

# **Electrochemical Direct Lithium Extraction: Materials, Mechanisms, and System Design for Selective Lithium-Ion Recovery**

Dissertation  
zur Erlangung des Grades  
der **Doktorin der Naturwissenschaften**  
der Naturwissenschaftlich-Technischen Fakultät  
der Universität des Saarlandes

von

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Saarbrücken  
2026

**Tag des Kolloquiums:** 09.06.2026

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*Hayatta en hakiki mürşit ilimdir.*

*Mustafa Kemal Atatürk*

*The truest guide in life is science.*

*Mustafa Kemal Atatürk*

## ABSTRACT

The rising demand for lithium necessitates extraction methods that are faster, more selective, and environmentally sustainable. This thesis demonstrates electrochemical  $\text{Li}^+$  extraction, exploring electrode materials, membrane design, and cell architecture to enhance selectivity, energy efficiency, and operational stability. At the material level, layered and two-dimensional electrodes, including layered double hydroxides and MXenes, achieve selective  $\text{Li}^+$  uptake and release through controlled interlayer environments and electrostatic/kinetic effects. Membrane integration via ceramic-based solid electrolyte and optimized cell architecture enables continuous  $\text{Li}^+$  separation from complex aqueous sources, with energy generation demonstrated in a fuel cell  $\text{Li}^+$  extraction system. These results show that rational material design, combined with optimized cell design and operational parameters, can deliver sustainable, scalable, and selective  $\text{Li}^+$  extraction. In summary, the work exemplifies novel approaches for designing electrochemical  $\text{Li}^+$  recovery technologies.

## ZUSAMMENFASSUNG

Der steigende Lithiumbedarf erfordert Extraktionsverfahren, die schneller, selektiver und ökologisch nachhaltiger sind. Diese Dissertation demonstriert die elektrochemische Extraktion von  $\text{Li}^+$ -Ionen und verknüpft Elektrodenmaterialien, Membrandesign und Zellarchitektur, um Selektivität, Energieeffizienz und Betriebsstabilität zu verbessern. Auf Materialebene ermöglichen schichtartige und zweidimensionale Elektroden - darunter geschichtete Doppelhydroxide und MXene - eine selektive Aufnahme und Freisetzung von  $\text{Li}^+$  durch gezielt eingestellte Zwischenlagenumgebungen sowie elektrostatische und kinetische Effekte. Die Einbindung von Membranen in Form eines keramischen Festelektrolyten und eine optimierte Zellarchitektur erlauben eine kontinuierliche  $\text{Li}^+$ -Abtrennung aus komplexen wässrigen Quellen. Dies wurde am Beispiel eines Brennstoffzell-basierten System gezeigt, das neben der  $\text{Li}^+$ -Extraktion gleichzeitig Strom erzeugt. Die Ergebnisse belegen, dass rationales Materialdesign in Kombination mit optimierten Zelldesign und Verfahrensparametern eine nachhaltige, skalierbare und selektive  $\text{Li}^+$ -Extraktion ermöglicht. Zusammenfassend zeigt diese Arbeit neuartige Ansätze zur Entwicklung elektrochemischer Technologien zur  $\text{Li}^+$ -Rückgewinnung.

## ACKNOWLEDGMENTS

*First and foremost, I thank my supervisor, Prof. Dr. Volker Presser, for welcoming me into his research group and for his continuous support throughout my Ph.D. journey, guiding both my academic growth and personal strength. During my time abroad, he was not only a mentor but also a “Doktorvater” in the truest sense of the word. I also acknowledge support from the European Regional Development Fund (EFRE) and the State of Saarland, Germany, for the eLiFlow and eWeWa projects.*

*I am grateful for the resources, facilities, and research environment at the INM – Leibniz Institute for New Materials, which were essential to the successful completion of this work. Special thanks to my colleagues in the INM Research Department, Energy Materials, for their support and stimulating discussions, as well as all colleagues at INM who made my time there both productive and enjoyable. Among those who became more than just colleagues are Varun, Ketaki, and Burcu. You made living in a foreign country easier and warmer for me.*

*I want to thank all my collaborators worldwide for their valuable contributions to my research. In particular, I am grateful to Prof. Dr. Michael Naguib for being a source of inspiration and for his insightful contributions to my work; to Dr. Antje Quade for the constructive feedback and continuous support provided through XPS measurements; to Dr. Mathew Suss for his valuable contributions to our fuel cell studies; and to Dr. Amir Razmjou and his team for their insightful contributions to our DLE study.*

*My deepest gratitude goes to my dearest mum and dad, who have supported my growth in every possible way, who can sense how I am doing from the tone of my voice alone, and who never stop trying to make me happy. Anıl and my twin sister, Ceyda, whose loving presence I feel every day despite the distance between us. To my little Sosa, whose smile always warms my heart. I am deeply thankful to all of you for standing by me, not only throughout my doctoral studies but in every moment of my life. Sizi seviyorum.*

*Finally, Marc, words do not always come easily, as whatever I write feels like it falls short. So, I simply want to say I am thankful to have you in my life. You were once a friend who made my life abroad warmer and more joyful, and you are now my life partner, giving me a sense of home I never expected. You cannot imagine how grateful I am for the sacrifices you have made for me, and for the care and support you have shown throughout my doctoral journey. I hope to spend the rest of our lives side by side, always supporting you just as you have supported me. Your presence has been the greatest comfort and strength, and with you, everything truly feels like home.*

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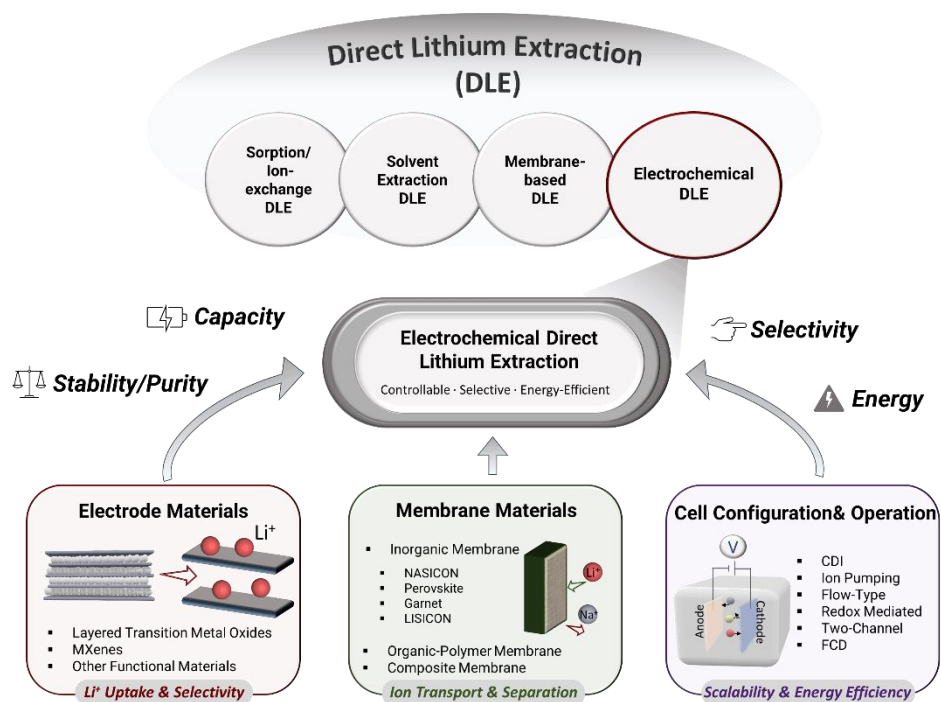
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# MOTIVATION

The demand for lithium is projected to increase roughly 2 to 4 times by 2030, driven by the rise of electric vehicles, grid-scale battery storage, and mobile devices.[1, 2] Currently, traditional evaporation ponds used for lithium extraction consume more than 100 m<sup>3</sup> of water per tonne of lithium carbonate equivalent (LCE) in Chile, and this creates a threat to underground freshwater resources due to salinization.[3] These processes often harm ecosystems and communities, highlighting the need for sustainable alternatives. Electrochemical ion separation technologies such as electrodialysis, electrodeionization, and capacitive deionization offer an alternative, providing promising selectivity values compared with traditional methods while consuming less energy, thus supporting sustainable development in the industry.[4-7] Specific energy consumption and the purity of recovered lithium are key indicators of process efficiency. Due to the similar chemical properties between Li<sup>+</sup> and Na<sup>+</sup>, achieving high selectivity in Li<sup>+</sup> extraction remains a significant challenge.

Therefore, the development of advanced electrode and membrane materials plays a critical role in improving parameters such as selectivity, purity, and energy efficiency because they influence ion selectivity, transport efficiency, and overall energy consumption. Over the decades, advancements in materials science have introduced new materials that shift the charge storage mechanism from electrosorption to Faradaic reactions, alternating carbon, the traditionally favored material in capacitive systems.[6, 8] The key difference between Faradaic and non-Faradaic processes is the presence or absence of charge transfer at the fluid-solid interface.[7] Li<sup>+</sup> selective materials, such as MnO<sub>2</sub>, Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, H<sub>2</sub>TiO<sub>3</sub>, and H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, have been studied extensively for lithium recovery due to their good selectivity and recovery yields.[9] Nevertheless, achieving the highest possible lithium purity remains the most desirable outcome for electrochemical extraction processes, as it directly influences the efficiency, performance, and commercial viability of the extracted product. This thesis investigates recent advances in electrode and membrane materials to improve the efficiency and selectivity of Li<sup>+</sup> extraction. Furthermore, it provides a critical evaluation of emerging technologies developed to enhance the overall performance of Li<sup>+</sup> recovery processes (**Figure 1**).



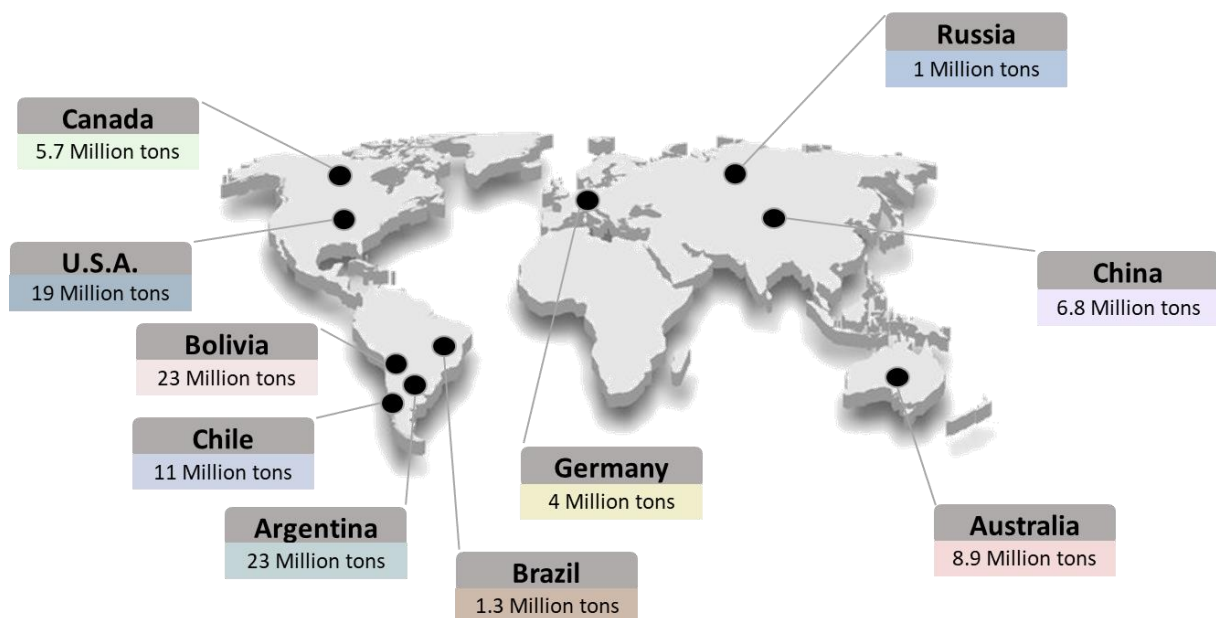
**Figure 1:** Motivation of this thesis.



# THEORETICAL BACKGROUND

## 1. Importance of Lithium Extraction

Lithium extraction is central to the global transition to clean energy and electrification, making it strategically and economically significant today.[10] As a crucial component of rechargeable lithium-ion batteries, lithium powers electric vehicles, enables grid-scale energy storage, and supports portable electronics, contributing to a sixfold increase in lithium production.[11] Additionally, it plays a critical role in reducing global carbon emissions. Ongoing exploration has led to a notable increase in the worldwide estimated and indicated lithium resources, currently totaling approximately 115 million tons.[12] These resources are primarily distributed across the lithium triangle (Argentina, Chile, and Bolivia), Australia, and the United States of America. At the same time, China handles more than half of global refining capacity (**Figure 2**).[12, 13] The global lithium mining market was estimated to be worth approximately €3.6 billion in 2025 and is expected to grow significantly, reaching around €7.3 billion by 2035.[2]



**Figure 2:** Distribution of world lithium resources.[12]

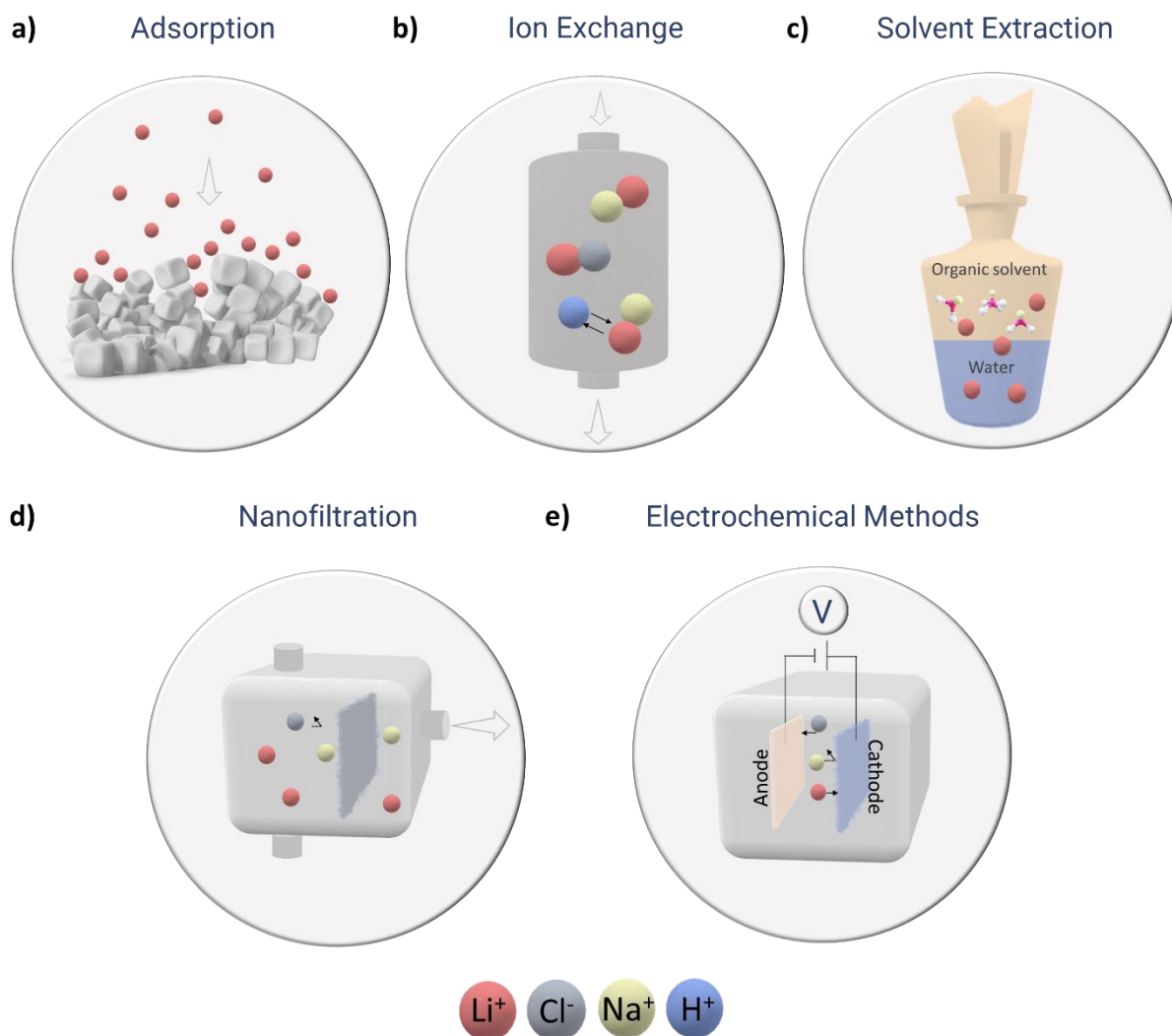
Conventionally, lithium has been extracted from lithium-bearing minerals like spodumene, lepidolite, and petalite, which are found in pegmatite formations.[14] The extraction process is energy-intensive and requires heavy equipment for digging pits, crushing rocks, and using concentrated chemicals.[14] Lithium extraction is typically carried out through two main methods: hard-rock mining and brine evaporation.[15] Hard rock mining primarily involves extracting spodumene through either the open-pit or underground methods.[16, 17] As a second method, lithium-rich brine is extracted from underground salars, which have been predominant in South America, such as Salar de Atacama, and then slowly evaporated in shallow solar ponds over 1-2 years to concentrate the lithium salts.[18] Hard-rock mining offers high lithium recovery and flexibility in producing battery-grade lithium, particularly lithium hydroxide (LiOH), but at the cost of high energy consumption, high emissions, and significant land and waste impacts.[19] Evaporation ponds have low energy input but are highly water-intensive and inefficient, resulting in limited recovery rates and significant environmental impacts in arid regions.[10] These methods are energy-intensive and require a significant amount of water, leading to potential environmental and social concerns; hence, there is a real need for more efficient, sustainable, and faster approaches to lithium recovery from brines. Technoeconomic analyses show high profitability for modern lithium extraction methods under certain conditions. For example, in favorable integrated cases, such as direct lithium extraction (DLE) from geothermal brine, lithium extraction can be achieved in less than a year with internal rates of return over 700%, and with a lower environmental impact than traditional mining and evaporation methods.[20] However, such outcomes are highly sensitive to fundamental assumptions, including lithium market prices, capital and operating costs, plant scale, brine composition, and the degree of integration with existing geothermal infrastructure. DLE may also reduce water use, land requirements, and carbon emissions by up to 95% compared to conventional techniques, making them appealing for sustainable development.[10]

## 2. Direct Lithium Extraction (DLE)

DLE explores new methods designed to reduce possible negative environmental impacts of traditional lithium mining by minimizing land and water disruption. Unlike open-pit mining or large-scale brine evaporation, which can damage ecosystems, deplete underground water resources, and threaten sensitive wildlife habitats, DLE allows the majority of the water and brine to be reinjected into the source without evaporation.[21, 22]

DLE targets selective extraction of lithium from brines using advanced methods like adsorption, ion exchange, or solvent-based systems (**Figure 3**).[7] These processes greatly reduce water and energy use and minimize land impact.[23] For example, DLE can reduce water consumption to less than 2 m<sup>3</sup> per ton of LCE, compared to over 100 m<sup>3</sup> per ton in evaporation ponds in places like Chile.[22, 24] By enabling faster production cycles and higher lithium recovery rates, DLE technologies are set to meet the increasing global demand for lithium, which is essential for batteries in electric vehicles and renewable energy storage, all while supporting sustainability goals.[25] In DLE processes, lithium is either captured by or transported through highly selective materials, including functionalized adsorbents, lithium-ion sieves, specialized ion-exchange resins, or lithium-selective membranes and electrodes.[14] Subsequently, Li<sup>+</sup> is released into a concentrated eluate or electrolyte, which enables most of the remaining brine to be processed and reinjected.[26]

DLE refers to any selective, non-evaporative process for recovering Li<sup>+</sup> directly from brines or dilute aqueous sources, including adsorption (**Figure 3a**), ion exchange (**Figure 3b**), solvent extraction (**Figure 3c**), nanofiltration (**Figure 3d**), and electrochemical methods (**Figure 3e**). In this thesis, we focused on electrochemical DLE methods, including the development of intercalation electrodes, membrane materials, and different electrochemical cell systems, because of their potential for high selectivity, energy efficiency, and compatibility with low-Li<sup>+</sup> feedstocks relevant to sustainable recovery.



**Figure 3:** DLE technologies. **a)** adsorption, **b)** ion exchange, **c)** solvent extraction, **d)** nanofiltration, **e)** electrochemical methods.[7, 14, 27, 28]

## 2.1. Sorption / Ion-exchange-based DLE

Sorption is the process by which solid materials take up substances, such as ions or molecules, either by attaching to their surfaces or by incorporating them into their structures.[29] Sorption includes both adsorption and ion-exchange processes. In adsorption-based DLE,  $\text{Li}^+$  is adsorbed to surface or near-surface sites by chemical or physical interactions. In contrast, ion-exchange-based DLE involves exchanging  $\text{Li}^+$  in a liquid phase with other positively charged ions, such as  $\text{H}^+$ , on a solid ion exchanger, typically a manganese or titanium-based sorbent.[30] Therefore, the recovery of  $\text{Li}^+$  using ion sieves is a specific type of  $\text{Li}^+$  recovery that relies on adsorption; it is an adsorption process governed by the crystal structure. While all ion sieves function as adsorbents,

not every adsorbent qualifies as an ion sieve.[31] Because sorption is controlled by kinetic and sometimes physical factors, the durations of adsorption and desorption can vary significantly, and thermodynamic equilibrium is often not achieved.[32] These methods provide a sustainable, fast alternative to traditional evaporation ponds, as well as a safer and less chemical-intensive option than solvent extraction.

Sorbents based on lithium manganese oxides (LMO), lithium titanium oxides (LTO), and aluminum-based layered oxides have been extensively studied.[15] LMOs are known for their high sorption capacity and rapid kinetics, making them a favorable choice in various applications. Lithium titanium oxides, such as  $\text{H}_2\text{TiO}_3$ , a monoclinic crystalline type of LTO, are common ion sieves for  $\text{Li}^+$  extraction via topotactic reactions.[33] Another type of LTO is spinel-structured  $\text{H}_4\text{Ti}_5\text{O}_{12}$ , which shows a similar structure to LMO.[34] Gao et al. reported LTO-based material showing a capacity of 24.4 mg/g after 24 h.[34] Chen et al. used powder hydrogenated titanate (HTO) with a  $\text{Li}^+$  adsorption capacity of 30.0 mg/g.[35] In another work, a  $\lambda$ - $\text{MnO}_2$ -based LMO material showed a capacity of 30.9 mg/g under highly basic conditions.[36] Recently, Zhang et al. reported a  $\text{H}_2\text{TiO}_3$ -based hybrid aerogel with an adsorption capacity of 30.3 mg/g.[37] Average capacity values for the LMO- and LTO-based adsorbents range from 20 mg/g to 50 mg/g for LMO and from 10 mg/g to 40 mg/g for LTO.[38]

Aluminate precipitation is more environmentally friendly and has shown recovery of lithium from brine with high  $\text{Mg}^{2+}/\text{Li}^+$  ratios. In a 2023 study by Jayanthi et al., an extraction efficiency of 86% and a maximum capacity of 37.9 mg/g were achieved in a single-step lithiation.[39] Aluminum-based layered oxides demonstrate a promising selectivity but relatively slow kinetics, whereas manganese-based layered oxides show faster kinetics with moderate selectivity.[7, 40, 41] Zhong et al. achieved an adsorption capacity of 7.3 mg/g and high selectivity with  $\text{Li}^+/\text{Mg}^{2+}$  of 125 in real brine for aluminum-based layered hydroxides through co-precipitation from natural Salt Lake.[42] Another study showed that a Fe-doped aluminum-based layered oxide achieved a capacity of 11.3 mg/g.[43]

In the ion-exchange process, the precursors can be produced via soft chemical and solid-phase synthesis techniques.[38, 44-46] The soft chemical synthesis approach involves dissolving  $\text{Li}^+$  and  $\text{Mn}^{2+}$  ions in aqueous solutions to form a mixture using synthesis methods like sol-gel, solid-phase combustion, molten salt synthesis, and hydrothermal method.[38] In solid-phase combustion, Li and Mn salts are mixed in stoichiometric

proportions, and calcination is performed at controlled temperatures to obtain the final product.[38] Subsequently, the ion-sieve is obtained through an acid treatment that removes nearly all the  $\text{Li}^+$ , while maintaining the unity of the product's spine structure as the process of  $\text{Li}^+$  is replaced by protons.

Certain drawbacks arise for the LMO-type ion-exchange process due to the powdered structure of the adsorbents. Therefore, specialized fabrication techniques are needed to process powder ion-exchange adsorbents. Thus, typical forming methods such as granulation, foaming, and membrane formation are used to produce LMO precursors.[31]

Layered  $\text{Li}_2\text{TiO}_3$  or spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  structures have been explored for LTO-based sorbents.[47] The production of LTOs generally employs a variety of techniques, including solid-state, sol-gel, and hydrothermal methods for preparing precursors, followed by acid treatment to create the ion-sieve material. In the traditional solid-state method,  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$  are combined, ground together, and then calcined at about  $700^\circ\text{C}$  before cooling to ambient temperature. This technique provides a relatively higher capacity than other methods for  $\text{Li}^+$  adsorption and ion selectivity.[48] In comparison to manganese-based sorbents, lithium titanate oxides exhibit less dissolution loss during acid treatment because of their enhanced durability in acidic conditions, making them more stable.[49] However, the speed of  $\text{Li}^+$  adsorption rate for LTOs tends to be slower than that of LMO sorbents.[14, 38] For layered structures, the underlying mechanism is less complex than that of spinel structures.[50] For instance, layered  $\text{H}_2\text{TiO}_3$  displays improved  $\text{Li}^+$  selectivity compared to other cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , attributed to its thin interlayer exchange sites.[48] As a result, the separation factor for  $\text{Li}^+$  relative to other cations exceeds several hundred.[51]

Commercially prevalent aluminum-based layered double hydroxide (Al-LDH) adsorbents represent another alternative for DLE technologies.[40, 52] In layered double hydroxides, the presence of octahedral vacancies particularly facilitates the adsorption of  $\text{Li}^+$ .[53] This specific attraction of  $\text{Li}^+$  in the process arises from its ability to infiltrate the  $\text{Al}(\text{OH})_3$  structure and occupy octahedral vacancies. It offers tunability of parameters such as the distance between layers, the presence of interlayer anions, crystal size, and the dimensions of the particles.[54] AL-LDHs do not require acidic substances or chemical reagents and have a minimal environmental footprint, achieving over 90% extraction

efficiency during commercial operations.[55] However, the kinetics of desorption are often limited by strong electrostatic interactions and barriers to interlayer diffusion.[56]

**Figure 4** represents selected advantages and disadvantages of the sorbent-based materials for adsorption-based DLE.

|               | Capacity      | Mechanism                                                       | Advantages                                                                                                                                              | Disadvantages                                                                                                                                                   |
|---------------|---------------|-----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>LMO</b>    | 20–50 mg Li/g | H <sup>+</sup> /Li <sup>+</sup> intercalation                   | <ul style="list-style-type: none"> <li>Fast kinetics</li> <li>High selectivity</li> <li>High capacity</li> </ul>                                        | <ul style="list-style-type: none"> <li>Mn dissolution</li> <li>Requires acid leaching</li> <li>Corrosion</li> <li>High waste formation</li> </ul>               |
| <b>LTO</b>    | 10–40 mg Li/g | Li <sup>+</sup> insertion/ extraction                           | <ul style="list-style-type: none"> <li>Stable</li> <li>Inexpensive</li> </ul>                                                                           | <ul style="list-style-type: none"> <li>Lower capacity</li> <li>Slower extraction process</li> <li>Solid state diffusion</li> </ul>                              |
| <b>Al-LDH</b> | <15 mg Li/g   | Li <sup>+</sup> /H <sup>+</sup> exchange with interlayer anions | <ul style="list-style-type: none"> <li>Single-step Li<sup>+</sup> extraction</li> <li>Commercial operation</li> <li>Low environmental impact</li> </ul> | <ul style="list-style-type: none"> <li>Require relatively high temperature (&gt;50°C)</li> <li>Interlayer diffusion</li> <li>Electrostatic retention</li> </ul> |

**Figure 4:** Selected advantages and disadvantages of common sorbent-based materials.[7, 27, 38, 55, 57, 58]

## 2.2. Membrane-Based DLE

Membrane-based DLE has emerged as an innovative alternative to traditional methods like evaporation ponds and chemical precipitation. The increasing demand for lithium in battery production and the need for sustainable, high-purity extraction from low-grade brines have gained interest in membrane technologies. In contrast to conventional techniques, membrane-based DLE enables selective separation of Li<sup>+</sup> under mild conditions.[59] For years, various types of membranes have been explored for lithium recovery through DLE, including ion-exchange membranes, nanofiltration membranes, and solid-state membranes that can effectively conduct Li<sup>+</sup>. [59] Nanofiltration (NF) operates under pressure. It can partially separate monovalent and multivalent ions, where the pore sizes or chemical coatings prefer lithium over larger ions.[28, 60] One limitation is that nanofiltration is effective at distinguishing Li<sup>+</sup> from multivalent cations,

such as  $\text{Mg}^{2+}$ , but is less effective at separating  $\text{Li}^+$  from other monovalent ions like  $\text{Na}^+$ . [61] Electrosorption occurs under an electric field, with cations moving toward the cathode, and anions toward the anode. While a membrane is not strictly required for electrosorption, its presence improves cation uptake efficiency. Membranes play a crucial role in electrodialysis, which can utilize either cation-exchange membranes (CEM) or anion-exchange membranes (AEM). [59]

Membranes can be classified as inorganic membranes and organic membranes. [28] Inorganic membranes such as solid-state ion-conductive membranes (e.g., lithium super ionic conductor (LISICON), sodium super ionic conductors (NASICON),  $\text{Li}^+$  conductive glass-ceramic (LICGC or NASICON-type), lithium titanium oxide, or lithium aluminum germanium phosphate (LAGP) are known for their high conductivity and selectivity, which result from their crystalline structure. [62-65] Their dense and rigid structure is their main disadvantage for operational conditions. [28, 66] Organic membranes are an alternative to inorganic membranes because of their flexibility, being more cost-effective, and easier to process. [7]  $\text{Li}^+$  selectivity can be obtained via mechanisms, including size exclusion, charge or Donnan effects, which will be discussed in detail later, coordination with functional groups, or ion-sieving channels engineered within polymer matrices. [67] Another approach involves inserting inorganic lithium particles into a polymer matrix, forming polymer composite membranes that can enhance  $\text{Li}^+$  selectivity and provide a flexible structure. [66, 68, 69]

### 2.3. Solvent Extraction

Solvent extraction employs an organic solvent that does not mix with water and contains specific extractant molecules to extract  $\text{Li}^+$  selectively from aqueous solutions. [28] This method is advantageous for being continuous, scalable, and compatible with low lithium sources. [70-73] The most extensively studied solvent extraction systems are tri-n-butyl phosphate (TBP) diluted in kerosene or methyl isobutyl ketone combined with ferric chloride ( $\text{FeCl}_3$ ). [74] Here,  $\text{FeCl}_3$  participates in the formation of chloro-complexes that facilitate  $\text{Li}^+$  extraction through coordination equilibria. At the same time, TBP functions as a neutral solvating agent that transfers these Li-Fe-Cl species into the organic phase. [73] Deep eutectic solvents (DES) and ionic liquids are alternatives to organic solvents, exhibiting low vapor pressure as well as thermal and chemical stability. DES are



liquid systems formed by mixing two or more components whose strong intermolecular interactions significantly lower the melting point relative to the individual components. Ionic liquids are salts composed entirely of ions that remain liquid below 100 °C. DES offer selective extraction of metal ions and enable high-purity recovery, while Ionic liquids offer low vapor pressure, good ionic conductivity, and thermal stability. However, regeneration is often required to address viscosity and interaction-related challenges.[75-77]

## 2.4. Electrochemical DLE Systems

Electrochemical systems offer a promising alternative for DLE, achieving high extraction rates while using electricity.[78] These systems utilize electricity as the driving force. When voltage or current is applied through a cell, ions move toward the electrode in the targeted area, or separation occurs via a specially designed membrane.[79, 80] Their notable ability to extract  $\text{Li}^+$  effectively with minimal environmental impact indicates that electrochemical systems are likely more cost-effective, especially for low  $\text{Li}^+$  concentrations, compared to precipitants or solvents.[14] The main drawbacks of electrochemical  $\text{Li}^+$  extraction involve considerable energy requirements, caused by slow  $\text{Li}^+$  intercalation and de-intercalation kinetics, as well as unwanted side reactions and low ionic conductivity.[78] Additionally, the high costs of durable electrode materials and specialized membranes can limit scalability and economic feasibility.[14, 78]

### 2.4.1. Electrodialysis (ED)

This method utilizes ion-exchange membranes (including cation and anion-exchange membranes) positioned between electrodes.[81] When an electric field is applied,  $\text{Li}^+$  moves through selective membranes, separating them from the other ions and concentrating in a recovery solution located in alternating compartments.[82] The efficiency of ED is influenced by factors such as operating voltage, temperature, pH, coexisting ions, and electrolyte concentration.[79, 83] ED is a technique that can be combined with other processes and stands out for its scalability and ease of design, reaching high recovery rates of 75% to 95%.[81, 82] It is effective in complex brines with multiple ions, such as those found in salt lakes; it exhibits low volumetric energy consumption, typically ranging from 0.2 kWh/m<sup>3</sup> to 5 kWh/m<sup>3</sup>, depending on ion

concentration and composition of brines when separating monovalent ions.[78, 84, 85] However, it is prone to membrane fouling, scaling, or degradation, and requires pre-treatment for divalent ions like  $\text{Mg}^{2+}$ . [14]

Combining electrodialysis with other separation methods has also been demonstrated for enhancing  $\text{Li}^+$  extraction.[79] Zhao et al. designed a liquid-membrane ED system that layers liquid-membrane extraction with ED, achieving over 60% current efficiency while efficiently isolating  $\text{Li}^+$  from  $\text{Na}^+$ . [86] In 2020, another group integrated nanofiltration and a bipolar membrane electrodialysis system to generate high-purity lithium hydroxide, achieving more than 92%  $\text{Li}^+$  recovery even from brines with elevated  $\text{Mg}^{2+}/\text{Li}^+$  ratios.[87] Kumar et al. developed a combined process utilizing nanofiltration, membrane distillation, and precipitation, allowing for effective removal of interfering ions and targeted recovery of  $\text{Li}^+$  as  $\text{Li}_2\text{CO}_3$ . [88] In summary, these hybrid systems demonstrate the improved efficiency and selectivity that can be achieved through multi-step membrane-based  $\text{Li}^+$  extraction.[79]

#### 2.4.2. Electrochemical Ion Pumping Systems (EIPS)

Electrochemical ion-pumping systems employ battery-like electrodes, such as LMO or lithium iron phosphate ( $\text{LiFePO}_4$ , LFP), which selectively intercalate  $\text{Li}^+$  through redox reactions.[89]  $\text{Li}^+$  is removed from the feed solution and then released into a recovery solution by reversing the applied voltage or alternating the solutions.[90] EIPS offers high  $\text{Li}^+$  selectivity, achieving purities as high as 99.9% with low energy usage.[89] Selectivity mainly depends on how well the cation radius matches the material structure and on the hydration energy of cations. For instance, LMO is less affected by competing cations, while  $\text{Na}^+$  has a stronger influence on EIPS.[89] The performance of electroactive materials in  $\text{Li}^+$  extraction is mainly determined by their intrinsic properties, which establish the upper limit of capacity achievable in each adsorption cycle.[91] Materials that facilitate reversible electrochemical reactions tend to exhibit enhanced cycling stability, whereas lattice distortion significantly contributes to capacity fade.[89] Overall energy consumption and cost are primarily influenced by the production expenses of electrode materials and the electrical energy needed for electrochemical  $\text{Li}^+$  extraction. However, transitioning the process from laboratory settings to large-scale industrial applications presents a considerable obstacle.[89]

### 2.4.3. Capacitive Deionization (CDI)

Capacitive deionization (CDI) utilizes carbon electrodes that electrosorb ions. This creates an electrical double layer (EDL), an essential interfacial structure that is formed when a charged surface encounters an electrolyte in classic CDI.[92, 93] When a voltage is applied (typically  $<1.23$  V), ions are adsorbed onto the electrodes. Reversing the voltage or short-circuiting the system leads to the desorption of these ions into a recovery solution.[94] Hybrid capacitive deionization (HCDI) uses ion-exchange membranes to enhance selectivity during the ion removal process.[95] Optimized cell designs, such as flow electrode CDI, HCDI, asymmetric cells, etc., can be used with advanced materials for higher  $\text{Li}^+$  selectivity, reduced energy consumption, and the ability to handle wide ranges of feed concentrations.[96] For instance, Xie et al. reported a flow-through HCDI cell, storing  $\text{Li}^+$  in  $\lambda\text{-MnO}_2$  with a  $\text{Li}^+$  uptake of 18.1 mg/g.[97] Yoon et al. proposed  $\text{Li}$ -selective hybrid CDI with LMO and Ag-coated active carbon electrodes.[98] Ag-coating increased  $\text{Li}^+$  uptake by approximately one-third compared to the pristine active carbon counter electrode. He et al. studied metal organic framework (MOF) in 2025, reporting a  $\text{Li}^+$  adsorption capacity of 59 mg/g in 10 mM LiCl with good capacity retention over 50 cycles.[99] Such advancements in electrode and cell system design highlight CDI technologies as a promising technique for  $\text{Li}^+$  recovery, offering advantages over traditional evaporation-based brine mining.[81] Nonetheless, this method has several drawbacks.  $\text{Li}^+$  adsorption generally decreases in environments with high salinity, and the electrodes may suffer from fouling or deterioration over time.[100] Also, the uptake capacity is rather limited, typically falling between 10 mg and 37 mg of  $\text{Li}^+$  per gram of electrode material, and the effectiveness greatly depends on the optimization of the electrode substances.[6]

### 3. Fundamentals of Electrochemical Lithium-Ion Extraction

#### 3.1. Electrochemical Ion Separation Mechanisms

The fundamental component of most electrochemical Li<sup>+</sup> extraction systems involves Li<sup>+</sup> selective electrodes that reversibly take in and release Li<sup>+</sup> through regulated reactions.[101] Upon application of voltage, these electrodes incorporate Li<sup>+</sup> from the feed solution towards the working electrode. When the voltage is reversed, the electrode polarity changes, and the stored Li<sup>+</sup> is released back to the recovery stream.[102] Recent developments in the field mainly focus on addressing critical issues related to selectivity and efficiency.[103] A notable challenge is the existence of competing cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, which are present in natural water sources.[104] To enhance selectivity, several strategies can be implemented, including tuning the electrode surfaces, the use of pulsed electrochemical techniques to modify surface adsorption sites, and the incorporation of advanced membrane technologies.[105, 106] By improving electrode designs, membrane configurations, and operational strategies, the field progresses toward scalable solutions that will be crucial for meeting future requirements for energy storage.[107] Li<sup>+</sup> removal processes differ depending on the underlying mechanism. Although electrosorption of Li<sup>+</sup> inherently involves charge storage (or charge recovery), it does not necessarily operate as a permselective process (**Figure 5**). The following sections will discuss various mechanisms based on the electrode model.

##### 3.1.1. Redox-active Mechanism

In redox reactions, inorganic materials act as redox centers by changing the oxidation state of transition metal ions reversibly, enabling the insertion and removal of Li<sup>+</sup> ions coupled with electron transfer.[108] This process converts electrical energy into chemical energy and vice versa. Materials commonly utilized for Li<sup>+</sup> extraction include spinel LMO, LFP, LiCoO<sub>2</sub> (LCO), and λ-MnO<sub>2</sub>. [101] All of these materials have distinct crystal structures with specific locations intended for the intercalation of Li<sup>+</sup> to the host structure via redox reactions. Simplified half-reaction is shown below;

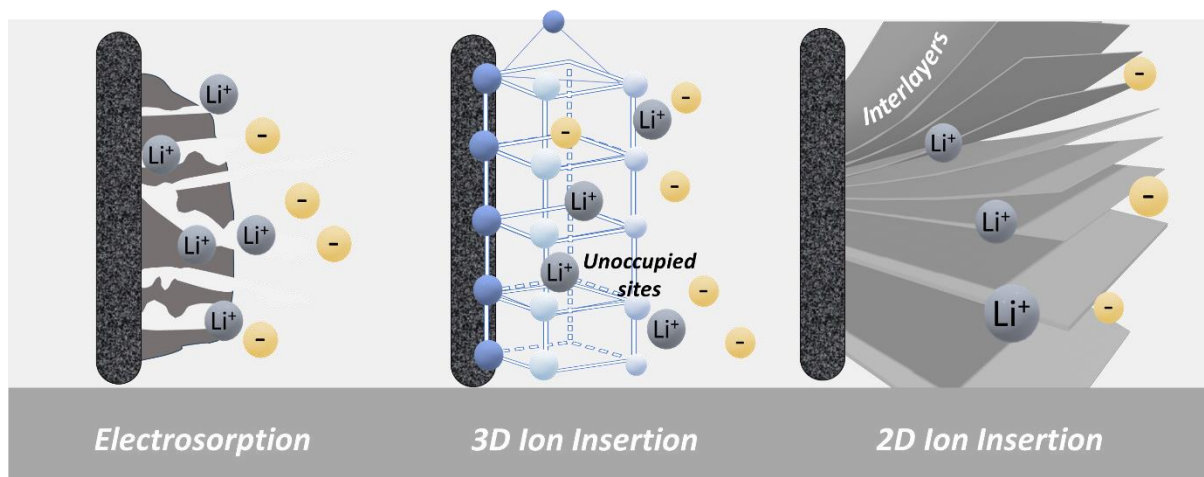


Some materials, such as LFP and LCO, which were originally developed as lithium-ion battery cathodes, have been repurposed for  $\text{Li}^+$  extraction due to their highly selective  $\text{Li}^+$  intercalation thermodynamics, compatibility with aqueous media, and well-defined diffusion pathways. During conventional battery charging,  $\text{Li}^+$  desolvates at the electrode-electrolyte interface before intercalating into the electrode material. In redox mediators, the charge-transfer process shifts from a heterogeneous process to a fast homogeneous chemical reaction.[109]

Redox-active couples have also been explored in electrolyte solutions, which are known as electrolyte redox reactions. A redox-coupled electrolyte can perform as the counter electrode, easing the redox involved in  $\text{Li}^+$  uptake.[110] Kim et al. proposed a redox couple ( $\text{I}^-/\text{I}^{3-}$ ) to achieve charge-transfer balance in an electrochemical cell for  $\text{Li}^+$  capture from seawater.[105] In another study, the redox couple  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  does not play a direct role in the capture or discharge of  $\text{Li}^+$ . Still, it serves as a donor or acceptor at the electrolyte-electrode interface by facilitating rapid electron transfer.[111]

### 3.1.2. Mechanism of Intercalation, De-intercalation, and Adsorption

$\text{Li}^+$  is mainly captured and released through a coupled intercalation and adsorption process in the current technical implementation. This process combines surface adsorption at the electrode-electrolyte interface with bulk ion insertion, or intercalation, within the crystal structure of the electrode (**Figure 5**).[101] When a negative potential is applied,  $\text{Li}^+$  migrates toward the electrode due to electrostatic attraction. At the interface,  $\text{Li}^+$  can adsorb onto surface-active sites via electrostatic or chemical interactions, or with transition-metal centers.[50, 112]



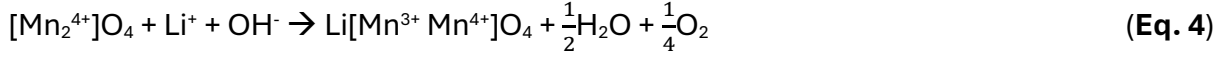
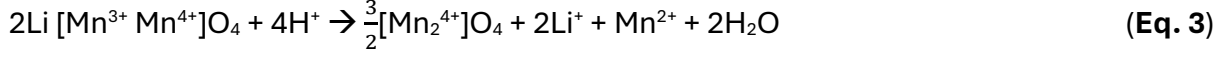
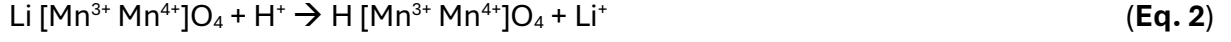
**Figure 5:**  $\text{Li}^+$  electrosorption, ion insertion into the crystal lattice, and ion intercalation between the layers, respectively.[113]

Ion insertion and intercalation are related electrochemical processes that differ in mechanism, structure impact, and reversibility.[113] Ion insertion refers to the general process of ions entering a host material's structure, which can involve structural distortion, lattice expansion, or even phase transformations in some cases, as seen in conversion reactions.[114, 115] Intercalation is a specific type of insertion in which guest ions (e.g.,  $\text{Li}^+$  or  $\text{Na}^+$ ) reversibly occupy preexisting sites in a host lattice, preserving the structural framework while causing minimal structural disruption and no new phase formation.[116, 117]

During intercalation/de-intercalation,  $\text{Li}^+$  can penetrate the crystal lattice or occupy the spaces between layers of the electrode material.[118] This process involves the insertion of  $\text{Li}^+$  into designated crystallographic positions, such as octahedral or tetrahedral voids found in spinel oxides, or interlayer spaces in layered oxides.[101] The intercalation occurs in a manner coupled with redox reactions, where electrons transfer between the external circuit and the redox-active metal centers within the host material.[119] During reverse polarization,  $\text{Li}^+$  ions are de-intercalated, meaning that they return to the electrolyte. This process reverses the redox reaction, permitting  $\text{Li}^+$  to move out of the lattice and detach from the surface back into the solution.[118-120]

Several types of LMO are effectively derived from precursors with high  $\text{Li}^+$  adsorption performance. These include spinel like  $\lambda\text{-MnO}_2$ , birnessite type  $\text{MnO}_2$  ( $\text{MnO}_2 \cdot 0.3\text{H}_2\text{O}$ , and  $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ ), which are obtained from  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  ( $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ), and  $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$  ( $\text{Li}_2\text{Mn}_2\text{O}_5$ ), respectively.[31] There is a two-stage process to synthesize

manganese-based sorbents, including the preparation of a precursor via heat treatment and the removal of  $\text{Li}^+$  from the spinel structure via acid treatment.[7] The reaction can be shown as follows;

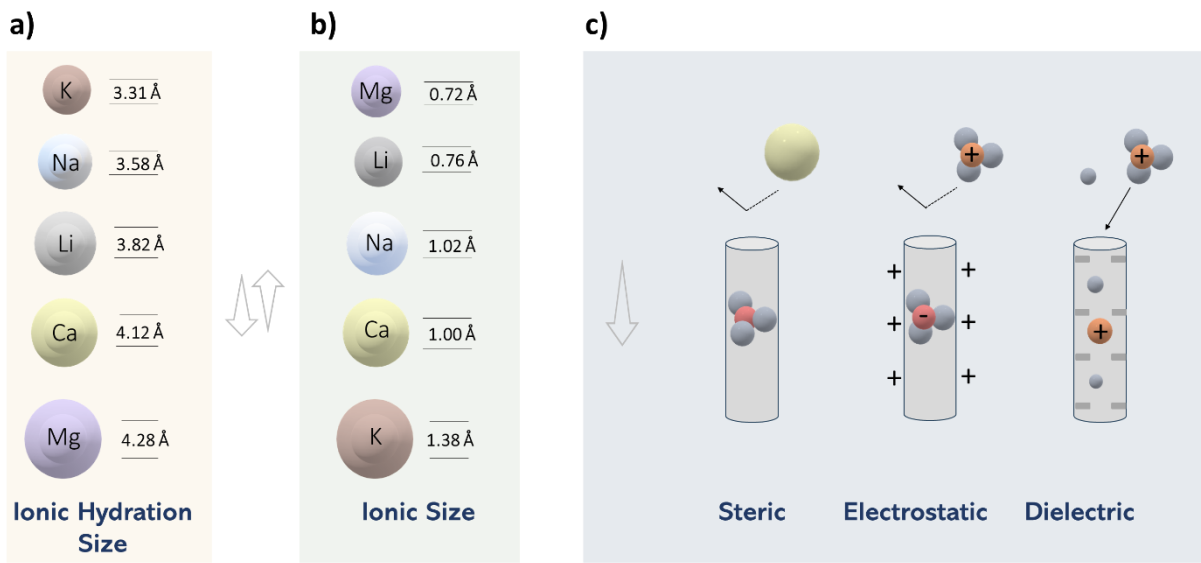


Adsorption influences kinetics at the interface while intercalation determines the thermodynamic preferences and overall capacity, as only ions that match the lattice structure can penetrate. In many cases, the overall rate is limited by solid-state diffusion or desorption kinetics when  $\text{Li}^+$  binds too firmly within the lattice or interlayer region.[119, 121] Consequently, to achieve high-rate capability, it is crucial to develop an active material structure that promotes fast ion transport and structural changes.[122]

### 3.1.3. Membrane Transport

Membrane transport is enabled by mechanisms that allow ions to move across selective barriers, driven by a variety of forces.[123] This selective permeability is influenced by several factors, including the size of the molecules, interactions based on electric charge, chemical affinities, and structural features such as the spacing between layers in the membrane.[28] For example, the majority of commercial nanofiltration membranes are constructed from polyamide and carry a negative charge at neutral pH. However, some membranes are positively charged, which enhances the separation of  $\text{Li}^+/\text{Mg}^{2+}$  or  $\text{Li}^+/\text{Ca}^{2+}$ , allowing them to repel divalent ions more effectively than  $\text{Li}^+$ . [124]  $\text{Li}^+$  has the highest hydration energy among alkali cations because of its small ionic radius and elevated charge density. It creates a highly stable hydration shell that is challenging to disrupt. As a result,  $\text{Li}^+$  is less mobile and more difficult to exchange or move across membranes or sorbents in comparison to other monovalent ions such as  $\text{Na}^+$  and  $\text{K}^+$ . [59] Understanding the sieving-size effect in membranes is important to increase  $\text{Li}^+$  selectivity.[59] The ionic hydration size follows the order:  $\text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$  (**Figure 6a-b**). This order differs from bare ionic size as follows:  $\text{Mg}^{2+} < \text{Li}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{K}^+$ . [125] This effect helps us understand ion dissociation through

steric hindrance (**Figure 6c**). Donnan exclusion refers to the electrostatic repulsion of ions of the same charge (co-ions) from a charged membrane or surface, which hinders their entry into the charged area (**Figure 6c**).<sup>[126]</sup> When ions lose their hydration shell and pass through the pore, the dielectric properties of the pore change the permeation energy barrier, allowing membranes to differentiate between similar monovalent ions (**Figure 6c**). After entering the pore, the transport of solutes is additionally hindered by surface friction and viscous drag, which result from the chemical attraction of the pore wall through van der Waals forces and electrostatic interactions.<sup>[127]</sup>



**Figure 6:** Cation size effect of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>. **a)** Ion Hydration Size, **b)** Ionic Bare size, **c)** Mechanism effect on the energy barrier for solute transportation.<sup>[28, 59, 128]</sup>

Ion transport is regulated by three main processes: migration, diffusion, and convective transport (also called convective flow). Migration is influenced by electric force and concentration, causing ions to migrate toward the membrane as described by the Nernst-Planck equation (**Eq. 5**). This process is called electrodifusion.<sup>[129]</sup>

$$J = D\Delta c + cv + \frac{Dze}{K_B T} cE \quad (\text{Eq. 5})$$

where  $J$  is the flux,  $\Delta c$  is the concentration gradient,  $v$  is the flow velocity,  $E$  is the electric field,  $D$  is the diffusivity,  $e$  is the charge of elements,  $T$  is the temperature,  $K_B$  is the Boltzmann constant, and  $z$  is the valence of ionic species.



Diffusion occurs due to concentration gradients, moving from areas of high concentration to those with low concentration, following Fick's law. Convective transport, or convective flow, involves the bulk movement of fluids driven by osmotic, hydraulic, or electroosmotic forces.[130] It plays a significant role in pressure-driven membrane processes and in electrochemical setups where electroosmotic drag may occur. In some systems, such as layered oxides, robust electrostatic interactions between  $\text{Li}^+$  and the surfaces within the layers can impede desorption, leading to kinetic limitations.[131] Interlayer diffusion resistance occurs due to closely packed or collapsed spaces. That complicates ion movement and slows down transport rates.[132] Concentration polarization occurs when ions accumulate at membrane surfaces, which can limit flux unless mitigated by improved mixing or the application of pulsed electric fields.[133, 134]

### **3.2. Key Performance Metrics**

Lithium extraction from sources including brines, hard-rock minerals such as spodumene, clay deposits, and geothermal fluids plays a key role in scaling the global battery supply chain. Given that lithium is not only chemically complex to isolate but also unevenly distributed in nature, the assessment and optimization of extraction processes require a comprehensive set of evaluation parameters.[22]

Evaluating these metrics allows operators to estimate resource quality, project feasibility, energy needs, water and environmental impacts, and the long-term sustainability of extraction projects.[2, 10] The following section outlines the main categories of these metrics, explains their components, and discusses their importance in lithium extraction.

#### **3.2.1. Lithium Concentration**

Lithium is a relatively rare element in Earth's crust, typically present at concentrations of tens of parts per million.[2] However, it becomes significantly enriched in specific pegmatitic hard-rock deposits and in closed-basin saline brines, where prolonged evaporation increases dissolved lithium to economically viable concentrations.[28] In conventional processes, brines are first subjected to solar evaporation for a long period

before lithium extraction. As evaporation continues, various salts such as NaCl, KCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and  $\text{Mg}(\text{OH})_2$  precipitate from the solution.[28] To prevent precipitation of these salts, pre-treatment is needed for higher efficiency. Moreover, CaO can be added to promote  $\text{Mg}(\text{OH})_2$  precipitation and prevent  $\text{Li}^+$  entanglement during the process.[135] Conventional salars contain 200 mg/L to 2000 mg/L of lithium.[12] The most common examples of conventional salars are: Salar de Atacama (Chile), exhibiting concentrations of 1.500 mg/L-2000 mg/L, and Salar de Uyuni (Bolivia), which contains concentrations of 200-600 mg/L.[12]

Oilfield brines, produced as a secondary product during oil and gas production, may have significant lithium concentrations, typically ranging from 10 to 600 mg/L.[136] As an example of the most common oilfield brine, Smackover (USA) has a lithium concentration of ~100 mg/L to 600 mg/L.[28] Similarly, geothermal brines are another type of brine category known to contain lithium at concentrations generally between 100 mg/L and 300 mg/L.[136] One of the most attractive high-quality brines is in the USA (Salton Sea), with a lithium concentration exceeding 100 mg/L and a low  $\text{Mg}^{2+}/\text{Li}^+$  ratio.[28]

Another lithium source is seawater, which contains an estimated  $2.3 \cdot 10^{11}$  tons.[61] There have been several studies exploring seawater for  $\text{Li}^+$  recovery.[62, 137, 138] However, the concentration of lithium in seawater is low, at approximately 0.1 mg/L to 0.2 mg/L, and it remains far from being a viable source for commercial technologies.[138] Extracting large quantities of lithium typically requires significant use of seawater and large-scale equipment.[28] Additionally, the water evaporation process poses a threat to the marine ecosystem.[22]

### 3.2.2. Uptake Capacity

The term uptake capacity refers to the maximum amount of  $\text{Li}^+$  that can be adsorbed or intercalated from a specified feed solution at equilibrium, normalized by the mass of the sorbent, the mass of the electrode, or occasionally the geometric area. It is usually shown as mg/g or mmol/g.[101]

$$\text{uptake capacity} = \frac{V \times c - c_{\text{Initial}}}{m_{\text{electrode}}} \quad (\text{Eq. 6})$$

When the concentration of  $\text{Li}^+$  is low, uptake capacity is restricted by the overall moles of  $\text{Li}^+$  delivered to the electrode during a cycle; as the concentration increases, it gets closer to the theoretical intercalation/adsorption capacity of the material.[139, 140] Recent continuous-flow electrode studies show that, at fixed current, increasing the inlet concentration of  $\text{Li}^+$  increases both extraction and the apparent “per-cycle capacity” until internal diffusion and ohmic limitations become the factors that limit the rate.[141]

Reported uptake capacities depend on current density and timescale, because faster cycling or higher current increases mass-transfer and solid-state diffusion limitations.[139] Uptake capacity can increase with the increasing geometric area ( $\text{mAh}/\text{cm}^2$ ) because this directly links to plant-scale throughput and reactor sizing, unlike gravimetric  $\text{mg}/\text{g}$  values alone.[141] However, very thick or highly loaded electrodes may suffer from severe  $\text{Li}^+$  transport limitations and mechanical instability over cycling, so electrochemical studies typically optimize an intermediate loading that balances high areal capacity with acceptable rate performance and long-term structural stability.[139, 141]

### 3.2.3. Selectivity

Selectivity or separation coefficient refers to the electrode, membrane, or system that adsorbs or transports  $\text{Li}^+$  over competing ions (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ).[101] It is a metric measured using the separation factor ( $\alpha$ ), which represents the ratio of  $\text{Li}^+$  concentration to the concentration of competing ions in the recovered solution, compared to the same ratio in the feed solution.[142]

$$\alpha = \frac{C_{\text{Li},r}/C_{M,r}}{C_{\text{Li},f}/C_{M,f}} \quad (\text{Eq. 7})$$

where  $C_{\text{Li},r}$  and  $C_{M,r}$  are the concentrations of  $\text{Li}^+$  and competing ion in the recovery solution, respectively.  $C_{\text{Li},f}$  and  $C_{M,f}$  are the concentrations of  $\text{Li}^+$  and competing ions in the feed solution, respectively.

In the literature on  $\text{Li}^+$  extraction from multicomponent brines or simulated feed solutions, selectivity factors vary depending on the extraction technique. Adsorbent-based systems, such as manganese oxide ion sieves and layered double hydroxides, typically report  $\text{Li}^+/\text{Na}^+$  separation factors in the range of 30-400, with higher values

achieved under optimized conditions and lower values when divalent cations such as  $Mg^{2+}$  or  $Ca^{2+}$  compete strongly for adsorption sites.[78] For example, Mn-based ion sieves have shown  $Li^+/Na^+$  separation factors up to 400:1, while LDH-type materials often report values below 100:1 in complex feed solutions.[54, 55] In contrast, liquid solvent extraction systems employing extractants exhibit higher selectivity, with reported separation factors frequently reaching the hundreds to thousands, reflecting strong lithium-specific complexation and efficient phase transfer.[57, 81, 143]

Electrochemical extraction systems, including capacitive deionization, electrodialysis, and lithium-intercalation electrodes, generally demonstrate moderate selectivity, with separation factors most commonly in the tens to hundreds, depending on electrode materials, membrane properties, and operating conditions.[59, 101] Overall, while solvent extraction offers higher ion selectivity, adsorbent and electrochemical systems provide competitive separation factors with advantages in process simplicity, environmental compatibility, and electrochemical controllability.

### 3.2.4. Current Efficiency and Energy Consumption

Current efficiency ( $\eta$ ), also known as Faradaic efficiency, measures the fraction of total charge passed through an electrochemical cell that contributes to  $Li^+$  extraction.[142] In most operations, electrochemical  $Li^+$  extraction occurs through charge-discharge cycles, where energy is supplied by the discharge step and consumed by the charging step.

$$\eta = \frac{F \times \Delta C \times V}{1000 \times M_{Li} \times \int_0^t I(t) dt} \times 100\% \quad (\text{Eq. 8})$$

where  $\Delta C$  is the concentration difference of  $Li^+$  in the recovery solution with a unit of mg/L,  $F$  is Faraday's constant (96485 C/mol),  $V$  (L) is the volume of the recovery solution,  $M_{Li}$  is the molar mass of lithium,  $I$  is the current (A), and  $t$  is the time.

Energy consumption is calculated by the total electrical energy required to extract a unit of lithium. It can be reported as kWh/mol  $Li^+$ .

$$\text{Energy consumption} = \frac{E}{V \times \Delta C_{Li} \times M_{Li}} \quad (\text{Eq. 9})$$

where  $E$  is the consumed electrical energy during the charge step,  $V$  is the cell voltage,  $\Delta C_{Li}$  is the concentration change in the recovery solution,[63]  $M_{Li}$  is the molar mass of

lithium. To accurately analyze energy use, the flow rate of the pumps, the duration of operation, and the energy consumed by the pumps should be considered.

### 3.2.5. Purity and Stability

Product purity is an important parameter and practical indicator of the composition and impurity level of the extracted  $\text{Li}^+$ , enabling the production of high-quality lithium salt as a product. In contrast, selectivity and recovery describe the extraction performance in terms of preferential  $\text{Li}^+$  transfer and overall yield, respectively. It can be described as the ratio of the concentration change of  $\text{Li}^+$  in the recovery solution to the concentration change of other competing ions, shown as M in **Equation 10**.

$$\text{Purity} = \frac{\Delta C_{\text{Li}}}{\Delta C_{\text{M}}} \times 100\% \quad (\text{Eq. 10})$$

Stability refers to whether a material or process can operate for a long period of cycles without losing selectivity, capacity, or efficiency.[142] Although initial uptake capacity and selectivity may appear promising, poor stability rapidly degrades these advantages due to material loss, structural damage, and increasing operational costs.[9] Numerous systems depend on optimal feed solutions, and their efficiency drops considerably in actual brines with high concentrations of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$ . [28] The compromise between  $\text{Li}^+$  flux and selectivity, along with issues related to scalable manufacturing and module integration, continues to hinder practical implementations.[28]

## 4. Electrode Materials for Lithium-Ion Extraction

Electrode materials are crucial for the selective capture and release of  $\text{Li}^+$ , and a specialized design can significantly enhance  $\text{Li}^+$  extraction performance.[144] To optimize the selectivity of  $\text{Li}^+$  towards other competing ions, several key factors should be emphasized, including the crystal structure and the ion sieve effect of  $\text{Li}^+$ .[61] For example, a spinel-structured  $\lambda\text{-MnO}_2$  creates three-dimensional tunnels after delithiation, and this structure is uniquely suited for the accommodation of  $\text{Li}^+$ .[82] Similarly, LTO displays a  $\text{Li}^+$  extraction due to its topotactic intercalation-deintercalation.[33] Furthermore, the one-dimensional channel in the olivine structure of LFP can be specifically designed for  $\text{Li}^+$  transport.[7] In the coming sections, a detailed discussion will be provided on the  $\text{Li}^+$  selective electrodes for efficient  $\text{Li}^+$  recovery.

