





Article

Microwave-Assisted Recovery of Spent LiCoO₂ Battery from the Corresponding Black Mass

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Abstract: The literature indicates that utilizing pyrometallurgical methods for processing spent LiCoO₂ (LCO) batteries can lead to cobalt recovery in the forms of Co₃O₄, CoO, and Co, while lithium can be retrieved as Li₂O or Li₂CO₃. However, the technology's high energy consumption has also been noted as a challenge in this recovery process. Recently, an innovative and sustainable approach using microwave (MW) radiation has been proposed as an alternative to traditional pyrometallurgical methods for treating used lithium-ion batteries (LIBs). This method aims to address the shortcomings of the conventional approach. In this study, the treatment of the black mass (BM) from spent LCO batteries is explored for the first time using MW–materials interaction under an air atmosphere. The research reveals that the process can trigger carbothermic reactions. However, MW makes the BM so reactive that it causes rapid heating of the sample in a few minutes, also posing a fire risk. This paper presents and discusses the benefits and potential hazards associated with this novel technology for the recovery of spent LCO batteries and gives information about real samples of BM. The work opens the possibility of using a microwave for raw material recovery in spent LIBs, allowing to obtain rapid and more efficient reactions.

Keywords: lithium-ion batteries; LCO; black mass; recovery; recycle; microwave treatment; lithium cobalt oxide; e-waste; pyrometallurgy; sustainability



Citation: Scaglia, M.; Cornelio, A.; Zanoletti, A.; La Corte, D.; Biava, G.; Alessandri, I.; Forestan, A.; Alba, C.; Depero, L.E.; Bontempi, E. Microwave-Assisted Recovery of Spent LiCoO₂ Battery from the Corresponding Black Mass. *Batteries* **2023**, *9*, 536. <https://doi.org/10.3390/batteries9110536>

Academic Editor: Carlos Ziebert

Received: 25 September 2023

Revised: 18 October 2023

Accepted: 25 October 2023

Published: 28 October 2023



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1. Introduction

The global new energy vehicle industry has witnessed rapid expansion, with the annual global sales of new energy vehicles showing a steady increase. One of the most critical technologies driving this growth are the lithium-ion batteries (LIBs) used for power storage. These batteries have seen a significant upsurge in production and sales, driven by the ongoing trend of electrifying transportation. Nonetheless, this surge in demand has also highlighted apprehensions about the availability of necessary materials. Considering the expected operational span of an LIB system, typically spanning 10 to 15 years, there is a notable expectation of a significant surge in end-of-life LIBs soon [1]. It is estimated that by the year 2030, the worldwide electric vehicle (EV) population will reach 140 million, leading to the collective disposal of approximately 11 million tons of depleted batteries [2]. Hence, the recycling of exhausted-power lithium-ion batteries will hold a significant position within the new energy industry ecosystem. Extracting and processing raw materials for battery production incurs environmental expenses. To illustrate, obtaining one ton of

pristine lithium necessitates 250 tons of ore or 750 tons of brine [3]. In addition, water consumption is another concern: in Chile, the primary source of lithium, the mining sector consumes 65% of the water resources [4]. Moreover, if depleted batteries cannot be repurposed for secondary energy-storage purposes, leading to a delay in their disposal, they convert into hazardous waste. This waste includes flammable organic solvents, polymer coatings, graphite, and metallic sheets, as well as compounds of transition metals such as Ni, Co, Mn, and/or Fe, along with Li ions [5]. Therefore, the impetus for LIB recycling arises from a variety of factors, spanning environmental, economic, and strategic considerations. Essentially, by preventing the disposal of hazardous substances like flammable electrolyte solvents and carcinogenic metals such as Ni and Co, an avenue is created to recover materials of substantial market worth [6]. Furthermore, a wide array of benefits derived from LIB recycling are not immediately measurable in financial value. The environmental and economic advantages vary over time, involving elements like energy preservation and the curbing of greenhouse gas (GHG) emissions achieved through recycling. These fluctuations stem from variations in recycling approaches, the advancement of innovative recycling methods, maintenance costs, shifts in the costs and sources of raw materials and energy, modifications in battery composition, and advancements in modeling techniques [7]. Still, the recovery of these precious and vital materials poses technological challenges due to the absence of standardization in LIBs, spanning differences in cathode compositions and physical dimensions. This leads to a complex blend of materials that are intricately intertwined, ultimately making LIB recycling a topic riddled with uncertainties about the best process setups. In this context, the frequently cited statistic for LIB recycling is that approximately 5% of LIBs are currently reclaimed at the culmination of their life cycle [8]. However, the share of recycled LIBs could potentially reach up to 50% [9].

Currently, considering LIBs, graphite is the most widely used anodic material. Several treatments have been proposed for graphite and degraded graphite recovery, including thermal and chemical methods [10] with different advantages and byproducts [11].

