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# Comparison of two approaches for discharging $LiFePO_4$ EV battery packs and comprehensive analysis of recovered cathodes for direct recycling purposes

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The recycling of spent Li-ion batteries has become a highly relevant research topic owing to increasing amounts of battery waste along with its toxic nature and significant content of valuable materials. Extensive research has been done on direct recycling of batteries with $LiFePO_4$ (LFP) chemistry, where the cathode active material (CAM) is collected and regenerated to be fit for use in new battery units. However, details on how the spent batteries should be handled, discharged and dismantled to collect the CAM are rarely discussed in research papers, despite being an integral part of any direct recycling application. Herein, we present a detailed description of two discharging methods of spent LFP batteries. Characterization of the CAM powders revealed the potential impact of the discharging method on CAM quality. Increased levels of copper and aluminum impurities in the CAM were observed after saline brine discharging, compared to discharging using an external electrical circuit. Considering the reduced number of process steps in the external circuit method, it is deemed more advantageous than the salt brine discharge method.

## 1. Introduction

The Li-ion battery (LIB) market has seen exponential growth during the past decades, owing to multinational efforts for electrification as a means of reducing the dependence on fossil fuels, especially in the mobility sector. In fact, the LIB market is projected to exceed 93 billion USD within the next two years.[1] At the same time, global Li resources are scarce and the mining for Li has been associated with serious environmental and human health issues.[2–4] Meanwhile, given the limited lifetime of electric vehicle (EV) batteries, large amounts of LIBs are being retired, generating a hazardous waste stream, the growth of which follows the market development. Recycling batteries is thus a necessity from environmental, economic, and human health perspectives.[5,6]

### 1.1. Present recycling strategies

Presently established recycling methods are far from perfect – the common and simple process of pyrometallurgy is unable to recover desirable amounts of Li and only hardly meets the goals for recovery of other valuable elements, while the more novel hydrometallurgy approach uses large volumes of chemical reagents and produces toxic chemical waste.[1,7–10] For $LiFePO_4$ (LFP) chemistry, which does not include metal elements of real economic value except for Li, these issues render the established recycling routes unsatisfactory.[1,11] LFP is, however, one of the most common LIB chemistries, expected to exceed 30% of the LIB market by 2030.[12] Hence, there is a need for the development of a greener, more economic, and more efficient recycling route for these types of batteries.

For the abovementioned purpose, the so-called direct recycling route has received increased attention in the scientific community, attempting to directly regenerate spent LFP cathodes, preferably in a non-destructive and green manner. A lot of effort has already been done in this relatively novel field, including solid-state thermal treatments,[5,11,13,14] hydrothermal treatments,[15–17] molten salt assisted regeneration,[18–20] and chemical or electrochemical relithiation of spent LFP cathode materials.[8,10,21–23] However, these methods have yet to find application on an industrial scale. Possible reasons for this include the high cost of the process compared to the potential revenue, market fluctuations in terms of material costs, unsatisfactory quality of the recycled cathode materials as compared to pristine ones (*i.e.*, low technological readiness), or fast development of new battery

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technologies and solutions, leading to hesitation among industrial sectors to invest in processes that cannot be universally applied to multiple battery chemistries.[1] Despite these shortcomings, research suggests that direct recycling may be the only reasonable strategy for low-cost battery chemistries, such as LFP chemistry from a circular economy perspective.[24,25]

Before discussing complete direct recycling process schemes, however, there is another practical obstacle to overcome in the pre-treatment stages of the processes. Broad and often justified concerns are frequently raised considering the safety aspects of handling and dismantling spent LIBs. Toxic electrolytes, highly flammable and volatile electrolyte solvents, flammable graphite anodes, and the risk of unpredictable thermal runaways followed by violent fires are some of the risk factors that prompt caution at all stages of the batteries' life cycle from research, through end-user applications, to end-of-life LIB handling.[26] Therefore, to minimize the electrical energy stored inside the batteries and thereby minimize the risk of accidents, such as electric shocks and fires, deep discharge prior to their dismantling is a necessity for any recycler or researcher.[10]

In today's recycling approaches, batteries are either loaded into furnaces, where explosions and violent fires are not an issue, or they are crushed in an inert atmosphere to minimize fire hazards.[1] In discussions about direct recycling, on the other hand, there is a need for collecting cathode materials from batteries in as pure and preserved form as possible to enable their regeneration. This often comprises manual dismantling of the batteries to obtain individual battery cells, followed by manual harvesting of the cathode sheets from the cells.[27] The absence of fireproof or fire-resistant equipment thus creates greater demands on the discharging protocol in terms of safety, efficiency, economy, and effect on the cathode materials. These (so far) manual processes may also need to deal with issues such as the rebound effect, where readings of increasing voltage appear after the completion of battery discharging[28] or swelling of the battery cells upon deep discharge.[29,30]

### 1.2. Discharging of LIB modules in the literature

Different discharging methods have been investigated. There are two main methods for removing residual charge from the battery, namely electrically using external resistors, or more traditionally, electrochemically using a saline solution (brine). In saline solution, the use of different salts has already been investigated, with sodium chloride (NaCl) being the one that presents the best results in relation to the complete discharge of batteries.[31,32] The advantage of this method is that it is not expensive, can be used on a large scale and depending on the conditions it is performed between 20 min and 24 hours.[31,33,34] The disadvantage is that during the process there is a release of hydrocarbons, carbon dioxide ($CO_2$), hydrogen ($H_2$) and chlorine gas ($Cl_2$), the latter causing external corrosion to the battery, and it can increase the impurity content in the active material of the electrodes. There is also a risk that the electrolyte will leak into the solution. In addition, the used solution requires further treatment to be recycled or discarded in a safe way, potentially generating a large waste stream.[30–32,35]

