Towards a More Sustainable Leaching Process for Li-Ion Battery Cathode Material Recycling: Mechanochemical Leaching of LiCoO 2 Using Citric Acid

Joshua Vauloup, Cécile Bouilhac, Nicolas Coppey, Patrick Lacroix-Desmazes, Lorenzo Stievano, Laure Monconduit, Moulay Tahar Sougrati

Towards a more sustainable leaching process for Li-ion battery cathode material recycling: mechanochemical leaching of $LiCoO_2$ using citric acid.

Joshua Vauloup,[1,*] Cécile Bouilhac,[1] Nicolas Coppey,[3] Patrick Lacroix-Desmazes,[1] Lorenzo Stievano,[1,2] Laure Monconduit,[1,2,*] Moulay Tahar Sougrati[1,2]

[1] *ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France*

[2] *RS2E, Réseau sur le Stockage Electrochimique de l'Energie, CNRS, Amiens, France*

[3] *SNAM, Viviez, France*

* laure.monconduit@umontpellier.fr, moulay-tahar.sougrati@umontpellier.fr

Abstract

Lithium-ion batteries (LIBs) require critical resources for cathode active materials production, including elements such as cobalt, nickel and lithium. Therefore, their recycling from spent LIBs is a priority for European countries. Current recycling technologies mainly consist in hydrometallurgical processes that require large amounts of inorganic acids, reducing agents and other chemicals for a selective recovery. In the present paper, an innovating and efficient process of Li and Co leaching from $LiCoO_2$ (LCO) cathode materials, which allows reducing the consumption of chemicals, is proposed. The combination of two bio-based organic acids, namely citric acid (H_3Cit) and ascorbic acid (AsAc), enables complete recovery of Li and Co in just one hour through mechanochemical leaching using ball milling. By using a relative molar ratio of H_3Cit:AsAc:LCO (1:0.5:1) this innovative approach offers an optimized leaching process, with a limited

water usage. This method holds promise for significantly reducing the carbon footprint of future lithium-ion battery recycling efforts..

Key words: recycling, mechanochemistry, Lithium-ion batteries, organic acids, cobalt

1. Introduction

Today's electric vehicles (EVs) market is building up fast to tackle down the fossil fuel consumption. The worldwide EV stock expanded from less than 1,600,000 units in 2015 to 17,400,000 units in 2021.[1] This trend is not going to slow down due to new regulations that will forbid, in the European Union (EU), the production and sale of new combustion-powered cars by 2035. Lithium-ion batteries (LIBs) emerge as the favoured energy storage technology due to their excellent performance. However, the large-scale production of new cathode materials for LIBs requires specific elements such as Co, Li and Ni, which are considered as critical by the EU owing to the supply risk they entail. Consequently, safeguarding sovereignty necessitates the recognition of end-of-life (EoL) LIBs as a strategic reserve of secondary raw materials. Given the limited lifespan of LIBs, estimated to be around 10 years, their recycling becomes of paramount importance, not only to alleviate environmental concerns associated with the disposal of spent batteries, but also to ensure a sustainable supply of critical metals for the production of new LIBs.[2–4]

Beyond resource scarcity and economic safety issues, recycling LIBs is beneficial in terms of energy consumption compared with the use of virgin resources.[5] Indeed, the metal extraction industry is known to be energy-intensive and to use large amounts of chemicals that are released in the environment, becoming additional sources of pollution. The production of cathode material for LIBs has proved to be twofold less energy-intensive using metal intermediates from LIB recycling rather than starting from virgin raw materials.[6] This is particularly true for Ni and Co.[2,7] This observation can be explained by the average concentration of strategic metals in LIBs, which is 100- to 1000 fold higher than in natural ores. For example, typical Co and Li contents in LIBs are 5-20 wt. % and 2-7 wt. %, respectively, based on the whole LIB.[8,9]

The most common process currently used for metal recovery is hydrometallurgy, either alone or combined with pyrometallurgy.[10] It consists of the acid leaching of metal oxides followed by multiple separation and purification steps to recover metals selectively with a sufficiently high purity for reusing them. This process is combined with pre-treatment steps such as discharging, dismantling, crushing, pyrolysis, size exclusion, magnetic separation as well as other physical separations. Many combinations of these steps are possible with different arrangements according to the industrial process. However, hydrometallurgical processes generate significant amounts of wastewater, emit toxic gases, are energy intensive and consume large amounts of chemicals. [11–13]

These activities are still at their infancy, and more advanced and efficient LIB recycling technologies are necessary to support the existing ones and to reach the upcoming legislation targets by limiting the secondary pollution emissions. [14,15] Mechanochemistry, consisting in using mechanical energy for activating chemical reactions by drastically reducing the solvent and chemical use, is one of the currently emerging alternative technologies.[16,17] The benefits of mechanochemistry are already under exploration for several processes of LIB recycling as recently summarized by Wang *et al.*[18] Different strategies have been proposed such as ball milling (BM) for the pre-treatment of the recycling feed in order to decrease the leaching activation energy. BM allows amorphization, particle size reduction and specific surface area increase due to the high energy delivered. These morphological and structural changes help the acidic proton attack for leaching the metal oxide. [19,20,21] Co-grinding agents may also be used for improving the leaching activation, for instance to reduce Co(III) and/or Ni(III) oxides,[21–27] or for solid-state chlorination to form soluble metal salts. [28–31] These methods, resumed in Table 1, allow diminishing chemicals consumption during leaching, using weaker acids and improving the leaching kinetics. [21,29] Mechanochemistry may be more than an

activation pre-treatment step, and was for example proposed for other innovative processes such as the direct synthesis of new materials from spent cathodes [32,33] or the direct recycling of cathode materials by relithiation without additional chemical separation steps.[34] Mechanochemistry using high energy ball milling was also studied to assist the leaching step of cathode active materials with organic acids (OAs) as solid reagents (Table 1).[13,35–38] This one-pot process for cathode powder activation and leaching assisted by ball milling is named mechanochemical leaching to differentiate it from mechanochemical activation prior to the leaching step. OAs have been widely studied in thermally-assisted hydrometallurgical processes as, unlike traditionally used inorganic acids, they do not emit toxic gases (SO_x, Cl_2, etc.), they are less corrosive, they may be recycled for further extraction,[39] and may also be bio-based.[40–42] Despite these benefits, OAs are not employed for industrial leaching mainly owing to their relatively high cost compared to mineral acids. However, mechanochemistry can allow limiting the consumption of reagents with solvent-free process, and the solid nature of such OAs make them the reagents of choice for an efficient mass and energy transfer during the mechanochemical reaction.[43] Few studies, listed in Table 1, explored the use of organic acids for mechanochemical leaching of cathode materials. Although citric acid demonstrated its ability to recover selectively Li from Fe, it has not yet been reported for the leaching of Co containing cathode materials such as LCO or NMC.

In this paper, the citric acid (H_3Cit) and ascorbic acid (AsAc) are associated to leach Co and Li from LCO cathode materials *via* mechanochemical leaching using a high energy planetary ball mill. This process associating both OAs has never been reported in the literature to the best of our knowledge. H_3Cit is supposed to play the role of both leaching and complexing agent, whereas AsAc mainly works as the reducing agent of pristine Co(III) to Co(II). Leaching conditions such as rotation speed, water addition, balls-to-powder mass ratio

(B/P), citric acid to LCO (H_3Cit/LCO) and ascorbic acid to LCO (AsAc/LCO) molar ratios as well as milling duration were studied for determining the optimal leaching conditions. This process proved to be very effective in limiting the quantity and the associated cost of reagents,[13] especially the OAs, as well as the energy consumption and the wastewater generation.

