

Review

Energy-Efficient Ion Recovery from Water Using Electro-Driven Membranes: A Comprehensive Critical Review

Akeem Adeyemi Oladipo ^{1,*}  and Mehdi Ahmad ² 

¹ Polymeric Materials Research Laboratory, Chemistry Department, Faculty of Arts and Science, Eastern Mediterranean University, TR North Cyprus, via Mersin 10, Famagusta 99628, Türkiye

² Mechanical Engineering Department, Eastern Mediterranean University, TR North Cyprus, via Mersin 10, Famagusta 99628, Türkiye; 23501398@emu.edu.tr

* Correspondence: akeem.oladipo@emu.edu.tr

Abstract

Amid concurrent pressures on water and material resources, recovering valuable ions like lithium and nutrients from brines and wastewater is a critical tenet of the circular economy. This review provides a critical assessment of electro-driven membranes (EDMs) as a key technology platform for achieving this goal with high energy efficiency. A comprehensive synthesis and analysis of the current state-of-the-art of core EDM technologies, including electrodialysis (ED) and membrane capacitive deionization (MCDI), is presented, focusing the analysis on the performance metrics of specific energy consumption and ion selectivity. The findings reveal that the optimal EDM technology is highly application-dependent, with MCDI excelling for dilute streams and ED for concentrated ones. While significant advances in monovalent selective membranes have enabled lithium recovery, achieving high selectivity between ions of the same valence (e.g., Li^+/Na^+) remains a fundamental challenge. Moreover, persistent issues of membrane fouling and scaling continue to inflate energy consumption and represent a major bottleneck for industrial-scale deployment. While EDMs are a vital technology for ion resource recovery, unlocking their full potential requires a dual-pronged approach: advancing materials science to design novel, highly selective membranes, while simultaneously developing intelligently integrated systems to surmount existing performance and economic barriers.



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Keywords: ion recovery; resource recovery; electro-driven membranes; electrodialysis; membrane capacitive deionization; energy efficiency; water treatment; circular economy

1. Introduction

The 21st century is defined by the intertwined global challenges of ensuring water security, meeting rising energy demands, and sourcing critical raw materials for a growing population and technological economy [1–3]. The escalating demand for clean water, projected to outstrip supply by 40% by 2030, coexists with an exponential need for materials like lithium, cobalt, and phosphate, which are foundational to modern agriculture and high-tech industries. These compounding pressures are forcing a fundamental paradigm shift away from a linear “take-make-dispose” model towards a circular economy, where waste streams are re-conceptualized as valuable resources [4–6]. Within this framework, water management is undergoing a critical transformation. Municipal and industrial wastewater, as well as rapidly growing volumes of brine from inland and coastal desalination plants, are no longer viewed simply as effluents requiring energy-intensive treatment for safe

disposal, but as rich, domestic repositories of valuable materials. This transition to resource recovery is driven by compelling economic incentives, geopolitical supply chain risks, and the urgent need for more sustainable environmental stewardship [4].

A diverse and economically significant array of valuable ions is present in these aqueous streams as presented in Table 1. For example, lithium (Li^+), the cornerstone of the burgeoning electric vehicle and grid storage battery industries, can be found in significant concentrations in geothermal and desalination brines, offering a potential domestic alternative to geographically concentrated and environmentally impactful conventional mining [7–9]. Nutrient recovery, particularly of phosphate (PO_4^{3-}) and nitrogen (as ammonium, NH_4^+) from municipal and agricultural runoff, holds the dual benefit of mitigating severe eutrophication in receiving water bodies while producing sustainable fertilizers to support global food security [4,10,11]. Similarly, industrial effluents from sectors like electroplating, mining, and electronics manufacturing often contain heavy metals (e.g., Cu^{2+} , Ni^{2+} , Zn^{2+}) that are both hazardous environmental contaminants and valuable secondary resources if recovered effectively [12,13]. The ability to selectively and economically extract these target ions from complex, multi-component aqueous matrices is therefore a key technological challenge for actualizing the circular economy.

Table 1. Valuable Ions, Their Primary Aqueous Sources, and Potential Market Value.

Target Ion	Typical Source(s)	Typical Concentration Range	Economic Value and Significance
Lithium (Li^+)	- Salt-lake Brines - Geothermal Brines - Oilfield Produced Water - Desalination Brine	- High: 100–500+ mg/L (Geothermal/Salt-lake) - Low: 0.2–0.4 mg/L (Desalination Brine)	Very High: Critical raw material for Li-ion batteries in EVs and electronics. Recovery offers a key alternative to conventional mining.
Phosphate (PO_4^{3-})	- Municipal Wastewater - Agricultural Runoff - Food Industry Effluent	5–30 mg/L (as P)	High: Essential, non-substitutable component of fertilizers. Phosphate rock is a finite resource. Recovery mitigates eutrophication.
Nitrogen ($\text{NH}_4^+/\text{NO}_3^-$)	- Municipal Wastewater - Agricultural Runoff - Industrial Effluent	20–70 mg/L (as N)	Moderate: Primary nutrient for fertilizers. Conventional production (Haber-Bosch process) is highly energy-intensive.
Potassium (K^+)	- Agricultural Runoff - Desalination Brine - Certain Industrial Brines	10–50 mg/L (Wastewater) ~400 mg/L (Seawater)	Moderate: Key component of fertilizers (potash). Recovery can supplement traditional mining sources.
Copper (Cu^{2+}), Nickel (Ni^{2+}), Zinc (Zn^{2+})	- Electroplating Rinsewater - Mining Effluent (Acid Mine Drainage) - Electronics Manufacturing	Highly variable: mg/L to g/L	High: Valuable base metals. Recovery is driven by both economic value and strict environmental regulations on heavy metal discharge.
Magnesium (Mg^{2+}), Calcium (Ca^{2+})	- Desalination Brine - Hard Industrial Waters	High: g/L range (Seawater Brine)	Low to Moderate: Lower commodity value, but their removal (softening) is often critical for preventing scaling in downstream processes, thus adding value by enabling higher water recovery.

Recent advancements in both laboratory and field research highlight electro-driven separation processes as a highly promising and versatile platform for water reuse and desalination. These processes offer several significant advantages over traditional pressure-driven methods like reverse osmosis. One key benefit of electro-driven processes is their

potential for energy savings, particularly when treating low-salinity waters. Furthermore, they provide enhanced cation or anion selectivity, allowing for more targeted removal of specific ions. This versatility enables fit-for-purpose treatment, where water can be tailored to meet specific quality requirements for various applications [14].

At the core of this technology are electro-driven membranes (EDMs). By applying an electrical potential difference, EDMs selectively transport charged ionic species across specially designed ion-exchange membranes [15–17]. This precise control over ion movement makes EDMs a powerful tool for advanced water treatment as shown in Figure 1. This fundamental mechanism offers distinct advantages over traditional separation methods. Unlike chemical precipitation, which often requires large quantities of pH-adjusting reagents and generates voluminous secondary sludge waste with high disposal costs [18,19], EDMs can operate with minimal chemical input. In contrast to pressure-driven membrane processes like reverse osmosis, which require high hydraulic pressures and are effective for dewatering but largely non-selective between ions of similar size [20], EDMs provide a direct pathway for targeted ion separation and concentration.

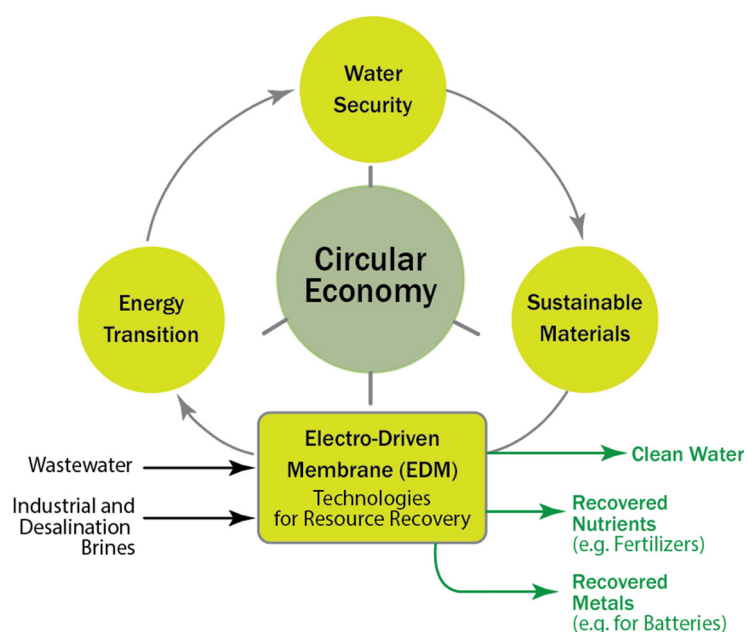


Figure 1. Illustration of the pivotal role of electro-driven membranes (EDMs) in the Water–Energy–Material nexus. EDMs are a key enabling technology for a circular economy, designed to transform wastewater and brines from environmental liabilities into valuable sources of clean water and recovered raw materials, such as critical metals and nutrients.

However, the field is not without its controversies and challenges. The practical application of EDMs is often hindered by a persistent trade-off between ion selectivity and permeability, and their performance is highly susceptible to the characteristics of the feed solution. Issues like membrane fouling by organic matter and scaling by sparingly soluble salts remain significant operational barriers that can drastically increase energy consumption and reduce the system’s lifespan [14]. Therefore, the primary aim of this review is to provide a comprehensive and critical assessment of the current state of electro-driven membranes, with a specific focus on their energy efficiency and practical applicability for ion recovery.

This work will not delve into the intricate details of polymer synthesis for membranes but will instead focus on the performance outcomes of different membrane types. The review begins by outlining the fundamental principles governing EDM processes before presenting a critical comparison of the leading technologies, including electrodialysis (ED)

and membrane capacitive deionization (MCDI). A detailed analysis of the key factors influencing energy consumption and a survey of recent applications in nutrient, metal, and acid/base recovery will be provided. Finally, this review highlights the principal conclusions that while EDMs represent a vital technology for resource recovery, future progress hinges on targeted innovations in robust membrane materials and integrated process design to bridge the gap between laboratory potential and industrial feasibility, thereby overcoming the critical barriers of selectivity and long-term operational stability.

2. Fundamentals of Electro-Driven Membrane Processes

Recent studies have extensively explored the application of electro-driven separation processes for recovering valuable metals and nutrients from diverse water sources, including industrial wastewater, municipal effluent, and agricultural runoff. This approach offers a sustainable pathway for resource valorization and pollution control. For example, Qiu et al. [15] engineered a closed-loop ultrafiltration-bipolar membrane electrodialysis system designed for the simultaneous capture and recovery of fluoride and silica from mixed wastewater. This innovative system successfully produced sodium silicofluoride and achieved zero liquid discharge, demonstrating a highly efficient and environmentally sound solution. In another study, Ge et al. [21] integrated electrodialysis with electrochemical oxidation for the sustainable extraction of Na_2SO_4 from rare earth extraction wastewater. Their research reported a significant water recovery of 46.5% and a Na_2SO_4 yield of 52.7 kg/m^3 . This highlights the potential for electro-driven processes to recover valuable chemicals from complex industrial streams.

Further showcasing the versatility of these technologies, Qiu et al. [15] developed an electro-driven membrane reactor for ex situ crystallization of fluoride/silica from microelectronic wastewater. This system produced high-purity fluorosilicates. An internal ultrafiltration membrane within the reactor played a crucial role by rejecting nanoparticles and organic matter while facilitating the migration of protons and SiF_6^{2-} ions. Under optimal conditions, the researchers verified over 99.5% Na_2SiF_6 purity and a 64.5% crystallization rate. These compelling studies provide robust experimental results, detailed process performance analysis, and a comprehensive discussion of the advantages and disadvantages of electro-driven separation technologies. Collectively, this research underscores the significant prospects and growing importance of this field in addressing global water and resource challenges. Figure 2 illustrates the timeline of key milestones in electro-driven membrane technologies, revealing a clear historical progression from general deionization to more specialized and selective applications for targeted resource recovery.

