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A review on assessment of ionic liquids in extraction of lithium, nickel, and cobalt *vis-à-vis* conventional methods

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This review discusses the extraction of critical metals (Li, Co, and Ni) using ionic liquids. Here, ionic liquids act as solvents for the separation and extraction of metals. In addition to extraction, they can be used as a lixiviant to leach out metals from spent lithium-ion batteries. Leaching and extraction of metals from the leachate can be performed using a single ionic liquid solvent. Lithium, cobalt, and nickel have been discussed in detail as per their reactivity towards an ionic liquid based on the extraction efficiency and reusability of the ionic liquid. Recycling and reusability of ionic liquids are crucial parameters to be considered while using them as solvents for extracting metals. Moreover, all the other methods such as solvent extraction, ion exchange, ionic liquids, and DES-based separation of metals are compared with respect to their extraction efficiency, cost-effectiveness, and reusability.

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Introduction

Ionic liquids are popularly known as “designer solvents” owing to their proficiency in tuning and modifying thermo-physical properties.¹ In recent times, ionic liquids are regarded as a new category of solvents having the ability to flow, consisting of an organic cation and inorganic or organic anions. Moreover, they have remarkable physicochemical properties, including inflammability, thermal stability, increased conductivity, non-volatility, and recyclability; hence, they are also referred to as “green solvents”. The term “green solvents” also refer to their characteristics of decreasing the possibility of polluting the atmosphere and minimizing the quantity of catalysts used for a reaction.^{2,3} Ionic liquids can be used in several fields such as electrolytes in batteries, metal plating, solar panels: solvents in reactions, extraction procedures in hydrometallurgy, coating materials and lubricants. This review will focus on ionic liquids and their applications in hydrometallurgy.

In recent years, metals have become an integral part of our daily lives; they have shaped the course of history through various applications. Consequently, the demand for ferrous and non-ferrous metals, rare earth metals, critical metals, and precious metals is increasing day by day.^{4,5} Critical metals play an essential role in energy industries, especially in battery storage, but are scarce in recent times. An economically significant metal at high supply risk is considered a critical metal. Natural resources of essential metals cannot be renewed and are exhausting owing to their high demand.^{6,7} Lithium,

cobalt, and nickel, among other metals, are distinguished as critical metals, and since the world is going further with substantial and material-based systems rather than fuel-based systems, the demand for these metals is rising.⁸ For the extraction of critical metals, the feasible alternative to hard rocks is saline water mining as saline water is loaded with dissolved metals.⁹

Critical metals such as Li, Co, Ni, and Mn are also used for the production of lithium-ion batteries and can thus be extracted from spent Li-ion batteries. The anode and cathode are the two main components of Li-ion batteries; the anode comprises graphite, whereas the cathode is layered with the lithium metal oxides LiCoO₂ (LCO), LiMn₂O₄ (LMO), LiFePO₄ (LFP) and LiNiMnCo₂ (NMC).^{10–13} Extracting metals from spent LIBs is a recycling process that is necessary not only for extracting critical metals but also for environmental reasons, as some metals and electrolytes present in the battery can harm the environment if released without any recycling treatment. Recycling can be done using pyrometallurgical or hydrometallurgical routes. Hydrometallurgy includes discharging, the dismantling of LIBs, and the separation of different components of the battery. After separating all the components, dissolution or leaching is done to recover critical metals. Hydrometallurgy includes less thermal treatment when compared to pyrometallurgy and helps to obtain pure metals.¹⁴ The dissolution of metals is followed by solvent extraction, precipitation, and other methods to get pure metal salts. Solvent extraction has been used recently to recover valuable metals using organic solvents, and metal recovery usually depends on the loading capacity of the organic solvent.¹⁵

However, metal separation can be performed using ionic liquids instead of organic solvents. This review discusses ionic

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liquids, their properties, synthesis, and advantages over organic solvents for extracting and separating Li, Ni and Co from the processed and synthetic solutions, primarily on batteries.

Ionic liquids

Structure and examples

An ionic liquid is a class of salt that behaves as a liquid at a low temperature (room temperature). NaCl, a salt, is made up of Na^+ and Cl^- ions that neutralize each other to form a stable compound. Similarly, ionic liquids are also made up of cations and anions.

Traditionally, at room temperature, salts do not exist in liquid state and are termed molten salts above 800 °C.

Table salts such as NaCl have small-sized cations and anions that are arranged in an orderly manner and packed closely, resulting in a crystalline structure. These ions have strong interactions with each other, forming a well-defined lattice structure. Displacing ions from their position requires high energy due to the tightly packed arrangement of ions in these salt crystals.

However, in ionic liquids, the cation size is more significant, and the anion size has variability. These irregularities in the sizes of cations and anions make it challenging to create a lattice structure, leading to their liquid state. The structures of molten salt and ionic liquid are shown in Fig. 1.

Fig. 2 illustrates that the cations used to synthesize ionic liquids are mostly heterocyclic rings with one or more N-atoms and can be paired up with the anions shown in the same figure.

History of ionic liquids

In 1914, Paul Walden pioneered the idea of ionic liquids by reporting the physical properties of ethyl ammonium nitrate ($[\text{EtNH}_3][\text{NO}_3]$) at a melting point of 13–14 °C.¹⁶ Ethylamine was made to react with concentrated nitric acid to give the neutralized product, ethyl ammonium nitrate, using distillation to remove water, as shown in Fig. 3.^{17–19} In the 1950s, a concept of halide salt ionic liquid with a mixture of aluminum chloride and ethyl pyridinium bromide (EtPyBr) was found in a mole ratio of 2/1 to form a low-temperature molten salt.²⁰ These molten salts were of high interest because of their negligible vapor pressure, high ionic conductivities, and wide temperature ranges. In some cases, these salts also behave as Lewis acid catalysts. Earlier, the findings focused on the imidazolium or pyridinium cations and their mixture with chloroaluminate anions.²¹ Chloroaluminate ions control the chemistry of these

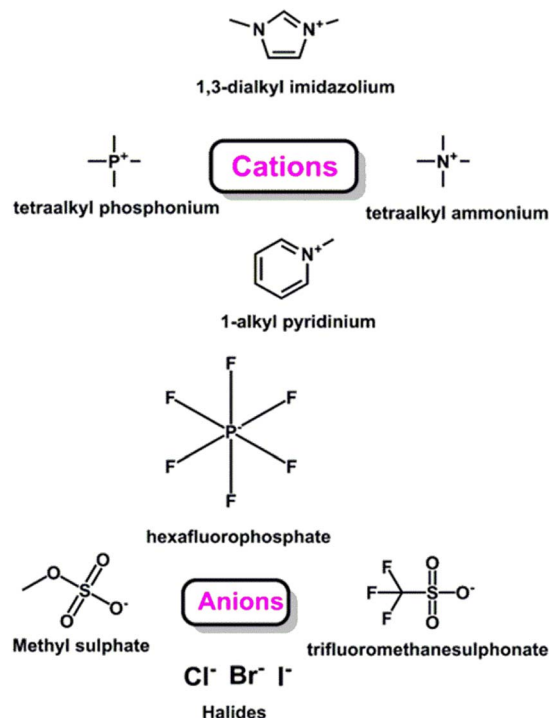


Fig. 2 Some commonly used cations and anions in ionic liquids.

ionic liquids with the change in their proportions. Changing the proportions can change the melt composition. These ionic liquids have been used for the deposition of metals and aluminum batteries, and they have helped to conduct several reactions as a medium.^{22,23} One example of chloroaluminate ionic liquid is given in Fig. 4, where *N*-ethyl pyridinium bromide is also a constituent of the ionic liquid with aluminum chloride.

