

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

New insights into the pretreatment of spent LiFePO_4 batteries for direct recycling purposes

Comparative experimental study of alternative strategies for discharging and dismantling of spent LiFePO_4 battery packs, recovery of the cathode active material and impurity removal for use in a feasible direct recycling process

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Gothenburg, Sweden 2026

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Cover: Illustration of the direct recycling process developed in this study.
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Abstract

The rapid electrification of the transportation sector is increasing the volume of spent lithium iron phosphate (LFP) batteries, yet direct recycling of LFP cathode active material (CAM) remains underdeveloped, despite spent LFP batteries starting to enter the recycling market. Direct recycling rests on a reduced number of process steps and a low impurity content in the recovered CAM, making the pretreatment chain a decisive factor for success. This work examined three successive pretreatment stages for spent LFP modules from real-life mild hybrid applications: discharging, delamination of the cathode from its current collector, and removal of impurities by solvent washing, followed by relithiation to restore electrochemical performance.

Salt brine discharging induced electrode corrosion, elevating Cu and Al impurity levels, whereas resistor-based discharging preserved CAM integrity better and produced no waste, making it the preferable option. Four delamination routes were compared: freeze-drying, ethylene glycol treatment, phytic acid treatment, and the novel LibriXer technology. Freeze-drying showed the highest peeling efficiency (93%), while LibriXer exhibited by far the lowest projected energy consumption and cost. All methods retained LiFePO_4 except for phytic acid, which leached Li and yielded mostly FePO_4 . Acetic acid emerged as the greenest solvent wash, though it traded Li losses for Cu removal. Relithiation with lithium acetate successfully regenerated the CAM, but overlithiation, unsuitable particle morphology, and residual Cu impurities limited electrochemical performance.

These findings outline more and less favorable pretreatment strategies for direct LFP recycling and identify the impurity control measures required to regenerate battery-grade CAM.

Keywords: Li-ion batteries, LiFePO_4 , LIB recycling, Direct recycling, LFP

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List of Abbreviations

AAM	Anode Active Material
ACN	Acetonitrile
CAM	Cathode Active Material
CE	Coulombic Efficiency
CRM	Critical Raw Material
CS	Center Shift
DEC	Diethyl Carbonate
DMC	Dimethyl Carbonate
EC	Ethylene Carbonate
EG	Ethylene Glycol
EI	Electron Ionization
EMC	Ethyl Methyl Carbonate
EoL	End-of-Life
EU	European Union
EV	Electric Vehicle
FP	Iron Phosphate (FePO ₄)
FT-IR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography with Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LFP	Lithium Iron Phosphate (LiFePO ₄)
LIB	Li-ion battery
MSD	Mass Selective Detector
NMP	N-Methyl-2-pyrrolidone
PC	Propylene Carbonate
PE	Peeling Efficiency
PG	Propylene Glycol
PVDF	Polyvinylidene Fluoride
QS	Quadrupole Splitting
R-LFP	Regenerated LFP
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy
SHE	Standard Hydrogen Electrode
S-LFP	Spent LFP (prior to regeneration)
SOC	State of Charge
SOH	State of Health
XRD	X-Ray Diffraction

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List of Publications

Paper I:

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Manuscript II:

Duda S., Barbosa de Mattos D.F., Segura-Bailón B., Altenschmidt L., Mikšovský P., Pierotti L., Lundgren E. and Petranikova M. "Effects of chemical, mechanical and cryogenic delamination methods and solvent washing on the quality of harvested LiFePO_4 cathodes for direct recycling purposes". Submitted to: *RSC Energy Advances* [2].

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1 Introduction

The Li-ion battery (LIB) market has been growing exponentially in the last decade, surpassing USD 130 billion in 2025, and is expected to continue growing to more than six times the size within the next eight years [4]. Simultaneously, batteries from electric vehicle (EV) applications are starting to enter the waste market, with predictions indicating a rise of End-of-Life (EoL) EV LIBs to 14 million units until 2030 [5]. Their content of rare and valuable materials along with their toxic nature necessitates the development of feasible recycling strategies and routes to safely treat waste LIBs and recover the valuable elements. Several of the constituent elements are on the European Union's (EU) list of Critical Raw Materials (CRM) [6] and measures are in place and under constant revision in order to enforce incentives on recyclers to responsibly treat EoL batteries [7].

Despite the incentives for battery recycling being present (and growing), many challenges need to be overcome before large-scale LIB recycling processes can be seen in the industry. Modern EV battery packs are mostly designed with energy density in focus, sparing little to no room for considering design for disassembly [8]. At the same time, constantly evolving battery chemistries improve the performance, but bring economic uncertainty into the recycling industry, where advanced recycling processes are often chemistry specific [8]. Moreover, the battery industry is gradually transitioning towards LIB chemistries with lower content of metals such as cobalt (Co), nickel (Ni) and manganese (Mn), pressing down the retail prices while simultaneously lowering their environmental and ethical impact caused by mining of the raw materials [8, 9]. This trend is driving a slow paradigm shift in the recycling industry, where more and more attention is given to strategies that hold the potential to recover valuable elements of EoL batteries in a more profitable/useful form and at a lower cost and environmental impact than the presently established pyrometallurgical and hydrometallurgical routes. Such a strategy is most widely discussed as "direct recycling" [3, 8].

Especially for genuine "low-cost" LIB chemistries, such as the Lithium Iron Phosphate (LiFePO_4 , LFP) chemistry, direct recycling is often viewed as the only feasible treatment strategy, with lithium (Li) being the only constituent

element of substantial economic value, thus rendering pyrometallurgy and hydrometallurgy not effective enough and too expensive, respectively [3]. Because of this, and because of the increasing popularity and market share of the LFP chemistry, research efforts in direct recycling of LFP batteries in the last decade have been extensive. Mostly, researchers tend to focus on the relithiation, i.e., the supplementation of Li into the LFP Cathode Active Material (CAM) in order to enhance its electrochemical performance to match that of a virgin material. This is understandable, since the electrochemical performance is what will ultimately decide the effectiveness of the proposed processes and their attractivity for industrial recyclers [3]. However, the way that the spent LFP CAM is obtained, from pack/module level down to CAM powder, may influence the outcome of the relithiation process, and is therefore of equally high importance. Its impacts are, however, not as explored in scientific literature and there is a knowledge gap in terms of what choices of pretreatment steps are appropriate for a recycler to make, should they invest in a direct recycling process of LFP batteries.

In this work, multiple aspects of pretreatment of spent LFP battery modules from mild hybrid applications were explored, with feasible direct recycling always in mind. Two discharging methods were compared to assess their impact on the chemical and mechanical integrity of the modules, cells and active materials, shedding new light on the question of what the appropriate choice of discharging strategy is for direct recycling (Paper 1). The dismantling process of these batteries from module to individual electrodes was described in detail, the display of which is rare in scientific literature, highlighting some of the bottlenecks that industrial recyclers can expect from EoL batteries that were not designed for easy disassembly (Paper 1). Further, the positive electrodes (referred to as "cathodes" from now on) were treated to explore and assess the impact of different washing and delamination methods on the recovered CAM. As was shown, washing the cathodes may be necessary to clean the material of impurities in order to enhance its electrochemical performance after relithiation (Paper 2). Additionally, one delamination method (freeze-drying) was developed into a more feasible and scalable mode of operation as compared to the previously demonstrated strategy. A fully novel delamination method was demonstrated as functional on an existing industrial equipment, on a prototype level (Paper 2). The aim of this study was to develop a functioning, feasible and scalable pretreatment process of spent LFP batteries that is fit for direct recycling purposes, i.e., that allows for CAM recovery without compromising on its purity and material integrity.

2 Background

LIB recycling is a topic with heavy focus in both academic and industrial research. Apart from the need for safe handling of EoL batteries, the incentive for the recovery and conservation of valuable battery materials, such as Li, Co and Ni, is growing. This is true particularly in Europe, where the virtually non-existent domestic supply of these metals, and LIBs in general, creates a strong dependence on import from non-EU countries, most notably China. The geopolitical tension that follows has prompted a push towards domestic LIB manufacturing and recycling, which becomes increasingly notable in all levels of the European battery supply chain - from retail to the European Parliament and Council.

The latter has recently updated the legislative framework widely known as the EU Battery Regulation (2023/1542), which mandates that large-scale LIB recycling be implemented within EU borders. Unlike its predecessor, the updated regulation sets goals for the recovery rates of several constituent elements commonly present in LIBs. Notably, the regulation stipulates that by 2031, the recovery rate of Li from spent LIBs should be 80% and that of Co, Ni and Cu should be 95%, while the overall recycling efficiency of spent LIBs should be 70% [7]. These goals are high enough to induce an intensive pursuit of feasible LIB recycling strategies among European LIB suppliers, recyclers and researchers alike.

2.1 Present LIB recycling strategies

2.1.1 *Pyrometallurgy*

Present production-scale LIB recycling strategies revolve mostly around pyrometallurgy; an established and well-understood technology with extensive industrial infrastructure ready to be used. Spent batteries are processed in a high-temperature environment (around 1000 °C), during which the metallic components melt and are recovered in the form of an alloy, while plastic and other organic components are pyrolyzed. Some metal oxides and phosphorus compounds are recovered as slag, while most of the lithium is volatilized, and therefore, lost.

Evident advantages of pyrometallurgical recycling include high production volumes, no necessary pretreatment of the spent batteries, as well as the versatility of the method, meaning a mixed stream of spent batteries can be processed. The main drawbacks are high energy consumption, high material losses which include lithium, and formation of hazardous gases such as hydrogen cyanide (HCN), hydrofluoric acid (HF) and carbon monoxide (CO). Moreover, because of the increased demands on material recovery in the current EU Battery Regulation, the current pyrometallurgical processes are unable to conform to its requirements [7].

Research in pyrometallurgical LIB recycling is focused primarily on the Li recovery, e.g., by the use of additives that cause the formation of less volatile alkali metal species, or by washing of the off-gases in aqueous media to leach the Li into a solution which can then be treated chemically to recover the Li in the form of a salt.

2.1.2 Hydrometallurgy

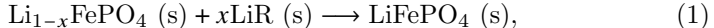
Hydrometallurgical LIB recycling has been largely investigated as an alternative to pyrometallurgical processing, mostly due to its potential to obtain significantly higher yields and purities of the recovered metals, such as Li, Co, Mn and Ni. It has been demonstrated on pilot and even production scale and is gaining attention by industrial recyclers thanks to its robustness, especially in China [3, 10].

The technology necessitates discharging of the spent batteries for safer handling, followed by crushing and milling. In the process, larger metallic, electronic and plastic components can be separated and recovered. Finally, a blend of the electrode active materials along with their binders and traces of the current collector foils, known as the black mass, is recovered. The black mass can then be treated chemically utilizing techniques such as acid leaching, solvent extraction, ion exchange and co-precipitation to separate and purify streams of individual metals, which are ultimately recovered as individual metallic salts [3, 10].

Research in hydrometallurgical recycling is focused primarily on improving the purity of the recovered metallic salts to conform to industry standards for battery-grade precursor materials [11, 12]. In addition, leaching strategies involving organic acids are readily developed and reported on. Examples involve the use of oxalic acid and formic acid for selective Li leaching [13, 14].

2.2 Direct recycling

The main challenge for hydrometallurgical recycling in combination with low-value chemistries, such as the LFP chemistry, lies precisely in what makes them attractive in the battery market, i.e., their low price. As Li is the only element of large economic value in LFP batteries, the recovered salt from a hydrometallurgical process (mostly Li_2CO_3 or LiOH) does not have enough economic value to cover the cost of the process. For this reason, direct recycling has been largely investigated as an alternative approach. The goal is to directly relithiate and regenerate spent LFP (commonly denoted as S-LFP) CAM, i.e., to compensate for Li losses and to repair crystal defects, thereby recovering the active material in a state in which its electrochemical performance would be up to par with a pristine cell. The relithiation reaction, in which partially delithiated LFP ($\text{Li}_{1-x}\text{FePO}_4$) is reacted with a source of Li, usually a salt, by which the Li is supplemented and the LFP phase relithiated according to reaction (1). As the delithiated LFP in reality often contains clusters of the completely delithiated FP (FePO_4) phase, full relithiation may demand either a reductive environment or an addition of reducing agents to help reduce the Fe^{3+} to Fe^{2+} .



