

# Deep Eutectic Solvents: Green Approach for Cathode Recycling of Li-Ion Batteries

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The overarching demand of modern electronics and electrification of transportation has tremendously increased usage of rechargeable lithium-ion batteries (LIBs). As a result, massive amounts of solid waste are generated from the end-of-life LIBs and expected to increase by two- to threefolds in the near future. Without proper recycling strategies and infrastructure, the immediate threat of environmental pollution and wastage of resources is clear. One way to circumvent these challenges is to recycle the spent LIBs and recover the components and materials, especially heavy metals for future repurposing applications. This review highlights the recent discoveries on the use of deep eutectic solvents (DESs) as an economical and environmentally friendly medium for metal recovery from spent LIBs. Herein, how the different hydrogen donors and acceptors affect the overall performance of DES in terms of leaching efficiency, time, temperature, and metal recovery rates are outlined. Very importantly, the mechanism of metal leaching from the metal oxides using DES is discussed. Finally, some potential strategies and opportunities for further development of novel DES for metal-recovery from not only spent LIBs but also other industries such as, mining, oil, and agriculture are outlined.

## 1. Introduction

Lithium-ion batteries (LIBs) are high-voltage, high-energy, and high-power density energy storage devices with long cycle life, therefore intensively applied in full and hybrid electric vehicles, portable electronic devices (computers, mobile phones, and tablet), and renewable (solar and wind) sector.<sup>[1,2]</sup> Typically, LIBs for such applications with estimated lifetime of around 3–10 years generate a vast amount of waste at their end-of-life.<sup>[3,4]</sup> It is estimated that over 11 million tonnes of spent LIBs will be discarded through to 2030, and only less than 5% of them are being recycled.<sup>[4]</sup> Moreover, due to rapidly increasing demand of LIBs, the price of crucial element resources (Li, Ni, and Co) is also significantly increasing. In contrast, the health and environmental concerns may arise in the event of large, accumulated


quantities of cobalt and lithium metals, which typically constitutes up to 20 and 7 wt%, respectively, of LIB cathodes, as well as toxic and flammable electrolytes (e.g., lithium hexafluorophosphate, LiPF<sub>6</sub>).<sup>[3–5]</sup> Therefore, efficient recovery of such raw materials in spent LIBs is extremely crucial.

At present, LIBs are recycled commercially using well-known processes such as pyrometallurgy, hydrometallurgy, and direct recycling.<sup>[4]</sup> However, these processes do not extract the maximum value from their feedstock. For instance, pyrometallurgy, or smelting operate at very high temperature (over 1100 °C), which eliminates several materials (carbon anode, plastic separator, and electrolyte solvents) through vaporization (electrolyte), combustion, and melting. The final product is a mixed alloy of cobalt, nickel, and copper. The concept of direct recycling is simple: keep the cathode crystal structure intact. The definition of direct recycling is the recovery, regeneration, and reuse of battery components directly without breaking down the chemical structure. It has also been called direct cathode recycling and cathode-to-cathode recycling. By recovering cathode material, several energy-intensive and costly processing steps can be avoided. Not only does recovery of more materials offer potential additional revenues, but also costs and other impacts from waste treatment can be avoided. Advantages include low temperatures and low energy consumption, and the avoidance of most impacts from virgin material production.<sup>[6,7]</sup> However, the electrode

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separation is still one of the important challenges.<sup>[7]</sup> In contrast, hydrometallurgy, or leaching, is considered as promising method as major battery components can be recycled. This method is simple, consumes less energy and provides high leaching efficiency.<sup>[8,9]</sup> It involves the dissolution of metals in both acid and alkaline solutions and subsequently can be recovered by precipitation, extraction, or electrodeposition methods.<sup>[1,10]</sup> Li et al. successfully recovered 89% of cobalt from the spent LIBs by a simple ultrasonic treatment followed by acid leaching and finally chemical precipitation.<sup>[11]</sup> However, recovery using hydrometallurgy route evolves large quantities of toxic gases and require longer leaching periods to recover the desired metals.<sup>[12]</sup> The use of stronger leaching agents generate a substantial amount of secondary pollutants (e.g., SO<sub>3</sub>, Cl<sub>2</sub>, NO<sub>x</sub>, etc.), which pose significant environmental and health risks.<sup>[13]</sup> Organic leaching agents are the promising alternative to these inorganic counterparts. Although the organic leachants pose less risk to the environment, they have their own challenges. They require stronger reducing agents, such as hydrogen peroxide, and moderate operating temperatures to achieve the good leaching efficiency. For example, oxalic acid as a mild leaching agent requires higher pyrolysis temperature due to its inability to fully dissolve metals at room temperature.<sup>[10]</sup> Similarly, malic acid needs an additional reducing agent to accelerate the process of metal-recovery from spent LIBs.<sup>[8]</sup> The leaching efficiency using succinic acid was increased with the presence of a reductant hydrogen peroxide at 70 °C.<sup>[14]</sup> These challenges clearly demonstrate the need of alternative simple, green, and economic solvents for the effective metal leaching and recovery process.

As well-known green solvents, ionic liquids (ILs) have been actively studied in the past decades. They are mainly liquids below 100 °C so basically molten at room temperature.<sup>[15]</sup> ILs were first reported by the Paul Walden in 1914, making a breakthrough in the history of chemistry.<sup>[16]</sup> Owing to unique physicochemical properties (e.g., chemical and thermal stabilities, non-flammability, better solvability, high ionic conductivity, and wide electrochemical potential window), ILs have widely contributed to chemistry as well as electrochemistry.<sup>[17–19]</sup> Moreover, ILs can be utilized as leaching agents for the metal recovery from spent batteries.<sup>[20,21]</sup> Although their leaching efficiency is quite good, they require expensive reducing agents as well as need to operate in specific inert environments.