### 4.1. Layered Transition Metal Oxides

$\text{LiMn}_2\text{O}_4$  has been widely explored as a host cathode material because of its structural benefits for  $\text{Li}^+$  extraction.[145] LMO has a spinel structure with the  $Fd3m$  space group, with  $\text{Li}^+$  occupying sites (8a sites of tetrahedra),  $\text{Mn}^{4+}/\text{Mn}^{3+}$  occupying sites (16d sites of octahedra), and oxygen anion occupying sites (32e sites of the face-centered cubes).[38] Early work established the uptake/release reaction of LMO with a rocking-chair battery, demonstrating an absorption capacity of 20.6 mg  $\text{Li}^+$  per 1 g  $\text{MnO}_2$  over 0.8 h.[146] Kim et al. reported a battery-recycling plant using an LMO-based electrode for  $\text{Li}^+$  removal from industrial wastewater. They obtained  $\sim 1900$  mg/L of  $\text{Li}^+$  at the end of the process with a lithium purity of 98.6 mol%.[147] Another work using LMO with activated carbon achieved a  $\text{Li}^+$  recovery capacity of 3.51 mmol/g with energy consumption of 3.8 Wh/mol.[148]

Current density and electric field intensity have also been studied to improve the performance of LMO electrodes. Zhao et al. found that the selectivity of  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  decreases at potentials above 0.8 V.[145]. Another study by Guo et al. proposed a rocking-chair electrode system for  $\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  by regulating the electrochemical driving mode.[149] They compared two operational modes: constant current-constant voltage (CC-CV) and self-driven-constant voltage (SD-CV), and found that CC-CV shows

better performance than SD-CV. They reached a  $\text{Li}^+$  extraction capacity of 34.69 mg/g with a selectivity of 555:1.

Lithium iron phosphate, another  $\text{Li}^+$  selective material, has been explored as an alternative electrode material to  $\text{Li}^+$  extraction because of its structural stability,  $\text{Li}^+$  intercalation barriers, and high  $\text{Li}^+$  affinity.[150, 151] The first LFP-based report in the literature was in 2012 by Pasta et al.[152] Wang et al. investigated a  $\text{LiFePO}_4$  electrode, using a rocking-chair cell configuration. They obtained a lithium extraction capacity of 21 mg/g with an energy consumption of 3.03 Wh/mol per  $\text{Li}^+$ .[153] Recently, Kong et al. used LFP/ $\text{FePO}_4$  electrode materials to intercalate  $\text{Li}^+$  electrochemically and obtained battery-grade  $\text{LiOH}$  as a product.[154]

Li-Al layered double hydroxides (Al-LDH) are extensively studied for  $\text{Li}^+$  recovery because of their minimal environmental impact, direct  $\text{Li}^+$  separation mechanism, which enables single-step  $\text{Li}^+$  extraction, and straightforward synthesis.[54, 155] Koplan et al. were the first to extract  $\text{Li}^+$  from Dead Sea brine through aluminum salt precipitation in 1963.[156] Since the 1970s, the structure of Al-LDHs has been the subject of ongoing research, leading to a more profound understanding of their layered structure and the pathways for lithium access.[54] Lv et al. utilized electrostatic interactions and the infiltration of anions into the interlayer to introduce interlayer anions, replacing chloride ions with phosphate ions to address structural degradation. [157] Jayanti et al. employed Al-LDH for DLE from geothermal brines and minerals. They showed that their material, Cl-LDH-A, can undergo complete delithiation within 2 h.[158]

To facilitate the mass production of Al-LDHs, numerous preparation techniques have been thoroughly explored, such as co-precipitation, impregnation, and ball-milling, which have been confirmed as effective methods for synthesis.[159-162] The production methods are varied and have their own advantages and disadvantages. For instance, coprecipitation offers benefits such as efficient product performance and versatile manufacturing, but it also has drawbacks, including reduced product stability and extensive equipment requirements.[159] The hydrothermal technique features an easy operational process; however, it suffers from issues including low yield and extended preparation times.[163]

Layered double hydroxides can show structural changes by calcination at different temperatures.[164] This thermal process enables the formation of LiCl from Li-layered metal oxides, specifically anions such as  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ . [165] A recent study by Kim et al. examined direct aluminate precipitation from Uyuni brine by combining a calcination process at temperatures ranging between 300-400 °C.[164] The presence of LiCl by calcination converts a layered sorbent into a tailored mixture of LiCl and Al oxide/aluminate phases.

Although sorption methods and mild elution techniques are widely explored in the literature, the electrochemical recovery of  $\text{Li}^+$  with Al-LDHs presents an attractive method, offering a straightforward, eco-friendly, and continuous operational procedure.[41] Abujayyab et al. evaluated  $\text{Li}^+$  recovery from desalination brine, examined LDH structure and performance, and compared LDHs among other layered sorbents.[166] The adsorbent demonstrated a  $\text{Li}^+$  uptake capacity of 49.7 mg/g, along with a desorption efficiency of 92%. Paranthaman et al. developed an electrode by optimizing temperature at 18 °C, 30 °C, 40 °C, and 90 °C, which minimized residual products and enhanced recovery efficiency from geothermal brine with Al-LDHs.[167] Another study on Al-LDHs with potential for electrochemical studies was conducted by Pan et al. in 2025.[168] They introduced an activated carbon-based pretreatment method, demonstrating that a sustainable preconditioning step can be performed without altering the adsorbent, while kinetic behavior remains unchanged.

In a recent study, Kök et al. utilized an Al-LDH electrode for chemical sorption of  $\text{Li}^+$ , followed by electrochemical desorption and regeneration with a mild, pH-neutral step in an electrochemical cell.[58] The average  $\text{Li}^+$  release capacity was found to be 13 mg/g compared to the  $\text{Na}^+$  release capacity of 3.8 mg/g. The reported selectivity factor for  $\text{Li}^+$  over  $\text{Na}^+$  was 2.5 times higher compared to the unmodified electrode across 15 cycles.

The limited number of electrochemical studies on Al-LDH can be linked to several reasons, such as the one-step chemical sorption method being more feasible than repeated faradaic cycling, stability in alkaline conditions, interference from other ions, and challenges in making electrodes.[169]

Beyond widely explored materials such as LMO, LFP, and Al-LDH, other layered oxide materials also play an important role in enhancing cycling stability and ion selectivity in



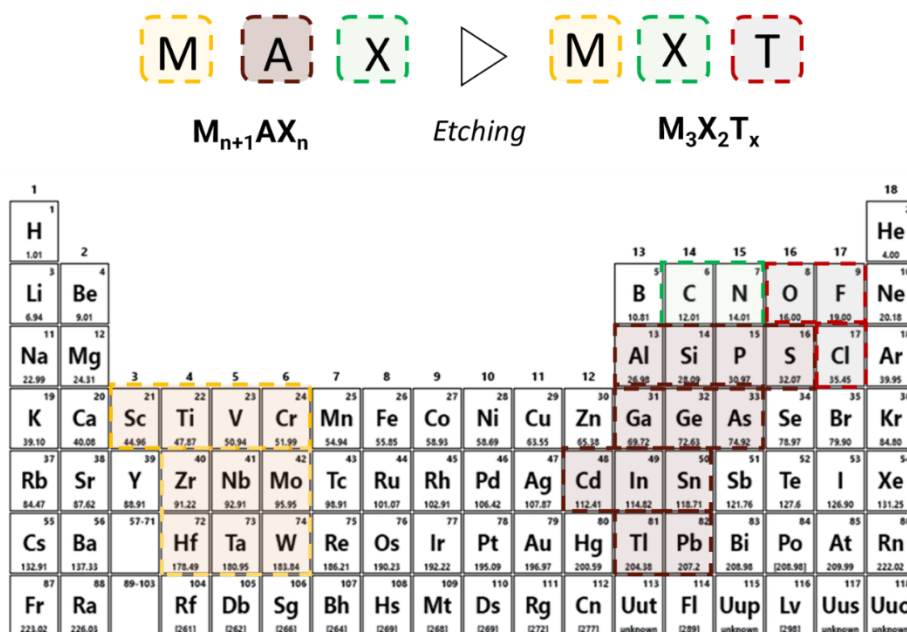
electrochemical  $\text{Li}^+$  separation. Strategies such as structural adjustment (including annealing processes, interlayer spacing in layered materials, and pre-lithiation treatment), surface coating, pore engineering, and metal element doping have been explored over the last decades to improve electrode performance significantly.[142, 170]

Strategies have been developed to reduce the Mn content in these materials to prevent distortion caused by Mn dissolution.[171, 172]  $\text{Li}[\text{NiCoMn}]$  (LNCM) has a close-packed oxygen framework similar to that of the spinel structure.[173] The oxidation states of nickel and cobalt adjust to maintain charge neutrality and enhance capacity when  $\text{Li}^+$  are removed in LNCM materials.[174] Wu et al. developed a powder material containing  $\text{LiNi}_{0.025}\text{Co}_{0.025}\text{Mn}_{1.95}\text{O}_4$ , and showed that Ni and Co doping can prevent  $\text{Mn}^{3+}$  reduction and improve  $\text{Li}^+$  diffusion.[175] Conversely, LNCMs suffer from several intrinsic drawbacks in aqueous electrochemical systems.[176] Due to the limited electrochemical stability window imposed by water splitting, only a single pair of redox peaks can be observed, indicating constrained redox activity. Moreover, LNCMs exhibit negligible electrochemical activity in lithium-free electrolytes, similar to  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$ , highlighting their strong dependence on  $\text{Li}^+$  participation. The presence of water further worsens material degradation by accelerating the reduction of  $\text{Ni}^{3+}$ , inducing lattice oxygen loss and structural transformation from a layered phase to a rock-salt structure, and promoting  $\text{LiOH}$  formation. These coupled effects significantly undermine the structural integrity and long-term electrochemical stability of LNCMs.

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , which has a NASICON structure, exhibits high thermal stability and good selectivity towards  $\text{Li}^+$ . [177] Zhou et al. first reported the use of carbon-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  as a cathode electrode.[177] The optimized electrode exhibited a maximum  $\text{Li}^+$  extraction capacity of 25.8 mg/g and retained 78% of its capacity after 50 cycles. Zhang et al. used Ti-doped  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  for the electrochemical extraction of  $\text{Li}^+$  and obtained an intercalation capacity of 100 mg/L for  $\text{Li}^+$ . [178] Despite their favorable thermal stability and  $\text{Li}^+$  selectivity,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  is hindered by low extraction capacity and poor cycling stability.

## 4.2. MXenes

MXenes are a family of two-dimensional (2D) materials composed of transition metal carbides, nitrides, and carbonitrides.[179] The general formula of MXene is  $M_{n+1}X_nT_x$ , where M signifies an early transition metal such as titanium, vanadium, or niobium, X represents carbon and/or nitrogen, and  $T_x$  represents surface terminations like -O, -OH, or -F, which are incorporated during the selective etching of the original MAX phases (**Figure 7**).[180] MXenes demonstrate promising performance across various fields, such as electrochemical energy storage (including Li-ion, Na-ion, and Zn-ion batteries and supercapacitors), electrocatalysis, water purification and ion separation, sensing technologies, and biomedicine.[180-182]



repeated use in electrochemical processes.[187, 188] In 2022, Li et al. assembled an LTO microsphere derived from MXene.[189] They reported that the mesoporous structure increased the electrode's specific surface area (above 180 m<sup>2</sup>/g) and revealed additional active sites for adsorption, thereby improving the rate of Li<sup>+</sup> adsorption. Faheem et al. recovered Li<sup>+</sup> through electrosorption utilizing pseudocapacitive composite materials made of polystyrenesulfonated MXene and sodium titanate/graphene oxide in a single-cell capacitive deionization system.[190] Recently, K k et. al. reported a two-step electrochemical strategy using alkyl-functionalized Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> electrodes to improve Li<sup>+</sup> selectivity.[184] Interlayer engineering with alkyl chains adjusted the channel size and surface chemistry, thereby enhancing Li<sup>+</sup> insertion and deinsertion behavior relative to pristine MXene. Their compatibility with organic, inorganic, and carbon nanomaterials expands the possibilities for creating multifunctional electrode materials that combine redox activity, capacitive properties, and nanochannel selectivity, highlighting the potential of MXenes for advanced, energy-efficient Li<sup>+</sup> recovery technologies.

### 4.3. Other Functional Materials

Metal-organic frameworks (MOFs) feature designable porous networks with high surface area and tunable ligands for Li<sup>+</sup> sieving.[191] While literature primarily focuses on membrane studies, recent studies have explored the use of MOFs as electrode materials due to their superior properties. Lim et al. synthesized a MOF-Carbon nanotube-based material for flow-electrode capacitive deionization (FCDI).[192] The operation with the MOF electrode reached a deionization performance 2.3-fold that of commercial active carbon for all targeted ions (e.g., lithium, sodium, nickel, and manganese) with a removal of 89.1%. He et al. designed a heterostructured MOF electrode using an in situ growth strategy.[99] The electrode material achieved Li<sup>+</sup> adsorption of 59.1 mg/g and a stability of 95.5% over 50 cycles. Hossain et al. achieved a Li<sup>+</sup> selectivity of 3.1 over Na<sup>+</sup> with a CDI system using Zeolitic imidazolate frameworks (ZIF).[193] Recently, He et al. constructed a hierarchical conductive MOF using Zn with the polyhydroxy ligand 2,3,6,7,10,11-hexahydroxytriphenyl.[194] They obtained a specific capacitance of 198.33 F/g with an adsorption capacity of 50.3 mg/g over 100 cycles in the CDI system. The capacity retention was reported as 87.5%.

Polymer-based electrodes enhance  $\text{Li}^+$  extraction by enabling structural flexibility, selective ion capture via tuning ion and electron transport, improving conductivity, and reducing energy consumption in processes for direct  $\text{Li}^+$  recovery from brines.[195-197] Xu et al. combined polyethylene glycol (PEG), a polymer featuring multiple hydroxyl groups, with polyvinylidene fluoride (PVDF), along with  $\text{LiFePO}_4$  to create a hydrophilic porous  $\text{LiFePO}_4$  electrode.[198] Their system maintained 27 mg/g adsorption capacity over 1000 cycles. Another  $\text{LiFePO}_4$  electrode with PEG modification was explored by Yin et al. in 2024.[199] PEG-modified electrode showed a current efficiency of 38.8% with an intercalation capacity of 28.4%.

Graphene creates conductive composites when combined with nanoparticles, improving charge transfer and packing density while reducing dissolution in electrodes for  $\text{Li}^+$  extraction. Yang et al. obtained LMO/graphene oxide flakes by hydrothermally lithiating  $\text{Mn}_3\text{O}_4$ . [200] The stability and adsorption capacity were improved compared with pure LMO. The reason for the improved stability of the graphene oxide electrode was due to the restriction of the distortion of LMO particles. Zhang et al. proposed a  $\text{Li}^+$  extraction CDI system using a ball milling strategy with LMO and graphene.[201] The 2023 LMO study by Yu et al. on graphene explored simulated seawater and demonstrated a capacity retention of 75.1%, which was higher than that of bare LMO over 50 cycles.[202] The purity of the electrode was 65.5%. Similarly, Hu et al. doped La particles in LMO and coated them with graphene oxide for lithium extraction via CDI.[203] Shang et al. designed a CDI electrode of  $\text{Li}_2\text{VO}_4$  on reduced graphene oxide to extract  $\text{Li}^+$ . [204] They demonstrated a  $\text{Li}^+$  extraction capacity of 39.5 mg/g under the cell voltage of 1.2 V.

Alongside inorganic ion sieves, polymer and graphene-based electrodes have emerged as key complementary materials for electrochemical extraction of  $\text{Li}^+$ . Recent composite designs that combine these materials have improved applicability, rate performance, and operational longevity.[142] With improved mechanistic understanding and demonstrations of continuous, low-energy electrochemical systems, functional materials are evolving from experimental concepts into technologically advanced components, underscoring their potential for large-scale, sustainable  $\text{Li}^+$  recovery.

## 5. Membrane Materials for Lithium-Ion Extraction

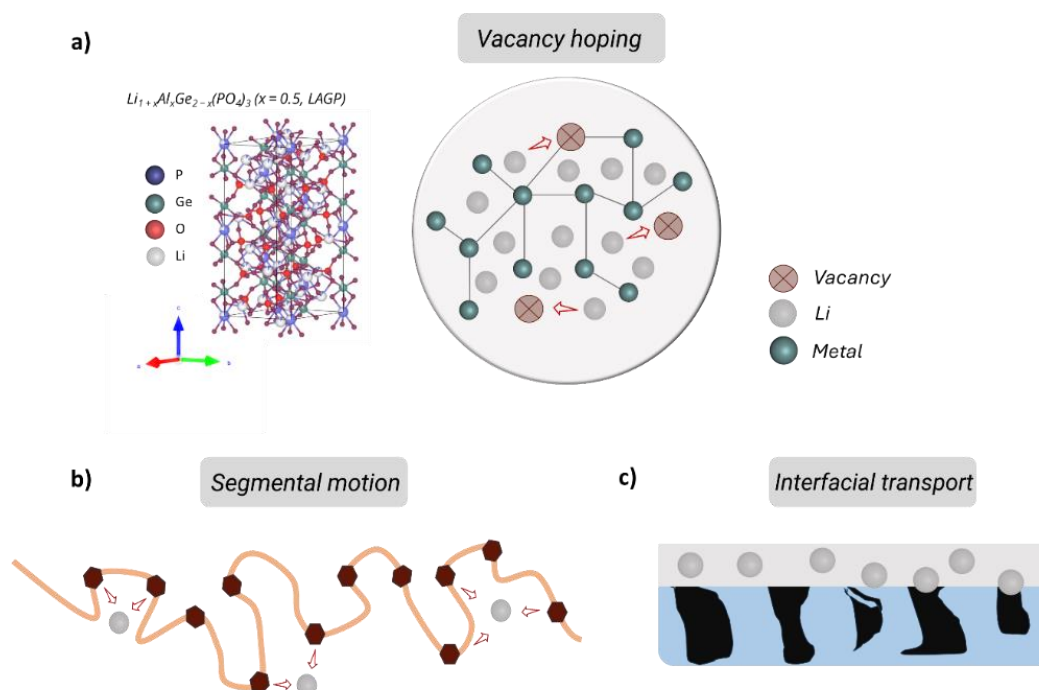
Membrane materials play a central role in determining the performance of  $\text{Li}^+$  extraction systems. An ideal membrane should exhibit high  $\text{Li}^+$  selectivity over competing ions, chemical stability, fast ion transport, and mechanical robustness.[59] Several types of membrane materials have been investigated to meet these requirements, including polymer, inorganic, and composite membranes.

Inorganic membranes, such as ceramics, oxides, or  $\text{Li}^+$  conducting solid electrolytes, offer superior chemical and thermal stability.[61] Materials like lithium lanthanum titanate (LLTO) and garnet-type oxides exhibit intrinsic  $\text{Li}^+$  conductivity, enabling highly selective  $\text{Li}^+$  transport.[62, 90] Despite their high selectivity, inorganic membranes are typically expensive, brittle, and difficult to scale up, limiting their large-scale industrial application.[28] Vacancy-mediated hopping is a dominant ion transport mechanism in inorganic and composite membranes, where  $\text{Li}^+$  migrates through a crystalline lattice by hopping between Li sites via pre-existing vacancies (**Figure 8a**).[205] Due to its small ionic radius and low migration barrier,  $\text{Li}^+$  exhibits a lower activation energy for vacancy hopping (depending on material, ranging from 0.25 eV to 1.0 eV) compared with competing monovalent and multivalent cations.[61, 206-208]

Polymer membranes have been extensively researched due to their flexibility, low cost, and ease of manufacturing.[61, 137] Functional polymers with ion-selective groups, such as crown ethers, sulfonic acids, or amide groups, can selectively interact with  $\text{Li}^+$  through size exclusion and coordination.[38, 60, 106] However, polymer membranes often have limited selectivity in high-salinity brines and may swell or degrade under harsh chemical conditions.[7, 13] Segmental motion occurs in transporting  $\text{Li}^+$  in polymer membranes (**Figure 8b**).[209]  $\text{Li}^+$  moves by binding to functional groups, such as ether oxygens or sulfonate groups, along flexible polymer chains. The efficiency of this segmental motion depends on how flexible the polymer chains are and the level of solvation.[209] Greater segmental mobility improves  $\text{Li}^+$  movement but usually reduces ion selectivity compared to transport in solid crystalline forms.[209]

To address challenges such as the low selectivity and brittleness of inorganic materials, composite membranes combining polymers with inorganic fillers or functional

nanomaterials have attracted increasing attention. By combining the processability of polymers with the selectivity and stability of inorganic materials, composite membranes can improve  $\text{Li}^+$  permeability and ion selectivity.[128]  $\text{Li}^+$  transportation takes place via an interfacial transport mechanism in the polymer-composite membranes (**Figure 8c**). The interface between the disrupted polymer packing and the distorted inorganic lattice creates a space-charge region rich in mobile  $\text{Li}^+$  ions and vacancies.[210] This environment facilitates rapid  $\text{Li}^+$  exchange between the coordination sites of the polymer and the lattice sites of the inorganic material.[211, 212] Despite their advantages, challenges remain. Issues such as membrane fouling, limited long-term stability, and trade-offs between permeability and selectivity continue to hinder large-scale applications.[28] Therefore, future research aims to develop membranes that allow for faster  $\text{Li}^+$  transport, exhibit durability in harsh brine conditions, and have scalable manufacturing processes.



**Figure 8:** Transport mechanisms of different types of membranes; **a)** Vacancy hopping. **b)** Segmental motion. **c)** Interfacial transport.

## 5.1. Inorganic Membrane Materials

Inorganic membrane-based materials have been extensively investigated for  $\text{Li}^+$  extraction owing to their intrinsic chemical robustness, thermal stability, and resistance to oxidative or highly saline environments, which are critical for extracting  $\text{Li}^+$  from complex brines.[213] These membranes show well-defined ion transport mechanisms such as lattice diffusion in  $\text{Li}^+$  conductive ceramics, sub-nanometer channel sieving, and electrostatic exclusion to preferentially transport  $\text{Li}^+$  over competing cations.[62] Crystalline inorganic membranes, including garnet-type oxides, NASICON/LISICON structures, and layered metal oxides, offer precise transport pathways with high conductivity exceeding  $1 \cdot 10^{-4} \text{ s/cm}$ . [214, 215]

### 5.1.1. NASICON-Type

NASICON, the sodium superionic conductor, refers to a family of polyanionic solid electrolytes with a three-dimensional framework that enables fast alkali ion transport and high chemical and electrochemical stability.[215] It was discovered in the early 70s as a rapid  $\text{Na}^+$  conductor. NASICON materials that conduct  $\text{Li}^+$  typically have the general composition  $\text{LiM}_2(\text{PO}_4)_3$ , where M can be Zr, Ti, Ge, Hf, Sn, or related metal cations. In this family,  $\text{LiTi}_2(\text{PO}_4)_3$  (LTP) and  $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  (LAGP) have been investigated most extensively because they combine high chemical stability with relatively low material cost.[216]

Wang et al. developed a  $\text{Li}^+$  extraction redox flow battery (LE-RFB) for continuous lithium recovery, reporting an extraction rate of  $0.04 \text{ mg/cm}^2/\text{h}$  and an energy consumption of  $2.5 \text{ Wh/g}$  for the system.[62] Kök et al. propose a fuel cell system that continuously extracts  $\text{Li}^+$  from seawater and real mine water while simultaneously generating electrical energy.[63] The system uses a ceramic-based solid electrolyte,  $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  ( $x = 0.5$ , LAGP) ceramic membrane as a  $\text{Li}^+$  selective solid electrolyte and advanced electrocatalyst electrodes, achieving a twofold enhancement in  $\text{Li}^+/\text{Na}^+$  selectivity compared with conventional approaches.

### 5.1.2. Perovskite-Type

$\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$  (LLTO,  $0 < x < 0.50$ ) is originally derived from a ferroelectric compound.  $\text{La}^{3+}$  and vacancies can be found at the A sites of the perovskite  $\text{ABX}_3$  structure, while  $\text{Ti}^{4+}$  is located at the B sites.[217] Li et al. investigated glass-type  $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$  (LLTO) membranes for  $\text{Li}^+$  recovery from seawater and demonstrated that lithium concentration reached approximately 9000 ppm after five treatment stages.[90] Golmohammadi et al. modified an LLTO membrane to enhance diffusion pathways within its structure.[218] The findings validated the influence of pH and temperature on the increase in LLTO pore size as well as the enhancement of  $\text{Li}^+$  movement across the membrane.

### 5.1.3. Garnet-Type

Garnet-type solid electrolytes, primarily based on  $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$  ( $\text{M}=\text{Nb}, \text{Ta}, \text{Zr}$ ), feature a cubic crystal structure that enables exceptionally high  $\text{Li}^+$  ionic conductivity (near  $10^3$ - $10^4$  S/cm at room temperature) and good chemical stability against lithium metal, making them promising as  $\text{Li}^+$  selective membranes for electrochemical  $\text{Li}^+$  extraction.[215, 219] Studies have explored LLZO and doped variants (e.g., Ta- or Al-LLZO) in  $\text{Li}^+$  selective membranes where flexible garnet-polymer hybrids can achieve stable cycling and high selectivity in solid-state extraction cells.[219, 220]

### 5.1.4. LISICON-Type

LISICON is a class of solid electrolytes, especially known as sulfide-based materials for high  $\text{Li}^+$  conductivity at elevated temperatures, originating from the garnet-like structure of  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ .[221] Recent advances include carbon-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  composites achieving uptake capacities influenced by voltage and brine composition.[177] Hoshino first proposed a  $\text{Li}^+$  extraction method from seawater using a lithium superionic conductor (LISM) as a separation membrane via dialysis, achieving a 7% increase in lithium recovery after 72 hours without external electrical input.[64]

Inorganic membrane materials face several challenges, including high interfacial resistance, brittleness, complex processing, and long-term mechanical stability.[222, 223] Consequently, current research is increasingly focused on developing organic and



hybrid membrane designs, as well as enhancing interfacial engineering and mechanical properties.

## 5.2. Organic-Polymer Membrane Materials

Organic polymer-based materials, primarily derived from polymers and covalent organic frameworks (COFs), leverage precise pore engineering at the sub-nanometer scale to separate  $\text{Li}^+$  from competing multivalent cations such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  based on hydration shell differences and electrostatic interactions.[224] Jiang et al. constructed an electro-membrane based on acid-functionalized COF for  $\text{Li}^+$  extraction.[225] Eden et al. developed a flexible, low-cost membrane based on a sulfonic acid-functionalized MOF using an electrochemical separation method.[226] In 2025, Baird et al. developed a sulfonated polymer membrane for electrochemical  $\text{Li}^+$  enrichment tested in mixed cation solutions.[227] The system removed 29% of  $\text{Na}^+$  and 41% of  $\text{K}^+$  while extracting only 9.5% of  $\text{Li}^+$ , generating a stream enriched in  $\text{Li}^+$  relative to non-Li cations. Another recent study on polymer membranes was demonstrated by Ying et al. using polyaniline (PANI) based CEM for electrodialysis.[228] They reached a selectivity of 5.26 for the  $\text{Li}^+/\text{Mg}^{2+}$  and 0.2  $\text{mmol}/\text{cm}^2/\text{h}$  lithium permeation rate.

## 5.3. Composite Membrane Materials

Composite polymer membranes have emerged as promising materials for selective  $\text{Li}^+$  separation in electrochemical processes, particularly for extracting  $\text{Li}^+$  from brines, salt lakes, and spent batteries, where high selectivity over competing ions like  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  is critical.[229] These membranes typically integrate polymers such as PVDF, polyethersulfone (PES), or quaternized polymers with functional additives like ion-imprinted polymers, polypyrrole (PPy), or  $\text{Li}^+$  conductors to create hybrid structures that enhance  $\text{Li}^+$  transport. For instance, the IIP@PPy/rGO@PVDF membrane achieves an adsorption capacity of 214  $\text{mg}/\text{g}$ .[230] It maintains performance over 10 cycles in acidic conditions under applied voltage, leveraging electric fields and 12-crown-4 ether for specific  $\text{Li}^+$  selectivity, with reduced graphene oxide and PPy providing mechanical stability and conductivity.[230] Similarly, PES-based composites with HMO exhibit  $\text{Li}^+/\text{Mg}^{2+}$  selectivity up to 11 without voltage and sustain high  $\text{Li}^+$  fluxes (0.0026  $\text{mol}/\text{m}^2/\text{h}$ ),

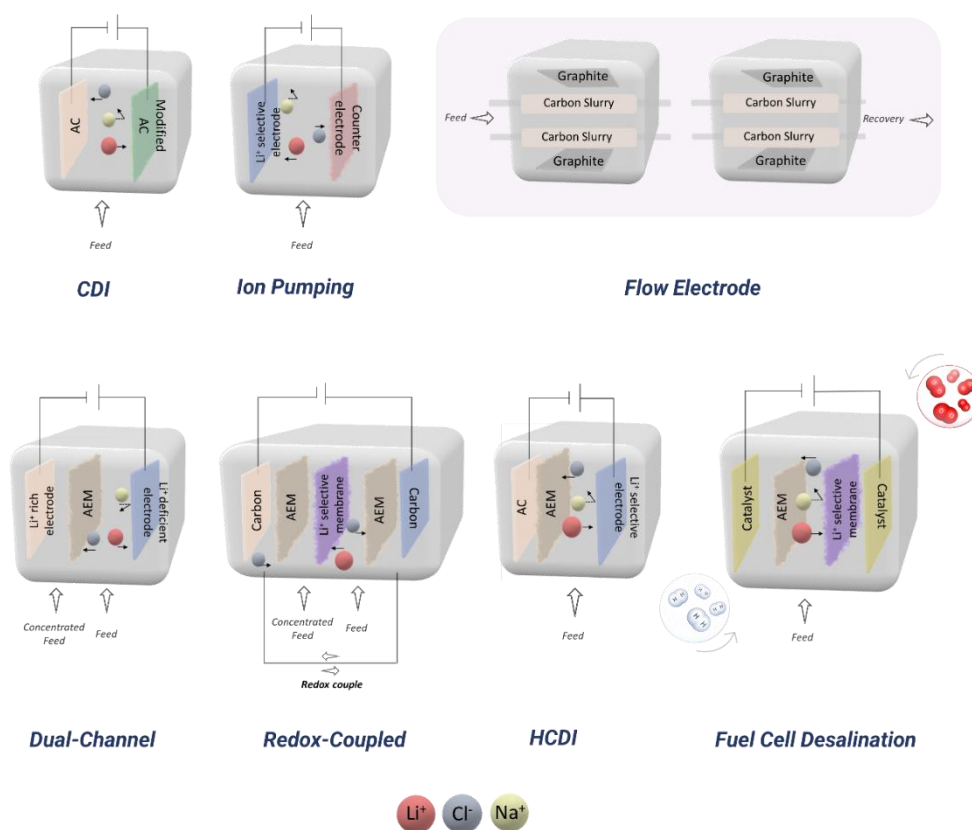
attributed to reduced polymer chain spacing, low glass transition temperatures, and uniform filler dispersion that facilitates ion diffusion.[229] Flexible  $\text{Li}^+$  selective composites combining quaternized polymers with  $\text{Li}^+$  conductors demonstrate  $\text{Li}^+/\text{Na}^+$  selectivity of 35.5 and flux of  $8.33 \times 10^{-10} \text{ mol/cm}^2/\text{h}$ , outperforming commercial monovalent cation exchange membranes by factors of 68 and 2.7, respectively.[231]

The selectivity mechanisms in these systems are based on the hydration energies of ions, with channel sizes designed to enhance the partial dehydration of  $\text{Li}^+$  in preference to the larger  $\text{Mg}^{2+}$ . [28, 128] They utilize electrostatic repulsion through charged functional groups such as sulfonates or crown ethers, along with improved pathways from conductive fillers, which facilitate effective electrochemical driving in processes like electrodialysis or membrane capacitive deionization.[128] Recent advances also incorporate crown ether-functionalized polymers, yielding  $\text{Li}^+/\text{Na}^+$  diffusion ratios up to 9.5 and a separation factor of  $>400,000$  for  $\text{Li}^+/\text{Mg}^{2+}$ , addressing scalability challenges through flexible, stable designs suitable for high-ion-ratio brines.[232] Overall, these literature examples highlight the collaboration between polymer matrices and nanomaterials for effective and selective recovery of  $\text{Li}^+$ .

## 6. Electrochemical Cell Designs and Operations

Electrochemical cell design for  $\text{Li}^+$  separation integrates principles from battery applications and electrochemical engineering to couple selective ion transport with controlled redox reactions that maximize selectivity, capacity, and energy efficiency.[233] These cells consist of one or more ion-selective compartments separated by ion-exchange or bipolar membranes, or  $\text{Li}^+$  selective electrodes in which  $\text{Li}^+$  is transported under an applied potential between a feed stream containing mixed salts (**Figure 9**).[7, 101]

A most preferred choice is either to design a  $\text{Li}^+$  selective phase with an intercalation electrode (e.g.,  $\text{FePO}_4$ , spinel, or layered oxides) or a permselective membrane (e.g., monovalent-selective cation exchange membranes or NF-like membranes). That determines if selectivity is dominated by solid-state insertion thermodynamics and kinetics or by Donnan exclusion, steric hindrance, and hydration effects in the membrane nanochannels.[60, 101, 234]



**Figure 9:** Different electrochemical cell design systems.[7, 91, 101, 233]

Intercalation-based “ion pumping” cells adapt  $\text{Li}^+$  battery electrodes to either static or flow-electrode architectures and operate by alternately polarizing the  $\text{Li}^+$  selective electrode to capture  $\text{Li}^+$  from a feed solution, then releasing it into a recovery or concentrating solution. In contrast, a redox couple or a counter electrode maintains charge balance and enables a continuous cycling process.[233]

The geometry of these cells, such as flow-by channels, flow-through porous electrodes, or slurry electrodes, has a strong influence on mass transport, as flow-through and semi-solid architectures can substantially increase electroactive area and effective mass loading relative to thin flow-by electrodes, thereby improving current efficiency and specific  $\text{Li}^+$  recovery at a given current density.[234] Electrochemical flow reactors designed for the direct recovery of  $\text{Li}^+$  frequently utilize 3D porous electrodes along with precisely adjusted flow rates to minimize concentration polarization.[235] In contrast, membrane-based selective electrodialysis cells arrange repeating recovery and feed compartments separated by CEMs and AEMs, and recent work on  $\text{Li}^+/\text{Mg}^{2+}$  separation has revealed the importance of a dense polyamide surface layer on CEMs to achieve monovalent selectivity by combining positive surface charge, small effective pore size, and favorable partitioning of  $\text{Li}^+$  over  $\text{Mg}^{2+}$ .[236]

More complex architectures, such as redox-flow desalination cells, integrate ion-exchange membranes functionalized with polyelectrolytes and redox-active electrolytes to simultaneously extract  $\text{Li}^+$  with a well-designed cell layout, such as the number and order of compartments, membrane type at each interface, and flow rate, which is used to combine monovalent-selective CEM transport with functionalized groups control so that only targeted ions can cross the membrane.[62] Zan et al. Introduced a flow device using a 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) redox couple and a flexible composite membrane for lithium extraction from seawater.[237] Combining redox chemistry with selective membranes via inorganic  $\text{Fe}(\text{CN})$  couples shows how molecular redox mediators can actively transport  $\text{Li}^+$  across interfaces in a flow configuration. Shan et al. coupled redox flow desalination with continuous Li recovery to recover  $\text{Li}^+$  from spent  $\text{LiFePO}_4$  battery material.[238] Kim et al. designed a combined CDI and redox flow battery system for desalination and  $\text{Li}^+$  capture.[111] The study demonstrates  $\text{Li}^+$  recovery with desalination in a flow electrochemical context, showing how RFB elements can be coupled to other flow separation modules.

Continuous lithium extraction is desirable for enhancing the efficiency of DLE processes. A fuel cell  $\text{Li}^+$  extraction system was developed that enables simultaneous  $\text{Li}^+$  recovery and electrical energy generation.[63] This system uses a ceramic-based membrane and advanced electrodes to extract  $\text{Li}^+$  ions continuously. This approach aims to replace the usual energy-consuming methods used in traditional battery processes.

These strategies reflect the ongoing evolution of electrochemical cell design for  $\text{Li}^+$  extraction, which includes a range of technologies, such as ion-pumping architectures and selective electrodialysis, resulting in improved systems that focus on  $\text{Li}^+$  selectivity, energy efficiency, and scalability.[239] Key advancements address challenges in complex brines by utilizing innovative materials and strategies to reduce energy use and unwanted side reactions. These developments facilitate sustainable  $\text{Li}^+$  recovery from low-grade sources such as seawater and support carbon-neutral supply chains, aligning with the increasing global demand for battery-grade lithium.

# APPROACH AND OVERVIEW

This thesis establishes the theoretical and technological basis of  $\text{Li}^+$  extraction, focusing specifically on direct lithium extraction and electrochemical  $\text{Li}^+$  extraction systems. Conventional processes are energy-intensive and exhibit low selectivity, whereas emerging DLE technologies are promising but remain far from practical application due to limited adsorption capacity and selectivity. Therefore, we examine advanced separation strategies that offer improved efficiency, selectivity, and sustainability. The chapters are structured to move from mechanistic understanding and material-level design to general system-level concepts. This aspect provides a clear framework for evaluating electrochemical  $\text{Li}^+$  extraction technologies.

The rational design of materials plays an important role in advancing  $\text{Li}^+$  extraction technologies, as it directly determines the selectivity, efficiency, and long-term stability of the extraction process. Building on insights into the importance of material design, we first focus on *material-driven strategies for selective electrochemical  $\text{Li}^+$  separation* in **Publication I**. In this initial work, we report a novel acid-free electrochemical regeneration strategy for Sandrose-like aluminum layered double hydroxide electrodes designed for selective  $\text{Li}^+$  recovery from mixed-ion solutions. The study demonstrates that these Al-LDH electrodes combine chemical adsorption affinity for  $\text{Li}^+$  with an electrochemically driven release process, enabling efficient cyclic uptake and release of  $\text{Li}^+$  without the need for harsh acidic or basic eluents. This gentle, pH-neutral regeneration preserves the structural stability of the electrode material and significantly reduces secondary waste and environmental impact compared to traditional extraction methods. The layered structure of the Al-LDH selectively favors  $\text{Li}^+$  over  $\text{Na}^+$ , resulting in promising selectivity and practical effectiveness for  $\text{Li}^+$  recovery from aqueous streams.

In addition to material-level advances in layered oxides such as Al-LDH, MXene-based electrodes have emerged as an attractive platform for many electrochemical applications due to their two-dimensional layered structure, high electrical conductivity, and tunable chemistry. Unlike conventional inorganic sorbents, MXenes can offer precise control over interlayer spacing and surface functionality, enabling selective ion transport and storage through structural design. In **Publication II**, by tuning the MXene interlayer

environment via organic molecule intercalation, the transport pathways can be engineered to preferentially accommodate  $\text{Li}^+$  while sterically and energetically excluding competing alkali ions such as  $\text{Na}^+$ . This tunability allows MXenes to combine fast electrochemical kinetics with high ion selectivity and operational stability in aqueous media. Consequently, MXene interlayer engineering represents a powerful complementary strategy to layered material systems, where selectivity arises from the intrinsic layered affinity, *highlighting how structure-guided material tuning can enhance electrochemical ion separation performance.*

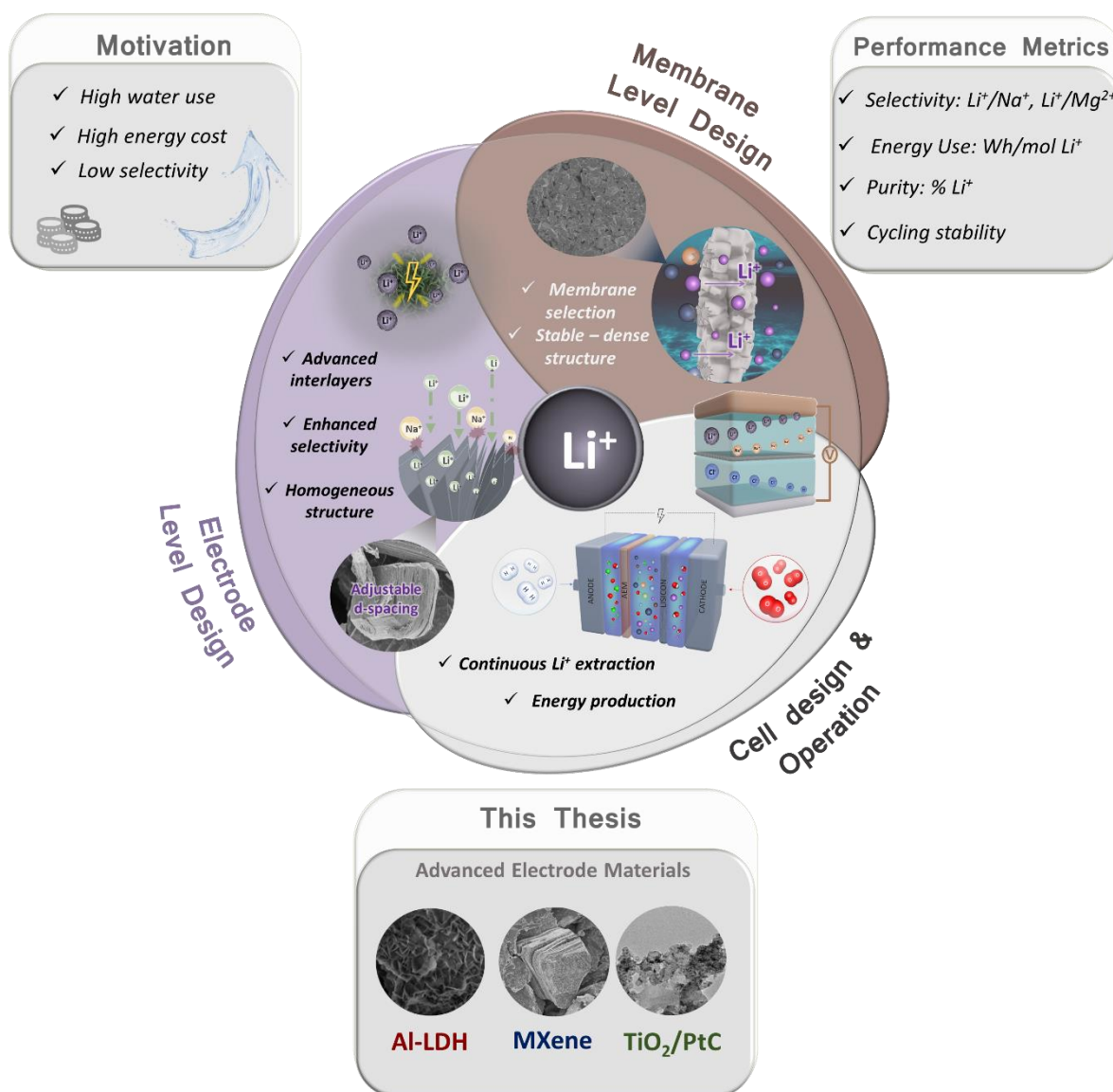
While material design plays a critical role in enhancing selectivity and capacity for  $\text{Li}^+$  separation, membrane selection, cell architecture, and operational strategies are equally important for a scalable, efficient electrochemical ion separation system. Optimizing these elements influences ion transport pathways, separation throughput, energy efficiency, and long-term stability, enabling continuous operation under realistic feed conditions. In this context, in **Publication III**, we introduce a continuous  $\text{Li}^+$  extraction system that combines a ceramic-based membrane with a fuel cell system architecture and advanced electrode coatings to achieve selective, continuous  $\text{Li}^+$  separation from complex aqueous sources such as seawater and mine water. By integrating a ceramic membrane that preferentially transports  $\text{Li}^+$  with a titania-coated electrode prepared via atomic layer deposition, the system demonstrates both enhanced  $\text{Li}^+/\text{Na}^+$  selectivity, doubling selectivity compared to a pristine electrode. Furthermore, it exhibited a high product purity of ~95%  $\text{Li}^+$  while simultaneously generating electrical energy throughout the process. *This work highlights how membrane chemistry, electrode surface engineering, and continuous cell operation* can be combined to improve practical extraction outcomes, positioning membrane and cell design as essential factors to advanced material development of efficient electrochemical  $\text{Li}^+$  separation.

Emphasizing the need for standardized evaluation of electrochemical ion separation, in **Publication IV**, we introduce a systematic framework for collecting, analyzing, and interpreting electrochemical desalination data, *setting the best practices for evaluating the performance of electrochemical ion separation systems.* To provide a mechanistic basis for system performance, we addressed this by defining key metrics, including salt removal efficiency, ion removal capacity, charge efficiency, energy

consumption, and the effect of operating parameters on these outputs. We also provided detailed guidance on how to calculate and normalize them in a reproducible way.

Complementing these advances, in **Publication V**, we wrote a comprehensive review of direct lithium extraction that systematically assesses key DLE technologies, including sorption, ion-exchange, solvent extraction, membrane-based, and electrochemical methods. ***This review establishes the broader DLE approach*** as a sustainable alternative to traditional mining and evaporation, providing a foundational framework ***that highlights our experimental innovations in previous papers*** within ongoing industrial and academic efforts to meet the increasing lithium demands for energy storage while reducing environmental impacts.





**Figure 10:** Overview of the strategies and focus of this thesis on electrochemical  $\text{Li}^+$  extraction. The schematic highlights three key design levels: membrane, electrode, and cell operation, highlighting performance metrics such as selectivity, energy use, purity, and cycling stability.

# PEER-REVIEWED RESEARCH PAPERS

## **Publication I:**

Acid-Free Electrochemical Regeneration of Sandrose-like Aluminum Layered Double Hydroxide Electrodes for Selective Lithium-Ion Recovery in Mixed Ion Solution

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## **Publication II:**

Interlayer-Tailored Alkyl-MXenes for Selective Electrochemical Lithium-Ion Extraction

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## **Publication III:**

Continuous Lithium-Ion Extraction From Seawater and Mine Water With a Fuel Cell System and Ceramic Membranes

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## **Publication IV:**

Best Practice for Electrochemical Water Desalination Data Generation and Analysis

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## **Publication V:**

Direct Lithium Extraction: A New Paradigm for Lithium Production and Resource Utilization

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# Publication I

## ***Acid-Free Electrochemical Regeneration of Sandrose-like Aluminum Layered Double Hydroxide Electrodes for Selective Lithium-Ion Recovery in Mixed Ion Solution***

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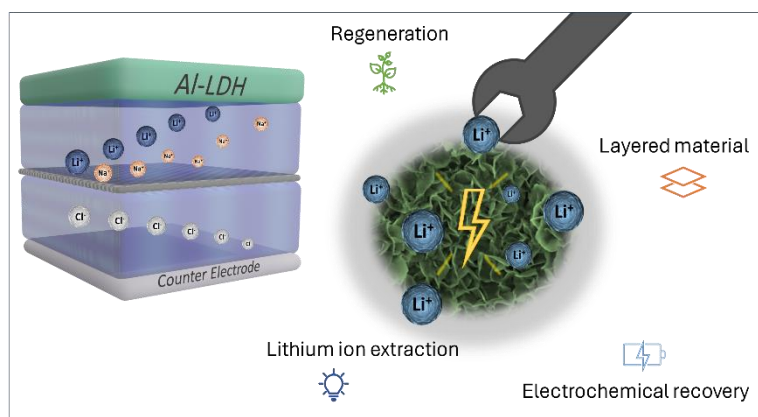
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### **Citation:**

C. Kök, P.V. Hernández, J.G.A. Ruthes, O. Janka, A. Quade, V. Presser, Acid-Free Electrochemical Regeneration of Sandrose-like Aluminum Layered Double Hydroxide Electrodes for Selective Lithium-Ion Recovery in Mixed Ion Solution, **ACS Sustainable Chemistry & Engineering** 13(44) (2025) 19218-19228.

### **Own contribution:**

Methodology, investigation, data curation, validation, writing–original draft, reviewing & editing.



# Acid-Free Electrochemical Regeneration of Sandrose-like Aluminum Layered Double Hydroxide Electrodes for Selective Lithium-Ion Recovery in Mixed Ion Solution

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Cite This: *ACS Sustainable Chem. Eng.* 2025, 13, 19218–19228

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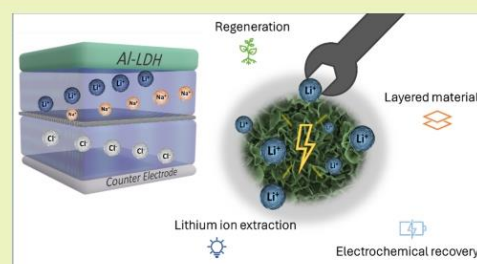
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**ABSTRACT:** The demand for lithium production has seen a significant rise, with the growing electric vehicle and stationary battery markets requiring further development of sustainable and scalable extraction methods. Direct lithium extraction technologies have been developed to address potential shortages, with adsorption emerging as a key method due to its efficiency and low environmental impact. Given that  $\text{Al}(\text{OH})_3$  is already utilized as an adsorbent in various industrial applications, the practical importance of Al-based alternative systems for lithium ion extraction is increasing, yet lithium ion recovery requires harsh chemicals. In this study, we report a novel lithium extraction method combining chemical adsorption and electrochemical release using a synthesized aluminum layered double hydroxide (Al-LDH) material, developed under mild reaction conditions. The performance of the Al-LDH electrode was evaluated against a commercial  $\text{Al}(\text{OH})_3$  adsorbent. Comprehensive characterization using techniques such as X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy revealed detailed insights into the crystalline structure, particle size distribution, and surface morphology of the materials. The Al-LDH electrode exhibited a lithium ion adsorption capacity, achieving an average chemical uptake of lithium ions of 57.6 mg/g. In contrast, lithium-ion uptake capacity for  $\text{Al}(\text{OH})_3$  was 1.0 mg/g over 15 cycles. Notably, this method operates under pH-neutral conditions, eliminating the need for harsh acidic or basic eluents. As a result, it prevents structural degradation and minimizes secondary pollution for potential future applications of lithium-ion recovery. The material's layered structure selectively allowed lithium ion intake while blocking sodium ions, demonstrating its high selectivity and utility in lithium ion recovery processes. The integration of pH-neutral regeneration and high selectivity shows that Al-LDH electrodes as viable candidates for next-generation, green lithium extraction technologies.

**KEYWORDS:** aluminum-layered double hydroxide, electrochemical regeneration, lithium ion recovery, selective adsorption, ion separation, lithium-ion extraction, intercalation materials



## 1. INTRODUCTION

The demand for lithium, strongly driven by battery production, is increasing from 32,000 tons in 2012 to a range of 850,000 to 1,200,000 tons by 2050.<sup>1</sup> Recent reports show a 23% annual rise in lithium production, which climbed from 146,000 tons in 2022 to roughly 180,000 tons in 2023.<sup>2</sup> The production of electric vehicles is a significant driving force for the growing demand for lithium-ion batteries.<sup>3,4</sup> Around 14 million electric vehicles (EV) were purchased in 2023, and the global sales are projected to reach 17 million in 2024.<sup>3</sup> Favorable policies, in addition to more positive consumer perception of electric mobility, are expected to further bolster EV sales to more than 40 million units by 2030.<sup>3</sup> Accordingly, investment in electric vehicles and battery manufacturing has risen to around 500 billion USD.<sup>3</sup> The corresponding increase in lithium consumption may deplete the currently available lithium resources,<sup>4,5</sup> which come primarily in the form of lithium

carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium oxide ( $\text{Li}_2\text{O}$ ), lithium hydroxide ( $\text{LiOH}$ ), and spodumene ( $\text{LiAlSi}_2\text{O}_6$ ) extracted from continental brines ( $\text{Li}_2\text{CO}_3$ ) and hard-rock minerals ( $\text{Li}_2\text{O}$ ,  $\text{LiOH}$ , and spodumene).<sup>4</sup>

The rising demand for lithium and its forecasted scarcity from the most common sources (such as hard-rock minerals and brines) necessitate the development of efficient methods for removing lithium from the environment.<sup>6</sup> Numerous commercial and laboratory-scale methods for direct lithium

Received: August 6, 2025  
Revised: October 23, 2025  
Accepted: October 24, 2025  
Published: October 31, 2025





extraction (DLE) exist, including evaporation, direct precipitation, membrane processes, solvent extraction, sorption, and ion exchange.<sup>7,8</sup> But these methods are hindered by high chemical consumption, cost, and scalability, and environmental impacts such as soil and water contamination, higher energy demands.<sup>9</sup> It is important to prioritize the efficient and environmentally friendly recovery of lithium.<sup>10,11</sup>

Among the various DLE technologies, adsorption is distinguished as the most advanced method, currently at technology readiness level (TRL) 9/9, due to its high theoretical lithium uptake capacity and low energy consumption.<sup>7,12</sup> Adsorption serves as a cost-effective technique for recovering lithium ions by selectively removing them from aqueous media. This process plays a crucial role in assisting a circular economy.<sup>13</sup> In the sorption-based DLE process, lithium ions are separated from complex, multi-ion aqueous environments through the use of aluminum-based sorbents that exhibit a high degree of selectivity for lithium ions over other competing ions. These specialized sorbents bind lithium ions from the solution, effectively concentrating the lithium ions while leaving other elements behind. Once the lithium ions have been sorbed, they are subsequently released or desorbed by flushing the system with fresh water, which facilitates the recovery of lithium ions in a purified form. Sorption offers several advantages, including the absence of hazardous chemical reagents and acids, a low environmental impact, an extraction efficiency of over 90%, and suitability for commercial operation.<sup>14,15</sup>

While several organic and inorganic sorbents, such as lithium manganese oxides, titanium oxides, aluminum hydroxides, iron oxide hydroxides, lithium iron oxide, clay minerals, and zeolites have been examined, lithium aluminum hydroxides stand out as particularly promising due to the structure of gibbsite-type aluminum hydroxides ( $\gamma\text{-Al}[\text{OH}]_3$ ).<sup>1,9,16,17</sup> These materials offer significant advantages, including consistent adsorption efficiency, lower production costs, simple manufacturing, durable adsorption–desorption cycles, and easy regeneration.<sup>18</sup> Lithium ions are attracted and adhere to the surface of gibbsite, which can occupy the central cavity of the hexagon formed by the six aluminum atoms in gibbsite; in contrast, larger alkaline earth metal ions are unable to do so due to steric hindrance.<sup>7</sup> Positively charged layers are induced when lithium ions diffuse into these vacancies.<sup>19</sup> Anions then intercalate into the interlayer to maintain charge balance. Dong et al. synthesized a porous LiAl-LDH material, intending to increase its adsorption capacity.<sup>20</sup> Kotsupalo et al. showed that they obtained high stability after more than 200 cycles in a large-scale column system (25 t) with an aluminum-based layered adsorbent.<sup>21</sup> Zhong et al. created two-dimensional Li/Al-LDHs with high lithium ion selectivity via coprecipitation to adsorb lithium ions at room temperature.<sup>22</sup> The effect of salinity on lithium ion adsorption by LiAl-LDHs adsorbents was studied at various magnesium chloride concentrations to explore  $\text{Li}^+/\text{Mg}^{2+}$  separation.<sup>16</sup> Results showed that increasing magnesium chloride from 0 to 500 g/L raised lithium ion adsorption capacity from 0.6 to 3.0 mg/g.<sup>16</sup>

However, there are environmental concerns regarding the commonly applied methods for lithium ion release. The most common approaches are to dispose of the saturated sorbent or to chemically regenerate it, which generally requires a relatively high temperature ( $>50\text{ }^\circ\text{C}$ ) and produces a lower eluate LiCl concentration compared to ion exchange.<sup>7,23</sup> Alternative regeneration methods, such as electrochemically assisted

regeneration, have been proposed to circumvent the chemical treatment of the sorbents.<sup>10,14,24,25</sup> Electrochemical ion separation enables energy and cost efficiency, a high extraction rate against selective ions, and minimal maintenance expenses.<sup>11,25,26</sup> While the electrochemical regeneration of ions like Sb(V) and Pb(II) has been explored in the literature, to the best of our knowledge, no studies have investigated the electrochemical recovery of lithium ions using aluminum-based adsorbent.<sup>14,27</sup>

This study focuses on the room-temperature synthesis of Al-LDH material with the goal of advancing a synthesis method to form a material that can be used for selective electrochemical lithium ion recovery. By leveraging the architecture of Al-based adsorbent, we aimed to create an electrode with high lithium-ion selectivity, thereby improving its electrochemical reversibility and enhancing the critical desorption stage through a pH-neutral washing step. Al-based adsorbents can desorb lithium ions using pure water which creates hydration shells that enable lithium ion release without the use of acids, thus lowering operational expenditures by removing the need for neutralization and waste treatment expenses.<sup>28</sup> Unlike traditional adsorption processes that typically require high temperatures and acidic conditions, this is a gentle yet effective method for achieving high lithium-ion selectivity and maintaining the electrode's performance in continuous lithium-ion extraction processes. By testing the performance under various operating conditions, we aim to understand how process parameters influence lithium ion separation efficiency and electrode stability. A systematic study was conducted to evaluate the uptake-release capacity and purity performance of the Al-LDH electrode over 15 cycles, achieved through controlled voltage application. The findings reveal that the Al-LDH electrode not only exhibited superior adsorption and electrochemical release capacity but also demonstrated enhanced selectivity for lithium ions toward sodium ions, marking its potential as a highly effective material in this application. In addition, the implementation of a neutral pH washing step allowed the recovery of lithium ions that could not be recovered during the electrochemical process. This mild electrochemical regeneration approach eliminates the need for corrosive eluents, strengthens the method's environmental compatibility, and positions Al-LDH as a promising material for sustainable lithium-ion extraction technologies.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis of the Al-LDH Material.** Al-LDH has been synthesized following previous work.<sup>29</sup> 0.81 g  $\text{LiOH}\cdot\text{H}_2\text{O}$  (Sigma-Aldrich,  $>98.0\%$ ) and 2.4 g  $\text{Al}(\text{OH})_3$  (Sigma-Aldrich; reagent grade) were mixed in a two-neck flask with approximately 75 mass % of deionized (DI) water. The mixture was saturated with argon gas and stirred at room temperature for 48 h. Next, ion exchange was performed by gradually introducing HCl (37% Sigma-Aldrich) at an equivalent mole ratio to the base into the solution. The mixture was stirred for 1–2 h to ensure completion of the reaction while maintaining the solution's pH above 5.5. After washing with deionized water and overnight vacuum filtration, the sample was subsequently ground into a granulated form.

**2.2. Al-LDH Electrode Preparation.** The Al-LDH electrode was prepared by mixing the as-prepared Al-LDH material, carbon black (Alfa Aesar, purity of 99.5 mass %), and polytetrafluoroethylene binder (60 mass % dispersion in water, Sigma-Aldrich) with a mass ratio of 8:1:1 in ethanol. The mixture is carefully ground to create a uniform paste. Then, the paste was rolled into a free-standing electrode with a thickness of 150–200  $\mu\text{m}$  using a hot rolling cylinder press (MTI HR01, MTI Corp). The Al-LDH electrode was dried at

40 °C under vacuum overnight. Punched electrode discs with a diameter of 26 mm were used as working electrodes.

**2.3. Material Characterization.** The morphology was analyzed using scanning electron microscopy (SEM). A ZEISS GEMINI 500 microscope with an EDX detector from Oxford Instruments was used in the experiments. The samples were ground in a mortar, fixed on the copper foil, and transferred to the sample holder. The micrographs were collected at an acceleration voltage of 1 kV with a 20  $\mu\text{m}$  aperture.

Transmission electron microscopy (TEM) was performed with a 2100F system (JEOL) at a voltage of 200 kV. A copper grid coated with lacey carbon was used as the sample holder. The samples were dispersed in ethanol via an ultrasonic bath, and then 10  $\mu\text{L}$  was drop-casted onto the grids and dried for 24 h. Phase analysis of the material was conducted using X-ray diffraction (XRD) with a D8 Discover diffractometer (Bruker) equipped with a copper source (Cu K $\alpha$ , 40 kV, 40 mA), a VANTEC two-dimensional detector covering a 20° 2 $\theta$  angular range, a Göbel mirror, and a 1 mm point focus. The detector was repositioned 4 times, with each measurement lasting 1000 s, to encompass an angular range of 10–80° 2 $\theta$ . All scans went through background subtraction and were normalized to (0–1). The samples were ground using a rotary motion in a mortar and transferred to the sample holder.

Additional X-ray diffraction measurements were carried out at room temperature on pulverized samples of all the compounds discussed, using a Bruker D8-A25 Advance diffractometer operating in Bragg–Brentano  $\theta$ – $\theta$  geometry (goniometer radius: 280 mm). The instrument employed nonmonochromatic Cu K $\alpha_{1,2}$ -radiation ( $\lambda$  = 154.0596 and 154.4425 pm). Diffraction data were collected over a 2 $\theta$  range of 6–130°, with a step size of 0.013° 2 $\theta$  and a total acquisition time of 1 h. A 12  $\mu\text{m}$  Ni foil served as a K $\alpha$  filter, and a variable divergence slit was installed on the primary beam side. On the secondary beam side, a LYNXEYE detector with 192 channels was utilized. The recorded data were evaluated using the Bruker TOPAS 5.0 software, employing both the fundamental parameter approach and the Rietveld method.<sup>30</sup>

Raman spectroscopy was conducted using a Renishaw inVia Raman microscope, which employed a neodymium-doped yttrium aluminum garnet laser operating at a wavelength of 532 nm. Each sample was placed on a glass slide, and spectra from 10 points were recorded with a 10 s exposure time and accumulated five times. The microscope employed a 50 $\times$  magnifying lens with a numeric aperture of 0.5. Spectra were treated by cosmic ray removal and normalized to (0–1).

The nitrogen adsorption analyses at –196 °C were carried out by using a Quadrasorb IQ system (Anton Paar, formerly Quantachrome). Before each measurement, the samples were outgassed for 12 h at 100 °C under vacuum.<sup>31</sup> The specific surface area was determined using the Brunauer–Emmett–Teller (BET) method, implemented through the Quadrasorb IQ software.<sup>32</sup>

Fourier-transform infrared spectroscopy (VERTEX 70v FT-IR Spectrometer, Bruker) was used to analyze the functional groups on the surface of the adsorbent material, including their bonding and interactions with adsorbates. The powders were directly analyzed under the lens without any additional modifications. The surface groups of the material were determined within the spectral range from 400 to 4000  $\text{cm}^{-1}$ .

The concentration of the feed and recovery solutions was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, ARCOS FHX22, SPECTRO Analytical Instruments).<sup>33</sup> 2 mL of samples were collected before and after the experiment, and they were injected into the system with a 1 mL/min sample flow rate. We established the connection between each ion concentration and the corresponding ICP-OES signal intensity. The calibration was performed with mixed ion solutions containing known concentrations of 0.1, 0.5, 1, 2, 5, and 10 mM of LiCl, NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>.

