Industrial and Laboratory Processing
of Spent Li-Ion Batteries
for
Efficient Materials Recovery

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Thesis to obtain the Master of Science Degree in

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Abstract

With the increasing number of electric vehicles on the road, the need to develop solutions to treat the batteries coming from these vehicles rose. The necessity to treat these batteries comes from the critical raw materials that constitute them, and a need for an alternative to the exploitation of such materials.

The objective of this work was to develop at an industrial scale, a deactivation process and dismantling procedure of batteries for further treatment, including mass balance of components that compose the battery. At the laboratory scale, the purpose of the work was to determine the percentage of each component, the type of chemistry used and morphologically characterise some of the cells, while studying the impact of the previously imposed treatments.

For deactivating the batteries an ohmic discharge and different brine/caustic solutions were used. Ohmic discharge will not influence the structure of the cells and it may be possible to deliver some of the charge back to the plant facilities. However, when there are low voltages, it may take several hours to reach safety levels of charge. When using solutions, one is always conditioned by the liquid effluents treatment, however, depending on the shape of the cell, the perfect solution conditions can be calculated for a faster discharge.

By analysing the 10 cells it can be concluded that the most used technology is in fact NMC, particularly NMC111. On average, the cell is responsible for 68.08% of the total weight of the battery, followed by the module (18.66%) and the battery periphery system that composes the pack (13.26%).

Keywords: Lithium-ion batteries, Dismantling, Deactivation, Recycling.

Resumo

Com o aumento do número de veículos elétricos em circulação, existe a necessidade de criar soluções para tratar as baterias provenientes destes veículos. A necessidade destas soluções prende-se com a quantidade de metais críticos presentes nas baterias e a importância de criar alternativas à exploração desses metais.

O objetivo deste trabalho é desenvolver, à escala industrial, um procedimento de descarregamento e desmantelamento das baterias para posterior tratamento, incluindo um balanço mássico dos componentes que compõe a bateria. À escala laboratorial, o objetivo é determinar a percentagem de cada componente, o tipo de química utilizada e caracterizar morfologicamente algumas das células, estudando o impacto dos tratamentos anteriormente impostos.

Para desativar as baterias, descargas elétricas e diferentes soluções salinas/causticas foram testadas. A descarga elétrica não vai influenciar a estrutura morfológica das células e pode possibilitar a reposição de alguma eletricidade à rede da empresa. Contudo, quando a diferença de potencial nas baterias torna-se baixa, pode demorar várias horas até atingirem níveis seguros de carga. Quando se usa soluções estaremos sempre condicionados pelo tratamento de efluentes líquidos, no entanto, dependendo da estrutura da célula, as condições da solução podem ser ajustadas de modo a permitir um descarregamento mais rápido.

Das 10 células analisadas, podemos concluir que a tecnologia mais usada é de facto a NMC, particularmente a NMC111. Em média a célula é responsável por 68,08% da massa total da bateria, seguida do módulo (18,66%) e do sistema periférico que compõe o pack (13,26%).

Keywords: Bateria iões lítio, Desmantelamento, Desativação, Reciclagem

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Acronyms

AB acetylene black

ACN acetonitrile

Ag silver

Al aluminium

APA Agência Portuguesa do Ambiente

Au gold

BEV battery electric vehicle

BMS battery management system

BMU battery management unit

CAD Computer Aided Design

CMC cell module controller

CO carbon monoxide

Co cobalt

CO_2 carbon dioxide

CRM critical raw materials

Cu copper

DMAC N-N-dimethylacetamide

DMC dimethyl carbonate

DMF N-N-Dimethylmethanamide

DMSO N-N-dimethyl Sulfoxide

DRC Democratic Republic of the Congo

EC European Commission

EI economical importance

EMC ethylmethyl carbonate

EN European Standard

EoL End-of-Life

EPR Extended Producer Responsibility

EU European Union

EV electric vehicle

F fluorine

FCEV fuel cell electric vehicle

Fe iron

GHG greenhouse gases

HCl hydrochloric acid

HDPE high-density polyethylene

HEV hybrid electric vehicle

HNO_3 nitric acid

ICEV internal combustion engine vehicle

LCA life cycle assessment

LCO Lithium cobalt oxide

LFP Lithium iron phosphate

Li-Air lithium-air

Li-S lithium-sulphur

LIB lithium-ion batteries

LiF lithium fluoride

LiSICON lithium super ion conductor

LMO Lithium manganese oxide

LNO Lithium nickel oxide

LTO Lithium titanate

Mg magnesium

Mg-ion magnesium-ion

Mn manganese

MP metal phosphide

Na-ion sodium-ion

NCA Lithium nickel cobalt aluminium oxide

Ni-MH nickel metal-hydride

NMC Lithium manganese cobalt oxide

NMHC non-methane hydrocarbon

NMP N-methyl-2-pyrrolidone

NOx nitrogen oxides

OEM original equipment manufacturer

Pb lead

PC propylene carbonate

PCB printed circuit boards

Pd palladium

PHEV plug-in hybrid electric vehicle

PM particulate matter

POE poly(oxyethylene)

PVC polyvinyl chloride

PVDF polyvinylidene fluoride

REEs rare earth elements

REEV range extended electric vehicle

SEI solid electrolyte interphase

SI(EI) Substitution Index for Economic Importance

SI(SR) Substitution Index for Supply Risk

SnO_2 tin oxide

SoH state-of-health

SR supply risk

SSB solid-state batteries

THC total hydrocarbon

Ti titanium

UN United Nations

WHO World Health Organization

Zn-Air zinc-air

Chapter 1

Introduction

1.1 Context and Problematic

Europe has a leading position among producers of motor vehicles. This sector employs around 13,8 million people: direct and indirect manufacturing account for 3,5 million jobs, 4,5 million belong to sales and maintenance workers and transportation represents 5,1 million jobs [1].

Even though there have been several technological developments when it comes to transportation, this sector is still responsible for a quarter of Europe's greenhouse gases (GHG) emissions. With this in mind, the European Union (EU) is committed in developing a decarbonized, and more sustainable economy around the transport system, aiming to bring down emissions by 2050 to 60% of 1990 levels[2, 3].

In 2016, The Strategy for Low Emission Mobility brought to light the need to deploy zero- and low-emission vehicles and set measures to support the transition. The European Commission (EC) also proposed revision to rules on the acquisition of clean vehicles (Directive 2009/33/EC), and an action plan to better implement the Directive on alternative fuel infrastructure (Directive 2014/94/EU) [4]. It becomes evident that electric vehicle (EV) are an essential technology to achieve the decarbonisation of the road sector. In fact, it is expected that by 2040, 54% of new car sales and 33% of the global car fleet will be electric, resulting in the displacement of up to 8,000,000 barrels of transportation petrol per day[5, 6].

At the moment, lithium-ion batteries (LIB) are the most common technology employed in EVs. However, they present many challenges, including, use of several different raw materials, some of which present supply risks and are of major economic importance. Besides, it is important to realise that manufacturing EVs entails different stages, and therefore, assessing the environmental impact of all stages, from cradle-to-cradle, becomes imperative. When comparing the impact during the production of EVs and internal combustion engine vehicle (ICEV), it becomes evident that producing EVs leads to higher GHG emissions, mainly due to the battery production (account between 33-44% of total production emissions [7]) that entails the extraction of raw materials and processing. To tackle problems at the supply chain, and production stage it is important to define what to do with these batteries at their End-of-Life (EoL).

Recycling poses an opportunity to improve resource efficiencies and raw materials available in Europe. With this in mind, since 2006 batteries and waste batteries have been regulated under the Batteries Directive (2006/66/EC), and in 2013 the Directive (2013/56/EU) imposed minimum collection rates for retired batteries. However, the demand for batteries is set to increase 14 fold by 2030. And so, in December 2020 the European Commission presented a proposal which aimed to improve collection and recycling rates of portable batteries by 65% in 2025 and 70% in 2030. This proposal also defined a framework that should facilitate the repurpose of batteries coming from EVs, in order to provide them with a second-life [3, 8].

Developing an effective and efficient recycling industry is mandatory to increase the sustainability of LIBs market. The recovery of critical materials would allow the industry to reduce the demand for these raw materials, reduce GHG emissions and local impacts from mining and refining, as well as, allow countries to reduce their dependency on the import of materials. Recycling rates, to date, have been hindered either by deficient legislation, inefficient collection systems (it is estimated that 95% of LIBs produced around the world remain untreated in households [9]) and low feasible recycling technologies. However, as the consumption of EVs increases, pressuring primary resources and thus increasing raw materials prices, materials recovered through recycling help stabilise the prices [10]. Although its widespread application is important, recycling processes for lithium batteries are very complex, especially because EV batteries come in a variety of shapes, and with different cathode compositions, making it harder to implement a systemic approach to their dismantling and recycling [5, 7, 11].

1.2 Research Questions and Strategies

This thesis was developed according to the mobilising programme *Baterias 2030*, taking into account the objectives of PPS2- Battery life cycle valorization and in a strategy study required by *Valorcar,SA*. It compromises 4 main objectives:

- Identification of dismantling, and deactivation operations paired with a critical analysis on their advantages and disadvantages;
- Specification- by materials and constituent metals- of the composition of LIBs, with particular interest in the cathode;
- Physical-chemical characterisation of EoL lithium batteries, aiming to define solutions for processing and recycling management;
- Assess importance of Eco-Design as an ally to recycling processes;

The end purpose of this study is to offer a panoply of guidelines for recycling procedures. Considering the main objectives set before, the development of the presented work was guided by the following research questions:

1. How should the deactivation and dismantling processes of spent LIBs be implemented to obtain a safe and efficient routine?
2. What is the weight balance between components, materials, and elements- interior and exterior- of cells?

1.3 Publications

The work developed in this thesis resulted in a publication, which is in submission to Journal of Waste Management.

D.O. Silva, R. Costa Neto, C.A. Nogueira, F. Margarido, M.F.C. Pereira. "Deactivation and Disassembling of Li-Ion Batteries".

1.4 Thesis Outline

This thesis is composed of 6 chapters.

In Chapter 1 an introduction to the problematic related to transportation and the electrification of the European fleet is given. The main objectives of these thesis are also provided.

In Chapter 2 an introduction to the problems of road transportation are presented to contextualise the reader. Electric cars are then presented as an alternative, with each model briefly described. Some types of LIBs technology are explained and described, emphasising different compositions, the critical raw materials (CRM) used, and future perspectives for these technologies.

In Chapter 3 the battery waste management hierarchy is presented, with emphasis on the legislation applied in the EU. Second-life alternatives are briefly explained, the main focus of the chapter being recycling. A thorough explanation is given regarding collection and transportation of LIBs followed by a step-by-step explanation of the pretreatments performed in spent batteries, both at industrial and laboratorial scale. Lastly, some established industrial recycling processes are presented.

In Chapter 4 the experimental methodology followed is described. The work was divided in two main parts: industrial and laboratory scale. This way, an emphasis is given on both works developed at companies (*Ambigroup* and *Palmiresíduos*) and at the laboratory (*IST* and *LNEG*). In addition, a brief explanation on the characterisation techniques used throughout the work are also presented.

In Chapter 5 the results obtained are presented alongside a discussion related to their meaning.

In Chapter 6 the main conclusions obtained from the work are presented. Moreover, some recommendations for future works are also given.

Chapter 2

Batteries for Electric Vehicles

2.1 Introduction

2.1.1 Problems with Road Transportation

Over the past decade, petrol has been the predominant energy source in the transport sector, providing 92% of final energy, a difference of only two percentage points when compared to 1973. Nowadays, it is well known the close relationship between petrol use and carbon dioxide (CO_2) emissions and the transportation sector accounts for a quarter of GHG emissions in Europe [11, 12].

Greenhouse Gases

As major economic sectors achieve massive reductions in GHG emissions, those related to transportation have increased. In fact, in the EU, emissions are 17% higher when compared to levels of 1990. However, increasing awareness of this problem has caused brands, and entities to further regulate emissions and new mandatory CO_2 standards were adopted in 2019 [2, 13]. For passenger cars, the average emissions will have to be reduced by 15% until 2025 and by 37.5% in 2030, respecting a 2021 baseline. This means that in 2021, manufacturers have to meet the average CO_2 target of 95g/km on newly registered cars. It is worth noticing, in Figure 2.1, that among the EU-28, Portugal has one of the lowest CO_2 emission levels (104 g/km)[13].

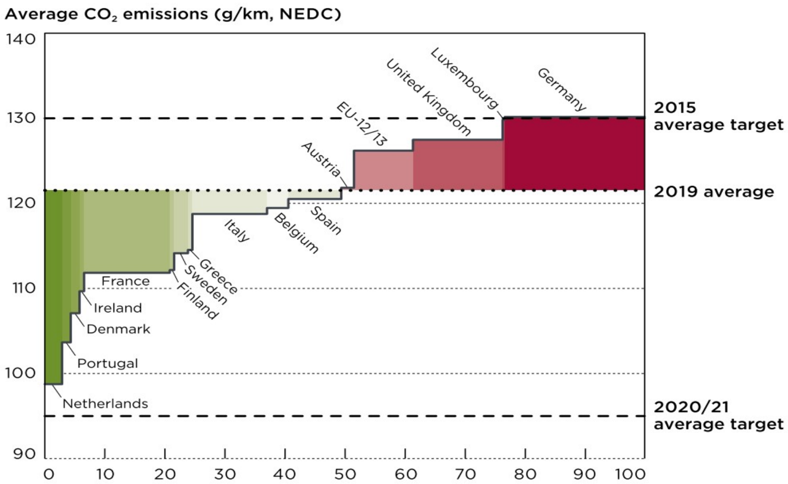


Figure 2.1: Passenger Cars: CO_2 emissions and market share by member state, 2019. Reproduced from Ref.[13].

Air Pollution

Emissions coming from vehicles are of particular importance to human health because these usually occur near populated areas, such as cities and towns. Road transport is a major source of harmful air pollutants such as nitrogen oxides (NOx) and particulate matter (PM), on average, traffic contributes 60% to the presence of NO_2 in the atmosphere.

With this in mind, the EU created different categories to set vehicles apart according to their emissions of NO_x, total hydrocarbon (THC), non-methane hydrocarbon (NMHC), carbon monoxide (CO), and PM under the 2007/46/CE Directive [14, 15]. NO_x emission limits for new diesel passenger cars have been dropping since 2000. They are now set at 0.08g/km for a Euro 6 level car (classification related to the year they were put on the market and the technology available at the time.). For gasoline models, the limit is set at 0.06g/km for the same classification [13]-[15] (Table 2.1).

Table 2.1: EU Emission limits for gasoline and diesel passenger cars (in g/km). Adapted from Ref.[13]

Gasoline Model	Effective Date	CO	HC	NMHC	NO_x	HC + NO_x	PM	PN
Euro 3	Jan 2000	2.30	1.00	-	0.15	-	-	-
Euro 4	Jan 2005	1.00	0.10	-	0.08	-	-	-
Euro 5	Sep 2009	1.00	0.10	0.068	0.06	-	0.0050	-
Euro 6	Sep 2014	1.00	0.10	0.068	0.06	-	0.0050	6.0×10^{11}
Diesel Model	Effective Date	CO	HC	NMHC	NO_x	HC + NO_x	PM	PN
Euro 3	Jan 2000	0.64	-	-	0.50	0.56	0.0500	-
Euro 4	Jan 2005	0.50	-	-	0.25	0.30	0.0250	-
Euro 5	Sep 2009	0.50	-	-	0.18	0.23	0.0050	-
Euro 6	Sep 2014	0.50	-	-	0.08	0.17	0.0050	6.0×10^{11}

PN: Particle Number

Noise Pollution

Noise pollution is considered a major environmental health problem in Europe, and road traffic is the most prominent source of noise. The harmful effects of noise are mainly related to an increase in stress caused to the human body, leading to cardiovascular disease, cognitive impairment, sleep disturbance, etc. The World Health Organization (WHO) recommends no exposure above the value of 40dB [16].

It is estimated that 100 million people are exposed to traffic noise exceeding the EU indicator of noise annoyance. Noise from vehicles comes mainly from two sources: the engine and the contact between tyres and the road. As speed increases the tyre's noise becomes dominant, however, over 50km/h the difference between an EV (have no engine) and ICEV becomes minimum.

2.1.2 Electric Vehicle's Market

It becomes evident that in the future a large share of the GHG emission reduction will have to come from road transport. This can be achieved by using new and cleaner technologies that contribute to the reduction in petrol consumption. With that being said, EVs are advertised as an alternative to ICEVs.

EVs were first presented in 1828, they had an advantage over the steam- and gasoline-powered vehicles that were characterized by loud noise, and the need to set the engine into an operating temperature before driving [17].

However, the invention of the internal combustion engine muffler, the electric engine starter in 1911, and the desire for higher autonomy and faster recharging contributed to the ramp-up use of internal combustion engines.

Between 1990-2005, the number of patents and new product launches regarding combustion engine technology showcased the focus of the European automakers in this technology over EV, being the latter only awarded 20% of patents related to pure battery EV and Hybrid EV.

There are several reasons to justify the low adherence of the public to this type of technology. When asked about their preference when buying cars, in 1996, consumers prioritized range and price (75% and 55%, respectively). At the time, EVs were mainly powered using lead (Pb)-acid batteries which resulted in limited lifetimes and driving ranges. Only in the latter part of the decade was there a shift towards nickel metal-hydride (Ni-MH) packs, which resulted in improved energy density but too high costs.

In addition, several automobile industries lobbied US Federal and EU legislators into pressuring them to loosen up emission restrictions. In fact, between 1998-2002 restrictions were even lifted, resulting in a market failure of EVs[18]. It is only with the introduction of lithium-ion batteries technology, later on, that consumers interest and acceptance rose again [12, 18, 19].

Data from 2019 shows that there were 17,9 million cars in the EU-28, and passenger cars account for 87% of the total share (Figure 2.2).

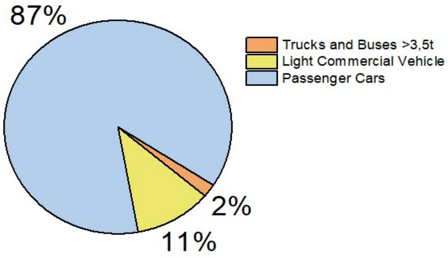


Figure 2.2: Market shares of passenger cars, light commercial vehicles, trucks and buses in EU-28, 2019. Adapted from Ref. [13]

In the same year, the electric vehicle's sales grew 44% (590,000 units), achieving the highest rate since 2016. Between the last quarter of 2019 and the first quarter of 2020, the sales also increased and the overall penetration rate of this technology rose to 7.5% [13, 20].

It is also important to mention that 9 out of 10 markets with the highest rates of EV penetration were placed in Europe, and as Figure 2.3 shows, Portugal was 7th between the fourth quarter of 2019 and the first quarter of 2020, with 4,8 thousand units sold in the first quarter of 2020 [20].

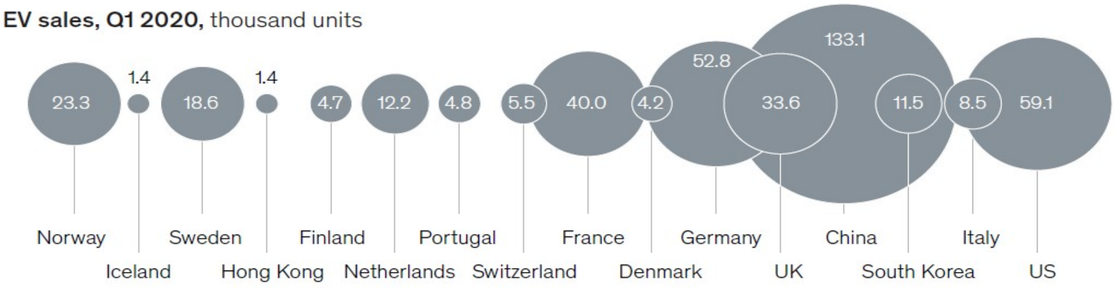


Figure 2.3: EV sales in the first quarter of 2020. Reproduced from Ref.[20]

More recent studies show that in the first half of 2020, 11% of the cars sold in Portugal were electric with hybrids and battery-only electric vehicles occupying similar positions in the automotive market [21]. In the same period, the most sold electric vehicles in Portugal were the Nissan LEAF, Tesla's Model 3 and the Renault Zoe [22].

2.2 Electric Vehicle's Types

Between different EVs, manufacturers present us with several technologies that vary in the way the onboard electricity is generated/recharged and the way the electric motor and combustion engine (if any) are coupled.

Battery Electric Vehicles (BEV)

These models have no engine are solemnly powered by one or more onboard traction batteries. These batteries must be regularly charged, even though they have the highest efficiencies, being able to convert 80% of the energy stored into motion. There are no exhaust emissions and the environmental performance can be increased if the energy used to power the vehicle comes from renewable energies. However, they need long times to recharge, have lower driving ranges (80-400km), the batteries used are more costly than the one's used in hybrids [2, 23, 24].

Hybrid Electric Vehicles (HEV)

Hybrids have two power sources, combining an internal combustion engine system with an electric propulsion system. This model is mainly powered by the conventional engine, so hybridisation can be regarded as an enhancer of fuel efficiency and reduced exhaust emissions. The conventional and electric motor can be joined using different configurations: in *Parallel Hybrids* the motors are connected and power the vehicle together, in *Series-Parallel Hybrids* the wheels are powered by both engines, but the vehicle can also be driven using the battery alone during short distances at low-speed [2, 23, 24]. Normally, the capacity of the batteries used in HEVs is relatively small within 2kWh [25].

Plug-in Hybrid Electric Vehicles (PHEV)

PHEVs allow both electric driving and combustion-fueled driving. The battery can be charged using power from the grid and the combustion engine supports the electric motor when more power is required. PHEVs batteries' capacity have to be larger (5-15kWh) [25] because at their fully charged state, the electric motor and battery are responsible for travel. In terms of environmental performance, if driven in the all-electric mode these vehicles produce zero exhaust emission. However, when using the combustion engine they can result in higher emissions than a convention vehicle due to the added weight of the batteries [2, 24].

Range Extended Electric Vehicles (REEV)

REEVs have a serial-hybrid configuration where the combustion engine has no direct link to the wheels. In this type of EV, the combustion engine is used to power the electric motor or recharge the battery- this can also be done using power from the grid. For these vehicles, the conventional engine can be of smaller dimensions, resulting in less weight. REEVs overcome the problem of restricted driving ranges because they can be fueled at conventional stations [2].

Fuel Cell Electric Vehicles (FCEV)

FCEVs are powered through a fuel cell which generates electricity from hydrogen and air. The fuel cell can substitute the battery or in combination with one to power the electric motor. This EVs achieve longer driving ranges and take shorter times to refuel. However, this technology is still at its early stages, and therefore few models are currently commercially available. Also, developments have to be made to improve the durability, cost and establish a hydrogen fuelling infrastructure [2, 23, 24].

2.3 Batteries

Batteries are electrochemical cells that store energy in chemical form and transform it into usable electrical energy. The electric current is provided through discharging processes coming from the use of different chemical compounds as cathodes and anodes.

2.3.1 Structure of Battery System

Batteries used in EVs have three main constituents (Table 2.2): Battery cells that contain the anode, cathode, electrolyte, separator, current collectors and casing. Modules which are clusters of cells paired with cooling systems and connectors and, finally, the modules are grouped in battery packs that have an outer casing, a battery management system, sensors, cooling systems and cables.

Table 2.2: Battery packs, modules and cells for EVs applications. Adapted from Ref.[26]

Pack	Casing, Battery Management System, Sensors, Cooling System	🔋
Module	Casing, Cooling System, Connectors	🔋
Cell	Anode, Cathode, Electrolyte, Separator, Current Collector, Casing	🔋

Table 2.3 shows the several types of external shapes and internal structures used for commercial single cells: cylindrical, prismatic and pouch, and their properties.

Cylindrical packaging is an early form of mass-produced batteries and is still very popular today. The biggest advantage of this design is its mechanical stability, that can naturally withstand internal pressures without deformation. In this design the cathode, anode and separator are cut into stripes and rolled. The biggest disadvantage of this configuration is the low packaging density when grouping several cells together. However, the air can easily circulate through the modules and packs, easing the cooling [27].

Prismatic cells have a box-like appearance and can contain one or more electrochemical cell units. In this design the cathode, anode and separator, are also cut into stripes, wound up and pressed into fitting the container. This configuration allows for more flexible designs and higher packaging density. Nonetheless, this design introduces more stress in the bend parts of the jelly roll at the corners and the thermal management becomes more complicated when in a pack [27].

Pouch cells have a minimalist approach to packaging. Cathodes, anodes and separators are stacked and do not have a rigid container involving them, this increases the energy density and lowers the weight of the cells. This design is very prone to swelling under charge/discharge cycles, this causes high stress on the cells. When compared to the prismatic design, pouch cells require better temperature management systems and better support structures when assembled into a module [27].

As mentioned before, LIBs have been used preferentially in energy storage applications ever since they were commercially produced by Sony Company in 1991 [23]. And since 2015, they have dominated the modern EV's market. They are the primary solution because of their high energy density, high energy efficiency, long life cycle, long charge retention and an unnoticeable memory effect [23, 25].

Table 2.3: Cell designs and properties. Adapted from Ref. [17, 27, 28]

Shape	Cylindrical	Prismatic	Pouch
Cross Section			
Electrode Arrangement	Wound	Wound	Stacked
Mechanical Strength	++	+	-
Heat Management	-	+	+
Specific Energy	+	+	++
Energy Density	+	++	+

2.3.2 Cell Materials

Batteries are amalgams of materials, in LIBs: lithium (Li), cobalt (Co), manganese (Mn), and Ni are usually used as cathode materials. Synthetic and/or natural graphite is usually used as the anode material. These materials are placed in copper (Cu) and aluminium (Al) foils. The separator and electrolyte are composed of volatile components and plastics [12]. Metals such as steel, aluminium combined with plastics and electronic materials are usually present in the system's periphery, like casings, pack enclosures and the battery and thermal management systems. In Figure 2.4, a generic composition of a battery system is presented as a percentage of total battery pack mass, the results reflect the average across different chemistries.

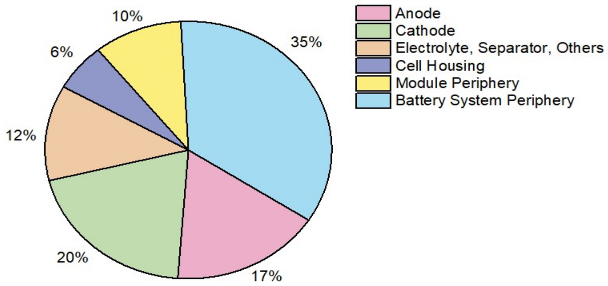


Figure 2.4: Generic battery components composition as a % of total battery pack mass. Adapted from Ref.[4]

Anode

The anodes are the negative electrodes that compose the battery cell. Usually, negative electrodes are made using lithium titanate, or carbon-based electrodes. However new types of anodes are being developed using lithium metal and lithium-metal alloys, and conversion electrodes [17, 29].

Carbon-Based

The use of graphite as an anode material dates back two decades ago, its low cost, good electrochemical performance, low volume expansion during cycles and the fact that it is a rather available material has contributed to this fact [30]. It also presents high specific capacity ($\sim$370 AhKg^{-1}) and low average voltage (150mV vs Li/Li^{+}) [17].

However, under specific conditions, if exposed to atmospheric oxygen in a thermal runaway event, it might explode.

Lithium Titanate ($Li_4Ti_5O_{12}$)

Lithium titanate (LTO) is considered a good anode material because it has a spinel structure that allows to have zero volume change during lithiation, which gives it a long lifetime, and it also makes it safer due to its charge/discharge plateau at 1.55V vs Li/Li$^+$. However, it has a higher price compared to graphite, a lower energy capacity, energy density ($\sim$ 175 AhKg^{-1}) and reduced cell voltage [17, 30].

Lithium Metal

This material presents a very high capacity ($\sim$ 3860 AhKg^{-1}) that, if used, could reduce the mass of the cathode and consequently reduce the battery mass by a third. Unfortunately, this material is very prone to the production of dendrites during Li plating/striping, which may lead to short-circuiting [17].

Silicon-Based

Lithium-silicon alloys, in its fully lithiated composition ($Li_{15}Si_{14}$), has a specific capacity of $\sim$ 4200 AhKg^{-1}. However, this material undergoes volumetric expansions, up to 300%, during lithiation. It also presents a low Li$^+$ diffusion coefficient and a high electrical resistivity [17, 30, 31].

Conversion

In conversion electrodes, instead of the usual Li$^+$ intercalation in the host material, an actual chemical reaction happens:

$$M_{\mathrm{a}}X_{\mathrm{b}} + (b*c)Li^{+} + (b*c)e^{-} \rightleftharpoons aM + bLi_{\mathrm{c}}X \tag{2.1}$$

where M is a transition metal and X an anionic specie. Anions that are oxides and sulphides have theoretical capacities ranging from 500-1500 AhKg^{-1} [32]. Another advantage would be the higher stability that would result in higher safety of the battery, decreasing the risk of thermal runaway [17, 30]. Examples of these materials are tin oxide (SnO_2) and metal phosphide (MP).

In Table 2.4, a resume of the information mentioned above regarding anode technology is presented.

Table 2.4: Comparison of most used anode technologies. Adapted from Ref.[17, 23, 30, 33]

Anode Material	Energy Density (Ah/Kg)	Lifetime	Cost
Carbon Based	370	Medium	Medium
LTO	175	High	High
Li Metal	3860	Low	High
Si Based	4200	Medium	Medium
Conversion	500-1500	High	Medium

Cathode

Cathodes are usually constituted by intercalation compounds from which Li$^+$ ions diffuse out/in from. The selection of material is highly dependent on the application itself, and the most important properties to consider are energy density, power density, cost and lifetime [17, 30].

Lithium Manganese Oxide ($LiMn_2O_4$)

Lithium manganese oxide (LMO) batteries were first introduced in the early 1980s, being the oldest commercially used electrodes due to their low cost. This material presents a 3D-spinel structure that improves flow on the electrode and consequently lower resistance. In addition, it also has better chemical stability. Unfortunately, it also has a lower capacity ($\sim$110 AhKg^{-1}) and a lower lifespan [17, 34, 30]. Most Li-manganese batteries blend with lithium manganese cobalt oxide (NMC) to increase the specific energy and lifespan. Research efforts in this area focus on developing composite electrodes using integrated spinel $LiMn_2O_4$ and layered Li_2MnO_3 ($xLi_2MnO_3(1\text{-}x)Li_{1+y}Mn_{2\text{-}y}O_4$). The combination of such structures improves structural stability during cycling, achieving also higher capacities and rate-capability[17].

