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Selective cobalt and nickel separation by bioacid-mediated electrowinning

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The increasing demand for cobalt (Co) and nickel (Ni) in energy storage and industrial applications highlights the need for their efficient separation from both primary mining and nonconventional sources. Electrowinning presents a greener alternative to incumbent solvent extraction but is hindered by the similar reduction potentials of divalent Co and Ni ions. We show that cost-effective and recyclable bioacids can modify ion solvation environments to amplify the reduction potential difference between Co and Ni, with tartaric acid achieving the highest selectivity through formation of a unique dinuclear complex. When applied to ternary lithium-ion battery leachates, the process achieves 99.1% Co purity in batch mode and, in a scalable flow system, stepwise recovery of metallic Co (95.1%), Ni (96.5%), and manganese dioxide (~100%) with high yields. Technoeconomic analysis and life-cycle assessment highlight superior economic and environmental benefits, establishing a sustainable, generalized electrochemical platform for selective Ni/Co separation from complex feedstocks.

INTRODUCTION

As the world transitions to renewable energy, critical elements cobalt (Co) and nickel (Ni) are experiencing a surging demand (1–3), driven primarily by their indispensable role in the rapidly expanding energy storage industry (4–6). Beyond batteries, they are also essential for superalloys in the aerospace sector and catalysts in electrochemical processes (7). As a result, Co demand reached nearly 0.2 million tonnes in 2023, more than doubling since 2016 (8). Meanwhile, Ni usage reached more than 3.1 million tonnes in 2023, maintaining an average annual growth rate of ~8% since 2009 (9, 10). Considering the constraints of limited metal reserves and mining output, this rising demand signals an impending supply shortage (11, 12). Moreover, geopolitical risks as well as environmental and ethical concerns surrounding the mining of critical elements further threaten supply chain stability (13), which can lead to marked price fluctuations and pose challenges to sustainable economic growth.

Given the frequent coexistence of Co and Ni in various primary (e.g., laterite ore) and secondary [e.g., spent lithium (Li)-ion batteries, produced water, and mining discharge] matrices, effective Co/Ni separation is crucial to meeting the growing demands (14, 15). As illustrated in Fig. 1A, state-of-the-art hydrometallurgical Co/Ni separation typically relies on solvent extraction (16, 17). However, the similar aqueous chemistries of Co and Ni limit selectivity, particularly when treating dilute, complex matrices characteristic of secondary resources (4). In addition, solvent extraction requires large chemical inventories, extensive pretreatment to remove competitor ions, and multiple extraction stages, making it costly, environmentally hazardous, and challenging to scale sustainably (11). Recent advances in selective precipitation that use more cost-effective chemicals offer a simpler,

lower-energy solution (18). However, its effectiveness in multicomponent solutions remains uncertain because of interference from non-target ions, while the resulting Co-rich precipitates require additional posttreatment before they can be used or commercialized, adding complexity to the workflow.

Electrochemical methods, such as electrowinning, present a promising alternative to chemical-based separations because of their inherent simplicity, precise tunability via applied current and potential, and compatibility with renewable energy sources (19). The performance of such techniques tends to be less sensitive to the feed conditions, making them ideal for treating dilute matrices. Therefore, electrowinning has been widely explored for water treatment and electronic waste recovery (20, 21). However, the nearly identical standard reduction potentials of divalent Ni²⁺ and Co²⁺ ions ($E^0_{\text{Co}} = -0.277$ V and $E^0_{\text{Ni}} = -0.250$ V versus standard hydrogen electrode) pose a fundamental challenge for selective electrodeposition (22).

Coordination chemistry has been shown to influence deposition potential (23, 24). For example, it has been reported that the addition of concentrated chloride (10 M) in aqueous media induces opposite charges in Ni²⁺ and Co²⁺ coordination complexes by forming cationic [Ni(H₂O)₅Cl]⁺ and anionic (CoCl₄)²⁻ species, thereby widening the electrodeposition onset potential difference to ~90 mV. In addition, coating electrodes with a positively charged polymer enhances electrostatic effects, further promoting Co deposition (25). Nevertheless, such approaches face challenges in Co/Ni selectivity, extraction efficiency, system complexity, and long-term scalability. In particular, the requirement for thousands of plating-stripping cycles and the use of high-concentration chloride electrolytes could limit broader applicability. Nonetheless, the design strategies provide valuable insights into advancing more sustainable and practical electrochemical separations.

The Irving-Williams series empirically defines the stability order of metal-ligand complexes for divalent first-row transition metal ions (26). Because of their distinct electron configurations (Co: 3d⁷; Ni: 3d⁸) and ionic radii, Ni²⁺ tends to form more stable coordination complexes than Co²⁺. As stronger complexes are more resistant to electroreduction, identifying ligand chemistries that amplify the stability

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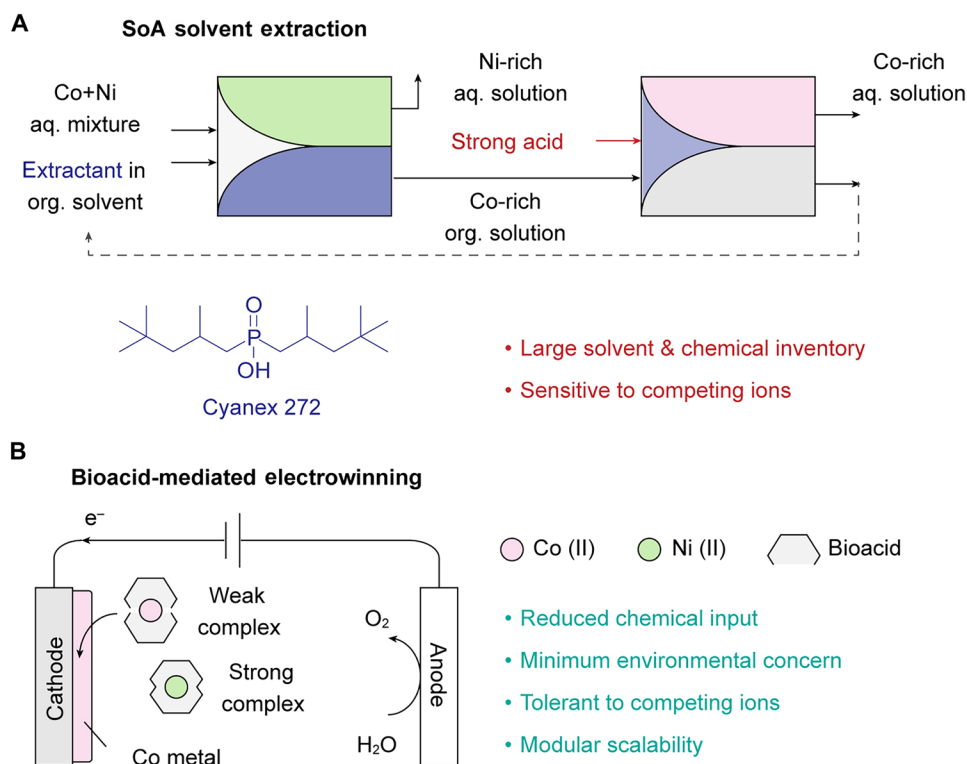


Fig. 1. Comparison of conventional solvent extraction and the proposed electrowinning strategy for Co/Ni separation. (A) Schematic illustration of conventional solvent extraction, highlighting its complexity and chemical intensity. (B) Proposed bioacid-mediated electrowinning platform, offering a greener and more selective alternative.

difference between Co^{2+} and Ni^{2+} coordination complexes presents a promising strategy to achieve efficient Co/Ni separation via electrowinning (Fig. 1B). However, designing such ligands with high selectivity, scalability, and environmental compatibility remains a substantial challenge.

Herein, we introduce bioacids, which are organic acids derived from biological sources, as low-cost, recyclable, and environmentally friendly ligands to modulate the solvation environments of Co^{2+} and Ni^{2+} during electrowinning (Fig. 1B) (27, 28). Electrochemical analyses and separation experiments identified tartaric acid as the most effective solvation regulator among various candidates. Through combined experimental validation and machine learning-guided analysis, we attribute the effect to the α -hydroxyl (α -OH) group adjacent to the carboxyl group of tartaric acid, which facilitates the formation of a unique dinuclear structure, $\text{M}_2(\text{H}_2\text{O})_4(\text{Tar})_2$ ($\text{M} = \text{Co}$ or Ni). Density functional theory (DFT) calculations further support the notion that the dimer structure maximizes the Gibbs free energy difference between Ni^{2+} and Co^{2+} coordination complexes, enhancing the Co/Ni separation factor. Benefiting from an optimized deposition-stripping protocol, we achieved 99.1% Co purity when refining a model battery waste leachate ($\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, NMC111) at a batch scale. Extending this strategy to a continuous flow system enabled the sequential recovery of Co, Ni, and Mn with purities of 95.1, 96.5, and ~100%, respectively, at high recovery yields. Notably, our method outperforms traditional solvent extraction and chemical precipitation both economically and environmentally, as validated by technoeconomic analysis (TEA) and life-cycle assessment (LCA). By providing a scalable, cost-effective, and sustainable alternative, this work establishes a universal strategy for the separation of critical transition metals,

addressing a key bottleneck in resource recovery and circular economy efforts.

