The application of deep eutectic solvents in lithium-ion battery recycling: A comprehensive review

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ABSTRACT

The extensive use of lithium-ion batteries (LIBs) in new electric vehicles has effectively alleviated the problems of insufficient oil and gas resources and environmental pollution. It is of great significance to realize the goals of "carbon neutrality" and "carbon peaking." As the key and last link in the use of power batteries, recycling waste LIBs is conducive to realizing resource return and avoiding pollution and potential risks of toxic and harmful substances in the environment. With the efforts of many researchers, the harmless treatment and resource recovery process of spent LIBs has been maturing. In recent years, some new recycling processes have appeared frequently to solve the problems of high energy consumption and secondary pollution in the traditional approach. Among these new technologies, green and inexpensive deep-eutectic solvents (DESs) have been particularly attractive due to their excellent selectivity and leaching efficiency. This review summarizes the dissolution mechanism of valuable metals from LIB cathode materials using DESs. At the same time, the advantages and challenges faced by DESs in cathode material recycling were analyzed, and an outlook was presented for the future development of DESs in the field of battery recycling.

1. Introduction

Due to the advent of the new energy era, lithium-ion batteries (LIBs), as one of the most commonly used energy storage devices, are increasingly used. Data show that by 2040, the global sales of electric vehicles (EVs) will reach 150–900 million, and the production of EVs is expected to reach 3 billion by 2050 (Tsiropoulos et al., 2018; International Energy Agency, 2021). LIBs are mainly composed of cathode materials, anode materials, collectors, separators, binders, conductive agents, and electrolytes. The most commonly used cathode materials are $LiCoO_2$ (LCO), $LiFePO_4$ (LFP), $LiNi_xCo_{y1-x-y}$ (NCM), and $LiNi_xCo_yAl_{1-x-y}$ (NCA) (Duarte Castro et al., 2021), while graphite is the most widely used anode material. Among these, LCO is the most expensive and has been widely used in portable electronic devices, thus having the highest economic value. LFP, NCM, and NCA are mainly used in energy storage devices for EVs. Compared with NCM and NCA, LFP with lower cost is more secure, but its actual capacity is much lower. The collectors of cathode and anode materials are composed of aluminum (Al) and copper foil, respectively,

which also have a specific economic value. However, the lifetimes of LIBs in portable electronics and EVs are 1–3 years and 8–10 years, respectively (Ma et al., 2021a; Jin et al., 2022). Therefore, excessive growth will lead to the generation of a large number of discarded LIBs and will also cause an insufficient supply of raw materials for LIB production and a sharp rise in prices. According to available data, from 2020 to 2050, the demand for lithium (Li), cobalt (Co), and nickel (Ni) will increase by 17–21 times, 7–17 times, and 11–28 times, respectively. The specific Li resource demand will increase by 0.584–0.734 Mt, Co resources 0.215–0.585 Mt, and Ni resources 1.37–3.57 Mt (Xu et al., 2020a). To alleviate this pressure, people in recent years have paid more attention to the recovery and reuse of spent LIBs. Generally speaking, when the capacity of a LIB is <80%, it is regarded as a spent LIB. According to forecasts, by 2030, the number of discarded LIBs will reach 11 Mt (Makuza et al., 2021). By recycling valuable metals from spent LIBs, the demand for Li, Ni, and Co will be saved by 20–23, 22–38, and 26–44%, respectively by 2050 (Xu et al., 2020a). Meanwhile, the electrolyte in spent LIBs contains many toxic and harmful substances, such

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as Li hexafluorophosphate, which is easily decomposed in the air to form fluorine-containing gas. Therefore, recycling LIBs efficiently can achieve the goals of a circular economy, safe environment, and carbon neutrality.

At present, the recycling and processing methods of spent LIBs mainly include echelon utilization and direct recycling (Fig. 1). Echelon utilization means that, when the remaining capacity of the battery cannot meet the requirements of EVs, the battery is repurposed to other energy storage devices for continued use, such as in electric bicycles and communication base stations, which do not destroy the structure and composition of the original battery. This strategy is simple, environment-friendly, low cost, and suitable for large-scale repurposing of waste LIBs. At present, this process is mainly suitable for the recycling of low-cost LFP batteries. According to data from the Ministry of Industry and Information Technology of China, the China Tower Corp. has repurposed spent LIBs in echelon utilization for nearly 120,000 base stations. At the same time, the State Grid of China also has used 1 MWh of spent LFP batteries for power generation and frequency regulation of renewable energy. (Ministry of Industry and Information Technology of the People's Republic of China, 2019) However, the various scales of LIBs and difficulty in assessing their interior health status present the process with certain limitations. Direct recycling mainly refers to pyrometallurgy, hydrometallurgy, and direct regeneration. Pyrometallurgy refers to recovering metals, such as Ni, Co, and other elements, in the form of an alloy from spent LIBs using high-temperature roasting technology, with Li ending up in the slag (Du et al., 2022; Thompson et al., 2020). At present, pyrometallurgy has been relatively well applied in Europe. This method is simple but has high energy consumption and poor metal recovery and purity (Thompson et al., 2021; Yu et al., 2022b). Therefore, developing a suitable method for extracting Li from slag will enable pyrometallurgy to obtain more significant economic benefits. Hydrometallurgy usually leaches metal oxides in cathode material in the form of ions into a solution using acid or alkali conditions, followed by separation and purification (Chan et al., 2021; Li et al., 2018; Ma et al., 2021a; Ma et al., 2021b; Santhosh and Nayaka, 2021; Raj et al., 2022). It has the features of low energy consumption, mature process, high purity, and low recovery cost and has been the most widely used in China. At the same time, compared with pyrometallurgy, hydrometallurgy has a longer recovery process, especially in the separation and purification of metals. The process requires many extractants and precipitants and becomes more complex as the number of metals involved increases. At the same time, a large amount of process acidic and alkaline wastewater is also produced. In addition, precipitation and purification of Li are often followed by residual elements. That is to say, the more complicated the separation and purification process, the more serious the Li loss. In addition to hydrometallurgy and pyrometallurgy, pyro-hydrometallurgy has gradually attracted research interest. For instance, some researchers have decomposed LCO and NCM cathode materials into Li_2CO_3 with a certain solubility and M_XO_Y (M: Ni, Co, and manganese, Mn) by mixing them with waste graphite (Fu et al., 2020; Lombardo et al., 2019; Xiao et al., 2017; Yue et al., 2018), biomass carbon (Chen et al., 2022; Zhao et al., 2020c; Zhou et al., 2022), and urea (Xiao et al., 2021). Then, Li and other metals are separated selectively by water leaching. However, Li_2CO_3 solubility is low and it is usually needed to pass carbon dioxide through the leachates to convert Li_2CO_3 to $LiHCO_3$ with higher solubility (Tao et al., 2022). Here, other metals are recovered by conventional hydrometallurgical methods. This mode reduces the temperature required for pyrometallurgy, preferential recycling of Li, and reduction of other high-valent metal elements. However, this process is still immature, which might be related to the formation of carbon monoxide (CO) gas during the reaction process, the low solubility of Li_2CO_3, and difficulty in controlling the final product during the calcination process.

In recent years, due to the uneven distribution of Co resources in the earth's crust, mainly in the geopolitically unstable Congo (Baars et al., 2021; Olivetti et al., 2017; Zeng et al., 2022), the price and supply of Co have been extremely expensive and unstable. Therefore, the cathode materials of LIBs are gradually being developed with low-Co and high-Ni, or Co-free materials, such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), NCA, and LFP (Gourley et al., 2020; Yu et al., 2022a), which make pyrometallurgy, hydrometallurgical, and pyro-hydrometallurgy processes less profitable. To balance the relationship between environmental protection and profit in the process of recycling and reusing waste LIBs, it is necessary to explore new recycling methods. One is direct regeneration, which means repairing the structure of Li-deficient cathode materials by supplementing Li salts. It has the characteristics of a simple process, environmental friendliness, and low energy consumption. Nevertheless, due to the uncertainty of the Li loss amount and difficulty in removing impurities with severe influence on the electrochemical properties of the regeneration materials (Zhang et al., 2020a; Zhang et al., 2020b; Zhao et al., 2020b; Zheng et al., 2021), it is still in the laboratory research and development stage. Another good choice is to
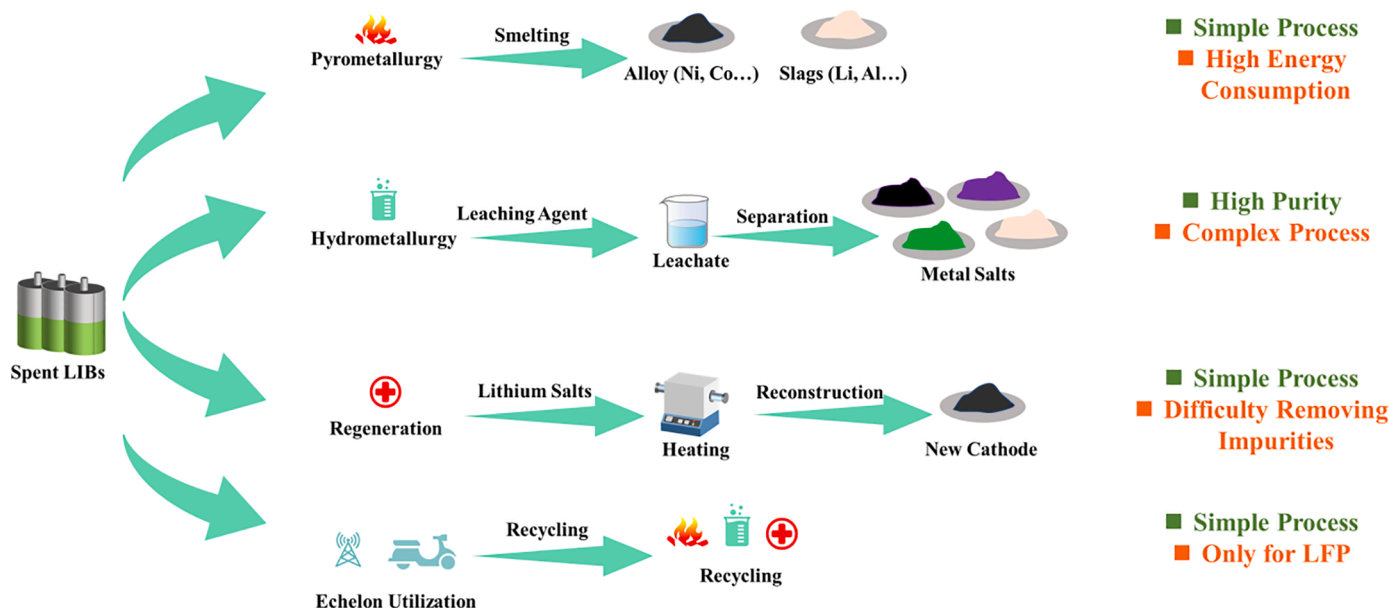

Fig. 1. Typical flowchart for spent Li-ion batteries.

recycle spent LIBs using the cheap and green deep-eutectic solvents (DESs). Like hydrometallurgy, they are a universal method and used in recent years in the field of LIB recycling. Interestingly, most DESs are reductive, which means that they can be regarded as both leaching reagents and reducing agents. The reducing agent can promote the reduction of high-valent metal oxides in the cathode material, reduce its lattice energy, and accelerate metal oxide dissolution. Currently, highly corrosive hydrogen peroxide is the most commonly used reducing agent in the leaching process (Fan et al., 2020; Li et al., 2017). Therefore, the use of DES can avoid the introduction of additional reducing agents, which thus reduces the cost and pollution to the environment. For example, Luo et al. leached over 99% Li, Ni, Co, and Mn from spent LIBs cathode materials by employing betaine hydrochloride/ethylene glycol DES without adding any reduced agents (Luo et al., 2022). In some cases, DES also exhibits similar or better leaching efficiency than hydrometallurgy, but also offers lower recovery costs and a greener process. Meanwhile, Tran et al. investigated DES recyclability and found that secondary recycled DES still has a dissolution effect on cathode material and there is almost no significant decrease in leaching efficiency. These characteristics are not available in traditional recycling methods (Tran et al., 2019). Compared with some traditional recycling methods, DESs are believed here to be more suitable for the recycling and reuse of new-generation battery materials. Therefore, this review summarized recent DES applications in the field of battery recycling. Combined with different physical and chemical properties of different DES, the dissolution mechanism and path of valuable metal elements in cathode materials were discussed from the perspective of kinetics and thermodynamics. Through economic and technical analysis, DESs were believed here to be greener, low-cost, and high-efficiency leaching

reagents and have prospects for future development and application.

