

Article

Environmentally Friendly Recovery of Lithium from Lithium–Sulfur Batteries

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Abstract: In the context of the rising demand for electric storage systems, lithium–sulfur batteries provide an attractive solution for low-weight and high-energy battery systems. Considering circular economy for new technologies, it is necessary to assure the raw material requirements for future generations. Therefore, metallurgical recycling processes are required. Since lithium is the central and most valuable element used in lithium–sulfur batteries, this study presents an environmentally friendly and safe process for lithium recovery as lithium carbonate. The developed and experimentally performed process is a combination of thermal and hydrometallurgical methods. Firstly, the battery cells are thermally deactivated to mechanically extract black mass. Then, water leaching of the black mass in combination with using CO₂, instead of emitting it, can mobilize lithium by >90% as solid product.

Keywords: battery recycling; lithium–sulfur batteries; metallurgical recycling; lithium recovery; recycling efficiency; lithium-ion batteries; circular economy



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1. Introduction

Lithium–sulfur batteries are a type of high-energy battery, reaching >500 Wh/kg [1]. Li-ion batteries in comparison reach their maximum energy density at ~300 Wh/kg [1]. This makes lithium–sulfur batteries (LiS) a relevant accumulator also in the mobility sector. Aviation weight is an especially critical parameter [2,3]. Nonetheless, several challenges are to be overcome before they enter the consumer market. Examples for this are the comparatively low lifetime or cycle stability due to self-degradation [4–6]. Lithium–sulfur batteries also differ from conventional lithium-ion battery cells in terms of their elemental composition (see Figure 1 [7]):

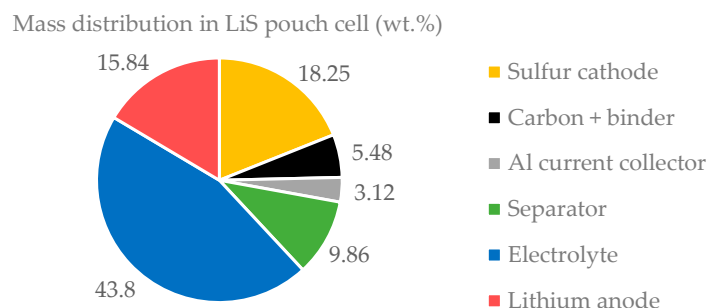


Figure 1. Lithium–sulfur cell composition based on built-in components. Based on: [7]. Reproduced with permission from Robinson, J. et al., (2021). 2021 roadmap on lithium–sulfur batteries. *J. Phys. Energy*, 3(3), [031501].

The lithium shares in the battery are higher (15.84%) in comparison to conventional lithium-ion batteries. Here, the lithium shares based on the cell level comprise ~2 wt.%

in an NMC ($\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z\text{O}_2$)-cathode-based cell system [8]. This has a direct influence on possible recovery options, a heavy dilution of an element within a system leads to a more challenging recovery [9,10]. Lithium itself is incorporated in lithium–sulfur cells in a metallic form as an anode. Beyond that, active carbon, graphene, reduced graphene oxide (RGO), carbon nanotubes or porous carbon replaces graphite, taking on the function of the cathode in lithium–sulfur cells together with sulfur [7,11]. Hence, no further valuable metallic components, such as cobalt or nickel, are incorporated. In conventional lithium-ion battery cells, the cathode matrix consists of transition metal oxides or iron-containing phases, relating thereto, heavy metals are incorporated in the intercalation electrode [7]. According to the EU's criticality assessment for evaluating a resource's relevance and supply risk from 2017 [12], no critical raw material was deployed in lithium sulfur batteries. This evaluation was revised by the European Commission in 2020, leading to the classification of lithium as critical element [13], making the recovery of lithium according to a circular economy approach even more relevant. However, for metallurgical recycling in general, the different chemistry of lithium–sulfur cells requires specific treatments. Firstly, metallic lithium is highly reactive and requires dry-room handling [5,14,15]. Secondly, besides its lower lithium dilution, higher gravimetric specific capacities, lower degree of material criticality, the elements in the cell are of lower monetary value making the production of batteries more cost efficient [5]. Therefore, a cost efficient recycling process is also needed to justify the metallurgical treatment [16,17]. An important discussion on the metallurgical process requirements is outlined within this study in the conclusions section.

A first recycling approach can be found in [18]. Here, lithium was recovered by conventional leaching. The maximum lithium recovery as a solid lithium product was 93% and further processing was performed of obtained solution. Li-losses in the different filter cakes were found and Li-losses in the residual filtrate and impurities in the product. An LCA (Life Cycle Analysis) of this process path for lithium-ion batteries demonstrated that pH-adjustment by NaOH, which was used in [18], significantly contributes to the GWP (global warming potential), TAP (terrestrial acidification potential) and FDP (fossil depletion potential) of this process [19]. NaOH production makes up the largest part in FDP and GWP, hence it demonstrates the highest impact regarding the environmental impact categories of the process [18,19].

Therefore, environmentally friendly methods were investigated to reach a carbonation of lithium by aqueous leaching and CO_2 -reaction. In [20], this was investigated for lithium-ion batteries, reaching lithium mobilization in the form of a solid lithium carbonate of up to 64% by aqueous leaching only. By treating the black mass and H_2O suspension with supercritical CO_2 (>73.8 bar [21]), a lithium recovery by 79% could be proven. In a similar set-up, a lithium leaching efficiency of 93.1% was obtained at an enhanced holding time and increased water volume by a factor 3 (3 h and $s/l = 1:90$ g/mL) [22]. Patents by Müller et al. from Albemarle Germany GmbH indicate the first several alternative approaches for lithium recovery from lithium–sulfur materials without acidic solutions [23,24]. For example, a lithium-containing black mass can be charged into an alkaline solution and heated to 100–150 °C in pressurized air. Here, detailed procedures and data are not shown. Nonetheless, high-pressure operations using supercritical fluids (SCF) are energy intensive [25] and their transformation to an industrial scale is challenging due to safety concerns, robust equipment demands and maintenance effort [26]. Therefore, the use of gaseous CO_2 for lithium–sulfur cells is to be investigated as well.

In [20], the possible, underlying mechanisms for CO_2 -supported lithium carbonation in aqueous media were discussed in detail, so a detailed elaboration of the chemical formula is not included in this paper.

Another option in contrast to carbonation in aqueous media (indirect carbonation), presented in a study by Wang et al. is the thermal carbonation of lithium by treating virgin black mass in a CO_2 -gas atmosphere (direct carbonation) [27]. After the thermal treatment, black mass is leached in H_2O . In this study, no lithium yields were given. Instead, the mass of lithium in black mass and in the product were given and were as

follows: 1.93 g and 1.735 g. The thermally induced phase transformations can also be promoted in an Ar-atmosphere or vacuum at elevated temperatures [28–32]. Hence, in [20], the influence of the thermal pre-treatment conditions on lithium leachability was shown by treating full cells. The lithium yields were higher when treating the cells in a reducing atmosphere [33]. Moreover, an influence on State of Charge (SOC) was demonstrated for lithium-ion batteries [34].

Independently from the type of hydrometallurgical treatment, namely acidic/alkaline leaching or aqueous leaching, a filter cake containing mainly aluminum and graphite/carbon materials [18] was obtained. To follow a circular economy, this material should be treated for raw material recovery. For lithium-ion batteries, flotation techniques are a possible solution to recover graphite for further resynthesis of anodes in LiBs [35]. Hereby, hydrophobic carbon particles can be separated from hydrophilic metallic components, such as aluminum [36]. The resulting fractions are carbon-containing concentrates and metal-containing tailings [37]. The importance of graphite and carbon material recovery is visible in the work of Engels et al. [38,39]. Flotation was also evaluated for lithium–sulfur batteries [40].

Therefore, approaches for the additive-free and environmentally friendly leaching of lithium should be investigated further as well as for lithium–sulfur batteries. The key questions in this study were as follows: How much lithium can be mobilized by a treatment in aqueous solution with or without gaseous CO₂? Is there a difference between lithium-ion and lithium–sulfur batteries? Can a thermal pre-treatment be set-up accordingly to lithium-ion batteries? The following article sums up the results of treating lithium-ion cells by indirect carbonation based on the results of lithium-ion batteries shown in [20].

2. Materials and Methods

To reach the target of an environmentally friendly lithium recovery with high yields, experimental studies based on lithium-ion batteries already performed by the authors were carried out for lithium–sulfur batteries. Hereby, the transferability and robustness of a recycling procedure to another battery system with metallic lithium anodes is possible. In this context, direct shredding was examined for lithium–sulfur batteries too, since lithium-ion batteries can also be directly shredded after an electric discharge [41]. However, the lithium–sulfur cells ignited during shredding and the thermally untreated black mass from lithium–sulfur batteries ignited during H₂O leaching. To ensure the safety of a recycling process, a thermal pre-treatment for deactivation and pre-conditioning is therefore recommended by the authors.

2.1. Recycling Concept with Thermal Pre-Treatment and Early Stage Li-Recovery (ESLR)

With such factors in mind, the recycling process within this study consisted of a thermal pre-treatment followed by H₂O-based hydrometallurgy. This process is shown in Figure 2a, and the reactor for as set-up for the thermal treatment is depicted in Figure 2b.

The thermal treatment was performed at a target temperature of 500 °C and 600 °C, based on the parameters chosen in [20]. Since for lithium-ion batteries, inert atmosphere leads to the highest lithium yields, this procedure was also performed here. Moreover, a CO₂ atmosphere was investigated since enhanced Li₂CO₃ formation by the reaction between metallic lithium, located on the anode side of LiS-cells, and CO₂ is possible according to FactSage (version 8.0, GTT Technologies, Herzogenrath, Germany) simulations (see Figure 3). Solid samples are marked in bold font since they have a direct meaning for explaining phases detected by XRD. Moreover, if the physical state (solid) was maintained, the lines are colored in the same color. FactSage provides different output values for different crystal lattices, but since this difference is not significant for this article the same colors were followed.