Table 1: Leaching assisted by BM with organic acids. Optimal conditions.

Ref.	Cathode materials	Acids/leaching agent	Optimal conditions
[13]	LCO	Alginic acids (from alginate degradation)	500 rpm, 4 h, AlgAc:LCO mass ratio of 10:1 (5:1 mole ratio), 2 mL of H_2O_2, 0.05 g of LCO
[36]	LFP	Oxalic acid	500 rpm, 2 h, OxAc:LFP mass ratio of 1:1 (1.75:1 mole ratio), B/P = 20, 1 mL of DIW
[37]	LFP	Citric acid	With H_2O_2 (selective toward Li) 400 rpm, 2 h, H_3Cit:LFP mass ratio of 20:1 (16.4:1 mole ratio), B/P = 25, 1 mL of H_2O_2 With H_2O (unselective) 300 rpm, 8 h, H_3Cit:LFP mass ratio of 20:1 (16.4:1 mole ratio), B/P = 45
[35]	LCO	EDTA	600 rpm, 4 h, LCO:EDTA mass ratio of 4:1 (1.3:1 mole ratio), B:P = 80:1
[38]	NMC	Ammonium persulfate (NHS) + Sucrose + Fe(0)	800 rpm, 3 h, 2 g, NHS:NMC mass ratio of 2:1, Suc:NMC mass ratio of 2:1, B/P = 20, 3 mm balls, 3 mL of DIW. Cast iron materials (with Fe(0), not efficient in ZrO_2 pots)

2. Experimental

2.1. Materials and reagents

For milling assisted leaching experiments, a Pulverisette 7 Premium Line (Fritsch) planetary ball mill with ZrO_2 jars of 45 mL was used. As a model cathode material, pristine commercial $LiCoO_2$ powder (ABCR, 98 %, 10 µm) was used. A representative black mass sample was provided by the recycling company SNAM (France). Citric acid (Aldrich, anhydrous, 99 %)

and L-Ascorbic acid (Aldrich, 99 %) were used as received. MilliQ deionized water was used for liquid assisted milling as well as for dilution and quantification of the recovered products. For the AAS (Atomic Absorption Spectroscopy) analysis, the dilution was performed with 2 % vol. HNO_3 solution to avoid cobalt precipitation and to limit the influence of matrix effects.

2.2. Experimental procedure

In the mechanochemical experiments, LCO (or black mass), H_3Cit, AsAc powders and water were initially introduced in a milling jar in defined amounts with a specific number of ZrO_2 5 mm balls. Milling cycles of 30 min followed by 5 min rest were implemented with a reverse rotation direction after each rest. The influence of several parameters on the milling process was studied, such as H_3Cit/LCO and AsAc/LCO molar ratio (0 - 3 mole eq.), solid/liquid ratio (S/L = 0 - 2 $g.mL^{-1}$)), time (0 – 3 h), balls-to-powder mass ratio (B/P = 10 to 40) as well as rotation speed (400 – 600 rpm). At the end of the milling experiment, the milled product was recovered by dissolution in 50 mL of MilliQ water for 15 min at room temperature. The solution was then filtered on a 0.20 µm PTFE syringe filter. Dilutions in 2 % vol. HNO_3 were performed to reach the defined AAS analytical range.

2.3. Analytical methods

The amounts of leached Co and Li were measured by AAS (Thermoscientific Ice3000), and the Co and Li leaching efficiency was calculated using Equation 1. The milled products were also analysed by X-ray diffraction (XRD) in Bragg-Brentano geometry with a PANalytical Empyrean diffractometer equipped with the Co K_α radiation ($K_{\alpha1}$ = 1.78901 Å and $K_{\alpha2}$ = 1.7929 Å) to identify the crystalline phases formed during ball milling. UV-Visible and FTIR spectroscopy measurements were carried out to study the formation of the cobalt complexes.

$$\%\, x = \frac{C_x \times DF}{m_{LCO} \times \%m_{x,LCO} \times V_{tot}} \times 100$$ Equation 1

With
- *% x: leaching efficiency of x (x = Co or Li)*
- *C_x: mass concentration of x ($g.L^{-1}$)*
- *m_{LCO}: mass of LCO (g)*
- *$\%m_{x,LCO}$: mass fraction of x in LCO (wt%)*
- *V_{tot}: volume of the milled solution after dissolution (L)*
- *DF: dilution factor*

1

2 ## 3. Results and discussions

3 ### *3.1. Water volume (L/S) influence*

4 For determining the optimal conditions for LCO leaching, experimental conditions
5 were studied by varying one parameter at a time. The water volume added to the system was
6 varied from 0 to 3 mL for 3 g of LCO, with H_3Cit/LCO = 1, AsAc/Co = 1. The ratio B/P was fixed
7 to 10, and the rotation speed to 400 rpm, for 60 min. The liquid/solid ratio (L/S) is the physical
8 value used for studying the water volume influence (Cf. SI for more details).Figure 1 represents
9 the Co and Li leaching efficiency as a function of this L/S ratio. It appears that L/S ≥ 0.27 is
10 required for an efficient leaching. With this ratio, a thick slurry is formed during the milling.
11 Water may help the leaching by creating a hydration sphere stabilizing aqueous metal
12 complexes, improving the reagents diffusion and limiting aggregation.[43] In the remainder
13 study, L/S was set to 0.33 to obtain optimal condition with the lowest water consumption.

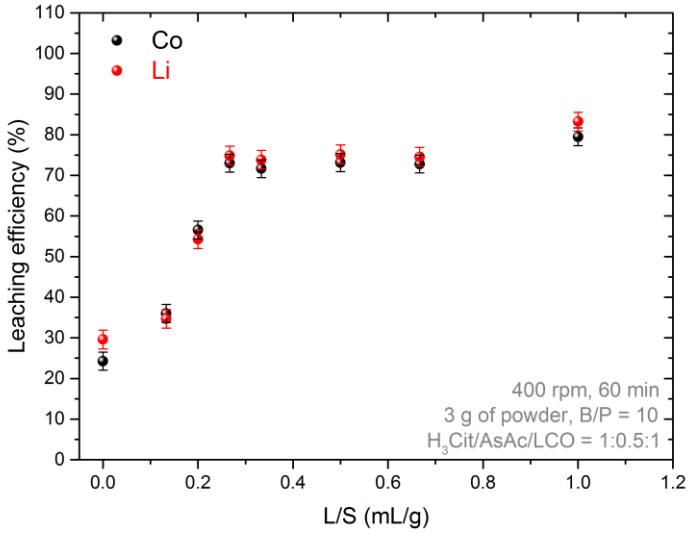

Figure 1: Leaching efficiency as function of L/S ratio. Fixed conditions: 400 rpm, 60 min, AsAc/Co = 0.5, H_3Cit/LCO = 1,3 g of powder and B/P = 10.