RESULTS

Selective Co electrowinning over Ni mediated by bioacids

We first studied the electrochemical behavior of Ni and Co by cyclic voltammetry (CV) in electrowinning electrolytes, focusing on the reverse scan after nucleation for metal deposition analysis. The theoretical Co/Ni selectivity at a given applied potential is defined as the ratio of Co and Ni deposition currents from the CV curve. As shown in Fig. 2 (A and B), Co and Ni exhibit similar deposition onset potentials in the absence of ligands (-676.3 mV versus Ag/AgCl for Co^{2+}/Co and -718.6 mV versus Ag/AgCl for Ni^{2+}/Ni), resulting in a theoretical selectivity of only 1.5 at an applied potential of -0.9 V versus Ag/AgCl, which highlights the challenge of direct electrochemical separation. To enhance selectivity, bioacids were introduced as solvation regulators because of their affordability and eco-friendly characteristics. Thirteen candidate bioacids, including mono-, di-, and tricarboxylic acids, as well as amino acids, were screened on the basis of solubility, accessibility, and compatibility with target ions (fig. S1). The corresponding deposition curves with varying bioacid concentrations are shown in Fig. 2 (A and B) and figs. S2 and S3, with theoretical selectivities shown in fig. S4.

To validate the reliability of theoretical Co/Ni selectivity derived from CV analysis, we used gluconic acid as a model ligand and conducted potentiostatic deposition in an equimolar $\text{Co}^{2+}/\text{Ni}^{2+}$ mixture on a titanium (Ti) substrate. The real Co/Ni selectivity, determined via inductively coupled plasma optical emission spectroscopy (ICP-OES)

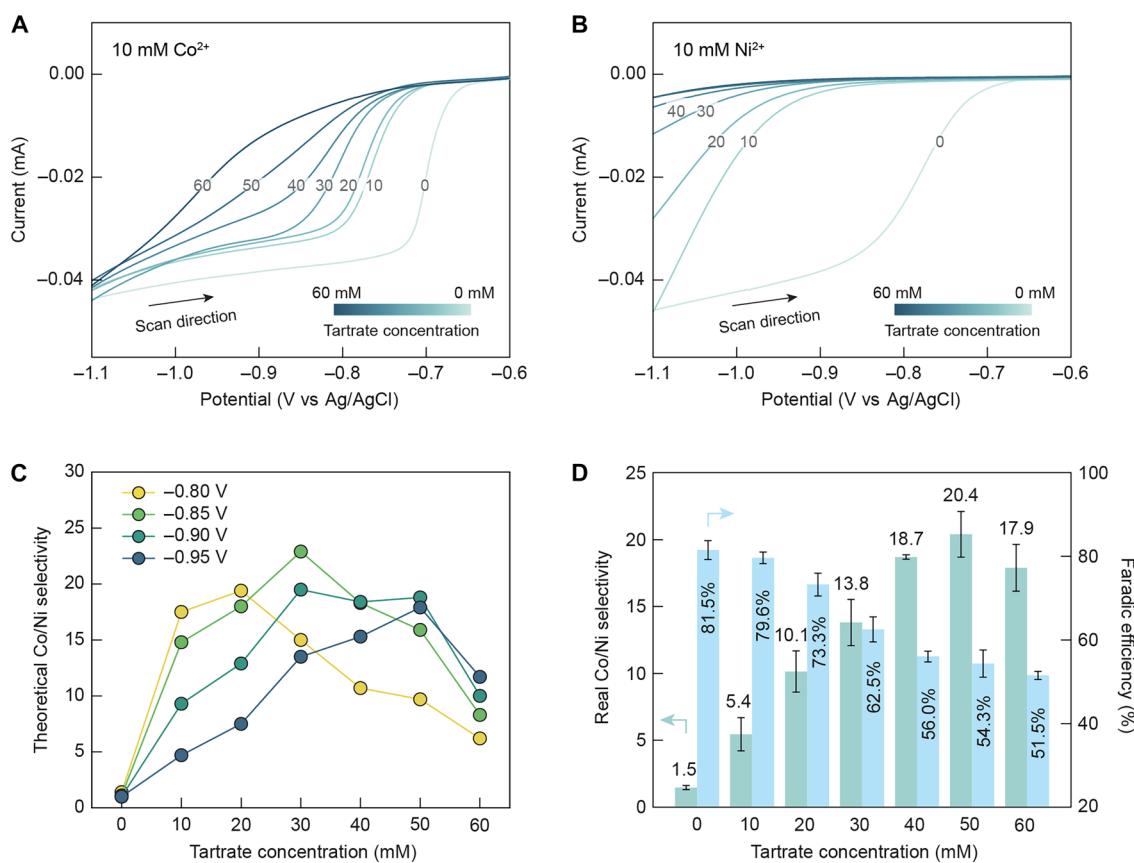


Fig. 2. Tartrate-mediated selective Co electrodeposition. (A and B) CVs of Co^{2+} (A) and Ni^{2+} (B) at varying tartrate concentrations, collected under nitrogen at a 10 mV s^{-1} scan rate. Electrolyte: 10 mM Co^{2+} or Ni^{2+} aqueous solution with 0.1 M LiCl as the supporting salt. (C) Theoretical Co/Ni selectivities at varying tartrate concentrations and applied potentials. (D) Real Co/Ni selectivities and faradic efficiencies at varying tartrate concentrations with an applied potential of -0.9 V versus Ag/AgCl. Electrolyte: 10 mM equimolar Ni/Co mixture with 0.1 M LiCl supporting salt. Deposition capacity: 1 mAh cm^{-2} . The error bars are standard deviations from three replicates.

measurements of the deposited electrodes after acid digestion, showed strong agreement with the theoretical values (fig. S5), confirming the robustness of the electrochemical screening approach.

In general, increasing the concentration of bioacids results in a cathodic shift in the deposition onset potential of both Ni and Co. Strongly coordinating ligands induce substantial cathodic shifts for both metals even at low concentrations. For instance, in the presence of 10 mM citric acid, the shifts in onset potential for Co and Ni are 96.0 and 199.8 mV, respectively, yielding a theoretical selectivity of 2.4 at an applied potential of -0.9 V versus Ag/AgCl (figs. S2H, S3H, and S4H). On the other hand, weakly coordinating ligands afford minimal changes in deposition behaviors. For instance, with 10 mM lactic acid, the shift in onset potential for Co is only 1.0 mV, while that for Ni is 39.7 mV, affording a theoretical selectivity of 1.0 at the same applied potential (figs. S2G, S3G, and S4G). Apparently, both extremes are suboptimal for selective deposition. An ideal bioacid ligand shall exhibit moderate coordination strength, interacting relatively strongly with Ni^{2+} while maintaining a lower affinity for Co^{2+} , thereby maximizing their reduction potential difference.

Among the bioacids tested, tartaric acid exhibits the most pronounced differentiation between Ni^{2+} and Co^{2+} . As the concentration of tartrate increases, a more substantial cathodic shift is observed for Ni^{2+} compared to Co^{2+} , indicating a greater suppression of Ni deposition (Fig. 2, A and B). For example, 10 mM tartaric acid results in a

191.1-mV difference in deposition potential, enabling a high theoretical selectivity of 9.3 at -0.9 V versus Ag/AgCl (Fig. 2C). This effect can be attributed to the higher formation constant (K_f) of the Ni-tartrate complex compared to that of Co-tartrate ($\log K_f = 3.02$ versus 2.77) (29). A higher K_f value corresponds to a more stable complex, which requires greater energy for desolvation and subsequent electroreduction. Consequently, Co deposition is thermodynamically favored in the presence of tartaric acid. By tuning the ligand concentration and applied electrodeposition potential, theoretical Co/Ni selectivity values above 20 can be achieved, outperforming all other bioacid candidates (fig. S4).

To maximize real Co/Ni selectivity from equimolar mixtures, the effect of tartrate concentration (0 to 60 mM) was evaluated at two constant potentials (-0.85 , -0.90 V versus Ag/AgCl) under a cutoff capacity of 1 mAh cm^{-2} (Fig. 2D and fig. S6). At -0.90 V , the real Co/Ni selectivity is limited to 1.5 in the absence of tartrate. Increasing tartrate concentration leads to a volcano-type trend in selectivity, achieving a maximum of 20.4 ± 1.7 at 50 mM tartrate (corresponding to 95.3% Co purity), accompanied by a decrease in deposition current density (fig. S7). Meanwhile, the faradic efficiency declines from 81.5 ± 2.3 to $51.5 \pm 1.0\%$ with increasing tartrate concentration, primarily due to constrained Co/Ni electroplating kinetics and increased competition from the hydrogen evolution reaction. Similarly, the selectivity at -0.85 V exhibits a maximum of ~ 20 at 40 to

60 mM tartrate, albeit with lower faradic efficiency and deposition rate than those at -0.90 V. On the basis of these results, we chose a constant potential of -0.9 V versus Ag/AgCl to balance the trade-off between energy efficiency, deposition throughput, and Co/Ni selectivity. Noticeably, the achieved selectivity surpasses that of previously reported electrowinning-based strategies for Co/Ni separation (table S1). As the deposition capacity increases to 5, 10, and 15 mAh cm^{-2} (corresponding to Co recovery yields of 46.5, 62.6, and 74.8%), the Co/Ni selectivity remains high at 13.3 ± 0.4 , 9.4 ± 0.7 , and 8.6 ± 1.3 , respectively (fig. S8). The gradual decline in selectivity is attributed to the depletion of Co^{2+} in the solution, which narrows the effective potential difference between Co and Ni. In addition, linear sweep voltammetry confirms that tartaric acid is stable within the anodic potential window used in our system (fig. S9), and no oxidation or degradation products were detected.

