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Research article

Microwave thermal treatment of industrial NMC 622 lithium-ion battery shredder and its influence on reaction products compared to conventional pyrolysis

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ABSTRACT

Thermal pre-treatment has been proven to be a relevant process step in lithium-ion battery recycling. The organic removal and phase transformations are beneficial for subsequent process steps. Recently, the innovative concept of microwave heating has been introduced as an alternative for conventional processes taking the example of black mass and artificial mixtures. This study investigates the transferability of the concept to an industrial NMC 622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) battery shredder, including foils and separator for the first time. The influence of treatment time, power and atmosphere are investigated and finally a scale-up is carried out. For all parameters, the influence on the resulting products off-gas and active mass and the subsequent mechanical treatment and water-based lithium recovery is investigated and compared to a conventional pyrolysis process. The gas analysis showed the enhanced decomposition of organics to shorter molecules compared to conventional heating and a successful organic removal. After a microwave treatment at 6 kW for 14 min, a mass loss of 14.7 % compared to 12 % in conventional pyrolysis at ~550 °C was achieved and the delamination of the collector foils was improved. Furthermore, the reduction degree of NMC is similar. Accordingly, the lithium recovery shows nearly equal results of 54.2 % (conventional) and 55.5 % (microwave). The microwave process can therefore achieve the same product quality as a conventional treatment and is highly efficient with a timesaving of ~88 %. Consequently, the study pooves the feasibility of a microwave treatment for complex battery shredder material.

1. Introduction

The thermal treatment of lithium-ion battery (LIB) scrap has gained high relevance and attention in the frame of recycling. The advantages, such as controlled organic removal, resulting in enhanced black mass separation (Pinegar and Smith, 2020; Zhang et al., 2019) and leaching behavior in hydrometallurgy (Pinegar and Smith, 2020; Vieceli et al., 2021), as well as the enabling of innovative recycling concepts like early-stage lithium recovery (ESLR) (Rouquette et al., 2023; Stallmeister and Friedrich, 2023a; Balachandran et al., 2021) and flotation (Vanderbruggen et al., 2022) make the thermal treatment an important step in the process chain. Therefore, studies investigating the reaction products generated under different process parameters such as temperature, holding time and atmosphere have been carried out with conventional heating methods (Rouquette et al., 2023; Stallmeister and Friedrich, 2023a, 2023b; Balachandran et al., 2021; Lombardo, 2019; Lombardo et al., 2019, 2020, 2021). Here, the temperature during the thermal treatment process was identified as one of the main influencing factors regarding the phase composition of the black mass product and the organic removal. With respect to targeted phase transitions of the contained metal oxides to metallic Ni and water-soluble Li_2CO_3 and in the presence of Al-foils, temperatures of around 600 °C have proven to be most suitable (Rouquette et al., 2023; Stallmeister and Friedrich, 2023a; Hu et al., 2017; Liu et al., 2019).

In conventional batch processes for thermal treatment, limited heating rates are possible. An opportunity for fast pyrolysis is the heating with microwaves, which is investigated for the treatment of biomass, coal and plastic waste (Suresh et al., 2021; Motasemi and Afzal, 2013; Lam and Chase, 2012). As LIB black mass contains elements with high microwave absorbing properties such as carbon and metal oxides (Lam and Chase, 2012; Rao and Smakula, 1965), heat generation with microwaves is a promising and innovative opportunity for a rapid and energy-saving thermal treatment process (Motasemi and Afzal, 2013). The heating starts from the inside of the material as a result of interface

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and dipole transformation polarization (Motasemi and Afzal, 2013; Lam and Chase, 2012; Zhao et al., 2020) and is therefore quick, direct and avoids the heating of the whole equipment first. Initial tests have already been carried out on battery material. Zhao et al. (2020) investigated the behavior of mixed Ni, Co and Mn containing active material in the microwave field. The cathode material showed differing dielectric parameters depending on the temperature range and carbon dosage. To ensure high microwave absorbance over the entire temperature range of the process, a sufficient amount of carbon in the input material is beneficial (Zhao et al., 2020).

Few researchers (Fu et al., 2020a, 2020b; Pindar and Dhawan, 2020a, 2020b, 2020c) have started to investigate the inert microwave thermal treatment of LCO, LMO and LMNO LIB black mass or manually mixed anode and cathode active material from spent LIB in the frame of recycling processes. They investigated the carbothermal reduction of the metal oxides in dependence on carbon content, microwave power and process time. Pindar et al. (Pindar and Dhawan, 2020a, 2020b, 2020c) found a correlation between the microwave power and the reduction degree; with rising energy input, the reduction of the metal oxides increased, which also resulted in higher Li yields in the following water leaching. The weight loss of the material is rising with higher C concentration in the material. Additionally, the magnetization and Li recovery rise with a C concentration of up to 25 %. In the case of process time, a decrease in magnetization and Li yield was observed after 8 min. By parameter optimization, 82 % (Pindar and Dhawan, 2020c) of the Li was recovered after the thermal treatment by water leaching. Fu et al., 2020a, 2020b made similar findings regarding the correlation between process parameters and the reduction degree of the cathode material. In comparison with conventional heating methods, they found a more effective and higher reduction degree (99.2 % vs. 80.35 %) of the metals contained. Due to the high efficiency and rapid heating, Pindar et al. (Pindar and Dhawan, 2020a) conclude energy savings of up to 94 % compared to conventional pyrolysis.

The referred studies show the potential of microwave treatment and provide insights into some of the reaction mechanisms and requirements that the input material should fulfil. It can be concluded that in presence of sufficient carbon content, a rapid heating of the material and desired reduction reactions of the cathode material to enhance Li recovery are possible. Nonetheless, it has to be considered that these known studies deal with fine powder fractions of the black mass from typical phone battery chemistries and NCA cathode foils, that were not generated industrially. In industrial processes, more complex input streams with higher proportions of accompanying elements and foil fractions are to be expected. Moreover, higher Ni-containing EV-battery chemistries gained great relevance in the meantime. These aspects require further exploration regarding their impact on a microwave thermal treatment process. Furthermore, a positive effect of binder removal on the delamination of the collector foils is known from common thermal treatment processes (Zhang et al., 2018, 2019) but was not investigated with microwave thermal treatment, yet. Therefore, the recent study deals with industrially shredded EV NMC 622 LIBs without further mechanical separation before the microwave treatment. It still contains the separator, electrolyte, collector foils and the fine black mass fraction. The influence of microwave parameters and atmosphere on the heating and delamination as well as on the phase-composition of the black mass including Li liberation are investigated for the first time for such a kind of material. Another aspect of this study is the analysis of the produced off-gas and its comparison to conventional pyrolysis because little is known about the influence of microwave treatment on off-gas generation and composition in the frame of battery material. Diaz et al. (2018) examined the off-gas generation during the microwave treatment of NCA cathodes, where significant differences compared to conventional pyrolysis were identified. During the conventional heating process, three main stages of gas release were detected. In the case of rapid microwave heating, one single gas evolution period with less complex molecules occurs (Diaz et al., 2018) what might be beneficial for further utilization. For end-of-life material no data is known, although it is essential for the evaluation and subsequent process design. Additionally, the accompanying elements F and Al are considered in the recent study, as they can have a major influence on the recycling steps and product quality. Accordingly, this study aims for a deeper understanding of the ongoing reactions and a step towards industrial processes and materials.

2. Materials and methods

The trials were carried out with an industrially NMC 622 LIB shredder. As described in a previous study by the authors (Stallmeister and Friedrich, 2023a), LIBs were shredded under N_2 atmosphere and dried below 100 °C under a slight vacuum. The material was analyzed as described in Stallmeister and Friedrich, 2023a, and the elemental composition is given in Table 1. A sieve classification showed a wide particle size distribution of the material. Around 30.0 wt% are larger than 2 mm and 45.8 wt% are smaller than 0.5 mm (Stallmeister and Friedrich, 2023a).

