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van de Ven, Johannes J.M.M.; Teeuwisse, Patrick J.; Hendrikx, Ruud W.A.; Yang, Yongxiang; Abrahami, Shoshan T.

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#### **RESEARCH ARTICLE**



# Simultaneous Recycling of Spent LiFePO<sub>4</sub> and LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> Li-Ion Batteries Under Mild Leaching Conditions

Johannes J. M. M. van de Ven<sup>1</sup> · Patrick J. Teeuwisse<sup>1</sup> · Ruud W. A. Hendrikx<sup>1</sup> · Yongxiang Yang<sup>1</sup> · Shoshan T. Abrahami<sup>1</sup>

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# Abstract

The growing demand for lithium-ion batteries (LiBs) for energy storage has intensified the need for the critical raw materials (CRMs) they contain, including Li, Co, Ni, and Mn. Consequently, the incentive to recycle LIBs is increasing. However, the commonly used hydrometallurgical processes often have a significant environmental footprint. Moreover, the relatively low value of certain battery materials (e.g., LiFePO<sub>4</sub>, LFP) results in a limited incentive for their recycling. This study explores the simultaneous recycling of LFP with various types of LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub>-containing Black Mass (BM). Leaching studies over time were conducted using stepwise additions of LFP and H<sub>2</sub>O<sub>2</sub> solution (1 vol%) to a mild lixiviant of 0.63 mol/L H<sub>2</sub>SO<sub>4</sub> at 50°C. For pristine NMC 532,  $\pm$ 95% leaching of Li, Ni, Co, and Mn was achieved. The Fe(II) present in LFP, as well as H<sub>2</sub>O<sub>2</sub>, acts as a reductant for the dissolution of Ni, Co, and Mn, later precipitating as FePO<sub>4</sub> to the leaching residue. The Al and Cu present in industrially treated BM further enhanced the dissolution of the transition metals via a catalyzed reaction with the iron from LFP. This resulted in complete leaching of Li, Ni, Co, and Mn for mechanically pre-treated industrial black mass samples. However, the leaching residues acquired from these samples were highly contaminated with graphite. Also, while pyrolysis of the black mass benefits the leaching of Co and Mn, it results in difficulties in subsequent removal of Fe from the pregnant leach solution. The chemical processes and their performance are described in this work.

#### **Graphical Abstract**



Keywords Lithium-ion batteries · Leaching · Hydrometallurgy · LiFePO<sub>4</sub> (LFP) · LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>2</sub>O<sub>2</sub> (NMC) · Recycling

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Extended author information available on the last page of the article

# Introduction

In our current society, lithium-ion batteries (LiBs) are widely used to store electricity, thereby contributing to the energy transition [1]. They are used in many applications, such as electric vehicles (EVs), portable electronics, and stationary energy storage [1]. LIBs contain many elements listed on the EU's critical raw materials (CRMs) list which are essential for their optimal functionality [2, 3]. Wellknown examples of these are Co, Mn, and Li [2, 3]. These elements are mainly present as oxides in the cathode, such as LiCoO<sub>2</sub> (LCO) or LLiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> (NMC) [4]. Hence, they are also known as cathode active materials (CAMs). Due to a high demand and geopolitical concerns, the supply of these CRMs is under pressure, yet they are crucial for the European economy [5–7]. However, the global market for LiBs is projected to grow significantly in the coming years, resulting in the need for more of these CRMs [8]. Also, the LiBs are mostly produced in China, which means most countries will rely on import of these batteries [9]. Therefore, apart from sourcing more of these raw materials, recycling will play a significant role in meeting future demands [10]. Also, landfilling of LiBs can cause harmful substances to leak in the environment, further emphasizing the need for recycling [11].

Although there is a range of possible routes to recycle LiBs, hydrometallurgical processes are emerging as the future choice of technology due to its ability to recover more materials compared to the traditional pyrometallurgy [12]. In hydrometallurgy, materials are selectively dissolved and then purified using aqueous and/or nonaqueous solutions [13]. There are various examples of hydrometallurgical processes that aim to extract and purify Li, Ni, Mn, and Co from LiBs [14–19]. However, these studies still present many limitations. For the case of LiBs, the starting material for the hydrometallurgical process is black mass (BM), a mixture of both anode and cathode containing graphite, metal oxides (Li, Mn, Co, Ni), and impurities such as Fe, Al, and Cu. Acquiring this material requires an extensive initial pre-treatment. In addition, LIBs are a family of different chemistries, leading to a heterogeneous waste stream of which the composition is prone to variations [20, 21]. Hence, there is a need for recycling processes capable to handle this complex waste stream [21].

