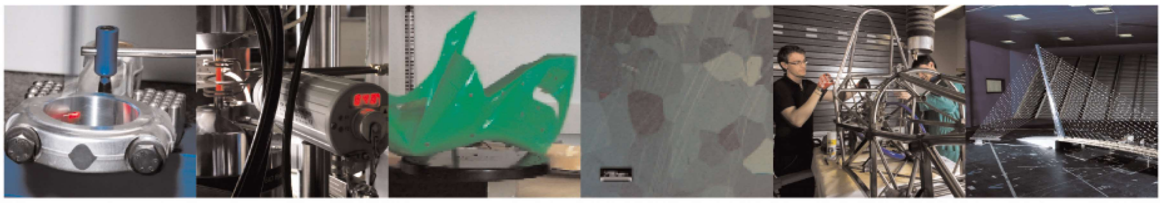

A novel mechanical pre-treatment process-chain for the recycling of Li-Ion batteries

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A novel mechanical pre-treatment process-chain for the recycling of Li-Ion batteries

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Li-Ion batteries are strategic components widely adopted in the e-mobility, electronics and building sectors. Although recycling of Li-Ion batteries has recently received increasing attention, the closed-loop recycling, aiming at supplying high quality materials to the battery manufacturing industry, remains a challenge, due to the inherent complexity in meeting target material specifications. This paper proposes a novel Li-Ion battery mechanical pre-treatment for improved selectivity and pre-concentration of the output streams. Machining processes are employed for battery cell case cutting and size-reduction and separation stages are applied on the isolated active winding. The developed process-chain is validated and benchmarked by experimental analysis.

Recycling, Machining, Sustainable Development

1. Introduction, motivation, objectives

Li-ion batteries are key storage solutions driving the ongoing transformation of strategic sectors such as the automotive, consumer electronics and building. Recent studies report that the worldwide market of Li-Ion batteries is expected to grow at a CAGR (Compound Annual Growth Rate) of 18% between 2022 and 2030 [1]. Despite of the positive contribution of these storage solutions to sustainable development during the product use phase, concerns about their environmental impact in the upstream battery critical material transformation phase and in the post-use treatment phase remain [2], [3].

This brings opportunities and challenges to closed-loop Li-Ion batteries circular economy solutions, aiming at recycling battery materials and precursors meeting the quality specifications demanded by battery production to close the loop in the same application [4]. If properly developed and scaled-up at industrial level, these solutions would have the combined benefit of positively impacting on recycling economics and rates, thus complying to legislation targets, and decreasing the dependency on primary material sources for battery manufacturing. Considering that, only in Europe, 25 new Gigafactories requiring million of tons of battery materials are expected to be established by 2025, the impact of closed-loop recycling solutions in the local European eco-system will be significant. Similarly, a recent study by the MIT has indicated battery recycling among the 10 most relevant technologies for the future [5]. However, limitations currently bound the industrial upscale of closed-loop circular economy solutions for Li-Ion batteries, mainly due to the variability in design, in terms of geometry, electrochemistry and material content, as well as in post-use degradation conditions.

Li-Ion battery systems are modular assembled architectures composed of pack, module, and cell levels. At cell level, different sub-components made of different materials are found, namely metallic cathode and anode current collectors, polymeric separator, binder, electrolyte, active anode material and cathodic mixture, giving origin to the specific electrochemistry of the battery (e.g. NMC - Lithium Nickel Manganese Cobalt Oxide and LFP - Lithium Iron Phosphate), enclosed in a steel or aluminium cell case [6]. In the literature and within industrial applications, the main circular economy strategies include combinations of pre-treatments and end-refining stages involving pyrometallurgical, hydrometallurgical and mechanical processes, compounded by upstream battery disassembly and safe discharge processes [7]. Pyrometallurgical solutions are thermo-chemical processes based on high temperatures, normally around 1500°, and comprising the phases of pyrolysis, metals reduction, and gas incineration. Despite the advantages in terms of recycling yields, these solutions bring environmental concerns due to material losses, hazardous gas generation, and the relevant energy consumption, as well as economic concerns, making the application to low valuable material battery chemistries infeasible [8]. Hydrometallurgical processes are flexible low temperature chemical processes, typically using organic or inorganic acids to selectively separate different elements by leaching the pre-sorted cathodic powder. The main advantages are the low energy consumption, the flexibility in recovering different materials, including Lithium in carbonate form, from various battery chemistries. The main drawbacks are related to the repeatability of the process, the dependency on pre-treatments to liberate pure battery "black mass", and the high costs of reagents [9]. Mechanical processes, based on a combination of wet or dry size-reduction and separation stages, are usually applied directly to battery modules or cells and adopted prior to hydrometallurgical processes as pre-treatment to pro-concentrate the black-mass from the other battery cell components. Despite of the low energy consumption, the purity of the produced black mass is relatively low, with direct impact on the cost of the downstream end-refining processes [10]. An emerging solution for closed-loop recycling is "Direct Recycling" applied to the pre-isolated battery active winding (inner roll), aiming at regenerating the cathodic mixture by re-lithiation without isolating the individual precursors [11]. Although promising, this solution is still limited at industry scale.