The external circuit method, on the other hand, uses a resistor circuit to discharge the battery. In this case, the discharge rate is controlled to avoid heating the battery and mitigate the risk of fire. In the case of batteries made from pouch cells, there may be swelling of the cells, possibly due to limited diffusion of ions.[30] In this method, there is no formation of gases and by-products that require treatment for disposal. In addition, the energy removed from the battery can be stored and reused. However, the discharge time can vary from 24 hours to days, which prolongs the pre-treatment time extensively.[30,35] Large-scale application has become feasible, though, as this is a cleaner way to discharge the battery, and much effort has been put into maintaining safety.[36,37]

The safety aspect of the discharge is undoubtedly the main driver for the inclusion of the step in basically any battery recycling process. In particular, when considering direct recycling, where battery modules need to be dismantled manually, the depth of discharge will correlate with the mitigation of incident risks – the deeper the discharge, the less energy left in the cells. However, studies have demonstrated that too deep a discharge will have an impact on the quality of the recovered materials, especially the electrode active materials. Previous studies have demonstrated the contamination of Cu from the anodic current collector in the CAM, due to the electrochemical dissolution of Cu into the electrolyte matrix and its subsequent deposition onto the CAM,[38–40] with a subsequent risk of internal short circuits if the discharging continues into negative states of charge (SoC).[40] Moreover, the presence of Cu in the CAM of directly relithiated samples has been linked to poor electrochemical performance and risks of internal short circuits in recycled CAMs and is thus important to keep at a minimum.[41,42] Despite the present efforts to investigate and compare different discharging methods, their reporting in the direct recycling-related literature, as well as reporting on the following dismantling and CAM-harvesting methods, is scarce and non-detailed. Researchers are then left to develop their own ways of dealing with harvesting of the material, delaying the work on its recycling. Also, different discharging methods have rarely been compared in terms of their effect on the quality of the recovered materials; something that is important especially for direct recycling purposes. This paper aims at filling this literature gap by presenting a detailed description of a developed laboratory-scale external circuit-based discharging and dismantling method, from whole, fully charged battery modules from a car battery pack to recovered LFP CAM powder. The external circuit protocol is then compared with the more traditional salt brine discharging in terms of the effect on the collected CAM to assess its feasibility for a direct recycling application.

## 2. Experimental

### 2.1. Materials and methods

Spent LFP batteries from mild hybrid applications were delivered by an established car manufacturer, as part of an ongoing recycling project in our group. Most of the modules were nearly

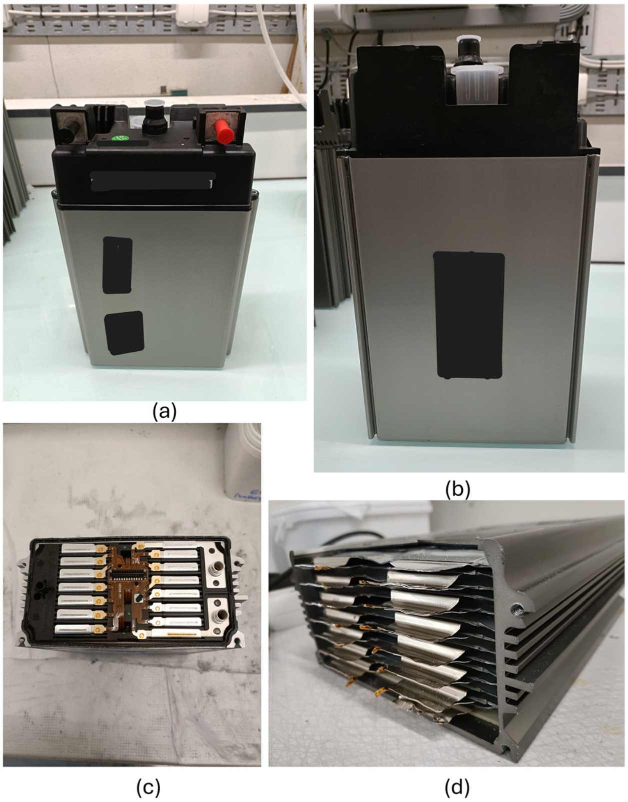

Fig. 1 As-delivered LFP battery from the front (a) and from the back (b); view of the battery after removing the top plastic head with (c) and without (d) the wirings and poles.

fully charged, *i.e.*, with a voltage of around 46 V, the full rated voltage being 46.2 V. The batteries also had a rated capacity of 8 Ah, a rated energy of 369.6 Wh, and a rated weight of 8.1 kg. Fig. 1a and b show an as-delivered battery from two angles.

For the discharging experiments, kitchen salt NaCl with added iodine and tap water were used to make the discharging brine. Electrical resistors were from Arcol (10 Ω), ATE Electronics (6.8 Ω) and VTM UK (1.8 Ω).

Characterization of the materials obtained from the batteries was performed using X-ray diffraction (XRD, Bruker TwinTwin diffractometer, Cu-$K_\alpha$), inductively coupled plasma–optical emission spectroscopy (ICP–OES, Thermo Scientific iCAP PRO Duo), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX, Phenom ProX) and Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Spektrum 3). Digestion with aqua regia was performed as a prerequisite for further characterization with ICP–OES using 65% $HNO_3$ from Sigma-Aldrich and 37% HCl from Sigma-Aldrich. Required standard solutions were prepared using 1000 ppm single-element standards from Teknolab Sorbent. A FreeZone 2.5 L benchtop freeze dryer (lyophilizer) was used for separation of the cathode active material from the current collector foil.