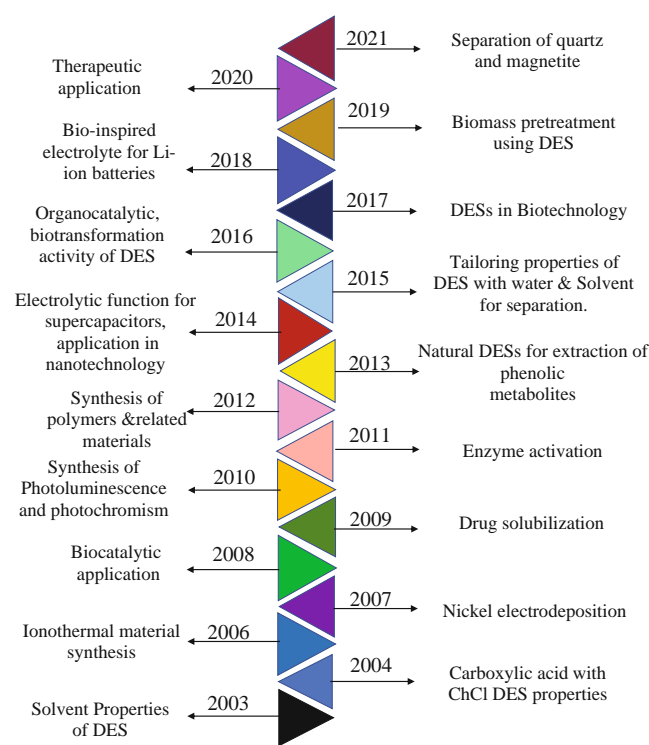
Deep eutectic solvents (DESs) are a new class of green solvents, first introduced in 2003 by Abbott<sup>[22]</sup> and exhibit several similar extraordinary characteristics like ILs such as, low cost, environmentally benign in nature, low volatility, biodegradable, and easy to synthesize.<sup>[23–26]</sup> They are primarily used for several applications, such as metal electrodeposition,<sup>[27]</sup> metal recovery, extraction, biocatalytic activity,<sup>[28]</sup> organic synthesis,<sup>[29]</sup> and so forth. Recently, they have been emerged as potential leaching agents for the metal recovery from spent batteries and considered as a promising alternative to inorganic/organic acids.<sup>[3,28]</sup> One of major benefits of using DESs in this research area is that there is no requirement for an extra step such as a reducing agent.<sup>[3,9,23]</sup>

Several efforts have been made to develop low-cost and green DESs for efficient leaching of metals from end-of-life rechargeable batteries, however, rarely been summarized. This focused review is an attempt to systematically outline recent advances in the DES-based metal recovery from spent rechargeable

batteries. The review begins with the definition and short history of DES as well as their recent applications. We highlight how the variation in the composition of DESs affects the solvent's properties and functions. For instance, how the hydrogen donors/acceptor and their ratio affect the properties of DESs and their consequent effect on metal recovery. We also outline the mechanism of metal leaching using DES. Finally, a brief outlook of the challenges and prospects for the future development of metal recovery using DES is provided, which will guide for the new applications of DESs.

## 2. History of Deep Eutectic Solvents (DES)

The term deep eutectic solvent was first introduced by Abbott and his coworkers where the authors explained the very large depression in melting point of two mostly used compounds to make the DES, which included choline chloride (ChCl) and urea.<sup>[30]</sup> After the first breakthrough in 2003, DESs have been explored and employed intensively in various research areas. **Figure 1**



**Figure 1.** Timeline of DES exploration of specific applications. Solvent properties of DES,<sup>[30]</sup> carboxylic acid with ChCl DES properties,<sup>[31]</sup> ionothermal materials synthesis,<sup>[32]</sup> nickel electrodeposition,<sup>[33]</sup> biocatalytic application,<sup>[34]</sup> drug solubilization,<sup>[35]</sup> synthesis of photoluminescence and photochromism,<sup>[36]</sup> enzyme activation,<sup>[37]</sup> synthesis of polymer and related materials,<sup>[38]</sup> natural DES for extraction of phenolic metabolites,<sup>[39]</sup> electrolytic function for supercapacitors<sup>[40]</sup> and application in nanotechnology,<sup>[41]</sup> tailoring properties of DES with water<sup>[42]</sup> and solvent for separation,<sup>[43]</sup> organocatalytic-biotransformation activity of DES,<sup>[44]</sup> application in biotechnology,<sup>[45]</sup> bio-inspired electrolyte for LIBs,<sup>[46]</sup> biomass pretreatment using DES,<sup>[47]</sup> therapeutic application,<sup>[48]</sup> and separation of quartz and magnetite.<sup>[49]</sup>

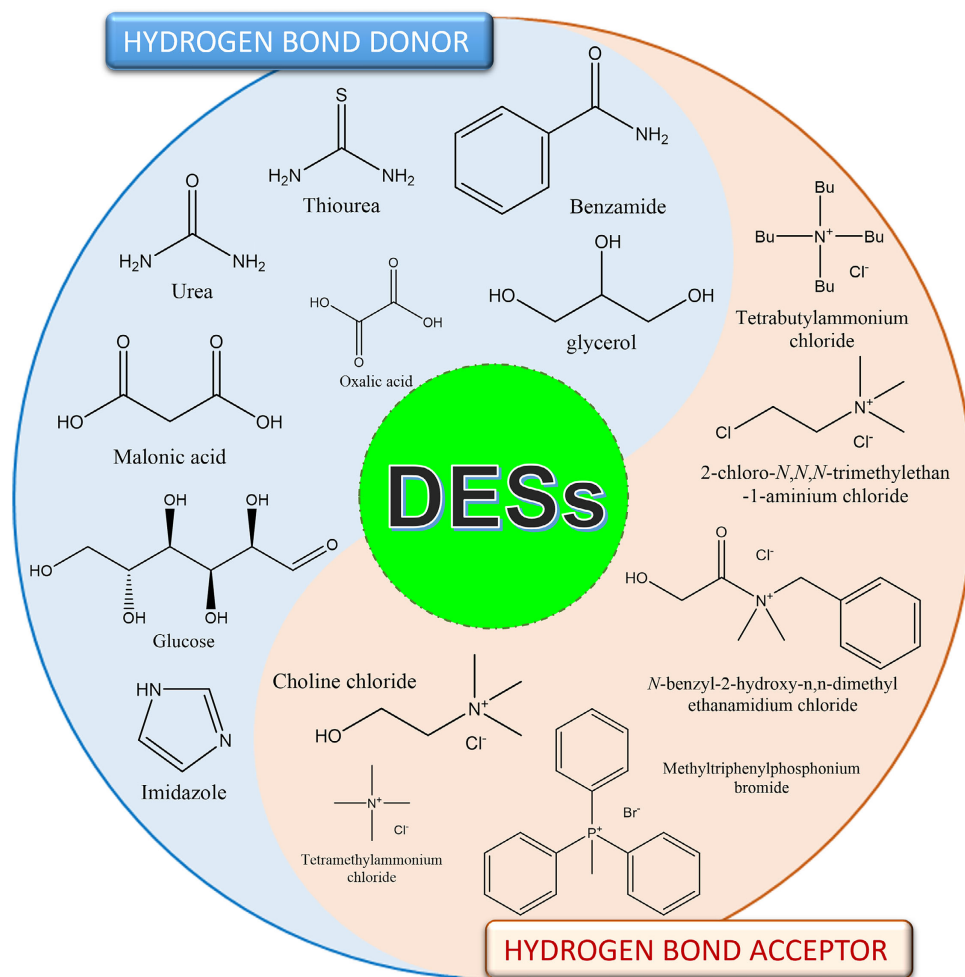
provides a summary of initial DESs applied in different topics by time.<sup>[30–49]</sup>

Generally, DESs are formed when the donor and the acceptor of compounds are bound by hydrogen bond at ambient temperature in a liquid state. A variety of common hydrogen donors and acceptors for the preparation of DESs were exhibited in **Figure 2**. Eutectic mixtures of salts have been widely used to lower the temperature for applications of molten salts. Under the extreme temperature, the formation of these molten salts by combining the quaternary ammonium salts with metal salts is used to obtain the deep eutectic mixtures from the complex anions, which reduces the lattice energy and maintains the low freezing point.<sup>[50]</sup> The very first DES reported, including ChCl and urea, can produce a eutectic mixture at ambient temperature and have the properties which are rare as solvents. The depression in freezing point is result of the interaction between urea molecules and ChCl ions at 1:2 molar ratio. It reported that the compounds which are capable of forming a hydrogen bonding with the chloride ions can highly exhibit the homogenous property of the solvents.<sup>[22]</sup> DESs demonstrate the similar characteristics as ionic liquids therefore are considered as ILs-subclass. However, DESs are economical, easily obtained, and biodegradable.

