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Decomposition of Deep Eutectic Solvent Aids Metals Extraction in Lithium-Ion Batteries Recycling

Pier Giorgio Schiavi,*[a] Pietro Altimari,[a] Elisa Sturabotti,[a] Andrea Giacomo Marrani,[a] Giulia Simonetti,[a] and Francesca Pagnanelli[a]

The application of deep eutectic solvents (DESs) to dissolve metal oxides in lithium-ion batteries (LIBs) recycling represents a green technological alternative to the mineral acids employed in hydrometallurgical recycling processes. However, DESs are much more expensive than mineral acids and must be reused to ensure economic feasibility of LIB recycling. To evaluate DES reusability, the role of the choline chloride-ethylene glycol DES decomposition products on metal oxides dissolution was investigated. The temperatures generally applied to carry on this DES leaching induced the formation of decomposition products that ultimately improved the ability to dissolve LIB metal oxides. The characterization of DES decomposition products revealed that the improved metal dissolution was mainly determined by the formation of Cl_3^-, which was proposed to play a pivotal role in the oxidative dissolution of LIB metal oxides.

Introduction

Driven by the green energy transition, the demand of lithium-ion batteries is predicted to vary from 500 in 2020 to 1.5 GW in 2030. To sustain this exponentially growing demand, it is mandatory to efficiently recover and recycle to the manufacturing sector the critical and strategic raw materials (Co, Ni, Li, graphite) composing the Li-ion batteries (LIBs) electrodes.[1] Hydrometallurgical recycling allows effective recovery of electrode metals but is characterized by a negative environmental footprint, mainly determined by the application of toxic mineral acids and by the generation of large wastewater volumes.[2] A competitive green alternative is represented by solvometallurgical processes, where deep eutectic solvents (DESs) are used to dissolve LIB metal oxides.[3,4]

DES are mixtures of two or more components with a melting point lower than those of its individual components, which include a hydrogen bond acceptor (HBA; typically a quaternary ammonium salt) and a hydrogen bond donor (HBD; e.g., alcohol or carboxylic acid). Synthesis of DESs is generally straightforward, and biodegradability, safety, and low price can be ensured by the proper selection of the DES components. For example, in most of the currently employed DESs, choline chloride, a cheap chemical widely used as an additive for chicken feed, is employed as HBA. Recently, attracted by these peculiarities, researchers have extended the application of DESs to the recycling of LIBs as metal leaching agents.[5] Different combinations of hydrogen bond donor and hydrogen bond acceptor in DES formulation were tested with the aim to maximize the metal extraction yields.[4,6–11] However, despite this interest of the scientific community, only very few studies attempted to develop a description of the mechanisms driving the dissolution of metal oxides in the employed DESs.[12,13] Among these few studies, an extensive experimental analysis was recently reported by Hartley and co-workers to evaluate the influence of proton activity and hydrogen bond donor on the solubility of metal oxides in DESs.[14] Different organic acids and ethylene glycol were separately tested as hydrogen bond donors while choline chloride was used as hydrogen bond acceptor. In accordance with the reported results, the ligand generated by the dissociation of the hydrogen bond donor can significantly influence the yield of metal oxide dissolution. Particularly, the solubility of any given metal oxide can be increased by the selection of organic acids that generate, through dissociation, an anion forming stable complexes with the metal cation. In addition, it was confirmed, like for aqueous systems, that increasing proton activity invariably increases the metal extraction yield and can enhance dissolution kinetics. Analogously to what was previously proposed for aqueous solutions of organic acids,[15] the authors concluded that dissolution in DES proceeds through the protonation of oxygen at the metal oxide surface, the complexation of metal (by either the ligand generated through hydrogen bond donor dissociation or the chloride ion from the choline chloride), and the dissolution of the complexed metals into the liquid phase.

On the other hand, ethaline, one of the most employed DES in metal processing and battery recycling composed by ethylene glycol and choline chloride, is characterized by a very low proton activity (ethylene glycol $pK_a \approx 15$ in water).[3,16,17] Consequently, the extraction of metals using ethaline takes place without oxygen protonation, differently from the mechanism proposed by Hartley and co-workers regarding DESs

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formulated with organic acids.[14] In addition, DESs are characterized by high metal extraction rate, low toxicity, safety, and biodegradability, but they have a cost much larger than traditional mineral acid-based metal extraction systems.[3] Therefore, the extensive reuse of DES is mandatory to ensure the economic feasibility of the recycling process, and this aspect is not addressed in the literature. The high cost of DESs combined with the lack of results about their possible reuse are the major obstacles to overcome their application on scale larger than laboratory. It is worth noting that the vast majority of the works reported in the literature involve the use of organic acid as hydrogen bond donor and, according to the above-described leaching mechanism, imply the consumption of proton with formation of water during the metal oxide leaching.[4,7,9–11] To all effects, DES is acting as reagent and is irreversibly consumed, compromising its reuse in following metal extraction cycles. In contrast, when poly-alcohols are used as hydrogen bond donor, high temperature were applied to reach satisfactory metal extraction yields and, to the best of our knowledge, both metal extraction mechanism and reusability have never been investigated.[5,8,9]

In a recent work, we demonstrated that selective extraction of Co and Mn (minimizing the extraction of Ni) can be attained during the leaching of LIB black mass with a choline chloride-glycol ethylene DES by appropriate selection of temperature and duration. The increased selectivity of Co extraction as compared to that of Ni excludes the complex separation of Ni and Co, considerably simplifying the downstream recovery of Co.[20] However, replicating the leaching with the residual DES left after the recovery of metals, we found an increase in the Ni extraction yield from about 10 to 40% without any significant change in the extraction of Co, corresponding to the loss of original DES extraction selectivity.[18] Above 90°C, DES is not stable, and we already reported several decomposition products after leaching the LIBs black mass at 180°C for 24 h.[18] More recently, using the same DES composition, Wang et al. obtained, already with pristine DES, an extraction yield higher than 90% both for Ni and Co by leaching the cathode material in a hydrothermal reactor at 190°C for 24 h.[21] This result seemingly contradicts the selective extraction of Co attained through our leaching test with pristine DES at 180°C. However, in view of our results of leaching with the reused DES, the faster thermal decomposition of DES induced according to Wang et al. by the larger leaching temperature could explain the apparent contradiction.[21]

