

Toxicity of lithium ion battery chemicals -overview with focus on recycling

2020-06-18

Mats Zackrisson
Steffen Schellenberger

RISE IVF

RISE IVF is a leading Swedish industrial research institute with materials, processes and production systems within manufacturing and product development as key areas. Our aim is to create commercial advantages and strengthen the competitiveness and innovation capacity of our members and customers. Rise IVF performs research and development work in close cooperation with industry and universities, nationally and internationally.

Our highly qualified personnel based in Mölndal and Stockholm work in the fields of:

- Working life, environment and energy
- Industrial production methods
- Materials and technology development
- Polymers and textiles
- Business development and efficiency (streamlining).

We work with applied solutions to real industrial needs. Our industry-experienced researchers and consultants are able to deliver the fast and robust results that companies require in order to secure their competitiveness on the market.

RISE IVF AB
P O Box 104
SE-431 22 Mölndal
Telephone +46 (0)31-706 60 00

Project Report 28132/1

© RISE IVF AB

Preface

This report contains an overview of toxicity risks with lithium ion batteries. It was performed in the context of the Swedish Scope-LIB project financed by Energimyndigheten, Dnr 2019-002597. Also contributions from BASE - Center for Swedish Batteries – An Alliance för Ultra-high Performance Batteries Vinnova project registration number 2019-00064, are gratefully acknowledged. The work was carried out by Mats Zackrisson and Steffen Schellenberger at RISE IVF with the aid of other participants in the Scope-LIB project. A list of acronyms and abbreviations used is provided below.

| | |
|--------------------|--|
| Ah | Ampere hours |
| BM | Black mass |
| CAS | Chemical Abstract Services |
| CO ₂ eq | Carbon dioxide equivalents |
| DC, DEC | Diethyl Carbonate |
| CF ₄ | Perfluorinated methane |
| DMC | Dimethyl carbonate |
| EC | Ethylene Carbonate |
| ECHA | European Chemicals Agency |
| FEP | Fluorinated ethylene propylene |
| EMC | Ethylmethyl carbonate |
| HF | Hydrofluoric acid |
| LCO | Lithium Cobalt Oxide |
| LFP | Lithium iron phosphate, LiFePO ₄ , battery cell |
| LIB | Lithium ion battery |
| LiPF ₆ | Lithium hexafluorophosphate |
| LMB | Lithium metal batteries |
| LMO | Lithium Manganese Oxide |
| NCA | Lithium nickel cobalt aluminium oxide |
| NMC | Lithium nickel manganese cobalt oxide battery cell |
| PBT | Persistent Bioaccumulative and Toxic substances |
| PFAAs | Perfluoroalkyl acids |
| PFAS | Perfluorinated alkylated substances |
| PFOA | Perfluorooctanoic acid |
| PFHxA | Perfluorohexanoic acid |
| POF ₃ | Phosphoryl fluoride |
| POPs | persistent organic pollutants |
| PVDF | Polyvinylidene fluoride |
| VC | Vinyl Carbonate |
| Wh | Watt hours |

Contents

| | |
|---|-----------|
| Preface | 3 |
| Figures | 4 |
| Summary | 5 |
| Chemical content of today's lithium ion cells | 6 |
| Production and use phase | 9 |
| End-of-life phase | 14 |
| LiPF ₆ forms hydrogen fluoride and phosphoryl fluoride | 17 |
| Thermal pre-treatment | 18 |
| Summary and recommendations for the end-of-life phase | 19 |
| Future outlook | 20 |
| References | 20 |

Figures

| | |
|---|----|
| Figure 1. The most common lithium chemistries 2015, 2016 och 2025 ⁹ | 7 |
| Figure 2. Production of LIB cells, adapted from ¹³ | 10 |
| Figure 3 Main construction types of LIB cells: a) wound cylindrical, b) button cell, c) wound prismatic and d) pouch cell ¹⁴ | 11 |
| Figure 4. Lithium ion traction battery pack..... | 12 |
| Figure 5. Diagnostic and disassembly phase..... | 15 |
| Figure 6. Pre-treatment phase..... | 16 |
| Figure 7. Decoking of black mass as envisioned in the ReLion project ¹⁹ | 16 |
| Figure 8. Smelting and lithium separation as envisioned in the ReLion project ¹⁹ | 17 |
| Figure 9. Four ways of thermal conditioning ²⁵ | 19 |

Tables

| | |
|--|----|
| Table 1. Electrolyte and PVDF content in NMC333 ¹ | 7 |
| Table 2. Electrolyte chemicals and binders in LIB cells-unreacted..... | 8 |
| Table 3 Electrolyte chemicals and binders in LIB cells - potential reactions | 13 |

Summary

In the end-of-life phase the risks related to toxicity, fire and high voltage inherent in the traction LIB life cycle become apparent and amplified. LIBs are a green technology but contain different hazardous substances, that can be emitted especially during fire events. These emissions are of high risks since chemical transformation processes are not well understood so far.

Additional risk occurs during production of raw materials such as highly fluorinated organic chemicals used in LIBs e.g. for binder materials. Due to the electrochemical stability of fluorinated materials their use might be unavoidable to produce batteries with a long life. However, their production, use and disposal need to be controlled. A high temperature treatment in recycling is a possibility to control emissions in the end-of-life phase.

Any laboratory, recycling facility or actor involved in the end-of-life phase of LIBs must carry out risk assessment for their unique activities and equipment and develop and maintain site specific safety protocols for their personal.

Many of the ingredients in modern lithium ion battery, LIB, chemistries are toxic, irritant, volatile and flammable. In addition, traction LIB packs operate at high voltage. This creates safety problems all along the life cycle of the LIB. This is a short overview of the health and safety risks during the life cycle of LIBs with a special focus on the end-of-life phase. It is recommended that any actor involved in the end-of-life phase of LIBs carry out risk assessment for their unique activities and equipment and develop and maintain site specific safety protocols for their personal.