Hence, they have been taken into account as an ideal solvent for green chemistry applications.<sup>[51,52]</sup>

Basically, DESs can be classified into four types as shown in **Table 1**.<sup>[27,53,54]</sup> They are described by the formula  $Cat^+ X^- zY$ ; where “Cat<sup>+</sup>” is a cation of any ammonium, phosphonium or sulfonium, X is a Lewis base, a halide anion “Y” is Bronsted acid. The complex anionic species are formed when X<sup>-</sup> reacts either with Lewis base or Bronsted acid “Y”, and “z” refers to number of Y molecules which interact with anion to form the final product.<sup>[55]</sup>

In type I, DESs formed from quaternary ammonium salts and  $MCl_x$  is mainly considered to be an analogous to study the metal halide/imidazolium salt. Few examples include the well-studied chloroaluminate/imidazolium salt and various metal halides such as  $FeCl_2$ ,  $AgCl$ ,  $CuCl$ ,  $LiCl$ ,  $LaCl_3$ ,  $CdCl_2$ ,  $CuCl_2$ ,  $SnCl_2$ ,  $YCl_3$ , and so forth.<sup>[53,56]</sup> Type-II DESs is hydrated metal halides and ChCl are sufficiently available which is contrary to type I where the nonhydrated metal halides are limited. Another advantage of type II is that they are relatively inexpensive and the metal salts are coupled with in-built moistness insensitivity, which makes them applicable at pilot scale processes.<sup>[53]</sup> Type III eutectics are the product of ChCl and hydrogen bond donors, which exhibits wide range of applicability and ability in solvation



**Figure 2.** Common hydrogen bond donors and acceptors for formation of DESs.

**Table 1.** Classification of DESs and its specific applications.

Type	Description	General formula	Example	Application	Ref.
Type I	A combination of metal and organic salts	$Cat^+ X^- z MCl_x$	$ZnCl_2 + ChCl$	Metal electrodeposition	[27]
Type II	A hydrate of metal salt and organic salt	$Cat^+ X^- z MCl_x yH_2O$	$CoCl_2 \cdot 6H_2O + ChCl$	Large scale industrial process	[53,61]
Type III	A mixture of hydrogen bond donor and organic salt	$Cat^+ X^- z RZ$	$ChCl + Urea$	Metal recovery, extraction, biocatalytic activity	[28]
Type IV	A mixture of metal salts in addition with hydrogen donor compound	$MCl_x + RZ = MCl_{x-1}^+ RZ + MCl_{x+1}^-$	$MCl_x + Urea/Ethylene Glycol/Acetamide$	Precursor for LnDES, materials for superconductors, lasers, magnets, and electronics	[28]

process of metal species such as chlorides and oxides. Type III DESs are very easy to prepare, relatively nonreactive with water and most of them are economical. Most importantly, they are environment-friendly.<sup>[22]</sup> Although type III DESs are versatile in terms of applications such as extraction of glycerol from biodiesel<sup>[57]</sup> and metal oxides administration, their electrochemical activities are less efficient as compared to the type I ones.<sup>[53]</sup> Lastly, type IV eutectics are the lanthanide based DESs (LnDESs). They are mixtures of salts with molecular components (e.g.,  $ZnCl_2:urea$ , etc.), which are useful to make few liquids mainly a hydrophobic DESs and metal salts.<sup>[58–61]</sup> Type IV ones are known as either low-melting mixtures (LMMs) or low transition temperature mixtures (LTTMs).

In general, the physical properties of DESs are supposedly featured by some significant factors such as molar ratio, density, viscosity, ionic conductivity, melting point, freezing point, and so forth.<sup>[62–65]</sup> Few DESs and their corresponding characteristics are listed in **Table 2**. According to the specific applications, their properties can be chemically tailored. For instance, the freezing point depends on the type of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) as well as its molar ratio. Taking  $ChCl:Urea$  DES as an example, the freezing point was estimated to be roughly 12 °C and greater than 50 °C in the molar ratio of 1:2 and 1:1, respectively.<sup>[64]</sup>

The strong ability of donating and accepting electrons or protons makes them ideal chemicals for the degradation process of

**Table 2.** Physicochemical and thermal properties of DESs.

DES	Molar ratio	Melting point [°C]	Freezing point [°C]	Density [g cm <sup>-3</sup> ]	Viscosity [cP]	Ionic conductivity [mS cm <sup>-1</sup> ]	Surface tension [mN m <sup>-1</sup> ]	Ref.
Urea:ChCl (reline)	2:1	134	12	1.25	632–750	0.199 (40 °C)	52	[27,85–87]
Ethylene glycol:ChCl (ethalene)	2:1	–12.9	–66	1.12	36–52	7.61 (20 °C)	49	[27,85–87]
Glycerol:ChCl (glyceline)	2:1	17.8	–40	1.18	259–376	0.75	55.8	[27,85–87]
Thiourea:ChCl	2:1	175	69	–	–	–	–	[85,87]
Malonic acid:ChCl	1:2	135	85	1.25	1124	0.55	65.7	[27,85,87]
Oxalic acid:ChCl	1:1	190	34	–	1500	–	–	[27,85,87,88]
Imidazole:ChCl	3:7	89	56	–	15	12	–	[27,85,87]
Benzamide:ChCl	1:2	129	92	–	–	–	–	[27,85,87]
Citric acid:ChCl	1:2	149	69	–	–	–	–	[27,85,87]
Adipic acid:ChCl	1:1	153	85	–	–	–	–	[27,85,87]
$ZnCl_2:ChCl$	1:2	–	–	–	85 000	0.06	–	[27,85,87]
DeTAB:HFIP	1:2	–	25	1.28	40	–	–	[86]
Benzoic acid:ChCl	1:1	122	95	–	–	–	–	[27,85]
2,2,2-Trifluoroacetamide:ChCl	1:2	72	–45	1.342	77	0.286	35.9	[27,85]
Acetamide:ChCl	1:2	80	51	–	–	–	–	[27,85]
Glucose:ChCl	1:1	–	–	–	34 000	–	–	[27,85,87]
Phenylactic acid:ChCl	1:1	77	25	–	–	–	–	[27,85,89]
Phenylpropionic acid:ChCl	1:1	48	20	–	–	–	–	[27,85,89]
Tricarballic acid:ChCl	1:1	159	90	–	–	–	–	[27,85,89]
Levulinic acid:ChCl	1:2	RT	–	–	–	–	–	[27,85,89]
Succinic acid:ChCl	1:1	185	71	–	–	–	–	[27,85]
$EtNH_3Cl:TFA$	1:1.5	–	–	1.041	64	0.688	46.3	[27,85]
$EtNH_3Cl:Urea$	1:1.5	–	–	1.14	128	0.348	52.9	[27,85]
EMIM:TFSI	–	–16	–	1.52	36	9	–	[86]



