Chapter 28

Simultaneous Selective Recovery of Lithium and Cobalt from Spent Lithium-ion Batteries Using Modified Bipolar Membrane Electrodialysis

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Abstract

The increasing use of lithium-ion batteries (LIBs) has led to significant volumes of battery waste and a growing demand for critical metals such as lithium (Li) and cobalt (Co). This study developed a selective electrodialysis process with bipolar membranes (EDBM) to simultaneously recover Li and Co from spent LIB cathode materials. Cobalt was converted into an anionic complex using a citric acid-based leaching system and hexacyanoferrate complexation, enabling its separation from Li under an applied potential. The optimised EDBM stack achieved recovery rates of >89% for Co and >93% for Li under a 25 mA cm^{-2} current density. The recovered Li was obtained as high-purity lithium hydroxide (LiOH, >98%) and Co as cobalt hexacyanoferrate, which may be reused into battery-grade precursors. The process eliminated selective precipitation, significantly reducing the consumption of toxic reagents and minimising secondary waste generation. A preliminary economic analysis indicated a 28% reduction in operating costs compared to conventional hydrometallurgical routes, while life cycle analysis showed a 35% lower carbon footprint. This approach offers an energy-efficient, scalable, and environmentally benign alternative for battery metal recovery, enabling circular resource use in the LIB industry. The successful demonstration of this technology strengthens its viability for downstream industrial integration.

Keywords: *Lithium-ion Battery, Recycling, Bipolar Membrane Electrodialysis, Cobalt Recovery, Sustainable Hydrometallurgy*

Introduction

The rapid expansion of electric vehicle (EV) production and the escalating demand for lithium-ion batteries (LIBs) have created a pressing global need for sustainable recovery of critical raw materials, particularly lithium (Li^+) and cobalt (Co^{2+}). EV sales are projected to reach 43 million units by 2040[1], with end-of-life LIBs expected to generate over 11 million tons of waste by 2030[2]. This waste stream presents not only an environmental concern but also a strategic opportunity, as spent LIBs are enriched

[1]BloombergNEF, *Electric Vehicle Outlook 2024*, BloombergNEF, 2024 https://about.bnef.com/electric-vehicle-outlook/.

[2]International Energy Agency, *Global EV Outlook 2023*, IEA, 2023 https://www.iea.org/reports/global-ev-outlook-2023.

with lithium and cobalt, making them a viable secondary resource. Their efficient recovery is essential to advancing circular energy technologies, reducing reliance on virgin mining, and ensuring a stable material supply chain. Current industrial LIB recycling utilised pyrometallurgy, an energy-intensive and toxic process[3], and hydrometallurgy, with large chemical consumption and high waste generation[4].

Electrochemical separation methods have emerged as a promising alternative that could overcome some limitations of traditional techniques. Electrodialysis (ED), in particular, is recognised as a 'green' separation technology that can selectively recover ions using electricity instead of added chemicals[5]. A recent study has applied ED to LIB recycling at laboratory scale, demonstrating that lithium can be efficiently separated from mixed-metal leachates given appropriate membranes and operating conditions[6]. Moreover, electrodialysis is a mature industrial technology and can be scaled by stacking membrane cell units, making it a promising candidate for industrial-scale LIB recycling[7].

Bipolar membrane electrodialysis (EDBM) is a specialised form of electrodialysis that integrates water-splitting bipolar membranes into the stack. An EDBM stack allows direct generation of acid and base from a neutral salt feed solution. The ability to produce acid and base in situ is highly attractive for battery recycling. EDBM thus enables a closed-loop process with minimal external reagents. However, simultaneous recovery of lithium and cobalt via EDBM has not been extensively studied.

In this work, the simultaneous selective recovery of Li and Co from spent LIB cathode leach solution using an EDBM process was explored. Key technical innovations include using a chelating strategy and modifying membranes to facilitate selective and efficient transport, and the integration of acid/base regeneration within the electrodialysis cell.