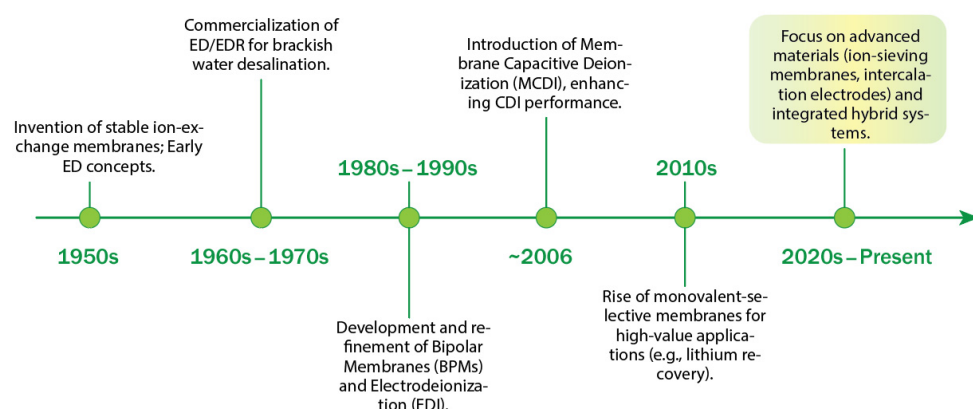


Figure 2. Timeline highlighting key milestones in the development of electro-driven membrane technologies. Historical progression shows a clear evolution from bulk deionization towards increasingly specialized and selective applications for targeted resource recovery.

A critical evaluation of electro-driven membrane technologies for ion recovery necessitates a robust understanding of the fundamental physicochemical principles that govern their operation. This section delves into these core concepts, laying the groundwork for the subsequent analysis of specific technologies and applications. The discussion begins by detailing the primary driving force of electromigration, followed by an in-depth look at the structure and function of the various ion-exchange membranes that provide the basis for selective separation. Finally, the section addresses the key transport phenomena and non-ideal effects that influence process efficiency and energy consumption in real-world scenarios.

2.1. Principle of Electromigration: The Movement of Ions Under an Electric Field

Electromigration is the fundamental transport mechanism underpinning all electro-driven membrane (EDM) technologies. It describes the net directional movement of charged species, or ions, through an electrolyte solution under the influence of an externally applied electric field [22–25]. When two electrodes, an anode (positive electrode) and a cathode (negative electrode), are placed in an ionic solution and connected to a direct current (DC) power source, they establish an electric field across the solution. This field exerts an electrostatic force on the dissolved ions, compelling them to migrate towards the electrode of opposite charge. Consequently, positively charged ions (cations) move towards the negatively charged cathode, while negatively charged ions (anions) are driven towards the positively charged anode [26].

The velocity and resulting flux of a specific ion are governed by several key factors, a relationship often described by the Nernst–Planck equation, which considers contributions from diffusion, convection, and electromigration. For the purpose of understanding the primary driving force in EDMs, the electromigration term is of central importance. The ionic flux (J_i) due to electromigration is directly proportional to the ion's charge (z_i), its mobility within the solution (u_i), its concentration (C_i), and the strength of the electric field gradient ($d\phi/dx$). The ion's mobility is an intrinsic property influenced by its size (specifically, its hydrated radius), its charge density, and its interactions with the solvent molecules (hydration shell) [27]. Furthermore, the properties of the bulk solution, such as viscosity and temperature, also play a crucial role, as they can either impede or facilitate ionic movement.

In the context of EDM processes, it is this differential migration of ions that enables separation. The electric field acts as a non-destructive, chemical-free force that sorts the components of the saline feed stream. While all cations are driven in one direction and all anions in the opposite, the rate of their movement varies based on the properties described above. It is the subsequent introduction of ion-exchange membranes, which act as selective barriers strategically placed between the electrodes, that harnesses this movement to achieve a desired separation. These membranes are designed to allow the passage of either cations or anions while blocking the other, thereby creating distinct channels where ions are either depleted (the diluate stream) or accumulated (the concentrate stream). Therefore, a comprehensive understanding of the principles of electromigration is essential for optimizing the design and operation of any EDM system to maximize separation efficiency and minimize energy consumption.

2.2. Ion-Exchange Membranes (IEMs): The Heart of the Process

While electromigration provides the driving force, it is the ion-exchange membrane (IEM) that imparts the critical functionality of selective separation in any EDM system. IEMs are dense, non-porous polymer sheets containing fixed charged functional groups that are covalently bonded to the polymer backbone. These membranes act as selective barriers,

ideally allowing the passage of ions with a charge opposite to their fixed charges (counter-ions) while rejecting ions with the same charge (co-ions) [28]. This property, known as permselectivity, is the cornerstone of creating the distinct diluate and concentrate streams in an EDM stack. The performance of any EDM process is therefore inextricably linked to the intrinsic properties of the IEMs used, including their ionic conductivity, selectivity, chemical stability, and mechanical strength.

2.2.1. Cation and Anion Exchange Membranes

The two primary types of IEMs are cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs). CEMs contain negatively charged fixed functional groups, typically sulfonic acid ($-\text{SO}_3^-$) or carboxylic acid ($-\text{COO}^-$) groups, attached to a polymer matrix such as polystyrene cross-linked with divinylbenzene. These fixed negative charges allow for the transport of positively charged cations (as counter-ions) while repelling negatively charged anions (as co-ions) based on the principle of Donnan exclusion [29–31]. Conversely, AEMs possess positively charged fixed functional groups, most commonly quaternary ammonium groups ($-\text{NR}_3^+$), which facilitate the transport of anions while excluding cations.

From a practical standpoint, a critical trade-off exists between a membrane's permselectivity and its ionic conductivity. Increasing the cross-linking density of the polymer matrix enhances the membrane's fixed charge density and thus its ability to exclude co-ions, leading to higher permselectivity. However, this also creates a more tortuous path for counter-ion transport, increasing the membrane's electrical resistance and, consequently, the overall energy consumption of the process [30]. Furthermore, AEMs, particularly those with quaternary ammonium groups, have historically exhibited lower chemical stability compared to the robust sulfonic acid-based CEMs, especially when exposed to alkaline conditions (high pH) or certain foulants, which can lead to degradation of the functional groups (Hofmann elimination) and a loss of performance over time [23].

2.2.2. Monovalent Selective Ion-Exchange Membranes

For many high-value recovery applications, such as separating lithium from magnesium-rich brines, simple charge-based separation is insufficient. This has driven the development of monovalent selective IEMs illustrated in Figure 3, which are engineered to preferentially transport monovalent ions over multivalent ions of the same charge [32]. The most common type used in recovery applications are Monovalent Selective Cation-Exchange Membranes (MCEMs). The mechanisms for achieving this selectivity are primarily based on two principles:

- **Steric Hindrance:** This approach leverages the difference in the hydrated ionic radii of ions. Multivalent ions like Mg^{2+} (hydrated radius ~ 0.43 nm) and Ca^{2+} (~ 0.41 nm) are significantly bulkier than monovalent ions like Li^+ (~ 0.38 nm) and Na^+ (~ 0.36 nm). By creating membranes with a dense, highly cross-linked surface layer, the physical transport of the larger, hydrated multivalent ions can be sterically hindered [33].
- **Electrostatic Repulsion:** A more common strategy involves modifying the surface of a standard IEM with a thin, oppositely charged polyelectrolyte layer. For example, modifying the surface of a CEM with a thin layer containing positive charges creates a repulsive electrostatic barrier. This barrier exerts a stronger repulsive force on incoming multivalent cations (e.g., Mg^{2+}) than on monovalent cations (e.g., Li^+) due to their higher charge, thus slowing their entry into the membrane [34].

In field applications, while these membranes have been instrumental in making processes like lithium recovery from brines are feasible, their performance is not ideal. The thin selective layer is susceptible to physical abrasion and chemical fouling, which can degrade

selectivity over the operational lifetime of the membrane. Achieving high selectivity often comes at the cost of increased membrane resistance and reduced ion flux, requiring careful economic optimization between recovery purity and processing throughput.

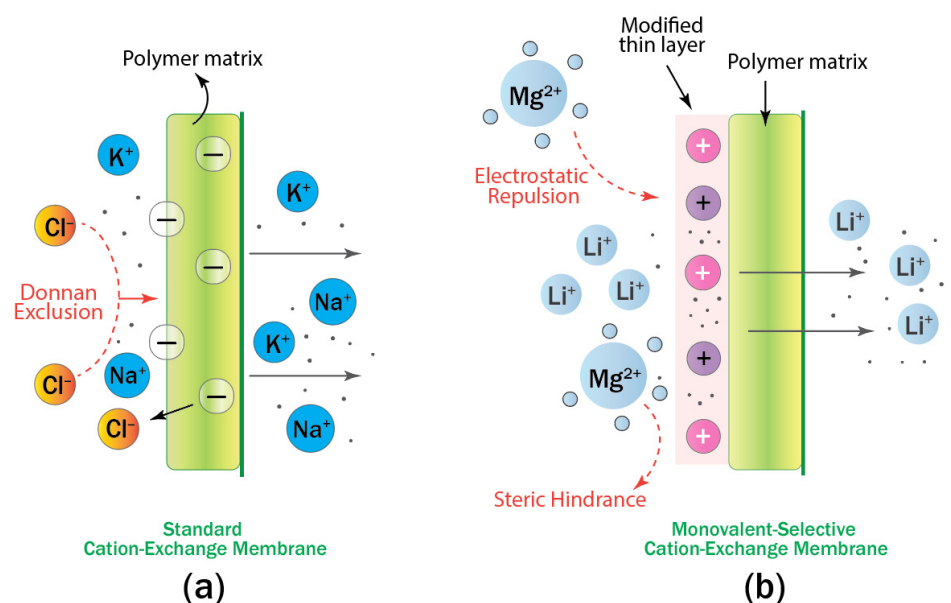


Figure 3. Mechanisms of selective ion transport in ion-exchange membranes. (a) A standard Cation-Exchange Membrane (CEM) allows cation transport while rejecting anions via Donnan exclusion. (b) A monovalent selective CEM utilizes a modified surface layer to preferentially transport monovalent cations over bulkier, more highly charged multivalent cations through a combination of electrostatic repulsion and steric hindrance.

2.2.3. Bipolar Membranes

Bipolar membranes (BPMs) represent a unique class of IEM, consisting of a CEM and an AEM laminated together to form a single composite membrane. Their defining characteristic is the ability to dissociate water molecules into protons (H^+) and hydroxide ions (OH^-) at the interface between the two layers when subjected to a reverse-bias electric field [35,36]. This reverse-bias condition, where the CEM side faces the anode and the AEM side faces the cathode, creates a depletion of mobile ions at the membrane interface. When the electric field strength becomes sufficiently high, it overcomes the activation energy for water dissociation, which is the rate-limiting step. Modern BPMs often incorporate a catalytic layer at the interface, containing metal oxides or other compounds, to lower this activation energy and accelerate the water-splitting reaction.

Under this field, water molecules that diffuse into the interfacial zone are split. The generated H^+ ions are then transported through the CEM layer, and the OH^- ions are transported through the AEM layer. This allows for the in situ generation of an acid and a base from a salt stream. For instance, in an electrodialysis with bipolar membranes system treating sodium chloride ($NaCl$), the BPMs will produce hydrochloric acid (HCl) on the anionic side and sodium hydroxide ($NaOH$) on the cationic side. This technology is particularly valuable for processes requiring pH adjustment or for producing valuable chemical commodities from waste salt streams without the addition of external chemicals [37]. The primary challenge for BPMs remains the significant potential drop (typically 0.8–1.0 V) required to drive the water-splitting reaction, which constitutes a major component of the overall energy consumption. The long-term stability and catalytic efficiency of the interfacial layer are critical areas of ongoing research to reduce this energy penalty.

2.3. Key Transport Phenomena Beyond Ideal Electromigration

While electromigration is the desired transport mechanism, the actual performance and energy efficiency of an EDM system are profoundly influenced by other concurrent transport phenomena. These non-ideal effects can limit process efficiency and must be carefully managed in any practical application.

- **Ohmic Resistance**

The total electrical resistance of the membrane stack is a primary contributor to energy consumption. This resistance is the sum of the resistances of all components: the IEMs, the diluate and concentrate solutions within the channels, and the electrode rinse solutions. According to Ohm's Law, the voltage drop across the stack is directly proportional to this resistance, and the energy consumed to overcome it is dissipated as heat [38]. In practice, minimizing this resistance is a key design goal, achieved by using highly conductive membranes and designing stacks with thin solution channels (typically < 1 mm). However, a critical engineering trade-off exists, as reducing channel thickness to lower resistance also increases the hydraulic pressure drop and elevates the risk of clogging by suspended solids.

- **Concentration Polarization**

Concentration polarization (CP) is an unavoidable phenomenon that occurs in the thin, stagnant boundary layers adjacent to the membrane surfaces. On the diluate side of a membrane, ions are transported away towards the membrane faster than they can be replenished by diffusion and convection from the bulk solution. This creates an ion-depleted boundary layer. Conversely, on the concentrate side, ions accumulate at the surface faster than they can diffuse away, creating an ion-concentrated boundary layer [39]. CP has several detrimental effects. It increases the local electrical resistance, adding to energy consumption. More critically, if the current density is too high, the ion concentration at the membrane surface in the diluate channel can drop to near zero. Any further increase in current will force the dissociation of water to carry the charge, a phenomenon known as exceeding the limiting current density (LCD). This leads to significant pH shifts, which can damage the membranes and drastically reduce process efficiency [40]. In practical systems, spacers are placed in the flow channels not only to provide mechanical support but also to induce turbulence, which disrupts the boundary layers and increases the LCD, allowing the system to be operated at higher, more productive rates.