The microwave trials were conducted in two different scales and microwaves. First, a parameter study with 10.0 g of input material in a microwave furnace (Panasonic NE-2740) equipped with four magnetrons was carried out. Therefore, the material was placed in an LT-crucible, which was placed in a sealed glass container with separate gas in- and outlet. Glass wool between glass and crucible walls was used for insulation. The glass container was purged with a continuous gas flow of 2 L/min of either N_2 or N_2+2.5% O_2 or 5% O_2. The described setup is shown in Fig. 1 (a). Before entering the two-stage scrubbing consisting of NaOH and H_2O, the off-gas was analyzed by Fourier-transform infrared spectroscopy (FTIR). For this purpose, the off-gas was continuously pumped to an N_2-dilution unit and afterward to the FTIR (DX 400, Gasmet Technology Oy, Vantaa, Finland). To avoid condensation, the whole system (pipe, pump, dilution and FTIR) was heated to 180 °C. In addition, a part of the gas was then fed into a condensation pump cooled to 5 °C, from where the gas was analyzed for hydrogen (CONTHOS 3-TCD, LFE GmbH & Co. KG, Bruchköbel, Germany) and oxygen (Oxygen Analyzer PMA 10, M&C TechGroup, Ratingen, Germany). The material was treated with a power of 340 W for 1–15 min and with a power of 1350 W for 1 and 3 min. Every trial was done minimum twice, some were repeated three or four times for statistical reasons.

Additionally, microwave trials were carried out in a batch microwave furnace (Fricke und Mallah, Microwave Technology GmbH, Peine, Germany) equipped with eight circular arranged magnetrons with a max. power of 6 kW, each. 120 g of the LIB shredder were placed in a similar setup as in the previous trials. Before the start of the trials, the furnace chamber was evacuated and afterward flooded with Ar. A continuous Ar flow of 6 L/min was adjusted during the trials at 6 kW for a trial duration of 14 min. The power was generated with two adjacent magnetrons switched on simultaneously. Every 2 min the magnetrons were switched to another pair, to promote a homogeneous treatment. A thermocouple type K, sealed in an alumina tube and protected with a copper foil at its top was used for temperature measurement. The trials were carried out in triplicate and the setup is given in Fig. 1 (b).

After the thermal treatment, the shedder material was weighed and sieved to 0.5 mm (small scale) and a sieve classification between 0.09 mm and 2 mm was carried out for the large-scale trials. The fine fraction <0.5 mm was then analyzed for its chemical composition by ICP-OES (Spectro ARCOS, Spectro Analytical Instruments GmbH, Kleve, Germany), IC (811 Compact IC pro, Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany) and combustion method (ELTRA CS 2000, ELTRA GmbH, Haan, Germany) and selected samples were analyzed for their phase composition by XRD.

Water leaching tests were carried out with the fine fraction of the black mass with a s/l of 40 g/L for 90 min with an input of 4 g (small scale) and 20 g (large scale). After filtration, the filter cake was washed with 40 ml (small scale) respectively 200 ml (large scale) of deionized

Table 1
The composition of the battery shredder in wt.%, analyzed by ICP-OES, combustion (Comb.) and ion chromatography (IC) (Stallmeister and Friedrich, 2023a).

Compound	Li	Ti	Mn	S	Co	Ni	Cu	Al	Si	P	Zr	F	C
Method	ICP-OES											IC	Comb.
Mean	2.51	0.01	4.26	0.19	4.56	14.20	4.51	5.04	0.11	0.57	0.15	3.51	34.55

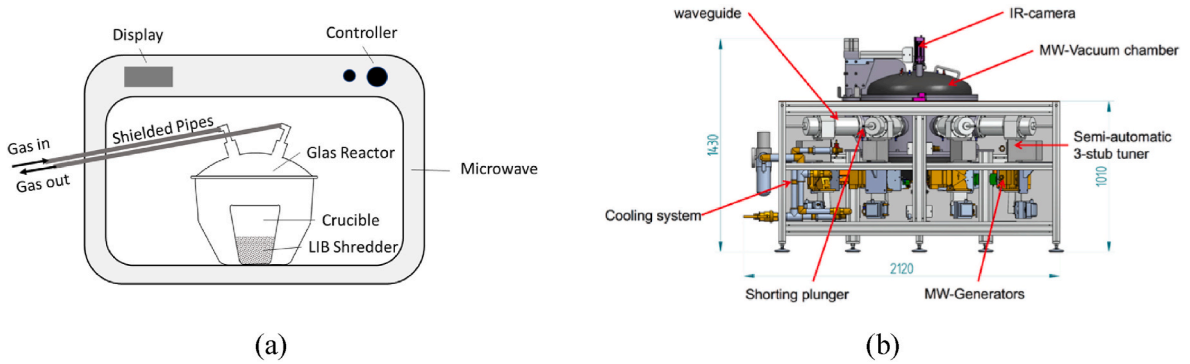

Fig. 1. (a) pyrolysis setup in small microwave and (b) large microwave furnace constructed by Fricke und Mallah, Peine, Germany (unit: mm). (Diaz et al., 2018).

water. In the case of the small-scale trials, the solution was analyzed for Li with ion-selective electrodes (ISE, DX207-Li and DX287-BF4, Mettler Toledo, Gießen, Germany and Metrohm Titrando 888, Deutsche Metrohm GmbH & Co. KG). A selection of 12 samples was analyzed by ICP-OES regarding Li and Al concentration additionally. In the case of Li-analysis, a comparison and compensational calculation between ISE and ICP-OES measurement was carried out. The ISE results were corrected by the equilibrium line equation as given in the supplementary material. For the large-scale trials, Li and Al analysis in the solution was carried out by ICP-OES, F analysis with ion-selective electrode (Metrohm Titrando 888, Deutsche Metrohm GmbH & Co. KG). Additionally, the filtrate was completely evaporated by heating to precipitate the Li salt. The salt was analyzed by XRD (Bruker D8 Advance, Cu Kα 0.154 nm) and IPC-OES. After the drying of the filter cake at 80 °C for 24 h, the filter cakes were analyzed for their chemical composition analog to the input material.

The results of conventional pyrolysis from a previous study by the authors with the same feedstock were used for comparison. The methodology can be found in the according paper (Stallmeister and Friedrich, 2023a).

3. Results and discussion

The following sections present the results of the two trial setups.

3.1. Off-gas analysis in small-scale microwave trials and comparison to conventional pyrolysis

The off-gas produced during the small-scale microwave trials was analyzed by a FITR. Due to the fast heating of the material, the gas evolution is rapid and reaches high concentrations in a short period. Therefore, it was necessary to include a dilution unit before passing the gas into the FTIR. Together with the complexity of the gas composition, possible lack of reference data for rare gas components, calibration of the FTIR for N_2-background, inhomogeneities of the input material and the microwave field, this can lead to inaccuracies in the absolute values of the gas analysis. Nevertheless, general, comparative and qualitative conclusions are possible.

