

Microstructure of Electrodeposited Lithium Metal Electrodes in Reservoir-Free Solid-State Batteries

*Mikrostruktur von elektrochemisch
abgeschiedenen Lithiummetallelektroden
in Reservoir-freien Feststoffbatterien*

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*Allein dein Mut zur Heiterkeit,
wirkt fort in alle Ewigkeit.*

Abstract

The transition towards renewable energy sources and the electrification of transportation are essential drivers for the development of advanced energy storage solutions with high energy and power densities. Conventional lithium-ion batteries based on liquid electrolytes have become the dominant technology for portable electronics and electric vehicles. However, they are rapidly approaching their theoretical physicochemical limits in terms of energy density. Solid-state batteries comprising lithium metal electrodes and inorganic solid electrolytes promise substantial improvements over conventional lithium-ion batteries, offering the potential to overcome current safety concerns, mitigate flammability risks inherent to liquid electrolytes, and increase both energy as well as power density.

A critical obstacle in implementing lithium metal electrodes remains the maintenance of the electrode|solid electrolyte interface during cell operation, which can lead to morphological instabilities during both charge and discharge. Furthermore, the storage of lithium metal and cell manufacturing must take place under inert gas atmospheres, which is costly. Otherwise, contact with atmospheric components such as moisture (H_2O), oxygen (O_2), and nitrogen (N_2) leads to the formation of resistive passivation layers on the surface, which impede cell performance. To address these challenges, reservoir-free cell concepts are being intensively explored. In these configurations, the lithium metal electrode is electrodeposited only during the initial charging step, with lithium sourced from the lithiated positive electrode. This approach substantially simplifies cell fabrication, as no lithium metal needs to be handled during assembly. However, electrodeposition is likewise associated with new morphological instabilities, and fundamental differences in microstructure and chemistry between conventionally produced and electrodeposited lithium remain insufficiently understood.

This dissertation focuses on the chemical and microstructural characterization of electrodeposited lithium, using reservoir-free model systems comprising steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interfaces. Chemical analysis revealed an exceptionally high purity compared to commercial lithium foils. Microstructural analysis on millimeter-sized cross-sections, based on electron backscatter diffraction, uncovered a dynamic evolution of the resulting lithium grain structure during both electrodeposition and subsequent electrodedissolution cycles. Finally, interlayer materials were introduced as an effective measure to control the resulting lithium microstructure.

Overall, the results presented in this dissertation significantly expand the understanding of electrodeposited lithium layers both in terms of their purity as well as their microstructure. Latter depends on electrodeposition parameters, cycling history, and current collector modifications. These insights aim to optimize the performance of reservoir-free cells and enable the development of advanced solid-state batteries.

Zusammenfassung

Der Übergang zu erneuerbaren Energiequellen und die Elektrifizierung des Verkehrssektors sind wesentliche Treiber für die Entwicklung fortschrittlicher Energiespeicher mit hohen Energie- und Leistungsdichten. Dabei nähern sich konventionelle Lithiumionenbatterien auf Basis flüssiger Elektrolyte ihren physikochemischen Grenzen. Feststoffbatterien mit Lithiummetallelektroden und anorganischen Festelektrolyten hingegen versprechen erhebliche Verbesserungen, indem sie Sicherheitsbedenken adressieren, keine entflammaren Flüssigelektrolyte verwenden, und die Energie- sowie Leistungsdichten gegenwärtiger Energiespeicher potenziell überschreiten können.

Ein wesentliches Hindernis bei der Verwendung von Lithiummetallelektroden ist der Erhalt einer intakten Lithium|Festelektrolyt-Grenzfläche, an welcher es zu morphologischen Instabilitäten beim Laden und Entladen kommen kann. Zudem müssen die Lagerung von Lithiummetall und die Zellherstellung unter Inertgasatmosphäre erfolgen, was mit hohen Kosten verbunden ist. Andernfalls führt der Kontakt mit atmosphärischen Bestandteilen wie Wasser (H_2O), Sauerstoff (O_2) und Stickstoff (N_2) zur Bildung von resistiven Passivierungsschichten auf der Oberfläche. Um diese Herausforderungen zu adressieren, werden Reservoir-freie Zellkonzepte erforscht. Hierbei wird die Lithiummetallelektrode erst während des initialen Ladeschritts elektrochemisch abgeschieden, wobei das Lithium aus der positiven Elektrode stammt. Dies vereinfacht die Zellherstellung, da kein Lithiummetall verwendet werden muss. Allerdings ist auch die elektrochemische Abscheidung mit neuen morphologischen Instabilitäten verbunden, und die grundlegenden Unterschiede in Mikrostruktur und Chemie zwischen konventionell hergestelltem und elektrochemisch abgeschiedenem Lithium sind noch nicht ausreichend erforscht.

Diese Dissertation befasst sich daher mit der chemischen und mikrostrukturellen Charakterisierung von Lithium, welches elektrochemisch in Reservoir-freien Modellsystemen an Stahl| $\text{Li}_6\text{PS}_5\text{Cl}$ Grenzflächen abgeschieden wurde. Chemische Analysen zeigten eine besonders hohe Reinheit im Vergleich zu kommerziellen Lithiumfolien. Mikrostrukturelle Analysen an millimetergroßen Querschnitten mittels Elektronenrückstreubeugung deckten eine dynamische Entwicklung der Kornstruktur während der elektrochemischen Abscheidung und der darauffolgenden elektrochemischen Auflösung auf. Des Weiteren wurden Zwischenschichten als effektive Methode zur Steuerung der Lithiummikrostruktur eingeführt.

Insgesamt erweitern die in dieser Dissertation präsentierten Ergebnisse das Verständnis von elektrochemisch abgeschiedenen Lithiumschichten hinsichtlich ihrer Reinheit und ihrer Kornstruktur erheblich. Letztere wird maßgeblich durch die elektrochemische Abscheidung sowie Auflösung, und Modifikationen des Stromableiters beeinflusst. Diese Erkenntnisse zielen darauf ab, die Leistung Reservoir-freier Zellen zu optimieren und die Entwicklung fortschrittlicher Festkörperbatterien zu ermöglichen.

List of Abbreviations

AM	Active material
BCC	Body-centered cubic
CC	Current collector
EBSD	Electron backscatter diffraction
FCC	Face-centered cubic
GEIS	Galvanostatic electrochemical impedance spectroscopy
LE	Liquid electrolyte
LIB	Lithium-ion battery
LiPON	Lithium phosphorus oxynitride
LLZO	$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$
LMB	Lithium metal battery
LME	Lithium metal electrode
LPSCl	$\text{Li}_6\text{PS}_5\text{Cl}$
MCI	Mixed ionic-electronic conducting interphase
RFC	Reservoir-free cell
SE	Solid electrolyte
SEI	Solid electrolyte interphase
SEM	Scanning electron microscope
SHE	Standard hydrogen electrode
SOC	State of charge
SSB	Solid-state battery
ToF-SIMS	Time-of-flight secondary-ion mass spectrometry
XPS	X-ray photoelectron spectroscopy

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1 Introduction

To minimize the impending consequences of man-made climate change, it is essential to prevent global warming.^{1,2} This goal is enshrined in the 2015 Paris Climate Agreement and the 194 participating parties are committed to acting accordingly.³ In concrete terms, this means that greenhouse gas emissions must be significantly reduced, and ultimately net-zero CO₂ emissions must be achieved globally. A key component is the transition from fossil fuels such as coal or oil to renewable energy sources such as solar or wind energy, both in primary energy production and in the transport sector.⁴ Due to the intermittency of these renewable energy sources, reliable energy storage systems are necessary at all levels: large-scale storage units to stabilize the electrical grid, traction batteries for electric vehicles, and compact storage devices for portable electronics such as smartphones and laptops.^{5,6}

Today, rechargeable batteries are the most widely used for mobile applications and are also gaining increasing interest in stationary energy storage. The battery market is dominated by lithium-ion batteries (LIBs), which can provide both high energy and power densities.⁷ However, the continuous optimization of this technology in recent years is bringing it ever closer to its physicochemical maximum. For further development of state-of-the-art LIBs, lithium metal is investigated as a negative electrode material. Due to its low electrode potential of -3.04 V versus the standard hydrogen electrode (SHE) and its high specific capacity of 3860 mAh g^{-1} the use of a lithium metal electrode (LME) could significantly increase the energy storage capabilities of next-generation batteries.⁸⁻¹² However, a combination of conventional liquid electrolytes (LEs) with LMEs suffers from lithium dendrite propagation and associated cell failure, including safety issues due to the flammability of the organic solvents of LEs.¹³ For this reason, solid electrolytes (SEs) are being investigated. Due to their solid nature, they are more stable towards dendrites, have no intrinsic flammability and are not affected by potential leakage.^{9-11,14} Another advantage of SEs is that they are generally single ion conductors with a transference number for lithium ions close to unity. This circumvents polarization effects, enabling higher charge and discharge rates. Furthermore, impurities are therefore not conducted through SEs.¹⁵⁻¹⁸

Lithium as an electrode material presents its own challenges, particularly due to its high reactivity. On the one hand, this leads to the formation of parasitic passivation layers on lithium itself. These, in turn, increase interfacial resistances between lithium and SEs.¹⁹⁻²¹ To prevent passivation and keep interfacial resistances as low as possible, lithium must be stored in inert atmosphere, which is costly. However, since degradation layers still form even in gloveboxes with an argon atmosphere containing water, oxygen and nitrogen traces in ppm range²¹, these must be laboriously removed during cell preparation, complicating cell manufacturing. On the other hand, due to the high reduction potential of lithium, a parasitic reaction occurs in contact with almost all SEs over time.²²⁻

²⁵ It is therefore important to keep the time between cell preparation and actual use of the battery cells as short as possible. For the reasons mentioned above, reservoir-free cells (RFCs) are being investigated.^{8,26–33} The omission of the lithium reservoir on the negative electrode is referred to in the literature as "anode-free". Since every electrochemical cell must have an anode, the term used here is *reservoir-free*.

These cell concepts completely avoid the use of lithium metal during assembly.^{11,26,28} Instead, similar to LIBs used today, they rely on the lithium content within the active material (AM) in the positive electrode. During the first charging step of RFCs, the LME is then electrodeposited at the current collector (CC) interface with the SE on the negative electrode side. As most AMs are synthesized in a fully lithiated state and thus the total amount of lithium for cycling is present already even without LME, a lithium reservoir represents only excess material. Accordingly, removing the reservoir further increases the energy density of RFCs.^{8,34,35} Furthermore, the above-mentioned handling of lithium metal, including costly storage and cell manufacturing, can be avoided. However, the electrodeposition of LMEs in RFCs often results in inhomogeneous and even dendritic lithium structures instead of a desired layer growth.^{27–29}

In addition, there are morphological challenges associated with the electrochemical dissolution of lithium even when using a homogeneous lithium layer, for example, in the form of a pre-applied reservoir.^{32,36,37} The newly acquired mechanical integrity of the SEs means that they cannot compensate for the volume changes that occur during stripping. If diffusion of the injected vacancies away from the lithium|SE interface is insufficient, *i.e.*, if the current density exceeds the rate at which lithium atoms replenish the interface, an accumulation of vacancies occurs. This leads to pore formation and ultimately to a loss of the electrode contact and thus to cell failure.^{36,37}

Results from the literature show that the risk of dendrite and pore formation can be mitigated by reducing the current densities. High external pressures are also often used to supplement lithium diffusion through mechanical creep, thus keeping the interface intact.^{36,38–40} However, both options are unsuitable for commercial applications. Reducing the current density would compromise the newly gained faster charge and discharge rates due to the lack of polarizability in SEs, while the necessary pressure systems would in turn reduce the newly gained energy density through LMEs. Consequently, increasing attention has shifted toward material-based approaches that can stabilize lithium plating and stripping without imposing restrictive operating conditions. In this context, (metallic) interlayers are widely investigated as a means to promote homogeneous lithium deposition during charging and to suppress pore formation during discharging.^{41–47} In parallel, growing efforts focus on tailoring the microstructure and chemistry of lithium itself, as it has been demonstrated that the lithium microstructure can substantially influence the discharge capacity and cycling behavior of LMEs.^{48–54}

Conversely, knowledge about the microstructure and chemical composition of electrodeposited lithium layers in RFCs with and without interlayers is mostly elusive.⁵² In general, the transferability of previous results obtained with commercially available lithium samples to lithium layers electrodeposited in RFCs is unclear. On an industrial scale, lithium is often extracted from LiCl using molten-salt electrolysis processes.⁵⁵ Depending on the purity and the exact process parameters, significant differences in the properties of the lithium samples can be expected, both microstructurally and chemically.^{55,56} Furthermore, the microstructure of commercial lithium samples is also influenced by the thermal and mechanical history^{51,57,58}, both of which are generally unknown to the user. In contrast, knowledge about the microstructure and the purity of electrodeposited LMEs was scarce at the beginning of this dissertation.

In this dissertation, lithium layers electrodeposited at CC|SE interfaces are analyzed in terms of their chemical composition and their microstructure, employing both chemical-analytical techniques and electron microscopy. The overall aim is to gain a fundamental understanding of microstructural processes within electrodeposited lithium layers during cell operation and how electrodeposited lithium layers may differ in comparison to their conventionally produced counterparts. Additionally, metallic interlayers are introduced to actively control the resulting microstructure of electrodeposited lithium in RFCs by employing them on the surface of the CC.

In the first publication, titled “*Purity of lithium metal electrode and its impact on lithium stripping in solid-state batteries*”, the influence of impurities in LMEs during stripping in solid-state batteries (SSBs) is investigated.¹⁸ Using a combination of X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and electrochemical measurements, it was demonstrated that sodium represents the predominant impurity in commercial lithium samples and that impurities accumulate at the interface towards the SE during stripping. This accumulation compromises morphological stability, reduces the accessible stripping capacity and causes earlier loss of contact during discharge. The SEs used, $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) and $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) selectively conduct lithium ions while blocking other species, such as sodium, effectively preventing impurities from being incorporated into electrodeposited lithium. In RFCs, this selective transport results in the formation of a high-purity lithium electrode during plating, even when the lithium source contains impurities. The SE thus acts as a filter, allowing only lithium ions to reach the plating side. In summary, these findings demonstrate that the purity of lithium metal critically influences lithium stripping. In RFCs, electrodeposition forms a highly pure electrode, potentially providing improved morphological stability and higher stripping capacities in subsequent cycles, being an intrinsic benefit of such RFC configurations.

In the second publication, titled “*Microstructure of lithium metal electrodeposited at the steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interface in “anode-free” solid-state batteries*”, the electrodeposition of lithium at

the steel|LPSCl interface was investigated to probe microstructural evolution of lithium in RFCs.⁵³ Steel|LPSCl|Li|steel cells were used as a model system to examine the influence of electrodeposition parameters on the resulting microstructure, focusing on lithium layer thickness and current density. By expanding a recently established workflow, analysis via scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) on millimeter-sized cross-sections revealed a dynamic microstructural evolution of the lithium grain structure during electrodeposition. Analysis of grain size and density demonstrated that lithium microstructure is governed primarily by layer thickness rather than electrodeposition current density, a phenomenon termed *specimen thickness effect*. Here, thicker layers exhibit larger grains, while thinner layers are composed of a higher number of smaller grains. Monte Carlo Potts simulations qualitatively reproduced the experimental observations, supporting the conclusion that microstructural evolution is driven mainly by layer thickness rather than deposition kinetics. Overall, this work provides insights into the relationship between electrodeposition parameters and lithium microstructure, deepening the understanding of microscopic processes taking place during electrodeposition in RFCs.

In the third publication, titled “*Microstructure of electrodeposited lithium and its evolution during cycling when using metal interlayers in “anode-free” solid-state batteries*”, metal interlayers were applied to the CC surface to control the resulting lithium microstructure in RFCs. Lithium was electrodeposited in an RFC on different interlayer materials such as gold, silver and bismuth, and the resulting microstructure was characterized using EBSD. The results demonstrate that each interlayer leads to a different lithium microstructure. Subsequently, the electrodeposited lithium layers were partially stripped, revealing that also stripping significantly affects the resulting lithium microstructure. Over multiple cycling steps, the microstructure continues to evolve, highlighting the dynamic interplay between interlayer selection, cycling history and resulting lithium microstructure. Overall, this work provides a detailed understanding of how interlayers govern lithium microstructure formation and its evolution during both plating and stripping, highlighting that cycling history also plays a decisive role in microstructure evolution of LMEs.

In summary, this dissertation significantly advances the understanding of electrodeposited LMEs in RFCs and elucidates key differences to conventional lithium foils. Lithium electrodes generated in RFCs exhibit exceptionally high purity due to the selective transport of lithium ions through single-ion conducting SEs, which contributes to improved morphological stability and stripping. Furthermore, it was demonstrated that the lithium microstructure changes dynamically during both electrodeposition and subsequent dissolution. Finally, metallic interlayers were introduced as effective measure to influence the resulting lithium microstructure. Overall, this work demonstrates that both the lithium purity and its microstructure represent critical parameters to consider for the successful development of RFCs.

2 Fundamentals

This chapter summarizes the current state of research on LMEs in SSBs. It provides an overview of the fundamental properties of lithium metal and discusses the main challenges associated with its use as an electrode material. Furthermore, the concept of RFCs is introduced. In this context, differences between electrodeposited lithium layers and conventionally produced lithium metal are discussed. A special focus is put on the microstructure of lithium, *i.e.*, grain size and grain orientation, and on how these properties can be influenced, which also is one main component of this dissertation.

2.1 Fundamental Properties of Lithium

Lithium plays a central role in modern energy storage. Today's commercial LIBs rely on lithium ions shuttling between host materials. In contrast, lithium metal was historically the first choice as an electrode material but was largely abandoned in LE systems due to safety issues like dendrite growth and associated flammability.^{13,59,60} However, lithium metal is still used in commercial primary batteries today.⁶¹ The development of SEs has renewed interest in LMEs for secondary batteries. LMEs offer a significantly higher specific capacity than graphite, while SEs offer reduced susceptibility to dendrite formation due to their mechanical rigidity.⁹ This makes lithium metal a key candidate for next-generation high-energy batteries. This chapter outlines the fundamental properties of lithium, including its production as well as mechanical and (electro)chemical characteristics that govern its behavior in SSBs.

2.1.1 Occurrence and Production of Lithium

Because of its high reactivity, lithium does not occur naturally in its elemental form. Instead, lithium was first discovered in 1817 in a mineral now known as petalite, from which its name is derived (Greek *lithos* = stone).^{12,19,55,62} Even today, minerals such as spodumene and petalite represent major natural sources of lithium compounds. In addition, lithium also occurs in significant concentrations in brine deposits in the form of dissolved salts.^{55,62} Overall, earth's crust contains about 20 ppm of lithium, as shown in comparison to other battery-relevant elements in **Figure 1a**.^{12,62,63} Commercially, lithium compounds are mainly extracted from mentioned brines found in South America. Solar evaporation concentrates the dissolved salts, followed by chemical purification steps that selectively remove interfering ions and precipitate lithium carbonate (Li_2CO_3).⁵⁵ The lithium carbonate is then reacted with hydrochloric acid (HCl) to produce lithium chloride (LiCl), which is subsequently dried to obtain the anhydrous form. To produce lithium metal, this anhydrous LiCl is mixed with potassium chloride (KCl) and subjected to molten salt electrolysis at temperatures between 450 °C and 500 °C. During electrolysis, lithium is deposited as a liquid at the cathode.⁵⁵ High purity is essential for battery applications, as impurities such as sodium, nitrogen, or oxygen can significantly alter mechanical properties and reduce electrochemical performance.

However, despite purification steps, trace amounts of potassium and sodium often remain because of their chemical similarity to lithium.^{55,56}

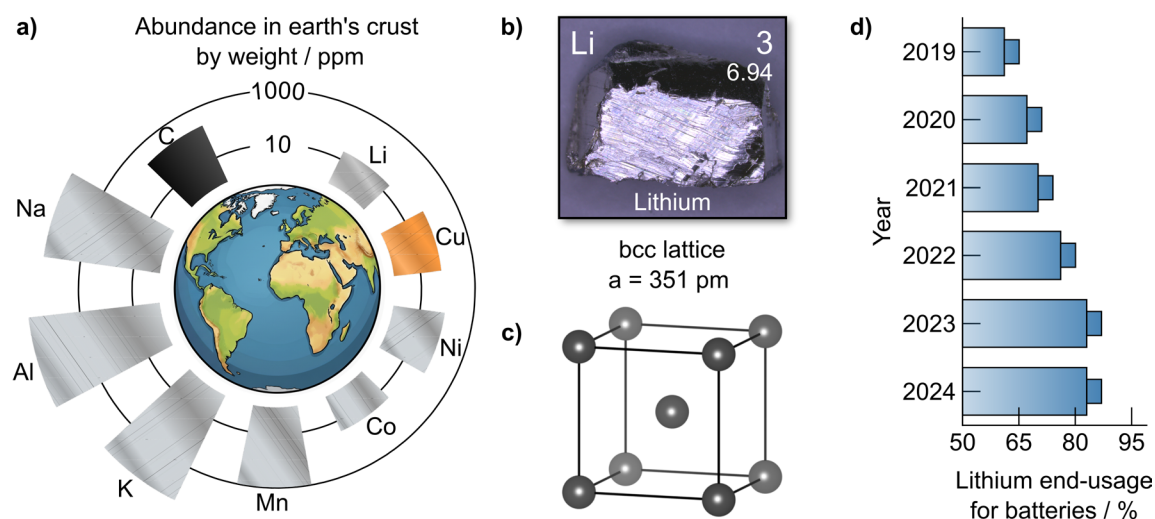


Figure 1: Occurrence and properties of lithium. a) Lithium abundance in earth's crust in comparison to other battery relevant elements. b) Photograph of a piece of lithium metal labelled with its atomic number 3 and atomic mass of 6.94 u. c) Schematic representation of the lithium crystal structure, which crystallizes in a body-centered cubic (BCC) structure with a lattice constant of 351 pm. d) Schematic representation of the end-usage for lithium, highlighting the dominance of the battery sector in the field of lithium use.^{64–69}

2.1.2 Properties of Lithium Metal

With a density of 0.534 g cm^{-3} , an atomic number of 3 and an atomic weight of 6.94 u, as shown in **Figure 1b**, lithium is the lightest metal in the periodic table.^{11,12,62,70} It crystallizes in a body-centered cubic (BCC) structure, which is shown schematically in **Figure 1c**.¹² The mechanical properties of lithium have important implications for the stable operation of SSBs, as they define which external stress is required to maintain a conformal contact at Li|SE interfaces. In the case of lithium, these properties are largely defined by its low melting point of $T_m = 180.5 \text{ °C}$.^{11,12,38} At room temperature T_{RT} , this corresponds to a homologous temperature of approximately 0.66 (T_m / T_{RT}). As a result, lithium metal is highly ductile even at room temperature, meaning that it can be easily deformed plastically. The measure of this is lithium's low yield strength, which is approximately 0.7 MPa.^{11,38,71,72} It should be noted, however, that the mechanical properties of lithium, and of metals in general, depend largely on the microstructure and the concentrations of impurities present.^{11,73} Nevertheless, it is evident that at typical pressures in SSBs, which in most cases are significantly above 1 MPa^{11,33,45,74}, lithium mechanics, in particular plastic deformation, must be considered. Herein, creep was identified as the dominant deformation mechanism for battery-relevant operating conditions.⁷¹

In addition, lithium has promising electrochemical properties. With its low molar mass and a molar volume of approximately $13 \text{ cm}^3 \text{ mol}^{-1}$, lithium has a theoretical specific capacity of 3860 mAh g^{-1} and a volumetric capacity of 2061 mAh cm^{-3} .^{11,12} In combination with the lowest standard reduction potential of all elements at -3.04 V versus the SHE, enabling high cell voltages when paired with high-voltage positive electrodes, lithium is considered the ultimate choice as negative electrode material.^{11,12} However, this low reduction potential also leads to intrinsic stability challenges in batteries. As it lies outside the thermodynamic stability window of nearly all liquid and solid electrolytes, spontaneous reduction reactions occur at lithium|electrolyte interfaces.⁷⁵ Furthermore, the high reactivity with atmospheric components necessitates rigorous handling in inert environments.^{11,19–25} Lastly, repeated plating and stripping leads to continuous volume and associated morphology changes, potentially decreasing longevity.^{11,27,32,33,36,48} These challenges arising when implementing LMEs will be discussed in more detail in the following chapter.

2.2 Challenges of Lithium Metal Electrodes

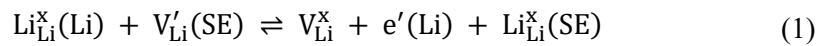
While the theoretical characteristics of lithium offer superior performance, its practical implementation is impeded by severe interfacial and morphological instabilities. This chapter examines the degradation mechanisms that currently hinder the commercial viability of reversible SSBs using LMEs, with a particular focus on morphological instabilities during stripping and interfacial reactivity.

2.2.1 Morphological Instabilities during Lithium Stripping

Upon complete dissolution during discharge, the LME undergoes a theoretically infinite relative volume change. In practice, targeted LME thicknesses of around 25 μm (corresponding to $\approx 5 \text{ mAh cm}^{-2}$) must therefore be reversibly stripped and plated with each cycle.^{11,26,34,76} At this point, first the stripping case will be examined more closely. Morphological instabilities during lithium deposition, such as dendrites, will be discussed in more detail later in this work, also as they are frequently a consequence of prior issues during stripping.

Due to the rigid nature of SEs, they cannot compensate for the resulting volume change of the LME during stripping as easily as LEs. Macroscopically, this can lead to the formation of pores at the Li|SE interface, resulting in an increased constriction resistance and, ultimately, a loss of contact.^{32,33,36,37,44,45} Microscopically, this is because the externally applied current density leads to the oxidation of a lithium atom from the LME during discharge. Consequently, a vacancy is created in the lithium crystal lattice. If this vacancy does not leave the interface sufficiently fast, multiple vacancies can accumulate, resulting in macroscopic pores.^{11,36,77–79} This kinetic phenomenon at solid-solid interfaces was characterized and described by Janek and Schmalzried⁷⁷ using silver electrodes and was further modified by Krauskopf *et al.*³⁶ to describe Li|SE interfaces.

The stripping mechanism can be described as follows: The oxidation of a lithium atom leaves a vacancy $V_{\text{Li}}^{\times}$ and an electron $e'(\text{Li})$ inside the metal, while the lithium ion migrates into the SE as described in equation (1). The ion then occupies either a vacancy $V'_{\text{Li}}(\text{SE})$ or an interstitial site $V_{\text{Li}}^{\times}(\text{SE})$ in the SE lattice. Equation (1) is formulated for occupying a vacancy in the SE lattice.



The vacancy created at the Li|SE interface diffuses into the bulk of the LME at a rate determined by the diffusion coefficient for vacancies D_v . This results in a vacancy diffusion flux, which is referred to as j_v in the following. The diffusion flux j_v competes with the lithium-ion flux within the SE, which in turn is determined by the applied current density i and is therefore referred to as j_{Applied} .

Now, two cases can be considered. First, if

$$j_{\text{Applied}} < j_V \quad (2)$$

the concentration of vacancies at the Li|SE interface reaches equilibrium, thus maintaining the morphological stability of the interface. In the second case, where

$$j_{\text{Applied}} > j_V \quad (3)$$

the injected vacancies accumulate at the interface faster than they can diffuse into the bulk. This supersaturation leads to pore nucleation, resulting in a morphologically unstable interface and potential cell failure. These two limiting cases are shown schematically in **Figure 2**. The schematic highlights not only the morphological evolution but also the impact on cell resistance as well as the cell voltage. Due to occurring current constriction at the remaining contact spots, the cell resistance increases with ongoing pore formation.^{80,81}

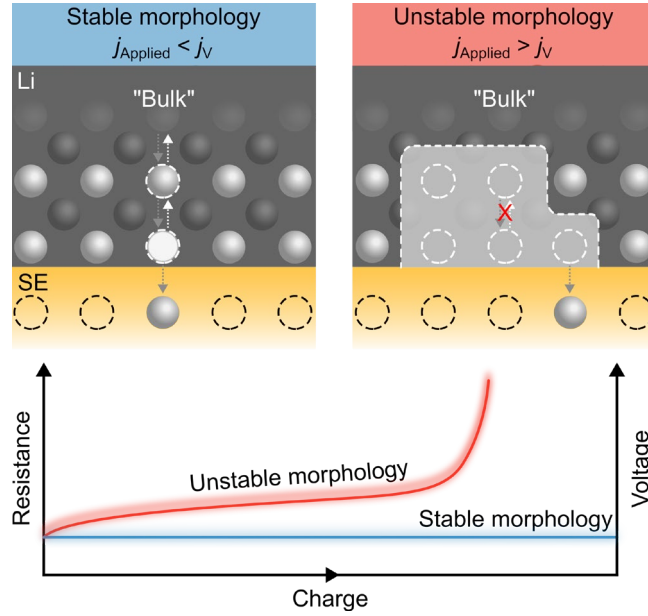


Figure 2: Schematic of the two limiting cases for resulting morphologies of LME during stripping. On the left, in blue, j_{Applied} is smaller than j_V . Here, injected vacancies diffuse into the lithium bulk without agglomerating at the interface towards the solid electrolyte (SE). Therefore, the LME|SE interface remains morphologically stable and thus the cell resistance remains constant. On the right, in red, j_{Applied} exceeds j_V . Here, injected vacancies do not diffuse into the lithium bulk fast enough. Therefore, they agglomerate at the interface, leading to pore formation and resulting in an unstable morphology and an increasing cell resistance.

The maximum current density at which the morphological stability of the interface can be maintained, often referred to in the literature as critical current density i_{crit} , is thus obtained when both fluxes are equal, as expressed in equation (4).

$$i_{\text{crit}} = z \cdot F \cdot j_V \quad (4)$$

$$j_V = \left(1 - \frac{c_{V,\text{Max}}}{c_V^0}\right) c_V^0 \sqrt{\frac{D_V}{\tau_V}} \quad (5)$$

Using equation (5), the limiting flux $j_{V,\text{crit}}$ can now be calculated for a maximum concentration of vacancies $c_{V,\text{Max}}$ at the interface, *i.e.*, when a certain supersaturation of vacancies compared to the equilibrium vacancy concentration is reached. Here, c_V^0 is the bulk concentration of vacancies in lithium at equilibrium and D_V is the diffusion coefficient of these vacancies. Further, τ_V denotes the relaxation time for establishing an equilibrium concentration of vacancies inside lithium. With $D_V \approx 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $c_V^0 \approx 8 \cdot 10^{-9} \text{ mol cm}^{-3}$ and $\tau_V \approx 5 \text{ s}$, Krauskopf *et al.* were thus able to estimate the critical current density of lithium metal at room temperature to be in the range of $50 \text{ } \mu\text{A cm}^{-2}$ to $200 \text{ } \mu\text{A cm}^{-2}$.^{36,82} Herein, reasonable values for the maximum vacancy supersaturation were assumed to be in the order of 10 times the equilibrium vacancy concentration. The results are largely consistent with experimental findings, although it should be noted that experimental data on the critical current density for LMEs vary widely.^{40,83,84} This is due to varying measurement conditions, such as different temperatures or externally applied pressures, or the choice between unidirectional and bidirectional test conditions.⁴⁰ In general, however, this assessment shows that the practically achievable discharge current density is far too low for commercial applications, and that measures are required to significantly increase it.

2.2.2 Reactivity of Lithium Metal Electrodes

Beyond morphological instabilities, lithium's pronounced reactivity toward atmospheric components poses significant challenges for its handling and processing.^{19–21,24} Upon exposure to moisture, oxygen, or nitrogen, lithium spontaneously forms parasitic surface layers consisting of lithium hydroxide (LiOH), lithium oxide (Li₂O) or lithium nitride (Li₃N).²⁰ Without targeted processing, these layers are inhomogeneous and impede a uniform lithium transport across Li|SE interfaces, thereby increasing interfacial impedance and deteriorating the overall electrochemical performance.^{21,85} Consequently, all processing steps involving lithium metal require strictly controlled inert environments, typically argon atmospheres with oxygen and water levels maintained below 1 ppm.^{11,21,27} However, even these trace amounts can induce surface passivation.²¹ Therefore, mechanical surface treatments (*e.g.*, polishing or scraping) are often necessary immediately prior to cell assembly to expose a fresh metallic lithium surface. In addition, the preparation of Li|SE interfaces also require the application of high pressures or high temperatures in order to ensure an intimate and thus low-resistance interface.^{11,36}

Beyond atmospheric sensitivity, the low reduction potential of lithium drives parasitic side reactions with most SEs.^{22,25,75,86–88} Ideally, the interface should be thermodynamically stable. However, in most practical material combinations, a reaction layer forms immediately upon contact. Based on

the electronic conductivity of these decomposition products, the resulting interphase is generally classified into two categories: (i) a solid electrolyte interphase (SEI), which acts as a kinetic barrier by being ionically conductive but electronically insulating, thus effectively passivating the interface, and (ii) a mixed conductive interphase (MCI), which conducts both ions and electrons.⁸⁹ As the latter fails to block electron transport, the decomposition reaction can propagate into the bulk electrolyte, resulting in continuous consumption of both AM and SE.⁸⁹ This reduces the storage capacity and ultimately causes cell failure. Both SEI and MCI formation can occur already during cell assembly or in the early stages of cycling, resulting in the formation of heterogeneous interphases.^{22,85,89} Furthermore, regardless of the specific mechanism, the formation of either interphase inevitably consumes lithium. While conventional LMEs can buffer this loss via a stoichiometric excess of AM, *i.e.* in form of the lithium reservoir, this degradation is particularly critical for RFCs. In these systems, the consumption of the fixed lithium inventory directly correlates with irreversible capacity loss, a central challenge that will be examined in Section 2.3.3.

2.3 Reservoir-Free Cell Concepts

This chapter introduces RFCs as a strategy to overcome the processing challenges associated with the high reactivity of LMEs, as detailed in the previous section. While RFCs offer the possibility to omit the handling of metallic lithium during cell assembly, they introduce distinct electrochemical challenges. The morphological instabilities described in section 2.2.1, *i.e.*, pore formation during stripping, remain relevant for RFCs. However, the absence of a pre-existing lithium reservoir shifts the critical challenge to the initial plating step which involves the nucleation and growth of lithium on a pristine substrate. This chapter thus focuses on the functionality of RFCs, their respective advantages and disadvantages, and strategies for overcoming the latter.

2.3.1 Working Principle of Reservoir-Free Cells

Scientific investigations of Li|SE interfaces typically rely on complex preparation protocols, involving argon atmospheres, surface polishing, and the application of high stack pressures or temperatures to minimize interfacial resistance.^{21,30,33,36} While effective for fundamental research, such elaborate procedures are cost-intensive and technically challenging for large-scale battery manufacturing. An alternative approach is offered by RFCs. Here, no metallic lithium is used during fabrication. Instead, the CC on the negative electrode side is in direct contact with the SE. During the first charge, the LME is electrodeposited at this CC|SE interface extracting the lithium ions from the AM in the positive electrode.^{11,26–30,36,90} This process results in the *in situ* formation of an LME. Consequently, a functional full cell configuration CC|Li|SE|AM|CC is established only after the initial charge. The working principle of RFCs is schematically depicted in **Figure 3**.

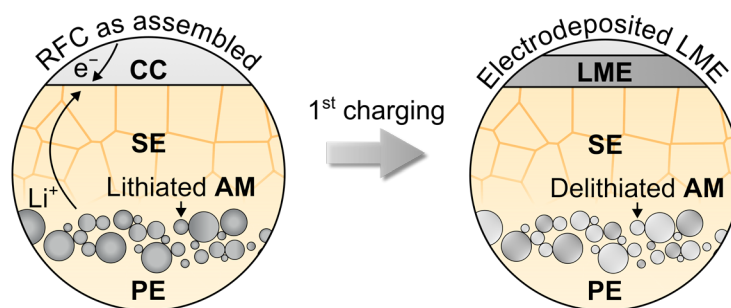


Figure 3: Schematic illustration of the working principle of a reservoir-free cell (RFC) configuration. After fabrication of the RFC, the current collector (CC) of the negative electrode is in direct contact with the solid electrolyte (SE). Using the lithium inventory provided by the active material (AM) in the positive electrode (PE), the lithium metal electrode (LME) is electrodeposited during the first charging step.

2.3.2 Advantages of Reservoir-Free Cells

The transition from conventional lithium metal batteries (LMBs) to RFC architecture offers significant benefits ranging from increased volumetric energy density to easier manufacturing processes and enhanced material purity. By eliminating the lithium reservoir, the cell volume is

minimized without sacrificing capacity, as the entire reversible lithium inventory is stored within the fully lithiated AM inside the positive electrode. Any additional lithium at the negative electrode would essentially constitute "dead weight" and volume. While the impact on gravimetric energy density is moderate due to the low density of lithium ($\rho = 0.534 \text{ g cm}^{-3}$), the gain in volumetric energy density is substantial. For instance, removing a 25 μm thick lithium foil can enhance the volumetric energy density of the cell by roughly 15%, depending on the exact cell geometry and material composition.^{26,34} For more information about the energy density calculation, the reader is referred to chapter 7.1 of this dissertation. However, in order to provide this energy in the long term, highly reversible lithium plating and stripping with efficiencies close to 100% are required to prevent rapid capacity decay, a challenge discussed in section 2.3.3.

The most significant motivation for RFC research is the possibility to completely exclude lithium from the cell assembly process. At first, this eliminates the need for energy-intensive production of battery-grade lithium foils via molten salt electrolysis and subsequent purification steps.^{8,11} Furthermore, handling and storing large quantities of reactive lithium metal, which requires costly inert environments and strict safety measures, is effectively eliminated for cell manufacturers. Instead, RFC production only involves the application of a CC to the SE, utilizing scalable techniques such as sputtering, thermal evaporation, or lamination.⁹¹ In addition, pre-assembled RFCs can be stored with fewer precautions, as there is no lithium metal present until the initial charging step. In addition, this allows RFCs to decouple cell production from the onset of aging. Since the contact between lithium and most SEs leads to the growth of resistive interphases (SEI or MCI), conventional SSBs employing lithium metal would degrade during storage. The thickness of these degradation layers increases with storage time.^{22,23,25,87} However, in the case of RFCs, these can be manufactured with the first charging step only being carried out immediately before use. This allows for precise determination of the start of operation and minimizes performance losses due to storage.

In addition to production and storage advantages, RFCs offer an additional intrinsic purification effect, when using single-ion conducting SEs for electrodepositing the LME in the first charging step.⁹² It has been hypothesized that impurities cannot migrate through the SE.^{11,32,92} As a result, electrodeposited LMEs should exhibit exceptionally high purity, even when the lithium source contains impurities. This hypothesis formed the basis of the first publication of this dissertation. Using LPSCl and LLZO as SEs, it was proven that high-purity lithium layers are electrodeposited in RFCs. Impurities contained in the lithium counter electrode, which was used as a model lithium source, accumulate at the interface with the SE. These impurities negatively influence the accessible lithium inventory, resulting in lower stripping capacities for less pure lithium foils and correspondingly higher stripping capacities for lithium foils with higher purity. This intrinsic

purification mechanism provides RFCs with a distinct electrochemical advantage over cells assembled with conventional lithium foils, as schematically summarized in **Figure 4**.

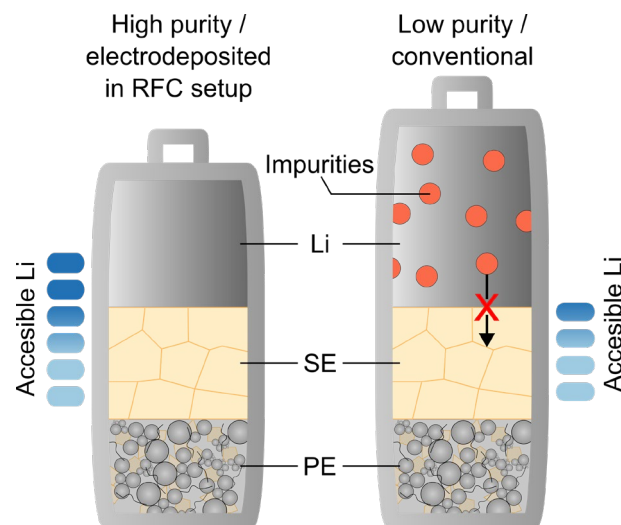


Figure 4: Schematic summary of the purity aspect in RFCs. As shown on the left, lithium electrodeposited using the positive electrode (PE) as a lithium source and a single ion conducting solid electrolyte (SE) has an exceptionally high purity, offering the maximum amount of accessible lithium. In contrast, as shown on the right, the accessible lithium inventory of conventionally manufactured foils is reduced by impurities. In addition, the figure schematically illustrates that eliminating the lithium reservoir in an RFC configuration can increase the volumetric energy density by approximately 15%.

2.3.3 Challenges of Reservoir-Free Cells

Besides the distinct advantages of RFCs, significant hurdles remain that hinder the widespread commercialization of these concepts. These challenges primarily stem from the unique architecture of RFCs, where lithium metal is initially absent and must be electrodeposited at the CC|SE interface during the first charge, or formation.

The central difficulty lies in controlling the morphology of this electrodeposited lithium. To achieve competitive cell performance, a dense and uniform lithium layer approximately 25 μm thick (corresponding to $\approx 5 \text{ mAh cm}^{-2}$) must be reversibly electrodeposited and stripped.^{8,34,76} In practice, however, lithium rarely forms a dense film. Instead, it tends to form undesirable morphologies such as islands, whiskers, or dendrites.^{11,26–29,93} Isolated, island-like structures cover the CC only partially, which significantly reduces the effective contact area with the SE compared to a uniform film. In addition, inhomogeneous electrodeposition morphologies can lead to different forms of protrusive growth: whiskers that extend into or along the CC, and dendrites that grow into the SE. Both phenomena can lead to mechanical damage of the electrode stack, including cracking or fracture of the SE and, ultimately, short-circuiting between the electrodes, thereby compromising the structural integrity and safety of the cell.^{27,94,95} The different failure growth modes are shown schematically in **Figure 5**.

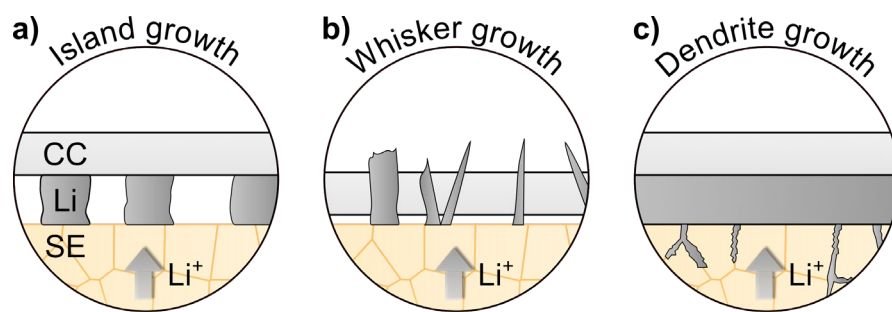


Figure 5: Schematic illustration of different failure growth modes in RFCs. a) Island growth mode: lithium is electrodeposited only locally along the CC|SE interface, resulting in a reduced coverage of the CC. b) Whisker growth mode: lithium grows locally in needle-like morphologies, which likewise keep the coverage low and can lead to penetration of the CC. c) Dendrite growth mode: filament-like structures grow into the interior of SE, damaging it and ultimately causing a short circuit between the two electrodes.

During the subsequent discharge step, the limited contact area becomes particularly critical. As lithium is stripped from the electrode, the current is focused at the remaining contact points, resulting in a local current density that is much higher than the current density calculated based on the total CC area.^{96,97} As extensively discussed in chapter 2.2.1, this locally increased current, j_{local} , can exceed the vacancy diffusion current, j_v , triggering morphological instabilities such as pore formation and contact losses. Therefore, ensuring uniform deposition during charging is essential not only to prevent mechanical damage during charging but also to maintain sufficient contact area for the subsequent discharge step. This continues for all subsequent charge and discharge cycles. If lithium is not stripped homogeneously and completely during the first discharge, there is an increased risk of dendrite growth in the second charging step due to preferential lithium electrodeposition at the remaining contact points.⁸⁴ This shows how immensely important it is to ensure homogeneous and reproducible lithium plating and stripping throughout all cycles.

In addition to morphological lithium losses, parasitic side reactions or diffusion into the CC can consume lithium, which in turn reduces the amount of AM.^{22–25,89} Omitting the lithium reservoir means that no lithium losses can be compensated for by excess material. Consequently, any lithium loss leads to a direct decrease in storage capacity.³⁵ This highlights the crucial importance of high Coulomb efficiency for stable operation, even more so for RFCs than for LMBs equipped with a reservoir. Although conventional LIBs also operate with a finite lithium inventory, they benefit from the stable host material graphite that reduces volume changes and stabilizes the interface towards the LE. RFCs lack this buffer, making the preservation of the limited lithium inventory decisive for long-term cycling stability.⁶⁰

2.3.4 Overcoming Challenges in Reservoir-Free Cells

To address the instabilities described above and homogenize the resulting lithium morphology, a wide range of strategies has been proposed. The approaches can broadly be divided into (i) the

optimization of operating conditions, which govern the electrochemical and mechanical boundary conditions during lithium plating and stripping and (ii) materials- and interface-based strategies, which aim to control lithium nucleation, growth, and stripping. It is essential to distinguish between nucleation and growth, even though the two terms are sometimes used interchangeably in literature. Lithium nuclei exist on the sub-nanometer scale and are therefore below the resolution limit of conventional imaging techniques. What is usually analyzed in literature are grown lithium structures, and the nucleation density is therefore inferred indirectly from the density of these grown lithium structures.^{27,98} As indicated, said strategies can also influence lithium stripping, which, like plating, is a prerequisite for stable cycling of RFCs. The following paragraphs therefore discuss one parameter at a time, beginning with its influence on lithium plating and subsequently on stripping. The parameters discussed are shown schematically in **Figure 6**.

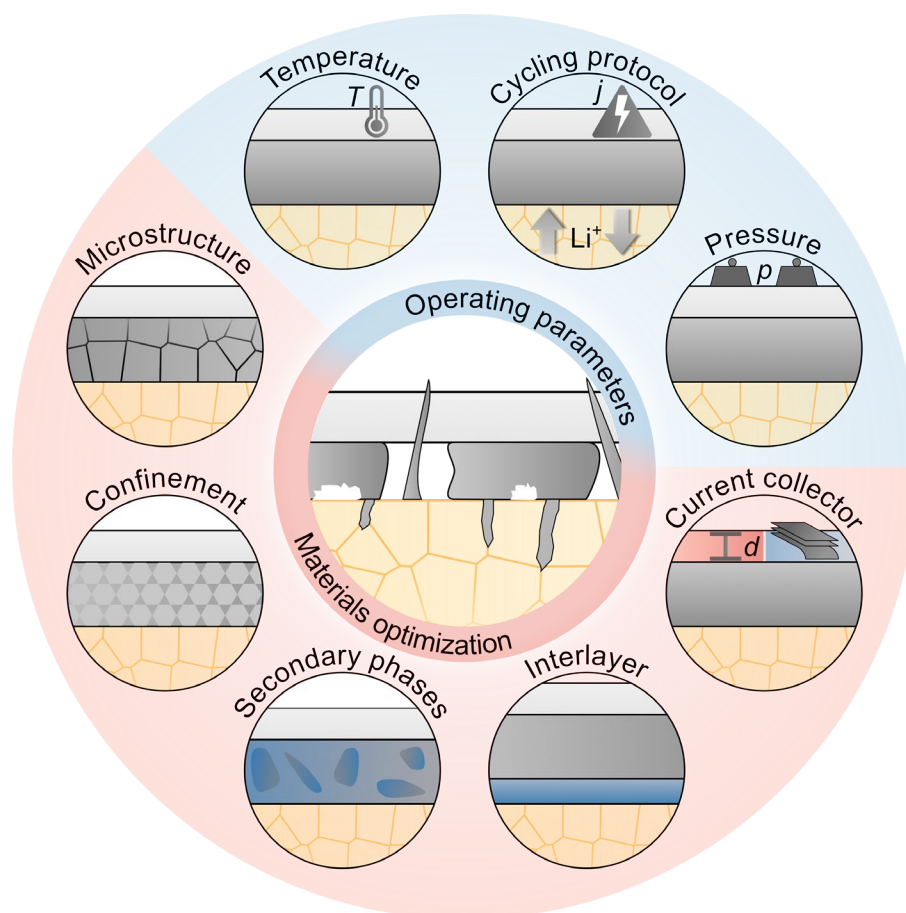


Figure 6: Schematic illustration of different strategies to ensure the functionality of RFCs. Highlighted in red, approaches are shown that aim to optimize the materials used and their interfaces, including the microstructural optimization of the LME, a (three-dimensional) confinement, the incorporation of secondary phases into the LME, and the implementation of interlayers. Highlighted in blue, strategies for optimizing the operating conditions during cell operation are depicted, including the choice of CC thicknesses and materials, the application of external pressure, the use of advanced cycling protocols and modification or increase of the operating temperature.

Within the optimization of operating conditions, temperature is a critical parameter during both lithium plating and stripping.^{29,99} Motoyama *et al.* propose that higher temperatures reduce the nucleation overpotential during plating, thereby decreasing the number of regions that can reach the supersaturation required for nucleation, which in turn leads to a reduced number of lithium nuclei.⁹³ This temperature dependence was experimentally verified by plating experiments on Cu|lithium phosphorus oxynitride (LiPON) interfaces, revealing a lower lithium particle density for higher temperatures and a higher lithium particle density for lower temperatures, respectively.²⁹ Temperature also significantly influences the stripping properties, as the vacancy diffusion coefficient D_V , the equilibrium vacancy concentration c_V^0 , and the relaxation time τ (revisit equation (5)) are all temperature-dependent.³⁶ The temperature dependence is therefore complex, but in general increased temperatures are found to improve stripping capabilities of LMEs and are used to ensure morphological stability throughout cycling.^{100,101} The exponential temperature dependence of the diffusion coefficient is particularly important here.¹¹

Like the temperature, the selected current density for plating also influences the resulting particle density. In accordance with the above-mentioned proportionality between nucleation overpotential and resulting nucleation density, higher current densities lead to an increased particle density by increasing the nucleation overpotential during lithium plating. This dependence on current density could be demonstrated not only in the amorphous Cu|LiPON system of Motoyama *et al.*²⁹, but also using polycrystalline LLZO by Fuchs and Becker *et al.*²⁷ During stripping, the current density defines the rate of vacancy injection. While lower currents favor interface preservation, they limit discharge power. As with plating²⁷, advanced stripping protocols are being investigated to ensure high discharge capacities even at high current densities.¹⁰² However, the applicable current density is ultimately dictated by the application requirements. Therefore, the discharge current density can only serve as an optimization parameter to a limited extent.

Externally applied pressure is utilized to influence lithium morphology. During plating, moderate pressures can flatten protruding islands and promote coalescence into uniform films. This facilitates a transition toward more uniform, film-like lithium growth.^{26,27,103} However, excessively high pressures may alter the resulting growth mechanisms and favor the formation of dendritic structures.⁷⁴ During stripping, applied pressure helps maintain Li|SE interfacial contact, as pressure can induce mechanical creep of lithium, which provides an additional material flux towards the interface.³⁶ Combined with vacancy diffusion, this creep-driven transport helps preserve the interfacial contact, mitigate pore formation, and maintain morphological stability throughout the stripping process. However, necessary pressure assemblies would introduce excessive mass and volume, making them impractical for application. Competitive cells must therefore also function at pressures in the order of approximately 1 MPa.¹⁰

Besides optimizing operating parameters, optimization of materials such as the CC is a key factor for controlling lithium morphology in RFCs. During plating, both the choice of CC material and its thickness strongly influence nucleation behavior and growth morphology.^{27,44,104} Chemical stability against both the SE and lithium is essential, while thin CCs are desired to minimize the fraction of electrochemically inactive material. At the same time, the CC must be mechanically robust enough to withstand stress and suppress the formation of whiskers.²⁷ During stripping, the CC must accommodate the resulting reduction in volume so that even when lithium is completely stripped, a homogeneous, electronically contacted CC|SE contact is restored. Accordingly, the CC should only undergo elastic deformation so that no plastic deformation occurs, which could lead to loss of contact over the course of several cycles. Ideally, this elasticity and the adhesion between the SE and CC also exert pressure on the LME, which improves stripping.

Given that lithium deposition in RFCs occurs directly at the CC|SE interface, the physicochemical properties of this interface largely determine nucleation, growth morphology, and cycling reversibility. Therefore, intensive research is being conducted to optimize this interface via material optimization. During plating, thin interlayers are widely employed to homogenize lithium flux, and provide preferred nucleation sites, thereby promoting more uniform lithium deposition.^{28,43,105,106} During stripping, interlayers help maintain intimate interfacial contact and distribute current more evenly, mitigating pore formation and minimizing the risk of contact loss.⁴⁴ By separating lithium and SE, they can also prevent chemical degradation between these two species^{107,108}, thereby enhancing morphological stability and Coulomb efficiency throughout repeated cycling.

In addition to interlayers, secondary phases are also frequently used. The distinction between interlayers and secondary phases is fluid, as interlayers can evolve into secondary phases within the lithium layer during operation. One of the most prominent examples from the recent past is described in the “*Samsung Paper*” by Lee *et al.*: Silver particles initially dispersed in a carbon matrix form a silver-lithium alloy during plating, introducing a secondary phase within the lithium layer.^{31,109} In general, secondary phases, like interlayers, aim to homogenize lithium deposition, guiding more uniform layer growth.¹¹⁰ Crucially for the stripping process, it was shown that secondary phases can increase the accessible lithium inventory.^{44,45,100,111} This can be explained primarily by two mechanisms. On the one hand, secondary (alloy) phases can alter the diffusion properties and thus contribute to morphological stability via higher effective diffusion of lithium towards the interface.^{11,100} On the other hand, secondary phases can act as contact mediators, ensuring that an electrically contacted interface is maintained during stripping.^{45,111} However, particularly in the case of ionically blocking layers, the underlying mechanism is still the subject of debate.

Another material-based approach involves the use of 3D-structured SEs. By spatially confining lithium growth within a porous host, the unconstrained vertical growth of *e.g.* whiskers is mechanically suppressed during plating.^{112–117} During stripping, the significantly increased Li|SE surface area reduces the effective local current density for a given total current, mitigating pore formation. However, these benefits come at the cost of reduced energy density and increased manufacturing complexity.

Finally, the lithium microstructure plays a decisive role. Initial studies suggest that the microstructure critically influences diffusion pathways as well as mechanical properties and thus the achievable discharge capacity.^{48–51} Since this aspect is a central component of this dissertation, it is discussed in a dedicated chapter below.

2.4 Microstructure of Lithium Metal Electrodes

While the previous chapter mainly dealt with the morphology of electrodeposited lithium layers, this chapter will focus on the microstructural properties, *i.e.*, the grain size, the number of grain boundaries, and the grain orientation of LMEs. Although these properties were difficult to access in the past due to experimental challenges, advanced preparation methods now allow for their detailed characterization. This enables systematic analysis of the microstructure of electrodeposited lithium and an investigation into how it can be influenced.

2.4.1 Effect of Microstructure on Diffusion in Polycrystalline Materials.

In general, diffusion in lithium occurs via a monovacancy transport mechanism.^{11,118,119} However, in polycrystalline materials, such as lithium, the diffusion can proceed through multiple pathways with different kinetics, as schematically shown in **Figure 7a**. Bulk diffusion along regular lattice sites represents the slowest pathway, characterized by the bulk diffusion coefficient D_{Bulk} . Diffusion is considerably faster along dislocations (D_{Dis}) and grain boundaries (D_{Gb}), due to the increased structural disorder in these regions. At surfaces, diffusion is most rapid, as D_{Surf} benefits from both the participation of adatoms and vacancies in the diffusion process. The hierarchy of diffusion coefficients in metals thus follows the relationship¹²⁰:

$$D_{\text{Bulk}} \ll D_{\text{Dis}} < D_{\text{Gb}} < D_{\text{Surf}} \quad (6)$$

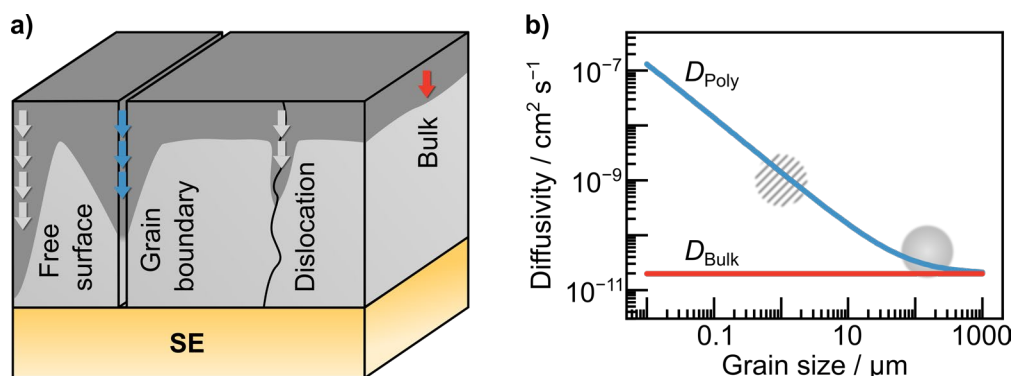


Figure 7: Microstructure-dependent diffusion in polycrystals. (a) Schematic illustration of different diffusion pathways in a polycrystal, including diffusion through the bulk, along dislocations, along grain boundaries, and along free surfaces. The dark grey shading indicates the different diffusion lengths at identical diffusion times to highlight the varying diffusivities. Figure adapted from H. Mehrer, *Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Processes*, Springer, Springer Series in Solid-State Sciences, Volume 155, 2007.¹²⁰ Copyright Springer-Verlag Berlin Heidelberg. Reproduced with permission from Springer Nature. (b) Theoretically calculated diffusivity as a function of the microstructure of a lithium polycrystal. The resulting polycrystalline diffusivity D_{Poly} as a function of grain size is shown in blue, while the bulk diffusivity is shown in red. Dark grey shading highlight experimental data from reference [100], and the grey-hatched region marks the target grain size of 1 μm and the corresponding diffusivity of approximately 10⁻⁹ cm² s⁻¹ as calculated by Yoon et al.¹²¹

Consequently, polycrystalline materials with smaller grain sizes, which exhibit a higher volumetric fraction of grain boundaries, are suspected to yield enhanced effective diffusivities. For LMEs, this

relationship has important implications as finer-grained structures should therefore withstand higher current densities without experiencing the morphological instabilities inherent to stripping. This dependence of electrochemical performance on microstructural features makes grain size control a promising optimization parameter for the stable operation of LMEs. Simulations by Yoon *et al.* suggest that for high-rate applications at current densities of $5 - 10 \text{ mA cm}^{-2}$ grain sizes below $1 \text{ }\mu\text{m}$ are required to sustain the necessary effective diffusivity of approximately $10^{-9} \text{ cm}^2 \text{ s}^{-1}$. This target range for diffusivities and grain size is shown in gray shading in **Figure 7b**. Practical diffusivities according to the results of Krauskopf *et al.*¹⁰⁰ (highlighted in gray in **Figure 7b**) are in the range of $5 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ and therefore roughly two orders of magnitude lower than needed. It should be noted, however, that changes in microstructure simultaneously alter the mechanics of the LME. Assuming a Hall-Petch mechanism, a lower grain size increases yield strength and in turn reduces deformability of the LME at a given pressure, which may impede the preservation of the LME|SE interface.⁷³ Therefore, both diffusional and mechanical properties must be considered in microstructural optimization.