- **Water Transport (Electro-osmosis and Osmosis)**

The transport of water across the membranes is a significant non-ideal flux that can limit the performance of EDM processes, particularly those aiming for high concentration factors. This transport occurs via two primary mechanisms:

1. **Electro-osmosis:** As ions migrate through the membrane, they drag along water molecules from their hydration shells. This transport is co-directional with the counter-ion flux and is proportional to the applied current density [21,41].
2. **Osmosis:** Driven by the difference in water activity between the concentrate and diluate streams, water naturally moves from the less concentrated diluate to the more concentrated stream to equalize osmotic pressure.

In any ion recovery application, both mechanisms result in an undesirable transfer of water into the concentrate stream. This "water leakage" dilutes the final product, increases the volume of the concentrate that must be managed, and represents a loss of treated water from the diluate stream. This is a particularly acute problem when treating high-salinity brines, where the osmotic pressure difference can be substantial, making it a key limiting factor in the maximum achievable concentration.

3. Core Electro-Driven Membrane Technologies for Ion Recovery

The successful recovery of ions from aqueous sources via electro-driven processes (Table 2) depends on the selection of an appropriate technology tailored to the specific feedwater composition, target ion, and desired purity. It is crucial, however, to first distinguish between the goals of water purification (e.g., desalination) and targeted resource recovery. While both utilize similar principles, their objectives differ: desalination aims to produce a purified water stream by removing the bulk of dissolved ions, whereas resource recovery aims to selectively isolate and concentrate specific, often valuable, ions from a complex mixture. Many of the advanced ion recovery technologies (Figure 4) discussed in this review are built upon the foundational platforms originally developed for desalination. Therefore, an understanding of these core technologies, such as electrodialysis, is essential for appreciating the innovations and specific challenges associated with adapting them for the more nuanced task of selective ion recovery.

Table 2. Comparison of Key Electro-Driven Membrane Technologies for Ion Recovery.

Technology	Driving Force	Primary Application Niche	Strengths	Limitations	Technology Readiness Level (TRL) ¹
ED/EDR	Electric Potential Gradient	Bulk deionization of moderately saline streams (>2000 ppm); brine concentration.	- Continuous operation - Commercially mature and robust - Effective for high concentrations	- Inefficient for dilute solutions - Prone to scaling and fouling - Low selectivity between same-charge ions	TRL 9
MCDI	Electrosorption via Electric Potential	Deionization of low-salinity/brackish streams (<2000 ppm); targeted ion removal.	- High energy efficiency in dilute feeds - Potential for electrode-based selectivity	- Inherently cyclic (batch) operation - Finite electrode capacity - Co-ion competition	TRL 6–7
S-ED	Electric Potential Gradient	Separation of monovalent from multivalent ions (e.g., Li ⁺ from Mg ²⁺ in brines).	- Enables separations not possible with standard ED - High product purity potential	- Higher membrane cost - Lower flux and higher resistance - Selective layer can be fragile/foul	TRL 5–7
EDBM	Electric Potential Gradient (with Water Splitting)	Conversion of salt streams into their corresponding acids and bases.	- In situ chemical production—Valorizes waste brines - Reduces need for purchased chemicals	- High energy cost due to water splitting - Higher capital cost - BPMs can have lower chemical stability	TRL 7–8
EDI/CEDI	Electric Potential Gradient (in resin-filled cells)	Production of ultrapure water; final polishing step.	- Achieves very low ion concentrations (ppb) - Continuous self-regeneration of resin - Low energy use for polishing	- Requires extensive pre-treatment - Resin is highly susceptible to fouling - Not suitable for bulk recovery	TRL 9

Notes: ¹ **Technology Readiness Level (TRL)** is a scale from 1 (basic principle) to 9 (fully commercial system). The TRLs are gauged as follows: **TRL 9 (ED/EDR, EDI)** is assigned due to decades of widespread commercial deployment in industries like desalination and ultrapure water production. **TRL 7–8 (EDBM)** reflects successful operation at the pre-commercial and pilot-plant scale for applications like brine valorization. **TRL 5–7 (MCDI, S-ED)** indicates that while the technologies are well-validated in relevant environments and at the pilot scale, they are not yet fully commercialized for all targeted ion recovery applications.

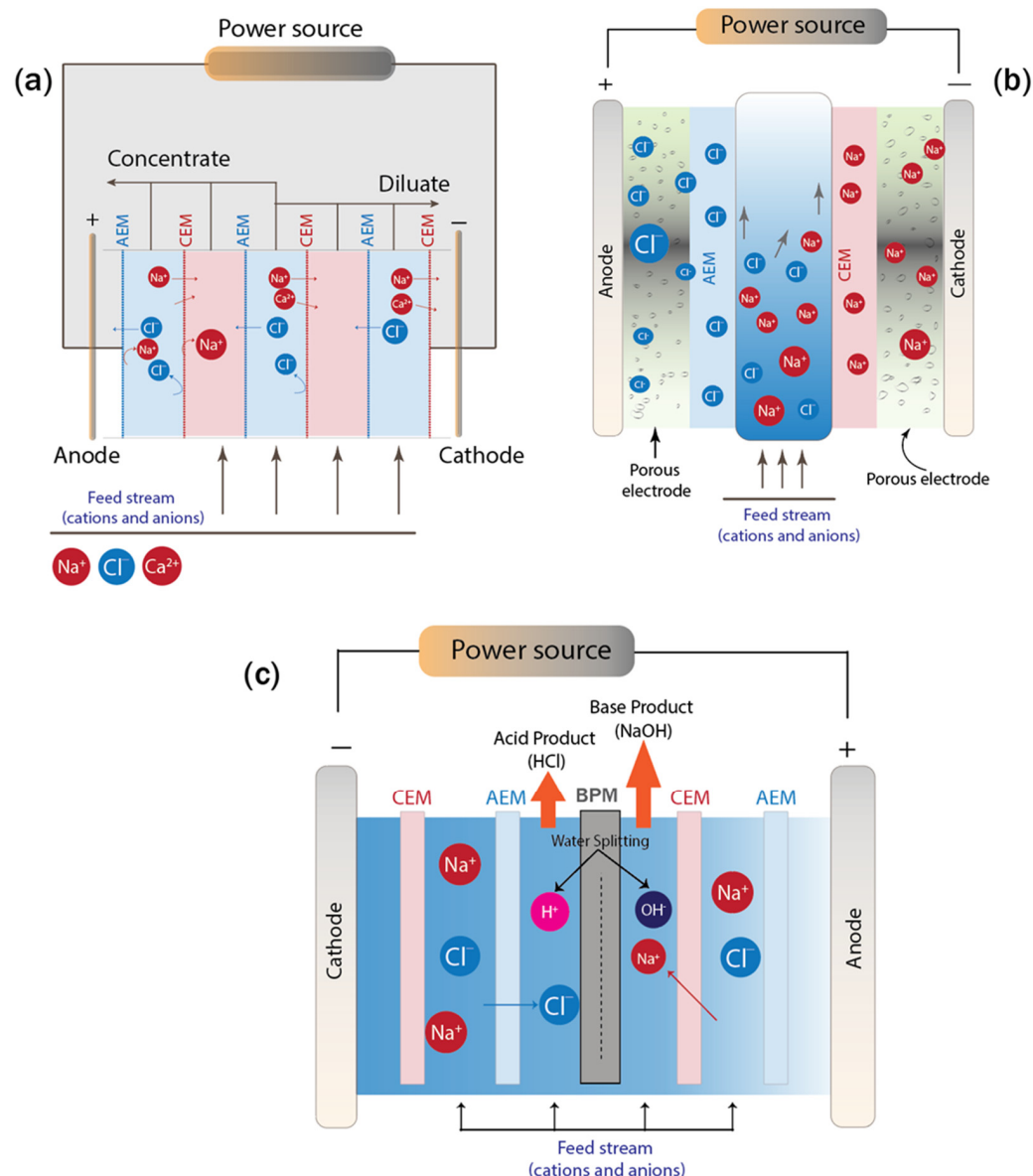


Figure 4. Schematic principles of core electro-driven membrane technologies. (a) Electrodialysis (ED), where alternating membranes separate ions into concentrate and diluate streams. (b) Membrane Capacitive Deionization (MCDI), where ions are temporarily stored via electro-sorption in porous electrodes. (c) Electrodialysis with Bipolar Membranes (EDBM), where water splitting at the bipolar membrane interface is used to convert a salt stream into its corresponding acid and base.

3.1. Electrodialysis Application in Water Treatment

Electrodialysis (ED) is one of the most established and commercially mature EDM technologies, with a long history of application in brackish water desalination and industrial process water treatment. Its operational robustness makes it a strong candidate for various ion recovery scenarios.

3.1.1. Working Principle: Standard Electrodialysis and Polarity Reversal Electrodialysis

A standard ED system consists of a stack of alternating cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs) positioned between an anode and a cathode. The spaces between the membranes form parallel flow channels. When a saline feed solution is pumped through these channels and a DC electric field is applied, cations migrate towards the cathode and anions towards the anode. The arrangement of the membranes dictates the outcome: as cations pass through a CEM, they enter the next channel

but are then blocked by an AEM. Similarly, anions pass through an AEM but are blocked by the subsequent CEM. This orchestrated movement effectively sorts the ions, creating a series of “depleted” or **diluate** channels and “enriched” or **concentrate** channels [42,43]. The result is two distinct output streams: one with a reduced salt concentration and another containing the concentrated recovered ions.

A common and critical enhancement to this process is Electrodialysis Reversal (EDR). In an EDR system, the polarity of the electrodes is periodically reversed (typically several times per hour). Simultaneously, the hydraulic valves redirect the flow paths so that the former diluate channels become concentrate channels, and vice versa. This periodic reversal is a highly effective in situ cleaning mechanism. It changes the direction of ion migration, helping to dislodge and flush out foulants and scale-forming precipitates that may have accumulated on the membrane surfaces, thereby significantly improving the system’s long-term operational stability and reducing the need for chemical cleaning [44,45].

3.1.2. Strengths: Continuous Operation and High Recovery Rates

From an industrial perspective, a primary advantage of ED and EDR is their ability to operate in a continuous mode. Unlike batch or cyclic processes, a continuous system is highly desirable for large-scale applications as it simplifies process control and integration, allowing for a steady and predictable output of both treated water and concentrated product. This makes it well-suited for integration with continuous industrial effluent streams or large-volume desalination plants.

Furthermore, ED is particularly effective for treating solutions that are already moderately to highly concentrated (e.g., >2000–5000 mg/L TDS). In these streams, the high ion concentration leads to high solution conductivity, which minimizes the ohmic resistance of the stack and allows for efficient ion transport with reasonable energy consumption [46,47]. This makes ED an excellent technology for concentrating brines from other processes, such as reverse osmosis retentate, or for recovering high concentrations of salts, acids, or bases from industrial process streams. For instance, Rögener and Tetampel [48] investigated the effectiveness of ED for concentrating lithium-containing brine solutions. Their research, conducted using a lab-scale ED plant, explored the impact of varying brine compositions, operational modes, and limiting factors. They found that ED was highly efficient, enabling an approximately 18-fold increase in lithium salt concentration. Additionally, their experiments quantified the water transport, showing about 0.05% to 0.075% of water transferred per gram of lithium chloride (LiCl) moving from the dilute to the concentrated solution.

3.1.3. Limitations: Scaling, Fouling, and Challenges with Dilute Solutions

Despite its strengths, ED faces significant limitations. The most pressing operational challenge is membrane fouling and scaling. The concentrate channels are particularly susceptible to the precipitation of sparingly soluble salts like calcium carbonate (CaCO_3) and calcium sulfate (CaSO_4), especially when operating at high recovery rates. The pH shifts that can occur near the membrane surfaces due to concentration polarization can exacerbate this scaling potential. Guo et al. [49] investigated calcium and magnesium scale precipitation on ion-exchange membranes within a laboratory-scale electrodialysis reactor. They fed the reactor with two high-strength wastewater streams: municipal waste liquid digestate and food waste liquid digestate. Their observations revealed that the scalants on cation-exchange membranes included struvite, amorphous calcium carbonate (ACC), and vaterite. Interestingly, ACC was not found on anion-exchange membranes. The researchers noted that membranes with high selectivity for divalent ions led to a rapid decrease in electric current, indicating severe membrane scaling. These findings clearly demonstrate

that membrane scaling due to calcium and magnesium precipitation is a pervasive problem in ED systems designed for nutrient recovery from wastewater.

