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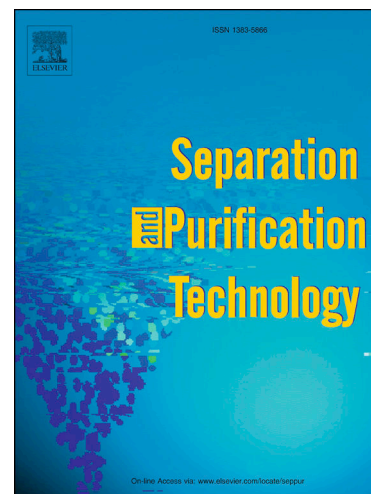
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Electrochemically-assisted leaching of active cathode materials from spent batteries with minimal pre-treatment using hydroxylated solvents

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Abstract

Spent lithium-ion batteries (LIBs) are a rapidly increasing source of waste that pose a hazardous and environmental problem. They are also a secondary source of valuable critical metals such as Li, Co, Ni and Mn. Their recycling often involves use of aggressive conditions, which challenge the sustainability character of the process. In this work, an electrochemically-assisted leaching process was carried out to dissolve valuable metals from pristine and spent LIB cathode materials under mild conditions without the need for any pre-treatment (removal of polymeric binder and current collector). Hydroxylated solvents were used as electrolytes, firstly in leaching of Co_3O_4 , demonstrating that the applied potential played a determinant role in achieving high Co dissolution (73.1 %). Subsequently, real spent cathodes were directly used, without pre-treatment, as working electrodes under mild working conditions. Up to 82 % Li, 62 % Co, 60 % Ni and 52 % Mn were leached at potentials up to 3V with fast kinetics in the first 30 minutes of the process. The structural changes caused by initial delithiation of the black mass, corrosion of the Al from the current collector, and the presence of binder, were identified as key in achieving competitive metal leaching efficiency values. This process can pave the way for new LIB recycling processes with less pre-treatment requirements, in milder conditions while still being scalable to an industrial setting.

Keywords: Metal recovery; Electrochemical extraction; Leaching; Recycling; Spent batteries

Introduction

The decarbonization of the global economy is heavily reliant on critical raw materials,^[1] which are widely present in the technologies currently driving this transition such as lithium-ion batteries (LIBs). Millions of these batteries are projected to enter the waste stream as they reach

their end-of-life, with this trend expected to significantly increase in the coming years.^[2] Recycling LIBs can be a valuable secondary source of critical raw materials, such as Li, Co and Ni, and partly reduce the pressure on their supply chain.^[3]

In line with the increased consumption of LIBs, the capacity for recycling significantly grew in recent years, with a number of strategies being implemented - from more conventional pyro- and hydrometallurgy, to emerging ones such as direct recycling.^[4] From these, hydrometallurgical processes often achieve some of the highest recovery and separation efficiencies for all LIB inorganic constituents.^[5] Nevertheless, some challenges remain, such as the dependence on hazardous chemicals and generation of secondary waste and emissions.^[6] The leaching step is often considered, by life cycle assessments (LCAs), to be one of the most impactful on the environment due to the excess use of reagents and their secondary emissions.^[7] LCAs also indicate that methodologies relying on electrochemical processes can provide better techno-economic and environmental impacts.^[6, 8] Improved efficiency or selectivity may also be achieved using electrochemical techniques. Recently, electrochemically-assisted methods were used to leach LIB chemistries (e.g. lithium iron phosphate (LFP), lithium manganese oxide (LMO) and lithium nickel cobalt manganese oxide (NMC)).^[9] These types of methods contrast with conventional methods by being less energy-intensive than pyrometallurgy and less dependent on corrosive chemicals than hydrometallurgy. Moreover, the potential for competitive leaching efficiencies and promising techno-economic and environmental performances has been demonstrated. They could also be used for metal separation and recovery, through strategies such as electrodialysis and electrosorption,^[10] enhancing the selectivity of existing materials. More important for this work, the combination of electrochemical methods and leaching enhanced dissolution of metals while allowing for more benign extraction conditions.^[11] For example, Yang *et al.* ^[12] used 0.05 M K_2SO_4 aqueous electrolyte to selectively recover Li with a high efficiency (95 %) from spent lithium-ion nickel cobalt manganese oxide (NMC) batteries, using the spent cathode as the working electrode. Watson and colleagues,^[13] on the other hand, achieved complete extraction of all target metals from a coating of NMC on a glassy carbon electrode, although the process required the use of hydrogen peroxide combined with HCl.

Alternative electrolytes, such as deep eutectic solvents (DESs), also emerged for electrochemically-assisted leaching. Pateli *et al.* used choline chloride:ethylene glycol as an electrolyte, applying an oxidative potential to coated metal oxides on the working electrodes.^[11b] This allowed an increase in the dissolution of nearly all metal oxides when compared to chemical use of the solvent, in some cases by multiple orders of magnitude.^[11b] Meng and colleagues also used an electrochemically-assisted leaching strategy reliant on malic acid at mild temperatures and high potentials to leach over 90% Co and 94% Li from lithium cobalt oxide (LCO).^[11a] Thus, the use of scalable electrochemical processes in the leaching step could be a viable route to achieve better LIB recycling processes. The direct usage of the spent cathodes as electrodes could significantly decrease the required hazardous chemicals, high energy requirements and time expenditure in the overall LIB recycling process.^[6] Ultimately one-pot strategies could arise as streamlined versions of these processes, in which not only leaching but also pre-treatment and recovery are performed. An example was reported by Liu and colleagues using hydroxylated solvents to affect both electrochemical oxidation of metal from a waste printed circuit board powder dispersion, followed by their electroplating in the same electrochemical cell.^[14] The use of ethylene glycol, similar to DESs, extended the electrochemical stability of aqueous leaching

solutions and improved metal recovery through changes in the coordination environment of transition metals such as cobalt and nickel.^[14-15] While these solvent systems are promising for application in electrochemically-assisted spent battery recycling, as providers of milder, efficient and selective conditions, further work must be carried out to understand their behaviour at different applied potentials and with different waste materials.

In this work, an electrochemically-assisted leaching process was investigated, using hydroxylated solvents as key components of the electrolytes, for the dissolution of cobalt oxide (Co_3O_4) from coated electrodes and subsequent application to real spent and pristine NMC622 cathodes. Importantly in the case of the latter, the cathodes were used without any pre-treatment, namely removal of the aluminium current collector and polymeric binder, greatly simplifying the processing. The obtained competitive electrochemical-leaching efficiencies reinforce the viability of electrochemistry in upstream hydrometallurgical application, benefiting from minimal pre-treatment of the spent cathode and reagent consumption as well as the straightforward scalability of the approach.

Experimental

Chemicals and instrumentation

Glycerol (Gly, > 99 %), ethylene glycol (EG, 99.8 %), hydrochloric acid (HCl, 37 %), cobalt (II,III) oxide (Co_3O_4 , ≥ 99.99 %) and silver nitrate (AgNO_3 , 99.0 %) were purchased from Sigma-Aldrich, and nitric acid (70 %) was acquired from Ajax Finechem (Australia). Lithium nickel cobalt manganese oxide (NMC) active material powder and cathodes ($\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ – NMC622) were acquired from Targray (Australia) and provided through Deakin University Battery Research and Innovation Hub (Australia). All chemicals were used without further purification.