2. Properties of deep-eutectic solvents

2.1. History and classification of DESs

DESs, proposed by Abbott et al. in 2003, are mainly liquids formed by heating two or more components, with simple preparation, wide source, and biodegradability. The first DES was prepared by mixing choline chloride (ChCl) and urea, which showed an extra low eutectic point (12 °C). Due to strong hydrogen bonding between ChCl and urea, their eutectic point was much lower than the melting points of ChCl and urea (302 °C and 133 °C, respectively) (Abbott et al., 2003). Subsequently, the physical and chemical properties of other types of DESs have been extensively studied, in terms of properties such as viscosity, pH, and conductivity. Recently, they have been widely used in electrodeposition (Bernasconi et al., 2020; Wang et al., 2021), nanoparticle synthesis (Exposito et al., 2020), organic extraction (Hatab et al., 2020), and metal oxides dissolution (Abbott et al., 2006; Chen et al., 2019), as well as other fields. The universal formation of DESs is $Cat^+ X^- zY$, where Cat^+ refers to organic cations containing ammonium, phosphorus, and sulfur and X and Y are Lewis bases and Lewis acids or Brønsted acids, respectively (Fig. 2) (El Achkar et al., 2021; Hansen et al., 2021; Padwal et al., 2022).

DESs are usually divided into four types, as shown in Fig. 2(a). In the first and second types, Y represents metal chloride and metal chloride hydrate salts, respectively. Generally speaking, type II tends to have a lower eutectic point and viscosity than type I due to the presence of crystalline water. At the same time, compared with anhydrous
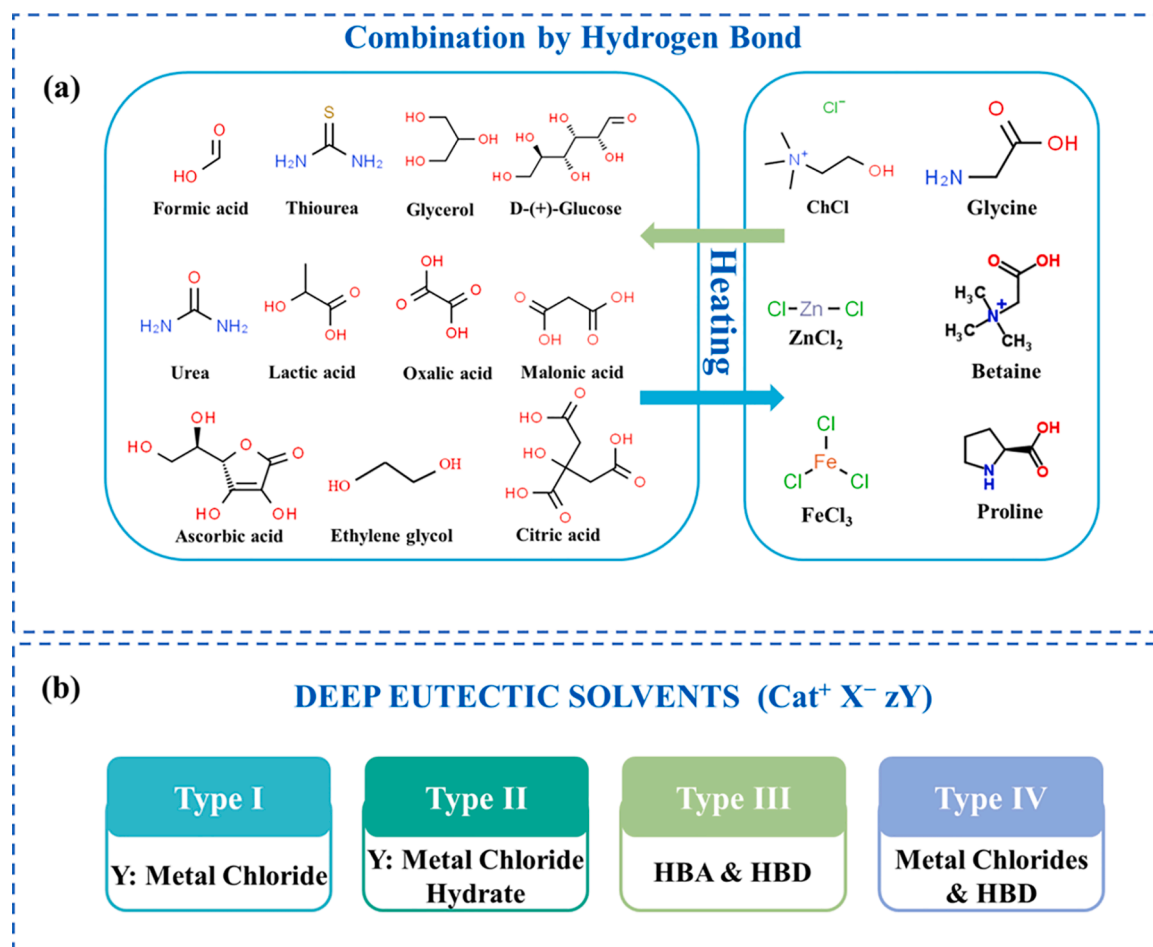

Fig. 2. Universal structures and classification of DESs (a). Typical compositions used for DESs preparation (b).

compounds, the price of hydrated metal salts is lower, which indicates that type II also has a lower cost than type I. Types III and IV consist of hydrogen bond acceptors (HBA) or metal chlorides and hydrogen bond donors (HBD). Among them, due to its low price and special biodegradability, choline chloride (ChCl), which is commonly used in feed additives, is currently the most commonly used HBA. The types of HBD are more diverse, including glucose, urea, carboxylic acid, and polyol (El Achkar et al., 2021; Hansen et al., 2021). In addition to the above classification, according to DES wettability, they can be divided into hydrophilic and hydrophobic solutions (Florindo et al., 2019). DESs composed of better water-soluble substances, such as urea, ChCl, and ethylene glycol (EG), tend to have better hydrophilicity. Hydrophobic DESs are comprised of some poorly water-soluble substances, such as capric acid and menthol, and include long-chain fatty acids and polyols. Such hydrophobic DESs show more excellent properties in extraction and separation. For example, Dannie et al. used a hydrophobic DES composed of lidocaine and decanoic acid to extract metal ions in some metal chlorides, such as $CoCl_2$, $NiCl_2$, and LiCl, from aqueous phases. Their results show that this type of DES has higher extraction efficiency for Ni and Co but lower extraction efficiency for Li, which indicates that it might be used for extracting and separating metal elements after leaching in the LIB recovery process (van Osch et al., 2016).

2.2. The application in metallurgy and LIBs recycling for DESs

For the dissolution of metal oxides, type III DESs are currently the most commonly used system. This is because they usually have essential metal oxides dissolution-promoting features, such as coordination ability, reducibility, and acidity. For example, in 2006, Abbott et al. used DESs, as mixtures of ChCl with urea, EG, and malonic acid, to dissolve metal oxides. They concluded that these metal oxides had higher solubility using malonic acid as HBDs (Abbott et al., 2006). Similarly, Pateli et al. also found the phenomenon that the leaching efficiencies for metal oxides, including vital metal elements in LIB cathode materials, such as Ni, Co, and Mn, were higher in these DESs with organic acids as HBDs (Pateli et al., 2020). This is because these DESs have a lower pH (Table. 1). Also, hydrogen ions act as oxygen atom acceptors, which accelerate metal oxide dissolution. Additionally, Damilano et al. demonstrated that the solubility of CoO, $LiCoO_2$, and NiO in ChCl/thioglycolic acid DES is 6, 6, and 24-fold that in ChCl:/glycolic acid DES, respectively. Meanwhile, the solubility of CoO in ChCl/thioglycolic acid DES was 18-fold that of NiO, indicating that selective leaching of Ni and Co can be achieved (Damilano et al., 2020). Through these important studies, DESs are believed here to have potential applications for recycling metals from spent LIB cathode materials, especially using type III DESs.

The history of DES in spent LIB recycling was summarized here (Fig. 3). In 2019, Wang et al. used ChCl/glycerol DES with a 2.3/1 molar ratio to degrade polyvinylidene fluoride (PVDF) in waste LIBs by heating at 190 °C for 15 min, thereby realizing the separation of Al foil and active cathode material. Traditional separation methods mainly include alkali dissolution, organic solvent immersion, and high-temperature pyrolysis (Hu et al., 2021). Among these, dissolving Al foil with an alkaline solution, such as NaOH, is efficient and straightforward. However, Al recovery requires a more complex process, which generates a large amount of hydrogen and acid-base wastewater (Zhang et al., 2016). Organic solvents, such as N-Methyl pyrrolidone, are highly toxic, expensive, and unsuitable for industrial use (Song et al., 2017). High-temperature pyrolysis involves heating cathode material adhered to Al foil above the PVDF decomposition temperature to achieve their separation. However, Al foil becomes brittle during this process and small amounts of Al impurities can inevitably be contained in the active cathode material during subsequent separation processes (He et al., 2021). In separating Al foil and cathode material, ChCl/glycerol DES has lower energy consumption and cost and does not damage the foil (Wang et al., 2019). Thus, this might be a greener method. In the same year, Tran et al. achieved the dissolution of valuable metals in LCO and NCM for the first time using ChCl/EG DES. The whole leaching process did not use any acidic or alkaline solution and added any reducing agents (Tran et al., 2019). Subsequently, Wang et al. pointed out the importance of DES reducibility for the leaching of cathode materials. They found that, when more reducing urea is used as the HBD, the leaching conditions of valuable metals from cathode material are milder (Wang et al., 2020b). The fly in the ointment is that the leaching conditions of LCO in these two types of DES are relatively harsh, requiring dozens of reaction hours above 180 °C to obtain better leaching efficiency. Therefore, in recent years, researchers have gradually paid attention to carboxylic acid-based DESs. Cathode materials tend to exhibit higher leaching efficiency due to the many free protons in such DESs and the strong coordination ability between carboxylate and metal elements. However, not all elements have high solubility in carboxylic acid-based DESs. Recently, Chang et al. have used ChCl/oxalic acid dihydrate DES to selectively dissolve Co and Mn in NCM, while Ni remained in the residue. Furthermore, different from the previous study, Chang et al. believed that ChCl, a common HBA in DESs, also took part in leaching reactions between ChCl/oxalic acid dihydrate DES and NCM cathode materials and acted as reducing agents because of the formation of chlorine gas (Chang et al., 2022). In addition to their applications in pretreatment and metal leaching, DESs also show good performance in extracting and separating valuable metals in leaching solutions. In 2020, Zante et al. used sulfates of Li, Ni, Co, and Mn to model the leaching solution of cathode materials. After Co and Mn were separated, they found that both lidocaine/decanoic acid DES and lidocaine/lauric acid DES could extract Ni^{2+} from the Li-containing leachate. When the pH of the leachate was <2, the extraction efficiency of Ni^{2+} was over 90% in

Table 1
Basic physical chemistry properties of some type III DESs.