X-ray photoelectron spectroscopy (XPS) was performed with the Kratos Axis Supra (Kratos Analytical). The photon source was a monochromatized Al K $\alpha$  line. Survey spectra were acquired with an analysis area of 300  $\times$  700  $\mu\text{m}^2$  and 160 eV pass energy at 15 kV. The

highly resolved measured spectra were acquired using a pass energy of 10 eV at 15 mA and 15 kV for Al 2p, C 1s, and O 1s scans. All spectra were analyzed using CasaXPS software (version 2.3.15). The peaks were calibrated to the aliphatic component in C 1s (285.0 eV). For measurements, the loose powders were spread onto the surface of a small piece (5  $\times$  5  $\text{mm}^2$ ) of carbon adhesive tape.<sup>34</sup> The flat side of a freshly cleaned spatula was used to press the powders firmly into the tape. After removing the loose powder from the surface of the sample holder, the holder was inserted into the XPS load lock.

Thermogravimetric analyses (TGA) were carried out in air with a Netzsch TG-209–1 Libra from 0 to 1000 °C at a heating rate of 10 °C/min. Five milligrams were taken from each sample and put into the alumina crucibles (Ceramic, TG F1 Libra). Then, crucibles were fixed to the device. Experiments have been performed in an argon (99.9%) atmosphere.

**2.4. Calculations.** The sorption capacity was calculated according to eq 1:

$$\text{sorption capacity} = \frac{(c_i - c_f) \times V}{m} \quad (1)$$

where  $c_i$  is the initial concentration,  $c_f$  is the final concentration of the uptake-release process,  $m$  is the mass of the sorbent, and  $V$  is the volume of the solution.

$$\text{capacity regeneration} = \frac{\text{Cation release capacity}}{\text{Cation uptake capacity}} \times 100\% \quad (2)$$

$$\text{purity} = \frac{\Delta C_{\text{Li}}}{\Delta C_{\text{all}}} \times 100\% \quad (3)$$

where  $\Delta C_{\text{Li}}$  and  $\Delta C_{\text{all}}$  are the concentration changes of lithium ions and all cations in the recovery solution.

The selectivity regarding the lithium-ion to sodium-ion ratio was calculated via:

$$\text{selectivity} = \frac{\Delta C_{\text{Li}}}{\Delta C_{\text{Na}}} \quad (4)$$

Here,  $\Delta C_{\text{Li}}$  and  $\Delta C_{\text{Na}}$  are the concentration changes of lithium and sodium ions in the feed solution with the unit of mmol/L, respectively.

Energy consumption was calculated according to eq 5:

$$\text{energy consumption} = \frac{E_{\text{electrical}}}{\text{cation release capacity}} \quad (5)$$

where  $E_{\text{electrical}}$  is the consumed electrical energy during one cycle.

**2.5. Electrochemical Characterization.** For electrochemical measurements of the cell, discs were punched from the prepared Al-LDH sheets and used as the working electrode (26 mm). An oversized commercially available microporous activated carbon cloth (Kynol ACC-507-10) was used as the counter electrode (26 mm) in a flow-through electrochemical desalination cell.<sup>35</sup> The electrodes were separated by a few layers of glass-fiber filters (GF/A, Whatman). The same cell setup was repeated for the Al(OH)<sub>3</sub> electrode. The electrodes' capacity to store and release lithium ions was evaluated using galvanostatic charge/discharge with potential limitation (GCPL) of +1 to –1 V with a 2 h holding time, conducted with a BioLogic VMP-300 potentiostat/galvanostat in a climate chamber maintained at 25  $\pm$  1 °C, and the pH of the solution was not adjusted. Anion exchange membranes (Fumasep, FAS-PET-130) were used to prevent the uptake of competing ions. The electrochemical cell experiment proceeded in three stages, using two different solutions.

Initially, a feed solution containing 10 mM NaCl and 50 mM LiCl was pumped through the cell for 24 h at a flow rate of 3 mL/min at zero applied potential, allowing the electrodes to chemically adsorb the ions. Afterward, the electrodes were rinsed for 30 min by pumping deionized water (purified using a Millipore Milli-Q lab water system) to remove any lithium ions and sodium ions that had not been adsorbed into the electrode material. Finally, a recovery solution of 10 mM KCl was pumped through the cell while applying the GCPL



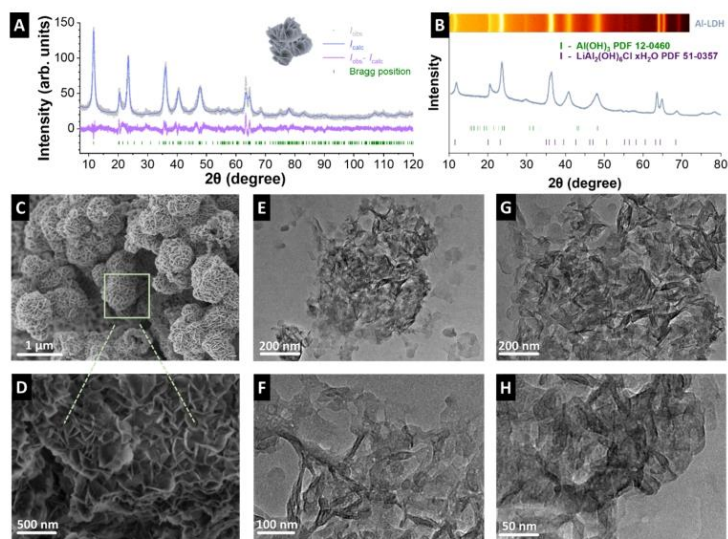


Figure 1. (A) X-ray diffractogram and associated Rietveld fitting of Al-LDH, (B) normalized X-ray diffractograms of Al-LDH, (C, D) scanning electron micrographs of Al-LDH in different magnifications, and (E–H) transmission electron micrographs of Al-LDH.

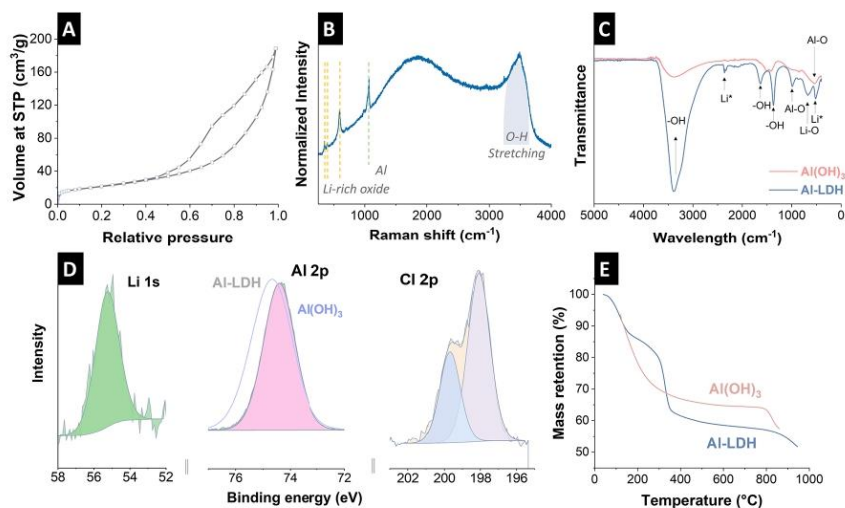


Figure 2. (A) Nitrogen gas sorption isotherm of Al-LDH at -196 °C (STP: standard temperature and pressure), (B) Raman spectrum of Al-LDH, (C) comparison of FTIR spectra of Al-LDH and Al(OH)<sub>3</sub>, (D) X-ray photoelectron spectra of Al-LDH, (E) TGA results of the Al-LDH and Al(OH)<sub>3</sub> in Ar atmosphere.

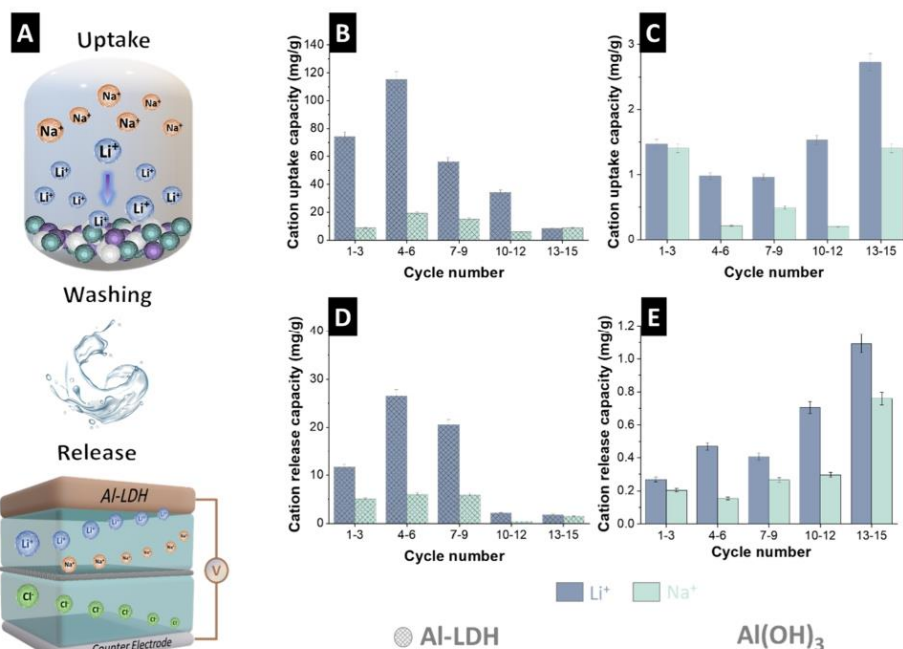
technique with a current of 0.1 A/g, with a 1 V limit to the potential difference between the electrodes. During this stage, the electrodes were expected to release the lithium ions into the recovery solution.

Two mL of aliquots of both solutions were collected before and after each step. These three stages constituted a cycle, and the process was repeated 15 times to assess the electrodes' ion storage/release capacity. The amount of lithium ions adsorbed and released during each cycle was determined using inductively ICP-OES. The Al-LDH

and Al(OH)<sub>3</sub> electrodes have been analyzed through chronoamperometry in 1 M LiCl solution. Measurements have been run for approximately 14 h at 0.8 V.

### 3. RESULTS AND DISCUSSION

In this study, an aluminum-based layered oxide material has been developed for the adsorption and electrochemical regeneration of lithium. The material has been synthesized at



**Figure 3.** (A) Schematic representation of the chemical uptake, washing step, and electrochemical release process, (B) ion uptake capacity of the Al-LDH, (C) ion uptake capacity of Al(OH)<sub>3</sub>, (D) ion release capacity of Al-LDH, and (E) ion release capacity of the Al(OH)<sub>3</sub>.

room temperature, ensuring that the process was carried out under mild and controlled conditions.

X-ray diffraction was used to prove that a crystalline material has formed during synthesis and to clarify which compound has formed, as the Pearson database (release 2023/2024) lists three different structures (Figure 1A,B). Anhydrous LiAl<sub>2</sub>Cl(OH)<sub>6</sub>, which crystallizes in the hexagonal crystal system with space group *P6<sub>3</sub>/mcm* and two hydrated forms, LiAl<sub>2</sub>Cl(OH)<sub>6</sub>·H<sub>2</sub>O and LiAl<sub>2</sub>Cl(OH)<sub>6</sub>·*n*H<sub>2</sub>O with *n* = 1.50 to 2.16.<sup>36,37</sup> While the monohydrate crystallizes with space group *P6<sub>3</sub>/m* the higher hydrated forms adopt the monoclinic crystal system with space group *C2/m*.<sup>38,39</sup> According to Rietveld analysis, the prepared compound is the monoclinic variant. The amount of crystal water could not be refined from the collected powder data. In addition, the preferred orientation along [001] is observed, which is expected in view of the layered structure. Some minor discrepancies remain between the refined model and the collected data, which can be attributed to disorder and partially occupied sites. A crystallite size of 8 ± 1 nm was deduced from Rietveld fitting. The scanning and transmission electron micrographs of the samples are shown in Figure 1C,D. In our comparative analysis, we noted that the Al-LDH material exhibits a distinctive sandrose-like flaky structure, which presents an interesting contrast to the Al(OH)<sub>3</sub> structure (Supporting Information, Figure S1A,B). This type of structure indicates that lithium ions will penetrate the material more effectively.<sup>20</sup> The transmission electron micrographs present in Figure 1E–H further display the sandrose-like structure of the material, along with the overlaid

hierarchical layers, which corroborate with the scanning electron micrographs and other reported Al-LDH materials.<sup>40–42</sup> Furthermore, the transmission electron micrographs suggest the formation of aggregates of the Al-LDH particles with different sizes. Micrographs indicate structures with hollow spots, characteristic of nonrigid aggregates, which could positively impact sorption–desorption, allowing more electroactive sites to be reached when compared with Al(OH)<sub>3</sub> powder (Supporting Information, Figure S1C–E).

Surface area analysis was utilized to interpret parameters such as pore volume, specific surface area, and pore size. Analysis showed that the material has an average BET surface area of 60 m<sup>2</sup>/g (Figure 2A). In comparison, Al(OH)<sub>3</sub> shows a value of 23 m<sup>2</sup>/g for the BET specific surface area, which is lower than that of the Al-LDH material (Supporting Information, Figure S2). The noticeable increase in specific surface area and pore volume indicates more accessible sites for Faradaic reactions and double-layer formation.<sup>43</sup> Based on the hysteresis loops of the materials by IUPAC, the Al-LDH material exhibits an H3 loop type.<sup>44</sup> This type of hysteresis loop is typically associated with nonrigid aggregates of plate-like particles, as observed in the transmission electron micrographs. The layered structure of Al-LDH consists of positively charged metal hydroxide sheets with anions and water molecules located in the interlayer spaces. This configuration provides both high surface area and accessible channels for lithium ions to enter, interact, and be selectively adsorbed within the structure.<sup>45</sup>



Raman spectroscopy (Figure 2B) showed three apparent bands from lithium-rich oxides at 351, 396, 595  $\text{cm}^{-1}$ .<sup>46</sup> The prominent vibrational mode observed at 595  $\text{cm}^{-1}$  is primarily associated with the  $A_{1g}$  and  $E_g$  symmetries from rhombohedral group  $R\bar{3}m$ , respectively.<sup>47</sup> Appeared peak in 1065  $\text{cm}^{-1}$  is the characteristic band for the presence of  $\text{Al}$ .<sup>48,49</sup> A typical bending mode  $\nu_2$  near 1595  $\text{cm}^{-1}$  from a single  $\text{H}_2\text{O}$  molecule and 3320–3600  $\text{cm}^{-1}$  range because of the O–H stretching band in the spectra.<sup>50,51</sup>

FTIR spectra were used to identify functional groups, with signals in the 2990–3600  $\text{cm}^{-1}$  range attributed to the stretching vibrations of –OH groups and bands in the 1380–1635  $\text{cm}^{-1}$  range corresponding to the bending vibrations of –OH groups. (Figure 2C).<sup>13</sup> The bands at 538 and 990  $\text{cm}^{-1}$  indicate the presence of the Al–O bond.<sup>20</sup> The bands between 980 and 650  $\text{cm}^{-1}$  can be attributed to the vibration of metal–oxygen bonding.<sup>20</sup> Bands typically observed around 3300–3600  $\text{cm}^{-1}$ , corresponding to O–H stretching of  $\text{Al}(\text{OH})_3$ .<sup>52</sup>

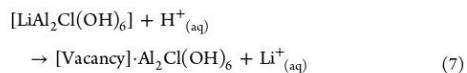
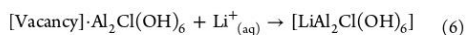
The chemical composition of the samples was also studied using XPS. According to the literature, the Al 2p signal of  $\text{Al}_2\text{O}_3$  is positioned at a binding energy (BE) of 74.1 eV.<sup>53</sup> However, a higher BE of 74.4 eV for Al 2p indicates the presence of a phase consisting of aluminum and lithium ions, which suggests the presence of the Al-LDH material (Figure 2D). Furthermore, the position of the Li 1s peak at a binding energy of 55.3 eV corresponds to the value published by Visser et al. for Li in Li-LDH.<sup>54</sup> The Cl 2p peak is positioned at a binding energy of 198.1 eV. Zhong et al. found a similar binding energy for Cl 2p and interpreted it as indicating that more lithium chlorides were intercalated into Li/Al-LDHs (Figure 2D).<sup>22</sup>

Figure 2E compares the thermograms of Al-LDH and  $\text{Al}(\text{OH})_3$ . Thermogravimetric analysis of the materials was performed in an argon atmosphere with temperatures ranging from 30 to 1000 °C. Al-LDH followed two steps of mass loss, including the initial weight loss due to the decomposition of physically adsorbed water molecules in the material.<sup>55</sup> Our material decomposed at around 300 °C, and the total mass loss was 47% for the Al-LDH. The second mass loss can be attributed to the dehydroxylation of  $\text{Al}(\text{OH})_3$ .<sup>56</sup>

### 3.1. Electrochemical Cell Performance of the Al-LDH.

The two-step process used by us to extract lithium ions is schematically illustrated in Figure 3A. Al-LDH enables effective lithium ion sorption due to its structure connected through hydrogen bonds, electrostatic interactions, and van der Waals forces.<sup>6</sup> In the initial step, the adsorption process involves the chemical sorption of lithium ions. The second step involves the electrochemical desorption of lithium. This process was conducted by first washing the electrodes with deionized water and applying an electric charge to the electrochemical cell. Upon charging the cell, ions sorbed by the Al-LDH electrode are released back into the recovery solution, facilitating the regeneration of the electrode. The central cavities of the hexagonal  $\text{Al}(\text{OH})_3$  structure enable the penetration of lithium ions into the material.

The adsorption and desorption mechanisms of Al-LDH can be represented as follows:



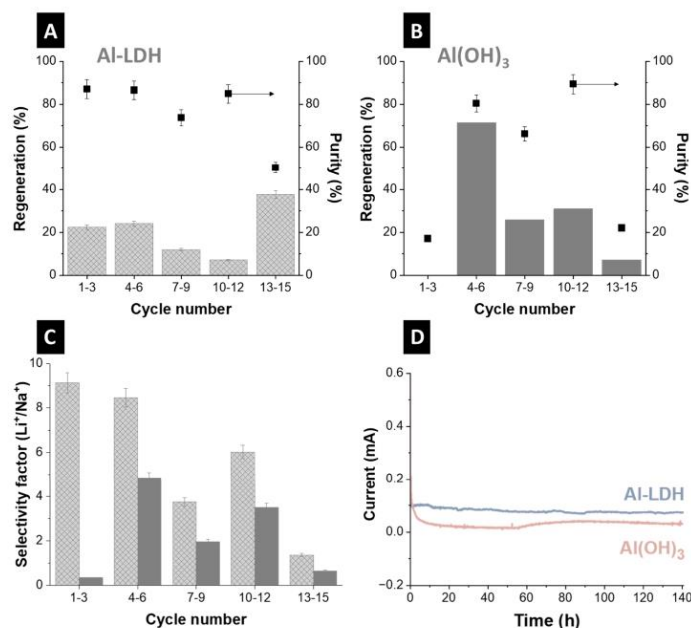
Here lithium ions enter the vacancies in the material structure coordinated with chloride ions. The adsorption of lithium occurs with charge balancing using chloride ions, while desorption can be triggered by the external voltage that replaces lithium ions with protons.<sup>57,58</sup>

Electrochemical recovery of lithium ions was conducted in a solution containing 50 mM of lithium ions and 10 mM of sodium ions. Initially, for each cycle, the solution was pumped at a rate of 3 mL/min for 24 h to facilitate the adsorption of cations onto the electrode surface and then flushed with deionized (DI) water. ICP-OES showed that the uptake capacity of the lithium ions was much higher than that of sodium ions for the Al-LDH electrode (Figure 3B). After 15 cycles, the average uptake capacity for lithium was 57.6 mg/g, while the average uptake capacity for sodium was 12.5 mg/g. After pH-neutral washing, a voltage of 1 V was applied to the electrochemical cell for 2 h to facilitate the electrochemical release of cations. At the end of 15 cycles, the average lithium ion release capacity was calculated as 13 mg/g. The corresponding value for sodium ions is 3.8 mg/g (Figure 3D).

The average lithium ion uptake capacity for  $\text{Al}(\text{OH})_3$  was 1.0 mg/g, while for sodium ions, it was 0.4 mg/g (Figure 3C). We found that the average lithium-ion release capacity of the  $\text{Al}(\text{OH})_3$  was determined to be 0.6 mg/g. In contrast, the corresponding release capacity for sodium was calculated at 0.3 mg/g (Figure 3E). Comparative analysis revealed that the lithium ion release capacity of  $\text{Al}(\text{OH})_3$  was notably lower than that exhibited by the Al-LDH electrode.

To assess the relative contributions of sorption and charge to the release capacity following 15 cycles, the cell was flushed for 1 h with DI water after the chemical sorption stage in each cycle. The samples from the washing solution were collected to get back any ions that were lost during the uptake and release processes (Supporting Information, Figure S3).

Considering the material's high adsorption capacity and its ability to undergo electrochemical regeneration, some ion loss was observed, which may reflect inherent trade-offs associated with the current system design. This loss is hypothesized to result either from the strong retention of ions within the material's structure, preventing their complete electrochemical desorption, or from modifications occurring on the electrode surface. The binding affinity of different anions to the layered structure varies, following the order of Hofmeister lyotropic series:  $\text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{HAsO}_4^{2-} > \text{CrO}_4^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$ . XPS analysis confirmed the presence of  $\text{CO}_3^{2-}$  anions within the material's layered framework (Supporting Information, Figure S4).<sup>59,60</sup> Furthermore, postexperimental XRD characterization of the electrode suggests the formation of lithium aluminum carbonate hydroxide hydrate (Supporting Information, Figure S5). The high lithium ion selectivity of the layered hydroxide material likely arises from strong electrostatic or coordinative interactions between lithium ions and functional groups such as  $\text{OH}^-$ . These strong interactions facilitate efficient ion capture but also increase the energy barrier for desorption, hindering ion release. These findings indicate the possibility of side reactions occurring during the process, as well as the inherent tendency of the adsorbent material to retain rather than fully release adsorbed ions. Moreover, post-mortem scanning electron micrographs of the electrode revealed significant structural degradation after 15 cycles (Supporting Information, Figure S6A–B).



**Figure 4.** (A) Regeneration and purity of recovery solution for Al-LDH, (B) regeneration and purity of recovery solution for Al(OH)<sub>3</sub>, (C) selectivity factor comparison of the feed solutions for Al-LDH and Al(OH)<sub>3</sub>, (D) chronoamperometry measurements of Al-LDH and Al(OH)<sub>3</sub> electrodes vs Ag/AgCl in 1 M LiCl.

The regeneration rate and purity were calculated to assess the reversibility of the electrodes and evaluate the efficiency of the lithium ion extraction process (Figure 4A,B). The regeneration ratio for Al-LDH generally ranged between 10 and 40%, which is consistent with the observed uptake-release capacity results. Despite Al-LDH demonstrating strong adsorption performance for lithium ions, it failed to fully release the captured ions during the electrochemical desorption stage. This asymmetry is attributed to the strong electrostatic interactions and coordination between lithium ions and the layered hydroxide host framework, which stabilizes the intercalated ions within the host framework.<sup>19</sup> Additionally, potential structural rigidity and diffusion limitations within the interlayer spacing may impede ion mobility during the release phase.<sup>58</sup> These findings suggest that while the material is highly effective for selective lithium ion capture, tuning interlayer spacing within the material structure and modifying host structure flexibility may be necessary to improve release efficiency.

The purity of Al-LDH generally ranged between 70 and 90% and dropped to 50% in the last 3 cycles (Figure 4A). These values were inconsistent for the unmodified material Al(OH)<sub>3</sub> (Figure 4B). Figure 4C plots the lithium ions selectivity factor toward sodium ions, highlighting that the selectivity factor for the Al-LDH electrode is higher than that of the Al(OH)<sub>3</sub> electrode. The difference can be attributed to the selective ion transport properties of the Al-LDH electrode, in which the vacancies generated by the deintercalation of primordial lithium ions during the desorption process act as highly selective active sorption sites for lithium ions.<sup>61</sup> Unlike Al-

LDH, the Al(OH)<sub>3</sub> electrode's behavior suggests that it facilitates the passage of both lithium ions and sodium ions. The adsorptive nature of the Al(OH)<sub>3</sub> electrode implies that while it may be efficient for general ion uptake, it does not possess the discriminative capacity necessary for lithium-ion-specific applications. This limitation highlights the importance of electrode composition and structure in achieving targeted ion selectivity. The cell corresponding to Al-LDH had a higher current compared to Al(OH)<sub>3</sub>, indicating the transport of cations. Chronoamperometry results provide that the current for Al-LDH is consistently higher than Al(OH)<sub>3</sub>, indicating ongoing electrochemical activity which can be attributed to the LDH layered structure in enabling sustained current flow, likely due to lithium ion transport within the layers (Figure 4D).

LDHs rely primarily on electrostatic interactions between positively charged hydroxylated layers and the exchanged anions, with a minor contribution from the free energy associated with hydration changes.<sup>62</sup> This is due to the presence of exchangeable anions and water molecules bonded within their interlayer spaces.<sup>63</sup> The characterization results of Al-LDH reveal the incorporation of carbonate anions within chloride ions in its structure. The carbonates in the LDHs structure exhibit a selective affinity toward anions. The substitution of chloride ions with carbonate reduces the interlayer spacing of LDHs, thereby enhancing the binding energy between the interlayer anions and the basal layer.<sup>11</sup> This structural modification decreases the interlayer gaps and improves the selectivity of the material toward elements with small ionic diameters, such as lithium.<sup>62,64</sup> This selective



Table 1. Comparison of the Al–Li Layered Materials in Different Lithium Extraction Studies

| material                                                                          | initial lithium ion concentration (mg/L) | lithium ion up take capacity (mg/g) | removal of lithium ions (%) | method                                          | ref       |
|-----------------------------------------------------------------------------------|------------------------------------------|-------------------------------------|-----------------------------|-------------------------------------------------|-----------|
| Al(OH) <sub>3</sub>                                                               | 1150                                     | 943.5                               | 92–94                       | adsorption                                      | 13        |
| Li/Al layered double hydroxides (Li/Al-LDHs)                                      | 399                                      | 7.3                                 | 72                          | adsorption                                      | 22        |
| magnetic Li/Al-LDHs doped with Fe <sub>3</sub> O <sub>4</sub> nanoparticles (NPs) | 397                                      | 5.8                                 |                             | adsorption                                      | 65        |
| granulated Li/Al-LDHs and NH <sub>4</sub> Al <sub>2</sub> (OH) <sub>6</sub>       | solution 1:500                           | solution 1:9.7                      |                             | adsorption                                      | 66        |
|                                                                                   | solution 2:969                           | solution 2:9.2                      |                             |                                                 | 66        |
| granulated porous Li/Al-LDHs                                                      | solution 1:300                           | solution 1:8.5                      |                             | adsorption                                      | 20        |
|                                                                                   | solution 2:999                           | solution 2:11.8                     |                             |                                                 | 20        |
| granulated Li/Al-LDHs                                                             | 1400                                     | 14.5                                | 83                          | adsorption                                      | 67        |
| Zn <sup>2+</sup> -doped Li/Al-LDHs                                                | solution 1:750                           | solution 1:13.1                     |                             | adsorption                                      | 45        |
|                                                                                   | solution 2:222                           | solution 2:6.1                      |                             |                                                 | 45        |
| Li/Al-LDHs doped with Fe <sub>3</sub> O <sub>4</sub> NPs                          | 397.1                                    | 13.4                                |                             | adsorption                                      | 68        |
| LiAl-LDH beads                                                                    | 200–500                                  | BLDH-P: 5.3 mg/g                    |                             | adsorption                                      | 69        |
|                                                                                   |                                          | BLDH-Cl: 4.7 mg/g                   |                             |                                                 | 69        |
| LDH-Si-BX                                                                         | 10–25–50                                 | 1.7 mg/g                            | 83%                         | adsorption                                      | 57        |
| Al-LDH                                                                            | 0.4                                      | 57.6                                | 60                          | chemisorption with electrochemical regeneration | this work |

interaction with carbonates enables a more targeted and efficient incorporation of lithium ions into the structure, thereby enhancing the overall performance of the cell. The layered structure of Al-LDH facilitates an optimal framework for the intercalation of anions between the layers. This structural arrangement preferentially permits the transport of lithium ions.<sup>59</sup> In contrast, the Al(OH)<sub>3</sub> electrode does not exhibit the same level of selectivity. Its more generalized cation uptake behavior suggests that it lacks the specialized ion transport mechanisms present in Al-LDH.

The Al-LDH electrode exhibited stable, low energy consumption across cycles, averaging ~0.5 μWh/g. In contrast, the Al(OH)<sub>3</sub> electrode showed significantly higher energy use, averaging 0.03 mWh/g per lithium ion, likely due to electrochemical inefficiencies and discharge energy losses. Elevated consumption in the first three cycles may result from the material's high adsorptivity and complex electrochemical behavior. Cyclic voltammetry in a three-electrode setup revealed quasi-reversible behavior for Al-LDH between 0 and –0.6 V vs Ag/AgCl (Supporting Information, Figure S6A).

Although the Al(OH)<sub>3</sub> sorbent is not electrochemically active, the quasi-reversible peak of the intercalated Al-LDH material between reduction and oxidation peaks can be associated with the insertion of lithium ions into the crystal structure of Al(OH)<sub>3</sub> and crystal growth of the material, causing expansion in the hexagonal structure.<sup>14,19</sup>

Table 1 displays various sorption studies on lithium-layered materials. The removal efficiency typically falls within the range of 70–95%. The study indicated that the Al-LDH material exhibited a release efficiency of 53% and an uptake efficiency of around 74%. Although the release efficiency is relatively lower compared to the uptake efficiency, the process is reversible, and the electrode's self-regeneration slows down after 15 cycles. The average regeneration ratio for the Al-LDH electrode is 35%, significantly surpassing the 29% value found for Al(OH)<sub>3</sub>. These results highlight the potential of Al-LDH as a regenerable material for electrochemical lithium ion extraction; however, further optimization is required to overcome current limitations and fully realize its practical applicability.

#### 4. CONCLUSIONS

In this study, the synthesis of the Al-LDH material was successfully carried out under mild reaction conditions, ensuring an environmentally friendly and energy-efficient process. Following synthesis, the Al-LDH material's structure has been characterized using a variety of advanced techniques to analyze its structural, morphological, and compositional properties. These techniques included X-ray diffraction for phase identification, Fourier-transform infrared spectroscopy for functional group analysis, and scanning electron microscopy for examining surface morphology. The characterization results provided a comprehensive understanding of the Al-LDH's crystalline structure, particle size distribution, and surface properties. Our findings reveal that the Al-LDH electrode showcased the adsorption–desorption capacity for lithium ions.

The two-step process, which involves chemical sorption followed by electrochemical desorption, enabled efficient lithium ion uptake from mixed-ion solutions, with Al-LDH significantly outperforming unmodified Al(OH)<sub>3</sub> in both selectivity and capacity. The layered structure of Al-LDH facilitated high lithium ion uptake (average of 57.6 mg/g), and its selectivity factor toward lithium ions over sodium ions was approximately 2.5 times higher than that of Al(OH)<sub>3</sub>. The desorption efficiency remained comparatively lower, with an average of 13 ± 3 mg/g of lithium ions released. This asymmetry is attributed to the strong electrostatic and coordinative interactions between lithium ions and the hydroxide layers, which enhance selectivity while also stabilizing intercalated ions and impeding their release. Lithium ions can be recovered by the additional step of pH-neutral washing, which is beneficial in preserving the performance of the electrode and thereby circumventing the dissolution damage to lithium-adsorbed adsorbents typically caused by acidic eluents. In particular, the electrochemical regeneration process demonstrated here proceeds under mild conditions and does not require the use of acidic eluents, making it both environmentally benign and operationally advantageous.

The layered structure of the Al-LDH material plays a crucial role by promoting the ingress of lithium ions while effectively

blocking the penetration of larger sodium ions. Selectivity comparison of the materials highlights the significance of electrode material choice in applications where selective lithium ion extraction is desired. The results confirm that Al-LDH electrodes provide a more effective and sustainable solution in electrochemical systems, owing to their higher release capacity and higher purity level. The findings have promising implications for sustainable lithium ion recovery, contributing to greener energy-storage systems and paving the way for scalable, environmentally conscious extraction technologies that address global demand while reducing ecological impact.

### ■ ASSOCIATED CONTENT

#### Data Availability Statement

All data can be accessed via [10.5281/zenodo.15575958](https://doi.org/10.5281/zenodo.15575958).

#### ■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsschemeng.5c08261>.

Additional material characterization of the electrodes: SEM and TEM of the Al(OH)<sub>3</sub>; nitrogen gas sorption analysis of the Al(OH)<sub>3</sub> electrode; analytical data set of washing steps; XPS of C 1s of Al-LDH; XRD of the Al-LDH and post mortem electrode after 15 cycles; and cyclic voltammogram of the Al-LDH electrode (PDF)

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curation, XRD analyses, writing, review & editing. A.Q.: Data curation, XPS analysis. V.P.: Visualization, writing—review and editing.

#### Notes

The authors declare no competing financial interest.

### ■ ACKNOWLEDGMENTS

Sincere thanks are given to Dr. Stefanie Arnold for her insightful feedback. The authors thank Peter Burger for conducting the thermal gravimetric analysis. We acknowledge the European Union's support for the eLiFlow project from the European Regional Development Fund (EFRE) and the State of Saarland, Germany.

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## Correction to "Acid-Free Electrochemical Regeneration of Sandrose-like Aluminum Layered Double Hydroxide Electrodes for Selective Lithium-Ion Recovery in Mixed Ion Solution"

Cansu Kök, Pablo Vega Hernández, Jean G. A. Ruthes, Oliver Janka, Antje Quade, and Volker Presser\*  
ACS Sustainable Chem. Eng. 2025, 13 (44), 19218–19228. DOI: 10.1021/acssuschemeng.5c08261



Cite This: ACS Sustainable Chem. Eng. 2026, 14, 848–849



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In the original Article, Figure 1C shows an image from a different, morphologically similar sample rather than the sample investigated in the other panels and throughout the manuscript. A corrected version of Figure 1 (with the correct image for panel C) is provided below. This correction does not affect the results, discussion, or conclusions of the Article.

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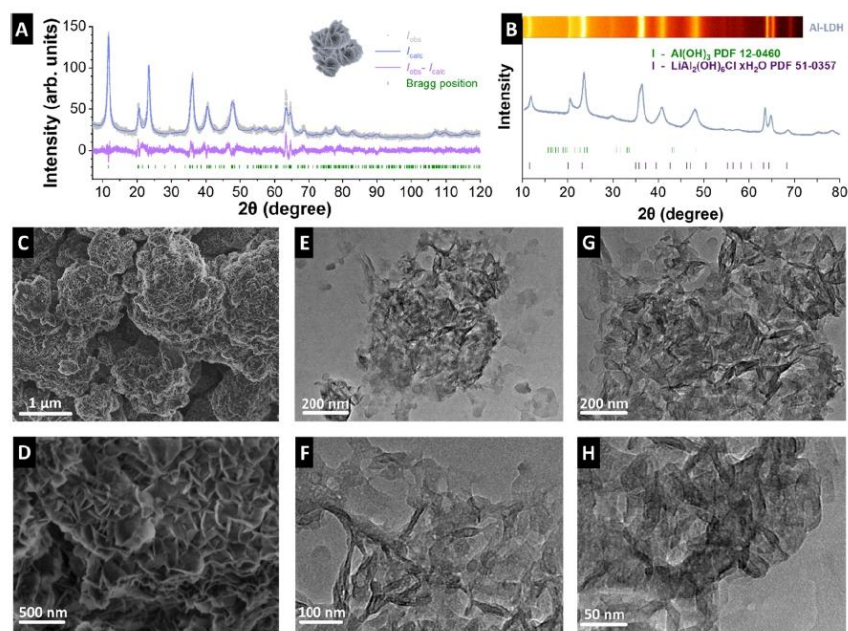
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Published: December 26, 2025





**Figure 1.** (A) X-ray diffractogram and associated Rietveld fitting of Al-LDH. (B) Normalized X-ray diffractograms of Al-LDH. (C and D) Scanning electron micrographs of Al-LDH at different magnifications. (E–H) Transmission electron micrographs of Al-LDH.



Supporting Information

**Acid-Free Electrochemical Regeneration of Sandrose-like  
Aluminum Layered Double Hydroxide Electrodes  
for Selective Lithium-Ion Recovery in Mixed Ion Solution**

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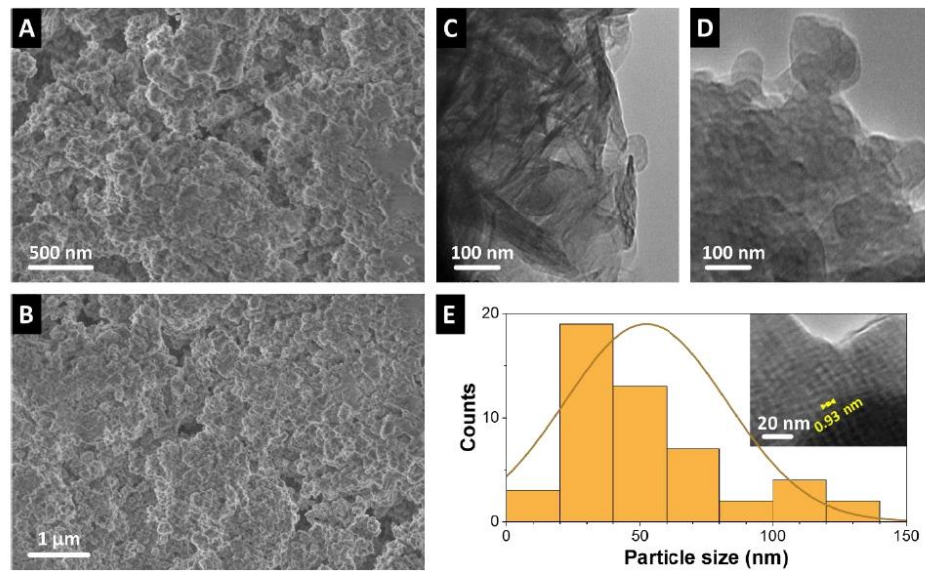
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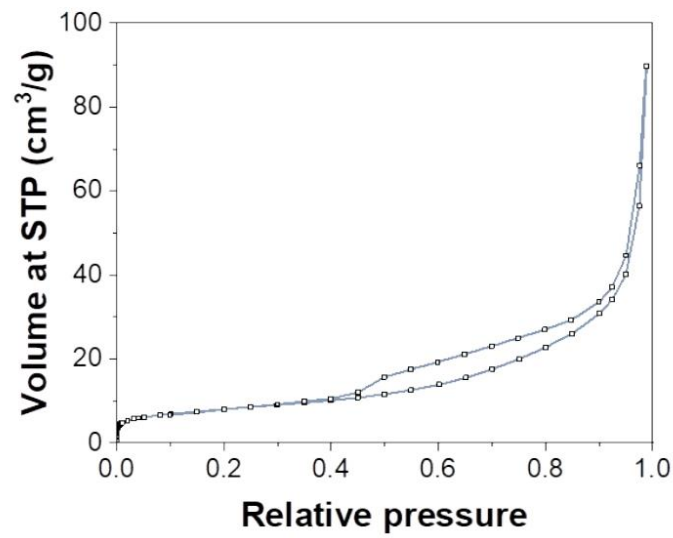
**Content (5 pages):**

Additional material characterization of the electrodes: SEM and TEM of the Al(OH)<sub>3</sub>. Nitrogen gas sorption analysis of the Al(OH)<sub>3</sub> electrode. Analytical dataset of washing stages. XPS of C1s of Al-LDH. XRD of the Al-LDH and post mortem electrode after 15 cycles. Cyclic voltammogram of the Al-LDH electrode.

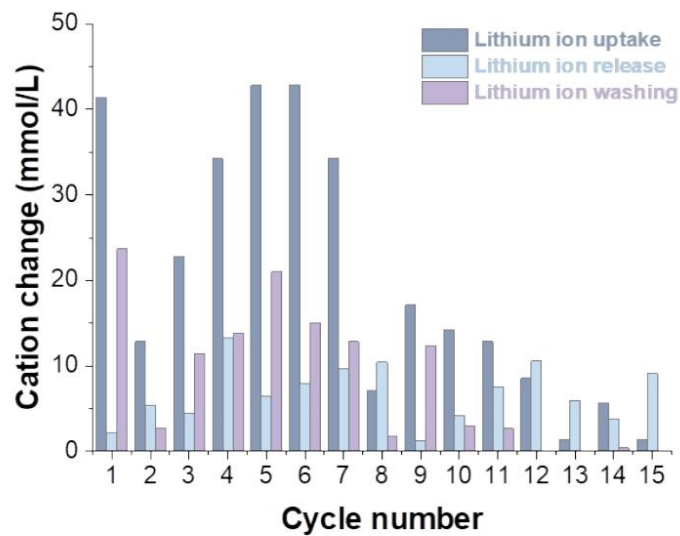
## 1. Supplementary Figures



**Fig. S1.** A-B) Scanning electron micrographs, C-D) Transmission electron micrographs, E) average particle size of the  $\text{Al}(\text{OH})_3$  of 60 counts.



**Fig. S2.** Nitrogen gas sorption isotherm recorded at  $-196^\circ\text{C}$  of the  $\text{Al}(\text{OH})_3$  electrode. (STP: standard temperature and pressure).



**Fig. S3.** Comparison of lithium ion amount after uptake, release, and washing steps.

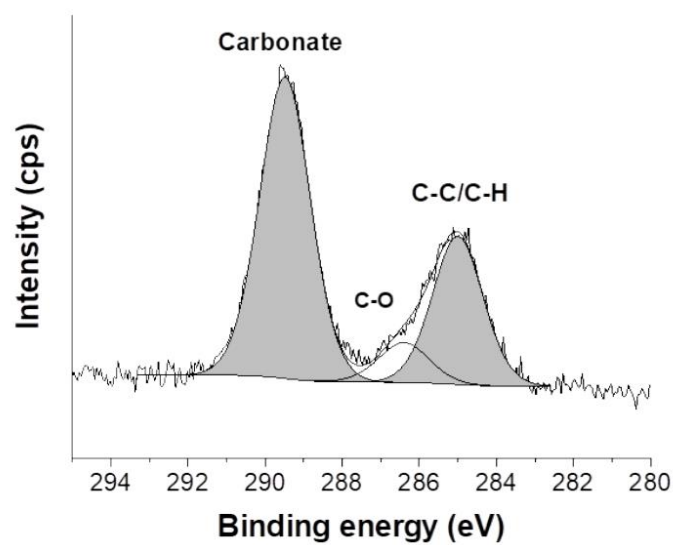


Fig. S4. X-ray photoelectron spectrum of C 1s of Al-LDH.

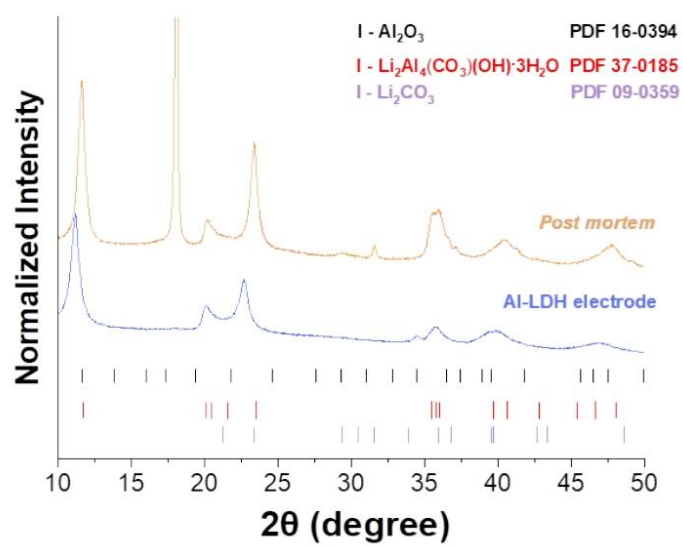
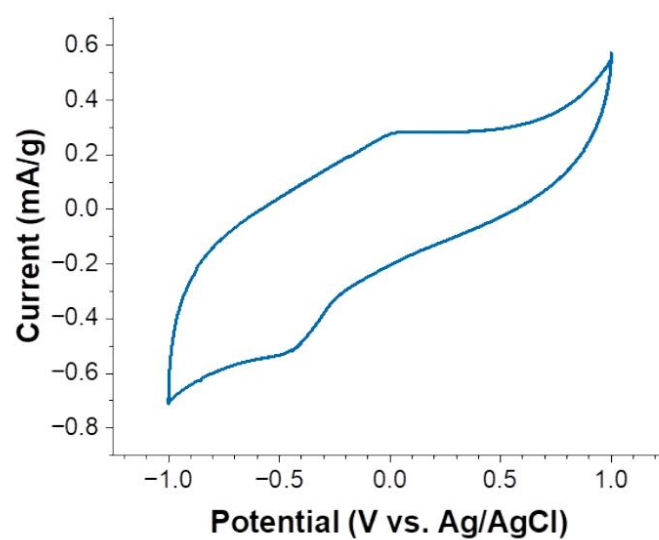


Fig. S5. X-ray diffractograms of the Al-LDH and post mortem electrode after 15 cycles.



**Fig. S6.** Cyclic voltammogram of the Al-LDH electrode at 10 mV/s in 1 M LiCl.

## Publication II

### *Interlayer-Tailored Alkyl-MXenes for Selective Electrochemical Lithium-Ion Extraction*

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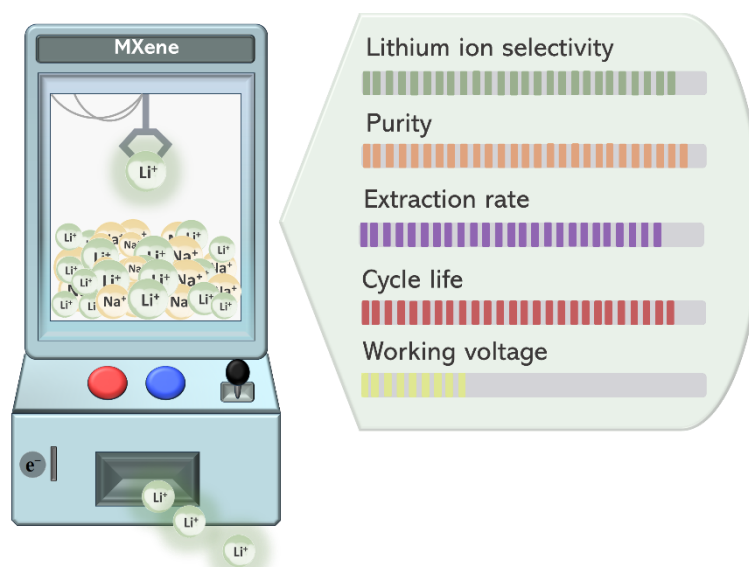
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#### Citation:

C. Kök, K. Eisawi, J.G.A. Ruthes, B. Tan, A. Quade, M. Naguib, V. Presser, Interlayer-Tailored Alkyl-MXenes for Selective Electrochemical Lithium-Ion Extraction, **ACS Energy Letters** (2025).

#### Own contribution:

Methodology, investigation, data curation, validation, writing–original draft, reviewing & editing.



# Interlayer-Tailored Alkyl-MXenes for Selective Electrochemical Lithium-Ion Extraction

Cansu Kök, Karamullah Eisawi, Jean G. A. Ruthes, Burcu Tan, Antje Quade, Michael Naguib, and Volker Presser\*



Cite This: *ACS Energy Lett.* 2026, 11, 508–516



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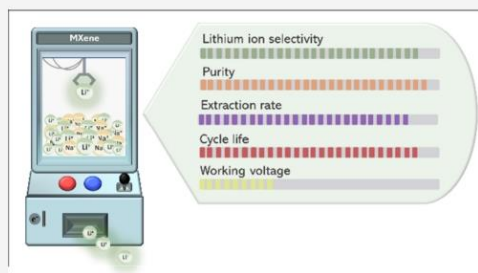
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**ABSTRACT:** The efficient and selective extraction of lithium ions from aqueous media is crucial for resource recovery, yet remains challenging due to the chemical similarity of coexisting alkali ions, such as sodium. In this study, we report a two-step electrochemical strategy that utilizes tailored MXene electrodes for lithium ion extraction with enhanced selectivity and extraction rates. By preintercalating hexadecylamine (HDA) and decyltrimethylammonium (C10), which are long-chain organic molecules, into the  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene structure, we tailored the interlayer environment to favor lithium ions over sodium ions. The HDA-intercalated MXene demonstrated high  $\text{Li}^+/\text{Na}^+$  selectivity with a lithium ion uptake of 2.2 mmol/L and a suppressed sodium ion uptake (<0.2 mmol/L). Extended cycling revealed that molecular preintercalation modulates ion transport pathways and influences structural and electrochemical stability. Both HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  and C10- $\text{Ti}_3\text{C}_2\text{T}_x$  maintained a lithium ion purity of nearly 100% over 50 cycles.



The increasing demand for lithium requires efficient and sustainable extraction technologies.<sup>1</sup> Conventional approaches, such as evaporation ponds and chemical precipitation, are limited by their inefficiency, high energy consumption, and environmental concerns.<sup>2</sup> As a promising alternative, electrochemical lithium ion separation offers high selectivity, low environmental impact, and scalability.<sup>3–5</sup> MXenes, which are two-dimensional transition metal carbides and nitrides, have attracted attention owing to their high electrical conductivity, surface chemistry tunability, and high affinity for cations.<sup>6,7</sup> Their layered structure with surface functional groups enables the precise tuning of their electrochemical properties for lithium-selective separation.<sup>8,9</sup> Furthermore, their high electrical conductivity ensures high charge/discharge rates with mechanical and chemical stability for prolonged electrochemical operations.<sup>10</sup> Recent studies have demonstrated the potential of MXenes in Li-selective electrosorption, revealing high capacity, fast kinetics, and high lithium ion diffusion mobility compared to traditional electrode materials.<sup>11</sup> Strategies such as doping, defect engineering, adjustable interlayer spacing, and composite formation with other nanomaterials can further enhance their lithium selectivity and durability, rendering MXenes a promising platform for sustainable extraction technologies.<sup>12,13</sup>

By modulating surface terminations, the interlayer spacing for ion sieving, and electronic characteristics, MXene-based

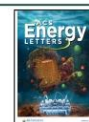
electrodes can achieve enhanced lithium ion adsorption and desorption, thereby facilitating the selective separation of lithium ions from complex brine solutions.<sup>14–17</sup> For example, Chen et al.<sup>8</sup> developed a hybrid membrane by immobilizing a titanium-based lithium ion sieve (HTO) on a polyvinyl chloride (PVC) film and used MXene to enhance its adsorption sites. The resulting HTO/MXene@PVC membrane demonstrated good lithium ion adsorption with a maximum capacity of 25.4 mg/g. Ge et al. proposed a MXene-based composite membrane by incorporating poly(sodium 4-styrenesulfonate) into MXene for  $\text{Li}^+/\text{Mg}^{2+}$  separation.<sup>15</sup> Abdelrahman et al. reported on hydrogel nanocomposite sorbents containing sulfonated graphene oxide (SGO), MXene, and alginate.<sup>16</sup> The sulfonic acid groups on SGO enable selective lithium ion binding by facilitating  $\text{Li}^+/\text{H}^+$  exchange while minimizing interference from other ions. Wang et al. fabricated a flexible hybrid film by embedding  $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$  nanoparticles into a 2D MXene/1D carbon nanofiber structure. The material facilitated rapid lithium ion transport

Received: September 18, 2025

Revised: October 5, 2025

Accepted: October 28, 2025

Published: December 12, 2025





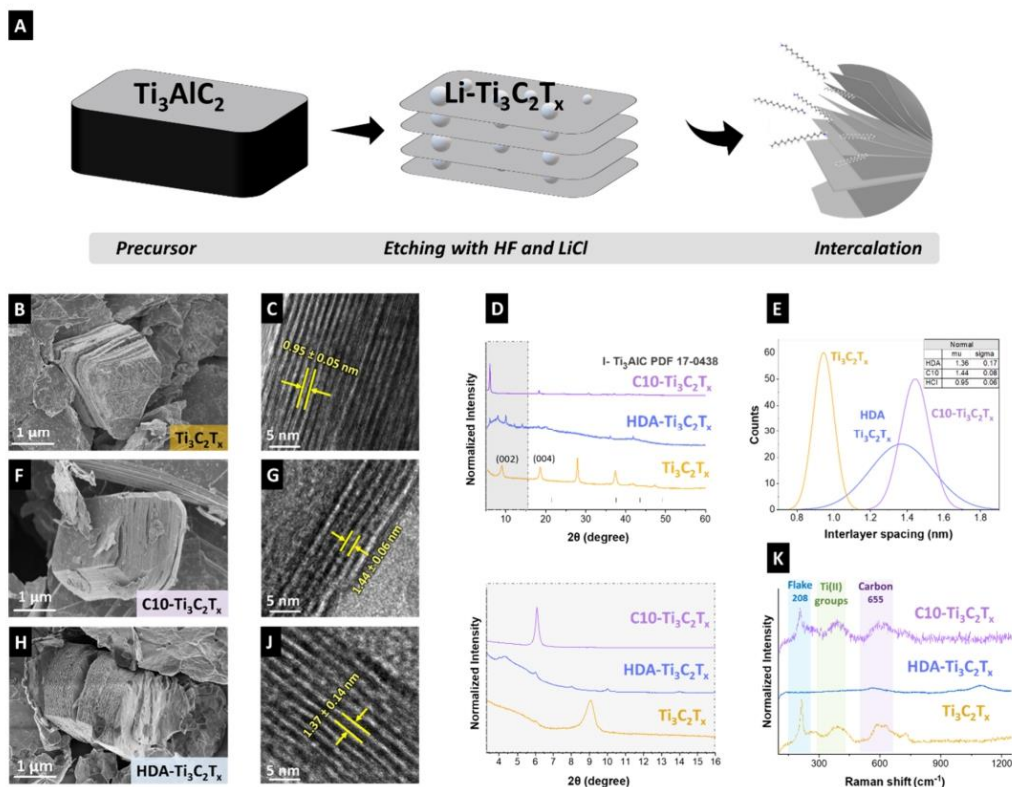


Figure 1. (A) Schematic representation of the synthesis of the MXene. (B–K) Material characterization of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{C10-Ti}_3\text{C}_2\text{T}_x$ , and  $\text{HDA-Ti}_3\text{C}_2\text{T}_x$ . (B,F,H) Scanning electron micrographs of the materials. (C,G,I) Transmission electron micrographs. (D) X-ray diffractograms. (E) Interlayer spacing values of the materials measured via transmission electron microscopy. (K) Raman spectra.

and enhanced lithium ion selectivity by blocking interfering ions through steric hindrance.<sup>17</sup> In particular, it achieved a sorption capacity of 21.4 mg/g, and lithium ion selectivity (e.g.,  $\text{Li}/\text{Na} = 29,232$  and  $\text{Li}/\text{Mg} = 3,606$ ).<sup>17</sup>

Ren et al.<sup>18</sup> employed a hydrogen bond interaction strategy to integrate 2D MXenes as interfacial agents between  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  and polysulfone, forming a composite membrane. Their design achieved a high lithium sorption capacity of 21.1 mg/g and stable cycling performance. In 2024, Fahem et al.<sup>13</sup> recovered lithium ions through electrosorption using pseudocapacitive electrodes. Composite materials of polystyrenesulfonated MXene (PM) and a sodium titanate/graphene oxide (NG) were synthesized and applied in a single-cell capacitive deionization system.<sup>13</sup> PM and NG electrodes tested in binary, ternary, and quaternary ionic solutions achieved a lithium ion recovery purity ranging from 59% to 96% and 60% to 77%, respectively.<sup>13</sup> The intercalation of alkylammonium ions into the MXene layers effectively modulates their interlayer spacing and surface chemistry, thereby unlocking new application opportunities for MXenes.<sup>19</sup> Particularly, alkylammonium ion preintercalation leads to the formation of pillars that expand the interlayer spacing, enabling the intercalation of large room-temperature ionic liquid cations

and resulting in high energy and power densities in MXene-based supercapacitors.<sup>20</sup>

Although MXene and MXene-based materials exhibit significant potential for lithium ion recovery, research in this area remains limited. To further advance the understanding and efficiency of selective electrochemical lithium ion recovery, our study explored a range of MXene-based materials, with a focus on tunable interlayer spacing. By controlling the interlayer structure, the selective uptake of lithium ions was optimized to enhance the selectivity and overall extraction performance for lithium ion recovery.

Our work highlights the advantages of modifying MXenes with organic molecules for lithium ion extraction. Unlike electrode-level strategies that primarily enhance ion pathways or electrode densities, organic intercalation enables the direct, molecular-level control of interlayer spacing, surface chemistry, and electrostatic environments.<sup>21</sup> This creates selective channels that facilitate lithium ion transport, linking fundamental insights into ion sieving with practical performance and positioning organic-modified MXenes as a highly promising ion-selective material. As illustrated in Figure 1A, a mixture of  $\text{HF}$  and  $\text{LiCl}$  was used during the etching process to simultaneously remove Al and intercalate lithium ions between

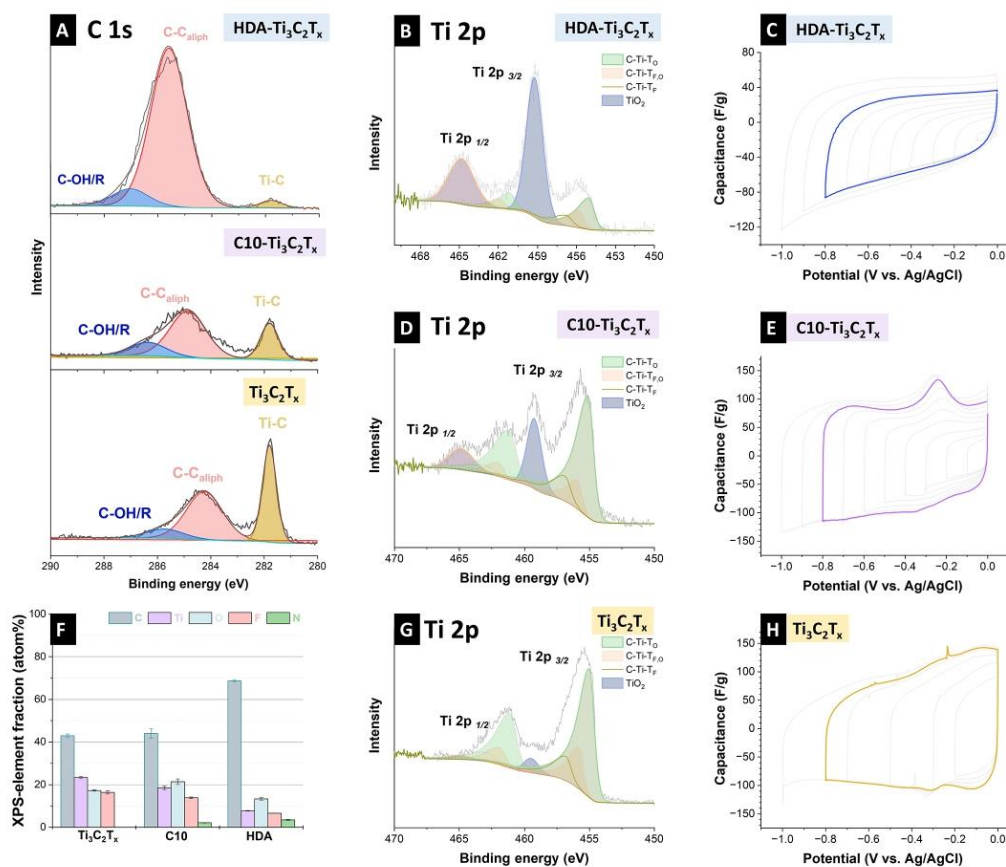


Figure 2. (A-H) Chemical composition and cyclic voltammograms of HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. (A) Comparison of X-ray photoelectron C 1s spectra. (B,D,G) Highly resolved measured Ti 2p peaks. (F) XPS data-derived elemental composition. (C,E,H) Electrochemical window opening via cyclic voltammetry.

the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> layers. Following etching, cation exchange was achieved by replacing lithium ions with ammonium salts or alkylamines, resulting in an increased interlayer spacing due to the incorporation of long alkyl chains. Figures 1B–J show the morphologies of the multilayered structure of pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. X-ray diffractograms of the pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> are presented in Figure 1D, where a progressive shift of the (002) reflection to lower angles was observed with increasing intercalant chain length, confirming the expansion of the interlayer spacing (Figure 1E).