However, the two ionic liquids discussed above demand complete, sophisticated handling as they are not water-stable and need an entire water-free state. Therefore, a new generation of ionic liquids came into the picture in 1992, as reported by Wilkes and Zaworotko, to overcome the handling issues. These ILs have air- and water-stable imidazolium cations with alkyl substituents and are inadequately coordinated with anions such as tetrafluoroborate $[\text{BF}_4]$ and hexafluorophosphate $[\text{PF}_6]$. These ions have been changed recently because of their restricted stability by a new set of stable anions such as tris(pentafluoroethyl)trifluorophosphate, triflate $[\text{CF}_3\text{SO}_3]$ or $[\text{OTf}]$, and particularly bis(trifluoromethanesulfonyl)amide $[(\text{CF}_3\text{SO}_2)_2\text{N}]$ or $[\text{NTf}_2]$, along with the halide-free anions methylsulfate $[\text{CSO}_4]$, acetate $[\text{C}_1\text{COO}]$, thiocyanate $[\text{SCN}]$, and others.^{24,25}

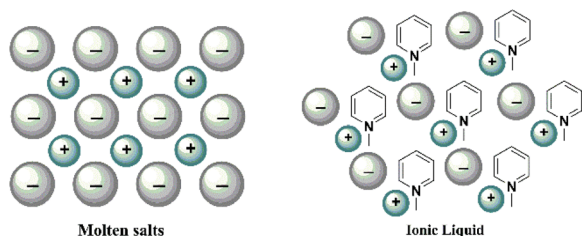


Fig. 1 Ionic structures of normal molten salts and Ionic liquids.

Properties of ionic liquids

Ionic liquids comprise an asymmetric organic cation and an anion, which can be organic or inorganic.²⁶ Various types of

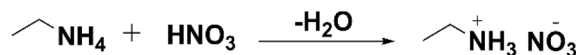


Fig. 3 Neutralization of ethyl amine.



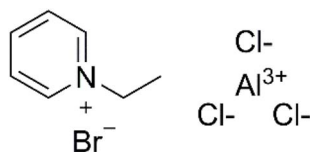


Fig. 4 Example of chloro-aluminate ionic liquids.

bonds link together these cations-anions. They relate to many properties including all the physical and chemical properties, making the vapor pressure almost negligible. These salts possess large ions due to the delocalization of charges, lowering the force of attraction between the ions and decreasing the melting temperature of ionic liquids.^{27,28} Its low vapor pressure does not allow it to evaporate at room temperature.²³ This is one of the properties of ionic liquids, which decreases the exposure risk factor compared to other volatile solvents. Moreover, this non-volatile property makes it less flammable under normal conditions.^{29,30} Nowadays, ionic liquids are also used in industries not just for their low vapor pressure but also for their air and water stability.³¹

ILs are environmentally friendly for many reasons. It is non-volatile, inflammable, mixes with other organic solvents or water, and has better solubility of organic and inorganic materials. Conventionally used volatile and toxic solvents can be replaced by ionic liquids. Moreover, ILs have high ionic conductivity, potential windows, and thermal stability.^{23,32}

All these properties of ionic liquids can be tuned or changed by a proper choice of anions and cations, which can also give us an enormous number of combinations. Thus, the properties of ILs are tunable and primarily dependent on the structure of cations and anions and can be called 'designer solvents'. Properties such as hydrophilicity-lipophilicity, viscosity, surface tension, and density depend on the length of the alkyl chain attached to the cation and its symmetry, including the type of anion.²⁷

These properties of ionic liquids can be studied with the help of a cation that has been used most recently. Methylimidazolium-based ionic liquids are considered the most favorable cationic species for this discussion. They are stable in air and water, hold a wide range of liquids, obviously stay liquid at room temperature, and have more significant viscosity and density. Moreover, *N*-methylimidazole is commercially available making its alkylation easier than any other cations and becomes one of the most popular cations used in the synthesis of ionic liquids.³³ It is also seen that adding alkyl groups or increasing the number of carbon atoms in the alkyl chain can change the properties of ionic liquids.^{34,35} The substituents linked to the imidazole molecule and the type of counter anion present decide the solubility of ionic liquids in water.²⁴

Synthesis of ionic liquids

Ionic liquids can be synthesized in two steps.

- (1) Formation of the desired action
- (2) Anion exchange

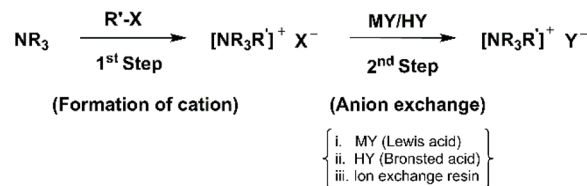


Fig. 5 General representation of ionic liquid synthesis using both steps.

Initially, the desired cation can be synthesized by the protonation of amine, alkylation, or quaternization of amines. In addition, the anions were exchanged by changing the halide through anion metathesis or using a Lewis acid to form a Lewis-acid-based ionic liquid.^{16,23}

A general representation of the synthesis of ionic liquids including both the steps is shown in Fig. 5.²³ Alkyl halide was used to form the desired cation from a N-based compound and anion was exchanged as the second step using any Lewis/Bronsted acids or *via* ion exchange resins.^{23,29}

One of the elementary ways to prepare imidazolium-based ionic liquids is the reaction of methylated imidazole molecules with alkyl halide. Eventually, desired room-temperature ionic liquids were achieved after a metathesis of halide salt.²⁴

In Fig. 6, several ionic liquids were synthesized, following the mentioned steps. To synthesize the cation, methylimidazole was taken with an alkyl halide and kept in reflux to get 1-alkyl-3-methylimidazolium chloride. The halide ion product was treated with several other acids and salt to change the anion.^{31,36}

Usually, alkylation, anion metathesis, acid-base reactions, and heterocyclic compound reactions were used to synthesize ionic liquids.

The amination of ionic liquids could be reached by the quaternization of ammonia, its derivatives and phosphine derivatives. Hydrophilic and hydrophobic products were formed during metathesis of an anion through an intermediate. The intermediate anion was then substituted by any other anion, giving the hydrophobic or hydrophilic ionic liquid products.

Application of ionic liquids in metal recovery *via* hydrometallurgy

Leaching

Depleted Li-ion batteries can be recycled using hydrometallurgy, including leaching, solvent extraction, and precipitation.

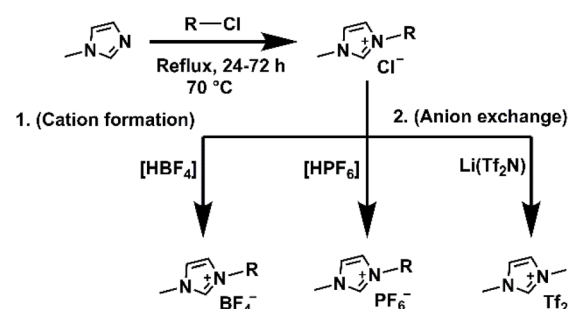


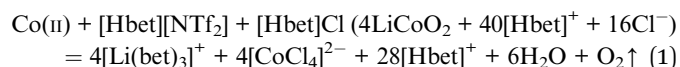
Fig. 6 Synthesis of ionic liquids using methylimidazole.