Chemical content of today's lithium ion cells

Nickel manganese cobalt oxide, NMC, chemistry will be the dominating battery chemistry for the coming decade, see production figures for 2015 and 2016 and prognosis for 2025 in Figure 1 below. An NMC333-cell will therefore be used as an example of chemical content of LIB cells. The other LIB chemistries, Lithium Iron Phosphate, LFP, Lithium Cobalt Oxide, LCO, Lithium Nickel Cobalt Aluminium Oxide, NCA and Lithium Manganese Oxide, LMO have very similar electrolyte and binder content, see for example bill of materials for NMC, LFP and NCA¹ and for LMO².

Many safety concerns with today's LIB chemistries are focused on the liquid electrolyte³. A very common LIB electrolyte is a 1-molar solution of Lithium hexafluorophosphate (LiPF₆) in 1:1 Ethylene Carbonate: Diethyl Carbonate and 2% Vinylene carbonate. Other Lithium conductive salts including compounds with highly fluorinated counter ions might be used in the production of LIB electrolytes as well. An overview of new Li- salts for LIBs is shown in a review by Bushkova et al⁴.

The amount of electrolyte needed is based on the volume of pores in the separator and in the cathode and can often reach 20% of battery cell mass or 10% of traction battery mass¹. Several chemicals used in LIBs are of high concern (see table 2). An example is Vinylene carbonate, an additive with high human and aquatic toxicity⁵. Another common LIB electrolyte ingredient is the flammable solvent Diethyl carbonate (DMC) which is likely to be an acute health hazard since it is suspected to be cancerogenic and toxic to reproduction according to European Chemicals Agency (ECHA)⁶. DMC is often used in a mixture with Ethyl methyl carbonate (EMC).

In addition, fluoropolymers such as Polyvinylidene fluoride (PVDF) or Fluorinated ethylene propylene (FEP) are used as binder materials for both the negative (anode) and positive (cathode) in nearly all commercial LIBs⁷. Fluoropolymers as well as highly fluorinated chemicals used in the electrolytes are a potential hazard when it comes to the emissions of persistent organic pollutants (POPs)⁸ related to LIBs. However, the potential risk of fluorinated chemicals associated with LIBs is so far not well understood. This report provides further insights into the chemicals uses in LIBs and their potential risk considering different life cycle phases.

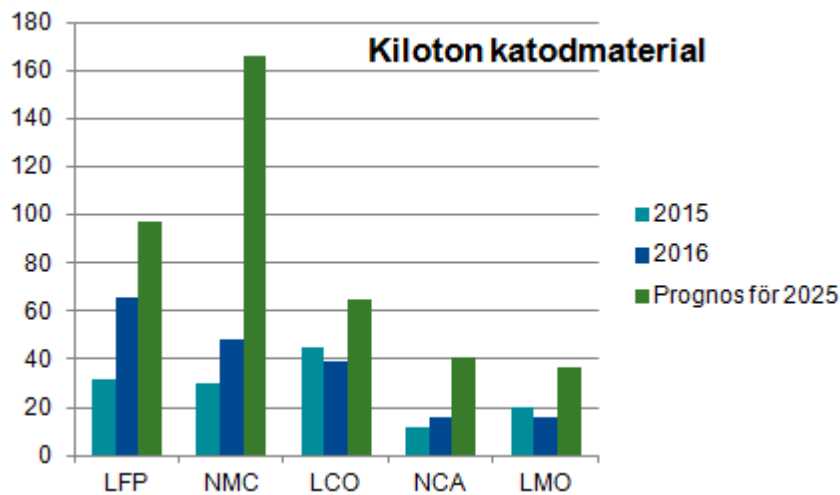


Figure 1. The most common lithium chemistries 2015, 2016 och 2025. Since it is approximately 10 years between production and recycling, what was produced 2015 will be available for recycling 2025.

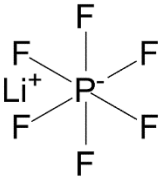
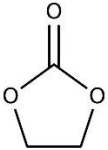
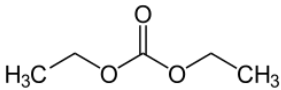
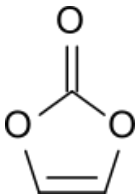
A typical NMC333-cell consist of 16% electrolyte distributed according to Table 1 below. An NMC333 consist of equal amounts of nickel, manganese and cobalt. The NMC333 cell in Table 1 is a 33 Ah cell weighing 800 grams. This is a cell size associated with traction batteries even though smaller cells are also common¹. Smaller cells would of course contain less electrolyte per cell but similar amounts per ton of cells.

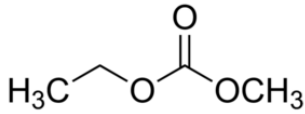
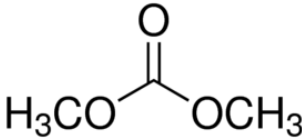
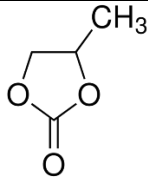
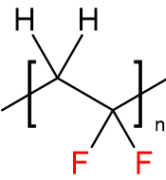
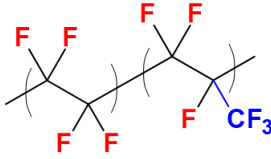
Table 1. Electrolyte and PVDF content in NMC333¹

| Material | % of electrolyte | % of cell | Gram per NMC333 cell from AESC weighing 800 g | Kg per ton NMC333 cells |
|--------------------------------|------------------|-----------|---|-------------------------|
| Lithiumhexafluorophosphate | 11 | 1,8 | 14 | 18 |
| Ethylene carbonate | 48 | 7,7 | 60 | 77 |
| Diethyl carbonate | 39 | 6,2 | 49 | 62 |
| Vinylene carbonate | 2 | 0,3 | 2,5 | 3 |
| Polyvinylidene fluoride (PVDF) | NA | 1,4 | 11,3 | 14 |

In Table 2, other commonly used chemicals for LIBs are included as well as hazard statement of the raw materials in the unreacted state.