2.4.2 Characterizing the Microstructure of Electrodeposited Lithium

Prior to the investigations presented in this thesis, knowledge regarding lithium microstructure was largely limited to commercial lithium foils.^{52,122–124} These typically exhibit coarse grain structures with grain sizes exceeding $100 \text{ }\mu\text{m}$, which is two orders of magnitude larger than the theoretical requirements for stable high-rate stripping derived in the previous section. At the same time, electrodeposition was identified as a promising approach for specifically adjusting the lithium microstructure and thereby achieving the grain sizes required for stable operation.^{49,54,121} However, the microstructure of electrodeposited lithium in RFCs remained largely unexplored. This lack of data was primarily due to the buried nature of the CC|SE interface and lithium's high sensitivity to oxidation.

To elucidate the relationship between deposition parameters and the resulting lithium microstructure, an advanced characterization workflow combining cryogenic ion beam polishing with inert gas transfer was utilized, as originally established by Fuchs and Ortmann *et al.*⁵² Building upon this initial work, the preparation protocol was further optimized within the scope of this dissertation. Specifically, the ion milling process was adapted to enable the preparation of significantly larger cross-sections in the order of several millimeters.⁵³ This advancement allows for the analysis of broader sample areas, thereby providing statistically more robust EBSD data on electrodeposited lithium layers. The experimental workflow is schematically depicted in **Figure 8**. First, cell preparation is carried out, followed by lithium electrodeposition and ion milling under cryogenic conditions, before finally analyzing the microstructure of the lithium layer using EBSD. In addition, an exemplary inverse pole figure map is shown, where the different colors represent different lithium grains with their respective orientations.

Herein, EBSD is a SEM technique that provides information on crystallographic orientation, phase distribution, and grain structure. When a stationary electron beam interacts with a tilted crystalline specimen, quasi-elastically backscattered electrons are diffracted according to Bragg's law, producing characteristic Kikuchi patterns on a phosphor screen.¹²⁵ These patterns are then captured and analyzed to determine local crystal orientations by comparison with simulated diffraction geometries. By scanning the beam across the sample surface, EBSD generates high-resolution orientation maps, revealing grains and grain boundaries as well as their respective orientation.

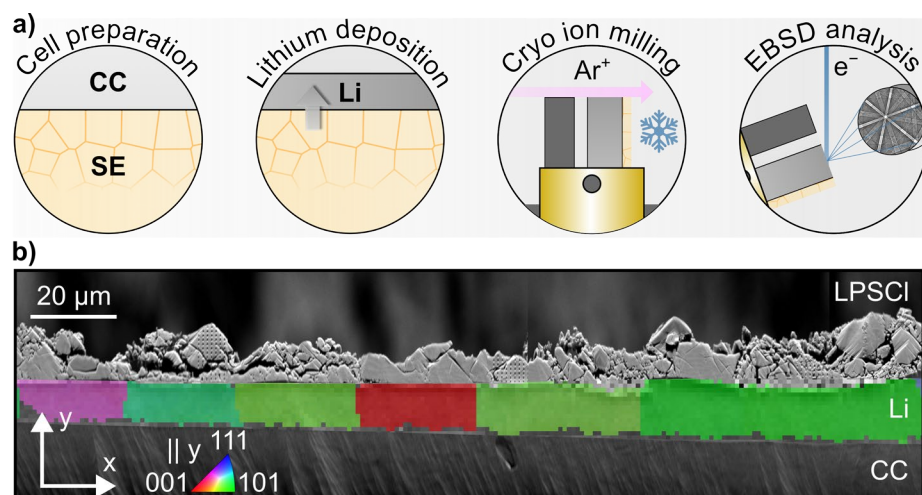


Figure 8: Workflow for the microstructural analysis of electrodeposited lithium. (a) Schematic illustration of the sample preparation procedure, comprising fabrication of the RFC, followed by lithium electrodeposition, subsequent cryogenic ion milling to prepare an analyzable lithium surface, and final analysis by electron backscatter diffraction (EBSD). (b) Representative EBSD map of an electrodeposited lithium layer, showing the CC at the bottom and the electrodeposited lithium layer on top, with individual lithium grains displayed in different colors. Residual LPSCI from the electrodeposition step is visible above the lithium layer. Figure adapted from Fuchs, T., Ortmann, T., Becker, J. et al. “Imaging the microstructure of lithium and sodium metal in anode-free solid-state batteries using electron backscatter diffraction.” *Nat. Mater.* **23**, 1678–1685 (2024), licensed under CC BY 4.0.⁵²

2.4.3 Influencing the Microstructure of Lithium Metal Electrodes

First investigations on electrodeposited lithium have revealed distinct microstructural differences compared to conventionally manufactured foils, including notably larger grain sizes in the latter.⁵² The microstructure of conventionally manufactured lithium foils is largely determined by their purity, thermal history, and mechanical processing.^{51,57,58} However, apart from purity, these parameters are mostly elusive to the user. While further processing steps during cell assembly, such as thinning, are likely to alter the microstructure, a systematic investigation of these processing parameters is currently lacking. In contrast, electrodeposited lithium layers exhibit characteristic microstructures, such as the majority of grain boundaries being perpendicular to the CC|SE interface.⁵² These microstructural differences are schematically illustrated in **Figure 9**. Crucially, initial studies have demonstrated that the resulting microstructure evolves dynamically and is influenced by the specific electrodeposition conditions.^{41,52}

Building on this, the ability to reliably characterize electrodeposited lithium now enables a systematic investigation into microstructural control. Based on approaches used to influence lithium morphology, strategies to tailor the microstructure can similarly be divided into two categories: (i) the variation of process and operating conditions, such as temperature, pressure, current density, and layer thickness, and (ii) material optimization through the choice of CC, spatial confinement of the lithium electrode, and the introduction of interlayers or secondary phases. The various approaches are shown schematically in **Figure 9**.

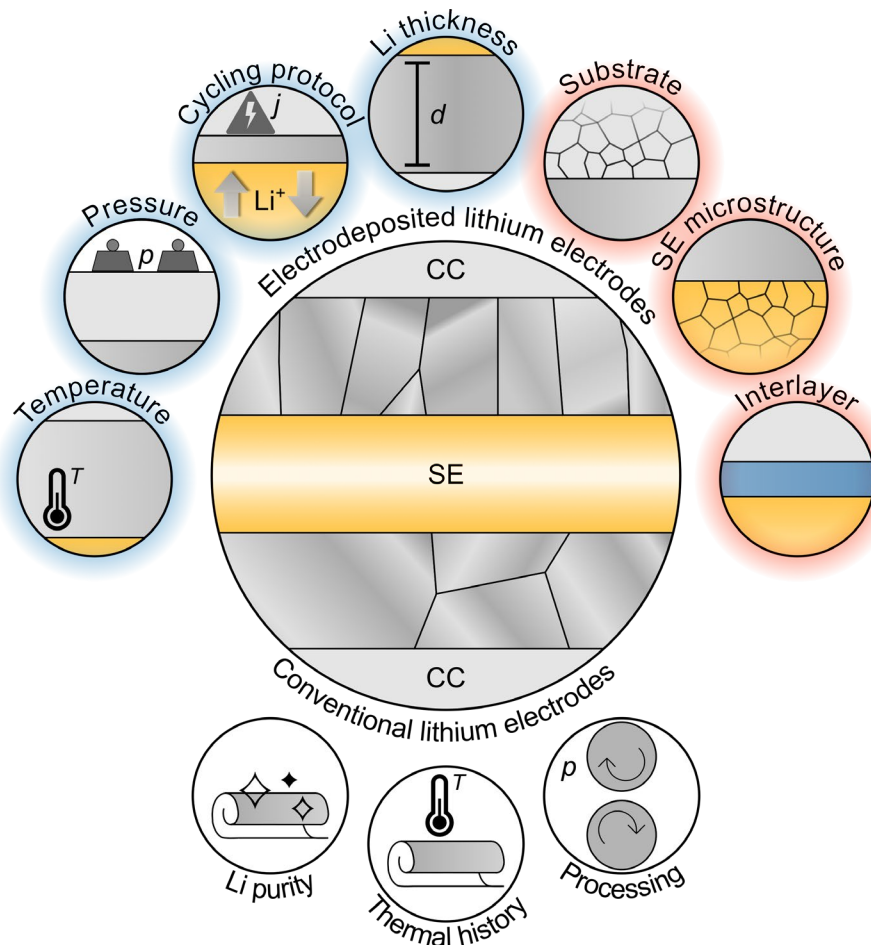


Figure 9: Schematic representation of the microstructural differences between electrodeposited lithium (top) and conventionally manufactured lithium foils (bottom) with their respective influencing factors. Highlighted in red are external operating conditions, including temperature, externally applied pressure, the selected cycling protocol, and the resulting lithium layer thickness. Highlighted in blue are material-based approaches, including the choice of substrate and its microstructure, the microstructure of the SE, and the application of interlayers at the CC|SE interface. Factors influencing the microstructure of conventionally manufactured lithium foils include lithium purity, thermal history, and mechanical processing.

First, the external deposition parameters are discussed. The found dependence of particle density on temperature suggests that the microstructure, *i.e.* the number of grains, can also be altered by varying the deposition temperature. Fewer grains are expected at higher temperatures, as the particle density decreases, and *vice versa*. Surprisingly, recent experimental results suggest the

opposite.^{126,127} More grains were detected at 80 °C than at 25 °C. Interestingly, a correlation between the deposition temperature and the resulting grain orientation was also observed.¹²⁶ In general, however, an influence of temperature on the resulting lithium microstructure appears to be present, but requires further investigation.

While the mechanical properties of lithium under external pressure have already been intensively studied, a direct correlation between pressure and resulting microstructure is still lacking.^{38,72,128} Conversely, Aspinall *et al.* have demonstrated, that the mechanical properties of conventional lithium foils are microstructure dependent.¹²² Furthermore, studies have shown that even full phase transformations from a BCC to a face-centered cubic (FCC) crystal structure can occur in lithium at pressures of approximately 7 GPa.¹²⁹ More generally, it is well established in metallurgy that the microstructure of metals can be influenced by the application of external pressure, suggesting a similar effect for lithium.^{130–133} Overall, additional experimental investigations are needed to elucidate the effect of pressure on the resulting lithium microstructure, especially for electrodeposited lithium at typical operating pressures in SSBs of several MPa.

Following the proportionality between current density and nucleation density, it was initially hypothesized that higher current densities yield finer-grained microstructures.³⁰ This hypothesis constituted the basis of the second publication of this dissertation.⁵³ Since EBSD analysis requires a minimum lithium thickness in the order of 5 µm, the study additionally examined the influence of layer thickness. The results reveal that the grain size increases with increasing layer thickness, whereas the grain density, defined as the number of grains per mm cross-section, decreases. Conversely, at the time of analysis, no correlation between the chosen current density and the resulting grain size or grain density could be observed. This suggests that, while higher currents may increase the initial nucleation density, this effect is masked by lithium grain growth during subsequent plating. This again highlights the importance of distinguishing between nucleation and analysis of subsequently grown lithium particles. Overall, the study demonstrates that deposition parameters can indeed be varied to influence the resulting lithium microstructure.⁵³ While layer thickness is an effective parameter to tune grain size, it is practically constrained by the cathode loading in RFCs, necessitating alternative control strategies, such as material-based approaches for targeted modification of the lithium microstructure.⁵³

The first apparent material-based parameter that influences the resulting lithium microstructure is the substrate on which deposition occurs, specifically the CC. Initial simulation results from the second publication of this dissertation suggest a substrate effect, particularly in the early stages where the lithium grain size is comparable to that of the underlying CC.⁵³ Experimentally, however, verifying this correlation proves difficult. As previously discussed, a minimum lithium thickness of ≈ 5 µm is required for microstructural analysis which is due to the low electron cross-section of

lithium.¹²² At the time this thickness is reached, the coarsening of lithium grains has likely outgrown the typically fine-grained microstructure of metal CCs. This potentially masks an initial substrate influence. Therefore, additional systematic investigations regarding lithium-substrate interaction are necessary to deepen scientific knowledge. It should be mentioned at this point that, in addition to the CC microstructure, the SE microstructure must also be considered, as it equally serves as a substrate during deposition.¹³⁴

In addition to a planar CC|SE interface, spatial confinement presents a further strategy to control the lithium microstructure. To date, no microstructural investigations have been reported for lithium electrodeposited within porous SE frameworks known from literature.^{112–117} While planar electrodeposition allows for continuous grain growth with increasing layer thickness, it is assumed that spatial confinement within significantly smaller pores imposes a geometric limit to this growth, therefore resulting in smaller grain sizes. Verifying this hypothesis remains a subject for future research.

In addition to the microstructural and spatial design of the CC, the chemical modification of the CC|SE interface via interlayers constitutes a further parameter for controlling the lithium microstructure. These interlayers not only alter the substrate but can also introduce secondary phases within the electrodeposited lithium, particularly when alloy-forming material combinations are utilized.^{41,44} In metallurgy, it is known that impurities, or more generally, secondary phases, influence grain growth in metals, resulting in smaller grains.^{73,135} A central model is *Zener pinning*, in which particles interact with the moving grain boundaries and thus influence grain growth.^{73,136} Building on the findings of the first and second publication of this dissertation, the observed grain growth was therefore partly attributed to the high purity of the electrodeposited lithium. Accordingly, the following hypothesis was derived: if high purity allows for grain growth, the targeted introduction of secondary phases should conversely inhibit it, resulting in a finer microstructure.

This hypothesis formed the basis for the third publication of this dissertation, in which gold, silver, and bismuth were investigated as interlayer materials. The study confirmed that interlayers induce different lithium microstructures, depending on the choice of the interlayer material and the resulting phase distribution. In the case of gold, lithium-gold alloy particles detached from the interface and dispersed throughout the lithium layer. These particles effectively acted as pinning sites, thereby decreasing the resulting grain size. For silver, the interlayer dissolved completely into the lithium layer, resulting in a contracted crystal structure. This lattice contraction is expected to generate internal stresses that may contribute to the observed reduction in lithium grain size. The lithium-bismuth alloy remained in direct contact with the SE, thereby separating lithium and LPSCl. Contrary to the smaller lithium grains observed with gold and silver, using a bismuth interlayer

resulted in even larger lithium grains, which was attributed to faster lithium diffusion kinetics along the formed Li_3Bi alloy. Overall, the third publication shows that the use of interlayers and secondary phases can indeed be used to modify the lithium microstructure. Furthermore, this work showed that the electrochemical history of the lithium layers also influences the resulting microstructure. Partially stripped lithium foils exhibited a different microstructure compared to their merely plated counterparts, namely smaller grain sizes and a preferred orientation in the $\langle 101 \rangle$ direction parallel to the stripping direction. This interplay between electrochemistry and the resulting microstructure will be discussed in more detail in the following chapter.

2.5 Electrometallurgy of Lithium Metal Electrodes

The previous chapters demonstrated various strategies for optimizing the microstructure of LMEs, including deposition parameters and interlayer design. These approaches primarily address microstructural evolution occurring during the plating process. However, microstructure and electrochemistry are coupled: the microstructure influences electrochemical performance, while electrochemistry drives microstructural changes through mass transport and mechanical stresses. Motivated by the grain shrinkage and reorientation in the $\langle 101 \rangle$ direction parallel to the stripping direction observed in the third publication of this dissertation, this chapter investigates the coupled electrochemical, mechanical, and microstructural changes during both plating and stripping.

The “mechanics of lithium plating” are relatively well understood through extensive studies on dendrite formation.^{11,71,90,95,137} Monroe and Newman initially hypothesized that SEs could suppress the formation of lithium dendrites due to their high shear modulus.^{138,139} However, it has since been discovered that dendrite formation can also occur in oxide SEs such as LLZO, whose shear modulus is ten times higher than that of lithium (LLZO $\approx$ 61 GPa, lithium $\approx$ 4.2 GPa). One contribution to this is high stress in existing defects during plating, leading to a Griffith-like failure mechanism.^{11,73} Furthermore, Porz *et al.* showed that the maximum stress is related to the overpotential and, accordingly, equation (7) can be used to estimate the maximum mechanical stress during plating at a given overpotential.⁹⁵

$$\sigma_{\text{Max}} \approx -\frac{F}{V_{\text{m}}^{\text{Li}}} \cdot \Delta\varphi \quad (7)$$

Herein F is the Faraday constant and V_{m}^{Li} the molar volume of lithium. Assuming an overpotential of $\Delta\varphi \approx 10$ mV, the maximum mechanical stress can reach up to 75 MPa. This value is large enough to enlarge surface defects, which can then form more complex networks, *i.e.*, dendrites.⁹⁵ However, even in the case of a perfect interface, it is evident that, at least at the beginning of the deposition process, mechanical work must always be performed in order to open the CC|SE interface or to create space for lithium.²⁶ In general, such mechanical contributions must always be considered in electrochemical experiments.

However, the microstructural level, *i.e.*, how the pressures that occur shape the resulting lithium microstructure, has been relatively little studied to date. Similarly, the coupling between stripping and microstructure remains largely unexplored. Publications 2 and 3 have shown that lithium grains grow with increasing layer thickness during plating under constant stack pressure. This was mainly attributed to curvature reduction, the associated energy minimization of the system, and thus thermodynamic reasons.^{53,140} Publication 3 revealed that stripping reverses the plating trend: grains shrink again, accompanied by a pronounced preferential orientation in the $\langle 101 \rangle$ direction parallel to the stripping direction. This is counterintuitive considering the thermodynamic explanation from

before, as new grain boundaries are created. While plating minimizes energy via grain growth, stripping increases the system's energy by creating new grain boundaries. Consequently, additional energy must be introduced into the system to drive this formation of additional grain boundaries.

Two mechanisms that put energy into the LME come into consideration, namely the externally applied stack pressure and the internal stress generated by stripping. Since both plating and stripping occur under the same external stack pressure, it appears unlikely that this parameter alone accounts for the fundamental difference in microstructural evolution. Furthermore, plating did not induce the strong preferred orientation observed after stripping despite being subjected to the same external pressure. This suggests that the stripping process itself, along with the resulting lithium flux, plays a crucial role in determining the observed grain refinement and the preferred orientation. This raises the question: What role does stripping play in chemo-mechanics, resulting stress, and ultimately in microstructure evolution?

Microscopically, stripping corresponds to the removal of atomic volume from the lattice, thereby injecting vacancies. This vacancy injection causes local distortion of the lattice.¹³⁵ Since the vacancy formation volume in lithium is significantly smaller than the atomic volume ($\Delta V \approx 0.5 \Omega_0$)^{118,141}, the lattice undergoes local inward relaxation, as schematically depicted in **Figure 10**. Here, Ω_0 is the volume of a lithium atom in a perfect lattice. Constrained by the adhering bulk material, this volume mismatch likely generates significant tensile stress within the metal. In the research field of electromigration, the relation between vacancy concentration and hydrostatic stress σ is used to predict when a critical stress level is reached and failure occurs (equation (8)).^{142–145} The cause of the locally increased vacancy concentration in electromigration is attributed to the so-called “electron wind” and is therefore fundamentally different from vacancy injection by stripping in the LME.¹⁴⁴ Nevertheless, it is assumed that the consequence, *i.e.*, the stress that builds up within the LME due to a locally increased vacancy concentration, is transferable. Accordingly, equation (9) is now used to estimate the stress that occurs in lithium at a given vacancy concentration.

$$c_{V,Max} = c_V^0 \exp\left(\frac{(1-f)\Omega_0\sigma}{kT}\right) \quad (8)$$

$$\sigma = \frac{kT}{(1-f)\Omega_0} \ln\left(\frac{c_{V,Max}}{c_V^0}\right) \quad (9)$$

Herein, k is the Boltzmann constant, T the absolute temperature in Kelvin, and $(1-f)$ accounts for the ratio between the volume of a vacancy and the atomic volume Ω_0 . Now, the resulting hydrostatic stress can be calculated for different ratios between the vacancy concentration in equilibrium c_V^0 and the vacancy concentration $c_{V,Max}$ increased by stripping, as shown in **Figure 10**. Please note that this consideration is simplified, as only a steady state is considered, assuming a constant

concentration of vacancies increased to equilibrium. The resulting vacancy concentration difference inside the material, the resulting vacancy flux and possible annihilation of vacancies are not taken into account. For a more in-depth analysis, the applied current density, the resulting vacancy injection rate, and the resulting vacancy diffusion should be coupled to better estimate the resulting stress.

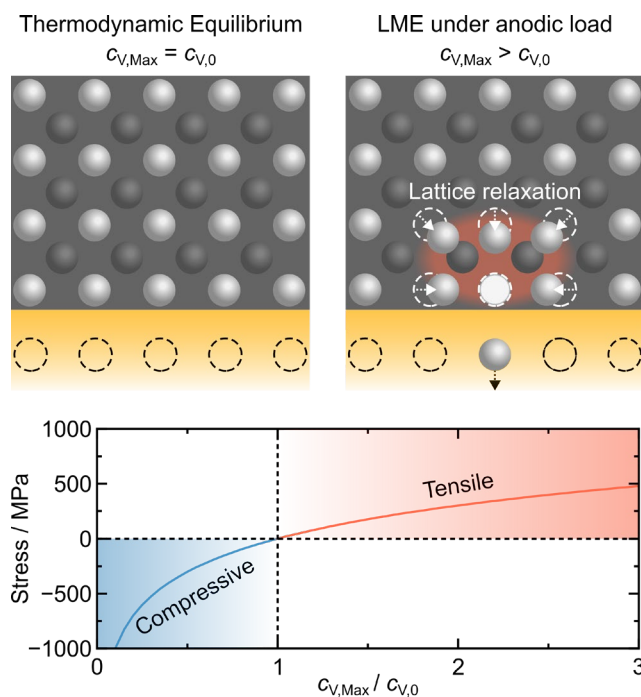


Figure 10: Vacancy injection during stripping and resulting stress in the LME. As shown above, vacancies are injected into the LME during stripping. This leads to local lattice relaxation. Depending on the vacancy concentration in relation to the equilibrium concentration, the resulting hydrostatic stress can be calculated as shown below.

The analysis shows that even doubling the vacancy concentration, already induces a hydrostatic stress of several hundred MPa within the electrode. Krauskopf *et al.* report that this concentration is still at the lower end of realistic values and can reach up to ten times the equilibrium level.³⁶ Nevertheless, it seems unlikely that the electrode will maintain this stress. Instead, it is hypothesized that the system relaxes this hydrostatic stress through microstructural reorganization processes, potentially involving plastic deformation or dislocation movement. Consequently, the material flux during stripping provides a plausible hypothesis for the missing driving force that leads to the formation of additional grain boundaries and the (101) preferred orientation, which is both the most densely packed plane and a slip plane in the BCC lattice. This mechanical perspective underscores the necessity of considering electromigration or “electrometallurgy” in future studies.

Finally, to evaluate the magnitude of the material flux and the potentially resulting stresses in a commercial RFC, the specifications of the *QuantumScape QSE-5B* cell serve as a case study. The

announced battery specifications, the calculated charge and discharge current densities and the resulting lithium height changes are shown in **Table 1**.¹⁴⁶

Table 1: Case study of the *QSE-5B* cell from *QuantumScape*. Relevant battery specifications are listed in the upper part of the table. The two sections below list the resulting current densities, and the resulting height changes of the LME during charging and discharging, respectively. A geometric electrode area of 1 cm^2 and a layer deposition is assumed for the calculations.

	Parameter	Value	Unit
Battery specifications	Cathode areal charge	6.2	mAh cm^{-2}
	Nominal Voltage	3.84	V
	LME thickness (100 % SOC)	30	μm
Charge ^a	Charge rate	4	$\text{C} \triangleq \text{h}^{-1}$
	Charge current density	17.4	mA cm^{-2}
	LME height change	1.4	$\mu\text{m min}^{-1}$
Discharge ^b	Discharge rate	0.2	$\text{C} \triangleq \text{h}^{-1}$
	Discharge current density	1.24	mA cm^{-2}
	LME height change	0.1	$\mu\text{m min}^{-1}$

^aThe charging parameters are calculated for fast charging between a state-of-charge (SOC) of 10% and 80% and consider 70% of the total cathode areal charge.

^bThe discharge parameters are calculated for complete discharge and consider 100% of the total cathode areal charge.

First, the calculated height changes of the LME reveal the extreme morphological demands placed on commercial RFCs. During fast charging, the LME grows at a rate of $1.4 \mu\text{m min}^{-1}$. While the height change during the stripping process (discharge) is significantly lower at $0.1 \mu\text{m min}^{-1}$, it remains substantial. Regarding potential microstructural changes associated with the stripping process, it is noteworthy that changes observed in the third publication already occurred at a current density of $100 \mu\text{A cm}^{-2}$, roughly one order of magnitude lower than the 1.24 mA cm^{-2} required for the *QSE-5B* sample. This implies that under realistic operating conditions, the driving forces for microstructural evolution are likely even more pronounced.

Now, the models previously used to estimate the resulting stress in LMEs are applied to the *QSE-5B* cell of *QuantumScape*. Accordingly, the supersaturation of vacancies is calculated that the LME would have to tolerate to remain morphologically stable at the given discharge current density of 1.24 mA cm^{-2} using equation (5). The corresponding vacancy concentration is 117 times greater than the equilibrium concentration, and the resulting stress in the material according to equation (9) is approximately 2 GPa. It is obvious that these values are unreasonably high and that the LME cannot withstand such high supersaturations of vacancies and high stress in the material. This highlights the limitations of the models, as additional influencing factors such as grain boundary diffusion in polycrystalline lithium, adatom diffusion, or mechanical contributions to the

preservation of the interface, for example via creep, are not considered. Furthermore, only hydrostatic contributions of the stress together with a constant relaxation factor $(1 - f)$ of the lattice are taken into account. On the other hand, it seems unlikely that these aspects alone, even if considered, would enable such high discharge current densities. If it is assumed that *QuantumScape* can indeed guarantee a stable lithium|SE interface at these high discharge current densities, this rather suggests additional contributions in the form of interlayers, host structures, or the microstructure. At the same time, *QuantumScape's* specifications show that RFCs might also function in larger-scale formats and are not limited to laboratory experiments, even if commercialization has yet to materialize.

3 Results

3.1 Publication 1: “*Purity of lithium metal electrode and its impact on the lithium stripping in solid-state batteries*”

In the first publication of this dissertation, the purity of electrodeposited lithium was systematically investigated by a combination of ToF-SIMS and XPS. Additionally, the purity of the electrodeposited lithium sample was compared with two commercially available lithium samples with different purity grades. The influence of purity on the accessible lithium inventory during stripping was investigated by galvanostatic electrochemical impedance spectroscopy (GEIS).

The complementary analysis using ToF-SIMS and XPS showed that commercial lithium samples can contain large amounts of impurities, particularly sodium (up to ≈ 1 at%). Lithium electrodeposited using single-ion conducting SEs such as LPSCl, in contrast, exhibits high purity with the sodium content being below ≈ 0.03 at%. Since the impurities cannot migrate through the SE, they accumulate at the Li|SE interface, resulting in a resistive sodium-rich layer after prolonged discharge.

Furthermore, electrochemical dissolution of the different lithium samples demonstrated that impurities can accelerate contact loss, lowering the accessible lithium inventory. An additional DRT analysis of the recorded impedance spectra revealed a distinct impedance contribution for impurity-containing lithium samples, potentially representing either a fingerprint of the impurities themselves or altered pore morphologies associated with their presence.

Overall, the first publication of this dissertation highlights the importance of accounting for lithium purity when investigating LMEs. Furthermore, the comparison of commercially available and electrodeposited lithium samples shows that RFCs using single-ion conducting SEs provide an intrinsic filtering effect resulting in lithium layers with high purity, which can improve discharge capabilities. The results underline the difference between conventionally produced and electrodeposited lithium samples, further contributing to a deeper understanding of electrodeposited metal electrodes and RFCs in general and advocate for better documentation of used lithium in related publications.

J. Becker designed and conducted all experiments together with T. Weintraut (ToF-SIMS) and S. L. Benz (XPS). Dr. T. Fuchs and C. Lerch supported experiments using LLZO as SE and participated in scientific discussions. P. Becker assisted in cell building. Dr. J. K. Eckhardt assisted in impedance analysis and participated in scientific discussions. Prof. A. Henß, Dr. F. H. Richter and Prof. J. Janek supervised the work and participated in scientific discussions. The original draft was written by J. Becker and edited by all co-authors except P. Becker.

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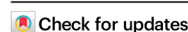


Purity of lithium metal electrode and its impact on lithium stripping in solid-state batteries

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Recent studies emphasize that incorporating lithium metal electrodes can increase the energy density of next generation batteries. However, the production of lithium metal with high purity requires multi-stage purification steps due to its high reactivity. Furthermore, subsequent handling under inert conditions is required to prevent degradation. To circumvent handling of lithium metal and further improve energy density, researchers are exploring reservoir-free cells often referred to as “anode-free” cells. Reservoir-free cells are assembled without using lithium metal. Instead, lithium is electro-deposited at the interface between a current collector and a solid electrolyte from positive electrode materials during the first charge. Despite the potential of reservoir-free cells, there is limited understanding of the purity of electrodeposited lithium metal and how impurities might affect the electrochemical kinetics. This study examines first the purity of electrodeposited lithium at the steel|Li₆PS₅Cl interface. Then, it shows how impurities in lithium electrodes affect stripping capacity when using commercial lithium metal foils with both Li₆PS₅Cl and Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ as solid electrolytes. By using time-of-flight secondary mass spectrometry and X-ray photoelectron spectrometry, we reveal that a lithium layer with high purity is electrodeposited at the negative electrode in reservoir-free cells and that common impurities in lithium metal (reservoir-type) electrodes like e.g. sodium negatively influence the accessible lithium capacity during discharge.

Growing demand for higher power and energy densities in batteries triggers extensive research toward solid-state batteries (SSBs)^{1,2}. The solid electrolytes (SEs) used in SSBs provide higher shear modulus than liquid or gel polymer electrolytes, potentially suppressing dendrite formation and increasing safety^{3–5}. Thereby, SEs could potentially enable the use of the lithium metal electrode. Lithium has a low redox potential of $E_{\text{H}} = -3.04 \text{ V}$ and a theoretical specific capacity of

$q_{\text{th}} = 3861 \text{ mAh g}^{-1}$, which could substantially increase the energy density compared to current cells with graphite electrodes^{6,7}.

Conventionally, lithium metal electrodes are studied using lithium foils produced via molten salt electrolysis in industry^{8–10}. These foils usually contain impurities in the 0.1% to 1% range, particularly sodium, which are challenging to remove during fabrication. Additionally, degradation layers form on the foils' surfaces even under practically

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relevant inert gas conditions, increasing the interfacial resistance to SEs^{11,12}. This issue complicates the preparation of reversible lithium|SE interfaces, often necessitating mechanical removal of the degradation layers or the use of high temperatures and pressures during cell assembly.

To circumvent the processing and safety challenges associated with reactive lithium foils, reservoir-free cell concepts (RFCs) are emerging^{13–16}. In RFCs, lithium is stored only in the discharged (lithiated) active material (i.e., the positive electrode), without excess lithium at the negative electrode. Instead, lithium metal is electrodeposited on the current collector (CC) of the negative electrode during the initial charge, which increases energy density and simplifies production by eliminating the need for inert gas storage of lithium and avoiding its degradation. Moreover, established SEs such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) or $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl), with lithium transference numbers near unity^{17–19}, may yield chemically pure electrodeposited lithium compared to industrially produced foils^{18,19}. This electrochemical purification effect and its influence on cell properties has previously been widely overlooked in battery research. As is shown in the following, the use of lithium metal even with a small fraction of impurities can seriously affect the kinetics of cells with lithium metal electrodes—particularly in fundamental research, where lithium metal foils of different origin are widely used.

In fact, much of the recent research on lithium|SE interfaces relies on the use of lithium foils^{6,20,21}, often without considering and specifying the impact of lithium purity. In particular, the kinetics and morphological development of lithium metal electrodes is often studied in apparently symmetric cells with two foil electrodes. In certain full cell concepts, such as lithium-sulfur or lithium-air batteries, the positive electrode materials are in their delithiated state during assembly^{22,23}, even necessitating the use of pre-formed lithium metal (e.g., lithium foil) at the negative electrode. We believe that lithium purity is a crucial factor across various cell types that has been largely disregarded so far. In contrast, in practical applications of RFCs, all cyclable lithium would initially be contained in the positive electrode materials, i.e., no lithium foils are used during assembly. After the initial charging step (i.e., after lithium metal electrodeposition) the high purity of the electrodeposited lithium layer likely affects continuous cycling of the cell much less. In practice, SSBs are often investigated with a minimal lithium reservoir on the negative electrode, aiming for the compensation of irreversible lithium loss. While these cells are still promising to achieve higher energy densities²⁴, the role of the impurity content in the lithium reservoir is not known.

Research on positive electrode active materials reveals that contaminants within these materials can significantly influence their electrochemical properties^{25–27}. Yet, little is known about the impact of lithium metal purity on its electrochemical performance in SSBs²⁴. Properties of metals in general vastly depend on their purity²⁸. This implies that lithium metal electrodes may also exhibit variations in chemo-mechanical and microstructural properties depending on their purity^{29–32}. As a result, the electrochemical properties, e.g., discharge capacity, of highly pure electrodeposited lithium in RFCs may also differ significantly from that of lithium foils produced industrially, which often contain impurities^{30,32}. While some studies have addressed the filtering of impurities using solid electrolytes^{19,33,34}, the implications for RFCs remain unexplored, but are crucial for practical applications^{28,32}.

In this work, we investigate the electrochemical “filtering” of lithium metal by LPSCl using a steel|LPSCl|Li|steel model-type RFC. Additionally, we examine the influence of impurities on the accessible lithium inventory (i.e., stripping capacity) in Li|LPSCl|Li and Li|LLZO|Li model-type symmetric cells using lithium foils. The purity of electrodeposited lithium and the concentration of impurities at the SE interface with a commercial lithium electrode after cell operation are analyzed using time-of-flight secondary ion mass spectrometry (ToF-

SIMS) and X-ray photoelectron spectroscopy (XPS). Our analysis confirms that electrodeposited lithium layers exhibit high purity. In contrast, when lithium foils containing impurities are used as the lithium reservoir, these impurities become more concentrated during the lithium dissolution process. They accumulate at the SE interfaces and cause kinetic hindrance. We note that diffusion of impurities in lithium metal, like e.g. Na, has already been studied in the 1970s, which we will consider in the discussion of our results. Ultimately, our results reveal a correlation between lithium purity and accessible stripping capacity using solid electrolytes. We identify lithium purity as a key factor to improve the electrochemical performance of lithium metal electrodes in SSBs.

Results and Discussion

Electrochemical deposition of lithium at the working electrode

To investigate the purity of electrodeposited lithium, a lithium layer with a thickness of at least about 30 μm is needed. Here, a steel|LPSCl|Li_{LP}|steel model system was used for electrodeposition, due to its suitability for electrodepositing thick lithium layers^{29,35,36}. The used cell setup and a characteristic voltage profile for electrodeposition of lithium are shown in Fig. 1.

The voltage profile confirms successful nucleation and electrodeposition of lithium at the steel|LPSCl interface. At the beginning of the measurement, a characteristic voltage minimum is observed, representing the nucleation overvoltage of Li_D at the WE when referenced to the following plateau¹³. The constant plateau afterwards demonstrates continuous lithium electrodeposition at the WE and stripping at the CE. After -12 mAh cm^{-2} of transferred Li, an increase in overvoltage is observed due to a contact loss at the CE despite application of external pressure, which indicates depletion of the Li_{LP} reservoir³⁷. With this procedure, Li_D films with a mean thickness of about 60 μm were electrodeposited at the WE, which were then examined for their purity in the following section. Due to lithium depletion at the CE and the resulting poor contact, the surface of the solid electrolyte was also accessible for surface analysis after being in contact with the lithium CE during stripping.

Chemical analysis of electrodeposited lithium and reference samples

The three different lithium samples Li_{LP}, Li_{HP} and Li_D were then investigated regarding their purity using ToF-SIMS and XPS. Analyses of Li_{LP} and Li_{HP} were carried out on lithium foils produced from two

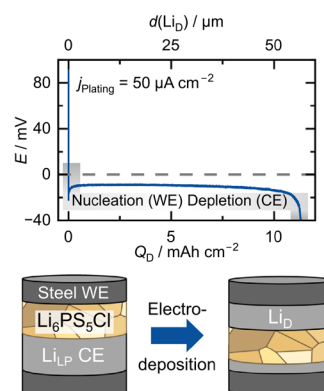


Fig. 1 | Electrodeposition of a lithium layer. Voltage profile during lithium electrodeposition at the steel|LPSCl interface using a current density of $50 \mu\text{A cm}^{-2}$ and schematic of the used cell setup steel|LPSCl|Li_{LP}|steel before and after the lithium deposition. Herein Li_{LP} is a lithium foil with low purity and Li_D the electrodeposited lithium.

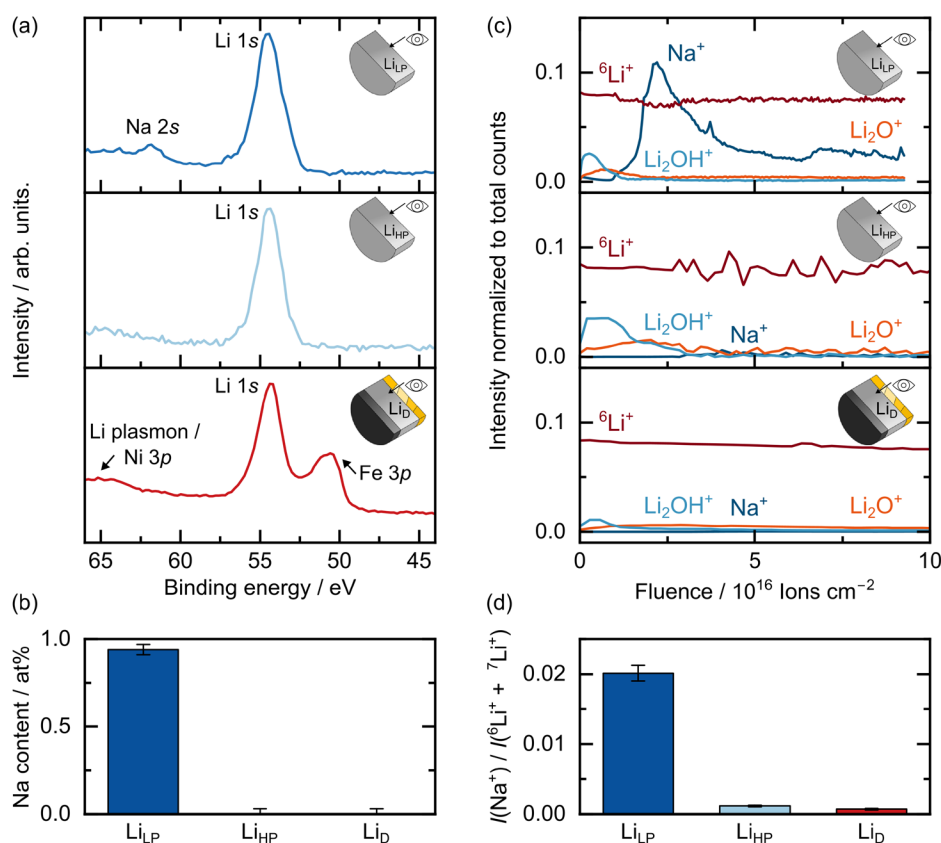


Fig. 2 | Measurement of the impurity content of various lithium samples.

a Acquired XPS spectra of Li_{LP}, Li_{HP} and electrodeposited Li_D. **b** Calculated sodium content from the XPS analysis. In case of Li_{HP} and Li_D, sodium impurities are below the detection limit, which is why only error bars are given. The error is ± 0.03 at% in all measurements, which is the detection limit of sodium within a lithium matrix using Al K α radiation based on the work of A. Shard⁴². **c** ToF-SIMS depth profiles of Li_{LP}, Li_{HP} and electrodeposited Li_D. The intensity of the signals was normalized to

the total counts. **d** Intensity ratios of the Na⁺ and Li⁺ signals (intensity I) from SIMS analysis. Data are presented as mean values from three measurements. The error bars correspond to standard deviation. All samples were measured in a cross-sectional geometry, as depicted schematically. Li_D was analyzed ex-situ after electrodeposition of 12 mAh cm⁻² lithium at a current density of 50 $\mu\text{A cm}^{-2}$ in a reservoir-free cell system on a steel electrode (see Fig. 1).

different commercial lithium rods and serve as a reference to the electrochemically deposited lithium Li_D (see Experimental section). According to the manufacturer's specifications, Li_{LP} is lithium with low purity (99%), while Li_{HP} has a higher purity (99.8%). To analyze Li_D, the electrodeposited layers (as shown in Fig. 1) were used. To avoid interference of surface passivation layers and LPSCl remnants, every sample was ion polished in a similar way and analyzed in a cross-sectional geometry. Although lithium contains various impurity species, including potassium, calcium, and magnesium, sodium was used as the reference signal for impurities in this study, as it is the most common impurity in lithium^{38,39}. The acquired XPS spectra, ToF-SIMS depth profiles and the resulting quantification from these analyses are depicted in Fig. 2.

The comparison of the acquired XPS spectra for the different lithium samples in Fig. 2a already hints toward a decreased sodium impurity level in Li_{HP} and Li_D when compared to Li_{LP}. While sodium is detected in Li_{LP} using the Na 2s signal, this signal is no longer visible for Li_{HP} and Li_D. For Li_D, additional signals for Fe 3p and Ni 3p are observed. This artifact originates from the steel foil used as working electrode (i.e., as current collector for lithium electrodeposition) and the sample

holder used for the previous ion beam milling. For clarification, a similar sample after disassembly is shown in Figure S1.

For a quantitative comparison of the sodium content, the respective sodium concentrations in the lithium foils Li_{LP}, Li_{HP} as well as the electrodeposited lithium Li_D were calculated using the XPS spectra. Interestingly, it was found that the measured sodium content depends on the sputtering process. As shown as an example for the Li_{LP} sample in Figure S2 and discussed in Supplementary Note 1, the intensity for the Na 2s signal increases with increasing sputtering time. After 360 s of sputtering with an acceleration voltage of 10 kV, the intensity approaches saturation. A subsequent increase of the acceleration voltage of the argon clusters to 20 kV significantly increases the Na 2s signal, indicating preferential sputtering or a mass related effect^{40,41}. Furthermore, increasing the accelerating voltage while keeping the argon cluster size constant could lead to an increased removal of inorganic degradation products during argon cluster sputtering, as shown by Shard and Baker⁴¹. Sputtering at an acceleration voltage of 20 kV leads to an overestimation of the sodium content of around 5.4 at% in Li_{LP}. The surfaces of the samples were therefore sputtered using an acceleration voltage of 10 kV in between

measurements. The following quantification is based on the XPS spectra after sputtering with an acceleration voltage of 10 kV.

In Li_LP , a sodium content of around 0.94 at% is calculated, as can be seen in Fig. 2b. This value is in good agreement with the manufacturer's specifications for the sodium content of around 7000 ppm. In the case of Li_HP the intensity of the Na 2s signal is too low to gain reliable values for the sodium concentration. Based on the work of Shard, the detection limit of sodium within a lithium matrix using Al K_α radiation is ~0.03 at%⁴². This limit is therefore assumed as measurement error for the measurements performed here. The manufacturer's specification for the sodium content of Li_HP is 820 ppm. Accordingly, sodium should be detectable. Deviations could stem from the measurement geometry, the surface sensitivity of XPS or the sputtering step. Nevertheless, the assumed measurement error of 0.03 at% is in the same order of magnitude as the manufacturer's specifications and is therefore used.

In the case of Li_D , no value for the sodium content can be specified based on the recorded XPS spectra either. Analogous to Li_HP , an error of 0.03 at% is assumed here. Clearly, Li_D has a higher purity than its counterpart Li_LP , which served as the lithium reservoir at the counter electrode for lithium deposition at the steel CC. A reduction of the sodium content from 0.94 at% to 0.03 at% corresponds to a factor of 31. The purification of lithium by the solid electrolyte LPSCI, by only allowing lithium ions to migrate through its crystal structure, is therefore evident.

To quantitatively compare the sodium impurity levels, the Na 1s signal can also be used instead of the Na 2s signal. However, the binding energy of the Na 1s signal at E_B = 1071 eV is roughly twenty times higher than that of the Li 1s signal at 55 eV. At a constant excitation energy of ~1487 eV (Al K_α source), the excited photoelectrons exhibit widely different kinetic energies. Accordingly, different penetration depths of the sample need to be considered for each signal. As shown in Figure S3, using the Na 1s signal results in a sodium content of 5.19 at% for Li_LP and 0.74 at% for Li_HP . For Li_D , no significant intensity for the Na 1s signal was found. Apparently, the sodium content is overestimated using the Na 1s signal. However, qualitatively, our results indicate that Li_D has an even higher purity than Li_HP .

The lithium cross-sections were further analyzed using ToF-SIMS, capable of detecting impurities at ppm to ppb levels, potentially distinguishing impurity contents between Li_HP and Li_D . Figure 2c presents the respective depth profiles. As reference, the $^6\text{Li}^+$ intensity is displayed as it is in the same order of magnitude as the intensity of the signals of interest, i.e., as Na^+ , Li_2OH^+ and Li_2O^+ . Please note that, based on our measurements, the intensity ratio $I(^6\text{Li}^+) / I(^7\text{Li}^+)$ is ~0.09. Despite ion beam polishing under vacuum and inert sample transfer conditions, a surface passivation layer is visible on all samples, with an increased intensity of Li_2OH^+ and Li_2O^+ . Notably, Li_LP shows a sodium-rich layer beneath this oxygen-rich layer. We note that sodium segregation out of lithium metal has early been reported by Schily et al. and Powell et al.^{43,44}. This layered structure could also be the reason for the strong increase in the Na 2s signal found following the sputtering step with 20 kV during the XPS analysis, in which more inorganic species such as LiOH and Li_2O are sputtered, exposing a sodium rich layer underneath⁴¹. In contrast, Li_HP and Li_D show no significant Na^+ intensity, already indicating a reduced sodium content. To avoid an influence of the passivation layer, quantification was performed on all samples after cleaning by sputtering.

Since ToF-SIMS analysis provides only semi-quantitative data, the intensity ratios $I(\text{Na}^+) / I(^6\text{Li}^+ + ^7\text{Li}^+)$ presented in Fig. 2d should only be seen as a qualitative comparison. The error bars reflect the average of three measurements taken from different sample locations. For the lithium foil used as the counter electrode (Li_LP), the ratio $I(\text{Na}^+) / I(^6\text{Li}^+ + ^7\text{Li}^+)$ is ~0.02. In the case of Li_HP the intensity ratio is 0.001. For the electrodeposited lithium layer (Li_D), this intensity ratio is the lowest at around 0.0007. It is important to note the high sensitivity of ToF-SIMS,

particularly for sodium detection. Therefore, it is not surprising that sodium contamination is also detected in electrodeposited lithium. This could result from redeposition during ion beam milling or sodium diffusion from the solid electrolyte into the electrodeposited lithium. Despite the semi-quantitative nature of this analysis, the data clearly shows a significant reduction in sodium content from Li_LP to Li_D , with the intensity ratio $I(\text{Na}^+) / I(^6\text{Li}^+ + ^7\text{Li}^+)$ decreasing by a factor of ~29. This confirms the purification by LPSCI, as already indicated during XPS analysis. Additionally, the result obtained from the XPS analysis of the Na 1s signals, indicating that the sodium content in Li_D is lower than in Li_HP , appears to be confirmed by the SIMS analysis.

The results are in good agreement with the reported high ion selectivity of solid electrolytes and was to be expected when considering the 60% difference in ionic radii for lithium and sodium. In LPSCI, lithium ions are tetrahedrally coordinated, have a single positive charge and an ionic radius of 0.59 Å⁴⁵. For the same coordination number and charge, the ionic radius for sodium ions is 0.99 Å and is therefore substantially larger⁴⁶, making a hopping transport of sodium ions through the solid electrolyte with its tetrahedral regular lattice sites energetically unfavorable and thus unlikely.

The two lithium samples, Li_LP and Li_HP were additionally analyzed using EDX to obtain information about the distribution of sodium within the lithium foil. The lithium samples were attached to an LPSCI pellet, a capacity of 5 mAh cm⁻² was stripped from one of the two lithium electrodes, and a crater was milled in the stripping electrode by using a focused ion beam. The EDX analysis reveals sodium precipitates within the lithium matrix of Li_LP (see Figure S4). In contrast, no such precipitates and almost no signal for sodium in general were found for Li_HP (see Figure S5). These precipitates likely stem from lithium metal production from the melt, in which sodium impurities are inevitably present. Based on the binary phase diagram, lithium and sodium form a monotectic at low sodium content (see Figure S6)⁴⁷. As lithium shows virtually no or minor solubility for sodium, the formation of sodium precipitates is to be expected, which is further discussed in Supplementary Note 2.

In summary, we conclude that only lithium ions can migrate through LPSCI, which is why a highly pure lithium layer with a sodium content below 0.1 at% is electrodeposited at the WE, even though roughly 1 at% of sodium is present in the lithium used as CE. Other impurities such as potassium, magnesium or calcium should also not be able to migrate through LPSCI, which is why they are also filtered out by electrodeposition^{19,33,34}. When using reservoir-free cells, a high-purity lithium layer is electrodeposited onto the WE during the initial formation step. This purer layer is likely to differ from conventional lithium foils in terms of mechanical properties, such as hardness, and electrochemical properties, such as stripping capacities. The latter is discussed in the final chapter of this work for further analysis.

Impurity analysis of lithium after lithium dissolution

Since impurities cannot migrate through the solid electrolyte, they must accumulate at the stripped CE. To investigate this, the surface of the solid electrolyte that has been in contact with an impurity containing lithium foil (Li_LP), acting as CE / lithium source for electrodeposition at the WE (see Fig. 1), is analyzed. Almost full lithium depletion allowed to peel off the Li_LP electrode³⁷, enabling analysis of the LPSCI pellet surface using XPS and ToF-SIMS. The acquired XPS spectra and ToF-SIMS depth profiles, along with a reference measurement of a pristine LPSCI surface, are given in Fig. 3.

A comparison of the XPS spectra for the reference sample (LPSCI surface without lithium contact, shown in blue) and the LPSCI surface after being in contact with a Li_LP counter electrode shown in red, reveals that a Na 2s peak is present only on the LPSCI surface that was in contact with Li_LP . This shows that an increased sodium concentration is present on the LPSCI surface after lithium stripping with an impure lithium foil. We attribute this to an accumulation of the sodium

impurities on the LPSCI surface as they are not able to migrate through the SE.

This finding is further supported by ToF-SIMS depth profiles. In the reference sample, the ${}^6\text{Li}^+$ signal remains consistently stronger than the Na^+ signal throughout the measurement. However, for the LPSCI surface that was in contact with a Li_{HP} counter electrode, the Na^+ signal becomes more intense than the ${}^6\text{Li}^+$ signal, confirming the formation of a sodium-rich layer on the solid electrolyte surface. Interestingly, also an enrichment of K^+ can be seen on top of this Na^+ rich layer. Notably, a sodium signal is detected in both measurements, suggesting the presence of sodium impurities within the solid electrolyte itself, potentially originating from precursor contamination.

These findings are in good agreement with the precipitates found inside the Li_{HP} sample using EDX (revisit Figure S4). As these precipitates are present within the lithium foil, they are consequently also

present at the interface during preparation. Furthermore, as the volume of the lithium electrode decreases during the stripping process, more and more of these precipitates approach the solid electrolyte surface.

To validate the accumulation of impurities at the solid electrolyte interface, additional experiments at an $\text{Li}_{\text{HP}}|\text{LLZO}$ interface were conducted. LLZO is studied as a potential separator SE for SSBs. It is practically stable in contact with lithium metal, allowing us to rule out degradation at the $\text{Li}|\text{LLZO}$ interface in this case⁴⁸. One electrode of a symmetrical $\text{Li}_{\text{HP}}|\text{LLZO}|\text{Li}_{\text{HP}}$ cell was electrochemically stripped until pores formed. This allowed the stripped Li_{HP} electrode to be peeled off and the surface of the LLZO pellet to be analyzed³⁷. Here, too, an enrichment of sodium on the surface of LLZO could be detected, which is even visible to the naked eye as a dark film on the SE. The results of this investigation using ToF-SIMS and XPS are summarized in Figure S7 and shortly discussed in Supplementary Note 3. In addition, EDX measurements were carried out at the edge of the electrode surface, which also show sodium accumulation for Li_{HP} in the area of the previous electrode contact. The results of the EDX analysis can be seen in Figure S8.

These results suggest that impurities such as sodium accumulate on SE surfaces during electrochemical lithium stripping. As only lithium ions migrate through the electrolyte, impurities concentrate on the CE side, leading to the observed buildup. The impact of these impurities on electrochemical performance is yet unclear and is discussed in the next section.

Influence of impurities on the discharge process of lithium electrodes

To investigate the influence of impurities on the electrochemical properties of lithium electrodes, the three analyzed lithium samples with different impurity contents (Na content in $\text{Li}_{\text{HP}} > \text{Li}_{\text{HP}} > \text{Li}_{\text{D}}$) are compared during electrochemical stripping in Fig. 4. Please note that all subsequent stripping experiments were carried out using galvanostatic electrochemical impedance spectroscopy with a current density of $100 \mu\text{A cm}^{-2}$ with no external pressure applied.

To compare stripping capacities, symmetrical $\text{Li}_{\text{HP}}|\text{SE}|\text{Li}_{\text{HP}}$ and $\text{Li}_{\text{HP}}|\text{SE}|\text{Li}_{\text{HP}}$ cells were built. Both LPSCI and LLZO were used as SE. Lithium was then stripped until pore formation occurred, as evident by a strong voltage increase to 1 V. To investigate the stripping performance of Li_{D} , a lithium layer with a capacity of 5 mAh cm^{-2} was initially electrodeposited at a steel|LPSCI interface with a current density of $100 \mu\text{A cm}^{-2}$ at an external pressure of 15 MPa. The voltage profile during electrodeposition is displayed in Figure S9. Subsequently, the external pressure was released, the current direction was reversed, and lithium was stripped until a pore formation occurred. The voltage profiles during stripping until pore formation are compared in Fig. 4.

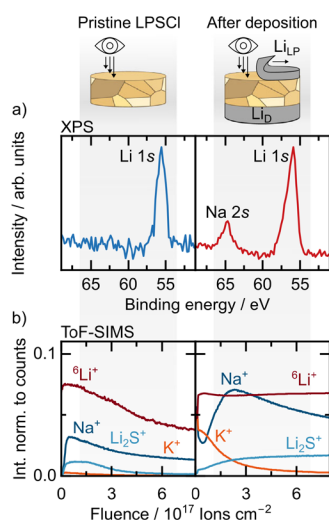


Fig. 3 | Analysis of residues on the solid electrolyte surface after lithium stripping. **a** XPS spectra of a pristine LPSCI surface on the left (in blue) and of an LPSCI surface that was in contact with Li_{HP} CE during stripping on the right (in red). **b** ToF-SIMS depth profiles of a pristine LPSCI surface on the left and an LPSCI surface that was in contact with Li_{HP} CE during stripping on the right. The intensity of the signals was normalized to the total counts. The LPSCI surface after deposition was analyzed ex-situ after stripping 12 mAh cm^{-2} of Li_{HP} in a reservoir-free cell (see Fig. 1).

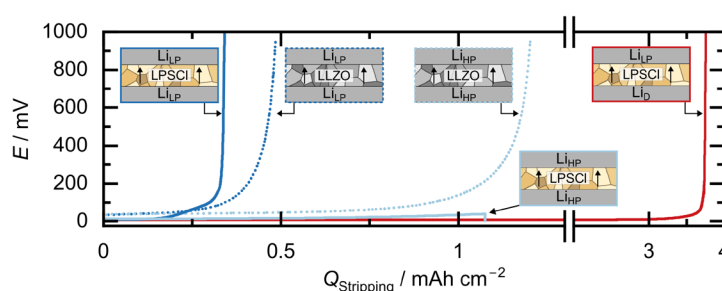


Fig. 4 | The influence of the impurity content on the accessible lithium capacity during stripping. Voltage profiles during stripping of lithium until pore formation in symmetrical $\text{Li}_{\text{HP}}|\text{SE}|\text{Li}_{\text{HP}}$ cells. Cells using LPSCI as SE are depicted with solid lines. For clarification, the respective cell system is schematically depicted next to the respective data.

Cells using LPSCI as SE are depicted with solid lines. For clarification, the respective cell system is schematically depicted next to the respective data.