|	Molar ratio	Eutectic points (°C)	Viscosity (cP)	pH	Conductivity (mS/cm)	Surface tension (mN/m)	Ref.
ChCl/Citric acid	1/1	69	9126	1.73	—	—	(Abbott et al., 2004; Hansen et al., 2021; Skulcova et al., 2018)
ChCl/Urea	1/2	12	750	8.91	2.31	64.14	(Abbott et al., 2003; Alabdullah, 2018; D'Agostino et al., 2011; Lapeña et al., 2020; Shah and Mjalli, 2014)
ChCl/EG	1/2	−36	37	6.89	7.63	52	(Alabdullah, 2018; Ibrahim et al., 2019; Klein et al., 2020)
ChCl/Glycerol	1/2	−17	281	7.48	0.985	58	(Alabdullah, 2018; AlOmar et al., 2016)
ChCl/Oxalic acid	1/1	34	597	1.32	0.38	—	(Abbott et al., 2004; Alabdullah, 2018)
ChCl/Malonic acid	1/1	10	721	—	—	—	(Alabdullah, 2018)
ChCl/Lactic acid	1/2	—	700	—	—	—	(Damilano et al., 2020)
ChCl/Thiolactic acid	1/2	—	100	—	—	—	(Damilano et al., 2020)
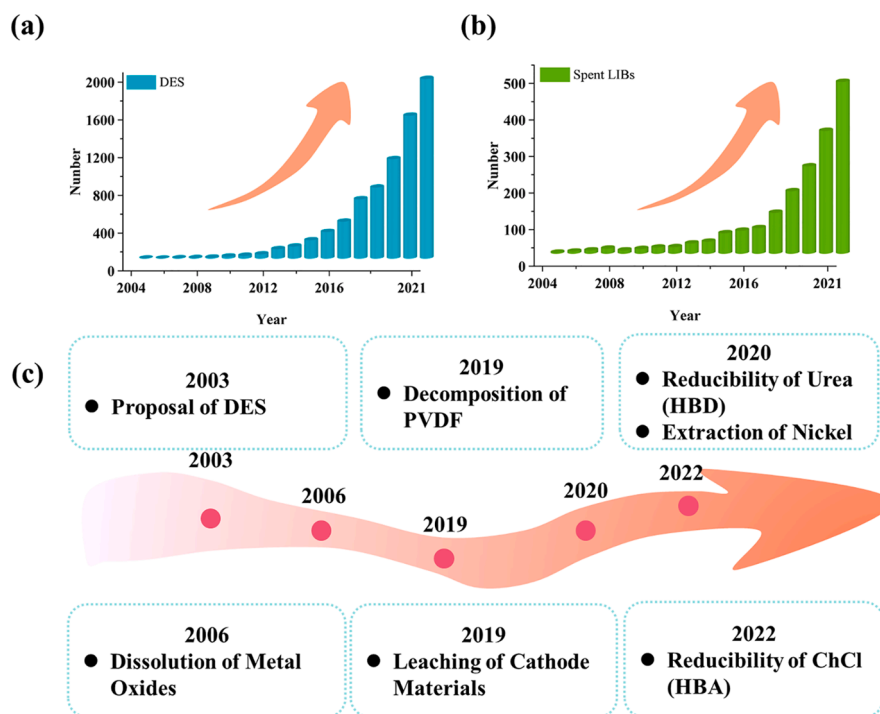
Fig. 3. Number of articles on DESs included in the web of science from 2004 to 2021 (a). Number of articles on recycling of spent LIBs included in web of science from 2004 to 2021 (b). Application and development for DES in spent LIBs recycling (c) (Abbott et al., 2003, 2006; Chang et al., 2022; Tran et al., 2019; Wang et al., 2019; Wang et al., 2020b; Zante et al., 2020).

both types of DESs, while the extraction efficiency of Li$^+$ was <10% (Zante et al., 2020).

2.3. The basic physical chemistry properties of some type III DESs

Based on the discussion above, some physicochemical properties of the type III DESs were summarized in Table. 1. Different from aqueous solutions, these DESs usually show higher viscosity. For instance, the viscosities in ChCl/urea and ChCl/citric acid are 750 and 9126 cP at 25 °C, respectively (D'Agostino et al., 2011). In general, with increased temperature, DES viscosity decreases. Usually, researchers adopt Arrhenius or VFT equations to describe DES relationships between temperature, as shown in Eqs. (1) and 2, respectively (D'Agostino et al., 2011; Yadav et al., 2014).

$$\eta_{\text{Arrhenius}} = Ae^{E/RT} \text{ and} \tag{1}$$

$$\eta_{\text{VFT}} = A' e^{B/(T-T_0)} \tag{2}$$

where E is the activation energy of viscous flow and A', B, and T$_0$ represent empirical constants.

However, too high viscosity is not conducive to a DES's practical application in recycling spent LIBs. On one hand, high viscosity hinders reaction molecule diffusion to unreacted particle surfaces and reduces the leaching reaction speed. On the other hand, it also makes the solid-liquid separation process more difficult, increasing energy consumption and processing steps in the recovery process. Usually, DES high viscosity is attributed to the larger radii of the molecules forming the DES than the radius of voids in the solution. To reduce DES viscosity, it is needed to increase the probability of voids in solution or use quaternary ammonium salt cations with a smaller radius and fluoride anions (Abbott, 2004, 2005). Meanwhile, selecting some sulfur-containing HBDs can also effectively reduce DES viscosity. For example, the viscosity value of ChCl/lactic acid DES is 7 times higher than that of ChCl/thiolactic acid DES (Damilano et al., 2020). In addition, electrical conductivity and surface tension are also related to DES viscosity. Generally speaking, the

lower the DES surface tension and higher the conductivity are, the lower their viscosity (Abbott, 2004, 2005). Besides these features, eutectic points can also significantly affect DES applications in the field of spent LIBs recycling. Lower eutectic points mean better savings and milder application conditions for DESs. In contrast, when DESs with high eutectic points are adopted for recycling LIBs, a higher temperature is required to avoid DES recrystallization. Fortunately, many DES eutectic points are relatively low, suggesting that they can act as desirable leaching solutions for dissolving valuable metals from LIB cathode materials.

In addition to the above characteristics, the pH value also impacts metal oxide leaching efficiency from cathode materials. Generally, metal oxides are poorly soluble in neutral DES, such as ChCl/EG DES (Abbott et al., 2006; Pateli et al., 2020). This is mainly due to the weak ability of such DESs to break down oxygen acceptors in metal oxides, which makes it difficult for metal ions to be released from the lattice. In some basic DESs, such as ChCl/urea DES, the formation of coordinated ligands in DESs and metal oxides is a critical condition for their dissolution. For acidic DESs, organic carboxylic acids are more commonly used HBDs. In general, acidic DESs are more effective in dissolving most metal oxides than neutral or basic DESs. This is because, on one hand, many free hydrogen ions in acidic DESs can well adsorb and destroy oxygen acceptors in metal oxides. On the other hand, carboxyl groups can form complexes with metal oxides to accelerate metal oxide dissolution.

3. DESs based metal recovery from spent batteries

3.1. Mechanism

The dissolution of high valence transition metal oxides, including Co, Ni, and Mn oxides, in LIBs is usually decided by the acidity, coordination ability, and reducibility of the DES. Among DESs, hydrogen ions act as oxygen acceptors. The attack of oxygen atoms by hydrogen ions leads to H$_2$O formation and dissolution of metal oxides surrounding them. Nevertheless, in neutral or basic DES leaching systems, hydrogen ion

action is severely weakened, while coordination ability and reducibility play a prominent role in their dissolution. Therefore, dissolution paths might be different for LIB cathode materials in different DESs. However, no matter which DES system, high valence transition metal oxides are finally dissolved in the form of coordination complexes with a lower valence (Table. 2). This is because, from a thermodynamic point of view, low valence transition metal oxides tend to form a more stable complex with coordination ligands than do high valence forms. Thus, the reducibility of DESs might have an irreplaceable effect on the leaching efficiency for LIB materials. For instance, Lu et al. depicted the leaching reactions of LCO cathode materials in ChCl/oxalic acid DES with reducibility. They believed that Li would be extracted by hydrogen ions in DES and formed $H-Co^{III}O_2$, firstly. Then the Co (III) from $H-Co^{III}O_2$ was reduced to Co (II) by $C_2O_4^{2-}$ and coordinated with Cl^- from ChCl. Finally, Co (II) dissolved in ChCl/oxalic acid DES in the form of $[CoCl_4]^{2-}$ (Lu et al., 2021).

For a long time, DES reducibility was generally considered to be related to HBDs, such that it is seen as an excellent choice for improving leaching efficiency from LIB materials in DESs, by adjusting reducibility using HBDs. For instance, in 2019, Tran et al. employed ChCl/EG DES to realize green recycling of LIBs. In this study, EG was deemed to be the reducing agent and oxygen acceptor that provided hydrogen ions, while chloride ions serve as coordination ions and form Co (II) $[CoCl_4]^{2-}$ (Tran et al., 2019). Based on this study, Wang et al. selected urea with stronger reducibility than EG as the HBD. They achieved a similar leaching result, with 100% leaching efficiencies for Li and Co, under reaction conditions shorter by half the time (~12 h) and lower temperature (180 °C). Meanwhile, urea and Co (II) coordinate and form Co $(urea)_2Cl_2$ in the leachate (Wang et al., 2020b). The improvement in leaching conditions demonstrated that enhanced reducibility might have an essential effect on the leaching process of valuable metals from LIBs.

After the reduction of high valence metal oxides, the lattice energy and stability of crystal structures start to decrease. Then, the effects of coordination ability and DES acidity on the dissolution of valuable metal oxides become more vital. Thus, to achieve enhancement of metal ion leaching efficiency, one good choice is to adopt some organic acid as the HBD. For example, when some organic acids, such as formic acid (Chen et al., 2021b), citric acid (Peeters et al., 2020), and p-toluenesulfonic acid (PTSA) (Roldán-Ruiz et al., 2020), act as HBD, the reaction temperature can decrease to <100 °C. Hua et al. selected L-ascorbic acid as HBD and achieved leaching efficiencies of valuable metals in NCM cathode material up to 96% with 50 °C for 1 h (Hua et al., 2021). Also, the coordination ability might also have a clear effect. Pateli et al. found that the solubility of Co_3O_4 is higher in a DES with a stronger coordination ability and pointed out that metal oxide dissolution paths in DES include four steps: (1) Hydrogen ions absorb oxygen atoms on metal oxide surfaces and form hydrated intermediate species, M-OH. (2) M-OH combines with coordination ligands and becomes $M-OH_2^+...X^{n-}$. (3) $M-OH_2^+...X^{n-}$ starts to dehydrate, solvate, and convert to $M-X^{n-1}$. (4) After $M-X^{n-1}$ diffuses into solution, coordination ligands in $M-X^{n-1}$ are replaced by others, and a more stable complex is formed in DES (Pateli et al., 2020). This again demonstrated the importance of reducibility, coordination ability, and acidity in DES on the leaching for valuable metals in LIBs.

In addition, some kinetics of processes for leaching valuable metals from LIB cathode materials in DESs were summarized here (Fig. 4 and Table. 2). Just like aqueous solutions, the leaching processes of Li, Ni, Co, and Mn were in line with the shrinking core model. This model is comprised of three steps: (1) mass transfer of molecules in the liquid, (2) diffusion between the intermediate layer and solid boundary, and (3) chemical reactions on particle surfaces (Jha et al., 2013; Wang et al., 2020a; Zhang et al., 2015). In these steps, DES viscosity and its acidity, coordination, and reducibility might have leading roles. The

Table 2
Several leaching kinetics processes and leaching efficiency of valuable metals in LIB cathode materials in DESs.