Some results about the decomposition of DES based on choline chloride and ethylene glycol in applications not related to metal extraction were reported, but no previous work systematically investigated whether and how decomposition products can influence the ability of DES to dissolve metal oxides.[22–25]

We found only few recent articles where the reuse of DES is analyzed. However, these works paid scarce attention to the decomposition of DESs during leaching. For example, Wang et al. applied the same DES and DES recovery strategy that we used in our work, but at higher temperature (190°C).[8,18] Likely, they had the same decomposition products we found in our
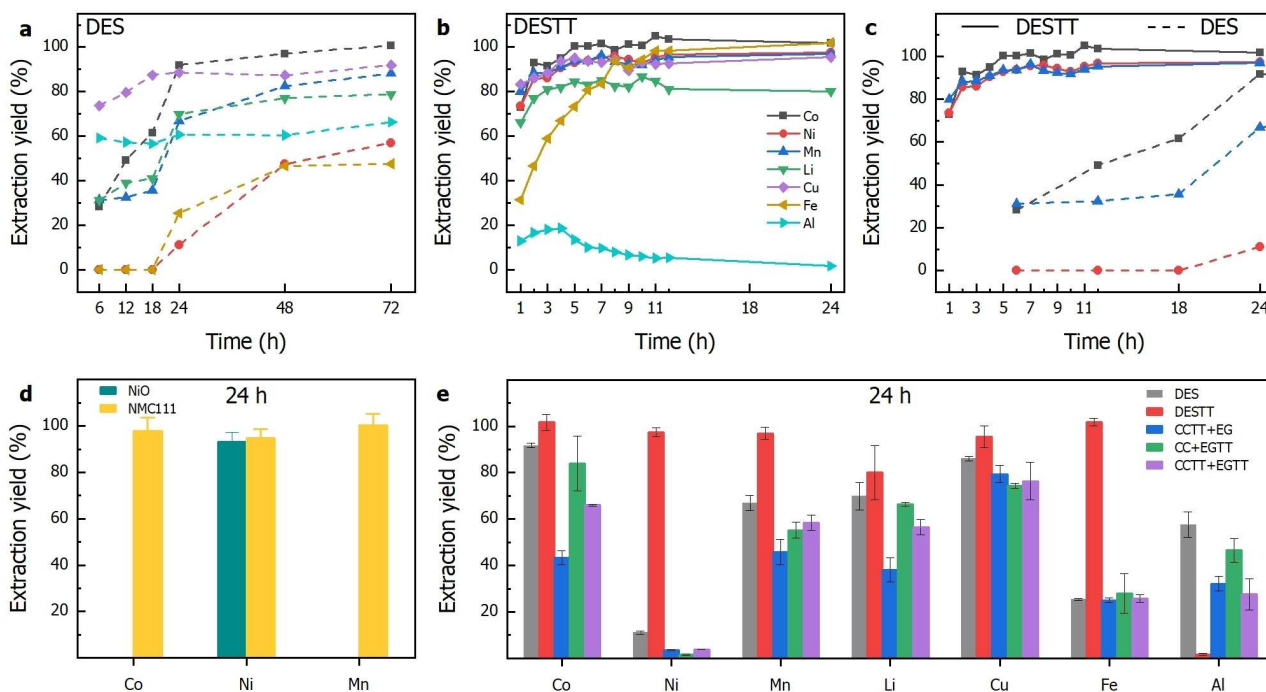
study, but any consideration about the decomposition of DES and the role of decomposition products in the extraction were not reported.[8] Morina et al. reported the reuse of a DES with an organic acid as hydrogen bond donor.[4] In their work, LIBs cathode materials were leached at temperatures up to 170°C and for 24 h. Again, in this latter works, no results about DES decomposition were reported, though Rodriguez et al. demonstrated the decomposition of DESs based on organic acid at milder condition (80°C; 2 h).[19]

In this work, thermally treated DES was used in the leaching of LIBs black mass allowing for extraction yields greater than 90% after only 4 h. Among the degradation products, the trichloride anion Cl_3^- is proposed to determine the enhanced metal dissolution by enabling an oxidative dissolution of the metal oxides. Metals were removed from the DES by solvent extraction, and the residual DES was reused in a subsequent leaching, reaching extraction yields for the different metals close to those attained by the first leaching. In fact, we found that after solvent extraction, most of the decomposition products were removed while Cl_3^- remained in DES. Here, we demonstrate that the thermal decomposition of DES effectively improves the dissolution of metals.

Results and Discussion

As recently reported, satisfactory metal extraction yields using DESs composed of choline chloride and ethylene glycol are attained at temperature values close to 200°C.[5,18,21] While these temperatures are about twice that used during the leaching with aqueous acidic solutions, chloride-ethylene glycol DESs have specific heat capacity (2.2 $J g^{-1} K^{-1}$) half that of acidic solutions ($\approx 4.2 J g^{-1} K^{-1}$). Therefore, comparable energy consumptions are needed to heat the employed DES and acidic solutions to the corresponding leaching temperatures. On the other hand, increasing the leaching temperature to about 200°C could induce a thermal decomposition of DES. In our previous work, we showed that DES is not stable above 90°C and found several compounds produced by DES decomposition after 24 h leaching at 180°C.[18] Under these leaching conditions, Co was quantitatively extracted (>90%) while a low Ni extraction was attained (<10%). By using the residual DES in a second leaching experiment, we found a generalized increase in the metal extraction yields. To elucidate the influence of DES decomposition products on metal oxide dissolution, the DES was maintained at 180°C for 72 h in a closed reaction vessel without any other component. This thermally treated DES is hereafter referred to as DESTT. After this thermal treatment, DESTT was used to perform the leaching of real waste LIBs black mass already characterized in our previous work and containing several cathode materials (LiNi$_a$Mn$_b$Co$_c$O$_2$=NMC, LiCoO$_2$=LCO, Li$_a$Mn$_b$O$_c$=LMO), carbon, graphite, and Al, Cu, and Fe impurities.[18]

Figure 1 reports the evolution of the extraction yields attained for the different metals contained in the black mass during the leaching tests with pristine DES (Figure 1a) and DESTT (Figure 1b). The extraction yields of all the metals