Results and Discussion

Selective Separation Mechanism

The EDBM process here effectively enabled the simultaneous recovery of Li and Co from spent LIB cathode leachates. Using a citric acid-based leaching system combined with hexacyanoferrate complexation, cobalt was converted into a stable anionic complex, allowing it to migrate under an applied potential while Li^+ selectively passed through cation-exchange membranes. Li and Co exhibited significantly higher adsorption capacities (Figure **1**a) than competing ions such as Ni^{2+} and Mn^{2+}, with Li^+ reaching ~1.6 mmol g^{-1} and Co^{2+} ~1.3 mmol g^{-1} after 30 min, while other ions remained below 0.2

[3]Brian Makuza et al., "Pyrometallurgical Options for Recycling Spent Lithium-Ion Batteries: A Comprehensive Review," *Journal of Power Sources* 491 (2021): 229622 https://doi.org/10.1016/j.jpowsour.2021.229622.
[4]E. Asadi Dalini et al., "A Review on Environmental, Economic and Hydrometallurgical Processes of Recycling Spent Lithium-Ion Batteries," *Mineral Processing and Extractive Metallurgy Review* 42 (2021): 628–651 https://doi.org/10.1080/08827508.2020.1781628.
[5]Alain Chagnes et al., "Lithium-Ion Battery Recycling: Metal Recovery from Electrolyte and Cathode Materials by Electrodialysis," *Metals* 12, no. 11 (2022): 1859 https://doi.org/10.3390/met12111859.
[6]Soumaya Gmar et al., "Application of Electrodialysis for the Selective Lithium Extraction towards Cobalt, Nickel and Manganese from Leach Solutions Containing High Divalent Cations/Li Ratio," *Recycling* 7, no. 2 (2022): 14 https://doi.org/10.3390/recycling7020014.
[7]Chagnes et al., "Lithium-Ion Battery Recycling," 1859.

mmol g^{-1}. Correspondingly, high selectivity coefficients were observed (Figure **1**b), with Li/Ni and Li/Mn ratios exceeding 200, and Co/Ni and Co/Mn also rising steadily over time, confirming strong preferential separation of Li^+ and Co^{2+} over competing species. The recovered product streams achieved high purity (Figure **1**c), with lithium hydroxide (LiOH) exceeding 98% and cobalt purity approaching 98% within 30 min of electrodialysis. Energy demand was modest (Figure **1**d), with specific energy consumption stabilising at ~3.2 Wh L^{-1}, equivalent to ~0.7–0.9 kWh kg^{-1} Li, which is comparable to reported values for similar electrodialysis systems[8]. The optimised five-unit EDBM stack (Figure **2**) operated at 25 mA cm^{-2}, achieving recovery rates of >93% for Li and >89% for Co. Li was recovered as LiOH (>98%), while cobalt was precipitated as cobalt hexacyanoferrate, both suitable for reuse as cathode precursors.

