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Strategic metals recovery from spent lithium-ion batteries is a critical step toward environmental sustainability and resource conservation. Our research introduces a new promising method to recover lithium from spent batteries. This process not only mitigates the ecological and economic impacts associated with mining and refining virgin materials but also fosters a circular economy. By enabling the reuse of valuable metals, we support the transition to renewable energy systems and contribute to lowering the cost of energy storage solutions. This research contributes directly to several UN Sustainable Development Goals: ensuring sustainable consumption and production patterns (SDG 12), building resilient infrastructure and fostering innovation (SDG 9), and supporting industry efforts to promote sustainable practices (SDG 11). Additionally, it underpins efforts to secure the availability and sustainable management of water and sanitation for all (SDG 6) by reducing the water-intensive processes of metal extraction and processing.

Thermal approaches based on microwaves to recover lithium from spent lithium-ion batteries.

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Abstract

During the energy transition, the demand for strategic metals has become a focal point due to their crucial roles in advancing cleaner energy technologies and sustainable practices. As a response to the potential supply vulnerabilities of critical raw materials, recycling has gained attention, despite some methods being more expensive than traditional mining. In this context, new technologies based on microwave radiation have been recently introduced to recover lithium from spent lithium-ion batteries.

This study highlights the innovative results achieved through the application of microwave heating to lithium cobalt oxide (LCO) black mass, showing that mass increase can support the possibility of proposing the technology as a new sustainable approach. The possibility of coupling carbon materials with magnetic materials, available in the black mass (BM) results in a strategic approach to increasing the final temperature of microwave-absorbing materials. The process proves highly efficient in lithium recovery, with a treatment at 600 W for 5 minutes, reaching a value higher than 80%, while also eliminating some labour-intensive pre-treatment steps. The research sheds light on both the advantages and potential challenges associated with this ground-breaking technology.

Keywords: Microwave, Black mass, lithium-ion battery, circular economy, metals recovery, e-waste

1. Introduction

Literature underscores that the availability of strategic metals, for example lithium, will pose a significant long-term sustainability challenge for the transportation sector unless a combination of measures is implemented to address this issue [1]. Among them, recycling is the most suitable option to avoid precious material loss. The advantages of recycling metals in lithium-ion batteries (LIBs) are not only limited to the mitigation of raw materials dependence and risks of shortage, but also include environmental and health benefits, and promotion of circular economy strategies [1]. Recycling can prevent environmental and health problems associated with the disposal of spent batteries [1] and helps to reduce the extraction of raw materials, such as cobalt, nickel, and lithium, which are limited resources and can be subject to supply chain disruptions [1]. By recycling LIBs, valuable metals can be recovered and reused, reducing the need for new mining and extraction [2]. This not only

1

43 conserves natural resources but also minimizes the environmental impact of mining
44 activities [3]. However, because of the delayed impacts associated with material recycling,
45 the recycling process is anticipated to have a substantial influence in addressing the long-
46 term material cost challenges in Electric Vehicle (EV) development [5]. Recycling is set to
47 increase the adoption rate of EVs from 59% to 67% by the year 2060 [5].

48 Then, recycling holds promise in tackling prolonged challenges related to critical material
49 prices, thanks to anticipated technological advancements and economies of scale that will
50 drive down recycling expenses. While recycling has the advantage of shortening supply
51 chains and cutting down on logistical expenses, it remains more cost-effective to extract
52 minerals through mining than to recycle them. Consequently, there is an urgent need to
53 explore cost-efficient and sustainable methods for reclaiming valuable minerals that can
54 compete with freshly mined ones [5].

55 Moreover, this is not straightforward, partly owing to the intricacies associated with spent
56 lithium-ion battery waste. For example, because the spent LIBs waste is made of complex
57 mixtures of different materials, and the classification and sorting of batteries by cathode
58 chemistry are extremely onerous, the automatization of the separation processes,
59 preliminary for the recovery, is quite complex [4]. Even if more than 95% in the efficiency of
60 lithium extraction and recovery can be found, the proposed processes are generally
61 addressed to specific cathodes [5]. Additionally, recycled materials often have a lower
62 market value compared to virgin resources [6]. This discrepancy can be attributed to several
63 factors, including the increase in mining activities, which are considered crucial for meeting
64 environmental targets for greenhouse gas (GHG) reduction. Furthermore, there is an
65 absence of explicit provisions for evaluating the environmental impacts of different mineral
66 sources, such as extraction from geothermal brines, coal, unconventional sources, the
67 ocean, spent electronics, and virgin mineral mining. This situation poses a significant threat
68 to environmental protection [7]. Therefore it is essential to make efforts towards establishing
69 a sustainable battery recycling system and providing resources for the continuous
70 development of new and advanced battery recycling technologies.

71 The primary objective of this paper is to introduce a novel approach, utilizing microwave-
72 based non-conventional heating systems, for the treatment of spent LIBs, highlighting the
73 potentialities of this technology. The efficacy of the process is demonstrated by the lithium
74 recovery, which allows making evidence occurring of the carbothermic reactions, induced
75 by thermal treatments. This is a significant contribution, also because existing literature
76 suggests separating lithium recovery from the other metals but doing so through traditional
77 thermal methods may present challenges [8]. This study is particularly dedicated to waste
78 samples, and there are limited comparable examples available due to the prevailing
79 tendency in the literature to adhere to ideal samples, obtained by using virgin materials.

