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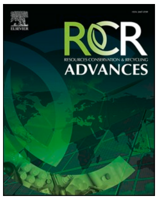

Intensification of lithium carbonation in the thermal treatment of spent EV Li-ion batteries via waste utilization and selective recovery by water leaching

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ABSTRACT

The recycling of lithium-ion batteries remains an essential question, the recovery of lithium is a central matter since the European Commission identified it as a critical raw material. This article proposes a more effective technology in which lithium will be recovered as lithium carbonate earlier in the recycling process using thermal pre-treatment and water leaching. Two thermal treatments are compared: incineration and pyrolysis, the whole cell (cathode, anode, current collector foils, and separator) is thermally treated in a first route, while the separator is removed, in a second route. The separator's presence showed a significant positive effect on the recovery, with an optimal recovery of 62% after pyrolysis at 700°C for 1 h and water leaching at 25°C with a solid-liquid ratio of 1:50 g/ml. Under these conditions, the solution purity was 92%, and aluminum was leached together with lithium. After evaporation, lithium carbonate and fluoride are found in the residue.

1. Introduction

At the end of 2020, there were 10 million electric vehicles (EV) on the world's roads, following a decade of rapid growth with an increase of EVs registrations of 41% (International Energy Agency (IEA) 2021). This increase in the EV market contributed to save, in 2020 alone, more than 50 Mt CO_2-eq of greenhouse gases emission globally (International Energy Agency (IEA) 2021). This rapid growth was possible thanks to energy storage systems' development and lithium-ion batteries (LiB), which given their performance in terms of energy and power density, were the technology of choice for the success of this growth (Armand et al., 2020) (Scrosati and Garche, 2010). Among the different types of LiBs, the NMC (Lithium Nickel-Manganese-Cobalt oxide) chemistry is nowadays the most popular technology used in EVs (Christian Julien et al., 2016). As a positive electrode, $LiNiO_2$, $LiMn_2O_4$, and $LiCoO_2$ are mixed with a polymer binder (polyvinylidene fluoride, PVDF) and coated onto an aluminum foil. The negative electrode is a graphite layer coated on a copper foil with the same polymer. The electrolyte in between is normally constituted by a mixture of one or more dipolar organic solvents and a lithium salt. A porous polymeric membrane usually made of polypropylene (PP) or polyethylene (PE) acts as a separator and prevents short circuits and ensures cell safety (Nunes-Pereira et al., 2015). Lithium, cobalt, manganese, and nickel play a central role in giving batteries greater performance, longevity, and high energy density (Scrosati and Garche, 2010) (International Energy Agency (IEA) 2021). In this dynamic, the total demand for some battery materials is expected to rise significantly and reaches over 40% for copper, 60-70% for nickel and cobalt, and almost 90% for lithium by 2040 (International Energy Agency (IEA) 2021). In what concerns lithium, in 2020, batteries represented 71% of its global end-use market and its global consumption was estimated to be 56,000 tons of lithium content, exported from Argentina, 55%; Chile, 36%; China, 5%; Russia, 2% (Ore et al., 2021). The European Union reacted by including lithium among the critical raw materials, which makes its recovery a central question (European commission 2020). Recycling spent LiBs is an obligation for multi-dimensional benefits such as keeping all the valuable metals in one place, re-using those metals during the manufacturing process, decreasing batteries' production cost, having a better environmental policy, saving natural resources, protecting the future, and conserving resources for future generations (Dewulf et al., 2010). However, nowadays only up to 3% of LiBs are recycled with the main focus on the recovery of more valuable metals, while the motivation for lithium recovery is almost nonexistent (Swain, 2017).

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2. Background about LiBs recycling processes

The recycling of LiBs is still limited, and current processes focus more on the recovery of cobalt, nickel, or other metals, leaving lithium aside. Current pyrometallurgical processes produce an alloy containing cobalt, nickel, copper, and iron, which can be separated by hydrometallurgical treatments. However, lithium, aluminum, and manganese are lost in the slag (Armand et al., 2020), (Umicore 2019). Research now focuses on hydrometallurgical methods to recycle LiBs, which include leaching, solvent extraction, precipitation, or electroreduction. In the leaching step, hydrochloric acid (Joulié et al., 2014, Shuva and Kurny, 2013, Contestabile et al., 2001), formic acid (Zheng et al., 2018), and sulphuric acid (Joulié et al., 2014) are mainly used and a reducing agent, such as hydrogen peroxide, can be added to reduce cobalt, nickel, and manganese to more soluble species. Still, in all those processes, lithium is recovered and purified at the end of the recycling flowsheet, as a by-product, resulting in a low total lithium recovery as losses are happening at every step. In the mining industry, the recovery of lithium from ores usually involves hydro/pyrometallurgy processes. First, the lithium-bearing mineral is concentrated and then treated by calcination or roasting, followed by a water leaching to dissolve lithium to the aqueous phase. Finally, Li_2CO_3 is produced through carbonation with reported yields above 85% (Swain, 2017).

The main goal of this study is to investigate an early-stage lithium recovery from spent LiBs using a thermal pre-treatment followed by water leaching. The optimization of lithium recovery was studied using two different waste materials; on the one hand, the whole battery cell was processed and on the other hand, the separator was removed from the active material. The objective is to determine the contribution of the separator during the lithium transformation. Moreover, the leaching selectivity towards lithium was observed and the evaporative crystallization was studied to identify the lithium compounds produced and the influence of the impurities on the purity.