In comparison to a conventional pyrolysis of the same LIB shredder under inert atmosphere, the same gas components were detected, but in different periods and concentration ranges, as shown in Fig. 2. In conventional pyrolysis, see Fig. 2 (a), with a heating rate of 300 °C/h,

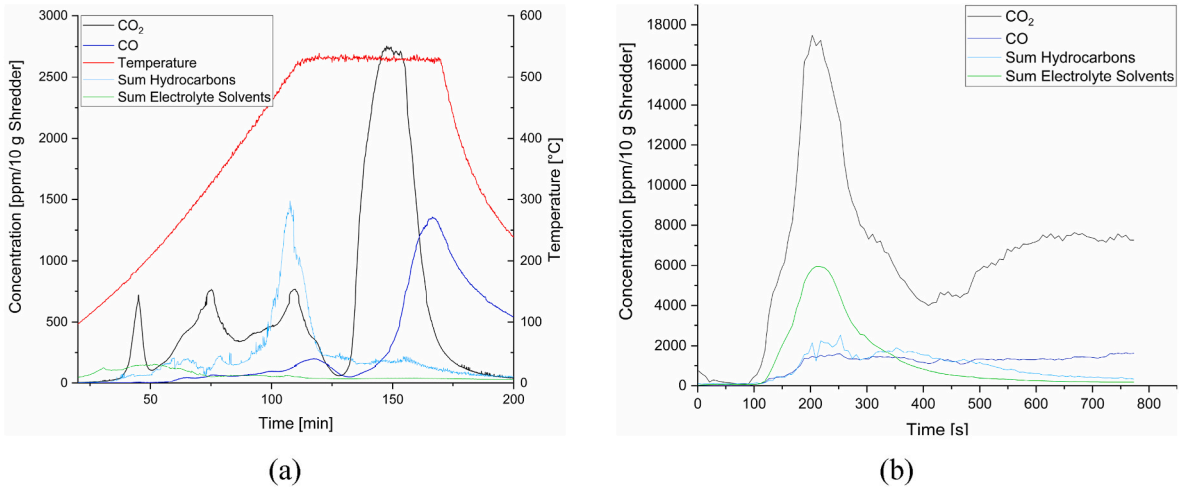

Fig. 2. Comparison of gas evolution in (a) conventional pyrolysis with (b) microwave pyrolysis under inert atmosphere (sum hydrocarbons including phenol).

different gas evolution periods, corresponding to the decomposition of LIB compounds at different temperatures are detectable, as described in a previous study (Stallmeister and Friedrich, 2023a). For example, CO_2 is released in four main stages due to different reaction mechanisms, which require different temperatures, such as the decomposition of the SEI or the decomposition of electrolyte components or separator. In the case of microwave heating, see Fig. 2 (b), most of the different gas compounds are released simultaneously and during a short period of around 300 s. The rapid heating results in simultaneous evaporation of electrolyte and decomposition reactions.

The comparison of the idealized produced gas amounts of different compounds between the conventional and the microwave pyrolysis under Ar, given in Fig. 3 and calculated by integrating the concentration curves with the Origin (OriginPro and OriginLab Corporation) integration tool according to equation (1), shows some significant differences.

$$V = \dot{V}\sum_{i=0}^{n}(t_{i+1} - t_i)(c_{i+1} - c_i)1 \Big/ 2 \quad (1)$$

V= Volume in NL, $\dot{V}$ = Ar flow rate (NL/min), c_i = concentration (vol %) at time t_i (min), c_{i+1} = concentration (vol %) at time t_{i+1} (min)

In conventional pyrolysis, a higher amount of water and hydrocarbons is released during the trial. In comparison, the rapid heating rate of the microwave treatment promotes the cracking of organics (Motasemi and Afzal, 2013; Menéndez et al., 2007), which results in the formation of higher amounts of CO and CO_2. Concerning Diaz et al. (2018), it can also be assumed that more hydrogen is formed during microwave pyrolysis. However, hydrogen could not be detected due to the dilution of the off-gas in the measurement device below the detection limit. Since the microwave heats the input material from its inside, a high temperature gradient between the material and the environment in the reactor chamber can be assumed. This leads to a short residence time of the pyrolysis gases in the hot region and to a quenching effect when the gases rise. This in turn, together with the higher heating rate, suppresses the formation of stable aromatic compounds, which is also reflected in the lower amount of aromatic gases produced, compared to conventional pyrolysis. Diaz et al. (2018) made similar findings when treating NCA cathode foils with microwaves.

Regarding HF, its amount is lower in microwave pyrolysis. HF is released due to the decomposition of the conducting salt $LiPF_6$ from the electrolyte according to equations (2)–(8) (Lamb et al., 2015; Tebbe et al., 2015; Stich et al., 2018) and the thermal degradation of the binder PVDF (Zulfiqar et al., 1994).

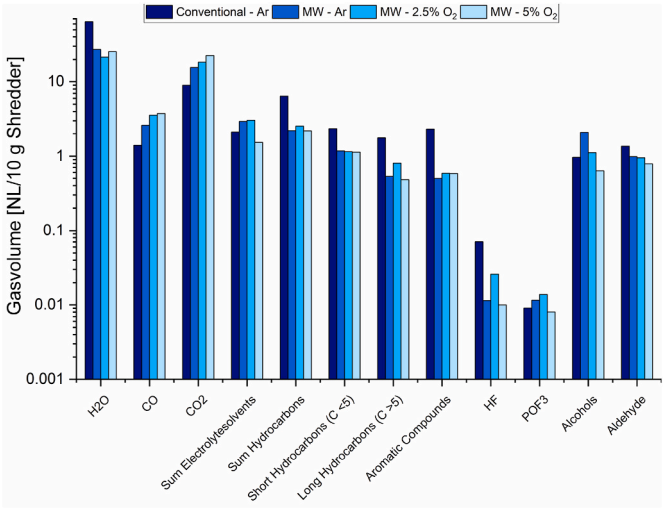

Fig. 3. Produced gas volumes of different compounds during different thermal treatments (Sum hydrocarbons including phenol; alcohols excluding phenol).

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \quad (2)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (3)$$

$$PF_4OH \rightarrow PF_3O + HF \quad (4)$$

$$POF_3 + H_2O \rightarrow POF_2OH + HF \quad (5)$$

$$POF_2OH \rightarrow PFO_2 + HF \quad (6)$$

$$POF_2OH + H_2O \rightarrow H_2PFO_3 + HF \quad (7)$$

$$H_2PFO_3 + H_2O \rightarrow H_3PO_4 + HF \quad (8)$$

A study by Bhandari et al. (Bhandari and Dhawan, 2023) investigated the influence of the H_2 concentration in the process atmosphere on the conventional thermal treatment of battery material. Their results indicate an influence of high H_2 concentrations on the decomposition mechanism of PVDF. Since in microwave pyrolysis a higher H_2 concentration is expected in general (Diaz et al., 2018; Ren et al., 2023), this could be an explanation for the lower HF emissions in the microwave trials. However, other possibilities such as the influence on PVDF decomposition or the reactivity of HF with other components should also be considered. For example, the reaction of PVDF with Li with the release of H_2 is reported in the literature (Du Pasquier et al., 1998).

$$C_2H_2F_2 + Li \rightarrow LiF + C_2HF + \frac{1}{2}H_2 \quad (9)$$

The comparison of the gas evolution between the microwave trials with different oxygen concentrations in the atmosphere also shows some differences. As expected, the amount of produced CO and CO_2 is rising with rising oxygen amount, as given in Fig. 3. Combustion reactions of organics and carbon with oxygen lead to this phenomenon. Taking the gas concentration over process time given in Fig. 4 (a) and (b) into account, the main difference in the CO and CO_2 production appears in the second half of the treatment period. In the case of CO_2, the concentration reaches a maximum after around 200 s and decreases afterward until a second increase starts between 300 and 400 s until the end of the trial. The first peak is related to decomposition reactions of the organics and is similar for all three oxygen concentrations. The second increase is due to the reaction of solid carbon or graphite with oxygen (see equations (10) and (11)) and, especially in the case of inert atmosphere, the carbothermic reduction of metal oxides. Higher oxygen concentrations in the atmosphere lead to higher concentrations of CO_2 and CO compared to an inert atmosphere, due to combustion. Therefore, this phenomenon is not observed in the study of Diaz et al. (2018), since they were treating NCA cathode foils without the carbon-rich anode.

$$C + O_2 \rightarrow CO_2 \quad (10)$$

$$2C + O_2 \rightarrow CO \quad (11)$$

The total amount of hydrocarbons is just slightly differing between the trials with different oxygen concentrations with 2.20 NL (Ar), 2.53 NL (2.5% O_2) and 2.19 NL (5 % O_2) and also the concentration curve over time is similar for all trials. This leads to the conclusion that nearly no combustion of the released organic compounds takes place with the added oxygen. In contrast, a previous study by the authors (Stallmeister and Friedrich, 2023b) proved the combustion of organic off-gases with inserted oxygen in a conventional thermal treatment in a moving bed reactor. In the microwave, the temperature gradient between the feedstock and the reactor environment is more decisive. Due to the cooling of the rising exhaust gases, there is no longer a sufficient temperature or energy available for their combustion with oxygen.