To determine the degree of active lithium loss, Mössbauer spectroscopy was performed. Measurements were carried out at room temperature on a spectrometer with a constant acceleration type of vibrator and a[43] CoRh source. About 16 mg cm$^{-2}$ of the sample were enclosed between Kapton. Calibration spectra were recorded using natural Fe metal foil at 295 K. The resulting spectra were analyzed using the least square Mössbauer fitting program Recoil and the values for the center shift (CS) *versus* α-Fe at room temperature, the quadrupole splitting (QS), Lorentzian linewidth $W$ and the spectral area $A$ were extracted.

### 2.2. Discharging in salt brine

The first effort to discharge the batteries was done using a NaCl salt brine, as per the manufacturer's recommendation. The goal was to discharge the batteries to below 0.1 V. The top plastic head of the battery was unscrewed (Fig. 1c), and the wirings underneath manually removed to uncover the cells from above, revealing a configuration with 14 (16 × 22.5 cm) pouch cells per battery module. This state is shown in Fig. 1d. Then, the module was fully immersed in 20 liters of the 10% NaCl brine for 36 hours. These conditions were recommended by the provider of the batteries as suitable for discharging. They were not further optimized because of the corrosive and wasteful nature of the method. Two modules in total were discharged in this way, the rest of them (46) were discharged using an external resistor circuit.

### 2.3. Controlled electric discharge with an external circuit

The top plastic head was manually unscrewed to reveal the wirings and the poles of the battery, as shown in Fig. 1c. Then, the battery was connected to an initial discharging device, consisting of two electric resistors comprising 20 Ω and a rheostat with a maximum resistance of 16 Ω and a maximum current of 3.7 A, as shown in Fig. 2a. For safety, the resistors were mounted on a metallic heat sink to avoid the build-up of heat near the battery.

Based on previous experiences within our group with discharging of NiMH batteries,[44] where a discharge current of 1–2 A was found to be optimal, a start current of 1.5 A was chosen and maintained with the help of a rheostat. Given Ohm's law (eqn (1)) and the rated maximum voltage ($U$) of 46.2 V, this gives a total resistance of 30.8 Ω. This is the reason for the design of the initial discharging device, as presented in Fig. 2a.

$$U = R{\cdot}I \tag{1}$$

Given the rated capacity ($C$) of 8 Ah of the batteries and eqn (2), this setup means discharging at about 0.2C.

$$C\text{-rate} = \frac{I}{C} \tag{2}$$

Furthermore, given eqn (3) and the rated energy ($E$) of the batteries of 369.6 Wh, this gives a discharge time ($t$) of about 5.3 h.

$$E = U{\cdot}I{\cdot}t \tag{3}$$

The discharging process was monitored through a voltage–time curve, such as the one shown in Fig. 2b. After successful discharge, a second, more permanent discharging device was

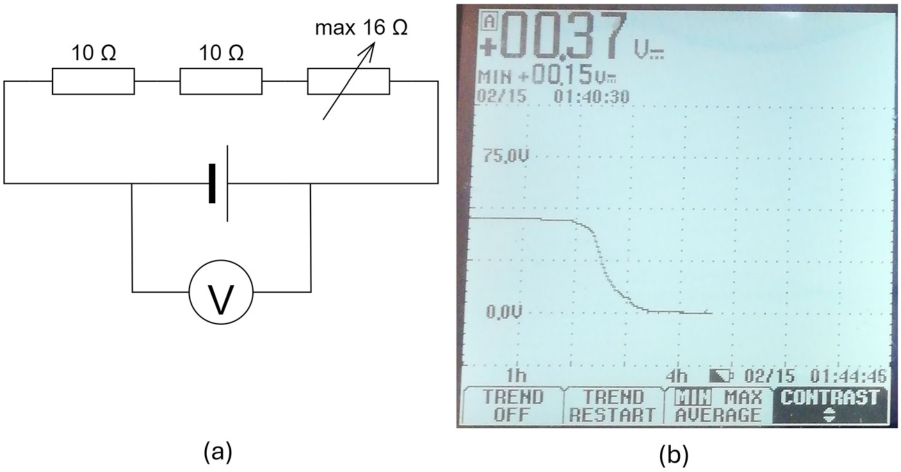

Fig. 2 Circuit diagram of the initial discharging device (a); example of a discharging curve (b).

built, consisting of a series of electric resistors, totally comprising 33.6 Ω. This setup was chosen based on the availability of resistors in the department and the electrical effect that they can withstand. Given eqn (1) and the maximum voltage ($U$) of the batteries of 46.2 V, this setup gives a maximum current ($I$) of 1.375 A. Eqn (2) and (3) thus yield a discharge rate of about 0.17C and a discharge time of about 5.8 h, respectively. This new setup is shown in Fig. 3a.

In either case, after approximately 5 hours, the recorded voltage over the batteries had decreased below 0.5 V. As observed from the voltage–time curve in Fig. 2b, the discharging process is now slow. To speed it up, the battery was connected to a second discharging device, consisting of a 1.8 Ω resistor, and a fuse to protect it from the sudden increase in current that inevitably follows such a drastic decrease in resistance. This setup is shown in Fig. 3b. Furthermore, Fig. 3c and d show a schematic overview of the circuits for the two discharging setups. The setup was left in this state overnight.

### 2.4. Battery and cell disassembly

After discharging, the wirings on top of the battery were manually disrupted and the plastic cover housing the wiring was manually removed, exposing the pouch cells from the top (Fig. 1d). The only feasible way to harvest the cells was to open the casing by cutting off one side of it with a multi-cut tool, as shown in Fig. 4a. This is because the cells were glued together, as well as to the walls of the battery casing, with strong silicone glue. Afterwards, the cells were manually separated and removed individually, taking care not to damage the plastic cell walls. For this, the silicone glue had first to be removed to the greatest feasible extent with the help of a thin, long screwdriver.