3.2. Balls-to-powder mass ratio (B/P)

Among the parameters related to the delivered energy, the Balls to Powder (B/P) mass ratio allows playing with the milling energy without varying the rotation speed.[44,45] To investigate the influence of B/P, L/S ratio was set to 0.33 mL.g^{-1} at 400 rpm for 60 min with H_3Cit:AsAc:LCO = 1:1:1. Here, B/P was adjusted by keeping constant the mass of powder and by varying the number of balls. The leaching efficiency of Co and Li as a function of B/P ratio, represented in Figure , clearly shows that increasing the B/P improves the leaching efficiency, which grows continuously from 62 to 89 % for cobalt when B/P goes from 5 to 20. As adding more balls allows increasing the balls impacts per unit of time, the reaction is then activated simultaneously in more points of the jar, improving the contact between the reagents. However, for B/P ≥ 20, the leaching efficiency is not improved further. A higher B/P ratio may in fact lead to more ball-ball contacts and consequently to a sterile dissipation of the energy, and/or restrain the balls movement for an optimal collision.[46]

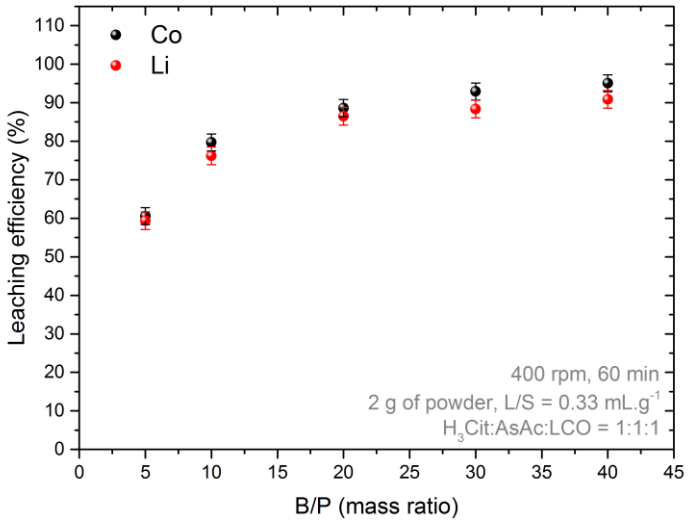

Figure 2: Leaching efficiency of Co and Li from LCO as function of B/P mass ratio. Fixed conditions: 400 rpm, 60 min, 2 g of powder, L/S = 0.33 mL.g^{-1} and H_3Cit:AsAc:LCO = 1:1:1.

3.3. Rotation speed (rpm)

The rotation speed of a planetary ball mill is the main parameter influencing the ball impact energy. Figure represents leaching kinetics of Li from LCO at increasing rotating speeds from 400 to 600 rpm, all the other parameters being kept constant. After 30 min, the leaching efficiency of Li increases from 58 to 88 % on going from 400 to 600 rpm, confirming that increasing the milling speed, and consequently the energy, allows improving LCO leaching. A higher impact energy acts by reducing the powder particle size and by amorphising LCO, leading to a decrease of the leaching activation energy.[23,24] Above 500 rpm, the leaching is already completed after only 1 h for 2 g of powder, B/P = 20, L/S = 0.33 mL.g^{-1} and H_3Cit:AsAc:LCO = 1:1:1. From an industrial point of view, a compromise has to be found between the energy consumption and process duration, as high rotation speed is required for a fast leaching.

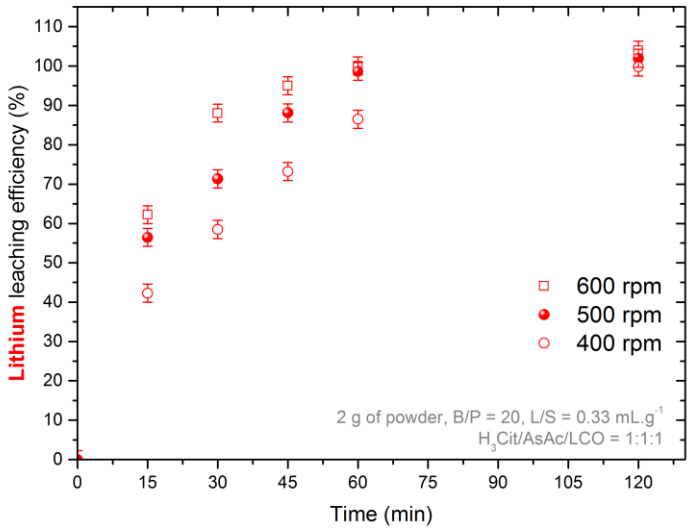

Figure 3: Leaching efficiency of Li from LCO as function of time for three different rotation speed: 400 rpm (hollow circle), 500 rpm (sphere) and 600 rpm (hollow square). Fixed conditions: 2 g of powder, P/B = 20, L/S = 0.33 mL.g^{-1} and H_3Cit:AsAc:LCO = 1:1:1.

3.4. AsAc/Co mole ratio

Another parameter that considerably affects the process cost is the reagents consumption. Consequently, the amount of reducing agent was an important parameter that must be evaluated. Figure 4a shows the leaching efficiency of Li and Co from LCO as function of AsAc/Co molar ratio at 600 rpm for 30 min with 2 g of powder and H_3Cit/LCO = 1. Without ascorbic acid, the leaching efficiency is very low with only 11 and 3 % for Li and Co, respectively. When AsAc/Co is set to 0.25, the leaching reaches more than 50 % of Li and Co. This observation indicates that the citric acid alone does not allow the reduction of Co(III) to Co(II), which is necessary in order to obtain stable aqueous complexes, and that a reducing agent is required (Equation 3Equation 2).[5,47] When AsAc/Co exceeds 0.75, the leaching efficiency reaches a plateau, and adding more AsAc does not improve further the leaching efficiency. Theoretically, 2 eq. of Co(III) can be reduced with 1 eq. of AsAc (Equation 4)

(AsAc/Co=0.5 molar ratio), which is in turn oxidized to dehydroascorbic acid[48] (DHA, extended formulae and redox couple of AsAc detailed in the SI).

