

The effect of waste material electrode on the properties of positive electrodes in lead-acid batteries

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Introduction

The increasing requirements for environmental protection constitute one of the most important aspects of the development of modern civilization. These requirements include creation of more effective materials and energy production technology as well as deployment of new solutions to facilitate the recycling of used materials or equipment. Also, in the area of chemical power sources, the described-above issues are of growing importance [1 ÷ 4]. Despite over 150 years of its history, the lead – acid battery is still the most widely used chemical secondary source of electric energy. The directions of its future evolution assume also the environmental factors [5 ÷ 8]. The lead – acid battery is a chemical power source, which can be recharged with electric current from an external power source, after being discharged.

The lead-acid batteries are mainly applied to the automotive industry, as the so – called starter batteries. They are also used as the primary power source in many systems that are sensitive to low power quality or voltage drops, for example, in electricity networks (stationary batteries) and in electric vehicles as forklift trucks, golf cars etc. (traction batteries) [8, 10, 11].

In order to reach high requirements of lead-acid batteries exploitation and environmental protection, the main components of these energy storage systems (e.g. active mass media, active mass, electrolyte etc.) are subjected to constant modifications. In case of the active mass, various research and development studies are carried out and cover the following issues:

- increase in the mechanical stability of the mass,
- increase in the resistance of the mass to the sulfation process,
- improvement of the accessibility of the active mass for electrode processes.

A particular attention was paid to study carbon material as an additive to the negative mass in order to increase the acceptance of the capacity load (it is the crucial feature for lead-acid batteries applied to cars with Start-Stop systems) and additives which enhance the stability of the mass (e.g. fibers placed on the surface in form of a special paper type used during pasting process) [12 ÷ 20]. One of the most important research directions is also the study on elements from wasted batteries and their use into production of new energy storage devices.

The aim of this study was to investigate the effect of addition of waste electrode materials obtained from technological processes to the positive active mass. The waste electrode material was prepared

according to one chosen method, the positive plates prepared in the laboratory were assembled in cells and were electrically tested. Physicochemical and structural analyses of the produced materials were performed at each stage of the study.

Experimental date

Materials

The commercial lead powder obtained from a spray-type Barton reactor and the waste electrode material from the positive active mass after the ageing process (Autopart S.A. Mielec – manufacture of batteries) were used in the study. Production negative plates (Autopart) as a counter electrode and a grid made of PbCaSn alloy with dimensions 142 × 113 mm (width × length), obtained by expanded metal exmet, used in the tests.

Research Methodology

The bulk density of lead powder and waste electrode material after mechanical treatment were determined using electrochemical volumeter WE-5 type, CLAIo. The phase composition of the lead powder and waste material was determined by XRD analysis using diffractometer Philips PW1050 with Cu α lamp with nickelic filter in the angular length range 5–50; 0.04; 2s. The surface area of both materials was also determined using a porosimeter Micromeritics type ASAP 2000. The active mass was left to degas at room temperature for 24h. During the measurement the sample was in nitrogen atmosphere at liquid nitrogen temperature.

After determination of the initial characteristics, a series of positive active mass with a different content of the waste material was prepared as well as mass without the waste material (the so-called reference cell) for comparison purposes. The paste was prepared from the lead powder, sulfuric acid, water and a small amount of polypropylene fibers. The paste had its penetration and density parameters corresponding to the positive mass applied in starting batteries. The produced active mass was manually pasted into a current medium. The produced positive plates were subjected to a two-step seasoning process: the first one, in high humidity and the second one, in the humidity < 10%.

During and after the seasoning process, the positive mass was subjected to the tests: phase composition (X-ray diffractometer Philips PW1050), specific surface area analysis by the BET method (ASAP2000) and microstructure analysis (scanning electron microscope Quanta FEG 250 FEI).

Next, the test systems, which consisted of a positive electrode, separator and two negative electrodes (production Autopart S.A. Mielec – battery manufacturer) were assembled. These systems were subjected to electrochemical conversion of electrode material (the so-called formation process) and electrical testing. All these tests were performed with use of Bitrode multiple

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tester, model SCN. Formation process was carried out at current intensity of 0.30A, 1.40A and 0.70A without any voltage limits. The charge introduced during the formation process was up to 49.1Ah. At each stage of the study an analysis of phase composition and microstructure was conducted.

