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Published in:
Separation and Purification Technology

DOI:
10.1016/j.seppur.2021.119903

Published: 15/01/2022

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
The interference of copper, iron and aluminum with hydrogen peroxide and its effects on reductive leaching of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$

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ARTICLE INFO

Keywords:
Li-ion battery (LIB) Leaching Material efficiency Recycling Metallic reducing agents Overconsumption of H$_2$O$_2$

ABSTRACT

Copper and iron are known to be effective alternative reducing agents to H$_2$O$_2$ in Li-ion battery leaching. The aim of this work is to study the effect of added H$_2$O$_2$ on its overconsumption to the side reactions such as oxidation of copper, iron, and aluminum in leaching of NMC 111 active material. The interactions between the reducing agents separately were first investigated ($T=30^\circ$C, $[H_2SO_4]=2$ M, $t=120$ min). Elemental copper was found to be a less efficient reducing agent (78%) compared to aluminum (100%) in terms of Fe$^{3+}$ reduced to Fe$^{2+}$. Nevertheless, copper exhibited much higher rate of iron reduction than aluminum. Additionally, aqueous copper ions were found to cement on aluminum surface and redissolve in the presence of iron, thus acting as the metallic reducing agent. In contrast, in the presence of H$_2$O$_2$ ferrous iron and copper were rapidly oxidized resulting in the consumption of all reducing agents. These effects were confirmed also during the leaching of NMC ($T=30^\circ$C, $[H_2SO_4]=1.5$ M, $t=120$ min), which demonstrated that the leaching efficiency markedly decreased (~63%) in the presence of H$_2$O$_2$ and Cu when compared to H$_2$O$_2$ alone (~78%). Furthermore, results from NMC leaching showed that when copper-iron reductant or H$_2$O$_2$ were added separately, a much higher leaching efficiency was achieved (~66% and ~78%, respectively) in contrast to being added together (~58%).

1. Introduction

Global environmental challenges have steadily moved to the forefront of the political agenda in recent years and as a consequence, increased efforts have been put toward clean electrical energy production and use to reduce the environmental footprint from the fossil fuels [1,2]. As a result of this drive towards electrification, there has been a growing interest in electric vehicles (EVs) that in turn, has required an increase in Li-ion batteries manufacturing. Nevertheless, despite the positive impact of this shift towards more sustainable lifestyles, a large fraction of end-of-life EV batteries are still being stockpiled [3,4] and/or not fully recycled. Due to the scarcity of cobalt mineral resources [5,6], high price and political uncertainties, alternative battery technologies have been developed that focus on either low cobalt or Co-free chemistries and these include NMC (LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$), LiFePO$_4$ and LiMn$_2$O$_4$ [6]. In NMC batteries, the ratio between Ni and Co display a large variation – NMC111 has equal amounts of these elements (LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$), whereas the following chemistries have a higher proportion of Ni compared to Co: NMC622 (LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$) and NMC811 (LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$). Cathode materials also have different microstructure and stability, for instance, LiCoO$_2$, LiNiO$_2$, NMC are layered, whereas LiMn$_2$O$_4$ and LiMn$_6$Ni$_4$O$_{12}$ have a spinel configuration [7]. Typically, NMC type of cathode chemistries have been utilized in power tools, e-bikes as well as EVs due to their higher specific energy densities as well as lower cobalt content [8,9]. In addition, EV batteries mainly utilize NMC and thus it is expected to dominate the future EV market [10] and consequently, the chemistries that require recycling at end-of-life (EoL). Hydrogen peroxide (H$_2$O$_2$) has been a commonly used reducing agent in the leaching of battery waste [11–14]. It readily reacts with LiCoO$_2$ and NMC types of LIB cathode chemistry, for example, NMC111 can be reduced by H$_2$O$_2$ according to Eq. (1) [15]:

$$6LiNi_{0.3}Mn_{0.3}Co_{0.3}O_{2} + 9H_2O + 3H_2 → 2NiSO_4 + 2MnSO_4 + 2CoSO_4 + 3Li_2SO_4 + 3O_2 + 12H_2O$$

(1)

Hydrogen peroxide reduces Co$^{3+}$ and Mn$^{4+}$ from the solid NMC oxide to Co$^{2+}$ and Mn$^{2+}$ in the aqueous form, whereas the overall valence of aqueous Ni (2–), remains the same as in the original NMC oxide [15]. The dissolution mechanism of NMC111 in sulfuric acid

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https://doi.org/10.1016/j.seppur.2021.119903

Received 3 August 2021; Received in revised form 6 October 2021; Accepted 6 October 2021

Available online 9 October 2021

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showed that the valence of Ni and Co during the leaching could vary in the range of 2+ to 4+ and 3+ to 4+, respectively.

