Article

Investigation of Potential Recovery Rates of Nickel, Manganese, Cobalt, and Particularly Lithium from NMC-Type Cathode Materials ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor

Stefan Windisch-Kern , Alexandra Holzer , Lukas Wiszniewski and Harald Raupenstrauch

Chair of Thermal Processing Technology, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria; alexandra.holzer@unileoben.ac.at (A.H.); Lukas.wiszniewski@unileoben.ac.at (L.W.); harald.raupenstrauch@unileoben.ac.at (H.R.)

* Correspondence: stefan.windisch-kern@unileoben.ac.at; Tel.: +43-3842-402-5819

Citation: 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 ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) by Carbo-Thermal Reduction in an Inductively Heated Carbon Bed Reactor. *Metals* **2021**, *11*, 1844. <https://doi.org/10.3390/met11111844>

Academic Editor: Srecko Stopic

Received: 28 September 2021

Accepted: 16 November 2021

Published: 17 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: Within the e-mobility sector, which represents a major driver of the development of the over-all 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

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 (H₂SO₄) [15–17], or phosphoric acid (H₃PO₄) [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 Montanuniversität 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 pur-

pose, 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 $\mu\Omega\text{m}$, 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 $\text{K}\cdot\text{min}^{-1}$, 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 alternately 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 stoichiometric composition of each cathode material. ² Total mass contribution of elements that are expected to be volatile (O₂, 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·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 Montanuniversität 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 Montanuniversität 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]:

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].

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]:

In case of NMC, i.e., $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, 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.

Said reducing conditions, namely high temperatures, low oxygen partial pressures ($p\text{O}_2$), 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 $p\text{O}_2$ and high CO/ CO_2 values [50].

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.

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 K·min^{−1}. For the interpretation of the InduMelt trials, where the heating rate is limited to less than 3.5 K·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 stoichiometric 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 28”), 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.

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.

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.

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.

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 whether 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 phase, 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.

Author Contributions: Conceptualization, S.W.-K. and A.H.; methodology, S.W.-K.; investigation, S.W.-K. and A.H.; resources, S.W.-K., A.H. and L.W.; writing—original draft preparation, S.W.-K. and L.W.; writing—review and editing, S.W.-K., A.H., L.W. and H.R.; visualization, S.W.-K.; supervision, H.R.; project administration, S.W.-K. and A.H.; funding acquisition, H.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Zukunftsfonds Steiermark with funds from the province of Styria, Austria, grant number GZ: ABT08-189002/2020 PN:1305.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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 EUO'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 LiCoO₂ 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.; Marschlok, 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.; Zaghbi, 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 LiCoO₂. *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.; Rodriguez, 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 LiCoO₂ 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. [\[CrossRef\]](#)