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Overview of funding sources and technologies for the recovery of raw materials from spent batteries and rechargeable batteries in Poland

Introduction

The development of the battery industry is a priority for EU policy as it was presented in COM and in Implementation of the Strategic Action Plan on Batteries: Building a Strategic Battery Value Chain in Europe COM/2019/176 final, and BATTERY 2030+ roadmap. The EU budget is already providing important funding opportunities to support research and innovation in batteries. The EU's Framework Programme for Research and Innovation for 2014–2020, Horizon 2020, has granted EUR 1.34 billion to projects for energy storage on the grid and for low-carbon mobility. In 2019, Horizon 2020 added a call to fund, under the European Battery Alliance, battery projects worth EUR 114 million. This will be followed by a call in 2020 amounting to EUR 132 million, covering batteries for transport and energy (Tsiropoulos et al. 2018). Moreover, in December 2019 the European Commission approved

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EUR 3.2 billion of public financing for: Belgium, Finland, France, Germany, Italy, Poland and Sweden aimed to support research and innovation across the common European priority area throughout all segments of the battery value chain. Poland will focus mostly on recycling. The dynamic development of the battery industry is associated with the wide use of batteries in portable devices such as: computers, mobile phones, power tools and other electronic devices. The new direction of applications is the growing market of electric and hybrid vehicles (Świętosławski 2016). The industry associated with the production of Li-ion batteries is considered one of the fastest growing in the modern world. It is estimated that from 2025, the potential of the European Union market will be EUR 250 billion per year. This trend is favoured by a newer and comprehensive legislative and energy union governance frameworks. Therefore, the Commission had identified batteries as a strategic value chain, towards which the EU must increase investment and stimulate innovation within an improved industrial policy strategy to build a sustainable and competitive industrial base (COM(2018)773).

1. Financial support opportunities for projects

Europe needs sustained and coordinated efforts to support investments in research and innovation in battery advanced materials and chemistries to enhance its performance on lithium-ion (Li-ion) battery cell technologies, and to pursue leadership in the next generation of battery technologies. The European Union has recently recognized the strategic importance and enormous business potential of metals related to energy storage, specifically to Li-ion batteries and their value chain. Since the battery industry is currently dominated by Asian countries, there is a huge risk that Europe is missing out the new business opportunities, whilst simultaneously becoming even more dependent on the foreign supply of both raw materials and end products. In order to avoid that risk and, instead, use the transition from fossil fuels to alternative sources of energy as an opportunity for Europe, the EU has encouraged the creation of the European Battery Alliance (EBA). EIT RawMaterials has been and will continue to be an active contributor to the European Battery Alliance (Strategic Agenda 2015, 2020). In the field of batteries, the EU mobilizes all its support instruments all round innovation cycle, analysis from basic research and prepared for projects demonstration, first implementation and commercialization. The European Regional Development Fund provides also the innovative research support aimed at promoting the energy sector and low carbon transport.

EU regions have expressed an interest in creating partnerships to implement joint projects and the further development of strong innovation ecosystems in the battery field. The EU budget is already providing important funding opportunities to support research and innovation (R+I) in batteries in Horizon 2020, Era-Net, KIC Raw Materials. Table 1 indicates selected financing options for projects related to innovative battery recycling technologies in EU.

Table 1. Selected financing options for batteries in EU

Tabela 1. Możliwości finansowania projektów w zakresie baterii w UE

Programme	Calls – support EUR	Chosen projects
H2020	EUR 1.34 billion – energy storage on the grid and low-carbon mobility	◆ Affordable High-Performance Green Redox Flow Batteries (HIGREEW) ◆ Copper-Based Flow Batteries for energy storage renewables integration (CUBER) ◆ Development of full lignin based organic redox flow battery suitable to work in warm environments and heavy multicycle uses (BALIHT) ◆ Membrane-free Low cost high Density RFB (MELODY)
H2020	EUR 114 million – European Battery Alliance	◆ Li-ion cell pilot lines network (LiPLANET) ◆ Competitive next-generation European lithium-ion battery technology (SeNSE)
H2020	EUR 20 milion – Next-generation batteries	◆ Advanced all Solid state safe lithium Metal technology towards Vehicle Electrification (SAFELiMOVE) ◆ All Solid-sTate Reliable battery for 2025 (ASTRABAT) ◆ Liquid-Processed Solid-State Li-metal Battery: development of upscale materials, processes and architectures (SOLiDIFY)
ERA-Net Smart Energy Systems	EUR 22 million in 2019 for transnational Research, Development and Innovation projects on integrated energy storage solutions	◆ Open Inter-DSO electricity markets for RES integration (CALLIA) ◆ DC Distribution Smart Grids (DCSMART) ◆ Rural Intelligent Grid (RIGRID)

Author's own study based on available data.