It has been previously established by Porvaili et al., 2020 [17] that LiCoO₂ can be reduced by Cu during leaching in acidic sulfate media according to Eq. (2), using dissolved iron as catalyst, i.e. Cu can reduce Fe³⁺ (Eq. (3)) generating Fe²⁺ [18], which then reduces the active material:

\[ 2\text{LiCoO}_2 + Cu + 4\text{H}^+ + 3\text{Fe}^{2+} \rightarrow 2\text{Li}^+ + 2\text{Co}^{2+} + \text{Cu}^{2+} + 2\text{H}_2\text{O} \]

It has also been demonstrated that metallic Fe can participate in the reduction of LiCoO₂ [19,20]. Furthermore, research by Peng et al., 2019 [21] has shown that Al, typically present in battery waste from current collector materials, can act as a reducing agent towards LiCoO₂ through its oxidation by ferric iron (Eq. (4)), in a similar way to that determined for Cu (Eq. (3)).

\[ \text{Cu} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+} \]  (3)

\[ \text{Al} + 3\text{Fe}^{3+} \rightarrow \text{Al}^{3+} + 3\text{Fe}^{2+} \]  (4)

Therefore, it can be hypothesized that NMC can also be dissolved (Eq. (5) and Eq. (7)) in the reductive leaching with the aid of Cu, Al and Fe²⁺/Fe³⁺ according to half reactions Eq. (8), Eq. (10), and Eq. (13). Moreover, the reduction process can theoretically occur via alternative routes, as thermodynamically Al can reduce also H⁺ to H₂ (Eq. (15)) or Cu²⁺ to Cu (Eq. (10)), and H₂ - if formed - Cu²⁺ to Cu or Fe³⁺ to Fe²⁺.

H₂O₂ is a strong oxidant [22] with a standard electrode potential of 1.83 V (Table 1, Eq. (6)), thus it may exhibit the properties of an oxidant in addition to its well-established reductive properties in the Li-ion battery scrap leaching sulfate system (Eq. (9)). The oxidation potential of H₂O₂ is above that of the other metallic components typically present in the leaching system, such as Cu, Al, Fe, Fe²⁺ and Fe³⁺, according to reaction equations (6), (8), (10), (11), (12), (13), therefore it can also oxidize and dissolve the metallic fragments in spent battery black mass.

In the absence of H₂O₂, metallic Cu (from current collectors) and Fe (from casing or iron containing active material) or even Al can act as reductants and will dissolve [17,23,24]. Even after sieving in attempt to remove the impurities, some copper, aluminum, and iron, will remain in the underflow and can benefit the leaching of active materials [24,25]. Even so, these beneficial elemental impurities only comprise a small fraction of black mass and are typically insufficient to fully reduce the active material during leaching, therefore their effect as reductants towards the active material and H₂O₂ are often overlooked. Nevertheless, the effect of metallic components present in larger fractions of black mass has been found to be significant [21,26] although the oxidative properties of H₂O₂ can hinder the utilization of this inherent reductive power, which can cause over consumption of H₂O₂.

So far, the implications of possible H₂O₂ overconsumption as well as safety concerns have been rarely addressed in the scientific literature [26,27], most likely due to a large part of battery recycling studies [28-33] involving the manual dismantling of battery cells as a method to separate the active materials. Selected black mass compositions utilized in LIB recycling research are summarized in Table 2. As can be seen, black mass can still contain a notable amount of Cu, Fe and Al, which can potentially interfere with the H₂O₂ when exposed to leaching.

The research work outlined here aims at acquiring more understanding of the interaction of different reducing agents during the leaching of NMC111 active material. An appropriate selection of the reducing agent, including tracking the dissolution of copper, iron and aluminum throughout leaching, can help prevent the loss of Cu, Al and Fe²⁺ due to the oxidation by H₂O₂. Moreover, reduced peroxide loss to overconsumption can have a significant positive environmental and safety benefits-from lower H₂O₂ demand during leaching, reduced production carbon footprint, transport, and storage-when considered on an industrial scale [24,39,40]. Consequently, this work investigates the interactions of NMC-battery elements with the typical metallic impurities and H₂O₂ in more detail to ascertain the extent of such potential benefits more readily.

2. Materials and methods

2.1. Raw materials

The active material used in leaching was NMC111 powder (<0.5 μm, MSE supplies). Metal content of NMC was Ni 21.2 wt%, Mn 20.3 wt% and Co 19 wt%, determined by total dissolution in aqua regia followed by analysis with atomic absorption spectroscopy (AAS, Thermo Fisher, ICE 3000, USA) using an air-acetylene flame. The particle size and morphology were studied using a scanning electron microscope (SEM, MIRA 3, Tescan, Czech Republic) equipped with an UltraDry Silicon Drift energy-dispersive X-ray spectrometer (EDS) and NSS microanalysis software (Thermo Fisher Scientific, USA). Surface morphology and characteristics of the active material was investigated by placing samples on a sticky carbon tape. The active material was found to be multi-crystalline (Fig. 1A) as its particles comprised of small crystals – in contrast to LCO which has smooth surface [41,42], therefore the dissolution behavior of NMC and LCO could be different in terms of reaction rate constant. Such a surface appearance for the active material agrees with that observed for other NMC type materials utilized [43-45]. Active material was also characterized using X-ray Diffraction (XRD, X’Pert Pro MPD Powder, USA) equipment with a PIXcel1D detector and Cu Kα source along with Fe beta filter without monochromator, was operated at 40 kV, 40 mA. The XRD pattern confirmed the active material to be NMC 111 (Fig. 1B) and the diffractogram correlated with that previously detailed in literature [16,46].