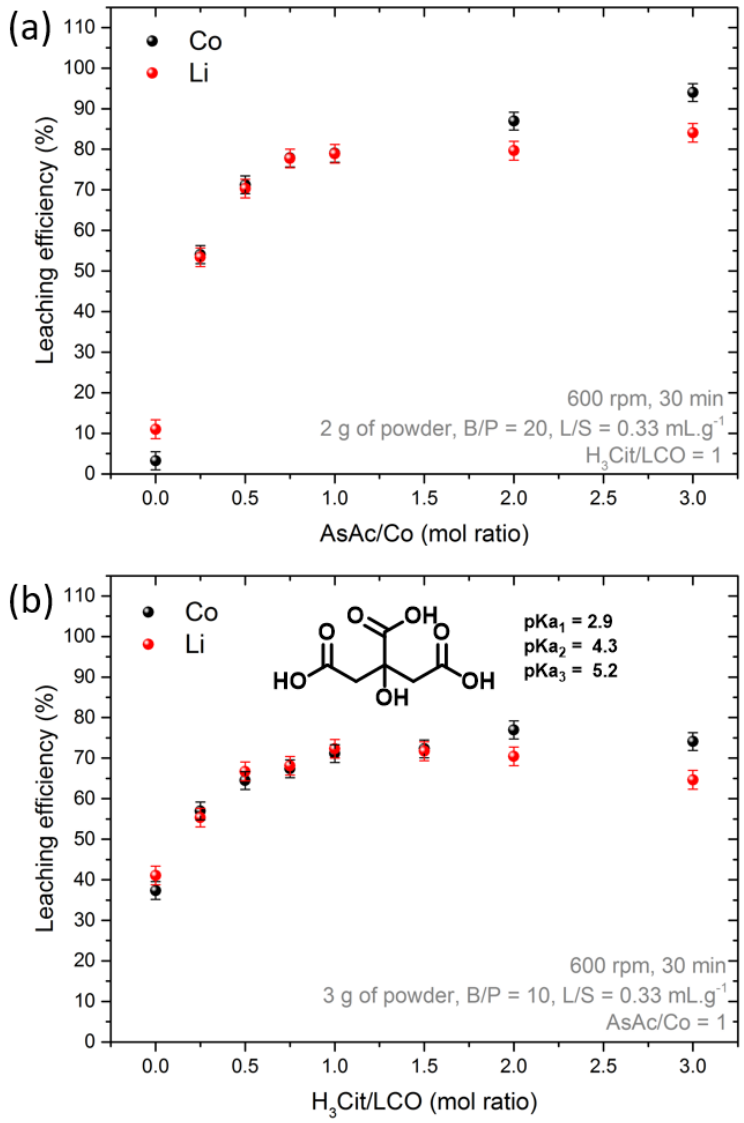

Figure 4: Leaching efficiency of Co and Li from LCO as function of AsAc/Co mole ratio (a). Fixed conditions: 600 rpm, 30 min, 2 g of powder, L/S = 0.33 mL.g^{-1} and H_3Cit:LCO = 1:1. Leaching efficiency of Co and Li from LCO as function of H_3Cit/LCO molar ratio (b). Fixed conditions: 600 rpm, 30 min, 3 g of powder, L/S = 0.33 mL.g^{-1} and AsAc:LCO = 1:1.

Co(III) reduction with ascorbic acid

$AsAc \rightarrow DHA + 2\,e^- + 2\,H^+$	(red)	(+0.4 V vs. SHE)	*Equation 2*
$Co^{3+} + e^- \rightarrow Co^{2+}$	(ox)	(+1.92 V vs. SHE)	*Equation 3*
$2Co^{3+} + AsAc \rightarrow 2Co^{2+} + DHA$	(redox)	Eq. (2) + Eq. (3)	*Equation 4*

3.5. H_3Cit/LCO mole ratio

The amount of citric acid was also varied to investigate its influence on the leaching efficiency. The leaching rate is plotted on Figure 4b for H_3Cit/LCO between 0 and 3 at 600 rpm for 30 min with 2 g of powder and AsAc/Co = 1. Without citric acid, the leaching efficiency is around 40 % for Co and Li. This means that AsAc plays the role of both reducing and leaching agent. Nevertheless, the addition of H_3Cit improves the leaching up to 90 % for H_3Cit/LCO = 1.

A larger excess of citric acid does not allow further increasing the leaching efficiency, which rather decreases. Different complex isomers with H_3Cit may be formed, as this molecule has three carboxylic acid groups. Therefore, three conjugated bases are likely formed along the deprotonation of H_3Cit (H_2Cit^-, $HCit^{2-}$, Cit^{3-}), as suggested by the decrease of pH measured (cf. Figure S5).[49]

3.6. Mechanism investigation

For the purpose of atom saving and for limiting the process cost as well as the environmental impact, the leaching mechanism has to be better understood. According to the general leaching equation of LCO, four acidic protons are required for one molecule of LCO (Equation 7). To confirm it, experiments with sub-stoichiometric conditions were carried out at 500 rpm with 2 g of powder and B/P = 20. The leaching efficiency of Co and Li as well as the pH of the solutions on the right axis of the graphs (milled product dissolved in 50 mL of MilliQ

water) are displayed in Figure . After 2 h of milling, Co and Li are completely leached for H_3Cit/AsAc/LCO = 1:1:1 (Cf. SI for repeatability). However, for H_3Cit/AsAc/LCO = 0.5:0.5:1 and 0.75:0.75:1, only 77 % and 90 % of metal leaching is obtained, respectively. Nevertheless, for a longer milling (3 h), a complete leaching of Co and Li is observed for a 0.75:0.75:1 ratio, whereas it reaches only 78 % for a 0.5:0.5:1 ratio (Figure 5a and b). On the basis of Equation 7, this limitation might be related to a lack of acidic protons to reach the complete LCO leaching. Theoretically, one molecule of AsAc is able to reduce two molecules of LCO as well as to provide two protons (Equation 4). Although the pKa_2 value is high for the reduced form of AsAc (pKa_1 = 4.1 and pKa_2 = 11.8), once oxidized to DHA after losing two electrons, the acid nature of this proton is increased, and pKa_2 becomes negative (pKa_2' = - 0.45).[50] Therefore, considering one molecule of LCO, one H^+ can be provided by 0.5 eq. of the oxidized form of AsAc, DHA. In the presence of water, moreover, DHA can undergo hydrolysis to 2,3-diketogulonic acid via the opening of the lactone ring, then releasing additional 0.5 eq. of H^+ per eq. of LCO.[51,52] Therefore at least 0.84 eq. of H_3Cit is required assuming that the three acidities of H_3Cit take part to the leaching. In terms of H_3Cit/AsAc/LCO molar ratio, this represents a ratio of 0.84:0.5:1. Thus, the theoretical maximum leaching efficiency when using a ratio of 0.5:0.5:1 and 0.75:0.75:1 is around 75 % and 100 %, respectively (cf. SI), assuming that the excess of AsAc remains in the reduced form and releases only one proton. Additional protons could be released in case of oxidation and degradation of such excess by reaction with ambient air,[53] as well as by the further decomposition of DKG in highly reactive ball milling conditions and the concomitant presence of transition metal cations in solution.[51]

Experimentally, a leaching efficiency of 90 % of Co and Li at 600 rpm for 1 h of milling and around 99 % at 500 rpm for 3 h is observed, confirming that the full leaching of LCO can be obtained with a 0.75:0.75:1 ratio (Figure 5), indicating that the third acidity of H_3Cit is

possibly involved in the leaching of LCO under these milling conditions. The general equation of LCO reductive leaching with H_3Cit and AsAc is given in Equation 11.

Cai L. et al.[13] suggested that AsAc does not allow the complete reduction of cobalt because its reducibility is lowered by its lack of deprotonation. In this paper, AsAc proved to be an efficient reducing agent. The determining factor is probably the amount of water that needs to be high enough for allowing both the reduction of Co(III) to Co(II) by AsAc and its leaching (Figure 1).