| Cathode	DES	Condition	Controlled step	Leaching efficiency (%)				Existing form of metal ions		Ref.
				Li	Ni	Co	Mn	Ni	Co	
LCO	ChCl/Urea	180 °C, 12 h	Mass transfer in the liquid	95	—	98	—	—	Co $(urea)_2Cl_2$	—	(Wang et al., 2020b)
NCM	ChCl/EG	180 °C, 24 h	Surface chemical reaction	92	95	93	95	—	—	—	(Wang et al., 2022)
NCM	ChCl/L-ascorbic acid	50 °C, 1 h	Mass transfer in the liquid and surface chemical reaction at higher temperature; Diffusion on the intermediate layer at lower temperature	96	99	98	99	—	—	—	(Hua et al., 2021)
LCO	ChCl/$H_2C_2O_4$	90 °C, 2 h	Diffusion on the intermediate layer	88	—	86	—	—	—	—	(Lu et al., 2021)
NCM	ChCl/Oxalic acid dihydrate	120 °C, 10 h	Surface chemical reaction	—	< 1	> 97	> 97	$NiC_2O_4 \bullet 2H_2O$	$[CoCl_4]^{2-}$	—	(Chang et al., 2022)
LCO	EG/ sulfosalicylic acid dihydrate (SA)	110 °C, 6 h	Surface chemical reaction	98	—	93	—	—	Co^{2+}-SA	—	(Tang et al., 2022)
NCM	EG/Citric acid	95 °C, 10 h	Surface chemical reaction	99	98	96	98				(Zeng et al., 2021)
LNCO	ChCl/Lactic acid	105 °C, 5 h	—	100	100	100	—	—	—	—	(Morina et al., 2022)
LCO	ChCl/Formic acid	70 °C, 12 h	—	—	—	99	—	—	$[CoCl_4]^{2-}$	—	(Chen et al., 2021b)
LCO	ChCl/ PTSA$\bullet$$2H_2O$	90 °C, 15 min	—	100	—	100	—	—	—	—	(Roldán-Ruiz et al., 2020)
LCO	ChCl/EG	220 °C, 24 h	—	—	—	94	—	—	$[CoCl_4]^{2-}$	—	(Tran et al., 2019)
LCO	PEG200/ Thiourea	160 °C, 24 h	—	—	—	60	—	—	—	—	(Chen et al., 2020b)
Mixed LIBs	ChCl/EG	180 °C, 24 h	—	60–80	11	90	60–70	—	$[CoCl_4]^{2-}$	—	(Schiavi et al., 2021)
LCO	ChCl/Citric acid/ H_2O (35 wt%)	40 °C, 60 min	—	—	—	98	—	—	—	—	(Peeters et al., 2020)
LCO	ChCl/SA/EG	140 °C, 16 h	Surface chemical reaction	100	—	100	—	—	$[CoCl_4]^{2-}$	—	(Huang et al., 2022)
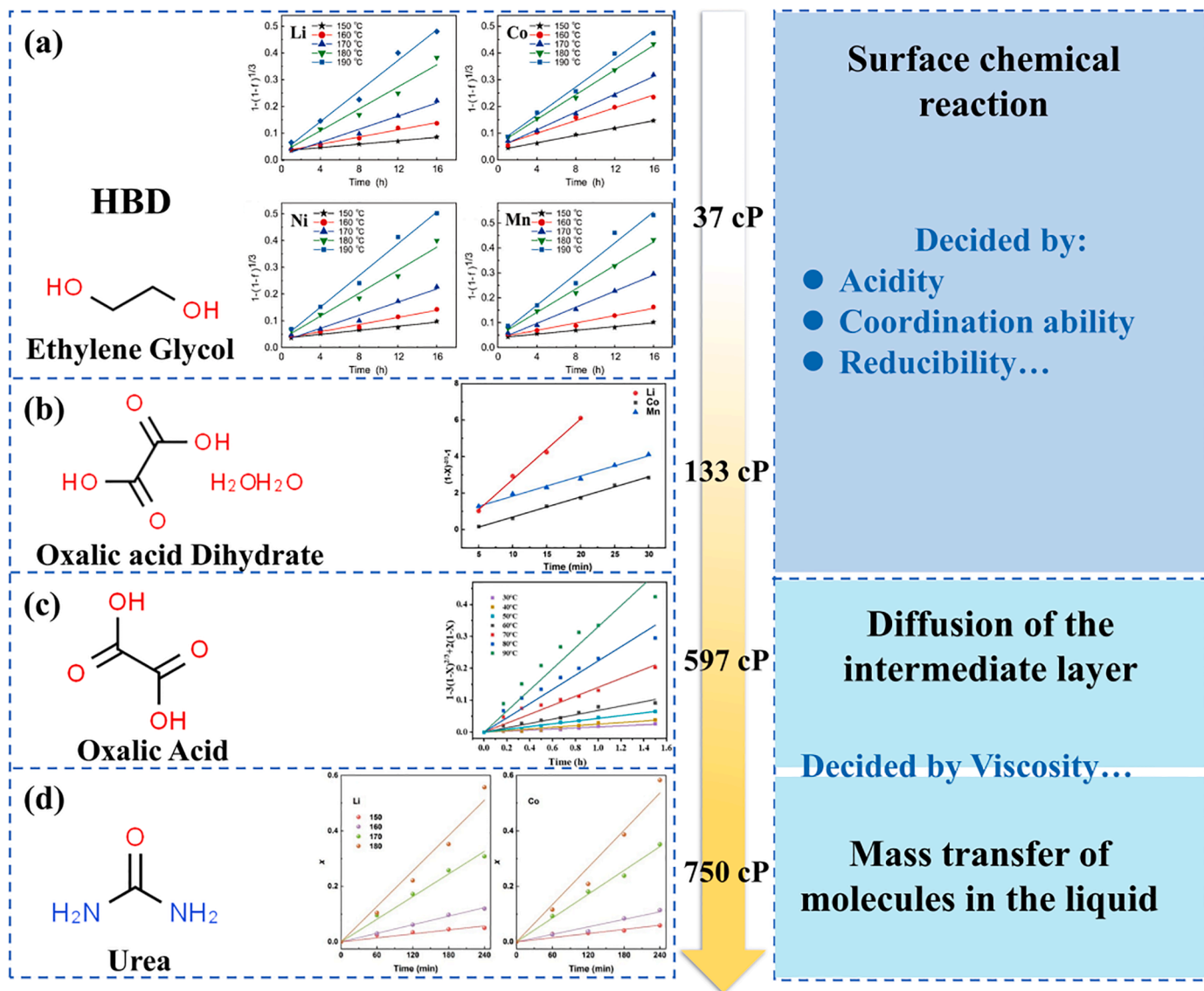
Fig. 4. Comparison of leaching kinetic models of LIBs in several DESs. ChCl/EG DES (a) (Wang et al., 2022); ChCl/Oxalic acid Dihydrate DES (b) (Chang et al., 2022); ChCl/Oxalic acid DES (c) (Lu et al., 2021); ChCl/Urea DES (d) (Wang et al., 2020b).

relationship between controlled steps and DESs viscosity was shown here. (Fig. 4). High viscosity can block mass transfer and diffusion, which causes a lower speed in these steps. Finally, the mass transfer and diffusion processes are the controlling steps in the whole leaching reaction. In contrast, in low viscosity DESs, chemical reactions were more the controlling step. For instance, the viscosity value of ChCl/urea (molar ratio 1/2) is 750 cP (D'Agostino et al., 2011). As shown in Fig. 4, the super high viscosity value for the leaching reaction of LCO in ChCl/urea is controlled by step (1). In ChCl/oxalic acid DES (597 cP) (Hansen et al., 2021) and ChCl/oxalic acid dihydrate DES (133.1 cP) (Chang et al., 2022), with molar ratios of 1/1 between HBD and HBA, steps (2) and (3) act as controlling steps in the leaching reaction, respectively (Lu et al., 2021). In ChCl/EG DES with a lower viscosity (37 cP), the leaching process is still controlled by surface chemical reactions. Therefore, with decreased DES viscosity, the controlling steps are concluded here to convert the process from mass transfer in the liquid and intermediate layer diffusion to surface chemical reactions. In the surface chemical reactions, the acidity, coordination, and reducibility of DES are believed here to decide the speed of surface chemical reactions.

To obtain the desirable leaching efficiency, it is necessary to design some acidic DESs with low viscosity and strong coordination and reducibility as leaching solutions. In one aspect, adding some low viscosity liquid, such as water and EG, or adopting these organic acids with crystal water as HBDs, can decrease the leaching system viscosity. Nevertheless, too much water destroys the DES hydrogen bond structure and affects the form of metal ions in the leachates. For instance, Amphlett et al. found that H_2O replaces EG ligand in the Ni complex with increased water content, a similar situation that also occurs in $[NiCl_4]^{2-}$ in a ChCl/malonic acid DES system. Conversely, H_2O would not displace Cl^- and urea for the $[CoCl_3(Urea)]^-$, but it will lead to hydrolysis of Co (Amphlett and Choi, 2021).

3.2. Li recovery

Due to the simple process and low cost, the chemical precipitation method is usually used to separate metal elements from leachates. In this step, Li recycling is often arranged after Ni, Co, and Mn separation (Yang et al., 2021) because many Li salts, such as LiOH and $Li_2C_2O_4$, are

soluble in aqueous solution, while $M(OH)_2$ and MC_2O_4 (M: Ni, Co, and Mn) are precipitates. Accordingly, with increased impurity-removal and solid-liquid separation steps, Li loss can become more severe. To avoid this phenomenon, selective recycling of Li from spent LIBs has attracted much research interest. For instance, using oxalic acid (Verma et al., 2020; Zhang et al., 2018a) and formic acid (Chen et al., 2021b; Ji et al., 2021; Mahandra and Ghahreman, 2021) in leaching solutions for recycling LCO or LFP allows Li to be dissolved in the first step, while Co or Fe remain in the leaching residues.

Unlike aqueous solutions, the study of Li recycling has been little regarding DESs, but a more interesting phenomenon has been observed, as shown in Fig. 5. For instance, Lu et al. found that Co and Li ions can be reprecipitated in leachates after being placed at room temperature for a specific time without any other processes. After that, the precipitate, a mixture of $CoC_2O_4 \bullet 2H_2O$ and $LiHC_2O_4 \bullet 4H_2O$, can be easily separated using H_2O and the resulting Li salt purity can reach 99% (Lu et al., 2021). As there were no precipitation agents used in this metal ion separation, the DES components are not destroyed and the DES can be reused for the next LIB leaching reaction after supplementing with oxalic acid. In addition, Hua et al. found that $Li_2C_2O_4$ tends to precipitate in ChCl/*L*-ascorbic acid DES, while it is soluble in aqueous solution. Therefore, they converted leachates to aqueous solution by first adding oxalic acid solution. Then, the transition metal ions, such as Ni, Co, and Mn, are precipitated as oxalates and Li ions remain in the leachate. After that, with water evaporation and ethanol addition, Li ions form $Li_2C_2O_4$ and precipitate in the DES (Hua et al., 2021). As oxalic acid is usually used as HBD for DES, this still did not affect the DES leaching abilities for LIBs.

In summary, recycling of Li from LIB cathode materials might exhibit a different result in DES with aqueous solutions, especially when oxalic acid is used as a precipitation agent. Therefore, there have been several methods for producing the separation of Li and transition metal ions in DES. One is to convert the DES leachates into water solutions. Then, Li can be separated from the leachates by conventional methods, such as chemical precipitation and extraction. The process is mature and simple, but it usually destroys the structure and property of DES, which affects its recyclability. For instance, Morina et al. prepared Li_3PO_4 using H_3PO_4 solution as the precipitant from the ChCl/lactic acid DES leachates (Morina et al., 2022). Also, adding some reagents that can act as HBD or HBA with no effect on the initial DES is a good choice. This means that the solubility of different Li salts in DESs should be explored. Unfortunately, to date, related studies have not attracted research interest. In addition, the pre-separation of Li from LIBs cathode materials before leaching them in DESs might be addressed. For example, Chen leached Li selectively using formic acid, while Co remained in the leaching residues with PVDF and carbon black. Subsequently, the ChCl/formic acid DES is applied for leaching and recycling of Co (Chen et al., 2021b). Although the two-step recycling process is complicated, the lower loss of Li made up for this disadvantage, especially for NCA and NCM cathode materials.

3.3. Other valuable metal recoveries

For NCA and NCM, Ni and Co are the most economically valuable materials in spent LIB, such that it is very important to obtain high-purity Ni and Co from these sources. At present, due to their similar physicochemical properties, it has been a challenge to achieve selective leaching of Ni and Co from cathode materials or separation from leachates (Kim et al., 2021). However, ideal results appear easily obtained using DES. For instance, Schiavi et al. utilized the characteristics of different formation conditions for $[Ni (EG)_3]^{2+}$ and $[CoCl_4]^{2-}$ to separate Ni and Co using ChCl/EG DES. The Li, Co, and Mn were dissolved in the ChCl/EG DES at 180 °C for 24 h, while Ni remained in the leaching residues due to the harsh forming conditions of $[Ni (EG)_3]^{2+}$ (Schiavi et al., 2021). The disappearance of Ni ions made the recycling of Co easier. Also, Pateli et al. found that the dissolution ability of CoO was more than 400 times that of NiO in ChCl/oxalic acid DES (Pateli et al., 2020). This also provided a new choice for the selective separation of Ni
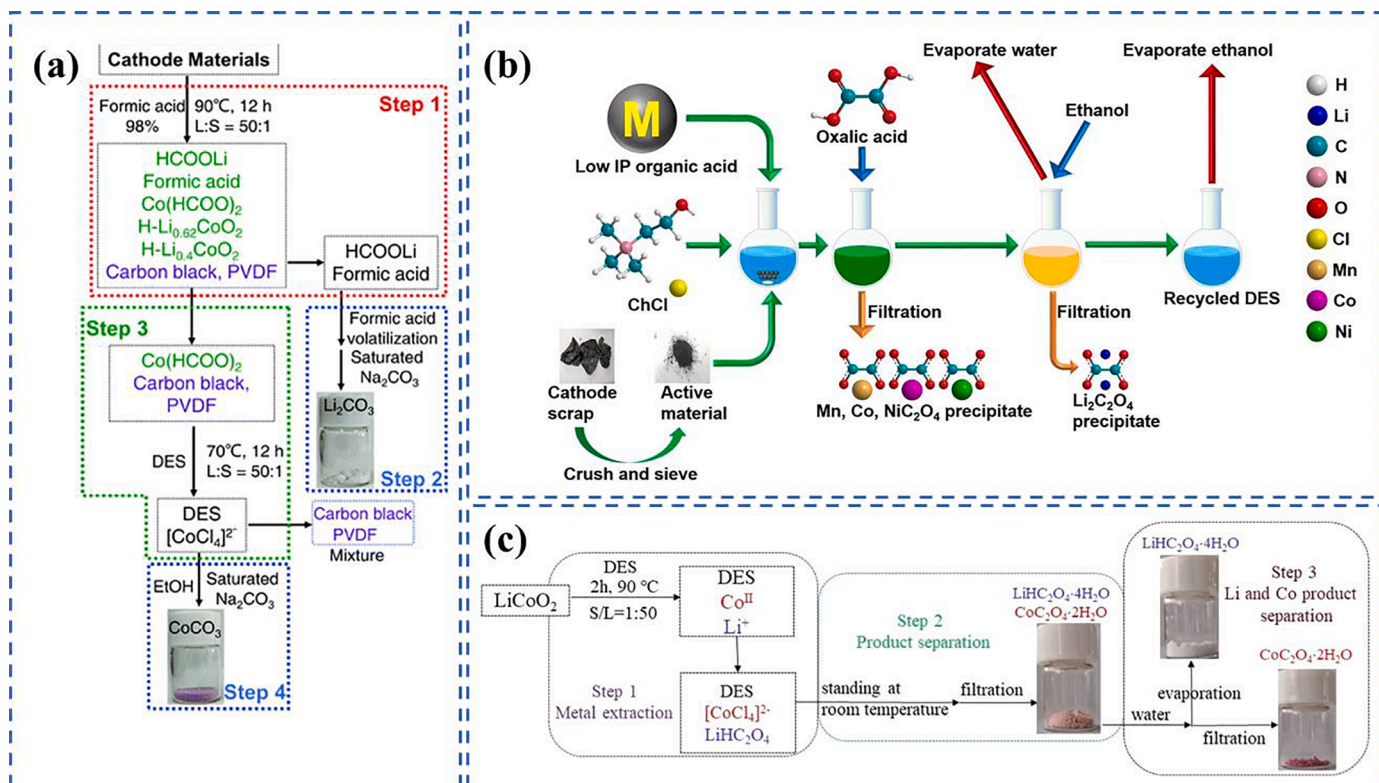

