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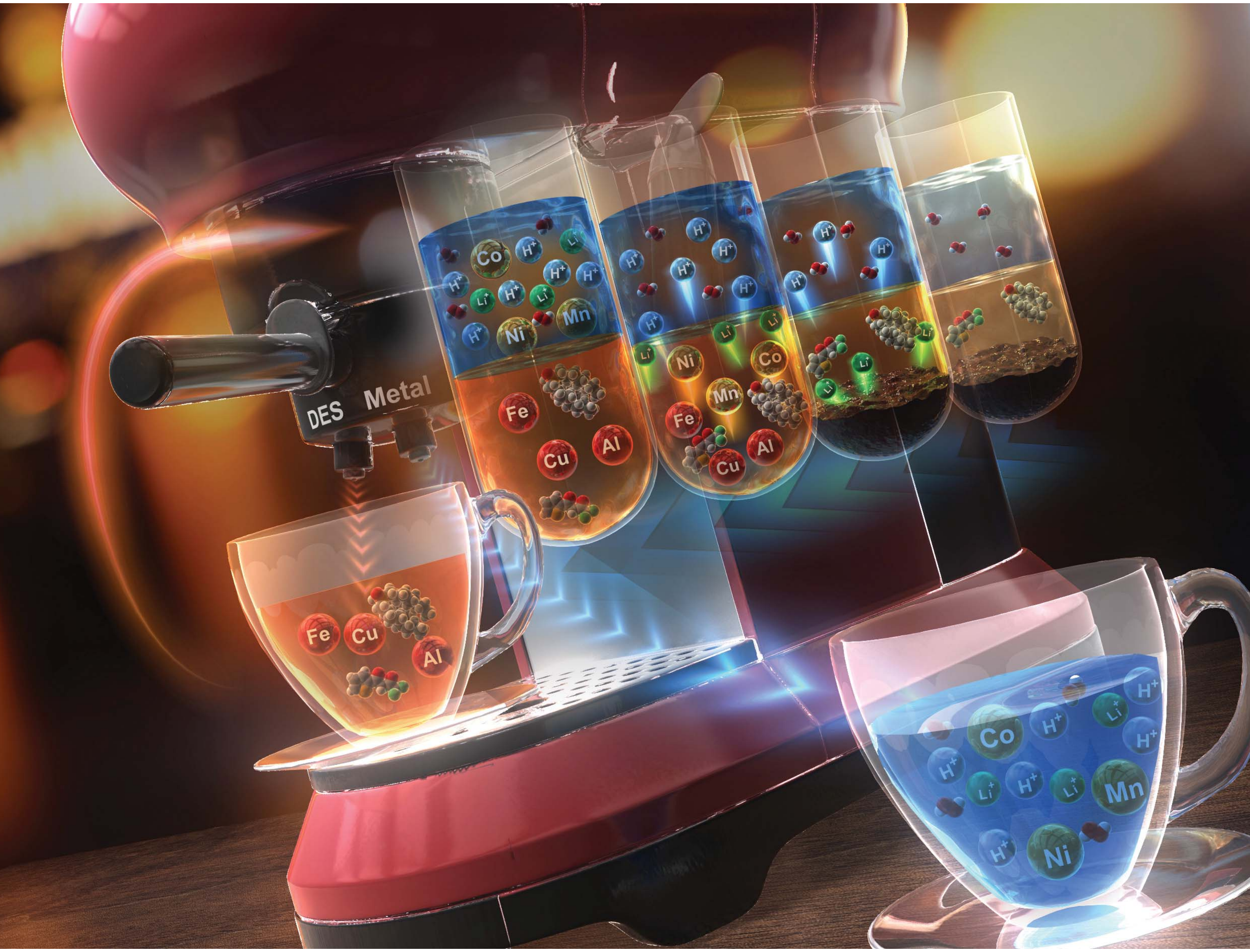

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Selective separation of critical metals from lithium-ion batteries in a two-phase leaching system based on a hydrophobic deep eutectic solvent and H_2O_2 solution

Kevin Septioga,[a] Adroit T. N. Fajar,[b] Rie Wakabayashi[a] and Masahiro Goto *[a]

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An efficient two-phase leaching system using a hydrophobic deep eutectic solvent (DES) composed of 2 mol of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and 1 mol of tri-*n*-octylphosphine oxide, with H_2O_2 as the aqueous phase, was developed for the selective recovery of Li, Co, Ni, and Mn from spent lithium-ion batteries. Under optimized conditions (80 °C, 30 min, 500 rpm, 10 mg per mL black mass loading, DES-to-aqueous ratio 1 : 1, and 5 M H_2O_2 as the aqueous phase), the two-phase leaching system achieved leaching efficiencies of 98% for Li, 94% for Co, 94% for Ni, 98% for Mn, with 73% Cu, 54% Al, and 76% Fe in the DES phase and minor amounts of Cu and Al in the aqueous phase, demonstrating pronounced phase-selective partitioning in a single-step process. The equilibrium pH (pH_{eq}) of the aqueous solution controlled the metal transfer behavior from the DES to the aqueous phase: Li was fully stripped at $pH_{eq} \leq 4$, while Co, Ni, and Mn migrated to the aqueous phase at $pH_{eq} < 2$. Furthermore, the DES exhibited stable performance over three successive cycles without regeneration or stripping, confirming its recyclability and operational robustness.

Sustainability spotlight

An efficient two-phase leaching system was developed to selectively recover Li, Co, Ni, and Mn from spent lithium-ion batteries using a hydrophobic deep eutectic solvent (DES) and an aqueous H_2O_2 phase. This system enables phase-selective leaching, driven by tunable equilibrium pH and proton exchange, under mild conditions (80 °C, 30 min). It achieves high selectivity and recyclability without requiring organic solvents or regeneration steps. This approach addresses the limitations of conventional leaching—namely poor selectivity, high reagent use, and waste generation—advancing sustainable metallurgy. The work aligns with SDG 12 (responsible production), SDG 9 (industry innovation), SDG 13 (climate action), and SDG 7 (clean energy) by promoting circular recovery of battery materials and reducing environmental impacts in critical metal supply chains.

Introduction

Lithium-ion batteries (LIBs) have been growing in popularity for many applications because of global efforts to mitigate climate change. The electrification of transportation and the expansion of energy storage systems are considered as essential strategies for reducing global emissions such as carbon dioxide (CO_2).[1] However, these advancements have significantly increased the demand for raw materials. The global demand for LIBs is expected to rise sharply – from 657 GWh in 2023 to 1103 GWh by 2028. In the automotive sector, more than 26 million electric vehicles were in service in 2022, representing a 60% annual increase.[2] Moreover, North America has announced plans for gigafactory-scale production, targeting 1 TWh of battery capacity.[1] Despite increasing environmental awareness, the global demand for metal ores has surged by 52% over the past two decades, showing no signs of slowing. This transition–coupled with relentless societal modernization and the aggressive advancement of renewable energy technologies—has intensified the strain on critical metal resources, exacerbating concerns over long-term supply security, environmental degradation, and geopolitical dependencies. To tackle these anthropogenic pressures on the environment, societies are forced to reconsider the unsustainable linear take-make-dispose model and shift toward a more environmentally friendly and holistic circular economy framework.[3]

Recycling LIBs is a practical and necessary approach to secure the supply of critical metals in the current era. By 2030, approximately 2 million tons of discarded LIBs are projected to accumulate globally. As metals such as lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn) in cathode materials become increasingly scarce, recovering them from end-of-life batteries

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[a] *Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan. E-mail: m-goto@mail.cstm.kyushu-u.ac.jp*