Table 2. Electrolyte chemicals and binders in LIB cells-unreacted

| Material/CAS | Chemical formula | Hazard | Comment |
|--|---|--|---|
| Lithiumhexafluorophosphate CAS 21324-40-3 |  | H302 Acute toxicity, oral H314 Causes severe skin burns and eye damage 372 Causes damage to organs through prolonged or repeated exposure | Other lithium ion salts based on highly fluorinated chemicals might be used |
| Ethylene carbonate (EC) CAS 96-49-1 |  | H302 Acute toxicity, oral H319 Causes serious eye irritation 372 Causes damage to organs through prolonged or repeated exposure | |
| Diethyl carbonate (DEC) CAS 872-36-6 |  | H226 Flammable liquid and vapour H315 Causes skin irritation H335 May cause respiratory irritation H351 Suspected of causing cancer H361 Suspected of causing cancer | |
| Vinylene carbonate (VC) CAS 872-36-6 |  | H302 Acute toxicity, oral H311 Acute toxicity, dermal H315 Causes skin irritation H317 May cause an allergic skin reaction H318 Causes serious eye damage 372 Causes damage to organs through prolonged or repeated exposure H411 Toxic to aquatic life with long lasting effects | |

| Material/CAS | Chemical formula | Hazard | Comment |
|--|---|--|---|
| Ethyl methyl carbonate (EMC) CAS 623-53-0 |  | H226 Flammable liquid and vapour H315 Causes skin irritation H319 Causes serious eye irritation H335 May cause respiratory irritation | Also commonly used in electrolyte |
| Dimethyl carbonate (DMC) CAS 616-38-6 |  | H225: Highly flammable liquid and vapour | Also commonly used in electrolyte |
| Propylene carbonate (PC) CAS 108-32-7 |  | H319 Causes serious eye irritation | Also commonly used in electrolyte |
| Polyvinylidene fluoride (PVDF) CAS 24937-79-9 |  | Inert polymer with low toxicity | Can contain highly fluorinated impurities from production (e.g. PFOA; PFHxA) that are SVHCs (substances of very high concern) |
| Fluorinated ethylene propylene (FEP) CAS 25067-11-2 |  | Inert polymer with low toxicity (alternative binder) | Can contain highly fluorinated impurities from production (e.g. PFOA; PFHxA) that are SVHCs (substances of very high concern) |

Production and use phase

The unreacted state is more applicable to the production phase of LIBs. PVDF and/or FEP are often used as binders in the cathode paste which is coated on a current collector, often in aluminium (see Figure 2 below). While these fluoropolymers are inert and have a low toxicity (see table 2) they cause large emissions of fluorinated surfactants during their production such as Perfluorooctanoic acid (PFOA) or perfluorohexanoic acid (PFHxA)^{10,11}. Some of these surfactants such as PFOA are persistent bioaccumulative and toxic substances (PBT) and are classified as POPs under the Stockholm convention¹². Impurities of these surfactants can stay in the binder material and get emitted for example during the cathode preparation.

Other hazardous chemicals are part of the electrolyte (table 2). Electrolyte emissions may occur during electrolyte mixing and filling and in connection with the formation (see Figure 2 below). During formation, gas is formed (mainly from electrolyte reduction/oxidation): H₂, CO, CO₂, methane, ethane, ethylene, propane, propylene, etc. It is the most safety-critical step during cell manufacturing. Gasses formed during the formation are highly flammable.

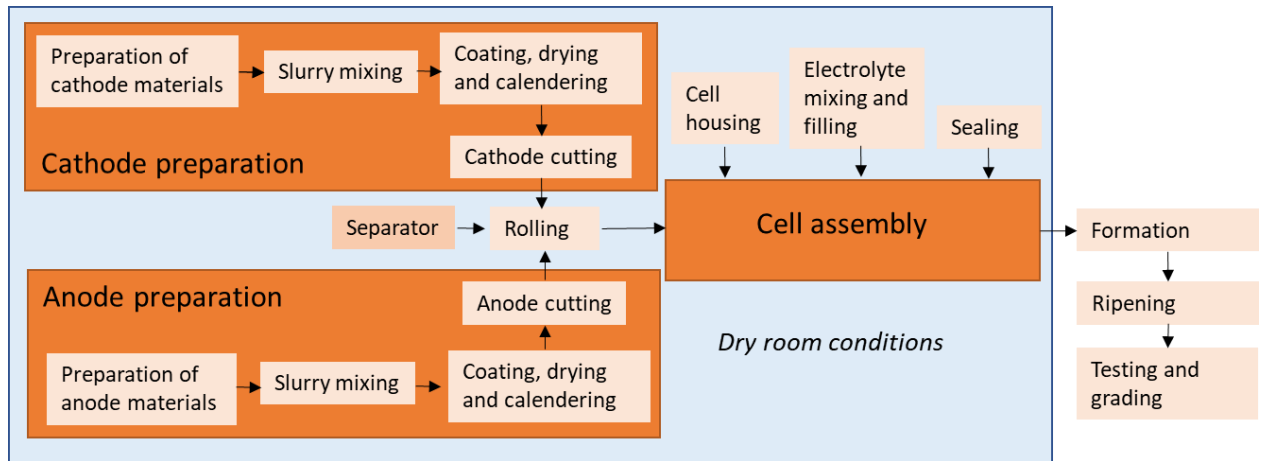


Figure 2. Production of LIB cells, adapted from¹³

Traction battery cells come in three different forms: cylindrical, prismatic or pouch, see Figure 3. Button cells are not used in traction batteries although depicted below.