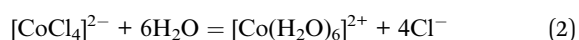
Traditionally, inorganic acids, organic acids, or oxidants were used to leach metals from depleted lithium-ion batteries (LCO, LMO, NMC, LFP, *etc.*), producing a large quantity of acidic waste. The separation of metals from the leachate was done using the solvent extraction method. Solvent extraction includes the use of organic solvents such as Cyanex, D2EHPA, and TBP, which again creates a problem as these solvents are highly volatile, and toxic for the environment, and multiple extractants are required to recover metals selectively.^{37,38} Therefore, to overcome these disadvantages, ionometallurgy is introduced, where ionic liquids play a major role as solvents, and their ability to coordinate strongly is highly important to dissociate the reactive metals. Leaching *via* ionic liquids may show a higher metal selectivity than that of inorganic or organic acids. Generally, Brønsted acidic ionic liquids are used for leaching, as this class of ionic liquids can donate H⁺ protons to the solution. The donated H⁺ in the solution reacts with metal oxides and can lead to the formation of water, showing the dissolution capability of metal oxides.^{39,40}

Lithium can be recovered from brines *via* solvent extraction, but to recover lithium as well as other metals such as Co and Ni from depleted lithium-ion batteries, leaching is a necessary step for the dissolution of metals. The dissolution of metals can be explained with the help of an example of extraction of cobalt from LCO batteries using ionic liquids. Approximately, 25–30 wt% of a portable lithium-ion battery consists of cobalt as a part of the cathode material in the LiCoO₂ (LCO) battery.^{41–43}

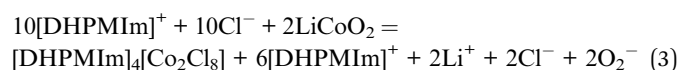
Ionic liquid [Hbet][NTf₂] was applied for the leaching of LCO but cobalt oxides do not have high solubility in pure [Hbet][NTf₂]. The addition of chloride increased the solubilities of cobalt oxides and improved the rate of dissolution. IL cation [Hbet]⁺ donated acidic protons to hydrate the oxygen atoms at the oxide surface, as shown in eqn (1) and the unused betaine coordinated the cobalt ions. This resulted in the diffusion of dissolved species into the solution; also, betaine got displaced by chloride as Co showed great affinity towards chloride in ligand exchange reactions. Cobalt(III) got reduced, leading to the formation of Cl₃[−] enabling the oxidative leaching of Co parallelly.^{44,45}



It took 2–3 hours to complete the dissolution of LCO, at 150 °C in a closed flask. The molar ratio of leaching reactants LCO/[Hbet][NTf₂]/[Hbet]Cl was 1/10/2. After the dissolution, [CoCl₄]^{2−} was formed as one of the products. Direct electrodeposition occurred to change [CoCl₄]^{2−} into [Co(H₂O)₆]²⁺ in the presence of water, as represented in eqn (2). [Co(H₂O)₆]²⁺ migrates to the cathode, displacing the chloride ions.^{44,45} The temperature of leaching does not exceed 150 °C, and this low temperature is advantageous to the IL reusability.⁴⁶ The reaction environment created by ionic liquids comprising only ions establishes exceptional dissolution properties for metals.^{44,45,47,48}



One more example of an ionic liquid as a lixiviant for the leaching of depleted lithium-ion batteries is an imidazolium-based ionic liquid, imidazolium glycol [1-(2,3-dihydroxypropyl)-3-methylimidazolium chloride]. To recover metals from spent LCO batteries, imidazolium glycol behaves as a non-decomposable leaching agent. Under heating conditions, imidazolium glycol can generate the oxygen anion redox of transition metal-ions as illustrated in eqn (3) and shows a high leaching efficiency of up to 100% Li and >99% Co. Imidazolium glycol can be easily recycled and reused as it does not go through redox decomposition. This procedure for the extraction of metals *via* imidazolium glycol is environmentally suitable and achievable, demonstrating significant and capable applications in LIB recycling.⁴⁹



Imidazolium glycol was recovered and reused after every cycle of leaching, as it does not decompose during the process without producing any toxic gases.³⁷

Solvent extraction

Solvent extraction refers to the diffusion of a solute between two non-miscible liquids, when in contact, distributing the solute into two phases. It is the most favored technique used for metal recovery due to its simplicity, speed, and wide range.²⁷ As metal ions have a wide range of applications in the industrial area of metallurgy, electronics, catalysis, synthetic chemicals, *etc.*, metal ion extraction has always driven ample recognition from researchers.⁵⁰ It has stimulated the rapid growth of industries and delivered a significant economic profit, yet also raised environmental problems. Metal extraction is applied for three primary business cases: (a) extraction of metal ions from natural resources, (b) recycling the materials from secondary resources, and (c) wastewater treatment.⁵¹

Solvent extraction employs water-immiscible organic solvents that can be toxic, flammable, or volatile. Given the rising costs for their eventual disposal and the growing awareness of the environmental impact associated with their use, replacing these solvents with less harmful alternatives is desirable.

Ionic liquid used as a solvent

Ionic liquids show various properties that make them sound like solvents including a wide liquid range, thermal stability, ability to dissolve an extensive range of solutes, absence of vapor pressure, and many more factors.²⁷ Moreover, it can be referred to as an environment-friendly solvent and less toxic than traditionally used organic solvents.²⁸ Nowadays, an essential aspect of research is its effect on the environment and whether it is green or not. Keeping these conditions in mind, the ionic liquid was designed to be safe, and its eco-friendly separation procedures have created a vital role in clean manufacturing processes and the cleanup of areas affected by manufacturing technology from an earlier generation.



Lately, significant attraction has been paid to the room-temperature ionic liquids as solvents for several reactions such as alkylation, acylation, and polymerization. This perspective allows the controlled production of wanted products from reactants with the least amount of waste generation *via* side reactions, as ionic liquids tend to repress the solvation.⁵²

The hydrophobic characteristics of some ILs allow the extraction of several heavy metals such as zinc, mercury, lead, cadmium, iron, chromium, copper, and nickel, from their aqueous solutions. Despite their hydrophobic character, ILs offer high solubility for salts and can be used to extract salts. The solubility of ILs in water strongly depends on the type of cations and anions. ILs possessing acid anions can also be used for the leaching of metals from ores.²⁷

The extraction of metals from brine solutions (lithium) or from spent lithium-ion batteries (lithium, cobalt, nickel, *etc.*) can be achieved using a pathway shown in Fig. 7. Leachates of lithium-ion batteries (cathode material) or brine solutions are taken as aqueous phases where the addition of ionic liquids is carried out to separate metals. Metals usually get transferred to an organic phase reacting with the anionic part of the ionic liquid and the ionic liquid cation gets transferred to the aqueous raffinate phase. After separation, the organic phase is stripped using an acid/base/salt to obtain an ionic liquid-free aqueous metal solution. Ionic liquids can be regenerated again for further separation and extraction of metals.

