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## **Towards a More Sustainable Leaching Process for Li-Ion Battery Cathode Material Recycling: Mechanochemical Leaching of LiCoO<sub>2</sub> Using Citric Acid**

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1 **Towards a more sustainable leaching process for Li-ion battery cathode material recycling:**  
2 **mechanochemical leaching of LiCoO<sub>2</sub> using citric acid.**

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10

11 **Abstract**

12 Lithium-ion batteries (LIBs) require critical resources for cathode active materials  
13 production, including elements such as cobalt, nickel and lithium. Therefore, their recycling  
14 from spent LIBs is a priority for European countries. Current recycling technologies mainly  
15 consist in hydrometallurgical processes that require large amounts of inorganic acids, reducing  
16 agents and other chemicals for a selective recovery. In the present paper, an innovating and  
17 efficient process of Li and Co leaching from LiCoO<sub>2</sub> (LCO) cathode materials, which allows  
18 reducing the consumption of chemicals, is proposed. The combination of two bio-based organic  
19 acids, namely citric acid (H<sub>3</sub>Cit) and ascorbic acid (AsAc), enables complete recovery of Li and Co in  
20 just one hour through mechanochemical leaching using ball milling. By using a relative molar ratio of  
21 H<sub>3</sub>Cit:AsAc:LCO (1:0.5:1) this innovative approach offers an optimized leaching process, with a limited

1 water usage. This method holds promise for significantly reducing the carbon footprint of future

2 lithium-ion battery recycling efforts..

3

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

5

## 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.<sup>1</sup> 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.<sup>2-4</sup>

Beyond resource scarcity and economic safety issues, recycling LIBs is beneficial in terms of energy consumption compared with the use of virgin resources.<sup>5</sup> 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.<sup>6</sup> This is particularly true for Ni and Co.<sup>2,7</sup> 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.<sup>8,9</sup>

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

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

1 activation pre-treatment step, and was for example proposed for other innovative processes  
2 such as the direct synthesis of new materials from spent cathodes<sup>32,33</sup> or the direct recycling  
3 of cathode materials by relithiation without additional chemical separation steps.<sup>34</sup>  
4 Mechanochemistry using high energy ball milling was also studied to assist the leaching step  
5 of cathode active materials with organic acids (OAs) as solid reagents (Table 1).<sup>13,35–38</sup> This one-  
6 pot process for cathode powder activation and leaching assisted by ball milling is named  
7 mechanochemical leaching to differentiate it from mechanochemical activation prior to the  
8 leaching step. OAs have been widely studied in thermally-assisted hydrometallurgical  
9 processes as, unlike traditionally used inorganic acids, they do not emit toxic gases (SO<sub>x</sub>, Cl<sub>2</sub>,  
10 etc.), they are less corrosive, they may be recycled for further extraction,<sup>39</sup> and may also be  
11 bio-based.<sup>40–42</sup> Despite these benefits, OAs are not employed for industrial leaching mainly  
12 owing to their relatively high cost compared to mineral acids. However, mechanochemistry  
13 can allow limiting the consumption of reagents with solvent-free process, and the solid nature  
14 of such OAs make them the reagents of choice for an efficient mass and energy transfer during  
15 the mechanochemical reaction.<sup>43</sup> Few studies, listed in Table 1, explored the use of organic  
16 acids for mechanochemical leaching of cathode materials. Although citric acid demonstrated  
17 its ability to recover selectively Li from Fe, it has not yet been reported for the leaching of Co  
18 containing cathode materials such as LCO or NMC.

19 In this paper, the citric acid (H<sub>3</sub>Cit) and ascorbic acid (AsAc) are associated to leach Co  
20 and Li from LCO cathode materials *via* mechanochemical leaching using a high energy  
21 planetary ball mill. This process associating both OAs has never been reported in the literature  
22 to the best of our knowledge. H<sub>3</sub>Cit is supposed to play the role of both leaching and  
23 complexing agent, whereas AsAc mainly works as the reducing agent of pristine Co(III) to  
24 Co(II). Leaching conditions such as rotation speed, water addition, balls-to-powder mass ratio

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

5

6 *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)

7

## 8 2. Experimental

### 9 2.1. Materials and reagents

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

1 and L-Ascorbic acid (Aldrich, 99 %) were used as received. MilliQ deionized water was used for  
2 liquid assisted milling as well as for dilution and quantification of the recovered products. For  
3 the AAS (Atomic Absorption Spectroscopy) analysis, the dilution was performed with 2 % vol.  
4 HNO<sub>3</sub> solution to avoid cobalt precipitation and to limit the influence of matrix effects.