Results and discussion

The first stage of the research consisted of analysis of waste material pre-treatment methods for their usefulness. On the basis of particle size and bulk density analyses, it was found that the proposed method of mechanical treatment allowed to obtain the waste material in powder with a suitable granulation to be used as a paste component of the assumed plasticity. The chemical composition of lead powder was significantly different from that of the waste material electrode. Analysis of the composition of waste material showed the presence of two varieties of crystallographic lead oxide (II): lead oxide (II) a tetragonal variety called red, designated as PbO_{tetr} and lead oxide (II) an orthorhombic variety called yellow, designated as PbO_{romb} .

In addition, indicated the presence of sulphates $3PbO \cdot PbSO_4 \cdot H_2O$ and $4PbO \cdot PbSO_4$. However, the phase analysis of the lead powder indicated the presence of lead oxide (II) a tetragonal variety called red, designated as PbO_{tetr} and metallic lead designated as Pb_{met} .

Table I

Relative phase content of lead powder and waste mass after milling

Sample	$3PbO \cdot PbSO_4 \cdot H_2O$ [%rel.]	$4PbO \cdot PbSO_4$ [%rel.]	PbO_{tetr} [%rel.]	PbO_{romb} [%rel.]	Pb_{met} [%rel.]
Lead powder	-	-	90.05	-	9.95
Waste material after pre-treatment	12.39	13.64	68.25	5.72	-

The differences were found in the powder density (after the milling process). The density of the waste material and the lead powder was respectively 1.59 and 1.90 g/cm³. This difference is probably due mainly to the shape of the particles.