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Figure 1. Metal extraction yields during time obtained leaching the black mass with (a) DES and (b) DESTT. (c) Comparison on the extraction yield between DES (dashed) and DESTT (solid) for Co, Ni, and Mn. (a–c) with associated errors are reported in Figure S1 of the Supporting Information. (d) Co, Ni, and Mn extraction yields obtained leaching NiO and NMC111 with DESTT for 24 h. (e) Metal extraction yields obtained leaching the black mass with solutions obtained separately treating EG and CC at 180 °C for 72 h.

considerably increase in the DESTT, proving that the decomposition products of DES significantly affect the metal oxide dissolution. In particular, the selectivity of extraction for Co, which was attained by leaching with pristine DES at 180 °C between 18 and 24 h, was completely lost (Figure 1c).[18]

Additionally, an extraction yield for any target metal (Co, Ni, Mn) higher than 90 % was attained after only 4 h, and a maximum extraction yield close to 100, 93, and 94 % for Co, Ni, and Mn, respectively, was reached after 6 h. To date the highest extraction yield was reported for Co (100 ± 3 %) using ethylene glycol:choline chloride (EG:CC) DES,[5,7,8,10,12] almost equal to that obtained using DES formulated using organic acid as hydrogen bond donor.[10,26]

To evaluate whether the dissolution of metals was influenced by unknown species contained in the real waste LIBs black mass, a leaching test with duration of 24 h was performed with DESTT by employing commercial NMC111 (LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$) and NiO. Extraction yields close to those attained with the black mass were found (Figure 1d), excluding that unknown species from the black mass could have influenced metals dissolution.

Since high extraction yields (>90 %) are attained in the DESTT already after a few hours of leaching, it can be hypothesized that the decomposition products responsible for the improved metal dissolution are already present in the DESTT before leaching starts and are formed in absence of the metals, that is, by reactions involving only DES components CC and EG. To clarify if the products enhancing the dissolution of

metals are generated by the decomposition of only CC, only EG, or by reactions involving both CC and EG, we separately treated CC and EG at 180 °C for 72 h and used the thermally treated compounds, here referred to as CCTT and EGTT, to prepare the three following solutions: CC + EGTT, CCTT + EG, and CCTT + EGTT. Figure 1e displays the metal extraction yields attained after 24 h leaching with these three solutions. In any of three solutions, the extraction yields of the different metals were not significantly different from those attained in the pristine DES. This indicates that decomposition products responsible for improved metal oxide dissolution should be sought in the reaction between CC and EG and/or between the decomposition products of the two DES components. To shed light on the reaction products coming from the thermal treatment of CC and EG, gas chromatography mass spectrometry (GC-MS) characterization of liquid and gas (head space) phases were carried out. Solutions obtained after the thermal treatment of CC and EG showed small peaks that can be related to ethanol, 2-methoxy-ethanol, and 1,2-dimethoxy-ethane. GC-MS of liquid DESTT shows an intense peak related to 2-methoxy-ethanol and 1,2-dimethoxy-ethane, as well as several other molecules with ether moieties and chlorinated compounds. To study the effect of thermal treatment on the DES, attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of the different solutions were recorded and shown in Figure 2b. No significant differences can be seen for the three solutions obtained by employing thermally treated CC and/or EG and, in fact, the recorded spectra remain very similar to that of the pristine DES
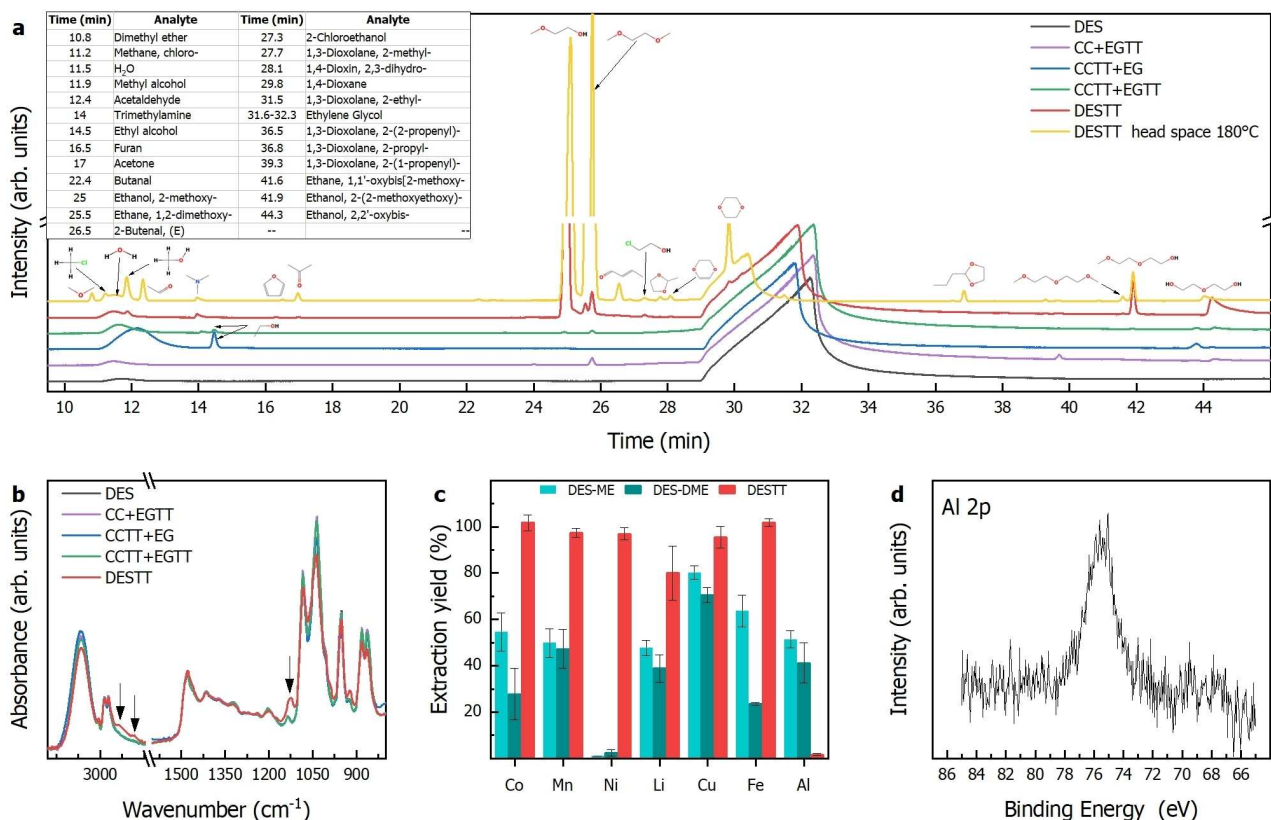
Figure 2. Total ion chromatogram in full scan acquisition (20–300 m/z) recorded by (a) GC-MS and (b) ATR-FTIR spectroscopy of the different solutions obtained by thermal treating DES and its single components. (c) Metal extraction yields obtained by leaching the black mass with DES added with 2-methoxy-ethanol (ME) and 1,2-dimethoxy-ethane (DME) for 24 h. (d) Al 2p region XPS spectrum of residual solid fraction after leaching with DESTT.