## 5 *2.2. Experimental procedure*

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

## 16 *2.3. Analytical methods*

17 The amounts of leached Co and Li were measured by AAS (Thermoscientific Ice3000),  
18 and the Co and Li leaching efficiency was calculated using Equation 1. The milled products  
19 were also analysed by X-ray diffraction (XRD) in Bragg-Brentano geometry with a PANalytical  
20 Empyrean diffractometer equipped with the Co K<sub>α</sub> radiation (K<sub>α1</sub> = 1.78901 Å and K<sub>α2</sub> = 1.7929  
21 Å) to identify the crystalline phases formed during ball milling. UV-Visible and FTIR  
22 spectroscopy measurements were carried out to study the formation of the cobalt complexes.

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

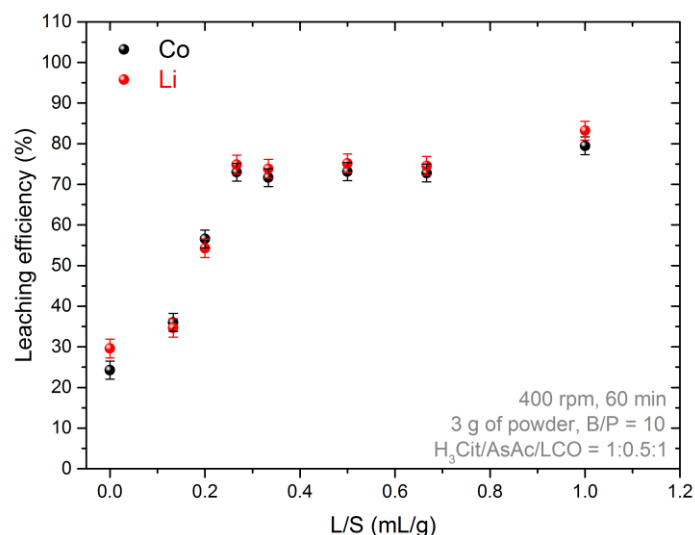
- With
- $\% x$ : leaching efficiency of  $x$  ( $x = \text{Co}$  or  $\text{Li}$ )
  - $C_x$ : mass concentration of  $x$  ( $\text{g.L}^{-1}$ )
  - $m_{LCO}$ : mass of LCO (g)
  - $\%m_{x,LCO}$ : mass fraction of  $x$  in LCO (wt%)
  - $V_{tot}$ : volume of the milled solution after dissolution (L)
  - $DF$ : 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  $\text{H}_3\text{Cit/LCO} = 1$ ,  $\text{AsAc/Co} = 1$ . 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  $\text{L/S} \geq 0.27$  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.<sup>43</sup> In the remainder  
13 study, L/S was set to 0.33 to obtain optimal condition with the lowest water consumption.



1

2 *Figure 1: Leaching efficiency as function of L/S ratio. Fixed conditions: 400 rpm, 60 min,*

3 *AsAc/Co = 0.5, H<sub>3</sub>Cit/LCO = 1,3 g of powder and B/P = 10.*

#### 4 *3.2. Balls-to-powder mass ratio (B/P)*

5 Among the parameters related to the delivered energy, the Balls to Powder (B/P) mass

6 ratio allows playing with the milling energy without varying the rotation speed.<sup>44,45</sup> To

7 investigate the influence of B/P, L/S ratio was set to 0.33 mL.g<sup>-1</sup> at 400 rpm for 60 min with

8 H<sub>3</sub>Cit:AsAc:LCO = 1:1:1. Here, B/P was adjusted by keeping constant the mass of powder and

9 by varying the number of balls. The leaching efficiency of Co and Li as a function of B/P ratio,

10 represented in Figure , clearly shows that increasing the B/P improves the leaching efficiency,

11 which grows continuously from 62 to 89 % for cobalt when B/P goes from 5 to 20. As adding

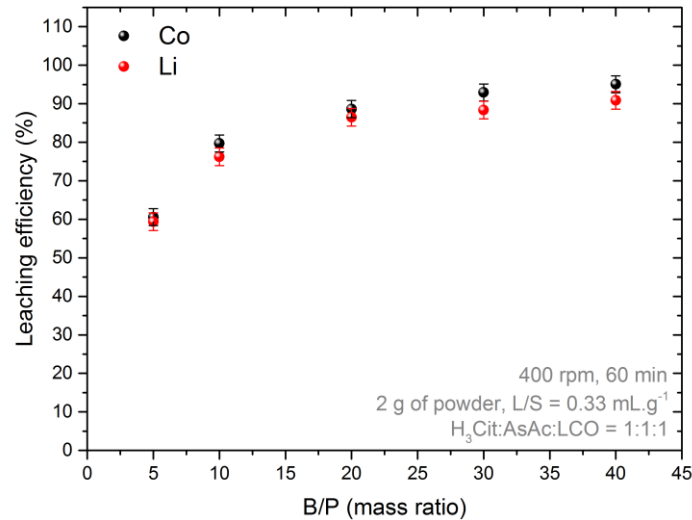
12 more balls allows increasing the balls impacts per unit of time, the reaction is then activated

13 simultaneously in more points of the jar, improving the contact between the reagents.