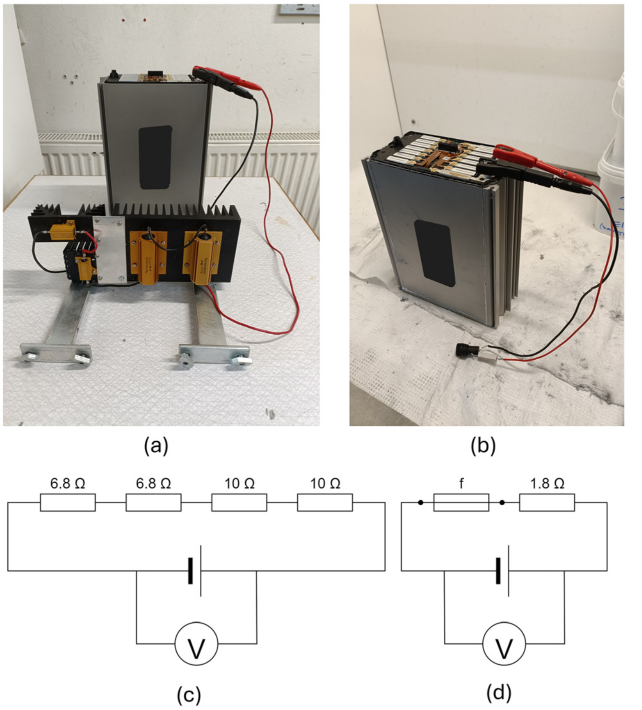

Fig. 3 Discharge setup in high voltage ranges (a) and low voltage ranges (b); scheme over the electric circuits in high voltage ranges (c) and low voltage ranges (d).

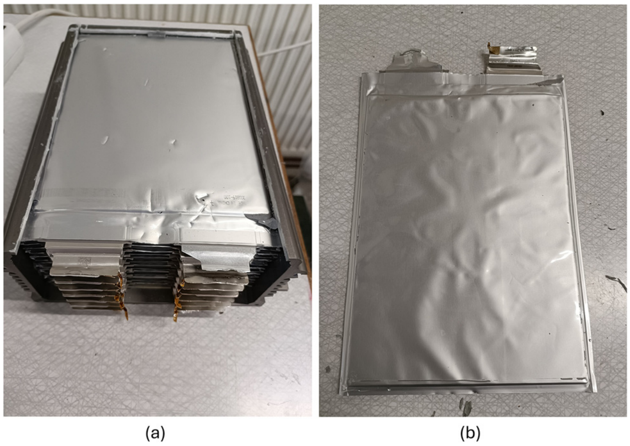

Fig. 4 Open battery after cutting the outer casing (a) and the separated individual battery cell (b).

Also, before separating out the individual cells completely, such as the one shown in Fig. 4b, a black rubbery plastic foil from in between the cells (as seen in Fig. 6), had to be peeled off from them.

The cells were then manually opened in air by cutting off the topmost part and opening up the cell casing by hand. The separator was then gradually unfolded, revealing a total of 26 individual cathode and anode sheets one by one, while the electrolyte was left to evaporate.

### 2.5. Separation of the CAM from the current collector foil

For the purpose of material characterization, the cathode active material (CAM) needed to be separated from the Al current collector foil. This was done on the basis of previous reports, using freeze drying after immersion in distilled water.[9]

## 3. Results and discussion

### 3.1. Discharging effectiveness

Immersing the battery modules into the discharging brine resulted in an immediate chemical reaction accompanied by extensive gas development lasting 3–4 hours and yielding considerably corroded battery cells with residues deposited on them (Fig. 5). Previous research suggests that the gas escaping the brine solution is composed of hydrogen and oxygen from a water splitting reaction at the positive and negative poles of the battery, as shown in eqn (3)–(5).[45,46] After 3–4 hours, gas development slowly ceased and the reaction seemed to have ended. The rest of the immersion period was mostly done as a safety precaution.

Anode (oxidation):

$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^- \tag{4}$$

Cathode (reduction):

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \tag{5}$$

Total reaction:

$$2H_2O(l) \rightleftharpoons O_2(g) + 2H_2(g) \tag{6}$$

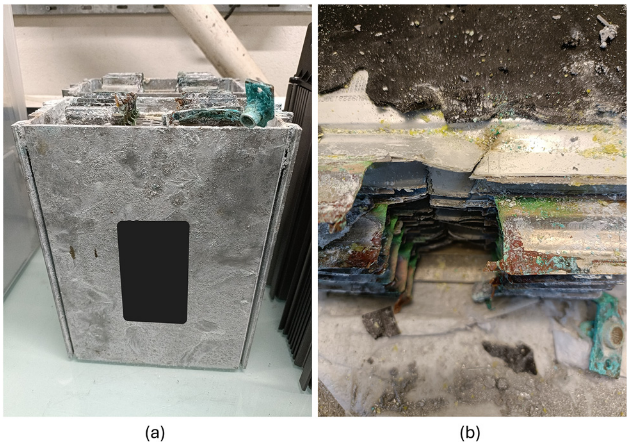

Fig. 5 Discharged battery module in salt brine (a) and a close-up of the deposited residue (b).