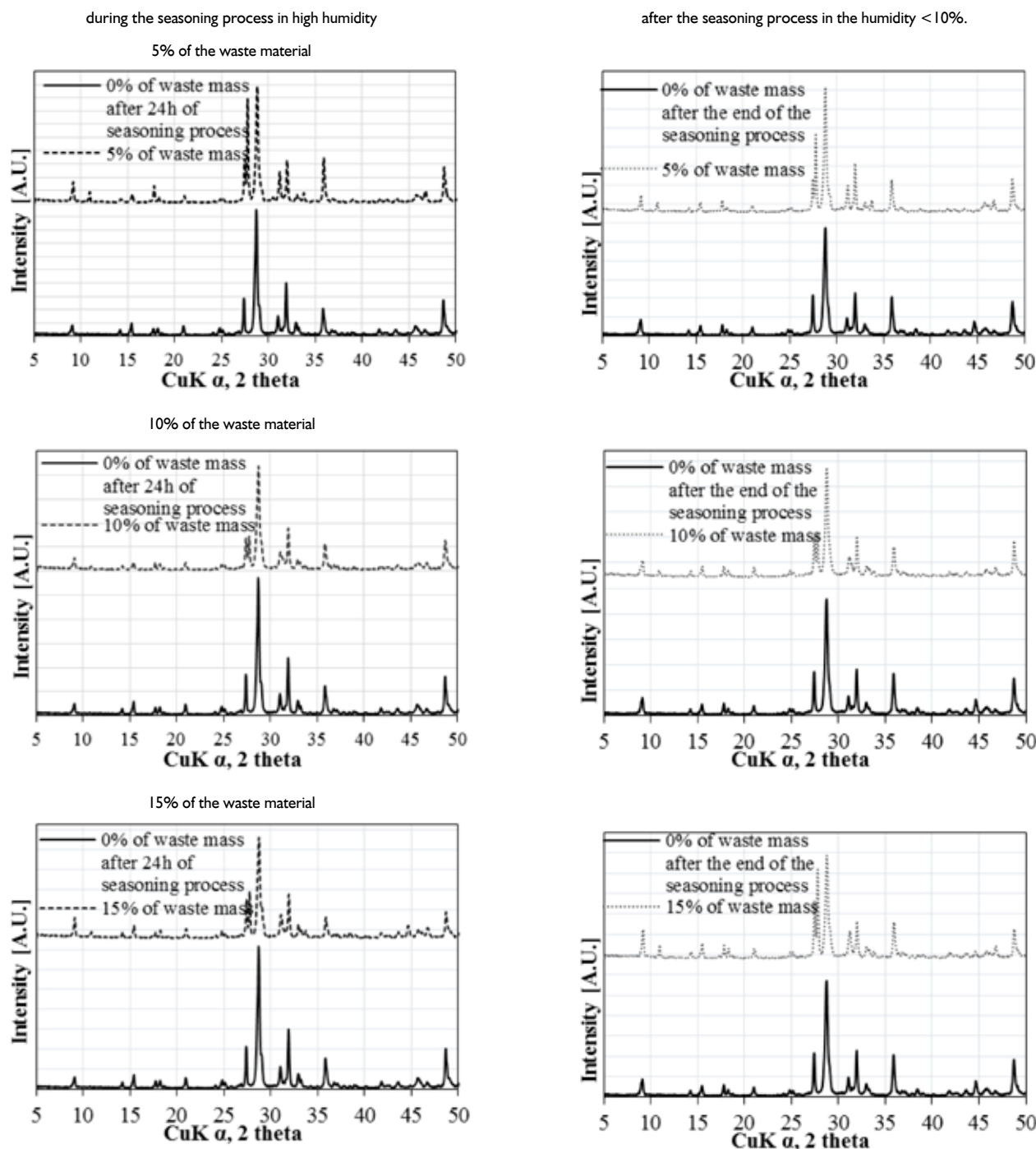


Fig. 1. X-ray diffraction spectra of the positive mass with and without addition 5, 10 and 15% of waste material during and after the seasoning process

After preparation of the positive active mass, the positive electrodes were made and they were subjected to ageing process. The changes in the phase composition during and after the process is shown in the XRD pattern (Fig. 1).

It could be noted that, despite some differences in the morphology of positive plates, the phase composition of positive plates with waste material addition examined after the seasoning process was similar to that of the reference group. As to plates containing the waste electrode material, the presence of $4\text{PbO}\cdot\text{PbSO}_4$ was

revealed, which was absent in the reference group, and a lower content of tetragonal phase PbO_2 was found. In order to evaluate changes in the material morphology after the ageing process, the SEM images were performed for the positive plates without and with 5, 10 and 15% of waste material addition (Fig. 2).

The material morphology indicates an increase in the mass of the added waste material, a presence of fine crystal structure with an elongated, slightly determined shape, and a loss of patch crystallites seen in the reference group.