Few of the many previous projects focused on recycling technologies, however, in the latest EU programmes (2019–2020), i.e. H2020-LC-BAT–2019–2020 it was emphasized that the complete electric rechargable batteries value chain and life-cycle must be taken into account, starting from the access to raw materials, innovative advanced materials and nanotechnologies to modelling, production, recycling, second life, life cycle and the environmental assessment. Moreover, in some projects, the increase in more sustainable products with a recycling efficiency going beyond the current legal requirements is expected. As it was established in the Batteries Directive, the perfect economic viability is greater than 50%. Many opportunities for financial support for the rationalization of innovative projects can be obtained through institutions such as KIC Raw Materials (KIC – Knowledge and Innovation Community) in the area of raw materials, established by the European Institute of Technology (EIT) in December 2014. The KIC Raw Materials will integrate and strengthen the innovation potential in the raw materials sector by introducing new solutions, products and services for the sustainable exploration, extraction, processing and recycling of natural resources. The next possibility to receive financial support is EIT InnoEnergy which enables and helps in the implementation of pioneering new technologies in the field of renewable energy sources. The European Battery

Alliance (EBA) was launched in October 2017. This is to ensure that all Europeans benefit from safer traffic, cleaner vehicles and more sustainable technological solutions. All this will be achieved by creating a competitive and sustainable value chain in the production of battery cells in Europe. Table 2 indicates selected financing options for projects related to innovative battery recycling technologies.

Table 2. Selected institutions supporting financing of projects in the field of raw materials

Tabela 2. Wybrane instytucje wspierające finansowanie projektów z zakresu surowców

Programme	Calls – support EUR	Chosen projects
Business Investment Platform (BIP) for the battery value chain	EUR 5 bilion investment	◆ E-BUS Battery (Impact) ◆ Nawacap Ultracapacitors &Ultra Fast Carbon Electrodes (NAWATechnologies)
EIT KIC Raw Materials	EIT funding EUR 328 milion (2019–2022)	◆ Automotive Battery Recycling 2020 (AutoBatRec2020) ◆ European Lithium Institute (ELI) ◆ Li-ion batteries for electric Vehicles (ReLieVe)
EIT InnoEnergy	EUR 104 milion in 2019	◆ FLS200: Floating LiDAR Solutions (EOLOS) ◆ Industrial energy efficiency (Gulplug) ◆ Energy-independent housing (ESC)

Author's own study based on available data.

There are many possibilities of financial support in Poland for innovative technologies of metal recovery from batteries. At present, support will be available to companies specializing in battery recycling in line with the introduced Circular Economy idea. The goal of the current projects is to increase the recycling capacity and extraction of elements from used batteries, and to bring them back into circulation. Under the EU funds (financial period 2014–2020) Polish entrepreneurs are implementing innovative projects in the field of the use of batteries and mobile devices under the Smart Growth Operational Programme, Infrastructure and Environment Operational Programme and 16 Regional Operational Programmes. Table 3 indicates selected Polish projects in the field of battery recycling.

Batteries and rechargable batteries have a significant raw material value, as they undergo recovery processes that can replace the extraction of fossil resources. The key ones: lithium, nickel, cobalt, manganese and graphite – are currently obtained from a small number of countries. In 1 Mg of mobile phones batteries, the average cobalt content is approx. 190 kg, while the nickel content – probably even more (Szamałek and Galos 2016). The unstable political situation in countries with sources of raw materials or high duties and taxes cannot only increase the cost of battery production, but also adversely affect their supply chain in Europe. The biggest challenges posed by new Li-ion on batteries are directly related to the replacement of expensive electrode materials (based on Co) with other less expensive materials, while extending their work time and extending the battery power (Bakierska

Table 3. Selected projects in the field of battery recycling in Poland

Tabela 3. Wybrane projekty z zakresu recyklingu baterii w Polsce

Programme	Calls – support EUR	Chosen projects
1.2. Sectoral R&D programs Smart Growth Operational Programme 2014–2020	EUR 20 milion in 2017 – Intelligent recycling	◆ Thermal conversion of WEEE, PCBs and lithium ion batteries with recovery of Cu, Ni, lanthanides ◆ Lithium cell and lithium ion processing technology ◆ Development of an innovative metal recycling technology, including metals critical, from scrap of used electrical and electronic equipment
Infrastructure and Environment Operational Programme 2014–2020	EUR 26 milion Municipal waste management	◆ Selective Waste Collection Point System

Author's own study based on available data.

and Chojnacka 2016). It is currently estimated that the cost of producing Li-ion batteries p/er 1 kWh is about USD 1000. There is a tendency to reduce this amount to several hundred dollars per 1 kWh. An important aspect in the battery and rechargable battery industry is the recovery of metals such as cobalt which comes from sources classified as exhaustive in the next decade (Pikoń and Bogacka 2017). Therefore, an important element is to enable the recovery of valuable raw materials in appropriate recycling processes. The variety of lithium cells, continuous technological progress in their construction can affect both the economics of processes and the safety itself of processing this type of waste. There is no company in Poland thad would develop the full recycling of the used batteries (Sobianowska-Turek et al. 2016). The most common technique available for processing of this type of waste is the elimination of burdensome waste and introducing its components to the pyrometallurgical process without any basic changes to phase parameters.