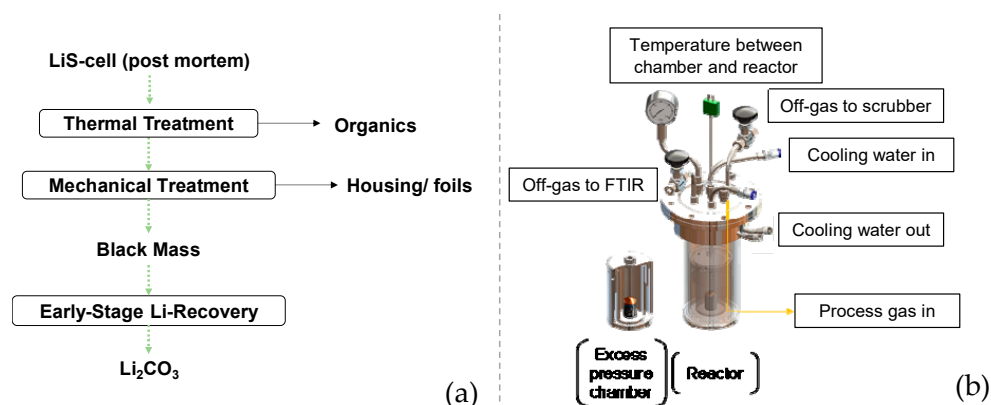


Figure 2. (a) Flowchart for the treatment of lithium–sulfur post-mortem cells. (b) Stainless-steel reactor with excess pressure chamber for safe lithium–sulfur cell thermal pre-treatment. In this set-up, different atmospheres can be created via “gas entry”.

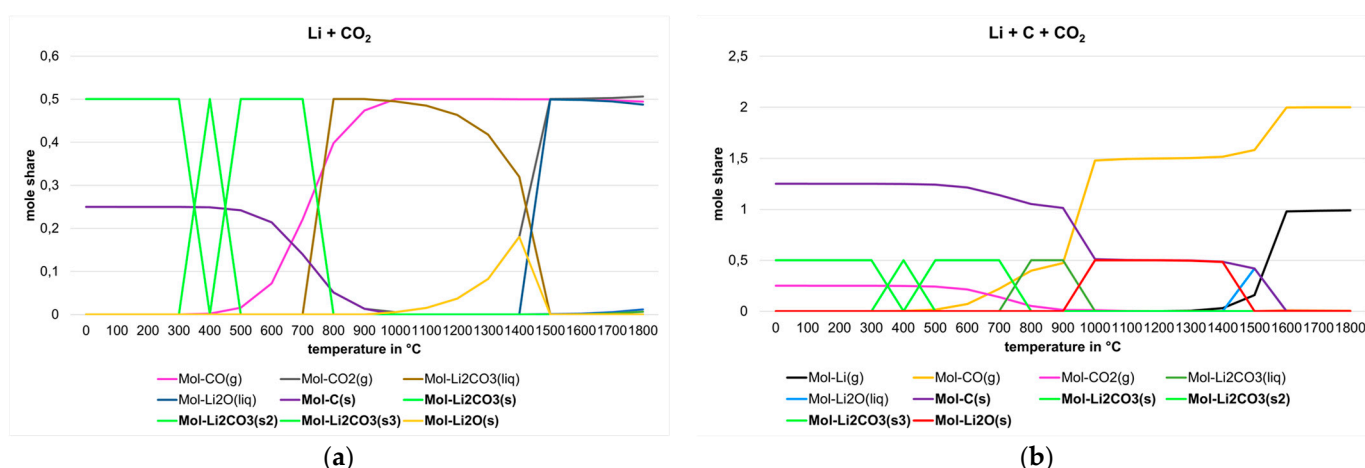


Figure 3. FactSage simulation (version 8.0) of possible products between 0 and 1800 °C using the Equilib-tool and the FactPS database (ideal gas and $p = 1$ atm). (a) reaction between 1 mol metallic lithium and 1 mol CO₂, (b) reaction between 1 mol metallic lithium, 1 mol CO₂ and 1 mol solid carbon from cathode.

The thermal treatment was performed with 3 L/min of carrier gas, hence a dynamic thermal treatment was performed. A heating rate of 300 °C/h in the resistance furnace by Thermo-Star (Thermo-Star GmbH, Aachen, Germany) was chosen and a holding time of 1 h at the target temperature was maintained. Figure 4a–c reveal the temperature and, for selected trials with specific equipment, the pressure curves obtained by the thermal pre-treatment. It is visible that three different temperatures and atmospheres were compared. For material 1, the target temperature of 500 °C was not reached due to a learning effect regarding the control of exothermic reactions. The effects on the resulting black mass are described in the following chapters.

After a thermal pre-treatment, the cells' components were shredded together (all cells of one cell type), manually sorted and grinded in a mortar. The shredded material was then sieved to extract black mass as the main product. Sieving was performed with a mesh width of 1 mm to extract black mass of a grain size of <1 mm. Afterwards, black mass was charged into the next process step, which was hydrometallurgical treatment based on the ESLR process. For a representative sampling, the black mass containers were rolled to homogenize the material before removing samples.

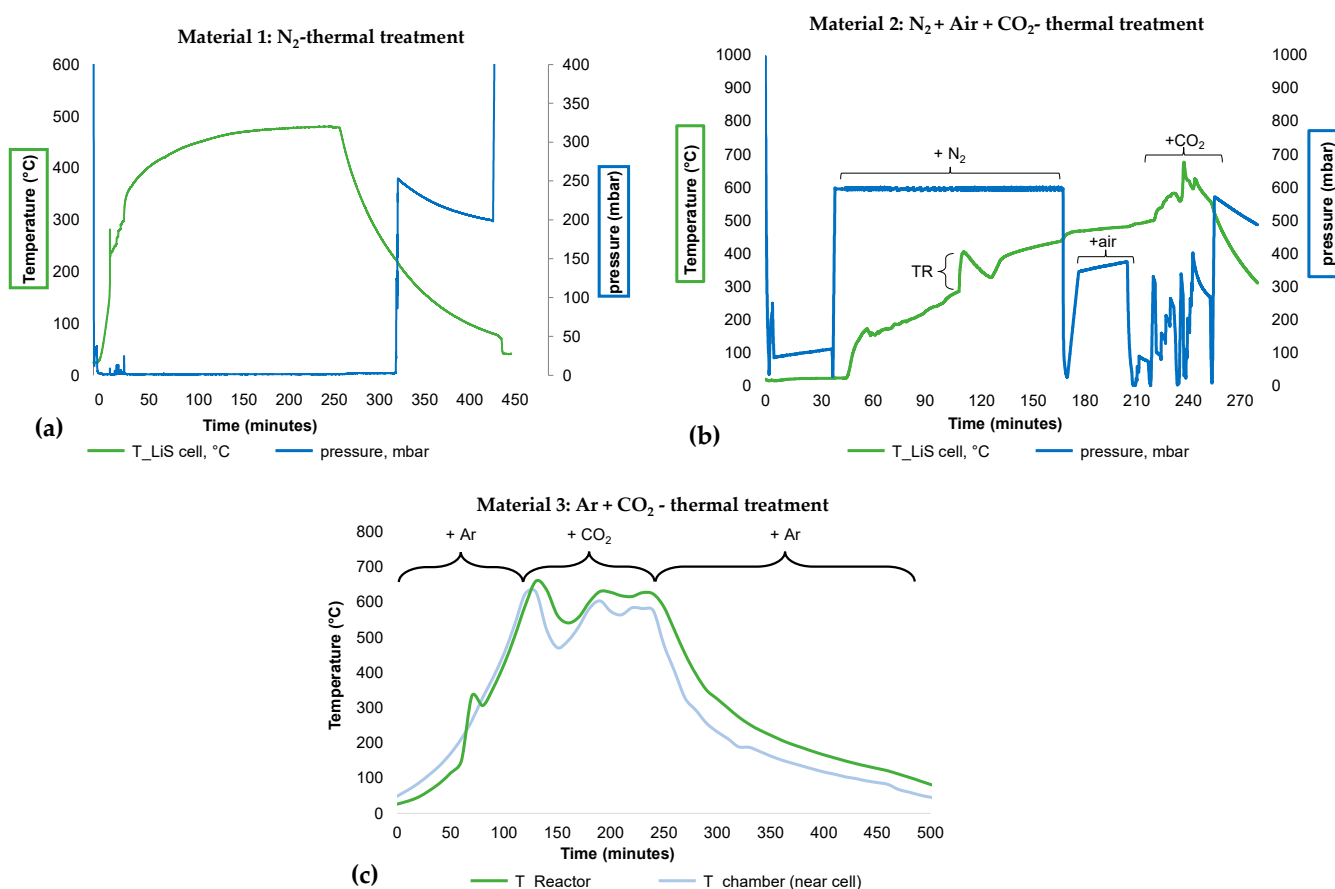


Figure 4. (a) Temperature and pressure over time of the thermal pre-treatment in inert atmosphere resulting in material 1. (b) Temperature and pressure over time of the thermal pre-treatment in N₂/air/CO₂- atmosphere resulting in material 2. TR = Thermal Runaway (exothermal reactions). (c) Temperature over time of the thermal pre-treatment in Ar/CO₂ atmosphere resulting in material 3.

To investigate the impact of lithium carbonation by means of CO₂-promoted H₂O leaching, this treatment (indirect carbonation) was compared to H₂O leaching without CO₂. Therefore, a glass beaker was used which was placed on a magnetic stirrer. A gas purging unit (glass frit) was placed into the liquid, which was connected to a CO₂-gas flow meter, which was in turn connected to a CO₂-gas bottle. Hereby, a constant gas flow rate was realized. During leaching, a defined volume and mass of deionized water and, respectively, black mass was mixed. Hence, the solid/liquid ratio of black mass/deionized water is one of the most important criteria for H₂O leaching. The solid/liquid volume was calculated based on the Li-share in the black mass assuming lithium to be available as Li₂CO₃ only. At 20 °C, the solubility of lithium carbonate was 13.3 g/L [42].