Lithium Cobalt Oxide ($LiCoO_2$)

This technology was first developed by Sony in 1991 and has been used since in most portable electronics. It is characterised by a high energy density, long life cycles and easy manufacturing and presents a capacity density around 140 $AhKg^{-1}$. Lithium cobalt oxide (LCO) batteries are very reactive, suffering from low thermal stability, this happens because as temperature increases, $LiCoO_2$ suffers dissolution of the metal in the electrolyte inducing oxygen release. Therefore, these batteries have to be monitored during use [17, 34].

Lithium Iron Phosphate ($LiFePO_4$)

Lithium iron phosphate (LFP) was discovered in 1996, this technology offers good electrochemical performance, low resistance, high current, the capacity of $\sim$170 $AhKg^{-1}$ and long cycle life. It is frequently used in combination with an LTO anode for a better overall lifetime of the battery [17, 30, 35]. The phosphate element helps to stabilize the electrode, allowing the battery to work in wider temperature ranges (-30°C to +60°C), decreasing the chances of thermal runaway.

Lithium Nickel Oxide ($LiNiO_2$)

Lithium nickel oxide (LNO) was first designed in 1954 and was considered a promising material for high voltage batteries (4V vs Li/Li^+) due to its low cost and high capacity $\sim$250 $AhKg^{-1}$ [17, 30]. However, the synthesis of LNO was considered rather difficult due to the instability of trivalent nickel at high temperatures. It also presented some irreversible phase transitions during charge-discharge cycles and release of oxygen at elevated temperatures [32, 34], thus, this technology is not in commercially available lithium-ion cells. This material can be mixed in solid solutions with cobalt (Co), iron (Fe), aluminium (Al), manganese (Mn), titanium (Ti) and magnesium (Mg), hence the development of other technologies discussed further ahead.

Lithium Nickel Manganese Cobalt Oxide ($Li(Ni_xMn_yCo_{1-x-y})O_2$)

Lithium manganese cobalt oxide (NMC) electrodes have gained massive attention to replace $LiCoO_2$ in Li-ion batteries, They present better stability during charge/discharge cycles, a higher reversible capacity ($\sim$160 $AhKg^{-1}$) [34]. The reason for such good performances lies within the combination of nickel and manganese: nickel is known for high specific energy but poor stability, and manganese has the capacity of forming a spinel structure that achieves low internal resistance but with a low specific energy. The problems that may arise with this type of technology come from the fact that Ni^{2+} ions have a similar radius to those of Li^+ and therefore the cation can mix between these two species in 3b crystallographic sites of the lattice [34].

Despite all of this, NMC electrodes are the most used in EV power-trains, and the mix of various metals is different between manufacturers. There have been several changes in composition, companies have gone from NMC111 (equal proportions of Ni, Mn and Co) with a capacity $\geq$154 $AhKg^{-1}$, passed through NMC442 and NMC622, and are now focused on NMC811 with a capacity $\geq$185 $AhKg^{-1}$ [17, 30, 34].

Lithium Nickel Cobalt Aluminium Oxide ($Li(Ni_xCo_yAl_{1-x-y})O_2$)

Lithium nickel cobalt aluminium oxide (NCA) is an available technology since 1999, it shares similarities with NMC such as high specific energy, specific power and a long lifespan. The exact mixture of these elements defines the properties of the cathode, however it stills presents thermal instability resulting in reduced safety. They are also more costly to produce and for this reason, the only EV manufacturer known to use this technology is TESLA. Some studies show that in these technologies (NCM and NCA) there can be some capacity lost because of changes in structures during charge/discharge cycles [32].

Table 2.5 a resume of the information regarding cathode technology is presented.

Table 2.5: Comparison of most used cathode technologies. Adapted from Ref.[17, 23, 36, 37]

Cathode Material	Avg. Potential (V vs Li^0)	Energy Density (Wh/Kg)	Gravimetric Capacity (mAh/g)	Lifetime	Cost
LCO	3.7-3.9	546	145	Medium	Medium
LMO	3.8	410-492	120	Low	Low
NMC	3.3	610-650	170	High	High
NCA	3.8	680-760	200	Medium	High
LFP	3.3	518-587	165	High	Medium

Electrolyte

The electrolyte is responsible for ensuring that Li^+ ions can shuttle between the two electrodes without being electronically conductive. Electrolytes affect the performance of the cell- cycling efficiency, rate capability, capacity retention, etc. Therefore it is to be carefully chosen. It has to endure the redox environment at both the cathode and anode sides and the voltage range to which is subjected without degradation or decomposition. It should also be inert and stable along with a considerable temperature range and, if possible, it should also be environmentally benign. The choice of electrolytes is less consequent than the choice of electrodes but both are highly dependent, and are chosen accordingly to the choice of electrodes[17, 35, 38].

Aqueous

This type of electrolyte is perceived as being safer and having lower potential environmental impacts, however, they present a more restricted electrochemical voltage window resulting in reduced cell potential. In order to try and improve performance aqueous mixtures of salts were tested, and even though the electrochemical window increased it is a technology far from commercialization [17, 39].

Organic Liquid

Due to the problems explained before regarding the electrochemical window, Li-ion batteries usually use organic-based solvents with lithium salts, for example, ethyl carbonate, propylene carbonate with dissolved $LiPF_6$ or $LiClO_4$. Normally, these materials are formulated and mixed according to some requirements of viscosity, conductivity and stability, for $LiPF_6$ a 50:50 w/w mix with ethylene carbonate is used. However, some of these materials have safety hazards, either high flammability, toxicity or even formulation of corrosive compounds. Additives can be used to increase stability and ensure the formation of a solid electrolyte interphase (SEI); this passivation layer comes from the decomposition products of electrolytes and it allows Li^+ transport while blocking consequent electrolyte decomposition [17, 35, 38].

Polymer

Polymer electrolytes are solvent-free and use high molecular weight-based polymers with lithium salts dissolved. This type of electrolytes present several advantages over liquid electrolytes: improved safety properties, design flexibility and could potentially eliminate the need for separators. Composite electrolytes based on poly(oxyethylene) (POE) and identical matrixes can have gel-like or solid properties. The problem with this type of electrolyte is the decreased conductivity (10^{-8} S/cm) when compared to that of liquid electrolytes (10^{-3} S/cm) [17, 35, 38].

Ceramic

More recently, ceramic electrolytes have been considered to be used in Li-ion batteries. The main advantages are, obviously, increased safety, ability to work in high service temperatures and pressures. The increasing conductivity as temperature increases- occurs due to the creation of movement and point defects that require energy, hence the increase. For this type of electrolytes sulfides, phosphates and oxides are used, some examples are the perovskite LTO, lithium super ion conductor (LiSICON). The conductivity of this materials is rather low ($\sim 10^{-5}$ to 10^{-6} S/cm), so they are mostly used in thin-film batteries [17, 35, 40].

Separator

Separators are commonly used in electrochemical systems with liquid electrolytes like fuel cells, capacitors and batteries. It exists to prevent direct physical contact between the cathode and the anode avoiding short-circuiting. It has, however, to allow Li^+ ions to pass between the electrodes. It has to be chemically stable and inert to materials composing the electrolyte and electrodes. It should be mechanically resistant to tension and punctures done by electrode materials, as well as, permeable, with a good wettability and cost.

Normally microporous polymer membranes are used with a thickness $\sim 25\mu$m and with an average porosity of 40%, allowing ionic conductivity with reduced resistance. This technology is expected to evolve into inorganic membranes and solid-state batteries (SSB) [35, 41].

2.3.3 Working Principles of LIBs

When initially discharged, Li^+ ions are in the cathode, hence the cathode being the source of lithium ions. To allow the migration of the ions the electrolyte is also enriched with lithium ions. During the first charging process, the electrons migrate from the cathode (oxidation) using an external conductor into the anode (reduction). As a result, a boundary phase (SEI) is formed at the interface between anode/electrolyte/cathode. After the formation of this layer, further lithium ions travel from the cathode through the electrolyte into the anode, being incorporated into the latter. During discharge, the reverse happens, as it can be seen in the following equations [42, 43]:

$$\text{Cathode: } LiMO_2 \rightleftharpoons Li_{1\text{-}x}MO_2 + x*e^- + x*Li^+ \tag{2.2}$$

$$\text{Anode: } C + y*e^- + y*Li^+ \rightleftharpoons Li_yC \tag{2.3}$$

$$\text{Overall Cell Reaction: } \frac{x}{y}C + LiMO_2 \rightleftharpoons \frac{x}{y}Li_yC + Li_{(1\text{-}x)}MO_2 \tag{2.4}$$

where, **M** represents a transition metal, for example: Al, Co, Mn or Ni.

This process is schematized in Figure 2.5.

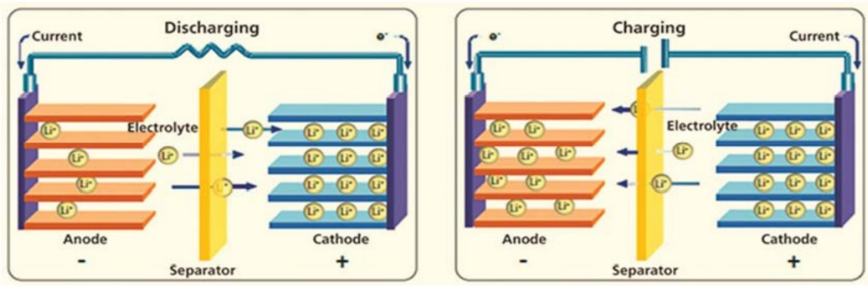


Figure 2.5: Basic working principle of a LIB. Reproduced from Ref.[42]

2.3.4 Critical Raw Materials

Of all the materials currently used in battery cells, three of them are featured in the 2020 list of critical raw materials[44]: cobalt, lithium and natural graphite.

This list intends to point-out supply risk (SR) of important materials to the EU economy, allowing the EU to prioritise needs and action to protect its industrial value chain. The criticality of these materials is based on a combination of their economical importance (EI) and their high SR disruptions. These materials are also classified according to its substitutability through a parameter called Substitution Indexes, this is important because in the event of a supply shortage it allows to reduce the potential impacts of such disruption [45].

Cobalt

Cobalt is a shiny, silver-grey transition metal with diverse applications. It is characterised by being a hard metal that retains its strength at high temperatures, has a high melting point, has magnetic properties and is also able to form alloys with other metals providing high wear-resistance. Cobalt is mainly produced as a by-product of nickel and copper production. In 2018, cobalt as a by-product of copper production represented 56% of the world total, 37% as a by-product of nickel production and only 7% was coming from mining operations that saw it as the main commodity[46]. It is estimated that global resources of cobalt are approximately 25 million tonnes, the world's most important reserves are placed in the central African Copper belt that runs across the Democratic Republic of the Congo (DRC) and Zambia. The DRC dominates the global mine supply, followed by China. In Europe, Finland mines nickel and copper, and cobalt is obtained as a by-product as well [26].

Cobalt demand has been increasing steadily for the last two decades, and more recently, the rising demand is related to rechargeable Li-ion batteries, initially in consumer electronics and now for EVs and energy storage. Currently, the market is experiencing a surplus due to the expansion of the mining capacity in the DRC. However, as new battery technologies rely on cobalt (NMC and NCA), the annual demand for cobalt in battery manufacturing is expected to go from 17kt in 2017 up to 350kt/year by 2030. This means that worldwide demand will exceed supply from 2025 onwards (Figure 2.6).

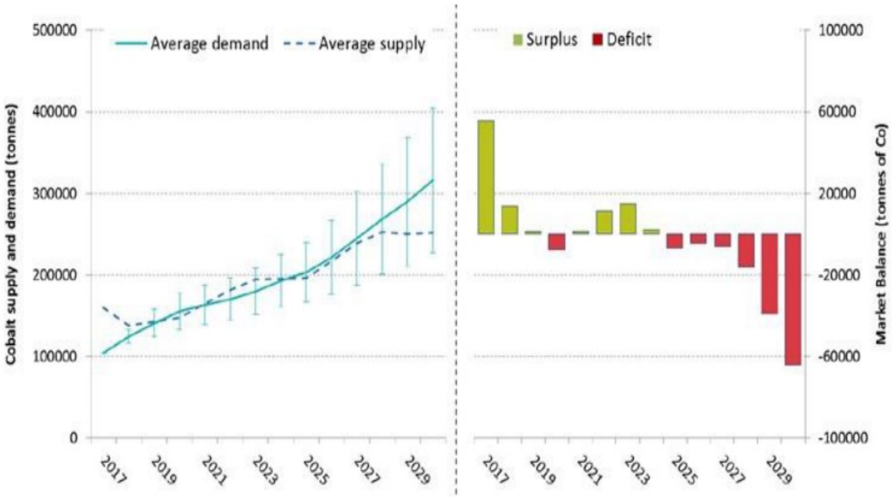


Figure 2.6: Average global supply-demand balances between 2017-2030. Reproduced from Ref.[47]

On a worldwide scale, the EU produces 1.5% of Co, this means that it still remains highly dependant on imports. Cobalt ores represent 86% of importations, whereas, concentrates and intermediates represent 27%. In Figure 2.7, the EU main sources for different types of cobalt are presented.

(a)

(b)

Figure 2.7: Top-10 cobalt exporting countries in 2017 for cobalt ores and concentrates (Figure 2.7a)) and for intermediates and refined cobalt (Figure 2.7b)). Adapted from Ref.[46]

In 2016, the EU used 36% of its demand for Co in superalloys manufacturing, followed by the production of hard metals for metal tooling and inks and pigments, information present in Figure 2.8.

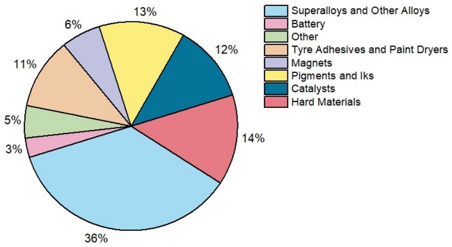


Figure 2.8: Cobalt application in the EU in 2015. Adapted from Ref.[46]

Cobalt is an essential raw material for the implementation of EU's plans for reaching climate-neutrality by 2050[47]. Its end of life products can be collected and recycled, and in 2016 the EU's input ratio for recycling cobalt was at 19% (Figure 2.9). The potential for increasing this number is high due to batteries coming from electric vehicles, however, due to their lifetimes, this will only be noticeable from 2025 into the future [46, 48]. The research to find a substitute for Co is mainly moved due to price volatility, geopolitics of supply and cost. In most applications substituting Co results in a lost of performance, however, it is possible, and Ni is its main substituent. The 2020 report of CRM[45] gave Co a classification of 0.92 on both Substitution Index for Economic Importance (SI(EI)) and Substitution Index for Supply Risk (SI(SR)).

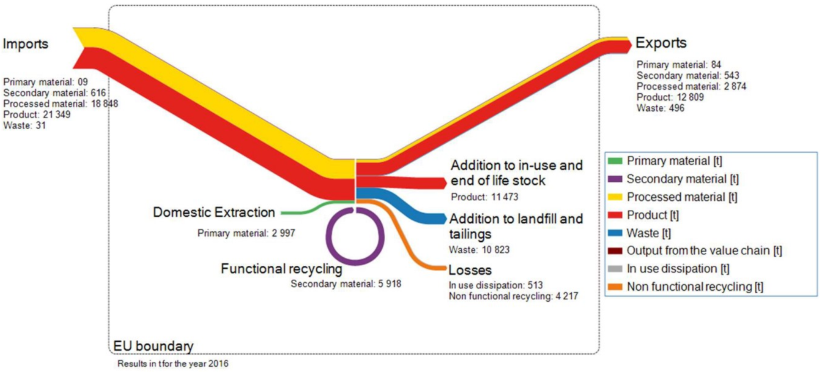


Figure 2.9: Sankey diagram of cobalt flows in the EU in 2016. Reproduced from Ref.[48]

The ability to recover this material through recycling will mean less dependency on imports from countries like the DRC, that from a socio-economic point-of-view have several issues like poor governance, political instability, trade restrictions. And since DRC uses artisanal and small scale mining it raises concerns regarding human rights abuse[46].

Lithium

Lithium is a metal placed in the alkali metal group. It has a density of 0.53g/cm^3, being the lightest metal and the least dense solid element at room temperature. It is also characterized by great electrical conductivity, high electrochemical potential and high reactivity, reason for only appearing in nature in the form of silicates or chlorine in brines and seawater [48]. Lithium can be extracted from mainly two distinct sources, hard-rock deposits and brines. Brines are mostly found in South America: Chile, Argentina and Bolivia compose the "Lithium Triangle" that contains half of the world's lithium resources and 70% of global reserves. On the other hand, most of the hard-rock mineral resources are located in Australia [46].

Between the 1950s and the 1980s, the global lithium production was rather stalled at levels of 5,000 tonnes annually. However, for the last years the world lithium mineral production rose to 36,5 kt in 2016 (31% lithium concentrates and 69% refined Li)[46]. This rapid growth is highly correlated to the strong growth in demand for Li-ion batteries. In 2018, the lithium produced from hard-rock surpassed the lithium coming from brines with a share of 55% of the global total.

Australia is the main producer of lithium mineral concentrates (spodumene) and this is largely exported to China. China has more than half of the world's refining capacity, making it the leader in imports and exports of lithium carbonates and hydroxides [46, 49]. On the other hand, Chile is the largest exporter of lithium carbonate, accounting for 61% share of these exports, followed by Argentina. China is also its main importer (24%), followed by South Korea and Japan (20% and 16%, respectively)[26, 46, 48].

The EU consumed between 2012-2016 about 3,208 tonnes of lithium per year (31% Li concentrate and 69% of refined Li). Australia is the main supplier for concentrates and Chile for refined lithium (Figure 2.10a). It should be brought to attention that since 2017, six mining sites of lithium were registered in Portugal: Alvarrões (Guarda), Gondiães (Braga), Alijó, Lousas, Mina do Barroso (Vila Real). From these mines, lepidolite and spodumene minerals are extracted. Portugal is the only country in the EU that currently mines lithium, it sources 11% of EU's Li concentrate imports (Figure 2.10b) and accounts for 0.5% of world production.

(a)

(b)

Figure 2.10: EU sourcing of refined lithium (Figure 2.10a)) and of lithium concentrates (Figure 2.10b)) between 2012-2016. Adapted from Ref. [46]

The 0.3 kt of Li supplied to the EU by Portugal are directly used in glass and ceramic manufacturing and respond to 17% of in-use demand of this EU sector, the remaining has to be imported [46, 48]. In the

EU the main end uses of lithium and compounds can be seen in Figure 2.11.

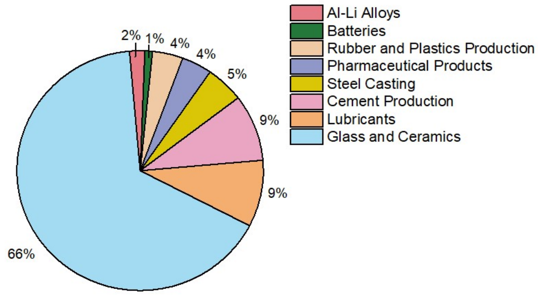


Figure 2.11: Lithium uses in the EU in 2012. Adapted from Ref.[46]

Since lithium is one of the essential raw materials used in battery production in EVs, there's a substantial opportunity for growth as many of the technologies employed use this material. In 2018 nearly 53% of Li end-use products were collected, however, the amount of recycled Li obtained was negligible and this is caused by several technical and economical issues (Figure 2.12). So it is important to invest in processes that increase the collection rates of this material. Li substitution is applicable in several fields, however, it's not very used because of Li's price and stability of supply. Sodium and potassium could substitute Li in the ceramic and glass industries, however, it entails a loss of performance [46]. In the 2020 report [45] on CRMs, Li was given a score of 0.93 on both SI(EI) and SI(SR).

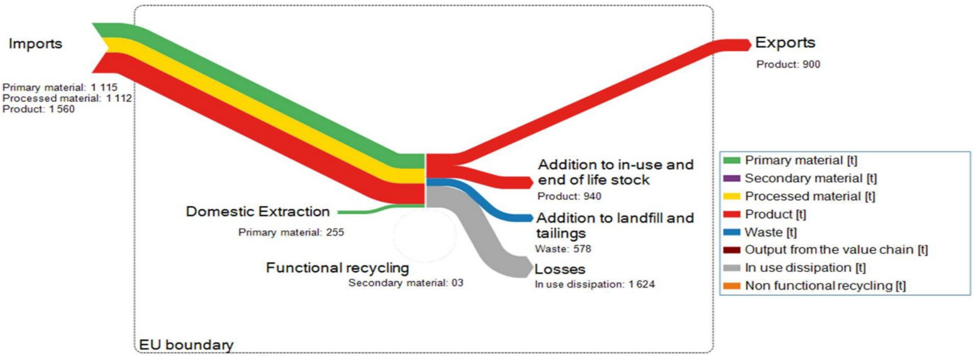


Figure 2.12: Sankey diagram of lithium flows in the EU (without UK) in 2016. Reproduced from Ref. [48]

Natural Graphite

Natural graphite is a carbon allotrope with both metallic and non-metallic properties, it consists of planar sheets with strong intra-planar bondings whereas inter-planar bondings are not as strong. Free electrons between layers make it a good thermal and electrical conductor with a high melting point (3650°C). There are three different types of natural graphite: crystalline/ flake graphite, microcrystalline/ amorphous graphite and vein/ lump graphite. These different ores require different processes after being mined, the mineral processing (occurs first) involves mechanical separation and flotation. Further processing is used for purer products such as anodes and includes milling, spheroidisation and purification [46, 48].

Natural graphite is mined in several countries. The global production of flake graphite is around 50%-60%, amorphous graphite represents around 40%-50% of total production and vein graphite accounts for less than 1% of total production. China concentrates almost all production with a share of 71% of the world production. In 2017, it had reserves estimated at 110,000kt, followed by India (12%) and Brazil

(8%) [46]. China produces approximately 70% of amorphous graphite, and 30% of flake graphite. It is also important to mention that China is the largest exporter of this material and it is the only commercial-scale producer of spherical graphite. In recent years, reserves were also found in Mozambique and Tanzania, each has 15% of the world's total. In Europe some reserves are found in Sweden, the Czech Republic and Finland.

The Eu reliance in the imports of natural graphite is around 98%, it consumes around 86kt, only 2% of which is sourced through domestic production. The main EU's supplier are China (47%), followed by Brazil (12%), Norway (8%) and Zimbabwe (7%), explicit in Figure 2.13.

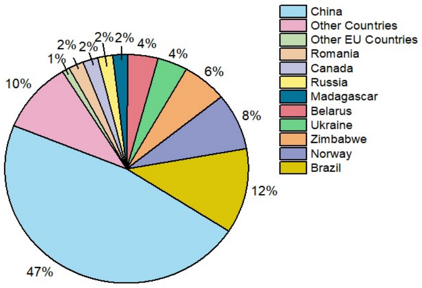


Figure 2.13: EU sourcing of natural graphite between 2012-2016. Adapted from Ref.[46]

EU uses natural graphite mostly in the steel industry for refractories. The second main application is batteries, followed by friction products and lubricants (Figure 2.14) [46, 48].

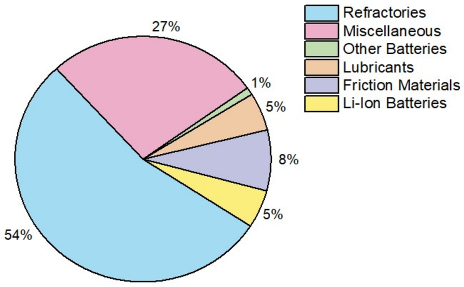


Figure 2.14: End uses of natural graphite in the EU between 2012-2016. Adapted from Ref.[46]

The graphite market is complex because it is not a homogeneous commodity. A large portion of the total demand for graphite is met using synthetic graphite (around 1,500-1,600kt)[46]. However, in the most recent years, the battery sector has been growing and is expected to continue growing to the point where China, in 2018, felt the need to start importing large quantities of flake graphite from Mozambique and Madagascar in order to meet the demand coming from the lithium-ion battery industry.

The need for graphite in domestic energy storage and EVs is expected to grow exponentially. In the EU it is projected that by 2035 the demand reaches 41kt and 98kt for energy storage and EVs, respectively, compared to 0.1kt and 0.07kt in 2015 [46, 50]. However, the supply of this material is positive as several companies continue to further develop mining projects in Australia, Canada, Sweden and countries in Africa.

As mentioned before, synthetic and natural graphite are competing in several applications, they are common substitutes for each other and some applications can even use both. The 2020 report [45] scored natural graphite, in both indexes, with a 0.99. Concerning the recyclability of this material, processing spent graphite-based products is a well known technology and the recycled materials are used in some applications as a full or partial replacement of virgin materials. In 2016, the EoL recycling input was around 3% [46] (Figure 2.15).

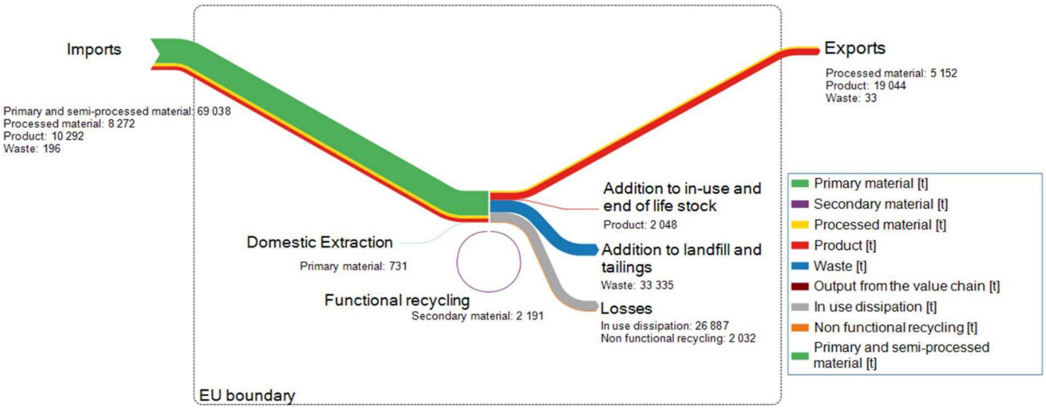


Figure 2.15: Sankey diagram for natural graphite in the EU (without UK), in 2016. Reproduced from Ref.[48]

2.3.5 Future Developments

Batteries are being more and more regarded as a solution to the decarbonization of transportation and as a way to provide electricity to off-grid communities. Between the years of 2010-2018, battery demand grew 30% annually, reaching a volume by the end of 2018 of 180GWh. As mentioned earlier, this number is going to keep growing and forecasts say it will reach, in 2030, a total volume of 2,600GWh, with an estimated 25% annual rate of growth [51]. The main drivers for this growth are the electrification of transportation allied with the deployment of batteries in electricity grids. Forecasts also say that by 2030 passenger vehicles will represent 60% of global battery demands [51, 52].

To date, the battery is responsible for around half of the total cost of a BEV. However, this expense, estimated in 2016, to be around 227$/kWh is expected to decrease potentially below 100$/kWh by 2030 (Figure 2.16).

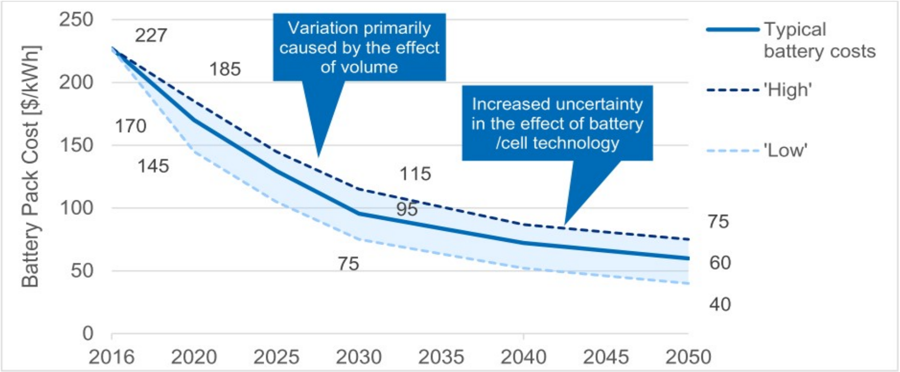


Figure 2.16: Current and projected future costs of Li-ion battery packs for BEVs up to 2030. Reproduced from Ref.[4]

This decrease in cost is highly due to falling component prices and assumed downsizing of 1% per year for the motor, and 2% per year for the battery pack[24]. This, consequently, means newer and different technologies for battery generations.

Nowadays LFP and LTO technologies are mostly used in heavy-duty vehicles because they present higher life cycle and can endure higher charging loads [4]. Another advantage is the use of iron over cobalt and nickel. In NMC811 the cathode production represents around one third of the manufacturing energy use, LFP technology offers a 50% reduction of energy use due to the high abundance of iron and phophorus. In addition, the LFP cathode offers a much lower toxicity score, when compared to NMC811, because of the use of non-toxic Fe rather than Co or Ni [53]. Even so, most predictions aim to a shift towards NMC technology across all vehicles types in 2030.

In the near future, there will be a change in the anode, cathode and electrolyte technologies that outperform the current Li-ion batteries. This includes lithium-sulphur (Li-S) and SSBs expected to be introduced in the market by 2025 [4, 54]. zinc-air (Zn-Air), lithium-air (Li-Air), sodium-ion (Na-ion) and magnesium-ion (Mg-ion) technologies and alternatives like supercapacitors for EVs are also being researched, however, these batteries will only be available for recycling by 2030-2050 (Figure 2.17).