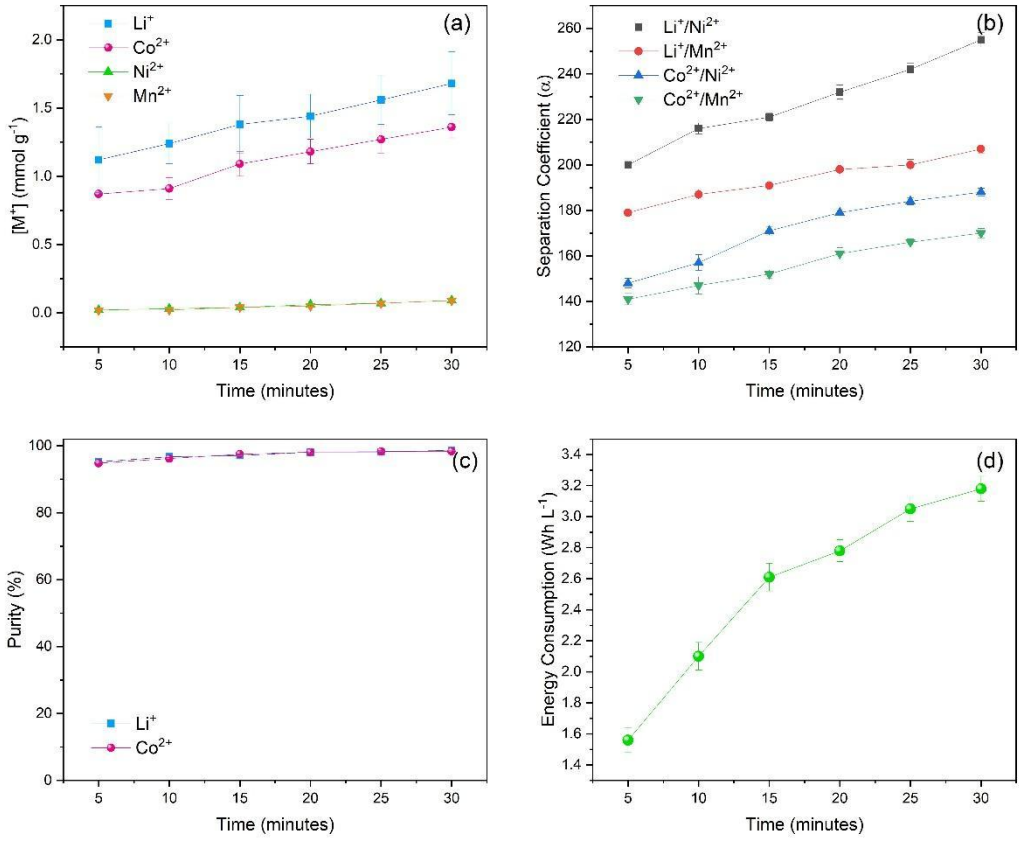

Figure 1: (a) Adsorption capacity of Li+ and Co2+ vs. other metal ions (Ni^{2+}, Mn^{2+}) on the modified membranes over time, (b) corresponding selectivity coefficients (Li/M, Co/M), (c) purity of recovered Li and Co as a function of electrodialysis time, (d) specific energy consumption of the EDBM process over time.

Figure **2** further illustrates the mechanism by which the EDBM process achieves this dual recovery. Cobalt complexed as hexacyanoferrate migrated through the modified anion-exchange membranes into the anode compartment, while Li^+ selectively traversed the modified cation-exchange membranes into the cathode compartment, where hydroxide ions generated by the bipolar membranes combined to form LiOH. This integrated configuration simultaneously produced high-purity LiOH and cobalt

[8]Adam Isaksson et al., "Zero-Waste Recycling of Lithium and Cobalt from Lithium-Ion Batteries by Three-Stage Electrodialysis," *Separation and Purification Technology* 368 (2025): 133060 https://doi.org/10.1016/j.seppur.2025.133060.

hexacyanoferrate, effectively performing two separations in a single unit operation. The process reduced chemical inputs and secondary waste by eliminating the multiple neutralisation and precipitation steps required in conventional hydrometallurgical flowsheets.