Before recycling, the Ni, Co, and Mn in the BM are typically present in the + II, + III, or + IV oxidation states [22, 23]. However, to efficiently dissolve these transition metals (TMs) during leaching, they all need to be reduced to the divalent state [24–26]. Therefore, the lixiviant needs to have a reducing nature, resulting in the reaction illustrated in Eq. (1) [24–27]. This can be established by the presence of an acid with reducing capabilities such as HCl [15, 28, 29], or additional reducing agents such as H<sub>2</sub>O<sub>2</sub>, glucose or ascorbic acid [25-27, 30-33]. In the study of Wang et al., 4 mol/L of HCl could both reduce and dissolve the elements in NMC cathode materials [34]. When leached for 60 min at 80 °C and a solid-to-liquid ratio (S/L) of 20 g/L, this resulted in leaching efficiencies exceeding 99.5% for Li, Ni, Co, and Mn. However, HCl comes with the drawback of chlorine gas formation during leaching, as well as high corrosiveness, which can result in damage to equipment [28]. Sattar et al. made use of 2 mol/L H<sub>2</sub>SO<sub>4</sub>, while adding  $H_2O_2$  to create a reducing environment [25]. The experiments were conducted at 50 °C for 3 h, with a S/L of +60 g/L. Without the reducing agent, leaching efficiencies did not exceed 45% for Mn and Co, and around 80% for Li and Ni. However, the addition of 4 vol%  $H_2O_2$ solution increased these values to > 98%. Similar results were found in the systems of Meng et al. and Peng et al. [30, 33], where glucose and ascorbic acid were added as reducing agents, respectively. However, the general drawback is that additional reagents are also accompanied by higher costs and extra indirect emissions. To lower the environmental footprint as well as some economic burdens of the recycling of LiBs, we need to find a way to reduce the consumption of chemicals without introducing any new impurities [35].

$$3LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 12H^{+}_{(aq)} + 3e^{-} \rightarrow 3Li^{+}_{(aq)} + Ni^{2+}_{(aq)} + Mn^{2+}_{(aq)} + Co^{2+}_{(aq)} + 6H_2O_{(l)}$$
(1)

LiFePO<sub>4</sub> (LFP) batteries are gaining popularity due to its high thermal and electrochemical stability, as well as a lower material cost [36, 37]. Due to its chemical nature, it can also be used as a reducing agent in recycling, instead of adding additional reducing compounds [38-40]. After its dissolution in  $H_2SO_4$  (Eq. (2)), the present Fe<sup>2+</sup> can be oxidized, hence releasing electrons (Eq. (3)) [38-40]. Jiang et al. showed that spent LiFePO<sub>4</sub> can be used as reagent in the leaching of LCO, which resulted in lower consumption of chemicals [38]. An acid concentration of only 0.5 mol/L ( $H_2SO_4$ ) was used, with a leaching time of 20 min at 50 °C and a total solid-to-liquid ratio of 30 g/L. These conditions resulted in over 99% extraction of Li, Fe, and  $PO_4^{3-}$ , and 92.4% for Co. Also, no additional reagents such as  $H_2O_2$  were necessary. The Fe<sup>3+</sup> could be removed by pH adjustment, due to the limited solubility of FePO<sub>4</sub> above pH 2 [38]. Similar findings were presented by Chen et Al. [39] and Liu et Al. [40], who used spent NMC-type cathode materials instead of LCO. Chen et Al. found that

a lixiviant composed of  $H_3PO_4$  (2 mol/L) and 4 vol%  $H_2O_2$  solution succeeded in leaching the Li, Co, Ni, and Mn from the waste cathode materials when reacting for 60 h at 60 °C and an S/L of 50 g/L. The Fe from LFP was left behind in the residue. They also showed the possibility of subsequent purification and regeneration of the cathode materials [39]. Liu et Al. found that with 0.25 mol/L  $H_2SO_4$  and an S/L of 32 g/L while leaching for 4 h at 80 °C also resulted in complete dissolution of Li, Co, Ni, and Mn. They even added 5 g/L of FePO<sub>4</sub>\*2H<sub>2</sub>O seed crystals during leaching, which resulted in simultaneous recrystallization of Fe from the PLS as phosphate.

$$LiFePO_{4(s)} + 2H^{+}_{(aq)} \rightarrow Li^{+}_{(aq)} + Fe^{2+}_{(aq)} + H_2PO^{2-}_{4(aq)}$$
 (2)

$$Fe_{(aq)}^{2+} \to Fe_{(aq)}^{3+} + e^{-}$$
 (3)

Using LFP to recycle other spent cathode materials is an elegant way to reduce the chemical consumption of the recycling process while increasing the recycling rates of both types of batteries, especially with simultaneous recovery of cathode materials. However, these proof-of-concept studies do not capture the complexity of the current industrial battery waste stream, especially coming from e-waste [21]. Consequently, the challenges arising from the heterogeneous composition of industrial battery waste are not addressed [41]. For example, the impact of impurities that are often present in black mass, such as graphite, Al and Cu, on the leaching and purification are not discussed [42].

Therefore, in this paper, we focus on recycling of various LiBs waste streams available on the current market. By studying the effect of varying waste composition and pretreatment on the leaching using LFP from spent LiBs, the following research question can be answered: Is it possible to leach a mixed LiB-waste stream aided by LFP, with less need of chemicals and limited additional contamination? To answer this question, we designed and tested an experiment that aimed for full dissolution of Li, Co, Ni, and Mn and monitored the reactions over time. This experimental procedure was then applied to 5 different types of battery waste, ranging from pristine NMC 532 to industrially pre-treated black masses. Next, we analyzed the leaching residues to highlight the impact of impurities from industrial LiB-waste. Following leaching, we used pH adjustment to selectively remove the Fe introduced by LFP addition from the pregnant leach solution (PLS). It was precipitated as FePO<sub>4</sub>, which is also a precursor in the synthesis of new LiFePO<sub>4</sub>

# **Materials and Methods**

#### **Battery Materials**

Within this study, we distinguish the terms cathode active material (CAM) and black mass (BM). CAMs are mixed oxides of Li, Co, Ni, and Mn, directly purchased from a manufacturer or manually removed from a battery. The term black mass (BM) is used for the combination of CAMs with impurities, retrieved via industrial pre-treatment. Industrial pre-treatment includes steps, such as shredding, magnetic separation, milling, and sieving.