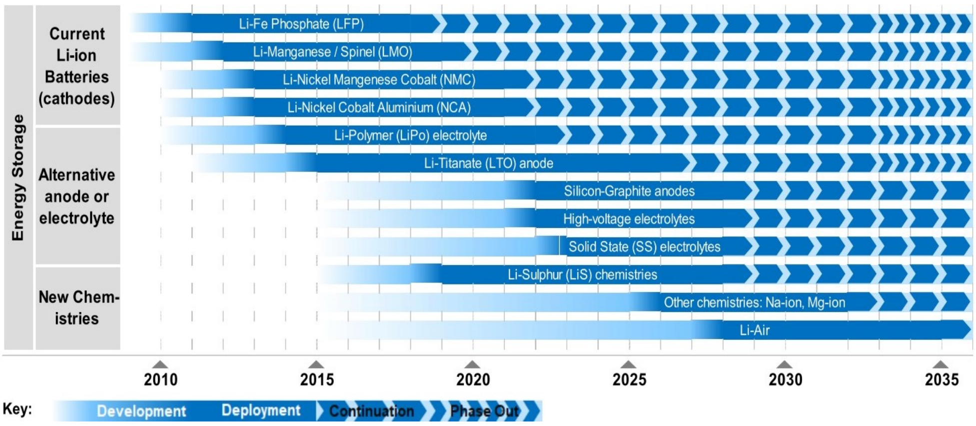


Figure 2.17: High-Level Technology Roadmap for EV Battery Chemistries. Reproduced from Ref.[4]

It is also important to understand how key performance indicators will evolve with these new technologies, and it becomes evident that higher energy densities, better performance under extreme temperatures and lower costs are what it can be expected. Generations 3a and 3b (Figure 2.18) consist of further optimisation developments of current Li-ion batteries, Generation 4 batteries concern new chemistries like Li-S and SSB.

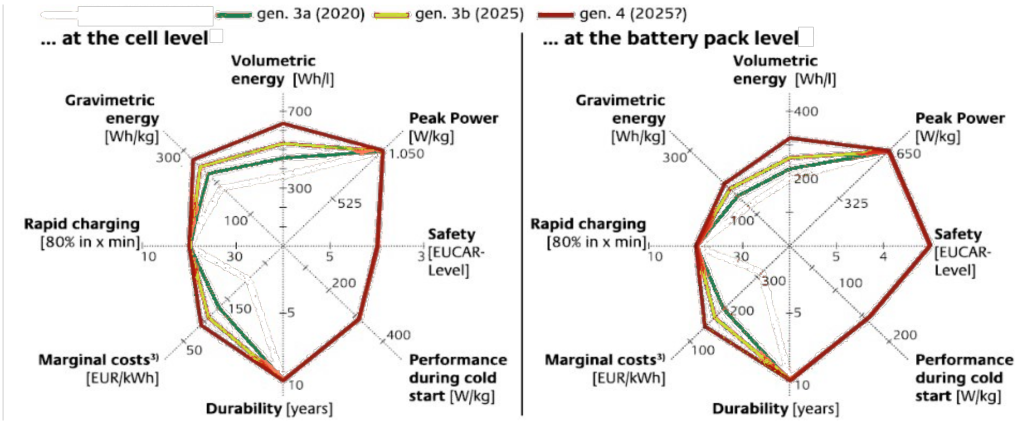


Figure 2.18: Forecast of key performance parameters of EV Batteries. Adapted from Ref.[4]

Chapter 3

Battery Waste Management

Every product, during its life cycle, has an environmental impact associated with it regarding all stages of that cycle. A helpful tool to assess this impact is a life cycle assessment (LCA). LCA allows us to better understand the upstream and downstream environmental impacts of products.

This analysis is performed considering the concept of circular economy. It considers the impacts of products during their life cycle and, in return, tries to find solutions throughout the system to maintain the value of materials and products. This will reduce material and energy inputs along the way and with higher benefits for solutions like: reuse, repair and remanufacture over recycling and energy recovery [7].

The battery market is no different. A sustainable way to reduce the impacts of battery production per unit of time is to extend their lifespan, including in other applications, at the cost of delaying the availability of materials for recycling (Figure 3.1) [55].

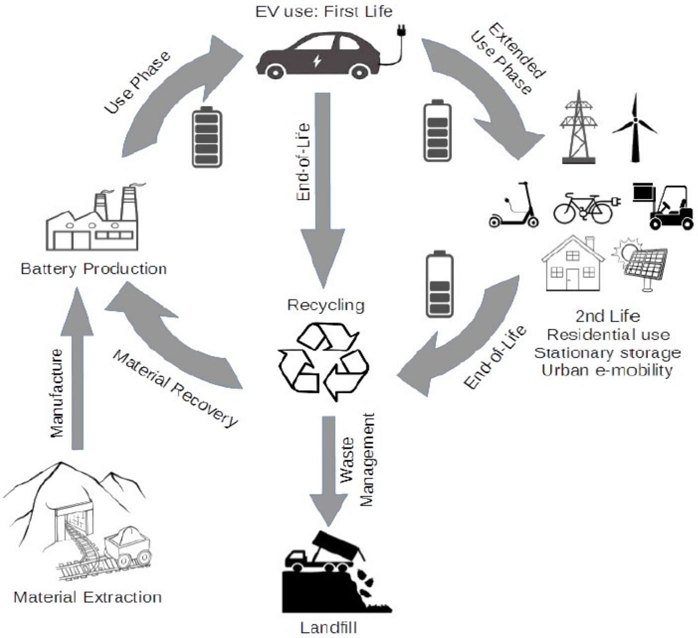


Figure 3.1: Batteries in a Circular Economy. Reproduced from Ref.[56]

3.1 Legislation

As mentioned in Chapter 2, the sales of EVs is expected to increase, and with them the number of batteries. EVs have a lifespan of about 10 years, decreased lifetime due to the battery, which degrades and shortens the driving range of vehicles to unacceptable levels [57, 58].

Disposal of these batteries in landfills represents an environmental hazardous. In LIBs most of the leachable metals (Ni, Co, Li) are confined in the cathode, however, if there's any damage to the outer casing, these metals become exposed. Landfill leachate is concerning because it can act as a medium for pollutant's transportation, and outside of landfills these can pose as threat to human health and the environment, if not dealt properly [59].

The EU, in order to make sure that the deployment of batteries did not hamper the efforts of a green transition, created major instruments to influence and regulate the management of batteries and EoL vehicles. According to the 2000/53/EC Directive, 95% by weight of an EoL vehicle has to be reusable and/or recoverable and 85% by weight has to be reusable and/or recyclable. This directive requires that automakers take extended responsibility for their vehicles and components after use, meaning that they either take back in their products for reuse, recycle or remanufacturing or either delegate the responsibility to a third party [57, 60]. Since 2006, batteries and waste batteries have also been regulated under the Batteries Directive (2006/66/EC), which stated that all the EU Member States should provide free collection systems to the public and required recycling efficiencies for LIBs at 50% of weight collected of all batteries.

In 2020, the EC proposed a modernisation of the EU legislation regarding batteries during the presentation of the european *Circular Economy Action Plan*. This new proposal aims to increase the collection rates for portable batteries, previously set at 45%, up to 65% in 2025 and 70% in 2030. Total prohibition of landfilling of waste batteries, restriction on the use of hazardous substances (particularly cadmium and mercury) are some of the additional measures contemplated in this proposal. It also sets new targets in recycling efficiencies and recovery of materials: by 2025 Li-ion batteries should have a recycling efficiency of 65% and by 2030 this number should increase up to 70%. Regarding material recovery, in LiBs, the targets for 2025 are 90% Co, 90% Ni, 35% Li and 90% Cu, in 2030 the figures change to 95%, 95%, 70% and 95%, respectively. Furthermore, the proposal intends to oblige manufacturers to use responsible sources of raw materials, inform about the content of recycled materials (12% of Co, 85% Pb, 4% Li and 4% Ni by 2030), present a carbon footprint declaration and labelling [8, 58].

In Portugal the control of batteries in the market and its recovery, treatment and disposal is regulated by the decree-law 152-D/2017 [61], this decree unifies residue's flux management laws with Extended Producer Responsibility (EPR) under the EU Directives. This decree states that battery producers are responsible for the environmental impacts and residues coming from the use and consequent disposal at the end-of-life. Producers are responsible for financing the management of battery residues, register as producers in SILiAMB and correctly label the batteries [61].

3.2 Collection

For recycling, and other second-life options, to be efficient it is important to have a strong and established collection infrastructure to meet the collection and recovery targets presented before.

In Portugal, the companies responsible for managing the integrated system of recycling of batteries and accumulators are Electrão, ERP Portugal, GVB and VALORCAR, the latter also being responsible for EoL vehicles. These companies and operators should aim to fulfill the following recycling rates: 65 wt% of Pb-batteries, 75 wt% of Ni-Cd batteries and 50 wt% of other chemistries [61].

Data from Eurostat shows that Portugal has since 2012 accomplished these recycling efficiency objectives [62]. A yearly report by Agência Portuguesa do Ambiente (APA) [63], shows that in 2018 Portugal placed 35,348 tonnes of batteries and accumulators on the market, collecting 33,640 tonnes and recycling 33,533 tonnes. Meaning that the collection targets were not met, but the recycling targets set by the EU were surpassed (Table B.1, Appendix B).

3.3 Transportation

Goods are considered hazardous if they are explosive, corrosive, flammable, toxic or radioactive. Batteries, and particularly Li-ion batteries, have corrosive, flammable, toxic and explosive characteristics and are classified under the United Nations (UN) category 9 as dangerous goods because of their thermal and electrical instability [64].

Throughout the years, there's been a surging number of stories regarding failures of EVs in car crashes, hard object intrusion, overcharge, over-discharge, water soak, overheat, battery leakage and electrical system failure, etc. Therefore, there's been an increasing search to understand the essence of unsafe behaviour of LIBs, showing that the exothermic reactions inside batteries are the main reasons. They generally include [65]:

- excessive delithiation of cathodes resulting in irreversible structure change of cathodes, oxygen release and oxidisation of organic solvents;
- lithium dendrites formed on anodes reacting with electrolytes to generate a large amount of gas, heat and continuous growth of lithium dendrites, which further penetrates the separator and hence resulting in an internal short circuit of batteries;
- the melting of PE-based separators when the temperature increases to above 130°C, which also leads to internal short circuit;
- the electrolyte being easily decomposed at high temperature (over 200 °C) and high voltage (about 4.6 V) due to the carbonate organic solvents with low flash points and low boiling points, which generate large amounts of heat.

When the amount of heat generation is higher than its dissipation in a battery, the exothermic reactions will cause a fast increase in internal temperature and pressure of batteries, which may result in thermal runaways, burning or even explosion of LIBs.

For these reasons, the transportation of batteries is highly regulated. Before being shipped batteries have to pass several tests described in UN38.3 Manual of Tests and Criteria (Appendix C) [64, 66].

European Standard (EN) follow most of the norms provided by the UN and the transportation regulations are largely covered by two EN standards: *EN 50272-1:2011-10* which defines safety requirements for secondary batteries (rechargeable) and battery installations, and *EN 62281:2013* defines the safety of Li-metal and Li-ion cells and batteries during transport and also specifies test methods and requirements for primary (non-rechargeable) and secondary Li-cells and batteries [64].

Lithium batteries can be commercially transported via road, rail, sea and air and are classified by the UN as [67]:

- **UN3480** Li Ion Batteries;

- **UN3481** Lithium Ion Batteries contained in Equipment;
- **UN3481** Lithium Ion Batteries packed with Equipment;
- **UN3090** Lithium Metal Batteries
- **UN3091** Lithium Metal Batteries contained in Equipment;
- **UN3091** Lithium Metal Batteries packed with Equipment;

When batteries pass the safety tests they are ready to be transported. For transporting these goods there are several packing instructions set by the UN: cells or batteries have to be individually packed so that they are protected against damage, they should be placed inside an impact resistant outer casing and the terminals must not support other elements.

If the batteries or cells are placed in the pack with equipment they have to be completely enclosed and secure against movement of the outer package. If they are placed within the equipment the casing must be built to avoid accidental operations during transportation [67, 68]. Batteries and cells have to be disconnected or electrically isolated. In addition, the packaging must contain several labels informing about its content (Figure 3.2).

(a) LIB handling label (*Place for UN numbers,
**Place for additional Information and Contact).

(b) Cargo aircraft only label.

(c) Class 9 hazard label.

Figure 3.2: Label placed in LIB packages. Reproduced from Ref.[64]

If it is an undamaged small-size lithium battery, for air transport, the only requirements are that cells and batteries are protected against short-circuiting, the package must present Figure 3.2a label and, in the case of containing equipment, it must be protected against accidental activation (Figure 3.3a). Non-small size lithium batteries follow the previous requirements and if sent via sea freight the container must have the same markings with the exception of Figure 3.2a) label (Figure 3.3b).

When the transportation concerns damaged and/or defective batteries some extra cautions must be met: each damage or defective cell/battery has to be individually packed in an inner package and placed inside an outer package. One of the packages has to be leakage-proof to prevent the release of the electrolyte, and if the battery is already leaking, sufficient inert absorbing material needs to be added. Individual inner packages must be surrounded by non-combustible and non-conductive material to protect against any increase of temperature. It is also important that these batteries and cells are packed inside form-fitting packages to avoid the effects of vibrations and shocks [64, 67]. The packages must not exceed the outside temperature of 100°C, no flames can occur outside of it and they must not contain projectiles. The packaging must contain a gas management system. A verification report must be available on request with the battery name, the cell/battery number, mass, type and energy content, as well as, the test data following the verification method set by the competent authority [68].

(a) Packaging containing batteries ≤100Wh, overpack Used.

(b) Packaging containing batteries >100Wh, overpacked Used.

Figure 3.3: Different packages for LIB air transportation. Reproduced from Ref.[69].

When batteries are transported for recycling/disposal they must be packed to prevent short-circuiting and dangerous risk of heat. This may include, individual protection of battery terminals, inner packaging to prevent contact between cells and batteries and this can be achieved by using non-conductive and non-combustible cushioning material inside the packaging. They must also be secured against excessive movement within the outer package. In addition, these packages must be marked as "Lithium Batteries for Disposal" or "Lithium Batteries for Recycling". Batteries being shipped for disposal/recycling are prohibited from air transport unless approved by the appropriate national authority [64, 68, 69].

In Europe, if the transportation is made by road and the vehicles carry less than 300kg, they are exempt from placards, and drivers are not required to carry hazmat endorsement/licensing [70]. They have to be, however, aware that the shipment contains Class 9 goods, requiring a dangerous goods shipping paperwork. In addition, vehicles should be equipped with a system capable of dealing with spillages, absorbent materials, and firework devices [71].

3.4 Second-Life

Moving away from a linear into a circular value chain can improve both environmental and economical footprint of batteries. After their use in EVs batteries present a residual capacity between 60%-80% of nominal capacity [4, 26], if batteries are properly collected, manufacturers can either: reuse them, recycle them for recovery of valuable metals, increasing their lifespan or dispose of them [55].

By 2030, second-life battery supply used in stationary applications can exceed 200 GWh/year (Figure 3.4), volume which exceeds the demand for Li-ion utility-scale storage for low and high cycle applications combined [72]. However, this is still a relatively new concept for EV manufacturers because only now the first batteries are reaching their end-of-first-life. Some difficulties arise from the fact that there are several battery-pack designs and chemistries increasing the complexity of refurbishing. Other difficulty is the decrease in prices for newer technologies meaning that the differential between an used and a brand new battery can lower from 30%-70% cost advantage up to only a 25% difference. Guaranteeing the quality of performance and quality of second-life batteries is also hard. Lastly, the lack of regulation creates uncertainty for original equipment manufacturer (OEM), companies and potential customers [4].

Once again, to tackle these issues, the EC in the proposal for modernisation of regulations presented a set of measures that may ease some of these problems by labelling the packs (with information regarding chemistry, lifetime, charging capacity, requirements on separation and collection, presence of hazardous substances and safety risks) [8, 58].

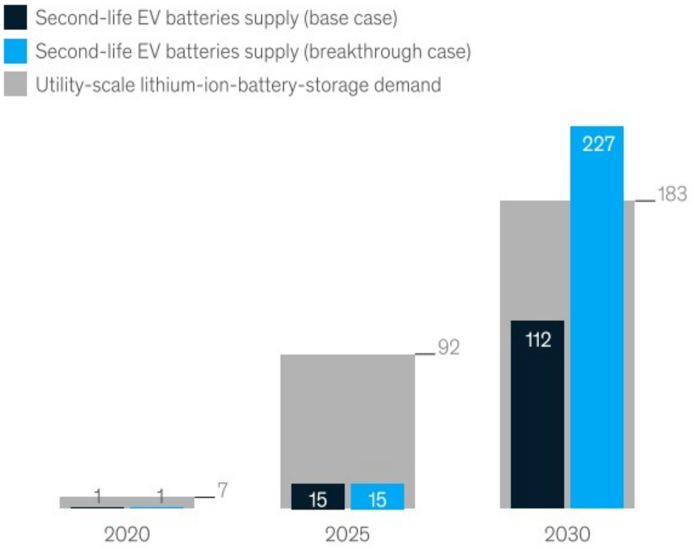


Figure 3.4: Utility-scale LIB demand and second-life EV battery supply (GWh/y). Reproduced from Ref. [72]

3.4.1 Reuse

Reusing batteries extends their lifetime, delaying the need for further EoL processes but not eliminating it [5, 7]. Using batteries for a second application (direct reuse) involves an assessment of individual modules within the cell. Normally up to 15% of the cells need replacing, but even with this intervention, 40% of direct costs can be saved when compared to the costs of producing new batteries [4, 7]. The removed cells are then disposed. This type of processes is highly hindered by the lack of optimisation due to the differences between warranties and life cycles of the batteries used in different vehicles.

Cascaded reuse involves using batteries in different and less demanding stationary applications, also known as repurposing. These batteries are normally used in energy storage systems, regulating the frequency and expediting the integration of renewable energies into the grid. This type of alternative reduces the need to invest in small application for residential energy storage. Repurposing is similar to reuse, all cells are assessed individually to determine their state-of-health (SoH), and since it does not require any change in design its costs are very low. It needs, however, reconfiguration of the modules and packs and the establishment of a new BMS to accommodate non-vehicle applications [7, 57]. This process is also favoured over recycling because it generates less waste and has a smaller environmental impact. The difficulties are also similar to the ones felt during reuse, such as, grading the SoH of packs and modules, dealing with different designs and performance metrics and cost, which must be competitive [4].

3.4.2 Remanufacturing

In remanufacturing, the batteries are intended to be reused in its original function with only a few parts replaced [57]. This technique returns a used product to almost new conditions, implying a complete disassembly of the EV battery, thorough cleaning, examination for damages and reprocessing to OEM specifications. Normally the cathode and anode have to be returned to their original state for reuse, this creates a closed loop of materials being considered the most environmentally friendly EoL option [4, 73].

3.5 Recycling

Aside from reducing the environmental toxicity from the production of virgin materials and the reduction of resource mining, recycling is a promising strategy for the future due to the increasing desirability of valuable products. Even though the recycling industry is still underdeveloped to respond to the immense surge of batteries in the next years, China has become the top-ranked country of recycling efforts (Figure 3.5) [74].

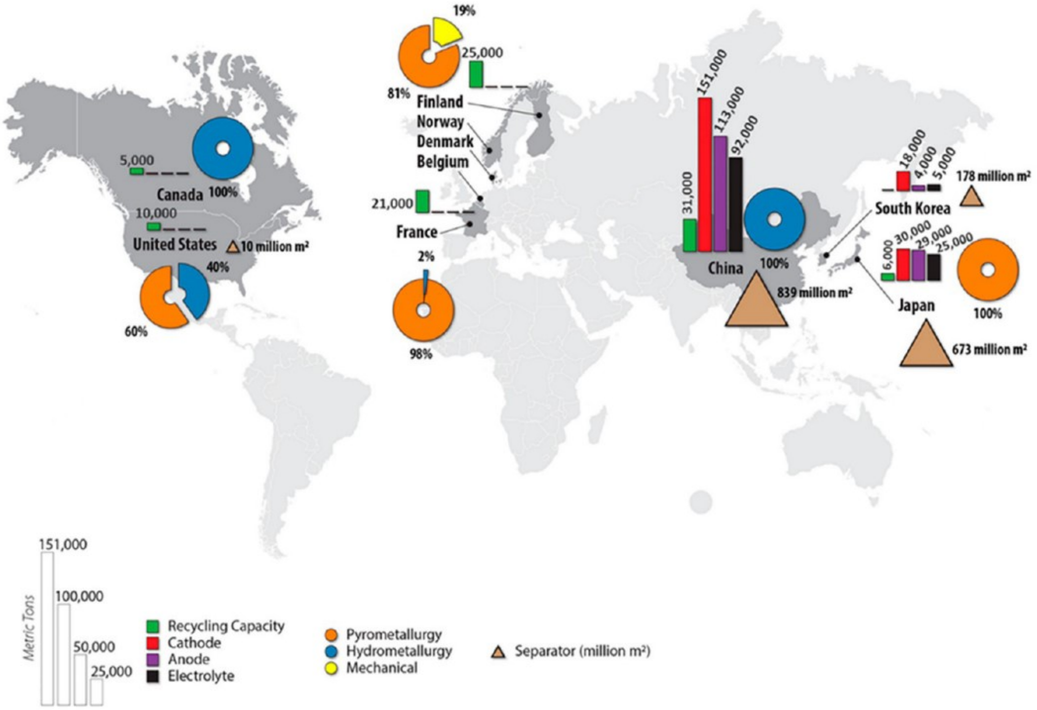


Figure 3.5: Battery (excluding Pb-acid) recycling capacities estimated in metric tons (MT) in the world, in 2019. Reproduced from Ref. [74].

For Europe, recycling poses as an opportunity to reduce its reliance on specific suppliers with poor social and environmental records. In addition, recycling is expected to become a prominent industry with billions of dollars in revenue, tax income and jobs [4, 75]. The goal of recycling processes is to separate the components of spent batteries into smaller fractions that can be reintroduced in the production of new materials [76]. Recycling processes are a combination of different unit operations, the existing approaches to recycling can be classified into [74, 77, 78]:

- **Pyrometallurgical Processes:** Use high-temperature furnace to reduce metal oxides into an alloy of Co, Cu, Fe and Ni while smelting the battery. The products obtained by these process are usually metallic alloys, slag and gases. This process is usually followed by hydrometalurgical steps to recover Al, Mn and Li from the slag, if not, the slag can be used by other industries as industrial cement. This process can be applicable to any battery chemistry and configuration without the need for any pre-treatment steps.
- **Hydrometallurgical Processes:** Usually involves a low-temperature leaching, purification and

separation process to recover pure metals. It is a process that accepts any type of battery chemistry and can specifically target certain metals. However, most processes require gas cleaning steps to avoid toxic emissions.

- **Direct Recycling:** It requires the separation and reconditioning of the cathode and/or anode materials from the electrodes to be reused in a remanufactured LIB. This process allows for an almost complete recovery of all materials. It requires more mechanical pretreatment steps and the quality of the recovered materials may not be as pristine.

In hydrometallurgical technologies and direct recycling a pre-treatment process is essential. These processes are capable of enhancing the recovery efficiency of the subsequent processes. Pretreatment involves the deactivation of the battery and some mechanical and thermo-mechanical procedures like dismantling, comminution, classification and separation of the battery components and thermal treatments. This work will describe typical processes/ unit operations that can be, and are, used in LIB recycling. Examples of current studies on lab- industrial-scale will be given and will follow the flowchart presented in Figure 3.6.

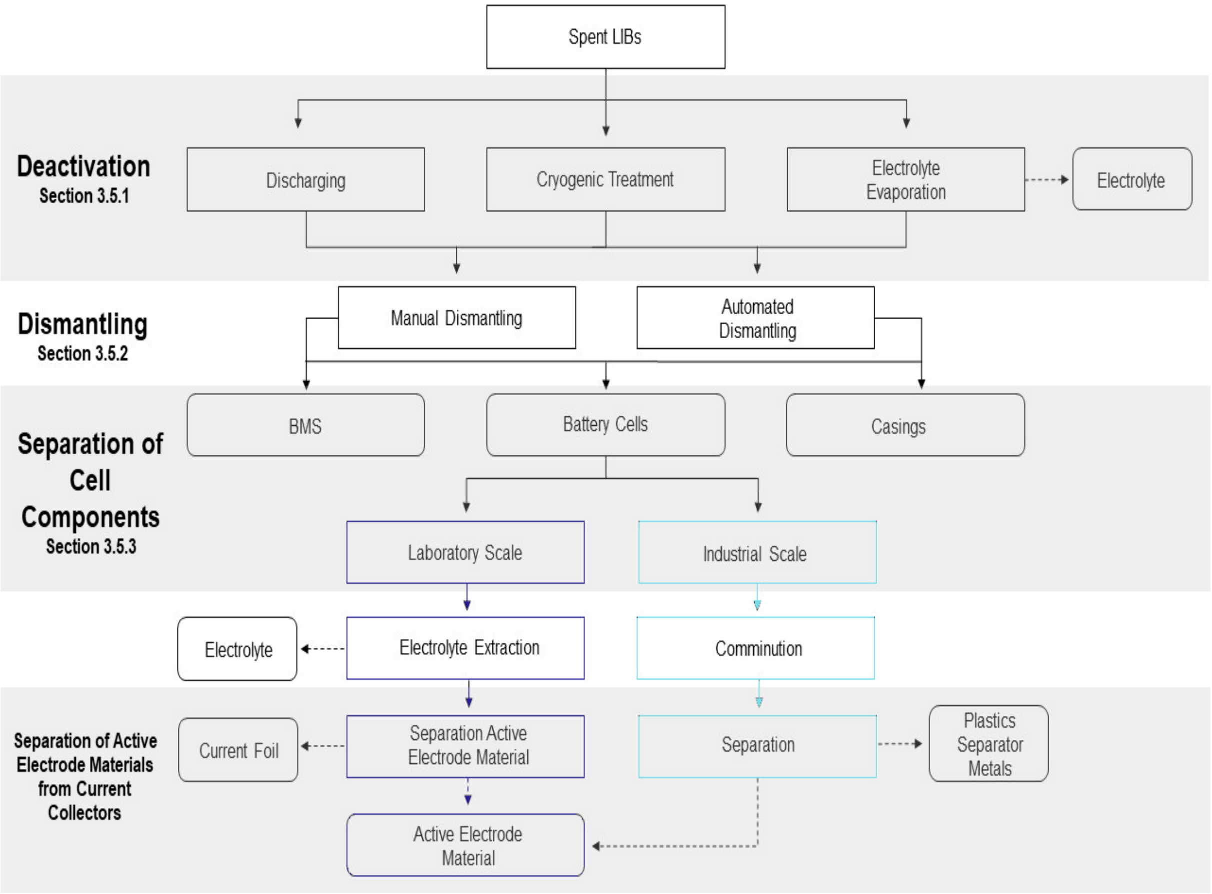


Figure 3.6: Flowchart of recycling pre-treatment processes of LIBs.

3.5.1 Deactivation

When batteries are charged they are usually reactive because of the presence of lithium atoms in the anode graphite layers, and therefore have to be deactivated before being treated for safety. The majority of them also contain organic electrolytes with fluoride-containing additives, that at high temperatures, can generate HF gases [79]. During deactivation the electrochemically stored energy is reduced, decreasing the chances of possible thermal runaways and other chemical reactions. Batteries can be deactivated by discharging, evaporation of the electrolyte or by cryogenic treatments [79, 80].

Discharge

When the cathode and anode, with some remaining capacity, come in contact with each other they cause a short-circuit current flow, this current generates Joule heat, igniting the solvents of the electrolyte. For this reason, when battery cells are to be dismantled and/or shredded without resorting to inert atmospheres or cryogenic freezing, they have to be discharged to reduce the risk of explosion [78, 79]. During the lifecycle of EVs the charge and discharge cycles are usually controlled by the battery management unit (BMU) (responsible for monitoring the voltage of each battery cell/module, controlling the current flow and measure temperatures), so it is only possible discharging and charging the battery through the BMU using a specific voltage range determined by the battery chemistry [80]. So to securely discharge a battery, a voltage superior to the end-of-discharge voltage is needed, however, this action is often prevented by the BMU because such deep discharges can be followed by a polarity reversion, inducing the formation of flammable gases in the cell.

When discharging a battery via standard resistor, where the energy is dissipated as heat, the energy can be reclaimed and repurposed. Here, since there is no damage to the parts, materials streams can be sorted at earlier stages reducing cross contamination, however, it is difficult to scale-up the energy recovery [81].

On lab-scale, batteries can be simply discharged by being placed in a stainless steel container with stainless steel chips [79] or by being submerged into a salt solution (brine) followed by a water-splitting reaction. This is a cheap solution to discharge batteries, with the disadvantage of not being possible to recover the energy and the liquid effluent may require some type of cleaning treatment. An experiment carried out using NaCl, $MnSO_4$ and $FeSO_4$ in solution at different concentrations (0.4mol/L, 0.8mol/L and 1.2mol/L) [82] concluded that the higher concentrations achieved better discharge efficiency. Even though they become more unstable, with registered fluctuations in residual voltage. It also stated that NaCl achieves the lowest voltages (0.5V in approx. 5h), followed by $FeSo_4$ (0.5V in approx. 14h) at a concentration of 0.8mol/L. Another experiment [83] used sulphate salts to discharge the battery leading to the formation of metallic precipitates. When stirring was added, the discharged rate was enhanced and the battery was completely drained after approximately 3h (20 wt% concentration). In this experiment iron flakes were also added to the solution with impressive results on the discharge speed, however, an undesired by-product was formed.

Halide salts (e.g.NaCl) usually end-up forming corrosion at the battery ends, alkali salts (e.g.Na_2CO_3) on the other hand, result in much less corrosion and water penetration, enabling the possibility for reuse. However, competing reactions still occur, oxygen, hydrogen and other gases may form at the end of the cathode and anode terminals, and for these reason, this method is not suitable for high-voltage modules because of the high rate of electrolysis and evolution of gases that may occur. In principle, on a lab-scale, this process could be more controlled offering a method where oxygen and hydrogen can be further recovered. But the probability of contamination of the cell contents is still high, hindering the down stream chemical processes [77, 79, 80].

Evaporation of the Electrolyte

Deactivation can also occur by evaporating the electrolyte using a thermal treatment usually at a range between 150°C - 300°C, in an inert atmosphere. This process rises the internal pressure of the cell, rupturing it and consequently separating some of the components. The range of temperatures is enough to evaporate the electrolyte, however, above 200°C there's a higher risk of electrolyte decomposition to CO, CO_2, etc [79, 80]. This process allows to simultaneously volatile different components with the downside of losing the electrolyte and the chance of producing toxic gases [81].

Nowadays, big recycling companies like Recupyl, Akkuser and Duesenfeld to name a few, usually use in-process stabilisation meaning that the batteries are shredded and/or crushed under an inert atmosphere (under 4% of molecular oxygen). This allows the formation of a passivating layer of Li carbonate while reducing costs. Retriev uses a water spray during the opening step because the hydrolysed water acts as a heatsink decreasing the risks of a thermal runaway [77].