80 ## 2. Pyrometallurgy recovery technologies

81 The prevailing recycling procedures for spent LIBs can be broken down into three key
82 stages: pre-treatment, the metallurgical processing of recycling, and the creation of new
83 materials. In the pre-treatment phase, the initial step involves discharging the spent LIBs to
84 prevent short circuits. Subsequently, they are roughly disassembled into various

85   components, such as cathodes, anodes, membranes, and metallic shells [4]. However, in
86   most cases, mechanical pre-treatment involves crushing the anodic and cathodic battery
87   parts, as it can be challenging to separate these components, making more complicate the
88   recovery of valuable materials. Thermal treatment is also commonly employed as a
89   preferred method for removing binders and electrolytes during the pre-treatment process.
90   Following pre-treatment, more advanced technologies are necessary to refine these mixed
91   products through chemical or physical techniques. The present metallurgical processing
92   methods predominantly encompass pyrometallurgical and hydrometallurgical technologies.
93   Nonetheless, the extensive use of chemicals and high energy consumption, along with the
94   associated high emissions during the metallurgical processes, can pose challenges in
95   achieving environmentally friendly and efficient recycling of various metals from spent LIBs
96   [4].

97   In particular, pyrometallurgical methods involve high-temperature procedures used to
98   extract and recover valuable materials from battery waste. Essentially, the pyrometallurgical
99   process entails exposing the battery waste to heat while utilizing a reducing agent, like
100 carbon. The main objective is to transform metal oxides into either their elemental form or
101 less complex metal oxides. This method has been proven to be especially efficient in the
102 recovery of metals such as cobalt, nickel, and copper, even if some problems can be
103 established with lithium recovery [9]which is usually present in the slag,
104 with other elements such as Al, Ca, and Si.

105 Carbothermal reduction of the lithium cobalt oxide ($LiCoO_2$ - LCO), lithium manganese oxide
106 ($LiMn_2O_4$ - LMO), and lithium nickel manganese oxide ($LiNi_{0.5}Mn_{1.5}O_4$ - LNMO) can occur
107 due to carbon present in the black mass (originating from the anodic part of the battery),
108 which is available for the reaction, promoted by the heat treatment. Indeed, the anodic part
109 of the LIBs is generally composed of graphite.

110 At high temperatures and in the presence of oxygen (derived from the cathodic material
111 decomposition), carbon oxidizes and can form CO and/or CO_2. The decomposition of LMO,
112 LCO, and LNMO can produce nickel, manganese, and cobalt oxides, which may be also
113 further reduced by C and CO at higher temperatures [10].

114 The thermal analysis following the kinetics of the reactions shows that, generally, until
115 about 600 °C cathode material seems to be stable (the weight loss of the black mass is quite
116 limited), and it is more evident beyond 600 °C [11]. Weight losses observed after 850°C are
117 generally associated with the formation of oxides of Mn and Co [11].

118 Although pyrometallurgical techniques offer the potential for metal reclamation, they have
119 certain limitations, mainly related to their energy demand [12]. High-temperature processes
120 require substantial energy input, leading to heightened environmental consequences and
121 elevated expenses in comparison to other recycling approaches. Furthermore,
122 pyrometallurgical methods might not be applicable for recovering all materials contained
123 within lithium-ion batteries, and specific hazardous constituents within the battery waste
124 could necessitate supplementary treatment and disposal.

125 In this frame, the advantages of microwave (MW) technology over traditional
126 pyrometallurgical processes are commonly recognized [13].

127
128
129 **3. Microwave treatments and the hybrid-heating mechanism**

130   MW technologies have been recently applied in various ways as new methodologies to
131   recycle metals in lithium-ion batteries (LIBs). One example is the MW-enhanced approach,
132   which uses a biodegradable and recyclable deep eutectic solvent to leach valuable metals
133   from spent LIBs [14]. The high electric field induced by MW heating increases the dipole
134   moments on the battery surface, allowing for fast leaching of metals such as lithium and
135   cobalt. MW was also used for sample leaching, in a closed vessel, to facilitate the dissolution
136   of the metals [15]. Another example consists of biomass pyrolysis supporting the recovery
137   of LIB from biomass waste, with the result of reducing the decomposition temperature of the
138   cathodic materials [16]. Finally, a very recent example concerns the use of the microwave-
139   assisted reduction roasting method to promote carbothermal reduction reactions [17,18]. In
140   particular, the use of a hybrid-heating mechanism has shown promising results in the direct
141   recovery of lithium from spent batteries. In this case, Li was shown to be available as lithium
142   oxide, then it is soluble in water.

143   Nonetheless, even though certain research findings showcase the potential of MW
144   technology for recycling metals from LIBs, efforts in this field remain relatively restricted.
145   Specifically, the impacts of MW heating on the treatment of spent cathode materials are not
146   yet comprehensively understood and necessitate further exploration. This is also because
147   the black mass (BM), based on carbon materials with microwave absorption properties,
148   brings both opportunities and challenges in providing new ways to recover strategic metals.
149   Then a deep understanding of the MW heating-related phenomena must be realized. In
150   particular, MW heating, with its distinctive internal heat mechanism, can mitigate the shadow
151   effect during material heating, alter the heat transfer mode, and significantly reduce reaction
152   times. Nevertheless, it's essential to emphasize that this heating mechanism differs from the
153   process that takes place in solutions.