in terms of peaks intensity and location. Conversely, small but reproducible spectroscopic variations are visible in the case of DESTT. In this case, the intensity of OH band decreases, together with that at 1080/1040, 952, 883, and 863 cm^{-1}, while a new band centered at 1125 cm^{-1} appears. The latter resonates in a region typical for the asymmetric stretching of C–O–C bond in aliphatic compounds,[27] and thus, it could be inferred that molecules bearing ether moieties in their structure are formed during the heating of DES, also confirming GC-MS results. In addition, ammonium salt of tertiary ammines (e.g., trimethylammonium ion) can be highlighted by the two weak bands at 2720 and 2470 cm^{-1}, which are associated to the N$^+$–H vibrational stretching. As for ethers, trimethylamine presence is confirmed by GC-MS analysis of DESTT. No additional information can be obtained by ^{1}H auclear magnetic resonance (NMR) spectra (Figure S7); in fact, besides choline and ethylene glycol peaks, the spectrum evidences the presence of ether and amino compounds in DESTT, confirming the results obtained from GC-MS and FTIR spectroscopy.

Ethers could be good ligands and form stable complexes with metals. This could enhance the extraction of Ni, which, unlike Co and Mn, exhibits a scarce tendency to form chloro-complexes and is, for this reason, only barely extracted by the pristine DES.[14,28]

Accordingly, the formation of ethers could contribute to explain the increased extraction yields with DESTT as compared to DES. We found several glycol diethers (i.e., glymes), which contain multiple ether type oxygen atoms similar to crown ethers and could solvate metal ions through oxygen-ion complexation/chelating mechanisms.[29] To evaluate the role of these diethers in metal extraction, two solutions were prepared by enriching the pristine DES with 2-methoxy-ethanol (30 g L^{-1}, DES-ME solution) and 1,2-dimethoxy-ethane (6 mg L^{-1}, DES-DME solution), which are the two most abundant ethers found in DESTT. However, the leaching of black mass with DES-ME and DES-DME led to extraction yield even lower than those attained with pristine DES (Figure 2c). Along with the almost quantitative extraction of Ni, Figure 1b reveals that the aluminum extraction yield decreases during the leaching with DESTT, becoming negligible after 24 h. Aluminum comes from the LIBs crushing and is determined by the application of metallic aluminum foils as current collector for the cathode materials. This is confirmed by the X-ray photoelectron spectroscopy (XPS) analysis (Figure S2), evidencing that the aluminum contained in the black mass is in the metallic form. Aluminum absence in the leachate could be attributed to its oxidation and precipitation as solid phase. The XPS survey spectra (Figure S3) of the residual black mass recovered after leaching with DESTT shows traces of Li, as LiPF$_6$ (Li 1 s, P 2p, and

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F 1 s regions) not dissolved in DESTT, and Al. Al is reasonably in the form of Al_2O_3 as evidenced by the major component that can be assigned to oxidized Al and falling at 76.6 eV binding energy in XPS Al 2p spectra (Figure 2d). It has been reported that aluminum impurities are typically leached along with the target metals during both hydrometallurgical and DES-based solvometallurgical recycling processes. To produce battery-grade cathode materials, aluminum can be removed by either the treatment of the black mass with NaOH prior leaching, or downstream separations (solvent extraction, selective precipitation) after leaching. Using DESTT, dissolution of Ni, Mn, and Co takes place while Al remains in the solid fraction allowing for a simplification of LIBs recycling.

The formation of Al_2O_3 and the dissolution of the metallic Cu current collector suggest the presence of oxidizing species able to oxidize Al and Cu but insufficient to oxidize Co, Ni, Mn. Depending on cathode material lithiation degree, Co, Ni, and Mn can have indeed oxidation state higher than (II) in the black mass, and they are therefore reduced during the leaching, being dissolved in DESTT and DES in their chloro-complex forms with oxidation state (II) (e.g., $Co[Cl_4]^{2-}$). In addition, as shown in Figure 1d, NiO was dissolved, and for this metal we found the typical thermochromic behavior of Ni^{II} including the formation of green/blue $[NiCl_4]^{2-}$ when the solution was heated to 180 °C and yellow $[Ni(EG)_3]^{2+}$ when the solution was cooled down to room temperature (Figure S4).[30] By analyzing the volatile DESTT decomposition products (Figure 2a), we found chlorinated products such as chloromethane and chloroethanol, suggesting the possible formation and presence of chlorine. On