Relithiation can be achieved through various techniques, among which the solid-state thermal relithiation is the most reported in the literature. It involves mixing of S-LFP with a Li salt, most often lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH), together with an addition of glucose or another carbon source for the carbon coating, followed by high-temperature treatment at 400-900 °C [3]. Current research in this field focuses on exploring alternative Li salts, such as organic salts to also act as a source of carbon, and on optimizing the reaction conditions for the best electrochemical performance of the regenerated LFP (commonly denoted as R-LFP). The major shortcoming of this method is the need of determining the exact stoichiometric amount of the Li salt needed for the reaction, as a deficit would mean incomplete relithiation, while an excess would most likely not be recoverable and reusable and could lead to the formation of unwanted impurity phases that may lower the performance of the R-LFP material [3]. At the same time, to determine the precise amount of the Li salt needed for each processed batch in an industrial setting would be impractical and unfeasible.

To partially overcome the challenge of the solid-state method and to lower the energy consumption from the high-temperature treatment, the molten-salt method has been reported in literature, although sparsely. Liu *et al.* reported using lithium nitrate (LiNO_3), iron oxalate (FeC_2O_4) and sucrose, where excess LiNO_3 could be washed off the relithiated material [3, 15]. Using the same salt, Wang *et al.* demonstrated the possible use of the same Li salt on LFP black mass, rather than pure LFP CAM, while simultaneously developing a way to achieve recrystallization of the LFP particles without a secondary high-temperature treatment step, but rather by centrifuging in a saturated zinc chloride (ZnCl_2) solution [3, 16]. A different molten-salt related recrystallization approach was reported by Zhu *et al.*, where a $\text{LiNO}_3\text{:LiOH}$ eutectic was used to increase the ion diffusion rate in the reaction environment, achieving competitive electrochemical performance of the R-LFP material despite also avoiding a sintering step [3, 17].

Other relithiation methods have been reported in the literature. The hydrothermal method, which utilizes elevated temperature (100-200 °C) and pressure (10-20 bar) in an aqueous Li-rich environment, has been explored for its higher scalability potential than the aforementioned methods [3, 18, 19]. An alternative to the hydrothermal method is to perform relithiation in organic (or aqueous) environments at mild conditions, i.e., ambient or slightly elevated temperature and/or pressure, commonly referred to as the chemical relithiation method [3, 20–22]. Relithiation has also been reported through the use of the electrochemical method, in which the reaction is driven by electrical cycling rather than chemically or physically, although the reported electrochemical performance of the relithiated LFP materials obtained in this way have struggled to reach competitive levels, as compared to the other relithiation strategies [3, 19, 23].

2.2.1 The hybrid approach - "Indirect-direct recycling"

Probably the main challenge for the various direct recycling strategies to overcome is their low scalability, and hence low industrial feasibility and attractiveness. An alternative approach, which is gaining increasing attention in scientific literature, obtains recovered and regenerated LFP by resynthesis, i.e., chemical synthesis of LiFePO_4 using materials directly recovered from the spent modules/cells - an indirect adaptation of the direct recycling philosophy of sorts [3].

In research, the precursor materials are often obtained by utilizing hydromet-

allurgical treatment of the spent LFP cathodes, i.e., by acid leaching, often accompanied by an oxidizing agent, such as hydrogen peroxide (H_2O_2) for higher yield. Fu *et al.* have employed sulfuric acid (H_2SO_4) and H_2O_2 to leach spent LFP cathode powder and recover FePO_4 and Li_2CO_3 , which were then used to resynthesize battery-grade LiFePO_4 [24]. Current research activities focus largely on developing and optimizing greener, milder and simpler leaching conditions for the hydrometallurgical part of the process, e.g., by exploring the possibilities of organic acid leaching [25], or decreasing the number of steps necessary for recovering the regenerated LFP material [26].

2.3 Pretreatment - current research overview

Despite the broad coverage of relithiation and regeneration strategies for LFP in the literature, the pretreatment steps that lead up to the recovery of pure spent LFP from whole spent modules are often overlooked and barely acknowledged. At the same time, research shows that impurities that either follow the material from the spent module, or are introduced during the pretreatment, can have detrimental effects on the performance of the regenerated material and/or on the safety of the process. Specifically, Al and Cu impurities have been reported to hinder efficient relithiation and lower the electrochemical performance of the regenerated CAM [27], while electrolyte and binder residues can either lower the purity of the recovered material to sub-battery-grade levels, or form hazardous off-gases such as HF upon heat treatment [28]. Therefore, any direct recycling technology that reaches even pilot-scale level will need to have a strategy for removing and/or mitigating these impurities in order to produce high-quality recycled LFP.

As mentioned, research in this topic is sparse and mostly concerned with other chemistries. Fink *et al.* investigated the use of solvents to wash additive and electrolyte residues off spent NMC cathodes, presenting a comparative study of the effects of several solvents, including diethyl carbonate (DEC), propylene carbonate (PC), acetone and isopropanol [29]. In a later study on the same type of material, they demonstrated the use of alkaline ultrasonication at high temperature for the removal of Al and Cu impurities [30]. Meanwhile, Zhou *et al.* reported the use of acid-base leaching for metal impurity removal from spent LFP material, producing battery-grade FePO_4 that was then used to resynthesize LFP [31].

Another crucial part of the pretreatment for direct recycling is the delamination, or the separation of the CAM from the current collector foil. Currently,

the most commonly reported method is pyrolysis-based thermal treatment, where the PVDF (Polyvinylidene fluoride) binder, present in most commercial LFP cells, is degraded at around 550 °C [32, 33]. Although efficient, the method suffers drawbacks in the form of generation of toxic gases such as HF and carbon monoxide [34]. Another readily employed delamination strategy is based on chemical dissolution of the binder, mostly using N-methyl-2-pyrrolidone (NMP), which is efficient but highly toxic and implies the need for proper waste handling of the used solvent [35–37]. For this reason, alternative solvents have been investigated. Bai *et al.* reported using ethylene glycol (EG) to weaken the PVDF-Al bond by preferential bonding to the Al foil, thereby achieving rapid delamination at 160 °C [38]. Solvent-based delamination has also been reported in terms of partial dissolution of the Al foil rather than the binder. Sulfuric acid (80 °C for 1 h) and phytic acid (25 °C for 5 min) have both been investigated and reported in literature [39, 40].

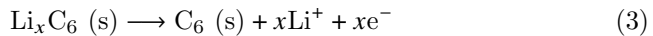
3 Theory

3.1 Basics of the Li-ion batteries

Rechargeable (secondary) Li-ion electrochemical cells follow the basic principle of alternating electrolytic and galvanic cells upon charging and discharging respectively, where the release and uptake of Li ions and corresponding electrons is based on redox reactions occurring at the two electrodes. The Li ions are transferred between the electrodes via an electrolyte, while corresponding electrons are led through an external circuit. Upon discharging, reduction and electron uptake take place at the positive electrode, or cathode, while oxidation and electron release take place at the negative electrode, or anode. Upon charging of the cell, the opposite electrochemical reactions occur, and the Li ion and electron transport move in the opposite direction. In the case of LFP batteries, the redox species is Fe, where during discharging, intercalation of active Li^+ at the positive electrode leads to gradual reduction of Fe from Fe^{3+} to Fe^{2+} according to reaction (2)



where $x \rightarrow 1$ as the battery progressively discharges. Simultaneously, at the negative electrode, active Li^+ is de-intercalated from active material, usually graphite, according to reaction (3)



Note that by electrochemical convention, the terms cathode and anode are defined strictly based on the redox reactions that take place (cathode = reduction, anode = oxidation), and thus switch places upon charging of the cell, while the terms positive and negative electrode are always on the same side of the electrochemical cell [41]. For simplicity and to avoid confusion, the positive and negative electrodes will be referred to as cathodes and anodes respectively in this thesis. This is based on the convention within the rechargeable battery community, where it is widely understood that the common nomenclature is based on the discharging state of the battery cell, as this is the state in which

the battery fulfills its primary purpose of releasing electrons for powering a device.

3.2 Design considerations - from material to module

Modern LIBs have evolved into a myriad of different chemistries and additives, but the basic principle has stayed the same. Cathode and anode active materials (CAM and AAM respectively) are deposited on current collector foils, normally made of aluminum and copper, respectively. The AAM is most commonly graphite, while the CAM varies, with the common denominator being that it naturally contains Li and allows for its reversible intercalation and deintercalation. In the original Li-ion cell developed in 1980 [42] that, together with the inventions of other LIB chemistries, led to a Nobel prize to its inventor John B. Goodenough in 2019 [43], Lithium cobalt oxide (LCO, LiCoO_2) was used. Nowadays, more advanced and safer chemistries are dominating the market, with the Lithium iron phosphate (LFP, LiFePO_4) being one of the most popular ones.

The main reason for the large scale success of the LFP chemistry is its relatively low production cost, which is directly linked to the avoidance of rare, expensive, and sometimes controversial, metals such as Ni, Mn and Co. The LFP chemistry is also inherently safer than its main competitors, as it is non-toxic and more chemically and thermally stable. The main drawback of using this chemistry is the relatively low performance, as compared to, e.g., the NMC chemistry. This issue arises from the crystal structure of LiFePO_4 , which is of a phospho-olivine type and only permits one-dimensional Li-ion transfer. In the case of NMC, the material is a layered oxide that allows for two-dimensional, and hence faster, ion transfer. Therefore, to promote better performance of LFP-based batteries, the material needs to be coated with a conductive carbon coating that increases the electronic conductivity of the material. In addition, manufacturers often incorporate undisclosed dopants into the LFP material, examples of which include Mn, V, and Cu.

The electrodes are separated with a separator which mostly consists of polypropylene or derivatives thereof, and in most cases, multiple cathode-anode pairs are put into a single battery cell to enhance its performance. The electrode-separator setup is placed in a cell casing, which could be of a cylindrical, prismatic, pouch, or even coin type geometry. In the work leading up to this thesis, pouch cells were used. Before sealing the casing of the cell, it is filled with the electrolyte, for which the most common standard is approximately

1 M Lithium hexafluorophosphate (LiPF_6) dissolved in a manufacturer-specific blend of organic solvents that could contain Ethylene carbonate (EC, $(\text{CH}_2\text{O})_2\text{CO}$), Propylene carbonate (PC, $\text{CH}_3(\text{CH}_2\text{O})_2\text{CO}$), Dimethyl carbonate (DMC, $(\text{CH}_3\text{O})_2\text{CO}$), Diethyl carbonate (DEC, $(\text{CH}_3\text{CH}_2\text{O})_2\text{CO}$) and Ethyl methyl carbonate (EMC, $\text{CH}_3(\text{CH}_2\text{O})_2\text{CO}$).

In industrially manufactured battery modules, multiple cells are typically placed in the module casing and wired together to form an inner circuit to improve the performance of the module. Especially in automotive applications, multiple modules are assembled into battery packs that are installed in the vehicle.

3.3 Measures of electrochemical performance

To communicate the electrochemical performance of a LIB cell or battery, several measures and measurement techniques are commonly used. Capacity is a measure of the cumulative charge that a cell can provide over a period of time according to equation (4)

$$Q = \int_0^t I dt \text{ [Ah]}, \quad (4)$$

where I is the current and t is the time during which the cell provides charge. In general, however, the capacity is normalized by the mass of the cell, and is thus commonly expressed as specific capacity [mAh g^{-1}]. Similarly, the energy of a cell or battery is defined as the cumulative work that it can provide over a period of time according to equation (5)

$$E = \int_0^t V(t) \cdot I dt \text{ [Wh]}, \quad (5)$$

where V is the voltage over the cell or battery. Communication of the battery energy is often more useful when normalized by its mass or volume, in which case it is expressed as the specific energy [Wh kg^{-1}] or the energy density [$\text{Wh } \ell^{-1}$], respectively.

Another common measure of a cell's performance, but also a means to communicate conditions for performance testing, is the C-rate, describing the rate at which the cell can be charged or discharged, relative to its capacity, and is expressed as according to equation (6)

$$C\text{-rate} = \frac{I}{Q} [\text{h}^{-1}]. \quad (6)$$

A common practice in electrochemical performance testing of battery cells is long-term cycling, in which the cell is charged and discharged at a constant C-rate in a large number of cycles, often 200-1000. Here, the specific discharge capacity and its long-term retention rate is of most interest. The reversibility of the electrode processes inside a cell can also be described using the Coulombic efficiency, which is a ratio of the measured charge and discharge capacities in a single cycle and can thus be expressed according to equation (7)

$$CE = \frac{Q_{discharge}}{Q_{charge}} \quad (7)$$

4 Materials and methods

A total of 48 spent LFP/Graphite modules from real-life mild hybrid vehicle applications were delivered by an established car manufacturer as part of a larger battery recycling project. The modules had a rated voltage of 46.2 V, a rated capacity of 8 Ah, rated energy of 369.6 Wh and a weight of 8.1 kg. Figure 1 shows the modules from different perspectives, both as-delivered and after removing the top plastic head part and the electrical connections between the cells. The modules contained 14 pouch cells each with 26 cathode/anode pairs in each cell, mounted in a zig-zag configuration with the separator.