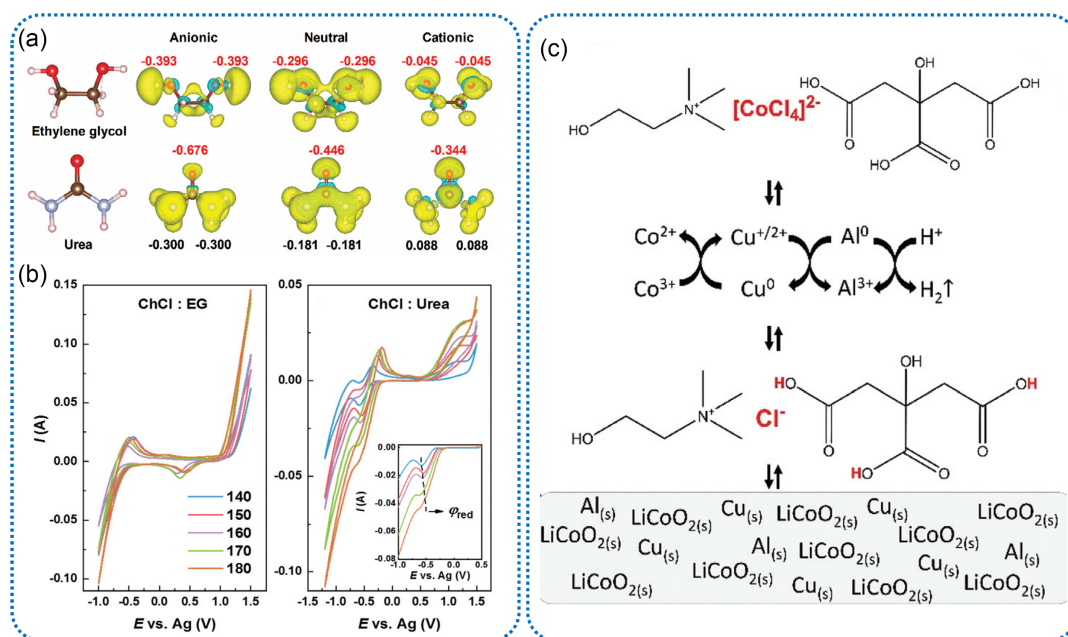
range of components such as sugars, polysaccharides, salts, drugs, proteins, and amino acids.<sup>[35,66,67]</sup> Owing to their unique characteristics, DESs have a wide range of applications from chemistry to biological viewpoint. For example, DESs can be used in chemical reactions such as electrodeposition, separation of metal, medical industry, biodiesel production, catalytic activity, cross-coupling synthesis, carbon capture, and so forth.<sup>[29,68–74]</sup> Among them, metal recovery by utilizing the DESs has gained much attraction recently, which mainly focuses on the present review. In parallel with benefits, DESs suffer from some drawbacks. First one is their own viscosity, which may limit the mass transfer.<sup>[23]</sup> It also results in poor diffusion of external components, leading to poor performance as a cause of less interaction with external species.<sup>[75]</sup> Next, in terms of metal recovery application, the shortage of knowledge related to the kinetics of leaching and the physicochemical properties of DESs has hampered the large-scale applications.

### 3. Mechanism of Metal Recovery from Spent Batteries Using DES

As discussed earlier, DESs have been widely used in metal electrodeposition, electropolishing, and extraction due to their high solubility of metal oxides. Although the exact mechanisms for dissolution of oxides by DESs have yet to be realized, Abbott et al. observed that the presence of an oxygen acceptor in the eutectic appears to be essential for digesting oxides, as it facilitates the cleavage of metal–oxide bonds.<sup>[76]</sup> In the first report of LCO leaching by ChCl:EG based DES, the tetrachlorocobaltate (II) anion complex was observed as dissolved species.<sup>[25]</sup> Such formation of chlorometalates is commonly proposed for certain metal oxides in the ChCl:EG eutectic.<sup>[76]</sup> However, the interesting fact was the

simultaneous reduction of Co(III) in LCO to Co(II) with the dissolution process. It was proposed that the dissolution of LCO in ChCl:EG involves the simultaneous oxidation of ethylene glycol and reduction of cobalt, based on the fact that the ethylene glycol is a common reducing agent. Thus, the leaching mechanism of metal oxide in DESs involves: 1) reduction of metal and 2) the formation metal chloro (chlorometalates) complexes.

The cathode materials of LIBs are composed of Li intercalated metal oxides with high valence Co(III) and/or Mn(IV) elements, which are usually insoluble. As mentioned earlier, it is anticipated that the reduction of Co and/or Mn elements play a critical role in their recycling from used LIBs. However, the reducibility (reduction potential) of ethylene glycol is relatively poor as the extraction reactions arise at high temperature (220 °C) for long periods of time (24 h). This suggests that pushing the reduction potential of DESs to more negative side will possibly accelerates the extraction reaction of valuable elements. To determine the reducibility of DESs (reduction potential), Wang and coworkers used Fukui functions calculations (density function theory) and supported by cyclic voltammetry technique.<sup>[75]</sup> In this article, the reduction potentials of ChCl:EG and ChCl:urea DES were explored. The composition of urea such as carbon and oxygen double bonds (C=O) and two amino groups (N–H) is crucial since these groups coordinate with metal ions to form metal–urea complexes via metal–O and metal–N bonds. In proposed ChCl:EG and ChCl:urea DESs, the abilities to reduce the metals is raised from the hydrogen bond donor components (ethylene glycol and urea). The atomic charges of ethylene glycol and urea were calculated using Fukui functions (**Figure 3a**) to evaluate the reducing powers of corresponding DESs. The findings suggest that the reducing power of urea is relatively higher than that of ethylene glycol, which was further proved by CV technique.



**Figure 3.** a) Fukui functions calculations (DFT) for ChCl:EG and ChCl:urea. b) Cyclic voltammograms of ChCl:EG and ChCl:urea DESs recorded at scan rate of 50 mV s<sup>-1</sup>. Reproduced with permission.<sup>[75]</sup> Copyright 2021, The Royal Society of Chemistry. c) Schematic representation of leaching of LCO using ChCl:citric acid DES, in the presence of aluminum and copper metal. Reproduced with permission.<sup>[28]</sup> Copyright 2021, The Royal Society of Chemistry.