[b] *Center for Energy Systems Design, International Institute of Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan*

becomes strategically important. This strategy lessens reliance on primary sources of critical metals while also reducing the environmental damage caused by primary mining. However, effective and environmentally friendly recycling methods are imperative to prevent ecological issues and enable a sustainable supply chain for strategic resources.[4]

Among the various strategies for improving LIB recycling, the development of environmentally benign leaching agents is receiving increasing attention. In this context, deep eutectic solvents (DESs) – a eutectic mixture of a hydrogen bond donor and hydrogen bond acceptor – have been pursued as a promising class of green solvents compared with conventional mineral acids in hydrometallurgy.[5] The hydrogen bond donor of the DES acts as an oxygen acceptor to facilitate the cleavage of metal–oxygen bonds, creating a chemically versatile medium for coordinating various metal ions.[6,7]

As early as 2006, Abbott *et al.*[8] investigated the solubility of metal oxides in DESs. In 2019, Tran *et al.*[9] employed a DES composed of ethylene glycol (EG) and choline chloride (ChCl) as the leaching agent, representing a key milestone in the application of DESs for LIB recycling. Since then, several studies have reported the excellent performance of this DES in dissolving the metals of LIBs.[6,10] For example, this ChCl-based DES has achieved remarkable leaching efficiencies of 99.5% Li and 99.2% Co at 80 °C within 5 h.[11] Other DES formulations have also shown promise. For instance, guanidine hydrochloride–lactic acid DESs, when supplemented with a reducing agent, demonstrated excellent leaching efficiency,[5] while betaine chloride-based DESs achieved high metal recovery at elevated temperature (140 °C).[12] Alcohol-based DESs composed of EG or polyethylene glycol have also been combined with thiourea,[13] *p*-toluene sulfonic acid,[14] ascorbic acid,[15] phytic acid,[16] and oxalic acid dihydrate[17] to enhance metal dissolution in LIB recycling. Although these systems show high metal dissolution performance, additional steps such as metal stripping or scrubbing are typically required to recover metal from the DES phase, highlighting the need for process optimization and improve recyclability.

Despite these advances, single-phase leaching suffers from poor selective recovery of individual metals from metal-rich DESs. Like conventional inorganic acids, DESs accumulate a broad range of dissolved metals following leaching. Selective separation of these metals typically requires additional downstream treatments such as precipitation,[18] crystallization,[19] electrodeposition,[20] and solvent extraction,[21] often involving further use of inorganic acids,[22] organic acids,[23] sodium hydroxide,[24] ammonia,[25] or DESs.[26] These steps are expensive and, importantly, diminish the green advantage of DES-based systems. Moreover, complete and efficient metal recovery is essential to ensure DES regeneration and reusability.[27] Sustainable LIB recycling strategies need to entail highly efficient, environmentally friendly, and economically viable processes.

Several one-step techniques are available for achieving DES-based selective metal recovery during LIB recycling. Carreira *et al.*[22] introduced one-pot leaching of LIBs with simultaneous Ni(II) precipitation by impregnating HCl into the hydrophobic DES. By employing water as the ternary component of dimethylthetin–oxalic acid, the DES provides selective separation of Li ions (99.98%).[28] Phosphate-based DESs are also effective in the separation of Li and Co from $LiCoO_2$ through the precipitation of $(CoHPO_4)_2\cdot 3H_2O$.[29] Therefore, modifying the DES system alters the behavior of metal complexes in the leachate, resulting in selective recovery.

In our previous research,[30] we used a two-phase leaching system comprising a hydrophobic DES and water to achieve direct separation of Li from others metals such as Co, Ni, Mn, Cu, Al, and Fe. This system promotes the migration of Li ions into the water phase, enabling *in situ* lithium stripping without relying on conventional multi-step recovery processes. Although this approach is highly selective (99% Li separation within 24 h), it primarily focuses on separating lithium and requires refinement for broader application to the separation of other valuable metals. Expanding this concept to efficiently dissolve and recover essential metals such as Co, Ni, and Mn, is of significant strategic interest. Effective separation of these metals without impurities (Al, Cu, and Fe) would improve the purity of the recovered metal stream, in addition to reducing downstream refining burdens. Moreover, this approach enhances the recyclability of the remaining solution, contributing to a sustainable close-loop recycling process.[24]

To implement this concept, the present study developed a novel two-phase system for the direct separation of target metals (Li, Co, Ni, and Mn). Importantly, we incorporated an oxidative agent (H_2O_2) into the system to promote proton transfer from the DES to the aqueous phase. This proton movement not only enhances the leaching kinetics but also facilitates spontaneous *in situ* metal stripping, eliminating the need for post-leaching stripping or DES regeneration. By systematically evaluating the factors governing metal partitioning, we optimized the system to provide an efficient, integrated, and scalable pathway for selective metal recovery from the black mass of DES-based LIB recycling systems.

Experimental

Reagents and chemicals

In this study, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (HTTA, purity > 98%) was obtained from Tokyo Chemical Industry, and tri-*n*-octylphosphine oxide (TOPO, purity > 98%) was purchased from Kanto Chemical Co., Inc. for DES preparation. The hydrogen peroxide (H_2O_2, 30%) supplied by Wako Pure Chemical Industries Ltd. was used as the aqueous phase in the two-phase leaching system. Separately, aqueous solutions of hydrochloric acid (HCl, 10 M), nitric acid (HNO_3, 5 M), and sulfuric acid (H_2SO_4, 5 M) as well as sodium hydroxide (NaOH, 10 M), all obtained from Kishida Chemical Co., Ltd., were also used as alternative secondary phases to investigate the effect of pH and acid type on metal migration behavior. Various diluents were employed to investigate the effect of DES dilution, including *N*-dodecane (98%), 1-decanol (97%), and hexane (96%), all supplied by Kishida Chemical Co., Ltd., as well as toluene (>99%) from Wako Pure Chemical Industries Ltd. Milli-Q water was used in all assays. The solid feedstock for the leaching experiment was obtained from industry and prepared by mechanically crushing spent LIBs, as previous studies.[31]

Black mass composition

The metals in the black mass were leached into 1 M H_2SO_4, 5 M HCl, and 5 M H_2O_2 at 80 °C for 4 h to determine the metal composition of the black mass. The resulting composition of black mass is presented in Table S1. This real-world black mass sample served as a source of critical and base metals targeted for selective recovery in the two-phase leaching system.

Preparation of hydrophobic DES

The hydrophobic DES was prepared by mixing HTTA with TOPO in a 2 : 1 molar ratio and then sealed in a glass vial. The mixture was treated with an ultrasonicator at 60 °C for 90 min, yielding a stable, clear, and homogeneous liquid at room temperature (Fig. S1). Furthermore, DES characteristics and leaching performance were investigated.

Metal leaching

The two-phase leaching system comprised distilled water and hydrogen peroxide as the hydrophilic phase. A mixture of the black mass, DES, and aqueous phase was combined in a specific ratio and then transferred into a glass vial. The vial was maintained at 80 °C with continuous stirring at 500 rpm. After leaching, the mixture was subjected to centrifugation at 20 000*g* and 25 °C for 30 min to separate the two immiscible phases. Finally, the aqueous and DES phases were collected and prepared for metal content determination.

Several parameters were investigated to understand their influence on the two-phase leaching system, including the pH of the aqueous phase, the type of inorganic acid, H_2O_2 concentration, reaction time, temperature, the ratio of DES to aqueous phase, and the influence of the diluent present were demonstrated. The initial aqueous pH was adjusted with 2 M NaOH or 2 M HCl prior to mixing with the DES phase. Inorganic acids such as HNO_3 and H_2SO_4 were used as the aqueous phase for comparison to the performance of H_2O_2 in the two-phase leaching system. Reaction time varied from 15 s to 60 min and temperature ranged from 50 to 80 °C. The effect of organic diluents and DES-to aqueous ratios (0.75, 0.5, and 0.375) was investigated.