To overcome these limitations, this paper proposes an innovative mechanical pre-treatment process-chain that exploits traditional machining processes to liberate the active winding from the battery cell case prior to size-reduction steps, thus achieving lower contamination and higher liberation of the output black mass with respect to existing mechanical pre-treatments, applied directly to battery modules or cells. The designed process-chain effectiveness and flexibility is validated through an experimental campaign applied to a sample of different battery cell chemistries and geometries.

2. Process-chain description

The developed mechanical pre-treatment process-chain is schematically represented in Figure 1, where the link with potential downstream processing stages, out of the scope of this paper, are also reported. As it can be noticed, differently from traditional mechanical pre-treatments, size-reduction and separation stages are applied on the battery active winding after extraction from the cell case. The rationale of this approach is to increase the selectivity of the pre-treatment by reducing the contamination of the black mass with case aluminium or steel granulates, difficult to separate when the entire cell is directly processed. Moreover, the prior removal of the cell case facilitates the size-reduction process, given the lower stresses involved. The individual process stages are described in detail in the following.

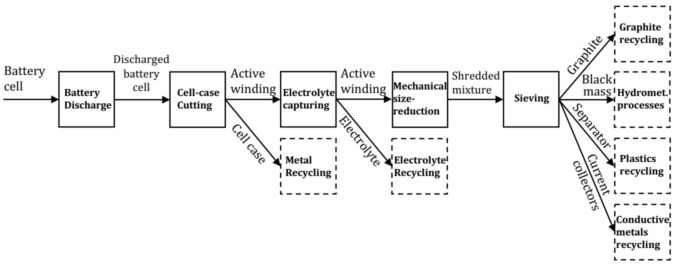


Figure 1. Representation of the mechanical pre-treatment process-chain.

2.1. Battery discharge

Applying a mechanical pre-treatment to charged batteries would cause the internal short circuit, with uncontrolled release of energy and heat. To minimize this risk, discharging the battery up to 0% of the State-of-Charge (SOC) may not be sufficient since the Li-ion cells still have a residual voltage of 2.5V. Therefore, the battery cells need to be over-discharged before disassembly and pre-treatment stages [10]. From 1V to 0V, the discharging become irreversible causing damages to the cathodic active material [12]. Different discharge strategies can be selected. The immersion of individual cells in salts solutions has been excluded due to its high degree of contaminations leading to a decreased metals recovery efficiency. A controlled discharge, instead, has been chosen to remove the residual voltage. This could also make it possible, to recover residual charge for other purposes.

2.2. Cell-case cutting

Cell-case cutting has the objective to selectively liberate the internal active winding of the discharged battery cell from the metallic case, that would then be recyclable by traditional metal recycling process stages. Given the novel requirements of this process stage, an in-depth analysis of alternative battery milling strategies has been conducted and reported in the next section. The liberated winding can in principle feed downstream direct recycling routes to regenerate cathodic mixtures for new battery production. However, especially for high metal content chemistries, the hydrometallurgical route seems promising in the short term. Therefore, the next processing stages are devoted to the further pre-concentration of high-quality black mass.