The right axis of Figure .a and b represents the pH of the milling residue dissolved in 50 mL of water as a function of the H_3Cit/AsAc/LCO. After 2 h of milling, for a ratio of 0.5:0.5:1, the pH is higher than for 0.75:0.75:1 and 1:1:1 ratio as almost all the acidic protons are consumed. This value further increases for longer milling time that proves the predominance of Cit^{-3} species.[54]

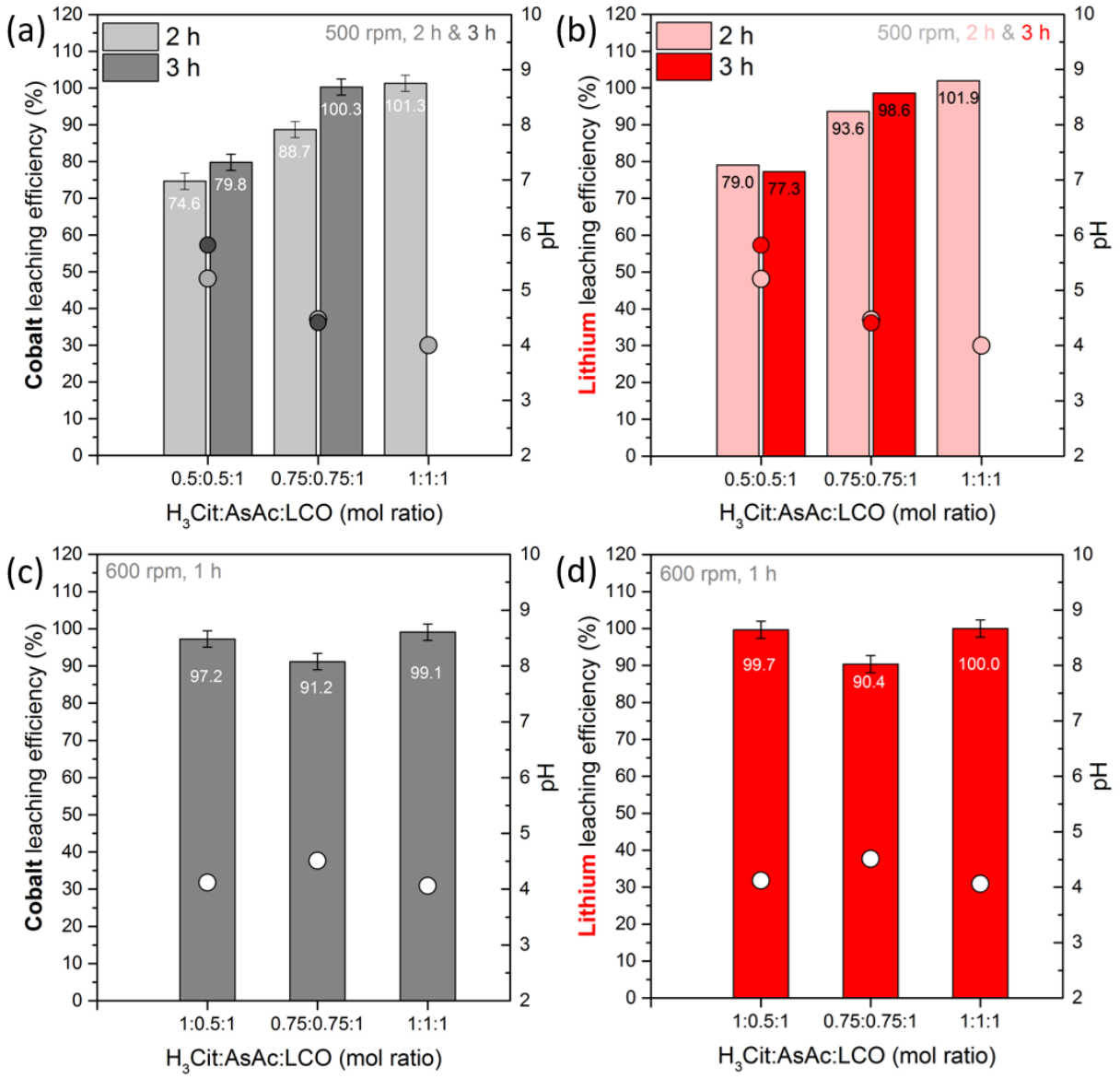

Figure 5: (Top) Leaching efficiency of Co (a) and Li (b) from LCO as well as pH evolution (circles) as function of H_3Cit/AsAc/LCO mole ratio. Fixed conditions: 500 rpm, 2 g of powder, B/P=20 and L/S = 0.33 mL.g^{-1}. (Bottom) Leaching efficiency of Co (c) and Li (d) from LCO as well as pH evolution as function of H_3Cit/AsAc/LCO mole ratio. Fixed conditions: 600 rpm, 2 g of powder, B/P=20 and L/S = 0.33 mL.g^{-1}.

Equations for describing the LCO leaching with H_3Cit and AsAc (Note: ascorbic acid = AsAc, dehydroascorbic acid = DHA, 2,3-diketogulonate = DKG).

- Reactions of ascorbic acid in water solution

$$AsAc \rightarrow DHA + 2\,e^- + 2\,H^+ \quad \text{Equation 5}$$

$$DHA + H_2O \rightarrow DKG + H^+ \quad \text{Equation 6}$$

- Reductive leaching of LCO

$$LiCo^{(III)}O_2 + 4\,H^+ + e^- \rightarrow Co^{2+} + Li^+ + 2H_2O \quad \text{Equation 7}$$

- Citric acid deprotonation

$$H_3Cit \overset{pKa_1}{\longleftrightarrow} H^+ + H_2Cit^- \quad \text{Equation 8}$$

$$H_2Cit^- \overset{pKa_2}{\longleftrightarrow} H^+ + HCit^{2-} \quad \text{Equation 9}$$

$$HCit^{2-} \overset{pKa_3}{\longleftrightarrow} H^+ + Cit^{3-} \quad \text{Equation 10}$$

- General equation of LCO reductive leaching with H_3Cit and AsAc

$$LiCo^{(III)}O_2 + \frac{5}{6}H_3Cit + 0.5AsAc \rightarrow Co^{2+} + Li^+ + \frac{5}{6}Cit^{3-} + 0.5DKG + 2H_2O \quad \text{Equation 11}$$

For the experiments with a low excess of acidic protons, the formation of a precipitate is observed when the solution is left resting for 48 h. In the case of the sample with a molar ratio of 0.75:0.75:1, 100 % cobalt efficiency is measured, filtering of the solution after 48 h reduces the cobalt leaching efficiency to 89 %, whereas lithium leaching is still at 100 %. This precipitation is most probably correlated to the formation of cobalt oxalate, a less soluble Co^{2+} species, as confirmed by TGA and XRD analyses of the recovered precipitate (Figure S6 and S7).