At this point, we note that varying impurity concentrations may alter the mechanical properties of lithium, potentially affecting the preparation of the Li|SE interface. However, the impedance spectra of both samples are similar, suggesting comparable interfaces (see Figure S10), with only a slight increase in the overall resistance in the case of $\text{Li}_{\text{HP}}|\text{LPSCI}$. This is likely as 15 MPa pressure were applied during electrode preparation with LPSCI, which is significantly higher than the yield stress of lithium at 0.7 MPa⁶. As a result, minor differences in the mechanical properties of the lithium samples are likely overshadowed by the high preparation pressure. A similar conclusion can be drawn for $\text{Li}|\text{LLZO}$ interfaces, which are prepared at an isostatic pressure of 400 MPa, ensuring optimal interfaces with minimal resistance in both cases (compare Figure S11)³⁷.

A comparison of the voltage profiles during stripping shows that when lithium with a low purity (Li_{LP} , see Fig. 2) is used for LPSCI and LLZO as SE, contact loss occurs after $\sim 0.34 \text{ mAh cm}^{-2}$ and 0.48 mAh cm^{-2} , respectively. In contrast, when lithium with a higher purity (Li_{HP} , see Fig. 2) is used, 1.1 mAh cm^{-2} is stripped for LPSCI, even though a slightly higher initial resistance was observed. Please note that the shown $\text{Li}_{\text{HP}}|\text{LPSCI}|\text{Li}_{\text{HP}}$ sample is short-circuited before reaching the cutoff potential. The reason for this is dendrite growth within the SE. In the case of $\text{Li}_{\text{HP}}|\text{LLZO}|\text{Li}_{\text{HP}}$, 1.2 mAh cm^{-2} can be stripped before reaching the cutoff of 1 V, which is close to experiments carried out in previous studies³⁷. In conclusion, for both SEs, a substantial increase in stripping capacity by a factor of about 3 is observed when lithium with a higher purity is used. To ensure the reproducibility of the results, a set of three cells was examined for each cell type. The additional cells using LPSCI as SE are shown in Figure S12, those using LLZO in Figure S13. For additional information, we refer the reader to Supplementary Note 4.

From this, we conclude that impurities commonly present in commercial lithium, such as Na and K, decrease the accessible capacity during stripping of lithium foils. We attribute this effect to the formation of sodium-rich precipitates within the lithium electrode, as shown in Figure S4, likely occurring during the fabrication process from the melt. During lithium stripping, the volume of the electrode decreases, causing an increase in the relative sodium content. Since sodium is almost completely insoluble in lithium (as illustrated in Figure S6), additional sodium-rich precipitates may form, most likely at the $\text{Li}|\text{SE}$ interface. This behavior aligns with recent findings by Mann et al., who reported the formation of a 3D sodium scaffold during the stripping process from a monotectic lithium-sodium mixture with 3 at % Na prepared through cold work⁴⁹. In contrast to our findings, the authors report improved lithium stripping kinetics which they attribute to the 3D structured Na interlayer formed during the first stripping step. A direct comparison with these results is difficult, as only garnet SE was used and most experiments were run at 60 °C. Similarly, Yoon et al. also investigated the influence of several at% of sodium in lithium during stripping. Under pressure, an increase in stripping capacity was observed with increasing sodium content, which the authors attributed to the greater plastic deformability of the sodium-lithium mixture⁵⁰. During stripping, there was also an accumulation of sodium at the solid electrolyte interface observed. As in the case of Mann et al., the resulting sodium layer appears to avoid current focusing in the subsequent plating step, as it keeps contact between the electrode and the solid electrolyte. Additionally, Park et al. reported an improved lithium stripping by introducing a Na-K interlayer at the $\text{Li}|\text{LLZTO}$ interface⁵¹. More work will be necessary to resolve this apparent contradiction. We suggest that small Na atom fractions, typical for a homogeneously dissolved impurity, will deteriorate the interface conformity, while a larger fraction of sodium, dispersed as a second phase, may form a thick interlayer.

Interestingly, when analyzing the lithium electrodes of the $\text{Li}|\text{LLZO}|\text{Li}$ samples after pore formation, a difference in the pore geometry seems evident (see Figure S14). One reason for this is the

increased stripping time in the case of lithium foil with higher purity (Li_{HP}). On the other hand, the impurities present could also lead to a changed pore geometry. This hypothesis is supported by the fact that sodium precipitates can be found in places on the lithium residues using EDX (see Figure S15).

Notably, the stripping capacity of 1.2 mAh cm^{-2} for $\text{Li}_{\text{HP}}|\text{LLZO}|\text{Li}_{\text{HP}}$ is comparable to the stripping capacity achieved by Krauskopf et al. in symmetrical $\text{Li}|\text{LLZO}|\text{Li}$ of 0.9 mAh cm^{-2} , using lithium with a similar purity of 99.8%⁵². This supports the purity dependence found in this study and highlights that the stripping capacity is primarily limited by the lithium electrode, rather than the solid electrolyte.

In the case of Li_{D} , an even higher stripping capacity of 3.74 mAh cm^{-2} is achieved, corresponding to 75% of the previously electrodeposited 5 mAh cm^{-2} of lithium. However, this increase in stripping capacity cannot be exclusively attributed to a higher purity of Li_{D} , as other parameters also change. On the one hand, the $\text{Li}_{\text{D}}|\text{LPSCI}$ interface contact could be more homogeneous due to the electrochemical deposition than is the case for the conventionally prepared $\text{Li}|\text{LPSCI}$ interfaces. In addition, the actual contact area between Li_{D} and LPSCI could be larger than the geometrically assumed one, since deposition within the SE could also have occurred during initial electrodeposition. This hypothesis is supported by a cross-section prepared on the $\text{Li}_{\text{D}}|\text{LPSCI}$ interface of a similar sample, revealing dendritic structures, i.e. lithium that has been deposited inside the solid electrolyte (see Figure S16).

For a more in-depth electrochemical analysis of the stripping properties of the investigated lithium electrodes, the impedance spectra during stripping are analyzed using the distribution of relaxation times (DRT). From this, contour plots are created, which are shown in Fig. 5 for each of the samples shown previously in Fig. 4. Additionally, to clarify how the contour plot is created, Fig. 5a includes selected impedance spectra in the Nyquist representation and all recorded impedance spectra during stripping in the Bode representation using the phase angle. The resulting DRT data for the $\text{Li}_{\text{HP}}|\text{LPSCI}|\text{Li}_{\text{HP}}$ sample are shown in Fig. 5b. During the continuous stripping of lithium, there is an increase in resistance, as evident from the growing semicircle in Nyquist representation with an apex frequency of 22 kHz. The corresponding data point is marked with a filled circle. This is complemented by a more negative phase angle in the Bode plot at the corresponding relaxation time ($\tau \approx 10^{-5} \text{ s}$). In the DRT representation (Fig. 5b), the increase in resistance results in an increasing maximum of the distribution function $\gamma(\tau)$. As the total resistance R corresponds to the area below this curve, the increase in resistance can also be seen here. This increase in resistance is finally shown in the contour plot by the corresponding color coding.

An analysis of the contour plot $\text{Li}_{\text{LP}}|\text{LPSCI}|\text{Li}_{\text{LP}}$ reveals a bulk transport impedance signal for LPSCI at $\tau \approx 10^{-7} \text{ s}$. Deconvolution of bulk and grain boundary (GB) contributions is not possible in the measured frequency range. For Li_{LP} , a broad interfacial signal ($\tau \approx 10^{-5} - 10^{-1} \text{ s}$) can be seen for LPSCI, which appears to be based on two different processes. Both signals are highlighted with black arrows and contribute to a similar extent to the resistance increase shortly before contact loss ($Q_{\text{stripping}} \approx 0.3 \text{ mAh cm}^{-2}$), as can be seen from the color coding. Additionally, the recorded impedance spectra during stripping, depicted in Nyquist representation in Figure S10, reveal two semicircles.

In the case of $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$, three distinct processes can be separated. For high frequencies, i.e., low relaxation times ($\tau \approx 10^{-7} \text{ s}$), the impedance contribution corresponds to the LLZO bulk transport. The resistance contribution is higher than in the case of LPSCI due to the lower conductivity of LLZO compared to LPSCI. At higher relaxation times ($\tau \approx 10^{-5} \text{ s}$), the impedance from the grain boundaries of the polycrystalline LLZO can be seen. These two contributions remain constant throughout the measurement, which is consistent with previous measurements on $\text{Li}|\text{LLZO}$ interfaces and shows that no lithium is

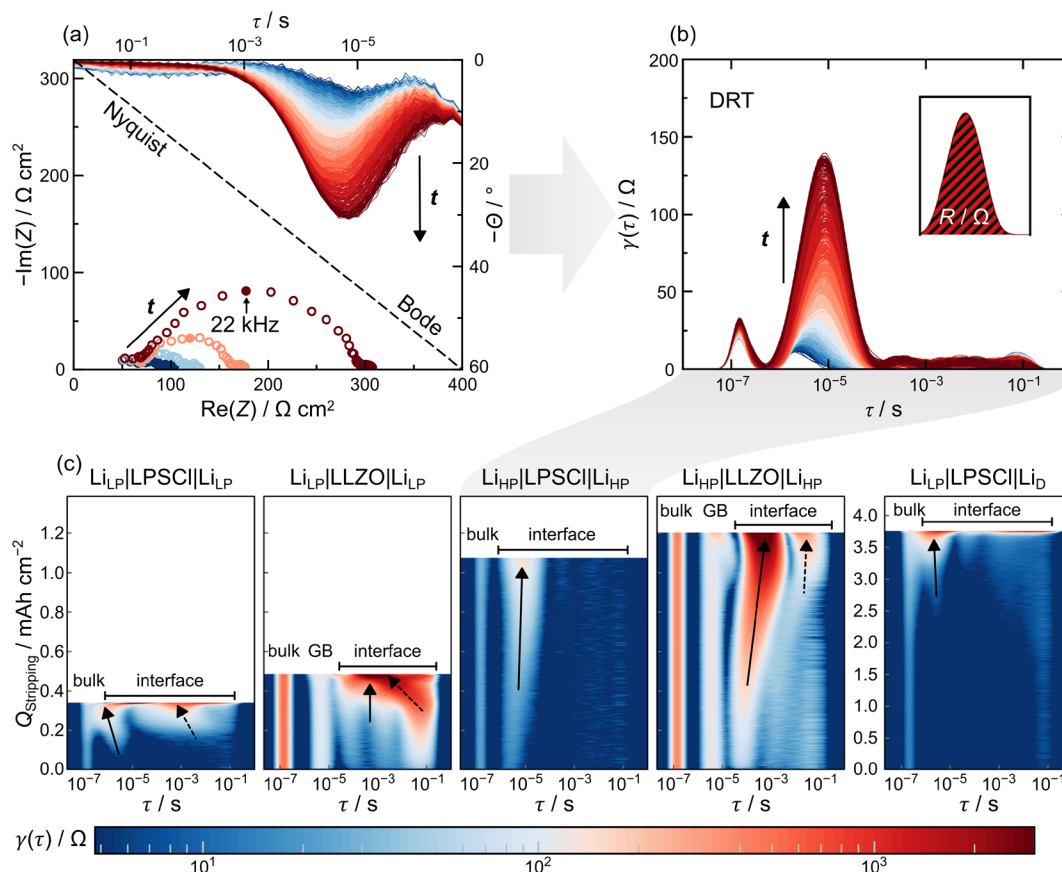


Fig. 5 | Impedance analysis of the different lithium samples during stripping. **a** Evolution of the impedance during stripping for the $\text{Li}_{\text{HP}}|\text{LPSC}|\text{Li}_{\text{HP}}$ sample showing all cycles in Bode representation (phase angle Θ versus relaxation time τ) in the upper part of the plot and selected cycles in Nyquist representation in the lower part of the plot. The characteristic frequency of the semicircle is marked with

a filled circle. **b** Resulting distribution of relaxation time curves of the acquired data in (a). As shown in the small insert, the area below the function $\gamma(\tau)$ is the total resistance R for a process at a certain relaxation time τ . **c** Contour plots for the different samples, as marked with the heading, from Fig. 4 during stripping. The arrows highlight different interfacial contributions during stripping.

deposited inside the SE but is plated homogeneously on the CE instead^{37,53,54}. Finally, at even higher relaxation times ($\tau \approx 10^{-4} \text{ s} - 10^{-1} \text{ s}$), impedance contributions, which can be attributed to interfacial processes, become apparent. The signal occurring here is also very broad and two different processes, highlighted with two black arrows, are responsible for the increase in resistance during pore formation. This is visible in the impedance spectra in Nyquist representation (see Figure S11). Here, a broadening of the respective semicircle is evident.

For the middle contour plot ($\text{Li}_{\text{HP}}|\text{LPSC}|\text{Li}_{\text{HP}}$), lithium with higher purity was used. As before, a constant bulk contribution is observed for LPSC as SE. The impedance contribution of LPSC is almost the same as for the $\text{Li}_{\text{LP}}|\text{LPSC}|\text{Li}_{\text{LP}}$ sample, highlighting the comparability between the two LPSC pellets. However, when using Li_{HP} , only one single dominant interface signal is found at $\tau \approx 10^{-3} \text{ s}$. The signal is highlighted with an arrow inside the contour plot. As visible from the color code, the resistance increase during contact loss ($Q_{\text{stripping}} \approx 1 \text{ mAh cm}^{-2}$) is solely attributed to this signal. This also agrees with the shape of the impedance data in Nyquist representation (see Fig. 5a and Figure S10). Instead of having a broadening of the semicircle as in the case of $\text{Li}_{\text{LP}}|\text{LPSC}|\text{Li}_{\text{LP}}$, only one semicircle is visible.

When using Li_{HP} in combination with LLZO, again, a constant bulk and GB contribution is observed. These impedance contributions of LLZO are almost the same as for the $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ sample, highlighting the comparability between the two LLZO pellets. However, when using Li_{HP} , only a single dominant interface signal emerges between $\tau \approx 10^{-4} \text{ s} - 10^{-1} \text{ s}$. Although there is a second signal at $\tau \approx 10^{-2} \text{ s}$ (highlighted with a dashed arrow), which also becomes larger shortly before contact loss ($Q_{\text{stripping}} \approx 1.2 \text{ mAh cm}^{-2}$), the resistance contribution is at least one order of magnitude smaller at any time than for the signal at $\tau \approx 10^{-4} \text{ s} - 10^{-3} \text{ s}$ (highlighted with a straight arrow). This observation is again supported by the impedance spectra in Nyquist representation (see Figure S11), where almost no broadening of the respective semicircle can be seen.

For the last contour plot ($\text{Li}_{\text{D}}|\text{LPSC}|\text{Li}_{\text{LP}}$), a slightly lower bulk contribution of the LPSC pellet is visible in the beginning. During stripping and especially just before contact loss ($Q_{\text{stripping}} \approx 3.8 \text{ mAh cm}^{-2}$) this resistance contribution increases. As discussed above, we assume that during electrodeposition, lithium is also electrodeposited inside the LPSC pellet, as shown for a similar sample in Figure S16. During the stripping shown here, this dendritic lithium is redissolved, decreasing the effective contact area between

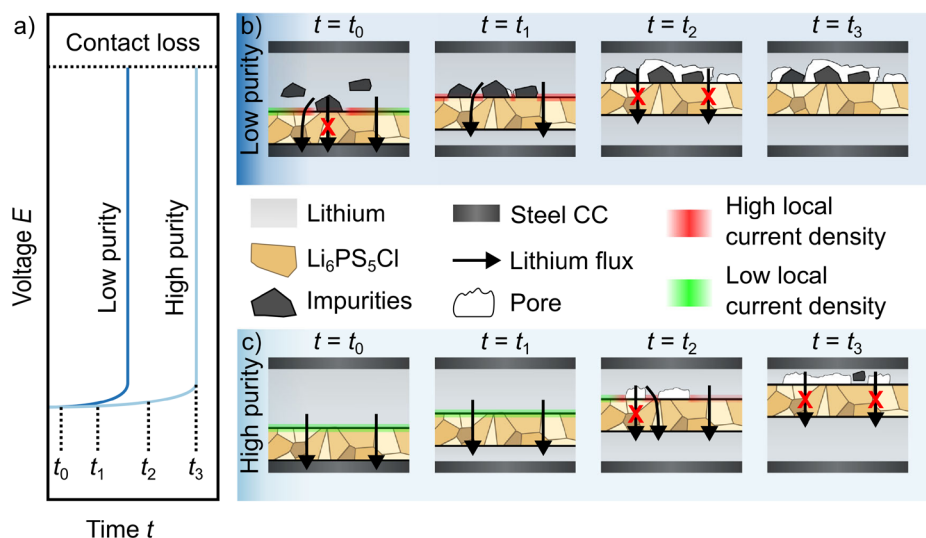


Fig. 6 | Impact of lithium purity in (reservoir-free) solid-state batteries. Scheme of the purification of lithium when using single-ion conducting SEs. **a** Voltage profile during lithium stripping for two different lithium samples, one with a high

and one with a low purity. **b, c** Interface evolution between the two respective lithium samples and the SE during ongoing stripping. The different times are marked within the given voltage profile in (**a**).

lithium and LPSCI, thus increasing the resistance. However, the interface signal at $\tau \approx 10^{-3}$ s is mainly responsible for an increase in resistance before contact is lost. This is consistent with the previous measurements using LPSCI. However, a second interface signal can also be seen for this sample at higher relaxation times, which only increases in intensity immediately before contact loss.

For both LPSCI and LLZO as SEs, the impedance evolution during stripping differs depending on the purity of the lithium used. With low-purity lithium, two (interface) processes contribute to the resistance increase during stripping, while high-purity lithium shows only one dominant interface signal. The impedance signal associated with pore formation during stripping—caused by kinetic limitations of the lithium electrode—occurs at $\tau \approx 10^{-4}$ s $\cdot 10^{-3}$ s for LLZO as SE. This is in good agreement with results from literature^{37,52,54,55}. In the case of LPSCI used as SE, this relaxation time is around $\tau \approx 10^{-5}$ s, which also aligns with previous studies⁵⁶. We hypothesize that the additional interface signals at higher relaxation times are due to impurities present at the lithium|SE interface. These impurities may stabilize additional pores with geometries different from those caused by kinetic limitations, as studies on constriction have shown that pore geometry strongly influences impedance signatures^{57–60}. The impurities may also act as nucleation sites for pores⁶¹. Alternatively, the additional signal could be caused by the impurity particles themselves, which locally impede the lithium flux. These sodium-rich particles act as a locally blocking layer, resulting in an additional constriction contribution or even a completely blocking electrode layer^{12,58,62}.

Impurities in reservoir-free model systems

In the following, the observed purification by single-ion conducting solid electrolytes together with the influence of impurities during stripping of lithium is discussed. The schematics in Fig. 6 serve as a visualization of the drawn conclusions from the results above.

The given voltage profile shows stripping of two different lithium samples, one with a low and one with a high purity. The small offset on the time axis only serves for better visualization. As depicted in Fig. 6b and c, before start of electrodeposition ($t = t_0$), a homogeneous interfacial contact is given in both cases. However, in the case of

impure lithium (Fig. 6b), impurities are already present at the interface with the SE.

With start of electrodeposition ($t_1 > t_0$), a lithium layer with high purity is electrodeposited at the working electrode for both samples, as only lithium ions can migrate through the solid electrolyte. The aforementioned impurities in case Fig. 6b lead to an increase of the local current density, as they block the local ion flux, decreasing the active electrode area.

For longer times of lithium stripping ($t_2 > t_1$), the lithium counter electrode with high purity Fig. 6c can still replenish the interface towards the SE, keeping contact. However, for the lithium electrode with impurities (Fig. 6b), voids already form at the interface. This is due to the accumulation of the contained impurities, increasing the local current density in their surroundings at remaining lithium contact spots and simultaneously blocking the local lithium flux where impurities are present, leading to a contact loss and an increase in the voltage as can be seen in Fig. 6a.

Prolonged electrochemical lithium dissolution ($t_3 > t_2$) eventually also leads to the formation of pores for the lithium electrode with high purity as shown in Fig. 6c. Reason for this is that the current density j exceeds the rate of replenishment through vacancy diffusion at the Li|SE interface^{37,63}. Thus, these vacancies accumulate at the interface and lead to the formation of pores, which ultimately leads to contact loss and an increase in the voltage as depicted in Fig. 6a. However, as indicated at $t = t_3$, the formation of impurity precipitates (i.e., sodium precipitates) might also occur in the case of lithium electrodes with high purity (Fig. 6c), as the lithium stripping increases the relative sodium content inside the electrode. According to the phase diagram, sodium precipitates should therefore form as lithium and sodium are not miscible. For the case of lower purity lithium (Fig. 6c), the interface does not change anymore, as pores were already formed at an earlier stage. The impurity enrichment likely also influences subsequent cycles. Studies of Na diffusion in Li by Mundy et al. suggest that Na may diffuse even faster than Li^{44,64}. This would mean that any stripping of Li will cause a homogeneous increase of the Na concentration rather than a local increase at the stripped interface. Once stripping leads to Na supersaturation, precipitates will form and can decorate the stripped

interface. Thus, depending on the Na concentration in Li metal, Na precipitates may always occur and influence the electrode kinetics—but after different times.

These findings are in good agreement with theoretical works by Agier et al. on the void formation in metal electrodes with impurity particles in their interior, showing that impurity particles block the lithium flux at Li|SE interfaces⁶¹. The authors hypothesize that this leads to an inhomogeneous deformation of the lithium electrode, an increased dislocation density around the impurities and therefore to a preferential void formation in their surroundings. However, based on the calculations, these voids should not grow larger than 10 μm , taking micrometer sized impurity particles into account. Agier et al. further hypothesize that the observed electrode failure is caused by the coalescence of several smaller voids due to the dispersion of impurity particles within the electrode. During ongoing stripping of lithium, these accumulate at the Li|SE interface, stabilizing the formed voids.

This hypothesis aligns with our experimental findings in this study, in fact showing an accumulation of Na-rich particles at the LPSCl and the LLZO interface. We like to note that Agier et al. did chemically not specify the impurity they considered. In the case of Li_{LP} this effect is more pronounced due to a higher content of impurities within the electrode, leading to a faster accumulation at the SE interface and a faster coalescence or formation of voids at the interface. For Li_{HP} , the impurity content is lower and therefore an accumulation of impurities at the interface leading to void formation is slowed down, if impurity driven at all. In the case of very pure lithium, contact loss may primarily result from the injection rate of vacancies at the Li|SE interface outpacing the replenishment rate of lithium to this interface. In a recent and apparently contradictory study mentioned above, Mann et al. intentionally prepared Li metal with a sodium fraction of 3 at%, which corresponds to the composition of the Li-rich monotectic. This fraction is significantly higher than in our case of Li_{LP} , and the authors observe a higher CCD than with their unmodified Li. After a complete stripping step of 21.6 mAh cm^{-2} a Na network at the interface is found, that must have formed through the accumulation of Na precipitates. The authors assume that this network supports high current densities. We believe that the apparent differences compared with this work might stem from the manufacturing process used by Mann et al., likely also influencing the resulting lithium microstructure. As suggested by Yoon et al., differences in mechanical properties could also be the cause of the increased stripping capacities of lithium-sodium electrodes⁵⁰. It remains to be clarified how the resulting sodium interlayer structure supports the lithium transfer. The mechanism might be similar as in the case of the Na-K interlayer introduced by Park et al.⁵¹. In our case, the typically low concentration of sodium in lithium clearly has a negative effect.

The impurity content likely influences the microstructure of different lithium samples⁶⁵. Previous studies have shown that the microstructure of electrodeposited lithium differs substantially from that of lithium foils, with electrodeposited lithium forming large columnar grains^{29,36}. This difference is likely accelerated by the high purity of electrodeposited lithium found in this study. Both the microstructure and the high purity of lithium are contributors to the observed differences in electrochemical behavior and may also influence the mechanical properties of lithium. Although we did not observe significant differences in interfacial resistances—potentially due to variations in Li|SE interfacial contacts resulting from different mechanical properties of the different lithium types—these differences might become more apparent under lower preparation pressures, approaching the yield strength of lithium of $\sim 0.7 \text{ MPa}$. Notably, the mechanical differences are expected to be even more pronounced in electrodeposited lithium due to its even higher purity and columnar microstructure. Further research focusing on the mechanical properties of lithium, particularly in relation to its microstructure and purity, is necessary to gain deeper insights.

In this study, we examined the ability of the single-ion conducting solid electrolytes LPSCl and LLZO to filter impurities when using reservoir-free cells. Specifically, we analyzed the sodium content—being the most prominent impurity in lithium—in electrodeposited lithium layers and compared it to that in lithium foils. This comparison was conducted using complementary XPS and ToF-SIMS analyses. The results revealed a significant reduction in sodium content in the electrodeposited lithium layers, highlighting that solid electrolytes effectively filter impurities during lithium electrodeposition. Conversely, when using impure lithium foils as counter electrode or as lithium source for electrodeposition, the stripping process leads to an enrichment of impurities, i.e., sodium, in this electrode and at the SE interface, strongly reducing the stripping capacity of this electrode.

By using two commercially available lithium foils with different impurity contents as well as an electrodeposited lithium layer, we found that impurities at the interface also affect the accessible lithium capacity before loss of contact. Herein, lithium foils with a higher purity showed a threefold higher stripping capacity. Accordingly, electrodeposited lithium layers will likely differ compared to commercially available lithium foils. This indicates that knowledge obtained from studying commercial lithium films may not be directly transferable to electrochemically deposited lithium films. This purity dependency needs to be considered in future studies, whether in model systems using lithium electrodes or in a possible application of lithium electrodes in lithium sulfur or lithium oxygen cell systems. Furthermore, the purity of the lithium used should always be specified when reporting cell data. We also like to note that true reservoir-free SSB cells will most probably be unaffected by any impurity accumulation at the solid electrolyte interface, provided that the positive electrode active material is sufficiently pure with respect to its lithium metal content. In fact, RFC may only operate well because of its inherent impurity filter effect. With additional deposition of dedicated metal interlayers, the electrodeposited lithium metal may be doped and modified such that improved electrode properties result. A better understanding of this will require in-depth studies of the impurity inventory of lithium metal before and after stripping and plating.

Methods

LLZO synthesis

LLZO was prepared using the reactants zirconium oxide ($\text{ZrO}_2 < 100 \text{ nm}$, Sigma-Aldrich), aluminum oxide (Al_2O_3 , 99.99%, ChemPur), lanthanum hydroxide ($\text{La}(\text{OH})_3$, 99.9%, Sigma Aldrich) and lithium carbonate (Li_2CO_3 , 99.998%, Puratronic). These were weighed with an excess of 3% Li_2CO_3 and homogenized using a ball mill (type: Fritsch Pulverisette 7 Premium Line, 10 Min @ 350 RPM, 20 Min break - 24 cycles) in a ball mill cup made of ZrO_2 inside and ZrO_2 balls as milling media. The intermediate product was pressed under air, using a steel die with a diameter of 25 mm, and calcined under an oxygen atmosphere at 1000°C . The pellets were transferred to a glove box (argon atmosphere, with traces of H_2O , $\text{O}_2 < 0.1 \text{ ppm}$ and $\text{N}_2 < 10 \text{ ppm}$ and ground there. The intermediate product was examined for impurities using an X-ray diffractometer. A further grinding step (10 Min @ 350 RPM, 20 Min break - 40 cycles) was carried out in the ball mill. The ground powder was pre-pressed manually using a steel die with a diameter of 10 mm in the glove box and then isostatically pressed at 400 MPa inside sonodomes. The pellets were covered with mother powder and transferred to an oven where they were sintered at a temperature of 1230°C for 1 h under an oxygen atmosphere³⁷. The product was transferred back into the glovebox and the excess mother powder was removed and the pellets were polished for further processing, resulting in LLZO pellets with a diameter of $\sim 8 \text{ mm}$ and a thickness of $\sim 2 \text{ mm}$.

Cell preparation

Cell preparation was conducted inside a glovebox (MBraun, Germany) with traces of H_2O , $\text{O}_2 < 0.1 \text{ ppm}$ and $\text{N}_2 < 10 \text{ ppm}$. For cell assembly, an

in-house fabricated casing was used. Steel stamps, which also serve as electronic contact, were used to press the cell components. A steel foil (thickness = 20 μm , AISI 304, Goodfellow, Germany), being the working electrode in the case of RFCs, was placed on top of one of the steel stamps. The $\text{Li}_6\text{PS}_4\text{Cl}$ powder (NEI Corporation, USA, particle size < 5 μm) was loaded onto the steel foil and compressed afterwards, using a second steel stamp. The cell was sealed using nitrile butyl rubber rings and compressed outside the glovebox, using a uniaxial press at 3 t for 1 min from each side. As a counter electrode, a freshly prepared lithium foil was used³⁷. To remove surface passivation layers, a piece of lithium was cut from a lithium rod and hand pressed between two pouch foils, resulting in a lithium foil with a thickness of ~100 μm . As far as Li_{LP} (LP = “low purity”) is concerned, a lithium rod from Goodfellow (Lithium rod, purity 99%, Goodfellow GmbH, Germany) was used. In the case of Li_{HP} (HP = “high purity”), a lithium rod from MaTeck (Lithium rod, purity 99.8%, Material, Technologie & Kristalle GmbH, Germany) was used. Analysis data from the manufacturers on the impurity content of the lithium rods can be seen in Table S1. One lithium electrode ($d = 9 \text{ mm}$) was placed on one surface of the compressed LPSCl pellet for electrodeposition experiments with RFCs. For symmetrical $\text{Li}|\text{LPSCl}|\text{Li}$ cells, a lithium electrode was placed on each side of the pellet. In all cases, an additional steel foil was placed between the steel stamp and the lithium electrode for easier cell disassembly. Finally, the cell was sealed, and an external pressure of 15 MPa was applied using an aluminum pressure frame. For electrodeposition within RFCs, electrochemical characterization was conducted within this pressure frame. For symmetrical cells, the pressure was released after an equilibration time of 12 h and lithium dissolution experiments were conducted without external pressure. Using LLZO as SE, lithium electrodes were prepared in the same manner as described above. After placing a lithium electrode ($d = 6 \text{ mm}$) on each surface of the LLZO pellet, it was transferred into a pouch bag and vacuum sealed. The pouch was then isostatically pressed at a pressure of 450 MPa for 45 min. Once pressed, the symmetrical $\text{Li}|\text{LLZO}|\text{Li}$ cell was removed from the pouch bag. The cell was then connected using nickel tabs, vacuum sealed again inside a new pouch and subsequently electrochemically characterized.

Electrochemical characterization

Unless otherwise stated, all electrochemical experiments were carried out in a climate chamber at a temperature of $25 \pm 0.1^\circ\text{C}$. Initially, the cells were equilibrated for 6 h. Within this resting time, potentiostatic impedance spectra were recorded at an interval of 30 min using a potentiostat (VMP 300, Biologic, France) at open-circuit voltage conditions. The frequency range was set between 7 MHz and 100 mHz with 7 points per decade in logarithmic spacing at an amplitude of 10 mV. After equilibration, lithium was electrodeposited at the steel|LPSCl interface using chronopotentiometry (CP) at a current density of $50 \mu\text{A cm}^{-2}$ in the case of RFCs for a capacity of roughly 12 mAh cm^{-2} . In the case of symmetrical $\text{Li}|\text{LPSCl}|\text{Li}$ or $\text{Li}|\text{LLZO}|\text{Li}$ cells, lithium was electrochemically deposited/dissolved, using galvanostatic electrochemical impedance spectroscopy (GEIS) at a current density of $100 \mu\text{A cm}^{-2}$. The frequency range was set between 7 MHz and 1 Hz with 6 points per decade in logarithmic spacing at an amplitude of 10% of the direct current. To ensure reproducibility of the observed trends, a set of three cells were examined for each symmetrical cell system.

Sample preparation

All preparation steps were carried out in the gloveboxes mentioned above. To examine Li_{LP} and Li_{HP} using XPS and ToF-SIMS, pieces were cut from the corresponding lithium rod and the passivation removed using the same procedure as described above. These pieces were then used to prepare cross-sections. To investigate Li_{D} , the cell used for lithium electrodeposition was disassembled. The working electrode was then removed from the LPSCl pellet using tweezers and

a cross-section of the entire working electrode was prepared. Please refer to the following paragraph for details on cross-section production. To investigate the LPSCl or LLZO surfaces after Li_{LP} contact, cells were disassembled after a loss of contact between the Li_{LP} electrode and the SE was caused by the stripping experiment. The electrode was removed using tweezers, exposing both the solid electrolyte surface and electrode surface. All transfer steps from glove boxes to any device were carried out using an inert transfer system (Leica VCT500, Leica Microsystems, Germany).

Cryogenic ion-milling

Cross-sections of electrodeposited lithium at the working electrode or the Li_{LP} and Li_{HP} samples were prepared using an ion beam milling system (Leica EM TIC 3X, Leica Microsystems, Germany). Using liquid nitrogen, the temperature during milling was decreased to -120°C . The device was operated at an accelerating voltage of 6 kV and an Ar^+ current of 2.2 mA. The prepared cross-sections were transferred to the SIMS or XPS systems using an inert transfer system (Leica VCT500, Leica Microsystems, Germany).

Focused-ion-beam cutting and scanning electron microscopy

Cutting with focused ion beams and imaging were carried out with an XEIA3 GMU/plasma machine from TESCAN, which works with a Xe plasma.

Scanning electron microscopy and energy-dispersive spectroscopy

Scanning electron microscopy was conducted within a Gemini SEM 560 from Carl Zeiss Microscopy GmbH. In case of energy-dispersive spectroscopy measurements an X-Max Extreme Silicon drift detector from Oxford Instruments was used.

Secondary ion mass spectrometry

Elemental analysis was performed using an M6 Hybrid secondary ion mass spectrometer (IONTOF GmbH, Münster, Germany). After disassembly of the cell, depth profiling of the LPSCl pellet surface was performed in positive polarity using 30 keV Bi^+ primary ions at 80 μs cycle time with non-interlaced DSC-S 2 keV Ar^+ sputtering between analysis steps. The analysis area was set to $100 \times 100 \mu\text{m}^2$ with 128×128 pixels while the sputter area was set to $300 \times 300 \mu\text{m}^2$ (total dose density $8.45 \times 10^{17} \text{ ions cm}^{-2}$).

All lithium metal samples were first sputter cleaned in a $300 \times 300 \mu\text{m}^2$ area with 1 keV Ar^+ ions (total dose density $1 \times 10^{17} \text{ ions cm}^{-2}$) to remove the native oxidation layer formed on the lithium metal during transfer to the SIMS machine. Please note that the $^7\text{Li}^+$ intensity was corrected using the $^6\text{Li}^+$ intensity. Three surface spectra per sample were recorded on the cross-sections of the electrodeposited lithium (prepared by ion milling) in areas of $50 \times 50 \mu\text{m}^2$ with 128×128 pixels. For the lithium metal reference measurements, a surface spectrum of $200 \times 200 \mu\text{m}^2$ area and 128×128 pixels was recorded at three different, previously cleaned areas. In all cases, i.e., the electrodeposited Li and the reference Li samples, the Na^+/Li^+ ratio was calculated by dividing the Na^+ counts by the sum $^6\text{Li}^+ + ^7\text{Li}^+$ of counts. All data evaluation was conducted with SurfaceLab 7.4 software (IONTOF GmbH, Münster, Germany).

X-ray photoelectron spectroscopy

Complementary to the SIMS investigations, the electrodeposited lithium as well as the lithium counter electrode was analyzed using a XPS machine of the type Phi Versaprobe IV. Monochromatic Al K_α radiation ($E_B = 1486.6 \text{ eV}$) was used for excitation. Bulk samples were analyzed with an excitation power of 50 W resulting in an X-ray beam diameter of 200 μm , while electrodeposited samples were excited with a power of 5 W, yielding a 20 μm beam diameter. Lower excitation power was balanced by increasing the measurement time per point by

the reciprocal factor. The samples were mounted electronically insulated from the stage. A combination of low energetic Ar⁺ ions and electrons was used for charge neutralization. Post referencing to the O 1s signal ($E_B = 529.0$ eV) ensured energy calibration. Survey spectra were recorded with a pass energy of 224 eV, while 55 eV were used for detail spectra. Alternating gas cluster ion bombardment was used to clean the surface in between spectra acquisition. The initial spectrum was recorded without sputtering beforehand. After acquisition, the surface was sputtered for 120 s and the second spectrum was acquired. This process was repeated multiple times. The acceleration voltage of the Ar clusters was either 10 kV or 20 kV. Data processing has been conducted with CasaXPS (Version 2.3.26rev1.1 P). The relative fractions X_i of Li and Na were obtained respecting the chemical sensitivity (employing tabulated relative sensitivity factors RSF_i of the XPS apparatus' manufacturer for orbital i), the transmission function of the apparatus $T(E)$ and the universal inelastic mean free path curve. A background correction has been applied using a Shirley-background.

DRT analysis

The collected impedance data were analyzed in the time domain using the commercial software RelaxIS 3 (version 3.0.22.29, rhd instruments GmbH & Co. KG). Data in the high- and low-frequency ranges that showed residuals greater than 3% in the Kramers-Kronig test were excluded from the analysis. Only the real part of the impedance was considered, as the residuals were limited to just a few 0.1%. No additional data points were generated through interpolation, and the second derivative of the distribution function $\gamma(\tau)$ with a lambda parameter of $\lambda = 10^{-3}$ was applied in the Tikhonov regularization problem⁶⁶.

Data availability

Source Data file has been deposited in "JLUPub" under accession code <https://doi.org/10.22029/jlupub-19895.2>⁶⁷.

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3.2 Publication 2: “Microstructure of lithium metal electrodeposited at the steel|Li₆PS₅Cl interface in “anode-free” solid-state batteries”

In the second publication of this dissertation, the microstructural evolution of lithium metal, *i.e.*, grain size and grain density, during electrodeposition was systematically investigated. For this, the microstructure of lithium layers, electrodeposited in RFCs at steel|LPSCl interfaces with different electrodeposition parameters was analyzed by EBSD. A workflow for microstructural characterization on large, millimeter-sized cross-sections using broad ion beam milling was established. This enabled, for the first time, a systematic analysis of electrodeposited lithium microstructure as a function of deposition parameters.

The resulting grain size is largely independent of the selected current densities for electrodeposition at the time of analysis ($j = 50 \mu\text{A cm}^{-2} - 500 \mu\text{A cm}^{-2}$ for $Q = 1 \text{ mAh cm}^{-2}$). In all cases, a similar columnar grain structure with grain sizes around $20 \mu\text{m}$ forms with grain boundaries being perpendicular to the growth direction. Increasing the lithium layer thickness by increasing the electrodeposited areal charge ($Q = 1 \text{ mAh cm}^{-2} - 10 \text{ mAh cm}^{-2}$ at $j = 100 \mu\text{A cm}^{-2}$) leads to the formation of grains with greater height. Moreover, the average grain width increases significantly while grain density decreases correspondingly. This observed grain coarsening results from reduction of grain boundary curvature, a thermodynamically favorable process that was qualitatively reproduced using a Monte Carlo Potts model.

Overall, the second publication extends the previously established workflow for microstructure analysis of electrodeposited lithium and is the first systematic parameter study of the lithium microstructure as a function of the electrodeposition parameters. The increased number of analyzed grains on millimeter-sized cross-sections allows statistically relevant conclusions, shows that the lithium microstructure depends on electrodeposition parameters and thus deepens the knowledge about electrodeposited LMEs.

J. Becker designed and conducted all experiments supervised by Dr. F. H. Richter and Prof. J. Janek. Dr. T. Fuchs and Dr. T. Ortmann supported EBSD experiments and contributed to scientific discussions. S. Kremer set up the model for microstructure simulation and also participated in scientific discussions. The original draft was written by J. Becker and edited by all co-authors.

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RESEARCH ARTICLE

Microstructure of Lithium Metal Electrodeposited at the Steel|Li₆PS₅Cl Interface in “Anode-Free” Solid-State Batteries

Juri Becker, Till Fuchs,* Till Ortmann, Sascha Kremer, Felix H. Richter, and Jürgen Janek*

Recent research shows that integrating lithium metal anodes can enhance battery energy density, but the high reactivity of lithium requires handling under inert conditions to avoid degradation. To overcome this, reservoir-free cells (RFCs) are explored, where lithium metal is electrodeposited at the current collector (CC) and solid electrolyte (SE) interface during initial charging. The electrochemical properties of electrodeposited lithium are influenced by its morphology and microstructure, which impact lithium discharge capacity and pore formation. However, little is known about how to control the microstructure of electrodeposited lithium. This work experimentally characterizes the lithium microstructure at the steel|Li₆PS₅Cl interface using cryogenic ion beam milling, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD), focusing on the effects of electrodeposition current density and lithium layer thickness. The results show that layer thickness, not current density, primarily governs the lithium microstructure. This “specimen thickness effect” is qualitatively described using a Monte Carlo Potts model and indicates that electrodeposited lithium metal quickly equilibrates at room temperature.

1. Introduction

Solid-state batteries (SSBs) are of primary interest as alternatives to conventional lithium-ion batteries as solid electrolytes (SEs) may enable the use of lithium metal as negative electrode material.^[1,2] Having a low redox potential of -3.04 V and a high theoretical specific capacity of 3861 mAh g⁻¹, the implementation of lithium metal would significantly increase the energy storage capability of next-generation rechargeable batteries, while SEs are expected to meet future safety standards.^[3–5]

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As lithium is highly reactive, degradation layers form on the surface of pristine foils when in contact with atmospheric constituents or SEs.^[6–9] To minimize the thickness of this degradation layer, storage under the exclusion of nitrogen, oxygen, and water is necessary. However, even in argon-filled gloveboxes with low partial pressures of reactive gases, degradation layers still form.^[6] These layers increase the resistance of lithium|SE interfaces, and significantly impact the electrochemical performance. To reduce this interfacial resistance, either high pressures of ≈ 400 MPa must be applied during preparation, or mechanical cleaning steps must be used to remove the degradation layers from the lithium surface beforehand. Both methods, as well as storage under inert gas, are costly and impede manufacturing.^[8,10]

To circumvent the challenging reactivity of lithium metal foils, avoid costly storage under an inert atmosphere, and further increase the theoretical energy density, reservoir-free cells (RFCs, often referred to as “anode-free”) are increasingly investigated and developed.^[7,11–13] Directly after cell assembly, RFCs consist in their discharged state only of lithiated positive electrode material, SE, and current collectors (CC). Their distinctive feature is that the CC at the negative electrode is in direct contact with the SE separator layer. No reservoir of lithium at the negative electrode is added, as the lithium available for cycling is contained in the lithiated active material in the positive electrode.^[14,15] Lithium metal is electrodeposited on the CC during the first charging step, with 5 μm of electrodeposited lithium corresponding to roughly 1 mAh cm⁻² of capacity. As a result, the reservoir-free electrode further increases the energy density compared to SSBs with an additional lithium layer.^[11] Sufficiently stable cells require a very high Coulomb efficiency,^[16] and ≈ 20 μm of lithium need to be reversibly cycled to meet an areal capacity of 4 mAh cm⁻².

The microstructure of electrodeposited lithium is of great interest because it influences the Coulomb efficiency, as shown by Singh et al. in Li|LLZO|Li cells.^[17,18] Under pressure, large-grained lithium foils exhibit higher stripping capacities and an increased electrode roughness after contact loss, while smaller-grained lithium foils have lower stripping capacities and a smoother electrode surface after contact loss. Moreover, it has been established that the lithium microstructure significantly impacts both its mechanical and electrochemical properties during

cycling as an anode material, when using foils.^[19–21] However, the microstructure of lithium foils is not tangible, as it is largely dependent on industrial manufacturing processes.

No lithium metal is required for the construction of RFCs, which simplifies the supply chain and storage beforehand. Additionally, electrodeposition allows for homogeneous lithium|SE interface contacts even at low stack pressures, in the range of 10 MPa or less, and enables precise determination of the battery's start of service life.^[11,22] We like to note that conventional lithium-ion batteries (LIBs) operate similarly with respect to the lithium inventory, as also here all lithium is initially stored in the positive electrode and transferred to the negative (graphite) electrode during the first charge step. Thus, balancing the lithium inventory in "reservoir-free" SSBs and minimizing the loss of lithium in any SEI is as relevant as in LIBs.^[23–25]

The primary challenge with RFCs arises from the morphology of the electrodeposited lithium layer, often resulting in non-uniform lithium structures in the form of islands, dendrites, or whiskers.^[26–30] Recent research indicates that external factors such as temperature, stack pressure, and current density can significantly impact the morphology of the electrodeposited lithium layer.^[22,31–34] For example, a higher electrodeposition current density leads to an increased nucleation density, leading to higher coverage of the current collector.^[22,31,32] The resulting microstructure of lithium layers electrodeposited in RFCs is a largely unexplored parameter although it has a large influence on the electrochemical and chemo-mechanical properties of the alkali metal.^[18,19,35]

As shown in previous reports, the microstructure of metals, including lithium, can be analyzed using electron backscatter diffraction (EBSD) without the influence of the analysis method itself.^[19,36–39] Going beyond the characterization of conventional metal foils, Fuchs and Ortmann et al. reported a well-reproducible workflow and presented a qualitative microstructure analysis of electrodeposited lithium by EBSD.^[39] They showed that the microstructure of electrodeposited lithium does not change over time at room temperature,^[39] allowing to analysis of electrodeposited lithium as a function of different electrodeposition parameters.

To the best of our knowledge, the influence of electrodeposition parameters on the lithium microstructure has not been studied yet, due to the buried nature of interfaces and the high reactivity of the metal during sample preparation. The electrodeposition of other metals such as Cu, Ag, or alloys like $\text{Ni}_{0.2}\text{Co}_{0.8}$ at liquid|solid interfaces, shows a correlation between the used electrodeposition parameters and the resulting microstructure, which in turn suggests that also the microstructure of electrodeposited lithium depends on the electrodeposition parameters.^[37,40,41]

Electrodeposition of lithium with controlled microstructure could be an effective method of modifying the cycling properties of the lithium electrode. By varying electrodeposition parameters such as current density, temperature, or capacity, microstructural parameters such as grain size or grain boundary distribution might be adjusted, potentially adapting the microstructure to the requirements for further cell operation.

This work aims to better understand the microstructure of lithium layers electrodeposited at the interface between steel and $\text{Li}_6\text{PS}_5\text{Cl}$ as a function of the current density used for electrode-

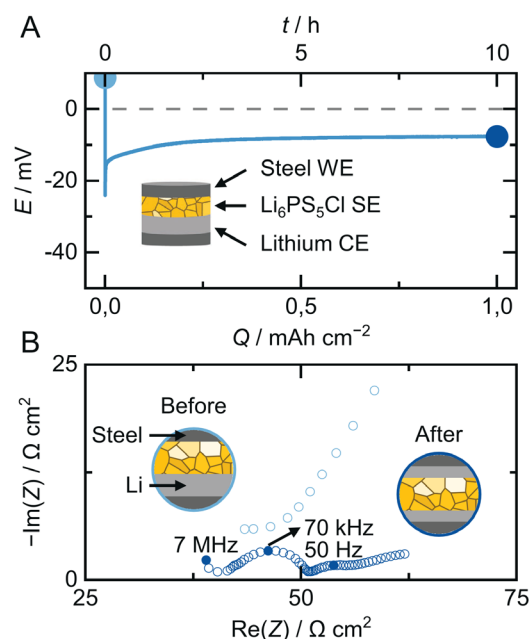


Figure 1. Illustration of the model system used and a representative lithium electrodeposition. A) Voltage profile of lithium electrodeposition at the steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interface using a current density of $100 \mu\text{A cm}^{-2}$ and schematic of the used cell setup steel| $\text{Li}_6\text{PS}_5\text{Cl}$ |Li|steel. B) Impedance data before and after the electrodeposition of lithium at the steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interface, as depicted in the schemes. Characteristic frequencies are highlighted with filled circles. The time of the measurement is marked in the voltage profile with enlarged dots.

position and to analyze the microstructural evolution during prolonged lithium electrodeposition, i.e., for different lithium layer thicknesses. The preparation of wide cross-sections allows for the analysis of many grains and obtain reliable statistics regarding grain size and grain orientation. In the second step, the experimental results are described with a Monte Carlo Potts model. The results reveal that the microstructure of electrodeposited lithium layers is mostly independent of the current density, i.e., electrodeposition kinetics. There is rather a specimen thickness effect, i.e., the layer thickness determines the lithium microstructure, offering to effectively adjust the microstructure of electrodeposited lithium to match requirements for further cell operation (i.e., lithium dissolution) by changing electrodeposition capacities.

2. Results and Discussion

2.1. Electrodeposition of Lithium at the Steel| $\text{Li}_6\text{PS}_5\text{Cl}$ Interface

To investigate the influence of electrodeposition parameters on the lithium microstructure, we built steel| $\text{Li}_6\text{PS}_5\text{Cl}$ |Li|steel cells to be used as a model system. A characteristic voltage profile for lithium electrodeposition at the steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interface with a current density of $100 \mu\text{A cm}^{-2}$ is shown in Figure 1A. First, the voltage profile passes through a minimum, which represents

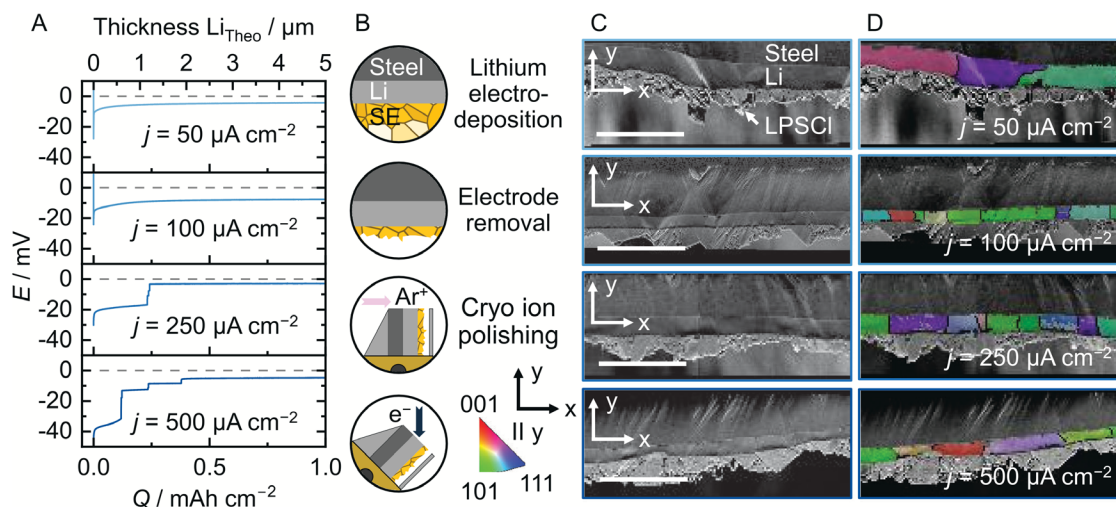


Figure 2. Current density-dependent lithium electrodeposition and microstructural analysis. A) Voltage profiles during lithium electrodeposition with current densities between $50 \mu\text{A cm}^{-2}$ and $500 \mu\text{A cm}^{-2}$ as well as the calculated lithium layer thickness. B) Schematic of the used workflow to prepare cross-sections. C) SEM images of representative steel|Li₆PS₅Cl cross-sections after electrodeposition of lithium with different current densities, see also Figures S1–S4 (Supporting Information). D) Overlay of the SEM images and IPF maps, which are given parallel to the y-direction as illustrated in (B). Grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between 2° and 10° are depicted in grey. The scale bar within the SEM images represents a length of $50 \mu\text{m}$ and also applies to the respective image overlaid with its IPF map.

the nucleation overvoltage relative to the following plateau, being in good agreement with previous studies on the electrodeposition of lithium at CC|SE interfaces.^[11,31] Here, lithium nucleation occurs.^[11] The voltage then stabilizes at ≈ 10 mV, which agrees with the IR drop of the solid electrolyte. At this point, the previously formed nuclei grow larger, forming the observed grains.^[11] Deviations stem from the resistances occurring at the two Li|Li₆PS₅Cl interfaces.

Additionally, exemplary impedance plots in Nyquist representation before and after the electrodeposition are shown in Figure 1B, recorded at the times indicated with two enlarged points within the voltage curve. The steel electrode is initially an ion-blocking electrode, which is why a capacitive response before electrodeposition is visible at lower frequencies (< 3 MHz). After electrodeposition, the cell has two lithium electrodes (i.e., two reversible electrodes for lithium ions), as indicated in the schematics in (B). As a result, several semicircles are now observed within the impedance data, which can be attributed to the charge transfer at the two Li|Li₆PS₅Cl interfaces, proving successful lithium electrodeposition.^[11]

The resistance contribution of the solid electrolyte has not changed significantly during nucleation and growth, indicating that no severe lithium electrodeposition or dendrite formation has taken place inside the solid electrolyte. However, due to a similar resistance contribution of thin lithium filaments and Li₆PS₅Cl, partial dendrite formation or lithium deposition inside of the Li₆PS₅Cl pellet cannot be completely ruled out. Nevertheless, the used model system is suited for investigating the electrodeposition of lithium with different current densities, which is presented in the following section.

2.2. Influence of Current Density on the Lithium Microstructure

Voltage profiles for lithium electrodeposition with $50 \mu\text{A cm}^{-2}$, $100 \mu\text{A cm}^{-2}$, $250 \mu\text{A cm}^{-2}$, and $500 \mu\text{A cm}^{-2}$, as well as exemplary SEM pictures and inverse pole figure (IPF) maps of the prepared cross-sections of the different layers are shown in Figure 2. Electrodeposition was limited to a capacity of 1 mAh cm^{-2} , theoretically resulting in a lithium layer thickness d_{layer} of $5 \mu\text{m}$. Please note that the charge per area is referred to as capacity in accordance with literature.

As in Figure 1A, the voltage profiles show a characteristic minimum, which represents the nucleation overvoltage when referenced to the following plateau. Electrodepositing lithium with current densities of $50 \mu\text{A cm}^{-2}$ and $100 \mu\text{A cm}^{-2}$ results in a continuous voltage profile during the electrodeposition process after nucleation. However, for higher current densities of $250 \mu\text{A cm}^{-2}$ and $500 \mu\text{A cm}^{-2}$, discontinuities occur in the voltage profile. These are caused by dendrite formation, as lithium filaments from the metal anode penetrate the solid electrolyte and (soft)-short-circuit the cell. This phenomenon is known for lithium metal anodes—especially at higher current densities—and resembles one of the main challenges for the initial charging step in RFCs if high areal capacities are applied.^[42,43]

Nevertheless, a dense and homogeneous lithium layer is observed for all current densities in the SEM images. The prepared cross-sections show a layered electrode arrangement, with the steel foil at the top, which was used as the WE as shown in Figure 1A. The electrodeposited lithium layer can be seen below. At the bottom, residual SE remains adhered to the electrode during cell disassembly. It is noteworthy that in all cases a homogeneous lithium layer had grown over almost the entire

width of the prepared cross-section (over several millimeters). For the full cross-section, we refer to the Supporting Information (Figures S1–S4, Supporting Information). Furthermore, homogeneous $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}|\text{steel}$ interfaces are visible along the entire cross-section, revealing continuous physical contact between the materials.

To exclude the influence of the layer thickness as much as possible, layers of approximately the same thickness d_{layer} were electrodeposited. The thicknesses of the electrodeposited lithium should theoretically be roughly $5\text{ }\mu\text{m}$ for $Q = 1\text{ mAh cm}^{-2}$. When compared with the SEM images, lithium layers thicker than $5\text{ }\mu\text{m}$ are found for all used current densities, as lithium is only electrodeposited on part of the electrode area, as can be seen in optical images of the SE pellet surface and working electrode surface of a similar sample in Figure S5 (Supporting Information). Interestingly, even for the cells in which a short circuit occurred during electrodeposition (i.e. $j = 250\text{ }\mu\text{A cm}^{-2}$ and $500\text{ }\mu\text{A cm}^{-2}$), a layer thickness larger than $5\text{ }\mu\text{m}$ is visible. In addition to the deviation between the total and used electrode area, another reason could be that even after the first discontinuity in the voltage profile, further lithium electrodeposition occurs, as only a “soft short” has been created. In this case, the resistance of the existing dendrite is approximately as high as the resistance of the solid electrolyte, so that current continues to be transported in the form of lithium ions.^[3] This is proven by further discontinuities, which are caused by further redox reactions at the electrodes (i.e., ongoing dendrite formation).

Analysis of the electrodeposited lithium layer via EBSD enables direct visualization of the different grains formed during electrodeposition. Different grains are colored according to an inverse pole figure color scheme in the y -direction (growth direction), i.e., each pixel is colored according to the crystal direction that runs parallel to the y -direction of the map. Noticeably, most grain boundaries are oriented perpendicular to the steel/ $\text{Li}_6\text{PS}_5\text{Cl}$ interface. This is particularly interesting as it represents a major difference to conventionally prepared $\text{Li}_{\text{foil}}|\text{Li}_6\text{PS}_5\text{Cl}$ interfaces. The grains of conventional lithium foils are usually oriented randomly,^[39] resulting in the presence of both vertical and parallel grain boundaries within the lithium metal attached to the SE. This has probably a significant influence on the dissolution of lithium after electrodeposition and the mechanics of the electrode.