Electrochemical experiments were carried out in a VMP-300 potentiostat (BioLogic, France). The metal slurries were prepared in a PM 100 ball mill (Retsch, Germany) using zirconium oxide balls and grinding jar. X-ray diffraction (XRD) was used to compare cathode materials at different stages with a Panalytical Empyrean (Malvern, UK) with $\text{Cu K}\alpha$ radiation operating with a Cu anode ($K_{\alpha 1} = 1.5406 \text{ \AA}$; $K_{\alpha 2} = 1.5444 \text{ \AA}$) at 45 kV. The resulting diffractograms were analysed using the X'pert Highscore Plus software package and the patterns matched against those in the International Centre for Diffraction Data (ICDD) database. A UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan) was used to confirm metal speciation in the solutions as well as provide a broad estimate of metal concentration prior to more sensitive analysis. Raman spectroscopy was performed using an inViaTM confocal Raman microscope (Renishaw, UK) with N PLAN Leica objectives, using an Ar+ laser (514 nm) with at least 64 scans and a resolution of 4 cm^{-1} . Inductively coupled plasma with mass spectroscopy or optical emission spectroscopy as detectors and quantification methods (ICP-MS or ICP-OES, respectively) were used for metal quantification. A NexION 350X (Perkin Elmer, USA) and Activa M (HORIBA Jobin Yvon, USA) instruments were used for ICP-MS and ICP-OES, respectively. In all cases, the solutions were diluted in a 2 % (v/v) nitric acid aqueous solution, after filtration through a $0.45 \text{ }\mu\text{m}$ PTFE membrane. External ICP grade calibration standards were provided by Perkin Elmer and an internal standard solution of In and Rh was used for quality control of the analysis and

correction of matrix effects. These calibration standards for all metals were prepared in 2 % HNO₃ as well.

Electrochemically-assisted leaching setup

A three-electrode setup was used in this work. A titanium mesh (grade 1, Titanium Suppliers Australia) was used as working electrode (WE) for experiments involving coating of the Co₃O₄ active material. The original mesh had a thickness of 1 mm, apertures of 3 mm per 6 mm and was cut into strips of about 70 mm by 10 mm. These electrodes were washed in 10 wt.% nitric acid aqueous solution and deionized water between experiments. During electrode investigation, a titanium mesh coated with IrO₂ was used as comparison, as well as a glassy carbon (GC) microelectrode, polished using the conventional water-alumina slurry.^[16] In all experiments, a platinum wire was used as a counter electrode, after being cleaned with a butane torch. The reference electrode was Ag⁺/Ag, using a silver wire immersed in a solution of 10 mM AgNO₃ in EG, separated from the electrolyte by a glass frit. When the working electrode was the spent cathode of NMC622 cells, a strip of 3 cm by 1 cm was supported by a polytetrafluoroethylene (PTFE) sample holder with titanium conductive material. A schematic representation of the experimental setup and preparation of the metal-coated titanium mesh working electrode is shown in **Figure 1**. The Co₃O₄ powder was mixed with EG in the ball mill for 30 minutes at 250 rpm and then painted on the titanium mesh, followed by drying at 40 °C for at least 3 hours prior to being used. The current density was normalised to the geometric surface area of the WE, in the cyclic voltammograms (CVs) during electrode investigation and electrolyte electrochemical window determination, as well as in the chronoamperograms during electrochemically-assisted leaching.

Electrochemically-assisted leaching of Co₃O₄

The electrochemically-assisted of leaching of Co₃O₄ coated on titanium electrodes was

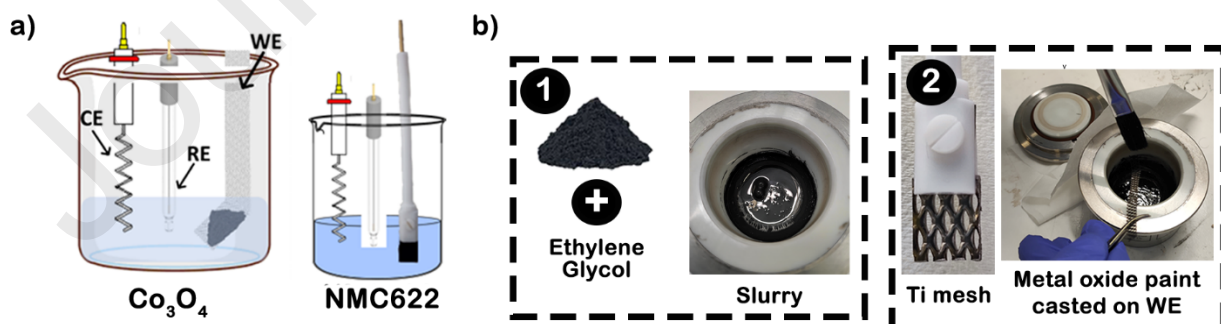


Figure 1. a) Schematic representation of the experimental setup used for electrochemically-assisted leaching experiments, using either a titanium mesh coated with a Co₃O₄ slurry (left) or the spent cathode from NMC622 cells (right) as working electrodes (WE), a platinum wire as counter electrode (CE) and a Ag⁺/Ag reference electrode (RE). b) Preparation of the Co₃O₄ slurries by mixing the active material with ethylene glycol, mixing in the ball mill for 30 minutes at 250 rpm and painting it on the titanium mesh, forming the WE after drying.

carried out in the experimental setup described in **Figure 1**, using either 0.5 M HCl in EG, 0.5 M HCl in 25 % (v/v) Gly in water or pure EG as electrolytes. All solutions were prepared gravimetrically and mixed, as in our previous work on chemical leaching,^[17] and bubbled with N₂ for 30 minutes prior to starting the electrochemically-assisted leaching experiments. These experiments were conducted for 24 hours at 40 °C at various applied potentials, ranging from -0.75 V to 6 V vs the reference electrode, using 3 mL of electrolyte. The leaching efficiency was calculated according to **Equation 1**:

$$\text{Leaching efficiency (\%)} = \frac{m_f(i)}{m_i(i)} \times 100 \quad (1)$$

where m_f and m_i correspond to the final leached mass and initial mass of a given metal, respectively.

Application to NMC622 cells

The NMC622 pouch cells were provided by Deakin University Battery Research and Innovation Hub (Australia), and were comprised of Li-metal anode and NMC622 cathodes and a 3.2 M lithium bis(fluorosulfonyl)imide (LiFSI) in *N*-propyll-*N*-methyl-pyrrolidinium bis(fluorosulfonyl)imide ([C₃mpyr][FSI]) ionic liquid electrolyte with a molar ratio of 1:1, for a total of 5 layers of cathodes separated from anodes by a Celgard 3501 separator, prepared according to their work.^[18] The commercial cathodes (Targray (Australia)) are composed of NMC622 active material, carbon black and polyvinylidene fluoride (PVDF) binder, all coated on an Al foil current collector, with an active material mass fraction of 96 %. The composition of NMC622 was confirmed to be LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ by total dissolution of the spent cathode in 8 M HNO₃ at 60 °C for 72 h and measurement by total reflection X-ray fluorescence spectrometry prior further studies, as well as by XRD as indicated below. The cells were dismantled in an argon-filled glovebox after 17 cycles (**Fig. S1**) and stored for further work. In each group of experiments carried out with these NMC622 cathodes, the same cathode layer was used for experimental consistency. The electrochemically-assisted leaching was then carried out at the same temperature without stirring and for 3 hours, at applied potentials of 1.0 V, 1.5 V and 2.0 V, to assess the best potential for highest leaching efficiency and/or selectivity.