Figure 3b shows the CV curves of the ChCl:EG and ChCl:urea DESs at temperatures between 140 and 180 °C. It is revealed that ChCl:EG DES exhibits reduction potential between 0.40 to 0.50 V (vs Ag) while that for ChCl:urea DES was between -0.45 and -0.35 V (vs Ag), suggesting higher reducing power for ChCl:urea DES than that of the ChCl:EG DES.

Similar metal leaching mechanism was formulated for ChCl: citric acid DES as shown in Figure 3c.<sup>[28]</sup> The study revealed that the protons of citric acid and chloride ions of choline chloride in the DES damaged the crystal structure of LCO. Different from previous studies, the leaching was accelerated by copper and aluminum metals. First, the cobalt(III) reduces to cobalt(II) in the presence of copper, which later oxidizes to copper(I). The copper(I) are in equilibrium with copper(II) and is stabilized by chloride anions. The copper(I/II) complexes formed during the dissolution reaction are reduced to metallic copper by metallic aluminum via cementation. This reaction partially regenerates copper, which becomes available for further cobalt(III) reduction until complete dissolution of LCO. Aluminum metal reduces protons as a side reaction, causing the evolution of hydrogen gas. Furthermore, chloride anions stabilize cobalt(II) by forming chloro-complexes, with tetrachlorocobaltate(II) being the predominant species. Although aluminum(III) and lithium (I) chloro-complexes could not be identified, the formation of

chloro-complexes with these metal ions can be excluded because of their strong affinity for water molecules

Thus, according to these studies, the leaching mechanism for metal oxides using DES involves: 1) a reducing agent to reduce high valance metal, 2) chloride anions to form metal chloro (chlorometalates) complexes, and 3) protons to react with oxide ions to form water molecules. It should also be noted that the dissociation of the hydrogen bond donors and the hydrogen bond acceptors have significant impact on the dissolution of the metal oxides. However, there is no exact information for the selective extraction of a target metal ion from either the hydrogen bond donors or the hydrogen bond acceptors in the applied DESs. Therefore, though different types of DESs might basically have a similar mechanism, the leaching efficiency and the selective recovery of metals may be varied because of the unique properties of each DES.

#### 4. DESs Based Metal Recovery from Spent Batteries

In this section, the current reports regarding the recovery of actual and model cathode materials from spent batteries using DESs as leaching agents are discussed (Table 3). In general, the study is still in the infant stage and the current attempts have

**Table 3.** A summary of metal leaching from spent batteries using DESs.

DES <sup>a)</sup>	Molar ratio	Time [min]	T [°C]	Additive	$R_{m/V}$ (g <sub>LCO</sub> /L <sub>DES</sub> )	$R_{m/m}$ (g <sub>LCO</sub> /g <sub>DES</sub> )	Type of spent batteries <sup>b)</sup>	Recovered Li [%]	Recovered Co [%]	Other metal [%]	Ref.
ChCl:malic acid	1:1	240	60	Water	20	–	LIBs	–	81.2	–	[28]
ChCl:malonic acid	1:1	240	60	Water	20	–	LIBs	–	24.4	–	[28]
ChCl:oxalic acid	1:1	240	60	Water	20	–	LIBs	–	19.6	–	[28]
ChCl: citric acid	1:1	240	60	Water	20	–	LIBs	–	99.6	–	[28]
ChCl: citric acid	2:1	60	40	Water	20	–	LIBs	–	98	–	[28]
ChCl:EG	1:1	240	60	Water	20	–	LIBs	–	2.1	–	[28]
ChCl:EG	1:2	1440	220	–	–	0.1:5.0	LIBs	–	94.14	–	[3]
ChCl:EG	1:2	1440	180	–	–	0.1:5.0	LIBs	89.81	50.30	–	[3]
ChCl:EG	1:2	1440	160	–	24	0.1:5.0	LIBs	28.4	23.8	–	[75]
ChCl:EG	1:2	1440	80	–	20	0.1:5.0	LIBs	–	-61 ppm	–	[80]
ChCl:urea	1:2	1440	160	–	24	0.1:5.0	LIBs	61.2	64.2	–	[75]
ChCl:urea	1:2	720	180	–	77.5	–	LIBs	95	95	–	[75]
PEG200:thiourea	2:1	1440	160	–	20	0.1:5.0	LIBs	–	60.2 (8440 ppm)	–	[80]
PTSA-H <sub>2</sub> O:ChCl	1:1:1	1440	80	–	20	0.1:5.0	LIBs	–	≈1283 ppm	–	[80]
PTSA-3H <sub>2</sub> O:ChCl	1:1	15	90	–	56	–	LIBs	91	97	–	[78]
PTSA-2H <sub>2</sub> O:ChCl	1:1	15	90	–	60	–	LIBs	100	100	–	[78]
PTSA-1H <sub>2</sub> O:ChCl	1:1	15	90	–	63	–	LIBs	85	88	–	[78]
AcChCl:urea	1:2	1440	70	–	50	–	SOBCB	–	–	Ag Ag <sub>2</sub> O	[90]
ChCl:EG	1:2	20	180	–	–	0.5:25	LIBs	–	90	Ni (10%)	[91]
ChCl:OA	1:2	15	75	–	0.1:5	–	LIBs	99%	–	Mn (96%)	[79]

<sup>a)</sup>ChCl = choline chloride; EG = ethylene glycol; PEG200 = polyethylene glycol; PTSA = *p*-toluenesulfonic acid; AcChCl = acetylcholine chloride; OA = oxalic acid;

