HELENA

Halide solid state batteries for **E**Lectric v**E**hicles a**N**d **A**ircraft

Deliverable 2.3 Recycling targets and safety requirements based on the chemistry of HELENA battery system

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Publishable summary

In this report, the main objective of defining the recycling target per element considering the material matrix in the HELENA Project was achieved. No deviation from the planned targets and activities on Task 2.4-subtask 2.4.3 "Testing and recycling target definitions"- "Definition of targets and safety requirements for recycling" is reported. Results from this deliverable have been transferred to T8.1 to define the recycling strategy and T8.3 to be considered for the evaluation of the validation experiments of the recycling process. In the following, the perspective of the study on the recycling process during the project is explained:

The HELENA project aims to design a solid-state battery that meets the requirements for use in electric vehicles and airplanes, while also being optimised for high currents and stable cycling. The project also aims to assess the environmental compatibility of the battery design and its potential for future recycling. The battery system contains various components, some of which are well-known for recycling, while others are experimental. The project proposes developing a recycling methodology that focuses on recovering base and strategic metals and achieving recycling efficiencies of 80% for copper and casing material, 90% for cobalt, and 60% for lithium, and 90% for manganese and nickel. The project will also explore the valorisation of materials contained in the solid electrolyte and assess the quality of products for industrialisation. The overall recycling rate are computed based on experimental data registered in the literature, experience and in accordance with EU battery directive regulations.

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Abbreviations

SYMBOL	SHORTNAME
Al	Aluminium
BAT	Best Available Technology
CC	Current Colector
Co	Cobalt
Cu	Copper
EOL	End-Of-Life
EU	EU
Li	Lithium
LIBs	Lithium Ion Batteries
Mn	Manganese
Ni	Nickel
NMC	Lithium Nickel Manganese Cobalt Oxide
wt%	weight percent

1 Introduction

The HELENA project is proposing a disruptive battery design with optimised performance at high currents and stable cycling that should fulfil the requirements for implementation in electric vehicles and airplanes. In addition, their properties for future recycling and the environmental compatibility should be quantified and properly assessed.

The studied systems contained different cell components such as anode materials (current collector, Li-metal foils), cathode materials (current collector, $LiNi_{0.6}Mn_{0.2}Co_{0.2}$ (NMC), binder, carbon black), separator, halide electrolyte (Li-Y-Cl-Br) and casing material. Some of these materials are well known in the manufacturing and further recycling of End-Of-Life (EOL) Lithium Ion Batteries (LIBs). In contrast some others like halide electrolytes are experimental materials and little information can be found regarding recycling. Therefore, due to the complexity of the system and unknown performance of the studied materials for recycling, an assessment of the material matrix has been done and possible recycling targets per element defined. In addition, a general safety handling operation was proposed to be considered in the technical evaluation of the recycling concept in WP8 (Task 8.1). the proposed values are also in line with the European Directive 2006/66/EC and current national regulations in member countries and the future requirements suggested to be adopted in 2026 and 2023. The HELENA project aims not only to fulfil all regulations but also to achieve the best standards for recycling in a sustainable manner. This report provides an overview of the main materials being considered for the battery design, and a preliminary description of the materials handling options based on Best-available-Technology (BAT) guidelines, which will serve as a guide for future developments in recycling within the project.

2 Recycling targets and safety requirements

2.1 Recycling targets definition

A Solid-state battery contains, in principle, the same type of materials required to build up the structure of a conventional battery. Figure 1, the matrix includes an anode system made out of a current collector (copper foil) and Li-metal as active material, an artificial protective layer made of Al_2O_3, TiO_2 and/or TiO_xN_y or a polymeric or hybrid polymer-inorganic, a halide electrolyte (Li(5-6%), Y(22-24), Cl (34-48%), Br (22-39%)), an active material coating made out of $Li(Ni_xMn_yCo_z)O_2$ (NMC) ($x + y + z = 1$), binder and carbon black, and a current collector at the cathode side, which will most probably be aluminium. The above-listed materials would remain at the EOL of the spent battery, and cells would need to undergo a recycling process aiming to extract valuable and relevant metals.