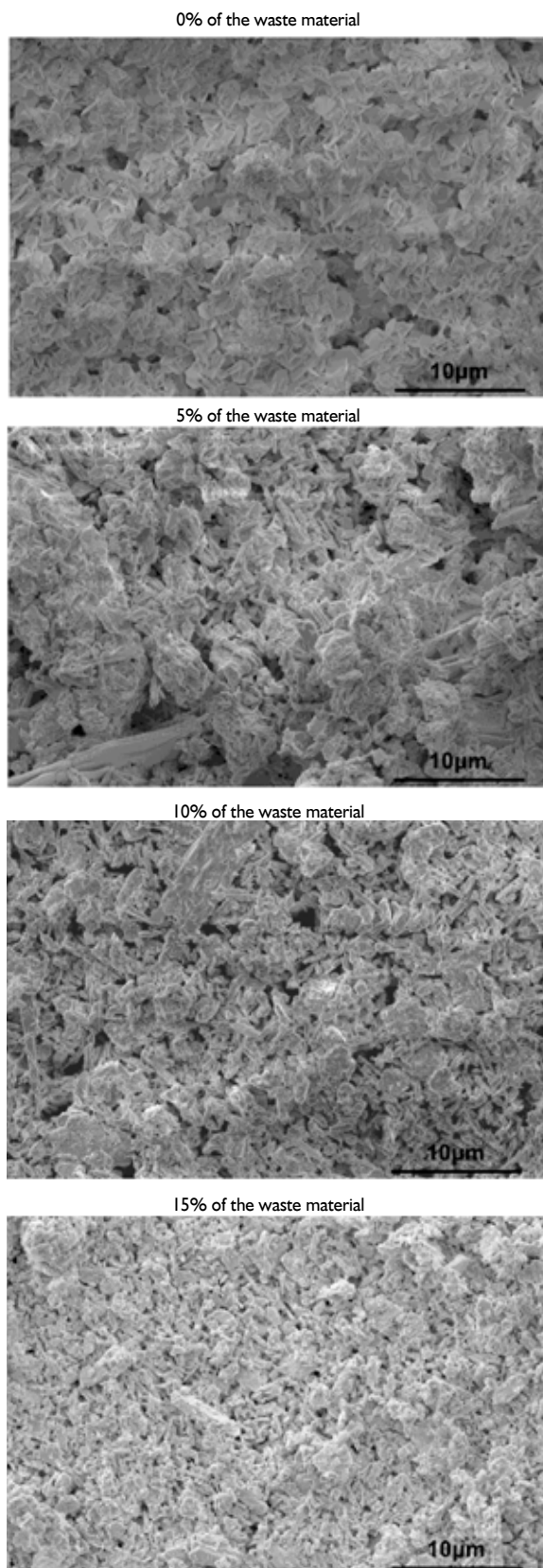


Fig. 2. Changes in the structure of the positive mass with and without addition 5, 10 and 15% of waste material after the aging process

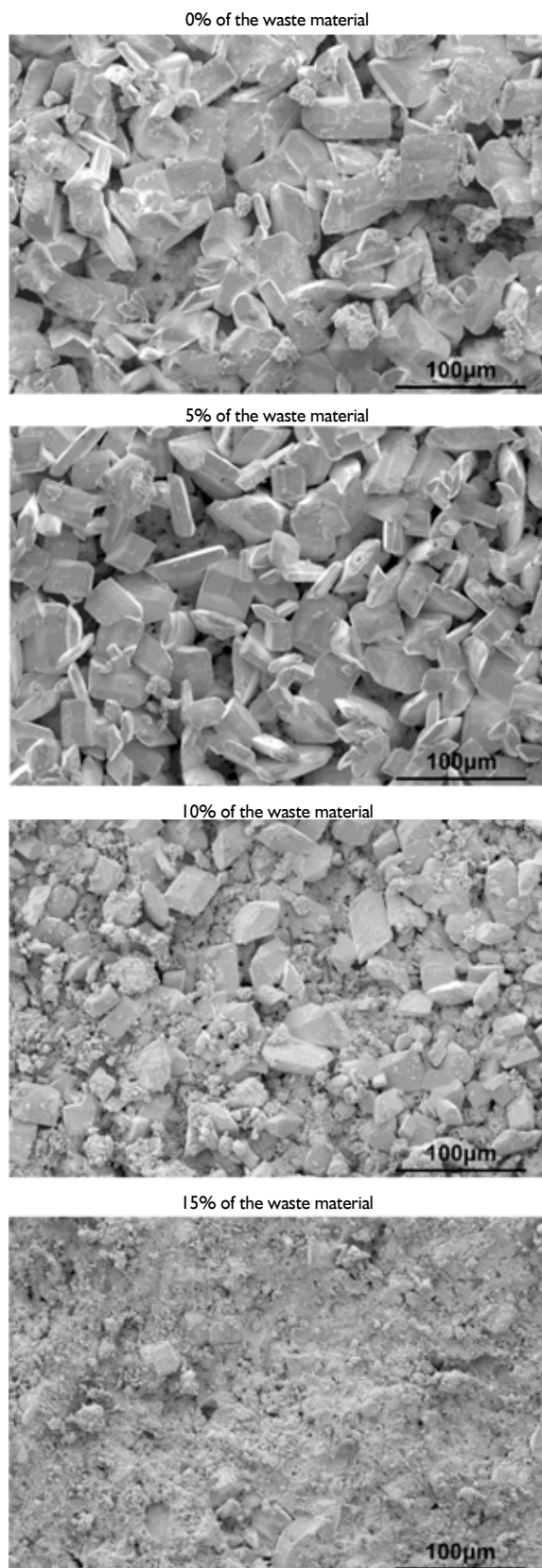


Fig. 3. Changes in the structure of the positive mass with and without addition 5, 10 and 15% of waste material after the end of the formation process