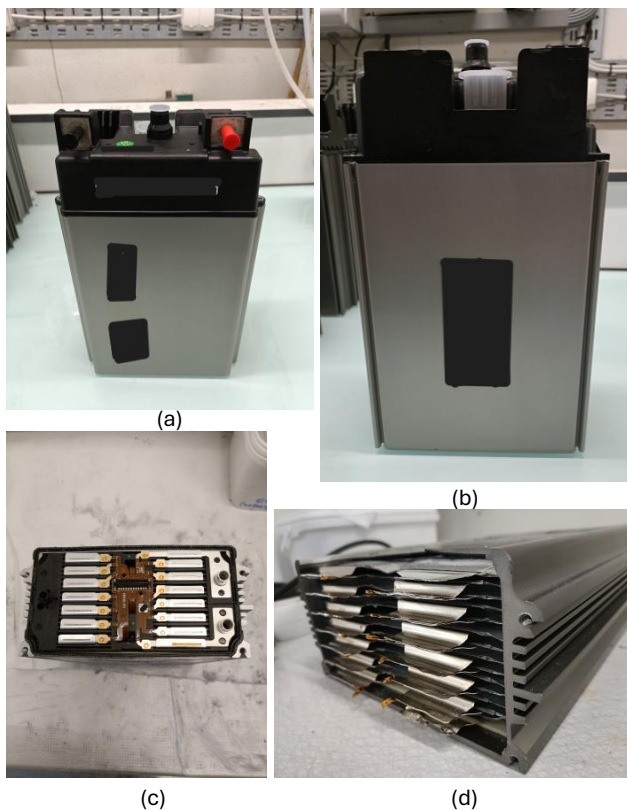


Figure 1: Delivered spent LFP modules from the front (a) and back (b), as well as from the top after removing the protective head part (c) and after also removing the electrical connections between the cells (d).

4.1 Discharging of spent LFP modules

Discharging of battery modules before manually opening them is a prerequisite for safe work, as otherwise sparks could occur, imposing a preventable fire hazard. First attempts at the discharging were done as per the manufacturer's recommendation and common industrial practice, i.e., by using salt brine. The top plastic head part of the modules was unscrewed and the wirings between the cells disrupted and removed, revealing the terminal pads of the cells. The modules were then fully immersed in 20 ℓ of 10% NaCl solution (iodized kitchen salt in tap water) for 36 hours. This setup with simple and available resources was chosen deliberately, in an attempt to mimic an approach that an industrial recycler would likely take, since the project aims at developing a feasible direct recycling route.

Brine discharging is undoubtedly efficient in terms of material throughput, but is challenged by an inevitably high waste generation, and, as described later in the thesis, also safety issues. Early in the process, it also became evident that this method corroded and damaged the battery cells, both from the outside and (partially) from the inside. The decision was therefore made to abandon the brine discharging and develop a protocol for resistor circuit based discharging. Based on previous experiences in the department with handling NiMH batteries [44], a discharge current of 1.5 A was chosen. After removing the top plastic head but keeping the wirings and poles intact, the modules were connected by their poles to a circuit consisting of a rheostat from Sandblom & Stohne AB with variable resistance and two aluminum clad power resistors from Arcol with a resistance (R) of 10 Ω each. The resistors were mounted on a heat sink suspended in the air to avoid heat buildup. The rheostat's resistance was adjusted to maintain the discharging current of 1.5 A. Throughout the discharging, voltage was monitored as a voltage-time curve using a digital multimeter. Figure 2a shows the initial setup with a module connected to it. Figure 2b shows a scheme of the corresponding circuit. Figure 2c shows an example of the recorded voltage-time curve, showing the time for discharging from 46 V to 0.4 V was approximately 4.5 h.

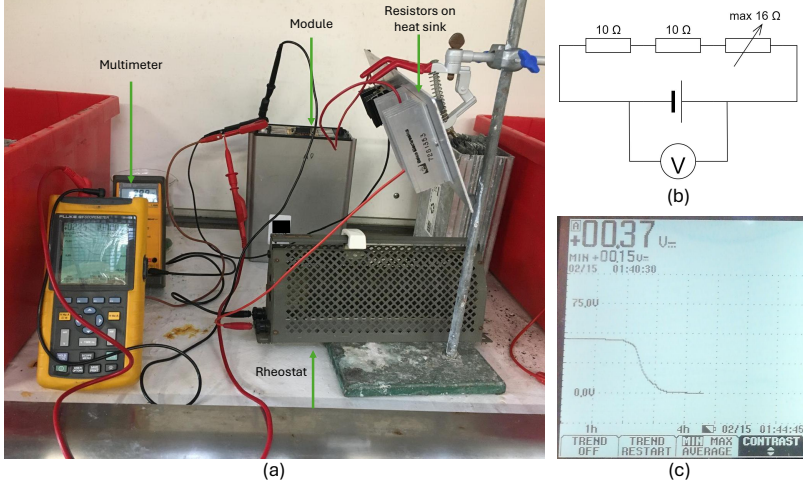


Figure 2: The initial discharging setup (a), the corresponding electrical circuit scheme (b), recorded voltage-time curve corresponding to discharging with this setup for 4.5 h (c).

After verifying that the setup was functional and able to discharge the modules successfully, a more permanent discharging setup was constructed without the rheostat to increase the throughput of modules being discharged at once. The new setup consisted of a series of aluminum clad resistors mounted on a heat sink ($2 \times 10 \, \Omega$ from Arcol and $2 \times 6.8 \, \Omega$ from ATE Electronics) of $R = 33.6 \, \Omega$ in total. Figure 3a shows a picture of this setup and Figure 3c shows its electrical circuit.

Both discharging devices gave rise to the same voltage behavior. After approximately 4-5 h, the voltage of the modules stabilized at around 0.5 V. This would technically be enough for safe dismantling, but due to limited knowledge about the behavior of the modules, as well as a strong voltage rebound effect that was observed, the decision was made to add a second step to the discharging protocol. This consisted of a single $1.8 \, \Omega$ resistor from VTM UK and a fuse to prevent damaging the resistor due to sudden current increase following the sudden resistance decrease. With this setup, the voltage over the modules quickly dropped to 0 V. The modules were left in this state until the occasion of dismantling. The final discharging setup can be seen in Figure 3b and its electrical circuit scheme in Figure 3d.

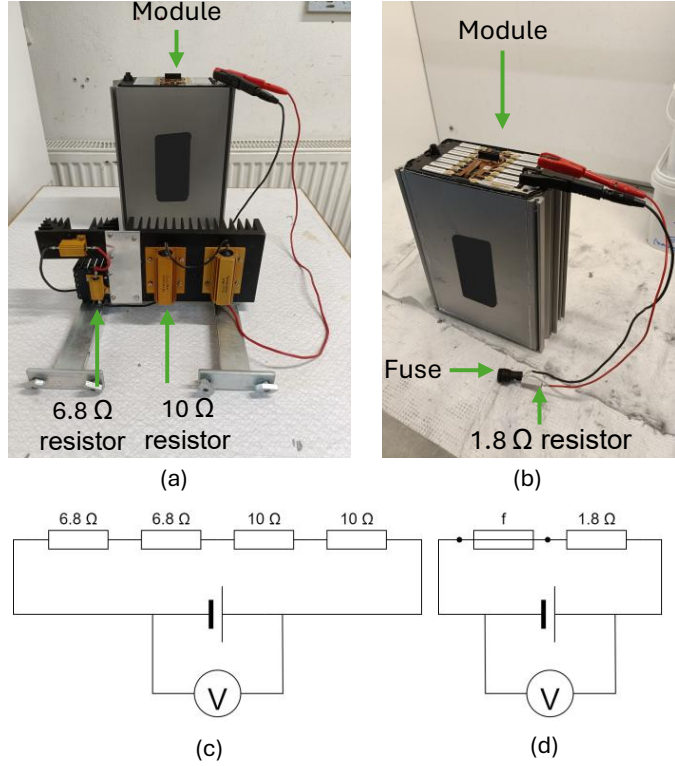


Figure 3: The second discharging setup (a), the corresponding electrical circuit scheme (c), the final discharging device used after reaching 0.5 V (b) and its corresponding electrical circuit scheme (d).

4.2 Dismantling of spent LFP modules to electrode level

After discharging, the modules were disconnected from the resistor setup and the electrical wirings between the cells were immediately disrupted to isolate the cells from each other. The plastic part that contained the wirings and poles was then removed and one long side of the modules was cut off using a multicut tool from Bosch. This allowed access to the cells, which were then removed from the module one-by-one. To remove the cells, it was necessary to remove silicon glue that had been used to restrict movement of the cells inside the module. The glue had to be scraped off using a long screwdriver. Figure 4a shows a module with the side cut off and the cells exposed and Figure 4b shows a pouch cell separated from the rest of the module.

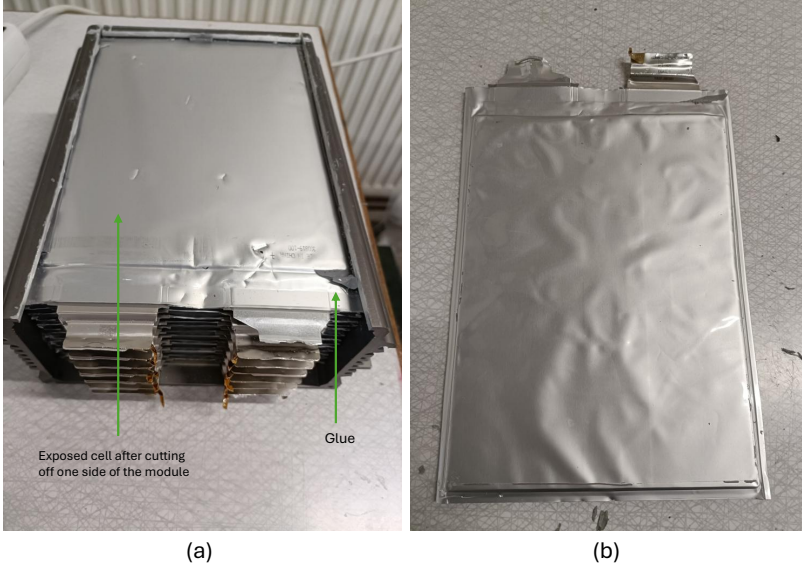


Figure 4: Open spent and discharged module with exposed cells (a), a single pouch cell separated from the module (b).

4.3 Delamination of CAM from the current collector

Delamination experiments were carried out using different techniques to investigate their achieved peeling efficiency and effect on the purity and integrity of the material, weighed against their industrial feasibility. Two different solvent-based strategies were tested, a cryogenic method was developed further from a single prior demonstration, and a fully novel, purely mechanical, technique was tested in an industrial setting as a proof of concept. Apart from the LibriXer process, all delamination experiments were performed in triplicate and a Peeling Efficiency (PE) along with a standard deviation was calculated according to equation (8)

$$PE = \frac{m_r}{m_i} \times 100 \text{ [\%]} \quad (8)$$

where m_r is the mass of CAM recovered after the delamination and m_i is the initial mass of CAM in the cathode prior to delamination. The initial mass m_i was estimated to 3.9 g by weighing untreated cathodes and the remaining Al current collector from three of the most complete delamination runs using the cryogenic method.

4.3.1 *Chemical delamination*

Probably the simplest strategy to delaminate CAM from its current collector would be a solvent-based approach, where the electrode is immersed in a solvent which, by reaction with the binder and/or the current collector disrupts the bonds between them, thereby releasing the CAM from the current collector. In this work, ethylene glycol and phytic acid were tested. Before the delamination, the cathodes were cut into smaller pieces of approximately 2×2 cm. In both cases, the cathode squares were immersed in the liquid for the shortest amount of time needed for visible separation.

Ethylene glycol was at an S/L ratio of 100 g/ ℓ and under heating at 160 °C, in line with previous research [38]. 2 g of the cathode squares were immersed in 20 g of heated ethylene glycol. Contrary to previously reported data, however, a few seconds was not enough for full delamination to occur and the pieces had to be left in the liquid for 2-3 minutes. The delaminated CAM was separated from the pieces of Al foil and collected using tweezers. After the delamination, the mixture was filtered and the liquid collected. The solid CAM was washed with 300 mL Milli-Q water and dried at 60 °C for 20 h.