154   Fig. 1 illustrates the difference between the heating mechanisms in a water-based solution
155   and a solid composed of carbon-based material. In the context of MW heating in a solution,
156   the primary process involves the rotation of polar solvent molecules. Conversely, for
157   electron-rich solids devoid of freely rotatable dipoles, such as carbon-based solids, the
158   literature suggests that heat is generated through electron motion, manifesting as joule
159   heating within the material's structure. This heat generation arises either due to collisions
160   triggered by graphite's delocalized pi-electrons moving within a confined region and
161   interacting with the oscillating field or as heat generated at grain/phase boundaries [19] due
162   to the interfacial polarization. Furthermore, the comprehensive mechanism behind the MW
163   heating of solids remains incompletely understood. Therefore, its potential applied to BM
164   treatments hasn't yet been highlighted in the literature.
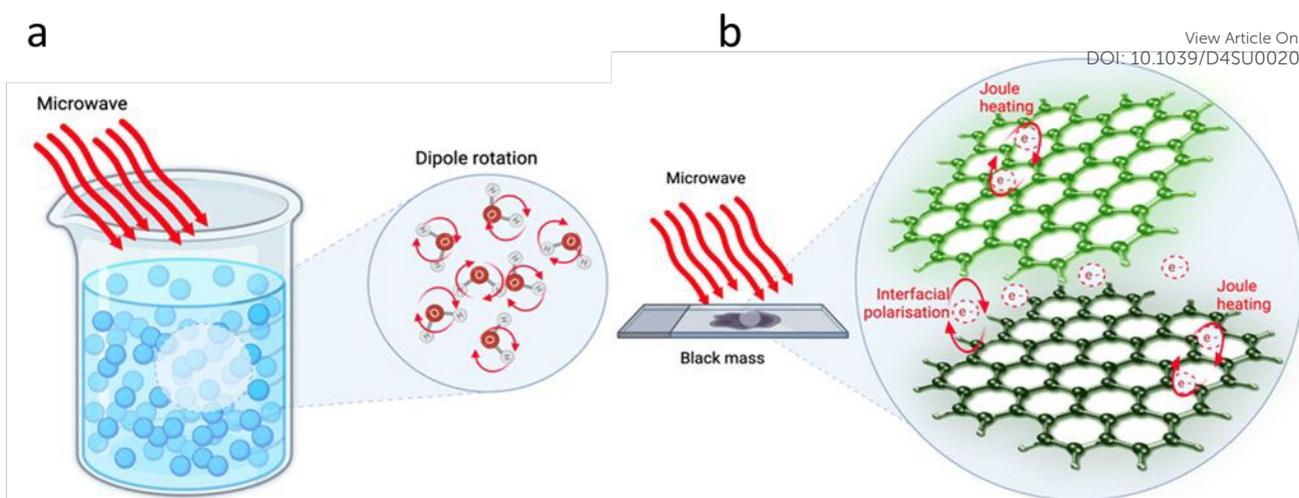
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Fig. 1: The MW heating mechanism in a water-based solution a) and a solid composed of carbon-based material b). In a solution, the primary process involves the rotation of polar solvent molecules. For electron-rich solids, such as carbon-based solids, the heat is generated through electron motion, manifesting as joule heating within the material's structure.

The main parameters used to model MW heating are permittivity, permeability, and loss tangent. Permittivity (ε) refers to a material's ability to engage with the MW electric field. It comprises both a real and an imaginary component. The real part (ε') signifies the extent to which the electric field permeates, often referred to as the dielectric constant or permittivity. The imaginary part (ε″) signifies the energy retained within the material and is known as the electric loss factor [20]. It dictates the material's capacity to transform electric energy into heat. Permeability, on the other hand, characterizes the material's aptitude to interact with the magnetic field. The substrate's reaction to converting microwave energy into thermal loss is denoted as the loss tangent (tan δ) and it is calculated as ε″/ε' [17]. The MW penetration depth (D_p) indicates the distance a wave travels before its energy diminishes to 1/e, and it is proportional to the MW wavelength and inversely proportional to (tan δ)$^{1/2}$. It can be calculated as reported in equation 1 [21]:

$$Dp = \frac{\lambda_0}{2\pi(2\xi')^{\frac{1}{2}}}\left\{\left[1 + \left(\frac{\xi''}{\xi'}\right)^2\right] - 1\right\}^{-\frac{1}{2}} \qquad (1)$$

On exposure to MW, the electromagnetic loss in a material is converted into heat. Moreover, with the temperature rise, the material's dielectric properties can change. This can alter the MW loss, with the consequence of changes in the heating characteristics [22]. As an example, alumina results transparent to MW up to 900 °C (resulting in high penetration depth of MW radiation), yet it starts to interact with microwaves at temperatures surpassing 1000 °C [20]. This makes it necessary to investigate suitable materials to be used for MW adsorbing and/or heat insulation applications.

