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Closing the battery loop: Choline citrate-based deep eutectic solvent to unlock direct cathode resynthesis via chlorine-free solvometallurgy

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HIGHLIGHTS

- Chlorine-free deep eutectic solvent made from choline citrate.
- It dissolves major cathodes including LCO, NMC, LMO, and LFP.
- Eliminating chlorine avoids side products during direct resynthesis.
- High leaching yields combined with direct resynthesis.
- LCA analysis support the sustainability of this strategy.

ABSTRACT

The science and technology behind end-of-life lithium-ion batteries (EoL-LIBs) is a fast-evolving field. Among various solutions proposed to recycle cathode active materials, the solvometallurgy exploiting deep eutectic solvents (DESs) for the leaching of cathode materials is one of the leading research technology due to high efficiencies, low costs of reagents, and absence of wastewater production. In literature, up to now, this method has been exploited to dissolve selected cathode materials and subsequently recover the critical raw materials in the form of salts to be reused for the synthesis of new cathodes. With this work, we propose and demonstrate the feasibility of an innovative and alternative solvometallurgical process, based on the design of a conceptually new DES formulation based on the presence of choline citrate substituting the always-exploited choline chloride, combined with ethylene glycol. This new method enables the leaching of the most relevant and common cathode materials - $LiCoO_2$ (LCO), $Li(Ni/Mn/Co)O_2$ (NMC), $LiMn_2O_4$ (LMO), $LiFePO_4$ (LFP), thus providing high flexibility combined with high efficiency. The leap forward and innovation is the new possibility of the direct resynthesis of cathodes, avoiding the step of metals separation; this is intrinsically linked to the new formulation of the DES, avioiding the presence of chlorine. This new strategy can open new ways for the further development of solvometallurgy and efficient recycling of EoL-LIBs.

1. Introduction

The widespread diffusion of lithium-ion batteries (LIBs) has started since their introduction on the market, and it continues to grow at a fast pace [1,2]. While the market share of portable devices and household appliances is today saturated by this kind of electrochemical energy storage system, the introduction and expansion in the sector of mobility and transportation is at the early stages, but it is expanding quickly [2]. Indeed, LIBs are the device of choice for the switch from the traditional combustion engine to electric transportation; the first LIBs-based car models appeared on the market in the first 2000's, the first electric vehicles' (EVs) millions of sales have been reached in 2017, and the global registration of new EVs in 2024 reached 14 million [3–6]. Moreover, one in five cars is expected to be electric on the roads in the European Union and in the United States, for a total of 23 million by 2030, with a 35% annual increase. Although LIBs are characterized by a combination of

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extremely favorable features, such as high energy density, scalability, reliability and long lifetime [4], the fading of performance is intrinsically unavoidable and dependent both on the LIBs peculiar composition and the employment history of the device. To match the value of the estimated sales, LIBs are expected to reach 0.2 million tons by 2023 [3], and around 8 million tons by 2040 [3,6,7].

Indeed, LIBs are discarded for several reasons (device obsolescence for many portable devices, fading of performance, failure of the device where LIBs are embodied). The question about the fate of the LIBs when they reach the end of their primary life (i.e., the application for which they were originally designed and exploited) is still open. Many strategies have been proposed, mainly for LIBs from retired EVs, ranging from second-life applications (exploiting the dumped but still relevant performance of the LIBs), reconditioning (with healing and/or substitution of specific damaged cells), efficient recycling (with the aim of overcoming today's limitations in metal recovery and environmental footprint) [7,8]. Indeed, today discarded LIBs are conveyed into two main trajectories: disposal in landfills, and low-sustainable recycling. In 2023, global battery recycling reached a capacity of 300 GWh [5]. Industrial recycling for such waste is patchy distributed worldwide, with the major companies operating in this sector (Li-Cycle, Eramet, Umicore, CATL, Accurec, SungEel HiTech) basing their operation on pyrometallurgical and hydrometallurgical procedures; these approaches are based on the smelting at high temperatures ($T > 1000^\circ C$) for the former, while imply the use of water-based inorganic acid solutions for the latter [7,9]. Both processes involve high energy consumption, production of large volumes of wastewater, secondary pollution due to hazardous gases formation, and allow for the recovery of only a fraction of the valuable elements embodied in the LIBs. One of the purposes of recycling is indeed not only avoiding the disposal of waste LIBs in landfills, but mainly the recovery of Li, Co, Mn, Ni, essential for the production of LIBs, but listed by different countries as strategic or critical raw materials due to their low natural abundance, geological scarcity in specific countries, uneven geographical distribution, and/or evidence that their extraction has severe environmental, social, and humanitarian implications [8,10]. The highest concentration of such elements is embodied in the cathodic compartment, as the cathode materials diffused at a commercial level for different target markets and applications are $LiCoO_2$ (LCO), $Li(Ni_x/Mn_y/Co_z)O_2$ (NMC), $LiMn_2O_4$ (LMO), and $LiFePO_4$ (LFP) [7,8,10,11]. Thus the development of improved recycling protocols that combine wide spectrum recovery of several elements, low energy consumption, and low environmental footprint, with high recovery yields, are of high importance to foster the implementation of always more sustainable energy storage technologies. In the very recent years, a great effort has been made in this direction with the development of recycling strategies and approaches based on the exploitation of organic acids [12], bioleaching procedures [13], solvometallurgical approaches [14], low temperature carbothermal treatments [15], generally proposed for the recycling of the cathodic materials [7,16,17]. Among these, the solvometallurgical processes belong to the class of wet metallurgical approaches and identify the branch of extractive metallurgy that uses non-aqueous solvents and/or solvents with a very low water content to extract since their introduction [18]. Typical solvometallurgical leaching media ranges from ionic liquids, organic solvents, deep eutectic solvents (DESs) and solvometallurgy is widely exploited (for example for metals recycling) due to the low water footprint, enhanced selectivity, high metal solubility [19,20]. In particular the use of deep eutectic solvents is encountering great success as DESs are inexpensive solvent, characterized by good thermal stability, low vapor pressure, low or null flammability and toxicity, combined with appealing leaching properties for the degradation of the most common cathode materials, and high metal solubility (thus involving a valuable high solid-to-liquid ratio) [14,21]. The solvometallurgical approaches are characterized by a degradation step where the considered cathode material is completely degraded to obtain a leached DES-based solution. Further steps are thus needed to process these products and isolate the desired metals with satisfying yields and purity; many papers report the possibility of recovering the DES as substantially unaltered and ready for several degradation cycles [22–24]. These subsequent passages are often onerous in terms of the increased complexity of the overall recycling procedure, consumption of reagents/solvents, and difficulty intrinsically connected with the separation of similar elements [25,26]. This effort is needed to obtain electrochemical grade materials, as - in the most common scenario - the recovered materials are reintroduced in the LIBs market circle to produce new cathodic materials. Moreover, it must be stressed that the recovery of CRMs is often performed through precipitation; this implies the addition of high-water volumes to dilute the DES solution and decrease its viscosity.

Analyzing this general scheme (briefly outlined in Fig. 1a), room for improvement can be found by introducing a radical change in the DES system. Indeed, to our knowledge, all the research on the exploitation of DES in the field of LIBs recycling has been based on the use of choline chloride as the Hydrogen Bond Acceptor (HBA) for the DES formation. The presence of chlorine, specifically, is considered and discussed as an essential component for the formation of Type III DES, as proposed in the commonly used classification [27,28]. Indeed, type III DES imply the presence of a Hydrogen Bond Donor (HBD) and an organic salt as per definition [14]; experimentally the choline chloride is always exploited as HBA [14,24,25].

In the present study, we propose a conceptually new DES composition, focusing our attention on the anionic component of the DES and thus substituting choline chloride with choline dihydrogen citrate (Fig. 1b); the final DES proposed in this study is based on choline citrate and ethylene glycol. This allows changing the paradigm in the solvometallurgical approach as the product of the degradation step does not contain chlorine, on the other hand, always expected when choline chloride is used. The presence of chloride moieties hindered the possibility to exploit the leached solution as starting point for resynthesis as chloride will lead to the formation of side products. When choline citrate is proposed the obtained leached solution mimics the composition and conditions of the sol-gel based synthesis as it contains citrate and ethylene glycol (and chlorine). Thus, the proposed method allows for exploitation for the direct resynthesis of the leached cathode material, prior analysis and eventual correction of the metal's concentration and mutual ratio, as schematized in Fig. 1. This enables avoiding the several, complex, time and reagents-consuming steps generally needed for metals' isolation. Moreover, we demonstrate that the DES system cannot be recovered unaltered as the solvent undergoes irreversible compositional changes; we fully characterize the starting DES as well as the DES after the leaching procedure through a multi-technique approach that enabled us to propose a degradation reaction mechanism. The degraded DES can thus be exploited as a matrix for the sol-gel-like synthesis procedure that can be tuned to optimize the composition and morphology of the cathode material considered. Moreover, as a further possibility, the recovery of CRMs by conventional precipitation method can also be implemented, thus incorporating the previously developed strategies. The novelty of this approach is embodied in the correlated patent [29].