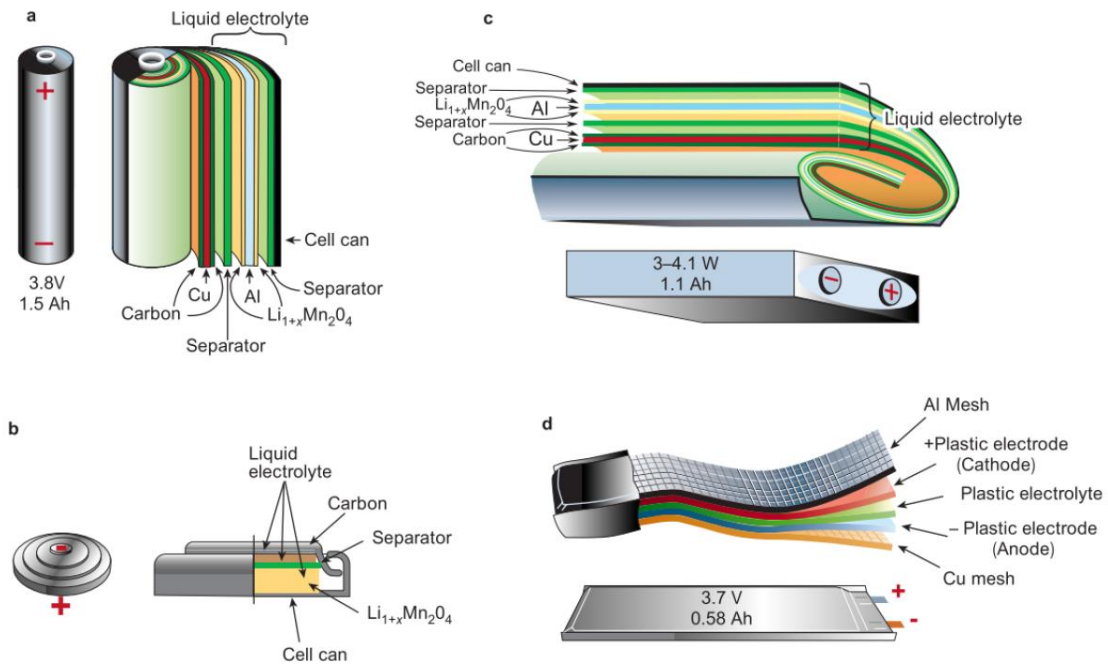


Figure 3 Main construction types of LIB cells: a) wound cylindrical, b) button cell, c) wound prismatic and d) pouch cell¹⁴

After testing and grading, the LIB cells are shipped as such or built into LIB systems which can comprise hundreds or even thousands of cells in one LIB high-voltage pack. The safety risk of a lithium-ion cell increases with age during operation because the voltage windows in which the electrodes are cycled shift, resulting in a higher possibility that at least one electrode is operated in a meta- or unstable state. Furthermore, higher impedances due to material degradations lead to increasing heat generation and therefore to an increase in the risk of failure¹⁵. In addition the high voltage of a LIB traction battery pack is a major safety concern throughout its installation and use in a vehicle and entering end-of-life treatment¹⁶.

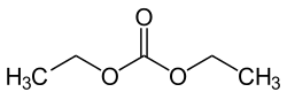


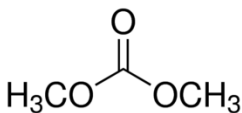
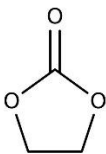
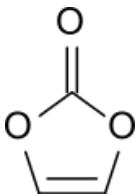
Figure 4 Lithium ion traction battery pack

Electrochemical processes during the use of LIBs might also cause the formation of toxic chemicals e.g. in the electrolyte. This can be of high risk if emissions into the environment occur, e.g. through leakage. Especially problematic is an event of a fire caused by e.g. collision of a vehicle. During this process hazardous chemicals will be formed and emitted¹⁶. Table 3, which shows possible reactions of chemicals in the cells, would then be more applicable than Table 2. The possible formation of hydrofluoric acid (HF) is a major hazard both in the use phase and the ensuing end-of-life phase due to its high toxicity. Moreover incomplete combustion (temperatures < 850°C) of fluoropolymer cathode materials but also fluorinated ingredients in the electrolyte can lead to the formation of various persistent PFAS¹⁷ (Perfluorinated alkylated substances) contaminants which are problematic when emitted. Reactions are complex and not completely understood¹⁸. Potential products of the thermolysis of fluoropolymer binder are:

- Short and long chain perfluoroalkyl acids (PFAAs); some of them are POPs and PBT substances. The formation will depend on the electrode binder material (PVDF or FEP)
- Fluorinated gasses such as perfluorinated methane, CF₄, which is extremely stable in the atmosphere and has a very high global warming potential (4950 kg CO₂eq/kg)

Table 3 Electrolyte chemicals and binders in LIB cells - potential reactions

| Material | Chemical reaction(s) | Hazard | Comment |
|---|---|--|---|
| LiPF ₆ | $\text{LiPF}_6(\text{s}) \leftrightarrow \text{LiF}(\text{s}) + \text{PF}_5(\text{g})$ $\text{LiPF}_6 + \text{H}_2\text{O} \leftrightarrow \text{LiF} + 2\text{HF} + \text{POF}_3$ $\text{PF}_5 + \text{H}_2\text{O} \leftrightarrow 2\text{HF} + \text{POF}_3$ | For HF H300 Fatal if swallowed H310 Fatal in contact with skin; Acute toxicity, dermal H314 Causes severe skin burns and eye damage H330 Fatal if inhaled Acute toxicity, inhalation | |
| DEC, C ₅ H ₁₀ O ₃ |  | H226 Flammable liquid and vapour H315 Causes skin irritation H335 May cause respiratory irritation H351 Suspected of causing cancer H361 Suspected of causing cancer | Fire hazard; will cause the combustion of other LIB components |
| PVDF or FEP | $(\text{C}_2\text{H}_2\text{F}_2)_n + \text{fire} \rightarrow \text{HF}$ Incomplete combustion in a fire event may result in persistent contaminants: → various PFAS → CF ₄ (and other) | HF (see above) For CF ₄ : Half-life (t _{1/2}) in atmosphere= 1000 years Global warming potential (GWP)= 4950 PFAS e.g. PFOA (may be formed during incomplete combustion) H302 : Acute toxicity, oral H332 : Acute toxicity, inhalation H351 : Suspected of causing cancer H360D : May damage the unborn child H362 : Reproductive toxicity H372 : Specific target organ toxicity, repeated exposure | Binder decomposition: May decompose to hydrogen fluoride when reaching 400 °C (Nissi 2019); Formation of PFAS if incomplete combustion at T < 850°C |
| Lithium ion salts based on highly fluorinated chemicals | Incomplete combustion in a fire event may result in persistent contaminants: → various PFAS → CF ₄ (and other) | see above | Formation of PFAS if incomplete combustion at T < 850°C |

| Material | Chemical reaction(s) | Hazard | Comment |
|--|--|--|--|
| DMC, C ₄ H ₈ O ₃ |  | H225: Highly flammable liquid and vapour | Fire hazard; will cause the combustion of other LIB components |
| EC, C ₃ H ₄ O ₃ |  | H302 Acute toxicity, oral H319 Causes serious eye irritation 372 Causes damage to organs through prolonged or repeated exposure | Complete combustion is likely even under 850 degrees |
| VC, C ₃ H ₂ O ₃ |  | H302 Acute toxicity, oral H311 Acute toxicity, dermal Acute toxicity, dermal H315 Causes skin irritation H317 May cause an allergic skin reaction H318 Causes serious eye damage 372 Causes damage to organs through prolonged or repeated exposure H411 Toxic to aquatic life with long lasting effects | Complete combustion is likely even under 850 degrees |

End-of-life phase

The end-of-life phase can be divided in a first diagnostic and disassembly phase and a second pre-treatment phase according to the figures below.