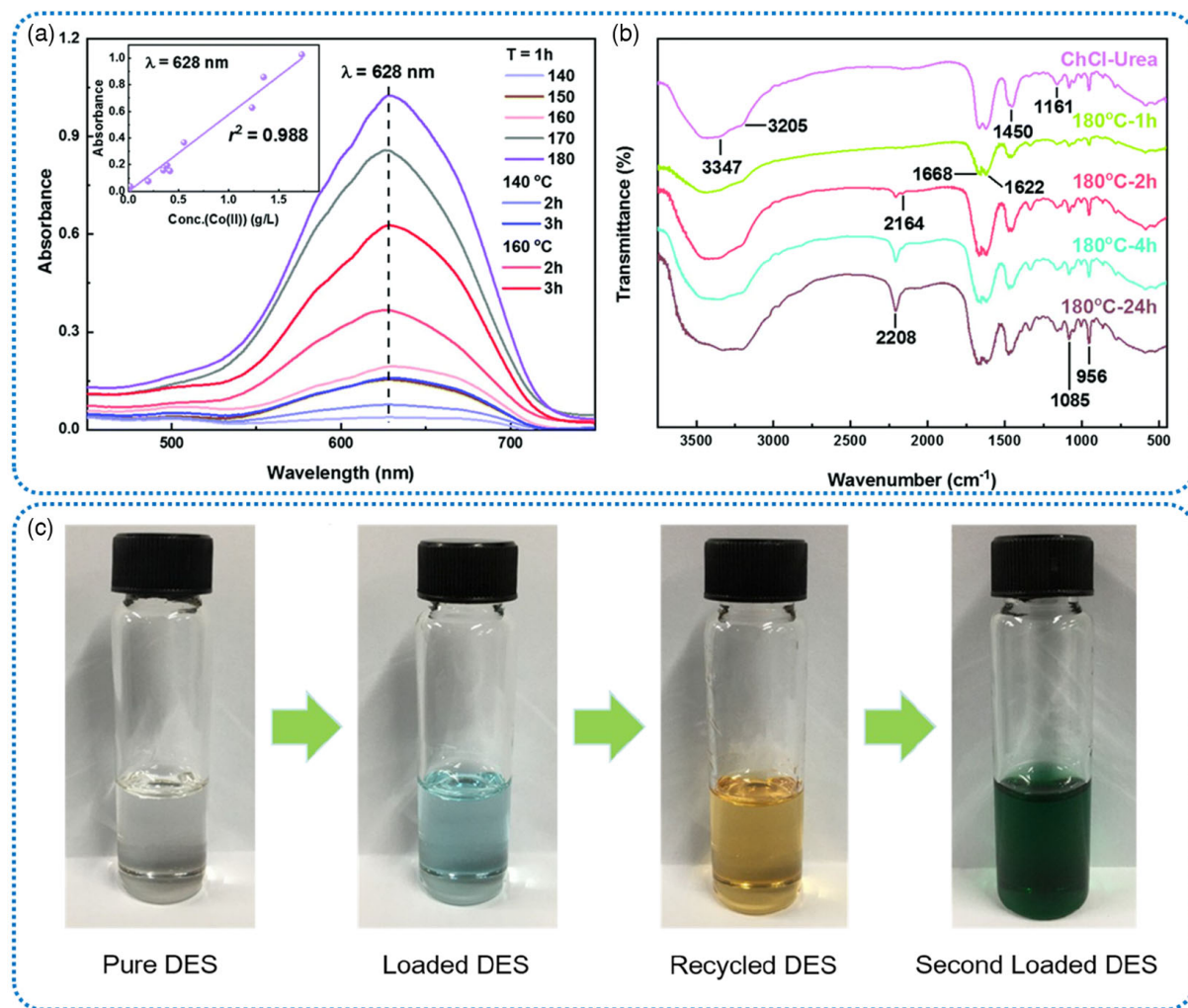
<sup>b)</sup>SOBCB = silver oxide button cell batteries.

worked on LIBs. There is a shortage of the recycling electrode materials from other types of commercial batteries. In the view of DESs, ChCl-based DESs are the most common solution to extract metal from spent LIBs and have provided high leaching efficiency in comparison with others.

Some earlier attempts using organic agents in leaching of lithium and cobalt from spent LIBs have been reported.<sup>[1]</sup> Among reported organic acids, oxalic acid is considered as an appropriate agent for leaching of cathode materials. For instance, the recovery rate of lithium and cobalt from spent LIBs were achieved about 98% and 97%, respectively.<sup>[77]</sup> However, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which is the most common reducing agent to boost the leaching efficiency, is hazardous.<sup>[1,13]</sup> Instead of using H<sub>2</sub>O<sub>2</sub>, the presence of ChCl hence is extremely vital because ChCl is economical, easily biodegradable, and not harmful for the environment. Interestingly, the mixtures of ChCl and carboxylic acids have formed a kind of DES, which have potential application for metal extraction.<sup>[50]</sup> Very recently, Peeters and co-authors prepared various DESs based on ChCl and a range of organic compounds with the aim of cobalt recovery from spent

LIBs.<sup>[28]</sup> According to this report, DESs composing of strong carboxylic acids combined with ChCl were able to leach cobalt. Apart from those DESs, a ChCl: citric acid DES was found to be an efficient lixiviant for LCO, which reached to 99.6% cobalt under identical condition. The result also suggested that the ChCl: citric acid DES leached more cobalt (II) than that of ChCl : malic acid ones because citric acids are higher acidity than malic ones. In the view of chemistry, the bulky molecules of citric acid resulted in the high viscosity when it was combined with ChCl. Water was hence used to reduce the viscosity of DESs. The authors also discovered that more than 98% cobalt were recovered under optimized leaching condition with 2:1 molar ratio of choline chloride-citric acid and diluted with 35 wt% water.<sup>[28]</sup>

Ethylene glycol (EG) is also one of promising hydrogen bond donors for DESs. Indeed, Tran et al. used a DES made of ChCl: EG to extract lithium and cobalt metals from spent LIBs.<sup>[3]</sup> The leaching efficiencies of 94.14% and 89.81% were obtained for cobalt and lithium, respectively. Particularly, the authors pointed out that time and temperature played significant roles in

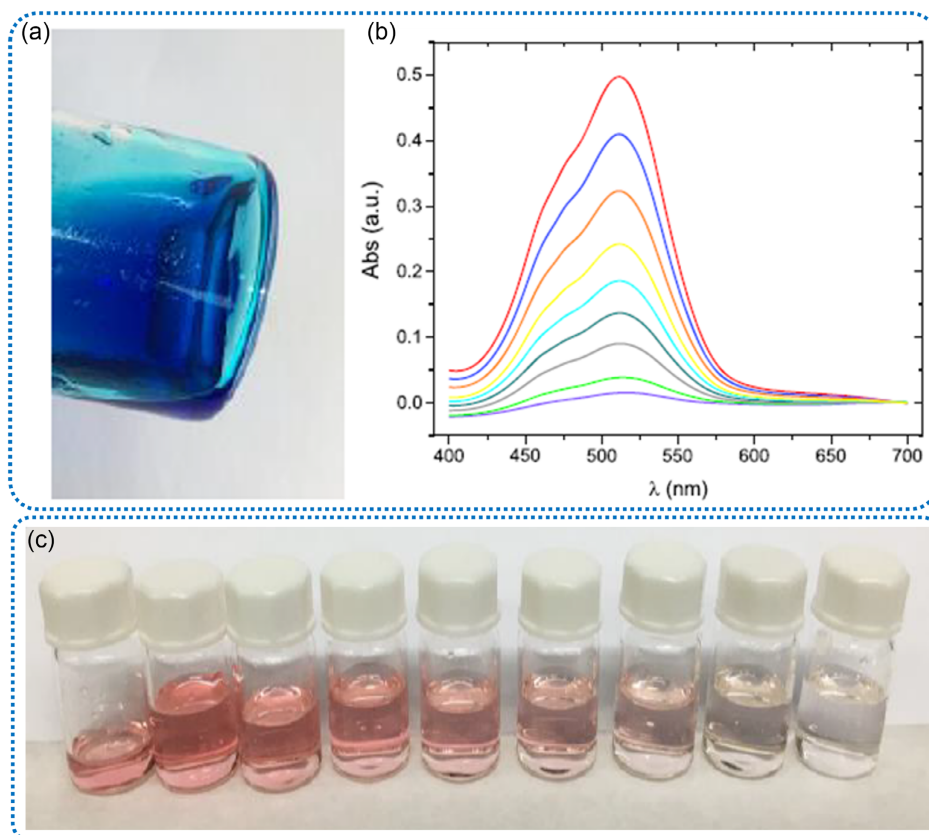


**Figure 4.** a) UV-vis and b) FT-IR spectra of the ChCl:urea DES and leachates at various extraction times and temperatures. c) Recyclability of ChCl:urea DES. Reproduced with permission.<sup>[75]</sup> Copyright 2021, The Royal Society of Chemistry.