14 However, for B/P ≥ 20, the leaching efficiency is not improved further. A higher B/P ratio may

15 in fact lead to more ball-ball contacts and consequently to a sterile dissipation of the energy,

16 and/or restrain the balls movement for an optimal collision.<sup>46</sup>

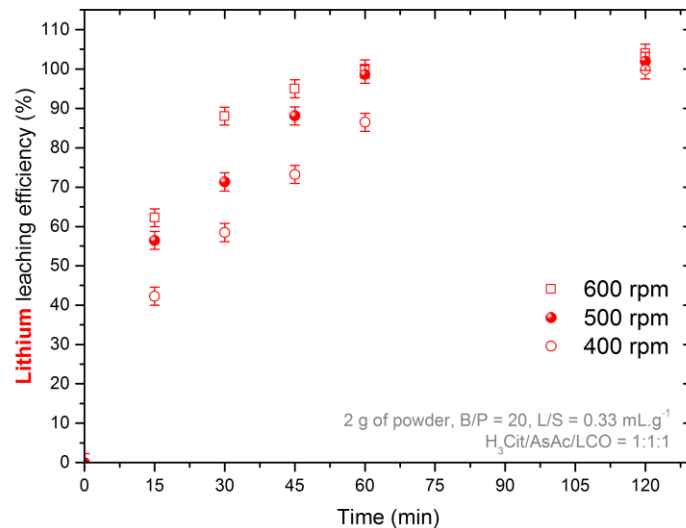


1

2 *Figure 2: Leaching efficiency of Co and Li from LCO as function of B/P mass ratio. Fixed*  
 3 *conditions: 400 rpm, 60 min, 2 g of powder, L/S = 0.33 mL.g<sup>-1</sup> and H<sub>3</sub>Cit:AsAc:LCO = 1:1:1.*

### 4 3.3. Rotation speed (rpm)

5 The rotation speed of a planetary ball mill is the main parameter influencing the ball  
 6 impact energy. Figure represents leaching kinetics of Li from LCO at increasing rotating speeds  
 7 from 400 to 600 rpm, all the other parameters being kept constant. After 30 min, the leaching  
 8 efficiency of Li increases from 58 to 88 % on going from 400 to 600 rpm, confirming that  
 9 increasing the milling speed, and consequently the energy, allows improving LCO leaching. A  
 10 higher impact energy acts by reducing the powder particle size and by amorphising LCO,  
 11 leading to a decrease of the leaching activation energy.<sup>23,24</sup> Above 500 rpm, the leaching is  
 12 already completed after only 1 h for 2 g of powder, B/P = 20, L/S = 0.33 mL.g<sup>-1</sup> and  
 13 H<sub>3</sub>Cit:AsAc:LCO = 1:1:1. From an industrial point of view, a compromise has to be found  
 14 between the energy consumption and process duration, as high rotation speed is required for  
 15 a fast leaching.