Scanning electron microscopy (SEM) images of electrodeposited metals with and without tartrate are shown in Fig. 3 (A and D). In the absence of tartrate, the deposit exhibits a dense, granular morphology (Fig. 3D). In contrast, the tartrate-mediated deposit displays randomly oriented triangular or needle-like structures (Fig. 3A). This morphological transition suggests that tartrate modulates the solvation environment of Co^{2+} and Ni^{2+} , which is known to directly influence deposition morphology (30, 31). The corresponding energy-dispersive x-ray spectroscopy (EDS) mapping provides additional evidence for selective Co deposition. With the same color bar, the tartrate-containing system (Fig. 3, B and C) reveals an elevated Co signal and minimized Ni signal compared to the ligand-free system (Fig. 3, E and F). The atomic Co/Ni ratio for the tartrate group reaches 14.8, markedly higher than the value of 4.1 for the control. These findings align with the ICP-OES results, confirming enhanced

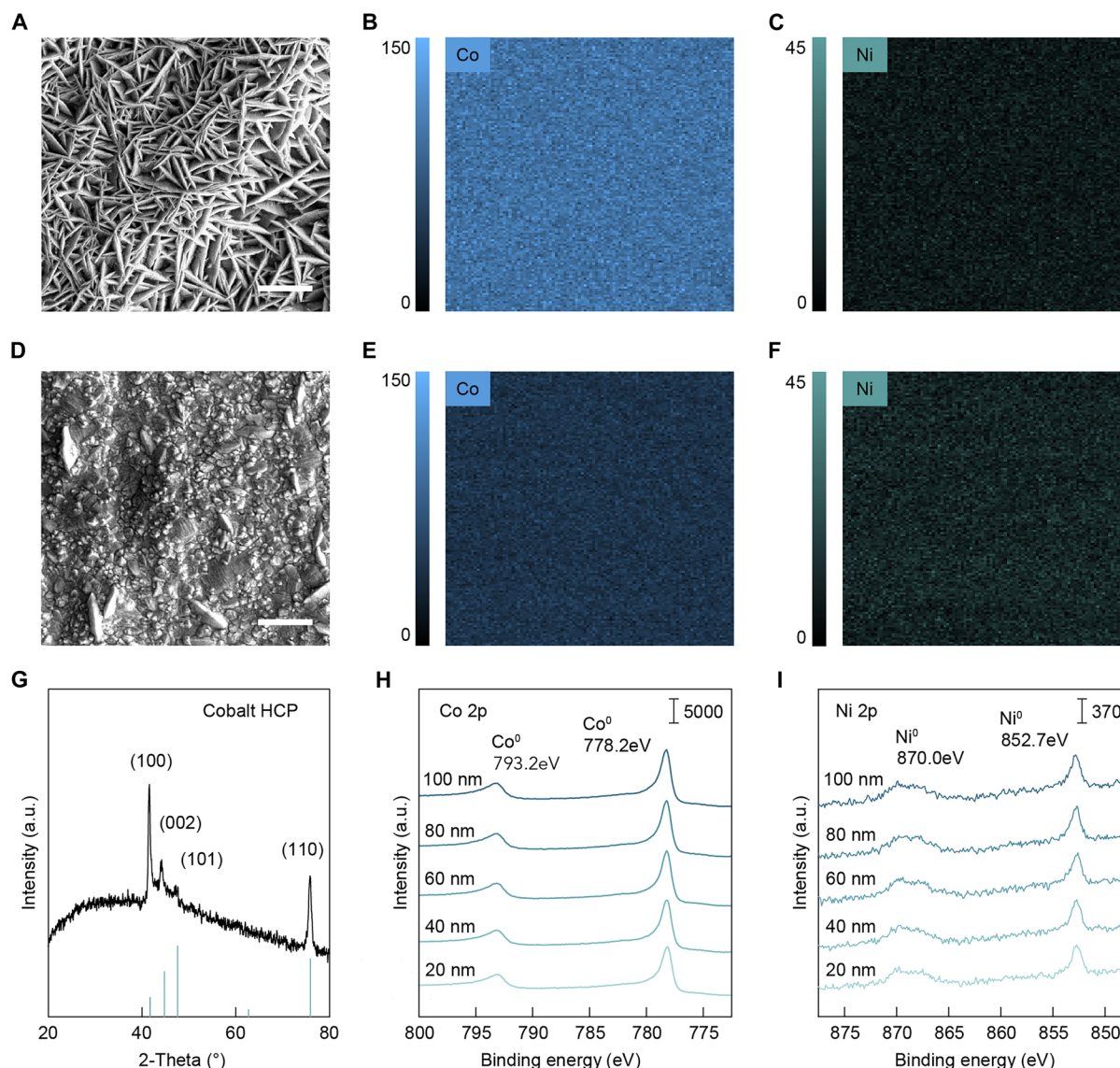


Fig. 3. Composition and phase analysis of electrodeposits. (A to C) SEM image (A) and corresponding EDS mappings of Co (B) and Ni (C) for tartrate-mediated electrodeposits. (D to F) SEM images (D) and corresponding EDS mappings of Co (E) and Ni (F) for additive-free electrodeposits. Scale bar, 2 μm . (G) XRD patterns of tartrate-mediated electrodeposits. a.u., arbitrary units. (H and I) Depth-profiling XPS spectra of Co 2p (H) and Ni 2p (I) in tartrate-mediated electrodeposits. The deposition capacity for these samples is 5 mAh cm^{-2} .

Co selectivity. The slight discrepancy between Co/Ni ratios obtained from EDS and ICP-OES may result from the limited analysis depth of the EDS technique.

X-ray diffraction spectroscopy (XRD) was performed to determine the phase composition of the electrodeposits (Fig. 3G). The spectrum shows distinct peaks corresponding to the HCP (hexagonal close-packed) phase of metallic Co, while no peaks corresponding to the face-centered cubic phase of Ni are observed. According to the binary Ni-Co phase diagram, the absence of distinct metallic Ni peaks is attributed to the formation of a NiCo solid solution phase at high Co/Ni ratios, further supporting the predominance of Co in the deposits (32). Apart from the characteristic metallic peaks, no additional peaks of metal hydroxides or oxides can be detected. To further examine the valence states of Ni and Co, x-ray photoelectron spectroscopy (XPS) depth profiling was conducted on the electrodeposits. Surface spectra reveal the presence of Co and Ni oxides resulting from the formation of a natural passivation film (fig. S10). After argon ion sputtering, XPS spectra at increasing depths display only Co^0 and Ni^0 signals, confirming that Co and Ni coexist in a metallic state throughout the bulk of the deposits (Fig. 3, H and I, fig. S11).

Machine learning and DFT-assisted mechanistic investigation

To elucidate the mechanism underlying the increased reduction potential difference between Co and Ni in the presence of tartrate, we conducted isothermal titration calorimetry (ITC) measurements (Fig. 4A). ITC quantifies the heat changes that occur when two species mix and interact in solution, providing thermodynamic insights into metal-ligand binding. As a control, titration of sodium acetate/acetic acid buffer into Co^{2+} and Ni^{2+} solutions produced negligible heat release, confirming its suitability as a noninteracting ITC buffer in our study (fig. S12). When tartrate was dissolved in the buffer solution, titrating Ni^{2+} with tartrate released more heat than titrating Co^{2+} , indicating a stronger binding interaction between Ni^{2+} and tartrate. The ITC results support the hypothesis that Ni^{2+} forms a more stable coordination complex with tartrate and provides a thermodynamic basis for the observed selectivity in electrodeposition.

We used ultraviolet-visible (UV-vis) spectroscopy to further probe the coordination environment (fig. S13). In the absence of tartrate, the Ni^{2+} spectrum exhibits a characteristic peak at 395 nm, corresponding to the octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ aqua complex (33). Upon the addition of tartrate, the peak gradually shifts to a higher wavelength, suggesting a disruption of the original hydration structure and the formation of Ni-tartrate coordination complexes. In contrast, the characteristic peak of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ at 511 nm remains largely unchanged with tartrate addition, indicating a much weaker interaction between Co^{2+} and tartrate (34). These findings confirm the preferential binding of tartrate to Ni^{2+} over Co^{2+} .

To further uncover the molecular features of ligands responsible for enhancing Co/Ni selectivity, we used a machine learning approach using experimental selectivity data of all 13 bioacid candidates. We generated extended-connectivity fingerprints (ECFPs) (35) for each molecule using RDKit (36), an open-source Python package for cheminformatics. ECFPs are binary molecular descriptors that encode the presence of particular topological substructures within a molecule, making them well suited for identifying structure-function relationships in ligand performance. Given that multiple concentrations of each bioacid were screened in this research, we introduced a weighting scheme to account for concentration effects. Each ECFP bit

was multiplied by the normalized concentration to get the weighted ECFPs (WECFPs). For example, data entries using 10 mM bioacid have a weight of 0.1667, while data entries using 60 mM bioacid have a weight of 1. WECFPs were used as input features for a random forest regression model.

To interpret the model's predictions, we used the Shapley Additive exPlanations (SHAP) analysis framework (37), which quantifies the contribution of each molecular feature to Co/Ni selectivity on the basis of game-theoretic Shapley values. A positive SHAP value indicates a feature that promotes higher selectivity, while a negative value denotes the opposite effect. SHAP analysis (fig. S14) showed that the top five ranked molecular fragments all have positive influences on Co/Ni selectivity. Notably, the more hydroxyl groups ($-\text{OH}$, feature_227) a bioacid has, especially α -OH groups adjacent to carboxyl groups (feature_1411 and feature_216), the higher the Co/Ni selectivity will be. Among these, the α,β -dihydroxyl carboxylic group (feature_605), which is a defining substructure of tartaric acid, emerged as the most impactful fragment to increase the Co/Ni selectivity, showing excellent agreement with our experimental findings. These results highlight key design motifs for engineering future ligands with enhanced separation performance.