For cathodic materials, in general, two main recycling methods have gained considerable prominence within the field: hydrometallurgy (which includes techniques like acid leaching) and pyrometallurgy (involving processes such as roasting and pyrolysis). These approaches are primarily derived from technologies utilized in mineral extraction [12]. As the significance of recycling spent LIBs continues to rise, a multitude of comprehensive review articles have been published, delving into the evolution of recycling technologies for these batteries. These reviews cover an extensive range of subjects, spanning from offering an overview of the general recycling process to evaluating the latest cutting-edge techniques, appraising their technoeconomic viability, and pinpointing future challenges. Importantly, these articles thoroughly contrast the advantages and disadvantages inherent in different methodologies.

Hydrometallurgical approaches involve employing aqueous solutions to separate the desired metals from cathode materials. A diverse range of chemical combinations have been documented for this purpose. Multiple investigations have been conducted to identify the optimal conditions that yield the highest leaching rates. These considerations encompass variables such as the concentration of leaching acid, leaching duration, solution temperature, the ratio of solids to liquids, and the introduction of a reducing agent. However, it is important to highlight that all these factors hinge on the specific cathode chemistry. The notable challenges inherent in all hydrometallurgical processes revolve around the quantities of chemicals required, the magnitude of waste generated, and the expenses associated with neutralization.

Pyrometallurgical technology encompasses a high-temperature procedure aimed at extracting metals or other compounds from used LIBs. The elevated temperatures employed in this process result in the batteries undergoing a “smelting” transformation. This methodology, a natural progression from techniques used for diverse battery types, is already commercially established for consumer LIBs. Its distinct advantages shine in the recycling of typical consumer LIBs, which are frequently a mix of cells with inadequate

sorting. This versatility extends to electric vehicle LIBs, where the approach proves its worth. A noteworthy advantage of this technique is that the presence of metal current collectors aids the smelting process, allowing it to handle intact cells or modules without requiring a preliminary passivation step [6]. Of significance, this technology demands minimal raw materials and generates minimal liquid waste throughout its operation. When compared to hydrometallurgy, pyrometallurgy has been proposed as highly viable for large-scale industrial recycling of used LIBs [6]. However, Li generally ends up in the slag, which has little economic value, so Li does not re-enter the battery chain [13]. Table 1 reports the most recent available studies on the carbothermic reduction of LCO, based on pyrometallurgy.

Table 1. Most recent studies about the carbothermic reduction of LCO that are based on pyrometallurgical processes.

| Reductant | Temperature (°C) | Time (min) | Atmospheric Condition | Product | Recovery of Li ₂ CO ₃ (%) * | Ref. |
|-----------|------------------|------------|-----------------------|---|---|------|
| Graphite | 1000 | 30 | N ₂ | Co, Li ₂ CO ₃ | n.a. | [14] |
| Graphite | 900 | 30 | Vacuum | Co, Li ₂ CO ₃ | n.a. | [15] |
| Graphite | 700 | 45 | Vacuum | Regenerated LiCoO ₂ | n.a. | [16] |
| Graphite | 700 | 90 | N ₂ | Co, CoO, Ni, NiO, Mn, Mn ₃ O ₄ , Li ₂ O, Li ₂ CO ₃ | n.a. | [17] |
| Graphite | 900 | 15 | Air | Co, Li ₂ CO ₃ | >95 | [18] |
| Graphite | 1500 | 180 | Ar | Co, Li ₂ CO ₃ | n.a. | [19] |
| Graphite | 1700 | 55 | Ar | Co, Li ₂ CO ₃ | 81.7–97.3 | [20] |
| Graphite | 500–1000 | 50 | N ₂ | Co, CoO, Li ₂ CO ₃ | >80 | [21] |

n.a., not available; *, not all papers report the percentage of recovery because they were mainly concerned with evaluating the thermokinetics of the reaction.

Generally, the process is realized in an inert atmosphere or in a reducing agent [14]. Moreover, although some studies on the carbothermic reduction of LiCoO₂ are available, only a few works deal with the study of carbothermic reduction in air, and no works are available concerning the possibility of using a microwave interaction to make the recovery process more sustainable. In addition, almost all works are devoted to the use of model samples by mixing standard pure materials.

This paper for the first time presents the use of microwaves to provide the carbothermic reduction of LiCoO₂ in air and shows the potential and limitations of the new recently proposed recovery technology. This work investigates the behavior of a real BM sample, then containing impurities from other cathodic materials. The technology used for this treatment has been proposed recently [22]. The reasons to study this process are also related to its sustainability, in comparison to treatments made in a controlled atmosphere. Indeed, the use of argon or nitrogen makes the process more onerous in terms of gas for the treatment. This paper opens the possibilities of new research devoted to microwave use in spent LIBs recovery.