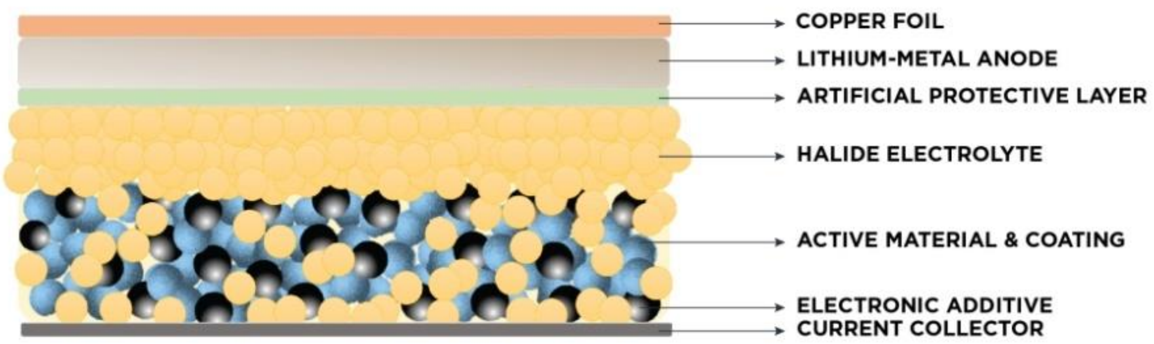

Figure 1: HELENA Battery structure

The definition of the recycling targets follows a strategy based primarily on the new EU regulatory framework for batteries and reported data on BAT for recycling of conventional LIBs. The first one consists of a series of suggested changes to the regulations of the European Parliament and the council concerning batteries and EOL batteries, which are currently regulated according to Directive 2006/66/EC and amending Regulation (EU) No 2019/1020 [1]. For instance, it is expected that from 2025, recycling of the whole LIB should reach at least 65 wt% and 70 wt% by 2030. Therefore, a total recycling rate of **75 wt%** has been set at HELENA. In addition, specific recycling requirements will also be introduced in the new regulation, for instance, for Li (35 to 70 wt% between 2026 and 2030), Co, Cu, Ni, and Pb (90 wt% from 2026). In Table 1, every battery segment is split into individual constituents. In the table, the expected recycling efficiency is set together with the expected material output to be recovered at the end of the recycling process. A general observation that should be considered during the design of the recycling concept is also given. As it can be seen, recycling targets are mainly set based on previous works on the recycling of NMC battery systems. Other experimental materials lacking data or with unknown behaviour regarding recycling at this project stage are initially set to zero without compromising the expected regulatory changes in the European Directive. It is recommended to follow and understand those materials' behaviour, especially in Task 8.1, working out the recycling concept and Task 8.3, evaluating the recycling concept via experimental validation. This special consideration would allow defining a guideline and suggest measures for the recycling of active experimental materials like the halide electrolyte and metallic Li foils.

Component: HELENA		Element target for recycling	Recycling target in [wt.%]	General observation	Ref
Anode	CC Copper	Cu	80 %	Metal foils should be separated mechanically before any chemical extraction method. Extraction and refining would follow traditional Cu recycling methods.	[2]
	Lithium-metal foils	Li	60 %	Proposal for a new directive repealing the EU Directive 2006/66/EC specifies a target recycling efficiency of 35% as a medium-level ambition. Trials with Li-metal-containing Li-S batteries have shown Li-Yields after thermal treatment, comminution, and CO_2-induced H_2O-leaching of >95%. Still, a more conservative target is formulated since the cathode and separator material differs. The recovery of metallic lithium still needs to be clarified since no work has been reported. It will be necessary to understand the behavior of this material through thermal and chemical treatment. Relevant questions to be solved are 1) Li-liberation from Cu foils, 2) Li2CO3 formation via thermal treatment with and extracted by neutral leaching CO2 3) Li oxidation and further extraction via acid leaching. 3) high-temperature behavior during pyrometallurgical treatment. Extraction via oxidation and agglomeration in the Cu-slag or flue dust. The presence of Cu and even Li would make the mechanical separation of Al from Cu not economically viable. This material will typically be accumutated in the slag during pyrometallurgical recycling of Cu. It can be used as fluxing material in the slag system.	[1]–[3]
Cathode	CC Aluminium	Al	0%	Aluminium combined with copper foils will be lost in the recycling process to make the process economicaly viable by prioritycing copper. Therefore, no targets on this sort of aluminium are placed here.	[3]
	NMC : $Li(Ni_xMn_yCo_z)O_2$ (x + y + z = 1)Li	Li	60 %	Reported work points out efficiencies higher than 60%. Nevertheless, due to the need for more data from the HELENA battery system, the recycling target for Li has been defined using the EU's expected regulation for 2026.	[2]–[6]
		Ni	90 %	Reported works indicate recycling efficiencies over the expected directive change of 90% efficiency for Ni and Co. In the case of manganese and even without a European definition for recycling, this material is expected to be recovered via hydrometallurgical recycling. NMC materials are commonly extracted together as salt during the selective precipitation process.	[1],[2],[4]–[6]
		Mn	90 %		
		Co	90 %		