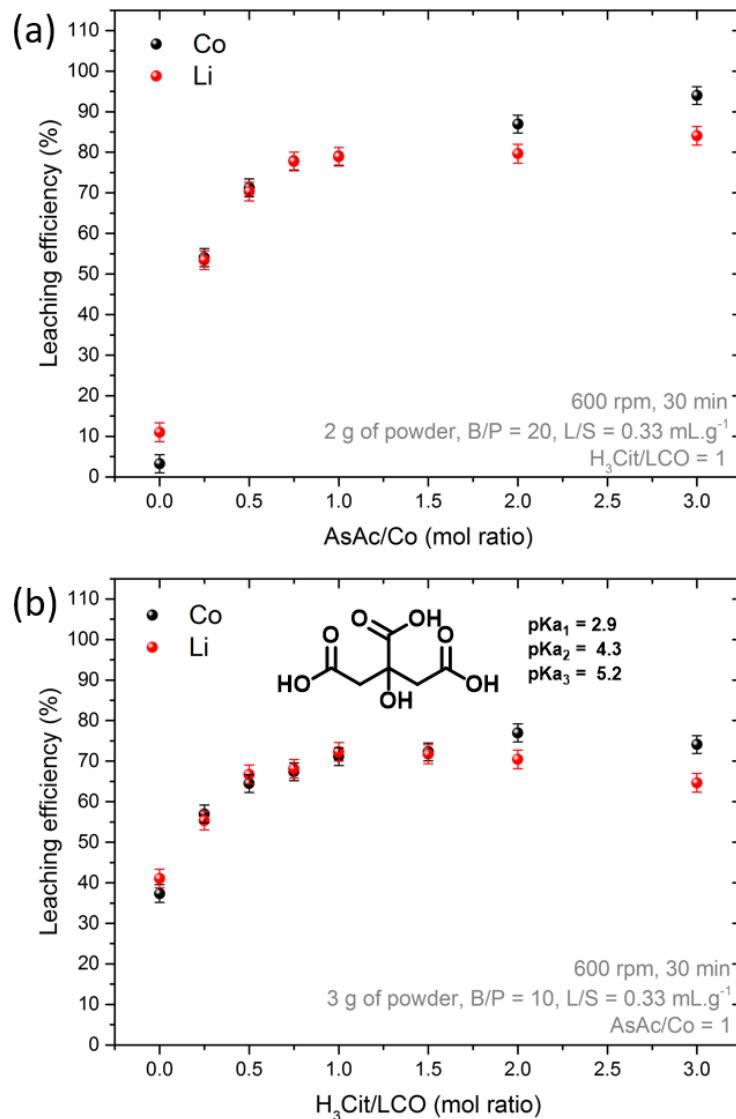
1

2 *Figure 3: Leaching efficiency of Li from LCO as function of time for three different rotation*  
 3 *speed: 400 rpm (hollow circle), 500 rpm (sphere) and 600 rpm (hollow square). Fixed*  
 4 *conditions: 2 g of powder, P/B = 20, L/S = 0.33 mL.g<sup>-1</sup> and H<sub>3</sub>Cit:AsAc:LCO = 1:1:1.*

### 5 3.4. AsAc/Co mole ratio

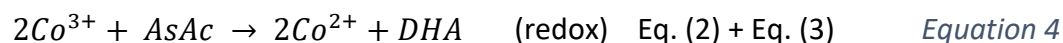
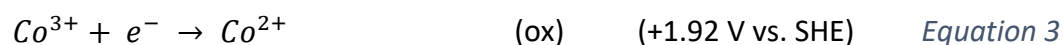
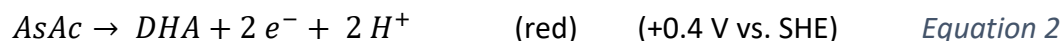
6 Another parameter that considerably affects the process cost is the reagents  
 7 consumption. Consequently, the amount of reducing agent was an important parameter that  
 8 must be evaluated. Figure 4a shows the leaching efficiency of Li and Co from LCO as function  
 9 of AsAc/Co molar ratio at 600 rpm for 30 min with 2 g of powder and H<sub>3</sub>Cit/LCO = 1. Without  
 10 ascorbic acid, the leaching efficiency is very low with only 11 and 3 % for Li and Co,  
 11 respectively. When AsAc/Co is set to 0.25, the leaching reaches more than 50 % of Li and Co.  
 12 This observation indicates that the citric acid alone does not allow the reduction of Co(III) to  
 13 Co(II), which is necessary in order to obtain stable aqueous complexes, and that a reducing  
 14 agent is required (Equation 3Equation 2).<sup>5,47</sup> When AsAc/Co exceeds 0.75, the leaching  
 15 efficiency reaches a plateau, and adding more AsAc does not improve further the leaching  
 16 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<sup>48</sup> (DHA, extended
- formulae and redox couple of AsAc detailed in the SI).



- 3
- 4 *Figure 4: Leaching efficiency of Co and Li from LCO as function of AsAc/Co mole ratio (a).*
- 5 *Fixed conditions: 600 rpm, 30 min, 2 g of powder, L/S = 0.33 mL.g<sup>-1</sup> and H<sub>3</sub>Cit:LCO = 1:1.*
- 6 *Leaching efficiency of Co and Li from LCO as function of H<sub>3</sub>Cit/LCO molar ratio (b). Fixed*
- 7 *conditions: 600 rpm, 30 min, 3 g of powder, L/S = 0.33 mL.g<sup>-1</sup> and AsAc:LCO = 1:1.*

### *Co(III) reduction with ascorbic acid*



### 1      *3.5. H<sub>3</sub>Cit/LCO mole ratio*

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

7            A larger excess of citric acid does not allow further increasing the leaching efficiency,  
8 which rather decreases. Different complex isomers with H<sub>3</sub>Cit may be formed, as this molecule  
9 has three carboxylic acid groups. Therefore, three conjugated bases are likely formed along  
10 the deprotonation of H<sub>3</sub>Cit (H<sub>2</sub>Cit<sup>-</sup>, HCit<sup>2-</sup>, Cit<sup>3-</sup>), as suggested by the decrease of pH measured  
11 (cf. Figure S5).<sup>49</sup>