2. Scenarios for the development of battery and rechargable battery market in Poland

The analysis of the battery market must take the current trends and the expected increase in demand and production of individual types of batteries and rechargable batteries into account. The paper has reviewed technology changes on the battery and rechargable battery market in Poland which was the basis for the foresight analysis. This method is utilized in many areas of the economy and politics to facilitate the process of making the best possible long-term decisions (Burt and Heijden 2008; Duin and Hartigh 2009), to support innovative activity (Amanatidou and Guy 2008) and strategic planning through the identification of alternative ways of development for emerging technologies, trends and the creation of future scenarios (Ofek and Wathieu 2010). Based on such strategic methods of prediction as the foresight analysis, a methodology whose aim is to examine the direction of the development of Polish battery and rechargable battery market was proposed. The scenario method has been selected, based on the premise that future events cannot be predicted with absolute accuracy and therefore various "scenarios" of the current situation's development should be prepared. On the basis of this method, the literature review and the analysis of the existing data (strategies, market analyses) probable scenarios for the battery and rechargable battery market in Poland have been built. Political, technological and social factors have been chosen as those exerting the strongest impact on the battery and rechargable battery market. Amongst the factors selected, trends and phenomena, theoccurrence of which in the future will be of vital importance, were defined. The assessment of phenomena was made through defining of the development directions. As a result of the tendency analysis, three scenarios were developed. An optimistic scenario was created by selecting in particular areas of the economic environment a trend with the highest potential of growth and positive impact on the economy. A pessimistic scenario was created based on processes with low potential of growth and that exert a negative impact on the market. The most probable scenario was built relying on trends with the stable potential of growth and the highest likelihood of occurrence, regardless of potential force of their negative or positive impact. Table 4 presents the directions of development for individual scenarios.

The scenarios presented in this chapter are the result of the analysis of trends in the environment of the battery and rechargable battery market in Poland. The optimistic scenario assumes that the greatest change on the battery and rechargable battery market

Table 4. Scenarios for the battery and rechargable battery market development in Poland

Tabela 4. Scenariusze rozwoju rynku baterii i akumulatorów w Polsce

Environmental factors/trends	Optimistic scenario	Pessimistic scenario	Probable scenario
	Directions of development		
Technological change	↑	↓	↔
Rate of change in production processes	↔	↔	↔
R&D cooperation	↑	↔	↑
Wealth of the society	↑	↓	↑
Environmental protection	↔	↔	↔
EU legislation	↔	↑	↔
Polish legislation	↑	↓	↑
Public procurement	↑	↓	↔
Financing of battery and rechargable battery projects	↑	↓	↔

Author's own study based on available data.

in Poland will concern the area of technology. Firstly, the increase in R&D cooperation will play a significant role in this sector's development. New technologies will emerge. A transfer of knowledge to entities in cooperation will occur resulting in the development of innovative solutions. A premise for optimism was the improvement in the social environment (increase in the society's wealth). In the regulatory and legal environment, the increase in the scope of public procurement and higher inlays on battery and rechargable battery recycling projects will be of great importance. In a pessimistic scenario for the battery and rechargable battery market in Poland, great difficulties in the social environment, with reduced society wealth in particular, may adversely affect the emergence of new businesses. The regulatory and legal environment may be affected by negative regulation which will result in decreased share of the public sector as regards to public procurement. Adverse effects will apply the least to the technological environment, the absence of increased rate of change in production processes, however, will cause difficulties in the development of new technologies. The overall result of these trends will be a decreased amount of modern and efficient solutions brought about by the aversion of risky decision making. a moderate development is assumed in the probable scenario on the battery and rechargable battery market in Poland. The technological environment is particularly conducive for the sector. The increase in the R&D cooperation as well as academic and research facilities will play a vital role. The sector will benefit from the favourable social environment as well, with increased society wealth in particular. Most likely, the regulatory and legal environment will also evolve towards a positive change on the battery and rechargable battery market in Poland. Assumptions were adopted that in line with the concept of a circular economy, activities in the field of recycling and obtaining metals from waste will be supported in Poland. This is realistic because in January 2019 a new National Intelligent Specialization – The Circular Economy – water, fossil raw materials, waste was created (Kulczycka et al. 2019). In Poland, there has been a broad discussion on the implementation of state policy in the field of raw materials for several years now, in which it in which obtaining raw materials from waste is also planned. Strong policy support in both battery production and recycling has already been implemented as part of EU policy.