Phytic acid (50% w/w in H₂O) was used at half the S/L ratio, i.e., 2 g of cathode squares were immersed in 40 g of the liquid, again for 2-3 minutes. Also in this case, the solid CAM was separated from the Al foil with tweezers, then dried at 60 °C for 20 h. In all cases, the recovered CAM was ground to fine powder using a Retsch RS200 Attrition Mill at 700 rpm for 30 s.

4.3.2 *Cryogenic delamination*

In an effort to move towards recycling methods that avoid chemical consumption and wastewater generation, cryogenic delamination based on freeze-drying was investigated. Specifically, 2×2 cm cathode pieces were immersed in Milli-Q water at different S/L ratios. The beaker was put in a freezer at either -20 °C or -80 °C until the water was completely frozen. It was then transferred into a freeze-dryer, or lyophilizer, (Labconco FreeZone) and left for 24 h at -54 °C and 0.014 mbar. The vacuum in the lyophilizer sublimed the ice and thereby rendered the cathode pieces dry. After the freeze-drying, the CAM was separated from the Al foil pieces with tweezers.

The first trials were mostly in line with previously reported results [45]. To further develop the method into a more practical form, whole cathode sheets were put individually in sealable plastic bags along with 20 mL Milli-Q water.

The bags were sealed shut, taking care to remove air bubbles to ensure the best possible contact between the cathode and the ice on both sides. The bags were frozen, then transferred to the lyophilizer. In many cases, the ice had partially melted during the transport, which made it difficult for the equipment to reach the correct conditions. To ease the process, an additional freezing step was added, where liquid nitrogen was poured over the frozen bags and left to evaporate immediately before being put into the lyophilizer. Also in the case of freeze-drying, the recovered CAM pieces were ground into fine powder using the attrition mill at 700 rpm for 30 s.

4.3.3 Mechanical delamination - The LibriXer process

The LibriXer process was only tested in a pilot setting at the LibriXer site in Skillingaryd, Sweden. Since only a smaller amount of the spent electrodes could be provided, relative to the design capacity of the equipment which is measured in hundreds of kg per hour, only small amounts of material could be collected for analysis. The variables that were varied in the tests were the size of the feed material (whole electrodes, 1 cm stripes or smaller squares), the rotational speed (between 1200 and 3500 rpm) and the direction of the rotation (clockwise and counter-clockwise). No replicates could be done and the tests were mostly done on a mixed stream, i.e., cathodes and anodes mixed in equal amounts. A small amount of a cathode-only stream was also processed, the material from which is what was primarily analyzed in the characterization. Figure 5a shows an image of the liberator equipment, along with a sketch of its working principle (Figure 5b).

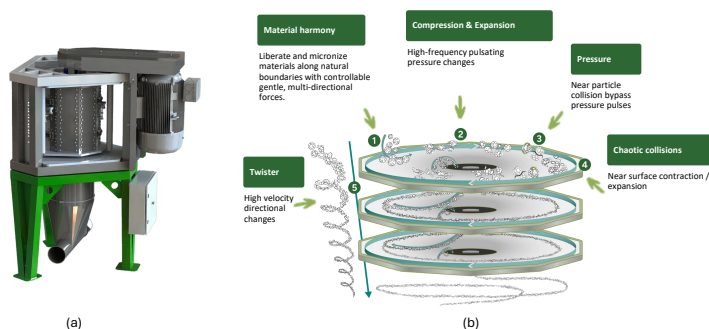


Figure 5: An image of the LibriXer liberator (a) and a sketch of its working principle (b). Kindly provided by LibriXer AB.

4.4 Investigations on impurity removal from the LFP CAM

To investigate the possibility to remove various impurities from the spent cathodes, a washing step was performed prior to the freeze-drying process, using and comparing different solvents from the perspective of their potential for impurity removal as well as their effect on the remaining CAM. Acetonitrile (ACN, CH_3CN) was used as a solvent due to its documented ability to dissolve LiPF_6 , which is an expected electrolyte-related impurity in spent cathodes [46]. Acetic acid (CH_3COOH) was used due to its ability to dissolve a variety of surface Cu oxides [47], while Cu is known to deposit on the cathode surface as an impurity caused by deep discharge, which was also observed in this work (see section 5.1). Ethanol (EtOH , $\text{C}_2\text{H}_5\text{OH}$) was also tested as a greener, cheaper, safer and more readily available alternative to ACN.

The washing was performed through momentary full immersion of the cathodes into the respective solvent, after which the cathodes were left to dry in air. The freeze-drying process was then carried out as described above, processing whole cathode sheets in individual plastic bags. For each solvent, washing was performed either once or three times. To explore whether a combination of solvents could enhance the impurity removal effect, a combination of a triple wash with ACN followed by a single wash with acetic acid was tested.

Additionally, as a frame of reference for total removal of non-volatile electrolyte solvents for comparison with the solvent washing, a pyrolyzed sample was prepared. Here, powdered CAM obtained by cryogenic delamination, was treated at 600 °C for 2 h in N_2 atmosphere with a 10 °C min^{-1} ramp-up rate, using a Nabertherm P330 furnace.

4.5 Regeneration of S-LFP by molten salt assisted relithiation

Based on results of the Mössbauer spectroscopy measurements, an approximate degree of delithiation of 15% was determined for the spent CAM powder. Lithium acetate (LiOAc , CH_3COOLi) was used as a Li source, due to its relatively low melting point of 286 °C and its content of an organic counterion, which has previously been exploited as a source of carbon for the repair of the carbon coating on the LFP particles, as opposed to adding additional glucose or other carbon source [48].

Given the determined degree of delithiation and the capacity of the furnace, 4 g of the spent LFP powder (S-LFP) were mixed with 0.64 g of LiOAc dihydrate (99%, Thermo Fischer Scientific) and treated thermally in a N_2 atmosphere,

being flushed with about 50 ml min⁻¹ N₂. The heat treatment was performed in two stages using a Nabertherm P330 furnace. The reaction stage, where the salt mixture was heated to varied temperatures above the melting point of the salt, namely 290 °C, 340 °C and 390 °C for varying times, namely 2 h, 4 h and 6 h, all at a 10 °C min⁻¹ ramp-up rate. Parameter variation was determined using a simplified 2² factorial design of experiments with a triplicate run in the central point (340 °C, 4 h). Table 1 shows an overview of the tested reaction conditions along with the nomenclature used for the experiments.

Table 1: Reaction conditions for the different relithiation samples.

Sample	Reaction temperature [°C]	Reaction time [h]
(1)_Ac	290	2
a_Ac	390	2
b_Ac	290	6
ab_Ac	390	6
c1_Ac	340	4
c2_Ac	340	4
c3_Ac	340	4

After the dwell time above has been reached, the samples immediately entered the annealing stage, where the temperature was raised to 675 °C at 10 °C min⁻¹ with an additional 6 h dwell time - a set of conditions that have been previously reported to have the best effect on the crystallinity of the recovered LFP material [49]. After completed treatment, the furnace was left to cool slowly to room temperature, where the regenerated LFP (R-LFP) was collected.

4.6 Analytical methods

4.6.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES measurements were performed using a Thermo Scientific iCAPTM Pro ICP-OES Duo to assess the elemental composition of the solid CAM samples. Solid samples were digested in aqua regia (1:3 v/v HNO₃ (65%, Sigma-Aldrich):HCl (37%, Sigma-Aldrich)) under magnetic stirring at 200 rpm at 80 °C for 4.5 h. Room-tempered solutions were filtered using 11 µm Grade 1 Whatman cellulose filters (Cytiva) and diluted to 100 mL with Milli-QTM deionized water. The samples were diluted 10 times in 0.1 M HNO₃ and spiked with 1 ppm Y internal standard to correct for possible fluctuations in sample introduction by the instrument. Calibration standards were prepared

in a dilution series using single-element 1000 ppm standards in 0.5 M HNO₃ matrix from Teknolab Sorbent. The standards were diluted in suprapur 0.1 M HNO₃ (Sigma-Aldrich), also spiked with 1 ppm Y as internal standard.

4.6.2 *X-ray Diffraction (XRD)*

XRD with standard Bragg-Brentano pattern matching was done primarily on a Bruker D8 Discover with a CuK_α radiation source ($\lambda = 1.5406 \text{ \AA}$) and an Eiger 2R-500K detector in a 2θ range of 10-80°. Because of the low energy resolution of the detector and the tendency of Fe to cause fluorescence in combination with a Cu radiation source, thus introducing high levels of background noise to the obtained diffractograms, a similar setup was utilized at Uppsala University. Here, a Bruker D8 Twin-Twin diffractometer with a Lynxeye detector was used instead. This was done to obtain diffractograms of better quality in terms of higher signal-to-noise ratio.

4.6.3 *Mössbauer Spectroscopy*

To determine the degree of delithiation of the spent CAM, Mössbauer spectroscopy was performed by Uppsala University. About 16 mg/cm² of sample were enclosed between two Kapton layers and measured at room temperature on a spectrometer with a constant acceleration vibrator and a ⁴³CoRh source. Calibration was done using a natural Fe metal foil. The obtained spectra were analyzed in the least-square fitting software Recoil, recording values for Center Shift (CS) *vs.* α -Fe at room temperature, the Quadrupole Splitting (QS), Lorentzian linewidth W , as well as the spectral area A .

4.6.4 *Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX)*

Morphological analysis and elemental mapping was done through SEM-EDX using a Phenom Pro X with a 15 kV acceleration voltage. Samples were mounted on stubs using a conductive carbon tape. The EDX mapping was done in a 250 × 250 px resolution unless stated otherwise.

4.6.5 *Fourier Transform Infrared Spectroscopy (FT-IR)*

FT-IR measurements were performed to confirm the presence of the PVDF binder in the recovered CAM samples using a PerkinElmer Spectrum 3 with PIKE GladiATR Attenuated Total Reflection. The measurements were carried out on the bandwidth between 4000 and 500 cm⁻¹ in a resolution of 4 cm⁻¹

and with a 16 scan accumulation.

4.6.6 Gas Chromatography with Mass Spectroscopy (GC-MS)

To measure the content of residues of the common cyclic electrolyte solvents ethylene carbonate (EC) and propylene carbonate (PC) in (mostly) washed CAM samples, GC-MS was employed using an Agilent Technologies 7890A GC system with a 5977A mass selective detector (MSD). Samples were treated with acetonitrile (ACN) at an S/L ratio of 20 g/ ℓ in a 40 °C ultrasound bath for 10 minutes. The samples were filtered using 0.45 μm PTFE syringe filters with prefilter (Thermo Fisher Scientific), then 1 mL GC samples were prepared by mixing 0.98 mL sample with 0.02 mL internal standard (20.330 mg decane/mL ACN). An Agilent HP-5MS capillary column (30 m $\times$ 250 μm $\times$ 0.25 μm) was used for separation. A calibration curve for dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), ethylene glycol (EG), propylene glycol (PG), EC and PC, was prepared in the range of 1.0 to 0.016 mg/mL ACN, also spiked with the decane internal standard.

Conditions GC: 1 μL injection volume, 20:1 split ratio, 1 mL/min He flow, 40 °C initial temperature, ramp 1: 3 °C/min to 60 °C, ramp 2: 20 °C/min to 270 °C, 5 min hold time.

Conditions MS: electron ionization (EI), MS source 230 °C, 2.20 min solvent delay, 30-500 m/z ratio, 5.8 scans/s.

4.6.7 Electrochemical performance evaluation

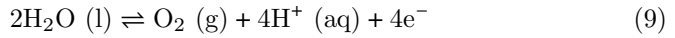
Electrochemical performance testing was performed in terms of long-term cycling, where specific capacity (mAh g⁻¹) and Coulombic Efficiency were measured over more than 100 cycles to partially assess the success of the relithiation experiments. The electrode slurry was prepared by mixing the R-LFP powders with carbon black and PVDF in a weight ratio of 8:1:1, using NMP as the solvent. The slurry was coated on carbon-coated Al foil. Coin cells were made in a half-cell configuration, using Li metal as the anode. The electrolyte was 1 M LiPF₆ in a mixture of EC and DMC (50:50 v/v).