### 12      *3.6. Mechanism investigation*

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

1 water) are displayed in Figure . After 2 h of milling, Co and Li are completely leached for  
2  $H_3Cit/AsAc/LCO = 1:1:1$  (Cf. SI for repeatability). However, for  $H_3Cit/AsAc/LCO = 0.5:0.5:1$  and  
3  $0.75:0.75:1$ , only 77 % and 90 % of metal leaching is obtained, respectively. Nevertheless, for  
4 a longer milling (3 h), a complete leaching of Co and Li is observed for a  $0.75:0.75:1$  ratio,  
5 whereas it reaches only 78 % for a  $0.5:0.5:1$  ratio (Figure 5a and b). On the basis of Equation  
6 7, this limitation might be related to a lack of acidic protons to reach the complete LCO  
7 leaching. Theoretically, one molecule of AsAc is able to reduce two molecules of LCO as well  
8 as to provide two protons (Equation 4). Although the  $pK_{a2}$  value is high for the reduced form  
9 of AsAc ( $pK_{a1} = 4.1$  and  $pK_{a2} = 11.8$ ), once oxidized to DHA after losing two electrons, the acid  
10 nature of this proton is increased, and  $pK_{a2}$  becomes negative ( $pK_{a2}' = - 0.45$ ).<sup>50</sup> Therefore,  
11 considering one molecule of LCO, one  $H^+$  can be provided by 0.5 eq. of the oxidized form of  
12 AsAc, DHA. In the presence of water, moreover, DHA can undergo hydrolysis to 2,3-  
13 diketogulonic acid via the opening of the lactone ring, then releasing additional 0.5 eq. of  $H^+$   
14 per eq. of LCO.<sup>51,52</sup> Therefore at least 0.84 eq. of  $H_3Cit$  is required assuming that the three  
15 acidities of  $H_3Cit$  take part to the leaching. In terms of  $H_3Cit/AsAc/LCO$  molar ratio, this  
16 represents a ratio of  $0.84:0.5:1$ . Thus, the theoretical maximum leaching efficiency when using  
17 a ratio of  $0.5:0.5:1$  and  $0.75:0.75:1$  is around 75 % and 100 %, respectively (cf. SI), assuming  
18 that the excess of AsAc remains in the reduced form and releases only one proton. Additional  
19 protons could be released in case of oxidation and degradation of such excess by reaction with  
20 ambient air,<sup>53</sup> as well as by the further decomposition of DKG in highly reactive ball milling  
21 conditions and the concomitant presence of transition metal cations in solution.<sup>51</sup>