2. Materials and Methods

This study uses recovered BM material derived from spent LCO batteries. The samples were provided by Spirit s.r.l. (Chiampo, Vicenza, Italy). The samples were treated in a PYRO Advanced Microwave Muffle Furnace (Milestone s.r.l., Bergamo, Italy). Thermal analysis of the BM was performed with a HITACHI-STA 200 in a nitrogen atmosphere until 300 °C and then in air, as shown in Table 2.

Table 2. Temperature program, temperature ramp, and gases used for thermal analysis.

| Temperature Range (°C) | Thermal Ramp (°C/min) | Atmospheric Condition |
|------------------------|-----------------------|-----------------------|
| 30–300 | 40 | N ₂ |
| 300–400 | 10 | Air |
| 400–800 | 5 | Air |
| 800–1000 | 15 | Air |

Before the treatment, 0.05 g of LCO as-received sample was digested in 3 mL of H₂SO₄, 2 mL of HClO₄, and 1 mL of V₂O₅ in an UltraWAVE microwave digestion system (Milestone, Bergamo, Italy) to investigate its chemical composition. The digested sample was analyzed by a total reflection X-ray fluorescence (TXRF) spectrophotometer equipped with Mo anode (S2 PICOFOX, Bruker AXS Microanalysis GmbH, Berlin, Germany) operating at 750 µA and 50 kV and by ion chromatography (IC), Metrohm 883 Compact IC plus (Metrohm AG, Herisau, Switzerland) and cation exchange column Metrosep C4-150/4.0 (Metrohm AG, Herisau, Switzerland). TXRF was used for the evaluation of metals present in the sample, and IC was used for the determination of Li that was not detectable by TXRF. Moreover, the samples were leached in water at 80 °C for 30 min with a magnetic stirrer set at 300 rpm using a solid/liquid ratio of 40 g/L [22]. The solid samples were separated by the solutions from water leaching, by vacuum filtration using a 0.45 µm nylon filter. After filtration, the residual solid parts were dried, and the Li concentration in the leached samples was determined by IC. Structural characterization before and after the microwave treatment and water leaching was performed by X-ray diffraction (XRD) with X'Pert PRO diffractometer (PANalytical, Malvern, UK) using Cu Ka (1.5406 Å) radiation and operating at 40 kV and 40 mA.

3. Results and Discussion

Figure 1 shows the results of the thermal analysis. It can be seen from the thermogravimetry (TG) curve and differential thermogravimetry (DTG) curve that the combustion process of the sample could be divided into some stages: before 450 °C, the mass loss was due to combustion of the residual binder (PVDF)/PE/PP and the electrolyte [23].

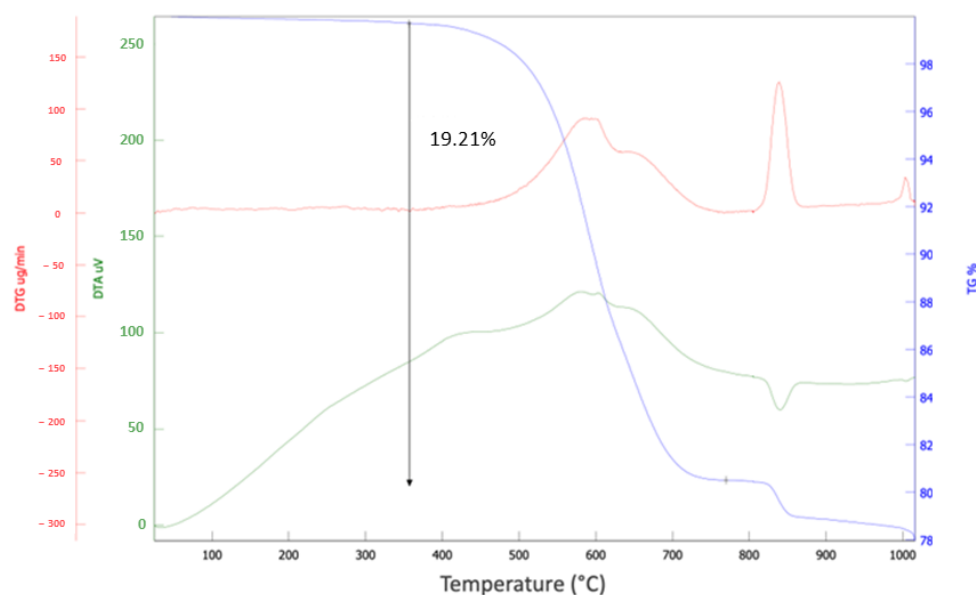


Figure 1. Results of the thermal analysis, reporting the thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA) curves. The 19.21% mass lost was due to the graphite burning and the corresponding carbon dioxide formation [24].

Between 450 and 800 °C, a sudden change in the weight of the sample was observed (TG%, blue line) due to the oxidation of the graphite in air. This percentage weight variation was attributed to the amount of carbon contained in the sample. In particular, in the stage ranging from 500 to 760 °C, a dramatic decrease in weight was due to the release of carbon dioxide, which could be attributed to the reduction of the cathodic material, better explained in the following.