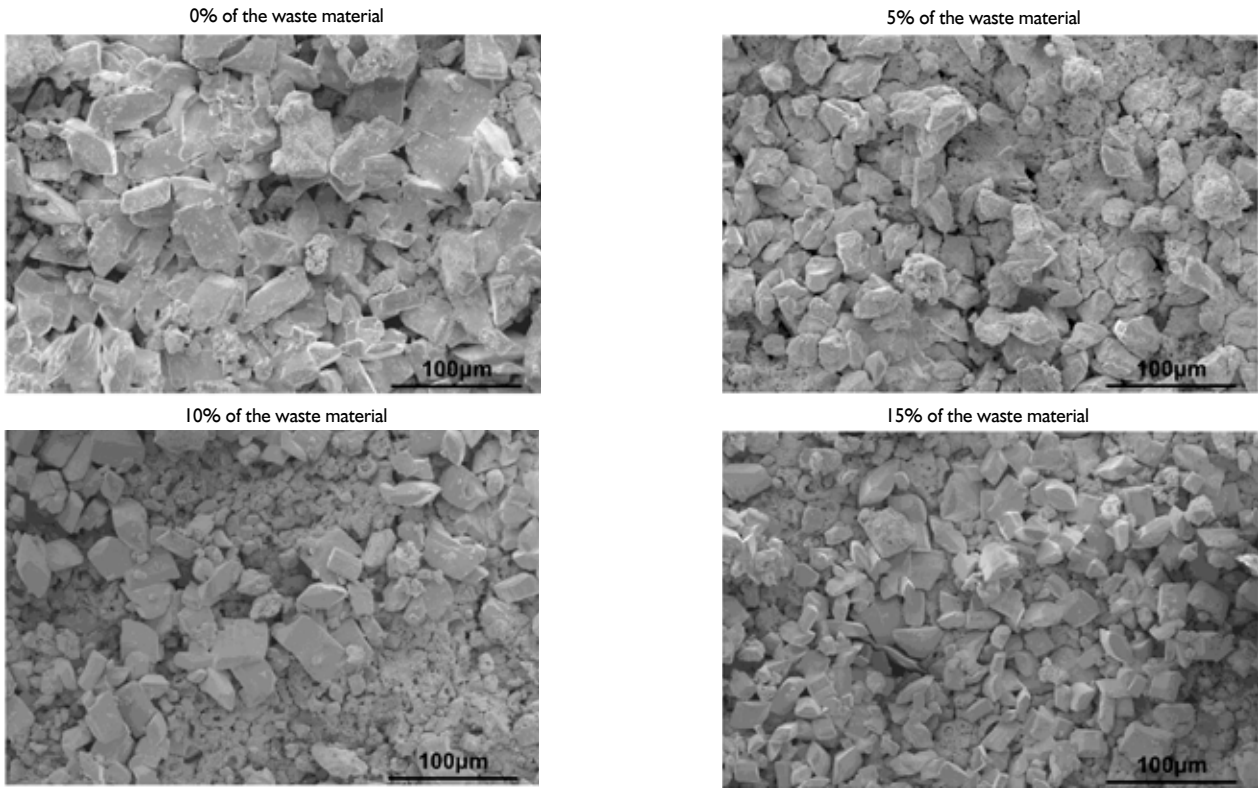


Fig. 4. Changes in the structure of the positive mass with and without addition 5, 10 and 15% of waste material after the discharge process