A defined leaching time and constant solution temperature were established. Into the solution, a gas purging unit (gas frit) was inserted to flush with a defined CO₂ flow rate of 2.5 L/min. After leaching, a filtration step was performed that separated the C-filter cake from the Li-bearing solution. This filter cake was then washed with a defined volume of 200 mL deionized water to ensure the enrichment of lithium cations in the product filtrate. Hence, physically entrapping dissolved lithium between the particles of the C-filter cake was avoided. Then, the filtrate's volume was measured and a sample was taken from the filtrate. Afterwards, the solution was filled into an empty and already weighed glass beaker. The solution was then boiled to obtain a solid lithium carbonate within the beaker. This means that all of the water needed to be boiled to detect the weight of the solid Li₂CO₃ product. The beaker can then be weighed again to extract the recovered lithium carbonate mass as the final product. This product was then analyzed via ICP-OES analysis to quantify

its purity. The sequence described here is shown in Figure 5a, whereas the set-up of the hydrometallurgical treatment is depicted in Figure 5b.

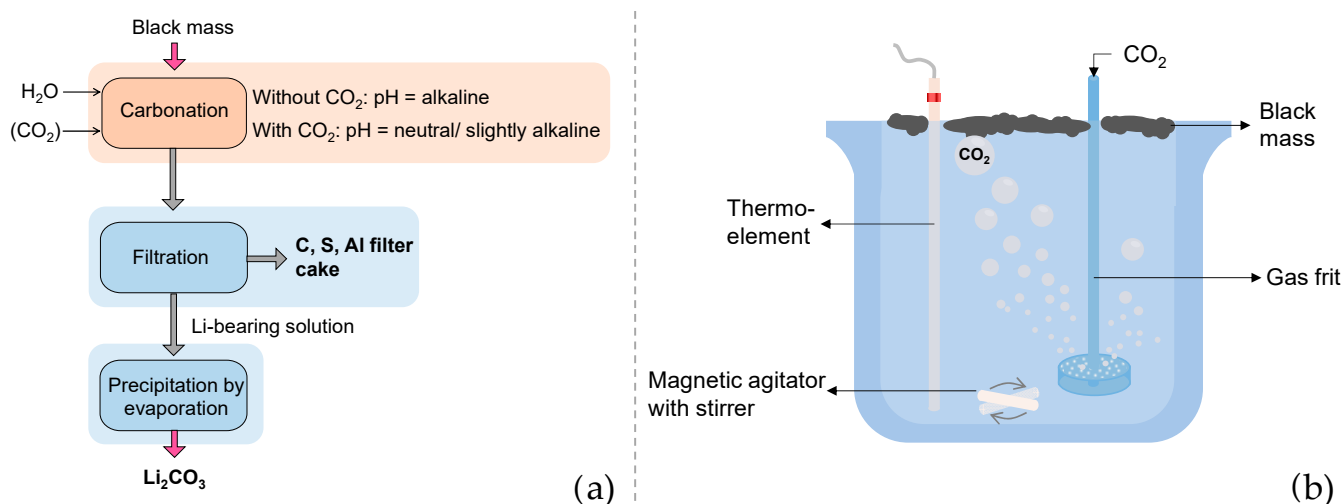


Figure 5. (a) Detailed depiction of the Early Stage Li-Recovery (ESLR) process after performing a thermal pre-treatment. (b) Set-up of ESLR in glass beaker for H₂O leaching with CO₂ bubbling.

Additionally, according to the flow chart shown, trials without the addition of CO₂ were performed as reference trials to benchmark the enhanced lithium yields by CO₂-gas purging (indirect carbonation). In these trials, the trial procedures were identical with the exception of not purging with CO₂.

Additionally, in Figure 6a–c the products of the ESLR process counting for the lithium yield (Li in %) are shown.

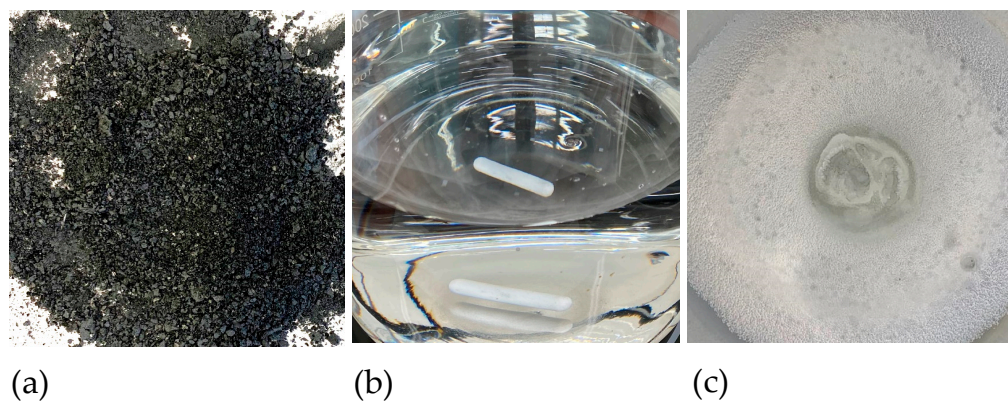


Figure 6. Products of the ESLR process with CO₂ bubbling: (a) C-filter cake (FKC), (b) filtrate, (c) Li₂CO₃ product.

2.2. Material Characterization and Lithium Yield Calculation

Material 2 was the main input material for the experiments shown in this article. Therefore, the ICP analysis, XRD analysis, particle analysis and EDS analysis of material 2 are detailed in this chapter. No information regarding the organic composition of the cells used is available, and if available is covered by NDAs (Non-Disclosure Agreements). The relevance of the pyrolysis parameters leading to material 1–3 was proven by the different obtainable lithium yields detailed in the Results chapter. Table 1 shows the results of the chemical analysis. Here, the elemental values were exemplarily since black mass was a heterogenous secondary material. Moreover, since the LiS cells used here were prototypes from cell research their elemental composition varied in terms of cell components used. For

example, Cu was not present in M2, meaning that no Cu-conductor foils were used. Since the anode consisted of metallic lithium, the cell design did not necessarily require Cu foils.

Table 1. Results of the chemical analysis of the different black mass materials 1–3. ICP-OES (Inductively Coupled Plasma—Optical Emission Spectrometry) analysis (Spectro, Kleve, Germany) of Li, Al and Cu. CIC (Combustion Ion Chromatography) analysis for F, and combustion method for C and S.

Materials	Li	Al	Cu	F	C	S
			wt. %			
M1	20.5	25	5.2	0.63	10.7	17
M2	16	13.2	0	1.76	17	13.9
M3	14.75	7.6	0.98	0.57	22.7	4.6

The solid/liquid ratio was the most relevant parameter for designing the leaching step of the ESLR (Early Stage Li-Recovery) process since lithium leachability must be ensured according to the solubility product of Li_2CO_3 . Therefore, 20 wt.% was taken for M1 as the reference to calculate the potential mass of Li_2CO_3 in the black mass. Hence, the minimum value of the required H_2O volume was derivable, resulting in the solid/liquid-ratio (s/l-ratio). M2 and M3 stem from the same cell type, hence the material comprises the same lithium share. Since another chemical analysis of M2 revealed a lithium share of 53.4 wt.%, the mean value of the three analyses (28 wt.%, hence 30 wt.%) was taken as the reference to calculate the s/l-ratio for M2/M3. Since one analysis revealed very high lithium shares, a slight over stoichiometric H_2O -ratio was chosen (+8%). Hereby, the heterogeneity of black mass was deduced. According to [20], the highest lithium yields were achieved when multiplying the minimal H_2O volume by 2 and 2.7. The minimal s/l-ratio can be derived from Table 2.

Table 2. Calculated solid/liquid-ratio dependent from the Li-content in black mass M1 and M2/M3. All concentration values are rounded.

Material	Reference Value for Li-Content (wt. %)	Minimal s/l-Ratio (g/mL)	Minimal s/l-Ratio $\times 2$ (g/mL)	Minimal s/l-Ratio $\times 2.7$ (g/mL)
M1	20	1:80	1:160	1:220
M2/M3	30	+8%: 1:130	1:260	1:350

Another important aspect is the determination of arising phases by means of an XRD (X-ray Diffraction) analysis. M1 was analyzed and evaluated externally. Therefore, only the results shown in Table 3 are available.

Table 3. Qualitative XRD analysis of M1. Since only the presence of phases was investigated no shares in % are available.

Characteristic Species	Li_2CO_3	LiF	Li_2SO_3	Li_2SO_4
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M2 and M3 were measured and evaluated internally at RWTH Aachen University. The X-ray Diffraction was performed at room temperature using an STADI P (STOE Darmstadt, Germany) powder diffractometer with an IPPSD detector and monochromatic $\text{Cu-K}\alpha 1$ radiation ($\lambda = 1.54059 \text{ \AA}$; flat sample; $1.5 \leq 2\theta \leq 116^\circ$ step rate 0.015° in 2θ) with a measuring time of 2 h. The evaluation was performed using the “Highscore+” software (Malvern Panalytical/Spectris, Egham, UK) and the ICDD database PDF-4/Axiom 2021 (ICDD, Newton Square, PA, USA). The results of two samples for M2 are depicted in Figure 7.