DES recovery and reuse in the two-phase system

The reusability of the DES was investigated to ensure sustainable metal recovery from LIBs in the two-phase leaching system under optimized conditions. After separation from the aqueous phase, the DES phase was washed with water (water volume was 2 times that of the DES volume) and vortexed for 15 s to remove residual H_2O_2 in the DES phase before using in the next cycle. The DES was then recovered by centrifugation at 10 000*g* and 25 °C for 10 min. Subsequent cycles were performed under the same conditions.

Characterization of DES and aqueous phase

The metals in the collected solutions were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 8300, PerkinElmer). The ICP-OES method was optimized in our previous work.[30] The leaching performance was evaluated on the basis of the leaching efficiency (% *L*), selectivity factor (*S*), and metal distribution (*D*), expressed as follows:

$$\%\ L = \frac{C_{\text{ICP}} \times d \times V}{C_{\text{cal}} \times m} \times 100\% \tag{1}$$

$$S_{\text{DES}} = \frac{\%\ L_{\text{Cu}} + \%\ L_{\text{Al}} + \%\ L_{\text{Fe}}}{\%\ L_{\text{Li}} + \%\ L_{\text{Co}} + \%\ L_{\text{Ni}} + \%\ L_{\text{Mn}}} \tag{2}$$

$$S_{\text{aq}} = \frac{\%\ L_{\text{Li}} + \%\ L_{\text{Co}} + \%\ L_{\text{Ni}} + \%\ L_{\text{Mn}}}{\%\ L_{\text{Cu}} + \%\ L_{\text{Al}} + \%\ L_{\text{Fe}}} \tag{3}$$

$$D = \frac{\%\ L_{\text{M(aq)}}}{\%\ L_{\text{M(DES)}}} \tag{4}$$

where C_{ICP}, V, C_{cal}, d, and m represent the concentration of metal M as determined by ICP-OES, volume of the hydrophobic DES, metal fraction based on molecular weight, number of DES dilutions, and mass of the black mass, respectively. Selectivity factors $S_{\text{(aq)}}$ and $S_{\text{(DES)}}$ were calculated to define the selectivity for targeted metals over impurity metals and *vice versa*. The distribution ratio *D* was defined as % *L* of the metal in the aqueous phase relative to that in the DES phase. Fourier-transform infrared (FTIR; Spectrum Two, PerkinElmer) spectra were acquired in the range of 400 to 4000 cm^{-1} to analyze molecular interactions. Nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR; ECZ400S, JEOL) was employed to observe the change in hydrogen and carbon bonds before and after leaching. UV-vis (V-750, Jasco) was used to observe metal–ligand complexation in both the DES and aqueous phase. A pH meter (HM-30R, DKK-TOA) was used to monitor the pH of the aqueous phase.

Results and discussion

Comparison of single-phase and two-phase systems for metal leaching of black masses

DESs in two-phase systems have the potential to compete with other solvents, despite the high leaching performance of mineral acids. Two-phase systems improve the leaching efficiency of DESs and enable the direct separation of specific metals into distinct phases, which is rarely achieved in single-phase systems. As listed in Table 1, conventional acidic solutions such as HCl, HNO_3, and H_2SO_4 demonstrated excellent performance in the metal leaching of black masses, with efficiencies exceeding 90% for most metals. The exception was iron (Fe), which leached only 20% in HCl and undetectable in HNO_3 and H_2SO_4. This low dissolution of Fe is attributed to its low content in the black mass and the heterogeneous nature of the material.[32] In contrast, H_2O_2 as the leaching agent provided higher selectivity. Only lithium (72%) and aluminum (32%) were leached, consistent with the results of water-based

Table 1 Leaching performance of various acidic solutions and HTTA–TOPO (DES) in both single-phase and two-phase systems. Experiments were conducted at 80 °C with stirring at 500 rpm for 1 h using a solid-to-liquid (S/L) ratio of 10 mg mL^{-1}. In the two-phase DES–H_2O system, the organic-to-aqueous (O/A) volume ratio was maintained at 1 : 1[a]

System		Single-phase					Two-phase	
Leaching agent		1 M HCl	1 M HNO_3	1 M H_2SO_4	5 M H_2O_2	DES	DES phase	H_2O phase
% leaching efficiency	Li	94.4% ± 3.1	87.9% ± 2.0	96.4% ± 3.2	72.5% ± 4.0	71.0% ± 1.2	48.1% ± 0.6	33.5% ± 1.0
	Co	98.8% ± 3.4	96.8% ± 1.1	93.8% ± 2.6	0.00%	54.6% ± 9.3	81.3% ± 0.5	0.00%
	Ni	98.1% ± 5.4	96.4% ± 0.5	92.6% ± 1.5	0.00%	35.7% ± 5.2	81.3% ± 1.7	0.00%
	Mn	100% ± 4.5	102% ± 1.2	98.5% ± 1.1	0.00%	64% ± 10.6	86.5% ± 1.2	0.00%
	Cu	91.8% ± 10.7	85.9% ± 3.0	86.1% ± 7.8	0.00%	32.4% ± 1.9	43.5% ± 1.0	0.00%
	Al	104% ± 6.3	91.8% ± 2.2	94.8% ± 3.7	32.2% ± 2.2	4.9% ± 0.9	66.9% ± 4.6	0.6% ± 0
	Fe	19.8% ± 3.3	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

[a] Values above 100% are due to experimental/analytical uncertainty for ICP measurements.

leaching in our previous research.[30] In contrast, HTTA–TOPO in the single-phase system showed moderate efficiency in leaching Li, Co, Ni, Mn, Cu, and Al, and negligible efficiency in leaching Fe. In a two-phase system with water as the aqueous phase, the DES phase exhibited leaching efficiencies of 48% for Li, 81% for Co, 81% for Ni, 87% for Mn, 44% for Cu, 67% for Al, and 0% for Fe. Moreover, the water phase was highly selective in extracting Li and a negligible amount of Al, indicating preferential partitioning of lithium into the water phase. This observation highlights the potential for tuning the conditions of the aqueous phase such as pH to promote the selective migration of critical metals like Li, Co, Ni, and Mn into the aqueous phase, effectively mimicking metal stripping during leaching.

Effect of aqueous phase pH on metal partitioning

The effect of aqueous phase parameters on metal partitioning in the two-phase system was investigated. As shown in Fig. S2, negligible differences in the leaching efficiencies Li, Co, Ni, Mn, Cu, Al, and Fe were observed within the aqueous-phase pH range of 2–12. Lithium preferentially partitioned into the DES at the initial pH (pH_0) ≥ 13 and was mostly distributed into the aqueous phase at $pH_0 \leq 2$. In contrast, the phase partitioning of Al consistently decreased under highly alkaline conditions (pH_0 > 12), likely owing to precipitation of $Al(OH)_3$.[33] Under extremely acidic conditions (pH_0 < 1), critical metals such as Li, Co, Ni, Mn, and Al were predominantly present in the aqueous phase, whereas Cu, Al, and Fe were enriched in the DES phase. In this case, HCl acts as a strong agent to leach metal oxides from the black mass, while the DES functions as an extractant in liquid–liquid extraction. Therefore, Cu, Al, and Fe were extracted from the aqueous phase because HCl was a stronger leaching agent than the DES (as shown in Table 1). Of particular interest, Li was fully distributed in the aqueous phase at pH_0 1, although Co (4%), Ni (2%), Mn (5%), and Al (5%) were present in trace amounts. It is plausible that distribution of these transition metals across the two phases is governed by the equilibrium pH (pH_{eq}) of the aqueous solution. In this case, proton transfer and proton-donating species modulate ΔpH, which reflects interfacial proton exchange,[34] a pivotal process governing metal separation within the two-phase leaching system.