To confirm the importance of the α -OH group, we conducted DFT calculations using succinic acid, malic acid, and tartaric acid, as they have similar backbone structures but differ in the number of α -OH groups (Fig. 4B). The octahedral aqua complex was used as the baseline for comparison. The CV onset potentials shift progressively to more negative values in the order of succinate > malate > tartrate, indicating increasing metal-ligand binding strength with a higher number of α -OH groups. For succinic acid, the replacement of two water molecules by one succinate anion resulted in Gibbs free energy changes (ΔG) of -17.76 and -18.74 kcal mol^{-1} for Ni^{2+} and Co^{2+} , respectively. With malic acid, substitution by one malate anion in the solvation sheath yielded more negative ΔG values of -19.52 and -20.88 kcal mol^{-1} for Ni^{2+} and Co^{2+} , respectively. In contrast, the most thermodynamically stable configuration for the metal-tartrate complex differs markedly. The ΔG values for $\text{Co}(\text{H}_2\text{O})_4(\text{Tar})$ and $\text{Ni}(\text{H}_2\text{O})_4(\text{Tar})$ are -17.59 and -18.63 kcal mol^{-1} , respectively, which are less negative than those of the other two bioacids and do not align with the potential shifts observed experimentally. This discrepancy suggests that the mononuclear complex is not the dominant species in solution. Instead, DFT calculation found that the preferred configuration is a dimer structure, $\text{M}_2(\text{H}_2\text{O})_4(\text{Tar})_2$ ($\text{M} = \text{Co}$ or Ni), where two metal ions are coordinated with two tartrate anions and four water molecules. The ΔG values for the Ni^{2+} and Co^{2+} dimers are -23.32 and -25.01 kcal mol^{-1} , respectively, indicating a greater energy difference and theoretically superior Co/Ni separation. The lower ΔG values of the dinuclear tartrate complexes compared to those of succinate and malate are consistent with experimentally observed potential shifts. One common route to understanding metal coordination is by inferring solution phase solvation from solid-state crystallography, and previous works have successfully isolated and structurally characterized dinuclear hydrated metal tartrate complexes (38, 39).

On the basis of the relationship between ΔG and the equilibrium constant ($\Delta G = RT \ln K$), the calculated theoretical separation factors (K_{sep}) for the monomeric succinate, malate, and tartrate complexes are 5.2, 10.0, and 5.7, respectively. In contrast, the metal-tartrate dimer structure exhibits a much higher K_{sep} of 17.4. Experimental

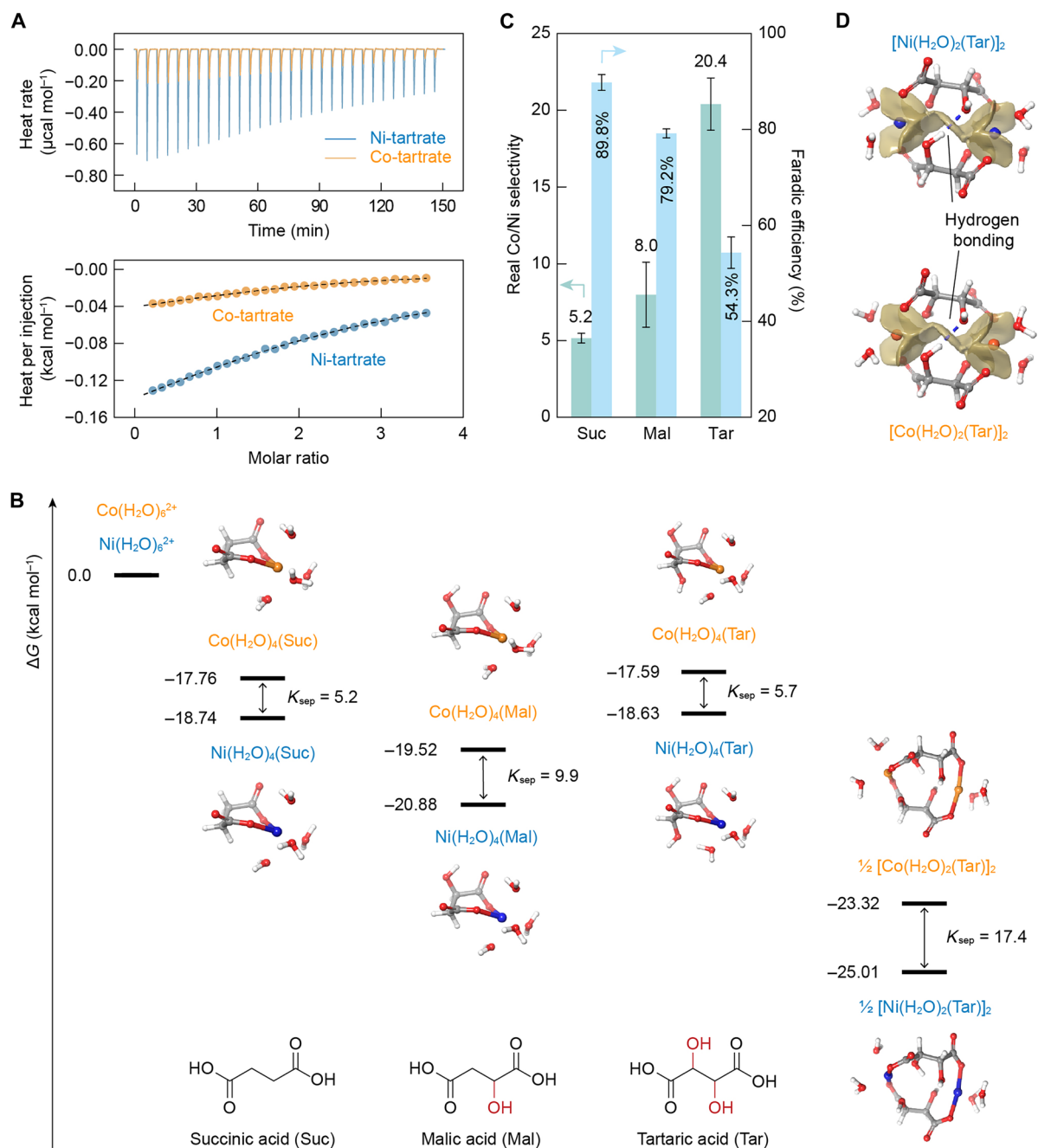


Fig. 4. Mechanistic investigation of tartrate-mediated selective Co electrodeposition. (A) ITC thermograms during the titration of Ni^{2+} and Co^{2+} with tartrate. Ni^{2+} is represented in blue and Co^{2+} in orange. (B) DFT-calculated energy profiles of metal-solvated complexes involving succinate, malate, and tartrate at a deposition capacity of 1 mAh cm^{-2} . The error bars are standard deviations from three replicates. The electrolyte contained a 10 mM equimolar Ni-Co mixture with 0.1 M LiCl supporting salt. Ti foil (1 cm^2) was used as the working electrode. Applied potentials were -0.8 V (succinate), -0.9 V (malate), and -0.9 V (tartrate) versus Ag/AgCl, selected on the basis of the condition of the highest theoretical Co/Ni selectivity at 50 mM. (D) Interaction visualization within the dinuclear metal-tartrate complexes.

measurements yielded Co/Ni separation factors of 5.2, 8.0, and 20.4 for succinate, malate, and tartrate, respectively (Fig. 4C), which closely match the DFT predictions. To understand why the dimer structure forms exclusively in the tartrate system, we visualized the atomic interactions within the complex (Fig. 4D). The α -OH groups in tartrate not only coordinate with metal ions but also form hydrogen bonds with each other between individual tartrate molecules. This additional stabilization promotes dimer formation, leading to a substantially high Co/Ni separation factor.

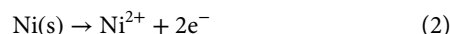
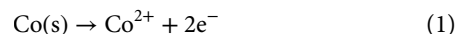
Co enrichment and up-concentration via controlled electrochemical stripping

Selective Co electrodeposition followed by subsequent dissolution enables effective up-concentration of Co^{2+} in solution for downstream processing, and through repetitive deposition-dissolution cycles, metallic Co can be progressively enriched on the electrode to enhance the final product purity. Compared to traditional acid digestion of electrodeposits, which raises environmental and scalability concerns, we established an electrochemical protocol to strip metals from the Ti substrate with high reversibility and minimal waste generation.

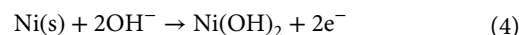
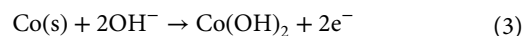
Achieving efficient stripping requires precise control of the electrochemical environment. We found that the choice of the counter electrode reaction critically affects stripping reversibility. The hydrogen evolution reaction is the most straightforward reaction for charge balancing (Fig. 5A). However, the associated pH increase impairs the stripping efficiency. Specifically, the produced hydroxide ions (OH^-)

react with oxidized Co^{2+} and Ni^{2+} , forming insulating hydroxide layers that passivate the deposit surface and impede electron transfer. This is reflected in the potential profile when stripping metallic NiCo electrodeposits using a carbon paper (CP) counter electrode, where the hydrogen evolution reaction occurs (Fig. 5C, blue curve). Two distinct plateaus are observed, corresponding to two different electrochemical reaction pathways, as shown below. Correspondingly, the stripping efficiency was only 77%, and pronounced residues could be observed on the Ti substrate after stripping (fig. S15A).