It was already shown that MW can penetrate the spent carbon cathode material (produced in the process of aluminum electrolysis) with a depth higher than 0,01 m [21], also reaching values higher than 0.3 m for cathodic materials and graphite [10] and 0,2 - 1 m for anthracite
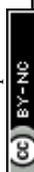
197 [23] and bituminous coal [24]. In particular, as the dielectric properties of the materials
198 depend on the temperature, it results that MW penetration depth also can be variable. It also
199 depends on the material density [24] and packing, making its evaluation extremely
200 complicated for a mixture of different materials, such as waste made of several compounds
201 and some contaminants, with variable chemistry.
202 In the case of MW heating the use of a solid-state material that can be excited by MW
203 radiation, such as carbon, allows a very efficient heating, because the target material
204 absorbs the MW energy. This is the case of LIBs, where the cathodic and anodic (generally
205 made in graphite) materials are both in black mass. Graphite has π-electrons, which are
206 responsible for heat generation (see Fig. 1). For carbon-based materials combined with
207 magnetic materials, these heating effects can be further enhanced. Magnetic materials can
208 absorb microwaves through magnetic losses, including hysteresis, eddy currents, and
209 relaxation losses [20]. The interplay between the magnetic losses and the Joule heating in
210 carbon can lead to efficient internal heating of the material. Finally, in MW processing of
211 various materials, a susceptor can be also employed to amplify the MW-absorbing
212 capabilities of the sample being treated. A susceptor material absorbs energy from the MW,
213 converting it into heat energy that is then transferred to the processed material. For example,
214 carbon can be used as a susceptor. For applications requiring reaching high temperatures,
215 such as high melting point materials treatments, Si is often used. Conversely, charcoal
216 powder is easily accessible at a significantly lower cost Fare clic o toccare qui per immettere
217 il testo..

218 A susceptor can be also external to the sample, but in its proximity: the heat will be
219 subsequently conveyed to the sample through conventional modes of heat transfer.
220 The susceptor assisted microwave heating is generally defined as "hybrid heating" (see Fig.
221 2). This was recently proposed for BM treatment [25] because graphite is generally used for
222 low-temperature applications [26], then the presence of an external susceptor can be
223 effective in the increasing of system temperature.
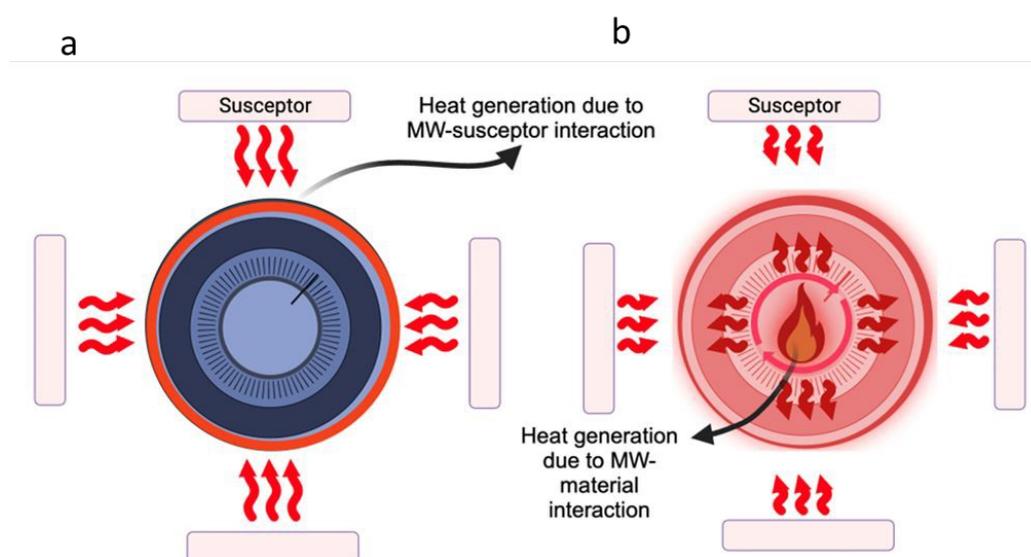224

225
226   Fig. 2: A susceptor external to the sample heats a material from its surface due to the MW excitation (a),
227   while when there is an interaction between the materials and MW, the material is heated from the centre (b).

228   The susceptor-assisted microwave heating, supporting the material heating (b) is generally defined as
229   "hybrid heating".

230

231

232 The effective and suitable configuration of a susceptor-assisted MW heating system needs
233 to couple a material that can be excited by MW with a thermal insulation system, which must
234 envelop it. Indeed, thermal insulation plays a fundamental role in any technology involving
235 a thermal process by limiting heat dissipation, especially at high temperatures. A suitable
236 thermal insulation for MW depends not only on the material thermal stability but also on its
237 ability to remain transparent to MW radiation across the entire temperature range. Alumina
238 is a commonly used insulation material due to its outstanding transparency to MW radiation
239 and its strong resistance to thermal and wear-related challenges over a wide range of
240 temperatures.
241 Concerning the drawbacks connected with thermal treatments, the main negative aspect is
242 pollutants gas generation, including electrolyte components, oxygenated hydrocarbons,
243 hydrocarbons, and others [27]. The formation of different gas species is due to electrolyte
244 volatilization, electrolyte degradation/decomposition, and pyrolysis of the organic separator
245 and binder, followed by complex radical reactions among the species formed by the
246 physicochemical reactions.