Extraction of metals using ionic liquids

Lithium extraction. Lithium is one of the most valuable and significant energy materials, also called an “energy-critical element,” and is broadly used in glass and ceramics as a raw material in rechargeable batteries,⁵³ metallurgical industries, and chemical industries. Moreover, the extraordinary evolution of electric vehicles is likely to increase the requirement for lithium in lithium-ion batteries.^{54,55} The possibility of less lithium availability and its commercial necessity makes it a critical metal.⁵⁶

Lithium exists in two states: mineral and liquid. The absence of adequate availability of lithium as a mineral has directed the

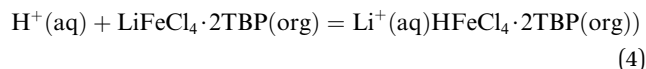
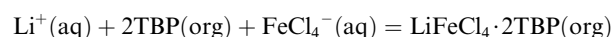
industries towards its other forms of resources. The other form is liquid, which contains 85% more retrievable lithium in the world.^{56,57}

One of the primary lithium resources is enclosed in the brines of lake sediments. Primarily, 60–65% of the lithium in total is stored in brines.^{53,55,58} Apart from brines, the use of lithium in lithium-ion batteries increased from 23% to 74% in the last few years, which exceeded the consumption of glass and ceramics.⁵³

Thus, the necessity of lithium is increasing for several applications, and there is a call for its treatment/extraction from all practical resources. The extraction procedure of lithium from minerals/ores consists of roasting and leaching, while its recovery from brines follows evaporation, precipitation, adsorption, and ion exchange. However, lithium extraction can be done from Li-ion batteries using hydrometallurgical methods, including leaching, precipitation, and ion exchange or solvent extraction.⁵⁴ Nowadays, solvent extraction is thought to be the most effective method for extracting lithium from its aqueous solutions (brine solution or Li-ion batteries) as it is eco-friendly, highly selective, easily accessible, and efficient.^{57–60}

Solvent extraction of lithium from its brine or aqueous solution was usually performed using the extraction system of tributyl phosphate (TBP)/FeCl₃ and kerosene. TBP is an organophosphorus extractant, highly popular for the traditional extraction procedure where kerosene is used as a diluent. Ferric chloride (FeCl₃) solution works as a co-extracting agent.^{57–59} Various analyses from the literature show that the TBP–Kerosene–FeCl₃ system satisfies the separation of lithium from its solution as explained in eqn (4).⁵⁷

Acidic conditions were needed for this system to work and to prevent the hydrolysis of the remaining Fe⁺³ ions in the aqueous solution, producing vast quantities of acidic wastage at the time of extraction. Moreover, the stripping process after solvent extraction required a high concentration of acids, which can harm the environment. Moreover, these highly acidic parameters can damage the equipment by corrosion.⁵³ Therefore, improvement in the extraction system is necessary with an alternative of green extraction methods, which can address and control the negative impact of traditionally used solvents on the environment.⁶¹



A better approach to decrease the usage of organic solvents is needed, and this can be done by researching a different system of extraction that can remove these unwanted characteristics. The ionic liquid is chosen as an alternative to organic solvents. ILs fulfill the desired requirements of the solvents for lithium extraction, and researchers nowadays are interested in ionic liquids because of their tunable properties such as hydrophilicity/hydrophobicity, low-flammability, non-volatility,

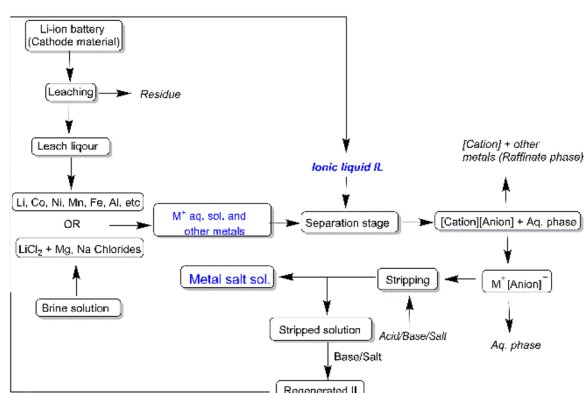


Fig. 7 General representation of metal (Li, Co, Ni, *etc.*) extraction *via* ionic liquids.





Table 1 Li extraction via ionic liquids

| Li (conc.) | Extraction (IL) | | Stripping of loaded IL layer | | | | | Ref. |
|-------------------------------------|--|--|------------------------------|---|---|----------------------|---------------------|----------|
| | ILs (conc.) | Conditions (T, t, pH) | IL/aqueous | Extraction% | Stripping agent | Stripping conditions | Stripping recovery% | |
| (0.5 g L ⁻¹) | [P ₄₄₄₄][BTMPP] (0.85 mol L ⁻¹) in 5 mL toluene | 30 min, 293 K, pH = 6.28 | 2 : 1 | 90 | HCl (0.5 mol L ⁻¹) | 293 K | 94.07 | 58 |
| (0.291 mol L ⁻¹) | [OHEmim][NTf ₂] (0.383 mol L ⁻¹) in TBP (2.197 mol L ⁻¹) | 30 min, 278.15 K, pH < 2 | 2 : 1 | 95.01 | HCl (1.0 mol L ⁻¹) | 278.15 K | 92.86 | 63 |
| 200 mg L ⁻¹ (1 : 1) | Omim-TTA (0.1 M) in Omim-TFSI (0.1 M) | pH ≈ 4.3, 120 min, EDTA : Co (1.1 : 1) | 1 : 3 | 82.4 | HCl | — | >90 | 62 |
| 0.5 g L ⁻¹ | [N ₄₄₄₄][DEHP] (1.06 mol L ⁻¹) in methylbenzene | 293 K, 30 min | 1 : 1 | 93 | HCl (0.5 mol L ⁻¹) | 293 K | >90 | Possible |
| 0.10 mol L ⁻¹ LiCl | [N ₁₈₈₈][P ₅₀₇] 0.025 mol L ⁻¹ + TBP (60%) + FeCl ₃ | 298 K, 30 min | 1 : 1 | 63.84 | HCl (1.5 mol L ⁻¹) | 298 K, 20 min | 90 | 64 |
| 0.5 g L ⁻¹ | [N ₄₄₄₄][EHPMEH] 0.6 mol L ⁻¹ In 10 mL methylbenzene | 298 K, 2 h | 2 : 1 | >90 | HCl (0.5 mol L ⁻¹) | 298 K | 94.2 | 65 |
| 2.088 g L ⁻¹ | [C ₄ mim][PF ₆] (TBP/IL of 9/1) (v/v) | 10 min, pH = 5.58 | 2 : 1 | 90.93 | HCl (0.1 M) | 80 °C | 96.28 | 66 |
| 3.85 g L ⁻¹ | (Carboxymethyl trimethyl bis(trifluoromethyl) sulfonamide) [(CH ₃) ₃ NCH ₂ COOH] + TBP | 20 min, 298.15 K, pH = 3 | 2 : 1 | 96.80 (after 5 stages) | H ₂ SO ₄ (1 M) | 298.15 K | 99.6 | 67 |
| LiNTf ₂ (1 M) | [BMim][NTf ₂] (0.5 M), 0.2 M crown ether, DCM. | 1 h, 293.15 K | 1 : 1 | 26.3 | — | — | — | 68 |
| LiCl (0.33 M) | [C ₄ mim][PF ₆] + TBP + kerosene (1 : 8 : 1) v/v | 298.15 K, pH = 5, 10 min | 2 : 1 | 74.14 | HCl (1 M) | 298.15 K | 86.36 | 69 |
| LiCl (0.3 M) | [C ₄ MIM][Cl] (0.8 M) + NaOH (1.6 M) | 298 K, 20 min | 3 : 1 | 52 | NaCl (5 M) | — | 100 (6 times) | Possible |
| LiCl (1 M) ⁶ Li | [EMim][NTf ₂] + DB ₁₅ C ₅ (0.2 M) + anisole | 60 min | 1 : 1 | 9.022 (20 stages) | HCl (1 M) | 1 h | 100 (3 times) | Possible |
| 0.766 g L ⁻¹ (brine sol) | [OHEMIM][Tf ₂ N] (0.09 mol L ⁻¹) + TOP | 30 min, pH = 7 | 3 : 1 | 83.16 in 1 st stage (99.09% in 5 stages) | NaCl (0.5 M), LiCl (0.1 M) | 1 : 1 | 99.90 | 6 |
| LiCl (250 mg L ⁻¹) | [Aliquat][DEHPA] (1 M) diluted in dodecane | pH = 5, 30 min | 1 : 1 | 83 | HCl (1 M) | 2 : 1 | 99.1 ± 2.2 | Possible |
| 1.5 g L ⁻¹ Li | 15% [OHEMIM][NTf ₂] + 85% Cyanex923 | pH = 10.68, temp. = 298 K, 20 min | 2 : 1 | 99 (2 stages) | HCl (0.5 M) | — | 80 | 74 |
| 0.16 mol L ⁻¹ | [Hmim][BTA] (0.5 M) in 2-octane | pH = 8.87, 6 min | 1 : 1 | 96 | LiCl (0.25 M), HCl (1 : 1 M) | 1 : 1 | 95.43 | >10 |
| 0.35 g L ⁻¹ | [Bmim]Bph ₄ + TBP + CH ₂ BrCl | 10 min, temp. = 298 K | 1 : 1 | 99.47 (4 stages) | NaCl (2.56 M), LiCl (0.10 M), Na ₂ CO ₃ (2 M) | 1 : 1 | 100 | >10 |

