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Chair of Thermal Processing Technology

Doctoral Thesis

Evaluation of the suitability of an inductively heated carbon bed reactor for the pyrometallurgical recycling of lithium-ion batteries

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AFFIDAVIT

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Abstract:

Due to the rapid market capitalization and the demand for valuable and sometimes critical raw materials, lithium-ion batteries (LIBs) are among the most relevant topics for the recycling industry in the short, medium and likely long term. The continuous development of the LIB technology will undoubtedly mean that the rules of the game for recyclers will change frequently and that processes will have to be highly flexible. In general, the processing and recovery of valuable raw materials from LIBs is a complex task that often involves a chain of processes and procedures. The challenges and scientific questions concerning LIB recycling are pervasive, both in number and content. This thesis, however, addresses one specific issue.

An intermediate product along the recycling chain of LIBs is so-called "black matter", a black powder enriched with valuable metal oxides, whose further processing can be regarded as one of the bottlenecks of LIB recycling. Recovering valuable metals such as nickel, cobalt, or lithium from this black matter can be achieved by various methods, with specific strengths and weaknesses. The present work focuses on the pyrometallurgical approach, which has, among many advantages, a very decisive cut. Lithium, which is now on the European Commission's list of critical raw materials, is almost entirely oxidized and slagged by the pyrometallurgical methods that are in use today. As the possibilities for later recovery from this slag are limited, primarily due to low concentrations, the lithium-containing slag is often utilized elsewhere. Thus, while pyrometallurgical processes can reliably recover nickel and cobalt, lithium is excluded and no longer useable for functional recycling, i.e. the production of new LIBs. As lithium's economic importance is high due to the predicted market growth in the LIB sector, and especially against the backdrop of future supply security, a more sustainable approach is probably inevitable in the future.

The present work particularly addresses this problem, and investigates a possibility to achieve simultaneous recovery of nickel, cobalt, the other transition metals and lithium by pyrometallurgical means. For this purpose, the so-called InduRed reactor concept is to be used, which has favorable properties and has already been successfully applied for other industrial and municipal residues. The work aims to investigate whether the reactor concept could be an alternative to conventional pyrometallurgical approaches, at which point it should be optimally integrated into existing recycling chains, and what contribution it could make to the future sustainability of the LIB technology. To determine the essential suitability and to evaluate potentially achievable recovery rates as well as possibly necessary adaptations of the process, a series of research, tests and analyses were carried out. The results can roughly be divided into three sub-areas.

The first part, which marked the start of the scientific work, deals with the high-temperature behaviour of currently used cathode materials. In several experimental series, the most common cathode materials with and without carbon addition, as well as black matter from a pre-treatment process, were examined in a heating microscope and subjected to thermogravimetric analyses. This showed that the desired reactions occur in a temperature range between 650°C and 900°C, which is compatible with the InduRed concept. However, a considerable difference in the behaviour of brand-new cathode materials and black matter from the pre-treatment step was identified.

The research and investigations to clarify the underlying cause of this phenomenon comprise the results' second part. A state-of-the-art review highlighted how crucial black matter's chemical and structural properties could be for downstream processes. For example, the pyrolysis step was identified as a key influencing factor that, depending on how it is carried out, can limit the suitability of metallurgical recovery processes, or even limit the efficiency of the entire recycling chain.

Finally, the investigation of potential recovery rates of valuable metals in black matter was the focus of the third part of the thesis. For this purpose, the already characterized cathode materials with an addition of 20 w.-% carbon were used in a lab-scale reactor inspired by the InduRed concept, and heated up to about 1,550°C. The product phases formed in the experiments were chemically analyzed to determine the corresponding transfer coefficients of the metals of interest. By comparing these results with values of currently used processes, it can be seen that the InduRed process can limit the otherwise almost complete slagging of lithium to less than 10% and simultaneously achieve high recovery rates for nickel and cobalt. Improving the quality of the previously mentioned product phases, and determining the necessary adjustments to the reactor concept, are among the crucial issues for future research work, the extent of which is described in detail in the concluding chapter of the thesis.

Kurzfassung:

Die rasante Marktkapitalisierung sowie der resultierende Bedarf an wertvollen, teilweise auch kritischen Rohstoffen, machen Lithium-Ionen-Batterien (LIB) kurz-, mittel- und wahrscheinlich auch langfristig zu einem der relevantesten Themenbereiche der Recyclingindustrie. Ansätze wie dieses Recycling aussehen kann gibt es viele, wovon einige schon industriell umgesetzt wurden, während sich andere noch in der Entwicklung befinden. Fest steht, dass sich die Spielregeln aufgrund der ständigen Weiterentwicklung der LIB - Technologie noch häufig ändern werden und die Verfahren ein großes Maß an Flexibilität aufweisen müssen. Allgemein stellt die Aufbereitung von bzw. die Rückgewinnung wertvoller Rohstoffe aus LIB eine komplexe Aufgabe dar, welche oft eine Kette von Prozessen und Verfahren beinhaltet. Da die dabei noch offenen Herausforderungen und wissenschaftlichen Fragestellungen sowohl in Anzahl als auch Inhalt äußerst umfangreich sind, nimmt sich die vorliegende Arbeit nur einem Teilaspekt dieses Problems an.

Entlang der Recyclingkette von LIB entsteht als Zwischenprodukt sogenanntes ‚Black Matter‘, ein mit Wertmetalloxiden angereichertes, schwarzes Pulver, dessen weitere Verarbeitung als Engpass des LIB-Recyclings angesehen werden kann. Die Rückgewinnung wertvoller Metalle wie Nickel, Kobalt oder auch Lithium aus diesem Black Matter kann durch verschiedene Methoden mit spezifischen Vor- und Nachteilen erreicht werden. Diese Arbeit konzentriert sich dabei auf den pyrometallurgischen Ansatz, welcher neben vieler Vorteile eine sehr entscheidende Schwäche aufweist. Lithium, welches mittlerweile auf der Liste kritischer Rohstoffe der Europäischen Kommission zu finden ist, wird in den bisher verbreiteten Verfahren beinahe ausschließlich oxidiert und verschlackt. Da die Möglichkeiten für eine spätere Rückgewinnung aus dieser Schlacke aufgrund niedriger Konzentrationen vor allem ökonomisch eingeschränkt sind, wird die lithiumhaltige Schlacke oft anderweitig verwertet. Während Nickel und Kobalt durch pyrometallurgische Verfahren also zuverlässig zurückgewonnen werden können, scheidet Lithium dabei zumindest für den für LIBs relevanten Stoffkreislauf aus. Da die wirtschaftliche Bedeutung von Lithium aufgrund der prognostizierten Marktzuwächse im LIB-Bereich aber hoch ist und besonders vor dem Hintergrund zukünftiger Versorgungssicherheit heraussticht, ist ein nachhaltigerer Umgang damit in Zukunft jedoch unbedingt anzustreben.

Die vorliegende Arbeit nimmt sich im Speziellen diesem Problem an und untersucht eine Möglichkeit, auf pyrometallurgischem Wege eine simultane Rückgewinnung von Nickel, Kobalt, den weiteren Übergangsmetallen sowie Lithium zu erreichen. Dafür soll das sogenannte InduRed-Reaktorkonzept zum Einsatz kommen, welches für diesen Zweck günstige Eigenschaften aufweist und bereits erfolgreich für andere wertstoffreiche Reststoffe angewendet wurde. Ziel der Arbeit ist es also zu untersuchen, ob das Reaktorkonzept eine Alternative zu konventionellen pyrometallurgischen Ansätzen darstellen kann, an welcher Stelle es sich optimalerweise in der Recyclingkette eingliedern sollte und welchen Beitrag es zur zukünftigen Nachhaltigkeit der LIB-Technologie leisten kann. Zur Feststellung dieser grundsätzlichen Eignung sowie der potentiell erzielbaren Rückgewinnungsraten und möglicherweise notwendigen Anpassungen des Verfahrens, wurde eine Reihe von Recherchen, Versuchen und Analysen durchgeführt. Die Ergebnisse können im Wesentlichen in drei Teilbereiche gegliedert werden.

Der erste Teil, welcher den Start der wissenschaftlichen Arbeit markiert, beschäftigt sich mit dem Hochtemperaturverhalten aktuell eingesetzter Kathodenmaterialien. In mehreren Versuchsreihen wurden die gängigsten Kathodenmaterialien mit und ohne Kohlenstoffzugabe sowie Black Matter aus einem Vorbehandlungsprozess in einem Erhitzungsmikroskop untersucht und thermogravimetrischen Analysen unterzogen. Dabei konnte gezeigt werden, dass die angestrebten Reaktionen in einem für das InduRed-Konzept problemlosen Temperaturbereich zwischen 650°C und 900°C ablaufen. Es wurde aber auch ein deutlich unterschiedliches Verhalten zwischen fabrikneuen Kathodenmaterialien und Black Matter aus dem Vorbehandlungsschritt festgestellt. Die Recherchen und Untersuchungen zur Klärung der Ursache dieses Phänomens stecken den zweiten Teilbereich der Ergebnisse ab. Im Rahmen eines Reviews zum Stand der Technik wurde hervorgehoben, wie entscheidend chemische und strukturelle Eigenschaften von Black Matter für nachgeschaltete Verfahren sein können. So wurde zum Beispiel der Schritt der Pyrolyse als wesentliche Einflussgröße identifiziert, welche je nach Art der Durchführung die Eignung metallurgischer Rückgewinnungsprozesse einschränken oder gar die Effizienz der gesamten Recyclingkette limitieren kann.

Die Untersuchung potentieller Rückgewinnungsraten für die in Black Matter enthaltenen Wertmetalle steht abschließend im Fokus des dritten Teilbereichs der Arbeit. Zu diesem Zweck wurden die bereits zuvor charakterisierten Kathodenmaterialien mit Zugabe von 20 m.-% Kohlenstoff in einem dem InduRed-Konzept nachempfundenen Reaktor im Labormaßstab eingesetzt und auf Temperaturen von etwa 1550°C erhitzt. Die in den Versuchen entstandenen Produktphasen wurden chemisch analysiert um die jeweiligen Transferkoeffizienten der Metalle von Interesse bestimmt. Vergleicht man diese Ergebnisse mit Werten aktuell eingesetzter Verfahren so zeigt sich, dass das InduRed-Verfahren die ansonsten beinahe vollständig ablaufende Verschlackung von Lithium auf weniger als 10% limitieren und simultan gewohnt hohe Rückgewinnungsraten für Nickel und Kobalt erreichen kann. Die Verbesserung der Qualität der Produkte und die Feststellung nötiger Anpassungen am Reaktorkonzept stellen die wesentlichsten Punkte der zukünftigen Forschungsarbeit dar.

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List of Publications

Journal Papers (peer-reviewed)

- Ponak, C., Mally, V., **Windisch**, S., Holzer, A., & Raupenstrauch, H. (2020). Phosphorus gasification during the reduction of basic oxygen furnace slags in a novel reactor concept. Advanced materials letters, 11(7).
- **Windisch-Kern**, S., Holzer, A., Nagovnak, P., Ponak, C., & Raupenstrauch, H. (2020). Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions. 20-25. 16. Minisymposium der Verfahrenstechnik 2020, ISBN:
- **Windisch-Kern**, S., Holzer, A., Ponak, C., & Raupenstrauch, H. (2021). Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept. Processes: open access journal, 9.2021(1). https://doi.org/10.3390/pr9010084
- Holzer, A., **Windisch-Kern**, S., Ponak, C., & Raupenstrauch, H. (2021). A Novel Pyrometallurgical Recycling Process for Lithium-Ion Batteries and Its Application to the Recycling of LCO and LFP. Metals: open access journal, 2021(11), 1-22. [149]. https://doi.org/10.3390/met11010149
- **Windisch-Kern**, S., Holzer, A., Ponak, C., Hochsteiner, T., & Raupenstrauch, H. (2021). Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach. Carbon Resources Conversion, 2021(4), 184-189. https://doi.org/10.1016/j.crcon.2021.04.005
- **Windisch-Kern**, S., Holzer, A., Wiszniewski, L., & Raupenstrauch, H. (2021). Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials (LiNixMnyCozO2) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor. *Metals: open access journal*, *2021*(11). https://doi.org/10.3390/met11111844
- **Windisch-Kern**, S., Gerold, E., Nigl, T., Jandric, A., Altendorfer, M., Rutrecht, B., Scherhaufer, S., Raupenstrauch, H., Pomberger, R., Antrekowitsch, H., & Part, F. (2021). Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies. Waste management, 2022(138), 125-139. https://doi.org/10.1016/j.wasman.2021.11.038

Articles and Papers (not peer-reviewed)

- Ponak, C., **Windisch**, S., Breuer, F., Holzer, A., Mally, V., Raupenstrauch, H., & Lasser, M. (2019). Vermeidung von Calciumsilikatzerfall und Förderung der Glasbildung bei vollständiger Reduktion von Konverterschlacken. Stahl und Eisen, 18-23.
- Holzer, A., Mally, V., Ponak, C., **Windisch**, S., & Raupenstrauch, H. (2020). Technologien zur Nutzung von Wertstoff- und Energiepotentialen in LD-Konverterschlacken. Berg- und hüttenmännische Monatshefte : BHM, 165.2020(7), 302-307. https://doi.org/10.1007/s00501-020-00992-1
- **Windisch**, S., Ponak, C., Mally, V., & Raupenstrauch, H. (2020). Phosphorrückgewinnung aus Klärschlammaschen mit dem RecoPhos-Prozess. Österreichische Wasser- und Abfallwirtschaft : ÖWAW , 72.2020(Oktober), 421-428. https://doi.org/10.1007/s00506-020-00696-3
- **Windisch-Kern**, S., Holzer, A., Ponak, C., Nagovnak, P., & Raupenstrauch, H. (2021). Recycling von Lithium-Ionen-Batterien: Herausforderungen und aktuelle Forschungsergebnisse. Berg- und hüttenmännische Monatshefte : BHM, 166.2021(3), 150-156. https://doi.org/10.1007/s00501-021-01091-5

Conference Papers

- Ponak, C., **Windisch**, S., Mally, V., Raupenstrauch, H., & Schönberg, A. (2018). Recovery of iron, chromium, manganese and phosphorus from steelmaking slags by carbothermal reduction. Paper presented at CleanTech 4, Bergamo, Italy.
- Ponak, C., **Windisch**, S., Raupenstrauch, H., & Schönberg, A. (2018). Methoden und Verfahren der Klärschlammbehandlung. In S. Thiel, E. Thomé-Kozmiensky, P. Quicker, & A. Gosten (Eds.), Energie aus Abfall (Vol. 15, pp. 669-678).
- **Windisch**, S., Ponak, C., Mally, V., & Raupenstrauch, H. (2018). Untersuchung der Möglichkeiten einer reduzierenden Behandlung von LD-Schlacke in einem induktiv beheizten Koksbett. In Schlackensymposium 2018
- Ponak, C., **Windisch**, S., Raupenstrauch, H., & Schönberg, A. (2018). Processes and Techniques for the Treatment of Sewage Sludge. In Waste Management Volume 8: Waste-to-Energy
- Ponak, C., **Windisch**, S., Mally, V., Raupenstrauch, H., & Schönberg, A. (2018). Rückgewinnung von Wertmetallen aus Stahlwerksschlacken im InduCarb-Reaktor. In Recy&DepoTech 2018

- **Windisch**, S., Ponak, C., Mally, V., & Raupenstrauch, H. (2019). Activation of hydraulic properties in BOF slags by carbo-thermal reduction with simultaneous phosphorus removal. In ESTAD 2019 - Environmental and energy aspects: Environmental and energy aspects in iron and steelmaking: Improvment, treatment and usage of Iron and steelmaking slags
- Ponak, C., **Windisch**, S., Mally, V., & Raupenstrauch, H. (2019). Recovery of Manganese, Chromium, Iron and Phosphorus from Basic Oxygen Furnace Slags. In Optimum utilization of resources and recycling for a sustainable solution (pp. 1311-1319)
- **Windisch-Kern**, S., Nagovnak, P., Holzer, A., Ponak, C., & Raupenstrauch, H. (2020). Lithium-Ionen-Batterien: Anforderungen an das Recyclingverfahren der Zukunft. In Conference proceedings of the 15th Recy & DepoTech conference

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Glossary

Al	Aluminium
AM	Active Material
Ar	Argon
BEV	Battery electric vehicle
BM	Black matter (also referred to as “AM” – active material)
BMS	Battery management system
BOFS	Basic oxygen furnace slag
C	Carbon
Co	Cobalt
Cu	Copper
CRMs	Critical raw materials
CSA	Cross sectional area [-]
DSC	Differential scanning calorimetry
EC	European Commission
EEE	Electrical, electronic and electromechanical equipment
EES	Energy storage systems
EoL	End-of-Life
EU	European Union
EVs	Electric vehicles
FeP	Iron phosphide
HTPT	High-temperature processing technology
LCA	Life cycle assessment
LCO	Lithium cobalt oxide ($LiCoO_2$)
LFP	Lithium iron phosphate ($LiFePO_4$)
Li	Lithium

LIB	Lithium-ion battery
LIBs	Lithium-ion batteries
LMO	Lithium-manganese oxide ($LiMnO_2$)
LTO	Lithium-titanate oxide
Me	Metal
MeO	Metal oxide
Mn	Manganese
MUL	Montanuniversitaet Leoben
NCA	Lithium nickel cobalt aluminium oxide ($LiNi_xCo_yAl_zO_2$)
Ni	Nickel
NMC	Lithium nickel manganese cobalt oxide ($LiNi_xMn_yCo_zO_2$)
OEMs	Original equipment manufacturer
P	Phosphorous
PHEVs	Plug-in Hybrid Electric Vehicles
SoC	State of Charge
SoH	State of Health
STA	Simultaneous thermal analysis
TGA	Thermogravimetric analysis
TPT	Chair of Thermal Processing Technology

List of Figures and Tables

1 Scope and Outline of the Thesis

As the title suggests, this thesis deals with the applicability of a pyrometallurgical recycling approach on lithium-ion battery (LIB) related waste streams. This opening chapter outlines the relevance of circular economy and recycling of valuables regarding end-of-life (EoL) LIBs. It strives to show how broadly this justifiably much-discussed field is positioned, and where the motivation lies to participate in the accompanying research. In addition, the subfield to which this work aims to contribute, and the hypotheses on which the thesis is based are explained. The first chapter ends with an explanation of the structure of the thesis and the applied methodology, and gives a brief outlook on the contents of the following chapters.

1.1 Research Relevance and Motivation

LIBs have become pervasive through portable electronic devices such as mobile phones, tablets, laptops and many others. Yet their increasing demand, primarily due to the introduction of electric vehicles, creates several environmental problems linked with mining and processing of the needed materials such as cobalt, nickel and lithium. Furthermore, given the current development of electric mobility, it can be assumed that the demand for more efficient and sustainable LIBs will even increase in the coming years. [1–3] The work from Placek (2021), for example, predicts that the size of the global LIB market will grow from 40.5 billion dollars in 2020 to more than 90 billion dollars by the year 2026. [4] Similar results of several other studies [5–7] generally forecast a market volume of more than 110 billion dollars in 2030. These numbers correspond to an increase of the annual global LIB demand from approx. 750 GWh in 2020, to more than 2500 GWh in 2030. With a view on Figure 1, which shows the trend of annual sales of passenger electric vehicles (EVs), it could be stated that this growth is particularly driven by the shift in the transport sector towards EVs and plug-in hybrid electric vehicles (PHEVs).

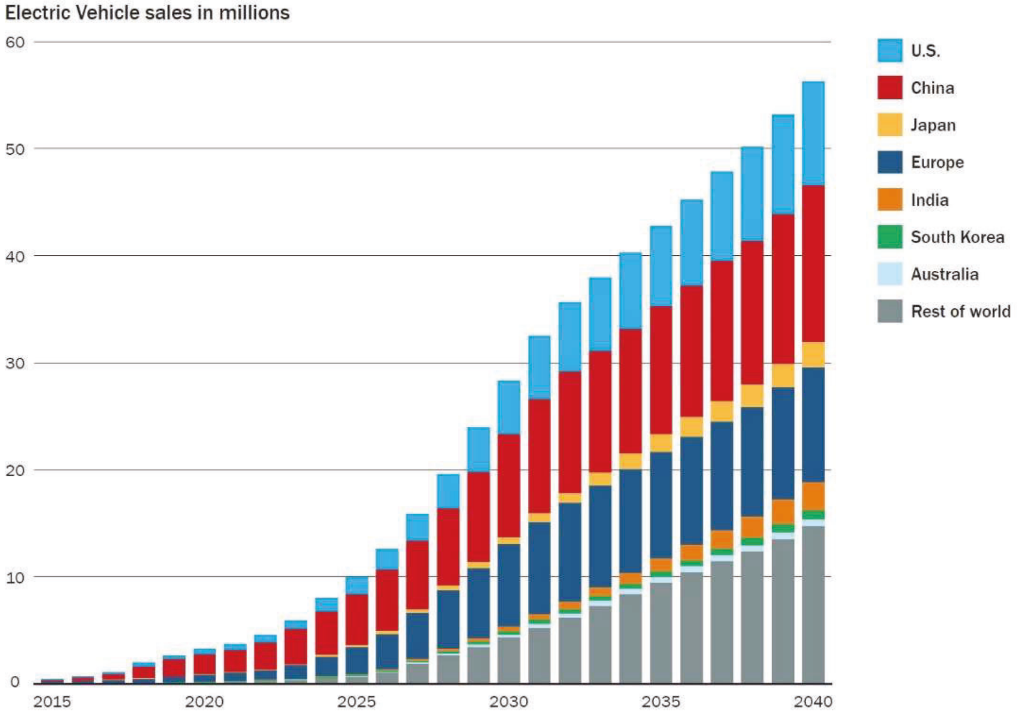

Figure 1: Trend of annual sales of passenger EVs including PHEVs. [8,9]

In addition to the projected demand and the associated waste stream to be processed in the future, the raw materials used in LIBs such as nickel (Ni), cobalt (Co) or lithium (Li) are not only valuable, but are listed as critical raw materials (CRM) by the European Commission. [10] Based on this alone, it can be concluded that the topic of LIB recycling is of great importance, both economically and ecologically. Among the many processes already in operation, countless new procedures and approaches are currently being developed to face up to this problem. [11–16] Mentioned processes usually concentrate on partial aspects of recycling. For example, some methods address the dismantling and pre-treatment of entire battery systems, while others are explicitly aimed at metal recovery from various intermediate products of said systems. The latter, namely metal recovery processes, can principally be based on pyro- or hydrometallurgical methods and aim primarily at recovering the valuable cathodic metals. With both approaches having their characteristic benefits and drawbacks, one particularly distinct disadvantage in pyrometallurgy stands out. While currently applied pyrometallurgical LIB recycling processes achieve high recovery rates for Ni and Co, Li becomes oxidized due to its high oxygen affinity. The resulting slagging of lithium leads to a situation in which lithium can hardly be kept in the functional material cycle but is used, e.g., as a construction material instead. Furthermore, while the proportion of nickel and cobalt is constantly changing and moving towards nickel-rich and cobalt-poor cathode technologies, the lithium demand remains relatively constant, even with newer chemistries, at around 150 g/kWh. Based on that, the Fraunhofer Institute for Systems and Innovation Research ISI calculated a global demand for lithium of 1 to 1.3 million tons for 2050. This contrasts with terrestrial lithium reserves of 14 million tons, and lithium resources that now amount to 62 million tons. So, while the basic availability of lithium continues to pose no threat, countries with low Li reserves still have an underlying strategic motivation and strive for a circular economy. The contribution that LIB recycling can make to the sustainability of the LIB technology as a whole is highlighted in Figure 2, which shows that the recovery of Li from spent batteries can not only drastically reduce energy and water consumption but also cut costs. Furthermore, if high collection rates are ensured, and 25% to 50% of the lithium from spent batteries is recovered, lithium from battery recycling could cover 10% to 30% of the annual demand by 2050. [17]

Figure 2: Benefits of recycling for lithium-ion batteries.[9,18]

In addition, according to the proposal published at the end of 2020 to amend EU Directive 2006/66/EC and amended version No. 2019/1020 regulating batteries and spent batteries, recycling quotas for disposed lithium-ion batteries will be prescribed in future for Li, Ni, Co and Cu. Adding to an overall recycling quota of 65% by 2025 and 70% by 2030, recycling quotas of 35% by 2025 and 70% by 2030 are to be achieved for lithium. The other elements mentioned above are to be recycled at 90% by 2025 and 95% by 2030.

With this in view and especially against the background of growing demand, the issue of lithium slagging in pyrometallurgical metal recovery processes can be considered a crucial challenge for state-of-the-art recycling chains and is therefore justifiably the center of attention of this doctoral thesis. To address this problem, the so-called InduRed reactor, an inductively heated graphite bed reactor with superior properties for the carbo-thermal reduction of metal oxides in complex waste streams, is to be evaluated as an alternative reactor concept with regard to its suitability as part of a LIB recycling chain. Thereby, its unique properties are supposed to counteract the slagging of lithium and enable a simultaneous recovery of all valuable metals. As mentioned before, some processes do not start with whole batteries, but use the products of upstream procedures as input material. In this respect, the InduRed reactor is no exception. For the desired process, the corresponding intermediate product is the so-called black matter, a black powdery mixture of former battery components. Black matter is generated during pre-treatment and ideally consists of the active materials of the electrodes, thus oxides containing the valuable cathodic metals as well as graphite from the anode and, in reality, also undesired residuals from other components. Finding an efficient way to recover those valuable metals from black matter does not only have economic and strategic incentives but is also of great relevance for ensuring future raw material supply, sustainability and environmental protection. [19–21] Within the scope of this doctoral thesis, it should be investigated whether black matter can be treated in the reactor at all and whether the desired simultaneous recovery of Li, Co and Ni can be achieved. Another motivation lies in the strive for continuous development of the InduRed concept, which could potentially benefit from another opportunity of application. Extending the portfolio of possible input materials for the InduRed concept could further increase its potential to contribute to sustainability and environmental protection.

1.2 Hypothesis and Research Questions

From what has been explained and demonstrated in the previous paragraph, a central hypothesis can now be formulated:

Due to the specific reactor characteristics, the InduRed concept could be a beneficial alternative for pyrometallurgical black matter recycling with superior capabilities regarding lithium recovery.

In order to refute or confirm this hypothesis, a number of underlying questions need to be answered. Not all of these questions were defined from the beginning of the research work, but partly arose from previous experiments and their results.

At the beginning of the work, the first question was about basic reactor design parameters, e.g., necessary temperatures to be prevailed for enabling the desired reactions in LIB black matter. For this evaluation, first it is necessary to investigate which reactions occur in black matter at certain temperatures. Furthermore, it must be clarified if impurities in the black matter affect aforementioned reactions. The associated questions were formulated as follows:

1a) What reactions are expected to occur in currently used cathode materials or black matter at high temperatures and under reducing conditions?

1b) Do the desired reactions occur under the conditions achievable with the InduRed concept?

Due to the ongoing strive for continuous improvement of LIB performance parameters such as energy or power density, the development of new materials leads to an everchanging and varying chemical composition of the later generated waste stream. Investigations into whether the InduRed reactor has this flexibility, and can potentially handle all currently used cathode technologies is a prerequisite, and the main component of the second research question, which is formulated as follows:

2. How do different cell chemistries affect the properties of black matter, and is the InduRed concept capable of handling all LIB cell chemistries used currently or in the near future?

Apart from the chemical composition of the batteries, the pre-treatment processes can also influence the properties and quality of black matter. Therefore, the following question arises for the intended use of the InduRed process, which is conversely dependent on the quality of the intermediate products of other processes:

3a) Is there a difference in the behaviour of black matter and factory new cathode materials and if so, what is the reason?

3b) What are desirable, what are rather counterproductive black matter properties and which pre-treatment processes are decisive for this?

Finally, some of the most relevant questions concern the actual achievable recovery rates when the InduRed concept is established as part of the LIB recycling chain. On the one hand, this involves the recovery of those metals that account for a large proportion of the total waste stream, e.g., Ni and Co, and thus are crucial in economic terms. On the other hand, the simultaneous recovery of Li would be a distinctive feature of the process and could overcome a yet unsolved problem. Thus, the fourth research question generally deals with the achievable recovery rates for the previously mentioned metals Ni and Co as well as Li in comparison with conventional pyrometallurgical procedures. Furthermore, it focuses on the recyclability of the obtained InduRed products.

4. What recycling rates can potentially be achieved for the metals of interest by applying the InduRed concept on LIB related wastes?

In summary, the investigations of the individual questions should facilitate the evaluation of the hypothesis. It should be noted that there were many other aspects and questions which will be described in the further course of the work. The questions defined above were chosen as they cover the key aspects of the work and provide a good overview of the issues under consideration.

1.3 Structure of the thesis

The **Introduction** section in chapter 2 mainly focuses on covering the fundamentals that will be relevant for later chapters. Therefore, it explains the very basics of the LIB technology, namely its working principle and the materials currently in use. From this information, the relevance of LIB recycling is derived, and an overview of currently used processes as well as their specific advantages, disadvantages and challenges are given. In a nutshell, the introduction strives to build a basic foundation of understanding the background of LIB recycling, summarises the current state of knowledge and provides a more detailed insight into those areas, which are essential for a proper comprehension of the thesis. Therefore, the focus in chapter 2 lies in introducing the InduRed reactor concept, which is the center of this scientific work and inevitable for all later discussions.

The outcome of the theoretical research and the results of all conducted experimental series and analyses are then presented in the third chapter, namely **Original Scientific Work**. This section is divided into three thematic sub-areas, which are based on the previously defined research questions and therefore cover the thermal properties of LIB related wastes, the influence of pre-treatment on the quality of intermediates and the achievable recovery rates for certain metals by using the InduRed concept. The results themselves are shown in the form of scientific publications, which are briefly placed in the context of the overall work.

As the name suggests, the following section, **Summary of Results**, restates the primary outcome of the scientific work.

Chapter 5, **Discussion and Assessment of Hypothesis,** then discusses all results holistically and strives to look at the results against each other again to draw new conclusions. Furthermore, some yet unpublished findings are added to increase the comprehensibility further. After the extensive discussion, the previously defined questions are answered, and the thesis hypothesis is subsequently evaluated.

At the end of the thesis, in the **Research Prospects and Outlook** section, some yet unsolved questions, further research perspectives and ideas on how future research in LIB recycling might be conducted are presented.

1.4 Methodology

Since each publication comprises an individual chapter with detailed information about the used materials and methods, this part is only intended to provide an overview of the conducted research.

An extensive literature review preceded the analyses and experiments. This was mainly aimed at identifying current bottlenecks and understanding their cause. From this, scenarios were derived in which way the InduRed reactor could be applied in the field of LIB recycling, and specific experimental plans were created to obtain significant results. The experimental investigations were essentially carried out in 3 apparatuses: the heating microscope, the simultaneous thermal analyser, and the InduMelt plant.

The first insights into the materials were gained in the **heating microscope analyses**. By observing superficial changes in the samples, temperature ranges could be defined in which apparent changes occur. The samples were analysed under inert and reducing conditions, i.e., with and without the addition of reducing agents and under an argon purge.

The **simultaneous thermal analysis** (STA) was the next step, in which the samples were subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The STA was also carried out under inert and reducing conditions and aimed to characterise the reactions that led to the changes observed in the heating microscope.

The third part of the experiments aimed to investigate potential recovery rates for Li, Ni, Co, and Mn by using the InduRed principle. But instead of using the original InduRed reactor that would currently allow for a material feed of 10 kg/h, a lab-scale version of the reactor was used. The mentioned furnace, the so-called **InduMelt plant**, has the same advantages as the InduRed reactor but is a discontinuous batch reactor that is much easier to work with. Consequently, the time needed to investigate one cathode material was cut significantly and thus allowed for more individual trials. However, all experiments and analyses used a similar maximum temperature of between 1550°C and 1600°C. The addition of carbon depended on the sample material and the type of analyses and contributed between 10 w.-% and 20 w.-% of the sample mass. More information on the individual settings is given in the corresponding publications later in this work.

Regarding the used materials, it is stated that the used black matter was provided by a LIB pre-treatment facility run by Redux GmbH in Germany. In addition to the black matter, analyses and experiments were also carried out with six currently used cathode materials. Lithium cobalt oxide (LCO, $LiCoO_2$) was chosen because it is still used in many electronic applications. Lithium nickel manganese cobalt oxide (NMC, $LiNi_xMn_yCo_zO_2$) and lithium nickel cobalt aluminium oxide (NCA, $LiNi_xCo_yAl_zO_2$) are currently used in EV applications and are very likely to hold this position at least in the near future due to their striking advantages. Furthermore, there are some modifications of NMC in which the contents of Ni, Co and Mn vary. To reflect the further development in the conducted studies, not only the standard 1-1-1 and 5-3-2 variants were analysed, but also the variants 6-2-2 and 8-1-1, which are relevant in the medium and long term. Because of its lower energy density, lithium iron phosphate (LFP, $LiFePO_4$) is more likely to be used in stationary energy storage systems. Nevertheless, it is also expected to have a significant share of the future battery market, which is why it should also be considered in the recycling sector and has therefore also been taken into account.

In general, all factory-new cathode materials used were directly purchased from the producer Gelon Energy Corp. in China. In addition to the samples, finely ground carbon powder obtained from voestalpine metal engineering GmbH (Austria) was used to serve as a reducing agent in the corresponding experiments. An overview of all conducted experiments and analyses is illustrated in Figure 3.

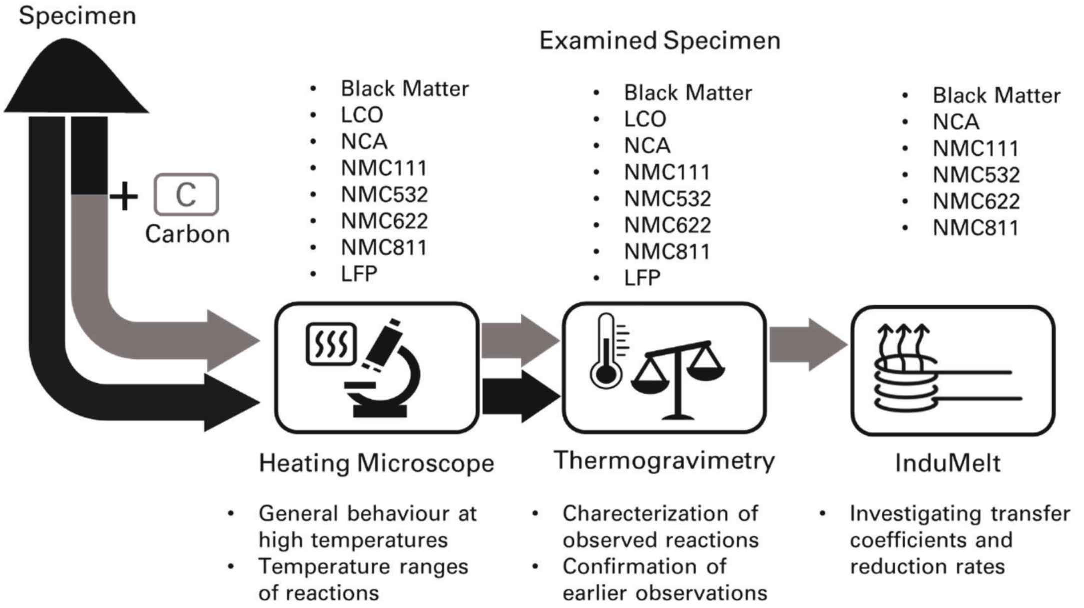

Figure 3: Overview of all experiments and analyses carried out for certain specimen in the course of this doctoral thesis. For an explanation of terms reference is made to Table 1.

For the sake of completeness, Table 1 explains all abbreviations used in figures and tables along the thesis.

Table 1: Overview of abbreviations used for materials, procedures and parameters.

Abbreviation	Designation	Chemical Formular or Explanation
LCO	Lithium cobalt oxide	$LiCoO_2$
LFP	Lithium iron phosphate	$LiFePO_4$
NCA	Lithium nickel cobalt aluminium oxide	$LiNi_{0.75}Co_{0.2}Al_{0.05}O_2$
NMC 1-1-1	Lithium nickel cobalt manganese oxide	$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$
NMC 5-3-2	Lithium nickel cobalt manganese oxide	$LiNi_{0.5}Co_{0.3}Mn_{0.2}O_2$
NMC 6-2-2	Lithium nickel cobalt manganese oxide	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
NMC 8-1-1	Lithium nickel cobalt manganese oxide	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$
CSA	Cross-section area [%]	see chapter 3.1.1
EM/HM	Heating microscope	see chapter 3.3.1
IM	InduMelt	see chapter 3.3.1
BM/AM	Black matter or active material	see chapter 3.3.1

2 Introduction and Fundamentals

The following introductory section aims to provide a basic understanding of the LIB technology and an overview of currently used recycling strategies with associated advantages, disadvantages and challenges. Special attention is being paid to the used materials as well as their further development and importance. Moreover, currently applied recycling methods are described and compared. In this regard, the focus lies on challenges and bottlenecks of the processes and the underlaying mechanisms. The chapter ends with a detailed presentation of the InduRed reactor, the concept and working principle of which is absolutely essential for understanding the rest of the work.

2.1 The LIB Technology

Lithium-ion batteries basically share their fundamental working principle with other battery types. A difference in the electrical potential of two electrodes, which are electrically isolated by a separator, forces electrons to flow over an external circuit so that the potential gradient becomes balanced. Basically, the name-giving causer for this potential gradient in LIBs are lithium (Li) ions which are able to pass the separator in each direction. To understand the system of a LIB cell in more detail, it is helpful to explain its working principle by using a schematic illustration of such a cell, as can be seen in Figure 4.

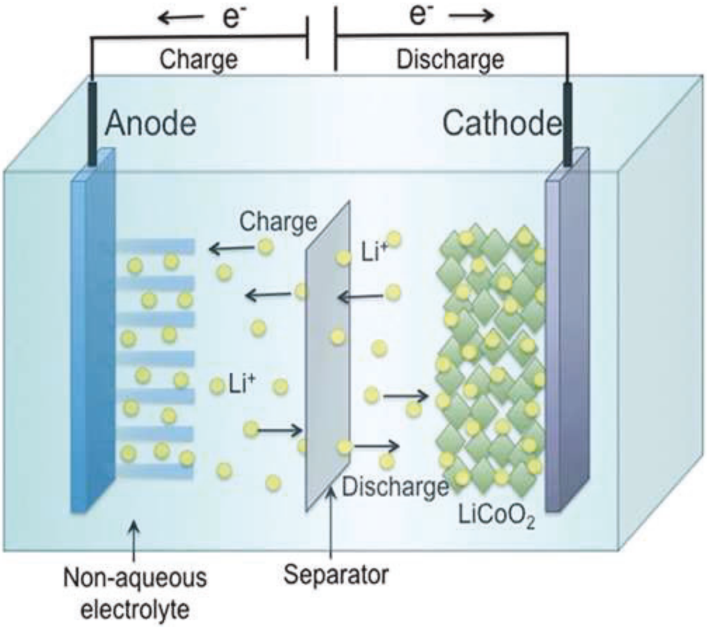

Figure 4: Schematic illustration of the working principle of a lithium-ion battery cell. [22]

In a nutshell, every LIB cell consists of two electrodes, a separator and an electrolyte. The electrodes are based on aluminium (Al) and copper (Cu) conductor foils, which are coated with active materials, thus either lithium metal oxides or lithium iron phosphate on one electrode and graphite or, less commonly, lithium titanite on the other one. [23] During the discharge, the anode emits electrons that migrate through the external circuit to the cathode. To compensate, positive lithium ions migrate from the anode into the electrolyte and flow to the cathode, where they are stored. The other way round, a voltage is applied externally during charging, which in turn creates an excess of electrons at the anode. The lithium ions now migrate from the cathode to the anode and are deposited in the anode again.

Despite an unchanged basic principle, the LIB technology came a long way since it was suggested and patented by Goodenough et al. [24] in the late 1970s. The original LIB was based on the previously mentioned LCO technology, which was more stable in air than its counterfeits and had better electrochemical properties. These advantages enabled LCO to become the preferred cathode material for decades. In the meantime, various reasons have led to LCO being replaced more and more by other materials. [25,26] This continuous development of the new LIB materials is primarily about positively influencing specific battery parameters. Typical parameters can be, for example, energy or power density, cycle stability or safety of the cell technology. In this respect, the main adjusting factor is the cell chemistry, i.e. the substances used as active materials or electrolytes. [27] Apart from the performance relevant attributes, other factors such as cost, sustainability, and social justice are of importance as well.

Since the composition of the cathode materials is of particular relevance for both battery parameters as well as all recycling-related activities, basic knowledge in this regard is required to comprehend certain explanations and conclusions in this thesis.

As already explained, the first commercially used LIB worked with a layer structured LCO cathode material. Since cobalt is not only considerably more expensive than its alternatives but also a critical raw material [28] that is extracted under questionable conditions, its substitution was intrinsically motivated. But replacing cobalt entirely, as for example in spinel layered lithium manganese oxide (LMO, $LiMn_2O_4$) cathode materials [29], lead to unwanted deterioration of key performance parameters such as safety. [30] So instead of omitting the cobalt, cathode materials have started to be developed in which cobalt is only partially substituted without compromising performance or safety. The result of this development, lithium nickel manganese cobalt oxide (NMC, $LiNi_xMn_yCo_zO_2$) and lithium nickel cobalt aluminium oxide (NCA, $LiNi_xCo_yAl_zO_2$), has not only partially improved properties but also led to significant cost reductions and thus to the further advance of the LIB technology. The lithium iron phosphate (LFP, $LiFePO_4$) accumulator has a cathode made of $LiFePO_4$ instead of conventional LiCoO2. It has a lower energy density but does not tend to thermal runaway, even in case of mechanical damage. Owing to its high reliability, LFP type batteries have a prominent position in new stationary energy storage systems for grid stabilisation. [31–37] A more detailed insight into the respective benefits and drawbacks of particular cathode materials, however, is later given in chapter 3.2.

2.2 Lithium-ion Battery Recycling

Before the principles and mechanisms of LIB recycling approaches are presented, first, the incentives for LIB recycling are to be derived:

- Economic incentive:

  The LIB market is about to increase drastically over the next decade. The corresponding need for raw materials, the value of which in the case of LIBs is high, to satisfy this demand could further increase raw material prices. Therefore, recovering those materials from EoL batteries is likely to remain a profitable business or even gain in lucrativeness and constitutes a corresponding economic motivation.

- Environmental incentive

  One thing that could be stated with certainty is that all LIBs currently produced and entering the product life cycle will someday return as waste batteries. Proper treatment of such waste batteries is vital to meet today's understanding of sustainability and environmental protection. On the one hand, for the sake of circular economy and the protection of resources, on the other hand, to protect the environment from being harmed by toxic ingredients of the EoL batteries.

- Strategic incentive

  While certain metals can be replaced and substituted by others, the name-giving lithium is crucial for LIBs. Despite contributing only a small part (less than 3%) to the total mass of a battery, lithium was added to the list of critical raw materials by the European Commission in 2020. [10] This means that lithium is not only of high economic importance but also bears a certain supply risk. Efficient recycling of EoL LIBs and particularly recovering lithium can, therefore, ensure future raw material supply for battery production and help conserve economic momentum.

The fact that there are sufficient incentives can be deduced from the large number of procedures and processes that are already established or currently being developed. These differ not only in their approach but also in their respective aims. In the following part of the thesis, the focus is precisely on this differentiation and the mechanisms underlying currently applied LIB recycling processes.

Broadly speaking, the processes can be arranged along a recycling chain and, in most cases, can be relatively clearly assigned to one of four sub-groups. As illustrated in Figure 5, those groups are collection and transport, pre-treatment, metal recovery, and refining. For the time being, only a brief explanation of each of the sub-groups will be given. This is intended to show where the current bottlenecks in the field of LIB recycling lie. However, a detailed review of the state-of-the-art technologies as well as interrelationships between specific process steps is presented in chapter 3.2.1.

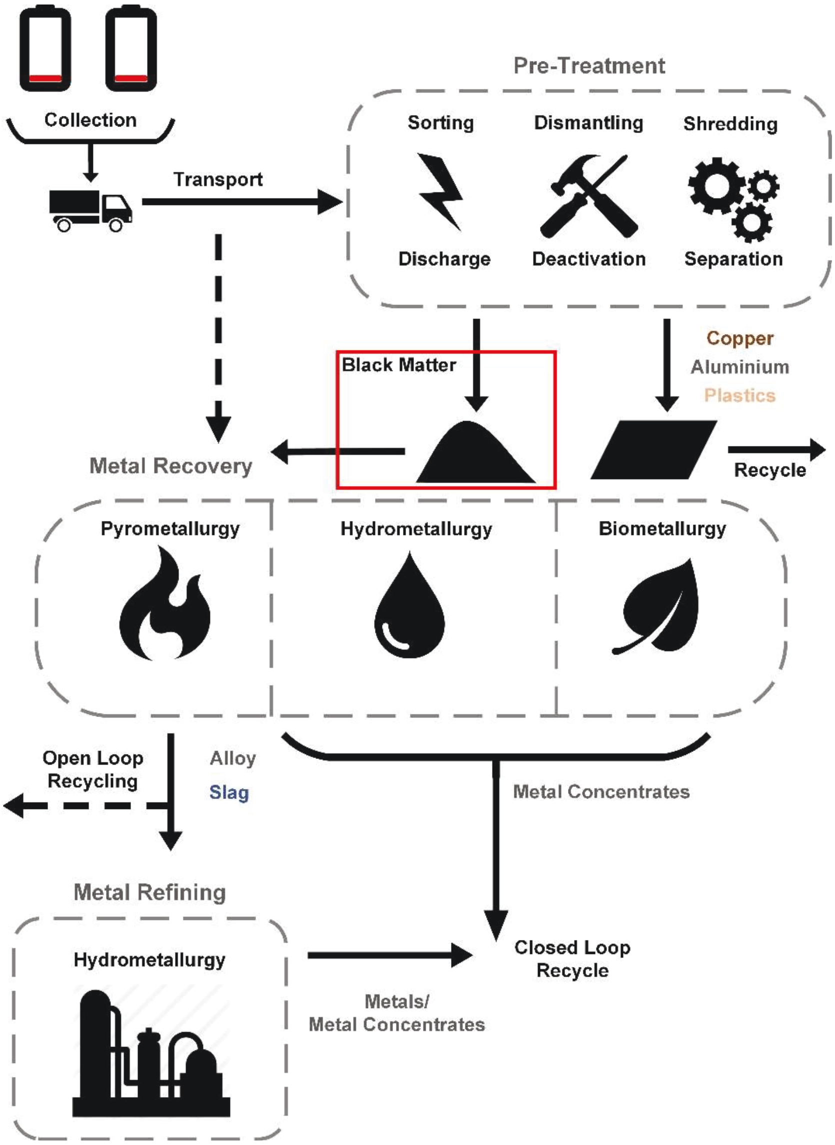

Figure 5: Schematic illustration of lithium-ion battery recycling chains. (cf. [38])

As one would expect, the area of collection and transport covers all activities that deal with the safe delivery of EoL LIBs to a facility entrusted with their further treatment. The transport of damaged batteries and the problem of incorrectly disposed batteries is particularly critical since both issues can pose a major safety risk and often cause problems.

Pre-treatment includes all process steps that basically aim at a rough separation of individual components of the battery system. There are several concepts for this, some of which have already been implemented on an industrial scale and process several thousand tons of used batteries every year. Typical process steps in pre-treatment can include, for example, discharging, deactivation, dismantling or mechanical processing, all of which can be carried out in different ways. The sequence, number of sub-steps, or their execution are variable, leading to many possible process concepts. In addition to the recovery of directly recyclable components such as steel from the housing or copper cables and other electronic parts, the pre-treatment is mainly aimed at producing so-called black matter. Black matter primarily consists of the active materials of the electrodes, i.e., usually graphite from the anode and the respective cathode materials. Furthermore, it includes cell residues that could not be separated after mechanical processing (e.g., shredding), such as aluminium or copper originating from the cell's conductor foils. Thus, black matter is enriched with the valuable cathodic metals and should be understood as an intermediate product along the LIB recycling chain that is crucial for economic feasibility. Moreover, pre-treatment procedures achieve to reduce the mass of input materials for subsequent processes significantly.

The previously obtained black matter is further treated in the downstream processes, which can be summarised under the name of metal recovery processes. This treatment can basically rely on pyro-, bio- or hydrometallurgical mechanisms. Biometallurgical procedures aim to use plants that selectively absorb and enrich certain metals. Due to poor throughput rates and yet low technical readiness level, industrial implementation of such methods is not yet foreseeable, which is why they were only mentioned for the sake of completeness and not further considered in this thesis. Hydrometallurgical approaches rely on methods like acidic leaching and precipitation. They are known to be highly selective and capable of achieving high recovery rates for all cathodic metals of 95% and beyond. On the other hand, these processes can be quite complex, often require large amounts of chemicals and are mostly not yet operating at an industrial scale. While bio- and hydrometallurgical processes always take black matter as an input feed, there are pyrometallurgical processes that do not need a pre-treatment but use whole LIBs from portables directly. This is primarily applicable when LIBs are used as secondary raw materials in already existing nickel or cobalt mills, like it is done by Umicore, Belgium. That fact could also be considered one of the strengths of pyrometallurgy since the mechanisms used are often already well researched and industrially sophisticated. Furthermore, the applied methods are generally less complex than the hydrometallurgical approaches but are more energy consuming on the other side. However, the most significant disadvantage of pyrometallurgical LIB recycling processes is their inability to recover lithium in a way that allows for functional recycling, i.e., for the production of new LIBs. Instead, Li becomes oxidized and accumulates in a resulting slag phase in which its concentration is too low to make further recovery steps economic feasible. [39–47] This yet unsolved issue is also one of the major drivers for the studies that have been conducted in the course of this thesis.

In general, the described process steps along the recycling chain are operated by different companies. An overview of the essential processes currently in use or under development was recently published by Mossali et al. [48]. Table 2 lists the respective operators, the methodological approach and the current capacities if data is available.

Table 2: Overview of currently applied processes by Mossali et al. [48].