While EDR mitigates scaling, it does not eliminate it entirely, and complex brines often require extensive pre-treatment (e.g., softening, antiscalant addition) to prevent severe scaling that can increase energy demand and permanently damage membranes [50–52]. Organic molecules and colloids present in wastewater can also adsorb onto membrane surfaces, causing organic fouling that blocks ion pathways and increases electrical resistance. Conversely, ED is generally inefficient and uneconomical for treating very dilute solutions (<500 mg/L TDS). In such feeds, the low ionic concentration results in a very high electrical resistance of the solution. According to Ohm's law, a significant voltage drop is required to drive the current, leading to prohibitively high specific energy consumption, most of which is wasted as heat. Finally, the selectivity of a standard ED system is entirely dependent on the properties of the membranes used. While it separates cations from anions effectively, it offers almost no intrinsic selectivity between different ions of the same charge (e.g., Na^+ vs. K^+ , or Cl^- vs. SO_4^{2-}). Achieving such separations requires the use of specialized and more expensive monovalent selective membranes, as discussed in Section 2.2.2, which fundamentally changes the process configuration and economics.

3.2. Membrane Capacitive Deionization

Emerging as a strong competitor to ED, particularly for specific application niches, Membrane Capacitive Deionization (MCDI) is an electrochemical technology that removes ions by temporarily storing them in porous electrodes. It represents a significant evolution from traditional Capacitive Deionization (CDI) through the strategic integration of ion-exchange membranes to improve charge efficiency. To address the inherent cyclic nature of MCDI, advanced configurations such as Flow-Electrode Capacitive Deionization (FCDI) have been developed, which utilize conductive carbon slurries as flowing electrodes to enable more continuous operation.

3.2.1. Working Principle: Electrosorption of Porous Electrodes

An MCDI cell consists of a pair of porous carbon electrodes (an anode and a cathode) separated by a flow channel, where each electrode is faced with an ion-exchange membrane (an AEM in front of the anode, a CEM in front of the cathode). The process operates in two distinct steps:

- **Adsorption (Ion Capture):** A low-voltage DC potential (typically 1.0–1.4 V) is applied across the electrodes. As the feed solution flows through the channel, anions are driven towards the anode and cations towards the cathode. The AEM allows anions to pass through and enter the porous anode structure but prevents cations from entering. Similarly, the CEM allows cations to enter the cathode but blocks anions. Once inside the porous electrodes, the ions are temporarily immobilized within the electrical double layers (EDLs) that form at the vast carbon-water interface. This process, known as electrosorption, removes ions from the flowing water, producing a purified diluate stream.
- **Desorption (Ion Release):** Once the electrodes approach their saturation capacity, the applied voltage is removed or reversed. This collapses the EDLs and releases the captured ions from the electrodes back into the flow channel, creating a concentrated brine stream that is flushed from the system [53,54].

The key innovation of MCDI over conventional CDI is the inclusion of the membranes. By preventing co-ions from leaving the electrodes during the adsorption step, the membranes significantly enhance charge efficiency, leading to higher salt removal capacity and lower energy consumption [54,55].

3.2.2. Strengths: Energy Efficiency in Dilute Streams and Potential for Selectivity

The most significant advantage of MCDI is its **superior energy efficiency when treating low-concentration or brackish water streams** (<2000 mg/L TDS) [55,56]. Unlike ED, where energy consumption is proportional to the bulk solution resistance (which is high in dilute feeds), MCDI's energy consumption is primarily proportional to the number of ions removed. While state-of-the-art brackish water reverse osmosis (BWRO) is also highly efficient in this range, typically operating at $0.5\text{--}1.5$ kWh/m³, MCDI can achieve even lower energy consumption levels (<0.5 kWh/m³) for very low salinity feeds (e.g., $500\text{--}1000$ mg/L), making it a more economical choice in its ideal operational window.

Furthermore, MCDI offers exciting prospects for selective ion recovery through the design of the electrode materials themselves. While standard activated carbon electrodes exhibit some natural affinity differences between ions, advanced research is focused on creating functionalized carbons or intercalation electrodes [57,58]. In a recent study, Rethinasabapathy et al. [59] developed high-performance electrodes for MCDI, aiming for the selective extraction of lithium ions (Li⁺). They achieved this by creating a composite of Li⁺-intercalating redox-active Prussian blue (PB) nanoparticles with a highly conductive, porous activated carbon (AC) matrix. Their "AC/PB-20%" electrode, characterized by uniformly anchored PB nanoparticles within the AC matrix, offered several advantages. It increased the number of active sites for electrochemical reactions, improved electron and ion transport pathways, and provided abundant channels for the reversible insertion and de-insertion of Li⁺ by the PB. These enhancements led to a stronger current response, a higher specific capacitance of 159 F g^{-1} , and reduced interfacial resistance for both Li⁺ and electron transport. These findings highlight the significant potential of combining intercalation pseudocapacitive redox materials with faradaic materials. This approach offers a promising pathway for designing advanced MCDI electrodes for practical Li⁺ extraction applications. Also, materials like λ -MnO₂ have shown a specific capacity to intercalate lithium ions into their crystal structure, offering a pathway for highly selective lithium capture from complex brines. Tan et al. [60] demonstrated this by developing a manganese dioxide (MnO₂)/hierarchical porous carbon composite for use as a capacitive deionization electrode. Their design aimed to enhance both brackish water desalination and water softening. This ability to tune selectivity at the electrode level, independent of the membrane, is a unique and powerful feature of the technology.

3.2.3. Limitations: Cyclic Operation, Electrode Capacity, and Co-Ion Competition

The most fundamental limitation of MCDI is its inherently cyclic (batch) operation [61,62]. The continuous production of purified water is interrupted by the necessary desorption step, which complicates process design for industrial-scale, continuous-flow applications. Typical electro-sorption cycles can range from minutes to hours, depending on the feed concentration and the electrode's capacity. During the desorption (regeneration) step, the membranes play a crucial role by preventing the transport of counter-ions (the ions being released) into the opposing electrode, ensuring they are efficiently flushed out into the concentrate stream. While multiple stacks can be operated out of phase to simulate continuous output, this adds to system complexity and capital cost.

Secondly, the performance is constrained by the finite salt adsorption capacity (SAC) of the porous electrodes. Typical carbon electrodes have capacities in the range of $10\text{--}30$ mg of salt per gram of carbon. This physical limitation dictates the length of the adsorption cycle and the system's overall throughput. For treating higher salinity streams, the electrodes become saturated very quickly, leading to short cycle times and a process dominated by frequent regeneration, which diminishes its efficiency and practicality. Finally, in multi-ionic solutions, ions directly compete for the limited adsorption sites within the electrodes.

Ions with lower hydration energy and higher charge density (e.g., divalent Ca^{2+} and Mg^{2+}) are often preferentially adsorbed over monovalent ions (e.g., Na^+ , Li^+), which can significantly hinder the recovery of a specific target ion unless highly selective electrode materials are employed.

3.3. Hybrid and Specialized EDM Configurations

To overcome the limitations of standard ED and MCDI and to target specific recovery challenges, a range of specialized and hybrid configurations have been developed. These systems combine elements of different technologies or utilize advanced membrane types to unlock new functionalities.

3.3.1. Selective Electrodialysis

Selective Electrodialysis (S-ED) is a modification of conventional ED that directly addresses the challenge of separating ions with the same charge but different valencies. Instead of standard IEMs, an S-ED stack incorporates monovalent selective ion-exchange membranes, as detailed in Section 2.2.2. The most prominent real-world application is the recovery of lithium (Li^+) from brines that have a high concentration of divalent cations like magnesium (Mg^{2+}) and calcium (Ca^{2+}) [8,63]. In this process, the monovalent selective cation-exchange membranes facilitate the transport of Li^+ into the concentrate stream while hindering the passage of the bulkier and more highly charged Mg^{2+} and Ca^{2+} ions.

Critically, the success of S-ED is highly dependent on the performance of these specialized membranes, which often present a trade-off between selectivity and permeability. Membranes with very high selectivity for monovalent ions tend to have a lower overall flux and higher electrical resistance, which increases energy costs and capital expenditure due to the larger membrane area required [33]. Furthermore, the thin selective layers that impart the monovalent selectivity are often more susceptible to physical damage and fouling than standard, robust IEMs, posing a significant challenge for long-term operational stability in complex, real-world brines.

3.3.2. Electrodialysis with Bipolar Membranes (EDBM)

Electrodialysis with Bipolar Membranes (EDBM) is a powerful technology that converts dissolved salts into their corresponding acids and bases, effectively valorizing a waste brine into valuable chemical commodities. The core of the technology is the bipolar membrane (BPM), which, as described in Section 2.2.3, splits water molecules into H^+ and OH^- ions under an electric field [64]. An EDBM stack typically consists of a repeating three-compartment unit cell: an AEM, a CEM, and a BPM. When a salt solution (e.g., NaCl) is fed into the central compartment, Na^+ ions migrate through the CEM and combine with OH^- ions from the adjacent BPM to form NaOH . Simultaneously, Cl^- ions migrate through the AEM and combine with H^+ ions from the BPM on the other side to form HCl [65–67].

The primary strength of EDBM is its ability to produce acid and base in situ without the addition of external chemicals, making it a cornerstone technology for circular economy applications. For instance, it can be used to treat RO brine to generate HCl and NaOH , which can then be used for pH adjustment or as cleaning agents within the same desalination plant [68,69]. The main limitation, however, is the high energy consumption associated with the water-splitting reaction in the BPM, which requires a significant voltage drop (0.8–1.0 V or more). This energy penalty, combined with the higher cost and lower chemical stability of BPMs compared to standard IEMs, currently restricts its application to high-value recovery scenarios where the market price of the generated acid and base can justify the operational cost.

3.3.3. Electrodeionization

Electrodeionization (EDI), also known as Continuous Electrodeionization (CEDI), is a hybrid technology that combines ED with conventional ion-exchange resins. In an EDI module, the diluate compartments of an ED stack are filled with mixed-bed (cationic and anionic) ion-exchange resins [70–72]. Its primary and most successful commercial application is in the production of ultrapure water for the semiconductor, pharmaceutical, and power generation industries. The ion-exchange resins serve two critical functions: they provide a conductive pathway that drastically lowers the electrical resistance of the diluate stream, overcoming the high-energy limitation of ED in dilute solutions; and they facilitate ion removal to trace levels (ppb).

While EDI excels at water purification, its inclusion in this review serves to highlight why it is generally *not* suitable for bulk ion recovery. The continuous electric field simultaneously regenerates the ion-exchange resins by pulling captured ions off the resin beads and transporting them into the concentrate channels. This eliminates the need for the chemical regeneration required in conventional ion-exchange systems. However, from a recovery perspective, EDI is designed to produce a highly concentrated waste stream, but one that is not necessarily pure in a single target ion. The process is also highly susceptible to fouling and scaling, particularly from hardness and organic matter, which can irreversibly damage the resin bed. Therefore, while EDI represents an extremely efficient polishing technology, its use as a primary ion recovery tool from complex streams is limited without extensive and costly pre-treatment.

3.4. Industrial Maturity and Existing Applications

While this review emphasizes emerging applications of electro-driven membrane systems for selective ion recovery, it is essential to position these developments within the broader context of existing membrane-based electroseparation technologies. Traditional Electrodialysis (ED), Electrodialysis Reversal (EDR), and Electrodeionization (EDI) are well-established, high Technology Readiness Level (TRL 9) technologies with decades of successful deployment in various industries [73–75]. Commercially, ED and EDR are widely used in the desalination of brackish water, particularly in arid and semi-arid regions where reverse osmosis is less cost-effective due to moderate salinity levels. For example, ED plants are extensively utilized in North America, Europe, and the Middle East, with some systems processing over 100,000 m³/day [46,75–78]. ED is also extensively applied in the food and beverage industry—for instance, in the demineralization of whey proteins and the deacidification of fruit juices [79].

EDI, on the other hand, dominates the ultrapure water market, particularly in semiconductor manufacturing, pharmaceutical formulation, and power generation, due to its ability to achieve resistivities exceeding 18 MΩ·cm without chemical regenerants [80–82]. However, the applications discussed in this review—particularly those involving advanced EDM architectures such as Selective Electrodialysis (S-ED) and Electrodialysis with Bipolar Membranes (EDBM)—focus on emerging and targeted ion recovery from complex matrices (e.g., lithium from brines, phosphorus from wastewater, and rare earth elements from mining effluents). These applications remain largely at laboratory or pilot scale, with only a few progressing toward demonstration-scale operations [83–85]. Therefore, while foundational EDM technologies are mature, their adaptation to highly selective, resource-recovery contexts present new material, economic, and operational challenges that warrant further development and validation under real-world conditions.