We here present the optimized degradation procedure for the most common cathode materials, i.e. LCO, NMC, LMO, and their subsequent direct resynthesis, enabling a closed-loop recycling scheme. The resynthesized materials have been electrochemically tested to provide proof-of-concept of the feasibility of such a closed-loop approach. The same procedure has been exported to a real cathodic black mass (CBM), mainly composed by LCO, thus confirming the possible exploitation under realistic environment. Each step of the process has been characterized via implementation of several techniques (thermal analysis, XRD, FTIR, ICP) to monitor the quality of the obtained product. To complement the experimental work, a Life Cycle Assessment (LCA) has been conducted to systematically evaluate the potential environmental impacts of the proposed recycling method. This approach supports a holistic understanding of its sustainability and enables comparison with

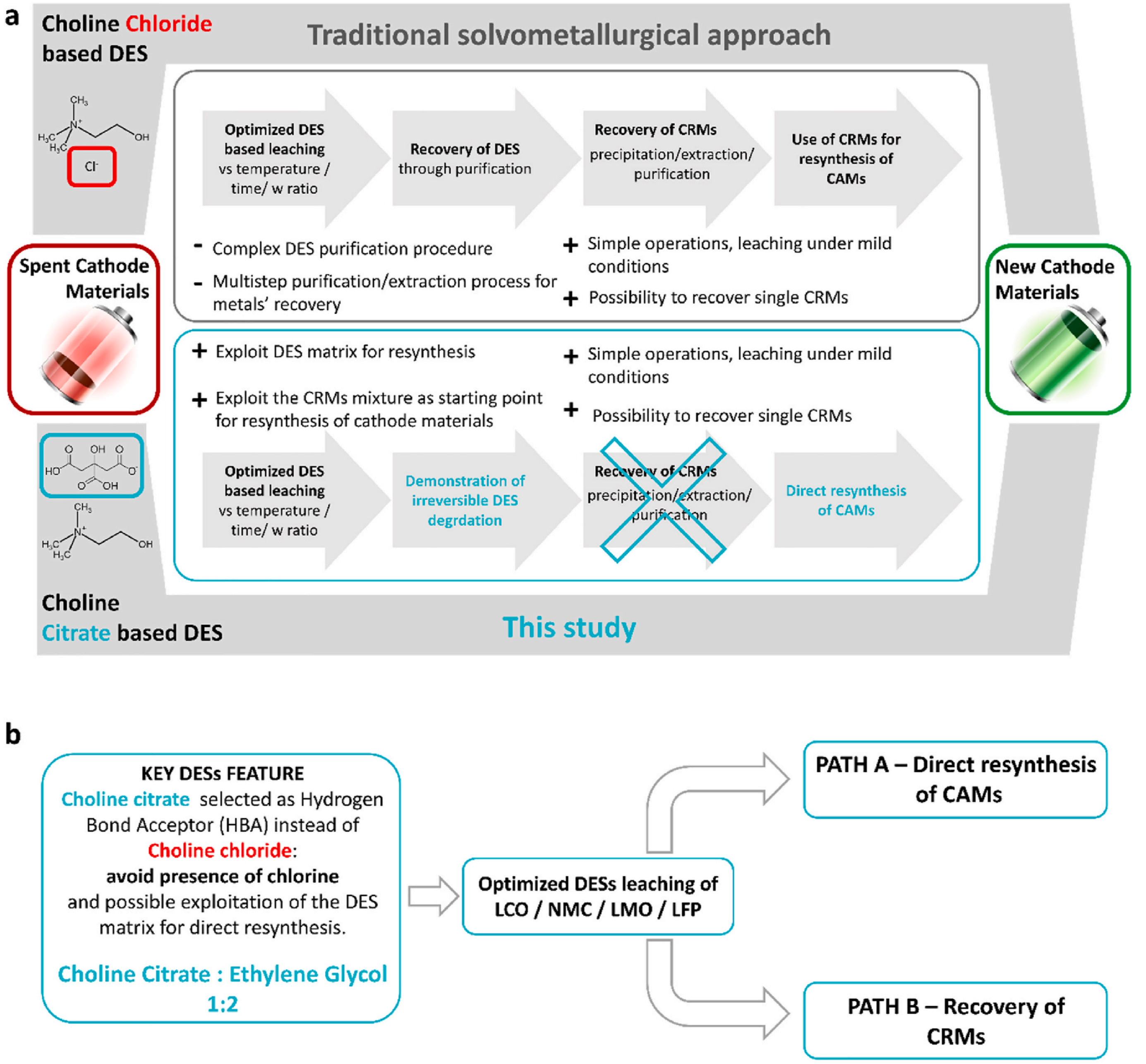

Fig. 1. – Schematic representation of the solvometallurgical approach emerging from the analysis of literature (upper panel) and the variation introduced by the present work; pro and cons are highlighted (a); possible strategies derived from the solvometallurgical approach presented in this study: path A (preferential) allows for the direct resynthesis of cathode materials, while path B is considered as a possible alternative and represent the recovery of critical raw materials (b).

conventional recycling processes [30]. Finally, some additional experimental steps (i.e., the detachment of the cathode from the current collector, the possibility of recovery of critical raw materials and their isolation, LFP leaching) have been considered and their feasibility demonstrated, further expanding the high potential of this new solvometallurgical method.

2. Methods

2.1. Chemicals and materials

Choline dihydrogen citrate (Sigma-Aldrich) and ethylene glycol (Sigma-Aldrich), without any further purification, have been used for the DES preparation. The considered pristine cathode active materials, characterized with XRD and SEM, are listed here:

- $LiCoO_2$ (LCO) 99.8% – Aldrich
- $LiMn_2O_4$ (LMO) 99.5% – Thermo Fisher Scientific
- $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) >98% – Sigma-Aldrich
- $LiFePO_4$ (LFP) – Hydro Quebec

2.2. Experimental section

2.2.1. DES preparation

The Choline citrate and ethylene glycol have been mixed in the desired molar ratio at 90°C for 1 h, or until dissolution of the solid components. For some compositions, it was not possible to obtain a limpid solution, due to the remaining presence of an undissolved part.

2.2.2. Leaching process

The proper amount of cathode powder (100 mg) has been weighed and put in a vial (25 mL volume), with the addition of DES (2-5 g range explored). The leaching process has been conducted in a climatic chamber (ATT DY110C), controlling the temperature and with no stirring. After heat treatment, the solution was filtered to collect the eventual solid residue. Both the solid and the solution have been analyzed through ICP-OES analysis.

2.2.3. Resynthesis

Before moving to the synthesis step, each solution was characterized by ICP-OES to verify that the ratio of the various elements corresponded to that of the desired active material. If an understoichiometry of lithium was detected, Li_2CO_3 was added to the solution to match the desired composition. The solution was then transferred in an alumina crucible and heated at 160°C under stirring on a magnetic plate until gel formation and complete removal of water. Afterward, the obtained gel was treated in a muffle furnace in air to complete the sol-gel synthesis at 750°C identified as the best temperature (range of tested temperature: 550°C-850°C) for 10 h; the obtained powders were characterized by XRD and SEM-EDX. In the case of LFP, the resynthesis process passed through a first hot treatment at 160°C under stirring to eliminate water, followed by a microwave treatment (400°C for 1 h) in air to eliminate the organic matrix. The as-obtained powder has been treated in a tube furnace in an inert environment for 5 h at 750°C, adding 30 wt% of glucose as carbon precursor.

2.2.4. Precipitation process

Oxalic acid (Sigma-Aldrich) was added to the leached solutions in large excess, considering a nominal ratio of Co: oxalic acid (1:10). The obtained solution was then stirred for 30 min at 40°C until complete precipitation of a pink solid, that has been washed and characterized. Both the liquid and solid phases have been tested through ICP-OES to assess the Co content.

2.2.5. CBM collection

The Cathodic Black Mass (CBM) was collected from spent smartphone batteries which have been discharged by immersion in saline water for a safe disassembly. After the opening of each cell, the cathode side was manually separated from the anode side, and the CBM was detached from the current collector by scratching with a spatula.

2.3. Characterizations

The TGA/DSC measurements have been performed on ~20 mg of DES solutions in alumina crucibles using a Mettler Toledo TGA/DSC1 STARe® SYSTEM. The analysis has been carried out in the 30–1000°C temperature range, with a heating rate of 10°C min^{-1} under constant air flux of 50 mL min^{-1}. For the determination of water concentration in the sample, DES solutions were treated at 100°C for 2h in air. The DSC analysis was carried out on ~ 20 mg of DES solutions in Al crucibles using a DSC1 Star® System Mettler Toledo; the samples were tested in the temperature range from −100°C to 180°C in N_2 atmosphere with a flux of 80 mL min^{-1} and with a heating ramp of 10°C min^{-1}. The TGA and DSC data were evaluated using STARe® Software. Viscosity measurements were performed with an Anton Paar rheometer. A parallel plate setup was used to perform shear tests with shear rate of 50 s^{-1}. The measurements were carried out at 25°C.

IR – FTIR analysis has been performed exploiting the Attenuated Total Reflectance (ATR) mode on a Thermo Fisher Scientific Nicolet iS20 instrument considering the 4000–550 cm^{-1} range, with 32 scans and a 2 cm^{-1} resolution. UV-visible data have been collected on a Cary 60 UV-Vis Spectrophotometer, equipped with a Xenon flash lamp (80 Hz).

NMR – ^{13}C hpdec spectra have been collected on the DES samples without any addition of water or solvent using a 9.4 T widebore Avance III Bruker spectrometer with a 4.0 mm probe under static conditions (MAS rotation hindered by high viscosity of the system). Reference solutions of the pure DES components (choline citrate dissolved in water and ethylene glycol) have been collected under static conditions.

SEM-EDX data have been collected on a Zeiss Gemini 500 field emission source (FEG). The microscope can operate with acceleration voltages of 0.5-30 kV, beam currents of 3 pA-20 nA, and has a nominal resolution of 0.6 nm at 15 kV.

The ICP-OES samples have been diluted with distilled water to have an estimated concentration of any metals between 0.5 ppm and 50 ppm and acidified with 2% HNO_3 (ultrapure 65% HNO_3, Merk) to prevent metal precipitation and adsorption. The calibration of the instrument has been operated using a multi-elements standard (Sigma Aldrich, Standard ICP multi-elements solution XVI Certipur®) considering five concentrations in the 0.5 - 30 ppm range. ICP-OES was performed by a Thermo-Scientific CAP7400 Duo, equipped with a quartz torch and charge injection detector. The nebulization gas flow has been set to 0.5 L min^{-1}, power RF to 1150 W, with a cooling gas flow at 12 L min^{-1}.

Leaching efficiency was evaluated using the following formula (Equation (1)):

$$Leaching_{M} = \frac{C_{M,ICP} * V_s * F}{m_M} * 100$$

with $C_{M,ICP}$ as the metal concentration from ICP analysis, V_s is the initial volume of the leached solution, F the dilution factor, m_M the amount of species M in the starting cathode material.