Proton movement between the aqueous phase and DES phase in the two-phase system is shown in Fig. 1a. Protons were predominantly reduced in the aqueous phase at pH_0 1 to 4 because protons were consumed in the formation of H_2O (Fig. 1b) in the aqueous phase during metal leaching.[27] In contrast, at pH_0 5 to 14, the direction of proton movement reversed, with the DES acting as the proton donor to the aqueous phase when pH_0 was higher than the pK_a of the DES components. Moreover, contact of the HTTA-based DES with water enabled proton donation, and the proton in the tautomer form of HTTA (Fig. 1c) was replaced with a metal, which resulted in exchange between protons and metal ions in the DES and aqueous phases.[35] Notably, pH_{eq} in the initial pH range of 2 to 12 was stabilized at an average of 4.4, at which Li and a small amount of Al remained in the aqueous phase. Then, at pH_0 13 and 14, the system exhibited the highest proton transfer—evidenced by a ΔpH of approximately 7.5—which corresponded to minimal lithium retention in the aqueous phase. This result indicates an inverse relationship between the extent of proton transfer from the DES phase to the aqueous phase and distribution of lithium in the aqueous phase. However, the leaching performance was not strongly affected except at pH_0 14 owing to disruption of the DES structure.[36] Under extremely acidic conditions, the aqueous phase stabilized the presence of Co, Ni, and Mn at pH_{eq} lower than 1.7. This suggests that decreasing the equilibrium pH of the aqueous phase is critical for extracting transition metals into the aqueous phase.

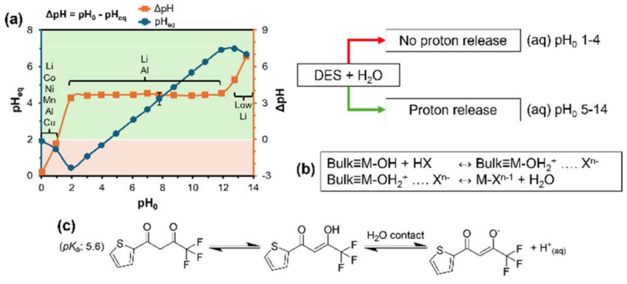

Fig. 1 (a) Effect of varying the initial pH of the aqueous phase on pH_{eq} and metal composition of the aqueous phase. (b) Reaction mechanism of metal oxides in acidic aqueous systems.[21] (c) Tautomerism of HTTA and its deprotonation form.

Comparison of inorganic acids and H_2O_2 in the two-phase system

Comparing the leaching performance of hydrogen peroxide with that of acid solutions is important because these agents promote metal dissolution through different mechanisms. In the single-phase system, hydrogen peroxide as a leaching agent was inferior to inorganic acids (Table 1). In the two-phase leaching system (Fig. S3a), % L of Li, Co, Ni, and Mn in the DES was lower than 1% with H_2O_2 as the aqueous phase, and this value was 2% with H_2SO_4 as the aqueous phase. Moreover, % L for Co, Ni, and Mn in the DES was 3–9% with HNO_3 as the aqueous phase. Metals such as Cu, Al, and Fe showed a high affinity for the DES phase, even when an acid solution was used as the aqueous phase. This indicates that the DES selectively extracted these metals over Li, Co, Ni, and Mn. These % L values revealed that the selectivity of the DES phase for Cu, Al, and Fe over Li, Co, Ni, and Mn depended on the nature of the aqueous phase in the order of H_2O_2 (86.8) > H_2SO_4 (35.1) > HNO_3 (9.1), which was calculated by dividing total % L of Cu, Al, and Fe to the total % L of Li, Co, Ni, and Mn as shown in eqn (2). In the two-phase leaching system (Fig. S3b), adopting H_2O_2, rather than traditional acid solutions like H_2SO_4 and HNO_3, as the secondary phase resulted in slightly superior leaching performance – particularly in the leaching of critical metals like Li, Co, Ni, and Mn, with over 94% leaching efficiencies. By using H_2SO_4, the leaching efficiency of Al was 67%, which affected the selectivity for Li, Co, Ni, and Mn over Cu, Al, and Fe. The calculated selectivity values (calculated by dividing total % L of Li, Co, Ni, and Mn by the total % L of Cu, Al, and Fe as shown in eqn (3)) indicated that the selectivity of the aqueous phase decreased in the order of HNO_3 (11.5) > H_2O_2 (9.4) > H_2SO_4 (5.1). Despite its highest selectivity ranking, HNO_3 exhibited the lowest overall leaching efficiency compared with H_2O_2 and H_2SO_4. Therefore, H_2O_2 acts synergistically with HTTA and TOPO in the DES to achieve high selectivity, with the DES phase rich in Cu, Al, and Fe and the aqueous phase rich in Li, Co, Ni, and Mn, which is the best option for efficient LIB recycling. Furthermore, H_2O_2 is comparable to inorganic acids in leaching performance and is an environmentally friendly leaching agent.[37] Instead of using strong mineral acids, incorporating oxidizing agents such as H_2O_2 may enhance proton release from the DES, offering an effective alternative for controlling metal separation.

Effect of H_2O_2 concentration on leaching performance

Determining how the concentration of H_2O_2 affects the two-phase leaching system is essential to optimize the leaching efficiency. This investigation enables identification of the direct transfer of critical metals like Li, Co, Ni, and Mn into the aqueous phase, improvement of the selectivity for target metals, and determination of the lowest effective concentration for sustaining high leaching performance. Indeed, the metal distribution was considerably influenced by the H_2O_2 concentration (Fig. 2a and b). The Li leaching efficiency in the DES phase (Fig. 2a) was 54% without H_2O_2 in the aqueous phase, and this value decreased as the H_2O_2 concentration increased, indicating that lithium was released into the aqueous phase. In addition, complete stripping of Li from the DES phase was achieved by using 1 M H_2O_2, and the highest accumulation of Co, Ni, and Mn in the DES phase was obtained by using 0.1 M H_2O_2, with % L of 91% for Co, 89% for Ni, and 92% for Mn. Direct stripping of Co, Ni, and Mn occurred at 1 M H_2O_2 in the two-phase leaching system, which marked the decline in the leaching efficiency. In contrast, the Cu leaching efficiency increased continuously and peaked at 3 M H_2O_2 before reducing to 64% at 5 M H_2O_2. Aluminum leaching showed a similar pattern, with the Al leaching efficiency in the DES phase increasing as the H_2O_2 concentration increased, although it declined to 45% at 5 M H_2O_2. Notably, Fe leaching depended on strong oxidative conditions, as evidenced by its ability to leach from the black mass at concentrations of 3 M H_2O_2 and higher. These results highlight the importance of the H_2O_2 concentration in maintaining metal selectivity and leaching efficiency of the two-phase leaching system, which arises from the significant effect of the H_2O_2 concentration on the distribution and recovery of metals in the aqueous phase – an aspect further examined in the following discussion.