A 5 M stock solution of H₂SO₄ was prepared from sulfuric acid (VWR Chemicals, 95%) and the concentration was confirmed by titration using standardized 2 M NaOH (Merck, Titirup). Subsequent lixiviants (1.5 M and 2 M H₂SO₄) were prepared based on this stock solution. Iron was added as Fe₂(SO₄)₃⋅9H₂O (VWR Chemicals, GPR Reacutop) to either 1.5 M or 2 M H₂SO₄ to achieve a concentration of ~20 g/L of Fe³⁺ in the solution and total iron concentration was confirmed by AAS analysis as the hygroscopic nature of iron(III) sulfate can result in weighing errors. Once prepared, a calculated amount of iron stock solution was added to the lixiviant during its preparation as required. Copper(II) was added as CuSO₄⋅5H₂O (ACS, ≥98%) during the lixiviant preparation stage. Copper powder (<425 μm, Merck, 99.5%) was added concurrently with Al granules (<1 mm, 99.7%, Merck), H₂O₂ (VWR Chemicals, 50%, GPR Reacutop) and the active material.

In order to ascertain the level of Fe²⁺, samples were added to sulfuric-phosphoric acid (85%, VWR Chemicals, AnalR Normapur) media, with diphenylamine (>99%, Riegel-de Haen) used as an indicator and titrated with K₂Cr₂O₇ (>99%, ACS). Hydrogen peroxide was determined using titration in sulfuric acid media with standardized

Table 1 Reduction potentials of the active materials and reducing agents (HSC Chemistry software, version 9.4.1).

<table>
<thead>
<tr>
<th>Half-cell reaction</th>
<th>Reduction potential at 30 °C (V vs. SHE)</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co³⁺ + e⁻ → Co²⁺</td>
<td>1.97</td>
<td>(5)</td>
</tr>
<tr>
<td>H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O</td>
<td>1.83</td>
<td>(6)</td>
</tr>
<tr>
<td>MnO₂ + 2H⁺ + 2e⁻ → Mn²⁺ + H₂O</td>
<td>1.22</td>
<td>(7)</td>
</tr>
<tr>
<td>Fe³⁺ + e⁻ → Fe²⁺</td>
<td>0.66</td>
<td>(8)</td>
</tr>
<tr>
<td>O₂ + 2H⁺ + 2e⁻ → H₂O₂</td>
<td>0.58</td>
<td>(9)</td>
</tr>
<tr>
<td>Cu²⁺ + 2e⁻ → Cu</td>
<td>0.33</td>
<td>(10)</td>
</tr>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>0</td>
<td>(11)</td>
</tr>
<tr>
<td>Fe²⁺ + 2e⁻ → Fe</td>
<td>0.44</td>
<td>(12)</td>
</tr>
<tr>
<td>Al³⁺ + 3e⁻ → Al</td>
<td>1.68</td>
<td>(13)</td>
</tr>
</tbody>
</table>
KMnO₄ (0.05 M, Merck, Titripur) diluted to 0.005 M. Standardized NaOH solution diluted to 0.2 M and methyl orange (Schering AG) indicator were used to establish the level of acidity in samples.

2.2. Leaching experiments

Experiments were carried out in a 500 mL glass round-bottomed reactor with a water jacket for heating (T = 30 °C for all experiments) and the initial lixiviant volume was 400 mL. Initial acidity (H₂SO₄) was 2 M for the leaching in NMC-free experiments and 1.5 M in the presence of NMC. The agitation rate was 300 rpm. Redox potential was measured from within the reactor vessel with an ORP electrode (Pt vs. Ag/AgCl in 3 M KCl salt bridge, Mettler Toledo, USA). Extraction was calculated using Eq. (14):

$$Y_{Me} = \frac{C_{Me} \cdot V_L \cdot x_0}{m_0} \times 100\%$$

where $C_{Me}$ is the concentration of metal (g/L) in solution, $V_L$ is the volume of the leach solution (L), $x_0$ is the fraction of metal in the concentrate (%), and $m_0$ is the initial weight of the concentrate introduced to the leaching reactor (g).