The main advantages of the thermal pretreatment are **(1)** the binder decomposition, which allows easy separation of the active material from the support foils (Neumann et al., 2022), which benefits the hydrometallurgical processes as it concentrates the black mass, and increases the contact surface between the cathode active material and the leaching agent; **(2)** the reduction of different oxides of the cathode by carbon at high temperatures and the formation of Li_2CO_3, which is water-soluble and can be readily used to manufacture secondary batteries (Christmann et al., 2015), moreover the reduced oxides are more easily leached, which avoid the consumption of reductant such as H_2O_2; **(3)** the decrease of waste volumes with a safe controlled process, which can help the transport, handling, and recycling of LiBs (Brian Makuza et al., 2021). Such pre-treatment can be performed, for example, by incineration in presence of airflow or by dynamic pyrolysis under an inert gas flow. This innovative approach to recover lithium from the LiBs has been investigated by several authors (Table 1). On the other hand, the main drawback of this pre-treatment is its gas emissions. Indeed, during incineration and pyrolysis with and without separator, CO_2, CO, and HF are emitted, as it will be seen in the following section in more detail. Therefore, some off-gases treatment methods must be incorporated into the process. However, CO helps to achieve the carbothermic reaction and HF reacts with metallic components, thus, the main off-gas is based on CO_2.

2.1. Incineration

Incineration involves mostly exothermic reactions (Brian Makuza et al., 2021). Lombardo *et al.* (Lombardo et al., 2020) investigated the incineration of EV LiBs as a recycling pretreatment, where the mechanism of the carbothermic reduction was studied. The authors concluded that during the incineration, the presence of oxygen causes the combustion of graphite and organic components to form CO and CO_2, the formation of the latter being mostly favored at a temperature below

Table 1
Summary of conditions for lithium extraction after thermal pre-treatment and water leaching from published studies (only the best conditions are reported; optimal parameters).

Material		Initial composition (w%)					Thermal treatment			Leaching					
Active material	Reducing agent	Li	Al	Ni	Co	Mn	Type	Temperature (°C)	Time (min)	Leaching reagent	S/L ratios (g/mL)	Temperature (°C)	Time (min)	Li recovery (%)	Reference
$LiMnO_2$ battery	Anode material	4.8	-	0.1	-	51.3	Incineration	650	60	Distilled water	1:25	Ambient	20	83	(Jandová et al., 2012)
$LiMn_2O_4$ $LiCoO_2$ NMC	Anode material	-	-	-	-	-	Vacuum Pyrolysis	700	45	Water	1:25	Ambient	30	82 83 66	(Xiao et al., 2017)
NMC 111	10% Coke	7.2		20.0	20.5	19.4	Pyrolysis	650	30	Water	1:30	25	60	94	(Liu et al., 2019)
NMC battery		6.0	0.3	25.6	10.2	14.0	Hydrogen roasting	500	15	Water	1:20	30	30	>97	(Liu et al., December 2020)
$LiCoO_2$	20% activated carbon	6.5	7.8	1.6	40.6	1.6	Pyrolysis	700	30	Coldwater	-	0	60	36	(Maroufi et al., 2020)
NMC	20% lignite	5.8	10.8	21.9	14.9	17.0	Pyrolysis	650	180	Carbonated water	1:20	Ambient	120	89	(Hu et al., 2017)
NMC		5.8	10.8	21.9	14.9	17.0	Pyrolysis	650	180	Carbonated water	1:10	Ambient	10	80	(Zhang et al., 2018)
$LiCoO_2$	Activated carbon	-	-	-	-	-	Pyrolysis	500	60	Water + ultrasonics	1:100	Ambient	60	98	(Kuzuhara et al., 2020)
$LiCoO_2$		3.7	2.8	2.7	23.6	1.7	- Nitration process - Pyrolysis	70 250	300 60	Water	1:20	Ambient	500	93	(Peng et al., Mar. 2019)
NMC	Negative electrode + excess 10% of graphite	2.2	6.2	-	-	-	Pyrolysis	700	60	Water	1:20	80	180	60	(Balachandran et al., 2021)

700°C. The metal oxides were reduced under the reducing atmosphere, $LiCoO_2$ was reduced by C and CO and formed Co_3O_4, Li_2CO_3, CoO, and CO_2. $LiMn_2O_4$ was reduced to Mn_3O_4, MnO_2, MnO, and Li_2CO_3. $LiNiO_2$ had the same behavior as $LiCoO_2$ and was reduced to Ni_3O_4, Ni, and NiO. Li_2O is also produced during this treatment (Brian Makuza et al., 2021).

2.2. Pyrolysis

Pyrolysis is reported to involve mostly endothermic reactions (Brian Makuza et al., 2021) (sung Kwon and Sohn, 2020). Lombardo *et al.* (Lombardo et al., 2019) investigated the pyrolysis of EV LiBs as a pre-treatment for recycling, where the mechanism of the carbothermic reduction was studied. It showed that during the pyrolysis, the carbon present in the samples triggered the carboreduction of the metal oxides. $LiCoO_2$ was reduced by C and CO and formed Co, CoO, and Li_2O which reacted with the CO_2 produced to form Li_2CO_3. $LiMn_2O_4$ was reduced to Mn_3O_4, MnO, Li_2O, and Li_2CO_3. $LiNiO_2$ had the same behavior as $LiCoO_2$ and was reduced to Ni and NiO. Li_2O and Li_2CO_3 were also produced. Less CO_2 was emitted during the operation, which is therefore considered a more sustainable process than the incineration.

Moreover, beyond a temperature of 500°C, the PP and PE from the separator are expected to undergo a complete decomposition forming CO, CO_2 and H_2O. Therefore, no additional contaminants are expected when the separator is processed with the rest of the battery cell, and the CO_2 formed is expected to react with Li_2O and contribute to the formation of Li_2CO_3.