In the leaching experiments, three types of battery products were used. The first material is a CAM with the chemical formula LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub> (High power Li-ion Battery Cathode Application, Nanographi) and is called NMC 532. Two other samples were manually prepared from spent LiBs, originating from end-of-life (EoL) consumer electronics. One of them is a material similar to the pristine sample, so it is called "spent NMC 532." The LiFePO<sub>4</sub> (LFP) used in this study is also retrieved in this manner. To acquire these materials, pouch-type battery cells were removed from their respective devices and discharged in a 10% K<sub>2</sub>CO<sub>2</sub> (>99.0%, Sigma-Aldrich) solution for 24 h. Then, the cells were opened with a box cutter. This revealed a roll of cathode, anode, and separator, which was removed and unrolled. The cathode foil was separated, since it contains the active materials used in this study. To liberate the cathode material from the aluminum foil, the cathode was cut into pieces of approximately 2 by 2 cm. These pieces were submerged in N-methyl-pyrrolidone (NMP, 99%, extra pure, thermo scientific) at 80 °C with ultrasonification to dissolve the binder. The slurry of NMP and cathode material was then allowed to settle for at least 24 h, after which it was decanted, and the remaining solvent was dried. This left behind CAMs with a relatively low amount of impurities. Thirdly, various BMs from industry were used in this research. The composition of all CAMs and BMs together with their abbreviation is listed in Table 1.

#### **Characterization Techniques**

The present phases in the battery materials, as well as the leaching residues and FePO<sub>4</sub> precipitates, were characterized by X-ray diffraction (XRD) analysis. The analysis was carried out with a Bruker D8 Advance diffractometer with Bragg–Brentano geometry and a Lynxeye position sensitive detector, using Cu K $\alpha$  radiation. The 2 $\theta$  range was 10–110°, with a step size of 0.04° and a counting time of 2 s per step. To analyze the data, the Bruker software DiffracSuite.EVA vs 7.1 and Profex BGMN 5.2 were used. Table 1Composition (wt%) ofall CAMs and BMs used in thisstudy

Abbreviation	Li	Со	Ni	Mn	Al	Fe	Cu	PO <sub>4</sub> <sup>3-</sup>	Note		
NMC 532	7.8	11.7	31.0	16.4	0.0	0.0	0.0	_	Pristine NMC 532		
Spent NMC 532	5.2	11.5	28.5	15.4	0.4	0.0	0.0	_	NMC 532 from spent LiBs		
LFP	4.0	-	-	-	0.3	32.6	0.0	52.2	LFP form spent LiBs		
BM P	4.2	17.8	12.0	4.5	2.8	0.4	2.1	*	Industrial BM, Pyrolyzed		
BM M	3.3	6.8	16.7	6.7	0.5	1.1	1.0	*	Industrial BM, mechanical**		
BM M+	4.5	7.9	22.0	8.0	1.3	0.9	3.0	*	Industrial BM, mechanical***		

\*For industrial BMs, the P from LFP batteries and P from electrolyte components could not be differentiated, and therefore was not included

\*\*Discharged LiBs, shredded, magnetic separation and sieving, \*\*\*BM M with extra milling and sieving step

To determine the elemental composition of the CAMs and BMs, they were analyzed with ICP-OES. Therefore, the samples were digested with aqua regia for complete dissolution. To account for the heterogeneity, each sample was analyzed at least three times, or at least four times when a high variance was seen. One gram of battery material was dissolved in 100 mL of aqua regia. This solution was prepared by combining 25 mL of HNO<sub>3</sub> (65%, VWR chemicals) with 75 mL HCl (37%, Merck). The digestion was carried out in a triple necked round bottom flask with reflux cooler, at 70 °C for 5 h, while stirring at 500 rpm. After digestion, the solid residue was separated through a Whatman 595  $\frac{1}{2}$  folded filter paper, and the solution was diluted to 1L using a volumetric flask at 20 °C. A sample of 0.5 mL from this solution was sent to ICP-OES analysis.

ICP-OES analysis was carried out using a Spectro Arcos-EOP-device with Modified Lichte nebulizer and mini cyclon spray chamber. For verification of complete dissolution of all metals after aqua regia digestion, the residue was analyzed to check any remaining residual metals with a Jeol JSM-IT100 scanning electron microscopy (SEM) in combination with energy dispersive X-ray (EDX) analysis. A small amount of the residue was applied on a piece of carbon tape and placed on the sample holder.

#### Leaching

For the extraction of Li, Ni, Co, and Mn from the black mass, a lab-scale leaching setup with a 500-mL triple necked round bottom flask was used as shown in the supplementary information (Fig. S1). The lixiviant had a total volume of 100 mL and contained  $H_2SO_4$  (95.0–97.0%, Sigma-Aldrich), diluted in Milli-Q water. The acid concentration was determined based on literature and preliminary experiments, and was 0.63 mol/L. 1 vol% of  $H_2O_2$  (30%, Sigma-Aldrich) was added after 90 minutes of leaching. The leaching was carried out for 2 h while stirring at 400 rpm with a magnetic stirring bar. At the end of the reaction, the slurry was filtered through a Cytiva ME 25 membrane filter with 0.45 µm pore size. The

residue was dried (50 °C, 8 h) and weighed, and the PLS was collected for further study on Fe precipitation. In one final leaching experiment with a lixiviant of 500 mL, a 1-L triple necked round bottom flask was used.