Regarding the residue that was deposited on the surface of the modules, it was identified by XRD as pure NaCl (Fig. S1). The green color of the residue suggests the presence of impurities. The analysis by ICP shows that this salt also contains around 3 wt% Al and Cu, respectively (Fig. S2). The salt residue was also analyzed by SEM-EDX (SI, Fig. S3). It can be seen that it mainly consists of Na, Cl, and O with traces of Al, consistent with the ICP results. This supports that the residue consists of mainly NaCl with traces of impurities of Cu, Al, and O. The brine water also acquired a yellow-greenish color and a sharp odor. Assuming the salt brine comes in contact with the battery current collectors during the immersion period, recent research on salt brine discharging of NCA ($LiNi_xCo_yAl_zO_2$) batteries suggests the formation of chlorine gas ($Cl_2$) along with the reaction between the chloride ions ($Cl^-$) and copper that was effectively leached into the solution from the cells.[46] This would also explain the sharp odor of the solution post-discharging. The overall chemical reaction of the gas formation could then be written as

$$2H_2O(l) + 2NaCl(aq) \rightarrow 2NaOH(aq) + Cl_2(g) + H_2(g) \tag{7}$$

Moreover, after harvesting individual cells, it was discovered that many of them were still wet with the residues of the discharging brine, months after discharging. This is likely because of the tightly packed pouch cells in the modules, where the brine had enough time to penetrate but was unable to evaporate efficiently afterwards. Also, upon opening the module and separating the cathode and anode sheets, the anodes were more fragile and easily torn as compared to ones discharged by the external circuit. This discharging method was therefore deemed unsafe and unfit for subsequent harvesting of cathode sheets and their regeneration.

Despite the corrosion occurring during salt brine discharging, the method seemed to have worked at least in terms of electric charge. As the cells were uncovered before immersion, there was no way to measure the voltage over the entire battery. However, upon measuring the voltage between the individual cells, it did not exceed 0.03 V. This held true even months after the discharge, when the electrically discharged batteries displayed a voltage of up to half of the original rated voltage due to the rebound effect, as discussed below.

Being able to better monitor the voltage behavior of the modules during the electrical discharge, it was observed that the measured voltage decreased to below 1 V within 5 h with the series of resistors (33.6 Ω), with some heat development being present, as the heat sink with the resistors was warm to touch. The voltage deceased further below 0.1 V within the next hour with the 1.8 Ω resistor. While still being connected to the discharging device on the occasion of opening the batteries, all of them reached below 0.05 V, most below 0.02 V. However, the voltage relaxation effect was strong, driving the voltage reading up to 3 V within minutes after disconnecting the discharging device. Therefore, the batteries were opened and dismantled immediately after disconnecting the resistor.

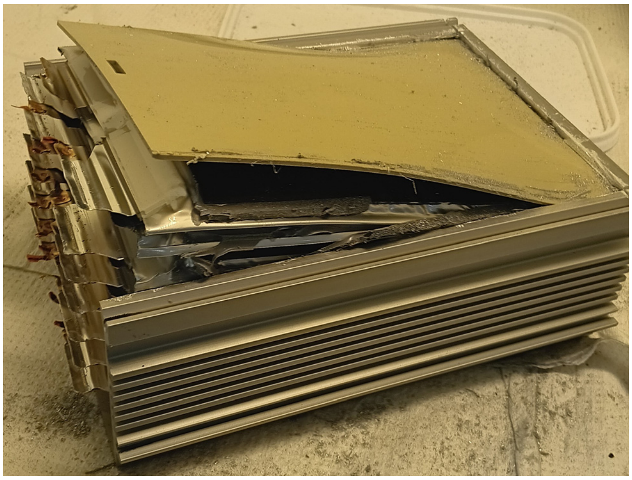

Fig. 6 Swollen battery cells after the module has been opened.

Voltage relaxation was also observed at this point, but was slow enough to allow for safe disconnection of the wirings between the cells, so that the cells were no longer in contact with each other by the time the voltage over the whole module would have risen up to levels where sparks would be visible.

#### 3.1.1. The rebound effect and cell swelling.

In electrically discharged batteries, the rebound (or voltage relaxation) effect was pronounced. Initially, after discharging, when the voltage reading of the batteries was 0.0 V, the batteries were disconnected from the resistors. In the very first trials, the modules were left idle, *i.e.*, disconnected from the resistors, after having reached 0 V, up until the disassembly, typically 2–3 days. It was observed that within the first few minutes after disconnection, the voltage reading increased to 3 V, increasing further, up to 10 V during the following days when the batteries were left idle. As a result, the 1.8 Ω discharging device was left connected to the battery until directly before disassembly, as previously stated. Note that it was only at this stage that the wirings were removed, and the individual battery cells thus disconnected from each other.

This new approach led to effective elimination of the rebound effect but tended to lead to more swelling of the cells instead. An image of a battery with strongly swollen cells taken immediately after opening the module is shown in Fig. 6. This not only meant more manually difficult harvesting of the cells, but also an increased risk of fires. This suggests that "too deep" a discharge, reaching down to 0 V, should be avoided to avoid excessive swelling of the cells. It further emphasizes the need to find a balance between the desirable depth of discharge and the acceptable degree of swelling of the cells.

### 3.2 Characterization of recovered CAMs

Table 1 shows ICP–OES results from measuring the elemental composition of the recovered CAM, given in wt% along with corresponding standard deviations. In the brine discharged samples, the amount of Li seems to be consistently slightly lower than in the resistor discharged ones, even when accounting for the variability within the sample set. If the overall state of health (SoH) of the modules prior to discharging is assumed to be equal, it also suggests that discharging was more efficient using the resistor circuit method. To assess possible variability in the cells prior to discharging, a heterogeneity study was conducted, where 2 cathodes from 2 different cells from 2 different modules were characterized separately. A schematic tree diagram can be seen in Fig. S4 and detailed ICP–OES results for each cathode sheet can be viewed in Fig. S5. The data in Table 1 present the ICP–OES results averaged over the whole series, *i.e.*, $2^3 = 8$ samples from each discharging method. All samples were measured in triplicate, meaning the average elemental contents and corresponding standard deviations given below are calculated over a population of 24 individual measurement points for each discharging method. In terms of the main elements, *i.e.*, Li, Fe and P, the ratios are similar in both cases, although the amount of Li is slightly lower in brine discharged samples, suggesting a less deep discharge than in the resistor case.