For the kinetic studies, the electrochemically-assisted leaching was conducted in a similar way (40 °C, 3 hours, 100 rpm, 50 mL of electrolyte) with aliquots of 1 mL each being collected at 15 min., 30 min. 1 h, 2 h and 3 h. These experiments were carried out at applied voltages of 1.0 V, 2.0 V or 2.5 V with an initial liquid:solid ratio of about 250:1. Each aliquot was filtered through a PTFE syringe filter with a pore size of 0.45 μm and diluted with the blank electrolyte, prior to metal quantification using ICP-OES. The remaining spent cathode was assessed by XRD and compared to material before electrochemically-assisted leaching and the pristine cathode before being assembled into a cell. A chemical leaching control experiment was carried out by dissolving

segments of these cathodes in the 0.5 M HCl in EG and 0.5 M HCl in 25 % (v/v) Gly in water solutions at 40 °C and 2000 rpm for 24 hours, to obtain the maximum values of dissolved metals.

Results & discussion

1. Electrochemically-assisted leaching of Co_3O_4

In our previous work,^[17] enhanced dissolution of metals available in LIB cathodes as oxides was demonstrated in a range of hydroxylated solvents in comparison with conventional acidic aqueous solution. Among those, 0.5 M HCl dissolved in either EG or 25 % (v/v) Gly in water stood out as promising for metal dissolution because of the higher atomic efficiency and safety. These not only demonstrated a high dissolution efficiency but could be more benign as Gly and EG can be less hazardous than conventional corrosive chemical (**Table S1**), and 0.5 M HCl in 25 % (v/v) Gly in water had a high-water content. Hydroxylated solvents can present various advantages for the dissolution of higher valency oxides due to their reducing capacity and their potential chelation of ions in solution. Furthermore, their presence was shown to increase the efficacy of metal oxide dissolution using dilute acid solutions such as HCl, permitting a reduction in the excess acid concentration required.^[17] Thus, in this work, these solvents were considered as electrolytes for the electrochemically-assisted leaching process. This combination allows for a more energy-efficient process design, less dependent on hazardous chemicals, that fits the ‘green’ chemistry principles.^[19]

To better understand the influence of process parameters on the leaching efficiency, a model system composed of a Co_3O_4 slurry painted on titanium mesh, as shown in **Fig. 1**, was studied prior to the application to real waste batteries. It is known that Ti is resistant to corrosive conditions,^[20] not only in terms of acidity but also the presence of chloride, two elements in the electrolytes. Based on these results, Ti mesh was selected as the working electrode for the electrochemically-assisted leaching of Co_3O_4 as a model system using 0.5 M HCl in EG, discussed further below.

A screening of potentials was carried out, as this allows for an understanding of the effect of applying oxidative or reductive potentials, and hence can also provide some insight into the dissolution mechanism. The values obtained for Co_3O_4 dissolution assisted by electrochemistry are depicted in **Figure 2a**, ranging from 29 ± 1 to 1170 ± 35 ppm, corresponding to leaching efficiencies from 2.1 % to 73.1 % - **Fig. S2**).

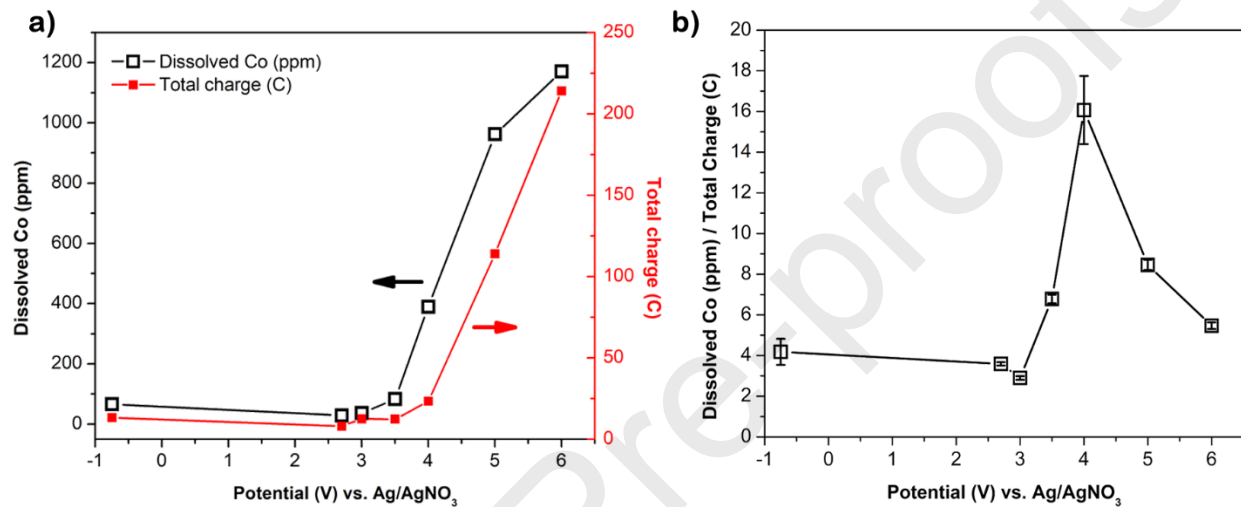


Figure 2. a) Effect of applied voltage on the amount of Co dissolved from Co_3O_4 in 0.5 M HCl in EG with electrochemically-assisted leaching for 24 h at 40 °C at different potentials vs. Ag/AgNO₃ (hollow black squares), along with the total charge passed (hollow red circles). **b)** Ratio of dissolved Co (ppm) per total charge passed during electrochemically-assisted leaching of Co_3O_4 in 0.5 M HCl in EG for 24 h at 40 °C.

The results indicate that the dissolution of Co does not greatly vary when using potentials from -0.75 V to 2.7 V vs Ag/AgNO₃ (from 56 ± 9 ppm to 29 ± 1 ppm), and then starts increasing as potentials are increased – first slowly up to 3.5 V (83 ± 2 ppm), and then significantly from 4 V onwards (376 ± 39 ppm). The highest Co dissolution values were achieved using 5 V and 6 V, 963 ± 29 ppm and 1170 ± 35 ppm, respectively. Although all the experiments were performed for 24 h, the application of 6 V was only stable for up to 7 hours, as the current exceeded the experimental limits at this high voltage.

UV-Vis spectra of the resulting leachates (**Fig. S3**) were compared to the blank electrolyte to assess Co speciation in the solutions produced at each applied potential. The presence of an octahedral catanionic cobalt complex was detected at 520 nm,^[21] but only in leachates obtained using potentials ≥ 4 V, consistent with the results in **Figure 2a**. Note that no assignment is made as to the nature of the other inner-sphere ligands, either water or EG, as there is water present in the electrolyte (≈ 2.7 wt.% by Karl-Fischer titration).

The dissolution of the metal ions in this process is a result of the synergistic effect between the applied oxidative potential and HCl. The applied potential can disrupt the spinel Co_3O_4 lattice as Co ions oxidize into Co^{3+} or highly unstable Co^{4+} and disturbs the charge balance in the structure.^[22] This lattice destabilization can be intensified at very high potentials (> 4 V) in which

oxygen evolution side reactions can take place. The exposure of the oxide surface to HCl results in its protonation, which further contributes to lattice destabilization. Finally, chloride ions interact with the exposed charged surface sites to stabilise the resulting species in the liquid.