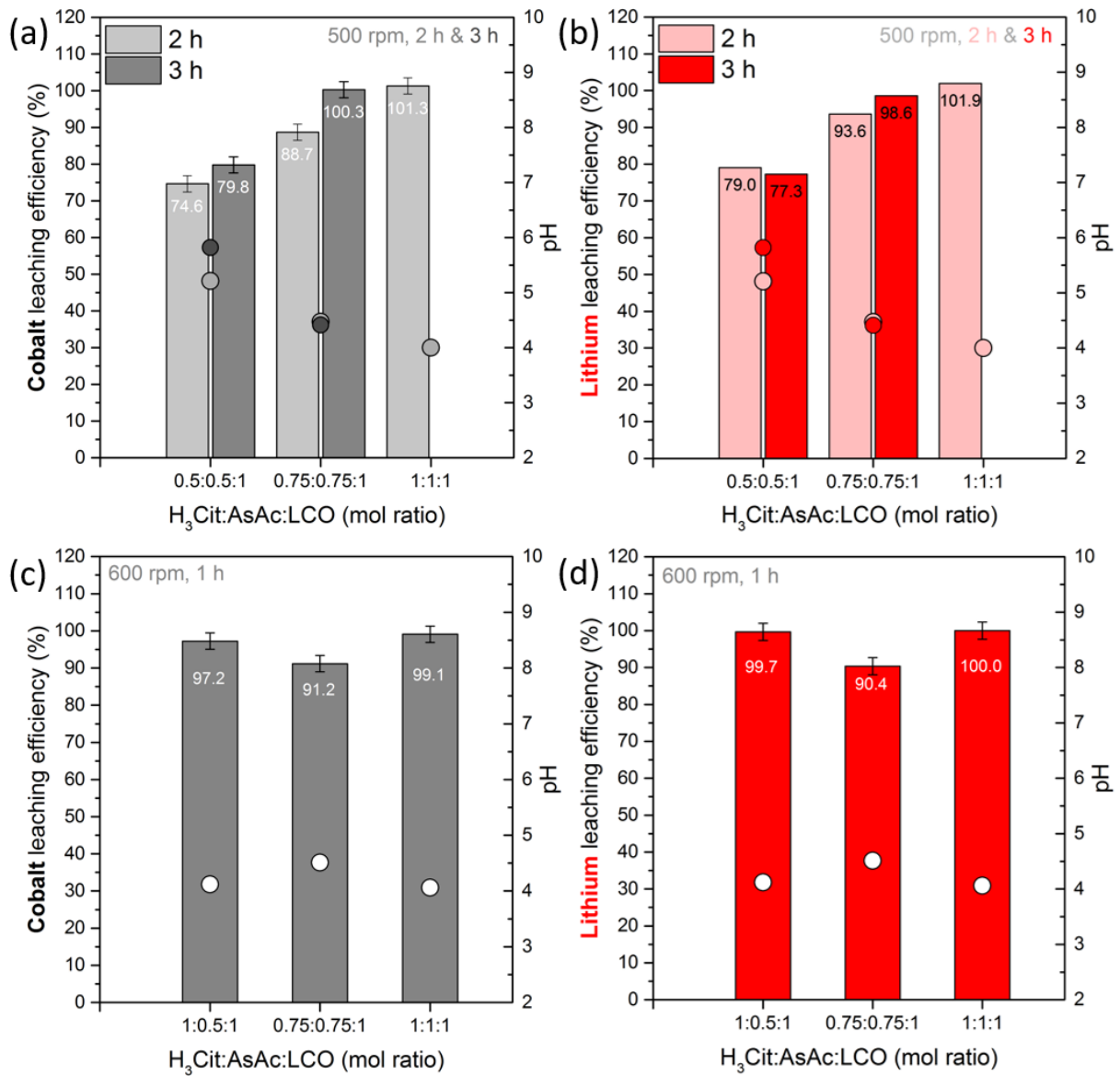
22 Experimentally, a leaching efficiency of 90 % of Co and Li at 600 rpm for 1 h of milling  
23 and around 99 % at 500 rpm for 3 h is observed, confirming that the full leaching of LCO can  
24 be obtained with a  $0.75:0.75:1$  ratio (Figure 5), indicating that the third acidity of  $H_3Cit$  is

1 possibly involved in the leaching of LCO under these milling conditions. The general equation  
2 of LCO reductive leaching with H<sub>3</sub>Cit and AsAc is given in Equation 11.

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

8 The right axis of Figure .a and b represents the pH of the milling residue dissolved in 50  
9 mL of water as a function of the H<sub>3</sub>Cit/AsAc/LCO. After 2 h of milling, for a ratio of 0.5:0.5:1,  
10 the pH is higher than for 0.75:0.75:1 and 1:1:1 ratio as almost all the acidic protons are  
11 consumed. This value further increases for longer milling time that proves the predominance  
12 of Cit<sup>-3</sup> species.<sup>54</sup>

1



2

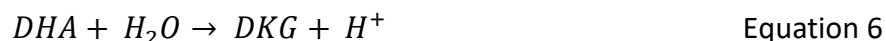
3 *Figure 5: (Top) Leaching efficiency of Co (a) and Li (b) from LCO as well as pH evolution (circles)*  
 4 *as function of H<sub>3</sub>Cit/AsAc/LCO mole ratio. Fixed conditions: 500 rpm, 2 g of powder, B/P=20*  
 5 *and L/S = 0.33 mL.g<sup>-1</sup>. (Bottom) Leaching efficiency of Co (c) and Li (d) from LCO as well as pH*  
 6 *evolution as function of H<sub>3</sub>Cit/AsAc/LCO mole ratio. Fixed conditions: 600 rpm, 2 g of powder,*  
 7 *B/P=20 and L/S = 0.33 mL.g<sup>-1</sup>.*