Raman spectroscopy showed the presence of the D-band and G-band of incompletely graphitic carbon (Figure 1K).<sup>22</sup> The characteristic signals at 215 cm<sup>-1</sup>, 394 cm<sup>-1</sup>, and 605 cm<sup>-1</sup> correspond to out-of-plane (A<sub>1g</sub>) and in-plane (E<sub>g</sub>) shifts, characteristics of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene flakes, documenting Al removal from the initial MAX phase and the successful synthesis of MXene.<sup>23</sup> The shifts at 394 cm<sup>-1</sup> were attributed

to the E<sub>g</sub> of Ti atoms, and the bands at 605 cm<sup>-1</sup> were in the range of carbon vibrations (A<sub>1g</sub>-E<sub>g</sub>).<sup>24</sup>

X-ray photoelectron survey spectra showed the presence of O, F, Ti, and C at the surface of the samples (Supporting Information, Figure S1). The C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> samples contained additional N and only traces of Cl (Figure 2F). In addition to aliphatically and hydroxidically bound carbon, all C 1s signals showed a distinct peak at a lower binding energy of 281.8 eV, which could be assigned to the carbide bond (Figure 2A). The highly resolved Ti 2p spectra were fitted with four doublets corresponding to the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> states in Ti-C with different surface terminations (C-Ti-T<sub>2</sub>O, C-Ti-T<sub>2</sub>F<sub>2</sub>O, C-Ti-T<sub>2</sub>F), and TiO<sub>2</sub> surroundings, respectively.<sup>25–27</sup> A Shirley background was selected for all peaks. Owing to their conductivity, asymmetric line shapes were employed for the MXene components, whereas a symmetric line shape was used for the oxide.<sup>25</sup> The energetic difference ΔTi 2p, which was due to spin–orbital splitting, was

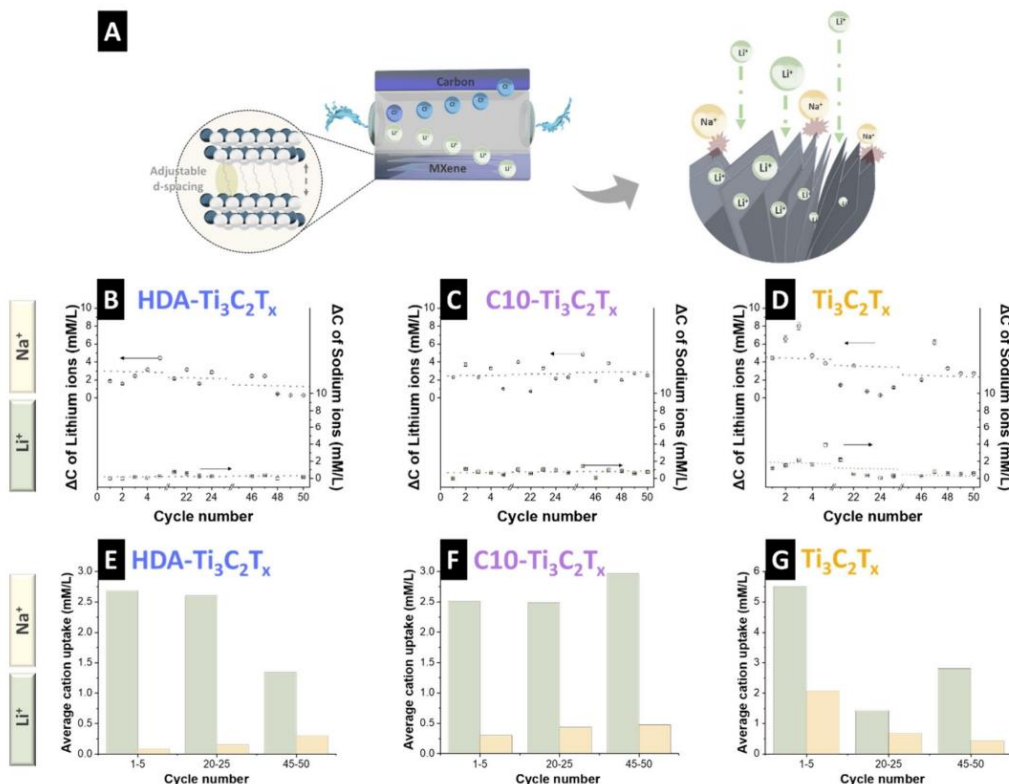


Figure 3. (A) Schematic representation of the electrochemical lithium ion extraction system. Cation uptake of the electrodes for (B) HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (C) C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and (D) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. Average cation uptake of the electrodes for (E) HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, (F) C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and (G) pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.

set to 6.1 eV for the MXene components. For the oxide component, ΔTi 2p was set to 5.6 eV.<sup>25,27</sup>

The Ti 2p<sub>3/2</sub> peak at 459.2 eV was attributed to TiO<sub>2</sub> species. The peaks located at 455.1, 455.9, and 456.9 eV were assigned to C-Ti bonded to O (C-Ti-TiO<sub>2</sub>), C-Ti bonded to both F and O (C-Ti-TiF<sub>2</sub>O), and C-Ti bonded only to F (C-Ti-TiF<sub>3</sub>) (Figure 2B-D,G).<sup>28</sup> The Ti 2p spectrum of the pristine sample exhibited the highest carbide content among the analyzed samples (Figure 2G). In contrast, HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> displayed the lowest carbide contribution and the most pronounced presence of TiO<sub>2</sub> (Figure 2B), suggesting that partial surface oxidation occurred during synthesis (Supporting Information, Figure S2). This oxidation was likely facilitated by the relatively elevated synthesis temperature (75 °C) employed in the preparation process of HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.

The N 1s spectra (Supporting Information, Figure S3) provided direct evidence of N-containing species in the C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> samples. The absence of any peaks at 396.5–396.8 eV corresponding to Ti–N confirmed that these N-species were intercalated rather than covalently bonded terminations of the MXene.<sup>29</sup> For C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, the N 1s at 402.1 eV corresponded to trimethylammonium group –N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>. For HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, the additional peak at 401 eV

could be attributed to protonated amine species R–NH<sub>3</sub><sup>+</sup>.<sup>30</sup> Therefore, both C10 and HDA intercalated as positively charged organic ions, electrostatically interacting with the negatively charged surface of the MXenes while displacing the lithium ions originally present between the MXene layers.<sup>19,31</sup> Evidently, the long alkyl chains stabilized the expanded interlayer spacing, which was consistent with the structural changes observed in the X-ray diffractograms.

Comparative electrochemical data demonstrated that the surface modifications of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene materials influenced their ion selectivity (Figure 2C,E,H). In 1 M NaCl, HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibited higher current responses across various scan rates, indicating faster kinetics than that of pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, which showed lower and less symmetric cyclic voltammograms (Supporting Information, Figure S4). In 1 M LiCl, all the samples display increased current densities relative to NaCl, with C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> showing prominent redox features, indicating favorable lithium ion intercalation.

The cyclic voltammograms revealed that HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> enhanced lithium ion intercalation over sodium ions in different electrolytes at 1 mV/s, while pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> demonstrated a stronger sodium ion response (Supporting Information, Figure S4G–J). This selectivity was attributed to



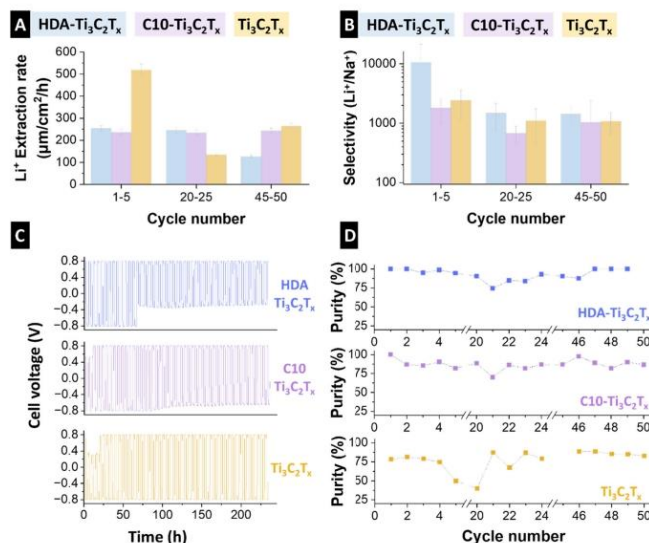


Figure 4. (A) Lithium ion extraction rate of the electrodes. (B) Lithium ion vs sodium ion selectivity of the electrodes. (C) Stability test of the electrodes for operation within  $-0.8$  V to  $+0.8$  V. (D) Purity of the recovery solution.

the electrostatic and coordination interactions between Li ions and the functional groups of the alkyl chains. Owing to their higher charge density and stronger Lewis acidity compared to sodium ions, lithium ions can establish more stable ion-dipole interactions with electron-rich sites along the alkyl chains. In contrast, such interactions are energetically less favorable for sodium ions.<sup>32</sup> The specific capacitance of the three MXene electrodes was evaluated at a scan rate of 1 mV/s over a 0–0.8 V window in 1 M LiCl (Supporting Information, Table S1). HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> yielded capacitances of 37 and 54 F/g, respectively, while the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> sample showed an intermediate capacitance of 23 F/g. Thus, the surface modification and synthesis approach significantly influenced the electrochemical performance.

The two-step lithium ion extraction process is illustrated in Figure 3A. In the first step, the application of an external potential drove lithium ion intercalation while rejecting sodium ions and reversing the potential released lithium ions back into the solution. Figure 3B–D presents the variations in the lithium ion and sodium ion concentrations observed for the different MXene-based electrodes over 50 cycles. HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> stably extracted lithium ions with minimal sodium ion uptake (2.2 mmol/L and 0.18 mmol/L, respectively) (Figure 3B–E). A comparable trend was observed for C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>; however, a small degree of sodium ion uptake was detected (2.7 mmol/L and 0.4 mmol/L, respectively) (Figure 3C–F). In contrast, the pristine electrode exhibited unstable cycling and the highest lithium ion uptake (3.3 mmol/L) (Figure 3D–G) but with significant sodium ion uptake (1.1 mmol/L), likely due to insufficient control over the interlayer spacing.

Although pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibited the highest lithium ion intercalation capacity, it also demonstrated lower selectivity, as evidenced by its substantial sodium ion uptake. Thus, expanding the interlayer spacing through molecular intercalation significantly enhanced the lithium ion selectivity. Among

the tested electrodes, HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibited the best performance, combining a high Li-ion uptake with pronounced Na-ion exclusion. These results indicate a compatibility threshold between the solvated ionic diameter and interlayer spacing of the layered materials.<sup>32</sup> Pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with a relatively narrow interlayer spacing of 0.95 nm (9.5 Å), likely restricted the intercalation of solvated ions, thereby limiting the uptake and desorption performance. In contrast, HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with larger interlayer spacings (1.37 and 1.44 nm, respectively), were more accommodating to solvated ions, potentially enabling more efficient ion diffusion and transport (Figure 1E).

The HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, and pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> materials showed high Li<sup>+</sup>-extraction rates of 207 μm/cm<sup>2</sup>/h, 235 μm/cm<sup>2</sup>/h, and 310 μm/cm<sup>2</sup>/h, respectively (Figure 4A). Although Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> had a high initial extraction rate during the first five cycles, its performance declined between cycles 20 and 25, likely because of its unmodified nature. In contrast, the extraction rates of HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> remained relatively stable.

All electrodes exhibited a higher initial Li<sup>+</sup>/Na<sup>+</sup> selectivity (Figure 4B) that decreased over time. HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibited the highest early cycle (~10,600) and late-cycle (~1,400) selectivities, confirming the effectiveness of HDA intercalation in favoring Li ions. For comparison, the late-cycle (i.e., cycles 45–50) Li<sup>+</sup>/Na<sup>+</sup> selectivities of C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> were lower (~1,000). The relatively high selectivity of pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is attributed to the LiCl treatment during synthesis, which preloads lithium ions into the interlayer galleries, effectively templating the structure and lowering the energy barrier for lithium ion insertion or exchange compared to other ions.<sup>33–36</sup> Post-mortem SEM confirmed structural degradation after 50 cycles, particularly for pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, where the intercalated structure was no longer visible (Supporting Information, Figure S5). The absence of distinct

X-ray reflections may indicate a significant expansion in the interlayer spacing beyond the detection limit of XRD used in this study. Alternatively, this could reflect the structural degradation and amorphization of MXene (Supporting Information, Figure S5).<sup>37</sup> The measured increase in the lithium ion extraction rate of pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  during cycles 45–50 may be attributed to electrochemically induced interlayer expansion over cycling. Unlike preintercalated materials, which initially benefit from expanded spacing, pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  appeared to undergo progressive structural activation, likely owing to gradual  $\text{Li}^+$ /solvent intercalation. This late-stage expansion enhanced the lithium ion mobility and temporarily improved the purity and extraction rates.

To investigate this phenomenon, we evaluated the electrode stability through extended charge–discharge cycling with the aim of elucidating the correlation between structural degradation and selectivity loss over time (Figure 4C). HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  exhibited a higher degradation rate than the other electrodes. Despite the tailoring effect of long-chain alkylamines, such as HDA, on the MXene structure, their incorporation may introduce trade-offs, including a reduced electrical conductivity, hindered ion transport, and limited electrochemical accessibility owing to the insulating and sterically bulky nature of the organic chains.<sup>7,38</sup> Degradation may also occur by the action of bulk aqueous electrolytes on the interlayer spacing, not just ions. Such a continuous exposure of the interlayer spacing to the aqueous electrolyte may accelerate MXene degradation.

A key challenge in Li extraction is maximizing both the rate and purity, because faster methods often reduce selectivity. The MXene electrodes exhibited both high purity and promising Li-ion extraction capacity (Figure 4D). HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  and C10- $\text{Ti}_3\text{C}_2\text{T}_x$  maintained nearly 100% purity after 50 cycles, whereas the purity of pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  significantly decreased to 30% with an unstable performance.

HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  and C10- $\text{Ti}_3\text{C}_2\text{T}_x$  exhibited an average  $\text{Li}^+/\text{Na}^+$  selectivity of approximately 1500, which is competitive with that of advanced lithium ion selective materials (Table 1). Lithium superionic conductors achieve a higher selectivity ( $10^4$ – $10^6$ ) but face flux and scalability challenges.<sup>39–41</sup> Diffusion-based methods and LFP electrodes report similar selectivity (900–1000), but with limited recovery or cycling

stability.<sup>5</sup>  $\text{LiMn}_2\text{O}_4$  exhibits high diffusion coefficients ( $10^{-9}$ – $10^{-11}$   $\text{cm}^2\text{s}^{-1}$ ), structural stability, and low cost, with optimized electrodes reaching selectivity near 1000.<sup>42</sup> Manganese-based adsorbents also show substantial selectivity ( $\text{Li}^+/\text{Na}^+ = 371$ ) in sodium-rich wastewater.<sup>43</sup> Although the HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  selectivity decreased with time, its initial performance rivals or exceeds that of leading membranes and adsorbents, underscoring its potential for practical lithium extraction where both selectivity and durability are important.

This study elucidates the efficacy of interlayer engineering in MXene-based electrodes for the selective extraction of lithium ions using an electrochemical cycling process. The tailored MXenes, particularly those preintercalated with HDA, exhibited an excellent combination of high lithium ion uptake and high sodium ion rejection, outperforming their C10- $\text{Ti}_3\text{C}_2\text{T}_x$  and pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  counterparts. The  $\text{Li}^+/\text{Na}^+$  selectivity observed for HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  highlights the role of alkyl chains in modulating the interlayer chemistry and enhancing ion sieving. Pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  exhibited the highest lithium ion uptake but lower selectivity and stability. Long-term cycling revealed a stable performance for C10- $\text{Ti}_3\text{C}_2\text{T}_x$ . Conversely, structural degradation was observed for HDA- $\text{Ti}_3\text{C}_2\text{T}_x$ , which was attributed to the oxidative instability of bulky organic chains that compromised the electrochemical accessibility and transport kinetics. HDA- $\text{Ti}_3\text{C}_2\text{T}_x$  and C10- $\text{Ti}_3\text{C}_2\text{T}_x$  retained lithium ion purity levels approaching 100% over 50 cycles, in contrast to the 30% decrease observed for pristine MXene. Therefore, interlayer functionalization is an effective strategy for advancing MXene electrodes toward high-rate, high-purity lithium ion extraction, thereby bridging the gap between ion selectivity and operational stability in aqueous electrochemical systems. This way, lithium ion harvesting from natural media<sup>4</sup> or within the context of lithium-ion battery recycling<sup>44</sup> may enable circular applications.<sup>39</sup>

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data can be made available upon request.

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenenergylett.5c03009>.

Experimental description, details on the material synthesis, XPS survey spectra of the electrodes, *post-mortem* SEM of the electrodes, *post-mortem* XRD of the electrodes, data obtained from cyclic voltammetry, and key performance metrics of the electrodes (PDF)

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**Table 1. Lithium-Ion Selectivity Values in This Study Compared to Existing Literature on Advanced Materials**

| Material                                                       | Lithium ion selectivity component | Lithium ion selectivity | Reference |
|----------------------------------------------------------------|-----------------------------------|-------------------------|-----------|
| M-T-LIS                                                        | adsorbent                         | 674                     | 45        |
| $\lambda$ - $\text{MnO}_2$                                     | adsorbent                         | $3.4 \times 10^4$       | 46        |
| 12-Crown-4 ether                                               | membrane                          | $(5-1.0) \times 10^2$   | 47        |
| Spiropyran crown ether                                         | membrane                          | $1.0 \times 10^3$       | 48        |
| Polyamide (PA)                                                 | membrane                          | $4.0 \times 10^3$       | 49        |
| $\text{LiTi}_2(\text{PO}_4)_3$                                 | membrane                          | ca. $2.6 \times 10^4$   | 39        |
| $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$     | membrane                          | $4.1 \times 10^5$       | 5         |
| $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$ (LLTO)          | membrane                          | $4.5 \times 10^7$       | 50        |
| $\text{LiMn}_2\text{O}_4/\text{Li}_{1-x}\text{Mn}_x\text{O}_4$ | electrode                         | $1.4 \times 10^3$       | 42        |
| $\text{TiO}_2$ -coated $\text{FePO}_4$                         | electrode                         | $1.8 \times 10^4$       | 40        |
| MXene (HDA- $\text{Ti}_3\text{C}_2\text{T}_x$ )                | electrode                         | av. $4.5 \times 10^3$   | This work |



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### Author Contributions

C.K.: methodology, investigation, data curation, validation, writing-original draft. K.E.: investigation, data curation, writing-review and editing. J.G.A.R.: data curation, review and editing. B.T.: data curation, review. A.Q.: data curation, XPS analysis. M.N.: writing-review and editing. V.P.: visualization, writing-review and editing.

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We acknowledge support for the eLiFlow project from the European Union, specifically the European Regional Development Fund (ERDF), and the State of Saarland, Germany. M.N. acknowledges the support from the Alexander von Humboldt Foundation through the Humboldt Research Award.

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Supporting Information

# **Interlayer-tailored alkyl-MXenes for selective electrochemical lithium-ion extraction**

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## Experimental description

### Synthesis of the $\text{Ti}_3\text{AlC}_2$ MAX phase

$\text{Ti}_3\text{AlC}_2$  was synthesized using powders of titanium (-325 mesh, 99%, Thermo Scientific), aluminum (-325 mesh, 99.5%, Thermo Scientific), and graphite (7-11  $\mu\text{m}$ , 99%, Alfa Aesar) in a molar ratio of 3.00:1.20:1.88. The powders were loaded into a high-density polyethylene (HDPE) bottle along with ten yttria-stabilized zirconia balls (10 mm diameter), then mixed using a Turbula T2F mixer at 56 rpm for 3 h. The resulting mixture was transferred to an alumina crucible and placed at the center of an alumina tube furnace. The crucible was heated to 1600 °C for 2 h under continuous argon flow (0.2 L/min), at a ramp rate of 5 °C/min. After thermal treatment, the furnace was allowed to cool naturally to room temperature under an argon atmosphere. The synthesized product, a lightly sintered  $\text{Ti}_3\text{AlC}_2$  brick, was ground and sieved to obtain particles smaller than 45  $\mu\text{m}$ .

### Synthesis of different alkylamine-based intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene

$\text{Ti}_3\text{C}_2\text{T}_x$  was synthesized by selective etching of Al from  $\text{Ti}_3\text{AlC}_2$ .  $\text{Ti}_3\text{AlC}_2$  powder (1 g) was slowly added to a 50 mL solution containing 10 mass% hydrofluoric acid (HF, 48-51%, Acros Organics) and 1 g of lithium chloride (LiCl, 99%, Thermo Scientific) in an HDPE bottle, which was stirred at room temperature for 24 h.(1, 2) The resulting etched powder was then divided into 50 mL centrifuge tubes at a ratio equivalent to 0.5 g of the starting  $\text{Ti}_3\text{AlC}_2$  per tube. To remove excess lithium ions and facilitate subsequent cation exchange, the powders were washed four times with 6 M hydrochloric acid (HCl, 37%, Fischer chemicals), followed by two washes with deionized water to remove residual acid. The protonated wet sediment was either vacuum-filtered to obtain a pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  sample or retained in its wet form for further AA intercalation. Alkylamine-based intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$  MXenes were prepared using a wet chemical approach and cation exchange.(1, 2)

For intercalation by decyl-trimethylammonium (C10), the wet  $\text{Ti}_3\text{C}_2\text{T}_x$  sediment was soaked in 0.5 M of decyl-trimethylammonium bromide ( $\text{C}_{13}\text{H}_{30}\text{BrN}$ , 99%, TCI America) for 4 days at room temperature, with 2 min of daily shaking. The sample was then washed four times with deionized water without shaking, followed by vacuum-assisted filtration and an additional wash with 100 mL of deionized water.

For intercalation by hexadecylamine (HDA), the wet  $\text{Ti}_3\text{C}_2\text{T}_x$  sediment was stirred in 0.5 M HDA ( $\text{C}_{16}\text{H}_{35}\text{N}$ , 95%, TCI America) at 75 °C for 24 h. The sample was then washed four times with deionized water, without shaking, followed by vacuum-assisted filtration, and an additional was with 100 mL of deionized water.

#### **Material characterization**

The structural morphology of the samples was characterized using scanning electron microscopy (SEM) with a ZEISS GEMINI 500 microscope equipped with an Xmax detector (Oxford Instruments). For imaging purposes and spectroscopic analysis, acceleration voltages of 2 kV and 15 kV, respectively, were employed. The samples were carefully mounted on aluminum stubs using copper tape, eliminating the need for additional conductive sputter coating.

High-resolution transmission electron microscopy was performed using a multi-purpose JEM-F200 microscope at an acceleration voltage of 200 kV. To prepare the samples, a copper grid coated with lacey carbon was used as the sample holder. Approximately 15 mg of the powder was dispersed in 15 mL of ethanol using an ultrasonic bath, and the sample was deposited dropwise onto a copper grid.

Phase analysis was performed using X-ray diffraction with a D8 Discover diffractometer (Bruker AXS) equipped with a  $\text{Cu-K}\alpha$  source (40 kV, 40 mA), a Göbel mirror, and a 1 mm point focus. A two-dimensional VANTEC detector captured an angular range of  $20^\circ 2\theta$  for 1000 s, with measurements repeated three times to cover the  $2\text{--}80^\circ 2\theta$  range. All scans underwent background subtraction and were normalized to (0,100). The system was calibrated using the NIST 1976b corundum standard.

Raman spectroscopy was conducted using a Renishaw inVia Raman microscope, which employed a neodymium-doped yttrium aluminum garnet laser with an excitation wavelength and power of 532 nm and 87  $\mu\text{W}$ , respectively, at the focal point of the sample. We chose a magnifying lens with a numeric aperture of 0.75. Before obtaining the measurements, a silicon standard was used to calibrate. Each sample was placed on a glass slide, and spectra from six points were recorded with a 10-s exposure time and accumulated five times. We employed cosmic ray removal and normalized the intensity range to 0-100%.

The concentrations of the feed (50 mM LiCl+ 10 mM NaCl) and recovery (10 mM KCl) solutions were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, ARCOS FHX22, SPECTRO Analytical Instruments). Samples (2 mL) were collected before and after the experiment and injected into the system at a flow rate of 1 mL/min. A correlation was established between the ion concentrations and corresponding signal intensities. Calibration was performed using mixed ion solutions with known concentrations of LiCl, NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> at 1  $\mu$ M, 5  $\mu$ M, 0.1 mM, 0.5 mM, 1 mM, 5 mM, and 10 mM.<sup>(3)</sup>

To detect material variations in the chemical composition and oxidation states at the surfaces, X-ray photoelectron spectroscopy (XPS) was performed using the Kratos Axis Supra system (Kratos Analytical). For sample preparation, loose powders were sprinkled over the surface of a small piece of carbon tape (5  $\times$  5 mm<sup>2</sup>). The powders were then firmly pressed into the tape using the flat side of a freshly cleaned spatula. After the loose powder was removed from the sample surface, a holder was inserted into the XPS load lock. The photon source was a monochromatized Al K $\alpha$  line. Survey spectra were recorded with an analysis area of 300  $\times$  700  $\mu$ m<sup>2</sup> and pass energy of 160 V at 15 kV and 10 mA. A pass energy of 80 eV was selected for acquiring the elemental spectra. The highly resolved measured spectra of Ti 2p and C 1s were recorded at a pass energy and power of 10 eV and 225 W, respectively. All spectra were analyzed using the CasaXPS software (version 2.3.15) and calibrated to the carbide component in the C 1s signal (281.8 eV).

Thermogravimetric analysis was performed using a Netzsch TG-209-1 Libra system to analyze mass changes as the temperature increased to 1000 °C at a heating rate of 5 °C/min in an oxidative (synthetic air) atmosphere within an alumina crucible.

#### **Electrode preparation**

The electrodes were fabricated using vacuum filtration to ensure a uniform structure and optimal performance. MXenes were combined with carbon nanotubes (Nanocyl, NC7000) without the need for binder. The composition mass ratio of the electrodes was 9:1. The material was mixed with carbon nanotubes in ethanol and treated with a tip sonicator (Branson Sonifier 450) for 30 min to obtain a homogeneous mixture at 30% of the maximum

power output. After vacuum filtration, the electrodes were dried in an oven overnight at 60 °C under 6 kPa.

#### Electrochemical characterization

For electrochemical measurements of the cell, discs (30 mm) were punched from the prepared electrode sheets and used as working electrode. An oversized commercially available microporous activated carbon cloth (Kynol ACC-507-20) was used as the counter electrode (30 mm) in a flow-between electrochemical desalination cell with a flow rate of 5 mL/min. (3, 4) The electrodes were separated using a 26 mm round glass fiber filter (GF/A, Whatman). Key performance metrics are listed in *Supporting Information, Table S1*.

Electrochemical window opening measurements were performed using a BioLogic VMP-300 potentiostat/galvanostat in a potential window of -1 V to +1 V vs. Ag/AgCl at a scan rate of 0.1 mV/s. Galvanostatic charge/discharge with potential limitation measurements were conducted in the potential range of -0.8 V to +0.8 V with a holding time of 2 h. Cycling stability tests were performed using chronoamperometry at 0.6 V. All the electrochemical tests were conducted in a climate chamber held at 25±1 °C.

#### Calculations

The lithium ion extraction rate was calculated according to **Eq. (1)**:

$$\text{Lithium ion extraction rate} = \frac{\Delta C_{Li} \times V}{t \times A \times M} \quad (\text{Eq. 1})$$

where  $\Delta C_{Li}$  is the concentration change of lithium ions,  $t$  is the time,  $A$  is the effective area of the electrode,  $M$  is the molar mass of lithium ions, and  $V$  is the volume of the solution.

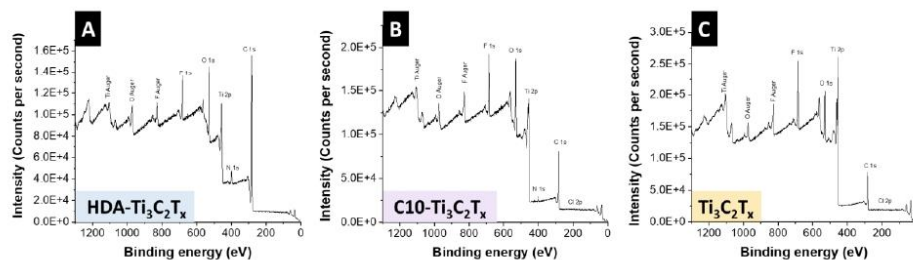
The selectivity in terms of the lithium ion to sodium ion ratio was calculated according to **Eq. (2)**:

$$\text{Selectivity} = \frac{\Delta C_{Li}}{\Delta C_{Na}} \times \frac{C_{Na} \text{ initial}}{C_{Li} \text{ initial}} \quad (\text{Eq. 2})$$

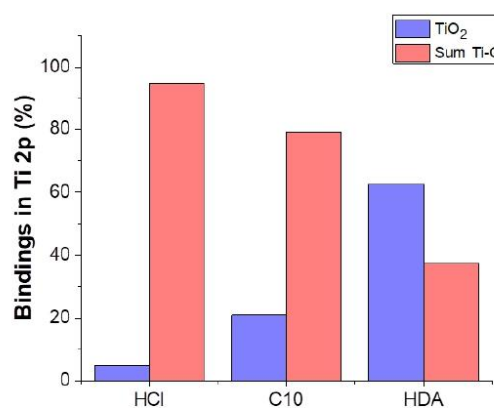
where  $\Delta C_{Li}$  and  $\Delta C_{Na}$  represent the concentration (mg/L) changes of lithium ions and sodium ions cations in the solution, respectively.



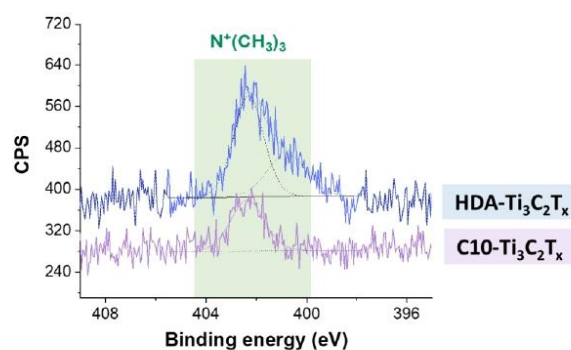
## Supporting Figures



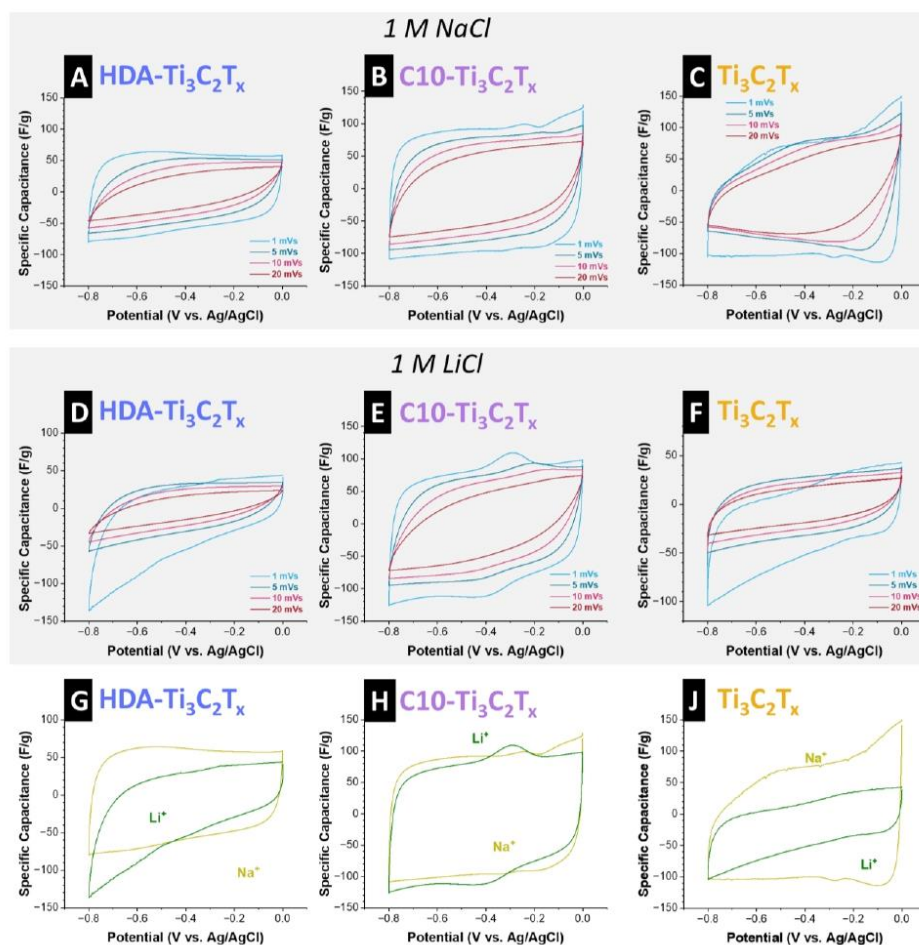
**Figure S1.** X-ray photoelectron survey spectra of the electrodes.



**Figure S2.** Binding values of the MXene materials.



**Figure S3.** N 1s region in the X-ray photoelectron spectra for C10 and HDA intercalated  $\text{Ti}_3\text{C}_2\text{T}_x$ .  
CPS: counts per second.



**Figure S4.** Cyclic voltammograms of the MXene electrodes in different scan rates in the range of 1 mV/s to 20 mV/s: A) HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, B) C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, C) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, D) HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, E) C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, F) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>. Comparison of the electrodes in 1 M NaCl and 1 M LiCl in 1 mV/s: G) HDA-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, H) C10-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, J) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.

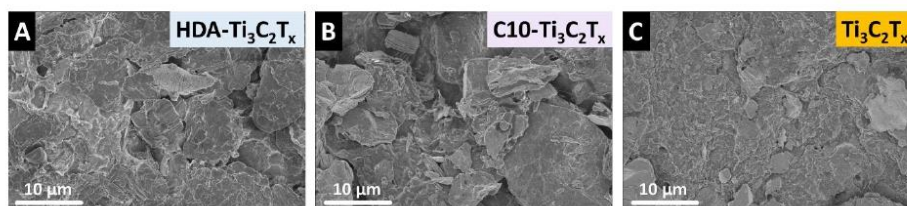


Figure S5. Post-mortem scanning electron micrographs of the electrodes.

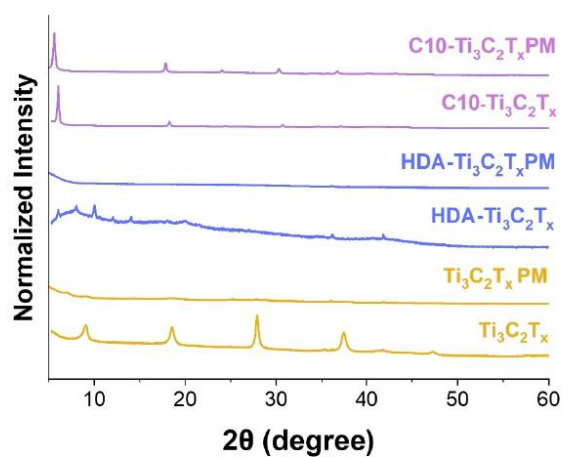


Figure S6. Post-mortem (PM) X-ray diffractograms of the electrodes.

## Supporting Tables

**Table S1:** Data obtained from cyclic voltammetry.

|                                                   | Scan rate<br>(mV/s) | Mass<br>(mg) | Voltage window<br>(ΔV) | Capacitance<br>(F/g) |
|---------------------------------------------------|---------------------|--------------|------------------------|----------------------|
| HDA-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> | 1                   | 16.69        | 0.8                    | 37 F/g               |
| C10-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> | 1                   | 23.56        | 0.8                    | 54 F/g               |
| Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>     | 1                   | 31.12        | 0.8                    | 23 F/g               |

**Table S2:** Key performance metrics of the electrodes.

|                                                        | Electrode<br>thickness (μm) | Mass loading<br>(mg/cm <sup>2</sup> ) | Conductivity<br>(S) | Geometric area<br>(cm <sup>2</sup> ) |
|--------------------------------------------------------|-----------------------------|---------------------------------------|---------------------|--------------------------------------|
| HDA-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>      | 290                         | 21.9                                  | 12.4                | 1.13                                 |
| C10-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>      | 284                         | 29.6                                  | 5.4                 | 1.13                                 |
| Pristine Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> | 302                         | 30.4                                  | 14.6                | 1.13                                 |

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## Publication III

### ***Continuous Lithium-Ion Extraction from Seawater and Mine Water with a Fuel Cell System and Ceramic Membranes***

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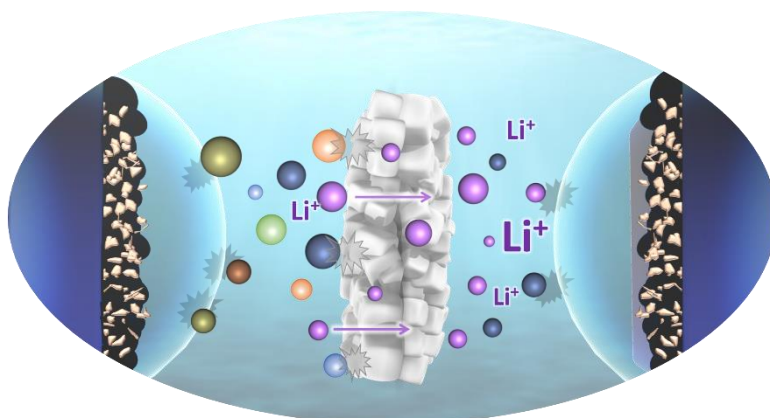
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#### **Citation:**

C. Kök, L. Wang, J.G.A. Ruthes, A. Quade, M.E. Suss, V. Presser, Continuous Lithium-Ion Extraction From Seawater and Mine Water With a Fuel Cell System and Ceramic Membranes, **Energy & Environmental Materials** 7(6) (2024) e12742.

#### **Own contribution:**

Methodology, investigation, data curation, validation, writing–original draft, reviewing & editing.





## RESEARCH ARTICLE

Energy &amp; Environmental Materials WILEY

Water Technology

# Continuous Lithium-Ion Extraction From Seawater and Mine Water With a Fuel Cell System and Ceramic Membranes

Cansu Kök<sup>1</sup>, Lei Wang<sup>1</sup>, Jean Gustavo A. Ruthes<sup>2</sup>, Antje Quade<sup>1</sup>, Matthew E. Suss<sup>3</sup>, and Volker Presser<sup>1\*</sup>

**The demand for electronic devices that utilize lithium is steadily increasing in this rapidly advancing technological world. Obtaining high-purity lithium in an environmentally friendly way is challenging by using commercialized methods. Herein, we propose the first fuel cell system for continuous lithium-ion extraction using a lithium superionic conductor membrane and advanced electrode. The fuel cell system for extracting lithium-ion has demonstrated a twofold increase in the selectivity of  $\text{Li}^+/\text{Na}^+$  while producing electricity. Our data show that the fuel cell with a titania-coated electrode achieves 95% lithium-ion purity while generating 10.23 Wh of energy per gram of lithium. Our investigation revealed that using atomic layer deposition improved the electrode's uniformity, stability, and electrocatalytic activity. After 2000 cycles determined by cyclic voltammetry, the electrode preserved its stability.**

## 1. Introduction

As technological advancements continue and the universal presence of electronic devices persists, the demand for lithium has experienced a substantial upsurge, establishing it as an indispensable constituent in nearly every type of electronic device.<sup>[1]</sup> There are approximately

20 million tons of lithium reserves worldwide, with 90 million tons available from land resources, but the production and conversion process of lithium is complex and time-consuming. It can take up to 16 years from mineral extraction to actual production, even if new mines are discovered.<sup>[2]</sup> For instance, approximately 0.4 million metric tons of lithium carbonate equivalent (LCE) were produced in 2020; production in 2021 exceeded 0.5 million metric tons, up 32% yearly. However, in 2030, the annual lithium demand of 3.3 million metric tons will only be met by 2.7 million metric tons.<sup>[3]</sup> Considering the assumed scenario that there will be a significant increase in the demand for lithium in the upcoming decades, to meet this demand, a total of 17.5 million tons of lithium production will be required between 2008

and 2100.<sup>[4]</sup> Given these constraints, it is crucial to discover efficient sources for extracting lithium.

Lithium extraction from ores is preferred as it allows for a simpler separation of the element and the production of a high-purity end product.<sup>[5]</sup> Although this approach has its benefits, it also has several drawbacks. It heavily relies on weather conditions and incurs high operational costs. Additionally, the brine extraction efficiency is only around 5%, and the method can cause harm to the environment due to the utilization of acid processes like chemical leaching.<sup>[6,7]</sup> Given such high demand and finite availability, new lithium extraction methods are in the spotlight of researchers.

Although the amount of lithium in the oceans is 230 billion tons, seawater's low concentration (approximately 0.2 parts per million, ppm) makes it challenging to extract lithium directly at high purity.<sup>[8,9]</sup> Various methods for extracting lithium directly from seawater include adsorption, ion exchange, and precipitation.<sup>[3]</sup> Electrochemical lithium extraction that utilizes electrodialysis, electrolysis, and capacitive or faradaic electrodes can offer many benefits, including fast ion capture, an easy process, a controlled reaction mechanism, and low energy consumption. However, low practical lithium-ion uptake capacity limits and poor selectivity of commercial membranes make scaling of electrochemical lithium extraction difficult.<sup>[10,11]</sup>

Ceramic membranes based on suitable crystalline materials have acquired great interest because of their high ionic conductivity, chemical stability, electronic area resistance, and thermal stability.<sup>[8]</sup> Hoshino proposed the extraction of lithium from seawater with Li superionic conductor as the Li separation membrane (LISM) by dialysis process.

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DOI: 10.1002/eem2.12742

Energy Environ. Mater. 2024, 7, e12742

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The lithium recovery rate increased by 7% after 72 h without an electrical supply.<sup>[12]</sup> Li et al. have studied glass-type  $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$  (LLTO) membranes to recover lithium from seawater. They have shown that lithium enrichment from seawater reached about 9000 ppm after a 5-stage treatment.<sup>[13]</sup> Shen et al. used a flexible LATP/PVDF-HFP composite membrane in an electrocatalytically driven lithium extraction device using Pt/C and  $\text{RuO}_2$  electrocatalysts. They reached  $4.8 \times 10^{-3} \text{ mol (m}^2 \text{ h)}^{-1}$  as the lithium extraction rate.  $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  (LAGP) structured lithium superionic conductor (LISICON) type materials with high Li-ion conductivity show high chemical and electrochemical stability with a wide electrochemical window.<sup>[14]</sup> Wang et al. have developed a redox flow battery (LE-RFB) for continuous lithium recovery. The lithium-ion extraction rate for LE-RFB is reported  $0.04 \text{ mg (hcm}^2)^{-1}$ , and the energy consumption is  $2.5 \text{ Wh g}^{-1}$  for the system.<sup>[15]</sup> Still, these devices continuously consume energy without any energy conversion.

Fuel cells are remarkable examples of energy production systems because of their renewability, accessibility, and zero carbon emissions.<sup>[16,17]</sup> The first energy conversion and storage system using seawater related to fuel cells was proposed by Khalla et al. in 2019. The system simultaneously desalinated water and generated electricity, with an output of up to  $23.5 \text{ kWh m}^{-3}$  of desalinated water.<sup>[18]</sup> Zhang et al. proposed a continuous desalination with a fuel cell. They generated  $67 \text{ mWh}$  of electricity by removing  $1 \text{ g}$  of NaCl using a Pt-based electrocatalyst.<sup>[19]</sup> One of the biggest obstacles affecting fuel cell performance is the low stability of the electrocatalyst.<sup>[20]</sup> Among the common catalysts, platinum has a long lifespan, can work at low temperatures, and only requires small amounts. However, particle size, particle migration and incorporation on catalysts, electrochemical Ostwald ripening, and dissolution/precipitation of Pt are known to reduce the power output of fuel cells.<sup>[21,22]</sup> Also, because the feed water used in the fuel cell is seawater,  $\text{Cl}^-$  ions are readily adsorbed on the Pt surface and block the catalyst's active site, thereby reducing the electrochemically active surface area for ORR.<sup>[23]</sup> Among transition metal oxides (TMOs) that are preferred to enhance the electrocatalytic activity and increase stability, titania is a good candidate for metal support, providing high chemical stability, catalytic activity, and mechanical resistance.<sup>[24,25]</sup> However, excessive deposition of the titania on the catalyst surface can prevent reactions on the electrode surface, leading to a decrease in the catalyst's performance. Atomic layer deposition (ALD) is a highly effective method that allows controlled dispersion of ultra-thin material thicknesses.<sup>[26,27]</sup>

Here, we propose a high-rate lithium recovery and electricity generation system enabled by a lithium-ion extraction fuel cell device (FCD-LE). We investigated titania-coated gas diffusion electrodes prepared by ALD to obtain homogeneous and ordered transition metal oxide layers. We also reported a highly selective LISICON ceramic membrane and tested the cell performance with various solutions. The findings indicate that the system reaches 95% purity compared to the ratio of lithium-ions to other cations and selectivity with the titania-coated electrode for  $\text{Li}^+/\text{Na}^+$  compared to the bare electrode.

## 2. Results and Discussion

### 2.1. Principle of the FCD-LE

Combining fuel cell operation (for energy generation) and lithium-ion extraction, our system consists of cells with three compartments: anolyte, catholyte, and feed water channel (Figure 1a). The LISICON and

anion-exchange membrane (AEM) were placed between electrodes, which separated the middle chamber (i.e., feed water channel) from the electrode chamber. In the FCD-LE system, hydrogen and oxygen sources are provided by the proton-exchange membrane (PEM) electrolysis cell, where water is split into  $\text{H}_2$  and  $\text{O}_2$  molecules by applying  $1.23 \text{ V}$  to the electrolysis system. The FCD-LE system is fed with hydrogen and oxygen gases. Simultaneously, HOR and ORR occur; hydrogen is oxidized on the anode side, and oxygen is reduced on the cathode side (Equations 1 and 2).



While the system is fed with feedwater and gases (hydrogen and oxygen),  $\text{Li}^+$  ions contribute to forming  $\text{LiOH (aq)}$  by passing into the cathode channel with the help of the lithium selective membrane.  $\text{Cl}^-$  ions migrate through the anion-exchange membrane into the anolyte channel and combine with  $\text{H}^+$  ions to form aqueous HCl.

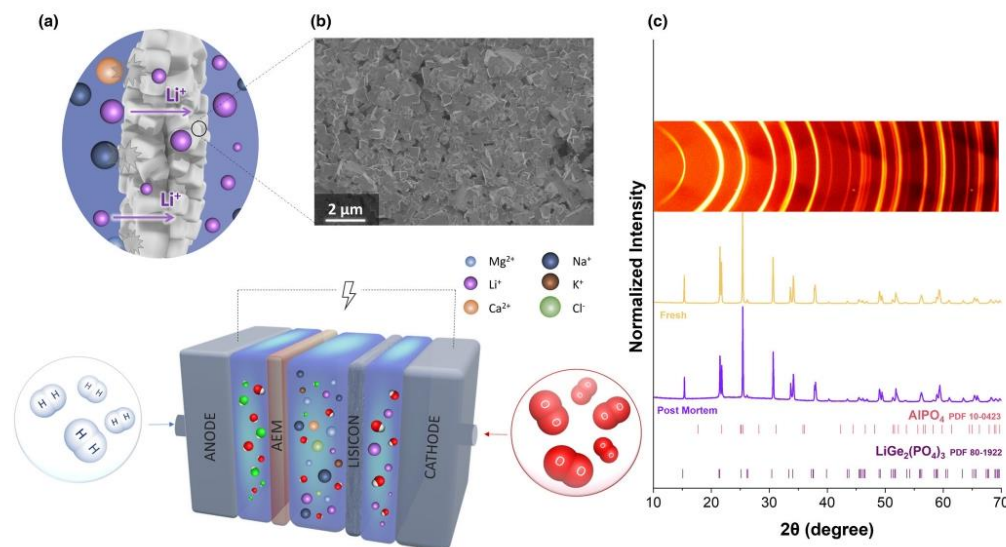
The  $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  ( $x = 0.5$ , LAGP) ceramic membrane accomplishes selective separation of  $\text{Li}^+$  ions toward the other cations from the lithium-ion-containing feedwater.<sup>[15]</sup> Cross-sectional and micrographs of the LISICON membrane and surface morphology of electrodes were characterized by scanning electron microscopy (SEM). The micrographs indicate that the membrane consists of dense, cuboidal-shaped interlocked crystals (Figure 1b). Higher magnification images exhibit interlocked granular forms with large and small grain sizes up to  $1 \mu\text{m}$ .

X-ray diffraction (XRD) and Rietveld analysis confirmed the successful synthesis of LISICON. No significant trace of impurities from  $\text{AlPO}_4$  was found in the structure, and the measured diffraction patterns match the LAGP structure. LISICON has a rhombohedral space group  $\text{R}\bar{3}\text{c}$  (167) with the lattice parameters  $a = 8.2782 \text{ \AA}$ ,  $c = 20.6306 \text{ \AA}$ . Smooth and continuous Debye rings observed in the scattering image exhibit that the structure is polycrystalline and fine-grained (Figure 1c).<sup>[15,28]</sup>

Titania was deposited on the PtC electrode with ALD to prevent platinum poisoning and to increase electrode stability during electrocatalytic reactions. Titania is homogeneously distributed on the PtC surface according to TEM images. The average particle number distribution supports that the structure is homogeneous (Figure 2a,b). X-ray diffractograms show  $\text{TiO}_2$ -related reflections overlapping the graphitic carbon (002) reflection. The reflections at  $20^\circ$   $2\theta$ ,  $30$ – $32^\circ$   $2\theta$ , and  $38^\circ$   $2\theta$  demonstrate the successful deposition of the anatase phase of  $\text{TiO}_2$  (Figure 2c). Scanning electron micrographs also indicated a homogeneous deposition of titania onto the electrode surface (Figure 2d,e). The characteristic Raman modes of carbon were observed at  $1354$  and  $1595 \text{ cm}^{-1}$ ,<sup>[29]</sup> and after titania coating, anatase shifts were observed at  $144$ ,  $327$ ,  $394$ ,  $456$ , and  $713 \text{ cm}^{-1}$  (Figure 2f,g).<sup>[30]</sup>

X-ray photoelectron spectroscopy (XPS) was used to examine the changes in the peak positions of the samples and the changes in the surface chemistry. Overview spectra confirmed the presence of Pt, C, F, O, N, and S (Figure S2, Supporting Information). The PtC sample contains only C, Pt, and F from the polytetrafluoroethylene binder and traces of O, N, and S, while the titania-loaded PtC samples additionally contain Ti. The peaks at  $458.6$  and  $464.3 \text{ eV}$  confirm the presence of  $\text{Ti}^{4+}$  ( $2\text{p}_{3/2}$  binding energy (BE):  $458.6 \text{ eV}$ ,  $2\text{p}_{1/2}$  BE:  $464.3 \text{ eV}$  (Figure 2h)).

In the FCD-LE system, fueled by oxygen and hydrogen gases, HOR occurs at the anode and ORR at the cathode (Figure 3a). The



**Figure 1.** a) Schematic representation of the Li-extraction fuel cell system fed via hydrogen–oxygen gases in seawater and the selectivity of the LISICON toward other ions, b) scanning electron micrograph of LISICON structure, c) normalized X-ray diffractograms and two-dimensional X-ray scattering image of the ceramic LISICON before and after 5 h measurements.

HOR/ORR electrocatalytic activities of the catalysts in alkaline media using a rotation disk electrode method with a three-electrode system in 0.1 M KOH (Figure 3b,c). TiO<sub>2</sub>/PtC exhibited a smaller half-wave potential ( $E_{1/2}$ ) of  $-0.11$  V with an onset potential of  $0.08$  V than PtC ( $-0.03$  V) with an onset potential of  $0.15$  V for ORR (Figure 3b). The electrochemical HOR activity of the TiO<sub>2</sub>/PtC electrode is significantly enhanced compared with that of PtC (Figure 3c). This difference in the curves indicates that stronger metal transition interactions improve electron-transfer kinetics and improved electrocatalytic activity enabled by titania layers deposited by ALD has been reported for other systems before.<sup>[31,32]</sup> To examine the ORR and HOR activities, cyclic voltammetry measurements were conducted on the TiO<sub>2</sub>/PtC electrode after saturating it with N<sub>2</sub> and O<sub>2</sub> gases (Figure S3a, Supporting Information). The electrode that was saturated with O<sub>2</sub> displayed a peak at approximately  $0.61$  V (Figure S4a, Supporting Information). Figure 3d and Figure S3b, Supporting Information reveal ORR-HOR activities of TiO<sub>2</sub>/PtC electrodes at different rotational speeds.

Stability tests were measured with chronoamperometry and cyclic voltammetry (Figure 3e,f). Cyclic voltammetry tests were performed at  $50 \text{ mV s}^{-1}$  for 5000 cycles. Even after 5000 cycles, there was slight degradation in the catalyst's performance for HOR (Figure 3f). Due to its corrosion resistance, homogeneous dispersions of titania particles on the electrode surface may act like a shield, preserving the electrode's lifetime. Chronoamperometric measurements examined the performance of the electrodes against time for ORR (Figure S4b, Supporting Information). The results established that the TiO<sub>2</sub> electrode provided significant stability.

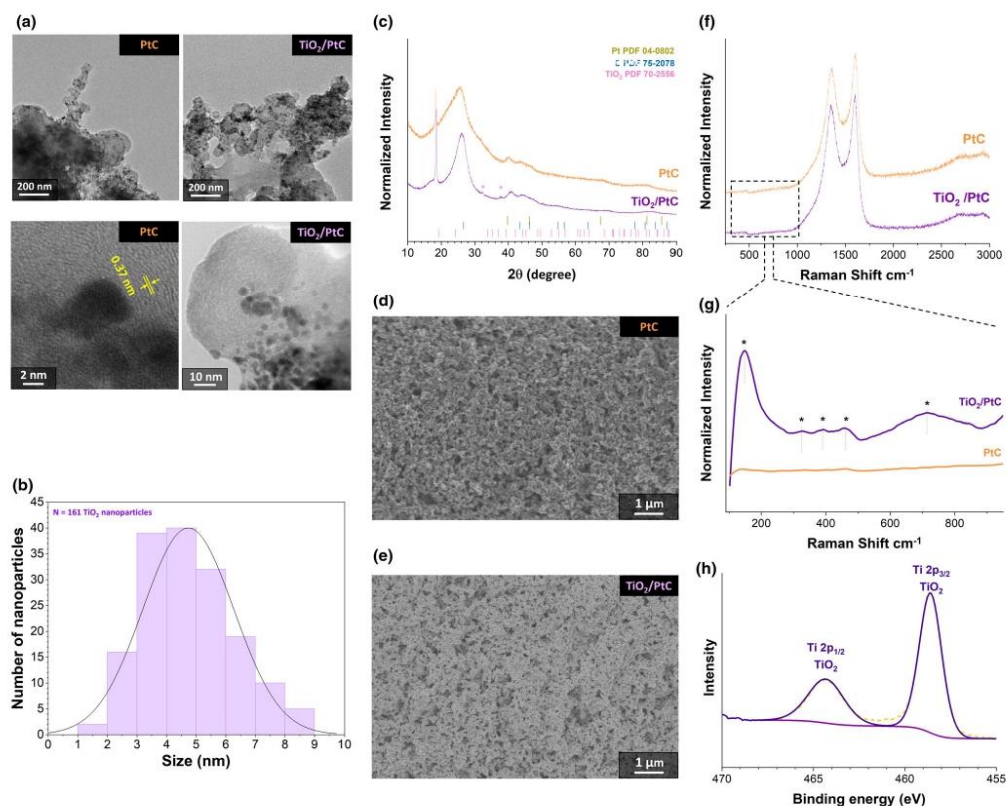
Thermogravimetric analysis (TGA) was performed to determine the thermal ejection of components and degradation of the material for

the electrodes and LISICON membrane. We observed a mass loss of 46% for PtC and 21% for TiO<sub>2</sub>/PtC. The degradation of the TiO<sub>2</sub>/PtC electrode was significantly reduced after titania coating (Figure S5a, Supporting Information). While the degradation of PtC increases linearly after  $560^\circ\text{C}$  for TiO<sub>2</sub>/PtC, the degradation remained more likely stable. We also examined the thermal behavior of LISICON in argon (Figure S5b, Supporting Information). The breakpoint at  $425^\circ\text{C}$  is probably the volatilization temperature of the lithium salt. The mass loss was 1.2%, which verifies that the LISICON membrane was very durable at the end of  $1000^\circ\text{C}$ .

## 2.2. Performance of the FCD-LE System

Polarization curves help to evaluate the fuel cell performance and analyze the relationship between current and cell voltage. There are three typical regions of potential loss, which vary depending on different factors such as catalyst type, membrane thickness, and electrical conductivity of cell components.<sup>[28]</sup> The activation losses, or kinetic polarization, related to the electrochemical reactions on the electrode surface hinges on the catalyst type, electrochemical active area, and catalyst stability. To examine the behavior of the catalysts in different solutions, measurements were conducted with both PtC and TiO<sub>2</sub>/PtC electrodes for 5 h separately in mine water and seawater. The titania-coated electrode's open-circuit voltage (OCV) is  $0.8$  V, lower than the PtC electrode with  $0.97$  V (Figure 4a). This may be due to increased internal resistance caused by titania coating. Although the cell with TiO<sub>2</sub>/PtC electrodes exhibits lower OCV value, it performed up to higher current density values. With an increase in the current density, the cell voltage





**Figure 2.** a) Transmission electron micrographs of PtC and TiO<sub>2</sub>/PtC catalysts in higher and lower magnification ranges, b) particle size distribution of the TiO<sub>2</sub>/PtC electrode, c) X-ray diffraction patterns of PtC and TiO<sub>2</sub>/PtC electrode, d, e) scanning electron micrograph of pristine PtC and TiO<sub>2</sub>/PtC electrode after 50 cycles of titania deposition, f, g) Raman spectra of PtC and TiO<sub>2</sub>/PtC at low- and high-frequency range (\* demarks the positions of TiO<sub>2</sub> anatase at 144, 327, 394, 456, and 713 cm<sup>-1</sup>), h) XPS Ti 2p peak of TiO<sub>2</sub>/PtC electrode.

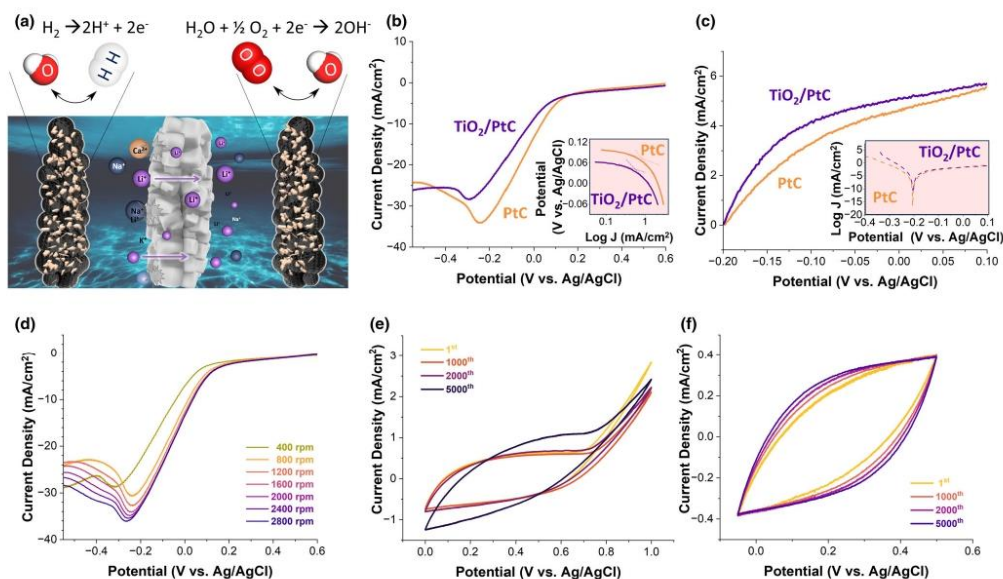
decreases linearly, indicating that the slight decrease in the performance of the fuel cell is primarily a result of electrochemical polarization in the region of low current density (Figure 4a).

Saarland mine water from Grube Viktoria consists of feed water with pH values close to 8. Usually, LISICON-derived ceramic membranes tend to show low oxidation potential (<4 V) and can easily corrode in an alkaline environment, leading to cell performance losses.<sup>[13,22,33–35]</sup> However, Figure 4b displays that the OCV behavior in mine water increased twice compared to seawater, suggesting a more electrochemical active environment. Also, the maximum power density reached the highest value. The power density can be calculated by multiplying the current density and the cell voltage values. The maximum power density at a current density of 1.04 mA cm<sup>-2</sup> was 0.40 mW cm<sup>-2</sup> for the PtC electrode and 1.11 mW cm<sup>-2</sup> at a current density of 1.06 mA cm<sup>-2</sup> for the TiO<sub>2</sub>/PtC electrode (Figure 4b).

Several factors can impact Ohmic losses, including the resistance to ionic transport through the electrolyte, the membrane's thickness, and

the cell's electrical conductivity.<sup>[36,37]</sup> The activation polarization is followed by a linear Ohmic polarization until a current density of 1.57 mA cm<sup>-2</sup> for TiO<sub>2</sub>/PtC. When the electrode is charged, it causes concentration gradients in the polarization curve, which result in overpotentials and related losses during mass transport in the electrolyte.<sup>[37]</sup> Both experiments revealed that even at higher current densities, there is no sign of concentration polarization caused by mass transport. This phenomenon indicates that the electrodes exhibit high efficiency in mass transportation, preventing the occurrence of concentration polarization. FCD-LE system generates two types of energy: electricity and neutralization enthalpy. The latter is the heat released when 1 g equivalent of the acid (HCl) in a dilute solution is completely neutralized by a base (LiOH). Generated energy from electricity and neutralization in the system were 0.1 and 9.7 Wh, respectively.

The concentration of all cations is determined by an inductively coupled plasma optical emission spectrometer (ICP-OES). The selectivity factors were investigated with two feed waters (seawater and mine



**Figure 3.** a) Schematic representation of HOR and ORR activities on the catalyst in FCD-LE system, b) ORR polarization curves of the electrodes. The inset figure shows the Tafel slopes of the electrodes in 0.1 mol L<sup>-1</sup> KOH at the rotating speed of 1600 rpm, c) HOR polarization curves and Tafel slopes (inset) of PtC and TiO<sub>2</sub>/PtC in 0.1 mol L<sup>-1</sup> KOH at the rotating speed of 1600 rpm, d) ORR polarization curves of TiO<sub>2</sub>/PtC at the different rotation speeds, e, f) stability of TiO<sub>2</sub>/PtC electrode for both ORR and HOR activities in 0.1 M KOH.

water). The selectivity factor can be calculated by the concentration change of Li<sup>+</sup> divided by the total concentration change of cations (mg L<sup>-1</sup>) (Equation 3).

$$K_{\text{Li}/\text{M}} = \frac{\Delta c_{\text{Li}}}{\Delta c_{\text{M}}} \quad (3)$$

Here,  $\Delta c_{\text{Li}}$  and  $\Delta c_{\text{M}}$  are the concentration change of Li<sup>+</sup> and the other cation in the catholyte with the unit of mg L<sup>-1</sup>, respectively. The titania-coated electrode exhibited a higher selectivity factor than the PtC alone. Viktoria mine water was collected from the Viktoria region of Saarland and analyzed for its composition (Figure 4c). Viktoria mine water has an alkaline pH of 8, and previous reports have indicated that LISICON-type ceramic materials are slightly dissolved in an alkaline environment, resulting in low selectivity.<sup>[38]</sup> However, results exhibited that the TiO<sub>2</sub>/PtC-coated electrode increased the Li<sup>+</sup> selectivity in mine water. While the selectivity factor of Li<sup>+</sup>/Na<sup>+</sup> was 1.9 for PtC, this value increased to 6.0 for TiO<sub>2</sub>/PtC (Figure S6, Supporting Information). Titania displays a unique stability property in highly alkaline media (pH 12.5), despite its dissolution at low pH values.<sup>[39]</sup> This characteristic significantly enhances the performance and selectivity of the TiO<sub>2</sub>/PtC electrode in mine water. Also, the robust metallic interactions of titania significantly enhance electron-transfer kinetics. Incorporating titanium with the catalyst fosters the development of a conductive network, leading to a substantial increase in reactive sites. Their selectivity factors between Li<sup>+</sup> and Na<sup>+</sup> ions were found to be  $K_{\text{PtC-seawater}}$  (10.2),

$K_{\text{PtC-mine water}}$  (1.90),  $K_{\text{TiO}_2/\text{PtC-seawater}}$  (20.5), and  $K_{\text{TiO}_2/\text{PtC-mine water}}$  (6.0), respectively (Figure 4d).