Fig. 5. Selective leaching of Li by using formic acid (a) (Chen et al., 2021b); recycling process of Li in ChCl/*L*-ascorbic acid DES (b) (Hua et al., 2021); and dissolution and precipitation processes of Li in ChCl/oxalic acid DES (c) (Lu et al., 2021).

and Co. Based on this research, Chang et al. studied the leaching behavior of NCM cathode materials in ChCl/oxalic acid dihydrate DES. A similar conclusion suggests that Ni remains in leaching residues as $NiC_2O_4 \bullet 2H_2O$, while dissolved Co in the leachates was $[CoCl_4]^{2-}$ (Chang et al., 2022). Therefore, the coordination ability between the different components in DES and valuable metal ions in LIB cathode materials might have an irreplaceable influence on their selective separation. After the separation of Ni and Co, processes of the precipitation and impurity removal become simpler, which reduces recycling costs, especially for NCM111 with almost the same Co and Ni content. Besides the selective separation of single elements, the coprecipitation of transition metal ions is another method for recycling metals from leachates. Usually, certain concentrations of NaOH and $NH_3 \bullet H_2O$ are selected as precipitants and chelating agents to produce the precursors of ternary battery materials (Zheng et al., 2018). For LCO, simple components have made Co recycling easier. Both chemical precipitation and electrodeposition methods are good for recycling Co from leachates. For instance, Wang et al. have adopted NaOH, Na_2CO_3, and $H_2C_2O_4$ solutions as precipitation agents for recycling Co from the ChCl/urea DES leachates. They found that the Co-based precursor prepared using NaOH and $H_2C_2O_4$ were more suitable for producing Co_3O_4 than Na_2CO_3 due to its better crystallinity (Wang et al., 2020b). The crystallinity of Co_3O_4 might have a severe effect on the electrochemical performance of regenerated LCO cathode materials. Therefore, the selection of precipitation agents is vital. Although NaOH has proven to be an effective precipitation agent, Na ions are difficult to remove from the products. An electrodeposition method can avoid the introduction of Na ions and other impurity elements and does not destroy the structure and properties of DES. However, while this requires greater energy consumption

than chemical precipitation, the DES obtained after the electrodeposition of Co ions can be used for the next leaching process (Tran et al., 2019; Wang et al., 2021).

3.4. DES recovery

Unlike traditional leaching and recycling methods, as mentioned in the above discussion, after a leaching experiment is completed, DESs can be recovered and reused by electrodeposition or by adding some nondestructive components, as shown in Fig. 6. Secondary DESs still have good solubility for metal oxides from cathode materials. In terms of electrodeposition, Tran et al. used Ag/AgCl as the reference electrode and stainless-steel mesh as the working and counter electrodes for recovering Co ions from ChCl/EG DES leaching solution using constant current electrodeposition at −4.5 mA. After the recovery of Co in the form of Co (OH)$_2$, DES can be used a second time. Under the same leaching conditions, there is no significant difference between the performance of the secondary DES and the original (Tran et al., 2019). In addition to the recyclability of ChCl/EG DES, Wang et al. also recovered Co from ChCl/urea DES leaching solution by constant-voltage electrodeposition (−0.9 V) and also achieved DES recovery. Subsequently, they leached LCO at 140 °C with the secondary DES, and the Co ion concentration in the leachate was 0.459 g•L^{-1}, which was not much different from the original DES (Wang et al., 2020b). In contrast, Hua et al. used oxalic acid solution as a precipitant to precipitate Li, Ni, Co, and Mn metal ions from ChCl/*L*-ascorbic acid DES leaching solution. The water and ethanol in the DES were then evaporated to realize DES recovery. H^1-NMR spectra have shown that the structure of DES does not change significantly (Fig. 6b). The leaching efficiency of NCM in
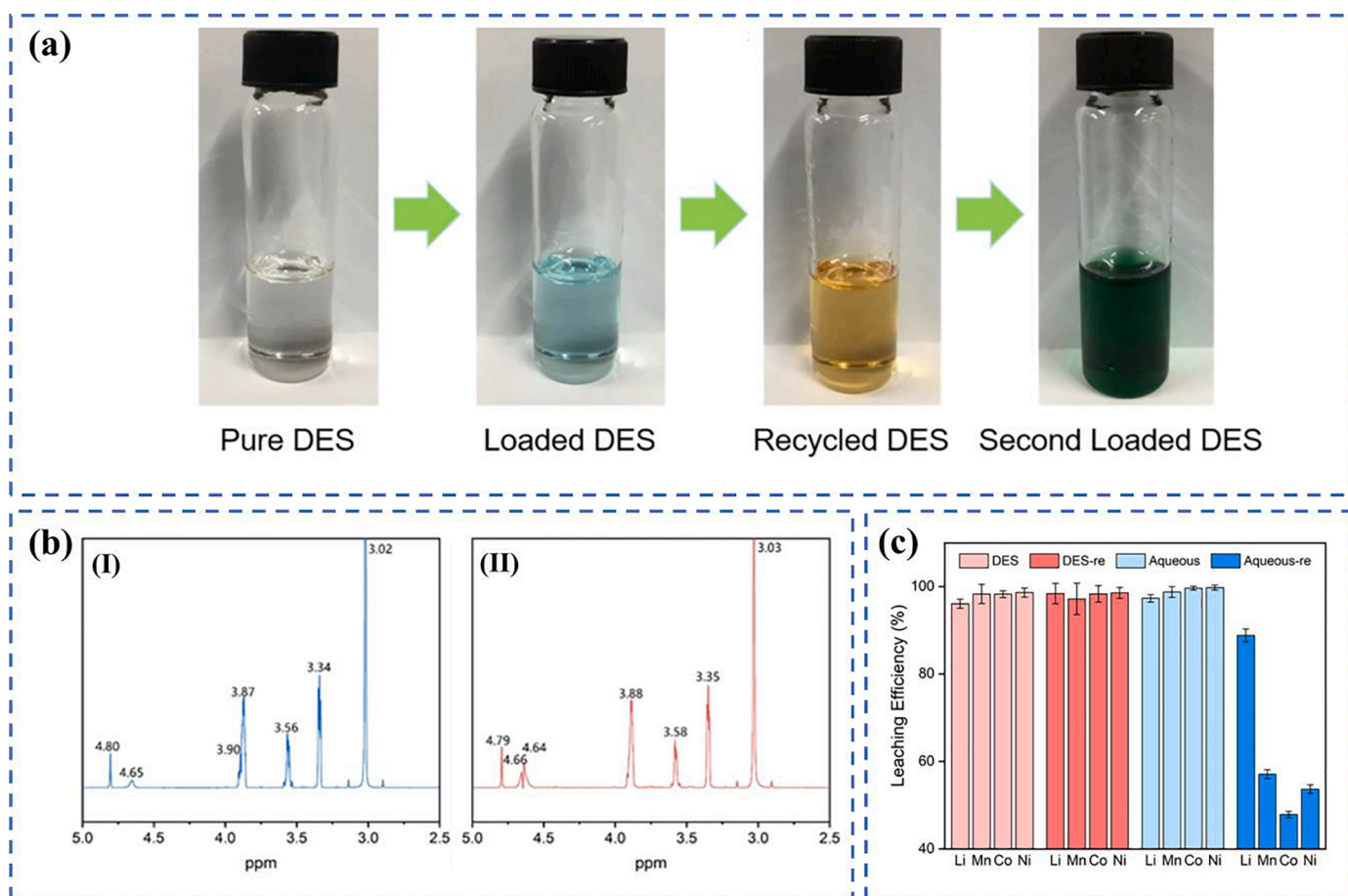

Fig. 6. Leaching effect for LCO in recycled ChCl/urea DES (a) (Wang et al., 2020b); The H^1-NMR spectra of initial DES (I) and recycled DES (II) (b); and leaching efficiency of NCM in initial and recycled DES and L-ascorbic acid aqueous solution (c) (Hua et al., 2021).

recycled DES is comparable to that of initial DES and higher than that of *L*-ascorbic acid aqueous solution. At the same time, they also recycled *L*-ascorbic acid aqueous solution and found that the leaching efficiency for Ni, Co, and Mn is less than half of the initial value. This showed that DES has more clear advantages than traditional aqueous solutions in terms of recycling (Hua et al., 2021). Li et al. adopted a similar method to Hua to recycle ChCl/oxalic acid DES. After LCO dissolution, deionized (DI) water was added to DES to precipitate Co. Then ChCl/oxalic acid DES can be recycled easily by evaporating water (Li et al., 2022).

For some of the less expensive DESs, such as ChCl/urea DES and ChCl/EG DES, the cost of electrodeposition might be higher than the cost of leaching reagents. However, the effective recovery of leaching reagents significantly simplifies the post-processing process of leaching solutions, such as acid wastewater neutralization, ammonia nitrogen wastewater treatment, and dilution of heavy metal ions remaining in the leachate after precipitation. Therefore, from the point of view of reusability, such DESs are far greener than traditional water-based leaching solutions. However, at present, the treatment of Li is often neglected in research regarding the recovery of metals from DESs using electrodeposition. With increased processing steps, such as solid-liquid separation, Li loss becomes increasingly serious. Therefore, it is believed here that verification of Li recyclability must be supplemented in recyclability demonstrations of DESs. Recently, Hua et al. have perfected this shortcoming. As we mentioned above, $Li_2C_2O_4$ exists in the form of a precipitate in a mixed solution of absolute ethanol and ChCl/*L*-ascorbic acid DES (Hua et al., 2021). Therefore, from the perspective of DES recyclability, it is also necessary to study the solubility of some Li salts, especially Li carboxylate salts, in DESs. At the same time, from a cost perspective, organic acids as HBDs yield DESs more expensive. Therefore, the recovery of metals from such DESs cannot only avoid complicated post-processing procedures but also significantly reduce the cost of leaching reagents.

4. Techno-economic analysis

From the conclusions obtained above, direct regeneration and echelon utilization are the best choices for reusing spent LIBs. In recent years, direct regeneration technology has made significant progress in the laboratory stage. Although the development of some technologies, such as hydrothermal repair (Jing et al., 2020; Xu et al., 2020b; Xu et al., 2021), microwave repair (Liu et al., 2022), and molten salt repair (Ma et al., 2020; Shi et al., 2019; Wu et al., 2021; Yang et al., 2020), has brought it one step closer to practical application, there is still a lack of practical application experience. For the echelon utilization of spent LIBs, the traditional recycling method must be considered when the capacity of waste LIBs cannot meet the capacity required by the equipment in the cascade utilization process. Accordingly, these two approaches were not analyzed here (Table. 3) from a technical and economic point of view.