Thermogravimetric studies investigated the influence of oxygen on the thermal decomposition of PVDF. It was showed that an increase in the proportion of O_2 in the atmosphere decreases slightly the maximum rate of decomposition, but it has a larger effect on the temperature at which initial decomposition occurs (M., 1982). It was also observed that the decomposition in O_2 is almost complete before severe decomposition in N_2 even begins.

One downside of thermal pre-treatments is the generation of gaseous substances that must be treated. Indeed, during the thermal treatment, lithium salts in the electrolyte, such as $LiPF_6$, can decompose into LiF and HF at a temperature higher than 200°C in presence of water (Armand et al., 2020). Additionally, the decomposition of PVDF also produces HF in the gas phase. Therefore, off-gasses are cleaned with water before being released into the atmosphere. Moreover, the formation of other lithium species such as LiF can affect the subsequent recovery of lithium by water leaching since the dissolution of lithium relies on the solubility of its salts in water.

2.3. Lithium solubility

Li_2CO_3, the principal lithium compound expected to be formed in the thermal pre-treatment, has a solubility of 13.3 g/L at 20°C that decreases to 7.2 g/L at 100°C, a behavior opposite of other compounds Schwich et al., 2021). Another compound formed during the thermal treatment is Li_2O, which will react with water to form LiOH, and is also water-soluble (110 g/L at 20°C and 161 g/L at 100°C). The gaseous HF can react with Li_2O or Li_2CO_3 to form LiF (Eqs. (1) and (2) which is only slightly soluble in water (1.2 g/L at 20°C and 1.3 g/L at 100°C). Therefore, the production of LiF can limit the lithium extraction with water.

$$Li_2O + 2\,HF \rightarrow 2\,LiF + H_2O \tag{1}$$

$$Li_2CO_3 + 2HF \rightarrow 2LiF + H_2O + CO_2 \tag{2}$$

Furthermore, although different studies demonstrate the successful recovery of lithium from LiBs using a thermal pre-treatment followed by water leaching (Table 1), several crucial questions related to the effect of the input material in the process have not been investigated yet. For example (1) Does the source of carbon provided during the thermal treatment influence the chemical transformation of lithium oxide? (2) Can the carbon present in LiBs be used for the carboreduction without adding any additional source of carbon? The main source of carbon in the spent LiBs are the graphite from the anode and the polymer constituting the separator (mainly PE and PP). Currently, the separators are removed from the battery waste, but their utilization is limited, and they represent a burden in waste management and handling.

In this study, the main goal is to investigate the effect of the separator as a source of carbon for the formation of lithium carbonate during the thermal treatment. The determination of the positive effect of the separator on the lithium recovery represents an innovative input that could benefit the industry to achieve a better material recovery by processing the whole battery cell. This approach also helps to decrease the waste generated during the recycling process and saves separator cost disposal. Two thermal treatments, incineration, and pyrolysis will be investigated and the operational conditions (temperature and time) allowing the higher lithium recovery will be identified. Moreover, the impurities co-extracted during the leaching step will be determined and the purification of lithium will be studied.

3. Material and method

3.1. Solid samples from EV LiBs

Spent NMC LiBs previously discharged were supplied by Volvo Car AB (Sweden). Two cells were manually dismantled (removing the plastic cover) and then followed distinct processes:

1. for the first route, the whole cell (cathode, anode, and separator) was kept in the black mass.
2. in the second route, the cathode and the anode were separated from the separator (PP), and, after the thermal treatment, the metal foils were separated from the black mass by sieving (0.5 mm).

The anode and cathode were cut together into 2 mm pieces in diameter using a manual hole punch before being thermally treated for both routes. A LECO CS744 instrument was used to determine the carbon content in the samples before thermal treatment. To determine the metal composition of the material, aqua regia (HCl/HNO_3: 3/1 - Merk Millipore Chloric acid 37% w/w and Merk Millipore Nitric acid 65% w/w) was used to digest the solid samples at 80°C during 4 h. The sampling was performed using the coning and quartering technique to divide an initial sample into halves until the desired sample weight was achieved. This procedure helps to reduce the uncertainty associated with grab sampling from a container (Gerlach et al., 2002). The obtained slurry was then left to cool down overnight. After filtration (filter VWR 516-0811 – 11 μm particle retention) and dilution in HNO_3 0.5 M (Merk Suprapure Nitric acid 69% w/w), the metal content was analyzed using inductively coupled plasma optic emission spectroscopy (ICP-OES, Thermo fisher). The concentration of fluoride was measured with a fluoride selective electrode (Ion-selective electrode, F, Metrohm) along with a reference silver/silver chloride electrode with a double junction system. The liquid sample is mixed with TISAB IV solution (volume ratio 1:1) before measurement to keep the pH and ionic strength constant. The TISAB also bound with interfering cations and therefore releases any complexed fluoride.

3.2. Thermal treatment

The solid samples were thermally treated in a horizontal tube (high purity alumina tube 65 cm alumina tube Degussit AL23 Aliaxis) furnace (Nabertherm GmbH Universal Tube furnace RT 50-250/11). Each sample (5 g of material for each experiment) was individually inserted into the furnace in an alumina crucible when the furnace was at the target temperature. Two different types of thermal treatment were performed: active pyrolysis (340 mL/min of N_2) and incineration (340 mL/min of air). For each thermal treatment type, a range of temperature between 400°C and 700°C was tested for 30, 60, and 90 min. The operational conditions used in each experiment are referred to in the results section. Once the experiment was finished, the samples were cooled down in the furnace under the same atmosphere. After grinding with an IKA M20 universal for 5 min, the metal content and composition of the homogeneous solid residue were determined after digestion using the same technique as the untreated material.