the other hand, head space GC-MS did not disclose the presence of Cl_2. The same result was observed by Haerens et al. when the DES was employed for the electrodeposition of Zn.[24] Oxidation of choline's Cl^- to Cl_2 in DES and ionic liquids containing a high concentration of Cl^- generates the equilibrium $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$.[31–33] Due to the high concentration of Cl^-, it was reported that the dominant product from the oxidation of Cl^- was the tri-chloride ion Cl_3^-, while, Cl_2 was not found as oxidation product.[24,31,32] Remarkably, Cl_3^- can act as oxidizing agents and could enable the dissolution of metal oxides by oxidative leaching.[34] Presence of Cl_3^- was also confirmed by UV/Vis analysis (Figure 3a) of DESTT and DES. A strong absorption band for DESTT was found at about 247 nm, which was close to that reported for the same DES (240 nm) and [BMIM]PF_6 ionic liquid (256 nm).[24,32] For comparison, UV/Vis measurements were carried out on a DES after Cl_2 bubbling (DES-CL3). A wide absorption peak at value (242 nm) close to that of DESTT was found with the addition of a weaker absorption band at about 362 nm, which could be attributed to dissolved Cl_2 in DES.[31] To prove the possible role of Cl_3^- in metal oxides dissolution, DES-CL3 was tested in leaching experiments of the LIBs black mass. The extraction yields of the different metals during the leaching with DES-CL3 are reported in Figure 3b. The extraction yields follow the same trend found with DESTT (Figure 1b). This corroborates the hypothesis that Cl_3^- formation could play a pivotal role in the enhancement of metal dissolution by enabling an oxidative leaching mechanism. Oxidative metal oxides leaching in the same DES was recently proposed by Pateli et al. by direct electrochemical oxidation of
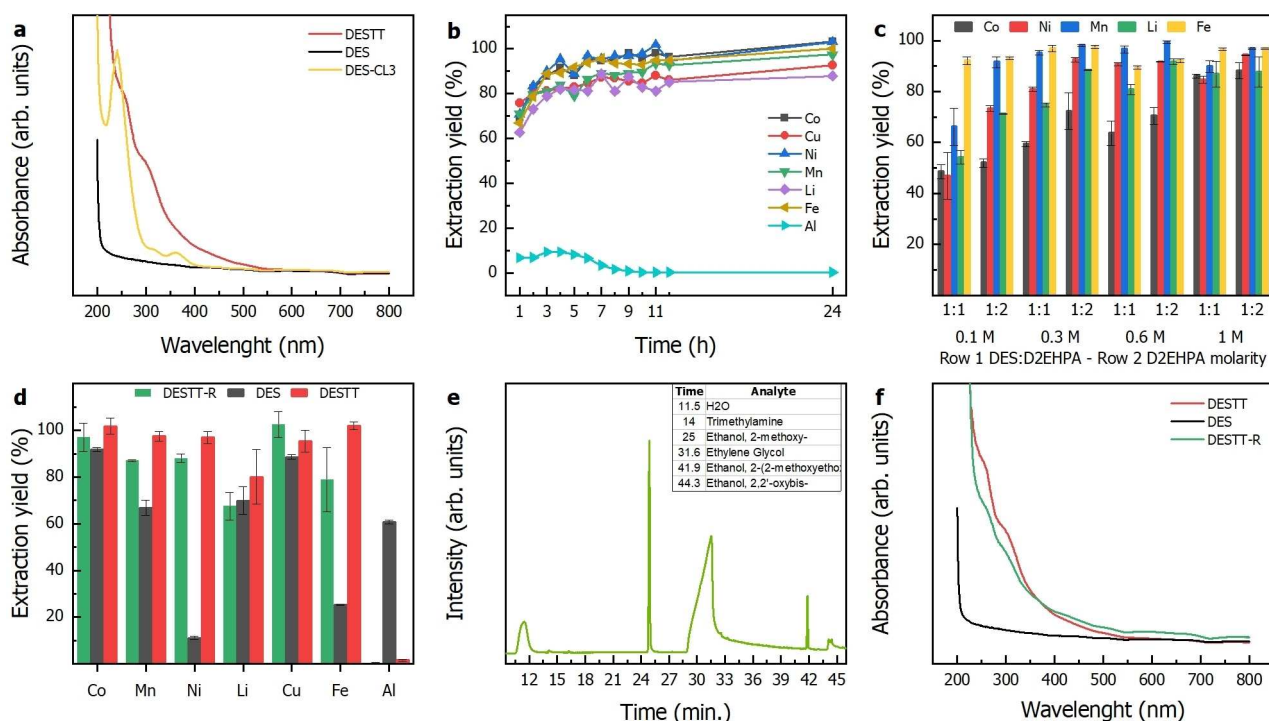

Figure 3. (a) UV/Vis spectra of DES, DESTT, and DES after Cl_2 bubbling (DES-CL3). (b) Metal extraction yields obtained leaching the black mass with DES-CL3. (c) Metal extraction yields obtained leaching the black mass with regenerated DESTT (DESTT-R) and (d) solvent extraction results on DESTT after leaching. (e) Total ion chromatogram in full scan acquisition (20–300 m/z) recorded by GC-MS and (f) UV/Vis spectra of DESTT-R.

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metal oxides.[35] Here, we propose Cl_3^- as oxidizing agent, and the suggested mechanism is reported. The first step is the oxidation of the Cl^-, coming from the choline chloride to Cl_2 [Eq. (1)], and the formation of Cl_3^- by the equilibrium reaction between Cl^- and Cl_2 [Eq. (2)]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^- \tag{2}$$

Cl_3^- acts as oxidizing agent with respect the oxygen in the oxide moiety of the metal oxides, allowing overcoming the lattice energy of the MeO (and LiMeO) and thus enabling the formation of chloro-complexes, without a further oxidation of metals ($E^0_{Me^{3+}/Me^{2+}} > E^0_{Cl^{3-}/Cl^-}$; Me=Co, Ni, Mn):

$$Cl_3^- + 2e^- \rightarrow 3Cl^- \tag{3}$$

$$2MeO + 8Cl^- \rightarrow 2[MeCl_4]^{2-} + O_2^- + 3e^- \tag{4}$$
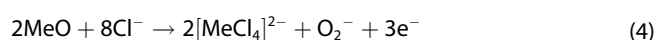
When $T = 180\,°C$, cooling down Ni forms $[Ni(EG)_3]^{2+}$. By appropriately combining Equations (3) and (4), we get the following Reaction [Eq. (5)]:

$$4MeO + 7Cl^- + 3Cl_3^- \rightarrow 4[MeCl_4]^{2-} + 2O_2^- \tag{5}$$

It should be remarked that the reduction of metals to their divalent oxidation state is a mandatory step for their solvation. It was previously reported that the reduction of metals can take place by the oxidation of EG.[5] However, we did not find compounds that can be related to the direct oxidation of EG from GC-MS and ATR-FTIR spectroscopy (Figures S5 and S6). It cannot be excluded that Co, Ni, and Mn, contained in the black mass at an oxidation state higher than (II), could be reduced by the oxidation of Cl^- to Cl_2 during the leaching. In addition, we found N,N-dimethylaminoethanol as additional reduction product of CC after black mass leaching (Figure S5). N,N-Dimethylaminoethanol could derive from the addition of an electron to CC, implying the oxidation of other species, with the formation of a methyl radical.[24] The latter can react with Cl_2 giving methyl chloride. The addition of an electron to CC could also lead to the formation of trimethylamine and ethanol radical, which, similarly to the above-mentioned methyl radical, endures chlorination. Both these reductions implying the oxidation of other species and could justify the presence of Cl_2. All those side products are visible in the GC-MS chromatogram of DESTT (Figure 2a). Methoxy and dimethoxy derivatives could be originated from the substitution reaction at high temperature of EG on chloride derivative, such as methyl chloride, at the electrophile site. A similar mechanism could be suggested for 2-(2-methoxyethoxy)ethanol, considering the presence of 2-chloroethanol. Regarding the formation of O_2^- [Eq. (4)], it is well known as superoxide is typically unstable, especially in water, and it is difficult to identify it analytically.[36] On the other hand, Pateli et al. have recently demonstrated that the stability of the superoxide ion, produced by electrochemical oxidation of metal oxides in the same DES applied in our work (EG:CC), is extended over the course of hours after its identification by means of UV/Vis spectroscopy.[35] Unfortunately, the application of UV/Vis spectroscopy to identify the superoxide ion is elusive in our system owing to the complexity of the sample: the superoxide ion absorbs in the range of 250–270 nm, where the absorption by several other species takes place (e.g., Cl_3^- absorbs in the same wavelength range). This does not allow identify unambiguously the absorption band of the superoxide ion by UV/Vis spectroscopy.

In summary, differently from DESs with an organic acid as hydrogen bond donor, for which the metals extraction takes place through the metal oxide protonation, the main responsible in metals extraction using CC:EG DES seems to be the hydrogen bond acceptor. In fact, the formation of Cl_3^- acting as oxidizing agent in the oxidative leaching is made possible by the oxidation of the chloride coming from CC. In addition, the chloride sustains the solvation of the metals by making possible the formation of stable metal chloro complexes.

To evaluate the possibility of DESTT reutilization, we performed a non-aqueous solvent extraction of Co, Ni, and Mn from DESTT using the common extractant di-2-ethylhexylphosphoric acid (D2EHPA) in kerosene. The solvent extraction results are reported in Figure 3d. Using D2EHPA at the highest investigated concentration of 1 M, we obtain the highest extraction yield for any target metal (Co=88%, Ni=95%, Mn=96%). Based on the extraction yield values obtained using DESTT and the solvent extraction results an overall recovery balance was calculated for Co, Ni, and Mn resulting, respectively, in 88, 86, and 90%. However, the solvent extraction procedure reported should be regarded only as a tool to remove metals from DES in order to evaluate the reuse DES, which is the main objective of the work.

After metal separation by D2EHPA, DESTT was reused in a new leaching experiment leading to extraction yields close to those attained with DESTT (Figure 3c). The GC-MS analysis of DESTT–R (DESTT after first stage leaching and extraction with D2EHPA) (Figure 3e) evidences the absence of many of the decomposition compounds found before solvent extraction. In particular, nonpolar molecules (e.g., ethers) soluble in kerosene are co-extracted and totally disappear from GC-MS chromatogram. The absence of the ethers in DESTT–R together with a metal extraction yields close to that of DESTT confirms the negligible effect of ethers on the dissolution capacity of DESTT. On the other hand, DESTT–R maintains the same UV/Vis absorption bands, suggesting the Cl_3^- is not extracted during D2EHPA treatment (Figure 3f).

It should be remarked that, while the Cl^- ions employed to form Cl_3^- are regenerated after oxidative leaching, DES decomposition includes reactions that determine a progressive consumption/degradation of EG and CC. These decomposition products can compromise green DES characteristics such as safety and non-toxicity. For example, after solvent extraction, the most abundant decomposition product that still remains is 2-methoxy-ethanol, which, even though widely employed in many industrial applications, is reproductive toxicant in sperm, leading to testicular pathology (Hazard statements: H226, H302, H312, H332, H360), and is flammable.[29,37] Therefore, there is a

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significant interest towards minimizing the extent of DES decomposition reactions, while maintaining unchanged the dissolution ability. In this respect, it is worth to notice that the leaching with DESTT could allow for milder conditions (e.g., lower temperature and shorter reaction times). This could allow slowing down the kinetics and reducing the extent of DESTT decomposition. Here, we have already demonstrated that leaching duration can be reduced with DESTT by 6 times with respect to fresh DES (from 24 to 4 h). We have preliminary quantified the decomposition of fresh DES after 24, 48, and 72 h by GC-MS and FTIR spectroscopy (Figures S8 and S9) in terms of 2-methoxy-ethanol and 1,2-dimethoxy-ethane, which are the main decomposition products. Their production rate follows a linear trend with the thermal treatment duration (Figure S10), and thus a reduction of the leaching duration by 6 times it is expected to proportionally reduce the consumption of CC and EG.

On the other hand, different approaches, other than thermal treatment, should be possibly explored to purposefully modify DES composition in a way that enhances the ability to dissolve metal oxides and excludes the formation of undesired products. An alternative way to eliminate the toxic compounds and retain the advantage of improved metal oxide dissolution could involve the preparation of DES with Cl_3^-, the only decomposition product that seems to have an effective role, without going through the thermal treatment of DES. For example, the formation of Cl_3^- could be induced by the electrochemical oxidation of DES (Cl^-) allowing for the formation of Cl_3^- without handling Cl_2, which, as demonstrated, quantitatively reacts with Cl^- and hence is not released from DES. In this way, by appropriately selecting the oxidation potential and an opportune reduction couple, a DES with only Cl_3^- could be prepared and safely used.

Conclusions

The decomposition of deep eutectic solvents (DES) during the leaching of the lithium-ion battery (LIB) black mass considerably increased the dissolution rate and yields of metal oxides. This improved dissolution was mainly determined by the oxidation of Cl^- to Cl_2 [Eq. (1)] and by the subsequent formation of Cl_3^- [Eq. (2)], which made possible the oxidative leaching of the metal oxides. DES decomposition led to the formation of a variety of ether molecules, most of which were removed during the recovery of metals by solvent extraction. On the other hand, Cl_3^- remained in the regenerated thermally treated DES (DESTT), ensuring the same initial extraction yields when it was reused.