From the environment-friendly aspect, a large amount of fluorine-containing and phosphorus-containing gasses would be generated in pyrometallurgy of LIBs due to the decomposition of the binder and electrolyte, which would cause severe environmental pollution (Neumann et al., 2022). For hydrometallurgy, this phenomenon decreased sharply due to the organic components being separated in pretreatment. Inorganic acids, such as HNO_3 (Chen et al., 2021a), H_2SO_4 (Chen et al., 2020a; Gao et al., 2019; Zhao et al., 2020a), and HCl (Yi et al., 2020), have been widely used due to lower cost and better leaching conditions than with organic acid and ammonia/ammonium salt systems. Nevertheless, Cl_2, SO_x, and NO_x are usually produced in such processes (Or et al., 2020; Zhang et al., 2018b). Also, the production of a large amount of acidic wastewater complicates post-treatment processes. Although Chang et al. have shown the emission of Cl_2 in the leaching process for NCM cathode materials in ChCl/oxalic acid dihydrate DES (Chang et al., 2022), components of DES are biodegradable and can be recycled, which are features that hydrometallurgy does not have. Meanwhile, it is easy to select an HBA without chlorine due to the broad types of DES. Accordingly, it is believed here that recycling processes can be environment-friendly using DESs as leaching solutions for recycling spent LIBs. In view of recycling costs, when a DES is composed of some cheap HBD, such as urea, and HBA, such as ChCl, its price is lower than an organic acid and similar to an inorganic acid. In contrast, organic acids used as the HBDs lead to increased DES costs. However, excellent leaching efficiency for valuable metal ions can be easily obtained from cathode materials using organic acids as HBDs. According to Pateli's research, the solubility of metal oxides, such as Ni, Co, and Mn oxides, in ChCl/oxalic acid DES is higher than in aqueous oxalic solution (Pateli et al., 2020). As discussed above, for other organic acids, such as *L*-ascorbic acid, leaching efficiency is similar between DES and aqueous solution, but DES shows superior recyclability. Thus, the higher leaching efficiency and recyclability are believed here to lead to a lower leaching cost in DES than with an organic acid. From recycling technology, Li tends to evaporate and be lost in slags due to the super high temperature (>1000 °C) in pyrometallurgy, while Fe, Ni, and Co are present in the product form of alloy (Murdock et al., 2021). Therefore, high energy consumption and low recycling efficiency of Li yield this method unsuitable for low economic value cathode materials, such as LFP and LMO. The recycling efficiency of Li is high in hydrometallurgy, but the selective separation of Ni and Co remains difficult. Fortunately, DESs can make up for this disadvantage. In summary, these recycling processes are believed here to be environment-friendly, low cost, and high efficiency, when DES is used as the leaching solution.

Table. 3
Comparison of the leaching features between DESs and others for LIB recycling.

Types	Hydrometallurgy			Pyrometallurgy	Deep eutectic solvents
	Organic acid	Inorganic acid	Ammonia/ammonium salt		
Solid-liquid separation	Easy	Easy	Easy	—	Hard
Selective separation of Ni & Co	Hard	Hard	Hard	Hard	Easy
Selective precipitation of	Hard	Hard	Easy	—	Hard
Solubility of Al	Low	High	Low	—	Low
Loss of Li	Few	Few	Few	Severe	Few
Leaching efficiency for LCO	High	High	High	—	High
Leaching efficiency for LFP	High	High	Fewer study	—	Few studies
Leaching efficiency for NCM	High	High	High	—	High
Leaching efficiency for NCA	Fewer study	Fewer study	Fewer study	—	Few studies
Energy-consumed in recycling	Low (<100 °C)	Low (<100 °C)	Low (<100 °C)	High (>1000 °C)	Low (50–220 °C)
Purity of products	High	High	High	Low	High
Emission of harmful gas	Low	Moderate	Moderate	High	Moderate
Demand for reducing agent	High	High	High	—	Unnecessary
Process maturity	Industrial application	Industrial application	Industrial application	Industrial application	In laboratory
Cost of leaching soln.	High	Low	Low	—	Moderate
Thermostability of leaching soln.	Low	Low	Low	—	High
Recyclability of leaching soln.	Hard	Hard	Hard	—	Easy

5. Conclusions and outlook

The increasingly tense supply relationship of critical raw materials for LIBs and the potential pollution and damage to the environment from spent LIBs make recycling imperative. However, at present, secondary pollution generated during the recycling of discarded LIBs remains unavoidable. Therefore, developing a green and cheap recycling technology is urgently needed to alleviate current recycling problems. Since 2019, green and affordable DESs have begun to show great application value in recycling discarded LIBs. These mixtures still have significant limitations in their application, as an emerging technology. For example, excessive viscosity limits the leaching reaction and requires high-temperature conditions (Wang et al., 2020b) or the participation of toxic diluents, such as dimethyl sulfoxide (DMSO) (Chang et al., 2022), in the solid-liquid separation process. The critical requirement for solving these problems lies in understanding the fundamental physicochemical properties of DESs and the pathways and mechanisms for the dissolution of valuable metals from LIBs into DESs. In this review, some physicochemical properties of DESs, such as viscosity, acidity, and coordination ability, were combined with the leaching kinetics of metal ions. At the same time, the precipitation and separation process of metal elements was summarized and analyzed. DES leaching solutions were found to be more suitable for acquiring high-purity single metal elements than traditional water-based leaching solutions. In battery recycling, this is helpful in the design and application of DESs to a certain extent. At the same time, a differential analysis of traditional hydrometallurgy, pyrometallurgy, and DESs was conducted from the perspectives of environmental friendliness, leaching cost, and technology. DESs were believed here to have significant advantages in some respects, such as in the selective separation of Ni and Co, recyclability, and lower leaching costs. However, in practical application, DESs still have features to be perfected and solved. 1) As mentioned above, it remains a challenge to solve the slow leaching reaction and filtration speed caused by high viscosity DESs. On one hand, a low viscosity DES can be designed as a leaching solution. On the other hand, it is also a suitable method to decrease leachate viscosity by adding diluent during filtration, while the diluent must be green and cheap and cannot cause secondary precipitation of valuable metal ions in the leachate. 2) More attention should be paid to DES recyclability. Undoubtedly, electrodeposition is a desirable choice for recycling neutral or alkaline DESs. However, few studies have focused on Li recycling from the leachate by electrodeposition. For the acid-based DESs with better leaching efficiency, electrodeposition might show undesirable results due to dissolution caused by hydrogen ions. Therefore, it is imperative to develop a method for recycling acid-based DESs. 3) The universality of DESs in LIB recycling needs to be further proven because research on recycling NCA and LFP by DESs is lacking. In general, organic acid solutions have poor solubility for Al, which means DESs composed of organic acids as HBD might exhibit specific selectivity during the leaching of NCA. For LFP, the desire for low prices leads to the need to choose a cheap and green recycling process. Therefore, inexpensive and biodegradable DESs are undoubtedly a good choice. 4) As is known, DESs are usually seen as great candidates for nanoparticle synthesis. And some nanoparticles, such as nano-Co_3O_4, show extreme application value in supercapacitor, catalytic, anode materials for LIBs, and other fields. Therefore, the preparation of nanoparticles with high value can be attempted after leaching valuable metals into DESs. 5) In recent years, the technology of all-solid-state LIBs has become increasingly mature. However, the recycling of Li metal anodes in all-solid-state LIBs is very difficult owing to the strong reactions between them and aqueous solutions. Nonaqueous solvent DESs might provide an excellent solution to this dilemma. 6) It is necessary to build a near-perfect system to evaluate the feasibility of DESs in spent LIB recycling from the aspect of the economy, environmental protection, and energy consumption. DESs currently used in LIBs recycling all have undesirable disadvantages. By detailed evaluation of DESs, DESs can be quickly graded and a more suitable DES selected for recycling spent LIBs, which would be beneficial for large-scale DES applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

References

Abbott, A.P., 2004. Application of hole theory to the viscosity of ionic and molecular liquids. Chemphyschem 5, 1242–1246. https://doi.org/10.1002/cphc.200400190.

Abbott, A.P., 2005. Model for the conductivity of ionic liquids based on an infinite dilution of holes. Chemphyschem 6, 2502–2505. https://doi.org/10.1002/cphc.200500283.

Abbott, A.P., Boothby, D., Capper, G., et al., 2004. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. J. Am. Chem. Soc. 126, 9142–9147. https://doi.org/10.1021/ja048266j.

Abbott, A.P., Capper, G., Davies, D.L., et al., 2003. Novel solvent properties of choline chloride/urea mixtures. Chem. Commun. 70–71. https://doi.org/10.1039/b210714g.

Abbott, A.P., Capper, G., Davies, D.L., et al., 2006. Solubility of metal oxides in deep eutectic solvents based on choline chloride. J. Chem. Eng. Data 51, 1280–1282. https://doi.org/10.1021/je060038c.

Alabdullah, S.S.M., 2018. pH measurements in ionic liquids.

AlOmar, M.K., Hayyan, M., Alsaadi, M.A., et al., 2016. Glycerol-based deep eutectic solvents: physical properties. J Mol Liq 215, 98–103. https://doi.org/10.1016/j.molliq.2015.11.032.

Amphlett, J.T.M., Choi, S., 2021. The effect of increasing water content on transition metal speciation in deep eutectic solvents. J. Mol. Liq. 332, 115845 https://doi.org/10.1016/j.molliq.2021.115845.

Baars, J., Domenech, T., Bleischwitz, R., et al., 2021. Circular economy strategies for electric vehicle batteries reduce reliance on raw materials. Nat. Sustain. 4, 71–79. https://doi.org/10.1038/s41893-020-00607-0.

Bernasconi, R., Panzeri, G., Firtin, G., et al., 2020. Electrodeposition of ZnNi alloys from choline chloride/ethylene glycol deep eutectic solvent and pure ethylene glycol for corrosion protection. The J. Phys. Chem. B 124, 10739–10751. https://doi.org/10.1021/acs.jpcb.0c04784.

Chan, K.H., Anawati, J., Malik, M., et al., 2021. Closed-loop recycling of lithium, cobalt, nickel, and manganese from waste lithium-ion batteries of electric vehicles. ACS Sustain. Chem. Eng. 9, 4398–4410. https://doi.org/10.1021/acssuschemeng.0c06869.

Chang, X., Fan, M., Gu, C.F., et al., 2022. Selective extraction of transition metals from spent LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ cathode via regulation of coordination environment. Angew Chem. Int. Ed Engl. https://doi.org/10.1002/anie.202202558.

Chen, D., Rao, S., Wang, D., et al., 2020a. Synergistic leaching of valuable metals from spent Li-ion batteries using sulfuric acid- L-ascorbic acid system. Chem. Eng. J. 388, 124321 https://doi.org/10.1016/j.cej.2020.124321.

Chen, H., Gu, S., Guo, Y., et al., 2021a. Leaching of cathode materials from spent lithium-ion batteries by using a mixture of ascorbic acid and HNO$_3$. Hydrometallurgy 205, 105746. https://doi.org/10.1016/j.hydromet.2021.105746.

Chen, L., Chao, Y., Li, X., et al., 2021b. Engineering a tandem leaching system for the highly selective recycling of valuable metals from spent Li-ion batteries. Green Chem. 23, 2177–2184. https://doi.org/10.1039/D0GC03820B.

Chen, W., Jiang, J., Lan, X., et al., 2019. A strategy for the dissolution and separation of rare earth oxides by novel Brønsted acidic deep eutectic solvents. Green Chem. 21, 4748–4756. https://doi.org/10.1039/c9gc00944b.

Chen, X., Wang, Y., Li, S., et al., 2022. Selective recycling of valuable metals from waste LiCoO₂ cathode material of spent lithium-ion batteries through low-temperature thermochemistry. Chem. Eng. J. 434, 134542 https://doi.org/10.1016/j.cej.2022.134542.

Chen, Y., Lu, Y., Liu, Z., et al., 2020b. Efficient Dissolution of Lithium-Ion Batteries Cathode LiCoO₂ by Polyethylene Glycol-Based Deep Eutectic Solvents at Mild Temperature. ACS Sustain. Chem. Eng. 8, 11713–11720. https://doi.org/10.1021/acssuschemeng.0c03624.

D'Agostino, C., Harris, R.C., Abbott, A.P., et al., 2011. Molecular motion and ion diffusion in choline chloride based deep eutectic solvents studied by 1H pulsed field gradient NMR spectroscopy. Phys. Chem. Chem. Phys. 13, 21383–21391. https://doi.org/10.1039/c1cp22554e.

Damilano, A.J., Laitinen, A., Willberg-Keyrilainen, P., et al., 2020. Effects of thiol substitution in deep-eutectic solvents (DESs) as solvents for metal oxides. RSC Adv. 23484–23490. https://doi.org/10.5281/zenodo.3750813.

Du, K., Ang, E.H., Wu, X., et al., 2022. Progresses in sustainable recycling technology of spent lithium-ion batteries. Energy & Environ. Mater. https://doi.org/10.1002/eem2.12271.