dictating the effectivity of the metal extraction. For example, while the cobalt leaching efficiencies reached 50.3% at 180 °C, the figure was achieved 94.14% at 220 °C under identical condition. Furthermore, they exhibited that the color of the DESs turned to blue after the leaching, being attributed to the formation of the  $\text{CoCl}_4^{2-}$  anion. Although, leaching efficiencies of ChCl:EG DES is  $\geq 90\%$  for both cobalt and lithium, the reaction temperature and time are still high (at 220 °C and 24 h), which are not attractive for commercial operations. According to metal leaching mechanism, if the reduction potential of DESs pushes toward more negative, the corresponding reduction reaction and hence extraction of valuable elements could be accelerated. In this context, Wang et al. used DFT calculations and cyclic voltammetry method to screen the DES with more negative reduction potential. It was found that ChCl and urea mixture as a DES possessed strong reducing power than that of ChCl:EG DES. As a results, Li and Co extraction efficiency was achieved to be 95% from spent LIBs at a reduced reaction temperature of 180 °C and reaction time of 12 h.<sup>[75]</sup> Thus, cyclic voltammetry (CV) was used as a rapid and effective electrochemical method to screen the reducibility of DESs. Moreover, the UV-vis spectroscopic measurement (Figure 4a) represented a d-d broad band peak at 628 nm, illustrating the formation of Co(II) complexes. In addition, the inset image exhibited that a linear relationship

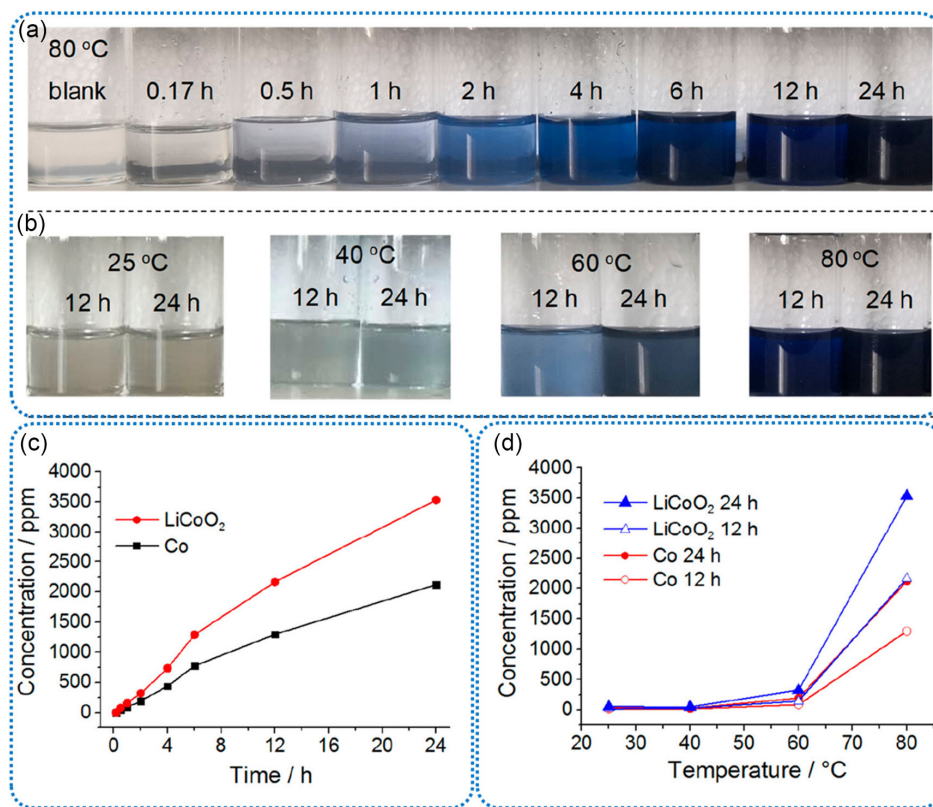
between the absorbance and Co concentration was found to be in good agreement with the Beer-Lambert law for this band. The FT-IR spectroscopy (Figure 4b) showed the presence and absence of Co(II) in DES, indicating the interactions between the various functional groups and identify structures using frequency shifts and absorption bands. Notably, ChCl:urea DES can be reusable as illustrated in Figure 4c.

Roldán-Ruiz and coworkers reported that a DES comprising *p*-toluenesulfonic acid (PTSA) monohydrate and choline chloride provided Co recovery efficiencies from spent LIBs (coming from Samsung and Nokia) of up to 94%.<sup>[78]</sup> As shown in Figure 5a, upon Co dissolution, the originally clear PTSA became blue. In addition, dilution with  $\text{H}_2\text{O}$  turned the blue solutions into pink ones (Figure 5b), the darkness of which could be linearly correlated to the Co concentration. PTSA:ChCl-based DESs offered a significant reduction of the solute to solvent ratio (in  $\text{g L}^{-1}$ ) needed for full Co dissolution, which brings benefits both in economic and sustainable terms that handling low solvent volumes has in industrial processes. Very recently, microwave-assisted treatment was employed to enhance the leaching efficiency using choline chloride-oxalic acid (ChCl-OA).<sup>[79]</sup> The report showed that the leaching efficiencies of both Li and Mn ions reached 99% and 96%, respectively, with only 15 min of microwave heating at 75 °C. Although the result



**Figure 5.** a) Picture of the solution obtained after dissolving  $\text{LiCoO}_2$  in PTSA- $\text{H}_2\text{O}$ -ChCl<sub>DES</sub>. b) Aqueous dilutions of (a) studied by UV-vis spectroscopy. c) UV-vis spectra of the different aqueous solutions depicted in (b), with concentrations of  $9.9 \times 10^3$  ppm (red line),  $7.9 \times 10^3$  ppm (dark blue line),  $6.6 \times 10^3$  ppm (orange line),  $4.9 \times 10^3$  ppm (yellow line),  $3.9 \times 10^3$  ppm (light blue line),  $3.0 \times 10^3$  ppm (dark green line),  $2.0 \times 10^3$  ppm (gray line),  $1.0 \times 10^3$  ppm (light green line), and  $0.5 \times 10^3$  ppm (purple line). Adapted with permission.<sup>[78]</sup> Copyright 2021, American Chemical Society.