Company	**Principle**	**Capacity [tons/year]**
Accurec GmBH, Germany	Pyro- and Hydrometallurgy	4000
AEA Technology, UK	Hydrometallurgy; Electrolysis	*Data not available*
Akkuser Ltd, Finland	Pre-treatment	*4000*
Batrec Industrie AG, Switzerland	Hydrometallurgy	*200*
Duesenfeld, Germany	Pre-treatment; Hydrometallurgy	*Data not available*
Glencore plc, Canada/Norway	Pyro- and Hydrometallurgy	*7000*
Inmetco, USA	Pyrometallurgy	*6000*
Lithorec, Germany	Hydrometallurgy	*Data not available*
OnTo Technology, USA	Pre-treatment	*Data not available*
Recupyl, France	Hydrometallurgy	*110*
Retriev (Toxco), USA/Canada	Hydrometallurgy	*4500*
SNAM, France	Pre-treatment	*300*
Sony, Sumimoto process, Japan	Pyro- and Hydrometallurgy	*150*
Umicore, Belgium	Pyro- and Hydrometallurgy	*7000*

2.3 The InduRed Reactor Concept

The InduRed reactor concept, schematically shown in Figure 6, and the idea behind it could be seen as the driving force behind this scientific work. Therefore, it is crucial to be familiar with the process, particularly its working principle and strengths and weaknesses, to comprehend the presented work.

The first prominent appearance of the InduRed concept, former also referred to as InduCarb reactor, was within an EU project. [49] In this project, several project partners under the lead of the Chair of Thermal Processing Technology (TPT) at the Montanuniversitaet Leoben (MUL) worked to establish the so-called RecoPhos process, the centerpiece of which is the aforementioned InduRed reactor. As part of the RecoPhos project, the reactor aimed for enabling phosphorus recovery from sewage sludge ashes by providing strong reducing conditions and a unique flow regime favorable for the desired reactions. Since then, TPT's team for High-Temperature Processing Technology (HTPT) has been continuously working on the further development of the original reactor. During that time, numerous improvements for enhanced performance, safety and efficiency have been implemented, as reported and documented by Ponak [50].

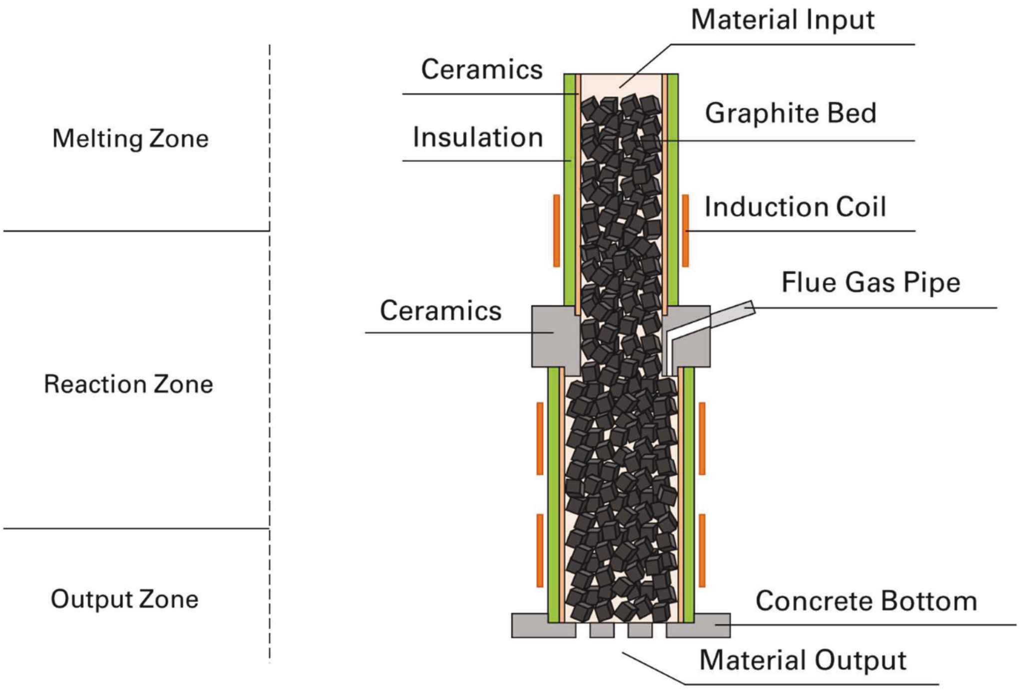

Figure 6: Illustration of the InduRed reactor concept (c.f. [50,51])

The InduRed reactor (Figure 6) is a continuously charged, inductively heated, fixed bed reactor that is particularly designed to handle metal oxide-containing input materials. The heat input is provided by three induction coils that surround a fixed bed of graphite particles within aluminium oxide (Al_2O_3) ceramic rings. The electromagnetic field, generated by the induction coils, induces an electric current in the graphite particles, which as a result, are heated due to ohmic heat. The induction coils cannot be controlled entirely independent from each other due to coupling effects but still allow to apply a particular temperature profile.

The continuous feed enters the reactor from the top and is melted in the uppermost part of the reactor, which is accordingly referred to as the melting zone. Within the melting zone, the temperature is controlled so that it is sufficiently high to melt the respective input material without enabling all reduction reactions immediately. The liquid material then forms a thin film on the surface of the reactor bed and flows downwards in the next zone of the reactor.

The reaction zone, which is marked by the second induction coil and the flue gas outlet, is where the aforementioned reactions are desired to occur and what makes the concept unique. If a gaseous reaction product, i.e., phosphorus (P) on the example of sewage sludge, is formed, it only needs to pass through a thin layer of molten material before becoming a part of the gas phase that is sucked out via the gas outlet. Therefore, an undesired reaction between gaseous products and residual metals in the liquid phase can be limited. For sewage sludge ash, an example of such an undesired reaction is the formation of iron phosphides that would limit the P recovery rate. [51]

At this point, it is also important to note that the carbon of the graphite bed is not supposed to take part in the reactions. Instead, an additional carbon source, usually fine powdered coke, is added to the input material as a reducing agent. The main objective of the graphite bed is to provide a large reaction surface and to serve as a heat source. If too much of the graphite bed is consumed during operation, issues with the power supply may occur, which is why the amount of C added is usually slightly over-stochiometric.

Furthermore, an argon (Ar) purge at both the feed at the top and the tap at the bottom is used to prevent the suction of false air and the resulting oxidization of graphite.

The third induction coil is designed to power the last part, namely the output zone, of the reactor. Depending on the input material, severe changes of physical properties, e.g., viscosity, could occur as a result of the altered chemical composition. Therefore, the power supply in the lower third is controlled so that the temperature is sufficient to allow the liquid phase to be transported towards the outlet of the reactor.

In summary, the most striking advantages of the concept are

- particularly low oxygen partial pressures to maintain strong reducing conditions,
- direct heat input into the graphite bed, which is where the power is needed,
- high CO/CO_2 ratio due to excess carbon supply and temperatures of up to 1750 C
- and the unique opportunity to directly remove gaseous reaction products without allowing intensive contact with non-volatile components of the liquid phase.

As explained, the reactor concept was developed to be the heart of the so-called RecoPhos process, which aimed to recover phosphorus from sewage sludge ashes. In the meantime, its applicability for other municipal and industrial wastes was under investigation. Especially the work of Ponak [50,52], which mainly focused on the treatment of basic oxygen furnace slag (BOFS) and considered other metallurgical slags, proved that the InduRed concept could potentially contribute to various issues within the field of pyrometallurgical metal recycling.

One of the primary goals of the present work is to determine whether the particularly strong reducing conditions are sufficient to prevent the slagging of lithium and solve one of the big bottlenecks in LIB recycling. Expanding the portfolio of potential input materials for the InduRed reactor can further allow far-reaching value creation due to its flexibility. Upon other things, this and the question of requirements regarding the necessary quality of black matter will be addressed in the following chapter.

3 Original Scientific Work

In this part of the thesis, all results of the undertaken research and the conducted experiments are presented. For the sake of comprehensibility, the chapter is further divided into three subchapters, each of which focuses on one of the main research fields. Within each subchapter, there is a brief introduction that explains how the results of the subchapters contribute to the overall research project and how they are interrelated with each other. The results themselves are then presented in the form of scientific publications. In the following chapter 4, the most important results from the publications are summarized to give an overview for the discussion in chapter 5.

3.1 The Behavior of LIB Cathode Materials at High Temperatures

For the development and evaluation of a carbo-thermal reduction process, fundamental technical questions arise at the beginning. As stated in the introduction, the InduRed concept is characterized in particular by the graphite bed and the mass transport taking the form of a thin melt film on the beds surface. The investigation of the melting properties, or thermophysical properties in general, of potential input materials for the process, is therefore of high priority.

In this subchapter, the results of the corresponding experiments and analysis to investigate said properties are presented. Namely, heating microscope experiments and simultaneous thermal analyses (STA) consisting of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted for this purpose. In the course of several experimental series, the cathode materials LCO, LFP, NCA, and NMC in the modifications 111, 532, 622 and 811, as well as black matter from a pre-treatment process, were investigated. Thus, the collected data covers all currently used cathode materials, including the promising modifications NMC622 and NMC811, which have great potential and are expected to have a significant share of the future LIB waste stream. [53–57] Since issues with standardized labelling lead to a situation in which a potential input materials for the InduRed reactor contain more than only one LIB type but are mixtures of several cell chemistries, the information about the thermophysical behaviour of all of the mentioned cathode materials is of great importance. Furthermore, it is crucial to investigate the temperature ranges in which certain reactions and changes in the materials occur in order to provide optimal conditions to enhance the desired reactions but to limit the undesired ones.

Therefore, the following publications precisely deal with that issue. In the first publication, “Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions” [58], the heating microscope experiments with LCO, LFP, NCA, NMC111 and black matter are described and discussed. The second publication, “Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach” [59], builds upon these results and adds STA results to further characterize specific observations that were made during the heating microscope experiments.

3.1.1 Publication 1

Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions

Windisch-Kern, S., Holzer, A., Nagovnak, P., Ponak, C., & Raupenstrauch, H.

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Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions

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Abstract

In this work, a brief overview of currently used lithium ion battery (LIB) cathode materials is given. These materials as well as active material, a fine powdered mixture from a pre-treatment step of spent LIBs, were investigated in a heating microscope. In order to estimate when reduction reactions of the lithium-metal-oxides start, another experimental series, in which highly reactive carbon powder was added to the samples, was performed. Since the said materials are very complex and thermodynamic data is hard to find, the gathered information and experience from these preliminary experiments are necessary for the development of a new pyrometallurgical approach to LIB recycling. For the basic reactor design, the state of the active material at high temperatures and, respectively, its solubility in a mineral slag is a crucial property, which was investigated in a third experimental series. The conducted experiments show that the reduction reactions of all tested cathode materials start at technologically manageable temperatures of about 800 °C. Furthermore, a significant difference between experiments in which carbon was added, compared to those with pure cathode materials could be observed. The behaviour of the active material from an existing pre-treatment process does not match the corresponding mixture of pure cathode materials. However, possible reasons could be identified and are the focus of the further research project.

Introduction

The EU climate and energy plan aims at a CO_2 reduction in the transport sector of at least 30 % by 2030. [1] Since lithium-ion-batteries (LIB) have some compelling advantages over other battery technologies, it is likely that they will play a crucial role in the decarbonization of the transport sector. Market forecasts, as shown in Figure 1, in which several trends predict an enormous increase of the global electric vehicles (EV) fleet within the next 20 years, give a feeling for the importance of this technology. On the other hand, there is still no satisfying solution on how to recycle crucial elements from the batteries of these vehicles in order to minimize waste streams and to meet the raw material requirements of the future. [3, 8]

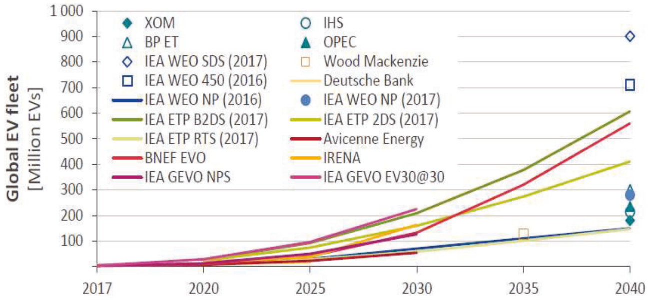

Figure 1: Forecast of the development of the global EV fleet [5]

In general, the LIB-technology has brought a variety of battery types, differing in their shape, size and - most importantly - their cell chemistry. Like other batteries, LIBs are also built up of cathode, anode, electrolyte and separator. [10] Different cell chemistries usually refer to different cathode materials, which for LIBs consist of lithium-metal-oxides. The cathode materials of LIBs are steadily evolving in order to make the batteries cheaper, safer and more efficient. Especially the amount of cobalt used in the cell must be emphasized, since its costs are above average compared to alternatives like nickel or manganese. Moreover, most of its mining takes place in politically unstable regions of the world and is often criticized. [3, 8] Thus, new technologies are trying to keep the proportion of cobalt as low as possible, without risking losses in battery safety or performance. [9]

In the mobility sector, currently used LIB types have cathodes with lithium-nickel-manganese-cobalt-oxides (NMC, $LiNi_xMn_yCo_zO_2$) or lithium-nickel-cobalt-aluminium-oxides (NCA, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$). [6] Figure 2 shows the proportion of raw materials varying by LIB type and emphasizes the significant reduction in the amount of cobalt used in common LIB types (NMC and NCA) compared to the older lithium-cobalt-oxide (LCO, $LiCoO_2$). Lithium-iron-phosphate (LFP, $LiFePO_4$), a relatively young cathode material, is considered to be one of the safest chemistries, due to its high thermal runaway temperature. While it does not need cobalt at all in its cell chemistry, it is still subject to further development. [5]

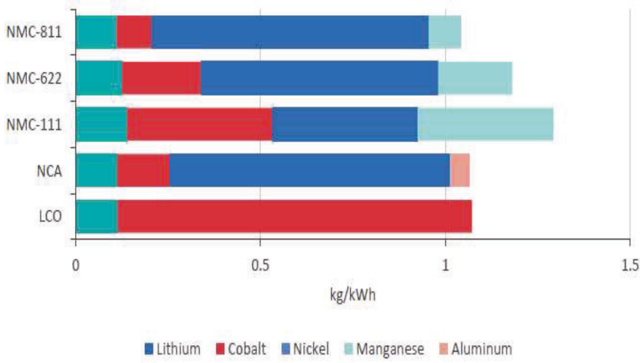

Figure 2: Proportion of raw materials by LIB type [5]

The variety of LIB types leads to a dynamic future waste stream that is difficult to predict and thus poses a challenge for developing new recycling processes. However, an efficient end-of-life concept for LIBs must be found in order to meet future raw material and sustainability requirements. End-of-life concepts can range from reuse over reprocessing to recycling. In this work the focus is on recycling, which can be divided into pre-treatment and hydro- or pyrometallurgical recycling processes. Common pre-treatment methods contain procedures like discharging, dismantling, thermal stabilization or crushing and aim for a separation of the main battery components. [4] Thus, the products of a pre-treatment process usually are plastics and metal shells from the battery casing, copper and aluminium from the conductor foils and active material (also called black matter) from the electrodes. This active material, which contains the valuable and crucial metals from the cathode and carbon from the anode is then processed in a following hydro- and/or pyrometallurgical recycling step. In this area, currently available recycling technologies are not yet in an industrial scale or are unable to recover all valuable metals with a reasonable effort. A novel pyrometallurgical approach, which is currently under development at the Chair of Thermal Processing Technology at the Montanuniversitaet Leoben, aims to close this gap in lithium ion battery recycling. [4, 7, 11]

Materials and Methods

The focus of this work is on the four cathode materials mentioned in the introduction, active material from an existing pre-treatment process as well as on a synthetic active material, which is based on the chemical composition of the pre-treatment active material and was generated by mixing the pure cathode materials and carbon.

- $LiCoO_2$ (LCO)
- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)
- $LiNi_xMn_yCo_zO_2$ (NMC)
- $LiFePO_4$ (LFP)
- active material (AM)
- reproduced (synthetic) active material (AM-R)

The NMC type used in the experiments has the momentarily most commonly used 1-1-1 configuration ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$). Newer NMC configurations like 6-2-2 or 8-1-1 are, as explained in the introduction, trying to decrease the proportion of cobalt but are not yet widely used and therefore only considered in the further course of this research project. Each material was tested in a heating microscope with an argon purge (Figure 3), in which it was placed on an Al_2O_3 sample holder and heated to a temperature of 1620 °C. The argon purge is needed to prevent reactions with oxygen from air. For the second experimental series, in which the behaviour of cathode materials under reducing conditions should be investigated, a high reactive carbon powder was added with a mass proportion of 10 % in order to enable reduction reactions. Those sample are indicated by addition of "_C" (e.g. LCO_C) to their sample name. A third series of tests aims to evaluate the behaviour of the active material (AM) at high temperatures. For this purpose, also several slag forming agents (SiO_2, CaO and FeO) in different quantities were added with up to 40 mass percent to the AM, in order to investigate if a molten phase can be formed. The AM_R sample (abbrev. for reproduced active material) consists of a mixture of NCA, NMC, LFP and carbon in a proportion that allows for a similar chemical composition as the AM sample. By this the influence of impurities, which are included in AM but are not added to AM_R, on thermophysical properties of the active material was investigated.

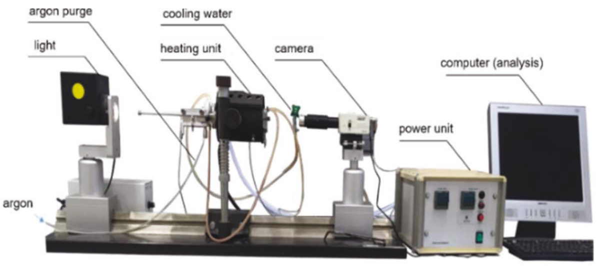

Figure 3: Heating microscope [2]

The experiments aim to determine the temperatures at which reduction reactions, phase transitions or melting processes take place, by analysing changes of the cross-sectional area of the sample during heating.

Results

The results can be subdivided into three parts according to the series of experiments:

- behaviour of pure cathode materials
- behaviour of pure cathode materials under reducing conditions
- behaviour of active material and slag formers

The changes of the cross-sectional area of the pure cathode materials are shown in Figure 4.

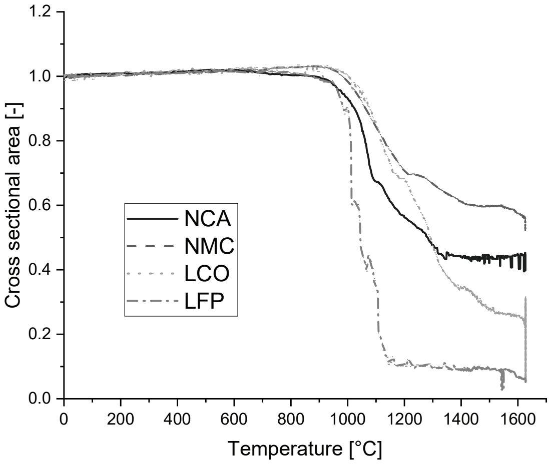

Figure 4: Comparison of the behaviour of pure cathode materials from lithium-ion-batteries during heating in a heating microscope

There is almost no change until the sample is heated to 950 °C, followed by a very similar linear decrease between 1000 °C and approximately 1300 °C. At 1600 °C, the sample's cross-sectional area has decreased to about 30 – 60 % of the initial value. LFP is an exception, since its decrease is steeper and its end value is clearly below 20 %.

None of the samples were magnetic, which indicates that nickel and cobalt are not metallic and the oxides were not reduced. In contrast, all samples from the second series of experiments that included carbon were magnetic and the curves (Figure 5) have significantly changed.

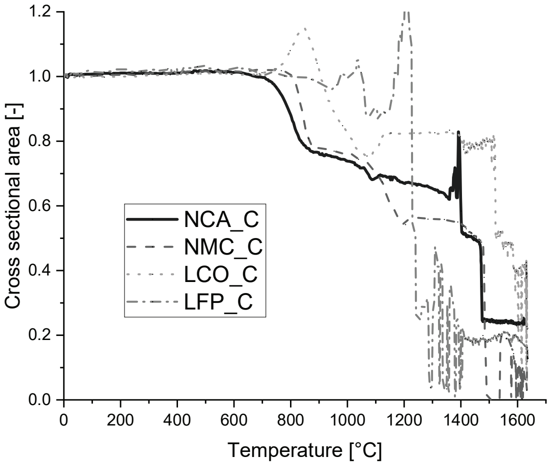

Figure 5: Comparison of the behaviour of cathode materials from lithium-ion-batteries with carbon powder during heating in a heating microscope

In general, Figure 5 shows that first changes occur at lower temperatures than in the experimental series without carbon and that the graphs of the cathode materials under reducing conditions differ more from each other than in Figure 4. For NCA, the first decrease can be observed at less than 800 °C, for NMC just slightly above. Basically, the curves of NMC and NCA are very similar. Both start at around 800 °C with a sharp decrease, followed by only small changes until 1400 °C and ending with an abrupt decrease to below 20 % of the initial area at temperatures of about 1470 °C, which pretty much concur with the melting temperature of pure nickel (1455 °C).

While - apart from the short slope at 800 ° C - the behaviour of LCO differs only slightly from NCA and NMC, LFP shows some differences, which can be explained by looking at the heating microscope recordings (Figure 6) and considering its chemical composition. First of all, $LiFePO_4$ has by far the highest proportion of oxygen, which – during reduction reactions – causes the release of a CO-rich gas phase. Figure 6 shows, that this gas release can cause a foaming of the sample, which explains the steep descent and the following rustling of the LFP_C curve in Figure 5.

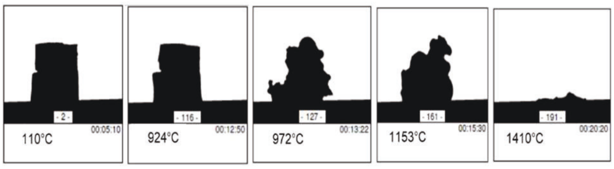

Figure 6: Heating microscope recordings from LFP_C

The last series of experiments concentrates on the behaviour of the active material from a pre-treatment step and how to convert it into a molten phase. A look at its chemical composition (Table 1) reveals that the carbon content, which comes from the graphite anode that is used in this type of LIBs, is very high. Nickel, cobalt, manganese, lithium and aluminium come from the cathode and their proportion suggests that the present active material mainly consists of NCA and NMC types. The high values for copper and aluminium can be explained by the conductor foils of LIBs, as they consist of these metals and a complete removal during pre-treatment was not achieved.

Table 1: Chemical composition of the active material from lithium-ion-batteries

Species		
C	29,5	wt.-% of dry matter (DM)
Ni	209000	mg/kg DM
Li	24200	mg/kg DM
Al	58300	mg/kg DM
P	3700	mg/kg DM
Mn	10800	mg/kg DM
Fe	5940	mg/kg DM
Co	41900	mg/kg DM
Cu	56900	mg/kg DM
Zn	7650	mg/kg DM
Pb	590	mg/kg DM

As mentioned in the introduction, it is necessary to investigate the aggregate state of the AM at high temperatures and the influence of slag formers in order to design the reactor for the desired pyrometallurgical recycling process. Therefore, first the AM was investigated in the heating microscope without any additives followed by several tests with slag forming agents with the following compositions:

- SiO_2/CaO in a 1:1 mass proportion (basicity B_2=1)
- SiO_2/CaO (B_2=1) with 10 mass percent FeO

Each composition was tested in proportions of 30, 40 and 60 mass percent based on the active material. Figure 7 exemplarily shows the recordings from three of these experiments.

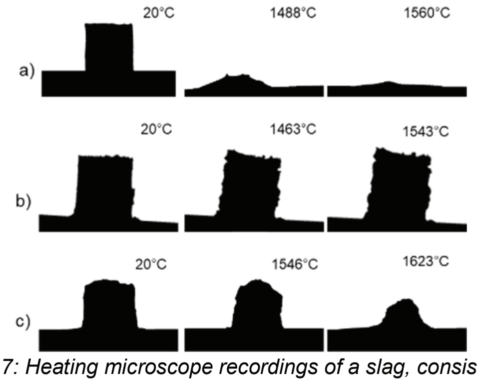

Figure 7: Heating microscope recordings of a slag, consisting of SiO_2/CaO (B_2=1) (a), active material from spent lithium-ion-batteries (b) and a mixture of active material and the slag from (a) in a mass proportion of 30 % (c) [2]

In Figure 7a, slag, consisting of SiO_2 and CaO in equal proportions, was tested. The mixture is completely molten at temperatures of 1560 °C. The active material shown in Figure 7b has not even shrunk let alone melted. Reasons, why there was no forming and melting of a nickel-manganese metal alloy, although there was a sufficient amount of carbon in the active material, will be discussed in the conclusion. Combining the materials from Figures 7a and b, the slag mixture from Figure 7a was added to the active material in a mass proportion of 30 % (Figure 7c). It was observed that the slag formers melted at slightly higher temperatures compared to Figure 7a, but no active material could be dissolved in the slag. This is also valid for higher proportions of additives and for additives with iron oxide addition, which was used to lower the melting temperature of the slag to about 1400 °C.

The changes of the cross-sectional area of active material and the reproduced active material are shown in Figure 8.

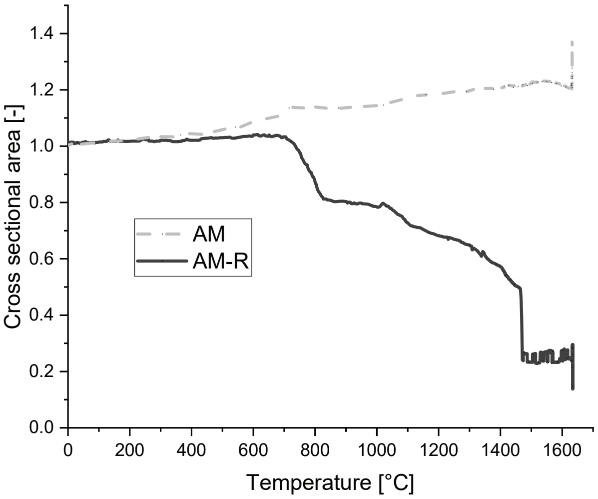

Figure 8: Comparison of the behaviour of active material from spent lithium-ion-batteries (AM) and a reproduced active material (AM-R)

The AM-R curve is very similar to the previously conducted experiments and lies between the curves of NCA_C and NMC_C in Figure 5. The sudden decrease at about 1450 °C can be considered as the melting of a nickel-manganese metal alloy. Since AM-R simply is a mixture of 75 % NCA, 20 % NMC and 5 % LFP, this seems reasonable but cross-reactions between these substances cannot be excluded. The AM curve indeed is the only curve that increases relatively steadily over the whole temperature range. All tests with slag forming additives also showed a slightly less pronounced increase between 400 °C and 1400 °C. Depending on the amount and type of additive there was a sharp decrease between 1400 °C and 1550 °C, ending at values of 30 to 60 % of the initial cross-sectional area.

Conclusion

Finally, there are many new findings that could be gained from the experiments. The original aim was to investigate if there are reactions between the cathode material and high reactive carbon powder and if they can be observed with a heating microscope. The comparison of the graphs in Figure 4 and Figure 5 shows significant differences. It is for example possible to observe the melting of the produced metal alloy after reduction and it could be determined that all residual samples from the reduction experiments were magnetic. This indicates that reduction reactions can occur in the heating microscope and that the argon purge is enough to disable re-oxidization reactions. The behaviour of the active material, however, raises some questions.

On the one hand, the carbon content in the AM is higher than would be stoichiometrically necessary for the reduction reactions but there is no sign that these reactions occur. The characteristic first decrease between 800 °C and 850 °C, which was similar in all reduction experiments, cannot be observed for the active material. The reason for this is most likely not due to cross-reactions between different cathode materials since the reproduced active material reacted like the cathode materials. A possible reason might be the presence of a non-neglectable proportion of aluminium and copper in the active material or changes in the material during the pre-treatment process. This could also be a reason for the difficulties to convert the active material into one or more molten phases (e.g. slag and metal). This is not absolutely necessary for the desired process, as long as the reduction reactions also take place in the solid phase and a corresponding reactor design can be found.

Outlook

In the next phase, the research project will be divided into two main fields of activity. On the one hand, it must be investigated why the behaviour of active material from the pre-treatment process is so contrary to the one of pure cathode materials or the reproduced active material. Therefore, more experimental series in the heating microscope are planned, in which the influence of aluminium and copper as well as the reactivity of the included carbon of the active material, are investigated. In order to evaluate the reactivity of the carbon it is first separated by density separation and then tested as reducing agent for the pure cathode materials.

The second work package concentrates on the reduction behaviour of the cathode materials. Hereby, the next step is to further analyse the reduction process itself and to confirm the temperature at which the reduction starts by performing a series of thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) tests. By analysing the mass loss of the samples, which for example occurs during the release of oxygen, the changes of the cross-sectional area at certain temperatures should be assignable to phase changes, melting processes, or reduction reactions. The differential scanning calorimetry is used to determine the energy consumption for the heating and reduction of the sample. This data is going to be used to estimate the power and energy demand of the desired pyrometallurgical recycling process.

References

[1] Bundesministerium für Nachhaltigkeit und Tourismus, 2019, Integrierter nationaler Energie- und Klimaplan für Österreich, https://www.bmnt.gv.at/dam/jcr:29ba927b-d36f-4cd4-8f56-8bec97a48c76/NEKP_final%2018.12.2019, checked on 18.02.2020.

[2] Holzer, A., Pyrometallurgisches Recycling von Aktivmaterial aus der Aufbereitung von Lithium-Ionen-Batterien in einem induktiv beheizten Schüttschichtreaktor, Master thesis, Montanuniversitaet Leoben, Leoben, 2019

[3] Baes, K., Kolk M., Carlot F., Merhaba A. and Ito Y., 2018, Future of batteries, available online at https://www.adlittle.com/sites/default/files/viewpoints/adl_future_of_batteries-min.pdf

[4] Huang, B., Pan, Z., Su, X. and An, L., Recycling of lithium-ion batteries, Journal of Power Sources 399 (2018), 274–286.
DOI: https://doi.org/10.1016/j.jpowsour.2018.07.116

[5] Lebedeva, N., Tarvydas D. and Tsiropoulos I., Li-ion batteries for mobility and stationary storage applications: Scenarios for costs and market growth, Luxembourg (EUR, Scientific and technical research series), 2018. DOI: https://doi.org/10.2760/87175

[6] Myung, S.-T., Maglia F., Park, K.-J., Yoon, C. S., Lamp, P., Kim, S.-J. and Sun, Y.-K., Nickel-Rich Layered Cathode Materials for Automotive Lithium-Ion Batteries: Achievements and Perspectives, ACS Energy Lett. 2 (2017), 1, 196–223. DOI: https://doi.org/10.1021/acsenergylett.6b00594

[7] Olivetti, E. A., Ceder, G., Gaustad, G. G. and Fu, X., Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals, Joule 1 (2017), 2, 229–243. DOI: https://doi.org/10.1016/j.joule.2017.08.019

[8] Chemali, E., Preindl M., Malysz, P. and Emadi A., Electrochemical and Electrostatic Energy Storage and Management Systems for Electric Drive Vehicles: State-of-the-Art Review and Future Trends, IEEE J. Emerg. Sel. Topics Power Electron. 4 (2016), 3, 1117–1134. DOI: https://doi.org/10.1109/JESTPE.2016.2566583

[9] Thielmann, A., A. Sauer and M. Wietschel, 2015, Gesamt-Roadmap Lithium-Ionen-Batterien 2030, Frauenhofer-Institut für System- und Innovationsforschung.

[10] Korthauer, R. (Ed.), Handbuch Lithium-Ionen-Batterien, Berlin, Heidelberg, s.l., Springer Berlin Heidelberg 2013, DOI: https://doi.org/10.1007/978-3-642-30653-2_4

[11] Xu, J., Thomas, H. R., Francis, R. W., Lum, K. R., Wang, J. and Liang, B., A review of processes and technologies for the recycling of lithium-ion secondary batteries, Journal of Power Sources 177 (2008), 2, 512–527. DOI: https://doi.org/10.1016/j.jpowsour.2007.11.074

3.1.2 Publication 2

Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach

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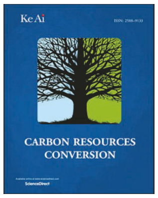

Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach

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ABSTRACT

Since pyrometallurgical approaches on lithium ion battery recycling are not yet capable of recovering lithium but only nickel, cobalt and manganese, the Chair of Thermal Processing Technology at the Montanuniversitaet Leoben started to investigate experimental reactor concepts on their suitability to overcome this major drawback. Therefor, the general behaviour of currently used cathode materials under reducing conditions and high temperatures is of great interest. This work expands previous performed heating microscope experiments by thermogravimetric analysis (TGA) to characterize the reactions that are responsible for certain changes in the cathode materials. By comparing the superficial changes of the samples in the heating microscope with the corresponding data from the TGA, it was possible to identify the temperature zones in which reduction reactions occured. For all investigated cathode materials, the reduction reactions started at technically feasible temperatures of approx. 1000 °C, which is favorable for the desired recycling process. On the other hand, this is some hundred degrees higher than the temperature at which first changes in the heating microscope could be observed and indicates that there are changes in the material before the reduction starts. Therefore, the results also emphasize the need for further analysis to clarify this offset and to complete the thermal characterisation of the cathode materials.

1. Introduction

The use of lithium ion batteries (LIBs) in e-mobility applications can potentially be a major part in the decarbonization of the transport sector in order to reach the EU climate and energy plan targets [1]. Like other batteries, LIB cells mainly consist of the components anode, cathode, separator and electrolyte [2]. However, the research on LIB-technology has brought several types of batteries which differ in their appearance, like size and shape as well as in their cell chemistry, the latter of which results from the variety of application in which LIBs can be used and the correspondingly varying needs in terms of performance and safety. The urge to continuously improve energy and power density also contributes to the rapid further development of the technology [3]. Furthermore, a substitution of cobalt is sought since its high price, which is also a driver for battery costs, and its mining, which is questionable in terms of social sustainability, are very unfavorable [4,5]. Thus, the main types of batteries that are currently used in the mobility sector have cathodes with lithium-nickel–cobalt-aluminium-oxides (NCA, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) or lithium-nickel-manganese-cobalt-oxides (NMC, $LiNi_xMn_yCo_zO_2$) [6]. The amount of cobalt used in this cathode material compared to older lithium-cobalt-oxide (LCO, $LiCoO_2$) is massively reduced. Due to its high safety standard, owing to the high thermal runaway temperatures, and its low price, caused by the full absence of cobalt, lithium–iron-phosphate (LFP, $LiFePO_4$) is also currently on the rise [4].

However, the expected increase of the whole LIB market, especially driven by electric vehicles, shows how important an efficient recycling chain, the exact implementation of which is not yet clear, will become [7,8]. Indeed, one thing can be said with certainty, the processes that will be used along the recycling chain must be able to deal flexibly with different chemical compositions of the LIB waste stream in both, the short and long term, as it can be assumed that the rapid development of new cathode materials will continue [5,9–11]. Current recycling concepts either process the LIBs directly or start with a pre-treatment step that includes processes like discharging, thermal deactivation and mechanical processing, with the aim of separating the battery's components. The materials received from these pre-treatment methods are

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metal shells, conductor foil consisting of aluminium and copper, plastics and black matter, which mainly consists of the active materials from the electrodes and contains most of the valuable metals [12].

Said black matter can then be further treated with pyro and/or hydrometallurgical procedures, with each of the approaches having its specific strengths and limitations [13–15]. In general, pyrometallurgical approaches on LIB recycling rely on methods like smelting, reduction smelting, roasting or calcination. On the hydrometallurgical side, the processes are based on leaching with inorganic as well as organic acids, solvent extraction or chemical precipitation. In broad terms, pyrometallurgical processes are already used on an industrial scale, while most hydrometallurgical processes are still under development. One of the reasons for this is that pyrometallurgical LIB recycling often uses conventional aggregates, known for example from other areas of metallurgy, or that black matter is only used as a secondary raw material in e. g. an already existing nickel production. The main advantage of hydrometallurgy is that it is in principle possible to recover all valuable materials from black matter. In pyrometallurgy, on the other hand, lithium is oxidized, slagged, and is only recycled non-functionally, for example if the slag is used as a construction material, lithium recovery from the slag is not yet economically feasible [16,17].

An alternative reactor concept, which aims for a simultaneous recovery of cobalt, nickel, manganese as well as lithium and therefore a possibility to overcome the common disadvantages of pyrometallurgical LIB recycling, is currently under investigation at the Chair of Thermal Processing Technology at the Montanuniversitaet Leoben [18,19]. One step in the evaluation of whether the desired reactor is suitable for black matter treatment or not, is the investigation of how the potential input materials of the process, i.e. LIB active materials, behave at high temperatures and under reducing conditions. Simplified, under reducing conditions, a reduction reaction of the lithium metal oxide compound as given in Eq. (1) is expected [16].

$$LiMeO_2 + C = Li_2CO_3 + Me + (MeO) \tag{1}$$

At higher temperatures, additional decomposition of the lithium carbonate into lithium oxide and carbon dioxide can be assumed. With regard to the transition metals, it is described in the literature that complete reduction can be expected for nickel and cobalt, while manganese, for example, can still be present as an oxide depending on the reaction conditions like atmosphere and temperature [20,21]. In experiments without carbon addition it is presumed that a thermal dissociation of the lithium metal oxide according to Eq. (2) will occur [20].

$$LiMeO_2 = Li_2O + MeO \tag{2}$$

The experiments aim to evaluate at which temperatures reactions in the materials occur and to further investigate which kind of reaction takes place at a certain temperature. Therefore, changes of the cross sectional area of a sample in the heating microscope are compared with the trends of the sample mass and the heat flow in the corresponding temperature range. By this, it is possible to distinguish between reduction reactions, phase transitions or melting processes. Furthermore, the used analysis, in particular the heating microscope and thermogravimetric analysis (TGA) with said settings, are evaluated regarding their suitability to achieve these desired statements.

2. Materials and methods

This paper, which extends the work presented in the “Minisymposium Verfahrenstechnik 2020” proceedings [22], again focuses on the currently most widely used cathode materials for LIBs and how they behave under reducing conditions and high temperatures. Therefore, the results from the first series of heating microscope experiments, which were performed in a Hesse Instruments EM 201 with an HR18-1750/30 furnace, are examined again more closely by taking TGA into account. The TGA was conducted in a Setaram Setsys Evo 2400 at the Chair of Physical Metallurgy and Metallic Materials at the Montanuniversitaet Leoben. In both, the heating microscope as well as the TGA, a maximum temperature of 1620 °C was reached, an argon purge to inhibit oxidization reactions were used and the samples were placed in or on Al_2O_3 crucibles respectively plates. The cathode materials $LiCoO_2$ (LCO), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) and $LiFePO_4$ (LFP) were analyzed with and without the addition of 10 w.-% carbon in order to be able to compare and describe their behavior under reducing conditions. As an indicator for reduction reactions, a simple magnetic strip was used directly after each experiment to check whether the samples were magnetic or not. The experiments with carbon addition are indicated by adding “_C” to the sample name, e.g. NMC_C.

Table 1
Furnace heating program used in the heating microscope experiments.

Temperature range	Heating rate
Start – 1350 °C	80 °C/min
1350–1550 °C	50 °C/min
1550–1650 °C	10 °C/min
1650 °C	5 min holding time

3. Results and discussion

In the heating microscope experiments, the samples with and without carbon addition were heated up to 1620 °C using the furnace heating program shown in Table 1 and an argon purge of approx. 2.5 L/min.

By looking at the graphs in Fig. 1, which show the trend of the cross sectional area (CSA) of the samples with respectively without a carbon addition of 10 wt.% during heating in the heating microscope, the results of this experimental series can be summarized. For the sake of understanding, it is important to mention that these experiments were only about finding temperature zones in which obvious changes in the sample occur. Considering the cross sectional area alone is not sufficient to draw conclusions about the mechanism causing the changes, but it is assumed that significant changes in the cross sectional area, i.e. volumetric changes in the sample, can be attributed to thermal effects, reactions, phase transformations or melting processes. In order to further specify which of the mentioned causes actually lead to changes in certain temperature ranges, the present results are considered along with those from the TGA and discussed in the further course of this work.

Starting with the samples with carbon addition, shown in Fig. 1a, one can see that first changes of the cross sectional area occur at temperatures of approx. 800 °C for NMC_C and NCA_C which generally have a similar behaviour. In both samples the cross sectional area decreases to about 60–70% of its initial value within a temperature of 1450 °C, followed by a steep decrease at approx. 1500 °C, which can be explained by the melting point of the resulting metal alloy. In comparison to LCO_C, apart from the short increase of the cross sectional area at 800 °C, only minor differences can be found. This similar behaviour may be caused by the fact that LCO, NMC and NCA have a common layered oxide structure. On the other hand, there is LFP_C which has an olivine structure and shows a significantly different trend. The first change occurs some hundred degrees later and is more striking than in other materials. At around 1200 °C, a rapid decrease of the cross sectional area can be observed, accompanied by a rustling of the curve. The latter can be explained by the high amount of oxygen in LFP, which can be released as CO respectively CO_2 due to reduction reactions and causes a foaming of the sample in this temperature range. This foaming can also be seen in Fig. 2, which shows the recordings of the heating microscope at certain temperatures. If the CSA becomes small due to complete melting of the sample, as seen in the 1410 °C image in Fig. 2, the CSA curve may also begin to noise as the microscope has difficulties finding the baseline [22].

In Fig. 1b, the trends of the cross sectional area of cathode materials

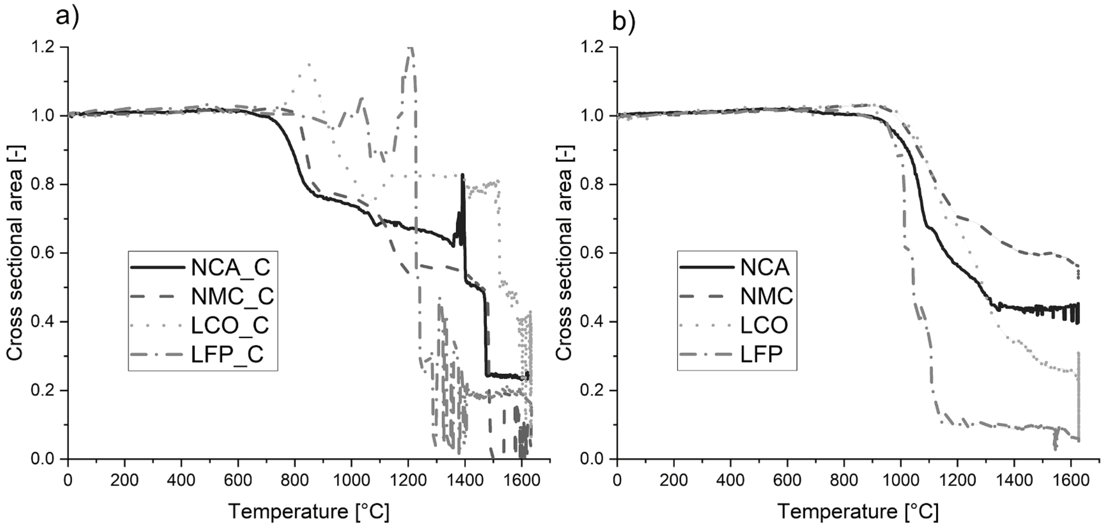

Fig. 1. Trends of the cross sectional area of lithium ion battery cathode material samples with (a) and without (b) carbon addition during heating to 1650 °C in a Hesse Instruments EM 201 heating microscope [22].

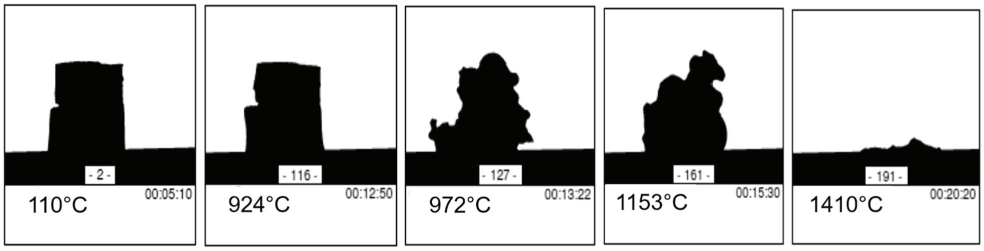

Fig. 2. Foaming of LFP_C during heating in a heating microscope experiment [22].

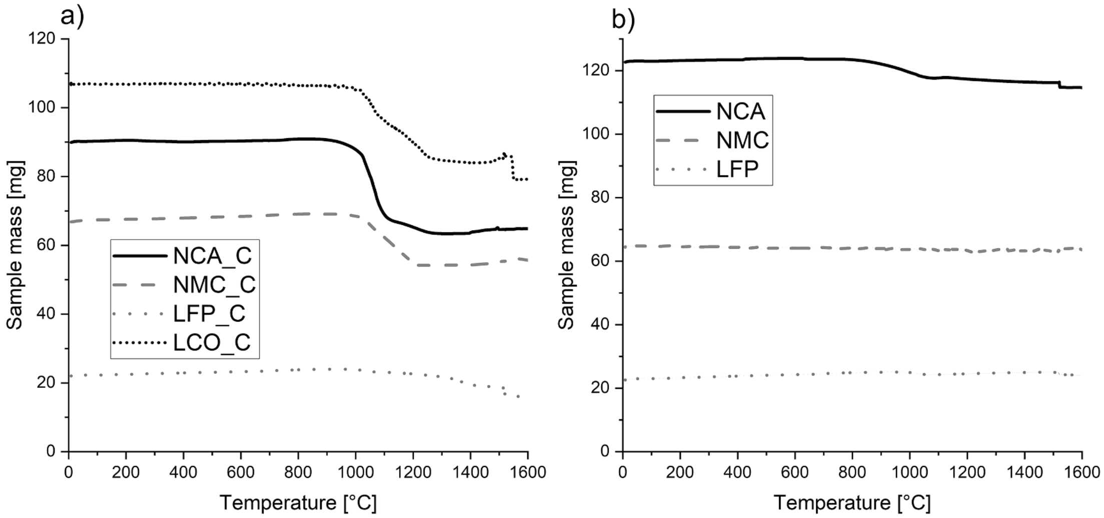

Fig. 3. Trend of the sample mass of lithium ion battery cathode materials with (a) and without (b) carbon addition during thermal analysis.

without carbon addition are shown. In comparison to those under reducing conditions, it can be seen that the first significant change occurs at higher temperatures (around 1000 °C) and that there is not the typical steep decrease at around 1450 °C as in the experiments with carbon addition which indicates melting processes. The difference between the layered structured NMC, NCA and LCO and the olivine type structured LFP are still noticeable but less pronounced than in Fig. 1a. The cross-sectional area has decreased to about 30–60% of the initial value for NMC, NCA and LCO respectively 20% for LFP and is less decrease compared to the experiments with carbon. In summary, the following can be concluded from the heating microscope experiments:

- Significant differences were shown between the experiments with and without carbon, which suggests reactions between carbon and the cathode materials.

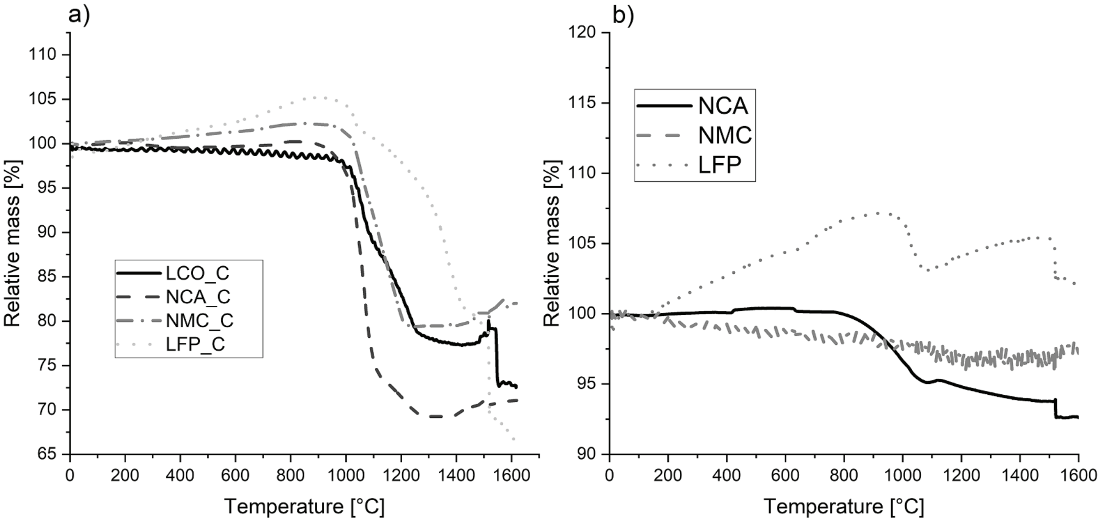

Fig. 4. Relative mass of lithium ion battery cathode materials with (a) and without (b) carbon addition during thermal analysis.

- The samples from the experiments with carbon addition were then magnetic, which did not happen without carbon. This is a clear sign of reduction reactions
- The reactions take place at technically feasible temperatures of around 800–1000 °C [22].

In any case, the heating microscope experiments have shown that the addition of carbon to the cathode materials led to reduction reactions. In order to investigate whether the observed initial decrease in cross sectional area was actually caused by those reduction reactions, thermogravimetric analysis were carried out. In Fig. 3 the trend of the mass of the cathode materials with and without carbon addition is shown. The reason for the different initial masses lies mainly in the density and packing density of the samples. However, a smaller amount was deliberately chosen for LFP because, should foaming occur, it should never escape from the sample crucible in order to protect the analysis device. Since it is known from reference measurements that the argon purge has an small effect on the gravimetric measurement (maximum deviation of approx. 1 mg), all measurements were corrected by the error term known from the reference measurements. At first glance, a difference between the samples with (Fig. 3 and without carbon addition (Fig. 3b) can be seen.