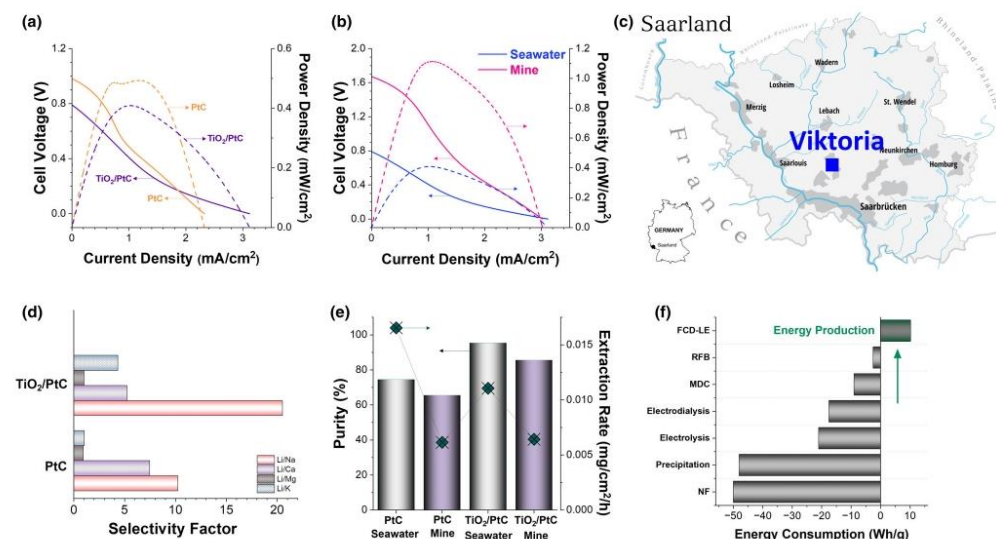
We define purity regarding lithium-ion selectivity. Purity can be calculated by dividing the lithium-ion uptake by the total cation uptake capacity, and the extraction rate of lithium can be calculated by indexing the system's performance (Equations 4 and 5).

$$\text{Purity} = \frac{\text{Li uptake}}{\text{Li uptake} + \text{Na uptake}} \times 100 \quad (4)$$

$$\text{Lithium extraction rate} = \frac{\Delta c_{\text{Li}} \times V}{t \times A \times M_{\text{Li}}} \quad (5)$$

where  $\Delta c_{\text{Li}}$  is the concentration change of Li<sup>+</sup> ions,  $V$  is the volume,  $t$  is the time,  $A$  is the effective area of the ceramic membrane, and  $M_{\text{Li}}$  is the molar mass of Li.

The findings indicate that the lithium-ion extraction rate was 0.017 mg (hcm<sup>2</sup>)<sup>-1</sup>, the highest when using the PtC catalyst with a purity level of 75% in seawater. With the TiO<sub>2</sub>/PtC catalyst, the extraction rate was 0.011 mg cm<sup>-2</sup> h<sup>-1</sup> with a purity level of 95% (Figure 4e). It has been proven that Li superionic conductor membranes offer superior purity to the system. For instance, Li et al. obtained 99.94% purity in the study where they performed Li extraction with glass-type Li<sub>0.33</sub>La<sub>0.56</sub>TiO<sub>3</sub> (LLTO) membrane.<sup>[13]</sup> Likewise, Wang et al.<sup>[15]</sup> received 93.5% purity in the RFB study with Li<sub>1-x</sub>Al<sub>x</sub>Ge<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> ( $x = 0.5$ , LAGP) membrane. However, the instability of lithium in an alkaline environment can cause a reduction in the durability of the



**Figure 4.** a) Polarization curves of  $\text{TiO}_2/\text{PtC}$  and  $\text{PtC}$  electrodes with seawater as the feed water, b) polarization curves of the cell with  $\text{TiO}_2/\text{PtC}$  electrode tested with different feed water compositions, c) geographic location of the mine Viktoria in the German State of Saarland at the German/French border, d) selectivity factors between  $\text{Li}^+$  and other cations in different electrodes, e) purity and lithium-ion extraction rate of electrodes in different feed waters, f) comparison of energy consumption of lithium extraction technologies.

membrane. After we conducted measurements with mine water with a pH of 8, the pristine  $\text{PtC}$  electrode exhibited 66% purity, while the purity provided by the  $\text{TiO}_2/\text{PtC}$  electrode to the system was 86%. Titania coating improved the cell's performance by increasing its electrocatalytic activity, leading to a greater metal-ion interaction. Additionally, it was observed that after 5 h of the experiment, there were minor distortions in the cubic shapes of the structure, but the material preserved its form, which means that the membrane is stable and could be operated for a longer time (Figure S7, Supporting Information).

To study the membrane further, we conducted H-cell experiments using solutions that contained lithium and sodium in one compartment and deionized water in the other compartment (separated by the membrane). We did not apply any external pressure or potential or modify the temperature (Figure S8, Supporting Information). Over time, there is a decrease in conductivity in the compartment with the concentrated salts, showing the ion transport ability of the ceramic membrane (Figure S9, Supporting Information). The preferred transport of lithium versus sodium was confirmed by ICP measurements (Figure S10, Supporting Information).

The voltage efficiency of the system can be found in the operating voltage by dividing the thermodynamic cell voltage. The voltage efficiency was 65.1% in the system for  $\text{TiO}_2/\text{PtC}$ . When hydrogen and oxygen undergo an electrochemical reaction in a fuel cell, it results in the production of both electricity and heat. Neutralization energy refers to the heat released when 1 kg equivalent of the acid (HCl) in a dilute solution is completely neutralized by a base (LiOH).

The energy consumption for the membrane-based lithium recovery process varies depending on the specific method used. For instance, the

nanofiltration (NF), precipitation, and evaporation processes require  $35\text{--}48\text{ Wh g}^{-1}$  of energy to recover lithium from brine, while the membrane distillation process (MDC) only requires  $9\text{ Wh g}^{-1}$ .<sup>[15]</sup> Electrolysis and filtration processes have an energy consumption of  $6\text{--}21\text{ Wh g}^{-1}$  of lithium.<sup>[40]</sup> Extracting lithium from seawater is more challenging because of the lower lithium concentration, leading to higher energy consumption requirements. Electrolysis-based technologies, for instance, demand  $2\text{--}50\text{ Wh}$  energy to extract 1 g of lithium from seawater.<sup>[15]</sup> FCD-LE generates energy from electricity, and neutralization in the system was found to be  $0.55$  and  $9.68\text{ Wh g}^{-1}$ , respectively (Figure 4f).

Achieving high extraction rates while maintaining product purity is a critical and challenging parameter that requires significant energy consumption. Although direct carbonation is a simple and effective method, it offers a recovery rate of approximately 75–85%. Processes such as precipitation or solvent extraction are disadvantageous in terms of excessive chemical use and excessive operational requirements.<sup>[41]</sup> Despite the disadvantages of the conventional method, electrochemical processes are advantageous as they promise high-purity products.<sup>[42]</sup> Although these systems have proven effective, these processes are not continuous and require significant energy consumption. With a purity rate of 99%, the FCD-LE system offers an effective alternative for future studies by providing a continuous process while minimizing energy use.

### 3. Conclusions

In this study, continuous  $\text{Li}^+$  extraction was investigated by the fuel cell desalination system. A titania-coated gas diffusion electrode has been



developed using the ALD method to prevent Pt poisoning caused by halides, increase the durability of the electrodes, and enhance the fuel cell's performance. Various feed water experiments displayed that the titania acts as a shield for the catalyst by creating a homogeneous thin layer on the catalyst and improving the surface area of the catalyst by preventing side reactions due to the undesirable sites on the catalyst. This leads to better cell performance and enhanced stability. In addition, we fabricated a highly selective superionic conductive membrane, LISICON, to enhance the selectivity of lithium toward other cations. After the 5 h experiment, the system displayed a high purity level of 95% following the deposition of  $\text{TiO}_2$ . The electricity produced during this period is  $0.55 \text{ Wh g}^{-1}$  equivalent reaction in mine water. This novel study, which combines fuel cell and electrochemical lithium recovery, displays considerable potential for future research.

#### 4. Experimental Section

**Materials and synthesis:** LISICON membranes were prepared according to previous studies.<sup>[15]</sup> The electrodes were coated with titania using an Oxford FlexAL ALD system.<sup>[43]</sup> Titania was grown on a commercial Vulcan carbon cloth supported by a 40% PtC gas diffusion electrode ( $0.3 \text{ mg cm}^{-2}$  loading; Fuel Cell Store). The precursor for depositing titania is tetrakis(dimethylamido) titanium (IV) (99% Purity, Pegasus Chemicals) with a pulse time of 20 s and purge time of 10 s. The deposition was carried out at  $180^\circ\text{C}$  for 50 cycles.

**Composition of feed waters:** We explored lithium extraction in simulated seawater and mine water collected from Saarland (Grube Viktoria; Table S1, Supporting Information). Before the usage, the mine water was filtered by a vacuum filtration setup with PVDF membranes (pore size,  $220 \mu\text{m}$ ) to remove the suspended solids. The concentration of cations and  $\text{Li}^+$  in the seawater and mine water in the experiment was determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, ARCOS FHX22, SPECTRO Analytical Instruments). The concentration change of cations was monitored as an offline method with ICP (Table S1, Supporting Information). Samples collected before and after the experiment were injected into the system with  $1 \text{ mL min}^{-1}$  sample flow rate.

**Material characterization:** Structure morphology was characterized by scanning electron microscopy (SEM) using a ZEISS GEMINI 500 microscope coupled with an Xmax detector from Oxford Instruments employing an acceleration voltage of 5 kV for imaging and 15 kV for spectroscopy with a  $20 \mu\text{m}$  aperture. Samples were prepared by fixing the electrodes on an aluminum sample holder with copper adhesive. Bright-field microscopy images were examined under a transmission electron microscope (TEM, 2100F system (JEOL)) at a voltage of 200 kV. For this analysis, a sample dispersion in ethanol ( $10 \mu\text{L}$ ) was deposited onto a 3-mm-diameter copper grid coated with lacey carbon.

Characterization of the crystal lattice structure via X-ray diffraction (XRD) was performed via D8 Discover diffractometer (Bruker AXS, Germany) with a copper X-ray source ( $\text{Cu-K}\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 40 mA), a Göbel mirror, and a 1 mm point focus. The samples were fixed to a glass sample holder at a desired amount for preparation. Another glass substrate was pressed onto the sample softly to ensure the sample was homogenous, and the excess sample was removed from the glass substrate.

X-ray photoelectron spectroscopy measurements were performed using Axis Supra, Kratos, Manchester, UK. The photon source was a monochromatized Al K $\alpha$  line. Survey spectra were acquired with an analysis area of  $300 \times 700 \mu\text{m}$  and 160 eV pass energy. The higher resolved measured spectra were acquired using a pass energy of 10 eV.

Raman spectroscopy was conducted with a Renishaw in Via Raman microscope employing an Nd-YAG laser (532 nm) at a power of 0.5 mW. For each sample, spectra from 10 points were recorded with 20 s of exposure time and 20 times accumulated with cosmic ray removal.

Thermogravimetric analysis experiments were performed using a Netzsch TG-209-1 Libra. Five milligram was taken from each sample and put into the crucibles. Then, crucibles were fixed to the device. Experiments have been performed in an argon ( $\pm 0.4$ ) atmosphere at a heating rate of  $20^\circ\text{C min}^{-1} \text{ L}^{-1}$  from 0 to  $1000^\circ\text{C}$ .

**Electrochemical characterization:** Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed via a BioLogic VMP-300 potentiostat/galvanostat in a rotating disk electrode (RDE) setup versus Ag/AgCl and platinum electrode as a reference and counter electrode, respectively. The scan rate for LSV measurements was  $20 \text{ mV s}^{-1}$  for all electrochemical tests. Before the rotating disk electrode testing, the PtC and  $\text{TiO}_2/\text{PtC}$  electrodes were cycled with a rotation rate of 1600 rpm in a nitrogen-saturated aqueous 0.1 M KOH electrolyte with a scan rate of  $100 \text{ mV s}^{-1}$  for 100 cycles, following the US Department of Energy protocol.<sup>[44]</sup>

Hydrogen oxidation reaction (HOR) activities were obtained through potential between 0 and  $+0.25 \text{ V}$  in  $\text{H}_2$ -purged electrolyte at a rotation speed of 1600 rpm. ORR activities were surveyed in a potential window of 0 to  $+1 \text{ V}$  with continuous  $\text{O}_2$  purging. The long-time stability tests of electrodes were taken at a rotation speed of 1600 rpm at a scan rate of  $20 \text{ mV s}^{-1}$  by both cyclic voltammetry for 5000 cycles and for chronoamperometric response at a potential of 0.6 V. The measurements and polarization curves were obtained in 0.1 M KOH. All measured potentials transformed to the reversible hydrogen electrode (RHE) measurement.

**Cell components and operation of the system:** The cell featured one pair of gas channels to feed hydrogen and oxygen, one pair of anolyte and catholyte, and a central water channel (Figure S1, Supporting Information). An anion-exchange membrane (AEM; Fumasep, FAS-PET-130) was placed between the anolyte and feed channel. A ceramic LISICON membrane (effective area  $1.5 \text{ cm}^2$ , thickness  $\sim 500 \mu\text{m}$ , geometric density  $3.26 \text{ g cm}^{-3}$ ) was placed between the catholyte and the water channel. The space of the anolyte, catholyte, and feed water had a 24-mm-diameter round shape and a 2 mm thickness and was filled with glass-fiber separators (Millipore, four pieces of  $380 \mu\text{m}$ ). Simulated seawater and Saarland mine water (Grube Viktoria) were used as feed water, and 0.6 M NaCl was used as anolyte and catholyte in the system. The feed water, anolyte, and catholyte were continuously circulated from and back to the reservoirs through the peristaltic pump (Masterflex L/S) with a  $1 \text{ mL min}^{-1}$  flow rate. To stabilize the system, open-circuit measurements ran for 2 h. Afterward, an external load ( $30 \Omega$ ) was connected to the system, and lithium-ion extraction occurred. Experiments were continued for 5 h, and samples were collected every 1 h to determine the change in lithium concentration in catholyte solution.

#### Acknowledgements

We acknowledge support for the eWeWa project by the European Union from the European Regional Development Fund (ERDF) and the State of Saarland, Germany. We thank Amr Radwan (INM) for the helpful discussions. We also thank the team of Prof. Zhaoyin Wen from the Shanghai Institute of Ceramics for providing the ceramic membranes. Open Access funding enabled and organized by Projekt DEAL.

#### Conflict of Interest

The authors declare no conflict of interest.

#### Author Contributions

Cansu Kök: Methodology, Investigation, Data curation, Validation, Writing—Original Draft. Lei Wang: Writing—Review & Editing. Jean Gustavo A. Ruthes: Data curation, Writing—Review & Editing. Antje Quade: Data curation, XPS analysis. Matthew E. Suss: Writing—Review and Editing. Volker Presser: Visualization, Writing—Review and Editing.

#### Data Availability

The data can be made available upon request.

#### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



## Keywords

atomic layer deposition, cation selectivity, electrochemical lithium-ion extraction, fuel cell

Received: October 22, 2023

Revised: December 9, 2023

Published online: February 20, 2024

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**Supporting Information**

**Continuous lithium-ion extraction from seawater and mine water  
with a fuel cell system and ceramic membranes**

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## 1. Supplementary Figures

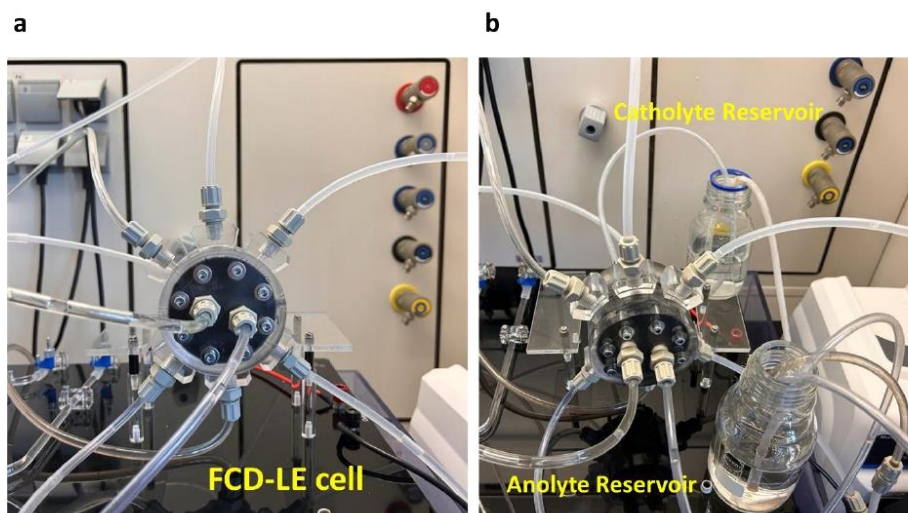


Fig. S1. Photograph of the setup of FCD-LE system.

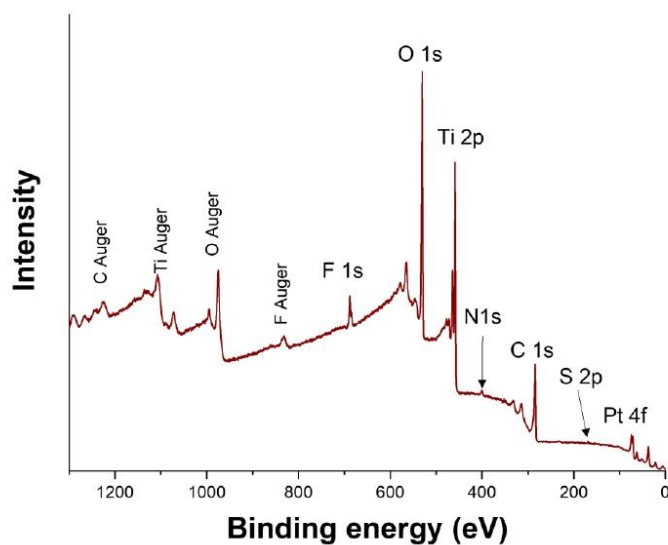
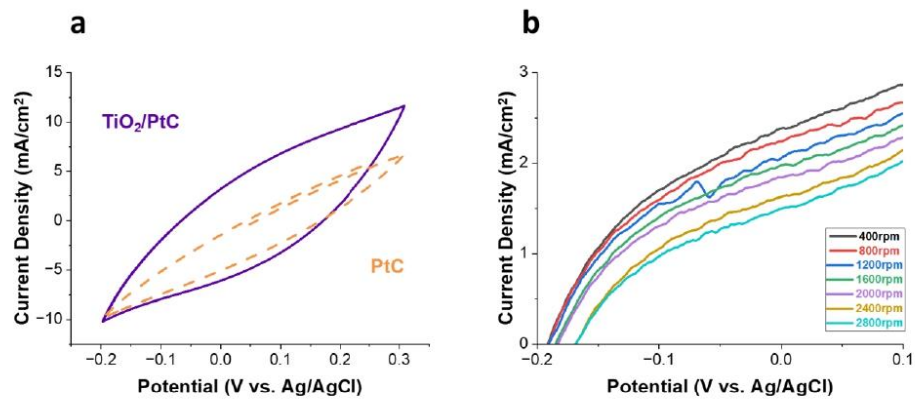
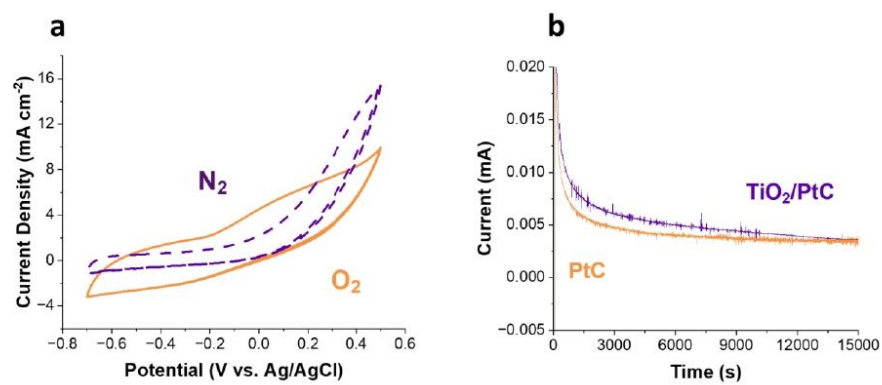


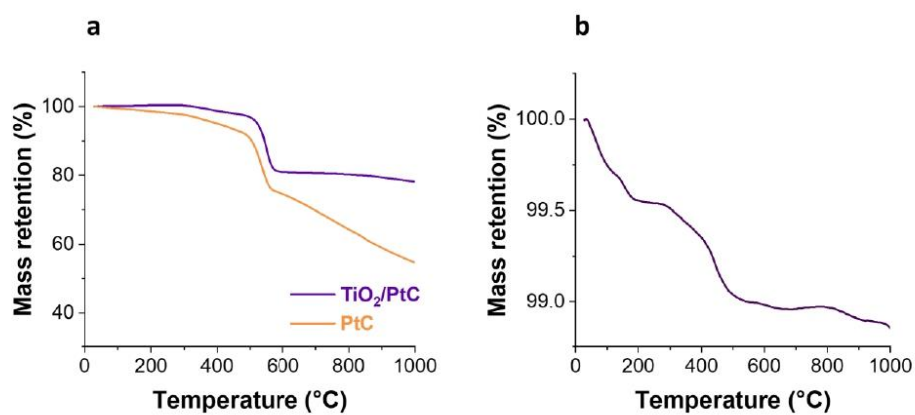
Fig. S2. X-ray photoelectron survey spectrum of the  $\text{TiO}_2/\text{PtC}$  electrode.



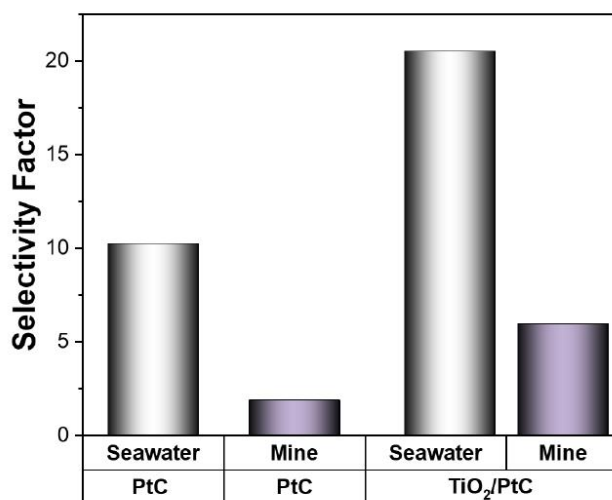
**Fig. S3.** **a** Cyclic voltammograms of PtC and TiO<sub>2</sub>/PtC electrodes after O<sub>2</sub> purging **b** HOR activity of TiO<sub>2</sub>/PtC at different rotation rates in 0.1 M KOH.



**Fig. S4.** **a** Cyclic voltammograms of TiO<sub>2</sub>/PtC after N<sub>2</sub> and O<sub>2</sub> purging, **b** Chronoamperometry of PtC and TiO<sub>2</sub>/PtC electrodes at 0.6 V at 1600 rpm.

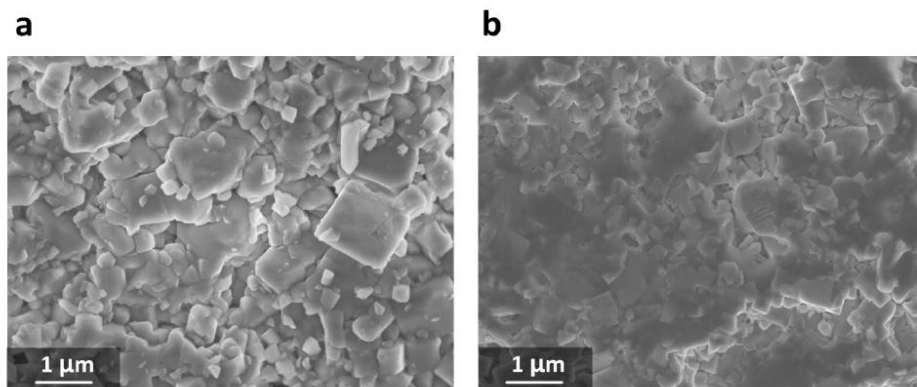


**Fig. S5.** TGA curves of **a** PtC and TiO<sub>2</sub>/PtC electrode **b** LISICON. The measurements were carried out in argon with a flow rate of 20 °C/min/L from 0 °C to 1000 °C at a heating rate of 5 °C/min.

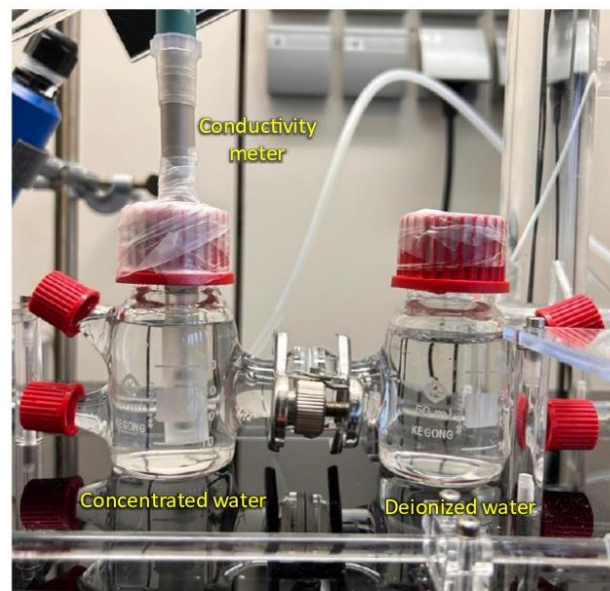


**Fig. S6.** Selectivity factor values of PtC and TiO<sub>2</sub>/PtC electrodes in different feeds.





**Fig. S7.** Scanning electron micrographs of LISICON membrane **a** before and **b** after 5 h experiment.



**Fig. S8.** Experimental Setup conducted with an H-cell

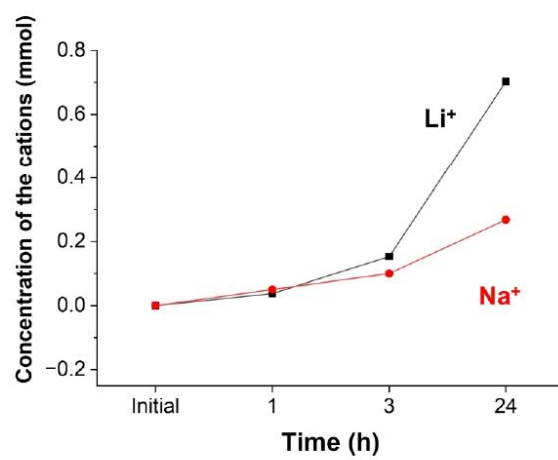


Fig. S9. Concentration changes of cations over time conducted with the H-cell

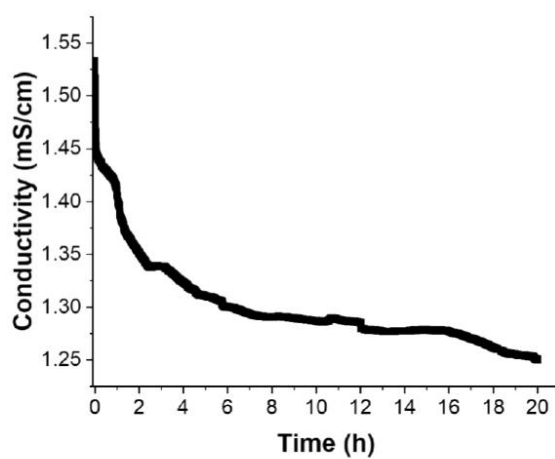


Fig. S10. Conductivity changes of the solution over time.

## 2. Supplementary Table

**Table S1.** The concentration of main cations and  $\text{Li}^+$  in the seawater and mine water in the experiment for lithium extraction from seawater. All concentrations are in mmol.

| Element          | Seawater | Mine water |
|------------------|----------|------------|
| $\text{Li}^+$    | 0.024    | 0.02       |
| $\text{Na}^+$    | 477.5    | 11.00      |
| $\text{K}^+$     | 9.3      | 0.54       |
| $\text{Ca}^{2+}$ | 10.5     | 0.76       |
| $\text{Mg}^{2+}$ | 54.6     | 4.70       |

**Table S2.** The measured concentration changes of sodium and lithium ions before and after the experiment in catholyte in different water via ICP.

| Electrode                          | Experiment | Li (mM) | Na (M) |
|------------------------------------|------------|---------|--------|
| PtC Seawater                       | Before     | 0       | 0.664  |
|                                    | After      | 0.267   | 0.691  |
| PtC Mine                           | Before     | 0       | 0.534  |
|                                    | After      | 0.099   | 0.586  |
| $\text{TiO}_2/\text{PtC}$ Seawater | Before     | 0       | 0.443  |
|                                    | After      | 0.179   | 0.452  |
| $\text{TiO}_2/\text{PtC}$ Mine     | Before     | 0       | 0.560  |
|                                    | After      | 0.104   | 0.578  |

## Publication IV

### ***Best practice for electrochemical water desalination data generation and analysis***

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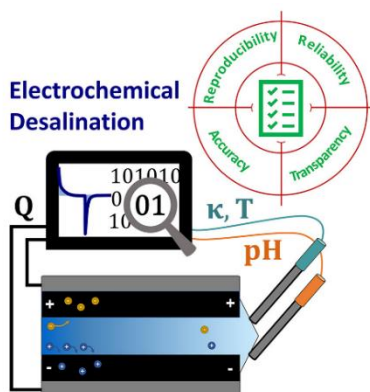
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#### **Citation:**

M. Torkamanzadeh, C. Kök, P.R. Burger, P. Ren, Y. Zhang, J. Lee, C. Kim, V. Presser, Best Practice for Electrochemical Water Desalination Data Generation and Analysis, **Cell Reports Physical Science** 4(11) (2023).

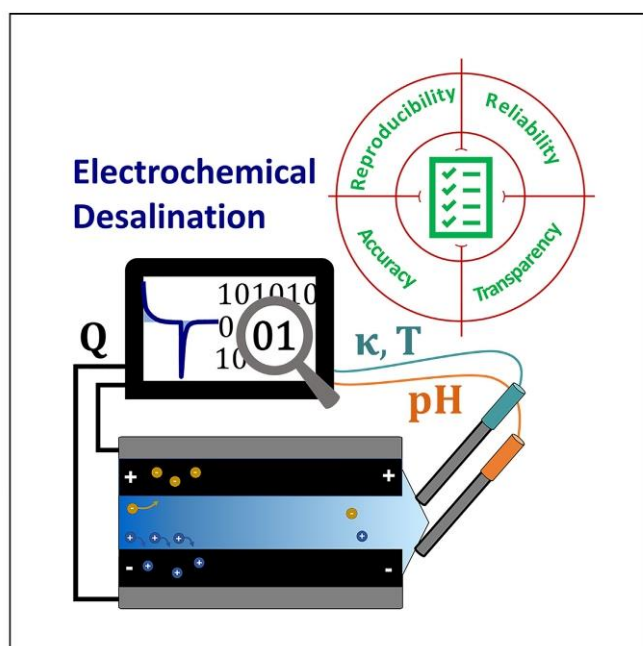
#### **Own contribution:**

Investigation, data curation, writing – review & editing.



## Article

# Best practice for electrochemical water desalination data generation and analysis



Electrochemical desalination shows promise for ion-selective, energy-efficient water desalination. Torkamanzadeh et al. provide a step-by-step guide on acquiring, processing, and calculating raw desalination data, emphasizing informative and reliable figures of merit.

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### Highlights

Detailed guide for acquiring and processing desalination data

Thorough demonstration for calculating critical desalination metrics

Insight on avoiding inaccuracies from leakage current and probe aging

Checklist and spreadsheet tools for enhanced test planning and accuracy

Torkamanzadeh et al., Cell Reports Physical Science 4, 101661  
November 15, 2023 © 2023 The Author(s).  
<https://doi.org/10.1016/j.xcrp.2023.101661>





## Article

## Best practice for electrochemical water desalination data generation and analysis

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## SUMMARY

Electrochemical desalination shows promise for ion-selective, energy-efficient water desalination. This work reviews performance metrics commonly used for electrochemical desalination. We provide a step-by-step guide on acquiring, processing, and calculating raw desalination data, emphasizing informative and reliable figures of merit. A typical experiment uses calibrated conductivity probes to relate measured conductivity to concentration. Using a standard electrochemical desalination cell with activated carbon electrodes, we demonstrate the calculation of desalination capacity, charge efficiency, energy consumption, and ion selectivity metrics. We address potential pitfalls in performance metric calculations, including leakage current (charge) considerations and aging of conductivity probes, which can lead to inaccurate results. The relationships between pH, temperature, and conductivity are explored, highlighting their influence on final concentrations. Finally, we provide a checklist for calculating performance metrics and planning electrochemical desalination tests to ensure accuracy and reliability. Additionally, we offer simplified spreadsheet tools to aid data processing, system design, estimations, and upscaling.

## INTRODUCTION

Electrochemical water desalination is a promising technology that removes the salt ions from aqueous saline media by applying electrical potential as the driving force. Electrodialysis and capacitive deionization are two powerful electrochemical desalination techniques that have the potential toward ion-selective,<sup>1,2</sup> low-energy-consuming,<sup>3</sup> high water recovery,<sup>4</sup> and economical<sup>5</sup> water remediation. In filtration processes such as reverse osmosis, by contrast, pressure serves as the driving force for ion migration; in thermal processes such as distillation processes, heat is the driving force that draws the water molecules out of a saline stream. In contrast, the fundamentally different driving force in electrothermal water desalination is the electrical field that draws the salt molecules out of a saline stream. As such, what makes electrochemical water desalination particularly interesting, among other factors, is that its energy consumption strongly depends on the initial salt concentration of the feed water, unlike other conventional thermal- or pressure-driven processes.<sup>6,7</sup> Comprehensive techno-economic analysis indicates that for a threshold between 3,000 and 30,000 ppm NaCl concentration levels in feedwater, a crossover point occurs for electrochemical water desalination and reverse osmosis. That is, electrochemical water desalination technologies below the mentioned threshold have become increasingly more economically attractive than reverse osmosis.<sup>7</sup>

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The energy and cost efficiency,<sup>8</sup> along with many other attractive unique capabilities, such as partially recovering the invested energy<sup>9</sup> or selective separation of ions,<sup>2,10,11</sup> have made electrochemical desalination the subject of numerous studies during the past two decades.<sup>12–15</sup> The key to making those studies reliable, comparable, and reproducible are clear guidelines on how electrochemical desalination data are acquired, processed, and reported. Yet such best-practice studies are limited in the literature, which could limit the rapid advancement of electrochemical desalination technology.

In a typical electrochemical desalination cell, a voltage is applied to a pair of electrodes, and an aqueous saline medium, commonly NaCl, is the electrolyte that continuously flows in and out of the cell. As such, an electrochemical desalination cell could be considered a supercapacitor/battery, only different in that the electrolyte flows through an electrochemical desalination cell. In contrast, it is stagnant in regular supercapacitors/batteries. The standard and probably simplest form of an electrochemical desalination cell is where the water stream passes between and tangentially to the two electrodes, known as the flow-by configuration (Figure S1). Upon polarization of carbon electrodes by applying a charging or discharging voltage, the system's response is commonly recorded in the form of the following key variables: (1) the amount of electric charge stored in the electrodes and (2) the change in the conductivity of the outflowing water. Depending on the available infrastructure, one might record additional variables, such as pH and temperature of outflowing water.

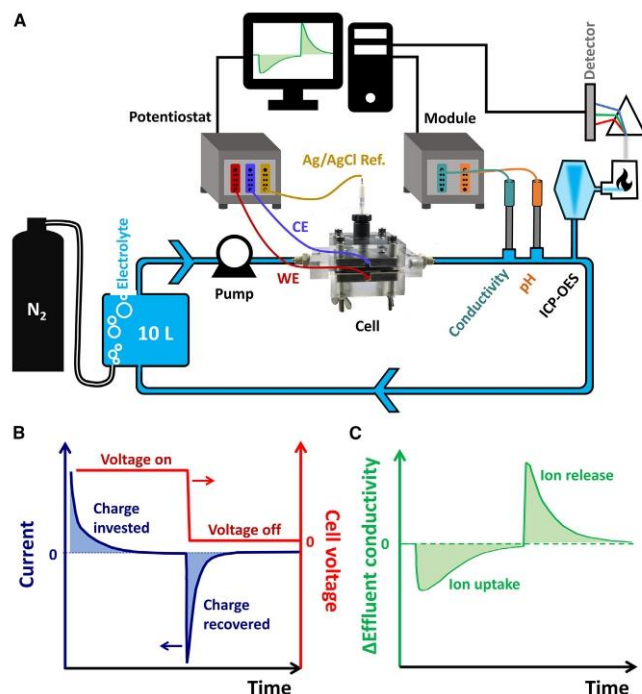
In the present study, we first deal with the conversion of the measured conductivity and pH data into actual salt concentration. We then establish the design of a typical electrochemical water desalination setup consisting of an electrochemical desalination cell with a pair of symmetric activated carbon electrodes in its core and conductivity and pH probes placed downstream of the cell. We show how the obtained conductivity and pH data can be related to the concentration and how the latter concentration obtained is further processed into commonly reported desalination performance metrics in the literature,<sup>16</sup> namely, desalination capacity, charge efficiency, and energy consumption. With the aid of an online elemental monitoring apparatus, we also investigate electrochemical desalination with a mixed-salt electrolyte and show how the preferential removal of specific ions could be quantified and reported in terms of selectivity metrics.

We then systematically investigate the effects of temperature and the aging of the conductivity probe over a 6-month period and how that influences the final reported desalination performance metrics. Finally, we recommend to the community of electrochemical water desalination researchers when and how to best calibrate the conductivity probes to avoid skewing the results. We also provide several simplified and easy-to-use spreadsheets that readily enable the synchronization between pH and concentration data, calculation of concentrations, conversion of standard concentration units ( $\text{mg L}^{-1}$ , ppm,  $\text{mmol L}^{-1}$ ) into one another, calculation of the electrode mass needed to achieve a desired water quality, and much more.

## RESULTS AND DISCUSSION

### Description of a typical desalination setup and experiment

Figure 1A schematically shows a typical electrochemical desalination setup. An electrolyte tank (in our case, typically 10 L) provides a practically constant concentration of saline water fed into the cell. However, the size of the tank needs to be adjusted for



**Figure 1. Electrochemical desalination setup and real-time response of the cell**

(A) Schematic representation of a typical electrochemical desalination setup; WE, working electrode; CE, counter electrode.

(B) The applied cell voltage profile and the current response of the cell.

(C) The corresponding conductivity profile during one full electrochemical desalination cycle.

the size of the desalination cell, and one must also consider the possible water evaporation over time during long-term operation. Such a setup is known as a single-pass mode of operation, in contrast to the batch mode.<sup>12</sup> A peristaltic pump continuously circulates the electrolyte from the tank to the cell through the conductivity and pH chambers and directs the electrolyte back to the tank. A nitrogen gas tube is inserted into the tank to constantly bubble the electrolyte with a small nitrogen gas flow to remove the air, and particularly the dissolved oxygen, from the water. The latter measure was taken to minimize carbon oxidation and performance degradation, since the dissolved oxygen in the electrolyte can take part in parasitic oxygen reduction reaction and peroxide formation during charge and discharge.<sup>17,18</sup>

As outlined before, two key datasets are commonly recorded in an electrochemical desalination experiment: (1) electrochemical data provided by the electrochemical workstation, which can include current-time (*I*-*t*), cell voltage-time (*V*-*t*), electrode potential-time (*E*-*t*), or energy-time (*U*-*t*) data, among others, and (2) the cell's effluent electrolyte properties provided by the probes installed at the downstream side of the cell, which can include conductivity-time, pH-time, or temperature-time data, among others.



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Figure 1B shows the cell voltage applied during charge and discharge, together with the current response of the cell. As will be shown later, the electric charge stored in the carbon electrodes can be calculated by integrating the area under the  $I$ - $t$  curve presented here. In a single-pass mode of operation, the concentration-time profile of the outflowing water from the cell resembles the scheme shown in Figure 1C. In the latter mode of operation, there is a quasi-infinite abundance of salt ions present in the circulating electrolyte, which is more than sufficient for the electrodes to take up. As a result, after applying a cell voltage for a while, the electrodes saturate with an overabundance of the present salt ions and reach their maximum (equilibrium) capacities, and the salt concentration of the water flowing out of the cell will finally reach the level of the water that flew into the cell. Likewise, the stored salt ions in the electrodes are ejected back to the circulating electrolyte (brine solution) upon applying the discharge voltage.

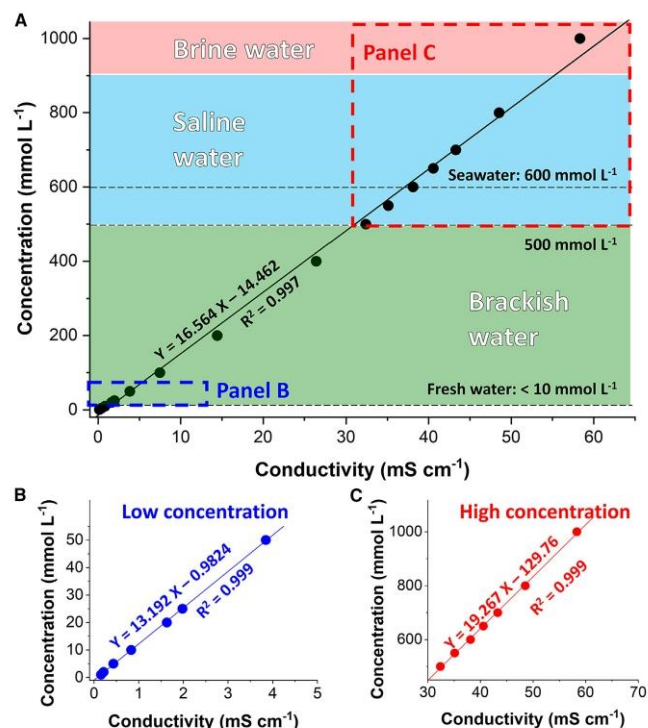
The conductivity change is translated into concentration change (see the section “calibration of conductivity probes”), and the integrated area under the concentration-time curve measures the capacity of the electrodes to remove salt ions, a merit called desalination capacity (DC). The electrode’s capacity to remove salt ions can then be compared with its capacity to store electric charge in the same cycle. A measure that reports the fraction of the former to the latter is called charge efficiency (CE). CE is not to be confused with Coulombic efficiency, which states the fraction of electric charge obtained during discharging to that while charging an electrochemical cell, a standard metric reported in battery research.

Finally, the energy consumed during the charging of the electrodes could be reported as normalized to the number of ions removed. Assuming no other losses, the net consumed energy in one complete cycle could be envisioned as the sum of the enthalpies of demixing the saline feed water into the desalinated solution produced during charging and the brine solution produced during discharging.<sup>19</sup> The consumed energy for demixing can be harvested again upon mixing the two latter solutions (the capmix process), giving rise to the concept of blue energy or osmotic power.<sup>20</sup>

#### Calibration of conductivity probes

To calculate standard desalination performance metrics, such as desalination capacity, one has to convert the obtained conductivity-time data (Figure 1C) into concentration-time data. As a first step, the conductivity probes should be calibrated (or standardized) using several NaCl stock solutions with known concentrations. Figure 2A shows a conductivity probe calibrated with 17 stock solutions of NaCl in pure water, ranging from 1 mmol L<sup>-1</sup> to 1,000 mmol L<sup>-1</sup>. For accuracy, the conductivity probes are best calibrated with stock solutions with concentrations around the target electrolyte desired to be tested in an electrochemical desalination experiment. In this study, since the target electrolyte for the subsequent electrochemical desalination tests is 20 mmol L<sup>-1</sup> NaCl, the calibration curve is constructed for the concentration regime of 1–50 mmol L<sup>-1</sup> (Figure 2B), resulting in a good coefficient of determination ( $R^2$ ) of 0.999 between conductivity and concentration values. Similarly, if an electrolyte simulating seawater-level concentrations of NaCl (~600 mmol L<sup>-1</sup>) is to be used, a calibration curve between 500 and 1,000 mmol L<sup>-1</sup> can be constructed (Figure 2C) and used.

Using the concentration-conductivity equation in Figure 2B, the conductivity data obtained in an electrochemical desalination experiment (Figure 3A) could be converted into concentration data (Figure 3B), enabling further calculations on the desalination capacity and CE.



**Figure 2. Construction of the calibration curves relating the conductivity to the concentration**  
Calibration curves were constructed to convert the measured conductivity into concentration in (A) the entire 1–1,000 mmol L<sup>-1</sup> range, (B) a low-concentration regime of 1–50 mmol L<sup>-1</sup>, and (C) a high-concentration regime of 500–1,000 mmol L<sup>-1</sup>.

#### Desalination capacity

Figure 3A shows the conductivity variations of a standard single-pass electrochemical desalination experiment during several cycles. In this study, we have used a symmetric cell composed of two activated carbon electrodes, charged and discharged at 1.2 V and 0.3 V, respectively. The experimental procedures section details the experimental and operational conditions used in the latter test. Figure 3B shows the typical concentration variations upon cycling of an electrochemical desalination cell. As illustrated in Figure 1A, the electrolyte solution is constantly bubbled by nitrogen gas to remove the dissolved oxygen, accelerating the electrolyte's evaporation over time. As a result, the concentration slightly increases and, hence, the feed concentration of ~22 mmol L<sup>-1</sup> is reached in Figure 3B instead of the initially made 20 mmol L<sup>-1</sup>. To alleviate electrolyte evaporation, one might pre-wet the dry nitrogen flow by passing it through a gas-washing water bottle.

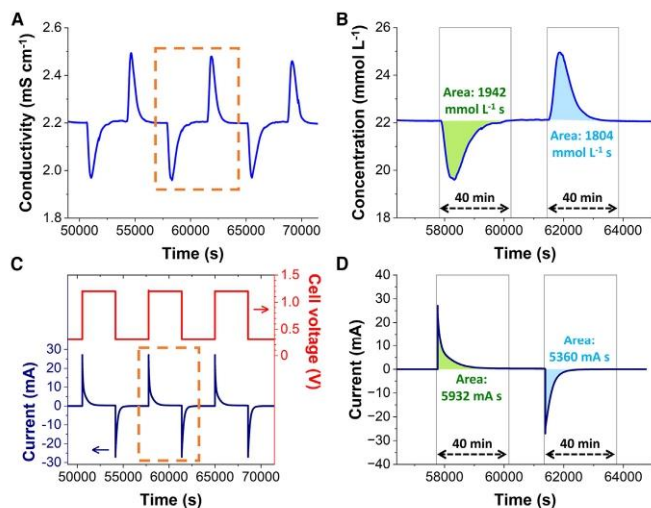
For the sake of simplicity, the x axis (time) in Figure 3B could be converted to cycle number by dividing the time by the cycle duration (a peak-to-peak separation), which is 7,220 s in the present case, as illustrated in Figure S2. Based on the





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**Figure 3. Integration of the area under the curves of concentration-time and current-time profiles**  
(A and B) Processing steps for converting the (A) raw conductivity-time data into (B) concentration-time data and the integration of the area under the curve for charging and discharging half-cycles. (C) The applied cell voltage during charge and discharge and the current response. (D) The integration of the area under the current-time curve for charging and discharging half-cycles.

decrease/increase in concentration curve versus time (Figure 3B), induced by charging/discharging of the cell by the electrochemical workstation, the DC ( $\text{mg}_{\text{salt}} \text{g}_{\text{electrode}}^{-1}$ ) is then calculated following Equation 1:

$$\text{DC} = \frac{\nu M_{\text{NaCl}}}{m_{\text{total}}} \int C dt, \quad (\text{Equation 1})$$

where  $\nu$  is the flow rate ( $\text{L s}^{-1}$ ),  $M_{\text{NaCl}}$  is the molar mass of NaCl ( $58.44 \text{ g mol}^{-1}$ ),  $m_{\text{total}}$  is the total mass of both electrodes combined (g), and  $t$  is the time (s) during which a concentration change ( $\text{mmol L}^{-1}$ ) occurs.

However, one commonly deals with more practical units at laboratory-scale electrochemical desalination, namely,  $\text{mL min}^{-1}$  for flow rate ( $\nu$ ) and mg for electrode mass ( $m_{\text{total}}$ ). Also, the collective term  $\int C dt$ , with the unit  $\text{mmol L}^{-1} \text{ s}$ , is obtained by integrating the area under each half-cycle in concentration-time curves. In this case, Equation 1 must be divided by 60 as a conversion factor to give Equation 2:

$$\text{DC} \left( \frac{\text{mg NaCl}}{\text{g}_{\text{electrode}}} \right) = \frac{\nu \left( \frac{\text{mL}}{\text{min}} \right) \times 58.44 \left( \frac{\text{g NaCl}}{\text{mol NaCl}} \right)}{60 m_{\text{total}} (\text{mg})} \int C dt \left( \frac{\text{mmol s}}{\text{L}} \right), \quad (\text{Equation 2})$$

which further simplifies into Equation 3:

$$\text{DC} \left( \frac{\text{mg NaCl}}{\text{g}_{\text{electrode}}} \right) = \frac{0.974 \nu \left( \frac{\text{mL}}{\text{min}} \right)}{m_{\text{total}} (\text{mg})} \int C dt \left( \frac{\text{mmol s}}{\text{L}} \right), \quad (\text{Equation 3})$$

Substituting in Equation 3  $1.6 \text{ mL min}^{-1}$  for the flow rate,  $270.6 \text{ mg}$  for the total mass of both electrodes ( $137.1 \text{ mg} + 133.5 \text{ mg}$ ), and  $1,873 \text{ mmol L}^{-1} \text{ s}$  as the average of



integrated areas under the two charging and discharging half-cycles in concentration-time curves  $\left(\frac{1.942+1.804}{2}\right)$ , will result in  $DC = 10.8 \text{ mg NaCl removal capacity per gram of electrode, or } 10.8 \text{ mg g}^{-1}$  in short.

In some cases, mainly where selectivity toward certain cations or anions is involved,<sup>11</sup> total NaCl salt removal capacity (DC) may be less relevant than specific removal capacities toward certain ions. If those ions are sodium and chloride,<sup>21</sup> the DC can be broken down to sodium removal capacity and chloride removal capacity following Equations 4 and 5, respectively.

$\text{Na}^+$  removal capacity:

$$\left(\frac{\text{mg Na}^+}{\text{g}_{\text{electrode}}}\right) = DC \left(\frac{\text{mg NaCl}}{\text{g}_{\text{electrode}}}\right) \times \frac{\text{mol NaCl}}{58.44 \text{ mg NaCl}} \times \frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} \times \frac{22.99 \text{ mg Na}^+}{1 \text{ mol Na}^+} = 0.39 \text{ DC,} \quad (\text{Equation 4})$$

$\text{Cl}^-$  removal capacity:

$$\left(\frac{\text{mg Na}^+}{\text{g}_{\text{electrode}}}\right) = DC \left(\frac{\text{mg NaCl}}{\text{g}_{\text{electrode}}}\right) \times \frac{\text{mol NaCl}}{58.44 \text{ mg NaCl}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} \times \frac{35.45 \text{ mg Cl}^-}{1 \text{ mol Cl}^-} = 0.61 \text{ DC,} \quad (\text{Equation 5})$$

For the example above,  $\text{Na}^+$  and  $\text{Cl}^-$  removal capacities would then be  $4.2 \text{ mg g}^{-1}$  and  $6.6 \text{ mg g}^{-1}$ , respectively. Adjustments must be made if a different salt system is investigated, such as KCl or  $\text{NaSO}_4$ .

#### Charge efficiency

After DC, another key metric of an electrochemical desalination system, not always reported in the literature, is the CE. CE is a unitless value between zero and unity (commonly given in percent) that gauges the portion of the invested electric charge that contributes to removing salt ions from the saline stream. The closer the CE to unity (or to 100%), the less the system suffers from parasitic losses. The latter parasitic losses stem from co-ion expulsion phenomena and electrode-electrolyte faradic side reactions.<sup>22</sup> As a result, side processes that do not contribute to the electrochemical desalination bottom line, that is, maximum net salt removal, will decrease the CE value. For a review of different sources of parasitic losses, readers are referred to other studies.<sup>12,23,24</sup>

The CE (%) can be formulated as Equation 6:

$$\text{CE (\%)} = \frac{DC}{\frac{M_{\text{NaCl}}}{Q}} \times 100\%, \quad (\text{Equation 6})$$

where  $F$  is the Faraday constant and  $Q$  is the average of total charge stored in the two electrodes normalized to the total mass of both electrodes combined. In Equation 6, the nominator expresses the population of salt ions taken up by the electrode, and the denominator expresses the population of invested electric charge. A critical point that needs to be stressed here is that the charge substituted in the CE formula should be obtained from the same cycle and the duration from which the DC was obtained. As such, the charge capacity/capacitance of the electrodes obtained via any other techniques performed prior to desalination experiments, such as cyclic voltammetry or charge/discharge, will be irrelevant to use here.





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For practical reasons, the term  $Q$  in Equation 6 can be defined as  $Q = \frac{q}{m_{\text{total}}}$ , where  $q$  is obtained by integrating the area under each half-cycle in current-time curves or readily obtained by the electrochemical workstation software (EC-Lab in this work). More discussion on the significance of employing either of the latter methods for calculating charge will follow later in this article (see the section "leakage current subtraction"). One might find the following units convenient to use at the laboratory-scale tests:  $96,485 \text{ C mol}^{-1}$  for the Faraday constant ( $F$ ), mg for electrodes mass ( $m_{\text{total}}$ ), mA s for charge ( $Q$ ), and  $58.44 \text{ g mol}^{-1}$  for the molar mass of NaCl ( $M_{\text{NaCl}}$ ). In that case, Equation 6 must be divided by 1,000 as a conversion factor to turn into Equation 7:

$$\text{CE (\%)} = \frac{\text{DC} \left( \frac{\text{mg NaCl}}{\text{g electrode}} \right) \times 96,485 \left( \frac{\text{C}}{\text{mol}} \right) \times m_{\text{total}} (\text{mg})}{1,000 \times q (\text{mA s}) \times 58.44 \left( \frac{\text{g NaCl}}{\text{mol NaCl}} \right)} \times 100, \quad (\text{Equation 7})$$

which simplifies into Equation 8:

$$\text{CE (\%)} = \frac{165.10 \text{ DC} \left( \frac{\text{mg NaCl}}{\text{g electrode}} \right) \times m_{\text{total}} (\text{mg})}{q (\text{mA s})}, \quad (\text{Equation 8})$$

Substituting in Equation 8  $10.8 \text{ mg g}^{-1}$  for DC,  $270.6 \text{ mg}$  for the total mass of both electrodes ( $137.1 \text{ mg} + 133.5 \text{ mg}$ ), and  $5,646 \text{ mA s}$  as the average of integrated areas under the two charging and discharging half-cycles in  $I$ - $t$  curves  $\left( \frac{5,932 + 5,360}{2} \right)$  will result in  $\text{CE} = 85\%$ .

In an ideal case, the DC or CE obtained in the charging half-cycle (desalination) should be equal to that in the discharging half-cycle (regeneration). Because of non-idealities and parasitic losses, such as leakage current (which will be dealt with later in this work), non-equal, but often close, values of DC or CE are obtained for the two half-cycles. In such a case, one might choose to average the two values, as done above. Without averaging, the DC and CE for the charging half-cycle would be  $11.2 \text{ mg g}^{-1}$  and  $84\%$ , respectively, and the DC and CE for the discharging half-cycle would be  $10.4 \text{ mg g}^{-1}$  and  $87\%$ , respectively.

As seen, the values calculated herein differ well below  $10\%$  between charging and discharging half-cycles. If those two values differ largely, that is,  $>10\%$ , one might need to check whether the baseline selection for integration of the area under the curves was precise. A simple method to get better baselines is to prolong the holding times for charging and discharging half-cycles (for relevant considerations, see also the section "leakage current subtraction"), which allows the concentration of the cell's effluent water to reach equilibrium. Moreover, one might also entertain the possible presence of detrimental faradic processes present significantly more in one half-cycle and absent in the other half-cycle. The latter phenomenon is often the case during the charging half-cycle, mainly when the cell is not carefully mass-balanced, and the electric potentials developed in one or both electrodes exceed their stability windows.

### Energy consumption

The energy consumed to accomplish the desalination is a key metric for comparing an electrochemical desalination system to other adjacent technologies. Also, within the realm of electrochemical desalination, the energy consumption analysis provides vital insight when comparing different system components, such as electrode materials, cell configurations, or electrolyte concentrations, as to which combination yields the most energy-efficient results. Such energy consumption analysis, for



instance, can reveal that while carbon electrodes show an increased energy consumption going toward higher electrolyte concentrations, faradic materials such as 2D transition metal sulfides or MXenes show a rather constant energy consumption across wide concentration ranges.<sup>16,21,25</sup>

Two approaches could be taken for energy consumption analysis: macroscopic and microscopic. The macroscopic approach involves the Wh energy required for producing  $x$  liters of freshwater, commonly reported in the unit  $\text{Wh L}^{-1}$ . The salt content of freshwater is variously defined as less than 500 ppm<sup>26</sup> ( $<9 \text{ mmol L}^{-1} \text{ NaCl}$ ) or less than 1,000 ppm<sup>27</sup> ( $<17 \text{ mmol L}^{-1} \text{ NaCl}$ ). The macroscopic approach is more common in reverse osmosis technology, although its application for electrochemical desalination systems must be cautiously employed. In the case of reverse osmosis filtration, more than 99% of the salt content in the feedwater is removed from the product water.<sup>28</sup> In contrast, in electrochemical desalination at the laboratory scale, only a few percent of the salt content is removed in each charging half-cycle in a single-pass mode of operation.<sup>29</sup> As such, calculating energy consumption for complete salt removal via an electrochemical desalination system might require extrapolation calculations which assume that the system consumes the same energy rate all the way down to a very-low-salt-content electrolyte. However, the latter assumption could be erroneous, as electrolytes of lower concentrations would show a higher solution resistance, resulting in more energy consumed as the concentration decreases.

The microscopic approach, however, eliminates the need for extrapolations or unreliable assumptions. The latter approach involves the energy consumed to remove one salt formula unit in a single electrochemical desalination cycle, which will also be dealt with herein. As outlined before, the energy consumed during the charging ( $U_{\text{charge}}$ ) of the electrodes are often considered the basis for energy calculations, even though part of that energy could be potentially recovered during the discharging of the electrodes.<sup>9,30</sup> Equation 9 can then be formulated to calculate the energy invested to remove a single salt molecule from the saline stream.

$$\text{Energy consumption per ion} = \frac{U_{\text{charge}}}{\frac{m_{\text{total}}}{\text{DC}}}, \quad (\text{Equation 9})$$

$$M_{\text{NaCl}}$$

where the nominator in Equation 9 provides the consumed energy normalized to the mass of both electrodes combined ( $\text{Wh g}^{-1}$ ), and the denominator gives the moles of salt ions removed normalized to the mass of both electrodes combined ( $\text{mmol g}^{-1}$ ).

The practical energy unit that one commonly deals with at laboratory-scale electrochemical desalination tests is Wh for energy consumed, while the desirable energy unit to report the energy values in molecular-scale systems is the product of the Boltzmann constant and temperature ( $k_B T$ ). Given that For  $T = 298 \text{ K}$ , 1 Wh is equal to  $8.75 \times 10^{23} k_B T$ , the substitution of the Avogadro number yields Equation 10:

$$\text{Energy consumption per ion} \left( \frac{k_B T}{\text{ion}} \right) = \frac{U_{\text{charge}} (\text{Wh})}{\frac{m_{\text{total}} (\text{mg})}{\text{DC} \left( \frac{\text{mg}}{\text{g}} \right)}} = \frac{U_{\text{charge}} (\text{Wh})}{m_{\text{total}} (\text{mg})} \times \frac{1,000 \text{ mg}}{1 \text{ g}} \times \frac{8.75 \times 10^{23} k_B T}{1 \text{ Wh}},$$

$$\frac{M_{\text{NaCl}} \left( \frac{\text{g}}{\text{mol}} \right)}{58.44 \left( \frac{\text{g}}{\text{mol}} \right) \times \frac{1,000 \text{ mg}}{1 \text{ g}} \times \frac{1 \text{ mol}}{6.02214076 \times 10^{23}}}$$

(Equation 10)



which, upon further simplification, yields Equation 11:

$$\text{Energy consumption per ion} \left( \frac{\text{kJ}}{\text{ion}} \right) = \frac{8.49 \times 10^7 U_{\text{charge}} (\text{Wh})}{m_{\text{total}} (\text{mg}) \times \text{DC} \left( \frac{\text{mg}}{\text{g}} \right)}, \quad (\text{Equation 11})$$

Referring to the electrochemical workstation software, the  $U_{\text{charge}}$  for the cycle studied above (Figure 3B) is  $2.08 \times 10^{-3}$  Wh. Substituting the latter value in Equation 11, along with  $10.8 \text{ mg g}^{-1}$  for DC and 270.6 mg for the total mass of both electrodes, will result in  $60.4 \text{ kJ}$  per single salt molecule (NaCl) removed.

### Ion selectivity

There has been an ever-growing interest in the electrochemical desalination research toward selective separation and recovery of ions from aqueous media, either to remove toxic/undesired species from water streams or to capture valuable elements.<sup>2,31</sup> Table 1 lists several works that have reported the selective electrochemical removal of certain ionic species from aqueous media in the presence of other competing ions in a cyclic manner. Lithium, nickel, cobalt, and manganese, for instance, are among the value-added elements that can be recovered from the leaching solution of spent lithium-ion batteries,<sup>32–34</sup> contributing toward a circular economy. The target ionic species in Table 1 are highlighted in a periodic system of elements with their significance and critical applications, as illustrated in Figure 4. As can be seen, the electrochemical desalination world is no longer limited to mere sodium chloride removal. Still, it has expanded in scope for selective removal of cations or anions of various types.

To calculate the performance metrics of an electrochemical desalination system, one has to determine the change in the concentrations of ionic species flowing out of the cell. However, when there is more than one salt species involved, the concentration cannot be related to the conductivity of the effluent water stream, as the measured conductivity is a product of the contribution of multiple ionic species (Figure 5A). Developing methods to quantify the individual ion concentration in a mixed-salt electrolyte is crucial in studying the system's selectivity. Inductively coupled plasma optical emission spectroscopy (ICP-OES), for instance, is a powerful and accurate tool that can individually quantify many ionic species simultaneously.

Techniques such as ICP-OES,<sup>71</sup> inductively coupled plasma mass spectrometry,<sup>72</sup> or ion chromatography<sup>37,45,73</sup> are methods to monitor individual ionic species. Alternatives include the EDTA titration of mixtures of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions,<sup>74</sup> or the colorimetric method for determining  $\text{Pb}^{2+}$  ions in the presence of alkali metal and alkaline earth metal ions.<sup>75</sup> The latter process required the treatment of lead ions with sulfide ions to convert the colorless lead ions into adsorptive lead sulfide, followed by UV-visible-near-infrared (UV-vis-NIR) spectrophotometry.