For the leaching experiments, monitoring the reactions over time was required. A syringe was used to extract 0.5 mL of the leaching system every 15 min. In order to separate the remaining solids, this slurry was filtered through a syringe filter (Chromafil Xtra PFTE-45/25), after which 0.1 mL was submitted to inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

To compare the performance of different leaching experiments, the leaching efficiency ( $\eta_L$ ) was calculated according to Eq. (4). In this formula,  $m_f^x$  represents the initial mass of element *x* in the feed. This was determined from aqua regia digestion of the sample in triplicates and subsequent ICP-OES analysis.  $m_{PLS}^x$  represents the mass of element *x* present in the pregnant leach solution (PLS) after leaching. This was determined by ICP-OES analysis of the PLS.

$$\eta_L = \frac{m_{PLS}^*}{m_f^*} * 100\%$$
(4)

# **Precipitation Stripping of Fe**

After filtration of the residue, the PLS was allowed to cool down for roughly 15 min. Then, its pH was measured, after which it was increased stepwise to 1.6, 2 and eventually 3 by the addition of a 1 mol/L NaOH solution. To correct the concentrations of the metals in the PLS, it was weighed before neutralization, as well as after reaching the aforementioned pH values. At each dedicated pH value, a sample of 1 mL was taken with a syringe and filtered through a syringe filter (Chromafil Xtra PFTE-45/25). This was submitted to ICP-OES-analysis to calculate the percentage of remaining elements in the PLS. After reaching pH 3, the precipitates were filtered using a Whatman 595 ½ folded filter paper. The precipitates were then dried at 50 °C for 8 h. In the last leaching experiment with 500 mL PLS, this approach was altered slightly. A 2 mol/L LiOH solution was used for neutralization. The resulting precipitate from this experiment was, after drying, also submitted to heat treatment in order to manifest crystallization. This was done at 600 °C for 2 h under N<sub>2</sub> atmosphere. Hence, the sample could be characterized by XRD analysis.

# **Results and Discussion**

Within this study, two types of experiments were conducted. Firstly, a leaching experiment was set up in which different battery materials were allowed to dissolve under mild leaching conditions while studying the reaction over time. The residues were then characterized to evaluate their purity, indicating of potential reuse in LiBs. Secondly, the iron that originated from the LFP was removed from the PLS by precipitation. The efficiency of the iron removal as well as the purity of the resulting precipitate was evaluated.

# Influence of Black Mass Composition on Leaching with LFP

The reducing capability of Fe(II) in LFP for reductive acid leaching has been demonstrated in literature [38–40]. Here, we test the feasibility of this leaching process for industrial LiBs waste recycling. An LFP:NMC ratio of 1:1 was chosen for this study. To ensure complete dissolution, 1 vol% of  $H_2O_2$  solution is added during the last phase of leaching. To show the individual impact of LFP and H<sub>2</sub>O<sub>2</sub> on leaching, they were added at different stages; LFP was added after 30 min, while  $H_2O_2$  was added after 90 min of reaction time. Then, the solution was left to react further for 30 more minutes, for a total leaching time of 2 h. To monitor the reaction progress, a sample was taken every 15 min. It was expected that LFP greatly benefits the dissolution of Ni, Co, and Mn. This should be seen in the shape of a sharp increase in leaching efficiency at the 45-min mark, 15 min after its addition. The addition of H<sub>2</sub>O<sub>2</sub> at 90 min should result in an increased leaching efficiency of all metals at 105 and 120 min. After conducting this experiment on the pristine NMC532, it was also applied to the other BM samples, the compositions of which are found in Table 1.

Figure 1 shows the results for the pristine NMC 532. It can be seen that the leaching efficiency of Ni, Co, and Mn after 30 min is rather low, reaching around 37%, while Li is extracted for 75%. After the addition of LFP to the mixture, a sharp increase in leaching efficiency can be seen, after only 15 min of reaction time. Also, even though the feed concentration of Li almost doubles upon the addition of LFP, its leaching efficiency still increases to 89%. This indicates a fast dissolution of LFP, as well as an efficient reaction



**Fig. 1** Dependence of the leaching efficiency of Li, Co, Ni, Mn, Fe, and  $PO_4^{3-}$  on time, as well as the presence of LFP and  $H_2O_2$ . LFP (34 g/L) and  $H_2O_2$  (1 vol%) were added to the leaching system at 30 and 90 min, respectively. The S/L of NMC was 20 g/L

between Fe<sup>2+</sup> and the TMs in NMC. After the sharp initial increase, the leaching efficiency continues to climb, albeit more gradually. A total reaction time of 90 min, of which 60 min are in the presence of LFP, results in 99% extraction of Li and around 94% for the TMs. Furthermore, the addition of H<sub>2</sub>O<sub>2</sub> at the end further enhances the dissolution of Li, Co, Ni, and Mn to roughly 98%, which is expected since the reducing ability of H<sub>2</sub>O<sub>2</sub> is well known. Fortunately, the extraction of the possibly contaminating iron is limited to 33%, with a concentration of 3.7 g/L in the PLS. This is a result of the limited solubility of FePO<sub>4</sub> [38, 39]. After Fe<sup>2+</sup> is oxidized (Eq. (3)), it largely precipitates as FePO<sub>4</sub>, as indicated by Eq. (5) [38].

$$Fe^{3+}_{(aq)} + H_2PO^-_{4(aq)} \to FePO_{4(s)} + 2H^+_{(aq)}$$
 (5)

These results are in line with our expectation. Without the presence of LFP, the Ni, Mn, and Co at higher oxidation states are not dissolved, resulting in the low leaching efficiency of approximately 35%. The presence of LFP from the 30-min mark onwards provides Fe(II) as a reducing agent, thereby enhancing the leaching efficiencies. Li dissolves relatively easily, resulting in 75% leaching without LFP. The efficient leaching of lithium is attributed to the good solubility of Li<sup>+</sup>, the lower binding energy between Li and O compared to the other metals and the fact that it does not need to be reduced before dissolution [26, 42].