Region I



Region II



To maintain a stable solution pH during metal stripping, we explored common electrode materials used in rechargeable alkali metal batteries. Li iron phosphate (LFP) stands out as an ideal candidate because of its favorable charge/discharge potentials within the water stability window, high redox reversibility, excellent aqueous stability, and low cost (Fig. 5B). The delithiated LFP (d-LFP) can be prepared

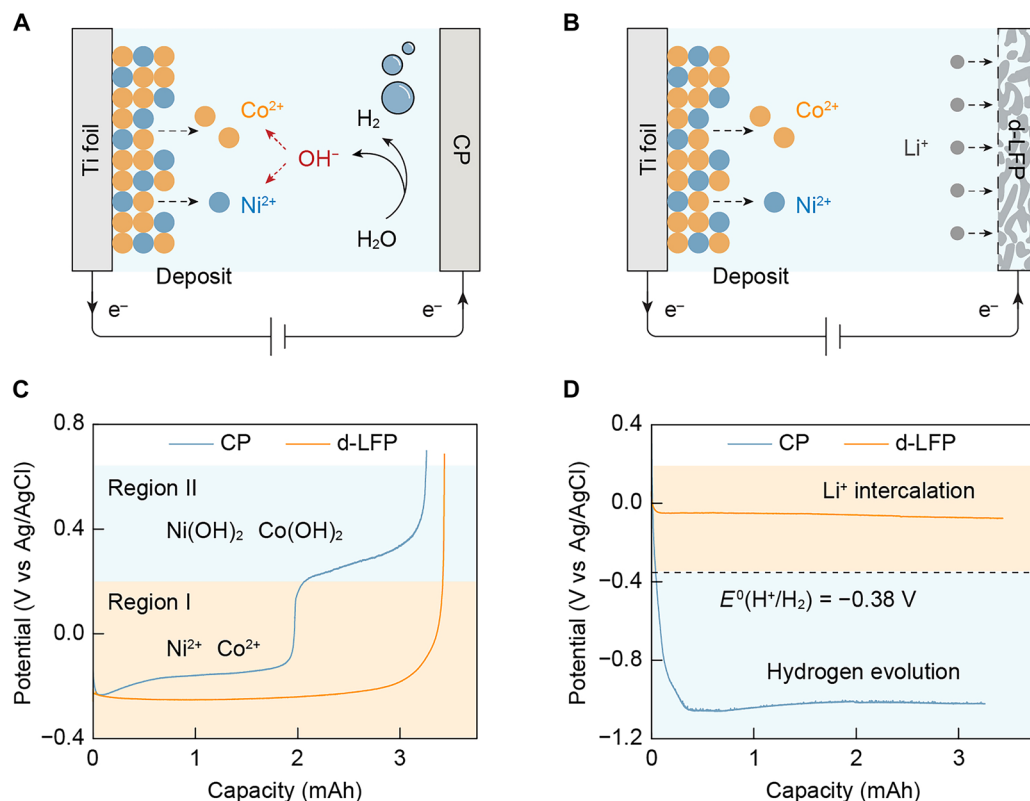


Fig. 5. Co enrichment and up-concentration via controlled electrochemical stripping. (A and B) Schematic representation of the stripping process using CP as the counter electrode at pH 6.0 (A) and d-LFP as the counter electrode at pH 3.0 (B). (C and D) Typical potential profiles of the anodic (C) and cathodic (D) reactions, comparing CP at pH 6.0 (orange) and d-LFP at pH 3.0 (blue). The dashed line in (D) denotes the standard redox potential of the H^+/H_2 couple at pH 3.0.

by chemical delithiation and used as the counter electrode (figs. S16 and S17). Stripping was initially performed at pH 6 when using the CP counter electrode, as lower pH conditions could obscure the detrimental effects of OH^- , particularly under limited stripping amounts. The CP potential stabilized at ~ -1.0 V versus Ag/AgCl, signifying continuous hydrogen evolution. In contrast, the d-LFP electrode operated at pH 3 to ensure an OH^- -deficient environment and exhibited a stable potential at around -0.06 V versus Ag/AgCl, consistent with Li ion intercalation, which does not alter the solution pH (Fig. 5D). This pH stability effectively suppresses OH^- formation, allowing the desired direct metal oxidation reactions (region I) to dominate (Fig. 5C, orange curve). As a result, complete metal stripping is achieved ($\sim 100\%$ stripping efficiency). No visible residue remains on the Ti substrate after stripping, and ICP-OES analysis confirms the complete removal of deposits (fig. S15B). In addition to improving stripping efficiency, the use of d-LFP also provides an energetic advantage. Because its redox potential is considerably more positive than that of the hydrogen evolution reaction, the overall energy input required for stripping is reduced as the process is thermodynamically spontaneous.

Batch extraction of Co from model battery waste

Our bioacid-mediated electrowinning strategy offers a potentially scalable and versatile solution to treating complex mixtures encountered in real-world Co/Ni separation scenarios. To exemplify its capability, we applied the approach to the recycling of NMC111, a representative cathode material used in Li-ion batteries.

The exponential growth of the Li-ion battery industry, driven largely by the electrification of the transportation sector, has heightened concerns over the limited availability of critical materials such as Li, Ni, and Co (5). Although recycling end-of-life Li-ion batteries can mitigate supply chain risks, the global recycling rate remains alarmingly low ($\sim 5\%$ in the United States), largely due to technical and economic barriers (40). Spent battery materials can be processed hydrometallurgically via acid leaching into ionic mixtures, followed by refining the valuable elements into raw precursor materials (41). Our electrowinning-based Co/Ni separation platform can serve as a drop-in replacement for conventional solvent extraction methods in the refining stage, offering improved selectivity, lower environmental impact, and better cost-effectiveness.

In our batch Co extraction scheme (Fig. 6A), commercial NMC111 powder, instead of spent battery material, was selected as model battery waste to eliminate variability in composition and avoid complex pretreatment steps. This choice allowed us to investigate the separation behavior under well-controlled and reproducible conditions. NMC111 powder was first leached using 2 M hydrochloric acid (HCl) with 4 vol % hydrogen peroxide (H_2O_2) (42, 43). The concentration of HCl was deliberately kept moderate to reduce chemical consumption and avoid the undesirable formation of tetrahedral CoCl_4^{2-} anions in the leachate (25), which may hinder the subsequent Co^{2+} coordination with tartrate. After filtration, a dark pink leachate solution was obtained. ICP-OES analysis confirmed efficient leaching, with the recovered elemental mass closely matching the theoretical composition of 0.5 g of NMC111 (table S2).

Concentrated leachate was diluted and adjusted to pH 6, in which electrowinning was performed by selectively reducing Co^{2+} on a Ti foil electrode in the presence of 200 mM tartrate at -0.9 V versus Ag/AgCl (fig. S18 and table S3). For a total leachate volume of 20 ml, 193-mAh charge was passed. The resulting deposit contained 355.4 μmol of Co, 18.8 μmol of Ni, and 1.1 μmol of Mn, corresponding to a metal

deposition faradic efficiency of 12.6%. This first deposition step produced a Co-rich deposit with 94.7% purity from a nearly equimolar Co-Ni-Mn solution and achieved a Co recovery yield of 80.1% (Fig. 6B).

Despite the high Co selectivity, the deposit still contained 5.0% Ni and 0.3% Mn as impurities. To further refine the product, the deposit underwent electrochemical stripping under the optimized conditions described earlier, followed by a second selective Co deposition. The metal was stripped into 20 ml of stripping solution containing 300 mM LiCl, affording a pink-colored solution characteristic of Co^{2+} (Fig. 6A). After the second electrowinning step in the presence of 100 mM tartrate (on the basis of the molar ratio between Ni + Co and tartrate) at -0.9 V versus Ag/AgCl, the Co purity elevated to 99.1% at a high recovery yield of 98.1% (Fig. 6B), with a faradic efficiency of 23.2%. Accordingly, the overall Co recovery reaches 78.6% relative to the initial Co feed. The final solution, now transparent, visually confirms the near-complete removal of Co^{2+} from the electrolyte (Fig. 6A), in agreement with recovery data.

Noticeably, there is a trade-off between Co recovery yield and purity, as evidenced by the ICP-OES results at varying deposition capacities (fig. S19). For instance, at a low cutoff capacity, extracting 23.9% of Co afforded a high purity of 96.4%. As the recovery yield increased to 65.8%, the purity dropped to 95.4% and further decreased to 94.9% at 76.4% Co recovery. The decline in selectivity is ascribed to the gradual depletion of Co^{2+} in solution during extended deposition, which increases the concentration polarization of Co deposition at the electrode surface and narrows the reduction potential difference between Co^{2+} and Ni^{2+} .

Energy consumption is a key metric in evaluating the feasibility of separation technologies (Fig. 6C and note S1). For our two-step electrowinning process applied to NMC111 leachate, the total electrical energy consumption was 76.4 kJ g^{-1} Co. As a predominantly electrochemical approach, this strategy substantially reduces energy demand compared to conventional Co supply chains (e.g., 2.11 MJ g^{-1} Co from primary refining and 0.48 MJ g^{-1} Co from recycling end-of-life Li-ion batteries) (5). In a potentiostatic electrowinning operation, energy consumption depends largely on the faradic efficiency of metal deposition and the polarization of the counter electrode. If the oxygen evolution reaction at the counter electrode is catalytically optimized, its overpotential can be minimized. Assuming the theoretical oxygen evolution potential of 0.667 V versus Ag/AgCl at pH 6, the corresponding energy consumption drops to 63.6 kJ g^{-1} Co. Further improving the faradic efficiency, possibly by enhancing Co^{2+} mass transport, yields substantial energy savings. At faradic efficiencies of 30, 50, and 70%, the projected energy consumption reduces to 34.9, 21.2, and 15.3 kJ g^{-1} Co, respectively. These findings highlight the potential for further optimization of the process through reaction engineering.