Table 1 Composition of the recovered CAM 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 |

Note that the ICP–OES results do not sum up to 100 wt% in either case. This is mainly due to the fact that ICP cannot measure certain elements, such as oxygen, carbon and fluorine, all of which are present in the material. Oxygen is present intrinsically as part of the phosphate groups, carbon follows from the carbon coating, carbon black, non-volatile electrolyte residues and the PVDF binder, in which fluorine is also present.

Concerning the impurities, the ICP–OES results reveal that the cathodes of the battery discharged in the saline solution have a higher copper and aluminum content compared to the ones discharged using an external circuit (Table 1). The main source of Cu in the battery is the anode current collector.[38–40] Despite discharging the batteries passively with a resistor load, there can be local differences in the state of charge (SoC) in different cells in the same module or even within a single electrode. This means that discharging with the same load can lead to local instances of pole reversal for some of the cells or parts thereof – a state that drives electrochemical Cu dissolution. The dissolved Cu can then be transported through the separator and deposited onto the cathode surface.[39,47,48] In literature, the Cu dissolution effect has been observed during electrical discharge of LFP pouch cells at voltages as high as 1.5 V,[49] posing a challenge to safe discharging and subsequent dismantling of LIB cells for direct recycling purposes. Research has shown that the formation of metallic Cu is avoidable if the discharge is not too deep and does not go into reversal, although this was only observed if the voltage was not allowed to reach near 0 V.[50] The higher content of Cu in the brine discharged cells can be explained by the salt solution causing corrosion of the copper current collector on the anodes. Since the cells were uncovered before the immersion, some contact of the electrodes with the brine is possible, which is confirmed by visible inhomogeneities on the surface of the electrodes after harvesting, as well as the fact that the anodes became very fragile in the brine discharged cells.

As for the other impurities, Al contamination is mostly attributable to incomplete separation of the CAM from the current collector. Despite our method of separation being effective and non-damaging to the material,[51] it is not 100% effective, and some Al contamination is expected. The higher amount of Al in the brine discharged cell can be explained by the same logic as the higher amount of Cu. The presence of V in the CAM suggests that it was used as a dopant by the battery manufacturer. Literature reports indicates possible positive effects of V doping on the performance of LFP battery materials by the decreasing of the unit cell volume of the material.[52–54] Also Si can be present as a doping agent in both electrode active materials, which could explain its presence in the samples.[55–58]

Fig. 7a and b show the XRD patterns of the recovered CAM obtained from the two discharging methods. It can be seen that in both samples the main phase is $LiFePO_4$ (LFP). However, in the case of the brine discharge method, the delithiated $FePO_4$ (FP) phase can also be clearly evidenced. The FP phase presents the characteristic (200) diffraction peak located at 18° 2$\theta$. It has to be noted that the FP phase might also still be present in the resistor discharge sample but in a low quantity below the detection limit by XRD or in a less crystalline form hindering its clear identification. While discharging the battery, Li-ions move to the cathode, which is accompanied by the reduction of FP to LFP. Thus, the presence of residual FP by XRD suggests that the brine discharge process is less complete than the resistor discharge, leading to a loss of Li. This is in agreement with the ICP results. However, inhomogeneities in terms of the FP content may also be present due to differences in the state of health (SoH) between different modules or even cells. Hence, the samples from the heterogeneity study were also characterized by XRD (Fig. S6). The brine discharged samples always present the FP phase, while in the resistor discharged samples the characteristic (200) diffraction peak of the FP phase cannot be unambiguously evidenced.

Interestingly, in the diffraction pattern of the sample obtained by the resistor discharge (Fig. 7b), three diffraction peaks (41.0, 42.9 and 45.8° 2$\theta$) can be evidenced, which cannot be assigned to either the LFP or the FP phase, but to an unknown phase. This impurity possibly arises from the residual electrolyte or are part of the SEI (solid electrolyte interface) that decomposes during the discharge process between 2.7 and 0 V (against $Li/Li^+$).[43] It appears that the presence of this phase varies on a modular level with the peaks being more pronounced in one module than the other (Fig. S7). FT-IR analysis (Fig. S8) also shows additional peaks of higher intensity in the resistor series than in the brine series. These suggest organic or carbonate species, pointing towards SEI decomposition products. Further work is currently ongoing in our group to identify the phase and its origin.

Furthermore, the samples were analyzed by Mössbauer spectroscopy (Fig. 7c and d) to determine the environment of the Fe-ions and possible impurities that were not detected by XRD. Regardless of the discharge method, the data can be fitted by three doublets and the results of the fits are presented in Table 2. For the main doublet, corresponding to site 1, the center shift (CS) and the quadrupole splitting (QS) of both samples can be assigned to $Fe^{2+}$ with values in the range expected for the LFP phase.[59] For the second doublet, the CS (0.49 mm $s^{-1}$ and 0.50 mm $s^{-1}$) and the QS (1.37 mm $s^{-1}$ and 1.20 mm $s^{-1}$) shows values close to those reported for the FP phase and can thus be assigned to the $Fe^{3+}$ in the FP phase.[59] In comparison to the typical values of FP (QS = 1.5 mm $s^{-1}$), the QS values deviate, which is probably caused by distortions in the local $Fe^{3+}$ environment, since the QS is very sensitive to the nearest neighbor. This shows that even the resistor discharged sample contains a small quantity of the residual FP phase (5%), which could not be unambiguously evidenced by XRD.