3. Technologies for recovering raw materials from used batteries

Technologies for the recovery of raw materials from used batteries are separation (mechanical), pyrometallurgical and hydrometallurgical methods (Sobianowska-Turek et al. 2014). Separation methods are most commonly used for batteries (industrial type) and as a preliminary operation in the field of processing technologies. They rely on mechanical loosening of the structure (body) of the battery with characteristic properties (density, size, magnetic properties). These activities are usually simple and cheaper than other processes, and therefore they are used to prepare the material stream for further chemical processing. Pyrometallurgical methods rely on the recovery of materials (basic metals) through their use at high temperatures for active condensed phases (including metal alloy) or for the gas phase with subsequent condensation. These methods are used for richer phases in the recovery of components, they can accumulate at elevated temperatures in the gas phase (applies to e.g. cadmium or zinc). The advantage of pyrometallurgical methods is the possibility of recycling various types of cells, including different materials (Sobianowska-Turek 2009). Hydrometallurgical methods usually involve acid or alkaline leaching of prepared battery waste (after mechanical treatment). It should be remembered that hydrometallurgical processes are less energy-consuming than pyrometallurgical ones, but the waste generated is more onerous. Recently, bio-metallurgical processes have become increasingly popular. Compared with the above-mentioned pyro- and hydrometallurgical processes, it is believed that biological processes have higher efficiency, lower cost and are safer for the environment (Espinosa et al. 2004; Xin et al. 2009). In recent years, an increase in the development of bio-metallurgical processes has been observed, which gradually began to replace hydrometallurgical processes. Unfortunately, their big disadvantage is the time and breeding of various types of bacteria. However, the treatment period of the bio processes is longer and different types of bacteria are required. Among the different types of bacteria and inorganic chemical solutions, the Acidithiobacillus ferrooxidans are extensively investigated for the battery waste treatment. Elemental sulfur and Acidithiobacillus ferrooxidans ferrous ions were used to produce metabolites, where the H_2SO_4 and ferric ion were responsible to recover Li and Co from $LiCoO_2$ of Li-ion batteries (LiBs). The results show that the metabolites enhanced the dissolution of metals and that, the bio-dissolution of Co was faster than the one of Li (Mishra et al. 2008). The bioleaching process of the spent LiBs at pulp densities ranging from 1% to 4% was investigated with exploration of the process controls. A bioleaching efficiency dec-rease from 52% to 10% was observed for Co, while a decrease from 80% to 37% occurred to Li recovery. This decrease was attributed to a pulp density increase from 1% to 4%, with an extraction efficiency of 72% for Co and 89% for Li at 2% pulp density (Wajda et al. 2015; Bajestani et al. 2014). Compared to the chemical leaching process and based on thermodynamic analyzes, the bioleaching process has great potential for recovering metals from spent LiBs.The bioleaching of heavy metals from spent Ni-Cd and NiMH batteries using Acidithiobacillus ferrooxidans was investigated (Bajestani et al. 2014). In order to investigate the effects of initial pH, powder size and initial Fe^{3+} concentration on the percentage of metals recovered, a Box-Behnken design was used. Under optimization of the experimental conditions a recovery of 87, 67, and 93.7% for Ni, Cd and Co, respectively, was obtained. It was confirmed that, Acidithiobacillus ferrooxidans is an effective toxin resistant microorganism for the bio-recovery of heavy metals. Other groups (Zeng et al. 2013) discuss the influence of silver ions on the bioleaching of cobalt from spent LiBs. Using the same bacteria type Acidithiobacillus ferrooxidans and a concentration of 0.02 g/L Ag^+ a 98.4% Co recovery was obtained, while in the absence of Ag^+ a 43.1% Co was observed. The proposed mechanism is based on catalytic interactions: firstly Ag^+ reacts with Co to form $AgCoO_2$, while an enhancement of the Co recovery using Acidithiobacillus ferrooxidans and Ag+ is explained (Zeng et al. 2013). Xin et al. (Xin et al. 2009) dealt with the recycling of spent Zn-Mn batteries via bio-metallurgy. Under optimum conditions a 96% of Zn extraction was achieved within 24 h, while 60% of Mn extraction was obtained using a biological mechanism with incubation for more than 7 days. For a better understanding of the mechanism of the leaching reaction a modified shrinking core model was proposed. The recovery of Cr and Ni using bioleaching of dewatered metal-plating sludge was subjected, showing that pH = 1, a pulp density of 9 g/l and initial Fe^{3+} concentration of 1 g/l are the optimum values and represent an recovery efficiency of 55.6% for Cr and 58.2% for Ni. However, even if the bioleaching process shows good results with respect to the recovery efficiencies, the procedure needs to be more effective by improving the methods and reducing cost for culturing the bacteria. Nevertheless, the bacteria need to be exchanged at a specific time intervals being unable to remain active in a concentrated waste solution. In order to bring the process to a commercial operation, the bio-metallurgy process remains challenging.

3.1. Lead-acid batteries

Lead-acid batteries are used as car batteries, gel batteries, forklifts batteries, cleaning machines batteries, UPS batteries, telephone exchange batteries, server rooms batteries, industrial batteries, submarine batteries. Figure 1 shows the composition of the lead-acid battery.

Lead acid batteries in Poland are processed by:

- Orzeł Biały in Bytom – processing capacity approx. 120 thousand Mg of scrap metal/year,
- Baterpol in Swietochlowice – processing capacity approx. 70 thousand Mg per year,
- ZAP Sznajder Batterien Inc in Pruszkow – processing capacity approx. 11 thousand Mg,
- Akros Llc in Stoczek Lukowski – permission for processing 1.5 thousand Mg/year,
- A.L.V. "LINK" Trade and Service Production Company.

Companies with higher processing capacities have a collection network for used batteries, therefore they also deal with the provision of equipment to the recipients with acid-resistant containers necessary for the transport of batteries. The recycling process of batteries

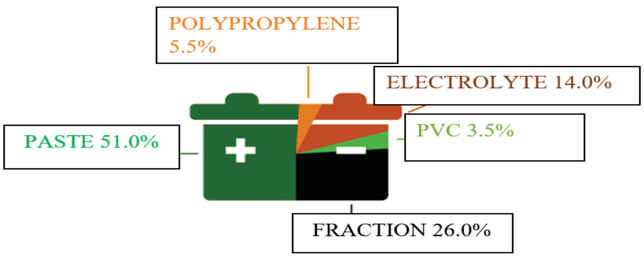

Fig. 1. Composition of a lead acid battery (http://www.orzel-bialy.com.pl/pl/oferta/proces-recyklingu)