When comparing the release of HF, no clear influence of the atmosphere on the concentration curves over time is observed. In all cases, one peak occurs which is highest for 2.5 % O_2. However, the general low

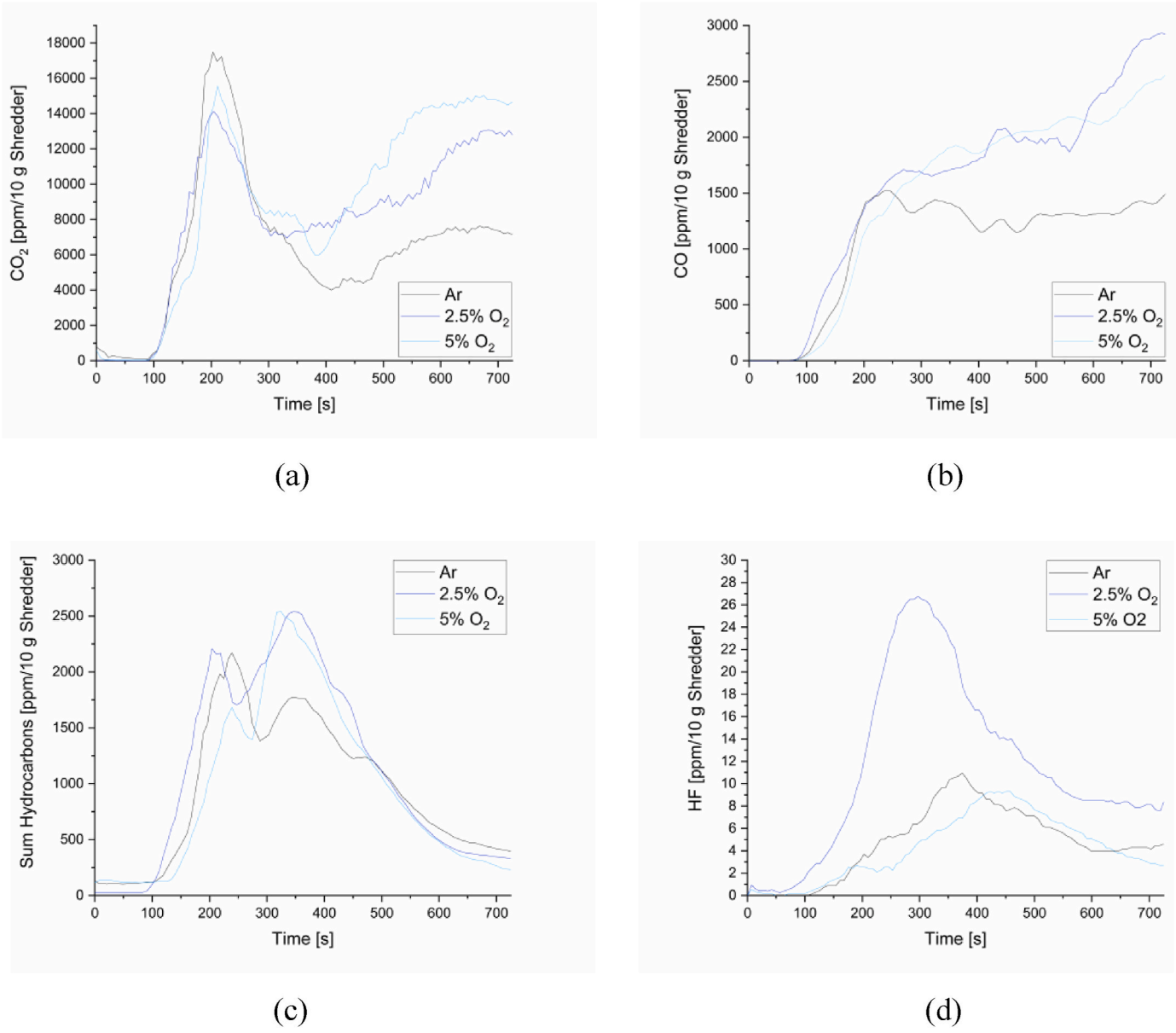

Fig. 4. Comparison of gas evolution of (a) CO_2, (b) CO, (c) hydrocarbons (including phenol) and (d) HF over microwave treatment time for different O_2-concentrations in the flow-gas.

HF concentration compared to most of the other measured gas compounds and the high reactivity of HF e.g. with the reactor or pipes could have affected this result. In a repetition of the trial, the concentration was lower. The evolution of alcohols like ethanol and methanol as well as the generation of aldehydes like acetaldehyde are decomposition products of electrolyte solvents (Kanayama et al., 2022; Fernandes et al., 2019). In both cases, a decreasing trend with rising O_2 concentration in the atmosphere is observed, as shown in Fig. 3. Both groups of substances require lower temperatures for their combustion than most of the hydrocarbons (Haynes, 2017). Accordingly, their partial reaction with oxygen is possible despite the temperature gradient.

3.2. *Weight loss and black mass characterization after small-scale microwave treatment*

After the microwave thermal treatment, the LIB material was weighed to measure its weight loss due to organic, fluorine and oxygen removal in dependence of treatment time, power and atmosphere. For all 3 atm investigated, the weight loss follows a limited growth function over time, as shown in Fig. 5(a). Up to a treatment time of around 11 min, the mass loss of the inert treated material is slightly higher than the loss for the material treated under O_2-Ar-mixtures. Possible explanations are the prevention of reducing and oxygen-releasing reactions of the cathode material and oxidation of aluminum in the presence of O_2. After the maximum treatment time of 15 min, the weight losses have equalized to 13.3 wt.-% (Ar), 13.9 wt.-% (2.5 % O_2) and 12.9 wt.-% (5 % O_2). Compared to conventional pyrolysis under Ar with the same input material, a similar weight loss occurs at maximum treatment temperatures between 580 °C and 600 °C (Stallmeister and Friedrich, 2023a). The increase of the microwave power to 1350 °W results in a larger weight loss after short treatment times, see Fig. 5 (b). The accompanying rapid increase in temperature in the material leads to an average weight loss of 14.2 wt.-% after just 1 min of microwave treatment, compared to 3.2 wt.-% in the case of 340 °W. After 3 min, the weight loss amounts to 19.2 wt.-% and is thus bigger than in conventional pyrolysis with 16.3 wt.-% at 717 °C (Stallmeister and Friedrich, 2023a). Even that a