This leaching process was repeated on the other BMs which are included in Table 1. The results for BM P and BM M + can be found in Fig. 2. The spent NMC 532 and BM M show similar results compared to the pristine NMC 532 (Fig. 1) and BM M + (Fig. 2a), and are therefore included in

**Fig. 2** Dependence of the leaching efficiency of Li, Co, Ni, Mn, Cu, Fe, Al, and  $PO_4^{3-}$  on time, as well as the presence of LFP and  $H_2O_2$ , for two different black mass samples; **a** BM M+(30.5 g/L), **b** BM P (33.5 g/L). LFP (34 g/L) and  $H_2O_2$  (1 vol%) were added to the leaching system at 30 and 90 min, respectively



the supplementary information (Fig. S2). For each experiment, the combined amount of Ni, Co, and Mn in the feed was kept constant at 0.2 mol, which was based on the experiment in Fig. 1. This was done to avoid a lower feed concentration of the target metals, which is a result of dilution by insoluble components, such as graphite in industrial BM samples. As a result, the S/L ratio varies between the leaching experiments of the different BM samples, being between 54 and 73 g/L total (LFP + NMC-type waste). Also, leaching efficiency sometimes exceeds 100%. This is of course not possible in practice and is a result of experimental uncertainties and the inherent heterogeneous nature of the samples.

When comparing the results of all the analyzed BM samples (Figs. 2 and S2), similar trends emerge. The addition of either LFP or  $H_2O_2$  results in a better leaching performance, albeit to a higher or lower extent. However, the various treatments applied to BMs as well as the different impurities they contain result in more complex leaching systems yielding different results.

Figure 2a depicts the results for BM M+. The leaching behavior is similar compared to the pristine NMC 532, but important differences are also present. After 30 min, Ni, Co, and Mn are extracted for around 50%, whereas Li reached 93%. At this point, the Cu and Al are extracted for 74%. When LFP is added, it first dissolves according to Eq. (2). After 30 min of Fe<sup>2+</sup> being present, the leaching of the Li, Ni, Co, and Mn is at 100% (Eqs. (1 and 3)). When Fe<sup>2+</sup> is oxidized to Fe<sup>3+</sup>, it mostly precipitates again as iron phosphate Eq. (5), which can be seen by its maximum leaching efficiency of 38% as well as by XRD analysis of the leaching residue (Fig. 4 in Sect. "Precipitation Stripping of Fe").

Since Al is also present in the LFP, its feed concentration increased at 30 min from 0.4 to 0.5 g/L. This results in a seemingly lower leaching efficiency after 45 min, although its total concentration in the PLS increases (0.30 g/L at 30 min, 0.34 g/L at 45 min). Al reacts slower, and its dissolution in sulfuric acid is already described in literature Eq. (6) [43]. However, both the dissolution of Al and Cu are facilitated by the presence of Fe<sup>3+</sup> in the solution. The latter is produced from the oxidation of  $Fe^{2+}$  originating from LFP. The reduction of Al and Cu can be found in Eqs. (7 and 8), respectively [43]. As a consequence, the dissolution of Al and Cu leads to reduction of Ni, Co, and Mn, through catalysis by the  $Fe^{3+}/Fe^{2+}$ -couple. This explains the higher leaching efficiency of Ni, Co, and Mn for the industrial BM M+(Fig. 2a), compared to pristine NMC 532 (Fig. 1). The latter has no reducing capacity that is generated by the dissolution of Al and Cu. It is important to note that the Cu is already partially extracted (73%) before LFP addition. This is most likely the result of Fe impurities present in the industrially processed feed, which can also reduce the Co, Ni, and Mn and hence start catalyzing the dissolution of Cu and Al. As a result, the addition of  $H_2O_2$  is not needed in this case. The dissolution of Al, Fe, and  $PO_4^{3-}$  after 120 min total reaction time reaches 77, 37, and 41%, respectively.

$$2Al_{(s)} + 3H_2SO_{4(aq)} \to 2Al_{(aq)}^{3+} + 3SO_{4(aq)}^{2-} + 3H_{2(g)}$$
(6)

$$Al_{(s)} + 3Fe_{(aq)}^{3+} \to Al_{(aq)}^{3+} + 3Fe_{(aq)}^{2+}$$
(7)

$$Cu_{(s)} + 2Fe^{3+}_{(aq)} \to Cu^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$$
(8)

Figure 2b depicts the leaching process of industrial BM P. The dissolution behavior of this BM differs significantly from all the other samples. Under the applied mild chemical conditions, Li, Mn, and Co are dissolved quickly, without any additional reducing agent. They reach leaching efficiencies of 102, 99, and 90%, respectively, which is very high compared to the other samples. This is most probably a result of the high temperature treatment the BM received. The industrial samples also contain graphite from the anode of LiBs. At high temperature, this can cause pre-reduction of the TMs [44]. Therefore, the reaction according to Eq. (1) has already been completed to a large extent before the leaching process. Ni, on the other hand, is only extracted for 42%. According to XRD analysis (Fig. S4), it is present as both NiO and metallic Ni. Hence, one part is already soluble (NiO) and another part needs to be oxidized (Ni), for which no reagents are present during the first 30 min.