Fig. 2b illustrates the dependence of metal partitioning on the H_2O_2 concentration, revealing an inverse relationship between the leaching efficiencies observed in the DES and aqueous phase. As the H_2O_2 concentration increased, most of the critical metals such as Li, Co, Ni, and Mn were stripped from the DES and transferred to the aqueous phase. In particular, the Li leaching efficiency showed a marked increase in response to H_2O_2. Similar to Co, Ni, and Mn, Li started to migrate into the aqueous phase at H_2O_2 concentrations of 1 M or higher, which indicated a direct stripping effect under oxidative conditions. At 5 M H_2O_2, the Cu and Al leaching efficiencies of the aqueous phase increased, suggesting that high H_2O_2 concentrations can compromise the selectivity of the DES by promoting broader metal migration into the aqueous phase. Furthermore, the presence of H_2O_2 strongly promotes proton transfer from the DES phase to the aqueous phase, as indicated by the ΔpH values of the aqueous phase (Fig. 2c), which averaged 4.898 compared with the average ΔpH (2.645) when water was used as the

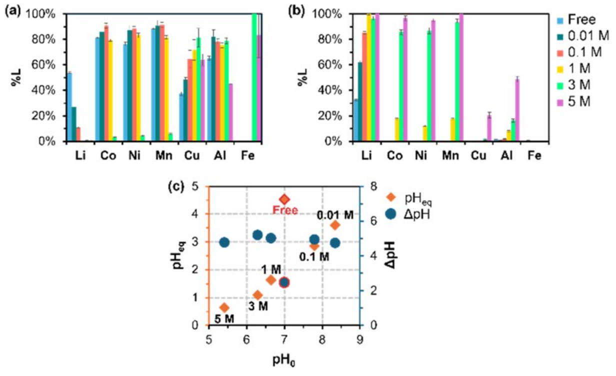

Fig. 2 Effect of varying the H_2O_2 concentration on the leaching efficiencies of the (a) organic phase and (b) aqueous phase. Leaching was conducted at 80 °C for 1 h with a solid-to-liquid ratio of 10 mg mL^{-1} and a DES-to-aqueous phase volume ratio of 1 : 1. (c) Change in aqueous phase pH at equilibrium after leaching.

aqueous phase. This suggests that the presence of H_2O_2 induces proton dissociation from the hydroxyl group of the keto–enol tautomeric form of HTTA by facilitating the formation of the corresponding enolate intermediate[38] (Fig. 1c). This deprotonation enhances the electron-donating ability of HTTA, promoting complexation with the metal ions.[35,39] Furthermore, equilibrium pH measurements confirmed that Li stripping occurred at pH 4 or lower, while Co, Ni, and Mn efficiently migrated into the aqueous phase at pH 2 or lower. *In situ* stripping of Co, Ni, and Mn needs an acidic environment to stabilize these metals in the aqueous phase.[40] These findings are consistent with the trends observed in Fig. 1a, reinforcing the role of acidic conditions in selective metal dissolution in two-phase leaching systems.

Effect of leaching duration and temperature on metal selectivity

The effect of leaching duration on the leaching efficiency of the two-phase system was investigated. The leaching efficiencies of both the DES and aqueous phase (Fig. 3a and b) indicated that leaching started in the DES phase, and the aqueous phase stripped the metals from the DES. Leaching of 19% Li, 39% Co, 45% Ni, and 57% Mn occurred in the DES phase within 15 s, and these metals completely moved to the aqueous phase after 30 min. The % *L* of Cu increased from 22% at 15 s to 71% at 15 min and then declined to 64% at 1 h. This indicated that stripping of Cu occurred after 15 min, which resulted in Cu migration into the aqueous phase. The Al content in the DES phase increased from 4% to 60% after 15 min, and the Al content of the aqueous phase increased from 2% to 27% after 4 min. A decline in the leaching performance of the DES phase after 15 min indicated that the stripping process occurred because of changes in the pH (pH_{eq} 0.64 at 60 min) of the aqueous phase, which resulted in 64% Cu and 45% Al in the DES phase at 60 min. Conversely, in the aqueous phase, metal stripping was observed within the first minute. The % *L* of the target metals was 61% Li, 5% Co, 5% Ni, and 8% Mn, with impurities of 3% Cu, 20% Al, and 52% Fe, after the first minute, which then increased to 100% Li, 97% Co, 95% Ni, and 100% Mn, with impurities of 21% Cu, 49% Al, and 0% Fe, at 60 min. In addition, 19% Fe was leached into the DES phase after 12 min, reaching 84% Fe at 60 min. Cu and Al were determined as impurities in this one-step leaching–extraction–separation process. Overall, 30 min of leaching was considered the optimized condition owing to absence of Li, Co, Ni, and Mn in the DES phase and relatively low impurities (9% Cu and 31% Al). As shown in Fig. S5b, the pH_{eq} of the aqueous phase continuously decreased during the reaction, consistent with our previous report.[30] The resulting H^+ displaced metals from the DES phase, facilitating their transfer into the aqueous phase.[41]

The effect of varying the temperature from 40 to 80 °C on leaching performance was investigated. As shown in Fig. 4, increasing the temperature improved overall metal transfer to the aqueous phase, as evidenced by the decline in the % *L* of each metal, except Fe, in the DES phase. This behavior indicated that increasing the temperature also increased molecular mobility and reaction kinetics,[42] which enhanced metal leaching from the black mass and promoted effective metal stripping into the aqueous phase. Notably, lithium was completely transferred from the DES at 40 °C. In contrast, the performance of the DES phase in leaching Cu and Al increased as the temperature increased from 40 to 60 °C and then tapered off at temperatures higher than 60 °C. The metal–DES interaction in the two-phase system was thermodynamically unstable at high temperatures and the acidified environment of H_2O_2. As a result, the metals were preferentially stripped from the DES and transferred to the aqueous phase. Interestingly, Al in the

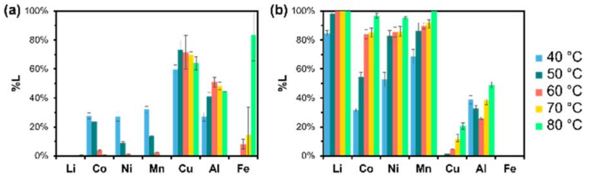

Fig. 4 Effect of varying the temperature on the leaching efficiencies of the (a) organic phase and (b) aqueous phase. Leaching was conducted for a fixed duration of 1 h using a solid-to-liquid ratio of 10 mg mL^{-1}, a DES-to-aqueous phase volume ratio of 1 : 1, and 5 M H_2O_2 as the aqueous phase.

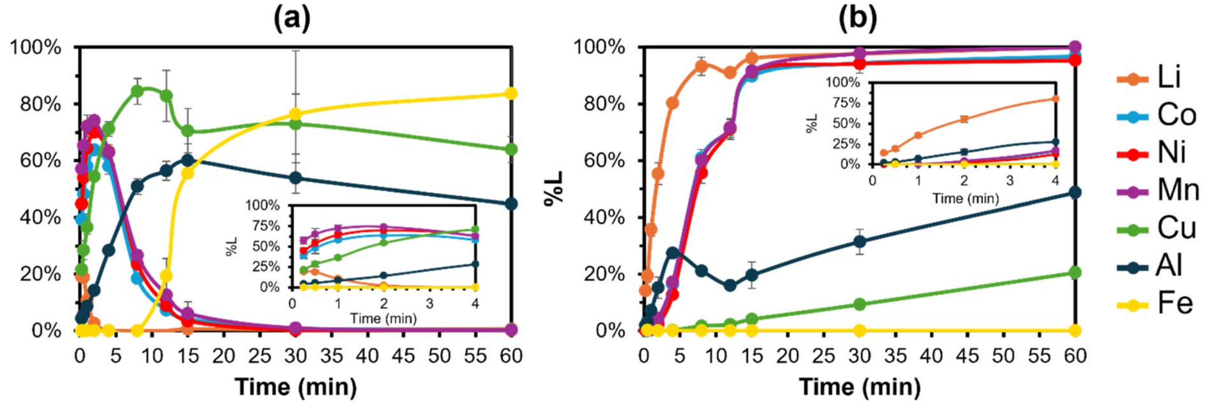

Fig. 3 Effect of varying the leaching duration on the leaching efficiencies of the (a) organic phase and (b) aqueous phase at 80 °C. Experiments were conducted using a solid-to-liquid ratio of 10 mg mL^{-1}, a DES-to-aqueous phase volume ratio of 1 : 1, and 5 M H_2O_2 as the aqueous phase.

aqueous phase exhibited a non-linear trend, which was attributed to competitive complexation between the DES and aqueous phase. This can be described as H_2O_2 leaching of Al (Table 1 and Fig. 4b), followed by DES extraction of Al from the aqueous phase at 70 °C or above, shifting the equilibrium towards the aqueous phase. Elevating the temperature reduced the stability of metal–DES interactions and promoted metal ion migration into the aqueous phase, indicating a temperature-driven shift in the metal distribution equilibrium. Therefore, increasing the temperature shifts the metal distribution equilibrium between the DES phase and aqueous phase, which balances the leaching efficiency, selectivity, and phase partitioning in the two-phase leaching system.