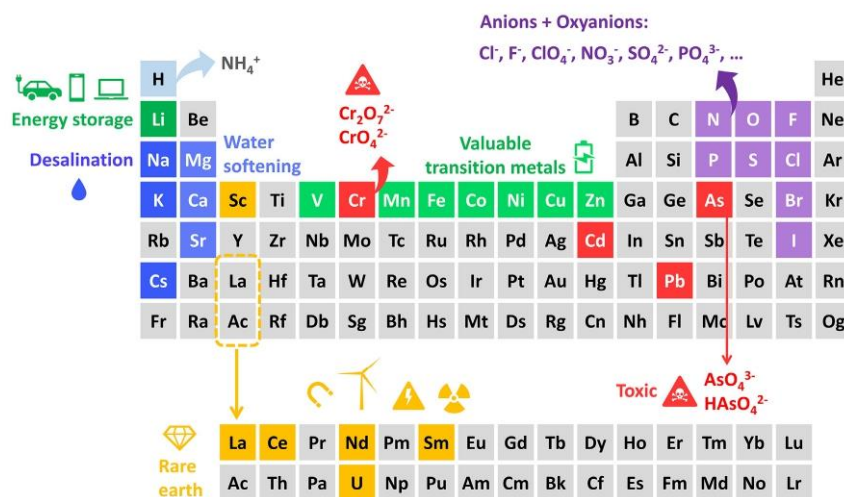
Ion-selective electrodes have been used when dual-salt electrolytes are involved. An example of the latter is surfactant-functionalized activated carbon electrodes developed to demonstrate a high affinity for  $\text{NO}_3^-$  compared to  $\text{Cl}^-$  ions.<sup>73</sup> Combined use of ion-selective electrodes and conductivity/pH measurements have also been shown for mixtures of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions<sup>53,76</sup> using the extended Onsager-Fuoss model.<sup>77</sup> The latter theoretical foundation helps to predict the complex conductivity changes that occur with concentration changes. This theoretical guidance provides calibration methods that consider the impact of ionic association on conductivity assessments, ensuring that accuracy and precision are maintained over a wide range of concentrations.<sup>78</sup>

Table 1. Overview of electrochemical desalination research on selective recovery of ions from aqueous media

| Target element                                                      | Competing ions                                                                                                                                                                                                                                                                                                                           | Electrode material                                                                                                       | References                                                                                |
|---------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| Li <sup>+</sup>                                                     | Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup>                                                                                                                                                                                                                                                                                      | LiFePO <sub>4</sub>                                                                                                      | Trócoli et al., <sup>35,36</sup> Pasta et al. <sup>35,36</sup>                            |
| Li <sup>+</sup>                                                     | Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                   | λ-MnO <sub>2</sub>                                                                                                       | Lee et al., <sup>37–39</sup> Trócoli et al., <sup>37–39</sup> Kim et al. <sup>37–39</sup> |
| Li <sup>+</sup>                                                     | Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup>                                                                                                                                                                                                                                                                                      | flow electrodes of (Fe(CN) <sub>6</sub> <sup>4-</sup> /Fe(CN) <sub>6</sub> <sup>3-</sup> ) redox pair + LISICON membrane | Wang et al. <sup>8</sup>                                                                  |
| Li <sup>+</sup>                                                     | Co <sup>2+</sup>                                                                                                                                                                                                                                                                                                                         | activated carbon fiber + MXene-based ion-sieving membrane                                                                | Jiang et al. <sup>40</sup>                                                                |
| Na <sup>+</sup>                                                     | Mg <sup>2+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                                                      | nickel hexacyanoferrate (NiHCF Prussian blue analog)                                                                     | Singh et al. <sup>41</sup>                                                                |
| Cs <sup>+</sup>                                                     | Na <sup>+</sup> , Sr <sup>2+</sup>                                                                                                                                                                                                                                                                                                       | copper hexacyanoferrate (CuHCF Prussian blue analog)                                                                     | Lee et al. <sup>42</sup>                                                                  |
| NH <sub>4</sub> <sup>+</sup>                                        | Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                   | nickel hexacyanoferrate (NiHCF Prussian blue analog)                                                                     | Tsai et al. <sup>43</sup>                                                                 |
| ClO <sub>4</sub> <sup>-</sup>                                       | Cl <sup>-</sup>                                                                                                                                                                                                                                                                                                                          | activated carbon cloth                                                                                                   | Xing et al. <sup>44</sup>                                                                 |
| PO <sub>4</sub> <sup>3-</sup>                                       | Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>                                                                                                                                                                                                                                                           | layered double hydroxide-reduced graphene oxide composite                                                                | Hong et al. <sup>45</sup>                                                                 |
| NO <sub>3</sub> <sup>-</sup>                                        | Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>                                                                                                                                                                                                                                                                                          | hierarchical carbon aerogel monoliths                                                                                    | Hawks et al. <sup>46</sup>                                                                |
| SO <sub>4</sub> <sup>2-</sup>                                       | Cl <sup>-</sup>                                                                                                                                                                                                                                                                                                                          | amine functionalized activated carbon                                                                                    | Zuo et al. <sup>47</sup>                                                                  |
| Cl <sup>-</sup>                                                     | SO <sub>4</sub> <sup>2-</sup>                                                                                                                                                                                                                                                                                                            | Bi                                                                                                                       | Chang et al. <sup>48</sup>                                                                |
| Br <sup>-</sup>                                                     | Cl <sup>-</sup>                                                                                                                                                                                                                                                                                                                          | activated carbon + ion-exchange membranes                                                                                | Li et al. <sup>49</sup>                                                                   |
| I <sup>-</sup>                                                      | Cl <sup>-</sup>                                                                                                                                                                                                                                                                                                                          | flow electrodes of activated carbon                                                                                      | Liu et al. <sup>50</sup>                                                                  |
| F <sup>-</sup>                                                      | SO <sub>4</sub> <sup>2-</sup>                                                                                                                                                                                                                                                                                                            | activated carbon + monovalent anion selective membrane                                                                   | Pan et al. <sup>51</sup>                                                                  |
| F <sup>-</sup>                                                      | Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>                                                                                                                                                                                                                                                                                           | graphene oxide-hydroxyapatite composite                                                                                  | Park et al. <sup>52</sup>                                                                 |
| Ca <sup>2+</sup>                                                    | Na <sup>+</sup>                                                                                                                                                                                                                                                                                                                          | H <sub>2</sub> SO <sub>4</sub> -treated activated carbon cloths                                                          | Uwayid et al. <sup>53</sup>                                                               |
| Sr <sup>2+</sup>                                                    | Na <sup>+</sup>                                                                                                                                                                                                                                                                                                                          | aryl diazonium salt-modified porous carbon                                                                               | Xiang et al. <sup>54</sup>                                                                |
| Cu <sup>2+</sup>                                                    | Na <sup>+</sup>                                                                                                                                                                                                                                                                                                                          | flow electrodes of activated carbon                                                                                      | Zhang et al. <sup>55</sup>                                                                |
| Fe <sup>3+</sup>                                                    | Na <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                                    | graphene nanoflakes                                                                                                      | Li et al. <sup>56</sup>                                                                   |
| Ni <sup>2+</sup>                                                    | –                                                                                                                                                                                                                                                                                                                                        | conductive graphite adhesive-activated ion-exchange resin composite                                                      | Wang et al. <sup>57</sup>                                                                 |
| Co <sup>2+</sup>                                                    | Li <sup>+</sup> , Ni <sup>2+</sup>                                                                                                                                                                                                                                                                                                       | electrodialysis with polymeric ion-exchange membranes                                                                    | Siekierka and Yalcinkaya <sup>58</sup>                                                    |
| Mn <sup>2+</sup>                                                    | –                                                                                                                                                                                                                                                                                                                                        | flow electrodes of dilute H <sub>2</sub> SO <sub>4</sub> with polymeric ion-exchange membranes                           | Soysüren et al. <sup>59</sup>                                                             |
| Zn <sup>2+</sup>                                                    | –                                                                                                                                                                                                                                                                                                                                        | activated carbon cloth                                                                                                   | Tang et al. <sup>60</sup>                                                                 |
| Pb <sup>2+</sup>                                                    | Mg <sup>2+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                                                      | thiol-functionalized graphene oxide-activated carbon composite                                                           | Huang et al. <sup>61</sup>                                                                |
| Pb <sup>2+</sup>                                                    | Co <sup>2+</sup> , Ni <sup>2+</sup>                                                                                                                                                                                                                                                                                                      | FeOOH                                                                                                                    | Wang et al. <sup>62</sup>                                                                 |
| Cd <sup>2+</sup>                                                    | –                                                                                                                                                                                                                                                                                                                                        | flow electrodes of δ-MnO <sub>2</sub>                                                                                    | Peng et al. <sup>63</sup>                                                                 |
| V <sup>5+</sup> (as VO <sub>3</sub> <sup>3-</sup> )                 | SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup> , SiO <sub>3</sub> <sup>2-</sup>                                                                                                                                                                                                                                           | resin-activated carbon composite                                                                                         | Bao et al. <sup>64</sup>                                                                  |
| Cr <sup>6+</sup> (as Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ) | Cl <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>                                                                                                                                                                                                                                                                                          | poly(vinyl)ferrocene-carbon nanotubes composite                                                                          | Su et al. <sup>65</sup>                                                                   |
| As <sup>5+</sup> (as AsO <sub>4</sub> <sup>3-</sup> )               | Cl <sup>-</sup>                                                                                                                                                                                                                                                                                                                          | poly(vinyl)ferrocene-carbon nanotubes composite                                                                          | Su et al. <sup>65</sup>                                                                   |
| Sc <sup>3+</sup>                                                    | Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Zn <sup>2+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup>                                                                                                                                                                                                          | electrodialysis with polymeric ion-exchange membranes                                                                    | Li et al. <sup>66</sup>                                                                   |
| Sm <sup>3+</sup>                                                    | Ag <sup>+</sup> , Cd <sup>2+</sup> , Co <sup>2+</sup> , Mn <sup>2+</sup> , Al <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Hg <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> | B <sub>12</sub> S nanoflakes                                                                                             | Xiang et al. <sup>67</sup>                                                                |
| La <sup>3+</sup>                                                    | Na <sup>+</sup> , Ca <sup>2+</sup>                                                                                                                                                                                                                                                                                                       | P-doped carbon                                                                                                           | Xiong et al. <sup>68</sup>                                                                |
| La <sup>3+</sup> , ND <sup>3+</sup> , Ce <sup>3+</sup>              | –                                                                                                                                                                                                                                                                                                                                        | sodium diphenylamine sulfonate-modified activated carbon                                                                 | Wang et al. <sup>69</sup>                                                                 |
| U <sup>6+</sup> (as UO <sub>2</sub> <sup>2+</sup> )                 | seawater (majorly Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> )                                                                                                                                                                                                                                               | BP nanosheets                                                                                                            | Chen and Tong <sup>70</sup>                                                               |

The selection of measurement techniques should align with experimental goals to ensure accurate and relevant results in electrochemical desalination investigations. In this work, we have used online ICP-OES monitoring to showcase a selectivity measurement and its relevant considerations and relationships. As outlined previously,





**Figure 4.** All elements targeted so far for electrochemical recovery from water

Periodic table showing elements targeted in electrochemical desalination (capacitive deionization, battery desalination) for selective recovery from aqueous media in a cyclic manner.

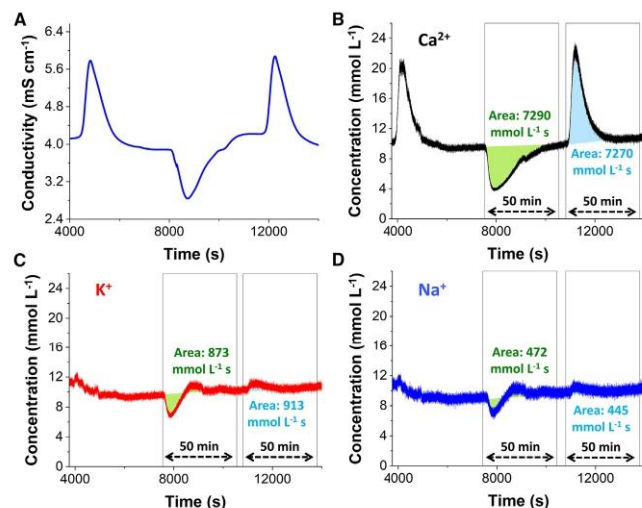
an electrochemical desalination cell with symmetric carbon electrodes was charged and discharged. The electrolyte in this case consisted of CaCl<sub>2</sub>, KCl, and NaCl, each with 10 mmol L<sup>-1</sup>, instead of the previously examined single-salt NaCl electrolyte.

To enhance the signal-to-noise ratio, one can increase the electrode mass and, if possible, a lower flow rate. The latter measures increase the amplitude of concentration change in each cycle, thereby maximizing the signal-to-noise ratio. A side-by-side comparison of raw ICP-OES data for two cells with carbon electrodes of significantly different masses is included in Figure S3. A noisy raw ICP-OES dataset will translate into less accurate concentration profiles (Figure S4), rendering further integrations and calculations inaccurate.

Further processing of raw ICP-OES data will result in Figures 5B–5D, individually showing the concentration-change profiles of calcium, potassium, and sodium ions. The process to convert raw ICP-OES data into the concentration of ions includes the calibration of the ICP-OES instrument with a set of samples with known concentrations (Figure S5) in the same manner shown previously to convert conductivity data into the concentration of a single-salt electrolyte (Figure 2).

The procedure to calculate the DC will be similar to what has been carried out to calculate the DC of a single-salt system (Figure 3B). For instance, to calculate the desalination capacity of the system for calcium ions (DC<sub>Ca<sup>2+</sup></sub>) using Equation 1, one has to substitute the molar mass of calcium ions (40.08 g mol<sup>-1</sup>) instead of the previously used molar mass of NaCl. Also, since the Ca<sup>2+</sup> ions are attracted to the negative electrodes, the  $m_{\text{total}}$  in Equation 1 has to be replaced by the mass of only the negative electrode. Substitution of the latter values, the average of integrated areas under the two charging and discharging half-cycles in concentration-time curves, and the flow rate gives DC<sub>Ca<sup>2+</sup></sub> = 7.4 mg g<sup>-1</sup>. Similarly, the desalination





**Figure 5. Online elemental monitoring of the effluent of an electrochemical cell**  
(A) Conductivity variations as a result of cycling a carbon/carbon electrochemical cell containing 506 mg of carbon cloth as negative electrode and 501 mg of carbon cloth as positive electrode in a mixed aqueous electrolyte containing  $\text{CaCl}_2$ ,  $\text{KCl}$ , and  $\text{NaCl}$ , and the corresponding change in the concentration of (B) calcium, (C) potassium, and (D) sodium ions measured online by ICP-OES.

capacity for potassium ions ( $\text{DC}_{\text{K}^+}$ ) and desalination capacity for sodium ions ( $\text{DC}_{\text{Na}^+}$ ) can be calculated by substitution of the respective molar masses and integration areas to result in  $\text{DC}_{\text{K}^+} = 0.9 \text{ mg g}^{-1}$  and  $\text{DC}_{\text{Na}^+} = 0.3 \text{ mg g}^{-1}$ .

Figures 5C and 5D show that for  $\text{K}^+$  and  $\text{Na}^+$  ions, after an initial dip in concentration induced by charging the electrochemical cell, a slight increase occurs in concentration. This is unlike the case for  $\text{Ca}^{2+}$  ions in Figure 5B, where the concentration profile is dipped and gradually reaches its past level to the feed concentration. This effect has been observed before in the electrochemical desalination of multicomponent electrolytes via activated carbon electrodes, where the monovalent ions are preferentially adsorbed initially but are gradually replaced by divalent ions.<sup>79</sup> The latter intricate information on such time-dependent ion dynamics is provided exclusively by online monitoring with ICP-OES, as offline manual sampling techniques can hardly reveal such behaviors.<sup>80</sup> For the calculation of  $\text{DC}_{\text{K}^+}$  and  $\text{DC}_{\text{Na}^+}$  in Figures 5C and 5D, during the charging half-cycle the integrated areas above and under the concentration profiles were subtracted from each other to result in a net removal capacity during the charging half-cycle.

The merit of a system for the preferential removal of a particular element against another elements could be formulated as Equation 12<sup>76</sup>:

$$\beta_{A/B} = \left( \frac{\text{DC}_A}{\text{DC}_B} \right) \left( \frac{C_{B,\text{feed}}}{C_{A,\text{feed}}} \right), \quad (\text{Equation 12})$$

where  $\beta_{A/B}$  is a unitless separation factor for element A with respect to element B,  $\text{DC}_A$  ( $\text{mg g}^{-1}$ ) is the desalination capacity of A ions,  $\text{DC}_B$  ( $\text{mg g}^{-1}$ ) is the desalination capacity of B ions, and  $C_{A,\text{feed}}$  ( $\text{mg L}^{-1}$ ) and  $C_{B,\text{feed}}$  ( $\text{mg L}^{-1}$ ) are the concentration of A



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and B ions, respectively, at the beginning of the process (that is, their concentrations in feedwater). One must note the use of consistent units in Equation 12 for concentrations and desalination capacities, which were, in this case,  $\text{mg L}^{-1}$  and  $\text{mg g}^{-1}$ , respectively. Alternatively, one could use  $\text{mmol L}^{-1}$  for concentrations, which then mandates the use of  $\text{mmol g}^{-1}$  for desalination capacities.

According to the latter definition, a system that removes both A and B ions indiscriminately, that is, non-selective, will have a separation factor of  $\beta_{A/B} = 1$ . Any value of  $\beta_{A/B}$  greater than unity indicates a favorable removal capacity toward A compared to B. In the example above, to calculate the separation factor for  $\text{Ca}^{2+}$  ions with respect to  $\text{Na}^+$  ions ( $\beta_{\text{Ca}^{2+}/\text{Na}^+}$ ), the following values have to be substituted in Equation 12:  $\text{DC}_{\text{Ca}^{2+}} = 7.4 \text{ mg g}^{-1}$ ,  $\text{DC}_{\text{Na}^+} = 0.3 \text{ mg g}^{-1}$ ,  $C_{\text{Ca}^{2+}, \text{feed}} = 400 \text{ mg L}^{-1}$ , and  $C_{\text{Na}^+, \text{feed}} = 230 \text{ mg L}^{-1}$ , which results in  $\beta_{\text{Ca}^{2+}/\text{Na}^+} = 14$ . Alternatively, one could use the following units to reach the same result:  $\text{DC}_{\text{Ca}^{2+}} = 0.185 \text{ mmol g}^{-1}$ ,  $\text{DC}_{\text{Na}^+} = 0.013 \text{ mmol g}^{-1}$ ,  $C_{\text{Ca}^{2+}, \text{feed}} = 10 \text{ mmol L}^{-1}$ , and  $C_{\text{Na}^+, \text{feed}} = 10 \text{ mmol L}^{-1}$ .

In a similar fashion, the separation factor for  $\text{Ca}^{2+}$  ions with respect to  $\text{K}^+$  ions ( $\beta_{\text{Ca}^{2+}/\text{K}^+}$ ) will be calculated as 8. This means that the water flowing out of the cell during charging will be calcium deficient, which is relevant for water-softening applications. Similarly, the water flowing out of the cell during discharging will be calcium-rich while being sodium- and potassium-deficient. The volume of the latter flow, the calcium-rich brine, could be minimized by shortening the discharge time for more efficient water softening.

In certain studies, the above process is carried out in a batch mode. In the latter case, the feedwater is introduced into a usually larger cell (also called an electrochemical reactor<sup>81</sup>). After applying the charging voltage and selective uptake of the desired ions from the solution into the electrodes, the solution is exchanged with a fresh solution of lower volume (and of higher purity than feedwater). The discharging is then accomplished in the latter solution, and the ions previously immobilized in the electrodes are released, yielding an enriched solution of the desired ions called the recovery solution. The recovery solution is again exchanged with a fresh feedwater batch, regenerating the cell for a new cycle.

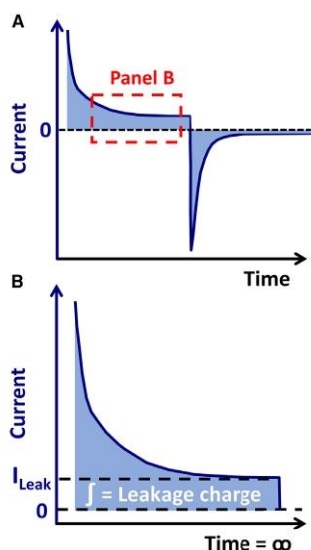
The batch-mode process, though interrupted, eliminates the need for online monitoring of elements, since one only needs to manually collect samples for elemental analysis at certain stages of the process, which are the feedwater and the recovery solutions.<sup>38</sup> In such a case, the separation factor expression can be reformulated as Equation 13:

$$\beta_{A/B} = \left( \frac{C_{A, \text{feed}} - C_{A, \text{final}}}{C_{B, \text{feed}} - C_{B, \text{final}}} \right) \left( \frac{C_{B, \text{feed}}}{C_{A, \text{feed}}} \right), \quad (\text{Equation 13})$$

where  $C_{A, \text{feed}}$  and  $C_{A, \text{final}}$  refer to the concentrations of A ions in the feedwater and the recovery solutions, respectively; and  $C_{B, \text{feed}}$  and  $C_{B, \text{final}}$  refer to the concentrations of B ions in the feedwater and the recovery solutions, respectively.<sup>41</sup>

#### Parameters affecting accuracy and meaningfulness of desalination performance metrics

Leakage current is one of the leading parasitic losses in the operation of electrochemical desalination cells, leading to energy loss.<sup>82</sup> We consider here the charging mechanism of a capacitor as an analogy to that of an electrochemical desalination cell. When a capacitor is being charged by applying a voltage to its terminals, once the electrodes are fully charged the current passing through the terminals



**Figure 6. Leakage current during cycling of an electrochemical desalination cell**

Schematic illustrations of (A) current response of an electrochemical desalination cell during charging and discharging half-cycles and the concomitant leakage current, and (B) calculation of leakage charge.

decays to zero. In an electrochemical desalination cell, the latter indicates that the electrodes are fully charged, that the maximum population of salt ions is drawn into the electrode, and that the electrode capacity is fully realized. The rate at which the current decays depends on the time constant ( $\tau$ ) of the capacitor known from classic resistor-capacitor circuits. The latter states that the "natural" current response of a capacitor follows an exponential function of time ( $I \propto e^{-t/\tau}$ ). For instance, the current falls to 37% of its initial value once a period equal to one time constant ( $1\tau$ ) has elapsed since the start of the application of potential bias to its terminals.<sup>83</sup> Likewise, the current should fall to less than 1% of its initial value after a lapse of a period equal to the five times the constant ( $5\tau$ ).

In practice, however, the  $I$ - $t$  curve of an electrochemical desalination cell typically approaches a non-zero value, known as the leakage current, as schematically shown in Figure 6. In this case, an electrochemical desalination cell can be modeled as an ideal capacitor (or other charge sources such as a battery) paralleled to a leakage resistance element.<sup>84</sup> When a voltage is applied to the cell, a relatively small (leakage) current constantly passes through the cell in the background. One approach to calculating the leakage resistance is to perform impedance spectroscopy measurements. Another approach, which takes less effort, is to prolong the voltage holding time so that the current contribution from the capacitor decays to zero. As a result, the remaining current could be approximated as the leakage current, as shown in Figure 6B.

The origin of the leakage current ( $I_{Leak}$ ) is partly due to the slightly conductive saline electrolyte (in contrast to an insulating dielectric in a capacitor), where the sodium and chloride ions constantly carry (leak) a small fraction of electronic charge across the separator from electrode/current collector on one side to those on the other side upon the polarization of the cell. Another possible origin of the leakage current



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could be water splitting, mainly when a cell voltage near 1.2 V is applied and held. More information on other possible sources of leakage current may be found elsewhere.<sup>85,86</sup> As illustrated in Figure 6A, the leakage current is larger during charging than in discharging, since the leakage current is mainly a voltage-dependent phenomenon.<sup>23</sup> As outlined above, one has to prolong the voltage holding time long enough to obtain the leakage current. Integration of the marked rectangular area under the  $I$ - $t$  curve (Figure 6B) then gives the charge leaked between the electrodes/current collectors via the electrolyte, also known as the leakage charge ( $q_{\text{Leak}}$ ).

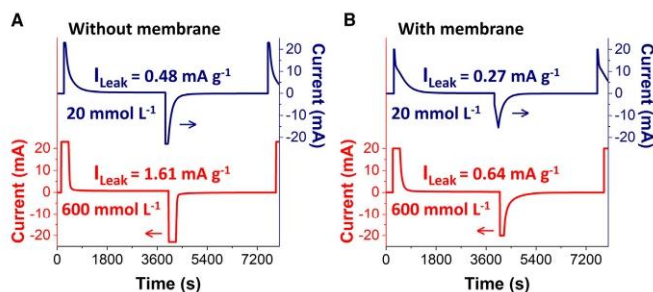
The leakage charge mentioned above should then be subtracted from the charge stored in the electrodes (obtained by the displacement current passing through the external circuit). Leakage charge considerations do not affect DC values. However, failure to consider the leakage charge in the calculations will result in inaccurate CE values, which follow further.

Zooming in on the  $I$ - $t$  profiles shown before (Figure 3D) reveals that the leakage current during the discharging half-cycle is insignificant and very close to zero. However, as expected, the leakage current is indeed significant during the charging half-cycle (Figure S6A), and its contribution to the overall charge invested by the power supply needs to be considered. Figure S6B shows how the leakage current is quantified and how the leakage charge can subsequently be obtained by multiplication of the latter to the duration of the cycle in the study, as indicated by the shaded area. Although the  $I_{\text{Leak}}$  of 0.241 mA may seem small, over time it yields a significant charge of  $q_{\text{Leak}} = 579 \text{ mA s}$  relative to the total charge of 5,932 mA s. Subtraction of the latter by the former gives a net charge of 5,353 mA s for the charging half-cycle, which is very close to that for the discharging half-cycle in Figure 3D (5,360 mA s). Averaging the latter two values (5,357 mA s) and substituting them in the CE formula gives a CE of 90%, a 5% increase from previously calculated without consideration of leakage charge.

To shed further light on the complications that might arise from failure to consider leakage charge subtraction, we base the DC and CE calculations this time on a different cycle duration, 60 min instead of 40 min. A glance at concentration-time profiles in Figures 3A and 3B reveals that the electrodes seemingly saturate after 40 min voltage holding time and reach their equilibrium. Calculations based on a 60-min time window for each half-cycle (Figure S7) yield an average CE of 83% and a DC of  $10.8 \text{ mg g}^{-1}$ . Leakage charge corrections, however, will result in the same CE of 90%, previously obtained for a 40-min half-cycle duration. As can be seen, leakage current considerations ensure accurate CE calculations regardless of the duration of the voltage holding step. Otherwise, the more extended voltage holding times will result in lower and lower calculated CE values.

The example above highlights the significance of leakage current considerations, although care must be taken to report it in the proper context. Leakage current is a highly system-dependent value, which depends on cell configuration, electrolyte concentration, and presence or absence of ion-exchange membranes, among others. As such, subtraction of leakage charge would help obtain more precise CE values, which in turn more accurately captures the mechanisms involved, such as the presence of co-ion-expulsion phenomenon or other faradic side reactions (decreasing the CE) or the absence of such phenomena (increasing the CE). Although leakage current considerations are educational within a research context, in a commercial setting where performance benchmarking of an electrochemical cell is being discussed or advertised, one must avoid subtracting the leakage charge.





**Figure 7.** Effect of electrolyte concentration and cell configuration on the magnitude of leakage current

Current-time profile for one full cycle of electrochemical desalination cells in electrolytes made of 20 mmol L<sup>-1</sup> and 600 mmol L<sup>-1</sup> NaCl solutions (A) without any ion-exchange membranes and (B) with anion- and cation-exchange membranes.

Reporting leakage charge-subtracted performance metrics in the latter case might lead to mischaracterization of the actual efficiency of the system.

To investigate the system dependency of leakage current, we have also examined the effect of electrolyte concentration and the presence of ion-exchange membranes in electrochemical desalination cells. Figure 7A shows the specific leakage current magnitude (that is, leakage current normalized to the mass of both carbon electrodes) of a single cell when cycled between 0.3 V and 1.2 V in 20 mmol L<sup>-1</sup> and 600 mmol L<sup>-1</sup> aqueous NaCl solutions. Swapping the electrolyte tank from a lower concentration to a higher concentration significantly increases the leakage current during the charging half-cycle. The latter observation is in line with the hypothesis outlined previously, which stated that one source of leakage current could be arising from the conductivity of the saline electrolyte. In 600 mmol L<sup>-1</sup> aqueous NaCl electrolyte, there will be more leakage of electronic charge from one electrode across the spacer channel to the other electrode.

In a fresh cell (Figure 7B), we introduced polymeric anion- and cation-exchange membranes before positive and negative carbon electrodes. It is seen again that the leakage current magnitudes scale with the concentration level. However, introducing such membranes has resulted in lower magnitudes of specific leakage currents than the membrane-less cell. Even though a barrier such as a membrane could constitute an extra resistive element in the cell, the membranes, which are electrically insulating, probably hinder the passage of electronic charges, resulting in a net diminishing effect on leakage current magnitude. In all cases, the leakage current magnitude during the discharging half-cycle has been shown to be negligible.

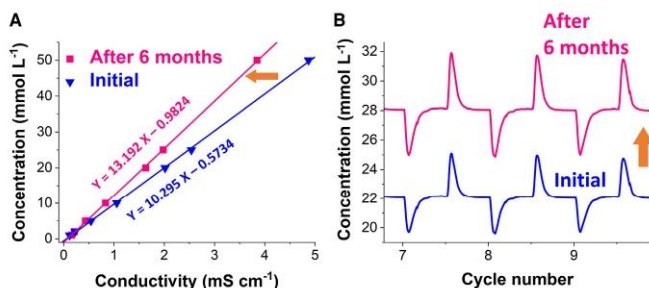
Next, we investigate the aging of conductivity probes and test whether it significantly changes the reported desalination metrics. Figure 8A shows two concentration-conductivity calibration curves performed on the same conductivity probe with an interval of 6 months. As understood by the slope change of the latter two curves, the sensitivity of the conductivity probes decreases over time, meaning that lower conductivity values are obtained for the same concentration as the probe ages. This slope change can affect the amplitude of concentration change when applied to an electrochemical desalination dataset. To test this, the linear equations of the fitted calibration curves are applied to the conductivity data shown in





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**Figure 8. Effect of aging of the conductivity probes**

(A) Calibration curves of the same conductivity probe, performed two times with a 6-month interval in between.

(B) The obtained concentration profiles of an electrochemical cell obtained from the latter two calibration equations.

Figure 2A to construct the concentration data presented in Figure 8B. As observed, two concentration profiles are obtained, which, although they follow the same trend, differ mainly in terms of both baseline concentration values (22 mmol L<sup>-1</sup> vs. 28 mmol L<sup>-1</sup>) and the amplitude of concentration change.

Performing the same calculations explained previously (Figure 3), DC and CE values of 13.8 mg g<sup>-1</sup> and 115% (after leakage charge subtraction) are obtained, respectively. The latter values vary primarily with the desalination metrics previously calculated, that is, an overestimation of DC by 3.0 mg g<sup>-1</sup> and CE by 25%. This pinpoints the importance of regular calibration of the conductivity probes before desalination experiments to avoid such inaccuracies. Assuming a monotonous loss of sensitivity for the conductivity probes tested herein within a 6-month interval, the inaccuracy could be approximated as 0.5 mg g<sup>-1</sup> per month for DC and around 4% per month for CE. As such, a calibration frequency of at least once per month is recommended to ensure the conductivity probes are fresh enough for reliable calculations.

More calibration curves for low and high-concentration regimes for two different conductivity probes with a 6-month interval may be found in Figure S8. Either of the two approaches may lead to inaccurate calculations: treating the old conductivity data with the equations obtained from a newly calibrated conductivity probe or treating the newly generated conductivity data with the equations obtained from an old formerly calibrated conductivity probe.

#### Relationships between pH, temperature, and conductivity

By definition, the conductivity of a solution  $\kappa$  (S m<sup>-1</sup>) measures its ability to conduct electricity. The said conductivity of the solution arises from the sum of conductivity contributions of all individual ions present in the solution. As such, one needs to consider the conductivity contributions of pure water and dissolved salt.

The molar conductivity  $\Lambda_m$  (S m<sup>2</sup> mol<sup>-1</sup>) of an electrolyte solution can be defined<sup>87</sup> as its measured conductivity  $\kappa$  (S m<sup>-1</sup>) divided by its molar concentration  $C$  (mol m<sup>-3</sup>) following Equation 14:

$$\Lambda_m = \frac{\kappa}{C}, \quad (\text{Equation 14})$$



In the case of an electrolyte with infinitely dilute concentrations of ions, Kohlrausch's law of independent ionic migration<sup>88</sup> can be applied to break down the molar conductivity into its contributions coming from each ion, as expressed in Equation 15:

$$\Lambda_m^\circ = \sum_i \nu_i \lambda_i, \quad (\text{Equation 15})$$

where  $\Lambda_m^\circ$  is the molar conductivity at infinite dilution, also known as limiting molar conductivity.  $\lambda_i$  is the limiting molar ionic conductivity of ion  $i$ , and  $\nu_i$  is the number of ions  $i$  in the formula unit of the electrolyte.

What causes ions to conduct an electric current is their ability to move in a solution, that is, their mobility. As such, the molar ionic conductivity of an ion ( $\lambda_i$ ) is a direct function of its electrical mobility ( $\mu_q$ ) following Equation 16:

$$\lambda_i = F z_i \mu_{q_i}, \quad (\text{Equation 16})$$

where  $F$  is the Faraday constant, and  $z_i$  is the ionic charge (unitless) for the ion  $i$ . Replacing Equation 16 in Equation 15 gives us Equation 17:

$$\Lambda_m^\circ = F \sum_i \nu_i z_i \mu_{q_i}, \quad (\text{Equation 17})$$

For a simple A:B electrolyte with monovalent ions, Equation 17 for this electrolyte can be written for  $A^+$  and  $B^-$  ions as Equation 18:

$$\Lambda_m = F (\mu_{qA^+} + \mu_{qB^-}), \quad (\text{Equation 18})$$

From the Einstein relation (the kinetic theory), we know that the mobility of a particle can be related to its diffusion coefficient via Equation 19:

$$D = \mu k_B T, \quad (\text{Equation 19})$$

where  $D$  is the diffusion coefficient,  $\mu$  is the mobility defined as the ratio of the particle's drift velocity to an applied force,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. In the particular case of a particle with electrical charge  $q$ , the electrical mobility term  $\mu_q$  can be related to the generalized mobility  $\mu$  in Einstein's relation as Equation 20:

$$\mu = \frac{\mu_q}{q}, \quad (\text{Equation 20})$$

where  $\mu_q$  is defined as the ratio of the particle's drift velocity per unit electric field.

Combining Equation 19 and Equation 20 gives the Einstein-Smoluchowski equation for the diffusion of charged particles,<sup>89</sup> also known as the electrical mobility equation, as expressed in Equation 21:

$$D = \frac{\mu_q k_B T}{q}, \quad (\text{Equation 21})$$

Solving Equation 21 for  $\mu_q$  gives Equation 22:

$$\mu_q = \frac{Dq}{k_B T}, \quad (\text{Equation 22})$$

The Nernst-Einstein<sup>90</sup> equation can then be written for the AB electrolyte by substitution of Equation 22 in Equation 18 to result in Equation 23:

$$\Lambda_m = F \left( \frac{D_{A^+} q_{A^+}}{k_B T} + \frac{D_{B^-} q_{B^-}}{k_B T} \right), \quad (\text{Equation 23})$$



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Given that  $A^+$  and  $B^-$  ions are monovalent ions,  $q_{A^+}$  and  $q_{B^-}$  will be equal to one elementary charge. Equation 23, thus, upon further simplifications and substitution of  $eN_A$  for  $F$ , becomes Equation 24:

$$\Lambda_m = \frac{Fe}{k_B T} (D_{A^+} + D_{B^-}) = \frac{e^2 N_A}{k_B T} (D_{A^+} + D_{B^-}), \quad (\text{Equation 24})$$

Replacing Equation 14 in Equation 24 gives Equation 25:

$$\kappa = \frac{e^2 N_A}{k_B T} (C_{A^+} D_{A^+} + C_{B^-} D_{B^-}), \quad (\text{Equation 25})$$

where  $C_{A^+}$  and  $C_{B^-}$  are molar concentrations of  $A^+$  and  $B^-$  ions, respectively.

In the case of hypothetically pure water with absolutely no contaminants, the weak self-ionization of water molecules into protons and hydroxide ions can be formulated as Equation 26:



$$K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ\text{C} \quad (\text{Equation 26})$$

where  $K_w$  is the equilibrium constant for the self-ionization of water. Given that  $H^+$  and  $OH^-$  ions will be responsible for the electrical conductivity of the electrolyte (water), Equation 25 can be written for them as in the form of Equation 27:

$$\kappa = \frac{e^2 N_A}{k_B T} ([H^+] D_{H^+} + [OH^-] D_{OH^-}), \quad (\text{Equation 27})$$

where  $[H^+]$  and  $[OH^-]$  in Equation 27 can be related to the pH as Equation 28:

$$[H^+] = 10^{-\text{pH}}, \text{ and } [OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-\text{pH}}} = 10^{\text{pH}-14}, \quad (\text{Equation 28})$$

Substitution of the relationships in Equation 28 in Equation 27 then gives Equation 29:

$$\kappa = \frac{e^2 N_A}{k_B T} (10^{-\text{pH}} D_{H^+} + 10^{\text{pH}-14} D_{OH^-}), \quad (\text{Equation 29})$$

Equation 29 then provides the relationship between the conductivity, temperature, and water pH.

As expressed by Equation 29, temperature and pH are the only variables influencing the conductivity of ideally pure water. Assuming a constant temperature of  $25^\circ\text{C}$  (298 K), the conductivity can then be plotted as a function of pH after substituting all physicochemical constants, as illustrated by Figure S9A. The V-shaped curve shows a weak pH dependency of water conductivity around near-neutral pH regimes. Approaching either of the acidic or basic extreme ends of the pH spectrum results in infinitely large conductivities (Figure S9). At pH 7, a theoretical conductivity of  $0.0549 \mu\text{S cm}^{-1}$  is obtained for ideally pure water free of contaminants, which is very close to the experimentally measured conductivity of ultrapure deionized water reported elsewhere ( $<0.0555 \mu\text{S cm}^{-1}$ ).<sup>91</sup>

The derivation of all the above expressions was based on the assumption that the  $H^+$  and  $OH^-$  ions are in dilute concentrations. Therefore, far deviations from the near-neutral regimes to either side of the pH range will negate the latter assumption for one of the ionic species and renders the calculations inaccurate. As such, a zoomed-in view of the near-neutral pH regimes (Figures S9B and S9C) would better



satisfy the starting assumptions regarding the dilute concentrations of both  $\text{H}^+$  and  $\text{OH}^-$  ions. As observed, within the pH range of 5–9, the conductivity is negligibly affected by the pH of the water, with a conductivity change of  $<0.005 \text{ mS cm}^{-1}$  in that pH window. Hence, while working within the pH window of 5–9, one could safely disregard the contribution of pH and be sure that the measured conductivity arises only from the presence of salt ions.

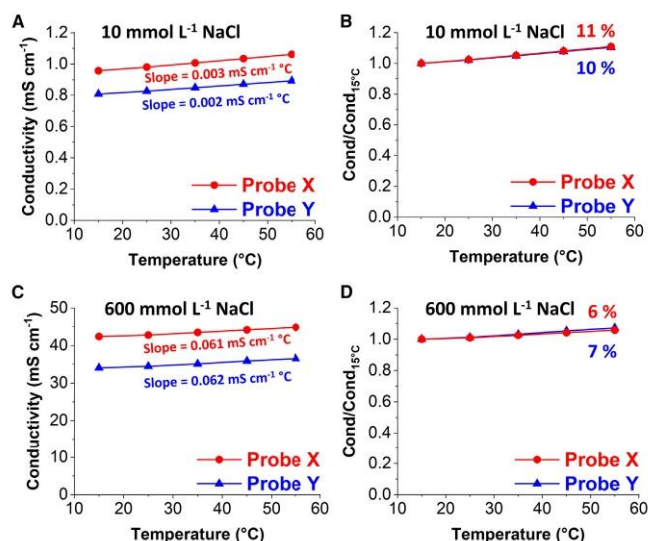
In contrast to pH, temperature variation has a much more complex effect on conductivity. Temperature variations change the self-ionization ( $K_w$ ) of water, as expressed in Equation 26, and shifts the pH values as a result. Consequently, the expression  $\text{pH} + \text{pOH} = 14$  will no longer hold. Temperature also affects the diffusion coefficients of  $\text{H}^+$  and  $\text{OH}^-$  ions in water, further making it less straightforward to plot a theoretical dependence of conductivity on temperature using Equation 25. As such, we measure the temperature dependency of conductivity experimentally in a wide temperature range of 15°C–55°C, as shown in Figure 9.

As expected, a steady increase in conductivity is observed upon increasing the temperature. Elevated temperatures increase the  $K_w$  in Equation 26, resulting in more populations of protons and hydroxide ions and thereby increasing the conductivity. The two different conductivity probes show very similar slopes in conductivity-temperature graphs. Going from 15°C to 55°C, we see that the gain in conductivity in the case of a low-concentration NaCl electrolyte ( $10 \text{ mmol L}^{-1}$ ) is 10%–11%, whereas it is 6%–7% in the case of the high-concentration NaCl electrolyte ( $600 \text{ mmol L}^{-1}$ ). The slightly higher conductivity gain in the case of low-concentration electrolyte indicates the conductivity contribution coming from the water as a result of temperature change, which becomes only significant when dealing with low-concentration electrodes ( $\leq 10 \text{ mM NaCl}$ ) and upon huge temperature variations such as 40°C. In the case of higher concentrations and slight temperature variations, it can be concluded that the temperature will not significantly influence conductivity and, hence, the concentration obtained.

In summary, the present work has illustrated in a step-by-step manner how a simple electrochemical desalination system is built and operated at the laboratory scale. At the heart of an electrochemical desalination setup, a cell houses a pair of electrodes that cyclically accomplish desalination when being charged and discharged. A conductivity meter monitors the conductivity change downstream of the cell. Once the conductivity meter is freshly calibrated with an array of stock solutions with known concentrations, it can reliably convert the measured conductivity of the cell's effluent water into the salt concentration, from which desalination capacity can be calculated. From the desalination capacity, the CE (and energy consumption) can also be calculated knowing the electronic charge data provided by the electrochemical workstation that applied voltage to the cell. The equations to calculate the said desalination metrics are also presented, which could be minimally modified for systems other than NaCl, such as LiCl.

We have emphasized that the conductivity meter has to be calibrated correctly and on time and have showcased how basing the calculations on 6-month-old calibration data could result in a significant deviation from actual performance metrics, specifically, 25%–30% relative error in final DC and CE values reported. We have additionally shown the significance of leakage current, how it is calculated, and how it could affect the CE values. We finally illustrated the relatively minimal effects of pH and temperature on the measured conductivities. The checklists provided in Notes S1 and S2 are developed to help the researchers have a quick overview of what is





**Figure 9. Wide variation of temperature and its effect on conductivity**

Experimental temperature dependency of the conductivity of two conductivity probes from 15°C to 55°C in (A) low NaCl concentration electrolyte and (B) its normalized gain in conductivity, and (C) high NaCl concentration electrolyte and (D) its normalized gain in conductivity.

needed when designing electrochemical desalination setups and what and how to report once the raw data are generated from such a setup.

## EXPERIMENTAL PROCEDURES

### Resource availability

#### Lead contact

Requests for further information, resources, or materials should be directed to and will be fulfilled by the lead contact, Volker Presser ([volker.presser@leibniz-inm.de](mailto:volker.presser@leibniz-inm.de)), upon reasonable request.

#### Materials availability

This study did not generate new unique materials.

#### Data and code availability

The data generated in this study are included in the manuscript and [supplemental information](#) and will be made available from the [lead contact](#) upon reasonable request.

### Conductivity and pH measurements

Aqueous stock solutions of sodium chloride with concentrations of 1–1,000 mmol L<sup>-1</sup> were prepared by first making 0.5 L of 1 mol L<sup>-1</sup> NaCl (VWR Chemicals) parent solution, followed by dilution with deionized water (Milli-Q, Merck Millipore) to the target concentration values. The solutions were kept in plastic centrifuge vials in a climatized chamber (BINDER) at constant temperatures of 25°C overnight to reach the equilibrium temperature before measuring.





The ionic conductivity of each solution was measured by the conductivity probe (Metrohm, 5-ring conductivity measuring cell with integrated Pt1000 temperature sensor) connected to a module (Metrohm, 856 conductivity module), which communicates the data to a desktop computer. Likewise, the pH was measured by a glassy pH probe (Metrohm, 3 mol L<sup>-1</sup> KCl electrolyte, with an integrated Pt1000 temperature sensor) connected to a module (Metrohm, 867 pH module) that communicates the pH data to the computer. Both conductivity and pH online data are shown in real time on the computer (Tiamo, Metrohm).

For temperature-dependent investigations of conductivity and pH, the aqueous stock solutions were kept in a climatized chamber (BINDER) at constant temperatures of 15°C, 25°C, 35°C, 45°C, and 55°C (each case:  $\pm 1^\circ\text{C}$ ). At each temperature, the solutions were left in the climatized chamber overnight to equilibrate with the target temperature before the measurements were made.

#### Electrode preparation

To prepare free-standing carbon electrodes, we followed the procedure outlined in our previous works.<sup>16,92</sup> Typically, the electrodes were made by adding enough ethanol to activated carbon (type YP-80F, Kuraray) in an agate mortar until it became entirely wet while manually stirring the mixture with a pestle. Once a homogeneous mixture was reached, polytetrafluoroethylene binder (60 mass % dispersion in water, from Sigma-Aldrich) was added to serve as a polymeric binder, using a carbon/binder mass ratio of 9:1. Stirring was continued under the fume hood until ethanol partially evaporated from the mixture to result in a carbon paste, which was further cold-rolled in a rolling machine (MTI HR01, MTI). The free-standing carbon films with a wet thickness of 600  $\mu\text{m}$  were then dried in a vacuum oven (Memmert) at 50°C overnight.

#### Electrochemical desalination tests

A pair of round pieces of the free-standing carbon electrodes were cut in 30-mm circular diameter and used as positive and negative electrodes for the electrochemical desalination cell. The carbon electrodes were sandwiched in a custom-made cell,<sup>93</sup> separated by a few round-shaped glass fiber filters (GF/A, Whatman) and nylon mesh pieces to allow the water stream to flow between the electrodes (flow-by configuration). To monitor the potential development in each electrode individually upon charge and discharge, a spectator Ag/AgCl reference electrode (3 M NaCl, BASi) was mounted on the cell near the electrodes. When needed, polymeric ion-exchange membranes with a diameter of 50 mm were cut and soaked into 20 mmol L<sup>-1</sup> NaCl electrolyte overnight. Anion-exchange membrane (Fumasep FAA-3-20, Fuma-tech) was placed in between the positive electrode and the flow channel, and the cation-exchange membrane (Fumasep FKE-20, Fuma-tech) was placed in between the negative electrode and the flow channel.

Ten liters of 20 mmol L<sup>-1</sup> aqueous NaCl solution was stored in a tank as the electrolyte, where it is constantly bubbled with a small nitrogen flow to minimize carbon electrode oxidation due to the presence of dissolved oxygen in the electrolyte. The electrolyte was pumped from the tank via a peristaltic pump (Masterflex) at flow rate of  $\sim 2 \text{ mL min}^{-1}$  into the cell. To ensure that accurate flow-rate values were obtained, the flow was collected manually using a 10-mL graduated cylinder for 5 min after each day of desalination measurements. The water stream flowing out of the cell went further into the chamber containing the conductivity probe, followed by the pH probe chamber, and finally cycled back into the tank to complete the loop (called a single-pass mode of operation). The entire setup was kept in a



climatized chamber at  $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$  to eliminate possible effects from day/night fluctuations in temperature.

Electrochemical testing was then carried out using an electrochemical workstation (Bio-Logic, potentiostat/galvanostat, type VSP300), programmed to repeatedly charge and discharge the cell at the rate of  $0.1 \text{ A g}^{-1}$  concerning the total mass of both carbon electrodes combined.

For selectivity measurements, a 1-L aqueous electrolyte of KCl (Sigma-Aldrich), NaCl (Roth), and  $\text{CaCl}_2$  (Sigma-Aldrich), each at  $10 \text{ mmol L}^{-1}$  concentration, was prepared. The electrolyte was constantly bubbled with nitrogen and pumped via a peristaltic pump (Masterflex Reglo ICC Digital Pump with independent channel control, 3-channel, 8-roller) into an electrochemical cell with symmetric carbon/carbon cloth electrodes (Kynol ACC-5092-20). The water stream flowing out of the cell first went into the chamber containing the conductivity probe and then proceeded to the ICP-OES instrument (ICP-OES, ARCOS FHX22, SPECTRO Analytical Instruments) before finally being discarded. The concentration of each ionic species was determined individually by intensity-concentration equations obtained by calibration of known samples beforehand (Table S1 and Figure S5).

#### SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2023.101661>.

#### ACKNOWLEDGMENTS

The INM authors acknowledge funding by the German Research Foundation (DFG, Deutsche Forschungsgemeinschaft) of the MXene-CDI project (PR-1173/11). Y.Z. acknowledges the financial support of the Alexander von Humboldt Foundation. C. Kim acknowledges the support of the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2021R111A3A040360).

#### AUTHOR CONTRIBUTIONS

M.T.: investigation, conceptualization, data curation, visualization, supervision, writing – original draft, writing – review & editing. C. Kök: investigation, data curation, writing – review & editing. P.R.B.: investigation, data curation, writing – review & editing. P.R.: writing – review & editing. Y.Z.: supervision, validation, writing – review & editing. J.L.: conceptualization, supervision, validation, writing – review & editing. C. Kim: supervision, validation, writing – original draft, writing – review & editing. V.P.: conceptualization, supervision, validation, resources, visualization, writing – original draft, writing – review & editing, project administration, funding acquisition.

#### DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: June 27, 2023

Revised: August 29, 2023

Accepted: October 5, 2023

Published: October 30, 2023

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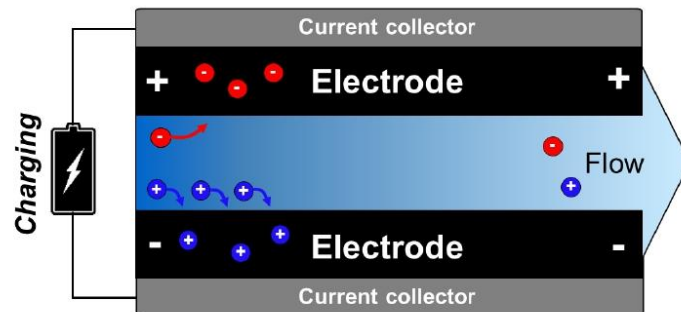
**Supplemental information**

**Best practice for electrochemical water  
desalination data generation and analysis**

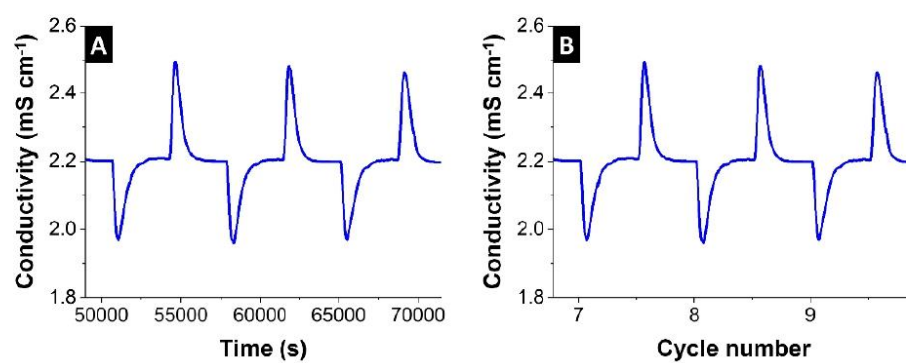
Mohammad Torkamanzadeh, Cansu Kök, Peter Rolf Burger, Panyu Ren, Yuan  
Zhang, Juhan Lee, Choonsoo Kim, and Volker Presser

## Supplemental Figures

Figure S1.

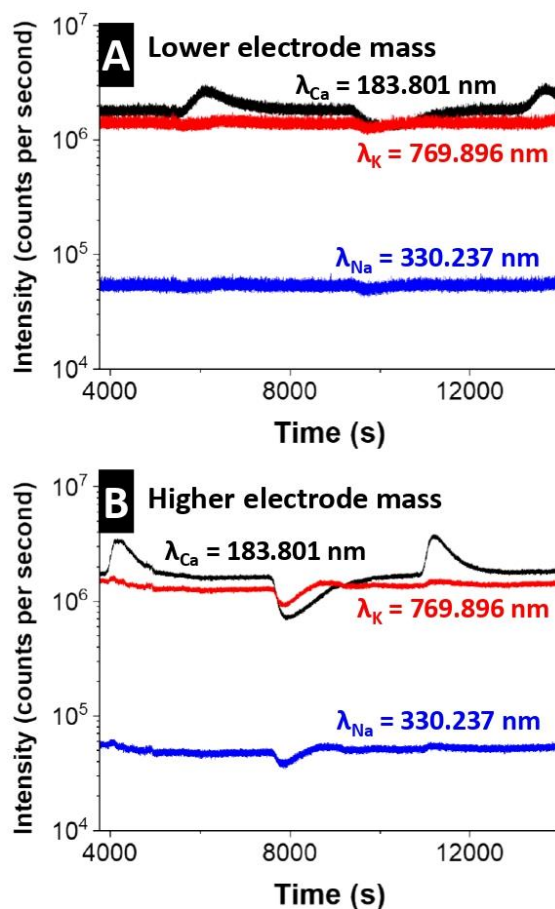


**Figure S1.** A simple electrochemical desalination cell. Schematic representation of an electrochemical desalination cell with flow-by configuration, where the water stream passes in between the two electrodes.

**Figure S2.**

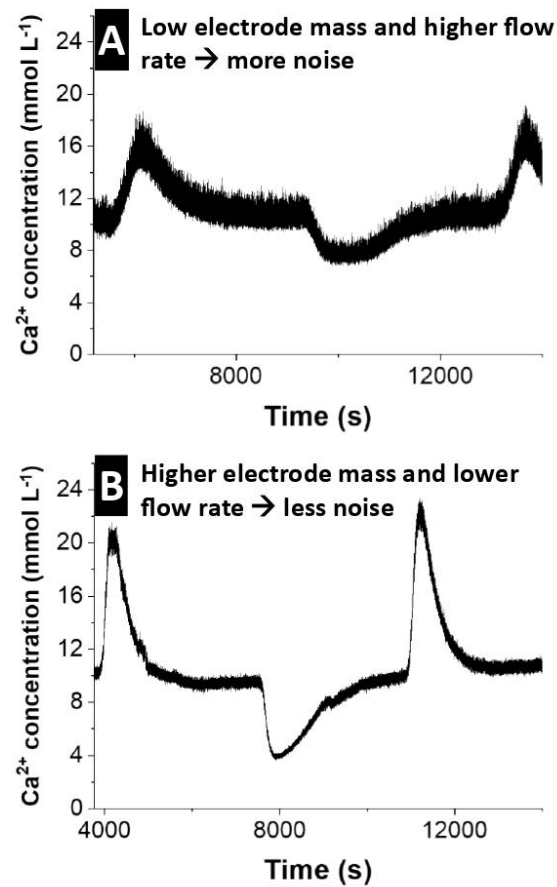
**Figure S2. Changing the time into cycle number.** Conversion of conductivity vs. time data (A) into conductivity vs. cycle number (B).

Figure S3.



**Figure S3. Raw online elemental monitoring data.** Variation of the intensities individually recorded from calcium, potassium, and sodium ions using online ICP-OES monitoring of effluent water stream of a carbon/carbon electrochemical cell showing (A) rather noisy data with a cell containing 294 mg carbon cloth as negative electrode and 293 mg carbon cloth as positive electrode, and (B) less noisy data with a cell containing 506 mg carbon cloth as negative electrode and 501 mg carbon cloth as positive electrode.

Figure S4.



**Figure S4. Improving the signal to noise ratio.** Calcium concentration change derived from raw ICP-OES intensity data (Figure S7) using concentration-intensity equations obtained from calibration curves (Figure S6): (A) a rather noisy concentration profile with a cell containing 294 mg carbon cloth as negative electrode and 293 mg carbon cloth as positive electrode and (B) less noisy concentration profile with a cell containing 506 mg carbon cloth as negative electrode and 501 mg carbon cloth as positive electrode.



Figure S5.

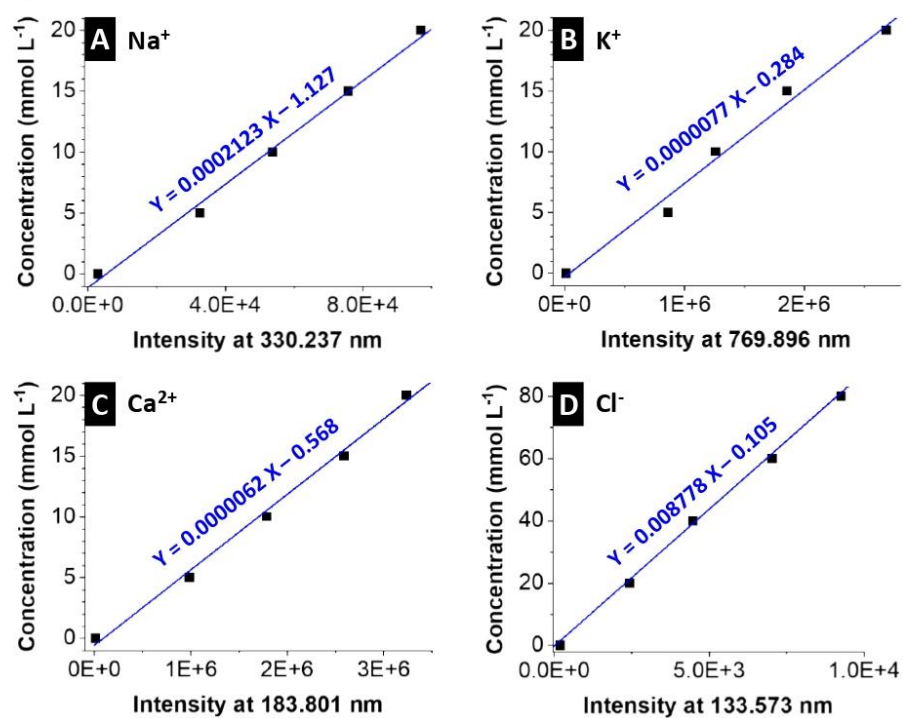
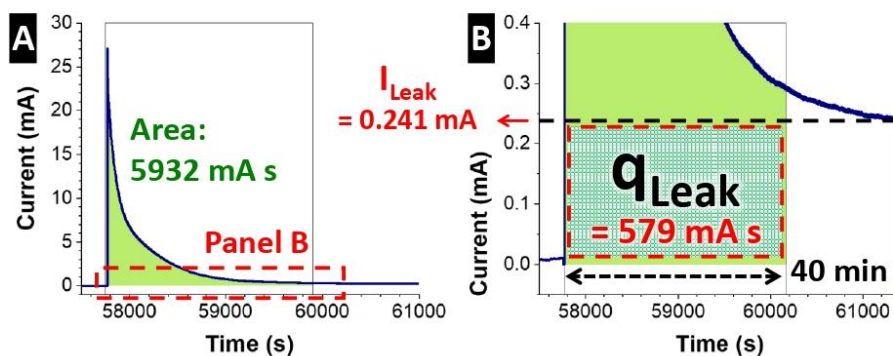


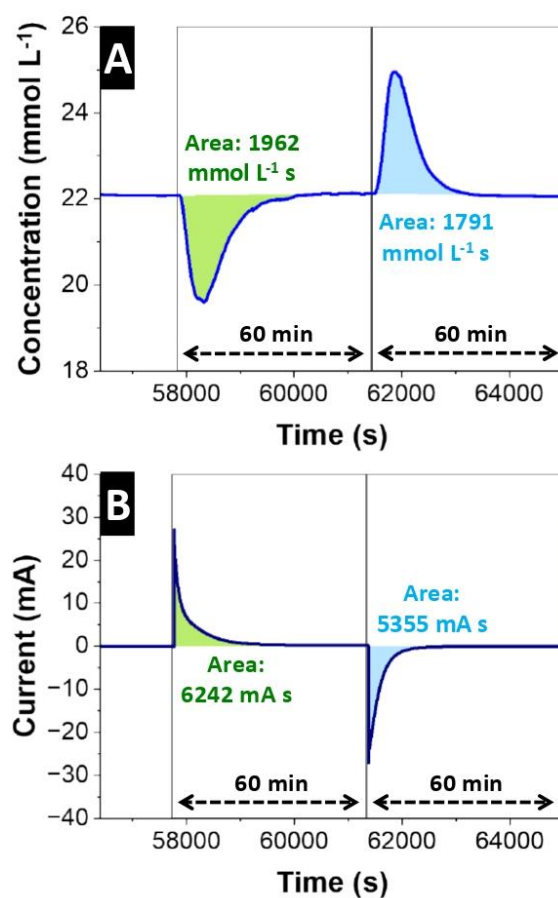
Figure S5. Construction of the calibration curves relating the ICP-OES intensity to the concentration. Concentration-intensity curves constructed using the solutions listed in Table S1 to calibrate the ICP-OES instrument so that the measured optical emission intensity of each element can be individually converted into its concentration for (A) sodium, (B) potassium, (C) calcium, and (D) chloride ions.

Figure S6.



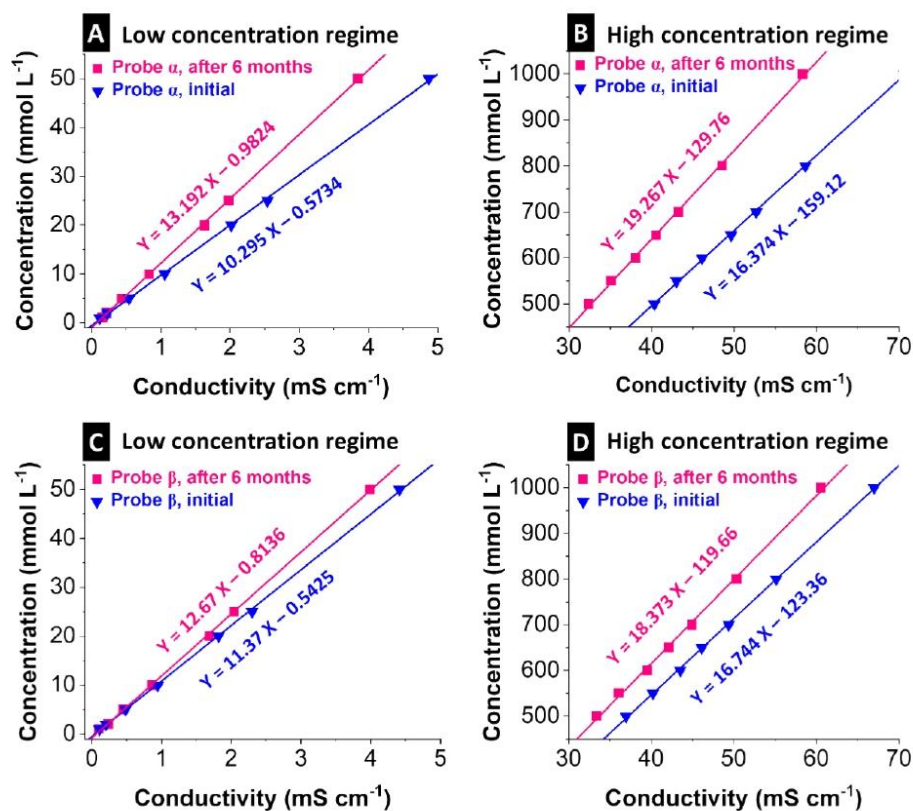
**Figure S6. Calculation of the leakage current of the electrochemical desalination cell in this study.** (A) Current-time profile for the charging half-cycle of an electrochemical desalination cell and (B) the zoomed view of the current-time curve showing the leakage current and leakage charge.