In the tests with carbon addition a significant decline can be detected at approx. 1000 °C for NMC_C, NCA_C and LCO_C while LFP_C remains relatively steady. In comparison, the tests without carbon addition (Fig. 3b) do not have a major mass decrease over the whole temperature for any of the cathode materials. For a closer look, the following Fig. 4 shows the relative mass, i.e. the respective mass signal in relation to the initial sample mass over sample temperature.

The previously mentioned decrease in mass becomes clearer in this representation. Between 1000 °C and 1200 °C the mass of NMC_C, NCA_C and LFP_C drop by 20–30% and remain relatively steady afterwards until 1600 °C. LFP_C also drops by a similar value in a similar temperature range but shows a steady mass increase before 1000 °C by almost 5%. This behaviour of LFP_C is also visible in Fig. 4b, the experiments without carbon addition. One explanation for this can be the influence of the argon purge on the gravimetric measurement, which has a stronger effect with a lower input mass and therefor especially on LFP_C.

One may also have noticed that there is no data for LCO without carbon addition in Fig. 4b. To explain this, it is necessary to compare the reactivity between the cathode materials and the Al_2O_3 ceramics, of which the sample holders for both, the heating microscope experiments as well as the thermogravimetric analysis are made of, by looking at the sample pictures in Fig. 5. In Fig. 5(a–c) the sample plates of the experiments with NMC_C, LFP and LCO_C are shown. It was seen, that the attack on the ceramic correlates with the chemical composition of the material examined and increases with increasing cobalt content. In the second to last thermogravimetric analysis with LCO_C this lead to the destruction of the sample crucible which is shown in Figs. 5(d–f). After reduction, the reactions between cobalt and the ceramic melted the bottom of the crucible and also destroyed the underlaying platinum rhodium thermocouple. Since the previous comparisons allow the assumption that LCO behaves similarly to NMC and NCA and in view that the behaviour under reducing conditions is in the foreground anyway, the measurement was not repeated in order to prevent further damage to the analysing device. Nevertheless, it is planned to repeat the analysis in graphite crucibles with the addition of sufficient carbon powder. By this, reactions between the sample holder and the sample itself should be avoided, which not only protects the analysis device but also provides the possibility of simultaneous thermal analysis to determine the energy intensity of the reduction reactions.

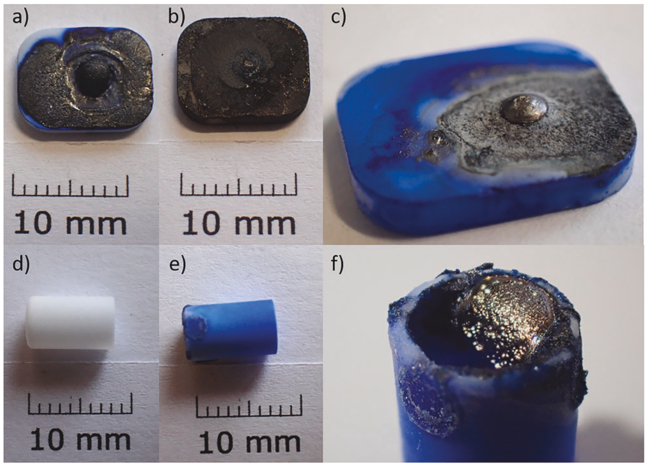

Fig. 5. Images of Al_2O_3 sample plates (a—c) from the heating microscope experiments: (a) NMC_C, (b) LFP and (c) LCO_C and images of Al_2O_3 sample crucibles (d–f) from the thermogravimetric analysis: (d) Reference measurement, (e and f) LCO_C.

For the time being, however, an important conclusion can be drawn from the thermogravimetric analysis. The difference between experiments with and without carbon addition are significant in means of

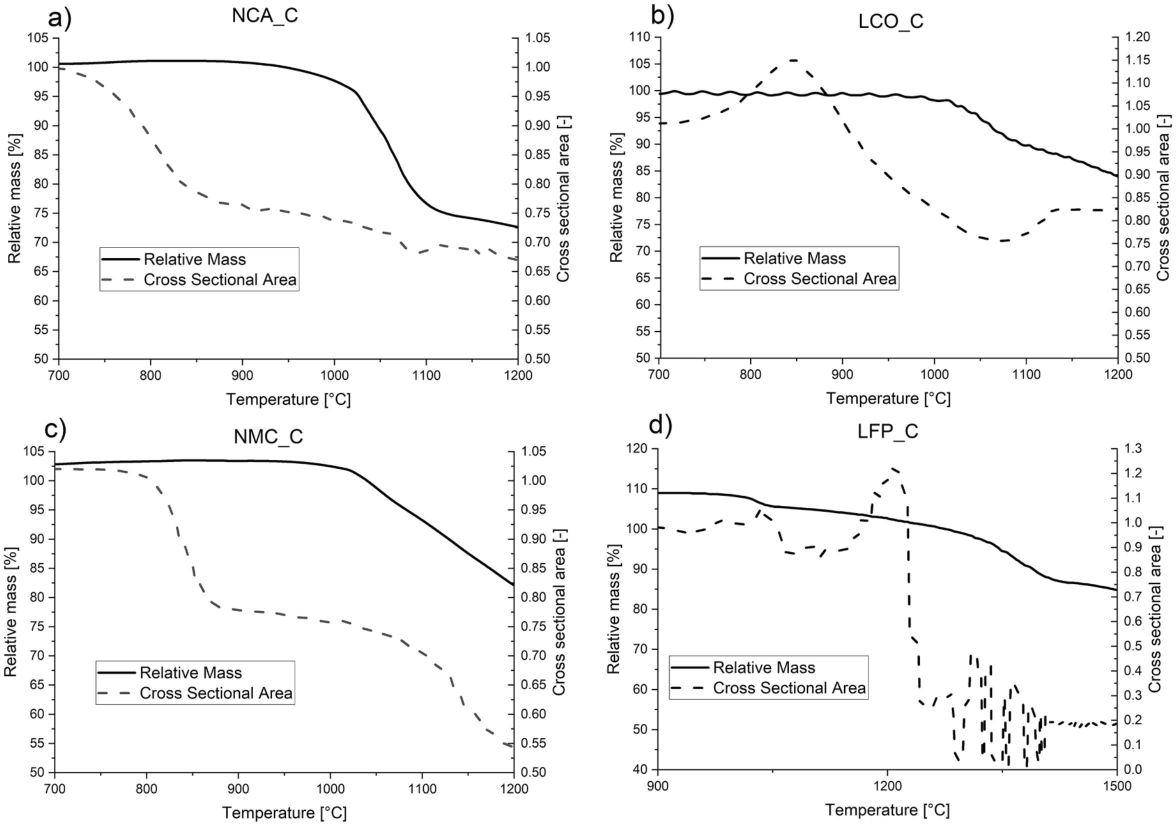

Fig. 6. Trend of the cross sectional area and relative mass of (a) NCA_C, (b) LCO_C, (c) NMC_C and (d) LFP_C during heating.

temperature range and magnitude of mass changes. This indicates that the carbon addition and argon purge are sufficient to allow for reduction reactions, with which the desired knowledge can be obtained from the experiments.

To finally be able to compare the results of both analyses to interpret the measured values in detail, the following Fig. 6 shows the relative mass and cross sectional area of each sample in the respective temperature range where the greatest changes occurred.

When comparing NCA_C and NMC_C, the similarity in the temperature range between 800 °C and 1100 °C is immediately apparent, which is an observation that has already been made on the basis of previous graphs. What is a new finding, however, is the delay with which the decrease in mass occurs compared to the change of the cross sectional area. It can be seen that the first mass decrease and the first cross-sectional area change appear to have an offset of about 200 °C, suggesting that there may be reactions prior to the desired reduction reactions. This can also be observed in the LCO_C sample, albeit less pronounced. It therefore seems that the first decrease in area in the heating microscope cannot be directly attributed to reduction reactions but probably to phase or structure changes. This behaviour also applies to LFP_C, which generally only shows signs of reactions at higher temperatures of 900–1400 °C. To investigate this offset in more detail, the next step is to heat the materials to a temperature before reduction reactions start and to perform a XRD analysis of these samples. Furthermore, the experiments need to be repeated with slower heating rates to evaluate its influence on the starting temperature of certain reactions. By this, the offset of changes of the cross sectional area and the sample mass might be clarified.

4. Conclusion

In this work, heating microscope analysis and thermogravimetric analysis were used to study the thermal behavior of the lithium ion battery cathode materials LCO, NCA, NMC, and LFP. The comparison of experiments with and without carbon addition revealed significant differences in the reaction behavior of the materials in regard to the temperature range in which the reactions occur as well as the extent of observed changes in the samples. When adding carbon, the thermogravimetric analysis results in a mass decrease of 10–25% in a temperature range of 1000–1200 °C for NCA, NMC and LCO and 1000–1400 °C for LFP. In comparison, much smaller or hardly any mass decreases were observed in the experiments without carbon addition. Also, the first changes of the samples in the heating microscope were detected at a temperature of about 1000 °C, which is approx. 200 °C higher than in the analysis with carbon addition. A problem that was seen in the experiments was the reaction between the resulting metal phase and the Al_2O_3 ceramics of which the sample plates and crucibles are made of. Thus, it can be concluded that the Al_2O_3 ceramic crucibles, which were supposed to be used for tests in the experimental reactor during the next phase of the project, need to be reconsidered and other materials such as MgO could come to the fore instead. However, the knowledge of the temperature ranges in which reactions occur is of decisive importance for the design of further experiments and the reactor concept itself. Hence, it can be stated that by completing the present experiments, enough results are available to carry out first test trials in the experimental reactor concept which initiates the next step in the overall process development project.

CRediT authorship contribution statement

Stefan Windisch-Kern: Methodology, Conceptualization, Visualization, Formal analysis, Writing - original draft. **Alexandra Holzer:** Conceptualization, Formal analysis, Writing - review & editing. **Christoph Ponak:** Project administration. **Thomas Hochsteiner:** Writing - review & editing, Writing - review & editing. **Harald Raupenstrauch:** Supervision.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

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References

[1] M.S. Whittingham, Lithium Batteries, 50 years of advances to address the next 20 years of climate, Issues (2020), https://doi.org/10.1021/acs.nanolett.0c04347.
[2] M. Yoshio, R.J. Brodd, A. Kozawa, Lithium-ion batteries, vol. 1, Springer. https://doi.org/10.1007/978-0-387-34445-4, 2009.
[3] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B. Lestriez, P. Novák, M. Petranikova, et al., Lithium-ion batteries–Current state of the art and anticipated developments, J. Power Sources 479 (2020), 228708, https://doi.org/10.1016/j.jpowsour.2020.228708.
[4] I. Tsiropoulos, D. Tarvydas, N. Lebedeva, Li-ion batteries for mobility and stationary storage applications scenarios for costs and market growth, Publications Office of the European Union:, Luxembourg, 2018, p. 72, https://doi.org/10.2760/87175.
[5] E. Chemali, M. Preindl, P. Malysz, A. Emadi, Electrochemical and electrostatic energy storage and management systems for electric drive vehicles: state-of-the-art review and future trends, IEEE J. Emerg. Sel. Topics Power Electron. 4 (2016) 1117–1134, https://doi.org/10.1109/JESTPE.2016.2566583.
[6] S.-T. Myung, F. Maglia, K.-J. Park, C.S. Yoon, P. Lamp, S.-J. Kim, Y.-K. Sun, Nickel-rich layered cathode materials for automotive lithium-ion batteries: achievements and perspectives, ACS Energy Lett. 2 (2017) 196–223, https://doi.org/10.1021/acsenergylett.6b00594.
[7] J.Y. Yong, V.K. Ramachandaramurthy, K.M. Tan, N. Mithulananthan, A review on the state-of-the-art technologies of electric vehicle, its impacts and prospects, Renew. Sustain. Energy Rev. 49 (2015) 365–385, https://doi.org/10.1016/j.rser.2015.04.130.
[8] L. Kavanagh, J. Keohane, G. Garcia Cabellos, A. Lloyd, J. Cleary, Global lithium sources–industrial use and future in the electric vehicle industry: a review, Resources 7 (3) (2018) 57, https://doi.org/10.3390/resources7030057.
[9] J. Baars, T. Domenech, R. Bleischwitz, H.E. Melin, O. Heidrich, Circular economy strategies for electric vehicle batteries reduce reliance on raw materials, Nature Sustainability 4 (1) (2021) 71–79, https://doi.org/10.1038/s41893-020-00607-0.
[10] E. Mossali, N. Picone, L. Gentilini, O. Rodrìguez, J.M. Pérez, M. Colledani, Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments, J. Environ. Manage. 264 (2020), 110500, https://doi.org/10.1016/j.jenvman.2020.110500.
[11] E.A. Olivetti, G. Ceder, G.G. Gaustad, X. Fu, Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals, Joule 1 (2017) 229–243, https://doi.org/10.1016/j.joule.2017.08.019.
[12] W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang, Z. Sun, A critical review and analysis on the recycling of spent lithium-ion batteries, ACS Sustainable Chem. Eng. 6 (2) (2018) 1504–1521, https://doi.org/10.1021/acssuschemeng.7b03811.
[13] X. Zheng, Z. Zhu, X. Lin, Y. Zhang, Y. He, H. Cao, Z. Sun, A mini-review on metal recycling from spent lithium ion batteries, Engineering 4 (3) (2018) 361–370, https://doi.org/10.1016/j.eng.2018.05.018.
[14] B. Huang, Z. Pan, X. Su, L. An, Recycling of lithium-ion batteries: Recent advances and perspectives, J. Power Sources 399 (2018) 274–286, https://doi.org/10.1016/j.jpowsour.2018.07.116.
[15] J. Xu, H.R. Thomas, R.W. Francis, K.R. Lum, J. Wang, B. Liang, A review of processes and technologies for the recycling of lithium-ion secondary batteries, J. Power Sources 177 (2008) 512–527, https://doi.org/10.1016/j.jpowsour.2007.11.074.
[16] H. Yin, P. Xing, Pyrometallurgical Routes for the Recycling of Spent Lithium-Ion Batteries, in: Recycling of Spent Lithium-Ion Batteries, Springer, 57–83, 2019, https://doi.org/10.1007/978-3-030-31834-5_3.
[17] J. Wang, Z. Guo, Hydrometallurgically Recycling Spent Lithium-Ion Batteries, in: Recycling of Spent Lithium-Ion Batteries, Springer, 27–55, 2019, https://doi.org/10.1007/978-3-030-31834-5_2.
[18] A. Holzer, S. Windisch-Kern, C. Ponak, H. Raupenstrauch, A novel pyrometallurgical recycling process for lithium-ion batteries and its application to the recycling of LCO and LFP, Metals 11 (1) (2021) 149, https://doi.org/10.3390/met11010149.
[19] S. Windisch-Kern, A. Holzer, C. Ponak, H. Raupenstrauch, Pyrometallurgical lithium-ion-battery recycling: Approach to limiting lithium slagging with the InduRed reactor concept, Processes 9 (1) (2021) 84, https://doi.org/10.3390/pr9010084.
[20] O.-S. Kwon, I. Sohn, Fundamental thermokinetic study of a sustainable lithium-ion battery pyrometallurgical recycling process, Resour. Conserv. Recycl. 158 (2020), 104809, https://doi.org/10.1016/j.resconrec.2020.104809.
[21] L. Shi, T. Qu, D. Liu, Y. Deng, B. Yang, Y. Dai, Process of thermal decomposition of lithium carbonate, in: Materials Processing Fundamentals 2020, Springer, 107–116, 2020, https://doi.org/10.1007/978-3-030-36556-1_10.
[22] S. Windisch-Kern, A. Holzer, P. Nagovnak, C. Ponak, H. Raupenstrauch, Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions, in: Proceedings of the 16th Minisymposium Verfahrenstechnik and 7th Partikelforum, 1–5, 2020, https://doi.org/10.34726/594.

3.2 About the Interrelationship of Pre-Treatment and Metal Recovery

The studies presented in the previous chapter revealed essential insights into the behaviour of black matter and LIB cathode materials at high temperatures and under reducing conditions. It was seen that significant differences could be observed if experiments with carbon addition were compared to those without. The underlying mechanisms, namely carbothermal reduction when carbon is added against thermal dissociation in tests without additives, clearly have different activation energies and result in different products.

However, the contrary behaviour of black matter was even more striking. From what was stated until then, it was assumed that black matter, which should also mainly consist of LIB active materials, thus a particular cathode material and graphite, will show similar behaviour as the factory new cathode materials with carbon addition. Despite some residual impurities that are left behind after pre-treatment, black matter clearly has a similar chemical composition. However, the sequence of processes that have generated this black matter has not been taken into account. It may be that some of these processes can lead to a chemical or structural alteration of the active materials and thus to an altered black matter quality.

In the following publication, with the title “Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities, and process dependencies” [38], the focus lies on precisely that issue. All currently used processes along the LIB recycling chain are characterized to assess a possible influence on the resulting black matter quality. From the standpoint of the overall objective of this thesis, the investigation of the suitability of the InduRed reactor for the recycling of LIBs, this step is enormously crucial to define a statement about quality requirements for future input materials.

3.2.1 Publication 3

Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities, and process dependencies

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Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies

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ABSTRACT

Lithium-ion batteries (LIBs) show high energy densities and are therefore used in a wide range of applications: from portable electronics to stationary energy storage systems and traction batteries used for e-mobility. Considering the projected increase in global demand for this energy storage technology, driven primarily by growth in e-vehicles, and looking at the criticality of some raw materials used in LIBs, the need for an efficient recycling strategy emerges. In this study, current state-of-the-art technologies for LIB recycling are reviewed and future opportunities and challenges, in particular to recover critical raw materials such as lithium or cobalt, are derived. Special attention is paid to the interrelationships between mechanical or thermal pre-treatment and hydro- or pyrometallurgical post-treatment processes. Thus, the unique approach of the article is to link processes beyond individual stages within the recycling chain. It was shown that influencing the physicochemical properties of intermediate products can lead to reduced recycling rates or even the exclusion of certain process options at the end of the recycling chain. More efforts are needed to improve information and data sharing on the exact composition of feedstock for recycling as well as on the processing history of intermediates to enable closed loop LIB recycling. The technical understanding of the interrelationships between different process combinations, such as pyrolytic or mechanical pre-treatment for LIB deactivation and metal separation, respectively, followed by hydrometallurgical treatment, is of crucial importance to increase recovery rates of cathodic metals such as cobalt, nickel, and lithium, but also of other battery components.

1. Introduction

Since the beginning of its commercialization 30 years ago, the lithium-ion battery (LIB) technology has asserted itself as a versatile energy storage device for a wide variety of applications. Due to their high energy-to-weight ratios, high open-circuit voltage, low self-discharge rate, low memory effect, and a slow loss of charge when not in use, LIBs are currently dominating the market of electric vehicles (EVs) as well as portable electronics (Qiao and Wei, 2012). Generally, batteries are classified according to their type of use: for electric and electronic equipment (EEE), such as laptops, e-scooters, e-bikes, and small household devices; for industrial use only (e.g., energy storage systems); or for EVs, such as motorized two-wheelers, plug-in hybrid, or battery electric vehicles. For the European Union (EU) it is reported that ca. 74,900 t of LIBs are placed on the EU market in 2019, of which ca. 49% are related to EEE applications, and 51% are industrial and automotive batteries (European Commission, 2019). In particular, the market of EV batteries is expected to have significant growth over the next decade (Baars et al., 2021). The International Energy Agency (IEA, 2021) estimates that the amounts of end-of-life (EoL) or spent LIBs,

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expressed in gigawatt hours (GWh), will increase from approximately 400 GWh in 2035 to 1,300 GWh in 2040. This development is intended to make a valuable contribution to the decarbonization of the transport sector and therefore play an important role in achieving the Paris climate goals. Nevertheless, much greater efforts must be made to recover metals through innovative recycling methods (Castelvecchi, 2020).

The resulting need for high-quality raw materials, such as cobalt, lithium, and graphite that are classified as critical raw materials (CRMs) by the European Commission (2020b), highlights the importance to pursue an efficient recycling strategy to ensure future raw material supplies through, in the best case, closed loop recycling in terms of a functioning circular economy. According to the Circular Economy Action Plan and the Green Deal (European Commission, 2020a), recycling rates of LIBs should increase and, as a consequence, the Directive 2006/66/EC on batteries and accumulators (European Parliament and Council of the European Union, 2006) is planed to be amended in 2022. According to the European Parliament (2021), the EU member states should achieve a minimum collection rate for LIBs of 70% by end of 2030. In addition, a “battery passport” will be introduced and specific material recovery rates for Lithium (Li), Nickel (Ni), Copper (Cu), Cobalt (Co), and further valuable materials will be set. To achieve a recycling rate of 95% for Ni, Cu, and Co, as well as 70% for Li until 2030, efficient recycling technologies need to be strengthened and adapted with regard to the predicted significant increase of LIBs (European Commission, 2020c).

Other literature reviews (Brückner et al., 2020; Doose et al., 2021; He et al., 2020; Liu et al., 2019; Lv et al., 2018; Velázquez-Martínez et al., 2019; Winslow et al., 2018) show that various process combinations of mechanical, pyrolytic and hydrometallurgical recycling techniques are possible to improve metal separation from polymer battery components and to achieve the material recovery rates for metals. All reports stressed the importance to consider the entire product life cycle and value chain of LIBs: from battery design and manufacturing to waste collection and recycling. For example, Mossali et al., 2020 highlights the importance and influence of product design as an early-stage measure to increase recyclability of LIBs. Yun et al. (2018) identified automated and intelligent recovery systems as one of the key research issues in LIB recycling. Another crucial research question is the impact of changing cell chemistries on recycling, which is addressed by Doose et al. (2021) who pays particular attention to the challenges of upcoming LIB generations (i.e., from LIBs with liquid electrolytes, to lithium sulfur batteries, or solid-state lithium batteries).

With regard to this increase of LIBs used for EVs and increased material recovery rates in the future, this review focuses on current (industrial-scale) waste management practices in LIB recycling with focus on the EU. Not only the constantly changing composition of the cell chemistry but also currently applied methods for waste collection and (mechanical or thermal) pre-treatment can have an impact on the quality of materials recovered by metallurgical refining technologies. Therefore, we reviewed the current state-of-the-art in waste collection, pre-treatment, and metallurgy and paid special attention on the interrelationships between each pre-treatment and post-treatment step to recover the currently most valuable alkali metals and metals from LIB packs, such as Li, Cu, Ni, Co, and also Manganese (Mn). This review aims to provide further insight into the impact of battery composition and different feedstock on LIB recycling, where graphite, polymers and various impurities can significantly affect the metallurgical processes.

2. Review scope and approach

This literature review focuses on LIBs from EVs and ESS (automotive and industrial batteries, respectively), and not on batteries used for portable electric devices, such as mobile phones or laptops. The review was conducted using various online databases such as PubMed, Science Direct, Web of Science, Google Scholar, and Scopus. The keywords “spent lithium-ion battery”, “battery electric vehicles”, “plug-in hybrid electric vehicles”, “waste management”, “battery recycling”, “separation techniques”, “recycling of critical raw materials”, “metal recovery”, “hydro- and pyrometallurgy” etc. were used to narrow down the search. The articles were then checked for quality, topicality, and relevance based on the journal’s impact factor, the year of publication, and the number of times the article was cited in another journal. During the literature search, we focused on peer-reviewed journal articles with impact factors according to the „Journal Citation Reports“ (JCR) and „Scimago Journal & Country Ranking (SJR) indicator“. In addition, the literature search was extended to include the principle of the so-called snowball system.

3. Lithium-ion battery types and material composition

Generally, LIBs are classified into cells, modules, and packs. A battery cell is a single power generating unit and consists of a cathode, an anode, a separator that is soaked in an electrolyte, and a robust housing. A battery module is a set of battery cells interconnected in series, in parallel, or in a combination of the two that is placed inside of a dielectric housing, whereas a battery pack is a set of battery modules (Warner, 2014). Depending on the requirements of a certain application, LIBs vary in shape (e.g., cylindrical, or pouch cells), size and configuration (i.e. at the level of a single cell, module, or pack). However, the most prevalent principle for discerning different types of LIBs is centred on the cathode material.

Table 1 lists different types of currently used LIBs, the distinction of which is based on the chemical composition of the cathode material. The first commercially used LIB type with liquid electrolytes was lithium cobalt oxide (LCO), which consists of layered $LiCoO_2$ as a cathode material, a graphite anode, and a conductive polymer as electrolyte (El Mofid et al., 2014; Zhao et al., 2021). While graphite materials remained the dominant anode material, the composition of cathode materials went through significant changes. The $LiCoO_2$ is reasonably easy to produce and has a stable discharge capacity. However, its relatively high costs, environmental and safety issues concerning the mining of Co or Li, which are furthermore on the EU’s CRM list for 2020 (European Commission, 2020b), prompted further development of the cathode materials (Chen et al., 2003; El Mofid et al., 2014). The trend for the next decades is thereby in particular to reduce the amount of Co (e.g., NMC622 to NMC811 having a molar ratio of Ni : Mn : Co of 6 : 2 : 2 and 8 : 1 : 1, respectively) or to use alternative technologies. Novel technologies, such as solid-state batteries with oxides, sulphides, or polymers as solid electrolyte compounds, are summarized for example in Doose et al. (2021), who discussed in more detail possible impacts on recycling. Lithium iron phosphate (LFP) are currently a popular alternative to NMC or LCO batteries, at which the used LFP cathode material has high structural stability that enables a long lifespan. Due to the relatively low nominal voltage and low energy density, the LFP batteries have been less frequently used for large traction batteries of EVs rather than for small EEE (Bharathraj et al., 2020; El Mofid et al., 2014), nonetheless the LFP battery technology tends to gain a significant market share in e-mobility, as LFP production is cost-effective. Lithium manganese oxide (LMO) on the other hand, has a high charge rate and cell potential at relatively low cost and environmental impact due to the absence of cobalt. The LMO batteries are used in a variety of portable electronic devices or small EEE as a single component, or are combined with NMC in electric vehicles like Chevy Volt, BMW i3, and Nissan Leaf (Bharathraj et al., 2020). Currently, the LIB types with the highest energy densities use NMC and lithium nickel cobalt aluminium oxide (NCA) type, in which Ni enables the increase in specific capacity and energy density and lowers its costs, and are therefore often used by the original equipment manufacturer (OEMs) like BMW, BYD Auto, Renault, Tesla, Volkswagen, etc. (Li et al., 2018; Wang et al., 2013). On the other hand, nickel-rich cathode materials suffer from a shorter lifespan, lower thermal stability and do have some minor technical issues like voltage decay, low initial Coulombic

Table 1
Characteristics and classification of lithium-ion battery cells based on their cathode chemistry.

Battery type based on cathode chemistry	Chemical formula and stoichiometry	Nominal voltage [V / cell]	Operating range [V / cell]	Energy density [Wh/kg]	Life cycles [#]	Areas of application	Sources
Lithium Cobalt Oxide (LCO)	$LiCoO_2$	3.60	3.0–4.2	150–200	500–1,000	• Small appliances, such as smartphones, laptops, e-readers, tablets, etc.	(Chen et al., 2021; Liu et al., 2018; Ma et al., 2018; Satyavani et al., 2016; Wang et al., 2020; Yan et al., 2020)
Lithium Iron Phosphate (LFP)	$LiFePO_4$	3.20	2.0–3.65	90–160	2,000–7,000	• Small appliances, such as power tools, medical equipment, hobby gadgets, etc. • Battery electric vehicles (BEVs), such as Tesla Model 3, Nissan Leaf, Porche Taycan, and others	(Chen et al., 2021; Lander et al., 2021; Liu et al., 2018; Liu et al., 2011; Satyavani et al., 2016; Vonsien and Madlener, 2020)
Lithium Manganese Oxide (LMO)	Li_2MnO_3	3.70	3.0–4.2	100–150	400–750	• Small appliances, such as power tools, etc. • Medical equipment • BEVs (combined with NMC types)	(Chen et al., 2021; Kim et al., 2016; Liu et al., 2018; Satyavani et al., 2016; Thackeray, 1997; Weng et al., 2020)
Lithium Nickel Cobalt Aluminium Oxide (NCA)	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	3.70	3.0–4.2	200–260	400–1,000	• BEVs mostly produced by Telsa, such as "Model 3", or "Model X"	(Chen et al., 2021; Chen et al., 2004; Liu et al., 2018; Togasaki et al., 2020; Vonsien and Madlener, 2020; Wang et al., 2016; Xu et al., 2015)
Lithium Nickel Manganese Cobalt Oxide (NMC)	$LiNi_xMn_yCo_zO_2$ (Ni:Mn:Co = 1:1:1, 6:2:2, or 8:1:1)	3.70	3.6–4.0	160–230	2,000–3,000	• BEVs, such as "BMW i3", "Audi e-tron GE", "BYD Yuan EV535", "BAIC EU5 R550", "Chevrolet Bolt", "Hyundai Kona Electric", "Jaguar I-Pace", "Jiangling Motors JMC E200L", "NIO ES6", "Nissan Leaf S Plus", "Renault ZOE", "Roewe Ei5", "VW e-Golf", "VW ID.3" etc. • Small appliances, such as smartphones, laptops, etc. • Battery storage power stations	(Chen et al., 2021; El Mofid et al., 2014; Liu et al., 2018; Maheshwari et al., 2018; Sun et al., 2020; Vonsien and Madlener, 2020; Zheng et al., 2016)

efficiency, capacity loss, poor rate capability, and dissolution of transitional metals (Xiang et al., 2019; Zhao et al., 2021). The lithium titanate oxide (LTO) cells are currently the only widely used type of LIBs that does not have graphite as anode material but replaces it with LTO (Nitta et al., 2015). The cathode material of LTO cells varies depending on the intended use and it is typically made of LCO, LMO, NMC, or NCA (Dubarry and Devie, 2018; Stroe et al., 2018). Nemeth et al. (2020) found that LTO anodes have several major technical advantages over graphite anodes, such as excellent rate capability at the expense of a reduced energy density, significantly better longevity (number of life

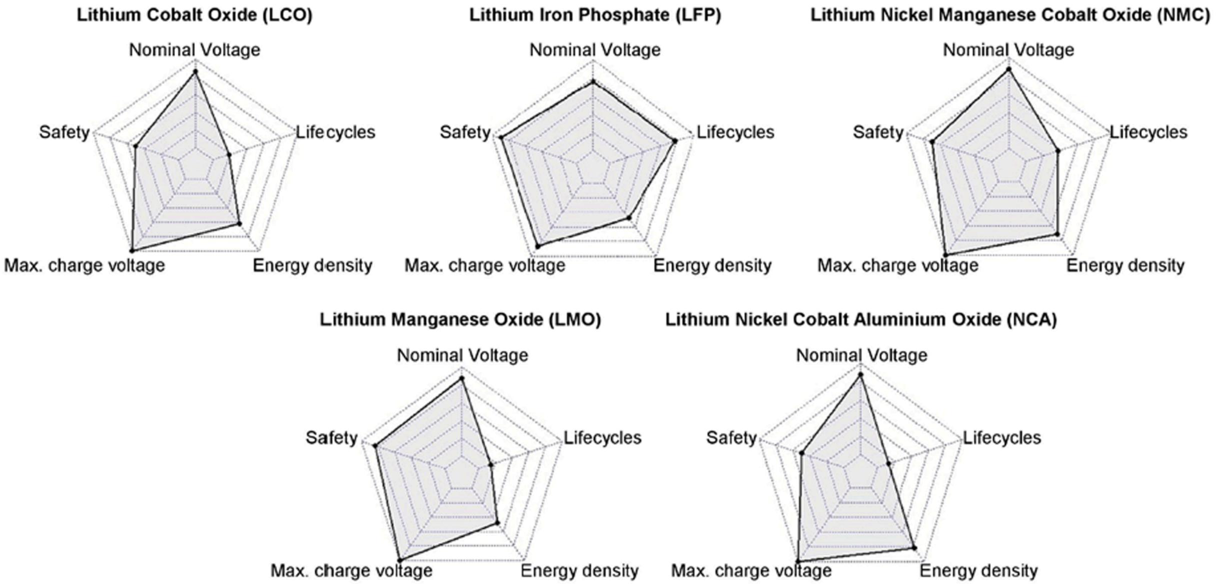

Fig. 1. Comparison of electrochemical characteristics of the most widely used lithium-ion battery types and cathode materials. Nominal voltage and maximum charge voltage are expressed on a scale from 0 to 4.2 V. The highest safety is defined by the highest unstable operation point of thermal runaways and expressed on a scale from 0 to 300° C. Energy density is the measure of how much energy can a battery type contain and it is expressed on the scale from 0 to 280 Wh/kg cells. Lifecycles approximate the expected lifespan of a LIB type and it is expressed on a scale from 0 to 4 000 full charge/discharge cycles.

cycles). However, the main obstacle to replacing graphite anodes with LTO are high production costs, which are 120–200% higher for LIBs with graphite anodes.

A general comparison of the main characteristics of the presented LIB types is shown in Fig. 1. With regard to battery safety, we have assumed that the higher the energy density of a battery type, the higher the probability of damage (e.g. caused by a thermal runaway). We additionally assume that the highest safety is defined by the highest unstable operation point of thermal runaways that can be up to ca. 300° C. An overview of the most widely used LIBs and their areas of application is provided in Table 1. In summary, NCA, MNC, and LTO batteries are mostly used by the OEMs. The innovations of cathodes of the last decades have shown that, for example, the stoichiometry of NMC has changed from 1 : 1 : 1 ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) since 2000 until 2010, to 6 : 2 : 2 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) from 2010 until today, whereby latest developments tend to a stoichiometry of 8 : 1 : 1 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) (El Mofid et al., 2014; Liu et al., 2014; Sun et al., 2020).

In addition, novel anode materials, such as graphene, or other nanocomposites, can be used to reduce heat development of LMO or LFP cathodes or to avoid ruptures of the anode caused by repeated charge and discharge cycles (Meng, 2019; Zhu et al., 2014). In summary, it must be highlighted that future LIB generations are going to have impacts on recycling processes and supply chains of the battery industry and therefore need to be considered (Doose et al., 2021). Fig. 2 shows a schematic overview of possible recycling routes for LIB recycling. The entire process chain begins with collection, which, like pre-treatment, can have a major influence on the output quality of metalurgical processes.

In addition, a battery is not only made of active materials but also requires electronic components, housing and an electrolyte, which must also be considered in recycling. For example, a dismantling analysis on two battery modules of end-of-life EVs by Arnberger (2016) shows that a module can consist on average of 66 wt% cells, 17% housing, 4% electronics, 3% cables, and 10% other components. A cell itself consists of up to 60% active material, including cathode material, anode material and the binder, and is therefore considered to be the potentially most valuable LIB component to be recycled. The weight of housing depends on whether it is made of a heavy steel alloy, aluminium alloy, or an even more lightweight multilayer composite material including plastics. The anode and cathode typically consist of thin Cu and Aluminium (Al) metal foils and can contribute up to 39% of the module weight (Arnberger, 2016).

Based on the complex composition, one can already imagine that specialized waste pre-treatment technologies (see Section 5) are needed to separate organic compounds, such as plastic housings and adhesions, from metallic fractions or alloys, which are in turn further processed using specialized metal recovery and refinery technologies (see Section 6). Prior to recycling, the EoL LIBs need to be collected and transported, at which it is very important to consider safety aspects with regard to thermal runaways, summarized in the following Section 4.

4. Safe waste collection, storage, and transport

According to the EU Battery Directive 2006/66/EC, it is mandatory to ensure a free of charge taking back of industrial and automotive batteries. In the EU, the collection of EoL LIBs from EVs are regulated by the End-of-Life Vehicle Directive 2000/53/EC (European Parliament, Council of the European Union, 2000), at which the manufacturers or OEMs must take back their own EVs including the battery. A contract with third parties (e.g. recycling companies, or car workshops), who take the recycling responsibilities, is permitted.

Safety aspects play an important role along the whole life cycle of LIBs, but particularly during the collection, storage, and dismantling of EoL LIBs. Incorrect handling or circumstances may result in leakage or outgassing of battery contents or thermal runaway where the LIB can catch fire or even explode. All of them are connected with potentially high damage to goods and a significant release of hazardous reaction products (e.g., hydrogen fluoride) and, thus, pose a threat to human

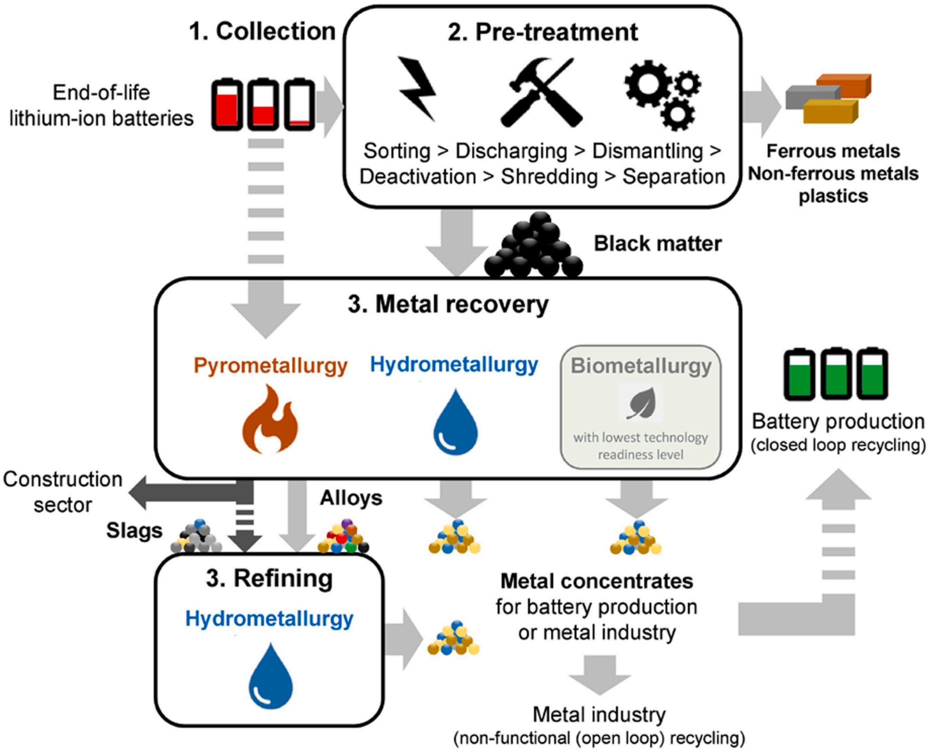

Fig. 2. Schematic overview of possible recycling routes for lithium-ion batteries. Metal recovery without pre-treatment results in non-functional (open loop) recycling (i.e. alloys not used for batteries), whereas pre-treatment followed by metallurgical processes can be applied in the sense of functional (closed loop) recycling. Biometallurgy is coloured in grey because this technology is currently not applied at industrial scale.

health and the environment. This is why safety-relevant research on LIBs was already of great interest – e.g. by Bravo Diaz et al. (2020), Chen et al. (2021), Chombo and Laoonual (2020), Golubkov et al. (2014), Nigl et al. (2020), Nigl et al. (2021), Sojka (2020), and Winslow et al. (2018).

In addition to the EU Battery Directive 2006/66/EC, the agreement concerning the International Carriage of Dangerous Goods by Road (ADR) (United Nations, 2020) regulates especially safety issues regarding transport, storage and packaging of goods at international level. LIBs need to be protected against extreme weather conditions, mechanical damage (e.g. by shock during relocation or transportation) and short circuit. Portable batteries should be packed into resistant foils or sacks and in specially marked drums. Packaging needs to be approved by the responsible authority working in line with the ADR agreement (United Nations, 2020). In Austria, for example, steel drums with inlay bag, lid and venting device are commonly used. Furthermore, cells and batteries must be secured within the outer packaging to prevent excessive movement during transport by e.g. embedding in a non-conductive and non-flammable padding material. In compliance with the ADR agreement (United Nations, 2020), portable LIBs can be collected and transported together with other non-lithium cells or batteries under certain conditions. It must be stressed that this does not apply to high-performance traction LIBs from EVs (i.e. for >500 g, >1 g Li per cell, >2 g Li per battery, >20 Wh nominal power per cell, or >100 Wh nominal power per battery), which must be collected separately from other battery types. Any containers with LIBs are to be set up inaccessible to third parties and at minimum distance from each other to comply with fire expert assessment. Such measures for the safe handling and processing of LIBs must be set not only for waste collection and storage, but also for all further waste pre-treatment and recycling processes to avoid financial risks and risks to human health (Nigl et al., 2021).

5. Pre-treatment processes and technologies

5.1. Sorting, disassembly and discharging

The variety of cell chemistries and designs leads to challenges for recycling processes. Not every cell chemistry can be recycled at any recycling route. Recycling companies are often specialised in particular battery chemistry types since mixing them has a negative influence on product quality. In the future, the planned amendment of the EU Battery Directive 2006/66/EC aims to provide in-depth information on the battery components and chemistry by the so-called “battery passport” (European Commission, 2020c) and thus should facilitate the safe handling during pre-sorting and deactivation. Common separating processes range from visual sorting followed by hand picking to magnetic separation, X-ray, electromagnetic, and UV-based sorting (Martens and Goldmann, 2016; Sziegoleit, 2013). A combination of visual and manual sorting is still the most common method across the EU. For example, ca. 50% of the portable batteries collected in Germany were sorted in this way according to Sziegoleit (2013). However, industrial batteries pose a challenge during existing (automated) processes due to their size, weight, and non-standard designs, which leaves visual and manual sorting by employees, followed by disassembly, as the most dignified options, resulting in high handling costs. This highlights the significance of labelling batteries and the need to further develop current sorting technologies towards automatic pre-sorting and material separation.

After sorting, EV battery packs must be disassembled. An advantage of dismantling LIB packs prior to recycling is the residual value of components, which are easily accessible and profitable. The disassembly of LIBs enables targeted recycling of individual components, where valuable materials, such as steel, copper, aluminum, selected plastics, and precious metals can be recovered from the housing, cable harness, cooling system, or other electronic parts. It also reduces volume flow and variety of material making recycling more efficient. A detrimental challenge of disassembly is standardization. It is closely interlinked with high time and personnel expenditure, as every EV battery must be manually disassembled by the staff with special training and tools due to the high voltage range and high energy density (Alfaro-Algaba and Ramirez, 2020; Rallo et al., 2020). Guidelines for a eco-friendly battery design would facilitate automation of dismantling processes (Harper et al., 2019). Knowledge transfer and information sharing between battery producers and recyclers is crucial and should be improved by the planned “battery passport”. The praxis is that recycling companies develop a patchwork of internal technical operating procedure comprising data bases including decision trees for LIB identification, dismantling guidelines and bill of materials (Peters et al., 2018; Saubermacher, 2020). Also, the choice of disassembly depth influences the choice of downstream recycling routes, as they either allow cells or modules as input (Gentilini et al., 2020; Schwarz and Rutrecht, 2018).

In general, disassembling should allow for discharging and diagnosing the current state-of-health (SoH) of the modules. The SoH is the very basis for decision-making if the battery qualifies for any further reuse, in the sense of repairing or refurbishing to extend the automotive LIB’s service life for so-called second life applications (Stein et al., 2020). Currently, no industrial standard to determine the SoH is available, however technical best-practice solutions do exist (Gentilini et al., 2020; Harper et al., 2019; Stein et al., 2020). There are two different ways to discharge a cell: The use of an ohmic resistor is the current state-of-the-art, especially for large ESS and EV batteries. The remaining charge in the LIBs is either dissipated as heat or optionally stored for further use in an on-site energy storage. The second method, the use of an electrically conductive liquid, is a niche application for small batteries (Arnberger, 2016; Harper et al., 2019; Rutrecht, 2015). Without thermally deactivating LIBs via pyrolysis, a low state-of-charge (SoC) is considered to be a safety advantage for subsequent waste treatment (Golubkov et al., 2015; Lee et al., 2019) and is often a prerequisite for downstream recycling processes. Exceptions are processes that apply cryotechnology at very low temperature or inert gas purging during pyrolysis (see Section 6.2).

5.2. Pyrolysis for deactivation

Currently, the LIBs are subjected to pyrolysis before mechanical treatment (Brückner et al., 2020; Vandepaer et al., 2017), which mainly aim to deactivate the cells for safety reasons. Thereby, the energy content can be reduced in a controlled manner while organic components are removed, and the content of halogenated substances is reduced by removing them via the exhaust gas stream. During pyrolysis, the active materials of the anode and cathode are detached from the copper or aluminium foil by removing the organic binder (Arnberger, 2016; Brückner et al., 2020; Zheng et al., 2018). Depending on the active material, it is advisable to discharge the cells first. The active material based on LFP-type cathode materials shows a low reaction and does not need to be discharged in advance while those based on LMO- or NMC-type cathodes are much more reactive and should be discharged before undergoing the pyrolysis process. After pyrolysis, the batteries can be stored temporarily and, as a consequence, mechanical treatment can be carried out at low risks of fire or thermal runaways (Arnberger, 2016).

The furnace is first placed under vacuum and then filled with high-purity nitrogen (Sun and Qiu, 2011; Zhang et al., 2018a). It is noted that experiments of pyrolysis at 600 °C under atmosphere did not achieve satisfactory results, as only parts of the cathode material could be detached, while the electrode was deformed, fragile and oxidised slightly at these high temperatures. This shows that pyrolysis under vacuum is necessary if the aluminium foil should be recovered in its metallic form (Sun and Qiu, 2011). According to Brückner et al. (2020), Sun and Qiu (2011) and Zhang et al. (2018c), the process takes place at about 500 °C to 600 °C. The separator melts due to the thermal exposure and a short circuit occurs, leading to further decomposition reactions and thus to a thermal runaway. The abrupt increase in the waste gas volume flow during a thermal runaway is also problematic for waste gas treatment, which is usually designed to handle constant gas flow rates. During the decomposition of plastics and partly organic solvents, fluorine-containing benzene and ester from the electrolyte are formed, which can be collected by condensation (Arnberger, 2016; Brückner et al., 2020; Zhang et al., 2018a).

Observed mass losses during pyrolytic processes can be divided into two main stages: The first mass loss, which results from the volatilisation of moisture and residual electrolyte, occurs during initial heating from 30 °C to 150 °C. The second stage is reported to take place in a temperature range of between 250 °C and 450 °C and 550 °C to 600 °C and is caused by decomposition of the organic binder (Diaz et al., 2018; Zhang et al., 2018a). Experiments show that about 20 to 24 wt% of the charged waste batteries migrate into the waste gas stream while the remaining 76 to 80 wt% can be transferred to further mechanical treatment (Arnberger, 2016). In the following comminution process, it can be seen, that pyrolysis significantly facilitates the liberation of the electrode material from the conductor foil. The pyrolysis temperature has also an impact on separation efficiency. According to the review by Zhang et al. (2018a), the optimal pyrolysis temperature for the cathode is 500 °C and for the anode 550 °C. There is a small difference in the separation efficiency of the anode, when the temperature ranges from 450 °C to 550 °C. At a pyrolysis temperature of 600 °C, the separation efficiency decreases because higher temperatures lead to aggregation, and thus, the formation of larger pyrolysis residues, which in turn hinder separation.

5.3. *Mechanical pre-treatment*

Mechanical pre-treatment of EoL LIBs is necessary prior to metallurgical processes. Its main task is to separate the valuable output fractions iron (Fe), Cu and Al alloys from the fines, called “black matter”. It mainly originates from active materials of the LIB’s anode and cathode (Windisch-Kern et al., 2021) and, therefore, contains valuable compounds, rich in Li, Co, Ni, Mn, etc. which are recovered by downstream metallurgical processes (see Section 6). It is important to note that battery packs should be either discharged or thermally deactivated prior to crushing processes or be somehow thermodynamically or chemically inhibited to avoid fire or explosion risks. State-of-the art methods for mechanical pre-treatment make use of rotary shears at low rpm using double shaft shredders, or impact crushing at high rpm using hammer mills. Depending on particle size and previously applied processing steps, shredding is combined with sieving, magnetic, and/or density separation, e.g. vibrating or drum screens, combined with float-sink separators (Velázquez-Martínez et al., 2019).

In case that no previous (thermal) deactivation of the cells is desired, crushing can be performed by shredding in inert atmosphere, cryogenic crushing, or electrohydraulic shredding. The effort required for this is reflected in higher investment and operating costs, but higher recycling efficiency is possible through pre-treatment. Once no thermal deactivation takes place, the recycling of currently low value components, such as plastics and the electrolyte, would be possible. It is not known exactly whether the reduction in processing costs by foregoing (thermal) deactivation outweighs the additional operating costs due to expensive operating equipment. Nevertheless, both methods, shredding in inert atmosphere and cryogenic crushing, are not affected by the SoC or SoH of the LIBs.

Shredding in inert atmosphere prevents the batteries from catching fire or exploding by displacing oxygen. For this, a closed chamber is filled with inert gas, such as CO_2, N_2, or Argon, before any comminution takes place. This method is applied for example at the battery recycling processes of Duesenfeld, Batrec, or Recupyl (Diekmann et al., 2017; Tedjar and Foudraz, 2008). A similar approach is used by Accurec, at which all organic volatiles, such as electrolyte and plastics, are evaporated and thus can be removed in a heatable evacuated chamber (Träger et al., 2012).

Cryogenic crushing takes advantage of low temperatures. By cooling the batteries using liquid nitrogen, dry ice (i.e., solid CO_2), or argon, battery materials become brittle and electro-chemically inactive (Grandjean et al., 2019). Next to the high safety level during this method, the battery materials become brittle and can be grinded more efficiently, as a fine powdery input can be beneficial for further metallurgical processes. The patented cryogenic cooling process of Smith and Swoffer (2014) is used as a pre-treatment step in the Toxco process, formerly known as Retriev. In this process, the batteries are cooled to between −175 °C and −195 °C with liquid nitrogen at atmospheric pressure (McLaughling and Adams, 1999). Since 2014, another patent by Retriev suggests to use a spray of water in addition to the liquid nitrogen (Smith and Swoffer, 2014).