4. Energy Efficiency: The Critical Performance Metric

While the technical feasibility of ion recovery using electro-driven membranes has been extensively demonstrated, the widespread industrial adoption of these technologies' hinges critically on their economic viability and environmental sustainability. Energy consumption is arguably the single most important factor governing both aspects. A high energy demand not only translates directly to high operational costs, rendering many recovery processes economically uncompetitive, but also carries a significant carbon footprint, potentially negating the environmental benefits of resource recovery. Therefore, a rigorous analysis of energy efficiency is not merely an academic exercise but a crucial step in evaluating the practical potential of any EDM technology. This section defines the key metrics used to quantify energy consumption, critically examines the multifaceted factors that influence it, and outlines the primary strategies being pursued to minimize it.

4.1. Defining and Quantifying Energy Consumption

To compare the performance of different EDM systems and processes, two key metrics are universally employed: Specific Energy Consumption (SEC) and Current Efficiency (η).

- Specific Energy Consumption (SEC):** This is the most direct measure of a process's energy demand, representing the amount of electrical energy required to achieve a specific separation task (illustrated in Figure 5). It is typically expressed in one of two ways, depending on the primary goal of the process:
 - kWh per cubic meter (kWh/m³)** of water treated or produced. This unit is most common in desalination and water purification applications where the volume of processed water is the key output.
 - kWh per kilogram (kWh/kg)** of the target ion or product recovered. This unit is more relevant for resource recovery applications, as it directly links energy input to the economic value of the recovered material.

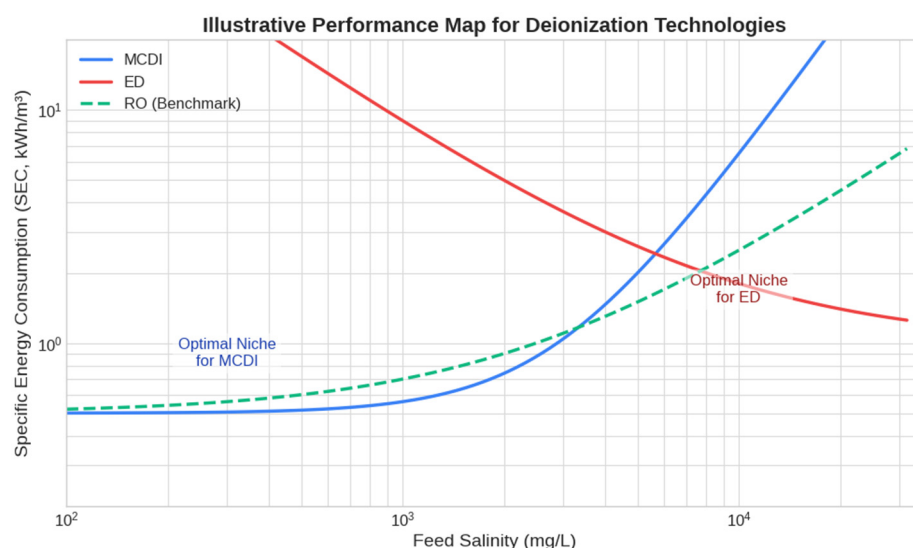


Figure 5. Comparative performance map of core deionization technologies. The specific energy consumption (SEC) is plotted against feed salinity, illustrating the optimal operational niche for Membrane Capacitive Deionization (MCDI) in low-salinity streams and Electrodialysis (ED) in higher-salinity streams. Reverse Osmosis (RO) is included as a benchmark pressure-driven process.

The total energy consumed (E) by an EDM stack is calculated as the product of the applied voltage (V), the current (I), and the operation time (t), and the SEC is derived from this value. The use of different units across the literature reflects the varied objectives of

the studies; a focus on kWh/m³ suggests a primary goal of water purification, whereas a focus on kWh/kg indicates a primary goal of resource recovery.

- **Current Efficiency (η):** Also known as Faradaic efficiency, this dimensionless parameter quantifies how effectively the electrical current is used to transport the desired target ions across the membranes. It is defined as the ratio of the charge carried by the target ions to the total charge passed through the system. An ideal system would have a current efficiency of 100%, meaning every electron supplied contributes to moving a target ion. In reality, current efficiency is always less than 100% due to several non-ideal phenomena, including the following:
 1. **Co-ion leakage:** The imperfect selectivity of membranes allows some co-ions to be transported in the “wrong” direction.
 2. **Water splitting:** At or above the limiting current density, a portion of the current is consumed by the dissociation of water into H⁺ and OH[−] ions.
 3. **Transport of non-target ions:** In multi-ion solutions, current is used to transport all ions, not just the target species.

A low current efficiency directly leads to a higher SEC, as a significant fraction of the supplied energy is wasted on these unproductive processes.

4.2. Factors Influencing Energy Consumption

The SEC of an EDM process is not a fixed value but is highly sensitive to a complex interplay of feedwater characteristics, operating parameters, and the physical properties of the system itself. It is important to clarify that the performance map presented in Figure 5 is an illustrative diagram based on established performance trends documented throughout the literature, rather than being plotted from a single, specific dataset. A log-log scale is employed as it is the standard and most effective method for visualizing and comparing performance trends that span several orders of magnitude for both salinity (X-axis) and the resulting SEC (Y-axis).

4.2.1. Feedwater Characteristics

The composition of the source water is a primary determinant of energy demand. The total salinity or ion concentration dictates the bulk solution’s electrical conductivity. For ED systems, treating highly dilute feeds (<500 ppm) is energetically unfavorable due to the high ohmic resistance of the water itself. Conversely, in MCDI, energy consumption is more directly related to the number of ions removed, making it better suited for such dilute streams. The presence of competing ions is a critical factor in selective recovery. For example, in lithium recovery from brines, the system must expend energy to transport not only the target Li⁺ ions but also the much more abundant Na⁺, Mg²⁺, and Ca²⁺ ions. This significantly lowers the effective current efficiency for lithium recovery and increases the SEC per kilogram of Li⁺ produced.

4.2.2. Operating Parameters

The way an EDM system is operated has a profound impact on its efficiency. The applied voltage or current density is a key parameter. While operating at a higher current density increases the rate of ion removal (throughput), it also quadratically increases energy losses due to ohmic resistance ($P = I^2R$). More importantly, exceeding the limiting current density (LCD) triggers water splitting, causing a sharp decline in current efficiency and dramatic pH changes that can precipitate scaling and damage membranes [22,86,87]. The flow rate of the feed solution influences the residence time and the thickness of the concentration polarization boundary layers. Higher flow rates create more turbulence, which can increase the LCD and allow for higher throughput, but this comes at the cost of

a higher hydraulic pumping energy demand. Finally, temperature plays a role, as higher temperatures decrease solution viscosity and increase both ionic mobility and membrane conductivity, generally lowering the required voltage and thus the SEC. However, actively heating process streams is rarely economically feasible.

4.2.3. System and Material Properties

The physical design of the EDM stack and the materials used are fundamental to its energy performance. The intrinsic resistance of the ion-exchange membranes is a major contributor to the total stack resistance. Significant research is dedicated to developing membranes with high conductivity without compromising their mechanical strength or permselectivity [88]. The design of the stack, particularly the thickness of the flow channels (the inter-membrane distance), is a critical trade-off. Thinner channels reduce the path length for ion transport and thus lower the ohmic resistance of the solution, but they are more prone to clogging and result in higher hydraulic pressure drops. The design of the spacers placed within these channels is also crucial. Modern spacers are engineered to promote efficient mixing and disrupt boundary layers to maximize the LCD, but their geometry must be optimized to minimize the energy required for pumping [89]. For MCDI, the properties of the electrode materials are paramount; high specific capacitance is needed to maximize ion storage, while low internal resistance is required to minimize energy loss during charge and discharge cycles.

4.3. Strategies for Minimizing Energy Consumption

Given the factors above, several key strategies are employed to enhance the energy efficiency of EDM processes.

- **Optimizing Operating Conditions:** The most straightforward strategy is to operate the system under conditions that maximize current efficiency, most notably by keeping the applied current density safely below the LCD. Advanced process control systems can dynamically adjust the current based on real-time measurements of conductivity or pressure drop to maintain optimal performance as feed conditions fluctuate.
- **Development of Advanced Materials:** This is a major frontier of research. The development of low-resistance IEMs and BPMs with high selectivity and stability is a primary goal [90,91]. For BPMs, incorporating catalysts into the interfacial layer to lower the voltage required for water splitting is a key area of focus. Zhang et al. [92] demonstrated this principle by incorporating $\text{Ti}_3\text{C}_2\text{Tx}$ nanosheets into the interfacial layers of bipolar membranes. These nanosheets served as advanced catalysts for water splitting. Their research revealed that these catalyst-infused bipolar membranes exhibited excellent inter-layer adhesion, strong thermal stability, and good alkali resistance, all while significantly enhancing the catalytic effect on water splitting. For MCDI, synthesizing novel nanostructured carbon electrodes or redox-active composites with higher capacitance and faster ion kinetics can significantly reduce the energy per ion removed [59,60].
- **Minimizing Water Transport:** Unwanted water transport across membranes via osmosis and electro-osmosis dilutes the recovered product and represents wasted energy. The design of membranes with lower water permeability is an important strategy, especially for high-salinity applications where osmotic pressure gradients are severe.
- **Process Integration and Hybrid Systems:** Often, the most energy-efficient solution involves integrating EDM with other separation technologies. For instance, a less energy-intensive process like nanofiltration (NF) can be used for the bulk removal of divalent ions or as a pre-concentration step. The resulting more conditioned feed

can then be treated by a more targeted (and expensive) EDM process like S-ED. This hybrid system approach allows each technology to operate in its optimal window, leading to a lower overall SEC for the entire process train compared to using a single technology for the entire task.

5. Critical Review of Practical Applications of EDMs in Ion Recovery

The theoretical advantages of electro-driven membrane processes are best evaluated through their performance in practical applications. The versatility of EDM technologies allows them to be adapted for a wide range of resource recovery challenges, from treating high-volume, low-concentration municipal wastewater to processing highly saline industrial brines. This section provides a critical review of the state-of-the-art applications, drawing on recent case studies from the literature to analyze the performance, highlight key successes, and identify the persistent challenges that must be overcome for broader industrial implementation. The discussion is structured around the primary types of resources recovered: nutrients, valuable metals from brines and batteries, and chemical commodities.

5.1. Recovery of Nutrients from Wastewater

The recovery of nutrients, particularly nitrogen (in the form of ammonium, NH_4^+) and phosphorus (as phosphate, PO_4^{3-}), from municipal and agricultural wastewater represents a cornerstone of the circular economy. It addresses the dual challenges of preventing eutrophication in surface waters and recapturing valuable components for fertilizer production, reducing reliance on energy-intensive synthetic fertilizer manufacturing. As summarized in Table 3, various EDM technologies have been extensively investigated for this purpose.

Electrodialysis (ED) has been shown to effectively concentrate both ammonium and phosphate, with studies like Meng et al. [19] reporting recovery efficiencies exceeding 84–90%. However, energy consumption, particularly for phosphate, can be extremely high, underscoring the challenge of recovering low-concentration species. Technologies like Membrane Capacitive Deionization (MCDI) and Flow-Electrode Capacitive Deionization (FCDI) have demonstrated high removal efficiencies (up to 98%) with more favorable energy profiles (e.g., 4.5–8.9 kWh/kg-N for FCDI) for dilute streams [93]. A key challenge in treating real wastewater is the severe potential for organic fouling. Dissolved organic matter, proteins, and humic substances present in municipal effluent readily adsorb onto the surfaces of ion-exchange membranes, particularly AEMs, increasing electrical resistance and reducing ion flux [94]. This necessitates robust pre-treatment or the use of fouling-resistant membranes, adding to the overall process cost and complexity. While EDM systems primarily serve to concentrate these nutrients, the resulting nutrient-rich brine is an ideal feedstock for a subsequent crystallization step to produce slow-release fertilizers like struvite (magnesium ammonium phosphate), creating a complete nutrient-to-product pathway.

A notable finding from the summarized data is the extremely wide range of Specific Energy Consumption (SEC) reported for phosphorus recovery, particularly the 16.8–1384 kWh/kg range observed by Meng et al. [19]. This significant variance underscores a key challenge in nutrient recovery: the SEC metric is highly sensitive to the initial concentration of the target ion. At the very low phosphate concentrations typical of municipal wastewater, a large amount of energy is expended relative to the small mass of material recovered, highlighting the energetic difficulties of scavenging trace nutrients.

Table 3. Summary of Recent Studies on Nutrient Recovery from Wastewater ¹.

