

Structure–Property Relationships in Mn-Based Sorbents for Direct Lithium Extraction

A Comprehensive Study of Synthesis, Structure, and Li-Sorption

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List of Abbreviations

APS	Anounced pledges scenario
BET	Brunauer–Emmett–Teller
CAPEX	Capital expenditure
CI	Competing ions
CTR	Controlled Thermal Resources
DLE	Direct Lithium Extraction
DMF	Dimethylformamid
DSC	Differential scanning calorimetry
EDX	Energy dispersive x-ray spectroscopy
EPC	Engineering procurement construction
FC	Field cooled
HS	Hydrothermal synthesis
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IEA	International energy agency
LCE	Lithium carbonate equivalents
LEOP	Lithium extraction optimization plant
LIS	Lithium ion sieve
LMO	Lithium manganese oxide
LMTO	Lithium manganese titanium oxide
LTO	Lithium titanium oxide
LDH	Lithium double layered aluminum Hydroxide
MAS NMR	Magic angle spinning nuclear magnetic resonance
MoU	Memorandum of understanding
m/V-ratio	Mass of sorbent to brine ratio
NaOAc	Sodium acetate
NMR	Nuclear magnetic resonance
NZE	Net zero emissions
OPEX	Operational expenditure
PEG	Polyethylenglykol
PVC	Polyvinylchlorid
SD	Spray drying
SEM	Scanning electron microscopy
SSA	Specific surface area
STEPS	Stated policies scenario
TDS	Total dissolved solids
TGA	Thermogravimetric analysis
TRL	Technology readiness level
URG	Upper Rhine Graben
XRD	X-ray diffraction
ZFC	Zero field cooled

Eidesstattliche Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit selbstständig verfasst habe, dass ich keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe, dass ich die wörtlich oder inhaltlich übernommenen Stellen als solche gekennzeichnet habe und dass ich die Satzung des KIT zur Sicherung guter wissenschaftlicher Praxis in der jeweils gültigen Fassung beachtet habe.

Karlsruhe, 1.11.2025

(Laura Herrmann)

Abstract

Lithium is considered a key raw material for the energy transition, particularly in the production of batteries for electric vehicles and stationary energy storage systems.^[62] Given the globally increasing demand for lithium, the development of alternative resources is of great importance.^[113] In this context, geothermal brines offer significant potential, as they can contain high lithium concentrations depending on the geological conditions.^{[112][111]} However, their high salinity poses a technological challenge, requiring suitable materials and processes for efficient and selective lithium extraction. Lithium manganese oxides (LMO) show promising properties as sorbents due to their high selectivity and sorption capacities.^{[24][115]}

In this thesis, the synthesis and optimization of LMO sorbents for lithium extraction from geothermal brines were investigated. The material was initially synthesized via hydrothermal methods.^{[23][115]} Targeted adjustments of synthesis parameters increased the sorption capacity from 1.19 mmol g⁻¹ to 1.61 mmol g⁻¹ and reduced manganese dissolution – an indicator of chemical stability – from 5.5 % to 3 %. Due to limited scalability of this method, a spray drying process was developed to enable large-scale production of LMO sorbents. The resulting material exhibited a sorption capacity of 2.03 mmol g⁻¹ and a reduced manganese dissolution of 2.9 %.

The chemical composition of the sorbent was determined by ICP-OES as Li_{1.6}Mn_{1.6}O₄. X-ray diffraction confirmed the cubic spinel structure (space group $Fd\bar{3}m$), while synchrotron XRD revealed an additional layered phase, Li₂MnO₃ ($C2/m$), accounting for 16.5 % of the material. This phase indicates a lithium deficiency in the main structure, which was identified by NMR spectroscopy as Li₄Mn₅O₁₂ – a well-known ion exchange material.

To improve chemical stability, manganese was partially substituted with titanium (<0.5 mol%), reducing manganese dissolution from 2.9 % (LMO) to 0.45 % (LMTO) and increasing sorption capacity to 2.22 mmol g⁻¹. The activated sorbents HMO and HMTO were tested in synthetic LiCl solutions and two geothermal brines from the Upper Rhine Graben. The influence of pH, mass-to-volume ratio (m/V), and lithium concentration on sorption capacity was systematically investigated. At an m/V ratio of 0.25 g L⁻¹, the highest capacities of 5.06 mmol g⁻¹ (LMO) and 5.66 mmol g⁻¹ (LMTO) were achieved.

The LMO granulate developed within the scope of this thesis was subsequently tested in long-term experiments under conditions close to those of a DLE pilot plant coupled with a geothermal system. The LMO-granules showed a significantly higher sorption capacity of 0.56 mmol g⁻¹ compared to commercial materials (Lithium double layered aluminum hydroxides (LDH): 0.01-0.12 mmol g⁻¹; Lithium titanium oxides (LTO): 0.10 mmol g⁻¹). Furthermore, significantly high lithium selectivity was observed for LMO, resulting in a high purity of the product solution.

Overall, these results demonstrate that the LMO and LMTO sorbents developed within the scope of this thesis are highly promising candidates for lithium recovery from geothermal brines.

Kurzfassung

Lithium zählt zu den Schlüsselrohstoffen der Energiewende, insbesondere im Hinblick auf die Herstellung von Batterien für Elektrofahrzeuge sowie stationäre Energiespeichersysteme.^[62] Angesichts des weltweit steigenden Bedarfs an Lithium ist die Erschließung alternativer Ressourcen von großer Bedeutung.^[113] Geothermalwässer haben in diesem Kontext ein hohes Potenzial, da sie – abhängig von der geologischen Beschaffenheit – teils hohe Lithiumkonzentrationen aufweisen und somit eine bedeutende Quelle darstellen.^{[112][111]} Der hohe Salzgehalt dieser Wässer stellt jedoch eine technologische Herausforderung dar, da für eine effiziente und selektive Lithiumextraktion geeignete Materialien und Verfahren erforderlich sind. Lithium-Mangan-Oxide (LMO) zeigen in diesem Zusammenhang vielversprechende Eigenschaften als Sorbenten mit hoher Selektivität und Sorptionskapazität.^{[24][115]}

In dieser Arbeit wurde die Synthese und Optimierung von LMO-Sorbenten zur Lithiumextraktion aus Geothermalwasser untersucht. Das Material wurde zunächst mittels Hydrothermalsynthese hergestellt.^{[23][115]} Gezielte Anpassungen der Syntheseparameter erhöhten die Sorptionskapazität von 1,19 mmol g⁻¹ auf 1,61 mmol g⁻¹ und senkten die Manganfreisetzung – ein Indikator für die chemische Stabilität des Sorbenten – von 5,5 % auf 3 %. Da diese Methode beschränkt skalierbar ist, wurde ein Sprühtrocknungsverfahren entwickelt, das die Herstellung von LMO Sorbenten im großtechnischen Maßstab ermöglicht. Das resultierende Material zeigte eine Sorptionskapazität von 2,03 mmol g⁻¹ und eine reduzierte Manganfreisetzung von 2,9 %. Die chemische Zusammensetzung wurde mittels ICP-OES als Li_{1,6}Mn_{1,6}O₄ bestimmt. Röntgendiffraktometrie bestätigte die kubische Spinellstruktur (Raumgruppe *Fd $\bar{3}m$*), während Synchrotron-XRD eine zusätzliche Phase mit Schichtstruktur Li₂MnO₃ (*C2/m*) identifizierte, die 16,5 % des Materials ausmacht. Diese Phase weist auf ein Lithiumdefizit in der Hauptstruktur hin, deren Zusammensetzung durch NMR-Spektroskopie als Li₄Mn₅O₁₂ identifiziert wurde – ein bekanntes Ionenaustauschmaterial.

Zur Verbesserung der chemischen Stabilität wurde Mangan partiell durch Titan (<0,5 mol%) substituiert. Dies reduzierte die Manganfreisetzung signifikant von 2,9 % (LMO) auf 0,45 % (LMTO) und erhöhte die Sorptionskapazität auf 2,22 mmol g⁻¹. Die aktivierten Sorbenten HMO und HMTO wurden in synthetischen LiCl-Lösungen sowie in zwei Geothermalwässern aus dem Oberrheingraben getestet. Dabei wurden der Einfluss von pH-Wert, Sorbent/Brine-Verhältnis (m/V) sowie der Lithiumkonzentration auf die Sorptionskapazität systematisch untersucht. Bei einem m/V-Verhältnis von 0,25 g L⁻¹ wurden die höchsten Kapazitäten von 5,06 mmol g⁻¹ (LMO) und 5,66 mmol g⁻¹ (LMTO) erreicht.

Anschließend wurde der LMO-Sorbent in Form eines Granulats unter geothermiekraftwerksähnlichen Betriebsbedingungen in Langzeitversuchen getestet. Er zeigte eine deutlich höhere Sorptionskapazität von 0,56 mmol g⁻¹ im Vergleich zu kommerziellen Materialien (Lithium double layered aluminum hydroxides (LDH): 0,01-0,12 mmol g⁻¹; Lithium titanium oxides (LTO): 0,10 mmol g⁻¹). Ebenso wurde für LMO eine besonders hohe Lithiumselektivität beobachtet, was sich in einer hohen Reinheit der Produktlösung widerspiegelt. Die Ergebnisse dieser Arbeit unterstreichen das hohe Potenzial der untersuchten LMO- und LMTO-Sorbenten für die Lithiumgewinnung aus Geothermalwässern.

Declaration of Collaborations

Collaborations

Throughout this doctoral research, several collaborative efforts were undertaken, including Master’s theses, co-authored publications, and a patent application. In addition to the author, multiple persons contributed significantly to these works. Their specific roles and contributions are outlined in the following sections.

During my doctoral research, I supervised the following Master’s theses and contributed to their conceptualization and scientific guidance:

- **Matthias Maier** – *Lithiumgewinnung aus Thermalwasser: Untersuchung verschiedener Formulierungstechnologien für das Adsorptionsmaterial.*
- **Tibor Feurer** – *Optimierung des Manganoxid-Adsorbenten zur Lithiumgewinnung aus Thermalwasser mithilfe von Doping- und Coating-Methoden.*

Selected results and insights from these theses have been integrated into this dissertation, with proper referencing and critical evaluation by the author.

As part of the doctoral work, a novel synthesis route for an LMO-based sorbent was developed, utilizing a spray drying method:

- **Dr. J.R. Binder, N. Bohn, Dr. F. Jeschull, L. Herrmann**
Herstellung des Mn-basierten Adsorbenten $Li_{1.6}Mn_{1.6}O_4$ im Sprühtrocknungsverfahren, application number 11360183DE

Based on this process, a scientific publication was prepared, covering the material synthesis, initial structural characterization, and lithium sorption behavior:

- **L. Herrmann, N. Bohn, A. Pfau, Dr. T. Kölbel, Prof. H. Ehrenberg, Dr. J.R. Binder, Dr. F. Jeschull**
Synthesis of lithium manganese oxide (LMO) and Ti-substituted LMO sorbents (LMTO) for lithium extraction in a spray drying process.

Dr. Fabian Jeschull, Dr. Joachim R. Binder, and Nicole Bohn made a significant contribution to the development of the spray drying synthesis method, which forms the basis of both the patent and the associated manuscript. Nicole Bohn operated the spray dryer for the synthesis of the LMO and LMTO precursors and conducted TGA of these materials. Prof. Helmut Ehrenberg supported the project through XRD data analysis, particularly in the context of Rietveld refinement. Alisa Pfau performed ICP-OES measurements and contributed to the evaluation of selected samples. Udo Geckle conducted scanning electron microscopy (SEM) analyses. Dr. Thomas Kölbel provided supervision for the manuscript.

The author of this dissertation, Laura Herrmann, was responsible for conceptualization, experimental design, data acquisition and analysis, interpretation of results, and manuscript preparation.

Further structural investigations of the spray dried LMO material are currently being compiled into a manuscript under preparation:

- **Dr. M. Gamba, L. Herrmann, Dr. B. Schwarz, Dr. H. Li, Dr. S. Mangold, Dr. S. Indris, Prof. H. Ehrenberg, Dr. G. Lener, Dr. F. Jeschull**
Reassessing the structure of the sorbent with nominal composition $Li_{1.6}Mn_{1.6}O_4$ used for Direct Lithium Extraction.

Dr. Martina Gamba was responsible for manuscript drafting, conceptual design and contributed to the data analysis and interpretation of results. Dr. Sylvio Indris and Dr. Hang Li carried out NMR measurements and contributed to the evaluation and interpretation of the data. Synchrotron and magnetic measurements were performed by Dr. Björn Schwarz, who also analyzed the magnetic data and supported the author in data evaluation and Rietveld refinement. Dr. Fabian Jeschull contributed to the manuscript through scientific supervision and co-writing.

The author of this dissertation, Laura Herrmann, was responsible for the experimental design and sample preparation and contributed to the data analysis and interpretation of the results.

A comprehensive magnetic characterization of the spray dried material is the subject of a forthcoming publication currently in preparation:

- **Dr. B. Schwarz, L. Herrmann, S. Mangold, Dr. H. Li, Dr. S. Indris, Dr. F. Jeschull, Prof. H. Ehrenberg**
Transition from Ferro- to Antiferromagnetism in $Li_4Mn_5O_{12}$ Spinel Induced by Li^+/H^+ Ion Exchange.

Magnetic measurements of pristine LMO and pristine HMO from this work were utilized in this dissertation to draw conclusions regarding the oxidation state of the materials. Synchrotron measurements and Rietveld refinements were performed and evaluated by Dr. Björn Schwarz and were integrated into the structural analysis. Furthermore, NMR analyses conducted by Dr. Sylvio Indris and Dr. Hang Li were incorporated into the structural evaluation. These contributions have been clearly indicated at the respective points within the dissertation and properly referenced.

Beyond the contributions mentioned above, further support was provided throughout the doctoral project. Dr. Fabian Jeschull offered continuous supervision and academic guidance. Dr. Timofey Kolesnikov provided technical support with the granulation of sorbent materials. Ferdinand Selbiger conducted SEM analyses of the LMO granules. Laboratory assistance was provided by Benedikt Schwalm, Ulf-Christian Rauska and Alisa Pfau in their roles as student assistants.

Chapter 1

Introduction

Lithium is a key element in the global energy transition, primarily due to its essential role in batteries for electric vehicles, stationary energy storage systems, and a wide range of electronic devices.^[113] In 2023, global lithium production reached approximately 200,000 tons,^[62] and projections indicate that demand will rise significantly to around 500,000 tons by 2030.^[62] Several forecasts predict that by 2035, conventional lithium extraction methods may no longer be sufficient to meet global demand.^[62]

Currently, lithium is predominantly extracted via hard rock mining in Australia and China (accounting for $\approx 60\%$) and solar evaporation from salt flats in South America, USA and China ($\approx 40\%$).^[134] Approximately 65 % of globally extracted lithium is currently exported to China, which hosts the majority of the world’s lithium refining capacity.^[64] This creates a strong dependency for regions like Europe, which today relies almost entirely on lithium imports.^[113] Therefore, the development of new technologies to extract lithium from alternative resources is becoming increasingly important—especially those that are sustainable and regionally deployable.^[113]

Geothermal brines offer a promising alternative source of lithium as there are several locations worldwide with significant high Li content. In Germany, the Upper Rhine Graben stands out due to high lithium levels in deep waters reaching up to 210 mg L^{-1} .^[112] However, these brines exhibit complex chemical compositions. In addition to lithium, they contain sodium chloride as well as considerable amounts of calcium, magnesium, and potassium, with total salinities often exceeding 100 g L^{-1} .^{[71][112]} This underlined one of the major challenges in development of Li-extraction technologies: the selective recovery of lithium from these highly saline and complex brines.^{[122][52]}

In this context, Direct Lithium Extraction (DLE) technologies are of particular interest. DLE encompasses various approaches such as solvent extraction,^[94] membrane separation,^[136] and sorption based processes.^[43] Among these, sorption methods have attracted considerable attention due to their relatively low energy consumption and good compatibility with geothermal systems.^[43] A particularly promising class of sorbents are lithium manganese oxides (LMO), such as $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, owing to their fast reaction kinetics, high lithium uptake capacity, and excellent selectivity.^{[75][163]}

However, several challenges must still be overcome to enable the practical application of LMO in geothermal brines. First, the synthesis of LMO sorbents has been successfully demonstrated at a laboratory scale using various methods including hydrothermal synthesis, solid-state reaction and sol-gel processing.^{[27][69][65]} However, these approaches are not suitable for large-scale production or industrial applications. Secondly, currently available LMO sorbents exhibit limited cyclability, primarily due to poor long-term stability caused by manganese dissolution.^[47] Several studies investigating $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ have reported manganese losses ranging from 1 % to 7.46 % after only a single sorption-desorption cycle.^{[47][23][6][139][123][95][98][29]} This implies a loss of active material, which results in a reduced extraction efficiency. The continuous release of Mn contributes to material degradation and ultimately leads to structural destabilization.^{[47][115]} Third, the sorbent material is typically obtained in powder form after synthesis, which requires shaping to ensure cyclability and processability in technical systems.^[81] Ideally, such formulations should retain both the sorption capacity and kinetics of the original material.^{[81][146]}

This thesis addresses those challenges by proposing a novel synthesis route based on a spray drying process. The method is characterized by fast reaction kinetics, high throughput, and compatibility with continuous operation, making it suitable for scalable production.^[57] As will be demonstrated herein, the synthesis approach also enables the incorporation of substituent transition metals into the crystal structure. Insights from battery research have shown that substituting Mn(IV) with Ti(IV) can significantly enhance the structural stability of manganese-based compounds.^[120] This approach is applied to the ion exchange material presented in this work. The structural composition of the material is investigated using x-ray diffraction (XRD), nuclear magnetic resonance (NMR) spectroscopy, and magnetic measurements, providing a comprehensive understanding of both the crystal structure and the overall material composition. The sorption behavior of the material is evaluated using both synthetic and geothermal brine from the Bruchsal and Soultz geothermal plant, providing insights into its ion exchange characteristics. Inductively coupled plasma optical emission spectroscopy (ICP-OES) is employed during the extraction experiments to quantify lithium depletion and assess the material's selectivity. Morphological and structural changes induced by the sorption and desorption cycles are analyzed using scanning electron microscopy (SEM) and XRD, revealing the stability and transformation of the material. Finally, the material is shaped into spherical granules which are chosen due to their mechanical stability, ease of handling, and suitability for packed-bed reactors commonly used in industrial applications. This shaping enables long-term cycling experiments and allows for direct comparison with commercially available sorbents, paving the way for future pilot-scale implementation.

Chapter 2

Fundamentals

2.1 Lithium demand and supply

Due to its strategic importance and limited availability, lithium is classified as a critical raw material.^[113] As the lightest metal, it offers significant advantages in a wide range of applications.^[22] For many years, lithium has played a key role in the production of glass and ceramics, lubricants, and pharmaceuticals.^[22] These industries continue to rely on lithium today. However, the introduction of lithium-ion batteries has led to an exponential increase of its demand.^[62] Today, around 80 % of the global lithium production is dedicated to the battery sector primarily for end use in electric vehicles, portable electronic devices, and energy storage systems.^[7] Between 2009 and 2019, the global lithium production increased by a factor of 4.^{[132][131]} In 2021, global production reached around 100,000 tons of lithium.^[133] By 2023, the demand had already risen to 200,000 tons.^[135]

The future outlook for lithium demand is characterized by significant uncertainty as a result of the development of alternative storage technologies, such as sodium-ion batteries, as well as the increasing demand for electric vehicles and the global expansion of renewable energy sources.^[62]

The International Energy Agency (IEA) has suggested three different scenarios (with at least 50 % probability), based on which a future outlook on Li-demand has been provided:^[62] The Stated Policies Scenario (STEPS¹) considers the existing policy frameworks of today.^[62] The Announced Pledges Scenario (APS²) is assuming that all climate-related commitments made by governments will be fully implemented on time.^[62] Third, the NZE³ scenario is aiming for Net Zero Emissions by 2050.^[62] A strong growth in lithium demand is anticipated for all scenarios, primarily driven by the production of electric vehicles. By 2050, demand is projected to reach 1,200 kt of lithium in the STEP scenario and 1,600 kt in the AP scenario. In the NZE scenario, demand is expected to increase to 1,700 kt of lithium by 2050.^[62]

¹STEP: In this scenario, global temperatures are projected to rise by 2.4 °C by 2100.^[62]

²APS: This scenario corresponds to a 1.7 °C temperature increase by 2100.^[62]

³NZE: This scenario considers a limit of global warming to 1.5 °C by 2100.^[62]

The forecasting of Li-supply also depends on various factors such as development of new mining projects, geopolitical risks and development of recycling technologies.^[113] The IEA analyzed future market coverage based on various demand and supply scenarios. In Fig. 2.1 the forecast of lithium demand (based on the STEPS, NZE scenario, and APS) is presented, as well as the expected supply from existing and announced projects in a conservative and optimistic scenario.^[62] As illustrated in Fig. 2.1 the implementation

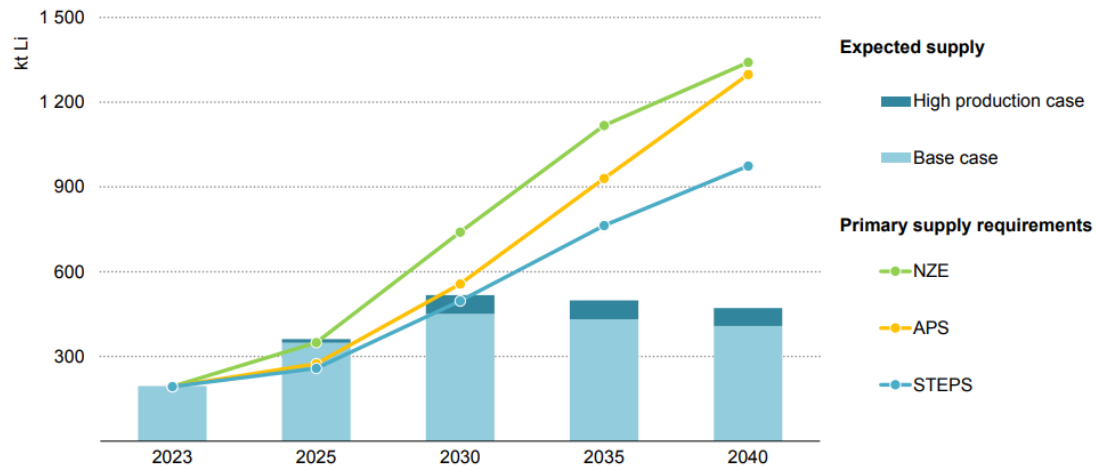


Figure 2.1: Global Li-demand and supply outlook. Figure reproduced from *International Energy Agency IEA, 2025*.^[62] Licensed under CC BY 4.0.

of planned projects in a high production case scenario is projected to meet the volume requirements outlined in STEPS for the year 2030. However, it will not be sufficient to maintain progress towards the APS and NZE scenario.^[62] Furthermore, the graph underlines that already in 2035 the demand cannot be covered by Li-production for any suggested scenario.^[62]

One reason for the increasing gap between supply and demand are significant price fluctuations in recent time that discourage investment in new lithium projects.^[33] Due to a sharp increase in lithium demand in 2021 and 2022 a temporary supply shortage was observed leading to a price peak of around 85,000 USD/t lithium carbonate in November 2022. This prompted producers to initiate new projects. However, the development of mines and refineries is a time-consuming process that typically requires several years. As a result, lithium production increased significantly more than expected in 2023 and 2024, causing an oversupply that drove prices down by up to 70–80 %.^[90] In August 2024 price of only 11,000 USD/t of lithium carbonate was reached. Since then, it has remained at a similarly low price level.^[33] This may not only discourage investment in new lithium projects but also lead to the closure of less economically viable mining operations, where production costs exceed market prices — thereby limiting future supply.^[113]

As the demand for lithium will increase significantly in the future and various projections indicate that conventional lithium production will not cover the demand, it is essential to investigate the extraction of lithium from alternative resources and ensure the supply of lithium as critical element for the energy transition.^[113]

2.2 Lithium extraction

Lithium is primarily obtained as lithium carbonate or lithium hydroxide, depending on the resource from which it is extracted and its further processing. This chapter presents an overview of different lithium extraction pathways, including conventional lithium extraction methods, identifies their inherent weaknesses, and assesses the potential of DLE as a sustainable alternative.

2.2.1 Conventional lithium extraction

Lithium is currently mainly extracted by hard rock mining and solar evaporation from salar brine. These processes are concentrated in a small number of countries because of the global distribution of lithium resources. In 2023, Australia was the largest lithium producer in the world providing approximately 48 % of the global lithium supply from hard rocks.^[134] The production of salars takes place mainly in South America with Chile contributing to almost 24 % of the total annual lithium production.^[134] In addition, China plays an important role in the extraction of Li, contributing to both salars and mineral deposits with a total share of 18 %.^[134] However, Li-extraction processes from salars and mineral deposits are fundamentally different and will therefore be discussed in the following chapter.

Li-extraction from salars

Salars, defined as salt-encrusted flats in arid regions, present an important source of lithium-rich brine. Significant lithium deposits have been identified in Chile, Argentina, and Bolivia. This region is called the Lithium Triangle. The brine in these regions contains significant high lithium contents between 0.02 % and 0.2 %.^[137] In addition to lithium, various other components, such as sodium, magnesium, and potassium, are present at high concentrations. To produce a pure lithium salt, it is necessary to separate these impurities. In particular, the removal of magnesium (Mg) is challenging due to atomic and ionic sizes being similar to those of lithium.^[59] The Mg/Li ratio is therefore set as one significant parameter to investigate the economical feasibility of the Li-extraction from a specific brine.^[130]

The lithium extraction process from salt flats is typically characterized by a standardized framework. However, the specific details of the process are adapted at each site

to account for the unique composition of the local brine, ensuring maximum yield.^[130] In Fig. 2.2 a schematic diagram of the Li-extraction process from Salar the Atacama in Chile is presented. The liquid is pumped to the surface and stored in large evaporation ponds. The brine is concentrated by solar evaporation for 12-18 months in total.^[137] During the processes of evaporation the brine concentrates leading to the precipitation of chlorides and sulfates as they reach the saturation limit. This allows a successive removal of alkali and earth alkaline metals from the brine.^[130] In a first pond calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$)

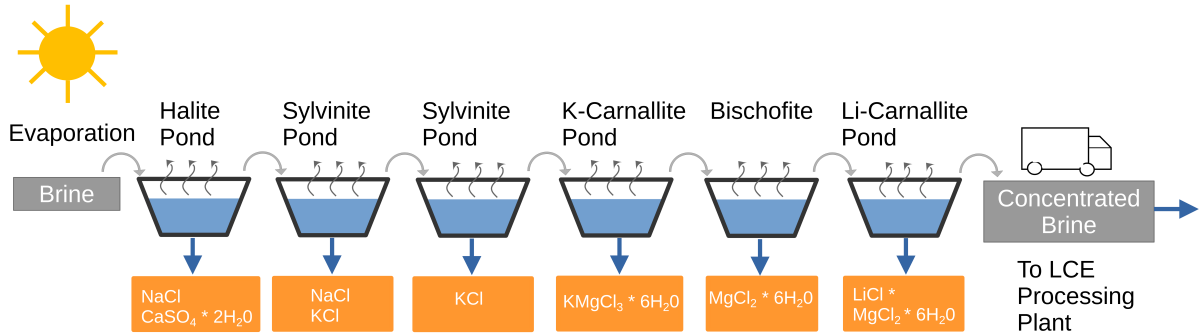


Figure 2.2: Li-extraction via solar evaporation from the Atacama salt flats. Adapted from Cerda *et al.*, Recovering water from lithium-rich brines by a fractionation process based on membrane distillation-crystallization, volume 41, page 102063, 2021, Elsevier.^[17]

and sodium chloride (NaCl) are precipitated.^[130] The highly concentrated brine is then transferred to a second pond where sylvite (KCl) and additional NaCl are precipitated known as the sylvinite systems ($\text{KCl} + \text{NaCl}$). With further concentration, potassium carnallite ($\text{KMgCl}_3 \cdot 6 \text{H}_2\text{O}$) is precipitated.^[130] In the bischofite stage, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ is removed followed by the Li-carnallite stage where $\text{LiCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ is extracted.^[17] In this evaporation and precipitation process the lithium content increases to approximately 1-6 %.^[17] Afterwards the Li-rich concentrate is refined and converted to battery grade lithium carbonate in a chemical factory. During this process, borates are removed as boric acid via liquid-liquid extraction using sulfuric acid. Subsequently, precipitation is used to remove sulfate, magnesium, and calcium ions.^[137] To finally obtain the final product, lithium carbonate (Li_2CO_3), sodium carbonate is added in a temperature controlled precipitation step.^[137]

Voigt *et al.* report typical ratios, using the example of the solution from the Salar de Uyuni.^[137] Producing 1 t of Li_2CO_3 generates 25 t of carnallite, 1 t of boric acid, 8 t of sulfates and 85 t of NaCl ; while some by-products are valuable, most are waste.^[137] A major limitation of this process is the loss of lithium through co-precipitation during the evaporation stages, resulting in an overall extraction efficiency of only about 50 %.^[63] The use of solar energy for evaporation enables a process that demonstrates a high degree of energy efficiency compared to conventional hard rock mining methods. However, it should be noted that up to 32.8 m^3 of freshwater is required for each tonne of lithium carbonate

produced.^[113] This has significant implications for water resources in arid regions, where water is already limited.^[113] In addition, the process requires large land areas for evaporation and takes up to 18 months.^[137]

Li-extraction from hard rocks

After salt flats, pegmatites represent the second largest lithium source, accounting for approximately 23-30 % of global reserves.^[31] Pegmatites are coarse-grained igneous rocks formed from the residual melt enriched in incompatible elements and volatiles.^[85] The lithium minerals present in these pegmatites are numerous, with their lithium content varying significantly. Australia is leading producer of lithium from pegmatites, specifically spodumene ($\text{LiAlSi}_2\text{O}_6$) which has a Li content of 1.9-3.7 %.^{[113][50]} The Li-extraction processes vary depending on the specific mineral.

The process for the production of lithium carbonate from spodumene, is illustrated in Fig. 2.3. Raw ores are mined through open-pit or underground mining.^[67] Firstly, the

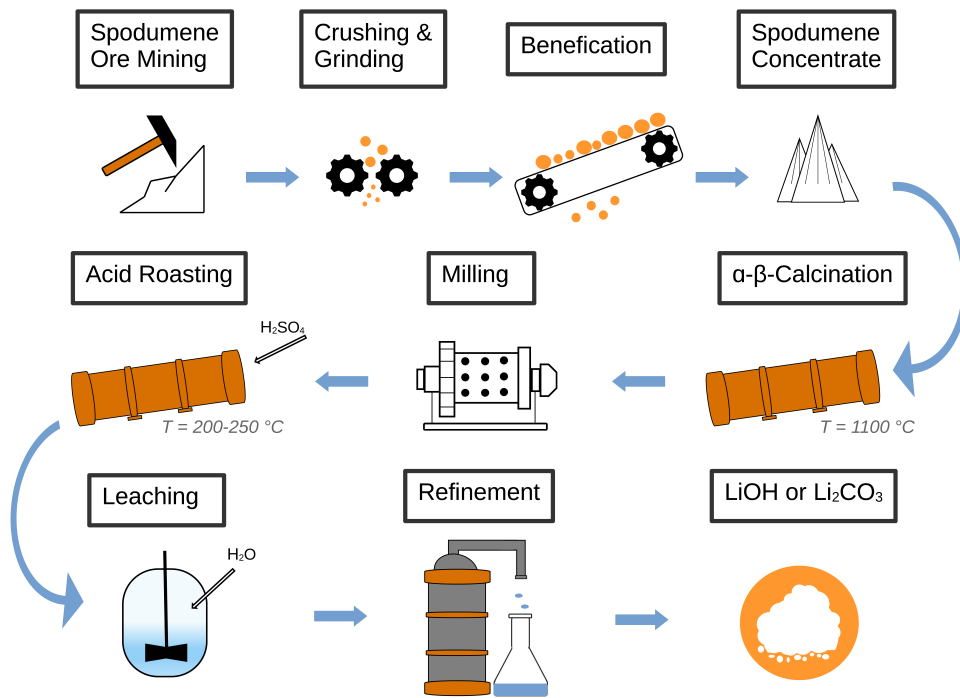


Figure 2.3: Schematic diagram of lithium extraction from hard rocks (own illustration).

overburden must be removed, which results in the production of 3-10 tons of waste material for every tone of ore.^[113] After crushing, a flotation process is commonly used to separate the minerals and produce a spodumene concentrate with a lithium oxide content ranging from 4-6 % Li_2O .^[91] These concentrates are mainly shipped to China for further processing, generating significant greenhouse gas emissions and transporting large amounts of tailings.^[113]

The traditional method for lithium carbonate production from Li-concentrates is known

as the sulfuric acid process. The ore is heated in a rotary kiln at 1100 °C, which converts α -spodumene into β -spodumene, a form that is more reactive and easier to process. During this process, the spodumene crystals expand by about 30 % in volume.^[31]

After cooling, the β -spodumene is ground to a fine powder and then mixed with concentrated sulfuric acid (H_2SO_4) at temperatures of 200–250 °C in a second rotary kiln. The kiln is leached with water for 60 minutes, leading to lithium sulfate (Li_2SO_4) as an intermediate product.^[67]

Subsequently, the process involves a purification step in which lime is used to precipitate the remaining magnesium and soda ash is added to remove any residual calcium. The pH is adjusted by adding H_2SO_4 . To achieve a high yield, it is necessary to concentrate the Li_2SO_4 solution through the evaporation process.^[128]

Finally, lithium is precipitated as lithium carbonate by adding soda ash at temperatures between 90–100 °C. The resulting lithium carbonate has a purity of approximately 95 %, which corresponds to a technical grade and can be further refined to produce battery-grade lithium salts.^[67]

The high temperatures required in this process make it highly energy intensive, requiring around 218,000 MJ per ton of Li_2CO_3 —approximately seven times more energy than extraction from salt flats. Furthermore, water consumption is 2-4 times higher than for salar extraction.^[68] Large amounts of chemicals are required, and the process produces chemical waste, leading to significant environmental impact.^{[113][68]}

2.2.2 Direct Lithium Extraction (DLE)

Conventional lithium production methods are criticized for generating large amounts of waste, requiring significant amounts of chemicals and involving long transportation distances that contribute to a high CO_2 -footprint (Ch. 2.2.1). Moreover, forecasts indicate that lithium extracted from these sources may not be sufficient in the future (Ch. 2.1). Consequently, there is an ongoing research focus on the development of novel methodologies for the extraction of lithium.^[93] In this context, Direct Lithium Extraction is of particular importance, as it offers environmentally friendly and efficient processes for lithium recovery from conventional resources such as salar brines, but also unconventional resources such as geothermal brines, seawater, or oil field brines.^[43]

DLE can be divided in several research fields like membrane processes, solvent extraction and sorption technologies.^[93] The membrane-based DLE separates lithium ions from brine by passing the solution through a selective membrane. This is challenging since it has high energy consumption and the high salt concentration of brines leads to membrane fouling and the need for pretreatment.^[136] Solvent extraction uses Li-selective organic solvents to separate lithium ions from brine. It faces challenges such as solvent recycling,

environmental concerns, and reduced efficiency in brines with low lithium concentrations or high impurities.^[94] Finally, adsorption/ion exchange describes the capture of lithium on or in a sorbent material. Lithium double layered aluminum hydroxides (LDH), lithium manganese oxide (LMO), or lithium titanium oxides (LTO) are often used.^{[43][105]} This method shows great promise due to the high lithium selectivity of the sorbent materials in highly saline brines, combined with the low energy requirements of the process.^[43]

Adsorptive DLE is already tested in some regions in field operation. The diverse pilot projects demonstrate the potential of DLE not only for conventional lithium extraction from salars but also for novel lithium sources such as geothermal brine, oil field brines and seawater. A comprehensive overview of the present state of the art for DLE is presented in Ch. 3.

DLE at a geothermal site

In recent years, the extraction of lithium from geothermal brine as a co-product in a renewable energy process has gained importance. The Upper Rhine Graben (URG) in Germany is known for its geothermal potential and also high Li contents in the brine.^[52] Currently, five geothermal plants in the URG are in operation. These facilities produce electricity, and in the case of the Bruchsal and Rittershoffen installation, a district heating system is combined.^[71] The deep geothermal fluids utilized in these systems contain lithium concentrations ranging from 163 to 190 mg L⁻¹.^[112] The site-specific flow rates of the geothermal power plants and the lithium concentrations of the brine are presented in Tab. 2.1. Based on these numbers a potential annual production of $\approx 5,700$ t of lithium carbonate equivalent (LCE) was determined (a lithium recovery of 90 % and an availability of the plants of 90 % was considered). This production capacity could support the annual

Table 2.1: Lithium concentration of geothermal brines in the Upper Rhine Graben.^[112] Possible annual production of LCE assuming 90 % of Li-extraction and an availability of the geothermal plant of 90 %.

Geothermal power plant	Li ⁺ concentration [mg L ⁻¹]	Flow rate [L s ⁻¹]	Potential production [t LCE/a]
Bruchsal	163	28	≈ 590
Soultz	173	30	≈ 680
Rittershoffen	190	80	≈ 2000
Insheim	168	70	≈ 1500
Landau	180	40	≈ 940

manufacturing of around 130,000 lithium-ion batteries, each with a 60 kWh capacity.^[18] This corresponds to around 0.6 % of today's global lithium demand and around 1 % of Europe's expected demand in 2030.^{[134][113]} However, the potential is significantly higher. Several additional geothermal drilling campaigns are planned for the coming years in the URG, for example in Germany through projects like WärmeWerk Wörth and GeoHardt.^{[35][34]} Also on the French side, ÉS and Eramet plan to drill for producing up to 10,000 t of LCE per

year.^[39] Other promising regions for extracting lithium from geothermal brines are also emerging across Europe, such as Cornwall in England.^[106]

A schematic diagram of the geothermal system with DLE unit is shown in Fig. 2.4. In the Bruchsal geothermal plant, hot brine ($T > 120\text{ }^{\circ}\text{C}$) is pumped to the surface and used for heating and power generation. After thermal usage, the cold brine with a temperature between $60\text{ }^{\circ}\text{C}$ - $80\text{ }^{\circ}\text{C}$ is sent to a DLE unit where Li-ions are extracted selectively. Then Li-depleted brine is reinjected in a second well to achieve a closed-loop system.^[136] The product of the DLE process is a Li-rich solution, which still contains some impurities and needs to be treated further in a purification step to be converted to battery grade lithium salt (e.g. lithium carbonate).^[71] In contrast to conventional Li-extraction, the CO_2 footprint

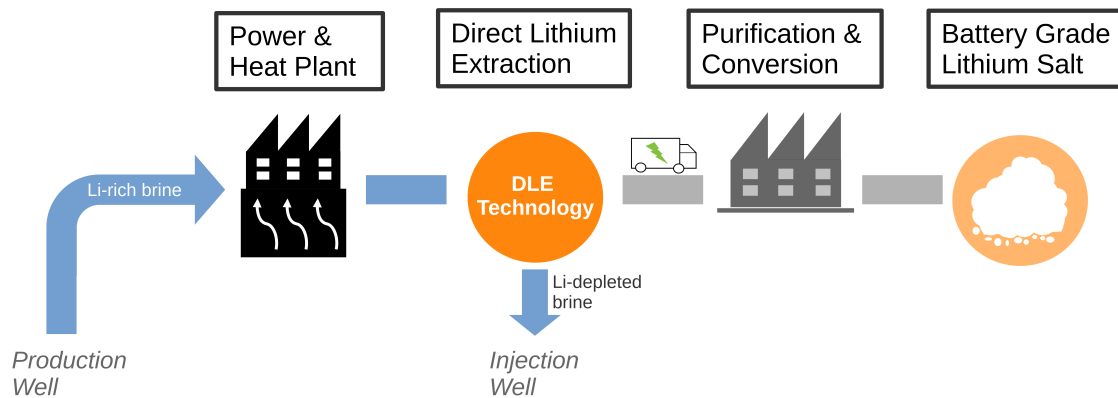


Figure 2.4: DLE unit in a geothermal system (own illustration).

per ton of lithium carbonate can be substantially reduced with DLE from geothermal brine.^[113] The coupling of lithium extraction with renewable geothermal power and heat supports low-emission processing. Furthermore, the potential for local production close to the end-use markets can reduce transport distances.^[113]

However, there are still challenges to overcome before DLE can reach its full potential for geothermal sites. Technologies require further development to become cost-competitive with conventional methods.^[52] One of the major challenges in geothermal lithium extraction lies in the complex composition of geothermal brines, containing high salt contents and a wide range of foreign ions.^[52] Selective and durable sorption materials must be developed that are capable of withstanding extreme conditions such as high temperature and pressure.^[52] Despite its limitations, DLE marks a significant advancement toward sustainable lithium production. It enables lithium extraction from a broader range of resources, such as salars, geothermal brine, and seawater. Additionally, DLE is faster than traditional solar evaporation methods and minimizes environmental impacts, making it a highly promising technology.

2.3 Geothermal brine from Bruchsal and Soultz

In this work geothermal brines from the Upper Rhine Graben were used. The brine samples originate from two different sites: the geothermal plant in Bruchsal, Germany (Energie Baden-Württemberg, EnBW)⁴ and the geothermal plant in Soultz, France (Électricité de Strasbourg, ÉS) which are located approximately 60 km apart. Both brines-typical for the URG-exhibit a high salinity level of $>100 \text{ g L}^{-1}$ TDS (total dissolved solids) and elevated gas contents.^[112] A liquid-to-gas phase ratio of 1:1.6 and of 1:1 was reported for Bruchsal and Soultz geothermal brines, respectively.^{[88][13]} The composition of the gas fraction in the brine is very similar at both sites. The gas phase consists of around 90 % CO_2 . For Bruchsal, a nitrogen content of around 8 % is reported, while for Soultz a range of 7 % - 9 % is stated.^{[88][13]} A somewhat smaller fraction of methane was stated for the Bruchsal site with around 1 % compared to 2 % for Soultz. In addition, noble gases are present in both brines with significantly lower concentrations.^{[88][13]} Both brines are mainly NaCl based. Since they are of natural origin, several additional elements are present. The elements with the highest concentration and greatest significance for this work are presented in Tab. 2.2.

Table 2.2: Composition of the geothermal brine Bruchsal (EnBW)^[71] and Soultz (ÉS)^[13].

	c	Li	Na	K	Mg	Ca	Sr	Ba	Pb	Mn
Bruchsal	[mg L ⁻¹]	155	36000	3200	320	6900	350	5.9	3.2	24.1
Soultz	[mg L ⁻¹]	163	26700	3350	123	7030	434	22	0.16	17

Due to operational conditions in geothermal systems, the brine is maintained under high pressure ($>20 \text{ bar}$), elevated temperatures ($>60 \text{ °C}$) and in absence of oxygen. These conditions are necessary to keep the brines chemically stable.^[88] The brines used in this research were stored for several months in the laboratory, leading to slight changes in the composition of the brine. Therefore, the concentrations of the relevant elements were measured immediately prior to the experiment with ICP-OES. The composition is presented in Tab. 2.3.