High voltage fragmentation (HVF) is another comminution method based on shock waves that are generated by pulsed spark discharges, transferred to the material via a liquid carrier medium (usually water) to electrically disintegrate aggregates. Short, violent impacts specifically attack weak points at material boundaries of the input material. After breaking down the battery cell in its’s components (i.e. cathode, anode, electrolyte, separator, cell, and battery housing), further selective separation is possible. Based on this type of comminution, various proof of concepts has been conducted: A sequence of battery recycling steps has been developed by e.g. the Fraunhofer IWKS project group, which is seen by their inventors as an alternative method for pyro- and hydrometallurgical processes. Öhl et al. (2019) claims the process to be energy efficient and that – without the use of additional chemistry – direct reuse of recovered material for battery manufacturing is possible. However, the direct reuse of the battery active material has so far only succeeded with capacity losses and is only possible when the input consists of a single LIB type (Öhl et al., 2019). The HFV method has already been applied to LIB components at laboratory scale: the cathode is separated from the anode by a poly-ethylene foil, for which high voltage pulses were used to separate this metal-polymer-composite material (Leißner et al., 2018). With regard to costs, throughput, energy consumption, availability and scalability, the research group concluded that HFV cannot currently compete with mechanical comminution beyond laboratory scale (Leißner et al., 2018). Typical throughput is ca. 0.5 t/h (Bittner, 2018), whereas Leissner et al. (2018) stated that a machine at industrial scale would need to reach a throughput of around 1 t/h. Additionally, it is unclear to what extent, and in which material quality, the electrolyte can be recovered and reprocessed (Sun and Qiu, 2011; Tedjar and Foudraz, 2008).

6. Refining technologies for metal recovery

The previous section already discussed pre-treatment methods as a substantial part of the whole recycling process chain. Most of the state-of-the-art recycling technologies, despite Umicore’s Valéas process, use black matter resulting from the pre-treatment as a starting point for chemical processes for metal recovery. Regardless of the principle applied by the respective recycling process, pyrometallurgical, hydrometallurgical, or biometallurgical, metal recovery methods for EoL LIBs have common goals and must consider both economic and environmental aspects (Zheng et al., 2018). For EoL LIBs especially the metal compounds, which contain Li, Ni, Co, and Mn and used in the cathode materials, are currently of economic interest. In addition, the release of these alkali and transition metals during recycling can cause adverse negative impacts because of their hazard properties – especially the toxicity of dissolved metal species (Bai et al., 2020; Part et al., 2018).

Pyrometallurgical processing with subsequent separation and refining steps on hydrometallurgical basis are considered to be today’s most common recycling routes (Pinegar and Smith, 2019). Pyrometallurgical methods mostly aim for a recovery of a Ni-Co alloy, which usually can be effectively achieved. One of the main reasons for this is that in pyrometallurgy it is possible to incorporate LIB-related waste into existing pyrometallurgical processes as a secondary raw material. A problem of pyrometallurgy in general is its low selectivity, since the metals are not recovered separately but as a metal alloy that – although potentially suitable as an alloying element in non-functional (not closed loop) recycling – usually requires further hydrometallurgical processing for purification. Furthermore, most of the contained Li and Al are transferred into the slag phase during the processes, from where they are usually not recovered for economic reasons. Upstream processing in order to recover Li is being investigated but has not yet been commercially used (Sabarny et al., 2020; Vest, 2016; Windisch-Kern et al., 2021). Higher selectivity, on the other hand, can be achieved by hydrometallurgical processes which are moreover capable of recovering Li directly and generally achieve high recycling rates of more than 90%. To reach this efficiency, different chemical processes, such as leaching, precipitation, extraction and crystallization, are conventionally applied. Various combinations of these basic process steps can be found in the literature, e.g. by Hanisch et al. (2015a), He et al. (2020), and Huang et al. (2018), in order to ultimately obtain a process sequence with high selectivity and efficiency.

6.1. Hydrometallurgy

6.1.1. Basic mechanisms

In order to recover the valuable transition metals Co, Ni, and Li from black matter, hydrometallurgical processes such as leaching, extraction, crystallization and precipitation are used. In addition, the application of such processes also occurs to re-synthesize battery-grade materials in the sense of closed loop recycling. The first step of a typical hydrometallurgical treatment is leaching of the black matter, whereby the transition metal compounds are dissolved in inorganic or organic acids to prepare the subsequent separation steps. The reduction of impurities and organic residues as well as the selective dissolution of the various product metals are the main objectives of this process step. In addition to commonly used inorganic acids, such as sulfuric acid (H_2SO_4), nitric acid (HNO_3), or hydrochloric acid (HCl), the application of hydrogen peroxide (H_2O_2) as a reducing agent is also frequently used to increase the leaching efficiency. The addition of H_2O_2 shows the possibility to significantly increase the extraction of Co and Li from 40% and 75%, respectively, to 85% for each. This effect can be explained by the reduction of Co^{3+} to Co^{2+}, which is leached more easily. In addition to the differences in used solvents, parameters such as temperature, solid–liquid ratio and leaching (residence) time play a significant role. Furthermore, organic acids have also been increasingly used in the recent past (Gao et al., 2019; Golmohammadzadeh et al., 2017). Citric acid ($C_6H_8O_7$), malic acid ($C_4H_6O_5$), and aspartic acid ($C_4H_7NO_4$) therefore promise adequate results. In addition to the choice of leaching medium, the pre-treatment of the material used also shows a significant influence on this process, as for example, thermal treatment of $LiCoO_2$ at 500 °C shows significant positive effects on the dissolution process (Li et al., 2014; Li et al., 2013; Li et al., 2009b; Li et al., 2009a).

In research, kinetic data obviously also play an essential role in the efficiency and effectiveness of the overall process. A number of different studies (Gao et al., 2018; Golmohammadzadeh et al., 2018; Golmohammadzadeh et al., 2017; Meshram et al., 2015) can be found in this fundamental field, whereby the availability of results and data situation must be clearly distinguished between the application of standard anorganic acids and organic acids. For the leaching mechanism with inorganic acids, such as HCl or H_2SO_4, statements can be found that the kinetics depends mainly on the heterogeneous phase transition between solid, liquid and gas, and that the addition of reduction agents allows a significant acceleration of the process. In addition to the solid–liquid ratio, parameters such as the reaction temperature and the concentration of the leaching agent also play a major role in this context. For the description of the kinetic data from leaching processes with organic acids, the time factor in particular can be found as an additional essential input parameter. In summary, it should be mentioned that in the field of organic acids as well as bioleaching, only a very limited data basis is currently available (Gao et al., 2018; Golmohammadzadeh et al., 2018; Golmohammadzadeh et al., 2017; Meshram et al., 2015).

To meet high quality requirements, especially for the application in traction batteries, car manufacturers and their battery suppliers agree on very strict material specifications. Therefore, the recycling processes to recover the secondary materials in high quality must also be designed accordingly. The removal of contaminants from the material mixture and the reduction of impurities represent key objectives of these processes to avoid (non-functional) downcycling of the pristine materials. The most common impurities include organic components (e.g., carbonates of the electrolyte and their decomposition products), graphite, metals (e.g., Co, Al, etc.) from current collector foils, iron, fluorine compounds, and other additives from the electrolyte like Mn. Due to the disruption of the material during conditioning, high Al contents in the leaching solutions are often particularly problematic. This led to novel approaches, such as a first pre-leaching step using sodium hydroxide (NaOH) to facilitate selectively separating Al compounds (Chen et al., 2011; Dhiman and Gupta, 2019). $LiCoO_2$ is also recovered by electrochemical processes, such as the so-called Etoile Rebatt process. The active material undergoes leaching in a solution of LiOH and KOH and is deposited on a platinum electrode and re-precipitated to provide high quality raw materials for material synthesis in battery production. Mixtures of dissolved Co and Li ions can also be separated with high selectivity using bipolar membrane electrodialysis with ethylenediaminetetraacetic acid (EDTA). However, a non-negligible fraction of the added metals is also absorbed on the ion exchange membranes and thus decrease recovery efficiency (Iizuka et al., 2013; Ra and Han, 2006).

Selective precipitation is a chemical process that has been extensively studied in the field of LIB recycling and applied to the extraction of metals from complex systems. The basis for this is provided by thermodynamics, with particular attention paid to E-pH diagrams, as these indicate the stable regions of the compounds to be precipitated. Since similar elements (e.g., cobalt and nickel) also exhibit thermodynamically analogous behaviours, there often occurs an overlapping of these stability regions which leads to co-precipitation. One possible approach is to change the oxidation state of the ion to be precipitated (e.g., converting Co^{2+} to Co^{3+}) to allow selective precipitation in this smaller region. This is done by the addition of oxidizing agents such as sodium hypochlorite (NaClO). In principle, several different precipitants find their use in this field, these include sodium salts such as hydroxides, phosphates and carbonates, oxalic acid but also other compounds (Chen et al., 2015a; Chen et al., 2015b; Gerold et al., 2020; Takacova et al., 2017). However, due to the strong influences of temperature, concentration, and leaching time, no final optimized parameter combinations and corresponding results can yet be deduced from the literature. Precipitation as a recovery method is not only used alone, but often in combination with a preceding solvent extraction to remove Ni and Mn, or precipitate Ni with dimethylglyoxime. Therefore, published results must always be critically evaluated with respect to the implemented process steps, since a very complex process combination is often required to achieve sufficient precipitation qualities and efficiencies. In summary, hydrometallurgical processes strive to recover materials at a quality suitable for battery production.

6.1.2. Current state of technology

Currently, the so-called Batrec process is applied Switzerland and France, whilst hydrometallurgy is also used by the company Duesenfeld in Germany (Pistoia and Liaw, 2018). Both processes mentioned are not strictly recycling processes but combined processes that link pre-treatment and metal recovery. Batrec Industrie AG has developed a special process for recycling EoL LIBs, which is made up of a combination of mechanical and hydrometallurgical processes and is depicted in Fig. 3. This schematic process scheme shows that LIBs are fed to a crusher for breaking up and energetic deactivation, which crushes them under a CO_2 protective gas atmosphere to avoid fire and explosions. The

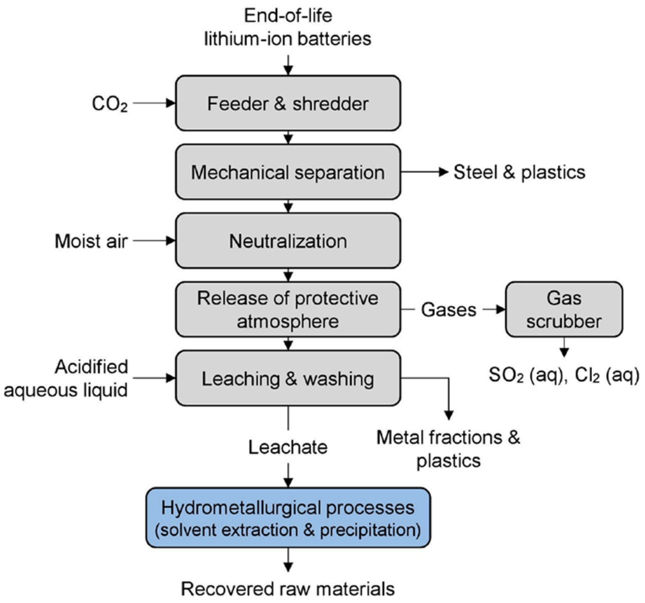

Fig. 3. The Batrec process for LIBs recycling, where mechanical treatment is combined with hydrometallurgical processes. Schematic process scheme is taken from the studies by (Conejo et al., 2015; Hanisch et al., 2015a; Meng et al., 2021).

CO_2 atmosphere serves to displace oxygen because the electrolyte would tend oxidize due to its high reactivity. This also prevents the release of highly toxic hydrogen fluorides. The CO_2 thus prevents strong exothermic reactions and is constantly refreshed during the shredding process. After shredding, the LIBs are divided into coarse and fine fractions by mechanical separation. The coarse fraction, which mainly consists of plastic and steel from housing components as well as non-ferrous metals, such as Cu or Al, is separated and made available to various recycling companies in the metal industry. The fine fraction, which contains the Co and Li of the electrodes, remains. The electrolyte is evaporated during the crushing and the resulting waste material is neutralized by adding moist air. The atmosphere is then condensed and cleaned in a gas scrubber to reduce possible pollutant emissions to a minimum. The fine fraction is leached with an acidified aqueous liquid in order to solubilize the cathode metals. Almost all the metal fractions of the neutralized waste material can be recovered using this process. A previous heat treatment such as pyrolysis to remove plastic residues can lead to a significant improvement in this process. In further steps, dissolved species are recovered from the metal based leaching liquid using a proprietary solvent extraction and precipitation process. More precise process parameters as well as a specification of the end product's quality could not be found in the literature (Conejo et al., 2015; Hanisch et al., 2015a; Meng et al., 2021; Pistoia and Liaw, 2018; Zhang et al., 2018a).

Duesenfeld GmbH combines mechanical, thermal and hydrometallurgical processes in a patented process (Hanisch et al., 2015b). The energy-efficient process claims to achieve very high material recovery rates of up to 91% related to the battery. This can be made possible by avoiding the meltdown, which is otherwise often used in battery recycling. Fig. 4 shows the patented process scheme of the Duesenfeld process that focuses on the recovery of high-quality cathode material from traction LIB modules (i.e. mainly from EV batteries). The recycling concept combines mechanical processing with a subsequent hydrometallurgical treatment of the electrode materials. At the beginning of the recycling chain, the EoL LIBs are discharged and manually dismantled into their main components. This removes the protective cover, plastics, cables, and possible other impurities. The LIBs modules are crushed in a 20 mm rotary shear crusher in a temperature range between 100 °C and 140 °C under an N_2 inert gas atmosphere. The existing solvents and the electrolyte are evaporated. The shredding process is connected to capacitors, which enable the recycling of the electrolyte and various solvents through vacuum distillation. The crushed modules are then broken down for classification in a zigzag classifier to separate Al, Fe, Cu, and plastics. Magnetic components as well as Cu and Al foils are separated by means of density and "eddy current" separation. It remains a fine-grained black matter, which implies the valuable electrode active materials and the fluorine containing conductive salt. A patented, specific pre-treatment step completely removes the fluoride before leaching, which prevents the formation of hydrofluoric acid (HF). Following the HF removal, the metals are leached and separated from the graphite. Li, Co, Ni, and Mn are separated by means of various extraction processes, cleaned and recovered in the form of salts (sulphates). These are finally fed to a calcination process, whereby a suitable precursor material for LIB production is produced (Duesenfeld GmbH 2020; Elwert et al., 2016; Lv et al., 2018; Pistoia and Liaw, 2018; Velázquez-Martínez et al., 2019).

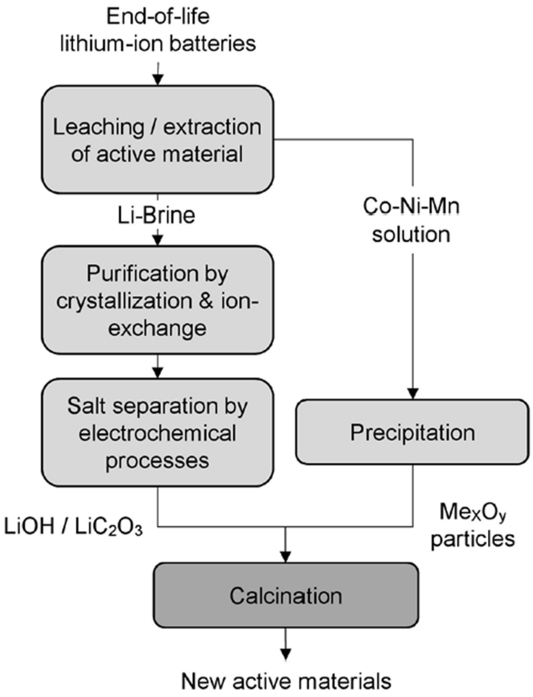

Fig. 4. The hydrometallurgical Duesenfeld process, which is preceded by mechanical preparation steps. The process scheme is taken from Elwert et al. (2016).

6.2. *Pyrometallurgy*

6.2.1. *Basic mechanisms*

Since pyrometallurgical approaches on metal extraction from different ores, minerals or secondary raw materials are widely spread and operate in large industrial scales, as for example in the iron and steel industry, there is a lot of experience in the handling of conventional pyrometallurgical processes which are partly also applicable to the field of LIB recycling. Calcination is one of these principal mechanisms, which is known from conventional pyrometallurgical operations, where it is used to pre-treat metal-containing carbonate minerals. In general, calcination is a thermal process in an oxygen-poor or even oxygen-free atmosphere that is applied to solid materials in order to remove volatile components, while the solid material undergoes phase changes or decomposition reactions (Yin and Xing, 2019). For LIB-related wastes, especially the decomposition of lithium metal oxides (e.g. $LiCoO_2$) into a metal oxide and lithium carbonate with simultaneous oxygen release is of interest (Kwon and Sohn, 2020). This, as well as the further decomposition of lithium carbonate into lithium oxide and carbon dioxide (Yin and Xing, 2019) will be discussed later in more detail. The applicability of these methods for recycling LCO type LIBs was shown, for example, by Li et al. (2016).

In contrast to calcination, roasting is a pyrometallurgical method in which the decomposition takes place in an oxygen-rich atmosphere and is often applied on sulfide minerals (Lin et al., 2018). The effects of roasting on LIB-related waste streams strongly depends on its previous treatment. If, for example, black matter with high carbon content is roasted, the carbon is likely to be completely oxidized. As mentioned, roasting originally aims for mineral treatment, and was also investigated as an alternative method for Li recovery from spodumene minerals by Medina and El-Naggar (1984) and Chen et al. (2011).

While roasting and calcination should be understood as preparatory methods, reduction processes aim for metal recovery from metal oxides, which for LIBs either origin from the cathode materials or are the result of possible oxidization reactions during pre-treatment. Carbo-thermal reduction uses carbon as a reducing agent and achieves to reduce these metal oxides to a metal alloy, while CO_x is formed (Makuza et al., 2021). In metallurgy, reduction primarily depends on the oxygen potential of the metal oxide compared to the reducing agent used. In a nutshell, this is also the reason why Ni and Co, which both have relatively low oxygen potentials, can easily be recovered by carbo-thermal reduction, whereas Li and Al with relatively high oxygen potentials are slagged. Different approaches using a combination or special designs of roasting, calcination and reduction to achieve a recovery of all valuable metals can be found in the literature but are not yet operating at industrial scale (Holzer et al., 2021; Windisch-Kern et al., 2021; Xiao et al., 2017).

6.2.2. *Current state of technology*

The so-called Umicore process is well-known and established, which includes a pyro- as well as a hydrometallurgical process step and is capable of treating not only LIBs but also Ni-based hydride batteries (Yazicioglu and Tytgat, 2011). In the Umicore process, EoL LIBs are fed together with additives (coke and slag formers) to a shaft furnace, which can be divided into three temperature zones. In the first zone, the so-called preheating zone, the electrolyte of the batteries is slowly evaporated at temperatures below 300 °C to increase the process safety and reduce the risk of explosions. The second zone, which has temperatures of up to 700 °C, utilizes the C-rich phases from the battery packs, e.g. plastics, and therefore enhances the process energy efficiency by lowering the energy requirement of the subsequent melting and reduction process. In the third zone, the smelting and reducing zone, Al and Li are oxidized and slagged, while Ni, Co, and Cu are reduced and obtained as a metal alloy which is further treated by acid leaching processes. The off-gas, leaving the furnace at a temperature below 700 °C, is first heated by a plasma torch to 1,150 °C and post combusted afterwards. During post combustion, calcium- or sodium-based additives can be injected to control halogens. Afterwards the gas is quickly cooled down to a temperature below 300 °C and for further treatment, a classical gas cleaning installation is used (Cheret and Santen, 2005). The biggest advantages of this process are that it does not require any pre-treatment and utilizes the C-rich compounds of the batteries, e.g. graphite from the anode or plastics, directly as both an energy source and a reducing agent. On the downside, the Umicore process particularly depends on the Co and Ni prices and their content in the input waste stream (Gaines, 2014). Another disadvantage is its high energy demand and the slagging of Li, which is typical for pyrometallurgical processes (Sonoc et al., 2015). Since the concentrations of Li in the slag are low and the energy demand for its recovery is high, the Li-containing slag is mostly used as an additive for construction materials (e.g. for the concrete pavement of motorways).

Analogous to the Umicore process, the Inmetco Process does also aim to recover Co and Ni, while Li and Al become slagged (Georgi-Maschler et al., 2012). The difference between the processes is that the Inmetco Process was originally designed to treat wastes from steel manufacturing and that EoL batteries are only used as a Co– and Ni-rich secondary feed. Therefore, the batteries need to be pre-treated in terms of dismantling, calcination and shredding before they are combined with the main material feed, consisting of milled stainless-steel waste. After the reduction takes place at 1,260 °C, the reduced metals are further treated in an electric arc furnace to form Fe-Co-Ni alloys while Li and Al are slagged (Pinegar and Smith, 2019).

Similarly, the Glencore (Xstrata Nickel) process also utilizes pre-treated LIBs as a secondary feed in a process which originally aims to treat Ni, Co, and Cu ores. Thus, Li, Al, and other components are again oxidized and slagged or utilized as an energy source (Georgi-Maschler et al., 2012).

The company Accurec follows the approach of a combination of mechanical, pyro- and hydrometallurgical steps. The focus is on separating components and recirculating pure fractions into existing recycling routes as early as possible (Vest, 2016). After deep discharge of the EoL LIBs, followed by dismantling, pyrolysis and mechanical treatment, the resulting fine fraction is pelletized. The pellets are used as feedstock for an electric arc furnace, if necessary, with the addition of slag formers. In addition to an alloy and slag, the Accurec process results in a Li-containing concentrate. In a downstream hydrometallurgical process, the obtained concentrate and alloy can be further processed to Li_2CO_3 and pure metal salts respectively. According to Vest, 2016, the generated slags can be used as additives in concrete materials and the construction sector (Accurec Recycling GmbH, 2018).

7. Relationships between pre-treatment and metal recovery processes

This literature reviews summarizes the complexity and relationships of process steps along the entire LIB recycling chain. After collection and transport, there are different recycling routes possible: one route aims to produce alloys, such as the Umicore process, without complex pre-treatment processes resulting in non-functional (open loop) recycling, while other routes aim for the recovery of certain metal compounds with highest possible degree of purities and thus can be used again for LIB production in the sense of functional (closed loop) recycling. Pre-treatment can include several process steps, which can be combined with each other in various ways. This has the appearance of an "over-supply" of possible pre-treatment options and a very large number of available technologies, some of which differ only slightly from each other. What all pre-treatment methods have in common is their goal, namely the recovery of ferrous and non-ferrous alloys and plastics as well as the production of black matter as a feedstock of further metallurgical processes. It is highlighted that black matter consists of graphite used for electrode materials, the Li-based metal oxide (e.g., $LiCoO_2$, $LiMn_2O_4$, etc.) or Li-Fe phosphate ($LiFePO_4$) from the cathode, and impurities that cannot be removed during separation (e.g., residuals of Al and Cu conductor foils or plastics). Since the majority of the valuable raw materials can therefore be found in the black matter, its further treatment is of great significance for the subsequent metallurgical processes. Fig. 5 summarizes schematically the interrelationships between pre-treatment and metal recovery technologies, especially possible consequences of mechanical or pyrolytic pre-treatment, at which parameters, such as temperature or atmospheric conditions, have a great impact on the quality of black matter. The resulting black matter properties are then considered in relation to the characteristics of pyro- and hydrometallurgical methods to show the influence of the black matter treatment on the efficiency and usability of the downstream metal recovery process.

In summary, pyrolysis temperature, oxidizing conditions, and the degree of impurities during pre-treatment steps have an influence on the subsequent metallurgical processes and therefore on the quality of recovered metals.

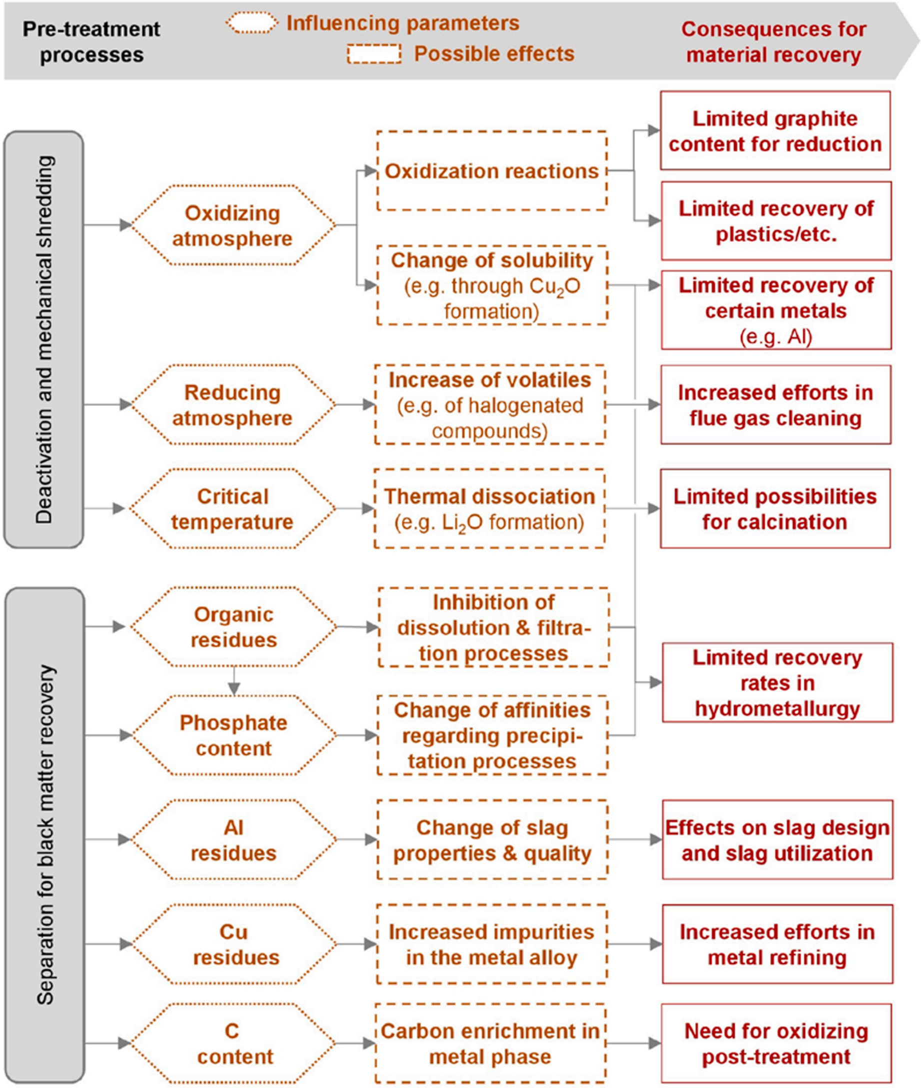

Fig. 5. Possible effects and relationships between pre-treatment and subsequent metallurgical processes during lithium-ion battery recycling.

7.1. Pyrolysis temperature

High temperatures during the thermal pre-treatment or pyrolysis for deactivation can cause significant changes in the black matter structure and chemistry, which have consequently an impact on recovery efficiency and purity of the obtained material. Pyrolysis between 500 °C and 800 °C can lead to thermal decomposition of cathode materials, at which e.g. $LiCoO_2$ can be transformed into LiO_2, CoO, or Co species (Kwon and Sohn, 2020; Zhang et al., 2018b). The consequences of thermal dissociation can be can be diverse and are particularly striking in processes which are designed to use unaltered lithium metal oxides as reagent for a certain chemical reaction. Examples for that could be sulfation roasting as investigated, for example, by Lin et al. (2020) or in other early-stage lithium recovery methods (Vest, 2016). The pyrolysis temperature can also influence later calcination processes, if C from the anode material acts as reduction agent and carbo-thermal reduction unintendedly already occurs during pre-treatment (Tang et al., 2019). According to Vieceli et al. (2021), hydrometallurgical methods could even benefit from promoted carbo-thermal reduction by exceeding a certain temperature, as they reported an enhanced leaching efficiency for incinerated EoL LIBs. In addition to pyrolysis, temperature increases can also occur during mechanical processing, although the influence can be considered minor compared to pyrolysis. However, the thermal decomposition of lithium metal oxides and the resulting formation of lithium oxide potentially poses a significant limiting factor to the effectiveness of further calcination processes (Holzer et al., 2021; Kwon and Sohn, 2020; Maroufi et al., 2020; Windisch-Kern et al., 2021).

7.2. Oxidizing conditions

It is very important to consider both temperature and oxidizing conditions during thermal or mechanical pre-treatment, as oxidation of e.g. Cu or Co can take place, resulting in a change of oxidation state as well as chemical and thermal stability (e.g., solubility or melting points, respectively) of the newly formed metal oxides. Such transformation can have a major impact on hydro- as well as pyrometallurgical processes and may cause necessity of costly post-treatment.

The precipitation of Cu by, for example, cementation with Fe is well described in the literature (Li et al., 2009a), whereby subsequent precipitation of the Fe as goethite is also necessary. This combination results in the almost complete removal of Cu and Fe with a recovery rate of 99 % from the solution, but it must be highlighted that 2–3 % of Ni, Co, and Mn are also lost by precipitation.

For pyrometallurgy, there is a need to provide an additional reducing agent in the case when there is an under-stoichiometric availability of C from the graphite anode materials. On the other hand, if C is utilized as a reducing agent or burned during pre-treatment, novel approaches to recover Li from lithiated graphite, as for example investigated by He et al. (2021), or methods to recover graphite in general as suggested by Gao et al. (2020) would not be applicable.

Furthermore, the presence of Al oxides can have impacts on the slags from pyrolysis which are further used for construction materials or must be landfilled. When Al-rich recycled or landfilled slags come into contact with water, Al hydroxides can be formed leading to chemical decomposition of construction materials or to the formation of toxic H_2 gas during landfilling. On the contrary, without oxidizing conditions during pre-treatment it is not possible to remove certain residues, such as organic compounds from the used electrolyte. In hydrometallurgy, particularly these organic residues cause problems in the individual process steps, as they inhibit the dissolution processes and slow down the filtration steps. In addition, organic compounds affect the chemical behavior of the acids used. In pyrometallurgy, this would result in increased processing costs for the exhaust gas that are rich in hydrofluoric acid or other halogenated compounds.

7.3. Residual impurities

As explained above, pre-treatment aims to separate certain material fractions of EoL LIBs in a way that each of them can be further processed or recycled efficiently. Since a complete separation cannot be reached with reasonable effort, one must consider that black matter consists not only of active materials but also of impurities such as Al or Cu from conductor foils, which may have an impact on the suitability of further processes or even the quality of the end-product and their realizable revenues.

For example, during pyrometallurgical metal recovery, residual Cu would become a component of the metal alloy, resulting in increased refining efforts if functional recycling of the metals is desired. A similar problem can be expected if a part of the black matter originates from the processing of LFP type batteries since phosphorus (P) can cause metal phosphide formation, the extent of which may not only depend on the black matter composition but also certain process conditions. On the other hand, Al that have a much greater oxygen potential is most likely slagged where it can alter the slag properties and probably call for slag design adjustments. Regarding the C content, it can be stated that, as long as it is not excessive or too low, it does not cause problems during pyrometallurgical processes and can be used as a reducing agent or as a source of energy.

Since nonmetallic components such as conductive carbon, or phosphates in the case of LFP cathode materials are usually separated or transformed by thermal or mechanical pre-treatment steps, problems or matrix effects due to high phosphate contents in hydrometallurgy can be avoided. The occurrence of matrix effects, such as kinetic inhibition of precipitation processes or the formation of complex buffer systems require a pretreatment step. The high affinity of phosphates to many metallic components of batteries or the precipitation agents are the biggest challenge here. In summary, these matrix effects, which are mostly influenced by the composition of the input materials or feedstock, should be considered during the development of novel recycling routes. This literature review shows that currently there is a lack of information about hydrometallurgical processing of cathode materials, such as LMO, LCO, and LFP. In the literature, information about the recovery of Co, Ni, Mn, and Cu can be found (e.g. Xu et al., 2008), but there are knowledge gaps about the behavior and final fate of minor components, such as P, Li, or graphite.

7.4. Future needs for research

Different process routes and recycling strategies for LIBs have been pursued by the recycling companies in Europe and worldwide. For the recycling of Ni- and Co-containing LIBs, these two valuable metals have so far been the main focus of the recycling activities in addition to the recovery of Cu. In recent years, European recycling companies have also focused on Li recovery, for which the current capacities of the recycling plants seems to have not sufficient capacities. The annual recycling capacities for LIBs in Europe are currently between approximately 54,200 and 81,500 tons per year (see Table 2). In the next 10 to 15 years, an enormous increase in EoL LIBs is forecasted and therefore it will lead to a growing demand for both larger recycling plants and optimized processes to specifically recover Li and graphite materials (Buchert and Sutter, 2020). For example, there are currently many approaches in research to advance the recovery of graphite, as it is currently listed as a CRM in the EU (European Commission, 2020b), for example by adapting thermal pre-treatment as well as hydrometallurgical processes accordingly. In this context, the ultrasonic treatment of the material is often mentioned, since an efficient separation before leaching processes is desirable. On the other hand, mechanical preparation, which certainly has its influence on subsequent battery recycling processes, is currently reaching its limits. Pyrolysis under vacuum, for the separation of highly volatile components (e.g. Li compounds, electrolyte) as well as electrohydraulic fragmentation seem to be promising possibilities to complement mechanical processing and to enable the recovery of raw materials that were previously unattainable. Especially the HVF approach seems to be promising with respect to an actual implementation of electrode material recovery and will certainly be a focus of future research projects. During current hydrometallurgical processes the active material is leached with inorganic or organic acids, whereby the graphite remains in the solid residue and is therefore currently not rated as valuable. The post-treatment to recover graphite from solid residues and slags would be very costly and technically very challenging, since this residue contains not only graphite but also other impurities such as Cu, Al, and other inorganic components of a LIB (Dutta et al., 2018; Pinna et al., 2017; Vieceli et al., 2018; Zheng et al., 2018). We therefore conclude that more research is still necessary, particularly to increase the recycling efficiency for Li- and graphite-containing materials.

8. Conclusions

The technologies used for currently available LIBs, as well as the quantity and value of the raw materials required for them, call for an efficient recycling solution capable of minimizing waste generation while producing recyclable products and thereby improving the sustainability of LIBs. However, a large number of LIB types and their constant further development pose a challenge regarding the subsequent recycling processes. Due to this rapid development, the technologies for waste pre-treatment and metallurgical post-treatment must be well coordinated in order to achieve maximum material recovery rates, particularly for the cathode materials (i.e., Co, Li, and Ni).

According to the current state-of-the-art in recycling, EoL LIBs are treated pyrometallurgically either without any waste pre-treatment or undergo a series of pre-treatment steps with the aim of recycling components of the housing or electronics and enriching the valuable materials of the cathodes in an intermediate product, which is generally known as black matter. The black matter obtained from pre-treatment is subsequently refined based either on pyro- or hydrometallurgical

Table 2
Current recycling capacity for LIBs in Europe (as of September 2021).

Country	Company	Capacity [t/a]
Belgium	Umicore	7,000
Germany	Accurec, Duesenfeld, Erlos**, Nickelhütte Aue, Promesa**, Primobius*, Redux (Saubermacher)	23,000–36,000
Finland	Akkuser Oy, uRecycle**	1,000–4,000
France	Eramet (Valdi, BASF, Suez), Euro Dieuze Industie, SNAM, TES-AMM (before Recupyl)	20,000–26,500
Switzerland	Batrec, Glencore, Kyburz**	3,200–8,000
Total		**54,200–81,500**

* expected start of operation 2021, ** no data available about plant capacity.

processes. The overall LIB recycling routes aim at separating the recyclable materials as far as possible and recovering them selectively in a high quality, so they can be used again in battery production in the sense of closed loop recycling. On the contrary to this functional recycling approach, current metallurgical processes often lead to non-functional (open loop) recycling where the product should at least be able to serve as a metal alloy that can be used in the metal industry. This literature review shows that currently there is a lack of information about hydrometallurgical processing of cathode materials, such as LMO, LCO, and LFP. Knowledge gaps about the behavior and final fate of minor components, such as P, Li, or graphite need to be closed.

Most importantly, our review highlights that the current recycling technologies or combinations of pre- and post-treatment steps need to be better coordinated with each other in order to better define first the quality of black matter from pre-treatment and then the quality of output fractions from metallurgical processes. For example, it has been shown that especially conditions during thermal pre-treatment processes, such as high temperatures or oxidizing conditions, can have a major impact on the physical–chemical properties of the black matter, of the black matter and the hydrometallugical processes required afterwards. In addition, separation and sorting before and after mechanical processing was also identified as a source of significant black matter modifications, since the presence or absence of certain components (e.g. graphite or copper residues) can also limit the quality or suitability for metal recovery processes.

Finally, it can be stated that properties resulting from the black matter history can lead to far-reaching consequences for the entire recycling chain. Currently, many different pre-treatment methods are established and produce black matter of different quality. For future recycling strategies, quality requirements of the metal recovery processes as well as the needed process flexibility regarding possible feedstock must be taken into account. In conclusion, the ambitious recycling rates of the EU for individual LIB components can only be achieved if current recycling routes are rethought and viewed holistically to better coordinate the combination of each process step. Furthermore, in the sense of eco-design and extended producer responsibility, recyclability has already to be considered during design and innovation processes to make lithium-ion batteries more sustainable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Alfaro-Algaba, M., Ramirez, F.J., 2020. Techno-economic and environmental disassembly planning of lithium-ion electric vehicle battery packs for remanufacturing. Resour. Conserv. Recycl. 154, 104461. https://doi.org/10.1016/j.resconrec.2019.104461.

Arnberger, A., 2016. Entwicklung eines ganzheitlichen Recyclingkonzeptes für Traktionsbatterien basierend auf Lithium-Ionen-Batterien. PhD Thesis. Leoben.

Baars, J., Domenech, T., Bleischwitz, R., Melin, H.E., Heidrich, O., 2021. Circular economy strategies for electric vehicle batteries reduce reliance on raw materials. Nat. Sustain. 4 (1), 71–79. https://doi.org/10.1038/s41893-020-00607-0.

Bai, Y., Muralidharan, N., Sun, Y.-K., Passerini, S., Stanley Whittingham, M., Belharouak, I., 2020. Energy and environmental aspects in recycling lithium-ion batteries: Concept of Battery Identity Global Passport. Mater. Today 41, 304–315. https://doi.org/10.1016/j.mattod.2020.09.001.

2018 Battery Recycling Datasheet. https://accurec.de/wp-content/uploads/8/04/Li-ion-RE_8.pdf.

Bharathraj, S., Adiga, S.P., Mayya, K.S., Song, T., Kim, J., Sung, Y., 2020. Degradation-guided optimization of charging protocol for cycle life enhancement of Li-ion batteries with Lithium Manganese Oxide-based cathodes. J. Power Sources 474, 228659. https://doi.org/10.1016/j.jpowsour.2020.228659.

Bittner, 2018. Neues innovatives Recyclingverfahren: Elektrohydraulische Zerkleinerung. Expertenforum - Recycling aktueller und zukünftiger Batteriespeicher, 2018, Karlsruhe.

Bravo Diaz, L., He, X., Hu, Z., Restuccia, F., Marinescu, M., Barreras, J.V., Patel, Y., Offer, G., Rein, G., 2020. Review—Meta-Review of Fire Safety of Lithium-Ion Batteries: Industry Challenges and Research Contributions. J. Electrochem. Soc. 167, 90559. https://doi.org/10.1149/1945-7111/aba8b9.

Brückner, L., Frank, J., Elwert, T., 2020. Industrial Recycling of Lithium-Ion Batteries—A Critical Review of Metallurgical Process Routes. Metals 10, 1107. https://doi.org/10.3390/met10081107.

Buchert, M., Sutter, J., 2020. Stand und Perspektiven des Recyclings von Lithium-Ionen-Batterien aus der Elektromobilität. https://www.oeko.de/fileadmin/oekodoc/Strategiepapier-Mercator-Recycling-Batterien.pdf (accessed 26 January 2021).

Castelvecchi, D., 2020. Electric Cars: The battery challenge, in: Nature, Vol 596.

Chen, C.H., Liu, J., Stoll, M.E., Henriksen, G., Vissers, D.R., Amine, K., 2004. Aluminum-doped lithium nickel cobalt oxide electrodes for high-power lithium-ion batteries. J. Power Sources 128 (2), 278–285. https://doi.org/10.1016/j.jpowsour.2003.10.009.

Chen, L., Tang, X., Zhang, Y., Li, L., Zeng, Z., Zhang, Y.i., 2011. Process for the recovery of cobalt oxalate from spent lithium-ion batteries. Hydrometallurgy 108 (1-2), 80–86. https://doi.org/10.1016/j.hydromet.2011.02.010.

Chen, X., Chen, Y., Zhou, T., Liu, D., Hu, H., Fan, S., 2015a. Hydrometallurgical recovery of metal values from sulfuric acid leaching liquor of spent lithium-ion batteries. Waste management (New York N.Y.) 38, 349–356. https://doi.org/10.1016/j.wasman.2014.12.023.

Chen, X., Xu, B., Zhou, T., Liu, D., Hu, H., Fan, S., 2015b. Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries. Sep. Purif. Technol. 144, 197–205. https://doi.org/10.1016/j.seppur.2015.02.006.

Chen, Y., Kang, Y., Zhao, Y., Wang, L., Liu, J., Li, Y., Liang, Z., He, X., Li, X., Tavajohi, N., Li, B., 2021. A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. J. Energy Chem. 59, 83–99. https://doi.org/10.1016/j.jechem.2020.10.017.

Chen, Y., Wang, G.X., Konstantinov, K., Liu, H.K., Dou, S.X., 2003. Synthesis and characterization of LiCoxMnyNi1−x−yO2 as a cathode material for secondary lithium batteries. J. Power Sources 119–121, 184–188. https://doi.org/10.1016/S0378-7753(03)00176-9.

Cheret, D., Santen, S., 2005. Battery recycling. US20050108321;EP20040076124; US20040563800P C22B7/00;C22B23/02;C22B23/06;C22B23/06.

Chombo, P.V., Laoonual, Y., 2020. A review of safety strategies of a Li-ion battery. J. Power Sources 478, 228649. https://doi.org/10.1016/j.jpowsour.2020.228649.

Conejo, A.J., Dahlquist, E., Yan, J. (Eds.), 2015. Handbook of clean energy systems: Intelligent energy systems. Wiley, Chichester, 6 bd.

Dhiman, S., Gupta, B., 2019. Partition studies on cobalt and recycling of valuable metals from waste Li-ion batteries via solvent extraction and chemical precipitation. J. Cleaner Prod. 225, 820–832. https://doi.org/10.1016/j.jclepro.2019.04.004.

Diaz, F., Wang, Y., Moorthy, T., Friedrich, B., 2018. Degradation Mechanism of Nickel-Cobalt-Aluminum (NCA) Cathode Material from Spent Lithium-Ion Batteries in Microwave-Assisted Pyrolysis. Metals 8, 565. https://doi.org/10.3390/met8080565.

Diekmann, J., Hanisch, C., Froböse, L., Schälicke, G., Loellhoeffel, T., Fölster, A.-S., Kwade, A., 2017. Ecological Recycling of Lithium-Ion Batteries from Electric Vehicles with Focus on Mechanical Processes. J. Electrochem. Soc. 164 (1), A6184–A6191. https://doi.org/10.1149/2.0271701jes.

Doose, S., Mayer, J.K., Michalowski, P., Kwade, A., 2021. Challenges in Ecofriendly Battery Recycling and Closed Material Cycles: A Perspective on Future Lithium Battery Generations. Metals 11, 291. https://doi.org/10.3390/met11020291.

Dubarry, M., Devie, A., 2018. Battery durability and reliability under electric utility grid operations: Representative usage aging and calendar aging. J. Storage Mater. 18, 185–195. https://doi.org/10.1016/j.est.2018.04.004.

Duesenfeld GmbH. Stoffliche Rückgewinnung beim Duesenfeld Recycling. https://www.duesenfeld.com/recycling.html (accessed 15 January 2020).

Dutta, D., Kumari, A., Panda, R., Jha, S., Gupta, D., Goel, S., Jha, M.K., 2018. Close loop separation process for the recovery of Co, Cu, Mn, Fe and Li from spent lithium-ion batteries. Sep. Purif. Technol. 200, 327–334. https://doi.org/10.1016/j.seppur.2018.02.022.

El Mofid, W., Ivanov, S., Konkin, A., Bund, A., 2014. A high performance layered transition metal oxide cathode material obtained by simultaneous aluminum and iron cationic substitution. J. Power Sources 268, 414–422. https://doi.org/10.1016/j.jpowsour.2014.06.048.

Elwert, T., Goldmann, D., Römer, F., Buchert, M., Merz, C., Schueler, D., Sutter, J., 2016. Current Developments and Challenges in the Recycling of Key Components of (Hybrid) Electric Vehicles. Recycling 1, 25–60. https://doi.org/10.3390/recycling1010025.

European Commission, 2019. Commission staff working document on the evaluation of the Directive 2006/66/EC on atteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC. https://ec.europa.eu/environment/pdf/waste/batteries/evaluation_report_batteries_directive.pdf.

European Commission, 2020a. A new Circular Economy Action Plan for a cleaner and more competitive Europe. https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1583933814386&uri=COM:2020:98:FIN.

European Commission, 2020b. Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0474&from=EN (accessed 10 February 2021).

European Commission, 2020c. Regulation of the European Parliament and the Council concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending regulation (EU) No2019/1020. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020PC0798.

European Parliament, 2021. New EU regulatory framework for batteries Setting sustainability requirements. Environment, Public Health and Food Safety. https://www.europarl.europa.eu/RegData/etudes/BRIE/2021/689337/EPRS_BRI(2021)689337_EN.pdf.

European Parliament, Council of the European Union, 2006. Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32006L0066.

European Parliament, Council of the European Union, 2000. Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles - Commission Statements L 269, 21/10/2000 P. 0034 - 0043. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32000L0053.

Gaines, L., 2014. The future of automotive lithium-ion battery recycling: Charting a sustainable course. Sustainable Mater.Technol. 1–2, 2–7. https://doi.org/10.1016/j.susmat.2014.10.001.

Gao, G., He, X., Lou, X., Jiao, Z., Guo, Y., Chen, S., Luo, X., Sun, S., Guan, J., Yuan, H., 2019. A Citric Acid/$Na_2S_2O_3$ System for the Efficient Leaching of Valuable Metals from Spent Lithium-Ion Batteries. JOM 71 (10), 3673–3681. https://doi.org/10.1007/s11837-019-03629-y.

Gao, W., Song, J., Cao, H., Lin, X., Zhang, X., Zheng, X., Zhang, Y., Sun, Z., 2018. Selective recovery of valuable metals from spent lithium-ion batteries – Process development and kinetics evaluation. J. Cleaner Prod. 178, 833–845. https://doi.org/10.1016/j.jclepro.2018.01.040.

Gao, Y., Wang, C., Zhang, J., Jing, Q., Ma, B., Chen, Y., Zhang, W., 2020. Graphite Recycling from the Spent Lithium-Ion Batteries by Sulfuric Acid Curing-Leaching Combined with High-Temperature Calcination. ACS Sustainable Chem. Eng. 8 (25), 9447–9455. https://doi.org/10.1021/acssuschemeng.0c02321.

Gentilini, L., Mossali, E., Angius, A., Colledani, M., 2020. A safety oriented decision support tool for the remanufacturing and recycling of post-use H&EVs Lithium-Ion batteries. Procedia CIRP 90, 73–78. https://doi.org/10.1016/j.procir.2020.01.090.

Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H., Rutz, M., 2012. Development of a recycling process for Li-ion batteries. J. Power Sources 207, 173–182. https://doi.org/10.1016/j.jpowsour.2012.01.152.

Gerold, E., Luidold, S., Antrekowitsch, H., 2020. Selective Precipitation of Metal Oxalates from Lithium Ion Battery Leach Solutions. Metals 10, 1435. https://doi.org/10.3390/met10111435.

Golmohammadzadeh, R., Faraji, F., Rashchi, F., 2018. Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review. Resour. Conserv. Recycl. 136, 418–435. https://doi.org/10.1016/j.resconrec.2018.04.024.

Golmohammadzadeh, R., Rashchi, F., Vahidi, E., 2017. Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects. Waste management (New York N.Y.) 64, 244–254. https://doi.org/10.1016/j.wasman.2017.03.037.

Golubkov, A.W., Fuchs, D., Wagner, J., Wiltsche, H., Stangl, C., Fauler, G., Voitic, G., Thaler, A., Hacker, V., 2014. Thermal-runaway experiments on consumer Li-ion batteries with metal-oxide and olivin-type cathodes. RSC Adv. 4 (7), 3633–3642. https://doi.org/10.1039/C3RA45748F.

Golubkov, A.W., Scheikl, S., Planteu, R., Voitic, G., Wiltsche, H., Stangl, C., Fauler, G., Thaler, A., Hacker, V., 2015. Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge. RSC Adv. 5 (70), 57171–57186. https://doi.org/10.1039/C5RA05897J.

Grandjean, T.R., Groenewald, J., Marco, J., 2019. The experimental evaluation of lithium ion batteries after flash cryogenic freezing. J. Storage Mater. 21, 202–215. https://doi.org/10.1016/j.est.2018.11.027.

Hanisch, C., Diekmann, J., Stieger, A., Haselrieder, W., Kwade, A., 2015a. Recycling of Lithium-Ion Batteries. In: Yan, J. (Ed.), Handbook of Clean Energy Systems. John Wiley & Sons Ltd, Chichester, UK, pp. 1–24. https://doi.org/10.1002/9781118991978.hces221.

Hanisch, C., Westphal, B., Haselrieder, W., Schoenitz, M., 2015b. Verfahren zum Behandeln gebrauchter Batterien, insbesondere wieder aufladbarer Batterien und Batterie-Verarbeitungsanlage. DE201510207843 H01M10/54;H01M6/52.