Duarte Castro, F., Cutaia, L., Vaccari, M., 2021. End-of-life automotive lithium-ion batteries (LIBs) in Brazil: prediction of flows and revenues by 2030. Resour. Conserv. Recycl. 169, 105502 https://doi.org/10.1016/j.resconrec.2021.105502.

El Achkar, T., Greige-Gerges, H., Fourmentin, S., 2021. Basics and properties of deep eutectic solvents: a review. Environ. Chem. Lett. 19, 3397–3408. https://doi.org/10.1007/s10311-021-01225-8.

Exposito, A.J., Barrie, P.J., Torrente-Murciano, L., 2020. Fast synthesis of CeO₂ nanoparticles in a continuous microreactor using deep eutectic reline as solvent. ACS Sustain. Chem. Eng. 8, 18297–18302. https://doi.org/10.1021/acssuschemeng.0c06949.

Fan, E., Yang, J., Huang, Y., et al., 2020. Leaching mechanisms of recycling valuable metals from spent lithium-ion batteries by a malonic acid-based leaching system. ACS Appl. Energy Mater. 3, 8532–8542. https://doi.org/10.1021/acsaem.0c01166.

Florindo, C., Branco, L.C., Marrucho, I.M., 2019. Quest for green-solvent design: from hydrophilic to hydrophobic (Deep) eutectic solvents. ChemSusChem 12, 1549–1559. https://doi.org/10.1002/cssc.201900147.

Fu, Y., He, Y., Yang, Y., et al., 2020. Microwave reduction enhanced leaching of valuable metals from spent lithium-ion batteries. J. Alloys Compd. 832, 154920 https://doi.org/10.1016/j.jallcom.2020.154920.

Gao, G., Luo, X., Lou, X., et al., 2019. Efficient sulfuric acid-Vitamin C leaching system: towards enhanced extraction of cobalt from spent lithium-ion batteries. J. Mater. Cycles and Waste Manag. 21, 942–949. https://doi.org/10.1007/s10163-019-00850-4.

Gourley, S.W.D., Or, T., Chen, Z., 2020. Breaking free from cobalt reliance in lithium-ion batteries. ISCIENCE 23. https://doi.org/10.1016/j.isci.

Hansen, B.B., Spittle, S., Chen, B., et al., 2021. Deep eutectic solvents: a review of fundamentals and applications. Chem. Rev. 121, 1232–1285. https://doi.org/10.1021/acs.chemrev.0c00385.

Hatab, F.A., Darwish, A.S., Lemaoui, T., et al., 2020. Extraction of thiophene, pyridine, and toluene from n-decane as a diesel model using betaine-based natural deep eutectic solvents. J. Chem. Eng. Data 65, 5443–5457. https://doi.org/10.1021/acs.jced.0c00579.

He, Y., Yuan, X., Zhang, G., et al., 2021. A critical review of current technologies for the liberation of electrode materials from foils in the recycling process of spent lithium-ion batteries. Sci. Total Environ. 766, 142382 https://doi.org/10.1016/j.scitotenv.2020.142382.

Hu, Z., Zhu, N., Wei, X., et al., 2021. Efficient separation of aluminum foil from mixed-type spent lithium-ion power batteries. J. Environ. Manag. 298, 113500 https://doi.org/10.1016/j.jenvman.2021.113500.

Hua, Y., Sun, Y., Yan, F., et al., 2021. Ionization potential-based design of deep eutectic solvent for recycling of spent lithium ion batteries. Chem. Eng. J. 133200 https://doi.org/10.1016/j.cej.2021.133200.

Huang, F., Li, T., Yan, X., et al., 2022. Ternary deep eutectic solvent (DES) with a regulated rate-determining step for efficient recycling of lithium cobalt oxide. ACS Omega 7, 11452–11459. https://doi.org/10.1021/acsomega.2c00742.

Ibrahim, R.K., Hayyan, M., AlSaadi, M.A., et al., 2019. Physical properties of ethylene glycol-based deep eutectic solvents. J. Mol. Liq. 276, 794–800. https://doi.org/10.1016/j.molliq.2018.12.032.

Inter-national Energy Agency, 2021. World Energy Outlook 2021. https://iea.blob.core.windows.net/assets/4ed140c1-c3f3-4fd9-acae-789a4e14a23c/WorldEnergyOutlook2021.pdf.

Jha, M.K., Kumari, A., Jha, A.K., et al., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. Waste Manag. 33, 1890–1897. https://doi.org/10.1016/j.wasman.2013.05.008.

Ji, G., Ou, X., Zhao, R., et al., 2021. Efficient utilization of scrapped LiFePO₄ battery for novel synthesis of Fe2P2O7/C as candidate anode materials. Resour. Conserv. Recycl. 174, 105802 https://doi.org/10.1016/j.resconrec.2021.105802.

Jin, S., Mu, D., Lu, Z., et al., 2022. A comprehensive review on the recycling of spent lithium-ion batteries: urgent status and technology advances. J. Clean. Prod. 340, 130535 https://doi.org/10.1016/j.jclepro.2022.130535.

Jing, Q., Zhang, J., Liu, Y., et al., 2020. Direct regeneration of spent LiFePO₄ cathode material by a green and efficient one-step hydrothermal method. ACS Sustain. Chem. Eng. 8, 17622–17628. https://doi.org/10.1021/acssuschemeng.0c07166.

Kim, K., Raymond, D., Candeago, R., et al., 2021. Selective cobalt and nickel electrodeposition for lithium-ion battery recycling through integrated electrolyte and interface control. Nat. Commun. 12 https://doi.org/10.1038/s41467-021-26814-7.

Klein, J.M., Squire, H., Dean, W., et al., 2020. From salt in solution to solely ions: solvation of methyl viologen in deep eutectic solvents and ionic liquids. The J. Phys. Chem. B 124, 6348–6357. https://doi.org/10.1021/acs.jpcb.0c03296.

Lapeña, D., Bergua, F., Lomba, L., et al., 2020. A comprehensive study of the thermophysical properties of reline and hydrated reline. J. Mol. Liq. 303, 112679 https://doi.org/10.1016/j.molliq.2020.112679.

Li, L., Fan, E., Guan, Y., et al., 2017. Sustainable recovery of cathode materials from spent lithium-ion batteries using lactic acid leaching system. ACS Sustain. Chem. Eng. 5, 5224–5233. https://doi.org/10.1021/acssuschemeng.7b00571.

Li, L., Lu, J., Zhai, L., et al., 2018. A facile recovery process for cathodes from spent lithium iron phosphate batteries by using oxalic acid. CSEE J. Power and Energy Syst. 4, 219–225. https://doi.org/10.17775/CSEEJPES.2016.01081.

Li, T., Xiong, Y., Yan, X., et al., 2022. Closed-loop cobalt recycling from spent lithium-ion batteries based on a deep eutectic solvent (DES) with easy solvent recovery. J. Energy Chem. 72, 532–538. https://doi.org/10.1016/j.jechem.2022.05.008.

Liu, Y., Yu, H., Wang, Y., et al., 2022. Microwave hydrothermal renovating and reassembling spent lithium cobalt oxide for lithium-ion battery. Waste Manag. 143, 186–194. https://doi.org/10.1016/j.wasman.2022.02.024.

Lombardo, G., Ebin, B., St. J. Foreman, M.R., et al., 2019. Chemical transformations in Li-ion battery electrode materials by carbothermic reduction. ACS Sustain. Chem. Eng. 7, 13668–13679. https://doi.org/10.1021/acssuschemeng.8b06540.

Lu, Q., Chen, L., Li, X., et al., 2021. Sustainable and convenient recovery of valuable metals from spent Li-ion batteries by a one-pot extraction Process. ACS Sustain. Chem. Eng. 9, 13851–13861. https://doi.org/10.1021/acssuschemeng.1c04717.

Luo, Y., Yin, C., Ou, L., et al., 2022. Highly efficient dissolution of the cathode materials of spent Ni–Co–Mn lithium batteries using deep eutectic solvents. Green Chem. https://doi.org/10.1039/D2GC01431A.

Ma, T., Guo, Z., Shen, Z., et al., 2020. Molten salt-assisted regeneration and characterization of submicron-sized LiNi0.5Co0.2Mn0.3O2 crystals from spent lithium ion batteries. J. Alloys Compd. 848, 156591 https://doi.org/10.1016/j.jallcom.2020.156591.

Ma, X., Azhari, L., Wang, Y., 2021a. Li-ion battery recycling challenges. Chem 7, 2843–2847. https://doi.org/10.1016/j.chempr.2021.09.013.

Ma, Y., Tang, J., Wanaldi, R., et al., 2021b. A promising selective recovery process of valuable metals from spent lithium ion batteries via reduction roasting and ammonia leaching. J. Hazard. Mater. 402, 123491 https://doi.org/10.1016/j.jhazmat.2020.123491.

Mahandra, H., Ghahreman, A., 2021. A sustainable process for selective recovery of lithium as lithium phosphate from spent LiFePO₄ batteries. Resour. Conserv. Recycl. 175, 105883 https://doi.org/10.1016/j.resconrec.2021.105883.

Makuza, B., Tian, Q., Guo, X., et al., 2021. Pyrometallurgical options for recycling spent lithium-ion batteries: a comprehensive review. J. Power Sources 491, 229622. https://doi.org/10.1016/j.jpowsour.2021.229622.

Ministry of Industry and Information Technology of the People's Republic of China, 2019. https://www.miit.gov.cn/gjsj/jns/zhlyh/art/2020/art_5a8da24dc673406992717f731e03ff3c.html.

Morina, R., Callegari, D., Merli, D., et al., 2022. Cathode active material recycling from spent lithium batteries: a green (Circular) approach based on deep eutectic solvents. ChemSusChem 15, e202102080. https://doi.org/10.1002/cssc.202102080.

Murdock, B.E., Toghill, K.E., Tapia Ruiz, N., 2021. A Perspective on the sustainability of cathode materials used in lithium-ion batteries. Adv. Energy Mater. 11, 2102028 https://doi.org/10.1002/aenm.202102028.

Neumann, J., Petranikova, M., Meeus, M., et al., 2022. Recycling of lithium-ion batteries—current state of the art, circular economy, and next generation recycling. Adv. Energy Mater. 12, 2102917 https://doi.org/10.1002/aenm.202102917.

Olivetti, E.A., Ceder, G., Gaustad, G.G., et al., 2017. Lithium-ion battery supply chain considerations: analysis of potential bottlenecks in critical metals. Joule 1, 229–243. https://doi.org/10.1016/j.joule.2017.08.019.

Or, T., Gourley, S.W.D., Kaliyappan, K., et al., 2020. Recycling of mixed cathode lithium-ion batteries for electric vehicles: current status and future outlook. Carbon Energy 2, 6–43. https://doi.org/10.1002/cey2.29.

Padwal, C., Pham, H.D., Jadhav, S., et al., 2022. Deep eutectic solvents: green approach for cathode recycling of Li-ion batteries. Adv. Energy and Sustain. Res. 3, 2100133 https://doi.org/10.1002/aesr.202100133.

Pateli, I.M., Thompson, D., Alabdullah, S.S.M., et al., 2020. The effect of pH and hydrogen bond donor on the dissolution of metal oxides in deep eutectic solvents. Green Chem. 22, 5476–5486. https://doi.org/10.1039/D0GC02023K.

Peeters, N., Binnemans, K., Riaño, S., 2020. Solvometallurgical recovery of cobalt from lithium-ion battery cathode materials using deep-eutectic solvents. Green Chem. 22, 4210–4221. https://doi.org/10.1039/D0GC00940G.

Raj, T., Chandrasekhar, K., Kumar, A.N., et al., 2022. Recycling of cathode material from spent lithium-ion batteries: challenges and future perspectives. J. Hazard. Mater. 429, 128312 https://doi.org/10.1016/j.jhazmat.2022.128312.

Roldán-Ruiz, M.J., Ferrer, M.L., Gutiérrez, M.C., et al., 2020. Highly efficient p-toluenesulfonic acid-based deep-eutectic solvents for cathode recycling of Li-ion batteries. ACS Sustain. Chem. Eng. 8, 5437–5445. https://doi.org/10.1021/acssuschemeng.0c00892.

Santhosh, G., Nayaka, G.P., 2021. Cobalt recovery from spent Li-ion batteries using lactic acid as dissolution agent. Clean. Eng. Technol. 3, 100122 https://doi.org/10.1016/j.clet.2021.100122.

Schiavi, P.G., Altimari, P., Branchi, M., et al., 2021. Selective recovery of cobalt from mixed lithium ion battery wastes using deep eutectic solvent. Chem. Eng. J. 417, 129249 https://doi.org/10.1016/j.cej.2021.129249.

