

## Primary cells as a source of environmental micropollutants and the method of comprehensive recovery of useful components from them

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### ABSTRACT

The aim of this paper was to develop method of recovery of valuable metals from used primary batteries with lithium-anode and to obtain a product in the form of lithium stearate through the synthesis of a lithium hydroxide solution with stearic acid. Pre-treatment of the battery with liquid nitrogen to reduce the reactivity of lithium, crushing and then leaching of the battery material with water, wet sieving and magnetic separation of the oversize product for the recovery of metal parts and plastic were carried out. Filtration of the liquid after wet sieving with the recovery of manganese dioxide, concentration of the filtrate and its synthesis with stearic acid solution to obtain lithium stearate were carried out. The paper presents the properties of lithium hydroxide and its phases formed as a result of leaching the battery material by X-ray diffraction and thermogravimetric analysis. Lithium stearate was analyzed by the Fourier-transform infrared spectrometry. The conceptual diagram and material balance of the process were presented.

*Keywords:* Recycling; Lithium batteries; Button cells; Hydrometallurgical process; Lithium hydroxide; Lithium stearate

### 1. Introduction

Small-size batteries and cells account for a growing proportion of the waste generated in households. According to Eurostat, 88,000 tons of small-volume batteries and cells were collected in the European Union (EU) in 2018, with 10,554 tons in Poland [1]. Uncontrolled disposal of batteries results in them ending up in municipal waste, which is then disposed of by landfilling, composting, or incineration. Toxic compounds from spent batteries can enter the local groundwater system and spread through the food chain in various ways [2,3]. Disposable galvanic cells with a potentially short product life cycle account for more than 75% of batteries placed on the market [4]. The content of elements such as cadmium, lithium, cobalt, zinc, and inorganic electrolytes such as: lithium tetrachloroaluminate ( $\text{LiAlCl}_4$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), lithium perchlorate ( $\text{LiClO}_4$ ), thionyl chloride ( $\text{SOCl}_2$ ) in organic carbonate

solvents: polypropylene, ethylene, dimethyl, dimethylsulfide, dioxolane, becomes a source of contamination of soil, water, and air [5]. Lithium is rare metal that are economically and strategically important to many countries. It was added to the list of critical raw materials in 2020. Critical raw materials are essential to the functioning and integrity of many different industrial ecosystems [6,7]. Demand for lithium is constantly increasing due to the growing market for electric vehicles and portable devices [8,9]. Worldwide consumption of lithium reached 82,500 tons in 2020 [10]. Therefore, every effort should be made to recover the lithium through the recycling process [11]. For example, the global lithium recycling rate is only <1% [12].

According to a new proposal for a Regulation of the European Parliament and of the Council concerning batteries and waste batteries, repealing Directive 2006/66/EC and Amending Regulation (EU) 2019/2020, by the end of 2025, 90% of cobalt, copper, lead, and nickel, and 35%

of lithium is to be recycled. By 2030, 95% of cobalt, copper, lead, and nickel, and 70% of lithium is expected to be already recycled [13].

A number of technologies have been developed to recycle waste small-size batteries, with pyrometallurgical or hydrometallurgical processes being the most common. The pyrometallurgical method does not require battery sorting, but it is very energy-intensive and results in high dust and gas emissions and a high cost of gas control [14,16]. Recycling of lithium primary batteries by pyrometallurgical methods leads to losses of metals such as lithium and manganese, which migrate into slags and are not recovered [15,17]. The hydrometallurgical method ensures more efficient recovery of the components of the metallic and non-metallic fractions, but it has some disadvantages such as the need to dismantle the battery and separate it into individual fractions [18,19]. According to Swain, hydrometallurgical processes have many advantages, such as smaller scale, minimal energy investment, and minimal carbon dioxide (CO<sub>2</sub>) emissions, and the installation can be designed based on available waste [12]. Among the technologies using the pyrometallurgical method, one can mention the Wealz process used worldwide, for example, in Poland to recycle waste zinc-carbon (Zn-C) and zinc-manganese dioxide (Zn-MnO<sub>2</sub>) batteries. This type of battery is also being processed by Inmetco (USA), Sumitomo (Japan), and Tera (Germany and Japan). Recycling of nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-NH) and lithium-ion batteries (Li-ion) is done on a large scale by Inmetco (USA) and Snam-Savan (France) technologies. Technologies such as Bartrecu (Japan and Switzerland), Citron (France) enable the recycling of all types of small-size batteries. Hydrometallurgical processes have been employed at BATENUS Technology (Germany) to process various types of batteries except those containing lead. The TNO process developed in Belgium (Netherlands, Germany, Japan) is used to process alkaline and Ni-Cd batteries, and the modified Zinces (MZP) process (Spain) allows for the processing of alkaline and zinc-carbon batteries [20]. There are only two processes dedicated as a solution for recycling button cells, which are implemented by MBM (Mercurie Boys Manufacture) and Duclos Environment, developed in France, with no literature data available. According to the available information, MBM's process consists of cryogenic pulverization button cells to obtain mercury/zinc amalgam, polymer joints and steel mantles and distillation of mercury in the amalgam which is then sold together with zinc and steel powder. The Duclos Environment company carries out the process of sorting, recovery of steel and plastics, thermal treatment: evaporation and condensation of mercury in a vacuum and recuperation of zinc in the form of powder [21].