Harper, G., Sommerville, R., Kendrick, E., Driscoll, L., Slater, P., Stolkin, R., Walton, A., Christensen, P., Heidrich, O., Lambert, S., Abbott, A., Ryder, K., Gaines, L., Anderson, P., 2019. Recycling lithium-ion batteries from electric vehicles. Nature 575 (7781), 75–86. https://doi.org/10.1038/s41586-019-1682-5.

He, K., Zhang, Z.-Y., Zhang, F.-S., 2021. Synthesis of graphene and recovery of lithium from lithiated graphite of spent Li-ion battery. Waste Manage. (New York N.Y.) 124, 283–292. https://doi.org/10.1016/j.wasman.2021.01.017.

He, Y., Yuan, X., Zhang, G., Wang, H., Zhang, T., Xie, W., Li, L., 2021. A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries. Sci. Total Environ. 766, 142382. https://doi.org/10.1016/j.scitotenv.2020.142382.

Holzer, A., Windisch-Kern, S., Ponak, C., Raupenstrauch, H., 2021. A Novel Pyrometallurgical Recycling Process for Lithium-Ion Batteries and Its Application to the Recycling of LCO and LFP. Metals 11, 149. https://doi.org/10.3390/met11010149.

Huang, B., Pan, Z., Su, X., An, L., 2018. Recycling of lithium-ion batteries: Recent advances and perspectives. J. Power Sources 399, 274–286. https://doi.org/10.1016/j.jpowsour.2018.07.116.

IEA, 2021. The Role of Critical World Energy Outlook Special Report Minerals in Clean Energy Transitions: World Energy Outlook Special Report. https://iea.blob.core.windows.net/assets/24d5dfbb-a77a-4647-abcc-667867207f74/TheRoleofCriticalMineralsinCleanEnergyTransitions.pdf.

Iizuka, A., Yamashita, Y., Nagasawa, H., Yamasaki, A., Yanagisawa, Y., 2013. Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electrodialysis coupled with chelation. Sep. Purif. Technol. 113, 33–41. https://doi.org/10.1016/j.seppur.2013.04.014.

Kim, S.-J., Kim, M.-C., Kwak, D.-H., Kim, D.-M., Lee, G.-H., Choe, H.-S., Park, K.-W., 2016. Highly stable TiO2 coated Li2MnO3 cathode materials for lithium-ion batteries. J. Power Sources 304, 119–127. https://doi.org/10.1016/j.jpowsour.2015.11.020.

Kwon, O.-sung., Sohn, I., 2020. Fundamental thermokinetic study of a sustainable lithium-ion battery pyrometallurgical recycling process. Resour. Conserv. Recycl. 158, 104809. https://doi.org/10.1016/j.resconrec.2020.104809.

Lander, L., Cleaver, T., Rajaeifar, M.A., Nguyen-Tien, V., Elliott, R.J., Heidrich, O., Kendrick, E., Edge, J.S., Offer, G., 2021. Financial Viability of Electric Vehicle Lithium-Ion Battery Recycling. iScience, 102787 https://doi.org/10.1016/j.isci.2021.102787.

Lee, C., Said, A.O., Stoliarov, S.I., 2019. Impact of State of Charge and Cell Arrangement on Thermal Runaway Propagation in Lithium Ion Battery Cell Arrays. Transp. Res. Rec. 2673 (8), 408–417. https://doi.org/10.1177/0361198119845654.

Leißner, T., Hamann, D., Wuschke, L., Jäckel, H.-G., Peuker, U.A., 2018. High voltage fragmentation of composites from secondary raw materials - Potential and limitations. Waste Manage. (New York N.Y.) 74, 123–134. https://doi.org/10.1016/j.wasman.2017.12.031.

Li, J., Li, X., Hu, Q., Wang, Z., Zheng, J., Wu, L., Zhang, L., 2009a. Study of extraction and purification of Ni, Co and Mn from spent battery material. Hydrometallurgy 99 (1-2), 7–12. https://doi.org/10.1016/j.hydromet.2009.05.018.

Li, J., Wang, G., Xu, Z., 2016. Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent $LiCoO_2$/graphite lithium batteries. J. Hazard. Mater. 302, 97–104. https://doi.org/10.1016/j.jhazmat.2015.09.050.

Li, J., Zhao, R., He, X., Liu, H., 2009b. Preparation of $LiCoO_2$ cathode materials from spent lithium–ion batteries. Ionics 15 (1), 111–113. https://doi.org/10.1007/s11581-008-0238-8.

Li, L., Dunn, J.B., Zhang, X.X., Gaines, L., Chen, R.J., Wu, F., Amine, K., 2013. Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. J. Power Sources 233, 180–189. https://doi.org/10.1016/j.jpowsour.2012.12.089.

Li, L., Zhai, L., Zhang, X., Lu, J., Chen, R., Wu, F., Amine, K., 2014. Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. J. Power Sources 262, 380–385. https://doi.org/10.1016/j.jpowsour.2014.04.013.

Li, Y.-C., Xiang, W., Wu, Z.-G., Xu, C.-L., Xu, Y.-D., Xiao, Y., Yang, Z.-G., Wu, C.-J., Lv, G.-P., Guo, X.-D., 2018. Construction of homogeneously Al3+ doped Ni rich Ni-Co-Mn cathode with high stable cycling performance and storage stability via scalable continuous precipitation. Electrochim. Acta 291, 84–94. https://doi.org/10.1016/j.electacta.2018.08.124.

Lin, J., Li, L., Fan, E., Liu, C., Zhang, X., Cao, H., Sun, Z., Chen, R., 2020. Conversion Mechanisms of Selective Extraction of Lithium from Spent Lithium-Ion Batteries by Sulfation Roasting. ACS Appl. Mater. Interfaces 12 (16), 18482–18489. https://doi.org/10.1021/acsami.0c00420.

Lin, J., Liu, C., Cao, H., Li, L., Chen, R., Sun, Z., 2018. Recovery of Spent Lithium Ion Batteries Based on High Temperature Chemical Conversion. Prog. Chem. 30 (9), 1445–1454. https://doi.org/10.7536/PC180424.

Liu, W.L., Tu, J.P., Qiao, Y.Q., Zhou, J.P., Shi, S.J., Wang, X.L., Gu, C.D., 2011. Optimized performances of core–shell structured LiFePO4/C nanocomposite. Journal of Power Sources. https://doi.org/10.1016/j.jpowsour.2011.05.046.

Liu, S., Xiong, L., He, C., 2014. Long cycle life lithium ion battery with lithium nickel cobalt manganese oxide (NCM) cathode. Journal of Power Sources 261, 285–291. https://doi.org/10.1016/j.jpowsour.2014.03.083.

Liu, C., Lin, J., Cao, H., Zhang, Y., Sun, Z., 2019. Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review. J. Cleaner Prod. 228, 801–813. https://doi.org/10.1016/j.jclepro.2019.04.304.

Liu, K., Liu, Y., Lin, D., Pei, A., Cui, Y., 2018. Materials for lithium-ion battery safety. Sci. Adv. 4, eaas9820. https://doi.org/10.1126/sciadv.aas9820.

Lv, W., Wang, Z., Cao, H., Sun, Y., Zhang, Y., Sun, Z., 2018. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. ACS Sustainable Chem. Eng. 6 (2), 1504–1521. https://doi.org/10.1021/acssuschemeng.7b03811.

Ma, J., Chen, B., Wang, L., Cui, G., 2018. Progress and prospect on failure mechanisms of solid-state lithium batteries. J. Power Sources 392, 94–115. https://doi.org/10.1016/j.jpowsour.2018.04.055.

Maheshwari, A., Heck, M., Santarelli, M., 2018. Cycle aging studies of lithium nickel manganese cobalt oxide-based batteries using electrochemical impedance spectroscopy. Electrochim. Acta 273, 335–348. https://doi.org/10.1016/j.electacta.2018.04.045.

Makuza, B., Tian, Q., Guo, X., Chattopadhyay, K., Yu, D., 2021. Pyrometallurgical options for recycling spent lithium-ion batteries: A comprehensive review. J. Power Sources 491, 229622. https://doi.org/10.1016/j.jpowsour.2021.229622.

Maroufi, S., Assefi, M., Khayyam Nekouei, R., Sahajwalla, V., 2020. Recovery of lithium and cobalt from waste lithium-ion batteries through a selective isolation-suspension approach. Sustainable Mater.Technol. 23, e00139. https://doi.org/10.1016/j.susmat.2019.e00139.

Martens, H., Goldmann, D., 2016. Recyclingtechnik. Springer Fachmedien Wiesbaden, Wiesbaden, p. 569 pp..

McLaughling, W., Adams, T., 1999. Li reclamation process.

Medina, L.F., El-Naggar, M.M.A.A., 1984. An alternative method for the recovery of lithium from spodumene. MTB 15, 725–726. https://doi.org/10.1007/BF02657295.

Meng, F., McNeice, J., Zadeh, S.S., Ghahreman, A., 2021. Review of Lithium Production and Recovery from Minerals, Brines, and Lithium-Ion Batteries. Miner. Process. Extr. Metall. Rev. 42 (2), 123–141. https://doi.org/10.1080/08827508.2019.1668387.

Meng, X., 2019. Recent Progress of Graphene as Cathode materials in Lithium Ion Batteries. IOP Conf. Ser.: Earth Environ. Sci. 300 (4), 042039. https://doi.org/10.1088/1755-1315/300/4/042039.

Meshram, P., Pandey, B.D., Mankhand, T.R., 2015. Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching. Chem. Eng. J. 281, 418–427. https://doi.org/10.1016/j.cej.2015.06.071.

Mossali, E., Picone, N., Gentilini, L., Rodrìguez, O., Pérez, J.M., Colledani, M., 2020. Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments. J. Environ. Manage. 264, 110500. https://doi.org/10.1016/j.jenvman.2020.110500.

Nemeth, T., Schröer, P., Kuipers, M., Sauer, D.U., 2020. Lithium titanate oxide battery cells for high-power automotive applications – Electro-thermal properties, aging behavior and cost considerations. J. Storage Mater. 31, 101656. https://doi.org/10.1016/j.est.2020.101656.

Nigl, T., Baldauf, M., Hohenberger, M., Pomberger, R., 2021. Lithium-Ion Batteries as Ignition Sources in Waste Treatment Processes—A Semi-Quantitative Risk Analysis and Assessment of Battery-Caused Waste Fires. Processes 9, 49. https://doi.org/10.3390/pr9010049.

Nigl, T., Schwarz, T.E., Walch, C., Baldauf, M., Rutrecht, B., Pomberger, R., 2020. Characterisation and material flow analysis of end-of-life portable batteries and lithium-based batteries in different waste streams in Austria. Waste Manage. Res.: The J. Int. Solid Wastes Public Cleansing Association, ISWA 38 (6), 649–659. https://doi.org/10.1177/0734242X20914717.

Nitta, N., Wu, F., Lee, J.T., Yushin, G., 2015. Li-ion battery materials: present and future. Materials Today 18, 252–264. https://doi.org/10.1016/j.mattod.2014.10.040.

Öhl, J., Horn, D., Zimmermann, J., Stauber, R., Gutfleisch, O., 2019. Efficient Process for Li-Ion Battery Recycling via Electrohydraulic Fragmentation. MSF 959, 74–78. https://doi.org/10.4028/www.scientific.net/MSF.959.74.

Part, F., Berge, N., Baran, P., Stringfellow, A., Sun, W., Bartelt-Hunt, S., Mitrano, D., Li, L., Hennebert, P., Quicker, P., Bolyard, S.C., Huber-Humer, M., 2018. A review of the fate of engineered nanomaterials in municipal solid waste streams. Waste Manage. (New York N.Y.) 75, 427–449. https://doi.org/10.1016/j.wasman.2018.02.012.

Peters, J.F., Baumann, M., Weil, M., 2018. Recycling aktueller und zukünftiger Batteriespeicher: Technische, ökonomische und ökologische Implikationen : Ergebnisse des Expertenforums am 6. In: Juni 2018 in Karlsruhe: Ergebnisse des Expertenforums am 6. Juni 2018 in Karlsruhe, p. pp.. https://doi.org/10.5445/IR/1000085778.

Pinegar, H., Smith, Y.R., 2019. Recycling of End-of-Life Lithium Ion Batteries, Part I: Commercial Processes. J. Sustain. Metall. 5 (3), 402–416. https://doi.org/10.1007/s40831-019-00235-9.

Pinna, E.G., Ruiz, M.C., Ojeda, M.W., Rodriguez, M.H., 2017. Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors. Hydrometallurgy 167, 66–71. https://doi.org/10.1016/j.hydromet.2016.10.024.

Pistoia, G., Liaw, B., 2018. Behaviour of Lithium-Ion Batteries in Electric Vehicles. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-319-69950-9.

Qiao, H., Wei, Q., 2012. In: Functional Nanofibers and their Applications. Elsevier, pp. 197–208. https://doi.org/10.1533/9780857095640.2.197.

Ra, D.-il., Han, K.-S., 2006. Used lithium ion rechargeable battery recycling using Etoile-Rebatt technology. J. Power Sources 163 (1), 284–288. https://doi.org/10.1016/j.jpowsour.2006.05.040.

Rallo, H., Benveniste, G., Gestoso, I., Amante, B., 2020. Economic analysis of the disassembling activities to the reuse of electric vehicles Li-ion batteries. Resour. Conserv. Recycl. 159, 104785. https://doi.org/10.1016/j.resconrec.2020.104785.

Rutrecht, B., 2015. Entladen von Lithium Ionen Batterien in flüssigen Medien. Bachelorarbeit, Leoben.

Sabarny, P., Peters, L., Sommerfeld, M., Stallmeister, C., Schier, C., Friedrich, B., 2020. Early-Stage Lithium Recovery (ESLR) for Enhancing Efficiency in Battery Recycling. DOI: 10.13140/RG.2.2.24566.55364.

Satyavani, T.V.S.L., Srinivas Kumar, A., Subba Rao, P.S.V., 2016. Methods of synthesis and performance improvement of lithium iron phosphate for high rate Li-ion batteries: A review. Eng. Sci. Technol., Int. J. 19 (1), 178–188. https://doi.org/10.1016/j.jestch.2015.06.002.

Saubermacher, 2020. Battothek. Denovo, Feldkirchen bei Graz, Feldkirchen bei Graz.

Schwarz, T., Rutrecht, B., 2018. Forecasting Real Disassembly Time of Industrial Batteries based on Virtual MTM-UAS Data. In: CIRP The International Academy for Production Engineering. The 25th CIRP Conference on Life Cycle Engineering in Copenhagen, 30 April 2018, Kopenhagen, Dänemark.

Smith, Swoffer, S., 2014. Reclaiming serviceable parts of waste accumulators.

Sojka, R., 2020. Safe Treatment of Lithium-based Batteries through Thermal Conditioning. In: Thomé-Kozmiensky, E., Holm, O., Friedrich, B., Goldmann, D. (Eds.), Recycling und Rohstoffe, vol. 13. Thomé-Kozmiensky Verlag GmbH, Neuruppin, pp. 506–523.

Sonoc, A., Jeswiet, J., Soo, V.K., 2015. Opportunities to Improve Recycling of Automotive Lithium Ion Batteries. Procedia CIRP 29, 752–757. https://doi.org/10.1016/j.procir.2015.02.039.

Stein, V., Arnberger, A., Nickl, A., Ungerböck, R., Werinos, M., 2020. Batterien aus der E-Mobilität in Second Life Anwendungen, in: Roland Pomberger (Ed.), Konferenzband zur 15. Recy & DepoTech Konferenz: 18.-20. November 2020. Eigenverlag, Leoben.

Stroe, A.-I., Knap, V., Stroe, D.-I., 2018. Comparison of lithium-ion battery performance at beginning-of-life and end-of-life. Microelectron. Reliab. 88–90, 1251–1255. https://doi.org/10.1016/j.microrel.2018.07.077.

Sun, L., Qiu, K., 2011. Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries. J. Hazard. Mater. 194, 378–384. https://doi.org/10.1016/j.jhazmat.2011.07.114.

Sun, X., Luo, X., Zhang, Z., Meng, F., Yang, J., 2020. Life cycle assessment of lithium nickel cobalt manganese oxide (NCM) batteries for electric passenger vehicles. J. Cleaner Prod. 273, 123006. https://doi.org/10.1016/j.jclepro.2020.123006.

Sziegoleit, H., 2013. Sortierung von Gerätebatterien. In: Thomé-Kozmiensky, K.J., Goldmann, D. (Eds.), Recycling und Rohstoffe. TK-Verl, Neuruppin, pp. 495–504.

Takacova, Z., Dzuro, V., Halvik, T., 2017. Cobalt Precipitation from Leachate Originated from Leaching of Spent Li-ion Batteries Acitve Mass: Characterization of Inputs. Inetrmediates and Outputs, in: World of Metallurgy - Erzmetall 70, 336–343.

Tang, Y., Xie, H., Zhang, B., Chen, X., Zhao, Z., Qu, J., Xing, P., Yin, H., 2019. Recovery and regeneration of $LiCoO_2$-based spent lithium-ion batteries by a carbothermic reduction vacuum pyrolysis approach: Controlling the recovery of CoO or Co. Waste management (New York N.Y.) 97, 140–148. https://doi.org/10.1016/j.wasman.2019.08.004.

Tedjar, F., Foudraz, J.-C., 2008. Method for the recycling of mixed batteries and cells compromising lilthium-based anodes.

Thackeray, M.M., 1997. Manganese oxides for lithium batteries. Prog. Solid State Chem. 25 (1-2), 1–71. https://doi.org/10.1016/S0079-6786(97)81003-5.

Togasaki, N., Yokoshima, T., Oguma, Y., Osaka, T., 2020. Prediction of overcharge-induced serious capacity fading in nickel cobalt aluminum oxide lithium-ion batteries using electrochemical impedance spectroscopy. J. Power Sources 461, 228168. https://doi.org/10.1016/j.jpowsour.2020.228168.

Träger, T., Friedrich, B., Weyhe, R., 2012. Recyclingtechnologien am Beispiel Batterien, in: Conference Proceeding of the 25. Aachener Kolloquium Abfallwirtschaft, 38th ed.

United Nations, 2020. ADR, applicable as from 1 January 2021: Agreement Concerning the International Carriage of Dangerous Goods by Road. United Nations, New York, 2 volumes.

Vandepaer, L., Cloutier, J., Amor, B., 2017. Environmental impacts of Lithium Metal Polymer and Lithium-ion stationary batteries. Renew. Sustain. Energy Rev. 78, 46–60. https://doi.org/10.1016/j.rser.2017.04.057.

Velázquez-Martínez, Valio, Santasalo-Aarnio, Reuter, Serna-Guerrero, 2019. A Critical Review of Lithium-Ion Battery Recycling Processes from a Circular Economy Perspective. Batteries 5, 68. https://doi.org/10.3390/batteries5040068.

Vest, M., 2016. Weiterentwicklung des pyrometallurgischen IME Recyclingverfahrens für Li-Ionen Batterien von Elektrofahrzeugen. Dissertation.

Vieceli, N., Casasola, R., Lombardo, G., Ebin, B., Petranikova, M., 2021. Hydrometallurgical recycling of EV lithium-ion batteries: Effects of incineration on the leaching efficiency of metals using sulfuric acid. Waste Manage. (New York N.Y.) 125, 192–203. https://doi.org/10.1016/j.wasman.2021.02.039.

Vieceli, N., Nogueira, C.A., Guimarães, C., Pereira, M.F.C., Durão, F.O., Margarido, F., 2018. Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite. Waste Manage. (New York N.Y.) 71, 350–361. https://doi.org/10.1016/j.wasman.2017.09.032.

Vonsien, S., Madlener, R., 2020. Li-ion battery storage in private households with PV systems: Analyzing the economic impacts of battery aging and pooling. J. Storage Mater. 29, 101407. https://doi.org/10.1016/j.est.2020.101407.

Wang, J., Yao, S., Yu, Y., Fu, T., Zhang, P., Zhao, J., 2016. Improving the stability properties of 5 V lithium nickel manganese oxide spinel by surface coating with cobalt aluminum oxides for lithium ion batteries. Electrochim. Acta 208, 310–317. https://doi.org/10.1016/j.electacta.2016.05.021.

Wang, K., Wan, J., Xiang, Y., Zhu, J., Leng, Q., Wang, M., Xu, L., Yang, Y., 2020. Recent advances and historical developments of high voltage lithium cobalt oxide materials for rechargeable Li-ion batteries. J. Power Sources 460, 228062. https://doi.org/10.1016/j.jpowsour.2020.228062.

Wang, Z., Liu, E., He, C., Shi, C., Li, J., Zhao, N., 2013. Effect of amorphous FePO4 coating on structure and electrochemical performance of Li1.2Ni0.13Co0.13Mn0.54O2 as cathode material for Li-ion batteries. J. Power Sources 236, 25–32. https://doi.org/10.1016/j.jpowsour.2013.02.022.

Warner, J., 2014. Lithium-Ion Battery Packs for EVs, in. Lithium-Ion Batteries. Elsevier, pp. 127–150.

Weng, D., Duan, H., Hou, Y., Huo, J., Chen, L., Zhang, F., Wang, J., 2020. Introduction of manganese based lithium-ion Sieve-A review. Prog. Nat. Sci.: Mater. Int. 30 (2), 139–152. https://doi.org/10.1016/j.pnsc.2020.01.017.

Windisch-Kern, S., Holzer, A., Ponak, C., Raupenstrauch, H., 2021. Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept. Processes 9, 84. https://doi.org/10.3390/pr9010084.

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. Resour. Conserv. Recycl. 129, 263–277. https://doi.org/10.1016/j.resconrec.2017.11.001.

Xiang, W., Zhu, C.-Q., Zhang, J., Shi, H., Liang, Y.-T., Yu, M.-H., Zhu, X.-M., He, F.-R., Lv, G.-P., Guo, X.-D., 2019. Synergistic coupling effect of sodium and fluorine co-substitution on enhancing rate capability and cycling performance of Ni-rich cathode for lithium ion battery. J. Alloy. Compd. 786, 56–64. https://doi.org/10.1016/j.jallcom.2019.01.264.

Xiao, J., Li, J., Xu, Z., 2017. Novel Approach for in Situ Recovery of Lithium Carbonate from Spent Lithium Ion Batteries Using Vacuum Metallurgy. Environ. Sci. Technol. 51 (20), 11960–11966. https://doi.org/10.1021/acs.est.7b02561.

Xu, J., Thomas, H.R., Francis, R.W., Lum, K.R., Wang, J., Liang, B., 2008. A review of processes and technologies for the recycling of lithium-ion secondary batteries. J. Power Sources 177 (2), 512–527. https://doi.org/10.1016/j.jpowsour.2007.11.074.

Xu, Y., Li, X., Wang, Z., Guo, H., Huang, B., 2015. Structure and electrochemical performance of TiO2-coated LiNi0.80Co0.15Al0.05O2 cathode material. Mater. Lett. 143, 151–154. https://doi.org/10.1016/j.matlet.2014.12.093.

Yan, S., Xue, Y., Shao, G., Liu, Z., 2020. Activity-structure relationship of electrocatalysts derived from lithium cobalt oxides for metal-air batteries. J. Power Sources 478, 228773. https://doi.org/10.1016/j.jpowsour.2020.228773.

Yazicioglu, B., Tytgat, J., 2011. Life Cycle Assessments involving Umicore's Battery Recycling process. Umicore. DG Environment -Stakeholder Meeting 18. July 2011.

Yin, H., Xing, P., 2019. Pyrometallurgical Routes for the Recycling of Spent Lithium-Ion Batteries. In: An, L. (Ed.), Recycling of Spent Lithium-Ion Batteries, vol. 4. Springer International Publishing, Cham, pp. 57–83. https://doi.org/10.1007/978-3-030-31834-5_3.

Yun, L., Linh, D., Shui, L., Peng, X., Garg, A., LE, M.L.P., Asghari, S., Sandoval, J., 2018. Metallurgical and mechanical methods for recycling of lithium-ion battery pack for electric vehicles. Resour. Conserv. Recycl. 136, 198–208. https://doi.org/10.1016/j.resconrec.2018.04.025.

Zhang, G., He, Y., Feng, Y., Wang, H., Zhang, T., Xie, W., Zhu, X., 2018a. Enhancement in liberation of electrode materials derived from spent lithium-ion battery by pyrolysis. J. Cleaner Prod. 199, 62–68. https://doi.org/10.1016/j.jclepro.2018.07.143.

Zhang, G., He, Y., Feng, Y., Wang, H., Zhu, X., 2018b. Pyrolysis-Ultrasonic-Assisted Flotation Technology for Recovering Graphite and $LiCoO_2$ from Spent Lithium-Ion Batteries. ACS Sustainable Chem. Eng. 6 (8), 10896–10904. https://doi.org/10.1021/acssuschemeng.8b02186.

Zhang, X., Li, L., Fan, E., Xue, Q., Bian, Y., Wu, F., Chen, R., 2018c. Toward sustainable and systematic recycling of spent rechargeable batteries. Chem. Soc. Rev. 47 (19), 7239–7302. https://doi.org/10.1039/C8CS00297E.

Zhao, S., Guo, Z., Yan, K., Wan, S., He, F., Sun, B., Wang, G., 2021. Towards high-energy-density lithium-ion batteries: Strategies for developing high-capacity lithium-rich cathode materials. Energy Storage Mater. 34, 716–734. https://doi.org/10.1016/j.ensm.2020.11.008.

Zheng, X., Li, X., Wang, Z., Guo, H., Huang, Z., Yan, G., Wang, D., 2016. Investigation and improvement on the electrochemical performance and storage characteristics of LiNiO2-based materials for lithium ion battery. Electrochim. Acta 191, 832–840. https://doi.org/10.1016/j.electacta.2016.01.142.

Zheng, X., Zhu, Z., Lin, X., Zhang, Y., He, Y., Cao, H., Sun, Z., 2018. A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. Engineering 4 (3), 361–370. https://doi.org/10.1016/j.eng.2018.05.018.

Zhu, J., Duan, R., Zhang, S., Jiang, N., Zhang, Y., Zhu, J., 2014. The application of graphene in lithium ion battery electrode materials. SpringerPlus 3, 585. https://doi.org/10.1186/2193-1801-3-585.

Glossary

ADR: Agreement concerning the International Carriage of Dangerous Goods by Road
Al: Aluminium
BEV: battery electric vehicle
BMS: battery management system
C: Carbon
Co: Cobalt
Cu: Copper
CRMs: critical raw materials
EDTA: ethylenediaminetetraacetic acid
EEE: electrical, electronic and electromechanical equipment
ESS: energy storage systems
EoL: End-of-Life
EU: European Union
EVs: electric vehicles
HVF: High Voltage Fragmentation
Li: Lithium
LCO: lithium cobalt oxide
LFP: lithium iron phosphate oxide
LIBs: lithium-ion batteries
LMO: lithium-manganese oxide
LTO: lithium-titanate oxide
Mn: Manganese
NCA: lithium nickel cobalt aluminium oxide
Ni: Nickel
NMC: lithium nickel manganese cobalt oxide
OEMs: original equipment manufacturer
P: Phosphorous
SoC: State of Charge
SoH: State of Health
UPS: uninterruptible power supply
WEEE: waste electrical and electronic equipment

3.3 Evaluation of the Suitability of the InduRed Process for LIB Recycling

The previous chapter showed that especially thermal processes during the treatment and separation of waste batteries could trigger chemical reactions. These changes can have far-reaching consequences and negatively influence the efficiency or even the suitability of downstream processes. The efficiency, one significant aspect of which with certainty are recovery rates for cathodic metals, is in the focus of this part of the thesis.

The investigation of potentially achievable recovery rates when feeding LIB related input materials into the InduRed reactor is possibly the most crucial part of examining its basic applicability for this task. The so-called InduMelt plant, a laboratory version of the InduRed concept that is operated in batch mode, was used to investigate said recovery rates. The results are presented within the scope of two papers. The first paper with the title “Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept” [60] generally investigates if the InduRed concept could improve the situation around Li slagging during pyrometallurgical treatment. In the second paper, “Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials ($LiNi_xMn_yCo_zO_2$) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor“ [61], moreover a possibility for an evaluation of the gas phase was implemented in the reactor concept. It was possible to investigate the transfer coefficients for Li, Ni, Co, and Mn into the obtained product phases. With this information, it is finally possible to compare the InduRed concept with conventional LIB recycling processes. Following these two publications, the results of all sub-areas of the research project are summarized before a holistic discussion and interpretation are carried out.

3.3.1 Publication 4

Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept

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Article

Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept

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Abstract: The complexity of the waste stream of spent lithium-ion batteries poses numerous challenges on the recycling industry. Pyrometallurgical recycling processes have a lot of benefits but are not able to recover lithium from the black matter since lithium is slagged due to its high oxygen affinity. The presented InduRed reactor concept might be a promising novel approach, since it does not have this disadvantage and is very flexible concerning the chemical composition of the input material. To prove its basic suitability for black matter processing, heating microscope experiments, thermogravimetric analysis and differential scanning calorimetry have been conducted to characterize the behavior of nickel rich cathode materials ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) as well as black matter from a pretreatment process under reducing conditions. Another experimental series in a lab scale InduRed reactor was further used to investigate achievable transfer coefficients for the metals of interest. The promising results show technically feasible reaction temperatures of 800 °C to 1000 °C and high recovery potentials for nickel, cobalt and manganese. Furthermore, the slagging of lithium was largely prevented and a lithium removal rate of up to 90% of its initial mass was achieved.

Keywords: lithium-ion-batteries; pyrometallurgical recycling; carbothermal reduction

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1. Introduction

Since 1979, when Goodenough et al. finally tested $LiCoO_2$ (short: LCO) as a cathode material, the development and commercialization of electrochemical energy storage based on the lithium-ion technology has been steadily pushed forward [1,2]. Lithium-ion-batteries (LIBs) basically consist of the same components such as anode, cathode, separator or electrolyte as can be found in other battery technologies. This basic principle has not changed since 1979 and therefore also applies to modern LIBs. However, the initially used LCO cathode material is now just one option on a long list of alternatives like NCA ($LiNi_xCo_yAl_zO_2$), NMC ($LiNi_xMn_yCo_zO_2$) or LFP ($LiFePO_4$) materials [3]. The variety of cathode materials is not only based on the fields of possible applications that reach from mobile electronics to e-mobility or stationary storages and their respective demand for performance (energy and power density) or safety aspects, but also on factors like raw material prices, supply risks or social and ecological sustainability. Concerning the development of the LIB market numerous publications can be found. Especially the electric automotive sector will benefit from decreasing costs made possible by mass production and optimized cell chemistry. Berckmans et al. [4] states that by 2030, the cut of fully electric or hybrid vehicles will rise to 25% of the total vehicles sold. In view of the high amount of valuable metals that are contained in LIBs, especially in their cathode materials, and the predicted market demand [5], an efficient recycling process in order to recover the mentioned valuable metals is absolutely necessary.

In general, the recycling of LIBs can be divided into three processing steps, namely pretreatment, metal extraction and metal refining. The recycling chain of LIBs usually starts with pre-treatment processing which aims to separate battery components like the battery management system or the housing and the corresponding materials such as plastics or iron from the active materials of the battery electrodes. For pre-treatment, various processes can be found which differ more or less from each other. Basically, steps during pre-treatment are sorting, dismantling deactivation and mechanical processing and separating. Said active materials–after pre-treatment they are also known as black matter–mainly consist of lithium metal oxides or lithium iron phosphate, carbon and residues from the electrode conductor foils. Umicore's Valéas process, for example, is an exception since it does not need a usual pre-treatment but uses the batteries directly in their pyrometallurgical process. [2,6–12].

While the obtained metal and plastic scrap can be recycled directly, the produced black matter that contains the valuable metals needs to be further treated in a metal extraction step to recover Li, Ni, Co and Mn, at best in a quality that is suitable for closed loop recycling. Therefore, pyro-, bio- and hydrometallurgical methods can be used. Biometallurgical processes like bioleaching are considered as environmentally friendly and low cost alternatives to conventional hydrometallurgy, capable of reaching recovery rates of more than 98% for Ni and Co and more than 80% for Li but suffering from low kinetics and resulting poor throughput rates [13–19].

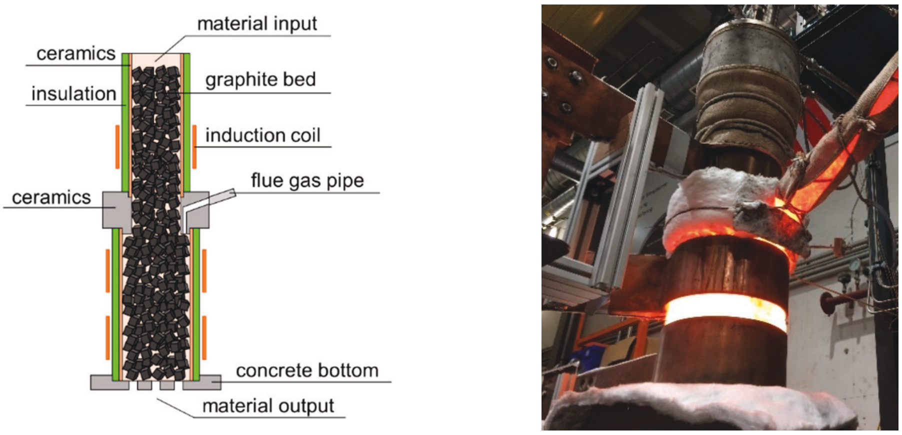
Typical hydrometallurgical procedures, used to recover metals from black matter, are leaching, solvent extraction, chemical precipitation or electrochemical deposition, with which a high selectivity and therefore product purity can be achieved [20]. The possible recovery rates for Ni, Mn, Co and Li, as for example reported by He et al. [21], can be close to or even higher than 99%. The obtained salts or concentrates can usually be directly used for the production of new cathode materials as it is the case for the Duesenfeld process described by Elwert and Frank [22]. An indication of the importance of hydrometallurgical recycling of spent LIBs is, among other things, the high intensity of research activities in this field. According to Huang et al. [23], more than half of the recycling processes that are currently under investigation are related to hydrometallurgical processing.

Pyrometallurgical approaches use high temperatures, usually above 1400 °C, and reducing conditions to recover valuable metals as a metal alloy. The advantages lie in the experience with and the properties of conventional pyrometallurgical units which are less complex and less vulnerable, e.g., to organic impurities in the black matter, than their hydrometallurgical counterparts. The decisive factor in this regard is the oxygen potential of the contained metals, which is for example low for Ni and Co, leading to a relatively low-effort recovery. On the other hand, the similarity of the oxygen potential between Ni and Co reduce the selectivity of pyrometallurgical processes since they cannot be recovered separately but only as an alloy. The oxygen potential is also responsible for one of the biggest disadvantages of pyrometallurgy. Lithium, which has a much higher oxygen affinity, cannot be recovered as part of the metal alloy but is bound as an oxide in the slag instead [2,20,24–26].

The refining step is usually based on hydrometallurgical methods and aims for a closed loop recycling. Hence, it mainly applies on the metal alloy and slag from pyrometallurgical processing, which without further treatment, cannot be used for the production of new LIBs. The treatment of the metal alloy aims for a separation of the contained metals, while the slag treatment's goal is to recover Li, which is often technically but not economically feasible due to the low Li content in the slag. [2,20,22,27]

However, it can be summarized that there are still a lot of uncertainties in the LIB recycling chain. Not only the development of the waste stream itself, also the number and diversity of pre-treatment processes lead to varying black matter compositions and qualities. For pyrometallurgy, the lack of Li recovery options is a major problem that is not yet solved, but however, gives the desired novel approach with the InduRed reactor a good opportunity to establish itself as an alternative to conventional processes.

The mentioned InduRed reactor might be a possibility to achieve a simultaneous recovery of Ni, Co, Mn as well as Li with a pyrometallurgical process. The existing pilot-scale reactor concept, shown in Figure 1a,b, consists of a packed bed of graphite pieces that is inductively heated by surrounding copper coils. The input material is fed continuously with up to 10 kg/h from the top onto the hot graphite bed. The uppermost induction coil powers the upper third of the reactor where the input material melts and forms a thin molten layer that moves downwards. A second induction coil, placed half way down the reactor, induces enough power so that reduction reactions can take place. Gaseous reaction products are then removed from the reactor via a flue gas pipe whereas the liquid products move further down. The third induction coil makes sure that the temperature within the reactor can be maintained well above the melting temperature of the mixture and enables a continuous flow out of the bottom of the reactor. The advantages of the reactor are the low oxygen partial pressure, the possibility to control different temperature zones, and the big reaction surface due to the graphite bed. Furthermore, the contact time and intensity between gaseous reaction products and the molten phase can be limited because they only need to pass a thin layer or droplets instead of a molten bath like in conventional pyrometallurgical furnaces. Originally, the reactor concept was developed for the recovery of phosphorus from sewage sludge ashes, which is described by Schönberg [28]. The concept was later also adapted by Ponak et al. [29,30] to treat basic oxygen furnace slag with limited iron phosphide formation.



(**a**) (**b**)

Figure 1. (**a**) Schematic illustration of the so called InduRed reactor and (**b**) said reactor operating at a test series for metal recovery from basic oxygen furnace slag. [29,30].

The aim of this work is to investigate if said reactor concept can potentially also provide a solution for LIB black matter recycling.

For the determination of the basic suitability of black matter as an input material for the InduRed reactor, thus its melting and reaction behaviour, heating microscope experiments, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out. Since black matter can have different properties and contents of impurities depending on the pre-treatment procedure, the influence of which on the properties being investigated is difficult to assess, the investigations are also carried out with pure cathode materials. The ability of the InduRed reactor concept to eliminate one of the biggest disadvantages of pyrometallurgical LIB recycling, namely lithium slagging, is finally evaluated by experiments in a lab-scaled batch reactor, which is based on the InduRed concept. The results, in particular the required reaction temperatures and the Li removal rate via the gas phase from the reactor, form the basis on which a decision is made about the fundamental suitability of the reactor to be part of the LIB recycling chain.

2. Materials and Methods

The cathode materials ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, sample abbreviation: NCA and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, sample abbreviation: NMC) which were used for the experiments have been produced by Gelon Energy Corporation in Linyi, China, while the black matter (sample abbreviation: AM) was provided by a LIB recycling facility operated by Redux GmbH in Bremerhaven, Germany. The chemical composition of said materials is summarized in Table 1 below.

Table 1. Chemical composition of used materials. (mass fraction, w/%).

Species	C	Li	Ni	Co	Mn	Al	P	Fe	Cu	Zn	Pb
AM [1]	29.5	2.4	20.9	4.2	1.1	5.8	0.4	0.6	5.7	0.8	0.1
NCA [2]	-	7.2	48.9	9.2		1.4					
NMC [2]	-	7.2	20.3	20.4	19.0	-					

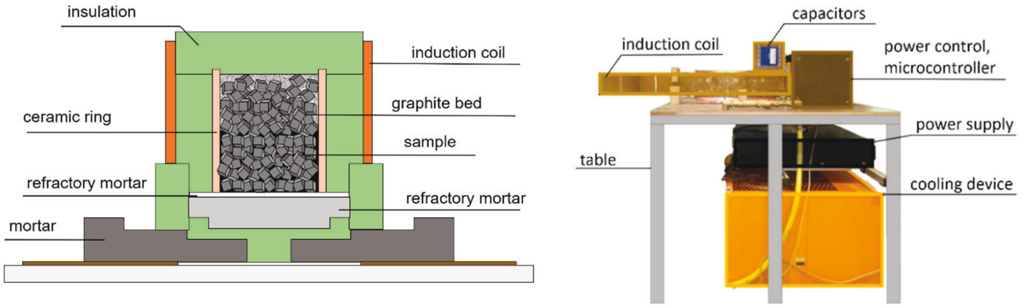
[1] Data from ICP-MS analysis. [2] Calculated from the molar composition of the cathode materials.

In experiments with NCA and NMC, where reducing conditions were desired (sample abbreviation: NCA_C, NMC_C), fine powdered coke was used as a reducing agent. Since AM already contains 29.5 w/% carbon there was no need to further add a reducing agent.

In order to investigate the general behavior of the cathode materials at high temperatures and under reducing conditions, the work started with two preliminary experimental series. First, heating microscope experiments were conducted in a Hesse Instruments EM 201 with an HR18-1750/30 furnace (Hesse Instruments, Osterode am Harz, Germany) to investigate at which temperatures reactions or transformations in the sample occur. In the heating microscope experiments, black matter and the cathode materials with and without carbon addition were tested at least twice to check the reproducibility of the results. In the reduction experiments, carbon was added in extents of 10 w/% to the NCA and NMC materials. An argon purge with a flow rate of approximately 2.5 l/min was used to inhibit oxidization reactions of the materials. The settings for the heating rate (80 °C/min until 1350 °C, 50 °C/min until 1550 °C and 10 °C/min until 1650 °C with a holding time of 5 min at 1650 °C), the used Al_2O_3 sample plates and the sample size of approximately 0.1 g of powder, pressed in a cylindrical shape, were the same for all experiments.

The second series were simultaneous thermal analyses (STA), more precisely thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), which have been conducted in a Setaram Setsys Evo 2400 at the Chair of Physical Metallurgy and Metallic Materials at the Montanuniversitaet Leoben. The aim of the STA was to confirm the temperature zones in which changes of the materials could be observed in the heating microscope and to further characterize the underlying reaction mechanisms. An argon purge was used to inhibit oxidization reactions of the materials. For carrying out the analyses, graphite crucibles and a carbon addition of 25 w/% were used in order to prevent damages to the analysis hardware. The need for this is due to reactions between standard Al_2O_3 crucibles and the produced metal alloy when carbon is added to the mixture. The reactions lead to a destruction of the Al_2O_3 crucible and the thermocouple underneath gets destroyed. The higher amount of carbon in the STA experiments is needed to prevent reactions between the cathode material and the graphite crucible, which would take part as a reductant.

To simulate the conditions of the InduRed reactor and check its suitability, a third set of experiments has been performed in the so-called InduMelt plant (sample abbreviation starts with: IM_). The InduMelt plant is a single coil induction furnace that is modeled on the InduRed reactor concept and used to perform preliminary experiments. This is due to the fact that the InduMelt plant is easier to use and requires less effort compared to the continuous InduRed reactor but still provides the same reaction conditions. The crucible concept used for these experiments is therefore based on the InduRed reactor and consists of a bed of packed graphite cubes (25 mm edge length) within an Al_2O_3 ceramics ring (70 mm radius, 100 mm height) and is shown in Figure 2a. In Figure 2b, the setup of the InduMelt plant is presented.



(**a**)

(**b**)

Figure 2. (**a**) Schematic illustration of the crucible concept used in the InduMelt experiments [29] and (**b**) setup of the experimental InduMelt plant.

During the preparation of the experiments, the ceramic ring is fixed on a mortar plate with refractory mortar and alternatingly filled with graphite cubes and input material. In the conducted experiments, the initial sample mass was 552.3 g for IM_NMC_C, 520.0 g for IM_NCA_C and 561.9 g for IM_AM. The filled crucible is then insulated, using 20 mm thick Cerachrome fiber wool with a classification temperature of 1500 °C and placed within the induction coil. The inductive energy input is controlled in such a way that the temperature increases at a maximum rate of 200 °C/h. For the measurement of temperatures of the reactor, two k-type thermocouples are used inside of the reactor to control temperatures up to 1200 °C. To keep track of the temperature after the k-type couples fail due to the high temperatures, two separate s-type couples are mounted on the outer wall of the Al_2O_3 ceramics ring. The temperature distribution in the reactor is known from previous experiments with other waste streams and can show a gradient of several 100 °C towards the end of the experiment, with the highest temperatures occurring at the top of the reactor. The s-type thermocouples are therefore placed at the lower third of the reactor in order to reach the necessary temperatures in the area in which the material is supposed to accumulate.

After the experiments, the reactor needs to cool down for at least 24 h before the sampling can start. Hereby, every graphite cube was picked from the reactor one after another and checked for any metal or slag depositions, which, if present, were removed from the cube's surface and collected. The difficulty to collect every little metal deposition and its influence on the overall mass balance of each experiment is discussed in the results section of this work.

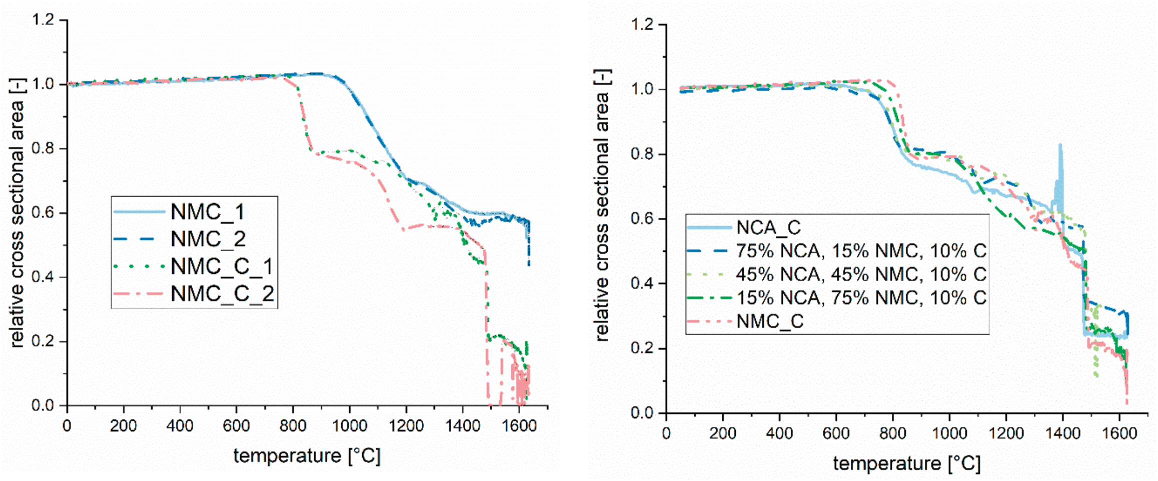
However, representative samples were taken from the collected products and the content of species of interest was examined using inductively coupled plasma mass spectrometry (ICP-MS). For all ICP-MS measurements, which were conducted at the Chair of Waste Processing Technology and Waste Management at the Montanuniversitaet Leoben, the sample preparation was done by aqua regia digestion according to the ÖNORM EN 13657 standard. The measurement of the respective species was carried out according to the ÖNORM EN ISO 17294-2 standard.

3. Results

3.1. Heating Microscope

In the heating microscope experiments, the relative cross-sectional area (CSA) of the sample, thus the trend of cross sectional area of the sample cylinder during heating in relation to its initial value, was observed to investigate at which temperatures changes in the material occur. In Figure 3a, where the results of the test series with NMC are shown, one can see a significant difference between the graphs of NMC_1 and NMC_2 without carbon addition and, respectively, NMC_C_1 and NMC_C_2 in which carbon was added. In this case, the first change of the CSA for NMC_C_1 and NMC_C_2 can be observed at approx. 800 °C, which is almost 200 °C lower than in the tests without carbon addition.

Moreover, the extent to which the change occurs is significantly higher in experiments with carbon addition. The steep decline of NMC_C_1 and NMC_C_2 at approx. 1500 °C was also observed with other cathode materials and can be explained by the melting point of the contained metals. The difference in the trends of the CSA with and without carbon addition can be explained by the origin of the changes. Mao et al. [31] and Kwon and Sohn [32] investigated and described the reaction behaviour of LCO ($LiCoO_2$) with and without carbon addition. According to their findings and due to the fact, that NCA and NMC are structurally identical to LCO, we assume that the changes in experiments without carbon addition are caused by thermal decomposition of the lithium metal oxides, while in experiments with carbon addition, reduction reactions with Li_2O formation led to the observed changes. About the reproducibility it can be said that in the repeated attempts the characteristic changes of the CSA appear at the same temperatures to about the same extent.



(**a**) (**b**)

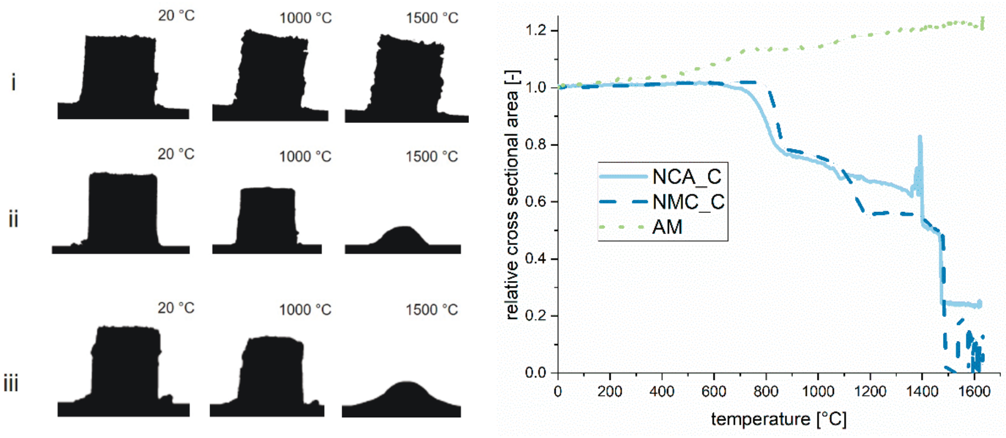
Figure 3. (**a**) Comparison of the cross sectional area of NMC with and without carbon addition in the heating microscope; (**b**) Comparison of the cross sectional area of different mixtures of NMC and NCA, each with carbon addition.

The results, mainly temperature zones and the extent of the correspondence of changes of the CSA, for NCA and NCA_C are very similar to those for NMC and NMC_C. However, since future waste streams are likely to consist of mixtures of different cathode materials, another set of experiments was performed in which NCA and NMC in different compositions and carbon were mixed to investigate if the materials influence each other. In Figure 3b, where the changes of the CSA of NCA_C, NMC_C and mixtures with varying composition are shown, no direct influence can be seen. The following Figure 4a,b show the NMC_C sample before and after the heating microscope experiment. In Figure 4b a perfectly molten metal sphere, indicated by the change of the CSA at approx. 1500 °C, and a fine white crystalline structure can be seen. The blue colour of the Al_2O_3 ceramic is most likely caused by reactions with cobalt and was also observed in all other experiments, especially in those with carbon addition.

(**a**) (**b**)

Figure 4. (**a**) NMC_C sample before and (**b**) after heating to 1600 °C in the heating microscope.