Two leaching series were conducted (Table 3 and Table 4). During the first leaching series the interaction between different reductants was studied. Metal salts were added dissolved in the lixiviant prior to leaching and reductants (Cu, Al and H₂O₂) were added simultaneously with the active material at the beginning of the experiment. Samples (10 mL each) were taken at 5 min, 30 min, 60 min and 120 min, with titration of Fe²⁺ and H₂O₂ was carried out immediately to minimize the oxidation of Fe²⁺ and decomposition of H₂O₂ with each titration repeated three times. The parameters used in the first experimental series are presented in Table 3.

During the second leaching series, the effect of reductants was investigated in the presence of NMC111 (Table 4). Lixiviant (300 mL)
was heated and 12.72 g of the active material was added to the reactor and rinsed into solution with the remaining 100 mL of the lixiviant. The experiment was initiated at a agitation rate of 300 rpm. Samples (6 mL each) were taken at 2 min, 5 min, 10 min, 15 min, 30 min, 60 min, and 120 min. Filtration of the samples was undertaken using syringe filter membranes (0.45 μm, VWR, polyethylene sulfone). Samples taken during leaching were diluted in 0.2 M HNO3, which was prepared from a concentrated stock solution (65%, VWR Chemicals, Analar Normapur).

3. Results and discussion

3.1. Interaction of reducing agents in the absence of NMC

After LIB leaching, the PLS generally contains small concentrations of iron, for example, in the study of Chen et al., 2015 [47] 1.96 g/L of dissolved iron was present in the PLS, whereas 1.29 g/L was found by Peng et al., 2018 [27]. For this work, the Fe(III) concentration was selected as 6 g/L (0.11 M). It is known that ferrous iron (Fe(II)) is an efficient reductant towards active materials in the LIB leaching process [17,23,40]. Iron has a unique property of being present in aqueous sulfuric acid solutions in both divalent (Fe(II)) and trivalent (Fe(III)) states, which enables effective charge transfer of electrons from less noble metals to the active materials, such as LCO and NMC. In this study, the reductive power delivered by different reductants— and combinations thereof— was observed in the form of Fe(II) generated from Fe(III) reduction.

Fig. 2 presents the analyzed reductive power i.e., Fe(II) as a function of leaching time in experiments T1–T5 and T7–T8. It can be seen that the highest reductive power (highest Fe(II) concentration of 5 g/L) with a final redox potential of 353–388 mV vs. Ag/AgCl was achieved in experiments T2 and T3 where copper or copper and aluminum were introduced to the solution. Experiments with aluminum (T1, T4) as well as copper with hydrogen peroxide (T5) resulted in slightly lower reductive power with final Fe(II) concentrations between 4.3 g/L and 2.8 g/L and redox potential between 438 mV and 474 mV vs. Ag/AgCl. Hydrogen peroxide was shown to negatively affect the reduction of Fe(II) in all instances. For example, the amount of Fe(II) generated by Cu was lower in the presence of H2O2 (Fig. 2) in T5 compared to T3 due to the simultaneous oxidation of Cu and Fe(II) as H2O2 was shown to instantly oxidize Fe(II) even in the absence of Cu or Al (Fig. 2, T8) and therefore also the reductive power of Fe(II) in the investigated system was lost (~620 mV vs. Ag/AgCl).

The redox potential of the final leach solution (t = 120 min) was shown to strongly correlate with the endmost ferrous iron concentration; Redox potential decreased with an increasing amount of ferrous iron (Figure S1 and Fig. 2, 350–470 mV). In contrast, the absence of externally added oxidants result in low redox potentials, which is indicative of a high reductive power. The lowest redox potential (~12 mV, Pt vs. Ag/AgCl) was found in T0 (Figure S1) along with H2 gas generation by Al reaction with H2O2. This first experimental series (T-series, Table 3) did not include the final active material to reduce (NMC), therefore it can be suggested that the final ferrous ion concentration reflects well the reductive power of the investigated system.

3.1.1. Copper and aluminum as reductants in the presence of dissolved iron

In the experimental T-series in the absence of NMC (Table 3), the studied concentrations of metallic Cu (5 g/L, 0.08 M) and Al (7.5 g/L, 0.28 M) were selected as being representative of their content in a PLS after leaching of typical LIB black mass (200 g/L or higher) [24]. The reduction of Fe(III) to Fe(II) by elemental copper is shown in Fig. 2, and due to reaction Eq. (3), copper will dissolve (Fig. 3A). Presence of aluminum alone (T0) in 2 M H2SO4 was shown to decrease the acid concentration to 1.99 M, which may indicate H2 generation (Eq. (15)), although aluminum can also be directly oxidized by Fe(II) generating Fe(III) ions in the solution (Fig. 2, T1). Furthermore, when copper was added as Cu2+ to the solution, its concentration decreased in the presence of Al from 5.38 g/L to 5.27 g/L (Fig. 3, T2), while Al3+ concentration in the solution increased (Fig. 3, T2 and T4). This shows that reductive power provided by Al can be at least partially transferred to copper, resulting in copper reduction (i.e. Cu cementation on Al surface) which subsequently can deliver the reductive power to Fe(II). Alternatively, Al can generate H2 gas (Eq. (15)), which potentially can cause (i) loss of reductive power or (ii) hydrogen reduction of more noble species such as Cu2+ or Fe(III).

\[
2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2 \quad \text{(15)}
\]

The study of Vieceli et al., 2021 [37], has previously shown that copper and aluminum extraction in leaching of crushed EV battery in sulfuric acid was low (Al < 20%), which could be caused by copper cementation covering the surface of aluminum. This observation can be explained by the absence of iron i.e. the studied system lacked the catalyzing agent that could support cobalt extraction, while simultaneously dissolving Cu and Al [17,24].