For comparison of the different current densities and to include statistics, the dimensions for all analyzed grains are summarized within a boxplot in Figure 3. At this point, it should be noted that when analyzing the grains, grains located at the edge of the cross-section were not considered if they were not visible over their entire width. Using millimeter-sized cross-sections, 70 grains were analyzed for a current density of $50\text{ }\mu\text{A cm}^{-2}$, 59 for $100\text{ }\mu\text{A cm}^{-2}$, 109 for $250\text{ }\mu\text{A cm}^{-2}$ and 51 for $500\text{ }\mu\text{A cm}^{-2}$. The boxplot in blue summarizes the measured grain widths w_{Grain} for the different current densities. It should be noted that the grain width w_{Grain} refers to the lateral dimension of the grains along the cross-section. Due to the slight deviation in layer thicknesses, as can be seen in Figure 3 in black above, we herein excluded the vertical dimension of the analyzed grains. Furthermore, we assumed for simplicity that the grains' cross-sections are rectangles, which only leads to negligibly small deviations in width due to the mostly vertical grain boundaries. Taking the cross-sectional

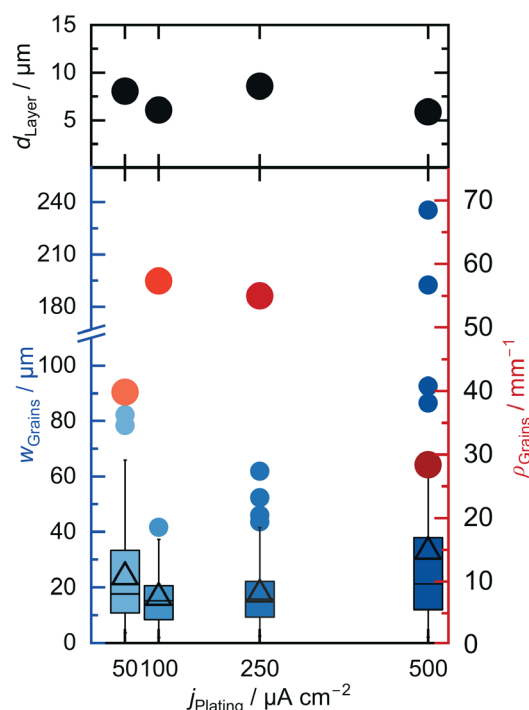


Figure 3. Summary of the analyzed lithium layers electrodeposited with different current densities. The average layer thickness is shown in black circles in the top part of the graph. The width of each lithium grain (w_{Grains}) as well as the calculated grain density (ρ_{Grains}) are depicted in the section beneath. The distribution of grain widths is shown in the boxplot in blue and summarizes 70 ($50\text{ }\mu\text{A cm}^{-2}$), 59 ($100\text{ }\mu\text{A cm}^{-2}$), 109 ($250\text{ }\mu\text{A cm}^{-2}$), and 51 ($500\text{ }\mu\text{A cm}^{-2}$) measured grains, respectively. The average width is represented with a triangle inside each box. Outliers (interquartile range factor = 1.5) are marked with blue points. The calculated grain density is depicted in red.

length into account, the grain density, i.e., the number of grains per millimeter of cross-section, was also calculated. This is shown in red.

From previous works on RFCs, it is known that an increased current density increases the nucleation density.^[22,31] If the microstructure of a lithium layer were determined by nucleation solely, one would expect that a higher current density would also lead to a smaller grain size and a higher grain density ρ_{Grains} . At this point, we like to note that the published nucleation experiments were carried out with $\text{Cu}|\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Cu}|\text{LiPON}$ model systems. As a first approximation, however, we assume that the steel/ $\text{Li}_6\text{PS}_5\text{Cl}$ system used here follows a similar current density dependence – even though copper and steel interact differently with lithium metal, as copper, unlike steel, can dissolve lithium.^[44] Due to the method of analysis (i.e., in a cross-sectional way), the data are referenced to a width instead of an area here.

When comparing the expected nucleation density and the resulting number of grains for the different current densities, however, a significant difference between the two quantities

shows up. Compared to an expected number of nuclei^[22] of around 320 mm^{-1} for $50 \mu\text{A cm}^{-2}$ and 700 nuclei per mm for $500 \mu\text{A cm}^{-2}$, we measured a considerably smaller grain density ρ_{Grains} of 40 grains per mm for $50 \mu\text{A cm}^{-2}$ and 28 grains per mm for $500 \mu\text{A cm}^{-2}$. Notably, these values cannot be directly compared, as not every nucleus results in a separate grain; neighboring nuclei may merge due to similar orientations to form a single grain upon contact. However, the difference of an order of magnitude strongly hints toward an influence of the subsequent grain growth after nucleation.

When comparing different current densities, no significant trend is found. The average grain width, marked with triangles, remains $\approx 20 \mu\text{m}$ for all current densities, with deviations falling within the range of measurement accuracy or within statistical variation. The grain density ρ_{Grains} , displayed in red, behaves analogously and shows no clear trend for the used current densities. Interestingly, both w_{Grain} and ρ_{Grains} are highest and lowest for $500 \mu\text{A cm}^{-2}$ respectively. The exact opposite would have been expected under the assumption that the nucleation density is highest for $500 \mu\text{A cm}^{-2}$.

In summary, the microstructure of electrodeposited lithium layers seems not to be solely determined by nucleation. Otherwise, a stronger correlation between the electrodeposition current density and the resulting grain size or grain density would arise. However, it should be noted that due to experimental limitations, the layers were only analyzed after the deposition of 1 mAh cm^{-2} . Thus, grain growth might have already taken place during deposition. The steel foil substrate appears to have no significant influence on the lithium microstructure. Compared to the average grain size of the steel foil, those determined for lithium are much larger (see Figure S6, Supporting Information). This is in good agreement with previous results of electrodeposited alkaline metal layers on different substrates.^[39] An influence of the $\text{Li}_6\text{PS}_5\text{Cl}$ SE on the nucleation or the microstructure shortly after the start of electrodeposition cannot be ruled out and is further discussed based on our simulations in the respective chapter. Possible further effects on the microstructure include the stack pressure that was applied to the cell during electrodeposition. More likely, however, is relatively fast lateral grain growth during continuous lithium electrodeposition, i.e., during vertical layer growth, which is examined in more detail below.

2.3. Influence of Electrodeposition Capacity on the Lithium Microstructure

First investigations by Fuchs and Ortmann et al. on electrodeposited alkali metal layers in an *operando* experiment already suggest that the microstructure is not solely determined by the initial nucleation of lithium. Instead, lateral grain growth appears to occur during ongoing electrodeposition.^[39] This agrees with the results summarized in the previous section. Hence, the microstructural evolution of lithium layers during prolonged electrodeposition is examined in the following.

For this, the capacity Q was increased to 2.5 mAh cm^{-2} , 5 mAh cm^{-2} , and 10 mAh cm^{-2} in additional measurements, changing the theoretical (mean) layer thickness from 5 up to $50 \mu\text{m}$, respectively, while keeping the current density constant at $100 \mu\text{A cm}^{-2}$. The voltage profiles during electrodeposition and examples of

the subsequent SEM analysis combined with EBSD are shown in Figure 4.

As with the first electrodeposition, a continuous profile can be seen in Figure 4A. For none of the selected capacities a short circuit occurs, showing that even thick lithium layers can be electrodeposited free of short-circuits with $100 \mu\text{A cm}^{-2}$ at the $\text{steel}|\text{Li}_6\text{PS}_5\text{Cl}$ interface. The measured layer thickness compared to the theoretically expected one is shown in Figure 4B. As discussed before, the actual thickness is slightly higher compared to the calculated one, due to the incomplete coverage of the steel electrode size. Interestingly, the largest deviation between the measured and theoretical values occurs at $Q = 10 \text{ mAh cm}^{-2}$. This may be due to an uneven growth rate of certain areas of the layer, caused by an inhomogeneous stack pressure distribution during electrodeposition. The uneven stack pressure distribution could either stem from cell preparation or faster growth in some areas, leading to poorer contact between the steel stamp and working electrode in slower-growing regions. Deviations in thickness align with observations of another thick lithium layer, where thinning occurs at the edges of the electrode (see Figure S7, Supporting Information).

Analysis of the electrodeposited lithium within the SEM reveals a dense layer in the region of interest, with only small local differences in layer thickness. For a complete view of the cross-section, the reader is referred to Figures S2, S8–S10 (Supporting Information). All layers retain the columnar structure, with almost exclusively vertical grain boundaries and grains spanning the entire layer thickness. Occasionally, as seen in the center of the IPF map for $Q = 10 \text{ mAh cm}^{-2}$ (see Figure 4D), smaller truncated grains appear between two larger neighboring grains. These V-shaped grains might result from the preferential growth of certain grains during prolonged electrodeposition or due to significant differences in growth rates. Their number is typically small.^[39]

When comparing the individual layers, both the grain height h_{Grains} and the grain width w_{Grains} differ between layers. For lower capacities, multiple grains are fully visible in the chosen image section in Figure 4D. The higher the capacity, the fewer grains are visible. For a more in-depth analysis, all grains are characterized both in terms of their grain height h_{Grains} and their width w_{Grains} . For a capacity of 1 mAh cm^{-2} , the number of grains amounts to 59, for 2.5 mAh cm^{-2} to 54, for 5 mAh cm^{-2} to 21, and for 10 mAh cm^{-2} to 16.

To gain a better understanding of possible deformations or stresses within the electrodeposited lithium grains, they were further analyzed for their misorientation. The measure used for this is the grain reference orientation deviation (GROD) angle, which indicates the misorientation of a pixel within the grain relative to the average orientation of the entire grain.^[45–49] The resulting boxplots, the calculated grain density ρ_{Grains} per mm cross-section, and the measured GROD angles are shown in Figure 5. As before, please note that partially visible grains located at the edge of the cross-section were not considered.

The upper boxplot, which shows the grain height, reveals that almost all grains in the individual layers have a similar height. The fact that the height of all grains approximately corresponds to the layer thickness (see Figure 4B), shows that the columnar structure is preserved for all electrodeposited layer thicknesses and that almost all grains span the entire layer thickness. For

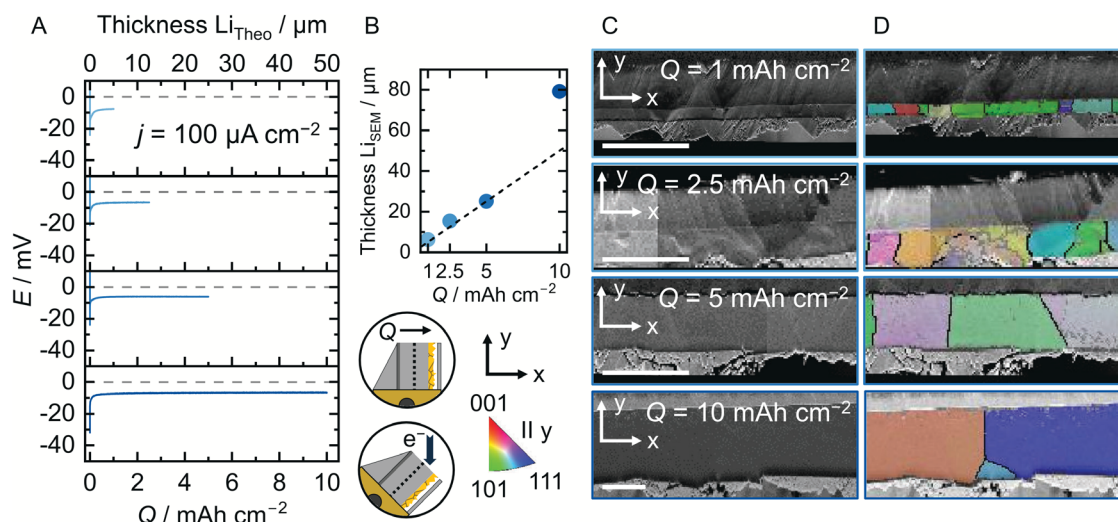


Figure 4. Layer thickness-dependent lithium electrodeposition and microstructural analysis. A) Voltage profiles during electrodeposition for four different capacities (1 mAh cm^{-2} , 2.5 mAh cm^{-2} , 5 mAh cm^{-2} , and 10 mAh cm^{-2}) using a current density of $100 \mu\text{A cm}^{-2}$. Please note that the sample for $Q = 1 \text{ mAh cm}^{-2}$ is the same one as in Figure 2, inserted here for direct comparison. B) Layer thickness determined by SEM, in which the expected theoretical thickness is depicted as a dotted line. A sketch of the following EBSD analysis is shown below. C) SEM images of representative steel/ $\text{Li}_6\text{PS}_5\text{Cl}$ cross-sections after electrodeposition of lithium for different capacities, see also Figures S2, S8–S10 (Supporting Information). D) Overlay of the SEM images and IPF maps, which are given parallel to the y-direction as illustrated in (B). Grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between 2° and 10° are depicted in grey. The scale bar within the SEM images represents a length of $50 \mu\text{m}$ and also applies to the respective image overlayed with its IPF map.

$Q = 10 \text{ mAh cm}^{-2}$, two outliers are found, which can be attributed to the truncated grains mentioned above.

There is a strong increase in the grain width with increasing layer thickness. While the average grain width for $Q = 1 \text{ mAh cm}^{-2}$ is $16 \mu\text{m}$, this increases to $194 \mu\text{m}$ for $Q = 10 \text{ mAh cm}^{-2}$. The same applies to the grain density, for a capacity of $Q = 1 \text{ mAh cm}^{-2}$ this is calculated to be 57 grains per mm. At $Q = 10 \text{ mAh cm}^{-2}$, the density decreases to 5 grains per mm, revealing a strong correlation between layer thickness and the resulting microstructure. This effect seems to be evident within individual lithium layers as well: the grain size appears to decrease in thin regions of an otherwise thick lithium layer (see Figure S7, Supporting Information). Additionally, the microstructure of the steel foil does not affect the microstructure of lithium at the investigated layer thicknesses, since the microstructure of lithium changes significantly while the steel foil is assumed to remain unchanged.

To investigate the influence of electrodeposition time and resulting microstructure, another lithium layer with a capacity of 1 mAh cm^{-2} was electrodeposited at a current density of $10 \mu\text{A cm}^{-2}$, requiring 100 h (see Figure S11, Supporting Information). This matches the electrodeposition time for the layer with a capacity of $Q = 10 \text{ mAh cm}^{-2}$ electrodeposited with $100 \mu\text{A cm}^{-2}$. As shown in Figures S12, S13 (Supporting Information), the resulting microstructure of the layer electrodeposited with $10 \mu\text{A cm}^{-2}$ for a capacity of $Q = 1 \text{ mAh cm}^{-2}$ is almost identical to the other lithium layers with a capacity of $Q = 1 \text{ mAh cm}^{-2}$.

This indicates that rather the electrodeposited capacity, and not the electrodeposition time, influences the microstructure. Additionally, our hypothesis from the previous section that the current density does not significantly affect the microstructure is confirmed. However, it is important to note that all lithium layers were analyzed after a certain deposition, storage, and preparation time. This means that no reliable statement can be made about the initial structure of the lithium layers. Results of *operando* experiments by Fuchs and Ortmann et al. indicate that the grains grow rapidly during electrodeposition, which means that in all cases we are likely analyzing a lithium layer in its fully annealed, i.e., equilibrium state.

Furthermore, this explains why no significant change in the microstructure could be observed in the current density-dependent experiments, even though different nucleation densities are expected. The grain growth following nucleation leads to certain grains preferentially growing both vertically and laterally. During this grain growth, certain grains are consumed, causing the mean lateral grain size to increase and grain density to decrease. This growth could be caused by a mechanism similar to grain ripening or “secondary recrystallization”, as suggested by Fuchs and Ortmann et al. The driving force is the natural tendency to minimize interfacial and grain boundary energies.^[50,51] Here, it should be noted that room temperature (25°C) corresponds to a homologous temperature of $T_H = 0.66$ for lithium, indicating that room temperature operation of lithium corresponds in principle to a *high-temperature* process, likely increasing the grain boundary velocity. Recrystallization in metals typically occurs at homologous temperatures between 0.4 and 0.6.^[52] This

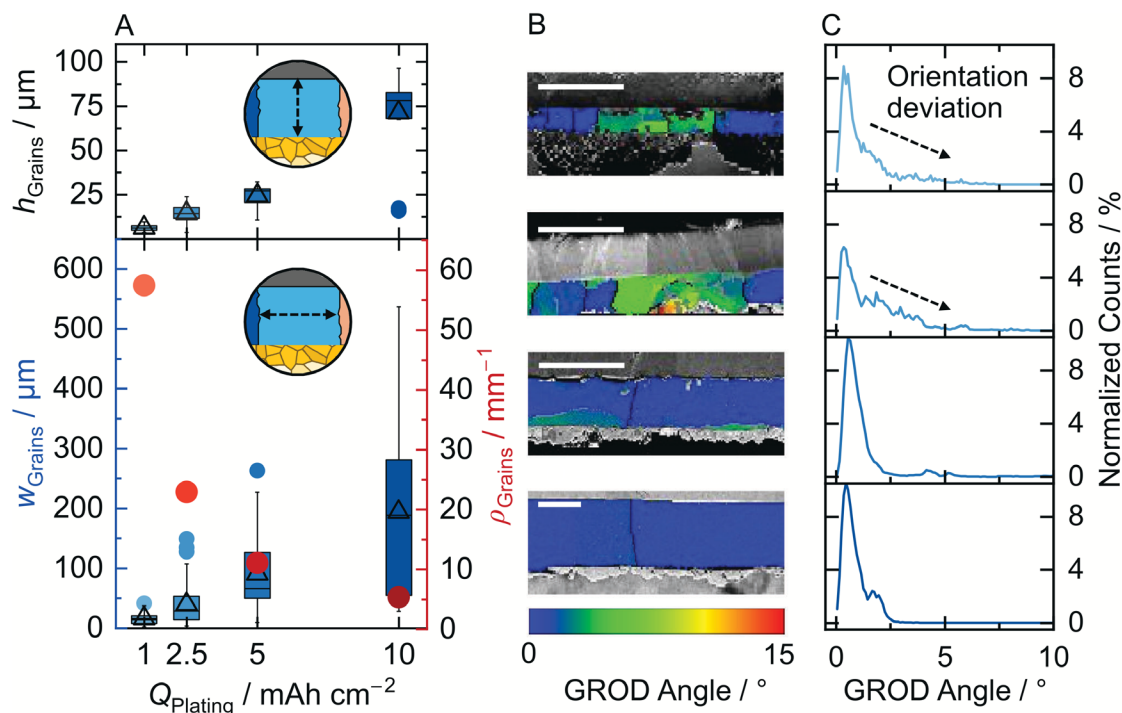


Figure 5. Summary of the analyzed lithium layers electrodeposited with different layer thicknesses. A) Boxplot of the analyzed lithium layers electrodeposited with $100 \mu\text{A cm}^{-2}$ for different capacities. The measured grain heights are summarized in the boxplot in black on the top graph. The measured grain widths are summarized in the boxplot in blue underneath. The dimension of interest for the respective boxplot is schematically depicted within the plot. Outliers (interquartile range factor = 1.5) are marked with blue points in both boxplots. The distribution of both grain heights and widths summarizes 59 (1 mAh cm^{-2}), 54 (2.5 mAh cm^{-2}), 21 (5 mAh cm^{-2}), and 16 (10 mAh cm^{-2}) measured grains, respectively. The average is represented with a triangle inside each box. The calculated grain density is shown in red circles in the lower section. B) Overlay of SEM images with GROD maps for the different layer thicknesses, see also Figures S14–S17 (Supporting Information). The shown scale bars correspond to $50 \mu\text{m}$. Angular deviations of individual pixels referenced to the mean orientation of the grain are shown according to the color scale below. C) Distribution of the measured GROD angles for all analyzed grains. The data is normalized to the total counts. The drawn arrows highlight the shift toward higher GRODs for lower capacities.

grain growth is potentially further enhanced by the fact that a high-purity lithium layer is electrodeposited, given that $\text{Li}_6\text{PS}_5\text{Cl}$ is a single-ion conductor – leading to the absence of impurities which would potentially hinder grain boundary motion.^[1,4,53,54]

Additionally, a lowering of the local degrees of misorientation and the associated strain within the grains could be a reason for the change in microstructure. As can be seen in Figure 5, the distribution of GROD angles shifts toward smaller values for higher layer thicknesses. This means that fewer grains show high GROD angles in their interior. The mean GROD angle is 1.35° for $Q = 1 \text{ mAh cm}^{-2}$, 1.78° for $Q = 2.5 \text{ mAh cm}^{-2}$, 1.12° for $Q = 5 \text{ mAh cm}^{-2}$, and 0.87° for $Q = 10 \text{ mAh cm}^{-2}$. Only the experiment with $Q = 1 \text{ mAh cm}^{-2}$ deviates from the trend, which could be because no severe (lateral) grain growth has yet taken place. Also, the GROD maps (see Figure 5B; Figures S14–S17, Supporting Information) show that there appear to be more grains with high GROD angles at lower layer thicknesses. In particular, the layer for $Q = 2.5 \text{ mAh cm}^{-2}$ shows multiple grains with high GROD angles and subgrain structures in their interior. Such subgrain structures are suspected to favor abnor-

mal grain growth.^[45–49] Interestingly, Omori et al. found similar columnar structures within high-temperature processed copper alloys.^[48] With increasing layer thickness, at $Q = 5 \text{ mAh cm}^{-2}$, such misorientations can only be recognized sporadically, and at $Q = 10 \text{ mAh cm}^{-2}$ there are almost no more grains that show misorientation angles. We herein conclude that the electrodeposited layers reduce their stress during vertical growth, which could be another driving force for the lateral growth observed.

The observed grain growth is in agreement with molecular dynamics simulations of Choi et al.^[55] and could potentially follow a normal grain growth mechanism described by Thompson,^[49] leading to a columnar grain structure and grain diameters in the range of 2–4 times the layer thickness, following a lognormal distribution.^[49] These assumptions fit well with the lithium grains analyzed here, as can be seen in the grain width distribution plot in Figures S18, S19 (Supporting Information). The grain size distribution for different current densities shows good agreement between the lognormal distribution and the experimental data, suggesting that normal grain growth has taken place. The same applies to the thicker lithium layer for $Q = 2.5 \text{ mAh cm}^{-2}$,

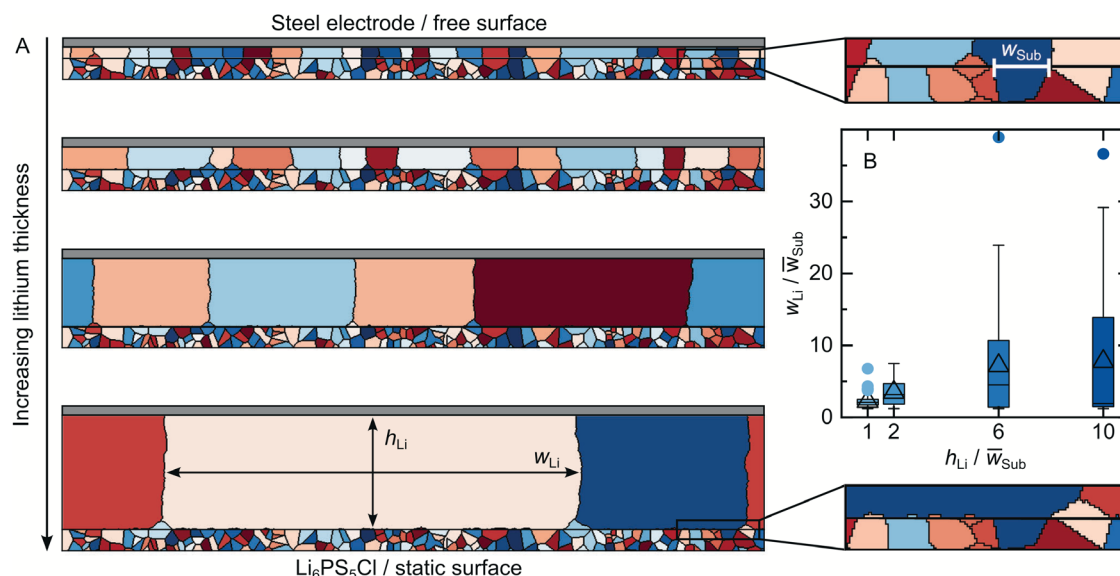


Figure 6. Simulation-based results on the microstructural evolution of lithium. A) Simulation-based microstructures of lithium layers of different thicknesses with a free surface toward the top (imitating steel foil) and a static interface toward the solid electrolyte at the bottom (imitating $\text{Li}_6\text{PS}_5\text{Cl}$). The two insets on the right show an enlarged section of the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ interface. B) Boxplot of grain width w_{Li} versus lithium thickness h_{Li} . Both values are referenced to the average width of the $\text{Li}_6\text{PS}_5\text{Cl}$ grains at the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ interface $\bar{w}_{\text{Sub}}$. The width of one $\text{Li}_6\text{PS}_5\text{Cl}$ grain (w_{Sub}) is highlighted in the upper inset as an example. For the boxplot, 5 structures, as shown in (A), were generated and analyzed for each of the different lithium thicknesses.

which also appears to be lognormally distributed. The continued growth of the grains for $Q = 5 \text{ mAh cm}^{-2}$ and 10 mAh cm^{-2} could either be due to the same mechanism or due to abnormal grain growth, which is described by both Thompson^[49] and Omori et al.^[48] Unavoidably, the quality of the statistics is reduced due to the decreasing number of grains for the thicker layers, which makes it difficult to draw more reliable conclusions. At this point, we like to note that the data presented here are the first of their kind and already require extensive analysis through a time-consuming workflow for the EBSD experiments on millimeter-sized cross-sections. More data will be generated in the future, including the role of other parameters like interface modification or seed layers.

2.4. Modelling of the Microstructural Evolution

To qualitatively describe the observed layer thickness dependence, a Monte Carlo Potts model is used in the following. Herein, we aim to model the microstructures for the different lithium layer thicknesses. To simulate the thickness dependence of the lithium microstructure after electrodeposition, the actual electrodeposition kinetics are disregarded. Instead, based on our previous results, we hypothesize that the lithium layer rapidly anneals during or after electrodeposition, as electrodeposition is conducted at a high homologous temperature of $T_{\text{H}} = 0.66$ for lithium. This hypothesis is supported by *operando* experiments of Fuchs and Ortmann et al.^[39] Consequently, when observing the metal layer using SEM, a fully annealed, i.e., equilibrated lithium

layer can be seen, with the microstructure primarily determined by the layer thickness d_{layer} . This approach aligns with our experimental findings, which show no significant differences in the microstructure based on the deposition rate (i.e., applied current density).

For each thickness, an identical $\text{Li}_6\text{PS}_5\text{Cl}$ grain microstructure with the same spatial distribution of orientations θ_i and a free surface imitating the steel electrode is attached to the lithium layer (see Figure 6; Figure S20, Supporting Information). Random orientation values θ_i are assigned to the lithium Monte Carlo Units (MCUs). We then anneal the structure via 10^6 Monte Carlo time steps, leading to grain growth as shown in Figure S21 (Supporting Information). After these 10^6 steps, the total energy and mean grain size reaches an equilibrium state (see Figure S22, Supporting Information).

The final microstructures for different layer thicknesses are shown in Figure 6. The layer thicknesses are given in units of w_{Sub} , which is the mean (interface) diameter of the $\text{Li}_6\text{PS}_5\text{Cl}$ grains at the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ interface. The color coding of the grains reflects their relative orientation θ_i , with low interfacial energies appearing between lithium and $\text{Li}_6\text{PS}_5\text{Cl}$ grains of similar colors (e.g., light blue and blue, or light red and red).

As visible in Figure 6A, the simulation results in columnar grains with boundaries perpendicular to both the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ and the steel|Li interfaces. Additionally, at the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ interface, smaller truncated grains remain, primarily forming triple junctions with the larger columnar grains, being in good agreement with our experimental data. The relative orientations θ_i of these smaller grains match those of the adjacent $\text{Li}_6\text{PS}_5\text{Cl}$ grains,

resulting in low interfacial energies. For small layer thicknesses, the lithium layer's grain orientation adopts the orientation of the adjacent SE grains.

In contrast, none of these truncated grains is visible at the upper interface toward the steel foil, which was modeled as a free surface. Comparing simulation and experiment, this highlights the necessity of introducing an interface interaction at the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ boundary to qualitatively reproduce our experimental results. However, it is important to note that SEI formation takes place at the $\text{Li}|\text{Li}_6\text{PS}_5\text{Cl}$ interface. Therefore, rather the SEI will influence the lithium microstructure instead of the $\text{Li}_6\text{PS}_5\text{Cl}$ itself. Nevertheless, it seems evident that the lithium microstructure is influenced by the interaction at the interface towards the $\text{Li}_6\text{PS}_5\text{Cl}$. Our simulations further indicate that these effects are more pronounced for thinner lithium layers. This is because the relative contribution of γ_{ij}^{int} to E_{tot} becomes more significant, given the increasing ratio between interfacial area and grain boundary area. This forces the lithium adjacent to the $\text{Li}_6\text{PS}_5\text{Cl}$ surface to favor crystal orientations with low interface energies (epitaxial growth). Conversely, the contribution of γ_{ij}^{gb} to E_{tot} becomes more significant for thicker grown layers, as the total grain boundary area increases in the course of electrodeposition, unlike the interfacial area with the substrate.

The mean width w_{ij} of columnar grains increases with increasing lithium layer thickness, as can be seen both in the generated structures in Figure 6A as well as in the boxplot in Figure 6B. Please note that only grains with a minimum width of 15 pixels were considered for the boxplot. This ensures that the analyzed grains are not artifacts of the simulation, e.g. grains that only consist of single pixels. Although no electrodeposition kinetics were considered in the model, the results are in qualitative agreement with the experiment, suggesting that the layer thickness is decisive for the resulting microstructure and that the observed layers are equilibrated. The underlying physics for the increasing grain width of the columnar grains is as follows: grains grow curvature-driven until their size matches the layer thickness. The driving force is the reduction of the total grain boundary area, associated with higher free energy of the layer. Then stagnation of the grain growth occurs (see Figure S22, Supporting Information) as the curvature of the grain boundaries approaches zero, eliminating the driving force for further growth. This leads to a linear relationship between grain width and layer thickness, as demonstrated by simulations on grain growth by Zöllner and experimental observations on thin layers.^[56–59] As shown in Figure 6, this linear relationship holds for the columnar grains in our simulation.

The simulations reveal that the experimental results can be qualitatively reproduced without taking electrodeposition kinetics into account, supporting the hypothesis that deposition rate (i.e., the current density) has no significant influence on the resulting microstructure. We conclude that the lithium layer anneals rapidly during or after electrodeposition in dependence on the lithium layer thickness. Furthermore, by implementing an interfacial energy between lithium and $\text{Li}_6\text{PS}_5\text{Cl}$, we induced the formation of truncated grains in the simulation. These truncated grains only occur at this interface and not on the side of the steel foil, both in the simulation and in the experiment. Thus, our hypothesis that the steel foil does not significantly influence the lithium microstructure is supported, but an influence of the

$\text{Li}_6\text{PS}_5\text{Cl}$ microstructure on the lithium microstructure is obvious. However, we would like to point out that the choice of other current collector materials might lead to a different outcome.

What remains an open question is the stagnating grain growth in 3D. Here, grain growth should slow down but not stop when the grain diameter matches the layer thickness due to residual boundary curvature. Possible explanations include the extremely slow coarsening of low-curvature grains, making the study's timeframe too short to observe changes. Surface grooving and rough interface topology might also pin grain boundaries, similar to 2D mechanisms.^[60] Additionally, orientation-dependent interface energies could lead to triangular grains that pin columnar grain boundaries at the SE|lithium interface. Further analysis is needed to understand the full effects of these factors, which may reveal additional insights.

2.5. Microstructural Evolution During Lithium Electrodeposition

In the following, the observed microstructural evolution is discussed. The scheme in Figure 7 serves as a schematic visualization of the conclusions drawn from the results presented above. The voltage profile in Figure 7A sketches lithium electrodeposition with two different current densities j_{low} and j_{high} . The small offset between the two curves only serves for better differentiation of the two. Initially, a nucleation overvoltage is visible for both current densities (point Q_0). Comparing (B) and (C), we assume that at higher current density (C) more nuclei are formed initially at the interface between steel and $\text{Li}_6\text{PS}_5\text{Cl}$, as has been demonstrated previously for RFCs.^[22,31]

During continuous electrodeposition (point $Q_1 > Q_0$), those nuclei grow and become grains. Because nuclei can have the same orientation, some nuclei grow together to form a single grain. At this point, grain growth occurs mostly in a vertical direction. A lateral grain growth before complete coverage of the solid electrolyte surface might be due to current constriction at the edge of the lithium grains. In addition, mechanical stress could also favor lateral growth. At this early stage of growth, the higher nucleation density for j_{high} may still result in a higher grain density compared to the lower current density j_{low} , as no significant grain growth has yet happened in both vertical and lateral directions. As shown schematically, however, we assume that misorientations and substructures already form within the grains, especially at contact points between two neighboring grains. Based on our simulations, we further assume that during this initial stage, the microstructure of lithium adopts the microstructure of the SE.

At higher electrodeposition capacity (point $Q_2 > Q_1$), we observe a harmonization of the microstructure, which means that – despite different nucleation densities – the same number of grains with a similar size is now present in both cases. We assume that a curvature-driven normal grain growth together with the reduction of misorientations inside the grains is the driving force, being schematically indicated by a reduction of highly misoriented regions in Figures 7B,C.^[46–49]

This effect is even more pronounced with longer electrodeposition (point $Q_3 > Q_2$). Existing grains further grow, increasing the average grain size and decreasing the grain density, also decreasing the surface-to-volume ratio of the remaining grains.

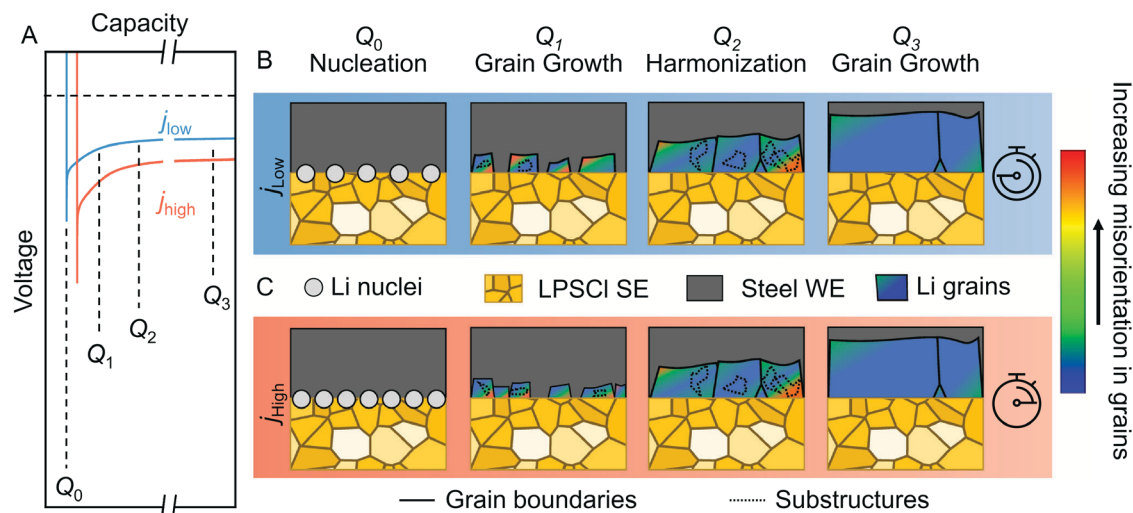


Figure 7. Schematic representation of the microstructural evolution of electrodeposited lithium. A) Sketch of voltage profiles for two different current densities j_{low} and j_{high} . The capacity-offset between the two curves serves for better differentiation. B, C) Microstructural evolution during electrodeposition of lithium for (B) j_{low} and (C) j_{high} . Please note that, as indicated by the stopwatches, electrodepositing the same capacity Q with a lower current density $j_{\text{low}} < j_{\text{high}}$ takes longer. The color code within the grains highlights misorientation, according to the color scale on the right of the image. Dotted lines indicate substructures that form within grains.

This leads to very large lateral grain sizes in the range of several hundred micrometers and some truncated grains, as visible in the analyzed layers within this work. Additionally, we found that the misorientation within grains further decreases for higher layer thickness, as indicated by a more homogeneous color gradient in Figure 7 at point Q_3 .

Based on our results and the work of Thompson, and Omori et al., we assume that the truncated grains are not caused by different growth rates of the grains.^[48,49] Instead, we assume that they are either caused by the fusion of neighboring grains, which is driven by the reduction of misorientations, or due to an interfacial interaction with the solid electrolyte, as indicated by our simulations. It remains elusive whether these truncated grains are formed at the beginning or during electrodeposition.

One possible mechanism for the observed grain growth is a curvature-driven normal grain growth. As postulated by Thompson,^[49] normal grain growth occurs in thin layers with grain sizes smaller than the layer thickness until the resulting columnar grains span the whole layer and grain sizes are in the order of the layer thickness, being referred to as a specimen thickness effect. This is in good agreement with both our experimental and computational results, indicating a similar grain growth mechanism. Additionally, as mentioned during the discussion of Figure 5, room temperature corresponds to a homologous temperature of $T_H = 0.66$ for lithium metal, making grain growth more likely due to a presumably high grain boundary mobility.

Furthermore, “secondary recrystallization” or abnormal grain growth could take place. Here a few grains grow preferentially at the expense of other surrounding grains.^[39,49] Abnormal grain growth has been observed in tantalum, molybdenum, and copper alloys, for example.^[46,48,61] In the case of copper alloys, a cyclic temperature treatment causes the formation of substructures and high GROD angles.^[48]

These in turn are suspected to be the origin of abnormal grain growth, leading to grain sizes in the millimeter range and, interestingly, also to a columnar structure. As discussed, such misorientations are also visible within electrodeposited lithium layers, as schematically depicted in Figure 7, or using GROD angle measurements (see Figure 5B; Figures S14–17, Supporting Information), potentially initiating abnormal grain growth here, too. In the case of abnormal grain growth, a preferential orientation of the abnormally grown grains is expected.^[49] An analysis of the thickest lithium layer (revisit Figure S10, Supporting Information) shows that the largest grains have a similar $\langle 111 \rangle$ orientation in the y -direction (blue), potentially caused by abnormal grain growth. For direct visualization of the orientation distribution, the inverse pole figure of this layer is shown in Figure S23 (Supporting Information). The thinner lithium layers are also shown for comparison. However, the large grain size for $Q = 10 \text{ mAh cm}^{-2}$ and thus poorer statistics on the one hand and the observation of the completely annealed state on the other hand makes it difficult to draw reliable conclusions on preferential growth. A deeper understanding of the detailed growth mechanisms is to be gathered in future studies, combining additional *operando* measurements, complemented by EBSD analysis.

Overall, we demonstrate that the microstructure of electrodeposited lithium can be controlled by varying the layer thickness. By decreasing the electrodeposition capacity (i.e., the layer thickness), a smaller grain size with a higher grain density can be electrodeposited. Assuming faster lithium diffusion along the grain boundaries, a higher power density can be achieved for small layer thicknesses. Furthermore, the microstructure differs significantly from that of commercially available foils, not only due to the reduced grain size of electrodeposited lithium layers

with practically relevant thicknesses of 20 μm (also resulting in a higher grain boundary density) but also because of the columnar structure of the layer. Both parameters likely influence the re-dissolvable amount of the lithium layer during cycling. In addition to electrochemical properties, mechanical properties are also determined by the microstructure. Assuming a Hall–Petch mechanism (i.e., grain boundary strengthening), it can be expected that thinner lithium layers are harder than thicker lithium layers, as the grain boundary density is inversely proportional to the layer thickness.^[52] Finally, the model system presented here enables further investigations of the lithium microstructure and how it can be influenced. Possible approaches include varying the temperature during electrodeposition or the use of seed layers, which could influence nucleation and grain growth.

3. Conclusions

In this study, we experimentally investigated the microstructure of electrodeposited pure lithium as a function of the current density and the electrodeposited layer thickness at steel|Li₆PS₅Cl interfaces using EBSD. Our experiments show that the steel|Li₆PS₅Cl|Li|steel cell setup is a suitable model system for RFCs, enabling the electrodeposition of lithium layers with a thickness of several tens of micrometers.

Varying the current density used for lithium electrodeposition does not influence the microstructure for the analyzed layer thicknesses of $\approx 5 \mu\text{m}$ of lithium. Despite an assumed higher nucleation density at higher current densities, the average grain size and density remain similar. Instead, the microstructure depends on layer thickness. For thicker layers, the lateral grain size increases, too. Thus, we conclude that – although the current density plays an important role in the morphology of electrodeposited lithium layers – its effect on the microstructure is overshadowed by grain growth during electrodeposition of practically relevant lithium layer thicknesses. This specimen thickness effect is further supported by our simulations based on a Monte Carlo Potts model, which qualitatively reproduces our experimental results without taking electrodeposition kinetics into account. In accordance with previous work, thinner electrodeposited lithium layers should therefore show a higher Coulomb efficiency (i.e., the amount of re-dissolvable lithium is higher) under equal current load, as the transport of lithium along grain boundaries is assumed to be faster.^[18,39,62]

Accordingly, particular attention should be paid to the choice of lithium layer thickness, as it significantly influences the resulting lithium microstructure and the electrochemical properties for subsequent investigations. To achieve higher power densities in practice, it might be better to stack several thin single cells rather than trying to develop thick cells with high areal capacity. In conclusion, our work provides a deeper understanding of electrodeposited lithium and its properties. Its microstructure is related to electrodeposition parameters, offering the perspective to be modified in future work to increase the amount of re-dissolvable lithium during cycling experiments.

4. Experimental Section

Cell Preparation: RFC (steel|Li₆PS₅Cl|Li|steel) preparation was carried out inside a glovebox (MBraun, Germany) with impurity contents of O₂,

N₂ and H₂O being below 1 ppm. An in-house casing was used for cell assembly. Steel stamps with a diameter of 10 mm were used to contact the electrodes. One of the steel pistons was fixed with the help of nitrile rubber sealing rings as well as polyether ether ketone cell components. A steel foil (AISI 304, Goodfellow, Germany) acting as the working electrode was placed on the fixed steel punch and 90 mg of Li₆PS₅Cl powder (NEI Corporation, USA) was filled in. The other opening of the cell housing was similarly sealed with a second steel punch to compress the SE and the powder was compacted using a uniaxial press at 3 t for 1 min from each side, resulting in a pellet with a thickness of roughly 1 mm. Lithium foil was freshly prepared by cutting a small piece of lithium from a lithium rod (99.8%, abcr GmbH) and removing the surface degradation layers by mechanical removal using a ceramic knife. The fresh piece of lithium was then pressed between a pouch foil to form a clean lithium foil with a thickness of $\approx 100 \mu\text{m}$ using a hand press.^[10] A lithium electrode ($d = 9 \text{ mm}$) was punched out and placed on the remaining surface (opposite to the steel working electrode) of the Li₆PS₅Cl pellet. An additional steel foil was placed between the steel punch and the lithium electrode. Finally, the cell was sealed and a stack pressure of 15 MPa was applied using an aluminum press frame for electrochemical characterization.

Electrochemical Characterization: The cells were electrochemically characterized using a VMP 300 potentiostat (Biologic, France) at room-temperature (25 °C). Initially, the cells were equilibrated for $\approx 6 \text{ h}$, and potentiostatic impedance spectra were recorded in a frequency range from 7 MHz to 100 MHz at an amplitude of 10 mV at an interval of 30 min. Subsequently, lithium was electrodeposited on the working electrode by galvanostatic electrochemical impedance spectroscopy (GEIS) using different current densities (50 $\mu\text{A cm}^{-2}$, 100 $\mu\text{A cm}^{-2}$, 250 $\mu\text{A cm}^{-2}$, and 500 $\mu\text{A cm}^{-2}$). For thickness-dependent measurements, the capacity was limited to 1 mAh cm^{-2} , 2.5 mAh cm^{-2} , 5 mAh cm^{-2} , and 10 mAh cm^{-2} while the current density was kept constant at 100 $\mu\text{A cm}^{-2}$. Unless otherwise stated, GEIS measurements were recorded with a frequency range from 7 MHz to 1 Hz at an amplitude of 10% of the direct current.

Cryogenic Ion Milling: For the preparation of cross-sections an ion beams milling system (Leica EM TIC 3X, Leica Microsystems GmbH, Germany) at temperatures below $-100 \text{ }^{\circ}\text{C}$ was used in combination with a Leica VCT500 (Leica Microsystems GmbH, Germany) transfer module. An accelerating voltage of 6 kV, resulting in an Ar⁺ ion beam current of $\approx 2.2 \text{ mA}$ was used to cut steel|Li cross-sections. Cross-sections were imaged using a field-emission scanning electron microscope GeminiSEM 560 system (SEM, Carl Zeiss Microscopy GmbH, Germany).

Electron Backscatter Diffraction (EBSD): For EBSD measurements, the sample was transferred into the SEM using an inert-transfer module (Leica VCT500, Leica Microsystems GmbH, Germany). Microstructural analysis was conducted at a beam voltage of 10 kV, a beam current of $\approx 12 \text{ nA}$, a working distance of 12.5 mm, and a tilt of 70° using an EBSD detector system (Symmetry S3) from Oxford Instruments (Oxford Instruments, United Kingdom).

Data Processing and Analysis: Acquired EBSD data were processed with the AZtecCrystal software from Oxford Instruments and the implemented Mapsweeper software package. The acquired electron backscatter patterns were indexed using a Hough algorithm with a resolution of 60 and 11 bands considering the cubic Li ($Im\bar{3}m$) phase. Dynamical template matching, refinement sweeps, and repair sweeps were executed against a master simulation of EBSD patterns of lithium to refine the measured patterns and remove artifacts such as pseudo-symmetries within grains. The grain reference orientation deviation (GROD) angle was calculated within AZtec Crystal. For this, the mean grain orientation was calculated by using every measured pixel of a grain. The angular deviation of the individual pixels were then referenced to the calculated mean value.

Grain Growth Simulations: The grain growth simulations were carried out using a Monte Carlo Potts Model, frequently used to simulate curvature-driven grain growth.^[56–59,63–69] In the model, the microstructure of the lithium metal was mapped onto a square lattice. Each lattice site is

called a Monte Carlo unit (MCU) and is assigned a state that corresponds to the particular grain orientation of the grain to which the lattice site belongs to. This means that grain boundaries were implicitly assigned to the boundary between two adjacent MCUs i and j with different orientations (see Figure S20, Supporting Information). The grain boundary energy per unit length γ_{ij}^{gb} in such models is typically assumed to follow the Read–Shockley-equation:

$$\gamma_{ij}^{gb} = \begin{cases} \gamma_{\max}^{gb} \frac{\theta_{ij}^{gb}}{\theta_{gb}^{b*}} \left(1 - \ln \left(\frac{\theta_{ij}^{gb}}{\theta_{gb}^{b*}} \right) \right) & \text{if } \theta_{ij}^{gb} \leq \theta_{gb}^{b*} \\ \gamma_{\max}^{gb} & \text{if } \theta_{ij}^{gb} > \theta_{gb}^{b*} \end{cases} \quad (1)$$

Here, θ_{ij}^{gb} represents the crystallographic misorientation angle between the neighboring lattice sites i and j , while θ_{gb}^{b*} denotes the critical misorientation angle that distinguishes small-angle grain boundaries from large-angle grain boundaries. This means that all grain boundaries with $\theta_{ij} \geq \theta^*$ exhibit the maximum grain boundary energy $\gamma_{\max}^{gb}$. In the analysis, this orientation dependence of γ_{ij}^{gb} was neglected for the interior of the lithium and thus only assume large angle grain boundaries ($\gamma_{ij}^{gb} = \gamma_{\max}^{gb}$). This assumption leads to a grain size evolution that closely approximates ideal grain growth, with the mean grain diameter following a square root time dependence (see Figure S21, Supporting Information). In such cases, grain growth was driven only by the local curvature κ of the grain boundary, i.e., the local grain boundary velocity v toward its center of curvature was proportional to κ .

To account for the potential influence of the SE, a polycrystalline layer was attached to one side of the lithium layer. This layer remains static during the simulation, with its MCUs defining the (static) boundary conditions on the SE side of the lithium layer (revisit Figure S20, Supporting Information). In contrast to γ_{ij}^{gb} , it was assumed that the interfacial energy γ_{ij}^{int} between a lithium MCU i and an adjacent SE MCU j follows Equation 1. Specifically, γ_{ij}^{int} was calculated using the maximum interfacial energy $\gamma_{\max}^{int}$ and an effective misorientation angle θ_{ij}^{int} that separates high energetic relative orientations of the SE MCUs and the lithium MCUs from low-energetic ones.

In 3D space, θ_{ij}^{int} is likely a complex function of the orientations (Euler angles) of the SE grains and their adjacent lithium grains. However, for a qualitative understanding of the experimental observations, a simplified approach similar to that of Zöllner et al. used for the calculation of grain boundary misorientations was adopted.^[67] In this approach, each lithium and SE MCU was assigned a relative misorientation θ_i ($\theta_i \in \mathbb{N}$; $\theta_i \leq 45$) with respect to a reference axis, and θ_{ij}^{int} was calculated according to:

$$\theta_{ij}^{int} = |\theta_i - \theta_j| \quad (2)$$

Given the lack of quantitative information on $\gamma_{\max}^{int}$, it was assumed to be equal to $\gamma_{\max}^{gb}$.

Due to the significantly smaller grain size of the steel foil compared to that of the deposited lithium layer (revisit Figure S6, Supporting Information), an isotropic interaction was assumed at the steel|Li interface. For simplicity, the attached steel electrode was modeled as a free surface with $\gamma_{ij}^{int} = 0$ between all lithium MCUs i and adjacent steel MCU j . For the boundaries perpendicular to the SE surface normal, periodic boundary conditions were applied, meaning that the nearest neighbor of an MCU at the edge of the lattice was the corresponding MCU on the other edge, and vice versa (see Figure S20, Supporting Information).

The total energy of the system E_{tot} , excluding contributions from the interior of the SE and steel layer, was given by summing up the energetic contributions of all N lithium lattice sites. Here, only interactions of each lattice side with their 8 nearest neighbors (nn) were considered. Lattice

sites with the same θ_i do not contribute to E_{tot} . Consequently, it was given as:

$$E_{\text{tot}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^{nn} (\gamma_{\max}^{gb} + \gamma_{ij}^{int}) (1 - \delta(\theta_i, \theta_j)) \quad (3)$$

Here, $\delta(\theta_i, \theta_j)$ is the Kronecker-delta which is equal to one if $\theta_i = \theta_j$ and zero if $\theta_i \neq \theta_j$. Obviously $\gamma_{ij}^{int} = 0$ for the lithium MCUs that are not in contact with the SE boundary units.

To update the orientations of the lithium MCUs, i.e., anneal the lithium, a Monte Carlo simulation was carried out. The corresponding algorithm works as follows: an MCU was chosen in a probabilistic way and its θ_i was changed to one of its 8 nearest neighbor states θ_j . Choosing the orientation only from neighbor states prevents the nucleation of new grains. A new θ_i was accepted with a probability P according to:

$$P = \begin{cases} 1 & \text{if } \Delta E_{\text{tot}} \leq 0 \\ \exp(-\Delta E_{\text{tot}}/k_b T_s) & \text{if } \Delta E_{\text{tot}} > 0 \end{cases} \quad (4)$$

where ΔE_{tot} is the energy difference between the old and the new lattice state calculated based on Equation 3, k_b is the Boltzmann constant, and T_s is the simulation temperature. T_s is a technical parameter and should not be confused with a real temperature.^[68] The proposal by Zöllner was followed and $k_b T_s$ was chosen to be equal to $0.66 \cdot \gamma_{\max}^{gb}$. A repetition of N reorientation attempts defines the time scale of the simulation, equivalent to one Monte Carlo step (MCS). The simulation was carried out in a parallel fashion by dividing the grid into four subunits with non-interacting MCUs.^[70] Consequently, four iterations were needed for N reorientation attempts, i.e., to perform one MCS. All simulation steps were carried out using Python.

It is important to note here that, strictly speaking, neither the time scale, the size scale, nor the energy scale of this model directly corresponds to the actual physical quantities of the experiments. Various methods have been proposed in the literature, such as those by Raabe,^[71] to translate the Monte Carlo parameters into real physical units. However, since the experimental results do not provide quantitative data on the grain growth kinetics of the lithium layers, such methods cannot be applied here.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

J.B. did conceptualization, methodology, investigation, validation, formal analysis, wrote the original draft, visualization, and did review & editing. T.F. did conceptualization, methodology, and did review & editing. T.O. did conceptualization, methodology, did review & editing. S.K. performed formal analysis, software, visualization, did review & editing. F.H.R. wrote the original draft, did review & editing, supervision. J.J. did conceptualization, methodology, resources, supervision, wrote the original draft, did review & editing, and funding acquisition.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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anode-free cells, electron backscatter diffraction, lithium metal, microstructure, solid-state battery

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3.3 Publication 3: “*Microstructure of electrodeposited lithium and its evolution during cycling when using metal interlayers in “anode-free” solid-state batteries*”

In the third publication of this dissertation, the impact of metallic interlayers on the microstructure of electrodeposited lithium was analyzed by EBSD. Building on the previously established broad ion beam milling workflow, the microstructure of lithium electrodeposited on pristine titanium foils as well as on three relevant interlayer materials, namely gold, silver and bismuth was analyzed. In addition, the microstructure of partially stripped lithium layers with and without interlayers and of repeatedly cycled lithium layers was examined.

EBSD analysis revealed that lithium electrodeposited on pristine titanium foils exhibit a similar columnar, large-grained microstructure as those electrodeposited on steel (Publication 2). In contrast, the presence of interlayers significantly modified the resulting lithium microstructure. When lithium is electrodeposited on gold, silver or bismuth interlayers, a different resulting microstructure is observed depending on the material used. While gold and silver result in smaller grain sizes, bismuth interlayers lead to an increased lithium grain size. To link these microstructural changes to the respective interlayers, the phase distribution of the interlayers was analyzed, *i.e.*, where the interlayer material is located after electrodeposition. To deconvolute the individual factors governing lithium microstructure formation, the proposed mechanisms were qualitatively assessed using 3D Monte Carlo Potts simulations.

In addition, the microstructure of partially stripped lithium layers was analyzed for the first time after only electrodeposited layers were analyzed in prior works. In the case of pristine titanium foil and using a bismuth interlayer, it was shown that the previously observed specimen thickness effect, *i.e.*, the increase in grain size with increasing layer thickness, is reversible. In the case of pristine titanium foil, in addition to the reduced grain size following stripping, a significant preferential orientation in the $\langle 101 \rangle$ direction parallel to the dissolution direction was observed. In contrast, the gold and silver interlayers seem to prevent grain shrinkage. Initial analyses following several electrodeposition and dissolution cycles further indicate that (mechanical) degradation of the SE or the SEI can also lead to a different microstructure by introducing secondary phases/particles into the lithium layer.

Overall, the third publication of this dissertation highlights the potential for microstructural modification of lithium layers using interlayers. The results further indicate that the grain growth observed in publication 2 seems to be related to the high purity of the electrodeposited lithium metal demonstrated in publication 1. Additionally, the study expands knowledge about the influence of stripping and repeated cycling on the resulting lithium microstructure. Finally, the study underlines the need to complement electrochemical research with metallurgical concepts and to consider (lithium metal) batteries as „electrometallurgical“ systems.

J. Becker and L. Schuster designed and conducted the experiments, contributing equally to this work. S. Kremer set up the Monte Carlo Potts model for the simulation of microstructures and was part of scientific discussions. Dr. T. Fuchs helped in designing experiments and was part of scientific discussions. This study was supervised by Prof. J. Janek. The original draft was written by J. Becker and edited by all co-authors.

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Microstructure of electrodeposited lithium and its evolution during cycling when using metal interlayers in “anode-free” solid-state batteries

Juri Becker,^{†a} Luca Schuster,^{†a} Sascha Kremer,^a Till Fuchs^{†b} and Jürgen Janek^{†a}

“Reservoir-free” construction of solid-state batteries could circumvent the handling of reactive lithium metal foils and further increase the energy density. Metallic interlayers could play an important role in the homogenization of the electrodeposited lithium layer by increasing the coverage of the deposit and additionally reducing the size of the lithium grains. To date, the influence of different interlayers and the influence of stripping on the lithium microstructure is still unknown. This work analyzes the influence of gold, silver and bismuth interlayers on the microstructure of electrodeposited lithium layers using electron backscatter diffraction (EBSD) on cross-sections prepared by broad ion beam milling. In addition, partially stripped lithium layers and thus the influence of stripping on the lithium microstructure are analyzed using the mentioned interlayers. Our findings reveal that different interlayer materials result in different lithium microstructures. In addition, stripping also causes a significant change in the lithium microstructure, both in terms of grain size and grain orientation, gaining a deeper understanding of the lithium microstructure and its impact.

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Broader context

The development of safe and durable batteries with high energy density is a prerequisite for the wider use of renewable energies. Solid-state batteries address these demands, particularly through reservoir-free cell designs that eliminate pre-formed lithium metal electrodes by electrodepositing lithium only during the first charging cycle. While this approach simplifies manufacturing and maximizes energy density, controlling the lithium morphology during charging is critical to prevent capacity loss and cell failure. Currently, metallic interlayers, such as gold, silver, and bismuth, are widely used to improve lithium morphology. However, their impact on the resulting lithium microstructure, *i.e.*, grain size and orientation, remains largely unexplored. Moreover, the microstructural evolution of lithium during electrodisolution (discharge) is unknown. Understanding these phenomena is essential, as the microstructure affects the resulting electrochemical performance. Using electron backscatter diffraction on lithium layers electrodeposited in reservoir-free cells, this study demonstrates that metallic interlayers strongly influence the grain size and orientation of lithium. Furthermore, discharging is shown to alter both the grain size and orientation of lithium, too. These results highlight that interlayers not only affect morphology but also the microstructure of electrodeposited lithium, establishing microstructure-driven design principles for the development of advanced solid-state batteries.