As a control, the same experimental set-up with no applied voltage yielded a negligible Co dissolution of less than 10 ppm (1.2 ± 0.3 % leaching efficiency), proving the vital role of electrochemistry in the dissolution step. A similar result was obtained when the chemical dissolution control experiment was carried out in another electrolyte, 0.5 M HCl in 25 % (v/v) Gly in water, with 6.8 ± 1.6 % leaching efficiency achieved. Additionally, electrochemically-assisted leaching at 4 V in EG but in the absence of the HCl electrolyte resulted in < 1 ppm of Co (2,500 times lower than in the presence of HCl, leaching efficiency < 0.1 %). Those two control studies demonstrate a synergistic effect of combining HCl as a leaching agent with an appropriate applied potential to significantly improve the anodic dissolution of Co_3O_4 .

Previous work by Pateli *et al.*, in electrochemical metal oxides dissolution was carried out using 2.7 V between a WE and a CE, in a EG:choline chloride deep eutectic solvent (molar ratio 2:1), at 50 °C for 48 hours.^[11b] In their case, their Co dissolution reached over 590 ppm, whereas we were able to leach almost double the amount by modification of the experimental conditions. Unfortunately, the leaching efficiency was not reported, making it difficult to compare the results. Further, in their work, a differential potential between two electrodes was used, while here we used a 3-electrode setup to measure the applied voltages.

Considering the tested potentials, a question remains regarding the dominant dissolution mechanism, namely the breakage of the metal-oxide bond *vs* metal reduction process. For instance, applying a reductive potential at -0.75 V did not lead to significant metal dissolution, so there was no confirmation that more negative potentials would be beneficial. For a better understanding of the effect of the potentials in the dissolution of Co_3O_4 , the total charge passed at the WE was investigated (**Fig. 2a**). When compared to the dissolved Co (**Fig. 2b**), this ratio can give information on the efficiency of the process, including any side reactions or degradation of the WE or the electrolyte.^[23] On average, it was observed that 3.6 ± 0.6 ppm of Co was dissolved per C up to 3 V *vs* Ag/AgNO₃. The electrochemically-assisted leaching process became more efficient by increasing the potential from 3 to 4 V (16.1 ± 1.7 ppm Co per C), and then decreased (8.5 ± 0.3 ppm Co per C). This trend suggests that around 4 V *vs* Ag/AgNO₃, a change occurred, enhancing Co dissolution, but after 4V, the process became less energetically efficient. Several factors could play a role in this detrimental electrochemically-assisted leaching performance at higher voltages, related to the electrochemical stability of the working electrode and/or of the electrolyte.

The Ti working electrode undergoes anodic dissolution at these high potentials and corrosive conditions.^[24] This was previously reported for Ti electrodes when chloride (from NaCl) and EG were part of the electrolyte, with the latter being involved in the formation of titanium glycolate complexes observed by UV-Vis in the literature at 340 nm.^[24] Here, a similar band was observed in leachates produced above 4 V (**Fig. S3**), with Ti ions also being semi-quantitatively detected in the leachates by ICP-MS as its signal had an intensity over 2 orders of magnitude higher than the blank. The dissolution and/or passivation of Ti could also promote detachment of Co_3O_4 on the surface of the working electrode, which would disperse in the electrolyte. In fact, at 5 V and 6 V, the resulting leachates had an amber colour (**Fig. S4**), different from the other transparent or pink-coloured leachates.

Another potential contribution to the behaviour over 4 V vs Ag/AgNO₃ could be the degradation of the electrolyte by electrochemical oxidation.^[25] This could also support the darker colour of the leachates. However, no changes could be observed in the Raman spectra of the electrolyte even up to 6 V compared to the pristine one (**Fig. S5**), apart from the possible coordination of Co by EG,^[26] discussed further in the Electronic Supplementary Information (ESI). Additionally, no bubbles were seen during the experiments that could indicate oxygen or chlorine gas evolution due to electrolyte degradation.^[27] In summary, the Ti dissolution and passivation could be the main culprit for the process to become more inefficient at higher voltages.

Nevertheless, it is important to note that the amount of dissolved Co and its leaching efficiency increased to values even comparable to chemical leaching from the literature. The highest leaching efficiency value achieved here (73.1 % at 6 V) was not far from the Co₃O₄ chemical leaching carried out by Eliseeva and colleagues, at 70 % Co, which required higher temperature and acid concentration although a much shorter time (0.57 M H₂SO₄ at 70 °C for 100 min).^[28] Kozhina *et al.*^[29] reported less than 2.5 ppm of dissolved Co from a Co₃O₄ electrode during a cyclic voltammogram in 1 M HCl, although the leaching efficiency was not reported. To the best of our knowledge, no other electrochemically-assisted dissolution of Co₃O₄ has been reported using comparable conditions.

Overall, the dissolution of Co₃O₄ benefits from electrochemically-assisted leaching, allowing Co dissolution using a lower acid concentration. The lack of significant solvent changes in these conditions also suggest a possible reuse of the solvents, which would further improve the sustainability and cost efficiency of the process (**Fig. S6**). Following these promising results, application of this methodology to commercial NMC622 powder and to pristine and spent NMC622 cathodes was investigated.

2. Chemical leaching of NMC622 matrices

The beneficial use of an anodic potential for higher dissolution of Co₃O₄ compared to its chemical counterpart encouraged investigation of its application in a realistic scenario, using spent batteries. It is important to note that the presence of Li, Ni and Mn as well as Co in NMC622 comprises a matrix that has different effects from the application of potential, in contrast with metal systems containing only one metal. Each redox pair has a different reduction potential (more similar between Co²⁺/Co and Ni²⁺/Ni than for manganese and lithium),^[30] with Li not undergoing anodic oxidation in the dissolution process. The layered lattice structure of NMC622 is also a significantly different factor, as it affects the dissolution of Li and consequently the transition metals, being less stable than metal oxides such as Co₃O₄,^[31] and consequently more prone to dissolution.

The PVDF binder could also affect the leaching process as its structure is disrupted by the applied potential and solvent interaction. Thus, this impact behaves differently depending on the leaching stage. Initially, it can act as a barrier to solvent contact with the NMC particles. As it swells and degrades, the leaching rate of metal ions from NMC will increase, maximizing the surface area between NMC particles and the solvent.^[32]

Prior to this direct application discussed below, here a chemical leaching study was carried out at 40°C for 24 hours and stirring at 2000 rpm to establish a chemical control. In this work, NMC622 pouch cells were used, with the NMC cathode rich in Li, Co, Ni and Mn. Those cathodes were prepared as detailed in the experimental section and cycled up to 17 cycles using a [C₃mpyr][FSI] ionic liquid-based electrolyte containing LiFSI. It is important to note that as opposed to the previous results where only the active material was present, these new set of experiments also contain the binder, carbon black and the Al current collector. Two different cathodes were assessed: a spent cathode and a pristine cathode, to evaluate the impact of chemical and electrochemical degradation during the pouch cell cycling on the dissolution process. Additionally, the NMC622 active material as a powder (without binder, carbon black or current collector) was also studied in this first set of experiments. The chemical dissolution results are given in **Table 1**.

Table 1. Leaching efficiency of target metals after chemical leaching of NMC622 active material powder, and NMC622 active material powder with binder and carbon black coated on an Al current collector forming the cathodes, either pristine or spent. These values were determined following quantification by ICP-MS.