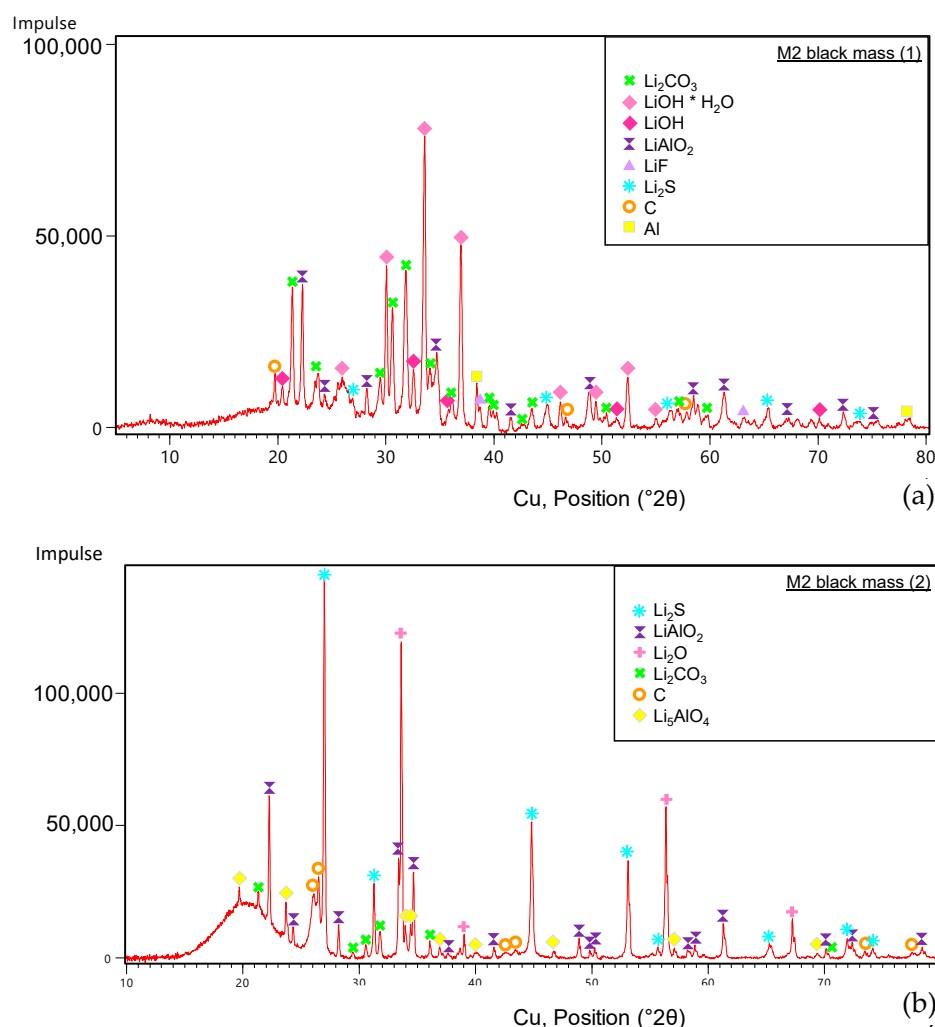


Figure 7. XRD evaluation of two samples: (a) M2 black mass (1) and (b) M2 black mass (2).

It can be seen that both samples contained Li_2S , Li_2CO_3 , C , and LiAlO_2 . Deviations in metallic aluminum can be explained by the samples' heterogeneity, the small X-ray contact surface and the low sample mass (~1 g). Since the metallic particles were large in relation to the carbon-containing cathode particles (see [20]), if an aluminum grain is included in the sample it can be detected by a high probability. Additionally, the lithium-aluminum-oxide phases, such as Li_5AlO_4 , together with LiAlO_2 , indicate the joint oxidation of metallic aluminum, which is located as a conductor foil below the anode, and hence metallic lithium. In M2 black mass (1), $\text{LiOH}/\text{LiOH} \cdot \text{H}_2\text{O}$ were also detected, and in M2 black mass (2) Li_2O was found.

This difference can also stem from the sampling. Both phases could be proven in the SEI (Solid Electrolyte Interface) [43,44], and once formed, Li_2O was obtained as pure phase until 700 $^{\circ}\text{C}$ [45]. The decomposition of LiOH occurs in favor of Li_2O surface formation inward over time, but re-hydroxidation can also be observed due to storage in air due to its humidity [46]. The formation of LiOH can also be proven for Li-ion batteries [33]. Both metallic lithium and lithium sulfide tend to react to Li_2O , Li_2SO_4 and Li_2CO_3 depending on the atmosphere and contact with solid carbon. Especially, if metallic lithium (anode side) or lithium sulfide (cathode side) is in contact with either C or CO_2 or both phases, lithium carbonate is formed. If no C or CO_2 are in place, metallic lithium (anode side) forms Li_2O with oxygen stemming from electrolyte degradation, and lithium sulfide (cathode side) forms Li_2SO_4 (see Figure 8).

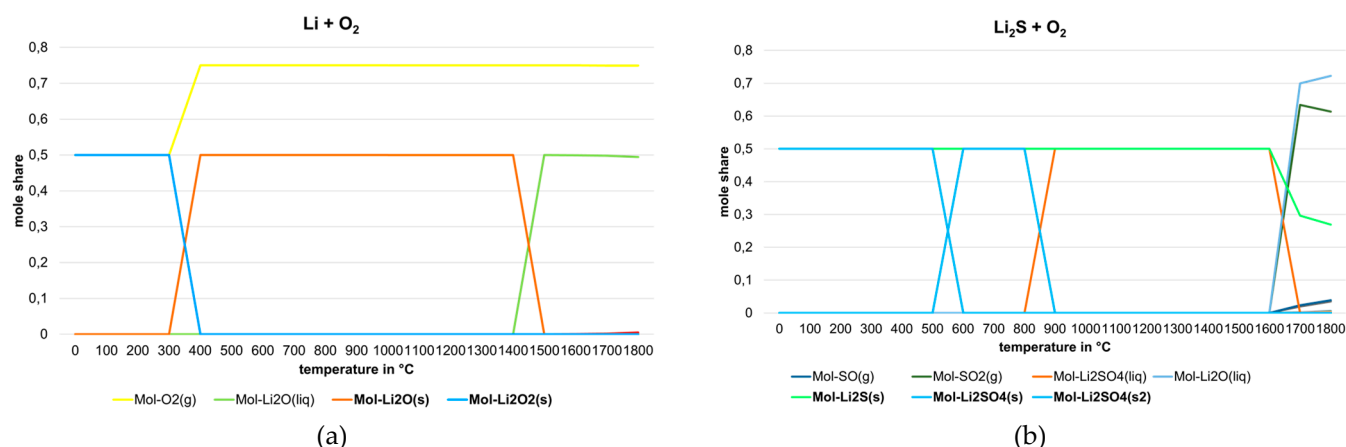


Figure 8. FactSage simulation (version 8.0) of possible products between 0 and 1800 °C using the Equilib-tool and the FactPS database (ideal gas and $p = 1$ atm). (a) reaction between 1 mol metallic lithium and 1 mol O₂, (b) reaction between 1 mol lithium sulfide and 1 mol O₂.

So, depending on the SOC, the equilibrium of reactions is either on the lithium-anode or cathode side. Moreover, once Li₂SO₄ is formed, it also remains stable when in contact with C or CO₂ (see exemplarily by the reaction with Li₂SO₄ and C in Figure 9a). Once Li₂CO₃ is formed from Li₂S, it remains stable until 300 °C. Then, the share of S (liq) decreases along with the Li₂CO₃ decrease. At the same time, Li₂S shares increase. Resulfidization can occur from 400 °C if the driving factor is simulated by the system Li₂CO₃ + C + CO₂ + S(liq), and the system Li₂S + C + CO₂ (see exemplarily by the reaction with Li₂S + C + CO₂ in Figure 9b) shows a high probability of resulfidization.

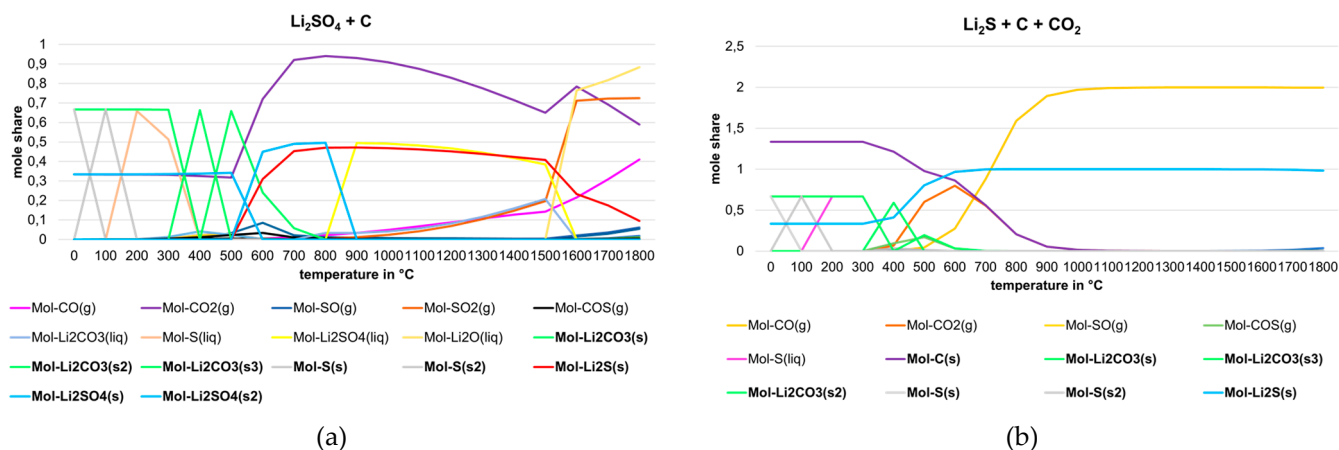


Figure 9. FactSage simulation (version 8.0) of possible products between 0 and 1800 °C using the Equilib-tool and the FactPS database (ideal gas and $p = 1$ atm). (a) Reaction between 1 mol lithium sulfate and 1 mol C, (b) reaction between 1 mol lithium sulfide, 1 mol C and 1 mol CO₂.

LiF on the other hand is only present at low shares, as the ICP-OES analysis demonstrated shares from 0.57 to 1.76 wt.%. An XRD evaluation can only detect phases which are present at a percentage of at least 2–3 wt.%. Therefore, depending on the sampling, LiF cannot be detected because the concentration is too low. However, LiF is likely formed in thermal pre-treatments according to [47].