Rys. 1. Skład akumulatora kwasowo-ołowiowego carried out in these enterprises consists mainly in the recovery of lead. Larger companies also have installations for neutralizing sulfuric acid, smaller ones (like Akros), only melt metallic lead and sell castings, and dross is managed in external companies (in rotary kilns). The volume of supply for processing lead-acid batteries in Poland is estimated at about 120,000. Mg and the processing capacity of these plants significantly exceeds it. The price of battery scrap ranges from PLN 2.8 to PLN 4 per kilogram. Almost 100% of used lead-acid batteries are currently being processed in Poland. An increase in the processing of one company can take place only at the expense of the other. The best solution would be import, which according to Polish regulations is prohibited (batteries qualify for hazardous waste). The Baterpol company purchases and processes battery scrap, while being a significant producer of refined lead and lead alloys. The company operates in two plants, the Battery Scrap Processing Plant located in Świętochłowice and the Lead Plant located in Katowice. The technological solutions used close the battery recycling cycle and allow for the economic use of over 95% of mass of battery scrap. Lead recovered from used batteries is used to produce refined lead, and electrolyte and sulfur from desulphurized paste are used to produce sodium sulphate – used in the chemical industry. Battery scrap processing is carried out using CX technology (the Italian company Engitec Technologies). The installation for the recycling of scrap metal in the Orzeł Biały enterprise uses the technology of separation and segregation with the use of heavy liquids, as well as melting of metal-bearing fractions in rotary-swing furnaces (Kamińska et al. 2014). In lead, paste, which constitutes about 51% wt. battery contains about 74% of lead, and in the metallic fraction, which is about 26% of the weight of the battery, there is about 98% lead. With such assumptions, it can be estimated that over 632 kg of lead can be recovered from 1 Mg of battery scrap. According to money.pl (www.money.pl) the price of 1 Mg of lead is a minimum of USD 2,000.

3.2. Rechargeable batteries and lithium ion batteries

LiBs that are used, among others, in electric and hybrid vehicles, they are made of housing (25%), cathode (25%), anode (14%), electrolyte (10%), copper foil (8%), aluminum foil (5%), separator (4%) and others (6%). In addition to vehicles, LiBs are used in laptops, power tools, vacuum cleaners, drones. The most popular version is lithium-cobalt, but manganese, titanium, aluminum or nickel in various blends and proportions, among others, can be used for the construction of cells. However, most of these options are unprofitable. Anode and cathode are the most important and the most valuable components of the battery, due to the presence of Co, Fe and Ni. The anode for lithium-ion batteries is made of graphite, carbon and polyvinylidene fluoride (PVDF), while the cathode consists of carbon, PVDF binder and lithium. Active cathode materials include lithium, which usually occurs as oxides $LiCoO_2$, $LIMnO_4$, $LiNiO_2$, LiV_2O_3 and $LiFePO_4$. The role of electrolyte in Li-ion batteries is played by an organic substance containing dissolved salts, including LIPF6, LiBF4. An important element of the battery is also a separator, maintaining an equal distance between the electrodes; it is made of PE or PP. Table 5 contains the material compositions of LiBs from three different manufacturers (Mantuano et al. 2006).

Table 5. Material composition of Li-ion batteries from three different manufacturers (% wt)

Tabela 5. Skład surowcowy akumulatorów litowo-jonowych trzech różnych producentów (% wag.)

Metal	I	II	III	Average content
Al	10.0	6.5	6.6	8 ± 3
Cd	0.03	0.01	0.03	0.02 ± 0.02
Co	42.9	30.8	34.2	36 ± 9
Cu	13	–	–	13
Fe	0.03	0.06	0.1	0.06 ± 0.05
Li	8.88	2.48	2.45	5 ± 6
Mn	not found	not found	0.01	< 0.01
Ni	0.02	0.02	0.02	0.02
Pb	not found	not found	not found	not found
Zn	0.01	not found	not found	< 0.01

LiBs are mainly subjected to recycling processes by hydrometallurgical methods (they include acid or base dissolution, solvent extraction, chemical precipitation, electrochemical methods and/or a combination of these processes, 57.3%), but also by mecha- nical methods (22.9%) and pyrometallurgical (thermal processes, 16.8%). On an industrial scale, recycling by hydro- and pyrometallurgical methods mainly carried out by means of processes is mainly used (Elibama: European Li-Ion Battery Advanced Manufacturing). The most common recycling methods are:

- Umicore – pyrometallurgical method – possibility of recovery, among others cobalt, nickel, copper, and iron; the disadvantage is the inability to recover lithium, magnesium and aluminum; high energy process,
- Sony-Sumitomo – hydrometallurgical method – possibility of cobalt recovery; the disadvantage is the inability to recover lithium,
- Toxco – hydrometallurgical method – the possibility of lithium recovery at 15–26%,
- Recupyl – hydrometallurgical method – the possibility of recovery of lithium, cobalt.

In recent years, biological technologies that use microorganisms to recover metals are developing techniques for recycling LiBs. Acidithiobacillus ferrooxidans are used, including Acidithiobacillus ferrooxidans, which transfer metals from solid to liquid phase by bio-oxidation and bioleaching (Marcincakova et al. 2016). Due to the growing share of electric and hybrid cars, possibilities of Li and Co recovery from LiBs used in the above mentioned are also being developed. The methods described below are in the phase of laboratory tests. Works were carried out on the possibility of recycling LiBs using the so-called fountain beds: in the first stage of the process, the batteries are mechanically crushed using a hammer mill to a particle size <10 mm and then screened on sieves with a mesh size of 0.211 mm (Wójcik et al. 2017). Metals, plastics and powdered materials are separated in this way. The separated fractions are subjected to a three-stage elutriation process by introducing them to a fountain bed with an air supply. During the initial elutriation, polymer fibers with a low content of Cu, Al, $LiCoO_2$ and graphite are separated, which are then screened on sieves. The material remaining on the fountain bed is subjected to a second degree of elutriation with separation of the Cu/Al fraction, which is subject to purification. In this way, polymers and fractions of different materials with larger dimensions are obtained, which are recycled. In the third stage of elutriation, the LiBs housing materials are separated. Another method is the ANVIL (Adhesion Neutralization via Incineration and Impact Liberation) process (Hanisch et al. 2015). The essence of the process is the weakening of the adhesion between the battery housing and the film due to the thermal decomposition of PVDF, which also affects the lower cohesion between particles of active materials.

3.3. Zinc-carbon and zinc-manganese batteries

Zn-Mn batteries (mainly) and Zn-C batteries are industrially processed using processes such as Batrec (Sumitomo), Recytec and using Waelz technology (Sobianowska-Turek 2009). The Batrec (Sumitomo) process was developed in the 1980s. It is a process of processing Zn-Mn batteries based on pyrometallurgical technology. The process can be divided into several stages. In the first stage, battery pyrolysis occurs. The batteries are subjected to high temperatures (up to 700°C), which allows water and mercury to evaporate, and all organic components (paper and plastics) contained in the batteries are gasified or burning. The resulting gas stream is directed to the after-burning in a separate reactor at a temperature of over 1000°C, which eliminates dioxins and furans. The gases formed during the after-burning are treated in a separate installation in the second stage. Gas purification is carried out using the wet method, and removal of impurities is accompanied by the condensation of mercury vapor after cooling the gases to 4°C. The sludge obtained in this way is directed for further processing in a separate mercury recovery (distillation) installation. In the third stage, metals are recovered. The material containing metallic components of the battery is placed in an electric induction furnace and heated to a temperature of 1500°C in a reducing atmosphere. Under these conditions, iron and manganese form an iron-manganese alloy, while zinc evaporates and is recovered in a condenser. The iron-manganese alloy drain is run cyclically. Cyanides, fluorides and heavy metals are removed from aqueous solutions after gas purification. Sludges from the purification system after filtration are recycled to the pyrolysis process. Purified water is directed to sewage. On the other hand, sludges containing mercury coming from gas treatment installations are subjected to moderately high temperatures, around 360°C. This allows the mercury to evaporate and to be recovered by condensation. Any mercury residues contained in the gases from this process are trapped on activated carbon filters. The periodically run mercury recovery process is a low-emission process. In 2002, Batrec Industrie factories in Wimmis, Switzerland, which use this technology, processed about 5,000 Mg of waste batteries. Approximately 360 kg of ferro-manganese alloy (Fe-Mn), 200 kg of zinc (Zn), 1.5 kg of mercury (Hg) and 20 kg of slag were obtained from one ton of charge. The process's energy expenditure is about 3.5 MWh/Mg of battery waste. The input material must not contain other types of batteries – in particular nickel-cadmium (Ni-Cd) batteries.

In Poland, zinc batteries are processed by BatEko Sp. z o.o, Eneris, Biosystem SA and KOS Sp. z o.o., the last two companies have joint management and process used batteries//rechargable batteries to a small extent. At Eneris Recupyl, there is a mechanical recycling process, and BatEko processes batteries using the hydrometallurgical method. At BatEko the crushing products are: ferromagnetic (metal housings, collectors), diamagnetic (battery components made of paper or plastics), paramagnetic (zinc anodes, cathode masses). The ferromagnetic fraction is sold to smelters, the diamagnetic fraction is treated as an alternative fuel, and manganese is recovered (by hydrometallurgical route: leaching, pressing, drying) from the paramagnetic fraction, which is about 50% – it is then sold in the form of oxide to battery manufacturers. Approximately 10,000 Mg of batteries are processed in BatEko annually (processing capacity is about 13,000 Mg). From the paramagnetic fraction, after manganese recovery, the waste is the scrubber, which is processed by other recyclers (waste code 11 02 02 – Sludges from zinc hydrometallurgy (including jarosite) – zinc recovery is possible from it. Zinc batteries, previously sorted from the battery stream, are processed at ENERIS Recupyl. The batteries are crushed, followed by fraction separation. About 3,000 Mg batteries are processed annually (processing capacity: sorting 4,000 Mg/year, processing 6,000 Mg/year (Sobianowska-Turek 2009). Steel and non-ferrous metals are transferred to smelters, the paper + plastics fraction is transferred as RDF, and the black mass is transferred to smelters where zinc and manganese in the form of oxide are recovered MnO is used as a component of silica slag, used as a mineral raw material for the production of building aggregates.

3.4. Nickel-cadmium batteries

Accurec, TNO, Everead, Inmetco and Sab Nife technologies can be used to recycle nickel--cadmium batteries (Szczepaniak and Sobianowska 2007). In Accurec technology, the first stage of conversion is to remove the electrolyte and then to separate the housings, mainly of plastics. The remaining material is subjected to vacuum distillation in an oven with a quartz tube, in which a container with the raw material is placed, induction heated (Kończyk et al.

2016). The process is carried out in two stages at a pressure of about 10 mbar. First, plastic elements are burned off and moisture removed, and the temperature does not exceed 500°C, then the temperature is raised to 850°C and cadmium is distilled off. A single operation lasts about 12 hours. Cadmium purity reaches 99.95%, as long as there are no other batteries in the charge. The processing plant is located in Mülheim, Germany, and its capacity probably reaches 1000 Mg per year (Szczepaniak and Sobianowska 2007). TNO technology (Toegepast-Natuurwetenschappelijk Onderzoek) was developed for the recycling of Zn and Ni-Cd batteries. Initially, it was focused on the recovery of cadmium, nickel and iron, and then it was also modified for the recovery of zinc and manganese. TNO technology allows for the recovery of approximately 275 kg of metallic nickel and 150 kg of metallic cadmium from every 1 Mg of battery. In the Sab Nife process, the electrolyte is removed first and the electrodes are cleaned and dried. Then the material (electrodes) goes to the reactor, where three subsequent operations are performed. In the first, the reactor is heated to 400–500°C and firing of organic matter is carried out in a controlled atmosphere of a mixture of nitrogen and oxygen. This stage lasts about 24 hours, and control of process conditions (especially oxygen potential) is associated with limiting evaporation of cadmium. Process gases are burned in a separate chamber. After the burning (gasification) of the organic substance, the temperature in the reactor is raised to about 900°C and cadmium distillation takes place. During this operation, a reducing atmosphere (a mixture of nitrogen and hydrogen) is maintained (Sobianowska-Turek 2009). This stage lasts about 20 hours, and after its completion the charge contains no more than 0.01% cadmium. In the last part, the temperature is raised to around 1300°C to obtain an Fe-Ni alloy. The purity of the cadmium obtained in this way is, as with other processing technologies, 99.95%. The material composition of nickel-cadmium batteries in% by weight is given in Table 6 (Mantuano et al. 2006).

Table 6. Material composition of Ni-Cd batteries from three different manufacturers (% wt)

Tabela 6. Skład surowcowy akumulatorów Ni-Cd trzech różnych producentów (% wag.)

Metal	I	II	III	Average content
Al	0.01	0.02	0.03	0.02 ± 0.01
Cd	39.4	35.3	28.4	34 ± 8
Co	2.08	2.56	1.43	2.0 ± 0.8
Cu	0.03	–	–	0.03
Fe	0.01	0.03	0.04	0.03 ± 0.02
Li	0.05	0.07	0.04	0.05 ± 0.02
Mn	not found	0.01	not found	< 0.01
Ni	14.3	19.8	33.3	22 ± 14
Pb	not found	not found	not found	not found
Zn	0.90	0.01	0.03	0.3 ± 0.08

The recycling of Ni-Cd batteries is associated with negative activities related to their collection and improper processing leading to obtaining nickel plates, the sale of which brings economic profit. Other demolition products are removed in an environmentally hazardous way, i.e. by pouring electrolyte into the sewage system or soil. Iron-cadmium plates are sent to steel mills as scrap. However, when the iron-cadmium plate, visually no different from steel scrap, goes to processing at the steel mill, it causes disorganized cadmium emission.

Conclusions

Effective and real recycling technologies with full life cycle analysis are under development and show the immediate need to develop comprehensive recycling solutions. The recycling of used batteries is not just about reducing the amount of generated waste directed to landfills, but above all reducing the use of non-renewable natural resources (Pyssa 2006). More and more lithium batteries are being used in the development of hybrid and/or electric vehicles. Along with the continuous development of hybrid technology, an increase in the return flow of used batteries is expected. However, commercially available batteries are not yet high enough to meet the power requirements of hybrid and/or electric vehicles. The most realistic scenario for the development of the battery and rechargable battery market in Poland assumes that the growth of innovative and modern technologies will be continued, with strong support from the academia. In the age when the economy transforms towards the electromobility and renewable energy sources, financial inlays on the implementation of supporting projects are of vital importance. UE activities are directed on financing R&D projects taking the entire value chain, ecodesign included, into account. It is also worth noting that Poland is becoming a better and better market for global investors while launching the European Battery Alliance plays a significant role in making the battery value chain more sustainable. A perfect scenario for the battery and rechargable battery market in Poland would purse solutions that will provide for an appropriate legal framework, ecodesign with recycling considered as well as maintained high quality standards. Challenges are facing the development of innovative concepts and technologies that can lead to battery development. Many innovative materials based on new chemicals, such as $LiFePO_4$, LiNiCoMnO, LiNiCoAlO, LiMnO, LiNiMnO, LiTiO, LiSi, LiSn, are intensively tested to increase the battery's performance to the level of the car. On the other hand, the economic and political implications of many countries around the world are considered important in budgeting funds to stimulate research and development of LiB technology. Developing innovative, cost-effective, simple, flexible and environmentally friendly solutions will be a challenge for future recycling processes. Sectors based on modern and efficient sources of electricity are also becoming more advanced. More and more electric buses are being introduced in Polish cities. The number of hybrid and electric vehicles in which batteries are used is also increasing. This means that the need for their proper management, recovery and recycling of batteries and rechargable batteries will increase proportionally. At present, it is possible to use a wide range of rechargeable batteries and batteries of different size, shape and type. Zinc-carbon and alkaline batteries constitute over 80% of the cells introduced to the Polish market. The battery market is associated with such types of rechargeable cells as nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), lead-acid and Li-ion. Ni-Cd batteries were one of the most popular electricity storage until recently. They were widely used in all types of power tools and in various electronic devices, such as flash lamps or radios. Ni-Cd batteries have been partly displaced by nickel metal hydride batteries. According to Rogulski and Czerwiński (2014), a rapid development of lithium cell technology has occurred, which after the displacement of nickel-metal hydride batteries from the segment of portable batteries used to power electronics begin to compete with them in automotive applications. Batteries/ /rechargable batteries contain many different materials that have a specific market value and, for rational resource management, waste batteries/rechargable batteries should be recycled. At the same time, virtually all batteries/rechargable batteries contain substances that are toxic and can pollute the environment. Therefore, some batteries and rechargable batteries that are included in the waste category hazardous substances should be subjected to the disposal process and, if possible, recycling. In the wake of the Paris agreement (COP21) and the Green Deal there is a need for significant reductions of greenhouse gas emissions in a short time span. Electric batteries are currently seen as important technological enablers to drive the transition towards a de-carbonised society, by integration of renewable and clean energy sources (such as wind energy and photovoltaics) in the electricity grid, and, in particular, by the electrification of transport. Energy storage is the common denominator: it includes both electro-mobility and stationary applications despite the different constraints applying to each of these applications in real life. Electric batteries have recently achieved considerable improvements in terms of their technical performance (such as energy density, power density, thermal stability and durability) and economic affordability (European Commission Decision C(2019) 4575). Such improvements are major contributors to the successful introduction of electric vehicles (which are becoming less expensive and have a longer range) and of stationary energy storage systems. But for a successful mass introduction of electrified mobility and renewable and clean energy systems with market competitive performances and – in the case of electric vehicles – fast charging capability, substantial improvements of the electric battery technologies are required. The competitiveness of new advanced energy storage systems or sustainable battery powered vehicles is strongly dependent on the performance and cost of the battery and battery cells and the materials used for the production of the cells. This is especially valid for the fast growing market of electric vehicles. However, the world production of automotive battery cells is dominated by Asian companies which represent more than 90% of the present world capacity.

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OVERVIEW OF FUNDING SOURCES AND TECHNOLOGIES FOR THE RECOVERY OF RAW MATERIALS FROM SPENT BATTERIES AND RECHARGEABLE BATTERIES IN POLAND

Keywords

recycling, raw materials, innovations, batteries and rechargable batteries

Abstract

Building a Strategic Battery Value Chain in Europe COM/2019/176 is a priority for EU policy. Europe's current share of global cell production is only 3%, while Asia has already reached 85%. To ensure a competitive position and independence in the battery market, Europe must act quickly and comprehensively in the field of innovation, research and construction of the infrastructure needed for large-scale battery production. The recycling of used batteries can have a significant role in ensuring EU access to raw materials. In the coming years, a very rapid development of the battery and rechargable battery market is forecast throughout the EU. In the above context, the recycling of used batteries plays an important role not only because of their harmful content and environmental impact, or adverse impact on human health and life, but also the ability to recover many valuable secondary raw materials and combine them in the battery life cycle (Horizon 2010 Work Programme 2018–2020 (European Commission Decision C(2019) 4575 of 2 July 2019)). In Poland, more than 80% of used batteries are disposable batteries, which, together with municipal waste, end up in a landfill and pose a significant threat to the environment. This paper examines scenarios and directions for development of the battery recycling market in Poland based on the analysis of sources of financing, innovations as well as economic and legal changes across the EU and Poland concerning recycling of different types of batteries and rechargable batteries.

PRZEGLĄD ŹRÓDEŁ FINANSOWANIA I TECHNOLOGII ODZYSKIWANIA SUROWCÓW Z ZUŻYTYCH BATERII I AKUMULATORÓW W POLSCE

Słowa kluczowe

recykling, surowce, innowacje, baterie i akumulatory

Streszczenie

Budowanie strategicznego łańcucha wartości w zakresie baterii i akumulatorów w Europie COM/2019/176 jest priorytetem dla polityki UE. Obecny udział Europy w globalnej produkcji ogniw wynosi zaledwie 3%, podczas gdy Azja osiągnęła już poziom 85%. Aby zapewnić konkurencyjną pozycję i niezależność na rynku baterii, Europa musi działać szybko i kompleksowo w dziedzinie innowacji, badań oraz budowy infrastruktury niezbędnej do produkcji baterii na dużą skalę. Recykling zużytych baterii może odgrywać znaczącą rolę w zapewnianiu dostępu UE do surowców. W najbliższych latach prognozowany jest bardzo szybki rozwój rynku baterii i akumulatorów w całej Uni Europejskiej. W powyższym kontekście recykling zużytych baterii odgrywa ważną rolę nie tylko ze względu na ich szkodliwą zawartość, niekorzystny wpływ na środowisko oraz zdrowie i życie ludzkie, ale także na możliwość odzyskania wielu cennych surowców w całym cyklu życia produktu (program prac „Horyzont 2010" na lata 2018–2020 (decyzja Komisji Europejskiej C (2019) 4575 z dnia 2 lipca 2019 r.)). W Polsce ponad 80% używanych baterii to baterie jednorazowe, które wraz z odpadami komunalnymi trafiają na składowisko odpadów, stanowiąc istotne zagrożenie dla środowiska. Celem postawionym w artykule jest opracowanie scenariuszy i kierunków rozwoju recyklingu rynku baterii w Polsce na podstawie analizy źródeł finansowania, innowacji oraz zmian ekonomicznych i prawnych w UE i w Polsce w zakresie recyklingu różnych typów baterii i akumulatorów.