A laboratory pyrometallurgical method for recycling lithium batteries was presented by Träger et al. [22]. The authors aimed to recover lithium (Li) from lithium batteries (both primary Li and Li-ion). To this end, they used Li reduction with carbon, evaporation, and recondensation, and manganese (Mn) recovery from slag by leaching. Implementing this process requires a lot of energy. In popular pyrometallurgical methods, slag is formed from lithium, which causes its loss in the raw material cycle [23]. Xiao et al. [24] proposed

a thermal reduction technology for lithium cobalt oxide (LiCoO<sub>2</sub>) to recover Li and Co from used lithium-ion batteries using urea as an ammonia (NH<sub>3</sub>) carrier. The authors obtained the reduction of LiCoO<sub>2</sub> to water-soluble lithium carbonate and water-insoluble metallic cobalt. Pindar and Dhawan [25] performed microwave reduction of cathode materials from lithium-ion batteries using graphite. Thermal treatment can handle a huge number of used lithium-ion batteries to effectively separate metal components [26,27]. However, after this process, it becomes necessary to apply several complex purification processes to obtain the expected products. For this reason, research is now focusing on improving the selective separation of lithium in metal extraction.

A great number of studies have been devoted to developing a single technological operation for recycling lithium-ion, lithium, nickel-cadmium, and other batteries. These are mainly hydrometallurgical operations involving leaching of electrode material with nitric, hydrochloric, sulfuric, and phosphoric acids. Guo et al. [28] and Barik et al. [29] conducted leaching with hydrochloric acid. However, chlorine (Cl<sub>2</sub>) produced during leaching is a difficult problem to solve due to its toxicity and corrosive effect. Acid leaching produces dissolved lithium and cobalt salts that require extraction and re-extraction processes to separate lithium from cobalt. According to Zhang et al. [30], 99.9% of cobalt and about 13% of lithium are extracted using a PC-88A solution. Pyrometallurgical and hydrometallurgical methods are often combined.

Paulino et al. [31] proposed calcination of lithium and lithium-ion batteries at 500°C followed by solvent extraction to recover lithium fluoride. The inert leaching method was proposed by Schiavi et al. [17] who used primary button and cylindrical lithium batteries to cryomechanical treatment and then recovered the metals through a hydrometallurgical process. In this technology, lithium was recovered in the form of lithium carbonate with a yield of 50%.

The typical composition of lithium-anode button cell is shown in Table 1 [32]. The dominant components are steel (30%–85%), manganese dioxide (12%–50%), and plastic (0.5%–10%). Electrolyte accounts for 4.5%–11.2%. The main components of the electrolyte are 1,2-dimethoxyethane (DME), lithium perchlorate (LiClO<sub>4</sub>) and an organic electrolyte from the carbonate group (propylene carbonate (PC)). The smallest percentage in the composition of the battery is the Li<sup>0</sup> lithium-anode at 0.5%–6%.

The purpose of this study is to develop method of recovery of valuable metals from used lithium-anode button cells

Table 1  
Typical composition of lithium-anode button cell [32]

Component	Material	Content (%)
Positive electrode	Manganese dioxide	12–50
Negative electrode	Lithium metal	0.5–6
Electrolyte	1,2-Dimethoxyethane	1.5–3.5
	Lithium perchlorate	0.2–0.7
Others	Organic electrolyte	2.5–7
	Steel	30–85
	Polypropylene	0.5–10

and to obtain a product in the form of lithium stearate by synthesizing of lithium hydroxide solution with stearic acid. Scope of paper includes presentation of method of recovery of useful components from lithium-anode button cells included discharge, cooling down, and grinding of the battery; determination of the timing and dynamics of hydrogen release and lithium hydroxide formation; leaching of the battery with water in an inert environment; wet sieving and separation of steel and plastics from the solution and  $\text{MnO}_2$  suspension; magnetic separation of the oversize product and separation into steel and plastics; filtration of the solution separating the  $\text{MnO}_2$  suspension from the filtrate containing lithium hydroxide; concentration of the filtrate and synthesis of lithium hydroxide with a heated stearic acid solution; separation of lithium stearate.

## 2. Materials and methods

### 2.1. Characteristics of button cells

Lithium-anode button cells collected from the point of their selective collection were used in the study. The batteries were placed in a sodium chloride ( $\text{NaCl}$ ) solution to completely discharge them and remove the residual voltage. The basic composition of the collected batteries was determined by taking them apart into individual components after cooling them down in liquid nitrogen to  $-200^\circ\text{C}$ . The percentages of each battery component were determined through successive test steps, including leaching of the crushed batteries, separation on a sieve, magnetic separation of the upper size fraction, and filtration of the lower size fraction.

### 2.2. Inert leaching of button cells

Research procedure is illustrated in Fig. 1. Deionized water was used to test the inert leaching of button cells. The process feedstock consisted of metallic lithium-anode batteries, which, after being discharged and cooled down in a nitrogen atmosphere to  $-200^\circ\text{C}$ , were ground in a knife mill.

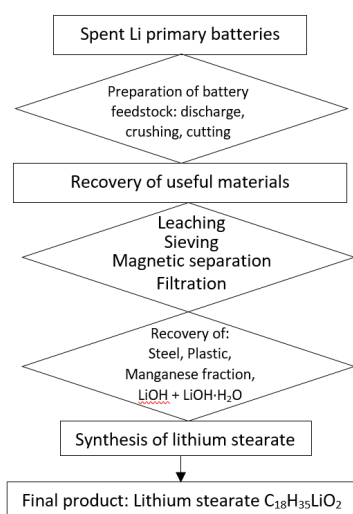


Fig. 1. Research procedure flow chart.