Introduction

Solid-state batteries (SSBs) can achieve higher energy and power densities compared to today's commercially available lithium-ion batteries by enabling the use of thin lithium metal electrodes (LMEs).^{1–3} Lithium has a high theoretical capacity of

$q_{\text{th}} = 3860 \text{ mAh g}^{-1}$ and the lowest potential of -3.04 V against the standard hydrogen electrode. Solid electrolytes (SEs) are intensively investigated, as they are often chemically and mechanically more stable against lithium metal and dendrite formation compared to liquid electrolytes.¹

Despite a variety of advantages, the use of LMEs is hindered by the high reactivity of lithium, which leads to formation of passivation layers on its surface.⁴ Minimizing the interfacial resistance in combination with SEs originating from these layers requires costly storage and manufacturing in an inert atmosphere.⁵ Alternative solutions, such as mechanically removing passivation layers or applying high temperature and pressure during cell preparation, also increase costs, making them less desirable.^{6,7}

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To address these challenges, reservoir-free concepts (RFCs), often referred to in literature as “anode-free” cell concepts are being explored.^{8–10} These cells consist of a lithiated positive electrode material, a SE, and current collectors (CCs). No lithium metal is present on the negative electrode side upon assembly. During charging, lithium is electrodeposited at the CC|SE interface on the negative electrode side. This concept eliminates the need to handle lithium metal, thereby simplifies fabrication, and increases energy density further. Additionally, electrodeposition using single-ion conducting SEs produces chemically pure lithium layers, enhancing discharge capacity.^{11,12}

However, RFCs suffer from morphology-driven cell failure during cycling. Inhomogeneous lithium deposition often leads to dendrite formation and poor CC coverage.^{13–15} Lithium stripping can cause pore formation and contact loss,^{16–18} as SEs cannot compensate for volume changes of the electrodes. A promising and widely-investigated strategy to mitigate these issues is the use of interlayers at the CC|SE interface.^{10,19–25} Alloying elements are intensively studied to homogenize the lithium morphology during plating and to mitigate pore formation during stripping.^{10,19,20,23,24,26–28} Gold and silver, in particular, are being investigated because they can increase lithium nucleation density and thereby prevent dendrite formation during lithium electrodeposition when using sulfide SE materials such as $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl).^{10,20,29} Furthermore, they can easily be prepared as chemically pure thin films. Additionally, alloy materials such as bismuth are also being investigated as cost-effective alternatives. In addition, the high Young's modulus of Li_3Bi alloys is expected to prevent dendrite formation.^{27,30} Beyond these effects, interlayers were recently linked to changes in the microstructure of electrodeposited lithium metal, decreasing its grain size and changing from a columnar microstructure to a less ordered one.³¹ Control of the microstructure of lithium is considered a crucial parameter to improve cycling stability of LMEs.^{32–34}

A key parameter of microstructure control is the grain size. Grain boundary (GB) density of electrodeposited lithium should be high, as GBs are predicted to act as fast diffusion pathways potentially preventing void formation during stripping.³⁵ However, for practically relevant lithium layer thicknesses of $\sim 25\text{ }\mu\text{m}$ of lithium (corresponding to $\sim 5\text{ mAh cm}^{-2}$), the deposited lithium typically exhibits large lateral grain sizes in the order of $\sim 100\text{ }\mu\text{m}$, whereas significantly smaller grains with a size of $\sim 1\text{ }\mu\text{m}$ would be more favorable.^{33–35} The introduction of interlayers provides a potential route to tuning this microstructure during electrodeposition.^{31,36}

Prior studies have primarily focused on the lithium microstructure after initial electrodeposition.^{31,33,34} However, its evolution during stripping is of equal importance, as changes in the lithium microstructure, such as preferential orientation, can directly affect stripping parameters such as available capacity and critical current densities. Recently, single-crystalline lithium films were used to show that lithium orientation influences the electrochemical properties of

lithium electrodes.³⁷ Furthermore, it was previously shown that the lithium microstructure changes during deposition.^{33,34} Conversely, stripping could also lead to microstructural changes and thus changes in the stripping properties during operation. Understanding these changes is essential for improving cycling stability.

To address this, we analyzed lithium layers electrodeposited onto various interlayers using Ti|interlayer|LPSCl|Li|Ti model-type RFCs, selecting gold, silver and bismuth as interlayer materials. Titanium was used as CC due to its chemical stability against LPSCl and lithium.³⁸ To gain deeper insight into the microstructural effects of these interlayers, wide cross-sections of the electrodeposited lithium layers were prepared and analyzed using electron backscatter diffraction (EBSD), revealing distinct mechanisms by which different interlayer elements influence the lithium microstructure. Additionally, lithium layers were analyzed after partial stripping of the electrodeposited layer to examine the effects of subsequent lithium stripping on the microstructure. A significant change in the preferential orientation of lithium was observed, especially in cells using pristine metal foils as CCs. Furthermore, the microstructural evolution of the electrodeposited lithium layers after multiple cycles was investigated. The results show that both interlayers as well as (repeated) stripping and plating cause notable changes in the lithium microstructure. Depending on the phase diagram of the lithium–interlayer system and the thickness of the interlayer, alloying interlayers can either completely or partially dissolve in deposited lithium, form intermetallic phases or remain virtually unchanged. We consider the resulting phenomena as a specific case of “electrometallurgy” in batteries.

Experimental

Cell preparation

Cell preparation was performed in a glove box (LABmaster pro, MBraun, Germany) under argon inert gas with residual water and oxygen contaminations $<1\text{ ppm}$, and nitrogen contaminations $<10\text{ ppm}$. Commercial LPSCl (POSCO Chemical Co, Korea) with a particle size of $5\text{ }\mu\text{m}$ was used as SE for the construction of all cells. The counter electrode (CE) was prepared by cutting lithium with a purity of 99.8% (MaTecK Material-Technologie & Kristalle GmbH, Jülich, Germany) from a rod. The passivation layer was then removed mechanically, and the material was pressed by hand between two pouch foils to form a foil with a thickness of approximately $100\text{ }\mu\text{m}$. Finally, circular electrodes were punched out from the foil ($d_{\text{CE}} = 9\text{ mm}$). A titanium foil (Goodfellow Cambridge Ltd, UK, 99.99% purity) with a thickness of $15\text{ }\mu\text{m}$ was used as the working electrode ($d_{\text{WE}} = 10\text{ mm}$). In instances where an interlayer was employed at the working electrode side, a thin film of gold, silver, or bismuth was deposited onto the titanium foil by using an in-house physical vapor deposition (PVD) chamber. For this, titanium foils were clamped inside a mask and a 160 nm thick layer of the desired interlayer material was

deposited onto the titanium with a deposition rate between $0.2\text{--}0.3\text{ nm s}^{-1}$. Cells were assembled using self-made press cell casings made out of brass with a polyether etherketone (PEEK) mantle of 10 mm diameter. The working electrode was placed on one of the steel stamps inside the press cell. Subsequently, 90 mg of LPSCl powder was filled in using a funnel. Both stamps were fixed and sealed using nitrile butadiene rubber (NBR) rings. The powder was then compacted uniaxially once for three minutes at a pressure of 380 MPa. The stamp was then removed on the CE side, a hand-pressed lithium foil was applied with a titanium foil on top and the stamp was reinserted. Finally, the finished press cell was clamped in an aluminum frame and a stack pressure of 15 MPa was applied. Before starting the electrochemical characterization, the cell was left to rest for at least five hours.

Electrochemical characterization

All electrochemical experiments were carried out using potentiostats from BioLogic (VMP3 or VMP300, BioLogic, France). Before characterization, all cells were equilibrated. During the resting period, potentiostatic electrochemical impedance spectroscopy (PEIS) was carried out between 7 MHz and 100 mHz at an amplitude of 10 mV. Subsequently, lithium was deposited using chronopotentiometry (CP). For the deposition of 7.5 mAh cm^{-2} of lithium with and without interlayers, and for the cycling experiments where 4.5 mAh cm^{-2} of lithium were electrodeposited and stripped for 10 cycles, a current density of $150\text{ }\mu\text{A cm}^{-2}$ was used. A current density of $100\text{ }\mu\text{A cm}^{-2}$ was used for the deposition of 10 mAh cm^{-2} and subsequent stripping of 5 mAh cm^{-2} of lithium. To assess the voltage profiles of various alloy phases during the initial stage of lithium electrodeposition onto an interlayer, a lithium deposition *via* CP with reduced current density was conducted. In this case, a current density of $3\text{ }\mu\text{A cm}^{-2}$ was applied until the maximum theoretical lithium areal charge for full lithiation of the interlayer was achieved, followed by lithium deposition. After successful electrodeposition, cells were disassembled for further analysis within the glovebox.

Cryogenic ion-milling

Cross-sections of electrodeposited lithium with and without interlayers were prepared *via* ion beam milling using a Leica EM TIC 3X (Leica Microsystems, Germany) at temperatures below $-100\text{ }^{\circ}\text{C}$. The working electrodes of the samples were detached from the cell stack and transferred into the Leica EM TIC 3X using an inert transfer system (Leica VCT500, Leica Microsystems, Germany). The milling was conducted at an accelerating voltage of 6 kV and an Ar^+ ion current of 2.2 mA.

Electron backscatter diffraction (EBSD)

To minimize passivation reactions, the polished cross-sections were immediately transferred to the SEM using the Leica VCT500. The lithium layer was then analyzed with a symmetry 3 EBSD detector (Oxford Instruments, England) at an accelerating voltage of 10 kV and a probe current of approximately 12 nA. All measurements were conducted at a working distance

of roughly 12.5 mm and a tilt of 70° . If the Kikuchi pattern quality was found to be insufficient, the accelerating voltage was increased to either 15 kV or 20 kV.

Data processing and analysis

Post-processing of the acquired measurement data was carried out using the AZtec Crystal software (Oxford Instruments, England) with the implemented MapSweeper tool. Indexing was done using a Hough algorithm with a resolution of 60 and 11 bands considering the cubic Li ($Im\bar{3}m$) phase. To refine the measured EBSD patterns of lithium and eliminate artifacts like pseudo-symmetries within grains, dynamical template matching, refinement sweeps, and repair sweeps were performed using a master simulation of EBSD patterns.

Grain growth simulations

Grain growth was simulated using a Monte Carlo Potts model, as frequently applied to simulate normal grain growth, the influence of texture, recrystallization, particle pinning, and many other phenomena.^{34,39–51} In our implementation, the lithium metal microstructure is discretized onto a cubic lattice, with each lattice site i , referred to as a Monte Carlo unit (MCU), assigned a grain orientation ϑ_i , represented as an integer between 1 and 240. Grain boundaries are implicitly defined at interfaces between neighboring MCUs i and j with differing orientations ($\vartheta_i \neq \vartheta_j$). The total energy of the system E_{tot} is computed as:

$$E_{\text{tot}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^{\text{nn}=26} \gamma_{ij}^{\text{gb}} (1 - \delta(\vartheta_i, \vartheta_j)),$$

where γ_{ij}^{gb} is the energy of a unit of boundary between MCU i and one of its 26 nearest-neighbor (nn) MCUs j (6 first nearest, 12 second nearest, and 8 third nearest-neighbors). N is the number of lattice sites, and $\delta(\vartheta_i, \vartheta_j)$ is the Kronecker delta, yielding 1 if $\vartheta_i = \vartheta_j$ and 0 otherwise. In practice the grain boundary energy, thus γ_{ij}^{gb} , is a function of the misorientation angle of adjacent grains.^{41,49,52} Anyhow, the orientation dependence of γ_{ij}^{gb} was neglected ($\gamma_{ij}^{\text{gb}} = \gamma_{\text{const}}^{\text{gb}}$), resulting in curvature driven grain growth.^{39,46} Grain growth proceeds *via* a Monte Carlo algorithm: a randomly selected MCU attempts to adopt the orientation of one of its 26 neighbors. The new configuration is accepted with a probability P based on the energy change ΔE_{tot} between the new and the old state:

$$P = \begin{cases} 1 & \text{if } \Delta E_{\text{tot}} \leq 0 \\ \exp(-\Delta E_{\text{tot}}/T_s) & \text{if } \Delta E_{\text{tot}} > 0, \end{cases}$$

Here, T_s is the simulation temperature, which is a technical parameter that determines the acceptance probability for state changes that increase the total energy of the system.⁵² We set $T_s = \gamma_{\text{const}}^{\text{gb}}$ throughout all simulations. A full Monte Carlo step (MCS) consists of N such reorientation attempts. For a domain size of $30 \cdot 250 \cdot 250$ MCUs, this corresponds to $\approx 2 \cdot 10^6$ updates per MCS.

To investigate the influence of the lithium film thickness, we followed an approach used by Zöllner *et al.*:^{41–43} free surfaces

were introduced as boundary conditions at the top and bottom surfaces (parallel to the CC|SE interface), such that MCUs on the surface have only 17 instead of 26 neighbors. As for all other simulations, periodic boundary conditions were used in the other two directions. Similar to our previous work,³⁴ the influence of the SE and CC interfaces was considered by attaching static polycrystalline layers to the lithium domain. These layers act as domains with fixed orientations and do not evolve during the simulation. The interfacial energy γ_{ij}^{int} between a lithium MCU i and an adjacent fixed MCU j is treated analogously to γ_{ij}^{gb} , yielding $\gamma_{\text{const}}^{\text{gb}}$ if $\vartheta_i \neq \vartheta_j$ and 0 otherwise. Hence, these fixed layers may be understood as thin lithium layers on top of the SE/CC that are forced into distinct low-energy orientations with respect to the SE/CC grains or SE/CC grain itself.

To study the effect of secondary-phase particles, we followed another common approach from the literature⁵¹ that is similar to the one used to incorporate the SE/CC influence: immobile spherical inclusions with a diameter of 3 MCUs were introduced. These MCUs were assigned a unique, fixed orientation/integer (250), which cannot be adopted by the lithium MCUs. This enforces a constant interface energy $\gamma_{ij}^{\text{int}} = \gamma_{\text{const}}^{\text{gb}}$ at the particle surface. The same strategy was used to explore the influence of interfacial roughness by placing two roughened layers (also with fixed orientation 250) adjacent to the lithium film.

To simulate large 3D structures within a feasible runtime, we adopted an approach discussed in more detail by Wright *et al.*⁴⁸ that enables efficient parallelization of some computation steps on a GPU. For parallelization, the lattice is partitioned into 8 sublattices with non-interacting MCUs, that do not share neighbors. In each update step, one sublattice is randomly selected, and all its MCUs are updated in parallel. Repeating this 8 times completes one MCS. All simulations were carried out in Python. Computationally expensive tensor operations were implemented using Pytorch.⁵³ In Fig. S1, the simulation approach and boundary conditions are schematically shown.

It is important to note that the Potts model used operates in arbitrary units, neglects the influence of electrodeposition kinetics, and does not provide direct access to physical time, length, or energy scales. Additionally, the Potts model relies on simplified, often arbitrary update rules and energy definitions and the simulated grain microstructure is influenced by the underlying simulation lattice (lattice pinning). Consequently, the results should be interpreted as qualitative insights into the evolution of curvature driven grown grain structures under special geometric and interfacial constraints (*e.g.*, thin-film geometries, pinning, substrate interaction, interface roughness), rather than quantitative predictions of experimental grain growth kinetics.

Results and discussion

Influence of interlayers on the resulting lithium microstructure

To study the influence of interlayers on the lithium electrodeposition and resulting microstructure, a Ti|interlayer|LPSCl|Li|Ti model system was used, as schematically depicted in Fig. 1a.

Additionally, as reference, cells without interlayer, *i.e.*, Ti|LPSCl|Li|Ti were also analyzed. The voltage profiles for lithium deposition using gold, silver and bismuth as interlayer as well as the titanium reference are shown in Fig. 1b. In all cases, an areal charge of 7.5 mAh cm⁻² (nominally 37.5 μm) was deposited at a current density of 150 $\mu\text{A cm}^{-2}$. A microstructural analysis of the electrodeposited lithium layers was conducted using EBSD on prepared cross-sections. Representative regions from the large area cross-sections are given in Fig. 1c.

Similar to steel, no additional lithium loss could be seen for titanium in CTTA experiments (see Fig. S2). Titanium³⁸ has the advantage that, unlike steel, it is a chemically pure metal. For the titanium foil without interlayer, the voltage profile first passes through a minimum, which is associated with lithium nucleation.⁸ Once the voltage stabilizes around 10 mV, agreeing with the IR drop of the cell, the previously formed lithium nuclei grow in size and the analyzed grains in Fig. 1b form.

Gold has already been established as a suitable interlayer material, due to its chemical stability and its ability to form a stable Li_xAu alloy during lithiation, which promotes uniform lithium electrodeposition.^{10,13,20,31,54} The voltage profile when electrodepositing lithium on a gold layer shows only two plateaus at 260 mV and 120 mV, despite passing through more phases in the phase diagram. As the potentials of the other phases are very close to each other, the transitions might be masked by the kinetics and the corresponding overpotentials. Furthermore, the relatively high current density of 150 $\mu\text{A cm}^{-2}$ could lead to a kinetic inhibition of some phases, which is why they are not observed here, despite being predicted by the phase diagram. In addition, some of the lithium-gold alloy phases appear to be unstable up to the δ -phase.^{26,55} After reaching a negative potential, lithium nucleates, as indicated by a small minimum in the voltage profile.³¹ To gain further insight in the lithiation process, the current density was decreased to 3 $\mu\text{A cm}^{-2}$ in a second cell. Furthermore, coulometric titration (CT) experiments coupled with an electrochemical impedance analysis were conducted on a third cell. Here, an additional plateau at 20 mV appears (see Fig. S3 and S4 and Note S1), corresponding to the Li₃Au|Li₁₅Au₄ two-phase region, underlining the kinetic inhibition of certain phases. At this point, we like to highlight that alloys investigated in binary phase diagrams are in most cases produced from a melt of the two constituent metals, while alloy formation at room temperature has often not been systematically investigated and is frequently based on data extrapolated from high temperatures. Therefore, their reliability at room temperature is uncertain and must be considered when interpreting phase stability and alloy formation.

Silver was also used as an interlayer material, due to its chemical stability and the formation of a stable Li_xAg alloy.^{10,19,28,31,54} This and faster lithium diffusion was shown to lead to a uniform lithium deposition and an increased cycle life of RFCs. The voltage profile when electrodepositing lithium on a silver layer, shows virtually no voltage plateaus, even if expected from the phase diagram.^{31,56} Here, again, kinetic limitations are likely the reason, as additional voltage plateaus

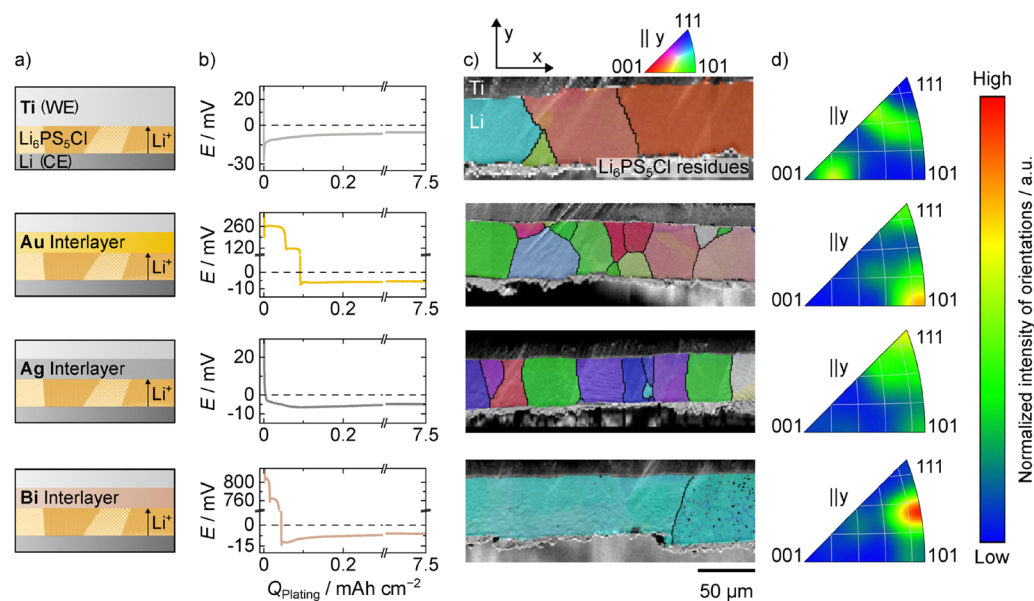


Fig. 1 Electrodeposition of lithium using (a) different interlayer materials. (b) Voltage profiles of the respective cell systems ($T = 25\text{ }^{\circ}\text{C}$, $j = 150\text{ }\mu\text{A cm}^{-2}$). As schematically depicted, titanium was used as reference (top row) and gold (2nd row), silver (3rd row) and bismuth (4th row) were used as interlayer materials. (c) Microstructure of the electrodeposited lithium layers using the different interlayer materials. The IPF maps are given parallel to the y -direction as indicated above. The shown scalebar represents $50\text{ }\mu\text{m}$ in all cases. (d) IPFs of the analyzed cross-sections showing the distribution of the orientation of all analyzed grains. The IPFs are given parallel to the y -direction. Please note that the IPFs were created based on the entire analyzed cross-section, which is shown in the SI.

can be resolved when decreasing the current density to $3\text{ }\mu\text{A cm}^{-2}$ as well as in the CT experiments (see Fig. S3 and S4). Interestingly, the voltage drops directly below 0 V without an additional (nucleation) overpotential.

Lastly, bismuth was chosen as interlayer material due to its affordability, and electrochemical activity, forming a Li_xBi alloy during lithiation with improved lithium diffusion.^{57,58} It could therefore be a cost-effective alternative to more established alloying interlayer materials such as gold or silver. The voltage profile when electrodepositing lithium on a bismuth layer, shows two plateaus at 800 mV and 760 mV before the potential drops below 0 V . These two voltage plateaus correspond to the two 2-phase regions Bi|LiBi and $\text{LiBi|Li}_3\text{Bi}$ in the Li-Bi phase diagram.⁵⁶ The experiment was repeated with a lower current density of $3\text{ }\mu\text{A cm}^{-2}$ and *via* CT. The potential profile can be seen in Fig. S3 and S4. After dropping below 0 V , electrodeposition of lithium metal takes place after passing through a small nucleation minimum.

Microstructural analysis of the electrodeposited lithium layer on the pristine titanium foil reveals large columnar grains with almost all grain boundaries being perpendicular to the SE interface with some truncated grains forming at the Li|LPSCl interface. This microstructure is in good agreement with previously studied lithium layers electrodeposited on various CC|SE interfaces.^{33,34} As the grain width is determined by the electrodeposited lithium layer thickness,³⁴ the large grain size

in this case, suggests similar trends for lithium layers electrodeposited at Ti|LPSCl interfaces. Another similarity is that the grown lithium grains do not appear to exhibit a pronounced preferential orientation, as can be seen in the inverse pole figures in Fig. 1d. However, the lithium microstructure on titanium foil appears to be slightly more distorted locally than on *e.g.* steel foil previously used.³⁴ This could be due to the different microstructure and larger average grain sizes of the titanium foil ($\bar{A}_{\text{grain}} \approx 150\text{ }\mu\text{m}^2$, see Fig. S5) compared to steel foil ($\bar{A}_{\text{grain}} \approx 0.8\text{ }\mu\text{m}^2$).³⁴ A detailed discussion of the influence of the substrate on the resulting lithium microstructure will follow below. For the inverse pole figures in parallel to the x - and z -axis, the reader is referred to Fig. S6 along with the full cross-sections displayed in Fig. S7.

The microstructural analysis of the lithium layer electrodeposited on a gold interlayer reveals a mix of thin columnar grains, multiple smaller grains at the Ti|Li interface and stacked grains as can be seen from the excerpt shown as well as the full cross-section in Fig. S8. While some columnar grains can be seen, the lithium microstructure deviates significantly from a mere columnar form, exhibiting more substantial deviations than what is observed on bare titanium CCs or on steel and copper CCs used in recent studies.^{33,34} These results are in line with those of Haslam and Fuchs *et al.* who found a similar microstructure of lithium electrochemically deposited at Cu|LLZO interfaces with a gold interlayer,³¹ despite the

different CC and SE. Thus, we conclude that the microstructure is influenced primarily by the interlayer and is apparently less dependent of CC and SE. Interestingly, making use of the better statistics due to large cross-sections, a preferred orientation in the $\langle 101 \rangle$ directions parallel to the y-axis is indicated in the inverse pole figure in Fig. 1d for the gold interlayer. For the inverse pole figures in parallel to the x- and z-axis, the reader is referred to Fig. S6. The full cross-section can be seen in Fig. S8.

For a silver interlayer, the microstructural analysis of the lithium layer reveals a mostly columnar structure, but with much thinner grains compared to the lithium grains electrodeposited without an interlayer. These differences in the aspect ratio, *i.e.*, the ratio of grain height to grain width, are summarized for all electrodeposited lithium layers in Fig. S9. This was already indicated in a previous study³¹ and is now proven here using the wide cross-sections. Additionally, the statistical analysis reveals that lithium grains exhibit a preferred growth direction when electrodeposited on a silver interlayer. In contrast to gold, the $\langle 111 \rangle$ direction parallel to the y-axis seems to be predominant in the case of silver as can be seen from Fig. 1d. For the inverse pole figures in parallel to the x- and z-axis, the reader is referred to Fig. S6. The full cross-section can be seen in Fig. S10.

Lastly, when using bismuth as interlayer, a columnar lithium microstructure can be found, similarly to the pristine titanium foil and the silver interlayer. However, unlike when other interlayer materials are used, the lithium grains are significantly larger, with a width even larger compared to that of the lithium layer electrodeposited on pristine titanium foil. The lithium grains show a preferred orientation in the $\langle 101 \rangle$ and $\langle 111 \rangle$ direction parallel to the y-axis as can be seen from the

inverse pole figure in Fig. 1d. Interestingly, one grain stands out, with a width of $811 \mu\text{m}$ (compare Fig. S11). The possible cause of its origin is discussed later in this chapter.

One important benefit of the wide cross-sections prepared *via* ion beam milling in this work, is the possibility of quantitative comparison of the lithium microstructures in each case. Therefore, the whole cross-sections spanning several millimeters (see Fig. S7, S8, S10 and S11) of the lithium layers electrodeposited with and without interlayer were analyzed in terms of their layer height and grain width. The results are summarized in a box plot in Fig. 2a. In addition, energy dispersive X-ray spectroscopy (EDS) measurements were carried out in the case of the bismuth and silver interlayers to obtain information on the distribution of the interlayer materials. For gold, an EBSD measurement was performed on particles found within the electrodeposited lithium layer. The results are shown in Fig. 2b–d.

As shown in the upper part of Fig. 2a, the layer thickness deviates between the measured samples, even though the same areal charge of 7.5 mAh cm^{-2} was electrodeposited in all cases. This is due to changes in the coverage of the CCs used, as can be seen in Fig. S12. While there are still pristine areas for titanium and bismuth, the coverage in the case of gold and silver is close to 100%. This increase in coverage for gold and silver interlayers aligns well with recent studies on interlayers,^{10,13,31} and leads to a reduced layer height compared to lithium plated at pristine CC metal foils.

Notably, the deposited lithium on a bare titanium CC exhibits the highest layer thickness, corresponding to the lowest degree of coverage. This could be attributed to the crystallographic mismatch between titanium (hexagonal) and lithium

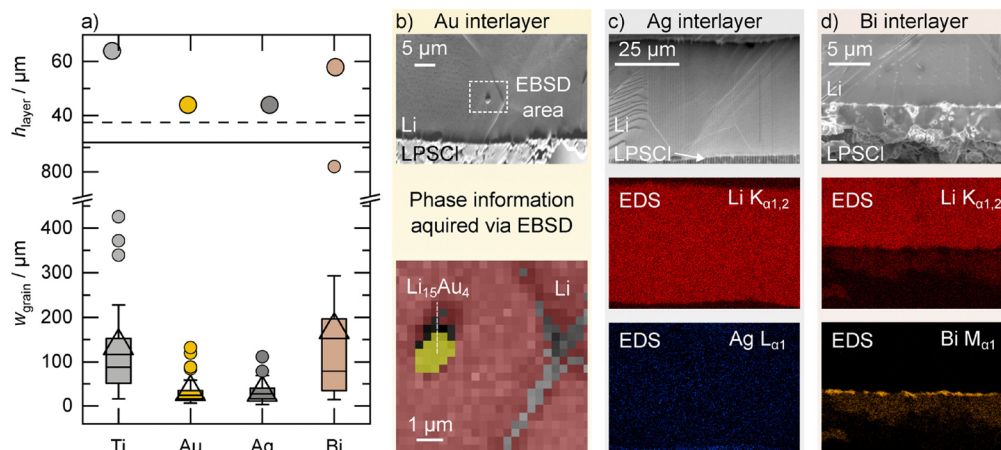


Fig. 2 Summary of the results from all analyzed lithium layers electrodeposited using different interlayers. (a) The average lithium layer thickness is shown in the upper part of the graph. The calculated (expected mean) height for 7.5 mAh cm^{-2} of $37.5 \mu\text{m}$ is depicted with a dotted line. The grain width of the analyzed lithium grains is depicted in the box plot underneath. Here, 18 grains were analyzed in the case of electrodeposition on a pristine titanium foil, 11 for the bismuth interlayer, 64 for the gold interlayer and 70 for the silver interlayer, respectively. The average is marked with a triangle inside each box. Outliers (interquartile range factor = 1.5) are marked with points colored in the same way as the respective box. (b) EBSD analysis of the lithium layer electrodeposited using a gold interlayer (top: SEM image). (c) EDS analysis of a lithium layer electrodeposited using a silver interlayer (top: SEM image). (d) EDS analysis of the lithium layer electrodeposited using a bismuth interlayer (top: SEM image).

(cubic),⁵⁹ which may inhibit widespread nucleation during the initial stages of deposition. The average grain width in the case of the pristine titanium foil is with 136 μm roughly twice as high as the layer height. This is also reflected in the aspect ratio of the grains, which is shown in Fig. S9 and is approximately 0.5 (ratio of height to width). This is in good agreement with previous results on electrodeposited lithium layers at a steel|Li₆PS₅Cl interface and indicates a curvature driven normal grain growth, as postulated by C. V. Thompson.^{34,60}

In the case of the gold interlayer, the average grain width decreases to 30 μm and is therefore significantly lower compared to the pristine titanium foil. At this point we would like to note that the layer thickness was shown to also influence the resulting grain width.³⁴ As the lithium layer electrodeposited with an gold interlayer is thinner compared to the one electrodeposited on a pristine titanium foil, this might further increase the difference in grain width between the two samples. However, the 4-fold decrease in grain width cannot solely be attributed to changes in the layer thickness. This is supported by the changed grain distribution and the higher aspect ratio of ≈ 1.3 .

In the case of the silver interlayer, the average grain width also decreases significantly to 30 μm . As in the case of gold, the thickness of the lithium layer deposited on the silver interlayer is significantly lower than the layer thickness on the bare titanium foil, which highlights the higher CC coverage during the deposition when using gold and silver as interlayer materials. Interestingly, the average grain width with silver interlayer is close to the one with gold interlayer. Since both lithium layers show also approximately the same thickness, this could indicate that the layer thickness effect mentioned above is also present when using interlayers. However, as with gold, the reduced grain size compared to the lithium layer deposited on pure titanium cannot be attributed solely to a thickness effect, but an additional influence of the silver interlayer is evident, changing the grain distribution and increasing the aspect ratio to ≈ 1.3 .

Interestingly, the layer height of lithium deposited on a bismuth interlayer is only slightly lower than that of lithium deposited on titanium. It might be expected that the interlayer would promote lithium nucleation and lead to a higher degree of coverage, as is the case for gold and silver. However, this is not observed for bismuth. Also, in the case of the bismuth interlayer, the average grain width is with 170 μm even higher as in the pristine titanium case, even though the layer thickness is slightly lower. The large grain mentioned above, is marked as the only outlier with a width of 811 μm . The aspect ratio of the bismuth sample, at ≈ 0.6 , is also very close to the value for the bare titanium foil.

In general, it could be shown that the microstructure of electrochemically deposited lithium is modified with the help of interlayers. Bismuth tends to increase the size of the lithium grains present, while silver and gold lead to a significant reduction in the grain size. The reduced grain size could improve the stripping behavior of the electrode, as is shown by simulation results.³⁵ This improvement is attributed to the

higher density of grain boundaries, which serve as fast diffusion paths for lithium atoms. According to the simulations, grain sizes below 1 μm are required to achieve current densities exceeding 1 mA cm^{-2} .³⁵ To gain more insight into the underlying mechanisms of the different alloying materials, the prepared cross-sections were further analyzed using EDS and EBSD. These analyses provide information about the position of the interlayers and their chemical composition across the interface, revealing that all three interlayer materials are located at different positions/regions within the cross-section. For gold, small clusters were detected predominantly near the Ti|Li interface in Fig. 2b, originating from the evaporated gold interlayer. EBSD revealed Kikuchi patterns corresponding to the Li₁₅Au₄ crystal structure. Although not visible in the voltage profile during electrodeposition, the alloy appears to form over time, indicating kinetic limitations during electrodeposition. These dispersed Li₁₅Au₄ particles likely affect lithium grain growth through a mechanism similar to Zener pinning: grain boundaries encountering these clusters experience drag forces that slow down their migration and hinder further grain coarsening.⁶¹

In contrast, EDS analysis of lithium deposited on a silver interlayer in Fig. 2c shows a homogeneous silver distribution within the lithium layer. According to the Ag–Li phase diagram, silver can dissolve into lithium up to about 1 at% at room temperature.^{22,62} Given the initial 160 nm thickness of the silver layer, its complete dissolution would occur beyond an areal charge of approximately 4.2 mAh cm^{-2} of lithium, which is less than the total amount of deposited lithium here. Therefore, a homogeneous solid solution of silver in lithium is expected. As silver is dissolved within the lithium lattice, the high density of grain boundaries may result from altered mechanical properties rather than Zener pinning. The dissolved silver could induce lattice strain throughout the lithium layer, modifying its surficial energy and impeding grain growth without silver accumulating at the Ti|Li interface. This energy change is expected, as lithium with 1 at% silver should have a slightly lower melting temperature than pure lithium.^{31,62} To analyze a possible change in crystal structure, a Li(Ag) solid solution with 0.7 at% silver in lithium was produced from a melt and examined using X-ray diffraction (XRD). As can be seen in Fig. S13 and Note S2, consistent with the literature,⁶² a decrease in the lattice constants of the lithium lattice by 0.21% and thus a lattice contraction is detected. Please note that the sample examined by XRD was produced from melt and not by electrodeposition; nevertheless, the results qualitatively show the effect of dissolved silver in a lithium host lattice.

In case of bismuth, a bismuth layer is found at the LPSCl interface in Fig. 2d, suggesting that lithium begins depositing behind the interlayer only after alloy formation is complete. This in turn suggests that lithium must pass through the Li₃Bi layer before accumulating at the Li₃Bi|Ti interface, and that bismuth probably has a low diffusion coefficient in lithium. This finding may help explain the low coverage found in Fig. 2a and Fig. S12: despite the presence of bismuth, lithium deposition occurs in contact with titanium. Since bismuth does not

dissolve into lithium, the deposited lithium forms a pure layer without remnants of the bismuth interlayer. However, unlike the deposition of lithium on a bare titanium CC, the presence of the bismuth-rich interlayer on the LPSCl prevents interaction of the lithium with the SE, which, as previously found, affects the resulting lithium microstructure.³⁴ It is noteworthy that separation of the two reactive species, *i.e.*, lithium and LPSCl, also influences SEI formation.⁵⁶

Simulations of factors influencing lithium microstructure

Building on our experimental observation that different interlayers result in different lithium microstructures, we use simulations to gain a qualitative understanding of how microstructures are influenced under varying boundary conditions in the thin-film geometry. Since various influencing factors can always occur simultaneously in the experiment, we apply a three-dimensional Monte Carlo Potts model to separate the effects of layer thickness, particle fraction, substrate grain size, and substrate roughness. In these simulations, deposition kinetics are neglected. Instead, a film is deposited instantaneously to a certain thickness and its microstructural evolution is then observed over time. The results are summarized in Fig. 3.

Fig. 3a investigates the influence of the layer thickness on the resulting lithium microstructure. As already visible from the 3D microstructures and the 2D cross-sections underneath, the average grain width increases when increasing the layer thickness from 10 Monte Carlo units (MCU) to 30 MCU. The grain height evolution further reveals that all layers develop columnar structures during the simulation, as reflected by the fact that the average grain height approaches and eventually equals the respective layer thickness (10, 20, and 30 MCU). A distinct change in the slope of the grain width growth with time occurs once the grain height matches the layer thickness. This is attributed to a reduction in curvature-driven grain growth along the height direction: once grains reach the full height,

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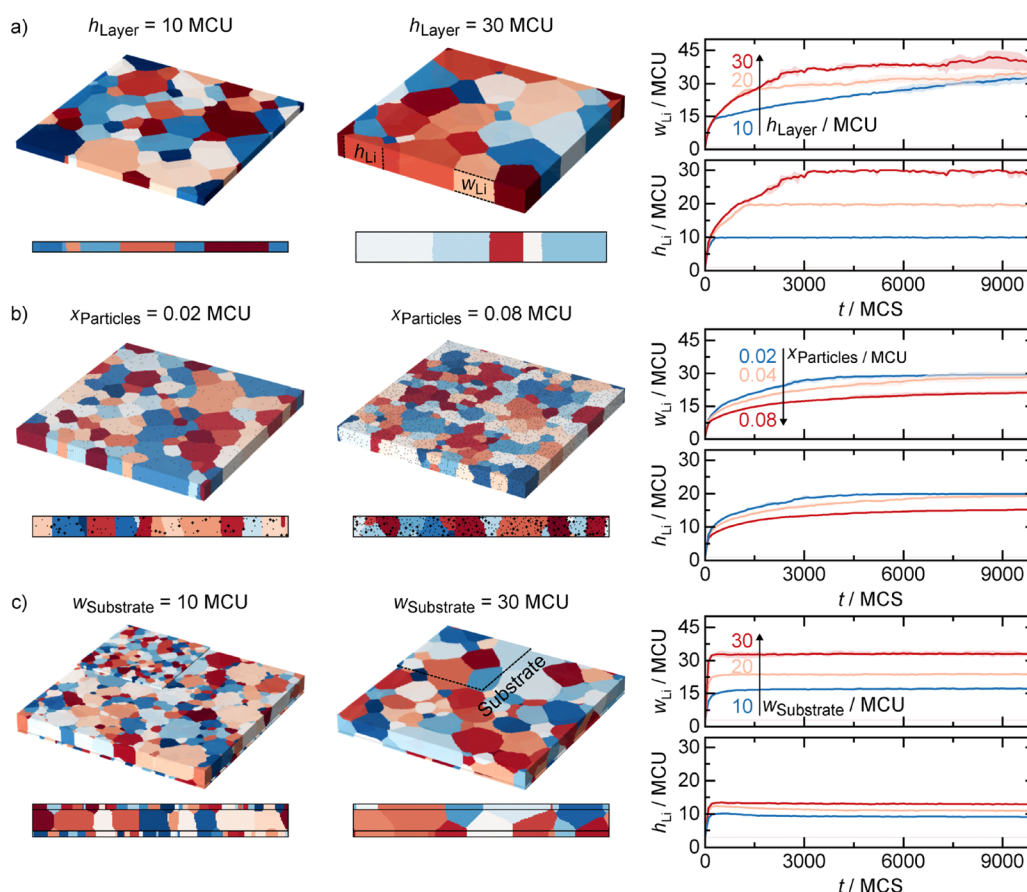


Fig. 3 Simulation results of lithium microstructure evolution under different conditions: (a) effect of lithium layer thickness, (b) secondary particle content and (c) substrate grain size. Each panel shows two 3D microstructures along with two 2D cross-sections underneath. On the right, the evolution of the average grain width (w_{Li}) and height (h_{Li}) versus simulation time in Monte Carlo steps (MCS) is shown.

further growth in that dimension no longer contributes to energy minimization. Consequently, growth continues only in-plane, driven by curvature reduction in that direction, resulting in a slower overall growth rate. Although grain growth slows down, it does not come to a complete stop in 3D. With sufficient simulation time and without other interactions, the system would ultimately develop into a single grain, which is a key difference from previous 2D simulations.³⁴ For the following simulations of the other influencing factors, the layer thickness is set to 20 MCU.

Fig. 3b shows the effect of secondary particles, mimicking the role of alloy inclusions in the experiment or other secondary phases within the lithium layer. Even a small fraction of 0.02 MCU reduces the average grain width compared to the pristine 20 MCU layer, and increasing the fraction to 0.08 MCU further suppresses grain growth. In this case, grains fail to develop into fully columnar structures, as reflected by the temporal evolution of grain width and height: at 0.08 MCU, the grain height no longer reaches the full layer thickness, indicating the presence of multiple stacked grains. This stagnation results from grain boundary pinning at the particles, which blocks curvature-driven growth in both height and in-plane directions and leads to a plateau in grain size over time.

Fig. 3c examines the influence of substrate microstructure. The attached substrates with average grain sizes of 10 MCU and 30 MCU reveal a reduction in lithium grain size compared to the case without substrate-layer interaction. Here, suppression of columnar growth originates from grain boundary pinning at the substrate rather than dispersed particles. Larger substrate grains result in fewer pinning sites, allowing larger lithium grains. This finding is particularly relevant for bismuth: the presence of a Li_3Bi interlayer at the SE|Li interface alters the substrate and, similar to substrate grain boundaries in the model, is expected to provide additional pinning sites that constrain lithium grain growth. For more information on the substrate microstructure, the pristine interlayers were analyzed by SEM and EBSD (see Fig. S14 and Note S3). All interlayers exhibit nanocrystalline structures with grain diameters below 200 nm and preferred orientation. After lithium plating, the lithium grains are therefore orders of magnitude larger than the substrate grains, suggesting that the layer thickness effect dominates and largely overshadows substrate-related effects. It should be noted, however, that the substrate microstructure may further evolve due to alloy formation. Future work should systematically tailor the substrate grain size to match lithium grain size, ideally using non-alloying substrates to isolate substrate effects, while separately addressing the microstructural evolution of alloying substrates during phase formation.

In addition to the microstructure of the substrate, its roughness can also influence the resulting lithium microstructure, as additional simulations in Fig. S15 show. In the experiment, the different substrate roughness could therefore further influence the lithium microstructure, particularly for bismuth, but also for all interlayers, as they were initially deposited onto the titanium foil. Furthermore, these two substrate effects could explain the slight differences mentioned above in the

microstructures of lithium on steel compared to lithium on titanium. These results highlight the impact of substrate selection on the resulting lithium microstructure. Please note that due to interactions with the substrate, simulation artefacts such as single-voxel grains may occur; therefore, only grains exceeding three voxels in both height and width were considered in the averages shown for the substrate microstructure simulations.

Overall, the simulations demonstrate that layer thickness, secondary particles (*i.e.*, inclusions) and the substrate can significantly affect grain growth dynamics and the resulting lithium microstructure. Enhanced layer thickness leads to larger grains and columnar structures, whereas inclusions and substrate interactions introduce pinning effects that hinder growth and the formation of columnar grain structures. Importantly, the results highlight that interactions with inclusions and the substrate are inevitable in real systems, as otherwise grain growth in 3D will proceed until a single grain is formed due to residual grain curvature.

Microstructural evolution during lithium stripping

Having shown that interlayers affect the lithium microstructure during the initial deposition, the question remains how the microstructure evolves during subsequent stripping of the electrodeposited lithium layer, both in case of pristine CC foils as well as CCs with an interlayer. Previous work has shown that the microstructure of (pure) lithium is largely determined by the layer thickness.^{33,34} Conversely, lithium stripping is expected to lead to a reduction in the average grain width. However, this would mean that existing grains would have to disintegrate, or new grain boundaries would have to be created, which would lead to an increase in energy in the system. Clearly, our knowledge on these microstructure issues is yet poor, and it is important to investigate the microstructural development of lithium during cycling in more detail.

To analyze the microstructural evolution of lithium during and after stripping, a lithium layer with an areal charge of 10 mAh cm^{-2} (nominally $50 \mu\text{m}$) was initially electrodeposited. To reduce the risk of dendrite formation at this high areal charge, the used current density was decreased to $100 \mu\text{A cm}^{-2}$. After successful electrodeposition, 5 mAh cm^{-2} of the 10 mAh cm^{-2} were stripped again using a current density of $100 \mu\text{A cm}^{-2}$ and the remaining lithium layer was analyzed using EBSD in the same way as before. Results of the EBSD analysis are summarized in Fig. 4. The different model systems are schematically shown in Fig. 4a. Additionally, a part of the respective IPF maps and an inverse pole figure, summarizing the orientation of all detected lithium grains is given.

In accordance with Fig. 1, the voltage profiles in Fig. 4b show that in all cases an areal charge of 10 mAh cm^{-2} could be deposited without indication of dendrite formation. Interestingly, in this case additional plateaus can be seen in the voltage profile for the silver interlayer. This could be due to the lower deposition current density of $100 \mu\text{A cm}^{-2}$ instead of $150 \mu\text{A cm}^{-2}$. The voltage profile during subsequent stripping of 5 mAh cm^{-2} looks similar in all cases. This was to be

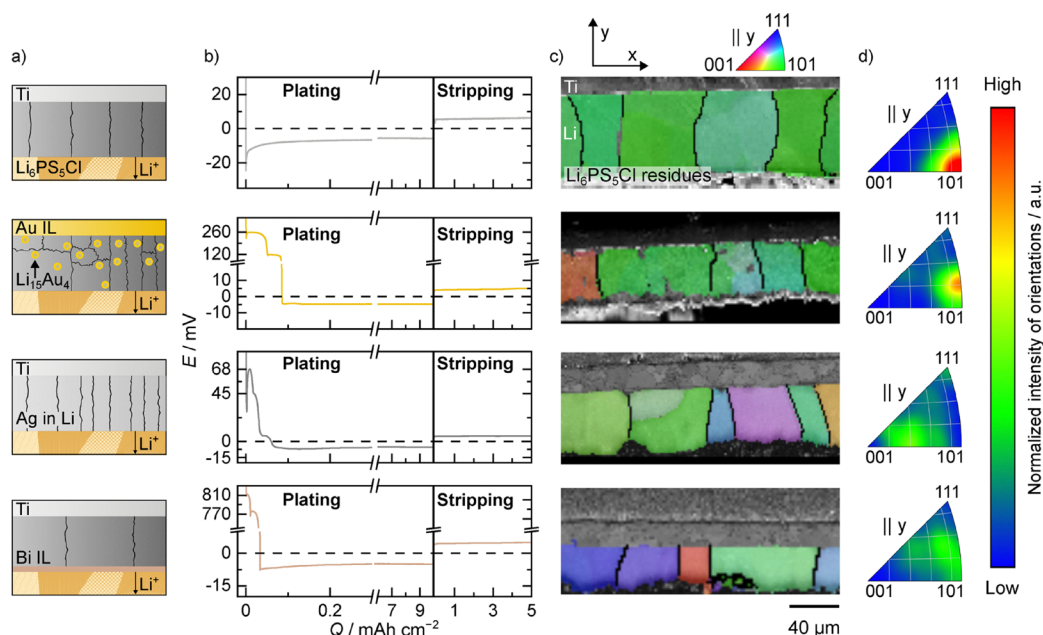


Fig. 4 Microstructure of electrodeposited lithium after partial stripping. (a) Cell setup used for stripping after electrodepositing 10 mAh cm^{-2} of lithium. The location of the interlayers is indicated schematically. (b) Potential profile during electrodeposition of 10 mAh cm^{-2} lithium on the left and subsequent stripping of 5 mAh cm^{-2} on the right. (c) Microstructure of the partially stripped lithium layers using the different interlayer materials. The IPF maps are given parallel to the y -direction as indicated above. The shown scalebar resembles $40 \mu\text{m}$ in all cases. (d) IPFs of the partially stripped lithium layers, showing the distribution of all measured grain orientations. Please note that the IPFs were created based on the entire analyzed cross-section, which is shown in the SI.

expected as no de-alloying takes place and a significant amount of 5 mAh cm^{-2} lithium remains after stripping.

The inverse pole figure maps reveal significant microstructural changes during the stripping process. For the pristine titanium foil, the columnar lithium grain microstructure remains intact, similarly to the electrodeposited lithium layer in Fig. 1. However, after stripping nearly all grains exhibit the same orientation, with the $\langle 101 \rangle$ directions aligned parallel to the y -axis. This uniform orientation is indicated by the green color of the grains in Fig. 4c and is confirmed by the inverse pole figure, shown in Fig. 4d, which considers the entire cross-section (see Fig. S16). For the inverse pole figures in parallel to the x - and z -axis, the reader is referred to Fig. S17. Interestingly, this preferred orientation is the orientation for which Chen *et al.* reported the highest critical current density, which the authors attribute to the lowest migration diffusion barrier and the lowest Young's modulus.³⁷ Furthermore, when comparing the lithium layer with an areal charge of 7.5 mAh cm^{-2} and the one with an absolute areal charge of 5 mAh cm^{-2} (10 mAh cm^{-2} plated and 5 mAh cm^{-2} stripped), a decrease in the average grain size is seen in Fig. S18. This trend is confirmed when this sample is compared with others subjected to single-step plating for areal charges of 5 mAh cm^{-2} and 10 mAh cm^{-2} (see Fig. S19). Notably, both samples with an absolute areal charge of 5 mAh cm^{-2} exhibit comparable average grain sizes, despite

their different cycling histories. Accordingly, stripping following plating leads to a decrease in the average grain size; apparently *vice versa* to the previously observed grain growth with increasing layer thickness.

For the gold interlayer, the overall decreased grain size and the more distorted lithium microstructure compared to the pristine titanium foil is retained. Here, too, there appears to be a change in the grain orientations with a preference close to the $\langle 101 \rangle$ direction, as can be seen from the excerpt of the analyzed cross-section shown in Fig. 4c and the inverse pole figure in Fig. 4d. Note that the inverse pole figure takes into account the whole cross-section displayed in Fig. S20. In contrast to titanium foil, however, there appears to be an increase in the average grain size during the stripping process, and not the decrease in grain size clearly observed with titanium (revisit Fig. S18).

In the case of silver, similar to gold, a reduced average grain size can be seen compared to the pristine titanium foil. A change in grain orientation is not as obvious as in the previous samples. Although the orientation of the 7.5 mAh cm^{-2} lithium layer plated on silver differs from the one shown here, no preferential orientation is recognizable after stripping on the whole cross-section in Fig. S21. As with gold, a higher average grain size can be seen in the box plot in Fig. S18 in the case of the stripped silver sample (10 mAh cm^{-2} plating followed by

5 mAh cm⁻² stripping) compared to the sample solely plated (7.5 mAh cm⁻² plating). In addition, another lithium layer with an areal charge of 7.5 mAh cm⁻² was deposited onto a silver interlayer, of which 3 mAh cm⁻² was then stripped again (see Fig. S22). Here, too, the average grain size is slightly higher for the sample which was partially stripped compared to the one subjected to a single-plating step.

Finally, the stripped lithium layer with a bismuth interlayer shows a more distorted microstructure compared to the bismuth sample previously analyzed after electrodeposition as well as the pristine titanium foil samples. While a preferential orientation of the lithium layer solely plated on a bismuth interlayer could be found (compare Fig. 1) – which is mainly due to very large individual grains – no preferential orientation of the stripped lithium layer with a bismuth interlayer is visible when analyzing the full cross-section in Fig. S23. Furthermore, a significant decrease in the average grain size of the lithium layer is visible when comparing the sample which was stripped after plating with the solely plated one using a bismuth interlayer, as can be seen in the box plot in Fig. S18. Interestingly, there are no longer any particularly large grains to be found. On the contrary, there is an area within the lithium layer that appears to be particularly disordered and to consist of many small grains. Please note that these particularly small grains were not included in the quantification of the mean grain width, as neighboring grains cannot always reliably be distinguished from one another in this area with the chosen measurement resolution.

In addition to the different microstructures found after electrodeposition, the choice of interlayers also appears to influence stripping performance and lithium microstructure evolution. For the pristine titanium foil and the titanium foil with a bismuth interlayer, unlike gold and silver interlayers, the average grain size decreases again during stripping, likely because the lithium layers remain chemically pure. Thus, it appears that the recently found layer thickness effect for lithium is reversible, potentially driven by external pressure forming new grains and grain boundaries during stripping. On the other hand, in the case of gold, Li₁₅Au₄ particles are found inside the lithium layer, while in the case of silver, dissolved silver is present. These lithium layers are therefore no longer chemically pure as the first plating step causes alloying with the interlayer element. Already during the investigation of the deposited lithium layers, it could be shown that these interlayer elements significantly change or suppress the grain growth within the lithium layers. Accordingly, the results obtained here suggest that the microstructural changes taking place in the pure lithium layers during stripping are suppressed in a similar way. Under this assumption, the microstructure of the lithium layers is “frozen” at an areal charge of 10 mAh cm⁻² and thus an increase in the average grain size compared to the layers at an areal charge of 7.5 mAh cm⁻² is to be expected. This hypothesis is further supported by the silver layer mentioned above, in which after a deposition of 7.5 mAh cm⁻², 3 mAh cm⁻² were stripped and yet a similar grain size was observed. The reason for the lack of microstructural changes in

the gold and silver interlayers could be the reduced grain boundary mobility or changed mechanical properties, such as alloy hardening, which means that the external driving force, the pressure applied, is no longer sufficient to cause these changes.

Microstructural evolution during cycling

To investigate the effect of cycling on the lithium microstructure, cells were cycled using a silver interlayer, which prevented the short-circuiting observed in cells without interlayer and allowed stable lithium deposition. In these experiments, 4.5 mAh cm⁻² of lithium was plated and stripped for ten cycles with a cutoff potential of 50 mV, ending with the 10th deposition step. The initial plating step was carried out at reduced current density to ensure that lithium deposition occurred only after complete alloy formation. Cycling results together with EBSD analysis after the final deposition step using a silver interlayer are shown in Fig. 5.

During the first plating step in Fig. 5a, several plateaus can be seen in the voltage curve, which are due to alloy formation. As cycling progresses, increasingly large (nucleation) overpotentials occur at the beginning of plating. We attribute this to an inhomogeneous silver distribution at higher cycle numbers. The absence of silver causes lithium nucleation at the bare titanium CC, resulting in the increasing nucleation overpotential.^{19,29} The increasing IR drop of LPSCl, indicating a higher cell resistance, is likely due to an increasing layer thickness of the SEI over time.^{63,64} Furthermore, mechanical degradation of the SEI or the LPSCl itself due to the volume change could lead to a partial loss of contact with the electrode and thus to higher constriction resistances.⁶⁵ Morphological analysis of the electrode following cycling in Fig. 5b shows that mechanical damage must have indeed occurred to the SE or the SEI, as LPSCl residues are found on the titanium electrode and within the lithium layer. This is accompanied by a decrease in the amount of deposited lithium that can be stripped again. As evident from the stripping curves, it is in the range of 90–95% of the plated amount and decreases with increasing cycle number.

Analysis of the lithium grains in Fig. 5c shows a clear deviation from a columnar structure after repeated deposition and dissolution. In contrast to the mostly uniform columnar structure observed after single dissolution, only three columnar grains remain, while numerous smaller grains emerge between them. This finer-grained microstructure may result from variations in interfacial energy at the Li|LPSCl interface as SEI thickness increases. More likely, however, is an influence of the observed mechanical degradation of the SEI or LPSCl during cycling, which introduces secondary phases into the layer. In line with our experimental findings with gold interlayers and our simulation results, secondary phases can impede grain growth and thereby decrease the grain size. In addition, the LPSCl residues on the titanium foil also lead to an increased roughness of the deposited lithium layer, which in turn was identified in our simulations as additional factor influencing the resulting microstructure. A contribution from

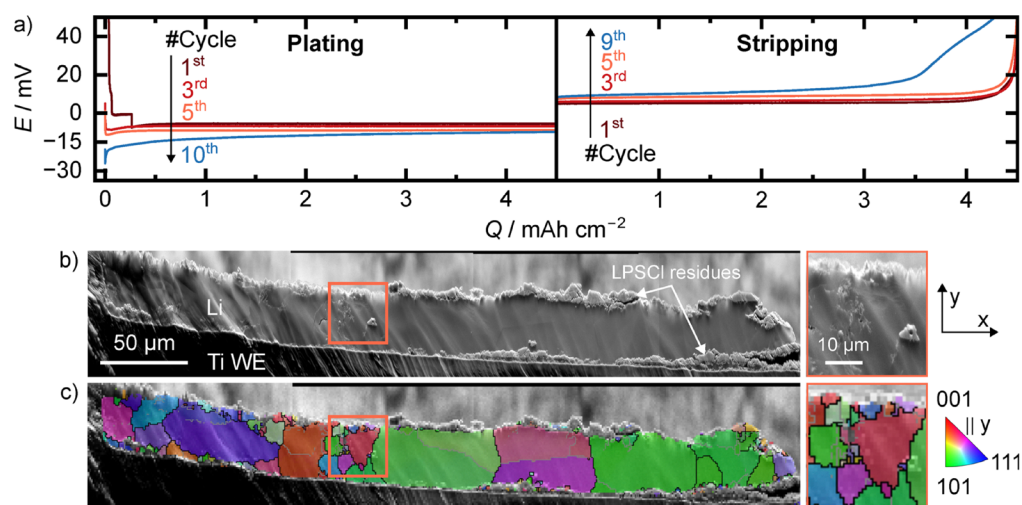


Fig. 5 Cycling results for repeated lithium plating and stripping on a silver interlayer. (a) Plating and stripping curves during lithium cycling. (b) SEM image of the lithium layer following the cycling experiment. (c) Overlay of the SEM image with the IPF map. The IPF map is given parallel to the y -direction as indicated on the right. To the right of (b) and (c), an enlarged section of the respective image is shown.

silver particles at low areal charges also cannot be excluded as full silver dissolution is expected only after $\sim 4.2 \text{ mAh cm}^{-2}$ of lithium deposition.

Overall, these observations highlight that the lithium microstructure during cycling is influenced by multiple complex and interdependent factors. While alloying with the silver interlayer enables stable cycling, repeated plating and stripping leads to mechanical degradation of the SEI and SE, secondary phase dispersion, and increasing roughness. These changes alter the lithium grains simultaneously, resulting in a finer, less columnar microstructure over time. This underscores that lithium microstructure is highly sensitive to the underwent cycling history and interfacial dynamics, emphasizing the need to consider multiple coupled mechanisms when investigating the lithium microstructure *post mortem*.

Interlayers in reservoir-free lithium cells

In the following, the observations made on the influence of gold, silver and bismuth interlayers on the resulting microstructure of plated and stripped lithium layers from the previous chapters are discussed in detail. The schematic in Fig. 6 serves as a graphical summary.

At the beginning of plating, depending on the binary phase diagram of the interlayer material and lithium, alloy formation and subsequent nucleation of lithium take place. While nucleation occurs at the Ti|LPSCI interface for the pristine titanium foil, in the case of gold and silver lithium nucleates at the interface between the forming gold–lithium or silver–lithium alloy and LPSCI, respectively. For bismuth, a bismuth–lithium alloy also forms first. According to the experiments presented, lithium nucleates between this alloy and the titanium foil.