5 Results and discussion

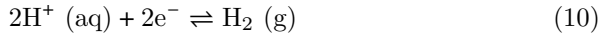
5.1 Discharging and dismantling of spent LFP modules

When comparing the two discharging methods, the salt brine-based one was tested first. An early observation of visible corrosion on the outside of the modules prompted the development of a resistor-based approach, as mentioned before. The corrosion and deposition of green substances on the surface of the modules were preceded by a chemical reaction accompanied by extensive gas development from the brine lasting for 3-4 hours [1]. This is explained by the presence of the water splitting reaction on the two poles of the modules (and cells within) according to reactions (9) through (11) [50, 51].

Anode reaction (oxidation):



Cathode reaction (reduction):



Total reaction:

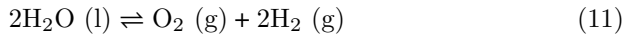


Figure 6a shows an image of the corroded discharged module, accompanied by Figure 6b, showing a close-up of the residue found deposited on its surface.

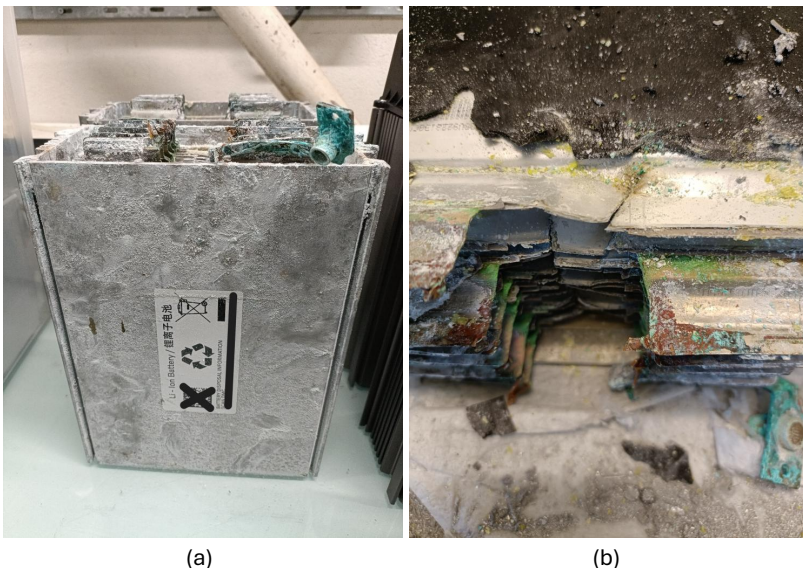


Figure 6: Module discharged in the salt brine (a) and a close-up of the deposited residue (b).

The residue was characterized with XRD as pure NaCl, while its green color clearly shows the presence of another phase. Analysis with ICP-OES showed the presence of approximately 3 wt% Al and Cu, which was later confirmed by SEM-EDX, ultimately suggesting that the residue consists mainly of NaCl, along with one or more impurity phases containing Al and Cu.

Apart from the deposited residue, the solution itself developed a yellow-greenish color and a sharp odor [1]. The electrodes themselves showed clear signs of corrosion near the terminal pads after dismantling of the cells, suggesting that the brine was able to come into contact with the current collectors. Given this, recent research on brine discharging of NCA ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$) batteries in similar conditions suggests the formation of chlorine gas (Cl_2) and hydrogen gas (H_2) according to reaction (12) and a reaction between the free chloride ions (Cl^-) with Cu leached from the anode current collector [51].



The above, along with the observation that the cells of the brine-discharged modules were wet even months after the discharging, when the modules were dismantled, was enough to discontinue discharging the modules in the salt

brine, and instead develop the resistor-discharge protocol. However, the brine method seemed to have worked in terms of discharging the modules. While the voltage over the whole module could not be measured due to the cells having been uncovered prior to the discharging, the voltage between individual cells never exceeded 0.3 V [1].

Interestingly, the brine-discharged cells did not exhibit a voltage rebound effect unlike the resistor-discharged ones, where the measured voltage of modules disconnected from the discharging device would rise up to 3 V within minutes of the disconnection, further rising up to 10 V within the following days. For safe handling, the modules were left idle on the smaller discharging device with $1.8\ \Omega$ resistance up to the dismantling occasion. While making sure that the modules were dismantled while the voltage was low, this approach also increased the swelling of the cells due to gas build-up at the extremely low voltages near 0 V. This suggests that discharging the modules to such low voltage is too deep [1]. A picture of a module with highly swollen cells, taken immediately after the removal of one of the outer casing walls, can be seen in Figure 7.



Figure 7: Swollen cells after resistor discharging.

The CAM recovered by cryogenic delamination was characterized with fo-

cus on the material differences caused by the different discharging methods. To account for possible initial heterogeneities in the cells before discharging, caused by their different thermal and electrochemical history and State of Health (SOH), a heterogeneity study was performed on a selection of CAM from different cells. Here, the material from two cathodes from two different cells, taken from two different modules from each discharging method was characterized using ICP-OES. All samples were measured in triplicates. Table 2 shows the results of the ICP-OES measurements, where each measurement value and its corresponding standard deviation is an average over a total of 24 samples for each discharging method. The full heterogeneity study can be seen in the Supplementary Information for the paper in which it is featured [1].

Table 2: Composition of the recovered CAM from the two different discharging methods measured by ICP-OES.

Analyte	Resistor discharge [wt%]	Brine discharge [wt%]
Li	3.64 ± 0.11	3.40 ± 0.21
Fe	26.78 ± 1.09	27.74 ± 0.77
P	16.09 ± 0.53	16.60 ± 0.40
V	0.90 ± 0.04	0.89 ± 0.04
Al	0.24 ± 0.07	0.61 ± 0.18
Cu	0.92 ± 0.10	2.68 ± 1.02
Si	0.65 ± 0.20	0.46 ± 0.12

The relatively high content of Cu in the resistor-discharged cathodes of about 0.9 wt% can be explained by electrochemical dissolution from the anode current collector upon reaching extremely low voltage [52–54]. This phenomenon has been previously reported and explained by local State of Charge (SOC) variations within the same cells or even cathodes, which, at very low voltage levels, cause local pole reversal instances, which in turn drive the dissolution of Cu and its subsequent transport over the separator and deposition on the cathode surface [53, 55, 56]. This has later been observed at voltages up to 1.5 V [57], while the modules in this study were discharged all the way to 0 V for safer handling. This poses a challenge for the research in direct recycling, where care must be taken to discharge the spent modules to safe levels, while simultaneously suppressing the Cu dissolution to the highest possible extent. In the case of brine discharging, however, the Cu content is considerably higher. This is attributed to the corrosion of the anode current collector by the brine itself, which seemed to have come into contact with the current collectors and electrodes in the cells [1].

Concerning the other impurities, the measured Al content was also higher in case of brine discharging, which can be justified by the same logic as for the higher Cu content. The presence of Al impurity in general can also be attributed to the incomplete delamination of the CAM from the current collector (see section 5.2). The presence of V and Si in the CAM can be attributed to the manufacturing process, as both elements have been reported to be used as dopants for performance improvement in LFP cells [58–63].

The higher content of Li in the resistor-discharged samples suggests that the resistor-based discharging was more effective in terms of reaching a lower SOC. This is in agreement with the XRD and Mössbauer spectroscopy characterization. Figures 8a and 8b show the diffractograms of a brine-discharged and a resistor-discharged sample, respectively. The brine sample features a distinctive FePO_4 (FP) phase, while this phase is barely distinguishable in the resistor sample. The same pattern is observed in the corresponding Mössbauer spectra in Figures 8c and 8d, where the characteristic FP doublet (Center Shift (CS) at 0.49 mm s^{-1} and 0.50 mm s^{-1} and Quadrupole Splitting (QS) at 1.37 mm s^{-1} and 1.20 mm s^{-1}) is much more pronounced in the brine sample, although still present in the resistor sample, albeit in a low quantity of about 5%. Interestingly, a third doublet was identified to fully fit the data. The exact origin of this third phase is not known, although there are reports that would suggest local instances of Fe^{3+} in the LFP lattice [64], or in amorphous olivine phases [65]. Work is in progress to identify this phase.

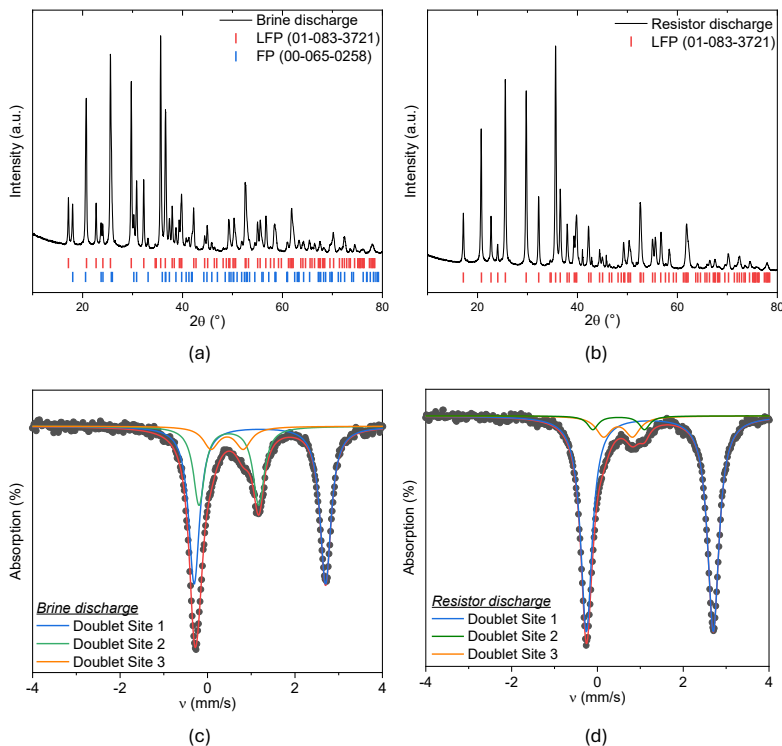


Figure 8: XRD diffractogram and Mössbauer spectrum of the brine-discharged sample (a) and (c), the corresponding results of the resistor-discharged samples (b) and (d).

Overall, the discharging method did not seem to alter the crystalline structure of the recovered LFP material. A similar observation can be made in terms of the morphology of the recovered particles. Figures 9b and 9c show SEM images of the powdered CAM from a resistor and brine-discharged sample, respectively. The samples, ground to powder using a mortar, exhibit a variety of particle shapes and sizes, ranging from units of μm to about 200 μm . Relatively large agglomerates can be observed in both, possibly caused by the PVDF binder still present in the material - something that would later be confirmed by FT-IR analysis [1, 2]. For comparison, Figure 9a shows an SEM image of an intact cathode, where much smaller particles can be seen. These observations suggest that the discharging method itself does not affect the morphology of the recovered particles, and that a better grinding method is needed to recover material fit for direct recycling, so that the CAM particles are smaller and have a more uniform size and shape distribution.

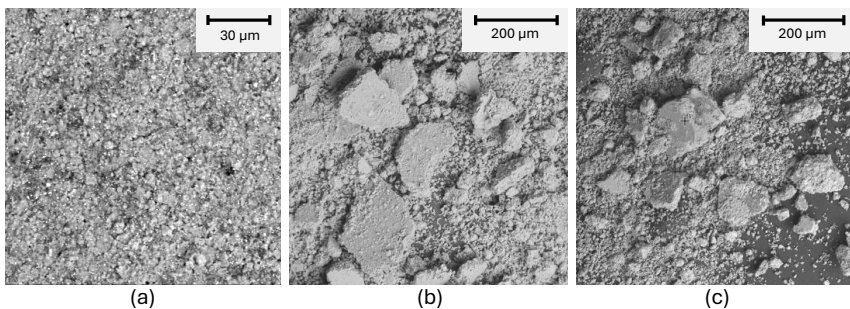


Figure 9: SEM images of the CAM still attached to the current collector (a), the delaminated and powdered CAM (by cryogenic delamination) from a resistor sample (b) and from a brine sample (c).

5.2 Delamination of LFP CAM from the current collector

The results of the delamination with ethylene glycol can be seen in Figure 10a, with phytic acid in Figure 10b, by freeze-drying in Figure 10c and a selection of results from two different conditions in the Libriker liberator can be seen in Figure 10d.