3.7. Optimal conditions

In order to determine if the process developed using H_3Cit and AsAc by ball milling is relevant in terms of atom economy, leaching conditions were optimized and compared to other leaching processes described in the literature. Leaching tests assisted by ball milling at 600 rpm for 1 h, carried out with L/S = 0.33 $mL.g^{-1}$ with different H_3Cit/AsAc/LCO ratios, have been performed. Figures 5c and 5d show Co and Li leaching efficiency for H_3Cit/AsAc/LCO of 1:0.5:1, 0.75:0.75:1 and 1:1:1 as well as the pH of the leached residue dissolved in 50 mL of water. As discussed earlier, different H_3Cit/AsAc/LCO ratios produce different amount of H^+ for LCO reductive leaching: (4.5 H^+, 4 H^+ and 5 H^+ for ratio of 1:0.5:1, 0.75:0.75:1 and 1:1:1, respectively, assuming the full deprotonation of H_3Cit). Lithium leaching is almost complete for ratio of 1:0.5:1 and 1:1:1 with 99.7 and 100.0 % of Li in solution. For 0.75:0.75:1, however, the leaching is lower with 90.4 %. Its kinetics seems slower due to a higher pH than for 1:0.5:1 (4.5 and 4.1, respectively). Considering that 4 H^+ are necessary for a complete LCO leaching, a leaching efficiency slightly lower than 100 % for 0.75:0.75:1 ratio is not unexpected. In terms of process cost, a small excess of H_3Cit is preferred as citric acid is cheaper than ascorbic acid (1.24 $ for H_3Cit anhydrous *vs* 3.3 $ per kg for AsAc in July 2023 in Europe, according to Chemanalyst).[55]

Referring to the literature (Table 2), thermally activated LCO leaching in solution requires more H_3Cit for an equivalent leaching efficiency (4 to 10 times more than the process discussed in this paper). Moreover, energy calculation should be carried out to evaluate the energy consumption of thermally activated leaching compared to ball milling activation. In fact, thermally activated leaching needs large amount of hot water above 80 °C for more than 90 min for reaching a complete leaching. Meng *et al*. [56] were able to leach around 90 % of Co and Li with a small excess of H_3Cit from a mixture with NMC, carbon, current collectors and

electrolyte, with no use of reducing agent, as Al is able to reduce Co^{3+} and Ni^{3+}. Ball milling was used as pre-treatment step by Qu L. *et al*.[26] prior to H_3Cit leaching without reducing agent. The milling with SiO_2 (500 rpm for 30 min) allowed decreasing the particles size, amorphizing the LCO and activating the Co^{3+} reduction to Co^{2+} due to the presence of carbon. The leaching time is considerably shortened to 30 min at 80 °C, but H_3Cit must still be used in large excess (*H_3Cit/LCO =6.6)*. Therefore, it appears that a one-batch system using ball milling for direct activation of the leaching appears relevant for at least decreasing the amount of chemicals.

Table 2: State of the art of cathode active materials leaching using citric acid and thermal activation.

Ref.	Cathode materials	Leaching efficiency	Optimal conditions
[57]	LCO	*Co = 86 %* *Li = 98 %*	*H_3Cit = 0.1 M, AsAc = 0.02 M, 0.2 g of LCO, S/L = 10 g.L^{-1} at **80°C for 6 h*** ⇨ *H_3Cit/LCO =5.3 ; AsAc/Co = 1 ; TA/LCO = 4.9*
[41]	LCO	*Co = 99.5 %* *Li = 97 %*	*H_3Cit = 1.5 M, **SA = 0.2 M**, + **6 % vol. H_2O_2**, S/L = 15 g.L^{-1} at 90°C for 90 min* ⇨ *H_3Cit/LCO =9.8 ; SA/LCO = 1.3 ; H_2O_2/Co = 3.8*
[58]	LCO	*Co = 81.3 %* *Li = 97.8 %*	*H_3Cit = 2 M**, Cu/Co = 1,** S/L = 50 g.L^{-1} at 70°C for 24 h* ⇨ Cobalt citrate precipitation for high citrate concentration. ⇨ *H_3Cit/LCO =3.9 ; Cu/Co = 1*
[59]	LCO	*Co = 81 %* *Li = 92 %*	*H_3Cit = 2 M, **1.25 % vol. H_2O_2**, S/L = 30 g.L^{-1} at 60°C for 2 h* ⇨ *H_3Cit/LCO =6.5 ; H_2O_2/Co = 0.4*
[60]	LCO	*Co = 100 %* *Li = 100 %*	*H_3Cit = 1 M, no reducing agents (presence of Al from current collector), S/L = 100 g.L^{-1} at 90°C for 2 h* ⇨ *H_3Cit/LCO =1*
[49]	LCO	*Co = 99 %* *Li = 99 %*	*H_3Cit = 1 M, 8 **% vol. H_2O_2**, S/L =40 g.L^{-1} at 70°C for 70 min (presence of Al from current collector)* *H_3Cit/LCO =2.5 ; H_2O_2/Co = 1.9*
[56]	NMC	*Co = 90 %* *Li = 91 %* *Ni = 94 %* *Mn = 89 %*	*H_3Cit = 0.5 M, S/L = 80 g.L^{-1} at 90°C for 80 min (presence of Al and Cu from current collector as well as electrolyte)* ⇨ *H_3Cit/NMC = 1.7*
[26]	LCO	*Co = 94.9 %* *Li = 97.2 %*	*H_3Cit = 1.25 M, no reducing agent, S/L =20 g.L^{-1} at 80°C for 30 min (presence of Al from current collector and graphene). Pre-treatment by ball milling with SiO_2.* *H_3Cit/LCO =6.6*
This study	LCO	*Co = 97.2 %* *Li = 99.7 %*	*60 min at 600 rpm with S/L = 775 g.L^{-1}* *H_3Cit/LCO = 1.0 and AsAc/Co = 0.5*

3.8. Preliminary tests with Black Mass (BM)

In this study, the leaching tests were performed and optimized for pure LCO. However, the leaching of strategic metals from spent LIBs usually takes place with a more complex medium, such as a black mass. *i.e.*, an intermediate product of battery recycling. Typical black masses consist of mixtures of carbon with metals from cathode (LCO and NMC) and anode parts obtained by calcination, crushing and sieving of disassembled spent batteries. The composition of the BM used here, determined by ICP-OES, is displayed on the SI.

Figure 6 represents the leaching efficiencies of Co and Li from a black mass produced from spent LCO/NMC LIBs. Ball milling-assisted leaching tests were carried out with the optimal conditions determined for pure LCO (600 rpm for 1 h with 2 g of powder and B/P = 20), by varying the H_3Cit/AsAc/[Co;Li] molar ratio (Figure 6a). Unlike with LCO, the leaching yield did not reach completion after 60 min of milling, the efficiency being only 55 and 67 % for Co and Li, respectively for H_3Cit/AsAc/LCO = 1:0.5:1. The presence of carbon (28 wt. %) probably influences the leaching kinetics as it absorbs some of the energy from the ball impacts. When the milling was extended for a longer period (2 h) with H_3Cit/AsAc/LCO = 1:0:1 (Figure 6b), the leaching efficiency of Co and Li was improved up to 80 and 98 %, respectively. This means that the kinetics is slower when a black mass is used, as the metal oxides are diluted by carbon powder. The leaching kinetics may also be improved by adding more citric acid as observed on Figure 6a where 78 and 94 % of Co and Li are leached after 1 h with H_3Cit/AsAc/LCO = 1.5:0:1. The addition of a larger excess of citric acid does not further improve the leaching efficiency. However, it is important to note that the use of ascorbic acid as a reducing agent is unnecessary in this case, as cobalt leaching efficiency remains the same with or without AsAc. This can be attributed to the presence of carbon or aluminum in the black mass, which can reduce Co(III) to Co(II). [26] Additionally, since the black mass is typically prepared through

an intermediate pyrolysis treatment, the original Co(III) oxides are already partially reduced to Co(II) species. (Cf. XRD of black mass Figure S8).