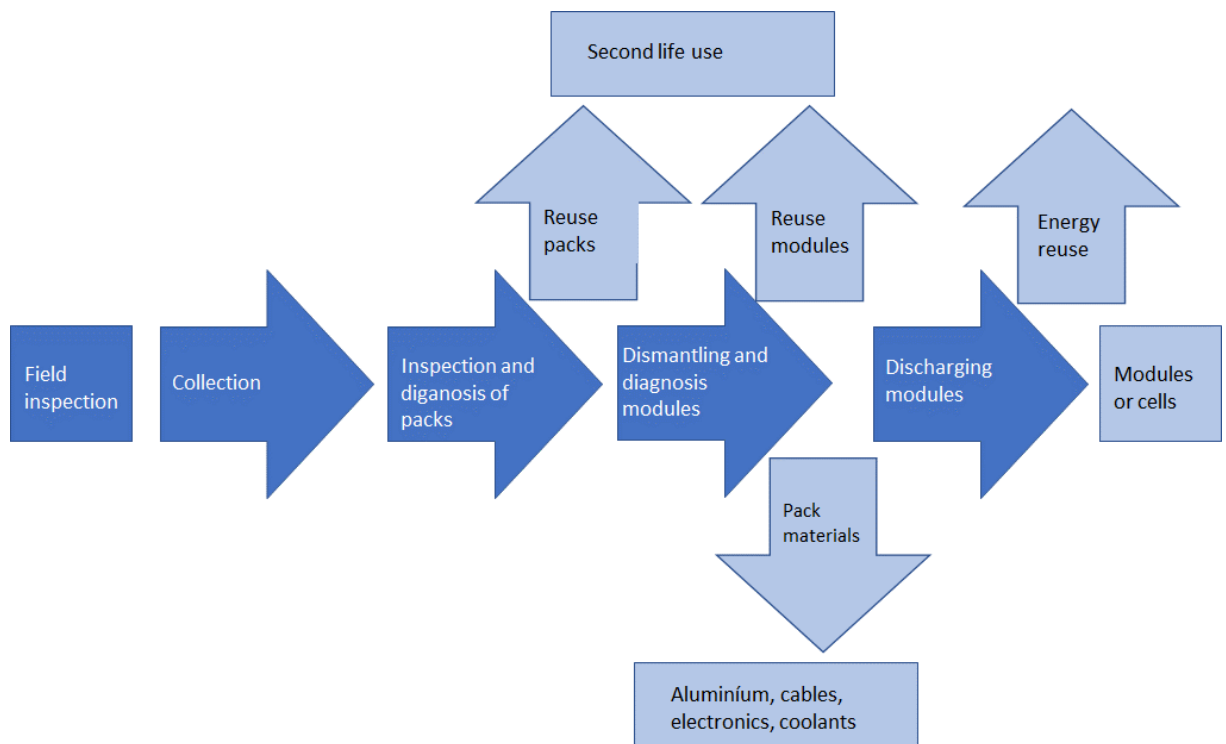


Figure 5. Diagnostic and disassembly phase

The end-of-life phase begins with the battery being unusable in a vehicle. A first action may involve field inspection to decide how to transport the battery pack safely and if its further fate is a second life or material recycling. Transportation of traction batteries are strictly regulated due to safety reasons. Inspection and diagnosis decide the further fate of the battery pack. It may be reused as a pack or as individual modules. Pack materials, around 50% of pack weight, is separated for material recycling. For an undamaged battery pack, safety risks during the first diagnostic and disassembly phase is mainly related to high voltage. After discharging, modules or cells are sent to the ensuing treatment phase.

With regards to the first action, *field inspection*, it is very important that traction battery packs contain the necessary data and information so that it can be handled safely and reused or recycled in the most economical and sustainable way. This data must be accessible to the person(s) carrying out the first inspection. It could be information on chemistry and chemical content, state-of-charge, state-of-health, usage history, automated disassembly, etc.

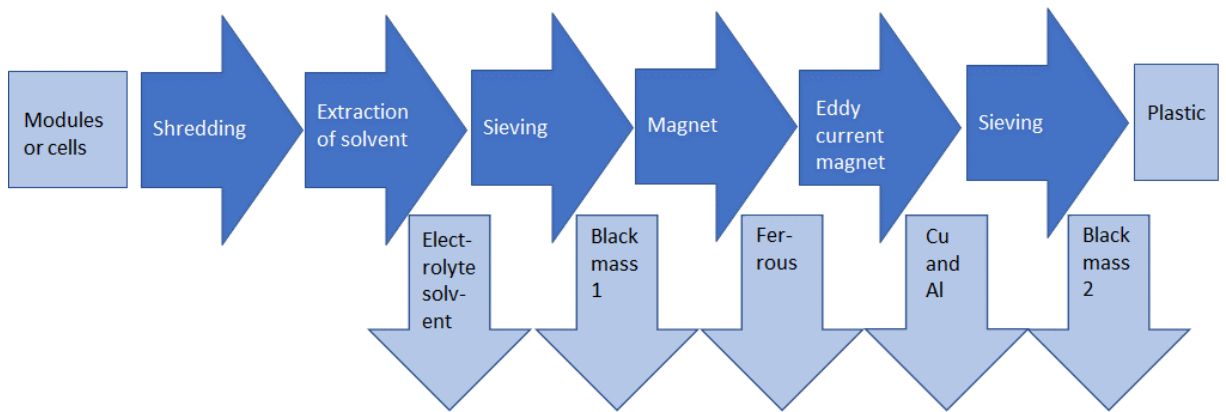


Figure 6. Pre-treatment phase

Modules may or may not be disassembled before treatment. Depending on cell content the shredding often take place in some form of protective environment, e.g. cryogenic for controlling fire hazards. Solvent extraction and recycling are envisioned for future, safe, recycling technologies. After sieving, black mass with or without metals and plastics will be produced and sent for pyrometallurgical and/or hydrometallurgical treatment.