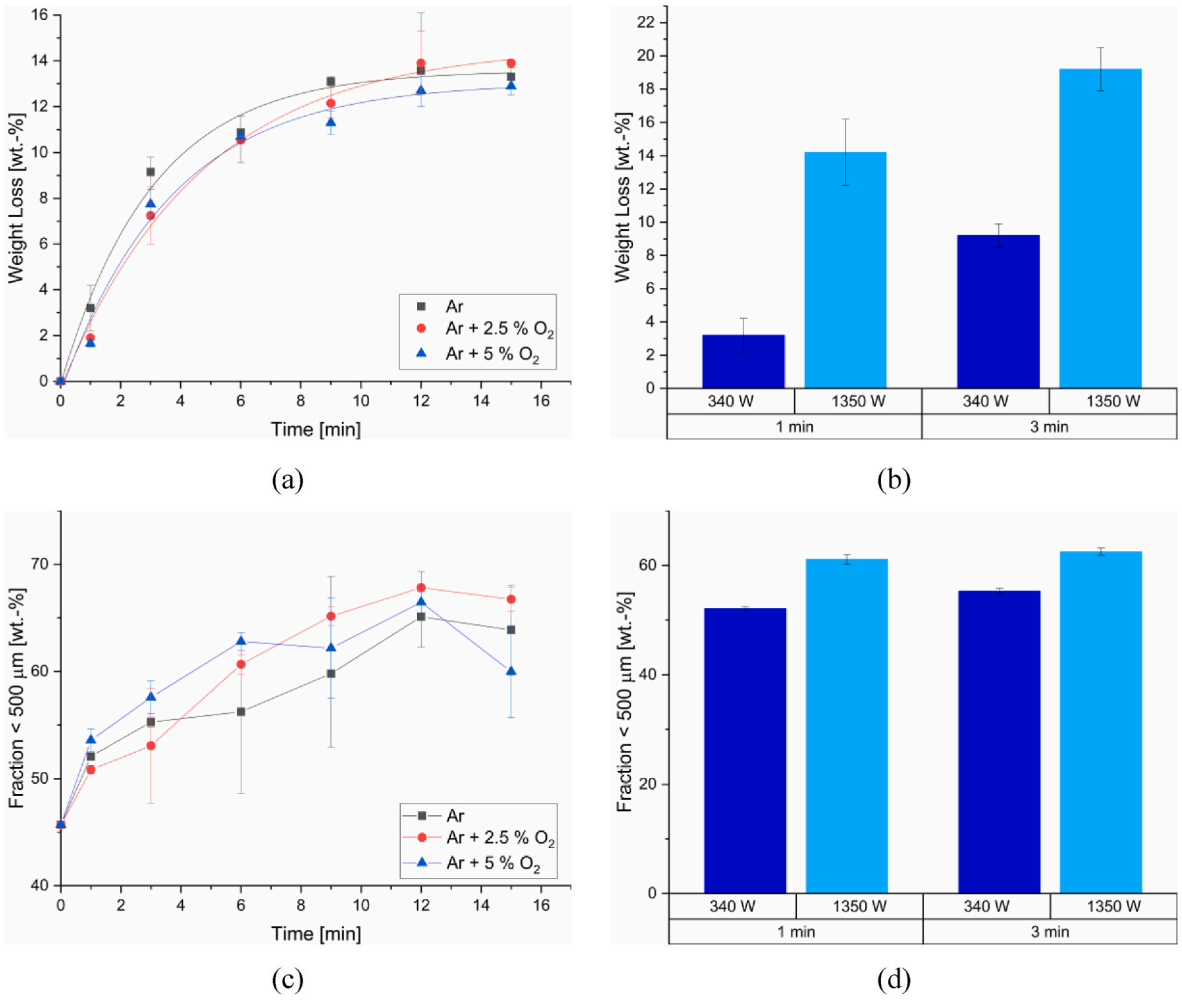

Fig. 5. Weight loss of the material treated in the small-scale microwave (a) over time and for different oxygen concentration in the atmosphere and (b) for different microwave power and treatment times und Ar and share of <500 µm fraction of the material after treatment in the small-scale microwave (c) over time and for different oxygen concentration in the atmosphere and (d) for different microwave power and treatment times under Ar atmosphere.

temperature measurement was not carried out in the small-scale microwave, it can be assumed that at least 660 °C was exceeded, as molten aluminum droplets are visible in the material.

The proportion of the fine fraction of the LIB shredder after thermal treatment, given in Fig. 5 (c), shows an increase with time. But the error bars, representing the largest and smallest value reached for each parameter setup, have a huge variance, especially under inert atmosphere. This is due to the inhomogeneity of the input material and the uneven heating in the microwave field. The shredder consists of different compounds with different microwave interaction parameters like metal foils, graphite and metal oxides (Pindar and Dhawan, 2020c). Additionally, the static sample placement in the microwave field lead to an inhomogeneous heat generation. Moreover, phase transformations during the treatment can lead to changes in the dielectric properties of the material, as described by Zhao et al. (2020). To increase the fine fraction share of the material output, it is crucial to decompose the binders which stick the active material on the collector foils and cause agglomeration. From previous research (Stallmeister and Friedrich, 2023a; de Jesus Silva et al., 2020) in conventional pyrolysis, it is known that temperatures above 500 °C are necessary to decompose the binder PVDF. Increasing the microwave power to 1350 W leads to an increase of the fine fraction share as shown Fig. 5 (d) and therefore indicates higher temperatures reached, similar to the weight loss observations. In addition to improved delamination behavior, the embrittlement of aluminum contributed to a higher proportion of fines.

The following XRD analysis of the fine fraction, given in Fig. 6, proves the already mentioned reducing reactions in the NMC active material. With rising time and temperature, the intensity of the lithium-containing NMC oxide is decreasing until it is not detectable after 15 min treatment time. Its decompo sition is proven to be stepwise: Initially, simpler mixed oxides such as LMO and LNO are formed. After prolonged microwave treatment, these are further decomposed to NiO and MnO, and the reaction product Li_2CO_3 can be detected. Besides Li_2CO_3, further Li-containing compounds such as Li_3PO_4 and Li_xC are formed. It can be assumed that LiF is also present due to reaction (2), but it is not detected in the XRD patterns.

In comparison to results from conventional thermal treatment with the same input material, the reduction of the metal oxides is less complete. In a previous study of the authors (Stallmeister and Friedrich, 2023a), metallic Ni was detected after a thermal treatment at 576 °C. Since the other results indicate that at least this temperature or even higher ones were achieved in the microwave, the reaction kinetics and inhomogeneities of the temperature distribution in the material are possibly the reasons for the less complete reduction. The derived overall reaction for this incomplete reaction could be according to equation (12), with subsequent Li_2CO_3 formation from the reaction of Li_2O with CO_2 (13).

$$10LiNi_{3/5}Mn_{1/5}Co_{1/5} + 2.5C \rightarrow 5Li_2O + 6\,NiO + 2\,MnO + 2CoO + 2.5\,CO_2 \quad (12)$$