Flow system for sequential metal recovery from model battery waste

Our batch extraction experiments confirmed the competitive Co selectivity of the bioacid-mediated electrowinning process and identified improving mass transport and minimizing reaction polarization as two primary pathways for further performance enhancement. To this end, we transitioned the system into a flow-based three-electrode configuration, leveraging its superior mass and charge transfer kinetics to boost deposition rates and faradic efficiency (Fig. 7A). A Ag/AgCl reference electrode was integrated within the flow chamber to maintain stable potential control during operation. To demonstrate the broader applicability of our strategy, we established a complete

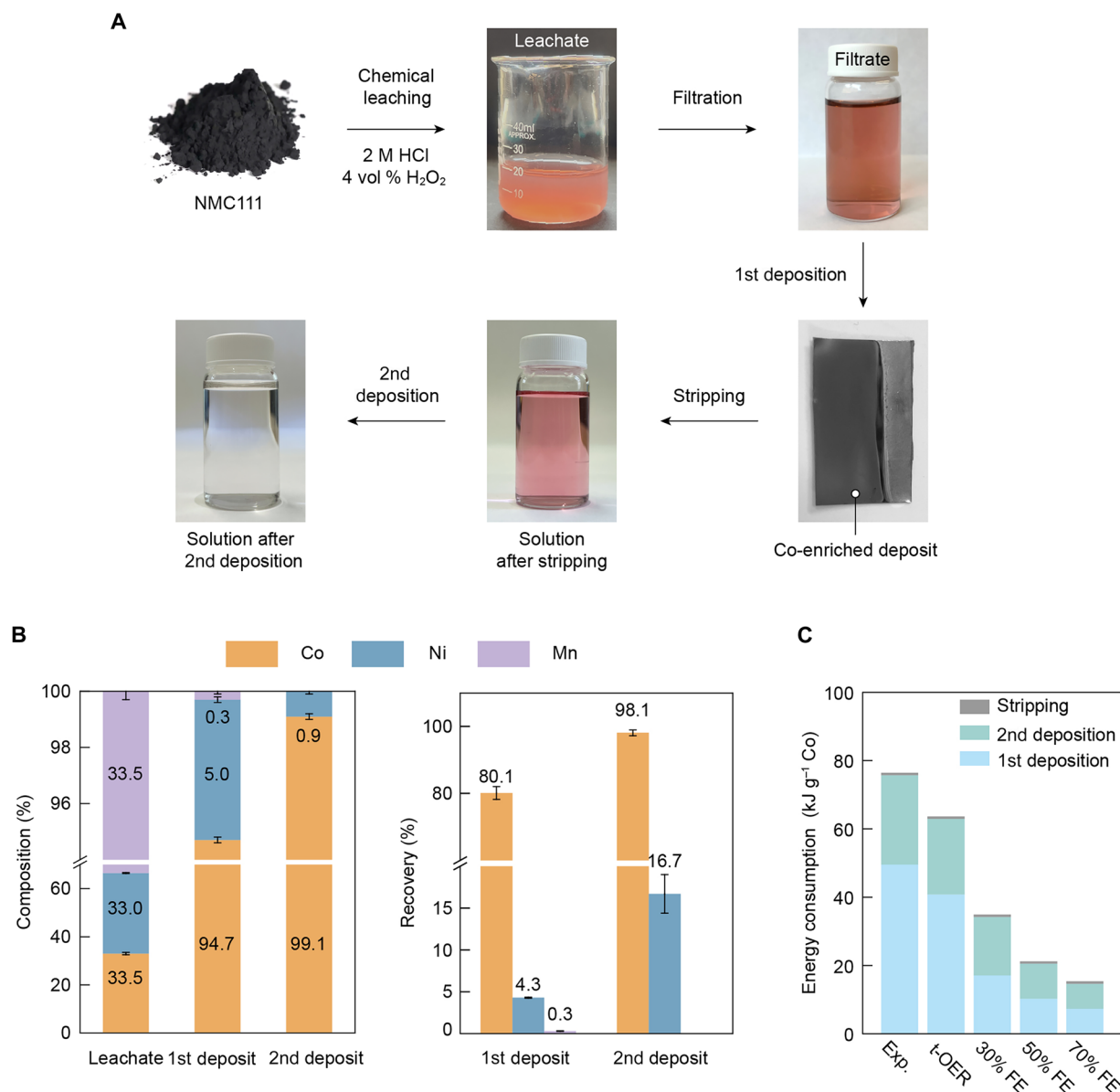


Fig. 6. Evaluation of batch-scale selective Co electrowinning from NMC111 leachate. (A) Workflow of recycling metallic Co from NMC111 powder at a batch-cell scale. (B) Elemental composition of the pretreated leachate, first deposit, and second deposit, along with recovery yields of Co, Ni, and Mn for the first and second deposits. The error bars are standard deviations from three replicates. (C) Comparative analysis of experimental and optimized energy consumption of the described Co electrowinning process. t-OER represents the theoretical oxygen evolution potential. FE stands for the faradic efficiency.

workflow for sequential separation and refinement of Co, Ni, and Mn from Li-ion battery leachate, showcasing the potential of bioacid-mediated electrowinning for tandem separation applications (Fig. 7B and figs. S20 and S21).

The workflow begins with selective Co deposition in the presence of 200 mM tartrate at an applied potential of -0.9 V versus Ag/AgCl to afford a Co-rich deposit (first Co deposition). As expected, the faradic efficiency is enhanced in the flow-based configuration ($\sim 29\%$ with 98.0% Co extraction). Similar to batch systems, a trade-off between recovery yield and purity was observed (Fig. 7C). At a Co recovery yield of 33.4% , a high separation factor of 13.8 can be achieved. As deposition progresses and more Co is extracted from

the leachate, the energy barrier for Co reduction increases, leading to reduced selectivity, especially beyond 80% Co recovery. At 98.0% Co recovery, the separation factor dropped to 5.4 , which was identified as the optimal cutoff point, balancing the Co purity of the first deposit while maximizing recovery. The Co-rich deposit was then completely stripped using a d-LFP counter electrode, followed by a second selective Co deposition. The relationship between Co/Ni selectivity and recovery yield during this stage was also studied (Fig. 7C). Notably, a high Co purity of 99.2% was achieved when 37.5% of Co was recovered from the stripping solution. Further extraction ultimately led to 95.1% Co purity at a 96.4% recovery (equivalent to 95% from the leachate), demonstrating the effectiveness of