Future recycling may consist of the processes successfully tried in the ReLion project shown below.¹⁹ First de-coking by partial combustion to get rid of the graphite which is an obstacle to down-stream winning of valuable metals. Then pyrometallurgy to win nickel, cobalt and manganese followed by hydrometallurgical winning of lithium, see Figure 7 and Figure 8.

De-coking by partial combustion

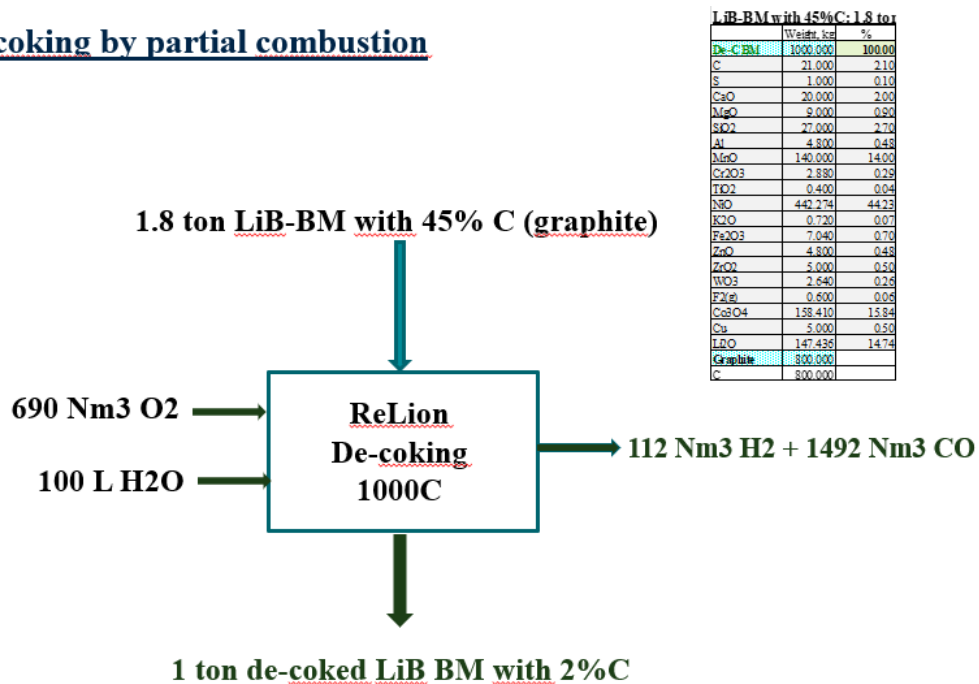


Figure 7. Decoking of black mass as envisioned in the ReLion project¹⁹

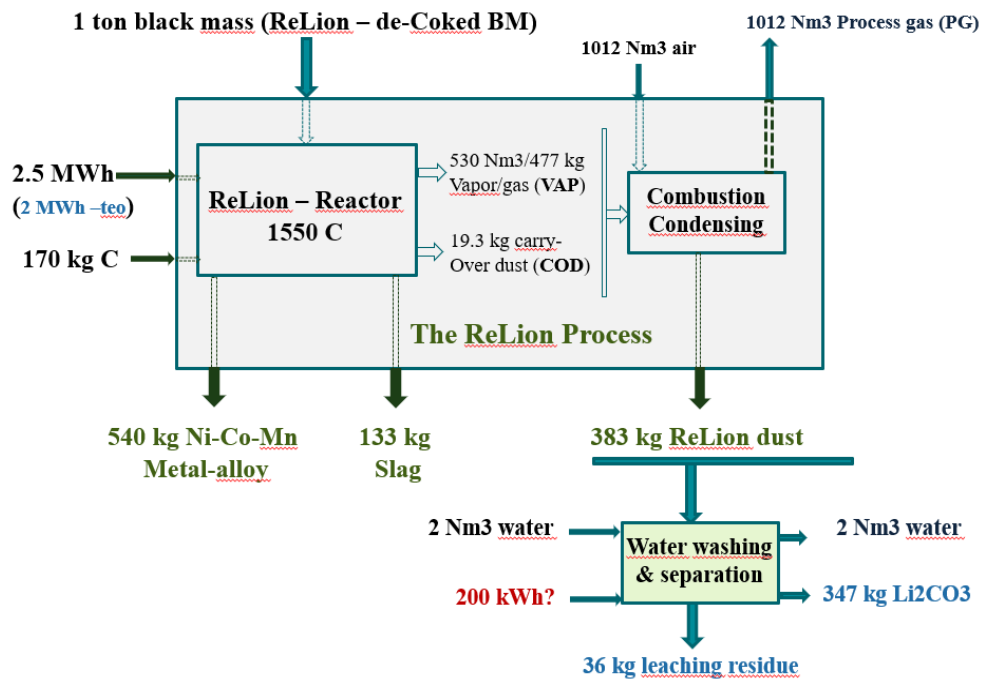


Figure 8. Smelting and lithium separation as envisioned in the ReLion project¹⁹

While the safety issues of LIBs related to toxicity, fire and explosion and high voltage exist more or less in all life cycle phases, they are more pronounced and have been more investigated in the end-of-life phase^{3,20,21}. The main toxicity issue is that the electrolyte containing lithiumhexafluorophosphate, LiPF_6 , forms hydrogen fluoride. If the temperature during the smelting and lithium separation process (see figure 8) is high enough (e.g. 1550°C) all organo fluorine chemicals will be mineralized and it is likely that no PFAS compounds are formed. The formation of HF remains a high risk.