In the current study, the reduction of copper on the Al surface (i.e. cementation) was further confirmed by SEM-EDS imaging. As can be seen in Fig. 4A, a particle of Al is almost completely covered with Cu as indicated by the lighter color (BSE mode).

The image of the surface (Fig. 4B) also reveals that Al dissolves as its surface shows signs of erosion in the location where Cu has reduced and partially redissolved. This observation shows the occurrence of cementation of Cu2+ by Al and the presence of Cu on Al particles was confirmed by EDS as shown by the presence of cemented copper (red spots) within the of Al particle (blue) matrix in Fig. 5. The additional presence of oxygen (purple) and sulfur (red) signals could indicate traces...
of lixiviant and oxidation of the surface.

It was demonstrated in T1 that Al can be oxidized by Fe$^{3+}$ (Fig. 3B) producing Fe$^{2+}$ (Fig. 2) according to Eq. (4). Additionally, Al can suppress the kinetics of Fe$^{3+}$ reduction by Cu in these experimental conditions (Fig. 2, T2 and T3) due to the cementation of Cu. Nevertheless, Cu has higher reduction kinetics of ferric iron compared to Al, thus providing the reductive power to NMC or LCO investigated in terms of ferrous iron concentration (T1, T2 and T3).

### 3.1.2. Hydrogen peroxide interaction with copper, aluminum, and dissolved iron

Recycling processes generally use H$_2$O$_2$ as a reductant for the leaching of battery waste, however, as battery waste contains elements other than active materials (Table 2) these may affect the efficiency of H$_2$O$_2$ as a reductant. Here, the interaction between H$_2$O$_2$ and reductive elements (copper, aluminum and iron) present in the battery waste were investigated (Fig. 2, T5 – T10). H$_2$O$_2$ concentration of 0.13 M, (0.4 vol%) was selected based on the stoichiometric amount of 1.65 H$_2$O$_2$ to Cu (mol/mol, Eq. (16)) to ensure that sufficient peroxide was present to oxidize also both Cu and Fe$^{2+}$. This level is much lower than that found in previous studies, where an excess concentration of H$_2$O$_2$ is used in black mass leaching – typically in the range of 3 to 8 vol% [32,38,48].

Results show that when added in the absence of any metal elements, H$_2$O$_2$ alone did not decompose in 2 M H$_2$SO$_4$ at 30 °C (T10). However, when Cu was introduced into the system (T6), H$_2$O$_2$ was found to rapidly consumed for the oxidation of Cu, which resulted in a 25% dissolution of metallic Cu (Fig. 6., T6 and T3).

For an industrial scale recycling process, such a phenomenon could result in an overconsumption of H$_2$O$_2$ (Fig. 7, T5 and T6) as well as loss of copper as a reductant. It is important to note that copper oxidation in the presence of H$_2$O$_2$ also involves H$^+$ (Eq. (16)), which was confirmed by decrease in the final acid concentration (Figure S1A).

A similar behavior was observed in experiment T8, where H$_2$O$_2$ was found to be rapidly consumed due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$ (Fig. 7). An additional experiment that utilized both elemental copper and ferric ions (Fig. 6, T3) found that approximately 10% less copper was dissolved cf. to the copper only experiment (T6). Moreover, the consumption of H$_2$O$_2$ in the presence of both Cu and Fe$^{3+}$ (T5) was even more rapid as Cu reduced Fe$^{3+}$ to Fe$^{2+}$, while H$_2$O$_2$ concurrently oxidized both Cu and Fe$^{2+}$.

Despite H$_2$O$_2$ acting as an oxidant towards Fe$^{2+}$, peroxide was also shown to be capable of reacting with Fe$^{3+}$ (Fig. 7, T7) as evidenced by
the formation of $\text{H}^+$ ions (Figure S1). From this finding it could be deduced that a Fenton-type reaction [49] may also occur in the lixiviant solution in the presence of Fe$^{3+}$, as outlined in Eq. (17):

$$\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^\bullet$$

(17)

These findings demonstrate that although $\text{H}_2\text{O}_2$ can suppress the reductive power of copper and iron in LIB leaching, the peroxide itself is also subject to enhanced levels of consumption due the presence of these metallic elements. In a LIB leaching process, this is undesirable as it results in the simultaneous loss of all valuable reducing agents, ferrous iron, copper, and hydrogen peroxide. Furthermore, it was also determined that Al can be partially oxidized by $\text{H}_2\text{O}_2$ (Fig. 7, T9), however this effect was found to be negligible compared to that observed for Cu and Fe$^{2+}$/Fe$^{3+}$.