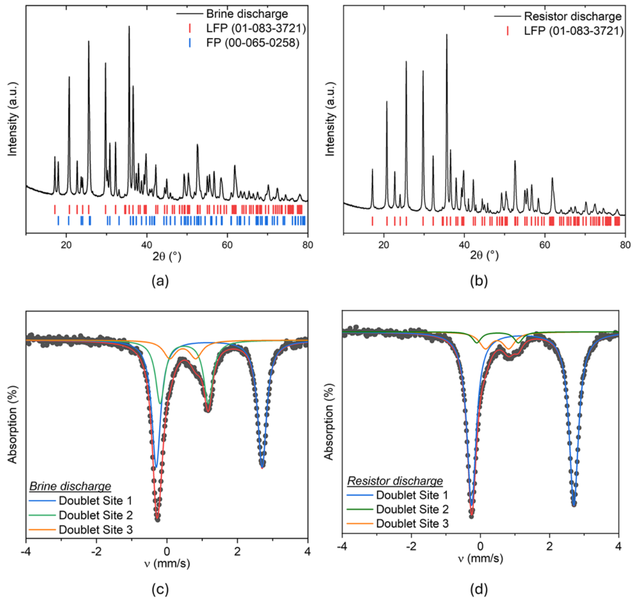

Fig. 7 (a) and (c) XRD pattern and Mössbauer spectrum of the sample obtained by brine discharge; (b) and (d) XRD pattern and Mössbauer spectrum of the sample obtained by resistor discharge.

Table 2 Hyperfine parameters CS and QS, Lorentzian linewidth *W* and relative spectral areas *A* obtained from the fits of the Mössbauer spectra

| | Doublet | CS (mm $s^{-1}$) | QS (mm $s^{-1}$) | *W* (mm $s^{-1}$) | Area (%) ± 2% |
|---|---|---|---|---|---|
| Brine discharge | 1 | 1.20(2) | 3.01(1) | 0.30(1) | 59 |
| | 2 | 0.49(1) | 1.37(1) | 0.31(1) | 30 |
| | 3 | 0.45(2) | 0.74(6) | 0.43(7) | 11 |
| Resistor discharge | 1 | 1.22(1) | 2.96(2) | 0.32(1) | 85 |
| | 2 | 0.50(2) | 1.20(5) | 0.3[a] | 5 |
| | 3 | 0.48(2) | 0.68(6) | 0.42(6) | 10 |

[a] The linewidth was fixed during the fitting.

Nonetheless, the main component of both samples is the LFP phase, in agreement with the diffraction data.

Surprisingly both samples present a third doublet to be able to fit the data completely. This third site shows CS values of 0.45 mm $s^{-1}$ and 0.48 mm $s^{-1}$ and a QS of 0.74 mm $s^{-1}$ and 0.68 mm $s^{-1}$, respectively. In previous Mössbauer studies on LFP, a CS of $0.3 - 0.5$ mm $s^{-1}$ and a QS of $0.7 - 1.1$ mm $s^{-1}$ are assigned to $Fe^{3+}$ in an LFP environment.[60] The origin of this component could be surface oxidation due to the exposure to air or the coexistence of both triphylite (LFP) and heterosite (FP) phases at the nanoscale. It is also proposed that this contribution arises from $Fe^{3+}$ in amorphous olivine phases.[61] The quantity of this phase is similar in both samples ($\approx 10\%$), which indicates that the discharge method has no influence on this phase but mainly on the LFP to FP ratio.

SEM analysis of the cathode materials from the two discharging methods did not reveal any significant differences between the two discharging methods (Fig. 8b and c). Fig. 8a shows an SEM image taken on the intact cathode, *i.e.*, before separating the CAM from the current collector. It can be seen that the active material particles are much smaller with more homogeneous sizes as compared to the separated materials. Both powdered samples, obtained by hand grinding in a mortar, contained particle agglomerates ranging from units of μm up to 200 μm in size, hence the larger scale in the images. The varying shapes and sizes, often larger than those commercial LFP batteries should have ($<100$ nm), suggest the CAM particles were disrupted and partially agglomerated, possibly caused by the grinding itself being insufficient and leaving chunks of the electrode material intact. Also, the residual presence of the binder could have an impact on the degree of agglomeration. This would suggest (i) that the discharging method *per se* does not influence the particle structure of the recovered material and (ii) that developing a better method of grinding the material into fine powder could be of importance for a direct recycling application, depending on how the CAM regeneration is performed.

Further, EDX mapping was performed on both samples, also without revealing clear differences between the two. Both samples contained Fe, P and O in an approximate 1 : 1 : 3 ratio (mol%), as well as residual amounts of Al and V. The EDX maps, along with the corresponding EDX spectra, are shown in the SI, Fig. S9c and d for the resistor discharged sample and in Fig. S9e and f for the brine discharged sample. All elements are regularly distributed over the measured areas. This is also true for V, which visibly follows the same distribution over the material as the LFP phase, most notably when compared to oxygen. This supports the theory that V was used as a doping agent by the battery manufacturer. The distribution of Al is, however, different from the rest, supporting the theory that it was introduced as an impurity during separation of the CAM from the current collector, also possibly from corrosion upon saline discharge.