Cryogenic Treatment

Cryogenic treatments are another way of decreasing the potential of exothermic reactions as low temperatures fix hazardous materials and chemical reactions are prevented [80]. This technique uses liquid nitrogen, and if the aim is to decrease the hazardous potential of the battery, temperatures around -65°C are advised. However, this treatment can also be used as a pre-treatment for transportation and safe handling of damaged batteries. Here the advised temperature is -60°C and it should be maintained constant. This creates the need for a cold chamber to be put into place with all its additional costs meaning that is not likely to be implemented at a large scale [81].

Another use for these low temperatures is to use them as a pre-treatment for mechanical separation techniques such as comminution. When this steps are performed at freezing temperatures (below the glass transition temperature) the components become brittle and easier to shatter, improving the efficiency of downstream separation processes [80, 81].

3.5.2 Dismantling

Once the battery is discharged, it is transferred to a controlled environment to be open safely, normally in a glove box filled with inert gas (e.g.argon) [84]. This happens because some chemicals inside the battery can react with oxygen and water, and some studies [85] have found that when dismantling battery, gases, predominantly esters and benzenes, are released. Carbonic esters were the most detected alongside dimethyl carbonate (DMC), the latter being a flammable liquid with a flash point of 17°C.

Disassembling involves all processes used to remove cell packaging and accessing the active materials either through manual or automated processes. It usually involves some basics steps such as [86, 87]:

1. Opening of the battery, usually the packs are held together by screws and nuts. Once it is opened it exposes the cell modules connected in series;
2. Cutting of electrical connections between electronic components and the battery modules, each module has its own cell module controller (CMC), after being disconnected they can be unbolted and removed;
3. Removal of mechanical connections between modules/electronics and the battery base, in this step there's the disconnection between the battery contacts and the wires;
4. Removal of electronic components;
5. Removal of battery modules;

6. Disassembly of battery modules and removal of battery cells. This last step starts by removing the rivets and that keep the metallic structure closed followed by the removal of wires on both sides, after that, the cell stacks are exposed;

This way, a clear separation of components and recovery of valuable materials is ensured. However, this step must involve high-voltage training and insulated tools to ensure the safety of workers, making it a labour intensive step and not practical in commercial operations [77, 79].

Automation

An obvious approach would be to automate this process eliminating the risk of harm to workers while reducing costs and possibly improving the mechanical separation of materials and components, resulting in higher purity and less intensive and more efficient downstream processes.

Some recent studies have been assessing the use of robots in the disassembly of battery packs[88]. With an industrial robot, with 6 degrees of freedom, equipped with a series of specially design tools was used to perform a number of operations like drilling, cutting and gripping. Initially the study starts by performing a set of experiments to define appropriate automated operations and movements. Once the depth of disassembly, sequence and movements are defined the disassembly is carried out using the robot. It was concluded that the non-destructive disassembly, using the robot, reduced the operation time. However, due to the high diversity of battery pack models it was recognised that fixturing and tools used might not be suitable for other designs.

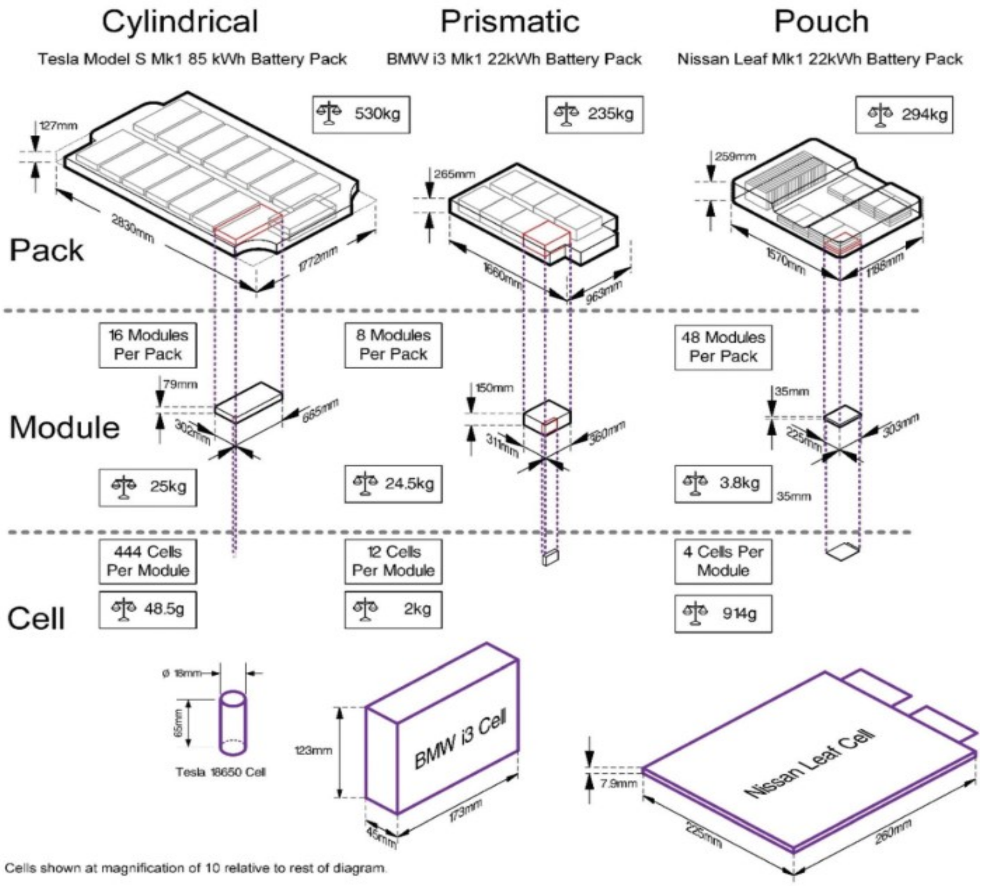
Another study [89], instead of using Computer Aided Design (CAD) models of the battery pack and components, relied on state-of-art 3D camera systems. This is a great advantage because, most of the times, when batteries reach recyclers they are different from CAD models due to maintenance, deformations and corrosion. Even though these systems (reinforcement learning and machine reasoning algorithms) are being more and more developed, they still present too high processing time, making the process economically unviable. The need of human assistance remains, which hinders production efficiency and the high inaccuracy of the vision system results in low success rate. Not to mention that if the batteries reaching the robot are differently assembled the machine would have to learn to identify the new model and its adequate disassembly sequence [88, 89].

At present, there's hardly any standardisation in the design of battery packs, modules and cells in the automotive industry, increasing the already existing difficulties in dismantling the batteries.

It should also be noted that not only do designs change, but chemistries as well, requiring different approaches for material reclamation and overall economics of recycling [77]. This becomes evident in Figure 3.7, a Tesla Model S has a 85kWh battery pack with 16 modules per pack and 444 cylindrical cells per module. BMWi3 with a 22 kWh battery pack is composed of 8 modules per pack only has 12 prismatic cells per module. Finally Nissan Leaf models use a 22 kWh battery pack with 48 modules and 4 pouch cells per module.

Robotics and automation in manufacturing operations require highly structured environments, where robots perform pre-programmed and repetitive tasks to known objects in fixed positions, contrasting, the development of intelligent robotic systems, capable of dealing with uncertainties is underdeveloped. So it is important to consider the complexity of these tasks in battery disassembly.

For automotive applications battery packs need to be power and energy dense. This is achieved by packing cells into modules and modules into packs, but the way through which they are assembled is one of the main issues for recycling. Cells are usually hermetically sealed and modules and packs



Cells shown at magnification of 10 relative to rest of diagram.

Figure 3.7: Different Battery Packs and Modules in Current EVs. Reproduced from Ref. [90]

are glued together with adhesives, the structures are clearly made to potential safety and cell longevity, hindering the speed at which the materials can be processed [90].

It is easy to comprehend the need for a robust outer pack, however, this should not difficult the opening of the cell, pack and module. As it becomes evident that manufacturers will not agree on an unique design, it is important to uniform fixing types to require only one tool to open. Normally, regardless of the design, cells in a module are permanently fixed to one another and are not intended to be broken down during service. Connections between modules are more processable, usually involving torque connections or mechanically push-fit connections. These makes modules easily replaceable and simpler to disassembly.

Semi-Automation

Due to the problems mentioned above, collaborative human-robot work is the most attractive possibility. Hybrid workspaces allow the implementation of a flexible production system where robots deal with monotonous and unergonomic tasks while humans perform tasks that require complex motions [77, 91]. One of the big challenges with this approach is to establish a certifiable safe technology without sacrificing the productivity due to high risk of collisions between robots and operator (Figure 3.8). Not all robots are equipped with sensors that facilitate human-robot collaboration and, therefore, for some applications, additional vision sensors have to be set in the workstation.

Once again, a robot was used to unscrew battery packs. In this case, they used a demonstrator

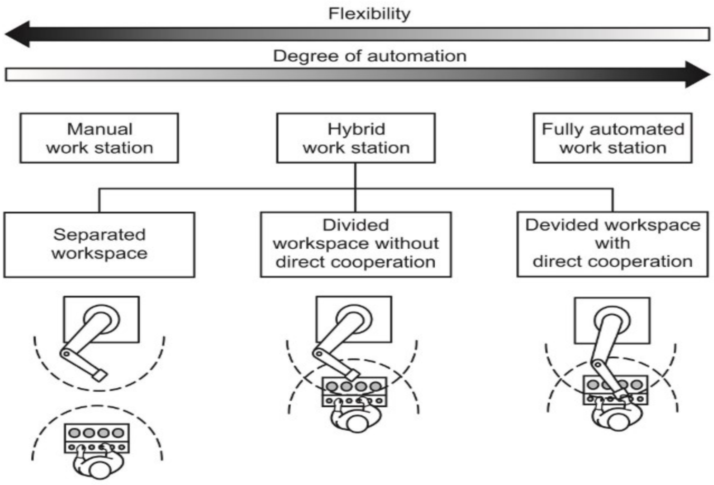


Figure 3.8: Classification of Hybrid Work Stations. Reproduced from Ref. [92]

that carried out the disassembly operations necessary, the operations/trajectories were computed using a 3D camera and transferred to the robot controller [91]. The intuitive operation reduced significantly the programming time of the robot. However, due to imaging processing errors the disassembly was constantly interrupted by the operator, decreasing the productivity. Nevertheless, the experiment showed that this type of collaboration is very promising. But it still needs to subject safety concepts to certification and improving imaging systems for higher accuracy.

At cell level the standardisation is even more difficult because cylindrical, pouch and prismatic cells are commonly used.

3.5.3 Separation of Cell Components

Lab-Scale Treatment

When the complete removal of the external metallic structure is achieved, cell stacks are exposed. Cell stacks consist on a series of carrier plates, each containing two cells. Between plates there are layers of isolating material [87]. During cell opening care must be taken to prevent internal short circuits inside the cell, these are more likely to happen during cutting of the cell due to penetration/ deformation of the electrode stack or by mechanical pressure. In most cases the cell components will be separated and analysed individually. Pouch cells are usually easier to open since the pouch can be simply cut. Prismatic cells have to be cut on one side and the remaining casing should be pulled, peeling the remaining casing using isolated pliers [93].

In case there is an electrolyte present, it can be extracted and further processed. The most challenging components are the anode and cathode materials, they are composed by a mixture of chemical components and require chemical and physical methods to be separated into pure materials [79, 84, 87, 93].

Electrolyte Extraction

As mentioned before, electrolytes used in LIbs have to fulfill several requirements such as a wide electrochemical stable window, high ionic conductivity and redox stability. The electrolyte system usually involves a conducting salt ($LiPF_6$, or $LiBF_4$) dissolved with a mixture of different carbonates: ethylene carbonate, ethylmethyl carbonate (EMC) and DMC, for example [94].

The electrolyte is introduced inside the battery as a liquid, however, during operation it starts penetrating the electrodes, and when the cell is opened the $LiPF_6$ salt can hydrolyse and produce HF, with adverse impacts on human health and the environment. For this reason, in recent years more focus has been given to the recycling of the electrolyte. It can be subjected to three possible recover methods: thermal drying step, application of sub/super-critical CO_2 and solvent extraction [84, 94].

Solvent Extraction

Solvent extraction aims to recover the electrolyte components while ensuring the requirements for subsequent steps in the recycling chain. In this technique the extraction agents are mixed with the battery material and the conducting salt and organic carbonates are transferred to a liquid phase, this allows to conduct the remaining processes in a safer way because it removes the toxic conducting salts and decomposition products.

A study conducted used acetonitrile, ethanol, acetone and DMC as solvents. After extraction, using a stainless steel vessel equipped with a pneumatic sample system at 2 bar of pressure, and 48h of storing at 8°C, the DMC solvent showed the higher concentration of hexafluorophosphate (PF_{6^-}) [95]. The fact that DMC already exists in the battery is an advantage because it discards the possibility of formation of additional substances.

After extraction the samples are mixed with the solvents, while the fluid exits the vessels through filters, the solid part remains in the vessel and new solvent is added. Extractions performed at different temperatures show that this parameter has a major impact on the decomposition of $LiPF_6$ but also on the dissolving of the conducting salt in solvent: higher temperatures maximise the concentration before it reaches a high level of decomposition. However, if the samples are to be handled for longer periods, a lower temperature is preferred because it avoids a quick degradation. It was concluded that $LiPF_6$ cannot be fully extracted with DMC because the major part of the residue is fluoride due to degradation but also $LiPF_6$, this happens because the product of $LiPF_6$, lithium fluoride, is very low in comparison to its solubility in water or mixtures with water.

Thermal Drying

This process relies on the different boiling points of components to separate them. Low boiling components like DMC and EMC accumulate in the gas phase, while high-boilers accumulate in the liquid phase. Along the process the low-boiling components are removed, leading to an increasing boiling temperature, however, this can be lowered if the pressure of the system is reduced. Experiments performed used a solvent extraction prior to the drying, the extracting agent was DMC, and since it is low boiling, it will be easily removed from the system while decreasing the content of high boiling components [95]. After that, the components were stirred, and the temperatures ranged from 20°C up to 120°C for 5-8 h.

Several problems were detected, such as, massive metal fragments can block the shovels, insufficient vacuum during drying prevents the drying of higher boiling components and if the temperature is not homogeneous throughout the apparatus the vapour can condensate and the high-boiling components may crystallize in these areas.

Supercritical CO_2

CO_2 is used to synthesize linear and cyclic carbonates for LIB electrolytes and it has been applied in Li-ion and Li-metal batteries as a SEI forming additive [94].

Aside from its standard phases, the supercritical phase is achieved by increasing the temperature and pressure above 304.1K and 74 bar. In this state CO_2 has the density equal to its liquid phase and the viscosity of gaseous CO_2 (Figure 3.9). These physical properties enhance greatly its dissolution characteristics and, therefore, carbon dioxide is used as supercritical medium for extraction. By using this method the extraction becomes a fast, highly selective and efficient process. To overcome limitations during extraction using subcritical CO_2 it is usual to add polar co-solvents, normally acetonitrile (ACN) or a mixture of acetonitrile and propylene carbonate (PC) [95].

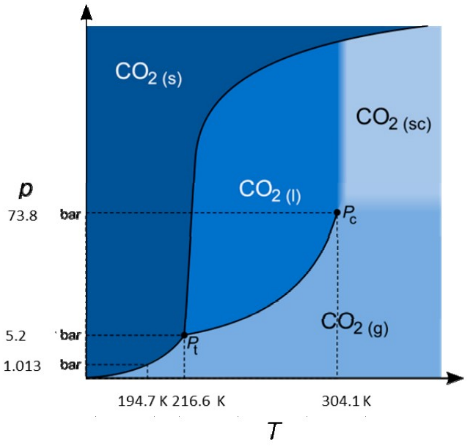


Figure 3.9: Pressure and temperature phase diagram of CO_2. Reproduced from Ref. [94]

In a study, supercritical dioxide carbon was studied as an extraction medium over a range of different pressures and temperatures, 15-35MPa and 30-50°C, respectively [94]. It was concluded that the increase in pressure of extraction resulted in increased extraction yield due to the high polarity of supercritical carbon dioxide. Regarding the temperature with its increase the overall extraction yield was also increased, however, when tested on EC its extraction remained stagnant, this happened because the polarity of the CO_2 was reduced, meaning that polarity plays a more important role in extraction compared to the density of the supercritical fluid. They achieved results of 88.71 ± 0.87 wt% regarding organic carbonate solvents, the conducting salt and aging products were not assessed.

It is important to keep in mind that it is not only the electrolyte that has to be removed undamaged. In a study performed [96], the purpose was to investigate the recovery of the graphite using three different electrolyte extraction techniques: subcritical and supercritical carbon dioxide- assisted removal with thermal treatment. Several analytical techniques were used to assess the electrochemical performance of the reclaimed graphite, and the best performance was found using the graphite that was retrieved using subcritical carbon dioxide assisted electrolyte extraction followed by thermal treatment. This technique obtained the best graphite performance and a recovery rate of 90% of the electrolyte. When compared to the electrolyte extraction, this technique eliminated the existence of inorganic residues coming from the conducting salt decomposition. When compared to the use of supercritical carbon dioxide in the extraction process, the former led to a critical crystallinity size of graphite particles, not present when subcritical CO_2 was used [74, 96].

Another study, aimed to create a way to exfoliate the electrode materials from metallic foils while recovering the electrolyte [97], used an aqueous solution, AEES, to peel off the electrode materials while it also substituted the organic solvent to reclaim the electrolyte while precipitating $LiPF_6$. After discharging the batteries and separating the anode plates, cathode plates, separators, shells and lugs the separators were transferred into the AEES. The electrode plates were placed on rotary screens and immersed in a separate solution. While the coated materials shed the electrolyte, being water soluble (242-248°C), could be reclaimed via dissolving and later on distilled. The dissolution of the electrolyte present at the surface of the electrodes happened very fast (3min), however, due to the porous structure of the electrodes the dissolution of the electrolyte placed within took longer to happen (10% was still dissolving after 27min).

$LiPF_6$ is very hard to separate from the electrolyte because this compound is soluble in the mixture of ethylene carbonate and PC. In addition, when exposed to moist air it hydrolyses becoming dangerous to the environment and the worker's health. Therefore it was necessary to convert $LiFP_6$ into a stabler compound, Li salt forms from the reaction of the electrolyte with the Na salt used to prevent the hydrolysis of PF_6^-.

The organics of the electrolyte were reclaimed from the solution via distillation, $NaPF_6$ and Li salt remained in the solution as sediment and were later recovered via filtration, achieving a recovery efficiency of 95.6% [74, 97].

Separation of Active Electrode Materials from Current Collectors

After the disassembly of the casing, and the safe extraction of the electrolyte it is important to retrieve the cathode, the current collector foil and the anode. After the electrodes have been separated from the other components they have to be split into their constituents, the main barrier being able to split the interface between the current collector and the active material is the binder.

The binder is a component used to hold the active material together and adherent to the current collector, the most used binder is polyvinylidene fluoride (PVDF) mixed with an additive acetylene black (AB). This material has a good electrochemical stability and adhesive properties, however, it is only soluble in a limited range of solvents making it harder to dispose of in the recycling process [36, 90]. Most of the times the importance of the binder is overlooked, but it has two main failure modes: breaking of the adhesive bond between the active material and the current collector or by breaking the cohesive bond between the active particles [79, 90]. Its removal is very important because the presence of the binder hinders the liberation of the electrode particles from foils. It may create agglomerates of active materials further down and, if the particles are covered by an organic layer, processes like flotation cannot be used because of the same hydrophilicity and hydrophobicity [98]. However, choosing water-soluble additives can result in pure waste streams with green solvents. Binders which are dispersed in water like carboxymethyl cellulose and styrene-butadiene rubber are implemented in the anode material to lower production costs and increase safety and recycling [90].

Separation of active materials from the current collector, binder and a conductive additive can be achieved using several methods. This section of the work will only focus on physical methods. Methods that put too much emphasis on chemistry are out of the scope of the current work.

An experiment carried out developed an automatic system to successfully separate polymer-laminated-aluminium films, separators and electrode sheets (Figure 3.10)[99]. In this study the batteries were discharged using salt water baths. Then the three sealed edges of the cell were cut, the remaining folded polymer-laminated aluminium film needs to be stretched and secured to the house removal module.

The device created consists in a three-grip apparatus, the transportation grip is design to hold and transport the trimmed pouch, the vacuum grip is used to secure the upper and lower side of the aluminium film housing and, finally, the clamping grip is used to guide the components. The vacuum conveyor holds the top layer of the z-folded separator and delivers it through a roller set, this pinch roller set squeezes the top layer of the separator as the vacuum is released. The first guiding post and skiving blade press down the separator, as this one is continuously fed forward. The components of the electrode-separator compound are then separated into three collecting bins for further treatment. Of course, this is still a highly limited disassembling apparatus, if the cells are heavily deformed or if by any chance the electrode and separator sheets are glued together.

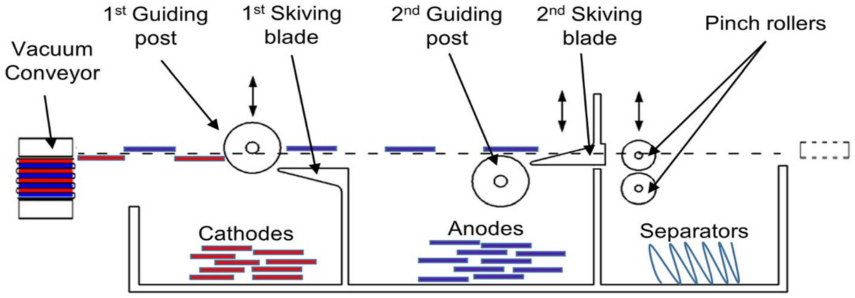


Figure 3.10: Schematic representation of the electrode sorting module. Reproduced from Ref.[99]

Ultrasonic Treatment

Ultrasonic cleaning is an efficient way to liberate the electrode materials from the aluminium/ copper foils because of the ultrasound forces can help breaking the adhesive forces between the electrode particles and the foils [98].

The mechanism used by this technology can be easily explained. Firstly, ultrasound waves promote convective currents in the solvent, the ultrasonic waves produces compression and rarefaction cycles. During rarefaction the pressure in the solvent becomes negative causing little vacuum holes, these holes will then be filled with solvent cavitation bubbles that expand when more gas enters the holes. At the compression stage these bubbles burst causing huge impact forces on the the interface of the cathode and solvent resulting in the peel-off from the foils [100]. It is important to point out that near a solid border the bubble dynamic changes. The disorientation in the spherical symmetry of the bubble creates a speed liquid jet that moves it. The bubble starts by increasing its size in an almost like spherical shape, at its maximum radius the part nearer to the rigid plate flattens and the jet hits the top of the bubble and consequently the rigid plate (Figure 3.11). However, when too much cavitation bubbles are formed on the surface, a barrier is created, resulting in a problem for the transmission of acoustic energy to the other parts of the bath. This phenomena is called decoupling, when the physical vibration at the transducer surface surpasses the ability of the fluid to stay in contact creating a gap between the fluid and the transducer [100, 101].

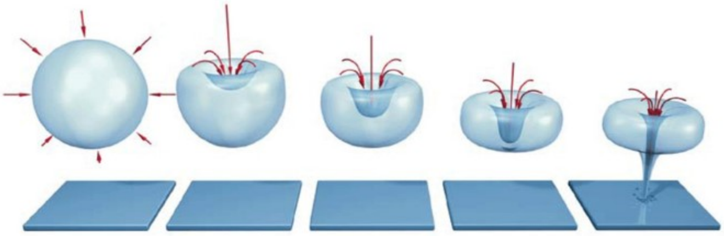


Figure 3.11: Asymmetric implosion of a cavitation bubble against a solid surface. Reproduced from Ref.[102]

Early experiments conducted on this subject [103] concluded that when the baths were performed only using agitation most of the electrode materials still clung to the foils and the same happened when only the ultrasonic waves were used. However, when the agitation and ultrasonic washing were employed simultaneously almost all of the electrode was separated. The explanation being that the ultrasonic waves generate greater pressure to destroy the insoluble substances and scatter them and the rinse effect of the agitation facilitates the process of separating both materials. Temperature was also tested, at 55°C, 92% of the electrode material was removed, but the efficiency (Equation 3.1) was reduced to 76% when carried out 85°. At higher temperatures the force coming from the collapse of the ultrasonic cavitation bubble is decreased, not being able to completely destroy the binding agent.

$$\text{Peel-off Efficiency :} \frac{m_{activesubstance}}{m_{activesubstance} + m_{foil}} x100\% \tag{3.1}$$

Other study used different organic solvents (NMP, DMF, DMAC, DMSO and ethanol) to separate the components (in a solid liquid ratio of 1:10 gmL^{-1}) in an ultrasonic clear powered by 160-400 W in a range of temperatures between 40-80°C during 90min [100]. The batteries studied used PVDF as a binder, and it was found that the most suitable dissolvent was strong polar- NMP- achieving high peel-off efficiencies, whereas weak polar components - ethanol- hardly dissolved the binder. This study also confirmed that the increase in temperature from 70°C to 80°C resulted in little improvement because of the volatization of the NMP. The increment in the ultrasonic power beyond 240 W decreased the peel-off efficiency because it leads to the formation of more invalid bubbles, resulting in the formation of a sound barrier that increases the attenuation of ultrasound, hindering the efficiency of the process. The results obtained pointed to a peel-off efficiency around ± 99%.

In more recent years there's been a growing concern with the environmental impacts and costs of these procedures. NMP solutions irritate the skin in case of exposure, its discharge in the sewers raises some concerns and has an increased cost [36, 101]. With this in mind a study was performed using only distilled water as a solvent while making thermal and ultrasonic treatment steps in series [101]. After discharging the batteries and separating the different components an electric furnace was used for the thermal treatment. This step allowed the removal of the organic fraction increasing the concentration of the remaining product. The optimum temperature for this pre-treatment was set at 550°C, temperatures above this resulted in deformation of the Al foil and precipitation of compounds at the interface [101]. Lower temperatures were not enough to completely dissolve the organic components, this step was performed during 15 minutes. The ultrasonic treatment used water at 25°C at 50 W for a maximum of 5 minutes. Increasing the power over 50 W proved to decrease the efficiency of the process due to the reasons mentioned previously. When the temperature was increased up to 45°C there was a significant improvement (optimum condition), beyond that there was a decrease in performance because it eliminated the creation of bubbles through sonication. Finally, the electrode powder can be separated from the foil pieces via filtration. This experiment was carried out on the cathode, obtaining removal efficiencies around 90%.

Industrial Scale Treatment

Laboratory protocols do not usually involve the requirements necessary to scale up processes of manual disassembly and separation of battery components. For industrial applications, where the amount of processing is enormous and a large volume of battery packs are involved, mechanical treatments, other than manual dismantling are feasible. However, as mentioned before, because of the several architectures of packs most of them are manually disassembled. This will become unfeasible with the expected increase in batteries reaching the recyclers in the coming years [36, 76].

Therefore, it is important to invest in high-level automated equipment to improve the efficiency of these process. In addition, it is important to keep in mind that recycling enterprises receive a mixture of batteries which involve different chemistries, this means that the recycling efficiency rates will be significantly lower when compared to laboraty-scale procedures where the purity is achieved through manual dismantling. To try and minimise the contamination impacts a preliminary classification is highly recommended [76]. Some of the equipment used at established recyclers will be presented forward.

Crushing

In order to decrease the volume of spent batteries and liberate important components from cells and modules, a crushing process is undertaken. Most cell-breaking techniques are continuous and involve crushing rotating devices. Different comminution processes result in different material sizes and shapes influencing downstream separation techniques. The comminution stage is also particularly important in hydrometallurgical processes [76, 78, 81]. In this process, because of the violent friction between components and high-speed the temperatures can increase up to 300°C, this means that the electrolyte can be easily decomposed and volatilize. Cathode and anode materials can also come into contact creating short-circuiting.

Wet crushing performs the shredding process in a brine solution to neutralize acid and other emissions of chemical reactions, this via when compared to dry crushing results in higher safety. However, it introduces more impurities to the finer fractions because of the scouring action of the water flow. A solution would be to perform this step under an inert atmosphere or at cryogenic temperatures to prevent the release and explosion of flammable gas components. Another route would be to perform a deactivation step prior to crushing using the alternatives previously mentioned (discharging in salt solution, removal of the electrolyte, battery freezing) [76]. This step can be done using several techniques, such as, hammer crushing, shear crushing, impact crushing and cutting milling. Shredding is widely used in waste electrical and electronic equipment, it uses high torque, interdigitated blades at low speed of rotation, granulating normally uses higher speeds.

Separation

After the disassembly and comminution processes physical separation are used to produce higher purity material streams. The usual materials obtained from these processes are plastics, separator, pouch material, steel casings, Al and Cu current collector foils and "black mass", the latter typically contains the active materials from the electrodes. The black mass is reclaimed later on for further processing and, since this mechanical procedures are not as good as the processes previously mentioned at lab-scale, when it comes to separating components it is important to perform these purification processes later on.

Sieving, or screening, is normally used to separate and concentrate the metallic fraction of spent batteries. Most of the times, coarser fractions of materials (>1mm) contain plastics, separator, current collector foil. Contrarily, the finer fraction (<1mm) will contain the electrodes active materials. This happens because the battery casing materials and current collectors are usually more ductile and difficult to crush, while the active materials already exist in powder form. Of course there's always risk of losing active material in the coarser fraction that is mixed with the metals from the battery casing and current collectors [36, 76, 81]. A series of sieves, with different size meshes, can be used. A study used five size fractions: <0.5 mm, 0.5-1 mm, 1-2.5 mm, 2.5-6 mm, >6mm [104]. This experiment concluded that this process can be easily scaled-up and entail low energy consumption. It sorted by size four different battery types, and it advises recyclers to pre-sort by cathode type these batteries to improve the segregation efficiency. In addition, separating these materials by size allows recyclers to decide upgrading technologies and recovery hierarchies that maximise mass to be recovered, for example, processes that target specific materials enriched in each size fraction.

Magnetic separation is used to separate magnetic susceptible materials such as Fe and Co using magnetic force, it usually removes non-magnetic impurities like plastics and separators [36, 81].

Density separation uses shaker tables, vibrating screens, flow of air or water to separate the low density materials from mixed cell waste. The air separation method is accomplished using methods such as cross-flow or zigzag sifting. In a zigzag sifter the mixed materials are put into zigzag tube at a certain height, an airstream uplifts materials to the top sifter and to the bottom by gravity, the geometry enables a cross-flow separation - the heavy fraction leaves through the bottom of the sifter and the lightweight fraction through the top[36, 81] .