Table 2.3: Composition of the geothermal brines used within the scope of this thesis. The presented values are based on ICP-OES measurements performed within this work.

	c	Li	Na	K	Mg	Ca	Sr	Ba	Pb	Mn
Bruchsal	[mg L ⁻¹]	143	35700	3091	382	8318	391	8.9	4.9	22.3
	[mmol L ⁻¹]	20.6	1552	79.1	15.7	207	4.5	0.07	0.02	0.41
Soultz	[mg L ⁻¹]	141	27870	3430	125	7443	479	6.2	0.3	16.5
	[mmol L ⁻¹]	20.4	1212	87.8	5.2	186	5.5	0.05	0.001	0.30

⁴The Bruchsal geothermal plant is jointly operated by EnBW and Stadtwerke Bruchsal.

2.4 Sorbent materials for DLE

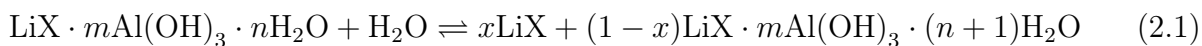
Sorption has been identified as one of the most promising DLE techniques for the extraction of lithium from brines.^[43] This process is promising due to its high Li-selectivity even in environments with high concentrations of competing ions. It is a fast process operated within hours compared to months or years in conventional methods. Furthermore, its energy consumption is low compared to membrane processes that require high pressures or hard rock extraction methods involving high temperatures.^[110]

Two distinct extraction mechanisms operate within sorption materials: (1) surface adsorption, and (2) bulk ion exchange. The first mechanism, surface adsorption, involves the physical or chemical binding of lithium ions to the sorbent material without altering the composition of the surrounding solution.^{[110][161]} Typical sorbents used for this type of adsorption are lithium double layered aluminum hydroxides (LDH). Second, lithium can be captured in an ion exchange process. Thereby lithium ions are exchanged with protons of the sorbent material.^{[110][23]} In this context, lithium manganese oxides (LMO) and lithium titanium oxides (LTO) are of particular importance. LDH is already utilized on a commercial scale (TRL 9) in lithium recovery from salars, whereas LMO and LTO are still under development but show promising potential.^[43] The following section provides an overview of the different sorbents used in DLE.

2.4.1 Aluminum-based sorbents

Lithium double layered aluminum hydroxides are one of the sorbents being studied for lithium extraction. These materials generally follow the chemical formula $[\text{Li}_x\text{Al}_2(\text{OH})_6]\text{Cl}_x \cdot n\text{H}_2\text{O}$, with $x = 0 - 1.5$.^[145] The structure of LDH consists of two-dimensional layers of aluminum hydroxide (Fig. 2.5). The $\text{Al}(\text{OH})_3$ layers feature ordered vacancies within the AlO_6 octahedrons.^[124] Lithium ions can occupy these vacancies, resulting in a positively charged layer. Larger alkaline earth metal ions can not enter due to steric hindrance. The $[\text{LiAl}_2(\text{OH})_6]^+$ layers are separated by water molecules and hydroxide ions.^[75] To keep the charge balance, the anions (e.g. Cl^-) are intercalated into the interlayer.^[124]

The sorption capacity of LDH lies $< 7 \text{ mg g}^{-1}$ which is significantly lower compared to LMO and LTO sorbents.^[162] Their main advantages compared to LTO and LMO is their easy fabrication and simple regeneration, which does not require acid or base treatments. In addition, sorption is largely pH independent, eliminating the need for alkaline additives and ensuring that the pH of the medium remains unchanged.^{[161][43]} The sorption and desorption mechanism can be summarized by the following equation, where X represents a halogen (e.g. Cl):^[161]



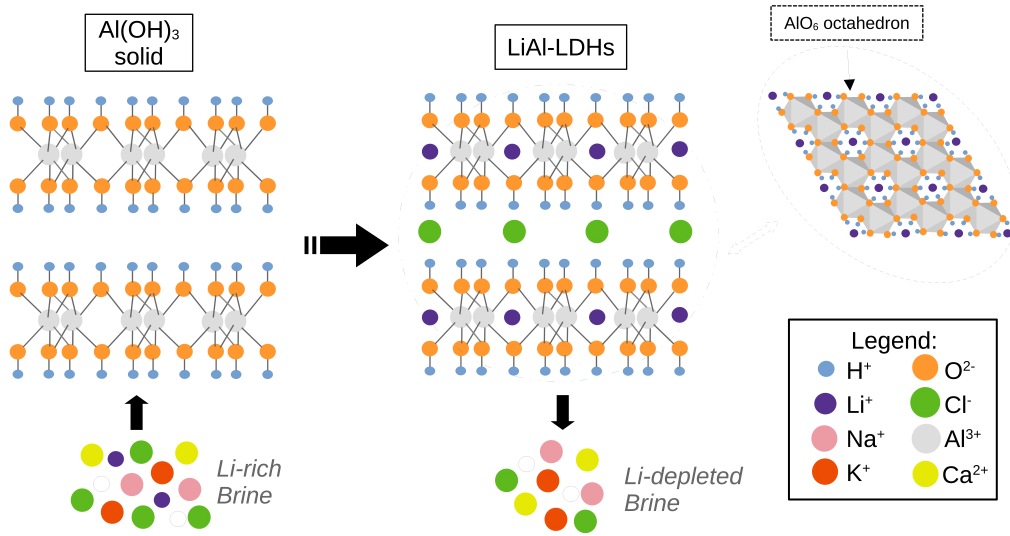


Figure 2.5: Selective LiCl-intercalation with Al-based sorbent. Structural model of lithium double layered aluminum hydroxide. Figure adapted from Sun *et al.*, Highly Efficient Lithium Recovery from Pre-Synthesized Chlorine-Ion-Intercalated LiAl-Layered Double Hydroxides via a Mild Solution Chemistry Process, volume 12, number 1968, 2019.^[124] Licensed under CC BY 4.0.

Currently, LDH is the only material available on an industrial scale for lithium extraction. However, due to their relatively low sorption capacity, moderate ion selectivity and suboptimal performance under extreme conditions (such as high temperature and high pressure) research is ongoing on LTO and LMO.^[43]

2.4.2 Titanium-based sorbents

Lithium titanium oxides are also considered as sorbents for lithium extraction due to their stable structure and high cycling performance. In this regard, layered Li_2TiO_3 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structures are of particular significance.^[82]

Spinel-type LTO. The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a well-known anode material in lithium-ion batteries. Recently, extensive research has also focused on its potential for lithium extraction from brines.^[150] This material is characterized by the $Fd\bar{3}m$ space group with cubic symmetry and has a chemical structure similar to the manganese based sorbent $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (see Ch. 2.4.3).^[149] In $\text{Li}_4\text{Ti}_5\text{O}_{12}$, lithium ions occupy the tetrahedral 8a sites. In addition, 1/6 of the octahedral 16d sites are occupied by lithium ions, while the remaining 5/6 are occupied by titanium. Oxygen anions occupy the 32e sites within the face-centered framework. It can be written as:^[43]



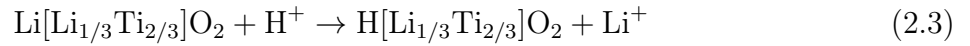
In terms of chemical stability, the material is superior over the Mn-based spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$, attributable to the more robust Ti–O bonds in comparison to the Mn–O bonds. Conse-

quently, the material exhibits reduced material dissolution during cycling experiments and an extended long-time performance.^[150]

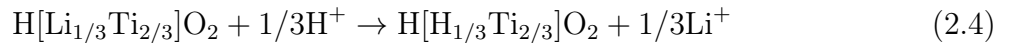
Layered-oxide-type LTO. The layered-structured Li_2TiO_3 has been extensively discussed as a highly promising material for electrochemical applications and photo-catalytic processes in pollutant degradation. Several studies have also investigated its capacity for the extraction of lithium from brines and report a high potential due to its high selectivity for lithium.^[150]

The crystal structure of Li_2TiO_3 with space group $C2/c$ is based on a cubic close-packed arrangement of oxygen atoms, with metal atoms positioned in octahedral voids (Fig. 2.6).^[25] Within this configuration, lithium and titanium form two distinct layers: one Li-layer consists solely of lithium atoms, while the other LiTi_2 -layer is occupied by one-third lithium and two-thirds titanium.^[25] The structure can be described by the formula $\text{Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_2$, emphasizing its distinct layered arrangement.

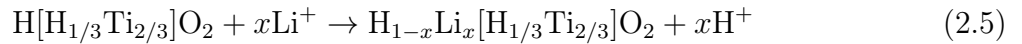
The lithium ions in the pure Li layer constitute 75 % of the total lithium ions in the Li_2TiO_3 structure, while the remaining 25 % are located in the LiTi_2 -layers.^[43] Lithium ions in this layered structure can be fully replaced by protons which is fundamentally different from the Li-intercalation mechanism observed in LDH. The exchange of Li^+ and H^+ takes place first in the Li-layer according to the following equation:^[30]



Subsequently, Li is extracted from the Li-layer:^[30]



The H_2TiO_3 is used as sorbent for Li-extraction from an aqueous solution. The Li-intercalation can be described by the following equations:^[150]



Ti-based sorbents exhibit a low dissolution rate during their desorption step, a property that confers significant advantages over other materials (e.g LMO). This characteristic is indicative of high chemical stability and optimal cycling performance.^[150] However, the reaction rates for LTO are comparatively lower than those for LMO, which is a significant process parameter for industrial application. Additionally, the manufacturing of LTO faces high raw material costs, which influence the economic feasibility of the process.^[43]

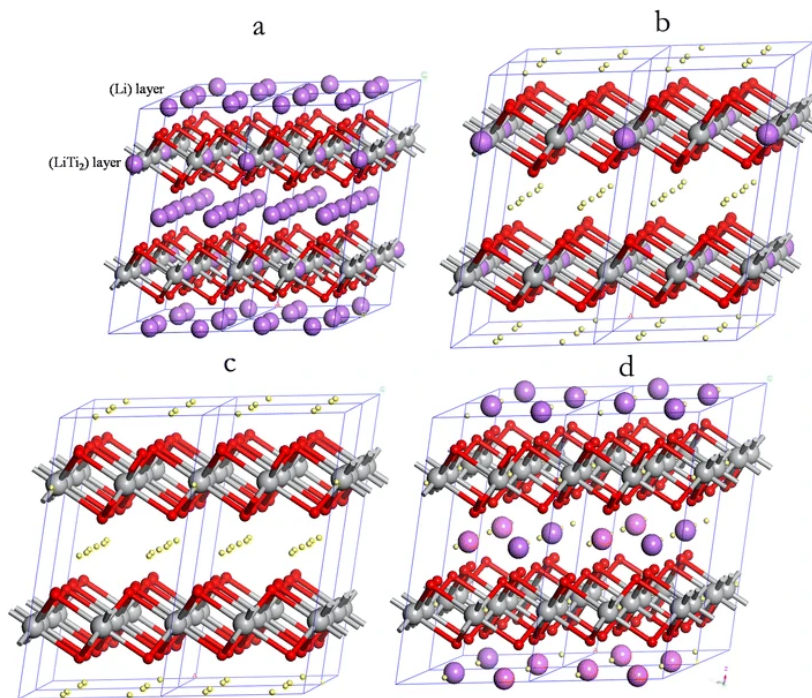


Figure 2.6: Crystal structure of a) layered Li_2TiO_3 , b) + c) pickled material, d) sorbent after lithium intercalation (Li: purple, H: yellow, O: red, Ti: gray). Figure reprinted with permission from Gang He *et al.*, The optimal condition for H_2TiO_3 –lithium adsorbent preparation and Li adsorption confirmed by an orthogonal test design, *Ionics*, Volume 21, pages 2219–2226, 2015, Springer Nature.^[56]

2.4.3 Manganese-based sorbents

Lithium manganese oxides represent an important class of sorbents in DLE applications. There are many different structures of Li-Mn-O compounds that can be formed depending on the oxidation state of manganese, Li/Mn-ratio, temperature and oxygen environment.^[99] In this work, lithium extraction using LMO sorbents is investigated. Therefore, the following section presents a detailed overview on lithium manganese oxides and their usage as materials for lithium recovery.

Li-Mn-O phase diagram. Paulsen *et al.*^[99] present a phase diagram of the Li-Mn-O system in air in a temperature range of 350 °C to 1060 °C (Fig. 2.7a) with several stability regions being highlighted. $\text{LiMn}_{1.75}\text{O}_4$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (with an oxidation state of Mn, $\nu = 4.0$) exhibit stability at temperatures below 400 °C. Cation-mixed spinels, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ (with $3.5 < \nu < 4.0$), remain stable at intermediate temperature ranges, while tetragonal $\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4$ (with $\nu < 3.5$) is stable at elevated temperatures.^[99]

LMO materials used in Li-extraction are primarily cubic spinels, characterized by the space group $Fd\bar{3}m$ (no. 227). Manganese occupies the 16d sites, where it is octahedrally coordinated by oxygen anions at the 32e sites. Lithium is positioned at the 8a sites, which

are tetrahedrally coordinated by oxygen atoms. A cation-mixed spinel (with $x > 0$) is formed by substituting some of the Mn atoms in the 16d sites with lithium atoms, denoted as $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$.^[99]

In Fig. 2.7b, an isothermal cross section of the Li-Mn-O phase diagram (20 °C) is shown according to Thackeray *et al.*^[129] Fig. 2.7b highlights the stoichiometric defect spinel

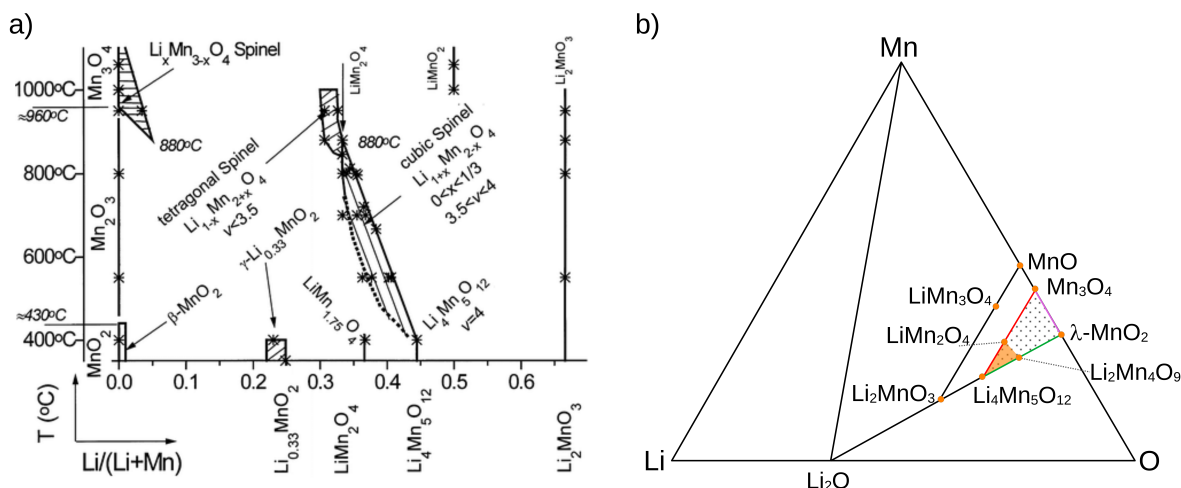


Figure 2.7: a) Li-Mn-O phase diagram of second kind. Figure adapted with permission from Paulsen, J.M., Dahn, J.R., 1999. Phase diagram of LiMnO spinel in air. Chemistry of Materials 11, 3065–3079. Copyright 1999 American Chemical Society.^[99]; b) Isothermal cross section of the Li-Mn-O phase diagram at 20 °C. Figure adapted with permission from Thackeray *et al.*, Spinel electrodes from the Li-Mn-O system for rechargeable lithium battery applications, volume 139, page 363, 1992, Journal of The Electrochemical Society.^[129]

phases by a dotted area. The stoichiometric spinel phases are represented as a red tie line connecting Mn_3O_4 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$. They can be written with the general formula $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ ($0 \leq x \leq 1.33$). Manganese oxide defect spinels are presented in purple between Mn_3O_4 and $\lambda\text{-MnO}_2$. They can be described by the formula $\text{Mn}_{3-x}\text{O}_4$ ($0 \leq x \leq 1$).^[150] The lithium manganese oxide defect spinels are on the green tie line between $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\lambda\text{-MnO}_2$ and have the general formula $\text{Li}_2\text{O} \cdot y\text{MnO}_2$ ($y > 2.5$). The orange area framed by LiMn_2O_4 , $\text{Li}_2\text{Mn}_4\text{O}_9$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ represents the relevant region for LMO-type sorbents for Li-extraction.^[150]

Mn-based sorbents. Manganese oxides are highly promising sorbents for Li-extraction from Li-bearing solutions since they offer high sorption capacities, high selectivity and fast kinetics.^{[100][148]} Commonly used LMO materials for Li-extraction are LiMn_2O_4 , $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ($\text{Li}_2\text{Mn}_2\text{O}_5$), and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ ($\text{Li}_4\text{Mn}_5\text{O}_{12}$) with their protonated species $\lambda\text{-MnO}_2$, $\text{MnO}_2 \cdot 0.5 \text{H}_2\text{O}$, and $\text{MnO}_2 \cdot 0.31 \text{H}_2\text{O}$. They exhibit Li-ion-sieving properties, enabling them to selectively capture specific Li-ions from a multi-ion solution.^[164] In theory, increasing the Li/Mn molar ratio in the precursors enhances the theoretical sorption capacity of the sorbents.^[43]

Table 2.4: Properties of different LMO spinels including lattice parameter LP, exchange mechanism, theoretical sorption capacity $Q_{sorb,th}$ and oxidation state of manganese Z.^[23]

LMO	LP [Å]	HMO	LP [Å]	mechanism	$Q_{sorb,th}$ [mmol g ⁻¹]	Z
LiMn ₂ O ₄	8.24	λ -MnO ₂	8.03	redox	5.7	3.5
Li _{1.33} Mn _{1.67} O ₄	8.14-8.19	MnO ₂ · 0.31 H ₂ O	8.06	ion exchange	8.5	4
Li _{1.6} Mn _{1.6} O ₄	8.14	MnO ₂ · 0.5 H ₂ O	8.05	ion exchange	10.5	4

For example, MnO₂ · 0.5 H₂O, with Li/Mn ratio of 1:1, demonstrates the highest theoretical sorption capacity with 10.5 mmol g⁻¹.^[23] Experiments have demonstrated (Ch. 3.1) that the actual sorption capacity is significantly lower than those theoretical values.^{[100][148][23]} Tab. 2.4 provides an overview of Mn-based sorbents, summarizing their properties including lattice parameters (LP), exchange mechanisms, theoretical sorption capacities ($Q_{sorb,th}$), and Mn oxidation states (Z).

LiMn₂O₄. The most well-known LMO compound in the context of lithium extraction is LiMn₂O₄. This compound crystallizes in a spinel-type cubic structure with the space group $Fd\bar{3}m$. Lithium ions occupy the tetrahedral 8a sites. Trivalent and tetravalent manganese ions are located in the octahedral 16d sites. In this spinel structure, manganese exhibits an average oxidation state of +3.5.^[150]

The LiMn₂O₄ spinel can be described by the structural formula (Li)_{8a}[Mn(III)Mn(IV)]_{16d}O₄, aligning with the general spinel composition AB₂O₄.^[150] The LiMn₂O₄ unit cell can be regarded as a complex cubic framework, where 32 oxygen atoms and 16 manganese atoms occupy half of the available octahedral interstitial sites (16d), while the remaining octahedral sites (16c) remain vacant. Lithium ions reside in 1/8 of the tetrahedral interstitial sites (8a).^[150] The Li⁺ ions can reversibly intercalate and de-intercalate through the three-dimensional network of vacant octahedral interstitial sites along the 8a-16c-8a-16c pathway, which serves as the structural foundation for lithium ion transport in the spinel LiMn₂O₄.^[150] Fig. 2.8 shows the arrangement of atoms in the crystal lattice. The theoretical sorption capacity of λ -MnO₂, the Li-free species of LiMn₂O₄, is 5.7 mmol g⁻¹.^[23]

Li_{1.33}Mn_{1.67}O₄. Depending on the preparation conditions, the equilibrium stoichiometry x of lithium in Li_{1+x}Mn_{2-x}O₄ can vary from $x = 0$ (LiMn₂O₄, stoichiometric spinel) to $x = \frac{1}{3}$ (Li₄Mn₅O₁₂). Consequently, the mean oxidation state of manganese varies from +3.5 when $x = 0$ to +4.0 in Li₄Mn₅O₁₂ (also denoted as Li_{1.33}Mn_{1.67}O₄).^[99] In the last case, one-sixth of the manganese ions occupying the octahedral 16d sites are substituted by lithium ions without disrupting the fundamental crystallographic framework.^[150]

Since Li_{1.33}Mn_{1.67}O₄ has a higher lithium content per mole of sorbent,^[23] a theoretical higher sorption capacity of 8.5 mmol g⁻¹ compared to LiMn₂O₄ (5.7 mmol g⁻¹) is expected. However, in neutron diffraction studies by Ammundsen *et al.*^[3] it was shown that lithium reinser-

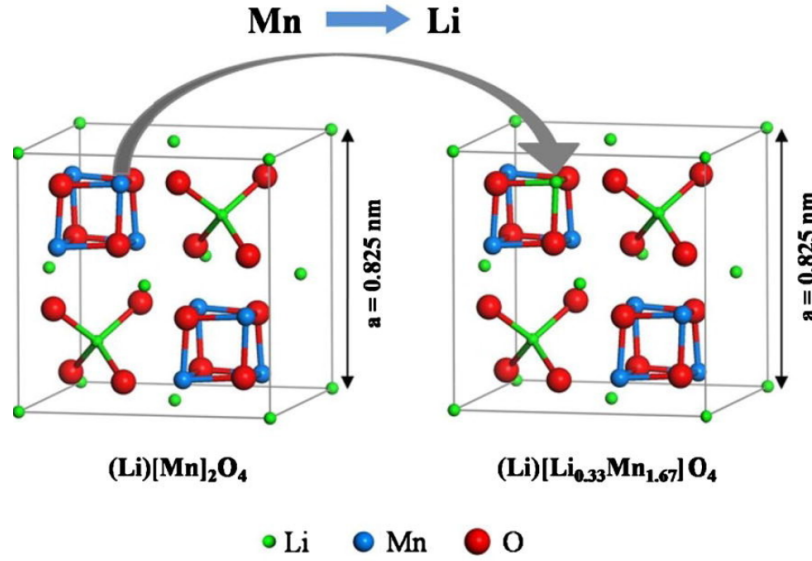
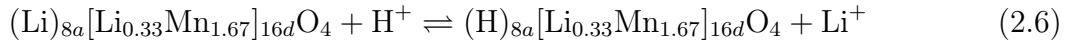


Figure 2.8: Structural evaluation of two quadrants in cubic spinel LiMn_2O_4 and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$. Figure reprinted with permission from Xu *et al.*, Extraction of lithium with functionalized lithium ion-sieves, volume 84, pages 276-313, 2016, Elsevier.^[150]

tion occurs preferentially at tetrahedral sites, with negligible occupation of octahedral sites. This observation suggests that the lithium extraction/insertion process can be described by the following reaction:^[150]



$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Another LMO spinel used for Li-extraction is $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ which can be converted into the sorbent $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (also denoted as $\text{MnO}_2 \cdot 0.5 \text{H}_2\text{O}$) by acid treatment. The ratio of anions to cations in $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ is 5:3 and therefore slightly different from typical standard spinel with 3:4. Several approaches have been proposed to address the location of the additional lithium. However, a structural model has not yet been published.^[23] Chitrakar *et al.*^[23] suggest a model with excess lithium at the 16c site, depicted as $(\text{Li})_{8a}[\text{Li}_{0.2}]_{16c}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16d}\text{O}_4$. In a second model they consider an oxygen deficiency, represented as $(\text{Li})_{8a}[\text{Li}_{0.5}\text{Mn}_{1.5}]_{16d}\text{O}_{3.75}$. These models refer to the structures of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ as a cubic-type phase with space group $Fd\bar{3}m$. A third model was proposed based on a hexagonal lattice model with cation deficiency, described as $(\text{Li}_{0.8}\square_{0.2})_{3b}(\text{Mn}_{0.8}\square_{0.2})_{3a}\text{O}_2$ with " $\square$ " corresponding to the vacant sites.^[23] This model corresponds to a layered structure with space group $R\bar{3}m$.^[23]

Decomposition temperature and lattice constant of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ as a function of x . Paulsen and Dahn describe that at a certain temperature (decomposition temperature T_C), a cation-mixed spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ undergoes a decomposition into a spinel with a smaller x and Li_2MnO_3 (Fig. 2.9).^[99] Thus, T_C is influenced by the lithium content x

and represents the upper stability boundary of the spinel with a specific composition.^[99] As shown in Fig. 2.9, the T_C decreases with increasing Li content. For example, at $x = 0$ a decomposition temperature of $T_C \approx 850$ °C is reported, whereas at $x = \frac{1}{3}$, a value of only $T_C = 400$ °C is indicated.^[99]

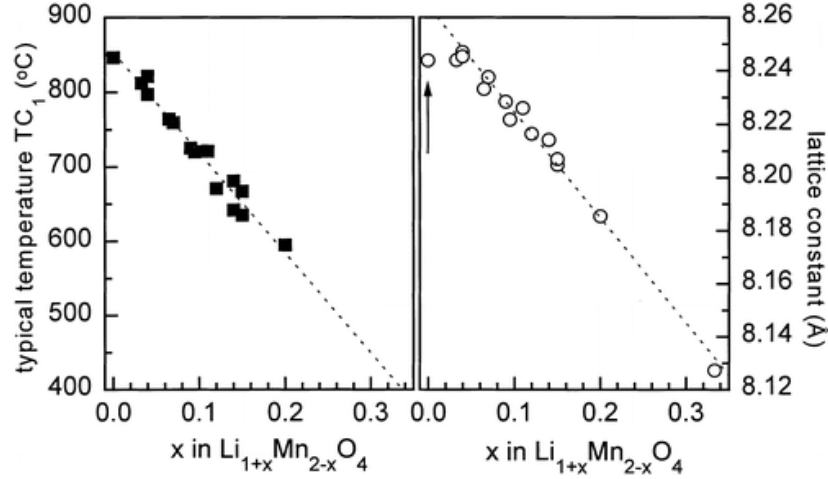


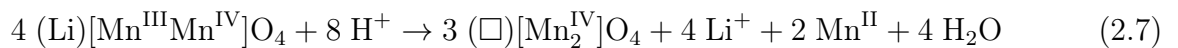
Figure 2.9: Decomposition temperature and lattice constant of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ as a function of x . Adapted with permission from *Paulsen, J.M., Dahn, J.R., 1999. Phase diagram of LiMnO spinel in air. Chemistry of Materials 11, 3065–3079. Copyright 1999 American Chemical Society.*^[99]

Li-intercalation/de-intercalation. For the intercalation and de-intercalation of Li^+ ions in spinel Mn-based sorbents, mainly two mechanisms are discussed: the redox mechanism and the ion exchange mechanism. Chitrakar *et al.*^[23] published a phase diagram that illustrates the oxidation state and exchange mechanism for various LMO materials and their lithium free derivatives (Fig. 2.10). In the diagram, the vertical plane corresponds to the redox reaction region, while the horizontal plane denotes the ion exchange region.^[23] The lithium storage in LiMn_2O_4 is predominantly described by the redox mechanism, whereas for $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, the ion exchange reaction is the dominant process.^[23]

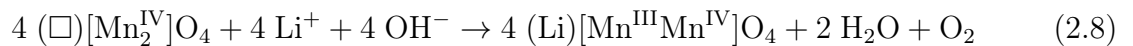
Redox-Mechanism

Xu *et al.*^[150] described the Li-sorption and desorption with LiMn_2O_4 based on Hunter *et al.*^[61] as redox reactions:

Li^+ -desorption/activation:



Li^+ -sorption:



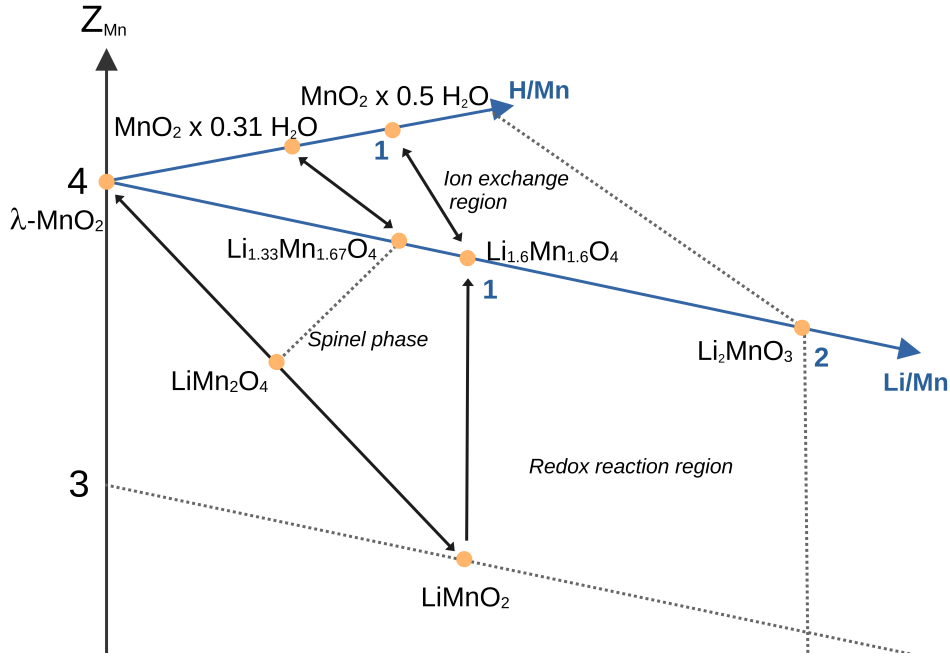
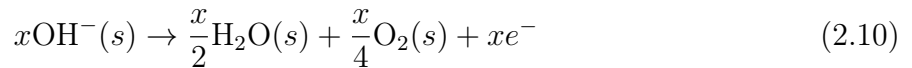
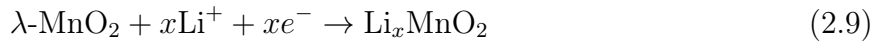


Figure 2.10: Oxidation state and Li-intercalation/de-intercalation mechanism of LMO and its delithiated derivatives. Adapted with permission from Chitrakar *et al.*. A new type of Manganese Oxide ($\text{MnO}_2 \cdot 0.5 \text{H}_2\text{O}$) derived from $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and its lithium ion-sieve properties. Chemistry of Materials 12, 3151–3157. Copyright 2000 American Chemical Society.^[23]

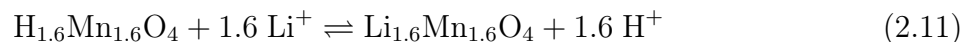
In this equation, "□" represents vacant sites. During the reaction, only surface Mn(III) undergoes transformation into Mn(II) and Mn(IV). Ultimately, the driving force behind the Li^+ insertion and removal process is the disproportionation of Mn(III), where Mn(IV) maintains the structural integrity of the crystal, while Mn(II) dissolves into the aqueous phase.^[97] Ooi *et al.*^[96] later explored the lithium intercalation mechanism in $\lambda\text{-MnO}_2$. Their findings highlighted the independent movement of lithium ions and electrons within the $\lambda\text{-MnO}_2$ framework. The periodic arrangement of Mn(III) and Mn(IV) in the spinel structure facilitates efficient electron migration. The overall intercalation process occurs in two distinct steps:^{[97][96]}



Here, x denotes the number of lithium ions intercalated per mole of Mn atoms in the solid, while (s) indicates surface interactions. However, because of the redox mechanism, manganese dissolves gradually in Mn-based lithium ion sieves (LIS) during repeated cycling, affecting the long-term stability of the spinel structure. This explains the gradual decline in the LIS sorption capacity over successive reuse cycles.^[97]

Ion exchange mechanism

Another approach to describe the lithium insertion mechanism is the ion exchange reaction. In this process, the spinel structure remains intact. According to Koyanaka *et al.*,^[70] lithium ions in the solid phase can be substituted for protons, while the oxidation state of manganese in the crystal lattice remains unchanged. The following equation represents the ion exchange reaction for the $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ sorbent:^[57]



This is an equilibrium reaction that strongly depends on the Li^+ concentration as well as the pH value (H^+ concentration). Lithium intercalation is favored at high pH and elevated Li^+ concentration. The gradient of proton concentration between the sorbent and the solution provides the driving force for this process. Buffering solution can be used to increase the Li-sorption since its usage results in a reduction in the decline of the pH value.^[100]

Conversely, at low pH, lithium is released, H^+ ions are incorporated, and the material is regenerated.^[143] Acid is used in this stage for desorption.

In this intercalation mechanism, only Li^+ and H^+ ions can be intercalated due to their small ionic radii, which makes the process highly selective. Other ions are excluded from intercalation due to their larger size (Fig. 2.11). Although it is theoretically assumed by the

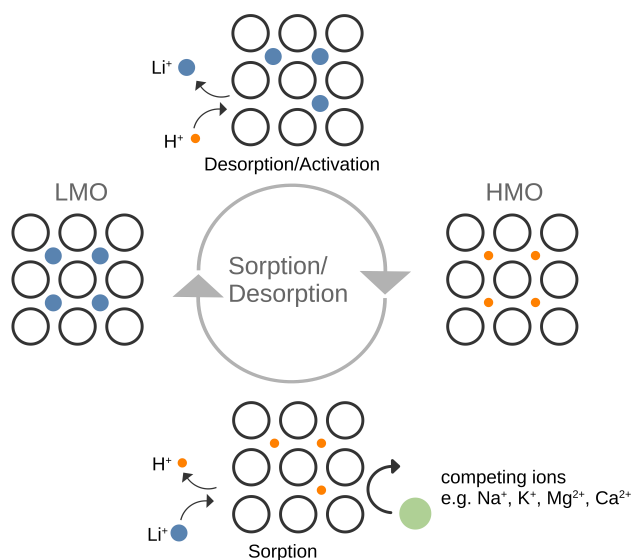


Figure 2.11: Selective Li-intercalation/deintercalation with Mn-based sorbents. Adapted with permission from Xu *et al.*, Extraction of lithium with functionalized lithium ion-sieves, volume 84, pages 276-313, 2016, Elsevier.^[150]

ion exchange mechanism that the cubic surface-centered structure remains intact during the ion exchange process, experimental observations indicate that Mn dissolution does

occur in practice.^{[143][58][47]} The inability to fully explain the dissolution of manganese and the gradual decline in performance over multiple recycling cycles showcases that there is still a lack of mechanistic understanding in the underlying degradation pathways in these materials.^[143]

Since not all phenomena can be fully explained by these two mechanisms, there are additional approaches to describe Li-intercalation and de-intercalation, including the composite mechanism. However, this mechanism is highly complex and has not been experimentally verified.^[150] Consequently, redox and ion exchange are assumed to be the primary exchange mechanisms in this thesis.

Material stability and Mn dissolution mechanism. The use of LMO for Li-extraction has great potential because high sorption capacities can be achieved and the material is very selective, leading to high product purity. However, there are still issues to be solved before the material can be used in real processes on an industrial scale. Mn dissolution represents one of the main challenges.^[102]

After the sorbent has captured Li (sorption), it has to be regenerated. For this purpose, an acid treatment is performed and Li is released. However, in addition to the release of Li, a release of Mn is also observed, indicating limited chemical stability.^[155] The loss of active material in each desorption step can result in a decrease in performance after some cycles and will eventually lead to gradual material deterioration or even a collapse of the entire crystal framework.^[8] To overcome this issue, it is important to investigate the Mn dissolution process, as it is not yet fully understood. One of the mechanisms contributing to the dissolution of Mn which has been widely discussed in the literature is the Jahn-Teller effect.^[101]

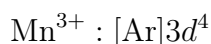
The Jahn-Teller effect describes the geometric distortion of molecules or crystals with distorted electronic states in order to reduce their energy. It is of particular importance for transition metal ions with partially filled d orbitals in an octahedral ligand field, especially trivalent Mn in the crystal structure of lithium manganese oxides.^{[47][107]}

The effect is of major significance for LiMn_2O_4 , where trivalent Mn is abundant (average oxidation number 3.5), but can also play a role in other LMO. Theoretically, in $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ no trivalent Mn is expected. However, small amounts are formed during synthesis and contribute to the Jahn-Teller effect.^[47]

Atomic manganese has an atomic number of 25, with the following electron configuration:^[49]



In Mn^{3+} , the atom first loses its 4s electrons. Following this a 3d electron is removed:^[49]



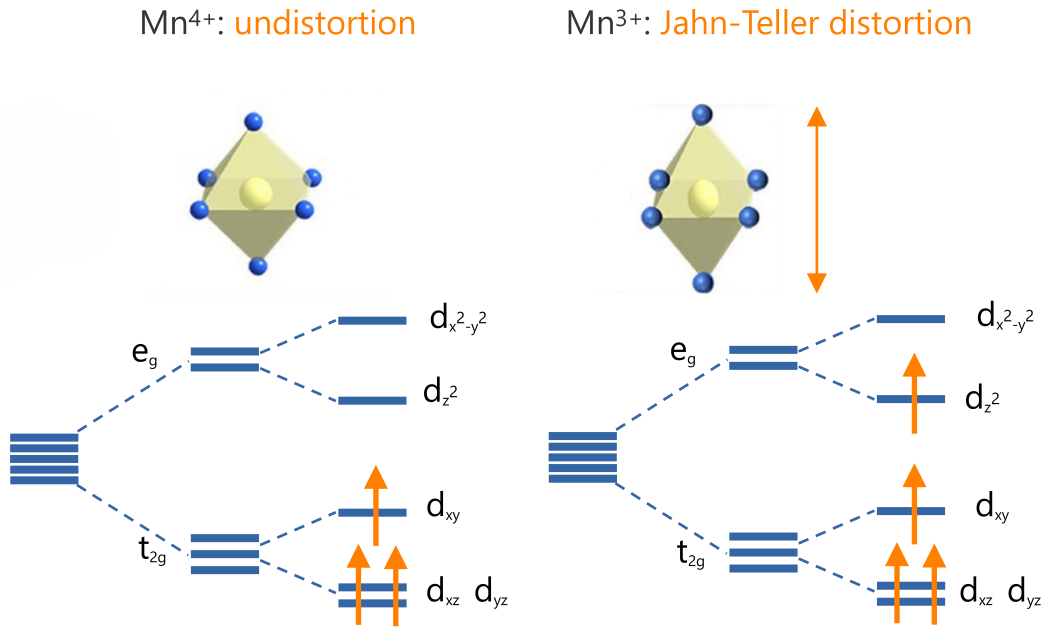


Figure 2.12: Illustration of Jahn–Teller distortion (elongation) of Mn³⁺ and undistortion for Mn⁴⁺. Adapted from *Bulou et al. 2025*^[14] and *Zhao et al. 2025*^[160] Licensed under CC BY 4.0.

In an octahedral ligand field (MnO₆), the five *d*-orbitals split up, leading to the configuration (*t*_{2g})³(*e*_g)¹ as presented in Fig. 2.12. Since the *e*_g orbitals directly interact with ligands along the axial directions, the presence of a single electron in these orbitals results in an instability, inducing the Jahn-Teller distortion.^{[152][107]}

This Jahn-Teller distortion leads to an energetically unfavorable configuration and triggers the following disproportionation reaction to reduce the energy of the system.



The release of Mn is particularly favored in the acidic environment (desorption step) and depends on the acid concentration. Therefore, mild desorption conditions can partly reduce Mn-loss.^[102] Besides the Jahn-Teller effect, Mn release also occurs when Li deintercalation takes place via the redox mechanism, as described by Hunter *et al.*^[61] (Eq. 2.7). To prevent Mn dissolution caused by the Jahn-Teller effect and the redox mechanism, it is crucial to minimize the Mn³⁺ content in the material formed in synthesis or operation to improve stability. One strategy to address this problem is the substitution of a small amount of trivalent Mn with dopant ions.

Substitution. Substitution is a process in which an atom or ion in a crystal lattice is replaced by another atom or ion of similar size. This modification can alter the properties

of the material, such as conductivity, stability, or catalytic activity without altering the matrix.^[21] Substitution approaches are used in various fields, such as materials science, electronics, and energy storage to enhance the properties of different substances.^{[83][153]} In some studies, doping approaches for LMO sorbents are presented to improve their performance. One of the primary challenges with LMO sorbents is the dissolution of manganese.^{[48][103]} Therefore, the main motivation for the Mn-substitution is to enhance the chemical stability of the sorbent to increase its lifetime and thereby enable industrial applications.^{[48][103][55]} Besides enhancing chemical stability, the introduction of foreign atoms can significantly influence the sorption capacity. Additionally, it modifies the lattice parameter, which may affect the selectivity towards lithium. Ion diffusion is also impacted, thereby influencing the kinetics of the system, which must be carefully considered.^[21]

Substitution approaches can be divided in cation doping using both monovalent and multivalent metal ions, as well as anion doping. The properties of the material can be controlled both by substituting anions or cations.^[21] Monovalent ions such as Na^+ and K^+ primarily replace Li^+ at the 16d sites without causing lattice distortion, maintaining the spinel structure. Na^+ tends to replace surface Li^+ due to its lower formation energy, while K^+ prefers bulk replacement. This doping improves the structural stability, since the Na-O and K-O bonds are stronger than the Li-O bonds. Furthermore, it reduces charge density at the 16d sites, which enhances the average valence of Mn and minimizes the risk of disproportionation of Mn^{3+} according to Eq. 2.12.^{[102][21][104]}

On the other hand, doping with multivalent ions such as Mg^{2+} , Zr^{4+} , Fe^{3+} , Al^{3+} , and Ti^{4+} primarily substitutes Mn^{3+} , leading to different effects on the material. Doping with cations slightly larger than Mn^{3+} can help to retain the original spinel structure, while causing lattice expansion and improving the average valence of Mn, improving stability.^{[8][140]} In contrast, ions which have smaller radii than Mn^{3+} can cause crystal shrinkage. Furthermore, these multivalent ions form stronger bonds (Al-O, Fe-O, Ti-O), further enhancing the stability and performance of the material.^{[21][156][48]}

In this thesis, Ti^{4+} was selected for substitution due to its ionic radius (0.605 Å), which is close to that of high-spin Mn^{3+} (0.645 Å), as well as its ability to form strong Ti-O bonds and improve the stability of the crystal framework.^[53]

Chapter 3

Sorbent materials and the state-of-the-art in DLE technologies

There are various activities in the field of sorption DLE, including basic research on sorbent materials, as well as transfer to field operations. A variety of sorbent materials have been investigated for their performance in lithium recovery from brines. Each material demonstrates a unique set of advantages and limitations. While lithium manganese oxides and lithium titanium oxides are still in research and development phase,^{[159][9][28]} lithium double layered aluminum hydroxides have already undergone preliminary field tests.^{[40][126]}

In this chapter a comprehensive overview of the current state of technology is provided. The text includes the most recent research on sorbent materials as well as insight into both planned and implemented on-site projects.

3.1 Research advances in DLE sorbents

In recent years, research has focused on optimizing the synthesis and recovery conditions for LDH, LMO, and LTO sorbents. When comparing different materials, the sorption capacity Q_{Sorb} is often used as a performance indicator. It is important to note that this parameter is highly dependent on operational conditions, such as pH, the Li^+ concentration of the solution c_{Li} , the temperature T , the reaction time t , and the ratio of the sorbent mass to the volume of the brine (m/V ratio).^{[115][23]} The results of relevant studies are presented in the Tab. 3.1.