The battery feedstock was stored in a sealed vessel under an argon atmosphere. This prevented the undesirable reaction of battery components with atmospheric air and moisture. Leaching tests were conducted in a closed reactor. The reactor was equipped with a valve that discharged gaseous products from the reaction environment and a valve that supplied argon to the space contained between the top cover of the vessel and the surface of the leaching liquid. The lid of the reactor contained a mechanical stirrer and a pipette for sampling the solution. Deionized water was supplied through a valve on the side of the reactor. Pre-leaching was carried out for 20.0 g of feedstock for 70 min to determine the dynamics of hydrogen evolution and determine the amount of lithium hydroxide. The basic leaching process was carried out for a battery feedstock of 250 g, which was introduced into a reactor filled with argon, then the vessel was closed tightly while argon feeding was continued. The reactor was filled with 1 dm<sup>3</sup> deionized water and the stirrer was turned on. The leaching process was carried out for 70 min and gaseous reaction products were discharged with argon gas supplied in the reaction zone. Solutions from the initial and main leaching were sampled every 10 min. The lithium hydroxide content of the collected samples was determined by acidimetric titration of its aqueous solution with 0.1 M hydrochloric acid against phenolphthalein. One milliliter of 0.1 M acid corresponds to 2.395 mg of lithium hydroxide. The solution after the main leaching was subjected to wet sieving using a sieve with a mesh diameter of  $\phi = 1$  mm. An upper size fraction consisting of metals and plastics and a lower size fraction were obtained. The upper size fraction was supplied to a magnetic separator and a magnetic fraction in the form of steel and a non-magnetic fraction in the form of plastic were obtained. The lower size fraction was filtered, yielding a manganese dioxide precipitate and a post-filtration solution. In the next stage of the study, the solution after filtration was concentrated by evaporation. The solution was heated to  $84^\circ\text{C}$ – $86^\circ\text{C}$  to remove dimethoxyethane DME. After 60 min, the solution was heated to  $90^\circ\text{C}$  and concentrated to a volume of 100 cm<sup>3</sup>. Lithium hydroxide was separated from the collected solution sample. For this purpose, isopropyl alcohol was added to the collected solution sample and lithium hydroxide was separated, which was next filtered and dried. The identification and purity of the resulting lithium hydroxide was examined by thermogravimetric analysis using SETARAM LABSYS TG-DTA/DSC derivatograph. The obtained product was also characterized by X-ray diffraction (XRD) using D8 Advance X-ray Diffractometer (the quantitative analysis used the Rietveld method). For XRD analysis the source wavelength was 0.15406 nm. The diffraction angle from  $10^\circ$  to  $110^\circ$  was determined with a step length of  $0.01^\circ$  and the step time of 0.6 s.

### 2.3. Preparation of lithium stearate

Studies on the preparation of lithium stearate were carried out by synthesizing a concentrated post-filtration solution with stearic acid. To ensure that the reaction occurred properly, 31 g of stearic acid was heated with a small amount of water at  $90^\circ\text{C}$ – $95^\circ\text{C}$  to obtain the acid in a liquid state. A concentrated filter solution of 2.6 g  $\text{LiOH}/100$  cm<sup>3</sup> was

introduced into the heated stearic acid solution, which was added gradually and slowly with continuous stirring for 60 min. Parallel molecular amounts of lithium hydroxide 1-hydrate and the corresponding fatty acid fuse together at elevated temperatures. The reaction mixture was stirred (1,000 rpm) for another 30 min to complete the dehydration reaction, with significant foaming observed. The next stage was to cool the reaction mixture down and filter the lithium stearate. The filter precipitate was dried and analyzed by Fourier-transform infrared spectrometry (FT-IR). The tests were carried out using the SHIMADZU IRAffinity-1S Spectrophotometer in the measuring range from 400 to 4,000  $\text{cm}^{-1}$ , 45 scans per measurement. The filtrate was submitted for chemical analysis by determination of mercury (Hg), manganese (Mn), nickel (Ni), cobalt (Co), copper (Cu), aluminum (Al), and lead (Pb). Analysis of the metal contents in the collected samples was performed using the ICP-OES method (inductively coupled plasma–optical emission spectrometry).

### 3. Results and discussion

#### 3.1. Characteristics of button cells

The basic components of the batteries that make up the feedstock for the leaching process are shown in Table 2. The dominant component of the batteries analyzed is steel and plastic, accounting for 62 wt.%. Manganese dioxide and  $\text{LiMnO}_2$  make up a total of 30 wt.%, electrolyte 6.48 wt.%, and lithium metal 1.52 wt.%.

The percentage composition of button cells presented in Table 2 determines the method of recovery of useful components, which consists of a mechanical and a chemical processes. Materials that are insoluble in water are recovered in a mechanical process: steel, plastics and manganese dioxide. Lithium is recovered in the form of hydroxide in the neutral leaching process.