According to TXRF and IC analyses, Table 3 shows the chemical analysis of the BM, reported as grams of element in 1 kg of LCO sample.

Table 3. Mass (g) of element in 1 kg of LCO sample.

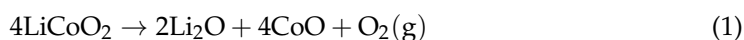
| Element | | g/kg | |
|---------|------|------|-----|
| Li * | 38.4 | ± | 0.6 |
| Co | 288 | ± | 18 |
| Mn | 5.2 | ± | 1.5 |
| Ni | 49 | ± | 3 |
| Cu | 4.8 | ± | 1.4 |
| Zn | 2.1 | ± | 1.6 |

* Li evaluation was performed by IC analysis. The other elements were evaluated by TXRF analysis.

Co and Li corresponded to about 28.8% and 3.8% of the total mass, respectively. Graphite represented about 19.2% of the total mass. Mn and Ni were also present (respectively, at 0.5% and 4.9%), probably due to contamination of the LCO BM from other cathodic materials, such as NCM. Indeed, the sample was provided by a recycling company that collects all the LIBs typologies. Cu and Zn were also present as used in battery production and they may have been not completely removed in previous dismantling and separation treatments. Traces of Al were also found. F may have also been present due to the residual binder and electrolyte.

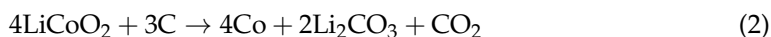
The samples were inserted into a refractory small chamber system with the presence of a susceptor according to the method proposed by [22]. Two different tests were performed using a quartz crucible: 4.5 g of BM in a single crucible for 5 min at 600 W, and 3 g of BM in three crucibles (1 g in each crucible) for 10 min at 1000 W. During the test, the last sample caught fire, and the temperature rose above 1000 °C; with the other sample, the temperature reached more than 650 °C.

The proposed microwave technology allowed the carbothermal reaction to take place. A typical thermochemical process can involve the decomposition of a metal oxide at high temperatures, in accordance with the following reaction (Equation (1)) [25]:



LiCoO_2 can decompose into Li_2O , CoO (or Co_3O_4 , which decomposes into CoO and O_2), and O_2 .

Considering the presence in the BM of a carbonaceous material, the overall reaction (Equation (2)) is a carbothermic reaction (the reducing agent is the graphite present in LCO):



Typically, oxygen reacts with graphite to form CO and/or CO_2 . Then, in an uncontrolled atmosphere, the oxygen in the air may react with the carbonaceous material, leading to combustion and the formation of carbon dioxide, which might interfere with the reduction process [26]. As long as CO can be found in the system, it can promote the formation of lithium oxide and it may also reduce cobalt oxide to metallic cobalt. Then, it is clear that the effect of carbon oxidation is a substantial step in defining the final products of lithium and cobalt, which are obtained.

For controlled carbothermic reduction experiments, researchers often use inert or reducing atmospheres to minimize oxidation and ensure the desired reaction takes place.

Common choices include using a controlled flow of gases like nitrogen, argon, or hydrogen, which can help maintain the desired environment for the reduction reaction without unwanted oxidation.

In the N_2 atmosphere, graphite was found to start oxidation from about 600 °C, as a consequence of O_2 generated by the decomposition of $LiCoO_2$ [17,26]. On the contrary, in the air atmosphere, it was found that graphite was more reactive at lower temperatures due to its oxidation before oxygen decomposition from $LiCoO_2$ [26]. Moreover, as previously mentioned, in an uncontrolled atmosphere, graphite may tend to react with the oxygen in the air rather than reduce $LiCoO_2$ [26]. Figure 2 shows the XRD pattern of the as-received LCO. Apart from the expected phases such as graphite and $LiCoO_2$, the XRD pattern showed that cobalt oxide (Co_3O_4 and CoO) peaks could also be detected. This may appear quite strange, but it could be explained by considering that thermal pretreatments were realized on the BM before the actual recycling processes to prepare the battery materials for further processing. Indeed, after battery dismantling, thermal treatment of battery materials is often performed. This process aims to break down organic binders, plastic components, and organic electrolytes into gases and volatile compounds, leaving behind solid residues containing valuable metals [17]. Moreover, the presence of graphite and the high temperatures can support the start of some carbothermic reductions, with the lowering of the $LiCoO_2$ phase [27].