Sorption capacity. Comparing different types of sorbents, LTO and LMO demonstrate higher sorption capacities than LDH. In the case of LDH, sorption capacities were frequently found to be below 7 mg g^{-1} .^{[109][108][19]} Zhong *et al.* achieved a remarkably high sorption capacity of 7.26 mg g^{-1} .^[162] In comparison, LTO and LMO show sorption capacities of $Q_{Sorb} \approx 20\text{-}40 \text{ mg g}^{-1}$ in most studies, depending on the synthesis route and experiment conditions.^{[76][20][103][72]}

Table 3.1: Overview of selected sorbent materials including shaping, molecular formula, Li^+ concentration (c_{Li}), kind of Li-bearing solution, temperature (T), pH, ratio of mass sorbent (m) to volume of brine (V), sorption capacity (Q_{Sorb}), reaction time (t).

Sorbent	Shape	Molecular formula	c_{Li} [mg L ⁻¹]	Li-rich-solution	T [°C]	pH	m/V [g L ⁻¹]	Q_{Sorb} [mg g ⁻¹]	t [h]	Source
LDH	Powder	$\text{Li}_m\text{Al}_2(\text{OH})_6\text{Cl}_m \cdot n \text{H}_2\text{O}$	399	salt lake brine	30	7	16.67	7.26	2	[162]
LDH-Na-Alginate	Granulate	$\text{Li}_2\text{Al}_4(\text{CO}_3)(\text{OH})_{12} \cdot 3 \text{H}_2\text{O}$	1400	salt lake brine	25	8	80	14.5	4	[74]
LTO	Powder	Li_2TiO_3	400	LiCl-LiOH	n.a	~12	1	34	24	[76]
LTO	Powder	$\text{H}_4\text{Ti}_5\text{O}_{12}$	~115	LiCl-buffered	25	9.2	2	39.4	120	[92]
LTO-PVP	Nanofibers	$\text{H}_4\text{Ti}_5\text{O}_{12}$	300	synthetic brine	25	11	1	59.1	0.5	[142]
LMO	Powder	LiMn_2O_4	50	LiCl buffered	18	10	0.2	24.7	12	[151]
LMO	Powder	LiMn_2O_4	50	LiOH	25	8	1.25	27.7	12	[20]
LMO	Powder	$\text{Li}_4\text{Mn}_5\text{O}_{12}$	424	LiCl	30	10.1	1	39.3	10	[147]
LMO	Powder	$\text{Li}_4\text{Mn}_5\text{O}_{12}$	300	synthetic brine	25	~7	1	37.9	28	[72]
LMO	Powder	$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	84	LiCl	25	12	1	32.3	48	[103]
LMO	Powder	$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	42	LiCl	25	12	1	26.1	48	[103]
LMO	Powder	$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	0.17	seawater	25	n.a.	0.001	40	~700	[24]
LMO	Powder	$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	156	salt lake brine	25	n.a.	5	33.2	24	[8]
LMO-Mg	Powder	$\text{Li}_{1.6}\text{Mg}_x\text{Mn}_{1.6-x}\text{O}_4$	156	salt lake brine	25	n.a.	5	35.6	24	[8]
LMO-Fe	Powder	$\text{Li}_{1.6}\text{Fe}_x\text{Mn}_{1.6-x}\text{O}_4$	84	LiCl	25	12	1	35.3	48	[103]
LMO-Co	Powder	$\text{Li}_{1.6}\text{Co}_x\text{Mn}_{1.6-x}\text{O}_4$	84	LiCl	25	12	1	35.4	48	[103]
LMO-Ni	Powder	$\text{Li}_{1.6}\text{Ni}_x\text{Mn}_{1.6-x}\text{O}_4$	84	LiCl	25	12	1	33.6	48	[103]
LMO-Al	Powder	$\text{Li}_{1.6}\text{Al}_x\text{Mn}_{1.6-x}\text{O}_4$	168	LiCl	45	12	1	40.9	48	[103]
LMO-Al	Powder	$\text{Li}_{1.6}\text{Al}_x\text{Mn}_{1.6-x}\text{O}_4$	600	synthetic brine	n.a.	12.8	1	46.8	24	[84]
LMO-Mg	Powder	$\text{Li}_{1.6}\text{Mg}_x\text{Mn}_{1.6-x}\text{O}_4$	600	synthetic brine	n.a.	12.8	1	45.8	24	[84]
LMO-PVC	Granulate	PVC-MnO ₂	70	LiCl	51	10.1	1	23.7	72	[146]
LMO-Epoxy	Granulate	$\text{Li}_4\text{Mn}_5\text{O}_{12}$	300	Brine buffered	25	~7	1	30.2	28	[72]

Among the manganese oxides, $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ exhibits the highest sorption capacity. In individual experiments, sorption capacities exceeding 40 mg g^{-1} were achieved under ideal conditions.^[24] However, these high values for LMO and LTO are only reached for high pH levels ($\text{pH} > 12$).^{[103][84]} Since the majority of LMO and LTO sorbents operate primarily via an ion exchange mechanism (Ch. 2.4.2; Ch. 2.4.3), the Li-insertion is mainly controlled by the present Li^+ - and H^+ -concentrations.^[23] High initial pH values or buffering solutions are required to control pH of the ion exchange reaction and enable high sorption capacities. In contrast, LDH intercalate lithium via adsorption in the layered structure, without being affected or altering the pH.^{[110][161]} Since natural waters typically exhibit neutral to slightly acidic pH values (salt lakes ≈ 7 -8; geothermal brines ≈ 5 -6),^{[162][74][88][13]} LDH offer a significant advantage, as no pH adjustment—and thus no additional chemical input—is required. Nevertheless, the high sorption capacities of LMO and LTO present them as attractive candidates for sorption processes, motivating continued research into material optimization and pH regulation of the process.

Selectivity. Another advantage of LMO and LTO is their high selectivity.^{[121][77]} Studies have shown that LMO and LTO materials exhibit high selectivity for Li^+ over competing cations such as Mg^{2+} and Na^+ , primarily due to their structural ion-sieving properties.^{[24][141]} In contrast, LDH tend to show only moderate selectivity and are more susceptible to interference from multivalent cations.^{[157][144][32]} However, a high selectivity is particularly important when processing natural brines, where elevated concentrations of competing ions are present, which can significantly impact the purity of the recovered lithium product.^[157]

Structural stability. A significant challenge associated with sorbent materials in the context of DLE is their long-term stability. It has been found that Li/Al-LDH undergo transformation into Gibbsite as a result of extensive lithium desorption.^{[161][60]} In the case of LMO, Mn dissolution is frequently observed during the desorption step, leading to a loss of active material and structural destabilization of the crystal lattice.^{[102][21][104]} Therefore, several studies are investigating modifications of the sorbents to improve the chemical stability of the sorbents. The results of selected substitution approaches using Mg, Fe, Co, Ni and Al as substituent are presented in Tab. 3.1.^{[8][103][84]} Some studies could successfully reduce Mn dissolution and as a side effect additionally increase the sorption capacity. In Bao *et al.* Mn dissolution could be reduced from 3.7 % (HMO) to 3.2 % (Mg-substituted) in the initial desorption cycle.^[8] Qian *et al.* investigated the substitution with Fe^{3+} and Co^{2+} and reduced Mn dissolution to 3.95 % (HMFeO) and 4.42 % (HMCoO) compared to undoped HMO (5.43 %).^[103]

Shaping of material. Most studies were working on optimizing synthesis conditions and investigated sorption capacity, kinetics and isotherms. So far long-term- (cycling-) tests were

conducted only over a few cycles and experiments were performed mainly under laboratory conditions. Powder cycling tests are limited by separation-induced material loss, hindering long-term evaluation.^[57] Recent research has focused on formulation of these materials into suitable shapes to improve handling and enable integration into plant operations.

A key challenge in integration of sorbents into matrices (e.g. PVC, Epoxy) is the potential blockage of active sites, reducing sorption capacity and affecting kinetics.^[154] Xiao *et al.* have reported promising results using PVC-MnO₂ granules with a sorption capacity of 23.7 mg g⁻¹ after 72 h.^[146] The highest sorption capacity reported to date for LMO granulates was published by Lai *et al.* using epoxy resin and Li₄Mn₅O₄ sorbent achieving 30.2 mg g⁻¹ Li-uptake.^[72]

However, there are still significant challenges to be addressed, particularly with regard to the scalability of the synthesis processes and the long-term cycling stability of the materials to bring them to an industrial scale application. These aspects are addressed within the scope of this thesis.

3.2 Pilot and industrial scale projects

Despite the ongoing research on optimization of sorbent synthesis, functionality, and shaping, certain materials have already progressed to pilot testing or even industrial applications. The subsequent chapter provides a comprehensive overview of the current state of the art of DLE technology. Tab. 3.2 summarizes the various projects currently underway in this field. Several sorption based DLE projects utilizing brines from salars and salt lakes are currently underway in South America and China.^{[40][126]} In the United States and Europe, numerous initiatives are also focusing on geothermal brines as a lithium resource.^{[41][15]}

Livent has been producing lithium at the Salar del Hombre Muerto in Argentina since 1997 using a DLE technology, making it one of the first companies to implement DLE at commercial scale.^[5] They aim to increase lithium carbonate production capacity from 18,000 to up to 100,000 t/a by the end of the decade.^[5]

Lilac Solutions is developing DLE technologies and has completed four pilot and demonstration plants.^[78] Lilac is the only company using ion exchange materials (e.g. Mn-based) in their DLE technology.^[119] In 2024 Lilac has introduced its fourth-generation ion exchange (Gen 4 IX) system.^{[78][119]} In 2025 the company has successfully commissioned a demonstration facility in Jujuy (Argentina) with a throughput of 42 t/a of LCE.^{[78][80][79]} Lilac's technology enables efficient lithium recovery from complex brine compositions, including those with low lithium concentrations and high impurity levels.^[78]

Table 3.2: Overview of selected industrial scale DLE projects worldwide

Project/ operator	DLE- technology	Brine source	Status (10.2025)	Planned capacity p.a.
Livent [5]	Sorption Al-based	Salar Argentina- Catamarca	Phase 1 operating	18 kt (Ph.1) 40 kt (Ph.2) 100 kt (Ph.3) LCE
Lilac Solutions [79]	Ion exchange Mn-based	Salar Argentina-Jujuy	operating	42 t LCE
Eramet – Tsingshan Centenario Ratones [40]	Sorption Al-based	Salar Argentina-Salta	Phase 1 operating	24 kt (Ph1.) 75 kt (Ph.2) LCE
Controlled Thermal Resources (CTR) [15]	Sorption sorbent unspecified	Geothermal brine USA-Salton Sea	Construction started (2024)	25 kt LiOH
Sunresin [126]	Sorption resin, Al-based	Salt-lake brine worldwide	operating	Zangge: 10 kt Minmetals: Ph. 1+2: 6 kt Jintai Lithium: Ph. 1+2: 7 kt LCE
Vulcan Energy [138]	Sorption VULSORB™ Al-based	Geothermal brine Germany-Upper Rhine Graben	planned	24 kt LCE
ExxonMobil [66]	Technology unspecified	Formation water USA-Smackover	Exploration phase	75 - 100 kt LCE
Eramet - ES AGELI [41]	Sorption Al-based	Geothermal brine France-Alsace	planned MoU signed	10 kt t LCE

In 2024, Controlled Thermal Resources (CTR) commenced construction of an integrated geothermal power and lithium extraction facility at the Salton Sea, California.^[15] The project combines renewable geothermal energy generation with DLE technology and is designed to produce up to 25,000 t/a of battery-grade lithium hydroxide monohydrate.^[15] They initially planned to implement an ion exchange based lithium extraction technology developed by Lilac Solutions. However, the company has switched to a sorbent-based DLE system to handle hotter brines.^[12]

ExxonMobil has announced their plans to extract lithium from the saline waters of the Smackover Formation, which are located in southern Arkansas. However, the specific DLE technology to be employed has not yet been published.^[42] ExxonMobil is currently in an exploration phase and wants to start production of lithium in 2027. The company declared

its intentions to become the leading lithium supplier with an annual production capacity of 75 kt - 100 kt LCE.^[66]

Sunresin is one of the leading producers of DLE sorbents (Al-based, Resin) in China.^[126] Furthermore, they offer engineering, procurement, and construction (EPC) solutions for DLE and have successfully completed several commercial-scale projects on Li-extraction from salt lake brines. Selected completed projects are presented in Table 3.2. They include a facility operated by Zangge, with a production capacity of 10 kt/a LCE,^{[4][126]} a project with Minmetals, producing 6 kt/a LCE^[125] and a Jintai Lithium project with a capacity of 7 kt/a LCE.^[127] Several additional projects are already in the planning and installation phase - also for the extraction from geothermal brine.^[126]

In December 2019, Eramet launched a pilot DLE project in Andean Highlands with a flow rate of 600 L h⁻¹. The pilot plant ran for 3 years in a 24/7 operation.^[38] The Eramet extraction technology is based on a DLE using Al-based sorbents.^[89] Together with Tsinghsan they work in the Centenario-Ratones Li-project on a industrial Li-production from brines in Salta Argentina.^[38] The project has an expected outcome of 24 kt/a in phase 1. They announced their first lithium carbonate produced in Argentina in December 2024.^[40] After phase 2 a total production capacity of 75 kt LCE/a is expected.^[40] Eramet is also active in the Li-extraction from geothermal brines. Within the EuGeLi-project a pilot plant was installed at geothermal sites in the Upper Rhine Graben. The project ended up producing the first lithium carbonate from geothermal brine in Europe in 2021.^[37] Furthermore, Électricité de Strasbourg and Eramet have signed an exclusive Memorandum of Understanding (MoU) to jointly assess the development of lithium production from geothermal brines in the Alsace region in an industrial scale. A production capacity of 10 kt/a of LCE has been announced.^[39] The project is currently in the planning and feasibility phase. It was officially recognized as a “strategic project” by the European Union in 2025.^[41]

Besides Eramet there are further active companies in the URG working on Li-extraction from geothermal brines. Vulcan Energy Resources investigates the Li-extraction using their in house developed sorbent VulsorbTM(Al-based).^[1] In April 2024, Vulcan commenced production of its first lithium chloride from their optimization plant (LEOP).^[138] An industrial plant is currently in the planning stage, which, according to Vulcan, is expected to deliver 24 kt of LCE in its first phase.^[138]

This work is linked to DLE projects conducted by EnBW Energie Baden-Württemberg, which also investigate lithium extraction from geothermal brine in the URG. EnBW tested Li-extraction at Bruchsal geothermal site in a pilot plant operation using various sorbents, including Al-, Ti- and Mn-based materials.^[71] In 2024, they became the first company in Germany which produced battery-grade lithium carbonate from geothermal brine with a (battery-grade) purity of 99.5 %.^[36]

This chapter underlines the significance of DLE on a global, European, and national (German) scale. A variety of DLE projects have already been implemented in South America (e.g., salars) and in salt lake regions of China.^{[40][126]} DLE enables a more environmentally sustainable and faster extraction process compared to traditional methods, such as solar evaporation.^[113] Moreover, DLE opens access to lithium from unconventional sources, including geothermal brines and salars or salt lakes with lithium concentrations too low for conventional recovery techniques (solar evaporation).^[117] According to current projections, global lithium production with DLE will increase by around 20 % between 2025 and 2035.^[16] Looking ahead, DLE is expected to play an increasingly important role in global lithium supply.

Chapter 4

Scope of the thesis

The global transition to renewable energies and the growing demand for energy storage systems have significantly increased the need for lithium, a key component in modern battery technologies.^{[62][113]} Direct Lithium Extraction represents an innovative and sustainable approach for lithium recovery from conventional resources, such as salar brines, while also enabling the utilization of alternative lithium sources.^{[113][16]} Among these, geothermal brines show great potential, as they allow simultaneous recovery of energy and lithium. However, they also have some challenges due to their high salinity and presence of competing ions, which require the development of advanced sorbent materials.^{[43][52]}

LMO sorbents (e.g. $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) have emerged as a promising sorbent material due to their lithium ion sieve properties.^{[100][148]} However, their industrial application and market readiness is hindered by several factors, including scalability issues of synthesis, chemical instability during desorption (Mn dissolution), and practical challenges in handling and cycling.^{[47][48][103]}

This thesis addresses these challenges by developing scalable synthesis methods for production of LMO sorbent for Li-extraction. To characterize the crystal structure and morphology of these sorbents, advanced techniques, such as x-ray diffraction, synchrotron x-ray analysis, NMR spectroscopy, magnetic measurement, and SEM analysis will be applied. In addition, substitution strategies will be explored to enhance the stability of the sorbent and reduce Mn dissolution. To optimize material utilization and understand its performance under varying conditions, the sorption behavior of LMO sorbents will be systematically studied, focusing on pH dependence, sorption kinetics, and mass-to-volume ratios. The success of the sorption experiments will be assessed via ICP-OES, measuring Li^+ concentrations to calculate sorption capacity and competing ions for selectivity analysis. In addition, granulation techniques will be applied to improve the handling of the sorbent and allow the material to be cycled for long-term testing.

By addressing these challenges, this thesis advances the development of Mn-based sorbents for efficient and sustainable lithium extraction from geothermal brines. The findings contribute to the development of industrial DLE processes and aim to reduce CO_2 footprint as well as strengthen independence from foreign imports.^{[62][113]}

Chapter 5

Experimental

5.1 Preparation of sorbent material

The following chapter provides an overview of various approaches for the preparation of sorbent materials for lithium extraction, including hydrothermal synthesis, spray drying process, and material granulation.

5.1.1 Hydrothermal synthesis

The conventional method for synthesizing the sorbent $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ is hydrothermal synthesis.^{[115][23][148]} In this work, the procedure was based on previous studies of Herrmann *et al.*,^[58] which combined the findings of Shi *et al.*^[115] and Chitrakar *et al.*^[23]. In general, the steps of the hydrothermal synthesis, as outlined in Fig. 5.1, can be categorized into roasting, hydrothermal autoclaving, calcination, and activation.

In the subsequent procedure MnO_2 (Sigma-Aldrich, 99 %) was calcined in a furnace at a temperature of 680 °C for 6 hours, using a heating rate of 655 °C/h to obtain Mn_2O_3 . Then, 2.5 g of Mn_2O_3 and 50 mL of 4 M LiOH solution (lithium hydroxide monohydrate, Alfa Aesar, 98 %) were mixed and placed in an autoclave with teflon inlet. The autoclave was subsequently heated for 24 h at 120 °C in a drying cabinet to obtain LiMnO_2 . After the reaction, the LiMnO_2 product was centrifuged at 8000 rpm for 1 min and washed twice with purified water. The LiMnO_2 was then dried in an oven at 80 °C for 12 h.

In the following step LiMnO_2 powder was milled and calcined at 400 °C for 4 h to obtain the pristine sorbent $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ with spinel structure. This was followed by a treatment with a 0.5 M HCl solution, causing an ion exchange between Li^+ and H^+ , forming the ready pristine sorbent $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Finally, the HMO material was dried for 12 h at 80 °C.

Optimization of synthesis parameters

As high Mn dissolution rates were observed in previous studies,^[58] the optimization of the synthesis was investigated within this chapter. Within the scope of this thesis, various experiments were performed that varied reaction parameters such as temperature and reaction

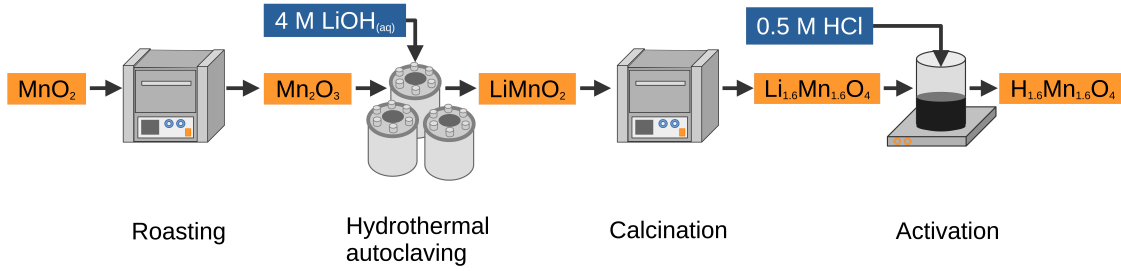


Figure 5.1: Schematic diagram of sorbent preparation with hydrothermal synthesis (own illustration).

time in the hydrothermal autoclaving step and the calcination step. The effects on sorption performance were examined. Furthermore, optimization of the synthesis conditions was examined at a structural level in the Master thesis supervised by the author and conducted by Tibor Feurer^[45]. Selected relevant findings from this work are presented in the subsequent chapters.

Hydrothermal autoclaving. Initially, the hydrothermal autoclaving step was optimized. This involved varying the temperature ($T=120^\circ\text{C}$, $T=170^\circ\text{C}$, $T=220^\circ\text{C}$) and reaction time ($t=12 \text{ h}$, $t=18 \text{ h}$, $t=24 \text{ h}$) as summarized in Tab. 5.1, followed by the calcination at 400°C for 4 h. Experiment 1 (E1) corresponds to the reaction conditions used in the previous study of Herrmann *et al.*^[58].

The selected conditions are evaluated by comparing the sorption capacities and the Mn dissolution of the pristine HMO sorbents. For this purpose, 200 mg of each HMO sorbent materials were brought in contact with 40 mL of buffered LiCl solution ($c_{\text{Li}}=143 \text{ mg L}^{-1}$, $c_{\text{NaOAc}}=1.5 \text{ g L}^{-1}$). The suspension was stirred for 24 hours, after which the sorbent was separated from the liquid. After this, the supernatant was analyzed using ICP-OES to determine the lithium depletion in the solution. Then, the sorption capacity was calculated according to Eq. 5.3. In a second step, the desorption was conducted. The lithium loaded LMO sorbent was exposed to 40 mL of 0.5 M HCl for 24 hours. Following this, the solid phase was separated from the liquid phase and the concentrations of Li^+ and Mn^{2+} in the supernatant were quantified using ICP-OES. The Mn dissolution was then determined using Eq. 5.6.

Furthermore, the x-ray diffraction patterns of the pristine LMO were used for evaluation of suitable synthesis parameters.^[45]

Calcination. After determining the optimum conditions for the hydrothermal autoclaving (E3: 220°C , 24 h), the calcination step (temperature and time) was optimized. First, the ideal temperature was determined. For this purpose, an in situ XRD analysis was conducted, in which LiMnO_2 was heated in 50°C increments from 200°C to 500°C . At each 50°C in-

Table 5.1: Optimization of the hydrothermal autoclaving step in hydrothermal synthesis: summary of the selected reaction conditions for roasting, hydrothermal autoclaving, and calcination. The conditions of E1 correspond to those in the preceding study by Herrmann *et al.*^[58].

Experiment	Roasting		Hydrothermal autoclaving		Calcination	
	T [°C]	t [h]	T [°C]	t [h]	T [°C]	t [h]
E1	680	6	120	24	400	4
E2	680	6	170	24	400	4
E3	680	6	220	24	400	4
E4	680	6	120	18	400	4
E5	680	6	170	18	400	4
E6	680	6	220	18	400	4
E7	680	6	120	12	400	4
E8	680	6	170	12	400	4
E9	680	6	220	12	400	4

crement, the temperature was kept constant for 1 h, and a diffractogram was recorded. This diffraction pattern was used to monitor the structural transformation of LiMnO_2 to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, and to determine an appropriate temperature for the calcination. The diffraction data show that full phase conversion did not occur at 400 °C, as previously suggested by Herrmann *et al.*^[58], but was completed at 450 °C (see Fig. 6.2). Consequently, 450 °C was established as the new optimal calcination temperature.

Once the optimum temperature has been set, the corresponding optimum calcination time is determined. For this purpose, LiMnO_2 was heated during an in situ XRD at a constant temperature of 450 °C for 12 h. The diffractograms were recorded at 1 hour intervals to monitor the time-dependent transformation of LiMnO_2 to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Significant reflections of LiMnO_2 are still observed below 3 hours, whereas after 3 hours reflections corresponding predominantly to the spinel phase $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ are evident. However, minor changes in the diffractogram with an increase in reaction time suggest that further experiments are required to determine the optimum calcination time. To this end, 500 mg of each LiMnO_2 material was calcined in an oven for 3, 4, 5, 6 and 7 h, resulting in the formation of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ -phase. The material was then activated with 0.5 M HCl to obtain the HMO sorbent. These materials were tested in sorption/desorption experiments as described in the previous section 5.1.1. The sorption capacities and Mn dissolution were calculated to determine the optimized calcination conditions. Further sorption experiments were performed with materials obtained using the conditions summarized in Tab. 5.2.

Table 5.2: Optimized synthesis parameters of hydrothermal synthesis

Roasting		Hydrothermal autoclaving		Calcination	
T [°C]	t [h]	T [°C]	t [h]	T [°C]	t [h]
680	6	220	24	450	5

5.1.2 Scale up: synthesis in spray drying process

Within this work a novel approach was developed for the large-scale production of LMO sorbent. This new method is based on a spray drying process that operates in continuous flow. Lithium acetate dihydrate and manganese acetate were used as starting materials for the synthesis of the LMO sorbent. In another approach, the partial substitution of Mn with Ti was investigated to increase the chemical stability of the sorbent. For this purpose, titanium isopropoxide was additionally introduced to the spray dryer to obtain the LMTO sorbent. The fundamental procedure for the synthesis of both LMO and LMTO is similar and is described below using LMO as a representative example. All corresponding material quantities are listed in Tab. 5.3. The individual steps of the synthesis process are illustrated in Fig. 5.2. For the preparation of the LMO sorbent, a total of 109.17 g (1.07 mol) lithium

Table 5.3: Weighed amounts for the synthesis of LMO and LMTO in the spray drying process

	Li-acetate		Mn-acetate		Ti-isopropoxide		product
	weighing [g]	water [L]	weighing [g]	water [L]	weighing [g]	acetic acid [L]	
LMO	109.17	0.4	262.25	0.8	-	-	231.3
LMTO	99.58	0.2	231.73	0.8	9.09	0.2	197.4

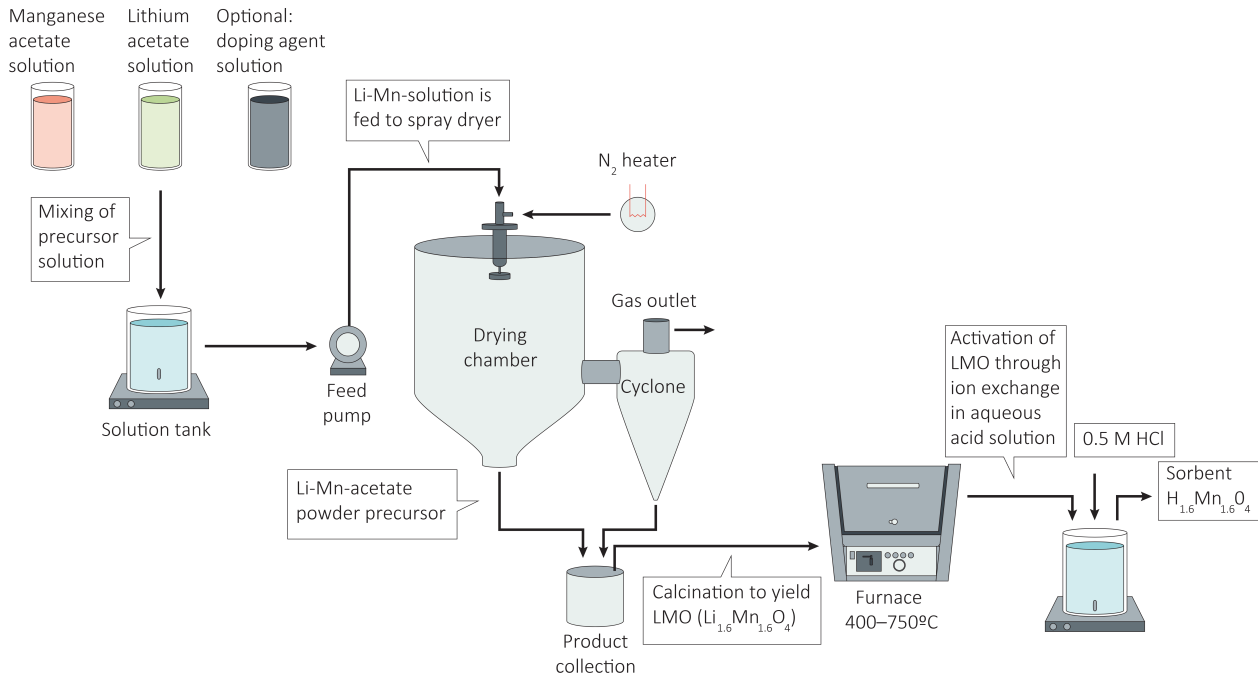


Figure 5.2: Schematic diagram of sorbent preparation ($\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$) including preparation of Li-Mn-solution, spray drying process, calcination and pickling of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ with 0.5 M HCl. Adapted from Herrmann *et al.* 2025.^[57] Licensed under CC BY 4.0.

acetate dihydrate ($\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$, purity 98 %, Acros Organics) was mixed with 0.4 L

of deionized water. Then, in a second container, 262.25 g (1.07 mol) manganese(II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, purity > 99 %, Sigma Aldrich) was added to 0.8 L of deionized water. The lithium acetate solution and manganese acetate solution were combined in a beaker. The solution was atomized in the spray dryer (GEA Niro MOBIL MINOR) using nitrogen as the carrier gas with a inlet temperature of $T_{\text{Inlet}} = 210^\circ\text{C}$ and a outlet temperature of $T_{\text{Outlet}} = 112^\circ\text{C}$. A total 231.3 g of dry LMO powder was obtained, hereinafter referred to as the LMO precursor. The precursor was calcined for 5 h at various temperatures of 450°C , 720°C and 800°C . In addition, a two-step heating process was performed at 720°C and 450°C , holding each temperature for 5 hours. After calcination, the LMO pristine material $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was obtained. An acid treatment (pickling) was applied to LMO pristine by exposing the material to 0.5 M HCl for 12 h. The sorbent $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was obtained by filtration and was subsequently washed with deionized water and dried for 24 h at 60°C . The LMO and HMO materials were examined by XRD and SEM to investigate their crystal structure and morphology.

The Ti-substituted sorbent material LMTO was synthesized using a similar route, beginning with the preparation of a lithium acetate dihydrate solution and a manganese acetate solution. Furthermore, titanium(IV)-isopropoxide was dissolved in acetic acid. Subsequently, the solutions were mixed and spray dried, and the LMTO precursor was treated similarly to LMO.

5.1.3 Granulation of sorbent material

To convert the sorption material into a suitable form for better handling during sorption/desorption processes, various shaping methods were tested in the master thesis supervised by the author and conducted by Matthias Mair^[86]. Granulation was selected as the most appropriate method. The optimal granulate composition identified in the mentioned work was used to produce formulated sorbents for various extraction experiments within this work. A schematic diagram of the granulation process is shown in Fig. 5.3.

First, 0.4 g polyvinyl chloride (PVC, Sigma-Aldrich, $M_W \sim 48.000$) was dissolved in 4.0 g *N,N*-Dimethylformamid (DMF, Sigma-Aldrich, 99 %). A total amount of 1.6 g HMO and 0.4 g polyethylene glycol (PEG, Sigma-Aldrich, $M_W \sim 200$) was added as pore-forming agent. Following this, the mixture was stirred with a magnetic stirrer to obtain a homogeneous slurry. In a next step, the slurry was dripped through a needle into ultrapure water, causing a phase inversion. The solvent escapes and the droplets form porous solid granules. Then, the granules were gently stirred in the water to completely remove the solvent and pore former. Finally, the granules were washed and dried at 80°C .

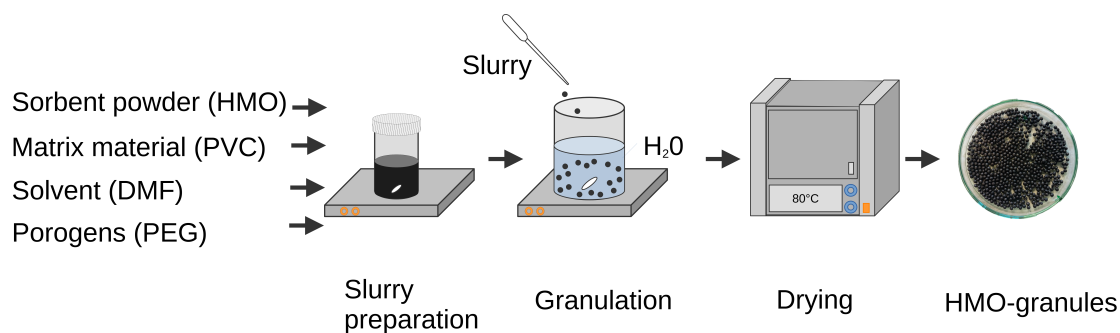


Figure 5.3: Schematic diagram of the preparation of HMO granules (own illustration).

5.2 Characterization of sorbent material and liquid solutions

Sorbent materials were characterized at distinct process stages: after synthesis (pristine LMO), after activation/pickling (pristine HMO), and after sorption/desorption cycles. Therefore, various analytical methods are used in this work. The structural, morphological, and surface properties were investigated by scanning electron microscopy with x-ray energy-dispersive spectroscopy, x-ray diffraction, synchrotron-XRD, Brunauer–Emmett–Teller surface area analysis, thermogravimetric analysis, nuclear magnetic resonance spectroscopy, and magnetic measurements.

The elemental composition of the sorbents was quantified by inductively coupled plasma optical emission spectroscopy after digestion. Furthermore, ICP-OES was utilized to determine ion concentrations in liquid samples, including synthetic and geothermal brines, both before and after the sorption experiments.

5.2.1 Scanning electron microscopy (SEM) - Energy-dispersive x-ray spectroscopy (EDX)

Scanning electron microscopy was performed to examine the surface morphology of the raw and treated sorbent material. A thermal field emission scanning electron microscope (FE-SEM, MERLIN, Zeiss) with x-ray energy-dispersive spectroscopy capability (EDX, Quantax 400 SDD, Bruker) was used. The samples were applied to a sample holder using a graphite adhesive disc and a silicon wafer. SEM micrographs were acquired at accelerating voltages between 3 kV and 5 kV and at magnifications of 10,000 $\times$ and 20,000 $\times$. Energy-dispersive x-ray spectroscopy was used to investigate the distribution of manganese and titanium in the pristine LMTO material and to evaluate the accumulation of foreign ions on the sorbent surface during cycling experiments with geothermal brine.

5.2.2 X-ray diffraction (XRD)

X-ray powder diffraction was performed to examine how variations of parameters in the hydrothermal autoclaving step affect the structural properties of LMO sorbents. The analysis was conducted in a powder diffractometer in transmission scan mode with a Cu-K $_{\alpha}$ radiation ($\lambda=1.54060$ Å) at 40 kV and 40 mA. In addition, the calcination process following hydrothermal synthesis was investigated using in situ x-ray diffraction with a heating function. This technique was employed to monitor phase transitions occurring at different temperatures and durations. In situ XRD was performed using a STOE Stadi P powder diffractometer with integrated oven in Debye-Scherrer scan mode. Similarly, monochromatic Mo-K $_{\alpha,1}$ radiation ($\lambda=0.7093$ Å) at 50 kV and 40 mA was used.

Furthermore, XRD was carried out to analyze the phase composition of the spray dried sorbent materials. The pristine and cycled materials of the spray drying process were analyzed using a STOE Stadi P powder diffractometer in transmission scan mode, using monochromatic Mo-K $_{\alpha,1}$ radiation ($\lambda=0.7093$ Å) at 50 kV and 40 mA.

5.2.3 Synchrotron XRD

Selected samples were further analyzed using synchrotron x-ray techniques to achieve higher resolution than in-house XRD with Cu-K $_{\alpha}$ or Mo-K $_{\alpha,1}$ radiation. The experiments were carried out on the P02.1 powder diffraction and total scattering beamline of the PETRA III synchrotron DESY in Hamburg. A photon energy (monochromatic x-ray beam) of approximately 60 keV, corresponding to a photon wavelength of 0.207337 Å was applied. The setup utilized a Varex XRD 4343CT detector with a pixel size of 150×150 μm^2 and a total pixel area of 2880×2880 . Featuring a CsI scintillator directly deposited on amorphous Si photodiodes, the detector ensures efficient signal conversion.

The sample material was received in 0.5 mm glass capillaries and the measurement time per capillary was approximately 60 seconds. LaB $_6$ was used as a reference material for calibration. Calibration was performed using the DAWN2 software. For the conversion of 2D data to 1D data (versus 2 Theta) DAWN2 and a Python script were used.

5.2.4 Brunauer, Emmett and Teller Analysis (BET)

The BET specific surface area of the material was determined using a surface analyzer Gemini VII 2390a from Micromeritics. Nitrogen was used as the adsorptive gas, and physisorption measurements were carried out at 77 K. The analysis was performed at a relative pressure of approximately $p/p_0=0.29$. The individual parameters of the BET measurement are shown in Tab. A.1.

5.2.5 Thermogravimetric analysis (TGA)

For bulk characterization, a simultaneous thermal analysis (TG-DTA/DSC) operated under synthetic air atmosphere (Netzsch Jupiter 449 C) was used. A sample is heated from 20 °C to 1000 °C at a rate of 5 K min⁻¹ in an open Al₂O₃ crucible. The mass change of the sample was recorded as a function of temperature, providing information on its thermal stability and decomposition behavior. On the basis of these findings, suitable calcination temperatures for the spray drying synthesis were selected.

5.2.6 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES, 700 Series-Agilent Technologies) was used to measure the concentrations of Li, Mn and further relevant ions of the geothermal brine. The chemical composition of the sorbent was also analyzed by ICP-OES. Therefore, the sorbent was digested by mixing the material with 37 wt% HCl (Merck KGaA) and 30 % H₂O₂ (Carl Roth GmbH). The samples were prepared by adding 1 mL of sample solution to 0.1 mL 65 % nitric acid (HNO₃) and 9 mL of distilled water. Three independent samples of the sorbent materials were analyzed, each subjected to separate sample preparation steps. The standard deviation of the cation concentrations determined by ICP-OES was 0.8 % for both lithium and manganese. The analyte solutions were characterized by ICP-OES in triplicate.

The calibration was performed using a Merck multielement standard with different concentrations (1 mg L⁻¹, 10 mg L⁻¹, 25 mg L⁻¹). In addition, the concentrations of ions in a blank and quality standard (QS) were determined. If the sample concentration was above the calibrated measurement range, it was diluted once more using distilled water.

5.2.7 Nuclear magnetic resonance (NMR)

The ⁷Li nuclear magnetic resonance analysis were performed to gain detailed insights into the structural characteristics of the sorbent materials. A Bruker Avance Neo 200 MHz spectrometer operating at a magnetic field strength of 4.7 T was used. Spectra were recorded using 1.3 mm rotors at a spinning speed of 55 kHz. A recycle delay of 1 s was applied, and the Larmor frequency was 77.8 MHz.

⁷Li magic-angle spinning (MAS) NMR spectra were acquired using a rotor-synchronized Hahn-echo pulse sequence (90°-τ-180°-τ-acquisition), with a 90° pulse length of 0.8 μs. The ⁷Li NMR shifts were referenced to 0 ppm using an aqueous 1 M LiCl solution. Normalization of the spectra was performed based on sample mass and the number of scans.

5.2.8 Magnetic measurement

To prepare the samples, sorbent material was filled into polypropylene sample capsules (QDS-4096-388 from Quantum design), which were fixed to the brass sample holder (QDS-4096-391 from Quantum design). Direct current (DC) magnetometry measurements were conducted using a Physical Property Measurement System DynaCool (Quantum Design), with an additionally installed vibrating sample magnetometry. The temperature dependence of the DC magnetic moment was measured from 2 K to 300 K at a constant magnetic field of $H=1000$ Oe, using the zero field cooled (ZFC) and field cooled (FC) method. The Settle mode was used in a temperature range from 2 K to 50 K. Following this, the temperature was increased at a constant heating rate of $2\text{ K}\cdot\text{min}^{-1}$ from 51 K to 300 K. Measurements were performed at temperature intervals of $\Delta T = 1$ K with a signal averaging time of 10 s per data point. Furthermore, field-dependent measurements were performed at 2 K and 300 K with a maximum magnetic field of $H_{max} = 70$ kOe. Zero field cooled conditions at 2 K were applied, followed by additional scans at 45 K (for HMO) and 300 K. The raw data was adjusted for diamagnetic contributions. The molecular formula of the sorbent, which was obtained from digestion of material ($\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$), was normalized to the formula $\text{LiMnO}_{2.5}$ with a single Mn.

5.3 Investigations into the Li-extraction behavior of HMO and HMT0 sorbents

In the following chapter, the lithium extraction behavior of various sorbents is investigated. To enable a systematic comparison of different sorbents, a standardized experiment was established. Based on these results, optimal synthesis conditions could be determined. The best-performing materials HMO-450 and HMT0-450 (produced via the spray drying process and calcined at $450\text{ }^{\circ}\text{C}$) were therefore selected for detailed investigations into their lithium insertion behavior, including investigations into the pH dependence of the sorbents, the effect of the mass-to-volume ratio on sorption capacity, and the influence of the initial lithium concentration of the brine. Furthermore, the ion exchange kinetics, long-term performance in terms of sorption/desorption capacities and Mn dissolution, as well as the Li^+ selectivity of the ion exchange process were evaluated. A comprehensive summary of the experiments is provided in Tab. 5.4.

Standard Li-sorption/desorption experiment. To enable a comparison of different materials, a standardized sorption experiment was established. A LiCl-NaOAc stock solution was prepared with a Li^+ concentration of 143 mg L^{-1} , and 1.5 g L^{-1} (18.3 mmol L^{-1}) sodium acetate (NaOAc) as buffering agent. For each test, 200 mg of sorbent was added to 40 mL of LiCl solution and stirred for 24 hours. Following the Li^+ sorption step, the solid was

Table 5.4: Overview of the various ion exchange experiments: type of experiments, amount of used sorbent mass (m_{Sorb}), concentration (c_{Li}), volume of brine (V) and temperature (T). Solutions with buffering agent are indicated by a (b). Table adapted from Herrmann *et al.*, 2025.^[57] Licensed under CC BY 4.0.

Experiment	m_{Sorb} [mg]	Li^+ solution	c_{Li} [mg L ⁻¹]	V [mL]	T [°C]
Standard sorption/ desorption	200	LiCl solution (b)	143	40	25
pH dependence	200 200 200	LiCl solution Bruchsal brine Bruchsal brine (b)	143	40	25
m/V ratio	10-1000	LiCl solution (b)	143	40	25
Variation of c_{Li}	200	LiCl solution (b) Bruchsal brine (b) Soultz brine (b)	46, 63, 142, 197 143 142	40	25
Kinetics	200	LiCl solution (b)	143	40	25
Cycling	200	LiCl solution (b), Bruchsal brine (b)	143 143	40 40	25
Selectivity	200	Bruchsal brine (b)	143	40	25
Operational conditions	2500 20000	Bruchsal brine (b/-) Bruchsal brine (b/-)	138-143 138-143	100 100	60 60

separated by centrifugation and the ion concentrations in the supernatant were analyzed with ICP-OES.