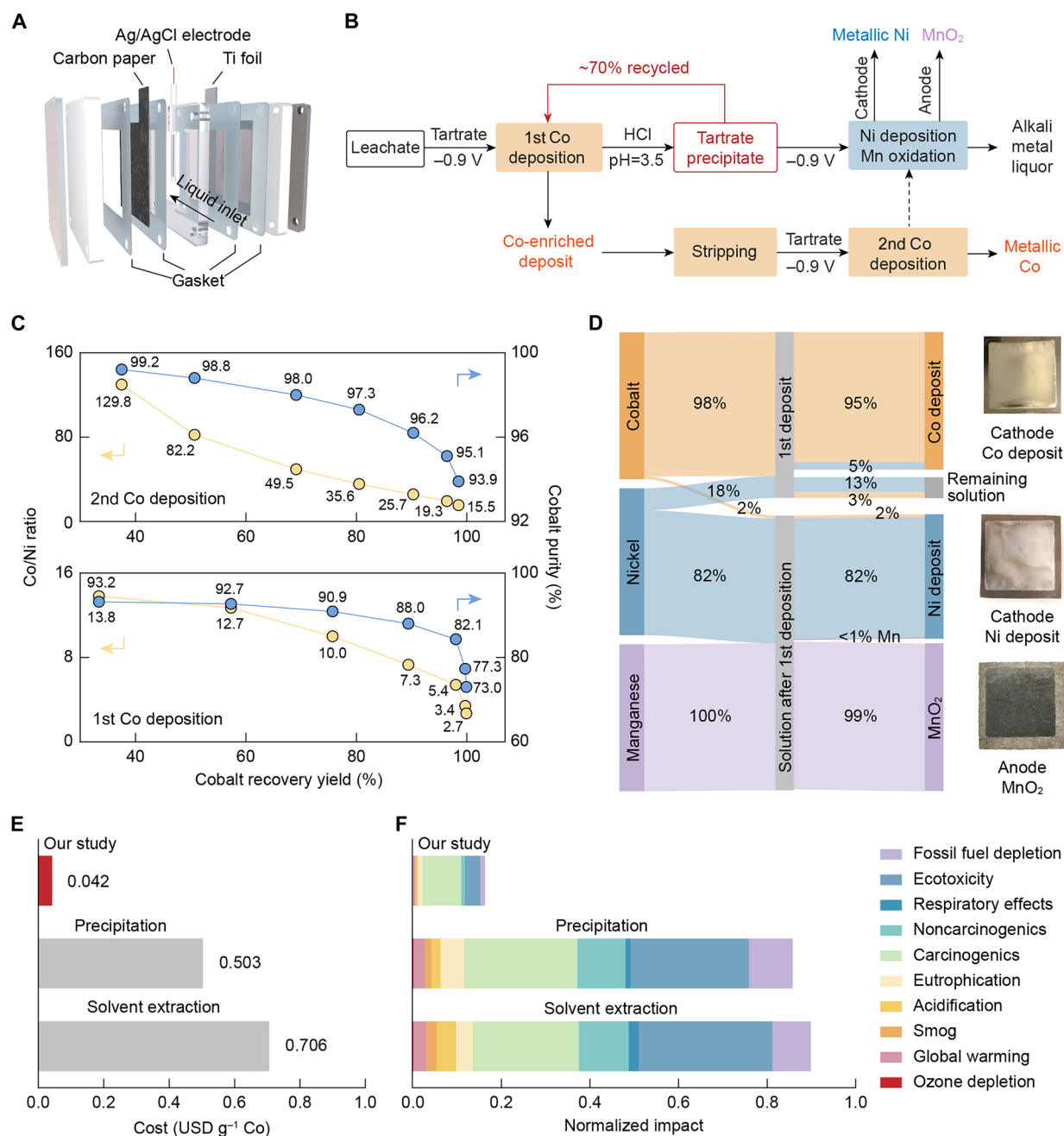


Fig. 7. Evaluation of the flow system for sequential metal separation. (A) Schematic configuration of the three-electrode flow cell setup. (B) Workflow for sequential separation of Co, Ni, and Mn from NMC111 leachate. (C) Co/Ni ratio in the deposit and corresponding Co purity as a function of Co recovery yield during the first and second Co deposition steps. (D) Sankey diagram illustrating the elemental flow of Co, Ni, and Mn throughout the process. (E and F) TEA (E) and LCA (F) comparing the developed strategy with traditional solvent extraction and chemical precipitation methods.

the tandem electrowinning process in achieving both high selectivity and yield.

Following the first Co deposition, metallic Ni was recovered from the leachate via electrodeposition. However, because of the strong coordination between Ni^{2+} and tartrate, direct deposition is hindered unless the ligand is removed. Otherwise, a large overpotential will be required, and the faradic efficiency will be compromised by the competing hydrogen evolution reaction. To address this, we developed a

strategy to precipitate and recycle tartrate ligands by exploiting the low solubility of potassium bitartrate under acidic conditions. By titrating the pH of 200 mM pure tartrate solution with HCl, we quantified tartrate precipitation by both weight measurements and nuclear magnetic resonance (NMR) spectroscopy (figs. S22 and S23). The optimal pH for precipitation was determined to be ~ 3.5 . A similar precipitation trend was observed in tartrate solutions containing Ni^{2+} and Mn^{2+} , simulating post-Co deposition leachates (figs. S24). These

findings align with literature reports indicating that bitartrate anions dominate in this pH range, promoting the formation of potassium bitartrate (44). Approximately 70% of the ligand can be recovered and reused for subsequent Co extraction, reinforcing the environmental sustainability of the process.

At lower pH, protonation of the carboxyl groups of tartrate weakens the Ni-tartrate complex, thus facilitating more effective Ni deposition. However, excess proton concentrations also promote hydrogen evolution, which compromises the faradic efficiency of Ni deposition. To balance these effects, pH 3.5 was selected for Ni recovery immediately after ligand precipitation without further pH adjustment. During this step, residual Co^{2+} in the leachate co-deposits with Ni^{2+} , slightly reducing metal purity. ICP-OES analysis reveals a Ni purity of 96.5%.

The reduced tartrate concentration after pH-controlled precipitation facilitates Mn^{2+} oxidation at the anode during Ni deposition at the cathode. In contrast, only trace amounts of Mn^{2+} are oxidized during Co deposition, likely due to the higher oxidation energy barrier imposed by the Mn-tartrate complex. Anodic products fill the pores of the CP electrode (fig. S25A), with manganese dioxide (MnO_2) identified as the dominant species on the basis of the Pourbaix diagram of Mn (fig. S25B). ICP-OES detects no metallic elements other than Mn, and EDS mapping shows a Mn:O atomic ratio of ~2:1, consistent with MnO_2 formation (fig. S25, C to E). The recovered transition metals were then used to synthesize NMC111 (note S2), which exhibited a comparable crystal structure and electrochemical cycling performance to its commercial counterpart (fig. S26) (45, 46), demonstrating the potential for cathode material regeneration.

Following Ni/Mn separation, the remaining solution contains alkali metal ions including Li^+ , K^+ , and Na^+ , the latter two of which were introduced because of the use of potassium sodium tartrate. The Li element can be easily extracted either electrochemically using a d-LFP electrode (47) or via chemical precipitation with saturated sodium carbonate (48). These downstream steps demonstrate the versatility of our process for recovering multiple critical elements in a sequential and resource-efficient manner.

The higher faradic efficiency of the flow system compared to the batch system reduces energy consumption. For Co recovery, the energy requirements are 47.2, 0.6, and 15.9 kJ g^{-1} Co for the first Co deposition, electrochemical stripping, and second deposition, respectively. This represents a 17.2% reduction compared to the batch process. In the case of downstream Ni/Mn separation, the total energy consumption is 116.3 kJ g^{-1} Ni (equivalent to 101.5 kJ g^{-1} Co). The Sankey diagram shown in Fig. 7D visualizes the complete elemental flow of the process.

TEA was performed to benchmark the cost-effectiveness of our approach against previously disclosed Co/Ni separation methods (Fig. 7E). Notably, comparative TEAs on metal extraction and recovery remain scarce because of the lack of detailed disclosures on key variables such as chemical dosage and process scales. However, a recent study comparing typical solvent extraction and an advanced chemical precipitation method for Co/Ni separation provided the necessary information, which we herein used for systematic comparisons under the same system boundaries (fig. S27) (18). For the conventional solvent extraction, the projected cost is 0.706 USD g^{-1} Co, while the chemical precipitation process achieves a modest improvement at 0.503 USD g^{-1} Co. In marked contrast, our electrowinning method reveals a much lower total cost of 0.042 USD g^{-1} Co, comprising 0.039 USD g^{-1} Co in chemical expenses and 0.003 USD g^{-1} Co in

energy consumption (tables S4 and S5). This represents a cost reduction by one order of magnitude compared to the other two techniques, primarily enabled by the use of readily available, low-cost bioacids and electricity as the driving force rather than specialized reagents. Applying an industrial electricity rate would further reduce the energy cost, although it is a minimal contributor to the overall expense.

To assess the economic feasibility of the full valorization process, we incorporated revenue from recovered products on the basis of market prices as of the end of 2024. The value-added products include Co metal, Ni metal, and MnO_2 . Excluding Li recovery from the downstream liquor, the net cost was calculated at 6.22 USD kg^{-1} Co, well below the market price of Co (24.30 USD kg^{-1}) used in the calculation. If assuming the complete recovery of Li as Li_2CO_3 , the process can generate a net profit of 33.68 USD kg^{-1} Co (table S6). The prices of these critical element products are currently far below their 10-year maximum. Considering the 10-year midpoint values for Co, Ni, and Li, the net profit increases substantially to \$190.01 kg^{-1} Co recovered. While actual margins will be affected by product purity, labor, and equipment depreciation, these results confirm the economic competitiveness of our electrowinning approach.

LCA was also conducted to quantify and compare the environmental impacts of solvent extraction, chemical precipitation, and our bioacid-mediated electrowinning process. The analysis was performed using impact models from TRACI 2.1 (Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts), developed by the US Environmental Protection Agency (49). Detailed results across 10 environmental categories are provided in table S7. The findings suggest that the electrowinning system has the potential to markedly curtail all considered categories of environmental impacts. For instance, compared with solvent extraction, respiratory effects decrease from 5.56×10^{-01} to 2.94×10^{-02} $\text{kg PM}_{2.5}$ (particles less than 2.5 μm in diameter) equivalent, which is a maximum reduction of 94.70%. This is followed by fossil fuel depletion (from $1.49 \times 10^{+03}$ to $1.74 \times 10^{+02}$ MJ surplus, an 88.26% reduction) and acidification (from 4.02 to 0.40 kg SO_2 equivalent, an 89.97% reduction). Compared with chemical precipitation, electrowinning also provides superior environmental performance across all impact categories, especially with regard to ozone depletion and noncarcinogenics, achieving reductions of 93.57 and 91.34%, respectively. We further normalized each environmental category to identify the most impactful ones on the basis of the US 2008 database (Fig. 7F and table S8) (50). Analysis of the normalized midpoint results reveals that ecotoxicity, carcinogenics, noncarcinogenics, and fossil fuel depletion exert the greatest influence on the overall environmental impact. This enhancement in environmental quality is primarily attributed to replacing the ammoniacal media with the bioacid-mediated electrowinning route for Co/Ni separation. In total, the electrowinning system has the potential to enhance the environmental performance by 81.91 and 81.05% relative to solvent extraction and precipitation, respectively, firmly establishing it as an economically and environmentally superior alternative for Co/Ni separation.

DISCUSSION

In summary, we developed a bioacid-mediated electrowinning platform that enables highly selective Co recovery from Ni-containing complex mixtures by modulating ion solvation environments. Leveraging the unique coordination chemistry of tartaric acid, we amplified the reduction potential difference between Co and Ni. Mechanistic

insights from machine learning-guided analysis and DFT calculations further revealed that dinuclear metal-tartrate complexes, stabilized by intramolecular hydrogen bonding, play a critical role in enabling selective deposition. By optimizing the deposition-stripping protocol, reactor design, and ligand recycling scheme, our flow system demonstrated scalable, energy-efficient recovery of Co, Ni, and Mn with high purity and recovery yield from real battery leachates, substantially outperforming conventional solvent extraction and precipitation methods as confirmed by TEA and LCA. Future work will focus on high-throughput screening of additives to generate larger datasets and integrating them with machine learning to predict optimal additives for enhanced electrowinning selectivity. Beyond Co/Ni separation, this strategy provides a blueprint for sustainable, electrochemically driven separations of critical elements, contributing toward circular resource utilization and a more resilient energy future.