Solvent system	Type of NMC622	Leaching efficiency (%)				
		Ni	Mn	Co	Li	Al ^a
0.5 M HCl in EG	Powder	99 ± 1	85 ± 3	93 ± 4	93 ± 6	N/A
	Pristine cathode	79 ± 2	78 ± 4	89 ± 4	87 ± 7	82 ± 6
	Spent cathode	69 ± 1	69 ± 4	68 ± 4	78 ± 8	72 ± 6
0.5 M HCl in 25 % (v/v) Gly in water	Powder	99 ± 1	85 ± 2	94 ± 2	95 ± 4	N/A
	Pristine cathode	72 ± 1	72 ± 4	70 ± 4	84 ± 8	91 ± 8

Spent cathode	71 ± 1	70 ± 4	71 ± 3	86 ± 7	66 ± 4
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^aThe extraction efficiencies were calculated considering the initial mass of each metal in the NMC622 matrix, after subtracting the mass of Al foil in the pristine and spent cathodes. This mass was calculated based on cathode dimensions, with a thickness of 0.0018 cm and density of 2.7 g.cm⁻³ of the Al foil.

Leaching the three NMC622 samples with 0.5 M HCl in EG produced a clear pink solution with the presence of cathode fragments, while the leachates of 0.5 M HCl in 25 % (v/v) Gly in water were black-coloured with suspended particles (**Fig. S7**). This already suggests important differences regarding NMC622 dissolution based on the chemical composition of the electrolyte.

The chemical dissolution experiments showed higher extraction efficiency values across all the metals present in NMC622 (Ni, Mn, Co and Li) for the powder in comparison to the cathodes, either spent or pristine. This difference likely arises from the presence of other cathodic components such as binder, carbon black and current collector. The binder could negatively affect the leaching process, despite its presence in a small percentage (up to 5 wt. % of the electrode coating), as it promotes interfacial interactions with the active particles and consequent adhesion to the current collector.^[33] In turn, this limits the surface area of the active cathode material particles to the leaching agent.

When 0.5 M HCl in EG was used as leaching agent, the metal extraction efficiency values were lower for the spent cathode (between 68 ± 4 % and 78 ± 8 %) compared to the pristine cathode (between 78 ± 4 % and 89 ± 4%). However, similar metal dissolution, from either pristine or spent cathode, was seen when using 0.5 M HCl in 25 % (v/v) Gly in water except for Al (**Table 1**). Thus, the difference between the dissolution of the pristine and spent cathode in EG-based systems seems to be related to solvent effects rather than any structural change that may have occurred during the brief cycling of the cathode.

Li⁺ dissolution is generally easier, than that of the transition metals or Al, due to its intercalating position between the NMC oxide layers^[34] and does not involve a change in oxidation state.^[35] As such, Li⁺ dissolution occurs to similar extents in both the solvent systems tested. The higher initial Li⁺ dissolution was also observed in other works extracting metals from NMC matrices.^[34, 36] This initial delithiation step can then affect the dissolution of the remaining transition metals, Ni, Co and Mn.^[37]

Thus, both solvent systems were concluded to be viable for the assessment of their performance as electrolytes in electrochemically-assisted leaching of spent NMC622 cathodes.

3. Electrochemically-assisted leaching of spent NMC622 cathodes

To further improve the practicality of the proposed approach, spent NMC622 cathodes from pouch cells (**Fig. S1**) were then used directly as the WE for electrochemically-assisted leaching experiments. The same 0.5 M HCl in EG and 0.5 M HCl in 25 % (v/v) Gly in water solvent were used, however an initial screening of conditions indicated that lower applied potentials than those previously utilised visually yielded a pink solution indicative of Co leaching, between 1 V and 2 V *vs* the Ag/AgNO₃. Those changes would be translated into lower energy intensiveness, as long as the process remains equally or more efficient, and would minimise the extent of eventual hazardous side reactions such as chlorine gas evolution.^[34]

The application of milder potentials in metal extraction from spent NMC622 cathodes was assessed by UV-Vis of the resulting leachates, to assess the presence and speciation of key metal ions such as Co²⁺ and Ni²⁺. The UV-Vis spectra from the resulting leachates after applying 1.0 V, 1.5 V and 2.0 V *vs* Ag/AgNO₃ are shown in **Figure 3**. The UV-Vis peaks at 392 nm, 660 nm and 724 nm are indicative of octahedral Ni²⁺ species,^[38] whilst that at 514 nm is characteristic of the similar cobalt complex, with water or the hydroxylated solvent involved in the coordination shell.^[39] A red shift of the octahedral Co²⁺ band from 514 nm in 0.5 M HCl in 25 % (v/v) Gly in water to 525 nm in 0.5 M HCl in EG was observed, most likely due to the partial dehydration of the cation inner sphere.^[21] In the 0.5 M HCl in 25 % (v/v) Gly in water electrolyte, the relative intensity of the double peak band in the 600 – 800 nm range is different when compared to 0.5 M HCl in EG, possibly due to the speciation change of nickel between the two media. The presence of manganese was not clearly seen in the UV-Vis spectra, although such could be related to a lower molar extinction coefficient or overlapping with the bands from other complexes in the system.^[38b]

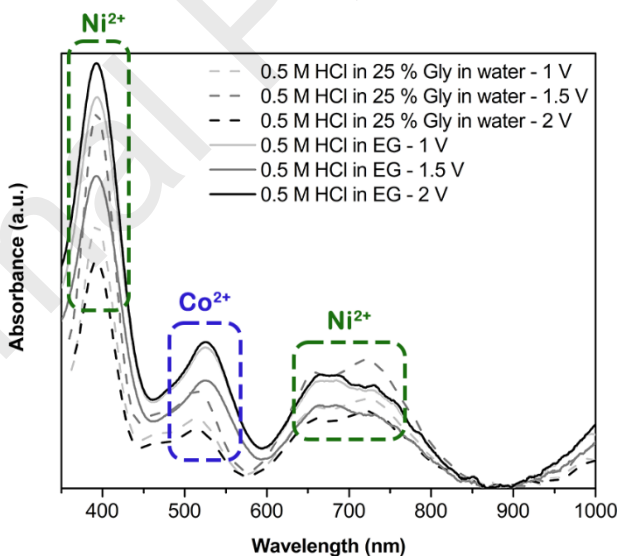


Figure 3. UV-Vis spectra after electrochemically-assisted leaching of NMC622 spent cathode for 3 h at 40 °C in either 0.5 M HCl in 25 % (v/v) Gly in water (dashed lines) or 0.5 M HCl in EG (solid lines) at potentials of 1 V, 1.5 V and 2 V.

The presence of Li⁺ was confirmed by ICP-MS (**Table S2**), as Li⁺ cannot be detected by UV-vis. The Li⁺ values ranged from 36.2 % to 57.9 % depending on the potential and the nature of the electrolyte used. The amount of Li extracted increased with the potential, as well as when using 0.5 M HCl in 25 % (v/v) Gly in water when compared to 0.5 M HCl in EG. The latter was

consistent with the solvent system comparison established during the chemical leaching, most likely due to a more corrosive environment for NMC matrices.^[17]

Despite the lower working potentials used, in all cases when the spent cathode material was used as working electrode during the electrochemically-assisted leaching process bubbles due to gas evolution were visible on the surface of the WE, probably due to dissolution of the Al current collector.^[40] In both electrolytes under study, the spent cathode split into two layers (**Fig. S8**). These layers were not the separation of the NMC coating layer from the current collector, as reported in the literature for acidic media,^[41] but rather disruption of the mechanical integrity of the overall material.