3.3. *Water leaching*

Water leaching was performed using Milli-Q water for each pre-treated sample with a solid/liquid ratio of 1:50 g/mL, this large excess of leaching agent was chosen to reach the maximum recovery of lithium after thermal treatment and to minimize the effect of the sampling. A magnetic stirring speed of 300 rpm was applied and the experiments were performed in 20 mL glass vials with a cap. All experiments were carried out in triplicates using 0.2 g of sample. The sampling was performed using the coning and quartering technique to divide an initial sample into halves until the desired sample weight was achieved. The leaching temperature varied, and specific conditions are presented in the results section. After leaching, the samples were immediately filtered (Syringe filter PTFE - Restek – 0.45 µm) to separate the solid residue from the liquid phase containing the lithium salts. The metal content of each leachate was analyzed using ICP-OES. The leaching efficiency was calculated by comparing the concentration of each element in the leachate to the elemental content of the solid samples determined by the total dissolution in aqua regia. The leaching efficiency (η_i) can be calculated according to Eq. (3):

$$\eta_i = (C_i \times V)/(m_0 \times w_i) \times 100 \tag{3}$$

where C_i is the concentration of the element i in the leachate (mg/L), V is the volume of solution (L), m_0 is the weight of the sample (mg) and w_i is the weight percentage of the element i in the sample (%).

The purity of the leachate was also estimated using Eq. (4):

$$P_i = (C_i \times V)/\left(C_j \times V + C_i \times V\right) \times 100 \tag{4}$$

where C_i is the concentration of the element i in the leachate (mg/L), C_j is the concentration of the other elements in the leachate (mg/L) and V is the volume of solution (L).

The leaching media was then filtered using gravity filtration through fiberglass to separate the solid residue and the leaching liquor. This solution was then heated up to 95°C to evaporate the water and collect the lithium salts. An elemental composition analysis of the obtained powder was performed using ICP-OES measurement after its dissolution in nitric acid 0.5 M. This powder was then analyzed using X-ray

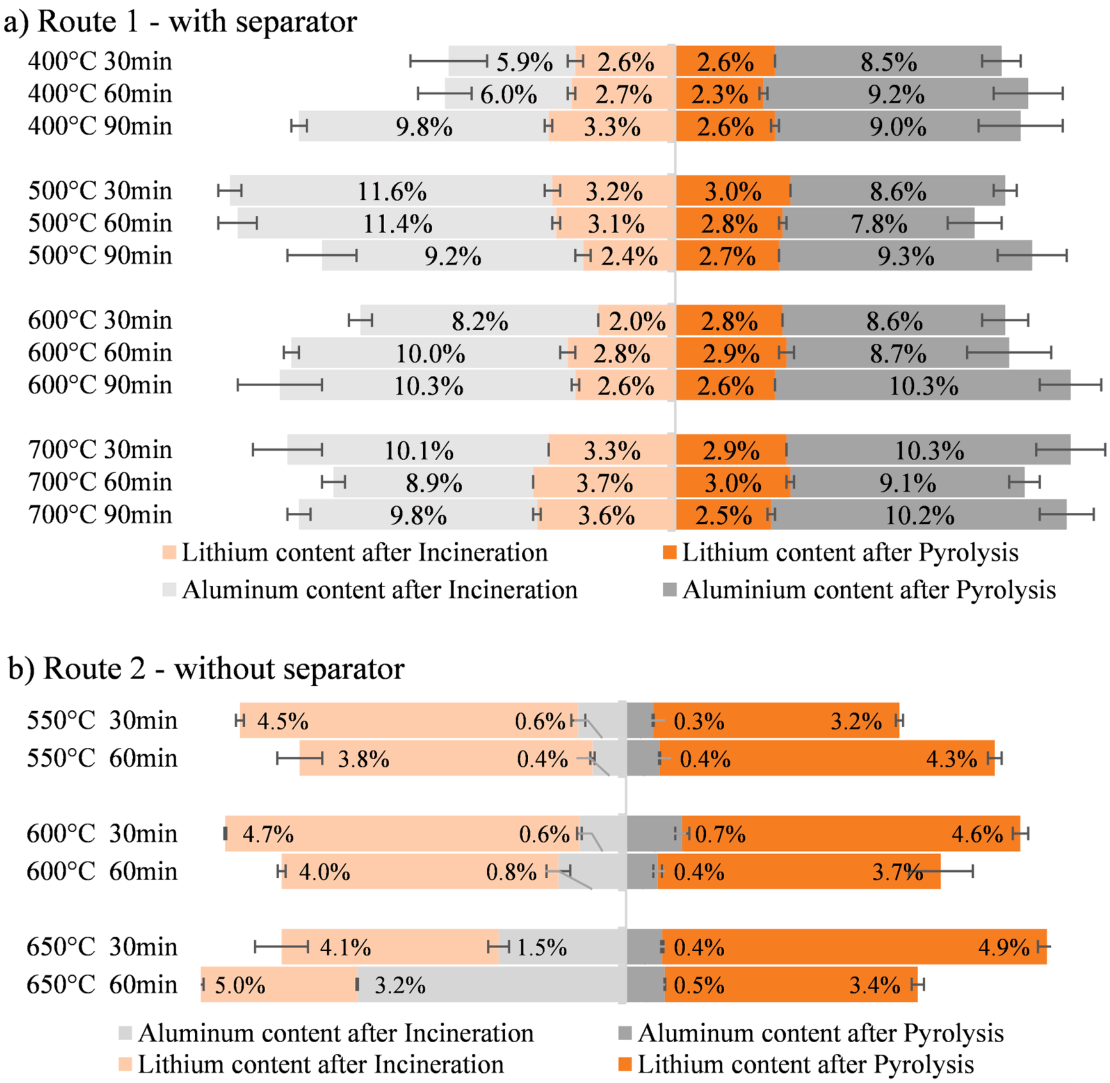

Fig. 1. Lithium (orange) and aluminum (grey) composition of the black mass after thermal treatment - Incineration (left) and Pyrolysis (right) for different treatment times and temperatures for Route 1 and 2.

diffraction to identify the different components.