### 3.1.3. Reaction mechanism and current efficiency

The first experimental series (T0 to T9) undertaken confirmed the dominating reduction reaction routes with their interactions in sulfuric acid solution and a schematic summary of the reaction routes is outlined in Fig. 8. In this work it was demonstrated that Al can directly reduce Fe$^{3+}$ to Fe$^{2+}$ (Route a). Additionally, previous [24] and current studies have indicated that in the presence of aqueous copper, the reduction of iron and thus the active material by the cemented copper on aluminum surface is also possible (Route b). In addition, Route c highlights that copper may directly result in Fe$^{3+}$ reduction and that the partial reduction of more noble elements such as Cu$^{2+}$ or Fe$^{3+}$ (Route $d$ and $e$, respectively) by hydrogen is thermodynamically possible in this system as confirmed by the observed hydrogen evolution in the presence of aluminum.

Traditionally, $\text{H}_2\text{O}_2$ has been used as reductant for active materials and black mass leaching (Route $f$), however, this work clearly demonstrates that $\text{H}_2\text{O}_2$ may also simultaneously act as oxidant thereby, decreasing the efficiency of reactions $a$, $b$, $c$, $d$, and $e$.

In order to investigate the current efficiency achieved via different
reaction routes described in Fig. 8, the related reduction efficiencies (current efficiency, $\eta$) were calculated using Eq. (18):

$$\eta = \frac{Fe^{2+}}{Mex} \times \frac{Fe^{3+}}{th} \times 100$$  \hspace{1cm} (18)

where $Fe^{2+}$ is dissolved ferrous iron (M) at $t = 2$ h, $Mex$ is dissolved Cu or Al (M) at $t = 2$ h and $Fe^{3+}$ is a theoretical amount (M) of ferric iron reduced by Cu or Al respectively (Eq. (3) and (4)).

Based on the results, (shown in Fig. 2) it is evident that most of the Cu reductive power is transferred to $Fe^{2+}$, whereas the remaining Cu is oxidized by the oxygen present in the system i.e., reaction Route $c$ proceeds with high current efficiency ($\eta = 78\%$, T3). The losses in the current efficiency may be explained by part of the $Fe^{2+}$ and the rest of Cu oxidation being facilitated by the presence of air within the lixiviant. In the presence of H$_2$O 2, the efficiency of reaction Route $c$ was calculated to reduce from 78% to 67% as the presence of H$_2$O 2 simultaneously oxidizes the $Fe^{2+}$ generated by Cu (T5) resulting in the loss of H$_2$O$_2$, $Fe^{3+}$ and Cu. In the case of Al, the reduction route was shown to occur either directly via $Fe^{3+}/Fe^{2+}$ ($\eta = 100\%$, Route $a$) or stepwise via $Cu^{2+}$ reduction to Cu and $Fe^{2+}/Fe^{3+}$ ($\eta = 107\%$, Route $b$). This indicates that the reductive power of Al is not lost through reaction Route $g$ – even though the dissolution reaction (Eq. (15)) would occur in acid generating H$_2$, it would further deliver its reduction power to the system in the presence of aqueous iron. In the absence of iron, Al produced H$_2$ and the associated redox potential was shown to be the lowest (Figure S1B, T0) among the investigated leaching tests. According to Eq. (15) and the amount of dissolved aluminum (0.0055 M), the theoretical quantity of H$_2$ that could be formed would be 0.008 M. Additionally, the amount of sulfuric acid consumed was experimentally determined to be 0.007–0.01 M, which suggests that the current efficiency of this reaction is ~100%.

Another hypothesis is whether H$_2$ in preference to or in parallel with Al could reduce ferric iron to ferrous (Eq. (19)):

$$2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+$$  \hspace{1cm} (19)

According to Eq. (19), the maximum amount of H$_2$ that could be produced from Al dissolution in sulfuric acid would be equivalent to 0.014 M of ferrous iron, whereas Al alone was found to generate significantly more ferrous iron (0.05 M) according to Eq. (4) and
therefore the reduction of ferric iron by H₂ could be a potential route. Theoretically, hydrogen gas generation could create localized low redox potential conditions that would allow Cu²⁺ to precipitate on Al surface, however Cu was found to only be cemented on the surface of Al particles. Consequently, metallic copper on the Al surface can redissolve and simultaneously reduce the active material via catalysis of the Fe²⁺/Fe³⁺ couple. The true efficiency of H₂O₂ as a reductant can only be assessed in the presence of the active materials due to their direct interactions.