Shah, D., Mjalli, F.S., 2014. Effect of water on the thermo-physical properties of Reline: an experimental and molecular simulation based approach. Phys. Chem. Chem. Phys. 16, 23900–23907. https://doi.org/10.1039/c4cp02600d.

Shi, Y., Zhang, M., Meng, Y.S., et al., 2019. Ambient-pressure relithiation of degraded LixNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (0 < x < 1) via eutectic solutions for direct regeneration of lithium-ion battery cathodes. Adv. Energy Mater. 9, 1900454 https://doi.org/10.1002/aenm.201900454.

Skulcova, A., Russ, A., Jablonsky, M., et al., 2018. The pH behavior of seventeen deep eutectic solvents. BIORES 13, 5042–5051.

Song, X., Hu, T., Liang, C., et al., 2017. Direct regeneration of cathode materials from spent lithium iron phosphate batteries using a solid phase sintering method. RSC Adv. 7, 4479–4783. https://doi.org/10.1039/c6ra27210j.

Tang, S., Zhang, M., Guo, M., 2022. A novel deep-eutectic solvent with strong coordination ability and low viscosity for efficient extraction of valuable metals from spent lithium-ion batteries. ACS Sustain. Chem. Eng. 10, 975–985. https://doi.org/10.1021/acssuschemeng.1c06902.

Tao, R., Xing, P., Li, H., et al., 2022. Recovery of spent LiCoO$_2$ lithium-ion battery via environmentally friendly pyrolysis and hydrometallurgical leaching. Resour. Conserv. Recycl. 176, 105921 https://doi.org/10.1016/j.resconrec.2021.105921.

Thompson, D., Hyde, C., Hartley, J.M., et al., 2021. To shred or not to shred: a comparative techno-economic assessment of lithium ion battery hydrometallurgical recycling retaining value and improving circularity in LIB supply chains. Resour. Conserv. Recycl. 175, 105741 https://doi.org/10.1016/j.resconrec.2021.105741.

Thompson, D.L., Hartley, J.M., Lambert, S.M., et al., 2020. The importance of design in lithium ion battery recycling - a critical review. Green Chem. 22, 7585–7763. https://doi.org/10.1039/d0gc02745f.

Tran, M.K., Rodrigues, M.F., Kato, K., et al., 2019. Deep eutectic solvents for cathode recycling of Li-ion batteries. Nat. Energy 4, 339–345. https://doi.org/10.1038/s41560-019-0368-4.

Tsiropoulos, I., Tarvydas, D., Lebedeva, N., 2018. Li-ion Batteries For Mobility and Stationary Storage Applications – Scenarios for Costs and Market Growth. EUR 29440 EN, Publications Office of the European Union, Luxembourg, JRC113360. https://doi.org/10.2760/87175. ISBN 978-92-79-97254-6. https://publications.jrc.ec.europa.eu/repository/bitstream/JRC113360/kjna29440enn.pdf.

van Osch, D.J., Parmentier, D., Dietz, C.H., et al., 2016. Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents. Chem. Commun. 52, 11987–11990. https://doi.org/10.1039/c6cc06105b.

Verma, A., Johnson, G.H., Corbin, D.R., et al., 2020. Separation of lithium and cobalt from LiCoO$_2$: a unique critical metals recovery process utilizing oxalate chemistry. ACS Sustain. Chem. Eng. 8, 6100–6108. https://doi.org/10.1021/acssuschemeng.0c01128.

Wang, H., Li, M., Garg, S., et al., 2021. Cobalt electrochemical recovery from lithium cobalt oxides in deep eutectic choline chloride+urea solvents. ChemSusChem 14, 2972–2983. https://doi.org/10.1002/cssc.202100954.

Wang, K., Hu, T., Shi, P., et al., 2022. Efficient recovery of value metals from spent lithium-ion batteries by combining deep eutectic solvents and coextraction. ACS Sustain. Chem. Eng. 10, 1149–1159. https://doi.org/10.1021/acssuschemeng.1c06381.

Wang, M., Tan, Q., Liu, L., et al., 2019. A low-toxicity and high-efficiency deep eutectic solvent for the separation of aluminum foil and cathode materials from spent lithium-ion batteries. J. Hazard. Mater. 380, 120846 https://doi.org/10.1016/j.jhazmat.2019.120846.

Wang, S., Wang, C., Lai, F., et al., 2020a. Reduction-ammoniacal leaching to recycle lithium, cobalt, and nickel from spent lithium-ion batteries with a hydrothermal method: effect of reductants and ammonium salts. Waste Manag. 102, 122–130. https://doi.org/10.1016/j.wasman.2019.10.017.

Wang, S., Zhang, Z., Lu, Z., et al., 2020b. A novel method for screening deep eutectic solvent to recycle the cathode of Li-ion batteries. Green Chem. 22, 4473–4482. https://doi.org/10.1039/D0GC00701C.

Wu, J., Lin, J., Fan, E., et al., 2021. Sustainable regeneration of high-performance Li$_{1-x}$Na$_x$CoO$_2$ from cathode materials in spent lithium-ion batteries. ACS Appl. Energy Mater. 4, 2607–2615. https://doi.org/10.1021/acsaem.0c03192.

Xiao, J., Li, J., Xu, Z., 2017. Novel approach for in situ recovery of lithium carbonate from spent lithium ion batteries using vacuum metallurgy. Environ. Sci. Technol. 51, 11960–11966. https://doi.org/10.1021/acs.est.7b02561.

Xiao, J., Niu, B., Xu, Z., 2021. Highly efficient selective recovery of lithium from spent lithium-ion batteries by thermal reduction with cheap ammonia reagent. J. Hazard. Mater. 418, 126319 https://doi.org/10.1016/j.jhazmat.2021.126319.

Xu, C., Dai, Q., Gaines, L., et al., 2020a. Future material demand for automotive lithium-based batteries. Commun. Mater. 1, 1–10. https://doi.org/10.1038/s43246-020-00095-x.

Xu, P., Dai, Q., Gao, H., et al., 2020b. Efficient direct recycling of lithium-ion battery cathodes by targeted healing. Joule 4, 2609–2626. https://doi.org/10.1016/j.joule.2020.10.008.

Xu, P., Yang, Z., Yu, X., et al., 2021. Design and optimization of the direct recycling of spent li-ion battery cathode materials. ACS Sustain. Chem. Eng. 9, 4543–4553. https://doi.org/10.1016/j.fluid.2014.01.028.

Yadav, A., Trivedi, S., Rai, R., et al., 2014. Densities and dynamic viscosities of (choline chloride+glycerol) deep eutectic solvent and its aqueous mixtures in the temperature range (283.15–363.15)K. Fluid Phase Equilib. 367, 135–142. https://doi.org/10.1016/j.fluid.2014.01.028.

Yang, J., Wang, W., Yang, H., et al., 2020. One-pot compositional and structural regeneration of degraded LiCoO$_2$ for directly reusing it as a high-performance lithium-ion battery cathode. Green Chem. 22, 6489–6496. https://doi.org/10.1039/D0GC02662J.

Yang, X., Zhang, Y., Meng, Q., et al., 2021. Recovery of valuable metals from mixed spent lithium-ion batteries by multi-step directional precipitation. RSC Adv. 11, 268–277. https://doi.org/10.1039/D0RA09297E.

Yi, A., Zhu, Z., Liu, Y., et al., 2020. Using highly concentrated chloride solutions to leach valuable metals from cathode-active materials in spent lithium-ion batteries. Rare Metals 40, 1971. https://doi.org/10.1007/s12598-020-01503-4.

Yu, L., Liu, T., Amine, R., et al., 2022a. High Nickel and No Cobalt - The Pursuit of Next-Generation Layered Oxide Cathodes. ACS Appl. Mater. Interfaces 14, 23056–23065. https://doi.org/10.1021/acsami.1c22091.

Yu, W., Guo, Y., Shang, Z., et al., 2022b. A review on comprehensive recycling of spent power lithium-ion battery in China. Etransportation. 11, 100155 https://doi.org/10.1016/j.etran.2022.100155.

Yue, Y., Wei, S., Yongjie, B., et al., 2018. Recovering valuable metals from spent lithium ion battery via a combination of reduction thermal treatment and facile acid leaching. ACS Sustain. Chem. Eng. 6, 10445–10453. https://doi.org/10.1021/acssuschemeng.8b01805.

Zante, G., Braun, A., Masmoudi, A., et al., 2020. Solvent extraction fractionation of manganese, cobalt, nickel and lithium using ionic liquids and deep eutectic solvents. Miner. Eng. 156, 106512 https://doi.org/10.1016/j.mineng.2020.106512.

Zeng, A., Chen, W., Rasmussen, K.D., et al., 2022. Battery technology and recycling alone will not save the electric mobility transition from future cobalt shortages. Nat. Commun. 13 https://doi.org/10.1038/s41467-022-29022-z.

Zeng, G., Yao, J., Liu, C., et al., 2021. Simultaneous Recycling of Critical Metals and Aluminum Foil from Waste LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cathode via Ethylene Glycol–Citric Acid System. ACS Sustain. Chem. Eng. 9, 16133–16142. https://doi.org/10.1021/acssuschemeng.1c04806.

Zhang, R., Meng, Z., Ma, X., et al., 2020a. Understanding fundamental effects of Cu impurity in different forms for recovered LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode materials. Nano Energy 78, 105214. https://doi.org/10.1016/j.nanoen.2020.105214.

Zhang, R., Zheng, Y., Yao, Z., et al., 2020b. Systematic Study of Al Impurity for NCM622 Cathode Materials. ACS Sustain. Chem. Eng. 8, 9875–9884. https://doi.org/10.1021/acssuschemeng.0c02965.

Zhang, X., Bian, Y., Xu, S., et al., 2018a. Innovative application of acid leaching to regenerate Li(Ni1/3Co1/3Mn1/3)O2 cathodes from spent lithium-ion batteries. ACS Sustain. Chem. Eng. 6, 5959–5968. https://doi.org/10.1021/acssuschemeng.7b04373.

Zhang, X., Cao, H., Xie, Y., et al., 2015. A closed-loop process for recycling LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ from the cathode scraps of lithium-ion batteries: process optimization and kinetics analysis. Sep. Purif. Technol. 150, 186–195. https://doi.org/10.1016/j.seppur.2015.07.003.

Zhang, X., Li, L., Fan, E., et al., 2018b. Toward sustainable and systematic recycling of spent rechargeable batteries. Chem. Soc. Rev. 47, 7239–7302. https://doi.org/10.1039/c8cs00297e.

Zhang, X., Xue, Q., Li, L., et al., 2016. Sustainable Recycling and Regeneration of Cathode Scraps from Industrial Production of Lithium-Ion Batteries. ACS Sustain. Chem. Eng. 4, 7041–7049. https://doi.org/10.1021/acssuschemeng.6b01948.

Zhao, J., Zhang, B., Xie, H., et al., 2020a. Hydrometallurgical recovery of spent cobalt-based lithium-ion battery cathodes using ethanol as the reducing agent. Environ. Res. 181, 108803 https://doi.org/10.1016/j.envres.2019.108803.

Zhao, S., Zhang, W., Li, G., et al., 2020b. Ultrasonic renovation mechanism of spent LCO batteries: a mild condition for cathode materials recycling. Resour. Conserv. Recycl. 162, 105019 https://doi.org/10.1016/j.resconrec.2020.105019.

Zhao, Y., Liu, B., Zhang, L., et al., 2020c. Microwave pyrolysis of macadamia shells for efficiently recycling lithium from spent lithium-ion batteries. J. Hazard. Mater. 396, 122740 https://doi.org/10.1016/j.jhazmat.2020.122740.

Zheng, Y., Zhang, R., Vanaphuti, P., et al., 2021. Unveiling the influence of carbon impurity on recovered NCM622 cathode Material. ACS Sustain. Chem. Eng. 9, 6087–6096. https://doi.org/10.1021/acssuschemeng.1c01510.

Zheng, Z., Chen, M., Wang, Q., et al., 2018. High performance cathode recovery from different electric vehicle recycling streams. ACS Sustain. Chem. Eng. 6, 13977–13982. https://doi.org/10.1021/acssuschemeng.8b02405.

Zhou, F., Qu, X., Wu, Y., et al., 2022. Vacuum pyrolysis of pine sawdust to recover spent lithium ion batteries: the synergistic effect of carbothermic reduction and pyrolysis gas reduction. ACS Sustain. Chem. Eng. 10, 1287–1297. https://doi.org/10.1021/acssuschemeng.1c07424.