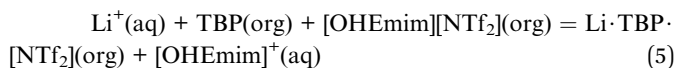
Table 1 (Contd.)

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|---|--|--|------------------------------|-------------|--|----------------------|---------------------|
| | ILs (conc.) | Conditions (T, t, pH) | IL/aqueous | Extraction% | Stripping agent | Stripping conditions | Stripping recovery% |
| 0.52 g L ⁻¹ Li in HCl | Cyphos IL-101 | Temp. = 60 °C, pH = 0–0.3, 1 : 1 10 min | 1 : 1 | 86.2 | HCl (2 M) | | 74.2 |
| [Li ₂ CO ₃ + NaCl + H ₂ O] Li (0.5 g L ⁻¹) | [A ₃₃₆]TTA (0.5 M) + TRPO | pH = 13.11, temp. = 298 K | 1 : 1.5 | 86.64 | HCl (0.5 M) | | 97.16 |
| 0.29 M | [OHEMIM][NTf ₂] (15% vol) in TBP | pH = 6, temp. = 303 K, 15 min | 2 : 1 | 94.2 | LiCl (0.6 M) + NaCl (1.8 M), HCl (1 M) | 1 : 1 | 98 |
| | | | | | | | 7 |
| | | | | | | | 77 |
| | | | | | | | 78 |
| | | | | | | | 79 |

high selectivity, high thermal stability, and greater efficiency towards solvent extraction.^{61,62}

Ionic liquids used in lithium extraction with their concentrations, extraction efficiency, conditions, stripping parameters, and reusability are shown in Table 1.

An example of lithium extraction with the chemical equation and structure is shown in eqn (5). Ionic liquid, [OHEMim][NTf₂] (1-hydroxyethyl-3-methyl imidazolium bis(tri-fluoromethylsulfonyl)imide) (Fig. 8) and TBP as diluents were employed to extract lithium from its aqueous brine solution containing Mg, Na, *etc.* Simply IL or TBP couldn't extract lithium effectively, but IL and TBP together as an organic media created a synergistic effect and extracted lithium efficiently.⁶⁵



The anion of IL (NTf₂) moved closer to the hydrated lithium in the aqueous solution from its organic phase due to the coulombic force of attraction and hydrogen bonding interaction initiating the extraction.

Since the structure of lithium in the aqueous solution got deformed, it facilitated the interaction of TBP with the lithium ion in the aqueous solution. Because of this interaction of TBP with lithium, the aqueous phase of lithium changed to the organic phase, and the IL cation [OHEMim] was left in the aqueous solution with other metals as the raffinate.⁶⁵

From Table 1, various similarities between extraction systems can be drawn, as the temperature used for extracting lithium was around 298 K in most of the extraction systems. The pH range is usually between 2 and 6, and the stirring time is 20–60 min. In addition to extraction, HCl was often used for the stripping process, and that too in a shallow concentration range of 0.5–1 M with satisfactory extraction results. In ionic liquids, when compared to organic solvent extraction systems, TBP was used in both approaches. Still, when TBP was used with an ionic liquid, its presence in an ionic liquid supported the extraction of lithium ions more than usual. Moreover, ionic liquids with nitrogen and phosphorus atoms attached to them gave better extraction results than ionic liquids containing only carbon due to the electronegative properties of N and P, which help in the comfortable distribution of electrons. The positive charge will mostly disperse on carbon atoms, and the positive charge dispersion increases the ionic liquid's extraction ability. Moreover, increasing or decreasing the hydrophobicity of ionic liquids can change the extraction efficiency. Hydrophobicity can be improved by increasing the alkyl chain length of the cation. However, further increasing the alkyl chain can also create steric hindrance and hamper the extraction.⁶⁸

For instance, 1-butyl-3-methyl imidazolium [BMIM]⁺, as shown in Fig. 9, is an imidazole-based cation containing two N-atoms and two alkyl groups bonded to the N-atoms. Here, the N-atoms can increase the dispersion of positive charge on the imidazolium cation and weaken the interaction between the cation and anion, allowing for an easy extraction route for lithium. Moreover, the butyl and methyl chains in the cation



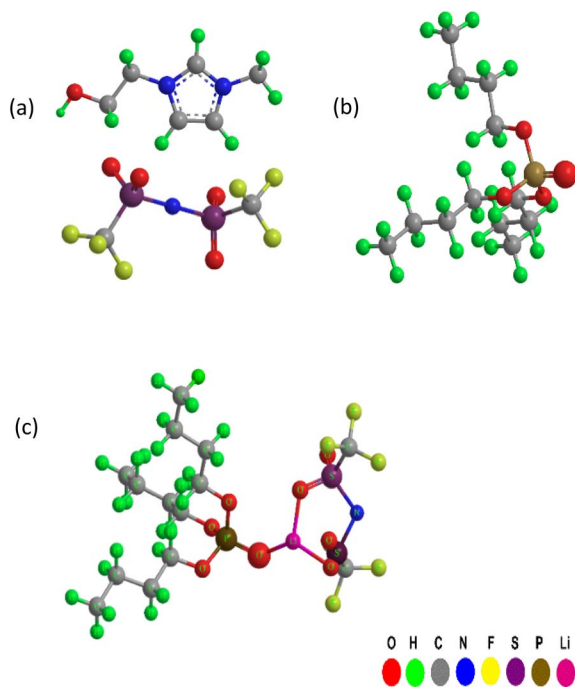


Fig. 8 Structure of (a) [OHEMim][NTf₂], (b) TBP and (c) Li⁺·TBP[NTf₂]; Li–O bond length = 1.87 Å.