Effect of the DES-to-aqueous phase ratio on leaching performance

The DES and aqueous phases of the two-phase leaching system synergistically enhance metal recovery. The configuration of the two phases, such as the organic-to-aqueous ratio and organic diluent–DES interaction, can influence metal recovery. Adjusting these parameters allows for fine control over metal distribution between the phases, in addition to enhancing the efficiency and selectivity of recovery. The effect of varying the organic-to-aqueous ratio on the leaching performance of the two-phase system was investigated (Fig. 5a and b). Metals such as Co, Ni, and Mn preferentially remained in the DES phase when the fraction of DES in the two-phase system was 0.75. This behavior can be attributed to the limited interfacial contact between the aqueous and DES phase, which likely hinders efficient metal stripping. This behavior is analogous to organic-to-aqueous ratio effects in conventional solvent extraction, where increasing the organic phase generally enhances metal retention in that phase.[43] Conversely, decreasing the DES fraction promoted metal partitioning in the aqueous phase, suggesting improved interfacial contact between the DES and aqueous phase. Interestingly, the % *L* of Co, Ni, and Mn at a DES fraction of 0.5 was marginally higher than that at a DES fraction of 0.375, indicating that the leaching mechanism was predominantly influenced by the DES content rather than the H_2O_2 content. However, transport of impurities such as Cu and Al into the aqueous phase was prominent at low DES fractions. In contrast, Li leaching in the two-phase system was found to be independent of the DES fraction. Furthermore, Fe leaching was observed at both 0.5 and 0.375 DES fractions but not at 0.75 DES fraction, similar to the behavior of single-phase DES leaching (Table 1). Notably, impurity migration was suppressed at high DES fractions, with 0% Cu and 4% Al in the aqueous phase. These findings indicate that increasing the DES content improves selectivity by minimizing impurity dissolution at the cost of lowering the recovery of Co, Ni, and Mn in the aqueous phase.

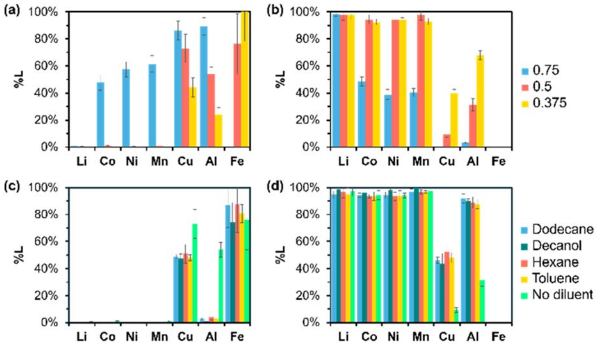

Fig. 5 Effect of varying the DES fraction on the leaching efficiencies of the (a) organic phase and (b) aqueous phase of the two-phase system. Effect of adding a diluent to the DES on the leaching efficiencies of the (c) organic phase and (d) aqueous phase. Leaching was conducted at 80 °C for 30 min using a solid-to-liquid ratio of 10 mg mL^{-1}, an organic-to-aqueous phase volume ratio of 1 : 1, a DES concentration of 50% v/v, and 5 M H_2O_2 as the aqueous phase.

The effect of diluent addition to the DES phase on the leaching performance of the two-phase leaching system was also investigated (Fig. 5c and d). The leaching performance of the system for Li, Co, Ni, Mn, and Fe appeared unaffected by the diluent, indicating that the integrity of the two-phase system was maintained. However, notable changes were observed in the behavior of Cu and Al upon diluent addition. Specifically, the Cu and Al leaching efficiencies in the aqueous phase markedly increased with diluent addition, corresponding to a decrease in the Cu and Al concentrations in the DES phase. In addition, the occurrence of emulsification in this system was unlikely because the diluent was specifically chosen for its immiscibility with water, and complete phase separation was achieved after centrifugation, confirming the biphasic nature of the two-phase system. This result suggests that diluting the DES weakens the interaction between the metal and DES components, thereby enhancing metal migration into the aqueous phase. Additionally, the added solvent decreases the DES viscosity, diminishing HBD–HBA interactions and facilitating metal transfer.[44]

Structural stability of DES upon contact with H_2O_2 in the two-phase system

The acquired FTIR spectra (Fig. 6) provided information on the molecular structure of the DES before and after leaching in the two-phase system with H_2O_2. The two strong bands at 2860 and 2928 cm^{-1} were assigned to the stretching of –CH_2– in the three alkyl chains of TOPO (Fig. S4). The peaks observed at 1145 and 1465 cm^{-1} were attributed to P═O and P–C stretching, respectively.[45] Peaks at 1110 and 1355 cm^{-1} corresponded to symmetric and asymmetric stretching of CF_3 in HTTA, respectively. Peaks at 1581 and 1638 cm^{-1} were assigned to the stretching vibration of the C═O group of β-diketones. The peak at 1065 cm^{-1} was assigned to the stretching vibration of the C–S group of HTTA.[46] In addition, a strong band was observed at approximately 1404 cm^{-1}, which was attributed to the thiophene ring. The peak at 3113 cm^{-1}, corresponding to the stretching vibration of the methylene group (–CH_2–) between two carbonyls group in HTTA, disappeared upon DES formation. Therefore, the DES was formed *via* enol tautomerism of HTTA rather than through its β-diketones.[47] This interpretation is further supported by the observed shift of the C═O stretching

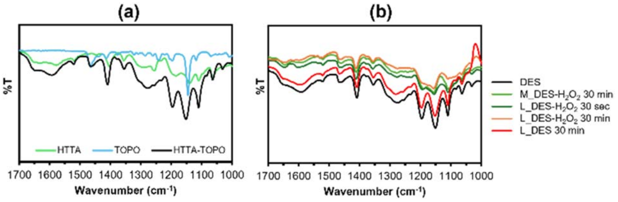

Fig. 6 FTIR spectra of the DES (a) before and (b) after contact with the black mass under different conditions: leaching (L) in DES–H_2O_2 (5 M H_2O_2 as the aqueous phase) or DES only, mixing (M) with 5 M H_2O_2 without the black mass for 30 min. All experiments were conducted at 80 °C.

bands to 1590 and 1651 cm^{-1}, indicating an increase in the double bond character of the carbonyl groups. This shift indicates altered intermolecular interactions and reduced hydrogen bonding, consistent with HTTA enolization and DES formation. Following leaching in the two-phase system with H_2O_2, notable spectral changes were observed at 1275 and 1590 cm^{-1}, attributed to metal complexation involving the keto–enol functionality of HTTA. In contrast, the overall FTIR spectra of HTTA and TOPO in the DES matrix remained unchanged, reflecting the stability of their core structures under oxidative leaching conditions.