Froth flotation relies on the difference of hydrophobicity between two materials, fine bubbles are introduced to a vessel with the materials to be separated. The hydrophobic materials are then collected by the bubbles and transported to the surface and remain in the stable froth; the desired hydrophobic fraction of materials is recovered. When the desired part stays in the slurry and the undesired fraction floats it is called reverse flotation. Frothing agents are used to stabilise the foam and the most common are pine oil, alcohols and cyclical carbonates. A common problem with this method happens when the components are still covered by hydrophobic binders, hindering the separation process. To maximise the separation using this method, surface modification through binder decomposition and surface treatments are important mechanisms [36, 81].

Finally, electrostatic separation can also be used to isolate polymer separators from current collector foils. Eddy current separators are used to differentiate between non-ferrous metals and non-metals [81].

3.5.4 Leaching

Hydrometallurgical processes are then often performed on pretreated battery scraps, this type of recovery is very promising on large-scale due to its low energy requirements. Upon leaching, valuable materials are recovered either using extraction and purification or direct resynthesis of material. Leaching aims to reduce impurities and organic residues and recover different product metals as pure as possible [36, 80]. Leaching can be performed using several means, either acidic or using microorganism to help the process.

Acid Leaching

Acid Leaching is used to leach out valuable metals present in the cathode materials, taking advantage of the chemical properties of metals in aqueous solutions to isolate and recover marketable products. This method usually uses inorganic acids (H_2SO_4, HNO_3, HCl), or various organic acids (succinic, ascorbic) as leaching agents often supported by reducing agents (H_2O_2, $NaHSO_3$, Na_2SO_3), in order to oxidize the metals to higher oxidation states [105, 106]. Numerous studies have tried to determine a set of conditions to maximise the rates of leaching, these include: acid concentration, time, temperature of solution, the solid-to-liquid ratio as well as the addition of a reducing agent [77].

A range of other possible leaching acids and reducing agents have been investigated. However, studies have shown that using inorganic acids, besides the high price, also shows some safety hazardous (release of toxic gases eg. Cl_2, NO_x, SO_3) resulting in serious environmental and human-health problems if special equipment installed to treat these gases is not available. Therefore, leaching solution may also be treated with an organic solvent to perform a solvent extraction.

Bio-Leaching

Bioleaching is a technique expected to replace traditional acid leaching with its environmental performance and low-cost. It uses microorganisms to digest metal oxides from the cathode selectively and to reduce these oxides to produce metal nanoparticles. The number of studies that have been performed thus far, however, are relatively small and there is plenty of opportunity for further investigation. Cobalt and nickel, in particular, are difficult to separate and require additional solvent extraction steps.

In bacterial bioleaching, the autotrophic cells involving iron(II), oxidizing bacteria and sulfur compound oxidation are often used to generate a number of metabolites like ferric ions and acid sulfuric. This method when studied for the first time, allowed to regain some critical metals from cathode materials (eg.$LiFePO_4$, $LiMn_22O_4$). According to the experiment, 98% of Li from $LiFePO_4$, 96% of Mn and 95% of Li from $LiMnO_2$ [107]. Fungal Leaching, when compared to Bacterial Leaching, has a higher ability to tolerate toxic materials. To date, a variety of fungi (eg. *Penicillium chrysogenum, Aspergillus niger*) have been employed to excrete metabolites as organic acids that play a role in dissolving metals from a variety of waste materials and ores. Studies performed with Aspergillus niger indicated that 38% of Ni, 45% of Co, 65% of Al, 70% of Mn, 95% of Li and 100% of Cu were recovered from a spent LIB [108].

This is an emerging technology for LIB recycling and metal reclamation and is potentially complementary to the hydrometallurgical and pyrometallurgical processes currently used for metal extraction.

3.5.5 Established Industrial Recycling Processes

This section reviews established industrial processes for the recovery and recycling of LIB components at companies like: Umicore, Recupyl, Retriev, Akkuser and OnTo Technology.

Umicore

Umicore is an enterprise placed in Belgium that specializes in materials technology and recycling. Its process is focused on the recovery of Co and Ni placed in lithium-ion and metal hydride batteries, using both pyrometallurgical and hydrometallurgical processes, with an annual processing capacity of 7,000 tons [109].

In this process the batteries are first dismantled to expose the cells. The cells are then placed in a shaft furnace alongside metallurgical coke, slag formers and some metal oxides. The shaft furnace is composed by three different sections: Pre-Heating Zone ($<300°C$), in this low temperature section the evaporation of the electrolyte is achieved; Plastic Pyrolyzing Zone ($< 700°C$), in this medium temperature section the pyrolysis of the plastics take place; Metal Smelting/ Reducing Zone (1200-1450°C), in this section the smelting and reduction take place. Oxygen-enriched air is supplied from the bottom of the furnace. The air is controlled so that in the melting zone the carbon and aluminium case are oxidised, and that cobalt and nickel are reduced. The offgas in the furnace is heated up to 1150°C and conveyed to a post-combustion chamber where halogens are captured using calcium or sodium-based products. After that, the offgas is quickly cooled down to avoid the recombination of organic compounds with halogen.

The resulting alloy from the shaft has Cu, Co, Ni and traces of Fe. On the other hand, the slag is composed of Al, Si, Ca, Fe, Mn, Li and rare earth elements (REEs). The metallic alloy is leached using acids to remove copper, zinc and manganese. Hydrochloric acid is used to separate the nickel from cobalt with high purity. This last two components may be used to reproduce a cathode precursor [109, 110]. This is a relatively simple process that has special attention to exhaust gases, with the big advantage of not requiring any type of sorting or mechanical treatment. The bottleneck of this process is its economical feasibility, which is highly dependant of the prices of cobalt and nickel. It only becomes economical if these two elements account for 30% of the feed. It also has the problem of not recovering other valuable metals like lithium because of the costs and energy demands of treating the slag [110].

Recupyl

Recupyl is a french recycling company which developed a low-temperature LIB recycling technology for primary and secondary LIBs, making use of mechanical and hydrometallurgical processes with a processing capacity of 110 t/year [80, 109, 110].

This process starts by sorting batteries and then crushing them. Crushing is performed in two steps: a rotary mill bellow 11rpm performs the first crushing, followed by the second crushing with an impact mill at 90rpm or less, to bring the particles to a size lower than 3mm. The crushing step is performed in a controlled atmosphere composed of CO_2 and argon (10-35 vol%). The presence of CO_2 in the atmosphere initiates the passivation of metallic lithium at the electrode surface, forming Li_2CO_3 [80, 109]. The mill discharge is screened. The oversize fraction is processed using magnetic separation to isolate the ferrous metals. The non-magnetic fraction is further processed using a shaking table, the high-density materials is composed of Cu and Al, while the low-density fraction contains papers and plastics. The fraction bellow 3mm are continuously sieved until reaching a 500μm opening size, this is expected to bring the presence of Cu below 0.3%.

The separated black mass is leached in stirred water under an atmosphere low in oxygen. The soluble lithium becomes dissolved in the water and the remaining solid is filtered. The dissolved fraction is precipitated as Li_2CO_3 or Li_3PO_4, depending if CO_2 or phosphoric acid is added [110]. The filtered solid is leached at 80°C with sulfuric acid to recover the cobalt. It is then cooled to 60°C and if there is any undissolved carbon the solution is filtered. After this, the solution undergoes a copper cementation and iron precipitation, the cobalt is then recovered by electrolysis, in this process manganese is also recovered as a precipitate. The remaining solution is sent to a lithium salt precipitation process [109, 110].

Retriev

Retriev, previously known as Toxco, is an American company that uses a combination of mechanical and hydrometallurgical processes to recover metals from spent LIBs, with a processing capability of 4,500 t/year [80, 109].

In Retriev's process the lithium batteries are cryogenically cooled using liquid nitrogen to deactivate them. After this, the batteries are crushed in a shredder or hammer mill and screened. The larger fractions containing mostly mixed plastics, steel cases, copper and aluminium foils are separated from the finer fraction [109, 110]. The small-size fraction, containing active electrode materials, is immersed in a solution of lithium hydroxide (LiOH) used to dissolve lithium salts. The undissolved metal oxides and graphite are separated from the solution via a carbon filter press. The filtrate is sent to an evaporator and storage, where the lithium salts are precipitated until their production exceeds the solubility. The Li-salts are then pumped and filtered [110]. LiOH, can be directly dewatered or converted to Li_2CO_3.

The downside of this process, even though it does not involve high-temperatures, is that it uses a cryogenic treatment which is in itself very energy intensive and hazardous [110].

Akkuser

Akkuser is a Finnish company which process involves only mechanical processing techniques, with a capacity of 4,000 t/year [109].

This process starts by pre-sorting the batteries by type. After this step the LIBs are processed by two cutting mills, the first mill operates at 40-50°C at 100-400rpm, achieving a particle size between 1.25-2.5cm. The occurring gases are extracted and filtered through a cyclonic system. At this stage it is possible to separate the plastics. The resultant shredded material is transferred to a secondary mill operating at 1000-1200rpm, this mill reduces the materials to particles $<$6mm. This mix is magnetically separated. The non-ferrous fraction is finally refined hydrometallurgically to recover Co and Cu.

OnTo Technology

OnTo Technology is an American company which specialises in the direct recycling and cathode healing processes of spent batteries.

The process starts by discharging the packs using a sodium bicarbonate brine solution. The electrolyte is extracted using a liquid carbon dioxide system that operates for 48h at 25°C and 900 psi. There's a disassembly step to decrease the contamination of iron and copper. The cells are then sent to a shear shredder, after this, the shredded particles are placed in a blender-vessel with an aqueous wash solution that deliminates the active material from the current collectors [111].

The electrode materials are separated from the plastic, metal casings and foils via froth flotation and filtering. The harvested material, consisting in a mixture cathode, carbon black, binder and graphite, undergoes a hydrothermal treatment where the binder is removed followed by another froth flotation step where the graphite is separated from the metal oxide [111].

In Table D.1 in Appendix D a summary of all the information provided can be seen.

3.5.6 Difficulties in Recycling

Ideally recycling should recover materials to their original condition in a closed-loop recycling cycle. However, most of the times recyclers down cycle, meaning that their output is sold to other industries. This solution is better than sending the spent batteries to landfills, but it does not relieve the pressure on the supply chain [75].

Another major problem is the competitive collection and recycling costs. To promote recycling, the profits coming from this activity should cover collection, transportation, storing and processing costs while being competitive with the cost of raw materials. More often than not, collecting and processing costs are higher than mining the raw materials. Moreover, recyclers have to operate in a volatile environment where virgin material prices are constantly changing making it less attractive [75]. As it can be seen, challenges associated with the logistics of recycling typically occur before the recycling processes themselves. Potential safety hazards associated to stored spent batteries could be reduced if pre-tretaments were performed in decentralised facilities. However, the lack of standardisation in spent battery sorting and dismantling hampers the whole process.

The difficulties start with the variety of EVs placed in the market, this means different pack configurations and different tools to remove these packs are required. Another problem with different vehicles is that not all of them will reach their EoL in the same conditions, meaning that it is not just about dismantling them like they were assembled. The workers at the recycling facilities will have to take into account the wear suffered from these vehicles and the damaged it may have caused to the batteries.

As the battery packs are disassembled other difficulties arise, the removal of electrical wirings, the high voltages until the modules are separated and the potential of other safety hazards puts a risk on workers, hence the need for specialised staff. At the module level, sealants an thermal glues difficult the disassemble, the cells may also be encased, soldered together and the SoH may be unknown. At the cell level the problems are already known: the clean separation of components, the fact that the chemistries are not stated, different designs, etc.

A solution would be to modify existing battery designs for recycling. Ecodesign is a method that encourages manufacturers to assemble a product that minimises their impact on the environment through their life cycle. In the EU, the Ecodesign Directive was adopted in 2005 (2005/32/EC) for energy-using products but it was later extended (2009/125/EC) to cover energy-related products. This Directive acts alongside other laws, allowing the EC to set minimum performance standards, pushing for innovation[112, 113]. The best start to optimise arrangements for end-of-life products is at the product design stage. If dismantling and component separation are foreseen at the design stage, components that make a battery harder to dismantle can be substituted [114].

At pack level, instead of adopting welded locking mechanisms, removable screw-off caps or perforated groovings would be better for disassembly. The change in materials used, from metals to plastics, ease the recycling of less valuable materials. The main problem with recovering metals is the purity of the input fraction and, consequently, the purity achieved in the final composition. A merge of materials implies loss of value and harder separation. Improved designs at module and pack level can improve the logistics of collection and dismantling, however, it is important to give some special attention to the cell and electrode designs where the critical materials are placed [114, 115].

At cell level it is important to perform some changes without loosing performance. Standardizing battery technologies is almost impossible as variety in designs and materials are thought to satisfy specific energy and power demands of a certain EV model, not to mention, that these differences are the basis of technological advantages and intellectual property rights [75]. New binder compositions that allow for a quick exfoliation and cost-effective separation of materials while avoiding fluorine-containing materials, single-crystal cathode materials which allow an easier direct regeneration are some of the material design strategies that can be adopted [115].

Chapter 4

Experimental Methodology

To better understand the work done, and for it to be as detailed as possible, the experimental methodology of this thesis is divided into two main parts: industrial and laboratory treatments (Figure 4.1).

The first part of this methodology follows the work done alongside two enterprises mentioned before, *Ambigroup* and *Palmiresíduos*. In their facilities, battery packs were assessed, opened, discharged and dismantled. The second part follows the work developed at both *Técnico* and *LNEG's* laboratories mainly, at the cell level, where battery cells were also discharged, dismantled and chemically and physically characterised using several different techniques.

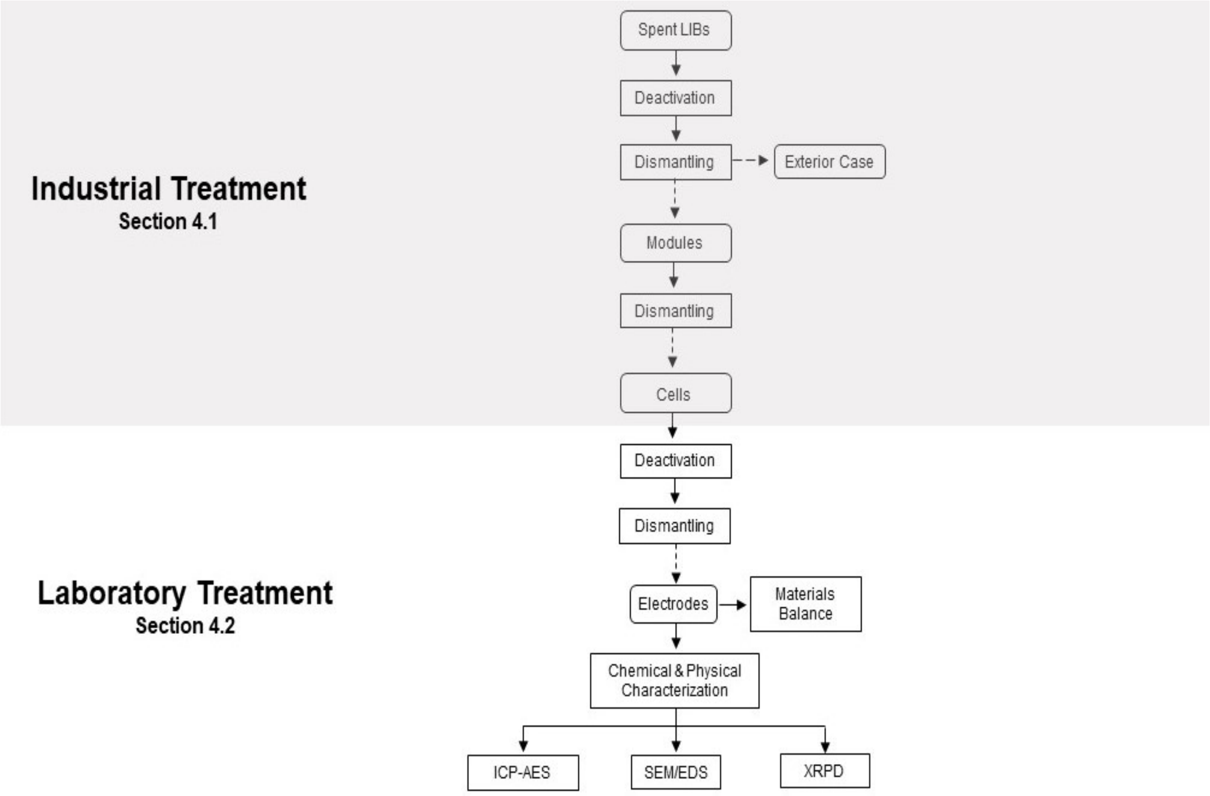


Figure 4.1: Flowchart of the experimental methodology.

For this thesis *Valorcar, SA* provided nine spent LIBs from several different electrical vehicles as a case study and *Addvolt* provided one spent battery pack as well, which was delivered at Técnico and all its dismantle procedures were performed there as well. As pack manufacturers cannot be disclosed, the different packs were attributed a digit to better follow their course throughout the work developed (Table 4.1).

Table 4.1: Summarized information of the LIBs used.

Enterprises	Battery Pack Nr.
Palmiresíduos	1, 2, 3, 4, 5, 9
Ambigroup	6, 7, 8
Técnico Laboratory	10

4.1 Industrial Treatment

When batteries are sent for recycling, they undergo three main processes: deactivation, opening and separation. With this in mind, at both enterprises, the work started by opening the containers where packs were transported according to all the rules mentioned in Section 3.3. After opening the containers, the batteries were tested using a multimeter to see if any electrical current was running through their outer case. When deemed safe, they were transported to the workstation using forklifts. Thereafter, the top exterior lid and all the external screws were retrieved and the pack was tested once more to verify its voltage (V) using a multimeter. In case the battery pack was considered charged (roughly above 15V, depending on the number of modules), the pack or modules were submitted to a deactivation process. In case they were discharged (usually below 15V) the following procedure was to dismantle it.

4.1.1 LIBs Deactivation

As mentioned before, deactivation can be achieved using several methods (ohmic discharge, brine/caustic solutions, etc) and it is made to ensure that the risk of explosion is reduced [77, 79].

The batteries processed at Palmiresíduos and Ambigroup were deactivated using either ohmic discharge (electric heaters as resistors, creating a simple circuit represented in Figure 4.2a) or brine solutions (200L tanks filled with water with a concentration of 0.3%wt of NaCl, Figure 4.2b). The criteria used to chose which path the pack would follow was rather simple (Figure 4.3): if the pack's terminals were easy to access, the pack was discharged. If not, the modules were individually separated and taken from the pack's external casing and placed inside the brine solution.

(a) Electrical circuit used for deactivation.

(b) Brine solution used for deactivation at industrial scale.

Figure 4.2: Deactivation methods used at the enterprises.

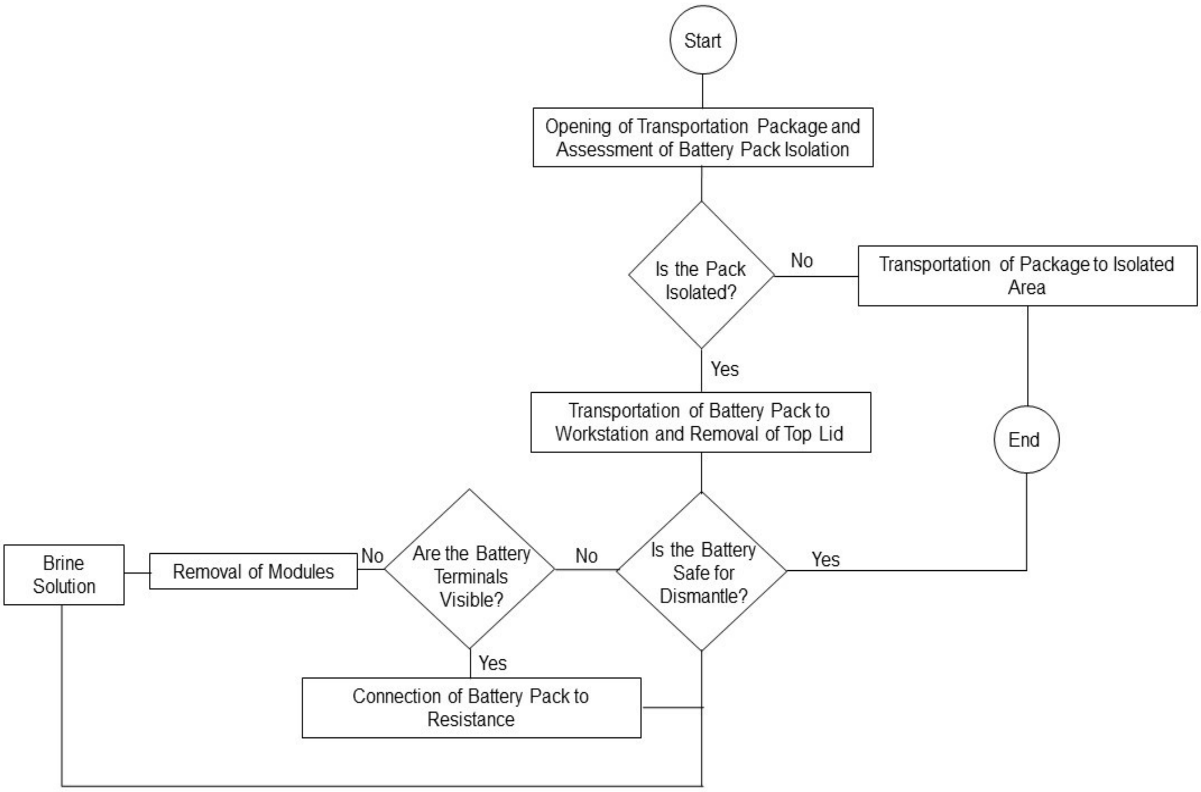


Figure 4.3: Deactivation procedure followed.

To ensure that the voltage was lowering, every hour, the batteries were measured using a multimeter, but with no registry of the pace at which it occurred.

4.1.2 LIBs Disassembly

When the battery packs were considered discharged (below 15V), or the modules had a voltage below 6V, their disassembly was set into motion. The purpose of disassembling battery packs into modules and modules into cells is to guarantee a clear separation of components, to easily target valuable materials for recovery [81].

This part of the work was solemnly performed using isolated hand tools with the help of *Ambigroup* and *Palmiresíduos* collaborators. This step starts by opening any covers that may still exist (some may have to be open beforehand to ensure access to the battery's terminals for discharging), followed by the retrieve of any electrical connectors. Then, all of the mechanical connections (screws, bolts, etc) are retrieved separating the modules from the battery's external cases. Finally, the modules are dismantled exposing the battery cells. This procedure is depicted in Figure 4.4.

4.1.3 Balance of Materials

As the batteries are being dismantled a variety of components and materials can be obtained. The aim of this step is to determine the average weight of different components to contribute to a more assertive report on the possible profit for recyclers.

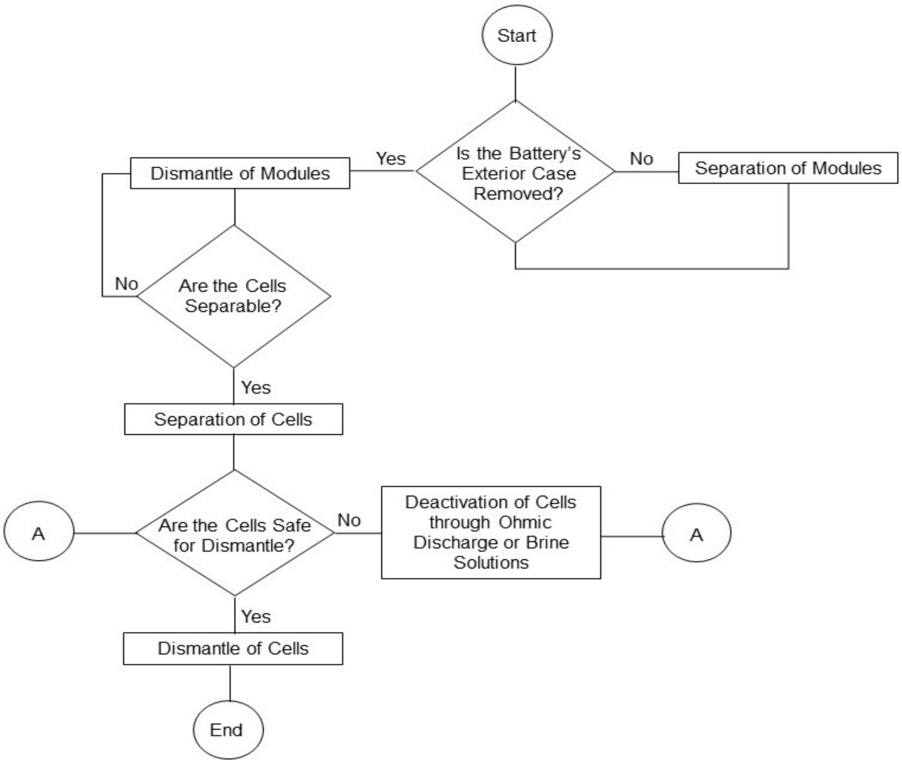


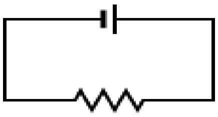
Figure 4.4: Dismantling procedure.

4.2 Laboratory Treatment

When the battery modules were dismantled and the cells were all separated, they were taken to the laboratory. Just like at the enterprises, the work carried out started by deactivating all cells, dismantling them and then all components were weighted and the black mass was analysed.

4.2.1 LIBs Deactivation

At the laboratory, the techniques used were similar but on a smaller scale (Figure 4.5), using lamps as resistors and caustic solutions. During deactivation the voltage was monitored to guarantee that the values would tend to zero, using a voltmeter.



(a) Representation of used circuit at the lab for deactivation.

(b) caustic solution used for deactivation at lab scale.

Figure 4.5: Deactivation methods used at the laboratory.

It is important to point out that caustic solutions with different concentrations were tested. In order to identify every cell clearly, a code number with two digits was attributed to every pack. Onwards, the first digits (which identify the packs), will be followed by a second set of digits which state the discharging method used:

- 1 means deactivation with caustic solution at a concentration of 20%wt NaOH where the cells' voltage was measured hourly;
- 2 means deactivation with caustic solution at a concentration of 20%wt NaOH but the cells's voltage was only measured after 24h and 48h;
- 3 means deactivation with caustic solution at a concentration of 10%wt NaOH where the cells' voltage was measured hourly;
- 4 means deactivation with caustic solution at a concentration of 15%wt NaOH where the cells' voltage was measured hourly;
- 5 means that the cell was deactivated using ohmic resistance;
- 6 means deactivation with caustic solution at a concentration of 0.3%wt NaCl;

In the event of repeated conditions a third digit will be used just to ensure that there are no mix ups between the battery cells.

4.2.2 LIBs Disassembly

After the cells are considered deactivated (below 1V), the next step (similarly to packs and modules) is to dismantle them. If it is a pouch cell, it can be simply cut, exposing the electrodes (Figure 4.6a). Cylindrical cells, on the other hand, have to be sawn to expose the electrodes, in a rather easy process due to its soft exterior (Figure 4.6b). Prismatic cells are the hardest to open due to their hard external case, so that, at the laboratory rotating discs had to be used to access their electrodes (Figure 4.6c).

(a) Dismantle of pouch cell. (b) Dismantle of cylindrical cell. (c) Dismantle of prismatic cell.

Figure 4.6: Dismantling process of three shapes of cells.

After the cells are opened, the components are dried in a ventilated furnace to ensure all electrolyte and residues from the baths (if applicable) are eliminated.

4.2.3 Characterisation of Cells

The following section describes in thorough detail the characterisation methods used on the electrode materials to assert the chemistry of the batteries and perform a morphological characterisation.

Elemental Composition by ICP-AES

In the case of atomic emission spectroscopy, the spectra emitted is used to determine a qualitative or quantitative elemental composition of the sample [116]. The qualitative information is given by emission at certain wavelengths characteristic of the elements present and of interest. On the other hand, the quantitative analysis is given by introducing a standard solution of the element with known concentration to the ICP. After that, the samples are analysed [117]. The intensities obtained are then plotted on the calibration curve and the concentration of the sample is determined accordingly.

For this technique, the samples are used in a liquid state. With that said, to analyse the electrode samples (solid) they have to go through a process called acid digestion to become liquid samples. For this purpose an *Aqua Regia* solution was used. It consists of hydrochloric acid (HCl) and nitric acid (HNO_3) in a proportion of 3:1, respectively. The samples are placed inside the solution and left to react for an hour. After that, the mixture is filtered and the obtained solution is sent to be analysed.

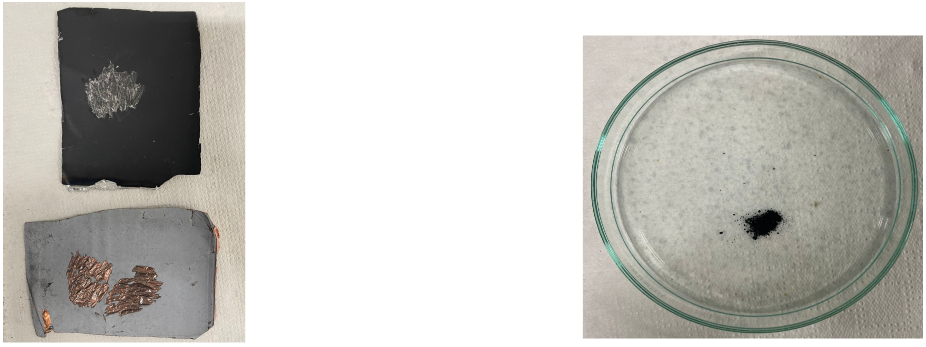
After a complete solubilisation of the electrodes, the weight percentage (%w/w) of the elements was calculated according to the Equation 4.1.

$$(\%w/w) = \frac{Concentration[mg/L] * InitialVolume * DilutionFactor}{Weight[mg]} \tag{4.1}$$

X-Ray Powder Diffraction (XRPD)

To analyse the electrode samples, the anode and cathode were separately scrubbed until the black matter detached from the foils. The black matter was crushed using a mortar until it became powder (Figure 4.7), it was placed in a sample holder and scanned between 5°-80°in a 2Θ range, using a CuKα radiation with generating step time of 75s with generating settings of 35mA and 40kV.

The samples belong to two different battery pack models, 2 and 3, and the samples were submitted to different deactivation conditions. Samples 2.1 and 3.2 were placed inside 20%wt NaOH bath and samples 2.5 and 3.5 were electrically discharged. In this case, the numbers are also followed by an A or C letter to distinguish between cathode and anode samples.