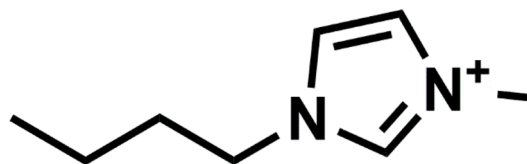


Fig. 9 Structure of [BMIM]⁺.

increase the hydrophobic properties, which is beneficial for lithium extraction. However, if these chains are increased in length to improve hydrophobicity, it can obstruct the extraction procedure by multiplying the steric crowd and creating hindrance.⁶⁸

Cobalt extraction. Cobalt is one of the most essential metals in the earth's crust and is widely used in industries,⁸¹ batteries, alloys, and ceramics. The highest use of cobalt is in the Li-ion batteries, at about 80%, along with the alloy materials.⁸⁰ Moreover, it is an evident element required as a nutrient for animals, and the pasture's cobalt deficit delayed their growth.⁸² Due to the diverse range of applications of cobalt, including all the above-mentioned requirements, its demand is increasing daily and needs to be extracted from its secondary sources.^{80,81} Cobalt can be manufactured from its primary sources by processing Co–Cu ore sediments as a product and Ni-mining as a byproduct.⁸³

Extraction from secondary sources can be possible using solvent extraction as a method, as it is a successful way of recovering Co, Ni, and many other metals.⁸³ Previously, CYANEX 301, CYANEX 302, CYANEX 921 and CYANEX 923 have been

extensively used as a solvent for Co extraction from its acetate and sulphate solutions.^{84–86} Cyanex 272 and D2HEPA are dissolved in cobalt from kerosene extract in its aqueous solution and separate from nickel.⁸⁷ Since Co(II) oxidizes to Co(III) in the presence of air, it becomes inert, and its stripping becomes difficult with the organic solvent taken for solvent extraction. Moreover, the extraction efficiency could be more satisfying when using these organic solvents.⁸⁸

Therefore, ionic liquids can be used as alternatives to organic solvents to extract cobalt from their aqueous solutions. Ionic liquids used in solvent extraction for Co extraction, along with their concentrations, extraction efficiency, conditions, stripping parameters, and reusability, are shown in Table 2.

Table 2 shows the application of different ionic liquids for solvent extraction of cobalt from its aqueous solution. These ionic liquids can be grouped into several categories according to the elements used in the cation formation. For example, ionic liquids [P₈₈₈₈][Cl], [P₆₆₆₁₄][SCN], and [P₄₄₄₁₄][Cl], all contain phosphorus in their cationic fractions along with long alkyl chains such as butyl, hexyl, and octyl. Therefore, these three can be categorized as a group of ionic liquids and can be compared with the other groups. Similarly, Cyphos 101 and [C101][Cl] (tri-hexyltetradecyl phosphonium chloride) can also be grouped in the category of ionic liquids containing phosphorus. For cobalt extraction, many ionic liquids containing phosphorus are assumed to give 95–10% extraction recovery of cobalt. All these ionic liquids work under different conditions with different temperatures, stirring times, and pH. The ratio of ionic liquids to the aqueous solution of cobalt was 1/1 in most cases and 2/1 in very few. They are now talking about the N-containing ionic liquids, which are also used very frequently for cobalt extraction, like [A₃₃₆][CA-12], R₄N–SCN, and [THN][Dca] with an extraction efficiency of 90–100%. The temperature range for most of the extraction systems was 298–308 K, and the pH varied from 4 to 8. Lastly, the imidazolium-based ionic liquids used for cobalt extraction were [Hmim][PF₆], [Hmim][BF₄], and [BBIM]Br, showing an extraction efficiency from 98% to 100%. In most extraction systems, water is used for stripping, providing 100% stripping efficiency. Most importantly, these ionic liquids can be regenerated and reused after the extraction for different cycles.

Nickel extraction. Nickel can be extracted primarily from nickel laterite ores and sulfide ores.^{104,105} Recently, secondary nickel resources have gained much more consideration because of the rapid reduction of primary resources. Traditionally, nickel is extracted using organophosphorus acids, chelating oximes, carboxylic acids, and amines with high molecular weights. The most widely used extractants are high-molecular-weight amines and chelating oximes, as these are commercially acceptable. Due to their high emulsion-forming tendency, amines and D2HEPA failed as extractants. In addition to the emulsifying property, D2HEPA and HEHEHP strictly depend on the pH for separation, as the carboxylic acids present in them create an inadequate environment for phase separation. The high solubility of carboxylic acids restricts their application as an extractant.¹⁰⁶ At very low pH, nickel can be extracted by Cyanex 301 and Cyanex 302, but these extraction systems are