^{1}H-NMR and ^{13}C-NMR analyses were conducted to compare the structural integrity of the DES before and after treatment with H_2O_2 *via* leaching and mixing (Fig. 7). In the ^{1}H-NMR spectrum of the untreated DES, the peak observed at 6.45 ppm was assigned to –CH_2– between the carbonyl groups of HTTA, while the peaks at 7.22, 7.77, and 7.85 ppm corresponded to protons on the thiophene ring of HTTA. Moreover, the peaks at 0.88 (–CH_3), 1.28 (aliphatic chain, C_2–C_7), and 1.65 ppm (P–CH_2– protons) were derived from TOPO. A weak singlet at 3.34 ppm was attributed to the enolic proton of the keto–enol tautomer of HTTA, supporting the formation of the enolized species in the DES and potential complexation during oxidative leaching.[48] The P–CH_2– peak shifted downfield from 1.65 ppm in the spectrum of the untreated DES to 1.72 ppm in the spectrum of the DES after mixing and to 1.75 ppm in the spectrum of the DES after leaching, indicating a change in the electronic environment around phosphorus. The core structure of HTTA and TOPO remained intact, although new aromatic peaks emerged at 7.11 and 7.57 ppm after leaching and at 6.98, 7.08, 7.30, and 7.54 ppm after mixing, suggesting the formation of new interactions. In addition, unidentified minor peaks appeared in the region of 4.5 to 2.5 ppm following mixing, which indicated the occurrence of mild degradation or formation of intermediate species.

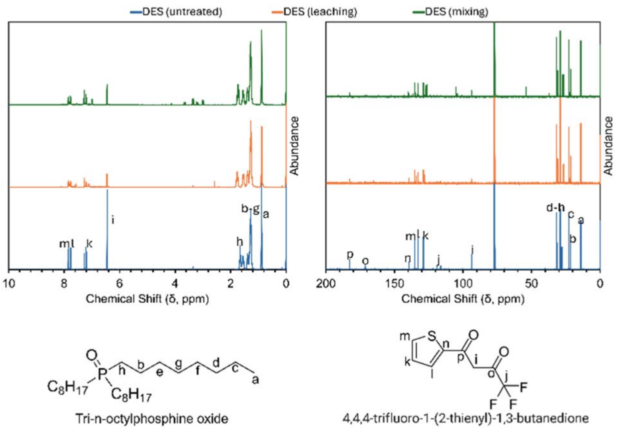

Fig. 7 ^{1}H-NMR (left) and ^{13}C-NMR (right) of the DES composed of HTTA–TOPO (untreated), DES after leaching, and DES after mixing with H_2O_2. Leaching was conducted at 80 °C for 30 min in the two-phase system, and mixing involved stirring at 80 °C for 3 h. 5 M H_2O_2 was used for both treatments.

The thiophene ring of HTTA is potentially susceptible to oxidative degradation by H_2O_2 *via* two main pathways: sulfoxidation/sulfone formation and ring cleavage. However, analysis of ^{13}C-NMR data indicated that the core structure of HTTA and TOPO in the DES system remained stable following treatment with H_2O_2, as evidenced by the retention of their characteristic carbon signals. Nonetheless, several new peaks were observed at 37.23, 53.89, 105.13, 126.66, and 134.17 ppm after leaching and at 165.34 and 134.17 after mixing, suggesting the formation of minor byproducts or transient species. The typical signals of aliphatic chains or acrylic-type structures were absent, indicating that cleavage of the thiophene ring did not occur. Additionally, the formation of thiophene *S*-oxide or *S*,*S*-dioxide would lead to pronounced de-shielding of aromatic carbons. However, corresponding changes were not clearly observed in the NMR data. These findings suggest that oxidation of the thiophene ring was minimal under these experimental conditions. This stability may be attributed to the presence of strong electron-withdrawing groups such as the trifluoromethyl and carbonyl substituents, which likely reduce the susceptibility of the thiophene ring to oxidation by H_2O_2. Nevertheless, under more aggressive conditions, the formation of sulfoxide or sulfone derivatives cannot be entirely ruled out.[49]

Proposed leaching mechanism in the DES–H_2O_2 two-phase system

Metal leaching in the DES-based system can be understood in terms of a complexation-driven mechanism. In the single-phase system composed of a DES based on β-diketone, metal dissolution occurs primarily *via* the formation of coordination complexes.[35] HTTA functions both as a hydrogen bond donor and a chelating ligand to extract transition metals like Co, Ni, Mn, Cu, and Fe. The extent of metal extraction in this system is influenced by the leaching duration and temperature. The β-diketone group of HTTA undergoes keto–enol tautomerization, and the deprotonated enolate form exhibited enhanced reactivity toward metal chelation.[39] Additionally, the two-phase leaching system can facilitate these formations (Fig. 6).

In the two-phase system ([HTTA–TOPO]–H_2O_2), metal dissolution proceeds through a combination of ion exchange, acid-driven bond cleavage, and phase-selective complexation. When the DES (HTTA–TOPO) was mixed with 5 M H_2O_2 at 80 °C, protons were released from the DES into the aqueous phase at pH_{eq} 0.9 after 30 min. These protons play three critical roles in the leaching mechanism: (i) promoting the exchange of cations such as Li^+ in the black mass *via* H^+/Li^+ ion exchange, (ii) assisting the cleavage of metal (M–O) bonds within the solid matrix, and (iii) liberating metal ions from the M–DES complex.

In the two-phase system, H^+/Li^+ ion exchange occurred across both the aqueous and DES phases, as evidenced by the leaching efficiencies listed in Table 1 and Fig. 3. However, Li was predominately found in the aqueous phase, indicating a high partitioning preference. In contrast, single-phase DES leaching resulted in the dissolution of all metals, except iron (Table 1). The observed competition between the aqueous phase and DES phase for Li^+ extraction indicates that the DES prefers to release protons rather than retain Li^+ ions. This interpretation is supported by the increase in the lithium content of the aqueous phase and the simultaneous decrease in the lithium content of the DES phase in the presence of 0.001 M H_2O_2 (Fig. 2). Furthermore, Li was completely transferred to the aqueous phase at pH_{eq} of 1.7, confirming that Li migration is strongly pH dependent.

In the single-phase system composed of H_2O_2 (Table 1), Li and Al were selectively extracted from the black mass, suggesting that in the DES–H_2O_2 two-phase system, the DES phase acted as the primary reducing and coordinating agent. This is consistent with previous studies reporting that the protonated form of the DES is more chemically reactive than its protonated counterpart.[30,50] In particular, the deprotonated form of HTTA facilitates the preferential extraction of transition metals such as Co, Ni, and Mn into the DES phase. This trend is clearly observed in Fig. 5, showing that these metals were primarily located in the DES phase within just 15 s of leaching. However, the metals were gradually distributed into the aqueous phase (Fig. S5a), indicating progressive stripping due to the decreasing pH_{eq} of the aqueous phase (Fig. S5b).

As leaching progressed, the pH of the aqueous phase decreased continuously (Fig. S5b), correlating with the onset and extent of metal stripping from the DES phase into the aqueous phase. According to the measured pH_{eq} and corresponding leaching duration, the pH_{eq} range of 2.0 to 1.5 limited stripping, as shown in Fig. S5a. However, when pH_{eq} dropped below 1.0, metal stripping became effective, indicating that extremely acidic conditions promoted the release of metals from the DES phase. This behavior is analogous to conventional acid scrubbing, where proton replace coordinated metals in the DES phase, releasing them into the aqueous phases.[41,51] In the present two-phase leaching system, the acidity of the aqueous phase is enhanced by proton transfer from the DES phase. It is plausible that peroxide-derived (*e.g.*, OOH^-), formed from H_2O_2 decomposition, participate in complexation and promote metal displacement, as supported by previous computational studies on Co-aqua complexes.[52]

UV-vis analysis further supports the above-mentioned mechanism. As shown in Fig. S5d, the UV-vis spectra of both the single-phase system and the DES phase of the two-phase system after 30 min of leaching contained a distinct absorption peak at 226 nm corresponding to a metal–DES complex. Interestingly, this peak was absent at 15 s, suggesting that initial metal–ligand interactions were relatively weak, particularly between Co, Ni, and Mn and the DES. These weak interactions likely facilitated subsequent stripping of these metals into the aqueous phase. The UV-vis spectra of the aqueous phase (Fig. S5c) contained a peak at 266 nm, confirming the presence of metal species after 30 min of leaching which may represent the metal complex with H_2O_2 or ^-OOH. However, the exact nature of their complexation in water remains unclear and warrants further investigation.