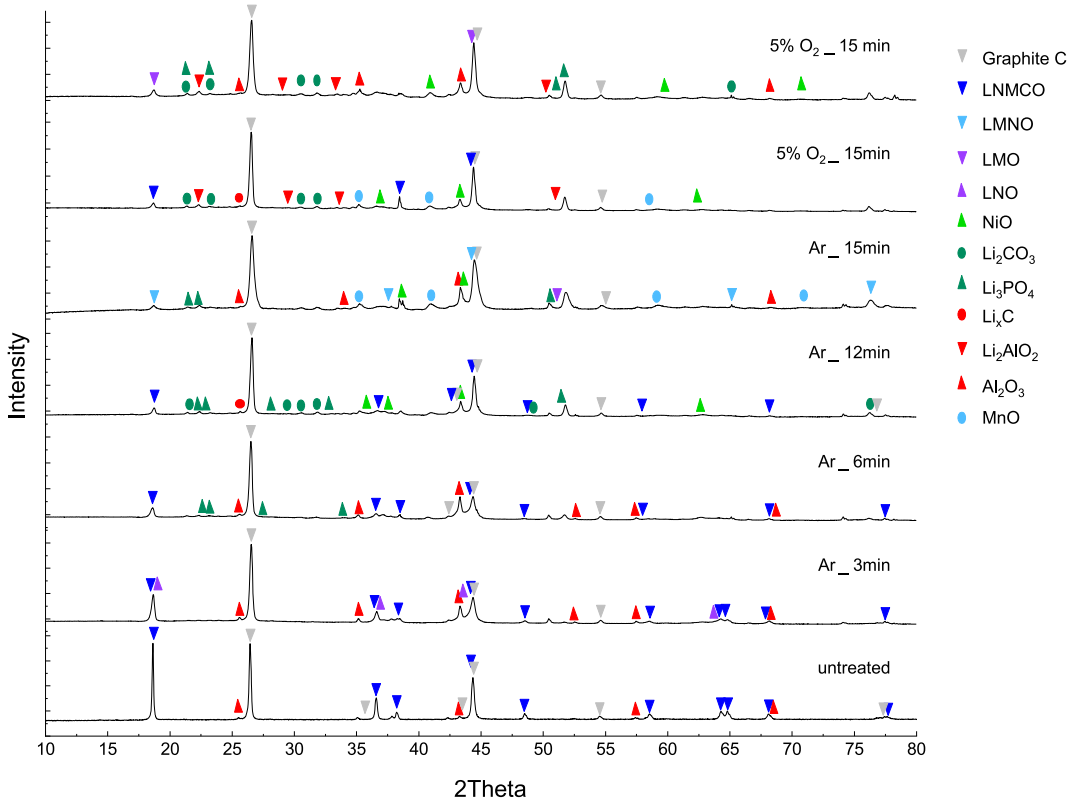

Fig. 6. XRD analysis of the active mass fraction after different microwave treatment times at 340 W under Ar and O_2-enrichted atmosphere.

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \quad (13)$$

Regarding the phase composition of the black mass after the treatment under different oxygen concentrations in the atmosphere, it can be seen from Fig. 6 that the reduction is less complete in the presence of oxygen compared to the inert atmosphere. LMNCO and LMO compounds are still detectable. Another difference is the proof of lithium aluminates which have formed in the presence of oxygen, due to the reaction of Li_2CO_3 with Al_2O_3 according to equation (14) (Bale et al.). The oxygen promotes the oxidation of aluminum and its transfer to the fine fraction, resulting in equation (15).

$$Li_2CO_3 + Al_2O_3 \rightarrow 2LiAlO_2 + CO_2 \quad (14)$$

$$Li_2CO_3 + 2Al + 1.5O_2 \rightarrow 2LiAlO_2 + CO_2 \quad (15)$$

3.3. Water leaching of black mass after small-scale microwave trials

The leaching efficiency (LE) of Li, calculated based on equation (16), shows a dependence on the previous microwave treatment time.

$$LE_{Li} = \frac{m_{Li}\ in\ solution\ [g]}{m_{Li}\ input\ to\ water\ leaching\ [g]} \bullet 100\% \quad (16)$$

As can be seen in Fig. 7, there is just a slight increase of the LE after the first 3 min for treatment under Ar and no change compared to the untreated material after this time in the case of oxygen presence. The oxygen hinders the reducing reactions of the NMC as shown in Fig. 6, which are necessary for Li_2CO_3 generation. After 3 min, a rapid increase of the Li LE occurs, which saturates after 10 min. This trend is most likely due to the similar temperature curve within the sample. From the temperature measurements of the large-scale microwave trials, see Figure A 1 in the appendix, it is known that the temperature of the material undergoes a limited growth function. Additionally, a strong dependence of Li leaching on the thermal treatment temperature is known from conventional pyrolysis trials (Rouquette et al., 2023; Stallmeister and Friedrich, 2023a) and is in accordance with the observed reduction behavior and Li_2CO_3 generation, presented in Fig. 6.

Overall, the average maximum Li LE achieved varies just slightly between the three different atmospheres investigated. It amounts to 53.3 % under Ar, 51.2 % under 2.5 % O_2 and 55.8 % under 5 % O_2 atmosphere. Taking the error-bars showing the maximum and minimum reached value from Fig. 7 into account, the results can be considered as the same. Also, the 3D plot of the leaching efficiency over microwave treatment time and O_2 concentration in Fig. 7 (e) demonstrates this behavior.

The influence of microwave power on the Li LE is huge. As presented in Fig. 7 (d), the Li recovery is 3–3.4 times higher in the case of the 4 times higher power of 1350 W microwave treatment compared to 340 W in the first 3 min. This is in accordance with the mass loss behavior and indicates a much faster temperature increase with higher microwave power, as observed by Zhao et al. (2020), who investigated the temperature profiles of a mix of cathode powder and anthracite at different microwave power. In our case, the higher power leads to a Li LE of 56.4 % after 3 min. A comparable value of 53.3 % is reached with less microwave power after 12 min, which seems proportional to the power increase. To validate and describe the correlation between power, treatment time and temperature mathematically, further data points would be necessary.

As known from conventional thermal treatment and water leaching tests, F and Al are the two main co-extracted elements during the leaching step. This can be confirmed for the treatment with microwaves. Al is dissolved during the water leaching due to the basic pH value of ~10–11 of the Li-containing solution (Bale et al.). F extraction is due to the dissolution of LiF and possibly other F-containing salts, or in the case of incomplete thermally treated material, to the dissociation of $LiPF_6$. Fig. 8 shows the co-extraction of the two elements depending on the microwave power, calculated based on equation (17).