Technology	Target Ion(s)	Feedstock	Removal/Recovery (%)	Energy Consumption	Ref.
ED (AEM/CEM)	N, P, K	Municipal Wastewater	N: >90, P: 84–90, K: >90	N: 4.1–16.2 kWh/kg P: 16.8–1384 kWh/kg	[19]
EDBM	NH ₄ ⁺	Synthetic Wastewater	72–83	2.7 kWh/m ³	[93]
ED Membrane Contactor	NH ₄ ⁺	Synthetic Wastewater	60–99	8.5–14.7 kWh/kg-N	[93]
FCDI	NH ₄ ⁺	Synthetic Wastewater	98	4.5–8.9 kWh/kg-N	[93]
MCDI	Phosphates	Municipal/Agri. Wastewater	10.1–86.4	0.87–2.1 kWh/kg-P	[95]
ED (CEM/AIEM)	NH ₄ ⁺	Municipal Wastewater	High	1.0–5.0 kWh/m ³	[23]
ED (IEMs)	NH ₄ ⁺ , PO ₄ ^{3−} , K ⁺	Municipal Wastewater	70–90	2.5–6.0 kWh/m ³	[96]
ED (AEM)	NO ₃ [−]	Synthetic Wastewater	96	Not Reported	[97]

Notes: ¹ **Abbreviations:** ED: Electrodialysis; AEM: Anion-Exchange Membrane; CEM: Cation-Exchange Membrane; EDBM: Electrodialysis with Bipolar Membranes; FCDI: Flow-Electrode Capacitive Deionization; MCDI: Membrane Capacitive Deionization; AIEM: Amphoteric Ion-Exchange Membrane.

5.2. Recovery of Valuable Metals from Brines

The extraction of valuable metals from saline solutions, including geothermal brines, desalination concentrate, and spent battery leachates, is a major economic driver for the development of advanced EDM systems.

5.2.1. Lithium Recovery

With the exponential growth of the lithium-ion battery market, extracting lithium from unconventional water sources—such as salt-lake brines, geothermal brines, and desalination brines—has become a major global research focus. It is important to contrast the emerging electrochemical methods with conventional technologies. For decades, the dominant method has been the use of particulate lithium-ion sieves (LISs) in packed column systems [98–101]. The most common LISs are manganese-based (LMO-type) and titanium-based (LTO-type) [102]. However, a primary disadvantage of this conventional adsorption route is its chemical-intensive nature; LISs often suffer from issues like manganese dissolution in acidic conditions and require significant quantities of acid and base for the lithium desorption and column regeneration steps. In contrast, electrochemical methods are being studied as a compelling alternative due to their significantly lower chemical usage. Furthermore, the applied electric field acts as a direct driving force for ion capture, which can shorten the time required to recover the same amount of lithium compared to passive adsorption processes [103,104].

While EDM technologies are promising, the challenge of lithium extraction varies significantly with the source. Salt-lake and geothermal brines, with Li⁺ concentrations in the hundreds of ppm, are the most economically attractive feedstocks. In contrast, seawater and desalination brines present a far greater challenge due to the extremely low lithium concentration (0.2–0.4 ppm) and the vast excess of competing cations. This introduces two severe and interconnected challenges: selectivity and biofouling [101]. The issue of selectivity is paramount; the Na⁺/Li⁺ mass ratio in seawater can exceed 20,000:1, meaning that even a membrane with 99.9% rejection of Na⁺ would still allow significant sodium leakage, contaminating the product and drastically lowering the current efficiency for Li⁺ transport. This directly inflates the specific energy consumption (SEC) per kilogram of

lithium recovered, posing a major economic barrier. Furthermore, treating raw seawater introduces the pervasive issue of marine biofouling. Microorganisms present in the water readily attach to membrane surfaces and excrete extracellular polymeric substances (EPS), forming a dense, slimy biofilm [101,105,106]. This biofilm physically blocks ion transport pathways, which can dramatically increase the stack's electrical resistance, and can also create localized pH changes that promote scaling. Combating biofouling requires an intensive and costly pre-treatment train (e.g., chlorination/dechlorination, ultrafiltration) and regular, aggressive chemical cleaning, which adds significantly to the operational complexity and cost of any potential seawater mining operation.

As shown in Tables 4 and 5, EDM technologies are at the forefront of this effort. The central challenge is separating the target Li^+ ion from a vast excess of competing cations, primarily Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . **Selective Electrodialysis (S-ED)**, using monovalent selective cation-exchange membranes (MCEMs), has emerged as the key technology. These membranes have proven highly effective at the separation of monovalent Li^+ from divalent Mg^{2+} and Ca^{2+} , a critical step where selectivity factors can be high [32,107]. However, the more difficult challenge lies in the separation of Li^+ from Na^+ , as both are monovalent ions with similar physicochemical properties. This remains a significant bottleneck, as achieving high lithium purity often requires multiple ED stages, increasing both capital cost and energy consumption. Recent breakthroughs in advanced materials, such as lithium-ion sieve membranes (e.g., LLTO- and LAGP-type), offer the potential for much higher selectivity. Studies like Yang et al. [108] report impressive recovery rates (>98%) from seawater. However, as the detailed techno-economic case study in Section 6 will explore, these advanced materials currently face significant challenges in terms of fabrication cost, scalability, and long-term stability in harsh brine environments.

Table 4. Summary of Recent Studies on Ion Recovery from Brines and Seawater ¹.

Technology	Target Ion(s)	Source	Recovery/Selectivity	Ion Flux ($\text{mg dm}^{-2} \text{ h}^{-1}$) ²	Energy Consumption	Ref.
ED (MCEM)	Li^+	Salt Lake Brine	94.5	Data Not Available	6.0–21.0 kWh/kg-Li	[33]
ED (MCEM)	Li^+	Salt Lake Brine	90	Data Not Available	Not Reported	[107]
ED (MCEM)	Li^+	Salt Lake Brine	94	Li^+ : 2.0–5.0	3.0–8.0 kWh/kg-Li	[109]
ED (LLTO Membrane)	Li^+	Red Sea Seawater	High	0.28	76.3 kWh/kg-Li	[22]
ED (LAGP-PE Membrane)	Li^+	Seawater	98	Li^+ : 5.1	17.4 kWh/kg-Li	[108]
EDBM	NaOH , HCl	Seawater Brine	NaOH : 84%, HCl : 63%	NaOH : ~1500, HCl : ~1013	NaOH : 1.5–3.1 kWh/kg HCl : 2.4–6.2 kWh/kg	[110]
SF-EDM (MCEM)	Bulk Salinity	Brackish Groundwater	93% Salinity Reduction	Data Not Available	7.14 kWh/ m^3	[111]
ED	Na^+ , Cl^-	Seawater Brine	55–74%	Na^+ : ~682, Cl^- : ~1053	1.0–3.7 kWh/ m^3	[112]
ED (MCEM)	NaCl	SWRO Brine	>90% divalent rejection	NaCl : ~1490	3.04 kWh/kg- NaCl	[113]
S-ED (MCEM)	NaCl	SWRO Brine	Na^+ Recovery: ~81%	Na^+ : ~1150, Cl^- : ~1770	0.20 kWh/kg- NaCl	[114]

Notes: ¹ **Abbreviations:** **ED:** Electrodialysis; **MCEM:** Monovalent Selective Cation-Exchange Membrane; **LLTO:** Lithium Lanthanum Titanium Oxide (membrane material); **LAGP-PE:** Lithium Aluminum Germanium Phosphate–Polyethylene (membrane material); **EDBM:** Electrodialysis with Bipolar Membranes; **SF-EDM:** Salt-Free Electrodialysis Metathesis; **SWRO:** Seawater Reverse Osmosis. ² **Ion Flux Calculation:** Where possible, ion flux was calculated or converted from data reported in the source paper. The flux represents the mass of the specified ion transported per unit of effective membrane area per unit of time. “Data Not Available” indicates that one or more of the necessary parameters (i.e., absolute mass recovered, membrane area, or operational time) were not reported in the publication.

5.2.2. Recovery of Other Metals from Brines and Leachates

Beyond lithium, EDM is applied to recover a host of other valuable metals. As shown in Table 5, the recycling of spent battery materials is a key application, with ED and

BMED used to recover cobalt (Co^{2+}), nickel (Ni^{2+}), and manganese (Mn^{2+}) from acidic leachate [115,116]. Here, the challenge is often managing a highly acidic feed stream and separating multiple valuable metals from one another. Specialized approaches, such as using cobalt-selective membranes, have shown promise but often struggle with co-transport of other ions, limiting final product purity [116]. The recovery of potassium (K^+), a key fertilizer component, from various brine sources is also an area of interest, although it receives less attention than lithium due to its lower market value.

Table 5. Summary of Recent Studies on Metal Recovery from Spent Battery Leachates ¹.

Technology	Target Metal(s)	Recovery/Selectivity	Energy Consumption (kWh/kg)	Ref.
ED	Li^+	90	27	[94]
BMED	LiOH	99	6–21	[116]
FCDI	Li^+ (over Co^{2+} , Ni^{2+})	Selectivity Factor: 12.88	9.9	[117]
BMED	Li^+	99	~7.9 kWh/m ³ (feed)	[32]
BMED	LiOH	>92	3.4	[64]
PIM-ED	Co^{2+}	>95.9	4.4	[118]
ED	Ni^{2+}	99.3	~164	[115]
ED (Co-selective)	Co^{2+} (over Li^+ , Ni^{2+})	Co: 91, Li: 48.8, Ni: 8	5.6	[119]

Notes: ¹ **Abbreviations:** ED: Electrodialysis; BMED: Bipolar Membrane Electrodialysis; FCDI: Flow-Electrode Capacitive Deionization; PIM-ED: Polymer Inclusion Membrane Electrodialysis.

5.3. Recovery of Heavy Metals from Industrial Effluents

The treatment of industrial effluents, particularly from the electroplating, mining, and electronics sectors, is driven by the dual imperative of meeting strict environmental discharge limits and recovering valuable metal resources. As summarized in Table 6, conventional ED is a robust and effective technology for this purpose, capable of achieving high removal efficiencies (>90–99%) for a wide range of metals including copper, nickel, zinc, and chromium. The primary challenge in this field is the complexity of the feedwater matrix. Industrial effluents are rarely clean, single-salt solutions; they often contain mixtures of metals, organic additives, and chelating agents at extreme pH values. This complex environment can lead to severe membrane fouling and requires careful process control to manage competing ion transport. While ED can effectively concentrate the total metal content, achieving a high-purity, saleable single-metal product from a mixed-metal waste stream often requires integration with other separation processes like solvent extraction or selective precipitation. The robustness of ED makes it an excellent pre-concentration step in such a hybrid process train.

Table 6. Summary of Recent Studies on Heavy Metal Recovery from Wastewater ¹.

Technology	Target Ion(s)	Feedstock	Removal (%)	Energy Consumption	Ref.
ED (IEMs)	Pb^{2+} , Cd^{2+} , Cr(VI) , Ni^{2+} , Cu^{2+} , Zn^{2+}	Industrial Wastewater	>99	2.0–5.0 kWh/m ³	[120]
iNF	CrO_4^{2-} , WO_4^{2-} , Ni^{2+} , Cd^{2+}	Synthetic Wastewater	96–97	Not Reported	[121]
ED	Pb^{2+} , Zn^{2+} , Hg^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Cr^{3+} , As	Synthetic Wastewater	~90	0.1–3.0 kWh/m ³	[122]
ED (CEM)	Ni^{2+} , Cr^{3+} , Fe^{3+}	Industrial Wastewater	>90	20–35 kWh/kg	[123]
ED (CEM)	Pb^{2+} , Cu^{2+} , Ni^{2+}	Synthetic Wastewater	Cu: 98.4, Ni: 84.1, Pb: 62.4	Not Reported	[124]
ED (CEM)	Cr^{3+}	Synthetic Cr solution	-	40.0–56.2 W/mol	[125]
PIM-ED	Cr(VI)	Simulated Wastewater	98.3	0.023 kWh (lab scale)	[126]

Notes: ¹ **Abbreviations:** ED: Electrodialysis; IEMs: Ion-Exchange Membranes; iNF: Ion Exchange-Nanofiltration; CEM: Cation-Exchange Membrane; PIM-ED: Polymer Inclusion Membrane Electrodialysis.

Note that, a critical evaluation of the literature reveals challenges in making direct energy comparisons between studies due to inconsistent reporting units. For instance, the energy consumption reported by Hosseini et al. [125] in W/mol, while technically valid, is not directly comparable to the more common kWh/m³ or kWh/kg metrics used in other studies. This lack of standardization can obscure direct assessments of process efficiency.

5.4. Production of Acids and Bases from Salt Streams

Electrodialysis with Bipolar Membranes (EDBM) enables one of the most compelling applications within the circular economy framework: the valorization of low-value waste salt streams into high-value chemical commodities. By using the water-splitting capability of bipolar membranes, EDBM can convert a salt like NaCl into streams of hydrochloric acid (HCl) and sodium hydroxide (NaOH) [67–69].