2.3. Electrolyte capturing

Liquid electrolytes used for commercial LIBs are a mix of lithium salts (lithium-hexafluorophosphate, lithium-perchlorate, and lithium-hexafluoroarsenate) and organic solvents (ethyl-methyl-carbonate, dimethyl-carbonate, diethyl- carbonate, propylene-carbonate and ethylene-carbonate) [6]. They typically have a boiling point in the 60 °C – 100°C range. The release of the cell active winding enables the evaporation of the electrolyte, facilitated by heat and venting. This ensures that the following size-reduction and sieving stages operate with dry and not sticky material. The electrolyte can eventually be recovered if its aspiration is performed in vacuum environment.

2.4. Mechanical size-reduction

The liberation of the black mass containing the key metal oxides and other recoverable streams is achieved by the comminution of the dry battery rolls. Common battery shredding equipment works at low rotary speed [7]. The earlier removal of the harder and more wearing battery component, i.e. the case, enables the introduction of high rotary speed cutting mill shredding. The exploitation of shearing phenomena to substitute impacts and compressions, together with a lower time into the shredding chamber, enable a better segregation of constituent components into dimensional fraction, especially regarding the reduction of contamination. Moreover, the heat generated within the process causes the binder dissolution, thus effectively liberating the black mass from the current collector foils.

2.5. Sieving

A strong limitation of traditional mechanical pre-treatments applied to batteries without prior case removal is the uncontrolled size reduction of ductile case metals. The resulting electrolyte-wet mixture can only be roughly sieved to segregate a highly contaminated black mass. The presented mechanical pre-treatment route overcomes this limitation, as the dry and cutting-mill reduced rolls better segregate in defined size-dependent fractions, thus facilitating sorting by sieving:

- Bigger particles are polymeric separator foils, whose non-rigidity limits the size reduction action induced by cutting tools.
- Intermediate size particles are ductile current collector foils, reduced in size and slightly folded by the cutting mill.
- Powder size fractions can be furtherly segregated as the porous anodic graphite, resulting in bigger particles with respect to cathodic metal oxides after shredding.

3. Cell-case cutting process stage

The cell case cutting stage is a key step of the innovative pre-treatment route presented in this paper, because it unlocks the downstream high-speed cutting mill shredding and selective sieving stages. The novelty of this task demanded a dedicated laboratory analysis to assess the most suitable cutting strategies, focusing on the following goals:

- Enable the effective release of the internal roll.
- Consider the removal of internal connections (metal wires / foils) between the roll and the poles.
- Limit the active material loss.
- Limit the uncontrolled electrolyte evaporation.
- Be amenable for implementation at high automation degrees.

Four cutting strategies per cell type have been investigated. Table 1 reports these strategies for cylindrical and prismatic cells together with a critical analysis of their strengths and weaknesses. The following paragraphs of this chapter further elaborate on the most promising cutting strategies for both cell geometries.

3.1. Evaluation of the optimal cutting process for cylindrical cells

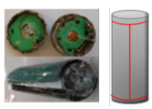
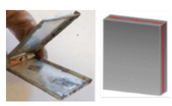
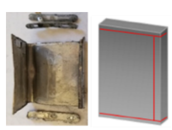
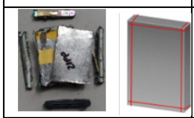
Concerning cylindrical cells, the most effective cutting strategy for the recovery of inner rolls, with adequate easiness of execution, resulted to be strategy *2C*, related to the full-depth peripheral milling of the two poles followed by a longitudinal etching of the steel cylinder. In this way, both the connections between the roll and the poles are removed, enabling the segregation between roll and case. Then, the longitudinal cut releases the internal roll pressure, easing its removal. Without longitudinal opening, the pressure between roll and case would block the sliding of the two surfaces, with no possibility of roll extraction.

Poles-etching-only (strategy *1C*) doesn't remove the roll-poles connections and is therefore not adequate. On the other side, if after the poles removal the cell full depth cutting is performed (strategy *3C*), the extensive stresses originated by the milling tool damage the roll and liberate part of the liquid electrolyte, resulting in a sticky and fragile inner winding difficult to detach from the case. This strongly limits the applicability of this strategy within an automated system. Moreover, experiments performed on the full longitudinal cutting strategy (*4C*) show a 5%wt case material losses. Finally, some cylindrical cells have a central solid bar, which complicates the full depth cutting strategy.