In contrast, the black matter material (AM) showed a completely different behavior, as can be seen in Figure 5a,b in which its CSA does not decrease during heating but increase to almost 120% of its initial value. The lack of the first change of the AMs CSA as well as the absence of any sign of melting at temperatures around 1500 °C indicates that pre-treatment might have a big influence on basic thermophysical properties of the produced black matter.



(**a**) (**b**)

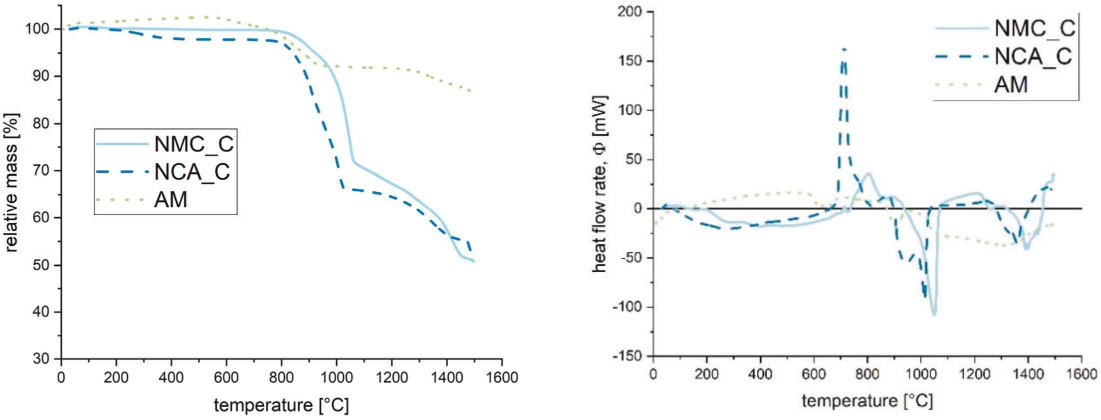
Figure 5. (**a**) Images of the samples AM (i), NMC_C (ii) and NCA_C (iii) at temperatures of 20 °C, 1000 °C and 1500 °C taken during the heating microscope experiments; (**b**) Trend of the cross sectional area of the samples AM, NMC_C and NCA_C during heating in the heating microscope.

Reasons for the deviating behavior of AM compared to NMC_C and NCA_C could lie in impurities, thus residues from the mechanical processing and separation step during pre-treatment, like Cu and Al from conductor foils. A closer look at the chemical composition of AM in Table 1 reveals that the mass content of Cu and Al with almost 6% each is much higher than anticipated. Moreover, the carbon content is much higher than would be stoichiometrically necessary for the reduction reactions. An example of a disruptive reaction could be the formation of aluminum oxide which, in the appropriate amount, could form a supporting structure and thereby reduce the informative value of the CSA. On the other hand, it is also possible that the anode graphite has a lower reactivity than the fine powdered coke which is used in NMC_C and NCA_C.

The origin of AM, a pre-treatment process that uses thermal deactivation before mechanical shredding, could also cause the observed differences, since some of the reactions might already have taken place if certain temperatures are overcome during this step. By this, the layered structure of the lithium metal oxides could probably have been changed, e.g., due to thermal decomposition which, as can be seen in Figure 3, occurs at approx. 1000 °C and could change the materials properties permanently. However, reliable information about these thermal processes is difficult to access. In our opinion, however, it is quite possible that at certain points in such a process, temperatures above 1000 °C can occur and that therefore the possibility of influencing the material must not be excluded.

3.2. Simultaneous Thermal Analysis

The experiments in the heating microscope gave some first impressions on how NMC, NCA and AM behave at high temperatures and under reducing conditions. For further characterization of the underlaying reactions that cause respective changes in the materials and to create a basis for a kinetics model in the long term, thermogravimetric analysis and differential scanning calorimetry was conducted. The results of the STA are summarized in Figure 6a, showing the trends of the relative mass of the samples, and Figure 6b, which shows the corresponding trends of the heat flow. The evaluation of the measurements, which also includes a correction of the data by reference measurements, was carried out in MATLAB.



(**a**) (**b**)

Figure 6. Results of the simultaneous thermal analyses of NMC_C and NCA_C with a heating rate of 40 K/min. (**a**) Trend of the relative mass of NMC_C and NCA_C during heating. (**b**) Trend of the heat flow of NMC_C and NCA_C during heating.

In Figure 6a the beginning of the mass loss at approximately 800 °C matches the observations from the heating microscope experiments. The first mass loss first declines slowly before it becomes steeper around 1000 °C and stops at approximately 70 % of the initial mass which was 40.1 mg for NCA_C and 39.8 mg for NMC_C. At the end of the thermogravimetric curve, the relative mass is about 55% of the initial mass. This means, that additionally to carbon, which had an initial mass content of 25 w/%, also components of the lithium metal oxide, most likely O_2 and Li, had been removed from the sample. Another indication for the presence of reduction reactions between 800 °C and 1000 °C is the trend of the heat flow, shown in Figure 6b. In both samples, the heat flow between 800 °C and approximately 1050 °C is endothermic with a negative peak around 1000 °C where also the biggest slope of the sample mass occurs. The outstanding exothermic peak in the NCA_C at 700 °C heat flow trend could be the result from Al_2O_3 formation whereby a significant amount of heat could be released. In order to confirm this, the samples must be heated in a controlled manner to or just above this temperature and analysed using XRD analysis, which is planned within the further scope of the research project.

As in the heating microscope experiments, the behaviour of the sample AM differs greatly from that of NCA_C and NMC_C. The overall mass loss only accumulates to around 10% and there are no sharp peaks in the heat flow trend. The lower mass loss is on the one hand due to the comparatively lower lithium metal oxide content (<60 w/%) compared to NCA_C and NMC_C (75 w/%) and the resulting decreased ability for CO or CO_2 generation. Since the heating rate was the same in all experiments, the less steep mass loss between 800 °C and 1000 °C and the absence of significant peaks in the heat flow trend indicate a lower reactivity of AM in general. The suspicion from the heating microscope experiments that certain reactions already took place during the thermal deactivation step has gotten stronger.

Finally, the results from the heating microscope experiments and the STA are summarized in Figure 7.

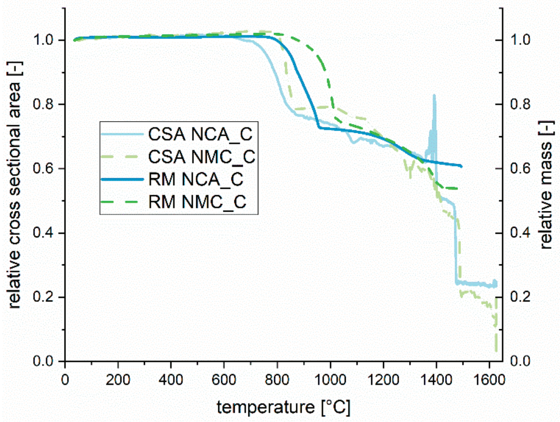
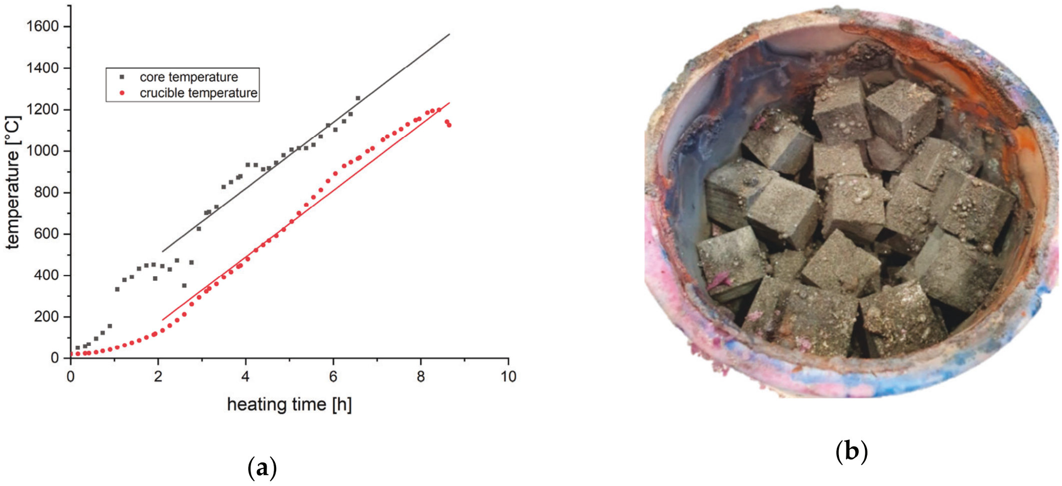


Figure 7. Trends of the cross-sectional area and the relative mass of NMC_C and NCA_C during heating in the heating microscope experiments and the simultaneous thermal analysis.

3.3. InduMelt Experimients

The last experimental series was conducted in the presented InduMelt reactor (Figure 2) to investigate the achievable transfer coefficients for Li, Ni, Co and Mn under the particular conditions of the reactor. The trend of the measured temperatures in- and outside of the reactor during one of the experiments is presented in Figure 8a. As explained in the materials and methods section, the slope of the outer s-type couples is used to control the temperature inside of the reactor after the operating temperature of the k-type couples is exceeded.



(**a**) (**b**)

Figure 8. (**a**) Trend of reactor temperatures during IM_NMC_C. (**b**) Picture showing the crucible and the packed bed of graphite cubes with metal depositions after IM_NMC_C.

In Table 2 the compositions of the input mixtures for the InduMelt experiments are shown. For NMC_C and NCA_C the composition matches the stochiometric proportion of the used cathode materials (NCA, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) with carbon addition of 10 w/%. If the whole added carbon is used and all oxides are removed the mass loss should accumulate to 40–46% of the input mass depending on the amount of Li that can be removed. For AM, which is a mixture of different cathode materials from LIBs and considering its composition most likely also other battery types, the volatile components also accumulate to around 42 w/%.

Table 2. Chemical composition of the input mixtures for the InduMelt experiments. (w/%).

Sample/Element	Li	Ni	Mn	Co	Al	O_2	C	Sum
AM	2.42	20.90	1.08	4.19	5.83	11.16 [2]	29.50	75.08 [1]
NCA_C	6.50	43.98	0.00	8.28	1.26	29.97	10.00	100.00
NMC_C	6.48	18.25	17.09	18.33	0.00	29.85	10.00	100.00

[1] Cu and other impurities are not specified here since they are not in focus of the experimental series. [2] Calculated on basis of the stochiometric Li-O_2 ratio.

Because the aim of the experimental series is to investigate possible recovery and removal rates for certain metals contained in the cathode materials, Cu and other impurities of the sample AM are not further analyzed.

For the first InduMelt experiments with LIB cathode materials and black matter a maximum temperature of approx. 1550 °C was chosen. At this temperature, no further changes of the CSA or mass during the STA and heating microscope were observed and the expected metal alloy's melting point is also some ten degrees lower. This temperature was then held for approx. one hour before the heat input was stopped.

In Figure 8b the reactor after the experiment is shown. All graphite cubes were removed and cleaned from metal and slag deposits which were subsequently weighed. The individual mass of input material and product phases for each experiment can be seen from Table 3.

Table 3. Masses of the input sample and the obtained products in InduMelt experiments. (g).

Experiment/Product	Input	Metal phase	Slag Phase	Powder	Product Sum
IM_NMC_C	552.3	244.2	37.7	11.6	293.5
IM_NCA_C	520.0	267.3	21.6	15.6	304.5
IM_AM [1]	561.9	-	-	396.1	396.1

[1] Neither metal accumulations nor slag depositions could be found.

The obtained product phases are subdivided into metal phase, slag phase and powder. On the first look at Table 3, one can see that the product distribution differs greatly between the experiments IM_NMC_C, IM_NCA_C and the experiment IM_AM. Therefore, the results are presented and discussed separately.

For IM_NCA_C and IM_NMC_C the metal and slag phase accumulates at the bottom of the reactor or can be found as depositions on the graphite cubes and the crucible. To achieve the best mass balance possible, the depositions have been rubbed of the graphite cubes and the metal particles were magnetically separated. By this, 244.2 g respectively 267.3 g of a metal product, which—if we assume that the metal phase only consists of Ni, Co and Mn—accounts for 81% and, respectively, 91% of the said metals in the input material of IM_NMC_C and IM_NCA_C. According to the oxygen potentials of the metals, the slag phase should mainly consist of Li_2O and Al_2O_3. With 37.7 g and 21.6 g of obtained slag for IM_NMC_C and IM_NCA_C compared to an input of approximately 36 g of pure Li alone one can say that this result looks promising, since the amount of oxygen—and of course Al—must also be taken into account. Furthermore, the refractory mortar and the crucible material also consist of Al_2O_3 and can take part in the reactions causing slag formation. Because this discussion is more complex than for the metal phase it will be continued later together with the chemical analyses of the phases. The powder phase of IM_NMC_C and IM_NCA_C is caused by abrasion during the removal of the small metal particles from the graphite cubes and therefore mainly consists of carbon. Summarized, the overall weight loss of IM_NMC_C and IM_NCA_C is 46.8% and, respectively, 41.4% of the input mass. If we assume that Li, O and C are the only volatile components in the input material a maximum weight loss of 47.2% for IM_NMC_C and 50.2% for IM_NCA_C is achievable. For IM_NMC_C, the obtained slag phase is shown in Figure 9a, the metal accumulation in Figure 9b.

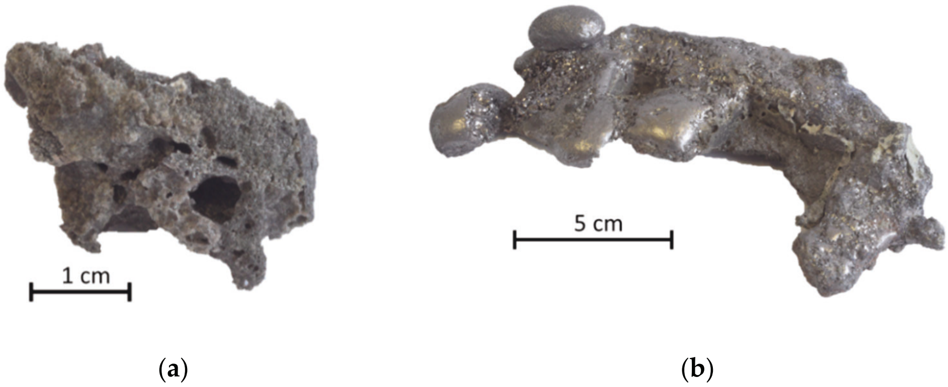


Figure 9. Obtained slag (**a**) and metal sample (**b**) from the experiment IM_NMC_C.

As can be seen, the separation of the metal and slag phase in IM_NMC_C for further chemical analysis was relatively easy since large specimens without fusions could be found. In contrast, the obtained products from IM_NCA_C were harder to separate as Figure 10a–d shows. Therefore, the ICP-MS analysis was performed for both, samples with and without inclusions, and the results weighted during data evaluation.

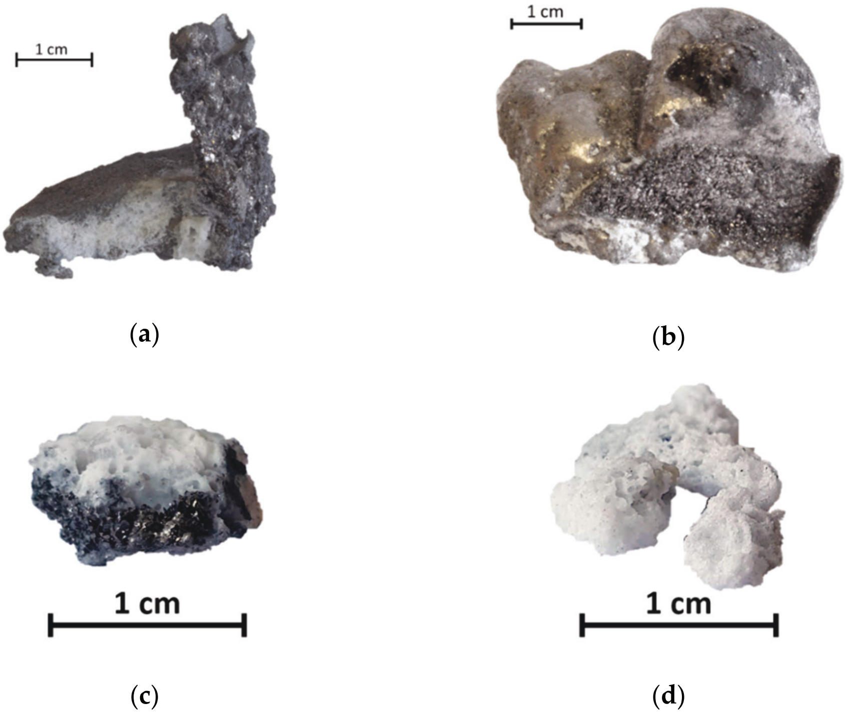


Figure 10. Obtained metal and slag samples from the IM_NCA_C experiment. (**a**) Metal sample 1 which is strongly fused with the produced slag. (**b**) Metal sample 2 with very little slag inclusions. (**c**) Slag sample 1 with metal depositions. (**d**) Slag sample 2 without inclusions or depositions.

To intensify this discussion, we need to look at the results of the chemical analysis, which were achieved by ICP-MS analysis. The discussion starts with the obtained metal phase from the experiments IM_NMC_C and IM_NCA_C for which the results are contained in Table 4.

Table 4. Mass fractions of certain metals in the obtained metal phases. (w/%).

Experiment/Species	Li	Ni	Co	Mn	Al
IM_NMC_C	0.09	38.40	36.10	28.10	0.01
IM_NCA_C_1 [2]	1.31	74.70	7.80	[1]	3.70
IM_NCA_C_2 [3]	0.05	92.20	9.89	[1]	[1]

[1] Species was not analyzed in this experiment. [2] Small inclusions of slag in the metal matrix need to be considered. [3] Slightly over-determined due to weighted consideration of residuals from the aqua regia digestion.

For IM_NMC_C the metal composition mostly matches the expected result. There is almost no Li and Al present in the metal alloy but Ni, Co and Mn. What is noticeable, however, is the significantly lower Mn content compared to Ni and Co. With an equal stoichiometric proportion and similar molecular weight—Mn is a little lighter—the difference should not be that high, which indicates that Mn also accumulates somewhere else than in the metal alloy.

As already explained, the sampling of NCA_C was not trivial due to small slag inclusions within the metal particles. In order to increase the informative value, metal samples with (IM_NCA_C_1) and without (IM_NCA_C_2) small slag particles were analyzed. By this it can be stated that also for IM_NCA_C there was hardly an accumulation of Li and Al in the metal alloy that mainly consists of Ni and Co.

A complete mass balance is hardly feasible due to the difficult collection of the small metal particles. In future experiments and respective analyses, ICP-OES as well as XRD analysis methods will be used to balance all the elements included in greater detail. Nevertheless, compared to the initial amount in the input material it was possible to find around 90% of Ni and Co and 76% of Mn in the metal phase of IM_NMC_C as well as more than 90% of Ni and Co in the metal phase of IM_NCA_C.

In order to investigate the whereabouts of Mn, to clarify whether Ni and Co can also be found in the slag and to finally check the question of whether Li removal from the reactor could be achieved or not we now look at the slag analysis shown in Table 5.

Table 5. Mass fractions of certain metals in the obtained slag phase. (w/%).

Experiment/Species	Li	Ni	Co	Mn	Al
IM_NMC_C	8.22	0.13	3.06	0.15	6.08
IM_NCA_C_1	9.85	1.31	[1]	[1]	7.45
IM_NCA_C_2	4.52	0.24	0.03	[1]	2.48

Species was not analyzed in this experiment.

Beginning with IM_NMC_C it can be said that Ni does hardly accumulate in the slag while a significantly higher but still low amount of Co could be found. For Mn, from which only 76% of its initial input were found in the metal phase, can also not be found in the slag phase. Since Mn is very reactive and has several oxidation states it is likely that parts of it were removed from the reactor via the gas phase. For IM_NMC_C, analogous to the metal phase results, there are again two samples, IM_NCA_1 with metal particles and IM_NCA_2 without metal particles. The data shows that only a small amount of Ni and Co is found in the slag while Li and Al accumulate to higher extents.

If we now compare the amount of Li that was initially inserted in the experiments, which was approx. 36 g for IM_NCA_C and IM_NMC_C with the amount of Li that was found in the metal and slag phase, a lithium removal of 96.72 w/% for IM_NCA_C and 90.76 w/% for IM_NMC_C was achieved.

Before these results are finally summarized, we have to take a look at IM_AM, which, as mentioned at the beginning, behaved differently than IM_NCA_C and IM_NMC_C. As can be seen in Table 3, neither a metal nor a slag accumulation was found but only a fine powder that was optically identical to the input material. The weight loss of 29,5% matches the initial carbon content exactly, which at first sight suggests that only the included carbon was burned in the reactor. However, analysis of the carbon content of the resulting powder revealed a mass content of still 22.6%, which indicates that also in IM_AM reduction reactions occurred. In the thermogravimetric analyses only a decrease in mass of 10% was achieved. This could be an indication that certain reactions proceed more slowly in AM and that longer holding times in the preliminary experiments would have provided better results, which is going to be investigated in the further course of the project. Furthermore, an increase of the average particle size was found that indicates at least an agglomeration of particles even if there was no molten phase. Because there was no slag or metal phase in IM_AM, the results are discussed by a comparison of the chemical composition before and after the InduMelt experiment, which is shown in Table 6.

Table 6. Chemical composition of AM before and after the InduMelt experiment. (w/%).

Experiment/Species	Li	Ni	Co	Mn	Al
AM before IM [1]	2.42	20.90	4.19	1.08	5.83
AM after IM [2]	0.77	35.00	7.00	1.76	4.12

[1] Total mass of input material: 561.9 g. [2] Total mass of product: 396.1 g.

The mass content of Ni, Co and Mn has risen by about 65% each which can only be caused by the mass loss of the sample. A statement about a possible discharge of Mn via the gas phase, as it was observed in IM_NMC_C, should not be made due to the already low concentration in IM_AM. Lithium had an input mass of 13.59 g and was reduced to 3.04 g in the product powder, which corresponds to a decrease of 77.6 w/%. This value is significantly lower than with pure cathode materials but in the light of the different behavior of AM compared to NCA_C and NMC_C in all experimental series still a promising result.

To finally summarize the InduMelt experiments, one must notice that the difficulties to achieve a complete mass balance and the absence of an off-gas analysis lead to the fact that the absolute numbers should only be considered to a limited extent. However, it is not the claim of this work to precisely define transfer coefficients for all species in cathode materials respectively black matter, but to evaluate the magnitude of possible recovery rates for the valuable metals Ni, Co, Mn and Li by using the InduRed reactor technology. In view of this, these tendencies are summarized in Figure 11.

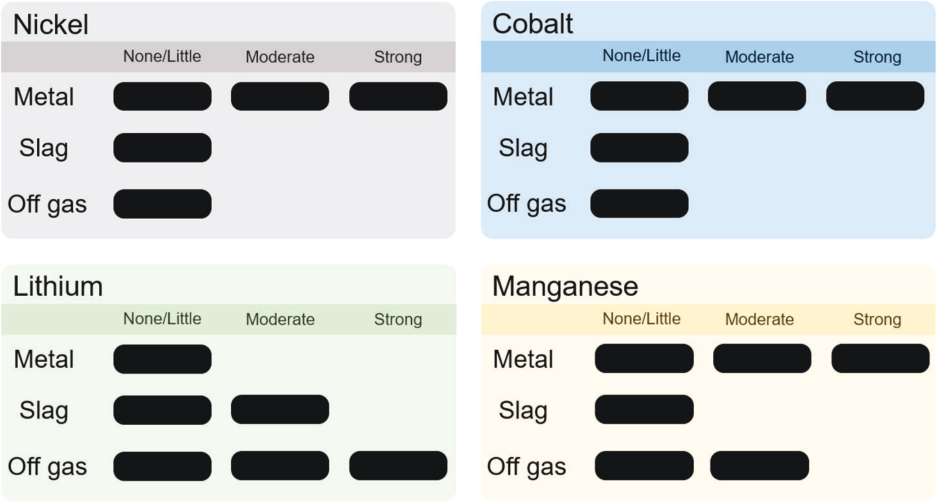


Figure 11. Qualitative consideration of the accumulation of Ni, Co, Mn and Li in the product phases obtained from the InduMelt experiments.

4. Conclusions

The literature research clearly shows that the possibility of simultaneous lithium recovery with a pyrometallurgical process would close a large gap in the recycling chain.

To evaluate if the presented InduRed technology can potentially provide a solution to this problem, a series of experiments have been conducted. By heating microscope experiments and simultaneous thermal analysis, the behavior of NCA and NMC cathode materials as well as black matter (AM) at high temperatures and under reducing conditions was investigated. The results showed that the significant reduction reaction between the lithium metal oxides and carbon take place between 800 °C and 1000 °C and that the produced metal alloy melts at approximately 1500 °C, which are technically feasible temperatures for the desired process.

Experiments, conducted in the InduMelt plant, a lab scale reactor modeled on the InduRed concept, were used to evaluate the transfer coefficients of Ni, Co, Mn and Li in qualitative terms. It was shown that Ni and Co seem to be fully recoverable by this technology while parts of manganese are removed from the reactor via the gas phase. For Li, which is considered to be the bottleneck of pyrometallurgical LIB recycling approaches, very promising results have been seen. In the InduMelt experiments with NCA and NMC more than 90%, respectively more than 75% in the experiment with black matter, of the initial Li were removed from the reactor. The fact that Li does neither accumulate in the slag nor in the metal phase indicates a high potential of the technology to enable new possibilities for Li recovery from the LIB waste stream. If Li is not obtained in small amounts in a slag phase, as in other processes, but can be collected in a separate material flow, its recovery from there can potentially be achieved with less effort and therefore represented more economically.

In order to better examine the removal of Li and Mn from the reactor, the experiments are going to be repeated using a gas vent with gas scrubbing. This should clarify in which form the Li can be obtained from the exhaust gas and how its recovery from there could be achieved. Furthermore, new cathode materials like NMC in other configurations (811, 622, 532 instead of 111) as well as LFP (lithium iron phosphate) are planned to be investigated regarding their suitability for treatment in the InduRed reactor.

The results from experiments with black matter (AM) showed some significant differences, which could partly be attributed to residues from the pre-treatment or excessively high temperatures during the thermal deactivation. Since the contrary behavior of AM in all experimental series cannot be fully elucidated with the available data, further research and experiments are necessary. In addition to that, it is planned to investigate black matter from different pre-treatment processes and the influence of interfering species like Cu or Al in general.

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References

1. Mizushima, K.; Jones, P.C. LixCoO$_2$ (0 <x <−1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* **1980**, *6*, 783–789.
2. Li, L.; Zhang, X. The Recycling of Spent Lithium-Ion Batteries: A Review of Current Processes and Technologies. *Electrochem. Energy Rev.* **2018**, *4*, 461–482. [CrossRef]
3. Ding, Y.; Cano, Z.P. Automotive Li-Ion Batteries: Current Status and Future Perspectives. *Electrochem. Energy Rev.* **2019**, *1*, 1–28. [CrossRef]

4. Berckmans, G.; Messagie, M. Cost Projection of State of the Art Lithium-Ion Batteries for Electric Vehicles Up to 2030. *Energies* **2017**, *10*, 1314. [CrossRef]
5. Arambarri, J.; Hayden, J. Lithium ion car batteries: Present analysis and future predictions. *Environ. Eng. Res.* **2019**, *4*, 699–710. [CrossRef]
6. Redux Smart Battery Recycling. Available online: https://www.redux-recycling.com/de (accessed on 28 December 2020).
7. Umicore Battery Recycling. Available online: https://csm.umicore.com/en/battery-recycling/e-mobility (accessed on 28 December 2020).
8. Lithium Batterie Recycling. Available online: https://accurec.de/lithium?lang=de (accessed on 28 December 2020).
9. Battery Recycling Datasheet. Available online: https://accurec.de/wp-content/uploads/2018/04/Li-ion-RE_2018.pdf (accessed on 28 December 2020).
10. Arnberger, A.; Coskun, E. Recycling von Lithium-Ionen-Batterien. In *Recycling und Rohstoffe*; Thiel, S., Thomé-Kozmiensky, E., Eds.; TK Verlag: Nietwerder, Germany, 2018; pp. 583–599.
11. Werner, D.; Peuker, U.A. Recycling Chain for Spent Lithium-Ion Batteries. *Metals* **2020**, *3*, 316. [CrossRef]
12. Liu, C.; Lin, J. Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review. *J. Clean. Prod.* **2019**, *228*, 801–813. [CrossRef]
13. Mishra, D.; Kim, D.-J. Bioleaching of metals from spent lithium ion secondary batteries using *Acidithiobacillus ferrooxidans*. *J. Waste Manag.* **2008**, *28*, 333–338. [CrossRef]
14. Xin, Y.; Guo, X. Bioleaching of valuable metals Li, Co, Ni and Mn from spent electric vehicle Li-ion batteries for the purpose of recovery. *J. Clean. Prod.* **2016**, *116*, 249–258. [CrossRef]
15. Zeng, G.; Deng, X. A copper-catalyzed bioleaching process for enhancement of cobalt dissolution from spent lithium-ion batteries. *J. Hazard. Mater.* **2012**, *199*, 164–169. [CrossRef]
16. Zeng, G.; Luo, S. Influence of silver ions on bioleaching of cobalt from spent lithium batteries. *Miner. Eng.* **2013**, *49*, 40–44. [CrossRef]
17. Bahaloo-Horeh, N.; Mousavi, S.M. Use of adapted metal tolerant Aspergillus niger to enhance bioleaching efficiency of valuable metals from spent lithium-ion mobile phone batteries. *J. Clean. Prod.* **2018**, *197*, 1546–1557. [CrossRef]
18. Ghassa, S.; Farzanegan, A. Novel bioleaching of waste lithium ion batteries by mixed moderate thermophilic microorganisms, using iron scrap as energy source and reducing agent. *Hydrometallurgy* **2020**, *197*, 105465. [CrossRef]
19. Heydarian, A.; Mousavi, S.M. Application of a mixed culture of adapted acidophilic bacteria in two-step bioleaching of spent lithium-ion laptop batteries. *J. Power Sources* **2018**, *378*, 19–30. [CrossRef]
20. Vest, M. Weiterentwicklung des Pyrometallurgischen IME Recyclingverfahrens für Li-Ionen Batterien von Elektrofahrzeugen. Ph.D. Thesis, RWTH Aachen, Aachen, Germany, 28 January 2016.
21. He, L.-P.; Sun, S.-Y. Recovery of Lithium, Nickel, Cobalt, and Manganese from Spent Lithium-Ion Batteries Using l -Tartaric Acid as a Leachant. *ACS Sustain. Chem. Eng.* **2017**, *5*, 714–721. [CrossRef]
22. Elwert, T.; Frank, F. 2020, Auf dem Weg zu einem geschlossenen Stoffkreislauf für Lithium-Ionen-Batterien. In *Recycling und Sekundärrohstoffe*; Thomé-Kozmiensky, E., Holm, O., Eds.; TK Verlag: Neuruppin, Germany, 2018; pp. 525–530.
23. Huang, B.; Pan, Z. Recycling of lithium-ion batteries: Recent advances and perspectives. *J. Power Sources* **2018**, *399*, 274–286. [CrossRef]
24. Yin, H.; Xing, P. Pyrometallurgical Routes for the Recycling of Spent Lithium-Ion Batteries. In *Recycling of Spent Lithium-Ion Batteries*; Liang, A., Ed.; Springer International Publishing: Cham, Switzerland, 2019; Volume 4, pp. 57–83.
25. Gao, R.; Xu, Z. Pyrolysis and utilization of nonmetal materials in waste printed circuit boards: Debromination pyrolysis, temperature-controlled condensation, and synthesis of oil-based resin. *J. Hazard. Mater.* **2019**, *364*, 1–10. [CrossRef]
26. Beheshti, R.; Tabeshian, A. Lithium-Ion Battery Recycling Through Secondary Aluminum Production. In *Energy Technology*; Zhang, L., Jaroslaw, W., Eds.; Springer International Publishing: Cham, Switzerland, 2017; pp. 267–274.
27. Dorella, G.; Mansur, M.B. A study of the separation of cobalt from spent Li-ion battery residues. *J. Power Sources* **2007**, *170*, 210–215. [CrossRef]
28. Schönberg, A. Mathematische Modellierung metallurgischer Prozesse—Induktive Erwärmung einer Graphitschüttung. Ph.D. Thesis, Montanuniversität Leoben, Leoben, Germany, 11 December 2014.
29. Ponak, C. Carbo-Thermal Reduction of Basic Oxygen Furnace Slags with Simultaneous Removal of Phosphorus via the Gas Phase. Ph.D. Thesis, Montanuniversität Leoben, Leoben, Germany, 2 September 2019.
30. Ponak, C.; Mally, V. Phosphorus Gasification during the Reduction of Basic Oxygen Furnace Slags in a Novel Reactor Concept. *Adv. Mater. Lett.* **2020**, *11*, 20071535. [CrossRef]
31. Mao, J.; Li, J. Coupling reactions and collapsing model in the roasting process of recycling metals from $LiCoO_2$ batteries. *J. Clean. Prod.* **2018**, *205*, 923–929. [CrossRef]
32. Kwon, O.; Sohn, I. Fundamental thermokinetic study of a sustainable lithium-ion battery pyrometallurgical recycling process. *Resour. Conserv. Recycl.* **2020**, *158*, 104809. [CrossRef]

3.3.2 Publication 5

Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials ($LiNi_xMn_yCo_zO_2$) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor

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Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials ($LiNi_xMn_yCo_zO_2$) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor

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Abstract: Within the e-mobility sector, which represents a major driver of the development of the overall lithium-ion battery market, batteries with nickel-manganese-cobalt (NMC) cathode chemistries are currently gaining ground. This work is specifically dedicated to this NMC battery type and investigates achievable recovery rates of the valuable materials contained when applying an unconventional, pyrometallurgical reactor concept. For this purpose, the currently most prevalent NMC modifications (5-3-2, 6-2-2, and 8-1-1) with carbon addition were analyzed using thermogravimetric analysis and differential scanning calorimetry, and treated in a lab-scale application of the mentioned reactor principle. It was shown that the reactor concept achieves high recovery rates for nickel, cobalt, and manganese of well above 80%. For lithium, which is usually oxidized and slagged, the transfer coefficient into the slag phase was less than 10% in every experimental trial. Instead, it was possible to remove the vast amount of it via a gas phase, which could potentially open up new paths regarding metal recovery from spent lithium-ion batteries.

Keywords: lithium-ion batteries; lithium recycling; carbothermal reduction

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1. Introduction

The ongoing transition towards a society based on clean and renewable energies, including an exponential increase of storage capacity within stationary and portable devices, has caused a surge in demand for lithium-ion batteries (LIBs) as a lightweight and energy-dense storage alternative [1,2]. By the year 2040, it is anticipated that almost 4000 GWh of LIBs will be installed, leading to a tremendous amount of wasted batteries which have to be recycled [3]. Due to previous economic conditions, the recycling of LIBs was primarily focused on valuable materials such as cobalt and nickel. However, as shown in the latest update of the European Union's list of critical raw materials (CRM), lithium has become a metal for which both a supply risk and economic importance is concerned [2]. The new proposal of the EU Directive 2006/66/EC concerning batteries and waste batteries tries to counteract this fact with a mandatory lithium recovery rate of up to 70% by 2030 [4]. However, due to economic limitations, lithium often remains in the slag. Therefore, alternative solutions which provide both high recovery rates for all materials and economic incentives for the industry are necessary [5].

At the end of the lifespan of a LIB, the battery materials are often too degraded to be used in subsequent applications. To recover the precious metals within the batteries, different recycling processes exist, which will generate products in different stages of the battery production chain [6]. State-of-the-art recycling processes are usually divided into a (thermal) pre-treatment process, metallurgical processing such as direct-, hydro-, or pyrometallurgical processes, and smelting processes [7]. Direct recycling methods such as gravity separation and flotation aim to recover, for example, unaltered cathode material for—as the name suggests—direct recycling. However, with each recycling process, performance losses can be obtained, representing a bottleneck within this recycling route [8].

Alternatively, hydrometallurgical extraction processes are known to be cost-competitive with little energy consumption and offering great recycling efficiencies and recovery rates [9,10]. Within this recycling route, the dismantled electrodes are dissolved in concentrated acids in which metal ions are recovered by precipitation [11]. While it is comparatively easy to achieve high metal-leaching efficiencies using inorganic acids such as hydrochloric acid (HCl) [12–14], sulfuric acid (H_2SO_4) [15–17], or phosphoric acid (H_3PO_4) [18,19], acidic wastewater and harmful gases for human and environment occur, which have to be tackled in a separate process. The use of organic acids such as citric acid [20,21], oxalic acid [22,23], or ascorbic acid [24–26] have been considered more eco-friendly, with the disadvantage of being more expensive and causing higher difficulties in metal separation from the leaching solvent [19]. From recent studies, e.g., those of Chen et al. [19,27], it is known that hydrometallurgical processes offer high recycling rates of more than 90% for lithium and other CRM. However, these processes are highly complex, and the efficiency strongly corresponds to the composition of the input material [24].

In pyrometallurgical treatments, as described by Makuza et al. [28], temperatures above 1400 °C are used to recover metals such as cobalt, nickel, and copper in a reducing atmosphere. Although the recycling process is highly efficient for these metals, lithium, aluminum, or organic compounds are commonly either burned or slagged and can only be recycled with an additional leaching process [29,30]. Potentially, pyrometallurgical processes could help to enhance the overall efficiency by decreasing the volume of waste that needs to be treated in hydrometallurgy, which then would only serve as a refining step [31]. However, the problem with lithium slagging in pyrometallurgy still exists and would require an extra leaching step, which is often not economically feasible.

To avoid this additional procedure, the Chair of Thermal Processing Technology at the Montanuniversitaet Leoben is currently working on a novel concept that aims to overcome that common disadvantage of pyrometallurgy. Said concept, referred to as the InduRed concept, mainly consists of a fixed bed of graphite cubes within ceramic rings. The ceramics are surrounded by induction coils that generate an electromagnetic field which then inductively heats the graphite particles of the bed. High temperatures of up to 1750 °C as well as a low oxygen partial pressure and an oversupply of carbon result in particularly strong reducing conditions that allow for carbo-thermal reduction of the metal oxides in the feed. The most striking advantage is the flow characteristic of the liquid phase within the InduRed reactor. After the input material, which is continuously charged from the top of the reactor, is molten, it forms a thin melt film on the bed's surface that flows downwards towards the reactor's tap. Gaseous reaction products that are formed in the liquid phase then only need to be transported through that thin film, which shortens the contact time between those gaseous products and certain metals in the liquid phase. Thus, undesirable reactions, e.g., between metal and metal-contaminating elements such as phosphorus, can be minimized. These advantages could also be exploited to allow for simultaneous recovery of all cathodic metals, including lithium, from end-of-life (EoL) LIBs.

The process idea is to prevent lithium from being slagged and to recover it as a part of the gas phase instead. First trials, presented in [5], already showed that the amount of slag obtained is significantly lower than what should be expected from other pyrometallurgical processes [32,33]. However, it has not yet been proven if lithium can actually be removed via the gas phase.

With the hindsight of a rapidly increasing share of electric vehicles within new registrations, spent LIBs from this market are of particular interest for future recycling operations. Since NMC-type batteries are currently the preferred choice for e-mobility applications [34], this work focuses on the recently available variants NMC532, NMC622, and NMC811 and aims to investigate possible recovery rates by applying the InduRed concept. For this purpose, a batch version of the InduRed concept titled the InduMelt reactor is used to analyze transfer coefficients of all cathodic metals into certain obtained product phases. This is to clarify if the InduRed concept could potentially enable simultaneous lithium recovery in a pyrometallurgical LIB recycling approach and if it could represent an alternative to currently used recycling processes.

2. Materials and Methods

Generally, the experiments conducted in the scope of this work can be divided into two parts. The main part of the research is based on trials in the so-called InduMelt plant, which is a batch version of the aforementioned InduRed concept, whereas the second part comprises simultaneous thermal analysis (STA). Both parts will be explained subsequently in more detail. With regard to the materials used in this work, it can be stated that all cathode materials (NMC532, NMC622, and NMC811) were produced by and purchased from Gelon Energy Corporation in Linyi, China. The decision to use factory-new cathode materials directly, instead of separating them from EoL batteries, allows to evaluate the results without considering possible side effects due to residual impurities of the separation process. Optically, all materials are fine black powders, with 90% of the particles (D_{90}) being smaller than 20 µm. Fine powdered coke was used as a reducing agent and was added to the cathode materials. The extent of coke addition differed between trials in the carbothermal reduction reactor, the so-called InduMelt, and for STA and was 20 wt.% and 25 wt.%, respectively. The amount of carbon added is the necessary stoichiometric amount to reduce all metal oxides under the assumption that only carbon monoxide is present after the reduction. In the following, the procedure for the two experimental apparatuses used within this test series is described in detail.

2.1. InduMelt Experiments

The equipment used for the investigations is based on the principle of the previously explained inductively heated packed bed reactor. The so-called InduMelt plant essentially consists of a crucible and an induction unit, as shown in Figure 1. The reactor is composed of a ceramic ring made of Al_2O_3 and a refractory concrete bottom, which are connected by refractory mortar. This reactor is filled with graphite cubes with a side length of 2.5 cm, a resistivity of 4–8 µΩm, and a density of 1.55–1.75 g cm^{-3}. The InduMelt plant is not charged continuously but still shares the same process-related advantages as the InduRed reactor since the conditions regarding temperature, oxygen partial pressure, and carbon monoxide to carbon dioxide ratio are the same as for the InduRed concept. The graphite cubes primarily serve as a heat source (susceptor for the electromagnetic field, generated by the induction coil) and are not supposed to take part in the reactions. The material to be investigated, i.e., a mixture of NMC532, NMC622, and NMC811 with coke, is located in the interstices of the graphite cubes. To reduce heat losses and to protect the copper coil, the reactor is insulated. Gas, which is produced due to chemical reaction, can leave the reactor via a ceramic tube installed in the lid. A water jet pump is used to force a partial flux of the exhaust gas to pass a gas wash bottle filled with 2.5 M H_2SO_4. During the experiments, the temperature is measured via s-type and k-type thermocouples which are located in and outside of the reactor. The heating rate of the reactor, which is limited by the used ceramics and supposed to be approximately 200 K·min^{-1}, is controlled via manually adjusting the power supply of the induction coil. For safety reasons, an additional suction is used to remove all gaseous products from the immediate surroundings of the experimental set-up.

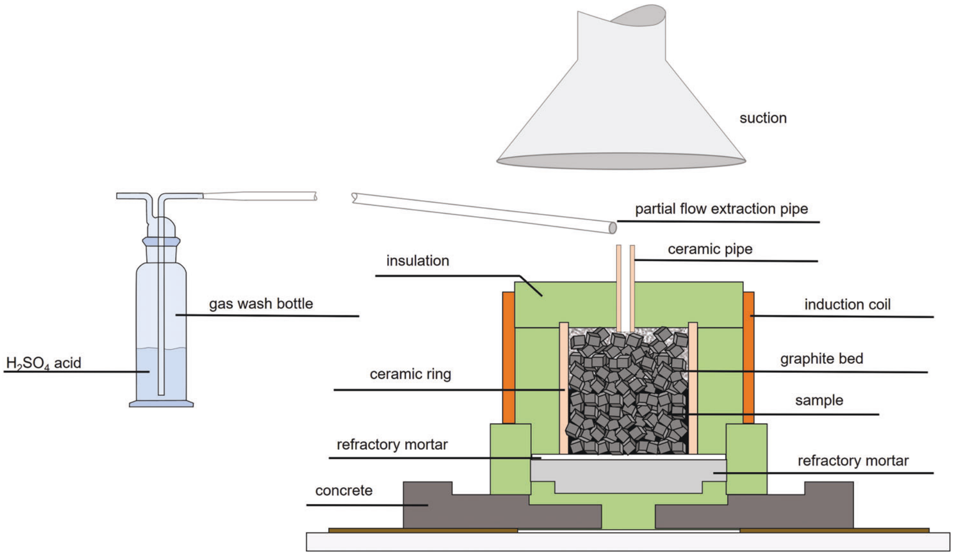


Figure 1. Schematic illustration of the InduMelt reactor used in the experimental trials with NMC532, NMC622, and NMC811.

2.1.1. Preparation

To enable comparability of the individual experiments, care was taken during preparation to ensure that all tests followed the same procedure. At the beginning, the ceramic ring, which can be seen in Figure 1, was fixed to the refractory concrete base with the aid of a refractory mortar. To guarantee the function of this bond, a drying time of at least 24 h was observed. Subsequently, the reactor was alternatingly charged with graphite cubes and the respective input material, the chemical composition of which for each trial can be taken from Table 1. In the interest of reproducible experimental performance and to allow for a uniform distribution over the whole reactor height, the reactor was continuously weighed during this procedure. In the experiments with NMC532, NMC622, and NMC811, the mass of input material charged was 502.3, 500.6, and 501.5 g, respectively.

Table 1. Chemical composition of the samples used in the experiments (mass fraction, wt.%).

Sample/Elements	Li [1]	Ni [1]	Mn [1]	Co [1]	O_2 [1]	C	n_v [2]
NMC532	5.8	24.3	13.7	9.8	26.5	20.0	52.3
NMC622	5.7	29.1	9.1	9.7	26.4	20.0	52.1
NMC811	5.7	38.6	4.5	4.9	26.3	20.0	52.0

[1] Calculated from the stochiometric composition of each cathode material. [2] Total mass contribution of elements that are expected to be volatile (O_2, C, and Li).

2.1.2. Experimental Procedure

After preparation, the heating phase was started. During heating, the power supply was regulated in such a way so that a heating rate of approximately 200 $K \cdot min^{-1}$ was maintained. A maximum temperature of 1500 °C was aimed for in each experiment, which takes a heating duration of seven to eight hours. The reactor temperature was then kept at that temperature for 30 min before the power supply was turned off. The temperatures inside the reactor were measured by three k-type thermocouples, which were positioned at different heights. However, these values were only valid until a temperature of approximately 1300 °C, which marks the maximum operating point of the k-type thermocouples. To keep track of the temperatures after this point is reached, three additional s-type thermocouples were used to measure the temperature at the outer wall of the crucible. A correlation between the measured temperatures outside and the actual temperatures inside of the reactor has been observed over dozens of tests and is known to be a good estimation and sufficient to retain the demanded heating rate. All data, thus temperatures, voltage, and amperage, were recorded using Excel and LabVIEW. Furthermore, certain striking observations that may occur during the experiment were noted and assigned to the respective time stamp. With this information, it should be possible to link certain events and observations during the experiment to certain reactions and therefore clarify their origin.

2.1.3. Sampling and Analyses

After a cooling period of at least 24 h, the reactor was unpacked and weighed in reverse order to the preparation. The products removed from the reactor chamber were subsequently separated into individual fractions by means of a sieve tower (2, 1, and 0.5 mm mesh size) and magnetic separation. The latter was simply achieved by using a magnetic tape to remove metallic particles step-by-step.For the sake of clarity, it is noted that the magnetic metal separation is only used for the batch version of the InduRed reactor. In the continuous process, the slag and metal phase are separated due to density differences after being tapped. Metal spheres adhering to the reactor and the graphite cubes were mechanically segregated. The fractions obtained were divided into metal alloy, slag, and powder. These fractions were then analyzed by ICP-MS and SEM. In addition, the scrubbing water of the exhaust gas was measured by ICP-MS analysis.

For the ICP-MS analysis, which was carried out in an Agilent 7500 CE, all samples were prepared using aqua regia digestion according to the ÖNORM EN 13657 standard. The ICP-MS measurements were carried out at the Chair of Waste Processing Technology and Waste Management at the Montanuniversitaet Leoben according to the ÖNORM EN ISO 17294-2 standard. For the scanning electron microscopy, a Jeol JSM-IT300 (Freising, Germany) was used. In Section 2.2, the results for each of these product phases are shown and discussed. Since the individual product phases are optically identical for all experiments, the figures in Section 3.2 exemplarily show a picture of the respective product from the trial with NMC622.

2.2. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

For the STA, TGA and DSC were carried out using a Setaram Setsys Evo 2400, located at the Chair of Physical Metallurgy and Metallic Materials at the Montanuniversitaet Leoben. To eliminate issues concerning unwanted reactions with the common Al_2O_3 sample holder, graphite crucibles with a volume of 90 µL were used instead. In this context, also the higher mass content of coke for STA can be explained, as it was needed to prevent the graphite crucible from taking part in the reduction reactions. All materials were analyzed twice, one time with a heat rate of 20 K/min and one time with a heat rate of 40 K/min. Each sample had an initial mass of approximately 40 mg and was heated to a maximum temperature of 1500 °C, at which it remained for 5 min. Furthermore, an argon purge was used in every analysis to inhibit re-oxidization reactions.

3. Results and Discussion

3.1. Simultaneous Thermal Analyses

So far, there are numerous studies that deal with the thermal stability of LIB cathode materials [35–40]. Since these are often only concerned with safety-related or performance-relevant issues, the analyses are usually carried out in temperature ranges below 300 °C. Pyrometallurgical recycling approaches on the other hand operate at temperatures of well above 1000 °C and cannot be adequately described by observed reactions and phenomena at lower temperatures [41–45].

By looking at thermokinetic studies and publications that conducted investigations at sufficiently high temperatures, it can be concluded that lithium metal oxides basically tend to thermally collapse according to Equation (1) [46–48]:

$$4\ LiMeO_{2(s)} \rightarrow 2\ Li_2O_{(s)} + 4\ MeO_{(s)} + O_{2(g)} \tag{1}$$

However, if a reductant, e.g., coke, is added, the reaction temperatures can be shifted towards lower temperatures and coupling reactions such as that in Equation (2) can occur.