#### 3.2. Inert leaching of button cells

A preliminary study preceding the main larger-scale battery leaching process was to determine the dynamics of

hydrogen release from the reaction medium and the amount of lithium hydroxide formed. To this end, 20.0 g of feedstock was reacted with deionized water in a closed vessel while the gas was collected and its amount was determined during the reaction 1 and 2 occurring according to the following pattern:



The dynamics of hydrogen release and lithium hydroxide formation in the inert leaching process vs time is illustrated in Fig. 2. The concentration of lithium hydroxide vs. leaching time in the initial test is shown in Table 3.

In the first 25 min of the process, more than 70% of hydrogen is released, while the yield of lithium hydroxide is about 65%. The reaction ends after 60 min. After this time, the release of hydrogen and the formation of lithium hydroxide are no longer observed. Both reaction curves are not very steep at the initial stage, which may indicate a reduction in lithium activity due to the cooling of the battery feedstock before leaching. The actual inert leaching was carried out in a reactor under an argon atmosphere, with the solution sampled every 10 min to determine the lithium hydroxide content (Table 3).

Table 2  
Composition of lithium-anode button cell using for the leaching process

Component	Material	Content (%)
Positive electrode	Manganese dioxide + $\text{LiMnO}_2$	30.0
Negative electrode	Lithium metal	1.52
	1,2-Dimethoxyethane	6.48
Electrolyte	Lithium perchlorate	
	Organic electrolyte	
Others	Steel	48.0
	Plastics	14.0

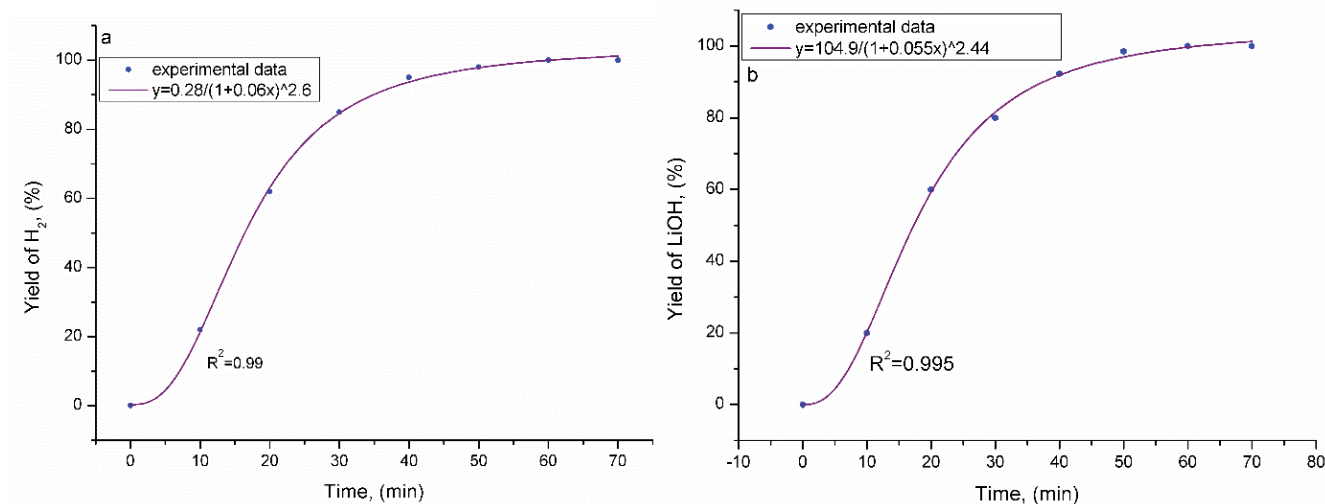
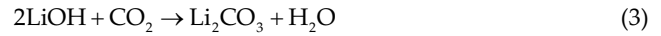


Fig. 2. Dynamics of hydrogen release (a) and lithium hydroxide formation vs. time (b).

The concentrations of lithium hydroxide in the obtained solutions were low. After running the process for 1 h, the concentration of lithium hydroxide in the solution was 2.6 g/dm<sup>3</sup> (Table 3). To obtain a higher concentration of LiOH, the solution, after leaching, sieving, and filtration, was concentrated to a volume of 100 cm<sup>3</sup> by evaporation while argon was introduced into the zone above the liquid. This helped avoid the reaction of the LiOH solution with CO<sub>2</sub> from ambient air. A concentrated LiOH solution of 2.6 g LiOH/100cm<sup>3</sup> was obtained. The results concern the laboratory-scale examinations. When conducting examinations on a semi-industrial scale, one can use leaching in a cascade or column system. Such a solution would be advantageous in terms of the amount of water consumption required for leaching and the concentration of lithium hydroxide in the final solution after leaching (to obtain 50–100 g LiOH/dm<sup>3</sup>). Reducing water

consumption would simultaneously reduce the operating costs of the future installation and its dimensions. Lithium hydroxide, which is formed in the leaching process, can absorb CO<sub>2</sub> from the air, leading to the formation of LiCO<sub>3</sub> according to reaction 3 [33]:



In the absence of CO<sub>2</sub>, lithium hydroxide can hydrate to LiOH·H<sub>2</sub>O according to the reaction 4 [34]:



In order to determine the phase composition of the lithium hydroxide present in the resulting solution after leaching the battery material and separation of the metal fraction, plastics and manganese dioxide, the precipitation of lithium hydroxide was carried out. A non-aqueous solvent in the form of isopropyl alcohol was used to precipitate and separate LiOH from the solution.