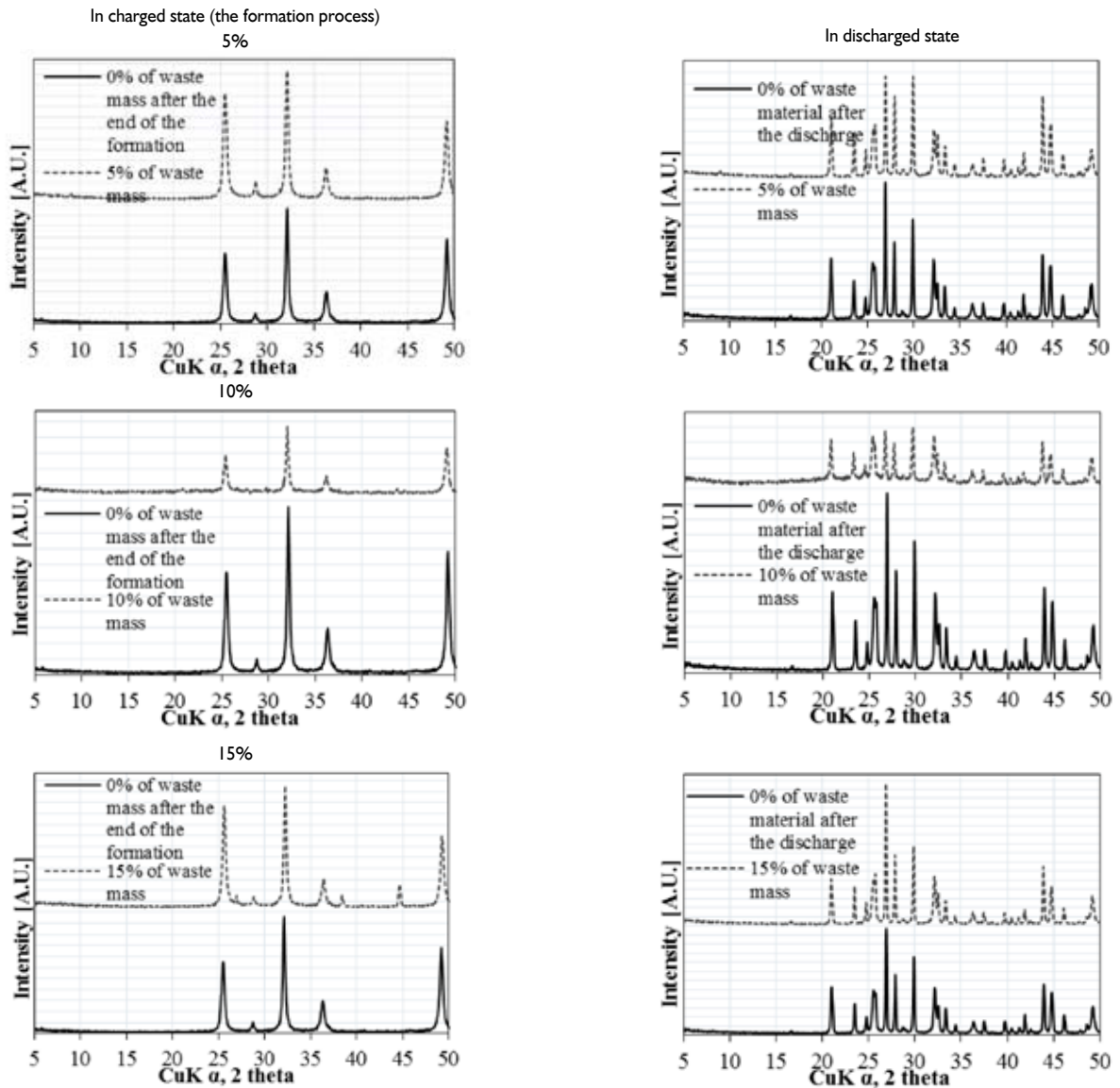


Fig. 5. X-ray diffraction spectra of the positive mass with and without addition 5, 10 and 15% of waste material after charge and discharge process

In the next stage, the cells with positive electrodes received after the ageing process and standard negative electrodes were tested. Figures 3 and 4 show SEM micrographs of the positive plates with different content of the waste material in two states: charged (the formation process) and discharged.

Along with a growing share of waste material in the mass, an increased participation of disordered structures is clearly visible. For mass with addition of 15% of waste material they significantly dominate the typical crystallites with dimensions of several dozen microns clearly visible in a sample without the waste material. After the discharge process one can observe a comparable content of the disordered structures in all masses regardless the waste material presence in mass.

Figure 5 shows the XRD spectra of charged (after formation) and discharged plates. The summary of phase composition for each group of plates is presented in Table 2.

Table 2
Relative phase content of the positive mass with and without addition 5, 10 and 15% of waste material after charge and discharge process

Sample	βPbO_2 [%rel.]	αPbO_2 [%rel.]	Pb_{met} [%rel.]	PbSO_4 [%rel.]
Mass 0% after charging	93.07	6.93	-	-
Mass 0% after discharge	-	-	-	100
Mass 5% after charging	89.70	8.02	2.28	-
Mass 5% after discharge	-	-	-	100
Mass 10% after charging	97.83	2.17	-	-
Mass 10% after discharge	-	-	-	100
Mass 15% after charging	96.04	4.87	-	-
Mass 15% after discharge	-	-	-	100

The differences in morphology of the tested materials were found after formation and discharge. After discharge in all tested positive mass the identified component was only lead sulphate. However, in a charged state the differences of phase composition between different groups of plates were insignificant (differences in the relative contents βPbO_2 and αPbO_2).