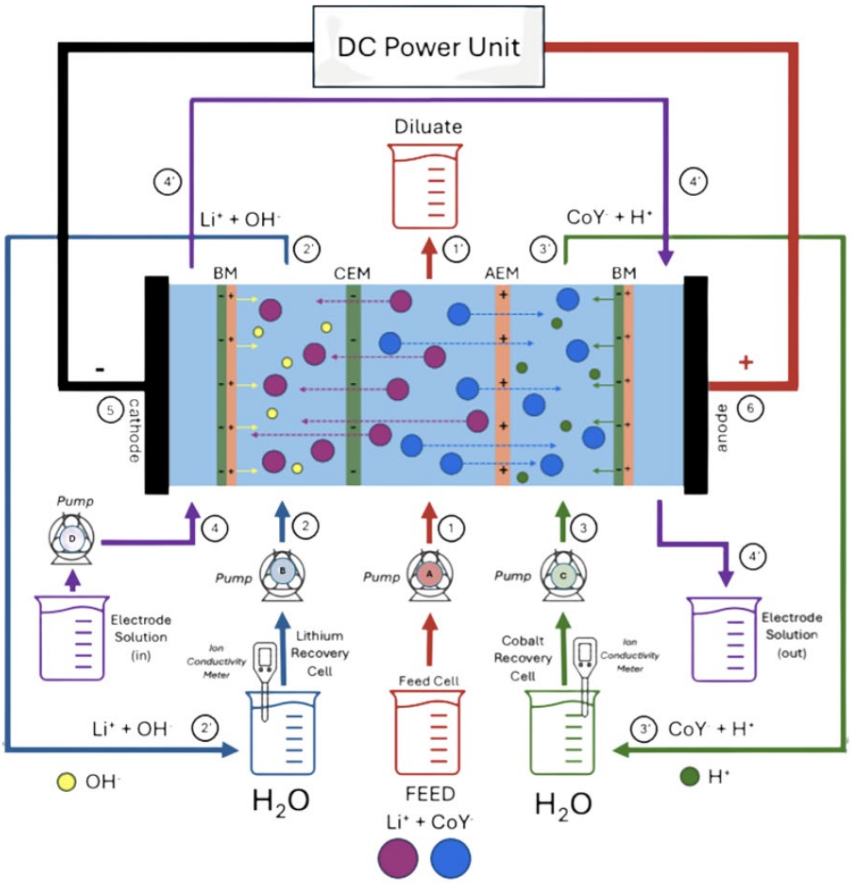

Figure 2: Schematic illustration of the bipolar membrane electrodialysis (EDBM) process for simultaneous Li and Co recovery.

Energy Consumption

An energy consumption was calculated from the electrical input required to drive ion transport and water dissociation in the EDBM stack, using $E = (V \times I \times t)/m$, where V is cell voltage, I is current, t is operation time, and m is the mass of lithium recovered. This gave a specific energy consumption of ~0.7–0.9 kWh per kg of Li, lower than reported ranges of 1–2 kWh kg^{-1} [9] for similar systems, and close to the 1.33 kWh kg^{-1} achieved with redox-mediated EDBM[10]. In contrast, the 35% smaller carbon footprint was determined by life cycle analysis (LCA) comparing EDBM to hydrometallurgy. Conventional processes incur high emissions from large-scale acid/base production, neutralisation reactions, and waste treatment. In EDBM, acid and base are regenerated in-situ, chemical use is minimised, and the main input is electricity, which can be partly renewable. Accounting for avoided

[9]Jie Yan et al., "Selective Electrodialysis with Bipolar Membranes for Cobalt and Lithium Recovery from Spent Lithium-Ion Batteries," *AIChE Journal* (2025, early view) https://doi.org/10.1002/aic.18786.

[10]Jeon et al., "Chemical Free pH Control for Efficient Lithium Recovery via Redox-Couple Mediated Bipolar Membrane Electrodialysis." *Desalination,* 603 (2025): 119145.

reagent production and reduced waste, the LCA showed that EDBM achieved a carbon footprint reduction of about one-third relative to conventional methods. The LCA used a cradle-to-gate boundary with inventories from Ecoinvent v3.9.1, analysed in openLCA 1.11 via ReCiPe 2016 Midpoint (H) and cross-checked against IPCC 2021 GWP factors.

Economic and Environmental Analysis

The EDBM process replaces most chemical reagents with electricity, which, though not cost-free, is modest in demand (<1 kWh kg^{-1} Li) and can be supplied by renewables. Unlike hydrometallurgical routes that consume large volumes of acids, bases, and solvents, producing tonnes of neutralised salts for disposal, EDBM regenerates its acid and base in situ, leaving only minor consumables such as recyclable hexacyanoferrate and water. The advantages are high-purity LiOH and Co recovery, very low waste, and reduced CO_2 footprint. A preliminary economic analysis indicated a 28% reduction in operating costs, largely due to lower reagent consumption, while an LCA showed a 35% smaller carbon footprint compared to conventional processes. Although membranes represent the main capital cost, their multi-year lifespan offsets recurring chemical expenses typical of hydrometallurgy. Moreover, eliminating neutralisation preserves reagent value and avoids secondary waste. When powered by renewable energy, the environmental benefits are amplified, making EDBM a closed-loop, greener, and economically competitive route for LIB recycling.

Conclusions

EDBM with the tailored as-prepared molecularly imprinted membranes has been shown to recover Li and Co from spent lithium-ion battery leachate with high efficiency and selectivity, producing >99% purity LiOH and achieving >90% recovery of both metals in under 30 min with negligible cross-contamination. By integrating hexacyanoferrate-assisted complexation in the electrochemical system, the process overcomes the co-extraction issues of conventional methods. Key advantages include minimised chemical use through in-situ acid and base generation, moderate electricity demand (<1 kWh kg^{-1} Li), direct production of battery-grade LiOH, regeneration of leaching agents, reduced greenhouse gas emissions and waste streams, and scalability through modular electrodialysis stacks. As a technically robust, energy-efficient, and environmentally benign alternative, EDBM has a strong potential for industrial adoption, either as a standalone process or as part of integrated recycling flowsheets, advancing sustainable and circular management of LIB materials.

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