8

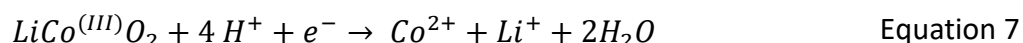
9

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



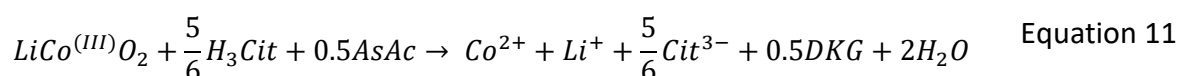
- Reductive leaching of LCO



- Citric acid deprotonation



- General equation of LCO reductive leaching with  $H_3Cit$  and  $AsAc$



1

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

### 3.7. Optimal conditions

In order to determine if the process developed using H<sub>3</sub>Cit 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<sup>-1</sup> with different H<sub>3</sub>Cit/AsAc/LCO ratios, have been performed. Figures 5c and 5d show Co and Li leaching efficiency for H<sub>3</sub>Cit/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<sub>3</sub>Cit/AsAc/LCO ratios produce different amount of H<sup>+</sup> for LCO reductive leaching: (4.5 H<sup>+</sup>, 4 H<sup>+</sup> and 5 H<sup>+</sup> for ratio of 1:0.5:1, 0.75:0.75:1 and 1:1:1, respectively, assuming the full deprotonation of H<sub>3</sub>Cit). 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<sup>+</sup> 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<sub>3</sub>Cit is preferred as citric acid is cheaper than ascorbic acid (1.24 \$ for H<sub>3</sub>Cit anhydrous vs 3.3 \$ per kg for AsAc in July 2023 in Europe, according to Chemanalyst).<sup>55</sup>

Referring to the literature (Table 2), thermally activated LCO leaching in solution requires more H<sub>3</sub>Cit 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.*<sup>56</sup> were able to leach around 90 % of Co and Li with a small excess of H<sub>3</sub>Cit from a mixture with NMC, carbon, current collectors and

1 electrolyte, with no use of reducing agent, as Al is able to reduce  $\text{Co}^{3+}$  and  $\text{Ni}^{3+}$ . Ball milling  
2 was used as pre-treatment step by Qu L. *et al.*<sup>26</sup> prior to  $\text{H}_3\text{Cit}$  leaching without reducing agent.  
3 The milling with  $\text{SiO}_2$  (500 rpm for 30 min) allowed decreasing the particles size, amorphizing  
4 the LCO and activating the  $\text{Co}^{3+}$  reduction to  $\text{Co}^{2+}$  due to the presence of carbon. The leaching  
5 time is considerably shortened to 30 min at 80 °C, but  $\text{H}_3\text{Cit}$  must still be used in large excess  
6 ( $\text{H}_3\text{Cit}/\text{LCO} = 6.6$ ). Therefore, it appears that a one-batch system using ball milling for direct  
7 activation of the leaching appears relevant for at least decreasing the amount of chemicals.