247

248 **4. Experimental**

249

250 LCO spent BM was provided by Spirit s.r.l., a company recycling battery located in Chiampo,
251 Vicenza, Italy.
252 The BM was obtained after conventional mechanical pretreatments to separate the battery
253 case, the plastic components, and the electrolyte.
254 The sample was digested to evaluate the concentration of Li, as described in [18]. The
255 composition results in 38.4 g/Kg of Li, 288 g/Kg of Co, 5.2 g/Kg of Mn, 49 g/Kg of Ni, and
256 4.8 g/Kg of Cu. The amount of graphite in the BM is 19.2% [18].
257 BM was treated at 600 W at 2.4GHz for 5 minutes, increasing the sample mass, in each
258 experiment, from 0.5 to 4.5 g (see Table 1 for the sample name with the corresponding
259 mass), in a PYRO Advanced Microwave Muffle Furnace (Milestone s.r.l., Bergamo, Italy),
260 which was equipped with a susceptor [25]. The tests were repeated three times. The
261 temperature of the samples, after the thermal treatment was provided by thermal imaging
262 camera testo 890.
263 The sample resulted in filling the sample holder to about 1 cm.
264 All the samples, after the MW treatments, were analysed by X-ray diffraction (XRD), using
265 a Panalytical diffractometer using Cu Ka (1.5406 Å) radiation and operating at 40 kV and 40
266 mA. The patterns were acquired from 10° to 70° (2Θ). For the leaching test, BM was mixed
267 with Milli-Q water in a heating plate at 80 °C for 30 min using a solid/liquid ratio of 40 g/L
268 [25]. After this time the solution was filtered with a vacuum filtration by using a nylon
269 membrane with 0.45 μm. Li^+ concentration was evaluated by ion chromatography (IC),
270 Metrohm 883 Compact IC plus (Metrohm AG, Herisau, Switzerland) and cation exchange
271 column Metrosep C4-150/4.0 (Metrohm AG, Herisau, Switzerland).

272

5. Results and discussion

5.1 A mass and sample heating correlation

$LiCoO_2$, in the presence of a carbon source, can decompose into LiO_2 and Co (or CoO), by increasing the temperature, showing the most favourable condition at about 700°C [28]. Graphite is converted into CO and CO_2. The reactions can be followed by analysing the sample mass loss, which is because CO_2 removes solid carbon contained in the BM, to form a gas.

However classical heating systems are more time-consuming in comparison to MW technologies, and the target temperature needs more time to be reached. To obtain an efficient heating system, it is fundamental to evaluate the MW penetration depth: if the penetration depth is not high, the heating efficiency may be low.

For an LCO BM, containing about 20% of graphite, the penetration depth of the microwave can be calculated based on (1) [17]. The results reported in Fig. S1 (see the Supporting) show that till to about 400 °C, the MW penetration depth decreases with the increase of the temperature, due to the rise of the MW-absorbing properties of the BM. This means that the loss factor (ε'') and the dielectric constant (ε') increase.

Fig. S1 shows that for the range of temperatures reached by these experiments, the penetration depth of MW radiation ranges from 0.025 to 0.065 m [17]. For a range of temperatures from 650 °C to 900 °C the penetration depth may also be higher than 0.06 m, depending on the BM density and dielectric parameters.

Concerning the samples investigated in this work, it is possible to conclude that all the samples were penetrated by MW radiation (see Fig. S1), with the consequence that an increase in the sample mass subjected to the treatment produces an increase in its temperature, due to the increase of the material that is excited by MW.

The temperature reached by the samples versus the different masses is reported in Fig. 3.
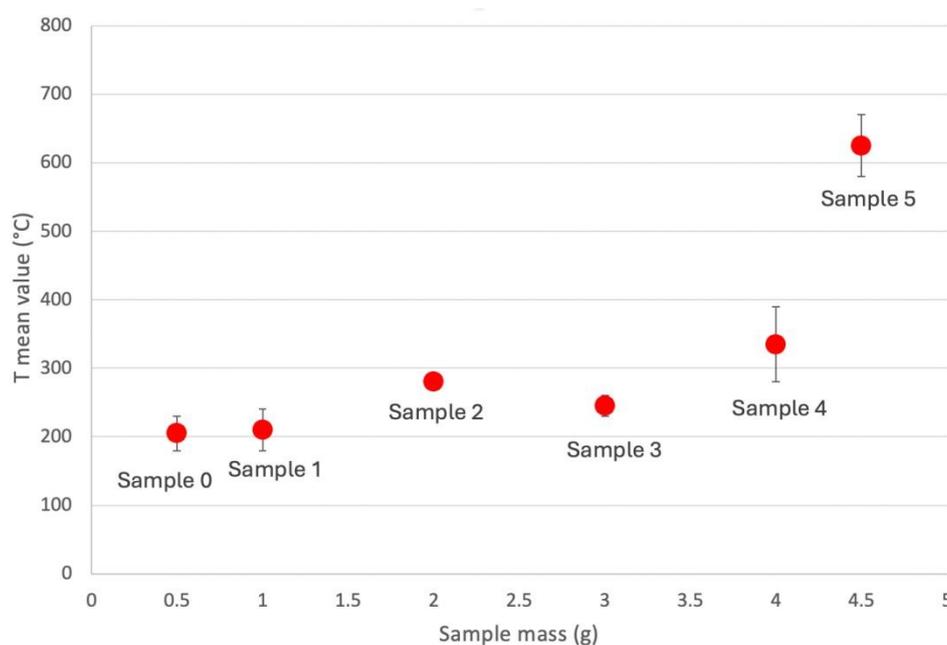
301   Fig. 3: Temperatures reached by the spent LCO battery samples, treated at 600 W for 5 minutes, as a
302   function of the samples' mass. Error bars correspond to the temperature variation inside the samples,
303   evaluated by the thermal imaging camera.
304
305