In summary, unlike the electrochemically assisted leaching process of the Co_3O_4 coated on a Ti mesh, for the spent cathode materials the use of 1.0 V to 2.5 V still allowed metal dissolution. While layered NMC is a more complex matrix, it is proposed that the initial delithiation, confirmed through ICP-MS, contributes to the overall metal dissolution of this matrix, being a less stable lattice than the Co_3O_4 spinel structure.^[37, 42]

To better understand the leaching process over time, a kinetic study was carried out by performing an electrochemically-assisted leaching of the spent NMC622 cathode in 0.5 M HCl in 25 % (v/v) Gly in water at 40 °C using the same electrochemical setup as described in **Fig. 1**. This electrolyte was selected as it showed highest metal leaching during the chemical control studies using NMC including Li, but also less Al dissolution (**Table 1**). Moreover, this solvent mixture could have better techno-economic and environmental impact characteristics^[17, 43] when compared to 0.5 M HCl in EG in a practical application due to the difference in water content (**Table S1**). The resulting leaching efficiency values are given in **Figure 4**. Using applied voltages from 1 V to 2.5 V vs Ag/AgNO₃, there was a slight increase in the maximum leaching efficiency at 3 hours for Co, Ni and Mn (49 % at 1 V and between 52 - 62 % at 2.5 V), and much higher in the case of Li (~ 82 % across all applied potentials). The lower leaching of Mn is consistent with the higher stability of metals at higher oxidations states, although this was not evident in the previous chemical control experiment (**Table 1**). It does not seem to be related to the formation of MnO₂ as this species was not detected in the XRD, discussed next.^[30, 37, 44] The Al current collector was still dissolved (**Fig. S9**), as high as 77 % regardless of potential, and similar to the chemical leaching.^[45] Nevertheless, the difference between the redox potential of Al and the target cathode transition metals is such that the presence of Al is not expected to influence a potential subsequent electrochemical separation in an optimized integrated process.^[46] Despite electrochemically-assisted leaching only being carried out for 3 hours, instead of the 24 hours for the chemical control process, the values for the leached Co, Ni and Mn represent between 74 % and 87 % of the values obtained by chemical leaching, and up to 95 % for Li. This highlights the benefit of using the electrochemically-assisted process. The latter is quite relevant as the leaching mechanism can be diffusion-controlled especially at the initial stages, as diffusion kinetics are affected by stirring, becoming more important with a short experimental time.^[17]

The fitting of leaching efficiency vs time values to four different kinetics models^[47] is summarised in **Table S3**. These show that the dissolution rate of both Li⁺ and transition metals increases with the potential, with a more noticeable increase from 1.0 V to 2.0 V than from 2.0 V to 2.5 V. Throughout the range of tested potentials and the various metals, the logarithmic-rate model ($R^2 = 0.99$ in the first 30 min. for all metals, $R^2 \geq 0.80$ in the remaining 2.5 h) was the most

representative of the dissolution mechanism, along with the mixed kinetics one ($R^2 \geq 0.98$ in the first 30 min., $R^2 \geq 0.75$ in the remaining 2.5 h). The kinetic model fittings support the existence of multiple contributions for the dissolution of the various metals, as seen once the kinetic model fitting are prepared separating the first 30 min. of dissolution from the remaining 2.5 hours. This was also seen in our previous work, in the chemical dissolution of NMC111.^[17] Here, in the first 30 minutes, a diffusion-controlled ($R^2 \geq 0.98$) mechanism seemed to have a higher contribution to the leaching kinetics of the four metals, when compared to the surface-controlled one ($R^2 \geq 0.93$). The remaining 2.5 h were better described by a logarithmic-rate kinetic model ($R^2 \geq 0.80$), although other models showed the multiple contributions effect at this slower dissolution stage. The kinetic rate of Li^+ dissolution, considering the mixed-kinetics model (**Table S3**), was over two times as high even at 1.0 V and in the first 30 minutes (0.102 h^{-1} vs. 0.048 h^{-1}), compared to the remaining 2.5 h. The same occurred for Co and Ni ions - 0.048 h^{-1} vs. 0.017 h^{-1} and 0.045 h^{-1} vs. 0.016 h^{-1} – respectively, although with a higher kinetic rate difference between both moments, approaching about 3 times as high, especially for Mn ions (0.032 h^{-1} vs. 0.010 h^{-1}).

These leaching efficiency values were then compared to other works based on NMC 622 materials. A comparative table is available in **Table 2**. It can be inferred from the different solvent systems and operating conditions that processes involving higher energy consumption (higher temperature, applied potential and longer reaction time), as well as higher corrosive chemical concentration, especially inorganic acids, are likely to represent a higher cost and environmental impact.

Table 2. Comparison between the leaching efficiency of the electrochemically-assisted leaching of NMC622 carried out in this work and existing works, considering key operating conditions.

Solvent system	NMC matrix	Type of process	Operating conditions	Leaching efficiency (%)	Ref.
0.5 M HCl in 25 % (v/v) Gly in water	NMC622	Electrochemical	Up to 2.5 V, 40 °C, 3 h	80% Li, 62% Co, 60% Ni, 52% Mn	This work
0.5 M HCl in 25 % (v/v) Gly in water	NMC111	Chemical	40 °C, 24 h	86% Li, 71% Co, 71% Ni, 70% Mn	[17]
0.05 M K ₂ SO ₄	NMC622	Electrochemical	Up to 3.0 V, 25 °C, 3 h	92% Li, 2% Ni, 1% Co, <1% Mn	[12]
2 M H ₂ SO ₄	NMC622	Chemical	50 °C, 45 min.	≈ 90% Li, 45% Co, 44% Ni, 35% Mn	[48]
4 M HCl	NMC811	Chemical	25 °C, 40 min.	≈ 100%, Li, Co, Ni and Mn	[36]
2 M HCl + 0.1 % (v/v) H ₂ O ₂	NMC532	Electrochemical	25 mA/cm ² , 3 h	≈ 100 % total metal extraction	[13]
1.25 M malic acid	LCO	Electrochemical	Up to 8 V, 70 °C, 3 h	94% Li, 90% Co	[11a]

Overall, our values were higher than those reported by Yang *et al.*^[12], who achieved a very small amount of transition metal dissolution using a differential potential of 3.0 V. In that case, the 0.05 M K₂SO₄ electrolyte does not seem to have the same extent of transition metal ion coordination, being more dependent on the higher potential that would be needed to disrupt the structure of the NMC material and reactions involving oxygen from the transition metal layers. Regarding a chemical leaching processes, Vieceli *et al.*^[48] achieved higher Li leaching (≈ 90 %), although only up to 40 % of Co, Ni and Mn were leached in 45 minutes using 2 M H₂SO₄ at 50 °C. At this timepoint, a higher amount of transition metals was obtained with our process, despite milder solvent conditions. Another work by Xuan and team^[36] reported complete leaching of Li, Ni, Co and Mn at 44 °C after almost 40 minutes, showcasing a faster dissolution rate of Li over

the other metals, and NMC622 over NMC111, although under agitation and with a more hazardous 4 M HCl solution. Nevertheless, a two-step leaching mechanism was also proposed, with the first stage being dependent on a significant phase change of the NMC structure as delithiation occurs, consistent with our process. It is important to note that compared to our previous work,^[17] at the 3 hours mark of the kinetics study at 40 °C using the same solvent, 39 % of Co, 44 % of Ni and 57 % of Mn were leached. The leaching rate was also faster in the electrochemically-assisted process in this work, in a shorter time, even at 1.0 V ($> 0.016 \text{ h}^{-1}$ vs. 0.003 h^{-1}) for Co and Ni, but not for Mn ($> 0.010 \text{ h}^{-1}$ vs. 0.197 h^{-1}). In that case, only the active cathode material powder of NMC111 was used, being a simpler matrix. Moreover, the higher dissolution of NMC622 when compared to NMC111 was consistent with the literature with the higher dissolution of transition metals in LIBs with higher Ni-content.^[36] Li was not measured in the previous work.