### 3.3. New light on the choice of the discharge method

The safety aspect of the discharge process is undoubtedly the main driver for the inclusion of the step in basically any battery recycling process. In particular, when considering direct recycling, where battery modules need to be dismantled manually, the depth of discharge will correlate with the mitigation of incident risks – the deeper the discharge, the less energy left in the cells. However, studies have demonstrated that too deep a discharge will have an impact on the quality of the recovered materials, especially the electrode active materials.[38–42] In the light of our results, mainly focusing on the quality of the recovered cathode active material (CAM), it can be seen that the external resistor circuit method yields higher quality CAM in terms of the content of impurities, especially Cu. The salt brine discharge is corrosive and destructive not only to the CAM, but also to other constituent materials, such as the current collectors, the separator, as well as the outer casings and poles of the batteries. Moreover, it generates a large amount of wastewater that needs to be treated properly and is potentially dangerous due to the release of hydrogen, oxygen, and possibly chlorine gas. In our case, 20 liters of the salt brine were used for one module (approximately 8.1 kg), as recommended by the battery supplier. If the salt brine would be reused for one more module, it would generate approximately 1.2 l of wastewater per kg of LIB feed. Of course, the process can be developed using other, less corrosive salt solutions as the discharging media, which is being reported in the literature.[45,62] However, even if the salt brine is developed to discharge the batteries efficiently and without degrading the materials, the

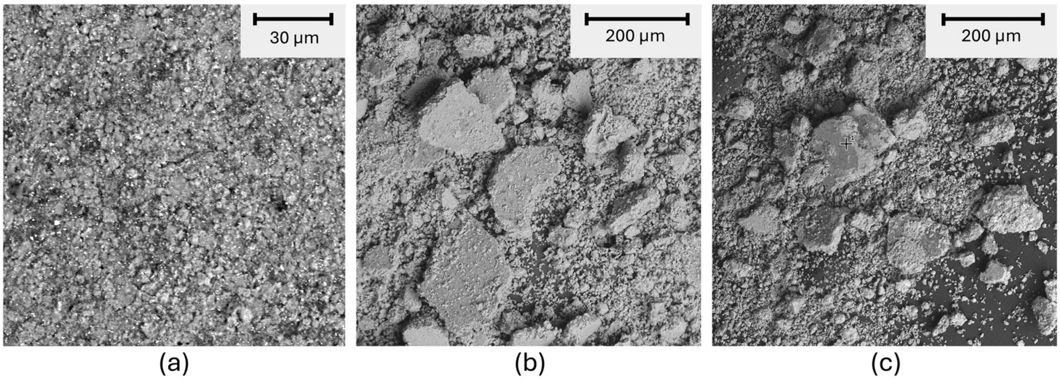

Fig. 8 SEM images of the cathode material still on the intact electrode (a), the separated cathode material after external circuit discharge (b) and after saline brine discharge (c).

waste generation and potential gas development would still remain. From this perspective, the resistor circuit method seems superior.

This is supported by the literature, where in a recent review, Shi *et al.* compared discharging methods in terms of several categories, including their effects on the cathode materials, waste emissions, efficiency and the potential adaptivity to different battery designs. They found the external circuit discharge to be the most advantageous in most of the categories, except for the adaptivity to different battery designs and the volume efficiency, where the saline brine discharge method performed better.[35] As a result, industrial recyclers have a tendency to prefer the brine discharging method, especially if the purpose of the recycling is material recovery based on the mass of the original batteries, and thus the purity/quality of the electrode materials is not of the most important. There is also an increasing political incentive for large-scale industrialization of LIB recycling, in which case, a discharging solution that can handle large volumes of LIBs with different chemistries, states of health (SoH) and states of charge (SoC) will need to be adapted. Even though the resistor circuit method is already being employed on an industrial scale, such as at a recycling company in Sweden, recyclers still tend to turn to the brine method, mainly because of the high cost and space demands of the resistor circuit method, and the high volume efficiency of brine discharging. In terms of industrial throughput, brine discharge has been superior thus far. However, we still argue that the resistor circuit method has a future in LIB recycling and is, indeed, the superior one, especially when considering direct recycling. Therefore, we recommend that future recyclers focusing on direct recycling should develop the resistor-based strategy further in order to increase its throughput, *e.g.*, by monitoring and optimizing the depth of discharge and by automating the connection and disconnection of the modules from the discharging device.

As previously demonstrated in the literature, the purity of the recovered CAM has a direct impact on the performance of the regenerated material, where impurities such as Cu may deteriorate the performance and even pose a safety risk.[39,47,48] This poses a dilemma to recyclers and researchers, as "proper" discharge is needed as a safety precaution before manual disassembly of battery modules and cells. At the same time, discharging too deeply leads to Cu contamination of the CAM regardless of the discharging method, although we demonstrated it to be lower when using the resistor circuit method. In future research, it would therefore be of interest to explore possibilities to either remove the Cu impurity altogether, or at least optimize the discharging process to a point where safe handling of the modules can be guaranteed, while keeping the Cu content in the CAM at sufficiently low levels for it to not pose problems for the recycled materials. Recent literature presents advances in this area, where the Cu dissolution behavior has been examined in terms of discharge current and cell potential in order to optimize the discharging process for minimizing the presence of the Cu impurity.[63] It would also be relevant to explore the technoeconomic and lifecycle aspects of the different discharging methods using data directly from related research activities, where modules of the same type were discharged in different ways. Also other discharging techniques may be worth considering, such as the electrochemical discharging method that was not considered in this work but has been reported in recent literature.[64]

## 4. Conclusion

The discharge of the residual charge of LFP batteries of electric vehicles was performed using a NaCl saline solution and an external circuit with resistors. Both were conducted in a safe manner mainly regarding the thermal runaway of the battery. In terms of the final quality of the electrodes, discharging with saline solution causes corrosion in the anode, causing the active material of the cathode to contain more copper as an impurity as compared to the resistor-based method. There is also a small increase in the concentration of aluminum in the CAM due to corrosion of the outer shell of the battery. Discharging with an external circuit is more advantageous because there is no waste to be treated later and it maintains the integrity of the battery electrodes better with lower levels of impurities and higher content of Li. This is important for recycling the cathode *via* the direct route, which is based on a reduced number of process steps and low content of impurities in the CAM, as well as for the retention of battery data for future use in battery passports.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

Raw data are available from the corresponding author upon reasonable request.

The data supporting the article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6ya00039h.

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