This technology is particularly well-suited for integration with large-scale desalination plants. The vast quantities of RO brine, typically considered a waste product, can be used as a feedstock for an EDBM unit. The produced acid and base can then be used directly on-site for membrane cleaning (CIP), pH adjustment, or pre-treatment, reducing the facility's reliance on and expenditure for purchased chemicals. As shown by Virruso et al. [110], a pilot-scale EDBM plant treating real seawater brine can achieve high production efficiencies. The critical barrier to widespread adoption remains the economic trade-off between the high energy cost of water splitting into the BPMs and the market value of the produced chemicals. This makes the process most attractive in regions with high chemical costs or low electricity prices, or where stringent brine disposal regulations add a significant “waste management” credit to the process economics. In addition to ion recovery, the successful application of electro-driven membranes for the remediation of organic pollutants is a significant area of research. As summarized in Table 7, these technologies have proven effective for removing contaminants ranging from glyphosate in industrial effluent to PFAS and pharmaceuticals in various water samples.

Table 7. Summary of Recent Studies on Organic Pollutant Removal from Water ¹.

Technology	Target Pollutant (s)	Feedstock	Removal (%)	Energy Consumption	Ref.
ED (PEM)	Bisphenol A (BPA), PFAS	Industrial Wastewater	90–99.9	5.1–6.7 kWh/m ³	[19]
EDBM	Glyphosate	Production Wastewater	95	2.7 kWh/kg of NaOH	[127]
Electroactive Membrane	NOM, phenol, antibiotics, pesticides, dyes	Contaminated Groundwater	>90	0.002–0.014 kWh/m ³	[128]
Electrochemical GAC Regen.	Phenols, pesticides, PFAS, NOM, dyes	Synthetic Wastewater	Dyes: 76–90, Phenols: 90	Phenol: 2.8 kWh/kg	[129]
G-EME	Pharmaceuticals, POPs	River/Tap/Wastewater	62–89	0.01–0.5 kWh/sample	[130]

Notes:¹ **Abbreviations:** ED: Electrodialysis; PEM: Proton-Exchange Membrane; EDBM: Electrodialysis with Bipolar Membranes; GAC: Granular Activated Carbon; G-EME: Gel Electro-Membrane Extraction; POPs: Persistent Organic Pollutants; NOM: Natural Organic Matter.

The application of these technologies to organic pollutant removal introduces further complexity in evaluating energy efficiency, as shown in Table 7. The use of mixed energy units—such as kWh/m³ for bulk water treatment, kWh/kg for a specific contaminant, and even kWh/sample for analytical-scale extractions—reflects the diverse goals of these studies. While each metric is appropriate for its specific context, this variance highlights the need for more standardized reporting protocols in future research to facilitate cross-study comparisons and to better evaluate the overall energy footprint of organic contaminant remediation using electro-driven membranes.

6. Overarching Challenges and Future Research Perspectives

Despite significant progress and promising results across a spectrum of applications, the transition of electro-driven membrane technologies from laboratory-scale validation to widespread, economically competitive industrial implementation is contingent upon overcoming several fundamental challenges. The long-term performance, stability, and cost-effectiveness of these systems are often constrained by the inherent limitations of the materials and the complexities of real-world operating environments. This section provides a critical analysis of these overarching challenges (Figure 6) and outlines the key future research directions required to unlock the full potential of EDMs for sustainable resource recovery.

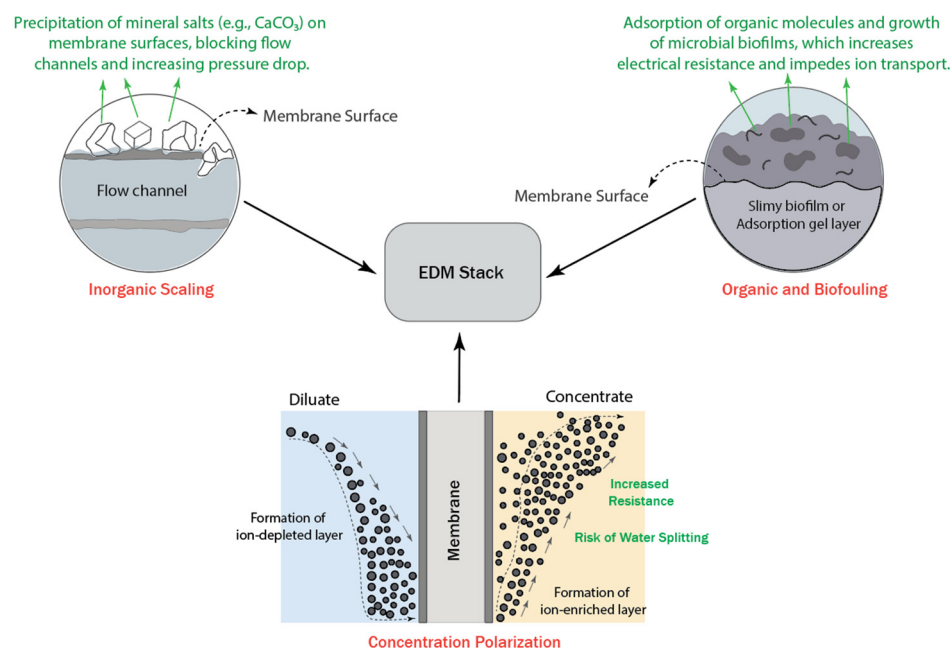


Figure 6. Schematic representation of the primary operational challenges affecting EDM performance. These include (a) inorganic scaling, where mineral precipitates can block channels and damage membranes; (b) organic and biofouling, where adsorbed layers increase electrical resistance; and (c) concentration polarization, which leads to increased energy consumption and can trigger undesirable side reactions if the limiting current density is exceeded.

6.1. Membrane Performance and Stability

The ion-exchange membrane is the functional heart of any EDM system, and its intrinsic properties dictate the ultimate performance of the process. While modern membranes are highly effective, significant hurdles remain.

- Challenge: The Selectivity–Conductivity Trade-Off:** The most critical challenge, particularly for high-value metal recovery, is achieving high selectivity between ions of the same valence, for example, separating Li^+ from Na^+ . Standard membranes offer little to no selectivity in this regard. While advanced monovalent selective membranes have been developed, they often exhibit a fundamental trade-off: enhancing selectivity by creating denser or more charged surface layers typically increases the membrane's electrical resistance (lowering its conductivity) and reduces its ion flux. This directly translates to higher energy consumption and requires a larger membrane area to achieve the same throughput, thereby increasing capital costs. Furthermore, the thin functional layers that impart this selectivity can be chemically or mechanically fragile. Advanced ceramic-based membranes, such as the LLTO type used for lithium recovery, are susceptible to mechanical stress and cracking, and their long-term durability in real-

world conditions has not yet been validated. There can also be safety concerns related to the flammability of certain electrolytes used in some electrochemical systems.

- **Future Direction: Advanced Material Design:** Overcoming this requires a move beyond simple surface coatings toward the rational design of novel membrane materials. Future research must focus on creating isoporous membranes with precisely controlled, sub-nanometer pore size distributions that can distinguish between ions based on their hydrated radii. Another promising avenue is the development of membranes with ion-sieving functional layers containing specific ligands or channels that have a chemical affinity for the target ion, enabling a more active transport mechanism. The integration of advanced nanomaterials, such as graphene oxide or metal–organic frameworks (MOFs), into the membrane matrix also holds potential for creating new transport pathways that could decouple selectivity from permeability [23].

6.2. Fouling and Scaling

Like all membrane processes, EDMs are highly susceptible to fouling and scaling, which remain the most common causes of performance decline and operational failure in industrial settings.

- **Challenge: Reduced Efficiency and Lifespan:** In wastewater applications, membrane surfaces, especially those of AEMs, are prone to organic fouling from proteins, humic acids, and other macromolecules, which increases system resistance and can be difficult to remove [94]. In the treatment of hard water or brines, inorganic scaling is a major issue. The increase in ion concentration and pH shifts at the membrane surface inside concentrate compartments can lead to the precipitation of sparingly soluble salts like CaCO_3 and CaSO_4 , blocking channels and potentially causing irreversible damage to the membranes. These issues lead to a direct increase in energy consumption, higher cleaning chemical costs, and a reduced operational lifetime for the membrane stack.
- **Future Direction: Surface Engineering and Pre-treatment:** The development of anti-fouling membrane surfaces is a key research priority. This includes creating highly hydrophilic surfaces that resist protein adsorption or grafting zwitterionic polymers that create a tightly bound hydration layer, preventing foulants from attaching. For scaling, the optimization of cleaning-in-place (CIP) protocols and the continued use of Electrodialysis Reversal (EDR) are crucial. Ultimately, however, the most effective strategy is the integration of robust pre-treatment steps. For many applications, particularly those involving complex industrial streams or high-hardness waters, the added cost of pre-treatment (e.g., clarification, media filtration, softening) is a necessary investment to protect the much higher capital cost of the EDM stack and ensure its long-term, stable operation.

6.3. Process Integration and Scale-Up

Bridging the gap from successful laboratory experiments to robust, large-scale industrial plants presents significant engineering and economic challenges.

- **Challenge: Capital Costs and Process Complexity:** EDM systems, particularly those using specialized membranes or complex configurations, have high capital costs driven by the price of the membranes and the intricate assembly of the stacks. Furthermore, industrial feed streams are rarely stable; they fluctuate in composition, concentration, and temperature. A system optimized for one set of conditions in a lab may perform poorly when faced with real-world variability. This makes scaling up a risky and capital-intensive proposition.
- **Future Direction: Hybrid Systems and Advanced Control:** For complex separation tasks, the most economically and energetically efficient solution often lies in hybrid

systems. Instead of relying on a single EDM process, an integrated approach—for example, using Nanofiltration (NF) for bulk removal of divalent ions before a more targeted S-ED step—allows each technology to operate in its ideal niche, lowering the overall cost and energy footprint. Critically, more rigorous techno-economic analyses (TEAs) are needed early in the research process to guide development toward economically viable applications. Finally, the development of standardized, modular EDM units and advanced feedback-based process control strategies are essential for creating robust systems that can automatically adapt to changing feed conditions, ensuring stable and reliable long-term operation at an industrial scale.

6.4. Energy and Electrode Limitations

While many energy limitations are tied to the membranes and system design, certain challenges are specific to the electrodes, particularly in MCDI systems.

- Challenge: Electrode Capacity and Selectivity:** The performance of MCDI is fundamentally limited by the salt adsorption capacity (SAC) of its porous carbon electrodes. For treating streams with higher salinity, the electrodes become saturated quickly, necessitating frequent regeneration cycles and lowering the overall water recovery and throughput [62]. Moreover, standard activated carbon electrodes offer limited selectivity, with co-ion competition often favoring the removal of divalent ions over target monovalent ions, hindering specific recovery efforts [131]. The challenge of selectivity in MCDI stems from the stronger interaction of divalent ions with electrode surfaces due to their higher charge density. This often leads to their preferential adsorption over monovalent ions [132,133]. While ion charge is a primary factor, the hydrated radius (the ion's size, including its surrounding water molecules) also plays a role. Smaller hydrated ions can more easily access and be adsorbed within the smaller pores of activated carbon electrodes. Nevertheless, the effect of charge typically dominates over the size effect, particularly when distinguishing between monovalent and divalent ions. This inherent lack of selectivity can significantly hinder the efficiency of MCDI in applications requiring specific ion recovery, such as extracting lithium from complex solutions like seawater that also contain divalent ions.
- Future Direction: Next-Generation Electrode Materials:** Research in this area is focused on moving beyond simple activated carbons. The exploration of novel carbon nanostructures, such as graphene aerogels or carbon nanotubes (CNTs), offers pathways to materials with higher specific surface area and better hierarchical pore networks for improved ion access and higher capacity [92]. The most exciting frontier, however, is in intercalation electrodes. Materials such as sodium manganese oxide (NMO) or lithium manganese oxide (LMO) can selectively insert specific ions (Na^+ or Li^+) into their crystal lattice via a Faradaic reaction, offering a dramatic improvement in both capacity and selectivity compared to EDL-based storage. The development of stable, scalable, and cost-effective versions of these advanced electrode materials is a critical step toward enabling highly selective and efficient ion recovery with MCDI.

6.5. Case Study: A Critical Analysis of the Techno-Economic Feasibility of Seawater Lithium Mining

To ground the preceding discussion of challenges in a practical context, this section provides a critical analysis of a techno-economic model for direct lithium extraction from seawater using a specialized electro-driven LLTO (Lithium Lanthanum Titanium Oxide) membrane, based on the process parameters described by Li et al. [22]. This case study serves to illustrate the immense scale and significant economic hurdles that must be overcome to translate a promising laboratory-scale membrane into an industrial reality.