Isopropyl alcohol was selected on the basis of the study by Khosravi according to which lithium compounds dissolve weakly in methyl alcohol, and ethyl alcohol, to varying degrees in 1-propanol, while they are practically insoluble in 2-propanol (isopropyl alcohol). LiOH, LiOH·H<sub>2</sub>O, Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub> are not dissolved in 2-propanol [35].

The phase composition of resulting lithium hydroxide separated from the concentrated solution is shown in Fig. 3.

The dominant component in the separated material is lithium hydroxide monohydrate LiOH·H<sub>2</sub>O and lithium

Table 3  
Concentration of lithium hydroxide vs. leaching time in the initial and main test

		Initial test						
Time, min		10	20	30	40	50	60	70
LiOH, g/dm <sup>3</sup>		0.04	0.13	0.17	0.19	0.2	0.21	0.21
		Main test						
Time, min		10	20	30	40	50	60	70
LiOH, g/dm <sup>3</sup>		0.52	1.56	2.1	2.4	2.55	2.6	2.6

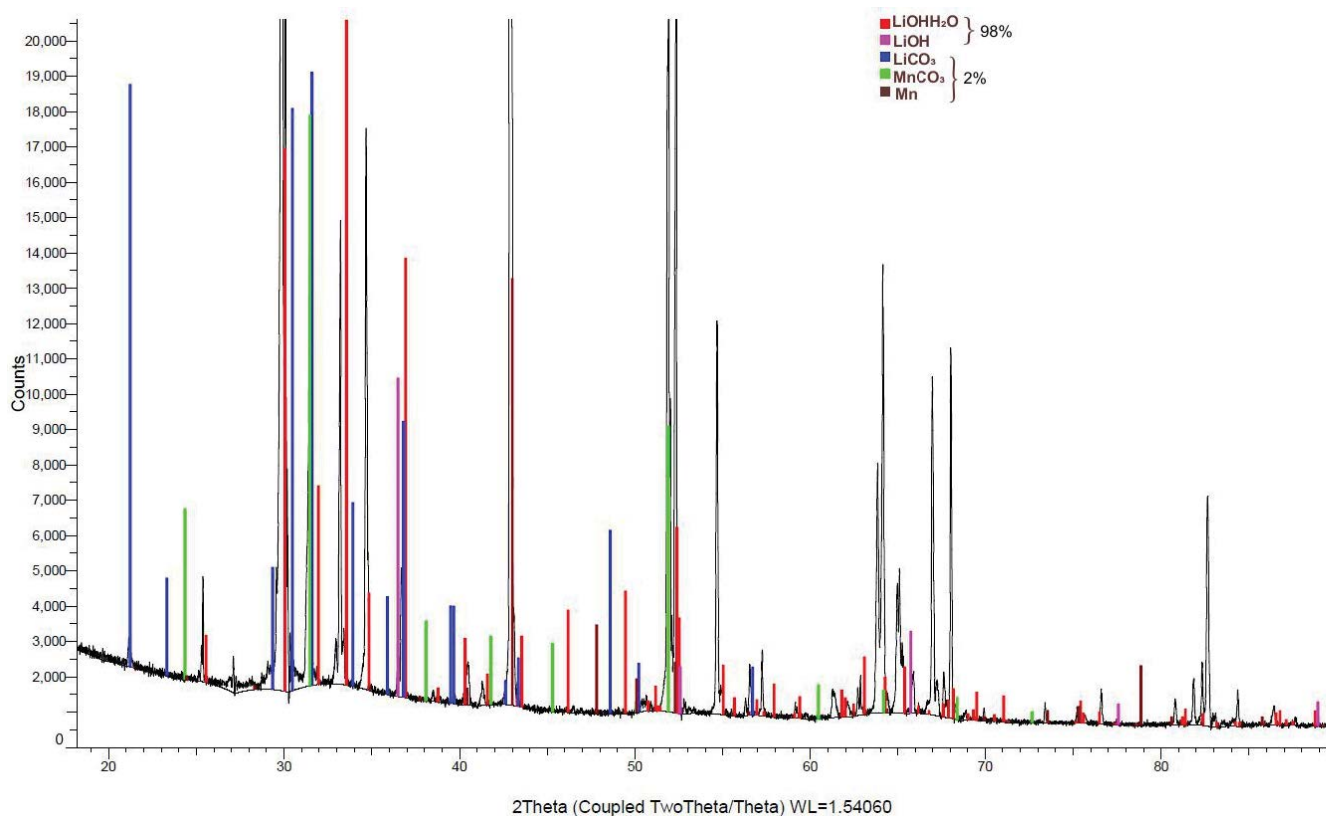


Fig. 3. X-ray diffraction pattern of lithium hydroxide.



hydroxide LiOH (accounting for 98 wt.%). Other ingredients constituting 2 wt.% are lithium carbonate  $\text{Li}_2\text{CO}_3$  and a small admixture of manganese compounds.

Thermogravimetric analysis of lithium hydroxide monohydrate is characterized by one dehydration reaction, visible in the graph as mass loss on the thermogravimetric (TG) and differential thermal gravimetric analysis (DTG) curves (Fig. 4). Dehydration of lithium hydroxide monohydrate begins at 50°C and ends at 250°C. Maximum of dehydration occurs at 125°C, which is revealed by the lowest point on the DTG curve. The TG curve shows a strong weight loss of 40%. lithium hydroxide monohydrate contains 42.93% water according to the chemical standard. The lower water content in the TG curve indicates that there are two phases in the leaching solution from which the test material was separated: lithium hydroxide monohydrate and lithium hydroxide (Fig. 4). This is also confirmed by the XRD phase analysis result where these two compounds are observed (Fig. 3).