In order to assess the influence of the differences in phase composition and microstructure of the plates on the electrical properties, the relative changes in specific capacitance of each positive active mass (100% – mass without waste material) in the first 3 cycles of charge/discharge are shown in Figure 6.

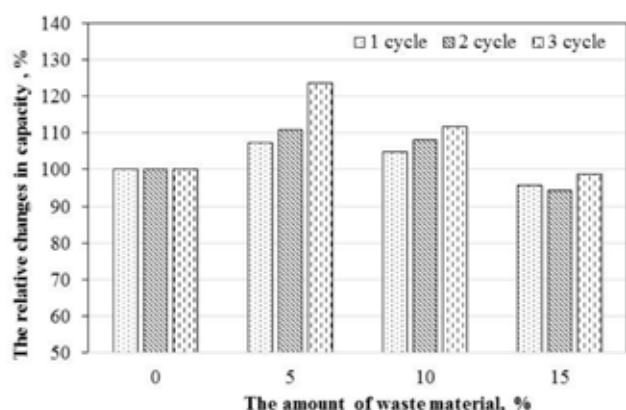


Fig. 6. Specific capacity of the positive active mass with and without addition 5, 10 and 15% of waste material in the first 3 charge/discharge cycles

Investigation of discharge capacity in the first three charge/discharge cycles showed some differences. The cells with addition of 5% of waste material showed the highest capacity values across the research group. The capacity measured for cells with 15% content of waste material was lower than for the referential system as well as for cells with 5 and 10% of waste material content. It results from the fact that the increased weight of waste material can lower the internal coherence of the mass in the electrode and impede the electrical contact between its parts.

Conclusion

As a part of studies it has been demonstrated that the addition of waste material containing of 5 – 15% causes changes in the morphology, microstructure and phase composition of the plates. Significant quantities of $4\text{PbO}\cdot\text{PbSO}_4$ were observed in the plates after the ageing process. Their presence was mostly associated with overheating of the electrodes during the process.

In this study, regarding an identical program of environmental changes during ageing and similar number of plates submitted to the described process, the presence of this component is related to the waste material addition. Certainly, the $4\text{PbO}\cdot\text{PbSO}_4$ was detected in the waste material but its amount measured after ageing indicated that some of $4\text{PbO}\cdot\text{PbSO}_4$ had formed during the process. According to the literature, $4\text{PbO}\cdot\text{PbSO}_4$ forms big crystals which are more difficult to convert to PbO_2 than $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$. It is worth to emphasize that neither the phase composition of positive electrodes after the formation process indicated any significant differences between particular groups, nor analysis of SEM micrographs after the ageing process demonstrated presence of big crystals specific for this compound. It could be assumed that $4\text{PbO}\cdot\text{PbSO}_4$ of small crystalline structure was successfully achieved in plates. Moreover, it was demonstrated that the plates with addition of 5 – 10% of waste active mass showed nominal capacities higher than standard plates. Nominal capacities of positive plates with 15% addition of waste electrode mass were lower than standard plates. It can be presumed that, in this case, a higher content of waste electrode material could lower the internal coherence of the electrode mass as well as inhibit the electric contact between its components. This, in turn, contributes to deterioration of its electric parameters. The analysis of the interior of the electrochemical cell carried out after the electric test confirmed this presumption. It was found that 15% addition of waste electrode mass weakened the electric contact between mass and current collector. This led to reduction in the specific capacity of plates. It should be noted that the processes taking place during paste mixing, seasoning and formation contribute to electroactive mass creation and have a significant influence on the performance parameters. All disorders at each stage can result in reduction of electric capacity, mechanical stability, etc. Since the physicochemical properties of the waste material are different from those of the new paste, the addition of waste material can affect the above-mentioned processes in many ways. The variability of the waste mass composition, a great number of possible links between the crystalline and morphology structure, chemical and physicochemical properties of paste and waste material additives – all of these elements make the analysis of the impact of the individual components on the final quality of the electrode material difficult.

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