Powder diffraction data have been collected on a Rigaku Miniflex 600 using Cu Kα radiation in the 10°-80° angular range, 0.02 step size and 0.5° per minutes of scan rate.

To evaluate the oxidation state, XAS data were collected at the Italian CRG XAS beamline LISA, BM08, of ESRF [31] in transmission mode, using two 1 bar N_2-filled Ionization chambers to measure the incoming and transmitted beam within the experiment IH-MA-634. The samples were encapsulated in a Kapton envelope and measured at the 3d metal edge, at the same time a metal reference was also measured to ensure good energy calibration. Due to the energy range investigated, the beam was monochromatized with a Si-111 Double Crystal Monochromator, and the harmonics were rejected with a Si mirror. The data were then analyzed with thelarch package, an open-source library and set of applications for processing and analyzing X-ray absorption and fluorescence spectroscopy data [32].

2.4. Electrochemical measurements

2.4.1. Electrode preparation

For each cathode, the electrode slurry for each cathode material has been prepared by using the newly resynthesized active material LCO, NMC, LMO mixed with conductive carbon black (Imerys, Ensaco 35P), and binder (PVDF 6020) in a 8:1:1 wt ratio. The binder is first dissolved in N-methyl-2-pyrrolidone (Sigma-Aldrich) by Ika T10 basic Turrax mixer for 15 min. After that, the conductive carbon and active materials have been added and mixed for 20 min. The so obtained slurry was then cast on an Al foil using a doctor blade (5 mils thickness) and then dried in two steps: overnight at room temperature, and under vacuum at 100°C for 3h the following day. Disks of 1.6 cm diameter have then been cut and used for assembling the coin cells (CR2032-MTI Corp) in half cell configuration, with lithium metal as counter electrode and LP30 as electrolyte (Sigma-Aldrich, 1 M $LiPF_6$ in ethylene carbonate: dimethyl carbonate, 50:50 vol%). As references, pristine cathodic materials have been used to produce cathodes to be tested in cells with the same configuration.

2.4.2. Electrochemical tests

To evaluate the electrochemical performance of the resynthesized active materials, the cells have been tested via constant current measurement. For all systems, 0.1C current have been used (0.14 mA g^{-1} for LCO and NMC, 0.15 mA g^{-1} for LMO, 0.17 mA g^{-1} for LFP) and oxidation and reduction have been limited to the 3-ited to the 3-4.5 (2.8-

3.7/for LFP) V vs Li^+/Li range.

2.5. Environmental sustainability assessment

Potential environmental impacts of producing RCMs are analyzed using a cradle-to-gate LCA for four scenarios, i.e., LCO, NMC, LMO, and LFP-based cathodes. The LCA method quantitatively assesses the different environmental impacts of a product, a synthetic process route, or a service according to ISO standards 14044 [30]. In this study, the functional unit is defined as 1 kg of RCM, and the system boundaries are set as cradle-to-gate, including raw material supply and chemical processing. Primary data for the foreground system are collected from laboratory-scale experiments, including the preparation and use of DES, as well as the energy consumption of equipment involved in leaching and synthesis steps. Energy inputs are calculated based on the rated power and operational time of laboratory devices such as the Milestone ETHOS UP microwave and Carbolite STF 16/180 furnace. Background processes, including energy production and chemical supply chains, are modeled using the ecoinvent v3.9 database within the openLCA v2.3 software. ENTSO-E (European Network of Transmission System Operators for Electricity) is selected as the electricity supply mix in the modeling. Environmental impacts are assessed using the ReCiPe 2016 midpoint (H) method, which includes 18 impact categories. Five impact categories—including global warming potential (GWP), terrestrial acidification (TA), mineral resource scarcity (MR), water consumption (WC), and particulate matter formation (PMF)—are selected for detailed analysis based on relevance in previous LCA studies focused on energy storage systems [33]. In addition, to better understand the influence of electricity consumption on environmental impacts, a sensitivity analysis is conducted using four scenarios combining variations in electricity use and renewable sourcing.

3. Results and discussion

The choline citrate – ethylene glycol 1:2 DES (ChCitG 1:2 in the following) has been prepared and fully characterized after a wide prescreening of possible choline citrate and ethylene glycol range of molar ratio from 3:1 to 1:20, as discussed in Supplementary Information Section 1.1; detailed information on preparation, selection, and properties are reported in Supplementary Information 1.2.

To summarize the main results, the ChCitG 1:2 DES can be successfully and easily obtained through mixing and heating the two commercial components illustrated in Fig. 2, where the ^{13}C NMR spectrum identifies the two molecules, and no extra peaks are detected, confirming it is a non-reactive physical mixture [34,35]. The resonances of the ChCitG 1:2 system do not show a significant shift with respect to the signals of choline citrate in aqueous solution and ethylene glycol (reported as references in Fig. 2a); it must be stressed that the ChCitG 1:2 data have been collected after water content equilibration (i.e. water uptake due to storage under ambient condition as discussed in the Supplementary Information Section 1), thus a dissociation of the citric moieties can be expected. The FTIR spectrum (Fig. 2b) presents the characteristic choline citrate signals (3200 cm^{-1} corresponding to OH stretching and ~3000 cm^{-1} corresponding to N-H stretching) that overlap with the ethylene glycol contribution (broad band in the 3300-3000 cm^{-1} range) [34–36]. The obtained DES is strongly hygroscopic, and when exposed to air it quickly equilibrates with a water uptake of ~20% as determined from thermal analysis (Fig. S1). The thermal stability is up to 150°C, and needless to say, the viscosity strongly depends on the water content, as reported in Fig. S1.

The hygroscopicity of several DES compositions has been previously observed and characterized, and the water content here described is in good agreement with the already reported trends [37]. Although DESs hygroscopicity is known, it is often not discussed or neglected in the specific field of application of lithium-ion battery recycling, as recently evidenced in the critical review work highlighting that an arbitrary amount of water is considered in DES formulation [14]. The presence of water can be considered beneficial for the application here proposed as it can drastically lower the viscosity of the system (moving from 7489 mPa*s to ~200 mPa*s the as prepared and water-equilibrated DES), as also discussed in our recent work on similar composition [35]. Moreover, the water is here expected to be strongly dissociated, thus favoring the degradation of the cathodic material, which is, in most cases, controlled by a diffusion mechanism and by the acidity of the solvent [28,38–42]. For this reason, the DES considered in the following is prepared and stored in air, with a water content in the above-mentioned range of 20-25% depending on the ambient conditions. This ease of preparation and storage can be considered as a propitious characteristic in view of the process scaling up.

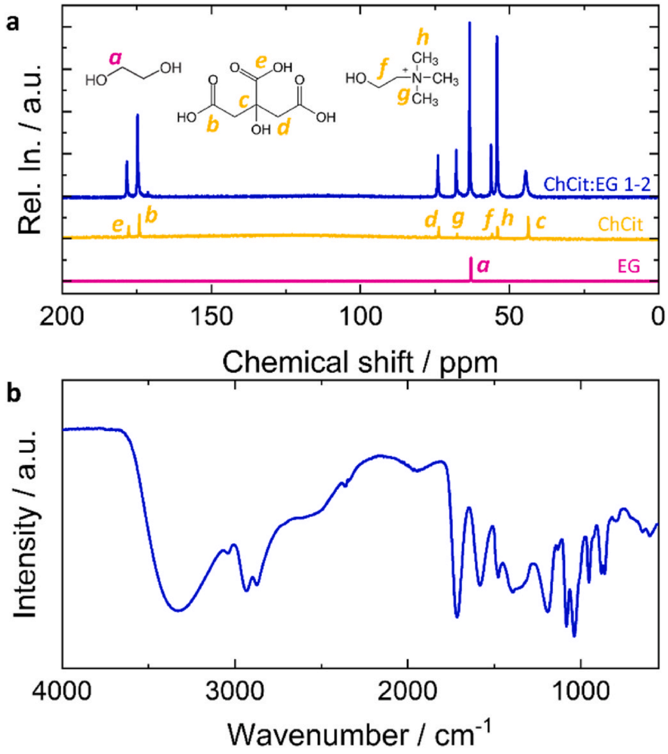

Fig. 2. ^{13}C hpdec spectra of the ChCitG 1:2 collected after 21 days from preparation under storage in air (blue trace) and reference spectra of choline citrate in aqueous solution (orange trace) and ethylene glycol (pink trace) together with resonance attribution (a); FTIR spectrum for the ChCitG 1:2 collected after 21 days from preparation under storage in air (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The so-obtained ChCitG 1:2 has been exploited for the degradation of different cathodic materials, namely $LiCoO_2$ (LCO), $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC-111), $LiMn_2O_4$ (LMO) selected as representatives of today's market share of LIBs and today's waste LIBs [6,43,44]. LFP is also considered, and results are reported in a dedicated section, Additional 3, later in the text. Pristine, commercial-grade cathode powders have been used for this first step as proof of concept to verify the efficiency of the DES in degrading the cathodic materials; their characterization is presented in Supplementary Information Section 2. As discussed in the introduction, the use of DES for degradation of cathode materials is now widely explored, and several studies have already been reported demonstrating that the main parameters in controlling the leaching reaction are the temperature, holding time, and the cathode-to-DES weight ratio [14,45]. We thus explored the effect of these parameters, and the optimization of the leaching procedure has been carried out for all the materials. Fig. 3 presents the leaching efficiencies in terms of Li% obtained in the DES-based solution as determined from ICP analysis.