Wet sieving was used to recover steel and plastic from the leaching solution, thus obtaining a steel and plastic upper size fraction and a lower size fraction. The upper size product underwent drying and magnetic separation. The process yielded steel as a concentrate in the amount of 120.25 g and plastic waste in the amount of 34.75 g. The results of magnetic separation are shown in Table 4.

The magnetic separation process resulted in a high steel yield of 99.59%. The lower size fraction was filtered

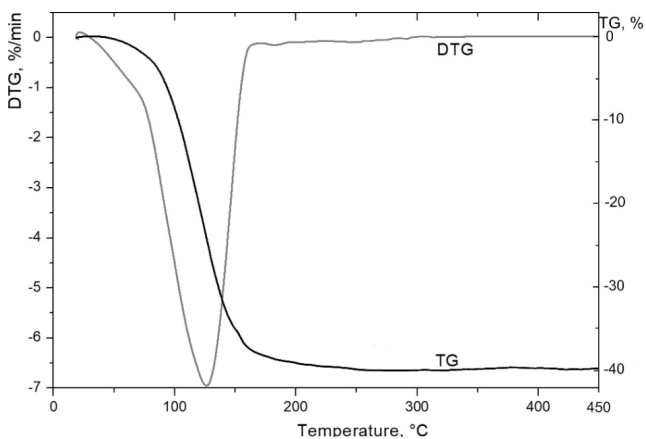


Fig. 4. Thermogravimetric and differential thermal gravimetric analysis of lithium hydroxide from process.

Table 4  
Magnetic separation of the upper size fraction

Product	Output, $\Upsilon$		Content of component, $\lambda$		$\Upsilon(\%) \cdot \lambda(\%)$	Yield (steel) $\varepsilon = \gamma(\lambda/\alpha)$
	g	%	Steel	Plastic		
			%	%		%
Waste	34.75	22.42	1.43	98.56	32.06	0.41
Concentrate	120.25	77.58	99.38	0.42	7,709.9	99.59
Feed	155.0	100	77.41 (=α)*	–	7,741.96	100.0

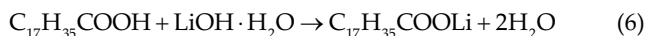
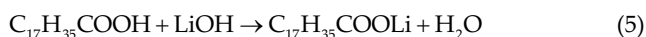
$$\alpha = \sum[\Upsilon(\%) \cdot \lambda(\%)] / 100\% \text{ (content of useful component in the feed).}$$

and manganese compounds were recovered in the amount of 74.8 g.

### 3.3. Preparation of lithium stearate

One of the reasons for the lack of technology for processing button cells is the low yield of lithium compounds ( $\text{Li}_2\text{CO}_3$  and LiOH) obtained during the processing of this type of battery. This is confirmed by research conducted by Schiavi et al. [17] who used primary button and cylindrical lithium batteries to cryomechanical treatment and then recovered the metals through a hydrometallurgical process. In this technology, lithium was recovered in the form of lithium carbonate with a yield of 50%, without specifying its purity. Analyse of the results of the research presented in the paper, 100% yield of lithium compounds was obtained because the post-process liquids are returned to the leaching node.

Lithium hydroxide compounds, they are difficult to store due to their high absorption of  $\text{CO}_2$  from the air [33]. Such a problem does not occur in the case of lithium stearate which storage is very easy, therefore such a solution was proposed in the paper. Lithium stearate obtained in presented research, was formed by the synthesis of LiOH and  $\text{LiOH} \cdot \text{H}_2\text{O}$  with stearic acid. Synthesis in an equimolar ratio occurs according to the reactions (5) and (6):



Recommended temperature for synthesis of lithium stearate is 90°C. Reactions (5) and (6) occur then at optimum speed and efficiency [36].

To ensure optimal conditions for the process of synthesis of lithium stearate conducted in presented research, it was necessary to concentrate the solution after leaching and filtration. For this purpose, less water during the reaction along with the alkali, heated by the concentration process was supplied. Thus, the heat required to heat stearic acid was reduced. Increasing the concentration of lithium hydroxide has affected the reaction speed, with its dynamics increasing with a concentrated substrate.

Based on the FT-IR spectrum, it can be concluded that the result of the synthesis is lithium stearate (match factor 98.9% – Li Stearate DuraSamp IR) (Fig. 5). The reaction yield is 102% for the stearic acid used. With full use of the filtration