4. Result and discussion

4.1. Characterization of the solid samples

The metal composition and carbon content of the solid residue before thermal treatment are presented in Table 1. The total carbon content without separator (Route 2) is measured at 22.6% when there is a clear increase of carbon content with the presence of separator (Route 1) with 40.8%. The carbon content of the separator alone was measured at 70% ± 3%.

A general weight loss of 5 to 10% was observed after the thermal treatment for Route 2 while a higher loss of 5 to 20% was verified for Route 1 (Lombardo et al., 2020), (Lombardo et al., 2019), without any significant influence on the running parameters. This is due to the conversion of carbon, from solid to gas, when reacting with the oxygen. The metal content increases after the thermal treatment for both routes, as the total mass of the sample was lifted from the carbon loss, as shown in Fig. 1, Table 2.

4.2. Pre-investigation of water leaching conditions

To define the effect of temperature on the leaching efficiency using water, experiments were performed at 3 different temperatures (25, 40, and 60°C) for the untreated material. Fig. 2 shows that the equilibrium was reached after 30 min. However, for further experiments, a leaching time of 1 h will be applied and kinetics studies will be performed on the optimal treatment to identify when the equilibrium is reached in the case of a thermally treated sample. No significant increase in the leaching efficiency can be observed with different leaching temperatures (Fig. 2). Based on this observation, the following leaching experiments were performed at 25°C using a water bath. This choice of parameter is part of an approach to reduce the energy costs of the process, also considering that lithium carbonate is more soluble at a lower temperature. The maximum lithium recovery without any thermal treatment after water leaching is around 7.5%. In this case, the lithium found in the solution could only come from the lithium salt used in the electrolyte ($LiPF_6$) or from the reaction between water and the remaining Li_2O from the manufacturing process.

4.3. The effect of the thermal treatment on lithium leachability (Route 1)

4.3.1. Effect of incineration

At 400°C, the leaching yield is around 20%, which is only 10% higher than the untreated material as can be observed in Fig. 3. This is possibly related to the fact that the carboreduction has not been completely achieved at this temperature. The carbothermic reduction of the oxide is happening beyond 500°C (Lombardo et al., 2020), and although the formation of CO starts around 400°C, the amount produced increases with the temperature. A more reductive atmosphere will be provided by using a temperature beyond 500°C (Brian Makuza et al., 2021). The treatment time is having a low influence on the recovery; therefore, shorter times will be preferred for further studies, reducing the energy consumption. At 700°C, a significant decrease in efficiency is observed. Over 660°C aluminum melts, which can coat the particles, making it even more difficult for the oxides to react with the gases and thus hindering their carboreduction. This behavior was also reported by others (Brian Makuza et al., 2021). The water leaching is not completely selective to lithium and some aluminum is also leached in a very low percentage compared to lithium. The purity of the solution after filtering the final residue was determined and it is possible to highlight the diminution of purity when increasing the treatment temperature regardless of the treatment time.

Table 2
. Metal and carbon composition of the battery cell with (Route 1) and without (Route 2) the separator.

Route	*w%* Li (%)	*w%* Al (%)	*w%* Cu (%)	*w%* Ni (%)	*w%* Co (%)	*w%* Mn (%)	*w%* C (%)
Untreated (Route 1)	2.2 ± 0.2	6.2 ± 0.3	15.0 ± 0.4	4.3 ± 0.4	4.3 ± 0.4	9.5 ± 0.8	40.8 ± 2.8
Untreated (Route 2)	3.1 ± 0.1	9.5 ± 0.9	12.7 ± 3.8	6.3 ± 0.3	6.1 ± 0.3	13.8 ± 0.6	22.6 ± 0.8

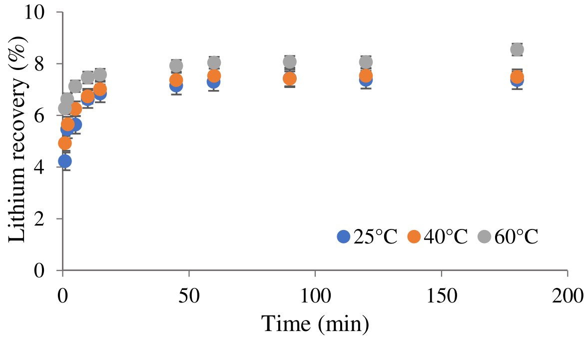

Fig. 2. Kinetic curves of water leaching for an untreated sample at 25°C, 40°C, and 60°C at a S/L = 1/50 g/mL and stirring of 300 rpm.

The optimal conditions observed in the present study using incineration are a thermal treatment of 90 min at 500°C, which leads to a lithium recovery of 43% and a solution purity of 90%. Under these conditions, the concentration of Li and Al in the leachate were 215 mg/L and around 25 mg/L, respectively. Thus, additional experiments should be performed to determine the conditions preventing the formation of water-leachable lithium compounds during the thermal pre-treatment and to further increase the recovery of lithium. The airflow for example could be a problem during incineration and being too intense, could remove the CO_2 and CO and prevents them from reducing the oxides, as reported by Lombardo *et al* (Lombardo et al., 2019). Moreover, investigations to reduce the leaching of Al or to prevent its presence in the final lithium product, which could be obtained for example by evaporative crystallization of the leachate, will be performed.