A direct comparison between M2 and M3 is possible by also considering M3, as shown in Figure 10:

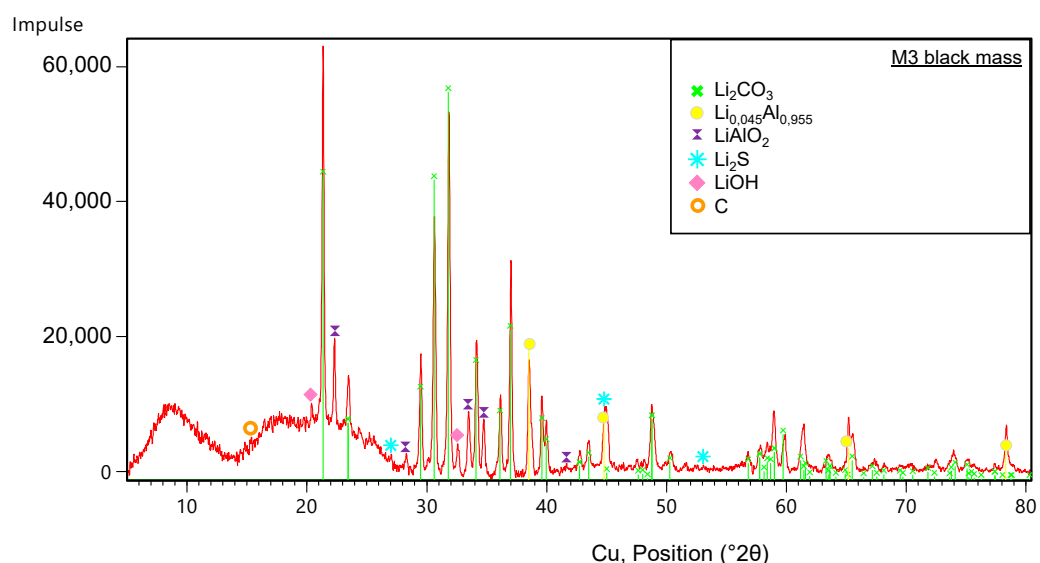


Figure 10. XRD evaluation of a black mass sample from M3.

Here, similar phases as found in M2 were detectable. When comparing M2/M3 (with CO_2 influence) to M1, it can be seen that a thermal pre-treatment generated in N_2 -atmosphere flooded in a vacuumized chamber pyrolyzed at $500^\circ\text{C} > T > 450^\circ\text{C}$ (M1) led to different phases. Here, no Li_2S was detectable. Instead, both Li_2SO_3 and Li_2SO_4 were found. Thermodynamically, this can be explained by the following context: Li_2S is present on the cathode side of the cell, hence, in a discharged state. Additionally, Polysulfides can dissolve in the electrolyte. As already described, Li_2SO_4 is only formed when no C and no CO_2 contact occurs. This means that lithium is present either on the anode side (charged state) or in the electrolyte in M1 since sulfates were formed instead of carbonates. If Li_2SO_4 is formed from Li_2S , it remains stable until 800°C . In the presence of C or CO_2 , the formation of Li_2CO_3 is rather favored. Additionally, once Li_2CO_3 is formed, the minimum temperature for a reverse reaction from lithium sulfide in lithium carbonate of 400°C is highly probable but should be proven in another simulation also containing $\text{Li}_2\text{CO}_3 + \text{S}$ (liq); therefore, M2 and M3 show a phase conversion towards Li_2S . These phenomena were proven by the FactSage simulations shown on the previous pages.

A dynamical particle analysis with QICPIC/L02 (Sympatec GmbH, Clausthal-Zellerfeld, Germany) of the heat-treated LiS black mass was performed, showing by the distribution sum (Q_3) a $d_{99.3}$ value of $101.46\ \mu\text{m}$ (see Figure 11).

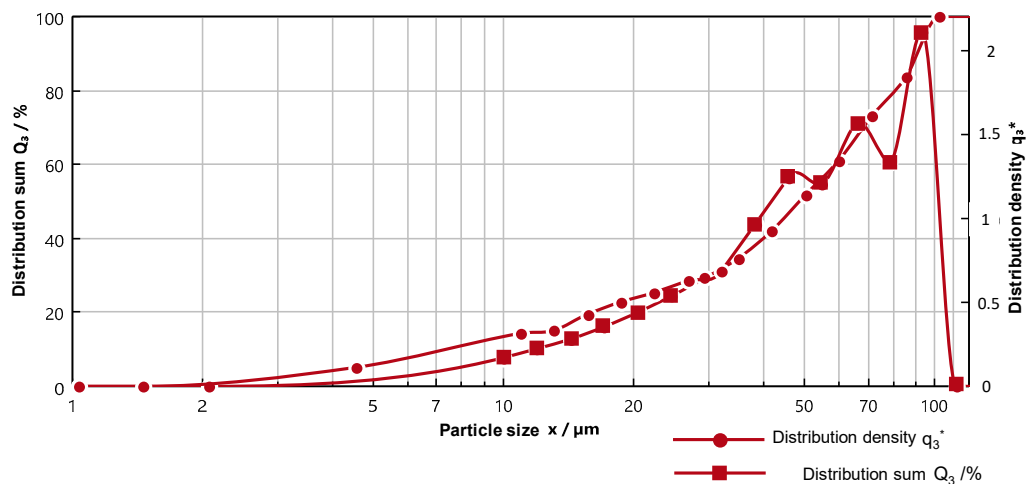


Figure 11. Dynamical particle analysis of CO_2 -pyrolyzed LiS black mass (M2).

The distribution sum and distribution density in this diagram are based on the EQPC (diameter of a circle of equal area to the 2D projection of a particle) value of the particles, which was indicated as particle size x.

Since the input material demonstrated a high degree of heterogeneity, the lithium yield was calculated for each trial by balancing the share in the C-filter cake and first filtrate against lithium, and finally in the solid lithium carbonate product. This is shown by Equation (1):

$$\text{Li [\%]} = \frac{\text{Li [g] in Li}_2\text{CO}_3}{\text{Li [g] in C-filter cake} + \text{Li [g] in filtrate}} \quad (1)$$

A similar method is the lithium yield calculation based on the leaching efficiency (“Li [g] in filtrate”), which is physically equivalent.

3. Results

Finally, Table 4 shows the experimental parameters investigated for the H₂O leaching of lithium–sulfur battery black mass and the resulting lithium yields. If a set-up was performed with an equal setting more than once, a mean value of the lithium yield was obtained. For M1, a coarse fraction (CF) was also considered with a grain size of >1 mm since pre-trials demonstrated that the lithium distribution between the coarse and fine fraction (<1 mm) can be also significant. Hereby, whether lithium is also recoverable when existing in coarse agglomerates can be investigated using the selected method. Sieving to <1 mm is performed in the process of Li-ion battery recycling to reduce the metallic impurities, especially in terms of Cu and Al from conductor foils.

Table 4. Experimental parameters and resulting Li-yields for H₂O leaching of Lithium–sulfur Battery black mass. 23.15 °C represents room temperature (indicated as RT). All trials without CO₂-addition were performed at room temperature due to the increased solubility of Li₂CO₃ at lower solution temperatures. FKC represents the C-filter cake.

Overview on Performed Trial Parameters					
Trial	FKC-Washing	Leaching Time, s/l-Ratio, if used: CO ₂ -Use, Leaching Temperature, Additives	Grain Size and Material	Li-Yield	Mean Value (Yield)
2.LS.1	FKC washed	120 min, 1:80	>1 mm (CF M1)	78%	
2.LS.2		120 min, 1:160	>1 mm (CF M1)	86%	
2.LS.3		120 min, 1:220	>1 mm (CF M1)	80%	
2.LS.4	FKC not washed	120 min, 1:80	>1 mm (CF M1)	65%	71%
2.LS.5		120 min, 1:80	>1 mm (CF M1)	70%	
2.LS.6		120 min, 1:80	>1 mm (CF M1)	78%	
2.LS.7		30 min, 1:80	>1 mm (CF M1)	75%	71%
2.LS.8		30 min, 1:80	>1 mm (CF M1)	68%	
2.LS.9		30 min, 1:80	>1 mm (CF M1)	71%	
2.LS.10	FKC washed	120 min, 1:130	<1 mm (M2)	72%	80% (with 2.LS.12)
2.LS.11		120 min, 1:260	<1 mm (M2)	40%	
2.LS.12		120 min, 1:130	<1 mm (M2)	87%	
2.LS.13		120 min, 1:260	<1 mm (M2)	81%	
2.LS.14		120 min, 1:350	<1 mm (M2)	87%	
2.LS.15	FKC not washed	120 min, 1:80, CO ₂ , 60 °C	<1 mm (FF M1)	80%	81%
2.LS.16		120 min, 1:80, CO ₂ , 60 °C	<1 mm (FF M1)	81%	
2.LS.17		120 min, 1:80, CO ₂ , 60 °C	>1 mm (CF M1)	73%	73%
2.LS.18		120 min, 1:80, CO ₂ , 60 °C	>1 mm (CF M1)	72%	
2.LS.19	FKC washed	120 min, 1:130, CO ₂ , RT	<1 mm (M2)	79%	
2.LS.20		120 min, 1:130, CO ₂ , 60 °C	<1 mm (M2)	87%	
2.LS.21		120 min, 1:260, CO ₂ , RT	<1 mm (M2)	88%	
2.LS.22		120 min, 1:260, CO ₂ , 60 °C	<1 mm (M2)	92%	
2.LS.23		120 min, 1:260, CO ₂ , RT, + H ₂ O ₂	<1 mm (M2)	91%	
2.LS.24		120 min, 1:260, CO ₂ , 60 °C, + H ₂ O ₂	<1 mm (M2)	91%	
2.LS.25		120 min, 1:350, CO ₂ , 60 °C	<1 mm (M2)	87%	

The solid/liquid-ratio is defined as mass of black mass [g] by volume of H₂O [mL].