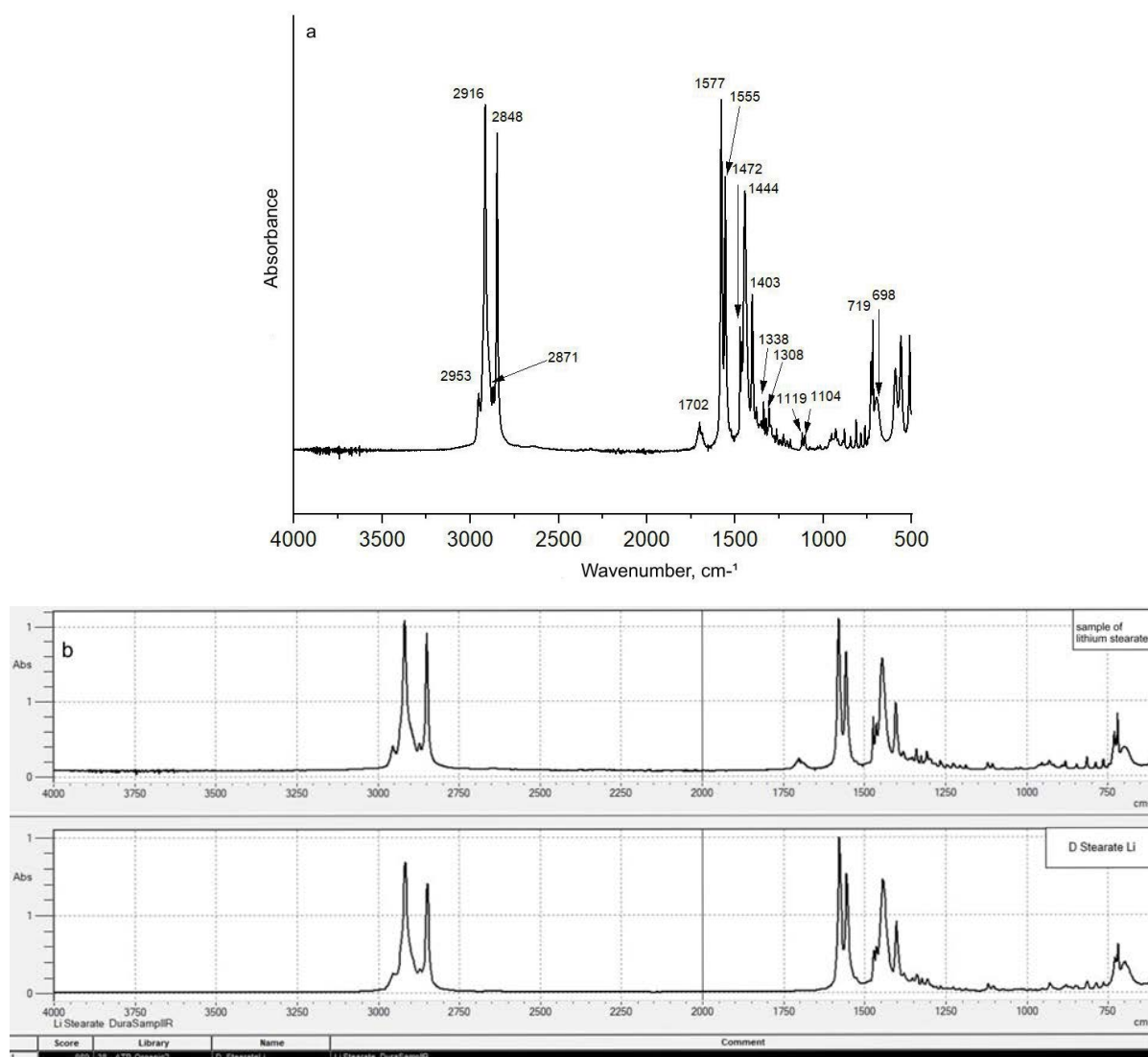


Fig. 5. FT-IR spectra of lithium stearate sample with wavenumbers (a) and FT-IR spectra of the sample compared to the source plot (b).

solution, 31 g of lithium stearate was obtained as a result of the synthesis. The market value of 94%  $C_{17}H_{35}COOLi/kg$  is about USD 100. This means that 1 Mg of lithium metallic anode button cells can yield 126 kg of lithium stearate with a market value of USD 15,000.

The metal content in the liquid after lithium stearate filtration is shown in Table 5. Manganese (1.04 ppm) is characterized by the highest proportion in the liquid tested, followed by copper (0.054 ppm) and nickel (0.005 ppm). Other metals (cobalt and aluminum) are present in trace amounts (<0.01 ppm). Lead and mercury were not found.

As a result of the research, a technological design for producing lithium stearate from waste primary batteries with lithium-anode was proposed (Fig. 6). Fig. 7 shows the mass balance of the process.

Recovered stainless steel can be a valuable raw material for steelworks (1 kg of stainless steel is about \$2). The plastic, mainly polypropylene, will be used in the production of alternative fuel or, after appropriate

Table 5  
Concentrations of metals in filtrate after synthesis of lithium stearate

Element	Concentration in filtrate, ppm
Mn	1.04
Ni	0.005
Co	<0.01
Cu	0.054
Al	<0.01
Pb	–
Hg	–

processing and regranulation, as a raw material for plastic production. The manganese fraction can be used to produce ferromanganese, which is used as an alloying additive and deoxidizer in the smelting of steel and cast