4.3.2. Effect of pyrolysis

After pyrolysis at 400°C, similar efficiencies were obtained for different treatment times with a recovery limitation of 20%, as can be observed in Fig. 3. The same trend was obtained after incineration at low temperature, which supports the hypothesis concerning the absence of a reducing atmosphere under 500°C. Moreover, the thermal decomposition of PVDF is known to occur at 450°C under a nitrogen atmosphere (M., 1982) (Gerlach et al., 2002). At 400°C, PVDF can still be partially present in the sample, which could prevent good contact between the particles and the leaching media (water). Moreover, Lombardo *et al.* (Lombardo et al., 2019) reported that after thermal treatment at 400°C and 500°C, the three lithium-metal oxides are still present in the black mass, the carbothermic reduction is not complete and lithium is not extractable by water from the present species.

On the contrary to incineration, pyrolysis temperature seems to have a positive effect on the recovery with a gradual increase in the lithium leaching efficiency. There is no limiting factor, and the amount of lithium carbonate increases with the treatment time. This behavior is also confirmed by Lombardo *et al.* (Lombardo et al., 2019), who observed a full decomposition of the active material beyond 700°C and 90 min. Longer treatment times do not promote an important improvement in recovery. In this case, aluminum is also leached along with lithium, and the purity decreases with the increase in the treatment time and temperature. The final leachate purity is increasing at a temperature of 700°C, which could indicate that aluminum is preferentially forming less water-soluble species over its melting point. Thus,

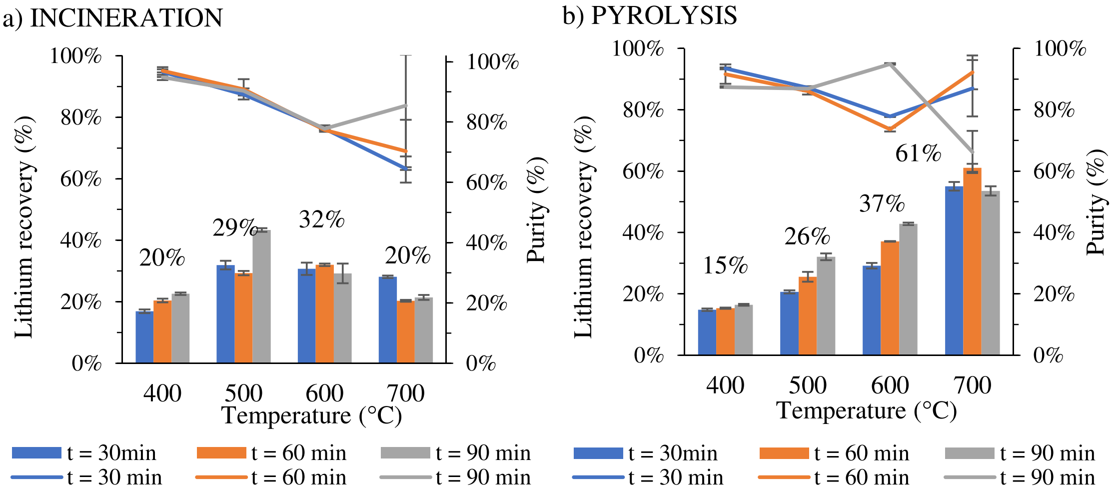

Fig. 3. Lithium recovery (Left axis - histogram) and purity (Right axis) after pyrolysis at different temperatures (400-700°C) and treatment time (30-90 min) followed by water leaching (S/L = 1/50 g/mL, 25°C, 1 h, 300 rpm). The first route of sample processing after incineration a) and pyrolysis b).

additional tests should be performed to investigate aluminum behavior and determine what are the water-soluble substances produced during the thermal treatment. The optimal conditions are a treatment time of 1 h at 700°C, which resulted in a recovery of 61% and a purity of 92%. Under these conditions, the concentration of Li and Al in the leachate were 370 mg/L and around 50 mg/L, respectively. Additional studies should be performed to optimize the recovery yield; increasing the temperature and time.

4.3.3. *Kinetic studies on the water leaching of lithium after thermal pretreatment*

Kinetics studies were made for the most promising temperature (700°C) for both incineration and pyrolysis at 3 different treatment times (Fig. 4). The recovery rate of lithium in water reaches an equilibrium after 20 min of leaching and there are no water-soluble forms of lithium remaining in the solid phase after this time at 25°C. The leaching behavior of nickel, cobalt, manganese, and copper was also followed and the selectivity of the water leaching towards lithium was once again proven since none of those elements was detected in the leachate (Supplementary material 1). Regarding aluminum, its leaching yield increases with the contacting time increasing, although its dissolution kinetics is slower than lithium. This is an important observation as it could lead to a more selective leaching by shortening the contact time and thus avoiding the extraction of aluminum.

4.3.4. *Solid residue composition*

After evaporative crystallization of the leachate, the solid obtained was analyzed using X-ray diffraction to identify the different salts present in the sample. Beforehand, the solid residue was dissolved in nitric acid and the elemental composition of the residue was measured using ICP-OES. Only aluminum and lithium were detected, and the purity between the 2 elements was the same as the one measured in the leachate which confirms that both elements are found in a solid compound (thus 92% of lithium purity after pyrolysis at 700°C for 60 min). Fig. 5 shows the obtained diffraction patterns for four samples (incineration and pyrolysis at 600°C and 700°C for 60 min). Those experimental patterns are compared to the database (ICDD) for two different lithium salts (Li_2CO_3 and LiF), and this indicates the presence of lithium carbonate as expected. The additional peaks have been assigned to lithium fluoride. The presence of aluminum was not detected using the XRD, which can be explained by the very small amount of aluminum in the residue (0.5 to 2.5 %*w/w*) which is under the limit of detection of the XRD.