Figure S7.



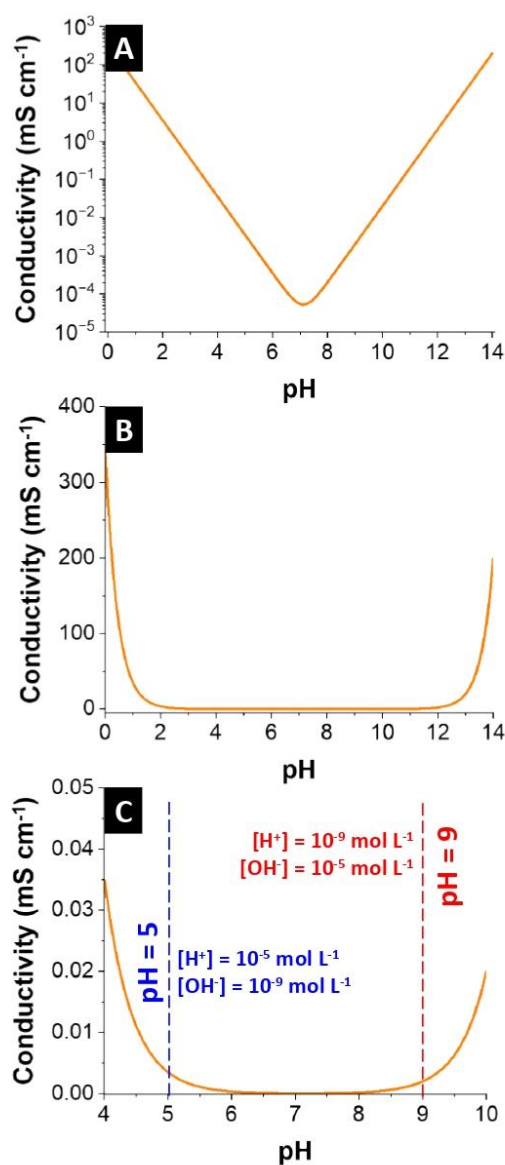
**Figure S7. Integration of the area under the curves of concentration-time and current-time profiles.** Integration of area under curve for charging and discharging half-cycles with 60 min duration each: (A) Concentration-time data and (B) current-time data.

Figure S8.



**Figure S8. Effect of aging of the conductivity probes.** Calibration curves of conductivity probe α, performed two times with 6 months interval in between for (A) low concentration and (B) high concentration regimes; calibration curves of conductivity probe β, performed two times with 6 months interval in between for (C) low concentration and (D) high concentration regimes.

Figure S9.



**Figure S9. How pH can theoretically affect the conductivity.** Theoretical dependence of the conductivity of ideally pure water on its pH is shown via (A) wide conductivity-pH scale, showing a conductivity of 0.055  $\mu\text{S cm}^{-1}$  at pH = 7; (B) narrower, and (C) narrower conductivity-pH scales showing a pH range where conductivity contribution of water is minimal.



**Supplemental Table****Table S1.** Composition and concentrations of the solutions used to calibrate ICP-OES instrument prior to ion selectivity measurements.

| Sample number | NaCl concentration (mmol L <sup>-1</sup> ) | KCl concentration (mmol L <sup>-1</sup> ) | CaCl <sub>2</sub> concentration (mmol L <sup>-1</sup> ) |
|---------------|--------------------------------------------|-------------------------------------------|---------------------------------------------------------|
| 1 (blank)     | 0                                          | 0                                         | 0                                                       |
| 2             | 5                                          | 5                                         | 5                                                       |
| 3             | 10                                         | 10                                        | 10                                                      |
| 4             | 15                                         | 15                                        | 15                                                      |
| 5             | 20                                         | 20                                        | 20                                                      |

**Supplemental Notes**

**Note S1.** The following is a checklist of what to report as the results of an electrochemical desalination experiment.

- Electrolyte parameters:
  - electrolyte concentration (mM, mg/L, or ppm)
  - electrolyte flow rate (mL/min)
  - de-aerated with an inert gas? (e.g., Ar or N<sub>2</sub>)
- Cell parameters:
  - cell configuration (e.g., flow-by, flow-through, or flow-electrode)
  - for each electrode: type, mass, thickness
  - types of membranes used, if any.
  - electrodes configuration (2-electrode system or 3-electrode system, half-cell or full-cell, with or without reference electrode)
- Other operational parameters:
  - single-pass or batch-mode
  - conductivity probe calibration status: when was it last calibrated? what was the concentration range used for calibration? how was the goodness-of-fit ( $R^2$  value)?
  - pH probe calibration status: when was it last calibrated?
  - pH variation: pH-time or pH-cycle curves, showing pH variation upon charge and discharge
- Electrochemical parameters:
  - specific current applied for charging and discharging (e.g., in A/g). it is important to specify here which mass was considered: the mass of both electrodes combined, the average mass of both electrodes, or the mass of a single electrode?
  - charging and discharging voltage, and voltage holding time in each step
  - number of cycles tested
- Performance metrics:
  - concentration-time or concentration-cycle curves
  - electrode potential-time (or cycle), cell voltage-time (or cycle), and current-time (or cycle) curves
  - average desalination capacity for each cycle, as well as the DC for charging half-cycle and for discharging half-cycle
  - the time duration considered for integration of C-t curve
  - charge efficiency, with and without leakage current subtraction
  - is the time duration considered for integration of I-t curve the same as that in C-t curve?
  - energy consumption (kT/ion removed)

**Note S2.** The following is a checklist of necessary items/considerations for an electrochemical desalination experiment.

- Hardware and infrastructure:
  - peristaltic pump: does the flow rate set on the pump match the real flow rate passing through its tubes? One can measure the flow rate manually by using a graduated cylinder and a simple chronometer.
  - conductivity probe: freshly calibrated with stock solutions
  - pH probe
  - temperature-controlled environment
  - inert gas source to bubble the electrolyte, as well as a gas washing bottle to minimize electrolyte evaporation
  - galvanostat/potentiostat that is capable of exporting outputs such as: electric charge stored in the electrodes during charging and the charge retrieved during discharging; energy consumed during charge; potential and current vs. time
- Software and other considerations:
  - reproducibility ensuring: does the software used for integration of area under concentration-time or current-time curves generate the same results when handled at a different time, or by a different user?
  - are the conductivity and pH probes close enough to the cell effluent to capture the characteristics of the outflowing water without long delays from the electrochemical results obtained by the galvanostat/potentiostat?

## Publication V

### ***Direct lithium extraction: A new paradigm for lithium production and resource utilization***

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#### **Citation:**

J. Farahbakhsh, F. Arshadi, Z. Mofidi, M. Mohseni-Dargah, C. Kök, M. Assefi, A. Soozanipour, M. Zargar, M. Asadnia, Y. Boroumand, V. Presser, A. Razmjou, Direct Lithium Extraction: A New Paradigm for Lithium Production and Resource Utilization, **Desalination** 575 (2024) 117249.

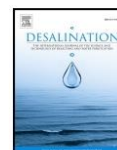
#### **Own contribution:**

Writing – original draft, Writing – review & editing



Contents lists available at ScienceDirect

Desalination

journal homepage: [www.elsevier.com/locate/desal](http://www.elsevier.com/locate/desal)

## Direct lithium extraction: A new paradigm for lithium production and resource utilization

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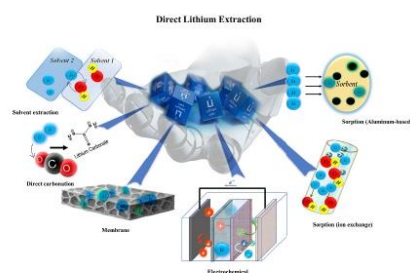
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### HIGHLIGHTS

- The lithium extraction is increasing through direct methods (i.e., sorption, membranes, electrochemical, and ion exchange).
- Industry professionals and researchers are working on the development of sustainable and efficient lithium production methods.
- Direct lithium extraction (DLE) has been challenged in cost reduction and environmental impacts of lithium production.
- Advancements in lithium production support a sustainable shift to a green economy over the past decade.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Direct lithium extraction  
Adsorption  
Membranes  
Electrochemical ion separation  
Ion exchange  
Solvent extraction

### ABSTRACT

The growing demand for lithium batteries in various applications has increased lithium production from multiple sources, including ores, brines, and spent batteries. Traditional extraction methods such as mining and evaporation ponds have significant environmental risks, such as air pollution and loss of habitats for aquatic and terrestrial animals. Furthermore, they cannot meet the ever-increasing demand for lithium in the global market. Consequently, industries have been exploring rapid and sustainable lithium recovery methods from these sources. Similar to what shale did for oil industry, Direct Lithium Extraction (DLE) represents a promising approach poised to enhance lithium production efficiency. This method not only reduces operation time but also brings added sustainability benefits. Various DLE methods have been proposed, such as adsorption, ion exchange, membranes, direct carbonation, and electrochemical processes. This paper comprehensively analyzes

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<https://doi.org/10.1016/j.desal.2023.117249>

Received 28 August 2023; Received in revised form 11 December 2023; Accepted 18 December 2023

Available online 27 December 2023

0011-9164/© 2023 Published by Elsevier B.V.



DLE technologies, including their fundamentals, principles, and applications. The focus is on various techniques used in DLE, highlighting their respective strengths and limitations. The study explores the potential of DLE for efficient and sustainable lithium recovery, considering the growing demand for lithium in the energy sector. Furthermore, the analysis examines the challenges associated with DLE, including cost, environmental impact, and scalability. This paper contributes to a greater understanding of the opportunities and limitations of DLE to inspire future crucial research efforts in this strategically important emerging technology.

## 1. Introduction

The rising demand for renewable energy and the global shift toward a low-carbon future have intensified the demand for energy-critical elements [1,2]. Lithium, in particular, has become pivotal to transitioning from fossil fuel-dependent industries toward cleaner and green energy sources [3]. It is assumed that over 12 years from 2016 to 2028, the worldwide consumption of lithium will grow considerably, from 37 k-tons (kt) of lithium in 2016 to an estimated 0.38 M-tons (Mt) of lithium by 2028 [4].

While lithium mining resources are the most abundant sources, water resources have emerged as a promising alternative reservoir. However, extracting lithium from aqueous sources using conventional technologies such as evaporation is challenging due to the lengthy process, low concentration of lithium in aqueous sources, and the presence of chemically similar ions, such as  $Mg^{2+}$ ,  $Na^+$ , and  $K^+$  [5,6]. These conventional techniques have been criticized for their high production costs and irreversible environmental implications. To address these concerns, numerous efforts have been made to extract lithium from aqueous sources in a more economically viable way [7–9]. In recent years, there has been a growing consensus on using DLE as a green technology to extract lithium from resources in a more efficient and eco-friendly manner, yielding higher efficacy. This can be achieved

through physical or chemical selective routes to separate lithium from the brine while leaving behind the other compounds [10–12].

New developments in DLE technologies provide an excellent opportunity to exploit lithium deposits that are supposed to be inaccessible or economically justifiable via conventional extraction approaches [13]. Over the past 50 years, numerous DLE technologies have been developed to separate lithium from other elements in brine without requiring water evaporation. While these DLE techniques can be effective for specific extraction sites, they cannot be interchangeable due to the varying nature and purity of brines. Therefore, the choice of each technique is tailored to the specific needs of each project. Researchers are investigating and developing different classes of DLE technologies worldwide. However, only a few techniques have advanced toward commercial deployment with a high technology readiness level (TRL) [14,15].

The techniques utilized in DLE were initially designed for desalination and wastewater treatment applications, contrary to a common misunderstanding that these technologies were newly developed for lithium extraction. DLE is essentially an adaptation of existing technologies, such as ion exchange, adsorption, and membrane separation, originally designed for desalination and wastewater treatment for mineral recovery. Recognizing this fact is crucial when discussing the development and implementation of DLE. Understanding the origin of

**Table 1**

The comparison of various DLE methods. Besides the mechanisms of adsorption, ion exchange, solvent extraction, membrane, precipitation, and electrochemical processes, the pros and cons of each method are discussed.

| DLE method                       | Mechanisms                                                                                         | Advantages                                                                                                                                                                                                                                                                                                                                                                                   | Disadvantages                                                                                                                                                                                                                                                                                                                                     | References      |
|----------------------------------|----------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|
| Adsorption<br>(TRL:9)            | Sorption of $LiCl$ onto the adsorbent                                                              | <ul style="list-style-type: none"> <li>- High selectivity</li> <li>- Global commercialization</li> <li>- Simple operation</li> <li>- Adaptability</li> <li>- Low energy usage</li> <li>- Low environmental impact</li> </ul>                                                                                                                                                                 | <ul style="list-style-type: none"> <li>- Dissolution loss</li> <li>- Time-consuming operation</li> <li>- Adsorbents are expensive and degrade in acid-based desorption</li> <li>- Complex regeneration of adsorbents</li> </ul>                                                                                                                   | [34,208,209]    |
| Ion-exchange<br>(TRL:8)          | Sorption of $Li^+$ into the ion-exchanger                                                          | <ul style="list-style-type: none"> <li>- High selectivity</li> <li>- High separation efficiency</li> <li>- Low initial investment</li> <li>- High theoretical lithium-uptake capacity</li> <li>- Relatively low energy usage</li> <li>- Environmental friendliness</li> </ul>                                                                                                                | <ul style="list-style-type: none"> <li>- High operating cost</li> <li>- Environmental hazards production</li> <li>- Weak virtual lithium-uptake capacity</li> </ul>                                                                                                                                                                               | [34,208]        |
| Solvent<br>Extraction<br>(TRL:7) | Based on the difference in partition coefficients of lithium between the liquid and organic phases | <ul style="list-style-type: none"> <li>- Simple and continuous operation</li> <li>- Adaptability</li> <li>- High <math>Li^+</math> selectivity</li> <li>- Low capital investment</li> <li>- Relatively simple equipment</li> <li>- Suitable for lithium recovery from brines with a high <math>Mg^{2+}/Li^+</math> mass ratio</li> </ul>                                                     | <ul style="list-style-type: none"> <li>- Risk of fire in high-temperature brines</li> <li>- High costs relative to other technologies</li> <li>- Complicated preparation</li> <li>- High environmental impact</li> <li>- Corrosive additives and solvents needed</li> <li>- High waste production</li> <li>- Toxic material production</li> </ul> | [27,28,208–210] |
| Membranes<br>(TRL:4–5)           | Pressure-driven (nanofiltration) or electrical potential-driven (electrodialysis) methods          | <ul style="list-style-type: none"> <li>- No contact between the extractant and brine</li> <li>- Low levels of impurities</li> <li>- Simple and continuous operation</li> <li>- High recovery rates</li> <li>- High efficiency</li> <li>- Relatively low energy usage</li> <li>- Environmental friendliness</li> <li>- No need for additional purification for industrial purposes</li> </ul> | <ul style="list-style-type: none"> <li>- Nascent</li> <li>- Fouling issues</li> <li>- Instability for geothermal brines</li> <li>- Pre-treatment requirement</li> <li>- High costs</li> <li>- High initial investment and operating costs for fabricating and regenerating different membranes</li> </ul>                                         | [34,72,208,210] |
| Electrochemical<br>(TRL:3–4)     | Reversible electrochemical processes, such as Lithium-ion intercalation in electrodes              | <ul style="list-style-type: none"> <li>- High efficiency</li> <li>- High selectivity</li> <li>- Environmental friendliness</li> </ul>                                                                                                                                                                                                                                                        | <ul style="list-style-type: none"> <li>- High amount of electrolyte is required (depending on setup configuration)</li> </ul>                                                                                                                                                                                                                     | [34,210]        |

these technologies and their pros and cons in DLE (Table 1) makes it possible to identify areas of potential improvement and innovation.

So far, only limited research has been conducted to comprehensively review the physio-chemical working principles, benefits, limitations, and opportunities and challenges associated with DLE technologies. Murphy et al. [16] reviewed the benefits and challenges of traditional and modern technologies for Li recovery from salt lake brine and seawater and presented DLE with a great potential strategy for large-scale Li production. Vera et al. [17] analyzed the environmental impacts and limitations of the current evaporitic and alternative strategies, particularly DLE, for lithium production from water sources. Reich et al. [18] investigated the potential application of several DLE methods, including sorption and ion exchange, for implementation in geothermal power plants at an industrial scale. Nonetheless, there is still a gap in the current literature when it comes to conducting an in-depth analysis of the challenges and advantages associated with DLE and identifying essential materials for enhancing these methods, particularly in sorption and membrane ion separation technologies. Furthermore, the

exploration of the direct carbonation process, considered a potential technique with low operational costs and high efficiency, has not yet been discussed in any research study. Additionally, the comprehensive examination of pre- and post-treatment techniques applied to DLE methods remains a subject that is insufficiently explored, and further information is imperative to gain a comprehensive understanding of these methods and their efficacy.

This study presents a comprehensive review of the latest developments in lithium extraction, specifically emphasizing DLE methods from water resources. Several DLE technologies, including sorption, ion extraction, membrane, electrochemical techniques, and direct carbonation process, have been reviewed and evaluated for their potential to enhance lithium extraction efficiency while minimizing environmental impact. Additionally, there is a limited number of published studies reporting on the commercial-scale implementation of these technologies. We believe there is a need to provide a thorough evaluation of the key characteristics and current commercial status of the various DLE methods, analyzing their potential applicability and highlighting the

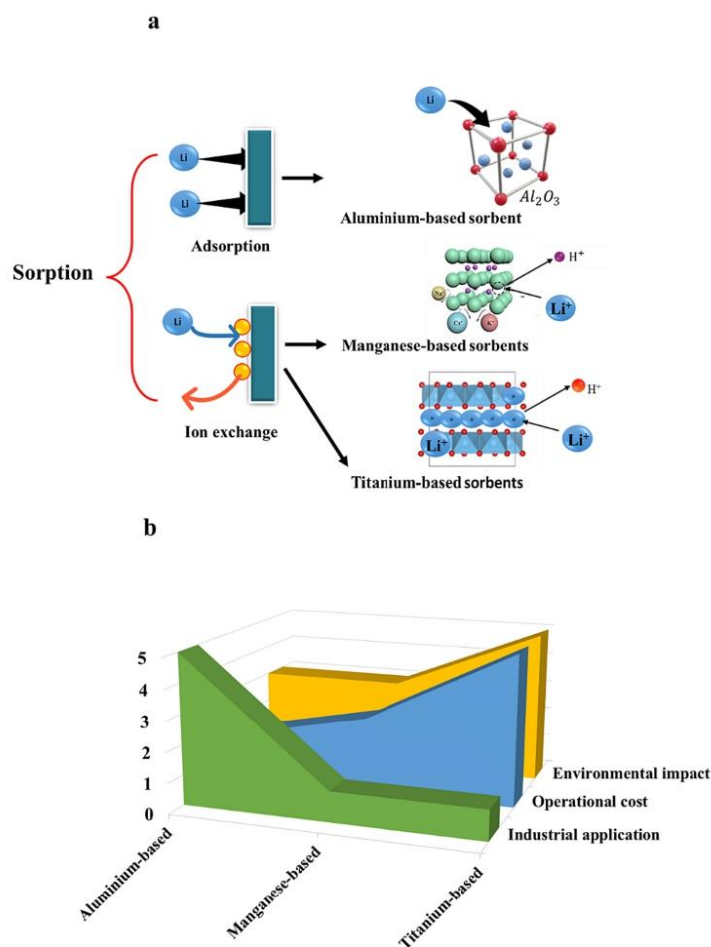


Fig. 1. (a) ion exchange and sorption mechanisms for lithium recovery with three different metals, including aluminum, titanium, and manganese-based sorbents, and (b) the comparison of three main metal-based sorbents based on three factors of i) industrial application, ii) operation cost, iii) environmental impact.



benefits of these technologies.

## 2. Technologies for DLE

### 2.1. Sorption (adsorption and ion exchange)

#### 2.1.1. Overview

Sorption-based DLE is a process that involves the selective attachment of targeted substances, or sorbates, here lithium, from an aqueous solution to insoluble materials, known as sorbents. Sorption is facilitated by either an adsorption (no ion exchange involved) or an ion exchange process (Fig. 1a). A common misunderstanding exists in the industry regarding sorption DLE, that defines it solely as an adsorption process primarily associated with aluminum-based sorbents. However, it is essential to clarify that sorption is a broader term encompassing both adsorption and ion exchange processes. In fact, sorption represents a parent terminology that includes not only adsorption but also ion exchange phenomena. While adsorption-DLE is the physical/chemical attachment of lithium onto the surface of solid particles, typically aluminum-based sorbents [19], ion exchange-DLE is a process where lithium ions in a liquid phase are swapped with ions of the same charge but with different chemical properties on a solid ion exchanger, mainly manganese-based and titanium-based sorbents [20].

Sorption is an efficient strategy for selective recovery of lithium from brines with a high  $\text{Mg}^{2+}/\text{Li}^+$  ratio, offering the advantages of high lithium selectivity, low energy consumption, straightforward operational procedure, and environmental friendliness [21–24]. These distinct advantages make sorption technology a promising approach to extract lithium efficiently and sustainably from different sources, thus supporting the progress of the lithium industry. Although sorption-DLE has achieved a high TRL compared to other DLE methods, such as the TRL of 9 for aluminum-based adsorption, there is some debate regarding its adaptability to different types of brines, mainly because of substantial variations in brine compositions depending on the location. Therefore, to ensure the efficacy of sorption-DLE for different types of brines, it is crucial to utilize an appropriate pre-treatment step customized to the specific brine being used [25]. In other words, each type of brine necessitates a unique pre-treatment approach to optimize the utilization of sorption-DLE technology; this will be thoroughly discussed in the pre and post-treatment section.

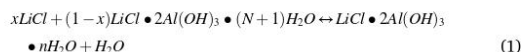
The key to successful sorption lies in selecting superior sorbents that demonstrate high sorption capacity, operational stability, and selectivity toward lithium. Sorbents used in DLE, including aluminum-based, manganese-based, and titanium-based, exhibit relative durability under harsh conditions throughout sorption operations such as high salinity, intense acidity, temperature fluctuations, and mechanical stress [26,27]. The primary principle behind the lithium selectivity of metal-based sorbents is based on their structural memory effect. Template ions are first incorporated into their structure through redox or ion-exchange reactions during their fabrication process. Subsequently, the template ions are removed from the structure, creating vacancies within the sorbent material that possess ion-specific properties toward lithium ions due to ion screening phenomena and the memory effect [2,28]. Currently, aluminum-based sorbents are being utilized commercially on a large scale, while manganese and titanium-based sorbents have only reached the pilot-scale stage of development. Prior research studies [29,30] have extensively reviewed the recent advancement in sorbent materials for lithium recovery and therefore, we will provide a brief overview of their process, feasibility, and potential applications.

#### 2.1.2. Aluminum-based sorbents (No ion exchange)

Aluminum-based sorbents, especially lithium-aluminum layered double hydroxides (LiAl-LDHs), have proven to be highly selective and efficient material for lithium recovery, possessing the general chemical formula of  $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ , where “X” represents anions, usually Cl, and “n” indicates the number of  $\text{H}_2\text{O}$  [31]. Aluminum-based sorbents are

fabricated by intercalating lithium ions, usually found from compounds like LiCl, LiOH, or lithium sulfate ( $\text{Li}_2\text{SO}_4$ ), into aluminum hydroxides, which are often present in naturally occurring minerals such as gibbsite ( $\alpha\text{-Al}(\text{OH})_3$ ) or bayerite ( $\beta\text{-Al}(\text{OH})_3$ ) [32]. The methods of their fabrication include coprecipitation, solid-state synthesis, and hydrothermal method [33].

LiAl-LDHs have a two-dimensional structure of aluminum hydroxide layers linked by electrostatic interactions, hydrogen bonds, and van der Waals forces. This structure facilitates the efficient adsorption of lithium ions within octahedral voids. Their strong selectivity toward lithium ions is primarily due to lithium's ability to enter the  $\text{Al}(\text{OH})_3$  structure and occupy the octahedral spaces, whereas larger alkaline earth metal ions cannot achieve due to steric hindrance effects [21,34]. Their mechanism of adsorption and desorption can be elucidated as follows:



While their adsorption capacity is lower than manganese and titanium-based sorbents, reported to <8–10 mg/g in a pH range of 3–8, LiAl-LDHs are the sole industrial sorbents with several advantages of easy fabrication, stable adsorption performance, relatively lower production costs, and easy regeneration without the need for acid or base treatments [2,25,27]. Besides, saturated LiAl-LDHs can be easily desorbed and regenerated using low conductivity neutral water, thus mitigating the risk of sorbent dissolution resulting from the use of acidic eluents [35].

In contrast to earlier research, which emphasized the need for pre-treatment to achieve effective adsorption, recent feasibility studies have shown that aluminum-based adsorption can reach a high TRL when three critical conditions are met: a specific lithium content, adequate salinity to drive the adsorption process, and elevated brine temperature [36]. Higher lithium concentrations are advantageous because they enhance the intercalation of lithium into the alumina layers [37]. In this regard, Hawash et al. [38] have provided evidence that higher initial lithium concentrations in treated solutions lead to improved efficiency in lithium adsorption, supporting previous findings. In terms of salinity, unlike other alkali ions that have a relatively weak level of hydration, lithium ions have a strong tendency to be surrounded by two layers of water molecules in aqueous solutions, which helps stabilize their electric charge within the solution [39]. In brines with high salinity, the double hydration of lithium ions is hindered due to the intense competition with other ions for water molecules, resulting in the accumulation and thus adsorption of lithium ions on the surface of sorbents during the loading process, while the other ions remain suspended in the brine [36]. Therefore, lithium adsorption is primarily suitable for high-salinity brines [40]. Regarding temperature, numerous studies have confirmed the endothermic nature of lithium absorption by aluminum-based sorbents, demonstrating that higher temperatures can result in increased adsorption capacity [41–44].

#### 2.1.3. Manganese-based sorbents (ion exchange)

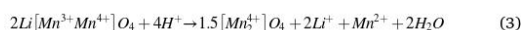
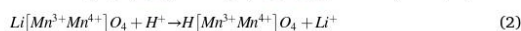
Manganese-based sorbents (LMOs) have attracted significant attention, due to their high sorption capacity and high selectivity for lithium [32]. These sorbents function effectively as ion sieves in different experimental setups and are also commonly employed as active additives in membrane processes and electrodes [2]. The precursors of manganese-based sorbents can be classified into three types based on different crystal structures and Li/Mn ratios:  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$  ( $\text{Li}_2\text{Mn}_2\text{O}_5$ ), and  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  ( $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ), resulting in the formation of  $\lambda\text{-MnO}_2$ ,  $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ , and  $\text{MnO}_2 \cdot 0.3\text{H}_2\text{O}$ , respectively [12,30]. In theory, increasing the Li/Mn molar ratio in precursors leads to a higher theoretical adsorption capacity of the corresponding sorbents. For instance,  $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$  exhibits the highest theoretical adsorption capacity among the types of manganese-based sorbents due to possessing a precursor with Li/Mn molar ratio of 1:1. However, in practical

applications, the adsorption capacity often does not meet the theoretical value [45].

The distinctive structure of LMOs plays a crucial role in their ability to selectively adsorb lithium, which is primarily due to the spinel structures found in their precursors. Among various precursor materials,  $\text{LiMn}_2\text{O}_4$  emerges as the most prominent example, showing a spinel structure with an  $\text{Fd}3m$  space group [46]. In this configuration, Li ions are situated in the 8a positions within tetrahedrons, while  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  alternate in occupying the 16d sites within octahedrons [24]. Simultaneously, oxygen anions occupy the 32e positions within the face-centered cubic crystal structure. The existence of empty octahedral and octahedral interstitial sites, linked in a repetitive 8a-16c-8a-16c pattern, enables the intercalation and de-intercalation of lithium ions within three-dimensional networks [28].

Manganese-based sorbents can be synthesized using a two-stage process comprising precursor preparation and acid treatment [12]. The precursor preparation process involves a heat treatment step (e.g.,  $\geq 400^\circ\text{C}$  [47,48]) that introduces lithium ions into the manganese complex, resulting in the formation of a spinel structure. The subsequent removal of lithium ions from the spinel structure is achieved by acid treatment, where a proton replaces the lithium ion without affecting the crystal structure, forming the lithium sieve manganese-based sorbent [32]. The sorbent can screen and recall lithium ions in the presence of numerous ions, known as lithium ion sieving [34].

Three mechanisms are suggested for the lithium adsorption of LMOs: ion exchange (Eq. (2)), redox (Eqs. (3)–(4)), and composite [34].



In the ion exchange mechanism, it is suggested that lithium ions are replaced by protons within the lattice structure, resulting in pH-dependent adsorption, while the Mn(III) and Mn(IV) sites remain unaffected. However, this mechanism does not predict any dissolution of manganese, indicating that the spinel structure should stay stable and maintain its performance during operations, which contradicts the observed results [45]. In the case of redox adsorption, the process of lithium intercalation and de-intercalation is mainly influenced by the uneven distribution of Mn(III) and Mn(IV) ions in an acidic environment. In such conditions, Mn(III) is expected to migrate to the surface and dissolve in the surrounding aqueous solution, while Mn(IV) is anticipated to remain within the crystal structure. This explains the experimentally observed manganese dissolution and the subsequent decrease in performance, but it does not completely clarify the pH dependency [2].

Despite their capacity to explain numerous phenomena of lithium recovery from aqueous solutions, both redox and ion exchange mechanisms have inherent limitations, resulting in the suggestion of the composite mechanism [2]. Ooi et al. [49] categorized lithium insertion sites into redox-type sites, lithium-ion-specific ion exchange sites, and non-specific ion exchange sites. The oxidation state of manganese in the precursor, following heat treatment, significantly influences the formation of these insertion sites. While the composite mechanism theoretically explains the intercalation and de-intercalation of lithium by LMO, its complexity hinders its practical verification [12].

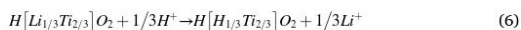
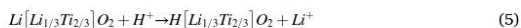
Modifications have been implemented to decrease dissolution loss while simultaneously enhancing the manganese sorption capacity to overcome the LMO dissolution. Overall, LMO sieves demonstrate sufficient ion exchange capacity and high levels of selectivity for lithium-ion extraction from various aqueous resources [27,50–52]. However,  $\text{Mn}^{2+}$  dissolution during acid regeneration presents a significant challenge that reduces ion exchange capacity and leads to poor cycling durability. This issue significantly limits the scalability of LMO technology at

present [27].

#### 2.1.4. Titanium-based sorbents (ion exchange)

Compared to LMOs, the application of titanium-based ion sieves for lithium extraction, particularly lithium titanium oxide (LTO), has not received much attention. Most studies have focused on layered  $\text{Li}_2\text{TiO}_3$  or spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  structures [53]. The crystal structure of layered LTO (Fig. 1a) can be characterized as an arrangement of oxygen atoms organized in a cubic close-packed pattern, with metal atoms situated within octahedral voids [24]. This structure consists of two layers created by lithium and titanium. The lithium layer is only formed by lithium atoms, which account for 75 % of the total lithium ions, while the ( $\text{LiTi}_2$ ) layer contains 2/3 Ti and 1/3 Li, which account for the remaining 25 % of total lithium ions [54]. Therefore,  $\text{Li}_2\text{TiO}_3$  can be described as  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_2$ , highlighting its distinct layered structure. The substitution of lithium ions with protons in layered  $\text{Li}_2\text{TiO}_3$  produces  $\text{H}_2\text{TiO}_3$ , which is suitable for lithium recovery from brines. The spinel structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is characterized by the  $\text{Fd}3m$  space group and cubic symmetry, in which lithium ions are situated in the tetrahedral 8a and 1/6 of the octahedral 16d sites [55]. The remaining octahedral 16d sites are occupied by titanium ions, resulting in a lithium-to-titanium ion ratio of 1:5. The 32e sites are also filled with oxygen ions [56]. Therefore, the spinel LTO can be represented as  $\text{Li}_{(8a)}[\text{Li}_{1/3}\text{Ti}_{5/3}]_{(16d)}\text{O}_{(32e)}$ . The octahedral 16c sites, the tetrahedral 8b, and the tetrahedral 48f sites remain vacant, offering suitable spaces for lithium ion insertion and extraction processes [55]. The synthesis methods of LTOs involve a range of approaches, including solid-phase, sol-gel, and hydrothermal techniques for precursor preparation, followed by acid treatment for ion-sieve fabrication [30]. In the conventional solid-phase method, a mixture of  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$  is first ground together and then heated at around  $700^\circ\text{C}$ , after which it is cooled to room temperature. This approach provides the benefits of achieving both high capacity and selectivity for the adsorption of lithium ions [54].

While spinel structures' intercalation and de-intercalation mechanisms are similar to LMOs, involving redox, ion exchange, and composite mechanisms, they are more straightforward for layered structures [24]. The superiority of lithium ion selectivity in layered  $\text{H}_2\text{TiO}_3$  over other cations is attributed to the presence of thin exchange site interlayers [28]. The mechanism underlying the behavior of the layered structure can be explained as follows [12]:



The main benefit of these sorbents lies in their eco-friendliness, as titanium ions are non-hazardous and easily removable [28]. Compared to manganese-based sorbents, LTOs exhibit limited dissolution loss during acid treatment due to their enhanced durability under acidic environments [57]. Furthermore, the stability of titanium valence ions throughout the processes of permeation and adsorption leads to higher theoretical adsorption capacity (127 vs. 68 mg/g [58]) and enhanced recyclability for continuous procedures (even >100 extraction cycles [59]) [27,60,61]. However, the rate of lithium adsorption for LTOs is relatively slower than that of LMO sorbents. Furthermore, applying an electrical potential limits their efficiency in recovering lithium ions from aqueous solutions [24].

The industrial utilization of LMO and LTO-based adsorbents for lithium recovery presents significant challenges due to the high cost of raw materials, the need for an acidic desorption process, their sensitivity to oxidation-reduction reactions, and the potential for dissolution loss [30]. These obstacles have limited their sustained usage over long-term periods. In order to address these issues, various modifications have been employed to create new adsorbents that enhance efficiency. These



modifications, which may involve altering synthesis conditions or introducing additives such as iron or nickel, hold notable importance for the industrial-scale utilization of these sorbents [62–65]. Some recent studies on the advancement of different lithium adsorbents have been reported in Table 2.

Table 2 indicates that Fe-doped and undoped  $\text{Li}_2\text{TiO}_3$  exhibit the highest adsorption capacity, reaching 53.3 mg/g and 50.5 mg/g, respectively, particularly at high initial lithium concentrations. According to the data in Table 2, titanium-based sorbents demonstrate higher performance compared to advanced materials like manganese and aluminum-based nanocomposites. Although porous  $\text{H}_4\text{Ti}_5\text{O}_{12}$  nanofibers exhibit a high adsorption capacity, their capacity has been evaluated under initial lithium concentrations. It is worth exploring the adsorption capacity of lithium with these porous nanofibers under higher initial lithium concentrations, as they may yield increased adsorption rates. Investigating various sorbents should be expanded to maximize efficiency under optimal operating conditions. However, these sorbents may have different operational costs and environmental impacts. From available data in the literature, the potential impacts and financial costs associated with the use of different sorbents, including aluminum, titanium, and manganese-based sorbents, have been concluded in Fig. 1b. This figure shows the significance of the sorbents mentioned above concerning their environmental impact, operational expenses, and their frequent use in the industry. According to this figure, aluminum-based sorbents are currently the leading sorbents used in the industry for lithium recovery. Hence, it can potentially play a significant role in meeting the growing demand for lithium.

## 2.2. Solvent extraction

Solvent extraction relies on the differential solubility of compounds in aqueous and organic phases [56]. This procedure involves several fundamental steps; first, the organic phase, which contains the extractant, is combined with a lithium-containing solution. As a result, lithium complexes are formed and transferred into the organic phase, along with some residual impurities. The phase containing the lithium complexes is then subjected to stripping to extract lithium, while the organic phase is recycled and regenerated. Various organic solvents, such as kerosene, m-xylene, p-xylene, chlorobenzene, benzene, dodecane, chloroform, cyclohexane, ketone, methyl-tertbutyl ether, and acetic ether, are utilized in lithium extraction. Green kerosene is a suitable solvent due to its lower volatility and toxicity [60,66]. Several variables can impact lithium extraction, including pH, extraction time, type of solvents and extractants, number of cycles, and temperature. According to previous reports [67–71], the optimal pH for lithium extraction is acidic, with a range of 0.86 to 6, although an alkaline solution has also proven efficient. The extraction duration varies from about 10 min to 4 h. Moreover, the optimum temperature in most experiments was around 25 °C, and the highest efficiency (96–98 %) was achieved in >5 cycles [56]. While solvent extraction is a cost-effective technique with simple equipment and operation, the cost of chemicals can be high. Using organic solvents can lead to environmental pollution and equipment corrosion [72].

Lithium solvent extraction techniques have three categories: multi-component solvent systems, ionic liquids, and crown ethers. Multi-component solvent systems consist of three elements: an extractant, a co-extractant, and a bulk solvent or diluent, such as xylene, kerosene,

**Table 2**

Recent studies on the adsorption capacity of novel advanced materials with high lithium adsorption capacity under different operating conditions, including lithium concentration, temperature, pH, and adsorbent dose.

| Sorbent                                                      | Operating C conditions               |             |       |                      | Lithium adsorption capacity (mg/g) | Equilibrium time (h) | Ref.  |
|--------------------------------------------------------------|--------------------------------------|-------------|-------|----------------------|------------------------------------|----------------------|-------|
|                                                              | Initial lithium concentration (mg/L) | Temperature | pH    | Adsorbent dose (g/L) |                                    |                      |       |
| Granulated Li/Al-LDHs                                        | 1400                                 | 298         | 8     | 80                   | 14.5                               | 4                    | [43]  |
| Li/Al-LDHs                                                   | 399                                  | 303         | 7     | –                    | 7.3                                | 2                    | [33]  |
| Al(OH) <sub>3</sub>                                          | 1150                                 | 295         | 4.5   | 1.15                 | 8.0                                | 4.5                  | [211] |
| Magnetic LiAl-LDHs                                           | 397.14                               | 298         | –     | 33.33                | 5.7                                | 4                    | [42]  |
| Magnetic LiAl-LDHs                                           | 397.14                               | 298         | –     | 33.3                 | 5.8                                | 4                    | [212] |
| Granulated LiAl-LDHs-SLS                                     | 300                                  | 298         | 7     | 10                   | 8.5                                | 0.66                 | [213] |
| Granulated LiAl-LDHs-SLS                                     | 1000                                 | 298         | 7     | 60                   | 11.8                               | 3                    | [213] |
| Granulated LiAl-LDHs                                         | 500                                  | 298         | 6     | 10                   | 9.7                                | 3                    | [44]  |
| $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$ -4%Al               | 600                                  | –           | 12.4  | 1                    | 46.8                               | –                    | [214] |
| $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$ -4%Mg               | 600                                  | –           | 12.4  | 1                    | 45.8                               | –                    | [214] |
| $\text{Li}_4\text{Mn}_5\text{O}_{12}$ powder                 | 300                                  | 298         | 6.5–7 | 1                    | 37.9                               | 28                   | [215] |
| Granular epoxy and $\text{Li}_4\text{Mn}_5\text{O}_{12}$     | 300                                  | 298         | 6.5–7 | 1                    | 30.2                               | 28                   | [215] |
| Branched rod-like $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$   | 150                                  | 298         | 11    | 1                    | 43.8                               | 24                   | [161] |
| Normal rod-like $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$     | 150                                  | 298         | 11    | 1                    | 35.3                               | 24                   | [161] |
| $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$                     | 41.6                                 | 298         | 12    | 1                    | 25.9                               | 48                   | [159] |
| Optimized $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$       | 50                                   | 298         | 8     | 1.25                 | 32.4                               | 12                   | [216] |
| $\text{LiMn}_2\text{O}_4$                                    | 50                                   | 298         | 8     | 1.25                 | 27.7                               | 12                   | [216] |
| Al-doped $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$            | 347                                  | 298         | –     | 5                    | 32.6                               | 24                   | [217] |
| Undoped $\text{Li}_1.6\text{Mn}_{1.6}\text{O}_4$             | 347                                  | 298         | –     | 5                    | 27.6                               | 24                   | [217] |
| RGONi3-doped $\text{MnO}_2$                                  | 50                                   | 303         | 12    | 0.4                  | 63.0                               | 10                   | [62]  |
| Cross-linked chitosan/ $\text{Li}_4\text{Mn}_5\text{O}_{12}$ | 25.78                                | 313         | 12    | 5                    | 8.9                                | 24                   | [218] |
| Fe-doped $\text{Li}_2\text{TiO}_3$                           | 1800                                 | 298         | 12    | 5                    | 53.3                               | 20                   | [219] |
| Undoped $\text{Li}_2\text{TiO}_3$                            | 1800                                 | 298         | 12    | 5                    | 50.5                               | 20                   | [219] |
| $\text{Li}_2\text{TiO}_3$                                    | 694                                  | 298         | 9.5   | 1                    | 40.0                               | 24                   | [220] |
| $\text{H}_2\text{TiO}_3$ @ carbon aerogel                    | 100                                  | 298         | 8     | 1                    | 30.3                               | 24                   | [221] |
| Yolk-shell structured- $\text{TiO}_2$                        | –                                    | 298         | 13.1  | 5                    | 28.5                               | 2                    | [222] |
| $\text{LiTi}_2\text{O}_4$                                    | 100                                  | 298         | 7     | 1                    | 9.5                                | 24                   | [223] |
| $\text{H}_2\text{TiO}_3$                                     | 1560                                 | 303         | 8.8   | 5                    | 36.3                               | 24                   | [224] |
| Porous $\text{H}_4\text{Ti}_5\text{O}_{12}$ nanofibers       | 300                                  | 298         | 11    | 1                    | 59.1                               | 0.5                  | [225] |
| Fe-doped $\text{H}_2\text{TiO}_3$                            | 1560                                 | 298         | 8.8   | 5                    | 34.8                               | 24                   | [226] |



or alkanes. Using co-extractants in multicomponent solvent systems creates a synergistic effect that increases the recovery efficiency or lithium extraction capacity [66]. Three categories of extractants are used for solvent extraction: acidic, neutral, and alkaline. Extractants typically have functional groups such as amines, phosphoric acid, and carboxylic acid that can be ionized [73]. Various acidic extractants, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA), mono-2-ethylhexyl-phosphonic acid (MEHPA), and bis-2,4,4-trimethyl pentyl phosphonic acid (Cyanex 272), have been used to extract lithium. Extractants such as Cyanex 272 can also be used independently, whereas other extractants are combined with solvents and acidic extractants to improve recovery efficiency and selectivity [73]. For selective lithium extraction, neutral extractants such as tri-*n*-butyl phosphate (TBP), tri-*n*-octyl phosphine oxide (TOPO), trialkyl-phosphine oxide (Cyanex 923), and methyl isobutyl ketone (MIBK) are promising [73]. One of the suitable extraction systems for lithium comprises TBP as the extractant, kerosene as the diluent,  $\text{FeCl}_3$  as the co-extractant, and lithium extraction efficiency [60].

Alkaline extractants such as tri-octyl methyl ammonium nitrate (Aliquat 336) are utilized to extract rare metals; however, they are infrequently employed in lithium extraction [74]. It has been demonstrated that multicomponent solvent systems are better suited for lithium recovery than other monovalent alkali metal ions due to the formation of complexes [75]. Despite the high efficiency and performance of multicomponent solvent systems, their use has some limitations. For instance, the partial dissolution of extractants results in environmental contamination and the loss of organics; furthermore, the polymerization of organics can reduce efficiency, increasing operational costs [60].

Ionic liquids have been used for extracting lithium and its isotopes from aqueous liquids. These ionic liquids, comprising both cationic and anionic components that maintain their liquid state below 100 °C, function as diluents with the characteristics of either an extractant or co-extractant [76]. Ionic liquids offer high separation efficiency, selectivity, and thermal stability. One of the key challenges associated with applying ionic liquids is the loss of these liquids in the final solution. Despite their potential to achieve near-perfect efficacy, using ionic liquids as extraction solvents is limited to laboratory scale due to high cost, solvent loss, and environmental contamination [60].

Crown ethers, a family of solvents, can selectively interact with lithium ions. The extent of the crown ring cavity determines the order of metal selectivity, with larger crown rings resulting in reduced lithium bonding. Benzo-14-crown-4 is among the many crown ethers, and it has the highest  $\text{Li}^+/\text{Na}^+$  ratio of 4.7 [25]. Crown ether derivatives with pendant arms have also been synthesized to create stronger complexes with cations [56]. However, the commercialization of crown ethers has been hampered by the high cost and corrosive nature of the chemical agents used in the process, which can shorten the lifespan of equipment and result in environmental pollution [56]. The 14-crown-4, 12-crown-4, and 15-crown-5 structures show good lithium selectivity with cations placed in the ether's center and oxygen atoms of crown ethers binding to lithium ions, which act as hard acid and hard base, respectively. The closeness of the cation diameter and the ring size of the crown ether leads to the optimal stability of the complexes formed between the crown ether and the cation so crown ethers with smaller ring sizes are more appropriate for lithium selectivity. Research has shown that ionic liquids can be combined with crown ethers, resulting in a synergistic effect [76]. Further investigation into the alkalinity of the pendant phenolic group, the size and structure of crown ether rings, and the geometry between pendant phenolic groups and crown ethers is necessary to understand lithium selectivity better. Supercritical carbon dioxide is utilized as a diluent for crown ethers in solvent extraction systems [77,78]. Supercritical carbon dioxide is considered a good solvent since it can be employed for extraction processes at high pressures and temperatures [79].

Table 3 showcases distinct investigations centered around diverse

solvent extraction approaches. It provides a concise overview of the efficacy of each technique along with the corresponding extractant and coextractant. This enhances comprehension of solvent extraction methods and their potential for future industrial implementation.

During the extraction process, lithium complexes are extracted into an organic phase. Then, they are recovered by using acidic stripping agents such as  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  [56]. The stripping stage is significant since it is possible to separate monovalent and divalent cations in this stage [76]. In addition, lithium extraction efficiency increases by repeating the extraction-stripping-extraction cycle [56]. In the solvent extraction technique, inputting fresh water is essential. In contrast to solvent extraction and ion-exchange resins, which use  $<1 \text{ m}^3$  of fresh water per ton of  $\text{Li}_2\text{CO}_3$ , ion sieve sorbents typically require significantly more water, often exceeding  $1000 \text{ m}^3$  per ton of  $\text{Li}_2\text{CO}_3$  [80]. Solvent extraction has shown adequate efficiency and lithium recovery, with many studies reporting over 90 % recovery through 6–10 cycles. However, ion-exchange resins show a wide range of lithium recovery, from 37.6 % to 99.98 %, with reported efficiency in terms of ion adsorption capacity ranging from 6.9 mg/g to 59.1 mg/g over 4 to 20 cycles [80]. The solvent extraction method eliminates the need for lithium pre-concentration, making it self-sufficient. The TBP +  $\text{FeCl}_3$  systems exhibit the highest potential among the various solvent extraction techniques. China is now playing a major role in providing a lithium supply chain with this [81]. Operational facilities like Qinghai Chaidamu Xinghua Lithium Salt Co., Ltd. have plants with an annual capacity of 10,000 tons of lithium carbonate. Crown ethers represent a prospective avenue for DLE, though additional research is required to confirm and evaluate their efficiency [25,60].

The solvent extraction method has not yet matured enough to compete with the sorption technique but has demonstrated adequate extraction efficiencies on the laboratory scale and recently in Qinghai Chaidamu Xinghua Lithium Salt Co. as industrial scale (TRL 3–4 when applied to natural water) [82]. The challenges of industrialization include the lithium-rich brine complexity and the large volume of brine that must be processed daily [80]. Actually, from an industrial viewpoint, some properties are significant for extractants such as stable structure, low cost, and high selectivity. In the future, further investigations are required to improve extractants [66].

### 2.3. Membrane technologies

Several reviews [25,60,72,83,84] have summarized applying conventional membrane processes and thus will not be covered here in detail. Membrane technologies play an important role in DLE [84] and are primarily used in the pre-treatment phase to reduce the presence of organic and inorganic contaminants in the brine. This is accomplished through pressure-driven processes such as ultrafiltration (UF) or microfiltration (MF). Another type of membrane technology that can be used to reduce the Total Dissolved Solids (TDS) of the feed by removing multivalent cations is nanofiltration (NF) [83]. In NF, it is widely recognized that the mass transfer is governed by a combination of factors: dielectric exclusion, steric hindrance, and Donnan exclusion. Based on the Donnan effect, anions can be effectively repelled by negatively charged NF membranes. However, these membranes demonstrate inadequate separation stability when processing positively charged solutes [5]. Successful examples of NF membranes utilized for lithium extraction include the positively and negatively charged NF membranes such as ethylenediaminetetraacetic acid (EDTA) modified NF membrane [85], NF90 membrane [86], and DK membrane [87]. Another application of membrane technology in DLE is reverse osmosis (RO) to recycle water throughout the flow sheet or concentrate the extracted lithium downstream. Applied potential-based membrane processes such as electrodialysis (ED) can be employed for refining or converting  $\text{LiCl}$  into final products [88] (Section 2.4). While conventional membranes (with  $\text{TRL} > 7$ ) can play a role in the pre-treatment or post-treatment stages of the DLE flowsheet for lithium extraction, it is important not to regard

**Table 3**  
Various types of research on solvent extraction DLE utilizing various extraction techniques and extractants. The efficiency of each system relies on the type of extractant and co-extractants used.

| System                                     | Extractant                                                                           | Co-extractant                                                      | Diluent                                                                     | Temperature                | Regeneration | Extraction time | Stripping solution                                                      | $\text{Li}^+/\text{Mg}^{2+}$ Separation factor | $\text{Li}^+$ Stripping efficiency | $\text{Li}^+$ Extraction efficiency | Ref.  |
|--------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------------|--------------|-----------------|-------------------------------------------------------------------------|------------------------------------------------|------------------------------------|-------------------------------------|-------|
| Multicomponent solvent systems             | N,N'-bis(2-ethylhexyl)-2-methoxyacetamide (NBEHMOA)                                  | $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$                          | Sulfonated kerosene                                                         | $25 \pm 1^\circ\text{C}$   | –            | –               | HCl 6 mol/L                                                             | 36,279                                         | 84.9 %                             | 96.7 %                              | [227] |
| Multicomponent solvent systems             | Methytriocetyl ammonium chloride and decanoic acid (DecA)                            | Bis(2-ethylhexyl) phosphate (DEHPA)                                | Deuterated dimethyl Sulfoxide ( $\text{DMSO}-d_6$ )                         | $25^\circ\text{C}$         | 10 cycles    | 65 min          | HCl 1 mol/L                                                             | 0.16                                           | 70.0 %                             | 80.0 %                              | [228] |
| Multicomponent solvent systems             | Trialkylmethylammonium di(2-ethylhexyl) orthophosphate + TBP (tri-n-butyl phosphate) | $\text{FeCl}_3$                                                    | Kerosene                                                                    | $25^\circ\text{C}$         | 6 cycles     | 30 min          | HCl 1.5 mol/L                                                           | 190.7                                          | 90 %                               | 61.0 %                              | [174] |
| Multicomponent solvent systems             | TBP                                                                                  | $\text{FeCl}_3$                                                    | Diethyl succinate                                                           | $25^\circ\text{C}$         | 10 cycles    | 11 min          | HCl 6 mol/L                                                             | 347.38                                         | $\geq 90$ %                        | 65.53 %                             | [77]  |
| Multicomponent solvent systems             | TBP                                                                                  | $\text{NaBPh}_4$                                                   | $\text{CH}_2\text{ClBr}$                                                    | $25^\circ\text{C}$         | 10 cycles    | 12 min          | –                                                                       | 2260.71                                        | 98.8 %                             | 87.65 %                             | [229] |
| Multicomponent solvent systems             | 2-Ethylhexyl phosphonic acid mono 2-Ethylhexyl + TBP                                 | $\text{FeCl}_3$                                                    | Kerosene                                                                    | $25 \pm 2^\circ\text{C}$   | Not require  | 60 min          | Water                                                                   | –                                              | 85 %                               | –                                   | [230] |
| Multicomponent solvent systems             | Tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate ([N4444][EHHP])     | –                                                                  | Dichloroethane                                                              | $19.85^\circ\text{C}$      | –            | 30 min          | HCl 0.5 mol/L                                                           | –                                              | 99.4 %                             | 94.64 %                             | [231] |
| Ionic liquids                              | 3-Benzoyl-1,1,1-trifluoroacetone (HBTA)                                              | Tri(n-octyl)phosphine oxide (TOPO)                                 | 1-Ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl imide ionic liquid | $25 \pm 1^\circ\text{C}$   | –            | –               | HCl 1 mol/L                                                             | –                                              | 77 %                               | –                                   | [232] |
| Ionic liquids                              | Carboxymethyl trimethylammonium bis(trifluoromethyl)sulfonimide                      | TBP                                                                | Chloroform                                                                  | $25^\circ\text{C}$         | –            | 30 min          | $\text{H}_2\text{SO}_4$ 0.5 mol/L + $\text{Li}_2\text{SO}_4$ 0.50 mol/L | –                                              | –                                  | 96.8 %                              | [233] |
| Ionic liquids                              | N-butyl pyridinium bis((trifluoromethyl)sulfonyl)imide (BD)                          | TBP                                                                | 1,2-dichloroethane                                                          | $25 \pm 2^\circ\text{C}$   | –            | 30 min          | –                                                                       | 74.86                                          | –                                  | 90.67 %                             | [67]  |
| Ionic liquids                              | TBP                                                                                  | $\text{NaNTf}_2$                                                   | $\text{HNO}_3$                                                              | $25 \pm 0.5^\circ\text{C}$ | 6 cycles     | 30 min          | HCl 0.2 mol/L                                                           | 33,000                                         | 98.0 %                             | 98.0 %                              | [234] |
| Crown ethers                               | 14-Crown-4 ethers                                                                    | Heptadecafluorooctanesulfonic acid tetraethylammonium salt (TPFOS) | Supercritical $\text{CO}_2$ ( $\text{ScCO}_2$ )                             | $60^\circ\text{C}$         | –            | 30 min          | HCl 1 mol/L                                                             | –                                              | –                                  | 38 %                                | [235] |
| Crown ethers                               | Benzo-9-crown (B9C9), benzo-12-crown-4 (B12C4), and benzo-15-crown-5 (B15C5) CEs     | –                                                                  | Dichloromethane                                                             | $25^\circ\text{C}$         | –            | 75 min          | –                                                                       | –                                              | –                                  | –                                   | [236] |
| Crown ethers                               | Benzo-15-crown-5 (B15C5) CEs                                                         | –                                                                  | Dichloromethane                                                             | $10-30^\circ\text{C}$      | –            | 75 min          | –                                                                       | –                                              | –                                  | –                                   | [237] |
| Crown ethers                               | Fluorinated 14-crown-4 (F14C4)                                                       | Bis(2-ethylhexyl) phosphate (HDEHP)                                | Supercritical $\text{CO}_2$ ( $\text{ScCO}_2$ )                             | $60^\circ\text{C}$         | –            | 75 min          | –                                                                       | –                                              | –                                  | 30.0 %                              | [78]  |
| Crown ethers + Supercritical $\text{CO}_2$ | Methylene-14-crown-4 paired with (M14C4)                                             | Bis(2-ethylhexyl) phosphate (HDEHP)                                | Supercritical $\text{CO}_2$ ( $\text{ScCO}_2$ )                             | $60^\circ\text{C}$         | –            | 75 min          | –                                                                       | –                                              | –                                  | 30.0 %                              | [78]  |



them as the primary technology for lithium extraction.

Rather, emerging ion-selective membranes (ISMs) have shown promising potential to serve as the core component of the DLE process, potentially replacing current high TRL DLE technologies. Recently developed ISMs have shown unique characteristics that allow for selective extraction of ions. These membranes feature nanometer-scaled channels with charged functional groups, enabling them to separate lithium ions from other monovalent and divalent ions in a solution. As a result, highly pure lithium ions can be recovered using ISMs with nanofluidic channels [5]. Various membrane design parameters, including geometry, surface charge, molecular structure, chemical affinity, nanochannel size, energy barrier, and driving force, can influence the lithium ion separation efficiency based on their separation mechanism (Fig. 2). Additionally, Eisenman suggests that the ion selectivity of nanochannels stems from the energy between the ion and a charged binding site within the channel, along with disparities in the ion's hydration energy [5]. ISMs have low energy consumption and require no additional purification. However, when selecting an ISM for a specific application, factors such as applied voltage, feed volume, coexisting ions, operating pressure, pH, and temperature should be carefully considered to optimize its performance and efficiency [83]. Highly efficient ISMs have been recently developed with different starting materials, including metal-organic frameworks (MOFs) [89], graphene oxide (GO) [90], MXene [91], polyethylene terephthalate (PET) [92], and vermiculate (VCT) [93–95]. Table 4 summarizes recent studies using novel ion-selective materials to separate lithium from lithium ion containing solution.

Membranes can also be effectively combined with other methods for lithium recovery. One such technology is the supported liquid membrane (SLM), which employs membrane support immersed in an organic phase to separate aqueous phases and transport substances from one

phase to another [96]. SLM is a prospective technique for lithium recovery due to its high selectivity, low solvent usage, and low energy consumption. However, the performance of the procedure can be affected by the liquid membrane's stability, pressure difference, solubility, and emulsion. Furthermore, a stable and efficient extraction solvent is essential for metal ions' complete and effective transfer [76,97].

Another hybrid membrane technology is the ion-imprinted membrane (IIM) technique, which involves the insertion of an ion-imprinted polymer (IIP) into the membrane's surface. This technique is considered one of the separation mechanisms in membranes for lithium extraction (Fig. 2). The IIP is synthesized by connecting functional monomers and template molecules, which are then removed to form binding sites through molecular recognition. Ion-imprinted membranes possess high specific selectivity, low energy consumption, antifouling properties, and easy regeneration, making them suitable for recovering rare-earth elements, heavy metals, and alkali metals [98]. However, challenges related to temperature dependence, pH sensitivity, extraction time, and the ratio of functional monomers, template ligands, and ions have hindered their commercialization [56,99]. The mixed matrix membrane (MMM) technology is another promising approach for lithium extraction that employs adsorption, a cost-effective and easy operation method. Inorganic lithium ion sieves, particularly the spinel structure of  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  ( $x = 0.3, 0.4$ , etc.), have demonstrated high stability, capacity, and selectivity for lithium adsorption. MMMs possess the advantages of both membranes and ion sieves, making them suitable for industrial operations [100]. Adsorption-based membrane processes, including IIM, SLM, and MMM, offer lower energy consumption and higher lithium adsorption capacity than the conventional solvent extraction methods with facile regeneration [72].

Membrane distillation crystallization (MDC) is another hybrid membrane technology that combines crystallization with MD to recover

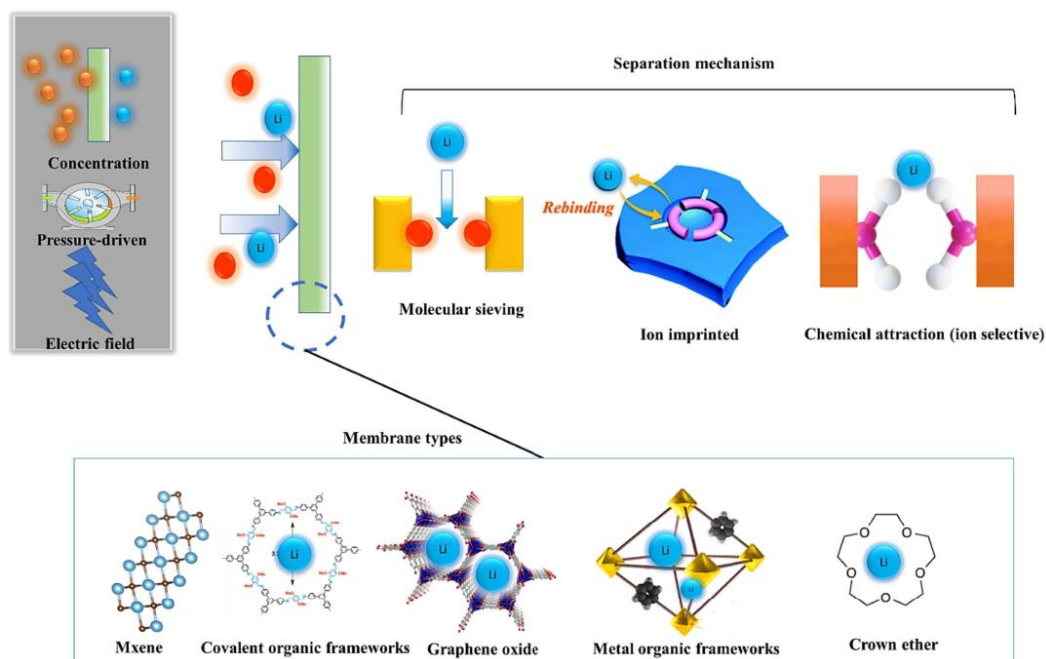


Fig. 2. Schematic of the metal recovery process and separation mechanism of membrane technologies. These processes rely on an electrical potential, pressure, or concentration difference to transport ions through the membrane [89,91–93,194–206].