MATERIALS AND METHODS

Electrochemical experiments

All electrochemical measurements were performed using a BioLogic VSP potentiostat (BioLogic Science Instruments). For CV experiments, a three-electrode configuration (Bioanalytical Systems Inc.) was used. The working electrode was a Ti disk electrode ($\varnothing = 3$ mm), the counter electrode was a platinum wire, and an Ag/AgCl electrode (3 M NaCl) served as the reference electrode. A 5-ml solution containing 100 mM LiCl was used as the supporting electrolyte, and 10 mM of either NiCl_2 or CoCl_2 was prepared for each test. The CV scans were conducted at a rate of 10 mV s^{-1} over a potential range of -1.2 to 0.5 V versus Ag/AgCl. Before each test, the solutions were purged with N_2 gas for at least 5 min to remove dissolved O_2 .

To obtain real Co/Ni selectivity, a 40-ml electrolytic cell was used with a Ti foil as the working electrode, a graphite rod as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The electroactive area of the working electrode was 1 cm by 1 cm, with its backside covered by Kapton tape to prevent unwanted deposition. A 20-ml solution containing 100 mM LiCl, 5 mM NiCl_2 , and 5 mM CoCl_2 was prepared for deposition, which was conducted under different bioacid concentrations, applied potentials, and capacities. Following the same protocol, batch-scale selective Co deposition was performed in NMC111 leachate. A larger piece of Ti foil ($\sim 2.5 \text{ cm}^2$) was used to accelerate the rate of deposition.

Metal deposits were electrochemically stripped at a current density of 2 mA cm^{-2} , with a cutoff potential of 0.7 V versus Ag/AgCl. This protocol is compatible with both batch and flow systems. The stripping electrolyte consisted of 300 mM LiCl or NaCl, serving as charge carriers to intercalate d-LFP. d-LFP was prepared by the chemical delithiation method, which uses a 0.1 M sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) solution with a 1:2 molar ratio of LFP to $\text{Na}_2\text{S}_2\text{O}_8$ (51).

Characterizations

XRD measurements were performed using a Malvern Panalytical Aeries Diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). SEM was conducted on a Thermo Fisher Scientific Helios G4 DualBeam instrument, equipped with an EDS detector with an accelerating voltage of 20 kV. UV-vis spectra were collected by a GENESYS 10S UV-vis spectrometer. NMR spectra were collected on a Bruker AMX400 (400 MHz) spectrometer and reported in parts per million (ppm). Tetramethylsilane was added as an internal reference, while deuterium oxide (D_2O) was used as the solvent for ^1H NMR spectroscopy. The chemical states of the

Co and Ni electrodeposits were characterized using XPS (Kratos Axis 165) with a monochromatic Al $\text{K}\alpha$ x-ray source. Monatomic Ar^+ sputtering was applied to etch the sample surface and perform depth profiling analysis. The heat released during a metal-ligand binding event was monitored by the MicroCal VP-ITC instrument with a sodium acetate/acetic acid buffer pair. All solutions were degassed before filling the syringe and cell.

Quantitative analysis of metal elements

To prepare for elemental analysis, samples were thoroughly washed with deionized water and ethanol, dried, and then digested using either 5% (w/w) trace metal-grade nitric acid or concentrated HCl, depending on the specific requirements for digestion. The quantifications of Co, Ni, Mn, and Li were performed by ICP-OES (Agilent 5800). Standard solutions at concentrations of 50, 200, 1000, 2000, and 5000 ppb (parts per billion) were prepared by diluting Assurance Grade single-element ICP standards (1000 ppm in 2% nitric acid; SPEX). A correlation coefficient (R^2) > 0.999 was ensured for the calibration linear fit. The wavelengths selected for elemental quantification were 231.604 nm (Ni), 238.892 nm (Co), 257.610 nm (Mn), and 670.783 nm (Li). Each sample was measured in six replicates to obtain reliable averaged results.

The purity of the deposit was defined as $\text{Purity} = n_x / (n_{\text{Ni}} + n_{\text{Co}} + n_{\text{Mn}}) \times 100\%$, where n_x represents the amount of a specific element of interest (in moles), and n_{Ni} , n_{Co} , and n_{Mn} are the amount of Ni, Co, and Mn, respectively.

The faradic efficiency of metal electrodeposition can be calculated from the ICP-OES measurements as $\text{Faradic efficiency} = nzF / Q_{\text{total}} \times 100\%$, where z is the moles of electrons involved in the reaction per mole of the product ($z = 2$ in this case), F is the Faraday's constant ($96,485 \text{ C mol}^{-1}$), n is the moles of product formed on the basis of ICP-OES analysis, and Q_{total} is the total charge passed through the system.

Acid leaching of NMC111

Commercial NMC111 powder was used as model battery waste to simulate the metal composition of spent Li-ion cathodes while avoiding the variability and additional pretreatment steps typically associated with real battery waste. This approach allowed us to focus on mechanistic insights under simplified and controlled conditions. A leaching solution (19.2 ml) consisting of 2 M HCl and 0.8 ml of H_2O_2 was added to the reactor to enhance chemical leaching and facilitate the reduction of high-valence metal ions. Subsequently, 0.5 g of NMC111 powder was gradually introduced under constant magnetic stirring to ensure uniform mixing. After a reaction time of 1.5 hours, the insoluble residues were separated via vacuum filtration. The filtrate was then collected and preserved for ICP-OES analysis and selective electrodeposition studies. Before Co deposition, the solution pH was adjusted to 6 using Li hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$) or sodium hydroxide (NaOH).

Machine learning-assisted identification of important molecular fragments

RDKit was used to convert the SMILES (Simplified Molecular Input Line Entry System) of bioacids to 2048-bit ECFPs (radius, 2). Then, using the normalized concentration as weight, each bit of ECFPs was multiplied by the weight to get the WECFPs. For example, if an experiment was performed with 10 mM bioacid, the weight would be 0.1667 and all bits of the ECFPs in this data would be multiplied

by 0.1667 to get the WECFPs; on the other hand, if an experiment was performed with 60 mM bioacid, the weight would be 1 and all bits of the ECFPs in these data would be multiplied by 1. Using the WECFPs as features and theoretical Co/Ni selectivity as the label, the random forest algorithm was used to train a model, followed by the SHAP analysis. With the top five ranked fragments in hand, RDKit was used to retrieve the substructures from the fingerprints. The code is available at <https://github.com/Liu-Lab-JHU/Selective-Cobalt-Nickel-Separation>.

DFT computational method

All DFT calculations were performed using Orca 6.0.0 (52, 53). All calculations featured the Truhlar M06-2x functional with D30 empirical correction to include van der Waals interactions (54). All atoms were described by the def2-svp basis set and effective core potential for optimization and def2-tzvp for energy calculation (55). The solvent environment was modeled via CPCM (56) with parameters matching H₂O. Vibrational frequencies were computed to predict such thermochemical properties as enthalpies, zero-point energies, and entropies. To account for librational modes hindered by the solvent environment, translational and rotational entropy modes were reduced by 50%. Note that the implicit solvation model has limitation while describing the hydrogen bond formed between anion ligands and H₂O; therefore, we used docking (57) results from Orca 6.0.0 as initial guesses for further optimization with explicit water. The independent gradient model based on Hirshfeld partition (IGMH) (58) analysis was applied on Multiwfn (59) to illustrate the hydrogen bond interaction between the two ligands in the dimer complex.

TEA and LCA

A cost comparison was conducted through TEA, focusing on the chemical expenses required to extract 1 g of metallic Co. Bulk pricing from vendors, reliable market data, and US-specific government reports were used to ensure a fair and scale-consistent evaluation. The environmental performance of different Co/Ni separation systems was assessed using the LCA method. The functional unit was defined as 1 kg of Co separation, taking into account the characteristics of the products. The system boundary encompasses all materials and energy inputs necessary for the Co/Ni separation process. Upstream infrastructure (e.g., equipment manufacturing) was excluded to facilitate a fair comparison with previous studies. Current models from TRACI 2.1 were used, which were developed using the midpoint-oriented LCA methodology by the US Environmental Protection Agency. The normalization results were then performed against the US 2008 database. The selected methodology encompasses the impact categories of ozone depletion, global warming, smog, acidification, eutrophication, carcinogenics, noncarcinogenics, respiratory effects, ecotoxicity, and fossil fuel depletion, providing assessment results that can inform environmental sustainability.

Sequential metal recovery

The flow-based sequential battery recycling system used a custom-built three-electrode configuration. Ti foil, CP, and Ag/AgCl were used as the working, counter, and reference electrodes for selective deposition, respectively. The electroactive area of the working electrode was 5 cm². The first selective Co extraction was carried out in NMC111 leachate at pH 6 and an applied potential of −0.9 V versus Ag/AgCl in the presence of 200 mM potassium sodium tartrate. Subsequent Co enrichment via controlled electrochemical stripping at

2 mA cm^{−2} using d-LFP as the counter electrode followed by second Co deposition yielded high-purity metallic Co. After the first selective Co deposition, concentrated HCl was added to the solution to adjust the pH to 3.5, precipitating potassium bitartrate, which can be recycled. At this pH, Ni deposition was conducted at −0.9 V versus Ag/AgCl, while MnO₂-dominated species formed on the CP anode, leaving behind an alkali metal liquor.

Supplementary Materials

This PDF file includes:

Figs. S1 to S27
Tables S1 to S8
Notes S1 and S2
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