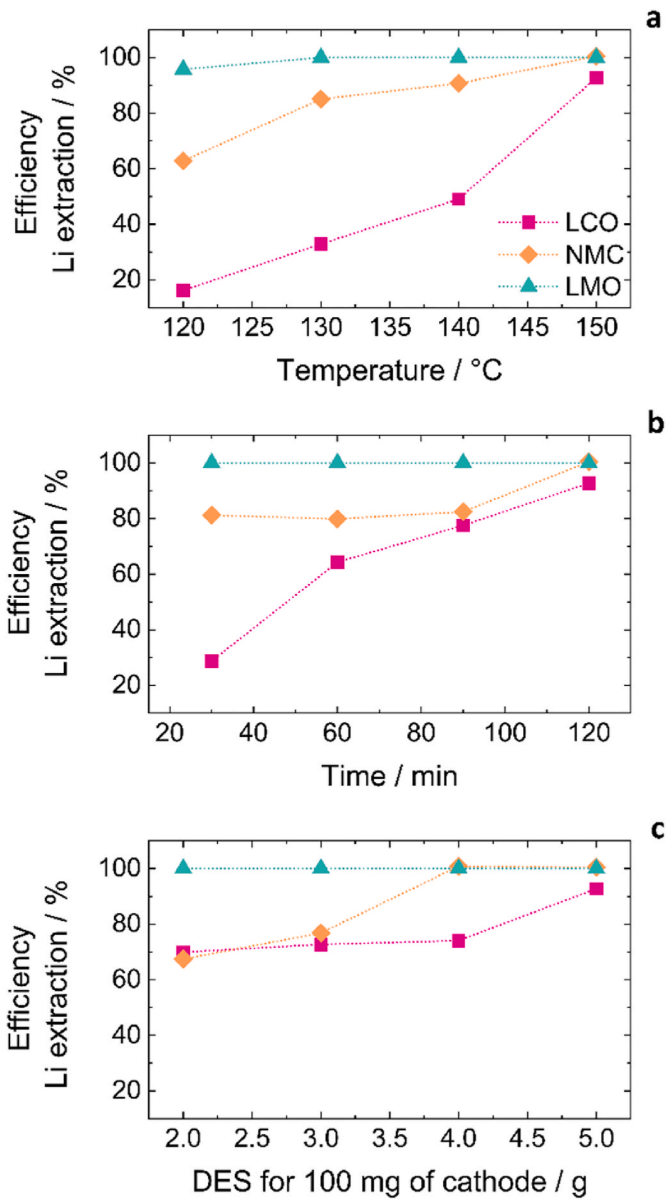

Fig. 3. – Leaching efficiency with respect to Lithium extraction as function of temperature (a), time (b), and weight ratio between DES and cathode material (c) as obtained from ICP analysis for LCO, NMC, LMO cathode powders.

Lithium has been selected as the descriptor of overall efficiency since it is the common element among all cathodic materials. The leaching efficiency yields for all the metals for each cathode are reported in Fig. S4 in Supplementary Section 3.

The results evidence that it is possible to optimize the leaching conditions, reaching efficiencies higher than 85% for all the cathode materials, as summarized in Table 1. At the same time, significant differences are observable. Indeed, LMO structure is fully degraded under milder conditions (optimal parameters 10 min at 130° with 1 g of DES for 100 mg of LMO). LCO is the one presenting the stronger dependence on temperature and time of the leaching process, and interestingly the NMC compound presents always higher efficiencies under the same experimental conditions when compared to LCO.

Table 1

– Optimized leaching conditions for LCO, NMC, LMO cathodes allowing for Leaching efficiencies above 85% with respect to Li.

Cathode	DES:Cathode w ratio/g:mg	Holding time/min	Temperature/ °C	Leaching efficiency (Li%)
LCO	5 : 100	120	150	92.2
NMC	4 : 100	120	150	99.5
LMO	1 : 100	10	130	98.7

Globally the leaching conditions are favorable, especially when compared with previous results. Most previous studies are focused on LCO and NMC leaching with a wide range of conditions depending on the DES compositions [41,46,47]. The LCO and NMC can be leached with the use of choline chloride-ethylene glycol DES [45,48] with harsher conditions in terms of temperature and time, maintaining the same DES: Cathode Active Material (CAM) weight ratio. As the HBD and HBA are extremely similar to those reported in the present work, the discrepancy in the experimental condition can be rationalized considering a different water content in the two DESs, although this cannot be further discussed as these details are not reported in these works [45, 48]. LMO has been only limitedly considered in the development of solvometallurgical approaches; generally, the leaching of this cathode material is obtained more easily with respect to the layered LCO and NMC systems, and the results presented in the present work are in line with this trend [49].

These results can be rationalized considering both the DES characteristics and the cathode materials' features. From the DES side, recently the key parameters for designing an optimal DES formulation for the leaching process have been recognized and critically discussed. The most relevant have been recognized as i) the presence of a reducing agent/component, ii) presence of an anion with good complexing properties; iii) favorable physicochemical properties such as low viscosity; iv) strong acidity that can enhance the leaching process [35, 50–52]. The leaching of cathode materials when DESs are exploited proceeds through a complex path and mechanisms, already reported as a combined effect of proton attack, coordination degradation, reduction stabilization. Initially the HBD provides protons that can cleave the transition metal-oxygen (TM-O) bonds and/or substitute with Li into the channels and layers of the cathode materials. The structure is strongly destabilized, and it is prone to rearrangement. The extensive hydrogen bond network formed by the DES components can further prompt particles cracking and TM dissolution, further promoted by the formation of reduced species, at the expense of the DES. The reduced species are stabilized in the DES-based solutions forming a wide range of complexes through coordination with water moieties, deprotoned HBAs, HBDs [53–56]. Finally, the leaching mechanism has been described as based on two steps: i) extraction of Li from the cathode structure, replaced by H+ derived from the HBD, ii) reduction of the transition metal species of the cathode with formation of complexes metal-anion of the HBA. The specific selection of HBD and HBA presented in this work (choline citrate – ethylene glycol formulation) and their molar composition has been designed and emerged among the explored compositional ranges (see Table S1–S3) based on these considerations. Indeed, ethylene glycol has good reducing properties and provides CO_2 as a byproduct of the leaching reaction (as recently demonstrated in our work [35] citrate is a good complexing agent, and for this reason widely exploited in sol-gel synthesis procedures, which is the ultimate goal of this work. The viscosity of the as-prepared dry DES is not particularly favorable, but the natural tendency for water uptake helps in improving this aspect. In several works, the intentional addition of water is considered to assist the transport steps and diffusion control of the leaching reaction [23,24, 37,42,52]. This combination of favorable characteristics can explain the overall excellent leaching performance under reasonable conditions for all the considered CAM.

From the CAM side, the differences observed among them must be ascribed to their different structure and behavior. As degradation can be described as a reductive leaching, the starting oxidation state of the different elements in CAMs must be considered. Pristine CAMs have been used in this section of the work thus $LiCoO_2$ includes Co^{3+}, NMC includes a mixture of Ni^{2+}, Co^{3+}, Mn^{4+} [57], LMO includes Mn^{3+}/Mn^{4+} [58]. [58] In the same way that in traditional leaching processes with inorganic acids, hydrogen peroxide [59,60] is added to promote the reduction of metals in oxide structures, so in this systems the presence of reducing ethylene glycol is exploited to promote the conversion of transition metals to more easily solubilized, reduced valence oxidation states (Co^{2+}, Ni^{2+}, Mn^{2+}) [57,58,61]. Co and Ni ions are revealed through UV-vis analysis (Fig. S5), where in the peak at ~510 nm can be seen as the hexa-acquo complex of Co (II) and Ni(II), with an intensity proportional to the relative cobalt content in the CAM (LCO > NMC). XAS data have been acquired on the leached solutions obtained from the dissolution of LCO, NMC, and LMO cathodes; results are reported in Fig. S6 and discussed therein. To summarize the results, the analysis of the edge position collected for each metal confirms that the reduced metal species are obtained after the leaching, confirming the reductive degradation mechanisms. Indeed, Co^{2+} is obtained after the dissolution of LCO, Mn^{3+} is obtained from LMO leaching, Ni^{2+}, Co^{2+}, Mn^{3+} are the products revealed in the leached NMC solution. This is in line with the hypothesis previously reported. As an example, the degradation process of LCO driven by the DES has been rationalized recently as a "dot-etching dissolution", where the reduction and complexation of the metals in the DES system act synergistically in determining the leaching efficiency [51]. From this, it follows that the possibility of reducing the transition metals present in the different CAM greatly increases the efficiency of the overall process. The stabilization of more soluble reduced cations in the DES solution with strong coordinating groups further improves the degradation rates [62]. An interesting comparison in the leaching efficiency in time can be done between LCO and NMC; indeed, as previously reported, the Li^{+} and Ni^{2+} similar ratios provoke a disordering effect which contributes to affecting the stability of the structure, accelerating the leaching process in comparison with the results obtained with LCO [63,64]. From the analysis of these results and investigation it is possible to confirm that the DES provides a unique combination of reductive properties, stabilization of metals in solutions, and high metals' solubility. To further support this, the leaching ability of choline citrate in aqueous solution and ethylene glycol were tested for the selected LCO case; results are reported in Table S4, demonstrating that it is not possible to reach the high leaching yields obtained with DES-performed leaching.

To summarize, the proposed DES is a new system allowing for the efficient dissolution of the most common cathode materials, i.e. LCO, NMC, LMO, here considered separately, and for each of them the leaching procedure has been optimized independently. It must be stressed that in industrially produced black mass, a mixture of different cathodes is often present in the black mass obtained from various pretreatment as no sorting based on cathode chemistry is generally implemented, although the production of black mass selected on specific cathode materials is now emerging as a trend [65]. Thus, the application of solvometallurgical approaches on actual mix cathode-based black mass can be challenging and need further development. At the same time the different leaching behavior of the diverse cathode materials under equal conditions discussed above can be exploited for a preliminary partial enrichment of leached solution of selected metals in view of a possible metals' separation.