The main challenge introduced by the application of DESs to run the leaching of LIB metal oxides should now be apparent. The design of the LIB recycling process should be performed to maximize the reuse of DES, maintaining satisfactory metal extraction yields over the successive DES reuses, and preventing the formation of toxic products, which would lead to the shifting of environmental impact. To this purpose, analyzing the kinetics of DES decomposition product formation

and the impact of DES decomposition on metal oxide dissolution is mandatory. Indeed, the characterization of these kinetics can make it possible to perform an integrated design and life cycle assessment of the whole recycling process.

In this respect, it is believed that future research, for any DES formulation, should address the complex problem of evaluating how the leaching performances change over successive cycles of the whole recycling process. Particularly, the analysis should be aimed at identifying the parameters optimizing the leaching performances, not by analyzing a stand-alone leaching unit operated with fresh DES, but rather the performances that are attained over successive cycles of the whole recycling process. This imposes a shift of the research philosophy, away from the analysis of the stand-alone leaching stage, which is currently followed by most of the studies in this area, and towards the integrated analysis of the whole recycling process.

On the other hand, with this approach, if only metal extraction kinetics are monitored, answering the question of whether the DES can ensure economic feasibility of the recycling process may require considerable experimental efforts: replication of the whole recycling process over numerous cycles should be performed. A more effective approach could be the application of experimental data to develop mechanistic kinetic models of DES degradation and metal oxide dissolution. To this purpose, detailed analyses should be performed, in addition to the measurement of metal concentrations, to evaluate whether DES degradation takes place. Experiments should be designed to identify the mechanisms of metal oxide dissolution and DES degradation and, particularly, evaluate how DES degradation can affect metal oxide dissolution. Once the species involved and the reaction mechanisms are confidently described, it will be possible to identify reliable kinetic models based on the species concentrations data. These models should be used to predict the evolution of DES composition and performances.

Experimental Section

Solutions

Solutions employed in the whole work are the following:

DES: DES was synthesized by choline chloride (Alfa Aesar 98%+) and ethylene glycol (VWR chemicals ≥99.0%). CC and EG were stored at 50°C prior to use. The required amount of CC and EG to obtain a molar ratio of 1:2 was added in a thermostatated reactor at 50°C and stirred until a homogeneous clear liquid phase was formed.

DESTT:	DES treated at 180°C for 72 h.
CC + EGTT:	Solution obtained by mixing EG treated at 180°C for 72 h with pristine CC.
CCTT + EG:	Solution obtained by mixing CC treated at 180°C for 72 h with pristine EG. A brown colloidal phase is formed.
CCTT + EGTT:	Solution obtained by mixing CC and EG separately treated at 180°C for 72 h. A brown colloidal phase is formed.

DES-CL3: Cl$_2$ produced by mixing MnO$_2$ and HCl (37%) was bubbled in the pristine DES. Following, to remove the excess of Cl$_2$, the solution was firstly purged with N$_2$ and then heated at 180 °C for 10 min in an open bottle. Without this latter treatment we found a boost oxidation of DES during leaching with the formation of a solid brown-black fraction.

DESTT-R: DESTT after black mass leaching and regeneration removing metals by using solvent extraction.

Electrodic powder

The employed electrodic powder used in this work was the same characterized in our recently published work.[18] End-of-life LIBs electrodic powder was obtained after the mechanical treatment of 50 kg of LIBs collected by an Italian waste disposal company (Seval srl). Mechanical pre-treatment has allowed the separation of the electrodic powder from copper and aluminum current collector, steel, and plastics case. Electrodic powder was separated by sieving the crushed batteries with mesh size of 0.5 mm. Characterization of the electrodic powder was attained by its microwave assisted leaching (Ethos Milestone srl) followed by the analysis of leachate. Microwave-assisted leaching was performed on six samples of 0.5 g of electrodic powder using 10 mL of aqua regia at 200 °C for 30 min. The performed characterization evidenced that cobalt was the metal with the largest concentration in the electrode powder (164.2 ± 3.1 mg g^{-1}) followed by manganese (78.6 ± 2.9 mg g^{-1}), nickel (42.7 ± 1.6 mg g^{-1}), and Li (39.2 ± 1.6 mg g^{-1}). Cobalt predominance is explained by the extensive application of LiCoO$_2$ as cathode oxide material over the last years. Copper (8.7 ± 0.5 mg g^{-1}), aluminum (3.1 ± 0.1 mg g^{-1}), and iron (19.1 ± 2.6 mg g^{-1}) impurities were found in the electrode powder, whose presence can be attributed, respectively, to metallic current collectors and steel case. Commercial LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (Aldrich, >98%, particle size <0.5 μm) and NiO (Aldrich, 99.999%) were used in comparison leaching experiments.

Leaching experiments

Leaching experiments with 24 h duration, with only one sampling at the end of the experiment, were carried out using 0.5 g of electrodic powder and 25 g of solution in a closed glass bottle of 50 mL. To evaluate the extraction yield as function of time, leaching tests were carried out using 5 g of powder and 250 g of solution. In the latter experiments, 3 mL of suspension was sampled every hour for the first 12 h and at the end of the experiment (12 + 1 sampling). In this case, during sampling, we removed a suspension of solution and powder, thus maintaining constant the powder/solution ratio during the experiment. Temperature was controlled by immersing the bottle in a thermostatated oil bath at 180 ± 1 °C. After any experiment, the metals bearing solutions was filtered and diluted in acidified water. Metals content was estimated by atomic absorption spectroscopy (AAS; ContrAA300 Analytic Jena GBH). The employed electrodic powder was obtained after the mechanical treatment of 50 kg of LIBs collected by an Italian waste disposal company (Seval srl). Mechanical pre-treatment has allowed the separation of the electrodic powder from copper and aluminum current collector, steel, and plastics case. The extraction yield for any metals was defined as Equation (6):

$$\text{Extraction yield } [\%_{Me}] = \frac{C_{Me} V}{m_p C_{PMe}} \times 100 \qquad (6)$$

where C_{Me} [mg L^{-1}] is the concentration of the metal Me (Me = Co, Ni, Mn, Li, Fe, Cu) estimated by AAS in the leachate, V [L] is the DES volume, m_p [g] is the mass of electrodic powder, and C_{PMe} [mg g^{-1}] is the concentration of the metal Me in the electrodic powder.