3.2. Evaluation of the optimal cutting process for prismatic cells

Different procedures have been tested for prismatic cells. A first attempt was made by acting on the thickness of the cell (*1P*), but a large set of battery cells are characterized by a lateral rounding that could hinder the automation of this step. Alternatively, it is possible to act on the front plane (*3P*), following the perimeter profile at a fixed distance, but this does not allow to cut the connections between the roll and the case and the active material is not removable. The only viable alternative for an easy roll extraction is the removal of the poles, possible with two different cutting procedures: one that identifies the poles, removes them and then another side of the cell, similarly to the most suitable strategy identified for cylindrical cells (*2P*), the other that does not identify poles and cut all the four sides (*4P*). Aiming at avoiding a preliminary and complex orientation of the cells or the adoption of a vision system identifying the poles, option *4P* has been selected.

Table 1: Different cutting strategies analyzed.

Cutting Strategy		**Pros**	**Cons**
Cylindrical Cells			
	1C- SURFACE MILLING Cell case limited milling, longitudinal and around poles.	Only cell case material is machined. No active material loss.	No removal of the internal connections. The active roll can be extracted upon case deformation.
	2C- POLES REMOVAL Poles are removed by a full depth milling. Longitudinal cell case limited milling is maintained.	Removal of the internal connections. Limited active material loss.	The active roll can be extracted upon case enlargement by deformation.
	3C- FULL DEPTH CUTTING The cell is longitudinally divided.	Easiness of the operation.	The electrolyte migrates from the roll to the roll-case interface, gluing the roll and inhibiting its release. Relevant material loss.
	4C - SURFACE MILLING II Cell case limited longitudinal milling along the cell.	Only case material is milled. No active material loss.	No removal of the internal connections.
Prismatic Cells			
	1P- SURFACE MILLING Cell case limited longitudinal milling over three sides.	Only case material is milled.	No removal of the internal connections. Roll extracted upon case deformation.
	2P- POLES REMOVAL Poles are removed by a full depth milling. Longitudinal case-limited milling.	Removal of the internal connections. Limited active material loss.	Roll can be extracted only after case enlargement by deformation.
	3P- SURFACE MILLING II rectangular etching of a cell case face.	Only case material is milled. No active material loss.	No removal of the internal connections. Challenging removal of the active roll.
	4P- FULL DEPTH CUTTING Through the four edges.	Simple case segregation. Removal of the internal connections.	Active material loss.

4. Real case study and experimental results

With the objective to assess the performance and technically validate the developed process-chain, an experimental campaign has been conducted on a sample of mixed Li-Ion batteries, representative of future post-use battery streams. The experimental activity was primarily dedicated to the fine tuning of individual process stage parameters and to the quantitative analysis of the process-chain benefits in terms of target output material recovery and grade rates.

4.1. Battery Sample Preparation

A representative sample of rechargeable Li-ion portable batteries coming from end-of-life household appliances has been used in the analysis, including all cell geometries (Table 2).

Table 2: Battery sample characteristics

Sample	**Cell geometry**	**Quantity**	
		Number	**%**
Portable batteries	Cylindrical	30	13,3
e-cigarette	Cylindrical, Pouch	40	17,9
Power tool	Cylindrical	14	6,3
Laptop	Cylindrical	10	4,5
Mobile phone	Pouch, Prismatic	130	58
Total		224 (14kg)	100

4.2. Application of the proposed pre-treatment solution

The developed process-chain described in Section 2 has been applied to the entire sample of 224 battery cells. Battery discharged has been implemented by connecting individually the cells to an electronic load, discharging at controlled C-rate to avoid any thermal degradation. Then, the battery cell case removal has been applied to the discharged battery sample. A state-of-the-art 4-axis milling machine has been adopted, with a peripherical milling tool with 48 teethes, a diameter of 32mm, and a depth of cut of 0.5mm for case etching steps, and a cutting speed of 40m/min in dry and Argon inert environment under gas capturing, resulting in a total cutting time of 8s to 20s, depending on the cell geometry. After each experiment, the active winding has been manually extracted by manual case deformation and sent to the further electrolyte capturing stage performed in an oven at 90°.
The dry active winding has been then processed by the size-reduction stage, performed with a cutting mill Retsch SM300, with high-resistance steel chamber and 18 carbide coated cutting tools. The addition of a cyclone aspiration system enhanced the powder extraction, minimizing the loss of active target material, both as residue inside the chamber and as emission during the process.
The final sieving processing stage has been conducted with a Retsch analytic sieve with 5 grids, in order to investigate the output distribution of the obtained fractions.