Addition of LFP does not have a significant impact on the dissolution of Ni, Co, and Mn. An increase of Li in the feed from 1.4 to 2.8 g/L leads to a lower leaching efficiency for this element (83% at 45 min), although the concentration in solution increases from 1.4 to 2.3 g/L. At 90 min, Li, Co, Mn, and Ni are extracted for 96, 95, 100, and 54%, respectively. It is unclear whether additional reaction time or the presence of LFP is causing this gradual increase in dissolution. Distinct behavior of Fe and  $PO_4^{3-}$  is also seen. The extraction of these entities is far greater than in the other experiments, reaching around 89% at maximum. This indicates that the Fe(II) from the LFP dissolves well Eq. (2). However, the target metals are already dissolved due to the pre-reduction during pyrolysis, and Fe<sup>2+</sup> is not required to act as a reducing agent. Thus, it remains in solution and does not turn into the less soluble Fe<sup>3+</sup> (Eq. (3)), hampering precipitation as FePO<sub>4</sub> (Eq. (5)).

After adding  $H_2O_2$  and reacting for another 30 min, the Ni extraction eventually reaches 78%. This increase is the result of metallic Ni being oxidized by  $H_2O_2$ , which can also act as an oxidizing agent according to Eq. (9) [45]. The addition of  $H_2O_2$  also results in a small amount of oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> Eq. (10) [46]. This has several consequences for the leaching system. Firstly, a small portion of the Fe and  $PO_4^{3+}$  precipitates, reducing their leaching efficiencies to around 85%. Secondly, the presence of Fe<sup>3+</sup> kickstarts the dissolution of Cu according to Eq. (8).

It is important to note that  $H_2O_2$  can engage in many side reactions, especially after forming radicals in combination with Fe<sup>3+</sup>-ions, such as shown in Eq. (11) [43, 46]. To verify that the Cu dissolution is truly a result of catalysis by Fe<sup>3+</sup>/ Fe<sup>2+</sup>, this experiment was repeated with the addition of pristine NMC 532 after 90 min, instead of  $H_2O_2$  (Fig. S3). The added CAMs should be able to react with the remaining Fe<sup>2+</sup>-ions in solution, hence forming Fe<sup>3+</sup> Eqs. (1 and 3), without the risk of side reactions. Subsequently, the Cu could then be dissolved according to Eq. (8). It can be seen in these results that the leaching efficiency of Cu increases to 29% upon addition of the pristine NMC 532. This confirms that the dissolution of Cu is indeed the result of its oxidation by Fe<sup>3+</sup>, which was generated from the reaction of Fe<sup>2+</sup> with the pristine NMC 532.

$$H_2 O_{2(aq)} + 2H^+_{(aq)} + Ni_{(s)} \to 2H_2 O_{(l)} + Ni^{2+}_{(aq)}(E^0 = 2.02V)$$
(9)

$$H_2 O_{2(aq)} + F e_{(aq)}^{2+} \to O H_{(aq)}^- + O H_{(aq)}^- + F e_{(aq)}^{3+}$$
(10)

$$H_2 O_{2(aq)} + F e_{(aq)}^{3+} \to H_{(aq)}^+ + H O_{2(aq)}^{\cdot} + F e_{(aq)}^{2+}$$
(11)

Fig. S2a shows the leaching results for the spent NMC 532. The trend looks very similar to the one seen for the pristine NMC 532 (Fig. 1), and the results and discussion

are therefore part of the supplementary information. It is interesting to note, however, that this sample requires more reducing agents in the form of LFP and  $H_2O_2$  compared to the pristine 532. This is presumably the result of TMs being present in compounds formed by side reactions during the use phase of these LiBs, as we previously have shown [21].

Fig. S2b shows the leaching behavior of BM M, which looks similar to the behavior of BM M+. The difference rises from the higher amount of graphite in BM M, resulting in a higher S/L ratio (38.4 compared to 30.5 g/L). Hence, the dissolution goes slower. A detailed description can be found in the supplementary information. The leaching behavior of Li is however noteworthy, since it does not reach full dissolution. This is likely because of its presence in the relatively large amount of graphite, which originates from the anodes in LiBs. These particles do not dissolve, resulting in the need for Li to migrate out of these particles. Hence, the leaching efficiency of Li is lower.

Overall, the leaching trends of these BM samples are similar. The addition of LFP greatly improves the dissolution of Ni, Co, and Mn and also benefits the dissolution of Li. However, samples such as the spent NMC 532 have a higher need for additional reducing agent. According to literature, this is largely the result of the oxidation state of the TMs in the BM, which are dependent on side reactions of the CAMs during use of the batteries [21]. Also, the Al and Cu which are present in industrial black mass samples have reducing capabilities, if catalyzed by  $Fe^{3+}/Fe^{2+}$ . When these elements were not present, additional  $H_2O_2$  was needed to complete dissolution. Since it is usual for industrially pre-treated BM to contain Cu and Al impurities, the use of  $H_2O_2$  can be minimized or avoided, reducing the need for additional chemicals in recycling.

#### **Analysis of the Leaching Residues**

Besides the content of the PLS, the purity of the leaching residue is of great importance in hydrometallurgical recycling. Hence, semi-quantitative XRD analysis with Rietveld refinement and ICP-OES analysis were performed on the leaching residues resulting from the experiments presented in Figs. 1, 2 and S2. The results are found in Table 2.