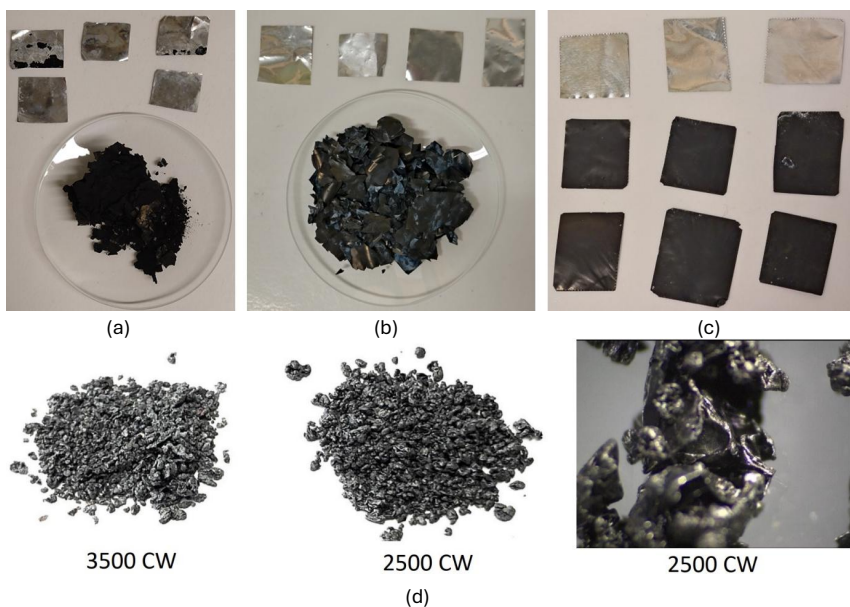


Figure 10: Results of delamination with ethylene glycol (a), phytic acid (b), by freeze-drying (c) and from two different experimental conditions in the Libriker liberator (d).

Note the incomplete delamination with ethylene glycol (Figure 10a), with

patches of the CAM still attached to the Al foil, as well as the complete delamination by phytic acid (Figure 10b) and freeze-drying (Figure 10c). Note especially that the recovered CAM is left mostly intact from the freeze-drying, unlike the material from the solvent-based delamination. The images from the LibriXer samples in Figure 10d can be seen as an illustration of the effect of the liberator on the Al foil, as well as the incomplete delamination, where large parts of the material are still left on the Al foil. In fact, it is not possible to accurately assess the Peeling Efficiency (PE) of the LibriXer method, as most of the recovered CAM was lost after the runs, however, an estimate suggests a PE of 20% or less.

Calculated PE values for the other three delamination methods can be seen in Table 3. Note that the data for freeze-drying come from the initial experiments conducted with small pieces in a beaker, for a fairer comparison with the chemical methods, which were conducted in the same fashion.

Table 3: Calculated peeling efficiencies from the different delamination methods.

Delamination method	Peeling Efficiency [%]	Standard deviation
Ethylene glycol	80.3	3.6
Phytic acid	28.6	19.9
Freeze-drying	92.7	3.9

Among the lab-scale delamination techniques, freeze-drying clearly exhibits the highest PE of about 93%. However, the solvent-based delamination using ethylene glycol also achieves a relatively high PE of about 80%, but in a much shorter time span of about 1 min, as opposed to freeze-drying, which took 24 hours only inside the lyophilizer. The delamination with phytic acid, on the other hand, showed only a low PE of less than 30%. This is attributed to a preferential leaching of Li from the material by the acid, which would later be confirmed by XRD.

5.2.1 *Material impact of the delamination methods*

Figure 11 shows diffractograms of the CAM obtained by the different delamination methods.

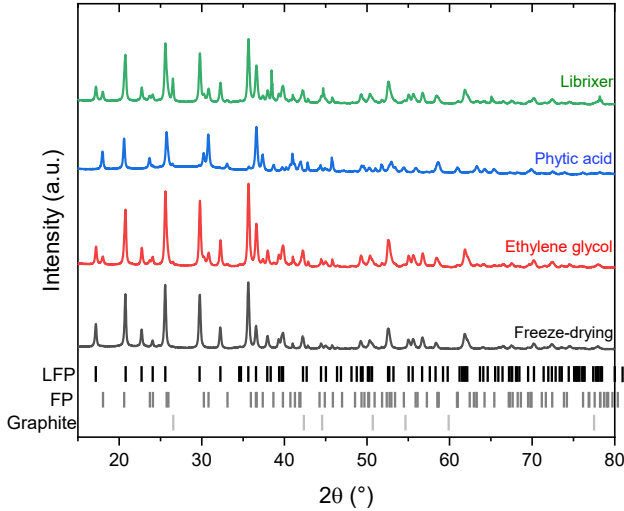


Figure 11: XRD diffractograms of the CAM recovered through the different delamination methods.

The samples from freeze-drying, ethylene glycol and Libriker share a similar pattern, i.e., with LFP being the dominant phase, with traces of FP and graphite being visible as well (although the FP phase is barely distinguishable in the freeze-dried sample). This suggests that there is some Li leaching in ethylene glycol, while no delithiation could be observed caused by freeze-drying. The relatively high intensity of the FP phase in the Libriker sample cannot be attributed to leaching, as no solvent was used, but rather to heterogeneities within the cathodes that were treated this way. Note that the Libriker data are results from a relatively large number of cathodes from different cells and modules, treated simultaneously, unlike in the other methods, where the cathodes were taken from the same cells for a fair comparison. The reason for this is that the Libriker liberator has a much higher material demand, as it is pilot-scale equipment. Another observation linked to Libriker is a relatively high intensity of the graphite phase, most clearly visible at 26.5° 2θ . This is attributed to indirect contamination in the liberator, as the Libriker facility had treated mixed-electrode streams prior to the cathodes-only runs. Despite having been cleaned in between the runs, it is likely that the adhesive properties of powdered graphite made some cross-contamination possible [2].

Interestingly, in the phytic acid sample, FP is the most dominant phase, with no clearly visible LFP peaks present. This supports the theory that phytic

acid leaches Li from the treated CAM and leaves behind intact FP. While this renders phytic acid an unsuitable delamination agent for direct recycling, it could be utilized for the hybrid, or indirect, approach, given its property to leave the FP phase intact. If the leached Li can be easily recovered as a pure salt, the two materials could be used as precursors for a resynthesis reaction [2].

SEM images of the four samples can be seen in Figure 12.

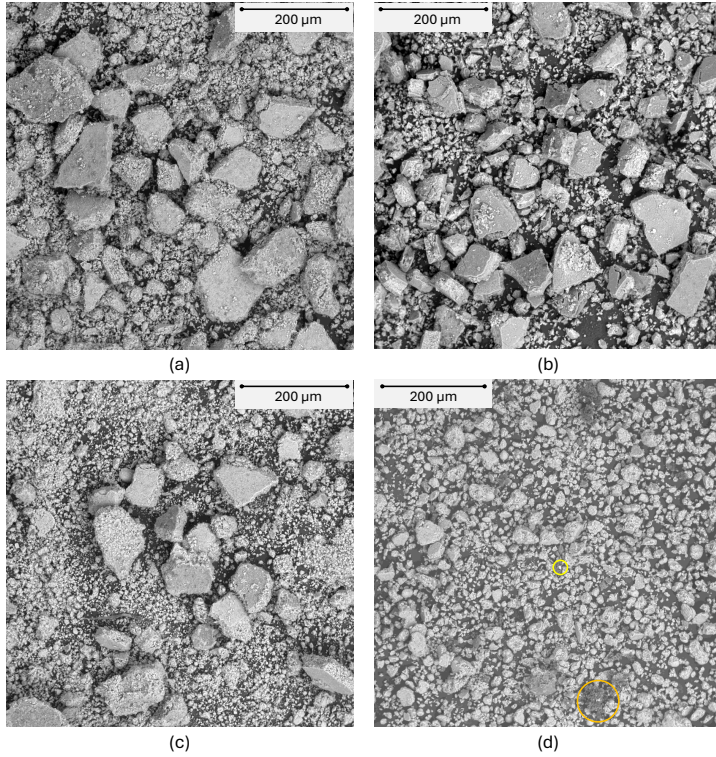


Figure 12: SEM images of recovered CAM from freeze-drying for 24 hours on whole cathodes (a), phytic acid delamination (b), ethylene glycol (c) and Librixxer treatment with highlighted impurities of Cu (yellow circle) and graphite (orange circle) (d).

Agglomeration of particles can be seen in all cases, where the particle sizes and shapes are similar in the three lab-scale methods, showing agglomerates of mostly up to 100 μm in size. This is attributed to the presence of the PVDF binder, as well as the manner in which the delamination occurred, i.e., in larger chunks of the material that were then ground to a finer powder in the attrition mill. The morphology of the particles seems to be similar as

well between the methods, likely due to a similar delamination mechanism, where the Al-PVDF bond is weakened in different ways, causing the CAM to spontaneously detach from the foil [2].

On the other hand, the LibriXer method utilized a different delamination mechanism, based solely on separating the materials by physical force, rather than chemically weakening the bond between them. Because of the strong forces applied (or injected according to the LibriXer terminology) to the material, the recovered CAM particles exhibit a more regular shape and size distribution, with the particles mostly having a regular round shape and not exceeding 50 μm in most cases. For direct recycling purposes, this is beneficial, as it approaches the common industrial practice of smaller LFP particles below 20 μm . However, because of contamination from previous runs, there are visible impurity particles within the recovered material, as highlighted in Figure 12d. EDX identified these particles as mostly consisting of Cu and graphite, respectively. Since the contamination is indirect and caused by improper sample handling at the LibriXer site, it would be possible to fully mitigate this issue in a real industrial setting, by either more rigorous cleaning in between runs, or by separating the cathode and anode streams altogether.

The presence of the PVDF binder was confirmed in all cases, as seen in Figure 13.

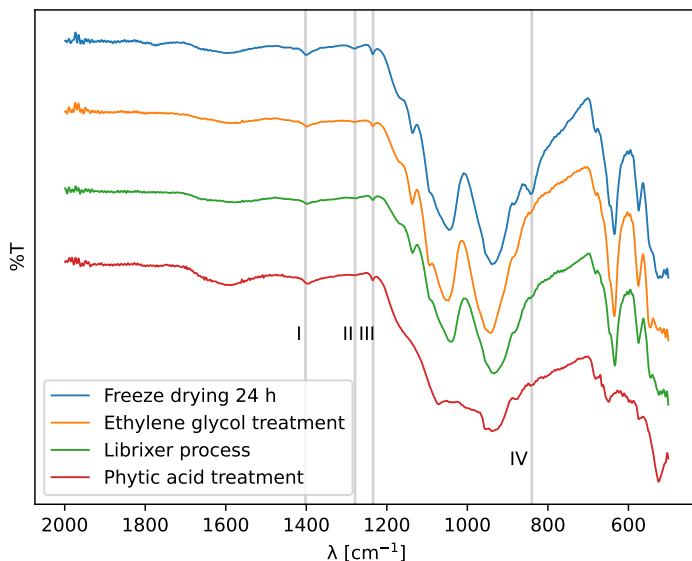


Figure 13: FT-IR spectra of the CAM recovered by the different delamination methods.

The spectra obtained from the FT-IR analysis were largely comparable across the samples, with the notable exception of the phytic acid-treated sample, which is expected given its different chemical composition. For the samples processed by freeze-drying, ethylene glycol and the LibriXer process, the characteristic bands of LFP are distinctly observed. Among these, the bands located at 1139 cm^{-1} , 1096 cm^{-1} , 1046 cm^{-1} , 966 cm^{-1} and 944 cm^{-1} stand out particularly, and they are all attributed to the intramolecular vibrational modes of the phosphate anion (PO_4^{3-}) [66]. Complementary bands appear at 636 cm^{-1} , 576 cm^{-1} and 546 cm^{-1} , corresponding to PO_4^{3-} bending modes [66]. In contrast, the spectrum of the phytic acid-treated sample exhibits a merging of the two well-defined bands at 1096 cm^{-1} and 1046 cm^{-1} into a single broad shoulder centered near 1082 cm^{-1} , accompanied by the displacement of the faint 966 cm^{-1} band towards a more pronounced peak at 956 cm^{-1} . Both of these changes are characteristic of FP and partially delithiated $\text{Li}_{1-x}\text{FePO}_4$ phases [66]. This observation is consistent with the XRD diffractograms and verifies that the dominant bulk phase in the phytic acid-delaminated sample is FP, whereas it is LFP in the other samples [2].

Furthermore, signals associated with PVDF are present in every sample, as mentioned before. Bands I and II at 1402 cm^{-1} and 1279 cm^{-1} originate from β -PVDF and correspond to CH_2 and CF groups, respectively [67, 68]. Band III at 1234 cm^{-1} is instead more indicative of out-of-plane CF deformation in γ -PVDF, while band IV at 840 cm^{-1} arises from CH_2 rocking characteristic of either the β - or γ -PVDF phase [68]. Taken together, these features indicate that both crystalline PVDF phases occur in the samples, demonstrating that the binder is carried over into the recovered cathode active material irrespective of the delamination method. A practical consequence of this finding is that, should the binder need to be removed prior to relithiation, an additional treatment — either thermal processing or solvent-based extraction, e.g., using supercritical carbon dioxide [69–71] — would most likely be required as a supplementary step subsequent to the delamination [2].