306   An increase in the mass undergoing treatment leads to a rise in sample temperature during
307   MW excitation because there's more BM to absorb the MW energy. This specific effect hasn't
308   been explored in spent LIBs, although it's documented in other contexts. According to the
309   literature, this may be attributed to the fact that a larger mass in the same container will have
310   a reduced surface area to volume ratio, thus lowering heat dissipation [29–31]. Unlike
311   conventional heating methods, where heat is applied externally, microwave systems
312   generate heat internally. As a result, it can be expected that the temperature of the material
313   will rise. Therefore, the loss of heat from the sample becomes a significant factor that
314   governs the heating process. In the present case, the rate of temperature increase is not
315   linear, probably because of the changes in the permittivity (ε'), and the electric loss factor
316   (ε'') that after 600 °C start to increase significantly.
317   The mass loss (%) of samples treated in this work is shown in Fig. 4 and is plotted against
318   the mean detected sample temperatures. The linear correlation observed in the data can be
319   explained by the fact that an increase in temperature, due to a more prolonged treatment,
320   more effectively promotes the oxidation of carbon. With the increase in the treatment time
321   and the temperature rise, the carbon within the samples reacts more readily with oxygen to
322   form carbon dioxide. This gas is released into the atmosphere, resulting in a carbon loss for
323   the sample (weight loss). This process highlights the occurrence of carbothermic reactions,
324   where the elevated temperatures facilitate the transformation of solid carbon into gaseous
325   carbon dioxide. Thus, higher temperatures enhance the efficiency of carbon oxidation,
326   leading to greater mass loss in the samples due to the emission of CO_2 (as described in
327   section 2).
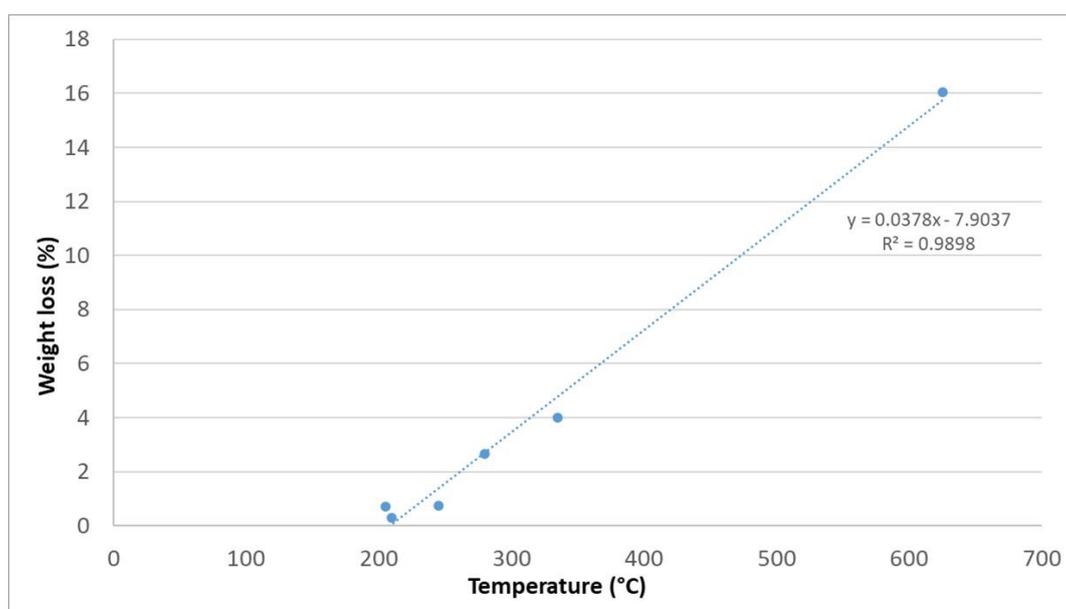328
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332   Fig. 4: Mass loss of the LCO BM samples, reported versus the final temperature.

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333

334   Fig. 5 shows the XRD patterns of LCO BM before (LCO_tq) and after MW treatments with
335   the mass increased (sample 2 and sample 5, see Figure 3). The results show that LCO
336   powder (before MW treatment) is characterized by graphite and lithium cobalt oxide
337   ($LiCoO_2$). Some peaks of Ni were also detected. This is also confirmed by the chemical
338   analysis reported in the experimental section, probably due to some other cathode
339   contamination. Also, some peaks of CoO, Co_3O_4, and Li_2O are present. The presence of
340   unexpected phases may be due to several reasons: first, it is important to highlight that the
341   BM used for this study is a real sample, provided by a recycling facility, then it also contains
342   Mn and Ni probably due to contamination of other cathodic materials. In addition, the pre-
343   treatment (performed at 800 °C) realised in the recycling facility, to remove the binder and
344   the electrolyte, can have partially promoted some carbothermal reactions [17].

345

346   After MW treatment, XRD patterns show an evident decrease in graphite peaks and the
347   reduction of $LiCoO_2$ with the formation of CoO. In the case of a sample with a higher mass
348   amount (sample 5), it is clear the increase in the CoO intensity. This means that the
349   carbothermal reactions are promoted by the mass increase, which is related to the higher
350   temperature rise (see Fig. 3).