With continuous lithium plating, the increasing layer thickness also leads to an increase in the lithium grain width, which is consistent with previous experimental and simulation results. For the pristine titanium foil, distinctive columnar lithium grains are formed, which have a width corresponding to approximately twice their height, which has already been observed for lithium layers plated at steel|LPSCI interfaces.³⁴

As shown schematically in Fig. 6a, volume expansion during lithium plating can lead to the dispersion of secondary phases. For example, in the case of gold interlayers, alloy particles ($\text{Li}_{15}\text{Au}_4$) can be found in the lithium layer. These lead to a more disordered microstructure and smaller grain size within the lithium layer, deviating from the columnar structure previously observed in chemically pure lithium layers. We assume that these differences are caused by the alloy particles mentioned *via* a mechanism similar to Zener pinning, *i.e.*, the grain boundary mobility is reduced, grain boundaries can be pinned to the particles and thus grain growth is prevented or restricted. These assumptions are underpinned by our simulation, showing a decreased grain size as well as multiple layers of grains when secondary particles are present. We like to emphasize that similar effects can also be caused by electrochemically inactive secondary phases, such as solid electrolyte (interphase) fragments. Therefore, electrolyte choice (both liquid and solid) can affect microstructure development through its mechanical properties and SEI formation.

Furthermore, as in the case of silver and shown in Fig. 6b, complete interlayer dissolution may occur in the course of lithium plating. This also leads to modification of the lithium microstructure. Compared to gold, however, the columnar structure of the lithium grains known from electrodeposition on pristine titanium or steel appears to be largely preserved,

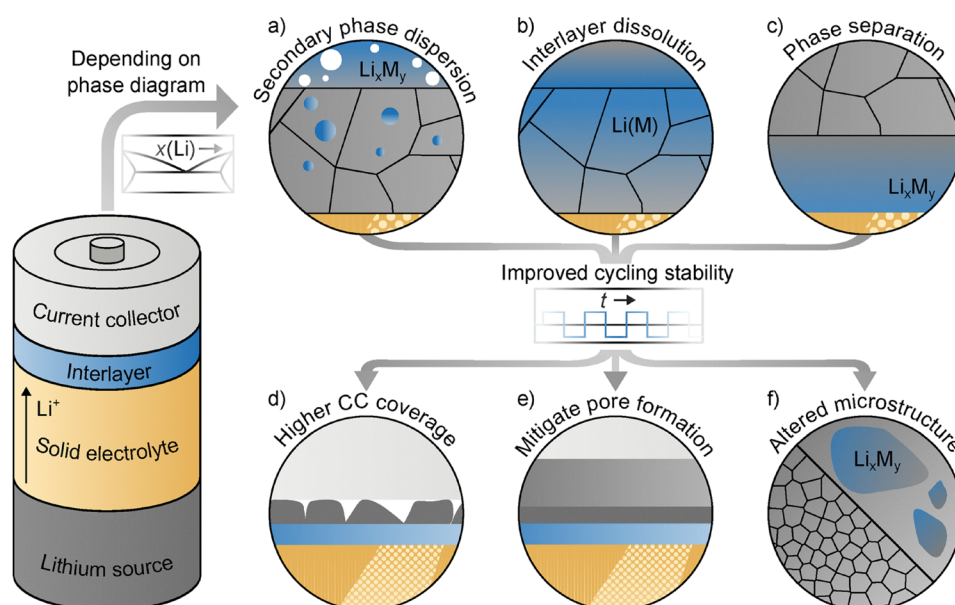


Fig. 6 Microstructural effects of interlayers in reservoir-free solid-state batteries. The model system used is shown schematically on the left. Depending on the phase diagram, different alloy reactions including (a) secondary phase formation, (b) interlayer dissolution and (c) phase separation can occur during ongoing lithium electrodeposition. These can improve the cycling stability by (d) increasing the current collector (CC) coverage, (e) mitigating pore formation and (f) altering the resulting lithium microstructure.

albeit with a significantly lower aspect ratio, *i.e.*, there are more grains that are taller than they are wide. Since lithium has residual solubility for silver and, in the samples examined here, silver is completely dissolved in lithium, a mechanism similar to Zener pinning seems unlikely at the point of examination. Instead, based on our XRD results for a Li(Ag) solid solution produced from melt, we assume that the dissolved silver induces lattice strain by changing lattice parameters, thereby causing the observed changes in microstructure. At this point, we like to mention that an additional mechanism similar to Zener pinning is likely to occur until all silver is completely dissolved in lithium.

Finally, phase separation may occur. This is shown in Fig. 6c and was observed for bismuth interlayers as an example. Here, the columnar structure of the lithium grains is largely preserved during plating. However, compared to the pristine titanium foil, the grain width appears to be even wider, with some grains that have grown particularly large, which could indicate abnormal grain growth. We assume that this is due to the deposition of lithium between the bismuth–lithium alloy and the titanium foil. As a result, the substrate differs and there is no direct contact between lithium and LPSCl. The Li|LPSCl interface alters the resulting lithium microstructure,³⁴ leading for example to the formation of truncated grains, as also found in Fig. 1c in this study. Without this interaction, it is conceivable that the grains could grow even wider. In addition, faster diffusion of lithium along the bismuth–lithium alloy could lead to the formation of larger grains.

In line with literature, interlayers can lead to improved cycling stability. This is caused, among other effects, by an increased CC coverage and a mitigated pore formation,^{10,13,20,25,31} as schematically illustrated in Fig. 6d and e. While these concepts have already been frequently observed and discussed in the literature, an altered microstructure is emerging as an additional influencing factor when using interlayers in RFCs, as shown in Fig. 6f. Specifically, the presence of interlayers can lead to a reduction in lithium grain size, as observed for gold and silver, which increases the density of grain boundaries within the plated layer. This, in turn, provides additional pathways for lithium diffusion.^{31,35} Translating these fundamental insights into design principles, our results indicate that interlayers resulting in a finer lithium grain structure, such as gold and silver, are preferable for enabling stable cycling in RFCs. The combination of smaller grain size, theoretically linked to enhanced diffusivity, and the experimentally observed higher initial CC coverage suggests that these metals facilitate more homogeneous lithium cycling than bismuth. However, it should be noted that in addition to the reduced grain size, the introduction of alloy phases with improved diffusion properties, as previously reported for Li₃Bi, likely also contributes to improved cycling stability.⁵⁷

Furthermore, our experimental results reveal for the first time that cycling itself significantly alters the lithium microstructure, too. For the pristine titanium foil, it was shown that, with decreasing layer thickness, the average grain size decreases again. Thus, the previously observed layer thickness

effect appears to be reversible.³⁴ In addition, in the case of pristine titanium, a strongly pronounced preferred orientation of the lithium grains occurs, which, following stripping, almost exclusively exhibit a $\langle 101 \rangle$ orientation parallel to the stripping direction. In contrast, the gold and silver interlayers appear to slow down grain boundary movement, and thus, the reversible growth and shrinkage of grains with layer thickness is suppressed. The lithium layer formed by plating 10 mAh cm^{-2} and stripping 5 mAh cm^{-2} has a larger average grain width than the layer formed by directly plating 7.5 mAh cm^{-2} . Accordingly, we assume that in this case, when analyzing the sample, we still see the grain microstructure that developed during the deposition of the 10 mAh cm^{-2} . The Zener pinning of the gold alloy particles or the lattice strain within the Li(Ag) solid solution prevents the expected decrease in grain size during stripping. For gold and silver, a well defined preferred orientation during stripping is also lacking. Although a slight change in orientation appears to occur here as well, it is less pronounced than in the case of the pristine titanium foil. Similarly, a preferred orientation is also lacking for the bismuth interlayer. However, a decrease in the mean grain size following stripping is again evident here. We assume that the reversible change of grain size with the layer thickness occurs also here, as in the case of titanium, since both cases involve chemically pure lithium and only the substrate differs. Interestingly, some very small grains with a more disordered microstructure were found for the bismuth interlayer following stripping, in contrast to the results after plating. We hypothesize that these areas could be areas where particularly large, possibly abnormally grown grains were previously located. During stripping, these then disintegrate into many smaller grains. In general, the cycling history also plays an important role in the resulting microstructure of lithium. This was further confirmed by first cycling experiments. In addition to the influencing factors already discussed, the mechanical degradation of the SE and the associated contamination of the lithium layer were identified as additional factors.

Conclusions

In this study, we deepen the understanding of how thin alloying interlayers affect the microstructure of electrodeposited lithium layers in reservoir-free produced SSBs, using EBSD on wide cross-sections prepared *via* broad ion beam milling. Lithium deposited on gold and silver interlayers exhibit a microstructure with a reduced grain size compared to lithium deposited at the titanium foil reference. The columnar structure with low-aspect ratio grains found for various metal CCs also vanishes when gold and silver are used. In contrast, the columnar structure of lithium layers deposited on bismuth interlayers is largely preserved with even increased grain size compared to lithium electrodeposited on pristine titanium foils. The smaller grain size should improve cycling for both gold and silver interlayers, with the effect for silver potentially being stronger due to its more uniform distribution within the lithium layer.

Additional EDS and EBSD analysis of the cross-sections provided information on the different modes of action of the interlayers. Gold and silver interlayers ensure that the deposited lithium is no longer chemically pure, which in turn suppresses grain growth. The bismuth interlayer, on the other hand, separates the lithium layer from the solid electrolyte LPSCl used here and thus changes the substrate and therefore the microstructure of the deposited lithium.

In addition, the microstructural change of remaining lithium caused by stripping of previously plated lithium was analyzed for the first time. In the case of chemically pure lithium, *i.e.*, pristine titanium foil and the bismuth interlayer, a reduction of the mean grain size could be observed, which shows that the previously observed layer thickness effect for plated lithium is reversible. In the case of gold and silver interlayers, however, this reversibility appears to be largely prevented and no decrease in grain size was observed during stripping. Interestingly, in the case of stripping lithium on titanium, a strong preferential orientation of the remaining lithium grains was also detected. Thus, in addition to alloying interlayer materials, the cycling history of LMEs can be identified as an influencing factor on the lithium microstructure. This is particularly evident in the lithium analyzed after cycling. Overall, our results emphasize that an “electrometallurgical” understanding is needed to describe the dynamic microstructural changes in LMEs during cycling and that additional microstructure analysis during cycling is necessary, especially when using interlayers.

Author contributions

The author contributions are given based on the contributor roles taxonomy (CRediT): J. B.: conceptualization, methodology, investigation, validation, formal analysis, writing – original draft, visualization, writing – review & editing; L. S.: conceptualization, methodology, investigation, validation, formal analysis, visualization, writing – review & editing; S. K.: formal analysis, software, visualization, writing – review & editing; T. F.: conceptualization, formal analysis, methodology, supervision, visualization, writing – review & editing; J. J.: conceptualization, methodology, resources, supervision, writing – original draft, writing – review & editing, and funding acquisition.

Conflicts of interest

The authors declare no competing interests.

Data availability

Data for this article, including electrochemical and EBSD data are available at “JLUPub” at <https://doi.org/10.22029/jlupub-20276>.

The SI contains figures (Fig. S1–S23) and notes (Note S1–S4). See DOI: <https://doi.org/10.1039/d5ee07230a>.

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4 Conclusions

In this dissertation, LMEs electrodeposited in RFCs were analyzed in depth. The purity compared to their conventional counterparts and the influence of purity on the available capacity during stripping was investigated. The microstructure of lithium metal was systematically analyzed using EBSD during both electrodeposition and electrodisolution and when employing metallic interlayers.

The first part of this work analyzed the chemistry of lithium electrodeposited at steel|Li₆PS₅Cl interfaces. An exceptionally high purity of the resulting LME was confirmed, which stands in contrast to conventionally produced lithium samples, in which sodium was identified as the dominant impurity. This finding reveals two important implications: first, electrodeposition in RFCs offers a distinct advantage over conventionally produced lithium in terms of chemical purity and reproducibility. Second, the accumulation of impurities at the interface with single-ion conducting SEs was identified as a further contributor to contact loss and associated constriction resistances during stripping, decreasing the accessible lithium inventory. Thus, lithium purity emerges as both an application-relevant parameter for battery performance and as a standardization parameter that must be considered when comparing research results obtained with lithium metal of varying purities. This systematic comparison reveals a current gap in the research field and highlights the importance of disclosing material purity.

The second part of this dissertation focused on characterizing the microstructure of electrodeposited lithium as a function of deposition parameters. By developing a workflow that allows the analysis of millimeter-sized cross-sectional areas, it was possible to demonstrate dynamic grain growth as a function of lithium layer thickness. This systematic approach reveals two key distinctions from conventionally manufactured lithium foils. First, deposition parameters provide an effective way to modify the lithium microstructure. Second, electrodeposited lithium exhibits microstructural evolution that is fundamentally different from conventionally produced material, whose structure is largely determined by prior thermal and mechanical history. These results not only validate the reliability of the microstructural analysis workflow for future parameter studies in alkali metal systems but also establish a methodological foundation applicable to other crystalline materials in batteries.

The final section of this dissertation addresses the influence of interlayers on lithium microstructure following electrodeposition and subsequent stripping. Gold and silver interlayers, previously studied in the literature primarily for improving lithium morphology during plating, resulted in a reduction of average lithium grain size to approximately 30 μm , representing a four-fold decrease compared to the deposition without an interlayer (yielding approximately 140 μm wide grains). Both values are given for a lithium areal charge of $\approx 7.5 \text{ mAh cm}^{-2}$. This finer-grained lithium

microstructure is expected to exhibit improved electrochemical properties based on existing simulations, though experimental confirmation remains to be established. Conversely, bismuth interlayers led to an increase in average grain size to approximately 170 μm . These results demonstrate that interlayers not only influence the resulting lithium morphology but also the microstructure. The choice of interlayer material, shown here using gold, silver, and bismuth as examples, is decisive for the resulting lithium microstructure, thereby enabling targeted microstructure design as a strategy for optimizing electrochemical performance.

Additionally, microstructural analyses performed for the first time following stripping and after repeated cycling revealed grain shrinkage and preferential crystallographic reorientation. While these observations are hypothesized to correlate with tensile stress in the LME during stripping, the underlying mechanisms still need to be investigated in more detail. In general, these findings demonstrate that both electrochemical and mechanical effects govern the formation and evolution of lithium microstructure and that these processes are coupled.

Overall, this dissertation expands the fundamental understanding of electrodeposited lithium in RFCs and highlights important differences from conventionally manufactured lithium foils. Comprehensive purity analysis addresses a parameter that has been largely overlooked in literature but significantly affects the reproducibility and comparability of research on LMEs. The systematic microstructural characterization highlights several options that can be used to specifically influence the lithium microstructure and touches upon the relationship between microstructural features and electrochemical properties. By demonstrating the interaction between electrochemical processes, mechanical effects, and microstructural evolution, this work provides both methodological advances and practical insights that are essential for optimizing the performance of LMEs in RFCs.

5 Outlook

While this work has clarified the critical roles of purity and microstructure in reservoir-free SSBs, the central question remains: will LMEs ultimately meet the extreme electrochemical and morphological requirements imposed by high-performance SSBs? A definitive answer is yet outstanding. However, building on the findings of this work, several promising directions for future research can be defined, spanning lithium purity, microstructure design, mechanical properties and interface phenomena.

Regarding lithium purity, the purification induced by single-ion conducting SEs in RFCs could ultimately represent an intrinsic advantage that improves stripping capabilities and reproducibility in research and application.^{18,33} In general, lithium purity should be consistently specified in future studies, together with all other relevant experimental parameters. This practice, which is well established in inorganic synthesis, would significantly improve the comparability and reproducibility of studies on LMEs. Moreover, the concepts developed here can be transferred to other metal|SE systems, for example sodium metal batteries employing single-ion conducting SEs such as NaSICON-based SEs.^{92,147–149} An additional open question concerns the role of impurities in systems that do not use single-ion conductors or even employ mixed-conducting SEs, as may be the case in K β -alumina-based cells.^{150,151} Systematic studies that vary impurity levels and types in different electrolyte environments could provide valuable insights into the interplay between purity, interfacial chemistry and electrochemical performance.

With respect to microstructure, this dissertation demonstrates that EBSD-based characterization of electrodeposited lithium yields reliable and reproducible results, even for highly reactive lithium. The established workflow enables systematic investigation of additional parameters governing lithium plating and stripping in RFCs. One important direction involves the controlled introduction of heterogeneities, such as alloy-forming elements (gold, silver, bismuth) or electrochemically inactive particles, to systematically modify nucleation and grain growth at the CC interface. Initial experiments with interlayers already reveal a clear correlation between interlayer chemistry and resulting microstructure. Although *ex situ* prepared lithium composite electrodes do not constitute RFC architectures, they provide well-defined model systems to decouple the influence of additive chemistry, phase distribution, and interfacial properties. Insights gained from such model systems can nevertheless contribute to the rational design of modified CCs and interlayers for RFCs. Ultimately, a central question remains: how do microstructure and electrochemical stripping correlate in detail? Are fine-grained LMEs indeed the key to achieving higher discharge rates, and if so, how can such microstructures be realized and maintained reversibly over multiple cycles?

However, the established methodology is not limited to LMEs. In general, EBSD characterization enables the investigation of a wide range of novel research questions in the battery field, including

the microstructural properties of SE, CC, positive electrode materials, and their impact on overall battery performance.^{134,152,153} Furthermore, as post-lithium energy storage systems based on sodium or potassium gain increasing importance, the EBSD characterization is readily transferable. Microstructural analysis of the crystalline components in these systems also enables a correlation between microstructure and electrochemical properties.

A further important aspect concerns the mechanics of electrodeposited lithium in RFCs. To date, no systematic mechanical investigations have been reported on lithium that has been electrodeposited in such configurations. However, both the very high purity and the significantly different microstructure compared to conventionally processed lithium foils suggest that the mechanical properties may differ substantially from already characterized reference foils. Future work should therefore address mechanical testing of electrodeposited lithium, for example via micro- or nano-indentation. Combining such measurements with detailed microstructural analysis would provide valuable insights into how purity, grain size, and grain orientation influence yield strength and creep tendency, and how these, in turn, influence morphological stability during cycling.

Overall, future research should aim to understand the chemo-mechanical coupling in SSBs employing RFC concepts in a comprehensive way. Lithium is a metal, albeit a special one, and therefore both metallurgical and electrochemical concepts should be combined to deepen understanding and guide the rational design of next-generation SSBs comprising LMEs.

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7 Appendix

7.1 Energy density calculation of cells with and without lithium reservoir

The following calculation is based on the work of Randau *et al.*³⁴ and illustrates the increase in energy density achieved by omitting the lithium reservoir in RFCs. A cell with a lithium reservoir (a 25 μm thick lithium foil) is used for comparison. In contrast, this is omitted in the case of RFCs, as the LME is formed from the lithium inventory of the AM on the positive electrode side. To calculate the energy density, an areal charge of the positive electrode of 5 mAh cm^{-2} is assumed. For simplicity, it is assumed that the positive electrode consists of 100% NCM active material and that the energy efficiency is 100%. Please note that neither cell housings nor other cell components such as catholyte or CCs were taken into account.

Table 2: Material parameters for calculating the potential energy density increase enabled by omitting the lithium reservoir in RFCs.

Parameter	Li	NCM	Li ₆ PS ₅ Cl	Stainless steel
Specific capacity / mAh g ⁻¹	3860	170	-	-
OCV vs. (Li ⁺ /Li) / V	0	3.8	-	-
Density / g cm ⁻³	0.534	4.78	1.64	8
Thickness / μm	0 (RFC) 25 (with reservoir)	62	40	20

Using the capacity values mentioned above and the parameters shown in **Table 2**, this results in volumetric and gravimetric energy densities of 1302 Wh L⁻¹ and 358 Wh kg⁻¹, respectively, for the cell with a 25 μm lithium reservoir. In the case of the RFC, the volumetric and gravimetric energy density increases to 1569 Wh L⁻¹ and 367 Wh kg⁻¹, respectively.

7.2 Supporting Information

7.2.1 Publication 1: “Purity of lithium metal electrode and its impact on the lithium stripping in solid-state batteries”

Supplementary Information

Purity of Lithium Metal Electrode and its Impact on Lithium Stripping in Solid-State Batteries

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Table S1: Summary of impurities in the two different commercially available lithium samples Li_{LP} and Li_{HP} . Contents of impurity elements are given in ppm and are based on the manufacturer's specifications.

Impurity	Content in Li_{LP} / ppm	Content in Li_{HP} / ppm
Al	5	5
Ca	400	300
Fe	50	55
K	80	80
Na	7000	820
Si	10	14

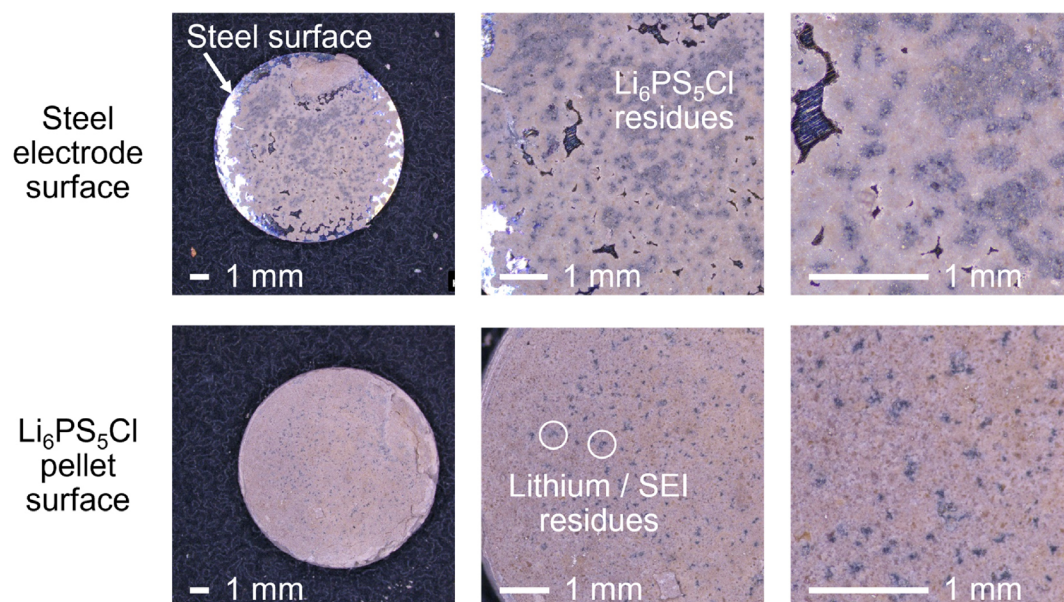


Figure S1. Optical images of a steel working electrode and a $\text{Li}_6\text{PS}_5\text{Cl}$ pellet surface after electrodeposition. Please note that this sample was used for reproduction of experiments and is not the same one that was analyzed using XPS and SIMS within the manuscript. In parts where no lithium deposition has taken place, the shiny steel electrode can still be seen. However, most of the electrode is covered with residuals of $\text{Li}_6\text{PS}_5\text{Cl}$ which adheres to the electrodeposited lithium. On the pellet surface some grey residuals of lithium or SEI products can be seen. Chipped edges on the pellet were produced during cell disassembly. This sample was analyzed ex-situ after electrodeposition of 1 mAh cm^{-2} lithium at a current density of $50 \mu\text{A cm}^{-2}$ in a reservoir-free cell system on a steel electrode.

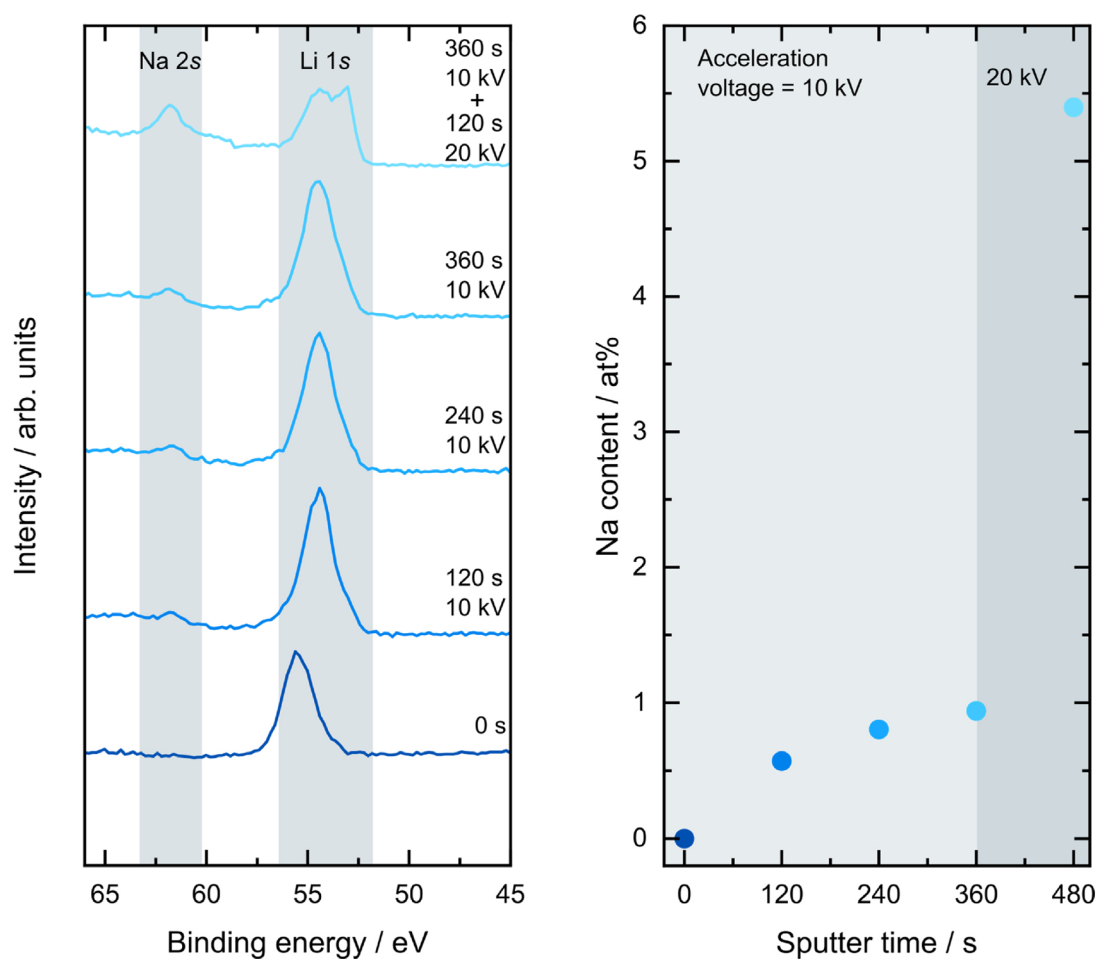


Figure S2: The influence of argon cluster sputtering on the acquired XPS spectra. The image on the left displays the acquired XPS spectra after the given sputtering times and acceleration voltages. Three sputter steps with an acceleration voltage of the argon clusters of 10 kV were conducted. After that, one additional sputtering step with an acceleration voltage of 20 kV was conducted. The image on the right displays the calculated sodium content (in at%) in dependence of the sputtering time.

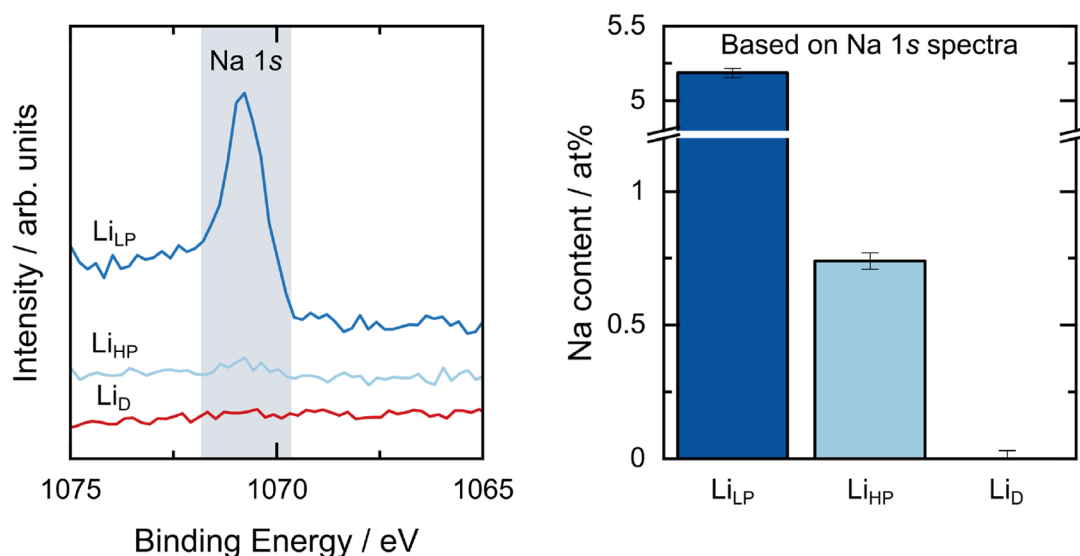


Figure S3: XPS analysis of different samples based on the Na 1s signal. Acquired Na 1s XPS spectra for the different lithium samples Li_{LP}, Li_{HP} and Li_D on the left. The corresponding sodium concentrations in at%, calculated from the Na 1s spectra on the left, are depicted on the right. The given error bars are based on the work of A. Shard², and indicate an error of 0.03 at% in all cases. In the case of Li_D no significant Na 1s signal is detectable. Therefore, only the error bars can be seen. Li_D was analyzed ex-situ after electrodeposition of 12 mAh cm⁻² lithium at a current density of 50 μ A cm⁻² in a reservoir-free cell system on a steel electrode (see Figure 1)

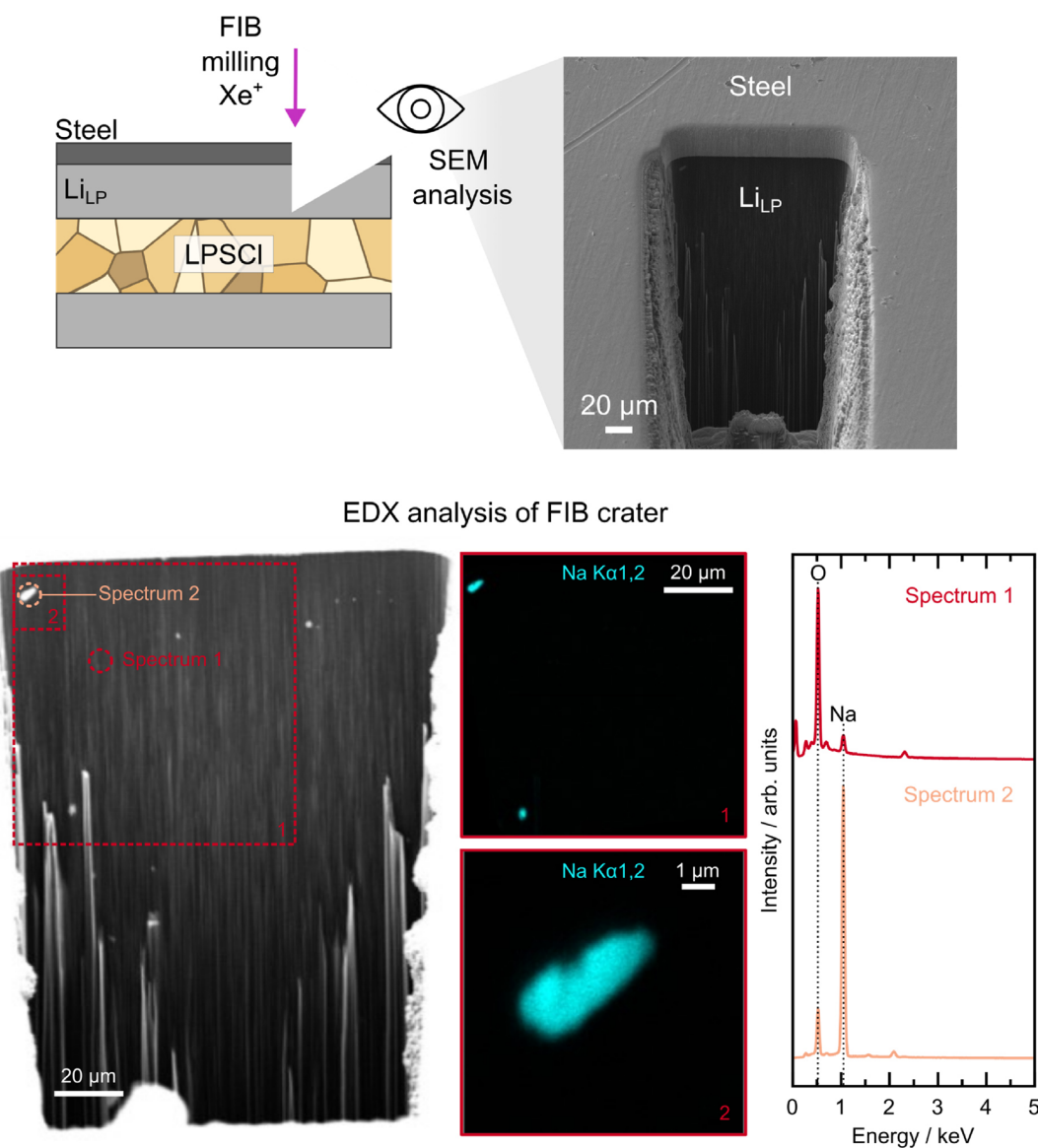


Figure S4: Sodium precipitates within a Li_{LP} electrode. EDX analysis of a crater inside a Li_{LP} metal electrode, being attached to a LPSCI pellet. As visible from the acquired EDX maps marked with red rectangles within the electron image, sodium is found in the form of a few μm sized regions inside the lithium foil. Spectrum 2 on the right side shows that the brighter appearing particles inside the lithium foil are in fact sodium precipitates. However, as visible from spectrum 1, a sodium signal is also found in areas of the sample where no such precipitates are directly visible. The sample was analyzed ex-situ after stripping of 5 mAh cm^{-2} Li_{LP} at a current density of $100 \mu\text{A cm}^{-2}$ in a symmetrical $\text{Li}_{\text{LP}}|\text{LPSCI}|\text{Li}_{\text{LP}}$ system.

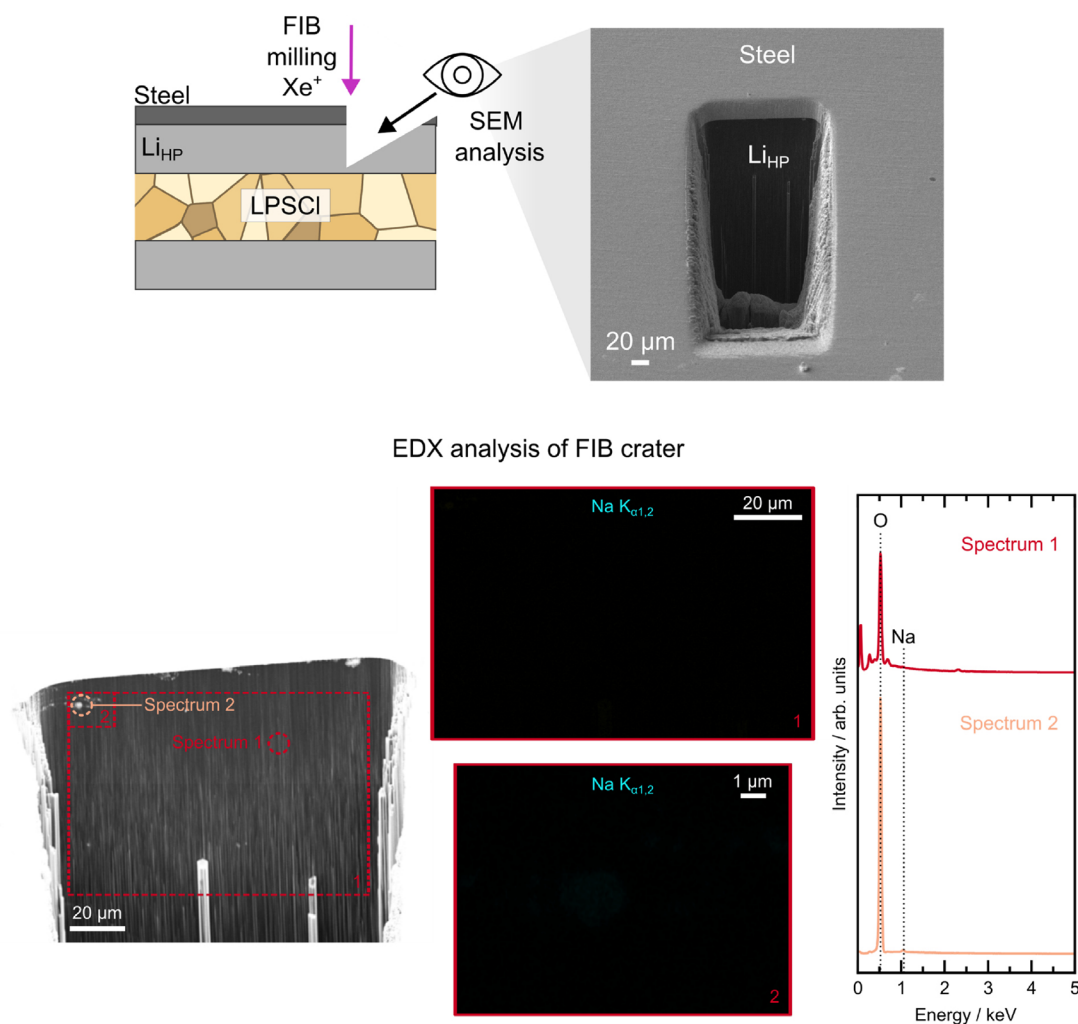


Figure S5: EDX analysis of a Li_{HP} electrode. EDX analysis of a crater inside a Li_{HP} electrode, being attached to a LPSCI pellet. As visible from the acquired EDX maps marked with red rectangles within the electron image, no sodium is found inside the lithium foil. This is further supported by two point spectra acquired in different locations inside the lithium foil. In both cases no sodium signal is found. As visible from spectrum 2, the white appearing particles within the lithium foil show a very intense oxygen signal, possibly due to some degradation products or artefacts from ion milling. The sample was analyzed ex-situ after stripping of 5 mAh cm^{-2} Li_{HP} at a current density of $100 \mu\text{A cm}^{-2}$ in a symmetrical $\text{Li}_{\text{HP}}|\text{LPSCI}|\text{Li}_{\text{HP}}$ system.

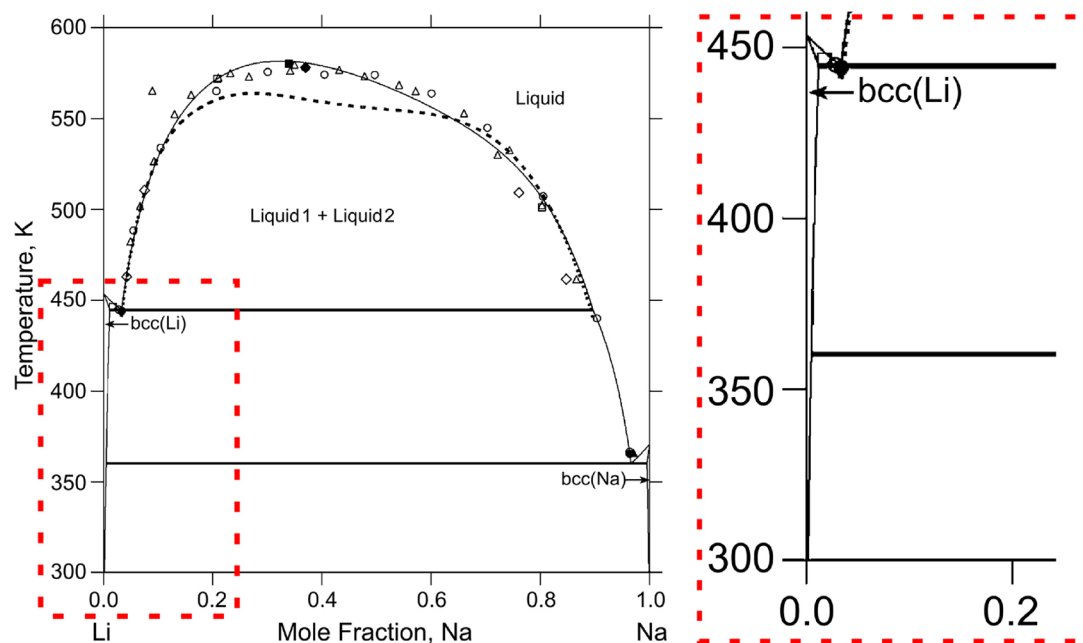


Figure S6: Phase diagram of the binary Li-Na system. The binary phase diagram of the Li-Na system is shown on the left. The magnified section on the right highlights the low sodium regime, revealing a monotectic at a sodium content of 3.4 at%. Reproduced and modified from Zhang et al.³ Copyright 2003 Elsevier.

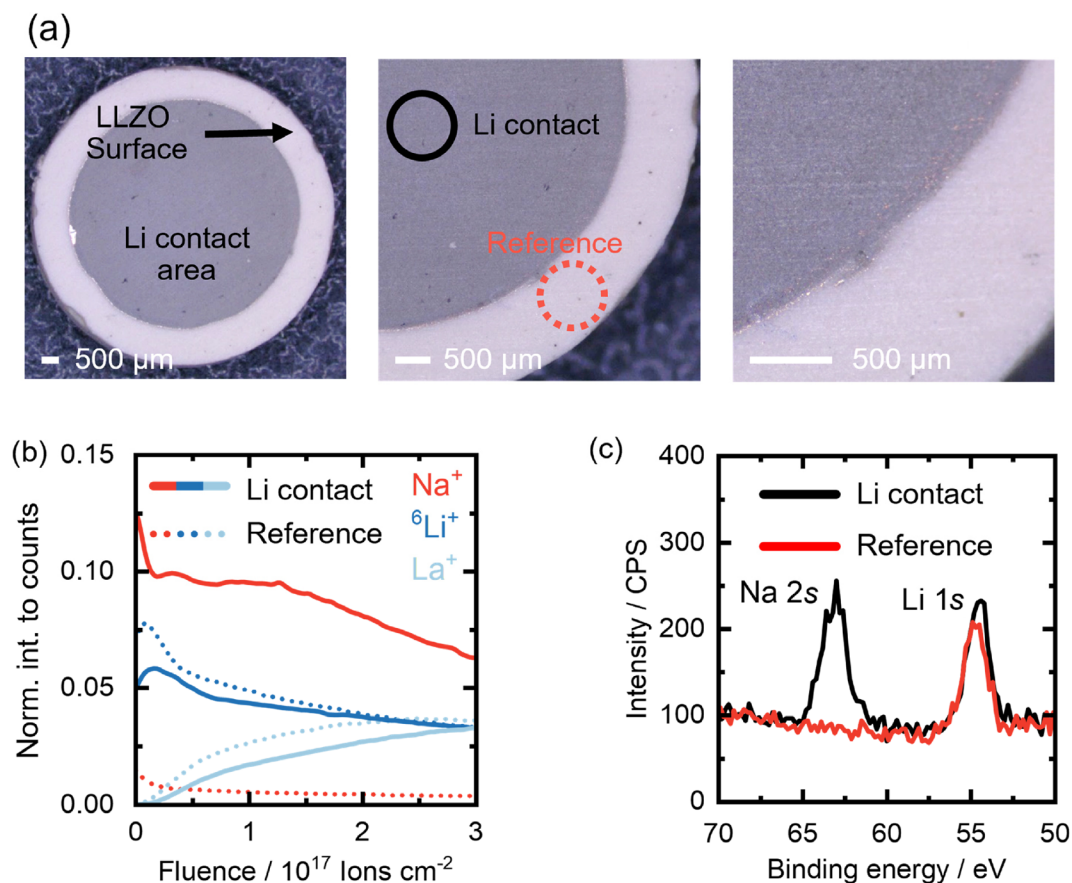


Figure S7. Residue analysis on the LLZO surface after Li_{LP} stripping using XPS and ToF-SIMS.

(a) Optical images of a LLZO surface after lithium stripping using a $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ cell. The lithium electrode was removed after pore formation (*i.e.*, contact loss) occurred, grey residues remain where the lithium electrode was. (b) SIMS depth profile conducted on the gray residues (straight line) and the pristine beige LLZO surface (dotted line). (c) XPS measurements on the two aforementioned areas. CPS: counts per second. The sample was analyzed ex-situ after stripping Li_{HP} at a current density of $100 \mu\text{A cm}^{-2}$ in a symmetrical $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ cell.

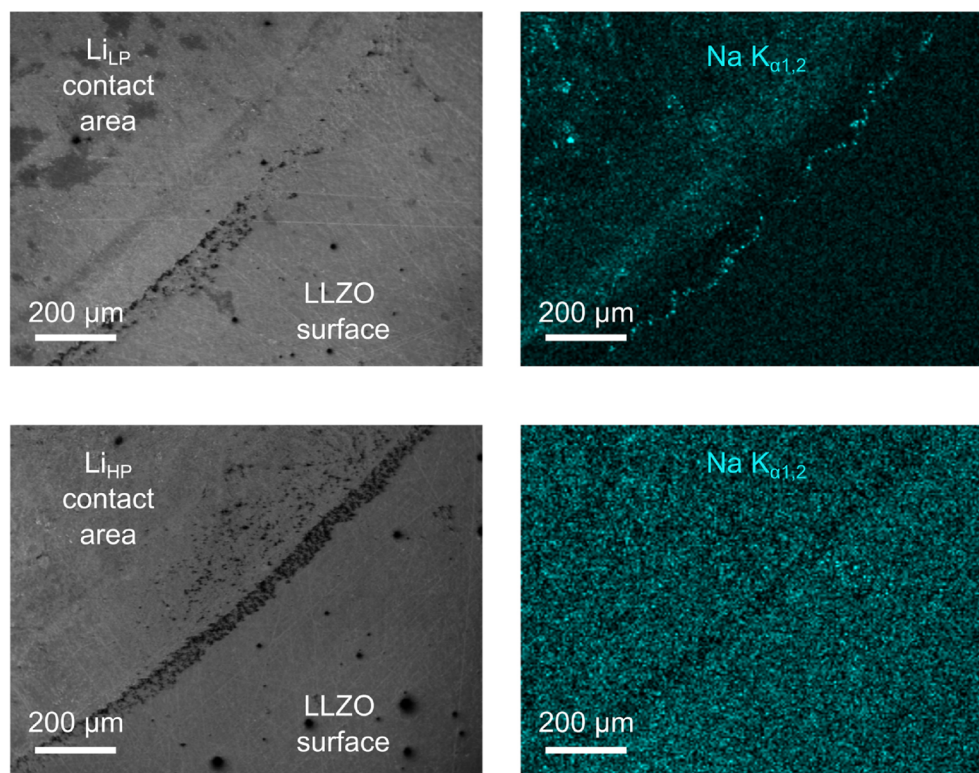


Figure S8: Residue analysis on the LLZO surface after Li_{LP} stripping using EDX. Top-view SEM and EDX analysis of a LLZO surface after being in contact with either Li_{LP} (top images) / Li_{HP} (bottom images) during lithium stripping (see Figure 4). The area, where the lithium electrode was in contact with the LLZO pellet can be seen in the left SEM images. The EDX map of the $\text{Na K}_{\alpha 1,2}$ signal on the right shows an increased intensity in the area where the Li_{LP} electrode was in contact with the LLZO pellet. Conversely, for the Li_{HP} electrode a homogeneous signal is visible, being only due to noise. Please note that the intensities of the two $\text{Na K}_{\alpha 1,2}$ signals have not been normalized with each other and therefore the intensities between the two images are not comparable. The sample was analyzed ex-situ after stripping Li_{LP} or Li_{HP} at a current density of $100 \mu\text{A cm}^{-2}$ for different capacities in symmetrical $\text{Li}|\text{LLZO}|\text{Li}$ systems (see Figure 4).

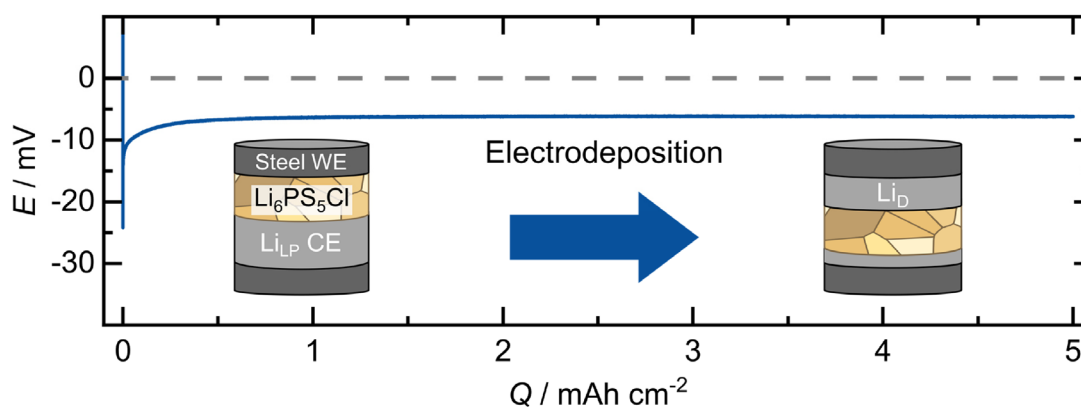


Figure S9: Electrodeposition of Li_D for stripping experiments. Voltage profile during electrodeposition of Li_D for the subsequent stripping experiment (see also Figure 4). Electrodeposition is conducted with a current density of $100 \mu\text{A cm}^{-2}$ at an external pressure of 15 MPa.

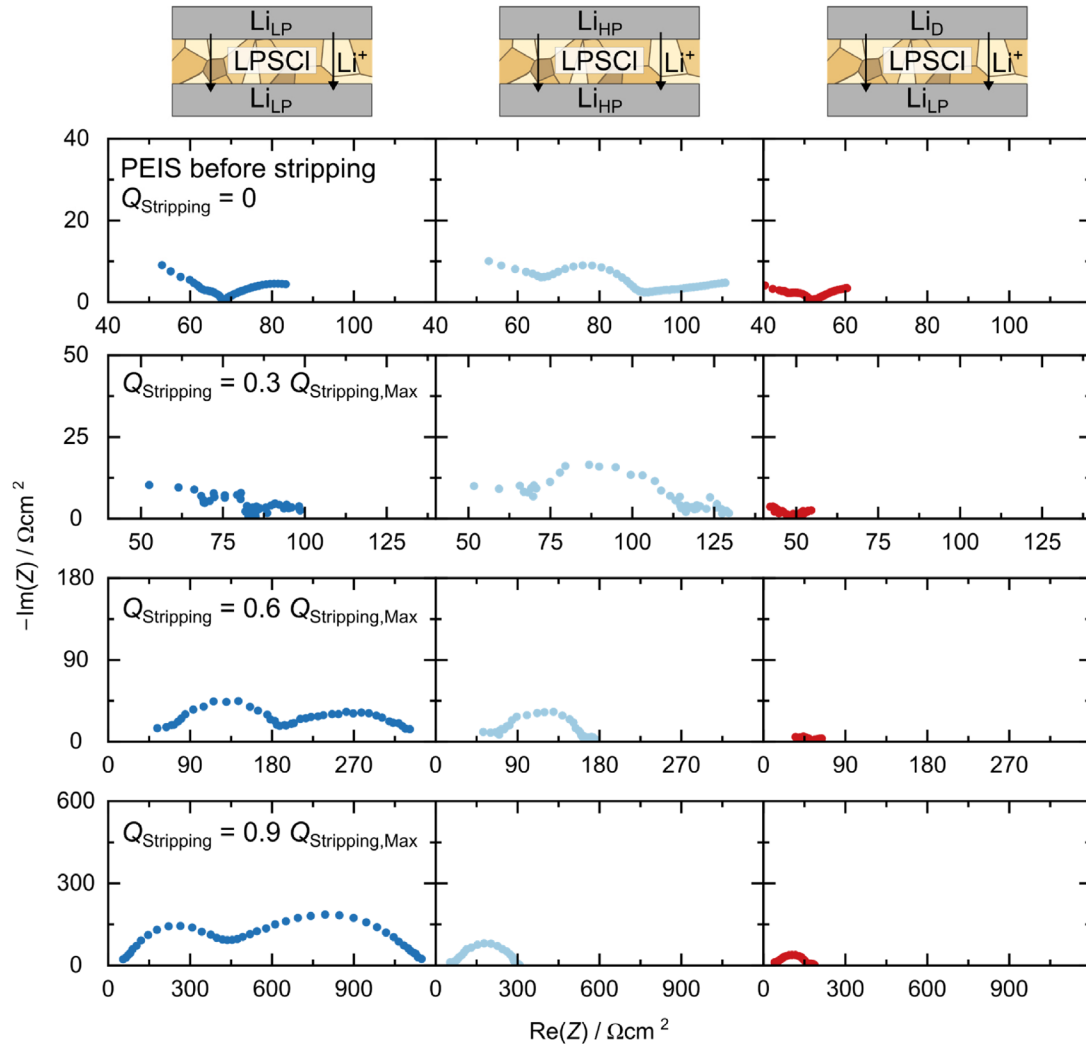


Figure S10: Impedance analysis of symmetrical Li|LPSCI|Li cells. Impedance spectra of three different Li|LPSCI|Li cells before and during lithium stripping in Nyquist representation. The cell setups with different lithium electrodes (Li_{LP}, Li_{HP}, and Li_D) are depicted above. As marked with the text, the first impedance spectra were recorded before applying a current using PEIS. The following spectra were recorded during the stripping process with an applied current of $100 \mu\text{A cm}^{-2}$ using GEIS. The times at which the spectra were recorded are given in fractions of the total stripping capacity $Q_{\text{stripping,Max}}$. Please consider the different scalings of the graphs.

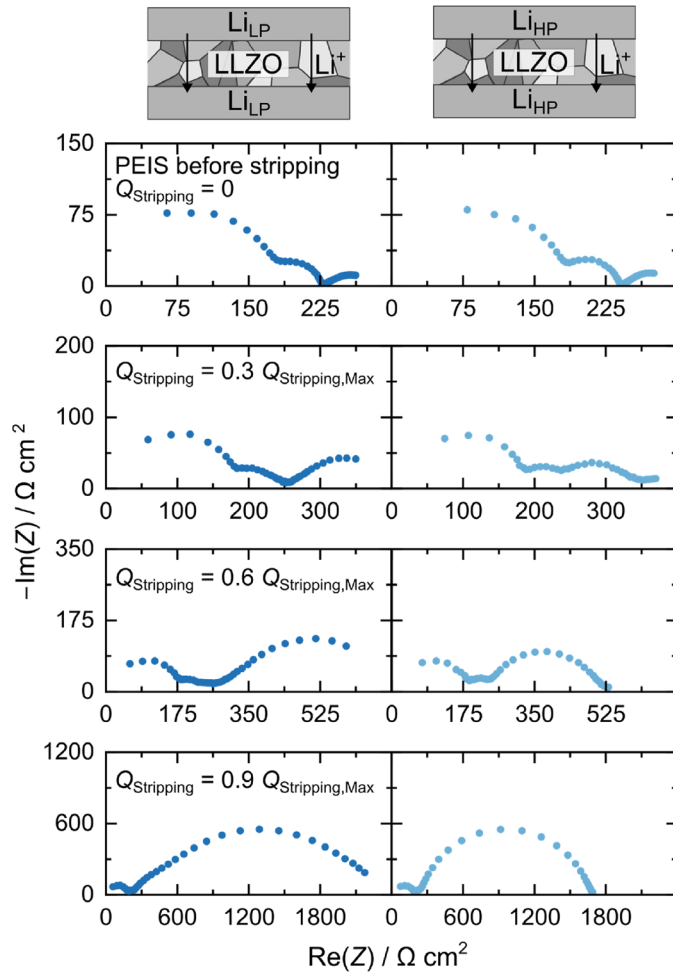


Figure S11: Impedance analysis of symmetrical Li|LLZO|Li cells. Impedance spectra of the symmetrical Li|LLZO|Li cells before and during lithium stripping in Nyquist representation. The cell setups with different lithium samples are depicted above. As marked with the text, the first impedance spectra were recorded before applying a current using PEIS. The following spectra were recorded during the stripping process with an applied current of $100 \mu\text{A cm}^{-2}$ using GEIS. The times at which the spectra were recorded are given in fractions of the total stripping capacity $Q_{\text{Stripping,Max}}$. Please consider the different scalings.

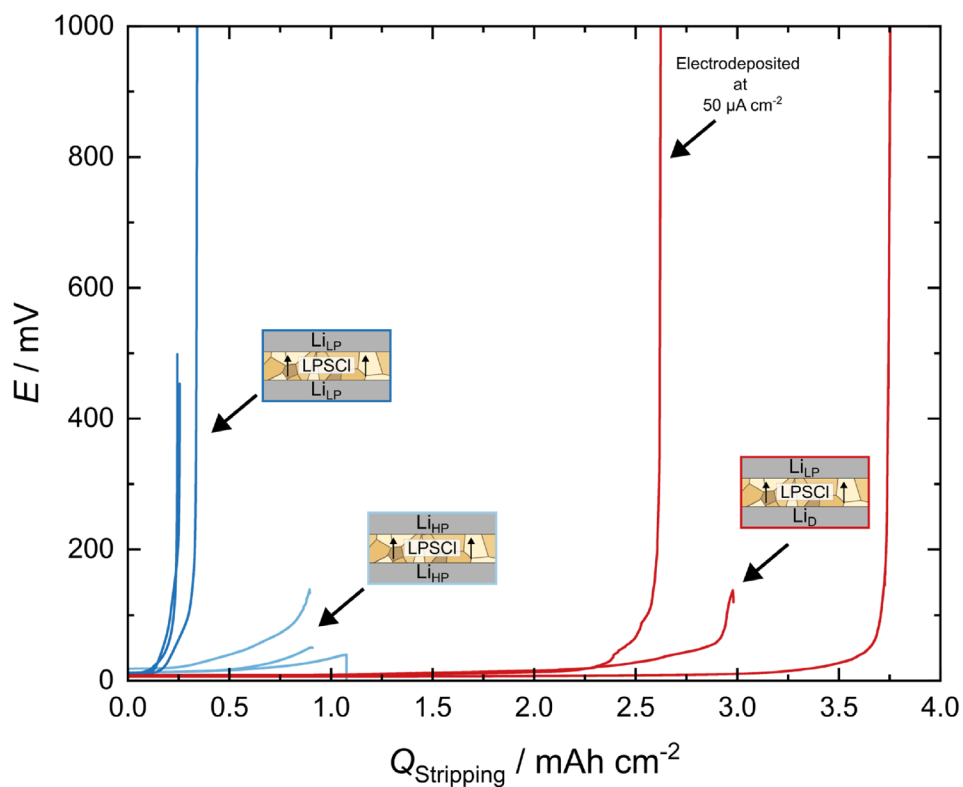


Figure S12: Reproduced cells using LPSCI as SE. Stripping curves of the cell systems examined using LPSCI as solid electrolyte. Three cells of type $\text{Li}_{\text{LP}}|\text{LPSCI}|\text{Li}_{\text{LP}}$, $\text{Li}_{\text{HP}}|\text{LPSCI}|\text{Li}_{\text{HP}}$ and $\text{Li}_{\text{LP}}|\text{LPSCI}|\text{Li}_{\text{D}}$ are shown. The respective cell system is shown schematically next to the corresponding stripping curves. In all cases a current density of $100 \mu\text{A cm}^{-2}$ was used for lithium stripping.