Optional desorption was performed by mixing Li-loaded sorbent LMO (200 mg) with 40 mL of 0.5 M HCl. The suspension was stirred for 24 hours followed by a solid-liquid separation. The liquid was analyzed with ICP-OES for its Li- and Mn-content.

pH dependence of ion exchange. For pH dependence experiments, a LiCl solution containing 143 mg L⁻¹ of Li⁺ was prepared. The pH was adjusted to values ranging from 1 to 12 by adding NaOH or HCl. A mixture of 200 mg of sorbent and 40 mL of the LiCl solution was stirred for 24 hours. After the reaction, the solid material was separated through centrifugation, and the ion concentrations in the resulting supernatant were measured using ICP-OES. In addition, a similar experimental setup was used with geothermal brine, both unbuffered and buffered with NaOAc at a concentration of 1.5 g L⁻¹.

Sorbent-to-brine ratio (m/V ratio). The correlation between the mass-to-volume ratio of the sorbent to the LiCl solution and its influence on sorption capacity and lithium extraction efficiency was systematically examined. Sorbent masses of 10 mg, 100 mg, 400 mg, and 1000 mg were individually suspended in 40 mL of a LiCl-NaOAc solution ($c_{\text{Li}} = 143 \text{ mg L}^{-1}$). The NaOAc concentration in the LiCl-NaOAc solution was varied, using $c_{\text{NaOAc}} = 1.5 \text{ g L}^{-1}$

(18.3 mmol L⁻¹) and $c_{NaOAc} = 15 \text{ g L}^{-1}$ (182.8 mmol L⁻¹). Following 24 h of stirring, centrifugation was used to separate the solid phase, and Li⁺ concentration in the supernatant was analyzed by ICP-OES to assess sorption capacity.

Li⁺-extraction using various Li⁺ concentrations and geothermal brine. The effect of the initial lithium concentration in the starting solution on the sorption capacity was evaluated. For this purpose, LiCl solutions with varying Li⁺ concentrations (46 mg L⁻¹, 63 mg L⁻¹, 142 mg L⁻¹, and 197 mg L⁻¹) were prepared. Additionally, experiments were conducted using natural brines from the geothermal plants in Bruchsal ($c_{Li} = 143 \text{ mg L}^{-1}$, EnBW) and Soultz ($c_{Li} = 141 \text{ mg L}^{-1}$, ÉS) to investigate the ion exchange process under conditions of high salinity and the presence of competing cations. In each experiment, 200 mg of HMO was suspended in 40 mL of brine and stirred for 24 hours. Subsequently, the solid phase was separated via centrifugation, and the ion concentrations in the supernatant were determined using ICP-OES.

Ion exchange kinetics. Kinetic studies were performed by suspending 200 mg of HMO or HMT0 in 40 mL of buffered LiCl solution ($c_{Li} = 143 \text{ mg L}^{-1}$, $c_{NaOAc} = 1.5 \text{ g L}^{-1}$). The contact times were varied systematically (5 min, 10 min, 15 min, 20 min, 30 min, 1 h, 2 h, 4 h, and 24 h) to investigate the ion exchange rate. After each time interval, the solid and liquid phases were separated via centrifugation, and the supernatant was analyzed for the lithium content using ICP-OES.

To describe the reaction kinetics, the experimental data were fitted to pseudo-first-order and pseudo-second-order kinetic models, as outlined in Eq. 5.1 and Eq. 5.2, providing insight into the underlying mechanisms of the ion exchange process.

$$\ln(q_e - q_t) = -k_1 \cdot t + \ln(q_e) \quad (5.1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot (q_e)^2} + \frac{t}{q_e} \quad (5.2)$$

The sorption capacity at a specific reaction time t is expressed as q_t , whereas the equilibrium sorption capacity is denoted as q_e . The reaction rate constants are represented by k_i . To analyze the data, the non-linear least squares method was applied using the SciPy library in Python (Fig. A.9).

Cycling experiments - sorbent aging. Cycling tests were carried out using HMO and HMT0 produced via the spray drying process (calcined at 450 °C), as well as HMO synthesized through the optimized hydrothermal process (Tab. 5.2). To evaluate the performance of the materials under repeated use (cycling), sorption/desorption was conducted for 5 cycles. For each test, 200 mg of HMO were mixed with 40 mL of either a buffered LiCl solution or a buffered geothermal brine (both: $c_{Li} = 143 \text{ mg L}^{-1}$, $c_{NaOAc} = 1.5 \text{ g L}^{-1}$). The mixture

was stirred for 30 minutes, after which the solid phase was separated via centrifugation. A sample of the supernatant was collected for ICP-OES analysis, while the solid material was washed twice with distilled water.

Desorption was performed by adding 40 mL of a 0.5 M HCl solution to the washed solid. The suspension was stirred for 30 minutes at room temperature, followed by separation and washing as in the previous step. The supernatant was analyzed for lithium, manganese, and other competing ions using ICP-OES. Sorption capacity calculations were based on the initial mass of the sorbent prior to the first cycle. This sorption-desorption process was repeated for a total of five cycles.

After cycling, the sorbent materials were examined by XRD and SEM to assess changes in crystal structure and morphology resulting from repeated use. In addition, selectivity analyzes that included determination of transfer factors (Eq. 5.5) were performed using the solutions obtained during the first cycle of long-term experiments.

Test under operational conditions - benchmark with commercial materials. In this series of tests, the LMO granulate produced in this thesis (Ch. 5.1.3) was compared to three commercial materials (LDH-1, LDH-2, and LTO) under conditions that closely simulate real-world applications. The sorbents were evaluated over 20 sorption/desorption cycles to assess their long-term sorption performance. For LDH, unbuffered geothermal brine ($c_{\text{Li}} = 143 \text{ mg L}^{-1}$) was used, while LMO and LTO were evaluated in buffered geothermal brine ($c_{\text{Li}} = 143 \text{ mg L}^{-1}$; $c_{\text{NaOAc}} = 1.5 \text{ g L}^{-1}$). Cycling experiments were carried out at two different m/V ratios (25 g L^{-1} , 200 g L^{-1}).

In a first experiment, the LMO-granulate, LDH-1, LDH-2, and LTO sorbents were used in a m/V ratio of 25 g L^{-1} . Therefore, 2.5 g of sorbent were mixed with 100 mL of geothermal brine at a temperature of $60 \text{ }^{\circ}\text{C}$ (returnline temperature of the geothermal plant, EnBW). The suspension was stirred for 30 min. Afterward, the sorbent was separated from the liquid phase. ICP-OES analysis was conducted to determine the change in Li^+ concentration and calculate the sorption capacity. For desorption, 100 mL of a 0.5 M HCl (for LMO-granule and LTO) and 100 mL of deionized water (LDH-1 and LDH-2) were added to the Li-loaded sorbent. Subsequently, the suspension was stirred for 30 minutes at $60 \text{ }^{\circ}\text{C}$. The desorption solution was analyzed for their Li- and competing ion concentration with ICP-OES. The results were used to evaluate the selectivity of the sorbents, including the determination of the transfer factor T_{CI} (Eq. 5.5) and the purity of the product solution.

In a second experiment performed using the same procedure, LDH-1, LDH-2 and LTO sorbents were tested with a m/V ratio of 200 g L^{-1} . Therefore, 20 g of sorbent were suspended in 100 mL of geothermal brine during the sorption step and 100 mL of desorption agent during the desorption step. Because the amount of active component in commercial granules was not disclosed by the supplier, the sorption capacity was calculated on the basis of the initial mass of the granules prior to the first cycle.

5.4 Calculations

Sorption capacity Q_{Sorb} .

The Li-sorption capacity Q_{Sorb} of the materials were determined using Eq. 5.3.

$$Q_{Sorb} \left[\frac{mmol}{g} \right] = (c_0 - c) \cdot \frac{V}{m_s \cdot M_{Li}} \quad (5.3)$$

Where V represents the solution volume, m_s denotes the initial mass of the sorbent, and M_{Li} is the molar mass of lithium. c_0 refers to the initial Li^+ concentration of the solution, while c indicates the Li^+ concentration after the sorption process.

Li^+ -depletion factor, R_D .

The degree of lithium depletion of brine in a sorption step was described by the depletion factor R_D . It is calculated by the change in Li^+ concentration before (c_0) and after sorption (c), divided by the initial Li^+ concentration (c_0), as shown in Eq. 5.4.

$$R_D[\%] = \frac{c_0 - c}{c_0} \quad (5.4)$$

Transfer factor of competing ions T_{CI} .

The transfer factor T_{CI} is defined as the molar fraction of competing ions originating from geothermal brines that are transferred into the desorption solution. It is determined by calculating the ratio between the concentration of a given competing ion (e.g., Na^+) in the desorption solution and its concentration in the initial geothermal brine, as expressed in Eq. 5.5.

$$T_{CI}[\%] = \frac{n_{Me,De}}{n_{Me,0}} \cdot 100 \quad (5.5)$$

The quantity of alkali and alkaline earth metals in the desorption solution is denoted as $n_{Me,De}$, while the initial amount of metal ions present in the geothermal brine is represented by $n_{Me,0}$.

Mn dissolution and Ti dissolution.

The dissolution of manganese was quantified using the ratio of the amount of dissolved Mn(II), calculated as the product of its concentration $c_{Mn,dis}$ and the volume of the desorption solution V_D , to the total amount of manganese present in the sorbent $n_{Mn,tot}$. The equation can be described by Eq. 5.6. A similar calculation applies for titanium.

$$D_{Mn}[\%] = \frac{c_{Mn,dis} \cdot V_D}{n_{Mn,tot}} \cdot 100 = \frac{n_{Mn,dis}}{n_{Mn,tot}} \cdot 100 \quad (5.6)$$

Chapter 6

Preparation and characterization of sorbent material

6.1 Hydrothermal synthesis

Hydrothermal synthesis as conventional route for producing the Mn-based sorbent LMO ($\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$) was carried out in previous work of Herrmann *et al.*^[58] according to Shi *et al.*^[115] and Chitrakar *et al.*^[23]. The long-term performance results showed high Mn dissolution during the desorption step, which can lead to instabilities in the crystal lattice, making the material unsuitable for cyclic usage. To increase the chemical stability of the material by retaining high sorption capacity, this work focused on optimizing the hydrothermal synthesis. As described in chapter 5, this process can be mainly divided into hydrothermal autoclaving and calcination. Initially, the hydrothermal autoclaving step was optimized, followed by the calcination step, with each process evaluated in terms of reaction time and ideal reaction temperature. Successful improvements are considered to be an increase in sorption capacity and a reduction in Mn dissolution during the desorption step. Additionally, results from the master thesis of Tibor Feurer^[45] were used to examine influence of reaction parameters on the crystal structure of the sorbent.

Optimization of hydrothermal autoclaving step. In the hydrothermal autoclaving step 4 M LiOH were mixed with Mn_2O_3 , placed in an autoclave and heated for various time intervals (12 h, 18 h, 24 h) in a drying cabinet at various temperatures (120 °C, 180 °C, 220 °C). The parameters are listed in Tab. 5.1. The resulting intermediates are subsequently calcined at 400 °C for 4 h and activated by HCl treatment to obtain HMO-sorbent. Sorption tests were conducted by mixing 40 mL of LiCl solution ($c_{\text{Li}} = 143 \text{ mg L}^{-1}$) with 200 mg of HMO. After 24 hours, the Li-depletion was determined and the sorption capacity was calculated. The Li-loaded sorbent LMO was mixed with 40 mL of 0.5 M HCl during the desorption step, and the concentrations of Li and Mn in the supernatant were determined. The Mn dissolution was calculated accordingly.

In Fig. 6.1a the sorption capacity as well as the Mn dissolution in the desorption step is

presented for experiments E1-E9 (Tab 5.1). An increase in temperature has been observed to coincide with an increase in the sorption capacity, while the Mn dissolution decreases. This suggests that high temperatures have a positive effect on the formation of the crystal lattice, resulting in better Li insertion and higher stability. This aligns with the findings of T. Feurer^[45], who investigated the influence of parameters from E1-E9 on the crystal structure and observed that reflections become sharper with increasing reaction temperature, as illustrated in Fig. 6.1b.^[45] Another effect that can be observed from Fig. 6.1a is that the

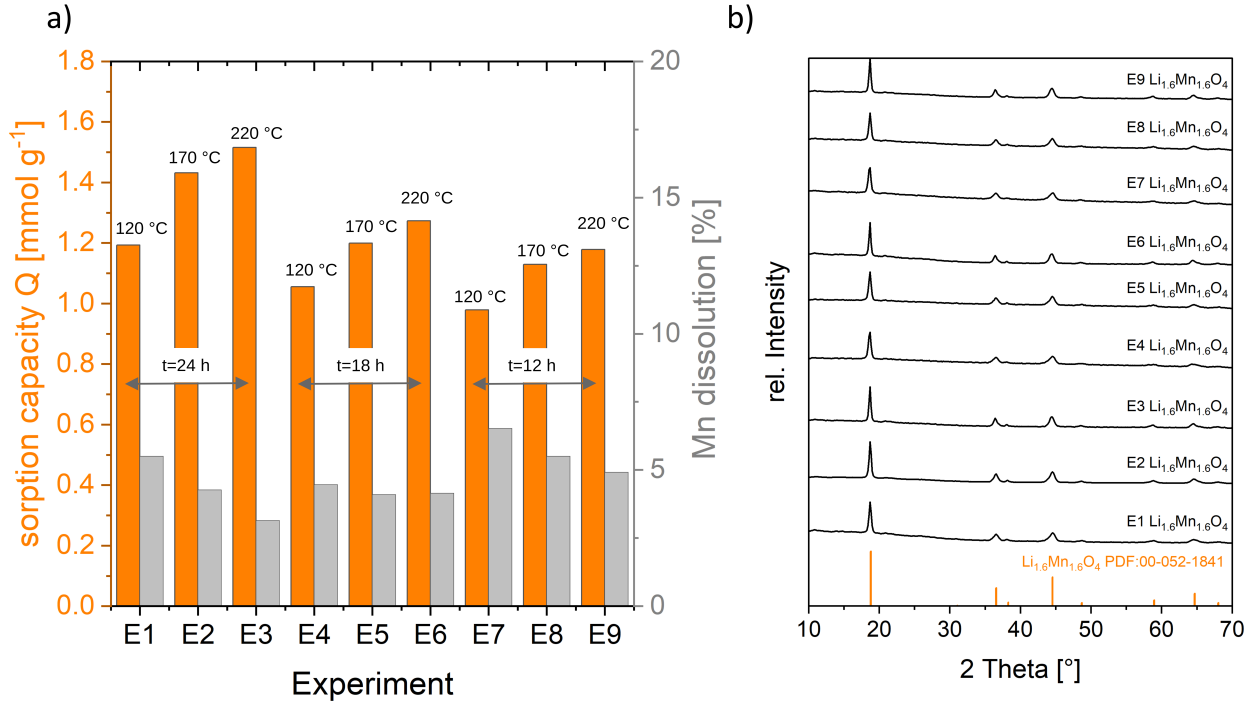


Figure 6.1: Optimization of hydrothermal autoclaving: a) sorption capacity and Mn dissolution of HMO sorbents obtained from E1-E9 b) XRD patterns of Li_{1.6}Mn_{1.6}O₄ obtained from E1-E9. Figure adapted from T. Feurer^[45].

sorption capacity increases with longer reaction times. This is also visible in the diffractogram (Fig. 6.1b), showing sharper reflections with increasing reaction time, suggesting higher crystallinity.^[45] The increase in sorption capacity, accompanied by a decrease in Mn dissolution, as well as sharper reflections in XRD with increasing reaction times, indicates that material continues to undergo structural transformation at reaction times below 24 hours. The highest sorption capacity (1.52 mmol g⁻¹) and the lowest Mn dissolution (3.1 %) were achieved in E3 with a temperature of T=220 °C and a reaction time of t=24 h. An improvement of 27 % was achieved regarding sorption capacity compared to the parameters used in the publication of Herrmann *et al.*^[58] (T=120 °C, t=24 h). Additionally, the Mn loss was significantly reduced from 5.5 % to only 3.1 %.

Optimization of calcination step. After optimal parameters for the hydrothermal autoclaving were established (T=220 °C and t=24 h), the calcination step was further optimized.

To this end, XRD data from T. Feurer^[45] were analyzed, sorption experiments were performed, and both sorption capacity and Mn release were quantitatively assessed.

Fig. 6.2a shows the XRD data of an in situ measurement presenting the transformation stages from LiMnO_2 to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at various calcination temperatures. It can be observed that at temperatures below 450 °C no fully conversion of LiMnO_2 to the target product $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ occurs. In contrast, at calcination temperatures of 450 °C and 500 °C, all re-

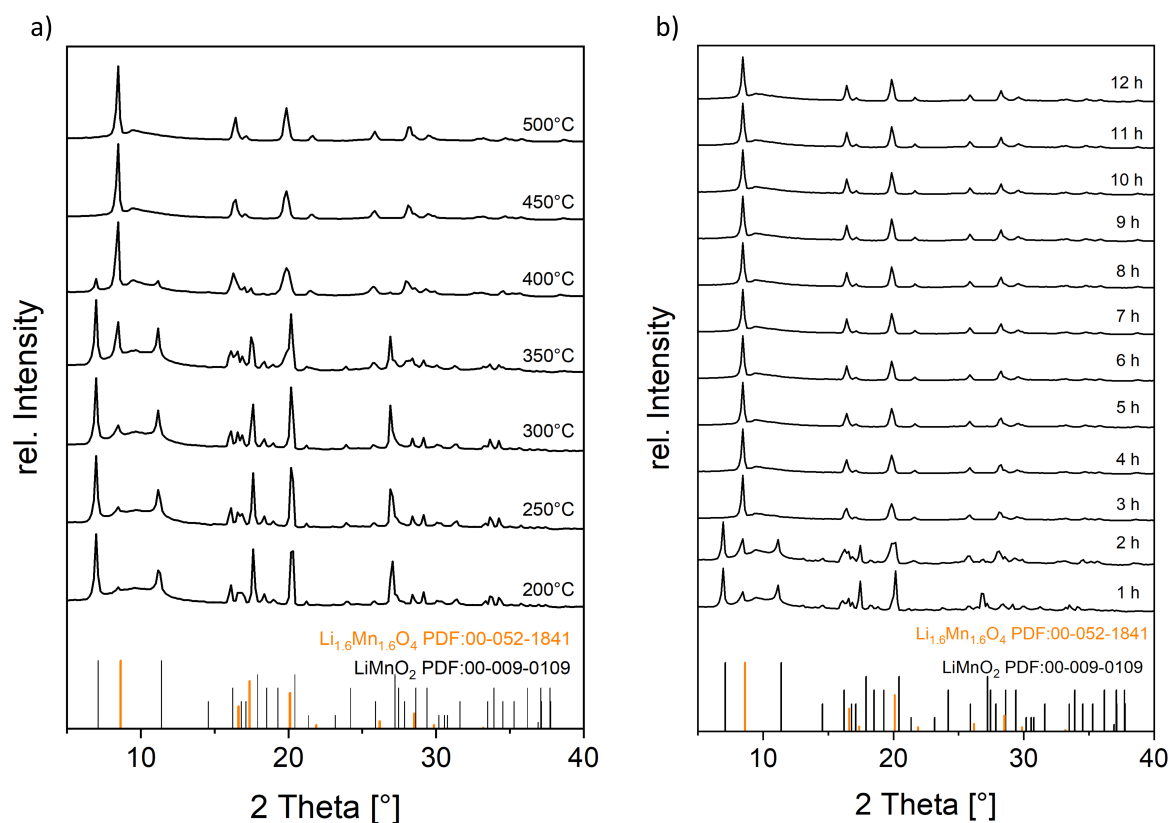


Figure 6.2: a) Transformation of LiMnO_2 to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at different calcination temperatures. b) Transformation of LiMnO_2 to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at 450 °C after different calcination times. Figure adapted from T. Feurer^[45].

flexions associated with LiMnO_2 disappear, and only the spinel phase reflections are visible, which match the reference of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (pdf: 00-052-1841). Therefore, 450 °C has been established as the optimal calcination temperature.

In the next step, the duration of the reaction was varied at a calcination temperature of 450 °C. An in situ XRD measurement was performed while maintaining the temperature for 12 hours, with a diffractogram recorded every hour (Fig. 6.2b). The diffractogram indicates that during the initial two hours, reflections corresponding to both phases LiMnO_2 and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ are observed. After 3 hours, the reflections associated with the LiMnO_2 phase disappear and in the subsequent hours, only minimal changes in the diffractogram are detected.

To identify the calcination duration that achieves highest sorption capacity and minimal

Mn release, sorption/desorption experiments were systematically performed for calcination times ranging from 3 to 7 hours. The results are presented in Fig. 6.3.

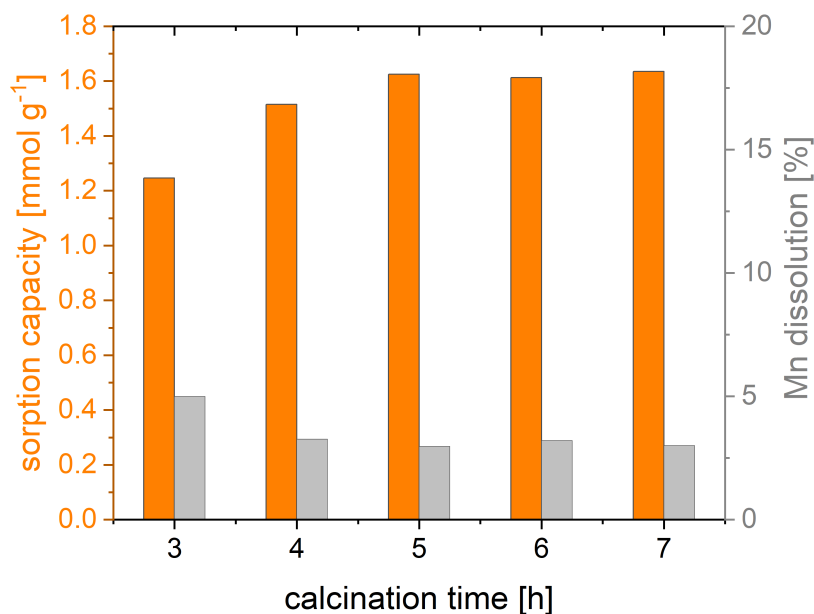


Figure 6.3: Sorption capacity and Mn dissolution for sorption experiments using HMO calcined for various time intervals.

Between 3 and 5 hours, an increase in sorption capacity accompanied by a decrease in Mn dissolution was observed. Beyond 5 hours, no further improvement in performance was detected. Consequently, optimized reaction parameters for LMO sorbent synthesis were established as 220 °C and 24 hours reaction time during the hydrothermal autoclaving step, followed by 450 °C and 5 hours reaction time during the calcination step. These optimized conditions resulted in a significant improvement in sorbent performance: the sorption capacity increased to a maximum of 1.62 mmol g⁻¹, while Mn release was reduced to 2.97 %.

6.2 Scale up: synthesis in spray drying process ¹

The use of the LMO sorbent at larger, potentially industrial, scale requires a synthesis route that is both scalable and yields a product with high chemical stability to enable long-term performance. The approaches of scaling up the hydrothermal synthesis using larger autoclaves led to an increase in the impurity phases in the material. This negatively affected performance, as indicated by reduced sorption capacity and increased Mn dissolution (Fig. A.1). In light of these findings, and because of a slow reaction time, the hydrothermal synthesis route is deemed unsuitable for scale-up and thus for large-scale production of the material. This work presents a newly developed synthesis method for the LMO sorbent that addresses the two critical requirements for industrial applicability: scalability and chemical stability.

Within the scope of this thesis, a novel synthesis route was developed that potentially enables continuous and high-throughput material production based on spray drying technology. Furthermore, to increase the chemical stability of the material and reduce Mn dissolution, a substitution approach was tested by the incorporation of a transition metal into the crystal structure. Therefore, Mn was partially substituted by titanium (less than 5 mol%) in the ion exchange materials. The influence on Li-sorption capacity as well as Mn dissolution was investigated. The following chapter is adapted from the publication of Herrmann *et al.*^[57]. The LMO sorbent with the target composition of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was synthesized using a two-step process, as detailed in Ch. 5.1.2 and schematically illustrated in Fig. 6.4. In the first step, a precursor was prepared by spray drying an aqueous solution containing manganese(II) acetate and lithium acetate. In the second step, the amorphous precursor needed to be transformed via calcination to spinel LMO (space group $Fd\bar{3}m$) with ion sieve properties. To identify a suitable calcination temperature for this transformation, thermogravimetric analysis of the precursor was conducted. Temperatures indicating phase transitions were identified and tested as calcination temperatures. After calcination at various temperatures, several LMO pristine sorbents were obtained and their crystal structure was analyzed using x-ray diffraction. A Rietveld refinement was performed to determine lattice parameters of the sorbents, to quantify the target phases, and to identify impurity phases. Furthermore, the particle morphology of the powder was investigated by scanning electron microscopy. The various materials were further activated through HCl treatment, converting them into their protonated form (HMO), and tested for their Li sorption capacity. LMO-450, identified as the most promising material, was further subjected to structural characterization using synchrotron XRD, magnetic measurements, and nuclear magnetic resonance spectroscopy. Finally, a Ti-substitution approach was also tested with this sorbent to further improve its

¹This chapter is based on the article by Herrmann *et al.* (2025)^[57], which is published under CC BY 4.0: Herrmann, L., Bohn, N., Pfau, A., Kölbel, T., Ehrenberg, H., Binder, J., Jeschull, F. (2025). Synthesis of Lithium Manganese Oxide and Ti-Substituted LMO Sorbents for Lithium Extraction in a Spray-Drying Process. *ChemSusChem*, 18: e202500530. <https://doi.org/10.1002/cssc.202500530>

material properties.

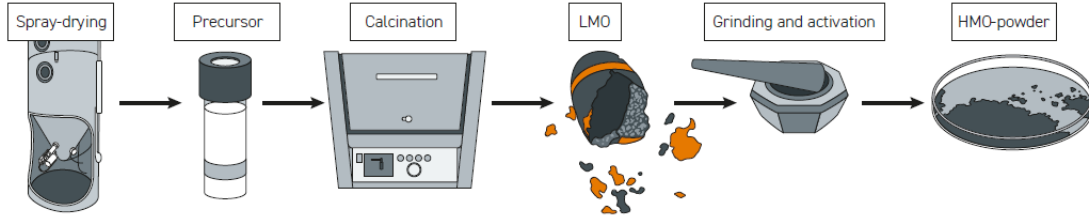


Figure 6.4: Steps for the synthesis of the LMO sorbent material: Spray drying of aqueous solution containing Li- and Mn-salts as well as an optional doping agent, calcination of spray dried precursor to receive LMO pristine, grinding and activation to obtain HMO-pristine sorbent. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Thermogravimetric analysis (TGA) & Differential scanning calorimetry (DSC).

The thermogravimetric and differential scanning calorimetry analyses of the precursor (Fig. 6.5) reveal a multi-step decomposition process. An initial minor mass loss of approximately 2 % is observed around 100 °C, corresponding to the evaporation of residual water. The DSC profile indicates an exothermic event at 163 °C, followed by two endothermic transitions at 203 °C and 237 °C, none of which are associated with further mass loss.

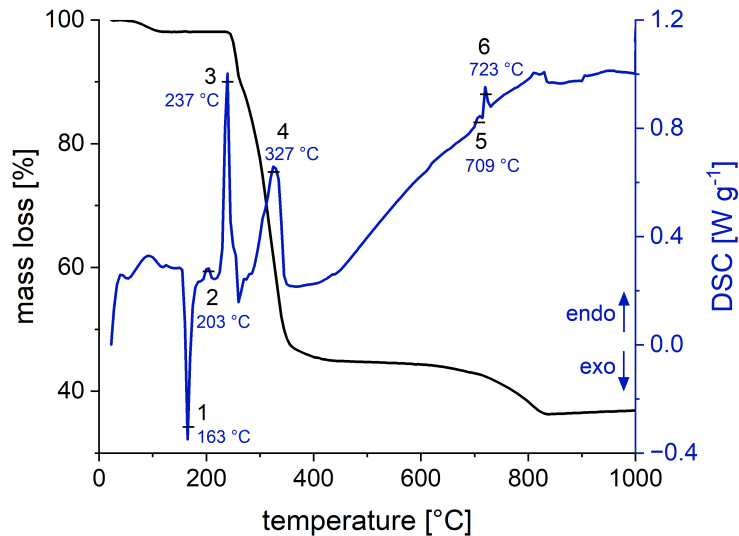


Figure 6.5: TGA of LMO precursor: Analysis of mass loss and heat flow during heating. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

The onset of major decomposition occurs above 250 °C and continues up to approximately 420 °C, accompanied by a substantial mass loss of about 55 %. The DSC signal exhibits pronounced tailing toward lower temperatures, suggesting an acceleration of decomposition with increasing temperature. This stage corresponds to the thermal degradation of organic components and the formation of the oxide phase, which remains stable with negligible mass change up to 700 °C. Subsequently, two distinct phase transitions are observed at 709 °C

and 723 °C, followed by an additional decomposition step (≈ 800 °C), resulting in a further mass loss of approximately 8 %. Based on these findings, calcination temperatures of 720 °C, and 800 °C were selected for the second step of the sorbent synthesis. In addition to the temperatures identified from the TGA analysis, a calcination temperature of 450 °C was selected, as this temperature was previously identified in this research as optimal for calcination step in the hydrothermal synthesis (Ch. 6.1). In addition, a stepwise calcination procedure involving sequential heating at 450 °C and 720 °C was applied. The duration of calcination was fixed at 5 hours, according to earlier reports by Chitrakar *et al.*^[27] and the findings of this work (Ch. 6.1).

Chemical composition and stoichiometry. The stoichiometric composition of the synthesized LMO compounds subjected to varying calcination conditions was investigated by digesting the materials and measuring the corresponding Li- and Mn-concentration in the solution using ICP-OES analysis. The calculated chemical formula of the sorbents is presented in Tab. 6.1. All sorbents are close to the target composition of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ with small deviations. At the lowest calcination temperature of 450 °C, the Li/Mn ratio was marginally higher (1.02) compared to the values observed at elevated calcination temperatures (0.98).

Structural analysis by x-ray diffraction and synchrotron measurements. XRD analysis was performed to analyze the crystal structure of sorbents calcined at various temperatures. The diffractograms of the pristine LMO and HMO samples are presented in Fig. 6.6a and Fig. 6.6b, respectively. The diffraction patterns of all LMO samples show the characteristic reflections of the spinel LMO with $Fd\bar{3}m$ space group. With increasing calcination temperatures, additional reflections emerge, with their intensity increasing as the temperature rises. These reflections are attributed to the formation of a secondary phase, a layered oxide with a monoclinic superstructure. This layered oxide phase corresponds to the composition Li_2MnO_3 , representing a lithium-rich phase (space group $C2/m$). The prepared LMO samples were subsequently activated by dispersing the powders in a 0.5 M HCl solution to obtain the sorbent HMO (Eq. 2.11).

The corresponding XRD patterns are shown in Fig. 6.6b. It can be observed that pickling generally causes a shift of the spinel reflections to higher angles, indicating a reduction in the lattice parameter. Notably, the Li-free HMOs derived from LMO-450, LMO-720 and LMO-720-450 exhibit only the spinel phase, with no evidence of the layered phase, suggesting that the HCl treatment selectively dissolves the Li_2MnO_3 impurity. Among the samples, HMO-800 is the only material that retains residual phase impurities after pickling. To quantify the phase fractions of $Fd\bar{3}m$ and $C2/m$, as well as to calculate the lattice parameters, a Rietveld refinement was performed (Fig. A.2). For LMO-450, the resolution obtained with $\text{Cu-K}\alpha$ or $\text{Mo-K}\alpha,1$ radiation was insufficient. Therefore, both LMO-450 and its protonated form HMO-450 were analyzed using synchrotron radiation to achieve higher resolution (Fig. 6.7).

Table 6.1: Synthesis parameters of the sorbent material including calcination time and temperature. Experiments were conducted using a buffered LiCl solution ($c_{Li} = 143 \text{ mg L}^{-1}$, $c_{NaOAc} = 1.5 \text{ g L}^{-1}$, $\text{pH} = 7.4$). Characterization of the sorbents: Lattice parameter (LP) of LM(T)O and HM(T)O, the calculated chemical formula (error Li: 0.8 %; Mn: 0.8 %), sorption capacity Q_{Sorb} and BET surface area. Table adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Sample	T_{calc} [°C]	t [h]	Lattice parameter LM(T)O [Å]	Lattice parameter HM(T)O [Å]	Calc. chemical formula	Q_{sorb} [mmol g ⁻¹]	Q_{sorb} [mg g ⁻¹]	BET [m ² g ⁻¹]
LMO-800	800	5	8.224	8.071	Li _{1.6} Mn _{1.64} O _{4-δ}	0.39	2.71	1.40
LMO-720	720	5	8.174	8.072	Li _{1.6} Mn _{1.64} O _{4-δ}	1.21	8.40	2.90
LMO-720-450	720, 450	5 h each	8.181	8.067	Li _{1.6} Mn _{1.63} O _{4-δ}	1.63	11.31	2.26
LMO-450	450	5	8.145	8.079	Li _{1.6} Mn _{1.57} O _{4-δ}	2.03	14.10	2.60
LMTO-450	450	5	8.155	8.067	Li _{1.6} Mn _{1.49} Ti _{0.04} O _{4-δ}	2.22	15.41	6.36

For LMO-450, LMO-720, LMO-720-450, LMO-800 and HMO-800 a mixed-phase model comprising both spinel and layered structures was employed. The initial structural model for the spinel phase was based on ICDD 1514017 (space group $Fd\bar{3}m$), while the layered impurity phase Li_2MnO_3 was modeled using ICDD 1514044 (space group $C2/m$). For x-ray data of HMO-450, HMO-720 and HMO-720-450 a single-phase spinel structure based on ICDD 1514017 (space group $Fd\bar{3}m$) was assumed. From the Rietveld refinement, it can be

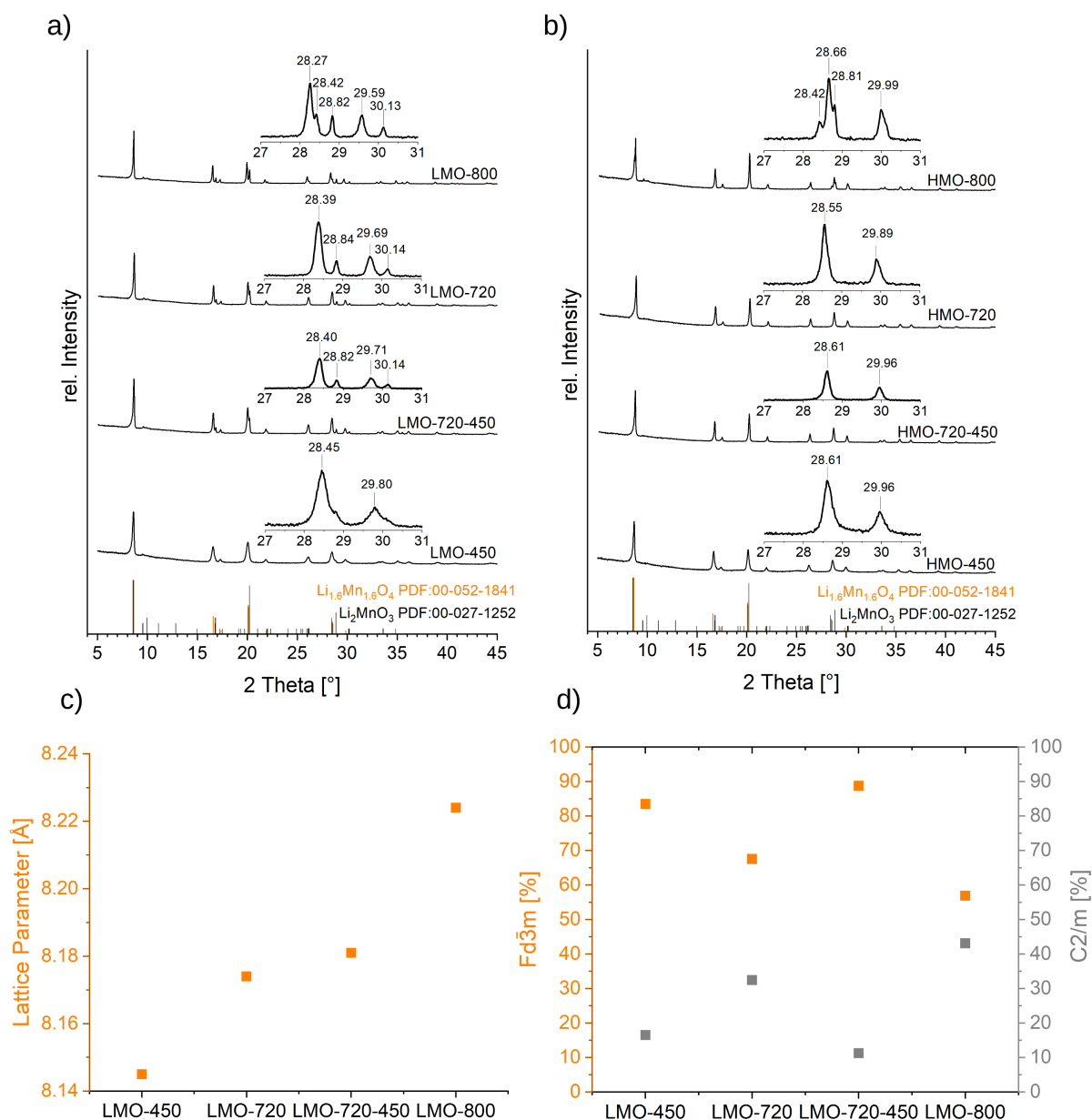


Figure 6.6: X-ray diffraction patterns of (a) LMO and (b) HCl-treated HMO synthesized at different calcination temperatures. (c) Lattice parameter and (d) phase fraction of $Fd\bar{3}m$ and $C2/m$ for sorbents calcined at various temperatures. The data was obtained through Rietveld refinement of the x-ray data (LMO-720, LMO-720-450 and LMO-800) and synchrotron data (LMO-450). Figure adapted from Herrmann et al. 2025.^[57] Licensed under CC BY 4.0.

seen that for the spinel phase, the lattice parameter increases with increasing calcination temperatures, as presented in Fig. 6.6c. For LMO-450, a lattice parameter of 8.145 Å was calculated that matches well the cubic spinel structure of the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ reference pattern (pdf 00-052-1841) with a $Fd\bar{3}m$ space group, which is the target phase of this synthesis.^{[27][23]} Meanwhile, for LMO-720 a lattice parameter of 8.174 Å was determined, while the one for LMO-800 was calculated as 8.224 Å. Parallel to the increase in the

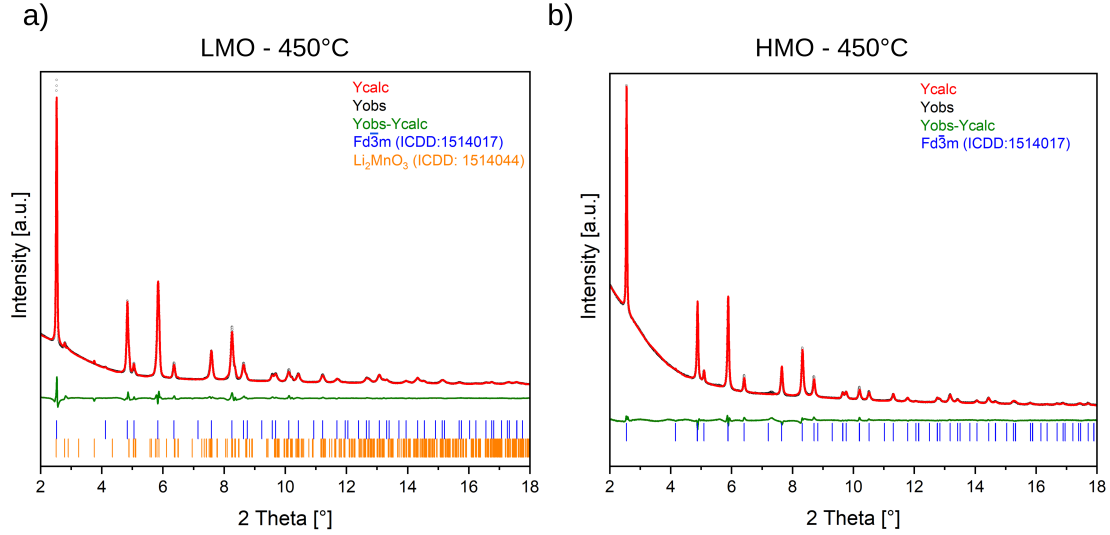


Figure 6.7: Rietveld Refinement of synchrotron data for (a) LMO-450 and (b) activated HMO-450.

temperature of calcination, a growth of the layered impurity phase Li_2MnO_3 is observed (Fig. 6.6d). For LMO-450 a phase fraction of the spinel with space group $Fd\bar{3}m$ of 83.5 % was calculated. In contrast, for LMO-720 only 67.5 % and for LMO-800 only 56.9 % of the powder can be attributed to the spinel phase. This aligns with findings reported by Paulsen *et al.*,^[99] which report that at a specific temperature T_C (Ch. 2.4.3), a cation-mixed spinel $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ decomposes into a spinel with a reduced x value and Li_2MnO_3 .^[99] The impurity phase Li_2MnO_3 is characterized as being particularly rich in lithium. The progressive formation of the Li-rich layered oxide at higher temperatures depletes the spinel phase of lithium leading to a reduction in lithium occupancy at the manganese sites which can explain the expansion of lattice parameter as previously reported in the literature.^{[11][10][3]} For the stepwise calcined material LMO-720-450, the lowest overall fraction of Li_2MnO_3 was observed (11.3 %), along with a lattice parameter of 8.177 Å.

Subsequently, the protonated materials (HMO) were analyzed using Rietveld refinement. A reduction in lattice parameters was identified for all protonated materials compared to their Li-rich derivatives. Specifically, for HMO-450, the lattice parameter decreased from 8.145 Å (LMO-450) to 8.079 Å. This value is slightly higher than the lattice parameter of the target composition $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ with 8.05 Å, as reported by Chitrakar *et*

al.^[27] This reduction is caused by the removal of Li^+ and the smaller H^+ ions that replace it, leading to lattice contraction. Furthermore, Rietveld refinement revealed that although no impurity phases were detected in HMO-450, HMO-720, and HMO-720-450, the impurity phase fraction for HMO-800 was still 39.5 % after pickling. This may be attributed to the fact that the pristine LMO-800 exhibited the highest level of impurities among the other sorbents and Li_2MnO_3 was not completely removed during acid treatment.

Particle characterization. Fig. 6.8a displays the SEM micrographs of LMO calcined at 450 °C, while Fig. 6.8b illustrates the morphology of the HCl-treated sorbent HMO-450. For both LMO and HMO calcined at 450 °C, the majority of particles exhibit sizes below 150 nm (Fig. A.4). The treatment of the sorbent with 0.5 M HCl only slightly affects the particle size. Despite the identification of 16.5 % Li_2MnO_3 as a secondary phase via Rietveld refinement in LMO-450, this phase is not optically distinguishable from the main LMO phase in SEM micrographs. This may be attributed to the relatively low calcination temperature, potentially resulting in small crystal sizes for the Li_2MnO_3 compared to higher calcination temperatures.