351
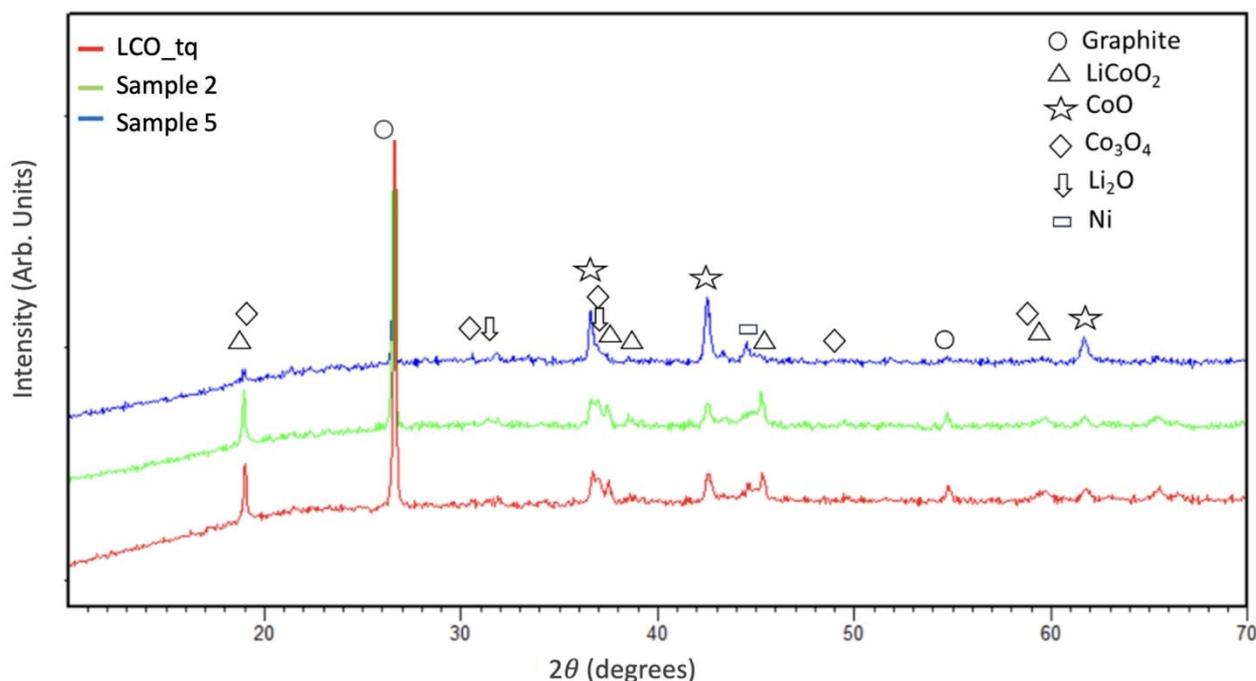
352
353   Fig.5: XRD patterns of LCO BM before (sample LCO_tq) and after MW treatment with the increase of black
354   mass (sample 2 and sample 5).

355

356

357   These results suggest that the heating mechanism is completely different in comparison to
358   conventional systems, where an increase in the mass needs a corresponding increase in
359   the energy that must be transferred for the increase in the sample temperature [32].
360   Carbon materials possess excellent electrical conductivity, which is crucial for microwave
361   absorption. When combined with magnetic materials, the interface between these two types

10

of materials increases [30]. This interface can act as a site for interfacial polarization, where the electric field can cause charges at the interface to oscillate, leading to energy dissipation as heat (see Figure 1). LCO exhibits some magnetic properties, even though it is not typically classified as a magnetic material for applications relying on strong magnetic interactions, such as magnetic storage devices or magnetic structural components. However, cobalt oxides, which are formed by carbothermic reaction (see Figure 3) are magnetic materials [33]. These cobalt oxides can significantly contribute to the magnetic loss mechanisms essential for effective microwave absorption, making them valuable as high-temperature microwave-absorbing materials [20]. When these materials interact with microwave radiation, they absorb the electromagnetic energy and convert it into heat, which typically increases their temperature. Magnetic loss materials dissipate electromagnetic energy through hysteresis loss, natural resonance, eddy current loss, magnetic hysteresis loss, domain-wall resonance, and other forms [20]. This effect was very recently demonstrated for cobalt oxide composite [34]. In this work, this effect is proposed, for the first time, to explain the heating mechanism of the black mass, induced by microwave.

To assess the potential of this technology, the amount of lithium that can be recovered is quantified.

For a simplified recovery of strategic metals from spent LIBs it is suggested to separate Li from transition metals. This is possible due to the high water solubility of Li_2O, which is formed after carbothermic reduction of LCO [35]. Then after the MW treatment, the samples were subjected to water leaching.

Table 1 shows the amount (%) of Li recovered by water leaching. As expected, an increase in the recovered Li corresponds to a higher mass treated in the MW oven. This demonstrates that higher temperatures promote carbothermic reductions and that this treatment can allow to recovery high amount of the lithium found in spent LIBs in a few minutes.

Table 1: Evaluation of the Li recovered by water leaching versus the mass increased. The analyses were realised by Ion Chromatography

Sample name	Sample mass (g)	Li (g/kg)			Li recovery (%)		
0	0.5	21.76	±	0.33	56.7	±	1.2
1	1	24.47	±	0.37	63.7	±	1.4
2	2	23.80	±	0.36	62.0	±	1.4
3	3	20.74	±	0.32	54.0	±	1.2
4	4	20.14	±	0.31	52.4	±	1.1
5	4.5	34.19	±	2.85	89.0	±	7.4

5.2 Revision of the pyrometallurgy characteristics associated with battery recovery

Literature indicates that hydrometallurgical methods are better suited for recycling specific cathodic materials since they must be optimized for the material to be recovered. On the

11

398 other hand, pyrometallurgical approaches are suitable for recycling different cathodic
399 materials, also in a mixture, due to the presence of carbon in the BM, which supports
400 carbothermic reactions [36].