To provide an example for one certain lithium metal oxide, reference is made to Kwon and Sohn [47], who present a detailed thermokinetic study on the behavior of LCO. The decomposition of lithium carbonate (Li_2CO_3), shown in Equation (3), is known to take place in two steps. First, from solid Li_2CO_3, which is expected to play a minor role, and the majority after Li_2CO_3 is melted [28,46,49].

$$4\ LiMeO_{2(s)} + 3C_{(s)} \rightarrow 2\ Li_2CO_{3(s)} + 4\ MeO_{(s)} + CO_{2(g)} \tag{2}$$

$$Li_2CO_{3(s/l)} \rightarrow Li_2O_{(s)} + CO_{2(g)} \tag{3}$$

The further reaction of the metal oxide clearly depends on the type of cathode material that is examined. In general, we expect that the reduction of metal oxide can be direct or indirect, as shown in Equation (4) and Equation (5), respectively [28]:

$$4\ MeO_{(s/l)} + 2\ C_{(s)} \rightarrow 4\ Me_{(s/l)} + 2\ CO_{(g)} \tag{4}$$

$$4\ MeO_{(s/l)} + 2\ CO_{(g)} \rightarrow 4\ Me_{(s/l)} + 2\ CO_{2(g)} \tag{5}$$

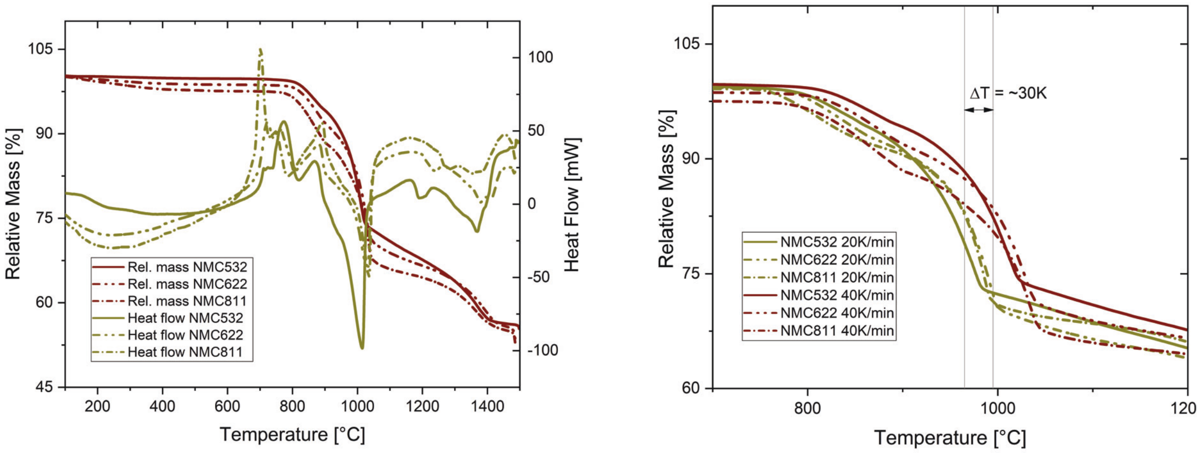
In case of NMC, i.e., $LiNi_xMn_yCo_zO_2$, we need to consider Ni, Co, and Mn, which have different oxygen potentials and call for different extents of reducing conditions. The reduction reaction of lithium oxide (Li_2O), formed during decomposition of Li_2CO_3, must also be considered. Thermodynamically, this reduction calls for higher temperatures and lower oxygen partial pressure values than for the other metals. If only thermodynamic considerations are made, we can expect nickel oxide and cobalt oxide to be reduced first. Manganese oxide, which can have various oxidation states and is reduced in several steps, is harder to predict. If Li_2O, which thermodynamically has the greatest requirements for its reduction, can be further reduced according to Equation (6), it should be possible to remove Li as a part of the gas phase, since the evaporation temperature of Li is only 1330 °C. This depends on whether sufficient reducing conditions can be reached or not.

$$Li_2O_{(s/l)} + C_{(s)} \rightarrow 2\ Li_{(g)} + CO_{(g)} \tag{6}$$

Said reducing conditions, namely high temperatures, low oxygen partial pressures (pO_2), and a high carbon monoxide (CO) to carbon dioxide (CO_2) ratio, must be provided by the InduMelt reactor. In this regard, the high temperatures of approximately 1550 °C and the excessive supply of carbon, see the Boudouard reaction in Equation (7), should be sufficient to maintain low pO_2 and high CO/CO_2 values [50].

$$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)} \tag{7}$$

However, from the statements above, we can make some preliminary assumptions on how the NMC variations with coke addition may react. Considering these, as well as the results from the STA, which are summarized in Figure 2, certain observations during the InduMelt experiments can be discussed and probably linked to certain reactions.



(**a**) (**b**)

Figure 2. Results of thermogravimetric analyses and differential scanning calorimetry of NMC532, NMC622, and NMC811 with a coke addition of 25 wt.% each. (**a**) Curve of relative sample mass and the corresponding heat flow with a heating rate of 40 K/min. (**b**) Comparison of relative sample mass curves with heating rates of 20 and 40 K/min.

At first sight of Figure 2a, it is worth mentioning that NMC532, NMC622, and NMC811 show a very similar behavior and share the same pattern. This indicates that the reaction scheme remains the same for all variants despite the significantly shifted ratios of Ni, Mn, and Co. As can be seen in Figure 2a, the first significant observation can be made at approximately 700 °C, where an exothermic peak without a corresponding change of the sample mass can be seen. The first main weight loss occurs between 800 and 1000 °C and is accompanied by a significant endothermic peak of the heat flow. In that phase, the sample mass drops by about 30%, which is most likely caused by the reduction reactions of the metal oxides, see Equations (4) and (5). In this regard, attention should be paid to the fact that at this point, the relative mass decrease of NMC532 is noticeably lower than for NMC622 and NMC811. It seems that the higher the main mass decrease is, the higher the relative content of Ni is. After the steepest slope, a transition phase with relative constant mass decrease develops before another, more intense phase between 1300 and 1400 °C occurs. Thereafter, the curve of the relative mass seems to flatten out. At the end of the analysis, at 1500 °C, the overall mass decrease summed up to 45%, 46%, and 47% for NMC532, NMC622, and NMC811, respectively. The overall weight loss is 5–7% less than the sum of all potential volatile components (n_V), which can be found in Table 1. This might be caused by insufficiently reducing conditions in the used laboratory analysis equipment that led to residual metal oxides, most likely containing Li or Mn.

From Figure 2b, it can be seen that there is a slight shift of reaction temperatures with varying heating rates of 20 and 40 $\text{K}\cdot\text{min}^{-1}$. For the interpretation of the InduMelt trials, where the heating rate is limited to less than 3.5 $\text{K}\cdot\text{min}^{-1}$, this effect needs to be considered.

3.2. InduMelt Experiments

In the InduMelt experiments, the cathode materials with 20 wt.% coke addition were heated to approximately 1500 °C under highly reducing conditions. As mentioned in Section 2, striking observations that could have been made during heating were noted for later discussion. The most important of these observations as well as the trend of the temperatures inside and outside of the reactor can be seen in Figure 3.

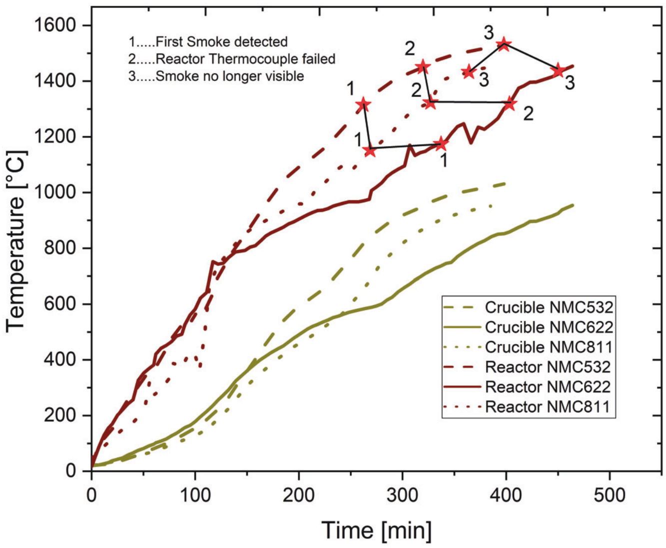


Figure 3. Curves of the temperature inside the reactor and at the outer wall of the crucible during carbo-thermal reduction experiments of NMC532, NMC622, and NMC811.

The first observation (1) that is highlighted in Figure 3 was the detection of visible flue gas leaving the reactor. The appearance of the flue gas was white to greyish, which might be caused by small particles. From other reduction experiments in the InduMelt, it is known that generated CO never resulted in a visible flue gas. Therefore, this observation indicates the removal of other gaseous reaction products or fine particles. However, the discussion on that will be continued in Section 3.3, where the gas phase is examined. For now, we wish to state that the phase of visible flue gas started at temperatures between 1100 and 1300 °C and ended between 1400 and 1500 °C, i.e., point (3) in Figure 3. By comparing this temperature range with the results of the STA, it can be seen that the detected flue gas corresponds to either the constant or the second steeper mass decrease between 1100 and 1400 °C rather than to the main change of the sample mass starting at 800 °C. Combined with the knowledge of the reaction kinetics and the high-temperature behavior of NMC cathode materials, we can assume that the observed flue gas might be related to reactions including Mn and Li.

To clarify this and to examine the original research question, namely the investigation of possible recovery rates for Ni, Co, Mn, and Li with the desired reactor concept, hereinafter, a detailed look at the obtained products is provided. In general, it was possible to distinguish between the following product phases after each of the experiments. Table 2 provides an overview on the masses of the charged input material and all obtained products that remained in the reactor.

- Metal phase, which occurs as small metal spheres on the graphite cubes and bigger accumulations at the bottom of the reactor.
- Slag phase, which can be found as thin, layered depositions on the graphite cubes.
- Powder phase, which is left after sieving and magnetic separation.
- Gas phase, which is not fully collected but is defined by the composition of the solution in the gas scrubber.

Table 2. Overview of the masses of the input material and the obtained products in each of the InduMelt experiments (mass, g).

Sample/Product	Input	Metal	Slag	Powder	Product Sum
NMC532	502.3	197	24	24.8	245.8
NMC622	500.6	206	18.9	36.8	261.7
NMC811	501.5	203.8	3.3	44.2	251.3

The metal phase is the largest contributor to the products in all conducted experiments and accounts for 77% to 80% of the found products. The amount of slag that was found differs noticeably more. In NMC811, only 3.3 g of slag was found, whereas in NMC532, the slag phase accumulated to 24 g. Thus, the slag phase contributes between 1.3% and 9.7% to the product sum. The mass of the obtained powder is again more uniform and accounts for 10% to 17% of the products. All in all, the mass loss that was observed in the experiments was 51.1%, 47.7%, and 49.9% for NMC532, NMC622, and NMC811 respectively, and therefore up to 6% higher than in the STA.

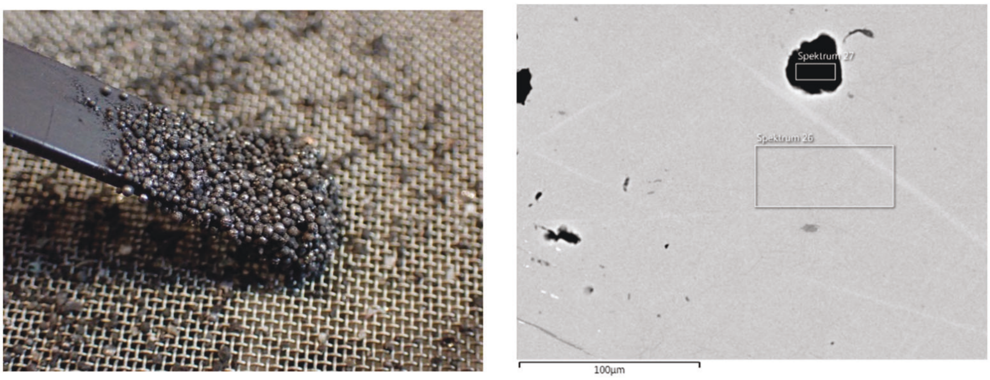
The detailed examination of the products starts with the metal phase, the chemical composition of which can be found in Table 3.

Table 3. Chemical composition of the obtained metal phase in the conducted experiments (mass fraction, wt.%).

Sample/Elements	**Li**	**Ni** [2]	**Mn** [2]	**Co** [2]
NMC532 [1]	0.05%	52.00%	28.50%	20.10%
NMC622 [1]	0.05%	64.70%	18.40%	19.90%
NMC811 [1]	0.06%	86.60%	9.00%	10.10%

[1] All values were measured using ICP-MS. [2] Slight over-determination due to weighted consideration of residuals from the aqua regia digestion.

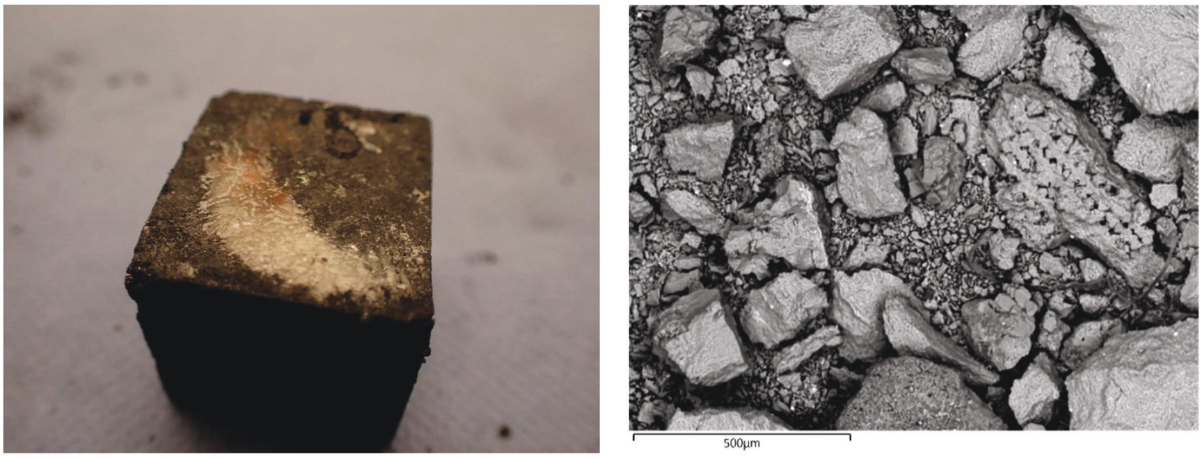
In terms of that, it can be stated that the chemical composition of the metal phase follows the expectations and consists mainly of Ni, Co, and Mn. For all trials, the ratio Ni:Mn:Co also correlates very well with the stochiometric ratio of the respective input material. Accordingly, only the proportion of Mn is somewhat lower than it actually should be, which might be caused by its more complex reaction behavior. Regarding the fourth metal of interest, Li, there is almost no accumulation in the metal phase, which is in line with our assumption that Li would rather be in a gaseous state instead of being a part of the metal alloy. In Figure 4a, an image of the small metal spheres is shown. The majority of the produced metal was found in this form, but there were also some bigger accumulations at the reactor bottom. In the SEM image in Figure 4b, two areas are highlighted, the darker of which (indicated with "Spektrum 27") consists almost exclusively of carbon. In the brighter spectrum (indicated with "Spektrum 27"), the conducted elemental analysis revealed a similar result as the ICP-MS analysis of the NMC622 metal phase. The metals in that area consists of 60.6 wt.% Ni, 20.0 wt.% Mn, and 19.4 wt.% Co. Therefore, the SEM analysis has shown that C mainly occurs sporadically as a particle enclosed in the metal phase. The statement regarding chemical composition and accumulation of the metallic products as well as the description of their optical appearance also applies for the experimental series with NMC532 and NMC811.



(**a**) (**b**)

Figure 4. (**a**) Accumulation of metal spheres on a magnetic tape during sampling of NMC622. (**b**) SEM image of the metal surface of NMC622 under 500-fold zoom, with "Spektrum 27" and "Spektrum 28" being elemental analysis points.

Metals that are not fully reduced during the experiment, and thus are still metal oxides, are expected to form a slag. Since we aimed to investigate possible recovery rates for said metals, the examination of the slag phase, illustrated in Figure 5a,b, can provide information on which of the metals still have potential for improvement.



(**a**) (**b**)

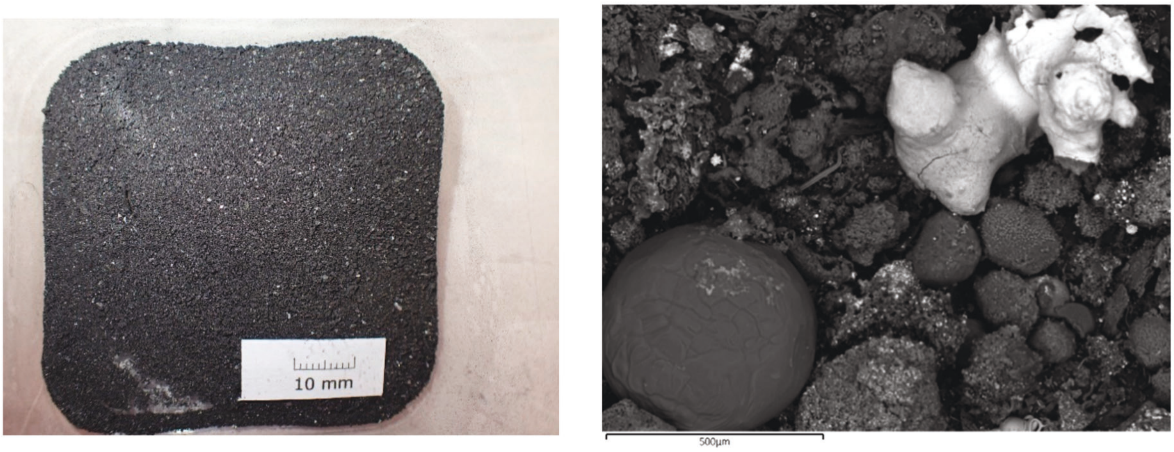
Figure 5. (**a**) Thin, layered slag deposition on a graphite cube from the experiment NMC622. (**b**) SEM image of the slag phase from NMC622 under 100-fold zoom.

Most of the slag that was found after the InduMelt experiments accumulated as a thin slag layer on the graphite cubes, as is shown in Figure 5a. Some small slag depositions on the inner wall of the ceramic crucible were also found and taken into account for the mass balance. The results of the ICP-MS analysis of the obtained slag phase in each of the trials can be seen in Table 4. Relating to the four metals of interest in NMC cathode materials, Li is the largest contributor to the produced slag phase and has a mass content of between 6.3% and 7.3%. Most likely, Li is found as Li_2O, which was formed during the thermal decomposition of Li_2CO_3 but not further reduced. However, other compounds cannot be completely ruled out either. For Ni, the mass content of which is laying between 2.5% and 3.7%, it is harder to assume in which form it is bound in the slag. It could be very fine metallic particles, unreduced nickel oxide, or even residual NMC, which for some reason has not reacted. The same accounts for Co and Mn, which contribute between 0.3% and 2% to the composition of the slag phase. However, analogous to the metal phase composition, the ratio of Ni, Co, and Mn is again approximately correlated to that in the respective original cathode material.

Table 4. Content of metals of interest in the obtained slag phase (mass fraction, wt.%).

Sample/Elements	Li	Ni	Mn	Co
NMC532	7.26%	3.65%	1.99%	1.48%
NMC622	6.30%	2.48%	0.80%	0.80%
NMC811	7.34%	2.77%	0.40%	0.33%

The third product that was found was the so-called powder phase, which is shown in Figure 6a,b. The powder phase is expected to consist of fine particles of both the metal and the slag phase, as well as carbon from the graphite cubes caused by abrasion during the product examination.



(**a**) (**b**)

Figure 6. (**a**) Image of the remaining powder after the product examination of the NMC622 trial. (**b**) SEM image of the powder phase from NMC622 under 100-fold zoom.

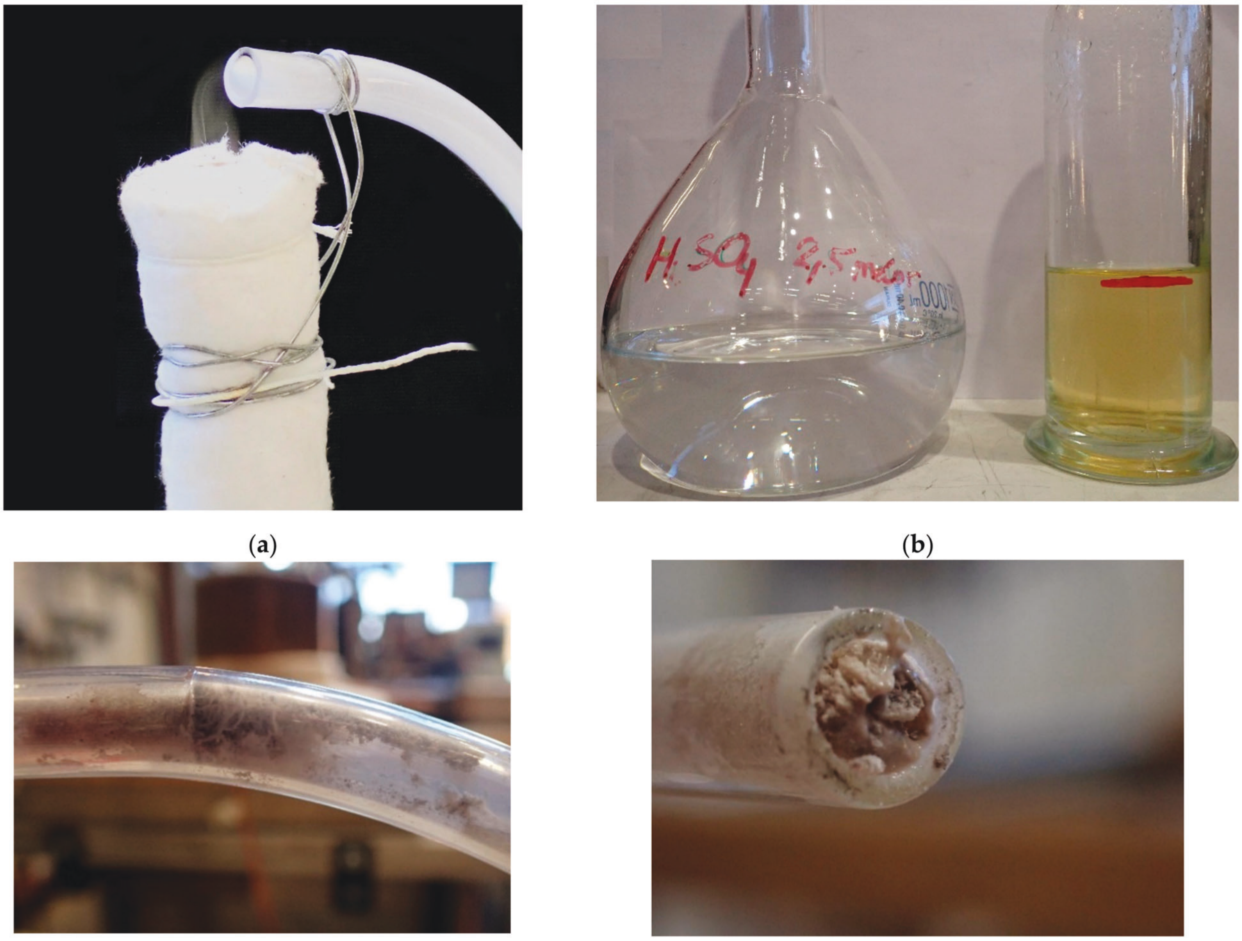
This assumption is also supported by a glance at the chemical composition of the powder phase, presented in Table 5. The largest contributor to the powder phase with a mass content of approximately 26 wt.% is carbon, which mainly results from the abrasion of the graphite cubes and leftover reducing agent, i.e., coke. Besides carbon, significant amounts of Ni, Mn, Co, and Li can also be found in the powder phase. The fact that these are remnants of the original NMC material can be ruled out based on the temperatures reached. An XRD analysis performed in parallel with the SEM also revealed that there was no detection of the original lithium metal oxide pattern anymore.

Table 5. Content of metals of interest in the obtained powder fraction in the InduMelt experiments (mass fraction, wt.%).

Sample/Elements	Li	Ni	Mn	Co	C
NMC532	1.10%	13.80%	8.70%	6.19%	25.50%
NMC622	1.09%	15.40%	5.21%	5.68%	26.60%
NMC811	1.13%	16.20%	1.69%	2.01%	25.60%

On closer inspection, the components apart from the C are probably mainly very small metal spheres, some of which are contaminated with slag and have therefore not been separated by the magnet. In contrast to the metal phase, which was obviously an alloy without slag inclusions, part of the manganese may still be present in the powder as an oxide, thus making magnetic separation more difficult and causing the issue. A clear identification, for example by further separation of metal and slag, is not feasible due to the small particle size. In the final determination of the recovery rates, however, the powder fraction is nevertheless considered.

The last product that needs to be discussed is the gas phase; thus, all gaseous reaction products and particles that left the reactor via the flue gas pipe. To visualize said product phase, a series of images is presented in Figure 7. Here, Figure 7a illustrates the already described observation (visible gas leaving the reactor) between 1100 and 1500 °C. In Figure 7b, the significant optical change of the scrubbing medium can be seen. Besides the visible gas, this was the second indicator for gaseous products, other than CO, leaving the reactor. The third indicator of this event can be seen in Figure 7c,d, where deposits inside the gas pipe are shown.



(**a**) (**b**)

(**c**) (**d**)

Figure 7. Images related to the gas phase. (**a**) Visible flue gas leaving the InduMelt reactor in the NMC532 experiment. (**b**) Gas scrubbing medium (H_2SO_4) before and after the experiment. (**c**,**d**) Deposits and clogging inside the gas pipe to the gas scrubber.

In order to obtain certainty about the cause of the above observations, both the deposits inside the gas tube as well as the gas scrubbing medium were analyzed. The results of these ICP-MS analyses are shown in Tables 6 and 7.

Table 6. Results of the ICP-MS analysis for Li, Ni, Mn, and Co of the H_2SO_4 acid in the gas scrubber after the InduMelt experiments (concentration, mg L^{-1}).

Sample/Elements	Li	Ni	Mn	Co
NMC532	1120.00	0.65	220.00	0.36
NMC622	1400.00	0.54	21.00	0.08
NMC811	820.00	1.30	36.00	0.19

Table 7. Chemical composition of the deposition in the flue gas tube which accumulated during the InduMelt experiments (mass fraction, wt.%).

Sample [1]/Elements	Li	Ni	Mn	Co
NMC532	8.26%	<0.01%	0.10%	<0.01%
NMC622	8.43%	<0.01%	1.97%	<0.01%

[1] In the experiment with NMC811, there was not enough deposition to obtain a representative sample for the ICP-MS analysis.

If we concentrate again on the four metals of interest in the NMC cathode materials, it can be seen that Li accumulated by far the most in the gas phase-related products. The amount of Li that was found in the scrubber medium is umpteen times higher than that of Ni or Co, which show almost no accumulation. For NMC622 for example, the value of Li measured was 1400 mg L^{-1}, which is more than 2000 times the value of Ni and Co. In comparison to that, the value for Mn lays between 20 and 220 mg L^{-1}, thus also showing a significant enrichment. If we now have a closer look at Table 7, we can see that this supports the first measurement. Additionally, for the deposition in the flue gas tube (see Figure 7c,d), Li is the most prominent of the desired metals, followed by Mn. For Ni and Co, the value was below the determination limit.

Finally, the results of the product examination are summarized in Figure 8, which will be used to discuss possible recovery rates.

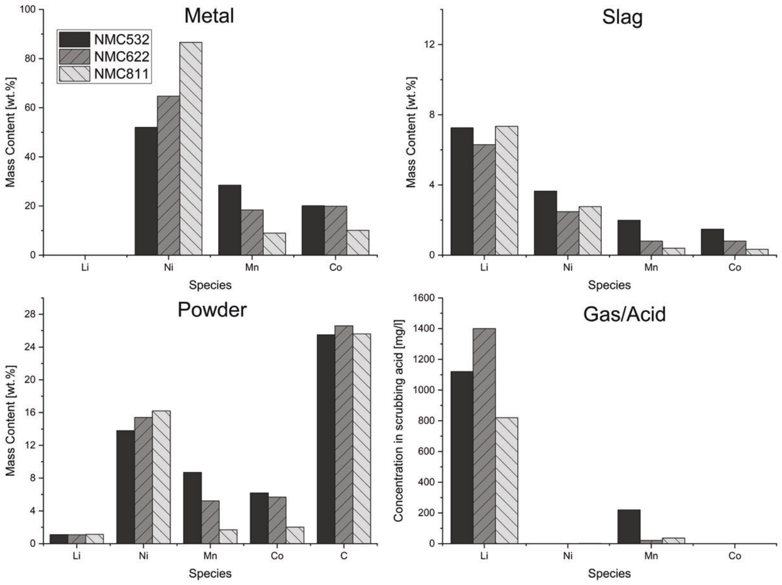


Figure 8. Overview on the analysis results for Ni, Mn, Co, and Li in the obtained product phases (metal, slag, powder, and gas) of the InduMelt experimental series.

3.3. Evaluation of Possible Recovery Rates

To finally derive potential recovery rates, we now need to combine the knowledge gained and the results from the previous sections. The key point is to relate the chemical analyses of the products to their mass, which was presented in Table 3. From that, it is possible to see to which extent the metals accumulated in a certain product phase and it can be discussed weather this is favorable for recycling operations or not. The result of this examination is summarized in Figure 9, which shows the transfer coefficients of Ni, Mn, Co, and Li in the different product phases. Since a complete mass balance is not possible because of the difficult product sampling and the fact that only a partial flue gas stream was used for analysis, we also need to consider that certain amounts of the metals were lost during the experimental procedure. This is indicated by adding “Not found” to the gas phase label, meaning that not everything which was not found in either the slag, powder, or metal phase was necessarily removed via the gas phase.

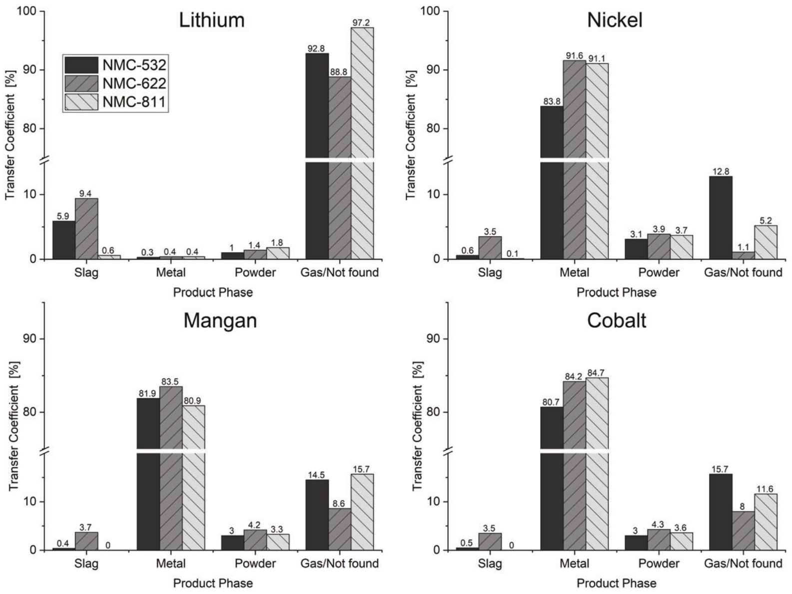


Figure 9. Overview of the transfer coefficients (= percentage of originally charged amount) of Li, Ni, Mn, and Co into the product phases during the InduMelt experiments with NMC532, NMC622, and NMC811.

To continue the discussion on sampling accuracy and the significance of the results, it is best to start the final evaluation with Ni and Co. Due to their properties and the given conditions of the reactor, both metals are expected to be fully reduced and therefore be almost exclusively transferred into the metal phase. In fact, Figure 9 reveals that between 83% and 92% of Ni and between 81% and 85% of Co were transferred into the metal phase. Despite NMC622, in which 3.5% of Ni and Co was found in the slag, there was no significant accumulation of Ni and Co in the slag phase. In the powder phase, the transfer coefficient for both Ni and Co lays between 3% and 4%. There, the majority is still considered to be metallic but just not separated due to the aforementioned reasons. However, there is also a significant amount of Ni and Co that is not found in these product phases. We can see that between 1% and 12% of the originally charged Ni and up to 15.7% of the originally charged Co were lost. In that regard, the value of Ni is always lower than that of Co. This is particularly distinct in the trial with NMC622. Based on the analyses in Tables 6 and 7, it can be excluded that parts of the metals were removed via the gas phase. In the case of Co, a strong reaction with the alumina sample holders could already be observed in previous analyses under the heating microscope. It is therefore possible that parts of Co reacted with the alumina ceramic crucible and are therefore missing from the mass balance. Furthermore, reactions with the porous mortar at the bottom of the reactor cannot be completely ruled out and could potentially cause further Ni and Co losses. However, since there are no analyses of the mortar, we need to generally consider a certain inaccuracy in our conclusions and must be particularly critical of absolute values.

If we look at the results for Mn, we see that again, the majority, i.e., between 80.9% and 83.5% of the amount fed, was transferred in the metal phase. Additionally, the transfer coefficients in the slag and powder are comparable to those of Ni and Co. Regarding the "gas/not found" phase, Mn has a significantly higher value than Ni and a similar or slightly higher value than Co. The higher proportion of Mn in this phase again supports previous measures in which Mn was also detected to a significant degree in the scrubbing medium and the deposits in the flue gas pipe. However, the underlying reaction or mechanism that particularly causes the Mn gasification is not yet clarified and needs further attention. The pattern in the diagram of Li is very clearly different from the others. Less than 0.5% of the charged Li was found in the metal phase. In the powder phase, which is assumed to partly consist of the metal alloy, the accumulation of Li is also correspondingly low, namely between 1% and 2%. Between 0.6% and 9.4% of the Li was found in the slag phase, which is much lower than in conventional pyrometallurgical recycling approaches. Between 88.8% and 97.2% of the charged Li was not found in the reactor after the experiments. Even if these numbers are not to be understood as definite, absolute values due to the problem of complete sampling, a clear trend can be shown and concluded.

4. Conclusions

The work presented in this paper aimed to investigate the possible recovery rates of Li, Ni, Co, and Mn from spent NMC-type LIBs with an unconventional, pyrometallurgical reactor approach. The results showed that, comparable to other pyrometallurgical approaches, recovery rates of at least 80% for Co and over 90% for Ni are achievable. Thus, both metals are mostly transferred to the metal phase, where they form a metal alloy with Mn, which generally shows a more complex behavior and is partly removed from the reactor via the flue gas. As in other pyrometallurgical processes, the Ni-Co-Mn alloy is assumed to need a further refining step before it can be utilized in battery manufacturing again.

The metal that is considered to be the most challenging to be recovered pyrometallurgically is Li. While Li is slagged and not available for functional recycling in so far established pyrometallurgical processes, less than 10% of Li was found in the slag phase in our experiments. The major part, on the other hand, was removed from the reactor via the gas phase and thus separated from the other metals. This can result in new approaches for the simultaneous recovery of all valuable metals. To further advance these efforts, it is planned to improve the gas analysis and sampling. By temporally divided sampling of the exhaust gas, which is linked to the observations of this work, more can be learned about the mechanism of lithium gasification, and thus, possible improvements can be derived. Furthermore, detailed thermodynamic and thermokinetic considerations as well as extended analyses of the product phases need to be conducted to improve our understanding of the reactions that take place. In addition, more focus is to be placed on the further processing of the obtained products and to investigate the way in which the InduRed concept can efficiently contribute to future LIB recycling chains.

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References

1. European Commission. Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0474&from=EN (accessed on 10 February 2021).
2. European Commission. Directorate general for internal market, industry, entrepreneurship and SMEs. In *Study on the EU0′s List of Critical Raw Materials (2020): Final Report*; Publications Office: Luxembourg, 2020.

3. Tsiropoulos, I.; Tarvydas, D.; Lebedeva, N. *Li-Ion Batteries for Mobility and Stationary Storage Applications: Scenarios for Costs and Market Growth*; Publications Office: Luxembourg, 2018.
4. European Commission. Regulation of the European Parliament and the Council Concerning Batteries and Waste Batteries, Repealing Directive 2006/66/EC and Amending Regulation (EU) No2019/1020. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020PC0798 (accessed on 17 November 2021).
5. Windisch-Kern, S.; Holzer, A.; Ponak, C.; Raupenstrauch, H. Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept. *Processes* **2021**, *9*, 84. [CrossRef]
6. Sita, L.E.; Da Silva, S.P.; Da Silva, P.R.C.; Scarminio, J. Re-synthesis of LiCoO 2 extracted from spent Li-ion batteries with low and high state of health. *Mater. Chem. Phys.* **2017**, *194*, 97–104. [CrossRef]
7. Sommerville, R.; Shaw-Stewart, J.; Goodship, V.; Rowson, N.; Kendrick, E. A review of physical processes used in the safe recycling of lithium ion batteries. *Sustain. Mater. Technol.* **2020**, *25*, e00197. [CrossRef]
8. Poyraz, A.S.; Huang, J.; Cheng, S.; Bock, D.C.; Wu, L.; Zhu, Y.; Marschilok, A.C.; Takeuchi, K.J.; Takeuchi, E.S. Effective recycling of manganese oxide cathodes for lithium based batteries. *Green Chem.* **2016**, *18*, 3414–3421. [CrossRef]
9. Jung, J.C.-Y.; Sui, P.-C.; Zhang, J. A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments. *J. Energy Storage* **2021**, *35*, 102217. [CrossRef]
10. Larouche, F.; Tedjar, F.; Amouzegar, K.; Houlachi, G.; Bouchard, P.; Demopoulos, G.P.; Zaghib, K. Progress and Status of Hydrometallurgical and Direct Recycling of Li-Ion Batteries and Beyond. *Materials* **2020**, *13*, 801. [CrossRef]
11. Ganesh, A.; Subramaniam, P.; Kaur, A.; Vaidyanathan, L. *Comparison of Hydrometallurgical and Hybrid Recycling Processes for Lithium-ion Battery: An Environmental and Cost Analysis*; Research Square: Durham, NC, USA, 2021.
12. Zhang, P.; Yokoyama, T.; Itabashi, O.; Suzuki, T.M.; Inoue, K. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy* **1998**, *47*, 259–271. [CrossRef]
13. Takacova, Z.; Havlik, T.; Kukurugya, F.; Orac, D. Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach. *Hydrometallurgy* **2016**, *163*, 9–17. [CrossRef]
14. Contestabile, M.; Panero, S.; Scrosati, B. A laboratory-scale lithium-ion battery recycling process. *J. Power Sources* **2001**, *92*, 65–69. [CrossRef]
15. Dorella, G.; Mansur, M.B. A study of the separation of cobalt from spent Li-ion battery residues. *J. Power Sources* **2007**, *170*, 210–215. [CrossRef]
16. Chen, L.; Tang, X.; Zhang, Y.; Li, L.; Zeng, Z.; Zhang, Y. Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy* **2011**, *108*, 80–86. [CrossRef]
17. Ferreira, D.A.; Prados, L.M.Z.; Majuste, D.; Mansur, M.B. Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries. *J. Power Sources* **2009**, *187*, 238–246. [CrossRef]
18. Pinna, E.G.; Ruiz, M.C.; Ojeda, M.W.; Rodriguez, M.H. Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors. *Hydrometallurgy* **2017**, *167*, 66–71. [CrossRef]
19. Chen, X.; Ma, H.; Luo, C.; Zhou, T. Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid. *J. Hazard. Mater.* **2017**, *326*, 77–86. [CrossRef]
20. Li, L.; Ge, J.; Wu, F.; Chen, R.; Chen, S.; Wu, B. Recovery of cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. *J. Hazard. Mater.* **2010**, *176*, 288–293. [CrossRef]
21. Musariri, B.; Akdogan, G.; Dorfling, C.; Bradshaw, S. Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries. *Miner. Eng.* **2019**, *137*, 108–117. [CrossRef]
22. Sun, L.; Qiu, K. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. *Waste Manag.* **2012**, *32*, 1575–1582. [CrossRef]
23. Zeng, X.; Li, J.; Shen, B. Novel approach to recover cobalt and lithium from spent lithium-ion battery using oxalic acid. *J. Hazard. Mater.* **2015**, *295*, 112–118. [CrossRef]
24. Nayaka, G.P.; Manjanna, J.; Pai, K.V.; Vadavi, R.; Keny, S.J.; Tripathi, V.S. Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids. *Hydrometallurgy* **2015**, *151*, 73–77. [CrossRef]
25. Nayaka, G.P.; Pai, K.V.; Santhosh, G.; Manjanna, J. Dissolution of cathode active material of spent Li-ion batteries using tartaric acid and ascorbic acid mixture to recover Co. *Hydrometallurgy* **2016**, *161*, 54–57. [CrossRef]
26. Nayaka, G.P.; Pai, K.V.; Santhosh, G.; Manjanna, J. Recovery of cobalt as cobalt oxalate from spent lithium ion batteries by using glycine as leaching agent. *J. Environ. Chem. Eng.* **2016**, *4*, 2378–2383. [CrossRef]
27. Chen, X.; Fan, B.; Xu, L.; Zhou, T.; Kong, J. An atom-economic process for the recovery of high value-added metals from spent lithium-ion batteries. *J. Clean. Prod.* **2016**, *112*, 3562–3570. [CrossRef]
28. Makuza, B.; Tian, Q.; Guo, X.; Chattopadhyay, K.; Yu, D. Pyrometallurgical options for recycling spent lithium-ion batteries: A comprehensive review. *J. Power Sources* **2021**, *491*, 229622. [CrossRef]
29. Hendrickson, T.P.; Kavvada, O.; Shah, N.; Sathre, R.; D Scown, C. Life-cycle implications and supply chain logistics of electric vehicle battery recycling in California. *Environ. Res. Lett.* **2015**, *10*, 14011. [CrossRef]
30. Werner, D.; Peuker, U.A.; Mütze, T. Recycling Chain for Spent Lithium-Ion Batteries. *Metals* **2020**, *10*, 316. [CrossRef]
31. Huang, B.; Pan, Z.; Su, X.; An, L. Recycling of lithium-ion batteries: Recent advances and perspectives. *J. Power Sources* **2018**, *399*, 274–286. [CrossRef]

32. Yin, H.; Xing, P. Pyrometallurgical routes for the recycling of spent lithium-ion batteries. In *Recycling of Spent Lithium-Ion Batteries*; An, L., Ed.; Springer International Publishing: Cham, Switzerland, 2019; ISBN 978-3-030-31833-8.
33. Accardo, A.; Dotelli, G.; Musa, M.L.; Spessa, E. Life Cycle Assessment of an NMC Battery for Application to Electric Light-Duty Commercial Vehicles and Comparison with a Sodium-Nickel-Chloride Battery. *Appl. Sci.* **2021**, *11*, 1160. [CrossRef]
34. Windisch-Kern, S.; Holzer, A.; Ponak, C.; Hochsteiner, T.; Raupenstrauch, H. Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach. *Carbon Resour. Convers.* **2021**, *4*, 184–189. [CrossRef]
35. Arbizzani, C.; Gabrielli, G.; Mastragostino, M. Thermal stability and flammability of electrolytes for lithium-ion batteries. *J. Power Sources* **2011**, *196*, 4801–4805. [CrossRef]
36. Huang, Y.; Lin, Y.-C.; Jenkins, D.M.; Chernova, N.A.; Chung, Y.; Radhakrishnan, B.; Chu, I.-H.; Fang, J.; Wang, Q.; Omenya, F.; et al. Thermal Stability and Reactivity of Cathode Materials for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7013–7021. [CrossRef]
37. Martha, S.K.; Haik, O.; Zinigrad, E.; Exnar, I.; Drezen, T.; Miners, J.H.; Aurbach, D. On the Thermal Stability of Olivine Cathode Materials for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2011**, *158*, A1115. [CrossRef]
38. Peng, P.; Jiang, F. Thermal safety of lithium-ion batteries with various cathode materials: A numerical study. *Int. J. Heat Mass Transf.* **2016**, *103*, 1008–1016. [CrossRef]
39. Wang, L.; Maxisch, T.; Ceder, G. A First-Principles Approach to Studying the Thermal Stability of Oxide Cathode Materials. *Chem. Mater.* **2007**, *19*, 543–552. [CrossRef]
40. Furushima, Y.; Yanagisawa, C.; Nakagawa, T.; Aoki, Y.; Muraki, N. Thermal stability and kinetics of delithiated $LiCoO_2$. *J. Power Sources* **2011**, *196*, 2260–2263. [CrossRef]
41. Zheng, X.; Zhu, Z.; Lin, X.; Zhang, Y.; He, Y.; Cao, H.; Sun, Z. A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. *Engineering* **2018**, *4*, 361–370. [CrossRef]
42. He, Y.; Yuan, X.; Zhang, G.; Wang, H.; Zhang, T.; Xie, W.; Li, L. A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries. *Sci. Total Environ.* **2020**, *766*, 142382. [CrossRef]
43. Li, J.; Li, X.; Hu, Q.; Wang, Z.; Zheng, J.; Wu, L.; Zhang, L. Study of extraction and purification of Ni, Co and Mn from spent battery material. *Hydrometallurgy* **2009**, *99*, 7–12. [CrossRef]
44. Li, L.; Zhai, L.; Zhang, X.; Lu, J.; Chen, R.; Wu, F.; Amine, K. Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. *J. Power Sources* **2014**, *262*, 380–385. [CrossRef]
45. Mossali, E.; Picone, N.; Gentilini, L.; Rodrìguez, O.; Pérez, J.M.; Colledani, M. Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments. *J. Environ. Manag.* **2020**, *264*, 110500. [CrossRef]
46. Mao, J.; Li, J.; Xu, Z. Coupling reactions and collapsing model in the roasting process of recycling metals from $LiCoO_2$ batteries. *J. Clean. Prod.* **2018**, *205*, 923–929. [CrossRef]
47. Kwon, O.; Sohn, I. Fundamental thermokinetic study of a sustainable lithium-ion battery pyrometallurgical recycling process. *Resour. Conserv. Recycl.* **2020**, *158*, 104809. [CrossRef]
48. Pindar, S.; Dhawan, N. Carbothermal Reduction of Spent Mobile Phones Batteries for the Recovery of Lithium, Cobalt, and Manganese Values. *JOM* **2019**, *71*, 4483–4491. [CrossRef]
49. Shi, L.; Qu, T.; Liu, D.; Deng, Y.; Yang, B.; Dai, Y. Process of Thermal Decomposition of Lithium Carbonate. In *Materials Processing Fundamentals 2020*; Lee, J., Wagstaff, S., Lambotte, G., Allanore, A., Tesfaye, F., Eds.; Springer International Publishing: Cham, Switzerland, 2020; pp. 107–116, ISBN 978-3-030-36555-4. [CrossRef]
50. Mianowski, A.; Radko, T.; Siudyga, T. The reactivity of cokes in Boudouard–Bell reactions in the context of an Ergun model. *J. Therm. Anal. Calorim.* **2015**, *122*, 1013–1021. [CrossRef]

4 Summary of Results

First of all, it was proven that the atmospheric conditions in the heating microscope were sufficient for the desired reduction reactions to occur, which was indicated by metallic residues on the sample plates after all experiments with carbon addition. All layer structured cathode materials, thus LCO, NCA and NMC, showed similar behaviour. Between 650°C and 900°C, a distinct first change of the cross-sectional area (CSA) was observed in all of those materials.

Another protruding change starts at between 1350°C and 1550°C, which correlates with the melting points of the produced metal alloy. In this regard, the melting temperature is shifted towards lower temperatures with increasing Ni content in the sample. However, from a process design point of view, the first temperature range is more important as these changes are likely to result from the carbothermic reduction reactions.

If compared with the first changes in experiments without carbon addition, a significant shift of the temperature range from between 650 and 900°C towards 850°C and 1000°C can be seen. The thermal dissociation of the cathode materials is responsible for these initial changes in the test without carbon addition and only occurs at distinctly higher temperatures than the reduction reactions. This finding is of great importance for further considerations, especially when evaluating the influence of pre-treatment processes, and will be discussed later.

The second rapid CSA change, which, as discussed, is due to the melting of the metal phase and leads to final relative CSA values of 20%-50%, does not occur in the experiments without carbon addition, as expected. Table 3 summarizes the described results from the heating microscope experiments with carbon addition and shows the main temperature ranges in which changes were observed.

Table 3: Summary of results of heating microscope analysis with carbon addition.

Sample*	Temperature ranges with maximum rate of CSA change	CSA value at 1550°C [%]
NCA	750°C – 825°C, ~1450°C	23.9%
NMC111	800°C – 850°C, ~1550°C	20.3%
NMC532	700°C – 800°C, 1500°C – 1550°C	36.2%
NMC622	~750°C, 1375°C – 1400°C	28.1%
NMC811	650°C – 750°C, 1350°C – 1400°C	33.2%
LFP	~1050°C, 1200°C – 1400°C	19.6%
LCO	850°C – 950°C, ~1525°C	48.5%
BM	550°C – 700°C	115.0%

*) For an explanation of terms, reference is made to Table 1.

In addition to the evaluation of temperature ranges in which the reactions occur, the heating microscope experiments revealed a clearly deviating behaviour of black matter. It was noticed that temperature ranges and corresponding CSA changes do not correlate with what was expected from the chemical composition and the observations with factory-new cathode materials. With black matter, the characteristic first decrease of the CSA was not observed. Perhaps this is due to the presence of a considerable amount of aluminium and copper in the black matter. Furthermore, despite having a carbon content that is significantly higher than stoichiometrically necessary, there was no sign that any reduction reactions occurred at all.

The erratic behaviour between BM and the cathode materials, as well as the difference between analyses with and without carbon addition, was also confirmed by the STA results. Upon addition of carbon, the thermogravimetric analysis shows a mass loss of 10-25 % in a temperature range of 1000-1200 °C for NCA, NMC and LCO, which deviates from the temperature ranges in which CSA changes were observed. From that, it can be concluded that the first CSA change is more likely to be caused by structural changes, phase transitions, or partial melting of the sample than by carbothermal reduction, which inevitably results in a mass loss.