It can be seen that particularly high lithium yields were obtained with M2 at a 120 min leaching time, as well as an s/l-ratio of 1:260 and CO₂ use. This was valid both for 60 °C (2.LS.22) or if H₂O₂ (10 mL, 35% concentration) was inserted, at both 23.15 °C (RT) and 60 °C (2.LS.23 and 2.LS.24). When comparing this yield to the lithium share in the black mass (30 wt.%), the minimum s/l-ratio for full lithium carbonate dissolution (1:120) was multiplied by 2 (1:260)/2.7 (1:350). This shows a good comparability between the pyrolyzed Li-ion battery black mass and pyrolyzed Li-S battery black mass. This is especially true in terms of trials 2.LS.13 and 2.LS.14 for M2 and 2.LS.2 and 2.LS.3 for M1, which can be directly compared to the best-case set-up in [20], particularly trial 1.A.25 with an s/l-ratio of 1:30, representing multiplication by 2, where no CO₂ was used for carbonation. The set-up of 2.LS.10 was repeated as in 2.LS.12 due to the large deviation in lithium yield. Since the difference was 47%, this set-up was not chosen as the best case. Kinetics are not crucial for lithium leachability, which was made evident by comparing 2.LS.4-2.LS.6 with 2.LS.7-2.LS.9. Washing of the C-filter cake is highly relevant: The lithium yield of 2.LS.1 is mostly higher than 2.LS.4-2.LS.9 and even in comparison to the CO₂-treated trials (2.LS.17 and 2.LS.18). Therefore, the key mechanisms detected in [19] for lithium-ion batteries can be proven here for Li-S black mass, too.

Hence, just by analyzing the yield, it can be seen that the mobilization of lithium was successful. Especially, an enhanced solid/liquid ratio led to increased lithium recovery. Moreover, the use of CO₂-gas is crucial for reaching satisfying yields. Finally, an enhanced leaching temperature of 60 °C in contrast to room temperature (RT) led to slightly higher lithium recovery.

In addition to the lithium yield, the purity of the obtained lithium product is also decisive. Connected to that, the resulting phases when using CO₂ and when using H₂O-solution only were compared with an XRD evaluation. In order to elucidate the crucial phenomena, the focus here was placed on M2. The following section highlights the lithium product impurities based on chemical analysis (see Figure 12) and the lithium phases based on XRD analysis (see Figure 13) for H₂O leaching without CO₂ bubbling.

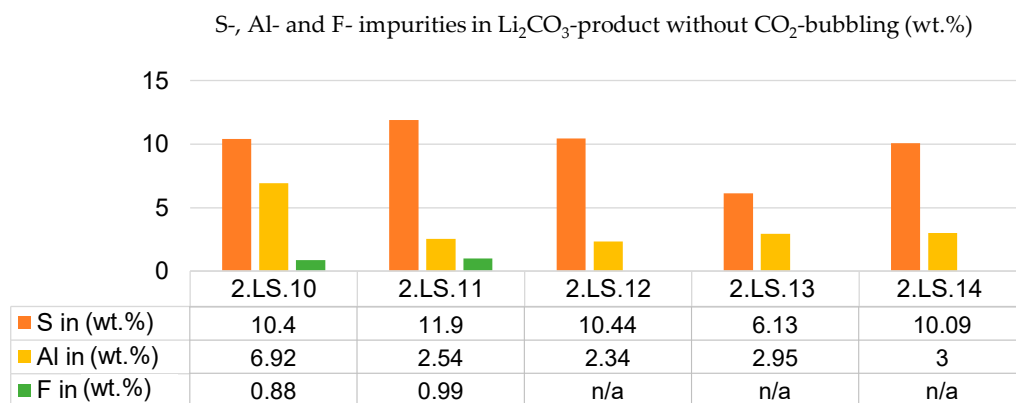


Figure 12. Summary of detected impurities (S, Al, F) within the final, solid lithium product with H₂O leaching without CO₂ bubbling.

The combined evaluation of lithium yield and impurity analysis shows the following output. The impurities of trial 2.LS.10-2.LS.14 are remarkable in terms of their high sulfur and aluminum contents. The aluminum contamination can be explained by the absence of CO₂, leading to a decrease in the pH value. Without CO₂, the components in black mass generate an alkaline solution of pH = 13, and with CO₂ bubbling the pH-value reaches pH = 7–9. This can be explained by the formed carbonic acid, which prevents aluminum from dissolving. In contrast to that, aluminum was dissolved in alkaline media only, due to its thin oxide layer on the surface [48], and this was the case when the set-up of H₂O leaching without CO₂ bubbling was investigated. The sulfur contamination can be explained by

the behaviour of S in aqueous media. In an acidic environment, gaseous H_2S is formed, whereas in basic areas sulfur tends to dissolve as hydrosulfide (HS^-), and then, at higher pH-value areas disulfide (S^{2-}) forming H^+ -ions are found [49,50]. In other words, S can be removed in acidic media, leaving as off-gas, and can dissolve in basic media, remaining in the solution. Here, the detected pH-value was pH = 13. This effect is promoted by the formation of dissolved sulfur-metal salts in OH^- excess, hence in basic media, such as $\text{M}_2\text{SO}_3/\text{M}_2\text{S}$ [51] or $\text{M}_2\text{S}_3\text{O}_3/\text{M}_2\text{S}$ [52]. A higher F-content in 2.LS.11 when compared to 2.LS.10 and 2.LS.11 can be explained by the reduced s/l-ratio. LiF has a low solubility of 1.2 g/L at 20 °C [42], hence solvent excess promotes dissolution.

A phase analysis was also used for LiS-Bs as a further assessment. For this purpose, trial 2.LS.13 is shown (s/l-ratio = 1:260). From 2.LS.13, it can be seen that only through H_2O leaching was the proportion of Li_2CO_3 reduced by phases such as LiOH , $\text{Al}_2(\text{SO}_4)_3$ or $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The same applies to an s/l-ratio of 1:130 (2.LS.10) and 1:350 (2.LS.14). The number of phases detected increases as the s/l-ratio increases. This means the Li product is not marketable despite the increased yield. Both the height of the interfering elements S and Al and the bandwidth of the resulting phases reduce the quality of the Li product.

In Figure 13, it can be seen that the obtained lithium product contained four phases besides lithium carbonate and lithium hydroxide. Therefore, the target of reaching a marketable product cannot be reached by H_2O leaching only. S specifically contributes to sulfate phases, containing both Li and Al. Moreover, in aluminium hydroxyfluoride hydrate and Li-Trifluoromethylsulfonate S and Al can be seen, which is attributed to the detected F-impurities. $\text{Li}(\text{CF}_3\text{SO}_3)$ is a common electrolyte salt used in LiS batteries as well [53], and $\text{Al}_2(\text{OH})_{2.76}\text{F}_{3.24}$ represents aluminium hydrofluoride hydrates, which can also occur in other stoichiometries [54]. Both phases show the necessity of lithium product purification when applying ESLR to LiS batteries.

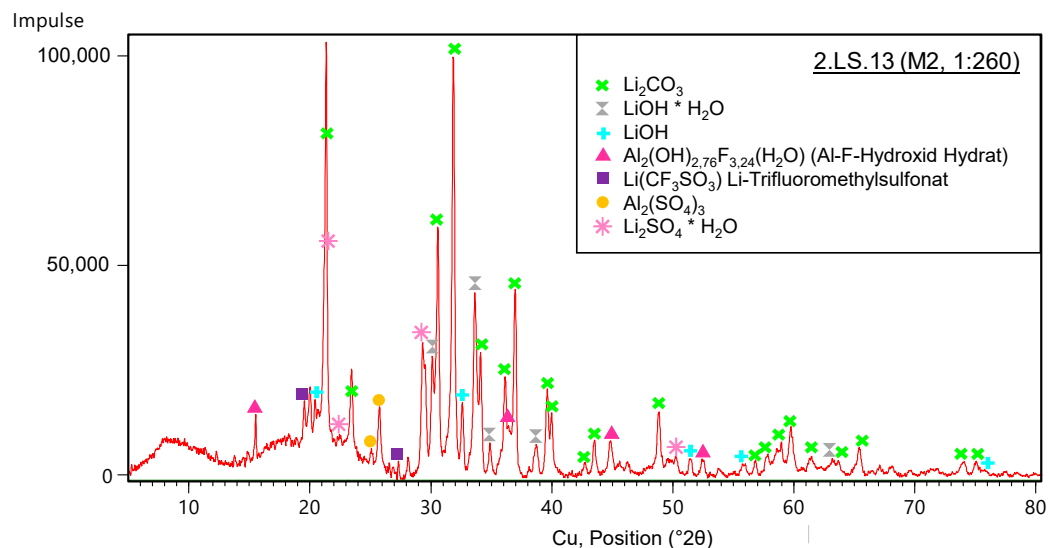


Figure 13. Diffraction pattern obtained by Highscore⁺-evaluation for trial 2.LS.13 (lithium carbonate product).

The same evaluation was required for the trials with CO_2 bubbling. Lithium product impurities were found based on chemical analysis (see Figure 14) and the lithium phases based on XRD analysis (see Figure 15) for H_2O leaching with CO_2 bubbling. For the XRD-analysis, trial 2.LS.22 was chosen because it was representative for the other trials as well.

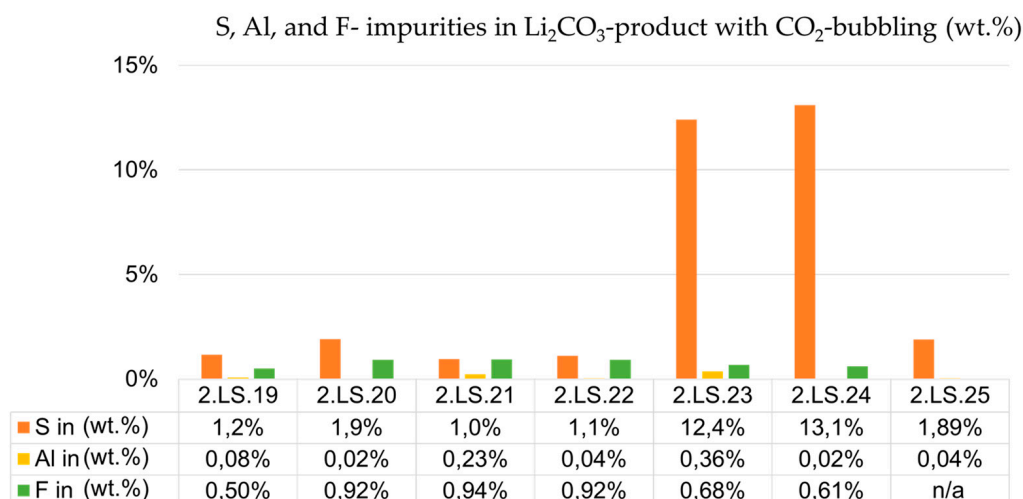


Figure 14. Summary of detected impurities (S, Al, F) within the final, solid lithium product with H_2O leaching with CO_2 bubbling.