401 However, traditional pyrometallurgical techniques employed in the recycling of LIBs have
402 numerous drawbacks, and there is a prevailing idea that these processes might not be
403 suitable for large-scale industrial implementation. Although they offer relative simplicity in
404 execution, these methods are not completely investigated. In particular, new technologies
405 involving the use of MW are still at low TRL.

406 Furthermore, literature also suggests that lithium is generally recycled in low quantities
407 through pyrometallurgical methods, while these techniques exhibit their highest
408 effectiveness in recovering particularly valuable metals like cobalt [8]. It is preferred to
409 extract Li, after the thermal treatment, by hydrometallurgy [37]. As battery technology
410 advances, the cobalt content in electrode materials is diminishing, while the utilization of
411 nickel and manganese is on the rise. This shift makes pyrometallurgy less attractive.

412 However, the treatment proposed in this paper, obtained by using MW radiation,
413 demonstrates that some drawbacks of the traditional pyrometallurgical procedures can be
414 overcome.

415 The advantages and improvements of the new proposed technologies are reported in the
416 following.

417 First, the dosage of a carbon source to have a carbothermic reaction is not necessary,
418 because in the BM the graphite is already present, and it can be used as the reducing agent.
419 This means that it is not mandatory to use onerous pre-treatment methods to separate the
420 cathode and anode materials.

421 Second, the reactions can be carried out also in an ambient atmosphere, even if the rapid
422 increase in the temperature of the samples must be monitored. Then inert atmosphere can
423 be not necessary for the reactions.

424 In addition, Li can be recovered directly after the thermal process by water leaching and
425 then precipitated as lithium carbonate (Li_2CO_3) by the carbonation of the water solution. After
426 water leaching and Li recover, the other metals (Mn, Co, Ni, etc.) can be precipitated through
427 hydrometallurgical processes, by using organic acids instead of inorganic ones [25]
428 Concerning the aspect connected with the management of gases generated by the
429 reactions, it would be possible to equip the treatment apparatus with suitable air treatment
430 systems, to recover and neutralize pollutant gases. For this aim, the organic gas species
431 may be recovered as liquids or solids. For example, a dedicated condensation system, with
432 a controlled temperature may be designed to recover the organic gaseous components via
433 low-temperature volatilization [38]. There is also the possibility of using an afterburner and/or
434 an adsorbent [38]. This must also be evaluated considering that it may allow to avoid some
435 onerous thermal pre-treatments which are generally realized to remove plastics,
436 electrolytes, and the binder. Finally, the possibility of recovering the carbon dioxide emitted
437 during the carbothermic reactions, after its partial purification of some pollutants, to be
438 reused for lithium carbonation seems quite attractive. A second way to face this drawback
439 would be to improve the pre-treatments: the organic solvents, binders, and separators would
440 be recovered with dedicated treatments, to improve the quality of the BM addressed to the
441 treatment.

In summary, the proposed technology would also allow a simplification of the entire recovery process, by reducing some pre-treatment steps. However, this requires more dedicated studies, involving considerations about all the pre-treatment steps (considering LIBs collection, separation, sorting, and preliminary thermal processes).

6. Conclusions and outlook

This work outlines both the benefits and hurdles associated with a novel MW heating approach for lithium recovery from spent lithium-ion batteries. The possibility of coupling carbon materials with magnetic materials in the BM appears to result in a strategic approach to increasing the final temperature of microwave-absorbing materials, by coupling dielectric loss with magnetic loss.

The application of MW allows for the rapid elevation of temperature in the BM, facilitating carbothermic reactions that yield lithium oxide and enable lithium separate recovery through a water solution. Experimental results obtained from a spent LCO BM sample reveal an efficiency higher than 80% within just a 5-minute treatment period. These findings support the proposition of this technology as a promising alternative to the traditional pyrometallurgical method and offer the opportunity to avoid several onerous BM pre-treatment steps. However, despite the evident advantages, full comprehension, and modelling of the mechanism of microwave heating are still in infancy and some open issues need to be addressed in the future:

i) The dielectric loss, and consequently the penetration depth of the BM has great importance for the energy conversion efficiency, nevertheless, BM is the result of a combination of the cathodic materials in graphite. Then, dedicated studies to promote the realization of a library containing the data of the loss capacity due to the different cathodic species mixed with graphite should be implemented;

ii) All the advantages of MW processes involved in LIBs recovery are not completely considered and investigated. For example, additional thermal effects, defined as the localized superheating effects are still not investigated for this waste [39];

iii) The possibility of recovering carbon dioxide generated during the carbothermic reactions, to be used as reactants to produce lithium carbonate must be exploited;

iv) The design and development of MW reactors operating in continuous mode for large batches of the process should be considered;

v) The introduction of susceptors may allow for the expansion of the applicability of MW technology to a range of applications, including the treatment of materials that are typically highly transparent to microwaves, for example, some ceramics, and materials that are highly reflective to microwaves, such as metals. This opportunity must be better investigated for BM recovery.

In conclusion, given the early stage of LIBs recovery efforts, MW-heating presents a highly promising method to be explored and developed to propose a sustainable approach for strategic metals recovery.

Author contribution

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

Conflicts of interest

There are no conflicts to declare

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The data supporting this article have been included as part of the Supplementary

Information

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