The temperature also influenced the stripping efficiency. At low temperatures, proton transfer from the DES to the aqueous phase occurred slowly, thereby limiting metal distribution into the aqueous phase. Additionally, copper remained in the DES phase for approximately 4 min before gradually migrating into the aqueous phase, indicating slow migration of Cu. In contrast, Al leached into both phases, indicating non-selective partitioning between the DES phase and H_2O_2 phase.

DES reusability in the two-phase system

To evaluate the reusability of the DES in the two-phase leaching system, leaching was conducted for three successive cycles without introducing an additional acid to the DES in the stripping and regeneration steps under optimized conditions (80 °C, 30 min, 500 rpm, 10 mg per mL black mass loading, DES-to-aqueous ratio 1 : 1, and 5 M H_2O_2 as the aqueous phase). Fig. 8a shows a schematic of closed-loop metal recovery, wherein the DES is reused directly with fresh aqueous solution (5 M H_2O_2) and black mass in each cycle. In all cycles, the leaching of Li, Co, Ni, and Mn into the DES phase was inefficient (3%) (Fig. 8b), while their recoveries in the aqueous phase were consistently efficient, exceeding 85% (Fig. 8c). Notably, a slight decline in the leaching efficiency was observed across the cycles. By the third cycle, recoveries of these metals in the aqueous phase decreased slightly to 90% Li, 85% Co, 87% Ni, and 86% Mn. The gradual increase in DES viscosity with each cycle (Table S2) likely reduced mass transfer, resulting in slightly lower leaching performances.[42] These results suggested that the DES maintained high extraction selectivity and functional stability with repeated use, albeit with minor performance loss, possibly owing to saturation effects, degradation of active sites, or accumulation of impurities.

The Cu and Al contents of the DES phase markedly decreased by the third cycle (Fig. 8d), indicating progressive migration of these metals into to the aqueous phase. Cu and Al in the aqueous phase reached maximum concentrations of 440 and 520 ppm, respectively (Fig. 8e). This accumulation was attributed to the absence of an intermediate stripping step between cycles, leading to gradual enrichment in the aqueous phase. In contrast to single-phase DES reuse, which typically requires an additional acidic solution to restore the leaching capacity of the DES by protonation,[53] the two-phase system exhibited stable performance without such intervention. Overall, these results demonstrated that the DES maintained its excellent leaching performance over three cycles without requiring regeneration or external stripping, highlighting its practical reusability for closed-loop metal recovery.

Conclusions

This work developed an efficient and selective leaching system comprising an oxidative solution as the secondary phase for the

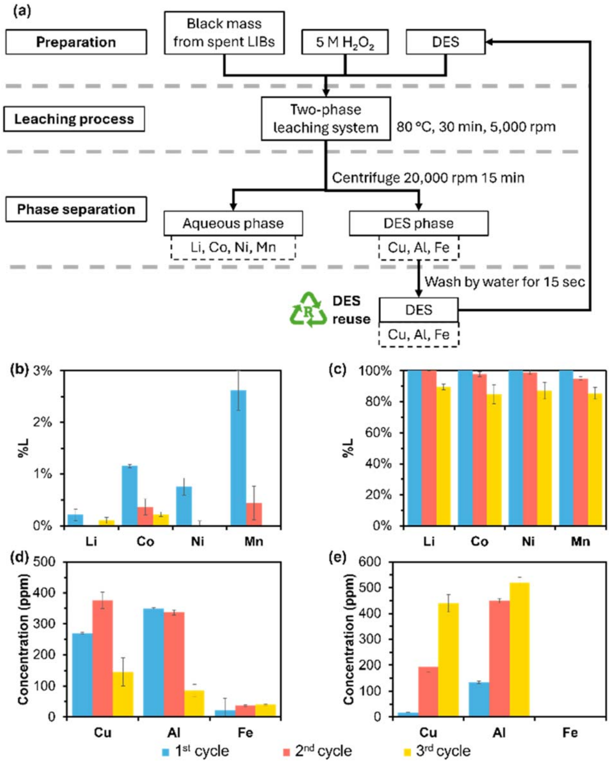

Fig. 8 (a) Schematic of closed-loop metal recovery from black masses using a reusable DES in a two-phase leaching system. Efficiencies of leaching Li, Co, Ni, and Mn into the (b) organic phase and (c) the aqueous phase over three cycles of leaching without additional stripping and regeneration of the DES. Concentrations of Cu, Al, and Fe in the (d) organic phase and (e) aqueous phase over three cycles of leaching. Leaching was conducted at 80 °C for 30 min using a solid-to-liquid ratio of 10 mg mL^{-1} and 5 M H_2O_2 as the aqueous phase.

recovery of Li, Co, Ni and Mn from black masses. The synergistic effect between HTTA–TOPO (DES) and H_2O_2 in the two-phase leaching system enabled leaching, separation, and stripping in a single-step process. Under optimized conditions (80 °C, 30 min, 500 rpm, 10 mg per mL black mass loading, DES-to-aqueous ratio 1 : 1, and 5 M H_2O_2 as the aqueous phase), this system exhibited excellent leaching efficiencies for Li (98%), Co (94%), Ni (94%), and Mn (98%) into the aqueous phase, with low extraction of Cu (9%) and Al (31%). Conversely, Cu (73%), Al (54%), Fe (76%) were predominately distributed into the DES phase indicating high phase-selective metal partitioning. The DES dilution, DES-to-aqueous ratio, type of aqueous solution, and aqueous solution pH were considered the key variables that appreciably influenced metal migration. Notably, the equilibrium pH played a decisive role: Li migration to the aqueous phase was preferred at $pH_{eq} < 7$ and optimal at pH_{eq} 4, while Co, Ni, and Mn were effectively transferred to the aqueous phase at $pH_{eq} < 2$. Li transmigration was related to proton transfer from the DES phase to the aqueous phase. In particular, the higher the number of protons transferred, the greater the number of Li ions trapped in the DES phase owing to replacement of protons. Cu and Al migration was influenced by the kinetics and thermodynamics of the leaching system. According to the structural analysis, the core structures of HTTA and TOPO in the DES were maintained after leaching in the two-phase system with H_2O_2 as the aqueous phase. Degradation of HTTA in the presence of the oxidative solution did not occur in this work. The DES maintained its excellent leaching performance over three cycles without requiring regeneration and external stripping. The concentrations of Cu and Al in the aqueous phase gradually increased with each successive cycle, which became a drawback in terms of selectivity for Li, Co, Ni and Mn over Cu, Al, and Fe in the two-phase leaching system. Ultimately, this research demonstrated an effective and efficient approach for the direct recovery of Li, Co, Ni and Mn from black masses.

Author contributions

Kevin Septioga: conceptualization, data curation, writing – original draft preparation, reviewing, and editing. Adroit T. N. Fajar: conceptualization, reviewing, and editing. Rie Wakabayashi: conceptualization, reviewing, and editing. Masahiro Goto: conceptualization, supervision, reviewing, and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the manuscript and supplementary information (SI). Supplementary information: details such as metal composition in the black mass, images of DES, additional variation condition for leaching reaction (*e.g.*, pH, type of aqueous phase), FTIR spectra, ^{1}H-NMR and ^{13}C-NMR results, and metal distribution data in the two-phase system. See DOI: **https://doi.org/10.1039/d5su00657k**.

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