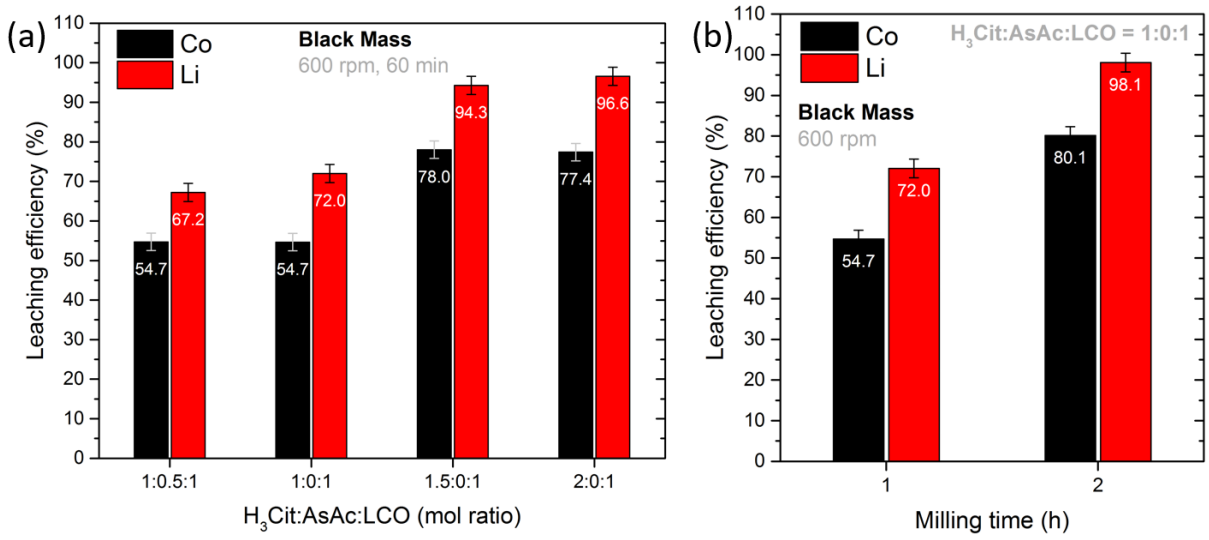

Figure 6: Leaching efficiency of Co and Li from black mass as function of H_3Cit/AsAc/LCO molar ratio (a) and as function of milling time (b). Fixed conditions: 600 rpm, 2 g of powder, L/S = 0.33 mL.g^{-1}, 1 h for (a) and H_3Cit/AsAc/LCO = 1:0:1 for (b).

4. Conclusion

Mechanochemistry proved to be a promising and efficient process for the leaching of cathode materials assisted by organic acids. Cobalt and lithium leaching from LCO reached efficiencies as high as 97.2 ± 2.2 % and 99.7 ± 2.2 %, respectively, using a mole ratio of H_3Cit/AsAc/LCO of 1:0.5:1, 2 g of powder and a B/P mass ratio of 20 at 600 rpm for 1 h. The process allows recovering metals from cathode materials of LIBs by reducing chemicals consumption and wastewater generation. The treatment of a representative black mass also showed promising efficiencies. Moreover, in the case of the black mass, the reducing agent consumption could be decreased owing to the possible reducing power of other species, *i.e.*,

carbon and aluminum, originally contained in the black mass. These findings underscore the potential of alternative methods such as mechanochemistry to significantly enhance the efficiency and sustainability of the recycling process of spent batteries. In particular, these approaches may help improving the efficiency of leaching processes of cathode materials, reducing chemical consumption and minimizing wastewater generation, thus rendering recycling more environmentally friendly and enabling the efficient recovery of strategic resources contained in spent LIBs.

Acknowledgments

The authors would like to acknowledge SNAM, the Région Occitanie as well as the French National Research Agency (project Labex STORE-EX, ANR-10-LABX-76-01) for financial support.

References

1 S. Jin, D. Mu, Z. Lu, R. Li, Z. Liu, Y. Wang, S. Tian and C. Dai, *J. Clean. Prod.*, 2022, **340**, 130535.

2 J. Neumann, M. Petranikova, M. Meeus, J. D. Gamarra, R. Younesi, M. Winter and S. Nowak, *Adv. Energy Mater.*, 2022, **12**, 2102917.

3 M. M. Cerrillo-Gonzalez, M. Villen-Guzman, C. Vereda-Alonso, J. M. Rodriguez-Maroto and J. M. Paz-Garcia, *Chemosphere*, 2022, **287**, 132020.

4 European Parliament Adopted Text, *Batteries and waste batteries-P9_TA(2023)0237*, 2023.

5 T. Or, S. W. D. Gourley, K. Kaliyappan, A. Yu and Z. Chen, *Carbon Energy*, 2020, **2**, 6–43.

6 L. Gaines, J. Sullivan, A. Burnham and I. Belharouak, *Transp. Res. Rec.*, 2011, 57–65.

7 E. Fan, L. Li, Z. Wang, J. Lin, Y. Huang, Y. Yao, R. Chen and F. Wu, *Chem. Rev.*, 2020, **120**, 7020–7063.

8 S. M. Shin, N. H. Kim, J. S. Sohn, D. H. Yang and Y. H. Kim, *Hydrometallurgy*, 2005, 79, 172–181.

9 B. Huang, Z. Pan, X. Su and L. An, *J. Power Sources*, 2018, **399**, 274–286.

10 D. Latini, M. Vaccari, M. Lagnoni, M. Orefice, F. Mathieux, J. Huisman, L. Tognotti and A. Bertei, *J. Power Sources*, 2022, **546**, 231979.

11 J. J. Roy, S. Rarotra, V. Krikstolaityte, K. W. Zhuoran, Y. D. Cindy, X. Y. Tan, M. Carboni, D. Meyer, Q. Yan and M. Srinivasan, *Adv. Mater.*, 2022, **34**, 2103346.

12 R. Golmohammadzadeh, F. Faraji and F. Rashchi, *Resour. Conserv. Recycl.*, 2018, **136**, 418–435.

13 L. Cai, J. Lin, E. Fan, F. Wu, R. Chen and L. Li, *ACS Sustain. Chem. Eng.*, 2022, **10**, 10649–10657.

14 J. Lin, X. Zhang, L. Cai, E. Fan, S. Wu, S. Ma, F. Wu, R. Chen and L. Li, *Adv. Energy Sustain. Res.*, 2022, **3**, 2100153.

15 L. Gregoir and K. Van Acker, *Eurometaux, KU Leuven*.

16 K. J. Ardila-Fierro and J. G. Hernández, *ChemSusChem*, 2021, **14**, 2145–2162.

17 N. Fantozzi, J. N. Volle, A. Porcheddu, D. Virieux, F. García and E. Colacino, *Chem. Soc. Rev.*, 2023, **52**, 6680–6714.

18 M. Wang, K. Liu, J. Yu, C. C. Zhang, Z. Zhang and Q. Tan, *Circ. Econ.*, 2022, **1**, 100012.

19 Y. Yang, X. Zheng, H. Cao, C. Zhao, X. Lin, P. Ning, Y. Zhang, W. Jin and Z. Sun, *ACS Sustain. Chem. Eng.*, 2017, **5**, 9972–9980.

20 Q. Zhang, J. Lu, F. Saito, C. Nagata and Y. Ito, *Adv. Powder Technol.*, 2000, **11**, 353–359.

21 M. Wang, Q. Tan and J. Li, *Environ. Sci. Technol.*, 2018, **52**, 13136–13143.

22 Y. Guo, Y. Li, X. Lou, J. Guan, Y. Li, X. Mai, H. Liu, C. X. Zhao, N. Wang, C. Yan, G. Gao, H. Yuan, J. Dai, R. Su and Z. Guo, *J. Mater. Sci.*, 2018, **53**, 13790–13800.