For the experiments using pristine and spent NMC 532, the residues primarily consist of  $\text{FePO}_4$  (>83 wt%) with minimal contamination from graphite, Al ,and Cu ( $\leq 1$  wt%). This low level of impurities can be attributed to the high purity of the starting materials. Pristine NMC 532, purchased directly from a supplier, contains very few impurities that could carry over to the residue. Similarly, the spent NMC 532 was manually liberated from a LiB and the CAMs directly removed from the cathode. Incomplete leaching, however, results in some CAMs still remaining in the residue, as is shown by the larger presence of Li, Ni,

**Table 2** Results of XRDanalysis (FePO4 and Graphite)and ICP-OES analysis (Al,Cu, and Li + Ni + Mn + Co) ofleaching residues, reported inwt%

Figures	BM sample	FePO <sub>4</sub>	Graphite	Al	Cu	Li, Ni, Mn, Co		
1	NMC 532	Main component	<1	0.0	0.0	0.4		
S2a	Spent NMC 532	83	1	0.1	0.0	4.6		
2b	BM P	13	74	2.0	0.8	6.6		
S2b	BM M	72	28	0.0	0.0	0.3		
2a	BM M+	72	28	0.1	0.1	0.1		

Mn, and Co (4.6 wt% total). The small amount of graphite that is present in these cases likely results from the carbon coatings of the CAMs which is applied to improve their conductivity during use [47]. For industrial black mass samples, impurities from other components of the LiB cells persist in the leaching residues. For the pyrolyzed BM, the residue primarily consists of graphite (74 wt%), followed by Al (2 wt%) and Cu (0.8 wt%). This is a result of the low amount of FePO<sub>4</sub> precipitation during leaching, as well as the poor leaching of Al and Cu. There is also a significant amount of elements from the CAMs present (6.6 wt%), as leaching was not complete. In mechanically pre-treated samples, the residue mostly consists of reprecipitated FePO<sub>4</sub> (72 wt%). However, graphite remains a significant contaminate, constituting of 28 wt%. Unlike the pyrolyzed BM, Al and Cu dissolved during leaching, which is why the residue from BM M+contains only 0.1 wt% of Al and Cu.

These results show that when industrial pre-treatment is absent, and the BM sample contains few impurities, the resulting residue is of higher purity. Previous studies conclude that such leaching residues are suitable for reuse in batteries, with minimal additional purification steps. However, our findings indicate that this is not possible in practice. Depending on the pre-treatment, Al and Cu often remain in the leaching residues and must be removed before FePO<sub>4</sub> can be repurposed. Moreover, the recovered FePO<sub>4</sub> is amorphous, so it would need to be recrystallized before being used in new LiBs. Apart from that, there is significant contamination by graphite. As the primary anode active material, graphite is always present in LiBs, and will inevitably contaminate the leaching residues unless completely removed during pre-treatment. While the removal of graphite has been studied by methods such as froth flotation, implementing this step in a practical and economically viable manner remains challenging [48]. Therefore, it is essential to address the presence of these impurities to ensure residue quality and viability for reuse.

# **Precipitation Stripping of Fe**

As is seen in the previous sections, the Fe(II) present in LFP is able to act as a reducing agent in the leaching of various NMC-based black mass samples. However, one very important aspect still needs to be studied; the use of LFP as a reducing agent should not be accompanied by the introduction of additional impurities. Therefore, the removal of Fe from the PLS is investigated. This was done by increasing the pH of the PLS by the addition of NaOH to precipitate the remaining Fe<sup>3+</sup> as FePO<sub>4</sub> [38]. The precipitation experiment was conducted on all previously reported systems, but most of them yielded similar results to the pristine NMC 532. Therefore, Fig. 3 only depicts the precipitation stripping results for the experiments on the pristine NMC 532 (Fig. 1) and BM P (Fig. 2b). The rest of the results can be found in Figs. S5-S7 in the supplementary materials.

The precipitation stripping from the PLS retrieved after leaching pristine NMC 532 is seen in Fig. 3a. These results show that Li, Co, Ni, and Mn are only slightly removed (around 4% on average) from the PLS during this process. The Fe, however, is completely removed from the PLS at

**Fig. 3** Precipitation stripping of Li, Co, Ni, Mn, Cu, Al, Fe, and  $PO_4^{3-}$ , after leaching of NMC 532 (**a**) and BM P (**b**), by pH adjustment



pH 3. The  $PO_4^{3-}$  follows the same trend as the Fe but is slightly more persistent. The resulting precipitate was dried and submitted to aqua regia digestion and ICP-OES analysis (Table 2). This showed that 8% of the precipitate consists of  $SO_4^{2-}$ . It could be that  $PO_4^{3-}$  is not completely removed because it is partly substituted by  $SO_4^{2-}$  from the lixiviant. Also, a combined 1.3 wt% of Li, Ni, Co, and Mn was found in the precipitate. These elements are not likely to co-crystallize since they do not precipitate at pH 3, but are rather present as physical inclusions in the fast-forming FePO<sub>4</sub> or leftover PLS that is dried together with the precipitate [49–51]. To verify these theories, the precipitate of the next pH-adjustment experiment was washed with demineralized water a few times (± 50 mL total) after filtration.