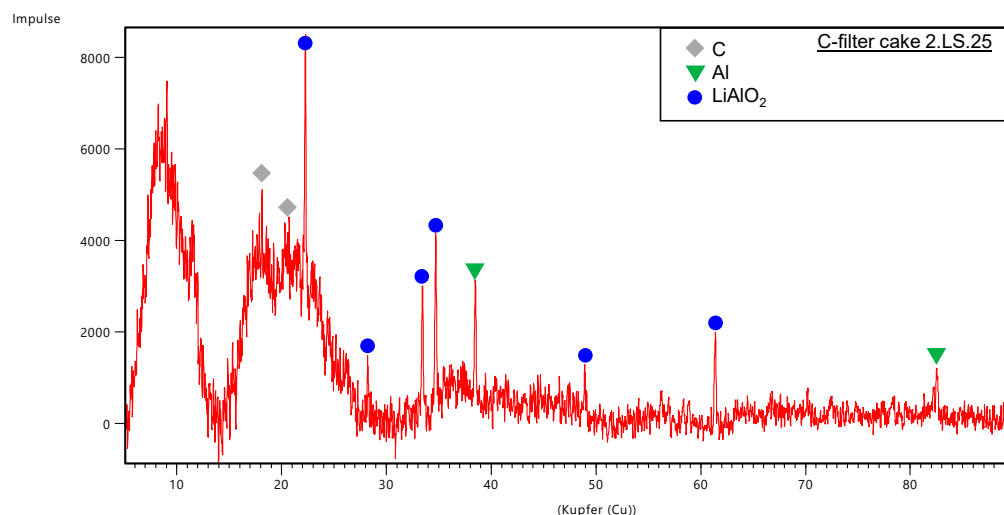


Figure 15. Diffraction pattern obtained by Highscore⁺-evaluation for trial 2.LS.25 (C-filter cake, FK).

The combined evaluation also revealed that, on the one hand, in terms of yields trials 2.LS.23 and 2.LS.24 are most successful together with 2.LS.22. On the other hand, in terms of impurities, it can be seen that both trials (2.LS.23 and 2.LS.24) show high sulfur contents in the lithium product. Hence, more sulfur-containing phases were dissolved during leaching by using H_2O_2 . For example, elemental sulfur can be oxidized to sulfates and then show an increased leaching efficiency. The process set-up does not have a significant influence on the F-impurities. For both with and without CO_2 bubbling, the Fluorine contents were in the range of 0.5–0.99 wt.%. At elevated solution temperatures (60 °C vs. RT) the formation of HF would be theoretically favored [55], while the dissolution of LiF is enhanced at higher temperatures. The phenomenon with a stronger influence could not be determined here. LiF, present in the black mass, shows a very poor solubility in H_2O , hence high lithium yields can also entail a good leaching efficiency of LiF by low s/l-ratios in that sense. As Figure 13 indicates, there are also non-lithium containing F-phases in the Li-product. The crystallization of aluminium hydroxyfluoride hydrates was also studied in [54,55], the occurrence of this phase was especially proven at 25 °C, thereby supporting the findings in this study [55]. For a further development, ion exchangers [55] or adsorbents [56,57] for F-removal from the filtrate should be incorporated into the process design. Moreover, the comparison between coarse fraction (>1 mm) and fine fraction (<1 mm) did not reveal any

significant changes in yields, or in Al-impurities. The Al-content in 2.LS.15 and 2.LS.16 was 0.02 wt.% (FF M1), in 2.LS.17 it was 0.39 wt.% and in 2.LS.18 it was 0.15 wt.% (CF M1). Eventually, lithium losses in the C-filter cake can occur leading to leaching efficiencies of < 100%. XRD analyses can provide an insight to determine responsible lithium phases, which do not dissolve into H₂O (see Figure 15).

It can be seen that LiAlO₂ was mainly responsible for lithium losses within the C-filter cake. Other XRD analyses revealed the phases LiF (2.LS.16) and Al₂O₃ (2.LS.18). An exemplarily XRD analysis of the best-case scenario, namely trial 2.LS.22, is depicted in Figure 16:

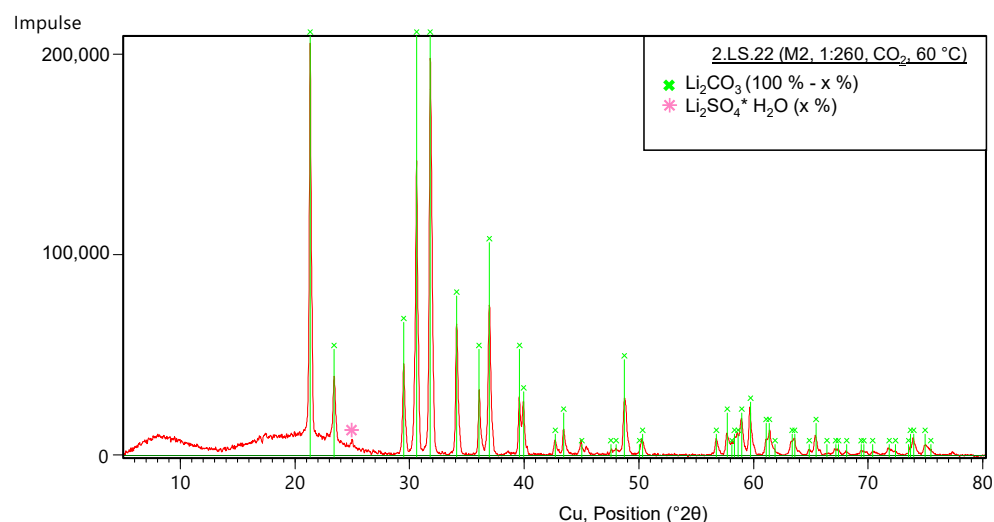


Figure 16. Diffraction pattern obtained by Highscore⁺-evaluation for trial 2.LS.22 (lithium product).

Technical grade Li₂CO₃ can be generated by CO₂ treatment at 60 °C. Just one low reflex, which cannot be assigned to Li₂CO₃, can be detected in 2.LS.22: Li₂SO₄ * H₂O, which is also in good accordance with the result of the element analysis in terms of impurities. The ratio of the molar mass of S to lithium sulfate hydrate (MS/MLi₂SO₄ * H₂O) is 25.06%. This results in a sulfate contamination of 4.39% by weight. The samples were in the air-dry state. A F-containing phase could not be detected, but 0.92 wt.% F in the Li product was measured by means of an elemental analysis. At 2.LS.21 (s/l = 1:260 at room temperature), XRD analysis detected, besides Li₂SO₄ * H₂O, LiF meaning LiF in 2.LS.22 LiF is highly probable. With this assumption and with a molar mass ratio (MF/MLiF) of 73.24%, the phase-wise LiF contamination accounted for 1.26 wt.% for 2.LS.22. A total of 5.65% by weight of phase-related impurities were therefore present in the Li₂CO₃ product, hence a lithium product with a purity of 94.35% was obtained in 2.LS.22.

Additionally, a further experimental series was performed since the Li-shares were heterogenous in black mass. Even the same type of black mass leads to different Li-shares. Hence, the calculations of the s/l-ratios were afflicted by uncertainties. Therefore, the fine fraction (<1 mm) of black mass of M1–M3 was leached using identical parameters. As a result, the influence of the thermal pre-treatment can also be evaluated more explicitly and the influence of material properties on lithium recovery. This set-up is presented in Table 5.

Table 5. Experimental parameters for H₂O leaching in combination with CO₂-gas promoted carbonation of Lithium–sulfur Battery black mass M1–M3 (validation trials).

Trial	FKC-Washing	Leaching Time, s/l-Ratio, Grain Size	Leaching Temperature and CO ₂ -Use/Flowrate
2.LS.26 (M1) 2.LS.27 (M2) 2.LS.28 (M3)	FKC not washed	120 min, 1:80, <1 mm	60 °C, CO ₂ -gas (2.5 L/min)

The resulting lithium yields can be derived from Figure 17:

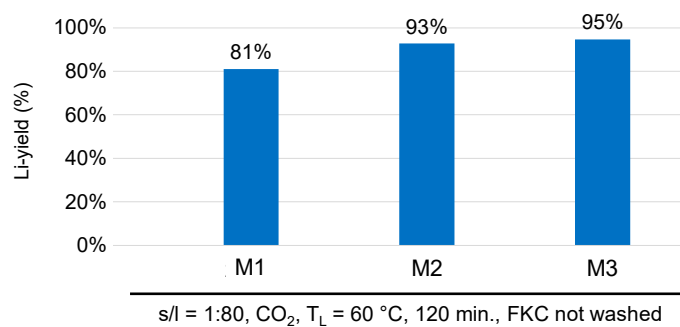


Figure 17. Lithium yields (%) referring on a solid lithium carbonate product based on different materials M1–M3. Leaching was combined with CO₂-gas.

Despite the different thermal pre-treatments, the Li-yields were >90% when treating M2 and M3 using the ESLR-process. M1 only reached an 81% lithium yield as a solid product. According to the XRD analysis of the black mass, sulphates were formed in M1, while in both M2 and M3 Li₂S formed instead. Since both phases show a high solubility in H₂O, the resulting LiS-phases are not decisive. However, during handling with M1, a sulphidic smell was noticeable. When connecting this fact to the lower resulting lithium yields, an elevated temperature and full oxidization and carbonation is recommended. Hence, the use of N₂ is not advantageous. Moreover, the optimal temperature for high (>90%) lithium yields is 600 °C.

The lower lithium yield of M1 might however be attributed to non-sulphidic, insoluble lithium phases, which were formed in the frame of the thermal pre-treatment. LiF on the other hand is poorly soluble in H₂O and was detected in M1. M2 shows LiF only in one sample and in M3 the presence of LiF could not be proven at all.

By comparing the lithium yields of M2 and M3, the following finding becomes visible: the most important difference in the thermal pre-treatment set-up was the air pressure before heating. For M2, the system was evacuated to an atmospheric pressure of ~100 mbar, while for M3 the atmospheric pressure of 1 bar was kept. Afterwards, both systems were flooded with inert gas.

Another important comparison is the transferability of the indirect carbonation by means of gaseous CO₂ between LiS- and LiBs black mass. Therefore, proof-of-concept trials were performed with thermally treated industrial black mass. This NMC111 black mass demonstrated a lithium content of 3.7 wt.% before thermal pre-treatment. The thermal pre-treatment was performed identically (600 °C, 3 L/min CO₂-flow rate and 1 h holding time) to the LiS-cells.

According to the lithium share in the black mass, the s/l-ratio was adjusted to keep it constant in comparison to the best-case trial with LiS-black mass (minimum solubility by factor 2.7). Moreover, the same leaching parameters were used (60 °C, 120 min, CO₂-flow rate of 2.5 L/min), thereby resulting in the following Li leaching efficiency (see Figure 18).

It can be seen that up to 76% of lithium can be dissolved into the aqueous solution by water leaching using indirect carbonation and 74% of lithium can be dissolved into the aqueous solution using H₂O only. CO₂ bubbling is hence advantageous in terms of lithium LE, and this difference can also increase to 7%. Moreover, it can be concluded that the lithium yields for LiBs were lower in comparison to LiS-black mass.

It can also be noted that the ratio of the CO₂-flow rate and black mass plays an important role in terms of lithium mobilization. Using 3 L/min in the thermal pre-treatment and 2.5 L/min in the indirect carbonation (CO₂ bubbling) led to a reduced Li-LE (9%) when inserting 100 g of black mass, hence the mass increase by a factor 10. Therefore, the volume of CO₂ offered is crucial in the thermal pre-treatment (trial C.3_1 vs. trial C.5_1) and also in terms of indirect carbonation (trial C.3_2 vs. trial C.5_2).

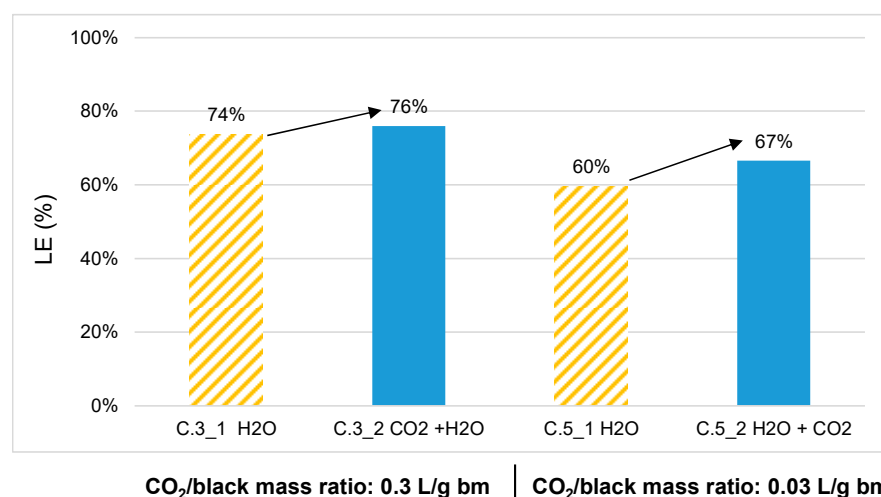


Figure 18. Leaching Efficiency (LE) of Li from LiBs black mass by H₂O leaching (orange, dashed lines) and H₂O leaching with CO₂-gas bubbling (blue, full color). Trials C.3_1 and C.3_2 represent a small scale (10 g), trials C.5_1 and C.5_2 an upscale (100 g) by constant CO₂-flow rate.

4. Conclusions

The developed process, with a combination of thermal pre-treatments, mechanical treatments and leaching in H₂O promoted by CO₂-gas, is a suitable tool for recovering lithium as a solid lithium carbonate product from LiS-battery cells. Yields of >90% are obtainable. At a H₂O-temperature of 60 °C, a purity of >90% can be reached. For industrial applications, however, a further refining step to remove residual impurities from the pregnant leaching solution is required. Therefore, according to primary lithium production, ion exchangers are an effective approach.

In detail, the following phenomena can be concluded:

The highest Li₂CO₃ shares in the product were found for trial 2.LS.22 and 2.LS.20, which were both leached at 60 °C with CO₂-gas bubbling. By applying XRD to the lithium product it was visible that the lithium carbonate reflexes of the diffraction pattern were dominant. Moreover, Li₂CO₃ does not comprise the dominant phase when no CO₂ bubbling is applied. In 2.LS.22, the highest yield and lowest reflexes of Li₂SO₄ · H₂O were present. In comparison to 2.LS.20, a lower s/l ratio (1:260) was applied. Therefore, more lithium can dissolve, explaining higher yields. The high lithium sulfate monohydrate phases in trial 2.LS.23 and 2.LS.24 were in good accordance with the ICP analysis detecting high sulfur contaminations and can be attributed to the use of H₂O₂ during leaching.

A finding in comparison to the results in [20] refers to the thermal pre-treatment of LiS-cells in comparison to LiBs. In both studies, an elevated thermal pre-treatment temperature led to higher lithium yields; however, for the atmospheres used, a different behavior of the lithium recovery was observed, whereby LiBs reached higher lithium yields in the inert gas (Ar) atmosphere, whereas for LiS-batteries a CO₂ atmosphere was found to be advantageous in terms of lithium recovery.

Future research will focus on the holistic recycling process that also considers carbon materials and aluminum particles in the black mass. This approach will be realized as part of the ecoLiga project, funded by the German Federal Ministry of Education and Research. Here, flotation in combination with the ESLR-process (ESLR-flotation) and subsequent acidic leaching in particular will be implemented to further purify the carbon materials on the cathode side. This will also lead to an increased recycling efficiency as more materials are recovered, also for LiBs. As this publication shows, the C-filter cake still contains impurities, which is why it can only be reused for the resynthesis of new cells following further processing. A second important target is the recovery of the contained electrolyte, which will also contribute to a higher recycling efficiency. The aluminum housing of the

cells was already removed manually and therefore provided a simulation of industrial separation techniques.

Besides, the statistical validation of the best-case scenarios for this recycling approach is pursued. Currently, only a limited mass of LiS-cells is obtainable since the batteries are currently still prototypes of the battery development phase. Moreover, it will be crucial to understand the phenomena of phase transformations with a detailed examination of the SOC (state of charge) when performing thermal pre-treatment. Especially for LiS-cells, this means a higher share of metallic lithium in contrast to a higher share of lithium sulfides in the input stream. The aspect of water resource efficiency is crucial. On the laboratory scale, the evaporation of H₂O was performed within this work. Further investigations should focus on the desalination and recirculation of H₂O by energy-efficient tools. Besides ion exchangers for impurity removal, membrane technologies are a good solution to obtain clean process water.

In fact, this publication, in combination with [18–20,58], provides a comparison between the LiBs and LiS batteries in terms of recyclability. When comparing LiBs and LiS-batteries in terms of their metallurgical recyclability, several benefits and drawbacks were observed. The specific benefits in terms of the recyclability of LiS-batteries can be described as follows:

- Lithium recovery from LiS-cells is comparatively facilitated due to fewer “contaminants” such as Ni, Co and Mn. When integrating lithium into acidic or alkaline leaching, lithium is only dissipated in the precipitates of the corresponding metal salts in low shares, see [18] in comparison to [58].
- This is also promoted by the use of metallic lithium in LiS-cells. Li does not have to be liberated from the transition metal oxides in the cathode material in LiBs by means of thermal decomposition. This is in accordance with an increased lithium yield because there are fewer insoluble phases in the thermally treated black mass, which is further exemplified in comparison to [20].
- In addition, there is an increased lithium concentration in LiS cells, which eases the Li-recovery by high yields during recycling, providing an interesting comparison with [20].

The specific drawbacks in terms of recyclability can be described as follows:

- A thermal pre-treatment specially designed for LiS-cells is necessary in order to achieve full oxidation of Li, otherwise the process safety during recycling is not assured due to the ignition of lithium during crushing of non thermally pre-treated cells, ignitions in the black mass when charging it into aqueous solutions, or ignitions when milling black mass without sufficient thermal pre-treatment.
- In hydrometallurgical processes, H₂S formation occurs during acidic leaching, which also makes process safety more challenging (see [18] in comparison to [58]).
- The intrinsic, monetary value of LiS-cells is largely determined by Li and is generally lower than the value of most LiBs. Because the viability of recycling is challenging, there are lower incentives for recycling. Therefore, a cost-saving recycling process is required for LiS-batteries.
- Connected to that, the Recycling Efficiency demanded by the EU, which is currently 50 wt.% based on a cell level, is not achievable only by recycling Li and Al. Considering the electrolyte, or activated charcoal and sulfur from the cathode material, would be necessary (see this publication in combination with [18]).

By analyzing the results in this publication alongside [18], two different scenarios for recovering lithium from LiS cells can be compared. In terms of lithium yields and purity, the results of this publication are to be favored over the approach in [18]. Moreover, in this publication, no additional additives besides gaseous CO₂ were required. The consumption of using CO₂ instead of emitting it is additionally advantageous. Besides, the process in this publication was H₂O-based, hence no leaching agents were necessary. Therefore, the ESLR process for LiS cells is recommended over acidic or alkaline leaching.

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