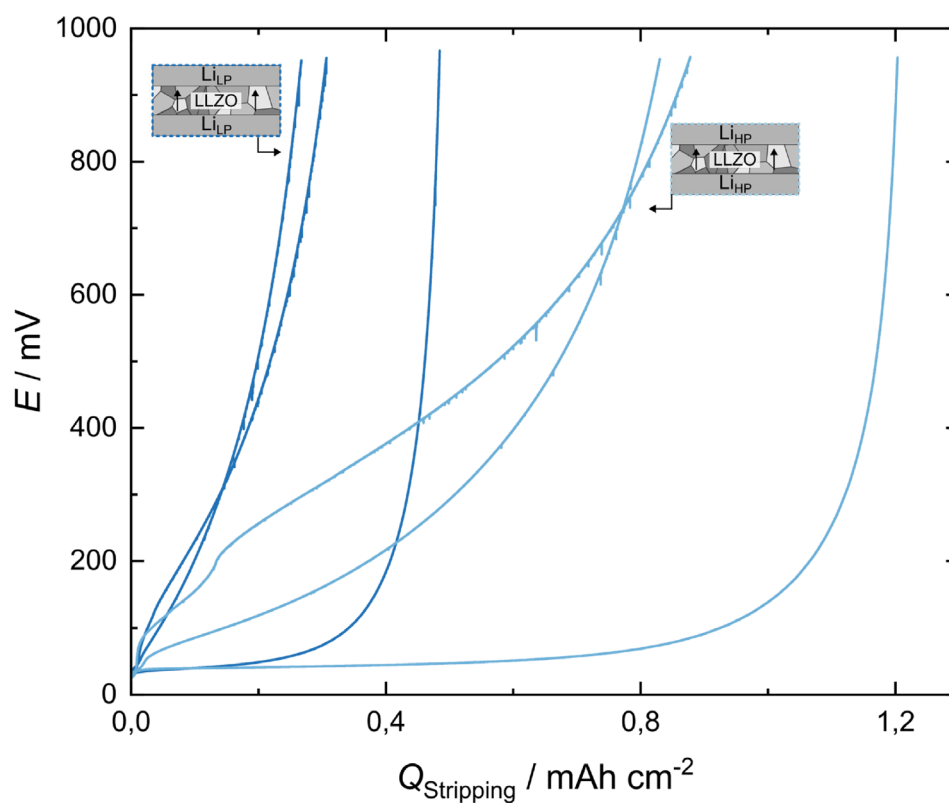


Figure S13: Reproduced cells using LLZO as SE. Stripping curves of the cell systems examined using LLZO as solid electrolyte. Three cells of type $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ and $\text{Li}_{\text{HP}}|\text{LLZO}|\text{Li}_{\text{HP}}$ are shown. The respective cell system is shown schematically next to the corresponding stripping curves. In all cases a current density of $100 \mu\text{A cm}^{-2}$ was used for lithium stripping.

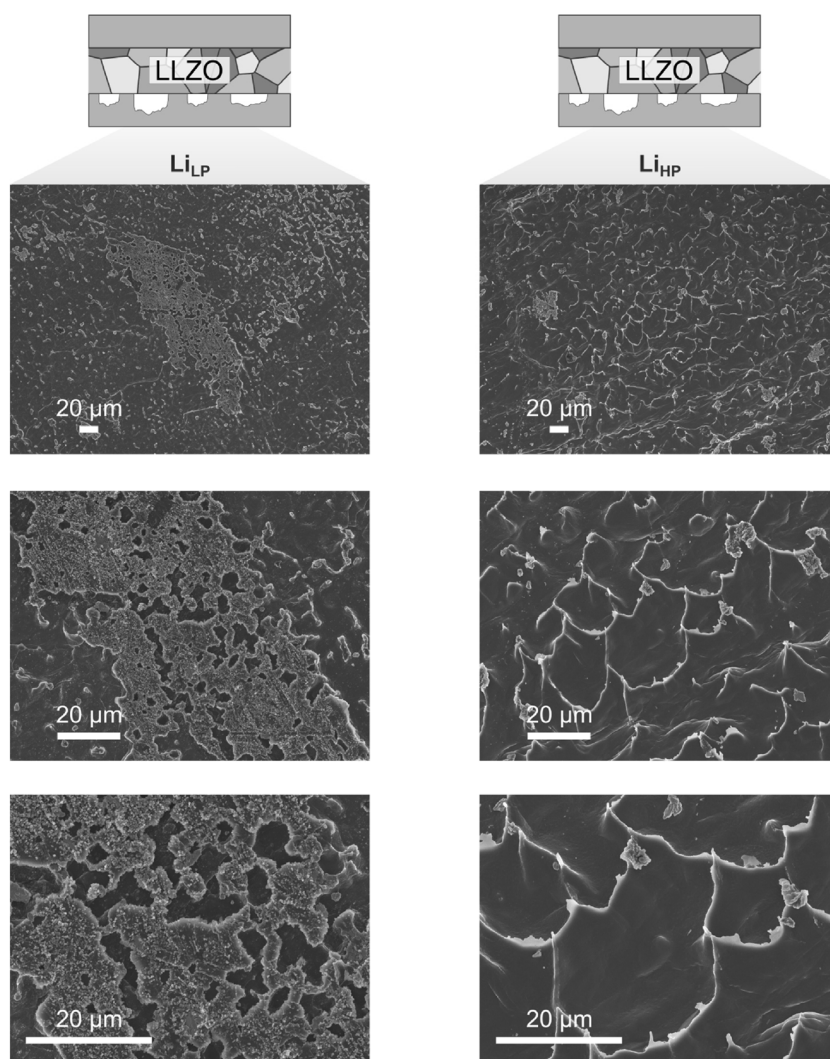


Figure S14: Pore morphology analysis of different lithium samples. Top-view SEM analysis of the stripped Li_{LP} and Li_{HP} electrodes from Figure 4 after contact loss. On the left side the Li_{LP} electrode can be seen, showing domains where seemingly remains of lithium are still present. On the right side the Li_{HP} electrode can be seen, showing almost no remaining lithium spots. The different panels show different magnifications. The sample was analyzed ex-situ after stripping Li_{LP} or Li_{HP} at a current density of $100 \mu\text{A cm}^{-2}$ for different capacities in symmetrical $\text{Li}|\text{LLZO}|\text{Li}$ systems (see Figure 4).

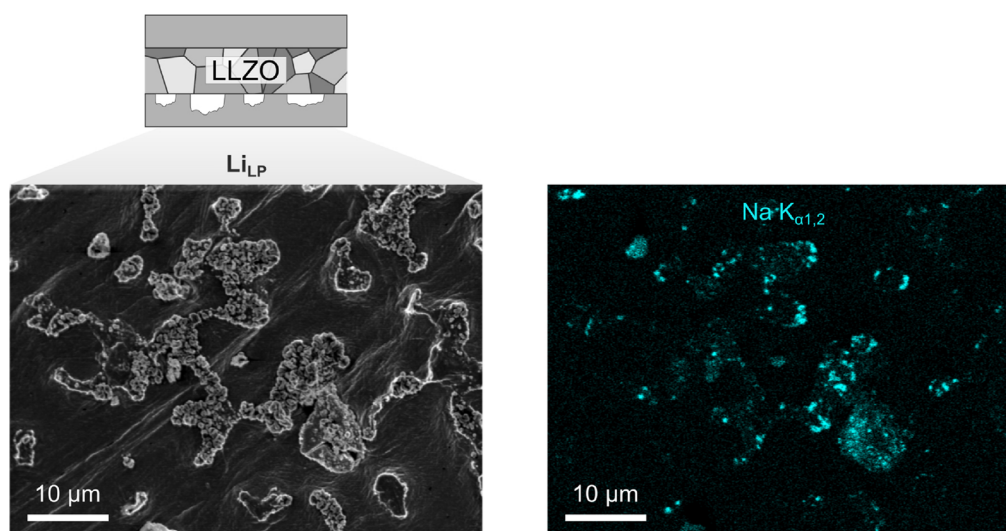


Figure S15: EDX analysis of a stripped Li_{LP} electrode. Top-view SEM and EDX analysis of the stripped Li_{LP} electrode from the $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ cell from Figure 4. On the left a SEM picture can be seen, showing some residual lithium after pore formation. The EDX map of the $\text{Na K}_{\alpha 1,2}$ signal on the right shows an enrichment of sodium where lithium remains. The sample was analyzed ex-situ after stripping Li_{LP} at a current density of $100 \mu\text{A cm}^{-2}$ for 0.48 mAh cm^{-2} in a symmetrical $\text{Li}_{\text{LP}}|\text{LLZO}|\text{Li}_{\text{LP}}$ systems (see Figure 4).

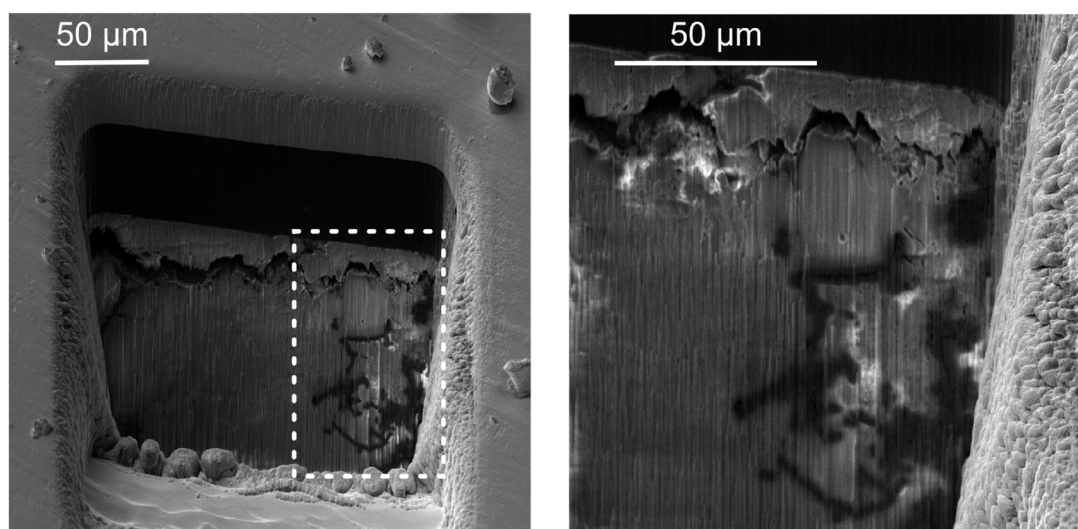


Figure S16: Cross-section analysis of the steel/LPSCI interface after electrodeposition. Cross-section of a $\text{Li}_{\text{D}}|\text{LPSCI}$ interface similar to the sample from Figure 4. As highlighted with the dashed rectangle and with a higher magnification in the right image, dendritic structures are visible near the surface of the solid electrolyte. This sample was analyzed ex-situ after electrodeposition of 5 mAh cm^{-2} lithium at a current density of $100 \mu\text{A cm}^{-2}$ in a reservoir-free cell system on a steel electrode.

Supplementary Note 1

Sputtering effect on the resulting XPS spectra

The change in shape of the acquired spectra in Figure S2 and the change in calculated sodium concentration during sputtering with 10 kV indicates that lithium is preferentially sputtered, leading to an apparent increase in sodium. Moreover, Shard and Baker¹ have demonstrated that increasing the accelerating voltage while maintaining a constant argon cluster size can enhance the removal of inorganic degradation products during argon cluster sputtering, which could explain the different shape of the XPS spectrum after the final sputtering step with an acceleration voltage of 20 kV.

Supplementary Note 2

Binary phase diagram of the Li-Na system

As can be seen from the phase diagram in Figure S6, only a very low amount of sodium can be dissolved homogeneously in solid lithium at room temperature. Accordingly, lithium production from a melt, inevitably containing sodium as an impurity, leads to sodium precipitation. The amount, size and distribution of the sodium precipitates will depend on the specific sodium content and processing route.

Supplementary Note 3

Residue analysis on the LLZO surface after Li_{LP} stripping using XPS and ToF-SIMS.

Using ToF-SIMS, a significant increase of the signal intensity for Na⁺ on the grey residues compared to the pristine surface can be observed in Figure S7.. In line with this, a strong enrichment of sodium is observed in the former contact area of the lithium electrode using XPS, which supports the SIMS results. From this we conclude that during stripping there is an accumulation of sodium at the interface to the LLZO pellet, which appears in the form of the gray residues.

Supplementary Note 4

Reproduced cells using LPSCl and LLZO as SEs.

Despite minor deviations within the respective cell systems, it is clear that the stripping capacities of Li_D > Li_{HP} > Li_{LP}. The drawn conclusions of the manuscript are therefore supported. At this point we like to mention that the stripping curve marked "Electrodeposited at 50 $\mu\text{A cm}^{-2}$ " was electrodeposited at a current density of 50 $\mu\text{A cm}^{-2}$. The other two Li_D samples were electrodeposited at a current density of 100 $\mu\text{A cm}^{-2}$. This observed trend is also confirmed by the measurements using LLZO as SE. Here too, there is an increase in the lithium stripping capacity of Li_{HP} compared to Li_{LP}. All layers were dissolved at a current density of 100 $\mu\text{A cm}^{-2}$.

Supplementary References

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7.2.2 Publication 2: “Microstructure of lithium metal electrodeposited at the steel| $\text{Li}_6\text{PS}_5\text{Cl}$ interface in “anode-free” solid-state batteries”

Microstructure of Lithium Metal Electrodeposited at the Steel| $\text{Li}_6\text{PS}_5\text{Cl}$ Interface in “Anode-Free” Solid-State Batteries

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Supporting Information

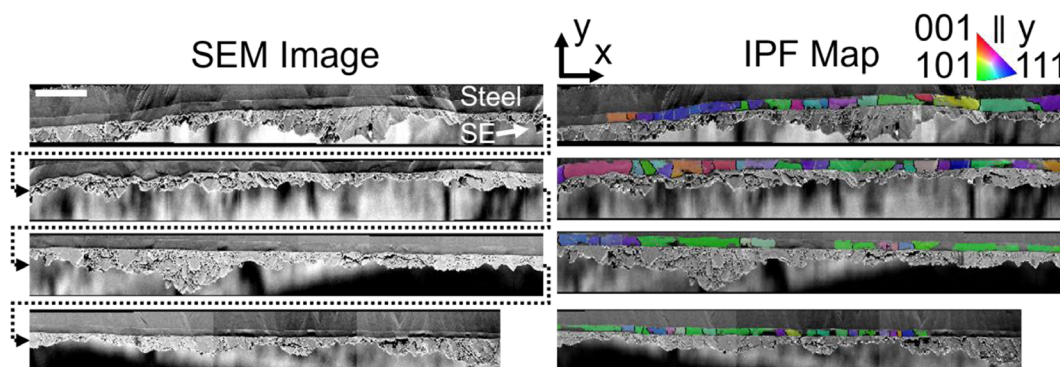


Figure S1. Full cross-section of a lithium layer electrodeposited with a current density of $50 \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} , related to **Figure 2**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The “reading direction” is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

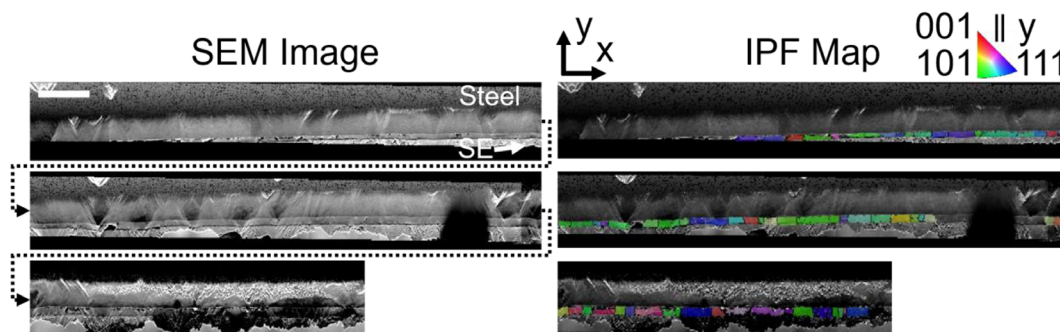


Figure S2. Full cross-section of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} , related to **Figure 2**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The

"reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling 50 μm .

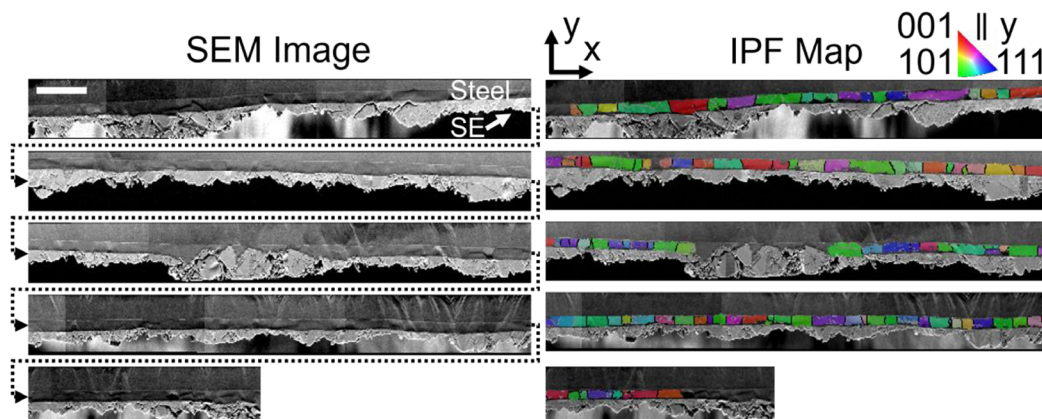


Figure S3. Full cross-section of a lithium layer electrodeposited with a current density of $250 \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} , related to **Figure 2**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

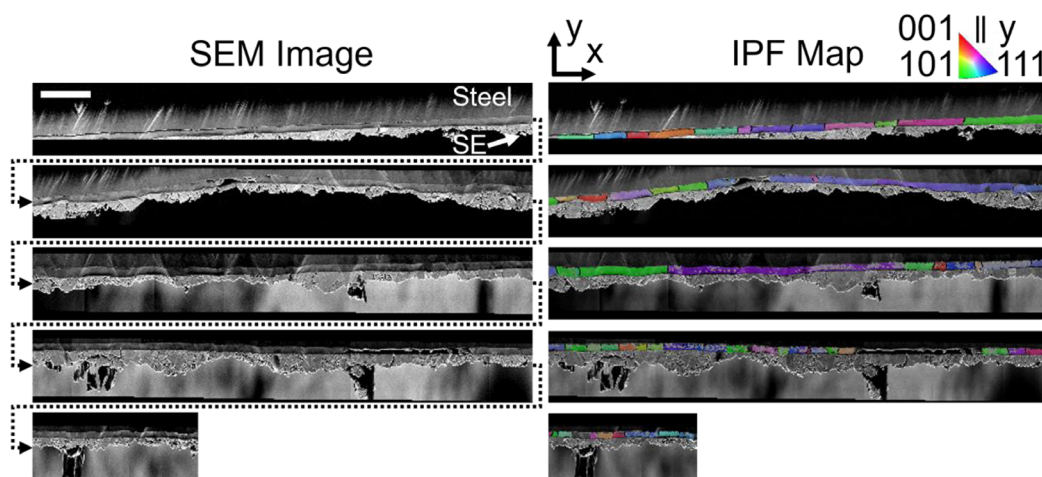


Figure S4. Full cross-section of a lithium layer electrodeposited with a current density of $500 \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} , related to **Figure 2**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

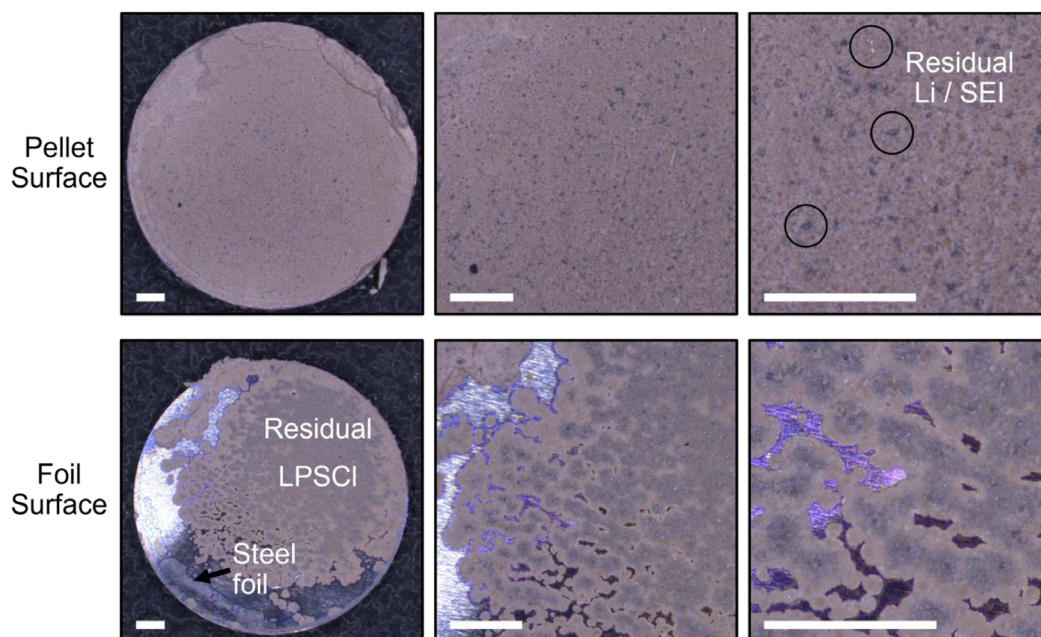


Figure S5. Optical images of a $\text{Li}_6\text{PS}_5\text{Cl}$ pellet surface and a steel working electrode after electrodeposition with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} . Please note that this is a sample used for reproduction of experiments and not the same one that was analyzed using EBSD within the manuscript. However, the surface morphology is comparable. Dark discoloration - sometimes shiny - can be seen on the pellet surface, which is attributed to residual lithium or degradation products, respectively. Chipped edges on the $\text{Li}_6\text{PS}_5\text{Cl}$ pellet were only caused during disassembly. The steel surface shows that not the entire electrode was electrochemically active. The bare steel foil can still be seen in some regions. However, most of it is covered by residual $\text{Li}_6\text{PS}_5\text{Cl}$, which adheres to the electrodeposited lithium behind it. The scale bars shown represent 1 mm in all images.

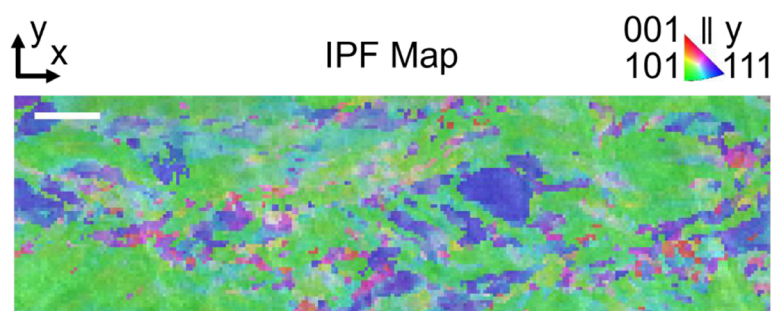


Figure S6. EBSD measurement on a cross-section of a steel foil, used as a working electrode within this work. The shown scale bar resembles $2 \mu\text{m}$. The average grain size is $0.762 \mu\text{m}^2$ and is therefore substantially smaller than the measured grain size of the analyzed lithium grains.

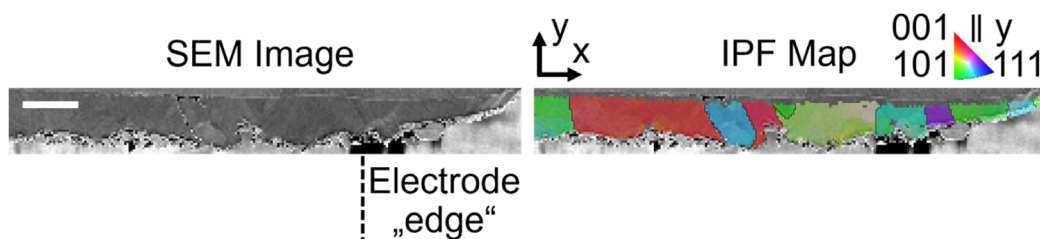


Figure S7. Cross-section and EBSD measurement of an edge piece of the used steel working electrode after lithium electrodeposition. A thinning of the lithium layer approaching the edge is visible. In addition, the grains at the edge of the electrode, where the lithium is thinner, also appear to become smaller laterally. The scalebar shown applies to both images, resembling 50 μm .

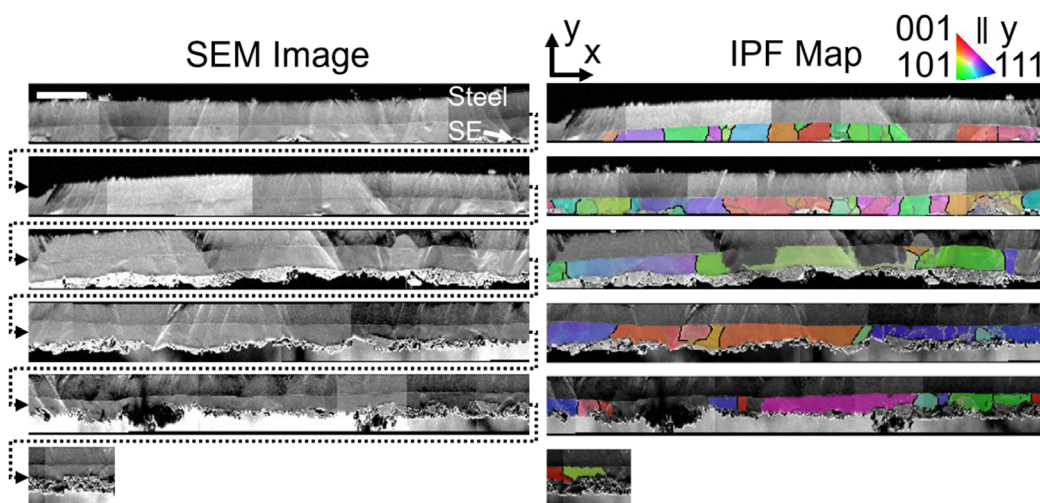


Figure S8. Full cross-section of a lithium layer electrodeposited with a current density of 100 $\mu\text{A cm}^{-2}$ for a capacity of 2.5 mAh cm^{-2} , related to **Figure 4**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling 50 μm .

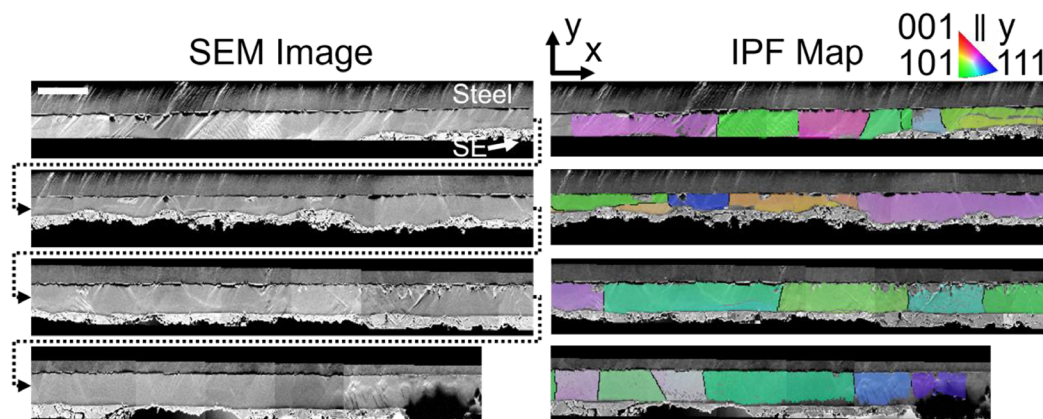


Figure S9. Full cross-section of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 5 mAh cm^{-2} , related to **Figure 4**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

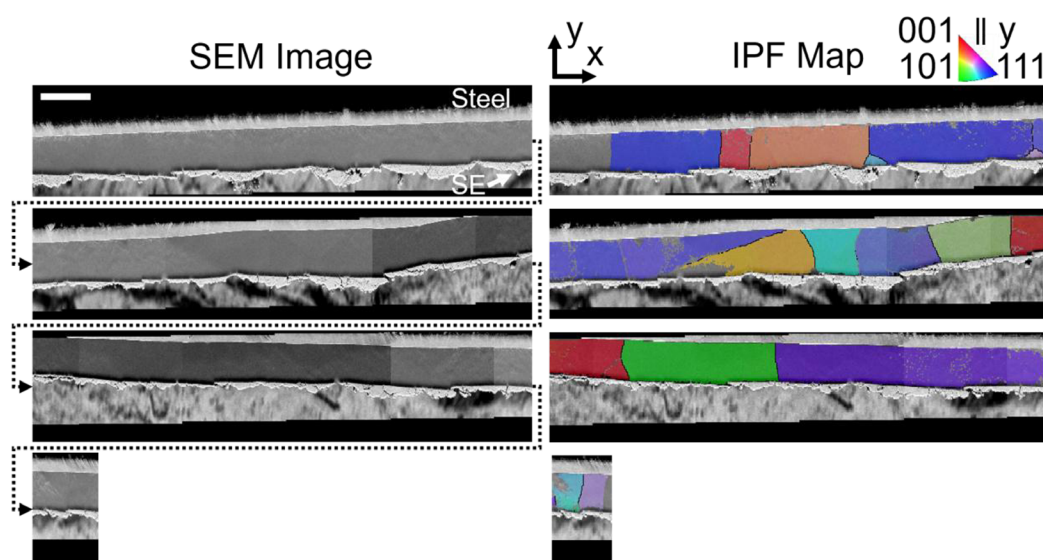


Figure S10. Full cross-section of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 10 mAh cm^{-2} , related to **Figure 4**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $100 \mu\text{m}$.

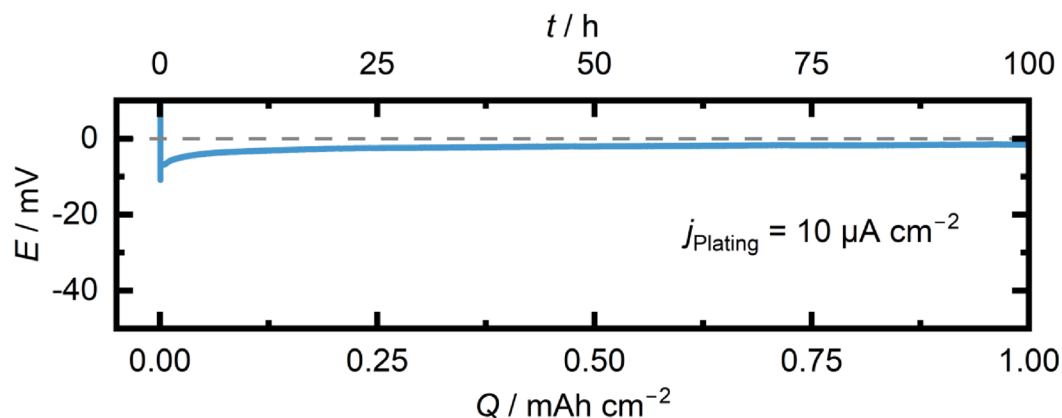


Figure S11. Potential profile during electrodeposition of a lithium layer with a capacity of 1 mAh cm^{-2} using a current density of $10 \text{ } \mu\text{A cm}^{-2}$. The electrodeposition time is 100 hours as shown above. This corresponds to the same deposition time as for a capacity of 10 mAh cm^{-2} at a current density of $100 \text{ } \mu\text{A cm}^{-2}$.

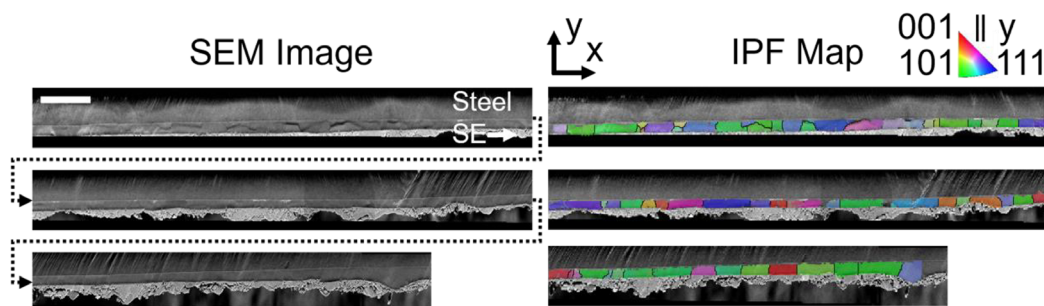


Figure S12. Full cross-section of a lithium layer electrodeposited with a current density of $10 \text{ } \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} . As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective IPF maps of lithium are displayed on the right side. The scalebar shown applies to all images visible, resembling $50 \text{ } \mu\text{m}$.

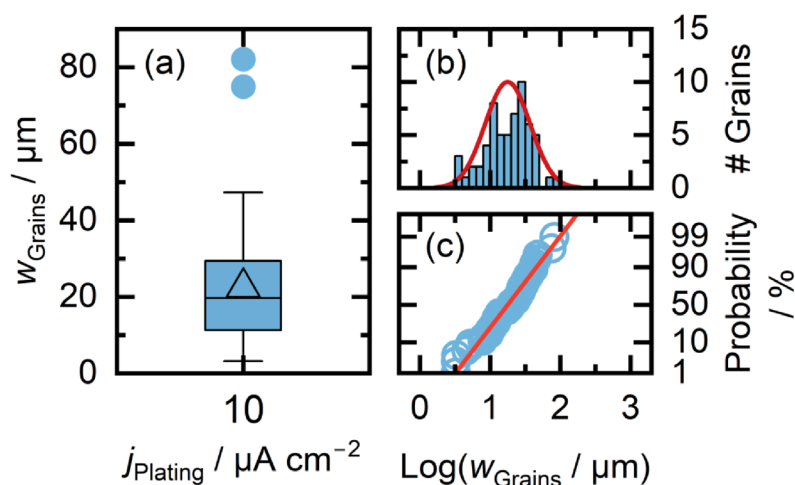


Figure S13. (a) Boxplot of the measured grain widths of a lithium layer with a capacity of 1 mAh cm^{-2} electrodeposited with a current density of $10 \text{ } \mu\text{A cm}^{-2}$. Outliers (interquartile range factor = 1.5) are marked with blue points in the boxplot. The distribution of grain widths summarizes 60 measured grains. The average is represented with a triangle inside the box. (b) Distribution of grains plotted against the logarithm of their sizes, with each class size being $\log(w_{\text{Grains}} / \mu\text{m}) = 0.1$. The red curve represents a fitted normal distribution, demonstrating a good match with the measured data and suggesting that grain sizes follow a lognormal distribution. (c) Probability plot of each grain width plotted against the logarithm of its size, confirming the approximate adherence to a lognormal distribution.

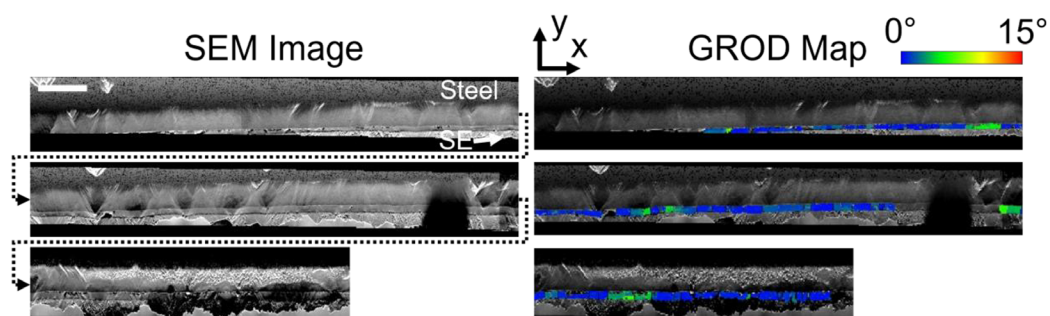


Figure S14. Angular GROD map of a lithium layer electrodeposited with a current density of $100 \text{ } \mu\text{A cm}^{-2}$ for a capacity of 1 mAh cm^{-2} , related to **Figure 5**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective GROD maps of lithium are displayed on the right side. Angular misorientations within a grain are colored as depicted in the colormap above. The scalebar shown applies to all images visible, resembling $50 \text{ } \mu\text{m}$.

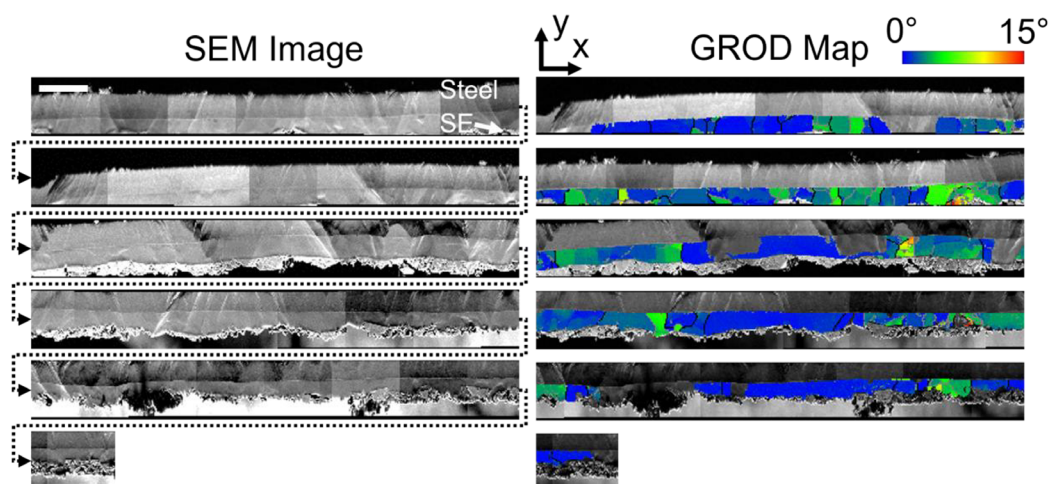


Figure S15. Angular GROD map of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 2.5 mAh cm^{-2} , related to **Figure 5**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective GROD maps of lithium are displayed on the right side. Angular misorientations within a grain are colored as depicted in the colormap above. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

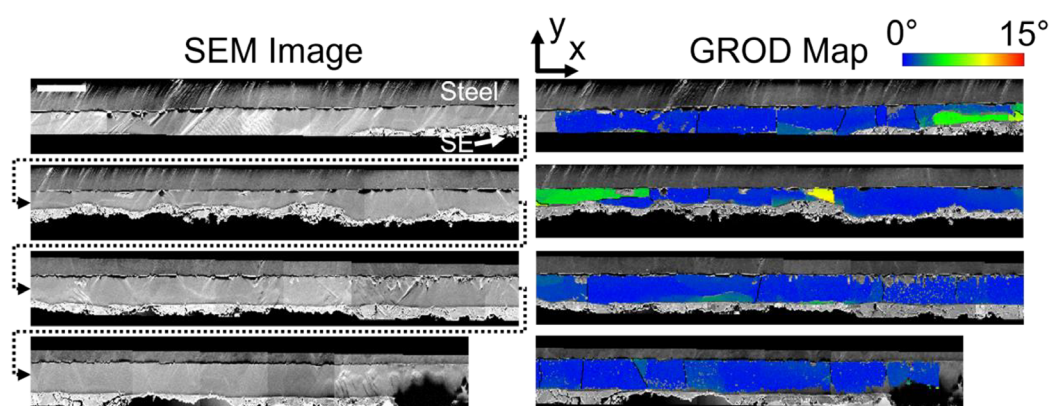


Figure S16. Angular GROD map of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 5 mAh cm^{-2} , related to **Figure 5**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective GROD maps of lithium are displayed on the right side. Angular misorientations within a grain are colored as depicted in the colormap above. The scalebar shown applies to all images visible, resembling $50 \mu\text{m}$.

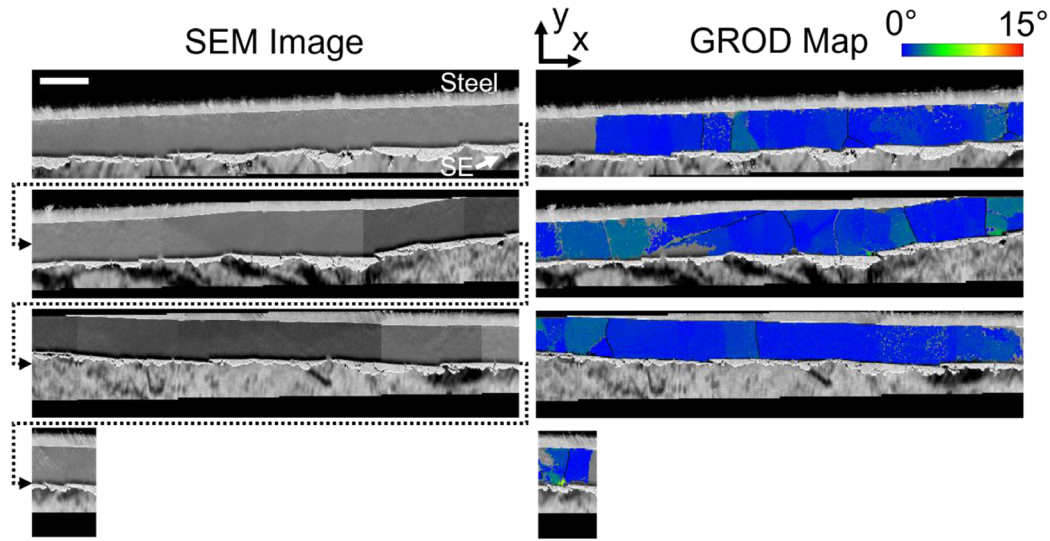


Figure S17. Angular GROD map of a lithium layer electrodeposited with a current density of $100 \mu\text{A cm}^{-2}$ for a capacity of 10 mAh cm^{-2} , related to **Figure 5**. As indicated, there is a layered structure with steel on top, lithium underneath and remaining $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large angle grain boundaries ($> 10^\circ$) are depicted with black lines. Misorientations between $2^\circ - 10^\circ$ are depicted in grey. The overall picture has been fragmented for improved visualization. Differences in contrast are due to the stitching mode used. The "reading direction" is labelled according to the arrows within the SEM image, respective GROD maps of lithium are displayed on the right side. Angular misorientations within a grain are colored as depicted in the colormap above. The scalebar shown applies to all images visible, resembling $100 \mu\text{m}$.

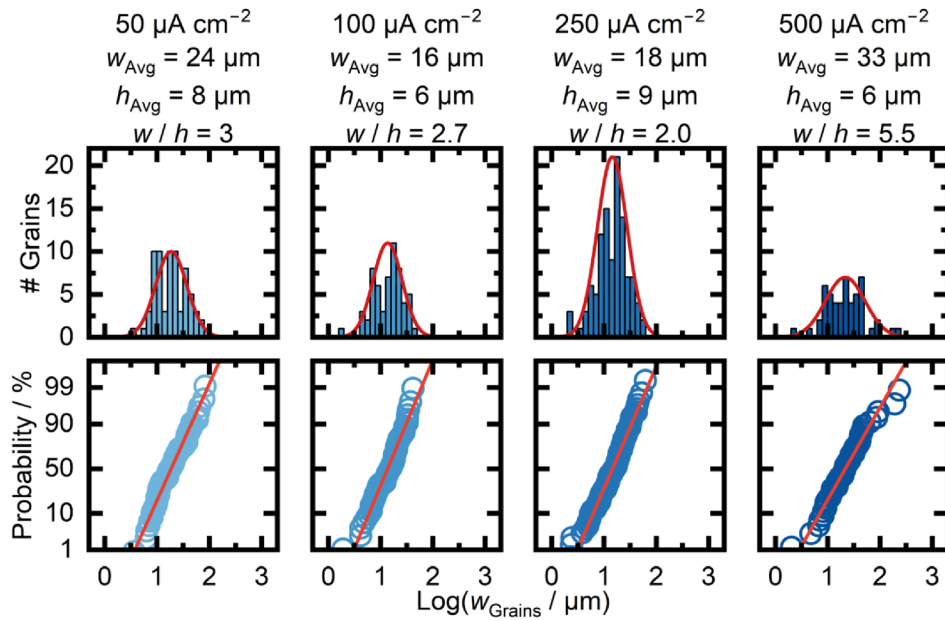


Figure S18. Distribution of grain widths for different plating current densities. Average widths, heights, and the width-to-height ratio are provided on top. Similar to the findings of Thompson¹, most ratios fall between 2 and 4, except for $j = 500 \mu\text{A cm}^{-2}$, which is slightly higher at 5.5. The bar chart depicts the number of grains plotted against the logarithm of their sizes, with each class size being $\log(w_{\text{Grains}} / \mu\text{m}) = 0.1$. The red curve represents a fitted normal distribution, demonstrating a good match with the measured data and suggesting that grain sizes follow a lognormal distribution. A probability plot below shows each grain's width plotted against the logarithm of its size, confirming the approximate adherence to a lognormal distribution, consistent with the hypothesis of normal grain growth by Thompson¹ in thin films.

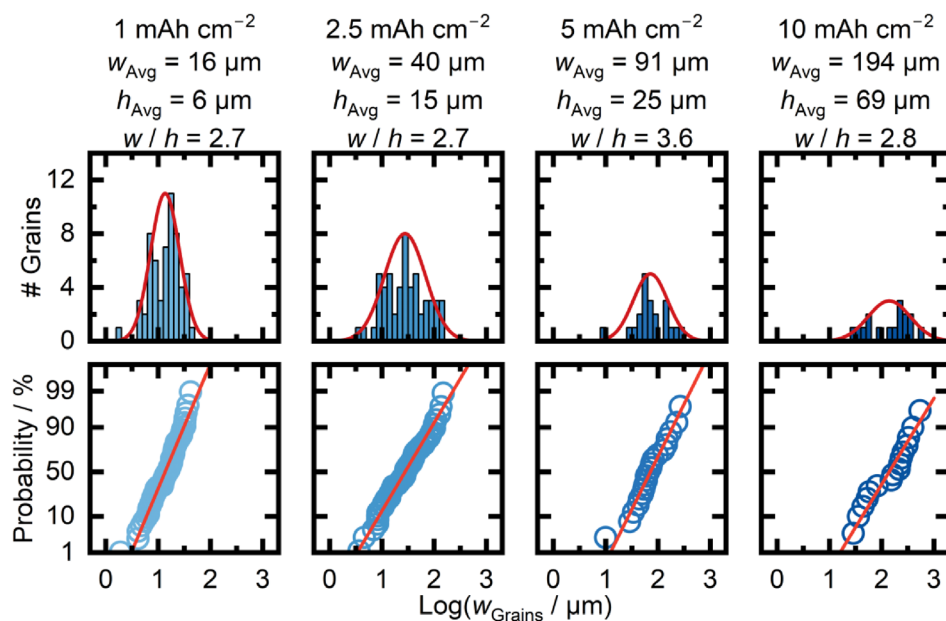


Figure S19. Distribution of grain widths for different plating capacities. Average widths, heights, and the width-to-height ratio are provided on top. Similar to the findings of Thompson¹, all ratios fall between 2 and 4. The bar chart depicts the number of grains plotted against the logarithm of their sizes, with each class size being $\log(w_{\text{Grains}} / \mu\text{m}) = 0.1$. The red curve represents a fitted normal distribution, demonstrating a good match with the measured data and suggesting that grain sizes follow a lognormal distribution. A probability plot below shows each grain's width plotted against the logarithm of its size, confirming the approximate adherence to a lognormal distribution, consistent with the hypothesis of normal grain growth by Thompson¹ in thin films. It is important to note that statistics for $Q = 5 \text{ mAh cm}^{-2}$ and $Q = 10 \text{ mAh cm}^{-2}$ are based on fewer grains, resulting in lower accuracy.

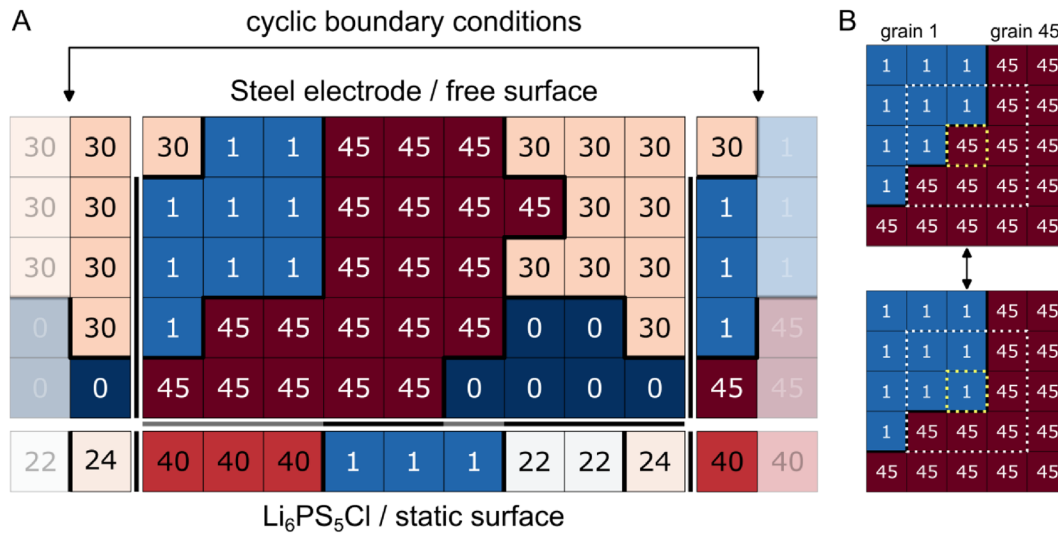


Figure S20. (a) Schematic representation of the applied Monte Carlo Potts model. A free surface is modelled above the lithium layer, which imitates the steel foil. There are no interactions assumed at this interface. The lithium layer can be seen underneath. The numbers inside the pixels indicate the orientation of the corresponding lithium pixel or lithium grain. Below the lithium, the microstructure of the Li₆PS₅Cl with its corresponding orientations can be seen. As indicated, cyclic boundary conditions are used. (b) Schematic of an “orientation” flip of the centered pixel. During the Monte Carlo steps only the nearest neighbors are considered, as indicated with the dashed white square around the centered pixel.

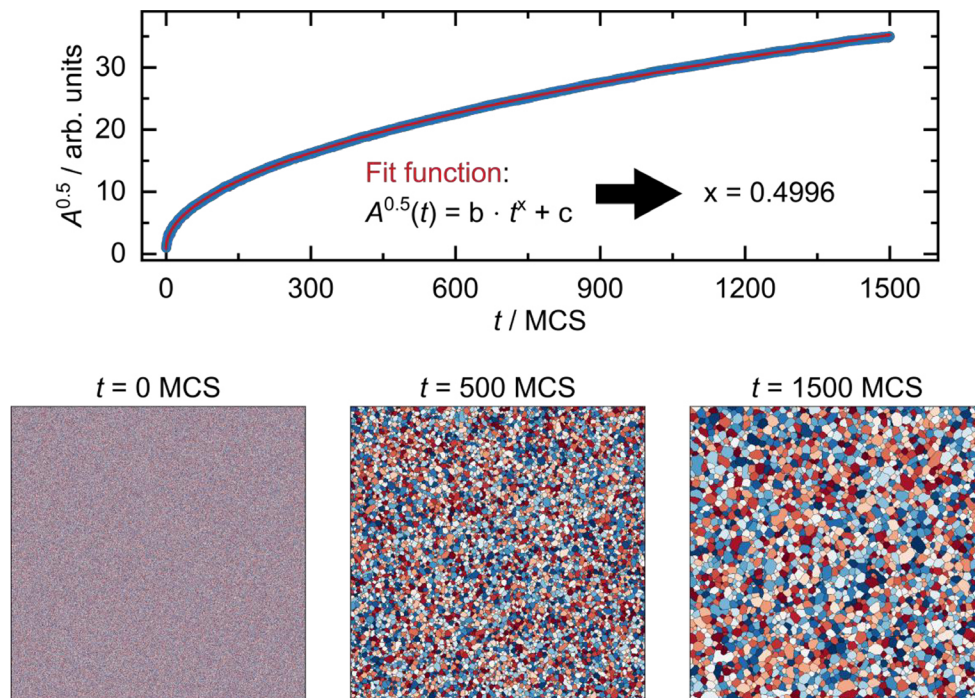


Figure S21. Schematic representation of the grain growth during the initial Monte Carlo steps. The square root of the mean grain area is plotted against the simulation time. The data is fitted with the shown fit function, revealing a square root of time dependency of the grain growth, which is expected for a normal grain growth. Exemplary grain structures at certain times are given below.

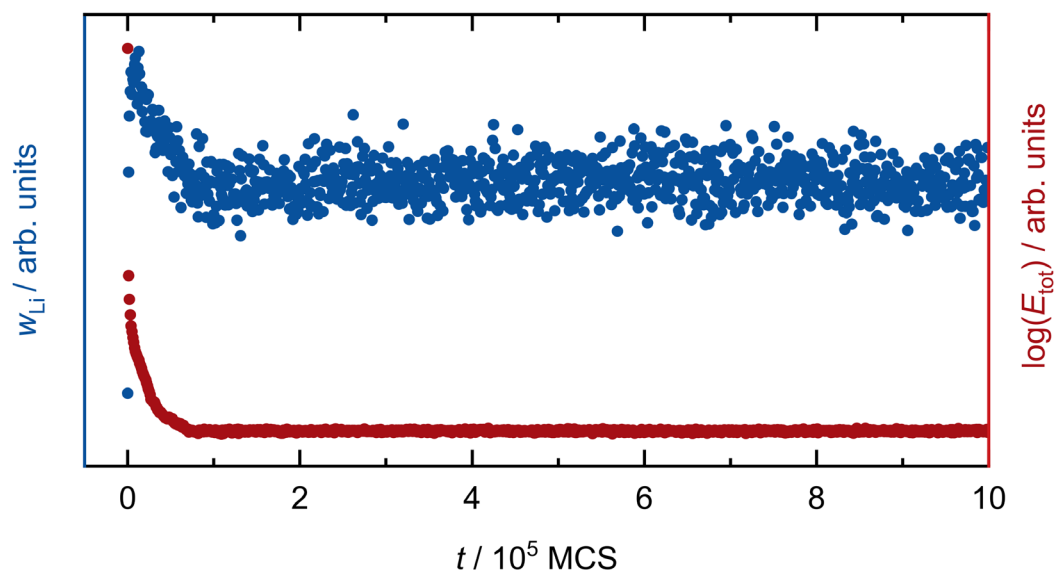


Figure S22. Evolution of the mean grain width w_{Li} and the logarithm of the energy E_{tot} plotted against the simulation time t . As can be seen from the graph, both w_{Li} and $\log(E_{\text{tot}})$ stagnate at the end of the simulation ($t = 10^6 \text{ MCS}$).

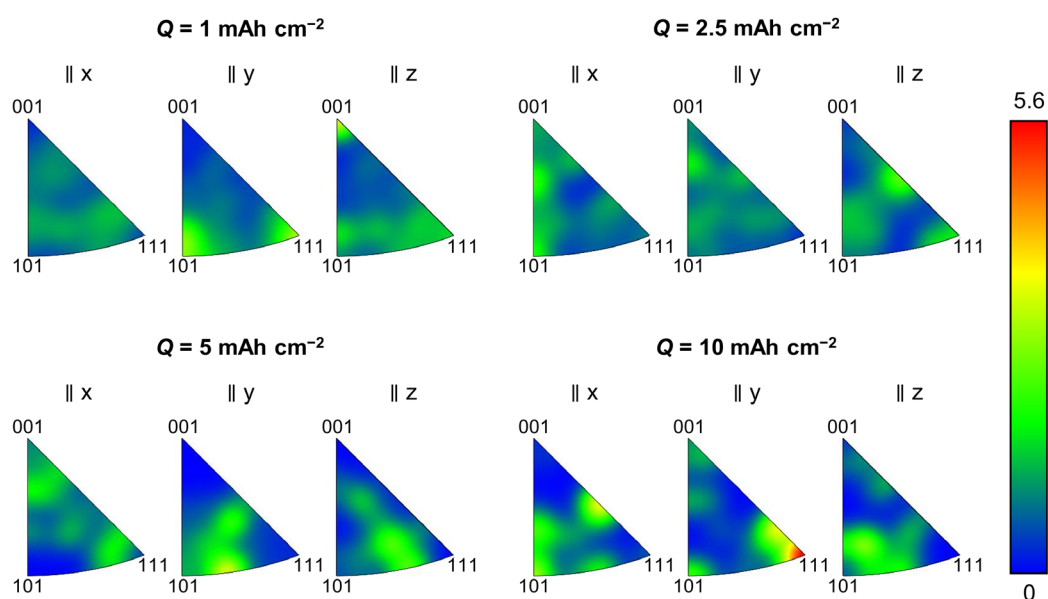


Figure S23. Inverse pole figures (IPFs) of the lithium layers electrodeposited with $j = 100 \mu\text{A cm}^{-2}$ for the shown capacities Q . The orientations parallel to the x , y and z directions are shown, as indicated above the IPFs. The normalized intensity of different orientations is shown according to the color scale on the right of the image.