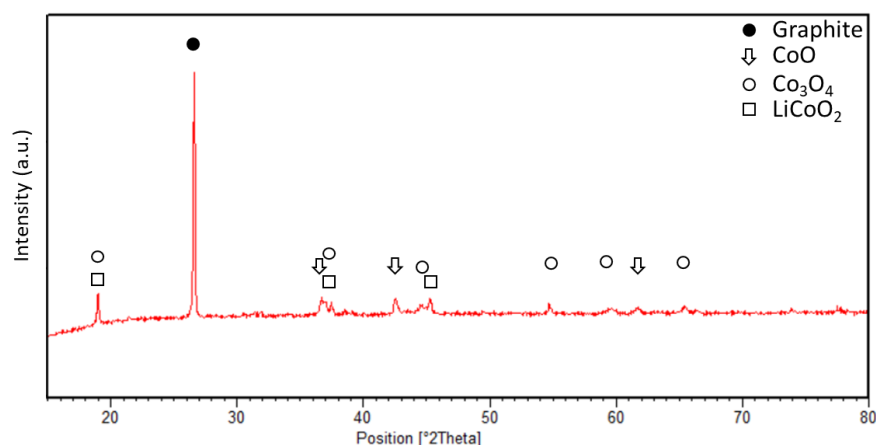


Figure 2. XRD pattern of the as-received LCO.

Figure 3 shows the XRD pattern of the sample treated at 600 W for 5 min. The pattern shows that only small peaks of the $LiCoO_2$ phase were still detectable and that the rise of cobalt oxide phases was evident. In addition, zabuyelite (lithium carbonate, Li_2CO_3) appeared in the pattern. This supports the conclusion that carbothermic reduction reactions allowed almost complete LCO decomposition in favor of the formation of Co_3O_4 , CoO , and Li_2CO_3 phases. In particular, comparing this pattern with that reported in Figure 2, the CoO XRD peak intensities were increased in comparison to the corresponding Co_3O_4 ones. This can be associated with a decomposition of this phase with the release of oxygen to form Co , in accordance with the thermal analysis (DTG) showing a peak centered at about 870 °C and a mass loss [25].

Figure 4 shows the XRD pattern of the sample treated at 1000 W for 10 min, which caught fire. The graphite peak was no longer visible, probably because it was completely burned during the test. The high temperature reached and the presence of zabuyelite support the conclusion that carbothermic reduction reactions took place, allowing almost complete LCO decomposition in favor of the formation of simple metal oxides like Co_3O_4 and CoO . Moreover, there was a presence of peaks related to Cu .

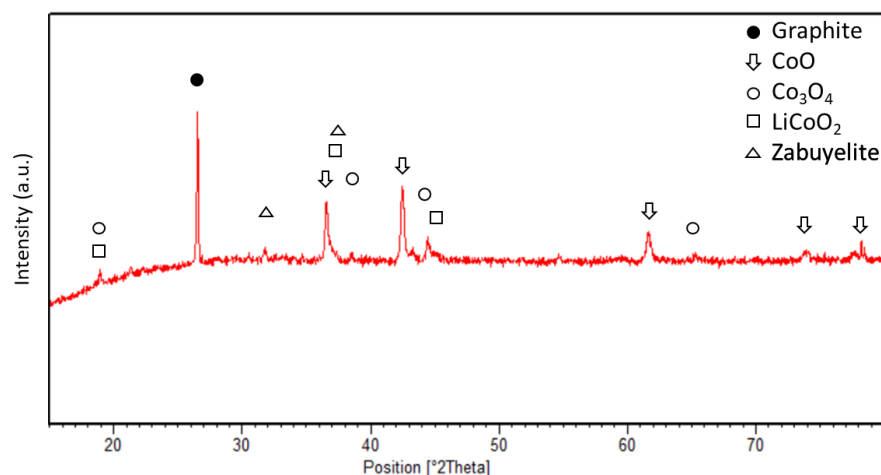


Figure 3. XRD pattern of LCO sample treated at 600 W for 5 min.

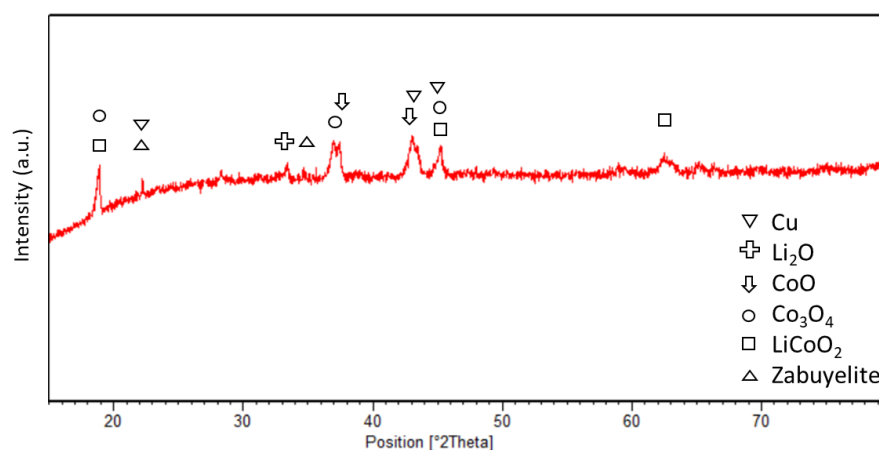


Figure 4. XRD pattern of LCO sample treated at 1000 W for 10 min. The sample caught fire.