	Binder	-	0%	The binder is assumed not to be recycled. Since it can impede the mechanical separation of the active material from the collector foils, which may result in reduced leaching efficiencies and slower kinetics in hydrometallurgical process stages, it is suggested to be removed via thermal treatment; During a possible thermal treatment, the binder could be decomposed at temperatures between 450 - 500 °C, depending on the binder material.	[7]–[15]
	Carbon Black	-	0%		[3],[16]
	A small part of the halide electrolyte		0%	The amount of Carbon Black inside the investigated cells is far below conventional LIB systems due to using a Lithium metal anode. Focus will lie on recycling metal-containing fractions such as Li, an NMC. Promising Li recovery yields are shown with a thermal treatment, with the prerequisite of reductive conditions during the treatment. Carbon black is most probably consumed during this process.	
Separator	Al_2O_3, TiO_2, TiO_xN_y polymeric or hybrid	- -	0 %	Typically, the cell structure's separator is only a small fraction, usually less than a few per cent. Consequently, the separation and recovery process is not practical for industrial use, and no recycling objectives are established in this project. However, since these ceramics are highly stable, they may serve as a significant source of impurities in the recycling products. Therefore, observing their behaviour during experimental validation is highly recommended to assess their influence on recycling and suggest remediation methods.	
Halide Electrolyte	Li (5-6%); Y(22-24%); Cl(34-48%); Br(22-39%))	Li	60 %	Since the electrolyte is soluble in polar solvents (e.g., ethanol), selective separation is conceivable before further process steps without the solvation of additional battery components. It remains to be investigated whether the electrolyte or precursors/sub-products is suitable for reusing new batteries in direct recycling. Similar approaches are proposed for ASSB with sulfide electrolytes. Experimental validation is yet to be conducted.	[3]
Casing	Pouch-Folie (PET, PP, Aluminum,Nylon)	Al	80 %	Recovery for secondary life products. The process will contemplate manual separation to concentrate the Al casing as recyclable aluminium. This can be feasible if the safety conditions allow this operation. Any steel or magnetic parts that belong to the casing can be separated manually or via magnetic separation. Shredding and further density separation of the aluminium could be considered. However, copper or other valuable or strategic metal losses should be avoided in order to keep the process sustainable.	
	Tabs	Al, Cu-Ni			
Total expected			75 %	This value is defined based on the projection for the recycling requirement being under study by the EU	[1]

Table 1: Recycling definition targets measured in the product that follows a dedicated recycling process

2.2 Safety and pre-handling concept for the recycling

Recycling involves a multi-step process that converts end-of-life products into various sub-products with value and waste. This process consumes resources and energy, affecting the new product's life cycle assessment and sustainability. Secondary resources are products from recycling that are introduced to the market, while waste must be safely disposed of or subjected to effective, usually expensive post-treatment. In designing a recycling process, the goal is to produce as many products as possible in an economically and environmentally sound way, minimising energy and material consumption and waste. Composite materials, such as lithium-ion batteries, must be separated from assembled devices using crushing or shredding techniques and sorted based on material properties, such as magnetic, eddy-current, density, or sensor-based separation [17]. Different material streams will follow specific recycling processes for the recovery stage. For example, copper-rich material streams undergo a copper-recycling process, while magnetic materials follow a steel-recycling process. If materials are incorrectly separated, metal losses will harm the recycling rate for that specific element. The recycling efficiency of the process strongly depends on the effectiveness of separating individual materials, calculated based on the unit's total weight or the concentration of individual elements. Separating elements in a multi-element-matrix system is sometimes limited by economics and the risk of losing valuable metals with a higher priority.