4.3. Experimental results

With the objective to investigate the optimal process settings during size-reduction, the influence of the output grate and the size-reduction time has been investigated at fixed rotor speed of 3000rpm. Indeed, two different mechanisms drive the detachment of the black mass from the current collector foils: i) the direct contact with the blades that break the ductile materials into smaller particles, and ii) the impacts with the chamber and the other grinded pieces that shake the foils and remove the cathode powder, after binder decomposition. A finer grid forces the material to recirculate in the chamber till it reaches the required dimension, strongly increasing the number of impacts with the cutting tools. Conversely, a larger grid reduces the operating times and the energy consumption. The average size distribution shown in Figure 2 were obtained after size-reduction carried out with three different grids (4, 6 and 10 mm) on the cylindrical cell sample, with crushing time of 4 min and screening time 30s.

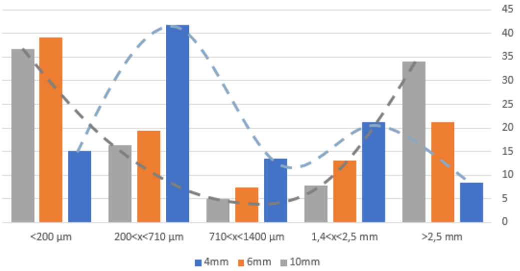


Figure 2: Weight distribution of grinded particles coming from cylindrical cells treated with different grids (4, 6, and 10 mm).

As visible from the dot curves, the amount of material present in the different fractions is extremely different for the 10 mm (grey) and the 4 mm (blue) grids: the first separates the material mainly in the two extreme fractions (i.e. the finer and the coarser), while the blue curve is characterized by two intermediate peaks. This behavior is explained by the electrochemical cell composition, and by the morphology of the materials constituting the electrodes. The active material, i.e. graphite or metal oxides, is a powder fixed on the current collector sheets of copper and aluminum by using of a polymeric binder, PVDF (polyvinylidene fluoride) or PTFE (Polytetrafluoroethylene), that dissolves at high temperatures. The detachment of the fine fraction, affected by the presence of this substance, can take place either heating the materials at 500-600°C or by friction. During crushing inside the mill, contact with the cutting edges and the collision between the particles facilitate the detachment, as well as a slight local increase in temperature, as a result of the mechanical stress induced, thus facilitating the dimensional segregation of treated materials.

This phenomenon explains the different curves. With the 10 mm grid, the residence time is quite low and the output material is divided mainly into two fractions, i.e. the dust detached during impact and the coarsely crushed fraction. With the 4 mm grid, the re-processing of the material not only increases the detachment of the active material but also crushes the metal sheets in smaller pieces that no longer maintain their rigidity but tend to bend and separate in fractions below 2.5 mm.

The quantitative analysis of the weight of the fractions is supported by the visual analysis of the sample in output, so with less intense crushing it is possible to identify the black mass and graphite still attached to the coarse fractions (Figure 3). The finest fraction (first bag from the left) appears as a very dark and homogeneous powder, while the second peak corresponds to mostly metallic fragments, recognizable by the orange color of copper and the silvery color of aluminum (3rd and 4th bags from the left). From the obtained results is possible to suppose that the black mass and the current collector sheets break up and separate into sufficiently different dimensional fractions, with intermediate fractions containing mostly graphite.

This preliminary analysis has been further confirmed by the quantitative chemical analysis performed on the samples processed with a 4mm grate size, reported in Figure 4. As it can be noticed, a Cobalt recovery rate close to 90% can be achieved in the finest fraction, compounded by a clear segregation of Al and Cu from the current collectors in the intermediate fractions. This proves the possibility to selectively segregate battery cell materials by adopting the proposed pre-treatment process-chain.