Table 2 Cobalt extraction via ionic liquids

| Co (conc.) | Extraction (IL) | | Stripping of loaded IL layer | | | | | Ref |
|--|---|--|------------------------------|-------------|--|----------------------|----------------------|-----|
| | ILs (conc.) | Conditions (T, t, pH) | IL/A | Extraction% | Stripping agent | Stripping conditions | Stripping recovery% | |
| 75 mg L ⁻¹ | [A ₃₃₆][CA-12] | 298 K, 1 h, 4.3 pH | 1 : 1 | 96 | H ₂ SO ₄ (8 × 10 ⁻⁴ mol L ⁻¹) | 298 K | 99 | 89 |
| 0.43 g (2 M H ₂ SO ₄) | R ₄ N-SCN (0.36 mol L ⁻¹ in kerosene) | pH – 5.6, 20 min, 308 K | 1 : 1 | 91.6 | Water (70 °C) H ₂ SO ₄ (2 M, 25 °C) HCl (3 M, 25 °C) | | 99.9 99.9 99.9 | 90 |
| 100 mg L ⁻¹ | 20 mL [P ₆₆₆₁₄][SCN] (0.1 M) in toluene | 2 h | 1 : 1 mole ratio (2.6 : 1) | 95 | EDTA (0.2 M) | (2–3) h | 100 | 91 |
| 0.05 mol L ⁻¹ | [THN][Dca] | 298 K, 12 h | 1 : 1 | 98.3 | Na ₂ SO ₄ (1 mol L ⁻¹) | — | 93 | 92 |
| 1 g L ⁻¹ | [P ₈₈₈₈][Cl] | 298 K, 10 min | 1 : 2 | 98.3 | H ₂ O | 298 K, 20 min | 100 | 93 |
| (1 M H ₂ SO ₄ , 5 M HCl) | [C101][Cl] | 75 °C, 45 min | 1 : 1 | >85 | HCl (0.1 M) | 30 min, 1 : 1 | >99 | 94 |
| (NH ₄) ₂ SO ₄ (3 M) | Cyphos IL-101 | 10 min, 60 °C | 1 : 1 | 90.5 | HCl (2 M) | | 87.4 | 77 |
| 5.12 g L ⁻¹ in HCl | P ₈₈₈₁₂ R ₂ POO (0.01–0.1 M) in toluene | 3 h | 1 : 2 | 99 | H ₂ O | | 99.8 | 95 |
| 100 mg L ⁻¹ in 5 M HCl | [P _{6,6,6,14}][BTMPP] (5 mmol) or [P _{6,6,6,14}][SCN] (5 mmol) | Temp. – 303 K, 6 h | 1 : 1 | 99 | H ₂ O | | | 96 |
| 5 mg L ⁻¹ (CoCl ₂ •6H ₂ O) | [HMIM][BF ₄] (0.7 g) and NaCl (0.5 g) | 5 min | | ~100 | H ₂ O or NaPF ₆ (15 mL of 0.02 M) | 20 °C | 90 | 97 |
| 100 mg L ⁻¹ (1 mL) | [BBIM][Br] (0.1 M) in DCM | Temp. – 25 °C, pH – 4.5, 3 min at 1200 rpm | 2 : 1 | 99.20 | NH ₃ (2 M) | | 93.4 | 98 |
| Co(SCN) ₃ ⁻ (25 mg L ⁻¹) and NH ₄ SCN (0.1 M) | [P ₈₈₈₈][oleate ⁻] | 2 h, 2500 rpm | 1 : 1 | 99 | Na ₂ CO ₃ (1 M) | | 98 | 99 |
| 1 g L ⁻¹ Co ²⁺ , (CoCl ₂ + NaCl) | Cyphos IL 101 (14 wt%) | 50 °C, 16 h, 750 rpm | 1 : 1 | 99 | H ₂ O | | >99.8 (3 stages) | 100 |
| 5 g L ⁻¹ Co ²⁺ (CoCl ₂) in 7.6 M HCl | [P ₄₄₁₁₄][Cl] (40 wt%)+ NaCl (11 wt%) | 25 °C | 1 : 1 | 98–101 | | | | 101 |
| 1.5 g kg ⁻¹ | [Hmim][PF ₆] (25 mg) NaPF ₆ (0.5 mL, 80 mg mL ⁻¹), ethanol (diluent), Schiff base (0.02 M) | pH = 7, 5 min | | | | | | 102 |
| 10 ng mL ⁻¹ | [Hmim][PF ₆] (0.8 mg μL ⁻¹ , 64 mg), and [Hmim][Tf ₂ N] (0.5 mg μL ⁻¹), ethanol (diluent), 5-Br-PADAP ligand (1.5 × 10 ⁻⁵ M), NaNO ₃ (8%) | 35 °C, 0 °C, 8 min, 2500 rpm, pH = 7.5 | | ~100 | | | | 103 |

not stable and can decompose. Many problems arise when utilizing a single extractant; therefore, a mixture of extractants is used to avoid the problems.¹⁰⁷

Table 3 discusses nickel extraction using ionic liquids such as Alamine 336 with Cyanex 272 and D2EHPA, imidazole-based ionic liquid [Bmim][PF₆] and amine-based ionic liquids. The conditions for nickel extractions are room temperature, a low pH range (1–6), and varying the stirring time of extraction from 5 min to 180 min to obtain >99.9% extraction efficiency. Stripping with acids (HCl and H₂SO₄) can regenerate the ionic liquid and separate the nickel metal from the organic solution. The regenerated solvent can be used again in further extraction cycles.

Comparative assessment among the various prevalent methods with IL-based separation

The high cost of ILs (exceeding up to \$800/kg) is the main concern for their low adaptation and industrial scaling, making several industrial utilizations unjustified and unsustainable. Currently, ILs are produced in small scales, which is one of the main reasons for their high price.^{112,113} In this section, our effort is to provide a lay-man's comparative outlook among the various processes employed in the separation of metals during spent LIB recycling. The process considered here takes into account an inorganic acid-based leaching process of 100 kg spent NMC-611 battery scrap from its cathode material as the starting feed, unless specified otherwise. The two majorly discussed and practised processes in critical metal extraction/separation from spent LIBs are solvent extraction and ion exchange, as depicted in Fig. 10. Solvent extraction (SX) is one of the most robust methods in metal separation, and thus, it is applied on an industrial scale. The major demerit is shown in Fig. 10, which is the number of sub-unit operations desired to first separate impurities, followed by Mn, Co, Ni and Li; however, there is an important merit of highly pure salts as well as high regeneration efficiency. Another widely used method is ion-exchange wherein functionalised metal-specific resin depending upon their efficacy adsorbs Cu, Ni, Co, Fe, Mn, Al and Li. The ion-exchange process still governs by the use of multiple functionalised resins in columns for adsorption followed by their preferential elution to recover the metal ion. The other two methods, namely ILs and DESs, discussed are relatively new, and thus, their implication or assessment among the existing ones is deeply desired. The merit of ILs is the use of QFLs and PIL or IMILs, which makes the separation among Mn–Ni and Co–Li possible. Another inherent method is the use of ILs in the leaching stage, which substantially reduces the acid consumption. Although it has been widely covered, the need for SX will be invariably still needed to separate these metals. DESs also function similar to ILs acting as leaching and separation agents. It has been effective for all battery metals and has shown non-reactivity towards Li. DESs containing only non-ionic species can be prepared easily, which exhibit more benefits than the polar or hydrophilic DESs as they are inexpensive, non-

Table 3 Nickel extraction via ionic liquids

| Ni (conc.) | Solvent extraction (IL) | | | Stripping of loaded IL layer | | | | Ref. |
|---|--|------------------------|-------|------------------------------|--|----------------------|---------------------|------------------------------|
| | ILs (conc.) | Conditions (T, t, pH) | IL/A | Extraction% | Stripping agent | Stripping conditions | Stripping recovery% | Regeneration of ILs (cycles) |
| 100 mg L ⁻¹ in 3 M HCl + 2 M NaCl (Ni, Li sol) | (0.1 M) Alamine 336 and Cyanex 272/ (D2EHPA) | pH 3.15 | 1 : 1 | >99.9 | 0.1 M H ₂ SO ₄ | A/O = 1 : 1 | >99.9 | 108 |
| 5.28 g in 2 M H ₂ SO ₄ | (0.36 M) R ₄ N–Cl in kerosene | pH 6.4, 110 min, 298 K | 1 : 1 | 9.2 | Scrubbing (0.1 M) HCl, 0.4 M HNO ₃ | O/A = 1 : 4 | >99.6 (5.2 g) | 90 |
| 0.110 g Ni | D2EHPA + Aliquat 336 + [Benzet][TCM] | pH 2.5, 318 K, 30 min | 1 : 1 | 84.5 | Stripping (0.02 M) H ₂ SO ₄ | 20 min, 323 K | 109 wt% | 109 |
| 1.40 g L ⁻¹ (chloride salt) | (6.7 g of IL in 15 cm ³ of toluene) [P ₈₈₈₈][oleate] + water (10 wt%) | 5 min, pH 1 | 1 : 1 | >99 | 0.5 M H ₂ SO ₄ | | ~100 | 110 |
| 1 mM | [Bmim][PF ₆] in 2-amino thiophenol | 180 min, 298 K, pH 4–6 | | 57 | 3% H ₂ O ₂ in 0.1 HNO ₃ | 20 min | >98 | 111 |