In Figure 4, Li_2O was not always detectable by XRD, probably due to its low amount. Indeed, in the literature, it is uncommon to find the Li_2O phase in treated LCO samples by XRD [28]. On the contrary, for both treated samples, some peaks that could be attributed to lithium carbonate appeared in the XRD pattern. This suggests that Li_2O derived from the decomposition of LCO may react with carbon dioxide to form the carbonate.

Considering the treatments performed with the MW, the presence of cobalt as an oxide (Co_3O_4 and CoO) confirmed that in carbothermic reduction occurring in air, Co cannot be found in the metal form [26]. On the contrary, in an inert atmosphere, metallic cobalt may be obtained [26].

Moreover, in the absence of an inert atmosphere, the lithium carbonate phase is expected to decompose to Li_2O and CO_2 from 930 °C. On the contrary, in air, Li_2CO_3 is evaluated as a stable phase until about 1200 °C [26]. This suggests that the presence of oxygen hindered the decomposition of lithium carbonate, justifying its presence also in the sample treated at 1000 W and subjected to fire, even if XRD peaks were quite low. The melting temperature of lithium oxide was reported to be lower than 1200 °C [29]. Then, Li_2O may vaporize congruently. This may justify the peak detected in the DTG after 1000 °C (see Figure 1).

All the samples were leached in MilliQ water to determine the percentage of Li recovered by the BM. The leached solution was analyzed by IC, while the solid residue was dried and analyzed by XRD. The results of IC analysis are reported in Table 4 as grams of Li in kilogram of LCO sample. The data in Table 4 show that Li could always be detected. This can be justified for all the samples by considering that Li may have been present as

an oxide in the BM, which is a phase soluble in water, explaining the presence of Li in the leaching solutions.

Table 4. Results of water leaching for LCO samples, reported as grams of Li in kilogram of LCO.

| Sample | | Li g/kg | |
|----------------------------------|------|------------|-----|
| LCO as-received | 24.4 | ± | 0.4 |
| LCO treated at 600 W for 5 min | 32.6 | ± | 0.5 |
| LCO treated at 1000 W for 10 min | 6.9 | ± | 0.1 |

The results in Table 4 show that Li was leached in the as-received sample as well. This may have been due to the thermal processes performed on BM during the pretreatments. The recovery percentage was about 63%. The result is very interesting. Indeed, to the best of the authors' knowledge, there are no works in the literature considering that BM pretreatments may have effects on Li leaching. This can also be of great interest for hydrometallurgy applied to LCO recovery.

The best result in terms of Li recovery was obtained for the sample treated at 600 W for 5 min. There was an increase in Li recovery, reaching almost 85%. LCO treated at 1000 W for 10 min had the worst result, with a recovery percentage lower than the as-received sample (18%); this was probably because the sample caught fire leading to the volatilization of Li.

After water leaching, an XRD analysis was performed on dried samples (the corresponding XRD patterns are reported in the Supporting Information). The XRD pattern of the as-received LCO after water leaching showed the same crystalline phases detected before the leaching, as well as the peaks related to the Li phase that was not completely leached. Furthermore, when the XRD pattern of the sample was subjected to treatment at 600 W for 5 min, the peaks observed after water leaching remained consistent with those detected prior to the leaching process (see Supporting Information). Only the peaks related to zabuyelite were no longer detectable by the high percentage of Li recovered in the leaching solution.

In summary, for the sample treated for 5 min at 600 W, the possibility of direct recovery of Li as lithium carbonate was evident. This is interesting also because the recovery of lithium carbonate may be preferable in comparison to the recovery of lithium oxide due to its applicability as a primary material for cathode manufacturing.

4. Conclusions

In this paper, for the first time, the use of a MW to provide the carbothermic reduction of LiCoO_2 in air was presented by investigating the behavior of the corresponding BM sample. The LCO sample was treated in a MW oven consisting of a refractory chamber and a susceptor, at 600 W for 5 min and 1000 W for 10 min. After the treatments, the samples were leached in water for Li recovery. Moreover, an as-received LCO sample was leached as a comparison. The results showed for the first time that Li could be recovered by the as-received LCO sample as well, with a recovery percentage of about 63%, due to BM pretreatment. However, it was also shown for the first time that the MW treatment at 600 W for 5 min increased Li recovery, reaching 85%. The sample treated at 1000 W for 10 min caught fire during the test, and the graphite was completely burned. In this case, judging by the lower Li recovery percentage (18%) obtained from this sample, the Li probably volatilized. The result showed that at low power and with reduced time, it is possible to obtain a high recovery of Li. This result is extremely promising, encouraging the development of MW technology that allows reaching high temperatures in a short time compared to pyrometallurgical processes.