Thus, it can be concluded that an electrochemically-assisted leaching can result not only in significant leaching efficiencies for both Li and transition metals in a short time and mild conditions, but also comparing well with chemical-focused processes. Once an optimized process is achieved and scaled-up to an industrial level, challenges regarding achieving uniform potentials across the system or impurity accumulation will require further measures. Such can include the disposition of electrodes; controlled electrolyte flow, filtration and recirculation; and real-time monitoring with modelling adaptations.^[32, 49] The resulting impurities either from the binder or other corrosion byproducts would also require not only a separation method, but also the determination of their composition for further processing into added-value materials.^[32, 49a] In the context of LIB recycling, this process can provide benefits comparable to other innovative approaches which focus on minimal chemical consumption, using renewable energy and allowing tunable selective metal recovery.^[50] These include using lower temperature processes and energy-efficient approaches,^[50b, 50c] as well as enhanced post-leaching metal separation,^[50a, 50d, 50e] which will be relevant in the expansion of this electrochemically-assisted leaching to an overall LIB recycling process.

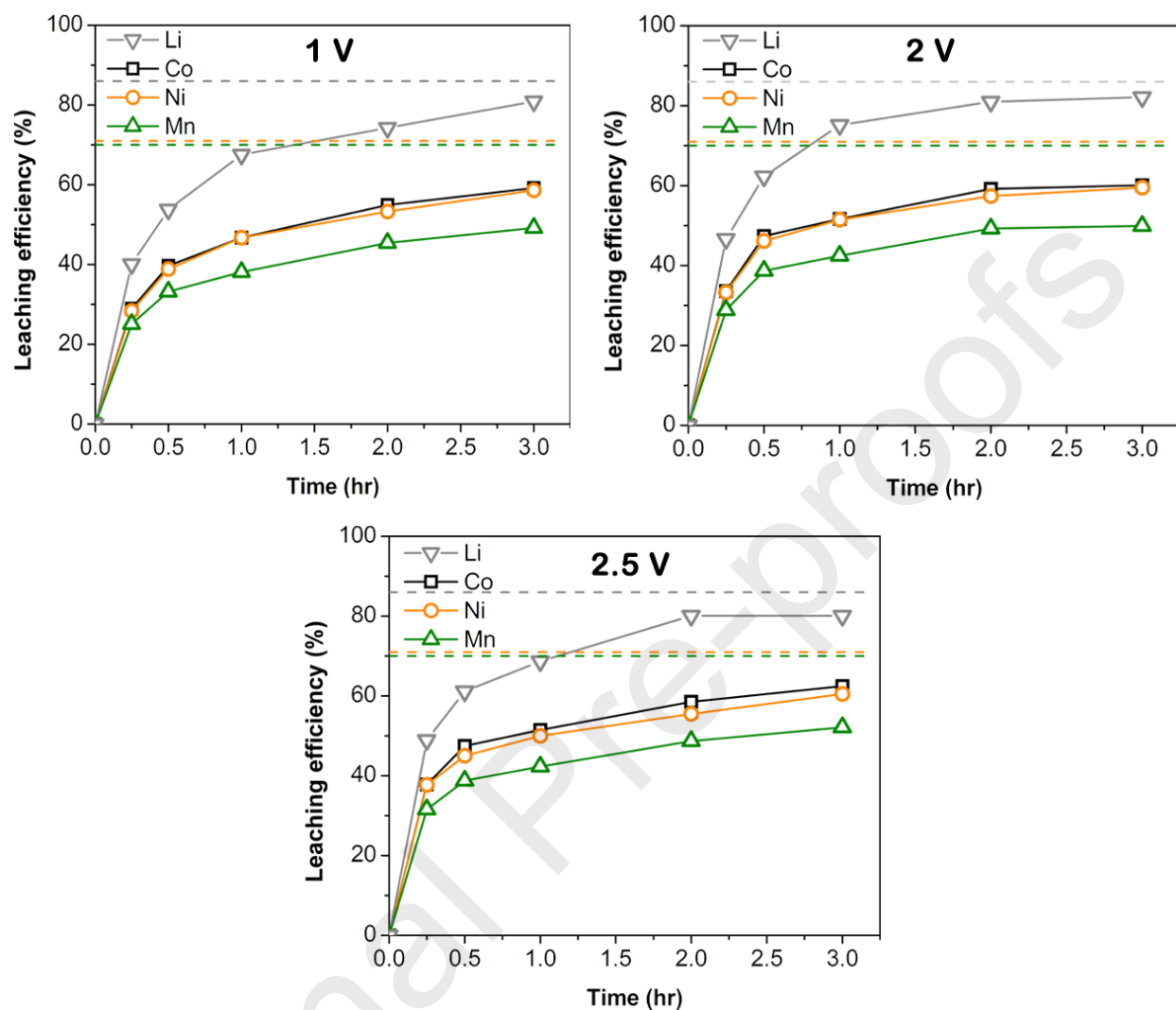


Figure 4. a) Leaching efficiency of Li, Co, Ni and Mn from electrochemically-assisted leaching of NMC622 spent cathode after applying 1.0 V, 2.0 V or 2.5 V vs Ag/AgNO₃ for 3 hours at 40°C, with aliquots collected at 15 min., 30 min., 1 h, 2 h and 3 h. Dashed lines are shown to indicate the corresponding chemical leaching value, for each metal, using also the spent NMC622 cathode and 0.5 M HCl in 25 % (v/v) Gly in water, after 24 h at 40 °C, as shown in Table 1.

For understanding the possible relationship between structural changes of the NMC622 cathodes and leaching efficiency of metals from them, the electrodes before and after leaching were analysed by XRD (Fig. 5a).

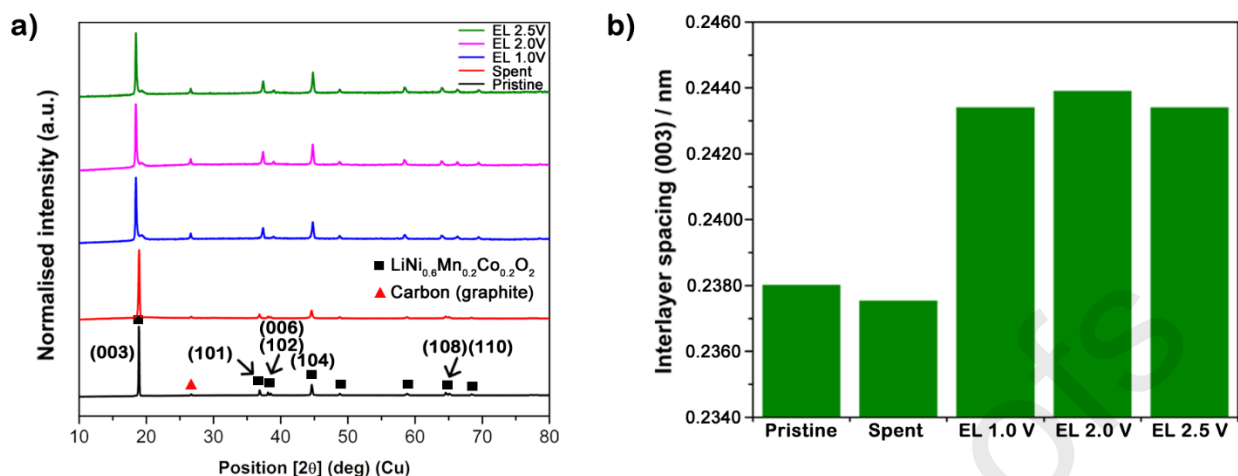


Figure 5. a) X-ray diffractograms of the NMC622 cathode material measured before assembly into the pouch cell (pristine), after disassembly of the pouch cell (spent) and after EL for 3 hours at 40 °C at either 1.0 V, 2.0 V or 2.5 V. **b)** Interlayer spacing of the NMC622 layered structure at each scenario, based on the (003) Bragg diffraction peak.