**Figure 6.** Effect of time on the concentration of Co and LiCoO<sub>2</sub> in DESs/LiCoO<sub>2</sub> mixture at 80 °C: color change (a) and concentration (c). Effect temperature on the concentration of Co and LiCoO<sub>2</sub> in DESs/LiCoO<sub>2</sub> mixture: color change (b) and concentration (d). Adapted with permission.<sup>[80]</sup> Copyright 2021, American Chemical Society.

was promising compared to conventional method, the mechanism was not reported in this article.

In addition to ChCl-based DESs, Chen and coworkers explored a new kind of DES, comprising polyethylene glycol and thiourea (denoted as PEG200/thiourea) with molar ratio of 2:1.<sup>[80]</sup> In this article, PEG200/thiourea DES was employed for Co leaching purpose. The impact of time on the color change of the DESs/LiCoO<sub>2</sub> solution was conducted. Figure 6a exhibited that the LiCoO<sub>2</sub> solubility in DESs increases with time in 24 h. While DESs and DESs/LiCoO<sub>2</sub> solution at 0.17 h (i.e., 10 min) are transparent, an obvious dissolution of LiCoO<sub>2</sub> in DESs was found at 2 h (i.e., blue). Afterwards, the color is completely black at 24 h. Furthermore, Figure 6b displayed the color alteration of DESs/LiCoO<sub>2</sub> solution with the temperature. In comparison with lower temperatures (25 and 40 °C), the color turned light blue and black quickly when exposing LiCoO<sub>2</sub> in DES at 60 and 80 °C, respectively, for 12 h, which indicates the influence of LiCoO<sub>2</sub> solubility in DES on temperature. Additionally, the resultant data showed that the leaching efficiency of Co achieved 15.1%, 24.8%, and 60.2% at 80, 120, and 160 °C, respectively, for 24 h. According to the comparison with other DESs under identical condition, the authors suggested that Co concentration in PEG200/thiourea (2:1) was higher about 2 and 35 times than those in *p*-toluenesulfonic acid/water/ChCl (1:1:1) and ChCl/ethylene glycol (1:2), respectively. Furthermore, the authors indicated that the increasing tendency of UV-vis absorbance

was consistent with the tendency of Co concentration by inductively coupled plasma optical emission spectroscopy (ICP-OES) under the identical conditions (as shown in Figure 6).

As considered green solvents, DESs' recyclability is also vital for large-scale applications. The electrodeposition and chemical precipitation methods are techniques to recycle metals from the loaded DES with the aim of DESs regeneration. For the electrodeposition method, the metal ions were electrodeposited onto a substrate, allowing the loaded DES to be recovered, which was reported by earlier attempts.<sup>[3,75]</sup> In the case of precipitation technique, the Co recovery was performed using the addition of an excess of Na<sub>2</sub>CO<sub>3</sub> to the solution after Co/Li extraction from spent LIBs, leading to the precipitation of CoCO<sub>3</sub>.<sup>[78]</sup>

## 5. Techno-Economic Analysis

The techno-economic and environmental analysis is crucial for the development of metal leaching using DESs. A brief comparison between hydrometallurgical and DESs-based metal leaching processes based on important factors (e.g., chemical cost, reaction temperature, reaction time, and so forth) is summarized in Table 4.<sup>[3,28,78,81–84]</sup> For instance, the chemicals used in traditional hydrometallurgical process are inorganic/organic solvent with high concentration while low concentrated green chemical are used for DESs. Likewise, large volume of solid

**Table 4.** A brief comparison between hydrometallurgical and DESs-based routes.

Factors	Hydrometallurgical process	DESs-based process
Chemicals	High concentration	Low concentration
Temperature	High	Intermediate
Reaction time	Intermediate	Short
Relative energy consumption	High	Moderate
Chemical cost	Intermediate	Low
Primary waste products	Liquid and solids	Liquid
Limitation	Corrosive acids	Viscosity
Recyclability	Non-recyclable	Partially or sometimes fully recyclable
Toxicity	High	Non-toxic (low)

and liquids are generated as primary waste products in the hydrometallurgy. Meanwhile, DESs route offers the regeneration of loaded DESs for further leaching steps, which reduces waste products. The comparison of other aspects such as limitations and cost are provided in Table 4.

## 6. Conclusions and Outlook

Deep eutectic solvents (DES) are new cheap and green solvents, which has attracted a large attention not only for the biomedical applications but also gaining a strong interest in metal recovery. Herein, we have discussed how the types of hydrogen donor and acceptor and ratios affect the properties of DES and their subsequent effect on metal recovery from batteries. The recent progress and future prospects for recycling of spent LIBs using eco-friendly DESs is highlighted. It is realized that although, DES are excellent solvents for metal recovery, their full potential is not yet harnessed. Several advancements are highly desirable to make them commercially viable. Some of the critical challenges in DESs for metal recovery from batteries are described as follows: 1) The properties of DESs (e.g., viscosity, conductivity, leaching efficiency and leaching temperature for metal recovery, and so on) are depends on the hydrogen donor and acceptors. However, there is not specific criteria for the selection of best among the DESs, which can deliver desired properties. 2) The detailed investigations of the relationship between type of DESs and metal leaching efficiency is essential. For instance, there is lack of the research on the effect of viscosity and/or conductivity on metal leaching efficiency. In addition, the influence of heat-treatment and time on the viscosity of DESs is needs to be elucidated. 3) The use of metal recovery using DESs is still infancy. Therefore, from industrial perspectives, DESs based on cost effective and non-toxic chemicals need to be developed for their mass-scale utilization for metal recovery from mining and recycled products. 4) It has been proposed that the DESs can be recovered after the metal extraction and can be re-utilized for second or third time, however, there are very few practical evidences which have been provided with proper methods and strategies. Further study in this space is required to realize

the potential of DES. 5) The combination between DES with other reducing agents should also be taken into account to achieve an economically and environmentally friendly ways for recycling of spent LIBs. For example, to lower viscosity and improve the separation process, a combination of DES and green reductants/additives should be investigated.

Thus far, only a narrow range of DESs have been utilized for the metal recovery from spent batteries; the future offers significant potential to expand the types of salts and hydrogen bond donors which are used and hence further increase the applications of these solvents.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

deep eutectic solvents, green solvents, metal recovery, spent lithium-ion batteries

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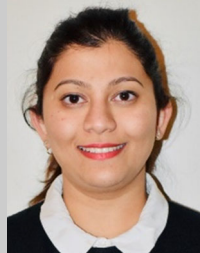
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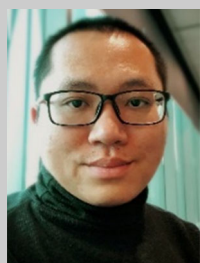
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