Fig. 6.8c and 6.8d compare the morphologies of LMO and HMO materials subjected to stepwise calcination at 720 °C and 450 °C. SEM micrographs of the LMO-720-450 sample reveal spherical particles smaller than 150 nm distributed across larger octahedral crystals, which can reach up to 1 μm in size. After pickling, only small crystals remain visible, while the larger ones appear to be dissolved. XRD analysis confirms that the Li_2MnO_3 phase is removed during the HCl treatment, suggesting that the large crystalline particles observed prior to pickling correspond to the Li_2MnO_3 phase. Interestingly, although Rietveld refinement indicates a slightly lower fraction of Li_2MnO_3 in LMO-720-450 compared to LMO-450, the layered structure is more clearly visible in the SEM image. This may be attributed to the higher calcination temperature of 720 °C, which likely promotes its crystal growth. Fig. 6.8e and Fig. 6.8f present SEM micrographs of HMO powders obtained after pickling LMO-720 and LMO-800. While HMO-720 (Fig. 6.8e) exhibits a morphology similar to HMO-720-450, minor residuals of the Li_2MnO_3 phase are visible as larger crystalline particles. Continually, the HMO-800 powder (Fig. 6.8f) contains the highest fraction of residual Li_2MnO_3 phase, despite undergoing treatment with 0.5 M HCl, which aligns with the Rietveld refinement results.

For all materials, an increase in particle size is observed with rising calcination temperatures. This trend aligns with XRD measurements, which indicate smaller crystallite sizes at lower calcination temperatures, as evidenced by the broadening of diffraction peaks. The BET specific surface area (SSA) measurements further support these findings, showing an inverse relationship between the calcination temperature and the SSA. As the calcination temperature decreases, particle size reduces, leading to an increase in SSA. For instance, the

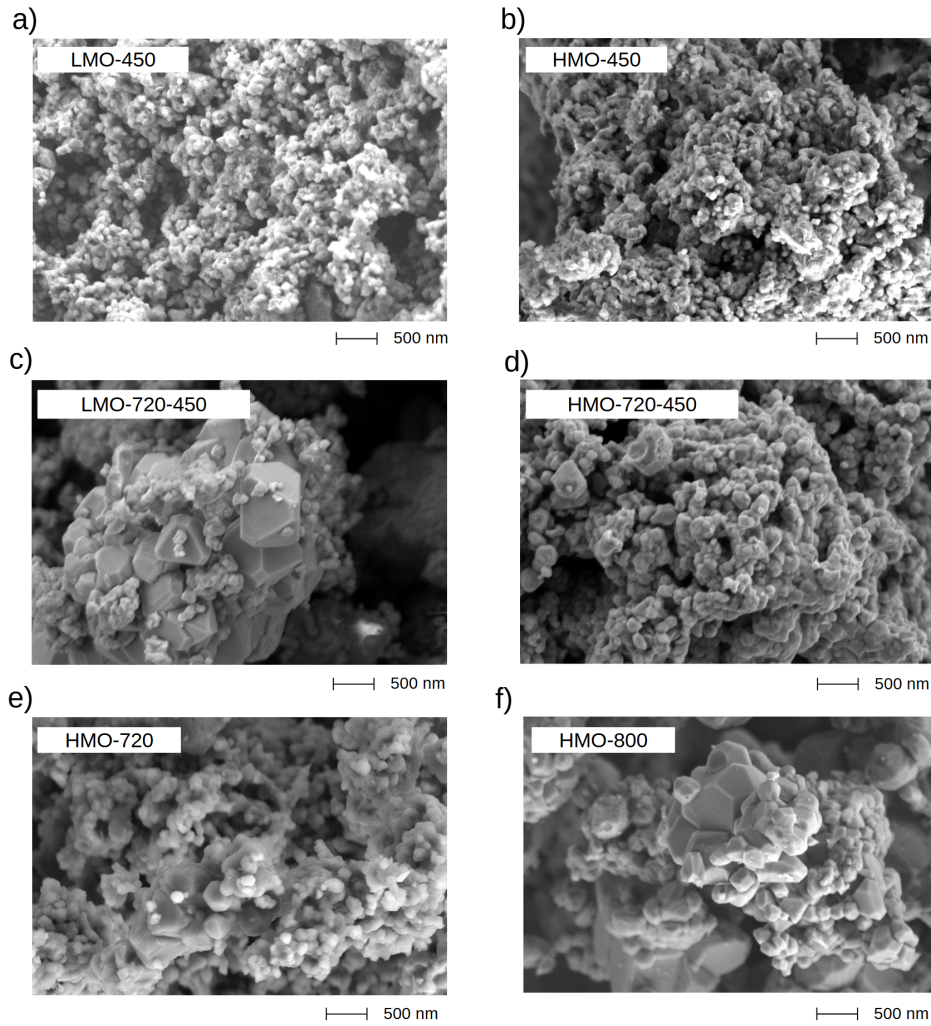


Figure 6.8: a) SEM of LMO pristine prepared at calcination temperature of 450 °C. b) SEM of HMO calcined at 450 °C after pickling. c) SEM of LMO pristine prepared at step-wise calcination at 720 °C followed by 450 °C. d) SEM of HMO prepared at step-wise calcination at 720 °C and 450 °C after pickling. e) SEM of HMO calcined at 720 °C after pickling. f) SEM of HMO calcined at 800 °C after pickling. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

LMO sample calcined at 450 °C exhibits an SSA of $2.60 \text{ m}^2 \text{ g}^{-1}$, whereas the SSA decreases to $1.40 \text{ m}^2 \text{ g}^{-1}$ for the sample calcined at 800 °C. The BET SSA values are summarized in Tab. 6.1. Additional details regarding the BET analysis parameters are provided in Tab. A.1, with corresponding isotherm linear plots and BET surface area curves shown in Fig. A.5 and Fig. A.6.

Ion exchange capabilities. The calcined LMO samples were evaluated for their lithium sorption performance. Following activation, the protonated HMO materials were suspended in a synthetic LiCl solution ($c_{\text{Li}} = 143 \text{ mg g}^{-1}$). The ion exchange capacity was determined by measuring the change in Li^+ concentration between the initial LiCl solution and the

supernatant after separating the sorbent. In this experiment, as well as in most subsequent tests, a buffering agent (sodium acetate, NaOAc) was added to the LiCl solution to form an acetate buffer in situ during the ion exchange process with HMO. This buffer was deemed essential, as the pH of the Li⁺-rich solution would rapidly decrease to acidic levels, thereby stopping the ion exchange process. The acetate buffer stabilized the pH to values characteristic of geothermal brines. Further details regarding the pH dependency of the ion exchange process are discussed in the following sections.

The sorption capacities obtained in this experiment are summarized in Tab. 6.1, with the highest capacity observed for LMO-450 ($Q_{Sorb} = 14.1 \text{ mg g}^{-1}$). The sorption capacity decreased progressively with increasing calcination temperature, reaching a notably low value for LMO-800 ($Q_{Sorb} = 2.71 \text{ mg g}^{-1}$).

Although the SSA of LMO-450, LMO-720, LMO-720-450 showed only minor variations, their sorption capacities differed significantly. The results suggest that lithium uptake is only marginally influenced by particle size. Instead, the diminished sorption performance is likely attributable to differences in the structural characteristics at the crystallographic level, such as variations in crystallinity and lattice parameters.

NMR measurement. LMO-450 was selected for detailed structural investigations due to its favorable crystallographic properties and high lithium sorption capacity. The overall chemical formula was determined to be $\text{Li}_{1.6}\text{Mn}_{1.57}\text{O}_4$, closely matching the target spinel composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (PDF 00-052-1841).^{[27][23]}

However, Rietveld refinement revealed the presence of 16.5 % Li_2MnO_3 as a secondary phase and a dominant spinel phase with $Fd\bar{3}m$ space group. Since Li_2MnO_3 is a lithium-rich layered compound, its presence implies that the spinel phase must be correspondingly lithium-deficient. This lithium deficiency in the spinel phase can be expressed by the general formula $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, with $x < 0.6$, indicating a reduced lithium occupancy of the 16d sites.

However, due to the high degree of structural similarity among various Li–Mn–oxide phases, particularly in their x-ray diffraction patterns, precise phase determination is not possible. To overcome these limitations and to gain deeper understanding of the local lithium environments, a ⁷Li MAS NMR spectroscopy was employed as a complementary technique. This approach enables the differentiation of lithium sites and provides further clarity regarding the nature and distribution of the coexisting Li–Mn–oxide phases. In addition, the protonated sorbent HMO was analyzed to see the remaining Li content in the material.

The NMR spectra of the LMO and HMO samples are depicted in Fig. 6.9. The peak positions, phase assignments, and corresponding area fractions of LMO-450 are shown in Tab. 6.2. For LMO-450, a weak resonance at 510 ppm is observed, corresponding to

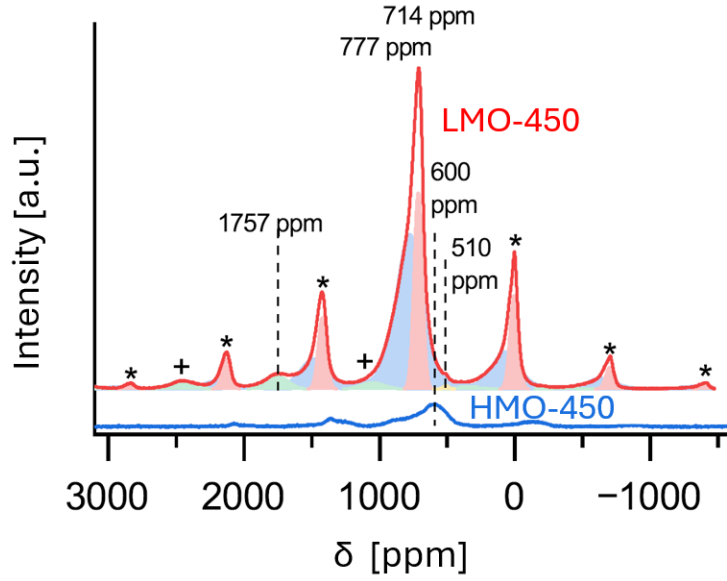


Figure 6.9: ^7Li MAS NMR spectra for the pristine LMO-450 and sorbent HMO-450. Phase-specific signal contributions are represented by colored integration areas in the NMR spectrum. Spinning sidebands are denoted by asterisks (*) and plus symbols (+). Figure adapted with permission from *Gamba et al.*^[46]

Table 6.2: ^7Li MAS NMR peak positions, phase assignments, and corresponding area fractions of LMO-450

Peak-position [ppm]	Phase	Area fraction [%]
510	LiMn_2O_4	0.14 % (yellow)
750	→ 714	29.5 % (red)
	→ 777	64.8 % (blue)
1754	$\text{Li}_4\text{Mn}_5\text{O}_{12}$	5.5 % (green)

LiMn_2O_4 , with an area fraction of only 0.14 %. The most intense signal appears at 750 ppm and exhibits noticeable asymmetry, which can be deconvoluted into two overlapping peaks at 714 ppm and 777 ppm. The broad resonance at 777 ppm, accounting for 64.8 % of the total signal, is assigned to the spinel phase $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ($\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$), a material known for its lithium ion sieve properties and Mn^{4+} oxidation state, making it a promising candidate for lithium extraction. The signal at 714 ppm is attributed to the layered phase Li_2MnO_3 , which was also identified by synchrotron x-ray diffraction as previously discussed. Rietveld refinement revealed that Li_2MnO_3 constitute 16.5 % of the sample. This corresponds to 14.3 % of the total Mn content being located within the additional Li_2MnO_3 phase. This result is in excellent agreement with the NMR analysis, which shows that 29.5 % of the overall lithium of the sample is associated with Li_2MnO_3 . Assuming a Li:Mn ratio of 2:1 in this phase, this corresponds to approximately 14.8 % of the total Mn, closely matching the value obtained from structural analysis. Furthermore, a minor resonance at 1757 ppm with

an area fraction of 5.5 % is also assigned to $\text{Li}_4\text{Mn}_5\text{O}_{12}$.

The pickled material HMO-450 was also investigated using ^7Li MAS NMR spectroscopy. The results show that lithium was effectively removed during activation, as evidenced by the fact that the HMO spectrum retains only 11 % of its original signal intensity, which corresponds to the remaining lithium content in the material. However, pickling did not completely remove lithium from the sorbent, which can limit the sorption capacity of the material.

Overall, NMR analysis provides the final piece of the puzzle in sorbent characterization. This allows the conclusion that the synthesized material predominantly consists of phase $\text{Li}_4\text{Mn}_5\text{O}_{12}$. In addition Li_2MnO_3 exists as impurity phase, which is removed after pickling. The capability of this material to extract lithium from Li-rich solutions, such as LiCl solution and natural geothermal brines, will be examined in detail in Chapter 7.

Magnetic measurement. Manganese in spinel structures can adopt multiple oxidation states, which significantly influence the chemical stability of the material. In particular, oxidation states below Mn^{4+} can lead to Mn dissolution during cyclic operation, mainly due to disproportionation reactions (Eq. 2.12) and the Jahn-Teller effect (Ch. 2.4.3).^[47] This process results in the loss of active material and a gradual decline in performance over time. Therefore, maintaining a manganese oxidation state of Mn^{4+} is essential to ensure long-term stability and functionality of the sorbent. To determine the oxidation state of Mn in pristine LMO-450 and pristine HMO-450, magnetic measurements were conducted.

Figure 6.10a shows the susceptibility χ versus temperature for both samples, measured in a magnetic field of 1000 Oe. At elevated temperatures (approximately 300 K), both samples exhibit nearly identical magnetic susceptibility values, which can be attributed to their comparable effective magnetic moments (see Curie–Weiss fit). In contrast, at lower temperatures, the LMO sample displays significantly higher susceptibility than the HMO sample. This difference arises from a change in the dominant magnetic coupling: while LMO is characterized by dominant ferromagnetic coupling (Weiss constant $\theta > 0$), HMO exhibits dominant antiferromagnetic coupling ($\theta < 0$). The temperature dependence of the inverse susceptibility (Fig. 6.10b) has been analyzed using the Curie–Weiss law (Eq. 6.1).

$$\chi^{-1} = C^{-1} (T - \theta) \quad (6.1)$$

The Curie–Weiss fits were performed in the temperature ranges of 100–300 K for LMO and 200–300 K for HMO. From the extracted Curie constants of $C=1.801(1) \text{ cm}^3 \text{ K mol}^{-1}$ and $C=1.740(4) \text{ cm}^3 \text{ K mol}^{-1}$ for LMO and HMO, respectively, effective magnetic moments of $3.80(1) \mu_B$ and $3.73(4) \mu_B$ were determined. These values are only slightly below the theoretical spin-only moment of $3.87 \mu_B$ for a spin state of $S=\frac{3}{2}$, indicating a manganese

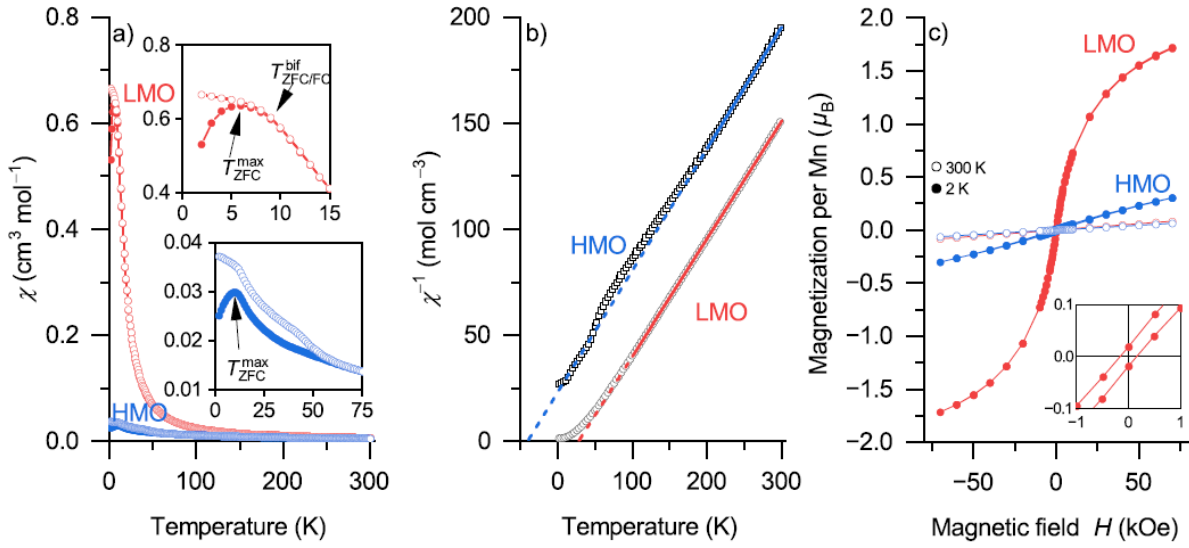


Figure 6.10: (a) Susceptibilities versus temperature for two distinct methods of zero field cooling (ZFC) and field cooling (FC), (b) inverse susceptibility as a function of temperature. (c) Full loop magnetization versus magnetic field scans with the inset showing an enlarged section around the origin for sample LMO at 2 K. Figure reproduced with permission from Schwarz *et al.*.^[114]

oxidation state close to +4 in both samples. This corresponds to an $[\text{Ar}]3d^3$ electronic configuration, resulting in three unpaired electrons ($S=\frac{3}{2}$) in octahedral coordination. For LMO, a positive Weiss constant $\theta=36(1)$ K was obtained, indicating dominant ferromagnetic interactions. This value was calculated by applying a linear interpolation method to account for the contribution of the Li_2MnO_3 secondary phase (Schwarz *et al.*^[114]), and is consistent with previous findings by Masquelier *et al.*^[87]. The dominant ferromagnetic coupling for LMO is further supported by the magnetic susceptibility curves, which show significantly higher values at low temperatures compared to HMO. Additionally, the bifurcation of the ZFC and FC branches at the Curie temperature of 9.0(5) K is characteristic of the onset of ferro-/ferrimagnetic ordering, confirmed by the s-shaped magnetization vs. field curve (Fig. 6.10c). In contrast, the HMO sample, consisting exclusively of the $\text{H}_4\text{Mn}_5\text{O}_{12}$ phase, exhibits a negative Weiss constant $\theta=-40(1)$ K. The negative Weiss constant reflects dominant antiferromagnetic interactions. This is further supported by the magnetization versus field scan for HMO, which exhibits a linear dependence on the magnetic field, which is typical for antiferromagnetic order. Although the Mn oxidation state remains close to +4 in both $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (main phase in LMO) and $\text{H}_4\text{Mn}_5\text{O}_{12}$ (HMO), the dominant magnetic coupling changes from dominant ferromagnetic to dominant antiferromagnetic. In $\text{Li}_4\text{Mn}_5\text{O}_{12}$, ferromagnetic $90^\circ \text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ superexchange couplings prevail over antiferromagnetic couplings of direct d-orbital overlap. Upon ion exchange, the lattice parameters slightly decrease from $\text{Li}_4\text{Mn}_5\text{O}_{12}$ to $\text{H}_4\text{Mn}_5\text{O}_{12}$, enhancing the direct overlap of the d-orbitals and ultimately leading to dominant antiferromagnetic coupling in $\text{H}_4\text{Mn}_5\text{O}_{12}$.

It can be concluded that both LMO and HMO samples contain manganese in the oxidation state Mn^{4+} , which represents a beneficial structural condition for ensuring chemical stability of the sorbent material.

Ti^{4+} substitution. Experiments conducted with the spray dried HMO material demonstrated a reduction in Mn dissolution compared to the hydrothermally synthesized sorbent. However, there was still Mn dissolution observed, which limits the long-term stability of the material. In a previous study of Gao *et al.* it was demonstrated that, in addition to Mn^{4+} , a small fraction of Mn^{3+} is present in $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, which contributes to Mn dissolution.^[47] Disproportionation reactions (Eq. 2.12) result in the formation of water-soluble Mn^{2+} , leading to an irreversible loss of sorbent material. Furthermore, the presence of Mn^{3+} in LMO is associated with the Jahn-Teller effect, which compromises structural stability.^[102] By substituting a small fraction of Mn^{3+} , these detrimental effects can be significantly suppressed, thereby improving the structural integrity of the material.

To address this issue and further improve the chemical stability of the spray dried material, a substitution strategy was considered. Several transition metals of similar atomic radii, including iron,^{[103][26]} aluminum,^[101] cobalt,^[103] nickel,^[103] and combinations such as iron and aluminum^[54] have already been tested for this purpose in previous studies. Furthermore, in related battery materials, replacing Mn(IV) with Ti(IV) has been shown to significantly improve the long-term stability of Mn-based cathodes.^[120] Within the scope of this thesis, Ti^{4+} was selected as the substituent due to its ionic radius (0.605 Å), which closely matches that of high-spin Mn^{3+} (0.645 Å)^[53], ensuring compatibility with the original lattice structure. Thereby, the incorporation of only a few mol% of the substituent proved effective in stabilizing the host lattice.^{[26][158][44]}

In this work, a target molar Li/Ti ratio of 32 and a Ti/Mn ratio of 0.032 were chosen. Ti^{4+} was incorporated into the precursor by first preparing a solution of titanium tetraisopropoxide and acetic acid, which was subsequently mixed with Mn- and Li-acetate solutions to ensure thorough mixing of the transition metals. This process yielded a homogeneous Li-Mn-Ti precursor after spray drying. As 450 °C was previously identified as the optimal calcination temperature for the LMO sorbent, this temperature was also selected for the present synthesis approach. Following calcination at 450 °C, a black powder was obtained, designated LMTO. Subsequently, the material was digested, and Li/Mn and Li/Ti ratios of 1.07 and 36.2, respectively, were determined, which served as the basis for the derivation of the chemical formula $\text{Li}_{1.6}\text{Mn}_{1.49}\text{Ti}_{0.04}\text{O}_4$. The BET specific surface area of LMTO was determined to be 6.36 m² g⁻¹, which is more than twice as high as that of the Ti-free LMO-450 material calcined at the same temperature. Subsequently, LMTO was treated with 0.5 M HCl to convert it into its protonated form, HMT0, which can be used

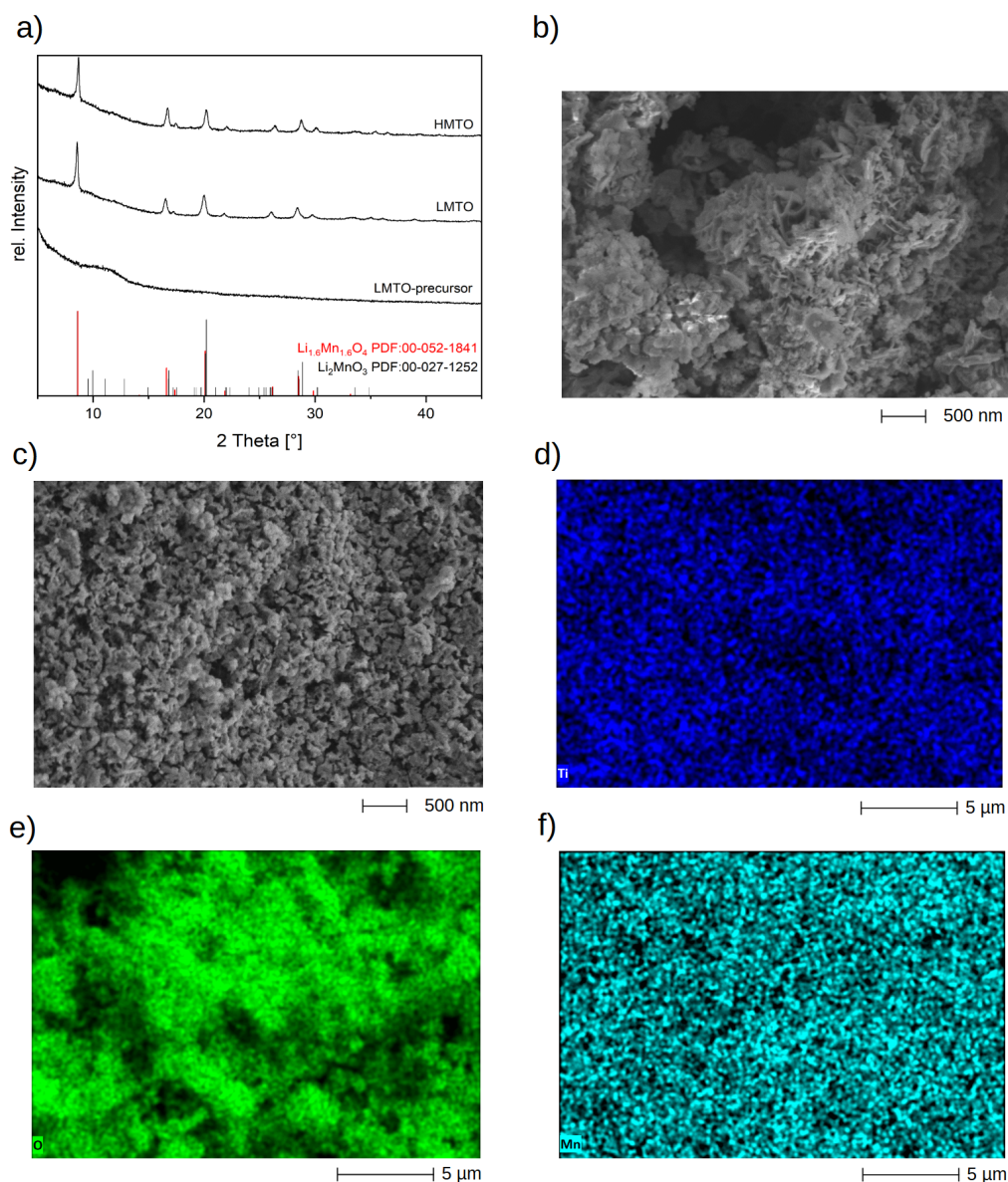


Figure 6.11: a) X-ray diffraction patterns of the LMTO precursor, pristine LMTO and activated HMTO. SEM micrographs of the as-prepared LMTO and activated HMTO powders are shown in b) and c), respectively. The elemental distribution in the LMTO powder is shown for Ti (d), O (e) and Mn (f). Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

for Li-extraction.

Subsequent structural characterization was performed using XRD to examine the crystallographic properties of the material. Fig. 6.11a presents the XRD patterns of the Li-Mn-Ti precursor, the calcined LMTO, and the activated HMTO, with the precursor exhibiting an amorphous structure with a broad background. The diffraction pattern of LMTO corresponds to a cubic spinel structure with the $Fd\bar{3}m$ space group. Notable

similarities can be observed between the material and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (pdf 00-052-1841). The lattice parameter of LMTO was determined to be 8.155 Å, which is slightly larger than that of LMO (8.145 Å), consistent with a slight shift of the reflections to lower angles.

The XRD pattern of the HMT0 revealed a shift of reflections to higher angles and a reduction in the lattice parameter to 8.067 Å, which is smaller than the Ti^{4+} -free $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (HMO, 8.079 Å). This reduction of the lattice parameter indicates an ion exchange process, in which lithium ions are removed from the structure and replaced by smaller protons (Eq. 2.11), leading to a contraction of the crystal lattice. In a next step the morphology and composition of the Ti-substituted LMTO material was investigated by SEM and EDX analysis. Fig. 6.11b presents an SEM image of the pristine LMTO. SEM analysis revealed the presence of small particles with platelet-like structures, exhibiting diameters in the range of approximately 50 nm to 200 nm. After the activation step (Fig. 6.11c), these platelet-like shapes were no longer observed. The activated HMT0 displayed more uniform, predominantly spherical particles, along with a narrower particle size distribution. Complementary EDX mapping (Fig. 6.11d-f) further confirmed a homogeneous distribution of Ti (d), O (e), and Mn (f), demonstrating the effectiveness of the synthesis approach in achieving uniform elemental distribution.

Finally, the Ti-substituted sorbent was evaluated for its Li^+ sorption performance in a standard sorption experiment (Ch. 5.3). A sorption capacity of 15.41 mg g^{-1} was measured, which exceeds the capacities of the Ti^{4+} -free materials (2.71 mg g^{-1} to 14.1 mg g^{-1} , Tab. 6.1), indicating enhanced ion exchange behavior compared to LMO.

In summary, the material is considered promising due to the successful incorporation of titanium into the crystal structure, as no secondary phases could be detected by XRD. Additionally, it shows a higher sorption capacity compared to Ti-free materials. Based on these findings, the material is selected for a more detailed investigation of its lithium extraction performance as presented in Ch. 7.

6.3 Granulation of sorbent material

From the synthesis routes presented in this thesis, including hydrothermal synthesis and the spray drying process, a powdery product is obtained, with the majority of particles being smaller than 1 μm . However, this fine powder presents several disadvantages in terms of material handling. Laboratory experiments showed that the powder form limits the number of testable cycles due to material loss during solid-liquid separation after each sorption/desorption step. Additionally, in technical applications, the powder causes high pressure losses and filter clogging, rendering it impractical for industrial use. Therefore, it is necessary to convert the sorbent into a more suitable form. One objective of this thesis was the production of granulates to improve the handling properties of the sorbent and enhance its technical applicability, while aiming to preserve its sorption capacity to the greatest extent possible. The method of granulation was thoroughly investigated and optimized in detail in Matthias Maier's Master thesis, supervised by the author, and the ideal conditions identified were applied for further studies carried out within the scope of this thesis.^[86]

Morphology of granulated sorbent. For the preparation of granules, a slurry was prepared consisting of PVC, DMF, and PEG (200 g mol⁻¹). Activated HMO powder obtained by spray drying and calcined at 450 °C was added, resulting in a granulate with an active material content of 80 %. After slurry preparation, the slurry was dropped into water, where precipitation of PVC-granules was observed. Following the drying process, the granulates were collected. Fig. 6.12a shows a Schott bottle containing the granulates, which predominantly formed small spheres with an average diameter of approximately 1.5 mm. The slight deviations from a perfectly spherical shape can be attributed to the manual addition of slurry droplets that, despite careful handling, introduced minor inconsistencies. Upon visual inspection, the surface of the granulates appears smooth and sealed. To obtain more detailed information about the particle surface, an SEM image of the granulate surface was captured. The corresponding image is presented in Fig. 6.12b. Small pores (≈ 100 nm) and larger pores in the micrometer range can be observed. Small pores can be explained by the selection of a water-soluble solvent DMF, which causes phase inversion after contact with water. DMF escapes from the polymer, causing the droplets to form solid porous granulates. Large pores in the micrometer range are caused by the pore-former PEG and enable effective infiltration of water into the granulate structure.^[86]

In Fig. 6.12c a SEM image of the cross section of a granule is shown, which reveals a distinct gradient in pore size distribution from the center to the periphery. Large macropores (>100 μm) are observed in the core, while the pore size decreases progressively toward the outer shell, with pores in the sub-micrometer to nanometer range (down to 100 nm). This can be explained by a rapid exchange between DMF and water molecules takes place at the droplet surface, leading to instantaneous phase separation and the formation of a dense,

finely porous structure in the outer layer. In contrast, delayed solvent exchange in the droplet interior results in slower demixing and the development of larger pores. The accumulation of PEG in the core region may further promote macropore formation.

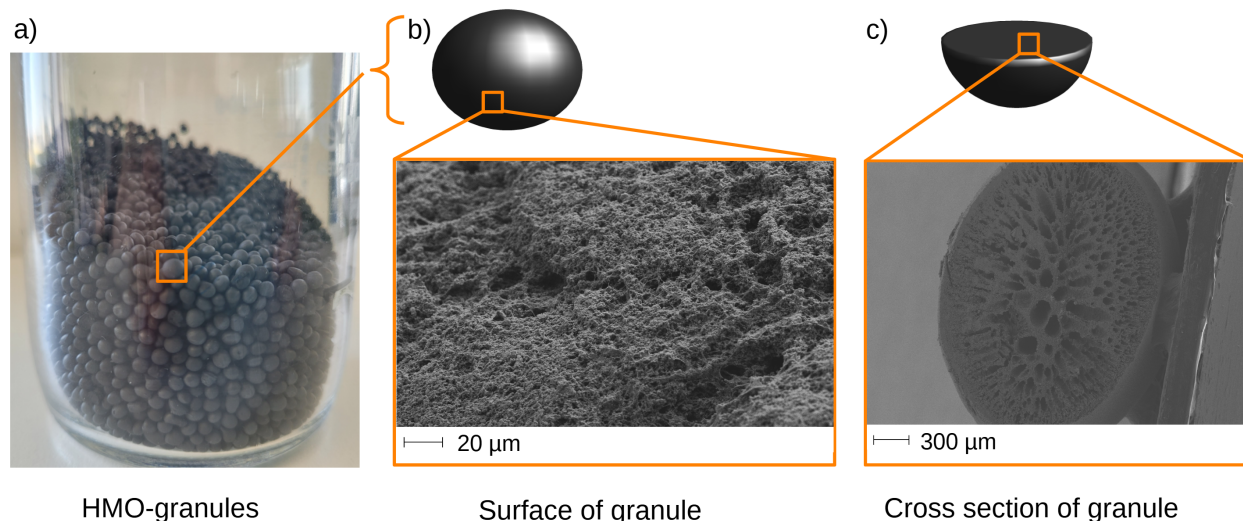


Figure 6.12: a) HMO granules after drying; b) SEM image of the granule's surface; c) cross section SEM image of granule.

Sorption/desorption experiment. Subsequently, the granules were tested in a standard sorption/desorption experiment (Ch. 5.3). Therefore, granules were mixed with buffered LiCl solution ($c_{Li}=143 \text{ mg L}^{-1}$, $c_{NaOAc}=1.5 \text{ g L}^{-1}$, $\text{pH}=7.4$) and stirred for 24 h. The Li-depletion of the brine was determined using ICP-OES and a sorption capacity was calculated according to Eq. 5.3. Afterwards, desorption was performed and the Mn dissolution of the material was calculated as an indicator for chemical stability of the material.

The results of the experiments including sorption capacity and Mn dissolution are presented in Fig. 6.13. Values for powdery sorbents obtained via hydrothermal synthesis and spray drying (with and without Ti substitution) are also included for comparison. The results represent the Li sorption per gram of active material, allowing better comparison of granule and powder values. For the granules, a maximum sorption capacity of 0.92 mmol g^{-1} (6.4 mg g^{-1}) was observed after sorption for 24 hours. This value is significantly lower than the sorption capacities of the LMO-powders (LMO-HS 1.61 mmol g^{-1} ; LMO-SD 2.03 mmol g^{-1} ; LMTO-SD 2.22 mmol g^{-1}). Since the active material LMO-SD is identical to the one in the granules, the reduction in sorption capacity can be attributed to the formulation process. One possible reason is that the active sites of the sorbent are partially covered by PVC, which prevents Li-insertion. Furthermore, the interaction between the active material and the Li-rich solution may be hindered by the characteristics of the pore system. Insufficient pore connectivity or limited permeability could restrict the effective transport of the solution to the reactive sites. Enhancing pore size or increasing pore

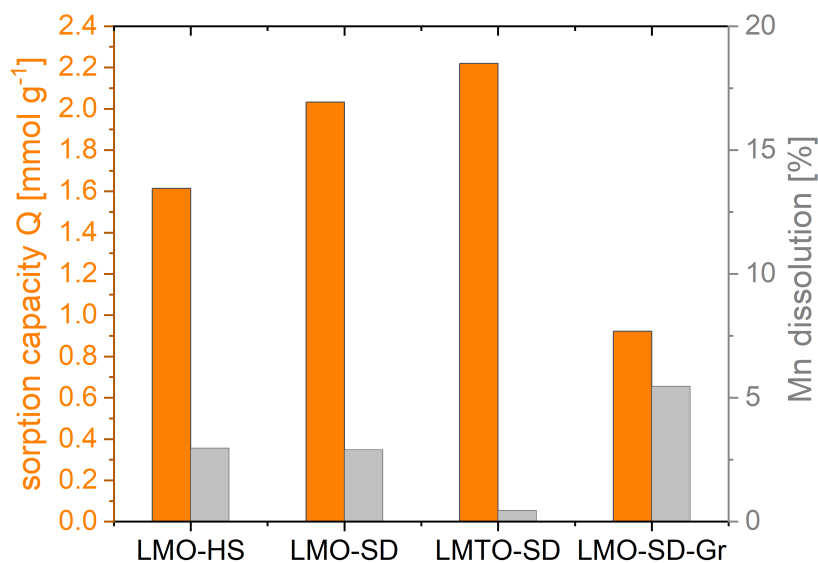


Figure 6.13: Sorption capacity and Mn dissolution of sorbents obtained from hydrothermal synthesis (LMO-HS), from spray drying process (LMO-SD) and the Ti-substituted material obtained from spray drying process (LMTO-SD). The granulated LMO from spray drying (LMO-SD-Gr) is also presented.

volume may improve mass transfer and facilitate more efficient contact.

It is further observed that Mn dissolution is significantly higher for the granulated material (5.5 %) compared to the powder (LMO-HS 3 %; LMO-SD 2.9 %; LMTO-SD 0.45 %). This could be attributed to the PVC, solvent (DMF) or pore-forming agent (PEG) used during slurry preparation, which may promote increased Mn dissolution. Further investigation is required to determine whether this is a phenomenon occurring only in the initial cycle or if consistently high Mn dissolution persists during cycling.

Within the scope of this thesis, the granulation process was not pursued as a primary research objective, but rather considered an enabling step to facilitate long-term performance evaluations of the sorbent material (Ch. 8). As a result, the obtained granulates do not represent an optimized state-of-the-art. Granulation is a mature field with commercially established expertise, which—although not yet specifically applied to LMO sorbents—could be readily transferred from other applications. Within the scope of this work, the aim was therefore to achieve a functional embedding with sufficient sorption capacity, rather than to realize a perfectly optimized material. Future improvements in granulation are expected to further reduce Mn dissolution and enhance sorption performance.

6.4 Summary

This chapter presents an overview of different routes for the preparation of LMO sorbents for lithium recovery from brines. A summary of the sorption capacity and Mn dissolution of these materials is provided in Fig. 6.13. The hydrothermal synthesis route, the most widely used method for producing LMO sorbents, was optimized to reduce Mn dissolution and improve chemical stability. Compared to the original synthesis parameters, the sorption capacity was improved from 1.19 mmol g^{-1} to 1.61 mmol g^{-1} . Additionally, Mn release was reduced from 5.5 % to 3 %, representing a significant reduction. Although this approach achieved improvements in sorption capacity and Mn dissolution, it is limited to small-scale production ($\approx 2 \text{ g}$ per batch), making it unsuitable for industrial applications. To address this limitation, a novel spray drying method was developed, enabling large-scale production. Rietveld refinement revealed that the best sorbent LMO-450 consists of approximately 16.5 % Li_2MnO_3 (space group $C2/m$) and 83.5 % spinel phase (space group $Fd\bar{3}m$). Solid-state NMR spectroscopy enabled the precise determination of the spinel's stoichiometry as $\text{Li}_4\text{Mn}_5\text{O}_{12}$, a compound known for its ion exchange capabilities. Magnetic measurements confirmed that manganese is predominantly in the +4 oxidation state. This is a crucial finding, as lower oxidation states of Mn are prone to disproportionation reactions and the Jahn–Teller effect, which can lead to structural instability and material degradation.

Furthermore, sorption experiments demonstrated that the material is suitable for lithium uptake and exhibits even higher sorption capacity (2.03 mmol g^{-1}) compared to the materials obtained via hydrothermal synthesis route (1.61 mmol g^{-1}). Additionally, Mn dissolution was further reduced to 2.9 %. These values for Mn dissolution are in a similar range, or even lower than those of previous studies.^{[8][58][103]} To achieve a further reduction in Mn dissolution, a substitution approach was tested. As demonstrated in this work, the novel developed spray drying synthesis is also well-suited for incorporating substituent transition metals, allowing flexible tuning of the material properties and thereby increasing the chemical stability. A portion of Mn in the crystal lattice was successfully replaced by Ti, leading to a Ti-substituted LMTO sorbent with composition of $\text{Li}_{1.6}\text{Mn}_{1.49}\text{Ti}_{0.04}\text{O}_4$. XRD analyses revealed a slight shift in reflections to lower angles, corresponding to an increase in lattice parameters (LMO: $8.145 \text{ \AA}$; LMTO $8.155 \text{ \AA}$). Furthermore, the Ti-substituted material demonstrated successful lithium uptake. Compared to other synthesis routes, the Ti-substituted material achieved the highest sorption capacity (2.22 mmol g^{-1}) and the most significant reduction in Mn dissolution to only 0.45 %.

In addition to material synthesis, shaping the sorbent to improve its handling was investigated. The material was integrated into a PVC matrix to form granules, addressing practical challenges such as ease of use and pressure drop in industrial processes. However, the integration partially covered active sites, leading to a reduction in sorption capacity (0.92 mmol g^{-1}) compared to the powder form (2.03 mmol g^{-1}). Furthermore, a high Mn dissolution (5.5 %)

was observed, likely due to interactions between the sorbent and other components of the slurry. However, the granulation approach facilitates repeated cycling tests within this thesis, which was not feasible in the powder form due to material loss during solid-liquid separation after each sorption/desorption step.

Chapter 7

Ion exchange behaviour of HMO and HMTO sorbents¹

In this chapter, HMO and HMTO materials calcined at 450 °C were evaluated for their Li-extraction performance using synthetic LiCl solutions and natural geothermal brines. Within the scope of this thesis, the effects of pH and initial Li⁺ concentration on sorption capacity, as well as the impact of the sorbent-to-brine ratio (m/V ratio) on Li-sorption were investigated. In addition, kinetic experiments were conducted. Based on these findings, suitable process conditions were identified and applied to cycling experiments with HMO and HMTO prepared via spray drying and hydrothermal synthesis. Thereby, the sorption capacity and Mn dissolution, as indicator of chemical stability, were tracked over five cycles. This following chapter is adapted from the publication Herrmann *et al.*^[57].

7.1 pH-dependence

The pH is an important parameter for the Li-extraction because the Li⁺/H⁺ exchange is governed by an equilibrium reaction that is highly sensitive to the H⁺- and Li⁺ concentration in the brine (Eq. 2.11). For natural brines, the pH values and buffering capacities can vary significantly depending on the specific composition at different extraction sites. Geothermal brines in the URG have less favorable extraction conditions due to their mildly acidic pH (≈ 5.5). Under such mildly acidic conditions, the sorbent's performance is reduced. For this reason, the effect of pH on the Li⁺ sorption capacity of HMO and HMTO was evaluated in an initial experiment.