5.2.2 *Energy requirement and cost estimations of the delamination methods*

To enable a more meaningful comparison of the various delamination routes with respect to their energy demands and chemical expenses, a set of simplified calculations was performed. It should be emphasised that these figures represent rough approximations at laboratory scale (LibriXer being the exception) and are intended merely as an initial basis of comparison. At pilot or

industrial scale, the outcome could deviate considerably. In the case of freeze-drying, the lyophilizer setup, including the vacuum pump, operates at 2.99 kW, corresponding to 72 kWh over a 24 h cycle. Given this, the electricity demand for treating 1 kg of material amounts to 1032 kWh/kg. Taking the Peeling Efficiency (PE) of 93% into account, the number increases to 1110 kWh/kg recovered CAM, rendering this the most energy-demanding of the methods. Using an electricity price of 0.2 EUR/kWh (a rounded value derived from the EU average for non-household consumers during the second half of 2025 [72]), the corresponding energy cost amounts to roughly 222 EUR/kg recovered CAM. Estimating the capital cost of the freeze-drying equipment is less straightforward, as industrial freeze-dryers span a wide price range. In addition, the apparatus would need to be carefully designed around the requirements of this process, i.e., the electrodes would have to be arranged in a configuration that allows for full and unobstructed electrode–ice contact so as to maximize the peeling efficiency [2].

For ethylene glycol, the energy requirement originates from heating the solution. The heating plate employed on lab-scale was rated at 1500 W, and the complete experiment ran for approximately 30 min, including the time to bring and hold the solvent to the required temperature. This corresponds to an electricity use of 0.75 kWh. Processing 1 kg of material would thus require 375 kWh/kg, a value which becomes 469 kWh/kg recovered CAM after accounting for the somewhat reduced PE of 80%. Applying the same electricity price of 0.2 EUR/kWh gives a cost of approximately 94 EUR/kg recovered CAM. Additionally, the chemical itself constitutes an expense. Taking a European price of roughly 0.97 EUR/ℓ [73] and a consumption of 12.5 ℓ/kg corrected for the 80% PE, the cost contribution of the solvent is estimated roughly at 12 EUR/kg recovered CAM.

As the phytic acid experiments were conducted at ambient temperature, no energy consumption is reported for this route. However, the cost of the chemical itself, and that of subsequent waste treatment, prevails. Given that the 50% phytic acid solution applied in this study carries a price of approximately 260 EUR/ℓ, and that the method entails a consumption of 20 ℓ per kg of material at a PE rate of 30%, the estimated chemical cost reaches 17300 EUR/kg recovered CAM, far exceeding that of ethylene glycol by orders of magnitude. This price should be understood as a laboratory-scale figure, as bulk prices applicable to industrial volumes are unavailable, implying that the true cost would presumably be substantially lower. Note that for both solvent-based

methods, the solvent could potentially be recycled within an industrial process, which would naturally reduce the associated cost. This possibility has not been explored so far but constitutes a possible topic for further research [2].

Assessing the energy intensity of the Libriker process is more challenging, primarily because the trials were carried out with quantities of material far below the throughput the equipment was engineered for. This hindered an accurate assessment of the material density, which had to be approximated to 0.2 kg/ ℓ . Operating the equipment at its full capacity of 2000 ℓ /h with a rated power of 68 kW would result in an electricity consumption of 0.17 kWh/kg of processed material. Assuming a PE of approximately 20%, this adjusts to 0.85 kWh/kg recovered CAM - a value far below those of the other methods. Converting this into an electricity operating cost at 0.2 EUR/kWh yields approximately 0.17 EUR/kg recovered CAM, the lowest among all methods considered. It should be noted, however, that this number cannot be directly compared to the corresponding numbers for the other methods, as it assumes production-level material throughput, while the numbers for the other methods were calculated on the lab-scale results. The capital cost, on the other hand, may surpass that of the other methods, given that the industrial Liberator used in this study has a capital price of approximately 400000 EUR [2].

5.3 Impurity removal by solvent washing

To evaluate whether solvent washing could eliminate various impurities from the CAM, and what consequences this would have for the material, entire cathodes were subjected to washing with a selection of solvents, subsequently delaminated by means of freeze-drying, and pulverized in a manner identical to the unwashed samples. XRD analysis was carried out to determine whether any phases had been eliminated through the washing procedure. Figure 14 presents a comparison of diffractograms from an unwashed sample, one washed three times with ethanol, one with acetonitrile (3x), one with acetic acid (3x), and one subjected sequentially to both acetonitrile (3x) and acetic acid (1x).

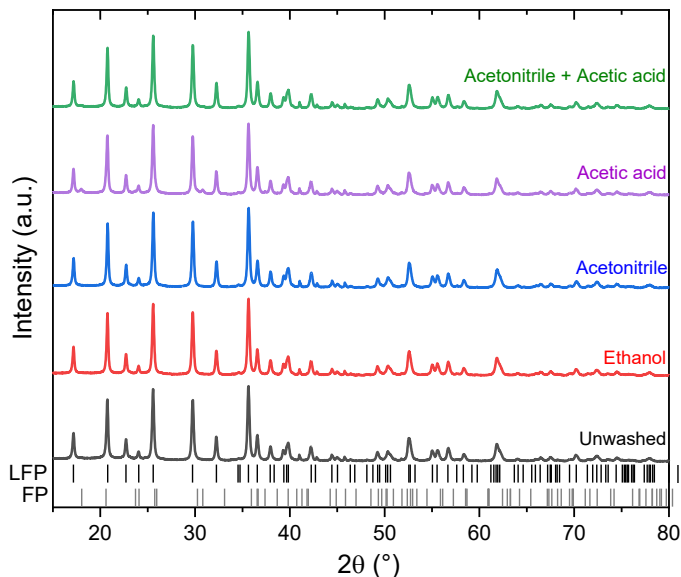


Figure 14: XRD diffractograms of freeze-dried samples washed in different manners.

The diffractograms of the samples are nearly indistinguishable from each other, indicating that solvent washing exerts no measurable influence on the crystalline phases contained in the material. An exception is the acetic acid-washed sample, in which the FP phase can be distinguished. Given that all cathodes employed in these experiments originated from the same cell, this points to partial leaching of Li from the material by the acid. In the combined acetonitrile–acetic acid treatment, this effect is not readily apparent. This is unsurprising, since this particular cathode underwent three acetonitrile washes followed by only a single acetic acid wash, whereas the remaining samples were washed three times with their respective solvent. The Li-leaching behavior of acetic acid is thus more pronounced when the washing is repeated more than once. ICP-OES confirmed this behaviour: the Li content of the solid samples dropped from 3.85 wt% (± 0.11) prior to washing to 3.56 wt% (± 0.07) after three acetic acid washes, equivalent to a 7.5% reduction in Li content [2].

Depending on the sample in question, ethylene glycol (EG), propylene glycol (PG), ethylene carbonate (EC), propylene carbonate (PC) and N-methyl-2-pyrrolidone (NMP) were identified by GC-MS, to assess the removal efficiency of the different solvents. Besides these compounds, minor quantities of unidentified substances appeared in some samples. EC and PC represent typical

low-volatility electrolyte solvents; those with greater volatility had already evaporated during cell opening and the subsequent processing stages. The occurrence of EG and PG, being common degradation products of EC and PC, is therefore unsurprising. NMP, on the other hand, is a standard solvent in cathode sheet manufacturing but does not serve as an electrolyte solvent, and its presence was hence not anticipated. Therefore, it was not included in the GC-MS calibration. Its presence is unexpected, as the solvent should have been eliminated during the manufacturing stage [2].

In order to quantify the washing effect of each solvent, the measured values were referenced against the identically treated unwashed sample and expressed as a removal efficiency [%]. Figure 15 illustrates the removal efficiencies of the two detected residual electrolyte solvents across the various washing methods.

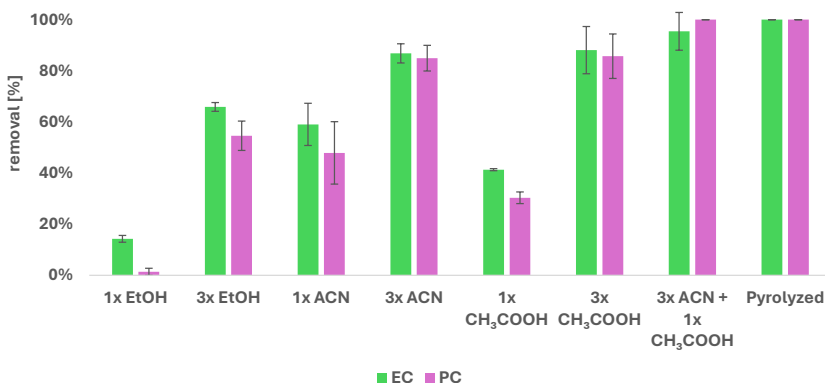


Figure 15: Removal efficiencies of EC and PC with the different washing methods.

The GC-MS data reveal that a single wash of the cathodes is insufficient to strip away appreciable quantities of the electrolyte residues. In the case of ethanol, even a triple wash fails to exceed 65% removal efficiency — an unfortunate finding, given that ethanol is the greenest, mildest and most affordable of the three solvents. An interesting observation is that triple washing with acetonitrile performs on par with acetic acid, the latter in fact slightly outperforming the former. This indicates that, for the purpose of washing electrolyte solvent residues from the recovered CAM, acetic acid could substitute for acetonitrile as a considerably greener and less costly alternative. A sequence of three acetonitrile washes followed by a single acetic acid wash appears to fur-

ther increase the removal efficiency. Whether this slight improvement justifies the added material consumption and waste handling entailed by employing two solvents rather than acetic acid alone is, however, debatable. Unsurprisingly, pyrolysis eliminates all traces of the electrolyte solvent residues. Should the recovered CAM be subjected to relithiation via a thermal route, solvent washing of the cathodes may therefore prove unnecessary [2].

Regarding the elimination of the Cu impurity by acetic acid, the washing operation itself provided an indication that the acid leaches some Cu, as the liquid took on a blue color almost immediately upon immersion of the electrodes. ICP-OES analysis of the acid following three successive cathode immersion stages revealed comparable concentrations in the first two (130 mg/ ℓ and 148 mg/ ℓ , respectively), followed by a decline to roughly 85 mg/ ℓ after the third stage. No Cu was detected post-washing in any of the other solvents. From this it follows that acetic acid is indeed capable of leaching Cu from the LFP material, and that room for optimization exists, as some Cu appears to remain in the CAM. At the same time, as shown earlier, acetic acid appears to leach Li as well. This constitutes a dilemma, since such an effect on the material and its value is undesirable. As discussed earlier, deep discharge of the battery modules constitutes an important safety measure for direct recycling, thereby making the occurrence of Cu impurities probable [1]. Consequently, a Cu removal step will most probably be required for any industrially implemented direct recycling process. Should acetic acid be employed for this purpose, some degree of Li loss is likely unavoidable — a factor that should be considered in future implementations of the process [2].

FT-IR measurements were likewise conducted on the washed samples to gain further insight into how the washing affects the composition of the recovered material. The acquired spectra are presented in Figure 16.

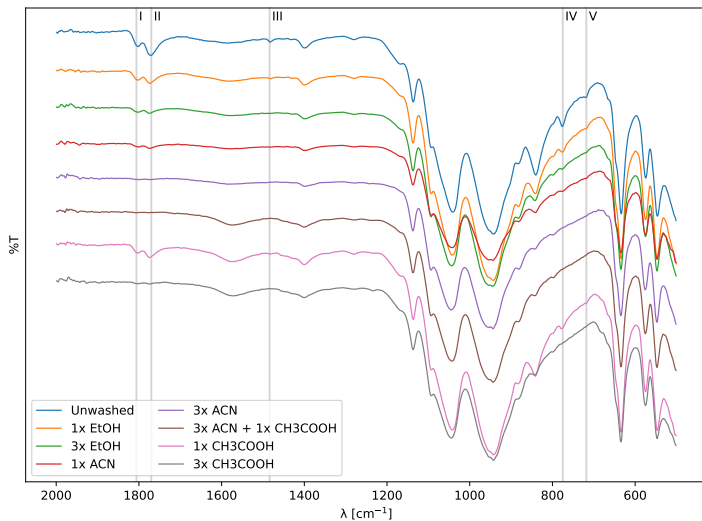


Figure 16: FT-IR spectra of samples washed in different manners.