DESTT regeneration

Metals were extracted from DESTT by non-aqueous solvent extraction. Di-2-ethylhexylphosphoric acid (D2EHPA; Sigma Aldrich, 97%) 0.1, 0.3, 0.6, and 1 M solutions were prepared by diluting D2EHPA in kerosene (Sigma Aldrich, reagent grade). We would want to remark that the only scope of the solvent extraction procedure here reported is to remove the metals from DES in view of its reutilization. The solvent extraction procedure should be seen only as a tool to remove metals from DES in order to evaluate the reuse DES, which is the main objective of the work. We are not proposing this procedure in a recycling process both only to regenerate and reuse DES. Solvent extraction using greener and more sustainable extractant and diluent was successfully applied in leaching of LIBs electrodic powder using DES.[10] D2EHPA was partially saponified (60%) by adding NaOH 10 M and 5% v/v of tributyl phosphate (98%, Sigma Aldrich) was added as phase modifier. 5 mL of DES was employed in any extraction experiments and different organic phase volumes were employed in order to have DES/D2EHPA ratio equal to 1:1 and 1:2. Shaking of the two phases was carried out for 0.5 h in a rotary shaker at 200 rpm. Raffinate DES was analyzed by AAS to determine the amount of extracted metals. Metals extraction yields was computed as follows [Eq. (7)]:

$$\text{Extraction yield } [\%_{Me}] = \frac{C_{Mei} - C_{Mef}}{C_{Mei}} \times 100 \qquad (7)$$

where C_{Mei} [mg L^{-1}] is the initial concentration of the metal Me (Me = Co, Mn, Li, Cu) into the DES and C_{Mef} [mg L^{-1}] is the concentration of metals into the DES after the solvent extraction.

Physical-chemical characterizations

UV/Vis spectra (Agilent Cary 50) were recorded in the range of 800 to 300 nm. DES samples were inserted into a 1 mm-pathlength quartz cuvette. Spectra were acquired at 25 and 180 ± 10 °C by controlling cuvette holder temperature for the evaluation of the thermochromic behavior of NiO leached with DESTT. Head space volume of DESTT was analyzed by injection of 100 μL in GC-MS. An HP GC 6890 coupled with an HP 5973 A single quadrupole mass-selective detector was used in electronic ionization (EI) mode, operating at 70 eV (Agilent Technologies, Palo Alto, CA). A VOCOL® Capillary GC Column (60 m × 0.25 mm film thickness 1.5 μm) was used for the separation, with He as carrier gas at a flowrate of 0.8 mL min^{-1}. The injector was set at 200 °C, in split mode (1:10). The temperature program was: 35 °C (initial temperature) held for 4 min, ramped at 4 °C min^{-1} to 210 °C and held for 10 min. Analysis of liquid decomposition products was carried out on DES after leaching at 180 °C for 24 h and on the same DES after volatile ammine stripping by bubbling N$_2$. 1 μL of liquid DES was injected to the GC-MS using the same GC method reported above but with a final oven temperature of 240 °C. The qualitative analysis was performed by NIST library. IR spectra of DES, DESTT, and several mixtures were collected using a Thermo Nicolet 6700 instrument (Thermo Scientific, Waltham, MA, USA), equipped with a Golden Gate diamond single-reflection device (Specac LTD, Orpington, UK). FTIR spectra, recorder in ATR mode, were collected at room temperature, between 4000–600 cm^{-1} with 200 scans per spectrum and 4 cm^{-1} resolution. To avoid moisture absorption, freshly

prepared samples were casted on diamond, closed with ATR-FTIR tool for volatile species, and analyzed. XPS results were obtained with an Omicron NanoTechnology MXPS system, equipped with a dual X-ray anode source (Omicron DAR 400) and an Omicron EA-127 energy analyzer. Spectra were acquired at a take-off angle of 21° with respect to the sample surface normal with achromatic Mg K_α photons ($h\nu = 1253.6$ eV) generated operating the anode at 14 kV × 14 mA. The Al 2p photoionization region was recorded using an analyzer pass energy of 20 eV, while for survey spectra a pass energy of 50 eV was used. The samples were attached to the stainless-steel sample holder with a conductive scotch tape. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer using D_2O as solvent.

Associated content

The Supporting Information contains XPS Al 2p spectra of pristine Al and survey spectra of black mass after leaching with DESTT, UV/Vis spectra of NiO in DESTT at 30 and 180 °C, GC-MS, ATR-FTIR, and ^{1}H NMR spectrum of DESTT after leaching, DES obtained for different durations of the thermal treatment, and concentrations of 1,2-dimethoxy-ethane and 2-methoxy-ethanol in DES treated at 180 °C for 24, 48, and 72 h.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

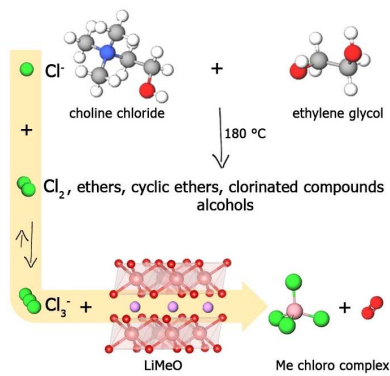The data that support the findings of this study are available from the corresponding author upon reasonable request.

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RESEARCH ARTICLE

Finding a (dis)solution: Thermal decomposition of chloride-ethylene glycol deep eutectic solvent taking place during the leaching of waste Li-ion batteries drives the dissolution of metals through an oxidative leaching mechanism enabled by the formation of Cl_3^-.

Cl⁻

choline chloride + ethylene glycol

180 °C

Cl_2, ethers, cyclic ethers, clorinated compounds alcohols

Cl_3^- +

LiMeO

Me chloro complex

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Decomposition of Deep Eutectic Solvent Aids Metals Extraction in Lithium-Ion Batteries Recycling