Supplemental References

Thompson, C. V. Grain Growth in Thin Films. *Annual Review of Materials Science* **1990**, 20 (1), 245–268. <https://doi.org/10.1146/annurev.ms.20.080190.001333>.

7.2.3 Publication 3: “Microstructure of electrodeposited lithium and its evolution during cycling when using metal interlayers in “anode-free” solid-state batteries”

Supplementary Information (SI) for Energy & Environmental Science.
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Microstructure of Electrodeposited Lithium and its Evolution During Cycling when Using Metal Interlayers in “Anode-Free” Solid-State Batteries

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Δ Equal contribution

Supporting Information

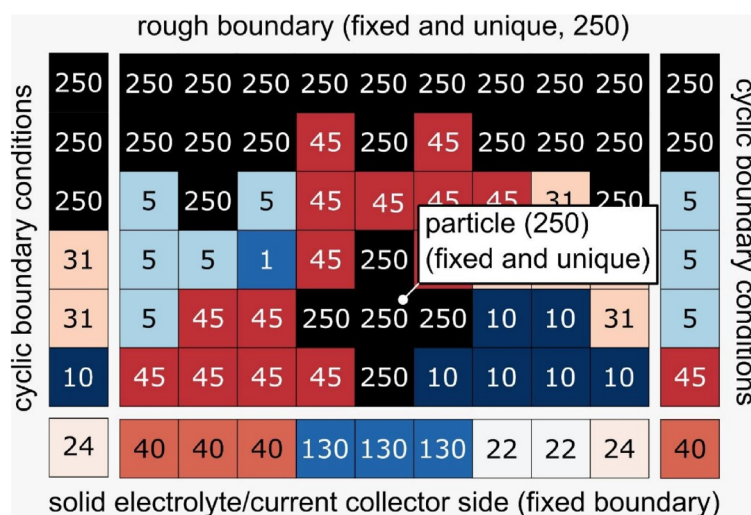


Figure S1: Scheme of the simulation approach and the cyclic boundary conditions for the Monte Carlo Potts model. The color and number within an MCU indicate the orientation of the respective MCU. The solid electrolyte on the bottom is simulated as a fixed boundary, i.e. its microstructure does not change throughout the simulation. Same is the case for the secondary particles introduced which are shown in black. Their orientation (250) is unique and fixed.

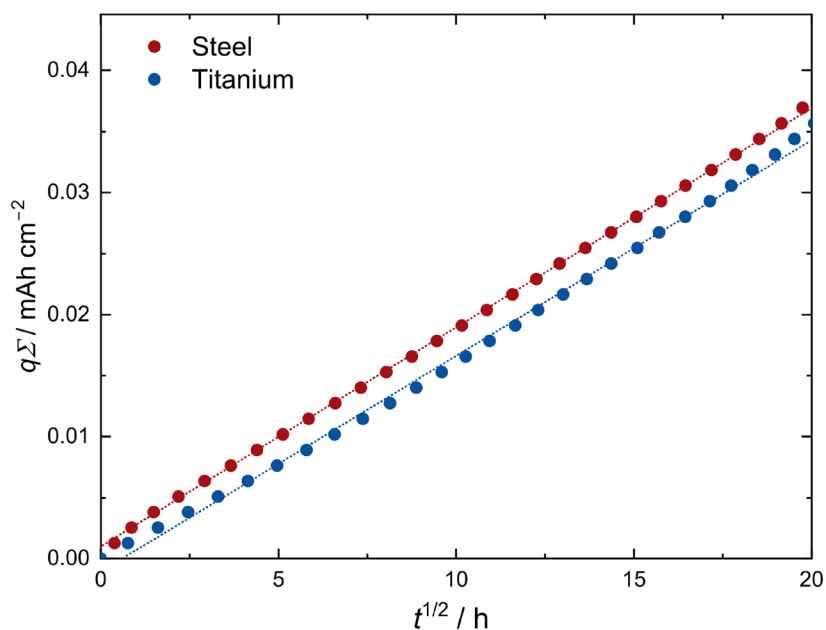


Figure S2. Results from coulometric titration time analysis (CTTA) performed on a steel and titanium current collector. The accumulated charge of lithium deposited on the WE is plotted against the square root of the overall elapsed time.

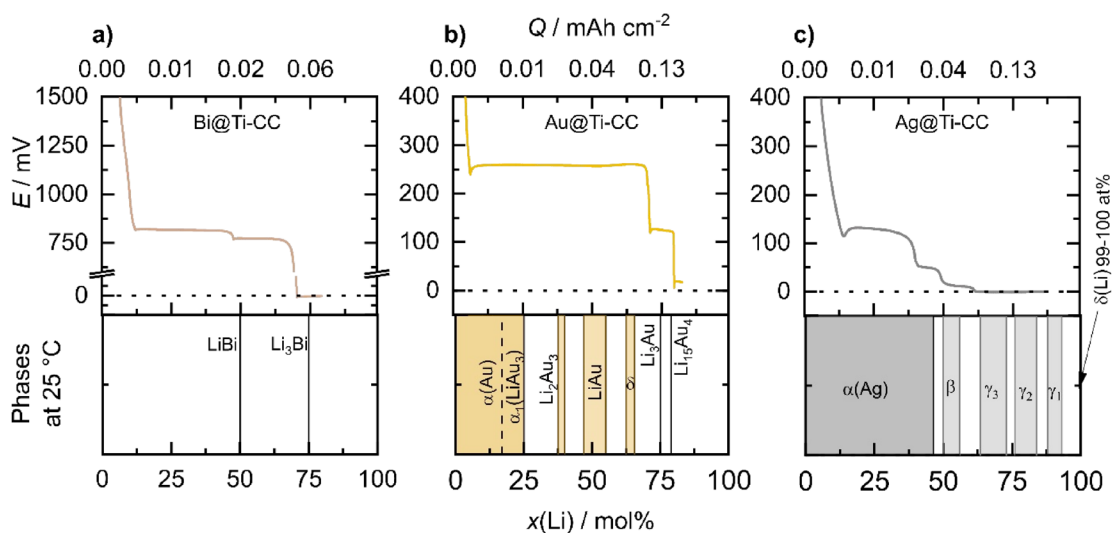


Figure S3. Voltage profiles during alloy formation on/with 160 nm of bismuth (a), gold (b), and silver (c) are shown, with an applied current density of $3 \mu\text{A cm}^{-2}$. The voltage is plotted against the lithium molar fraction and accumulated charge. Below the profiles, the distinct alloy phases at 25 °C, taken from published phase diagrams¹⁻³, are displayed as a function of lithium molar fraction.

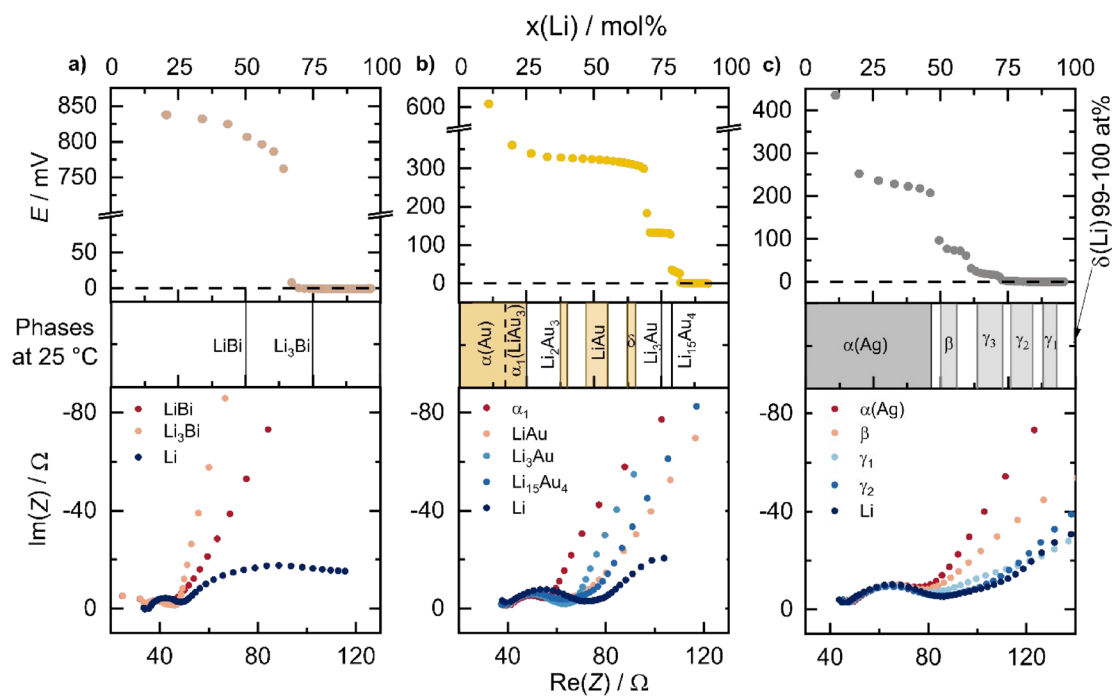


Figure S4: Electrochemical characterization of the alloying steps when plating lithium on a 160 nm thick bismuth interlayer (a), gold (b), and silver (c) using coulometric titration. On the top, the voltage during the resting period is shown at different stages of lithiation. Below the profiles, the distinct alloy phases, as taken from published phase diagrams^{1–3}, at 25 °C are displayed as a function of lithium molar fraction. At the bottom, electrochemical impedance spectra, acquired at times where the distinct alloy phases are present, are shown. For more information, we refer to **Supplementary Note 1**.

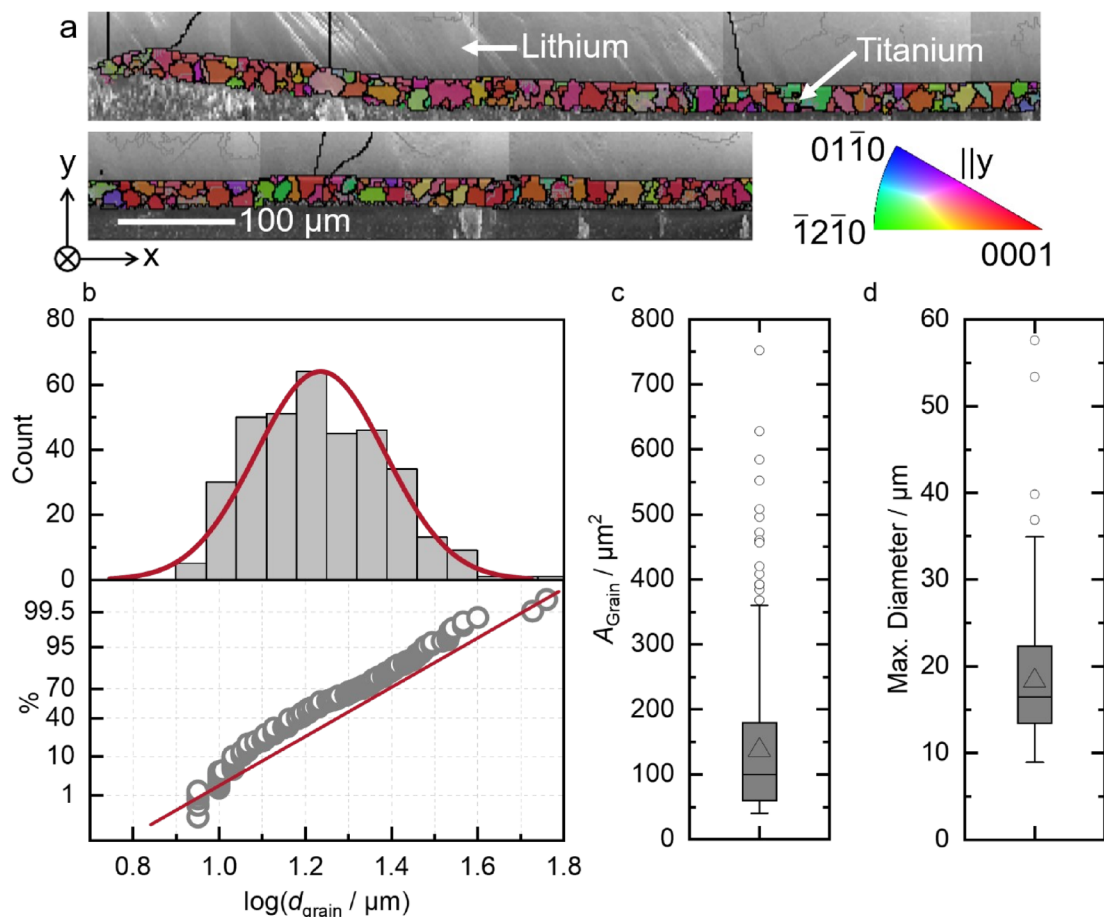


Figure S5: EBSD analysis of a cross-section of the titanium foil used in this study. (a) shows the inverse pole figure (IPF) map parallel to the y-direction. (b) presents the distribution of grain widths on a logarithmic scale. (c) and (d) display box plots of the grain areas and maximum grain diameters, respectively. Box plots of the grain surface areas and maximum grain diameters are shown in panels (c) and (d), respectively.

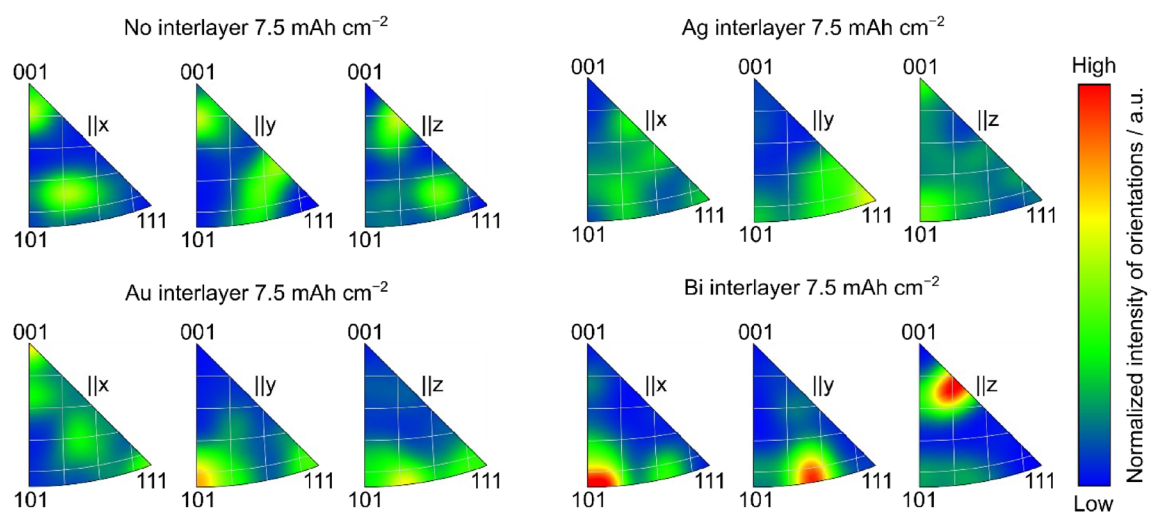


Figure S6. Inverse pole figures (IPFs) of the lithium layers electrodeposited at a current density of $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} with and without interlayers. The orientations parallel to the x, y and z

directions are shown, as indicated above the IPFs. The normalized intensity of different orientations is shown according to the color scale bar on the right of the IPFs.

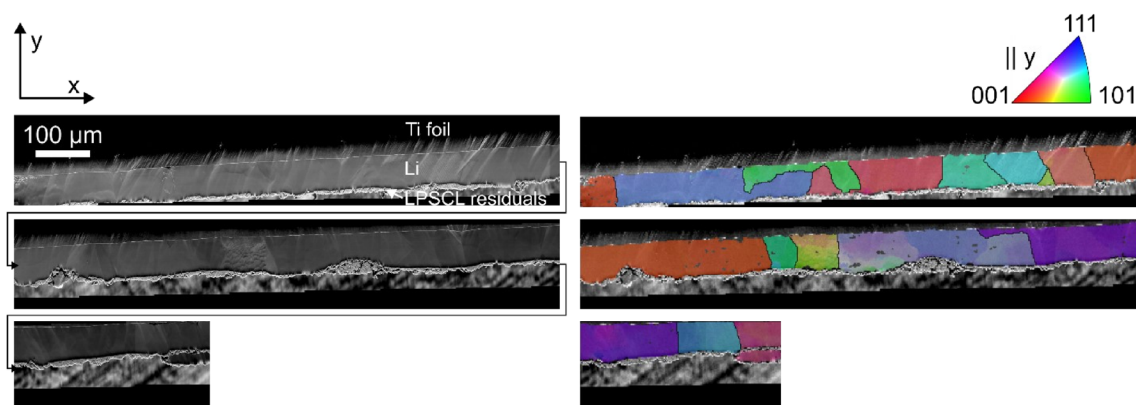


Figure S7. Full cross-section of a lithium layer electrodeposited at $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} on a titanium foil without interlayer (related to Figure 1). The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into several small sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps for lithium on the right are given parallel to the y -direction. The scalebar represents $100 \mu\text{m}$ in all images.

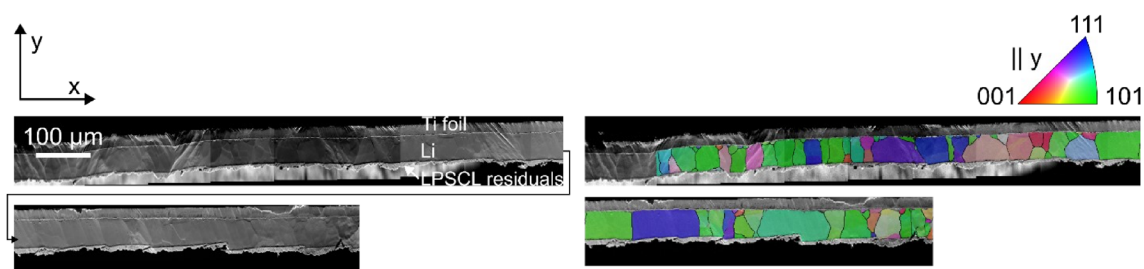


Figure S8. Full cross-section of a lithium layer electrodeposited at $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} on a titanium foil with a gold interlayer (related to Figure 1). The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into two smaller sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps on the right for lithium are given parallel to the y -direction. The scalebar represents $100 \mu\text{m}$ in all images.

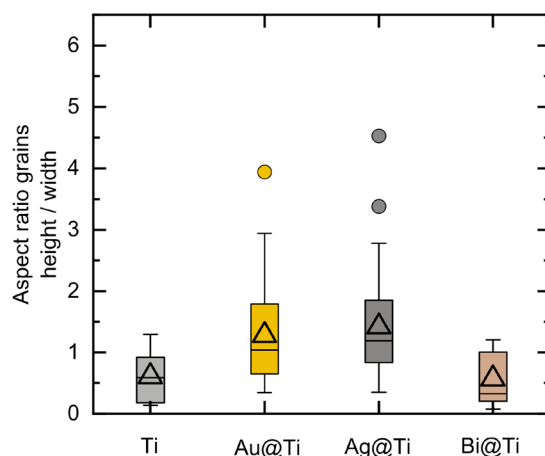


Figure S9. Aspect ratios (grain height divided by grain width) of the analyzed lithium grains electrodeposited with a current density of $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} using different interlayer materials.

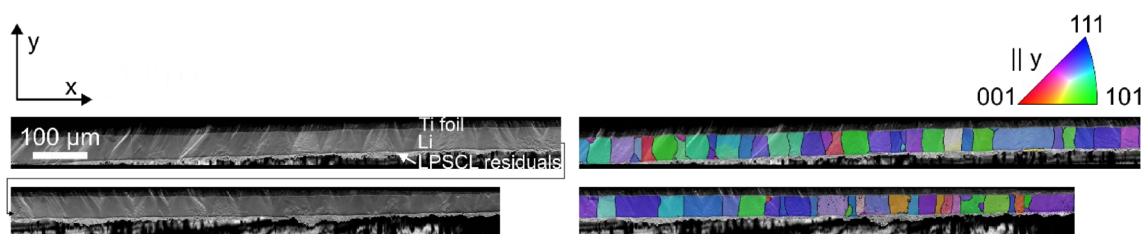


Figure S10. Full cross-section of a lithium layer electrodeposited at $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} on a titanium foil with a silver interlayer (related to Figure 1). The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into two smaller sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps on the right for lithium are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

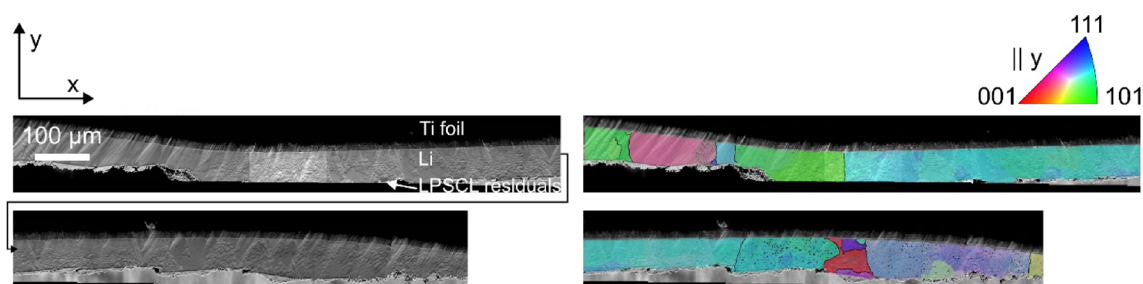


Figure S11. Full cross-section of a lithium layer electrodeposited at $150 \mu\text{A cm}^{-2}$ for 7.5 mAh cm^{-2} on a titanium foil with a bismuth interlayer (related to Figure 1). The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into two smaller sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps on the right for lithium are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

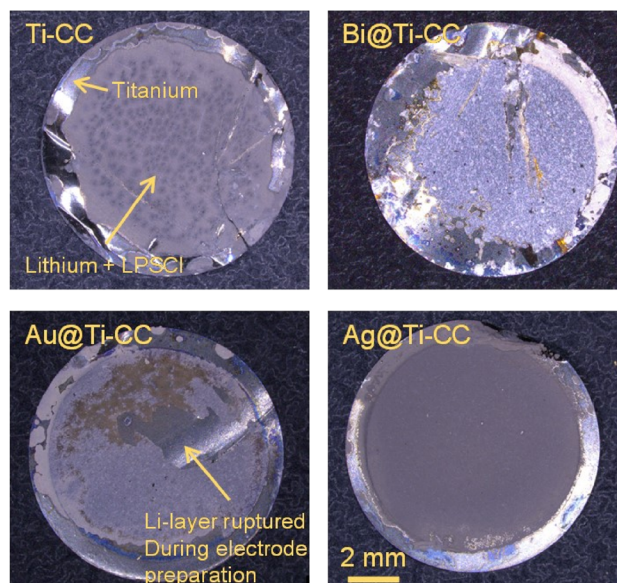


Figure S12. Optical images of the working electrodes after lithium electrodeposition and cell disassembly. The scalebar in the bottom right picture resembles 2 mm and is valid for all pictures. Please note that in the case of the pristine titanium foil, the whole electrode ($d \approx 10$ mm) was in contact with $\text{Li}_6\text{PS}_5\text{Cl}$. The diameter of the interlayers was only 8 mm.

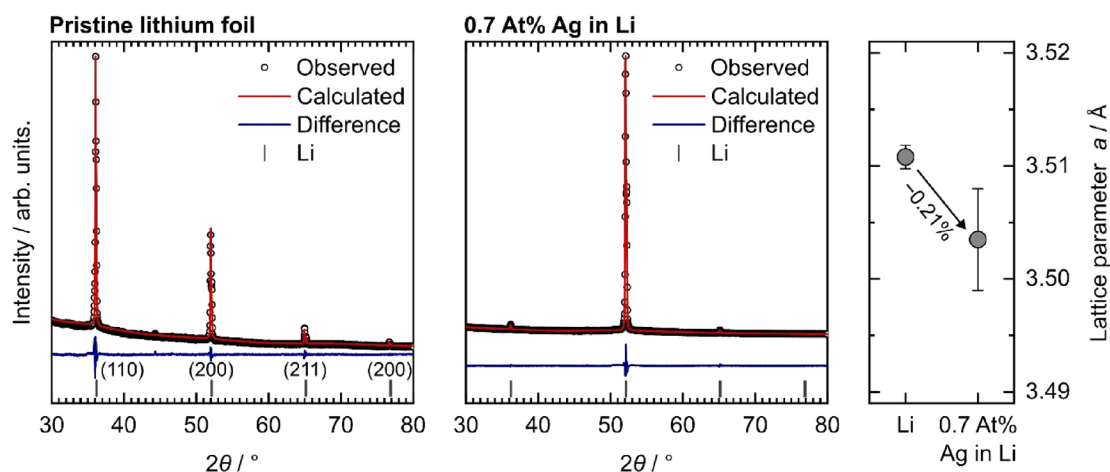


Figure S13: Comparison of X-Ray diffraction data acquired for pristine lithium foil (left plot) and a lithium foil with 0.7 At% dissolved Ag within (middle plot) with results of a Pawley-Fit. On the right, the extracted lattice parameter a shows a decrease with addition of Ag. For more information, we refer to **Supplementary Note 2**.

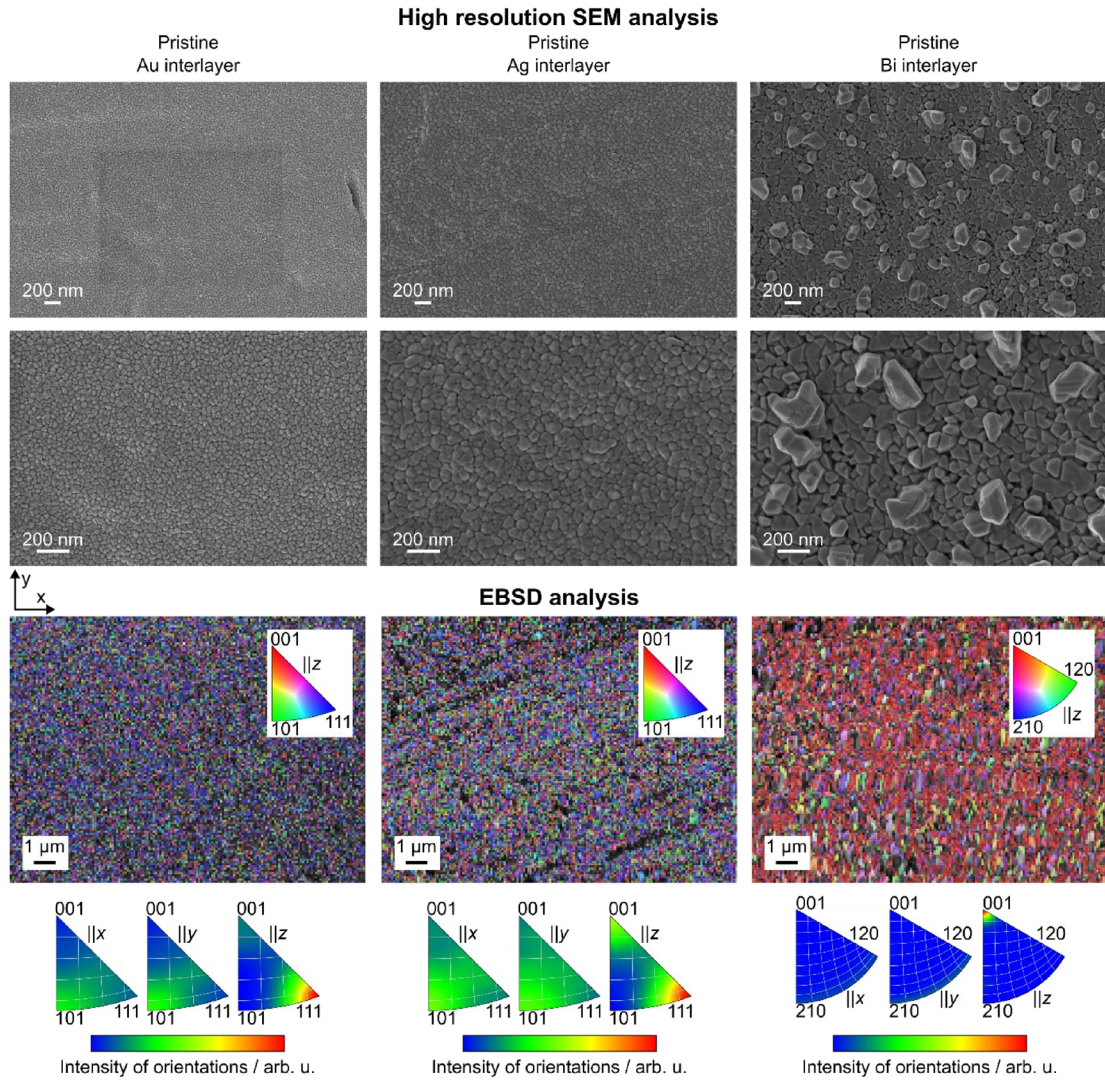


Figure S14: Microstructural analysis of the pristine interlayers. Columns correspond to the gold, silver, and bismuth interlayer, respectively. High-resolution SEM images are shown in the top row, while EBSD maps with the corresponding inverse pole figures are displayed below. Please note that the EBSD maps were acquired at different sample locations than the SEM images due to the distinct measurement geometries. Furthermore, the intensities of orientation were not normalized and cannot be compared in between different interlayer materials. More details are provided in **Supplementary Note 3**.

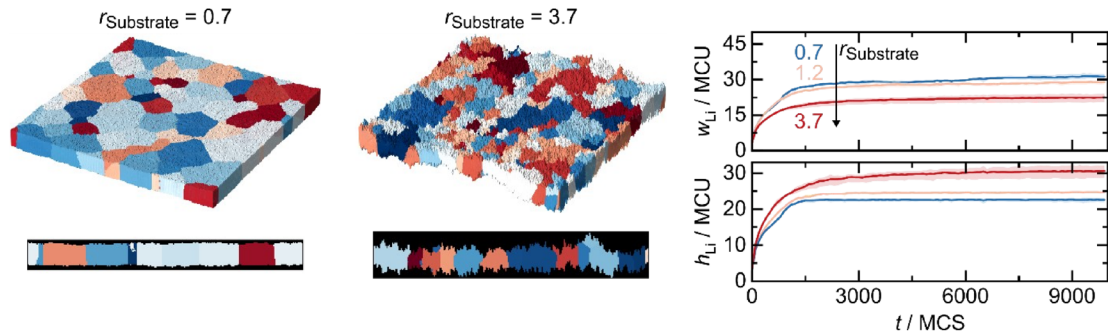


Figure S15: Simulation results of lithium microstructure evolution with different surface roughnesses of the substrate. The panel on the left shows two 3D microstructures with respective two 2D cross-sections

underneath. On the right, the evolution of the average grain width and height versus simulation time in Monte Carlo steps (MCS) is shown. For more information, we refer to **Supplementary Note 4**.

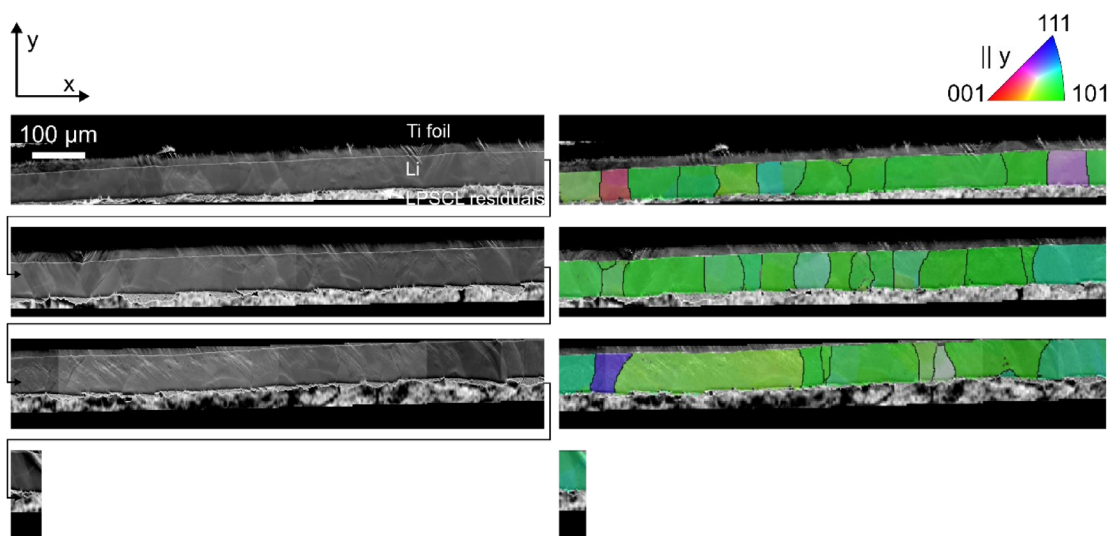


Figure S16. Full cross-section of a lithium layer electrodeposited at $100 \mu\text{A cm}^{-2}$ for 10 mAh cm^{-2} on a titanium foil with no interlayer (related to Figure 3) with subsequent stripping of 5 mAh cm^{-2} at the same current density. The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into several small sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps for lithium on the right are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

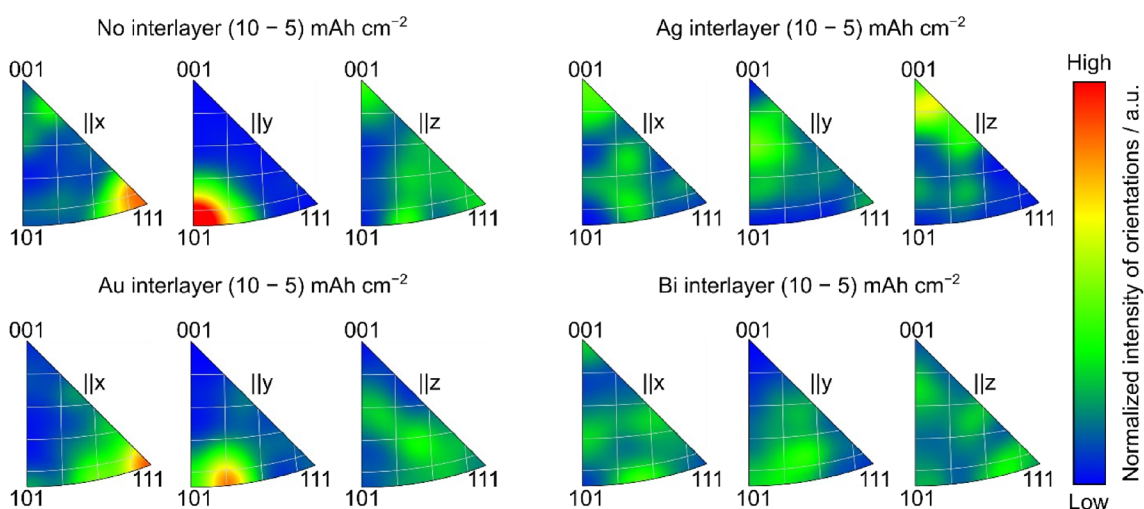


Figure S17. Inverse pole figures (IPFs) of the lithium layers electrodeposited on various substrates at a current density of $100 \mu\text{A cm}^{-2}$ for 10 mAh cm^{-2} and subsequent stripping of 5 mAh cm^{-2} using the same current density. The orientations parallel to the x, y and z directions are shown, as indicated above the IPFs. The normalized intensity of different orientations is shown according to the color scale bar on the right of the IPFs.

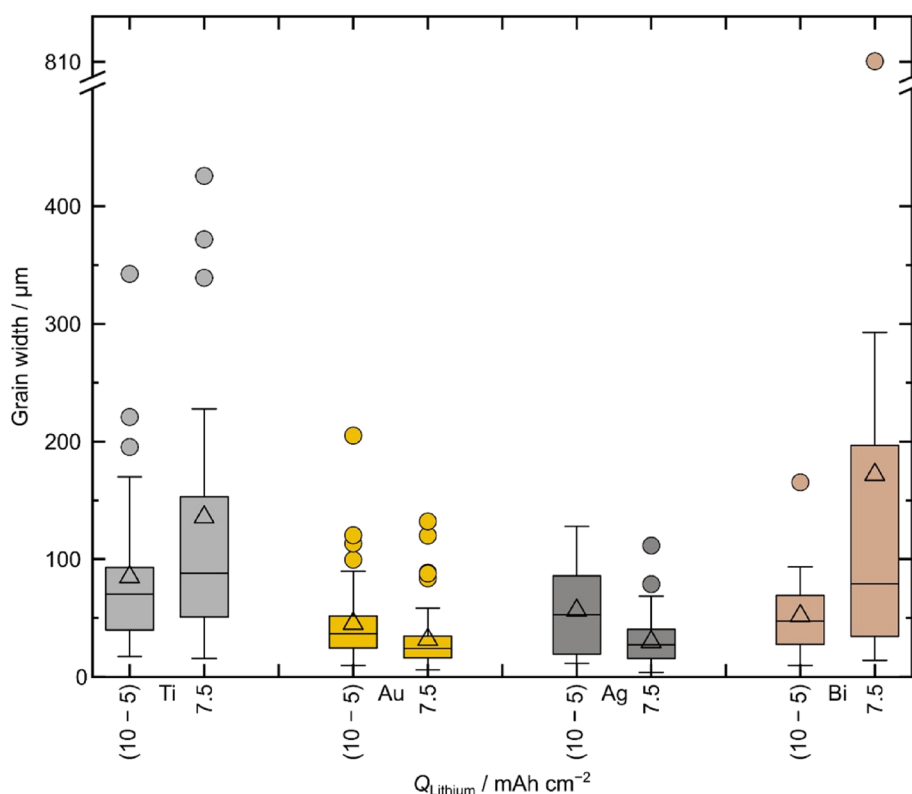


Figure S18: Grain widths of the lithium grains within the lithium layer with a total areal charge of 7.5 mAh cm^{-2} (after a plating step) or 5 mAh cm^{-2} (after a plating step followed by a stripping step). The samples denoted with $(10 - 5) \text{ mAh cm}^{-2}$ refer to the layers in which initially 10 mAh cm^{-2} of lithium were plated and subsequently 5 mAh cm^{-2} of these 10 mAh cm^{-2} were stripped again using a current density of $100 \mu\text{A cm}^{-2}$ (see Figure 3). The samples denoted with 7.5 mAh cm^{-2} refer to the layers in which solely a plating step was conducted for 7.5 mAh cm^{-2} of lithium at a current density of $150 \mu\text{A cm}^{-2}$ (see Figure 1). The used substrate for each case is given on the x-axis between the areal charges.

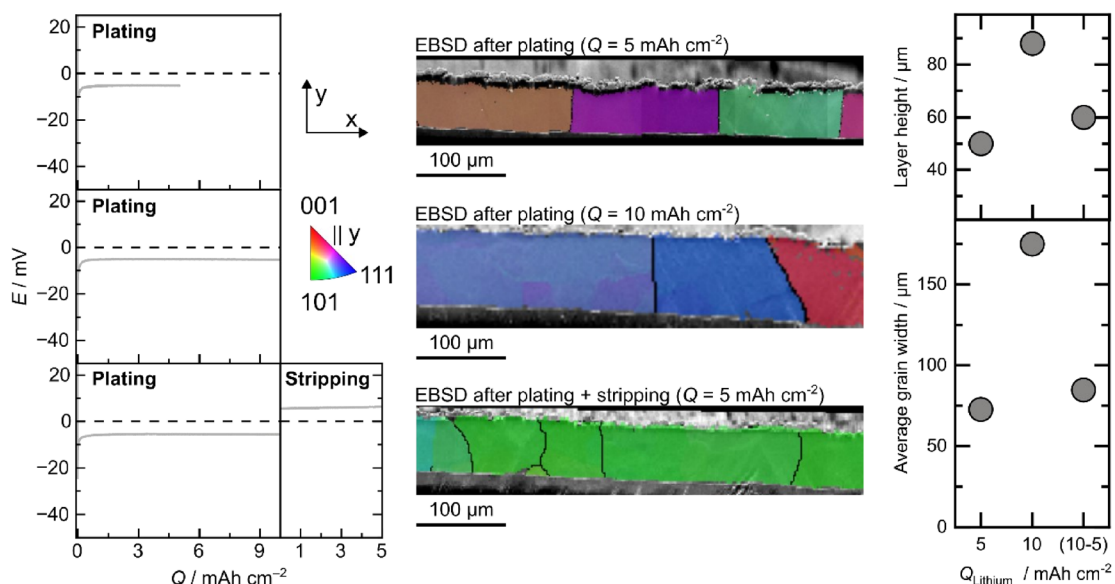


Figure S19: Grain size analysis of lithium deposited on pristine titanium foil. On the left, the voltage curves during lithium plating for samples with an areal charge of 5 mAh cm^{-2} and 10 mAh cm^{-2} are shown. For the sake of completeness, the voltage curve for plating and stripping of the

(10 – 5) mAh cm⁻² sample from Figure 4 of the main text is also shown. In the middle, representative sections of large IPF maps for the three samples are shown. On the right, the extracted layer height and average grain width is shown. As evident from the average grain width plot, the average grain width for both samples with an absolute areal charge of 5 mAh cm⁻² is comparable, despite their different cycling history.

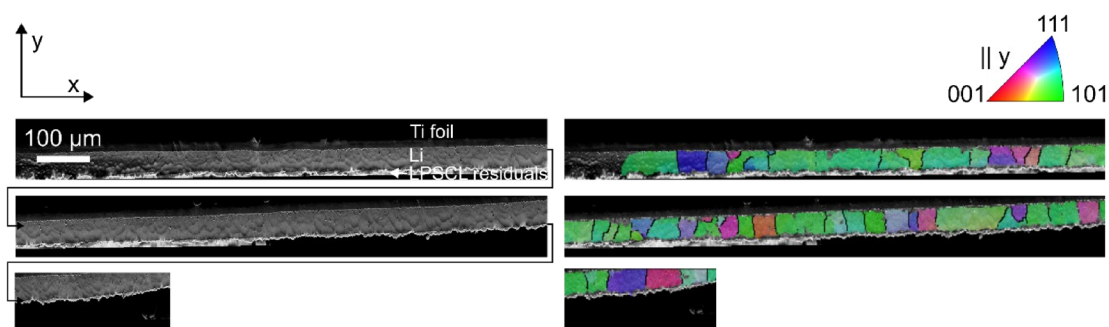


Figure S20. Full cross-section of a lithium layer electrodeposited at $100 \mu\text{A cm}^{-2}$ for 10 mAh cm^{-2} on a titanium foil with a gold interlayer (related to Figure 4) with subsequent stripping of 5 mAh cm^{-2} at the same current density. The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into three smaller sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps for lithium on the right are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

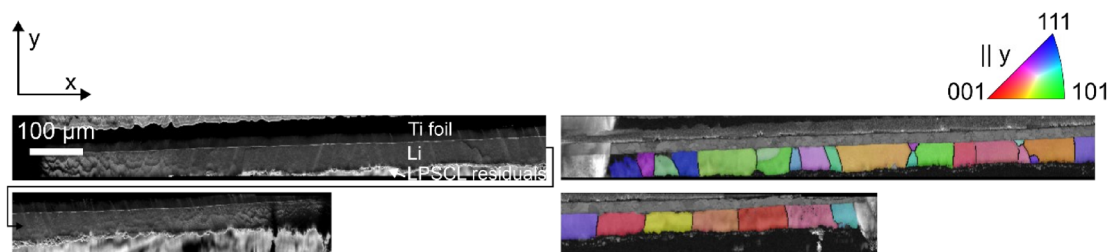


Figure S21. Full cross-section of a lithium layer electrodeposited at $100 \mu\text{A cm}^{-2}$ for 10 mAh cm^{-2} on a titanium foil with a silver interlayer (related to Figure 4) with subsequent stripping of 5 mAh cm^{-2} at the same current density. The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into two smaller sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps for lithium on the right are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

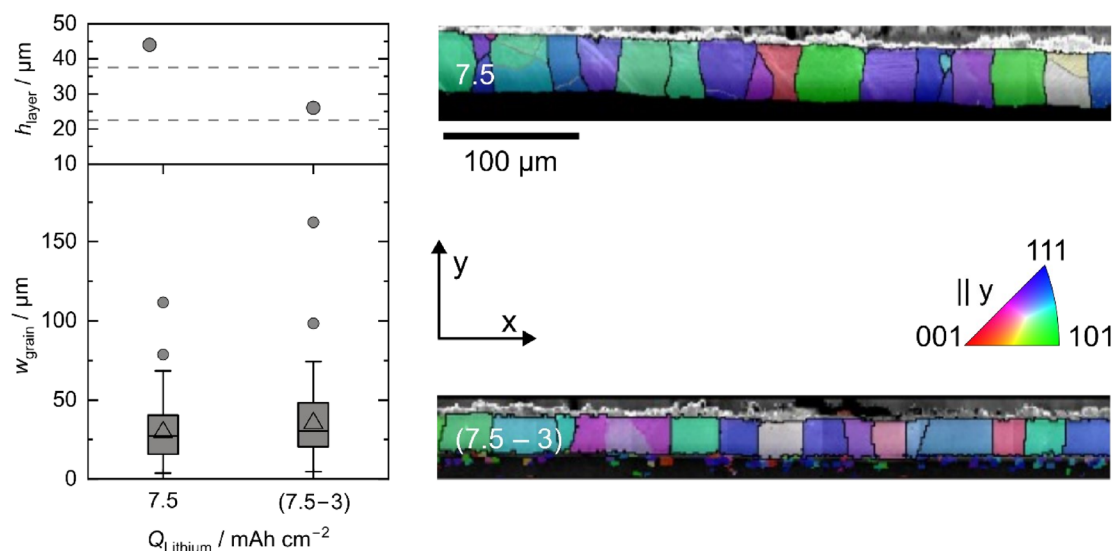


Figure 22: Grain size analysis of lithium deposited on titanium foil with a silver interlayer. The box plot on the left compares the layer thickness and grain size of a lithium layer plated on a silver interlayer for an areal charge of 7.5 mAh cm^{-2} and a lithium layer plated on a silver interlayer for an areal charge of 7.5 mAh cm^{-2} with subsequent partial stripping of 3 mAh cm^{-2} . Representative excerpts from larger IPF maps are shown on the right. Please note that the entire maps were analyzed to create the box plot.

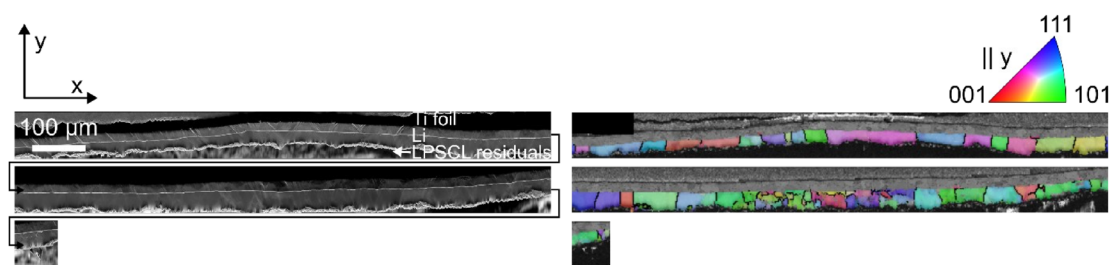


Figure S23. Full cross-section of a lithium layer electrodeposited at $100 \mu\text{A cm}^{-2}$ for 10 mAh cm^{-2} on a titanium foil with a bismuth interlayer (related to Figure 4) with subsequent stripping of 5 mAh cm^{-2} at the same current density. The cross-section reveals a layered structure with the Ti foil at the top, lithium in the middle, and residual $\text{Li}_6\text{PS}_5\text{Cl}$ particles at the bottom. Large-angle grain boundaries ($> 10^\circ$) are marked with black lines. Due to the large width of the cross-section, it was divided into two small sections for illustration purposes. The “reading direction” is shown with arrows in the SEM image. The overlaid IPF maps for lithium on the right are given parallel to the y-direction. The scalebar represents $100 \mu\text{m}$ in all images.

Supplementary Note 1 (Coulometric Titration)

To further analyze the potential evolution of distinct alloying phases, we conducted coulometric titration (CT) experiments. Here, an areal charge of $5 \mu\text{Ah cm}^{-2}$ of lithium was incrementally deposited onto the negative electrode. Each deposition step was followed by a 15-minute relaxation period, during which the open-circuit voltage was recorded to capture its evolution with lithium concentration throughout the alloying process. After every relaxation step, potentiostatic electrochemical impedance spectroscopy was performed. Particular attention was given to changes in the low-frequency regime, as these may reflect differences in lithium transport behavior between coexisting or sequential alloy phases. The impedance spectra collected during lithium titration show distinct low-frequency behavior depending on the interlayer material. For bismuth, a pronounced increase in low-frequency impedance is observed as LiBi and Li_3Bi form, with the rise becoming steeper at higher lithium content. In the case of gold, the low-frequency slope evolves gradually with increasing lithiation, reflecting changes in the spectra as successive Au-Li alloy phases appear. For silver, the low-frequency region shows little variation once high lithium contents are reached, with spectra remaining nearly identical where the final alloy phases would be expected. These observations indicate material-dependent differences in the evolution of impedance during lithium titration across the three systems.

Supplementary Note 2 (Ag-Li alloys)

To measure the influence of dissolved silver on the lithium crystal structure, 0.0579 g silver was added to a stainless steel crucible containing a melt of 0.5126 g lithium resulting in a

composition of 0.7 At% silver and 99.3 At% lithium. The molten mixture was held at 260°C for three hours before cooling. After the mixture solidified and cooled to ambient temperature, it was transferred from the steel crucible to a glass jar. All steps were performed inside a glovebox under argon atmosphere. For the XRD measurement, a piece of the produced Li(Ag) solid solution was freed from passivation and pressed into foil form using a uniaxial press in the glove box. A spacer was used during pressing to ensure comparability of the sample heights. The sample thickness was approximately 350 μm in all cases. For the structural analysis of the produced foil, it was placed on a (911)-oriented silicon zero background holder and covered with Kapton polyimide foil inside the glove box to minimize reactions with the humidity outside the glove box. The sample was then transferred to an Empyrean powder diffractometer (PANalytical) with a copper K_α radiation source ($\lambda_1 = 1.5405980 \text{ \AA}$, $\lambda_2 = 1.5444260 \text{ \AA}$). The measurements were performed in a 2Θ range from 10° to 90° with a step size of 0.026° . The measurement time per angle step was 200 s. A Pawley fit was performed using Bruker's TOPAS-Academic V6 software to analyze the lattice parameters of the sample. The same procedure was repeated with pristine lithium samples, i.e., without dissolved silver. In this case, the lithium foils were pressed directly from the lithium rod and analyzed in the diffractometer. A total of three samples were analyzed for pristine and silver containing lithium. The mean value for the lattice parameter a was calculated from the three respective Pawley fits. Please note that during the fitting, the other lattice parameters b and c were set equal to a due to the cubic crystal structure.

Supplementary Note 3

To characterize the microstructure of the interlayers prior to lithium plating, SEM and EBSD analyses were performed on interlayers deposited on titanium foils (**Figure S14**). High-resolution SEM images were acquired at 2 kV and a working distance of 2 mm, while EBSD was conducted at 20 kV with a 70° sample tilt, a working distance of 12.5 mm, and a step size of 100 nm. All three interlayers are nanocrystalline with grain sizes (maximum Feret diameter) below 200 nm, following the order $\text{Au} < \text{Ag} < \text{Bi}$. With the chosen EBSD step size of 100 nm, most grains span only a single pixel, leading to a slight overestimation of the actual grain size. The acquired SEM images suggest that the actual grain sizes are even smaller. Interestingly, the inverse pole figures reveal a preferential orientation for all deposited interlayers, characterized by an alignment of the $\langle 111 \rangle$ direction parallel to the z -direction for Au and Ag, and the $\langle 001 \rangle$ direction for Bi. For the FCC metals (Au, Ag), this orientation corresponds to the most densely packed (111) lattice planes lying parallel to the substrate. This configuration

typically minimizes the surface free energy. Although the crystal structure of bismuth is more complex, the preferred orientation in the $\langle 001 \rangle$ direction suggests an analogous thermodynamic driving force, likely favoring the exposure of the stable, low-energy planes of its crystal structure during growth.

Supplementary Note 4

Figure S15 investigates the influence of substrate surface roughness on the resulting lithium microstructure. The 3D microstructures and corresponding 2D cross-sections on the left illustrate two cases with roughness values of 0.7 and 3.7. These values correspond to the arithmetic average of the profile height deviations from the mean line. The plot on the right shows the temporal evolution of average grain width and height for these surface roughnesses. An increased substrate roughness reduces the effective grain size, as grains grow more irregularly and fail to develop fully columnar structures. At a roughness of 3.7, the average grain height reaches a lower value than at 0.7, indicating that taller surface features act as pinning sites that restrict vertical growth. This pinning mechanism is similar to that caused by impurities and substrate microstructure. The surface asperities locally block curvature-driven growth, slowing both height and in-plane expansion of grains. Consequently, while grains continue to coarsen over time, the overall growth stagnates earlier compared to smoother surfaces, resulting in a finer and more constrained microstructure.

Supplementary Literature

- (1) Sangster, J.; Pelton, A. D. The Bi-Li (Bismuth-Lithium) System. *Journal of Phase Equilibria* 1991, 12 (4), 447–450. <https://doi.org/10.1007/BF02645966>.
- (2) Pelton, A. D. The Au-Li (Gold-Lithium) System. *Bulletin of Alloy Phase Diagrams* 1986, 7 (3), 228–231. <https://doi.org/10.1007/BF02868994>.
- (3) Pelton, A. D. The Ag-Li (Silver-Lithium) System. *Bulletin of Alloy Phase Diagrams* 1986, 7 (3), 223–228. <https://doi.org/10.1007/BF02868993>.

7.3 Scientific Contributions

7.3.1 List of publications published online as checked on the 27th of March 2026

^ΔIndicates shared first authorship

2026	Becker, J.^Δ , Schuster, L. ^Δ , Kremer, S., Fuchs, T., Janek, J., Microstructure of Electrodeposited Lithium and Its Evolution During Cycling When Using Metal Interlayers in “Anode-Free” Solid-State Batteries, <i>Energy & Environmental Science</i> , 2026 .
2025	Raj, H., Aktekin, B., Becker, J., Janek, J., Pralong, V., Understanding the Role of Oxygen Substitution in Lithium Conduction and Air/Interfacial Stability of LGPS-Structured Oxy-Sulfide Electrolytes, <i>ACS Applied Materials & Interfaces</i>, 2025. Becker, J., Weintraut, T., Benz, S. L., Fuchs, T., Lerch, C., Becker, P., Eckhardt, J. K., Henß, A., Richter F. H., Janek, J., Purity of lithium metal electrode and its impact on lithium stripping in solid-state batteries, <i>Nature Communications</i>, 2025. Haslam, C. G.^Δ, Fuchs, T.^Δ, Liao, D. W., Becker, J., Dasgupta, N. P., Janek, J., Sakamoto, J. The Effect of Alloying Interlayers on Lithium Anode Morphology and Microstructure in “Anode-Free” Solid-State Batteries, <i>ACS Energy Lett.</i>, 2025.
2024	Becker, J., Fuchs, T., Ortmann, T., Kremer, S., Richter, F. H., Janek, J. Microstructure of Lithium Metal Electrodeposited at the Steel Li₆PS₅Cl Interface in “Anode-Free” Solid-State Batteries, <i>Adv. Energy Mater.</i>, 2024. Fuchs, T.^Δ, Ortmann, T.^Δ, Becker, J., Haslam, C. G., Ziegler, M., Singh, V. K., Rohnke, M., Mogwitz, B., Pepler, K., Nazar L. F., Sakamoto, J., Janek, J. Imaging the microstructure of lithium and sodium metal in anode-free solid-state batteries using electron backscatter diffraction, <i>Nat. Mater.</i>, 2024. Kremer, S., Rekers, R., Sigar, U., Becker, J., Schubert, J., Eckhardt, J. K., Bielefeld, A., Richter, F. H., Janek, J. A Simple Method for the Study of Heteroionic Interface Impedances in Solid Electrolyte Multilayer Cells Containing LLZO, <i>ACS Appl. Mater. Interfaces.</i>, 2024. Aktekin, B.^Δ, Kataev, E.^Δ, Rieger, L. M., Garcia-Diez, R., Chalkley, Z., Becker, J., Wilks, R. G., Henss, A., Bär, M., Janek, J. Operando Photoelectron Spectroscopy Analysis of Li₆PS₅Cl Electrochemical Decomposition Reactions in Solid-State Batteries. <i>ACS Energy Lett.</i>, 2024.
2022	Fuchs, T. ^Δ ; Becker, J.^Δ ; Haslam, C. G.; Lerch, C.; Sakamoto, J.; Richter, F. H.; Janek, J. Current-Dependent Lithium Metal Growth Modes in “Anode-Free” Solid-State Batteries at the Cu LLZO Interface. <i>Adv. Energy Mater.</i> , 2022 .

7.3.2 List of Conference Contributions

2025	Oral Presentation: Microscopy & Microanalysis 2025, Salt Lake City, UT, USA (07/2025): <i>Microstructural evolution of electrodeposited lithium metal in anode-free solid-state batteries</i>
2024	Oral Presentation: Bunsen Meeting on Solid-State Batteries VI, Frankfurt, Germany (11/2024): <i>Microstructure of Lithium Metal Electrodeposited at the Steel Li₆PS₅Cl Interface</i>
	Oral Presentation: 245th ECS Meeting 2024, San Francisco, CA, USA (05/2024): <i>Plating-Dependent Lithium Metal Microstructure in “Anode-Free” LPSCl Cells</i>
2023	Poster Presentation: German-Israeli Battery School 2023, Ein Gedi, Israel (02/2023): <i>Current-Dependent Lithium Metal Growth Modes in “Anode-Free” Solid-State Batteries at the Cu LLZO-Interface</i>

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I would like to thank all my colleagues and friends within the Janek group for creating such a pleasant and fun working atmosphere. Unless someone had overfilled the liquid waste container, it was always a great time, both in the lab and outside university. Special thanks go to Dr. Till Fuchs and Dr. Till Ortmann, *die Tillies*, both for their constant scientific support and for all the completely pointless conversations we had.

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Finally, I would like to express my gratitude to my family and especially to Lena, who has always supported me unconditionally. Thank you for every distraction, every boost of motivation, and for always making me laugh. Danke für Alles!