge time, h.

Table 4. Peukert coefficients

k	

Standard	1.246
SG	1.250
CG	1.317
CG+CB	1.293

Based on Equation (1), it can be concluded that the lower the Peukert coefficient, the higher is the available capacitance during high current discharge. Standard and SG batteries showed the lowest Peukert coefficients. However, high-power discharges are rare in semi-traction systems.

A more important factor is the endurance of the system for operation in charging/discharging (CH/DCH) mode. Cyclic life test included endurance cycles. At first, fully charged batteries were discharged for 2 h with

a current of 11.25 A, next charged at $U_{con} = 15.6$ V, total charge $Q=1.08$ (108% of discharge capacitance) and again discharge. The CH/DCH cycle was repeated until voltage during discharge fell below 10.5 V. Fig. 9 presents the results of cyclic life test in relation to the standard battery.

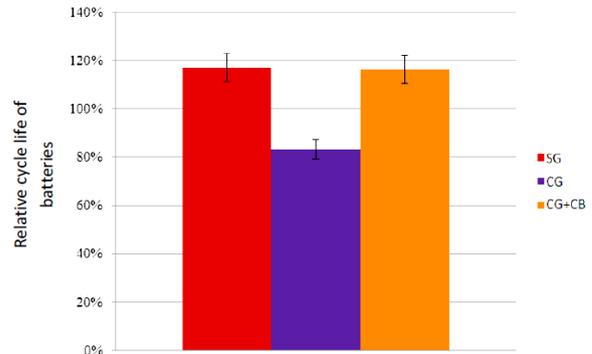


Fig. 9. Relative cycle life of batteries (100% - cell containing NAM without additives)

Batteries with NAM and SG or CG + CB demonstrated the highest cyclic resistance. The improvement in cyclic resistance was 17% and 16%, respectively, relative to the reference cell. In contrast, cells with the addition of CG had an approximately 18% lower durability cycle life test result.

CONCLUSIONS

Due to the practically unlimited number of types of carbon material precursors and modifications of the conditions for obtaining these materials, it is possible to constantly search for new additives to active masses. Based on presented experiments, it can be concluded that mixtures of carbon materials with different physicochemical properties are a very promising area of research. Studies of the physicochemical and electrochemical properties of pure carbon materials do not allow to predict their effect on the performance properties of plates in the battery. The 2+1 plate Pb/PbO₂ single-cell systems are more useful in the preliminary estimation of the electrochemical properties of modified electrode materials and their selection. However, owing to the complex relationships between the active mass (PAM, NAM) and the electrolyte, as well as thermal phenomena, it is necessary to verify the obtained data on multi-cell and multi-plate systems.

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NOMENCLATURE

LAB – lead-acid battery;
PAM – positive active mass;
NAM – negative active mass;
RES – renewable energy sources;
OCV – open circuit voltage [V];
IR – internal resistance [$m\Omega$].

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