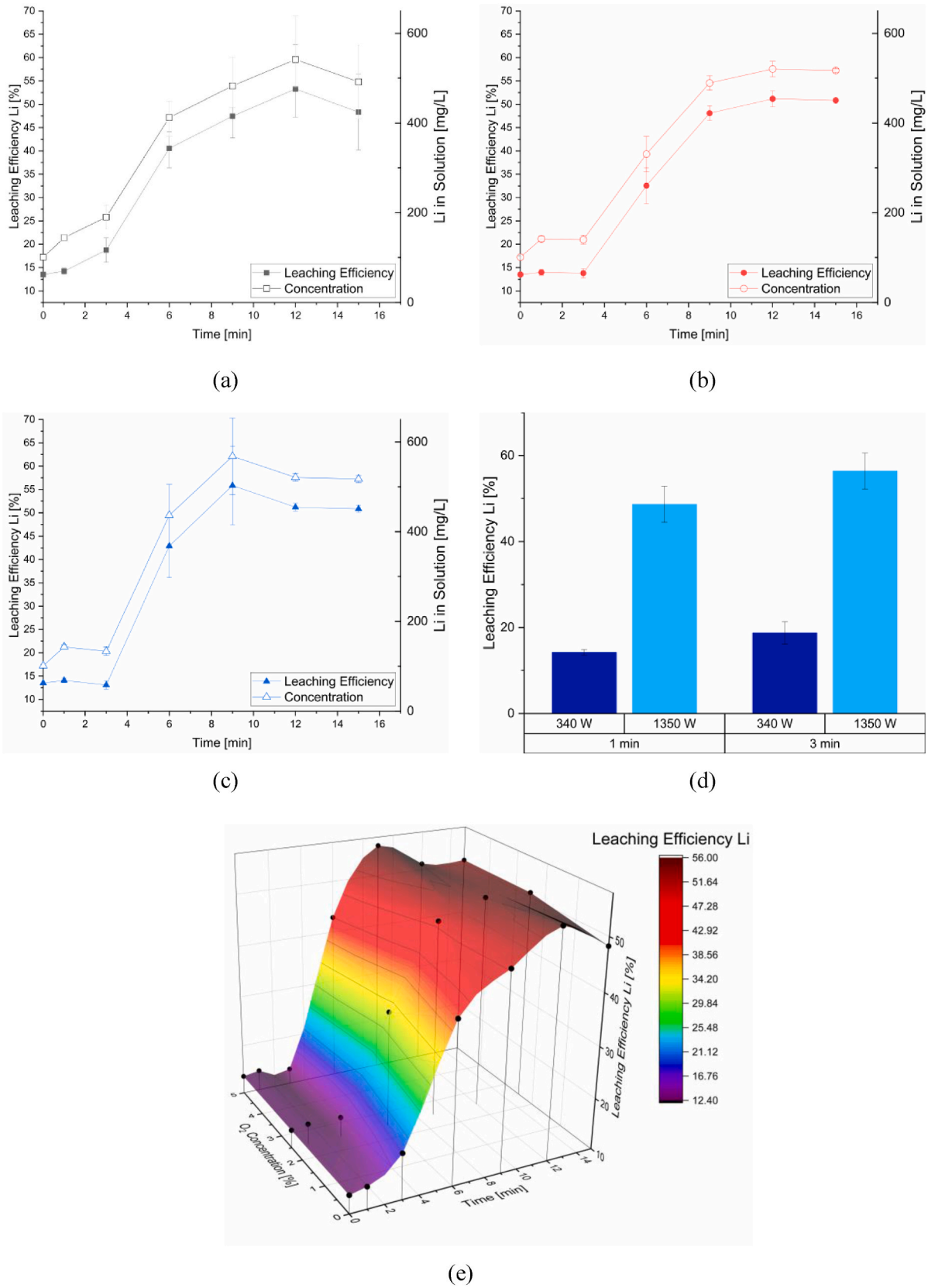

Fig. 7. Leaching efficiency and concentration of Li in solution after water leaching of small-scale microwave treated LIB shredder in dependence of microwave thermal treatment time under (a) Ar and 340 W, (b) Ar with 2.5 % O_2 and 340 W, (c) Ar with 5 % O_2 and 340 W, (d) Ar 340 W compared to Ar 1350 W and (e) 3D plot of leaching efficiency of Li in dependence of treatment time and O2-concentration at 340 W.

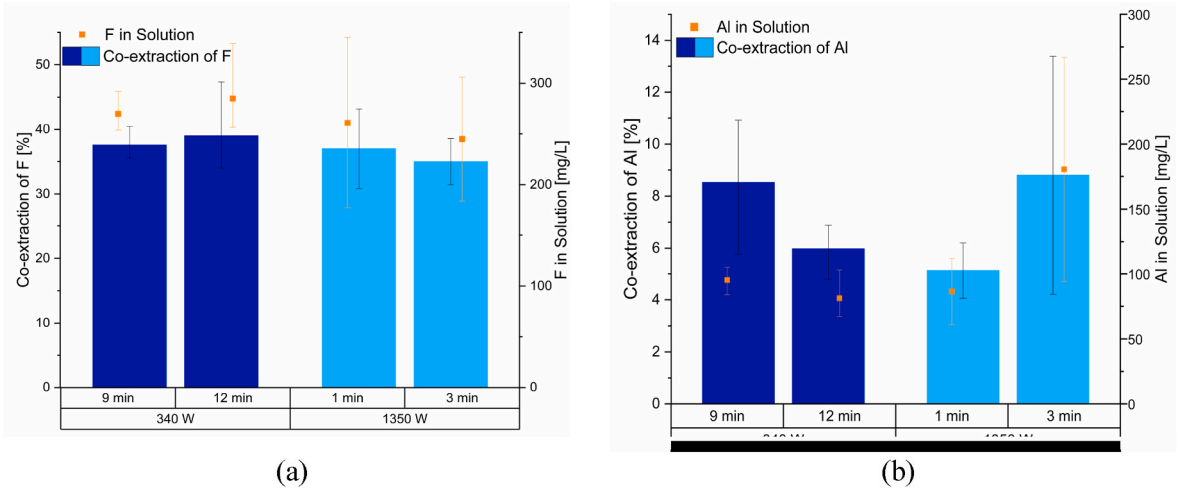

Fig. 8. Concentration of (a) fluorine and (b) aluminum in solution after water leaching in dependence of different microwave treatment times and power under Ar.

$$\text{Co} - \text{Extraction}_{Al\ or\ F} = \frac{m_{Al\ or\ F}\ in\ solution\ [g]}{m_{Al\ or\ F}\ in\ solution\ [g] + m_{Al\ or\ F}\ in\ filtercake\ [g]} \bullet 100\% \quad (17)$$

In this case, no clear trend can be observed. Especially the Al extraction takes place in small proportions of up to 8.8 % and concentrations of 181 mg/L. The deviations between the trials, shown in Fig. 8 (b) can be explained by the inhomogeneities of the input material and the microwave field. For F, the analysis itself is subject to an error of around 10 %. Together with the inhomogeneities described above, this also explains the partly large error bars in Fig. 8 (a). The leaching efficiencies of the two elements are in good accordance with the results achieved in conventional pyrolysis trials with the same material in a previous study (Stallmeister and Friedrich, 2023a), but the concentration in the solution is higher, which is due to a higher Al amount in the fine fraction after the thermal treatment. In conventional pyrolysis of the same material, the Al share in the fraction <500 µm is between 1.8 wt.-% and max. 5.3 wt.-%. In the case of the microwave treatment, Al shares of up to 8.5 wt.-% are detected in the fine fraction. During some trials, hot spots, sparks or plasma were observed at the edges of Al-foils. The interaction with the microwave field also led to partial melting of aluminum, especially at high power and longer holding times. As a result, the Al became brittle and partially oxidized. This in turn leads to the transfer of aluminum into the fine fraction.

3.4. Scaleup of microwave trials and comparison to small microwave and conventional pyrolysis

To investigate the scalability of the microwave thermal treatment process, three trials in a larger microwave reactor were carried out with 120 g of input material. The power and treatment time were set after a series of pre-tests, where the necessary power to reach around 550–600 °C and the treatment time to stabilize the final temperature was tested. This resulted in a power of 6 kW and a treatment time of 14 min. The corresponding temperature curves are given in Figure A 1 in the appendix. The results of the trials and the following water leaching are given in Table 2 in comparison to the small microwave trials and conventional pyrolysis trials with the same shredder material at two different temperatures.

After the microwave treatment, an average weight loss of 14.7 wt.-% was achieved, mainly due to organic removal, which is around 1 wt.-% higher than in the small tests at 0.34 W after 12 min. But it has to be considered that the upward deviation occurring in the small tests amounts to 2.5 %. This is primarily due to the quantity of input material and its wide range of particle size distribution. The results of the water leaching about Li recovery of 55.5 % and the co-extraction of Al with 5.9 % and F with 39.2 % show good agreement between the small-scale tests and the scaleup. To investigate the relation between specific energy supply and the amount of material and its mathematical description, additional trials with a wider parameter set would be necessary.

A difference between the two setups is the resulting black mass phase composition. The XRD pattern of the black mass treated in the large microwave furnace proves a better reduction behavior of the material during the trials. In contrast to the material treated in the small microwave, metallic Ni is detectable and the intensity of the remaining Li-NMC oxide is very low, as can be seen in Fig. 9.

The comparison between microwave and conventional pyrolysis shows a smaller mass loss of 12 % in the conventional trials at 551 °C but similar values for Li and F leaching under the same conditions. In this case, the use of microwaves results in a timesaving of around 1:45 h, respectively 88 %, compared to conventional pyrolysis. The best Li recovery after conventional pyrolysis was reached when the shredder was pyrolyzed at 642 °C and amounts to 62.4 %. In this case, the achieved

Table 2
Comparison of the mass loss and water leaching results between conventional pyrolysis and the two microwave setups.