The spectra are largely indistinguishable, being dominated by bands arising from LiFePO_4 together with visible traces of PVDF (see previous discussion in section 5.2.1). Certain visible differences between the samples do, however, exist. Five bands appear in the unwashed samples with lower or absent intensity in the washed ones. The intensity of these bands appears to track, in approximate terms, the removal efficiencies derived from GC-MS, in that greater removal efficiency in the corresponding GC-MS sample coincides with lower band intensity. Bands I and II, at 1806 cm^{-1} and 1770 cm^{-1} , stem from carbonyl-containing phases, most likely acid anhydrides or dialkyl phosphates, and thus point to non-volatile electrolyte solvents or their degradation products. Band III at 1484 cm^{-1} relates to carbonate species, pointing towards decomposition products of the SEI. Bands IV and V, situated at 775 cm^{-1} and 718 cm^{-1} , correspond to C-H bending and hence cannot be confidently assigned to any particular organic compound.

5.4 Regeneration of S-LFP by molten-salt assisted relithiation

Relithiation experiments yielded recovered LFP CAM (R-LFP) with an average 18% lower mass, as compared to the initial total mass of the samples going in to the relithiation experiment. This is explained by the relithiation reaction taking place, as well as some electrolyte- and binder-related residues leaving the material. Figure 17 shows the measured electrochemical performance in

terms of long-term cycling for a selection of samples.

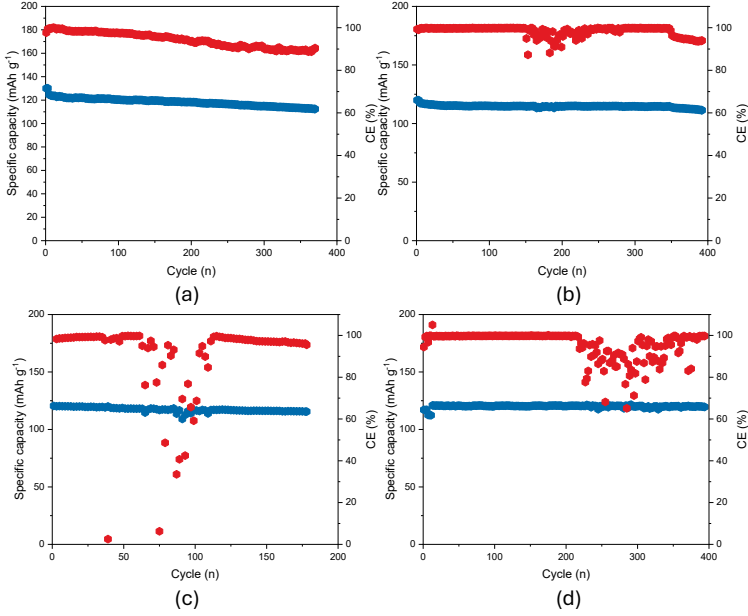


Figure 17: Long-term cycling results at 1C from the samples b_Ac (a), ab_Ac (b), (1)_Ac (c) and a_Ac (d).

It becomes clear that the electrochemical cycling performance varies over the population of the samples, although no clear pattern was recognized, mostly due to parts of the dataset never having been delivered. What can be said is that the cycling performance is not up to par with commercial battery-grade LFP. Even the best performing cell (Figure 17a) exhibits an initial discharge capacity of approximately 130 mAh g⁻¹, which quickly drops to slightly above 120 mAh g⁻¹. The Coulombic Efficiency (CE) also decreases quickly to about 95% after 380 cycles, showing an overall low reversibility of the electrochemical reaction within the cell. In the other cells (Figure 17b-d), the capacity performance is overall lower and the CE measurements show chaotic behavior, most likely caused by inhomogeneities in the sample in terms of purity and/or morphology.

Morphological inhomogeneities are confirmed by SEM, as seen in Figure 18 below.

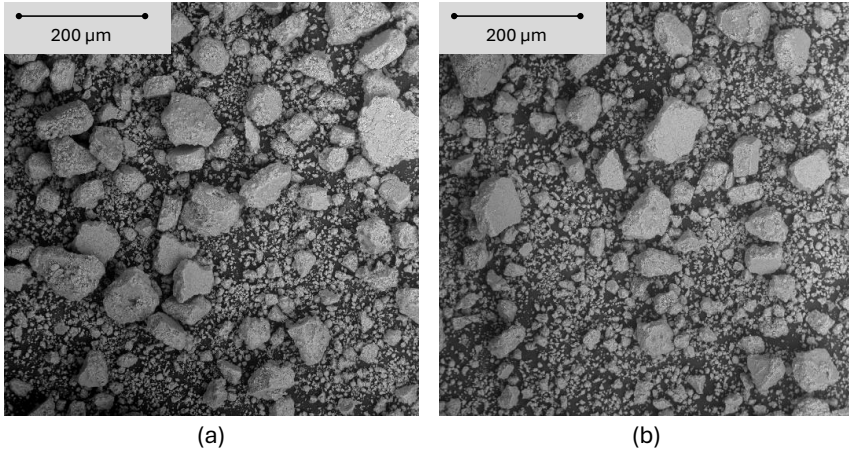


Figure 18: SEM images of relithiated samples (1)_Ac (a) and a_Ac (b).

Both samples exhibit mostly suitable particle morphology in terms of mostly round particles with even elemental distribution (confirmed by EDX). However, the particles were generally too large, some up to 100 μm , as opposed to the common industrial practice with particles closer to 20 μm or less in size. The uneven size distribution may be a reason for the low and chaotic performance as seen in Figures 17c-d. This suggests that post-relithiation treatment, e.g., in the form of ball-milling and spray drying, may be necessary to achieve a more suitable particle morphology.

In terms of the crystal structure of the R-LFP samples, the diffractograms can be viewed in Figure 19, which also features the diffractogram of the S-LFP sample prior to relithiation, as well as a Fresh LFP (F-LFP) sample from commercial, battery-grade LFP (Sigma-Aldrich).

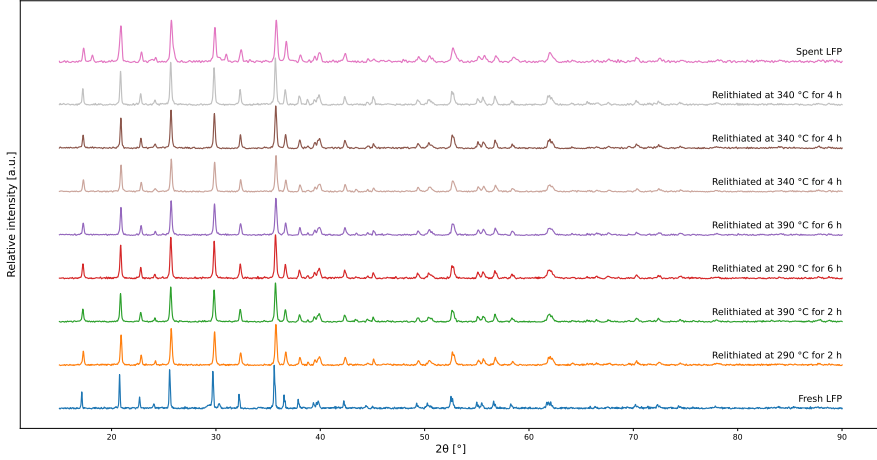


Figure 19: XRD diffractograms of regenerated, spent and fresh LFP samples.

An important observation that can be made from the diffractograms upon comparing the relithiated samples to the spent sample, is the complete disappearance of the FP phase in all the relithiated samples (most visible at 18° and 32° 2θ). This clearly suggests that the relithiation reaction itself was successful. However, there seemed to be an introduction of a lithium fluoride (LiF) phase visible at 46° 2θ , pointing towards possible overlithiation of the samples. A $\text{Fe}_2\text{P}_2\text{O}_7$ phase was detected in the F-LFP sample at 30.5° 2θ , the origin of which is unclear. Overlithiation of the samples was later supported by ICP-OES, where the measured content of Li in the R-LFP samples was on average 6.1 wt% - a 41% increase compared to the S-LFP sample. When converted into molar amounts, this yields an average Li:Fe ratio of 1.51:1, significantly exceeding the ideal 1:1 ratio. The impurity introduction caused by this is believed to be a factor contributing to the relatively low performance of the R-LFP samples. Another factor is the previously discussed Cu impurity, which was found in all samples at about 1 wt% rate.

6 Conclusions and future work

This work has examined three successive stages in the pretreatment chain of spent LFP batteries from real-life mild hybrid applications intended for direct recycling: the discharging of the spent modules, the delamination of the cathode active material from its current collector, and impurity removal by solvent washing. Moreover, relithiation of spent samples was performed in an attempt to restore their electrochemical performance.

Discharging of the spent LFP modules was performed using both a NaCl saline brine and an external resistor circuit. With respect to the resulting electrode quality, brine discharging induces corrosion of the electrodes, whereby the cathode active material (CAM) acquires a higher Cu impurity content than in the resistor-based method. A slight increase of the Al concentration in the CAM, arising from corrosion of the battery's outer casing and the cathode current collector, was likewise observed. Discharging through an external circuit emerges as the preferable option: it generates no waste requiring subsequent treatment and preserves the integrity of the recovered CAM better, giving lower impurity levels and a higher Li content. This is of importance for direct recycling of the cathode, which rests on a reduced number of process steps and a low impurity content in the CAM.

Four routes for delaminating spent LFP CAM from the Al foil were investigated, and the recovered material was characterized with respect to the impact of the delamination methods on the integrity of the recovered CAM. XRD and FT-IR analyses jointly confirmed that the freeze-dried, ethylene glycol-treated and LibriXer-processed samples retained LiFePO_4 as the main bulk phase, whereas phytic acid treatment yielded mainly FePO_4 , as a consequence of Li leaching by the acid. PVDF was detected in the recovered CAM irrespective of the delamination technique employed, implying that binder removal prior to relithiation would demand an additional thermal or solvent-based step. Simplified cost and energy estimates identified freeze-drying as the most energy-intensive route, but the most promising overall for direct recycling purposes given the highest measured peeling efficiency of 93%, combined with the retained chemical integrity of the recovered CAM. Ethylene glycol delivered a competitive performance, reaching 80% peeling efficiency, although

solvent recovery and reuse remain unexplored and could lower its cost. Phytic acid proved unsuitable for direct recycling purposes and expensive at lab-scale pricing despite requiring no energy input. The novel LibriXer technology was tested and evaluated, exhibiting by far the lowest projected energy consumption and operating cost. Nevertheless, it must be developed further for higher peeling efficiency and reduced granulation of the current collector foils.

Solvent washing of whole cathodes prior to delamination removed parts of the electrolyte-related impurities, with triple washing by acetonitrile and acetic acid performing comparably well, and acetic acid standing out as the greener and cheaper candidate. Acetic acid, however, simultaneously leached both Li and the Cu impurity, presenting a trade-off that must be weighed in future process designs. Pyrolysis removed all electrolyte residues, suggesting that solvent washing may be redundant where thermal relithiation is implemented. Even so, a greener means of cleaning electrodes of electrolyte residues and other impurities should be developed.

Relithiation of the spent LFP using lithium acetate proved to be successful, although the electrochemical performance of the regenerated samples was not up to par with what would be expected commercially. Overlithiation that caused the introduction of a LiF impurity as well as unsuitable particle size distribution and a persisting Cu impurity were identified as the most likely reasons for the relatively low performance of the R-LFP samples. These results point to a need to more precisely assess the degree of delithiation in the spent samples, as well as a need for post-relithiation treatment for better particle morphology. Moreover, the results underline the importance of developing an effective pretreatment route that eliminates various impurities from S-LFP samples subjected to relithiation.

Taken together, these results constitute novel insights into the pretreatment process of spent LFP batteries for direct recycling purposes, outlining more and less preferable pretreatment strategies in terms of their impact on the recovered CAM. This work also identifies challenges for direct regeneration of spent LFP CAM that arise from inadequate pretreatment handling. Future work is set to focus on further optimization of the pretreatment and relithiation processes in order to produce R-LFP with an electrochemical performance up to par with commercially available LFP cells. Furthermore, the hybrid approach is set to be tested in practice, employing acid leaching to recover Li and FePO_4 separately, subsequently using the recovered materials directly as precursors for the resynthesis of battery-grade LiFePO_4 .

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