The solutions obtained after the leaching procedure with ChCitG 1:2 can be exploited for two kinds of processes as reported in Fig. 1b. Path A (direct resynthesis of cathode materials) is the primary track developed within this work, while path B (recovery of critical raw materials, as traditionally performed with solvometallurgy) has been explored as an alternative route, demonstrating the flexibility of the proposed method. Path A is thus discussed hereafter in more details, while Path B is discussed in a dedicated section "Additional 4- Recovery of Raw Materials – Path B". Within this global scheme, the recovery of the spent DESs has been considered, based on previous literature proposing this step to increase the sustainability of the overall recycling process [66–69]. The recovery of the spent DES and its purification is actually a complex procedure requiring addition of large volume of water (1-10 times the DES volume) to decrease the DES viscosity and allowing for filtration and separation procedures. This actually cancels one of the main benefits of the solvometallurgy, i.e. the very low water footprint. Moreover, the spent DES has chemical composition and physical properties (specifically viscosity) significantly different from those of the pristine DES, as also demonstrated by our recent publication [35]. This is associated with the leaching process itself, involving the reduction of the TMs and degradation of the cathodes, inevitably associated with the oxidation of the DES counterpart. Globally, due to the deterioration of the DES composition and the complexity of the operation for its recovery and purification, the DES recycling is not considered sufficiently sustainable and valuable. At the same time, the DES-based solution obtained as a result of the leaching process is the ideal starting precursor for a sol-gel-like synthesis of new batches of LCO, NMC, and LMO materials. While the formation of the gel matrix is ensured from the specific composition of ChCitG DES - designed specifically to meet this requirement - the metal composition is derived from two factors: i) the starting composition of the cathode powders, determining element's type and its maximum concentration; ii) the efficiency of the degradation process, determining the actual concentration of each metal in solution.

For this reason, it is crucial for the here proposed recycling scheme to work with selected waste cathodic materials of a single cathodic type, as the elemental composition (i.e. which metals are present) is controlled by this step; this point will be discussed in more detail in the conclusion and perspectives. On the contrary, the metals concentrations can be monitored and then regulated to meet the desired metal-to- metal ratio.

The metal concentrations in solution need to meet the final desired stoichiometric ratio of the final compounds and can be easily adjusted after quantitative analysis (ICP-OES) by adding the proper amount of the needed element. In the present case, as we started from commercial grade LCO, NMC, LMO materials, there was no need for correction of transition metals' concentrations. For direct resynthesis, well-established sol-gel routes reported in literature for these materials have been considered without any further optimization [70,71]. In this synthesis, an excess of Li is generally introduced to compensate for the eventual losses at high temperatures. We recall here that the extra Li source can be obtained from the leached ChCitG-based solutions as discussed later in the section "Additional 4 - Recovery of Raw Materials – Path B″, further demonstrating the flexibility of the proposed scheme.

For each cathode material, the resynthesis has been performed following procedures previously reported in literature, and results are in Fig. 4 [72–74]. From the patterns shown in the figure, by comparison with the references and patterns obtained for the starting powders (Fig. S2), it can be seen that the resynthesis process resulted in the formation of the expected structures for the three oxide cathodes, without any presence of contaminating structures. From SEM analysis, it is possible to appreciate the formation of particles in the range of 500 nm and 1 μm in the case of LCO, and a few hundred nm in the case of NMC and LMO (300 nm and 160 nm, respectively; in this case the comparison with the pristine powders' morphology (Fig. S3) reveal significant differences. The morphology of the particles plays a role in determining the final electrochemical properties; thus it is expected that significant differences can be found [71,75,76].

As proof of concept of the feasibility of the closed-loop recycling scheme, the resynthesized materials have been electrochemically tested as cathodes in a half-cell configuration, results are reported in Fig. 4(g and h-i). The resynthesized materials present the characteristic charge/discharge profiles of the LCO, NMC, and LMO materials demonstrating the validity of the direct recycling scheme. The specific capacity values obtained are not at the level of theoretical values, while the cycling performances at the lower rate conform to the values expected from the respective materials, although a decrease in specific capacity can be observed as cycles increase (in Fig. 4, the comparison between the first cycle and 41st). This may be attributable to a lack of control over the size of the synthesized particles, as already discussed, and not to the structure, as the recorded charge and discharge profiles demonstrate the

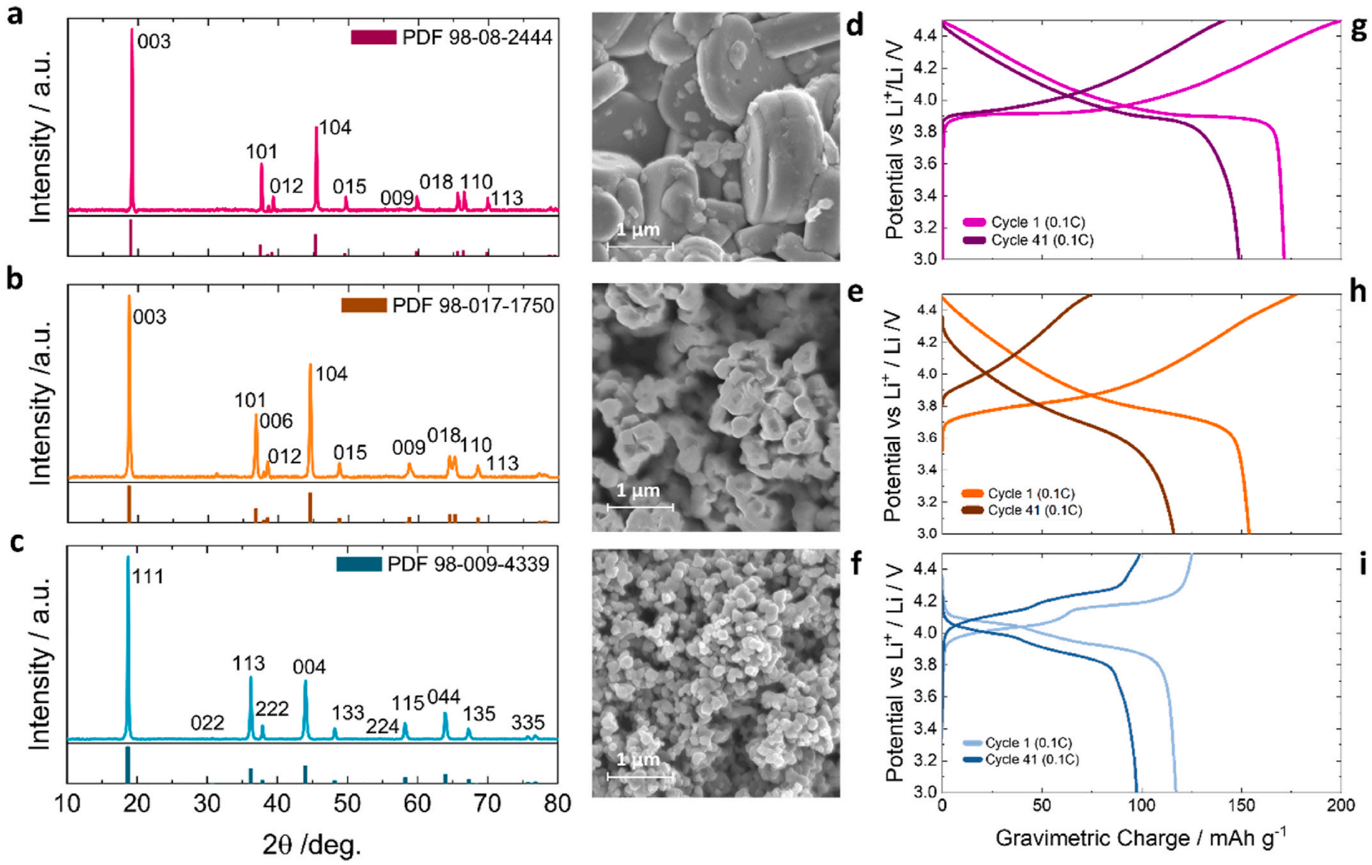

Fig. 4. XRD (a, b, c) and SEM images (d, e, f) of the resynthesized LCO, NMC, LMO cathode materials. Electrochemical profiles at 0.1C of resynthesized LCO (g), NMC (h), LMO(i).

correct electrochemical mechanism, thereby supporting the results of the XRD analysis. Another possible explanation, valid for LCO and NMC, is that related to the degradation of the cathode material and the release of molecular oxygen, a phenomenon known when the potential exceeds a certain threshold (about 4.3 V for nickel-rich NMC).

A final and fundamental part of the study is the evaluation of the environmental sustainability of the proposed project. Fig. 5 presents the LCIA results across five selected impact categories for the resynthesized cathode materials (RCMs): LCO, NMC, LMO. The full results across all 18 categories are summarized in Table S5. Among the three materials, LMO consistently demonstrated the lowest environmental impacts, especially in water consumption (41.2 m^3) and mineral resource scarcity (4.58 kg Cu-eq).

In the case of LMO under the GWP category, while electricity consumption in both leaching and resynthesis steps remains the main hotspot, the DES used also plays a significant role. As shown in our process-level analysis, the total GWP contribution of EDS amounts to 171.4 kg CO_2-eq, with 145 kg CO_2-eq from choline dihydrogen citrate and 25.36 kg CO_2-eq from ethylene glycol. This finding highlights the importance of both energy optimization and solvent recovery strategies in reducing climate change impacts.

Given that electricity consumption emerged as a major contributor across several impact categories (e.g., GWP, acidification, and particulate matter), a sensitivity analysis was conducted to assess how electricity source and consumption levels influence environmental outcomes. The four considered scenarios were.

Scenario 1: Baseline Scenario (S1-BL)

In this scenario, the electricity supply chain used was ENTSO-E. This scenario represents the current situation and serves as the baseline for comparison.

Scenario 2: Reduced Electricity Consumption (S2-REC)

This scenario evaluates the effect of reducing electricity consumption by 20% during the re-synthesis stage, while keeping the electricity supply chain the same as in the baseline scenario (ENTSO-E).

The 20% reduction was assumed without any changes in production efficiency, meaning that the same amount of product is obtained with lower electricity input.

Scenario 3: Renewable Electricity Mix (S3-RE)

To explore the potential benefits of replacing conventional electricity with renewable sources, the electricity supply chain in this scenario consists of a custom electricity mix: 50% wind power (CH) and 50% solar power (CH).