5. Patents

This technology was patented (Italian patent pending n. 102022000002351 and PCT/IB2023/051034).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries9110536/s1>, Figure S1: XRD pattern of the as-received LCO after water leaching; Figure S2: XRD pattern of LCO sample treated at 600 W for 5 min after water leaching; Figure S3: XRD pattern of LCO sample treated at 1000 W for 10 min after water leaching.

Author Contributions: Conceptualization, M.S., A.C., A.Z. and E.B.; methodology, M.S., A.C., A.Z. and E.B.; validation, M.S., A.C., A.Z. and E.B.; formal analysis, M.S., A.C., A.Z., D.L.C. and G.B.; investigation, M.S., A.C. and A.Z.; resources, A.F. and E.B.; data curation, M.S., A.C., A.Z., A.F. and C.A.; writing—original draft preparation, M.S., A.C. and A.Z.; writing—review and editing, I.A., A.F., C.A. and E.B.; visualization, A.C., A.Z., D.L.C. and G.B.; supervision, I.A., L.E.D. and E.B.; project administration, I.A. and E.B.; funding acquisition, E.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was realized with the support of Fondazione CARIPLO to “Tech4Lib—Spent Lithium-ion battery recovery” (CUP D73C23000170007) and MITO Technology (23_BONTEMPI_PROGRESS).

Data Availability Statement: The data are reported within the article and in Supporting Information.

Acknowledgments: The authors thank Milestone s.r.l. for the support in sample digestion. The graphical abstract was created with [BioRender.com](https://www.biorender.com), accessed on 16 October 2023.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Masias, A.; Marcicki, J.; Paxton, W.A. Opportunities and Challenges of Lithium Ion Batteries in Automotive Applications. *ACS Energy Lett.* **2021**, *6*, 621–630. [\[CrossRef\]](#)
- Thompson, D.L.; Hartley, J.M.; Lambert, S.M.; Shiref, M.; Harper, G.D.J.; Kendrick, E.; Anderson, P.; Ryder, K.S.; Gaines, L.; Abbott, A.P. The Importance of Design in Lithium Ion Battery Recycling—A Critical Review. *Green Chem.* **2020**, *22*, 7585–7603. [\[CrossRef\]](#)
- Liang, Z.; Cai, C.; Peng, G.; Hu, J.; Hou, H.; Liu, B.; Liang, S.; Xiao, K.; Yuan, S.; Yang, J. Hydrometallurgical Recovery of Spent Lithium Ion Batteries: Environmental Strategies and Sustainability Evaluation. *ACS Sustain. Chem. Eng.* **2021**, *9*, 5750–5767. [\[CrossRef\]](#)
- Baum, Z.J.; Bird, R.E.; Yu, X.; Ma, J. Lithium-Ion Battery Recycling—Overview of Techniques and Trends. *ACS Energy Lett.* **2022**, *7*, 712–719. [\[CrossRef\]](#)
- Wagner-Wenz, R.; van Zuilichem, A.J.; Göllner-Völker, L.; Berberich, K.; Weidenkaff, A.; Schebek, L. Recycling Routes of Lithium-Ion Batteries: A Critical Review of the Development Status, the Process Performance, and Life-Cycle Environmental Impacts. *MRS Energy Sustain.* **2023**, *10*, 1–34. [\[CrossRef\]](#)
- 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. [\[CrossRef\]](#)
- Lv, W.; Wang, Z.; Cao, H.; Sun, Y.; Zhang, Y.; Sun, Z. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2018**, *6*, 1504–1521. [\[CrossRef\]](#)
- Woollacott, E. Electric Cars: What Will Happen to All the Dead Batteries? Available online: <https://www.bbc.com/news/business-56574779> (accessed on 22 September 2023).
- Maisch, M. Lithium-Ion Recycling Rates Far Higher than Some Statistics Suggest. Available online: <https://www.pv-magazine.com/2019/07/12/lithium-ion-recycling-rates-far-higher-than-some-statistics-suggest/> (accessed on 22 September 2023).
- Gao, Y.; Zhang, J.; Jin, H.; Liang, G.; Ma, L.; Chen, Y.; Wang, C. Regenerating Spent Graphite from Scrapped Lithium-Ion Battery by High-Temperature Treatment. *Carbon* **2022**, *189*, 493–502. [\[CrossRef\]](#)
- Li, T.; Tao, L.; Xu, L.; Meng, T.; Clifford, B.C.; Li, S.; Zhao, X.; Rao, J.; Lin, F.; Hu, L. Direct and Rapid High-Temperature Upcycling of Degraded Graphite. *Adv. Funct. Mater.* **2023**, *33*, 2302951. [\[CrossRef\]](#)
- Nkuna, R.; Ijoma, G.N.; Matambo, T.S.; Chimwani, N. Accessing Metals from Low-Grade Ores and the Environmental Impact Considerations: A Review of the Perspectives of Conventional versus Bioleaching Strategies. *Minerals* **2022**, *12*, 506. [\[CrossRef\]](#)
- 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*, 1–21. [\[CrossRef\]](#)
- Kaya, M. State-of-the-Art Lithium-Ion Battery Recycling Technologies. *Circ. Econ.* **2022**, *1*, 100015. [\[CrossRef\]](#)
- Mao, J.K.; 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. [\[CrossRef\]](#)