The model explores the feasibility of achieving a target extraction rate of 1 kg/h of lithium by scaling up a small laboratory prototype. A summary of the key assumptions underpinning the model, from material costs to energy inputs, is presented in Table 8. The analysis proceeds by exploring three scenarios of increasing scale to evaluate the impact on financial metrics such as Net Present Value (NPV) and Internal Rate of Return (IRR), with the key findings summarized in Table 9.

Table 8. Key Assumptions for the LLTO Membrane Techno-Economic Model (Based on [22]).

Parameter	Assumption/Value	Source/Rationale
Material Costs	LiNO ₃ : \$3.11/g; La(NO ₃) ₃ : \$1.80/g; Citric Acid: \$0.12/g; Ti(IV) Butoxide: \$0.18/g.	Sourced from Sigma-Aldrich (lab scale).
Energy Costs	Electricity Price: \$0.15/kWh; Process Energy: \$5.00/kg-Li.	Assumed market rate; Process energy as reported.
Manufacturing	Sintering and Ball Milling included in membrane cost.	Based on reported lab process parameters.
Product Market Prices	Lithium Phosphate (99.94%): \$9.00/kg; Hydrogen Gas: \$8.00/kg; Chlorine Gas: \$0.15/kg.	Assumed market prices for analysis.
Financial	Discount Rate: 4.75%; Plant Operational Period: 20 years.	U.S. market rate; Standard project lifetime.

Table 9. Summary of Feasibility Scenarios for Seawater Lithium Extraction.

Parameter	Scenario 1	Scenario 2	Scenario 3
Target Li Production	8.7 tons/year	87.6 tons/year	876 tons/year
Required Membrane Diameter (m)	31 (m)	97 (m)	308 (m)
Initial Membrane Cost	\$1.0 M	\$3.1 M	\$10.0 M
Net Present Value (NPV) ¹	\$0.52 M	\$13.8 M	\$162 M
Internal Rate of Return (IRR) ¹	9%	40%	132%
Simple Payback Period (SPP) ¹	8.9 years	2.5 years	7 months

Notes: ¹ Financial metrics calculated assuming a 20-year operational period and no membrane replacement costs.

While the model's scenarios—particularly Scenario 3—project a highly favorable NPV and IRR, a critical perspective is required. From a project finance standpoint, the 9% IRR of Scenario 1 is borderline for a novel technology, which would typically require a higher return (>15–20%) to attract investment given the inherent risks. Conversely, the exceptionally high returns projected for Scenarios 2 and 3 (40% and 132% IRR, respectively) would likely be viewed with considerable skepticism, as they stem from a model with significant underlying uncertainties. The assumption of a fixed market price for lithium products ignores the well-documented volatility of the commodities market. More importantly, the model's scope is narrow, focusing primarily on membrane and energy costs while excluding several major real-world cost centers. For instance, the extensive pre-treatment required for raw seawater to prevent catastrophic biofouling of the membranes is not included, nor are the significant capital and operational costs associated with pumping millions of liters of water. Furthermore, the model relies on the assumption that the membrane's lifespan will be multiple years yet concedes that this is an unknown variable. A short membrane lifespan would dramatically alter the economic outlook due to high replacement costs. Consequently, while the model is a useful illustration of the technology's potential at scale, the projected financial returns should be interpreted as an optimistic upper-bound estimate that does not yet account for the comprehensive costs and risks inherent to large-scale industrial water processing.

This case study effectively highlights the critical factors identified in this review. While novel materials like LLTO show immense promise for overcoming the selectivity challenge (Section 6.1), the path to commercialization is fraught with challenges in scale-up and capital cost (Section 6.3). The analysis underscores that for such technologies to become viable, future research must not only focus on improving membrane extraction rates but also on drastically improving membrane durability and reducing manufacturing costs to withstand the economic pressures of industrial application.

7. Economic and Environmental Considerations

The viability of electro-driven membrane systems for ion recovery hinges not only on their separation performance and selectivity but also on their economic competitiveness and environmental sustainability. This section presents a comprehensive evaluation of key techno-economic and ecological parameters—including capital and operational costs, membrane lifespan and durability, and the results from recent life cycle assessments (LCA). Understanding these dimensions is essential for the transition of EDM technologies from laboratory-scale innovation to scalable and commercially viable resource recovery platforms.

7.1. Capital and Operational Costs

The total cost of an EDM system comprises Capital Expenditure (CAPEX) and Operational Expenditure (OPEX), both of which are highly dependent on the specific application, process design, system scale, and the required level of ion selectivity.

- **Capital Expenditure (CAPEX):** The membrane stack is the central cost element in EDM systems. This includes cation exchange membranes, anion exchange membranes, and in certain configurations, bipolar membranes. Costs vary significantly depending on membrane type and performance. For example, monovalent selective membranes, critical in lithium recovery or nutrient separations, command premium prices due to complex fabrication and limited manufacturing scale [85,111,134]. In addition to membranes, electrodes (e.g., titanium, platinum-coated, or carbon-based), spacers, and the stack frame contribute significantly to CAPEX. The balance of plant—encompassing feedwater pumps, hydraulic and electrical control systems, power supplies, sensors, instrumentation, and chemical pre-treatment units—can represent up to 40–60% of the total capital investment, depending on plant design complexity and automation level [46,135,136]. Notably, pre-treatment is often mandatory to reduce the risk of scaling, fouling, and oxidation damage, especially in wastewater or mining brine applications, thereby adding to the upfront cost burden.
- **Operational Expenditure (OPEX):** The dominant OPEX component in EDM processes is electrical energy consumption, which directly correlates with membrane resistance, process current density, and system recovery rate. As detailed in Section 4, specific energy consumption (SEC) can range from 0.5 to 10 kWh/m³ depending on the application (e.g., nutrient recovery vs. salt removal vs. lithium concentration) [22,65,109,110]. Other recurring OPEX elements include:
 - Membrane cleaning chemicals (e.g., acids, bases, anti-scalants) and clean-in-place operation labor,
 - Scheduled membrane replacement (based on performance degradation),
 - Pump maintenance and occasional component replacement (e.g., electrode corrosion, valve failure),
 - Monitoring and process control instrumentation calibration.

For emerging applications, particularly those operating in extreme conditions (e.g., high salinity or low pH), OPEX may increase due to higher membrane wear rates and

cleaning frequency. Economic optimization models suggest that improving membrane selectivity and stability can significantly reduce both CAPEX (by reducing stack size) and OPEX (by minimizing cleaning and energy costs) [137].

7.2. Membrane Lifespan and Stability

Membrane longevity is a critical determinant of the levelized cost of treatment or ion recovery. Under optimized operating conditions, standard ion-exchange membranes used in ED/EDR systems can last between 3 and 7 years, or even longer, depending on membrane material, feedwater characteristics, and operating protocols [73]. However, real-world performance often falls short due to three main degradation mechanisms:

- **Fouling and Scaling:** As described in Section 6.2, biofouling, organic adsorption, and inorganic scaling (e.g., CaCO_3 , CaSO_4 , Fe(OH)_3) can clog membrane pores and increase resistance. While some of this fouling is reversible through chemical cleaning, irreversible fouling necessitates premature membrane disposal [14,101].
- **Chemical Attack:** Ion-exchange membranes, especially AEMs, are prone to degradation when exposed to oxidizing agents (e.g., chlorine, hydrogen peroxide), extreme pH, or organic solvents. These attacks cleave the polymer backbone or functional groups, degrading ionic conductivity. BPMs can also delaminate or degrade under prolonged water splitting conditions, particularly at high current densities [14].
- **Mechanical Stress:** Improper handling during installation, hydraulic shocks, abrasive particles in feedwater, and uneven spacer-induced pressure distribution can cause membrane warping, pinholes, or delamination. Specialized membranes with ultra-thin or composite layers (e.g., surface-coated selective membranes) are particularly vulnerable [138–141].

Due to these factors, the effective lifespan of high-performance membranes used in selective ion recovery can be significantly shorter than in classical desalination applications—often under **2–3 years**, depending on the level of stress and fouling encountered. These considerations must be integrated into techno-economic feasibility studies and lifecycle cost models [142,143].

7.3. Environmental Aspects and Life Cycle Assessment (LCA)

EDM technologies offer substantial environmental advantages over conventional treatment methods, particularly in applications targeting resource recovery, zero-liquid discharge, and circular economy pathways. Key benefits include:

- Minimal chemical consumption, due to the absence of stoichiometric reagents,
- Selective separation with reduced sludge generation,
- Direct recovery of valuable components (e.g., nutrients, lithium, acids, and bases), enabling waste valorization.

These features make EDM an attractive choice for sustainable water treatment and resource recovery initiatives, especially in alignment with SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production). However, environmental trade-offs also exist. Chief among them is electricity demand. If the energy used is sourced from fossil fuels, EDM processes can exhibit non-negligible carbon footprints, potentially offsetting sustainability gains. Consequently, integration with renewable energy sources (e.g., solar PV, wind) is increasingly recognized as essential for sustainable deployment [15,144]. Recent Life Cycle Assessments have demonstrated that:

- The manufacturing phase, especially membrane production, contributes significantly to the total environmental burden.

- The operational phase, dominated by energy consumption, is the key determinant of global warming potential and acidification potential.
- End-of-life impacts, such as membrane disposal (e.g., incineration, landfill), also contribute, though advances in membrane recycling and reuse are being explored [145,146].

LCAs have also underscored that system efficiency improvements (e.g., energy recovery, high-recovery operation, smart process control) can substantially reduce environmental impacts. Ultimately, eco-design principles, combined with circular economy strategies and renewable energy integration, are essential to unlocking EDM's full environmental potential.

8. Conclusions

Electro-driven membrane (EDM) technologies represent a versatile and powerful platform for advancing the goals of a circular economy, demonstrating significant potential for recovering valuable ions from a wide range of aqueous sources, including industrial effluents, municipal wastewater, and natural brines. This review has critically examined the state-of-the-art, revealing that the optimal technology choice is highly dependent on the application: conventional Electrodialysis (ED) is robust for concentrating saline streams, while Membrane Capacitive Deionization (MCDI) offers superior energy efficiency for more dilute feeds. Specialized configurations, such as Selective Electrodialysis (S-ED) and Electrodialysis with Bipolar Membranes (EDBM), have unlocked new capabilities for separating specific monovalent ions and converting waste salts into valuable chemical commodities, respectively.

The successful application of these technologies underscores their significant potential to provide more sustainable alternatives to conventional extraction and treatment methods, reducing chemical consumption and, under the right conditions, lowering the energy footprint of resource management. However, this review also highlights that the transition from laboratory promise to widespread industrial reality is impeded by several persistent and interconnected challenges. The performance and economic viability of all EDM systems are fundamentally limited by the trade-offs between membrane selectivity and permeability, the pervasive issues of fouling and scaling, the high capital costs, and the engineering complexities of scaling up.

To unlock the full potential of EDMs, future research must be strategically focused on a few critical areas. The foremost priority is the development of next-generation membrane materials with enhanced selectivity—particularly between ions of the same valence—and superior chemical and mechanical stability to withstand long-term operation in aggressive industrial environments. Concurrently, greater emphasis must be placed on the design and optimization of integrated hybrid systems, which couple EDMs with appropriate pre-treatment technologies to mitigate fouling and allow each component to operate at its peak efficiency. Finally, it is imperative that future research is guided by rigorous and holistic techno-economic analyses that consider the entire process lifecycle. Only by addressing these fundamental challenges in material science, process engineering, and economic feasibility can electro-driven membranes truly become a cornerstone of sustainable water and resource management in the 21st century.

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Abbreviations

The following abbreviations are used in this manuscript:

AEM	Anion-Exchange Membrane
BMED	Bipolar Membrane Electrodialysis
BPM	Bipolar Membrane
CEM	Cation-Exchange Membrane
CEDI	Continuous Electrodeionization
ED	Electrodialysis
EDBM	Electrodialysis with Bipolar Membranes
EDI	Electrodeionization
EDM	Electro-Driven Membrane
EDR	Electrodialysis Reversal
FCDI	Flow-Electrode Capacitive Deionization
GAC	Granular Activated Carbon
G-EME	Gel Electro-Membrane Extraction
IEM	Ion-Exchange Membrane
iNF	Ion Exchange-Nanofiltration
IRR	Internal Rate of Return
LAGP	Lithium Aluminum Germanium Phosphate
LLTO	Lithium Lanthanum Titanium Oxide
MCDI	Membrane Capacitive Deionization
MCEM	Monovalent Selective Cation-Exchange Membrane
NOM	Natural Organic Matter
NPV	Net Present Value
PEM	Proton-Exchange Membrane
PIM	Polymer Inclusion Membrane
POPs	Persistent Organic Pollutants
S-ED	Selective Electrodialysis
SEC	Specific Energy Consumption
SPP	Simple Payback Period
TEA	Techno-Economic Analysis
TRL	Technology Readiness Level

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