Scenario 4: Renewable Electricity + Reduced Consumption (S4-RE + REC)

This scenario combines the measures from Scenario 2 and Scenario 3: the electricity supply is based on the same renewable mix as in Scenario 3, and the electricity consumption during the re-synthesis stage is reduced by 20%, assuming no change in production efficiency.

The results, illustrated in Fig. 6, show that shifting to renewable electricity and reducing consumption leads to substantial GWP reductions, ranging from 81.5% (LCO) to 83.9% (LMO). These findings underscore the strong leverage that electricity-related decisions offer in improving environmental performance. Additionally, the influence of these scenarios on other impact categories is provided in Tables S5–S9,

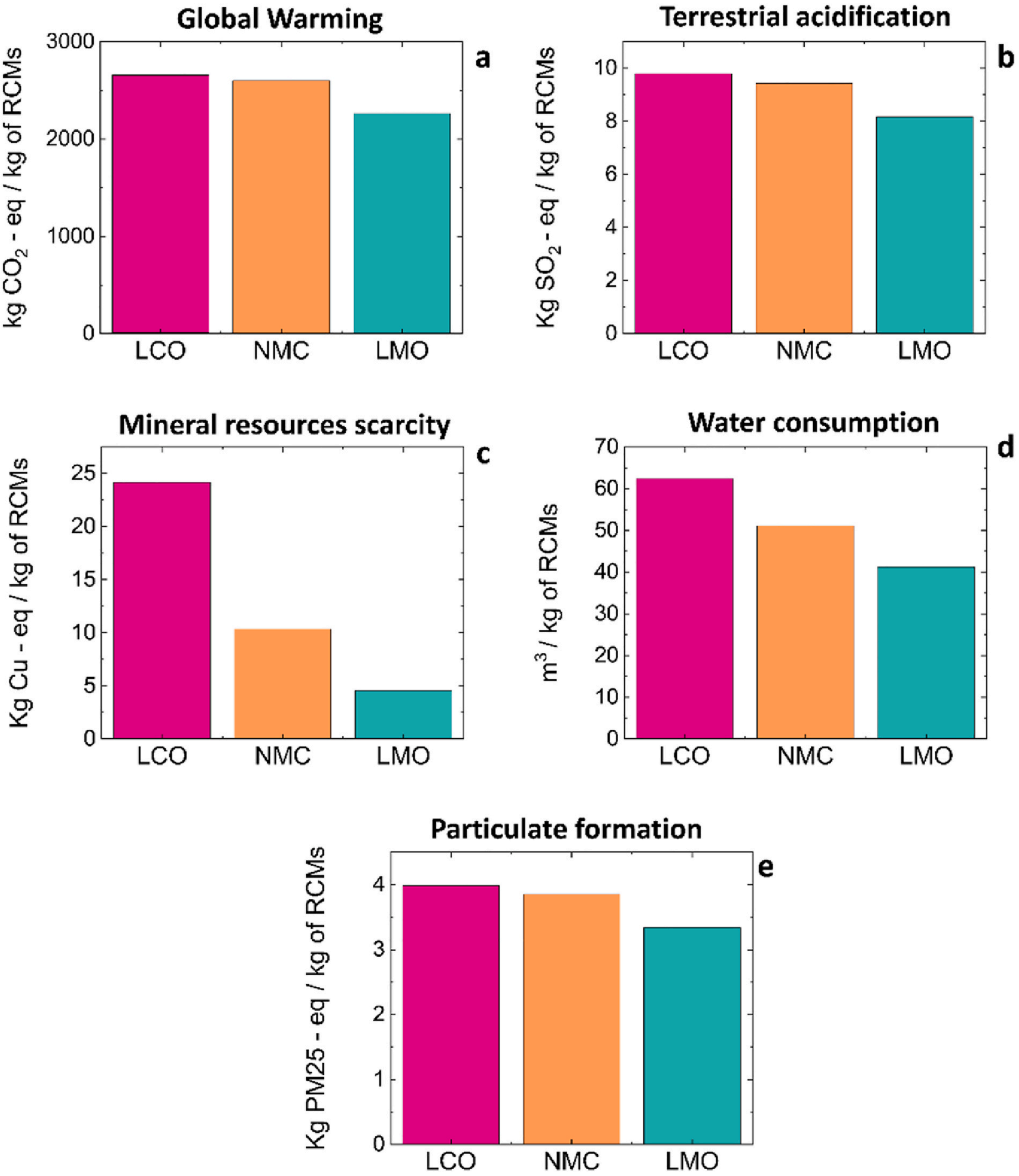

Fig. 5. LCIA results using the ReCiPe method. Values are presented per 1 kg of RCMs as the functional unit.

revealing similarly significant reductions, especially in acidification, fossil resource use, and particulate matter formation.

These findings are consistent with previous studies. For example, Maritz et al. (2024) [77] emphasized that lab-scale energy consumption is often 2 to 5 times higher than pilot-scale due to small batch sizes, non-optimized heating devices, and inefficient energy transfer. Similarly, Tian et al. [78] and Iturrondobeitia et al. [79] reported that electricity and heating are dominant contributors in battery recycling LCAs and noted that process optimization in pilot-scale setups (e.g., heat recovery, modular design) can reduce environmental impacts by up to 70%.

For instance, Iturrondobeitia et al. reported a GWP of only 1.92 kg CO_2-eq per kg of recovered NMC cathode using a hydrometallurgical process—two orders of magnitude lower than the values obtained in our lab-scale study. Such contrasts emphasize that our results should be interpreted as conservative, worst-case benchmarks, useful for identifying environmental hotspots such as thermal energy use and solvent production that must be addressed during scale-up.

Taken together, this analysis suggests that if electricity is sourced renewably and if thermal processing is optimized in scaled-up operations, the solvometallurgical approach presented here has the potential to become an environmentally competitive and circular alternative to conventional recycling methods—well-aligned with the goals of the EU Battery Regulation and the Critical Raw Materials (CRM) Strategy.

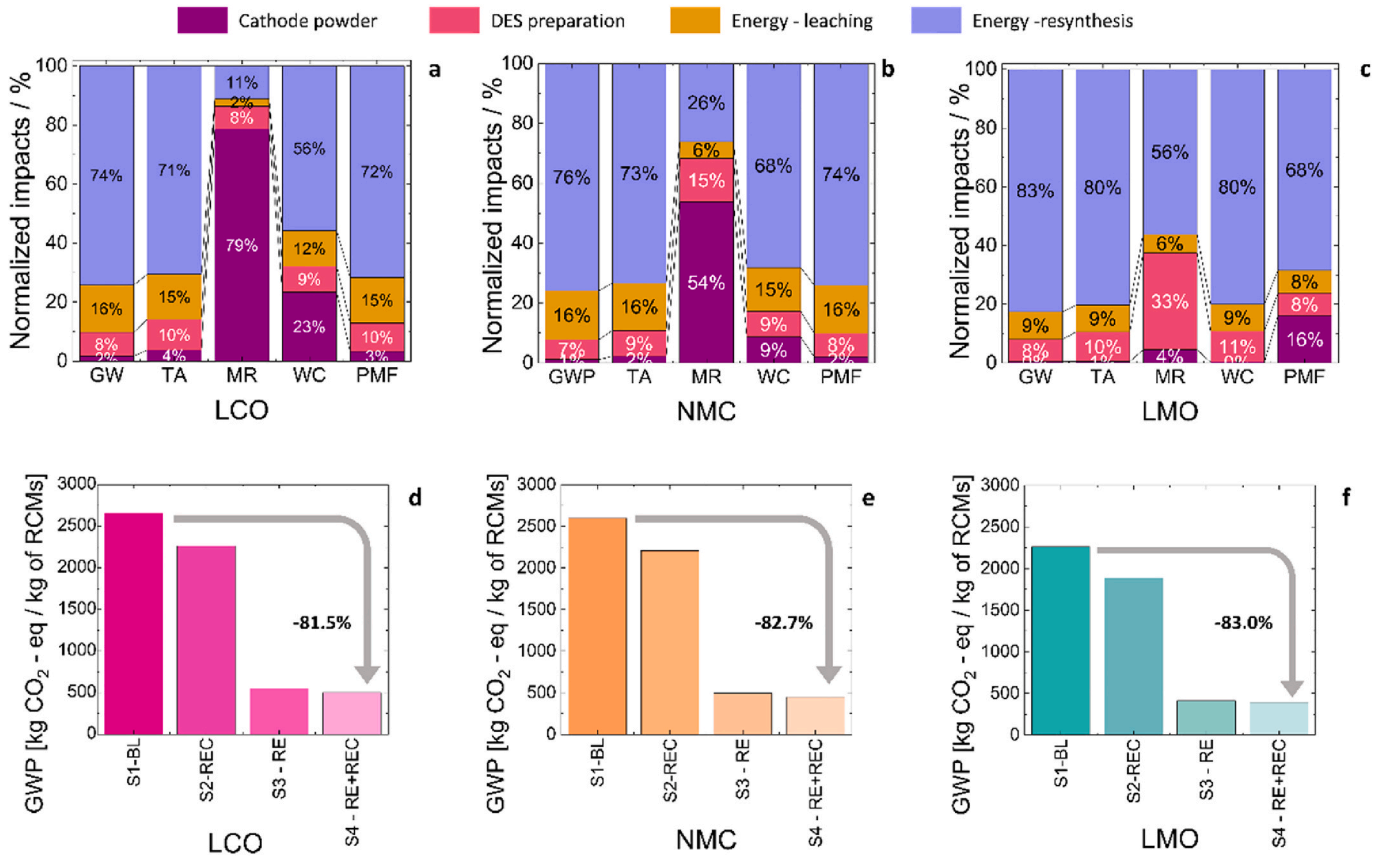

Fig. 6. Contribution analysis of the synthesis process to the environmental impact of three RCMs (a-c) and comparison of Global Warming Potential (GWP) under four scenarios: baseline (S1-BL), 20% reduced electricity consumption in the resynthesis process (S2-REC), renewable electricity mix (S3-RE), and combined scenario (S4-RE + REC) (d-f).