(a) Scrubbed electrode foils: anode [bottom], cathode [top].

(b) Powdered electrode sample.

Figure 4.7: XRPD and SEM/EDS sample preparation.

Scanning Electron Microscopy/ Energy Dispersive Energy (SEM/EDS)

The samples used for the XRPD analysis were also used in this analysis, the main difference being that samples are covered by sputtering with gold (Au) and palladium (Pd) to ensure their electrical conductance.

Chapter 5

Results & Discussion

5.1 Industrial Treatment

As explained in Chapter 4, 10 different battery packs were provided by *Valorcar, SA* and *Addvolt* for this work. 9 of which were first treated at both *Ambigroup* and *Palmiresíduos* facilities.

This work starts by assessing the conditions in which the battery packs arrive. If the transportation package is intact, following all rules, it is opened to reveal the battery itself. After that, the exterior lid is accessed to ensure its electrical isolation and, if considered safe, the battery is then transported to the workstation and its voltage is measured.

The first step is to deactivate the battery, however, since no measurements were taken at the facilities regarding the rate at which they discharged, this step will be ignored for now. The conditions used to deactivate the packs at the enterprises were explained previously in sub-chapter 4.1.1.

5.1.1 LIBs Disassembly

Disassembling a battery pack is a very labour intensive step. For this thesis, this stage of the work was performed both at the *Ambigroup* and *Palmiresíduos* facilities with the help of their collaborators. The difficulties of this process start with the transportation of the battery to the work station, with the need to use forklifts and hence a worker specialised in it (Figure 5.1). After that, the choice of tools has to be planned to remove the external case.

Figure 5.1: Placing battery pack onto workstation using forklift.

The second stage of this process is to remove every screw and bolts which differ in all packs, hence the need to use different hand tools. It is not a difficult task, however, it can take up to 10min to remove all the visible screws and attachments. This task is hampered when manufacturers use glue to avoid the screws of becoming loose, hence making it harder to remove them.

After removing all of the screws and bolts, the next stage is to remove the modules from the pack. This is supposedly an easy step, however, sometimes manufacturers use a sort of thermal glue that helps the heat escape through the structure but attaches the modules to the external lid (Figure 5.2). In this case, only the use of force will be able to separate parts. Another difficulty found was when parts were welded together, this made them impossible to separate using only force, and more tools had to be used like rotating discs for cutting.

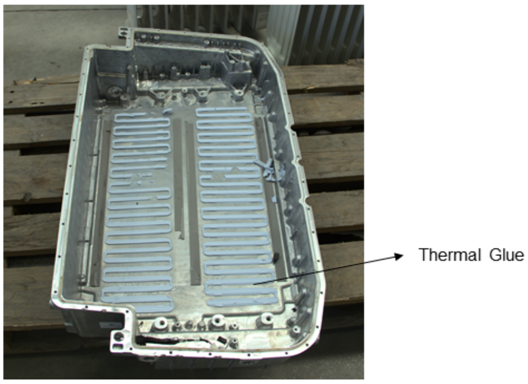


Figure 5.2: Thermal glue on exterior lid of battery pack.

When the modules are separated they have to be dismantled which requires more and smaller tools to remove all screws. To avoid trepidation of the cells, more often than not, they are encased in plastic frames that have to be cut or broken by applying force, taking up to 20min to dismantle all parts (Figure 5.3).

(a) Opening cell without cutting.

(b) Sawing cell.

Figure 5.3: Opening battery cells.

Even though the steps are more or less the same to every battery presented, in this thesis, the lack of a standardised design requires that, upon opening a pack, a thorough analysis has to be made in order to define a safe and more efficient disassembly sequence. Otherwise, a lot of time will be lost in trying to discover which part should have come off first, etc. On average, between the placing of the battery at the workstation and the separation of the last piece it takes four workers around 40-50 minutes to perform this operation.

Another important aspect that should be mentioned is the fact that most batteries opened in this work were all relatively new (with less than five years). This is important because if the batteries reaching the recyclers happen to be older or coming from crashed vehicles they may be damaged, therefore, the working conditions may be worst and harder to intervene.

At the end of this step all cells were retrieved, allowing the elaboration of Table 5.1. Here the number of modules, number of cells per module, the type of cell and its weight are presented. It becomes evident that prismatic cells, with their metal external case have the highest weight, but require less cells as they are characterised by higher energy densities. As expected, cylindrical cells have the lowest weights but exist in higher number as they have lower energy density. Pouch cells are the most common, and since they need a plastic frame to support and connect them, they are usually assembled in bigger modules. They are the easiest to open and have an average weight when compared with the other two cell shapes. This happens because even though they use metals in the external cases, these are much thinner and lower in density.

Table 5.1: Summarized information of the LIB modules used.

Battery Pack	Enterprises	Cell Type	Cell Weight (Kg)	Nr of Cells/ Module	Nr of Modules
1	Palmiresíduos	Prismatic	1.702	8	1
2	Palmiresíduos	Prismatic	0.722	13	8
3	Palmiresíduos	Pouch	0.530	9	1
4	Palmiresíduos	Prismatic	0.563	8	1
5	Palmiresíduos	Pouch	0.698	50	2
6	Ambigroup	Pouch	0.745	48	4
7	Ambigroup	Pouch	1.269	30	3
8	Ambigroup	Pouch	0.965	24	6
9	Palmiresíduos	Pouch	0.745	48	4
10	Técnico Laboratory	Cylindrical	0.044	196	1

5.1.2 Balance of Components and Materials

Batteries are composed by different components and materials, entailing different weights and monetary value. Based on the separation of components performed at the companies, Table 5.2 summarises the main components and materials obtained from the dismantling processes.

This table is divided in two main sections, the external case of the battery where the weights of all the external screws, lids and BMS are presented, followed by the main components and materials that compose the module, including: plastics, metals, electric and refrigeration cables, some more screws and printed circuit boards (PCB), which are really important due to their economic value.

Most of the periphery of the battery system is composed by the biggest and heaviest components and entail a considerable value. All lids are composed by metals and this material is the easiest to recycle and is well quoted on the scrap market: aluminium and steel are priced around 1050\$/t and 155\$/ton [118], respectively. Modules have a lower monetary interest, the fraction of plastics is much higher, meaning lesser weight and less valuable components that can be retrieved. Polymers like polyvinyl chloride (PVC) and high-density polyethylene (HDPE) are sold, as new granules, at prices around 835\$/t and 815\$/t [119], respectively. However, one must remember that these materials at the recyclers have to be shredded, made into pellets and will be sold at lower values.

For recyclers some of the most interesting components are the BMS, PCB and the electric cables. These parts entail several valuable and critical metals: PCBs are composed by gold (Au), palladium (Pd), silver (Ag), etc [120]. The electric cables have a high content in Cu and can be easily reused [121] and the BMS can be reprogrammed and placed on another battery[122] or sold.

Table 5.2: Balance of obtained materials and components of modules.

		1 wt (kg)	2 wt (kg)	3 wt (kg)	4 wt (kg)	5 wt (kg)
Ext. Case	Lids	-	9.909	1.106	-	17.000
	BMS	-	0.921	-	-	1.145
	Screws	-	1.194	-	-	NA
Module	Plastics	0.543	2.160	2.740	NA	1.277
	Metals	0.904	43.096	0.070	1.839	4.600
	Screws	0.232	3.160	-	0.129	NA
	PCB	-	0.136	0.110	-	NA
	Cables	-	5.518	NA	0.147	0.391

NA: Not Analysed

Table 5.2: Balance of obtained materials and components of modules (continued).

		6 wt (kg)	7 wt (kg)	8 wt (kg)	9 wt (kg)	10 wt (kg)
Ext. Case	Lids	4.120	22.470	42.850	4.000	3.936
	BMS	NA	NA	0.980	NA	NA
	Screws	0.220	1.885	0.690	0.144	0.437
Module	Plastics	0.155	1.770	1.280	0.155	0.195
	Metals	4.365	6.035	2.840	3.230	0.265
	Screws	0.645	0.255	1.950	0.370	-
	PCB	NA	NA	NA	NA	0.061
	Cables	1.122	0.170	2.400	1.122	0.422

NA: Not Analysed

5.2 Laboratory Treatment

5.2.1 Cells Deactivation

In order to start operating the cells, they have to be deactivated until they reach a safe open circuit voltage (below 1V) to be handled.

At the lab, cells were both deactivated using ohmic discharge and caustic solutions. In Table 5.3 the discharging values can be seen when a lamp was used to discharge some of the cells coming from packs number 2 and 5.

Other cells coming from different batteries were discharged using caustic solutions. Conductivity depends on the ionic nature of the compounds dissolved, and its corresponding capacity to dissociate into charged ions to carry the charge [123]. The concentration of the bath was chosen accordingly to the conductivity of the salt in solution (Annex A, Figure A.1). If a solution has higher conductivity the lower

Table 5.3: Measured operating voltage of batteries during discharging process using a lamp.

Batteries	**0h**	**1h**	**3h**	**7h**	**18h**	**22h**
2.5	2.835 V	2.726 V	-	-	0.820 V	0.738 V
3.5	3.223 V	-	1.982 V	0.84 V	-	-

its resistance (Equation 5.1). Consequently, the faster the ions move, the quicker the discharge of the cell is until the equilibrium of components is reached [123].

$$R(\Omega) = \frac{1}{Conductivity(S.m^{-1})} * k(m^{-1}) \tag{5.1}$$

K stands for the cell constant, which is equal to the distance in metres (m) between the probe's electrodes divided by the surface area of the electrodes in m^2.

Most studies use NaCl saline solutions for discharging the batteries. However, it produces hydrogen and chlorine gas when electrolyzed, and chlorine ions accelerate the aqueous corrosion of steel[123]. With that in mind, solutions between a range of 10%-20%wt of NaOH and distilled water were tested. When the batteries are placed inside the NaOH solution, the cell's negative terminal evolve hydrogen gas according to Equation 5.2:

$$H_2O + 2e^- \rightleftharpoons \frac{1}{2}H_2 + OH^- \tag{5.2}$$

To complete the circuit generated, normally, the water reduction positive cell terminal (anode) forms oxygen gas and electrons, according to Equation 5.3:

$$4OH^-(aq) \leftrightharpoons O_2 + 2H_2O + 4e^- \tag{5.3}$$

The fact that oxygen is formed hinders the creation of an inert environment. However, there's only a hazardous situation if the presence of hydrogen surpasses 4%vol in the gaseous mix [123].

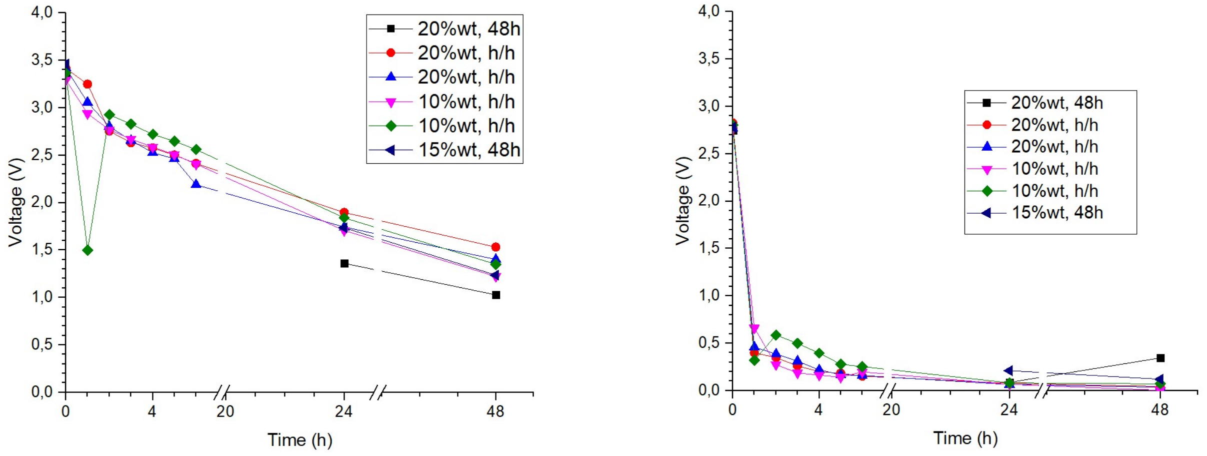
Table 5.4 was assembled to confirm the hypothesis given by Equation 5.1. Here, an average value is given regarding the measured distance between the electrodes and their surface area. When it comes to the resistance of the bath, it is important to notice that the conductivity values are given for solutions at 25°C and the baths were actually at 27°C. This is done so that a correlation between the shape of the cells and their discharging rate can be done.

Table 5.4: Description of the bath conditions used to discharge different battery cells.

Bath 1 (20%wt NaOH)	**Batteries**	**Conductivity (S/m)**	**Path Length (m)**	**Surface Area (m^2)**	**k (m^{-1})**	**Resistance (Ω)**
m_{H2O}= 2511.40g	1.1	38.0	0.09	4.9x10^{-4}	183	4.8
m_{T1}= 502.28g	2.1	38.0	0.09	12x10^{-4}	75	2.0
m_{R1}= 502.43g	3.1	38.0	0.085	6.75x10^{-4}	126	3.3
T= 27°C	4.1	38.0	0.09	4.9x10^{-4}	183	4.8
Bath 2 (20%wt NaOH)	**Batteries**	**Conductivity (S/m)**	**Path Length (m)**	**Surface Area (m^2)**	**k (m^{-1})**	**Resistance (Ω)**
m_{H2O}= 5139.90g	1.2.1	38.0	0.09	4.9x10^{-4}	183	4.8
	1.2.2	38.0	0.09	4.9x10^{-4}	183	4.8
m_{T2}= 1027.98g	2.2.1	38.0	0.09	12x10^{-4}	75	2.0
	2.2.2	38.0	0.09	12x10^{-4}	75	2.0
m_{R2}= 1027.30g	3.2.1	38.0	0.085	6.75x10^{-4}	126	3.3
	3.2.2	38.0	0.085	6.75x10^{-4}	126	3.3
T= 27°C	4.2	38.0	0.09	4.9x10^{-4}	183	4.8
Bath 3 (10%wt NaOH)	**Batteries**	**Conductivity (S/m)**	**Path Length (m)**	**Surface Area (m^2)**	**k (m^{-1})**	**Resistance (Ω)**
m_{H2O}= 4952.20g	1.3.1	35.5	0.09	4.9x10^{-4}	183	5.2
	1.3.2	35.5	0.09	4.9x10^{-4}	183	5.2
m_{T3}= 495.22g	2.3.1	35.5	0.09	12x10^{-4}	75	2.1
	2.3.2	35.5	0.09	12x10^{-4}	75	2.1
m_{R3}= 495.00g	3.3.1	35.5	0.085	6.75x10^{-4}	126	3.5
	3.3.2	35.5	0.085	6.75x10^{-4}	126	3.5
T= 27°C	4.3	35.5	0.09	4.9x10^{-4}	183	5.2
Bath 4 (15%wt NaOH)	**Batteries**	**Conductivity (S/m)**	**Path Length (m)**	**Surface Area (m^2)**	**k (m^{-1})**	**Resistance (Ω)**
m_{H2O}= 1512.80g	1.4	41.0	0.09	4.9x10^{-4}	183	4.5
m_{T4}= 226.92	2.4	41.0	0.09	12x10^{-4}	75	1.8
m_{R4}= 226.40g	3.4	41.0	0.085	6.75x10^{-4}	126	3.1
T= 27°C						

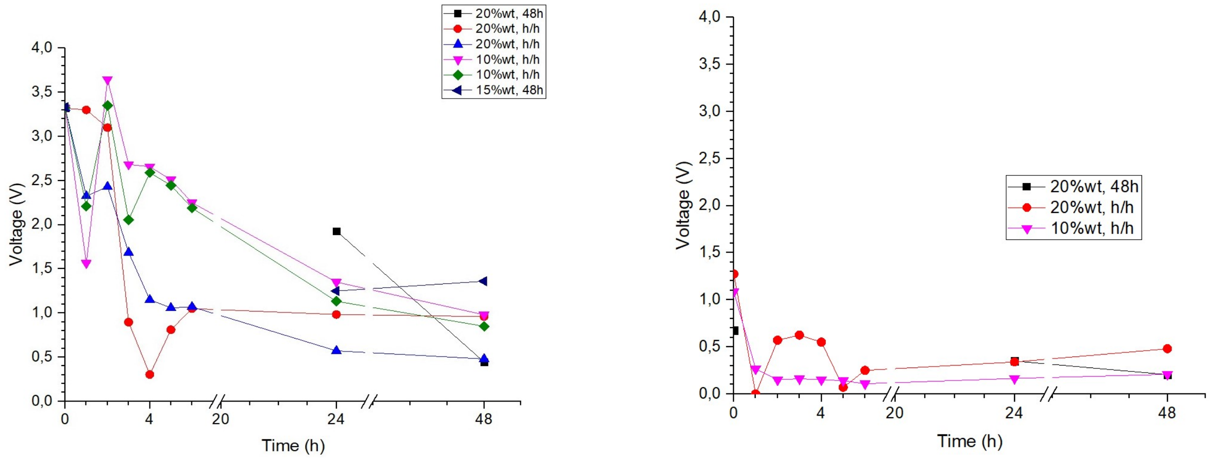
In Figure 5.4 the different discharging profiles can be seen for every battery type. In batteries 1, 2, and 3 there are some repeated bath conditions (upward blue triangle and green rhombus) just because two samples of the same battery type were placed inside the solution. It can also be seen that for Battery 3 there are some discrepancy in values, this happens because the exterior electrodes were corroded and disappeared, making the measurements more difficult to perform.

Nonetheless, Figure 5.4 emphasises the fact that different bath conditions do not result in significant difference between discharging profiles. Batteries 1 and 2 drop around 1V in the first 4h, maintaining a sustained discharge during the remaining 20h. After that, no significant change is registered as values remain more or less stable between 24h and 48h. Another remark is that checking the cells every hour, which involves retrieving them from the solution, does not seem to hinder the discharging process. Meaning that leaving the cells inside the solution continuously does not result in better discharging rates.



(a) Cell type 1

(b) Cell type 2



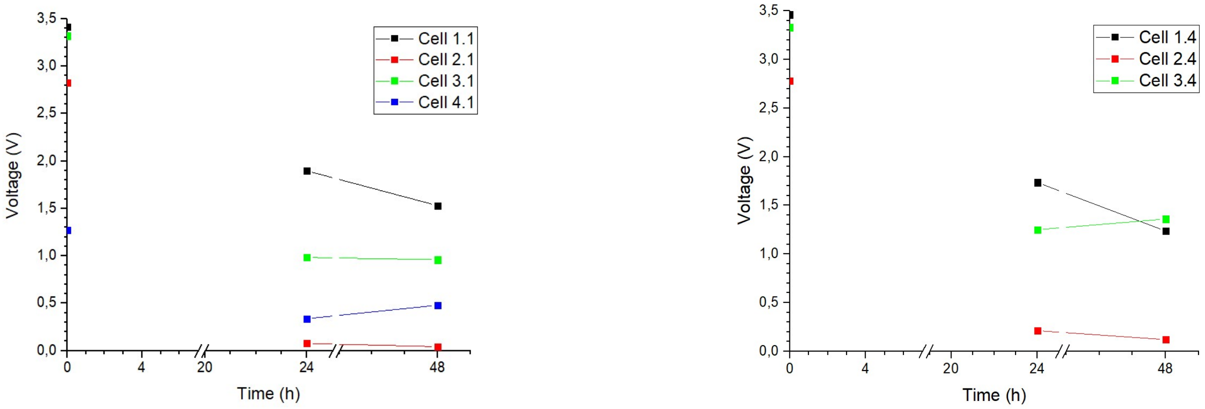
(c) Cell type 3

(d) Cell type 4

Figure 5.4: Discharging profile under different conditions.

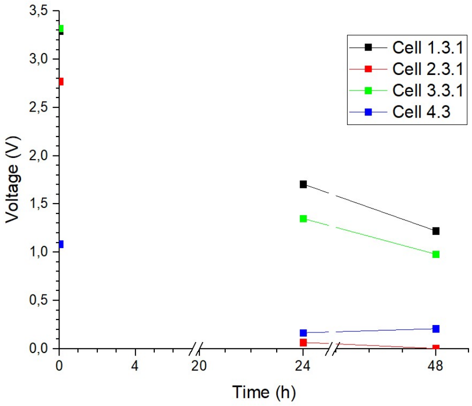
In Figure 5.5 the behaviour of each cell in different solutions is analysed. Once again, is important to mention that more than one equal cell were placed inside the solutions, hence the third digit in the cells nomenclature.

Here, the caustic solutions are presented, and the discharging profile of each cell type becomes evident, demonstrating the correlation between the shape of the cell and the discharge efficiency. Cells which were predicted to have the higher resistance (type cell 1) have indeed more difficulties in discharging. On the other hand, the cells which discharged the fastest (type cell 2) had the lowest theoretical resistance. This happens because, according to Equation 5.1, the cells with the highest distance between the electrode probes and the lowest surface area result in higher resistance, slowing the discharge process.



(a) caustic solution 20%wt NaOH.

(b) caustic solution 15%wt NaOH.



(c) caustic solution 10%wt NaOH.

Figure 5.5: Discharging of cells by caustic solutions with different concentrations.

The discrepancies measured for cell type 4 are highly related to the conditions in which the cells were retrieved from the caustic solutions (Figure 5.7). It becomes evident that all data presented related to cell 4 should be overlooked.

Figure 5.6: Cell 4 after discharging bath and drying process.

5.2.2 Balance of Components and Materials

Given the work developed at laboratory, it is also important to present an estimate of components and materials at cell level (Table 5.5). The values were obtained at the laboratory facilities after opening and drying randomly picked cells from different batteries.

Cells 1 and 2 have the weights of the anode and cathode presented together, because they are prismatic and their electrodes are rolled up together, meaning that if they were to be unrolled, material would be loss compromising the results.

Table 5.5: Balance of obtained materials and components of cells.

		1 wt (kg)	**2** wt (kg)	**3** wt (kg)	**4** wt (kg)	**5** wt (kg)
Cell	Anode	1.033	0.440	0.191	NA	0.230
	Cathode			0.255	NA	0.293
	Plastics	0.007	0.012	-	NA	-
	Separator	NA	NA	0.025	NA	0.058
	Case	0.463	0.154	0.021	NA	0.021
Before Dismantling (kg)		1.702	0.719	0.554	1.827	0.698
Mass Loss (%)		11.67	15.87	8.34	NA	13.66

NA: Not Analysed

Table 5.5: Balance of obtained materials and components of cells (continued).

		6 wt (kg)	**7** wt (kg)	**8** wt (kg)	**9** wt (kg)	**10** wt (kg)
Cell	Anode	0.284	0.461	0.342	0.245	0.013
	Cathode	0.317	0.514	0.458	0.333	0.017
	Plastics	-	-	-	-	0.001
	Separator	0.043	0.126	0.042	0.090	0.003
	Case	0.026	0.037	0.027	0.026	0.005
Before Dismantling (kg)		0.742	1.269	0.965	0.748	0.044
Mass Loss (%)		9.70	10.31	9.92	7.11	10.57

NA: Not Analysed

Regarding the materials that compose the cell structure, most cells use metals as their external case. The separator is a porous polymer membrane impregnated with the electrolyte that is dried after opening. The plastics refer to the wrappings that some manufacturers use in the prismatic cells to close the rolled electrodes. In fact, the disassembly of these cells demonstrated that prismatic and cylindrical cells are very similar in their assembly, only differing in the cross section resultant of the rolled electrodes.

Concerning the materials used in the anode and cathode, a precise estimation cannot be given at this stage of the work since the chemistry and the proportions of each metal used are still unknown. These results will later be revealed by an ICP analysis. The materials used in the anode are probably graphite and Cu at the current collector foil. At the cathode the options are much wider and, depending on the metals used, the value of cells can vary. This means that different chemistries entail different costs. A LFP battery will cost less when compared to a NMC because it uses less critical metals. Regarding recyclers, the only thing that can be said is that extracting the metals from the black mass is still a time-consuming and not so efficient process meaning that, at this stage, the focus of recyclers should be in the disassembly of packs and processing the materials used in the external case and modules, and sell the cells to second-life businesses, after assessing them and their SoH.

The cells were weighted at two different moments, firstly before opening and after all the components separation. There is some material loss, mostly related to the drying of the electrolyte. This data can be corroborated by Figure 5.7, which explicitly presents the drying process that the cells have gone through. On average, the cells lost 10.79% of their weight and any deviation from the results presented by Figure 5.7 probably indicates material loss during the handling of the cells.

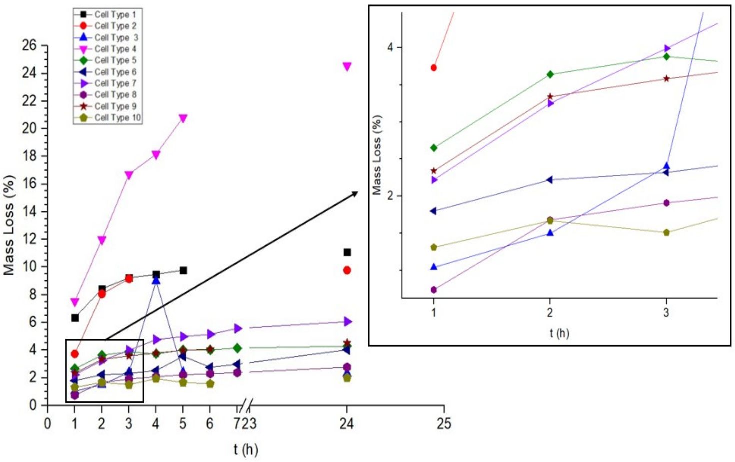


Figure 5.7: Mass loss (%) during drying process of cells.

After performing this part of the work, an average components composition of a battery can be given (Figure 5.8), obtained from the results presented fully in Table E.1, Annex E. The exterior case contributes for 13% of the weight, the module 19% and the cells 68%. From these 68%, the anode accounts for 22%, the cathode 26%, the electrolyte 11% and the exterior case with 6%, with the separator and plastics accounting for less than 5% of the weight of the cell. When comparing these results with (Hill *et.al*, 2018) where: the anode represents 17% of the weight, the cathode 20%, the electrolyte around 8% and plastics below 4%, with the cell casing representing around 6% of the weight, we can conclude that the average cell composition is similar. The more significant differences begin when moving away from the cell structure, the external lids, cables and electronics account for 35% of the weight and the modules 10%, which significantly differs from the 13% and 19% presented in this work, respectively.

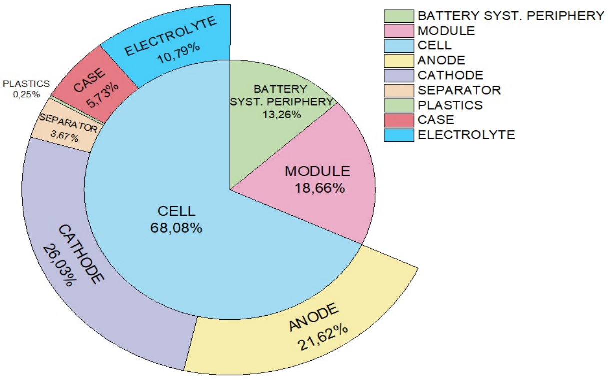


Figure 5.8: Average battery pack components.

5.2.3 Cell Characterization

Elemental Chemical Composition

A quantitative elemental chemical analysis of different electrode materials was carried out using ICP analysis at REQUIMTE at FCT-NOVA University. Table 5.6 presents the concentration of each element in each sample using Equation 4.1.

Table 5.6: Elemental chemical composition (%w/w) of electrodes.

	Sample	% Al	% Co	% Fe	% Li	% Mn	%Ni		% Li	% Cu
Cathode	1.1	10.88	5.28	0.01	3.78	41.28	4.81	**Anode**	1.09	23.12
	2.1	13.82	11.75	0.02	5.60	18.62	14.69		0.50	48.58
	3.2	13.96	-	9.56	0.93	-	-		4.12	58.68
	5.5	6.95	16.20	0.02	6.05	14.79	16.24		0.52	32.35
	6.6	11.79	8.20	0.02	3.18	15.91	23.41		3.68	45.70
	7.5	17.77	15.15	0.01	5.15	11.85	14.00		0.50	29.62
	8.5	7.19	10.69	0.02	5.78	9.03	31.54		0.66	18.80
	9.6	8.02	7.84	0.01	4.38	15.79	23.21		0.88	35.83
	10.5	15.34	7.69	0.02	5.61	4.66	35.42		0.60	49.55

It is possible to see that cell 3.2 differs from all the other because it has higher content of Fe and no Co, Mn, and Ni meaning it is a LFP battery. The copper content is really high in the anode because the current foils were cut and placed inside the *aqua regia* solution.

One can confirm that the most used technology is NMC due to the constant presence of atoms such as Ni, Mn, and Co. The proportions in which these elements are present may differ. Sample 1.1, for example, is considered a Mn-rich LIB $({}_xLi_2MnO_3\cdot(1\text{-}x)Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2)$ that uses a mixture of LMO-NMC as the cathode. The presence of Al is probably related to it being the main component of the current collector foil on the cathodic side. To determine the proportions of the cathodic material composition, Table 5.7 is presented.

Table 5.7: Cathodic material composition of NMC cell samples.

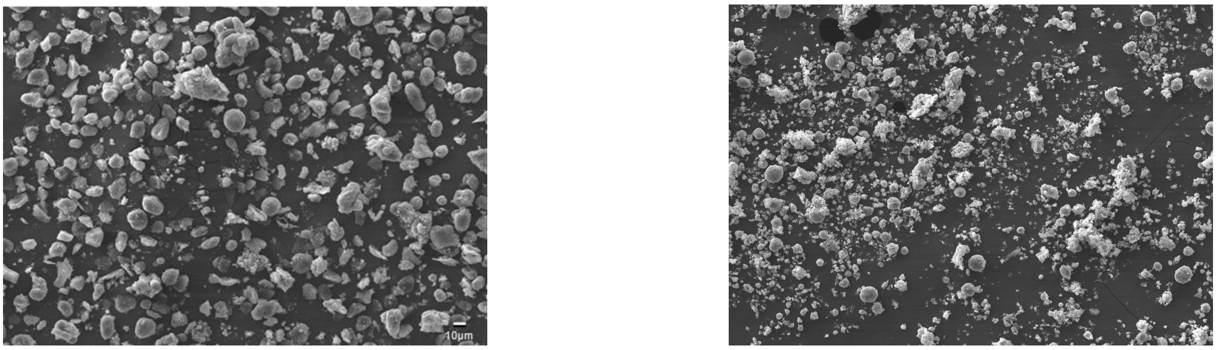
Sample	Cathodic Composition
1.1	LMO-NMC111
2.1	NMC333 / NMC111
5.5	NMC333 / NMC111
6.6	NC532
7.5	NMC333 / NMC111
8.5	NMC622
9.6	NMC532
10.5	NMC811

It is important to remember that no data is given for pack manufacturer 4 since the sample regarding this type of battery was very damaged after exiting the caustic solutions (see Figure 5.6).

Morphological and Chemical Characterisation of Phases

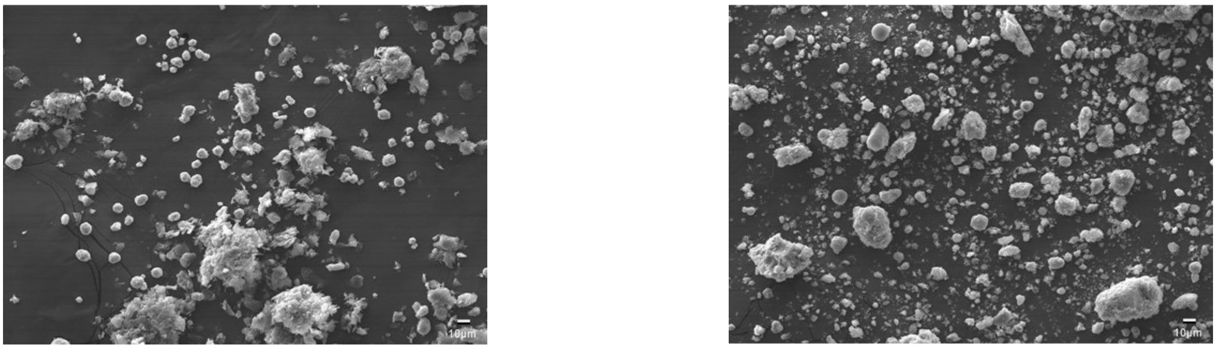
The samples analysed using SEM/EDS are the same samples used in the XRPD analysis, hence the same terminology. Firstly, an understanding of how the bath conditions affected the surface properties and morphology of the electrode materials was required. And since there are different battery technologies involved, it would also be interesting to see their differences.

To compare the surface morphology of different battery technologies, Figure 5.9 is presented. Here, a broader view of the surface of the electrode materials is given and both cells (2.5 and 3.5) were electrically discharged, guaranteeing that the only differences seen regard the materials themselves and not bath conditions. The main differences observed are that cell 2 has more evenly sized particles with predominantly rounder shapes. Cell 3 on the other hand, has bigger agglomerates of particles with not so uniform shapes.



(a) Sample 2.5 anode.

(b) Sample 2.5 cathode.



(c) Sample 3.5 anode.

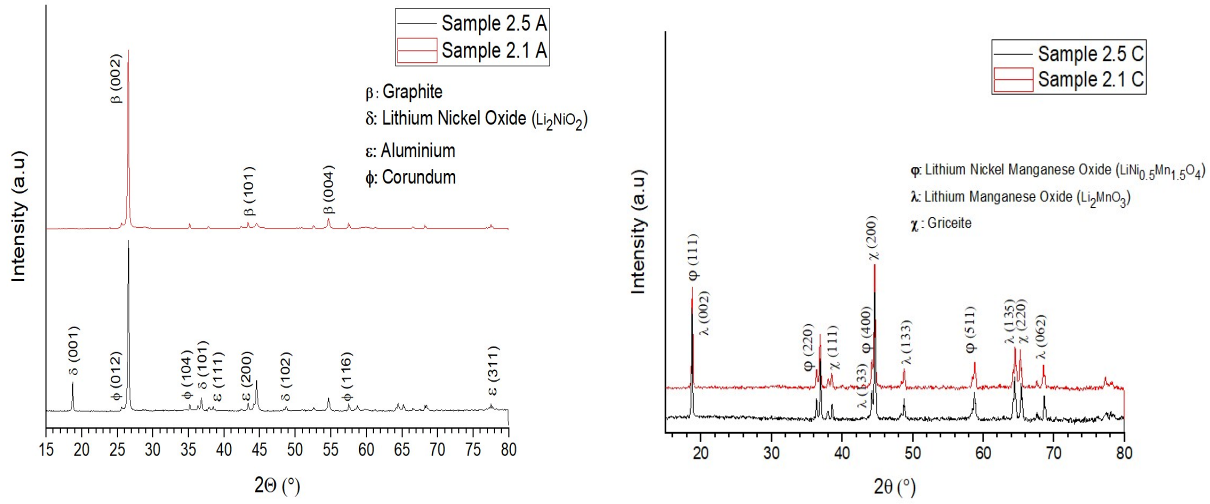
(d) Sample 3.5 cathode.

Figure 5.9: Morphological analysis of electrodes by SEM.

The main compounds found at the anode of cell 2 (Figure 5.10a) are graphite, aluminium, corundum and lithium nickel oxide. To no surprise, graphite was detected as the anode material as it is characterised by its good electrochemical performance and good specific capacity. Aluminium is present because it composed the exterior connectors that eroded during the NaOH bath, hence being present in the electrode material. Corundum, or Al_2O_3, is a very well known crystalline form of aluminium oxide that could have formed due to the interaction of aluminium with the NaOH atoms and water since it is an amphoteric substance meaning that it could react with both acids and bases.

Finally lithium nickel oxide, or Li_2NiO_2, is very used as a layered lithium transition metal oxide. This happens because cathodes layered with lithium transition metals oxides present higher theoretical capacity ($\approx$ 270mAh/g), and higher average operating voltages ($\approx$ 3.6V vs Li^+/Li) [124]. The reason it is showcased in the anode material and not the cathode material is probably related to some cross contamination while handling the samples for testing.

Regarding the cathode sample (Figure 5.10b), the presence of lithium nickel manganese oxide is explained by the nature of this battery, as the ICP analysis proved, this battery in particular uses NMC cathode technology. Lithium manganese oxide is characterised by the abundance of its raw materials,



(a)

(b)

Figure 5.10: XRPD patterns of battery 2: a) anode; b) cathode.

environmental friendliness, low cost, relatively facile manufacturing process and higher potential when compared to $LiCoO_2$ or $LiFePO_4$ as cathode materials [125].

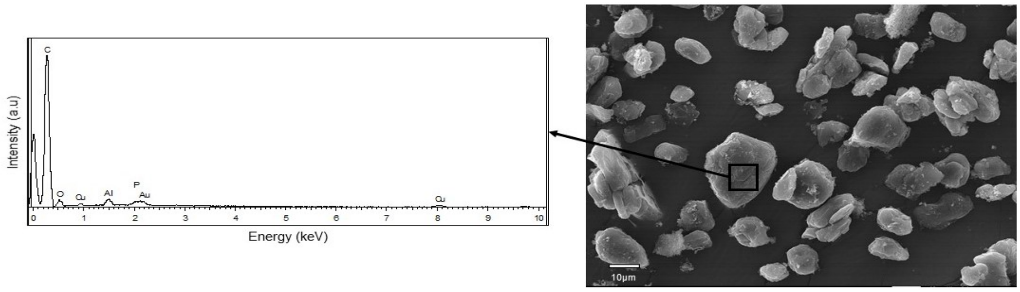
Griceite, also known as lithium fluoride (LiF), is used as an additive to improve surface diffusion of metal ions at the SEI layer during electrodeposition and as a source of ^{6}Li isotopes [126]. Another suggestion for its appearance is that it results from the leaching of the anode material combined with the reaction of NaOH with HF [123].

It is possible to see in Figure 5.11 the anode samples of cell 2. The EDS spectra presented corroborate the XRPD analysis where carbon is the most prominent element. Followed by oxygen, related to the discharged method used, and aluminium stemming from the foils where the black mass is deposited. The presence of gold is explained by its use as a conductor for SEM analysis.

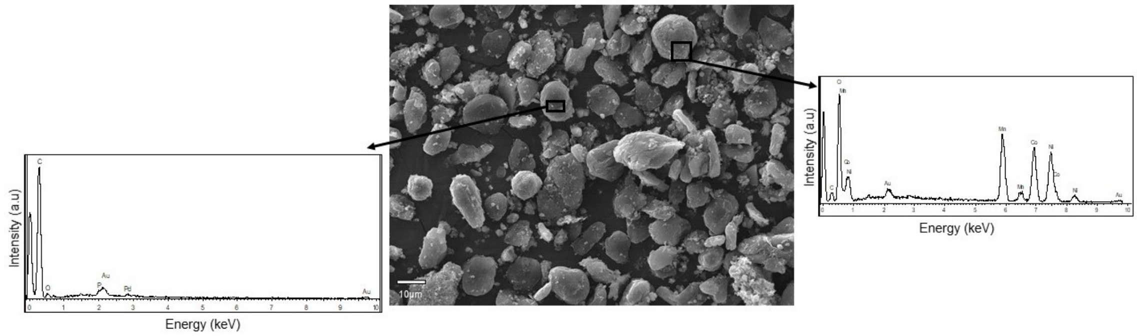
One important aspect that should be mentioned is that, in Figure 5.11b, two spectras are presented. This happens because at the first try analysing the sample a contamination was detected, cathode material was found in the anode sample (Co, Ni and Mn). This had been an hypothesis while performing the XRPD, and since the samples used for both analysis are the same, it can now be confirmed.

In Figure 5.12 it is possible to see the cathodic samples of cells 2.1 and 2.5. On a closer look, given by the EDS spectra, the elemental chemical analysis report can be confirmed. It is in fact an NMC sample, confirmed by the spectra presented in Figure 5.12a and Figure 5.12b. The differences between both samples are not very significant, so it can be concluded that the bath conditions do not affect the morphology of cell 2 samples. This might be good news, meaning that modules or cells can be discharged using such solutions, while not compromising the integrity of the material for further treatment.

Comparing both the anode and cathode, we can see that the graphite has a much rounder shape and does not form agglomerates. The cathode, however, agglomerates several particles acquiring more irregular shapes.

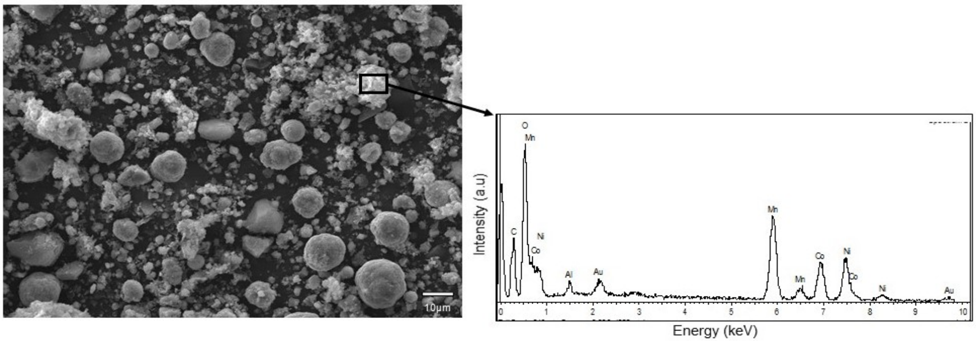


(a) Sample 2.1 anode.

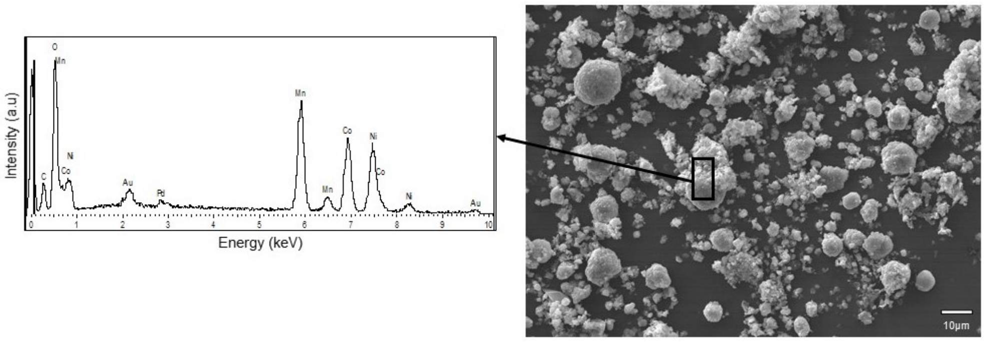


(b) Sample 2.5 anode.

Figure 5.11: SEM/EDS analysis of sample 2 anodic material.



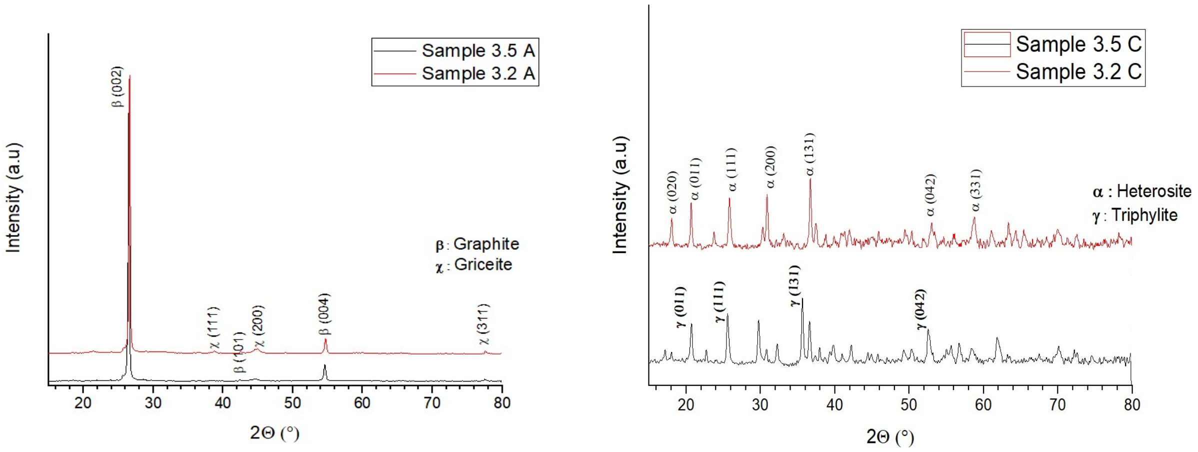
(a) Sample 2.1 cathode.



(b) Sample 2.5 cathode.

Figure 5.12: SEM/EDS analysis of sample 2 cathodic material.

Moving on to the samples of cell 3, the patterns obtained (Figure 5.13) also correlate the elemental chemical analysis performed. The main compounds found at the anode are graphite and griceite, which presence was explained previously.



(a) (b)

Figure 5.13: XRPD patterns of battery 3: a) anode; b) cathode.

The main compounds identified in the cathode were heterosite ($FePO_4$) and tryphilite ($LiFePO_4$) (Figure 5.13b). These minerals crystallise in the core of granite pegmatites (heterosite-purpurite and triphylite-lithiophilite series, respectively). The phosphate of thriphylite series is a olivine-type of mineral, with a grayish-blue colour. These minerals are often subjected to aqueous rest liquid and suffer step-wise alterations. One of these altered minerals is heterosite, found in secondary, weathered pegmatites. Firstly the oxidation of Fe^{2+}, combined with reduction of lithium content, followed by the oxidation of Mn^{2+} and complete depletion of lithium leads to the formation of these isomorphous heterosite-purpurite series. The crystal structure of heterosite is based on the same hexagonal close packing of oxygen atoms as tryphilite but with ordered vacancies in the cation position left by the lithium (Figure 5.14).

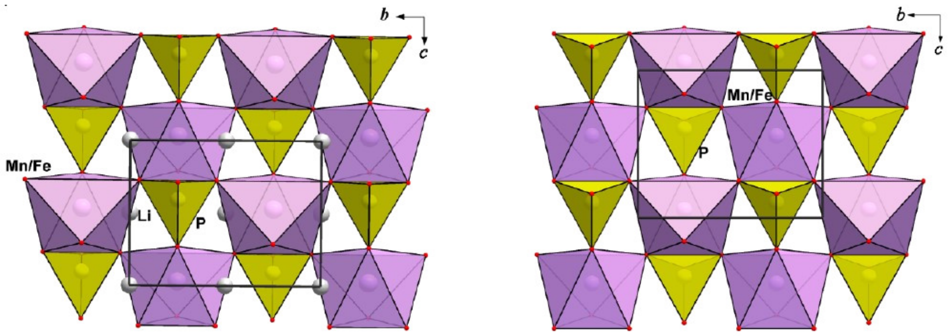
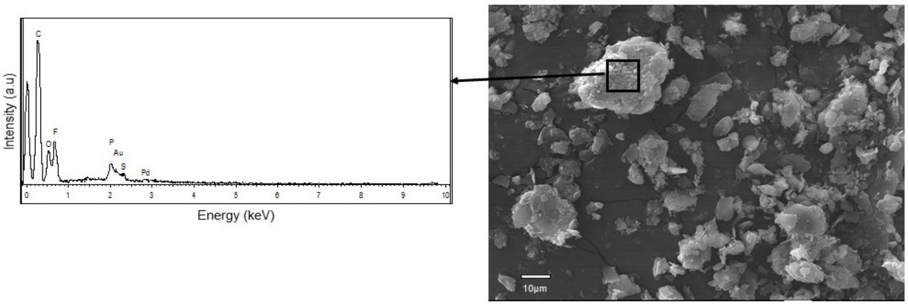


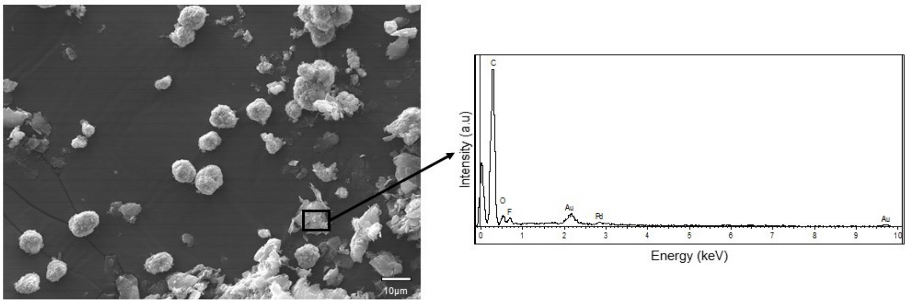
Figure 5.14: Layers of Mn/Fe centred octahedra and PO_4 tetrahedra parallel to *yz* plane in lithiophilite [left] and purpurite [right]. Reproduced from ref. [127]

In Figure 5.15, it is possible to identify the major components of these samples which are C coming from the graphite and fluorine (F) present in the griceite. As it was mentioned before, cathodic samples 3.2 and 3.5 were composed of triphylite ($LiFePO_4$) and heterosite ($FePO_4$), respectively (Figure 5.16a and Figure 5.16b). The EDS spectra found the main elements (Fe, P, O) but also V.

Some works have suggested that if a trivalent cation could be incorporated on the Fe site in heterosite, then that would lead to vacancies on the lithium site in order to balance charge. Consequently having enhanced lithium mobility and higher power capabilities. Vanadium would then be a great candidate, and was found to enhance the electrochemical performance of the cell, even though it occupied the P site and not Fe, decreasing the unit cell in size [128]. However, this hypothesis cannot be proven as V was not detected during XRPD analysis nor within the structure.

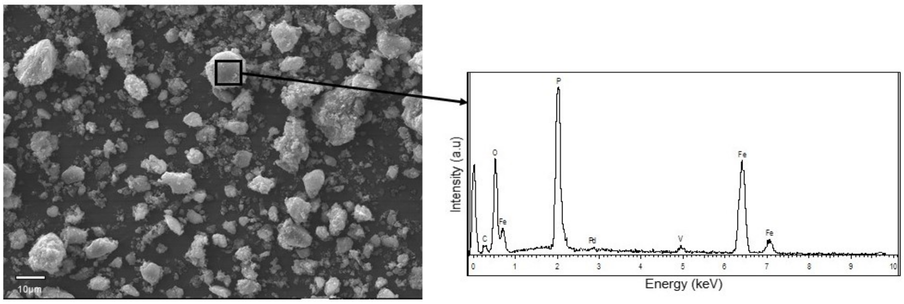


(a) Sample 3.2 anode.

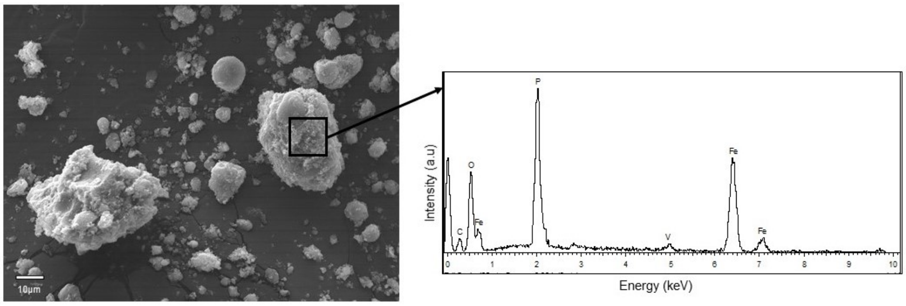


(b) Sample 3.5 anode.

Figure 5.15: SEM/EDS analysis of sample 3 anodic material.



(a) Sample 3.2 cathode.



(b) Sample 3.5 cathode.

Figure 5.16: SEM/EDS analysis of sample 3 cathodic material.

Chapter 6

Conclusions & Future Work

With the work developed in this thesis, it was possible to comprehend the full extent of procedures related to dismantling EV batteries on both an industrial and laboratory scale. Working closely with recyclers gave an unique perspective on the problems coming from the batteries and how to create an efficient disassembly line.

The fact that these batteries are characterised by high voltages, required that at the start of this work a discharging procedure was established. By being at the companies facilities it was possible to understand the difficulties of disassembling an EV battery pack, starting by their large dimensions and the numerous safety procedures that have to be followed. The difficulties in understanding how the modules are connected and which disassembly sequence will guarantee the collaborators safety, followed by the challenges of dismantling each and every piece without damaging the cells and other components. It goes to show the importance of eco-design.

Eco-design should not just be a concern for end-of-life businesses. One of the circular economy premises is the reuse or recondition of certain objects in the same or other applications. When it comes to LIBs coming from EVs, they are usually applied in another field. This means that there's a lot more of other businesses dependent on the dismantle and recondition of batteries. Therefore, it is of the utmost importance that manufactures re-think their assembling strategy to help the downstream businesses that are dependent of the shapes, materials and components coming their way. Of course, the difficulties start to arise when one starts to think of the implications of having a standardise design, the loss of certain performance features (essential to patents) have to be accounted for and resolved. Not only that, but this work also allowed to understand that the shape at cell level is also important when it comes to discharge these batteries.

When caustic solutions were used, the distance and surface area of the electrode probes combined with the conductivity of the solutions allowed to see a correlation regarding the pace at which the cells were discharged. If the electrode probes result in an higher resistance, the cell will take longer to discharge.

Working at the companies allowed the building of a dismantle and discharging procedure, possible to follow whatever the conditions available. The dismantling procedures set into motion, allowed for an efficient material recovery, while performing a mass balance, it was possible to see that the anode accounts to 21.6% of the cell weight, while the cathode contributes with 26.03% and the electrolyte with 10.79%. The module, in this work composed by screws, metals, plastics, circuit plates, and cables compose 18.66% of the total weight, and the battery system periphery containing the lids, BMS, and some screws accounts for 13.26%.

When it comes to the profit coming the recyclers way, no opinion was made on this matter due to the impossibility of coming to an accurate conclusion. At the companies the materials retrieved could not be known accurately and at cell level, the fact that this thesis does not cover the recovery of metals in the black mass, hindered the possible conclusions. For now, recyclers should focus on recovering the materials that compose the external battery case, which are mainly metals and where the commodity price is higher. In addition, retrieving PCBs, electrical cables, and the BMS may also pose as an opportunity.

Concerning the morphological characterisation and the caustic solution influence, in terms of new compound forms some new minerals were formed. The NMC cell batteries were as affected by the baths as the LFP samples, independently of the shape of the cells (one are prismatic and the other pouch) and their components being more prone to react than others. The discharging method, is safe to say, is the one that will allow batteries to maintain their most original form, even with some delithiation. Another concern regarding the deactivation through caustic solutions is what to do with the liquid effluents.

At the end of this thesis is possible to suggest some future work. An essential step would be to continue the work and try and retrieve the black mass from the foils. This work should be first done at laboratory scale to try and define the best conditions to retrieve these materials. After that, the procedures should be scaled up and implemented at industrial scale.

Not only that, but an optimization to the posterior purification of metals contained in the black mass should also be addressed. Keeping in mind that the ideal situation would be to scale up the process and integrate them in the recyclers facilities.

Another interesting work would be to try and maximize the gains coming the recyclers way. This approach should involve a way to give back to the factory grid the energy retrieved from charged batteries, and some physical separation steps to be able to better distinguish the different materials used, enhancing the purity of materials being treated.

Finally, another interesting approach would be to focus on the design of batteries. As mentioned throughout this thesis, designing a product with its EoL in mind is very important and will help the downstream processes throughout. Therefore, studying better solutions for dismantle and the materials used can improve the feasibility of taking these products through a second life and disposal.

Bibliography

[1] E. Commission", “Automotive industry.” `https://ec.europa.eu/growth/sectors/automotive_en`. Acessed March 10, 2021.

[2] E. E. Agency, *Electric Vehicles in Europe - Approaching adolescence*. No. 20, European Environment Agency, 2016.

[3] M. Abdelbaky, J. R. Peeters, J. R. Duflou, and W. Dewulf, “Forecasting the EU recycling potential for batteries from electric vehicles,” *Procedia CIRP*, vol. 90, pp. 432–436, 2020.

[4] N. Hill, D. Clarke, L. Blair, and H. Menadue, “Circular Economy Perspectives for the Management of Batteries used in Electric Vehicles,” *JRC Publications Office of the European Union*, 2019.

[5] E. Drabik and V. Rizos, “Prospects for electric vehicle batteries in a circular economy,” *Ceps*, p. 33, 2018.

[6] McKerracher, C, “Electric Vehicle Outlook 2020,” *Bloomberg New Energy Finance*, no. July, p. 20, 2020.

[7] K. Hampshire, R. German, A. Pridmore, and J. Fons, “Electric vehicles from life cycle and circular economy perspectives,” no. 13, p. 78, 2018.

[8] European Commission, “Green Deal : Sustainable batteries for a circular and climate neutral economy,” no. December, pp. 10–11, 2020.

[9] J. Heelan, E. Gratz, Z. Zheng, Q. Wang, M. Chen, D. Apelian, and Y. Wang, “Current and Prospective Li-Ion Battery Recycling and Recovery Processes,” *Jom*, vol. 68, no. 10, pp. 2632–2638, 2016.

[10] IEA, “Global EV Outlook 2020,” *Global EV Outlook 2020*, 2020.

[11] O. Velázquez-Martínez, J. Valio, A. Santasalo-Aarnio, M. Reuter, and R. Serna-Guerrero, “A critical review of lithium-ion battery recycling processes from a circular economy perspective,” *Batteries*, vol. 5, no. 4, pp. 5–7, 2019.

[12] L. A.-W. Ellingsen and C. R. Hung, *Part 2: Research for TRAN Committee - Resource and climate aspects of lithium-ion traction batteries and battery electric vehicles*. 2018.

[13] P. Mock, “European Vehicle Market Statistics: Pocketbook 2020/21,” *International Council on Clean Transportation*, 2019.

[14] P. Mock, “EU CO2 standards for passenger cars and light-commercial vehicles,” *International Council on Clean Transportation*, no. January, pp. 1–9, 2014.

[15] Parlamento Europeu e do Conselho da União Europeia, “Diretiva 2007/46/CE,” *Jornal Oficial da União Europeia*, no. 5 de Setembro, p. 160, 2007.

[16] European Environment Agency, “Managing exposure to noise in Europe,” *European Environment Agency*, p. 4, 2017.

[17] Y. Miao, P. Hynan, A. Von Jouanne, and A. Yokochi, “Current li-ion battery technologies in electric vehicles and opportunities for advancements,” *Energies*, vol. 12, no. 6, pp. 1–20, 2019.

[18] M. Dijk, R. J. Orsato, and R. Kemp, “The emergence of an electric mobility trajectory,” *Energy Policy*, vol. 52, pp. 135–145, 2013.

[19] S. Steinhilber, P. Wells, and S. Thankappan, “Socio-technical inertia: Understanding the barriers to electric vehicles,” *Energy Policy*, vol. 60, pp. 531–539, 2013.

[20] T. Gersdorf, P. Hertzke, P. Schaufuss, and S. Schenk, “McKinsey Electric Vehicle Index: Europe Cushions a Global Plunge in EV Sales,” *McKinsey Company*, vol. July, no. July, pp. 1–12, 2020.

[21] P. News, “Portugal with the fifth highest percentage of electric car sales in europe.” `https://tinyurl.com/tphm7kc`, 2020. Acessed April 15, 2021.

[22] Z. Shahan, “Portugal ev market share = 12%.” `https://cleantechnica.com/2020/07/12/portugal-ev-market-share-12/`, 2020. Acessed April 15, 2021.

[23] X. Sun, Z. Li, X. Wang, and C. Li, “Technology development of electric vehicles: A review,” *Energies*, vol. 13, no. 1, pp. 1–29, 2019.

[24] P. Wolfram and N. Lutsey, “Electric vehicles: Literature review of technology costs and carbon emissions,” *The International Council on Clean . . .* , no. July, pp. 1–23, 2016.

[25] X. Zeng, M. Li, D. Abd El-Hady, W. Alshitari, A. S. Al-Bogami, J. Lu, and K. Amine, “Commercialization of Lithium Battery Technologies for Electric Vehicles,” *Advanced Energy Materials*, vol. 9, no. 27, pp. 1–25, 2019.

[26] S. B. J. Huisman, T. Ciuta, F. Mathieux and D. P. K. Georgitzikis, *RMIS – Raw Materials in the Battery Value Chain*. 2019.

[27] E. Maiser, “Battery packaging - Technology review,” *AIP Conference Proceedings*, vol. 1597, no. February, pp. 204–218, 2014.

[28] T. Horiba, “Lithium-ion battery systems,” *Proceedings of the IEEE*, vol. 102, no. 6, pp. 939–950, 2014.

[29] K. Kinoshita and K. Zaghib, “Negative electrodes for Li-ion batteries,” *Journal of Power Sources*, vol. 110, no. 2, pp. 416–423, 2002.

[30] G. Berckmans, M. Messagie, J. Smekens, N. Omar, L. Vanhaverbeke, and J. V. Mierlo, “Cost projection of state of the art lithium-ion batteries for electric vehicles up to 2030,” *Energies*, vol. 10, no. 9, 2017.

[31] X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B. W. Sheldon, and J. Wu, “Silicon-Based nanomaterials for lithium-ion batteries: A review,” *Advanced Energy Materials*, vol. 4, no. 1, pp. 1–23, 2014.

[32] H. J. Kim, T. N. Krishna, K. Zeb, V. Rajangam, C. V. Muralee Gopi, S. Sambasivam, K. V. G. Raghavendra, and I. M. Obaidat, *A comprehensive review of li-ion battery materials and their recycling techniques*, vol. 9. 2020.

[33] M. A. Hannan, M. M. Hoque, A. Hussain, Y. Yusof, and P. J. Ker, "State-of-the-Art and Energy Management System of Lithium-Ion Batteries in Electric Vehicle Applications: Issues and Recommendations," *IEEE Access*, vol. 6, pp. 19362–19378, 2018.

[34] C. M. Julien, A. Mauger, K. Zaghib, and H. Groult, "Comparative issues of cathode materials for Li-ion batteries," *Inorganics*, vol. 2, no. 1, pp. 132–154, 2014.

[35] D. Deng, "Li-ion batteries: Basics, progress, and challenges," *Energy Science and Engineering*, vol. 3, no. 5, pp. 385–418, 2015.

[36] S. W. D. Gourley and Z. Chen, "Recycling of mixed cathode lithium - ion batteries for electric vehicles : Current status and future outlook," no. November 2019, pp. 6–43, 2020.

[37] F. Larouche, F. Tedjar, K. Amouzegar, G. Houlachi, P. Bouchard, G. P. Demopoulos, and K. Zaghib, "Progress and status of hydrometallurgical and direct recycling of Li-Ion batteries and beyond," *Materials*, vol. 13, no. 3, 2020.

[38] K. Xu, "Nonaqueous liquid electrolytes for lithium-based rechargeable batteries," *Chemical Reviews*, vol. 104, no. 10, pp. 4303–4417, 2004.

[39] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, and K. Xu, ""Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries," *Science*, vol. 350, no. 6263, pp. 938–943, 2015.

[40] J. W. Fergus, "Ceramic and polymeric solid electrolytes for lithium-ion batteries," *Journal of Power Sources*, vol. 195, no. 15, pp. 4554–4569, 2010.

[41] S. S. Zhang, "A review on the separators of liquid electrolyte Li-ion batteries," *Journal of Power Sources*, vol. 164, no. 1, pp. 351–364, 2007.

[42] N. Chawla, N. Bharti, and S. Singh, "Recent advances in non-flammable electrolytes for safer lithium-ion batteries," *Batteries*, vol. 5, no. 1, 2019.

[43] E.-L. Innovations, "The working principle of the lithium-ion battery!." `"https://e-lyte-innovations.de/working-principle-lithium-ion-battery/"`. Acessed February 9, 2021.

[44] Bobba, S., Carrara, S., Huisman, J., MAthieux, F., Pavel, C., "Critical Raw Materials for Strategic Technologies and Sectors in the EU: A Foresight Study," *Publications Office of the European Union*, pp. 1–27, 2015.

[45] L. A. Tercero Espinoza, A. Loibl, S. Langkau, A. de Koning, E. Van der Voet, and S. Michaux, "Report on the future use of critical raw materials," *Scrreen*, no. 730227, 2019.

[46] European Commission, *Study on the review of the list of Critical Raw Materials - Critical Raw Materials Factsheets*. 2020.

[47] P. Alves Dias, D. Blagoeva, C. Pavel, and N. Arvanitidis, *Cobalt: demand-supply balances in the transition to electric mobility. EUR 29381 EN, Publications Office of the European Union*. 2018.

[48] F. Matos, C.T.; Ciacci, L; Godoy León, M.F.; Lundhaug, M.; Dewulf, J.; Müller, D.B.; Georgitzikis, K.; Wittmer, D.; Mathieux, *Material System Analysis of five battery related raw materials: Cobalt, Lithium, Manganese, Natural Graphite, Nickel* . 2020.

[49] P. Christmann, E. Gloaguen, J.-F. Labbé, J. Melleton, and P. Piantone, *Chapter 1 - Global Lithium Resources and Sustainability Issues*. Elsevier, 2015.

[50] L. A. Tercero Espinoza, A. Loibl, S. Langkau, A. de Koning, E. Van der Voet, and S. Michaux, “Report on the future use of critical raw materials,” *Scrreen*, no. 730227, 2019.

[51] World Economic Forum; Global Battery Alliance, “A Vision for a Sustainable Battery Value Chain in 2030 Unlocking the Full Potential to Power Sustainable Development and Climate Change Mitigation including photocopying and recording, or by any information storage and retrieval system. 3 A Vision for a S,” no. September, 2019.

[52] G. Giordano, “Electric vehicles,” *Manufacturing Engineering*, vol. 161, no. 3, pp. 50–58, 2018.

[53] S. S. Sharma and A. Manthiram, “Towards more environmentally and socially responsible batteries,” *Energy and Environmental Science*, vol. 13, no. 11, pp. 4087–4097, 2020.

[54] M. G. Idc, *Advanced Technologies for Industry – Methodological report*. No. May, 2020.

[55] F. Di Persio, J. Huisman, S. Bobba, P. A. Dias, G. A. Blengini, and D. Blagoeva, *Information gap analysis for decision makers to move EU towards a Circular Economy for the lithium-ion battery value chain*. 2020.

[56] Y. Kotak, C. M. Fernández, L. C. Casals, B. S. Kotak, D. Koch, C. Geisbauer, L. Trilla, A. Gómez-Núñez, and H. G. Schweiger, “End of electric vehicle batteries: Reuse vs. recycle,” *Energies*, vol. 14, no. 8, pp. 1–15, 2021.

[57] M. O. Ramoni and H. C. Zhang, “End-of-life (EOL) issues and options for electric vehicle batteries,” *Clean Technologies and Environmental Policy*, vol. 15, no. 6, pp. 881–891, 2013.

[58] E. Commission, “Questions and Answers on Sustainable Batteries Regulation,” no. December, 2020.

[59] K. M. Winslow, S. J. Laux, and T. G. Townsend, “A review on the growing concern and potential management strategies of waste lithium-ion batteries,” *Resources, Conservation and Recycling*, vol. 129, no. November 2017, pp. 263–277, 2018.

[60] S. Blömeke, S. Lawrenz, P. Sharma, L. Kintscher, G. Bikker, M. Nippraschk, H. Poschmann, and C. Scheller, “Recycling 4.0,” pp. 66–76, 2020.

[61] D. D. E. Pilhas, N. Legal, M. D. E. Aplica, E. S. Do, and M. D. E. Aplica, “(rpa),” 2019.

[62] Eurostat, “Waste statistics - recycling of batteries and accumulators,” *Eurostat*, pp. 1–14, 2020.

[63] I. Financeiros, “R (rpa),” vol. 2018, no. 1, pp. 2018–2020, 2018.

[64] H. Huo, Y. Xing, M. Pecht, B. J. Züger, N. Khare, and A. Vezzini, *Safety requirements for transportation of lithium batteries*, vol. 10. 2017.

[65] J. Duan, X. Tang, H. Dai, Y. Yang, W. Wu, X. Wei, and Y. Huang, *Building Safe Lithium-Ion Batteries for Electric Vehicles: A Review*, vol. 3. Springer Singapore, 2020.

[66] E. Rahimzei *Lithium-Ion Batteries: Basics and Applications*.

[67] International Air Transport Association, “Lithium Battery Guidance Document: Transport of Lithium Metal and Lithium Ion Battery,” pp. 1–27, 2014.

[68] United Nations, *Recommendations on the Transport of Dangerous Goods – Model Regulations Volume II*, vol. 21. 2019.

[69] S. E. C. Ib and S. E. C. Ia, “Shipping Guidelines for Lithium Ion Batteries,” no. April, pp. 1–13, 2019.

[70] Tesla, “Powerwall 2 Transportation and Storage Guidelines,” 2017.

[71] Valorcar, “Guia de desmantelamento de Veículos em Fim de Vida,” p. 94, 2015.

[72] “Second-life EV batteries: The newest value pool in energy storage,” *McKinsey Company*, no. April, 2019.

[73] M. Chen, X. Ma, B. Chen, R. Arsenault, P. Karlson, N. Simon, and Y. Wang, “Recycling End-of-Life Electric Vehicle Lithium-Ion Batteries,” *Joule*, vol. 3, no. 11, pp. 2622–2646, 2019.

[74] F. Arshad, L. Li, K. Amin, E. Fan, N. Manurkar, A. Ahmad, J. Yang, F. Wu, and R. Chen, “A Comprehensive Review of the Advancement in Recycling the Anode and Electrolyte from Spent Lithium Ion Batteries,” *ACS Sustainable Chemistry and Engineering*, vol. 8, no. 36, pp. 13527–13554, 2020.

[75] A. Beaudet, F. Larouche, K. Amouzegar, P. Bouchard, and K. Zaghib, “Key challenges and opportunities for recycling electric vehicle battery materials,” *Sustainability (Switzerland)*, vol. 12, no. 14, pp. 1–12, 2020.

[76] X. Zhang, L. Li, E. Fan, Q. Xue, Y. Bian, F. Wu, and R. Chen, “Toward sustainable and systematic recycling of spent rechargeable batteries,” *Chemical Society Reviews*, vol. 47, no. 19, pp. 7239–7302, 2018.

[77] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, and P. Anderson, “Recycling lithium-ion batteries from electric vehicles,” *Nature*, vol. 575, no. 7781, pp. 75–86, 2019.

[78] S. Kim, J. Bang, J. Yoo, Y. Shin, J. Bae, J. Jeong, K. Kim, P. Dong, and K. Kwon, “A Comprehensive Review on the Pretreatment Process in Lithium-ion Battery Recycling,” *Journal of Cleaner Production*, vol. 294, p. 126329, 2021.

[79] H. Pinegar and Y. R. Smith, “Recycling of End-of-Life Lithium-Ion Batteries, Part II: Laboratory-Scale Research Developments in Mechanical, Thermal, and Leaching Treatments,” *Journal of Sustainable Metallurgy*, vol. 6, no. 1, pp. 142–160, 2020.

[80] C. Hanisch, J. Diekmann, A. Stieger, W. Haselrieder, and A. Kwade, “Recycling of Lithium-Ion Batteries,” *Handbook of Clean Energy Systems*, no. 2011, pp. 1–24, 2015.

[81] R. Sommerville, J. Shaw-Stewart, V. Goodship, N. Rowson, and E. Kendrick, “A review of physical processes used in the safe recycling of lithium ion batteries,” *Sustainable Materials and Technologies*, vol. 25, p. e00197, 2020.

[82] L. P. Yao, Q. Zeng, T. Qi, and J. Li, “An environmentally friendly discharge technology to pretreat spent lithium-ion batteries,” *Journal of Cleaner Production*, vol. 245, p. 118820, 2020.

[83] S. Ojanen, M. Lundström, A. Santasalo-Aarnio, and R. Serna-Guerrero, “Challenging the concept of electrochemical discharge using salt solutions for lithium-ion batteries recycling,” *Waste Management*, vol. 76, pp. 242–249, 2018.

[84] J. Marshall, D. Gastol, R. Sommerville, B. Middleton, V. Goodship, and E. Kendrick, “Disassembly of Li ion cells—characterization and safety considerations of a recycling scheme,” *Metals*, vol. 10, no. 6, pp. 1–22, 2020.

[85] J. Li, G. Wang, and Z. Xu, “Generation and detection of metal ions and volatile organic compounds (VOCs) emissions from the pretreatment processes for recycling spent lithium-ion batteries,” *Waste Management*, vol. 52, pp. 221–227, 2016.

[86] K. Wegener, W. Hua, F. Dietrich, K. Dröder, and S. Kara, “Robot Assisted Disassembly for the Recycling of Electric Vehicle Batteries,” *Procedia CIRP*, vol. 29, pp. 716–721, 2015.

[87] H. Rallo, G. Benveniste, I. Gestoso, and B. Amante, “Economic analysis of the disassembling activities to the reuse of electric vehicles Li-ion batteries,” *Resources, Conservation and Recycling*, vol. 159, no. February, p. 104785, 2020.

[88] J. Li, M. Barwood, and S. Rahimifard, “Robotics and Computer – Integrated Manufacturing Robotic disassembly for increased recovery of strategically important materials from electrical vehicles,” vol. 000, no. March 2016, pp. 1–10, 2017.

[89] B. Pack, “metals Task Planner for Robotic Disassembly of Electric Vehicle Battery Pack,” 2021.

[90] D. L. Thompson, J. M. Hartley, S. M. Lambert, M. Shiref, G. D. Harper, E. Kendrick, P. Anderson, K. S. Ryder, L. Gaines, and A. P. Abbott, “The importance of design in lithium ion battery recycling-a critical review,” *Green Chemistry*, vol. 22, no. 22, pp. 7585–7603, 2020.

[91] R. Gerbers, K. Wegener, F. Dietrich, and K. Der, “Safe , Flexible and Productive for Disassembly of Lithium-Ion Batteries,”

[92] C. Herrmann, A. Raatz, S. Andrew, and J. Schmitt, “Scenario-Based Development of Disassembly Systems for Automotive Scenario-based Development of Disassembly Systems for Automotive Lithium Ion Battery Systems,” no. April, 2014.

[93] T. Waldmann, A. Iturrondobeitia, M. Kasper, N. Ghanbari, F. Aguesse, E. Bekaert, L. Daniel, S. Genies, I. J. Gordon, M. W. Löble, E. De Vito, and M. Wohlfahrt-Mehrens, “Review—Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis Techniques,” *Journal of The Electrochemical Society*, vol. 163, no. 10, pp. A2149–A2164, 2016.

[94] S. Nowak and M. Winter, “The role of sub- and supercritical CO2 as "processing solvent" for the recycling and sample preparation of lithium ion battery electrolytes,” *Molecules*, vol. 22, no. 3, 2017.

[95] S. Editors, C. Herrmann, and S. Kara, “Sustainable Production, Life Cycle Engineering and Management- Recycling of Lithium-Ion Batteries The LithoRec Way,” *Springer International Publishing*, 2018.

[96] S. Rothermel, M. Evertz, J. Kasnatscheew, X. Qi, M. Grützke, M. Winter, and S. Nowak, “Graphite Recycling from Spent Lithium-Ion Batteries,” *ChemSusChem*, vol. 9, no. 24, pp. 3473–3484, 2016.

[97] K. He, Z. Y. Zhang, L. Alai, and F. S. Zhang, “A green process for exfoliating electrode materials and simultaneously extracting electrolyte from spent lithium-ion batteries,” *Journal of Hazardous Materials*, vol. 375, no. March, pp. 43–51, 2019.

[98] Y. He, X. Yuan, G. Zhang, H. Wang, T. Zhang, W. Xie, and L. Li, “A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries,” *Science of the Total Environment*, vol. 766, p. 142382, 2020.

[99] L. Li, P. Zheng, T. Yang, R. Sturges, M. W. Ellis, and Z. Li, “Disassembly Automation for Recycling End-of-Life Lithium-Ion Pouch Cells,” *Jom*, vol. 71, no. 12, pp. 4457–4464, 2019.

[100] L. P. He, S. Y. Sun, X. F. Song, and J. G. Yu, “Recovery of cathode materials and Al from spent lithium-ion batteries by ultrasonic cleaning,” *Waste Management*, vol. 46, pp. 523–528, 2015.

[101] M. Jafari, M. M. Torabian, and A. Bazargan, “A Facile Chemical-Free Cathode Powder Separation Method for Lithium Ion Battery Resource Recovery,” *Journal of Energy Storage*, vol. 31, no. December 2019, p. 101564, 2020.

[102] J. A. Sarasua, A. Sandá, C. Villasante, and E. Aranzabe, “Non-immersion ultrasonic cleaning for heliostats,” *AIP Conference Proceedings*, vol. 2033, no. April 2020, 2018.

[103] J. Li, P. Shi, Z. Wang, Y. Chen, and C. C. Chang, “A combined recovery process of metals in spent lithium-ion batteries,” *Chemosphere*, vol. 77, no. 8, pp. 1132–1136, 2009.

[104] X. Wang, G. Gaustad, and C. W. Babbitt, “Targeting high value metals in lithium-ion battery recycling via shredding and size-based separation,” *Waste Management*, vol. 51, pp. 204–213, 2016.

[105] E. Gratz, Q. Sa, D. Apelian, and Y. Wang, “A closed loop process for recycling spent lithium ion batteries,” *Journal of Power Sources*, vol. 262, pp. 255–262, 2014.

[106] L. Li, J. B. Dunn, X. X. Zhang, L. Gaines, R. J. Chen, F. Wu, and K. Amine, “Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment,” *Journal of Power Sources*, vol. 233, pp. 180–189, 2013.

[107] L. Yun, D. Linh, L. Shui, X. Peng, A. Garg, M. L. P. LE, S. Asghari, and J. Sandoval, “Metallurgical and mechanical methods for recycling of lithium-ion battery pack for electric vehicles,” *Resources, Conservation and Recycling*, vol. 136, pp. 198–208, 2018.

[108] N. B. Horeh, S. Mousavi, and S. Shojaosadati, “Bioleaching of valuable metals from spent lithium-ion mobile phone batteries using aspergillus niger,” *Journal of Power Sources*, vol. 320, pp. 257–266, 2016.

[109] O. Velázquez-Martínez, J. Valio, A. Santasalo-Aarnio, M. Reuter, and R. Serna-Guerrero, “A critical review of lithium-ion battery recycling processes from a circular economy perspective,” *Batteries*, vol. 5, no. 4, pp. 5–7, 2019.

[110] H. Pinegar and Y. R. Smith, “Recycling of End-of-Life Lithium Ion Batteries, Part I: Commercial Processes,” *Journal of Sustainable Metallurgy*, vol. 5, no. 3, pp. 402–416, 2019.

[111] S. Sloop, L. Crandon, M. Allen, K. Koetje, L. Reed, L. Gaines, W. Sirisaksoontorn, and M. Lerner, “A direct recycling case study from a lithium-ion battery recall,” *Sustainable Materials and Technologies*, vol. 25, p. e00152, 2020.

[112] C. Egenhofer, M. E. Drabik, A. Rizos, and V., “Stakeholder’s Views on the Eco-design Directive: An assessment of the successes and shortcomings,” *Centre for European Policy Studies*, p. 38, 2018.

[113] E. Drabik and V. Rizos, “Prospects for electric vehicle batteries in a circular economy,” *Centre for European Policy Studies*, no. July, p. 33, 2018.

[114] R. Lee, U. of Birmingham Stephen Gifford, and F. Institution, “The importance of coherent regulatory and policy strategies for the recycling of EV batteries,” p. 8, 2020.

[115] D. H. S. Tan, P. Xu, and Z. Chen, “Enabling sustainable critical materials for battery storage through efficient recycling and improved design: A perspective,” vol. 7, no. 1, pp. 1–13, 2020.

[116] “Introduction to Inductively Coupled Plasma Atomic Emission Spectrometry,” *Introduction to Inductively Coupled Plasma Atomic Emission Spectrometry*, vol. 1, 1989.

[117] C. B. Boss and K. J. Fredeen, “Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry,” *PerkinElmer*, vol. 997, pp. 1–125, 1999.

[118] S. Monster, “High purity metal prices.” `https://www.scrapmonster.com/metal-prices/high-purity-metals`. Acessed October 4, 2021.

[119] alibaba.com. `https://www.alibaba.com/showroom/recycled-pvc-granules.html`. Acessed October 4, 2021.

[120] I. SVTronics, “How much does a pcb cost? factors that will affect the price, howpublished = `https://svtronics.com/blog/how-much-does-a-pcb-cost-factors-that-will-affect-the-price/`, note = Acessed October 4, 2021,.”

[121] alibab.com. `https://www.alibaba.com/countrysearch/CN/used-electric-cable.html`. Acessed October 4, 2021.

[122] O. BMS, “Orion bms 2.” `https://www.orionbms.com/products/orion-bms-standard`. Acessed October 4, 2021.

[123] J. Shaw-Stewart, A. Alvarez-Reguera, A. Greszta, J. Marco, M. Masood, R. Sommerville, and E. Kendrick, “Aqueous solution discharge of cylindrical lithium-ion cells,” *Sustainable Materials and Technologies*, vol. 22, p. e00110, 2019.

[124] J. Xu, E. Hu, D. Nordlund, A. Mehta, S. N. Ehrlich, X.-Q. Yang, and W. Tong, “ Understanding the Degradation Mechanism of Lithium Nickel Oxide Cathodes for Li-Ion Batteries,” *(BES)*, 2017.

[125] A. H. Marincaş and P. Ilea, “Enhancing lithium manganese oxide electrochemical behavior by doping and surface modifications,” *Coatings*, vol. 11, no. 4, 2021.

[126] D. S. Suarez, E. G. Pinna, G. D. Rosales, and M. H. Rodriguez, “Synthesis of lithium fluoride from spent lithium ion batteries,” *Minerals*, vol. 7, no. 5, pp. 1–13, 2017.

[127] O. Yakubovich, N. Khasanova, and E. Antipov, “Mineral-inspired materials: Synthetic phosphate analogues for battery applications,” *Minerals*, vol. 10, no. 6, pp. 1–29, 2020.

[128] J. Hong, C. S. Wang, X. Chen, S. Upreti, and M. S. Whittingham, “Vanadium modified LiFeP O4 Cathode for Li-ion batteries,” *Electrochemical and Solid-State Letters*, vol. 12, no. 2, 2009.

[129] R. Analytical, “Conductance Data For Commonly Used Chemicals,” *Emerson Process Management*, no. December, 2010.

Appendix A

Appendix A

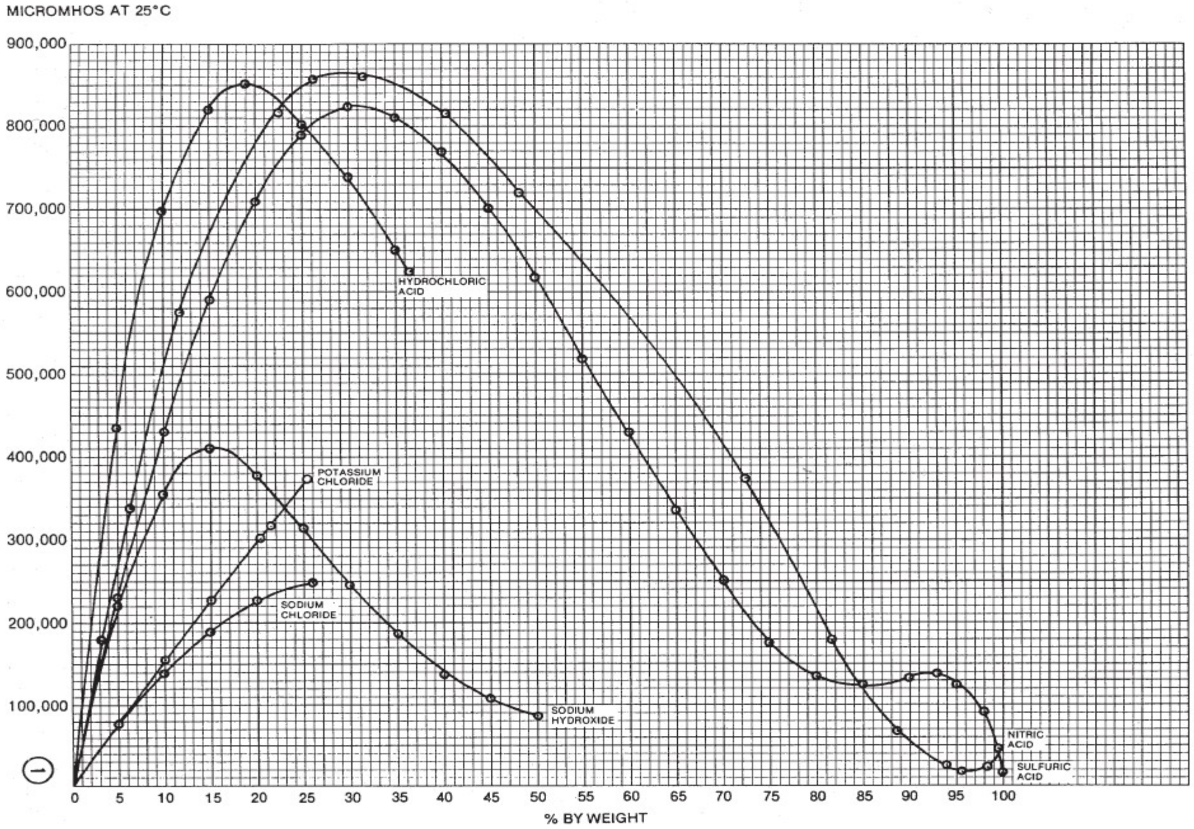


Figure A.1: Conductance Data of NaOH at 25°C. Reproduced from Ref. [129].

Appendix B

Appendix B

Table B.1: Batteries and accumulator fluxes in Portugal, in 2018. Adapted from Ref.[63]

Batteries and Accumulators Placed on Market (t)			**35.348**
Portable Batteries and Accumulators	2 456		
Industrial Batteries and Accumulators	6 678		
EV Batteries and Accumulators	26 214		

Collection of Batteries and Accumulators (t)			**33.640**
Portable Batteries and Accumulators	669		
Industrial + EV Batteries and Accumulators	32 971		

Collection Targets for 2018 (%)	**Target**	**Achieved**	
	45%	31,0%	

Recycling of Batteries and Accumulators (t)			**33.533**
Portable Batteries and Accumulators	610		
Industrial + EV Batteries and Accumulators	32 923		

Recycling Efficiency in 2018 (%)	**Target**	**Achieved**	
Pb- Acid	65%	72%	
Ni-Cd	75%	76%	
Other Chemistries	50%	79%	

Appendix C

Appendix C

T.1 Altitude Simulations: Batteries are stored at a pressure of 11.6kPa or less for a minimum of 6h at room temperature.
T.2 Thermal Test: Batteries are stored for at least 6h at 72°C ± 2°C followed by a storage at -40°C ± 2°C for at least another 6h. This process is repeated 10 times at which point the battery is stored in a room at 20°C ±5°C for 24h.
T.3 Vibration: Batteries are secured to a platform and vibrated between 7Hz and 200Hz during 15 minutes in 12 cycles.
T.4 Shock: Batteries are firmly secured to a mount and subjected to a half-sine wave shock. For small batteries the shock generates a peak acceleration of 150g, for larger batteries the shock generates peaks of 50g.
T.5 External Short Circuit: Batteries are stabilized at 57°C ±4°C and subjected to a short circuiting using a resistance under 100 milliohms during an hour.
T.6 Impact: A bar with 15.8mm of diameter is placed across the cell and a 9.1kg mass is dropped on it from a 61±2.5 cm.
T.7 Overcharge: This test is conducted 24h throughout with a charge current twice the manufacturer's recommendation.
T.8 Forced Discharge: Each cell is connected in series to a 12V DC power supply at an initial current equal to the maximum discharge current specified by the manufacturer.

Appendix D

Appendix D

Table D.1: Summary of LIB Recycling Processes. Adapted from Ref.[109]

Processes	**Pretretament**	**Mechanical Processing**	**Main Recoveries**	**Secondary Recoveries**	**Losses**
Umicore	Dismantling	-	Co,Ni,Cu,Fe, $CoCl_2$	Slag: Al, Si, Ca, Fe, Li, Mn, REE	Electrolyte, Plastics, Graphite
Recupyl	-	Crushing, Vibrating Screen, Magnetic Separator, Densimetric Table	Li_2CO_3, $LiCO_2$, Li_3PO_4	Steel, Cu, Al	Graphite
Retriev	Dismantling	Wet Comminution, Screening, Filtration	Li_2CO_3, MeO	Steel, Cu, Co, Al	Plastic
Akkuser	Sorting	Cutting , Air Filtration, Magnetic Separator	Co, Cu Powder, Fe	Non-Ferrous Metals	Plastics
OnTo Technology	Discharge, Dismantling	Shear Shredder, Filtration, Froth Flotation	Fe, Cu, Graphite	Plastics, Li	Electrolyte

Appendix E

Appendix E

Table E.1: Balance of obtained components and materials of whole battery pack.

		1 wt (kg)	**2** wt (kg)	**3** wt (kg)	**4** wt (kg)	**5** wt (kg)
Ext. Case	Lids	-	9.909	1.106	-	17.000
	BMS	-	0.921	-	-	1.145
	Screws	-	1.194	-	-	NA
Module	Plastics	0.543	2.160	2.740	NA	1.277
	Metals	0.904	43.096	0.070	1.839	4.600
	Screws	0.232	3.160	-	0.129	NA
	PCB	-	0.136	0.110	-	NA
	Cables	-	5.518	NA	0.147	0.391
Cell	Anode	1.033	0.440	0.191	NA	0.230
	Cathode			0.255	NA	0.293
	Plastics	0.007	0.012	-	NA	-
	Separator	NA	NA	0.025	NA	0.058
	Case	0.463	0.154	0.021	NA	0.021
Cell Mass Before Dismantle (kg)		1.702	0.719	0.554	1.827	0.698
Calc. Mass Total (kg)		13.706	142.922	8.553	24.039	103.191
Mass Loss (%)		11.67	15.87	8.34	NA	13.66

Table E.1: Balance of obtained components and materials of whole battery pack (continued).

		6 wt (kg)	**7** wt (kg)	**8** wt (kg)	**9** wt (kg)	**10** wt (kg)
Ext. Case	Lids	4.120	22.470	42.850	4.000	3.936
	BMS	NA	NA	0.980	NA	NA
	Screws	0.220	1.885	0.690	0.144	0.437
Module	Plastics	0.155	1.770	1.280	0.155	0.195
	Metals	4.365	6.035	2.840	3.230	0.265
	Screws	0.645	0.255	1.950	0.370	-
	PCB	NA	NA	NA	NA	0.061
	Cables	1.122	0.170	2.400	1.122	0.422
Cell	Anode	0.284	0.461	0.342	0.245	0.013
	Cathode	0.317	0.514	0.458	0.333	0.017
	Plastics	-	-	-	-	0.001
	Separator	0.043	0.126	0.042	0.090	0.003
	Case	0.026	0.037	0.027	0.026	0.005
Cell Mass Before Dismantle (kg)		0.742	1.269	0.965	0.748	0.044
Calc. Mass Total (kg)		154.946	152.408	209.787	157.748	12.983
Mass Loss (%)		9.70	10.31	9.92	7.11	10.57