3.2. Reducing agent interaction in LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ leaching

In the second experimental series (L1–L9) the active material (NMC 111) was subjected to a leaching process under similar conditions to series T (interaction between the reducing agents). The leaching behavior of NMC 111 was shown to resemble that of LiCoO₂ as, in general, dissolution was shown to cease after the first 20 min of leaching time. In the case of NMC111, the extraction profiles of Ni, Mn and Co were all found to be similar (Fig. 9A–C, Fig. 10A–C). Also, the reducing agents, H₂O₂ or Cu with Fe²⁺/Fe³⁺ catalyst have been shown to enhance the dissolution of LiCoO₂ and can assist the leaching of NMC according to exp. L2 and L3 (Fig. 9A–C). However, Fe and Cu, elements typically present in minor amounts in black mass, affect also the consumption of H₂O₂ because Fe³⁺ and Cu were rapidly oxidized by H₂O₂ (Fig. 9D) resulting in the loss of all three useful reductants. Hydrogen peroxide itself has a low current efficiency (η = 21%) as the increase in extraction of e.g. Ni – and by inference NMC - was only 38% (Fig. 9A, L1 and L3). Eq. (20) was used to calculate its current efficiency:

\[
\eta = \frac{(\text{H}_2\text{O}_2)_i \times \times 0.38 \times 100}{NMC_i}
\]

where \((\text{H}_2\text{O}_2)_i\) is the added amount of hydrogen peroxide (0.1 M) multiplied by the number of mols of NMC that can be reduced with 1 mol of H₂O₂ (Eq. (1)), \(NMC_i\) is the initial amount of the active material (0.33 M) multiplied by the extraction difference in L1 and L3.

The presence of Cu is associated with overconsumption of H₂O₂, decreasing the extraction of Ni from 76% to 61%, Mn from 80% to 61% and Co from 78% to 63% (exp. L3 and L4). In addition, dissolved ferrous iron was shown to have a larger impact on H₂O₂ consumption as H₂O₂ was shown to oxidize Fe²⁺ instantly, thus decreasing the leaching efficiency of NMC due to the accelerated consumption of both useful reductants H₂O₂ and Fe²⁺. This was shown as decrease metal extraction for Ni from 76% to 53%, Mn from 80% to 61% and Co from 78% to 58% (L3 and L6). Additionally, Fe³⁺ alone (1.2 g/L) was shown to decompose H₂O₂ (Eq. (17)) which can negatively affect the leaching efficiency. This

![Fig. 9. Metal concentration in leaching for (A) Ni, (B) Mn, (C) Co and (D) Cu (T = 30 °C, t = 120 min, [H₂SO₄] = 1.5 M).](image-url)
can be seen in Fig. 9A–C (L3 and L5) where extraction decreases for Ni from 76% to 66%, Mn from 80% to 73% and Co from 78% to 71%. This effect was also observed in the first experimental series as H2O2 concentration decreased from 0.13 M to 0.09 M (Fig. 7, exp. T7).

In the current study, H2O2 was rapidly consumed for the oxidation of Fe2+ as well as reduction of NMC, which resulted in a significant amount of Cu remaining unreacted (Fig. 9D, exp. L6). The oxidation of Cu by H2O2 at the beginning of leaching is pronounced in the presence of dissolved iron (exp. L2 and L6) but Cu oxidation is not as significant as in the absence of dissolved iron (exp. L4). This confirms that H2O2 is rapidly consumed for Fe2+ oxidation preferentially to Cu. The remaining copper continued to reduce NMC through Fe2+/3+ couple (exp. L6, Fig. 9A) after H2O2 has been consumed. The reduction of NMC 111 by Fe2+ can be described in Eq. (21) [34]:

$$6LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2 + 12H_2SO_4 + 6FeSO_4 \rightarrow 2NiSO_4 + 2MnSO_4 + 2CoSO_4 + 3Fe_{2}(SO_4)_3 + 3Li_{2}(SO_4)_3 + 12H_2O \quad (21)$$

Consequently, the reaction of Cu with NMC 111 through Fe2+/3+ catalyst can be summarized in reaction Eq. (22), similar to that of LiCoO2 (Eq. (2)):

$$3LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2 + 6H_2SO_4 + 1.5Cu \xrightarrow{Fe^{2+}/Fe^{3+}} NiSO_4 + MnSO_4 + CoSO_4 + 1.5Li_{2}SO_4 + 1.5CuSO_4 + 6H_2O \quad (22)$$

The reductive performance of H2O2 in the presence of lower amounts of Cu and dissolved iron is illustrated (Fig. 10). In the presence of 0.053 M or 0.1 M of H2O2 (L9 and L7, Fig. 10A–C) the extraction is slightly higher (by ~2%) in the first hour compared to L8, where only Cu and Fe were present. This indicates that H2O2 reduces the active material but oxidizes also Cu and Fe2+ simultaneously. After 1 h, however, the reaction started to cease (L7 and L9, Fig. 10A) because a significant amount of Cu was oxidized by H2O2 (Fig. 10D) and thus less Cu was remaining to react with NMC compared to L8 without added H2O2 where the dissolution of NMC continued at a higher rate after 1 h as more copper was present to react with NMC (Fig. 10D).