Additional 1 – Detachment of cathode black mass from current collector

Another interesting application that highlights the versatility of the here proposed DES concerns the separation of the current collector from the electrode. The separation of the cathode black mass from the other cell components formally falls into the so-called pretreatments, i.e. all the steps needed to isolate the component of interest that will undergo the recycling process. The detachment of the electrode form current collector is not done at industrial scale (only grinding and sieving, allowing for coarse separation of smaller particles but not avoiding cross contamination), while at laboratory scale it is usually involved the use of NMP as a solvent for the binder, facilitating also the removal from current collector. The use of NMP represents an additional step in the procedure, further complicated by its toxicity.

We here demonstrate that it is possible to completely detach the cathode black mass and recover the intact current collector by exploiting the same DES then used for the leaching but under milder conditions [80–82]. Specifically, a portion of LCO-based commercial electrode has been immersed in the ChCitG 1:2, under stirring and heating at 140°C. After 15 min it is possible to obtain a clear DES matrix containing black powder and the Al foils with no visible residue of electrode. The Al foils can thus be recovered and potentially reused, while the ChCitG 1:2 suspension containing the electrode can undergo further heating to realize the LCO leaching. A portion of the DES solution was analyzed with ICP-OES to determine its metal content to check any eventual Al contamination, and aluminum turns out to be below the detectability threshold of the instrument, thus demonstrating that the detachment occurs without affecting the current collector, which remains uncorroded.

Additional 2 – Leaching of a CBM

With the aim to go beyond the proof-of-concept stage, the same DES and procedure has been tested for the treatment of actual cathodic black mass (CBM), collected as reported in *Materials and methods.*

The XRD pattern in Fig. 7 (a) shows that the CBM is composed of a layered cathode, compatible with delithiated $Li_{0.7}Co_1O_2$ (JCPDS: 98-017-2912), with the presence of Co_3O_4 evident in the peaks at 36.7° and 44.7°. ICP-OES analysis confirmed the elemental composition of this sample, which is reported in the table below (Table 2). CHNS results in a 2.61 wt% of carbon, attributed both to conductive carbon and polymeric residues, since no additional washing steps are performed on the CBM after the collection. The manual separation from the current collector guarantees a minor and negligible Al contamination.

The leaching result with the ChCitG 1:2 DES has been assessed through ICP analysis, and the yield is more than 96% for both Li and Co. The obtained solution has been used for directly resynthesizing the cathode material, accordingly to the Path A, employing the same conditions identified as optimal through the study of leaching and resynthesis starting from commercial LCO material. The obtained powder (CBM res.) is characterized by an XRD pattern coherent with the LCO reference (Fig. 7b), and the ICP analysis confirms the desired stoichiometric ratio between Li and Co. The electrochemical behavior has been checked in a half-cell configuration, and the voltage profiles recorded at 0.1C are reported in Fig. 7c. The same observations previously made regarding the resynthesis of LCO from commercial material also apply in this extension, as the specific capacity values are unstable and decrease with increasing cycles, probably due to a lack of control over morphology and particles' dimension during the sintering step.

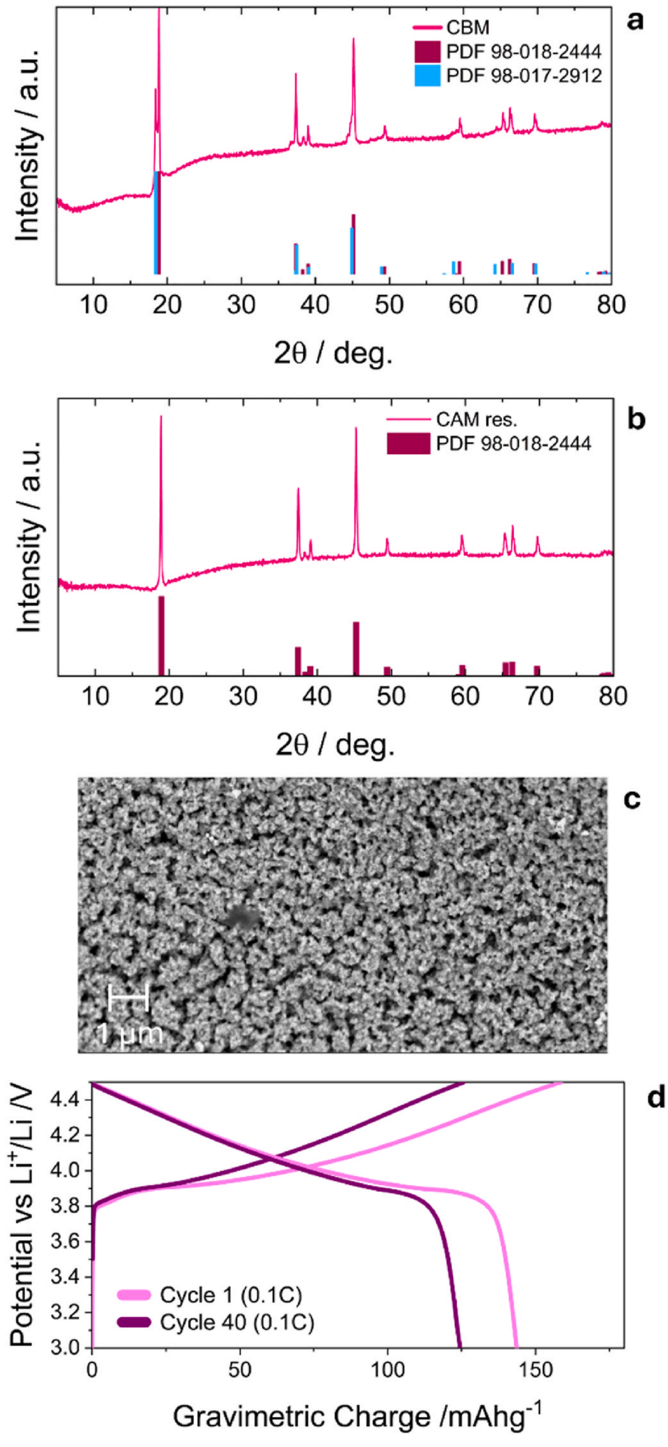

Fig. 7. – XRD pattern of the as-collected CBM (a). XRD pattern (b) and electrochemical profiles at 0.1C (c) of the resynthesized LCO, together with a SEM image of the product (d).

Table 2
– Summary of elemental content expressed in wt% calculated from ICP analysis for the CBM sample.

Sample	Co/%	Li/%	Ni/%	Mn/%	Al/%	Fe/%	Cu/%
CBM	63	5	-	<0.4	0.1	-	-

Additional 3 – Leaching of LFP material

LFP is a well-known cathode material, emerging in terms of market share for its lower cost and intrinsic safety. From the chemical point of view, it differs from the other cathode materials (layered and spinel structure oxides) as it belongs to the class of polyanionic compounds. From the point of view of recycling it is characterized by low content of critical raw materials; for this reason the traditional recycling of this cathode is explored in less extent with respect to LCO, NMC, and LMO in favor of direct recycling strategies appeared recently (i.e. procedure that aims to regenerate and/or heal the initial properties of the cathode instead of dissolve it) [83–85]. Although these strategies are the most effective and sustainable in the short-term view, the possibility to dissolve the LFP powder was here considered to foresee the necessity -at certain point-to finally recycle a cathode with no further possibility of healing. The leaching of LFP based on ChCitG 1:2 DES was then optimized similarly to the other cathodes and results are reported in Fig. 8. The optimal conditions for LFP dissolution are 5 g of DES for 100 mg of cathode powder upon heating for 10 min at 150°C; this leads to the peculiar result of obtaining >98% of Li in solution and 40% of Fe while a solid residue is also observed. Attempts to push further the leaching in terms of time and temperature have been considered, the solid residue is always obtained. Further investigation of such products was thus carried out through XAS analysis at the Fe K-edge, results are reported in Figs. S7 and S8 and discussion therein. The results confirm that Fe is present in solution as a mixture of Fe^{3+} and Fe^{2+} while the solid residue presents Fe^{2+}. Although the dissolution of the iron phosphate matrix is not complete, the Li leaching is obtained with high yield and under fast leaching conditions. The LFP leaching can thus be explored for a simple recovery of Li. The possibility to resynthetize LFP cathode materials exploiting the solid residue and the leached solution was also considered; results are reported in Fig. S9. The LFP olivine phase is successfully obtained, demonstrating that the paths reported in Fig. 1 are conceptually exploitable. It must be stressed that for LFP cathode the control of the morphology and carbon content (as residue of the sol gel synthesis) is extremally relevant for its final electrochemical performance. The full optimization of the synthesis with these respects, as for the other cathodes discussed in the main texts, have not been addressed in the present paper although we are aware of their relevance (see Fig. S9 for comparison of commercial and resynthesize LFP morphology). The environmental assessment of 1 kg of resynthesized LFP revealed trends consistent with those observed for other cathode materials, with electricity emerging as the dominant contributor across most impact categories. Full results across all impact categories are provided in Table S5. The sensitivity analysis demonstrated that the GWP can be significantly reduced by optimizing electricity consumption and adopting renewable energy sources (Table S9). This substantial 83.5% reduction underscores the critical role of energy-related decisions in minimizing the environmental impacts of LFP recycling and highlights the potential of direct recycling approaches to support sustainable battery end-of-life management.

Additional 4 -Recovery of Critical Raw Materials – Path B

As discussed in the previous section, the main aim of this work is the direct resynthesis of cathode materials. Nevertheless, ensuring that it is possible to recover the critical raw materials from the leached solution is of potential interest as this is considered the state-of-the-art strategy in solvometallurgy.

This more traditional approach has thus been explored with the aim of recovering critical raw materials through a precipitation step, as reported for similar LCO leaching procedures exploiting DESs.