Therefore, a LiCl solution with $c_{Li}=143 \text{ mg L}^{-1}$ (pH=7.1) was prepared, and its pH was adjusted to values ranging from 1 to 12 using HCl or NaOH. HMO and HMTO sorbents

¹This chapter is based on the article by Herrmann et al. (2025)^[57], which is published under CC BY 4.0: Herrmann, L., Bohn, N., Pfau, A., Kölbel, T., Ehrenberg, H., Binder, J., Jeschull, F. (2025). Synthesis of Lithium Manganese Oxide and Ti-Substituted LMO Sorbents for Lithium Extraction in a Spray-Drying Process. *ChemSusChem*, 18: e202500530. <https://doi.org/10.1002/cssc.202500530>

were suspended in these solutions for 24 hours, after which the pH and Li^+ concentration of the solutions were measured. The resulting sorption capacities, Q_{Sorb} , are presented in Fig. 7.1a. For HMO, a negative sorption capacity was detected at pH values below 2,

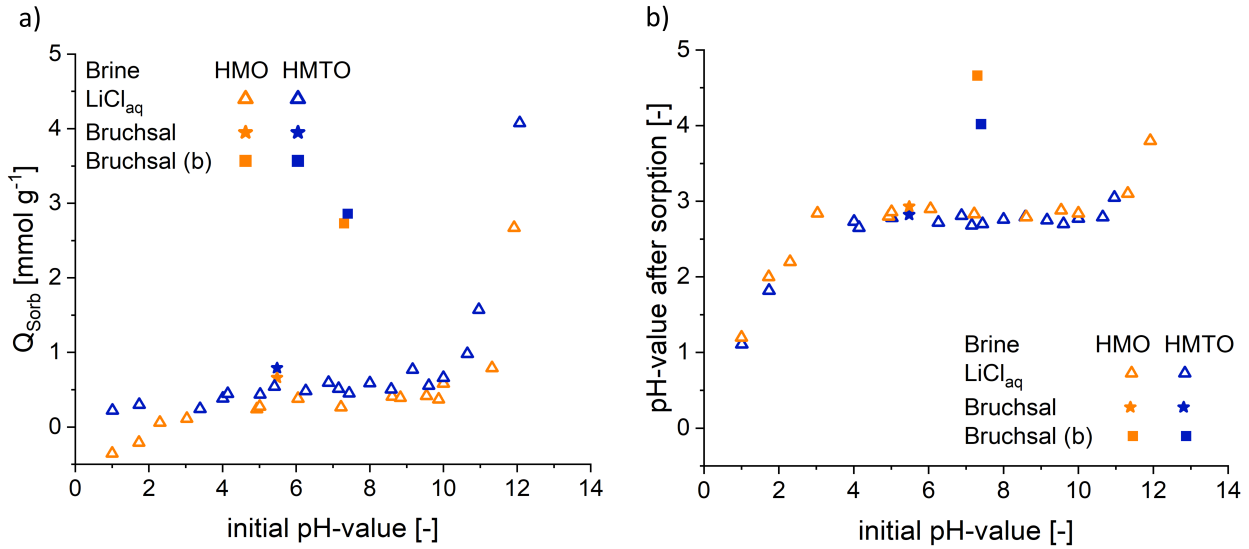


Figure 7.1: a) Sorption capacity of HMO and HMTO at different initial pH levels, b) pH values before and after sorption. In both graphs HMO data is shown in orange, and HMTO sample data is shown in blue. Experiments conducted with unbuffered geothermal brine are indicated with stars, those conducted with buffered geothermal brine with squared data points and (b). Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

suggesting that Li^+ ions were released from the sorbent material. As the pH increased, Q_{Sorb} showed a gradual rise up to a pH of 10, followed by a pronounced increase. The highest sorption capacities were observed at a pH of around 12, with HMO reaching a maximum Q_{Sorb} of 2.67 mmol g^{-1} (18.5 mg g^{-1}). In comparison, HMTO exhibited a significantly higher maximum Li^+ content, achieving $Q_{\text{Sorb}}=4.08 \text{ mmol g}^{-1}$ (28.3 mg g^{-1}). The results indicate that the exchange process benefits from elevated pH levels. This is because during Li intercalation, protons are released, and their neutralization by OH^- at a higher pH enhances the thermodynamic driving force for the conversion of HMO to LMO.

Subsequently, these findings were placed in the context of prior publications. Tab. 7.1 provides an overview of Q_{Sorb} values at various pH levels for a selection of sorbent materials with substituent ions, HMXO, as reported in the literature. These include trivalent ions such as Al^{3+} ^[101], Ni^{3+} ^[103], Fe^{3+} ^[103], and Co^{3+} ^[103].

At low pH (pH=4), HMTO demonstrated the highest sorption capacity in this comparison, achieving 0.45 mmol g^{-1} compared to the other materials ranging from 0.19 to 0.36 mmol g^{-1} . However, in the mildly basic region (pH=10), other HMXO materials exhibited higher Q_{Sorb} compared to HMTO. Furthermore, at high pH levels (pH = 12),

Table 7.1: Comparison of pH dependence on Li^+ -sorption capacities of HMTO and literature values for selected substituted HMXO ($\text{X} = \text{Al}^{3+}$, Fe^{3+} , Co^{3+} , Ni^{3+}) materials. Table adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

	Substituent	pH				m/V [g L ⁻¹]	Source
		4	7	10	12		
Q_{Sorb} [mmol g ⁻¹]	Al	0.19	0.4	1.61	4.24	1	[101]
	Fe	0.36	0.55	1.41	3.31	1	[103]
	Co	0.3	0.45	1.46	3.96	1	[103]
	Ni	0.35	0.59	1.51	3.36	1	[103]
	Ti	0.45	0.52	0.82	4.08	5	Fig. 7.1

HMTO again exhibits a higher sorption capacity compared to Fe-, Co- and Ni-substituted materials, and a slightly lower capacity than Al-substituted sorbents. This indicates that HMTO is particularly efficient in slightly acidic to neutral conditions, as well as in strongly basic environments. For application in geothermal water from the URG, which has a pH of approximately 5.5, the sorbent is therefore well suited.

For all extraction experiments conducted at varying initial pH values, the pH was measured again after the sorption process. The corresponding results are presented in Fig. 7.1b. For initial values of $\text{pH} < 3$, the initial pH and the pH after sorption are very similar. This phenomena is consistent with the calculated sorption capacity, indicating negligible sorption or even a slight release of Li ($Q_{\text{Sorb}} < 0$). In contrast, at an initial $\text{pH} > 3$, a decrease in pH after sorption was observed, reflecting successful Li uptake. It can be observed that across a wide range of initial pH levels, the sorption process ends at an equilibrium pH of approximately 2.8 for HMO and 2.7 for HMTO. These findings align with earlier results reported by Shi *et al.*^[115], who investigated synthetic LiCl solutions with varying initial pH values (adjusted using LiOH or HCl) to determine the equilibrium pH. In particular, the pH after sorption remains at a constant level until the initial pH of the LiCl solution transitions to more strongly basic conditions (Fig. 7.1b). For an initial pH above 11, the pH does not return to the equilibrium value after sorption but remains higher. This is due to the elevated concentration of OH^- ions, which are not sufficiently neutralized by H^+ ions released through Li^+/H^+ ion exchange to reach equilibrium pH.

Beyond the experiments involving LiCl solutions, sorption experiments were performed using pure geothermal brine ($\text{pH} \approx 5.5$) under otherwise identical conditions. The resulting sorption capacity and the change in pH after extraction are shown in Fig. 7.1 (star data points). Both the sorption capacity and the equilibrium pH were slightly elevated when using geothermal brine, relative to the LiCl solution at a similar pH. This difference can be due to the high total dissolved solids amount ($\text{TDS} > 100 \text{ g L}^{-1}$) and the carbonate content in the geothermal brine, which act as a natural buffer system. A similar effect was

previously reported by Zhang *et al.* [159] in studies on salt lake brines.

The results indicate that in batch-type extraction processes, the pH tends to drift significantly without additional pH regulation. However, adjusting the pH of geothermal brines to values above $\text{pH} > 10$ would lead to substantial precipitation, making such an approach impractical. As an alternative, buffering the brine during the Li^+ -sorption process at a pH above the equilibrium pH of 2.7 (2.8) can be considered as a feasible approach. In this study, sodium acetate (NaOAc , $\text{pK}_s = 4.76$) at a concentration of 1.5 g L^{-1} was added to the brine prior to sorption experiments. The acetate buffer was generated *in situ* through the release of protons from the ion exchange material. This addition increased the initial pH of the geothermal water from 5.5 to approximately 7.4. This buffered (b) geothermal brine was used in a sorption experiment with otherwise identical experiment parameters. The results are presented as squared data points in Fig. 7.1. After the sorption step, equilibrium pH values of 4.7 for HMO and 4.0 for HMTO were recorded, which are significant higher compared to the unbuffered system. Furthermore, the sorption capacities improved significantly, reaching 2.7 mmol g^{-1} for HMO and 2.9 mmol g^{-1} for HMTO, compared to 0.3 mmol g^{-1} (HMO) and 0.5 mmol g^{-1} (HMTO) in unbuffered solution. In subsequent sections, the NaOAc buffer will be employed and further examined as a method for effective pH control during the sorption process.

7.2 Sorbent-to-brine ratio (m/V ratio)

A further critical parameter in lithium sorption experiments is the sorbent-to-brine ratio, as it governs the concentration gradient between the sorbent and the Li-rich solution, thereby significantly affecting the sorption equilibrium that is established. Higher sorbent mass or smaller brine volumes can lead to faster pH changes, potentially stopping the ion exchange process (Eq. 2.11). To investigate this effect, the m/V ratio was adjusted within a range of 0.25 to 25 g L^{-1} . Therefore, HMO or HMTO amounts between 10 and 1000 mg were mixed with a fixed volume (40 mL) of LiCl solution. The brines were buffered with either 1.5 g L^{-1} or 15 g L^{-1} of NaOAc , resulting in initial pH values of 7.4 and 8.2, respectively (as shown by the circles in Fig. 7.2c). Fig. 7.2a presents the resulting sorption capacities, calculated using Eq. 5.3, as a function of the m/V ratio, based on the residual Li^+ content in the LiCl solution. The second axis in Fig. 7.2a represents sorbent utilization, calculated as the ratio between Q_{Sorb} and the theoretical maximum sorption capacity $Q_{\text{sorb,th}}$ (10.5 mmol g^{-1}), which corresponds to the complete conversion of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Fig. 7.2b illustrates Li^+ depletion (Eq. 5.4), while Fig. 7.2c shows the associated pH changes. The data reveal that Li^+ sorption is highest at the lowest m/V ratio, reaching approximately 5.7 mmol g^{-1} or 39 mg g^{-1} for HMTO. This value exceeds the Q_{Sorb} determined in the titration experiments and represents about 57 % of the theoretical sorption capacity of LMTO. Despite the high material utilization at small m/V ratios (Fig. 7.2a), the total amount of extracted lithium

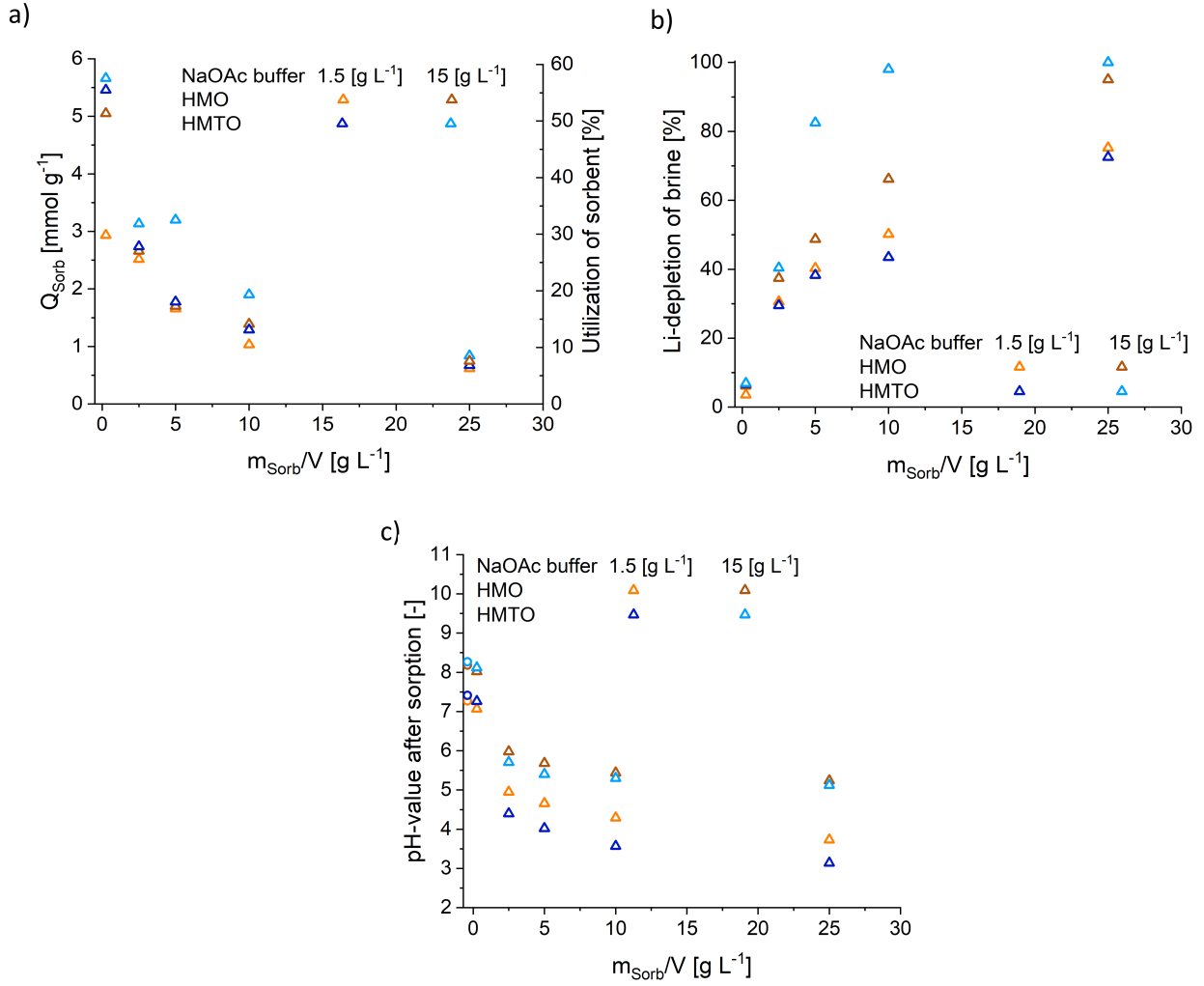


Figure 7.2: Variation of mass-to-volume ratio: a) sorption capacities and corresponding utilization of sorbent ($Q_{\text{Sorb}}/Q_{\text{theo}}$), b) Li^+ -depletion of brine c) initial pH values (circle) and pH values after sorption (triangle) are presented. Data for HMO is highlighted in orange, while data for HMT0 samples is highlighted in blue. Figure adapted from Herrmann *et al.* 2025.^[57] Licensed under CC BY 4.0.

remains low (Fig. 7.2b) due to the limited sorbent mass in the defined volume. Additionally, the large brine volume prevents significant pH changes caused by exchanged protons (Fig. 7.2c). Interestingly, for $m/V = 0.25 \text{ g L}^{-1}$, the sorption capacity of HMO (1.5 g L^{-1} NaOAc) is notably lower than other values. This discrepancy can be attributed to two factors: the very small sorbent mass at this ratio, which increases measurement inaccuracies, and the minimal change in Li^+ concentration, leading to higher relative uncertainty. To ensure reliability, this value was confirmed through five independent experiments.

At higher m/V ratios, the available Li^+ ion inventory per gram of sorbent becomes limited or insufficient, resulting in significantly lower sorption capacities. However, the relative depletion of Li^+ ions is high, leading to substantial pH changes. In a batch-type extraction

process, this scenario is impractical, as it disrupts the balance between material utilization and extraction yield. The goal is therefore to identify an optimal balance that ensures efficient extraction within a reasonable circulation interval. As shown in Fig. 7.2b, using a NaOAc concentration of 15 g L^{-1} and 0.4 g of HMT0 sorbent ($m/V=10 \text{ g L}^{-1}$), nearly all Li^+ ions were extracted from the LiCl solution, achieving a Li^+ depletion of 98 %. Under the same conditions, the HMO sorbent material achieved a lower depletion rate of 66 %. By further increasing the m/V ratio for HMO ($m/V=25 \text{ g L}^{-1}$), the extraction yield approached that of HMT0, making HMT0 the more cost-effective and efficient material. The results in Fig. 7.2b also emphasize the influence of NaOAc concentration on extraction yield. At a lower initial NaOAc concentration of 1.5 g L^{-1} , both HMO and HMT0 exhibited extraction yields below 50 % at a $m/V=10 \text{ g L}^{-1}$. Interestingly, under these conditions, HMO demonstrated slightly higher extraction yields compared to HMT0.

The pH values presented in Fig. 7.2c for sorption experiments with 15 g L^{-1} NaOAc stabilize at approximately $\text{pH}=5.4$ (m/V ratio of 10 g L^{-1}). This value is notably higher than the pK_a of acetic acid (4.76). Complementary to the measured pH values, the equilibrium pH was theoretically estimated using the Henderson-Hasselbalch equation. The detailed calculation is presented in the appendix (Ch. 9). For both HMO and HMT0 sorbents at a m/V ratio of 10 g L^{-1} and a concentration of 15 g L^{-1} NaOAc, an equilibrium pH of ≈ 5.7 was calculated, closely matching the experimental observations. In contrast, when using 1.5 g L^{-1} NaOAc, the pH exhibited a more pronounced pH drop within the m/V -range of $10\text{-}25 \text{ g L}^{-1}$. For HMT0 at a m/V ratio of 25 g L^{-1} , the pH decreased to 3.14, marking the lowest pH observed in this experiment and approaching the limiting pH of 2.7 identified in Fig. 7.1. This significant pH reduction is attributed to the lower buffering capacity, indicating that the buffer was nearly depleted under these experimental conditions. Also for this case ($m/V=25 \text{ g L}^{-1}$ HMT0; 1.5 g L^{-1} NaOAc), the equilibrium pH was calculated using the Henderson-Hasselbalch equation to allow comparison with the experimentally determined value. Interestingly, the measured pH of 3.14 is lower than the theoretical value of 3.7. This discrepancy may arise from additional acidic effects introduced by the sorbent itself, which could further contribute to the observed pH decrease beyond what is expected from the release of H^+ ions during the Li^+ ion exchange process.

In comparison to unbuffered systems (Fig. 7.1), the use of a buffering agent significantly enhanced sorption capacities, achieving values of 1.5 mmol g^{-1} compared to $<0.5 \text{ mmol g}^{-1}$ (Tab. 7.1) at the same m/V ratio. This improvement is attributed to the buffering agent's ability to mitigate the pH decrease during the ion exchange process. However, this approach necessitates sufficiently high concentrations of the buffering agent (NaOAc) to effectively stabilize the pH throughout the reaction. To balance sorbent utilization and minimize chemical consumption in a batch-type extraction process, an optimal trade-off must be established. The ideal conditions were determined to be a sorbent content of approximately 0.2 g per 40 mL of LiCl solution combined with a NaOAc concentration of 1.5 g L^{-1} . These param-

eters will be employed in the subsequent experiments to further investigate the extraction process.

7.3 Impact of initial Li^+ concentration

Since Li sorption occurs via an ion exchange mechanism (Eq. 2.11), the equilibrium position is influenced not only by pH but also significantly by the initial Li^+ concentration. Using the optimized extraction conditions established earlier ($m/V = 5 \text{ g L}^{-1}$ and 1.5 g L^{-1} NaOAc), the sorption capacities of HMO and HMTO were evaluated as a function of the initial lithium concentration in buffered synthetic LiCl solutions, ranging from 40 to $200 \text{ mg}_{\text{Li}} \text{ L}^{-1}$. In Fig. 7.3a sorption capacities are represented by triangular symbols. Additionally, the sorption capacities of both sorbent materials were assessed in two different buffered geothermal brines, as shown in Fig. 7.3a (star-shaped symbols). The buffered Bruchsal geothermal brine had a lithium concentration of 143 mg L^{-1} and a pH of 7.4, while the buffered brine from Soultz contained 141 mg L^{-1} lithium and had a pH of 6.9 (Tab. 2.3). The corresponding pH changes before and after the sorption step are depicted in Fig. 7.3b and c. In the LiCl solutions, sorption capacities increased approximately linearly within the range of $50\text{--}150 \text{ mg L}^{-1}$, indicating a direct correlation with the initial Li^+ concentration. However, solutions with an initial lithium concentration of 200 mg L^{-1} exhibited slightly lower sorption capacities, suggesting a deviation from the linear trend at higher concentrations. As the Li^+ concentration increased, more Li^+ ions were exchanged during the sorption process, leading to a corresponding rise in H^+ concentration. This increase in H^+ resulted in lower pH values for brines with higher initial Li^+ content after the sorption step. Although HMTO achieved higher sorption capacities compared to HMO, the supernatant from HMTO extractions consistently maintained a pH close to the pK_a value of NaOAc/HOAc (4.76) across the tested range of LiCl concentrations. In contrast, suspensions with HMO exhibited a more pronounced pH drop, decreasing by approximately 1.5 pH units from the lowest to the highest Li^+ concentration. The relatively stable pH values in HMTO extractions contribute to its higher sorption capacities. Consequently, in geothermal brines, HMTO achieved sorption capacities of 2.4 mmol g^{-1} in the Soultz brine and 2.3 mmol g^{-1} in the Bruchsal brine. In comparison, HMO reached similar sorption capacities of 2.2 mmol g^{-1} only in the Bruchsal brine, highlighting HMTO's superior performance in lithium extraction.

HMO exhibited significantly lower sorption capacities (1.3 mmol g^{-1}) when using Soultz brine, not only in comparison to HMTO with Soultz brine, but also to HMO with Bruchsal brine. The overall salinity of the lithium-bearing solution (approximately 100 g L^{-1} in Soultz^[51]; around 130 g L^{-1} in Bruchsal^[112]) likely influences the resulting sorption capacities. Interestingly, high salinity had minimal impact on the pH values of the brines after the sorption process, as shown in Fig. 7.3b and c. While a detailed investigation

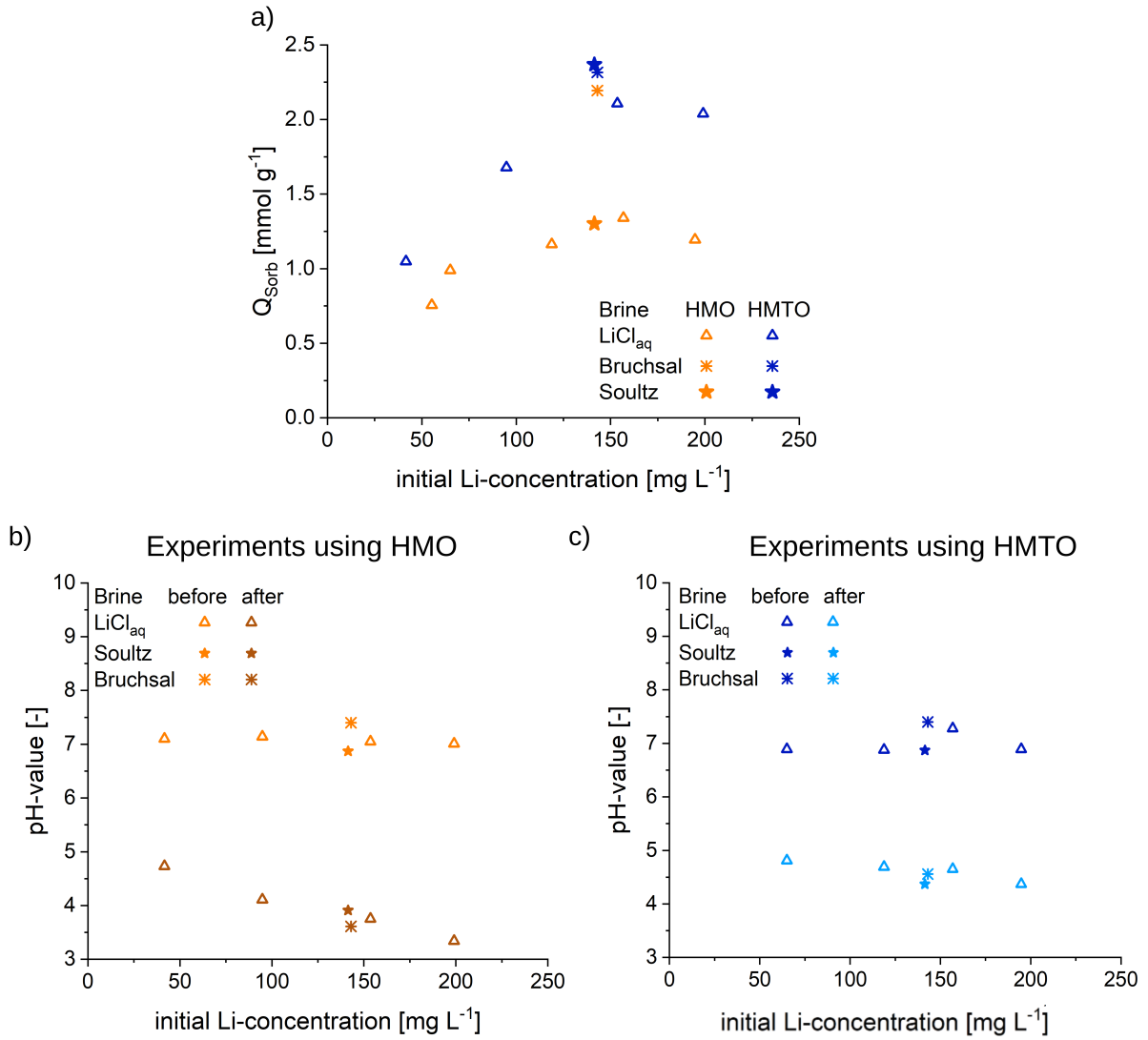


Figure 7.3: a) Sorption capacity for LiCl solutions (triangles) with various Li⁺ concentration and natural brines (stars). Data associated with HMO is marked orange; data for HMTO samples is marked blue. The corresponding changes in pH values before and after the sorption step are provided in b) for HMO and c) for HMTO. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

of these matrix effects lies beyond the scope of this thesis, it remains highly relevant for developing a deeper understanding of how salinity and chemical composition of geothermal brines, which are chemically unique at each site, affect ion exchange equilibria.

7.4 Ion exchange kinetics

The duration of an extraction cycle is a critical factor in optimizing extraction yields, as it directly impacts the size and cost of industrial scale processes. Ion exchange kinetics play a key role in determining the efficiency of the extraction process. To investigate this, sorption

experiments were conducted to measure the sorption capacity at various time intervals under the previously described extraction conditions.

Fig. 7.4a illustrates the Li^+ -sorption capacity over different reaction times for HMO and HMTO, while Fig. 7.4b shows the corresponding pH values at the end of the sorption step. The rapid increase in Q_{Sorb} , coupled with the associated pH decrease due to proton release into the buffered brine, highlights the fast ion exchange kinetics of both materials. HMTO demonstrated superior performance, achieving 87 % of its equilibrium sorption capacity ($q_{e,\text{exp}}$) within just 15 minutes. In comparison, HMO reached only 76 % of $q_{e,\text{exp}}$ during the same time frame. The equilibrium sorption capacity was experimentally determined after a reaction time of 24 hours. Additionally, at shorter sorption times, HMTO consistently delivered approximately 10 % higher sorption capacities than HMO, further emphasizing its faster kinetics and greater efficiency. In agreement with the measured

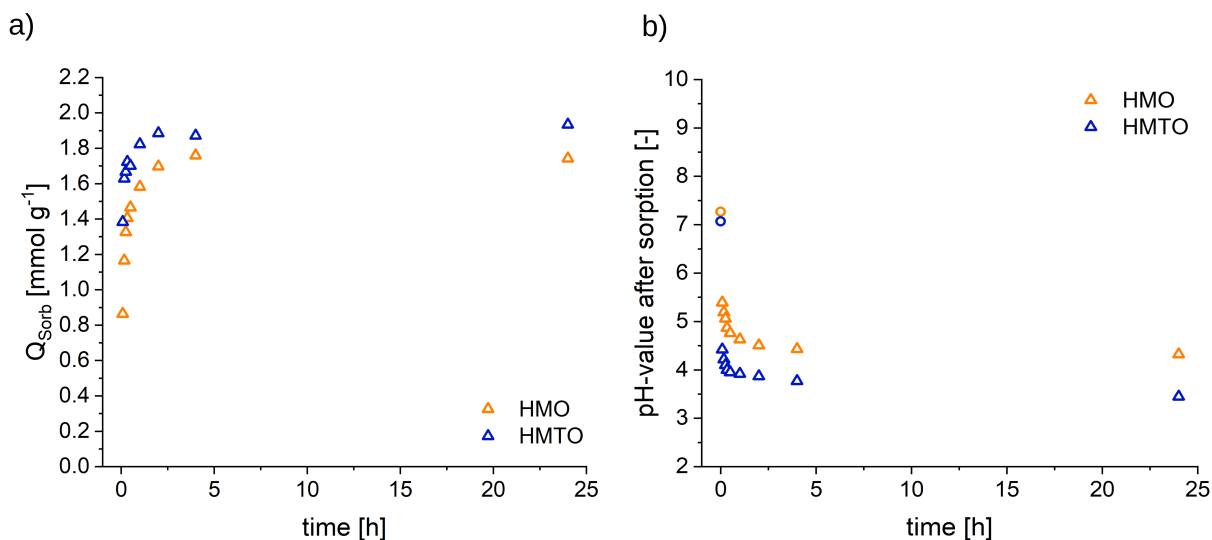


Figure 7.4: a) Sorption capacity for various reaction times and b) pH values after sorption for various time intervals are presented as triangle, the initial pH of the LiCl solution prior to sorption is shown as circles. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

sorption capacities, the pH decreased more rapidly for HMTO samples compared to HMO samples. Due to the lower Q_{Sorb} observed in HMO experiments, the pH remained generally higher by approximately 0.5–1 pH unit. As expected, the lowest pH values were recorded for both HMTO and HMO samples after the longest sorption time of 24 hours, corresponding to the highest Q_{Sorb} and the greatest proton release during the experiment. To gain a more quantitative understanding of the ion exchange kinetics, reaction parameters were derived using a pseudo-second-order model (Eq. 5.2). The calculated equilibrium sorption capacity $q_{e,\text{calc}}$ showed strong agreement with the experimental data ($q_{e,\text{exp}}$), as presented in Tab. 7.2 and Fig. A.10. A better goodness-of-fit was observed for HMO, which may be attributed to

Table 7.2: Kinetic parameters of pseudo-first-order and pseudo-second-order kinetic models. Table reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Material	Experimental	Pseudo-first-order			Pseudo-second-order		
	$q_{e,exp}$ [mmol g ⁻¹]	$q_{e,calc}$ [mmol g ⁻¹]	k_1 [h ⁻¹]	R^2 -	$q_{e,calc}$ [mmol g ⁻¹]	k_2 [h ⁻¹]	R^2 -
LMO	1.74	1.67	7.18	0.89	1.76	6.56	0.99
LMTO	1.93	1.82	15.41	0.73	1.89	16.98	0.95

the fact that HMTO sorption capacities at shorter reaction times (<10 minutes) exhibited minimal variation, indicating limited time dependency. For both sorbents, the kinetic data derived from the pseudo-second-order model provides valuable insights for process optimization, including reactor sizing and the determination of residence time parameters to ensure efficient extraction performance.

7.5 Sorbent aging in synthetic and geothermal brines upon repeated cycling

The durability of sorbent materials over multiple extraction cycles is an essential parameter, as issues such as Mn dissolution in the desorption step, as well as the formation of impermeable surface layers (caused by deposits from competing ions in geothermal brines) can inhibit Li⁺ capture. In this study, the sorption capacity and stability of HMO and HMTO materials from spray drying synthesis, as well as HMO from hydrothermal synthesis were evaluated over five sorption/desorption cycles. In this experiment, the cycle number was limited due to the small particle size of the HMO and HMTO powders, which led to significant material loss during the solid-liquid separation step in each cycle. For the spray dried materials synthetic LiCl solution and Bruchsal geothermal brine were used as Li-bearing solutions, for the HMO obtained from hydrothermal synthesis only LiCl solution was used. Desorption was performed using 0.5 M HCl as eluent. Based on kinetic data, a sorption and desorption duration of 30 minutes each per cycle was selected, because it ensures relatively high lithium uptake while maintaining a reaction time sufficiently short for practical application.

Sorption Capacity. The sorption capacities of the materials cycled with LiCl solution and Bruchsal geothermal brine are shown in Fig. 7.5a. In the first cycle using LiCl solution, the lowest sorption capacity among all tested materials was observed for HMO produced by hydrothermal synthesis (HS), with 0.86 mmol g⁻¹. In contrast, the spray dried (SD) materials HMO and HMTO exhibited higher capacities of 1.1 mmol g⁻¹ and 1.6 mmol g⁻¹, respectively. Interestingly, when using geothermal brine, significantly higher sorption capacities were observed and the results were in a similar range for both HMO (SD) and

HMTO (SD), with approximately 2.2 mmol g^{-1} . Over five cycles, the sorption capacity Q_{Sorb} remained stable for HMO (SD) and HMTO (SD) in geothermal brine. However, in LiCl solution, Q_{Sorb} exhibited a slight decline across all materials, with the smallest decrease observed for HMTO (SD). The results obtained with geothermal brine are consistent with the values in the literature, where long-term sorption capacities of 2.66 mmol g^{-1} for HMO and 3.14 mmol g^{-1} for Mg-substituted HMO were reported using salt lake brine.^[8] These findings highlight the promising performance, especially for spray dried materials for lithium recovery in particularly complex brines.

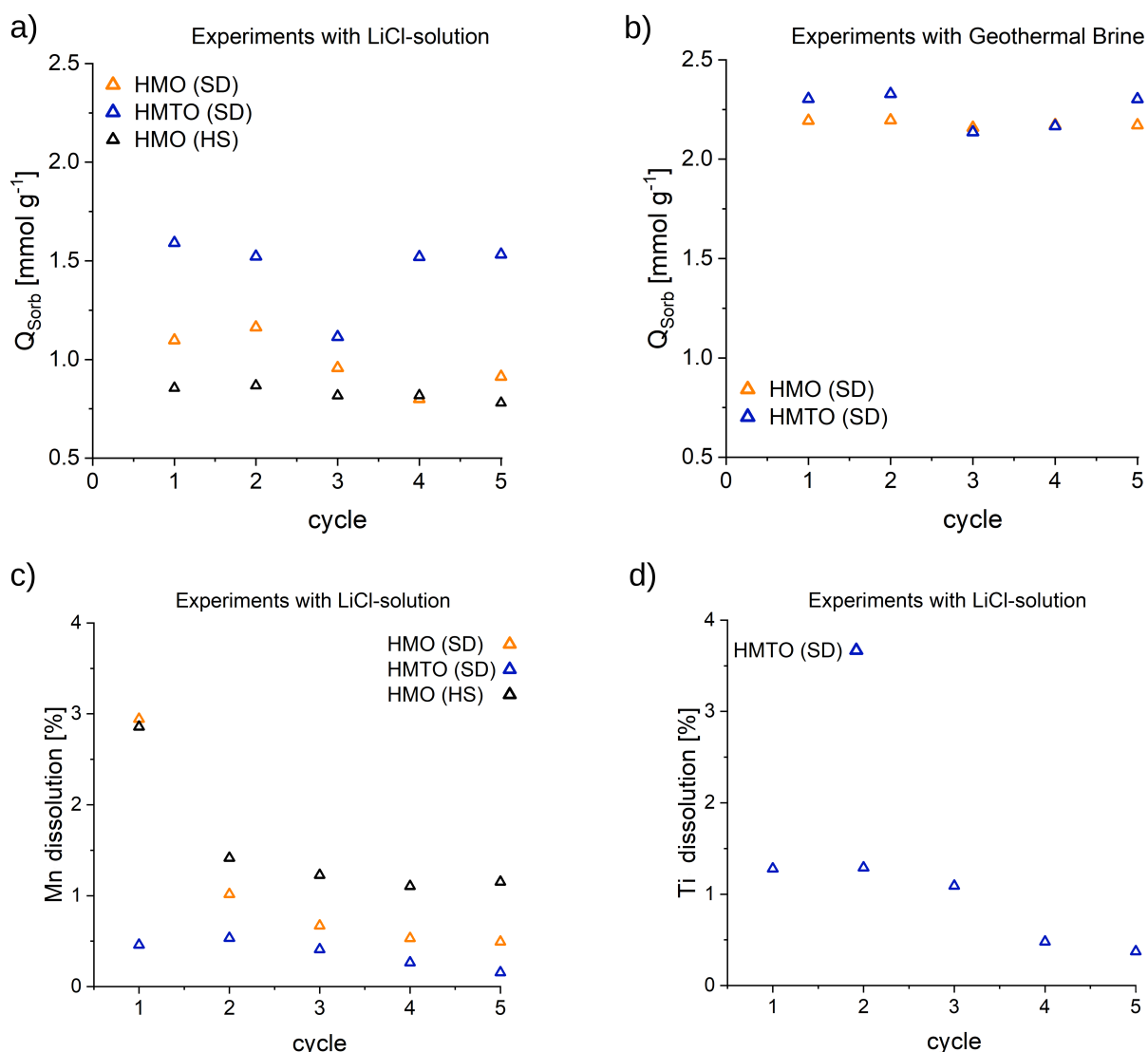


Figure 7.5: Long term performance of sorbents obtained from hydrothermal synthesis (HS) and spray drying (SD) using LiCl solution and geothermal brine: a+b) sorption capacity, c) Mn dissolution, d) Ti dissolution. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Dissolution of Mn^{2+} and Ti^{4+} . Subsequently, manganese and titanium release was analyzed over five cycles as an indicator of the chemical stability of the materials. Fig. 7.5c illustrates the Mn dissolution over five extraction cycles. After five cycles, the cumulative Mn dissolution was measured to be 7.8 % for HMO (HS), 5.6 % for HMO (SD) and significantly lower for HMTO with 1.8 %. The results indicate that the hydrothermally synthesized material exhibits the lowest chemical stability, followed by the Ti-free spray dried HMO. In contrast, the Ti-substituted HMTO shows significantly higher stability, confirming its superior performance under cyclic conditions. Notably, Mn-losses were most pronounced during the first cycle for the HMO sorbents from hydrothermal synthesis and spray drying method, both with a Mn dissolution of around 2.9 %. In contrast, HMTO consistently exhibited low Mn dissolution across all cycles. In the first cycle, Mn release was limited to just 0.45 %, representing a substantial improvement over the HMO sorbents and previously reported literature values, such as the 3 % dissolution observed for Mg-substituted HMO.^[8]

Furthermore, for HMTO the Ti-dissolution was investigated (Fig. 7.5d). During the first cycle, Ti-dissolution in the desorption step was measured at 1.3 % in experiments with LiCl solution. However, a clear trend of decreasing Ti release was observed over subsequent cycles. By the 5th cycle, Ti-dissolution had significantly reduced to just 0.4 %. This continuous decline in Ti-dissolution suggests that the material stabilizes over repeated use, further enhancing its suitability for long-term lithium extraction applications.

Changes in morphology. Geothermal brine contains substantial concentrations of dissolved salts besides lithium ($\text{TDS} > 100 \text{ g L}^{-1}$, Bruchsal), which can significantly affect the lithium sorption process. The competing ions from geothermal brine can either enter the sorbent structure or accumulate on its surface. To investigate surface deposits and morphological changes after multiple sorption-desorption cycles, SEM and EDX analyses were performed on spray dried sorbents treated with geothermal brine. The Ti^{4+} -free material LMO was analyzed in its Li-loaded state, while the Ti-substituted material HMTO was examined in its desorbed state, both after the 5th cycle. The SEM and EDX images for LMO and HMTO are presented in Fig. 7.6a and b, respectively.

For cycled LMO the EDX maps primarily show Mn and O as elements from the material itself along with Na, Cl, Ca, and K as the main residual ions originating from the geothermal brine (Tab. 2.3). This observation is consistent with findings from a previous study of Herrmann *et al.*^[58], where surface deposits on hydrothermally synthesized LMO sorbents included mainly Na, Ca, and K when exposed to Bruchsal geothermal brine. Furthermore, Fe was detected in the brine-cycled material in the previous study, whereas no such signal was observed in the present work. This discrepancy may be attributed to the prolonged storage time of the geothermal brine used herein, which led to the precipitation of Fe-containing compounds. This was evidenced by the formation of an orange precipitate and was taken into account during data evaluation.

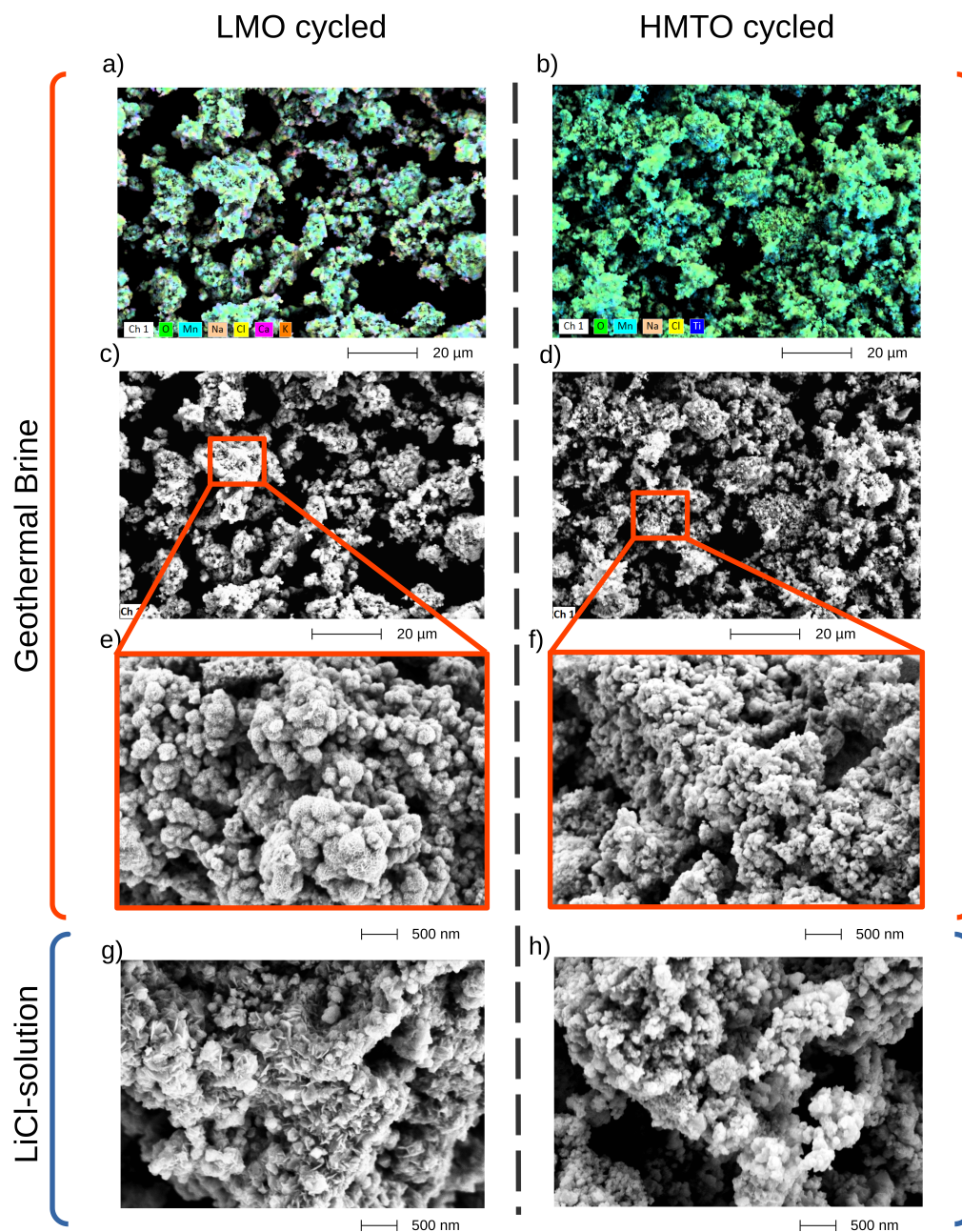


Figure 7.6: a) EDX of LMO material cycled with geothermal brine. b) EDX of HMT0 material cycled with geothermal brine. c+e) SEM micrograph of LMO after 5th sorption/desorption cycle using geothermal brine. d+f) SEM micrograph of HMT0 after 5th sorption/desorption cycle using geothermal brine. f) SEM of LMO after 5th sorption/desorption cycle using LiCl solution. g) HMT0 after 5th sorption/desorption cycle using LiCl solution. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

For cycled HMT0, the dominant residual ions were only Na and Cl, which correspond to the major constituents of the geothermal brine. The presence of fewer residual ions on the material may be attributed to its protonated state, resulting from an additional HCl treatment following contact with geothermal brine. This acid washing step likely facilitated

the removal of bound foreign ions. Furthermore, the energy diagrams of HMO and HMTO (Fig. A.8) reveal additional peaks for other elements present in the geothermal brine. However, these quantities are negligible compared to the primary components detected. Analysis of the distribution of residual ions in the EDX images reveals that Na and Cl are evenly distributed across the particle surfaces, whereas the Ca signal is localized in distinct regions, suggesting the formation of Ca-rich surface deposits.