LiPF_6 forms hydrogen fluoride and phosphoryl fluoride

LiPF_6 in the electrolyte is always in equilibrium with the gaseous phosphorus pentafluoride, PF_5 , via the reaction $\text{LiPF}_6(\text{s}) \rightleftharpoons \text{LiF}(\text{s}) + \text{PF}_5(\text{g})$ ²². Both LiPF_6 and PF_5 are very sensitive to water, even traces of moisture and forms hydrogen fluoride, HF and phosphoryl fluoride, POF_3 via the reactions $\text{LiPF}_6 + \text{H}_2\text{O} \rightleftharpoons \text{LiF} + 2\text{HF} + \text{POF}_3$ and $\text{PF}_5 + \text{H}_2\text{O} \rightleftharpoons 2\text{HF} + \text{POF}_3$.

Lebedeva et al³ found that one cell containing 18-35 g electrolyte, i.e. considerably less than the cell in Table 1, could, in the event of an accidental release form a potentially toxic atmosphere in enclosed spaces. Hydrofluoric acid has serious health hazard having both acute and cumulative toxicity²³. Larsson et al²¹ presents quantitative measurements of heat release and fluoride gas emissions during battery fires for seven different types of commercial lithium-ion batteries. The results showed large amounts of hydrogen fluoride (HF), ranging between 20 and 200 mg/Wh¹ of nominal battery energy capacity. In addition, 15–

¹ 20-200 mg HF per Wh translates to 4-400 g HF per kg cell or 4-400 kg HF per ton cell (with energy density 200 Wh/kg at cell level).

22 mg/Wh of another potentially toxic gas, phosphoryl fluoride (POF_3), was measured in some of the fire tests. Gas emissions when using water mist as extinguishing agent were also investigated. Fluoride gas emission can pose a serious toxic threat and the results are crucial findings for risk assessment and management, especially for large Li-ion battery packs. Fluorine-containing compounds can be present also in the separators and electrode materials²¹. Nissi²³ notes that the PVDF binder material may decompose to hydrogen fluoride when reaching 400 °C. Degradation processes related to PVDF and other fluoropolymers cause the formation of persistent PFAS contamination which is an additional risk.

Hamuyuni et al²⁴ presents an analysis of the contents and chemistry of the components of the commercially employed electrolytes for lithium-ion batteries revealing that:

- Most currently used lithium-ion battery electrolytes on exposure to the environment are toxic, irritant or harmful in addition to being flammable. While flammability associated risks of electrolytes are well researched and documented such that they are well known by handlers, hazards and risks associated with their toxicity are less often addressed.
- Typical commercial lithium-ion battery electrolyte solvents are volatile, with volatility ranging from moderate to extremely volatile. Several studies have now shown that even small amounts of some of these solvents when exposed to the environment have irreversible serious health effects.
- The reactions of salts including the most commercially successful— LiPF_6 —when in contact with water, for example, is known to result in the generation of gaseous HF, which is very toxic and corrosive compound posing a serious health risk.
- In addition to salts and their resultant toxic products, many of industrial available electrolytes comprise numerous additives which could also be volatile and toxic.

Thermal pre-treatment

Friedrich et al²⁵ compares four ways of thermal conditioning (pre-treatment) of recycled Li-batteries for safe and highly material efficient processing, see figure below.

| Pre-treatment processes: Comparison | | | | |
|-------------------------------------|-------------------------------------|-------------------------------------|---------------------------------|---|
| Process | Avoidance potential for toxic gases | Contribution to Resource efficiency | Contribution to Cost efficiency | Benefits for post-processing |
| Distillation | +++* | +++ | o | <ul style="list-style-type: none"> • Safe handling • Possible electrolyte recovery |
| Pyrolysis | ++ | +++ | + | <ul style="list-style-type: none"> • Safe handling • Reductive potential in pyrometallurgy (C) • Eased mech. Post processing |
| Thermolysis | +++ | ++ | ++ | <ul style="list-style-type: none"> • Safe handling • No carbon in hydrometallurgy • Eased mech. Post processing |
| Combustion | + | + | o | <ul style="list-style-type: none"> • Safe handling |

*no Thermal Runaway








Figure 9. Four ways of thermal conditioning ²⁵

Thermal treatment of charged LIBs requires an off-gas treatment system to avoid harmful emissions²⁰ and to recover electrolyte. According to Pinegar et al²⁰ LIB electrolyte can be recovered at around 160 °C; temperatures above 200 °C have a higher risk of electrolyte decomposition to CO, CO₂, and hydrocarbons. Highly toxic or flammable substances such as POF₃, CF₄, HF, COF₂, and C₃H₄O also form at temperatures above 200 °C, although some of the generated gases, such as CH₄, C₂H₄, or H₂, are energetically usable. Some of these gases (e.g. CF₄) are extremely stable in the atmosphere and have a very high global warming potential as noted above (table 3).

Summary and recommendations for the end-of-life phase

In the end-of-life phase the risks related to toxicity, fire and high voltage inherent in the traction LIB life cycle become apparent and amplified. LIBs are a green technology but contain different hazardous substances, that can be emitted especially during e.g. fire events. These emissions are of high risks since chemical transformation processes are not well understood so far.

Additional risk occurs during production of raw materials such as highly fluorinated organic chemicals used in LIBs e.g. for binder materials. Due to the electrochemical stability of fluorinated materials their use might be unavoidable to produce batteries with a long life. However, their production, use and disposal need to be controlled. A high temperature treatment in recycling is a possibility to control emissions in the end-of-life phase.

Any laboratory, recycling facility or actor involved in the end-of-life phase of LIBs must carry out risk assessment for their unique activities and equipment and develop and maintain site specific safety protocols for their personal. For inspiration, see for example Nissi²³.

Future outlook

Future cell designs may include metallic lithium, which is an acute fire hazard, and/or solid electrolytes, potentially with less acute risks compared to liquid electrolytes. Thus, the safety problems of future lithium cell designs will be different from today's design, but hardly eliminated. Some commercial solid-state lithium batteries and/or lithium metal batteries already exist. At least those containing metallic lithium must be treated separately.