This demonstrates that a significant part of H2O2 contributes to the oxidation of Cu and Fe while acting as a reductant towards the active material. Various effects of the reducing agents present together in the beginning of leaching are summarized in Table 5.

From a circular economy point of view, it may be unnecessary to use H2O2 to dissolve the active material and metallic parts of the black mass.
simultaneously as Fe and Cu efficiently dissolve the active material. Instead, peroxide could be used after Fe, Cu and Al have dissolved to complete the reduction of NMC, or additional copper (e.g. current collector scrap) could be introduced to the leaching process to completely reduce the active material. This way the negative effects of combined reducing agents can be avoided or minimized as in the case of H$_2$O$_2$*Cu, complete the reduction of NMC, or additional copper (e.g. current collector scrap) could be used after Fe, Cu and Al have dissolved to present in leaching in aqueous form and react with H$_2$O$_2$.

Alternatively, larger fractions of black mass (e.g. 1250 µm) that contain a significant amount of metallic Cu, Al and Fe could be used in leaching [26]. Ideally, copper and iron only could be used as reducing agents as Al is known to cause challenges in solution purification stage. In order to implement such strategy, Al would have to be separated from coarse fractions and recycled separately together with the active material on its surface, which is not feasible. Moreover, the chemical energy of Cu and catalytic properties of Fe would be effectively employed to reduce the active material thus lower the need to utilize H$_2$O$_2$, or at least minimize its overconsumption. Additionally, the sieving of black mass in attempt to remove Cu, Fe and Al impurities would be unnecessary. Therefore, an improved strategy can be the addition of H$_2$O$_2$ after all metallic components have been dissolved if the aim is to use H$_2$O$_2$ or to add iron sulfate and Cu/Al current collector scrap as reductant instead.

<table>
<thead>
<tr>
<th>Reductant combination</th>
<th>Effect on leaching efficiency of the active material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^+$Fe$^{2+}$/Fe$^{3+}$</td>
<td>Positive</td>
</tr>
<tr>
<td>H$_2$O$_2$/Fe$^{2+}$</td>
<td>Negative</td>
</tr>
<tr>
<td>H$_2$O$_2$/Fe$^{3+}$</td>
<td>Negative</td>
</tr>
<tr>
<td>H$_2$O$_2$/Cu$^+$</td>
<td>Negative</td>
</tr>
<tr>
<td>Al$^+$H$_2$O$_2$</td>
<td>Negative</td>
</tr>
<tr>
<td>Al$^+$Fe$^{2+}$/Fe$^{3+}$</td>
<td>Positive</td>
</tr>
<tr>
<td>Al$^+$Cu$^{2+}$/Cu$^{2+}$</td>
<td>No effect</td>
</tr>
<tr>
<td>Al$^+$Cu$^{2+}$Fe$^{2+}$/Fe$^{3+}$</td>
<td>Positive</td>
</tr>
</tbody>
</table>

4. Conclusions

Synthetic active material NMC111 was leached in the presence of added H$_2$O$_2$. Metallic Cu and Al as well as Fe$^{3+}$ were added to mimic potential impurities present in battery waste. The reducing power of metallic Cu and Al and Fe was assessed. The results in this work demonstrate that a significant part of H$_2$O$_2$ is consumed to the concurrent oxidation of Cu and Fe$^{2+}$, which reflects on the leaching efficiency of the active material as all reducing agents consume each other. It is of the essence to select either Cu-Al-Fe or H$_2$O$_2$ as a reducing agent, especially when recoverable valuable metals determine the particle size of the feed and hence the amount of Cu, Fe and Al present in black mass concentrate. Alternatively, the metallic components in the black mass leaching could be allowed to dissolve completely while transferring their chemical energy to the dissolution of active material through redox reactions followed by the addition of a lower amount of H$_2$O$_2$ to complete the leaching of the active material to utilize all materials efficiently.

Author contributions

The research was primarily conducted by AC (mineralogical analysis, SEM-EDS analysis, leach solution sample analysis, data analysis), in association with YZ who performed additional experimental investigations (leaching experiments, leach solution sample analysis). Conceptualization was undertaken by AC and ML, and methodology by AC and YZ. Validation and analysis of results was performed by AC, YZ and ML. The original draft was written by AC and reviewed and edited by AC, YZ, BPW, ML. Project administration and supervision was provided by BPW and ML, with funding acquisition and resources by ML.

Declaration of Competing Interest

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

Acknowledgements

This research work has been supported by Business Finland Bat-Circle2.0 project (grant number 44886/31/2020), and the Academy of Finland’s RawMatTERS Finland Infrastructure (RAMI) based at Aalto University. The KIC InnoEnergy SE (KIC-IE) supported by the EIT a body of the European Union is thanked for supporting the project.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2021.119903.

References