Recycling lithium-ion batteries involves important safety considerations due to the presence of flammable substances, such as organic electrolytes, binders, metallic lithium, and high concentrations of halogen elements like fluorine, chlorine and bromine, which combined with electrical charges that remain from non-fully discharged batteries represent a risk for handling. Lithium-ion batteries are also known to cause unexpected explosions or thermal runaways that can put humans and the environment at risk [18]. Therefore, a discharging or deactivation process should occur before recycling lithium-ion batteries. Some of these methods correspond to thermal treatments like pyrolysis. During pyrolysis, organic compounds are broken down into smaller molecules in a neutral atmosphere, and halogenated compounds are safely condensed and removed from the input material. Gaseous products, including combustible gases like CO, CH4, and H2, can be used for energy, while solid materials containing metals, oxides, coke, or graphite remain after pyrolysis.

For HELENA, the first consideration for recycling will be directed into safety testing for recycling. This experimental work should involve mechanical abuse tests of synthetic material and prototype cells under a controlled atmosphere and continuously monitoring generated gases. According to the material's matrix chemistry, the reactivity of metallic lithium and the presence of organic compounds, including solid binders at room temperatures and air atmosphere, will be studied under mechanical abuse. If necessary, mechanical processing under an inert or CO_2-supported atmosphere should be considered.

After inertization, the material undergoes defined liberation and sorting techniques, and material streams follow targeted metallurgical extraction processing for individual strategic elements.

Manipulation of synthetic material for the elaboration of preliminary recycling tests might demand some safety measures. For this, the corresponding safety data sheets have been listed and indicated in the following table. However, it is recommended that the list should be updated and revised by the person manipulating materials when working in the laboratory.

Material	Safety data sheet
Lithium ≥99,5 %	[19]
Lithium carbonate	[20]
Nickel/ Nickel hydroxide	[21],[22]
Aluminium oxide	[23]
Manganese/ Manganese hydroxide	[24],[25]
Cobalt/ Cobalt hydroxide	[26],[27]
$LiNiCoMnO_2$	[28]
Titanium(IV) Oxide	[29]
Copper	[30]
Aluminium	[31]

Table 2: List of safety data sheets of main battery components used in the HELENA battery system.

3 Conclusions

A set of recycling targets considering safety and recycling have been defined using HELENA chemistry cells as the foundation. The primary objectives for the recycling concept are focused on the recovery of base metals such as copper and aluminium, as well as strategic materials for Europe like 90% for cobalt, and 60% for lithium, and 90% for manganese and nickel. In addition, efforts will be made to explore the valorisation of materials contained in the solid electrolyte to identify potential remediation or recovery pathways, alongside those fractions of metals that may not meet the required quality standards or acceptable recycling efficiencies for industrialisation. Experimental results will be used to validate the anticipated targets, and an overall recycling rate will be computed based on the experimental data, in accordance with the current EU battery directive.

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Project partners

#	PARTICIPANT SHORT NAME	PARTNER ORGANISATION NAME	COUNTRY
1	CICE	CENTRO DE INVESTIGACION COOPERATIVA DE ENERGIAS ALTERNATIVAS FUNDACION, CIC ENERGIGUNE FUNDAZIOA	Spain
2	AIT	AIT AUSTRIAN INSTITUTE OF TECHNOLOGY GMBH	Austria
3	SGR	SAINT GOBAIN RECHERCHE SA	France
4	UMI	UMICORE	Belgium
5	LV	LIONVOLT B.V.	Netherlands
6	TNO	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK TNO	Netherlands
7	FHG	FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.	Germany
8	CCI	CUSTOMCELLS HOLDING GMBH	Germany
9	RWTH	RHEINISCH-WESTFAELISCHE TECHNISCHE HOCHSCHULE AACHEN	Germany
10	MIMI	MIMI TECH GMBH	Germany
11	IFPEN	IFP ENERGIES NOUVELLES	France
12	PVS	PIPISTREL VERTICAL SOLUTIONS DOO PODJETJE ZA NAPREDNE LETALSKE RESITVE	Slovenia
13	LDO	LEONARDO - SOCIETA PER AZIONI	Italy
14	FEV	FEV EUROPE GMBH	Germany
15	EDLP	FEV eDLP GmbH	Germany
16	ZAB	ZABALA INNOVATION CONSULTING, S.A.	Spain

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