References

- (1) Zackrisson, M. *Life Cycle Assessment of Long Life Lithium Electrode for Electric Vehicle Batteries – Cells for LEAF, Tesla and Volvo Bus*; Stockholm, 2018.
- (2) Cusenza, M. A.; Bobba, S.; Ardente, F.; Cellura, M.; Di Persio, F. Energy and Environmental Assessment of a Traction Lithium-Ion Battery Pack for Plug-in Hybrid Electric Vehicles. *J. Clean. Prod.* **2019**, *215* (April), 634–649. <https://doi.org/10.1016/j.jclepro.2019.01.056>.
- (3) Lebedeva, N. P.; Persio, D.; Kosmidou, T.; Dams, D.; Pfrang, A.; Kersys, A.; Boon-brett, L. Amount of Free Liquid Electrolyte in Commercial Large Format Prismatic Li-Ion Battery Cells. *J. Electrochem. Soc.* **2019**, *166* (4), 5–12. <https://doi.org/10.1149/2.1151904jes>.
- (4) Bushkova, O. V.; Yaroslavtseva, T. V.; Dobrovolsky, Yu. A. New Lithium Salts in Electrolytes for Lithium-Ion Batteries (Review). *Russ. J. Electrochem.* **2017**, *53* (7), 677–699. <https://doi.org/10.1134/S1023193517070035>.
- (5) PubChem. Vinylene carbonate <https://pubchem.ncbi.nlm.nih.gov/compound/13385> (accessed Jun 11, 2020).
- (6) ECHA. Classifications - CL Inventory of Diethyl carbonate <https://echa.europa.eu/sv/information-on-chemicals/cl-inventory-database/-/discli/details/135702> (accessed Jun 11, 2020).
- (7) Gardiner, J. Fluoropolymers: Origin, Production, and Industrial and Commercial Applications. *Aust. J. Chem.* **2015**, *68* (1), 13–22. <https://doi.org/10.1071/CH14165>.
- (8) Lallas, P. L. The Stockholm Convention on Persistent Organic Pollutants. *Am. J. Int. Law* **2001**, *95* (3), 692–708. <https://doi.org/10.2307/2668517>.
- (9) Zackrisson, M. *De Vanligaste Litiumjonbatterierna*; Stockholm, 2017.
- (10) Dauchy, X.; Boiteux, V.; Rosin, C.; Munoz, J.-F. Relationship between Industrial Discharges and Contamination of Raw Water Resources by Perfluorinated Compounds. Part I: Case Study of a Fluoropolymer Manufacturing Plant. *Bull. Environ. Contam. Toxicol.* **2012**, *89* (3), 525–530. <https://doi.org/10.1007/s00128-012-0704-x>.
- (11) Wang, P.; Zhang, M.; Lu, Y.; Meng, J.; Li, Q.; Lu, X. Removal of Perfluoroalkyl Acids (PFAAs) through Fluorochemical Industrial and Domestic Wastewater Treatment Plants and Bioaccumulation in Aquatic Plants in River and Artificial Wetland. *Environ. Int.* **2019**, *129*, 76–85. <https://doi.org/10.1016/j.envint.2019.04.072>.
- (12) Wang, T.; Wang, Y.; Liao, C.; Cai, Y.; Jiang, G. Perspectives on the Inclusion of Perfluorooctane Sulfonate into the Stockholm Convention on Persistent Organic Pollutants. **2009**.
- (13) Northvolt. Northvolt – Anläggning För Storskalig Batteritillverkning Skellefteå. Underlag För Samråd Enligt 6 Kap Miljöbalken. Skellefteå 2017.
- (14) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414* (November), 359–367.

- (15) Kleiner, K.; Ehrenberg, H. Challenges Considering the Degradation of Cell Components in Commercial Lithium-Ion Cells : In *Topics in Current Chemistry*; Springer International Publishing, 2017; pp 1–45. <https://doi.org/10.1007/s41061-017-0139-2>.
- (16) Bisschop, R. Fire Safety of Lithium-Ion Batteries in Road Vehicles. RISE Report 2019:50 2019.
- (17) Huber, S.; Moe, M.; Schmidbauer, N.; Hansen, G.; Herzke, D. *A Literature Survey, Emissions from Incineration of Fluoropolymer Materials, OR 12/2009*; Norsk institutt for luftforskning, 2009; p 65.
- (18) Tsang, W.; Burgess, D. R.; Babushok, V. On the Incinerability of Highly Fluorinated Organic Compounds. *Combust. Sci. Technol.* **1998**, *139* (1), 385–402. <https://doi.org/10.1080/00102209808952095>.
- (19) Zackrisson, Mats. *Life Cycle Assessment of Lithium Ion Battery Recycling - The ReLion Process*; RISE research institutes of sweden, 2019.
- (20) Pinegar, H.; Smith, Y. R. Recycling of End-of-Life Lithium-Ion Batteries, Part II: Laboratory-Scale Research Developments in Mechanical, Thermal, and Leaching Treatments. *J. Sustain. Metall.* **2020**, *6* (1), 142–160. <https://doi.org/10.1007/s40831-020-00265-8>.
- (21) Larsson, F.; Andersson, P.; Blomqvist, P.; Mellander, B. Toxic Fluoride Gas Emissions from Lithium-Ion Battery Fires. *Sci. Rep.* **2017**, 1–13. <https://doi.org/10.1038/s41598-017-09784-z>.
- (22) Berg, H. *Batteries for Electric Vehicles - Materials and Electrochemistry*; Cambridge University Press, 2015.
- (23) Nissi, J. Development of Safety Protocols in Aalto University LIB Recycling Laboratory, 2019.
- (24) Hamuyuni, J.; Tesfaye, F. Advances in Lithium-Ion Battery Electrolytes : Prospects and Challenges in Recycling. In *Secondary and Byproduct Sources of Materials, Minerals, and Metals*; Springer International Publishing, 2019; pp 265–270.
- (25) Friedrich, B.; Peters, L.; Diaz, F. Thermal Conditioning of Recycled Li-Batteries – Pre-Treatment for Safe and Highly Material Efficient Processing. In *Circular Economy of Battery Production and Recycling*; Gothenburg/Sweden, 2018. <https://doi.org/10.13140/RG.2.2.16211.22560/1>.