23 J. Xie, K. Huang, Z. Nie, W. Yuan, X. Wang, Q. Song, X. Zhang, C. Zhang, J. Wang and J. C. Crittenden, *Resour. Conserv. Recycl.*, 2021, **168**, 105261.

24 Y. Jiang, X. Chen, S. Yan, Y. Ou and T. Zhou, *Green Chem.*, 2022, **24**, 5987–5997.

25 J. Guan, Y. Li, Y. Guo, R. Su, G. Gao, H. Song, H. Yuan, B. Liang and Z. Guo, *ACS Sustain. Chem. Eng.*, 2017, **5**, 1026–1032.

26 L. QU, Y. HE, Y. FU, W. XIE, C. YE, Q. LU, J. LI, J. LI and Z. PANG, *Trans. Nonferrous Met. Soc. China*, 2022, **32**, 1325–1335.

27 J. Yang, L. Jiang, F. Liu, M. Jia and Y. Lai, *Trans. Nonferrous Met. Soc. China*, 2020, **30**, 2256–2264.

28 S. Saeki, J. Lee, Q. Zhang and F. Saito, *Int. J. Miner. Process.*, 2004, **74**, 373–378.

29 S. Zhang, C. Zhang, X. Zhang and E. Ma, *ACS Sustain. Chem. Eng.*, , DOI:10.1021/acssuschemeng.2c00276.

30 M. Wang, Q. Tan, L. Liu and J. Li, *J. Clean. Prod.*, 2021, **279**, 123612.

31 K. Liu, Q. Tan, L. Liu and J. Li, *Environ. Sci. Technol.*, 2019, **53**, 9781–9788.

32 S. Dang, P. Zhou, P. Shi, Y. Min and Q. Xu, *ACS Sustain. Chem. Eng.*, 2021, **9**, 15375–15385.

33 Y. Yang, H. Yang, H. Cao, Z. Wang, C. Liu, Y. Sun, H. Zhao, Y. Zhang and Z. Sun, *J. Clean. Prod.*, 2019, **236**, 117576.

34 X. Meng, J. Hao, H. Cao, X. Lin, P. Ning, X. Zheng, J. Chang, X. Zhang, B. Wang and Z. Sun, *Waste Manag.*, 2019, **84**, 54–63.

35 M.-M. Wang, C.-C. Zhang and F.-S. Zhang, *Waste Manag.*, 2016, **51**, 239–244.

36 E. Fan, L. Li, X. Zhang, Y. Bian, Q. Xue, J. Wu, F. Wu and R. Chen, *ACS Sustain. Chem. Eng.*, 2018, **6**, 11029–11035.

37 L. Li, Y. Bian, X. Zhang, Y. Yao, Q. Xue, E. Fan, F. Wu and R. Chen, *Waste Manag.*, 2019, **85**, 437–444.

38 Z. Liang, G. Peng, J. Hu, H. Hou, C. Cai, X. Yang, S. Chen, L. Liu, S. Liang, K. Xiao, S. Yuan, S. Zhou and J. Yang, *Waste Manag.*, 2022, **150**, 290–300.

39 M. Cera, S. Trudu, A. Oumarou Amadou, F. Asunis, G. Farru, G. Pietro De Gaudenzi, G. De Gioannis and A. Serpe, *Int. J. Refract. Met. Hard Mater.*, 2023, **114**, 106249.

40 J. Becker, A. Lange, J. Fabarius and C. Wittmann, *Curr. Opin. Biotechnol.*, 2015, **36**, 168–175.

41 M. Xu, S. Kang, F. Jiang, X. Yan, Z. Zhu, Q. Zhao, Y. Teng and Y. Wang, *RSC Adv.*, 2021, **11**, 27689–27700.

42 J. Zhang, X. Hu, T. He, X. Yuan, X. Li, H. Shi, L. Yang, P. Shao, C. Wang and X. Luo, *Waste Manag.*, 2023, **165**, 19–26.

43 J. L. Howard, Q. Cao and D. L. Browne, *Chem. Sci.*, 2018, **9**, 3080–3094.

44 H. X. Kho, S. Bae, S. Bae, B.-W. Kim and J. S. Kim, *J. Korean Powder Metall. Inst.*, 2014, **21**, 155–164.

45 D. Dong, Y. Zhang, M. Shan, T. Yin, T. Wang, J. Wang and W. Gao, *J. Clean. Prod.*, 2022, **348**, 131351.

46 F. Hirosawa and T. Iwasaki, *Chem. Eng. Res. Des.*, 2021, **167**, 84–95.

47 X. Cheng, G. Guo, Y. Cheng, M. Liu and J. Ji, *Energy Technol.*, , DOI:10.1002/ente.202200039.

48 G. Gao, X. Luo, X. Lou, Y. Guo, R. Su, J. Guan, Y. Li, H. Yuan, J. Dai and Z. Jiao, *J. Mater. Cycles Waste Manag.*, 2019, **21**, 942–949.

49 M. Yu, Z. Zhang, F. Xue, B. Yang, G. Guo and J. Qiu, *Sep. Purif. Technol.*, 2019, **215**, 398–402.

50 Y.-J. Tu, D. Njus and H. B. Schlegel, *Org. Biomol. Chem.*, 2017, **15**, 4417–4431.

51 R. A. Dewhirst and S. C. Fry, *Biochem. J.*, 2018, **475**, 3451–3470.

52 S.-O. Kang, H. Sapper and W. Lohmann, *Z. Naturforsch. C*, 1982, **37**, 1064–1069.

53 X. Yin, K. Chen, H. Cheng, X. Chen, S. Feng, Y. Song and L. Liang, *Antioxidants*, 2022, **11**, 1–20.

54 H. M. Sharada, S. A. Abdel-Halim, M. A. Hafez, I. A. Ibrahim, T. A. Elbarbary and Y. Abdel-Fatah, *Biointerface Res. Appl. Chem.*, 2022, **12**, 8406–8425.

55 Market Analysis - Demand & Supply.

56 F. Meng, Q. Liu, R. Kim, J. Wang, G. Liu and A. Ghahreman, *Hydrometallurgy*, 2020, **191**, 105160.

57 G. P. Nayaka, Y. Zhang, P. Dong, D. Wang, K. V. Pai, J. Manjanna, G. Santhosh, J. Duan, Z. Zhou and J. Xiao, *Waste Manag.*, 2018, **78**, 51–57.

58 M. del M. Cerrillo-Gonzalez, J. M. Paz-Garcia, M. Muñoz-Espinosa, J. M. Rodriguez-Maroto and M. Villen-Guzman, *J. Power Sources*, 2024, **592**, 233870.

59 R. Golmohammadzadeh, F. Rashchi and E. Vahidi, *Waste Manag.*, 2017, **64**, 244–254.

60 L. S. Martins, S. Rovani, A. B. Botelho Junior and D. C. Romano Espinosa, *Ind. Eng. Chem. Res.*, 2023, **62**, 18672–18682.

TOC Entry


Green taz' - A High-Energy milling for Recycling
EoL LIB
Critical metals source