Figure 7.6c and e shows SEM micrographs of the brine-cycled LMO material at different magnifications, while Figure 7.6d and f presents the brine-cycled HMTO material. For LMO, the particles appear to be coated with a surface layer, likely resulting from precipitates formed during exposure to geothermal brine. In contrast, such deposits are not observed on the HMTO material.

Fig. 7.6g and h show the LMO and HMTO material cycled exclusively in LiCl solution after 5th cycle. Its morphology appears to be mostly unchanged compared to the pristine materials, whereas the brine-cycled samples, particularly LMO, exhibit pronounced alterations.

Structural evolution. Previous experiments (Fig. 7.5) confirmed the leaching of Mn^{2+} and Ti^{4+} from the crystal lattice during cycling and morphological changes could be observed by SEM analysis, particularly for brine-cycled materials. To assess whether these alterations are also reflected at the crystallographic level, XRD analysis was performed on the cycled materials and compared to their respective pristine counterparts. Rietveld refinements for LiCl-cycled LMO and geothermal brine-cycled LMO were performed, and the lattice parameters of the cycled materials were determined.

The resulting XRD patterns are presented in Fig. 7.7 and the results of Rietveld refinement are attached in Fig. A.3. The XRD data clearly show that after five cycles, the characteristic spinel reflections remain present for all materials. However, slight changes in intensity can be observed. For cycled LMO, a noticeable reduction in the intensity of the reflection at 19.9° is detected compared to pristine LMO. In addition, a change in the lattice parameter was observed. While the LiCl-cycled sample showed only a slight increase from $8.145 \text{ \AA}$ (LMO-450 pristine) to $8.157 \text{ \AA}$, the geothermal brine-cycled material exhibited a more pronounced shift to $8.181 \text{ \AA}$, indicating a stronger structural impact from brine exposure. The observed lattice expansion indicates structural alterations within the spinel framework, with several factors potentially contributing to this phenomenon. One reason could be the partial co-intercalation of foreign cations from geothermal brine. In particular, Na^+ and K^+ , which are present in high concentrations in the brine, may be incorporated at defect sites under cycling conditions. Although their intercalation is relatively unlikely, even small amounts can significantly contribute to the observed lattice expansion.

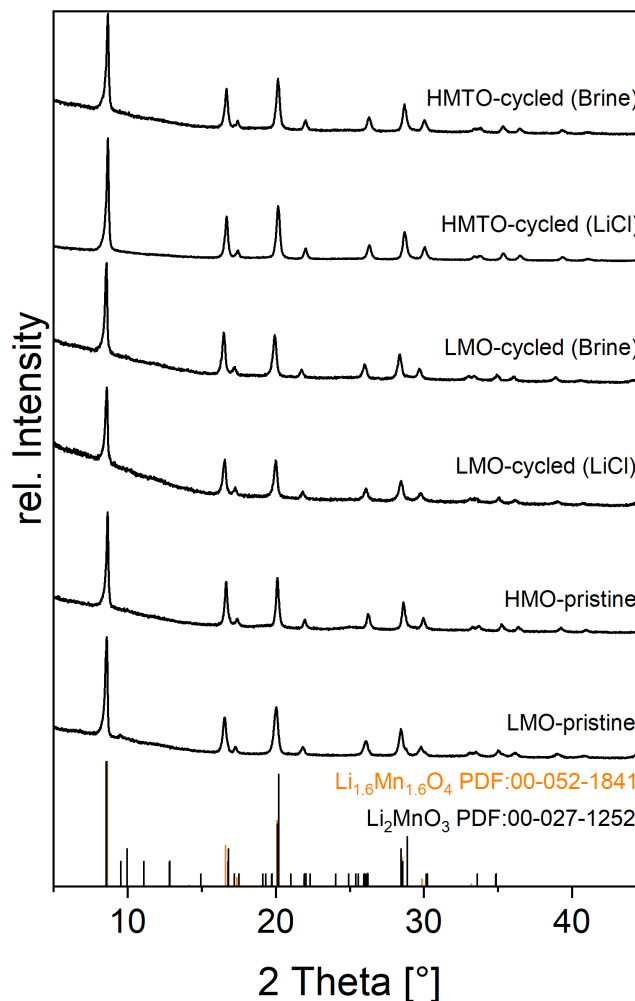


Figure 7.7: X-ray diffraction patterns of pristine and cycled LMO and HMTO using LiCl solution or geothermal brine after 5th sorption/desorption cycle. Figure adapted from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Another possible explanation is that relithiation may lead to the development of spinel phases with lower lithium content relative to pristine LMO. Paulsen et al.^[99] reported a correlation between the lithium content x in cation-mixed spinels of the type $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ and their lattice parameters. As the value of x decreases, the lattice increases and the structure tends to incorporate a higher proportion of Mn^{3+} . For example, for classical spinel-type LiMn_2O_4 a typical lattice parameter of approximately 8.25 Å has been reported.^{[99][2]} The repeated intercalation and de-intercalation of lithium ions may thus lead to a shift in the manganese oxidation state in the sorbent from Mn^{4+} to Mn^{3+} . Since Mn^{3+} has a larger ionic radius than Mn^{4+} , an increased Mn^{3+} content results in lattice expansion, consistent with the crystallographic changes observed after cycling.

In addition, previous experiments and studies have shown that during sorption experiments, only a fraction of the original lithium content can be achieved depending

on the experiments conditions. The maximum of re-intercalation which was performed within this work under ideal conditions was $\approx 51\%$ (35.05 mg g^{-1}), matching well with various literature values.^{[27][103][8]} The materials discussed in this chapter with respect to structural changes were obtained from the 5th cycle of long-term experiments, which were conducted under conditions that were not idealized, but rather designed to reflect more realistic operational scenarios. Therefore, these samples exhibited significantly lower degrees of lithium re-insertion. The LiCl-cycled LMO material exhibits a lithium sorption capacity of 0.91 mmol g^{-1} after the 5th cycle which corresponds to only 9% of the original lithium content of the pristine LMO material. In contrast, the LMO material cycled with geothermal brine shows a slightly higher sorption capacity of 2.17 mmol g^{-1} after the 5th cycle, which corresponds to a loading of 21% relative to the pristine material. When comparing the lattice parameters, it must therefore be taken into account that differences in lithium loading alone already lead to variations in the lattice constants. The inability to achieve higher lithium loadings, such as 51% , is not yet fully understood and may be attributed to thermodynamic limitations under operation conditions, particularly when using brines with mildly acidic pH values. Alternatively, it can be due to the fact that not all lithium sites within the spinel lattice are reversibly accessible. Another reason, as outlined above, could be related to the formation of lithium-deficient spinel phases during relithiation.

In contrast, the Ti-substituted HMTO samples exhibit well-preserved reflection intensities and positions, indicating high structural stability even after cycling. The lattice parameter changed from $8.067\text{ \AA}$ (HMTO pristine) to $8.085\text{ \AA}$ for LiCl-cycled HMTO and $8.087\text{ \AA}$ for geothermal brine cycled HMTO. The deviation from the pristine value may result from either material degradation or incomplete desorption processes. Furthermore, after five cycles, the LiCl-cycled sorbent exhibits structural features that more closely align with those of the sorbent exposed to geothermal brine, in contrast to the Ti-free reference material. This suggests that geothermal brine induces less structural changes in the Ti-substituted sorbent compared to the Ti-free material.

Besides the changes in lattice parameters, a general trend observed for cycled sorbents is the narrowing of reflections compared to pristine materials. This phenomenon may be linked to the loss of fine (nano-)crystallites during the separation process in the cycling experiments, as supported by SEM micrographs. The gradual material loss during cycling currently poses a challenge for long-term stability and cycling tests, highlighting the need for further optimization of the sorbent shaping and separation processes.

7.6 Summary

This chapter explores the Li-intercalation from synthetic LiCl solutions and geothermal brines under varying conditions using HMO and HMT0 materials calcined at 450 °C. The results highlight a strong dependence of pH and initial lithium concentration on the sorption capacity. Higher pH values and lithium concentrations lead to increased Li-intercalation, as the process is governed by an equilibrium reaction based on Li^+/H^+ exchange (Eq. 2.11). In pH-dependence experiments, HMT0 achieved the highest sorption capacity at pH 12, reaching 4.08 mmol g^{-1} (28.3 mg g^{-1}).

Lithium extraction from natural geothermal brines, such as Bruchsal ($\text{pH} \approx 5.5$), is challenging due to their natural acidity and artificial pH adjustment leading to precipitation issues. As an alternative, buffering agents such as NaOAc were tested within the scope of this thesis and proved effective in stabilizing pH during lithium intercalation, significantly enhancing sorption capacity compared to unbuffered systems. A NaOAc concentration of 1.5 g L^{-1} was identified as sufficient for this purpose.

Additionally, the sorbent-to-brine ratio was investigated. At the lowest m/V ratio of 0.25 g L^{-1} , maximum sorption capacities of 5.66 mmol g^{-1} (39.28 mg g^{-1}) for LMT0 and 5.05 mmol g^{-1} (35.05 mg g^{-1}) for LMO were achieved — values that are high compared to other studies conducted at similar pH levels ($\text{pH} \approx 5.5$)^[115], and represent the highest capacities observed throughout this work. Furthermore, m/V tests revealed that lower m/V ratios result in higher sorption capacities but limit lithium depletion. An optimal balance between material utilization and extraction yield was established at an m/V ratio of 5 g L^{-1} .

In addition, ion exchange kinetics were examined, showing that both HMO and HMT0 exhibit rapid reaction times. HMT0 demonstrated superior performance, achieving 87 % of its maximum sorption capacity within 15 minutes, compared to 76 % for HMO. Kinetic data derived from the pseudo-second-order model provide valuable insights for process design, including reactor sizing and residence time optimization.

Based on previous experiments and with the aim of simulating realistic conditions, cycling tests over five cycles were conducted using HMO synthesized via spray drying, as well as HMO produced under optimized hydrothermal conditions. Additionally, HMT0 was included in the cycling experiments for comparison. In contrast to a previous study of the author^[58] with LMO from a hydrothermal synthesis process, where a Mn dissolution between 1 % and 5 % was measured, it could be demonstrated that HMO from the optimized hydrothermal synthesis delivers material with reduced Mn dissolution of only 1-3 %. The Mn dissolution of the novel spray drying process achieved even smaller Mn dissolution rates of 0.5-3 % and therefore enables higher chemical stability during long term cycling. In general, the Ti-substituted material shows by far the lowest Mn dissolution rates ($<0.5 \%$),

which is likely attributed to a stabilizing effect of Ti^{4+} on the crystal structure. However, crystallographic analyses of the spray dried materials revealed a pronounced change in lattice parameters for HMO after five cycles, particularly under brine cycling conditions. In contrast, HMT0 exhibited significantly less structural alteration, which aligns with reduced Mn release and thus indicates higher structural stability.

Overall, HMT0 stands out as a promising candidate for lithium extraction applications due to its higher sorption capacity, faster kinetics, and enhanced efficiency in geothermal brines. Further cycling is necessary to make more precise statements about long-term performance. However, the loss of powder in each separation step during cycling limits the number of cycles that can be performed with the powder. Granulation of the material may enable long term cycling.

Chapter 8

Tests under operational conditions - Benchmark with commercial material

In the previous chapter (Ch. 7.5), cycling experiments with LMO and Ti-substituted LMO (LMTO) powders were conducted over 5 cycles to evaluate their ability for repeated lithium loading and unloading. Additionally, the experiments aimed to quantify manganese release as an indicator of chemical stability and to assess the impact of multiple cycling using geothermal brine and synthetic brine (LiCl solution) on the crystal structure and morphology. However, cycling over more than 5 cycles was not possible due to loss of powder in the solid-liquid separation step after sorption and desorption. Granulation of the material was tested to improve its handling properties and, to minimize material loss by fixing the powder within a matrix, thereby enabling cycling over an extended number of cycles. This chapter aims to examine the cycling of the LMO granulated material over 20 cycles to determine whether any decline in sorption capacity can be observed. The experiments were conducted close to realistic conditions of a DLE pilot plant coupled with a geothermal system. This involved using geothermal brine (Bruchsal), maintaining an elevated temperature of 60 °C, and ensuring a short contact time between the sorbent and geothermal brine while maintaining a high sorption capacity. Based on kinetic experiments, 30 minutes were selected (Fig. 7.4).

In addition to the LMO granulate produced in this thesis, three other commercial materials in the form of granulates were tested: two different lithium double layered aluminum hydroxides (LDH) and one lithium titanium oxide (LTO). The matrix and exact composition of the commercial granulates cannot be disclosed herein. Since the fraction of active material in the granules is not known, sorption capacities are related to the mass of granulate, not the mass of the active component in this chapter. This value is particularly critical in the design of the DLE process, as it influences the dimensions of the reactor and therefore has a direct impact on capital expenditure (CAPEX).

Together with sorption capacity, selectivity represents another crucial material property, as it directly impacts the composition of the resulting product solution. The product solution is obtained after the bound lithium is released back into the solution (desorption solution).

The purity of this solution is crucial for the effort required in further processing in the post-DLE process up to the final product, battery-grade lithium salt (lithium carbonate/lithium hydroxide). High purity levels in the desorption solution reduce the complexity and cost of subsequent purification steps, making the overall process more efficient and economically viable. Consequently, this chapter examines how different materials influence product composition.

8.1 Cycling tests under operational conditions

In a first experiment, granulated LMO sorbent and 3 different commercial materials (LDH-1, LDH-2, LTO) were tested over 20 sorption/desorption cycles for their long-term sorption behavior. A mass of sorbent to brine ratio (m/V ratio) of 25 g L⁻¹ was selected, targeting a lithium depletion of brine ≈ 70 %. The experiments were conducted in geothermal brine at 60 °C

For LDH, unbuffered geothermal brine was used, since their mechanism of Li uptake involves an adsorption process (Ch. 2.4.1) and do not alter the pH of brine. In contrast LMO and LTO work based on ion exchange mechanism. As shown in Ch. 7.1 LMO reveals a strong pH dependence and results indicate that buffering is essential to maintain consistent performance. Therefore buffered geothermal brine ($c_{Li}=143$ mg g⁻¹; $c_{NaOAc}=1.5$ g g⁻¹) was used in all experiments involving LMO and LTO.

In Fig. 8.1a the sorption capacity Q_{Sorb} over 20 cycles is presented for LMO, LDH and LTO sorbents. The results indicate that the LMO granules prepared in this thesis present significant improved performance compared to commercial LDH and LTO. In the initial cycle LMO's Q_{Sorb} is higher by a factor of 5 compared to LDH-2 and LTO and 35 times higher than that of LDH-1. A close examination of the development of the LMO values over 20 cycles reveals that, despite some fluctuations in individual measurements, the overall level of sorption capacity remains approximately constant. In particular, a sorption capacity of 4.1 mg g⁻¹ (0.59 mmol g⁻¹) is observed after cycle 20, which is similar to the value of first cycle (3.9 mg g⁻¹; 0.56 mmol g⁻¹).

The profiles are provided in the insights of Fig. 8.1c for better visualization. For LDH-2, a sorption capacity of 0.8 mg g⁻¹ (0.11 mmol g⁻¹) was measured in the first cycle. Subsequently, a slight decline was observed in the following cycles, followed by an almost constant level between cycles 6 to 18, before declining again. Further cycling experiments are required to assess whether the observed decline continues or if the curve recovers. LTO exhibited a sorption capacity of 0.7 mg g⁻¹ (0.11 mmol g⁻¹) in the first cycle, followed by a gradual decline over 20 cycles, potentially due to material degradation or incomplete desorption. The results for LDH-1 show a sorption capacity of only 0.1 mg g⁻¹ (0.02 mmol g⁻¹) in the first cycle. However, the capacity increases over subsequent cycles and stabilizes around cycle 5, suggesting that an equilibrium state may have been reached.

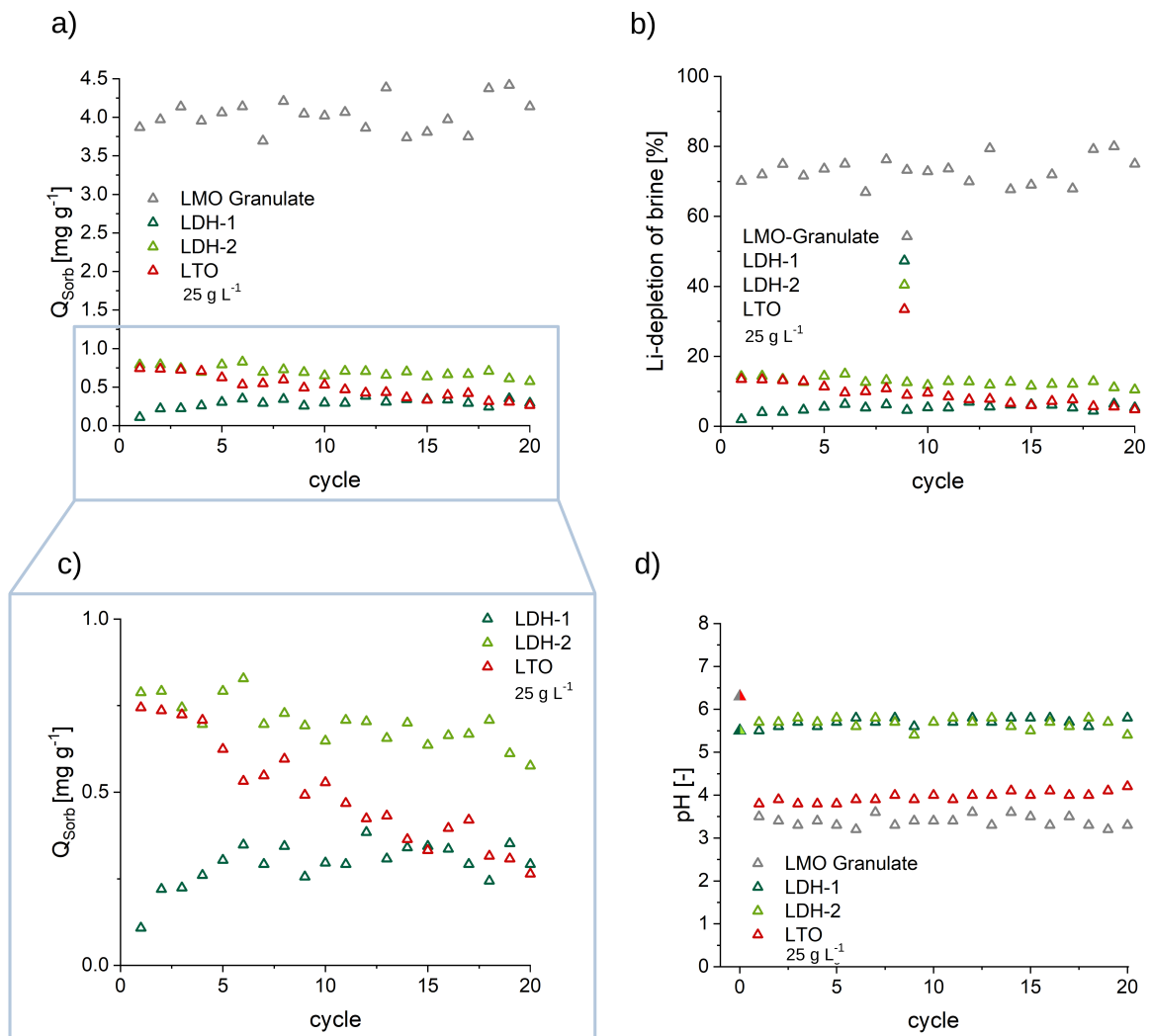


Figure 8.1: (a+c) Sorption capacity of LMO, LDH and LTO granules over 20 cycles for a m/V ratio of 25 g L⁻¹. (b) Corresponding Li-depletion and (d) pH values.

Fig. 8.1b shows the lithium depletion of geothermal brine after sorption with various sorbents. Using LMO granulate, between 66 % (cycle 7) and 80 % (cycle 19) of the lithium can be captured. In comparison, under an identical m/V ratio, significantly less lithium can be extracted with the other sorbents (<15 %) due to their lower sorption capacities. In the first cycle, a Li-recovery of 13 % (LTO) and 14 % (LDH-2) was measured, which was the highest value among those materials in this cycling experiment. After 20 cycles, the values for lithium depletion reflects development in sorption capacity (Fig. 8.1a). As the sorption capacity for LDH-2 decreased slightly between cycles, a decrease in Li depletion to only 10 % (cycle 20) could be observed. LDH-1 and LTO exhibited lithium removal of only 5 % in 20th cycle.

Fig. 8.1d shows the initial pH of the geothermal brine in both buffered (gray and red-filled triangle) and unbuffered (green-colored triangle) conditions. The open triangles represent the pH values after sorption over 20 cycles. It can be observed that the pH remains stable

after sorption with LDH. This stability is attributed to the intercalation of LiCl into the layered structure, which has only a minimal impact on the pH. This represents one of the major advantages of LDH sorbents, as they do not require any pre- or post-treatment of the solution for pH stabilization.

In contrast, significant pH changes are observed using LTO and LMO for sorption experiments. This behavior is due to the release of protons during lithium intercalation, as described by Eq. 2.11, leading to a drop in pH. To mitigate this effect, the geothermal brine was buffered prior to sorption (see Ch. 7.1). For LTO, the pH decreases from 6.3 to 3.8 after the first cycle. With increasing cycle number, the pH drop is less significant. By cycle 20, the pH drops from 6.3 to only 4.3. The reduced pH drop with increasing cycle number can be attributed to the decrease in sorption capacity. As fewer lithium ions are intercalated, correspondingly fewer protons are released, resulting in a less pronounced pH decrease. The pH after using LMO is significantly lower than with LTO, indicating a greater degree of ion exchange, which is consistent with higher sorption capacity for LMO granules compared to LTO.

Since only low lithium recovery ($<15\%$) was achieved with LDH and LTO at a m/V ratio of 25 g L^{-1} , an additional experiment was conducted using a higher m/V ratio for these materials. The m/V ratio was set to 200 g L^{-1} , again targeting a lithium depletion of approximately 70% , as previously achieved only by the LMO granulates under the lower m/V conditions. The resulting sorption capacities are shown in Fig. 8.2a, in comparison to the corresponding Li depletion in Fig. 8.2b for LDH and LTO with m/V ratio of 200 g L^{-1} . For better comparison, the results obtained with LMO granulate at $m/V = 25\text{ g L}^{-1}$ are also added to this graph.

As shown in Fig. 8.2a, the sorption capacities at a m/V ratio of 200 g L^{-1} follow a similar trend to those observed at the lower m/V ratio of 25 g L^{-1} . In general, the sorption capacities at 200 g L^{-1} are slightly lower. This can be attributed to the reduced availability of lithium per gram of sorbent material. These findings are consistent with the results presented in Ch. 7.2, where the influence of the m/V ratio on the sorption capacity of LMO powder was investigated.

The corresponding lithium depletion in Fig. 8.2b is significantly higher for a m/V ratio of 200 g L^{-1} compared to 25 g L^{-1} . Using LDH-2, more than 70% lithium recovery was achieved in the first cycle, which is in a similar range comparable to LMO granulate. However, it should be noted that to achieve a similar lithium recovery rate with LDH-2 compared to LMO required approximately eight times more sorbent material. This highlights a major advantage of using LMO granulate in the extraction process. In terms of plant design, the higher sorption capacity of LMO enables smaller equipment dimensions, reduced material handling requirements, and ultimately lower CAPEX.

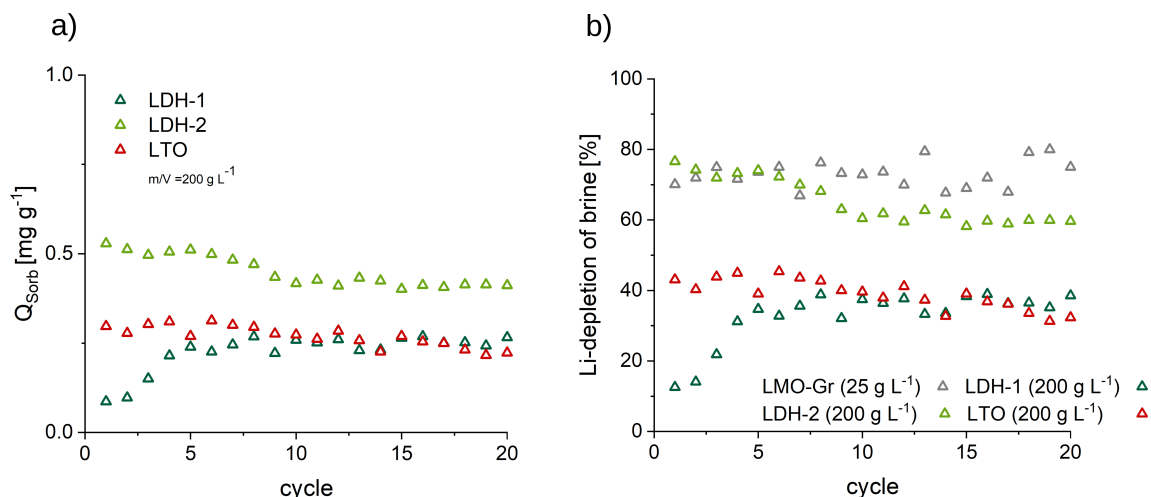


Figure 8.2: In (a) the sorption capacity of LDH and LTO granules over 20 cycles is presented for a m/V ratio of 200 g L^{-1} . In (b) the corresponding Li-depletion is shown for LDH and LTO at a m/V ratio of 200 g L^{-1} and for LMO with a m/V ratio of 25 g L^{-1} from the previous experiment.

As the sorption capacity of the LDH-2 sorbent decreases with increasing number of cycles, lithium recovery also decreases, reaching only 60 % after 20 cycles. In contrast, the recovery achieved with LMO granulate remains approximately constant throughout the cycling. The consistent sorption performance of LMO ensures reliable process operation and minimizes the risk of performance fluctuations that could compromise lithium recovery efficiency. The stable sorption capacity over multiple cycles indicates high material stability and long-term usability, reducing the need for frequent replacement or regeneration. This predictability not only lowers operating costs (OPEX), but also minimizes downtime associated with maintenance, further enhancing the economic attractiveness of LMO granulate compared to LDH-2. For the LTO and LDH-1, increasing the sorbent concentration to 200 g L^{-1} also led to a significant improvement in lithium depletion, reaching up to 43 % for LTO and 38 % for LDH-1.

8.2 Selectivity

In DLE processes, the target product is a lithium-rich aqueous solution, ideally containing only lithium ions in the form of LiCl . However, in practical applications, this solution often contains co-extracted impurities such as Na, K, Mg, and Ca, which must be removed in downstream purification steps to meet battery-grade specifications. In this regard, an important factor in the evaluation of sorbent materials is their selectivity, as it directly influences the quality and purity of the final product. In this study, LMO granulate, as well as commercial LDH and LTO were compared with respect to product purity. Furthermore, the selectivity of LMO and LMTO powders was investigated to understand the influence of

the active material and the formulation on the selectivity. The selectivity of the materials was assessed based on two factors. First, the composition of the product solutions obtained with different materials. Second, the transfer of foreign ions from the geothermal brine into the product solution (transfer factor).

To analyze material selectivity, results from the 10th cycle of the cyclic experiments (steady state conditions) were used for LMO granulate, LDH, and LTO. In contrast, the data for LMO and LMTO powders were obtained from the first loading cycle as equilibrium was already reached.

In the sorption step, the materials were exposed for 30 minutes to either buffered geothermal brine (LMO, LMTO, LTO) or unbuffered geothermal brine (LDH). Subsequently, desorption was carried out for 30 minutes using 0.5 M HCl (LMO, LMTO, LTO) or deionized water (LDH).

Purity of product solution. The molar fraction of cations in the product solution are presented in Fig. 8.3. The results indicate that in addition to lithium, various other ions present in the geothermal brine are co-extracted into the product solution.

For the LMO granulate, lithium is the dominant cation in the product solution, accounting for almost 64 mol% of the total cation content, while the LDH product solutions contain only 3.3 mol% (LDH-1) and 5.1 mol% (LDH-2) of lithium, respectively. Similarly to LMO, LTO also exhibit lithium as the major component in the product solution, with a lithium content of 66 mol%. The high product purity observed for LMO and LTO is attributed to their lithium ion sieve mechanism, which relies on size exclusion during insertion into the crystal lattice. Lithium ions are small enough to enter the interstitial sites. Other ions are sterically hindered and cannot pass through the diffusion channels. In contrast, LDH can accommodate various cations within their layered structure, which reduces selectivity and leads to material degradation and contamination of the product solution. However, the product solutions obtained from LMO and LTO are not entirely free of foreign ions. This residual presence is likely due to surface-related phenomena, such as the adsorption of non-lithium ions onto the material surface or might be related to the presence of residual geothermal brine on the sorbent.

Sodium represents the main impurity across all sorbents, which can be attributed to its high concentration in the geothermal brine (1550 mmol L^{-1}) and its carryover primarily via residual process water. Calcium, identified as the impurity cation with the second highest concentration of 200 mmol L^{-1} was found to constitute 5 % of the product solution using LMO granules. In contrast, 11 % of the product consisted of calcium for LDH-1 and 14 % for LDH-2. Interestingly, no calcium was found in the product using LTO, suggesting a particularly efficient separation of Li and Ca for this material. When examining the potassium content in the product solutions, it is evident that it is particularly low for LMO at 2 %,

below 5 % for LDH, and comparatively high for LTO with 8 %. The high potassium content in the product solution with LTO can be attributed to its monovalent nature, similar to lithium.

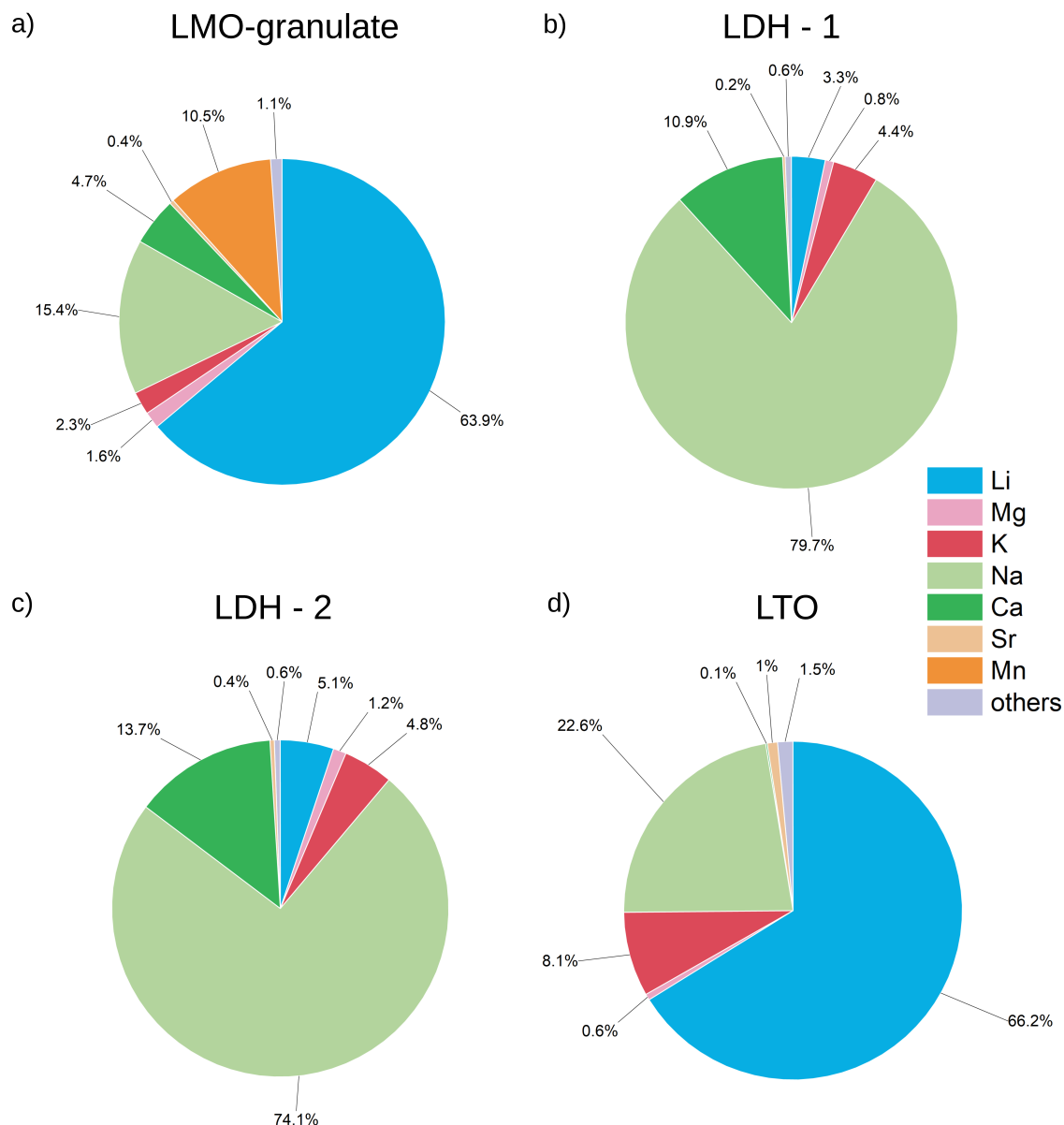


Figure 8.3: The molar fractions of cations in the product solution, obtained from 10th cycle, is presented for (a) LMO-granules, (b) LDH-1 , (c) LDH-2 and (d) LTO .

In contrast, divalent cations were separated with high efficiency using LTO. Magnesium is often discussed as a particularly challenging interfering ion in conventional lithium extraction due to its chemical similarities to lithium, including a comparable ionic radius.^[118] For this study, the magnesium content in the product solution remained consistently low across all sorbents, demonstrating the effectiveness of our approach in minimizing interference from magnesium. Furthermore, the product solution obtained from LMO granules contains manganese. This is primarily attributed to Mn dissolution from the sorbent. Although

manganese is also present in the geothermal brine, its transfer via sorption can be ruled out, as the Mn concentration in the geothermal brine remains constant during the sorption process. The use of Ti-substituted HMT0 sorbent may lead to reduced Mn contamination in the product solution, as previous experiments have shown significantly lower Mn dissolution from this material (HMO: 2.9 %; HMT0: 0.45 %). In addition to the contaminants listed in the pie chart, Pb and Ba were also detected in trace amounts ($< 0.02 \text{ mmol L}^{-1}$).

The results clearly demonstrate that using ion exchange materials such as LMO and LTO enables the production of a high-purity product solution with a lithium content of 64 % for LMO and 66 % for LTO. In contrast, LDH achieved a maximum lithium content of only 5 %. High product solution purity is essential, because impure solutions require additional downstream processing steps such as further concentration, purification, or removal of competing ions. These procedures are technically demanding and substantially increase OPEX.

However, it should be noted that, as this thesis is focusing on Mn-based sorption materials, the experimental methodology has been tailored accordingly. Alternative process conditions may potentially yield improved performance for the other sorbents as well.

Transfer factors. In addition to the product purity another parameter is introduced to evaluate the selectivity of the sorbents: the transfer factor T_{CI} . The transfer factor indicates the percentage of competing ions (CI) transferred from the geothermal brine into the product solution. It provides valuable insights into the material's sorption ability for various ions present in the geothermal brine. Furthermore, the transfer factor allows predictions about how the material might perform with geothermal brines of other compositions. A low T_{CI} value is desirable for achieving a lithium-enriched, high-purity product solution. However, even small T_{CI} -levels for ions present in high concentrations in the geothermal brine (e.g. Na: 36 g L^{-1} , Ca: 8 g L^{-1} , K: 3 g L^{-1} , Tab. 2.3) can lead to significant contamination in the final product. An evaluation of transfer factor was performed for LMO- and LMTO powder from the spray drying process, for LMO-granules and the commercial materials LDH-1, LDH-2, as well as LTO. It is important to note that the powder was washed twice with water between the sorption and desorption steps to remove residual geothermal brine, whereas the granulates (LMO, LDH and LTO) were not subjected to intermediate washing. This lack of washing can result in a greater transfer of foreign ions due to residual geothermal brine adhering to the granulates. The transfer factors for the most relevant contaminants in the product solution are presented in Tab. 8.1.

Table 8.1: Percentage transfer of competing ions originated from Bruchsal geothermal brine into the desorption solution

	T_{Na} [%]	T_{K} [%]	T_{Mg} [%]	T_{Ca} [%]	T_{Sr} [%]	T_{Ba} [%]	T_{Pb} [%]
LMO-powder	0.02	0.11	0.15	0.21	0.54	27.1	5.3
LMTO-powder	0.01	0.01	0.02	0.03	0.01	1.2	0.24
LMO-granule	0.2	0.6	2.1	0.5	2.0	1.6	4.7
LDH-1	10.7	11.7	10.9	11.0	11.2	1.5	53.1
LDH-2	10.6	13.5	17.6	14.7	20.5	2.7	77.6
LTO	0.2	1.2	0.5	-	2.7	1.7	30.6

Examining the major elements in the geothermal brine (Na, K, Mg, Ca, Sr) reveals that for LMO powder and LMTO powder, very low transfer factors of less than 1 % were observed. This demonstrates the high selectivity and efficiency of the materials in minimizing the presence of these ions in the final product. Overall, LMTO shows greater selectivity in comparison to LMO, as it transfers fewer foreign ions to the desorption solution. LMO granulates, as well as LTO granulates, exhibit higher T_{CI} values compared to powders, but remain significantly lower than those observed for LDH. This can be attributed to the ion-sieving effect of the LMO- and LTO-based materials. In general, the higher T_{CI} values observed for granulates can be attributed to the lack of washing between the sorption and desorption steps. However, different ions exhibit varying behaviors, indicating that the washing effect is not the sole contributing factor.

Considering sodium as the main foreign ion present in geothermal brine, notable differences between powder and granules become evident. While only 0.02 % (LMO) and 0.01 % (LMTO) of sodium were transferred to the product solution when using powder materials, the transfer increased tenfold to 0.2 % for both LMO and LTO granules. This highlights the significant influence of material shaping on ion selectivity. Potential contributing factors could include adherence of salts and ions on the surface or within the pore structure of the granules. For LDH, the transfer was even higher, as up to 11 % of the sodium present in the geothermal brine was transferred into the product solution. This can be attributed to the differing incorporation mechanisms of LMO and LTO compared to LDH. LMO and LTO are more selective than LDH, because their crystalline tunnel structures incorporate only small cations like Li^+ with a suitable ionic radius, while larger ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} or Sr^{2+} are sterically hindered. In contrast, LDH sorbents have a more flexible structure with larger interlayer spacings, allowing them to accommodate cations primarily through nonspecific electrostatic interactions. This leads to a more pronounced incorporation of foreign ions into the sorbent structure.

Comparing the transfer factor for barium for various sorbents shows that the separation of Li^+ from Ba^{2+} is more challenging compared to Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Sr^{2+} . Using LMO 27 % of Ba^{2+} was transferred from brine to the desorption solution. With substitution

and granulation it was possible to greatly reduce the transfer factor to only 1.2 % with LMTO and 1.6 % with LMO-granule. The commercial materials removed 1.5 % of Ba^{2+} with LDH-1, 2.7 % with LDH-2, and 1.7 % with LTO. The low selectivity towards Ba^{2+} could pose a challenge, as bound barium is prone to substitution by radium, a radioactive element commonly found in natural brines.^[73] This issue becomes particularly critical when barium accumulates within the sorbent over extended operational periods, potentially leading to increased radiological exposure and safety concerns.

Furthermore, the transfer for Pb^{2+} was evaluated. Lead is a relevant contaminant, as radioactive isotopes such as Pb-210 exist in natural brines. These isotopes can be transferred to the product solution, potentially leading to radiological risks and posing challenges for downstream processing. The results show that the transfer factor of lead is quite high for LMO with 5.3 %, but could be significantly reduced by Ti substitution to only 0.2 % (LMTO). This significant reduction could be attributed to a contraction of lattice parameters due to Ti-substitution from 8.079 Å for LMO to 8.067 Å for LMTO. Comparing LMO powder with LMO granules, the transfer of Pb^{2+} is slightly smaller for LMO granule with 4.7 % compared to 5.3 % for LMO powder. The granulation process partially covers the LMO powder, making parts of the active surface inaccessible to Pb^{2+} ions and thereby reducing overall lead sorption. The commercial materials accumulated high amounts of Pb^{2+} with 53 % (LDH-1), 78 % (LDH-2) and 31 % (LTO). Although these T_{CI} -values were significantly high, no substantial impact on the product solution composition was observed under the experimental conditions given. This can be attributed to the low Pb^{2+} content in the geothermal brine of Bruchsal. However, in brines with higher lead concentrations, such a high transfer factor could become a serious issue — potentially even a showstopper for process implementation.^[58]

8.3 Summary

In this chapter, the LMO material synthesized using the spray drying process developed within the scope of this PhD study was embedded in a PVC matrix to improve handling and mechanical stability. The resulting LMO granulate was tested under operating conditions similar to those of a geothermal power plant in lithium extraction experiments and compared to commercial materials (LDH and LTO), which were also tested under identical conditions. The materials were subjected to 20 cycles of lithium loading (sorption) followed by regeneration (desorption). The sorption capacity of the materials was analyzed over 20 cycles, and the percentage of lithium depletion from the geothermal brine was calculated. The LMO granulate demonstrated the ability to extract up to 80 % of the lithium from geothermal brine (m/V ratio of 25 g L⁻¹), whereas the commercial materials achieved less than 15 % lithium extraction. The sorption capacity of the LMO granulate was measured

at 3.9 mg g^{-1} (0.56 mmol g^{-1}), which is five times higher than LDH-2 (0.11 mmol g^{-1}) and LTO (0.11 mmol g^{-1}), and 35 times higher than LDH-1 (0.02 mmol g^{-1}). In addition to sorption capacity, the selectivity of the materials was also investigated and compared to powders obtained from the spray drying process (LMO powder and LMTO powder). The ion exchange materials exhibited significantly higher selectivity for lithium compared to LDH. Both the LMO granulate developed in this thesis and the commercial LTO granulate yielded high-purity product solutions, with lithium making up approximately 64 % and 66 % of the total cation content, respectively. In contrast, the use of LDH-based sorbent resulted in a product solution containing no more than 5 % lithium.

Transfer factor analyses revealed that LMO and LMTO powders transferred only 0.02 % and 0.01 % of sodium, respectively, into the product solution, despite sodium being the predominant interfering ion in geothermal brine. In contrast, LMO granulate and commercial LTO granulate transferred approximately 0.2 %, while the commercial LDH transferred more than 10 % of sodium. Furthermore, all commercial materials showed a particularly high transfer of lead into the product solution compared to those of Mn-based materials, which could pose a critical issue due to the potential for radioactive contamination of the product solution.