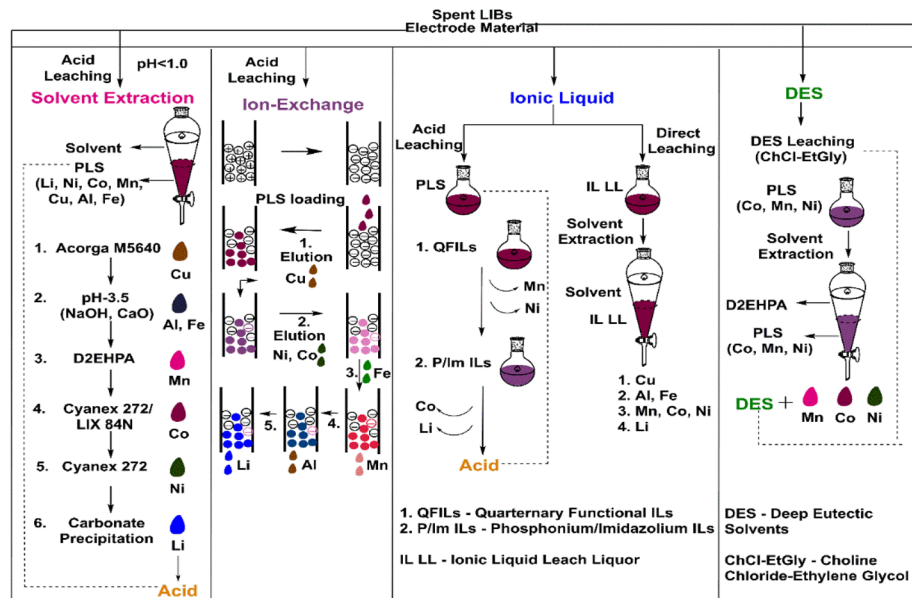


Fig. 10 Comparative outlook on the various processes involved in spent LIB recycling (composition of the NMC 111 electrode material: nickel 33%, manganese 32%, cobalt 34%, lithium 5.6%, copper 0.9%, aluminium + iron: 1%).

toxic in nature, and can be regenerated by evaporation only. The extraction of alkali or transition metals or polycyclic aromatic hydrocarbons from water can be done using non-ionic DESs. Metal ions or metal salts can be removed from water using non-ionic DESs containing decanoic acid and lidocaine in a molar ratio of 2/1. Positively charged metal ions probably exchanged with the moderately charged lidocaine ion executing an ion exchange process removing all the transition metals. Moreover, the non-ionic DES can be regenerated using $\text{Na}_2\text{C}_2\text{O}_4$ and reused by increasing the decanoic-to-lidocaine ratio.¹¹⁴

Since ILs and DESs are more expensive than organic solvents and have complexities in synthesis, their reusability and recyclability can only promise their economic feasibility for large-scale applications. The cost-competitiveness of ILs can be achieved by the regeneration of ILs and their reuse for different applications without creating any additional changes in the functionality of ILs. ILs are likely to be judged. They have the potential to lower the environmental impact of solvents in metal extraction when compared to organic solvents and DES reagents.¹¹²

Conclusions

In this review, the importance and usefulness of ionic liquids have been discussed, as well as their usage in the extraction of Li, Co, and Ni from their different sources. The ionic liquid is a solvent that is liquid at room temperature, as its volatility is very low or negligible. This is one of the main reasons for considering ionic liquids more than conventional solvents for metal extraction. Ionic liquids can be synthesized according to one's own choice and can be tuned by changing the anions or adding substituents to the cation molecule. For metal extraction, the choice of solvent and the extraction parameters

depend on the behavior of the metal ion in the aqueous solution, whether it is acidic or alkaline. The structure of an ionic liquid determines its properties, such as hydrophobicity/hydrophilicity and weak interactions between cations and anions. According to the previously published works, extraction parameters are mild when compared to the traditionally used solvents. For instance, temperature and stirring time used for extraction vary between 293 and 298 K and 20 and 60 min with a pH range of 2–6. In addition to parameters, the extraction efficiency shown by the ionic liquid extractants was highly satisfying. For stripping, HCl was frequently used to strip >90% of lithium ions from the organic phase. The critical part is the regeneration of ionic liquids after the extraction procedure. All the ionic liquid extractants can be recycled and reused for further extraction cycles for Li, Co, and Ni.

Future directions of research

Solvents such as ionic liquids contain only ions rather than any other neutral molecules, and have a low vapor pressure, and are almost non-volatile. This absence of volatility shows that ILs are safer to use and are environment-friendlier than any other traditionally used organic solvents, which are usually volatile organic compounds.¹¹⁵ However, as we compare other aspects of organic solvents and ionic liquids, viscosity is one of the factors that increases in ionic liquids. The viscosity of a solvent can disturb the transfer of ions and decrease the rate of chemical reactions. Similarly, high production costs are also a factor that can be seen as a disadvantage for ILs.^{116,117} ILs can be used as a solvent in metal extraction, not only for separation purposes, but also for leaching. They can also be used in the electro-winning and electro-refining of metals acting as electrolytes.¹¹⁷



Abbreviations

| | |
|------------------------------|--|
| IL | Ionic liquid |
| LIB | Lithium-ion battery |
| D2EHPA | Di(2-ethylhexyl)phosphoric acid |
| TBP | Tributyl phosphate |
| Cyphos 101/ [C101][Cl] | Trihexyl(tetradecyl)phosphonium chloride |
| [P ₈₈₈₈][Cl] | Tetraoctylphosphonium chloride |
| [P ₆₆₆₁₄][SCN] | trihexyl(tetradecyl)phosphonium thiocyanate |
| [P ₄₄₄₁₄][Cl] | Tributyl(tetradecyl)phosphonium chloride |
| [A ₃₃₆][CA-12] | Tricaprylmethylammonium <i>sec</i> - octylphenoxy acetic acid |
| R4N-SCN | Tetraalkylammonium thiocyanate |
| [THN][Dca] | Tetrahexylammonium dicyanamide |
| [Hmim][PF ₆] | 1-Hexyl-3-methylimidazolium hexafluorophosphate |
| [Hmim][BF ₄] | 1-Hexyl-3-methylimidazolium tetrafluoroborate |
| [Bmim]Br | 1-Butyl-3-methylimidazolium bromide |
| [P ₈₈₈₈][oleate] | Tetraoctylphosphonium oleate |
| LCA | Life cycle assessment |
| LCO | Lithium cobalt oxide |
| NMC | Lithium nickel manganese cobalt Oxide |
| LFP | Lithium iron phosphate |
| LMO | Lithium manganese oxide |
| [Hmim][NTf ₂] | 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide |
| CoCl ₄ | Cobalt tetrachloride |
| [OHEmim][NTf ₂] | 1-Hydroxyethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide |

Data availability

No primary research results, software or code has been included and no new data were generated or analysed as part of this review.

Author contributions

Pratima: supervision, software, project administration, funding acquisition, and formal analysis. Nikita: writing – original draft and investigation. Abhilash: writing – review & editing, validation, supervision, resources, methodology, data curation, and conceptualization.

Conflicts of interest

There are no conflicts to declare.

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