16. Tang, Y.; Xie, H.; Zhang, B.; Chen, X.; Zhao, Z.; Qu, J.; Xing, P.; Yin, H. Recovery and Regeneration of LiCoO₂-Based Spent Lithium-Ion Batteries by a Carbothermic Reduction Vacuum Pyrolysis Approach: Controlling the Recovery of CoO or Co. *Waste Manag.* **2019**, *97*, 140–148. [\[CrossRef\]](#)
17. Lombardo, G.; Ebin, B.; St Foreman, M.R.J.; Steenari, B.M.; Petranikova, M. Chemical Transformations in Li-Ion Battery Electrode Materials by Carbothermic Reduction. *ACS Sustain. Chem. Eng.* **2019**, *7*, 13668–13679. [\[CrossRef\]](#)
18. Vishvakarma, S.; Dhawan, N. Recovery of Cobalt and Lithium Values from Discarded Li-Ion Batteries. *J. Sustain. Metall.* **2019**, *5*, 204–209. [\[CrossRef\]](#)
19. Kwon, O.; Sohn, I. Fundamental Thermokinetic Study of a Sustainable Lithium-Ion Battery Pyrometallurgical Recycling Process. *Resour. Conserv. Recycl.* **2020**, *158*, 1–12. [\[CrossRef\]](#)
20. 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. [\[CrossRef\]](#)
21. Li, J.; Lai, Y.; Zhu, X.; Liao, Q.; Xia, A.; Huang, Y.; Zhu, X. Pyrolysis Kinetics and Reaction Mechanism of the Electrode Materials during the Spent LiCoO₂ Batteries Recovery Process. *J. Hazard. Mater.* **2020**, *398*, 1–9. [\[CrossRef\]](#)
22. Fahimi, A.; Alessandri, I.; Cornelio, A.; Frontera, P.; Malara, A.; Mousa, E.; Ye, G.; Valentim, B.; Bontempi, E. A Microwave-Enhanced Method Able to Substitute Traditional Pyrometallurgy for the Future of Metals Supply from Spent Lithium-Ion Batteries. *Resour. Conserv. Recycl.* **2023**, *194*, 1–10. [\[CrossRef\]](#)
23. Zhong, X.; Liu, W.; Han, J.; Jiao, F.; Qin, W.; Liu, T. Pretreatment for the Recovery of Spent Lithium Ion Batteries: Theoretical and Practical Aspects. *J. Clean. Prod.* **2020**, *263*, 1–10. [\[CrossRef\]](#)
24. Gomez-Moreno, L.A.; Klemettinen, A.; Serna-Guerrero, R. A Simple Methodology for the Quantification of Graphite in End-of-Life Lithium-Ion Batteries Using Thermogravimetric Analysis. *iScience* **2023**, *26*, 107782. [\[CrossRef\]](#)
25. She, X.F.; Zhu, K.; Wang, J.S.; Xue, Q.G. Product Control and a Study of the Structural Change Process during the Recycling of Lithium-Ion Batteries Based on the Carbothermic Reduction Method. *J. Chem. Res.* **2022**, *46*, 17475198211066533. [\[CrossRef\]](#)
26. Nuraeni, B.A.; Avarmaa, K.; Prentice, L.H.; Rankin, W.J.; Rhamdhani, M.A. Carbothermic Reduction of LiCoO₂ Cathode Material: Thermodynamic Analysis, Microstructure and Mechanisms. *Sustain. Mater. Technol.* **2022**, *34*, 1–17. [\[CrossRef\]](#)
27. Wang, H.; Liu, C.; Qu, G.; Zhou, S.; Li, B.; Wei, Y. Study on Pyrolysis Pretreatment Characteristics of Spent Lithium-Ion Batteries. *Separations* **2023**, *10*, 259. [\[CrossRef\]](#)
28. Chen, S.; Xie, D.; Liu, G.; Mwizerwa, J.P.; Zhang, Q.; Zhao, Y.; Xu, X.; Yao, X. Sulfide Solid Electrolytes for All-Solid-State Lithium Batteries: Structure, Conductivity, Stability and Application. *Energy Storage Mater.* **2018**, *14*, 58–74. [\[CrossRef\]](#)
29. Ma, S.; Jiang, M.; Tao, P.; Song, C.; Wu, J.; Wang, J.; Deng, T.; Shang, W. Temperature Effect and Thermal Impact in Lithium-Ion Batteries: A Review. *Prog. Nat. Sci. Mater. Int.* **2018**, *28*, 653–666. [\[CrossRef\]](#)

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