The formation of LiF precipitates could be explained by the presence

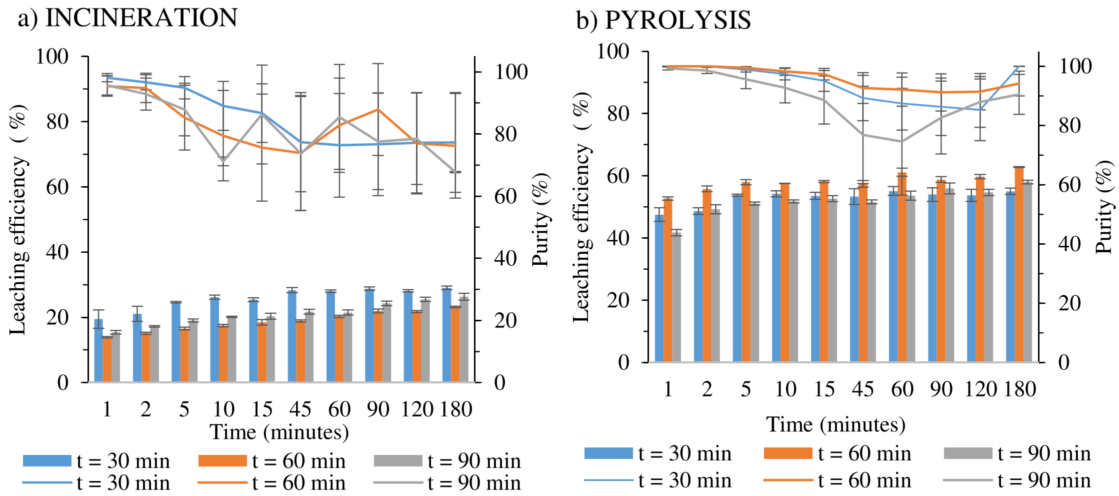

Fig. 4. Lithium recovery (right axis – histogram) and purity (left axis) after incineration a) and pyrolysis b) at 700°C for 3 different treatment times and water leaching at 25°C, S/L = 1/50 g/mL with a gradual increase of leaching time for Route 1 (with separator).

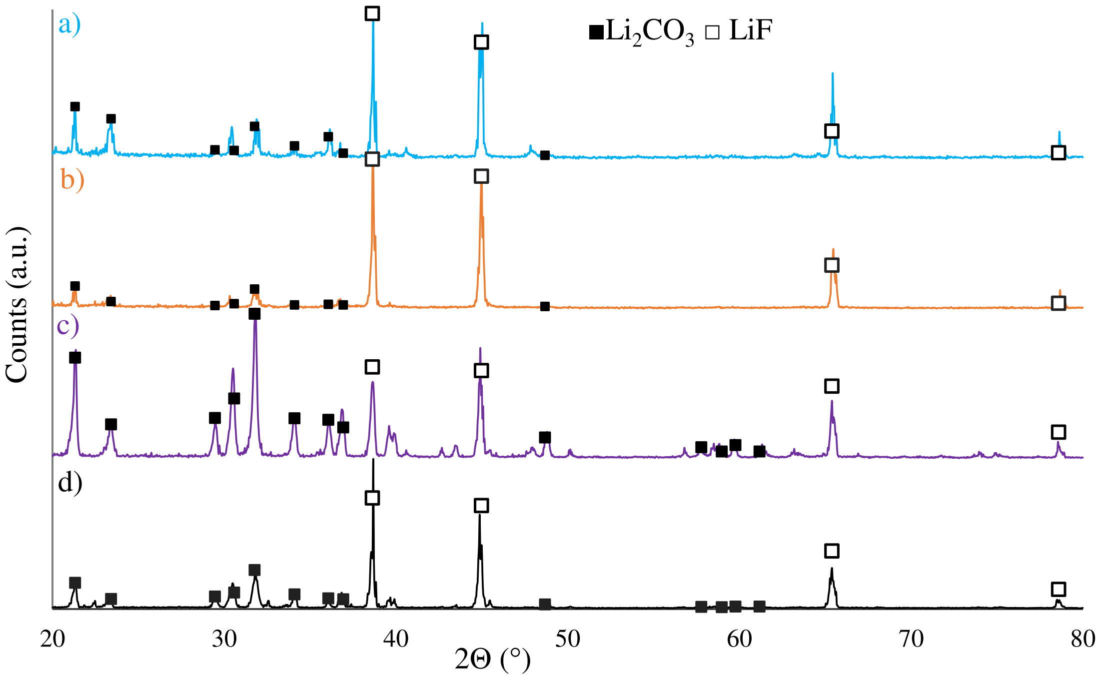

Fig. 5. X-ray diffraction pattern of residue obtained after evaporative crystallization of the leachate. The leaching (25°C, S/L = 1/50 g/mL for 60 min) was realized on different treated materials obtained after a) Incineration at 700°C for 60 min, b) Incineration at 600°C for 60 min, c) Pyrolysis at 700°C for 60 min and d) Pyrolysis at 600°C) for 60 min.

of fluorine in the leachate solution, which would react with lithium ions coming from the dissolution of Li_2CO_3. The fluoride content in the solid produced is measured by ion selective electrode in order to quantify the amount of LiF produced. It is about 1 mmol of fluoride per gram solid, after a pyrolysis at 700°C for 60 min, which represent 2.3 % of lithium fluoride formation against 97.7% of lithium carbonate. Therefore, additional experiments should be performed to determine the conditions promoting the formation of LiF in the residue and mapping the presence of anions such as fluorides in the process as they can be a limitation in the final product purity.

The obtained powder is therefore not a pure lithium salt and needs to be purified with aluminum removal and converted into pure lithium hydroxide to be reintroduced in the electrode manufacturing process. The use of sodium hydroxide to removed aluminum from the leachate will be explore in futures work.