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

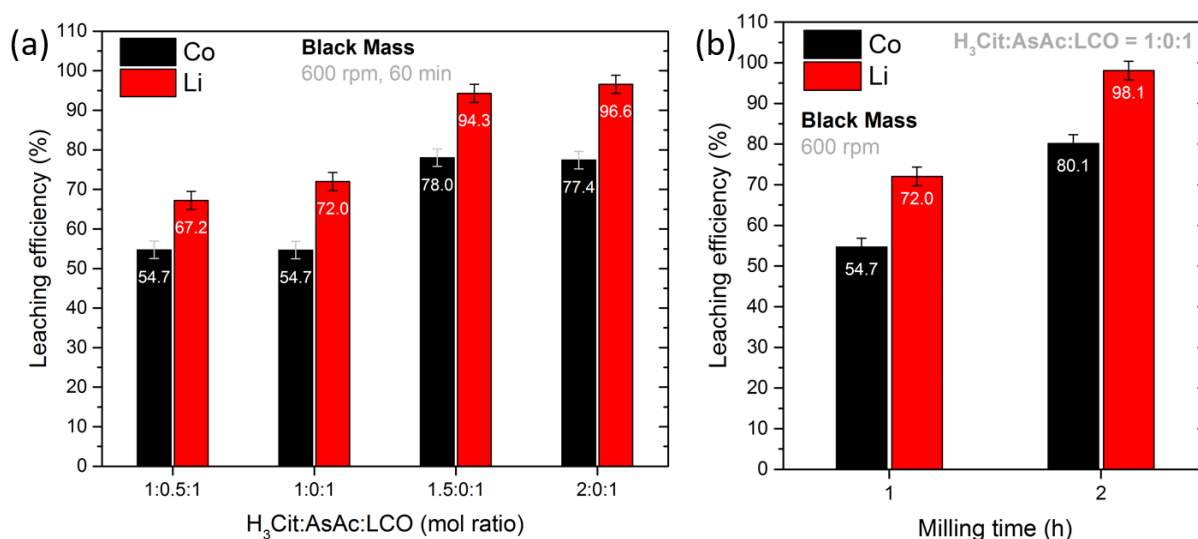
Ref.	Cathode materials	Leaching efficiency	Optimal conditions
57	LCO	Co = 86 % Li = 98 %	H <sub>3</sub> Cit = 0.1 M, AsAc = 0.02 M, 0.2 g of LCO, S/L = 10 g.L <sup>-1</sup> at 80°C for 6 h ⇒ H <sub>3</sub> Cit/LCO = 5.3 ; AsAc/Co = 1 ; TA/LCO = 4.9
41	LCO	Co = 99.5 % Li = 97 %	H <sub>3</sub> Cit = 1.5 M, SA = 0.2 M, + 6 % vol. H <sub>2</sub> O <sub>2</sub> , S/L = 15 g.L <sup>-1</sup> at 90°C for 90 min ⇒ H <sub>3</sub> Cit/LCO = 9.8 ; SA/LCO = 1.3 ; H <sub>2</sub> O <sub>2</sub> /Co = 3.8
58	LCO	Co = 81.3 % Li = 97.8 %	H <sub>3</sub> Cit = 2 M, Cu/Co = 1, S/L = 50 g.L <sup>-1</sup> at 70°C for 24 h ⇒ Cobalt citrate precipitation for high citrate concentration. ⇒ H <sub>3</sub> Cit/LCO = 3.9 ; Cu/Co = 1
59	LCO	Co = 81 % Li = 92 %	H <sub>3</sub> Cit = 2 M, 1.25 % vol. H <sub>2</sub> O <sub>2</sub> , S/L = 30 g.L <sup>-1</sup> at 60°C for 2 h ⇒ H <sub>3</sub> Cit/LCO = 6.5 ; H <sub>2</sub> O <sub>2</sub> /Co = 0.4
60	LCO	Co = 100 % Li = 100 %	H <sub>3</sub> Cit = 1 M, no reducing agents (presence of Al from current collector), S/L = 100 g.L <sup>-1</sup> at 90°C for 2 h ⇒ H <sub>3</sub> Cit/LCO = 1
49	LCO	Co = 99 % Li = 99 %	H <sub>3</sub> Cit = 1 M, 8 % vol. H <sub>2</sub> O <sub>2</sub> , S/L = 40 g.L <sup>-1</sup> at 70°C for 70 min (presence of Al from current collector) H <sub>3</sub> Cit/LCO = 2.5 ; H <sub>2</sub> O <sub>2</sub> /Co = 1.9
56	NMC	Co = 90 % Li = 91 % Ni = 94 % Mn = 89 %	H <sub>3</sub> Cit = 0.5 M, S/L = 80 g.L <sup>-1</sup> at 90°C for 80 min (presence of Al and Cu from current collector as well as electrolyte) ⇒ H <sub>3</sub> Cit/NMC = 1.7
26	LCO	Co = 94.9 % Li = 97.2 %	H <sub>3</sub> Cit = 1.25 M, no reducing agent, S/L = 20 g.L <sup>-1</sup> at 80°C for 30 min (presence of Al from current collector and graphene). Pre-treatment by ball milling with SiO <sub>2</sub> . H <sub>3</sub> Cit/LCO = 6.6
<b>This study</b>	LCO	Co = 97.2 % Li = 99.7 %	60 min at 600 rpm with S/L = 775 g.L <sup>-1</sup> H <sub>3</sub> Cit/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<sub>3</sub>Cit/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<sub>3</sub>Cit/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<sub>3</sub>Cit/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<sub>3</sub>Cit/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).<sup>26</sup> Additionally, since the black mass is typically prepared through

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



3  
4 *Figure 6: Leaching efficiency of Co and Li from black mass as function of H<sub>3</sub>Cit/AsAc/LCO molar*  
5 *ratio (a) and as function of milling time (b). Fixed conditions: 600 rpm, 2 g of powder, L/S =*  
6 *0.33 mL.g<sup>-1</sup>, 1 h for (a) and H<sub>3</sub>Cit/AsAc/LCO = 1:0:1 for (b).*

7

#### 8 4. Conclusion

9 Mechanochemistry proved to be a promising and efficient process for the leaching of  
10 cathode materials assisted by organic acids. Cobalt and lithium leaching from LCO reached  
11 efficiencies as high as  $97.2 \pm 2.2$  % and  $99.7 \pm 2.2$  %, respectively, using a mole ratio of  
12 H<sub>3</sub>Cit/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  
13 process allows recovering metals from cathode materials of LIBs by reducing chemicals  
14 consumption and wastewater generation. The treatment of a representative black mass also  
15 showed promising efficiencies. Moreover, in the case of the black mass, the reducing agent  
16 consumption could be decreased owing to the possible reducing power of other species, *i.e.*,

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

8

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13 document and will be applied to all subsequent versions up to the Author Accepted  
14 Manuscript arising from this submission, in accordance with the grant's open access  
15 conditions.

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1 TOC Entry

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**Critical metals source**