Starting from the LCO-based leachate, the addition of oxalic acid leads to the formation of a precipitate, the cobalt oxalate [86]. This procedure has been previously reported as an effective separation method for the subsequent recovery of Co and Li from LCO degradation with organic acid -based DES, such as succinic or maleic acid. [87,88]. In these cases, a small excess of oxalate ions was needed to fully recover the

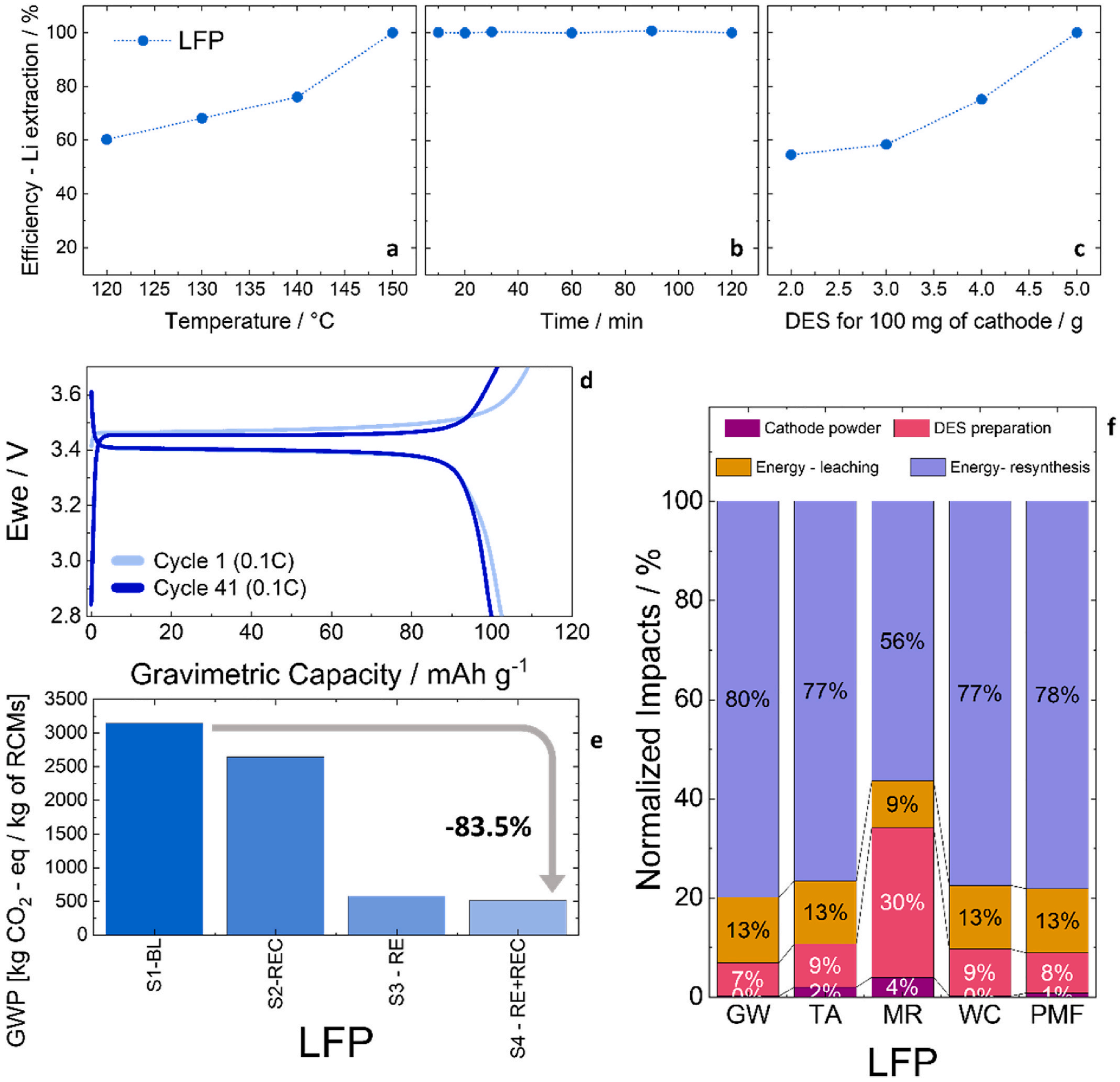

Fig. 8. Li extraction yields vs temperature (a), time (b), and DES-to-cathode weight ratio (c); the electrochemical profiles at 0.1C of resynthesized LFP (d); Global Warming Potential (GWP) under four scenarios described above (f).

cobalt from the aqueous solution.

Unlikely, in this case, a large excess of oxalate (1:10 M ratio with respect to cobalt) is needed; this unfavorable ratio is ascribed to the fact that the cobalt oxalate solubility in the DES systems is strongly dependent on the DES compositions itself. Moreover, oxalic acid is often used as an HBD component for DES preparation [46,89–91], thus a large portion added to the ChCitG DES is expected to be soluble in the system, modifying its composition before the Co oxalate starts to precipitate. Another possibility is to add an excess of water (1:20 w DES: water ratio) that leads to the formation of a water-based solution starting from the DES-based matrix. In this case, adding oxalic acid in a small excess compared to the molar Co content leads to the precipitation of cobalt oxalate, as previously reported [92].

The powder precipitate can be recovered by filtration and subsequent water washing; the final product has been characterized, and the remaining limpid solution has also been recovered and characterized, with results reported in Fig. S11. XRD measurements (Fig. S11a) confirm that the pink solid is composed of cobalt oxalate in good agreement with the reference entry 98-015-0589. The TGA profile (Fig. S11b) reveals that in the 100°-220°C temperature range, a weight loss of 16-18% is observed, compatible with the removal of crystallization water corresponding to the formula $CoC_2O_4*2H_2O$. Finally, the ICP analysis of the solid powder and the DES leached liquid confirm the absence of cross contamination (<1%). To further confirm this, UV-Vis characterization was also performed on the liquid phases to verify the absence of the signal of Co in water (510 nm), as reported in Fig. S11.

The proposed process can be exploited for the recovery of pure CRMs only for the LCO-derived leachate. In the case of NMC it is still possible to exploit the precipitation route but, in this case, it leads to obtaining mixed oxalate salts due to the similar behavior of Ni, Co, and Mn. This product is of high interest as mixed Ni/Co/Mn oxalates are now emerging as suitable precursor for recently reported synthesis of NMC.

The reported results confirm that it is possible to isolate Co oxalate with purity >99% and at the same time recover a ChCitG-based solution containing Li in the range of $2*10^{-4}$ m with low content of Co (<1%). The purity of this solution is sufficient to be used as a source of lithium in the process of direct resynthesis with the advantage of having the same DES composition of the leachate solution thus being fully compatible.

We want to stress the relevance of the flexibility of the proposed process as the combination of these two strategies can lead to a fully closed-loop circular economy scheme, as reported in Fig. 1. Indeed, the resynthesis of the materials can request the correction of the metal's compositions and generally addition of extra source of Li is mandatory in preparation of CAM, especially when high temperature step is involved [93–95].The possibility to use the same DES-based precursor for both the supply of metal sources and the resynthesis (Path A and B in Fig. 1) is a powerful tool for the scalability of the process.

4. Conclusions

Solvometallurgy is ramping up among the strategies for recycling cathode materials from spent lithium-ion batteries. In the present paper a conceptually new deep eutectic solvent formulation is designed with the aim of allowing a new possibility: the direct resynthesis of cathode materials after solvometallurgical recycling. The key feature is the switch from choline chloride, proposed as hydrogen bond acceptor in all the previous DESs formulation, to choline citrate. Although the presence of chlorine was considered essential for the DESs formation, through the physico-chemical investigation of the choline citrate-ethylene glycol compositional range, we were able to demonstrate that a DES system is formed for the 1:1-1:20 M ratio range. The as obtained DES was then successfully tested for the leaching of the most common cathode materials today present in spent and newly produced LIBs, i.e. LCO, NMC, LMO, LFP, highlighting the huge flexibility of the method proposed. The leached solutions obtained from the dissolution of LCO, NMC, LMO, and LFP have then been exploited as a starting point for the direct resynthesis of new cathode materials and, as a secondary possibility, for the recovery of lithium and other metals. The same approach has also been applied to a real CBM to assess the possibility of exploiting this method in the presence of an understoichiometric or defective starting material. The resynthesized cathode materials have been electrochemically tested, fully supporting the feasibility of the implementation of the direct recycling method. Finally, the cradle-to-gate life cycle assessment enables demonstrating the environmental sustainability of the process when renewable energy sources are considered. The proposed method represents a new alternative in the LIBs recycling panorama, with advantages and drawbacks. The main advantage is the possibility to avoid the separation of the different CRMs, typically challenging and one of the most demanding steps in terms of mechanical procedures, involved expensive chemicals, and the production of wastewater. For this reason, can be particularly appealing for production of NMC where separation of each transition metal is extremely complex for the LFP case, where the low amount of valuable elements hindered complex and costly recycling procedures. At the same time the lack of separation steps inevitably involves careful control of the impurity level in the starting black mass. High grade black mass with very low contamination from different cathode active materials, current collectors, polymeric fraction is needed to ensure that the resynthesize materials meet the requirement of electrochemical grade purity. As a perspective, this approach can be appealing for in house recycling from battery producers, involving dismantling of selected cells with known chemistries and complete knowledge of the battery cell composition. Overall, this study opens the way for a new recycling route, putting in contact the solvometallurgical methods (traditionally devoted to the recovery of CRMs) and the research trend of healing of cathode materials, offering a new possibility for direct recycling.

CRediT authorship contribution statement

Riccardo Morina: Conceptualization, Investigation. **Eleonora Carena:** Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Nicolò Pianta:** Data curation. **Jacopo Orsilli:** Data curation. **Francesco d'Acapito:** Supervision. **Fatemeh Bahmei:** Data curation, Formal analysis. **Anna Galli:** Supervision. **Marcel Weil:** Supervision. **Chiara Ferrara:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Chiara Ferrara reports financial support was provided by University of Milano-Bicocca. Chiara Ferrara reports a relationship with University of Milano-Bicocca that includes: employment. Chiara Ferrara, Riccardo Morina has patent pending to Chiara Ferrara, Riccardo Morina. No other relationship or activity that may be interpreted as a conflict of interest by the reader have to be reported. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2026.240716.

Data availability

Data will be made available on request.

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