4.4. Effect of the pyrolysis and incineration on the lithium leachability without separator (Route 2)

Additional tests were performed to investigate the effect of removing the separator from the black mass before the thermal pre-treatment, considering that the separator (PP or PE) could also play a role, as a carbon source, in the carbothermic reduction of NMC oxides. In both processes, incineration, and pyrolysis, it is possible to observe a limitation in the recovery of Li, which did not exceed 35% (Fig. 6), and the temperature and time did not show any significant effect. The presence of the separator seems to have a positive influence on the carboreduction of the oxides, possibly enhancing the formation of lithium carbonate given the presence of higher content of carbon in the system available to react. Higher leaching yields for lithium were observed in the presence of the separator (Route 1, results in Section 4.4) – an increase of around 7% for pyrolysis and incineration after pre-treatment at 600°C for 60

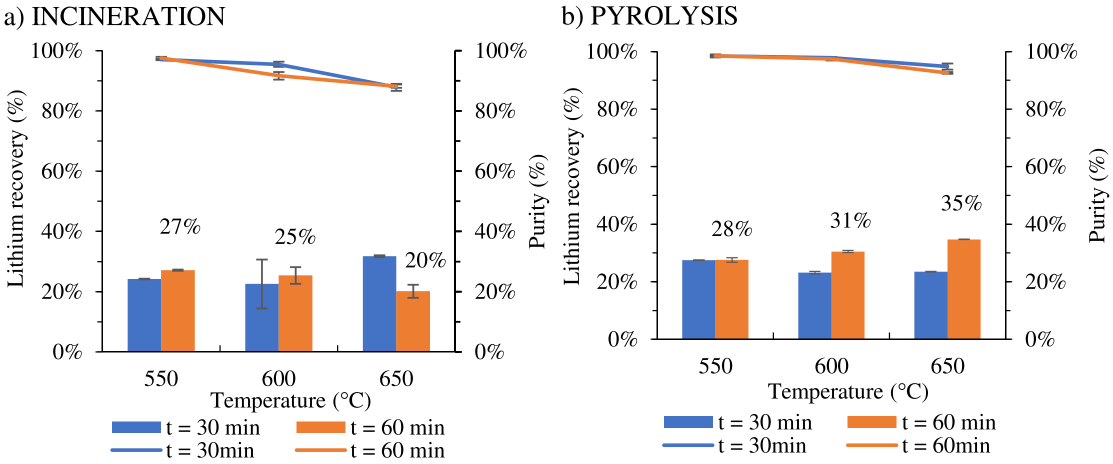

Fig. 6. Lithium recovery (left axis – histogram) and purity after the leaching step (S/L ratios = 1/50 g/mL, 25°C, 1 h, 300 rpm) for different treatment temperatures and times. The Second route of sample processing after incineration a) and pyrolysis b).

min. Furthermore, no significant impact on the purity is observed, which also decreases with the temperature increase, following the same trend as route 1. Although the lithium recovery is lower without separator, higher purities are obtained in this route, for a thermal treatment at 600°C for 60 min an increase of around 17% for incineration, and 24% for pyrolysis is observed. The separation of active material from the current foil is having a positive influence on the leaching selectivity.

5. Conclusions

The positive effect of the separator as a source of carbon for the formation of lithium carbonate was determined in this work. Processing the black mass without the separator lead to approximately 30% of lithium recovery while its presence allowed 62% of lithium recovery after pyrolysis at 700°C for 60 min. Taking advantage of the carbon sources present in the waste itself for the carbothermic reduction should be considered a central goal when designing recycling processes for Li-ion batteries combining pyrometallurgical and hydrometallurgical technologies. This approach not only reduces the volumes of waste to be handled but also helps to decrease the consumption of reagents in the hydrometallurgical route (the need for reducing agents could be avoided and the consumption of acid could be decreased when some elements can be leached with water or become more easily leached).

Furthermore, increasing treatment temperature and time of pyrolysis has a positive effect on the subsequent leaching efficiency of lithium since the cathode active material was reduced and the water-soluble lithium carbonate was formed. A maximal lithium recovery of 62% was obtained after pyrolysis at 700°C for 60 min and a water leaching at room temperature with a solid/liquid ratio of 1:50 g/mL. An increase of the recovery is expected when increasing the temperature. A lithium purity of 92% was measured in the leachate. The only impurity co-extracted with lithium is identified to be aluminum. The aluminum extraction is increasing with the increase temperature and time. Beyond 650°C a decrease in aluminum extraction is observed, the aluminum melting could form less water-soluble species. The aluminum water-soluble species has not been determined but further studies will be done. Moreover, the aluminum extraction by the water is slow, shorter leaching times lead to a decrease in the aluminum extraction. A lithium purity of 97.3 % was measured in the leachate after 15 min instead of 60 min. Therefore, shorter leaching time should be applied in future work to increase the selectivity of the process.

Finally, water was evaporated from the leachate after filtration to give a white solid. ICP-OES measured the presence of both aluminum and lithium in the residue, with the same purity that in the leachate. X-ray diffraction analysis showed that is a mix of lithium carbonate and lithium fluoride, aluminum is not detected due to the limit of detection. Fluoride was detected in the solid residue with a concentration of 1 mmol/g which represents 2.3 % *w/w* if lithium fluoride produced. Mapping the presence of anions such as fluorides in the process will be of good interest as it can be a limitation in the final product purity.

CRediT authorship contribution statement

Léa M.J. Rouquette: Investigation, Writing – original draft. **Tom Lemaître:** Investigation, Writing – review & editing. **Nathália Vieceli:** Supervision, Writing – review & editing. **Martina Petranikova:** Supervision, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.rcradv.2022.200125.

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