	Conventional 1 (Stallmeister and Friedrich, 2023a) (200 g)	Conventional 2 (200g) (Stallmeister and Friedrich, 2023a)	Small microwave (10 g)	Large microwave (120 g)
Parameters	551 ± 3.7 °C ~2 h process time	642 ± 3.9 °C ~2.3 h process time	0.34 kW, 12 min process time	535–600 °C, 6 kW, 14 min process time
Mass Loss [wt.-%]	12.0 ± 0.2	15.4 ± 0.5	13.6 + 2.5/-1.6	14.7 -0.6/-1.0
Fraction <500 µm [wt.-%]	52.9 ± 0.4	59.5 ± 3.3	65.1 + 4.2/-2.8	58.3 + 1.6/-1.2
LE Li [%]	54.2 ± 1.3	62.4 ± 0.5	53.3 + 9.6/-6.0	55.5 + 0.3/-0.5
Al-extraction [%]	3.4 ± 0.3	3.6 ± 0.4	6.0 ± 1	5.9 + 0.9/-0.5
F-extraction [%]	39.9 ± 5.6	43.2 ± 3	39.0 + 8/-5	39.2

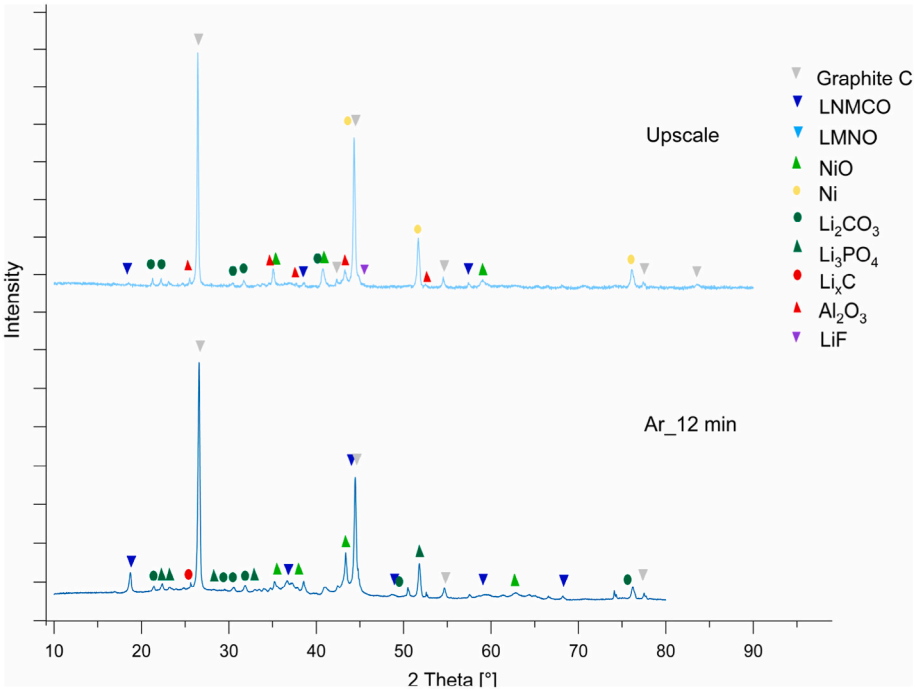

Fig. 9. Comparison of XRD pattern of active mass between small and upscale pyrolysis trial in microwave under Ar.

mass loss is similar to the microwave trials. A further deviation occurs for aluminum extraction, which is around 6 % in the case of microwave treatment and 3.4–3.6 % after conventional pyrolysis. This indicates a stronger attack of the aluminum foils in the microwave and their embrittlement and transition into the active mass as described above. Finally, the leached Al ends up in the Li-salt product, where its share is 2.95 %, see Table A 1 in the appendix. For the battery elements Mn, Ni and Co, the process is very selective, since they were not detected in the final Li-product, mainly consisting of Li_2CO_3.

When comparing these results to the few previously published studies dealing with microwave thermal treatment, lower Li recovery was achieved, but several differences need to be considered. Previous studies were working with manually extracted LMO, LCO and LMNO cathode material milled to <53 µm (Pindar and Dhawan, 2020a, 2020b, 2020c). It is known from conventional thermal treatment and water leaching tests, that this kind of idealized material performs better in the water-based Li recovery but it does not represent industrial material. Moreover, different leaching conditions were chosen in this study. Previous works operated with 20 g/L and with CO_2 injection during the leaching (Pindar and Dhawan, 2020a, 2020b, 2020c), whereas in this work 40 g/L and a process without gas injection was chosen for resource savings.

4. Conclusion

In this study, for the first time, an EoL NMC 622 battery shredder was thermally pre-treated using microwaves. The effects of microwave power, treatment time, oxygen content in the process atmosphere and upscaling on the products black mass and off-gas were investigated and compared to a conventional heating. The conducted experiments demonstrated a strong influence of treatment time and power on the resulting products, whereas the presence of oxygen has just a slight and negative influence. Time and power are correlated to the temperature reached during the trials, which has the biggest influence on the process and its products. Using XRD, it was shown that microwave treatment under an inert atmosphere achieved a similar degree of reduction of the NMC oxides as conventional pyrolysis. In connection with this, the LE of Li in subsequent water leaching of 55.5 % is almost identical to the 54.2 % achieved in conventional pyrolysis at a similar temperature of 551 °C. F also behaves in a similar way to conventional pyrolysis and is leached to 39.2 % (microwave) vs. 39.9 % (conventional). In the frame of off-gas production, the microwave treatment seems even more beneficial than the conventional pyrolysis, as smaller gas-molecules are produced which favors a potential subsequent usage. A further benefit of the microwave is the timesaving of around 88 % and the prospect of relevant energy savings. The study was thus able to show that the transfer of the thermal treatment process of industrial shredder material with included metal fractions and accompanying elements to a microwave heating is possible and promising. There is even potential for improvement, as so far, it has not been possible to guarantee a homogeneous temperature profile across the entire feed material bed, which can lead to the formation of hotspots and an uneven active mass quality. Future work will be focusing on further process optimization regarding homogeneous temperature profiles, different input material fractions, upscaling and continuous processing.

CRediT authorship contribution statement

Christin Stallmeister: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Niklas Mehl:** Writing – review & editing, Validation, Investigation, Formal analysis. **Bernd Friedrich:** Supervision, Project administration, Funding acquisition.

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Declaration of competing interest

There is no conflict of interest between the authors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2025.124616.

Appendix

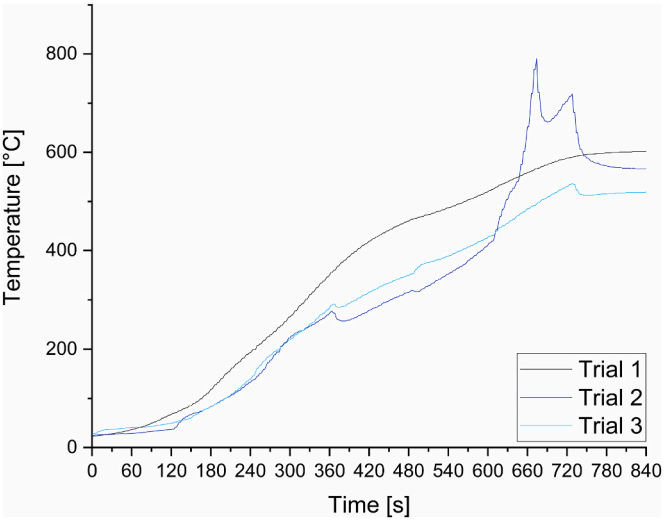

Fig. A 1. Temperature curve during the large microwave trials (peaks in trial 2 are probably due to the coupling of the thermocouple to the microwave field).

Table A 1
Chemical composition of lithium salt in wt.%.

Compound	Li	Al	Cu	Co	Ni	Mn	Ca	Si	P	S	Na
Mean	16.79	2.95	0.00	0.00	0.01	0.00	0.01	0.04	0.00	0.33	0.19

Data availability

Data will be made available on request.

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