Figure 3b shows the precipitation of Fe from the PLS acquired after the leaching of BM P, which yields drastically different results. Although the Li, Co, Ni, and Mn are only slightly removed from the PLS (5% average), the removal of Fe is very inefficient. At a pH of 3, 54% of the Fe remains in the solution. This can be attributed to the fact that a large percentage of Fe was not used to reduce any TMs from the BM during leaching (as in Eq. (3)). Therefore, a large portion of the Fe is still present in the divalent state instead of the less soluble trivalent state. This hampers its precipitation stripping by pH adjustment. Precipitation of Cu (12% removed) and Al (38% removed) is also seen. The precipitate was filtered and washed with demineralized water. This resulted in a far lower amount of Li, Ni, Co, and Mn in the FePO<sub>4</sub>-precipitate, being 0.3 wt. % in total (Table 3). This indicates that these elements are most likely not cocrystallized. Also interesting to see is that Al (1.5 wt%) and Cu (0.3 wt%) are not washed out of the precipitate. This indicates that these elements can co-crystallize with, and hence contaminate, the FePO<sub>4</sub>.

In order to research the transformation of LFP to  $FePO_4$ in more detail, a larger experiment with 500 mL PLS using BM M+ was set up. After stripping, the precipitate was calcinated to manifest crystallization, enabling characterization by XRD analysis. Also, it was investigated if pH adjustment with a 2 mol/L LiOH solution worked as well. In this way, the complexity of the PLS does not increase by adding another ion-type. The resulting PLS after Fe removal can be found in Table S1. This shows that Fe is almost completely removed, and only Al and Cu impurities remain. Also, the Li, Ni, Mn, and Co are present in a large amount compared to these other impurities. After heat treatment (600 °C, 2 h,  $N_2$  atmosphere), the precipitate was again submitted to XRD analysis. The diffractograms of LFP before reaction, the leaching residue, and the precipitate are found in Fig. 4. This shows that before leaching, the recovered LFP from spent batteries is indeed mostly LiFePO<sub>4</sub>. In the residue, this is converted to FePO<sub>4</sub>. The calcinated precipitate consists of FePO<sub>4</sub> as well. Hence, it is shown that the LFP added during leaching indeed transforms to FePO<sub>4</sub>. However, this product contains impurities regardless of whether a washing step is applied and would require further purification before it can be reused in a new LiB.

# Conclusions

Our findings demonstrate that the simultaneous recycling of LFP and NMC provides substantial benefits in terms of chemical consumption. At optimal conditions, this approach eliminates the need for an additional reducing agent, enabling an effective dissolution of Ni, Co, and Mn at mild conditions (0.63 M  $H_2SO_4$ , 50 °C) from various battery waste compositions. By repurposing LFP, a waste product with limited economical value, as a reagent, the method not only minimizes chemical usage but also offers a sustainable solution to recycle LFP without requiring prior separation.

LFP acts as an efficient reducing agent in reductive acid leaching by dissolving in  $H_2SO_4$ , releasing Fe<sup>2+</sup>, which facilitates the dissolution of the tri- or tetravalent Ni, Co, and Mn. Key results are as follows:

When leaching *Pristine NMC 532* without any reducing agent, dissolution of Ni, Mn, and Co reached 36% in 30 min. Upon addition of LFP, this increased to about 80% in just 15 min. Leaching of *Spent NMC 532* yielded similar results. *Mechanically pre-treated BM* exhibited slightly higher efficiencies compared to pristine and spent NMC 532, achieving complete leaching within 30 min with LFP. The presence of Cu and Al impurities in this BM enhances the leaching efficiencies of TMs through catalysis with Fe<sup>3+</sup>/ Fe<sup>2+</sup>. Pre-reduction of Ni, Co, and Mn during pyrolysis *in the pyrolyzed BM* resulted in 90–100% leaching efficiencies without any additional reducing agent. Consequently, adding LFP did not significantly affect metals extraction.

Consequently, Fe introduced via LFP can be effectively removed by pH adjustment with NaOH or LiOH, yielding FePO<sub>4</sub> precipitates with minimal losses of Li, Co, Ni,

Table 3Elementalcomposition (wt%) of theresulting precipitates from thepH-adjustment experiment inFig. 3

BM sample	Precipitation study	Washing	Li	Co	Ni	Mn	Al	Fe	Cu	PO <sub>4</sub> <sup>3-</sup>	$SO_4$
NMC 532	Figure 3a	x	0.2	0.2	0.5	0.4	0	22.9	0	35.6	7.7
BM P	Figure 3b	$\checkmark$	0.02	0.1	0.1	0.1	1.5	21.8	0.3	44.8	0.6

It is also indicated whether the precipitates were washed with demineralized water directly after filtration





and Mn (0.3 wt% in total) after washing. Residue analysis revealed differences in impurity levels based on the starting waste composition. Leaching pristine or manually liberated NMC 532 produced residue primarily consisting of FePO<sub>4</sub>, while residue from industrially pre-treated BMs contained up to 74 wt% graphite and smaller amounts (0.1 to 2 wt%) of Al and Cu, necessitating further purification steps. However, challenges remain. In pyrolyzed BM, unutilized Fe<sup>3+</sup> from LFP remains in the PLS at pH 3, complicating PLS purification from iron.

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**Data Availability** The datasets used and/or analyzed during the current study are available at the 4TU Research data repository. https://doi.org/10.4121/de23a97d-b0c7-475a-85fc-b922a7732a15

# Declarations

**Competing Interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Johannes J. M. M. van de Ven<sup>1</sup> · Patrick J. Teeuwisse<sup>1</sup> · Ruud W. A. Hendrikx<sup>1</sup> · Yongxiang Yang<sup>1</sup> · Shoshan T. Abrahami<sup>1</sup>

Shoshan T. Abrahami S.T.Abrahami@tudelft.nl <sup>1</sup> Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands