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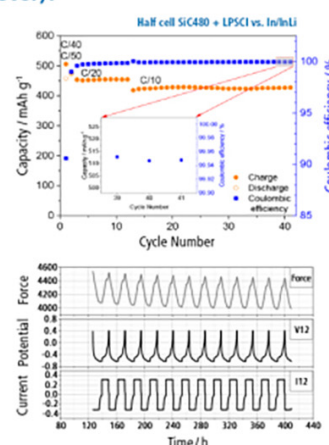
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Selective Electrochemical Recovery of Valuable Metals from Spent Lithium-Ion Batteries Using a Betaine-Based Deep Eutectic Solvent

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The rapid growth in lithium-ion battery (LIB) deployment has led to increasing volumes of end-of-life batteries, creating an urgent need for sustainable recycling technologies capable of recovering critical metals from complex waste streams. Although leaching has been successfully shown in various DES systems, selective recovery of metals/metal oxides still remain a challenge. In this study, a deep eutectic solvent (DES) of betaine hydrochloride and ethylene glycol is employed as a green medium for both dissolution of valuable metals and selective electrochemical recovery from LIB black mass. Rapid dissolution of Li, Ni, Co, and Mn together with 86% Cu was achieved within 30 min at 100 °C. Based on electrochemical studies, it was observed that temperature and potential/ current can be adjusted for selective metal recovery. Copper was selectively deposited at 40 °C, while increasing the deposition temperature to 60 and 80 °C enabled deposition of Ni–Co alloys. Manganese was recovered from the remaining electrolyte via carbonate precipitation. The integrated process achieved overall recovery efficiencies of approximately 98% for Cu, ~90% for Ni and Co, and ~80% for Mn. Thus, this work demonstrates a selective and environmentally benign strategy for recovering valuable metals from complex LIB waste streams, providing a promising pathway toward circular battery recycling.

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Lithium-ion batteries (LIBs) are essential to modern energy storage, underpinning applications ranging from portable electronics to electric vehicles and grid integration of renewable energy. Their high energy density, extended cycle life, low self-discharge and compact form factor have accelerated their deployment worldwide. However, the inevitable end-of-life of these devices is creating a rapidly expanding stream of spent batteries. Global projections estimate that by 2040, annual waste generation will exceed 8 million tons, coinciding with more than 23 million electric vehicle sales expected by 2030.^{1–9} Spent LIBs contain toxic electrolytes and transition metals that pose serious environmental risks if untreated, yet they also represent a valuable secondary resource. Cathode active materials and associated components contain 5%–25% Co, 5%–10% Ni, 5%–10% Mn, 5%–7% Li, 15%–20% Al, 5%–7% Cu and graphite.^{1,10,11} Effective recycling of these metals is therefore critical both to mitigate environmental hazards and to reduce reliance on primary mining, which is concentrated in geopolitically sensitive regions.^{8,12–15}

Recycling of LIBs is currently dominated by pyrometallurgical and hydrometallurgical processes.^{16–19} Pyrometallurgy, operating at temperatures exceeding 1400 °C, yields alloys rich in Co, Ni and Cu but requires large energy inputs, produces greenhouse gases and volatile emissions, and fails to recover light metals such as Li and Al efficiently.^{17,18,20–22} Hydrometallurgy, involving acid or alkaline leaching followed by precipitation, solvent extraction or electrochemical recovery, is attractive due to lower energy consumption and the potential for high-purity product recovery. However, it typically employs strong mineral acids (HCl, H₂SO₄, HNO₃) and reducing agent (H₂O₂), which are hazardous to handle, corrosive to equipment and generate secondary wastes requiring neutralisation.^{18,19,23–25} While organic acids such as citric, tartaric or aspartic acid have been tested as greener leaching agents, their efficiency remains limited and often requires additional steps, such as the use of ultrasonic treatment or reducing agents, thereby increasing overall recovery costs.^{23,26–28} These limitations highlight the urgent need for

more sustainable leaching strategies capable of achieving high metal recovery while reducing energy and chemical inputs.

In recent years, deep eutectic solvents (DESs) have emerged as promising green alternatives. DESs are mixtures of hydrogen bond donors (HBDs) and acceptors (HBAs) that form a eutectic system with a melting point significantly lower than that of the individual components, due to extensive hydrogen bonding.^{29,30} Their advantages include low volatility, non-flammability, low toxicity, biodegradability, and simple, low-cost preparation.^{24,29,31} Importantly, their physicochemical properties are highly tuneable through the selection of HBA and HBD components, enabling the design of solvents with desirable acidity, viscosity, coordination ability or reducing strength.^{15,32,33} DESs have already shown strong potential for metal dissolution due to their intrinsic redox activity, allowing them to leach transition metal oxides without additional reducing agents.^{15,27,29} Their wide electrochemical windows (EWs) also make them suitable electrolytes for electrodeposition, enabling selective recovery of metals from solution and facilitating solvent reuse.^{19,24}

Several DES formulations have been investigated for the recovery of LIB cathode materials. Yang et al.³⁴ employed a guanidine hydrochloride-formic acid DES to leach spent LIBs, achieving efficiencies of 99.79% for Li, 98.86% for Ni, 99.51% for Co and 96.12% for Mn. Li et al.³⁵ reported a maleic acid-ethylene glycol DES capable of dissolving LiCoO₂ with Co and Li recovery rates of 98.3% and 98.4%, respectively. Zhang et al.³⁶ demonstrated the use of a tetraethylammonium chloride-ascorbic acid DES, which achieved leaching efficiencies above 99% for Li, Ni, Co and Mn. Similarly, Zhen et al.³⁷ developed a ternary choline chloride-DL-malic acid-glycerol DES, reporting recovery rates of 94.6% for Ni, 96.8% for Co, 93.8% for Mn and 96.4% for Li. Among the DES systems investigated, a betaine hydrochloride-ethylene glycol (Bet-HCl:EG) DES has also recently been reported to exhibit excellent leaching capability.^{38,39} Luo et al. demonstrated that this system can rapidly dissolve NMC cathode materials, achieving leaching efficiencies close to 99% within 10 min at 140 °C, while a subsequent study using the same DES recovered metals from the leachate via precipitation.

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Despite this progress, most reported studies recover dissolved metals by precipitation, which can compromise solvent integrity and reduce recyclability.⁴⁰ Several reports have demonstrated the feasibility of electrochemical recovery, but these have been largely restricted to simplified or single-component systems. For instance, Cheng et al.⁴¹ employed a multistage process combining formic acid leaching with a ternary DES (choline chloride, ethylene glycol, tartaric acid), enabling selective precipitation of Ni and electrodeposition of Co(OH)₂ from NMC811 cathodes. Similarly, Chen et al.⁴² used choline chloride-succinic acid and choline chloride-oxalic acid DESs to electrochemically recover Co(OH)₂. Wang et al.³¹ and Aldana-Gonzalez et al.⁴³ demonstrated Co recovery from LCO using choline chloride-urea. These examples illustrate that while electrodeposition from DESs is feasible, current approaches are constrained by narrowly defined feedstocks. Therefore, development of a robust process capable of handling complex, mixed-battery waste streams remains a critical challenge for advancing DES-based recycling towards scalable application.

Herein, we present a sustainable strategy for selective recovery of metals from black mass (BM) using a Bet-HCL:EG DES. The solvent enables rapid leaching of transition metals under mild conditions, followed by sequential electrodeposition for selective recovery of Cu and Co/Ni alloys, and precipitation of Mn. This approach integrates efficient dissolution with electrochemical selectivity, offering an environmentally benign alternative to conventional hydrometallurgical methods.

Materials and Methods

Materials.—Black mass (BM) was obtained from a domestic recycling company, Lithium Ion Battery Recycling Ltd. Betaine hydrochloride ($\geq 99\%$), ethylene glycol ($\geq 99.5\%$), cobalt (II,III) oxide (Co₃O₄, 99.7%), and nickel (II) oxide (NiO, 99%) were purchased from Thermo Scientific. Manganese (III) oxide (Mn₂O₃, 99.4%) was purchased from Nanografi, and copper foam (99.9%) was sourced from PI-KEM. All reagents and solvents used in the study were of analytical grade and used without further purification.

Methods.—*Representative sample preparation of BM.*—Representative sampling is a critical step in the recycling of LIBs. This study utilized the CAPCO sample divider to ensure precision and reliability in sample preparation. A specific amount of BM was weighed and introduced into the feed hopper of the CAPCO divider, following the manufacturer's guidelines. The device has a rotating mechanism that equally spreads the material into six containers. To get a representative sample, three symmetrical containers were chosen, and the contents were repeatedly subdivided to attain a representative sample.

Preparation of the DES.—Mixtures of Bet-HCl and EG were prepared in molar ratios ranging from 1:4 to 1:10. The components were placed in a four-neck conical flask and heated to 100 °C in an oil bath under continuous magnetic stirring at 300 rpm. Heating and stirring were maintained until a clear, homogeneous and transparent liquid was obtained. The mixtures were then cooled to room temperature and stored in sealed containers for further investigation.

Experimental.—Leaching experiments were carried out to extract metal ions from the BM using the described DES. The One-factor-at-a-time (OFAT) experimental approach was employed to examine the influence of leaching time, temperature, and solid-to-liquid (S/L) ratio on metal dissolution efficiency. In each experiment, 5 ml of the DES was preheated to the target temperature (80 °C, 100 °C, or 120 °C) after which, a defined amount of BM corresponding to S/L ratios of 10 g l⁻¹, 50 g l⁻¹, and 100 g l⁻¹ was added. Leaching was performed at the set temperature under constant agitation at 500 rpm using a magnetic stirrer. The leaching time was varied across four intervals: 15, 30, 45, and 60 min. Following leaching, the slurry was centrifuged at 10 000 rpm for 30 min to separate the liquid

leachate from the remaining solid residues, including undissolved particles and binder materials. The supernatant was then collected and analyzed using ICP-OES to quantify the leaching efficiency of the target metals.

Calculation of leaching efficiency.—The leaching efficiency (η_M) was calculated:

$$\eta_M = \left(\frac{C_M \times V}{m_0 \times w_M} \right) \times 100$$

where η_M is the leaching rate of the corresponding metals in the leachate, C_M (mg l⁻¹) is the concentration of metals in the leachate, V (L) is the volume of the leachate, m_0 (mg) is the cathode materials initial mass, and w_M is the mass fraction of metals in the cathode materials.

Electrochemical studies and metal recovery.—Electrochemical measurements and metal recovery experiments were carried out using a standard three-electrode cell configuration. Graphite sheets (RS Pro) were used as both the working and counter electrodes. A platinum wire was used as a quasi-reference electrode. All electrochemical experiments were performed using a Biologic VSP-3e potentiostat, with control and data acquisition managed via EC-Lab software. To investigate the electrochemical behavior of metal species in the DES, cyclic voltammetry (CV) was used. Galvanostatic and potentiostatic techniques were used for selective recovery of metals/ alloys.

Precipitation of manganese and lithium separation.—After sequential electrodeposition, manganese was recovered from the residual leachate by chemical precipitation. A 1 M sodium carbonate (Na₂CO₃) solution was added dropwise under constant stirring at ambient temperature, resulting in the selective precipitation of manganese carbonate (MnCO₃). Lithium remained dissolved in the DES owing to the high solubility of Li₂CO₃, enabling effective separation from manganese.

A schematic flowchart summarizing the overall experimental procedure for DES preparation, BM leaching, and metal recovery is provided in Fig. S.1.

Metal recovery rate calculation.—The recovery rates of individual metals were quantified based on the mass of recovered metals and the initial metal concentrations in the leachate, as determined by ICP-OES. Each metal's recovery efficiency was calculated using the following equation:

$$\text{Recovery Rate (\%)} = \left(\frac{C_M \times V}{C_{0,M} \times V_{\text{Leachate}}} \right) \times 100$$

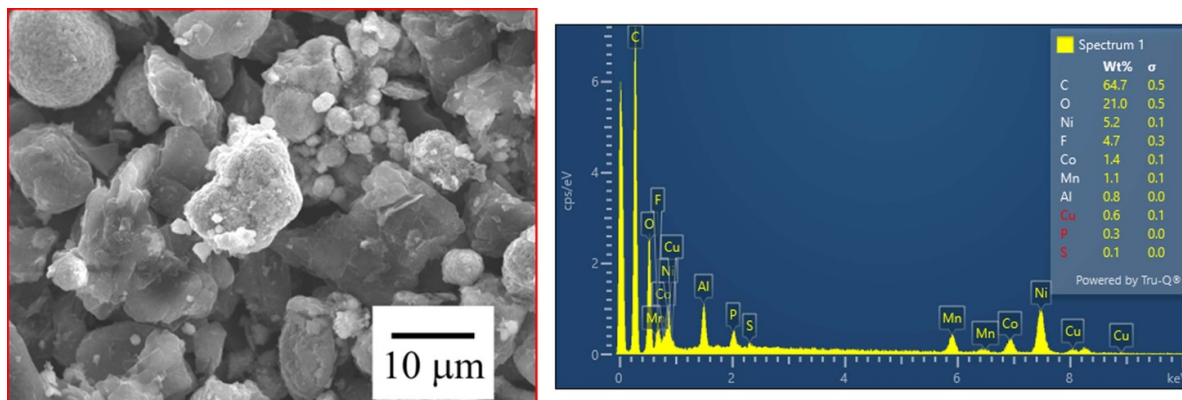
where C_M (mg l⁻¹) is the concentration of the recovered metal in the digested solution (diluted HNO₃), V (L) is the volume of the digested solution, $C_{0,M}$ (mg l⁻¹) is the initial concentration of the metal in the leachate, and V_{Leachate} (L) is the total volume of the leachate.

Unless otherwise stated, all experiments and measurements were performed in triplicate to ensure reproducibility, and the reported results represent the mean values of three independent measurements.

Characterisation.—*Thermal stability of DES.*—The thermal stability of the mixtures was evaluated using thermogravimetric analysis (TGA) on a Mettler Toledo system. For dynamic measurements, a defined mass of mixture was placed in an alumina crucible and heated from 25 to 230 °C at 5 °C min⁻¹ under a constant nitrogen flow (20 ml min⁻¹). The resulting thermograms were used to determine decomposition behavior and establish the operational temperature limits of the solvent system. Complementary isothermal TGA experiments were performed on DES at 25, 40, 60,

Table I. Elemental mass fractions (wt%) of the BM, determined by ICP-OES.

Element	Al	Co	Cu	Fe	Li	Mn	Ni	P
Mass Fraction (%)	1.59 ± 0.04	2.25 ± 0.05	3.18 ± 0.18	0.74 ± 0.06	1.89 ± 0.04	2.06 ± 0.06	7.84 ± 0.12	1.22 ± 0.04

**Figure 1.** SEM and corresponding EDS spectra of the as-received BM.

80, and 100 °C for 24 h under the same nitrogen atmosphere (20 ml min⁻¹). These measurements enabled evaluation of long-term stability and mass retention under constant operating conditions relevant to leaching and recovery experiments.

Spectroscopic analysis and speciation studies.—FTIR spectra were collected using an IRSpirit-X spectrometer (Shimadzu, Japan), while Raman measurements were performed on a confocal Raman microscope (Stellar-REN) equipped with a 514 nm excitation laser and a diffraction grating of 1800 lines mm⁻¹. Spectral detection was achieved using a Renishaw CCD camera. UV–Vis absorption spectra were collected using a Shimadzu UV-1900i UV-Vis Spectrophotometer operating over a wavelength range of 190–1100 nm with a double-beam optical configuration and a spectral bandwidth of 1 nm.

Viscosity measurements.—The viscosity of the DES was measured between 40 and 100 °C using an automatic rolling-ball micro-viscometer (Anton Paar GmbH, Graz, Austria). Each measurement was performed in triplicate, and the average values are reported.

Structural and morphological characterisation.—Crystalline phases of the samples were characterized using X-ray diffraction (XRD). The XRD was carried out on a Bruker D8 Advance diffractometer (Germany) equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a LynxEyeTM silicon strip detector. Surface morphology and microstructural features were examined using a scanning electron microscope (JEOL IT200LV, USA), equipped with an Oxford Instruments energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis.

Elemental analysis.—Elemental composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) to quantify metal concentrations in the BM, leachates, recovered products and residual solutions. These data were used to evaluate leaching efficiency and calculate metal recovery at each process stage.

Analyses were performed on an FMX46 SpectroGreen ICP-OES (SpectroAmetek) equipped with dual side-on interface and ASX520 autosampler. Samples were introduced via a cross-flow nebulizer and Scott-type spray chamber at a flow rate of 2 ml min⁻¹, with nebulizer argon flow at 0.8 l min⁻¹. The torch was operated

at 1150 W with coolant and auxiliary argon flows of 13 l min⁻¹ and 0.8 l min⁻¹, respectively. Optical ranges of 285.9–770.6 nm and 163–285.7 nm were measured for 8 s and 28 s, respectively, with three replicate measurements. Sample uptake and stabilization time was 60 s. Calibration was carried out between 0–10 ppm for Al (167.078 nm), Co (228.616 nm), Cu (224.700 nm), Fe (238.204 nm), Li (670.780 nm), Mn (257.611 nm), Ni (231.604 nm) and Zn (206.200 nm), and between 0–250 ppm for P (177.495 nm). All calibration curves had correlation coefficients (*r*) greater than 0.996.

Results and Discussion

BM characterisation.—**Elemental composition of BM by ICP-OES.**—The elemental composition of the BM was determined by ICP-OES following microwave-assisted acid digestion. Measurements were conducted in triplicate to account for the compositional heterogeneity of spent LIB waste, and the average concentrations are summarized in Table I. The analysis revealed that the BM contained Nickel with an average mass fraction of 7.84%. Copper (3.18%) and cobalt (2.25%) were also present from current collector residues and cathode materials, respectively. Manganese (2.06%) and lithium (1.89%) were present in moderate amounts, while aluminum (1.59%) and iron (0.74%) were attributed to contributions from Al current collectors and either LFP-type cathodes or Fe introduced during the crushing process. The presence of phosphorus (1.22%) further supports the contribution of LFP-derived phases, although its slightly elevated content may also reflect residues from the electrolyte.

Morphological and elemental characterisation of BM by SEM/EDS.—Figure 1 shows the SEM/EDS of the as-received BM. The material exhibited a heterogeneous microstructure composed of flake-like graphite and agglomerated cathode particles with typical sizes of 5–10 µm.^{44,45}

EDS analysis of selected regions corroborated the multi-phase composition. Carbon was the dominant element (64.7 wt%), consistent with the extensive presence of graphite. Oxygen (21.0 wt%) was also abundant, likely originating from metal oxides and degradation products of the polymer binder. Nickel was present at 5.2 wt%, representing the most abundant transition metal in the sample. Cobalt (1.4 wt%) and manganese (1.1 wt%) were detected at lower concentrations. Fluorine (4.7 wt%) was present at significant levels, attributed to polyvinylidene fluoride (PVDF). Aluminum (0.8 wt%)

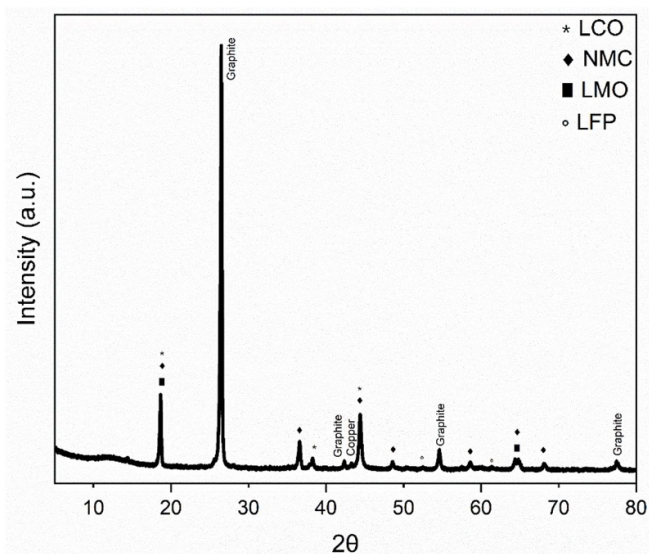


Figure 2. XRD pattern of the as-received BM, identifying crystalline phases present in the sample.

and copper (0.6 wt%) were detected, corresponding to fragments of current collectors, suggesting incomplete mechanical separation. Phosphorus (0.3 wt%) and sulfur (0.1 wt%) are associated with residual LiFePO_4 and sulfur-containing electrolyte components, respectively.

Structural characterisation of BM by XRD.—The crystalline phases present in the BM were investigated by XRD, and the resulting diffraction pattern is shown in Fig. 2. The major phases were assigned to graphitic carbon and layered transition-metal oxides, particularly nickel-rich lithium nickel manganese cobalt oxide (NMC; ICSD 8362) and lithium cobalt oxide (LCO; PDF 00-016-0427).^{46,47} Minor reflections were attributed to spinel LiMn_2O_4 (LMO; JCPDS 35-0782), olivine LiFePO_4 (LFP; ICSD 072545), and metallic copper.^{48,49} The coexistence of these crystalline phases indicates that the BM originated from a mixture of different LIB cathode chemistries.

DES preparation and characterisation.—The Bet-HCl:EG DES was prepared by mixing the components at different molar ratios and heating until a homogeneous liquid was obtained. The stability of the mixtures was strongly dependent on the molar composition, with stable and transparent liquids obtained for ratios $\geq 1:7$. Thermal stability, spectroscopic analysis, and viscosity measurements were performed to confirm DES formation and evaluate its physicochemical properties. The results indicate that the DES remains thermally stable up to approximately 110 °C and exhibits decreasing viscosity with increasing temperature, which is favorable for mass transfer during leaching and electrochemical recovery. Detailed characterization data, including optical observations, TGA analysis, FTIR spectra, and viscosity measurements, are provided in the Supporting Information (Figs. S2–S4 and Table S1).

Leaching optimization.—Leaching parameters for the recovery of metals from BM were optimized by evaluating the effects of leaching time, S/L ratio, and temperature. Efficient dissolution of Li, Ni, Co, and Mn were achieved within short leaching times, while Cu exhibited slightly lower but still significant recovery. Increasing the solid loading beyond a threshold reduced metal recoveries, likely due to increased viscosity and limitations in metal-ligand interactions within the DES. Temperature strongly influenced leaching kinetics, with optimal dissolution obtained at 100 °C. Based on these

results, the optimal leaching conditions were identified as 30 min at 100 °C with a S/L ratio of 50 g l⁻¹. The complete optimization data and detailed discussion are provided in the Supporting Information (Fig. S5).

Post leaching BM characterisation.—SEM of the BM after leaching (Fig. 3a) showed a morphology dominated by flake-like graphite layers. The more homogeneous surface compared to the untreated material is seen in Fig. 3a indicating removal of cathode-derived phases by selective dissolution. EDS spectra (Fig. S.6) confirmed this, showing dominant C and O peaks with residual Al.

XRD patterns of the post-leaching BM (Fig. 3b) revealed substantial structural changes. Reflections from layered transition metal oxides were markedly suppressed, consistent with their dissolution. The peaks at $2\theta \approx 26.4^\circ$, 42.3° , 54.5° and 77.4° correspond to the (002), (100), (004) and (110) planes of graphitic carbon, confirming the presence of graphite in the solid residue.

Spectroscopic analysis of the DES Before and after leaching.—Spectroscopic analyses were performed to evaluate possible changes in the chemical speciation of the DES after metal dissolution from the BM. FTIR and Raman spectra of the leachate (Figure S.7 and S.8) showed no significant changes compared with the blank solvent, indicating that the overall molecular structure of the DES remained largely preserved after leaching. However, a noticeable color change of the solvent from transparent to dark green suggested the formation of metal-DES complexes (Fig. S.9). UV–Vis analysis further confirmed the presence of chloride-based metal complexes in the leachate, consistent with speciation behavior previously reported for Bet-HCl: EG DES system (Fig. S.10).^{38,39}

Electrochemical studies.—The electrochemical window (EW) of the DES was systematically examined using CV at 40 °C, 60 °C, and 80 °C. Figure 4 shows the CV of the DES at different temperatures. At 40 °C, the DES exhibits a wide EW of ~ 2.25 V with cathodic decomposition commencing at -1.6 V and anodic decomposition occurring at $+0.65$ V. At 60 °C, cathodic decomposition shifted to -1.3 V, with anodic breakdown initiating at $+0.75$ V, reducing the EW to ~ 2.05 V. At 80 °C, decomposition began earlier, at -1.2 V and $+0.8$ V, narrowing the window further to ~ 2.00 V. The progressive reduction in EW with temperature reflects the behavior of hydrogen-bonded solvent systems, where elevated temperature lowers the overpotentials for decomposition due to increased ionic mobility and weakened hydrogen bonding.^{50,51}

Electrochemical responses of model systems.—To identify the electrochemical behavior of individual metals in the DES, CV was first performed using model systems containing individually dissolved Cu, Ni, Co, and Mn species Figs. (5–8).

The Cu-containing DES exhibited well-defined redox features within the EW. All CVs shows two distinct reduction/oxidation processes, which are consistent with the literature.^{52–55} At 40 °C (Fig. 5a), two cathodic processes were observed. The first cathodic peak appeared between -0.5 and 0.0 V (centered near -0.2 V), corresponding to the reduction of Cu^{2+} to Cu^+ . A second cathodic process occurred at more negative potentials between -1.0 and -1.4 V, which corresponds to reduction of Cu^+ to metallic Cu. During the reverse scan, two corresponding anodic stripping peaks were detected. The first stripping feature appeared between -0.8 and -0.1 V (centered near -0.5 V) corresponding to oxidation of Cu^0 to Cu^+ , while a second oxidation peak was observed between 0.0 and 0.6 V attributing to oxidation of Cu^+ to Cu^{2+} .

The two-step redox behavior arises from the stabilization of both Cu(I) and Cu(II) species in the chloride-rich DES through complex formation with Cl^- ions.⁵³ Accordingly, copper reduction proceeds via sequential electron-transfer reactions involving chloro-complexes:

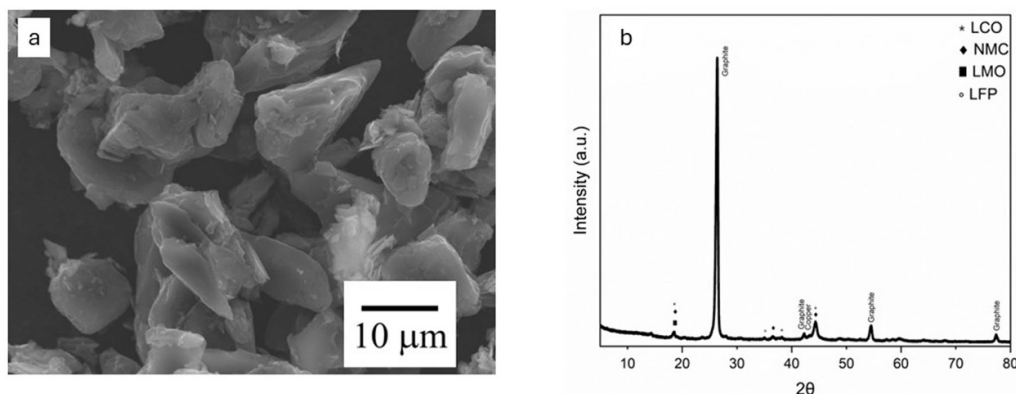


Figure 3. (a) SEM image and (b) XRD pattern of post-leaching BM.

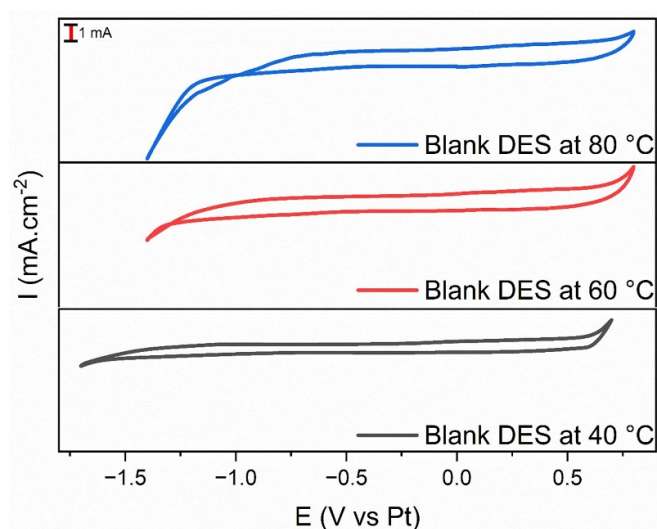
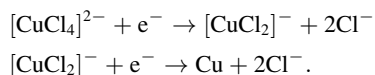


Figure 4. Cyclic voltammograms of blank DES recorded at different temperatures at a scan rate of 10 mV s⁻¹.



Increasing the temperature to 60 °C and 80 °C shifted the Cu reduction peak slightly towards less negative potentials with increased current densities (Figs. 5b and 5c).

The CV of Mn-containing system exhibited broad and weakly resolved Mn redox features. At 40 °C (Fig. 6a), only a weak cathodic feature was observed near -0.25 V and a shoulder starting near -1.0 V, together with three small anodic peaks at approximately -0.90, -0.70 and 0.00 V, indicating limited Mn deposition and kinetically hindered reoxidation. At 60 °C (Fig. 6b), the cathodic feature near -0.15 V and the anodic peak at about -0.70 V became more pronounced. At 80 °C (Fig. 6c), the Mn response was further enhanced, and two anodic peaks at approximately -0.85 and -0.70 V could be distinguished, reflecting improved Mn deposition kinetics at elevated temperature. Notably, a clear current loop observed during the reverse scan at 60 °C and 80 °C is indicative of a nucleation overpotential associated with Mn deposition on the graphite electrode. Such behavior is characteristic of metal electrodeposition on a foreign substrate, where an additional overpotential is required to initiate nucleation.⁵⁶ Overall, the presence of broad cathodic waves, shoulder features, and incomplete anodic stripping is consistent with literature reported for Mn in ionic liquids and DESs,

where Mn reduction is nucleation-controlled and the deposited Mn is re-oxidised only partially.^{56–59}

The CV of Co-containing system (Figs. 7a–7c) exhibit typical features of cobalt electrodeposition in deep eutectic solvents.^{60–62} At 40 °C, a broad cathodic wave corresponding to Co(II) reduction to metallic Co is observed, accompanied by an anodic stripping peak. The presence of a single cathodic and anodic peak pair suggests a one-step, two-electron transfer process. Increasing the temperature to 60 °C enhances both cathodic and anodic currents, reflecting improved mass transport and charge transfer. Additionally, the reduction peak shifts towards more positive potentials, which can be attributed to decreased viscosity and increased ionic conductivity of the DES at elevated temperatures. This reduces polarization effects and facilitates electron transfer, while higher thermal energy accelerates the mobility of electroactive species.⁶¹ At 80 °C, the electrochemical response becomes more pronounced, confirming facilitated cobalt deposition. Notably, a nucleation loop is observed at all temperatures at more negative potentials, indicating that the deposition process follows a nucleation and growth mechanism.⁶⁰ Overall, the behavior is consistent with a diffusion-controlled, quasi-reversible Co(II)/Co(0) system governed by nucleation and growth kinetics.

Similar to the Co-containing system, the CVs of the Ni-containing system (Figs. 8a–8c) exhibit a strong temperature dependence. At 40 °C, a broad cathodic wave with minimal anodic stripping indicates sluggish kinetics and a high overpotential requirement for Ni(II) reduction. Increasing the temperature to 60 °C and 80 °C leads to a significant enhancement in current densities and a shift of the reduction onset towards less negative potentials, reflecting improved electrochemical kinetics. Notably, the reduction feature becomes more distinct at 80 °C compared to 40 and 60 °C, indicating facilitated Ni deposition at elevated temperature. Concurrently, the anodic peak shifts towards more positive potentials with increasing temperature, suggesting improved stripping behavior and increased deposit stability.

A nucleation loop observed at higher temperatures confirms that Ni deposition proceeds via a nucleation and growth mechanism. The increase in peak currents at elevated temperatures is attributed not only to improved conductivity of the DES but also to enhanced electrochemical kinetics, which have been associated with the increased presence of tetrahedral $[\text{NiCl}_4]^{2-}$ species in chloride-rich systems.⁶³

Electrochemical responses of leachate.—CV was used to investigate the redox behavior of the leachate in the DES at 40, 60 and 80 °C (Fig. 9). At all temperatures, a distinct peak (c_1) was observed between -0.1 and -0.5 V (centered at -0.25 V), consistent with the reduction of Cu and/or Mn, as confirmed by the Cu and Mn reference systems. At more negative potentials, broad cathodic shoulders (c_2) between -1.0 and -1.3 V became more pronounced at

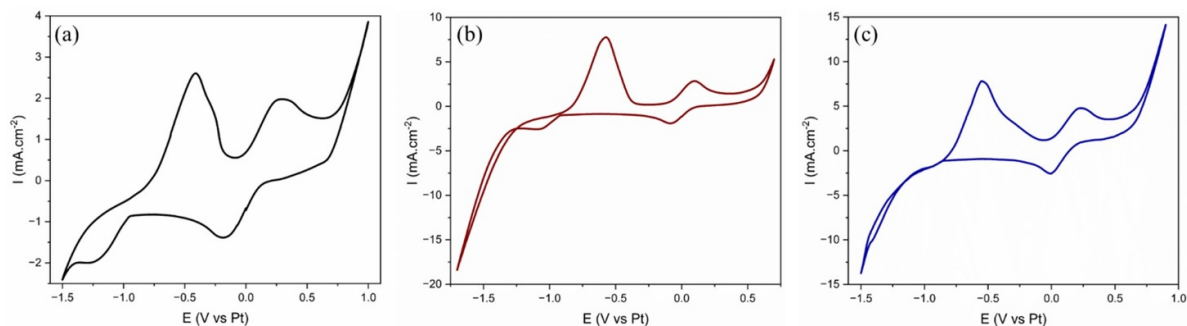


Figure 5. Cyclic voltammograms of Cu-containing DES at different temperatures: (a) 40 °C, (b) 60 °C, and (c) 80 °C at a scan rate of 10 mV s⁻¹.

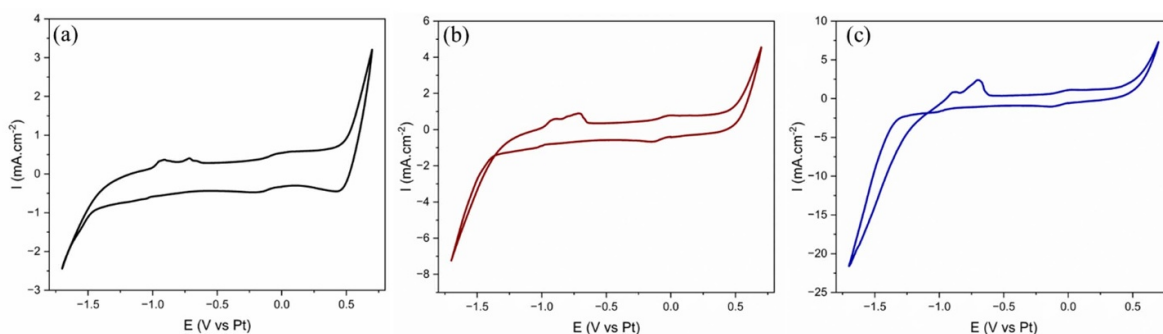


Figure 6. Cyclic voltammograms of Mn-containing DES at different temperatures: (a) 40 °C, (b) 60 °C, and (c) 80 °C at a scan rate of 10 mV s⁻¹.

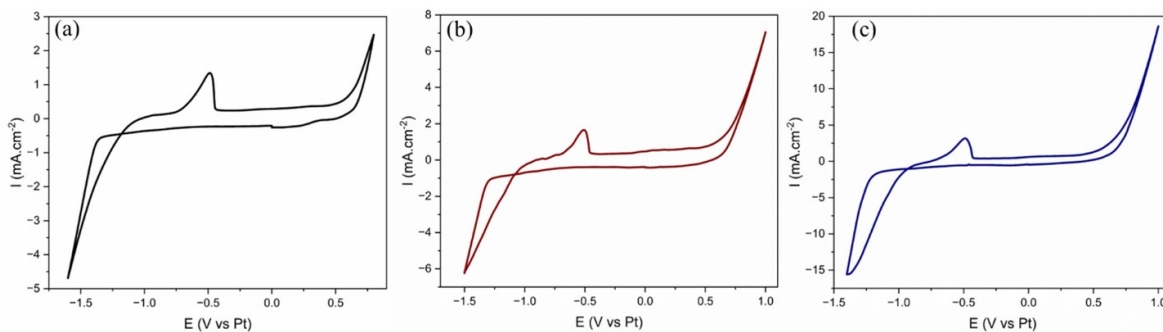


Figure 7. Cyclic voltammograms of Co-containing DES at different temperatures: (a) 40 °C, (b) 60 °C, and (c) 80 °C at a scan rate of 10 mV s⁻¹.

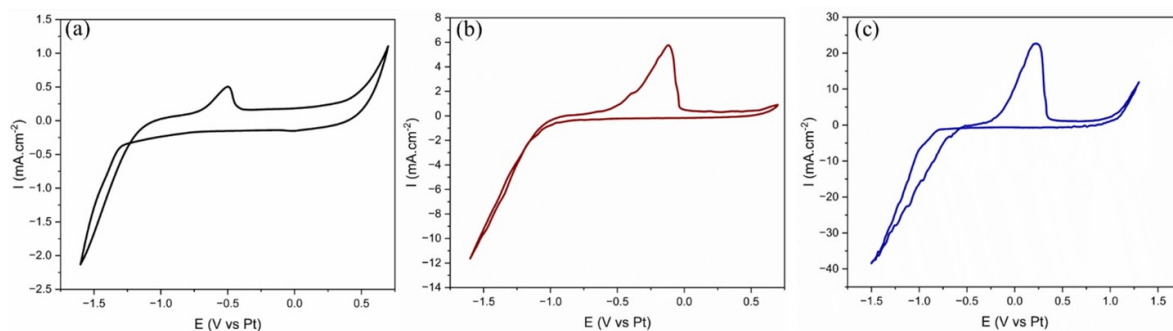


Figure 8. Cyclic voltammograms of Ni-containing DES at different temperatures: (a) 40 °C, (b) 60 °C, and (c) 80 °C at a scan rate of 10 mV s⁻¹.

elevated temperatures, corresponding to transition metals reduction with contributions from electrolyte decomposition. In the anodic scans, additional features were observed. At 60 and 80 °C, an oxidation peak (a_1) between -0.8 and -0.4 V (centered at -0.6 V)

developed a distinct shoulder (a_1^*) that was absent at 40 °C. A further oxidation peak (a_2), common to all three temperatures, appeared between -0.2 and 0.3 V (centered at 0.1 V). The combination of these anodic and cathodic signals suggests overlapping processes

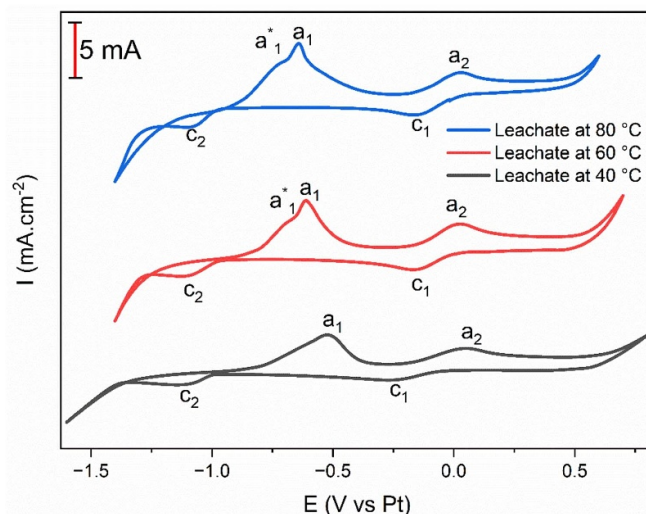


Figure 9. Cyclic voltammograms of leachate at different temperatures at a scan rate of 10 mV s^{-1} .

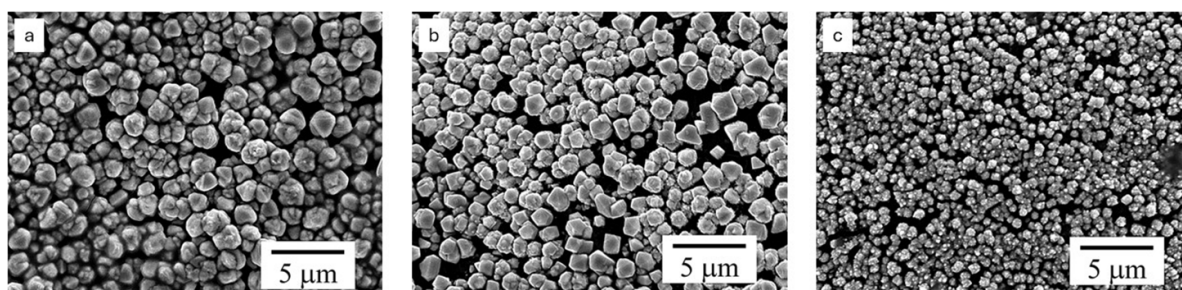


Figure 10. SEM images of copper deposits obtained during sequential electrodeposition: (a) first step, (b) second step, and (c) third step.

associated with transition metal deposition and stripping, with possible alloy deposition at higher temperatures. Comparing the CV of BM and model systems, copper can be selectively recovered at 40°C , while Ni and Co are co-deposited as alloys at higher temperatures.

Selective metal recovery.—Copper recovery at 40°C .—For Cu recovery, three sequential galvanostatic deposition steps were carried out at 40°C under a constant current of 1.8 mA , each lasting 3 h .

To assess the morphology and elemental purity of the deposits, SEM and EDS analyses were performed after each step. SEM images of copper deposits are presented in Fig. 10 and the corresponding EDS spectra are provided in Fig. S.11. In the first deposition step, the deposit surface was uniform with spherical to cauliflower-like copper particles. The average particle size ranged from 300 to 600 nm , with agglomerates reaching $\sim 2 \mu\text{m}$. In the second deposition step, the surface displayed less dense coverage with clear signs of particle faceting. Average particle sizes were ~ 300 – 600 nm . The third step resulted in a reduction of average particle size (~ 100 – 200 nm). The surface appeared more compact, with homogeneous coverage and few visible voids. Across all three steps, the morphology remained nanocrystalline and granular, with uniform texture and no evidence of irregularities or structural breakdown.

EDS spectra for each deposition step confirmed that copper was the dominant element present, validating the success of selective recovery during the first three deposition steps. Trace amounts of nickel and cobalt were also detected, consistent with overlapping redox potentials and possible minor co-deposition from the leachate. The presence of oxygen is attributed to mild surface oxidation of copper upon air exposure. Carbon signals come from both the graphite substrate and some organic components of the DES.

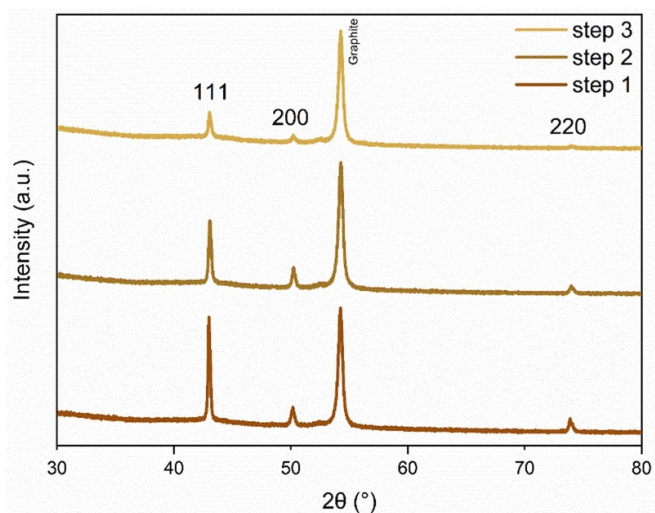


Figure 11. XRD patterns of deposits obtained during three stages of selective copper recovery.

EDS elemental mapping of the copper deposit obtained in deposition step 1 was performed to evaluate the elemental distribution, and the corresponding results are presented in Fig. S12 of the Supporting Information.

XRD analysis was conducted on the copper deposits obtained after each of the three sequential electrodeposition steps (Fig. 11).

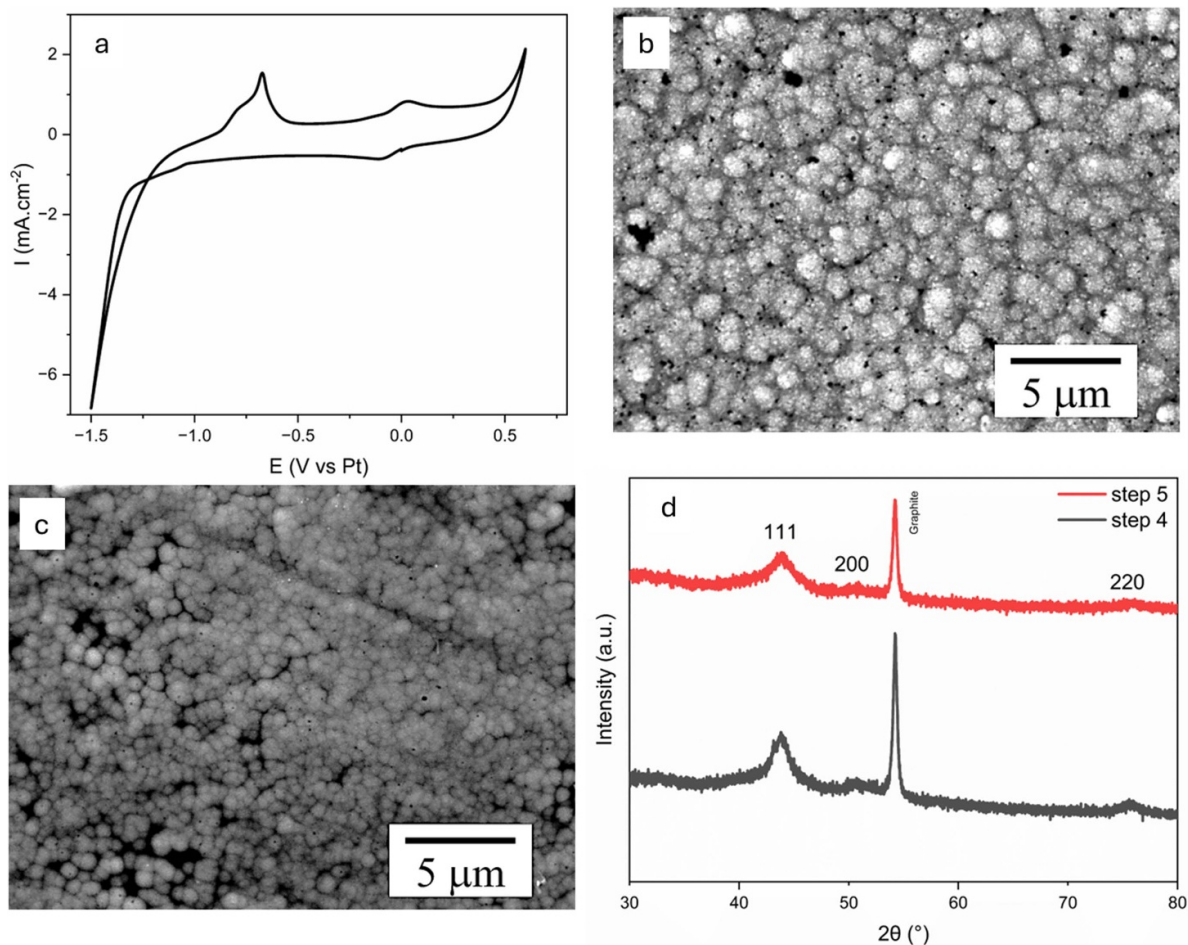


Figure 12. (a) Cyclic voltammogram of the electrolyte at 60 °C after Cu recovery at a scan rate of 10 mV s⁻¹; (b) SEM image of the Ni/Co deposit obtained at step 4; (c) SEM image of the Ni/Co deposit obtained at step 5; (d) XRD patterns of the deposits from steps 4 and 5.

All patterns were recorded over the 2θ range of 30°–80° and reflect both phase composition and crystal texture evolution of the recovered metallic copper. Well-defined peaks were observed around 43°, 50°, and 74°, corresponding to the (111), (200), and (220) planes of face-centered cubic (FCC) metallic copper (ICDD 04-0836). In all three stages, the (111) reflection is dominant, indicating a preferred growth orientation along this plane, which is commonly observed in FCC metals like copper due to its lowest surface energy and highest atomic packing density.^{64,65} Peak intensity declined progressively from the first to the third deposition, reflecting the declining availability of Cu²⁺ ions in the leachate following each recovery cycle. Importantly, no peak broadening was observed, indicating that crystalline quality remained high across all three depositions, despite declining deposition mass.

ICP-OES analysis of the deposits obtained after each electrodeposition step further confirms the progressive change in composition and purity of the recovered copper. In the first deposition step, the deposit exhibited high copper purity (~88.4%), with minor contributions from Co (~5.6%), Ni (~5.1%), and trace amounts of Mn (~0.6%) and Li (~0.3%). In the second step, the copper content decreased to ~82.2%, accompanied by increased incorporation of Co (~9.4%) and Ni (~7.1%), indicating gradual co-deposition of transition metals as Cu²⁺ concentration declined in the electrolyte. This trend became more pronounced in the third step, where copper purity further decreased to ~75.3%, while Co (~13.5%) and Ni (~9.3%) contents increased, along with slight enrichment of Mn (~1.2%) and Li (~0.7%).

Ni/Co alloys recovery.—After completion of copper recovery, the electrolyte temperature was increased to 60 °C, and a CV was recorded to assess the remaining electroactive species in the leachate (Fig. 12a). In this scan, the Cu²⁺-associated peak near -0.25 V was markedly reduced, confirming effective depletion of copper ions from the solution. The cathodic response at lower cathodic potentials was almost completely suppressed. A nucleation loop at -1.3 V is observed in the anodic scan at -1.25 V, followed by oxidation peaks at -0.8 V and -0.65 V, indicating the deposition and stripping of Co/Ni alloys. To recover Co/Ni alloys, two potentiostatic deposition steps were carried out at -1.3 V for 2 h each at 60 °C. These constituted steps 4 and 5 of the recovery sequence.

The morphology and compositional profile of the Ni/Co alloy deposits were systematically examined after each sequential deposition steps. The step 4 and 5 depositions yielded dense, compact layers of fine-grained Ni/Co alloys (Figs. 12b and 12c). SEM images revealed a uniformly distributed particulate coverage with minimal surface porosity. The deposits consisted of predominantly spherical to sub-spherical nanoparticles with average diameters ranging from 50–150 nm. The morphology remained continuous and well-packed, indicating high nucleation density and consistent lateral growth across the substrate surface.

EDS spectra are presented in Figs. S.13a and S.13b which confirmed that both nickel and cobalt were successfully co-deposited, with only trace levels of residual copper detected. This is consistent with the incomplete elimination of Cu²⁺ ions following the initial recovery stage. EDS elemental mapping of the Ni/Co deposit

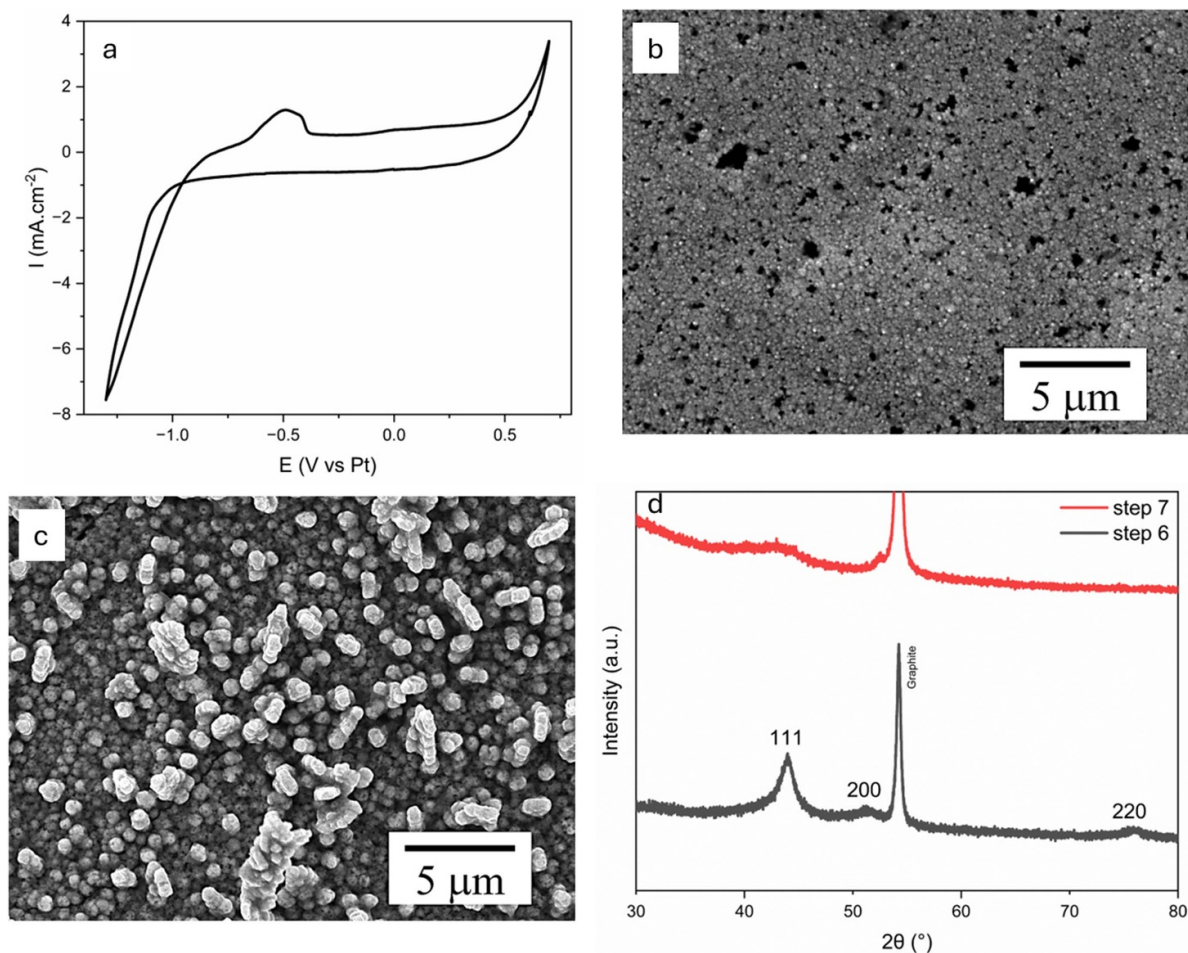


Figure 13. (a) Cyclic voltammogram of the electrolyte at 80 °C after step 5 at a scan rate of 10 mV s⁻¹; (b) SEM image of the Ni/Co deposit obtained at step 6; (c) SEM image of the Ni/Co deposit obtained at step 7; (d) XRD patterns of the deposits from steps 6 and 7.

obtained in deposition step 4 was conducted to confirm the distribution of Ni and Co, with the corresponding results provided in Fig. S14 of the Supporting Information.

The XRD patterns of steps 4 and 5 (Fig. 12d) display three broad but distinct diffractions at $\sim 44^\circ$, 51° , and 76° , corresponding to the (111), (200), and (220) planes of FCC nickel (ICDD 04-0850). Among these, the reflections near 51° and 76° are less pronounced than the dominant peak at 44° . The absence of peak splitting or shoulders indicates cobalt substitution into the nickel lattice, forming a homogeneous Ni-Co alloy. The broad peak profiles in both samples suggest nanocrystalline alloy formation.⁶⁶

ICP-OES analysis of the deposits obtained in steps 4 and 5 reveals the transition from Cu-dominated deposition to Ni-Co alloy formation at 60 °C. In step 4, the deposit is composed predominantly of Ni ($\sim 61.5\%$) and Co ($\sim 30.9\%$), corresponding to the possible formation of Ni₆₇Co₃₃ alloy, with a small amount of residual Cu ($\sim 6.5\%$) and trace levels of Mn and Li, indicating the onset of Ni-Co co-deposition following copper depletion. In step 5, the Ni content increases significantly to $\sim 73.6\%$ while Co decreases to $\sim 21.5\%$ which corresponds to the formation of Ni₇₈Co₂₂ alloy, confirming preferential deposition of Ni over Co under these conditions. Residual Cu is further reduced ($\sim 2.3\%$), and Mn ($\sim 2.3\%$) becomes more noticeable in the deposit. Overall, these results demonstrate progressive Ni enrichment at 60 °C, although Co remains a significant component, indicating competitive co-deposition behavior.

Following step 5 deposition, the leachate was further heated to 80 °C and re-examined by CV to evaluate the electrochemical activity of the remaining species (Fig. 13a). The voltammogram showed further attenuation of the cathodic features. The Cu peak was absent, and the previously dominant Ni/Co reduction wave displayed a reduced current response. A slight shift toward less negative onset potentials was observed. The remaining electroactive features were confined to the -1.1 V region, indicating that Ni and Co were still present, albeit at diminished concentrations. At 80 °C, a similar nucleation loop to that at 60 °C is observed, along with comparable oxidation peaks. For complete recovery of Ni and Co as alloys, two additional potentiostatic deposition steps were performed at -1.2 V for 2 h each at 80 °C (steps 6 and 7).

Transitioning to 80 °C for the sixth deposition led to approximately similar morphology to steps 4 and 5 (Fig. 13b). The particle size decreased, and the deposit exhibited rougher texture. SEM analysis indicated that particles became increasingly aggregated, with a size distribution ranging from 50 to 150 nm. EDS (Figs. S.13c and S.13d) confirmed the continued presence of Ni and Co.

The step 7 produced the most morphologically distinct deposit (Fig. 13c). SEM revealed the emergence of vertically oriented, flower-like and rod-stacked structures with feature sizes ranging from 500 nm to 1 μ m. These anisotropic features were spatially isolated and grew in clusters, contrasting with the compact spherical morphology of earlier steps. EDS analysis confirmed Ni and trace level of Co remained in the deposit, consistent with near-complete depletion of these species from solution and minimal electrochemical

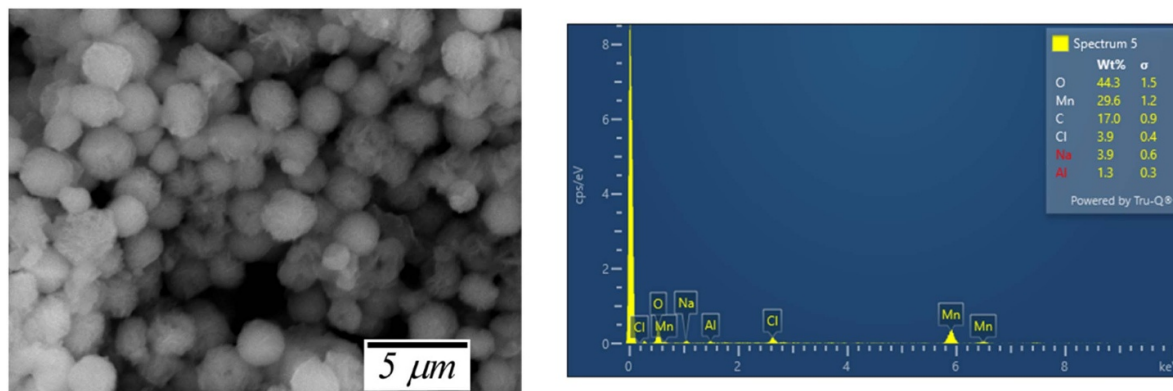


Figure 14. SEM image and EDS elemental analysis of the MnCO_3 precipitate recovered from the leachate after carbonate precipitation.

activity during the final recovery step. EDS elemental mapping of the Ni/Co deposit obtained in deposition step 6 was also performed, and the corresponding elemental distribution maps are presented in Fig. S15 of the Supporting Information.

The XRD patterns of steps 6 and 7 (Fig. 13d) exhibited similar reflections, with step 6 showing higher overall intensity, consistent with a thicker or denser deposit. In contrast, the reflections in step 7 decreased significantly in intensity, corresponding to diminishing Ni^{2+} and Co^{2+} ion concentrations in the DES after repeated recovery cycles. The thinner, more dispersed metal layers produced under these conditions yielded weaker diffraction signals. The shift toward larger, anisotropic surface features observed in SEM (e.g. flower-like rods) is not reflected in crystallographic changes.

ICP-OES analysis of the deposits obtained in steps 6 and 7 highlights a pronounced shift towards Ni-rich compositions at 80 °C. In step 6, Ni reaches its highest purity (~87.4%, accompanied by a substantial decrease in Co (~9.8%) and negligible Cu (~0.17%), indicating highly selective Ni deposition at elevated temperature. Minor incorporation of Mn (~1.3%) and Li (~1.3%) is also observed. In step 7, Ni remains the dominant component (~82.2%, although slight increases in Co (~6.7%), Mn (~4.0%), and Li (~7.1%) are detected. Overall, these results confirm that higher temperatures strongly favor Ni selectivity, leading to the formation of Ni-rich alloys with reduced Co incorporation.

Electrochemical comparison between blank DES and post-recovery DES.—CV was also employed to evaluate the electrochemical integrity of the DES before and after the complete sequence of metal recovery steps. CVs of the blank DES and the used DES at 40 °C are compared in Fig. S16. The blank DES exhibited a stability window of ~2.25 V, with cathodic decomposition initiating near -1.60 V and anodic near + 0.65 V. In contrast, the DES sampled after sequential Cu and Ni/Co recovery showed an earlier cathodic onset at -1.15 V, while anodic decomposition shifted positively to + 0.8 V, narrowing the electrochemical window to ~1.95 V. This reduction indicates a decline in solvent robustness after processing, likely due to structural changes in the DES matrix from prolonged exposure to elevated temperatures and applied potentials. Partial oxidative degradation of ethylene glycol or disruption of the hydrogen-bonding network may have contributed to reduced cathodic resilience.

Figure S.17 presents optical images of the DES at successive stages of the recovery process, showing a gradual color change from dark green to pale blue. This visual observation reflects changes in the solution composition during metal extraction

Mn selective recovery.—Although manganese recovery was demonstrated from the model system, its concentration in the leachate was too low to enable electrodeposition. Mn was instead

recovered through selective precipitation using 1 M Na_2CO_3 . Lithium remained dissolved in the DES owing to the high solubility of Li_2CO_3 , enabling effective separation from manganese.

The recovered Mn salt was analyzed using SEM and EDS analysis (Fig. 14). SEM image revealed spherical particles with rough, porous surfaces and typical sizes of approximately 2 μm. Elemental analysis by EDS showed the presence of O (44.3%), Mn (29.6%), and C (17.0%). In addition, Na (3.9%) and Cl (3.9%) were detected, originating from the reaction between Na_2CO_3 and the Bet-HCl based DES during the precipitation process. A small amount of Al (1.3%) likely originates from trace impurities in the BM.

Metal Recovery efficiency: ICP-OES analysis.—Figure 15 reflect cumulative and stepwise extraction efficiencies for Cu, Ni, Co, and Mn from the DES leachate. Copper was selectively recovered during the first three deposition steps. Recovery efficiencies decreased progressively, with 44.54% in the first, 27.38% in the second, and 16.83% in the third step, consistent with stepwise depletion of Cu^{2+} ions. Minor co-deposition of Ni ($\leq 0.78\%$) and Co ($\leq 3.55\%$) was observed, likely due to overlapping redox potentials or surface adsorption. Trace Mn and Li were also detected, possibly due to minor electrolyte entrainment.

During alloy deposition, Ni and Co recoveries reached 14.76% and 27.84% in step 4, increasing to 37.45% and 40.98% in step 5 under optimized conditions. Residual Cu (5.17% and 3.82%) indicated incomplete removal in earlier steps. Mn and Li remained negligible. Step 6 yielded 29.76% Ni and 12.51% Co, while final recoveries dropped to 3.29% and 1.01%, respectively, reflecting near-complete depletion. Copper was absent in these steps, confirming full removal. Slightly elevated Mn ($\leq 1.87\%$) and Li ($\leq 1.78\%$) may be attributed to DES entrainment or analytical variation. ICP-OES of the MnCO_3 precipitate confirmed a recovery rate of 71.52%. The shortfall from theoretical recovery likely reflects prior Mn loss during deposition or incomplete precipitation, with additional contributions from dissolution or handling losses. Lithium remained largely in the DES, with 66.7% of the original content detected in the final leachate. Minor Li detected in earlier steps ($\leq 5.17\%$) is consistent with solvent residue on electrodes or analytical variability. Lithium retention in the liquid phase aligns with lithium carbonate's high solubility. Slight underestimations in Mn and Li recovery may arise from experimental limitations, including sequential leachate volume losses, electrolyte retention on solids, and sample handling during ICP-OES preparation.

Conclusions

In this work, a sustainable and selective recycling strategy for spent LIBs was developed using a DES composed of betaine hydrochloride and ethylene glycol. The DES exhibited good thermal

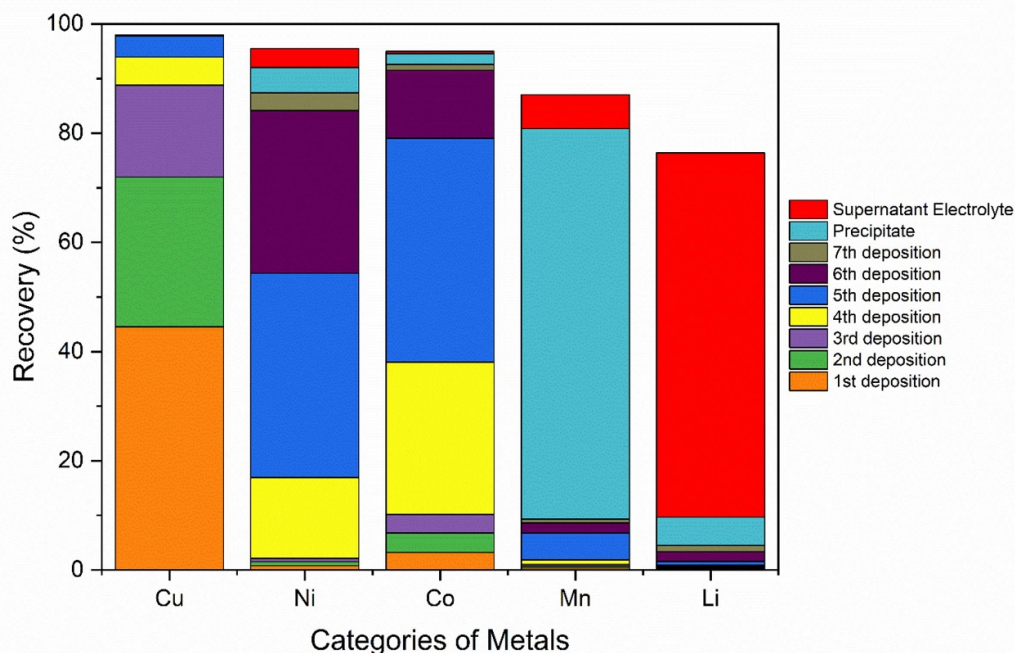


Figure 15. Recovery efficiencies of individual elements.

stability and enabled efficient leaching of transition metals at optimized conditions (100 °C, 30 min, 50 g l⁻¹ S/L ratio). Sequential electrodeposition steps facilitated selective recovery of copper at 40 °C using galvanostatic control, followed by cobalt-nickel alloy deposition at 60 °C and 80 °C via potentiostatic methods. Manganese was recovered as manganese carbonate via precipitation, and lithium remained in solution. Cumulative recovery efficiencies reached ~98% for Cu, ~90% for Ni and Co, and ~80% for Mn. Minor co-deposition of metals was observed at each stage, consistent with CV and ICP-OES data. Post-process analysis revealed a reduction in the electrochemical stability window of the DES, suggesting partial degradation after extended use. This study demonstrates the feasibility of a green, betaine-based DES for efficient, stepwise recovery of valuable metals from LIB black mass, offering a viable and scalable alternative to conventional hydrometallurgical methods.

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Data availability statement

The link to the data is provided in <https://doi.org/10.17633/rd.brunel.30465077>.

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References

- E. Ebrahimi, M. Kordloo, G. Khodadadmahmoudi, A. Rezaei, M. Ganjali and G. Azimi, "Solvometallurgical recycling of spent LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM) cathode material using ternary choline chloride-ethylene glycol-p-toluenesulfonic acid deep eutectic solvent." *Hydrometallurgy*, **2023**, 222 (2023).
- B. Behnadjy, J. Y. Seyf, S. Karimi, M. Moradi and M. Sohrabi, "Molecular dynamic (MD) simulation and density function theory (DFT) calculation relevant to green leaching of metals from spent lithium-ion battery cathode materials using glucose-based deep eutectic solvent (DES)." *Hydrometallurgy*, **2024**, 223 (2024).
- X. He, Y. Wen, X. Wang, Y. Cui, L. Li and H. Ma, "Leaching NCM cathode materials of spent lithium-ion batteries with phosphate acid-based deep eutectic solvent." *Waste Manage.*, **157**, 8 (2023).
- R. Liu, J. Li, Y. Yue, X. Yin, Z. Gai and Y. Yang, "A weakly acidic and reductive deep eutectic solvent used for one-step efficient separation of Li and Co from spent lithium-ion batteries." *Waste Manage.*, **197**, 76 (2025).
- Y. Luo, L. Ou and C. Yin, "High-efficiency recycling of spent lithium-ion batteries: a double closed-loop process." *Sci. Total Environ.*, **875**, 162567 (2023).
- B. Lu, R. Du, G. Wang, Y. Wang, S. Dong, D. Zhou, S. Wang and C. Li, "High-efficiency leaching of valuable metals from waste Li-ion batteries using deep eutectic solvents." *Environ. Res.*, **212**, 113286 (2022).
- Y. Luo, C. Yin and L. Ou, "Recycling of waste lithium-ion batteries via a one-step process using a novel deep eutectic solvent." *Sci. Total Environ.*, **902**, 166095 (2023).
- A. Zhu, X. Bian, W. Han, Y. Wen, K. Ye, G. Wang, J. Yan, D. Cao, K. Zhu and S. Wang, "Microwave-ultra-fast recovery of valuable metals from spent lithium-ion batteries by deep eutectic solvents." *Waste Manage.*, **156**, 139 (2023).
- R. Cui, Y. Ran, D. Shu, Q. Huang, Q. Song, H. Wang, J. Zhu and W. Yuan, "Recent advances in green deep eutectic solvents for lithium-ion battery recycling: a perspective on bibliometric analysis." *J. Environ. Manage.*, **377**, 124670 (2025).
- Y. Lai, X. Zhu, J. Li, Q. Gou, M. Li, A. Xia, Y. Huang, X. Zhu and Q. Liao, "Recovery and regeneration of anode graphite from spent lithium-ion batteries through deep eutectic solvent treatment: structural characteristics." *Chem. Eng. J.*, **457**, 141196 (2023).
- Y. Fan, Y. Kong, P. Jiang, G. Zhang, J. Cong, X. Shi, Y. Liu, P. Zhang, R. Zhang and Y. Huang, "Development and challenges of deep eutectic solvents for cathode recycling of end-of-life lithium-ion batteries." *Chem. Eng. J.*, **463**, 141196 (2023).
- Y. Luo, L. Ou and C. Yin, "Extraction of precious metals from used lithium-ion batteries by a natural deep eutectic solvent with synergistic effects." *Waste Manage.*, **164**, 1 (2023).
- R. Liu, J. Li, X. Liu, X. Yin and Y. Yang, "Novel ternary deep eutectic solvents used for recycling lithium and cobalt from waste lithium-ion batteries." *Sep. Purif. Technol.*, **354**, 128934 (2025).
- P. G. Schiavi, P. Altamari, M. Branchi, R. Zanoni, G. Simonetti, M. A. Navarra and F. Pagnanelli, "Selective recovery of cobalt from mixed lithium ion battery wastes using deep eutectic solvent." *Chem. Eng. J.*, 417 (2021).

15. B. Li et al., "High-efficiency leaching of valuable metals from waste lithium-ion ternary batteries under mild conditions using green deep eutectic solvents." *Green Chem.*, **27**, 163 (2024).
16. X. Chang, M. Fan, C. F. Gu, W. H. He, Q. Meng, L. J. Wan and Y. G. Guo, "Selective extraction of transition metals from spent LiNi_xCo_yMn_{1-x-y}O₂ cathode via regulation of coordination environment." *Angew. Chem., Int. Ed.*, **61**, e20220558 (2022).
17. Y. Li, M. Sun, Y. Cao, K. Yu, Z. Fan and Y. Cao, "Designing low toxic deep eutectic solvents for the green recycle of lithium-ion batteries cathodes." *ChemSusChem*, **17**, e202301953 (2024).
18. S. Wang, Z. Zhang, Z. Lu and Z. Xu, "A novel method for screening deep eutectic solvent to recycle the cathode of li-ion batteries." *Green Chem.*, **22**, 4473 (2020).
19. S. Ashoka Sahadevan, M. Shahid, S. Sankarasubramanian and V. Ramani, "Solvometallurgy: design of ternary deep eutectic solvents for the electrochemical recovery of nickel from lithium-ion cathode materials." *J. Mater. Chem. A*, **13**, 12625 (2025).
20. M. Shahid, S. A. Sahadevan, V. Ramani and S. Sankarasubramanian, "Recommended practices for the electrochemical recovery of cobalt from lithium cobalt oxide: a case study of the choline chloride: ethylene glycol deep eutectic solvent." *ChemSusChem*, **18**, 3 (2025).
21. D. L. Thompson, I. M. Pateli, C. Lei, A. Jarvis, A. P. Abbott and J. M. Hartley, "Separation of nickel from cobalt and manganese in lithium ion batteries using deep eutectic solvents." *Green Chem.*, **24**, 4877 (2022).
22. D. Yetim, L. Svecova and J. C. Lep  tre, "Lithium-ion battery cathode recycling through a closed-loop process using a choline chloride-ethylene glycol-based deep-eutectic solvent in the presence of acid." *Chem. Open*, **13**, e202300061 (2024).
23. L. Chen, Y. Chao, X. Li, G. Zhou, Q. Lu, M. Hua, H. Li, X. Ni, P. Wu and Y. Zhu, "Engineering a tandem leaching system for the highly selective recycling of valuable metals from spent li-ion batteries." *Green Chem.*, **23**, 2177 (2021).
24. B. Li, Q. Li, Q. Wang, X. Yan, M. Shi and C. Wu, "Deep eutectic solvent for spent lithium-ion battery recycling: comparison with inorganic acid leaching." *Phys. Chem. Chem. Phys.*, **24**, 19029 (2022).
25. M. Jafari, S. Z. Shafaei, H. Abdollahi and A. Entezari-zarandi, "Green recycling of spent li-ion batteries by deep eutectic solvents (DESs): leaching mechanism and effect of ternary DES." *J. Environ. Chem. Eng.*, **10**, 6 (2022).
26. Y. Wen, X. He, T. Kang, K. Gu, S. Di, L. Li and Y. Cui, "Simultaneous separation and leaching of cathode materials from spent lithium-ion battery using ternary deep eutectic solvents." *J. Environ. Chem. Eng.*, **12**, 6 (2024).
27. W. H. Gao, C. C. Nie, L. Li, S. Yan, W. T. Zhou and X. Zhu, "Sustainable and efficient deep eutectic solvents in recycling of spent lithium-ion batteries: recent advances and perspectives." *J. Clean. Prod.*, **464**, 142735 (2024).
28. C. Cao, Z. Yuan, H. Liu, X. Fei and Q. She, "Lactic-acid-based deep eutectic solvent for sustainable recovery of critical metals from spent lithium-ion batteries under mild conditions." *J. Clean. Prod.*, 505 (2025).
29. M. Chen, Y. Zhou, L. Wang, G. Xue, J. Guo and Y. Wang, "Recycling spent LiNi_{1-x-y}Co_xMn_yO₂ cathodes to efficient catalysts for the oxygen evolution reaction." *Green Chem.*, **26**, 2912 (2024).
30. N. Peeters, K. Janssens, D. de Vos, K. Binnemans and S. Ria  o, "Choline chloride-ethylene glycol based deep-eutectic solvents as lixivants for cobalt recovery from lithium-ion battery cathode materials: are these solvents really green in high-temperature processes?" *Green Chem.*, **24**, 6685 (2022).
31. H. Wang et al., "Cobalt electrochemical recovery from lithium cobalt oxides in deep eutectic choline chloride + urea solvents." *ChemSusChem*, **14**, 2972 (2021).
32. F. Zhou, D. Shi, W. Mu, S. Wang, Z. Wang, C. Wei, R. Li and T. Mu, "Machine Learning models accelerate deep eutectic solvent discovery for the recycling of lithium-ion battery cathodes." *Green Chem.*, **26**, 7857 (2024).
33. F. Zhou, Y. Tian, H. Zhang, Y. Yin, Z. Wang, R. Qin, Y. Chen, Z. Li and T. Mu, "Enhanced rapid and efficient recycling of lithium-ion battery cathode by synergistic effects of ternary deep eutectic solvents ChCl/MClx/Levulinic acid." *ACS Sustain. Chem. Eng.*, **12**, 18090 (2024).
34. H. Yang, Y. Sun, J. He, J. Li, J. Li, Z. Ding and Y. Ren, "Efficient recovery and regeneration method of spent LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode materials based on novel deep eutectic solvent design." *J. Power Sources*, **610**, 234731 (2021).
35. H. Li, N. Chen, W. Liu, H. Feng, J. Su, D. Fu, X. Liu, M. Qiu and L. Wang, "A reusable deep eutectic solvent for the regeneration of Li and Co metals from spent lithium-ion batteries." *J. Alloys Compd.*, **966**, 171517 (2023).
36. T. Zhang, J. Dao, J. Wang, R. wan, C. Li, D. Wang, C. Bao, Y. Zhang, Z. Zhang and P. Dong, "Efficient leaching of valuable metals from NCM cathode materials by green deep eutectic solvent." *J. Clean. Prod.*, **438**, 140636 (2024).
37. S. Zheng, S. Xu, Z. Wang, H. Duan, D. Chen, M. Long and Y. Li, "Efficient leaching of valuable metals from spent lithium-ion batteries using green deep eutectic solvents: process optimization, mechanistic analysis, and environmental impact assessment." *J. Clean. Prod.*, **480**, 144128 (2024).
38. Y. Luo, C. Yin, L. Ou and C. Zhang, "Highly efficient dissolution of the cathode materials of spent Ni-Co-Mn lithium batteries using deep eutectic solvents." *Green Chem.*, **24**, 6562 (2022).
39. Y. Luo, L. Ou and C. Yin, "A green and efficient combination process for recycling spent lithium-ion batteries." *J. Clean. Prod.*, **396**, 136552 (2023).
40. T. Hu, T. Li, X. Liu, Z. Wang, L. Lou, S. Jing, X. Yan, Y. Xiong, J. Xiong and X. Ge, "Realizing the reusability of leachate for the hydrometallurgical recycling of spent lithium cobalt oxide by dynamically regulating the solubility product." *Green Chem.*, **26**, 2653 (2024).
41. J. Cheng, C. Zheng, K. Xu, Y. Zhu, Y. Song and C. Jing, "Sequential separation of critical metals from lithium-ion batteries based on deep eutectic solvent and electrodeposition." *J. Hazard. Mater.*, **465**, 133157 (2024).
42. S. C. Chen, F. C. Chou, S. Shirke, S. Y. Lin and Y. C. Lin, "Efficiency comparison of succinic acid and oxalic acid with choline chloride deep-eutectic solvent through response surface methodology." *J. Taiwan Inst. Chem. Eng.*, **174**, 106230 (2025).
43. J. Aldana-gonz  lez, A. Sampayo-garrido, D. Hern  ndez-p  rez, M. G. M. de Oca-yemha, E. M. Arce-estrada, M. T. Ram  rez-silva, P. Morales-gil, M. Romero-romo, V. Mugica-  lvarez and M. Palomar-pardav  , "Electrochemical nucleation and growth of cobalt after leaching waste lithium-ion batteries using a deep eutectic solvent." *J. Electrochem. Soc.*, **169**, 102504 (2022).
44. A. Shen, J. Zhang, Y. Chen and C. Wang, "Recycling spent lithium ion batteries by flash joule heating: preferential lithium recovery and Li-phase conversion mechanism under ultra-temperature." *Resour. Conserv. Recycl.*, **222**, 108433 (2025).
45. L. Wang, X. Jiao, T. Xie, H. Bian, J. Ma and Z. Zhang, "Waste treats waste: an efficient co-pyrolysis approach for the preferential li extraction from spent lithium-ion battery powder utilizing coffee grounds." *Chem. Eng. J.*, **520**, 165670 (2025).
46. X.-G. Sun, C. J. Jafra, S. Tan, A. Borisevich, R. B. Gupta and M. P. Paranthaman, "Facile surface coatings for performance improvement of NMC811 battery cathode material." *J. Electrochem. Soc.*, **169**, 020565 (2022).
47. Z. Qi and G. M. Koenig, "High-performance LiCoO₂ sub-micrometer materials from scalable microparticle template processing." *ChemistrySelect*, **1**, 3992 (2016).
48. A. Li, Z. Shao, S. Yang, X. Li and A. Zhang, "Precipitation synthesis and enhanced electrochemical performance of graphene-modified LiMn₂O₄ for lithium-ion batteries." *Ionics*, **26**, 3231 (2020).
49. M. T. Nguyen, T. L. Pham, H. T. K. Tuyen, H. N. Dai and M. L. P. Le, "Effect of conductive carbon additives and negative/positive capacity ratio on graphite/LiFePO₄ full-cells performance." *Energy Storage*, **5**, 6 (2023).
50. K. C. Lethesh, A. Bahaa, M. Abdullah, M. O. Bamgbopa and R. A. Susantyo, "Temperature-dependent electrochemical stability window of Bis(Trifluoromethanesulfonyl)Imide and Bis(Fluorosulfonyl)Imide anion based ionic liquids." *Front. Chem.*, **10** (2022).
51. M. Hu, J. Zhou, L. Jiang, Z. Wang, Y. Bao and S. Cui, "Correlation between hydrogen bond strength and temperature: a quantitative single-molecule study over a broad temperature range." *J. Phys. Chem. B*, **129**, 4547 (2025).
52. P. Sebasti  n, E. Vall  s and E. G  mez, "Copper electrodeposition in a deep eutectic solvent. first stages analysis considering Cu(I) stabilization in chloride media." *Electrochim. Acta*, **123**, 285 (2014).
53. O. I. Zaytsev, M. R. Ehrenburg, E. B. Molodkina, P. Broekmann and A. V. Rudnev, "Over- and underpotential deposition of copper from a deep eutectic solvent: pt(1 1 1) single crystal versus polycrystalline Pt substrates." *J. Electroanal. Chem.*, **926**, 116940 (2022).
54. Z. Tan, S. Liu, J. Wu, Z. Nan, F. Yang, D. Zhan, J. Yan and B. Mao, "Copper deposition on Au(111) in a deep eutectic solvent: an *In Situ* STM Study." *ChemElectroChem*, **9**, 4 (2022).
55. A. P. Abbott, A. I. Alhaji, K. S. Ryder, M. Horne and T. Rodopoulos, "Electrodeposition of copper-tin alloys using deep eutectic solvents." *Trans. Inst. Met. Finish.*, **94**, 104 (2016).
56. P. Y. Chen and C. L. Hussey, "The electrodeposition of Mn and Zn-Mn Alloys from the room-temperature Tri-1-Butylmethylammonium Bis(Trifluoromethane)Sulfonyl)Imide ionic liquid." *Electrochim. Acta*, **52**, 1857 (2007).
57. N. M. Pereira, C. M. Pereira, J. P. Ara  jo and A. F. Silva, "Electrodeposition of Mn and Mn-Sn alloy using choline chloride-based ionic liquids." *J. Electrochem. Soc.*, **164**, D486 (2017).
58. J. K. Chang, C. H. Huang, W. T. Tsai, M. J. Deng, I. W. Sun and P. Y. Chen, "Manganese films electrodeposited at different potentials and temperatures in ionic liquid and their application as electrode materials for supercapacitors." *Electrochim. Acta*, **53**, 4447 (2008).
59. M. J. Deng, P. Y. Chen and I. W. Sun, "Electrochemical study and electrodeposition of manganese in the hydrophobic Butylmethylpyrrolidinium Bis(Trifluoromethyl)Sulfonyl)imide room-temperature ionic liquid." *Electrochim. Acta*, **53**, 1931 (2007).
60. A. Serr  , P. Sebasti  n-pascual, M. Landa-Castro and E. G  mez, "Electrochemical assessment of high active area of cobalt deposited in deep eutectic solvent." *J. Electroanal. Chem.*, **896**, 115177 (2021).
61. X. Cao, L. Xu, Y. Shi, Y. Wang and X. Xue, "Electrochemical behavior and electrodeposition of cobalt from choline chloride-urea deep eutectic solvent." *Electrochim. Acta*, **295**, 550 (2019).
62. M. Landa-Castro, P. Sebasti  n, M. I. Giannotti, A. Serr   and E. G  mez, "Electrodeposition of nanostructured cobalt films from a deep eutectic solvent: influence of the substrate and deposition potential range." *Electrochim. Acta*, **359**,

- 136928 (2020).
63. G. Qadr, M. I. Awad, K. Haji, J. A. Jumaa and H. H. Abdallah, "Nickel electrodeposition from deep eutectic solvents containing copper ions at a high temperature." *J. Mol. Liq.*, **378**, 121584 (2023).
64. Y. N. Wen and J. M. Zhang, "Surface energy calculation of the Fcc metals by using the MAEAM." *Solid State Commun.*, **144**, 163 (2007).
65. T. C. Liu, C. M. Liu, H. Y. Hsiao, J. L. Lu, Y. S. Huang and C. Chen, "Fabrication and characterization of (111)-oriented and nanotwinned Cu by Dc electrodeposition." *Cryst. Growth Des.*, **12**, 5012 (2012).
66. L. Hosseinzadeh, J. Baedi and A. K. Zak, "X-ray peak broadening analysis of Fe 50 Ni 50 nanocrystalline alloys prepared under different milling times and BPR using size strain plot (SSP) method." *Bull. Mater. Sci.*, **37**, 1147 (2014).