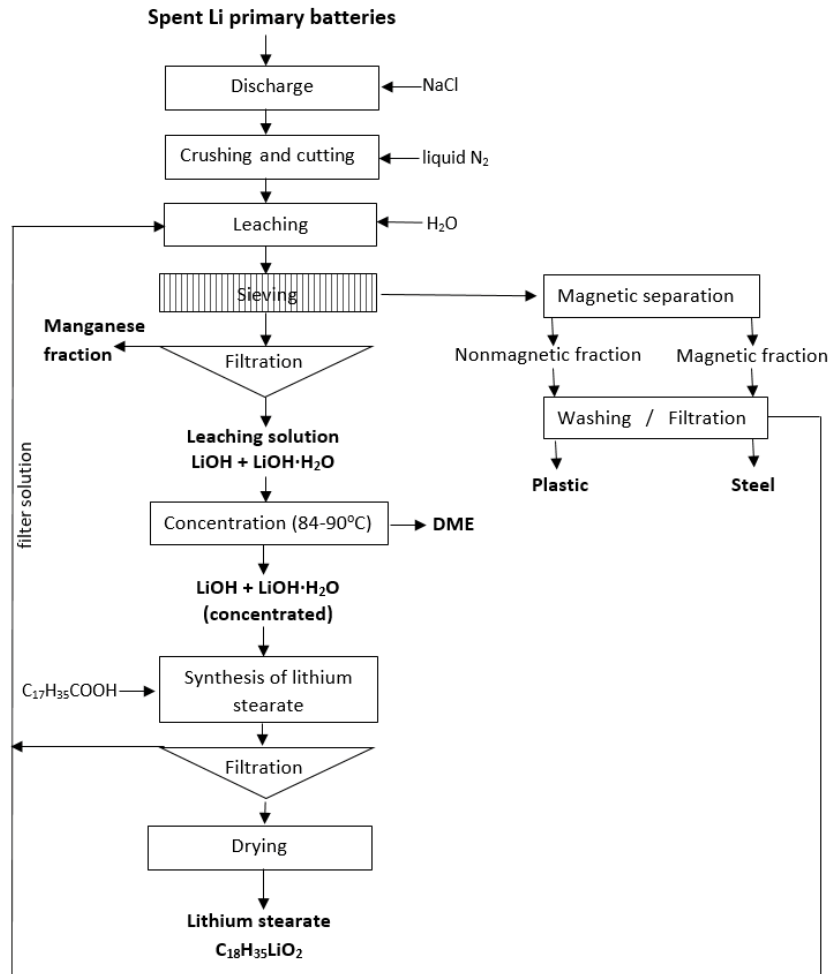


Fig. 6. Technological design for producing lithium stearate.

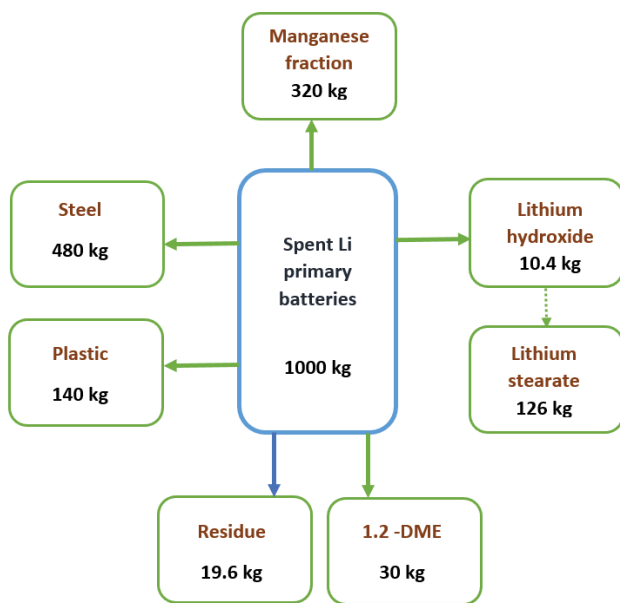


Fig. 7. Mass balance of the process.

iron. The manganese fraction can also be purified by oxidation of accompanying compounds, thus obtaining pure  $MnO_2$ . The market price for 78%  $MnO_2$  is USD 8–10/kg. Separated DME is an oxygen solvent that will find use as an ingredient in paints and varnishes, engine and hydraulic fluids, and cleaning and degreasing formulations. The post-process liquid residue contains propylene carbonate, an organic electrolyte that is non-toxic and biodegradable [37]. The proposed hydrometallurgical acidic lithium battery recycling technologies mostly use hydrochloric acid and sulfuric acid. The resulting products of acid leaching are  $Li_2SO_4$  or  $LiCl$ , synthesized into  $LiOH$  and  $Li_2CO_3$ , the most marketable lithium compounds. For lithium chloride, sodium carbonate is used to secrete it in a carbonate form, with  $NaCl$  being the secondary product. In the case of lithium sulfate, sodium hydroxide  $NaOH$  is used to secrete it in the form of  $LiOH$ . The waste product is sodium sulfate. Secondary waste salts require additional process operations to separate them and treat the wastewater before it is discharged, which increases the cost of obtaining lithium salts.

Current methods of recovering useful components from lithium batteries are associated with their costly processing



and, at the same time, obtaining low-value products. In the process of processing lithium batteries, their deep segregation plays a very important role. In this way, it is possible to limit the number of processes for processing homogeneous batteries and reduce the costs of recovering useful components from them.

#### 4. Conclusions

- The use of inert leaching of ground button cells allows for the complete recovery of useful materials.
- Obtaining high-purity lithium hydroxide depends on maintaining an inert atmosphere in the reaction environment to prevent it from absorbing CO<sub>2</sub> from the ambient air.
- The inert leaching process does not generate wastewater or secondary waste salts, thus allowing for closing the water cycle.
- The final product of the process can be used in the production of lithium lubricants, detergents, and emulsifiers in cosmetics as a thermal stabilizer of plastics.
- The process does not use thermal treatment and does not emit dust and gases or wastewater, which is of particular importance to the environment.
- Propylene carbonate undergoes biological degradation that can be carried out periodically for the leaching liquid. This will be the topic of future research.

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