The spectra show the presence of the NMC622 matrices as well as carbon traces from carbon black. A shift of the pristine NMC diffraction peak (003) at $2\theta = 18.9^\circ$ (**Figure S10a**) to higher degrees was registered upon battery cycling. The same peak shifted to lower degrees following electrochemically-assisted leaching. The downshift of the (003) peak suggests an expansion of the lattice structure in the *c* direction, consistent with the occurrence of delithiation after electrochemically-assisted leaching,^[30, 37] which is also demonstrated by an increased interlayer spacing (**Figure 5b**). This structural change leads to exposure of the oxygen moieties in the transition metal oxide layers, which will repulse each other electrostatically, increasing the distance between them.^[51] At the same time a contraction can occur in the *a* direction and this is in agreement with the (101) peak shift to higher degrees.

The apparent new shoulder of the (003) peak at $2\theta = 19.3^\circ$ was reported to indicate the protonation of the transition metal oxide layers.^[37] Both effects – increased distance between transition metal layers, and their protonation – are also correlated by the distancing between the peaks (108) and (110) (**Figure S10c**).^[37] This separation indicates that the layered structure is still ordered in an hexagonal arrangement simply with larger spacing between layers. Further insights from transmission electron microscopy have also indicated that this increase in the interlayer spacing is coupled with fractures in the NMC particles, which decreased in size as their exposure to the solvent was increased.^[9a, 37]

For the spent cathodes, the interlayer spacing was only slightly lower than for the pristine cathodes, probably related to its final discharge state and hence being mostly lithiated. Prior to electrochemically-assisted leaching, both pristine and spent cathodes had similar XRD spectra, with only slight differences in the (003) peak being noted, as discussed. After electrochemically-assisted leaching, the clear influence of the delithiation process in the structure of NMC622 is consistent with the high Li^+ leaching reported before (**Table 1** and **Figure 4**), as Li dissolution impacts the overall leaching of transition metals. The increase of the relative intensity of the carbon peak at $2\theta = 26.6^\circ$, four-fold between the pristine and spent cathodes (0.06) and the electrochemically-assisted leached samples (0.24), also corroborates the leaching of metals.

The direct use of these spent cathodes, XRD results and lack of mechanical processing with co-agents can allow mechano-activation phenomena to be considered negligible, highlighting the importance of the applied voltage above a certain threshold. Overall, structural changes in the spent cathode lattice during electrochemically-assisted leaching seemed to be independent of the potential used above 1 V. Coupled with the leaching efficiency results, this shows that potentials as low as 1 V vs Ag/AgNO₃ reference electrode could be used for an electrochemically-assisted leaching in 0.5 M HCl in 25 % (v/v) Gly in water.

Considering the relevance of the lattice structure in the metal dissolution mechanism, this work could also be expanded to other layered LIB chemistries, such as NMC811 and NMC111 and even lithium cobalt oxide, as similar dissolution profiles were demonstrated in the literature, for example when dissolving four types of NMC cathodes in HCl-based media.^[36]

Although higher leaching efficiency values were reported in other electrochemically-assisted processes,^[9a, 12, 52] these were obtained under more energy-intensive conditions (higher applied voltages) and required extensive pre-treatment prior to metal recovery.

Following this work, various selective metal recovery routes could be applied, including directly on the electrochemically-assisted leaching setup, such as controlled potential, functionalizing the electrodes through pH or additive changes, temperature and even electrode rotational speed.^[53] The possible reuse of the electrolytes used in this work, as hinted by the lack of significant changes in the solvent, appears as another advantage although further work is required to close the processing cycle. Thus, the proof of concept reported in this work provides an alternative to less chemical-demanding and streamlined processes with potential for industrial application.

Conclusions

In this work, an electrochemically-assisted leaching process was used to enhance the leaching of valuable metals from model Co₃O₄ coated on Ti meshes, as well as untreated spent NMC cathode from used pouch cells with minimal pre-treatment required. The dissolution of Co from Co₃O₄ increased with more positive potentials, achieving up to 1170 ppm of Co or 73.1 % leaching efficiency at 6 V, being competitive with electrochemical and chemical-based leaching.

Following these promising results, segments of real spent cathodes of NMC622 from cycled pouch cells were directly used as working electrodes in milder conditions. The extraction efficiency of Li from the cathode was as high as 82 % using just 2 V vs. Ag/AgNO₃ in only 3 hours, at 40 °C in 0.5 M HCl in 25 % (v/v) glycerol (Gly) in water. Kinetic studies further revealed that similar extraction efficiency values can be attained at potentials as low as 1 V vs. Ag/AgNO₃ in the same solvent, including for Co, Ni and Mn. Despite competing with other metals for dissolution, the presence of Al and the initial delithiation process could also promote the overall leaching efficiencies by disrupting the NMC lattice, as indicated by XRD after the electrochemically-assisted leaching process. These were also better than the results obtained when using only Co₃O₄, as the initial delithiation process in the NMC contributes to the extraction of the other metals, as well as being a more sensitive lattice structure than the cobalt oxide spinel. These

results were promising, considering the direct use of the spent cathode including binder, carbon black and current collector. Ultimately, these electrolytes could be tested for their reuse capacity for multiple cycles, with electrodeposition of Co and Ni between cycles. Once an optimized and streamlined process is achieved, considering any challenges regarding downstream separation or purification arising from less pre-treatment, a full life-cycle and techno-economic assessments should be carried out to benchmark the applicability of this strategy on a larger scale.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data availability statement

The data supporting this article have been included in this article and as part of the Supplementary Information.

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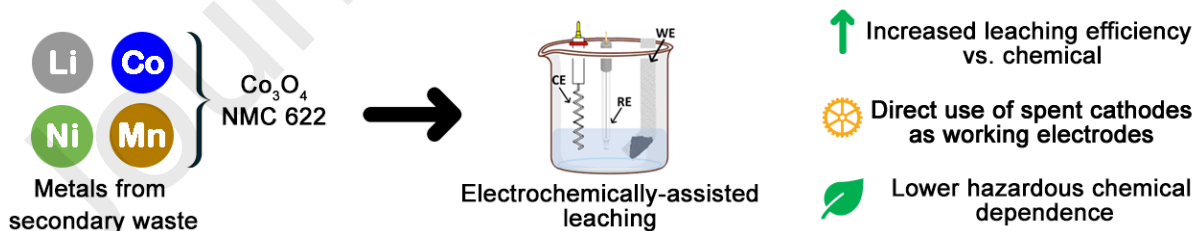
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Table of Contents

TOC description: The use of electrochemically-assisted leaching allowed an enhancement of the overall leaching efficiency of critical metals such as Li, Co and Ni from Co_3O_4 and NMC matrices when compared to a chemical leaching. The direct use of spent NMC 622 cathodes as working electrodes provided a simple and environmentally friendly way of extracting these metals from spent batteries, as less hazardous chemicals such as *N*-Methyl-2-pyrrolidone are required.



Declaration of interests

- 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.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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