On the other hand, in the series without carbon addition, much lower or hardly any mass losses were observed, which is in line with the expectations drawn from the literature research. Furthermore, it was seen that the olivine structured LFP cathode material varies significantly regarding the temperature range in which the reactions occur and the extent of observed changes. Since it is expected that LFP will have an increasing market share in the future, this is something that needs to be further considered. Analogous to the results from the heating microscope, the most important above-described data are summarized in Table 4.

Table 4: Overview of the results of the thermogravimetric analysis.

Sample**	**Temperature range with maximum rate of mass loss**	**Relative mass value at 1550°C [w.-%]**
NCA*	1025°C – 1100°C	71.9%
NMC111*	1000°C – 1220°C	73.9%
NMC532	950°C – 1025°C	55.9%
NMC622	950°C – 1025°C	53.4%
NMC811	950°C – 1025°C	52.9%
LFP*	1500°C – 1525°C	72.6%
LCO*	1000°C – 1275°C	83.3%

*) TGA and DSC analysis have been conducted using Al2O3 crucibles, which later turned out to affect the results due to undesired reactions negatively.

**) For an explanation of terms, reference is made to Table 1.

Additionally, one problem that became apparent in the STA has been the chemical reaction between the emerging metal phase and the aluminium oxide (Al_2O_3) ceramics of which the sample plates and crucibles are made. From that, it can be concluded that the Al_2O_3 ceramic crucibles that ought to be used for the experiments in the InduMelt reactor must be reconsidered.

In conclusion, most expectations made upon literature research were met by the results of Thermal analysis. However, the substantial difference between black matter and the factory-new cathode materials was unforeseen and requires further consideration. The most obvious explanation for the difference in the behaviour was the distinction in their chemical composition. At that point, an undesired reaction between the cathodic metals and residual copper and aluminium was made exclusively responsible for the unexpected deviations that could have been measured in the heating microscope. With ongoing investigations and more knowledge about the actual chemical reaction at certain temperatures, the pre-treatment process itself came more and more in focus. At the end of the day, the preliminary analyses were of great importance for the design of experiments in the later phase of the project. Furthermore, the varying data measured for black matter has initiated research in the direction of process-technical interrelationships, which was the second sub-area of the research project.

Thus, the third paper illustrated the severe impact that certain processes could have on the quality of the produced black matter. In particular, the conditions during thermal pre-treatment, such as high temperatures or oxidizing conditions, have been shown to have a severe influence on the physical-chemical properties of intermediates. Moreover, it was found that segregation after mechanical processing needs to be considered as a crucial step since the presence of certain components (e.g., aluminium or copper residues) might limit the efficiency of subsequent metal recovery processes. In general, the study suggests that current recycling technologies need to be better coordinated to determine the quality of black matter better. Since the InduRed process requires this black matter as a feedstock, defined grades, as well as information about the processing history, are indispensable to be able to design the process efficiently and to achieve the targeted recovery rates.

In the third research sub-area, a lab-scale version of the InduRed reactor was used to evaluate achievable recovery rates. Beside investigating recycling rates, the experiments also aimed to evaluate product qualities, identify the reactor design's drawbacks, and recognize possibly necessary process adjustments. In summary, four main product phases could have been obtained in the InduMelt experiments, namely a metal, a slag, a powder, and a gas phase. In the fourth paper, NCA and NMC111, as well as black matter were first tested, and tendencies for transfer coefficients of Ni, Co, Mn and Li could have been drawn.

The possibility to also analyze the gas phase and therefore improve the quality of the mass balance was only added in later experiments, in which NMC532, NMC622 and NMC811 were examined, and the results of which were presented in the fifth paper. The corresponding results are provided in Table 5. The temperature ranges of reduction reactions were confirmed in the InduMelt experiments and were identified by certain observations, e.g., visible off-gas. The reactions between products and the Al_2O_3 ceramic crucible, comparable to those that already occurred in the thermal analyses, were also noticeable. A holistic discussion of all results is carried out in the next chapter.

Table 5: Potential recovery rates for each cathodic metal as examined in the InduMelt experiments

Sample*/Metal	**Nickel**			**Cobalt**			**Lithium**			**Manganese**		
Product phase	**Metal**	**Slag**	**Removed**	**Metal**	**Slag**	**Removed**	**Metal**	**Slag**	**Removed**	**Metal**	**Slag**	**Removed**
NCA	>95%	<0.1%	<0.1%	61.2%	<0.1%	<0.1%	0.4%	2.9%	>95%-	-	-	-
NMC111	93.0%	<0.1%	6.9%	87.0%	<0.1%	12.9%	0.6%	8.7%	90.8%	72.7%	1.2%	26.1%
NMC532	83.8%	0.6%	12.8%	80.7%	0.5%	15.7%	0.3%	5.9%	92.3%	81.9%	0.4%	14.5%
NMC622	91.6%	3.5%	1.1%	84.2%	3.5%	8.0%	88.8%	9.4%	88.8%	83.5%	3.7%	8.6%
NMC811	91.1%	<0.1%	5.2%	84.7%	<0.1%	11.6%	>95%	0.6%	97.2%	80.9%	<0.1%	15.7%
BM	>95%	-	<0.1%	>95%	-	<0.1%	22.4%	-	77.6%	>95%	-	<0.1%

*) For an explanation of terms, reference is made to Table 1.

5 Discussion and Assessment of Hypothesis

In this chapter, the results are considered as a whole and discussed against each other. This is intended to place the work in a broader context and answer the questions defined at the outset. Finally, building on this, the work's hypothesis is discussed and evaluated, and a final conclusion is stated.

5.1 Evaluation of Research Questions

The research questions defined in the first chapter aim to enable a holistic assessment of the suitability of the InduRed concept for the treatment of LIB residues. They have been selected so that all aspects of general technical feasibility are considered. In the following, they are now dealt with in their original order.

1a) What reactions are expected to occur in currently used cathode materials or black matter at high temperatures and under reducing conditions?

1b) Do the desired reactions occur under the conditions achievable with the InduRed concept?

First concerned within the thermal analyses presented in chapter 3.1.1 and chapter 3.1.2, the general behaviour of cathode materials and black matter was a central research question throughout the whole project. Through extensive literature research, it was expected from the beginning that significant differences would occur between samples with and without carbon addition. The results, which are illustrated by the synoptic heat map charts in Figure 7, also met this expectation. There, the rate of the relative CSA change, measured in the heating microscope, is plotted over the temperature for all investigated cathode materials with (left) and without (right) carbon addition.

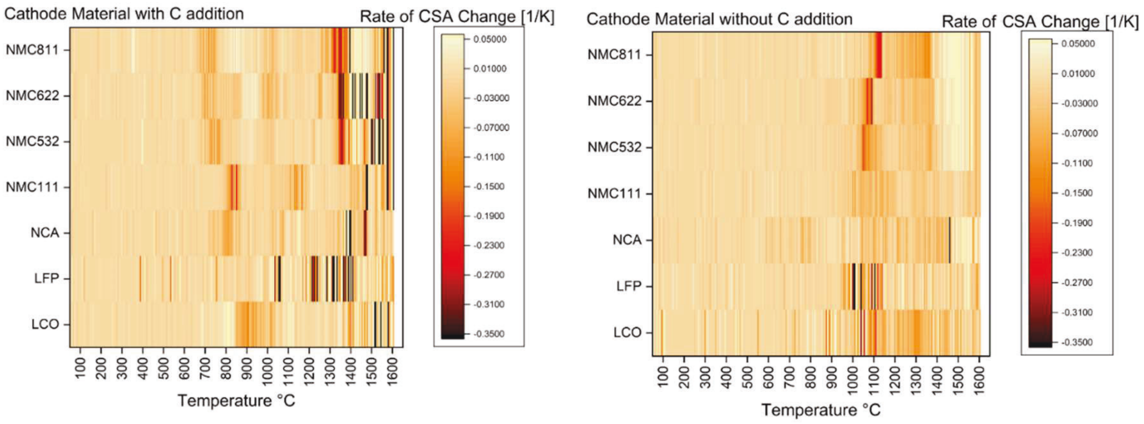

Figure 7: Heatmap showing the rate of the relative CSA change during heating microscope experiments for cathode materials with and without carbon addition. For an explanation of terms, reference is made to Table 1.

The most important finding drawn from the heat map is the temperature range in which reactions obviously occur. Despite LFP, all cathode materials with carbon addition show first changes between 650°C and 900°C. In experiments without carbon addition, this was only observed at some hundred degrees higher temperatures of between 1000°C and 1150°C. The reason for the varying behaviour can be explained by looking at the very basic reactions that occur in lithium metal oxides while heating. LFP must be excluded from this discussion due to its different chemical and structural composition but will be discussed in the course of the second question. When heated, the lithium metal oxide samples without carbon addition thermally dissociate at a certain temperature according to equation 5.1. On the other hand, carbothermal reduction, according to equation 5.2, occurs in the samples with carbon addition and dominates the dissociation reaction. [46]

$$4\ LiMeO_{2(s)} \rightarrow 2\ Li_2O_{(s)} + 4\ MeO_{(s)} + O_{2(g)} \qquad \text{Eq. 5.1}$$

$$4\ LiMeO_{2(s)} + 3C_{(s)} \rightarrow 2\ Li_2CO_{3(s)} + 4\ MeO_{(s)} + CO_{2(g)} \qquad \text{Eq. 5.2}$$

The second temperature range in which striking changes were observable, namely between 1400°C and 1550°C, only occurs in the samples with carbon addition. This correlates with the melting temperature of the metal alloy that results from the further reduction of the metal oxides according to equation 5.3 and equation 5.4.

$$4\ MeO_{(s/l)} + 2\ C_{(s)} \rightarrow 4\ Me_{(s/l)} + 2\ CO_{(g)} \qquad \text{Eq. 5.3}$$

$4\ MeO_{(s/l)} + 2\ CO_{(g)} \rightarrow 4\ Me_{(s/l)} + 2\ CO_{2(g)}$ Eq. 5.4

The fact that in the experiments with carbon addition, most of the oxygen of the lithium metal oxides is converted to gaseous products (CO or CO_2) and volatilized enables further characterization using TGA. The result of this analysis is summarized in Figure 8.

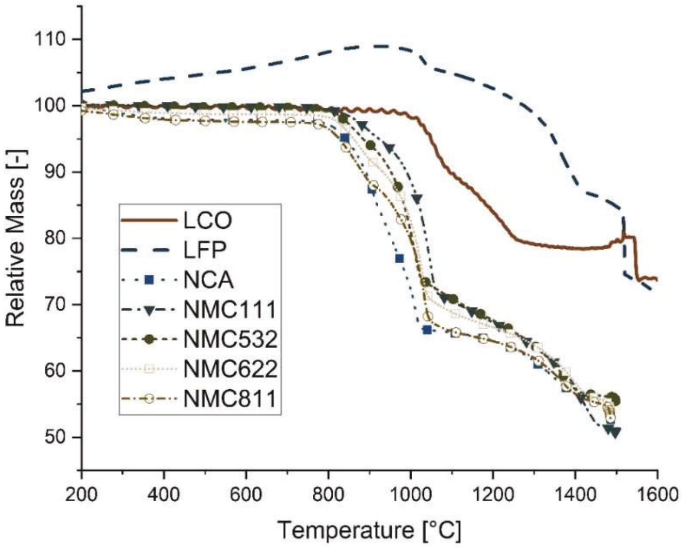

Figure 8: Comparison of thermogravimetric analysis data of all investigated cathode materials with carbon addition. For an explanation of terms reference is made to Table 1

From these data and the fact that all experiments with C addition led to magnetic products, it is clear that the conditions in the heating microscope and the STA were already sufficient to enable the carbothermic reaction. In the InduRed concept, in which an oversupply of carbon is given, the Boudouard reaction (equation 5.5) furthermore improves the reducing conditions since its equilibrium at high temperatures is in favour of CO and therefore helps to maintain a high CO/CO_2 ratio.

$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)}$ Eq. 5.5

Thus, it can be concluded that the reducing conditions provided by the InduRed concept are sufficient to enable the basic reduction reactions for at least Ni and Co and therefore allow to produce a metal alloy that correlates with the composition of the respective input material. Manganese which occurs in all NMC cathode materials has a higher oxygen affinity than Ni and Co and eventually requires stronger reducing conditions than provided in the thermal analyses. In the InduRed reactor, however, it is known from experiments with basic oxygen furnace slag (BOSF) that Mn gets reduced and becomes part of the metal alloy. Whether the conditions are also sufficient to reduce the base metal Li (equation 5.6) or prevent its oxidation (equation 5.7) cannot be determined by heating microscope and TGA tests due to the generally low proportion but must be answered by InduMelt experiments.

$$Li_2O_{(s/l)} + C_{(s)} \rightarrow 2\ Li_{(g)} + CO_{(g)} \qquad \text{Eq. 5.6}$$

$$Li_2CO_{3(s/l)} \rightarrow Li_2O_{(s)} + CO_{2(g)} \qquad \text{Eq. 5.7}$$

2. How do different cell chemistries affect the properties of black matter, and is the InduRed concept capable of handling all LIB cell chemistries used currently or in the near future?

The thesis described in detail which changes in the cell chemistry of LIBs can be expected in the future and what the drivers for these developments are. As a result, a certain flexibility of the future recycling process concerning the chemical composition of its input material is required. In this context, it must be remembered that new cell technologies are only found in the waste stream after a certain time, as the batteries are only disposed of after the end of their service life, e.g., after about ten years in the case of EVs. Thus, at least in the mid-term, it is possible to estimate which cell chemistries will be prevalent in the waste stream based on the technologies currently in use.

While the aged LCO is still used in mobile electronics applications, LFP is especially prevalent in applications where the lower energy density is irrelevant, i.e., stationary energy storage. Nickel-rich cathode chemistries, thus NCA and NMC are used particularly in the transport sector. It can be assumed that due to the growth of e-mobility, recyclers who specifically focus on the relatively large battery systems from EVs will emerge. This might result in a waste stream of old EV LIBs in which, as explained, nickel-rich cathode materials will predominate. Since LIBs from e-mobility are particularly important, chapters 3.3.1 and 3.3.2 also focused on the correlated cathode materials.

The chemical composition of the used samples in the corresponding experiments is given in Table 5. It can be seen that the cell technologies used in EVs differ mainly in the ratio Ni : Co or Ni : Co : Mn. Structurally, all NCA and NMC variants are layered lithium metal oxides, which, as can be seen in Figure 8, have very similar reaction characteristics. The content of lithium and volatile components is also very close in these materials, i.e., between 5.7% and 6.5% and between 50% and 52.7%, respectively.

Table 6: Metal contents in the input materials of the InduMelt experiments. [w.-%]

Sample/Elements	Li	Ni	Mn	Co	O	C
NCA	6.5%	44.0%	-	8.3%	30.0%	10.0%
NMC111	6.5%	18.3%	17.1%	18.3%	29.9%	10.0%
NMC532	5.8%	24.3%	13.7%	9.8%	26.5%	20.0%
NMC622	5.7%	29.1%	9.1%	9.7%	26.4%	20.0%
NMC811	5.7%	38.6%	4.5%	4.9%	26.3%	20.0%

With the chemical composition in view, the second research question can already be answered for the LIBs used in the field of electromobility. Due to the significant similarities in the chemical and structural properties as well as the reaction behaviour, the InduRed process can deal flexibly with all nickel-rich cathode materials. Furthermore, in chapter 3.3.1, it was also shown that even with mixtures of NCA and NMC, no results deviate from the expectations.

But since LCO continues to be used in mobile electronics applications and LFP is increasingly used in stationary energy storage systems, these materials should not be forgotten. In general, Holzer et al. (2021) [45], who investigated the possibility to treat these cathode materials with the InduRed concept, reported slightly deviating results within the InduMelt experiments. The thermal analyses also found differences between LCO and LFP and the other technologies. While LCO, which also has a layered structure, shows only minor deviations, LFP, which has an olivine structure, behaves entirely differently. However, it should be noted that, in principle, for both LCO and LFP, sufficiently reducing conditions are provided by the InduRed reactor.

In summary, the InduRed reactor can treat waste streams from all cell technologies currently in use. Experiments with mixtures of several nickel-rich cathode materials also turned out to be trouble-free, which should not change even with the addition of LCO. It can be assumed that the reactions in mixtures of NCA, NMC and LCO occur in the same temperature range as in the single-variety tests. LFP must be excluded from this perspective and could cause problems in pyrometallurgical processes if it is part of the waste stream. This is mainly due to the expected influence on the quality and composition of the most important products of the desired process, namely the metal and gas phases. If LFP contributes to the composition of an input feed for a pyrometallurgical process, the reactivity of phosphorus must be considered. Its high affinity to produce metal phosphides, particularly with iron (FeP), might negatively influence the quality and recyclability of the produced Ni – Co – Fe – Mn alloy. Due to the reaction conditions in the InduRed reactor, parts of the phosphorus will also be removed via the gas phase, where it might cause difficulties with the desired lithium recovery. Overall, the behaviour of LFP as part of black matter still needs to be better researched to be able to make clearer conclusions. With regard to the defined research question, however, LFP is to be classified as rather problematic for the time being.

3a) Is there a difference in the behaviour of black matter and factory new cathode materials and if so, what is the reason?

3b) What are desirable, what are rather counterproductive black matter properties and which pre-treatment processes are decisive for this?

In addition to the cell-technological origin of black matter, another crucial influencing parameter has emerged in the course of the research work. As shown in chapter 3.2.1, there is an inevitable connection between the processing history of black matter and the quality of the finally obtained products. Thus, the first part of the question, whether black matter and factory-new cathode materials show similar behaviour, must be clearly negated on the basis of the results from chapter 3.1.2, chapter 3.2.1 and chapter 3.3.1.

The reasons for that can be explained by chemical and structural differences, of which both can be influenced by upstream processes in the recycling chain. To demonstrate this influence, all pre-treatment procedures are divided into processing, e.g., shredding or pyrolysis, and separating treatments, e.g., magnetic separation or sieving. Then, processing treatments often affect the chemical structure of cathode materials, for example, the oxidation state of certain metals. In this regard, particularly thermal or mechanical processes that could lead to a heat release must be considered carefully. If, for example, a critical temperature is exceeded, thermal dissociation reactions might already occur according to equation 5.1. Specific processes, for example, those who aim for early-stage lithium recovery or those who try to prevent the formation of lithium oxide like the InduRed concept are then less effective or might even not be applicable at all.

Separation processes, on the other hand, influence the chemical composition of the black matter. Depending on their efficiency, the content of impurities in the black matter can differ substantially. These impurities could be residuals from other battery components that are left behind after shredding and could originate from the housing, the EMS or the electrode conductor foils. The latter, which consist of Al and Cu, can influence, for example, the thermal behaviour of the black matter or reduce the quality of later obtained products. If Cu, for example, becomes a part of the metal alloy, it causes the need for additional refining procedures to allow for functional recycling. Due to the strong reducing conditions, this is very likely to occur if Cu containing black matter is treated in the InduRed process.

Attention should also be paid on the graphite content in the black matter, which originates from the anode material. Being able to separate graphite from black matter for functional recycling and use alternative reducing agents instead could bear another strategic incentive since graphite also belongs to the list of CRMs. Furthermore, too high C contents in black matter negatively affects the melting process of the produced metal alloy and must be kept within a certain range.

4. What recycling rates can potentially be achieved for the metals of interest by applying the InduRed concept on LIB related wastes?

One problem in assessing recycling rates is the definition of recycling itself. When is a substance considered recycled? Is it enough to create a saleable product or should the requirement be greater? In terms of LIB recycling, for example, a claim could be that the recyclables should be recovered in a way that they can be used again in battery production.

In the InduMelt experiments, different product phases, namely metal, gas, slag and powder phase, were obtained. The metals of interest, thus Ni, Co, Mn and Li, accumulate in different ratios and different forms in those product phases. In the slag phase for example, the majority of the metals found there is found in an oxidic form (MeO). In the metal or powder phase, the metals accumulated as a metal alloy. However, to discuss and compare recovery rates for the InduRed concept, it is necessary to first define which form of a certain metal is the most suitable for functional recycling.

The powder phase was largely caused by graphite abrasion during sampling and thus consists of carbon and very small agglomerations of metal and slag particles. In the continuous process, the powder phase is therefore not expected to occur at all. Due to that and due to the anyway relatively small contribution of the powder phase to the total mass of products, it is not considered in this discussion. This leaves the metal phase, the slag phase and the gas phase. In the slag phase, as explained, the metals are primarily present in their oxidic form. Eventually, there are also some small metallic particles trapped within the slag matrix, but the majority of the slag is made of oxides. If the slag can be utilized as a construction material, the included metals could be considered recycled.

However, since this is tantamount to a far less valuable utilisation, this work places emphasis on the fact that the valuable metals shall be recycled functionally. In other pyrometallurgical processes the majority of Ni and Co are recovered as a metal alloy. Therefore, it is also considered for the InduRed process that the aim regarding Ni and Co is to recover them as an alloy. For the corresponding results it must be noted that due to the weighted consideration of residuals from the aqua regia digestion a slight over-determination in some analyses was observed. This led to calculated transfer coefficients of slightly more than 100%. This fact and the resulting inaccuracy were also described in detail in chapters 3.3.1 and 3.3.2.

However, by looking at the graphs for Ni and Co in Figure 9 it can be seen that the goal for Ni and Co can largely be achieved. In all experiments with factory-new cathode materials, it was possible to transfer between 83% and more than 95% of the initially present Ni and between 65% and 85% of the initially present Co in the metal phase. The lower recovery rates for Co can be explained by undesired side-reactions between Co and the Al_2O_3 crucibles, which consumed between 10% and 40% of the contained Co.

To optimize the recovery of Ni and Co, new refractory materials need to be considered. This is necessary to be able to compete with other pyrometallurgical processes which have Ni and Co recovery rates of well above 90%.

Regarding the gasification rates, as expected, there were no traces of Ni or Co in the gas phase. In general, Mn is going to be less present in future black matter mixtures since its content in NMC cathode materials is continuously reduced. Namely from a Ni:Mn ratio of 1:1 to a ratio of 8:1 in NMC811. However, since this only becomes noticeable after some time in the recycling plants, it should not be neglected at this stage. Due to a higher oxygen affinity and the presence of several oxidation states, Mn showed a more complex behavior. While also between 72% and 84% of Mn were transferred to the metal phase, there was one striking difference. In contrast to Ni and Co, there was a significant transfer of Mn into the gas phase which needs to be considered in view of the further treatment of the gas phase in an continuous process.

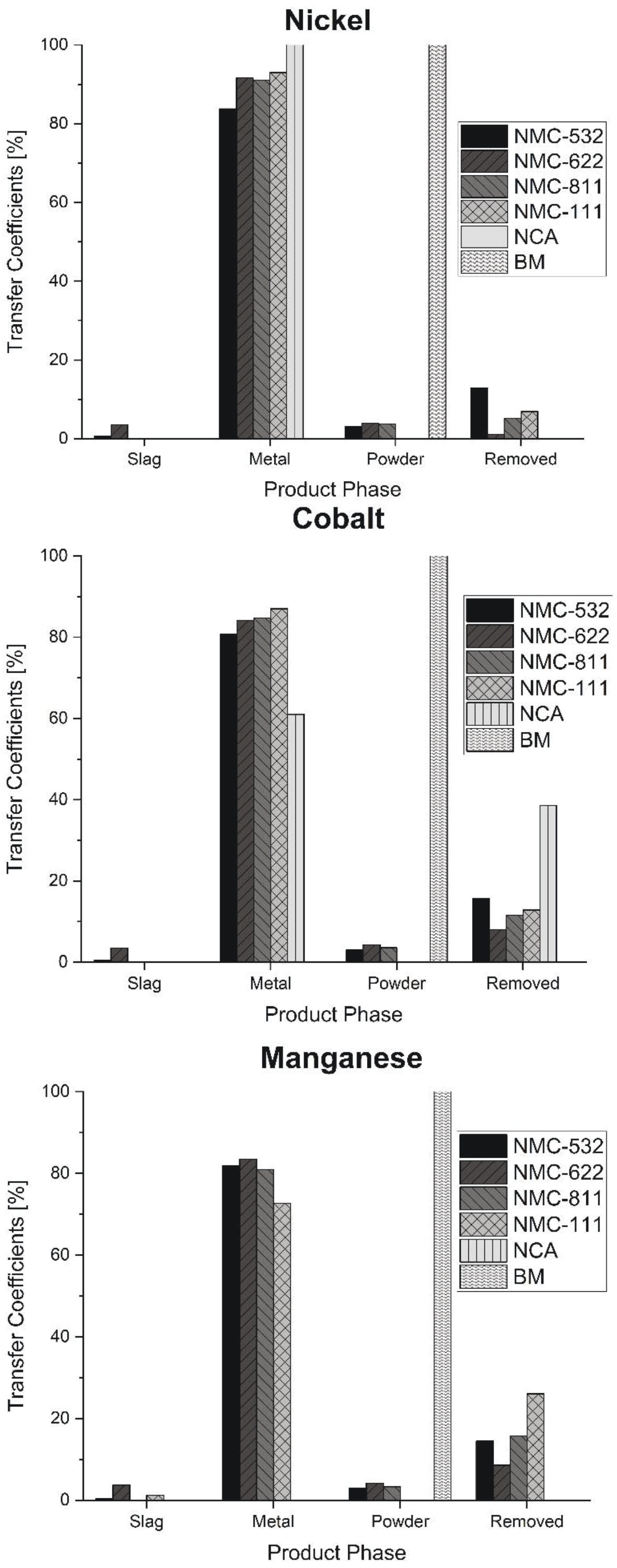

Figure 9: Comparison of transfer coefficients of Ni, Co and Mn into the obtained products during the InduMelt experiments. For an explanation of terms reference is made to Table 1

As described already at the beginning of the thesis, the slagging of Lithium is considered as one of the major drawbacks of pyrometallurgical approaches. Therefore, the aim of the InduRed process is to prevent the oxidization of Li, to separate it from the other metals and to make it available again for LIB production. Indeed, the transfer coefficients for Li, shown in Figure 10, are a complete contrast to those of the other metals. In all conducted experiments, between 80% and more than 95% of the originally charged Li was removed from the reactor. There was no accumulation of Li in the metal phase which was expected from the literature study. Most importantly, it was possible to limit the slagging of Li to values between 1% and 10% of the amount of Li in the respective input material.

This is an enormous improvement compared to conventional pyrometallurgical processes applied to date, in which almost 100% of Li is slagged.

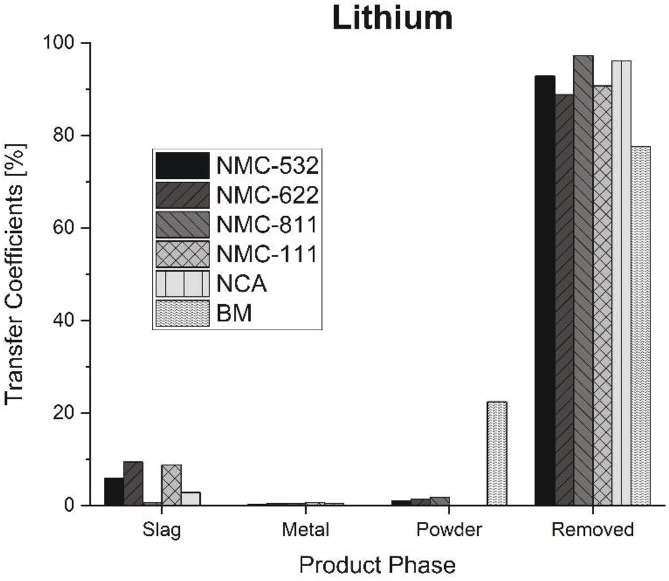

Figure 10: Transfer coefficients of Li into obtained products in the conducted InduMelt experiments. For an explanation of terms reference is made to Table 1

In conclusion, the InduRed process is capable of transferring large amounts of the metals of interest in a product phase that potentially allows for functional recycling. Some uncertainties, e.g., the gasification of Mn or the Co losses due to reactions with the crucible, however, need further research, which will be described in the last chapter of the thesis.

5.2 Conclusion

In the beginning of the thesis, it was shown that LIB recycling, especially the recovery of Li, can make a large contribution to the sustainability of the LIB technology as a whole. It conserves primary resources, drastically reduces energy and water consumption and helps to make LIBs more affordable by cutting costs. In the conclusion, the focus will now be on the hypothesis placed in the first chapter of the work. The hypothesis, the evaluation of which aims to clarify if the InduRed reactor could contribute to the complex task of LIB recycling, was formulated as follows:

Due to the specific reactor characteristics, the InduRed concept could be a beneficial alternative for pyrometallurgical black matter recycling with superior capabilities regarding lithium recovery.

Indeed, the InduRed concept distinguishes itself clearly from other pyrometallurgical processes in the field of LIB recycling and has some striking advantages. Especially its strong reducing conditions were expected to have an impact on the achievable recovery rates. The conducted experiments revealed that for Co and Ni, which are economically the most important cathodic metals, also fewer reducing conditions are sufficient. Accordingly, conventional pyrometallurgical procedures, e.g., operated by Glencore or Umicore, already achieve recovery rates of above 95% for these metals. So, if metal recovery from spent LIBs was only about Co and Ni, the competitiveness of the InduRed process compared to currently applied procedures would be questionable.

However, with Li coming more in focus, the disadvantage of lithium slagging in state-of-the-art pyrometallurgy must be considered. The experiments revealed that the InduRed concept is capable of limiting the slagging of Li to values below 10%, while comparable processes almost exclusively transfer Li to the slag phase. Instead, it was possible to remove up to 95% of the contained Li from the reactor. Thus, it can be stated that the InduRed concept has superior capabilities regarding the recovery of Li from LIB related wastes.

Nevertheless, there are also some disadvantages to be mentioned. Apart from the complexity of the process compared to a conventional shaft furnace as used by the Umicore process, the strong reducing condition also led to the accumulation of, e.g., Mn, in the metal phase. Thus, while Co or Ni mills, in which black matter for example is used as a secondary raw material, are capable of producing an alloy of adequate quality, the metal phase of the InduRed process most likely needs some further refining. But it should be noted that a possibly necessary post-treatment of the metal phase is not a criterion for generally excluding the

InduRed concept. It just needs to be clarified at what stage of the recycling chain an optimal usage of the reactors special characteristics can be achieved.

The mass balance in the InduMelt experiments revealed that the process can achieve a mass reduction of about 50%. If the InduRed concept could be used as a primary metal recovery process, the waste stream in a downstream hydrometallurgical refining step would be drastically reduced which positively affects its environmental impact due to a reduced consumption of chemicals.

In conclusion, the InduRed reactor shows great potential for its application along the LIB recycling chain. There are still some research questions to be answered in order to find the best solution for how such application should look, but the reactor can potentially close the gap regarding simultaneous recovery of all cathodic metals from spent LIBs. In the following last chapter of the thesis, further research questions that arose along the way are presented, and an outlook of the future work is given.

6 Research Prospects and Outlook

The results of this thesis have proven that the InduRed reactor concept is able to make a contribution to the sustainability of the LIB technology. Closing the gap in the circular economy of lithium is crucial for several reasons, and not yet achieved by established pyrometallurgical processes. However, there are still numerous questions that need to be answered before the InduRed concept can prove its ability to solve this issue. Some of the key research points along that way are noted in this last chapter.

- **Definition of black matter qualities**

It was shown that not only the chemical composition but also the processing history of black matter can influence its properties. The interrelationship between certain process steps during pre-treatment and downstream metallurgical processes can influence the overall efficiency of recycling chains. Thus, knowledge and certainty about the feed material is inevitable for metal recovery processes during both, the design as well as the operating phase.

Two basic steps can be derived from this for the follow-up research project at TPT. With regard to the chemical composition of the black matter, the influence of Cu and Al residues must be investigated. With the help of a further study in the heating microscope, limit values for the contained impurities should also be determined. The second point concerns the general definition of black matter qualities. To this end, contact should be established with operators of pre-treatment processes in order to demonstrate the practical influence of certain process steps on overall recycling rates. Finding a solution here requires the collaboration of all actors involved in the LIB recycling chain. Apart from that, the role of graphite needs to be reconsidered. Since graphite is also considered to be a critical raw material, it should also be recovered in a way that allows for functional recycling instead of being utilized as a heat source or reducing agent. In this regard, also the suitability of alternative reducing agent needs to come in focus with special attention on carbon-free industry approaches. Finally, the further development of cell technologies must be constantly monitored in order to react to emerging materials at an early stage. Thus, the continual investigation of the influence of new cathode materials on existing recycling chains is of great importance.

- **Process development**

The further development of the process is certainly one of the most important issues in the near future. Apart from the influences that arise from the definition of the future input material, the research work for this thesis has identified a couple of issues that require attention in this respect.

The first point concerns the selection of a suitable refractory material for the next reactor scale. Already in the thermal analysis it was observed that there is a strong reaction between the aluminium sample holders and Co. In the InduMelt experiments, the mentioned reaction caused significantly reduced recovery rates for Co but also Ni, which reacted with the porous Al_2O_3 mortar at the bottom of the reactor. Therefore, the usage of Al_2O_3 needs to be reconsidered and other refractory materials like MgO need to be tested. One of the next steps should also be to conduct an experimental trial in the continuous reactor. This allows to identify weaknesses or potentials for improvement of the reactor concept. Finding the optimal control of the reactor's temperature zones could be one such example for improvement. Also, the energy efficiency of the induction system in general must be enhanced in order to be economically competitive, also in a larger plant scale. The last point regarding the process development is directly linked with the product quality and comprises the definition of further processing routes for the reactor's products.

- **Product quality**

The third and last issue concerns the topic of product quality. Until now, only the extent to which valuable metals can be transferred into certain product phases has been investigated without focusing on their further processing. This involves the metal phase, for which the question arises if, and to what extent hydrometallurgical refining is necessary to fulfil quality requirements for functional recycling. In this regard, special attention should be paid to Mn from NMC materials and Fe and FeP from LFP materials. Equally significant, albeit smaller in quantity, is the gas phase, in which a large part of the lithium is discharged from the reactor. The development of a suitable gas post-treatment has a major impact on the quality of the Li product, thus the unique selling proposition of the process, and is one of the major challenges that is in focus in later stages of the research project.

References

1. Costa, C.M.; Barbosa, J.C.; Gonçalves, R.; Castro, H.; Del Campo, F.J.; Lanceros-Méndez, S. Recycling and environmental issues of lithium-ion batteries: Advances, challenges and opportunities. Energy Storage Materials 2021, 37, 433–465, doi:10.1016/j.ensm.2021.02.032.
2. Martin, G.; Rentsch, L.; Höck, M.; Bertau, M. Lithium market research – global supply, future demand and price development. Energy Storage Materials 2017, 6, 171–179, doi:10.1016/j.ensm.2016.11.004.
3. Sterba, J.; Krzemień, A.; Riesgo Fernández, P.; Escanciano García-Miranda, C.; Fidalgo Valverde, G. Lithium mining: Accelerating the transition to sustainable energy. Resources Policy 2019, 62, 416–426, doi:10.1016/j.resourpol.2019.05.002.
4. Placek, M. Projected size of the global lithium-ion battery market from 2020 to 2026, 2020. Available online: https://www.statista.com/statistics/1011187/projected-global-lithium-ion-battery-market-size/.
5. Markets and Markets. Lithium-Ion Battery Market with COVID-19 Impact Analysis, by Type (Li-NMC, LFP, LCO, LTO, LMO, NCA), Capacity, Voltage, Industry (Consumer Electronics, Automotive, Power, Industrial), & Region (North America, Europe, APAC & RoW) - Global Forecast to 2030, 2021. Available online: https://www.marketsandmarkets.com/Market-Reports/lithium-ion-battery-market-49714593.html.
6. Winslow, K.M.; Laux, S.J.; Townsend, T.G. A review on the growing concern and potential management strategies of waste lithium-ion batteries. Resources, Conservation and Recycling 2018, 129, 263–277, doi:10.1016/j.resconrec.2017.11l.001.
7. Tsiropoulos, I.; Tarvydas, D.; Lebedeva, N. Li-ion batteries for mobility and stationary storage applications: scenarios for costs and market growth; Publications Office, 2018.
8. Bloomberg New Energy Finance. Long-Term Electric Vehicle Outlook 2019, 2020. Available online: https://bnef.turtl.co/story/evo-2020/page/3?teaser=yes.
9. Federal Consortium for Advanced Batteries FCAB; U.S. Department of Energy. National Blueprint for Lithium Batteries 2021-2030, 2021.

10. European Commission. Directorate General for Internal Market, Industry, Entrepreneurship and SMEs. Study on the EU's list of critical raw materials (2020): final report; Publications Office, 2020.
11. Peters, J.F.; Baumann, M.; Weil, M. Recycling aktueller und zukünftiger Batteriespeicher: Technische, ökonomische und ökologische Implikationen : Ergebnisse des Expertenforums am 6. Juni 2018 in Karlsruhe: Ergebnisse des Expertenforums am 6. Juni 2018 in Karlsruhe, Karlsruhe, 2018.
12. Harper, G.; Sommerville, R.; Kendrick, E.; Driscoll, L.; Slater, P.; Stolkin, R.; Walton, A.; Christensen, P.; Heidrich, O.; Lambert, S.; et al. Recycling lithium-ion batteries from electric vehicles. Nature 2019, 575, 75–86, doi:10.1038/s41586-019-1682-5.
13. Öhl, J.; Horn, D.; Zimmermann, J.; Stauber, R.; Gutfleisch, O. Efficient Process for Li-Ion Battery Recycling via Electrohydraulic Fragmentation. MSF 2019, 959, 74–78, doi:10.4028/www.scientific.net/MSF.959.74.
14. Grandjean, T.R.; Groenewald, J.; Marco, J. The experimental evaluation of lithium ion batteries after flash cryogenic freezing. Journal of Energy Storage 2019, 21, 202–215, doi:10.1016/j.est.2018.11.027.
15. Bittner. Neues innovatives Recyclingverfahren: Elektrohydraulische Zerkleinerung. Karlsruhe, 2018.
16. Hanisch, C.; Diekmann, J.; Stieger, A.; Haselrieder, W.; Kwade, A. Recycling of Lithium-Ion Batteries. In Handbook of Clean Energy Systems; Yan, J., Ed.; John Wiley & Sons, Ltd: Chichester, UK, 2015; pp 1–24, ISBN 9781118991978.
17. Thielmann, A.; Wietschel, M.; Funke, S.; Grimm, A.; Hettesheimer, T.; Langkau, S.; Loibl, A.; Moll, C.; Neef, C.; Plötz, P.; et al. Batterien für Elektroautos: Faktencheck und Handlungsbedarf, Karlsruhe, 2020.
18. Gaines, L.; Dai, Q.; Vaughey, J.T.; Gillard, S. Direct Recycling R&D at the ReCell Center. Recycling 2021, 6, 31, doi:10.3390/recycling6020031.
19. Doose, S.; Mayer, J.K.; Michalowski, P.; Kwade, A. Challenges in Ecofriendly Battery Recycling and Closed Material Cycles: A Perspective on Future Lithium Battery Generations. Metals 2021, 11, 291, doi:10.3390/met11020291.
20. Jung, J.C.-Y.; Sui, P.-C.; Zhang, J. A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments. Journal of Energy Storage 2021, 35, 102217, doi:10.1016/j.est.2020.102217.
21. Lander, L.; Cleaver, T.; Rajaeifar, M.A.; Nguyen-Tien, V.; Elliott, R.J.; Heidrich, O.; Kendrick, E.; Edge, J.S.; Offer, G. Financial Viability of Electric Vehicle Lithium-Ion Battery Recycling. iScience 2021, 102787, doi:10.1016/j.isci.2021.102787.
22. Balasubramaniam, B.; Singh, N.; Verma, S.; Gupta, R.K. Recycling of Lithium From Li-ion Batteries. Encyclopedia of Renewable and Sustainable Materials; Elsevier, 2020; pp 546–554, ISBN 9780128131961.
23. Korthauer, R. Handbuch Lithium-Ionen-Batterien; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013, ISBN 978-3-642-30652-5.
24. Goodenough, J.B.; Mizushima, K.; Wiseman, P.J. Electrochemical cell and method of making ion conductors for said cell. EP19800300876 19800320, March 20, 1980.
25. Reddy, M.V.; Mauger, A.; Julien, C.M.; Paolella, A.; Zaghib, K. Brief History of Early Lithium-Battery Development. Materials (Basel) 2020, 13, doi:10.3390/ma13081884.
26. Whittingham, M.S. Lithium Batteries: 50 Years of Advances to Address the Next 20 Years of Climate Issues. Nano Lett. 2020, 20, 8435–8437, doi:10.1021/acs.nanolett.0c04347.

27. Pistoia, G. Lithium-ion batteries: Advances and applications; Elsevier: Amsterdam [etc.], op. 2014, ISBN 9780444595133.
28. European Commission. Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0474&from=EN (accessed on 10 February 2021).
29. Thackeray, M.M. Manganese oxides for lithium batteries. Progress in Solid State Chemistry 1997, 25, 1–71, doi:10.1016/S0079-6786(97)81003-5.
30. Chen, Y.; Kang, Y.; Zhao, Y.; Wang, L.; Liu, J.; Li, Y.; Liang, Z.; He, X.; Li, X.; Tavajohi, N.; et al. A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. Journal of Energy Chemistry 2021, 59, 83–99, doi:10.1016/j.jechem.2020.10.017.
31. Wang, K.; Wan, J.; Xiang, Y.; Zhu, J.; Leng, Q.; Wang, M.; Xu, L.; Yang, Y. Recent advances and historical developments of high voltage lithium cobalt oxide materials for rechargeable Li-ion batteries. Journal of Power Sources 2020, 460, 228062, doi:10.1016/j.jpowsour.2020.228062.
32. Weng, D.; Duan, H.; Hou, Y.; Huo, J.; Chen, L.; Zhang, F.; Wang, J. Introduction of manganese based lithium-ion Sieve-A review. Progress in Natural Science: Materials International 2020, 30, 139–152, doi:10.1016/j.pnsc.2020.01.017.
33. Yan, H.; Zhang, D.; Qilu; Duo, X.; Sheng, X. A review of spinel lithium titanate (Li4Ti5O12) as electrode material for advanced energy storage devices. Ceramics International 2021, 47, 5870–5895, doi:10.1016/j.ceramint.2020.10.241.
34. Zheng, X.; Li, X.; Wang, Z.; Guo, H.; Huang, Z.; Yan, G.; Wang, D. Investigation and improvement on the electrochemical performance and storage characteristics of LiNiO2-based materials for lithium ion battery. Electrochimica Acta 2016, 191, 832–840, doi:10.1016/j.electacta.2016.01.142.
35. Chen, C.H.; Liu, J.; Stoll, M.E.; Henriksen, G.; Vissers, D.R.; Amine, K. Aluminum-doped lithium nickel cobalt oxide electrodes for high-power lithium-ion batteries. Journal of Power Sources 2004, 128, 278–285, doi:10.1016/j.jpowsour.2003.10.009.
36. Skeete, J.-P.; Wells, P.; Dong, X.; Heidrich, O.; Harper, G. Beyond the EVent horizon: Battery waste, recycling, and sustainability in the United Kingdom electric vehicle transition. Energy Research & Social Science 2020, 69, 101581, doi:10.1016/j.erss.2020.101581.
37. Scrosati, B.; Hassoun, J.; Sun, Y.-K. Lithium-ion batteries. A look into the future. Energy Environ. Sci. 2011, 4, 3287, doi:10.1039/C1EE01388B.
38. Windisch-Kern, S.; Gerold, E.; Nigl, T.; Jandric, A.; Altendorfer, M.; Rutrecht, B.; Scherhaufer, S.; Raupenstrauch, H.; Pomberger, R.; Antrekowitsch, H.; et al. Recycling chains for lithium-ion batteries: A critical examination of current challenges, opportunities and process dependencies. Waste Management 2022, 138, 125–139, doi:10.1016/j.wasman.2021.11.038.
39. Brückner, L.; Frank, J.; Elwert, T. Industrial Recycling of Lithium-Ion Batteries—A Critical Review of Metallurgical Process Routes. Metals 2020, 10, 1107, doi:10.3390/met10081107.
40. Zhang, G.; He, Y.; Feng, Y.; Wang, H.; Zhang, T.; Xie, W.; Zhu, X. Enhancement in liberation of electrode materials derived from spent lithium-ion battery by pyrolysis. Journal of Cleaner Production 2018, 199, 62–68, doi:10.1016/j.jclepro.2018.07.143.

41. Guo, X.; Cao, X.; Huang, G.; Tian, Q.; Sun, H. Recovery of lithium from the effluent obtained in the process of spent lithium-ion batteries recycling. J. Environ. Manage. 2017, 198, 84–89, doi:10.1016/j.jenvman.2017.04.062.
42. Sabarny, P.; Peters, L.; Sommerfeld, M.; Stallmeister, C.; Schier, C.; Friedrich, B. Early-Stage Lithium Recovery (ESLR) for Enhancing Efficiency in Battery Recycling, 2020.
43. Huang, B.; Pan, Z.; Su, X.; An, L. Recycling of lithium-ion batteries: Recent advances and perspectives. Journal of Power Sources 2018, 399, 274–286, doi:10.1016/j.jpowsour.2018.07.116.
44. He, Y.; Yuan, X.; Zhang, G.; Wang, H.; Zhang, T.; Xie, W.; Li, L. A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries. Sci. Total Environ. 2020, 142382, doi:10.1016/j.scitotenv.2020.142382.
45. Holzer, A.; Windisch-Kern, S.; Ponak, C.; Raupenstrauch, H. A Novel Pyrometallurgical Recycling Process for Lithium-Ion Batteries and Its Application to the Recycling of LCO and LFP. Metals 2021, 11, 149, doi:10.3390/met11010149.
46. Yin, H.; Xing, P. Pyrometallurgical Routes for the Recycling of Spent Lithium-Ion Batteries. In Recycling of Spent Lithium-Ion Batteries; An, L., Ed.; Springer International Publishing: Cham, 2019; pp 57–83, ISBN 978-3-030-31833-8.
47. Zheng, X.; Zhu, Z.; Lin, X.; Zhang, Y.; He, Y.; Cao, H.; Sun, Z. A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. Engineering 2018, 4, 361–370, doi:10.1016/j.eng.2018.05.018.
48. Mossali, E.; Picone, N.; Gentilini, L.; Rodrìguez, O.; Pérez, J.M.; Colledani, M. Lithium-ion batteries towards circular economy: A literature review of opportunities and issues of recycling treatments. J. Environ. Manage. 2020, 264, 110500, doi:10.1016/j.jenvman.2020.110500.
49. European Commission. Recovery of Phosphorus from Sewage Sludge and Sewage Sludge Ashes with the thermo-reductive RecoPhos-Process, 2015. Available online: https://cordis.europa.eu/project/id/282856/de.
50. Ponak, C. Carbo-thermal reduction of basic oxygen furnace slags with simultaneous removal of phosphorus via the gas phase. PhD Thesis; Montanuniversität, Leoben, 2019.
51. Schönberg, A. Mathematische Modellierung metallurgischer Prozesse - Induktive Erwärmung einer Graphitschüttung. PhD Thesis; Montanuniversität, Leoben, 2014.
52. Ponak, C.; Mally, V.; Windisch, S.; Holzer, A.; Raupenstrauch, H. Phosphorus Gasification During The Reduction Of Basic Oxygen Furnace Slags In A Novel Reactor Concept. AML 2020, 11, 20071535, doi:10.5185/amlett.2020.071535.
53. Warner, J. Lithium-Ion Battery Packs for EVs. Lithium-Ion Batteries; Elsevier, 2014; pp 127–150, ISBN 9780444595133.
54. Zhao, S.; Guo, Z.; Yan, K.; Wan, S.; He, F.; Sun, B.; Wang, G. Towards high-energy-density lithium-ion batteries: Strategies for developing high-capacity lithium-rich cathode materials. Energy Storage Materials 2021, 34, 716–734, doi:10.1016/j.ensm.2020.11.008.
55. Vonsien, S.; Madlener, R. Li-ion battery storage in private households with PV systems: Analyzing the economic impacts of battery aging and pooling. Journal of Energy Storage 2020, 29, 101407, doi:10.1016/j.est.2020.101407.
56. Sun, X.; Luo, X.; Zhang, Z.; Meng, F.; Yang, J. Life cycle assessment of lithium nickel cobalt manganese oxide (NCM) batteries for electric passenger vehicles. Journal of Cleaner Production 2020, 273, 123006, doi:10.1016/j.jclepro.2020.123006.

57. Chen, W.; Liang, J.; Yang, Z.; Li, G. A Review of Lithium-Ion Battery for Electric Vehicle Applications and Beyond. Energy Procedia 2019, 158, 4363–4368, doi:10.1016/j.egypro.2019.01.783.
58. Windisch-Kern, S.; Holzer, A.; Nagovnak, P.; Ponak, C.; Raupenstrauch, H. Pyrometallurgical recycling of lithium ion batteries: Preliminary experiments to investigate the behaviour of cathode materials under reducing conditions. In Proceedings of the 16. Minisymposium Verfahrenstechnik & 7. Partikelforum: September 21-22, 2020, 1st edition; Jordan, C., Ed.; chemical-engineering.at: Wien, 2020, ISBN 978-3-903337-01-5.
59. Windisch-Kern, S.; Holzer, A.; Ponak, C.; Hochsteiner, T.; Raupenstrauch, H. Thermal analysis of lithium ion battery cathode materials for the development of a novel pyrometallurgical recycling approach. Carbon Resources Conversion 2021, doi:10.1016/j.crcon.2021.04.005.
60. Windisch-Kern, S.; Holzer, A.; Ponak, C.; Raupenstrauch, H. Pyrometallurgical Lithium-Ion-Battery Recycling: Approach to Limiting Lithium Slagging with the InduRed Reactor Concept. Processes 2021, 9, 84, doi:10.3390/pr9010084.
61. Windisch-Kern, S.; Holzer, A.; Wiszniewski, L.; Raupenstrauch, H. Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials (LiNixMnyCozO2) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor. Metals 2021, 11, 1844, doi:10.3390/met11111844.