**Table 4**

The result of lithium enrichment ratio (i.e.,  $\text{Li}^+/\text{K}^+$ ,  $\text{Li}^+/\text{Na}^+$  and  $\text{Li}^+/\text{Mg}^{2+}$ ) in recent ISM studies.

| Membrane                                          | Method                            | Lithium enrichment ratio (in permeate or feed compartments) |                           |                              | Reference |
|---------------------------------------------------|-----------------------------------|-------------------------------------------------------------|---------------------------|------------------------------|-----------|
|                                                   |                                   | $\text{K}^+/\text{Li}^+$                                    | $\text{Na}^+/\text{Li}^+$ | $\text{Li}^+/\text{Mg}^{2+}$ |           |
| UiO-66                                            | ISM with 3D channel configuration | 0.63                                                        | 0.806                     | –                            | [194]     |
| ZIF-8                                             | ISM with 3D channel configuration | 0.46                                                        | 0.730                     | –                            | [194]     |
| ZIF-7                                             | ISM with 3D channel configuration | –                                                           | –                         | –                            | [194]     |
| MOP-18                                            | ISM                               | 0.59                                                        | –                         | –                            | [238]     |
| Sulfonated HKUST-1                                | ISM                               | 0.015                                                       | 0.029                     | 1.815                        | [239]     |
| PET                                               | ISM                               | 0.06 <sup>b</sup>                                           | 0.096 <sup>b</sup>        | –                            | [240]     |
| PET                                               | ISM                               | 1.30 <sup>b</sup>                                           | 1.23 <sup>b</sup>         | –                            | [241]     |
| PET                                               | ISM                               | 1.30                                                        | 1.11                      | –                            | [194]     |
| GO                                                | ISM                               | 1.20                                                        | 1.299                     | –                            | [242]     |
| GO                                                | ISM                               | 1.19                                                        | 1.075                     | –                            | [194]     |
| Sulfonated-rGO                                    | ISM                               | –                                                           | 1.190                     | 5.27                         | [198]     |
| Vermiculite                                       | ISM                               | 0.63                                                        | 0.794                     | –                            | [93]      |
| MXene                                             | ISM                               | 0.67                                                        | 1.099                     | –                            | [243]     |
| UiO-66-SO <sub>3</sub> H@PVC                      | ISM                               | 1.66                                                        | –                         | –                            | [200]     |
| Graphite/hBN/MoS <sub>2</sub>                     | ISM                               | 2                                                           | –                         | –                            | [201]     |
| MXene                                             | ISM                               | 1.25                                                        | –                         | –                            | [202]     |
| MXene                                             | ISM with 2D channel configuration | 1.12                                                        | 1.104                     | 2.306                        | [91]      |
| UiO-66-SO <sub>3</sub> H                          | ISM                               | 2.86                                                        | –                         | –                            | [244]     |
| MOF-808-SO <sub>4</sub> @PVC                      | ISM                               | 1.43                                                        | –                         | –                            | [200]     |
| Covalent organic frameworks (COF)                 | ISM with 3D channel configuration | 4.2–4.7                                                     | –                         | –                            | [204]     |
| MOF-808@PVC                                       | ISM                               | 1.67                                                        | –                         | –                            | [200]     |
| Asymmetric UiO-66-NH <sub>2</sub> /ZIF8 (PVP)     | ISM                               | 9.63                                                        | 6.27                      | –                            | [245]     |
| Asymmetric UiO-66-NH <sub>2</sub> (PSS)/ZIF8(PVP) | ISM                               | 84                                                          | 80                        | 0.035                        | [245]     |
| rGO@SAPS                                          | ISM                               | 1.5                                                         | –                         | 0.26                         | [206]     |

minerals from high-concentration brine using low-grade heat. MDC provides a high level of control over nucleation kinetics and enables rapid crystallization rates [101]. The process can be applied to lithium extraction from brine by transferring water across a hydrophobic membrane under a thermal gradient, leading to induced crystallization in the crystallizer. MDC has the advantages of using various energy sources and simultaneous salt and fresh water production, while membrane wetting and fouling are some substantial disadvantages of the MDC method [72]. The  $\text{Li}^+/\text{Mg}^{2+}$  separation factor for NF membranes usually ranges between 2.6 and 10.4. In addition, the separation factors of  $\text{Li}^+$  over  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  for IIM range from 4 to 51, whereas separation factors for MMM range from 99 to 5312. Furthermore, the lithium recovery rate of SLM and MDC is over 95 % and 73 %, respectively (more detailed information in Table 5) [72]. Advanced ISMs comprise various materials and membranes, resulting in a wide variety of  $\text{Li}^+/\text{Mg}^{2+}$  separation factors ranging from <1 to 1815 [88]. NF and RO have been widely used on an industrial scale among various membrane technologies. MDC has not yet been implemented on a large scale and is on a pilot scale, while SLM, IIM, and MMM are still in the laboratory stage [72]. Energy consumption of producing lithium carbonate

from brines using NF membranes is reported as 35–48 kWh/kg [72]. There is no water consumption in MDC, however, one of the by-product that can be obtained through the process is fresh water [82]. Recovery rates of fresh water for MDC are  $3.5 \text{ kg m}^{-2} \text{ h}^{-1}$  and  $22.5 \text{ kg m}^{-2} \text{ h}^{-1}$  for higher and lower salinity feeds. Due to the cost of membrane replacement and thermal energy, MDC has a higher operating cost, while MMM is a cost-effective technology [80]. To reduce the thermal energy in MDC, a heat exchanger could be used, resulting in 85 % recovery of the thermal energy [102].

Although hybrid membranes improve extraction performance, several obstacles must be addressed. These include solvents and absorbers degradation in technologies such as SLM, IIM, and MMM, the complexity and high cost of membrane production, the need for lithium resolution with acids, and pore-clogging [82]. Future studies should prioritize the development of membrane fabrication and material design, focusing on factors such as stability, flexibility, and strength of the membrane material. These aspects are crucial in achieving efficient lithium extraction. [72]. NF offers some advantages, such as a smaller footprint, but its main disadvantages are its high operating costs and susceptibility to membrane fouling. SLM, on the other hand, has a low footprint but has some limiting factors, such as the absence of an organic solvent and the need to use chemical reagents. IIM, like SLM, encounters obstacles such as using chemical reagents for desorption and a low desorption capacity. [72]. Moreover, some obstacles hinder the commercialization of IIM, including ion recognition sites, temperature, extraction time, and sensitivity to pH [56]. MMM provide benefits, such as chemical stability, high selectivity, and large adsorption capacity. Despite the advantages outlined above, using chemical reagents for adsorption and the potential leakage of inorganic particles remain drawbacks of MMM [72].

The inherent limitations and challenges associated with membrane-based technologies for lithium recovery necessitate a comprehensive investigation of strategies to surmount these limitations and improve the process's efficiency. These techniques can be advanced to the commercial level by conducting further investigations to identify and tackle the limitations of these technologies. Utilizing molecular dynamics simulation can provide valuable insights into ion-selective membranes and their potential for future success. Such investigations could pave the way for developing these techniques and their advancement to the commercial level.

#### 2.4. Electrochemical lithium ion capturing systems (ELiCS)

##### 2.4.1. Overview

Electrochemical lithium ion capturing systems (ELiCS) have emerged as sustainable procedures for the selective extraction of lithium and other valuable compounds, such as nickel [103], cesium [104], and copper [105–107]. In all ELiCSs, the driving force for lithium capturing is applying an electrical potential bias between electrodes [108]. Based on the configuration, ELiCSs can be classified into three general categories: battery-based, battery-based combined with the membrane, and electro-membrane-based (Fig. 3). Battery-based ELiCSs use at least one Faradaic electrode [109]. In battery-based combined with membrane ELiCSs, a similar configuration is used, but the set-up includes both membranes and Faradaic electrodes for lithium ion capturing [14]. Electrodialysis (ED) techniques represent a well-established illustration of the third category of ELiCSs, which is called electro-membrane-based approaches [110,111].

##### 2.4.2. Battery-based ELiCSs

The electrochemical extraction of lithium ions requires two electrodes (often called working electrode and counter electrode) and their properties strongly influence the process, including efficiency and kinetics [112]. In all battery-based methods, the lithium ion selective electrodes use a Faradaic process for capturing lithium ions. For example, lithium manganese oxide (LMO;  $\text{LiMn}_2\text{O}_4$ ) or lithium iron

**Table 5**  
Comparison of different membrane technologies (including NF, SLM, IM, MMM, and MDC) and their efficiencies.

| Membrane                                                                                               | Method | Mg <sup>2+</sup> rejection rate | Li <sup>+</sup> rejection rate | Li <sup>+</sup> /Na <sup>+</sup> selectivity | Li <sup>+</sup> /K <sup>+</sup> selectivity | Temperature °C | Water permeability (L/m <sup>2</sup> h <sup>-1</sup> bar <sup>-1</sup> ) | Separation factor (Li <sup>+</sup> /Mg <sup>2+</sup> ) | Pore size   | Li <sup>+</sup> separation efficiency | Ref.  |
|--------------------------------------------------------------------------------------------------------|--------|---------------------------------|--------------------------------|----------------------------------------------|---------------------------------------------|----------------|--------------------------------------------------------------------------|--------------------------------------------------------|-------------|---------------------------------------|-------|
| NF90-2540 membrane                                                                                     | NF     | 100 %                           | 15 %                           | —                                            | —                                           | 22.0 ± 0.1 °C  | 15.0 ± 0.1                                                               | —                                                      | —           | 85 %                                  | [246] |
| Composite NF hollow fiber                                                                              | NF     | 46.0 %                          | 40.7 %                         | —                                            | —                                           | 25.0 ± 1.0 °C  | 40–50                                                                    | 2.6                                                    | 0.83 nm     | —                                     | [86]  |
| NF-90 membrane                                                                                         | NF     | 60.5 %                          | 15 %                           | —                                            | —                                           | 25.0 ± 1.0 °C  | —                                                                        | 2.1                                                    | —           | —                                     | [86]  |
| Desal nanofiltration membrane (DL-2540)                                                                | NF     | ~60 %                           | <–10 %                         | —                                            | —                                           | 20.0 ± 2 °C    | —                                                                        | >2.86                                                  | 0.468 nm    | —                                     | [247] |
| PEI-TMC composite NF membrane                                                                          | NF     | 95 %                            | 19 %                           | —                                            | —                                           | 25 °C          | 5.02                                                                     | 20                                                     | 0.48 nm     | —                                     | [248] |
| EDTA modified NF membrane                                                                              | NF     | 92.3 %                          | <30 %                          | —                                            | —                                           | 25 °C          | —                                                                        | 9.2                                                    | 0.20 nm     | —                                     | [85]  |
| PES/PIP-PHF/TMC                                                                                        | NF     | 90 %                            | 16.3 %                         | —                                            | —                                           | 20 ± 0.5 °C    | 6.7                                                                      | 13.1                                                   | 0.639 nm    | —                                     | [249] |
| Polymer membrane/ <i>n</i> -acetyl- <i>n</i> -dodecylacetophenone/tri- <i>n</i> -octyl phosphine oxide | SLM    | —                               | —                              | —                                            | —                                           | 20 °C          | —                                                                        | —                                                      | 50 × 190 nm | 95 %                                  | [97]  |
| PVDF membranes/1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide/TBP                       | SLM    | —                               | —                              | —                                            | —                                           | 25 °C          | —                                                                        | —                                                      | 20–450 nm   | 80 %                                  | [250] |
| CTA polymers/2-ethylhexyl phosphonic acid mono 2-ethylhexyl/TBP                                        | SLM    | —                               | —                              | 13.2                                         | 32                                          | 25 °C          | —                                                                        | 10.2                                                   | —           | —                                     | [251] |
| calix[4]arenes functionalized dual-imprinted mesoporous film (DMFz)                                    | IIM    | —                               | —                              | 72.05                                        | 93.35                                       | 25 °C          | —                                                                        | 193.20                                                 | 5.196 nm    | —                                     | [252] |
| Li <sup>+</sup> -imprinted polymers/PDA/SiO <sub>2</sub> nanoparticles                                 | IIM    | —                               | —                              | 1.85                                         | 2.07                                        | 25 °C          | —                                                                        | —                                                      | 220 nm      | —                                     | [253] |
| PDMS-PDA                                                                                               | IIM    | —                               | —                              | 0.58                                         | 0.22                                        | 25 °C          | —                                                                        | —                                                      | 500 nm      | —                                     | [254] |
| PVA/12-crown-4                                                                                         | IIM    | —                               | —                              | 1134.38                                      | 156.38                                      | 30 °C          | —                                                                        | 815.79                                                 | —           | —                                     | [255] |
| PVDF/ <i>N,N</i> -dimethylacetamide                                                                    | MMM    | —                               | —                              | —                                            | —                                           | 25 °C          | —                                                                        | 4.7                                                    | —           | —                                     | [256] |
| PVC-Li <sub>10</sub> Mn <sub>10</sub> O <sub>4</sub>                                                   | MMM    | —                               | —                              | 4555                                         | 454                                         | 25 °C          | —                                                                        | 1114                                                   | —           | —                                     | [257] |
| poly(acrylonitrile)/H1.6Mn1.6O4                                                                        | MMM    | —                               | —                              | 5312                                         | 234                                         | 25 °C          | —                                                                        | 99                                                     | <300 nm     | —                                     | [258] |
| polypropylene (PP)                                                                                     | MDC    | —                               | —                              | —                                            | —                                           | 30–50 °C       | —                                                                        | —                                                      | 200 nm      | —                                     | [259] |
| polypropylene                                                                                          | MDC    | —                               | —                              | —                                            | —                                           | >60 °C         | —                                                                        | —                                                      | —           | 73.8 %                                | [260] |
| CTA polymers/P507/TBP                                                                                  | SLM    | —                               | —                              | 0.03125                                      | 0.0757                                      | 25 °C          | —                                                                        | 21.8                                                   | —           | —                                     | [251] |
| Li <sup>+</sup> -imprinted polymers/PDA/SiO <sub>2</sub> nanoparticles                                 | IIM    | —                               | —                              | 9.86                                         | 7.39                                        | 25 °C          | —                                                                        | —                                                      | —           | —                                     | [253] |
| PDMS-PDA                                                                                               | IIM    | —                               | —                              | 3.80                                         | 1.71                                        | 25 °C          | —                                                                        | —                                                      | —           | —                                     | [254] |



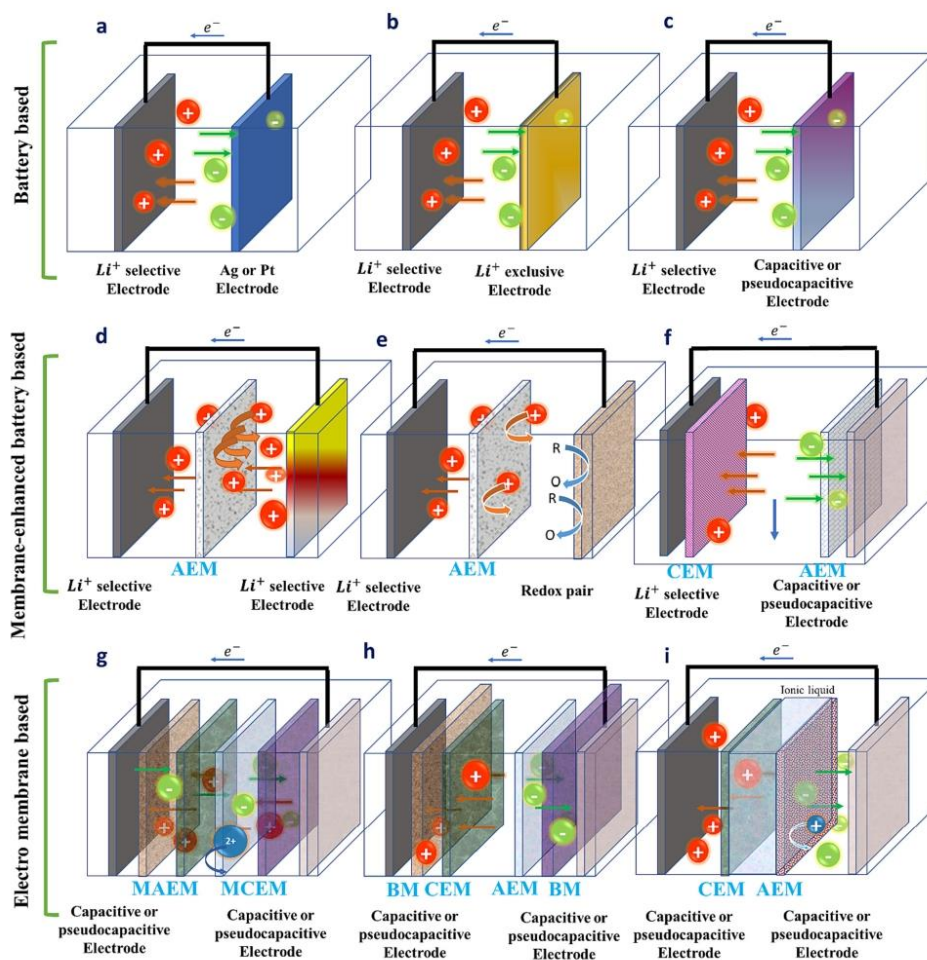


Fig. 3. Different configurations of ELiCSs: a) battery operating, b) mixed ion battery, c) ESIX, d) rocking chair, e) Redox battery, f) MCDI, g) SED, h) BMED, and i) ILMED [116].

phosphate (LFP;  $\text{LiFePO}_4$ ) can be used as lithium ion selective electrode in battery-based systems to capture lithium ions [113,114]. Battery-based ELiCSs can be divided into electrochemical ion-pumping systems (EIPS; Fig. 3a–b) and electrochemical switched ion exchange (ESIX; Fig. 3c). The key distinction between EIPS and ESIX system is the type of counter electrode (the electrodes that are not selective to lithium ions and have positive charge when applying voltage) [115]. EIPSs are classified as battery-operating EIPS Fig. 3a and mixed-ion battery EIPS Fig. 3b [116]. The counter electrode, non lithium ion selective electrode, in EIPS is a Faradaic electrode, whereas, in ESIX, a non-Faradaic counter electrode can be applied [117]. Electrodes can be broadly categorized into two major groups: Faradaic (battery-like or capacitor-like = pseudocapacitive) and non-Faradaic (capacitive) electrodes. This classification is based on the specific electrochemical processes that occur at the electrode/electrolyte interface [118,119]. The difference between Faradaic and non-Faradaic processes is the transfer or non-transfer of charge across the fluid-solid interface [120]. Charge-transfer reactions

may then exhibit clear redox-peaks in their electrochemical signature or exhibit rather a pseudocapacitive (capacitor-like) behavior [121]. In battery operating EIPS, a lithium ion selective electrode is paired with an electrode made from Pt or Ag (which by default does not react with lithium ions; Fig. 3a). Moreover, a general lithium ion exclusive material (where other ions are preferred over lithium ions; this electrode can be Faradaic or capacitive; Fig. 3b and Fig. 3c, respectively) is usually applied in both EIPS and EISP systems for lithium ion extraction. The operation of such devices is cyclic by which lithium ions are up-taken by the lithium ion-selective electrode (but not the counter electrode) and released upon discharging. In total, there are four steps: 1) extraction of lithium ions from a lithium ion containing feedwater solution into the lithium ion selective electrode, 2) exchange of the solution with a recovery solution and 3) release of the lithium ions from the lithium ion selective electrode. Finally, 4) the recovery solution is replaced with a fresh feed containing lithium ions, and the cycle can recommence from the beginning. In these systems, the ion selectivity is not enabled by a

membrane but by the properties of the lithium ion selective electrode material directly. A hybrid electrode configuration containing a Faradaic intercalating electrode (like the two EIPS methods) and a non-Faradaic electrode provides the benefits of both battery and capacitor-based behavior, such as low self-discharge, a large capacity of Faradaic, and fast removal rates of the non-Faradaic electrodes [117].

#### 2.4.3. Battery-based combined with membrane ELiCSs

The second type of ELiCSs called battery-based combined with membrane, represents an advanced form of ELiCSs and feature a similar configuration to battery-based ELiCSs. In this system, both electrodes and membranes work together to capture lithium ions. They can be divided into three categories: rocking chair, redox battery, and membrane capacitive deionization (MCDI), as illustrated in Fig. 3d-f [122]. In the rocking chair system (Fig. 3d), there are two Faradaic electrodes that intercalate lithium ions, and the cell is divided into two compartments by an anion exchange membrane (AEM). By applying an electric potential between the cathode and anode, one electrode captures lithium ions from the solution compartment and releases it into the recovery solution to the other electrode. Lithium ions can be cyclically recovered by switching the current direction appropriately. In Fig. 3e, similar to rocking chair system, an AEM separates the system into two compartments, one of which captures and releases lithium ions from the lithium ion selective electrode. In the other compartment, different materials electrodes can be used. For example, the  $\text{I}^{3-}/\text{I}^-$  [67] and  $\text{Zn}/\text{Zn}^{2+}$  couple undergo redox processes [123]. In the MCDI systems (Fig. 3f), the electrode array includes a lithium ion selective electrode as the working electrode and a capacitive electrode as the opposing electrode, with a cation and an anion exchange membrane surrounding each electrode. After passing through the cation exchange membrane, lithium ions are captured by the intercalating electrode. While passing through an anion exchange membrane, anions can be stored, for example, via ion electrosorption at the electrode interface [124,125].

#### 2.4.4. Electro-membrane based ELiCSs

Electro-membrane-based approaches, also known as electrodialysis (ED) systems, are depicted in Fig. 3g-i [126]. This technique is an electrochemical separation process in which ions are transferred through a sequence of cationic and anionic exchange membranes using a DC voltage through non-Faradaic electrodes [126]. In ED systems, separating ions with the same charge, such as  $\text{Mg}^{2+}$  and  $\text{Li}^+$ , is generally impossible. To address this issue, selective electrodialysis (S-ED; Fig. 3g) has been developed with a monovalent selective ion-exchange membrane. Bipolar membrane electrodialysis (BMED, Fig. 3h) [127] is another form of ED in which a bipolar membrane and ED are combined and used for lithium ion extraction. Bipolar membranes are a special class of ion-exchange membranes constituted by a cation- and anion-exchange layer, allowing the generation of protons and hydroxide ions via a water dissociation mechanism [128]. In ionic liquid membrane electrodialysis (ILMED; Fig. 3i), an ionic liquid is employed as the membrane. Ionic liquids are compounds with negligible volatility, high stability, and high selectivity [129].

#### 2.4.5. Comparison of different ELiCSs and perspectives

Among ELiCSs, EIPS shows potential for effective lithium recovery from liquid sources in the future due to their simple operation, sustainability, high efficiency, and low energy consumption. For these technologies to be useful for large-scale applications, researchers need to optimize the electrochemical system's performance. This optimization includes determining the ideal composition of the feed solution, electrode arrangement, current density, and applied potential. Among the ED methods, SED and BMED offer the maximum recovery of lithium ions. A summary of the characteristics of the most commonly used ELiCSs is presented in Table 6.

By now, electrochemical methods have been commercially applied in some industries for water purification and extracting valuable metal ions

from waste and other resources. Although intercalation and deintercalation have been studied before [130,131], more understanding of this mechanism, its recovery process, and long-term stability are essential in guiding the design and selection of suitable electroactive materials. For effective electrochemical extraction, the set-up should be developed based on the kinetics of the particular electrode material. However, the key challenges for the commercialization and industrialization of this process are the operating costs and energy consumption. To overcome these challenges, developing new materials for electrodes and membranes with high lithium ion selectivity and long-term stability is critical. Additionally, selective separation of lithium ions in the presence of other ions with high concentrations, such as magnesium, sodium, and potassium ions, is another important and challenging aspect that must be addressed.

#### 2.5. Carbonation processes

Using carbon dioxide ( $\text{CO}_2$ ) in producing lithium carbonate via the carbonation process has gained attention over the past several years as  $\text{CO}_2$  emissions continue to rise globally. In principle, released  $\text{CO}_2$  can be harnessed and incorporated into the carbonation process for lithium recovery, especially in ores (mineral carbonation) [132]. In brines,  $\text{CO}_2$  can be generated in two forms,  $\text{CO}_2$  and supercritical  $\text{CO}_2$  ( $\text{SC-CO}_2$ ), aiming to recover lithium with lower operation costs while speeding up the lithium extraction process as a result of their excellent diffusivity and low viscosity [25,78,133].  $\text{SC-CO}_2$  followed by solvent extraction method has been reported with up to 30 % extraction improvement [133].

Lithium recovery with  $\text{CO}_2$  in brines can also be done with different procedures and methods. In the most straightforward method, direct carbonation involves reacting the brine with concentrated lithium directly with  $\text{CO}_2$  at elevated temperatures and then moving to an alkaline situation to produce lithium carbonate [134]. After the carbonation reaction, solid lithium carbonate is separated from the remaining brine solution through filtration, centrifugation, or by allowing the lithium carbonate to settle out of the solution over time. The final step in the direct carbonation process is to refine the solid lithium carbonate product into a usable form [135]. A promising method for carbonating lithium from brine (as the performance was proven in ion battery lithium recovery [136]) is indirect carbonation, in which the lithium-containing brine is first treated with an acid. Then,  $\text{CO}_2$  reaches a high-temperature point and forms as  $\text{SC-CO}_2$  (usually at temperatures  $>31.1^\circ\text{C}$  and pressure higher than 81.2 bar). At this point, the  $\text{SC-CO}_2$  is bubbled into the solution containing lithium carbonate. The high solvating power of the  $\text{SC-CO}_2$  allows it to dissolve the lithium carbonate, forming a solution of lithium carbonate in  $\text{SC-CO}_2$ . However, when the pressure and temperature are lowered below the threshold point, the  $\text{SC-CO}_2$  returns to its gaseous state, causing the lithium carbonate to precipitate out of the solution and form a solid [137,138]. This method has been frequently used to separate other metals (i.e.,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) from brine, but it can also be used for the recovery of lithium [139].

Reverse carbonation may be promising for lithium recovery from brines since it was proven in other technologies, such as solar energy storage [140]. The lithium-containing brine is first reacted with a salt solution ( $\text{Na}_2\text{CO}_3$ ) to produce isolated lithium carbonate, which is then further processed as described in the previous method. Finally, there is electrochemical carbonation. This method is potentially used in ion batteries to increase the electrodes high storage stability by producing  $\text{Li}_2\text{CO}_3$  [141]. Briefly, a voltage is applied to an electrode immersed in a lithium-containing solution, causing lithium ions to move to the electrode surface. Then,  $\text{CO}_2$  is introduced to the system, which causes lithium carbonate to precipitate out of the solution [134].

The effectiveness of different carbonation methods for extracting lithium from brines can vary depending on various factors, including the nature of the starting material, the processing conditions, temperature,



**Table 6**  
important characteristics of most common ELICs considering their advantages for lithium extraction. The table is categorized into methods and mechanisms and their corresponding configurations.

| Method | Configuration |           |                                 | Technical development | Advantages                                                                                             | Voltage     | Extraction time | SEC       | Recovery | Ref           |
|--------|---------------|-----------|---------------------------------|-----------------------|--------------------------------------------------------------------------------------------------------|-------------|-----------------|-----------|----------|---------------|
|        | Electrode     |           | Membrane                        |                       |                                                                                                        |             |                 |           |          |               |
|        | WE            | CE        |                                 |                       |                                                                                                        |             |                 |           |          |               |
| ESIX   | FE            | CE        | —                               | Bench/pilot scale     | -Complex sources<br>-Ease of upscaling<br>-No membrane fouling<br>-Extraction from lower concentration | −0.25–3.5 V | 25 min–18 h     | 1.4–18.5  | 60–96 %  | [261–263]     |
| CDI    | FE            | CE        | CEM AEM                         | Bench scale           | -Simple<br>-Low voltage<br>-Eco-friendly<br>-High separation                                           | 0.6–3.5 V   | 3 min–3 days    | 1.3–160.7 | 15–45 %  | [264–266]     |
| SED    | CE or PCE     | CE or PCE | selective ion-exchange membrane | Bench scale           |                                                                                                        | 5–20 V      | 2–3 h           | 5–2400    | 68–80 %  | [116,267,268] |
| BMED   | CE or PCE     | CE or PCE | Bipolar membrane                | Bench/pilot scale     | -High perm-selectivity<br>-No chemical additive                                                        | 15–35 V     | 20–120 min      | 3–19      | 60–98 %  |               |
| ILMED  | CE or PCE     | CE or PCE | Ion liquid membrane             | Bench scale           | -High selectivity of membrane toward $\text{Li}^+$                                                     | 2–3 V       | 12 h            | 110–130   | —        |               |

FE: Faradaic electrode, CE: Capacitive electrode PCE: pseudocapacitive electrode, SEC (kWh/kmol): specific energy consumption.

the pressure of  $\text{CO}_2$ , and the desired purity and yield of the final lithium product. The direct carbonation process is the simplest and most effective method as a novel lithium recovery approach with approximately 75–85 % recovery rate. However, the electrochemical approach has shown a higher  $\text{Li}_2\text{CO}_3$  production with >95 % recovery rate, according to Harrison et al. [25,134,141–143]. Carbonation has generally gained attention as a potentially more environmentally friendly alternative to traditional methods, such as direct acid leaching because it can utilize waste  $\text{CO}_2$  from industrial processes and does not produce toxic by-products. Results showed that the carbonation process to produce 1 kg lithium carbonate had significantly less energy usage, material consumption, wastewater generation, and emission rates than the conventional techniques for extracting mined lithium. Specifically, in a comparative study, the carbonation process used only 1.4  $\text{m}^3$  of steam (compared to 6.4  $\text{m}^3$  for traditional methods), 5.9 kg of water (compared to 26.3 kg), 4.7 kg of wastewater (compared to 20.6 kg), and 0.2 kg of solid waste (compared to 12.9 kg) [144].

### 3. Pre-treatment and post-treatment methods

#### 3.1. Overview

As of currently available data, lithium-bearing brines with high concentrations of lithium ions, are typically found in arid and semi-arid regions (i.e., the Andes Mountains of South America, Salar de Uyuni in Bolivia (80–1500 mg/L of  $\text{Li}^+$ ), the Salar de Atacama in Chile (2700 mg/L of  $\text{Li}^+$ ), the Clayton Valley in Nevada (320 mg/L of  $\text{Li}^+$ ), Zabuye Lake (1500 mg/L of  $\text{Li}^+$ ), and the Hombre Muerto salar in Argentina (700 mg/L of  $\text{Li}^+$ ) [145–152]. The characteristics of lithium-bearing brines can vary widely depending on the location and geological formation of the source. Some of the key properties that determine the economic viability of extracting lithium from brines include the concentration of lithium, the concentration of other metals and minerals that may interfere with the extraction process, the brine's temperature and pH, and the brine deposit's total volume. The lithium concentration in brines was found in the range from as low as 70 mg/L to as high as 8000 mg/L, with an average concentration of around 200 mg/L [153–155]. It was also found that the concentration of other metals, such as magnesium, potassium, and sodium, can vary widely, ranging from around 100 mg/L to tens of thousands of mg/L [66,146]. Adsorption and ion exchange processes showed that the solubility of lithium in brines increases with temperature up to a certain point, beyond which the solubility begins to decrease. It was found that the optimum temperature range for lithium extraction from brines is between 10 °C and 80 °C, which increases the lithium recovery from 15 % to 70 % depending on the specific

composition of the brine [156]. Other studies also showed improved recovery with increasing temperature via ion exchange [157–161]. The pH of brines can also impact the extraction process. The optimum pH range for lithium extraction from brines was typically found between 9 and 11, although this can vary depending on the specific composition of the brine [161]. It was also found that the size of the brine deposit is a key factor in determining the overall economic viability of lithium extraction, with larger deposits generally being more cost-effective to extract [162,163]. Doing pre-treatment and post-treatment techniques to optimize the abovementioned factors while considering the unique characteristics of brine location and situation can effectively improve lithium recovery through the DLE process. Hence, it is essential to consistently evaluate and select precise pre and post-treatment approaches to optimize factors mentioned earlier in lithium recovery processes.

#### 3.2. Pre-treatment strategies

Pre-processing strategies (pre-treatment methods) are typically used to address the feed composition diversity (location dependency) with various characteristics (i.e., suitable pH, temperature, and impurities content). These processes involve separating and removing unwanted impurities from the brine feedstock, such as magnesium, potassium, sodium, and other metals, and conditions that can interfere with the extraction process [164,165]. Various pre-treatment methods have been explored for brine feedstock, precipitation, ion exchange [166], solvent extraction [167], softening, pH adjustment (i.e., acidification), and membrane filtration (i.e., pressure-driven membrane [72] or electrically-driven membrane [83]) which has been briefly depicted in Fig. 4a. Precipitation is a common pre-treatment method that involves the addition of chemicals (i.e., sodium carbonate) to form insoluble compounds, which can be then removed through filtration or settling. Softening removes or reduces the concentration of divalent cations, such as calcium and magnesium, by adding a chemical reagent, typically sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). In membranes, semi-permeable films separate some parts of brines and concentrate the rest to improve the recovery efficiency in the main DLE process [168].

In some cases, NF membranes have been used in the preprocessing step to pre-treat brine and concentrate lithium while separating other materials, such as  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , from lithium. NF is a good candidate to separate  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from lithium ions, with the ability of rejecting divalent ions from brine being up to 90 % and in the range of 40–50 % for monovalent ions [169]. In other cases, membrane distillation (MD) has been utilized in several studies, demonstrating the effectiveness of pre-treatment strategies in obtaining a concentrated

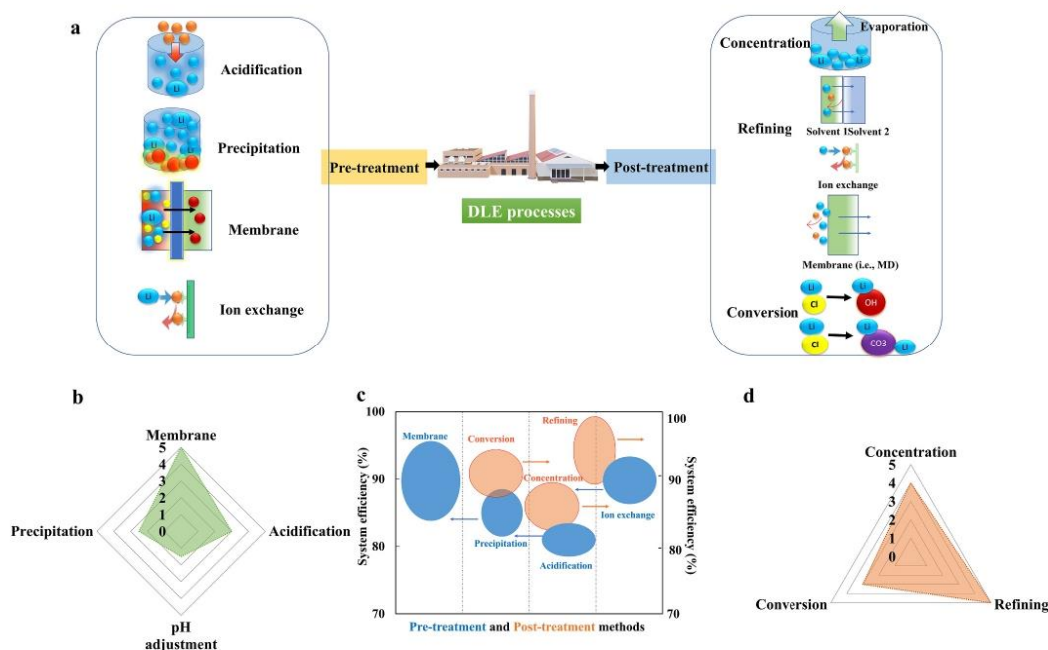


Fig. 4. The various strategies currently applied for the pre and post processing DLE process including acidification, precipitation, membrane, ion exchange for pre-treatment and concentration, refining (i.e., solvent extraction, ion exchange, and membranes), and conversion for post treatment, b) the importance of different pretreatment methods based on their efficiency and environmental impact based on current available data, c) the efficiency of pre and post treatment strategies d) the importance of post treatment plants based on their important factors (i.e., operational costs, environmental impact, and performances).

lithium solution and purified water. The employed MD for the enrichment of treated brine before lithium recovery in a two-stage precipitation process as an NF/MD hybrid system showed up to 90 % rejection of divalent ions (i.e.,  $Mg^{2+}$  and  $Ca^{2+}$ ) using NF and 80 % water recovery supported by MD [170]. Seawater was also pre-treated for lithium chloride recovery with MD process under three pre-treatment stages, including oxalic acid treatment, granular activated carbon, and MD, followed by ion exchange as the main lithium ion extraction phase [168]. Ion exchange is another pre-treatment method that eliminates undesirable ions using anion or cation resins. Nishihama et al. [171] used an ion exchange process to extract lithium from seawater. At first, an ultrafiltration membrane was used for the pre-treatment to separate suspended materials in the solution. In the second step, it was followed by ion exchange to replace unwanted ions, and in the final step, sorption was used as the main DLE for lithium recovery [171,172]. Acidification processes are commonly used as one of the primary preprocessing methods in producing lithium from brines to adjust the pH of the solution and remove impurities that may interfere with the extraction process [173]. Commonly used acids include sulfuric acid, hydrochloric acid, and nitric acid. The choice of acid will depend on the brine's specific composition and the lithium's required concentration. It was found that sulfuric acid is often the preferred acid for acidification of brines due to its high solubility and low cost [144]. Another method for pH adjustment is the addition of alkali chemicals such as sodium hydroxide or lime [172].

The selection of an appropriate pre-treatment method depends on the characteristics of the brine and the desired final product. An ideal pre-treatment method should be able to increase the lithium concentration as much as possible to reduce the impurities load from DLE. It

also should be restructured to require a minimal amount of reagents such as NaOH to reduce the cost and energy of the crystallizer. For example, to select the optimum pre-treatment step, it is important to consider the geothermal brine composition and its location.

The importance of these strategies and their efficiencies for lithium ion recovery has been discussed in Fig. 4b-c. Although various pre-treatment methods have been studied for direct lithium extraction from brine, some challenges still need to be addressed to achieve efficient and cost-effective lithium recovery. First, most pre-treatment methods target calcium, magnesium, and sodium impurities, which can compete with lithium for sorption sites. However, achieving selectivity for lithium remains a challenge, as the sorbents used for lithium extraction may also interact with other ions in the brine, leading to decreased efficiency and selectivity. Second, some pre-treatment methods require high energy input, such as pH adjustment using sodium hydroxide or lime, which can increase the process's overall energy consumption and cost. Third, pre-treatment methods that involve adding chemicals, such as precipitation and softening, can increase the overall cost of the process. Moreover, the cost of the sorbents used for lithium ion extraction can also be a limiting factor in the commercialization of direct lithium extraction from brine. Besides, some pre-treatment methods, such as pH adjustment and softening, can generate large amounts of sludge or waste, which can have negative environmental impacts if not properly disposed of or treated. Finally, it is notable that most of the pre-treatment methods have been tested on a laboratory scale, and their scalability to a commercial level is still uncertain. The efficiency and cost of the pre-treatment methods may change significantly when scaled up to a commercial level, making it challenging to determine their feasibility for large-scale DLE from brine.

Addressing these challenges is key to achieving efficient and cost-effective DLE from brine and applying it in an industrial applicable scale. Further research and development are needed to optimize and scale up the pre-treatment methods and identify new, more selective, cost-effective approaches. One emerging trend is using new solvents, such as ionic liquids [174] and deep eutectic solvents [175,176], which offer improved selectivity and efficiency in lithium extraction and can be used as pre-treatment plans for brines.

### 3.3. Post-treatment strategies

Post-treatment strategies are an important part of the lithium extraction process from brines. These strategies involve the concentration [177], refining [25], and conversion [178] of lithium salts, mainly lithium chloride, to produce high-purity lithium products (Fig. 4a). There are two main concentration processes for lithium chloride solutions: evaporation and crystallization [27]. Evaporation involves heating the solution to evaporate the water, leaving a concentrated lithium chloride solution behind. Crystallization processes involve cooling the solution to induce crystallization of the lithium chloride. The process selection depends on factors such as energy efficiency, product purity, and process scalability. The process parameters such as temperature, pressure, and residence time can affect the efficiency and purity of the product [179]. Typically, the concentration processes can achieve a concentration factor of 1.1–1.3 for evaporation processes and up to 1.6 for crystallization processes [180].

Refining lithium chloride solutions involves the removal of

impurities such as magnesium, calcium, and sodium. Solvent extraction, ion exchange, and precipitation are commonly used in refining processes [181]. Refining processes can achieve up to 90 % impurity removal efficiencies, with membrane and ion exchange being the most effective method for certain impurities such as sodium, potassium, calcium, and magnesium [182]. The process selection depends on the type and concentration of the impurities present in the solution. The conversion of lithium chloride solutions into lithium carbonate or hydroxide involves using various processes such as Solvay, Lime soda, and carbonation processes [183]. The process selection depends on factors such as product purity, energy efficiency, and process scalability. The process parameters such as temperature, pressure, and residence time can affect the efficiency and purity of the product [184]. The conversion of lithium chloride solutions to lithium hydroxide involves the use of various processes such as the Lime process, the  $\text{Li}_2\text{CO}_3$  process, and the electrochemical route (Fig. 5). The Lime and electrochemical route results in the production of pure battery grade  $\text{LiOH}$  while the  $\text{Li}_2\text{CO}_3$  route produces technical and battery grade level of  $\text{Li}_2\text{CO}_3$ . The selection of the process depends on various factors such as the number of impurities, energy efficiency, and being more environmentally friendly. The process parameters such as temperature, pressure, and residence time can affect the efficiency and purity of the product. Conversion to lithium carbonate or hydroxide can typically achieve purity levels of 99.5–99.9 % [184,185].

The challenges associated with post-treatment processes in DLE include the high energy consumption of some processes, such as the electrochemical process with the electrolysis section, the complexity of

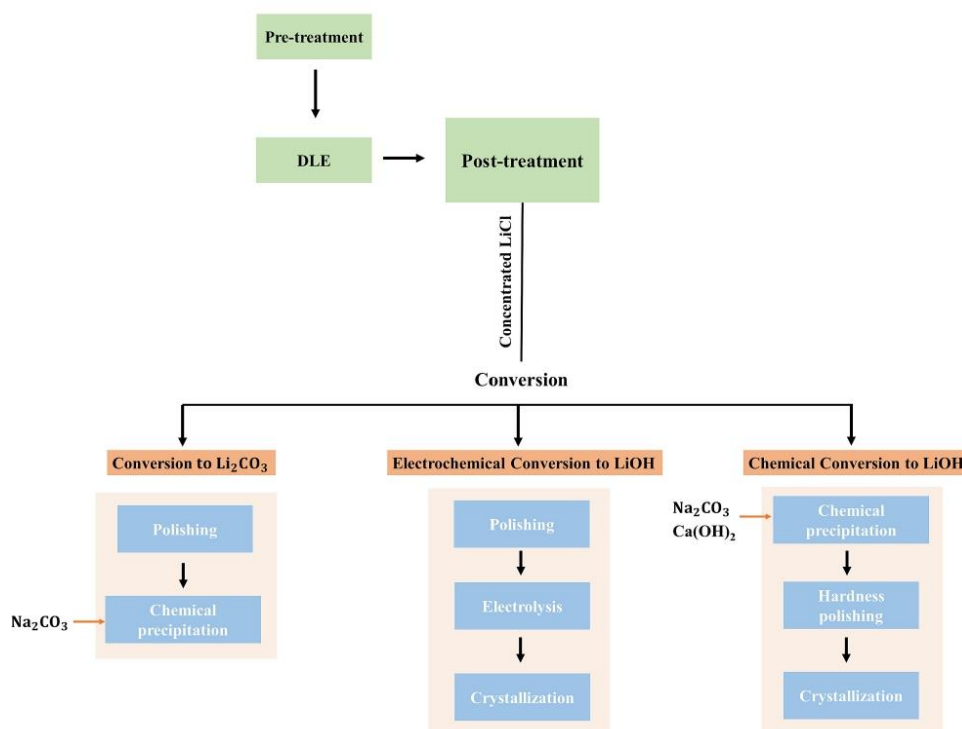


Fig. 5. post treatment processes with three different conversions including electrochemical (with the aim of producing battery grade  $\text{LiOH}$ ), lime route (with the aim of producing battery grade  $\text{LiOH}$ ), and  $\text{Li}_2\text{CO}_3$  route (with the aim of technical grade or battery grade production of  $\text{Li}_2\text{CO}_3$ ).



such routes, and the difficulty in achieving high product purity (either LiOH or Li<sub>2</sub>CO<sub>3</sub>). All process has significant improvement and effectiveness in DLE strategies that depend on factors such as the brine location, operational cost, environmental impact, etc.). Fig. 4c-d categorized different post-treatment strategies and highlighted the most important one for the final lithium recovery step. Emerging trends and future directions in DLE technology include the development of new and more efficient processes for concentration, refining, and conversion, as well as using renewable energy sources to power these processes.

#### 4. DLE Commercial implementation

##### 4.1. Overview

The TRL of DLE methods provides a quick view of how easy it will be to convert a process into a commercial or industrial process. The readiness level of these technologies varies, with sorption (TRL 9) and ion exchange methods (TRL 8) being the most commercialized or fully demonstrated technologies (Fig. 6). Aluminum-based sorbents have already reached a TRL of above 9 at full scale. However, some sorbents, such as manganese-based and titanium-based ones, are still in the pilot stage for DLE [186]. Energy sources use alumina-based sorbents for DLE processes, and pilot trials have shown that they can recover approximately 90 % of lithium with the ability to produce 99.9 % pure lithium [187]. In addition, PurLucid is currently developing a method to extract lithium from water that is produced during oil sand mining in Canada using titanium oxide-based sorbents [25]. Lithium can be extracted using a solvent extraction process, resulting in either lithium aluminate or lithium carbonate (LCE) precipitation. This method is cost-effective, at approximately 2800 US\$/t LCE from the Dead Sea, with a recovery rate of 65 % to 96 % [188]. Alternatively, membrane-based technologies can be used to remove ions and separate water. These technologies have been evaluated at TRL 4 [189]. The estimated operational costs for membrane processing of lithium from brines are approximately 3000 US \$/t of LCE. While these methods hold potential, further research is needed to improve their efficiency and economic viability for large-scale production [188].

The electrochemical lithium recovery methods; ED, ESIX, and MCDI,

are shown in TRL 4 at the applied research level. Up to now, only 4.3 % of these processes have shown the potential for the pilot scale. Nevertheless, a higher percentage (54.4 %) of studies have validated processes at the bench scale; another 21.7 % of studies demonstrated high system stability in continuous operation mode. In MCDI methods, most of them are in TRL 4 and TRL 5, while only 22.2 % of MCDI processes are in TRL 6 with no system reaching TRL of 7 [190]. In many DLE projects worldwide, sorption and ion exchange techniques are the primary methods used. China, Australia, and Argentina are significantly emphasizing their lithium production.

Additionally, with the growing demand for lithium, several new lithium DLE projects have been announced in countries like the USA, Germany, and Canada [191]. The annual LCE output is mainly at 20 kt based on current data. The USA aims to produce LCE at up to 90 kt/a, while Germany and Argentina target production at 40 kt/a and 50 kt/a, respectively (Table 7).

DLE technologies offer much faster lithium production that can be achieved within a few hours or days compared to the evaporation pond process, which takes a whole year for production [192]. Additionally, DLE technologies can significantly reduce water consumption and environmental impact, resulting in a smaller environmental footprint. Furthermore, with the use of DLE methods, it is possible to achieve a lithium recovery rate of 70–90 %, resulting in the production of approximately 18–23 kt/a LCE, which is a remarkable improvement compared to traditional processes that usually yield only 40–60 % recovery and produce around 10–15 ktpa LCE [193].

##### 4.2. DLE for recovery of lithium from discarded batteries

Considering the life span of a lithium ion battery which could last up to 3–5 years in small electronic devices such as laptops and up to 5–10 years in large devices such as electronic vehicles, it is expected that discarded lithium ion batteries become a challenging e-waste stream soon [2]. lithium concentration in waste batteries is about 3–6 mass%, representing them as an essential source for recovery. However, due to the elemental diversity and composition complexity of batteries [3], selectively recovering lithium requires several energy-intensive processes such as solvent extraction [4] and co-precipitation [5].

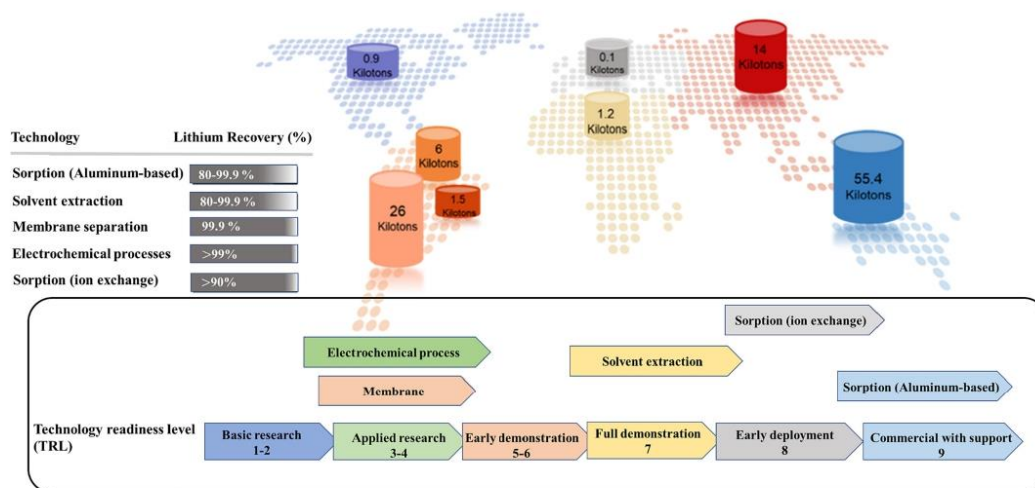


Fig. 6. Global lithium production in different regions of the world with different brine properties and ores. The selected area used different DLE methods including Sorption, solvent extraction, membrane, electrochemical, and ion exchange processes. The respected TRL and the amount of lithium production has been reported in the map [207].

Table 7

Global DLE projects with various lithium recovery rates to reduce environmental impact as compared to conventional methods.

| Company                | DLE technology     | Capacity (kt/a LCE) | 2023 stage    | Country   |
|------------------------|--------------------|---------------------|---------------|-----------|
| Anson Resources        | Ion Exchange       | 15                  | Production    | Australia |
| Berkshire Hathaway     | Ion Exchange       | 90                  | Pilot         | USA       |
| Compass Minerals       | Ion Exchange Resin | 20–25               | Pilot         | USA       |
| CTR                    | Ion Exchange Resin | 20                  | Offsite Pilot | USA       |
| E3 Metals              | Ion Exchange       | 20                  | Pilot         | Canada    |
| Energy Source Minerals | Ion Exchange Resin | 20                  | Pilot         | USA       |
| Eramet/Tsinghan        | Sorption           | 24                  | Construction  | Argentina |
| Lake Resources/Lilac   | Ion Exchange Resin | 20–25               | Offsite Pilot | Argentina |
| Jintai lithium         | Sorption           | 7                   | Production    | China     |
| Lanke lithium          | Sorption           | 20                  | Production    | China     |
| Livent                 | Sorption           | 20                  | Production    | Argentina |
| Pure Energy Minerals   | Solvent Extraction | 12                  | Bench Scale   | Canada    |
| Standard lithium       | Ion Exchange Resin | 21                  | Demo          | USA       |
| Rio Tinto              | Sorption           | 50                  | Pilot         | Argentina |
| Vulcan Energy          | Sorption           | 40                  | Pilot         | Germany   |
| Zange lithium          | Sorption           | 20                  | Production    | China     |
| Xinghua Lithium        | Solvent extraction | 10                  | Production    | China     |

Lithium is mainly available in the cathode electrode in different phases, such as NMC ( $\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ ), LCO ( $\text{LiCoO}_2$ ), and LFP ( $\text{LiFePO}_4$ ) [6]. Although recovering other metals, such as Nickel and Cobalt, brings more value to the recycling processes, their co-extraction calls for selective recovery technologies such as DLE.

Recently, the concept of ED, borrowed from biological purification technologies and desalination industries, has inspired scientists and industries to utilize it as a DLE technique for lithium recovery from discarded batteries. Through the recovery of a waste NMC battery, lithium, alongside nickel and cobalt as other critical elements in the battery, has been recovered using the monovalent cation exchange membrane (CEM). Using Ethylenediamine tetra acetic acid (EDTA) as the complexing agent at a controlled pH has resulted in the recovery of lithium as  $\text{Li}_2\text{SO}_4$ . Multi-stage CEM and anion exchange membrane (AEM) processing and consuming extensive amounts of reagents for pH adjustment and decomplexation of Nickel and Cobalt make the scalability of this technology challenging [7]. In addition, recovered  $\text{Li}_2\text{SO}_4$  should be converted to  $\text{Li}_2\text{CO}_3$  or  $\text{LiOH}$  as the main raw materials for battery manufacturing.

Recovery of spent LCO batteries using an H-shape electrochemical cell and without the addition of chemicals has also shown that selective extraction of lithium could be carried out under 3.5 V and 90 °C after 48 h. Although the recovery time seems slack, the lithium and Cobalt have both been recovered as  $\text{LiOH}$  and  $\text{Co(OH)}_2$ , which requires less post-processing to be used as raw materials [8]. Recycling of LFP batteries has also been investigated using the ED method.  $\text{LiOH}$  has been produced where cathode materials of an LFP battery were exposed to the 60 mA/cm<sup>2</sup> at 50 °C for 4 h. Kinetic data has revealed that the initial 1.5 h of the process provides more extraction efficiency before the internal diffusion controls the leaching through the remaining time.  $\text{FePO}_4$ , as the by-product of the extraction, has also been formed on the anode chamber [9]. DLE, one of the promising sustainable techniques for lithium recovery, has shown its feasibility for processing different types of waste batteries, such as NMC, LCO, and LFP. As the formulation of waste batteries gets more complicated with the presence of other heavy metals, further research is required to investigate to prove its scalability.

## 5. Summary and future perspectives for DLE

DLE technologies have the capability to significantly enhance the lithium supply derived from brines, while also providing sustainability benefits. In this review, we have discussed the fundamental aspects of DLE technologies, including their faster production timeframe and the potential for brine reinjection into the aquifer in comparison to traditional lithium processes that rely on evaporation ponds.

Among DLE technologies, aluminum-based adsorption is the most widely utilized and technologically advanced method for lithium extraction. It offers several advantages, including the elimination of reagents such as acids for lithium chloride extraction, reduced sensitivity to brine composition and weather conditions, and the potential to achieve over 90 % lithium extraction efficiency. However, aluminum-based adsorption LDE suffers from some drawbacks. It requires temperature above 40 °C and involves additional purification steps and water recycling. Contrasted with aluminum sorbent-based DEL, ion exchange-type DLE exhibits significant potential due to its higher recovery rate and reduced dependence on water. While several pilot studies are underway, the ongoing challenge lies in maintaining the stability of the sorbent. Addressing the acid/base dependency of ion exchange-type DLE should also be a priority for consideration.

On the other hand, solvent extraction-DLE can achieve high lithium concentration regardless of weather conditions, resulting in lower operating costs. However, its commercial development has been limited due to certain challenges. These include concerns over environmental contamination, the risk of fire with high-temperature brines, significant capital expenditure (CAPEX) for initial filling, issues of corrosion, and the potential for solvent leaching into the product.

Lithium selective membranes, although in early-stage development, demonstrate significant potential for use in DLE processes. One notable advantage is the absence of direct contact between the brine and extractant, resulting in a lower carbon and water footprint. Moreover, these membranes offer scalability and modularity. However, several challenges need to be addressed to facilitate their future development. These include enhancing membrane stability, reversibility, and durability, as well as improving lithium selectivity while maintaining sufficient ionic permeability.

Electrochemical processes relying on membranes and electrodes have demonstrated great potential for industrial-scale lithium recovery, offering reduced environmental impact and carbon footprints. However, their widespread adoption of these processes has been hindered by the limited progress in the development of lithium-selective membranes and electrodes.

Carbonation processes, especially direct carbonation, offer several advantages over traditional lithium extraction methods. These include simplicity, cost-effectiveness, and environmental sustainability. Direct carbonation can be integrated with other technologies, such as geothermal or solar energy, to create efficient lithium and sustainable lithium extraction processes. Nonetheless, there are certain drawbacks to consider. These include a lower lithium recovery rate and the requirement for operating under controlled atmosphere, often involving elevated temperature and pressure.

**Future research** in DLE should be prioritized for both material and process development to drive advancement in the field. For sorption based DLE, it is crucial to focus on the development of advanced materials that can serve as building blocks for innovative adsorbents. These materials should exhibit higher adsorption capacity, enhanced stability, and reduced reliance on heat and reagents during stripping stages. Specifically, the aluminum sorbent DLE exhibits a restricted stripping capacity of approximately 10 %, and excessive unloading of lithium could potentially harm the sorbents. Hence, additional research is imperative to minimize both the water dependency of the sorbent DLE and to bolster the stability of the sorbent. Furthermore, enhancing the reloading capacity of the sorbent during the stripping solution is essential.



Despite achieving high lithium recovery rates, the stability of the adsorbent in ion exchange DLE remains a primary obstacle preventing its commercial implementation, necessitating further investigation. Reducing its reliance on reagents during the stripping stage is essential, not only to decrease OPEX but also to minimize Scope 3 emissions. Although membrane technology has recently shown promising outcome, material innovation is essential for the improvement of lithium-selective membranes, ensuring their stability, durability, and scalability. The current lithium-selective membranes have demonstrated promising results when exposed to very low TDS solutions or simulated brines with low salinity. However, the majority of lithium-bearing brines typically exhibit high TDS and salinity levels, which could lead to fouling on the membrane surface, thereby compromising the immediate performance of these lithium-selective membranes. Consequently, practical implementation of deployed ion-selective membranes for real brines remains uncertain. Additionally, membranes constructed from advanced materials like MOF or COF tend to be expensive. Thus, designing membranes from cost-effective starting materials with a well-established supply chain becomes crucial for the commercial implementation of membranes.

Reverse osmosis membrane technology has been incorporated into DLE flowsheets. Nevertheless, alternative pressure-based membranes like NF and UF can also be viable options for purposes such as water recycling, purification, or concentration. NF, in particular, has received significant attention in research literature; however, there has been comparatively less effort dedicated to its utilization within commercial DLE settings.

The exploration of thermally driven membrane processes, such as membrane distillation or pervaporation, holds significant promise for DLE. These methods exhibit substantial potential for applications in water recycling, concentration, and even crystallization within the realm of DLE.

In the case of solvent extraction-DLE, the emphasis should be on developing environmentally friendly solvent and extractant components, promoting a more sustainable process overall. Moreover, continuous improvements in process design and flow sheets are necessary to optimize extraction efficiency, minimize environmental impacts, and reduce costs associated with DLE technologies. By addressing these key areas of material and process development, the DLE field can advance significantly and pave the way for more efficient, sustainable, and cost-effective lithium extraction.

Lastly, it is essential to conduct research that explores the potential of integrating DLE processes with other technologies, such as renewable energy sources and battery recycling, to establish a more sustainable and circular lithium supply chain. Currently, the majority of DLE processes are primarily limited to laboratory or pilot-scale operations, expect sorbent DLE. It is crucial to scale up these processes to a commercial level. This will involve optimizing the process for large-scale operations, and addressing any technical and economic challenges that may arise during scale-up.

Moreover, DLE processes should be integrated with existing lithium production methods, including brine evaporation, brine pumping, and hard rock mining. Investigating how DLE can complement or potentially replace these methods will help enhance overall lithium production efficiency. Such investigations will facilitate the identification of synergies and the development of integrated approaches to maximize the benefits of DLE technology within the existing lithium production infrastructure.

#### CRedit authorship contribution statement

**Javad Farahbakhsh:** Writing – original draft, Writing – review & editing. **Faezeh Arshadi:** Writing – original draft, Writing – review & editing. **Zahra Mofidi:** Writing – original draft, Writing – review & editing. **Masoud Mohseni-Dargah:** Writing – original draft, Writing – review & editing. **Cansu K  k:** Writing – original draft, Writing – review & editing. **Mohammad Assefi:** Writing – original draft, Writing – review

& editing. **Asieh Soozanipour:** Writing – original draft, Writing – review & editing. **Masoumeh Zargar:** Writing – review & editing. **Mohsen Asadnia:** Writing – review & editing. **Yasaman Boroumand:** Writing – original draft, Writing – review & editing. **Volker Presser:** Writing – review & editing. **Amir Razmjou:** Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

#### Acknowledgments

AR appreciates the funding support from the AusIndustry and Australian government. CK and VP acknowledge support for the eLiRec project by the European Union from the European Regional Development Fund (EFRE) and the State of Saarland, Germany.

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## CONCLUSIONS AND OUTLOOK

My doctoral work demonstrates that material and system design are essential for advancing electrochemical  $\text{Li}^+$  extraction toward higher selectivity, efficiency, and sustainability. In these studies, material development, electrode and membrane engineering, system architecture, and performance evaluation provide practical strategies for selective  $\text{Li}^+$  recovery from complex aqueous environments.

At the material level, this thesis establishes layered materials as a versatile and selective class for electrochemical  $\text{Li}^+$  separation. An aluminum layered double hydroxide electrode was shown to enable selective  $\text{Li}^+$  uptake combined with an electrochemical regeneration process, in addition to gentle acid-free washing. Compared to conventional adsorption-based DLE technologies that rely on chemical regeneration and harsh eluents, this approach allows reversible  $\text{Li}^+$  extraction under mild, pH-neutral conditions, thereby improving material stability and reducing secondary waste. In parallel, MXene-based electrodes were explored as an alternative to the layered-material platform for electrochemical  $\text{Li}^+$  separation, where interlayer engineering via organic-molecule intercalation enables preferential  $\text{Li}^+$  transport while suppressing competing ions. These results highlight how layered structures with tunable chemistries can be effectively designed for selective electrochemical ion separation.

Beyond material design, this thesis highlights the role of membrane choice, electrode surface engineering, and cell configuration for achieving continuous  $\text{Li}^+$  extraction. By integrating a ceramic-based solid electrolyte membrane and coated electrodes into a fuel cell system configuration, selective and continuous  $\text{Li}^+$  recovery from seawater and mine water was achieved, with 95% purity and improved  $\text{Li}^+/\text{Na}^+$  selectivity. In this context, my work examines how electrochemical systems originally developed for energy storage and conversion can be effectively adapted for desalination applications, particularly for  $\text{Li}^+$  selective ion separation.

To support meaningful comparison and system optimization, a standardized framework for evaluating electrochemical ion separation performance was also developed in the best practice for electrochemical water desalination paper. By defining key metrics and calculation methods, this paper enables reproducible evaluation of efficiency, capacity,

and energy consumption across different systems. Finally, a comprehensive review of direct lithium extraction technologies addresses these findings within the broader context of sustainable lithium supply, highlighting DLE approaches as promising alternatives to conventional mining and evaporation.

Overall, this work shows that combining material design with optimized system architecture and standardized evaluation of electrochemical DLE technology can compete by offering mild operating conditions, high selectivity, and compatibility with continuous processing. While some challenges remain, such as long-term stability, extraction kinetics, and scale-up, this thesis provides concrete design principles that distinguish electrochemical approaches from conventional DLE methods. Future research should focus on improving long-term stability and kinetics, deepening mechanistic understanding of ion–material interactions, and scaling continuous systems under realistic operating conditions. These advances will be essential for developing sustainable and efficient  $\text{Li}^+$  extraction technologies to meet the growing demand for energy storage materials.



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