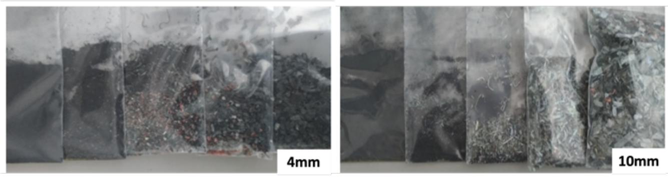


Figure 3: Output fractions by using 4mm and 10mm grate sizes.

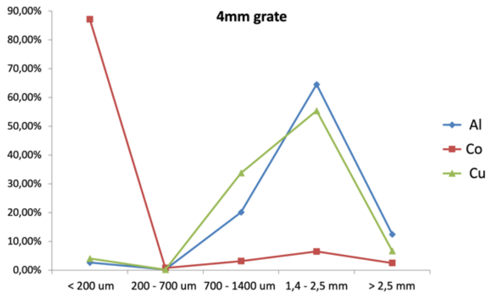


Figure 4: Recovery rates of different metals at grid size of 4mm.

5. Conclusions

The paper presents a novel pre-treatment process-chain for the high-quality recycling of Li-Ion batteries, based on the selective separation of the battery cell case from the active winding by traditional machining processes, followed by size-reduction and dimensional separation. The process-chain validation, conducted over a representative set of battery geometries, shows the benefits of the developed solution over existing pre-treatments in terms of homogeneity of the obtained output streams and recovery rates of high-value materials, thus paving the way towards the application of closed-loop recycling within battery manufacturing processes. Future research will be devoted to the design of innovative flexible machining systems for cell case cutting over the entire set of battery cell geometries, endowed with innovative fixtures and tooling to support the future industrial upscale of the developed process-chain at target processing rate scales. Moreover, the achieved benefits in terms of environmental and economic performance will be assessed, having validated the technical feasibility and output results of the process-chain. This solution paves the way to the industrial implementation of novel routes for high quality closed-loop recycling of Li-ion batteries.

References

[1] Pillot, C., 2021, The rechargeable battery market and main trends 2020-2030, Batteries Event, Lyon, France.
[2] Yuan, C., Deng, Y., Li, T., Yang, F., 2017, Manufacturing energy analysis of lithium ion battery pack for electric vehicles, CIRP Annals - Manufacturing Technology, 66/1: 53-56.
[3] Thiede, S., Turetskyy, A., Loellhoeffel, T., Kwade, A., Kara, S., Herrmann, C., 2020, Machine learning approach for systematic analysis of energy efficiency potentials in manufacturing processes: A case of battery production, CIRP Annals - Manufacturing Technology, 69/1, 21-24.
[4] Colledani, M., Tolio, T., Duflou, J., Seliger, G., Bernard, A., Kara, S., Battaia, O., Takata, S., 2017, Design, Management and control of demanufacturing and remanufacturing systems, CIRP Annals - Manufacturing Technology, 66/2: 585-609.
[5] 10 Breakthrough Technologies, 2023, MIT Technology Review.
[6] Zubi, G., Dufo-López, R., Carvalho, M., Pasaoglu, G., 2018, The lithium-ion battery: State of the art and future perspectives, Renew. Sustain. Energy Rev., 89: 292–308.
[7] Mossali, E., Picone, N., Gentilini, L., Rodriguez, O., Pérez, J. M., Colledani, M., 2020, Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments, Journal of Environmental Management, 264.
[8] Winslow, K.M., Laux, S.J., Townsend, T.G., 2018. A review on the growing concern and potential management strategies of waste lithium-ion batteries, Resources, Conservation and Recycling, 129, 263–277.
[9] Gaines, L., Richa, K., Spangenberger, J., 2018, Key issues for Li-ion battery recycling, MRS Energy Sustainability, 5/12, 1-9.
[10] Kwade, A., Diekmann, J., 2018, Recycling of Lithium-Ion Batteries, Springer International Publishing.
[11] Gaines, L., Dai, Q., Vaughey, J.T., Gillard, S., 2021, Direct Recycling R&D at the ReCell Center, Recycling , 6/31.
[12] Shu, J., Shui, M., Xu, D., Wang, D., Ren, Y., Gao, S., 2012, A comparative study of overdischarge behaviors of cathode materials for lithium-ion batteries, J. Solid State Electrochem., 16/2, 819–824.