Chapter 9

Conclusion and outlook

This thesis addresses key challenges in the development of LMO sorbent materials for lithium extraction from various aqueous lithium sources, with a particular focus on geothermal brines. LMO is a highly promising sorbent due to its unique combination of high selectivity, high sorption capacity, and fast kinetics.^{[75][163]} However, several challenges, such as the scalability of the synthesis, the chemical stability of the material and handling of the sorbent, were encountered, which currently hinders market readiness. Through systematic optimization of the material synthesis, this work has demonstrated significant advances in material performance and scalability, bringing these materials closer to practical application. The Mn-based sorbent $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was previously synthesized by Herrmann *et al.*^[58] using a hydrothermal method, a conventional approach for producing LMO sorbents, following procedures described by Shi *et al.*^[115] and Chitrakar *et al.*^[23]. In this thesis, the synthesis parameter were optimized and the sorption capacity was improved from 1.19 mmol g^{-1} to 1.61 mmol g^{-1} and the Mn dissolution was significantly reduced from 5.5 % to 3 %. However, despite these improvements, the hydrothermal synthesis approach was limited by its small-scale production capabilities, making it unsuitable for industrial applications.

To address this limitation, a novel spray drying process was developed, enabling the production of sorbents on an industrial scale. This process not only increased sorption capacity to 2.03 mmol g^{-1} but also further reduced manganese dissolution to 2.9 % in the first cycle. However, the level of dissolution remains relatively high when considering the long-term operation. Drawing inspiration from substitution strategies used in battery research to stabilize manganese-based cathodes, this research explored the partial substitution of manganese with titanium (<0.5 mol%).^[120] The results demonstrated that the newly developed spray drying process is highly suitable for incorporating such modifications. The partial substitution of manganese with titanium further enhanced the chemical stability of the material, reducing manganese dissolution to just 0.45 % while simultaneously increasing the sorption capacity to 2.22 mmol g^{-1} . These findings highlight the flexibility of the spray drying process in tailoring material properties to meet specific performance requirements and demonstrate its potential for large-scale production.

In addition, this thesis provided critical insights into the chemical structure and phase com-

position of the synthesized materials. Using ICP-OES, the overall chemical structure of the sorbent was identified as $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. X-ray diffraction studies with Cu-K_α - and Mo-K_α -radiation confirmed that the measured reflections closely match the reference $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (PDF: 00-052-1841), characterized by a cubic spinel structure and space group $Fd\bar{3}m$. However, higher-resolution synchrotron XRD measurements revealed that the material consists of multiple phases, which were not detectable using in-house x-ray diffraction. In addition to the dominant spinel main phase, a secondary phase with a layered structure, Li_2MnO_3 (space group $C2/m$), was identified, accounting for 16.5 % of the material as determined by Rietveld refinement. The formation of Li_2MnO_3 is considered unfavorable, as it reduces the overall synthesis yield of the main spinel phase due to its leaching during sorbent activation. Since Li_2MnO_3 is a lithium-rich layered oxide, its presence implies a corresponding lithium deficiency in the main phase ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, with $x < 0.6$). NMR analyses further characterized the spinel phase, identifying it as $\text{Li}_4\text{Mn}_5\text{O}_{12}$, a known ion exchange material. These findings provide a deeper understanding of the material's structure and phase composition, while also demonstrating that conventional XRD techniques, although widely used in the literature to reference these material structures, are insufficient to fully characterize complex sorbents like $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$.^{[23][115][47]}

The spray dried activated sorbents HMO and HMT0 were examined in detail to assess their lithium insertion behavior under varying experimental conditions. The findings demonstrate a pronounced influence of pH and lithium concentration on sorption capacity. Elevated pH levels and higher lithium concentrations promoted lithium intercalation, consistent with the Li^+/H^+ exchange mechanism that governs the process. However, lithium recovery from natural geothermal brines—such as those from Bruchsal ($\text{pH} \approx 5.5$)—remains challenging due to their inherent acidity. Attempts to adjust pH artificially often result in precipitation, complicating the extraction process. To overcome this limitation, buffering agents like sodium acetate (NaOAc) were employed. These proved effective in maintaining a stable pH during lithium intercalation, leading to significantly improved sorption capacities compared to unbuffered systems. The sorbent-to-brine ratio was also optimized. At the lowest tested ratio of 0.25 g L^{-1} , maximum sorption capacities of 5.66 mmol g^{-1} (39.28 mg g^{-1}) for HMT0 and 5.05 mmol g^{-1} (35.05 mg g^{-1}) for HMO were achieved. These values are notably high in comparison to other studies conducted under similar pH conditions,^[115] and represent the highest capacities observed within the scope of this thesis. HMT0, in particular, shows strong potential for lithium recovery from geothermal brines, offering superior sorption capacity, faster kinetics, and improved performance under acidic conditions.

To address practical challenges such as handling and mechanical stability, the sorbent was incorporated into a PVC matrix as spherical granules. Granulation led to a reduction in sorption capacity, likely due to partial coverage of active sites within the material. Nevertheless, the resulting LMO granules exhibited significantly higher lithium sorption capacity of 0.56 mmol g^{-1} compared to commercial reference materials (LDH-1: 0.02 mmol g^{-1} ; LDH-

2: 0.11 mmol g⁻¹; LTO: 0.11 mmol g⁻¹). Furthermore, LMO granules exhibited significantly higher lithium sorption selectivity compared to LDH and were comparable to LTO. In the resulting product solution approximately 64 % of all dissolved cations were lithium. In comparison, LTO reached 66 %, while LDH achieved a maximum of only 5 %. Such high lithium purity in the desorption solution reduces the complexity and cost of downstream purification steps, contributing to a more efficient and economically viable overall process.

While this research has demonstrated significant advancements in the development and scalability of HMTO sorbents, several aspects require further investigation to ensure their practical applicability and industrial implementation. Due to time constraints, long-term cycling of HMTO beyond five cycles could not be performed within the scope of this thesis. Future investigations are required to assess the chemical stability and structural integrity of HMTO under extended operational conditions. Furthermore, although the synthesis of the sorbent powder has been successfully scaled up, the granulation process is still performed manually. For future applications in large-scale lithium extraction, it will be essential to develop a reproducible and scalable granulation method that ensures the formation of mechanically stable and efficient sorbent granules. In addition, to assess the practical applicability of the developed sorbents, preparations were made for pilot-scale use, and a corresponding plant was constructed. However, due to renovation work at the Bruchsal geothermal facility, pilot tests could not be conducted within the time frame of this thesis. These tests are planned and will be crucial for evaluating the long-term performance of the sorbents under real operational conditions, providing valuable insights into their behavior in industrial scale lithium extraction processes.

Overall, this PhD thesis provides a robust framework for advancing sustainable lithium recovery technologies. The developed materials and processes have the potential to play a pivotal role in addressing the growing global demand for lithium, contributing to the development of a more sustainable and resilient energy system.

Appendices

Appendix A

Scale up of hydrothermal synthesis

In an attempt to scale up the hydrothermal synthesis, the input quantities for a 125 mL autoclave were linearly increased to a 1 L autoclave. Accordingly, the substrate amounts were adjusted proportionally. The hydrothermal synthesis was carried out under the optimized conditions described in Ch. 5.2. An XRD analysis revealed the appearance of additional reflections, indicating the presence of impurities. A sorption experiment was conducted following the same procedure outlined in Ch. 5.1.1. The results were compared in terms of sorption capacity and Mn release. When using the larger autoclave, a significantly lower sorption capacity of only 0.96 mmol g^{-1} was observed, compared to 1.62 mmol g^{-1} in the 125 mL setup. Additionally, Mn release was higher by a factor of 2.8, suggesting reduced chemical stability of the material.

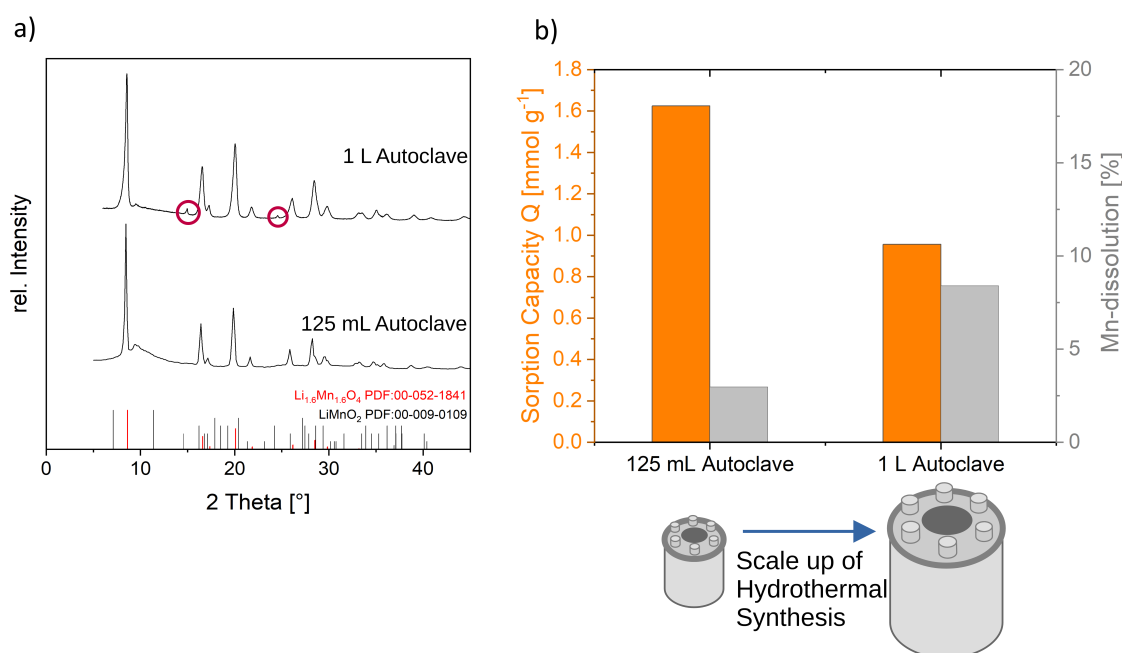


Figure A.1: (a) XRD pattern of LMO sorbent obtained from hydrothermal synthesis (optimized conditions) in a 125 mL and 1 L autoclave. (b) Sorption capacity and Mn-dissolution for LMO obtained from different sizes of autoclave

Rietveld refinement of LMO and HMO calcined at various temperatures

A Rietveld refinement was performed using FullProf Software for calcined LMO and HMO calcined at 720 °C and 800 °C as well as stepwise calcined sample LMO-720°C-450°C. For LMO-720°C, LMO-800°C, LMO-720°C-450°C and HMO-800°C both a spinel structure (space group $Fd\bar{3}m$, ICDD 1514017) and a layered Li_2MnO_3 impurity phase (space group $C2/m$, ICDD 1514044) were considered. For HMO-720°C and HMO-720°C-450°C a single-phase spinel structure was assumed with space group $Fd\bar{3}m$.

The profile function used for all refinements was function number 7, corresponding to the Thompson-Cox-Hastings pseudo-Voigt profile convoluted with an axial divergence asymmetry function. The refinement parameters included zero shift, scale factor, lattice parameters, isotropic temperature factor (B_{ov}) and asymmetry parameters S_L and D_L. For all LMO samples, the refinement focused on zero shift, scale, lattice parameters, and selected profile parameters. For HMO samples, additional refinement of background points and half-width parameters (U, W) was performed. The results of the fitting are shown in Fig. A.2.

Rietveld refinement of synchrotron data of LMO-450 and HMO-450

The LaB_6 refinement was conducted to determine the U, V, and W Caglioti instrumental resolution (irf file). The profile function used was number 7 which corresponds to the Thompson-Cox-Hastings pseudo-Voigt convoluted with an axial divergence asymmetry function. For all sample refinements, U, V, and W were taken only from the irf file, while X (mainly strain) and Y (mainly size) were refinable parameters. The background points and lattice parameters were refinable parameters.

Starting with the 'normal' cubic spinel (space group $Fd\bar{3}m$, no. 227) as used for previous analysis (ICDD 1514017), the lattice parameter a and Wyckoff positions 32e fully occupied by oxygen, 16d (0.5, 0.5, 0.5) fully occupied by Mn, and 8a (0.125, 0.125, 0.125) fully occupied by Li were considered. Modification was made by allowing partial occupation of the 16d site by Li.

The structural model included an isotropic overall temperature factor (B_{ov}) for all sites, which was refined as a 'fudge' factor and resulted in negative values. Individual fixed isotropic temperature factors were used for Li ($1.18 \text{ \AA}^2$), Mn ($0.78 \text{ \AA}^2$), and O ($1.51 \text{ \AA}^2$). As second phase a layered Li_2MnO_3 impurity phase (space group $C2/m$, ICDD 1514044) was considered. Special reflections associated with the layered Li_2MnO_3 phase were explicitly considered in the refinement to enhance the quality of the fit. Fig. 6.7 shows the XRD Rietveld refinement pattern.

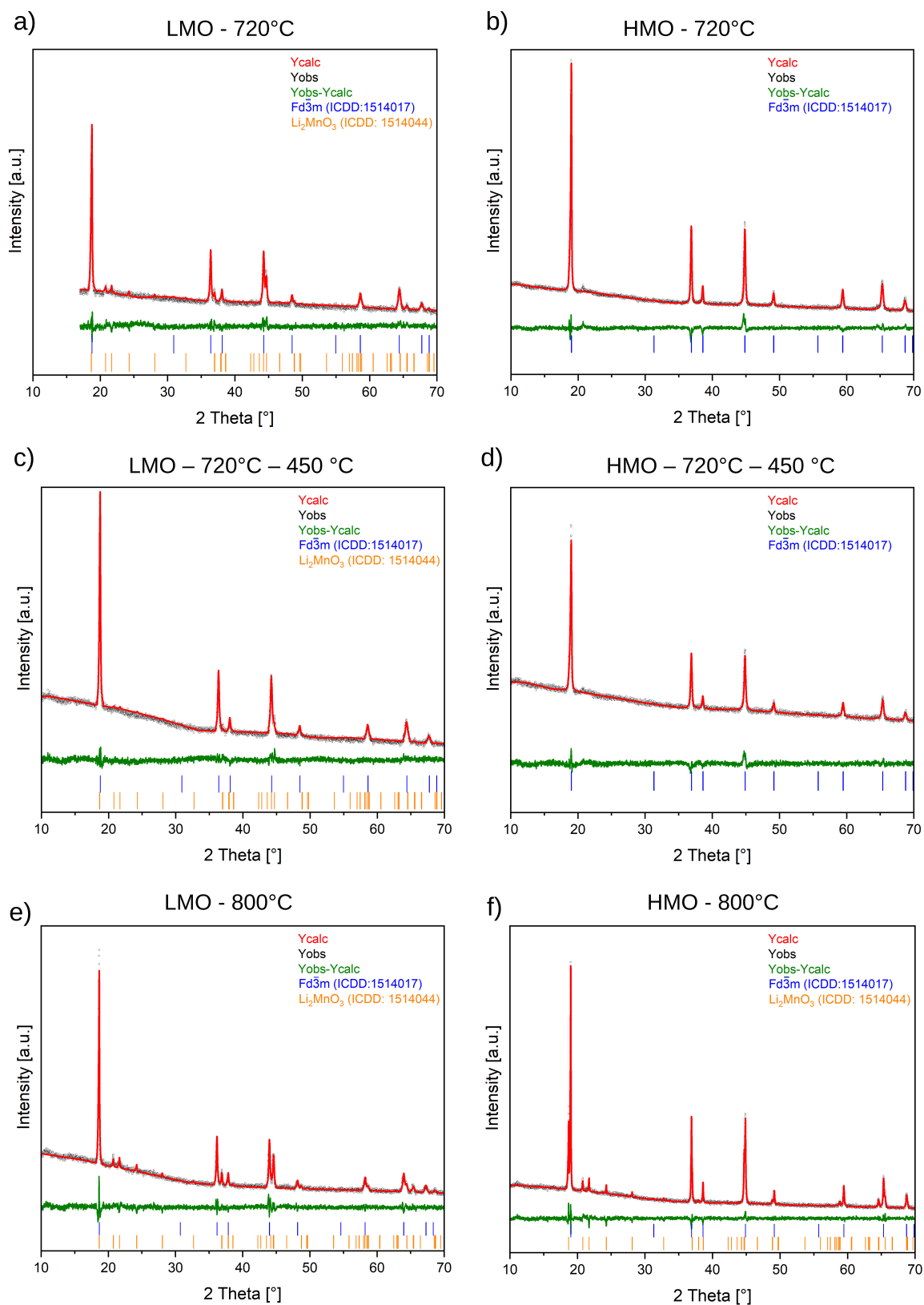


Figure A.2: Rietveld refinement of (a) LMO-720°C, (b) HMO-720°C, (c) LMO-720°C-450°C, (d) HMO-720°C-450°C, (e) LMO-800°C, (f) HMO-800°C

Rietveld refinement of cycled LMO

A Rietveld refinement was performed using FullProf Software for brine-cycled LMO-450 and LiCl-cycled LMO-450. A single phase spinel structure (space group $Fd\bar{3}m$, ICDD 1514017) were considered for the structural model. The Rietveld refinements were carried out using profile function number 7 in FullProf, which corresponds to the Thompson-Cox-Hastings pseudo-Voigt function convoluted with an axial divergence asymmetry correction. For both cycled materials, the refinement parameters included zero shift, scale factor, lattice parameters, background points, strain (X) and asymmetry parameters S_L and D_L. For brine cycled LMO, additional refinement of half-width parameters (U, W) and isotropic temperature factor (B_{ov}) was performed. The results of the fitting are presented in Fig. A.3.

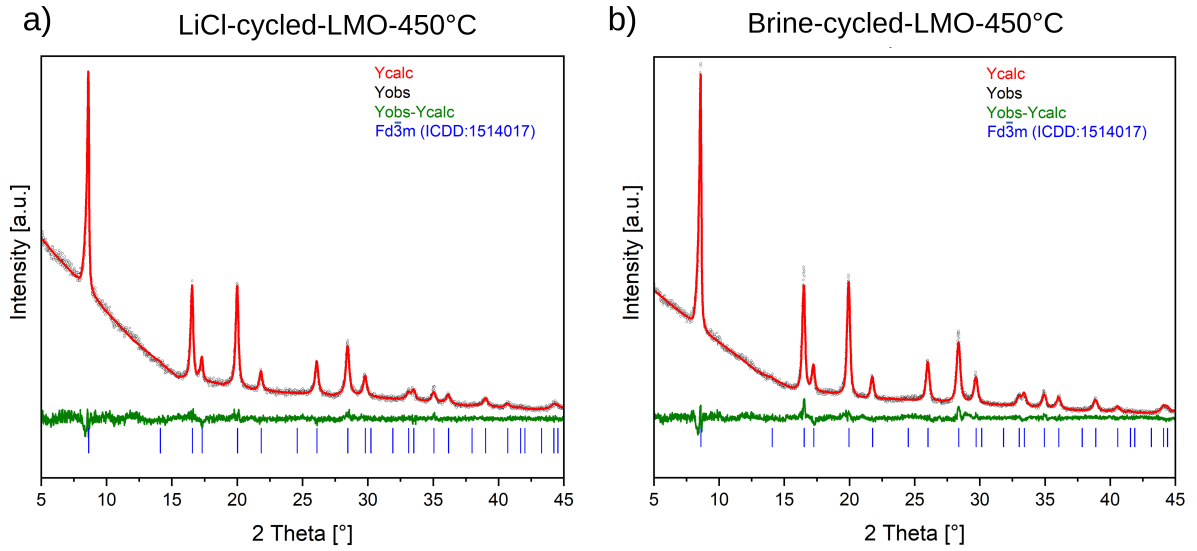


Figure A.3: Rietveld refinement of (a) LiCl-cycled LMO-450°C and (b) geothermal brine cycled LMO-450°C.

Particle Size distribution (PSD)

An analysis of particle size distributions for the precursor, pristine LMO, and activated HMO was performed. The results are shown in Fig. A.4.

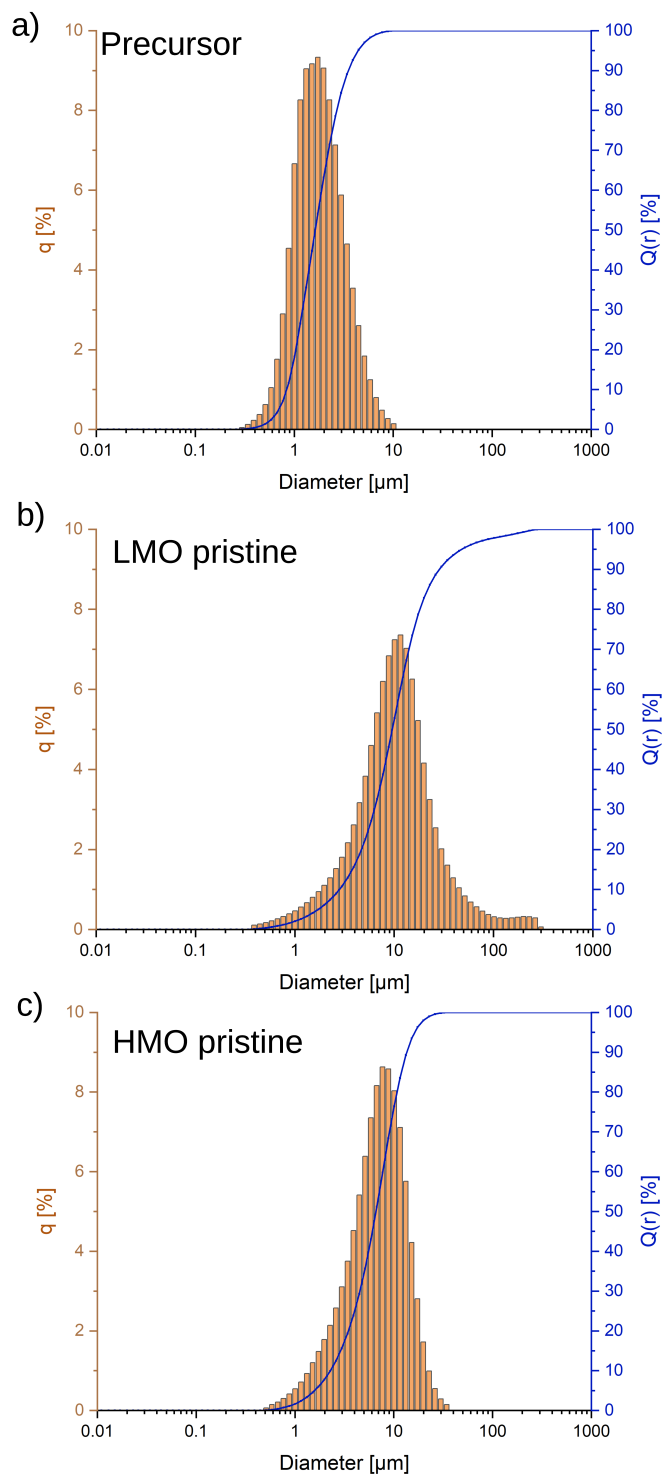


Figure A.4: PSD including differential distribution (q) and cumulative distribution (Q) for (a) precursor (b) pristine LMO and (c) pickled HMO. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

BET-Parameters The Brunauer–Emmett–Teller (BET) equation, an empirical model developed to evaluate the specific surface area of porous materials, is expressed as follows [116]:

$$\frac{p}{n^a(p_0 - p)} = \frac{1}{n_m^a \cdot C} + \frac{C - 1}{C} \cdot \frac{p}{p_0} \cdot \frac{1}{n_m^a} \quad (.1)$$

Here, n^a denotes the amount adsorbed at a given relative pressure p/p_0 , while n_m^a represents the monolayer adsorption capacity. According to BET theory, the constant C is exponentially related to the enthalpy of adsorption in the first adsorbed layer. A molecular cross-sectional area $a_m = 0.1620 \text{ nm}^2$ was assumed for the calculations.

Table A.1: Parameters of BET Analysis

Sample	n_m^a mmol g ⁻¹	C -	p/ p ₀ -	Y-Intercept g mmol ⁻¹	Sat. pressure mmHg
LMO-800	0.0143	139.657	0.2916	0.501 ± 0.026	777.96
LMO-720	0.0297	110.843	0.2921	0.303 ± 0.006	764.44
LMO-720-450	0.0231	136.290	0.2918	0.317 ± 0.015	777.96
LMO-450	0.0265	122.212	0.2915	0.308 ± 0.008	777.96
LMTO-450	0.0652	133.945	0.2913	0.114 ± 0.006	761.84

Linear isotherm plots and BET surface area plots for calcined LMO materials and LMTO are shown in Fig. A.5 and A.6.

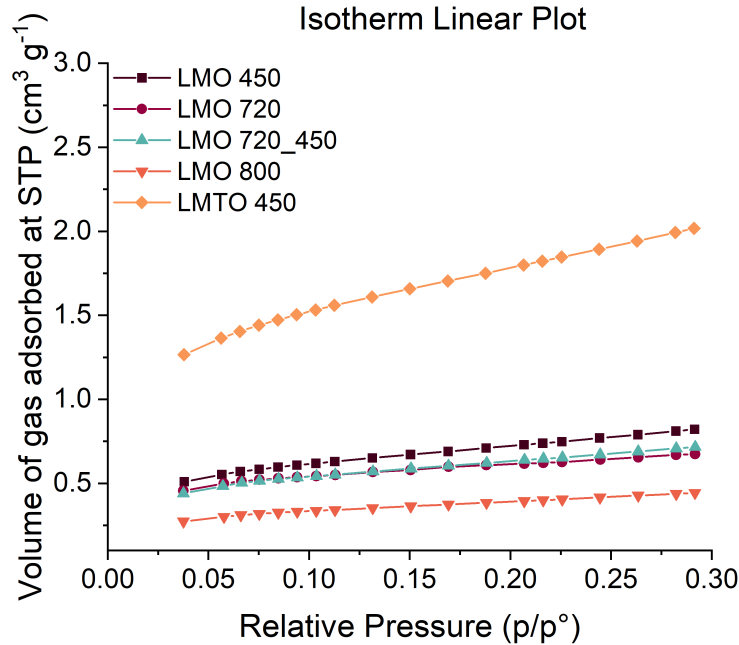


Figure A.5: BET: Isotherm linear plot. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

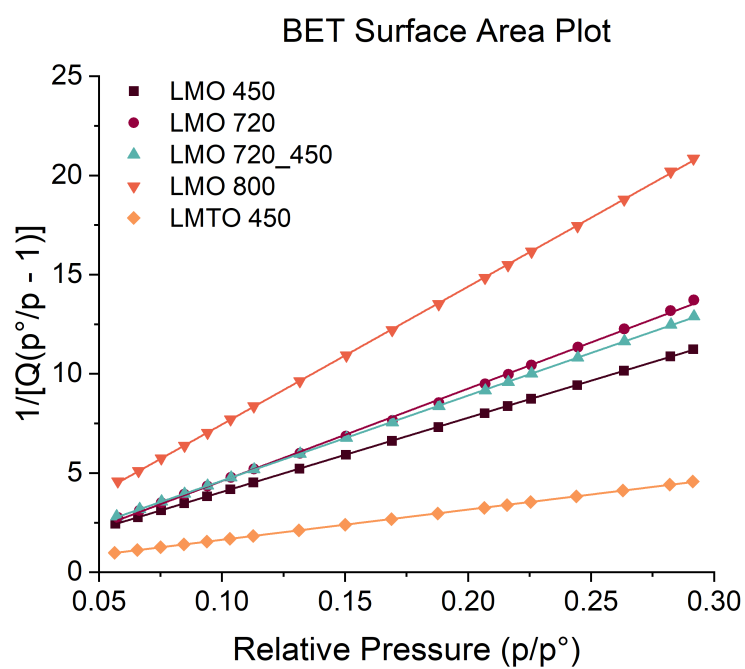


Figure A.6: BET: Surface area plot. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

TGA

A TGA of the LMTO precursor was performed. The results are presented in Fig. A.7.

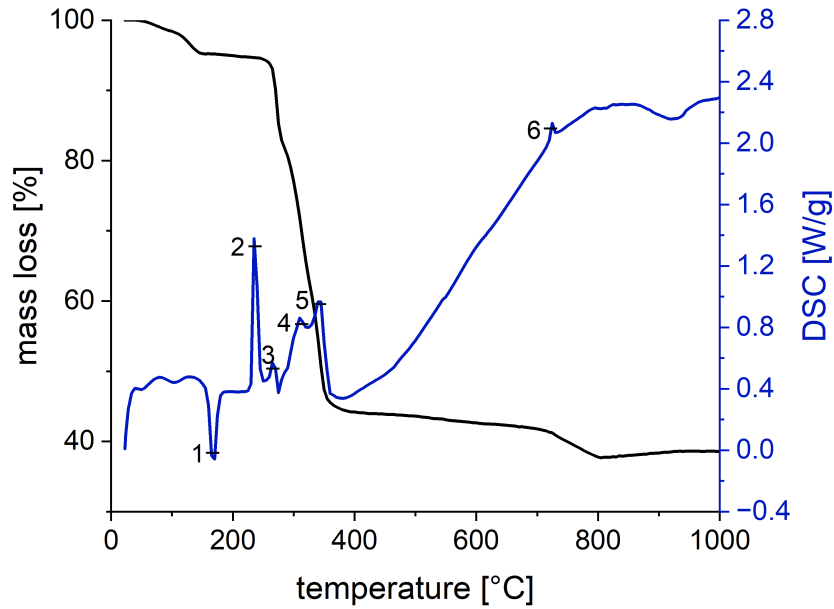


Figure A.7: TGA of LMTO. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

Tab. A.2 presents the corresponding peaks that are considered relevant in the context of this analysis.

Table A.2: TGA: Significant Peaks

Peak	T [°C]	Reaction Type
1	167	exothermic
2	237	endothermic
3	268	endothermic
4	311	endothermic
5	343	endothermic
6	727	endothermic

EDX-Energy diagram

EDX-Analysis was conducted for the brine-cycled sorbents HMO and HMTO. The Energy diagram is shown in Fig.A.8.

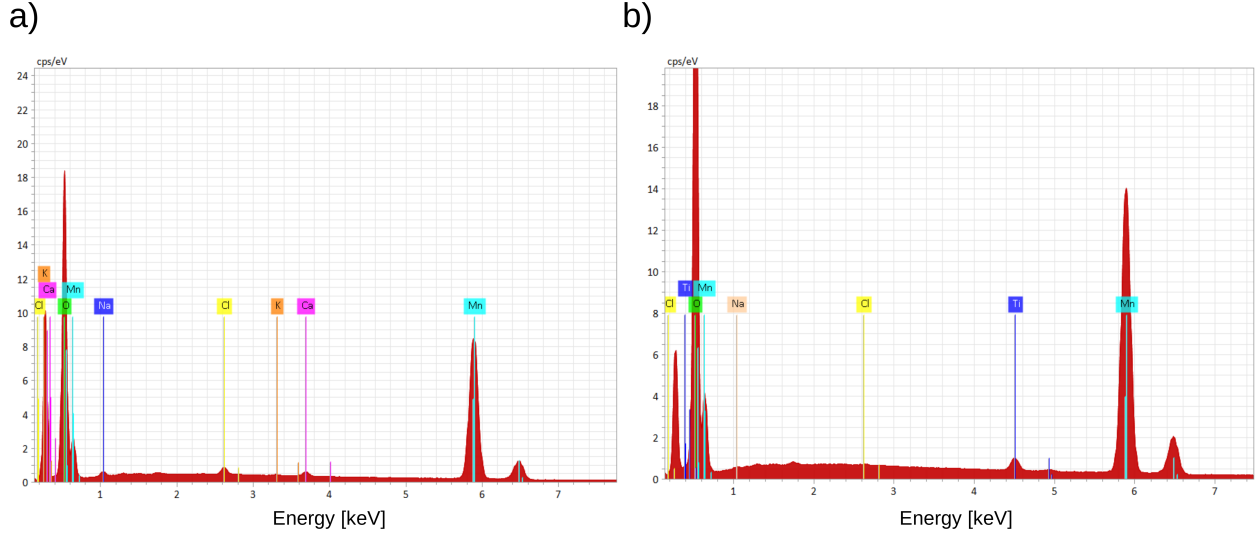


Figure A.8: Energy diagram of sorbent cycled with geothermal brine a) HMO and b) HMTO. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

pH value after sorption in a buffered system

To estimate the expected pH after adsorption, the following example is considered: A LiCl solution containing 150 ppm of Li was prepared, and sodium acetate (NaOAc) was added at a concentration of 1.5 g L^{-1} , corresponding to approximately 0.018 mol L^{-1} . The initial pH of the solution was measured to be 7.41. Given that the acid dissociation constant of acetic acid (HA) is $pK_a \approx 4.76$, the ratio of acetate ions $[A^-]$ to undissociated acetic acid $[HA]$ can be calculated using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

By substituting the known values into the Henderson–Hasselbalch equation, the following expression is obtained:

$$\begin{aligned} 7.41 &= 4.76 + \log \left(\frac{[A^-]}{[HA]} \right) \\ \log \left(\frac{[A^-]}{[HA]} \right) &= 7.41 - 4.76 = 2.65 \\ \frac{[A^-]}{[HA]} &= 10^{2.65} \approx 446,68 \end{aligned}$$

Rearranging the equation yields the following expression:

$$[\text{HA}] = \frac{[\text{A}^-]}{446,68}$$

For 0.04 L of the solution, the molar amount of NaOAc is:

$$n(\text{A}^-) = 0.018 \text{ mol/L} \times 0.04 \text{ L} = 0.00072 \text{ mol}$$

The molar amount of acetic acid ($n(\text{HA})$) is:

$$n(\text{HA}) = \frac{0.00072 \text{ mol}}{446,68} \approx 1.61 \times 10^{-6} \text{ mol}$$

The sorption process involves an ion exchange mechanism between lithium Li^+ and protons H^+ . In this experiment a release of 0.6728 mmol H^+ was detected (Fig. 7.2a), which results in:

$$n(\text{A}^-)_{\text{new}} = 0.00072 \text{ mol} - 0.0006728 \text{ mol} = 0.0000590 \text{ mol}$$

$$n(\text{HA})_{\text{new}} = 1.61 \times 10^{-6} \text{ mol} + 0.0006728 \text{ mol} = 0.0006744 \text{ mol}$$

This corresponds to a concentration of:

$$[\text{A}^-]_{\text{new}} = \frac{0.0000590 \text{ mol}}{0.04 \text{ l}} = 0.0014738 \text{ mol L}^{-1}$$

$$[\text{HA}]_{\text{new}} = \frac{0.0006744 \text{ mol}}{0.04 \text{ l}} = 0.0168598 \text{ mol L}^{-1}$$

By substituting the values into the Henderson-Hasselbalch equation, we get the following expression:

$$\text{pH}_{\text{new}} = \text{p}K_a + \log \left(\frac{[\text{A}^-]_{\text{new}}}{[\text{HA}]_{\text{new}}} \right)$$

$$\text{pH}_{\text{new}} = 4.76 + \log \left(\frac{0.0014738}{0.0168598} \right)$$

$$\text{pH}_{\text{new}} = 4.76 - 1.06 = 3.7$$

The expected pH value after the ion exchange is 3.7.

Fitting kinetic models

The Python script used for kinetic fitting is provided in Fig. A.9.

```

1
2 import numpy as np
3 from scipy.optimize import curve_fit
4 import matplotlib.pyplot as plt
5 from sklearn.metrics import r2_score
6
7
8 def first_order(t, q_e, k_1):
9     return q_e * (1 - np.exp(-k_1 * t))
10
11 def second_order(t, q_e, k_1):
12     return t / ((1 / (k_1 * q_e * q_e)) + t / q_e)
13
14 t = np.array([5/60, 1/6, 0.25, 1/3, 0.5, 1, 2, 4, 24])
15 data = [
16     {
17         'name': 'LMO',
18         'qt': np.array([0.86344, 1.16493, 1.326512968, 1.40567, 1.465763689, 1.58286, 1.697636888, 1.759913545, 1.742420749]),
19         'qt_errors': np.array([0.246973, 0.365481, 0.370584598, 0.2987643, 0.314758807, 0.2456782, 0.317932795, 0.230323481, 0.194741936])
20     },
21     {
22         'name': 'LMT0',
23         'qt': np.array([1.3837, 1.6291, 1.667896254, 1.72346, 1.700417867, 1.8233, 1.885677233, 1.871080692, 1.933962536]),
24         'qt_errors': np.array([0.13567, 0.11482, 0.137307926, 0.12567, 0.121903305, 0.11473, 0.115005228, 0.117812957, 0.113148441])
25     }
26 ]
27 orders = [{'name': 'first', 'method': first_order}, {'name': 'second', 'method': second_order}]
28
29 for material in data:
30     for order in orders:
31         popt, pcov = curve_fit(order['method'], t, material['qt'], sigma=material['qt_errors'], absolute_sigma=False)
32         q_e, k_1 = popt
33         q_e_error, k_1_error = np.sqrt(np.diag(pcov))
34         label = f"Original data {material['name']} {order['name']} order with absolut_sigma=false"
35         t_fit = np.linspace(min(t), max(t), 100)
36         qt_fit = order['method'](t_fit, q_e, k_1)
37
38         r2 = r2_score(material['qt'], order['method'](t, q_e, k_1))
39
40         with open("results.txt", "a") as file:
41             file.write(f"{label}\n")
42             file.write(f"q_e = {q_e} +/- {q_e_error}\n")
43             file.write(f"k_1 = {k_1} +/- {k_1_error}\n")
44             file.write(f"R^2 = {r2}\n")
45             file.write("\n")
46
47         plt.figure()
48         plt.errorbar(t, material['qt'], yerr=material['qt_errors'], fmt='o', label=label)
49         plt.plot(t_fit, qt_fit, 'r', label='Fitted curve')
50         plt.xlabel('Time t (h)')
51         plt.ylabel('q_t (mmol/g)')
52         plt.legend()
53         plt.savefig(f"{label}.png", dpi=300)

```

Figure A.9: Python code: Fitting of kinetic model pseudo first and pseudo second order. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

The fitting results are presented in Fig. A.10

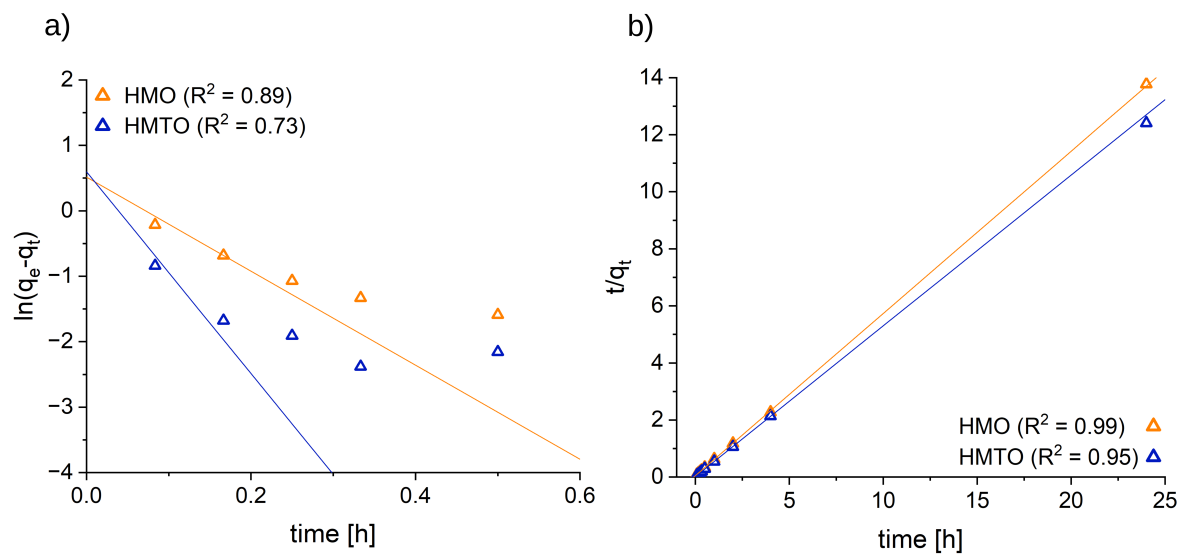


Figure A.10: a) Fitting of k_1 and $q_{e,calc}$ using pseudo-first-order kinetic model. b) Fitting of k_2 and $q_{e,calc}$ using pseudo-second-order kinetic model. Figure reproduced from *Herrmann et al. 2025*.^[57] Licensed under CC BY 4.0.

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Publications and Patents

Patents	Applicant-number	Status	Applicant
Cascade novel process for lithium extraction	AN: 11360179US-20240523	granted	EnBW
Herstellung des Mn-basierten Adsorbenten $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ im Sprühtrocknungsverfahren.	AN: 11360183DE	filed	EnBW + KIT
Effizientes Pre-Treatment von Batterien als Recycling-Vorstufe	DE102021117319A1	filed	EnBW
Verfahren zum Freimachen einer durch ein Adsorbens zugesetzten Tiefbohrung	EP4098715A1	granted	EnBW
Lithiumgewinnung mit CO_2	DE102022130083A1	filed	EnBW
Verfahren zur Herstellung eines Lithium-Adsorbens	EP4066935A1	filed	EnBW
Verfahren zur Gewinnung von Lithium aus Sole und zur Rückgewinnung von Lithium beim Recycling von Li-Ionen-Akkumulatoren	EP4063527A1	filed	EnBW

Publication	Journal	Status	Authors
Lithium recovery from geothermal brine – an investigation into the desorption of lithium ions using manganese oxide adsorbents	Energy Advances	Published 2022	<u>L. Herrmann</u> , H. Ehrenberg, M. Graczyk-Zajac, E. Kaymakci, T. Kölbel, L. Kölbel, J. Tübke
Universal and efficient extraction of lithium for lithium-ion battery recycling using mechanochemistry	Communications Chemistry	Published 2023	O. Dolotko, N. Gehrke, T. Malliaridou, R. Sieweck, <u>L. Herrmann</u> , B. Hunzinger, M. Knapp, H. Ehrenberg
Lithium extraction from geothermal brines in the Upper Rhine Graben: A case study of potential and current state of the art	Hydro-metallurgy	Published 2023	L. Kölbel, T. Kölbel, <u>L. Herrmann</u> , E. Kaymakci, I. Ghergut, A. Poirel, J. Schneider
Lithium extraction from geothermal brines: Adsorption-desorption studies on ^{226}Ra (^{228}Ra) and ^{210}Pb on lithium-titanium-oxides (LTO)	Applied Geochemistry	Published 2024	L. Kölbel, <u>L. Herrmann</u> , T. Kölbel, J. Schneider
Synthesis of Lithium Manganese Oxide and Ti-Substituted LMO Sorbents for Lithium Extraction in a Spray-Drying Process	ChemSusChem	Published 2025	<u>L. Herrmann</u> , N. Bohn, A. Pfau, T. Kölbel, H. Ehrenberg, J. R. Binder F. Jeschull
Reassessing the structure of the sorbent with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ used for Direct Lithium Extraction	-	submitted	M. Gamba, <u>L. Herrmann</u> , B. Schwarz, H. Li, S. Mangold, S. Indis, G. Lener, H. Ehrenberg F. Jeschull
Transition from Ferro- to Antiferromagnetism in $\text{Li}_4\text{Mn}_5\text{O}_{12}$ Spinel Induced by Li^+/H^+ Ion Exchange	-	submitted	B. Schwarz, <u>L. Herrmann</u> , H. Li, S. Indis, N. Bohn S. Mangold, F. Jeschull H. Ehrenberg

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