

Matthias Geiß

- Dissertation -



Sacrificial interlayers for all-solid-state batteries

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Sacrificial interlayers for all-solid-state batteries

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Der Mensch hat dreierlei Wege, klug zu handeln:
Erstens durch Nachdenken – das ist der edelste;
zweitens durch Nachahmen – das ist der leichteste;
und drittens durch Erfahrung – das ist der bitterste.

– Konfuzius

EIDESSTATTLICHE ERKLÄRUNG

Die vorliegende Arbeit wurde im Zeitraum vom 01.03.2015 bis 31.07.2019 am Physikalisch-Chemischen Institut der Justus-Liebig-Universität unter Betreuung von Prof. Dr. Jürgen Janek angefertigt.

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Ortenberg, den 24. 03. 2020

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Kurzfassung

Ziel dieser Dissertation ist es, ein tieferes Verständnis für die Reaktionsschichten zwischen metallischem Lithium und lithiumionenleitenden Festelektrolyten zu erlangen und das Konzept der Opferschichten zur Passivierung der Lithium|Festelektrolyt-Grenzfläche zu erläutern und anhand praktischer Beispiele zu belegen.

Zunächst werden die Lithium|Festelektrolyt-Grenzfläche und die an ihr auftretenden Phänomene diskutiert. Das Hauptaugenmerk liegt dabei auf der Bildung der Reaktionsschicht zwischen Lithium und dem Elektrolyten. Diese Bildung erfolgt sowohl in Batterien mit flüssigem Elektrolyten als auch in Batterien mit Festelektrolyten. Beide Systeme werden ausführlich erläutert und die Unterschiede zwischen diesen Fällen werden analysiert. Eine folgende Literaturzusammenfassung zeigt, mit welchen Materialien und Methoden in der Forschung versucht wird, die Grenzfläche zu stabilisieren und in wieweit sie die Zielsetzung erreichen, bzw. wo sie versagen.

Ausgehend davon wird diskutiert, über welche Eigenschaften eine Grenzfläche verfügen muss, damit sie den Elektrolyten vor Zersetzung in Kontakt mit Lithium bewahrt. Da davon ausgegangen wird, dass nur die wenigsten Festelektrolyte über die intrinsische Eigenschaft verfügen, eine stabile Grenzfläche zu Lithiummetall auszubilden, wird der neu entwickelte Opferschichtmechanismus zur Stabilisierung der Grenzfläche erläutert. Es wird aufgezeigt, welche Aufgaben diese Opferschichten erfüllen müssen und welche Materialien in Frage kommen.

Der Experimentaltail dieser Arbeit beschäftigt sich schließlich mit der Erzeugung dünner Schichten verschiedener Opferschichtmaterialien und der Herstellung der Testbatterien, sowie der verwendeten Nachweismethoden.

Die Idee des Opferschichtmechanismus leitet sich aus der Untersuchung von „LiPON“ ab, einem Festelektrolyten, der eine passivierende Reaktionsschicht in Kontakt mit Lithium bildet. Mittels Röntgen-photoelektronenspektroskopischer (XPS) Messungen wird die Bildung dieser Reaktionsschicht untersucht und sowohl ihre Zusammensetzung als auch ihre Dicke wird in Abhängigkeit der Elektrolytstöchiometrie experimentell ermittelt. Diese

Untersuchungen geben Aufschluss darüber, wie eine Reaktionsschicht beschaffen sein muss, um eine passivierende Wirkung zu entfalten.

Als zweites Material wird in dieser Arbeit Triphosphorpentanitrid (P_3N_5) eingesetzt. Aufgrund seiner Zusammensetzung sollte dieses Material in der Lage sein, in Kontakt mit Lithium eine Reaktionsschicht zu bilden, die die gleichen positiven Eigenschaften aufweist wie im Falle von „LiPON“. Der Spannungsabfall über die Reaktionsschicht sollte jedoch kleiner sein. Die Reaktionsschicht von P_3N_5 und Lithium sollte eine bessere ionische Leitfähigkeit besitzen, da im Gegensatz zu „LiPON“ kein schlecht leitfähiges Lithiumoxid Li_2O gebildet wird.

Zunächst muss jedoch die Gültigkeit des Opferschichtmechanismus für P_3N_5 nachgewiesen werden, wobei diese Untersuchungen zum Vergleich sowohl mit dem pulverförmigen Ausgangsmaterial als auch mit hergestellten Dünnschichten durchgeführt werden. Mittels struktureller und elektrochemischer Messungen wird dann gezeigt, wie sich diese Opferschichten auf die Zelleigenschaften und die Lithium|Elektrolyt-Grenzfläche auswirken. Dazu werden sowohl symmetrische $Li|LPS|Li$ -Feststoffzellen gebaut, als auch Vollzellen des Typs $NCM:LPS|LPS|P_3N_5|Li$.

Abschließend folgt ein Ausblick auf weitere Maßnahmen zum Schutz der Grenzfläche. Diese reichen von einer Verbesserung der Schichtqualität der in dieser Arbeit verwendeten Materialien über weitere Vorschläge für Opferschichten bis hin zu Multischichtsystemen.

Der Anhang dieser Arbeit umfasst neben einer ausführlichen Diskussion der Kenndaten herkömmlicher Lithiumionenbatterien, mit denen sich Feststoffbatterien werden messen müssen, zusätzliche Daten, die für das Verständnis der Argumentation förderlich sind. Dazu gehören zusätzliche Signale aus den XPS-Messungen von „LiPON“ und P_3N_5 , als auch die Vergleichsmessungen des P_3N_5 -Pulvers, aber auch Untersuchungsergebnisse weiterer möglicher Schutzschichtmaterialien.

Abstract

The aim of this dissertation is to gain a deeper understanding on the interface between lithium metal and lithium-ion conducting solid electrolytes and to introduce the concept of sacrificial interlayers as a method of passivating such interfaces. The applicability of sacrificial interlayers is discussed with respect to experimental results.

The first part of the dissertation comprises the theoretical background of this work and discusses the necessity of all-solid-state batteries.

As the interface between highly reactive lithium and any other adjacent phase is considered to be one of the most severe impediments for the realization of all-solid-state batteries, it is discussed in the second chapter of this dissertation. Several phenomena occurring at the interphase are explained and their influence on the battery properties is pointed out.

Then a chapter concerning protective layers and protection concepts gives a brief overview on various materials and concepts known from literature and discusses the applicability for the prevention of electrolyte decomposition. It will be examined to what extent these concepts fulfill the requirements for a thermodynamic or kinetic stabilization of the interface and what their limitations are.

Based on the properties of the interface, the thermodynamic and kinetic quantities that cause interphase formation are derived. Only if the reasons for a reaction are understood, possible methods to prevent this reaction can be suggested and experiments be developed.

In consequence, a working protective layer may cause lithium plating. Therefore, also this phenomenon will be explained briefly.

Afterwards, the concept of sacrificial interlayers is introduced and its mechanism is explained using „LiPON“ as a reference material. „LiPON“ forms a naturally stabilized interface with lithium metal. The properties of „LiPON“ that enable a stable interface are discussed. As phosphorous nitrides should be able to offer the same benefits, they are discussed as suitable interlayers, in particular P_3N_5 , the material that is examined in this work.

The experimental section of this work comprises the preparation of thin-films of various protective layers by ion-beam sputtering and radio-frequency magnetron sputtering. It also contains the fabrication of symmetric Li|LPS|Li transference cells with and without interlayer, and full cells of the type NCM:LPS|LPS|P₃N₅|Li.

A closer look at the interface between „LiPON“ and lithium metal is provided to learn more about the metastable interphase formation of this system. Especially the nature and the thickness of the naturally formed interphase are of major importance because any artificial interlayer must possess the same quality. Interlayers that are thicker than a natural SEI may not be fully converted into an ion conducting SEI. The unreacted film may add additional overpotentials to the cell depending on the transport properties of the interlayer.

Then phosphorous nitride is applied as interlayer. First, the reaction between P₃N₅ and lithium metal and the validity of the concept of sacrificial interlayers is demonstrated by means of X-ray photoelectron spectroscopy. Then the effect of a P₃N₅ interlayer in solid-state cells is demonstrated via lithium plating/stripping, battery cycling and impedance spectroscopy.

The final part of this dissertation comprises a summary of the obtained results and an outlook on further experiments on „LiPON“, phosphorous nitrides, metal nitrides and other promising interlayers.

The appendix comprises a review on the properties of lithium-ion batteries that are required to successfully promote electric mobility and an evaluation of aspects that might be improved by applying all-solid-state batteries. In addition, the appendix comprises more detailed photoelectron spectroscopy results on „LiPON“ and phosphorous nitride.

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Introduction

It is often claimed that all-solid-state batteries (ASSB) are the future battery technology that will enable affordable electric vehicles with large driving ranges and a long life time. Any all-solid-battery that will be used in electric vehicles must be able to compete with current state-of-the-art batteries. The purpose of this first chapter is to take a short look at the significance of battery research, solid electrolytes (SE) and lithium metal anodes.

The significance of battery research

The significance of battery research can easily be understood if one tries to live a day without using any portable energy storage. Batteries are included almost everywhere: alarm clocks, electric tooth brushes, smartphones, and even vehicles. They can be used in door bells, radios, entertainment electronics, hearing aids, laptops, flashlights and many other applications. The more applications, the more batteries are needed. There are various battery types like lead-acid batteries, nickel-metal hydride (NiMH) batteries, nickel-cadmium batteries (NiCd), zinc batteries or lithium-ion batteries, each of which have a different application area.

The most frequently used batteries are lithium-ion batteries. They benefit from their high energy density and power density which exceeds those of the other battery types.

The energy density w describes how much energy can be stored in a battery. The energy density is usually referred to as volumetric energy density (unit: Wh/L) or gravimetric energy density (Wh/kg). The power density p describes how fast this energy can be released during

the discharge process. The energy and power density are usually calculated with respect to the active material that stores the energy; values that are suitable for research and lab scale processes. For real application, usually the energy and power density are given with respect to the entire battery volume and battery weight. As batteries are typically used in applications where there is no conventional plugged energy supply, a high energy density and power density are required.

Why all-solid-state batteries?

All-solid-state batteries may not necessarily be required to bring electric vehicles to the market (for a detailed discussion of state-of-the-art batteries in electric vehicles the reader is kindly referred to **Appendix B** of this work), but they may play a key role in reducing the battery volume and weight and increasing the energy and power density, and simultaneously increase the battery safety.

The energy W (Wh) of a battery is described by the product of the battery voltage U and the battery capacity Q .

$$W = U \cdot Q \quad (1)$$

The power P is the product of the battery voltage and the current I .

$$P = U \cdot I \quad (2)$$

True to the slogan *Citius, Altius, Fortius*, manufacturers would like to sell smaller, lighter devices with elongated lifetime. For that, higher energy densities are required. To achieve higher energy or power densities, one has to increase either the battery voltage or the battery capacity/peak current.

Changing the battery voltage is only possible when different electrode materials are used, as the voltage depends on the difference of the chemical potential of lithium in both electrodes (cf. **chapter 2.4**). Also the capacity of an electrode depends on the electrode material. Every electrode material has a certain lithium uptake that defines its capacity; e.g. carbon can (depending on its modification) take up lithium up to LiC_6 , delivering a capacity of 372 mAh/g [1]. Once this limit is reached, a further increase of the capacity is not possible

without destroying the structure. Whereas engineering can be done to reach the physicochemical limit, higher capacities require different electrode materials.

One way to increase the power of a battery is the application of high-voltage cathode materials. The most common electrode material, lithium cobalt oxide LiCoO_2 , has a capacity of 140 mAh/g and can be charged to voltages of up to 4.2 V vs. Li^+/Li [2].

By applying other cathode materials like lithium nickel manganese oxide $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) or lithium cobalt phosphate LiCoPO_4 the battery voltage may be increased up to 5 V [3]–[7]. Unfortunately, conventional liquid electrolytes (a conductive lithium salt like LiPF_6 or LiClO_4 dissolved in an organic solvent like ethylene carbonate [8]) are unstable against these high potentials and decompose. In addition, liquid electrolytes are inflammable and, in case of an accident or a defective device, can pose a huge safety risk. To overcome the stability and safety issues, liquid electrolytes might be replaced by solid electrolytes. Many solid electrolytes are oxide materials and cannot be ignited and many of them are stable against potentials above 4.2 V vs. Li^+/Li [9], [10]. In terms of ionic conductivity, the best solid electrolytes are thiophosphates [11]. However, their safety is yet not proven.

Why the lithium metal anode?

Solid electrolytes may increase the safety of a battery, especially in combination with high-voltage cathode materials, but they will decrease the gravimetric energy and power density of a battery. Typical solid electrolytes form a rigid metal-oxide framework in which lithium ions are mobile. This framework contains heavy transition metal ions. They will increase the mass of the electrolyte.

Lithium metal as anode material can increase the energy density. Not only has lithium metal the lowest standard electrochemical potential (-3.04 V vs. standard hydrogen electrode, SHE), which further increases the battery voltage; it also has the highest gravimetric energy density (3860 mAh/g) of all electrode materials, increasing the energy density of the anode by a factor of 10, and a volumetric energy density of 2100 mAh/cm³ [12]. By applying lithium metal, the energy density of a battery might be enhanced drastically, making ASSBs competitive to state-of-the-art lithium-ion batteries.

Major aim of this thesis

It is general knowledge that alkaline metals are highly reactive and lithium is no exception to that rule. No matter whether in batteries with liquid or solid electrolytes, lithium tends to react with the electrolyte and the interface between the lithium-metal electrode and the electrolyte is changed. In addition, similar reactions can occur on the cathode side of the battery. Whereas in batteries with liquid electrolyte, usually a stabilizing solid electrolyte interface (SEI) is formed, in batteries with solid electrolytes, a reaction with lithium can lead to the decomposition of the entire electrolyte. This problem necessitates the characterization of battery interfaces and the modification of such interfaces. Only well-known, stable interfaces will lead to reliable performances of ASSBs. It is the aim of this thesis to examine the interface between lithium metal and “LiPON” solid electrolyte and to derive guidelines for the creation of artificial interlayers and to apply these guidelines on artificial interlayers based on phosphorous nitride P_3N_5 .

Anode Interfaces & Interphases

The following chapter provides an insight on interfaces and interphases in lithium metal batteries. At first, the most common interfacial phenomena (e.g. surface roughness, lattice strain and lattice impurities) are briefly described. The focus is set on the thermodynamic aspect of interface formation. The stabilization of the anode|electrolyte interface will then allow the use of a plentitude of material combinations and processes. Therefore, this chapter includes a literature review of the two most prominent concepts for the interface modification in lithium-metal batteries: The application of a stable electrolyte layer between lithium and an unstable electrolyte, and the formation of lithium alloys. For a successful passivation of the interface, it is necessary to understand the thermodynamic driving force for the decomposition. For that reason, the basic thermodynamic quantities and relations are discussed in this chapter, and guidelines for a stabilization of the anode|electrolyte contact are derived.

This chapter introduces the concept that is examined in this work: The application of sacrificial interlayers. The concept is derived from „LiPON“, a commercially employed thin-film solid electrolyte that forms a passivating interlayer in contact with lithium metal. After providing a brief summary of the properties of „LiPON“, the material characteristics of phosphorous pentanitride P_3N_5 are described. In this work, P_3N_5 is used to mimic the intrinsic stabilization behavior of „LiPON“.

2.1 Introduction to interfaces

Any scientist who tries to determine the influence of an interface on the properties of a system will support the statement that an ideal interface does not exist. An ideal interface is electrochemically stable, clean, free from defects, perfectly flat and homogeneous. In a battery, it does not inhibit the flux of charge carriers and therefore should not be detected electrochemically. When faced with mechanical issues, whether they be caused by thermal or mechanical stress, the ideal interface does not influence the properties of a system. There are no voids between two phases and no impurities incorporated. Only the bulk properties should determine the performance of a system. With such specific standards, it is no wonder an ideal interface has yet to come into existence. When attempts are made to examine systems consisting of various parts, e.g. batteries with their electrodes and the electrolyte in between, the interface poses problems. There are multiple phenomena, intrinsically and extrinsically, that bring about these imperfections and make creating an interface that does not to some extent influence the properties of a system, seem nearly impossible. Some of these phenomena are discussed below.

Constructing a well-defined interface is a challenging aspect of scientific research because it needs to fulfill a series of requirements that can be difficult to balance. An ideal interface should:

- Be thermodynamically and kinetically stable
- Be free from resistive impurities
- Have a precisely defined morphology
- Be homogenous

In the case of batteries and especially between the anode and the electrolyte it should also

- Prevent dendrite formation
- Have a negligible charge transfer resistance (if any)

A researcher's task is to understand all the effects of phenomena that could potentially have a negative impact on the ideal properties and to find strategies how to minimize them.

Depending on the origin and consequences, interfacial phenomena can be divided into several groups.

By their dimension:

- Two-dimensional or three-dimensional

By their origin:

- Chemical incompatibility [13], [14]
- Fabrication
- Application

By their impact:

- (Thermo-)Mechanical
- Thermodynamic [14]
- Kinetic [15]
- Electro-chemo-mechanical (e.g. volume change during battery cycling) [16]

An interface can be described as a two-dimensional defect because at the surface, the continuous phase is interrupted and suddenly atoms find themselves without binding partners. Therefore, the reactivity at a surface will differ from the bulk reactivity. Most interfaces were once surfaces until they were brought in contact with a second phase and became "buried surfaces". By bringing two surfaces in contact with one other, a few problems can occur.

Some of these problems are governed by the battery chemistry, while others are due to the fabrication and handling of the systems. It is the aim of this thesis to propose a strategy to overcome interfacial instability in batteries caused by chemical incompatibility, followed by a chapter discussing experimental issues caused by the handling of the systems.

2.2 Interface phenomena

Some of the most important interfacial phenomena are depicted in **Figure 1**. Each can cause significant problems during battery cycling. Since this thesis deals with the protection of the interface and the prevention of reactions, only these phenomena will be discussed in detail. However, for the evaluation of model systems it is necessary to know about mechanical problems as well as effects that occur upon battery cycling. These phenomena will be briefly introduced.

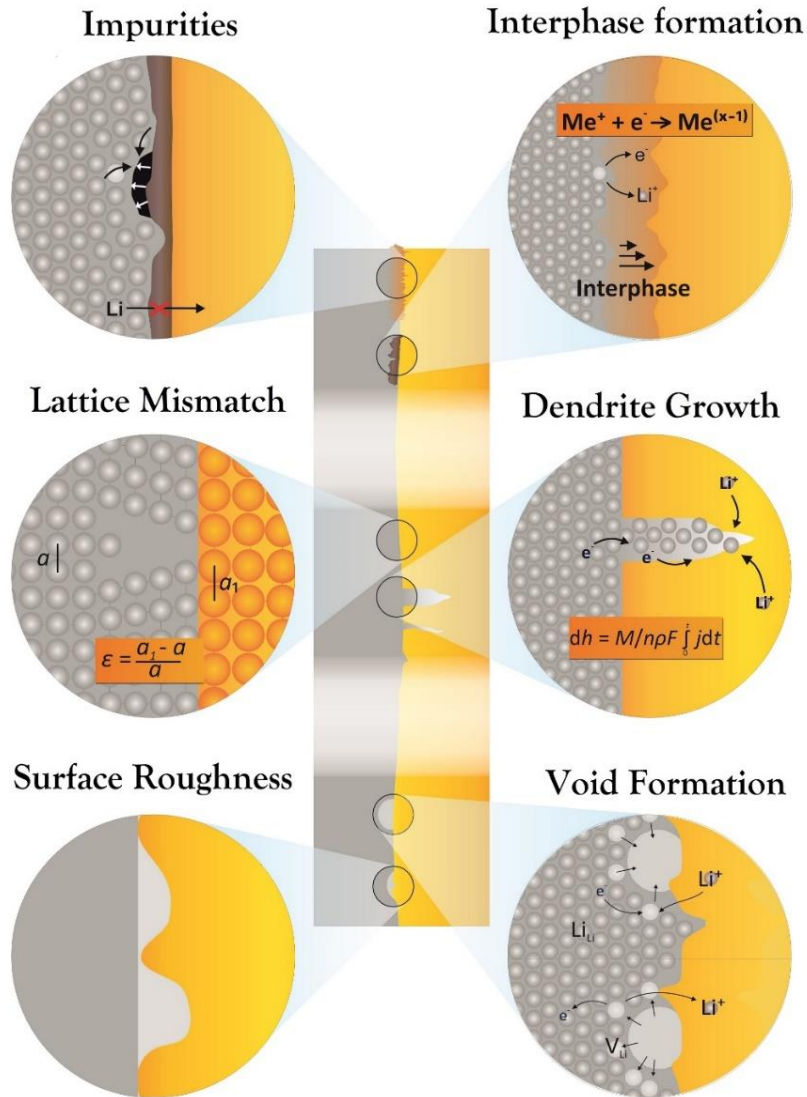


Figure 1: Frequent interfacial phenomena occurring in batteries.

2.2.1 Surface Roughness

Two cases of surface roughness need to be distinguished when two phases are brought in contact with one another:

- i) A rough surface can be in contact with a flat surface. (cf. **Figure 1**).
- ii) A rough surface can be in contact with a rough surface.

Rough surfaces add complications in predicting the behavior of a material. Many phenomena depend on the microscopic surface area of a material, which can deviate strongly from the macroscopic surface of e.g. a pellet. Bringing rough surfaces in contact with each other can also inhibit the transport properties across the interface. Charge carriers can only cross the interface in regions where both phases are in direct contact with each other (constriction resistance). If there are voids, charge carriers cannot cross the interface.

Rough surfaces can also be problematic when thin layers are supposed to be deposited on top. Only a few thin-film deposition methods (e.g. Atomic Layer Deposition, ALD) are conformal and will cover the entire surface. Other methods, such as sputtering, are directional and parts of the surface can be shielded during deposition if the surface roughness is too high. This results in a non-conformal layer. An effect related to the inhomogeneous surface of a material that occurs during battery cycling is the formation of voids. During the discharge of a battery, lithium is transferred from the anode side to the cathode side, with lithium-ions migrating through a solid electrolyte and electrons through an external circuit, and lithium is directly removed from the anode|electrolyte interface leading to a morphologically instable interface. If the ductile lithium metal is not pressed against the electrolyte by application of an external force, voids can be formed that hinder subsequent transport of lithium. These void formations can lead to mechanical stress, non-uniform lithium deposition in a subsequent charging step, and higher current densities due to the current focusing [17].

2.2.2 Lattice strain

When two phases are brought in intimate contact with one another, they can form one out of three different interfaces: a coherent interface, a semi-coherent interface or an incoherent interface (**Figure 2**).

At a coherent interface, every atom of phase 1 shares a bond with an atom of phase 2. If the atoms have different atomic radii, the atoms will be displaced from their equilibrium position. The phase with a larger lattice constant will experience a contraction of the lattice constant at the interface whereas the phase with the smaller lattice constant will experience an expansion of the lattice constant at the interface. This displacement from the equilibrium position causes mechanical stress in the lattice. The bigger the difference of the radii, the bigger the stress. To release this stress, a semi-coherent interface can be formed. In a semi-coherent interface not every atom from one phase shares an atomic bond with an atom from the other phase (cf. dislocation in solid state physics). At the third type, the incoherent interface, there are no bonds between atoms of phase 1 and atoms of phase 2.

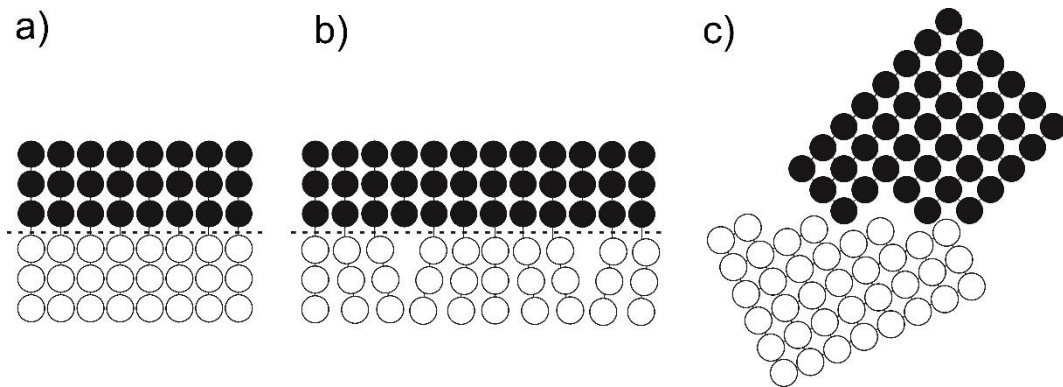


Figure 2: a) Coherent interface, b) semi-coherent interface, c) incoherent interface (redrawn from [18]).

Usually, the bulk properties of the material are not significantly influenced by lattice strain. However, lattice strain can have an influence, e.g. on the transport properties in the phase. This is especially the case in systems where the ratio between the surface area and the bulk volume of a material is relatively high.

Thin-films can be used to examine phenomena caused by lattice-strain because depending on the thickness of the films, most of the film can be seen as an interface and the distortion of the lattice parameters can be in the range of the film thickness. Especially in the case of ion conductors, thin films are used to examine the influence of lattice parameters on transport processes across the interface [19], [20].

In battery systems, lattice mismatch usually causes negative effects because at the interface where the lattice parameters are changing, the transport properties will also be affected. Crossing the interface usually costs the Li ion more energy than moving through a phase, and the interface forms a “bottleneck”, a limiting factor for the charge flux. When the current across the interface is high, this limitation can cause severe issues, e.g. unwanted lithium plating on the active electrode materials (see **chapter 2.3**). Lattice strain can also be caused by battery cycling. Most of the electrode materials are layered intercalation materials, which have a layered metal oxide framework. Lithium can be (de-)intercalated into these layers. Changing the amount of lithium in these layers causes an expansion or contraction of the lattice. Due to this change of the lattice, subsequent charging and discharging of the battery can cause lattice strain and contact loss between the electrode and the electrolyte. It can also result in the collapse of the electrode structure [21]. It is possible to create an intimate interface with various thin-film techniques like evaporation, sputtering, and ALD; but even an intimate contact can cause problems when both adjacent phases have different lattice constants.

2.2.3 Impurities

Impurities cause unpredictability in terms of how they influence any given system. They first need to be distinguished from doping or substitution of materials. Doping of materials and substitution describe the intentional inclusion of atoms or molecules in order to influence the properties of a phase. The difference between these terms lies in the concentration of the introduced atoms or ions. Doping is used to describe the incorporation of very small numbers of atoms (e.g. in semiconductor physics) whereas substitution describes the replacement of large fractions of ions. Impurities are not intentionally introduced and can influence the properties in many ways. In this particular case the term “impurities” describes

every species or phase that is present in the battery but is not responsible for its desired function. At the interface, even small amounts (i.e. very thin layers) of impurities are enough to alter the properties (cf. **chapter 3.3.2**). Impurities can have various different origins. They can originate from material synthesis, handling or chemical incompatibility.

The way in which interfacial properties can be influenced by impurities can be a bit abstract, but it basically governs all other phenomena shown in **Figure 1**. Impurities will not so much influence the lattice parameters but will cause a disturbance of the lattice as the phases have to rearrange around the impurities. Impurities can be crystallites of the same material with a different crystal structure (cf. **chapter 3.3.1**), foreign materials (e.g. carbonates [22]) or very thin oxide-layers on top of a metal surface. They can be responsible for lattice mismatch, voids at the interface and a disordering of adjacent phases; and therefore influence the mechanical properties of a material (e.g. hardening of steel [18]). At the interface they can be even more troublesome, for they can worsen the transport properties across the interface and cause chemical instability. Impurities at the interface can block the transport of charge carriers, when they do not have good conductivity for the respective species. If impurities partially block the interface (which can already be caused by a partial coverage with an oxide layer), the actual local current density during operation can be much higher than expected as charge carriers can only pass a fraction of the interface. Higher current densities can damage the interface and lead to battery failure. A more detailed look at the respective phenomena is given in **chapter 2.4**. Impurities can also induce reactions at the interface, either with themselves or by catalyzing reactions between the two different phases.

2.2.4 SEI formation

SEI formation occurs in systems with liquid electrolytes as well as in systems with solid electrolytes. In both systems, the formation of reaction layers can have a strong influence on the properties of the interface, especially in batteries, where the crossing of the interface is a process that must be carried out. However, although the same phenomenon occurs in both systems, there are a few very important differences that in consequence strongly influence the battery performance.

i) SEI formation in systems with liquid electrolytes

First findings of the SEI were reported in the late 1970s [23]. The SEI is an interphase that forms on the lithium metal anode in contact with liquid electrolytes at potentials below 1.0 V vs. Li^+/Li . Liquid electrolytes which consist of one or more organic solvents and a lithium-containing conducting additive decompose in contact with lithium and form an interlayer with a typical thickness of around 20 nm [24]–[27]. Although this phenomenon has been known for many years, it is not fully understood and questions regarding the formation, composition and properties of this interphase have yet to be answered. Though there is much to learn, it is known that the composition of the electrolyte solution influences the formation and composition of the SEI and therefore the properties of the battery [28].

There are several mechanisms to describe the formation of the SEI between lithium metal and a liquid electrolyte [23], [29]. Over time, they have become more and more detailed. These models all involve the reaction of lithium with at least one of the components in the electrolyte solution and the formation of a solid layer on the lithium anode.

The main components of the SEI are lithium compounds like Li_2S , LiOH , LiF , and Li_2O_3 , and organic species like ROLi , RCOOLi and various others (R = alcyl group), depending on the applied liquid electrolyte [30], [31]. The lithium species are usually located on the inner surface of the SEI (close to the lithium anode) whereas the organic species can be found on the outer surface (close to the electrolyte) [32]–[34]. Determining the exact properties of the SEI is rather difficult as the composition and thickness vary largely; so only average parameters are determined from observations [35].

In combination with liquid electrolytes, the SEI formation is advantageous because it enables a stable cycling behavior by passivating the anode surface and therefore preventing further decomposition of the electrolyte. In batteries with graphite anodes, during the first charge of the battery, the electrolyte is reduced at the graphite surface by forming an SEI, which prevents further decomposition [36]. Other parasitic reactions such as co-intercalation and exfoliation of graphite layers can also effectively be suppressed [37].

However, if the SEI is not a dense layer, dendrite formation and decomposition of the electrolyte can still occur. In systems where a large volume change of the electrode occurs

during charging and discharging, the SEI can burst, which may lead to further decomposition along the cracks.

The composition and morphology of the SEI in batteries with liquid electrolyte strongly depends on the composition of the electrolyte solution. Different conductive salts, solvents and additive combinations significantly influence the reaction products and thus the composition of the SEI. It can govern the formation of dense, solid, porous or spongy interlayers, and influence the ionic and electronic conductivities of the SEI. A detailed description of the SEI composition and morphology is given in literature [38], [39].

Usually, the formation of an SEI can be used to stabilize the cycling behavior of a lithium-ion battery. However, the SEI formation is a parasitic process that includes more than just the desired reaction products of the electrolyte additives. If phenomena like inhomogeneous lithium plating or dendrite formation occur and a fresh lithium surface is exposed to the liquid electrolyte, an interface layer forms again, consuming active material and lowering the cell performance. Other undesired components can become a part of the SEI as well, such as when interactions between the cathode material and the anode material cause SEI growth with unfavorable properties. During cycling, transition metal ions like manganese on the cathode side are reduced and become soluble in the electrolyte, especially when the electrolyte contains HF [40]. When they are transported to the anode side, these ions can be incorporated into the SEI [41]. This behavior influences the cell performance as well as the role of the SEI on the anode side. A more prominent example of such “parasitic” SEI components is the polysulfide shuttle in lithium-sulfur batteries. During discharge of the battery, the sulfur on the cathode side will be reduced from S_8 to form Li_2S . This reaction occurs in two steps, which form intermediate products Li_2S_n ($4 < n < 8$). These polysulfide species are soluble in the electrolyte and can be transported to the anode side, where they can form an SEI layer. The reaction not only consumes active cathode material but also leads to capacity fading and short cycle life [42], [43]. A more detailed insight on the shuttle-effect of lithium-sulfur batteries is given in literature [44].

SEI formation in batteries with liquid electrolytes can be used to tailor the cell properties if suitable electrolyte additives are used and parasitic reactions with the cathode side are prohibited (e.g. [45]). The mechanisms of SEI formation in solid electrolytes differ from those in liquid systems.

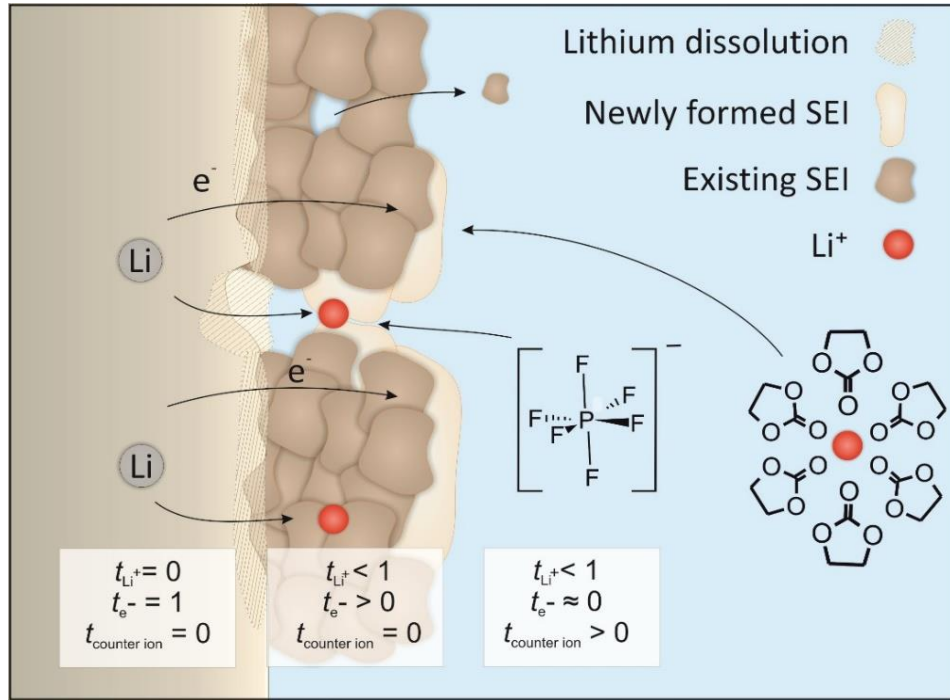


Figure 3: Formation and properties of the SEI in batteries with liquid electrolyte (exemplary LiPF_6 in EC). The SEI can grow in both directions as lithium ions, counter ions and solvent molecules are mobile in the liquid electrolyte. The SEI forms a stable layer that blocks the motion of electrons and solvents. The SEI often is a porous layer and parts of it can break off and float in the electrolyte. If cracks appear due to heavy changes of the lattice parameter of the anode during cycling or due to dissolution of lithium metal, anode and electrolyte can further react to close the gaps.

ii) SEI formation in systems with solid electrolytes

In contrast to batteries with liquid electrolytes, where the SEI is needed to enable a stable cycling behavior, in batteries with solid electrolytes the SEI is often problematic. Wenzel et al. have shown that there are three different types of interfaces between lithium metal and solid electrolytes: stable interfaces, unstable interfaces and metastable interfaces [46]. Which type of interface exists between electrolyte and electrode, depends on the nature of these two phases. When there is a thermodynamically stable two-dimensional interface, the electrolyte does not react in contact with the anode material. It must be noted that because of the high reactivity of lithium, this case only occurs on very rare occasions (e.g. the binary lithium compounds [47]). Most materials form either a metastable or an unstable interface.

The second type of interface is the mixed conducting interface (MCI) or mixed ionically and electronically conducting interface (MIEC). At this interface, a reaction between lithium and the electrolyte takes place, leading to a mixed-conducting phase, as the reaction products conduct electrons as well as ions. This is especially the case when transition metals are involved, which upon reduction to neutral metal atoms form a percolating network for electrons (e.g. in LGPS [50]). This can also occur at the cathode side of an all-solid-state battery, where carbon is added as an electron-conducting additive that also promotes the decomposition of the electrolyte [12]. If both conductivities are in the same order of magnitude, the reaction can spread out over the entire electrolyte given enough lithium is provided. In this case a two-dimensional interface becomes a three-dimensional interphase and the interphase formation can lead to short-circuiting of the cell [48].

The third type of interface is the meta-stable interface. It also forms a three-dimensional interphase. Similar to an MCI, there is an initial reaction between the two adjacent phases, e.g. lithium and the electrolyte. The difference is that the reaction products only conduct one charged species. In the case of a lithium battery, the interface is ionically conducting but does not conduct electrons. For a redox reaction both charge carriers are necessary, if the reaction is to continue. The meta-stable interface results in the formation of a stable SEI.

The formation of an SEI as well as an MCI has a thermodynamic driving force. The difference is the electronic conductivity, which limits the interfacial reaction. Studies on the interfaces between lithium metal and solid electrolytes are quite rare, particularly studies on the thermodynamic and kinetic stability of electrolytes in contact with lithium metal. The studies that do exist report the phenomenological stability or instability of electrolytes but only few give reasonable explanations based on fundamental thermodynamics.

Zhu et al. have made First Principles Calculations on the thermodynamic stability of solid electrolytes in contact with electrode materials [47], [49]. Their purpose was to explain the stability of electrolytes like „LiPON“, which had been mentioned in a previous publication by Schwöbel et al. [50]. In contact with lithium metal this electrolyte decomposes by forming Li_3N , Li_3P and Li_2O in varying amounts depending on the stoichiometry of the electrolyte. The decomposition happens because the anode potential is not within the thermodynamic stability window of the electrolyte. The stability window is often explained as the difference between the highest unoccupied molecular orbital (HOMO; or valence band edge, from a

semiconductor physicist's point of view) and the lowest unoccupied molecular orbital (LUMO; conduction band edge) of the electrolyte from which an electron can be extracted or into which an electron can be inserted [9]. However, this model neglects that fact that for the electrolyte reduction not only electrons need to be transferred to the interface between lithium and the electrolyte but also Li^+ ions are needed. So even if the stability window is not big enough, a reaction does not necessarily have to take place.

Bron et al. have examined the conduction behavior of different sulfide superionic conductors in contact with Li by using impedance spectroscopy [35]. They brought the sulfur-based solid electrolytes $\text{Li}_{10}\text{Si}_{0.3}\text{Sn}_{0.7}\text{P}_2\text{S}_{12}$ (LSnPS), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$ (LSiPS), and 95 (0.8 Li_2S · 0.2 P_2S_5) 5 LiI (LPSI) in contact with a lithium metal foil and performed time dependent impedance measurements. Their experiments showed that three out of four electrolytes were unstable in contact with lithium metal and formed a mixed conducting interphase (MCI). Only the LPSI electrolyte did not show a significant change of the impedance over time. They suggested that this happened due to the formation of a stable SEI. The SEI was ionically conducting but electronically insulating. Thus, the decomposition reaction was self-limiting.

According to the considerations of [47], [49] and the experimental results of [51] and [52], LSnPS, LGPS and LSiPS contain transition metal ions that will be reduced to their metallic state and induce an electronic conductivity. In contrast to these materials, LPSI does not contain transition metal ions. By reacting with lithium metal, binary lithium compounds like Li_2S , Li_3P and LiI will most likely be formed. These binary compounds often have a negligible electronic conductivity [53] and thus prevent the electrolyte from further decomposition. As they often also have a low ionic conductivity, they will cause an increase of the interfacial resistance if the interphase reaches a critical thickness. Determining the thickness of an SEI or MCI is challenging, as the surface is buried beneath the electrode. The thickness also depends on the reaction time, the lithium diffusion coefficient and the amount of lithium in the system. If the reaction time is long enough and enough lithium is present in the system, the whole electrolyte might decompose. Wenzel et al. determined the thickness of their interphases to be between 2 nm and 20 nm, whereas Bron et al. obtained values of a few micrometers [35]. But as they only estimated a value of the permittivity ϵ_r , their results can be inaccurate. Regardless, an MCI will be thicker than an SEI as the growth mechanism of the MCI is not self-limiting. To obtain a stable interface for an unstable electrolyte, the

interface must be tailored in a fashion that only ionically conducting species are present, which do not decompose when in contact with lithium.

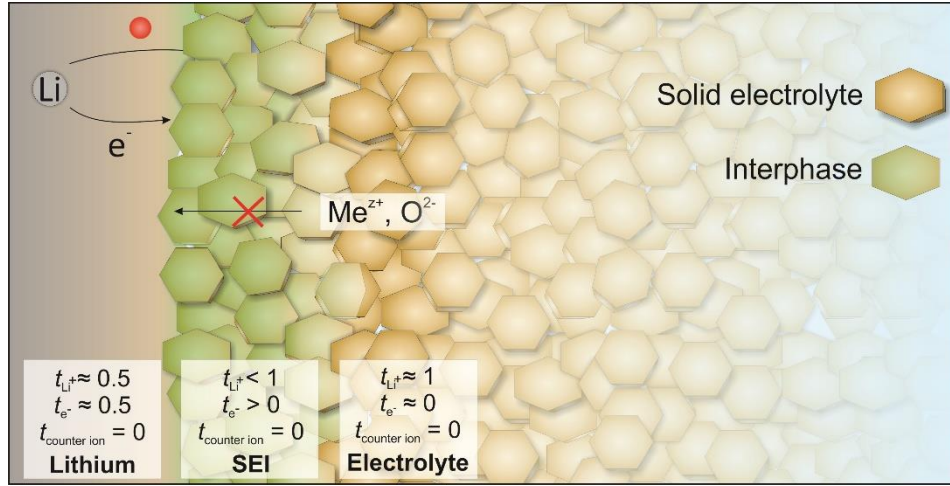


Figure 4: In a solid-state battery, only lithium ions are mobile in the electrolyte. Oxygen anions and other cations are bound in the rigid electrolyte framework. Thus, the SEI can only grow from the anode side into the electrolyte. Depending on the transference number of electrons in the newly formed SEI, the growth might proceed through the electrolyte or stop after forming an insulating layer.

iii) Comparison of the SEI formation with solid and liquid electrolyte

Figure 3 & 4 show the schematic interphase formation in batteries with liquid and with solid electrolytes. They depict the case of lithium metal anodes, but the considerations are valid for batteries with other anode materials as well.

The biggest difference in the interphase formation between systems with liquid or solid electrolyte is the growth direction of the interphase. The SEI formation in systems with liquid electrolytes is schematically depicted in **Figure 3**. LiPF_6 in ethylene carbonate (EC) is chosen as the electrolyte. Typical transference numbers of lithium ions in liquid electrolyte are < 1 because in liquid systems, anions, cations and the electrolyte molecules are mobile. Each of these species getting in contact with the lithium|electrolyte interface can contribute to the SEI formation, which can occur at the lithium|SEI interface as well as at the SEI|electrolyte interface. The SEI can grow into the electrolyte as well as into the lithium anode. Due to an unspecified decomposition of electrolyte compounds, the SEI has a complex and often porous structure. If cracks appear due to severe changes of lattice parameters of the anode

material during charging/discharging, further decomposition of the electrolyte and a reformation of the SEI can occur. Furthermore, parts of the SEI might break off and become mobile in the electrolyte. Many detailed studies of the interface formation, based on experimental results as well as theoretical calculations, are given in the literature [54]–[57].

Figure 4 shows the SEI formation in a system with a solid electrolyte. In systems with solid electrolytes, only lithium ions are mobile with a transference number close to unity. All the counter ions are bound in a rigid framework. The slight deviations from $t_{\text{Li}^+} = 1$ origin from electronic partial conductivity and due to defect formation and migration in the solid electrolyte on a short range. The growth direction of the SEI is determined by the direction of migration of the lithium ions, as the mobility of the other ions can be neglected at typical operation temperatures of batteries [58]. Most often, the SEI is formed at the lithium surface and grows into the electrolyte, depicted by the color shading of the electrolyte particles in **Figure 4**. Even if reaction products in solid-state batteries did not induce a partial electronic conductivity in the cell, the instability of the electrolytes against lithium metal remained a problem: Reaction products in all-solid-state batteries are fixed locally at the interface between lithium and the electrolyte and cannot be removed. Even small amounts of these products can have a large influence on the transport properties of the cell if the conductivity of the interphase differs significantly from the conductivity of the electrolyte. The prevention of the aforementioned interface phenomena, especially SEI formation, is very important for the construction of reliable ASSBs. One way to influence the properties of an interface in batteries is the application of an additional interlayer. The following chapter summarizes various attempts to modify the interface, which are known from literature.

2.3 Artificial anode | electrolyte interlayers in literature

The modification of battery interfaces has been a notable challenge for battery research since the earliest findings of the SEI formation and dendrite growth. Different approaches on how to protect the lithium metal anode in batteries with liquid electrolyte have been examined [45], [59]–[71]. These concepts can generally be divided into three different ideas:

- The use of electrolyte additives;
- The ex-situ modification / pretreatment of lithium metal with gases or electrolyte solutions, and
- The introduction of a polymer / solid electrolyte protective layer on lithium metal.

The research on the combination of lithium metal and a solid electrolyte, however, is still in its infancy. Though few publications on the topic exist at present, an increase in research interest can be expected since many scientists believe that all-solid-state batteries are the future of lithium batteries. There are several patents concerning protective layers in all-solid-state batteries with lithium metal anode but only recent scientific findings give a possible explanation on their mode of operation.

The ideas behind these patents and publications can roughly be divided into two main strategies:

- i) The application of a stable electrolyte layer between lithium and an unstable electrolyte.
- ii) The formation of lithium alloys.

In the following these concepts are explained and discussed.

i) Stable electrolyte as interlayer

The most straightforward way to improve the properties of a phase is to incorporate a second phase that offers the required beneficial properties. Depending on the properties to be enhanced, this approach can include a wide variety of materials. The formation of dendrites can be suppressed by combining a polymer electrolyte with high ionic conductivity with a glassy electrolyte or ceramic electrolyte, which has lower a conductivity than the polymer electrolyte but provides the mechanical stiffness that is required [72]–[75].

One example of how to achieve a thermodynamically stable interface is the application of a thin „LiPON“ layer between the lithium electrode and the electrolyte. West et al. proposed this method in 2004, and it has since been applied for different systems [76]. West and his co-workers used Ohara glass-ceramic, a patented solid electrolyte, which consists of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$ with a NASICON (Sodium Super Ionic Conductor)-type crystalline structure. The glass-ceramic electrolyte reacts with lithium metal and cannot be used in batteries with a lithium metal anode because under reaction an electronic conductivity is induced. West et al. applied a 1 μm thick layer of „LiPON“ with the approximate stoichiometry of $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$ and it successfully prevented the Ohara electrolyte from decomposing. Although the conductivity of the „LiPON“ was only in the range of $10^{-6} \text{ S cm}^{-1}$, the conductivity of the bilayer composite was still around $1 \cdot 10^{-4} \text{ S cm}^{-1}$ and not lastingly decreased by the „LiPON“ layer.

A patent from *PolyPlus Company* covers the same idea but includes several glassy materials such as $6\text{LiI}-\text{Li}_3\text{PO}_4-\text{P}_2\text{S}_5$, $\text{B}_2\text{O}_3-\text{Li}_2\text{CO}_3-\text{Li}_3\text{PO}_4$, $\text{LiI}-\text{Li}_2\text{O}-\text{SiO}_2$ [77].

While recent findings showed that some of these materials are unstable when in contact with lithium metal (e.g. „LiPON“), they can still be used as protective layers. They can be utilized if they form a stable interface when in contact with lithium and the reaction is self-limiting. This is amplified in the case of „LiPON“ and electrolytes in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ system [50], [76]. There have also been attempts to create a pure lithium nitride layer on the lithium metal electrode [80], [81]. The creation of Li_3N is supposed to have the same passivating effect as the reaction between lithium and „LiPON“. However, it has only been applied in batteries with liquid electrolyte and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [82]. The Li_3N layer stabilizes the cycling behavior by protecting the lithium metal from reacting with the liquid electrolyte and

forming an SEI. In contrast to the „LiPON“ decomposition products, pure Li_3N has a higher ionic conductivity [83]. Applying this method to an ASSB could be challenging because the lithium needs to be nitrided before bringing it in contact with the electrolyte. An intimate contact between the metal and the electrolyte needs to be ensured, and the high pressure that is needed to achieve this intimate contact may cause the Li_3N layer to break due to mechanical deformation of the lithium foil. In batteries with liquid electrolyte, the morphology is not important for the nitridation.

Zhu et al. performed density functional theory (DFT) calculations and examined the stability of various nitride, sulfide, oxide and fluoride materials that are either used as electrolyte or coating material for the lithium anode [84]. They discovered that nitride compounds have lower reduction potentials vs. lithium metal than the respective oxides, sulfides and fluorides. Some of these materials even had negative reduction potentials (e.g. AlN : -0.0004 V vs. Li^+/Li , and Li_3AlN_2 : -0.32 V) and may be intrinsically stable in contact with lithium metal.

Reinacher et al. also showed that garnet type electrolytes can be used to protect instable electrolytes in contact with lithium metal [85]. They deposited a 200 nm thick layer of $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ (LBLTO) on top of an Ohara glass-ceramic sheet by Pulsed Laser Deposition (PLD) and covered the sheet with lithium metal for 12 hours. After removing the lithium, the Ohara was clearly visibly degraded, as it had turned black, yet the parts that were covered by LBLTO showed no sign of degradation. Typically, the applied interlayers have a lower conductivity than the actual electrolyte in the cell. Even a conductivity in the range of $10^{-6} \text{ S cm}^{-1}$ or lower is tolerable, if the protective layer is very thin (in the range of a few nanometer). If the transport is blocked by a thicker interlayer, however, lithium plating may occur and destroy the battery (cf. **chapter 2.4.3**).

ii) The formation of lithium alloys

Several research groups reported the application of a metal layer between lithium metal and the solid electrolyte to be a feasible method to stabilize the interphase. The basic idea is to use these interlayers to solve a few problems that occur at the interphase: High interfacial resistances, high differences in the chemical potential, and decomposition reactions in contact with lithium metal. The formation of a lithium/metal alloy might passivate the

lithium|electrolyte interface because it has a lower chemical potential than lithium metal and leads to a thermodynamic stabilization of the interface. The creation of a lithium/metal or lithium/oxide compound may result in the formation of a solid lithium-ion conducting phase that itself is stable against lithium [84], [86]. However, this concept is not valid for every kind of alloy and depends on the composition of the alloys.

Two different types of alloys have to be distinguished: The formation of a homogeneous alloy (solid solution) and the formation of two-phase systems.

In a solid solution, two metals are completely soluble in each other and form one single crystalline phase with a homogenous composition. Elements that form solid solutions have the same crystal structure, similar atomic radii, and the difference in their electronegativity is small. Due to the excellent solubility, the lattice parameter a of a solid solution consisting of the metals A and B can be estimated by Vegard's law

$$a_{A_{(1-x)}B_x} = (1-x) a_A + x a_B, \quad (3)$$

with x being the molar fraction of element B in the solid solution. It can be linearly extrapolated from the lattice constants of the two involved elements.

In two-phase alloys, two metals can also form mixed crystals but not with any composition. The solubility of B in A can be limited by the difference between the atomic radii or different crystal structures. Instead of a single phase with homogeneous composition, two different phases with distinct compositions are formed, whose ratio depends on the fraction of B in A. Only one of these two different types of alloys can have a protective effect on the lithium|electrolyte interface.

A solid solution containing lithium metal in contact with a lithium metal anode will have the same chemical potential as the pure lithium metal. The reactivity between lithium and the electrolyte will remain unchanged. An alloy like that cannot protect the electrolyte from decomposition.

However, a two-phase alloy can be used as protective layer. In such an alloy the chemical potential of lithium is different from the potential of pure lithium metal. This reduces the thermodynamic driving force for the electrolyte reduction. This concept is already widely applied in battery research. One common material for the anode side that forms a two-phase alloy with lithium metal is indium [87]–[89]. Usually a layered electrode consisting of an

indium foil on top of the electrolyte and a lithium foil on top indium is used for battery cycling. By applying a layer of indium the battery voltage is reduced by roughly 0.6 V but the chemical stability and cycling stability increases.

A study of the phase formation and redox potentials of the indium–lithium electrode has been carried out by Santhosha et al. [90]. It provides a deeper understanding on how the reduction of the electrolyte decomposition by using indium foil is achieved.

Santhosha et al. performed a coulometric titration of indium by lithium in three–electrode cells using a liquid electrolyte (1 M lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) in a 1:1 mixture of dioxolane (DOL) and dimethoxyethane (DME)). They applied several current pulses (1 h, $\approx 280 \mu\text{A cm}^{-2}$) followed by a 0.5 h rest period during which they recorded the OCV. The change of the OCV and the amount of inserted lithium was compared to the In–Li phase diagram. They monitored three plateaus in the OCV curve, that could be attributed to different two phase regions of In + InLi, InLi + In₄Li₅, and In₄Li₅ + In₂Li₃. An additional slope of the OCV was attributed to a small one phase region consisting of InLi.

The In + InLi region, which is present at lithium contents from nearly 0 at% up to 47 at% lithium has an OCV of 0.62 V vs. Li⁺/Li, the OCV of the other two phase regions decreases with increasing lithium content and ultimately the OCV reaches a value of almost 0 V vs. Li⁺/Li. A reduction of the thermodynamic driving force for the reaction can therefore only be achieved in InLi electrodes with a lithium content of less than 47 at%.

From lithium insertion/deinsertion experiments with symmetric solid state cells using β -Li₃PS₄ solid electrolyte and indium and lithium foil on either side of the electrolyte, Santhosha et al. learned that the atomic ratio of In and Li is a crucial aspect for the long-term electrolyte stability. Using an InLi anode with an In:Li atomic ratio of 1.26:1 (corresponding to 44 at% Li), they could perform these experiments for more than 200 hours without seeing a significant rise of the total areal resistance of the cell.

Using an anode with an In:Li atomic ratio of 0.36:1, the total areal resistance increased to 200 $\Omega \text{ cm}^2$ in less than two days. During the lithium insertion/deinsertion experiments, the lithium and indium foil formed alloys. In the first case, the lithium content of the alloy was still in the range of the In–InLi plateau region of the In–Li phase diagram. In the second case, the lithium content was in the InLi₂–InLi₃ region of the phase diagram. In this region the redox potential may get too low to effectively suppress the electrolyte decomposition.

That means a protective effect will only be observed in lithium/metal alloys if the applied metal layer is thick enough and the lithium content of the alloy is not too high.

Another example of a metal interlayer has been given by Liu et al. [91]. They applied a thin Ge layer between $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{0.5}\text{P}_3\text{O}_{12}$ (LAGP) electrolyte via sputtering. The film had a thickness of around 60 nm, which was thick enough to fully cover the electrolyte pellet.

They were able to show that lithium plating and stripping for more than 200 hours was possible without showing the slightest hint of side reactions and change of resistivity; whereas the uncoated electrolyte pellet exhibited voltages of up to 2 V (at 0.1 mA cm^{-2}) after only 60 hours. They also showed that the resistance of the electrolyte pellet had only increased by a factor of 3 after 300 cycles, in comparison to the uncoated electrolyte that showed a 100-fold increase of the resistivity after only 32 cycles.

However, the origin of the protective effect is currently not understood, taking into account the experiments conducted by Santhosha et al., that were discussed above. As the phase diagram shows, lithium should be able to form several phases with germanium [92] and a similar behavior than in the In-Li system should be expected. Then the redox potential of the alloy depends on the lithium content. Liu et al. do not provide precise information on the thickness of the lithium foil but assuming the same thickness than in the case of Santhosha et al. (0.5 mm), the Ge content of the anode should be in the range of only a few per mill and not sufficient enough to suppress the electrolyte decomposition.

2.4 Thermodynamic and kinetic aspects of batteries

From a thermodynamic point of view, there are three different types of interfaces. They have already been discussed in **chapter 2.3**. Not every type of these interfaces is capable of protecting the solid electrolyte from decomposing in contact with lithium metal. Generally, inert interphases as well as metastable interphases can be used as a protective layer to avoid a reaction with lithium. An inert interface would be the easiest method. A protective layer that does not react with lithium, is deposited conformally on the electrolyte and prevents the contact between the electrolyte and lithium. In batteries with liquid electrolytes, a plentitude of protective layers is used for that very purpose on the cathode side. As lithium is the most reductive species, it is unlikely to find materials that are stable. So, on the anode side only a few materials have been proven to be stable [47]. The binary lithium compounds Li_aX_b are stable in contact with lithium metal at a potential of 0 V vs. Li^+/Li because they cannot be further lithiated. The only other solid electrolyte material that has sufficient stability is the garnet LLZO because it has a reduction potential of only 0.05 V vs. Li^+/Li and a stabilization may be achieved due to kinetic effects. It's stability can also be influenced by introducing various dopants [93]. A material that is metastable can also be used as protective layer if it does not react completely or the reaction products lead to a cessation of the reaction. However, for the purpose of improving the battery, materials that are metastable in contact with lithium metal can only be used as protective layers, if the reaction products do not worsen the battery performance. Thus, ionic conductivity is a priority.

To describe decomposition and SEI formation in thermodynamic terms and to find strategies how to prevent them, it is necessary to briefly introduce the fundamental thermodynamic quantities that are required to describe these effects.

2.4.1 Fundamental thermodynamic considerations

As shown in **Appendix B**, a battery consists of an anode, a cathode, and an electrolyte that separates each electrode from the other. For the application as an anode several different materials are considered: metal electrodes, intercalation electrodes or conversion electrodes. As the aim of this work is to discuss various concepts for the realization of Li-metal electrodes, only this case is considered. The thermodynamic aspects are not limited to the Li anode and can be transferred to other electrode materials in a similar fashion. Basic differences are pointed out briefly in the following paragraphs.

Mainly metal oxides are used as cathode materials, in which lithium can be inserted. In this work they are only discussed as far as necessary to explain the fundamentals of battery cycling. The basic considerations on stability criteria as outlined in the following are not limited to the anode side and can be transferred to the cathode side and must be applied in a similar way if protection layers for the cathode side are required.

For reasons of simplification, only a linear one-dimensional model is described though it is also applicable for a two-dimensional interface. To derive the basic thermodynamic quantities, the case of a stable electrolyte under open circuit conditions is discussed first.

Lithium ions are the mobile species in a lithium-ion battery. In each component of the battery an electrochemical potential of the lithium ions $\tilde{\mu}_{\text{Li}^+}$ can be defined. In the thermodynamic equilibrium the electrochemical potential of the lithium ions in all components must be equal or a particle flux and current flux will appear:

$$(\tilde{\mu}_{\text{Li}^+})_{\text{Anode}} = (\tilde{\mu}_{\text{Li}^+})_{\text{Electrolyte}} = (\tilde{\mu}_{\text{Li}^+})_{\text{Cathode}}. \quad (4)$$

The electrochemical potential of the lithium ions consists of the chemical potential μ_{Li^+} and the electrical (Galvani)potential φ :

$$\tilde{\mu}_{\text{Li}^+} = \mu_{\text{Li}^+} + z \cdot e_0 \cdot \varphi, \quad (5)$$

where e_0 is the electric charge and z the charge number. In the case of electrons and lithium ions, z is ± 1 and thus omitted in the following discussion.

The chemical potential depends on the activities a_i of the involved species, namely the activity of the lithium ions in the electrodes and the electrolyte:

$$\mu_{\text{Li}^+} = \mu_{\text{Li}^+}^0 + RT \ln a_{\text{Li}^+}, \quad (6)$$

with $\mu_{\text{Li}^+}^0$ = standard chemical potential of Li^+ .

R = universal gas constant ($8.31447 \text{ J/K mol}^{-1}$)

T = absolute temperature [K]

The chemical potential is inaccessible so the values shown in **Figure 5** are only relative values. As the activity of lithium ions in lithium metal is unity, lithium ions have the highest chemical potential in lithium metal.

The electric potential describes the potential energy of a species with charge q in an electric field E . The inner electrical potential (or Galvani potential) consists of two terms: the surface potential χ and the outer potential or Volta potential ψ . The surface potential depends on the crystal orientation, as different lattice planes have different surface charges depending on the kind of ion that exists at the surface and the number of mirror charges that are formed when an ion is brought in contact with the surface.

The absolute Galvani potential of a charge carrier is not accessible experimentally, as only differences of the Galvani potential can be measured. The potential needs to be lower on the anode side than on the cathode side, as no spontaneous charge transfer would occur otherwise.

The open-circuit voltage or electromotive force (EMF) is a measure for the maximum non-volumetric work done by the cell. It is derived from the difference in the chemical potentials of the neutral lithium compound in both electrodes when no current is flowing.

$$EMF = -\frac{\Delta_r G}{z F} \quad (7)$$

$$\left(\frac{\partial G}{\partial n_{\text{Li}}} \right)_{p, T, n_j \neq n_{\text{Li}}} = \mu_{\text{Li}} \quad (8)$$

The chemical potential μ_{Li} is the measure of the change of the free enthalpy G of a homogeneous phase that is required or released for adding or by removing a lithium atom to or from an electrode when pressure p , temperature T and the amount of all other substances n_j remain constant. During the charge/discharge process in a battery, the free Enthalpy changes by the value of

$$\Delta\mu_{\text{Li}} = (\mu_{\text{Li}})_{\text{Cathode}} - (\mu_{\text{Li}})_{\text{Anode}}. \quad (9)$$

Thus, the potential difference can be calculated from the EMF. For the chemical potential absolute values cannot be given. To enable calculations, a virtual zero line can be added to the energy scale, which is often set to the theoretical Galvani potential of the anode, i. e. the redox couple Li^+/Li .

As a lithium atom can be described as the sum of the positively charged lithium ion and the negatively charged electron, the chemical potential of the neutral lithium μ_{Li} is composed of the electrochemical potential of the lithium ions $\tilde{\mu}_{\text{Li}^+}$ and electrons $\tilde{\mu}_{\text{e}^-}$. By knowing μ_{Li} and $\tilde{\mu}_{\text{Li}^+}$, the potential of the electrons can be calculated:

$$\mu_{\text{Li}} = \tilde{\mu}_{\text{Li}^+} + \tilde{\mu}_{\text{e}^-}, \quad (10)$$

whereas the electrochemical potential of the electrons is equal to the Fermi level of the electrons in the electrodes.

The calculation of the electrochemical potential of the electrons is analogous to equation 5, except for the prefix:

$$\tilde{\mu}_{\text{e}^-} = \mu_{\text{e}^-} - z \cdot e_0 \cdot \varphi. \quad (11)$$

In thermodynamic equilibrium equation 4 is valid. In that case, inserting equation 10 in equation 9 shows that the difference of the chemical potential of lithium in both electrodes is determined solely by the difference of the electrochemical potential of the electrons in both electrodes and results in the open circuit battery voltage U .

$$\Delta\mu_{\text{Li}} = (\tilde{\mu}_{\text{e}^-})_{\text{Cathode}} - (\tilde{\mu}_{\text{e}^-})_{\text{Anode}} = U \quad (12)$$

As the discussion of the cathode side is excluded in this work, it is considered that there are local equilibria and that the potentials in this phase are constant. In the case of the lithium anode, ideal behavior is assumed. Contacting anode, electrolyte and cathode with one another generates a voltage, resulting from the different lithium potentials in the electrodes. Between the electrodes the potential needs to decline from $\mu_{\text{Li, Anode}}$ to $\mu_{\text{Li, Cathode}}$ and a change of the Galvani potential must occur at the interface. Simultaneously, a change of the chemical potential of lithium across the electrolyte needs to develop. A hint what the slope of the chemical potential of lithium may look like has been given by Nakamura et al. [94].

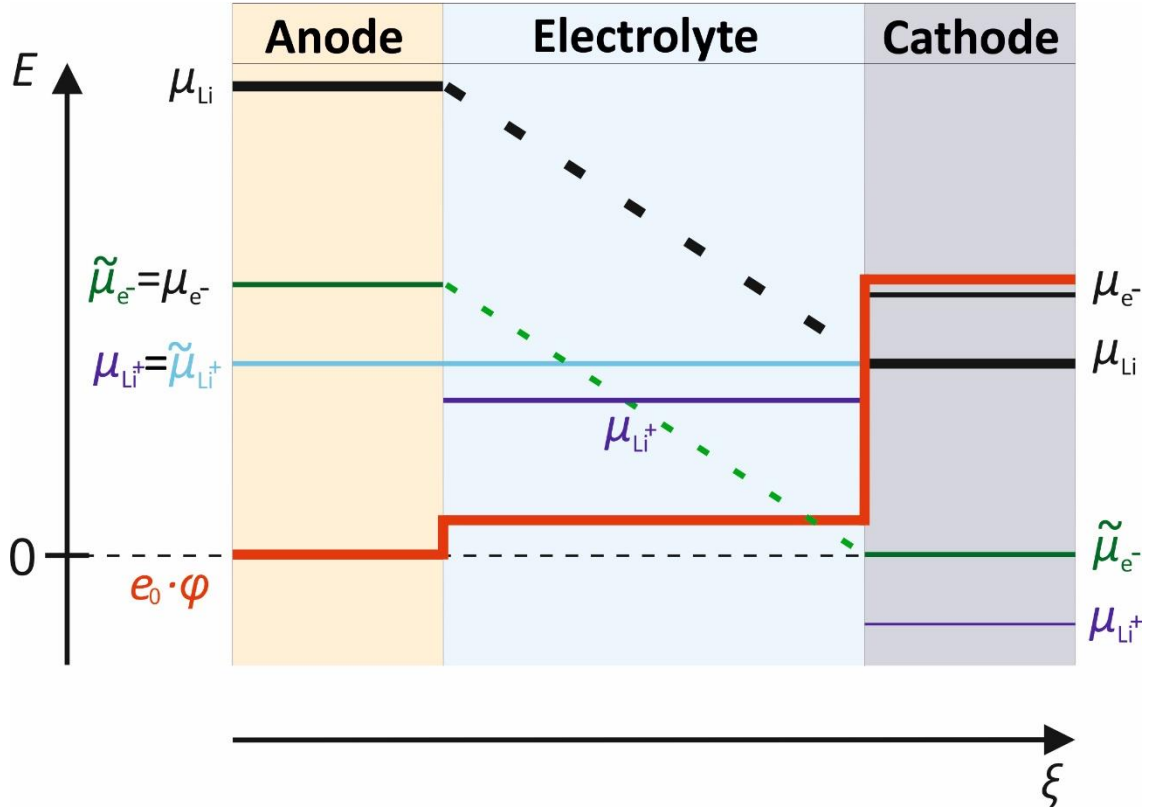


Figure 5: Schematic depiction of the potentials in a lithium ion battery. Between anode and cathode, a decline of the lithium potential μ_{Li} needs to occur. The electrochemical potential $\tilde{\mu}$ is the sum of the chemical potential μ and the Galvani potential $z \cdot e_0 \cdot \varphi$. As the electrochemical potential of the ions is constant in all phases (otherwise, a particle flux must occur), the difference of the chemical potential is due to different Galvani potentials in the three phases. The virtual zero line is depicted as dashed line and fixed to the Galvani potential of the anode. Thus, on the anode side the chemical and the electrochemical potential of the electrons are identical and the chemical and electrochemical potential of the Li ions are identical, too. The decay of μ_{Li} across the electrolyte is solely determined by the change of the electrochemical potential of the electrons $\tilde{\mu}_{e^-}$. As in an ideal electrolyte $\tilde{\mu}_{e^-}$ cannot be formulated, the virtual change of the two values is depicted as dashed lines.

They developed a model to calculate potential profiles by using the transport properties of the electrolyte and an adjacent layer, e.g. a second electrolyte or a protective layer. The hypothesis of their work was evaluated using oxygen ion conductors, as one requirement for the estimations is the knowledge of the activity dependence of the transport properties. These quantities are known for oxygen ion conductors but currently unknown for typical battery materials. Nakamura et al. showed that the potential drop has a sigmoidal shape. Its width depends on the electronic partial conductivity of the two phases. A smaller electronic

conductivity leads to a stronger potential drop across a phase and the thickness of the phase influences the width of the potential drop. A thin phase causes a narrow drop; a thick phase causes a wide drop.

This potential decline is difficult to determine, and it is indicated as a dashed line. For simplification, a linear drop of the potential in **Figure 5** is assigned, but since the potential is a function of $\tilde{\mu}_e$ (the Fermi level) in the electrolyte, which is not constant, a non-linear decay can be expected. As the potential of the lithium ions $\tilde{\mu}_{Li^+}$ is the same in all battery components, the entire potential drop across the electrolyte must be caused by the change of the electrochemical potential of the electrons (equation 10). This behavior is only valid, if the electrolyte has an (although possibly negligible) electronic partial conductivity. Only in this case can an electrochemical potential of the electrons be defined. As this is not the case in an ideal solid electrolyte, this curve is only indicated as a green dotted line.

Details about the steps of the Galvani potential at the interfaces are unknown, as they cannot be measured. The steps in **Figure 5** are only schematic sketches. Their values as well as directions can be different. As at the interface the counter ions of the electrolyte are in contact with the electrode (due to surface charges), a linear potential decay analogous to the Helmholtz layer in aqueous systems should occur. A logarithmic decay is expected only in diffuse interlayers. The width of the steps should be in the range of the Debye length.

For all these considerations it is assumed that no space charge layers exist in the system. In real system they generally cannot be excluded generally [95].

2.4.2 SEI formation

Reactions at the interface either need to be prevented completely or controlled to create interphases with enhanced properties. Whereas the properties of the SEI in liquid electrolytes can be tailored by including proper additives or applying thin oxide layers to increase the stability against lithium metal, similar systematic studies on the anode|electrolyte interface and its properties have yet to be published up to our knowledge.

From a thermodynamic point of view, the formation of a stable reaction layer, the application of a protection layer, and the presence of impurities at the interface can be treated similarly. Crucial for the stabilization of the interface are the ionic and electronic conductivity.

The potential difference $\Delta\varphi$ between the two electrodes acting as the driving force for the movement of charge carriers across the electrolyte is constant. However, the change of the potential from φ_{Anode} to φ_{Cathode} is split up into two contributions, when an interlayer is present:

$$\Delta\varphi = \Delta\varphi_{\text{SEI}} + \Delta\varphi_{\text{SE}} \quad (13)$$

When a current flows during discharge of the battery, the potential drop across each phase depends on the current density i and the electronic conductivity of the SEI and the solid electrolyte according to

$$\Delta\varphi = \Delta\varphi_{\text{SEI}} + \Delta\varphi_{\text{SE}} = -i \left(\frac{1}{\sigma_{\text{el, SEI}}} + \frac{1}{\sigma_{\text{el, SE}}} \right). \quad (14)$$

In this case, the potential drop across the electrolyte depends on the potential drop across the interlayer and vice versa. The pivotal property is the electronic conductivity in the electrolyte and the interlayer. Two general cases need to be considered (**Figure 6**):

- The interlayer has a larger electronic conductivity than the electrolyte.
- The interlayer has a smaller electronic conductivity than the electrolyte.

If the electronic conductivity in the interlayer is larger than the one of the electrolyte, the potential drop across the interlayer will be smaller than the potential drop across the electrolyte (**Figure 6 top**). If the electronic conductivity of the interlayer is smaller than the one of the electrolyte, the potential drop across the interlayer will be larger than the potential drop across the electrolyte (**Figure 6 bottom**).

An electron can energetically pass from the electrode into the electrolyte, if the electrochemical potential of the electrons $\tilde{\mu}_{\text{e-}}$ in the anode is higher than the LUMO in the electrolyte or if $\tilde{\mu}_{\text{e-}}$ is lower than the HOMO. If this is the case, a reaction between the anode and the electrolyte can occur. A reaction does not necessarily have to take place because electrons are only one required species and also lithium ions are needed but it is energetically possible. However, to avoid a reaction with certainty, electrons need to be prevented from

crossing the interface.

A reaction cannot take place, if $\tilde{\mu}_{e^-}$ is between the HOMO and LUMO of the electrolyte, two values that are often described as the electrochemical stability window of the electrolyte. Similar, a reaction between lithium and an interlayer cannot take place if $\tilde{\mu}_{e^-}$ lies in the stability window of the interlayer.

Equation 14 suggests that a proper selection of electrolyte and interphase materials is necessary to ensure that the potential at the SEI|electrolyte interface lies in between the stability windows of both phases. Only if the potential difference across the SEI is large enough to fulfill this requirement will the electrolyte be stable. If that is not the case, further decomposition will occur. In an ideal case, the interlayer should not have an electronic conductivity so no electrons can pass. However, if the potential drop across the SEI is too large, the strength of the electric field could lead to a decomposition of the SEI or tunneling effects (for films of only a few nanometer thickness). As the potential difference $\Delta\mu_{Li}$ between the electrodes is solely depending on the electrode materials, the use of different electrodes may require a specifically tailored electrolyte multilayer structure for each combination of electrode materials in which the kind of SEI as well as its thickness are crucial. As the electrochemical stability window of most electrolytes is smaller than the potential difference between the lithium metal anode and cathode materials, a combination of different electrolytes may be required to ensure the stability of the battery. Concerning Li anodes, electrolytes that are stable at potentials of around 0 V vs. Li^+/Li are needed. According to [47], only binary compounds fulfill this requirement because they cannot be further reduced. The garnet material LLZO has a reduction potential of 0.05 V and could possibly be used as well. On the anode side, either one of these materials or an artificial layer that will react with lithium metal by forming the binary compounds should be applied.

Thus, a thermodynamic stabilization of the lithium|electrolyte interface is only possible if the interphase does not conduct electrons. Any attempt to stabilize the interface in literature that employs electronically conducting interlayers must be doomed to failure. These materials may be able to achieve a short-term kinetic stabilization but not a long-term thermodynamic stabilization.

It is important to keep in mind the influence that transport properties across an interface can have on the battery performance. A successful thermodynamic stabilization of the

interlayer may cause another problem: unwanted lithium plating between SEI and electrolyte.

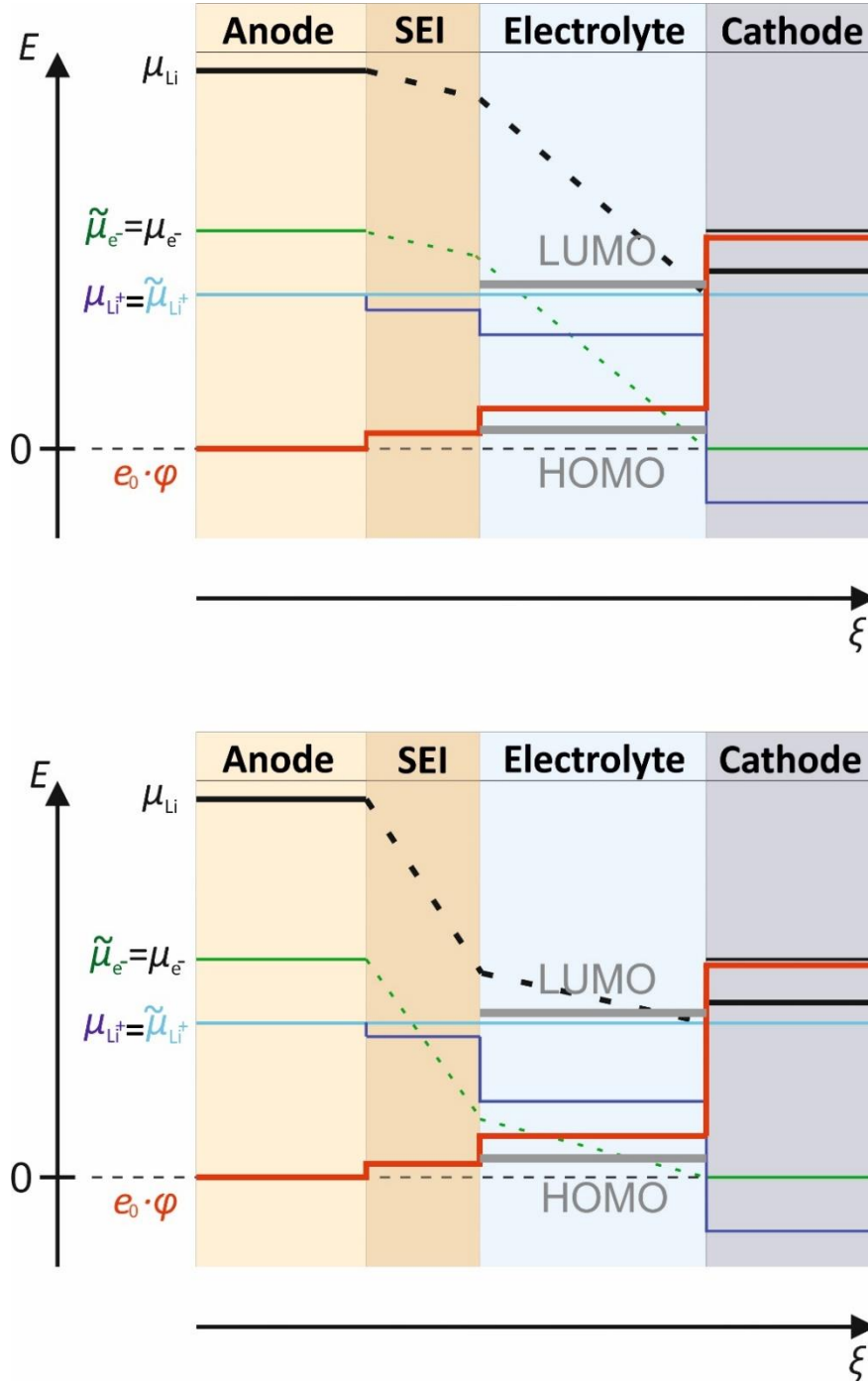


Figure 6: Schematic depiction of the changes of the potentials in a lithium ion battery with an additional SEI. The potential drop across a phase depends on the conductivity of the phase. The smaller the electronic conductivity, the higher the potential drop. Top: The SEI has a superior electronic conductivity than the electrolyte and the potential drop across the SEI is small. Bottom: The SEI has an inferior electronic conductivity than the electrolyte and the potential drop is large. As long as $\tilde{\mu}_{e^-}$ at the interface is not between HOMO and LUMO, a reaction at the interface can occur, if lithium ions are present.

2.4.3 Lithium plating

As discussed above, protective layers should have a negligible electronic conductivity. On the anode side, these protective layers are in direct contact with lithium metal, which has a high electronic conductivity. The drastic change of the transport properties from high to negligible conductivity can cause unwanted lithium plating, which in this case acts as a failure mechanism.

Lithium plating is a widely examined process and describes the deposition of lithium metal at an interface of two phases, either a solid electrolyte and an electrode or current collector or at an electrode surface in batteries with liquid electrolyte [72], [96]–[105], [107]–[113]. To induce lithium plating, two phases with precisely defined properties are put in contact with one another. One phase needs a large ionic conductivity and a small electronic conductivity whereas the other phase needs to have a good electronic conductivity but a negligible ionic conductivity.

Lithium plating can be a desired or an undesired process. For directed lithium plating in batteries, the two adjacent phases are a lithium-ion conducting electrolyte (el) and a metal current collector (cc). The current collector possesses a high electronic conductivity but shows an ion-blocking behavior whereas the electrolyte possesses a high ionic conductivity and a negligible electronic conductivity. Absolute values for the conductivities are less important than the respective transference numbers t_{Li^+} and t_{e^-} in the electrolyte and the current collector. In an all-solid-state battery, in which only Li^+ and e^- are mobile, $t_{\text{Li}^+} + t_{\text{e}^-} = 1$. A charge carrier flux in the electrolyte toward the current collector will result in a charge transfer resistance at the interface, as the lithium ions cannot penetrate the current collector without difficulty. Electrons enter the electrolyte with just as much resistance. Only the fraction $\frac{t_{\text{Li}^+, \text{cc}}}{t_{\text{Li}^+, \text{el}}}$ of ions can pass from the electrolyte into the current collector. Concurrently

only the fraction $\frac{t_{\text{e}^-, \text{el}}}{t_{\text{e}^-, \text{cc}}}$ of electrons can pass from the current collector into the electrolyte.

The remaining $\frac{t_{\text{Li}^+, \text{el}} - t_{\text{Li}^+, \text{cc}}}{t_{\text{Li}^+, \text{el}}}$ ions and $\frac{t_{\text{e}^-, \text{cc}} - t_{\text{e}^-, \text{el}}}{t_{\text{e}^-, \text{cc}}}$ electrons accumulate at the interface. For an ideal interphase between the electrolyte and the current collector, $t_{\text{e}^-, \text{el}}$ and $t_{\text{Li}^+, \text{cc}}$ should be zero, at a real interphase always a small fraction of electrons may pass from the current

collector into the electrolyte and ions into the current collector. At low current densities even for an almost completely blocking interface only a few charge carriers of either species remain at the interface. The higher the current density, the higher the accumulation of charge carriers at the interface. From a certain “threshold” concentration, electrons and ions will combine by forming lithium metal. In the case of a negligible electronic conductivity in one phase, even negligible current densities are sufficient to cause lithium plating.

If the transference numbers for the lithium ions and the electrons are the same in both phases, no lithium plating will occur. As soon as $\frac{t_{\text{Li}^+, \text{Phase 1}}}{t_{\text{e}^-, \text{Phase 1}}} \neq \frac{t_{\text{Li}^+, \text{Phase 2}}}{t_{\text{e}^-, \text{Phase 2}}}$, lithium plating can occur as fractions of the charge carriers will remain at the interface. At this point only the difference in the transference numbers of each species determines when lithium plating starts. The higher the current density and the bigger the difference of the transference numbers, the sooner lithium plating occurs. In the ideal case, when lithium plating is a desired process, the ionic conductivity in the current collector should be insignificant, like the electronic conductivity in the electrolyte. If these requirements are fulfilled, even small current densities and charge carrier concentrations at the interface will result in lithium plating. Similar thoughts on transport properties of interfaces in solid electrolytes have already been made in literature a few decades ago [114], [115].

Especially in terms of the directed application in lithium-free batteries, lithium plating is an interesting phenomenon [96], [98], [104], [118], [119]. As depicted in **Figure 7**, the anode current collector in a lithium-free battery is directly positioned on the electrolyte without inserting an anode layer. The lithium anode is formed *in situ* during the first charging of the battery by removing the lithium ions from the cathode and depositing them between the current collector and the electrolyte. As all the lithium in this kind of battery is stored in the cathode, no excess lithium is present. Therefore, measures must be taken to prevent lithium loss during the first charging due to SEI formation or side reactions, as well as the further consumption of lithium during each cycle needs to be prevented. To ensure a reversible cycling behavior, the lithium deposition on the current collector must take place homogeneously.

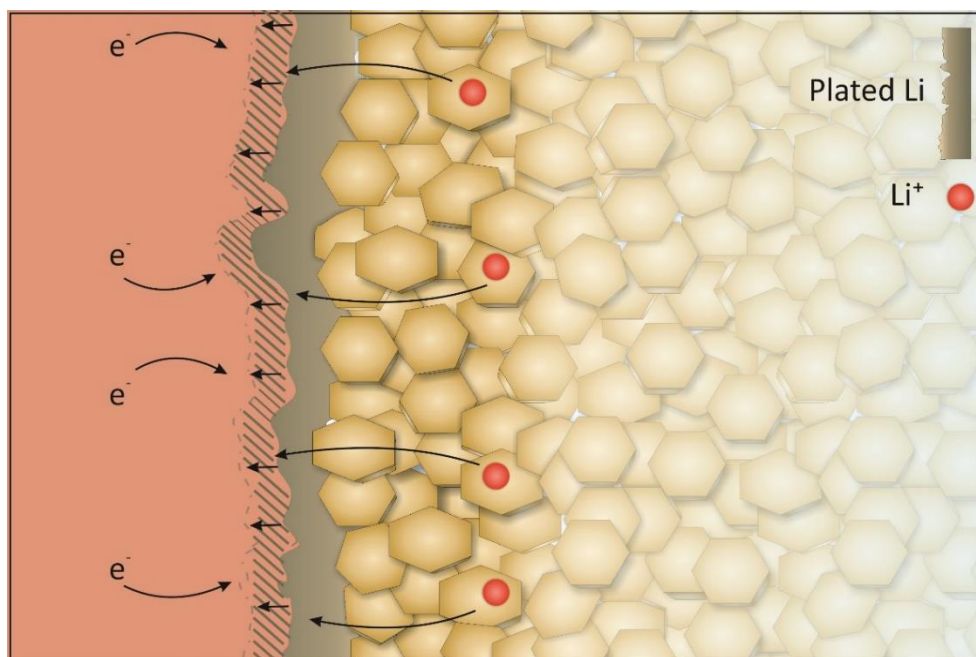


Figure 7: Lithium plating between a copper foil (red) and a solid electrolyte. Different transport numbers of Li^+ and e^- in a solid electrolyte and an adjacent phase lead to the precipitation of lithium metal at the interphase when charge carriers cannot cross the phase boundary. The higher the difference in the transport numbers, the lower the current that is needed to initiate lithium plating. Plating of lithium leads to the deformation of at least one of the phases at the interface.

When artificial interlayers are applied to stabilize the anode|electrolyte contact, lithium plating can also be a cause of degradation in lithium batteries. As lithium plating solely depends on the transport properties of two adjacent phases, it can occur even between two electrolyte layers if they have different electronic and ionic partial conductivities and if the current densities are sufficiently high. This makes the point that lithium plating – although it is a kinetic phenomenon – can have an influence on the thermodynamics in lithium batteries. **Figure 8** schematically shows the potentials in a lithium ion battery consisting of a lithium anode, a cathode and two electrolytes with different transport properties before and after lithium plating. Before lithium plating, there is a potential gradient in both the electrolytes and the potential decay in each phase depends on the conductivities in both phases (equation 14). If unwanted lithium plating occurs due to different transport properties, one can assume that a second lithium anode is formed at the interface between electrolyte 1 and electrolyte 2. This results in a change of the potential gradient in both electrolytes. Due to the formation of a second lithium anode phase, the potential decay across

electrolyte 1 vanishes as the potential of lithium at both sides of the electrolyte is equivalent. This means there is no driving force for the ionic motion in electrolyte 1 anymore.

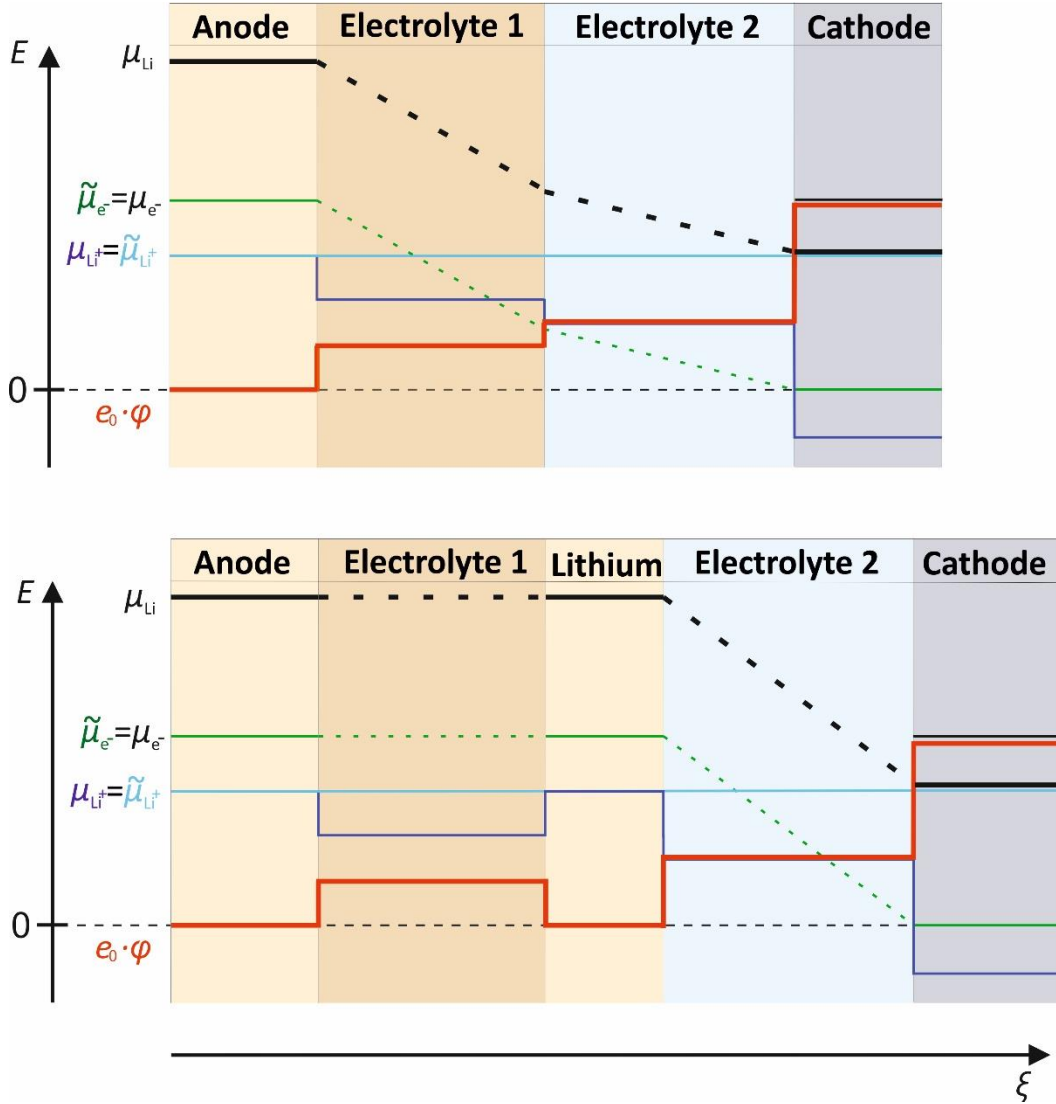


Figure 8: Schematic depiction of the potentials in a lithium ion battery before and after lithium plating between two electrolytes with different transport properties. Lithium plating at the interphase leads to the formation of a phase with a high lithium potential. Between the newly formed lithium and the cathode is a large potential gradient which increases the driving force for lithium plating. After the formation of lithium there is no potential gradient between the anode|electrolyte 1 interface and the electrolyte 1|lithium interface, which means there is no driving force for ion migration. Only if the plated lithium is fully removed, lithium from the anode is involved in the charge transfer process again.

Concurrently, the overall potential difference between anode and cathode then needs to be reduced across electrolyte 2. This results in a larger potential gradient and a larger driving force for the ionic motion between the cathode and the newly formed lithium anode. To

prevent unwanted lithium plating (and subsequent dendrite formation) in composite electrolytes, it must be ensured that electrons and ions at the interface cannot form lithium metal.

Taking these findings into account, it is questionable whether the long-term electrochemical (thermodynamic) stability, as demanded by Liu and co-workers can be improved by applying metal interlayers [91]. A thermodynamically unstable interface will decompose, as long as the decomposition is not kinetically hindered. As long as both electrons and Li ions can get in contact with the electrolyte, the interlayer will not serve as a diffusion barrier, and a decomposition has to take place. Germanium, like silicon, is able to form an alloy with lithium and it can be assumed that lithium will diffuse upon cycling into the Ge layer to form an alloy [92]. If lithium gets in contact with the electrolyte again, or if the potential vs. Li^+/Li gets low enough, the decomposition reaction will continue. The rate of alloy formation depends on the diffusion coefficient of lithium in germanium (which is determined as the reduced diffusion coefficient of the lithium ions and electrons). Haro et al. used a thin Ge layer to increase the lithium uptake in Si nanotubes as battery anodes [119]. They suggest that this result is governed by the good electronic conductivity of germanium. Germanium transports electrons that are necessary to form lithium metal. The material can therefore not function as a protective layer to stop the reaction between lithium and the electrolyte. Metal interlayers can only be able to stop an interfacial reaction on the short-term scale but the reaction will still occur after longer/elongated cycling times and the protective effect will only be due to kinetic effects but not due to thermodynamic stabilization.

The purpose of the examined interlayers in this thesis is to prevent the electrolyte decomposition in contact with lithium metal. As discussed above, to fulfill this purpose, these interlayers need to have a good ionic but negligible electronic conductivity. That means the artificial interlayer will most likely have different transport properties than the unstable solid electrolyte. In this case it must be ensured that the interlayer is not too thick. Otherwise, lithium plating between the electrolyte and the interlayer may occur. Then the electrolyte can still react with newly formed lithium metal and the interlayer will not fulfill its purpose. In general, materials are rare, that are thermodynamically stable in contact with lithium metal, and therefore, this work presents the concept of sacrificial interlayers.

2.5 Sacrificial interlayers

In addition to the two groups of interlayer materials presented in **chapter 2.3**, there is a third group of materials proposed in this work: sacrificial interlayers or in-situ formed protective layers.

This approach uses a “designed” reaction with lithium metal to create an artificial interphase. The formed interphase is stable in contact with lithium metal and prevents the electrolyte from degradation. If a material is chosen that forms an interlayer with sufficient good ionic conductivity, then the interlayer might also decrease the interface resistance [120]–[122].

The application of sacrificial interlayers is a relatively new concept in the field of battery research and originates from findings that were made with „LiPON“ solid electrolyte. „LiPON“ itself may be regarded as the first sacrificial interlayer, although it has never been used for this purpose intentionally. It has long been considered as stable against lithium metal until, a few years ago, Schwöbel et al. reported the reaction with lithium metal [50]. The apparent stability of „LiPON“ is due to the fact that the decomposition is a self-limiting reaction. A detailed description of „LiPON“, its properties and its behavior in contact with lithium metal is provided in **chapter 2.6**.

The stabilization of the lithium | “LiPON” interface after forming a reaction interlayer led to the development of the concept of sacrificial interlayers in the present work. The concept can be described by three essential elements:

- 1) The interlayer decomposes in contact with lithium.
- 2) The decomposition products lead to a passivation of the interface.
- 3) The decomposition products show sufficient ionic conductivity such that the interface impedance does not rise critically (i.e. the conductivity of the decomposition products must not be worse than the conductivity of the electrolyte).

As most materials are unstable in contact with lithium metal, the idea of using an unstable layer comes naturally and the number of possible materials is huge. In contrast to stable interlayers, these materials do not need to have a high ionic conductivity if the reaction products do. They can also be electronically conducting if the reaction products are electronically insulating and limit the decomposition reaction.

From a technical point of view, the application of a sacrificial interlayer does not require major considerations. As the material is supposed to react, it does not matter whether it is crystalline or amorphous and the deposition should not require high temperatures, enabling low-cost processing.

The decomposition products should act as a diffusion barrier for lithium (as neutral component Li^0), thus, the ion-conducting reaction products must be electronically insulating. In the case of „LiPON“, this behavior occurs naturally. A similar behavior can also be observed for phases within the quasi-binary Li_2S - P_2S_5 system [78], [123].

The critical aspect in terms of sacrificial interlayers is their thickness. If the interlayer is thicker than a critical thickness d_{crit} , parts of the interlayer remain between electrolyte and lithium anode unreacted. If the original interlayer does not have ionic conductivity, it will remain in the system as highly resistive interlayer, inhibiting the battery performance. If the interlayer is too thin, it may lead to incomplete local protection.

Finding metastable materials, which react in contact with lithium metal by forming only good lithium-ion conducting and electronically insulating compounds is the major challenge in the realization of sacrificial interlayers.

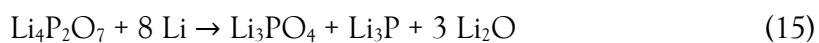
In order to exemplify the design of artificial interlayers, the properties of „LiPON“ will be discussed before deducing parameters that sacrificial interlayers need to possess to create a stable interphase.

2.6 „LiPON“ solid electrolyte

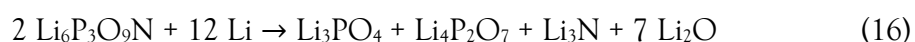
LiPON” is the most widely used thin-film solid electrolyte. Since its first synthesis in the early 1990s [124]–[127], it has gained an outstanding position in the field of thin-film batteries. The term „LiPON“ does not relate to the sum formula of the material but is an acronym for the elements that are included. „LiPON“ is amorphous, nitrogen-doped lithium phosphate. The structural backbone is lithium phosphate, which forms PO_4 -chains in which phosphorous is tetrahedrally coordinated by four oxygen atoms, and lithium ions are coordinated to the phosphate groups. „LiPON“ is usually formed by sputter deposition from a Li_3PO_4 target in reactive nitrogen atmosphere [50], [79], [124], [128]–[137]. During the deposition, oxygen of the phosphate group is partially substituted by nitrogen. The incorporation of nitrogen results in two different nitrogen species that are distinguishable via X-ray photoelectron spectroscopy (XPS). Nitrogen can form three single bonds to three adjacent phosphorous atoms (triply coordinated nitrogen, N_t) $\text{P} - \text{N} \begin{smallmatrix} \text{P} \\ \text{P} \end{smallmatrix}$ or it can be present as doubly coordinated nitrogen (N_d) with one single bond and one double bond to two adjacent phosphorous atoms ($\text{P} - \text{N} = \text{P}$). The smaller the nitrogen content in „LiPON“, the larger the fraction of $\text{P} - \text{N} \begin{smallmatrix} \text{P} \\ \text{P} \end{smallmatrix}$. If the nitrogen content increases, more $\text{P} - \text{N} = \text{P}$ is formed. Although lots of research has been conducted to explain the ionic conductivity of „LiPON“, the conduction mechanism remains yet unexplained. Due to its glassy nature, the prediction of conductivity mechanisms or reactions in contact with electrode materials are rather difficult. In literature, calculations are usually performed assuming different structures for different stoichiometry of the material [14], [50], [138]. However, one general remark on the conductivity of the material can be made. The conductivity of „LiPON“ depends on the nitrogen content of the films and is typically in the range of 10^{-7} to $3 \cdot 10^{-6} \text{ S cm}^{-1}$ [129], [137], [139]–[143]. The higher the nitrogen content of the films, the higher the ionic conductivity. Although the ionic conductivity of „LiPON“ is up to three orders of magnitude lower than the conductivity of good solid electrolytes, its straightforward deposition at room

temperature has led it to become the most prominent thin-film solid electrolyte. In thin-film separators the ionic conductivity is less important than in thick films ASSB cathode and anodes because the electrolyte thickness of thin separators is usually in the range of a few micrometers or less [144]–[148]. On this scale, even a low ionic conductivity contributes little to the overall cell resistance. „LiPON“ has also been used due to its excellent long-term stability in contact with lithium metal [148].

However, the long-term stability of „LiPON“ is questionable. Recent findings carried out by researchers from TU Darmstadt have shown that „LiPON“ is not stable against lithium metal [50]. Like Wenzel et al. they carried out an *in situ* XPS experiment. They measured the signals of a „LiPON“ thin-film and subsequently deposited a small amount of lithium on top of the film. From the changes of the measured binding energies they concluded that a reaction between lithium and the electrolyte layer took place. They suggested a reaction for two different specific „LiPON“ phases, i.e. $\text{Li}_4\text{P}_2\text{O}_7$ and $\text{Li}_6\text{P}_3\text{O}_9\text{N}$. Li acted as a reducing agent and lead to a decomposition of these two phases. In the case of the nitrogen-free phases, the following reaction took place:

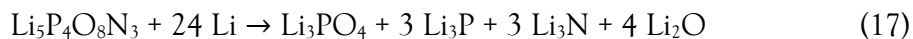


The nitrogen-free sample decomposed into lithium phosphate and the binary compounds lithium phosphide and lithium oxide. For the nitrogen-containing sample they predicted the following reaction:

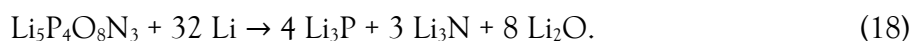


In this case, the $\text{Li}_4\text{P}_2\text{O}_7$ could further react according to equation 15 and in addition to the binary compounds Li_3PO_4 was found again. The contact with lithium lead to a decrease of the amount of network forming phases and the formation of simpler and mostly binary phases. These results are supported by the theoretical computations of Sicolo et al. [138]. By means of Density Functional Theory (DFT) they calculated the defect formation energies for „LiPON“ in contact with lithium metal. They found out that at the interface of lithium and „LiPON“, neutral interstitial lithium defects are formed which cause a disruption of the electrolyte network. The Fermi level at the interface between lithium and „LiPON“ is located at the upper region of the band gap of „LiPON“ and close to the conduction band minimum [51]. Electrons can easily access the conduction band and therefore induce a reaction.

The driving force for the decomposition and the question of the nature of the interfacial reaction has also been discussed by Albe et al. [14]. For the DFT studies they examined a „LiPON“ with the stoichiometry of $\text{Li}_5\text{P}_4\text{O}_8\text{N}_3$. They examined two different reaction paths:



and



They calculated that the complete reduction of „LiPON“ and the formation of the binary compounds alone had a formation energy of -24.16 eV and was therefore thermodynamically favored over the partial reduction (equation 17; -18.45 eV).

The Albe team also reported that the lithiation energy gets more negative upon lithiating „LiPON“, therefore the lithiation gets even more favored when lithium is inserted. Hence, they could show theoretically as well as experimentally that the thermodynamically favored decomposition into the binary compounds does not take place. Instead, Li_3PO_4 is formed and remains at the interface. They suggested that some sort of kinetic barrier prevented the decomposition of Li_3PO_4 .

Although these recent findings have proven the interfacial instability of „LiPON“, the reaction does not lead to a decomposition of the entire electrolyte. Otherwise, there would not be batteries containing „LiPON“ that run for more than 1000 cycles. The reason for the long cycle life of these batteries is that the reaction products Li_3PO_4 , Li_2O , Li_3N , and Li_3P have in parts a high ionic conductivity ($\text{Li}_3\text{P} \sim 10^{-4} \text{ S/cm}$ [53], $\text{Li}_3\text{N} \sim 10^{-4} - 10^{-3} \text{ S/cm}$, [149]–[152]), but a negligible electronic conductivity. The formed interphase acts indeed as a diffusion barrier. The reaction rate ceases and the formed interphase has a thickness of only a few nanometers. The cycling data proves that such an interphase is able to effectively protect the lithium|electrolyte interface and an application of such an interphase in ASSBs should help to increase their stability and efficiency. A further discussion of the electrochemical examinations on “LiPON” thin-films is provided in **chapter 4.1.4** of this thesis.

For the aforementioned reasons „LiPON“ is examined as a model system in this work. Although the work of Schwöbel, Albe and Sicolo has already shed light on the reaction

between „LiPON“ and lithium, their results are still lacking detailed information on the structure and thickness of the SEI. Does the reaction lead to a multilayer-system consisting of different layers of Li_3PO_4 , Li_3P , Li_2O and Li_3N or is the SEI a homogeneous mixture of all these components? Does the stoichiometry of the electrolyte influence the SEI formation? How thick is a natural passivating interface and how thick can sacrificial interlayers be? From detailed examinations of the $\text{Li}|\text{“LiPON”}$ interface these questions will be answered and guidelines for the creation of artificial protection layers will be derived.

2.7 Phosphorous nitride P_3N_5

One promising candidate as sacrificial interlayer is triphosphorous pentanitride P_3N_5 . The material has not attracted much attention in literature so far. Most publications include information on the structure and different polymorphs of the material but little is known about its properties and applications.

Phosphorous nitride consists of edge-sharing PN_4 tetrahedra. The structure contains two different nitrogen species. Two fifth of the nitrogen atoms have covalent bonds with three adjacent phosphorous atoms, three fifth of the nitrogen atoms are connected to only two phosphorous atoms [153].

The material can be synthesized by reacting stoichiometric amounts of hexachlorocyclotriphosphazene and ammonium chloride in an evacuated quartz ampule [153]. After heating the material to 700 K for 12 h and 1050 K for 24 h, the educts react to P_3N_5 under formation of hydrochloric acid according to equation 19.



A second synthesis route uses phosphorus pentachloride instead of $(PNC\ell_2)_3$ [154]:



The formed HCl is condensed and removed by cooling the ampules in liquid nitrogen. The reactions yield a powder with a color ranging from white to orange.

P_3N_5 is used in combination with lithium nitride to synthesize a variety of lithium-containing phosphorous nitrides which have been examined with respect to their ionic conductivities [154]–[156]. By this, compounds like Li_7PN_4 , $Li_{12}P_3N_9$, $Li_{10}P_4N_{10}$, and $LiPN_2$ where synthesized, whose ionic conductivity varies between 10^{-7} to 10^{-5} S/cm (at 400 K). It has also been used as a gate insulator in GaAs transistors.

For these reasons – the formation of lithiated phases and their low electronic conductivity – P_3N_5 is a possible candidate for sacrificial interlayers in lithium batteries. The advantage of

P_3N_5 is, that if a reaction with lithium and a full conversion takes place, only Li_3N and Li_3P are formed, which are both good ionic conductors. If an SEI is formed, it should have a high ionic conductivity but only a small electronic conductivity. Even if the conversion into the binaries is not completed and lithiated phosphorous nitride species are formed, the resulting interphase could still be conductive for lithium ions, as these compounds exhibit ionic conductivities which are surpassed by only a few electrolyte materials and should not inhibit the battery performance.

As it only consists of phosphorous and nitrogen, finding deposition parameters for the thin-films should be comparably easy. Even if the stoichiometry cannot be fully transported from the target onto the thin-film, there will still be only two components, which both lead to an ionically well conducting interphase. There are no metallic compounds, which from a certain volume fraction on create percolating pathways for electrons and therefore need to be oppressed.

The deposition process does neither need high temperatures nor retaining a crystal structure. As the material is supposed to decompose in contact with lithium metal it actually is not important whether the thin-film is crystalline or amorphous. The only prerequisite is that in the end the film will be converted into Li_3N and Li_3P and that the thickness is small enough to fully react but enough to cover the entire electrolyte. In the end, phosphorous nitride layers will be much thinner than typical electrolyte layers.

Experimental Section

Nature gives the best examples for scientists, and from looking at natural phenomena one can often deduce parameters that might be helpful to create materials with distinct properties. In this case, the start was looking at „LiPON“ solid electrolyte thin-films as model systems. Following the work of Schwöbel et al. [50], a closer look at the interface between „LiPON“ and lithium metal, the formed reaction products, their properties, and the thickness of this interphase is taken. From these findings parameters for the application of artificial interlayers are derived. The choice was made to employ P_3N_5 thin-films that might be able to mimic the natural behavior of the „LiPON“ interphase. Therefore, the first part of this experimental section comprises the deposition of these thin-films by sputter deposition and ion beam sputtering, followed by a detailed description of the P_3N_5 target preparation and the battery assembly. The second part of this section comprises the structural, chemical and electrochemical characterization of the „LiPON“ thin-films, the P_3N_5 films and the electrochemical cells. In addition, this chapter comprises a few guidelines and tips how to circumvent problems that can occur when working with „LiPON“ and thiophosphate electrolytes.

3.1 Sample preparation

3.1.1 „LiPON“

“LiPON” thin-films were prepared using a SLS *Twin* sputtering chamber, depicted in **Figure 9**. Silicon (100) wafers and float glass with a thickness of 500 μm and 1 x 1 cm in size were employed as substrates. The substrates were mounted at 5.3 cm distance from the sputter target. The base pressure of the process chamber was in the low 10^{-7} mbar range. The chamber consisted of a loadlock (LL) attached to an in-house made glovebox (GB), a transfer module (TM) and two process modules (PM I and PM II).

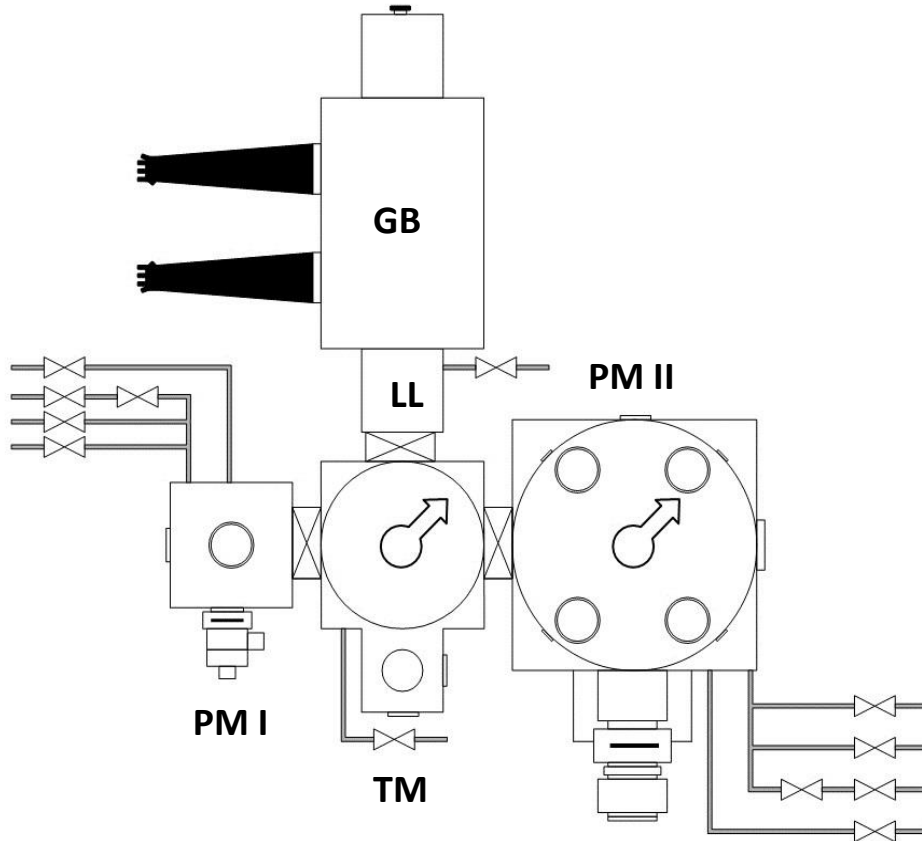


Figure 9: Schematic of the RF magnetron sputtering machine *SLS Twin*. Samples are introduced into the chamber via a load lock (LL) that is connected to a glovebox (GB). From the load lock the samples are transferred into one of the process modules (PM) via a transfer module (TM). The three locks included in this system ensure that the amount of impurities in the process modules is quite low and their base pressure is typically in the 10^{-7} mbar range.

Due to the sample transfer across three chambers, it could be ensured that any atmospheric impurities will have a negligible influence on the atmosphere of the deposition chamber. „LiPON“ films were deposited in the PM II chamber. This chamber contained four different target sites for targets of 3“ to 4“ diameter, the lithium phosphate target (*Kurt J. Lesker*, purity 99.95 %) had a diameter of 3“. In this deposition chamber the targets were located above the substrates and the substrates were placed on a transferable metal plate. „LiPON“ films were deposited by reactive RF magnetron sputtering without intentional heating of the substrate. N₂ (99.99 %) and argon (99.99 %) were used as sputtering gases. The working pressure and gas ratio were varied in order to achieve different stoichiometry of the „LiPON“ films. The sample holder had a diameter of 8“ but due to the inhomogeneous deposition, the maximum sample size was limited to roughly 5 cm. The RF power was set at 100 W, resulting in a power density of 2.19 W/cm². The deposition parameters of the „LiPON“ films are shown in **Table 1**. No active substrate cooling or additional heating was applied. The deposition chamber was attached to an argon-filled glovebox so the samples could be removed without contact to ambient atmosphere. The samples were sealed in pouch bags and transferred to a second glovebox with an attached evaporation chamber in which lithium metal and gold were thermally evaporated, respectively. The oxygen and water content in the glovebox were kept below 0.1 ppm, respectively.

Table 1: Deposition parameters of the „LiPON“ thin-films.

Gas	Gas flow / sccm	p / mbar	P / W	U_{RF} / V	t_{dep} / min
Ar	105	$2.90 \cdot 10^{-2}$	100	278	120
N ₂ / Ar	4 / 200	$5.50 \cdot 10^{-2}$	100	300	120
N ₂ / Ar	5 / 150	$4.40 \cdot 10^{-2}$	100	267	120
N ₂ / Ar	8 / 32	$1.10 \cdot 10^{-2}$	100	740	120
N ₂ / Ar	16 / 32	$1.50 \cdot 10^{-2}$	100	150	120
N ₂ / Ar	16 / 16	$8.60 \cdot 10^{-3}$	100	140	120
N ₂ / Ar	16 / 8	$5.80 \cdot 10^{-3}$	100	125	120
N ₂	16	$1.50 \cdot 10^{-3}$	100	110	120
N ₂	31	$9.10 \cdot 10^{-3}$	100	90	120
N ₂	54	$1.90 \cdot 10^{-2}$	100	68	120
N ₂	86	$3.00 \cdot 10^{-2}$	100	56	120

3.1.2 Phosphorous nitride P_3N_5

Phosphorous nitride powder (purity 99.9 %) was purchased from *alfa chemistry*. The powder had to be used to prepare a sputtering target that was later used for the thin-film deposition.

i) P_3N_5 target preparation

A target was prepared by grinding 7 g of powder in a mortar and giving it into a 1.5" press mold. The applied pressure was 30 kN and the pressure was kept constant for 30 minutes. As the target diameter needed to be at least 1.5", only uniaxial pressing could be performed. The target was too large to fit into the isostatic press. Sintering of the target material could not be performed as the target could not be heated under dry nitrogen atmosphere in order to avoid nitrogen loss and decomposition during heat treatment.

ii) Thin-film preparation

Depositions were carried out in a vacuum chamber designed by *Surface systems+technology GmbH & Co. KG*. A schematic of the chamber is shown in **Figure 10**. The chamber consists of a target holder with four rotatable target positions. Each position can hold a target with a maximum size of 2" and a maximum thickness of 1/4". The targets were rotated anticlockwise with a rotation speed of 20 rpm during deposition. It is also possible to move the targets back and forth during deposition to achieve a homogenous material removal. Directly above the center of the target holder is the substrate holder, which was rotated during deposition with a rotation speed of 5 rpm. The substrate holder contained a platinum coil which can heat up the substrate to 950 °C with a maximum heating ramp of 10 K/min but all depositions were carried out at room temperature. The working distance between the substrate holder and the target was kept at 44 mm.

The chamber contained a *Kaufman&Robinson KDC 10* ion source running with argon. For the deposition, the working distance was 44 mm, the argon flow was set to 4 sccm (varied between 1 – 4 sccm) resulting in a pressure of $\sim 3.4 \cdot 10^{-3}$ mbar. To create a reactive atmosphere and to compensate nitrogen loss during deposition, an additional *Gen-II* plasma

source by *tetra* was used to ignite a nitrogen plasma in the deposition chamber. A nitrogen flow of 75 sccm resulted in a working pressure of $6.8 \cdot 10^{-2}$ mbar. Due to the geometry of the deposition chamber, the minimum distance between the plasma source and the substrate was ~ 11 cm. The deposition chamber was attached to an argon-filled glovebox (MBraun, $O_2 < 0.1$ ppm; $H_2O < 0.1$ ppm) so the samples could always be kept under protective atmosphere. The fixed deposition parameters are shown in **Table 2**. The deposition time was varied from 15 min to 4 h in order to achieve different film thicknesses.

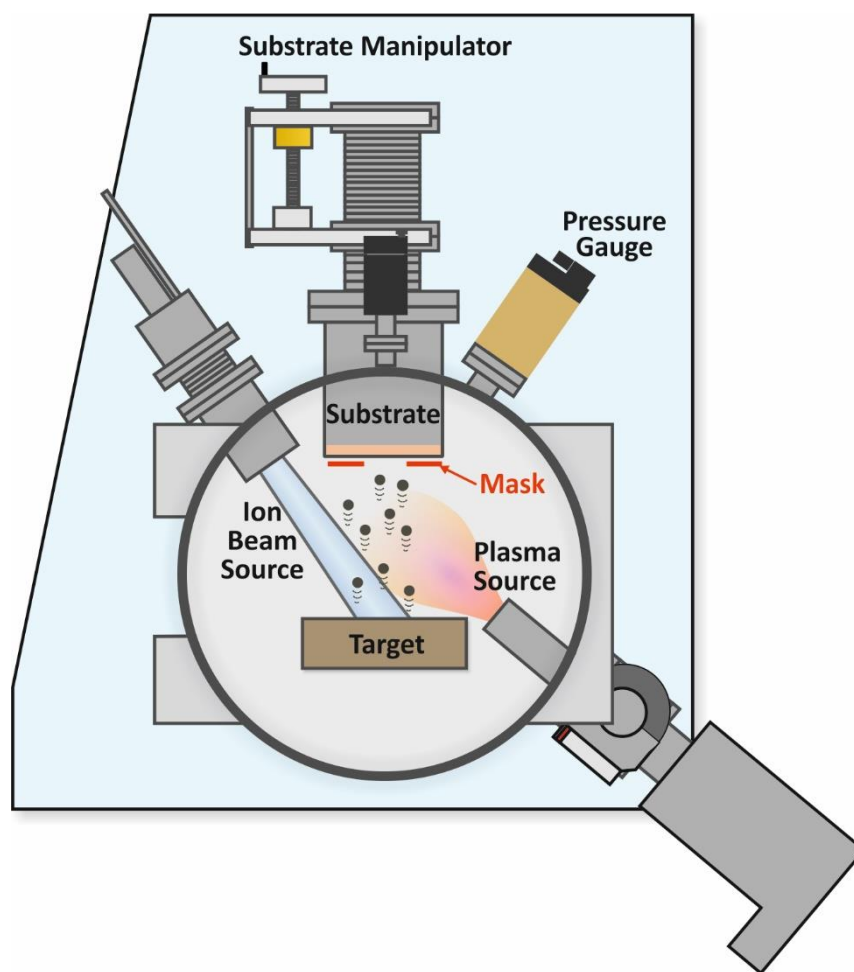


Figure 10: Schematic of the *Surface* ion beam sputtering chamber. The chamber contained a rotatable target holder, a rotatable substrate holder with an AC heater, an ion beam source and an additional plasma source to create a reactive atmosphere.

Table 2: Parameters for the ion beam deposition of P_3N_5 .

$U_{\text{discharge}} / \text{V}$	40
$I_{\text{discharge}} / \text{A}$	0.2 – 0.25
$U_{\text{Beam}} / \text{V}$	600
$I_{\text{Beam}} / \text{A}$	0.01

The deposition rate of the P_3N_5 layer was determined by measuring the film thickness after different deposition times using the *KLA D-600* surface profiler by *tencor*.

3.1.3 ASSB fabrication

The all-solid-state batteries were assembled in a home-designed cell casing, which has already been used in previous studies [13], [16], [157]. To be able to insert the battery into the deposition chamber, the polyether ether ketone (PEEK) part of the casing had to be modified. The unmodified part is 20 mm high, and has deep trenches on both sides for the rubber rings. These trenches might lead to only partial coverage of the sample during deposition and might therefore lead to an inhomogeneous film thicknesses. The left part of **Figure 11 a** shows the unmodified PEEK part of the all-solid-state battery. In order to deposit a thin layer on one side of the pellet, the frame was split into two pieces of which one had a flat surface so no shadowing effects occurred during the deposition. Both pieces were 10 mm high, so the total height of the inner PEEK part did not change. For the fabrication of symmetric cells with interlayers on both sides, the PEEK part was split into three parts (**Figure 11 b**). The smallest one in the middle was only 3 mm high, small enough to press powder and later have the opportunity to apply an interlayer on either side. **Figure 11 c** and **d** show the cell parts mounted on the substrate holder of the deposition chamber.

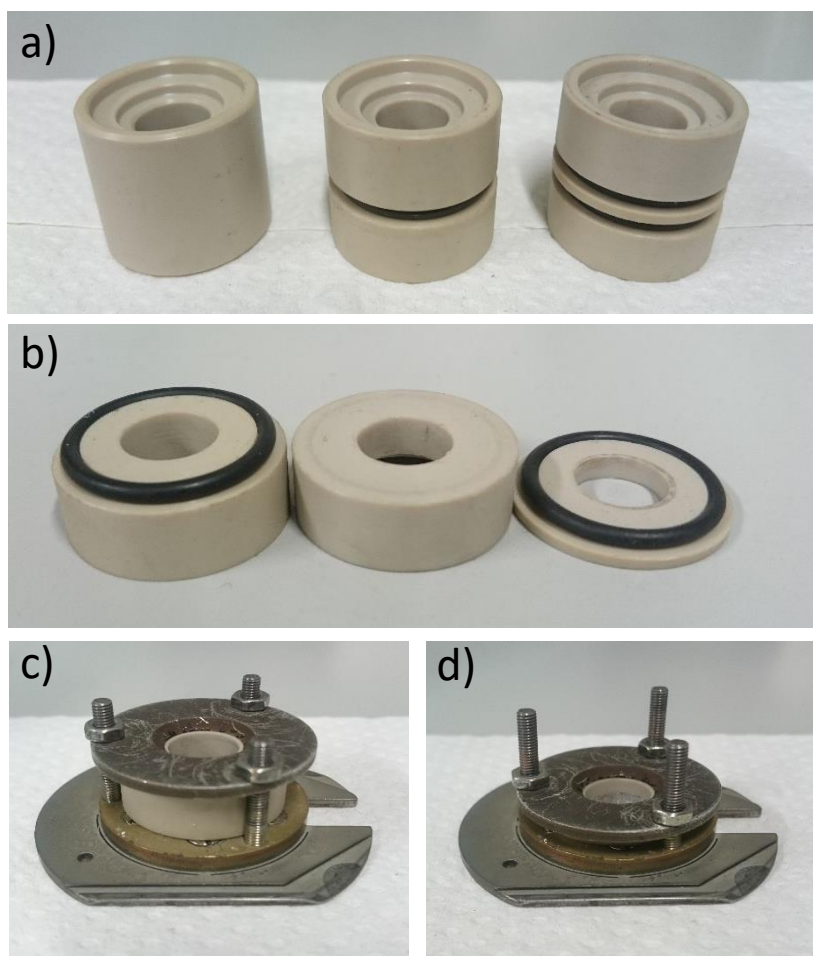


Figure 11: Modified sample holder.

- a) Left: Standard PEEK housing; middle: Two-piece modification for one-sided depositions; right: Three-piece modification for the fabrication of symmetric cells.
- b) Three-piece modification for the fabrication of symmetric cells.
- c) PEEK casing for full cells mounted on the sample holders.
- d) PEEK casing for symmetric cells and layer ablation on both sides of the electrolyte.

All ASSBs and all symmetric cells were assembled using the thiophosphate electrolyte β - Li_3PS_4 (LPS). First, 60 mg of the LPS powder (provided by BASF SE) were filled into the PEEK casing with an inner-wall diameter of 10 mm and cold pressed with 3 t for 5 min. To be able to remove the stamp from the electrolyte later on, a mirror-polished metal plate was placed in the battery casing. The composite cathode was prepared by mixing the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622, provided by BASF SE) and LPS in a weight ratio of 70:30. The powders were hand ground for 15 min, in order to achieve a homogeneous mixture. Next, 10 mg of the composite cathode were distributed on one side of the preformed LPS electrolyte, followed by uniaxial pressing with 3 t for 5 min. The inner part of the housing

was removed, disassembled and placed in the deposition chamber. The P_3N_5 layer was deposited on the electrolyte using the aforementioned deposition parameters. The covered half-cell was put back in the cell housing and lithium foil (*Rockwood Lithium GmbH*) was pressed on the covered electrolyte with 6.4 Nm using a torque wrench, resulting in a pressure of 520 bar.

Symmetric cells were prepared similarly. For practical reasons the pellets had to be slightly thicker. Hence, 100 mg of electrolyte were used.

The thickness of the interlayer in both symmetric cells as well as ASSBs was varied to examine whether there is a minimum interlayer thickness $d_{\min}$ that is necessary to achieve an interface passivation or a maximum thickness $d_{\max}$ that must not be exceeded in order to improve the battery performance.

3.2 Characterization

3.2.1 Structural characterization

The samples were characterized using several different methods. It was necessary to determine the thickness, the deposition rate and roughness of the thin-films.

For the precise calculation of electrochemical data, it was necessary to determine the sample geometry (cell constant). However, obtaining a precise value for the film thickness can be rather challenging and most methods can have a large error. Especially the film thickness is difficult to determine. Therefore, several methods were used.

Whenever possible, the thicknesses and roughnesses of the samples were determined via surface profiling using a KLA D-600 from *KLA Tencor* and samples that were partially masked during deposition. Usually a minimum of 6 measurements were taken from each sample to see the deviation of the thickness across the sample. The average value of these measurements was taken and divided by the deposition time to obtain the deposition rates. In addition, the cross-sections of the thin-film substrates were examined in the scanning electron microscope and these results were compared to the thicknesses obtained from surface profiling, when possible.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed using a *MERLIN* electron microscope from *Carl Zeiss SMT-Nano Technology Systems Division* and a *Xmax-50* detector from *Oxford Instruments*.

3.2.2 XPS analysis

Key part of this work was the observation of the reaction of the proposed materials in contact with lithium metal. As in solid thin-film systems phenomena like precipitation, segregation, and color change cannot be expected, the only chance to monitor the reaction with lithium

is to observe the change of the oxidation state of the materials and their binding energies during the stepwise introduction of lithium. Therefore, the *in situ* XPS experiment was performed according to the description given by Wenzel et al. [48]. For this experiment Li metal foil (*Rockwood Lithium GmbH*) was used.

XPS measurements were carried out with a *PHI Versaprobe II Scanning ESCA Microprobe* (*Physical Electronics PHI/ULVAC-PHI, USA*) with a monochromatized Al K α X-ray source (Beam diameter 200 μm , X-ray power of 50 W) at a chamber pressure below 10^{-7} Pa. The samples were transferred to the vacuum chamber under argon atmosphere in an airtight transfer vessel. The pass energy of the analyzer was set to 23.5 eV for detail spectra, to 46.9 eV for *in situ* measurements and to 187.6 eV for survey scans. During the measurements, the sample was flooded with low energy electrons and argon ions using the built-in ion sputter and electron guns in order to compensate surface charging effects. The samples were mounted with an insulating adhesive tape (floating potential) to avoid any electrical field gradient across the “LiPO(N)”, P_3N_5 thin-film or P_3N_5 powder. For data evaluation, the signal of adventitious carbon (C 1s, see **Figure A 9** in **Appendix D**) of the pristine sample (i.e. before lithium deposition) was set to 284.8 eV to correct for charging effects. This correction was then applied to all subsequent spectra. The *CasaXPS* software package (Version 2.3.17) was used for data analysis and elemental quantification was performed using the sensitivity factors provided by the instrument manufacturer. A Shirley background and GL (30) line-shapes were used for data evaluation and for signal fitting.

To investigate the reactions *in situ* (during interphase formation), lithium metal was deposited onto the “LiPO(N)” or P_3N_5 films, followed by an XPS acquisition step. These experiments again were conducted analogously to previously reported experiments [48]. Sequential lithium deposition and surface analysis steps were performed. After recording XPS spectra, lithium was deposited on top of the electrolyte using the built-in argon sputter gun. This procedure was repeated multiple times by an automated process and the sequential change of the substrate signals was monitored. Thereby, a set of spectra as a function of the lithium deposition time was recorded.

These experiments were carried out with pristine P_3N_5 powder as well as thin-films prepared by ion-beam sputtering.

3.2.3 Electrochemical characterization

After applying the artificial interlayers, it was necessary to determine their influence on the battery performance.

Impedance spectroscopy on „LiPON“ films

Impedance measurements were carried out to evaluate the resistances of the samples and to monitor their evolution. For these measurements, two potentiostat/galvanostat VMP-3 and VMP-300 devices from *Biologic Science Instruments* were used.

The conductivity of the „LiPON“ films was determined by potentiostatic electrochemical impedance spectroscopy (PEIS). The films were deposited on Si|SiO₂ substrates on which a small gold bar had been deposited by thermal evaporation as bottom electrode. A second Au electrode was used as top electrode. The film thickness varied between 800 nm and 2 μ m after 2 h of sputtering, depending on the working pressure, and for each sample the electrode area was 0.02 cm². The sample geometry is shown in **Figure 12**.

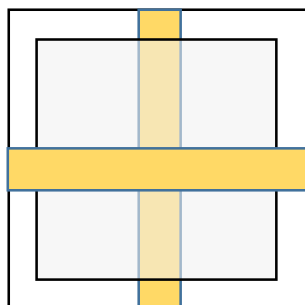


Figure 12: Sample geometry for impedance measurements on LiPO(N) thin-films.

PEIS was also used to monitor the time-dependent change of the resistance of the ASSBs. The frequency range for all measurements was 7 MHz – 100 mHz. The voltage amplitude was 10 mV for the ASSBs and 60 mV for the thin-film samples.

Charging/discharging of the samples and lithium plating and stripping experiments were carried out using a VMP-3 and VMP-300 device from *Biologic Science Instruments*. The samples were kept at constant temperatures in climate chambers from *Binder GmbH*.

Plating/Stripping

In a lithium plating and stripping experiment, a constant current is applied for a given time interval in both directions. A positive current will dissolve lithium on one side of a symmetrical cell (anode) and cause the deposition of lithium on the other side (cathode). Changing the direction of the current will switch the direction of these reactions. Long-term plating and stripping can shed light on the processes that happen at the interfaces. It is used to examine the influence of the anode|electrolyte interface on the battery performance without having to consider the cathode side. Only if the resistances do not change, a conformal and highly reversible behavior can be assumed. It is also a good way to monitor dendrite formation. In this case a current of 70 μA (100 $\mu\text{A}/\text{cm}^2$) was applied for two hours in each direction, respectively. By choosing a longer process time it can be ensured that an actual charge and mass flux takes place (in this case corresponding to $\sim 36 \mu\text{g}$ of lithium or a roughly 870 nm thick layer). Short measurement times of only a few minutes are critical because they do not present typical operating conditions of a battery and cannot be used to draw conclusions on the effect of protective layers in real batteries. The experiments were carried out at 25 °C and 60 °C. The measurements at 60 °C were started after a temperature equilibration time of 60 min.

Battery cycling

Cycling of the ASSBs was performed applying a constant current of $\pm 140 \mu\text{A}$ (200 $\mu\text{A}/\text{cm}^2$) between an upper cutoff potential of 4.3 V vs. Li^+/Li and a lower cutoff potential of 2.6 V vs. Li^+/Li . The charge/discharge steps were separated by a 10 min rest at open-circuit voltage (OCV).

3.3 Experimental Issues

An important aspect of science and research is failure. Often failure is not reported because only a proven theory is regarded as success. However, in practice one can find that knowing about potential problems can help to gain a deeper understanding of measurement artifacts and to distinguish between results that are due to expected phenomena and results influenced by side effects. The purpose of this chapter is to briefly summarize a few aspects that have been observed with the materials mentioned in this thesis.

The issues comprise surface anomalies on „LiPON“ solid electrolyte that were formed during deposition. These structures make the examination of model surfaces difficult and are but one example of how important a high-quality interface is. Another challenging aspect in the manufacturing of ASSBs is the strong degradation of the solid electrolyte even under protective atmosphere. These degradation phenomena can superimpose the degradation of the batteries caused by cycling when the cell housing is not completely gas-tight and impede the data evaluation.

3.3.1 Flower-like structures on „LiPON“ solid electrolyte

The first phenomenon addressed in this chapter is the morphological change of „LiPON“ electrolyte thin-films. This topic has found hardly any attention in literature. Only the Indian Institute of Science has reported the observation of structures on the thin-film surface [158]. However, as these structures can have a huge influence on the properties of the interface between „LiPON“ and any adjacent phase, they will be discussed below.

During this work, the formation of surface anomalies was visible. Directly after removing the samples from the deposition chambers, the samples occurred to be opaque (**Figure 13**). These anomalies were not just single deposits, isolated on the substrate, but many deposits spread all over the substrate.

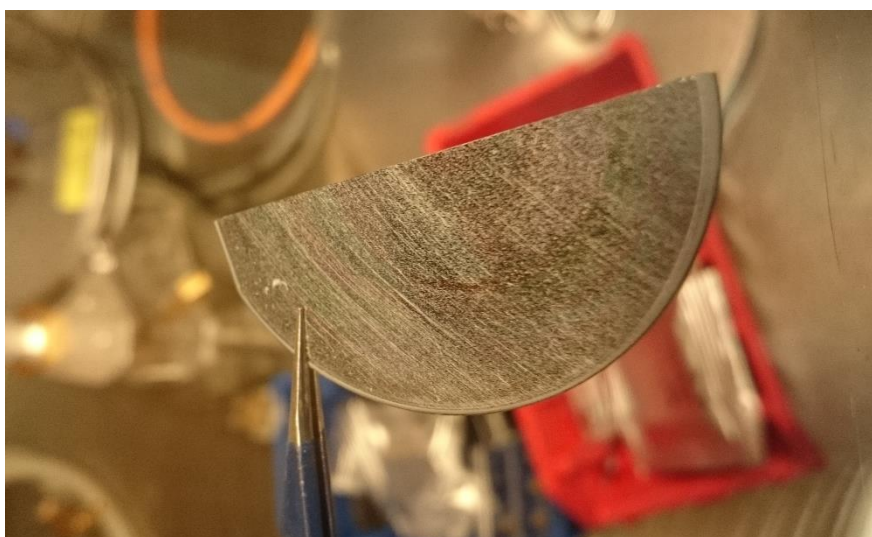


Figure 13: „LiPON“ film after deposition for 2 h on silicon (100) substrate.

The morphology of the observed surface anomalies had a variable size and shape. Deriving from the most common shape these structures are referred to as “„LiPON“ flowers”. Their size was depending on the film thickness but was typically in the range of 2 μm – 10 μm in diameter. As **Figure 14** shows, they could also reach diameters of more than 20 μm and were large enough to be observed with the bare eye.

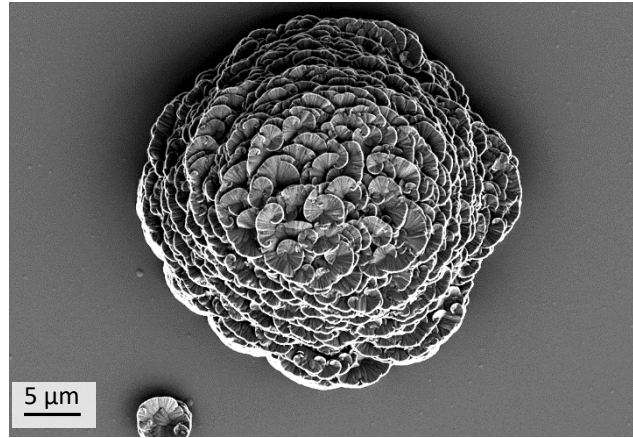


Figure 14: Flower-like structures on „LiPON“ solid electrolyte.

The shape and orientation of these structures varied depending on their position on the sample. Only in the center of the sample they were perfectly round. The closer they were located to the sample edge, the more they were shaped crescent-like. It could also be observed that these structures were always oriented toward the edge of the sample (as shown in **Figure 15**).

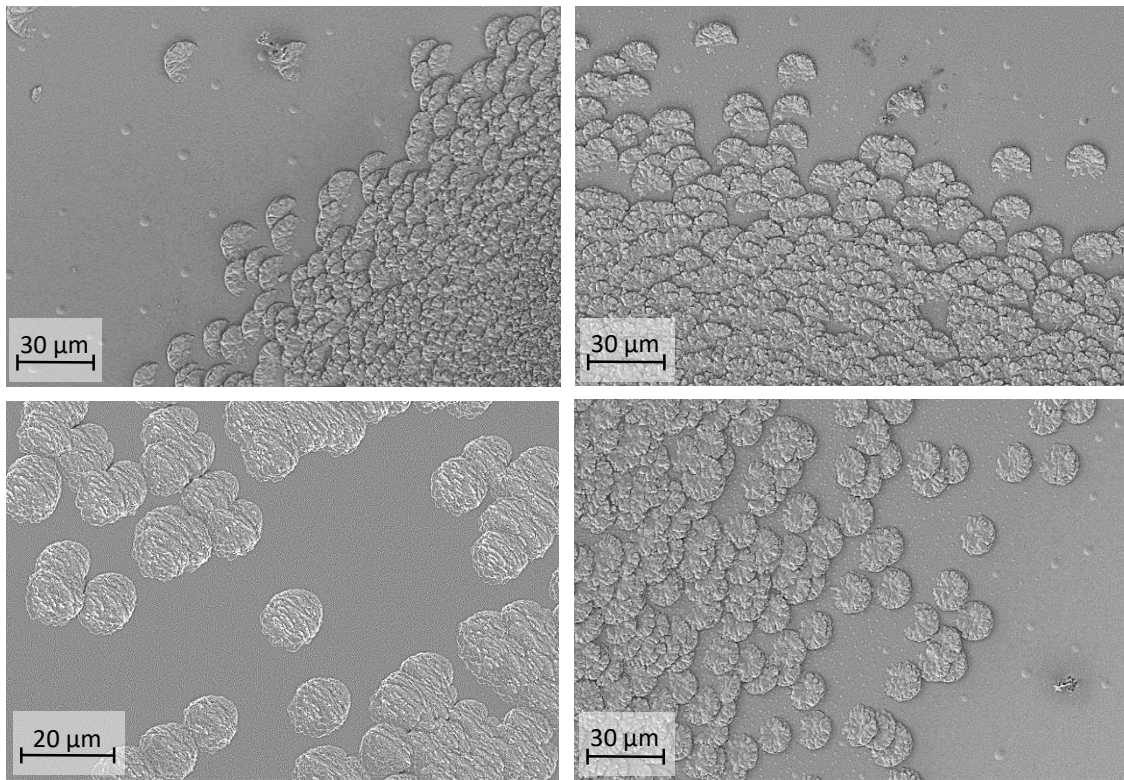


Figure 15: Orientation of „LiPON“ flowers in dependence of the position on the substrate. SEM images.

The origin of these structures is currently unclear. The cross-sectional image suggests that their formation is initiated during the sputtering process (**Figure 16**). By creating a cross-section of the sample it was possible to get a side-view on one of these structures. The first observation was that these structures were growing on top of the electrolyte layer but not instead of it. In **Figure 16** the smooth electrolyte is still visible below the surface deposit. It is interesting to see that the thickness of the electrolyte below is not constant. Instead it is gradually decreasing from the edge to the center of the structure and these structures seem to grow in a certain angle to the surface. This finding suggests that, from a certain point during the deposition on, the formation of these structures begins on top of the electrolyte layer and they are not formed right from the beginning. There must be an initiation for the formation of these structure. Then they seem to spread out across the electrolyte leading to the covering of a linearly growing electrolyte layer. This assumption is supported by the fact that „LiPON“ layers with a thickness of around 100 nm do show hardly any surface anomalies (see **chapter 4.1**). The way the structures grow suggests that in line with nucleation theory a threshold needs to be overcome to initiate the growth of these „LiPON“ structures. It could also be observed that sometimes anomalies were formed in areas where there were scratches from substrate handling. However, when attempts were made to create artificial nucleation sites (e.g. by creating scratches on the sample surface) no preferred growth of structures in these areas could be observed.

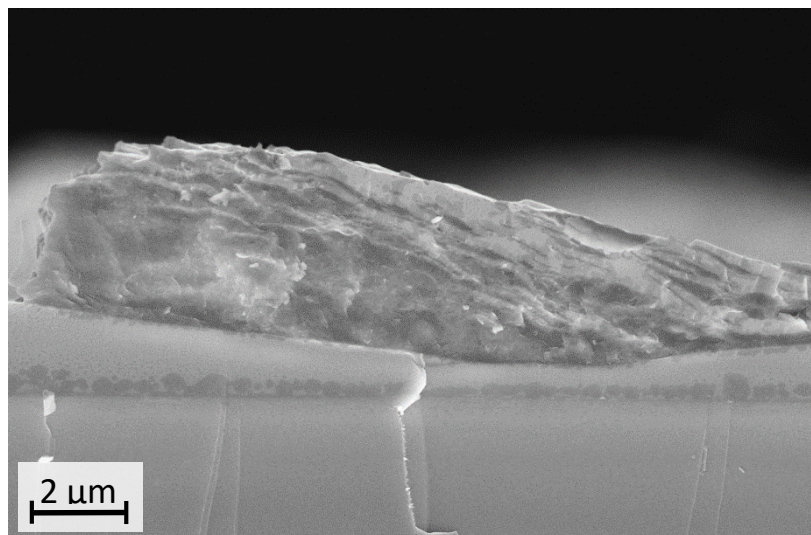


Figure 16: Cross-sectional SEM image of a surface anomaly on „LiPON“ electrolyte.

In addition to the growth of these structures also their composition was examined. Determining the stoichiometry of the surface via XPS was not possible. Although the deposits (“flowers”) were comparably large, they were still smaller than the lateral resolution of the method. The average stoichiometry of the film surface in an area with many structures compared to a surface area with less structures did not show any difference bigger than the error of the measurement. To further examine the composition of these structures, EDX was used as an additional method.

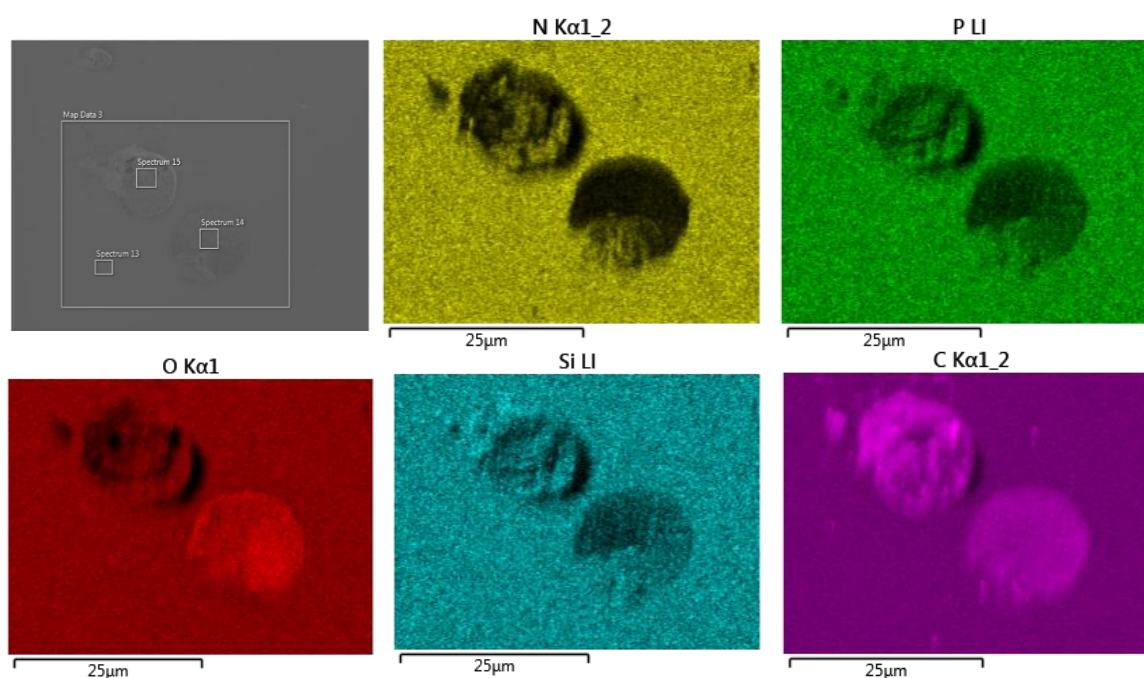


Figure 17: EDX image of the „LIPON“ surface, a surface deposit and an area where a surface deposit had been removed.

A sample was examined where there was a surface deposit and in one position a structure deposit to have broken off during handling (**Figure 17**). With this sample, the stoichiometry of the films could also be compared to „LiPON“ below these structures. The results are summarized in **Table 3**. The O/P ratio of the „LiPON“ film was around 3.8 whereas the N/P ratio was 1.1. This is in good agreement to the results that can be obtained by varying the nitrogen flow and with respect to the accuracy of the detecting method. However, the oxygen ratio is slightly higher than expected, probably due to surface impurities. The amount of carbon is around 4.5 %. Only traces of Si, probably due to holes in the film, are visible. The stoichiometry of one of the „LiPON flowers“ differed strongly from the surface stoichiometry. The oxygen content was reduced by about one third and was only 41.4 at%.

The nitrogen content was reduced by almost 2/3 and the phosphorous content decreased to only 3.1 at%. The carbon content of the structures was much higher (45.6 at%). In the area where there was no deposit, the oxygen content was the highest with 73.2 at%. The nitrogen and phosphorous content were just as high as in the deposit but the carbon content was reduced to 15.1 at%.

Table 3: Comparison of the elemental contents of a „LiPON“ electrolyte surface, a deposit and an area where a deposit is missing (shown in **Figure 17**).

At%	Surface	Deposit	Deposit missing
O	61.1	41.4	73.2
N	17.7	6.8	6.4
P	16.2	3.1	2.3
C	4.5	45.6	15.1
Si	0.5	3.1	2.9

However, a second line scan on another sample was performed and led to contradicting results (**Figure 18**). In this case the nitrogen and carbon content remained more or less the same but the phosphorous content in the surface deposit was smaller than in the „LiPON“ thin-film, whereas the phosphorous content was higher. Although the composition of these surface deposits could not finally be determined, it can be concluded from the results above that they do not consist of „LiPON“ and therefore might possess different properties than the flat films.

Nimisha et al. suggest that these deposits are formed due to contact with humid air [158]. However, in the present study humidity as the origin of these structures can be excluded. The samples were always kept under protective atmosphere. The PM II chamber had a very low base pressure (10^{-8} mbar) and the plasma led to a high temperature during the deposition. Therefore, the fraction of water in the sample should be very low, even though the deposition chamber needs to be vented to change one of the four targets. Even if there was still residual humidity in the chamber, it should not be enough to create surface deposits of more than 10 μm in diameter and thicknesses larger than the electrolyte films in the time-frame of the deposition.

If these deposits were formed in contact with atmosphere, humidity could be a reasonable explanation. However, the presence of surface deposits could already be observed with the

bare eye directly after removing the samples from the deposition chambers. For the above mentioned reasons it can be assumed that the humidity was too low and that the deposits must have a different origin.

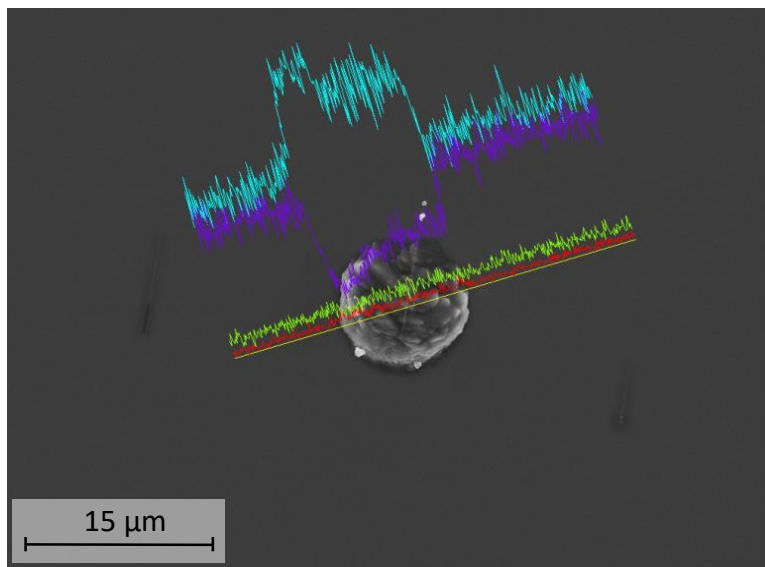


Figure 18: SEM image and EDX signals of a „LiPON“ film with surface deposit. The nitrogen (green) and carbon signal (red) show no difference between the films and the surface deposit. The phosphorous signal (violet) decreases on the deposit whereas the oxygen signal (blue) increases.

The only clear dependence that could be found was the dependence of the size of these deposits on the deposition times. Films deposited for only a few minutes had an almost perfectly flat surface. Only a few deposits were visible and they were very small (diameter < 100 nm). This finding suggests that „LiPON“ films should have very homogeneous properties as long as they are thin enough but from a certain thickness on, surface anomalies will occur that will influence the electrolyte properties and performance of cells. In the case of „LiPON“ as an interlayer, it must be ensured that these deposits do not form during deposition.

3.3.2 Degradation of the LPS solid electrolyte

Thiophosphates are highly sensitive to moisture and must always be kept under protective atmosphere. The following example is given to underline the importance of material storage. Small amounts of oxygen, water or solvent molecules can be sufficient to cause a reaction even in an argon-filled glovebox, changing the electrolyte properties drastically. These reactions made it difficult to see whether the interlayers worked.

One electrolyte pellet was prepared from Li_3PS_4 powder. For this, 100 mg of the powder were given into a press mold with a diameter of 10 mm and pressed with a weight of 3 t for 2 min. Then 200 nm Au were evaporated on both sides of the pellet. The pellet was connected with Al current collector tabs and sealed in a pouch bag. After sealing, time-dependent impedance measurements were done. Four months later, a second pellet was prepared in similar fashion but was stored in the glovebox for one week before evaporating Au electrodes. The results of the impedance measurements conducted on both samples are shown in **Figure 19**. The black data points belong to the sample prepared from pristine Li_3PS_4 , the red data points belong to the aged sample. Although the very same material was used, a large difference can be seen in the impedance spectrum. The spectrum of the pristine material consists of a small semicircle in the high-frequency range and a low frequency tail. These two contributions can be attributed to the electrolyte resistance (a semicircle is caused by a parallel circuit consisting of a resistor and a capacitance or constant phase element) and the Li-ion blocking behavior of the gold electrodes. However, the impedance spectrum of the aged Li_3PS_4 shows two more contributions. There are two semicircles in the high-frequency region and one larger semicircle, which partly overlapped with the linear part, in the mid-frequency region, and the linear contribution of the blocking Au electrodes. To distinguish between the different contributions, the capacitances C of the elements were calculated from the constant phase elements Q according to equation 21:

$$C = \left(\frac{Q}{R^{\alpha-1}} \right)^{\frac{1}{\alpha}} \quad (21)$$

with Q = the value of the constant phase element (CPE)

R = Ohmic resistance

α = alpha value of the CPE

The capacitance of the first high-frequency semicircle was in the range of $2 \cdot 10^{-11}$ F. Taking into account the geometry of the samples, and equation 22 as relation of the geometric capacitance

$$C = \epsilon_0 \cdot \epsilon_r \cdot \frac{A}{d} \quad (22)$$

with ϵ_0 = dielectric constant

ϵ_r = permittivity of „LiPON“

A = electrode area ($\hat{=}$ pellet surface)

d = electrode distance ($\hat{=}$ thickness of the electrolyte pellet),

this low value can be attributed to the bulk electrolyte (the same value was measured for the pristine electrolyte). The capacitance of the second high-frequency semicircle was in the range of $1 \cdot 10^{-10}$ F, suggesting that it is another contribution caused by a bulk material. The capacitance of the mid-frequency semicircle was in the range of 1 μ F. Values in the microfarad range can usually be attributed to an interface, probably to the interface between Li_3PS_4 and the gold electrodes.

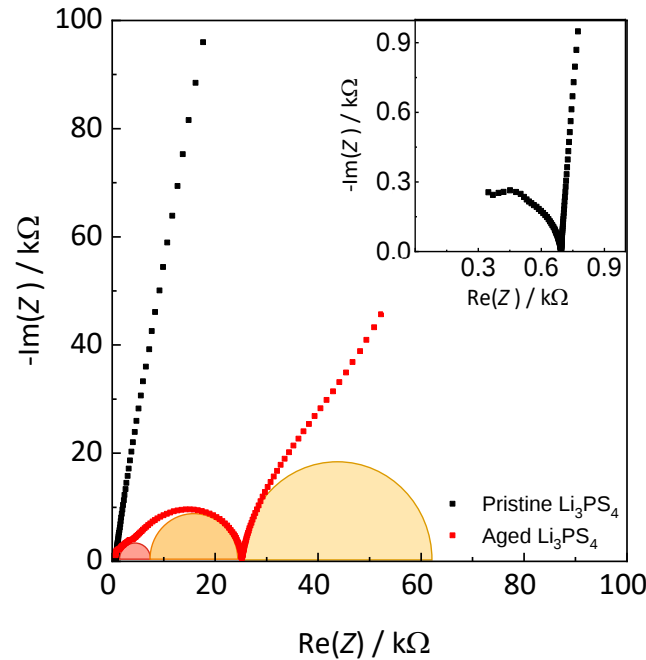


Figure 19: Nyquist plot of the pristine (black) and degraded (red) Li_3PS_4 powder.

Although the material has always been kept under argon, the additional contributions in the impedance spectrum are possibly due to a degradation of the electrolyte that was induced by

trace impurities in the glovebox atmosphere. When Li_3PS_4 reacts with oxygen or moisture, it may form Li_2O or LiOH , both being components with low electronic and ionic conductivity. Thus, the decomposition reaction may be a self-limiting process leading to a core-shell structure of a Li_3PS_4 particle core and an $\text{Li}_2\text{O}/\text{LiOH}$ -containing shell with a lowered conductivity (**Figure 20**).

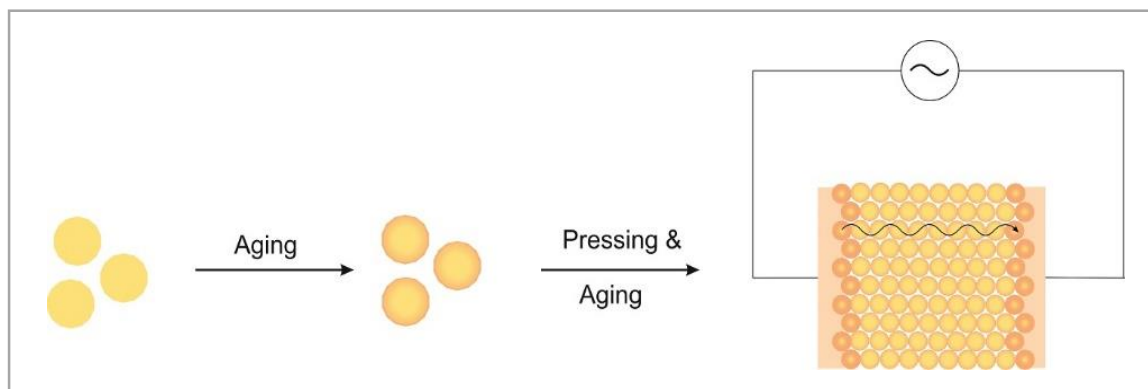


Figure 20: How aging of the electrolyte may cause additional contributions in the impedance spectra.

If the powder particles are pressed to form a pellet, the pellet contains grain boundaries, formed by the shells of the electrolyte particles, leading to a second impedance contribution of the bulk electrolyte. The third impedance contribution could be caused by a further reaction of the pellet surface with impurities in the glovebox atmosphere. This assumption is supported by results received after grinding the aged electrolyte before pressing a pellet. Grinding the electrolyte in a mortar for 5 minutes lead to a decrease of the resistances (of all three components) by a factor of three (**Figure 21**).

Grinding might break the shells of the electrolytes reducing the highly resistive interface between the particles. However, grinding did not fully remove the contributions because the reacted electrolyte has a lower conductivity than the pristine one. In addition, the semicircle in the mid-frequency range was still visible, indicating that a degradation of the pellet surface still took place.

Grinding also lead to smaller particles, which enabled a better densification of the pellet. The density increased from 1.3 g/cm^3 to 1.45 g/cm^3 .

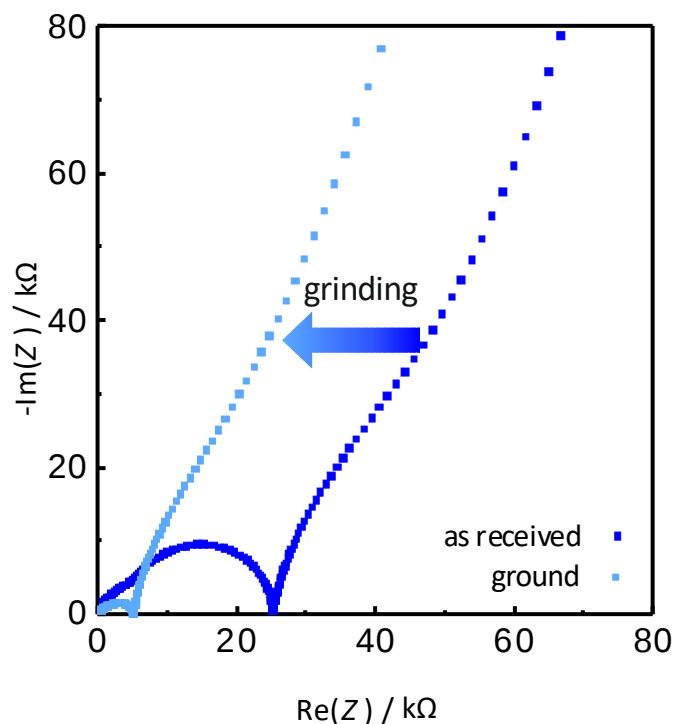


Figure 21: Influence of the powder treatment on the conductivity of the Li_3PS_4 powder. Grinding reduces the resistance significantly.

Therefore, special care needs to be taken to keep the electrolyte clean, even under protective atmosphere. It cannot be excluded that some changes in the impedance spectra are related to the aging of the electrolyte. When working with thiophosphates, quality control in regular intervals is necessary. Also cells with thiophosphate electrolyte should be examined quickly and composite cathodes should always be prepared freshly.

4 Results & Discussion

This chapter is divided into two subchapters. Firstly, „LiPON“ is examined. „LiPON“ is a material that has a metastable interface toward lithium metal and enables batteries with more than 4000 charge/discharge cycles [145]. This apparent stability is achieved by the formation of a passivating SEI [50]. The first task was to learn more about the behavior of „LiPON“. How does the passivation work, what are the main components of the SEI and how thick is the SEI, had been questions to be addressed to find suitable parameters for the application of artificial interlayers. Based on the „LiPON“ results, the application of P_3N_5 as possible sacrificial interlayer was examined. The quality of the deposited thin-films was determined before monitoring the reaction of P_3N_5 with lithium metal. After clarifying that the material showed a behavior similar to „LiPON“ and was suitable as interlayer, it was applied in symmetric cells and in all-solid-state batteries, and its effect on the cell properties was analyzed.

4.1 SEI formation on „LiPON“

A model system is a system that is both chemically and structurally well-defined and that can be used to examine unexplained phenomena in a more reproducible way. For that reason, it is necessary to evaluate the characteristics of the deposited electrolyte thin-films and to understand the influence of the deposition parameters on the sample properties. Only if certain requirements can be achieved reproducibly, the material can be applied as model system.

4.1.1 General characterization of „LiPON“

First it needed to be checked whether the films prepared in this work were comparable to films known in literature. Therefore, the deposition conditions were varied to obtain films with different properties. The stoichiometry of the films and the conductivity of the samples were determined and also the morphology of the samples was examined. For the examinations „LiPON“ films with different stoichiometry ought to be compared and it was investigated whether the stoichiometry (i.e. the nitrogen content) had an influence on the properties of the SEI. The varied deposition parameters were the background pressure and the gas composition during the depositions. The sputtering power as well as the sputtering time were kept constant. The base pressure was usually in the range of $(8 \cdot 10^{-8} - 2 \cdot 10^{-7})$ mbar. The deposition parameters as well as the elemental ratios N/P, Li/P and O/P of the prepared films are given in **Table 4**. The elemental compositions were obtained from the integrated intensities of the respective photoemission signals of the XPS measurements. The stoichiometry of all „LiPON“ films in this work is normalized to phosphorous.

Stoichiometry

As can be seen in **Table 4**, the composition of „LiPON“ could be adjusted over a wide range. By sputtering in pure argon, the resulting stoichiometry is $\text{Li}_{1.33}\text{PO}_{2.75}$, rather corresponding to a meta-phosphate Li_1PO_3 than to a (ortho-)phosphate like the target stoichiometry Li_3PO_4 , meaning that the resulting films are lithium and oxygen deficient compared to the target material. This result is in accordance with observations known in literature [132], [134], [137], [142]. In general, lithium deficiency is caused by the deflection of the light lithium atoms and ions in the plasma due to collisions with the heavier gas atoms. The lithium content of the films is in most cases lower than in the target material and decreases with increasing nitrogen content.

Table 4: Deposition parameters and resulting stoichiometry of „LiPON“ solid electrolyte thin-films. The bold samples were used for further investigations.

Gas	Gas flow / sccm	p / mbar	U_{RF} / V	t_{dep} / min	N/P	Li/P	O/P
Ar	105	$2.90 \cdot 10^{-2}$	278	120	0.00	1.34	3.41
N₂ / Ar	4 / 200	$5.50 \cdot 10^{-2}$	300	120	0.43	2.23	3.23
N ₂ / Ar	5 / 150	$4.40 \cdot 10^{-2}$	267	120	0.47	3.93	5.63
N ₂ / Ar	8 / 32	$1.10 \cdot 10^{-2}$	740	120	0.76	1.83	2.33
N₂ / Ar	16 / 32	$1.50 \cdot 10^{-2}$	150	120	1.29	1.30	1.62
N ₂ / Ar	16 / 16	$8.60 \cdot 10^{-3}$	140	120	0.89	1.77	1.96
N ₂ / Ar	16 / 8	$5.80 \cdot 10^{-3}$	125	120	0.95	1.73	2.03
N ₂	16	$1.50 \cdot 10^{-3}$	110	120	1.00	1.58	1.77
N ₂	31	$9.10 \cdot 10^{-3}$	90	120	1.23	1.40	1.50
N ₂	54	$1.90 \cdot 10^{-2}$	68	120	1.11	1.71	1.87
N ₂	86	$3.00 \cdot 10^{-2}$	56	120	0.97	1.95	2.22

The influence of the nitrogen flow during deposition on the N/P ratio is shown in **Figure 22**. As can be seen, the nitrogen content in the films increases with increasing nitrogen flow during deposition. As the background gas is the only nitrogen source, an increase of the gas reservoir should logically result in an increased incorporation of nitrogen into the film. This behavior is in accordance with observations in literature [132], [142]. However, the resulting nitrogen contents of the films are much higher than values obtained from similar deposition parameters in literature. A gas flow of as little as 16 sccm can result in an N/P ratio of 1 and further increasing the nitrogen flow does result in even higher ratios up to a maximum of

1.2. However, this result is in accordance with Su et al. who used the same machine for their sputter depositions [136]. It was also observed that the nitrogen content reaches a maximum at a nitrogen gas flow of 31 sccm and increasing the nitrogen flow beyond 40 sccm does not further increase the nitrogen content of the films. The errors of the determined stoichiometry are in the range of 5 – 10 % and are calculated from the measurement errors of the experimental data. The reproducibility of the stoichiometry for a certain set of deposition parameters lies within the measurement error

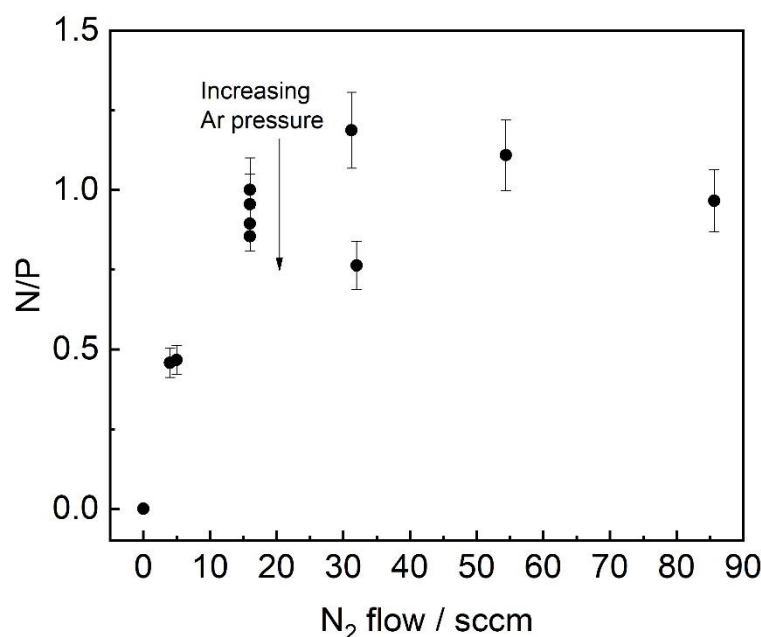


Figure 22: Influence of the gas flow during deposition on the N/P ratio (determined by XPS) of the „LiPON“ films. Up to 31 sccm, a higher nitrogen flow increases the nitrogen content in the films. Additional Argon during the sputtering decreases the nitrogen content of the films. The errors are in the range of 5 – 10 % and are calculated from the measurement errors of the experimental data. The reproducibility of the stoichiometry lies within the measurement error.

An increased Ar flow while using gas mixtures led to a decrease of the nitrogen content. Using a constant N₂ flow of 16 sccm and increasing the Ar flow from 0 to 32 sccm lead to a reduction of the N/P ratio from 1 to 0.85. Increasing the partial pressure of Ar typically increases the deposition rate as the heavier Ar⁺ ions remove more material from the target surface but the two gaseous species compete for the ionization during the deposition and less nitrogen is incorporated into the films. However, in the present case the challenge was not to get thin-films with a high nitrogen content but to get films with a low nitrogen content. Even when using a mixture of N₂/Ar of 4 sccm/200 sccm, the N/P ratio was still 0.42. As

the Ar flow could not be further increased and reducing the N₂ flow was not possible either, this stoichiometry is used as the nitrogen-poor sample.

For the conductivity experiments, three different samples are compared: A nitrogen-free lithium phosphate film, a „LiPON“ film with a low nitrogen content and a „LiPON“ film with a high nitrogen content. For this comparison, the three compositions marked with bold letters in **Table 4** are used. For further discussion, the nitrogen-free films will be denoted as *LiPO*, the films with a low nitrogen content will be denoted as *LiPON-low* and the films with a high nitrogen content as *LiPON-high*. It is pointed out that the major focus of this work is not to obtain films with very high conductivities or very high nitrogen contents and for such aims different deposition conditions may be needed.

Deposition rate

To estimate the thickness of the samples, the substrate was partially covered with a mask during the deposition and the film thickness was determined across one edge of the thin-film via surface profiling. As the films have all been sputtered for the same time, the thicknesses can be compared and the differences can be related to the working pressures. Usually, the deposition rate is determined from depositing samples with different deposition times. In this case, multiple samples were deposited simultaneously and the thickness was determined via surface profiling of a partly masked substrate after each deposition. This ensures a more precise determination of the thickness. The thicknesses of the samples after 2 h of sputtering are shown in **Table 5**. The deposition rate did slightly vary depending on the position of the sample on the sample holder. A more or less homogenous deposition could be achieved in a spot with a diameter of 2“. However, even for the same deposition parameters, the thicknesses typically varied by around 5 %.

Table 5: Film thickness of the three „LiPON“ species after two hours. The thickness was determined via surface profiling from each sample. Deviations from inhomogeneous sputtering are around 5 %.

Sample	Thickness after 2 h / nm
LiPO	1250
LiPON-low	700
LiPON-high	1650

The deposition rates are highly dependent on the pressure in the sputtering chamber during deposition. The lowest working pressure (LiPON-high) leads to the highest deposition rate and the highest working pressure (for LiPON-low) leads to the lowest deposition rate due to the deflection of the sputtered atoms, ions and molecules in the gas phase.

Scanning electron microscopy

Typical SEM images of „LiPON“ films are depicted in **Figure 23**. The left image shows the surface of a film after 8 min of deposition, the right image shows the surface of a film after 2 h of deposition. Unsurprisingly, the roughness of the films corresponds to the deposition time. Thinner films have a smoother surface because less building defects during the formation of the film had the chance to form. However, there are spherical structures on the films and their number and size grew with the deposition time. These structures are not important for the application of „LiPON“ as an interlayer, when the thickness is supposed to be in the range of only a few nanometers but they could not be eliminated in this work (cf. **chapter 3.3.1**). A cross-sectional SEM image shows that the films are dense and have a homogeneous thickness (**Figure 24**).

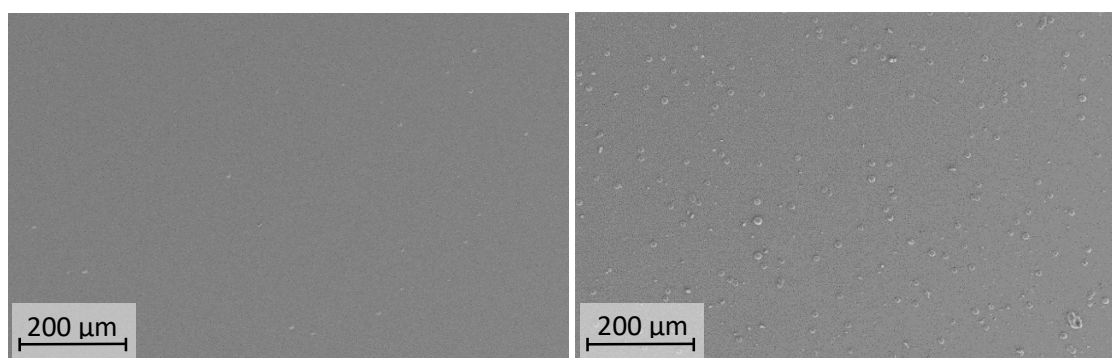


Figure 23: Surface of a „LiPON“ sample after (left) 8 min and (right) 2 h of deposition.

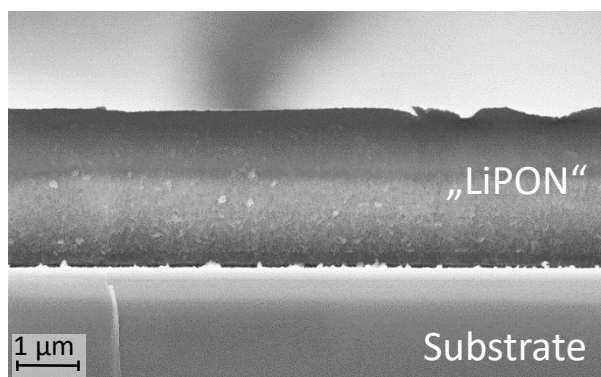


Figure 24: Cross-section of a „LiPON“ film on silicon. The film is dense and has a homogeneous thickness. The film appears in different shadings because breaking the substrate lead to a crooked cross-section.

Ionic conductivity

Ionic conductivities were determined from impedance spectroscopy measurements and are shown in **Table 6**. The respective Nyquist plots can be found in **Figure A 5** in **Appendix C**. A clear dependence of the conductivity with respect to the film stoichiometry can be observed: The higher the nitrogen content, the higher the resulting ionic conductivity. The nitrogen free lithium meta-phosphate (LiPO) has a conductivity of around 0.35 $\mu\text{S}/\text{cm}$, whereas the conductivity of nitrogen-added „LiPON“ films can reach up to 1.7 $\mu\text{S}/\text{cm}$. This behavior is in accordance with literature where the maximum conductivity of „LiPON“ is given as 3 $\mu\text{S}/\text{cm}$ [126], [132]. However, if a certain nitrogen content is exceeded the conductivity decreases again, probably due to the formation of less dense films.

Table 6: Deposition parameters and conductivities of the prepared „LiPON“ films.

Name	N ₂ flow / sccm	Ar flow / sccm	Pressure / mbar	Stoichiometry	Conductivity / $\mu\text{S cm}^{-1}$
LiPO	0	105	$2.90 \cdot 10^{-2}$	Li _{1.33} PO _{2.75}	0.35
LiPON-low	4	200	$5.50 \cdot 10^{-2}$	Li _{2.29} PO _{3.03} N _{0.42}	1.7
LiPON-high	31	0	$9.10 \cdot 10^{-3}$	Li _{1.40} PO _{1.50} N _{1.23}	1.4

4.1.2 Chemical analysis

Chemical analysis of the films in their as deposited states by means of XPS reveals that all elements are present in their expected bonding states. In particular, the lithium signal (Li 1s) at 56 eV is symmetrical (cf. **Figure A 8, Appendix D**), suggesting that only one Li species exists in “LiPO(N)”. A shoulder on the high binding energy side of the oxygen signal (O 1s, **Figure A 6 & A 7, Appendix D**) can be attributed to bridging oxygen species O_b as expected for the glassy network structure of the films. Moreover, a small carbon signal (C 1s, **Figure A 9, Appendix D**) was observed in all samples and reveals a surface contamination (< 5 at%) with hydrocarbons as well as with carbonate-like species although none of the samples had been exposed to the lab atmosphere before analysis. Consequently, these species also contribute to the shoulder of the O 1s signal at high binding energies.

For all films phosphorous (P 2p signal) was present in mainly one chemical state, the phosphate group of the “LiPO(N)” network. To account for small discrepancies of the measured signals from the ideal Gaussian/Lorentzian shape of the photoemission lines, it was necessary to add a very small second component at lower binding energies. This contribution may originate from surface atoms with different binding situations. Due to the different chemical environment of the P-atom in “LiPO” and „LiPON“ the P 2p binding energy was observed at 134.0 eV (“LiPO”) or at 132.5 eV (LiPON-low, LiPON-high).

As expected for the „LiPON“ samples, the nitrogen signal (**Figure 25**) consists of two main components: the doubly coordinated $-N=$ and triply coordinated $-N<$ at 398.0 eV and 400.0 eV, respectively. The sample LiPON-high contains only a minor contribution of $-N<$. The dependency of the $-N<$ fraction from the N/P ratio has already been observed in literature [142]. The higher the N/P ratio the lower the fraction of triply coordinated $-N<$ and the higher the fraction of $-N=$. As the nitrogen content of LiPON-high is higher than most values reported in literature, also the fraction of $-N=$ is higher than reported. In addition, also the O_b fraction is smaller in LiPON-high than in literature. This result suggests that O_b is preferentially replaced by nitrogen during thin-film formation.

4.1.3 SEI formation at the Li|“LiPON“ interface – *in situ* XPS

To investigate the formation of the Li|“LiPO(N)” interphase, lithium metal was deposited stepwise on the “LiPO(N)” films in the XPS analysis chamber, each time followed by an acquisition step. For all samples, a similar behavior could be observed: Due to the high reactivity of Li metal, all elemental signals drastically change upon lithiation of the surface evidencing the formation of new species in the course of a solid-state reaction.

Figure 25 shows the P 2p and N 1s detail spectra of “LiPO”, LiPON-low and LiPON-high for Li deposition times of 1080 s, 2160 s and 3240 s, and the as-deposited films. The C 1s detail spectra and the evolution of the O 1s and Li 1s signal of the three different samples can be found in **Figure A 9 in Appendix D**. In accordance with the observations from Schwöbel et al., the decomposition of “LiPO(N)” can be clearly observed: New components evolve in the P 2p spectrum. These components can be attributed to lithium phosphide (Li_3P) as well as to lithium phosphate (Li_3PO_4) [14], [159] and to small amounts of partially lithiated phosphorous species (Li_xP_y). For „LiPON“ samples, also the N 1s signal is heavily altered by the reaction: Triply coordinated $\text{P} - \text{N} \begin{smallmatrix} \text{P} \\ \text{P} \end{smallmatrix}$ species disappear during the first deposition steps and a new component at low binding energies attributed to the formation of lithium nitride (Li_3N) evolves. The oxygen signal undergoes similar changes as the component at high binding energies (bridging oxygen) vanishes first, accompanied by the formation of lithium oxide (Li_2O). To summarize, the reaction of lithium with “LiPO(N)” causes the formation of an interphase (SEI) containing the respective binary compounds (Li_2O , Li_3N , Li_3P) as well as Li_xP_y and Li_3PO_4 .

In contrast to previous works on the Li|“LiPON“ interface, the *in situ* XPS technique allows for a much more detailed analysis of the SEI formation: Firstly, due to intermittent Li deposition and XPS analysis, a “deposition profile” reflecting the interphase formation and – for the case that a thin and stable reaction layer is formed – the following attenuation of signals from the “„LiPON“ substrate” allows further insights into the chemistry and kinetics of the occurring reactions. Secondly, a systematic evaluation of the signal intensities of non-reacting species can reveal the thickness of the formed SEI.

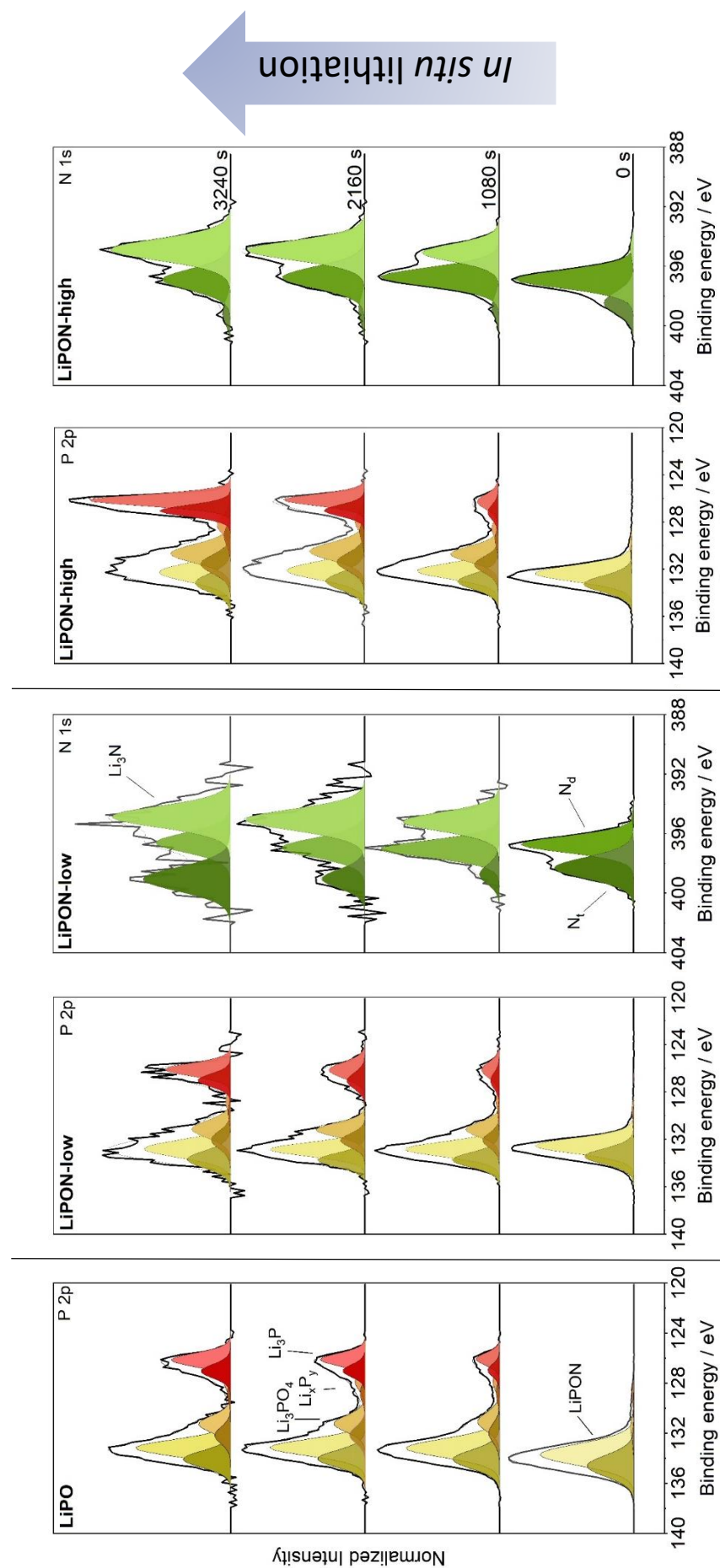


Figure 25: Evolution of the P 2p signals and the N 1s signals of the LiPO, LiPON-low and LiPON-high thin-films during the *in situ* experiment. In contact with lithium, LiPO and „LiPON“ form Li_3PO_4 before decomposing into the binary compounds Li_2O (see Figure 26) and Li_3P . All spectra are normalized to the maximum signal intensity at time t after subtracting the background intensity.

Deposition Profiles

To further investigate the SEI formation process, profiles of the evolution of different species in the course of lithium deposition were created from the respective intensities obtained from peak fit analysis. In general, the deposition of any kind of material on a substrate leads to the attenuation of the photoemission signals of the substrate material. For cases where no reaction between substrate and surface layer takes place, the intensity of the substrate signal is diminished exponentially and can be described by a simple absorption law (Beer–Lambert law). This directly allows for the calculation of the thickness of a surface film [48]. **Figure 26** depicts the integrated intensities of the photoelectron signals from different SE and SEI species in dependence of the lithium deposition time. The y-axis has a logarithmic scale and easily allows the distinction between different reactions. If no reaction took place one would assume a linear decay of the intensities of the electrolyte species and an increase of the lithium metal intensity and – in the presence of water or oxygen in the deposition chamber – an increase of the Li_2O signal.

The reaction of the solid electrolyte with lithium metal should result in a decrease of the intensities of all signals attributed to the SE that are converted and covered by an overlayer, and the rise of signals attributed to reaction products. A superposition of these two processes, interphase formation and creation of an overlayer, will result in a curve with pronounced maximum prior to a final decay of the intensity.

Indeed, for long Li deposition times all signals (besides oxygen, see below) are attenuated and it is clear that SEI formation is either finished and a stable interphase has formed or that reaction rates for further SE decomposition are too low to be observed within the time-frame of the experiment. Interestingly, all profiles show a distinct behavior of the film growth. As can be seen in **Figure 26**, the evolution of the different SEI components of the “LiPO” film in contact with lithium does not happen simultaneously. Regarding the phosphorous species, a signal attributed to the formation of Li_3PO_4 arises first followed by a further reaction step toward Li_3P [14]. The maximum intensity for Li_3PO_4 was observed after about 500 s of lithium deposition (dotted line) and for Li_3P after 1200 s (dashed line) hinting at a layered structure of the SEI. As Sicolo et al. have shown by combining theoretical and experimental studies, „LiPON“ with an average stoichiometry of $\text{Li}_6\text{P}_3\text{O}_9\text{N}$ first decomposes by forming Li_3PO_4 before further reacting to Li_3P [14]. This is probably related to the fact that LiPO films

are lithium deficient compared to the Li_3PO_4 and the deposition of Li helps to compensate this deficiency. In a second step, the surface of Li_3PO_4 then will decompose in contact with Li and form the binary compounds Li_2O and Li_3P . In **Figure 26**, it can also be seen that for longer lithium deposition times, the slope of the curves for different components are different. This is another indication that more than one reaction takes place. Whereas the reaction of Li_3PO_4 seems to be finished (the slope of $\text{P}(\text{Li}_3\text{PO}_4)$ is almost the same as the slope of the $\text{P}(\text{LiPO})$ signal), the slope of $\text{P}(\text{Li}_3\text{P})$ is less steep, indicating that although the total intensity is attenuated by the evolving overlayer, more Li_3P is formed.

The examination for LiPON-low and LiPON-high shows similar results. Again, Li_3PO_4 is formed prior to Li_3P . In addition, simultaneous to the reduction of „LiPON“ to Li_3PO_4 and Li_2O , Li_3N is formed. For LiPON-low – in contrast to the “LiPO” sample – the decay of the intensities already sets in after 600 – 900 s of lithium deposition and the formed interphase is expected to be thinner than that of “LiPO”. The reaction of LiPON-high happens for much longer Li deposition times: Not until lithium has been deposited for 2000 s, the intensities related to SEI species begin to decrease. Therefore, we conclude that the interphase on top of the nitrogen-rich sample is thicker than for the other two solid electrolytes.

It is important to note that unavoidable water and/or oxygen impurities in the residual gas atmosphere of the vacuum chamber heavily affect the *in situ* XPS experiment and lead to the partial oxidation of the freshly deposited lithium metal. Most importantly, the interpretation of the oxygen signal is complicated as Li_2O can either be formed as reaction product of Li and „LiPON“ or due to the reaction of “LiPO(N)” with H_2O or O_2 from the gas phase. This is reflected in the significantly less steep slope in the Li_2O profile as well as in the O 1s spectra (see **Figure A 7, Appendix D**), which comprise an Li_2O component with almost constant intensity even after long Li deposition times – confirming the re-oxidation of the Li film. Moreover, additional components from LiOH or from Li_2O (reaction of Li with H_2O or O_2 residual gas) contributing to the O 1s signal cannot be excluded. However, expected binding energy differences to signals from these species are too small to be resolved and, due to the blindness of (lab-scale) XPS for hydrogen, the existence of LiOH cannot be proven. The incorporation of oxygen can also cause difficulties in determining the SEI thickness and the lithium deposition rate of lithium (see sections below): If instead of pure lithium metal a

mixture of lithium and lithium oxide is deposited on top of the electrolyte, not the entire lithium layer can contribute to the interface reaction. Consequently, the data evaluation will reveal a smaller growth rate than expected because more lithium is needed to achieve a certain SEI thickness. Secondly, lithium oxide with its poor transport properties can lead to a passivation of the SEI and impede the SEI growth. If that happens, even electrolytes that would undergo full decomposition in contact with lithium metal might be stabilized. Nevertheless, being aware of these external influences, the contribution of additional Li_2O can be corrected by a careful data treatment, and a reliable interpretation of the data is still possible.

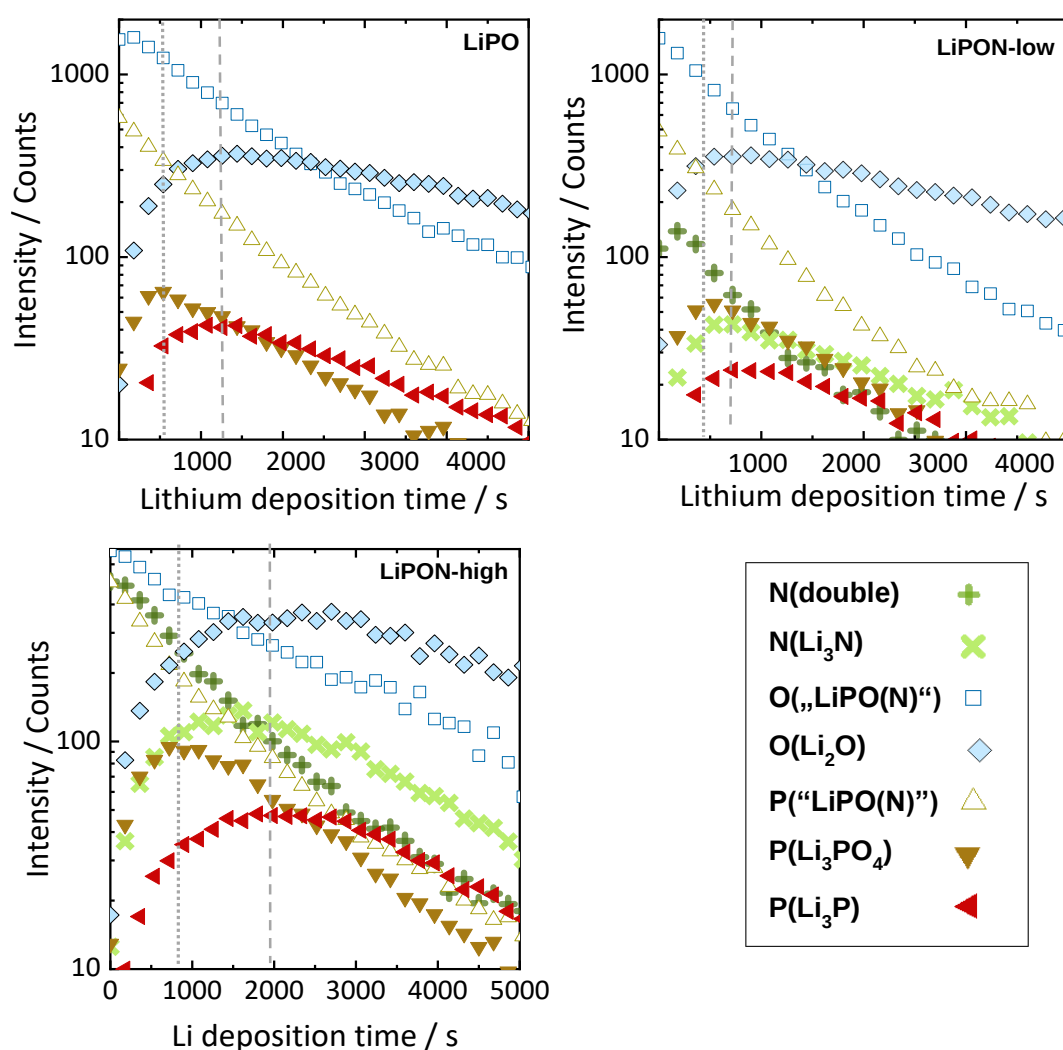


Figure 26: Change of the intensities of SE and SEI signals as a consequence of the step-wise deposition of lithium in dependence on the deposition time. Substrate signals are shown as empty data points. The dotted line depicts the maximum intensity of $\text{P}(\text{Li}_3\text{PO}_4)$ the dashed line depicts the maximum intensity of $\text{P}(\text{Li}_3\text{P})$.

The time-dependent evolution of the relative fractions of different phosphorous and nitrogen species reveals further interesting insights on the reaction. **Figure 27** shows the evolution of the phosphorous signals of the three different samples. In the beginning, almost exclusively $P(\text{LiPO}(\text{N}))$ can be found as no reaction took place yet. Directly after the first Li deposition step the $P(\text{LiPO}(\text{N}))$ signal decreases and the $P(\text{Li}_3\text{PO}_4)$ signal increases. The formation of Li_3P sets in later. As can be seen, the $P(\text{Li}_3\text{PO}_4)$ signal results in a constant fraction after 1000 s of lithium deposition whereas the $P(\text{LiPO}(\text{N}))$ signal decreases continuously and the Li_3P signal increases. This finding suggests that Li_3PO_4 is formed from “LiPO(N)” and then, upon further lithiation, Li_3PO_4 is transformed into Li_3P . At the same time the formation of Li_3PO_4 continues. The reduction of Li_3PO_4 to Li_3P seems to occur without large amounts of intermediate products as the fraction of partially reduced Li_xP_y remains very small ($< 3\%$). The same observations can also be made for the nitrogen-containing „LiPON“ samples. The Li_3PO_4 formation always occurs prior to the formation of Li_3P . However, for the nitrogen-containing samples, a constant ratio of the different phosphorous species is achieved after 3000 s of lithium deposition. Note, that only the absolute intensities of all signals decrease (compare **Figure 26**) and that, once the relative ratio of different phosphorous species is constant, no further decomposition of the electrolyte or SEI formation occurs. This finding suggests that the SEI formation ceases and the lithium | electrolyte interphase is passivated.

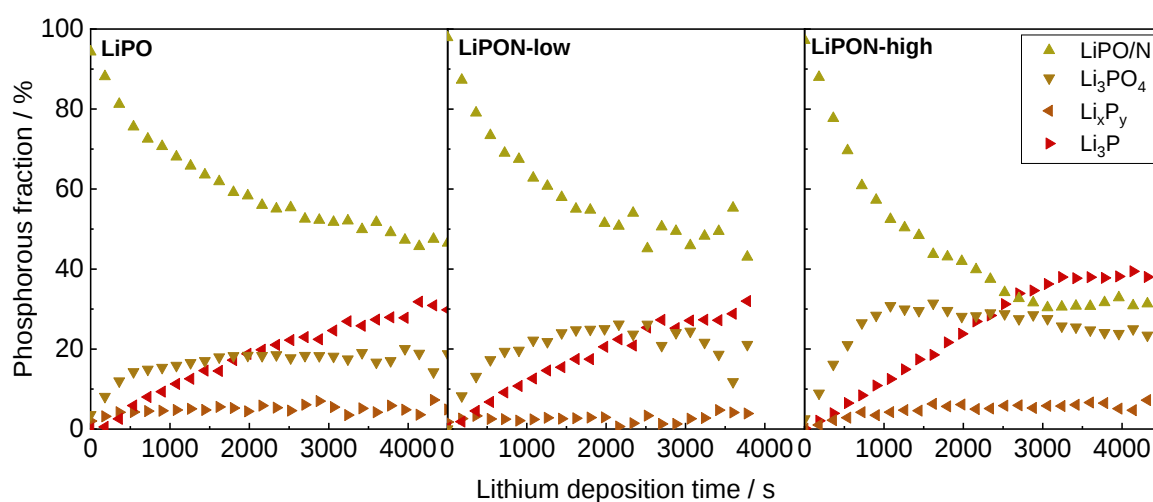


Figure 27: Evolution of the relative fractions of phosphorous species in the “LiPO(N)” samples.

In addition to phosphorous, also the change of the relative intensities of nitrogen is interesting (**Figure 28**). Exemplarily shown for LiPON-high, the relative intensities of N_d , N_t and $N(Li_3N)$ also change upon lithiation. In the case of LiPON-high, the initial N_t signal vanishes instantly after the beginning of the lithium deposition. Also N_d decreases but Li_3N is formed. It is interesting to note that the relative fraction of $N(Li_3N)$ begins to cease around the time when the Li_3PO_4 formation reaches a constant value, suggesting that the decomposition of „LiPON“ stops.

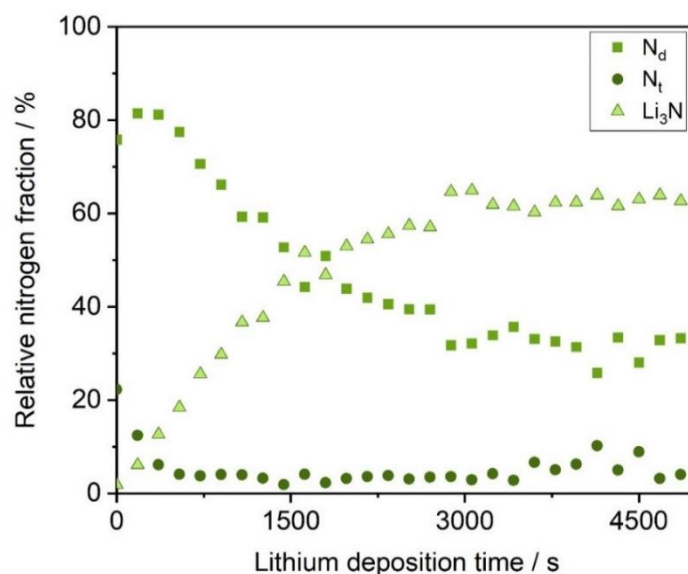


Figure 28: Evolution of the relative fractions of nitrogen species in LiPON-high.

Thermodynamic considerations

The thermodynamic driving force for the reaction is the Gibbs free enthalpy

$$\Delta_r G = \Delta_r H - T \Delta_r S. \quad (23)$$

The entropy is a function of the heat capacity at either constant pressure or constant volume:

$$S = \int_0^T C_p d \ln T \quad S = \int_0^T C_V d \ln T \quad (24)$$

In the case of solid state reactions between lithium metal and the electrolyte or interlayer, no gases are formed or consumed. The molar heat capacity of solids is determined by their degrees of freedom and can be estimated as $3 R (\approx 24 \frac{J}{mol \cdot K})$, with R being the universal gas constant. Therefore, it can be assumed that the change of the entropy during the reaction is

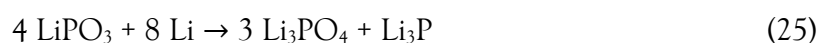
small compared to the change of the enthalpy and that the entropic contribution to ΔG is negligible. In the present study only the molar standard formation enthalpies $\Delta_f H_m^0$ are used for judging the plausibility of a reaction.

The thermodynamic driving forces for the reactions of “LiPO(N)” in contact with lithium can easily be estimated if the heats of formation of the products and educts are known (**Table 7**). For the estimations of the reaction enthalpies, the calculated values from [160] and [161] were used and compared to the species that come closest to the stoichiometry of the three films examined in this work.

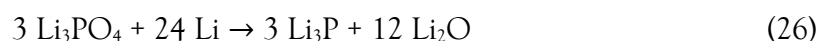
Table 7: Standard heats of formation (from the elements); adapted from [160] and [161].

	$\Delta_f H_m^0$ [kJ/mol]
Li	0
β -Li ₃ PO ₄	−2048.4
Li ₂ O	−588.6
α -Li ₃ N	−154.4
Li ₃ P	−334.8
LiPO ₃	−1230.2
Li _{2.5} PO ₃ N _{0.5}	−1608.4
Li ₂ PO ₂ N	−1165.5

As described above, a time-delayed formation of Li₃P compared to the formation of Li₃PO₄ can be observed. Consequently, this observation suggests a two-step reaction. The first step is the reaction of LiPO₃ to Li₃PO₄.



The second step is the subsequent decomposition of Li₃PO₄ to Li₃P and Li₂O.



Although Li₃P is already formed in the first step, the amount of formed Li₃PO₄ is higher and the intensity of the Li₃PO₄ signal (**Figures 26 & 27**) shows a steeper increase. When, in a second step, Li₃PO₄ is decomposing into Li₃P and Li₂O, the intensity of the phosphate signal decreases and the intensity of Li₃P further increases. The heat of formation for these reactions

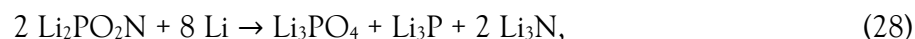
can be calculated according to $\sum_i v_i \cdot \Delta_f H_{m,i}^0$. The resulting heat of formation is -3481.6 kJ (-1559.2 kJ for the first step and -1922.4 kJ for the second step), or -870.4 kJ per mole LiPO_3 , clearly indicating the driving force of the reaction.

The same calculation for LiPON-low (with a simplified stoichiometry $\text{Li}_{2.5}\text{PO}_3\text{N}_{0.5}$) leads to a decomposition into Li_3PO_4 and Li_3N :



This reaction is followed by the decomposition of Li_3PO_4 according to equation 26. In total, a heat of formation of -2277.6 kJ ($\cong -569.4$ kJ/mol) is calculated. This value is still a large driving force for the decomposition of „LiPON“, however, the heat of formation for the first step is only -355.2 kJ, and therefore much smaller than for pure Li_3PO_4 in contact with lithium.

The decomposition of LiPON-high (here simplified to $\text{Li}_2\text{PO}_2\text{N}$) in contact with lithium metal can be described by the following reaction:



resulting in a heat of formation of -361 kJ. This first step is followed by the decomposition according to equation 26, resulting in a total heat of formation of -1001.8 kJ (-500.9 kJ/mol with respect to $\text{Li}_2\text{PO}_2\text{N}$). So regardless of the stoichiometry, all reactions have a thermodynamic driving force to happen spontaneously and a conversion of „LiPON“ into the binary compounds should occur in contact with lithium.

The XPS results suggest that a two-step reaction can be formulated although thermodynamics dictate a favored formation of the binary lithium compounds, also determined from first principles calculations carried out by Zhu et al. [47]. However, the thermodynamically favored reaction might be limited by kinetic factors and the results of the *in situ* XPS experiment must not necessarily describe the SEI formation in a real battery.

The amount of lithium that is deposited on the sample during each step is limited, whereas in a real battery the lithium anode can be seen as an endless lithium reservoir. The amount of lithium should therefore have an influence on the interface reactions and a limited lithium reservoir should not support a reaction that consumes a lot of lithium. Therefore, in the case of the *in situ* experiment, the formation of Li_3PO_4 is favored over the formation of the binary

compounds because it requires more lithium and the Li_3PO_4 formation sets in earlier. Only when after multiple lithium deposition steps enough lithium is present, Li_3PO_4 can be converted into the binary compounds. In a real battery system, the amount of Li_3PO_4 may be smaller than found during the XPS experiment. As lithium always needs to diffuse from the lithium metal anode into the electrolyte and is steadily hindered by the limited transport properties of the continuously growing SEI, it can still be expected to find a lithium-poor Li_3PO_4 layer in batteries with „LiPON“ electrolyte.

Calculation of the SEI thickness

After clarifying the chemical reactions in the course of SEI formation, the thickness of the reaction layer is addressed. The evaluation of the thickness of a thin overlayer on a substrate by XPS is a routine procedure, e.g. [162], in microelectronics (thickness of SiO_2 layer on Si) and has also been extensively studied for oxidation or surface passivation of other materials [139]–[148]. These methods are based on the intensity ratio of the substrate signals and overlayer signals but have different presumptions. While some consider a single layer on top of a substrate with homogeneous composition, others like the model from Lubenchenko et al. consider the formation of a multilayer system with varying composition [163]. These multilayer considerations are of particular interest in the case of the oxidation of a metal where a stepwise oxidation takes place. In this case the oxygen content changes across the interphase and the metal cations exist in different oxidation states. Depending on the system that is examined, the assumption of a multilayer comprises a few, several nanometers thick layers with distinct differences or the summation of many layers with infinitesimal differences, leading to slight deviations of the determined thicknesses. In addition to the examination of multilayered systems, which are predominantly used for the monitoring of a reaction, also angular-dependent photoelectron spectroscopy can be performed to distinguish between the topmost surface-layer signals and signals from underneath. The change of the angular dependent signal intensities can be used to examine already formed reaction layers.

For the following analysis some simplifying assumptions have been made: Firstly, the substrate (here the SE) is assumed as homogeneous and semi-infinite with an atomically flat

surface. Therefore, any effects of surface roughness and compositional inhomogeneities are neglected. Moreover, for each deposition step the growing SEI overlayer is considered to be perfectly flat and as a homogenous mixture of its components. Assuming a thin overlayer with thickness d on a solid electrolyte substrate (SE), the intensities of the respective photoelectron signals of the elemental transition from a given subshell i from substrate ($I_{i,SE}$) and transition j from overlayer ($I_{j,SEI}$) can then be calculated as

$$I_{i,SE} = I_{i,SE}^{\infty} \cdot \exp\left(\frac{-d}{L_{i,SEI}}\right) \quad (29)$$

$$I_{j,SEI} = I_{j,SEI}^{\infty} \cdot [1 - \exp\left(\frac{-d}{L_{j,SEI}}\right)] \quad (30)$$

with $L_{i,j,SEI} = EAL_{i,j,SEI}(KE) \cdot \cos \vartheta$

$EAL_{i,j,SEI}(KE)$ = energy-dependent effective attenuation length of photoelectrons from transition i or j in the SEI,

ϑ = photoelectron emission angle with respect to the surface normal (here $\vartheta = 45^\circ$).

$I_{i,SE}^{\infty}$ and $I_{j,SEI}^{\infty}$ denote signal intensities for the respective materials assuming infinite thickness and can be calculated as

$$I_{i,SE/SEI}^{\infty} = \sigma_i \cdot N_{i,SE/SEI} \cdot EAL_{i,SE/SEI}(KE) \cdot \cos \vartheta \cdot J_{hv} \cdot T(KE) \quad (31)$$

The factors contributing to the signal intensities can be grouped to those affected by instrumental properties (J_{hv} : X-ray flux density, $T(KE)$: energy-dependent transmission function of the analyser), to those being governed by the transition itself (σ_i : elemental photoionization cross-section for transition i) and to sample dependent factors ($N_{i,SE/SEI}$: number of atoms of element i , $EAL_{i,SE/SEI}(KE) \cdot \cos \vartheta$: effective attenuation length for electrons of elemental transition i in the respective material). The number of atoms N_i can be calculated from the molar volume V_{mol} and the atomic concentration X_i .

In the following the signal intensities of the P 2p signal of different P-species from SE and SEI are used to calculate the SEI thickness as P solely originates from the solid electrolyte film and is not present in the chamber atmosphere. In this case $i = j = P\ 2p$ and the energy dependence of the EALs can be neglected ($L_{i,SEI} = L_{j,SEI} = L_{P\ 2p,SEI}$)

To extract d from equation 30, the ratio of both intensities can be used.

$$\frac{I_{SEI}}{I_{SE}} = \frac{I_{SEI}^{\infty}}{I_{SE}^{\infty}} \cdot \frac{[1 - \exp(\frac{-d}{L_{P\ 2p,\ SEI}})]}{\exp(\frac{-d}{L_{P\ 2p,\ SEI}})} \quad (32)$$

After rearranging, the thickness d can be calculated according to [164] and [165]:

$$d = L_{P\ 2p,\ SEI} \cdot \ln \left(\frac{I_{SE}^{\infty}}{I_{SEI}^{\infty}} \cdot \frac{I_{SEI}}{I_{SE}} + 1 \right) \quad (33)$$

$$\text{with } \frac{I_{SEI}^{\infty}}{I_{SE}^{\infty}} = \frac{N_{P\ 2p,\ SEI}}{N_{P\ 2p,\ SE}} \cdot \frac{L_{P\ 2p,\ SEI}}{L_{P\ 2p,\ SE}} = \frac{V_{mol,\ SE}}{V_{mol,\ SEI}} \cdot \frac{X_{P,\ SEI}}{X_{P,\ SE}} \cdot \frac{L_{P\ 2p,\ SEI}}{L_{P\ 2p,\ SE}}$$

$$d = L_{P\ 2p,\ SEI} \cdot \ln \left(\frac{V_{mol,\ SEI}}{V_{mol,\ SE}} \cdot \frac{X_{P,\ SE}}{X_{P,\ SEI}} \cdot \frac{L_{P\ 2p,\ SE}}{L_{P\ 2p,\ SEI}} \cdot \frac{I_{SEI}}{I_{SE}} + 1 \right) \quad (34)$$

The values $V_{mol,\ SE}$, $X_{i,\ SE}$, and $L_{i,\ SE}$ depend on properties of the SE and are assumed to be constant for each SE sample in the course of the experiment. However, $V_{mol,\ SEI}$, $X_{i,\ SEI}$, and $L_{i,\ SEI}$ are functions of the SEI composition and change in the course of the experiment. This equation is also valid for intermediate layers as in the case of an SEI between solid electrolyte and electrode. Equation 34 now allows for the calculation of the SEI thickness after each deposition step.

According to the results of the chemical analysis the SEI has to be described as a complex multi-component composite with increasing Li concentration toward the surface and with the lowest Li content at the SEI|SE interface. Moreover, the average molar volume of the SEI will obviously differ from that of the SE. Depending on the chemical nature of the SEI species, the interphase formation leads to a contraction or expansion of the material. Finally, for each subsequent deposition step, electrons from SE and SEI are attenuated differently. The available data do not allow to determine a precise stoichiometry of the formed SEI as species close to the surface will always be detected with a higher intensity than species below. Moreover, additional surface species lead to an overestimation of the Li_2O content. Also the energy dependence of the EAL can lead to different relative intensities of the various reaction products and to a misinterpretation of the data. To address these complications, some assumptions can be made as SEI thickness and EALs for the relevant signals are both in the same range (2 – 3.5 nm): Firstly, an average SEI signal intensity is calculated as sum of the photoemission intensities from the respective species ($Li_3PO_4 + Li_xP_y + Li_3P$) resulting in a

single value for the SEI thickness. Moreover, this average SEI composition can be used for calculating $V_{\text{mol, SEI}}$, $X_{\text{i, SEI}}$, and $L_{\text{i, SEI}}$.

Figure 29 shows the evaluation of the SEI thickness in the course of Li deposition for all samples. Three main observations can be made at this point:

- The SEI thickness is about 2 – 3.5 nm for all samples (similar to $\text{Li}_7\text{P}_3\text{S}_{11}$ [78]).
- The SEI thickness reaches a constant value (in the timeframe of the measurement, less than one day).
- LiPON-high forms a thicker SEI than the other two samples.

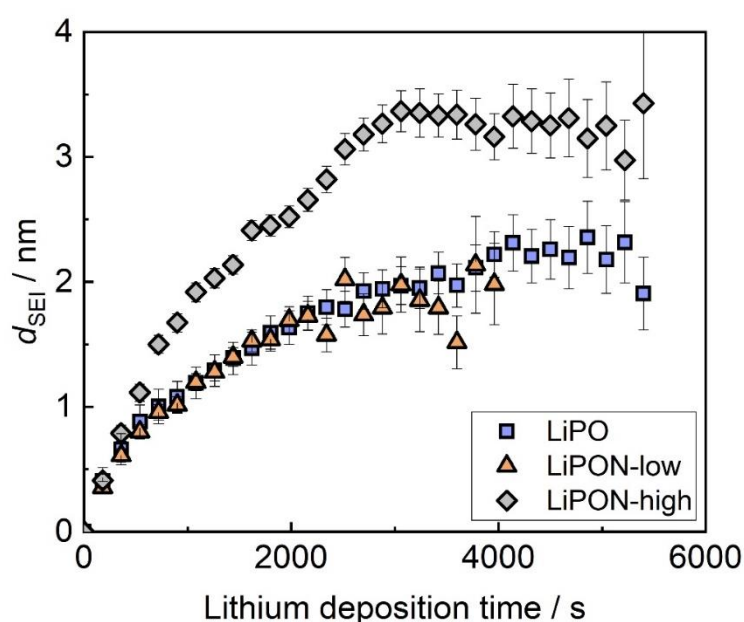


Figure 29: SEI growth in dependence of the deposition time for the different “LiPO(N)” films.

It must be pointed out that d_{SEI} as determined by *in situ* XPS describes the lower limit of the thickness and that the real SEI might be thicker. According to Wenzel et al. the *in situ* XPS experiment can only be used when the kinetics of the reaction fulfill certain requirements. The kinetics of the experiment must be either very fast, so that the reaction is already completed when the measurement step after lithium deposition starts or the kinetics must be very slow so that no change of the sample occurs until the measurement is finished [48].

However, as the experiment consisted of subsequent lithium deposition and analyzing steps, the reaction between the electrolyte and lithium does not necessarily have to be finished during the analyzing step and might still proceed during the measurement if enough lithium is present. To clarify whether the decomposition is an ongoing process, one would have to perform several measurements with different analyzing times between each lithium deposition step and see whether the intensity ratio changes over time.

Estimation of Li thickness

The *in situ* experiment also allows to calculate the Li deposition rate by applying equation 29 on the intensity of the attenuated SE and SEI signals, which can be used as internal reference. Note that the calculated deposition rate is much more sensitive to various instrumental parameters (e.g. slight changes in the experimental geometry, instabilities of the ion gun, residual atmosphere in the UHV chamber) than the determined SEI thickness and has to be calculated for each experiment. In particular, additional Li_2O species in the overlayer (see above) need to be taken into account. **Figure 30** shows the total P 2p signal intensity on a logarithmic scale plotted against the Li deposition time for all samples.

As can be seen best for LiPON-low, for each sample the signal attenuation curve can be split into two regions with different slopes. The first region corresponds to the formation of the SEI (i.e. transformation of $\text{P}(\text{LiPO}(\text{N}))$ to $\text{P}(\text{Li}_3\text{P})$ and $\text{P}(\text{Li}_3\text{PO}_4)$) and to the simultaneous damping of the unaffected SE signal by the growing SEI layer. In the second region the reaction is finished and the SEI reaches a constant composition. Here, further damping of the intensity of both SE and SEI phosphorous species is caused by the growth of the Li layer on top of the SEI, resulting in a rate of

$$r_{\text{mix}} = m \cdot L_{\text{Overlayer}} \quad (35)$$

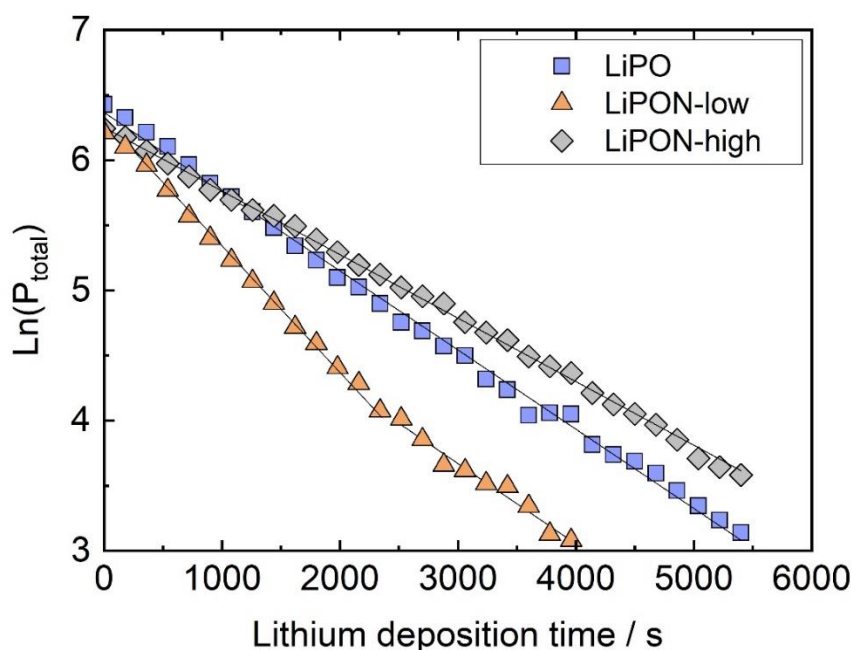


Figure 30: Attenuation of total P signal. Once the SEI has reached a stable thickness, the slope of the curve can be used to calculate the deposition rate of the Li/Li₂O overlayer.

The average effective attenuation length of the overlayer can be calculated from its stoichiometry (Table 8). In equation 35, m is the slope of the photoemission intensities for all P species. The thereby determined value r_{mix} is the deposition rate of the Li/Li₂O mixture, which now needs to be corrected for the Li₂O component. For long deposition times, this mixture has a constant composition of $X_{\text{Li}_2\text{O}} = 20 - 25$ mol% as determined from the ratio of the intensities of the O 1s signal of Li₂O and the total Li signal. This ratio was calculated as an average value from data recorded from 3000 s of Li deposition time until the end of the measurement, assuming that at this point mainly the overlayer contributes to the signal. Consequently, the damping of the P 2p intensity is also caused by both Li and Li₂O. It has to be noted that the EALs of O 1s and Li 1s are different. Therefore, the damping of the intensity caused by these components is different. In the case of “LiPO” and LiPON-low where a thick overlayer is assumed, these difference lead to negligible errors of the SEI composition and growth. In the case of LiPON-high, where the reaction proceeds longer than for the other two samples, the overlayer is thinner and therefore the different EALS in

the overlayer may cause a bigger error. However, this error may be smaller than the error of the SEI stoichiometry derived from the data fitting.

Table 8: Mol percentage of Li_2O in the lithium overlayer calculated from the $\text{Li}_2\text{O}(\text{O } 1s)$ and $(\text{Li } 1s)$ signals after 3000 s of Li deposition time till the end of the measurement; and average EAL thereof.

Material	mol% Li_2O	$\text{EAL}_{\text{P } 2p} \cdot \cos 45^\circ / \text{nm}$
“LiPO”	17.9	3.33
LiPON-low	17.2	3.34
LiPON-high	21.9	3.27

From r_{mix} and $X_{\text{Li}_2\text{O}}$, the growth rate of pure Li metal can be calculated. The volume fractions of the overlayer components can be calculated from the molar fractions with $X_{\text{Li}_2\text{O}} = \frac{I_{\text{Li}_2\text{O}(\text{O } 1s)}}{I_{\text{Li}(\text{total})}}$, the ratio of the intensities of the O 1s signal of Li_2O and the total Li signal. The approximation via the oxygen signal is necessary because the intensity of the Li signal is too small to be fitted with multiple signals and to determine the fraction of $\text{Li}(\text{Li}_2\text{O})$.

The damping of the P 2p intensity is caused by both Li and Li_2O and the growth rate in equation 35 is the growth rate of the $\text{Li}_2\text{O}/\text{Li}$ layer. From this value, the growth rate of pure Li metal can be calculated. The volume fractions of the overlayer components can be calculated from the atomic fractions using the molar volumes $V_{\text{M},i}$:

$$V_{\text{Li}_2\text{O}} = X_{\text{Li}_2\text{O}} \cdot V_{\text{M},\text{Li}_2\text{O}} \quad (36)$$

$$V_{\text{total}} = V_{\text{Li}_2\text{O}} + V_{\text{M},\text{Li}} \cdot (1 - X_{\text{Li}_2\text{O}}) = V_{\text{Li}_2\text{O}} + V_{\text{Li}} \quad (37)$$

A certain amount of the growth rate r_{mix} is caused by Li_2O

$$r_{\text{mix}} = r_{\text{Li}} + r_{\text{Li}_2\text{O}}, \quad (38)$$

with

$$r_{\text{Li}_2\text{O}} = \frac{V_{\text{Li}_2\text{O}}}{V_{\text{total}}} \cdot r_{\text{mix}} \quad (39)$$

Combining (34),(37) and (38) leads to

$$r_{\text{Li}} = r_{\text{mix}} - r_{\text{Li}_2\text{O}} = r_{\text{mix}} - \frac{V_{\text{Li}_2\text{O}}}{V_{\text{total}}} \cdot r_{\text{mix}} = m \cdot L_{\text{Overlayer}} \cdot \left(1 - \frac{V_{\text{Li}_2\text{O}}}{V_{\text{total}}}\right) \cdot 60\text{s/min} = r_{\text{Li,late}} \quad (40)$$

Adding the factor 60s/min results in a more convenient growth rate per minute. As discussed above, the thermodynamic driving force for the reaction between lithium and the electrolyte

is bigger than for the reaction of lithium and oxygen or water. The formation of Li_3PO_4 (and Li_3N) out of “LiPO(N)” is thermodynamically more favorable than the formation of Li_2O from the elements (**Table 7**). If the formation of Li_2O and/or LiOH is due to the reaction of lithium with water in the deposition chamber, the resulting reaction enthalpy is -303.0 kJ and the reaction with the chamber atmosphere instead of the electrolyte should be even less favorable. Therefore, it can be concluded that the reaction rate for forming Li_2O from residual oxygen in the chamber atmosphere will be negligible as long as impinging lithium can instantaneously react with the electrolyte surface. As a consequence, lithium that would form Li_2O for higher deposition times will react with the electrolyte at the beginning of the experiment. Therefore, the deposition rate of active lithium will be higher for the first deposition steps and the rate needs to be corrected. As the overlayer consists of x mol% Li_2O and $(100 - x)$ mol% Li, and for each Li_2O molecule two lithium atoms are needed, the total fraction of Li is therefore $(100 - x + 2x) \% = (100 + x) \%$ of the value determined via XPS, leading to a correction factor of $\frac{100 + x}{100 - x}$ for the lithium deposition rate at the beginning of the experiment.

$$r_{\text{initial}} = r_{\text{late}} \cdot \frac{100 + x}{100 - x} \quad (41)$$

In the intermediate region where the kinetic limitation of the SEI formation starts to decrease the deposition rate of active lithium, an average deposition rate will be between the values from equation 40 and equation 41. A precise value cannot be calculated, leading to a slightly erroneous value of the total lithium thickness.

For a precise determination of the thickness of the lithium layer, it is important to determine the time after which a transition from the initial to the late deposition rate sets in. A helpful indicator for this transition point is the ratio of total intensities of the oxygen and phosphorous signals in the course of the *in situ* experiment (**Figure 31**). Without additional oxygen from the residual atmosphere, this ratio should be constant in SE and SEI. Additional oxygen, however, will form Li_2O on top of the sample whereas all phosphorous species stem from SE and SEI and their signal intensities are attenuated once the top-layer begins to form. Consequently, the O/P intensity ratio reacts extremely sensitive to the formation of additional Li_2O as can be seen in **Figure 31**.

In this figure, it can be seen that the ratio is almost constant during the first 600 s of lithium deposition time before increasing to a ratio of almost 10. In the beginning all lithium directly reacts with „LiPON“ and no oxygen from the atmosphere is trapped. Minor changes of the ratio are attributed to parts of lithium oxide that originate from the oxidized surface of the lithium foil that was used for lithium deposition. The following increase of the O/P ratio is due to the subsequent formation of additional Li_2O (whose intensity is proportional to $(1 - e^{-d})$) due to kinetic limitations caused by the growing SEI and the exponential decay of the P intensity that is buried under Li_2O . To summarize, the increase of the O/P ratio sets in at the time when the interphase growth of the sample LiPON-high changes from a reaction-controlled mechanism to a diffusion-controlled mechanism as will be discussed below in further detail.

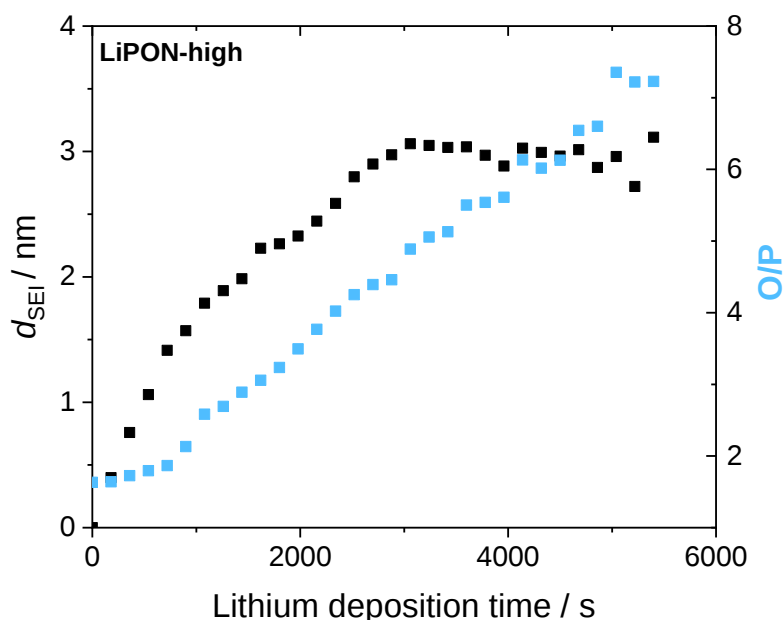


Figure 31: Evolution of the O/P intensity ratio of the LiPON-high sample depending on the lithium deposition time. The ratio starts to increase when the reaction-controlled interphase formation turns into a diffusion-controlled process and lithium has enough time to trap water from the chamber atmosphere. Note that this ratio does not describe the elemental composition as O and P signals stem from different depths leading to much higher intensities from surface-near species (Li_2O) compared to signals from the SE and SEI.

After SEI formation, the Li metal film is partly oxidized by oxygen or water traces and for all samples an average composition and an average electron attenuation length could be determined. The values are summarized in **Table 9**.

For the calculation of the average effective electron attenuation lengths of the SEI, the average SEI composition is required. The average SEI composition determined from XPS measurements will always be erroneous, as the information depth during each measurement step is bigger than the SEI thickness created during the previous Li deposition step. At short deposition times and very low SEI intensities, the ratio is adulterated by the high intensity of the electrolyte signals. After long deposition times, the incorporation of additional Li_2O falsifies the results. For that reason, the average EALs were calculated from the ratio of SEI signals at Li deposition times of 540 s – 1080 s. As the ratio of LiP is always < 3 %, it is neglected in these calculations.

Table 9: SEI composition, electron attenuation lengths of different SEI species and average values of the interphases calculated from the data after 540 s – 1080 s of lithium deposition time.

Species	$\text{O}_{\text{Li}_2\text{O}}$	$\text{P}_{\text{Li}_3\text{PO}_4}$	$\text{P}_{\text{Li}_3\text{P}}$	$\text{N}_{\text{Li}_3\text{N}}$	Li_{Li}
$\text{EAL}_{\text{P}_{2\text{p}} \cdot \cos 45^\circ} / \text{nm}$	2.29	2.41	2.29	2.28	3.59
$\text{Vol}\%_{\text{LiPO}}$	32.4	51.2	16.4	0	0
$\text{Vol}\%_{\text{LiPON-low}}$	37.0	43.0	9.9	9.2	0
$\text{Vol}\%_{\text{LiPON-high}}$	18.3	51.5	10.5	19.6	0
$\text{EAL SEI}_{\text{LiPO}}$		2.35			
$\text{EAL SEI}_{\text{LiPON-low}}$		2.34			
$\text{EAL SEI}_{\text{LiPON-high}}$		2.35			

The EAL is always dependent on the emission angle θ and therefore subject of the respective XPS machine. The values given in **Table 9** are corrected by the emission angle of the machine used in this work. The EAL for the three different SEIs are quite similar. The differences of the stoichiometry are small as oxygen is only replaced by nitrogen when the stoichiometry is changed. The main difference is caused by the variable amount of Li_3PO_4 that is formed and the average EAL is always in between the values of Li_2O and Li_3PO_4 . To evaluate the plausibility of these estimations, it is necessary to compare the obtained values to the

theoretical maximum SEI thickness obtained after the deposition of a certain amount of lithium.

Estimation of the theoretical SEI thickness

As long as the thermodynamic driving force of the decomposition does not change, and as long as the decomposition is a reaction-controlled or interface-controlled reaction, the SEI growth should proceed with a constant rate. However, from **Figure 29** it is clear that the growth rate is limited. If the assumption is made that the overall difference of the chemical potential of lithium $\Delta\mu_{\text{Li}}$ between the substrate (silicon) underneath and the deposited lithium metal does not change during the experiment, the decrease of the growth rate must be caused by kinetic limitations. A simple calculation can be used to estimate a thickness of the formed SEI between “LiPO(N)” and lithium for the case of an unlimited growth (i.e. all Li reacts; see **Appendix E**). This estimation requires a few assumptions: The volume change is only one-dimensional and all participating compounds have the theoretical density of 100 %. If the density of the real SEI is lower (which is very likely), the calculation might slightly underestimate the SEI thickness. In addition, two different boundary conditions need to be regarded: i) Li_3PO_4 does not decompose into the binary compounds (only equations 25, 27 and 28 are valid). ii) Lithium phosphate fully decomposes into the binary compounds (equation 26). Considering the amount of lithium that is needed to completely transform “LiPO” into Li_3PO_4 and Li_3P the calculation leads to a 0.41 nm thick reaction layer if 1 nm of Li reacts with “LiPO” in a stoichiometry as shown above.

If in a second step Li_3PO_4 reacts to Li_3P and Li_2O , 1 nm of Li should lead to a 0.79 nm thick reaction layer. The same calculations for LiPON-low and LiPON-high lead to the SEI thicknesses summarized in **Table 10**.

When only Li_3PO_4 is formed, the SEI growth per nm Li depends on the nitrogen content of the thin-film. The more oxygen is replaced by nitrogen, the smaller is the amount of Li_3PO_4 that is formed and the higher is the amount of Li_3P and Li_3N . The sum of the molar volumes of Li_3P and Li_3N is bigger than the molar volume of Li_3PO_4 , therefore, the interface gets thicker. Forming the binary species requires a lot more volume resulting in a thicker interphase. Interestingly, the theoretical growth rate of the SEI shows no linear dependence

on the nitrogen content. Although Li_3N has a higher volume than Li_2O it also needs more lithium per molecule, so with each nanometer of lithium, less SEI is formed. However, the theoretical thickness of the SEI of a nitrogen-containing sample is always higher than that of the nitrogen-free sample.

Table 10: Interphase growth per nanometer lithium for the different “LiPO(N)” samples.

	Formation of Li_3PO_4	Formation of Li_3P , Li_3N , Li_2O
LiPO	0.41 nm	0.79 nm
LiPON-low	0.51 nm	0.86 nm
LiPON-high	0.64 nm	0.81 nm

Figure 32 shows a comparison of the theoretical thickness (unlimited growth) of the SEI of the three different samples and the measured values. Without kinetic limitations (i.e. a mixed conducting interphase is formed) the SEI grows linearly with the amount of deposited lithium either due to the formation of Li_3PO_4 (dark blue line) or due to the formation of the binary compounds (light blue line). At the beginning of the experiment, the real thickness is close to the value that is expected for a complete reaction into the binary compounds and increases linearly. For “LiPO” the growth decelerates after the deposition of roughly 1 nm of lithium. The growth rate slows down even earlier for LiPON-low. The SEI growth of LiPON-high follows a linear trend for almost 4 nm of lithium deposition. Whereas the results for “LiPO” and LiPON-low are in good agreement with the respective theoretical values, the SEI growth rate of LiPON-high is slightly higher than predicted.

However, after depositing around 5 – 6 nm of lithium, the SEI reaches a constant thickness for all three samples. In the case of “LiPO” and LiPON-low, a 2 – 2.5 nm thick SEI has formed, in the case of LiPON-high, the SEI is more than 3 nm thick.

Deviations of the measured SEI thickness from the theoretical one at low d_{Li} are most likely due to some of the assumptions that were made to calculate the theoretical thickness. According to equations 25, 27 and 28, the films should first form Li_3PO_4 before decomposing into the binary compounds and the growth rate should be smaller than observed. However, the theoretical estimation assumes a theoretical density of 100 % whereas the uncontrolled

decomposition will most likely lead to a less dense SEI layer. This assumption will then lead to a slight underestimation of the SEI thickness.

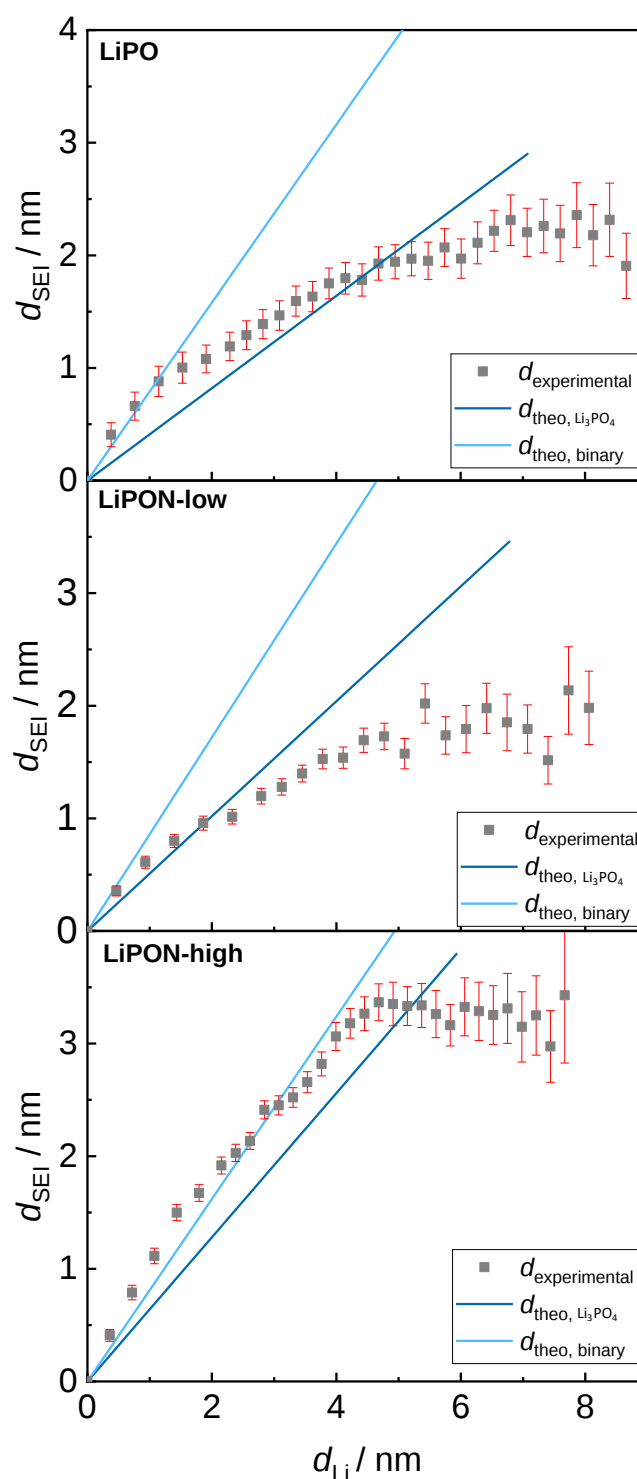


Figure 32: Comparison of the theoretical and practical interphase growth in dependence of the deposited lithium thickness for the different LiPO(N) samples. Solid dark blue line: Theoretical thickness of an SEI consisting of only Li_3PO_4 (and Li_3N). Light blue line: Theoretical thickness of an SEI consisting of Li_3N , Li_3P and Li_2O . Error bars: Errors determined from XPS measurements.

The shape of the plots in **Figure 32** suggests a limitation of the growth rate. For a continuous SEI growth according to equations 25 – 28, the presence of lithium metal at the interface is necessary. Only if both lithium ions and electrons are present, a reaction can occur. At first lithium is in direct contact with lithium metal and a thin reaction layer can form. As soon as this layer is formed, the reaction can only proceed if lithium metal can cross the SEI and get in contact with the electrolyte. The reaction can therefore only proceed if both lithium ions and electrons cross the SEI. As the growth rate declines, one can assume that the transport of the charge carriers is hampered by the SEI and the different onset of the growth limitation in the three different samples suggests that the stoichiometry of the electrolyte and the SEI influence the transport properties of the SEI.

If it is assumed that according to Wenzel et al. [78] the molar flux of lithium as neutral compound j_{Li} depends on (in case of diffusion control) [166]

$$j_{\text{Li}} = \frac{\sigma_{\text{e}^-} \cdot \sigma_{\text{Li}^+}}{F^2 (\sigma_{\text{e}^-} + \sigma_{\text{Li}^+})} \cdot \nabla \mu_{\text{Li}} \quad (42)$$

with both electronic as well as ionic conductivity σ_{e^-} and σ_{Li^+} of the interphase components, the Faraday constant F and the gradient of the chemical potential of lithium $\nabla \mu_{\text{Li}}$ across the SEI with the thickness d_{SEI} , this flux is limited by the conductivity of the minority charge carriers; in the case of a passivating SEI the electrons. Although the ionic conductivity of the major SEI components differs by several orders of magnitude, j_{Li} will not lead to a significant SEI growth rate as long as $\sigma_{\text{e}^-} \ll \sigma_{\text{Li}^+}$ for the average SEI compositions of the LiPO(N) samples.

The binary compounds formed during the reaction of the electrolyte and Li (Li_2O , Li_3N) are known as poor electronic conductors (for Li_3P no reliable data can be found). Electronic and ionic conductivities of the interphase components are given in **Table 11**. If only lithium ions are mobile in the SEI, the lack of electrons leads to a ceasing of the SEI formation. The thicker the SEI gets, the more hampered the transport process will be. That behavior is typically described using a parabolic growth mechanism [166].

Table 11: Conductivities of the main SEI components.

Material	$\sigma_{\text{ion}} / \text{S cm}^{-1}$	Ref	$\sigma_{\text{el}} / \text{S cm}^{-1}$	Ref
Li_3PO_4	$6 \cdot 10^{-8}$	[141]	$10^{-15} - 10^{-14}$	[136], [167]
Li_2O	$1.5 \cdot 10^{-9}$	[168]	10^{-13}	
Li_3P	10^{-4}	[53]	–	
Li_3N	$10^{-4} - 10^{-3}$	[74], [140], [141], [152],	$10^{-12} - 10^{-4}^\dagger$	[83], [150], [151], [169]
LiP	Insulator	[53]	–	

[†]depending on the hydrogen content in Li_3N .

Reliable conductivity values are scarcely reported in literature, especially for the electronic partial conductivities in lithium electrolytes. However, one can relate the interphase growth to the transport properties of the SEI components. Two different cases need to be distinguished:

i) Li_2O is the major component of the SEI (for “LiPO”). The reduced conductivity $\frac{\sigma_{\text{e}^-} \cdot \sigma_{\text{Li}^+}}{(\sigma_{\text{e}^-} + \sigma_{\text{Li}^+})}$ is determined by its conductivity and for this system the ionic conductivity lies at around $1.5 \cdot 10^{-9} \text{ S/cm}$. As can be seen in **Figure 32**, especially the oxygen content of the films plays an important role in the formation of the interface and has a big influence on the thickness of the SEI. The sample LiPON-low has a very high initial oxygen content and its SEI an initial Li_2O fraction of 37 vol%, calculated from the signals obtained after 540 s – 1000 s of Li deposition compared to 32.4 vol% for “LiPO” and 18.3 vol% for LiPON-high. The high Li_2O content leads to a rapid kinetic limitation of the SEI growth and to deviations from the theoretical SEI thickness already after the second lithium deposition step. For the other samples, the limitation sets in after longer lithium deposition times because the initial Li_2O formation is weaker than for LiPON-low.

ii) Li_3N and Li_3P form a percolating network and determine the transport properties of the SEI (LiPON-high). Here the ionic conductivity is in the range between $(10^{-4} - 10^{-3}) \text{ S/cm}$. The electronic conductivity depends on the amount of hydrogen present in the system and can vary between 10^{-12} and 10^{-4} S/cm . In this work, reliable assumptions on the hydrogen content of Li_3N cannot be made but if it is assumed that incorporation of hydrogen into

„LiPON“ during the thin-film preparation occurs, and the hydrogen induces an electronic conductivity. The higher amount of Li_3N and Li_3P in the sample LiPON-high explains the thicker interphase. The higher partial electronic conductivity of Li_3N leads to a stronger interphase growth compared to “LiPO” or the sample with less nitrogen.

Taking the stoichiometry of the samples from **Table 4**, it can be found that after a full conversion of the electrolyte into the binary lithium compounds, the samples “LiPO” and LiPON-low contain 44 vol% and 52 vol% of highly conductive Li_3N and Li_3P , respectively. The volume fraction of Li_3N and Li_3P in LiPON-high is around 67 vol%. According to Kirkpatrick, the volume fraction that is necessary to form a percolating 3D network, is around 30 % [170], but this value can be significantly higher depending on the crystal structure of the material and the mechanism of the charge transport. However, the amount of highly conductive species in the SEI of LiPON-high is much higher than for the other samples. Therefore, it can be assumed that enough volume is occupied to provide a better conductivity and – in combination with a significant amount of hydrogen in Li_3N – a MCI is formed that leads to an increased decomposition of the SE. It is interesting to note that even in the case of an uncompleted reaction and the formation of Li_3PO_4 , the SEI of LiPON-high would consist of 64 vol% of highly conductive Li_3N and Li_3P and the SEI of nitrogen-rich „LiPON“ should always exhibit a better ionic conductivity than the SEI of nitrogen-poor „LiPON“ or lithium phosphate.

In summary the finding suggests that by influencing the properties of the SEI in „LiPON“, one is caught between *Scylla* and *Charybdis*: An SEI which offers good transport properties for the lithium ions results in a stronger self-decomposition because also the electronic conductivity is higher, whereas an SEI that has a low ionic conductivity is bad for the transfer of lithium ions but is also more stable because the electronic conductivity is much lower. However, even a thick SEI might not be a disadvantage because a Li_3N -rich and Li_3P -rich SEI has an ionic conductivity that is much better than that of Li_2O .

This conclusion contradicts all the efforts reported in literature to increase the ionic conductivity of the SEI in order to reduce the charge transfer resistance as long as hydrogen is present. In the case of the examined “LiPO(N)” films, clarifying the origin of the hydrogen is difficult. The characterization was performed in an analysis chamber with a base pressure of $< 10^{-10}$ mbar. The deposition of the films was carried out in a sputtering chamber with a

base pressure of $< 10^{-7}$ mbar. The chamber is always kept under vacuum, except when the target needs to be replaced. There is also a transfer system consisting of three different chambers which should further reduce the impact of humidity from outside and the samples are directly transferred into a glovebox. Therefore, it can be assumed that the hydrogen content in the films originating from humidity is very low. However, there might be a significant amount of hydrogen at the surface of the thin-films, originating from the glovebox atmosphere. Although the water content in the glovebox was < 0.1 ppm, it might still be sufficient to provide enough hydrogen that can be incorporated in the formed Li_3N during the *in situ* XPS experiment and induces the partial electronic conductivity.

Nevertheless, if lithium nitride is formed without a significant amount of hydrogen incorporation, the SEI might still profit from the high ionic conductivity but an electronic partial conductivity would not occur.

4.1.4 Electrochemical properties of the „LiPON“ SEI

From the latest findings of SEI formation on various different electrolytes, the question arises, why there has been little evidence of the SEI formation in the cycling data of batteries. Simple mathematics show that finding electrochemical evidence of the interphase formation is rather challenging as its properties make it difficult to distinguish between the interphase and the electrolyte. In most cases the electrolyte has a thickness of more than $1\text{ }\mu\text{m}$, whereas the SEI is suggested to have a thickness of roughly 10 nm and, according to the calculations in this work, is even thinner than that. The interfacial contribution to impedance spectra is rather small and highly depending on the properties of the interphase itself as will be shown below.

The peak frequency ω_p of a RC semicircle in the Nyquist plot is the reciprocal value of the time constant τ and depends on the ohmic resistance R and the capacitance C of the sample.

$$\omega_p = \frac{1}{RC} = \frac{1}{\tau} \quad (43)$$

If one assumes geometric relations for both R and C ($R = \frac{1}{\sigma} \cdot \frac{l}{A}$ and equation 22 for C), the peak frequency is independent from the sample geometry and only depends on the conductivity and the permittivity of the film. There are no precise values of the permittivity of most battery materials given in literature but if ϵ_r is assumed to be in the range of 10 – 100 for most battery materials, the peak frequency for the interface between lithium and „LiPON“ can be estimated.

If Li_3PO_4 reacts with lithium, the major component of the SEI will be Li_2O with around 62 % of the SEI volume. If Li_2O is the major contributor to the SEI conductivity, the conductivity of the SEI layer will be in the range of $10^{-8} - 10^{-10}$ S/cm resulting in a peak frequency of

$$\omega_p = \frac{10^{-9} \text{ S/cm}}{\epsilon_0} \cdot \frac{1}{\epsilon_r} = \frac{113 \text{ Hz}}{\epsilon_r} \quad (44)$$

An interphase with Li_2O will be influencing the impedance of the system in the range of a few dozen Hz, depending on the value of ϵ_r . If the SEI is thick enough, it should be visible as a contribution in the impedance spectrum; if not, it will most likely be hidden in the electrolyte contribution.

However, if the nitrogen content in the „LiPON“ film is high enough and the combined volume fractions of Li_3N and Li_3P are high enough to form a percolating network, the conductivity of the interface will be in the range of 10^{-3} S/cm resulting in a peak frequency of $10^7 - 10^9$ Hz which cannot be seen with most impedance devices. If the thickness of the SEI is assumed to be in the range of 1 nm – 3 nm as calculated from the XPS measurements, for the present sample geometry, the resulting resistance would be 3.3 k Ω – 10 k Ω for Li_2O and 5 m Ω – 15 m Ω for $\text{Li}_3\text{N}/\text{Li}_3\text{P}$. That means the interphase will only be visible if very thin films are prepared as its contribution to the overall resistance will only be around 1 %. Very thin films, which fully cover the substrate, are very hard to prepare.

If the interphase contains a lot of nitrogen, the fraction of Li_3N formed in contact with lithium will be much higher. The interphase will have a higher ionic conductivity than the electrolyte and its contribution will not be visible in the common frequency ranges. Even if

the conductivity is lower, the smaller thickness may result in a transport process, which cannot be seen in the spectrum as it might overlap with the ionic transport across the electrolyte. These values explain why „LiPON“ has been considered to be stable in contact with lithium metal. The reaction layer was usually so thin that the most common detection methods were not able to detect the interphase.

However, there are a few evidences of the „LiPON“ SEI reported in literature. Larfaillou et al. examined thin-film batteries containing „LiPON“ solid electrolyte [171]. They compared commercial batteries consisting of LiCoO_2 , „LiPON“ and a lithium metal anode with batteries of the same scheme prepared in the lab. Their impedance analysis showed that the interface between lithium and „LiPON“ led to a contribution to the impedance spectrum, which was much bigger when aged cells, which had been stored in the fully charged state at $60\text{ }^\circ\text{C}$ for 60 h were used. They found that this contribution was formed during a first charging of the battery suggesting that the transport of lithium across the electrolyte led to a modification of the interface. They also suggested that this modification was partly reversible as lithium deposition during a subsequent battery cycle led to a decrease of this contribution in the impedance spectrum. However, they did not take into account that these batteries were assembled at an indefinite point before the testing. In accordance with Schwöbel et al. the interface between „LiPON“ and lithium was already passivated. Probably the cycling of the battery led to breaking of the SEI or lithium plating underneath the SEI and ongoing SEI growth.

Schichtel et al. prepared all-solid-state thin-film batteries based on lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and „LiPON“ as an electrolyte. They performed various experiments to determine the different elements present in the impedance spectra of this system. One of their findings was a contribution in the high-frequency range caused by the transport of the ions across an interface between the lithium electrode and the „LiPON“ solid electrolyte. They performed impedance measurements at different states of charge and after different “cycling properties” and found out that this contribution at high frequencies was independent from the state of charge and the applied C-rate, suggesting that the interphase is stable [172].

An ideal SEI that only consists of Li_3P and Li_3N should not be visible in the impedance spectrum as its contribution is too small to be resolved. However, the effectiveness of the

interface passivation may be visible by the absence of a contribution of the reaction layer between the electrolyte and lithium to the impedance spectrum. If P_3N_5 can be successfully applied as interlayer, its effect may have to be derived from cycling data rather than impedance measurements.

4.2 Phosphorous nitride P₃N₅ as a sacrificial interlayer

From the investigation of „LiPON“ solid electrolyte, the principle guidelines for the creation of artificial interlayers were derived and the creation of P₃N₅ layers with the same properties is the next step. There is no report on phosphorous nitride thin-films in literature up to our knowledge. Hence, a comprehensive characterization of these films is necessary. This chapter comprises the determination of the deposition rates during ion beam sputtering and a detailed XPS analysis. First the stoichiometry of the thin-films was determined before performing the *in situ* XPS experiment and electrochemical measurements to monitor the influence of the P₃N₅ thin-film on the battery properties.

4.2.1 Deposition rates

The deposition rates are determined from surface profiling of partially masked substrates. Films were deposited for 1 h, 2 h and 4 h, and the thickness of each sample is determined from five different measurements along the edge of the thin-film. The average value of the determined thickness after each deposition is used for the determination of the sputtering rates and is shown in **Figure 33**. The error bars depict the largest deviation of the measured film thickness from the average value.

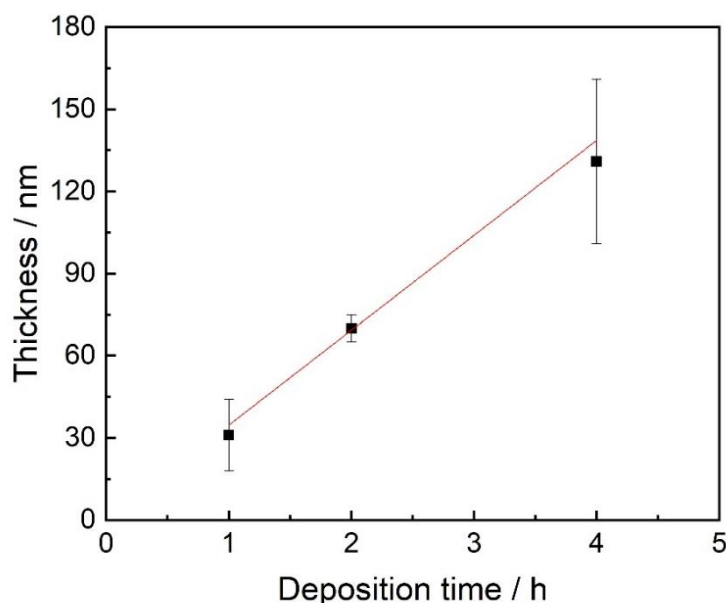


Figure 33: Thickness of the P₃N₅ films in dependence of the deposition time.

These values result in a deposition rate of 35.6 nm/h. The error of the thickness measurement can reach values up to 30 %. At low thicknesses, the deviation is due to the fact that the cantilever cannot be protected from atmospheric vibrations. Therefore, small oscillations caused by noise in the lab lead to a relatively high error. At larger thicknesses, the error is due to the inhomogeneous deposition of material on the sample surface. The used ion beam has a diameter of only 10 mm. It is widened to ~ 30 mm until it hits the target, so the deposition rate is strongly depending on the number of ions that hit a certain surface area of the target. Therefore, even in a deposition chamber with a perfectly aligned ion beam the area of homogeneous deposition will not be bigger than the diameter of the ion beam. In the case of the small ion beam, the deposition rate already varies over the sample area of 1 cm. In addition, also thermal impact can influence the film growth. The substrate is heating up during deposition when it is hit by the deposited material. The longer the deposition, the higher the temperature. The variation of the film thickness can possibly cause potential deviations across the sample but it can be assumed that for the deposition times used in this work, the deviation may be in the range of only 1 – 2 nm or less. However, it needs to be pointed out that it is hard to validate the influence of thickness variations on cycling properties in such a small scale, especially in terms of buried interfaces.

4.2.2 XPS Analysis

Chemical analysis

The following chapter comprises the evaluation and discussion of results obtained from thin-film examinations. A detailed discussion of the XPS examinations on the P₃N₅ powder, which are referenced below, can be found in **Appendix F**.

The phosphorous signal of the P₃N₅ films consists of a single peak at 134.0 eV. This signal is attributed to the one existing phosphorous species in P₃N₅, a P atom, which is tetrahedrally coordinated by four nitrogen atoms. Due to the peak splitting into P 2p ³/₂ and P 2p ¹/₂, the signal consists of the two brown and beige components in Fehler! Verweisquelle konnte nicht gefunden werden.. There is no evidence that there is an oxidized P-O species at higher binding energies like the one observed in the powder sample (**Figure A 11**).

The N 1s signal shows three different contributions. Two of them can be attributed to the two different nitrogen species in P₃N₅. Phosphorous nitride forms an alternating network of corner sharing PN₄ tetrahedra [153]. In this structure, each P atom is coordinated by three nitrogen atoms. Nitrogen can either be coordinated by two P atoms (P-N-P; N_{double} at 399.0 eV) or by three different P atoms (P-N<^P_P; N_{triple} at 397.5 eV). In the ideal structure, the ratio of the nitrogen species N_{double} : N_{triple} is 60 : 40. The ratio of these components in the P₃N₅ powder as well as in the thin-films is in good agreement with literature. The third component at 401.0 eV can be attributed to NO_x at the surface of the sample. However, in the case of the thin-film, the amount of NO_x seems to be much higher than for the powder sample.

The stoichiometry of the powder as well as the deposited thin-films was determined via XPS. A comparison of the elemental composition of the phosphorous nitride powder and thin-films is given in **Table 12**.

Table 12: Elemental composition of the P₃N₅ powder and thin-films determined via XPS.

	Powder	Film
P 2p / at%	30.3	22.8
N 1s / at%	52.1	31.5
O 1s / at%	10.1	30.1
x (P ₃ N _x)	5	4.2

As can be seen, with 30.3 at% phosphorous and 52.1 at% nitrogen, the powder has a P : N ratio of almost 3 : 5. However, the powder also contains a significant amount of oxygen (10.1 %). The elemental ratio is hard to judge by XPS because the information depth is only a few nanometers. The overall oxygen content of the powder and thin-films may be much lower but on the surface it is around 10 % for the powder and 30 % for the thin-film. As the overall oxygen content of the film surface is higher than the oxygen content of the powder surface, it can be assumed that the increased oxygen content originates from the deposition process. A certain fraction of the nitrogen at the surface must have reacted with oxygen. Not only does humidity during the deposition lead to an increased incorporation of O into the thin-film, it can also be assumed that the target incorporated oxygen while being stored in the deposition chamber. Oxygen is most likely incorporated as carbonate because also the carbon content (7.5 at% in the powder) did increase to 15.6 at%. Unfortunately, it was not possible to keep the target free from oxygen and carbon. The oxygen in the thin-film must be considered during the discussion of the results.

In situ XPS

During lithium deposition, large changes of the elemental signals can be observed. Fehler! Verweisquelle konnte nicht gefunden werden. shows the change of the P 2p and N 1s signal. Before lithium deposition, the phosphorous signal consisted of only one species. After lithium deposition on the P₃N₅ film, three different contributions can be observed. Directly after the first lithium deposition step the fraction of the P₃N₅ phosphorous species decreases

drastically from 100 % to only 12.5 %. Two other contributions are formed simultaneously. These signals can be attributed to the stepwise reduction of P₃N₅ via Li_xP_yN_z to Li₃P. Li_xP_yN_z describes the sum of all components that can be attributed to various partly lithiated phosphorous nitride species, e.g. LiPN₂, Li₇PN₄, Li₁₈P₆N₁₆, Li₁₂P₃N₉, and Li₁₀P₄N₁₀ (cf. **Appendix G**). From the collected data it is impossible to predict a precise stoichiometry of these compounds. But as the P 2p signal continuously shifts toward lower binding energies, it must be attributed to components whose degree of lithiation lies between P₃N₅ and Li₃P.

It is interesting to see that the P signal of P₃N₅ disappears completely after the second lithium deposition step and only the lithium phosphide signals are left. The signal that is attributed to Li_xP_yN_z contributes to 93 % of the phosphorous signal, whereas Li₃P is only around 7 % of the signal. This observation may be due to the fact that the deposited thin-films are very thin and already a small amount of lithium is enough to completely reduce the film in a range that is at least as thick as the information depth of the analysis method. Between the third and the fourth measurement there is no change of the relative intensities of these two species visible but the absolute intensities decreases. The amount of Li₃P reaches only around 7 %, indicating that at least under the conditions of the measurement, the conversion to Li₃P is not completed and that no further reaction of Li_xP_yN_z to Li₃P occurs after 600 s of lithium deposition time. The change of the absolute intensities indicates that a layer of Li is deposited on top of the thin-film that dampens the intensities of the thin-film signals. In contrast to the powder sample, a limitation of the reaction can be seen. The thin-film has a smaller surface area than the powder and thus, a smaller amount of lithium is necessary to convert P₃N₅. After the conversion lithium diffusion into the film is hindered and the reaction ceases.

From the previous discussion on „LiPON“ it is known that the thermodynamic driving force to form the binary compounds is very high but in „LiPON“ also only a partial reduction of the phosphorus signal could be observed.

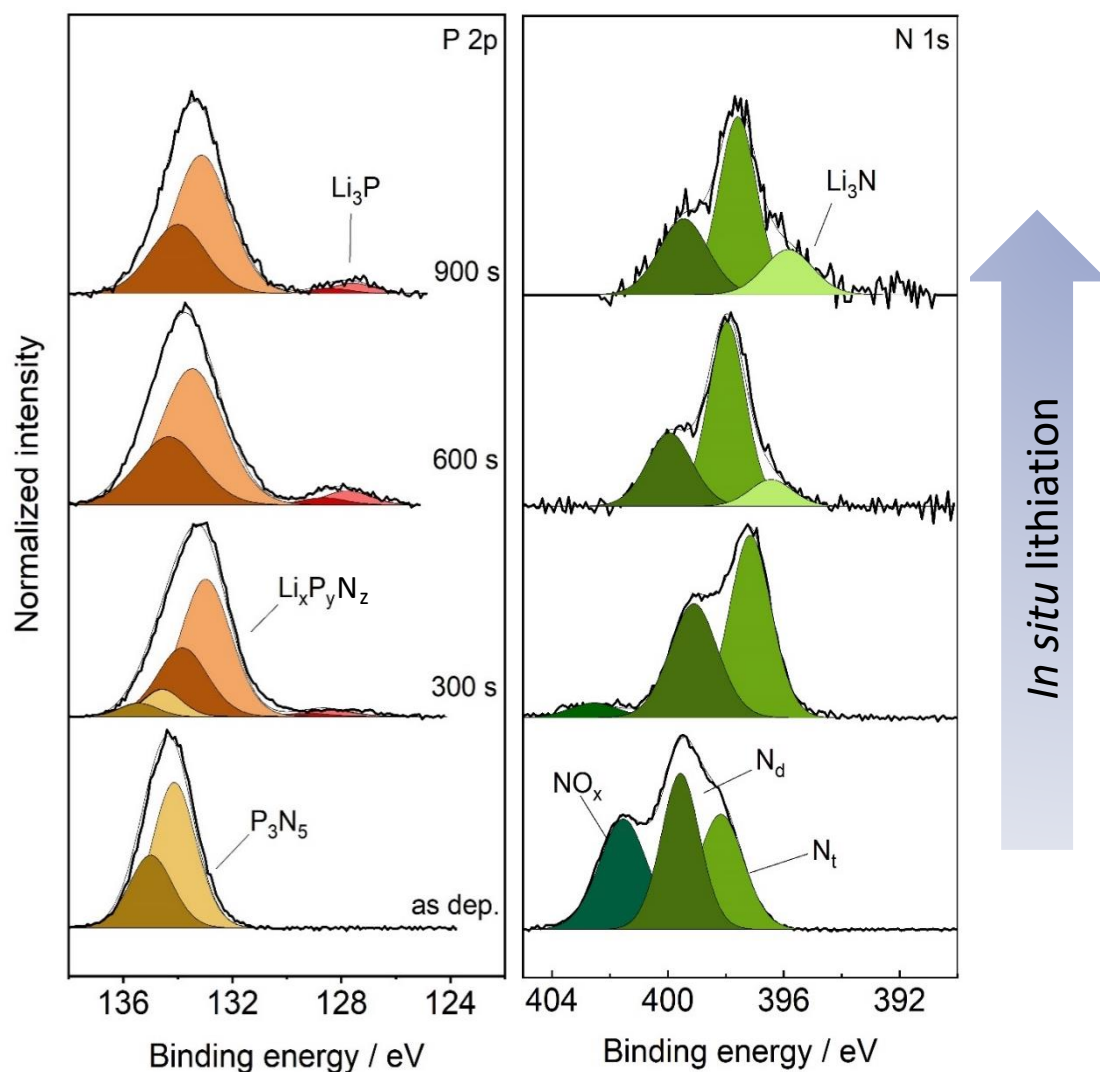


Figure 34: Evolution of the P 2p signal and N 1s signal of P₃N₅ during *in situ* lithiation. A stepwise reduction of P₃N₅ via Li_xP_yN_z to Li₃P can be observed as well as the disappearance of the N_t signal and the formation of Li₃N.

A complete reaction of P₃N₅ and the decomposition into the binary lithium compounds can be described as follows:



Taking the formation energies from **Table 13**, this reaction has a reaction enthalpy of -1371.2 kJ/mol, indicating that the decomposition of P₃N₅ has a strong driving force. From a thermodynamic point of view, the interphase should only consist of Li₃P and Li₃N.

Table 13: Standard formation enthalpy of P₃N₅ and the binary lithium compounds.

Material	$\Delta_f H_m^0$ [kJ/mol]
P ₃ N ₅	-405.2 [173]
LiP	-50.7 [173]
Li ₃ P	-334.8 [160]
Li ₃ N	-154.4 [160]
Li ₂ O	-588.6 [160]

The simultaneous presence of Li_xP_yN_z and Li₃P cannot be deduced from thermodynamic calculations, which predict the formation of only Li₃P. Again, as in the case of „LiPON“, the information depth of the XPS method is higher than the thickness of the SEI. Therefore, it is likely that the spectra show a Li₃P layer and the lithium-deficient layer below. For the reaction to proceed, more lithium needs to be transported across the interface into the electrolyte. If P₃N₅ successfully works as sacrificial interlayer, this transport should be limited per definition. P₃N₅ under the topmost layer may react with lithium and form a lithium polyphosphide layer but the lithium for a subsequent reaction is missing. After 600 s of lithium deposition, the intensity ratio between Li₃P and Li_xP_yN_z does not change anymore, indicating that the conversion is stopped.

The fact that various different Li_xP_yN_z species are formed, can explain the ceasing of the reaction. If it is assumed that the SEI has a layered structure and a chemical potential difference of lithium exists across the Li|P₃N₅ interface, Li₃P does only exist directly in contact with lithium metal. Going deeper into the P₃N₅ film, Li_xP_yN_z can only react to Li₃P if lithium ions and simultaneously electrons pass the already existing Li₃P interphase. According to literature, these components are ion-conducting but their conductivity is several orders of magnitude lower than that of the most commonly examined solid electrolytes [174], [175]. When partially lithiated phosphorous nitride is present and also exhibits a negligible electronic conductivity, electrons are prevented from migrating through

the SEI and the reaction is stopped. As in the case of „LiPON“, this process is diffusion-controlled. That may be the reason why the relative Li_xP_yN_z/Li₃P ratio does not change after 600 s of lithium deposition, but only the absolute intensities decrease. In addition, the reaction layer is buried under a mixture of lithium and Li₂O, further slowing down the decomposition. This behavior is in accordance with the „LiPON“ study.

Secondly the comparison of the thin-film experiment with the powder results shows that the reaction of the P₃N₅ powder is not finished after more than 9000 s of lithium deposition. The powder has a higher surface area than the thin-film and therefore needs more lithium to react. If there was enough lithium, P₃N₅ might be fully converted into Li₃N and Li₃P.

The N 1s signal also changes during the *in situ* experiment (**Figure 35**). Similar to the P 2p signal, the NO_x component decreases directly after the beginning of the lithium deposition; it decreases from more than 30 % to 5 % and vanishes completely after the second lithium deposition step. The second component, N_{double} varies between 30 % and 35 % over time but does not show a clear trend, probably due to the formation of partially lithiated Li_xP_yN_z whose signal overlaps with N_{double}. The N_{triple} signal starts to increase. It is assumed that the oxygen of the NO_x reacts with lithium and leaves unsaturated nitrogen which is on the same position as the N_{triple} signal. The N_{triple} component does not decrease as much as N_{double}. As no Li₃N signal can be seen after the first lithium deposition step, this signal may also include Li_xN_y. After another lithium deposition step, when more lithium is present, this material can further incorporate lithium and form Li₃N, which can be seen after the second lithium deposition step. After 600 s of lithium deposition only minor changes of the relative intensities can be seen but the absolute intensities decrease due to the formation of a Li/Li₂O

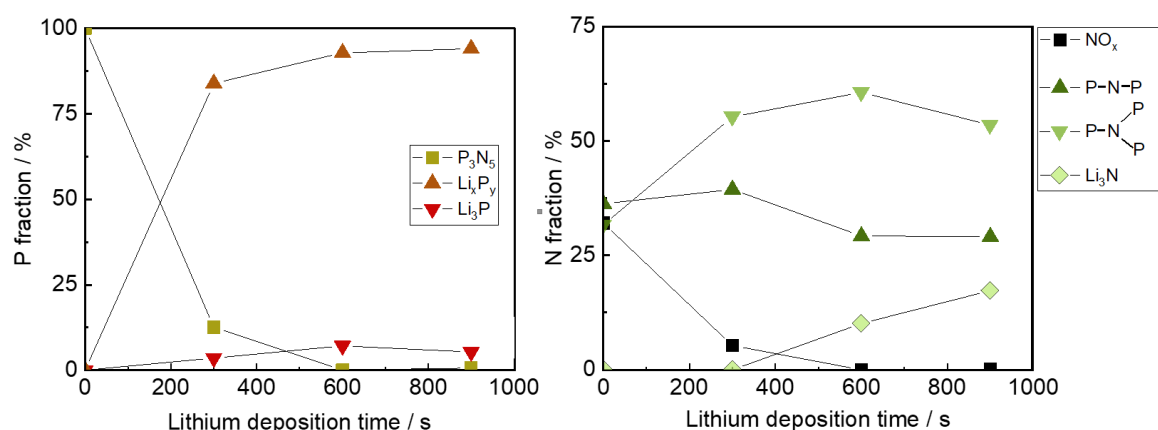


Figure 35: Evolution of the phosphorous and nitrogen fractions during *in situ* lithiation.

layer on top. Li₃N is also formed but the formation of Li₃N is not seen before the second lithium deposition step. However, the fraction of Li₃N is steadily increasing.

As in the powder, the oxygen signal of the thin-film consists of two species located at almost the same positions (cf. **Figure A 13**). In comparison to the powder, the O_{high} signal of the film is shifted to a higher binding energy of 534.0 eV, the O_{low} signal is still at 531.5 eV. During lithium deposition, the O_{high} signal decreases and vanishes completely after 900 s. Also, the O_{low} signal decreases. The signal attributed to Li₂O increases after each Li deposition step. Li₂O is formed, first from the O_{high}-oxygen and then from the O_{low}-oxygen. The behavior of O_{high} is again linked to the behavior of the NO_x signal. Both components are only found at the surface and again the lower surface area compared to the powder explains the rapid diminishing of the signal. With an ionic conductivity of $1.5 \cdot 10^{-9}$ S/cm, Li₂O is not beneficial for the transport process across the interphase. If the film contains 30.1 at% as mentioned in **Table 12** the resulting Li₂O corresponds to 21.5 vol%, but this fraction should not be enough to inhibit the charge transport. For a proof of concept of the applicability of sacrificial interlayers, the Li₂O content of the thin-films may be neglected. It must be pointed out that Li₂O might reduce the thickness of the SEI because its low conductivity might additionally inhibit the lithium transport. From the XPS results on P₃N₅ two different conclusions can be drawn:

- i) **The formed interface is thinner than the information depth of the X-rays (Al K α , $E = 1486.6$ eV).**

The presence of Li_xP_yN_z signals and Li₃P signals does not necessarily mean that both species are homogeneously distributed across the SEI. Li_xP_yN_z may be formed on top of the P₃N₅ layer and the topmost part of Li_xP_yN_z reacts further to Li₃P, indicating a layered kind of interphase similar to the Li|“LiPON” interphase.

It must again be pointed out that there may be a difference between the *in situ* experiment and a real battery. As the supplied amount of lithium in the experiment is limited, the SEI in a real battery may be thicker as the estimated values and it may also completely consist of Li₃P and Li₃N. However, determining the optimized film thickness is a key requirement due to the second finding:

ii) **The conversion is self-limiting.**

The formation of lithium metal hints toward the limitation of the reaction. Lithium metal will not be formed as long as it can react with P₃N₅. The observation of lithium metal indicates that not the entire deposited lithium reacted. The increase of the oxygen signal means that instead Li₂O is still formed. The decrease of the intensity of the P signal and N signal means that both species are buried and do not further react with lithium.

If the reaction was not self-limiting, the original signals of P₃N₅ would disappear completely. If the thickness of the reaction layer exceeded the information depth of the XPS, it would be impossible to judge whether the interlayer reached a constant thickness. In a subsequent experiment, the reacted layer would have to be removed by sputtering and the remaining signals would have to be measured. In the present case the original signals are still visible and the reaction layer is very thin. This means, that the reaction layer has a negligible electronic partial conductivity and that P₃N₅ shows the expected protective behavior.

4.2.3 Protective effect

Testing the protective effect was done by several different methods. First of all, to optically show the protective effect, an Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O₁₂ membrane (Ohara) was used because in contact with lithium metal the membrane turns black in contact with lithium metal due to the reduction of the Ti(IV) [48]. A mask was used to cover a round area of the membrane with a thin layer of phosphorous nitride. After the P₃N₅ deposition, the Ohara membrane is still white (**Figure 36 a**). No deposited layer is visible, not even a slight coloring due to interference of the light with the thin layer. The deposition took 30 min, so according to **Figure 33** the thickness of the P₃N₅ layer should be around 17 nm and no interference with visible light should occur.

Afterward, 100 nm lithium were thermally evaporated onto the entire membrane. **Figure 36 b** shows the membrane right after the deposition of lithium. The inner grey part is the area that is covered with phosphorous nitride. The outer part of the membrane is still the bare LATP surface. **Figure 36 c** shows the same membrane 24 hours after lithium deposition.

As can be seen, the color of the membrane changed completely. The inner P₃N₅-covered part turned white, the outer part turned black. The blackening is caused by the reduction of the metal ions in LATP to metallic titanium, germanium and aluminum. The reaction was only observed in the uncovered section of the membrane. The covered part turned white again, partly due to the formation of Li₃N and Li₃P and partly due to the reaction of lithium with residual impurities in the glovebox atmosphere leading to Li₂O and carbonate species.

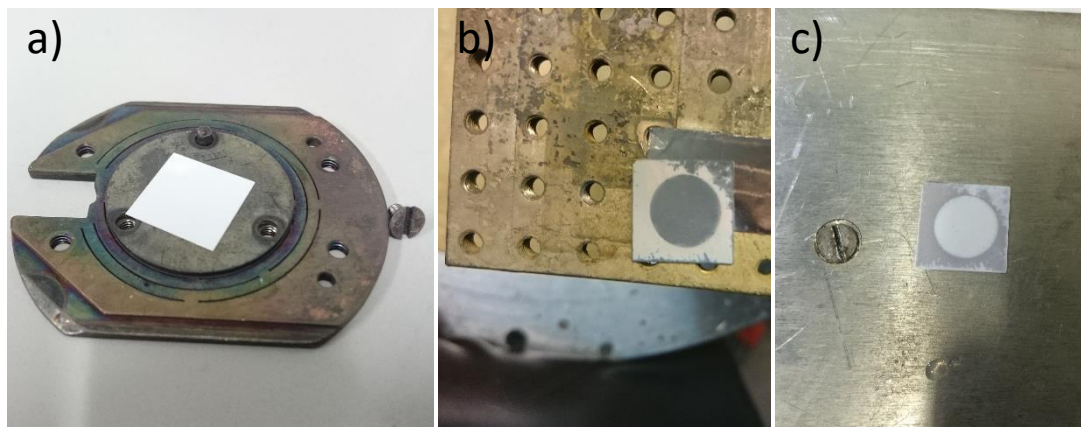


Figure 36: Test of the protective effect of P₃N₅ on an Ohara membrane.

- a) Membrane after P₃N₅ deposition.
- b) Partially protected membrane directly after lithium vapor deposition.
- c) Partially protected membrane 24 h after lithium vapor deposition.

It could indeed be shown that a very thin layer of phosphorous nitride is sufficient to prevent the electrolyte from decomposition. But only if the electrochemical performance of batteries with the protected electrolyte is superior than the performance of batteries without interlayer, the material may be applied in larger scale. The next step was to examine the electrochemical properties of the interlayer. For that, lithium plating/stripping experiments in symmetric transference cells were carried out as well as cycling of full cells.

4.2.4 Electrochemical behavior

The electrochemical behavior of the interlayer was tested building symmetric Li|LPS|Li cells with and without interlayer between the electrolyte and the alkaline metal, and performing long-term stability tests, by plating and stripping lithium at the electrode|electrolyte interface. Later on, the electrochemical behavior of the interlayer was tested in full-cells with NCM as a cathode material and a lithium metal anode.

Symmetric transference cells

As can be seen in **Figure 37**, it is possible to use bare, unprotected LPS to run a symmetric cell for more than 2000 hours at room temperature. Applying a current of 70 μA ($\cong 100 \mu\text{A cm}^{-2}$) results in an overpotential of initially 35 mV. Upon plating/stripping for 2 h in each direction, this value slightly increases to more than 50 mV. The short decrease of the potential after 120 hours is due to a disruption of the power supply. Afterward, the potential increases again. It is therefore assumed that parts of the overpotential are caused by polarization of the electrode|electrolyte interface. However, this polarization seems to be hindered by an interphase formation/passivation during cycling because a second break of the measurement of around 4 hours duration did not cause a drop of the potential after around 1500 hours. Although the cell can be cycled for around 500 times, the shape of the curve is not very smooth, indicating that different processes led to changing resistances during lithium plating and stripping. A closer look at the potential during each plating/stripping step shows that at the beginning of the measurement the potential remains constant during each cycling step. After 2000 hours it can be seen that the potential slightly increases, which can be explained by inhomogeneous lithium plating and stripping. Although the cell could be run for 2000 hours, the shape of the $U(t)$ curve indicates that several failure mechanisms occurred. A sudden breakdown of the overpotential after 1250 h may be caused by microdendrites that are formed and after a few steps are dissolved again.

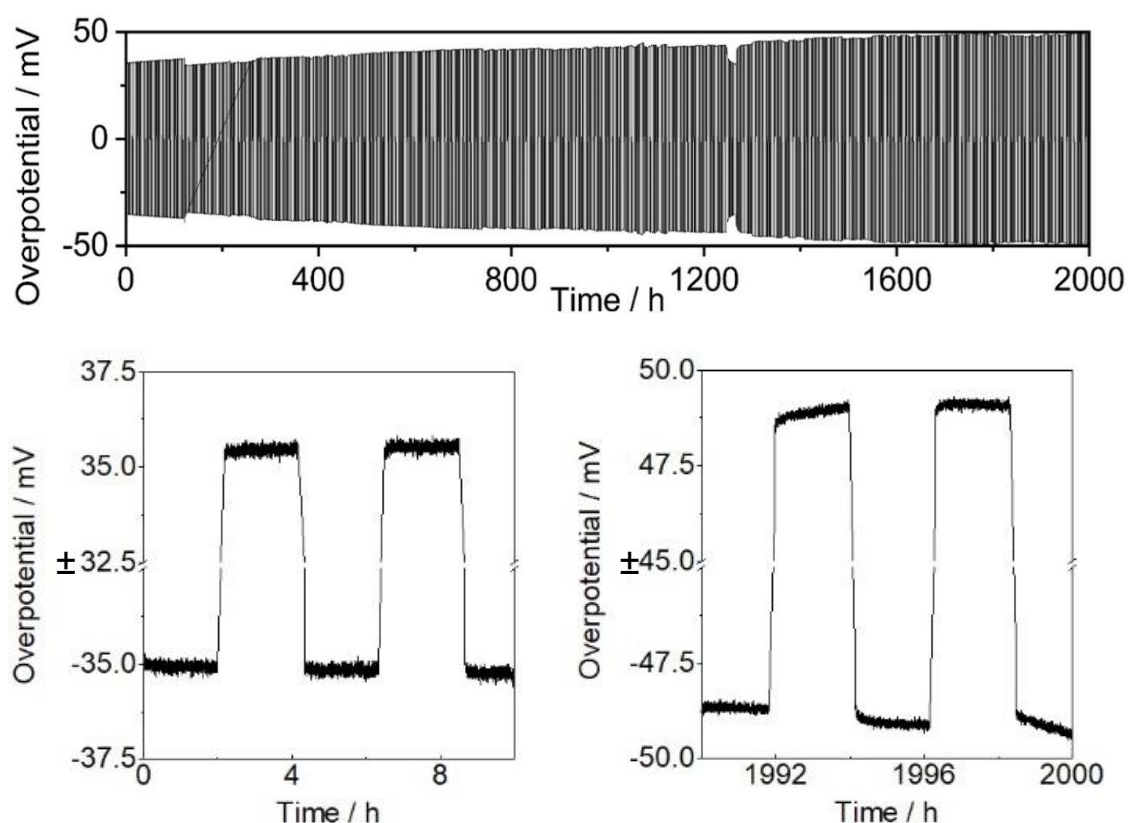


Figure 37: Lithium plating and stripping of a Li|Li₃PS₄|Li cell without interlayer at room temperature. For the experiment 100 $\mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction. During each step, an 870 nm thick layer of lithium was plated and removed. The experiment could be performed for more than 2000 h. Close-ups of the beginning and the end of the measurement show that the overpotential increases over time and that the plating/stripping is less uniform after 2000 h. The edges of each step are not perfectly horizontal due to the OCV step in between.

In contrast, **Figure 38** shows the plating and stripping data of a symmetric Li|LPS|Li cell with P₃N₅ on both sides of the compressed electrolyte powder. To ensure to get a dense covering layer, 17 nm of P₃N₅ were deposited on either side of the electrolyte. It needs to be pointed out that a sacrificial layer according to the definition of this work may need to be thinner to protect the battery without inhibiting the transport properties but the surface of pressed LPS powder requires a thicker surface layer.

As can be seen, the cell with interlayer can be cycled with the same settings as the cell without interlayer for over 2000 hours. The potential increases over time, again indicating an increasing cell resistance but the absolute increase of the potential is around 17 mV; as much

as for the sample without interlayer. The shape of the curve also shows less fluctuations of the overpotential during each plating/stripping step suggesting that a more homogeneous lithium plating and stripping takes place. It is assumed that applying a homogeneous surface layer leads to a more homogenous potential distribution at the interface and cycling behavior because impurities of the LPS powder (e.g. reaction products with atmosphere and carbon impurities that are present up to a certain amount no matter how clean the glovebox atmosphere is), are circumvented and do not hinder the charge transfer anymore.

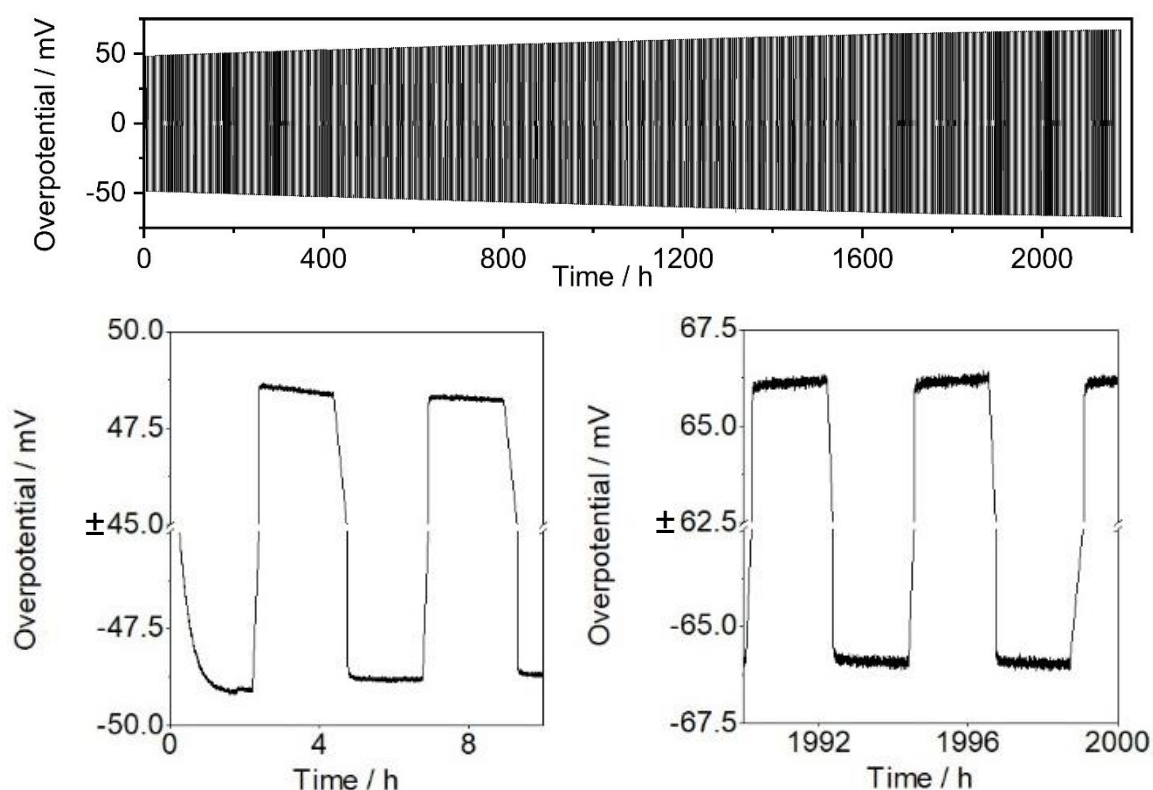


Figure 38: Lithium plating and stripping of a Li|P₃N₅|Li₃PS₄|P₃N₅|Li cell with a 17 nm thick interlayer at room temperature. For the experiment 100 $\mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction. During each step, an 870 nm thick layer of lithium was plated and removed. Thickness of the interlayer: 17 nm. The overpotential is higher than in a cell without interlayer and also increases over time. After 2000 h, plating/stripping is still homogeneous. The edges of each step are not perfectly horizontal due to the OCV step in between.

With an initial value of 50 mV, this cell has a higher overpotential than the cell without interlayer and it increases up to 66 mV after 2000 h. The additional overpotential results from the P₃N₅ layer between the electrolyte and the lithium electrode. A part of the P₃N₅ layer is converted into Li₃N and Li₃P, but as the reaction products limit the electron diffusion

through the interface, the conversion ceases, and the SEI growth is limited. A part of the P₃N₅ layer remains unreacted at the interface, inhibiting the charge transfer and increasing the cell resistance. Plating/stripping experiments were also performed at 60 °C (**Figure 39**). As can be seen, the initial potential of the sample without interlayer at 60 °C is only 10 mV. Due to the increased temperature, the cell resistance and overpotential are much lower than at room temperature. The potential remains almost constant for around 120 hours. Then it starts to increase to more than 25 mV, before the cell is short circuited after around 900 hours. This increase of the potential slows down between 250 and 800 hours leading to a parabolic change over time. When in accordance with the observations of the SEI growth on „LiPON“ the interphase shows a parabolic growth, the resistance should show the same behavior. It can therefore be suggested that the increased overpotential is caused by a decomposition of the electrolyte. Taking a closer look at the data, it can be seen that at the beginning the potential at which lithium plating and stripping happens, remains virtually constant during each 2 h step. In comparison it can be seen that after 800 hours, the potential slightly increases during each step.

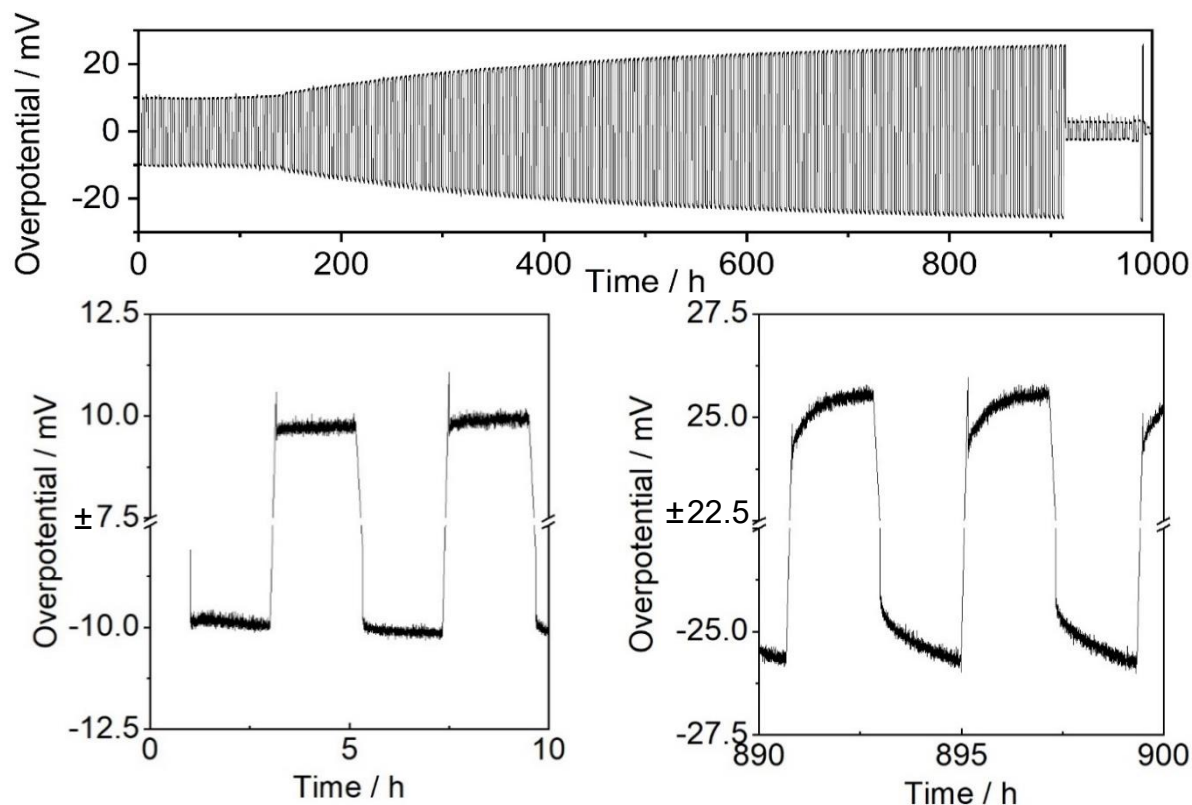


Figure 39: Lithium plating and stripping of a Li|Li₃PS₄|Li cell without interlayer at 60 °C. For the experiment 100 $\mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction. During each step, an 870 nm thick layer of lithium was plated and removed.

This behavior can be due to different phenomena. It can be caused by a contact loss between lithium and the electrolyte during lithium dissolution, resulting in a smaller interface area and a less homogeneous plating/stripping behavior. It may also be caused by the diffusion of lithium ions through a growing reaction layer.

In comparison, **Figure 40** shows data of the best running cell with an interlayer at 60 °C. The initial overpotential is at 10 mV but after a few plating/stripping steps increases to 14 mV, higher than for the sample without interlayer. The steep increase after a few hours was caused by a breakdown of the power supply overnight and it is unclear what happened. Aside from that, the observed homogeneous increase of the potential during plating/stripping with constant current is smaller than for the sample without interlayer. The increase of the potential slows down after around 200 hours but continues across the entire duration of the measurement.

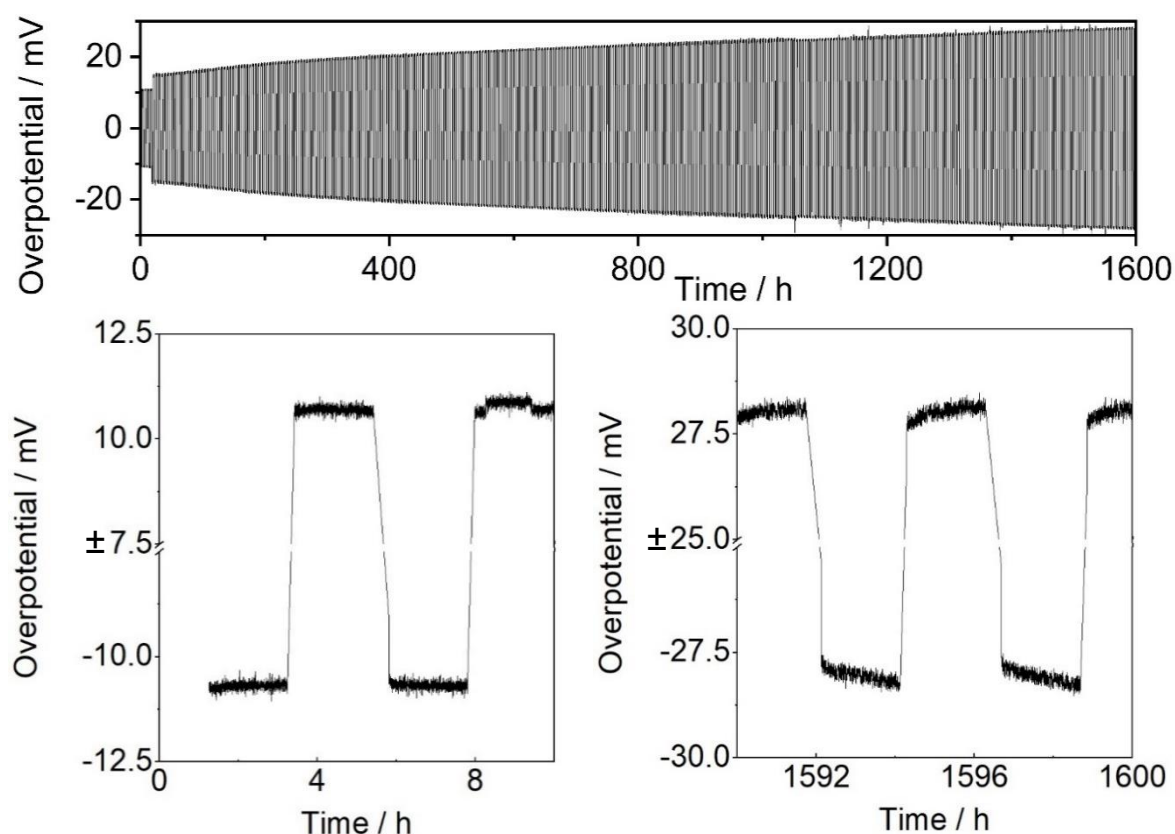


Figure 40: Lithium plating and stripping of a Li | P₃N₅ | Li₃PS₄ | P₃N₅ | Li cell with interlayer at 60 °C. For the experiment 100 $\mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction. During each step, an 870 nm thick layer of lithium was plated and removed. Thickness of the protective layer: 17 nm. The results are from the best running cell.

Again, a parabolic increase can be seen but it is almost the same as for the sample without interlayer. Although the resistance increases from cycle to cycle, the potential during each plating and stripping step remains almost constant, indicating that the process is more homogenous than at the unmodified interface.

To determine the influence of the film thickness of the interlayer on the cell performance, the deposition time of P₃N₅ was decreased to 15 min, reducing the film thickness to ~ 8 nm. **Figure 41** shows a comparison of the plating and stripping data of two samples with P₃N₅ layer (i.e. the sample from **Figure 40** and one with a thinner interlayer) with different film thicknesses at 60 °C and **Figure 42** a comparison between a sample without interlayer and the one with an 8 nm thick interlayer.

As can be seen, the overpotential is reduced by 5 mV when the film thickness is halved, indicating that also the cell resistance is decreased. Assuming that 17 nm of P₃N₅ are too thick to fully react, this observation is reasonable. Still, lithium plating and stripping increases the potential and therefore the cell resistance over time. In the beginning, this increase seems to be slower than in cells with a thicker interlayer, indicating a better protection of the cell or a better plating/stripping behavior. An interlayer of P₃N₅ with 8 nm thickness may still be thicker than the optimal calculated thickness of the natural passivating material „LiPON“ but it can be expected that the rough inhomogeneous surface of the pressed LPS powder leads to a less conformal deposition than on a smooth thin-film and requires a thicker interlayer.

The sample using 8 nm of P₃N₅ as interlayer has as high an initial overpotential as the sample without interlayer (**Figure 42**). Therefore, it can be assumed that the formation of the interphase was prior to the start of the first measurement and must have been finished during the temperature stabilization at 60 °C. Whereas the sample without interlayer does not show an increase of the overpotential and resistance during the first 150 h but increases afterward, the overpotential of the sample with P₃N₅ layer increases continuously. Compared to the sample without interlayer, this increase is not parabolic but linear and smaller than for the sample without interlayer. A parabolic increase is due to the interphase formation. The absence of a parabolic increase can be explained by two different effects:

- a) The electrolyte is protected from decomposition. When no decomposition is caused, the increase of the resistance can be attributed to regular mechanical degradation

mechanisms of the cell during plating/stripping, e.g. volume changes of the electrode, changes of the interface area, and the creation of cracks and pores and relaxation of the electrolyte thickness. In this case the interlayer effectively negates the thermodynamic driving force for the decomposition and thermodynamically stabilizes the lithium|electrolyte contact.

- b) The decomposition of the electrolyte is slowed down drastically. If the interlayer does not cover the entire electrolyte surface, a decomposition in contact with lithium metal may still take place but it is so slow that it is superimposed by the regular mechanical degradation.

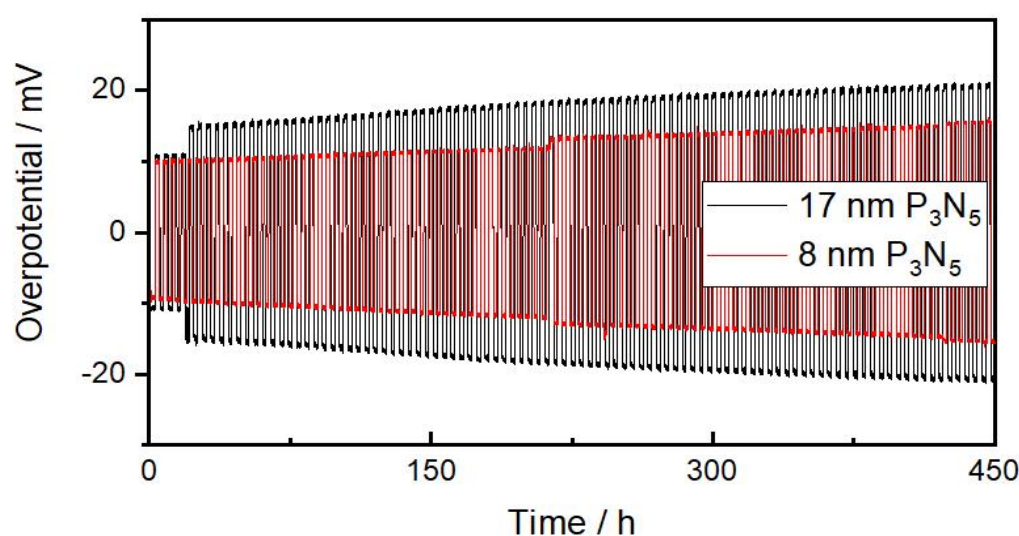


Figure 41: Comparison of two samples with two different interlayer thicknesses. Plating/stripping experiments at 60 °C. For the experiment 100 $\mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction

The 8 nm thick interlayer is still more than twice as thick as the optimal layer thickness that was determined from examinations on „LiPON“. A thinner layer may also protect the electrolyte from decomposition without leading to an increased cell resistance. However, applying a homogeneous interlayer with a thickness smaller than 8 nm on a rough electrolyte surface by IBS is on one hand technically challenging. On the other hand, films with a thickness < 5 nm may lead to problems. In a thickness range of less than a few nanometers, the interlayers may lose their protective effect because electrons may be able to tunnel through the protective layer. In ASSBs, a distinction between failure due to an inhomogeneous interlayer or tunneling through the interlayer is currently not possible.

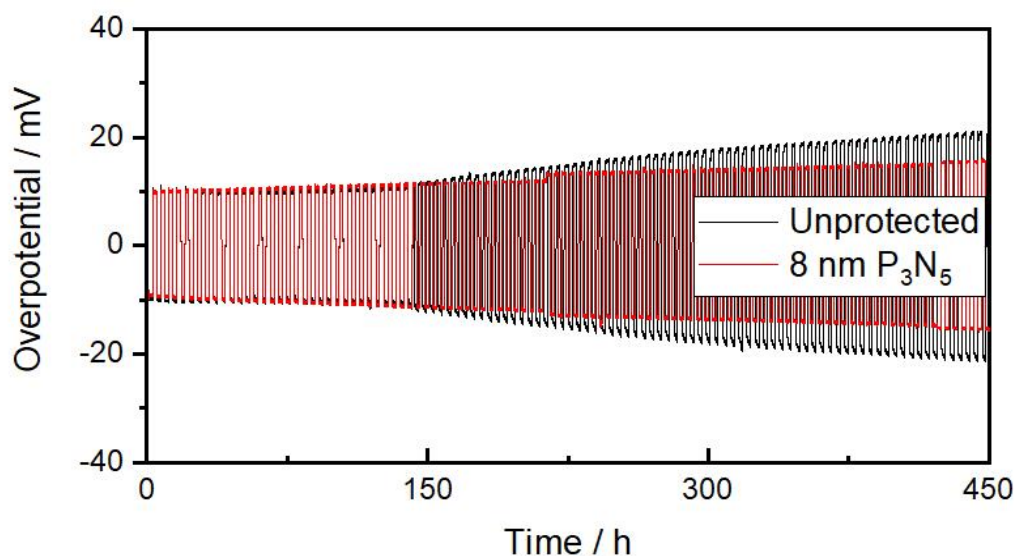


Figure 42: Comparison of a symmetric cell with and without interlayer. Plating/stripping experiments at 60 °C. For the experiment $100 \mu\text{A}/\text{cm}^2$ were applied for 2 h in each direction.

Cycling of all-solid-state batteries

All-solid state batteries with and without P₃N₅ interlayer were built to examine the influence of the interlayer on the performance of ASSBs. The interlayer thickness was varied to examine whether there is a minimum interlayer thickness d_{min} that is necessary to achieve an interface passivation or a maximum thickness d_{max} that must not be exceeded in order to improve the battery performance.

The analysis of ASSBs is a difficult task as many different components are involved, many different degradation mechanisms can occur and the fabrication of ASSBs comprises many different steps, which can lead to strong statistical spread of the performance data.

These phenomena include volume change of the electrode active materials during charging & discharging, interface reactions between the electrode active materials and the electrolyte and variation of the conductivities depending on the particle size [157], [176]–[179]. The examination of ASSBs is always a superposition of all these phenomena and the state of the cathode active material (CAM) can make the examination of the anode side difficult. These effects can be even more severe, when the examinations are carried out at different temperatures. As some of them also had an influence on the battery performance in this

work, they will be discussed below. It is pointed out that all specific capacities are given with respect to the mass of the CAM.

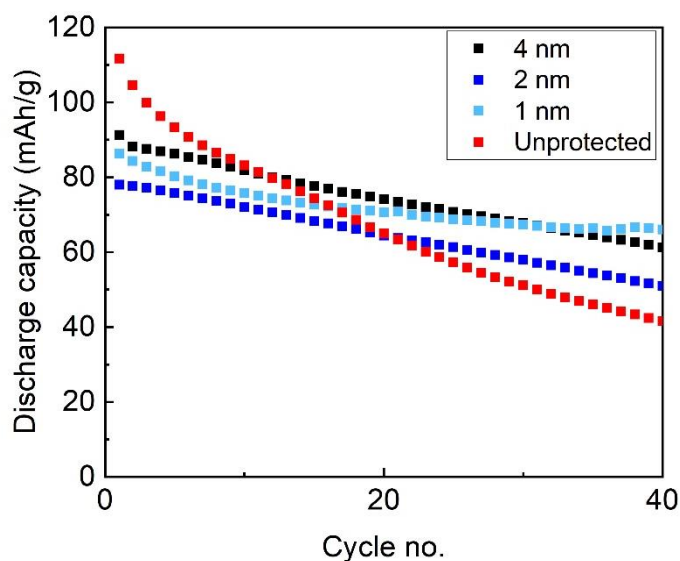


Figure 43: Comparison of the discharge capacities of ASSBs with interlayers with different thicknesses. As precise thicknesses for short deposition times cannot be given, the deposition time of P₃N₅ is given instead. The batteries with interlayer have a smaller discharge capacity than the battery without interlayer. The interlayer decreases the capacity fading during the first 40 charge/discharge cycles. A dependence of the capacity retention on the interlayer thickness cannot be seen.

The batteries consist of an NCM611:LPS composite cathode with a mass ratio of 70:30, LPS solid electrolyte and a lithium metal anode. Battery cycling was performed between an upper cutoff potential of 4.3 V vs. Li⁺/Li and a lower cutoff potential of 2.6 V vs. Li⁺/Li by applying a constant current of $\pm 140 \mu\text{A}$ ($200 \mu\text{A}/\text{cm}^2$). The battery without interlayer between electrolyte and anode has a specific discharge capacity of 110 mAh/g (**Figure 43**). The discharge capacity decreases strongly during the first 20 cycles. The capacity loss is around 50 mAh/g or 45 % of the initial discharge capacity. The capacity fading continues but slows down after 40 cycles. At that time the discharge capacity is only 40 mAh/g. The difference in the degradation rate is probably caused by different degradation mechanisms. During the first charge/discharge cycles a reaction between both electrodes and the electrolyte takes place, leading to the formation of an SEI at both electrode|electrolyte interfaces. This SEI is passivating the interface but increasing the interface resistance, leading to an impeded transport of lithium ions, which reduces the capacity. A second contribution to the capacity

loss, is the loss of CAM. Upon subsequent cycling, the volume change of the CAM leads to a contact loss between the CAM and the electrolyte and less CAM can be addressed. The volume change and contact loss will also occur during the first 20 cycles but its effect is superimposed by the SEI formation.

The batteries with interlayer have a lower initial discharge capacity of only 80 mAh/g to 90 mAh/g. The smaller discharge capacity may be due to overpotentials caused by the modified interface. In the impedance spectra of the assembled cells before cycling, a higher interfacial resistance can be seen than in the case of the cells without interlayer (cf. **Appendix I**). The cause may be the interlayer that need to be converted into Li₃N and Li₃P in the first couple of cycles before providing a protective effect and a decreased interfacial resistance. A smaller cathode utilization can be excluded as the composite cathode is not in contact with the interlayer.

Although the initial capacity of the batteries with interlayer is smaller than that of the batteries with unmodified interface, the capacity loss is also smaller. The discharge capacity decreases with prolonged cycling of the battery but it decreases steadily. After 40 cycles, the slope of the capacity fading is the same for the batteries without interlayer and batteries with interlayer, indicating that after 40 cycles the capacity fading is not caused by the formation of an SEI but by the degradation of the composite cathode.

The coulombic efficiency – the ratio between the electric charge that is retrieved during the discharge step and the charge that is needed for the charging step – is in the range of 98 % – 99 % for the batteries without interlayer but also shows some fluctuations (**Figure 44**). For the batteries with interlayer, the coulombic efficiency is also in the range of 99 % but slightly higher. Although the difference is only 99.8 % for the cells with interlayer compared to 99.2 % for the cells without interlayer, the energy loss during each cycle decreases by almost an order of magnitude. In addition, the cells with interlayer reach such a high coulombic efficiency after around 10 cycles, whereas the cells without interlayer need more than 40 cycles to reach a coulombic efficiency of > 99 %. After 40 cycles, the coulombic efficiencies of the cells with and without interlayer are virtually the same. The interlayer reduces the loss of charge carriers during the first 40 battery cycles. We suggest that the increased coulombic efficiency is due to the prevention of the electrolyte decomposition in contact with lithium metal. This observation indicates that the drastic capacity loss during

the first 60 charge/discharge cycles is caused by the interphase formation between the anode and the electrolyte whereas the capacity loss during subsequent cycling is only due to mechanical issues of the cathode side.

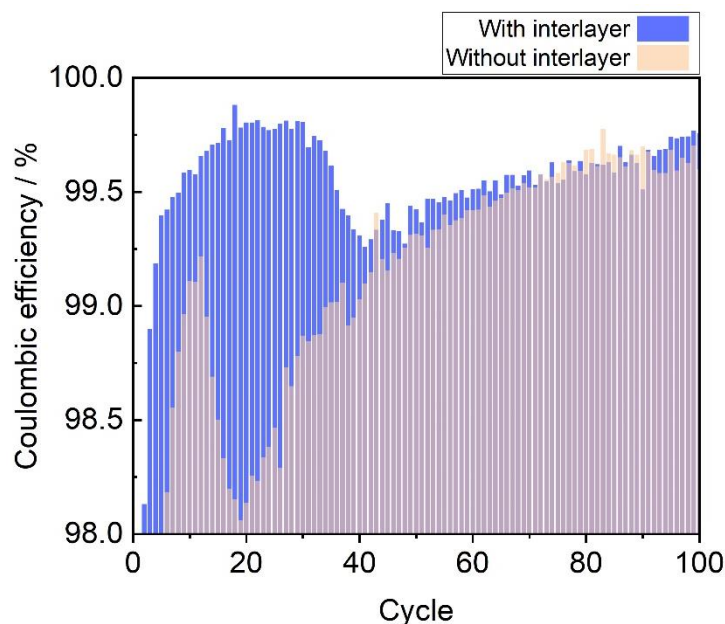


Figure 44: Coulombic efficiency of an ASSB with P_3N_5 interlayer (blue) and without interlayer (yellow). Batteries with an interlayer exhibit a higher coulombic efficiency during the first 60 charge/discharge cycles. After 60 cycles the efficiencies are similar.

The variation of the thickness of the P_3N_5 interlayer does not have a significant influence on the performance of the battery. The variation of the properties of batteries prepared with the same material under the same conditions (around 10 cells) is just as big as the difference in the discharge capacity of batteries with different interlayer thicknesses. The reasons for these differences are plentiful: They can originate from differences of the particle distributions in the composite cathode after manual mixing and grinding of the powders, from the size of the CAM primary and secondary particles, from differences in the glovebox atmosphere during cell fabrication, especially during the handling of lithium metal, and due to differences of the pressure that is applied during cycling. This pressure changes during cycling; during each cycle the pressure changes according to the volume change of the CAM and the lithium anode and it also changes when during subsequent cycling the utilization of the CAM decreases. Aging of the cell housing and frames may also alter the battery performance. An aged housing may not be fully gastight anymore and may cause a reaction between the battery materials and the atmosphere. The surface of the stamps, which are used

to press the powders, influences the roughness of the electrolyte surface and can also cause different current densities during cycling. As can be seen in **Figure 45**, these differences in the discharge capacity for cells that were prepared the same day from the same powder can already be as big as 15 mAh/g after 30 cycles (dark blue and light blue data). For a profound evaluation of the influence of a protective layer on the battery properties, a standardized cell manufacturing procedure and a statistic evaluation with an increased number of cells is necessary. A statistical approach is of outmost importance because also the preparation of the interlayer can lead to varying results depending on the state of the deposition chamber. Humidity in the chamber atmosphere can cause impurities in the interlayer.

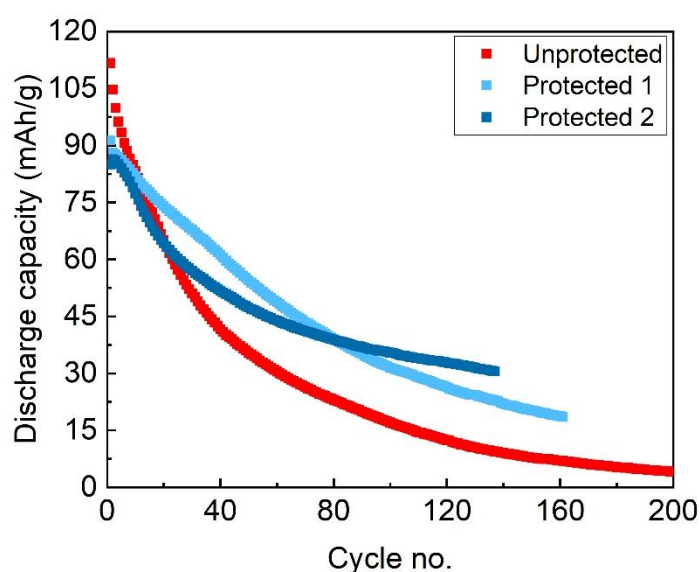


Figure 45: Discharge capacities of batteries with and without interlayer. The initial discharge capacity of a battery without interlayer is around 20 mAh/g higher than that of batteries with interlayer. Two batteries with an interlayer of the same thickness can exhibit a difference in the discharge capacities by 10 mAh/g and a different capacity retention due to the complex fabrication.

In ASSBs, there is no clear dependence of the battery performance on the thickness of the interlayer. For a thickness of the interlayer between 1 nm and 4 nm (2 min – 8 min deposition time) the initial discharge capacity varies between 80 mAh/g and 90 mAh/g. The reason that the thickness of the interlayer does not have a clear influence on the battery performance may be due to the fact that the pressed electrolyte powder is rough and the interlayer is not thick enough to fully cover the electrolyte surface. In that case, parts of the surface are covered and protected from decomposition, while other parts are still exposed to

lithium metal and undergo a reaction. To cover a rough surface, a thicker interlayer may be necessary but it may come along with an increased resistance if the layer becomes too thick. The differences in the capacity retention of the cells with different interlayers may also be caused by an inhomogeneous interlayer thickness. Although the thickness should not exhibit large lateral differences, even slight differences (e.g. caused by randomly ablated bigger particles) can cause lateral potential distributions across the interface (cf. **chapter 2.4**) and lead to a locally higher driving force for decomposition.

Further evidence of the protective effect of the interlayer is given by the impedance spectra of the batteries with and without interlayer.

Although the procedure is not optimized, the positive influence of the interlayer on the ASSBs is visible. A more effective protection may be achieved by using a more conformal deposition method, e.g. ALD.

Impedance spectroscopy

The evaluation of impedance data is always difficult. For a reliable data interpretation, it is necessary to create equivalent circuits that describe the system under examination. A system like an all-solid-state battery easily results in a complex equivalent circuit. The system consists of the cathode, the electrolyte and the anode, each of which provides one contribution to the equivalent circuit. Each interface in the system will also contribute to the impedance spectrum leading to two more contributions (electrolyte|cathode interface and anode|electrolyte interface). In the case of the batteries with interlayers, one more contribution of the interlayer can be expected as well as (depending on the thickness of the interlayer) one contribution of the interlayer|electrolyte interface and one of the anode|interlayer interface. In addition, also the current collectors and the wires can contribute to the impedance spectrum.

The resulting impedance spectrum (Nyquist plot) of an ASSB with and without interlayer after 100 charge/discharge cycles is shown in **Figure 46** in the charged (blue) as well as in the discharged state (black). The data can be described by three different semicircles, each simulated by a parallel resistor R and a CPE. Of all the possible contributions discussed above, only three seem to contribute to the impedance spectrum. The reason is that some

contributions (e.g. wires and current collectors) have a good electronic conductivity and are too small to be resolved. Other contributions, e.g. the lithium anode are large enough to be measured but their time constant so small that they only appear in a frequency range above 10⁶ Hz. The upper frequency limit of the VMP 300 is 7 MHz, therefore these contributions cannot be detected. Other contributions may have similar time constants and cannot be resolved as the respective semicircles overlap, resulting in one larger contribution. For all these reasons, a reasonable data evaluation was performed using three semicircles in the equivalent circuit. The Nyquist plot of a battery with interlayer after 100 cycles has the same shape as the Nyquist plot of the battery without interlayer but the overall resistance of the battery with interlayer is smaller.

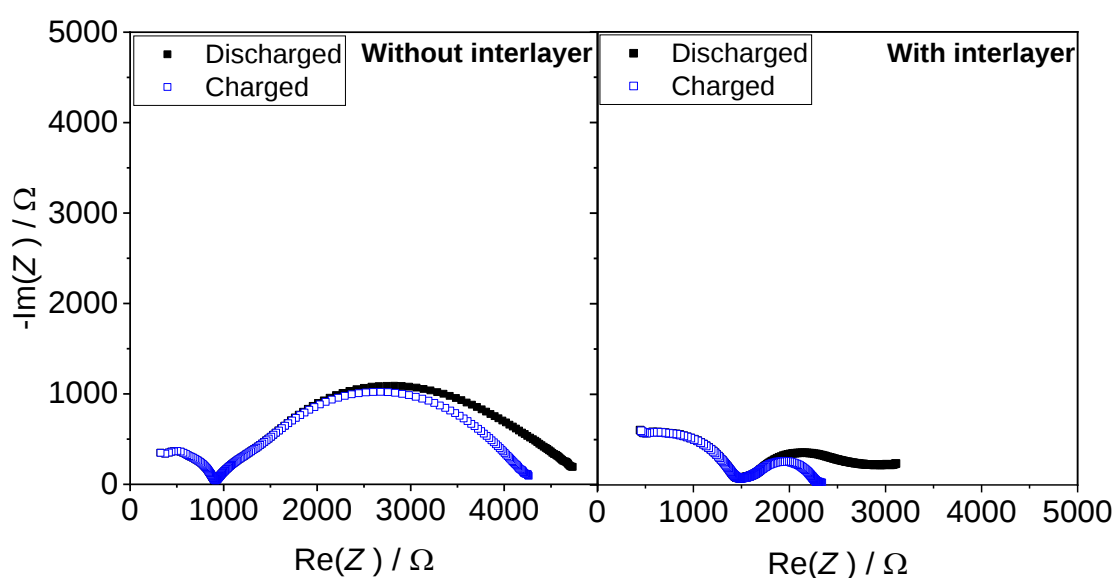


Figure 46: Nyquist plot of a battery without anode|electrolyte interlayer after 100 cycles in the charged (blue empty data points) and discharged (black filled data points) state.

From the differences in the impedance spectra of the charged (delithiated cathode) and discharged (lithiated cathode) battery and the values of the capacitances for the three semicircles, it is possible to attribute the semicircles to the different battery components (**Figure A 16**). The first semicircle at high frequencies is independent from the state of charge (SOC). Therefore, it can be concluded that this semicircle is caused by the solid electrolyte. This suggestion is supported by the capacitance that was calculated from the CPE, and which

is in the range of 10^{-11} F – 10^{-10} F, a typical value for the bulk electrolyte (cf. **chapter 3.3**) and the resistance (denoted as R_1) leads to a conductivity of $1.1 \cdot 10^{-4}$ S/cm, which is in good agreement with the conductivity values of LPS known from literature [180], [181]. Differences in the electrolyte resistance are due to weighing errors during cell fabrication. Any change of the electrolyte contribution must be caused by the measurement. It can be due to the volume change/densification of the electrolyte during charging/discharging which may differ due to different cell housings or due to reaction with atmosphere that can occur if the housings are not fully gas tight.

The two contributions at lower frequencies depend on the SOC of the battery. They must be attributed to the cathode material. The anode consists of lithium metal and all changes of the resistance during charging and discharging should be small as the conductivity of lithium does not change. The conductivity of the cathode material depends on the state of charge and should therefore lead to an altering contribution to the Nyquist plot. Both impedance contributions at mid to low frequencies have capacitances in the range of 10^{-6} F, which is typical for the geometric capacitance of an interface. Therefore, these contributions cannot be due to the bulk electrode materials but must be due to both electrolyte|electrode interfaces. It has to be pointed out that due to the large overlapping of these two contributions, fitting of the data is difficult, especially during the first few battery cycles, when these two contributions are not well pronounced yet. For that reason, the values for the second semicircle may be erroneous, as they are influenced by the large third semicircle at low frequencies.

For an assignment of these contribution, a battery with and without interlayer are compared. **Figure 47** depicts the change of the different contributions of the cell resistance in dependence of the charge/discharge cycles.

As discussed above, the discharge capacity of a battery without interlayer decreases drastically during cycling due to the SEI formation at the anode|electrolyte interface and due to the degradation of the electrolyte|cathode interface. Latter effect also occurs in cells with anode|electrolyte interlayer causing a similar capacity fading during long-term cycling. As the cathode side has a more severe impact on the cycling data, it can be assumed that the contribution that shows the strongest changes in the impedance spectrum is caused by the cathode side. Hence, R_3 is attributed to the electrolyte|cathode interface. The fact that the

resistance of this component in the lithiated state conforms to the delithiated state, suggests that the volume change during cycling causes a destruction of the composite cathode leading to higher resistances.

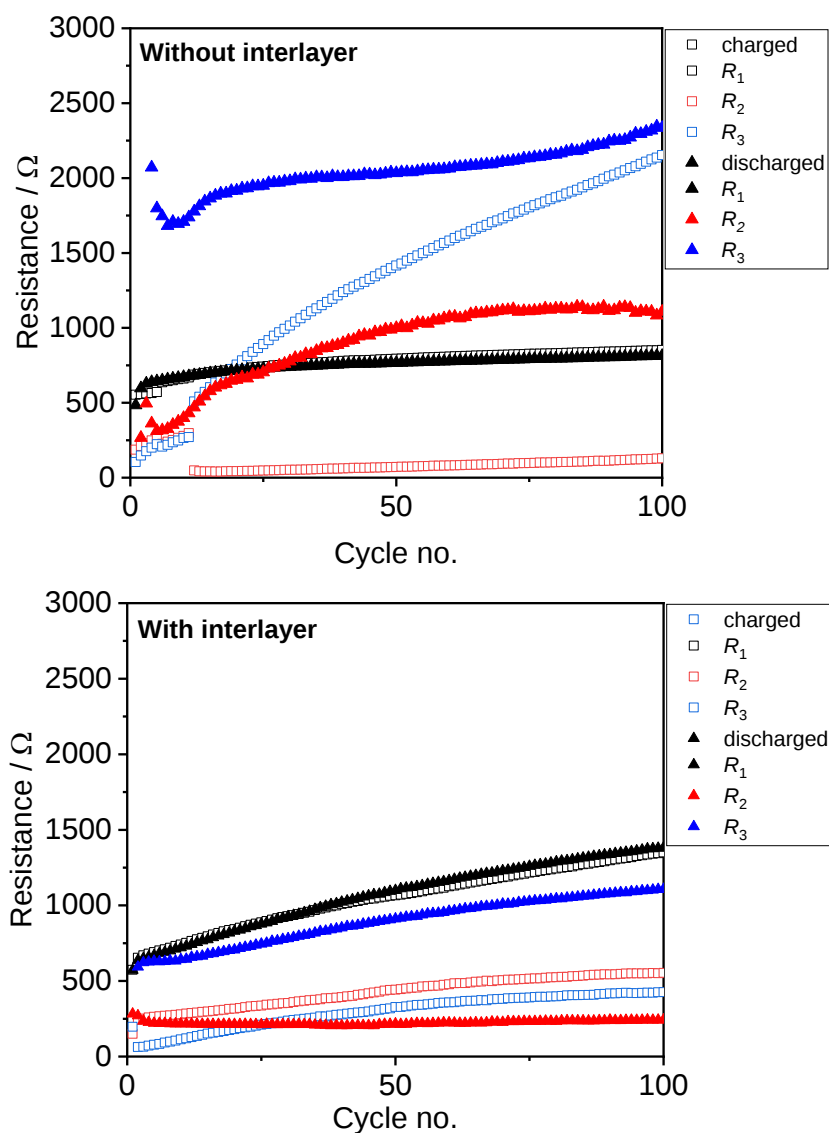


Figure 47: Evolution of the resistances of a battery with and without anode|electrolyte interlayer within several charging/discharging cycles of a battery. An impedance measurement was performed after each charging and discharging step.

On the other side, R_2 is attributed to the anode|electrolyte interface. In the battery without interlayer, this contribution is also increasing, suggesting that an interface is formed. But the increase of R_2 shows a parabolic behavior in the discharged state. This suggests that the

growth of R_2 is limited. It may therefore be due to the formation of a passivating SEI at the anode|electrolyte interface. On the cathode side, the transition metal ions of nickel, cobalt and manganese should prevent a passivation due to the formation of metal atoms. It can therefore be suggested that R_2 is due to the anode|electrolyte interface. However, this resistance is bigger in the discharged state of the battery than in the charged state. If lithium is transported from the anode side to the cathode side of the battery during discharge, voids are formed at the lithium|electrolyte interface and these voids increase the interface resistance. During the first 10 cycles, the data is not according to the trend because due to the small contributions R_2 and R_3 , the same equivalent circuit leads to fitting errors.

All resistances of the battery with interlayer do also increase over time. The increase of the electrolyte resistance R_1 is bigger than in the case of the battery without interlayer. As the initial values of R_1 are similar in all batteries (**Appendix I**) and differences are not caused by the intrinsic properties of the electrolyte, this behavior may be due to different pressure on the cell housing. Statistically, the increase of R_1 is not bigger than for the cells without interlayer. It has to be pointed out that the values of R_1 of the battery without interlayer in **Figure 47** do slightly deviate from the apparent diameter of the semicircle in **Figure 46**. The difference is caused from fitting errors caused by high-frequent noise. As the information from frequencies above 7 MHz is lacking, there is no information on possible additional serial resistances.

R_2 does increase in the case of a charged battery with interlayer but stays constant in the discharged state. This observation may be due to the fact that the lithium|electrolyte interface is enhanced by the protective layer and the contact is more homogeneous. When the battery is charged, additional lithium is transported to the anode side and causes a volume expansion of the anode, which increases the resistance. When the additional lithium is removed during discharge, the resistance is decreased again and the anode|electrolyte interface is retrieved as before.

The resistance R_3 also increases during cycling. Although R_3 is also bigger in the discharged state than in the charged state, in the case of an interlayer, they do not seem to converge. Therefore, the application of an interlayer on the anode side does not only have an influence on the anode|electrolyte interface but also on the cathode side. A detailed study on the reasons still needs to be carried out. It may be possible that according to the thermodynamic

discussion in **chapter 2.4**, the potential drop on the anode side has an influence on the potential drop on the cathode side. A large potential drop across the SEI creates a strong electric field that can cause a decomposition of the electrolyte. The anode|electrolyte interlayer with a negligible electronic conductivity should cause a strong potential drop across the interlayer. In that case the potential drop on the cathode side should be smaller, leading to a less pronounced decomposition. The change of R_3 is then only due to the volume change during cycling.

We conclude that the application of P₃N₅ as interlayer is an effective way to modify the lithium|electrolyte interface. The material does not only protect the electrolyte from decomposition in contact with lithium metal (**Figure 34**), it also has a positive influence on the capacity retention of full cells. These experiments with P₃N₅ successfully prove the concept of sacrificial interlayers in ASSBs.

Summary

The present work consists of three different parts:

In the first part (**chapter 2**), a closer look at the concept of surface modification of the solid lithium | electrolyte interface has been taken. The reasons for the thermodynamic interfacial instability analyzed. After that, criteria for the successful thermodynamic stabilization of the lithium | electrolyte interface have been given and the concept of sacrificial interlayers (based on „LiPON“ solid electrolyte and phosphorous nitride P_3N_5) has been introduced.

In the second part (**chapter 4.1**), insight on the interface formation of „LiPON“ solid electrolyte in contact with lithium metal is provided by means of X-ray photoelectron spectroscopy and a model for the SEI growth was postulated. Thin-films of this material with varying nitrogen content were deposited by radio-frequency magnetron sputtering. By stepwise lithium deposition in the analysis chamber and subsequent measurements it was possible to show a decomposition reaction between „LiPON“ and lithium. This decomposition reaction consisted of two different steps: First the decomposition of „LiPON“ into Li_3PO_4 , Li_3P and (depending on the amount of nitrogen) Li_3N followed by the decomposition of Li_3PO_4 into Li_3P and Li_2O . Although the complete conversion into the binary compounds is thermodynamically favored, Li_3PO_4 can always be found due to the limited amount of lithium present during the experiment. This amount is not enough to fully convert „LiPON“. From the ratio of the intensities of the phosphorous signals of the surface layer and the electrolyte layer it was possible to monitor the SEI growth and to

determine the SEI thickness after each lithium deposition step. The SEI growth did not proceed linearly as expected when a constant mass of lithium is deposited during each sputtering step. Instead the SEI growth follows a parabolic law. This behavior can be explained by the fact that the reaction products are only ionically conducting but electronically insulating, leading to a kinetic hindrance of the reaction. Only when both ions and electrons can pass the interphase, a reaction will occur and proceed. The limited electronic conduction leads to a gradually decreasing growth rate of the SEI and the parabolic increase of the SEI thickness. Increasing the nitrogen content of the „LiPON“ films leads to a thicker SEI layer, presumably due to an increased electronic conductivity caused by proton incorporation into Li_3N from residual humidity during the deposition of lithium in the analysis chamber. However, in the time-frame of the measurement, the thickness of the SEI ranged between (2 – 3.5) nm.

It was also possible to determine the lithium deposition rate from the damping of the XPS signal intensities of the electrolyte caused by the creation of a $\text{Li}/\text{Li}_2\text{O}$ overlayer. Although the amount of lithium deposited during each step remained constant during each experiment, the amount of active lithium changed. The amount of non-active lithium could be determined from the $\text{Li}_2\text{O}/\text{Li}$ ratio of the overlayer. As soon as the reaction of lithium and the electrolyte is kinetically hindered, a fraction of the lithium will react with residual water in the analysis chamber, reducing the amount of active lithium.

These examinations led to the conclusion that „LiPON“ is a metastable electrolyte in contact with lithium metal, forming a passivating layer consisting of Li_3N , Li_3P and Li_2O , that successfully prevents the electrolyte from further decomposition and leads a stable battery performance for thousands of cycles. Any reaction layer that also consists of solely the lithium binary compounds should be able to provide the same passivating effect, presenting a range of materials that may act as potential anode|electrolyte interlayers. The results on „LiPON“ also suggest that the thickness of these interlayers is crucial. As long as the sacrificial interlayers do not conduct lithium ions, any layer that is thicker than the determined 2 ~ 4 nm will impede the ion migration and decrease the battery performance.

The third part of this work is the preparation and characterization of P_3N_5 as sacrificial interlayer (**chapter 4.2**) Phosphorous nitride was examined toward its application as a sacrificial interlayer. For this, thin-films of the material were prepared by ion-beam

sputtering using argon as sputter gas and nitrogen as working gas. Oxygen was always incorporated into the films during deposition instead of nitrogen but the thin-film deposition was optimized to achieve a high amount of nitrogen in the films and as little oxygen as possible.

Photoelectron spectroscopy was used to monitor the reaction of P_3N_5 in contact with lithium metal and a decomposition similar to „LiPON“ – the formation of Li_3P and Li_3N – could be observed. This observation led to the conclusion that a thin layer of P_3N_5 could successfully protect a solid electrolyte from decomposition. The protective behavior was tested using an Ohara glass-ceramic membrane. A thin layer of P_3N_5 was deposited on top of a partially masked membrane and then lithium metal was evaporated. The unprotected parts of the membrane turned grey due to the reduction of the metal cations in the electrolyte, the protected parts remained white.

To validate whether also the electrochemical properties of a protected electrolyte in contact with lithium metal can be improved, symmetric $Li|LPS|Li$ cells with and without protective layer were built and lithium plating/stripping experiments were carried out. Upon varying the thickness of the interlayer we observed that exceeding a critical thickness d_{crit} of the interlayer led to an increase of the overall cell resistance. The films were too thick to fully react to Li_3N and Li_3P . Reducing the thickness led to an improvement of the plating/stripping behavior for more than 2000 h. The trend of the increasing overpotential during the experiments suggests that the films successfully prevented the thermodynamic interphase formation. The overpotential increased linearly, not parabolic, suggesting that this increase was caused by a change of the mechanical properties of the system but not by thermodynamic instability. Cycling of full cells showed that a P_3N_5 protective layer as thin as 1 nm was enough to improve the capacity retention of the cell. This increase comes along with a decrease of the initial discharge capacity of the cell which is around 15 % smaller than for the unprotected cell. This decrease may be caused by factors unique to the deposition method and may be subject of future research.

It can be concluded that the concept of sacrificial interlayers poses a promising approach for the modification of the lithium|electrolyte contact in ASSBs and that the concept enables a variety of materials that may be used to create ASSBs with improved long term stability.

6

Outlook

The present dissertation has outlined the concept of sacrificial interlayers for lithium metal anode protection. Starting from “LiPON” as a natural metastable material, the basic concept was explained and examples were given on how a passivation of the lithium | electrolyte interface can be achieved. These ideas have been validated by using phosphorous nitride as a potential material for protective layers and a positive influence could be observed. However, this thesis is only the first step on the long and winding road toward a deeper understanding of controlled interfacial decomposition.

There are different aspects of this work that need a more detailed examination and will be subject of further research. The application of phosphorous nitride, especially in all-solid-state batteries requires further research and the layer thickness still needs to be optimized.

Phosphorous nitride is only one possible candidate as artificial interlayer. Different other (lithium) phosphorous nitrides may also be applicable as protective layer. It is also possible to take a look at different solid electrolytes as possible interlayers. Another group of materials are metal nitrides, that in parts were already subject of research during this project. The final concept that will be discussed is the combination of different interlayers in bi- or multilayer systems. All these concepts may not only be useful in preventing the electrolyte decomposition but can also have a few more positive effects on the battery properties.

6.1 *In situ* XPS experiment

Since the first application by Wenzel et al., the *in situ* lithiation XPS experiment has proven to be a valuable tool for the examination of interfacial reactions of battery systems. The present work has provided a more detailed insight on the parameters that can be derived from the experiment and the information that can be gained. However, to fully understand the reaction between a solid electrolyte and lithium metal, even further examination is necessary.

One drawback of the *in situ* XPS method is that the determined SEI thickness is only a lower limit. The real SEI can be thicker. The determined values for the thickness are only valid in the time frame of the measurement. If the reaction proceeds slow, it may not be completed when the measurements after each lithium deposition step are started and the estimated value may be smaller than it actually is. To solve this problem, one must perform multiple measurement steps between the lithium deposition steps. If the interphase formation is kinetically limited the intensities might still change over time because the reaction – although slowly – continues. If the reaction is stopped, there should not be a change of the line intensities over time. Such an experiment consumes a lot of time and is only recommended for well-known systems.

The fact that the information depth of the XPS method is in the range of the thickness of the SEI and especially at the beginning of the measurements even higher than the layer thickness also causes a problem. As discussed above, the results suggest a two-step decomposition of „LiPON“ leading to a multilayer SEI consisting of a lithium-poor layer which only decomposes into Li_3PO_4 and Li_3P (and in the case of nitrated samples into Li_3N) close to the electrolyte and a lithium-rich layer that fully decomposes into the lithium binary compounds. It is possible that this apparent behavior is only due to the limited amount of lithium that is deposited during each deposition step and that prevents a direct formation of the binaries because not enough lithium is present. Also a time-delayed reaction may be interpreted as a layered SEI. To verify whether there is indeed a layered SEI, it is necessary

to vary the information depth of the XPS. By varying the angle of the X-ray source it is possible to achieve different information depths and to clarify whether there is a layered SEI or not.

6.2 Optimization of the P_3N_5 layer

Phosphorous nitride has been used in first experiments and has shown to have a positive influence on the battery performance. Yet, the deposition still needs to be optimized. The deposited layers should have a stoichiometry of P_3N_5 but due to nitrogen loss during the sputter deposition the stoichiometry with the highest nitrogen content was $P_3N_{4.2}$. Although the material can still be used as a protection layer, increasing the amount of nitrogen and reducing the oxygen content is desirable. In the present case it requires a reconstruction of the sputtering chamber and the gas supply, which might be a task for future research.

Although the first results suggest that P_3N_5 has a beneficial influence on the stability of the lithium|electrolyte interface, many open questions remain that need to be addressed:

1. Can the film thickness be optimized?

The thickness of the P_3N_5 layer was scaled down to roughly 8 nm. Ion beam sputtering is a method that can be used to create very thin-films because the sputtering rate is precisely adjustable via the applied gas flow but it is still a method using a directed ion beam. Therefore, this method might be suitable to create a film on a flat substrate, but uniformly covering rough substrates or powders is not possible. To create a layer that considers the roughness of a surface, other methods need to be employed.

One possible method for the fabrication of these thin-films may be Atomic Layer Deposition (ALD). The ALD process uses different precursors to deposit different atoms and by alternating the precursors complex molecules can be formed. The formation of very thin P_3N_5 layers should therefore be possible. The ALD also allows an even more precise control of the interlayer thickness.

2. How does the conversion reaction take place?

The XPS examinations showed that a reaction between lithium and the interlayer takes place. However, during the *in situ* experiment lithium was step-wise deposited onto the electrolyte, and, besides impurities originating from the chamber atmosphere, the lithium was free from impurities. In a real battery the ideal case would be a reaction between lithium foil and the interlayer leading to the formation of Li_3P and Li_3N . If the surface of the lithium foil is passivated, this reaction will not take place. In that case, the conversion of the interlayer will only take place if fresh lithium is plated on the anode side during the first charging step of the battery. Time-dependent impedance measurements at elevated temperatures of a fabricated, uncycled cell, like the ones used in this work should be able to reveal the formation mechanism. If the interlayer does not protect the battery, the interfacial resistance should increase due to the decomposition of the electrolyte and the formation of Li_2S . If the interlayer is converted in contact with lithium metal, the interfacial resistance should decrease because the highly resistive P_3N_5 reacts to Li_3N and Li_3P . If no conversion takes place, the resistance should not change. Elevated temperatures will reduce the time for this experiment.

3. What happens to the interlayer during battery cycling?

The optimized thickness for the P_3N_5 layer will be well below 10 nm. Creating a conformal layer of such a minor thickness is difficult but possible. For the use in batteries it is not only necessary to create such a layer, it is also important that the layer remains intact during battery cycling. From experiments on various electrode materials it is known that battery electrodes can undergo large volume changes. These changes cause mechanical stress and battery failure. Although lithium metal should not as strongly be affected as metal alloy electrodes, it is currently unknown how the phosphorous nitride coating changes upon cycling. It can be assumed that volume changes of the electrode during the cycling will lead to a less homogeneous interlayer and impinge the effectiveness of the interlayer. In that case, an interlayer material needs to be found that can compensate these volume changes or a flexible host structure for the lithium anode needs to be added [182]–[185]. However, any

additional component on the anode side will reduce the energy density.

4. Can different electrolytes be protected as well?

The results obtained in this work were determined from cells with thiophosphate electrolyte. These electrolytes are supposed to develop a meta-stable interphase as the reaction products are mostly Li_3P and Li_2S , including minor impurities of Li_2O and – in the case of Argyrodites – LiCl , LiBr or LiI [102], [126]. Especially Li_2S is a poor ionic and electronic conductor. A conversion of Li_3PS_4 into Li_3P and Li_2S should result in an interphase consisting of around 70 vol% Li_2S and the SEI properties should thus be dominated by Li_2S . An interlayer might be necessary to reduce the charge transfer resistance across the interface but it should not be needed to generally stabilize the interface.

Other electrolytes like LATP, LAGP and LGPS, which decompose and form metallic components in contact with lithium, will need a protective layer, because otherwise the entire electrolyte will decompose in contact with lithium metal. Therefore, the application of P_3N_5 in these systems is highly recommended and should be addressed in future experiments.

6.3 Alternative sacrificial materials

Phosphorous nitride is only one possible candidate for the application as sacrificial interlayer. There are several different groups of materials that can possibly have a protective effect on the battery. One group of materials are solid electrolytes that are related to „LiPON“ and should exhibit similar properties. Another group of potential interlayers could be metal nitrides, which may act similar to P_3N_5 . If one single layer does not provide the necessary stabilization of the interface, the application of multilayer systems may prove to be a valid approach. Although artificial interlayers were only discussed in this work with respect to their ability of preventing SEI formation, they may also be applicable to overcome various other interfacial issues.

6.3.1 Electrolyte thin-films

There is a plentitude of different materials that could also be used as sacrificial layers and that have not been used in this work. A prerequisite for industrial application is a low-cost process, which only allows inexpensive, abundant materials, and a low-energy process. Therefore, materials that need high temperatures during thin-film synthesis are excluded from this discussion

Only „LiPON“ was examined as a possible electrolyte-based interlayer but there are a few more materials that could also be used. Several electrolytes, which are closely related to „LiPON“ are currently under investigation [187], [188]. These materials are based on lithium sulfate instead of lithium phosphate or are derived from a mixture of both. „LiSON“ is supposed to have an ionic conductivity that is one order of magnitude higher than that of „LiPON“ [189]. In the case of „LiPON“, its use as a protective layer has been confirmed in several applications [74], [190].

However, these materials may be unstable in contact with lithium metal, too. But as these materials are closely related to „LiPON“ they should also form a passivating reaction layer. Yet, the ionic conductivity of the formed interlayer might be inferior to „LiPON“ due to the smaller amount of phosphorous in the sum formula. Whereas „LiPON“ with an average stoichiometry of $\text{Li}_3\text{PO}_3\text{N}$ decomposes into 42 vol% Li_2O , 34 vol% Li_3P and 24 vol% Li_3N , in the case of „LiSON“ ($\text{Li}_3\text{SO}_3\text{N}$), only 26 vol% of Li_3N will contribute to conduction of the interphase and 74 vol% will have a low ionic conductivity.

The same goes for Li_3PS_4 which forms 24.8 vol% of highly conductive Li_3P and 75.2 vol% of poorly conductive Li_2S interphase. Therefore, if applied, these materials should act as an inferior protective layer than „LiPON“ but rather need a protective layer to reduce the charge transfer resistance.

Another possible choice as interlayers are lithium phosphorous nitrides. There are a few compounds like LiPN_2 and Li_7PN_4 , and $\text{Li}_{10}\text{P}_4\text{N}_{10}$ and $\text{Li}_{12}\text{P}_3\text{N}_9$. Although their conductivities are not much better than those of lithium phosphate [191], they could be checked for the application as interlayer. If they are unstable in contact with lithium metal, they should also only decompose into lithium nitride and lithium phosphide.

6.3.2 Metal nitride layers

Metal nitrides were also considered as possible interlayers. As metal oxides are often used as artificial interlayers in batteries [192], [193] the idea of applying metal nitrides comes naturally. The major drawback of metal oxides is their often bad ionic conductivity that causes an increase of the resistance and limits the thickness of the applied layer to only a few nanometers. Metal nitrides could also act as protective layers after a conversion reaction with lithium. These materials will only have a protective effect on the lithium | electrolyte interface, if they do not conduct electrons. Therefore, the use of metal nitrides was evaluated by the examples of copper nitride and aluminum nitride.

Copper nitride as sacrificial interlayer

Polyplus company patented the use of Cu_3N as an interlayer in their batteries. However, not much is known about the protective effect of this material. Polyplus suggest that the material reacts similar to P_3N_5 and decomposes into Cu and Li_3N in contact with lithium metal. The formed lithium nitride should be the reason why they achieved a smaller overall cell resistance [194]. However, together with lithium metal also copper metal is formed. Copper metal does not lithiate, a reason why it is used in “lithium-free” batteries where the lithium metal anode is formed via lithium plating on the copper current collector during the initial charging step of the battery [195]; but copper is an electronic conductor. If a reaction takes place according to equation 46



the resulting interphase would contain 45.8 vol% of Cu metal, which would be enough to form a percolating network for electronic conduction. One would therefore expect that copper nitride does not prevent a decomposition of the electrolyte as the SEI consists of one phase that conducts electrons and a second phase that conducts ions. To better understand the applicability of metal nitrides as protective layers in batteries, first experiments on Cu_3N were carried out. The results are summarized in **Appendix J**. Copper nitride can be used to reduce the interface resistance between lithium and the solid electrolyte but it does not prevent the growth of the resistance and the decomposition of the electrolyte. The volume fraction of metallic copper in the reaction layer is high enough to induce an electronic conductivity.

Aluminum nitride

An alternative to copper nitride could be aluminum nitride. Its metal content is only 1/3 compared to that of Cu_3N . Although the molar volume of aluminum is higher than the one of Cu ($10 \text{ cm}^3/\text{mol}$ vs. $7.11 \text{ cm}^3/\text{mol}$), the volume fraction of aluminum in the reaction layer is only 28.4 %. As 30 vol% are considered to be the threshold concentration that is necessary to form a percolating network [170], the aluminum content of nitrogen-rich AlN might not be enough to induce an electronic conduction and the material might be able to suppress the electrolyte decomposition. In addition, Zhu et al. have calculated that the material should

be intrinsically stable against lithium metal and even when overpotentials are applied to create a lithiated Li_3AlN_2 phase, these two phases should act electronically insulating and thus passivate the interface [84].

In addition, aluminum is known to form alloys with lithium and it might lead to a reduced potential gradient at the interface. AlN could also be an interesting candidate for protective layers on the cathode side. Coatings of LiCoO_2 with aluminum oxide are known in literature [192], [196]–[203] but aluminum oxide is an insulator. If the coating is too thick, it will have a negative influence on the transport properties. However, it is assumed that in parts the aluminum is incorporated into the LiCoO_2 , stabilizing its structure and leading to a more stable cycling behavior. For that reason aluminum is used in NCA materials [203]–[205]. AlN could fulfill the same purpose but it might probably react by forming a lithium aluminum nitride phase, which is ionically conducting. It could be an interesting interlayer for the system „LiPON“ | LiCoO_2 because the aluminum might be incorporated into the LiCoO_2 whereas the nitrogen might be incorporated into the „LiPON“, increasing the nitrogen content and thereby lowering the resistance at the interface.

6.4 Combination of interlayers

There is strong evidence that different kinds of interlayers serve different purposes. As mentioned in **chapter 2.3**, many groups apply metal layers between lithium and the electrolyte to increase the battery performance. However, these layers will not stop the electrolyte from decomposing in contact with lithium because they do not serve as a diffusion barrier. Instead they promote a more intimate and homogeneous contact between the electrolyte and the anode, decreasing the risk of dendrite formation. To stop the degradation in such systems a combination of two or more layers may be a suitable strategy.

A promising idea could be the combination of a material like P_3N_5 and a metal layer, e.g. Sn. P_3N_5 stabilizes the lithium|electrolyte contact by forming Li_3N and Li_3P , whereas the metal layer increases the contact area and reduces the interfacial resistance. The metal layer does not serve as a diffusion barrier for lithium. Even when the metal layer is deposited on P_3N_5 , the lithium can still reach it and convert it into the binary compounds. Thus, no highly resistive layer will remain buried between the electrolyte and the electrode. As the experiments have shown, the risk of incorporating oxygen into the interlayer is high when water is present. In the case of lithium/metal alloys, lithium could be prevented from reacting with oxygen on one side of the electrode but still react with P_3N_5 on the other side of the electrode.

Although Cu_3N has not proven to protect the electrolyte from decomposition, it could be worth revisiting Cu_3N as a material for the application in such a multilayer system.

This dissertation is the first to discuss the concept of sacrificial interlayers in all-solid-state batteries. The present examinations are only the starting point for a vast and promising field of subject. The urge of applying interlayers in ASSBs will get more important in the future and will spark interest in sacrificial interlayers. This dissertation may provide suggestions and guidelines for future research toward thermodynamically stable anode|electrolyte interfaces.

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Appendix

Appendix A

Symbols and abbreviations

Table A 1: Scaling factors.

Unit	Name	Value
G	Giga	10^9
M	Mega	10^6
K	Kilo	10^3
C	Centi	10^{-2}
m	Milli	10^{-3}
μ	Micro	10^{-6}
N	Nano	10^{-9}
Å	Angström	10^{-10} m

Table A 2: Units.

Unit	Name	Physical Quantity
A	Ampere	Current
At%	Atomic percent	Atomic fraction
Bar	Bar	Pressure
C	Coulomb	Charge
°C	Degree Celsius	Temperature
eV	Electron volt	Energy
F	Farad	Capacitance
G	Gram	Mass
H	Hour	Time
J	Joule	Energy
Kg	Kilogram	Mass
K	Kelvin	Absolute temperature
L	Liter	Volume
M	Meter	Length / Distance
Min	Minute	Time
Mol	Mol	Quantity
Ω	Ohm	Electrical resistance
Pa	Pascal	Pressure
Rpm	Rounds per minute	Rotational speed
S	Second	Time
S	Siemens	Conductivity
S/cm	Siemens/centimeter	Specific conductivity
Sccm	Standard Cubic Centimeter	Gas flow
V	Volt	Electric potential
Vol%	Volume percent	Volume fraction
W	Watt	Power
Wh	Watt hour	Energy

Table A 3: Abbreviations.

Unit	Name
AC	Alternating Current
ADAC	Allgemeiner Deutscher Automobilclub
ALD	Atomic Layer Deposition
ASSB	All-Solid-State Battery
CAM	Cathode Active Material
CC	Current Collector
CPE	Constant Phase Element
DFT	Density Functional Theory
e^-	Negatively charged electron
El	Elektrolyte
EMF	ElectroMotive Force
HOMO	Highest Occupied Molecular Orbital
IBS	Ion Beam Sputtering
ICE	Internal Combustion Engine
Li^+	Positively charged lithium ion
LIB	Lithium-Ion Battery
LUMO	Lowest Unoccupied Molecular Orbital
MCI	Mixed Conducting Interphase
MIEC	Mixed Ionic and Electronic Conducting
NEDC	New European Driving Cycle
OCV	Open Circuit Voltage
Q	Constant Phase Element
RF	Radio Frequency
SE	Solid Electrolyte
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscope
SHE	Standard Hydrogen Electrode
SOC	State Of Charge
SOD	State Of Discharge
Tof-SIMS	Time-of-flight Secondary Ion Mass Spectrometry
WLTC	Worldwide Harmonized Light-Duty Vehicles Test Cycle
XPS	X-ray Photoelectron Spectroscopy

Table A 4: Chemicals.

Material	Name
95 (0.8 Li ₂ S · 0.2 P ₂ S ₅) · 5 LiI	LPSI
DMC	Dimethyl carbonate
DME	Dimethoxyethane
DOL	Dioxolane
EC	Ethylene carbonate
HF	Hydrofluoric acid
LAGP	Lithium aluminum germanium phosphate
LBLTO (Li ₆ BaLa ₂ Ta ₂ O ₁₂)	Lithium barium lanthanum tantalum oxide
LGPS (Li ₁₀ GeP ₂ S ₁₂)	Lithium germanium thiophosphate
LLZO (Li ₇ La ₃ Zr ₂ O ₁₂)	Lithium lanthanum zirconium oxide
LiPF ₆	Lithium hexafluoro phosphate
„LiPON“	Lithium phosphorous oxynitride
“LiSON”	Lithium sulfurous oxynitride
„LiPSO“	Mixture of „LiPON“ and LiSON
LiSiCON	Lithium super ionic conductor
LiSnPS (Li ₁₀ Si _{0.3} Sn _{0.7} P ₂ S ₁₂)	Lithium silicon tin thiophosphate
LiTFSI	Lithium bis (trifluoromethane-sulfonyl)imide
LPS	Lithium thiophosphate Li ₃ PS ₄
LLTO	Lithium lanthanum titanate
LSiPS (Li ₁₀ SiP ₂ S ₁₂)	Lithium silicon thiophosphate
LTO	Lithium titanate
NASICON	Sodium super ionic conductor
NCA81.50.5	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂
NCA90.50.5	LiNi _{0.9} Co _{0.05} Al _{0.05} O ₂
NCM111	LiNi _{0.33} Co _{0.33} Mn _{0.33} O ₂
NCM622	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂
NCM811	LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂
PC	Propylene carbonate
PEEK	Polyether ether ketone
PEO	Polyethylene oxide
PLD	Pulsed Laser Deposition
Pvdf	Polyvinylidene fluoride
PMMA	Poly(methyl methacrylate)
PVC	Polyvinyl chloride

Table A 5: Variables and constants.

Unit	Name	Value
a	Activity	
BE	Binding energy	
C	Capacitance	
C_V, C_p	Heat capacity	
d	Thickness	
E	Electric field	
e_0	Electric charge	$1.602 \cdot 10^{-19} \text{ C}$
$EAL (KE)$	Energy-dependent effective attenuation length of photoelectrons	
EMF	Electromotoric force	
F	Faraday constant	$96,485 \text{ C/mol}$
I	Current	
I	Current density/Flux	
I	Intensity	
j	Particle flux	
J_{hv}	X-ray flux density	
KE	Kinetic energy	
M	Molar mass	
M	Mass	
N_i	Number of atoms i	
N	Amount of substance	
P	Power	
P	Pressure	
Q	Energy	
Q	Constant phase element	
R	Universal gas constant	$8.31447 \text{ J/K mol}^{-1}$
r_i	Growth rate of species i	
T	Absolute temperature	
t_x	Transference number	$0 < t < 1$
V	Volume	
V_m	Molar volume	
W	Energy density	

Table A 6: Variables and constants.

Unit	Name
X_i	Atomic concentration of species i $0 < X < 1$
x	Molar fraction $0 < x < 1$
Z	Impedance
Z'	Real part of the impedance
Z''	Imaginary part of the impedance
z	Charge number
$\Delta_r G$	Free Gibbs reaction energy
$\Delta_r H$	Reaction enthalpie
$\Delta_r S$	Reaction entropy
∇	Gradient
ϑ	Photoelectron emission angle with respect to the surface normal
$\tilde{\mu}_x$	Electrochemical potential of species x
μ_x	Chemical potential of species x
Σ	Elemental photoionization cross- section
Σ	Conductivity
φ	Galvani potential
χ	Surface potential
ψ	Volta potential

Appendix B

What is a good lithium-ion battery?

In 2017, Toyota announced its intention to launch an electric vehicle with an all-solid-state battery [206]. They expected to begin a new era of electric mobility; a matter of utmost urgency with respect to globally rising energy costs. All-solid-state batteries are designed to increase driving ranges for electric vehicles at reduced space, weight, and cost. The sheer amount of batteries that is needed to electrify only a small fraction of the vehicles that are licensed every year shows that the battery type which will be used in future vehicles, will become the future standard, just as the current lithium-ion battery has been for a long time. In order to compete with the market, however, the new battery system must adduce evidence that it can meet, and eventually exceed, the standards set by current state-of-the-art batteries.

The fundamental question is: How good does an ASSB need to be to compete with the liquid-based systems that are currently available?

To answer this question, one must consider the features of the cells currently used in electric vehicles: lithium-ion batteries. In order to succeed these batteries, ASSBs must prove superior in reliability, efficiency, cost and safety.

In conjunction with electric mobility, often the deficient performance of conventional lithium-ion batteries is mentioned. The realization of ASSBs is regarded to be the premise for the successful establishment (or the failure) of electric mobility.

Despite some criticism lithium-ion batteries have proven to be a generally reliable system. Thus, consumers will expect comparable or improved dependability in ASSBs.

The first aim of this chapter is to look at currently available EVs and their included battery technologies.

A conventional lithium-ion battery consists of an anode, a cathode and a liquid electrolyte that separates the two electrodes. Lithium cobalt oxide (LiCoO_2), a material that can incorporate lithium ions into a layered metal-oxide framework, is often used as cathode material [1].

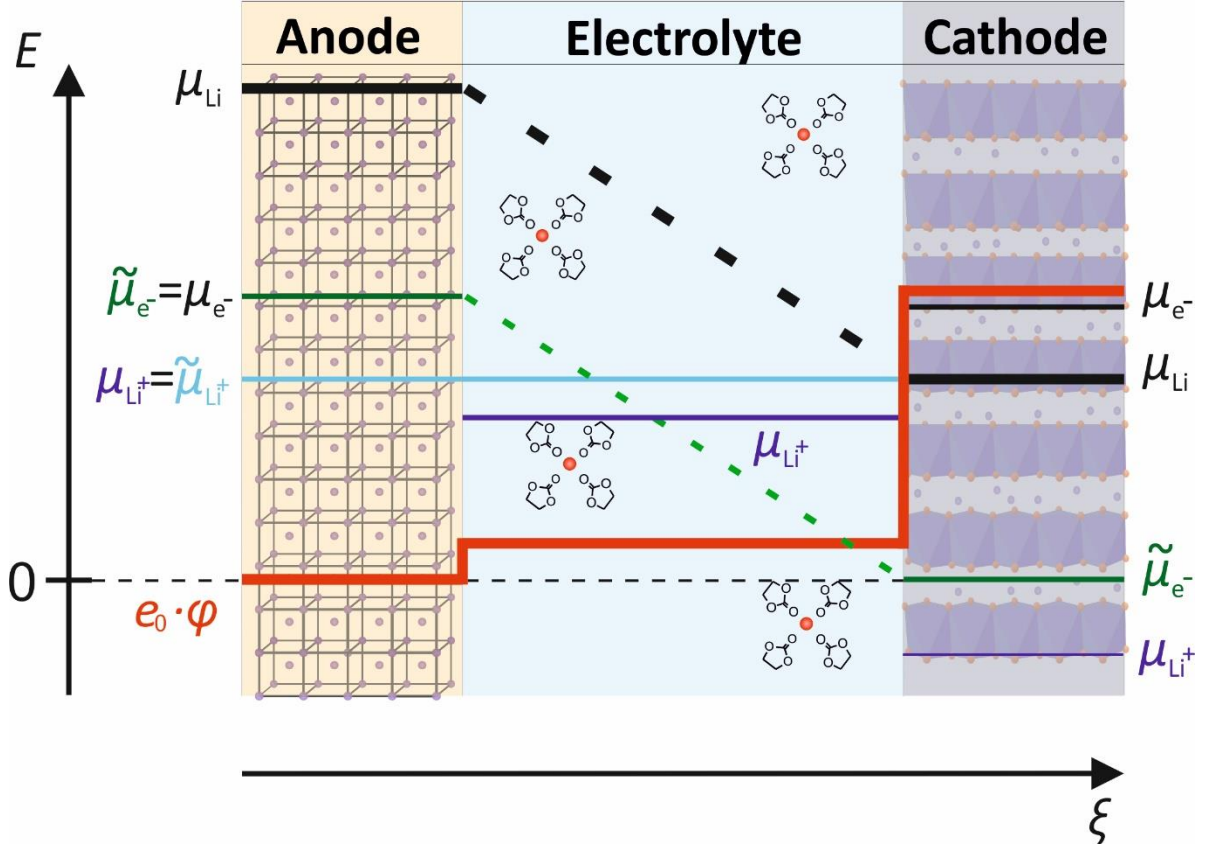
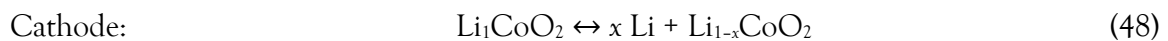


Figure A 1: Schematic of a conventional Li-ion battery. The anode material is lithium metal, the cathode material is LiCoO_2 . A lithium-ion conducting liquid electrolyte with carbonate solvents is used. The potential profiles in this battery are depicted as well.

Graphite, which also possesses a layered structure that can incorporate lithium, is usually used as anode material. The electrode reactions that take place are:



Typically, $x < 0.5$ because if too much lithium is extracted from LiCoO_2 , the structure will collapse and the cathode material will no longer work. The lithium uptake of carbon can be higher and reach up to LiC_6 , delivering a capacity of 372 mAh/g [1]. The electrodes are separated by a liquid electrolyte consisting of an organic solvent that provides the mobility, e.g. ethylene carbonate (EC) or propylene carbonate (PC), and a lithium-containing conducting salt e.g. LiPF_6 or LiClO_4 . To avoid mechanical contact between the electrodes, a separator sheet drenched in the electrolyte solution is included. These batteries typically deliver a voltage of 3.6 V.

Besides the chemical requirements, there are a few other characteristics that will determine whether and when a new battery technology will be applied:

- Power/energy
- Weight
- Volume
- Life time
- Charging time
- Cost
- Safety

Only if the sum of all these properties surpasses those of conventional batteries will ASSBs win recognition and acceptance in the marketplace.

The focus is to figure out what electric vehicles are capable of. The most prominent parameters to be taken into account are driving ranges and the amount of energy consumed while covering a set distance. From these values and typical battery specifications, estimations on the number of battery cells needed in a vehicle can be made, and the weight, volume, charging needs and cost can be calculated. These estimations are necessary as car manufacturers often do not publish details concerning the technologies used in their electric vehicles. For this reason, it needs to be pointed out, that all values given in this chapter – especially concerning the battery volume, weight, and cost – are only rough estimates.

It is premature to make a finalized conclusion about electric mobility based on present observations of conventional batteries and ASSBs, as both systems still lack long-term data on battery performance. But to get a sense of the performance of conventional lithium-ion

batteries thus far, **Figure A 2** presents a comparison of practical driving ranges for a few commercially available electric vehicles. The listed data is taken from the *Allgemeine Deutsche Automobilclub* (ADAC), and the specifications that are provided by the car manufacturers [207].

Figure A 2 and **Table A 7** show the typical energies that electric vehicles of various manufacturers need to cover 100 km. Green represents the values provided by the ADAC, orange the values stated by the manufacturers. The ADAC tests were performed using the *Worldwide Harmonized Light-Duty Vehicles Test Cycle* (WLTC 5.3), which is considered to be one of the most realistic driving tests [208], the test procedure for the values given by the manufacturers was the *New European Driving Cycle* (NEDC). The test values typically range from 12 kWh to 25 kWh per 100 km. The energy per 100 km is a proper value to estimate the battery properties that are necessary to allow a car to cover a certain distance.

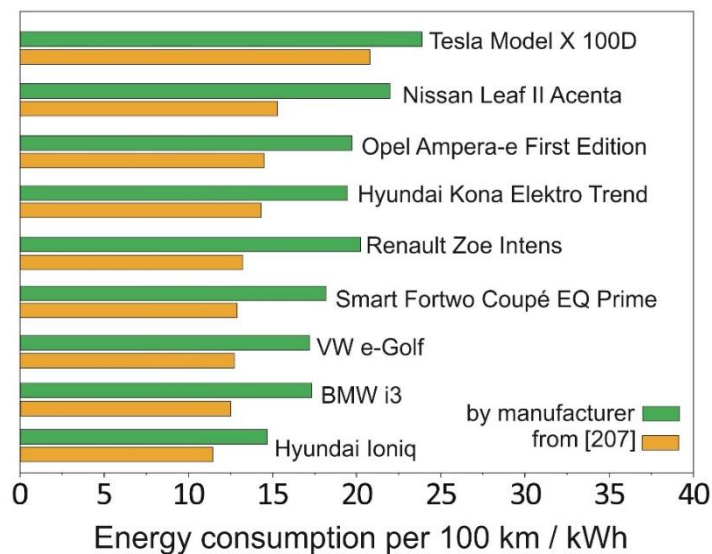


Figure A 2: Comparison of practical driving ranges of various electric vehicles. Green values are provided by car manufacturers, orange values were determined in [207].

The energy consumption depends on multiple factors, including the test region, driving style, car weight and various other applications (e.g. air condition, radio, heating, satnav). Due to inconsistencies between the values stated by the car manufacturers and the ADAC, the following estimations cover a more “pessimistic” scenario and a higher energy consumption

per 100 km is assumed. Nonetheless, these numbers provide a basis for the driving range that is solely dependent on the conduction of the vehicle.

For example, take the calculations for a Tesla Model S 100D. According to the ADAC, the Tesla Modell S 100D has a battery capacity of 100 kWh, which results in a driving range of 416 km. The “magical threshold” an electric vehicle’s driving or the distance a car should cover before needing to recharge the battery, is 500 km. This distance is regarded as the value that is necessary to convince consumers to buy electric vehicles and drive with the confidence that they will not “run out of gas”.

Table A 7: Energy consumption (according to manufacturer), battery capacity, and driving range of various currently available electric vehicles [207].

	Energy/100 km (kWh)	Battery capacity / kWh	Driving range / km
BMW i3	12.6	27.2	188
Smart Fortwo	12.9	17.6	112
Coupé EQ Prime			
Hyundai Kona	14.3	64	375
Elektro (64 kWh)			
Trend			
Opel Ampera-e	14.5	60	342
First Edition			
Renault Zoe Intens	13.3	41	316
Nissan Leaf II	15.2	40	201
Acenta			
Tesla Model X	20.8	100	451
100D			
Hyundai Ioniq	11.5	28	211
Elektro Style			
VW e-Golf	12.7	35.8	201

The Tesla S 100D contains 8,256 Panasonic 18650 batteries [209], each of which contains 12.1 Wh of power. With a nominal voltage of 3.6 V, the nominal capacity equals 3,365 mAh per cell. Compared to the values given in the data sheet of the respective battery type by Panasonic (NCR-18650B) the capacity of 3,350 mAh or 12 Wh, is similar to the Tesla calculations [210]. With a stated mass of 47.5 g and a volume of 17.55 cm³ per cell, the resulting gravimetric energy density is 252.6 Wh/kg and the volumetric energy density is 683.7 Wh/L on cell level, respectively.

With an energy consumption of 24 kWh/100 km the Tesla therefore needs 120 kWh to cover a driving range of 500 km. To generate that power, the car must contain 10,000 NCR-18650B battery cells.

To calculate the total weight and volume of a battery, several factors must be considered in addition to the cell weight. Battery cells need to be connected to cell modules, which require stable housing as well as a cooling and monitoring system. According to the manufacturer, the current Tesla S 100D includes 16 modules containing 516 battery cells each; totaling a weight of 392.16 kg [211]. Reliable information on the battery weight of the Tesla S 100D are scarce. If one assumes a similar ratio between the battery module weight and the cell weight as for the Tesla models with smaller driving range (the weight of a 90 kWh battery is given as 540 kg [212], the housing accounts for additional 49 % of weight. Based on these statistics, the total weight of a battery capable of a 500 km driving range is 708 kg; compared to the cell level weight of 475 kg. The cells alone would have a volume of roughly 175.5 L; and if it is assumed that the volume increases by the same ratio as the weight, the total volume can be estimated at 261.5 L.

Weight and volume are important considerations when constructing a car, and electric vehicles have an advantage in this department. In comparison to a conventional car, an electric vehicle has room to spare due to its independence from components required in a car with an internal combustion engine. For example, in the Tesla S 100D, the battery volume is only slightly bigger than the additional luggage compartment found under the engine hood [213]. ASSBs will have an even lesser volume than their lithium-based counterparts as a thin solid-electrolyte replaces the separator sheets. The free space under the engine hood could be used to store a heavier, more voluminous battery, though that is not the only technical solution for the implementation of batteries in electric vehicles. As

the demand for production of electric vehicles increases, so will the competition to streamline packaging as well as design more novel battery shapes and arrangements. Ideas such as switching from cylindrical to prismatic cells and placing batteries in the frame of the car are already being discussed as options for future vehicles [214]–[216].

Figure A 3 shows a comparison of four models of the different battery technologies (from left to right): all-solid-state battery, lithium-oxygen battery (Li-O₂), lithium-ion battery (LIB), and lithium-sulfur battery (Li-S). These models were designed to show the difference of the volumes of the battery components in each system. All models have the volume (and mass) that is required to let an electric vehicle cover a distance of 10 km. ASSBs, Li-O₂ and LIB depict the optimized case, Li-S depicts the current state of the art where a large part of the battery consists of the housing. As can be seen by switching from LIB to ASSB, the volume of the battery can be reduced by a factor of almost 3. A good deal of this reduction is attributed to the lower amount of housing that is needed to protect the battery. Also the volume of the anode side can be reduced by using lithium metal instead of carbon. Although the mass does not change due to the heavy electrolyte, the space that is required to store the battery is reduced drastically. As the space is a limiting factor in a car, applying ASSBs will have a beneficial impact on car manufacturing. The amount of cathode material can be improved if different cell chemistries are applied. However, the thickness of the separator / solid electrolyte might stay the same, because current LIB are already optimized to use a very thin separator [217], [218]. Another advantage of ASSBs is, that they can be used to realize a multitude of different cell geometries. Whereas conventional batteries are mostly fabricated as cylindrical cells, which cannot achieve a high packing density, even if the housing is driven to the lowest necessary amount, ASSBs can achieve higher volume fractions. Different concepts for 3D battery applications are discussed in literature and could help to change the way we think of batteries today [219], [220].

In the end, the battery volume is not crucial for the application in electric vehicles. For both, batteries based on liquid electrolytes as well as ASSBs, the battery weight will be the crucial aspect as any additional weight further increases the energy consumption. However, the battery volume can have a stronger negative influence on the efficiency of electric vehicles than the battery weight because additional weight can be used to recuperate energy during braking. The battery volume does not affect this process.



Figure A 3: Comparison of battery models for different battery types (From left to right: All-solid-state batteries, lithium-oxygen batteries, state-of-the-art lithium-ion batteries and lithium-sulfur batteries). Although all-solid-state batteries have a high cell weight, they require the least space. Each model (15 x 15 cm) depicts the volume that is needed for an average EV to drive 10 km.

The lifetime of a battery is another crucial aspect in the decision to buy an electric vehicle. The battery, as the most expensive component of the car, should remain reliable for many years. The cycle life strongly depends on the depth of discharge (DOD) and depth of charge (DOC) of the battery. The less deeply a battery is discharged, the less it is damaged. Likewise charging a battery to only 80 % of its maximum capacity also reduces the amount of damage. If it is assumed that electric vehicles batteries have a comparable cycle life to those used in consumer electronics, one can expect a battery to serve for 1000 to 3000 cycles without any problems. Based on the Tesla battery capacity, the energy consumption per 100 km and 1000 battery cycles produces a minimum driving distance of 416.000 km. By using a battery with a capacity of 200 kWh, the same distance can be reached when the battery is only discharged to 50 % state of charge (SOC). A less deep discharge will increase the cycling stability. Driving ranges of 1 – 1.5 million km will then be possible.

If the newly developed batteries have as long a cycle life as the latest battery technologies from Samsung SDI [221], it can be assumed that these batteries are also capable of around 4600 charge/discharge cycles. In the case of a 200 kWh battery as in the Tesla, this would result in a kilometric performance of almost 4.5 million kilometers. From these data, it can be

assumed that the driving range of an electric vehicle does not pose any problems, even with current battery technologies, as they overcome by far the lifetime of most vehicles.

In the end, the driving range of an electric vehicle will be determined by the size and weight of the battery. A large battery will guarantee a large driving range. But even small batteries can be interesting applications for compact cars as long as they can be discharged and first and foremost charged quickly. Then even long distances can be covered with a few short breaks (which will make driving much more comfortable for the driver). As a consumer will expect a battery lifetime comparable to that of a conventional vehicle, so will they expect equivalent “fueling” time. The aim of the electric vehicle industry is to create a battery with a charging time that mimics that of consumers filling their tank with gas. Ideally, an 80 % state of charge (SOC) will be achieved within an approximate 5-minute window.

SOC over 80 % are not desirable because they would reduce the lifetime of the battery, since overcharging as well as a deep discharge damage the battery. Additionally, though a charging step with constant current is much faster than a charging step with a constant voltage, a constant current charge creates over-voltages which prevent the battery from reaching 100 % SOC. Charging a battery to 100 % SOC is only possible by using a constant current charging step followed by a subsequent step with a constant voltage, which is why 80 % SOC is the ideal target.

The quantity that is suited best to describe the charging time is the so-called C-rate. A rate of 1 C means that the entire battery can be charged in 1 hour. A rate of 2 C means that the battery can be fully charged in 30 minutes. The rate does not describe an absolute current but the ratio between the current and the absolute capacity of a battery.

Charging a battery to 80 % SOC in 5 minutes equals a C-rate of 9.6. For the Tesla S 100D, this equals to a charging power of 1 MW. At present, a charging rate of that velocity has yet to be achieved. The main problem is that the carbon anode in the batteries has a limit of 1 – 5 C, depending on the modification (graphite, graphene, nanotubes), the temperature and the SOC [222], [223]. This problem can be circumvented by using lithium metal because then lithium plating does not cause a battery failure. In addition, the usage of solid electrolytes with a transference number of $t_{Li^+}=1$ may be helpful to increase the charging rate. But even then, in addition to the battery system, the charging infrastructure needs to provide

enough power for quick charging. The Tesla S 100D has a C-rate of 1.6, which shows that for now, electric vehicles need half an hour to be charged to 80 % SOC.

The cost of a battery system varies from year to year. In 2018, Andrew Ulvestad tried to estimate the costs of different battery components in order to predict the future development of battery prices [224]. The prices given in his publications are the total prices for the production of batteries, including the raw materials, processed materials and processing costs. First, he examined the price evolution of batteries in the years from 2010 to 2016; then showed how the production costs changed over time. He concluded that the average production cost of batteries dropped from \$ 1000/kWh in 2010 to under \$ 300/kWh in 2016, a factor of more than two-thirds. Although manufacturing costs decreased, they still exceed the \$ 100/kWh, a number that is commonly regarded as cost parity line. When batteries are cheaper than \$ 100/kWh that would make electric vehicles less expensive than vehicles with internal combustion engine (ICE).

In his publication, Ulvestad provided values for the weights of different components of a conventional battery stack with a capacity of 52 Ah in order to itemize the costs [224]. The cost of this stack sums up to \$ 30.58. With a nominal voltage of 3.6 V the total cost comes to \$ 136.35/ kWh. This value includes the raw material costs and the manufacturing costs. To estimate the future development of battery prices, it is necessary to look at various aspects that influence the costs.

Judging the future development of battery prices is challenging because they are not really predictable. In the following, two different aspects are discussed: raw material prices and manufacturing.

Table A 8 summarizes the prices per kilogram of the most commonly used metals in cathode materials for batteries. The final price of the cathode mixture depends on the amount of each metal that is used. Cobalt is the most expensive component in the cathode material, so in order to reduce production cost, manufacturers are trying to substitute it with nickel. By decreasing the Co-content by a factor of 6 and replacing Mn by Al, the cost of the raw material is reduced by nearly half. However, the increased demand for batteries can cause drastic changes of the commodity prices, making predictions difficult.

Table A 8: Raw material prices for battery materials. Prices taken from [219].

Material	Raw mat./ \$/kg	Lithium \$/kg	Nickel \$/kg	Cobalt \$/kg	Mn/Al \$/kg
Price per kg		16.50	10.83	55.25	2.06
NMC 1:1:1	14.30	1.19	2.20	10.49	0.42
NCM 6:2:2	11.62	1.19	3.93	6.71	0.23
NCM 8:1:1	9.89	1.19	5.23	3.35	0.12
NCA 8:1.5:0.5	11.59	1.19	5.29	5.08	0.03
NCA 9:0.5:0.5	8.87	1.19	5.96	1.69	0.03
Aluminum	1.93				
Copper	6.18				

Figure A 4 compares the price trends of the materials shown in **Table A 8** over the past 40 years. The strong price fluctuations could have been caused by a variety of factors, including an increased demand for a commodity, climate change, catastrophes, oligopoly, economic crisis or political instability in the countries of raw-material suppliers. Yet even with all these variables, the rule of supply and demand still stands: an increase in demand for batteries will increase the price of battery materials. These price changes will continue to affect all battery production, as both ASSBs and batteries with liquid electrolytes use the same group of cathode materials.

An entirely accurate assessment of the second factor, battery production costs, can be difficult, as reliable numbers are hard to come by when there is only scarce information published to estimate the production costs. Nonetheless, a rough estimate can be made using the information that is available, such as construction and energy demand of the factory, and employee costs.

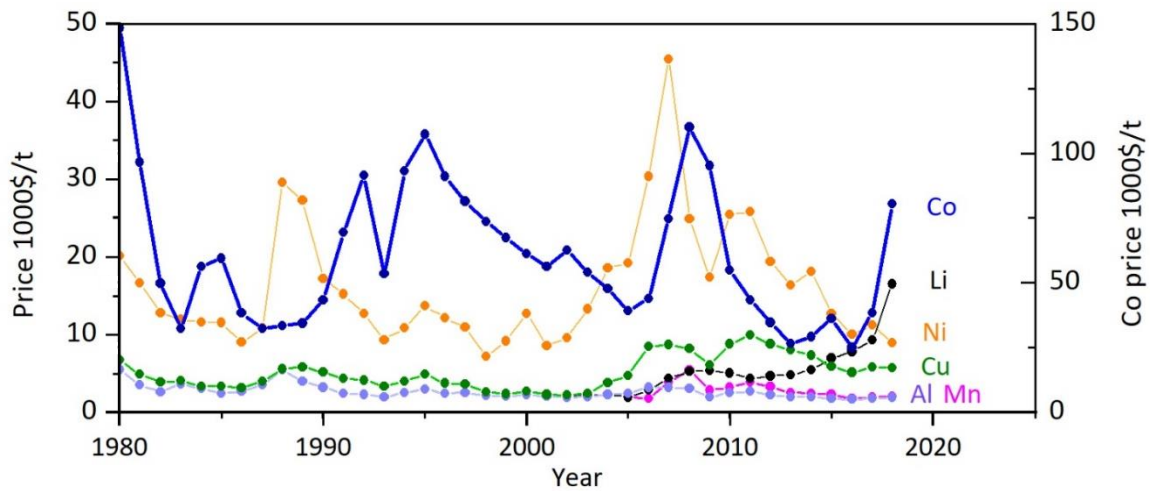


Figure A 4: Evolution of various prices of materials needed for battery fabrication from 1980 to 2018. Values taken from [219].

Take the “Gigafactory” by Tesla, for example. Erected in Nevada, the construction costs of this factory are estimated to be around \$ 5 billion. As the energy demands of the factory are fully covered by renewable energies, the only other major factor that needs to be considered is the salary of the employees. Tesla plans to employ around 6,500 people to build batteries with a capacity of 35 GWh per year. If it is assumed that the production will last for 10 years and each of the employees causes the average labor expense of \$ 38/h (estimated from [226]) and average annual hours worked [227], each employee causes costs of \$ 67,640 per annum and the annual production cost in the “Gigafactory” will be \$ 940 million, resulting in production costs of \$ 27/ kWh. As the company wants to generate profit, the number will be somewhat higher than the estimated value but less than 50 % of the final battery price and the prices given by Ulvestadt. Looking at data from **Table A 8**, it can be expected that upon replacing costly components, batteries will eventually reach the cost parity line. If Tesla reaches the goal of producing 50 GWh per year for more than 10 years, the production cost will further be reduced [228].

Table A 9 summarizes the specifications of conventional state-of-the-art batteries. In conclusion it can be said that besides the charging time, even conventional batteries can be sufficient to realize electric mobility. Especially the charging time will be one factor that ASSB cannot enhance as long as no advanced electrode and electrolyte materials are used. At this

juncture, most solid electrolytes have inferior an ionic conductivity than liquid electrolytes and charging might take longer.

Table A 9: Specifications of a state-of-the art battery for Tesla Model S 100D (conservative estimations) with a theoretical driving range of 500 km.

Volume / L	261.5
Weight / kg	708
Charging time (to 80 %) / h	0.5
Cost per kWh / \$	136
Life time / km	>1.2 million

Yet still consumers are not convinced to buy electric vehicles and currently electric mobility seems to be star-crossed. Although their characteristics are sufficient for electric vehicles, the discussion of batteries ignores one important factor: safety. Concerning batteries, safety is only discussed when negative events draw attention to it. Mobile phones that start to burn because their batteries experienced a thermal runaway are but one problem. Unfortunately, there are few studies on battery safety in cars, for conventional or electric.

The study of car battery safety is lacking because it depends on perceived values rather than concrete ones, as well as because too few electric vehicles are sold to track trends and draw significant conclusions. This should not discount the importance of consumer safety. Buyers deserve to know, for example, how many vehicles catch fire and how dangerous the battery can be in case of a fire. A study could address the flammability of a battery's liquid electrolyte, which is comparable to that of fuel. Even if only 1 out of 1 million battery cells experienced a thermal runaway and began to burn – taking into account that there will be around 8,300 battery cells in a car – it could cause 1 out of 120 electric vehicles to burst into flames. It might be a negligible fraction of risk for the battery manufacturer; but for the car owner could mean life-changing loss.

Consider the safety of lithium-based batteries in electric vehicles. Batteries based on lithium metal are employed because these batteries have a higher voltage compared to cells with carbon anode. Only by applying lithium metal can batteries achieve energy densities that will make electric vehicles competitive to vehicles with ICE. Amorphous carbon can reversibly take up to 0.6 lithium atoms per formula unit C_6 , resulting in a specific capacity of

200 mAh/g with respect to the active material. Lithium metal, however, has the highest gravimetric capacity (3860 mAh/g) and a volumetric capacity of 2100 mAh/cm³. These values correspond to the pure lithium metal, as no host structure is needed. As the space is limited in vehicles and the weight will influence the energy consumption, reducing both weight and volume of the battery is necessary and carbon electrodes will have to be replaced by lithium metal. Using pure lithium, however, increases the risk of flammability in a battery and consequently reduces the safety of a vehicle.

Car manufacturers believe that the application of ASSBs in electric vehicles will bring about significant progress in terms of battery safety. This hypothesis is built on the knowledge that solid electrolytes have a higher electrochemical stability than liquid electrolytes and are largely based on oxide materials, which are not flammable and can bear higher temperatures. This will provide manufacturers with less liability, and consumers with a greater peace of mind.

Appendix C

Nyquist plot of the „LiPON“ thin-films

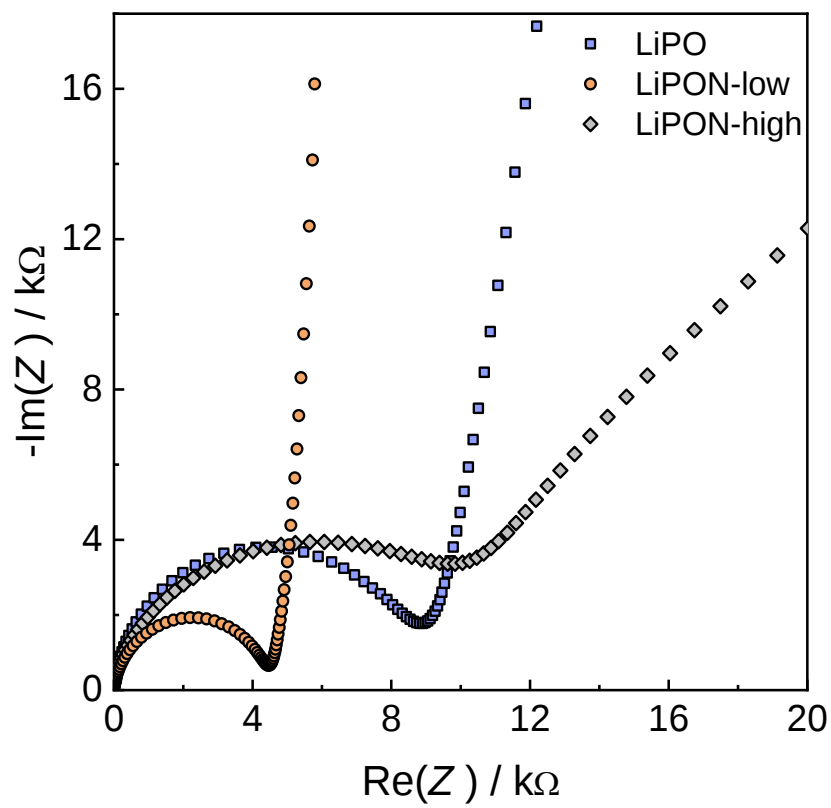


Figure A 5: Nyquist plot of the three examined „LiPON“ films.

Appendix D

XPS-Spectra of “LiPO(N)” samples

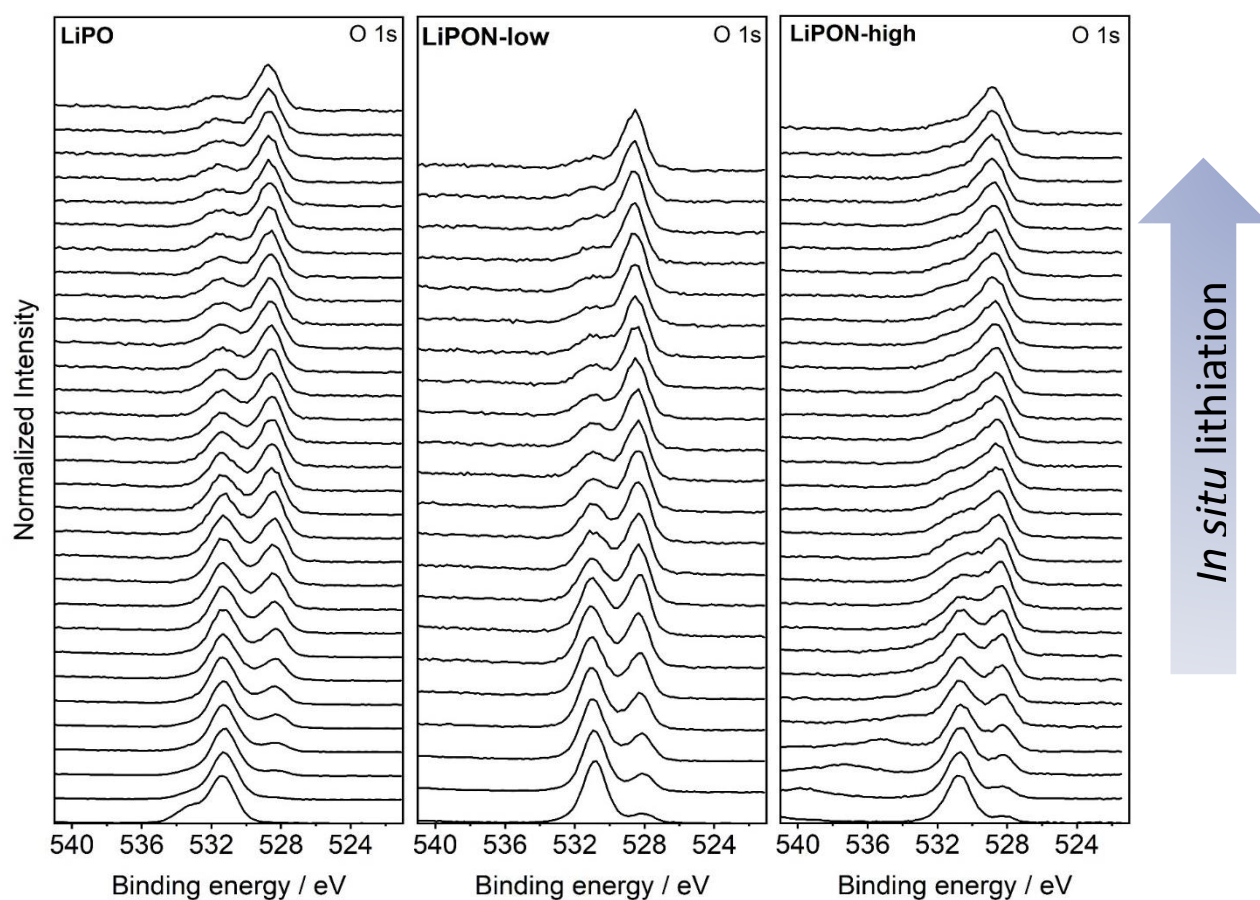


Figure A 6: Evolution of the O 1s signal during the lithiation experiment.

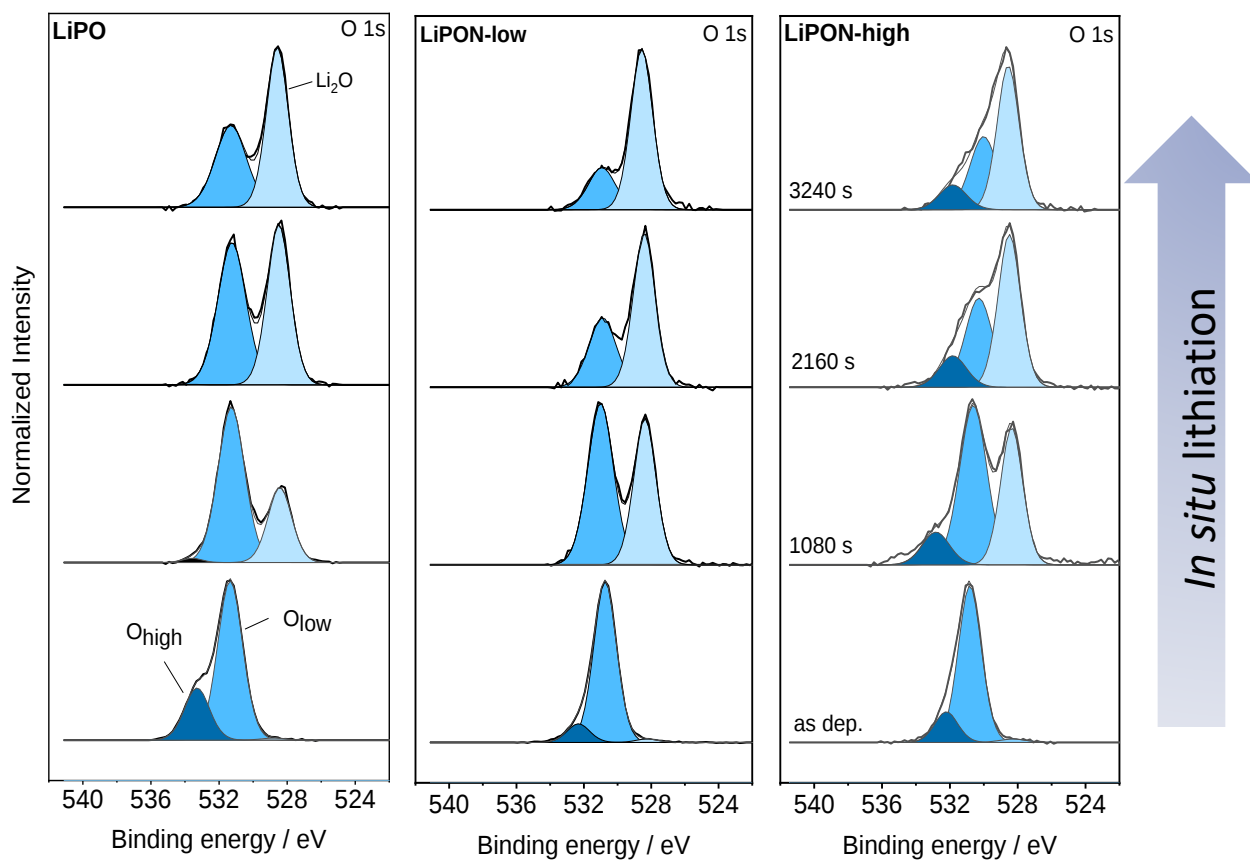


Figure A 7: Evolution of the O 1s signal during the lithiation experiment. The bridging oxygen vanishes rather quickly after the beginning of lithiation. Instead Li₂O is formed.

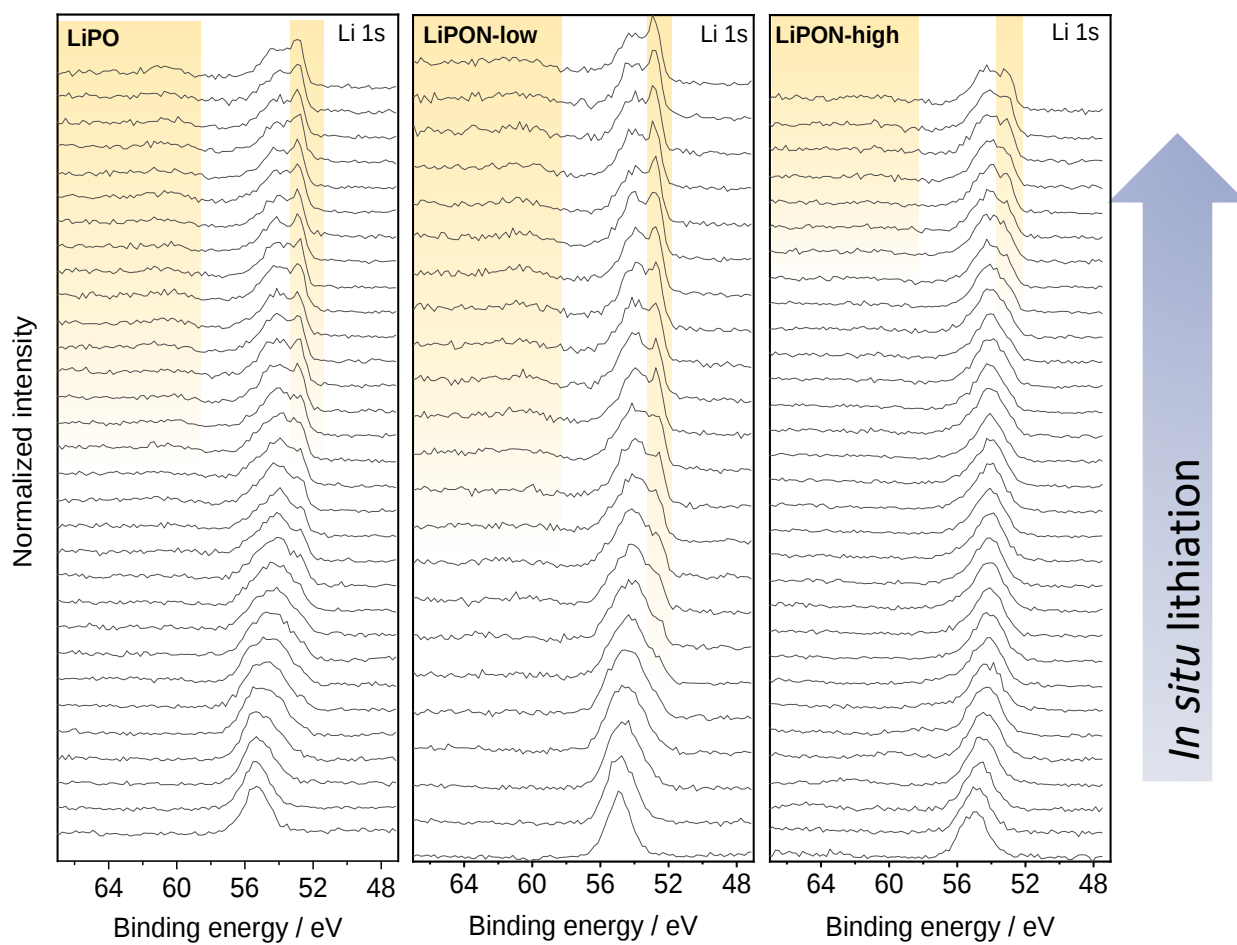


Figure A 8: Evolution of the Li 1s signal during the lithiation experiment.

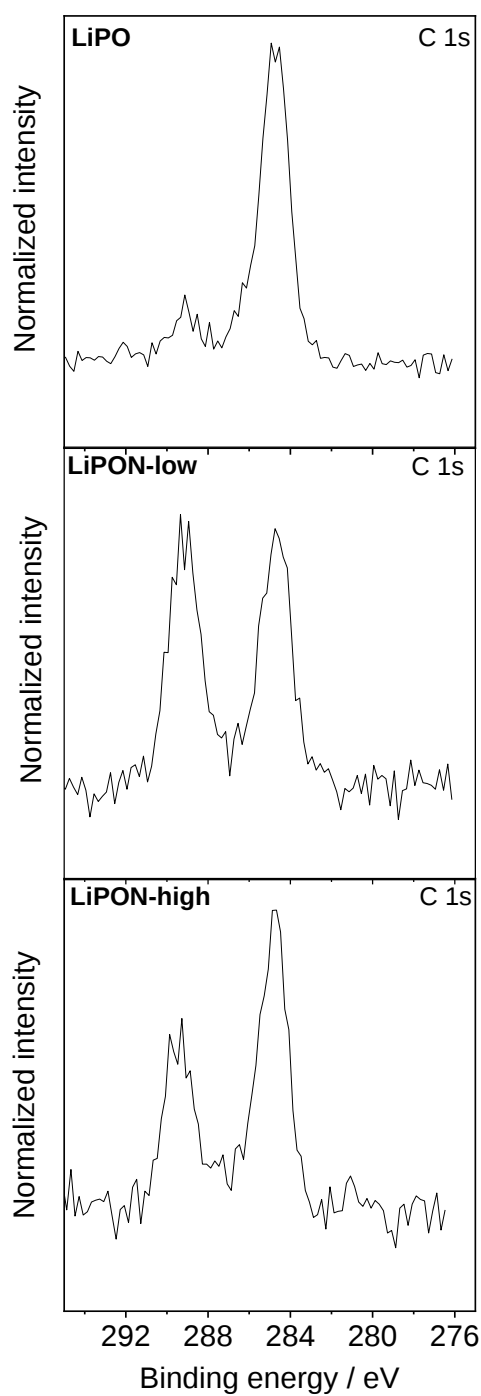


Figure A 9: C 1s signal of the pristine LiPO(N) samples.

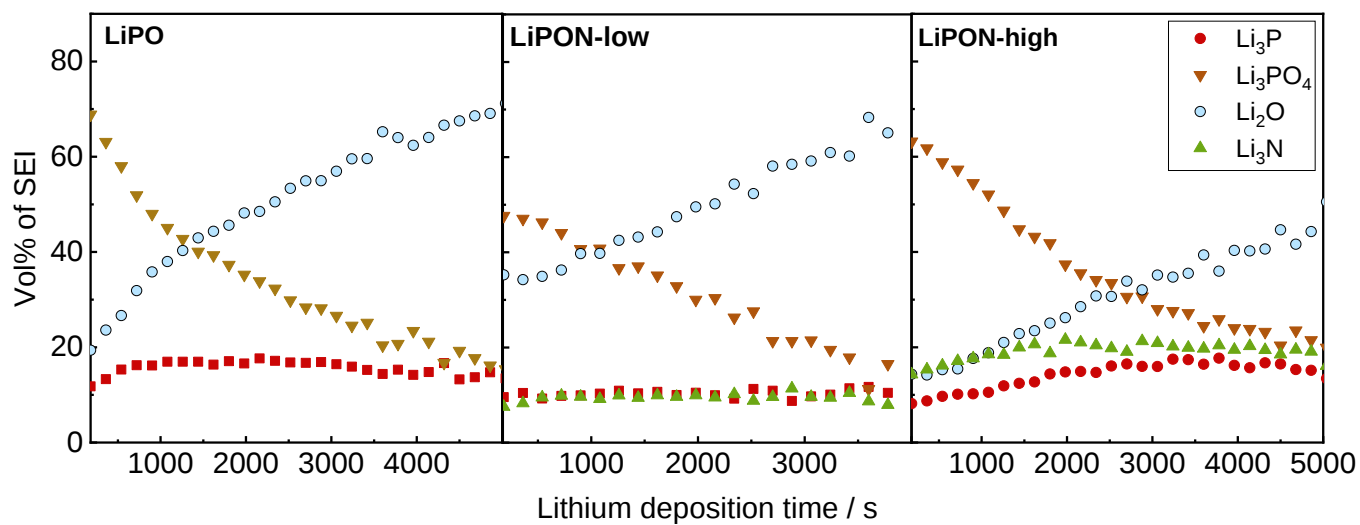


Figure A 10: Change of the average volume fractions of the reaction products in the SEI as determined from the intensities of the XPS signals.

Appendix E

Estimation of the theoretical SEI thickness in „LiPON“

It is possible to estimate the SEI thickness in dependence of the thickness of the deposited lithium layer in the case of a kinetically unhindered growth.

If the thickness of the deposited lithium is known, the thickness of the formed SEI can be calculated. The calculation is fairly simple using the molar volumes of lithium and the SEI components (**Table A 10**). However, a few assumptions have to be made for reasons of simplification:

First, 100 % density of the interphase, the „LiPON“ film and the deposited lithium layer is assumed. In addition, it is assumed that the growth is only in z -direction whereas there is no expansion (or contraction) along the x - and y -direction.

For the estimations also fully crystalline components and a formation of only Li_3PO_4 and the binary compounds are assumed.

First an electrolyte area, which is covered by lithium and in which the electrolyte will decompose needs to be defined. All calculations presented below are normalized to an area of 1 cm^2 .

It is also assumed that there are no impurities in the lithium or the electrolyte. However, carbon impurities derived from the stoichiometry of the electrolyte films can easily be included. For reasons of simplification, they are excluded in this calculation. Two different possibilities for the SEI formation are considered:

- i) The interphase consists of the binary compounds Li_3N , Li_3P and Li_2O (equation 26).

- ii) The interphase consists only of Li_3PO_4 , Li_3P (and Li_3N) but Li_3PO_4 does not decompose into Li_3P and Li_2O (equations 25, 27, 28).

The decomposition into Li_3PO_4 and Li_3N should describe a lithium-insufficient reaction, where a complete decomposition does not occur. The decomposition into the binaries describes a reaction path where enough lithium is present.

Table A 10: Molar volumes of the SEI components.

Molar volume / $\text{cm}^3 \text{mol}^{-1}$				
Li_3PO_4	Li_3P	Li_3N	Li_2O	Li
45.591	36.599	25.239	14.866	12.998

For each reaction path the calculation will be given for $\text{Li}_{1.34}\text{PO}_{3.41}$ („LiPO“) exemplarily.

- i) Formation of Li_3N , Li_3P and Li_2O .

If a Li layer thickness of 1 nm is assumed, the volume of deposited lithium is $1 \cdot 10^{-7} \text{ cm}^3$, which equals $7.693 \cdot 10^{-9} \text{ mol}$.

When 1 mol „LiPO“ decomposes completely into the binary compounds, 1 mol Li_3P and 3.41 mol Li_2O are formed. For this reaction, 9.82 mol of lithium are needed. The electrolyte already delivers 1.34 mol; therefore, 8.48 mol Li are still needed to complete the reaction.

A one nanometer thick Li layer contains enough lithium to convert $9.073 \cdot 10^{-10} \text{ mol}$ $\text{Li}_{1.34}\text{PO}_{3.41}$ into the binary compounds.

The reaction thus leads to the formation of $9.073 \cdot 10^{-10} \text{ mol}$ Li_3P and $3.094 \cdot 10^{-9} \text{ mol}$ Li_2O . Taking the molar volumes of these binary components, the entire SEI volume therefore must be $7.920 \cdot 10^{-8} \text{ cm}^3$, resulting in an SEI thickness of 0.792 nm.

The same calculation for $\text{Li}_{1.30}\text{PO}_{1.62}\text{N}_{1.29}$ („LiPON-high“) leads to an interphase thickness of 0.814 nm. The higher molar volume of Li_3N is compensated by the fact that 50 % more lithium are needed to form Li_3N instead of Li_2O . The influence of the electrolyte composition on the thickness of the interphase is smaller than the measuring error.

ii) Formation of Li_3PO_4 .

A reaction according to equation 25 is assumed and also a 1 nm thick Li layer. Taking the molar volume of Li_3PO_4 and Li_3P , the resulting interphase will be 0.413 nm thick. Compared to the complete conversion into the binary compounds the SEI thickness is much smaller.

The same reaction for $\text{Li}_{1.30}\text{PO}_{1.62}\text{N}_{1.29}$ leads to a 0.641 nm thick SEI.

When Li_3PO_4 does not decompose, the resulting SEI is smaller than in i) but the influence of the electrolyte composition on the SEI thickness is stronger. The reason is that in the case of i) for each Li_3PO_4 molecule one molecule Li_3P and 4 molecules Li_2O are formed which require more space. When O is replaced by N, less Li_3PO_4 is formed but Li_3N and Li_3N has a higher molar volume.

Appendix F

Effective attenuation lengths for “LiPO(N)” and the SEI components

Table A 11: Effective attenuation lengths for P 2p (KE = 1354 eV) in “LiPO(N)” and the different SEI components. Values are determined for Al-K α -radiation (middle) and corrected by the photoelectron emission angle with respect to the surface normal (right).

	EAL (practical 0–4 nm, P 2p, Al)	• cos 45
LiPO ₃	3.02	2.14
LiPON-low	2.95	2.09
LiPON-high	2.93	2.07
Li ₃ PO ₄	3.41	2.41
Li ₃ N	3.23	2.28
Li ₃ P	3.24	2.29
Li ₂ O	3.25	2.29
Lithium	5.07	3.59

Appendix G

X-ray photoelectron spectroscopy of P_3N_5 powder

The P 2p signal showed one single signal at a binding energy of 132 eV – 136 eV (Figure A 11). This signal was slightly asymmetric toward higher binding energies and two contributions were used to fit the data (each consisting of two Gaussian peaks due to the peak splitting into P 2p_{1/2} and P 2p_{3/2}). The first contribution (brown and yellow) at 133 eV and 134 eV is attributed to the one phosphorous species present in P_3N_5 . The second contribution (black and grey) at higher binding energies suggests that phosphorous was slightly oxidized. As the powder also contained certain fractions of oxygen, it is assumed that this contribution is due to P–O bonds at the surface of the powder particles. To account for small discrepancies of the measured signals from the ideal Gaussian/Lorentzian shape of the photoemission lines, it was however necessary to add a very small second component at lower binding energies as was also done for the P 2p signal of „LiPON“.

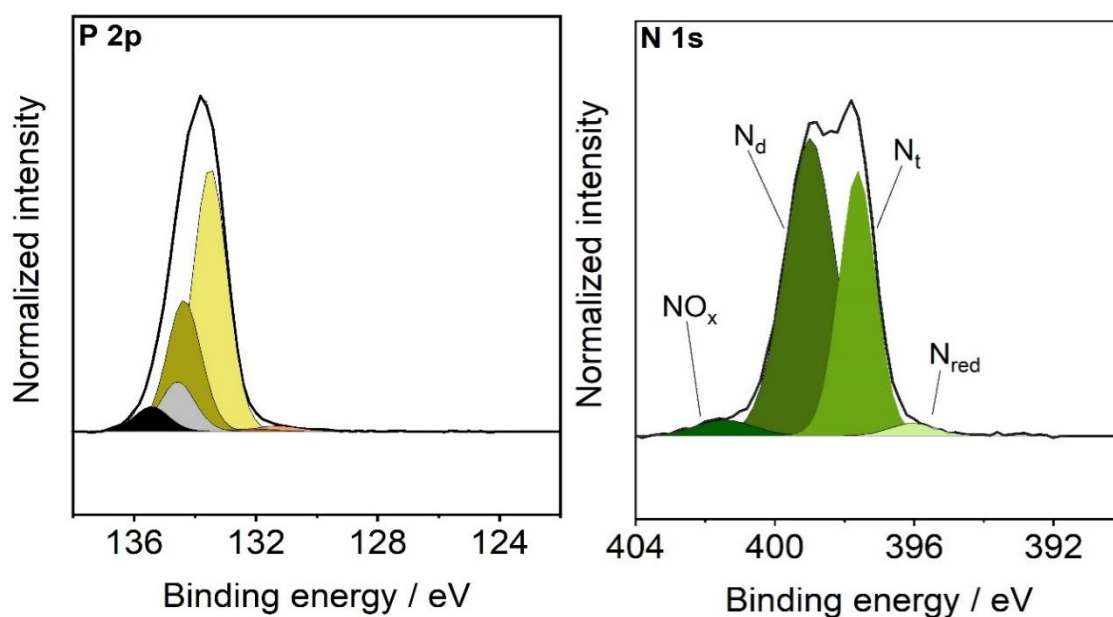


Figure A 11: P 2p and N 1s detail spectra of pristine P_3N_5 powder.

The P_3N_5 structure contains two different nitrogen species: Nitrogen that is coordinated by two phosphorous atoms (N_d) and nitrogen that is coordinated by three phosphorous atoms (N_t). In the perfect P_3N_5 structure, as is the case in the examined powder, the ratio of these species is $N_d:N_t = 3:2$.

For nitrogen, four different chemical species could be identified in the spectrum, two large contributions at 399.5 eV and 397.5 eV and two minor contributions at 396 eV and 401.5 eV. It is assumed that the two major contributions are due to the two different nitrogen species in P_3N_5 . The larger one (medium dark green) is due to N_d and the medium green contribution is due to nitrogen N_t . The ratio of the integrated intensity of these two major contributions is 60:40 which is in accordance with the theoretical assumptions. The minor contribution at 401.5 eV is attributed to NO_x . As there is a certain amount of oxygen in the powder, the existence of P-O as well as N-O can be expected. This oxygen incorporation can originate from the synthesis of the powder. The amount of oxygen determined by XPS is around 10 at%. The manufacturer *Alfa Chemistry* states that less than 0.1 % water can be found in the product and it can be assumed that the oxygen stems from a reaction between water and the powder. The oxygen that was detected appears to be significant but as XPS is a very surface-sensitive technique and only detects the topmost few nanometer of the material, even slight impurities on the powder surface can cause high signal intensities. The average oxygen content may be much lower. As the X-ray diffractogram does not indicate the presence of large quantities of impurities (**Appendix H**), it can be assumed that the oxygen is indeed only at the surface. The surface of the powder has been exposed to environmental atmosphere and it cannot be excluded that the surface is slightly oxidized.

A fourth contribution to the nitrogen signal can be found at 396 eV. It is only a small contribution causing a broadening of the base of the N_t signal toward lower binding energies. This signal is close to the position of Li_3N (as will be discussed later) and could be attributed to nitrogen at the surface of the powder particles. Nitrogen at the surface of an P_3N_5 particle should have unsaturated bonds as corresponding P binding partners are missing.

In situ XPS

Only if the material reacts with lithium metal and forms Li_3N and Li_3P , P_3N_5 can be employed as sacrificial interlayer. At first the stability of this material had to be examined. As in the case of „LiPON“, the *in situ* XPS experiment was used to validate the behavior. The powder was examined first to get an internal reference for the behavior of the thin-films and then the same examinations were carried out on the thin-films. Lithium has been sputtered on top of the powder for 9000 s. Each single sputtering step had a duration of 300 s. The elemental spectra of P 2p and N 1s before sputtering and after 3000 s, 6000 s, and 9000 s are shown in **Figure A 12**. The phosphorous signal show big changes over time. Upon Li deposition, phosphorous is reduced. The P–O signal at 135 eV (black and grey) vanishes immediately so it can be assumed that this species does only originate from a thin surface layer that is reduced in contact with lithium immediately. The evolution of two new signals can be observed, one signal at 130 eV – 132 eV and a second one at 127 eV. With respect to the previous examinations on „LiPON“ (cf. section 4.1) these signals can be attributed to the stepwise formation of Li_3P . The intensity of both signals increases during Li sputtering. According to the „LiPON“ examinations, where Li_3PO_4 reacts with lithium and forms a lithium polyphosphide Li_xP_y followed by the reaction to Li_3P , a similar phosphorous reduction can be expected in the case of P_3N_5 . As the amount of lithium during each sputtering step is limited, a formation of a lithium polyphosphide layer with a lower lithium content than Li_3P is plausible. However, a binding energy of 131.5 eV is higher than typical values of phosphorous with a negative oxidation number and a complete reduction of phosphorous from +5 to 0 and further during the deposition of a small amount of lithium is unlikely. In addition, the width of the signal is around 6 eV. It can therefore be expected that this signal consists of the overlapping contributions of various partially lithiated phosphorous species. These signals are hard to deconvolute. It is possible that upon lithiation P_3N_5 forms lithium phosphorous nitride. There are various species with different lithium content e.g. $LiPN_2$ [191], Li_7PN_4 [191], $Li_{18}P_6N_{16}$ [175], $Li_{12}P_3N_9$ [156] and $Li_{10}P_4N_{10}$ [221]. With such a variety of the stoichiometry, it is likely that one of these species is formed during *in situ* lithiation, especially as no change of the oxidation state of P (+V) occurs during lithiation and therefore shifts of the P 2p signal should only be minor. XPS examinations on these components have not been carried out yet, so a precise assignment is not possible. For

that reason, this contribution is denoted as $Li_xP_yN_z$.

The nitrogen signal also changes during lithium deposition. The NO_x signal vanishes like the P–O signal, another indication that the impurities exist only at the topmost surface layer. The intensity of the N_{double} signal increases over time, but the N_{triple} signal does not show a significant change. However, a new nitrogen species at a lower binding energy of 395 eV is formed. Again, this behavior can be compared to the behavior of „LiPON“. When P_3N_5 reacts with lithium, lithium nitride is formed. The change of the intensities of the two N species in P_3N_5 suggests that the P–N–P nitrogen species is less stable than N_{triple} . It is possible that the presence of lithium causes the breaking of a P–N–P bond. The broken bond is “unsaturated” and probably more reactive than the N_{triple} bond and therefore lithium preferentially reacts with the “unsaturated” nitrogen. It may also be possible that another stepwise reaction of N takes place but the signal intensities of Li_xN species is overlapping with the N_{triple} signal and cannot be deconvoluted.

In the case of a powder where the sample surface is large, a large amount of lithium is needed for the reaction. Even after 9000 s of lithium deposition, the decomposition reaction is not finished yet. Li_3P and Li_3N could be observed but also partially lithiated polyphosphides $Li_xP_yN_z$ and the P and N species of the thin-films are still visible. However, although the reaction is not completed, the presence of Li_3N and Li_3P suggests that the formed interphase – if there is enough lithium to react – will only consist of the binary species Li_3N and Li_3P and therefore exhibit a high ionic conductivity and a beneficial influence on the battery performance.

The oxygen signal contains two components at binding energies of 531.5 eV and 533 eV (**Figure A 13**). As pure phosphorous nitride should be free from oxygen, it is assumed that the oxygen stems from partial substitution of the two nitrogen species of P_3N_5 due to humidity during the synthesis and handling of the material. For the discussion the species at 533 eV is labelled O_{high} and the species at 531.5 eV is labelled O_{low} . In contact with lithium metal the intensity of the O_{high} signal decreases drastically. As the same observation is made for the N 1s signal, the assumption that this signal stems from doubly coordinated oxygen (P–O–P bonds) is plausible and it can therefore be assumed that O_{low} is caused by triply coordinated oxygen.

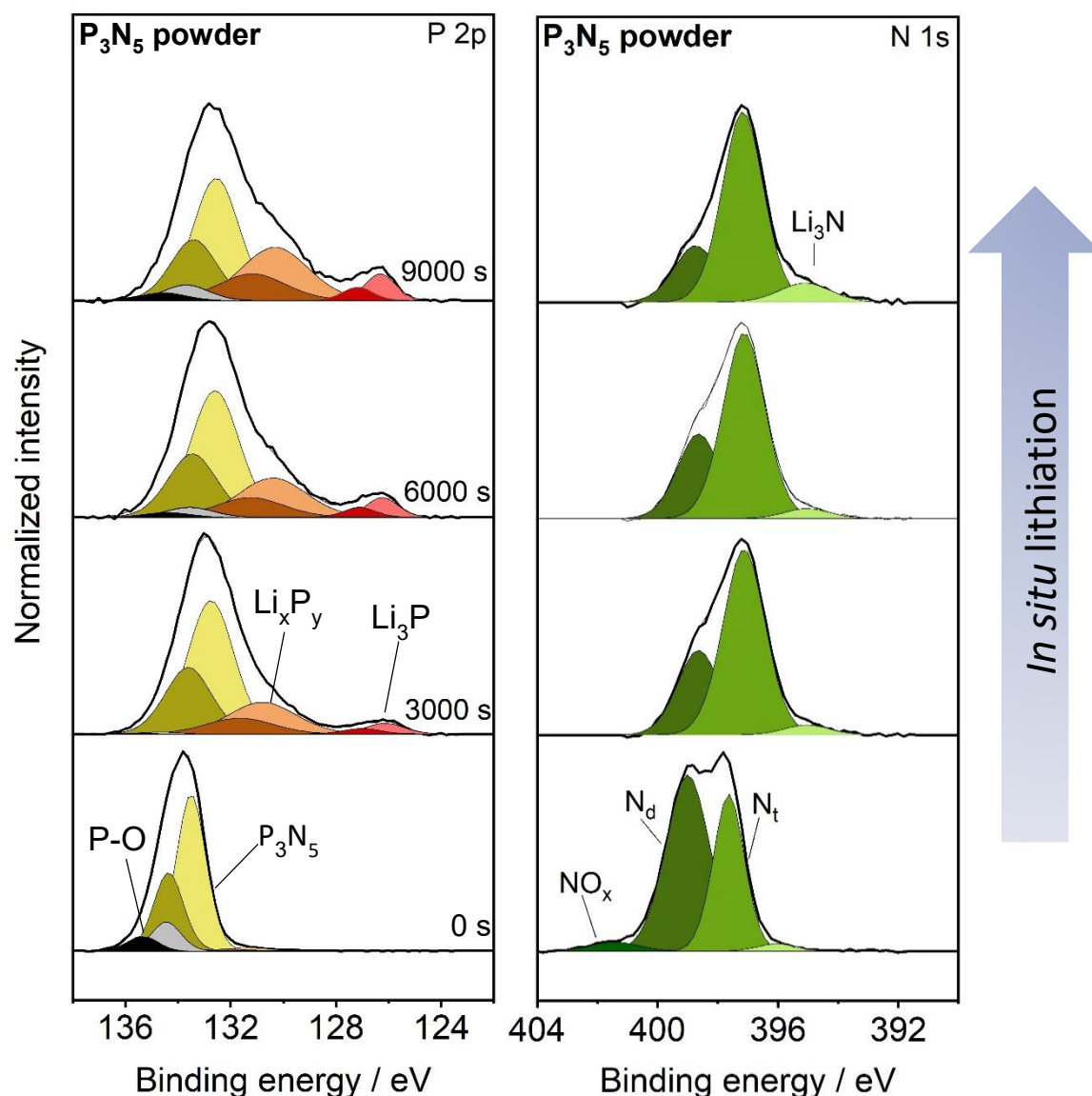


Figure A 12: Evolution of the P 2p and N 1s signal of P_3N_5 powder during *in situ* lithiation. Phosphorous is reduced and the formation of Li_3P via lithium polyphosphides $Li_xP_yN_z$ can be observed. In addition, Li_3N is formed.

The P-O-P bond seems to be more likely to break in contact with lithium metal but the XPS signals are difficult to judge as the partial reduction of O_{high} may lead to a signal that overlaps with O_{low} . The formation of a third signal at a binding energy of 528.2 eV can be seen. This signal is attributed to lithium oxide. Due to the different chemical environment, the binding energy of this signal is around 0.5 eV lower than in „LiPON“. As in the case of „LiPON“ also LiOH may be formed that cannot be distinguished from Li_2O due to the blindness of the detection method for hydrogen. The absolute intensities decrease by around 12 % over the

duration of the *in situ* experiment but a significant diminishing as caused by the growth of a dense overlayer cannot be seen.

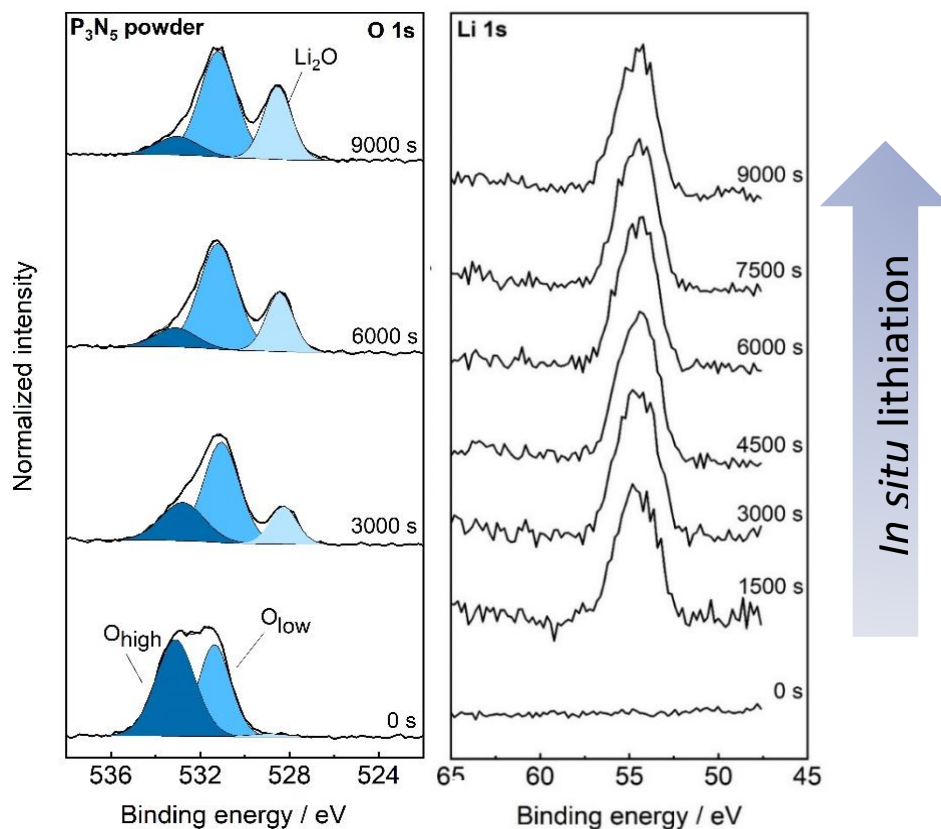


Figure A 13: Evolution of the O 1s and Li 1s signal during *in situ* lithiation of P_3N_5 powder. The O_{high} signal is decreasing whereas Li_2O is formed. The Li 1s signal does not indicate the evolution of lithium metal suggesting that the reaction is still proceeding after 9,000 s.

As long as the reaction does not cease and lithium continues to react with phosphorous nitride, the formation of lithium metal is not observed (**Figure A 13**). Even after 9000 s of lithium deposition, the reaction still proceeds as no indication for the presence of Li metal in the signal can be made. There is neither a sharp increase of the Li signal at low binding energies nor the formation of plasmons at higher binding energies. As discussed in **chapter 4.1**, the formation of lithium metal goes along with trapping of water from the chamber atmosphere and the increase of the oxygen signal. The O/P ratio in dependence of the lithium deposition time is shown in **Figure A 14**. Even the pure powder has an O/P ratio of 0.7. In contrast to „LiPON“ (**Figure 31**) where the O/P ratio shows a strong increase, the O/P ratio of the phosphorous nitride powder increases slowly but linearly. The linear increase

suggests that although oxygen is trapped, the phosphorous nitride signal is not dampened exponentially by an overlayer.

The reason for the low damping of the signal is that the XPS signal is an average over a certain surface area as well as the lithium deposition rate is an average value over a certain area. A rough inhomogeneous powder surface needs more lithium to react than a smooth thin-film surface. In addition, the rough surface leads to local differences of the lithium deposition rate and the conversion reaction. Parts of the powder surface that are directed toward the lithium surface will react faster than parts that are not directed toward the lithium surface. These parts may soon develop a passivating overlayer which then leads to the formation of lithium metal and Li_2O , whereas other parts still react with lithium and form Li_3N and Li_3P . In that case, the O/P ratio does only show minor changes.

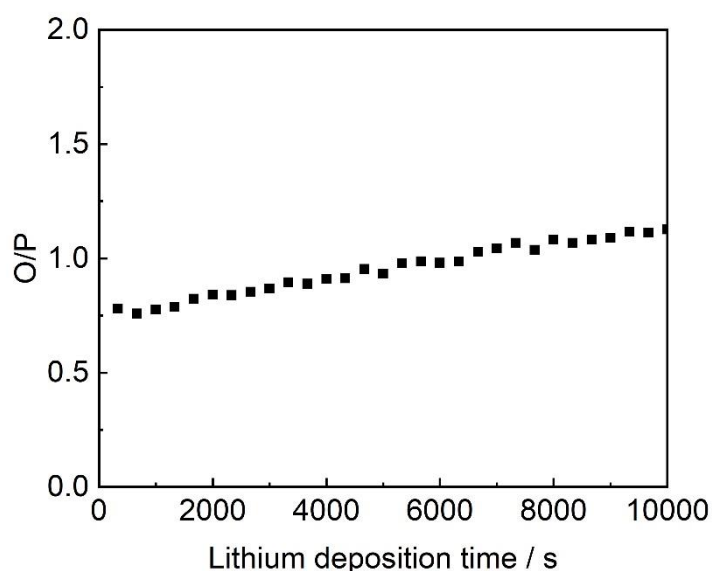


Figure A 14: Evolution of the O/P ratio of P_3N_5 powder. The change of the ratio is slow, suggesting that the interphase formation of P_3N_5 powder is not finished after 10,000 s and hardly any reaction with water takes place.

In conclusion it can be said that phosphorous nitride reacts with lithium metal under forming Li_3N and Li_3P . Due to the large amount of powder and the surface area the reaction did not cease during the time-frame of the experiment. However, it can be expected that the examination of the thin-films with a smaller surface area shows a passivation of the surface (cf. chapter 4.2).

Appendix H

X-ray powder diffractogram of phosphorous nitride powder

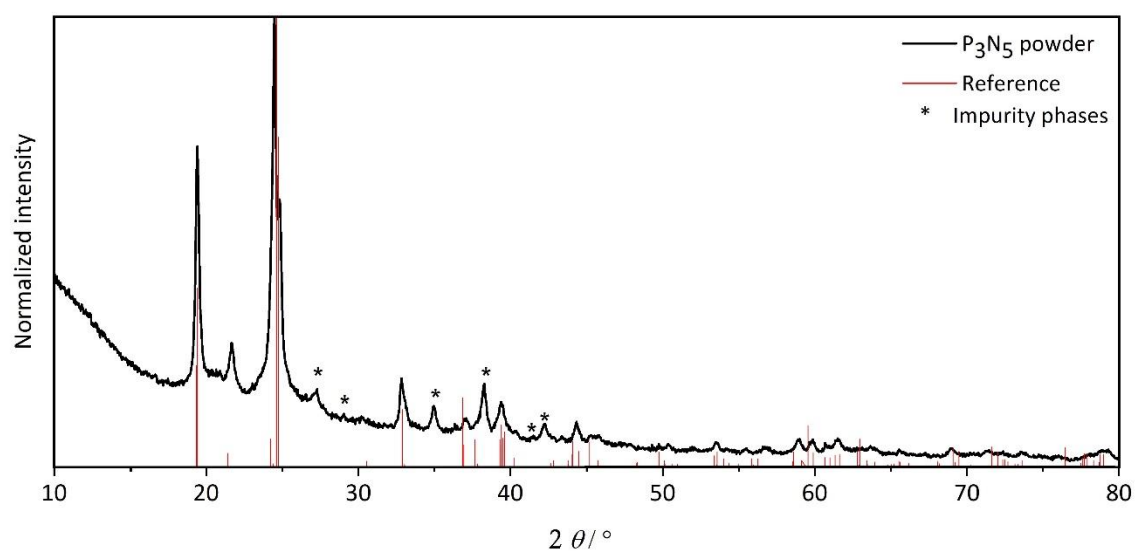


Figure A 15: X-ray diffractogram of the P_3N_5 powder. Reflections that are not due to P_3N_5 are marked with *.

Appendix I

Impedance spectra of assembled all-solid-state batteries

The Nyquist plot of the batteries directly after cell assembly shows that there is only one semicircle, which can be attributed to the electrolyte, whose resistance is almost the same for the battery with and without interlayer. Both cells also show a second, very small semicircle in the mid-frequency range. This contribution is bigger in the battery with interlayer. It can be assumed that this contribution is due to the applied interlayer. In the battery without interlayer, the SEI formation has started but is not finished yet and the contribution is small. In the battery with interlayer, the conversion of the interlayer is not finished yet and the highly resistive P_3N_5 layer still exists. The linear contribution at low frequencies is due to the lithium|electrolyte interface that has not formed an intimate contact yet.

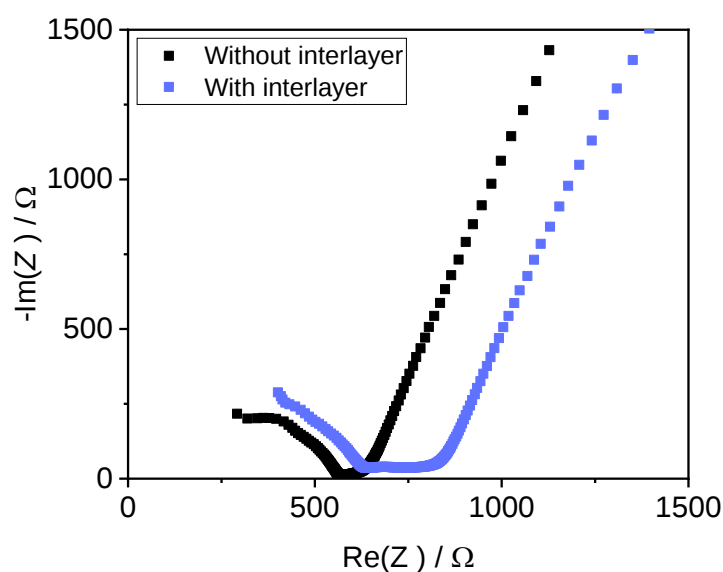


Figure A 16: Nyquist plots of ASSBs with (blue) and without (black) interlayer directly after cell assembly.

Appendix J

Copper nitride as sacrificial interlayer

All films were deposited by radio-frequency magnetron sputtering. All depositions were done at room temperature under variation of the gas composition and the sputtering power. The deposition parameters are summarized in **Table A 12**.

Table A 12: Deposition parameters for Cu₃N.

Sample	1	2	3	4
Substrate	FG	FG	FG	FG
Base pressure / mbar	$1.20 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$
Working pressure /mbar	$3.00 \cdot 10^{-2}$	$3.00 \cdot 10^{-2}$	$4.20 \cdot 10^{-2}$	$4.20 \cdot 10^{-2}$
Gas	Ar / N ₂	Ar / N ₂	N ₂	N ₂
Gas flow / sccm	70 / 30	70 / 30	200	200
Power / W	100	30	100	30
RF-Bias / V	240	130	112	111
Sputtering time / min	10	10	10	10

The film quality was examined via SEM. As can be seen in **Figure A 17**, the film consists of needle-shaped particles with a size of around 200 nm. This film was deposited for 10 min with the parameters of sample 1 in **Table A 12**. As can be seen, with a sputtering power of 100 W even 10 min of deposition result in a dense film. For the application as interlayer a smaller sputtering power of 30 W may result in a homogeneous film thickness and smaller particles.

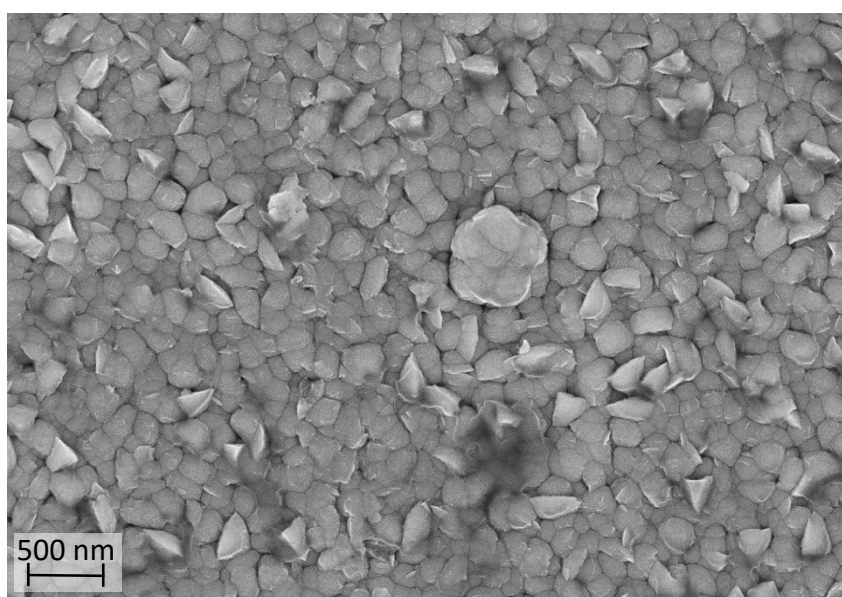


Figure A 17: SEM image of a Cu₃N film deposited by sputtering deposition.

From XPS measurements the nitrogen content of the films could be determined. It is in good agreement with the theoretical value of 25 % for all different deposition parameters. Also the reaction between Cu₃N and Li was examined via XPS. **Figure A 18** shows the XPS spectra of the elemental signals of Li, N, O and Cu, and the copper LMM Auger signal during the *in situ* experiment and a comparison of the copper signals to copper foil. The N 1s signal of Cu₃N shows one peak at 398 eV belonging to the one nitrogen species in Cu₃N. In contact with lithium metal this signal immediately shifts to a lower binding energy of 396 eV, corresponding to the formation of Li₃N. Simultaneously, the Cu 2p_{3/2} signal also shifts from 933.5 eV to 931 eV, suggesting the reduction of Cu₃N to metallic copper.

The same behavior can be observed for the Cu LMM Auger line. A comparison of the initial and final Cu LMM line with copper foil shows that the final copper signal is similar to the one of the copper foil. Therefore, it can be deduced that copper is completely reduced. During the experiment the evolution of the lithium signal is observed, too. It has to increase because lithium is deposited on top of the substrate. However, although the intensity increases, neither the evolution of Li^0 nor the existence of plasmons in the Li 1s signal is observed, therefore it is assumed that the reduction reaction is not fully completed and lithium is still oxidized. The oxidation of lithium can be attributed to the reaction with water again. There are always small impurities of oxygen in the Cu_3N films because the formation of CuO instead of Cu_3N from water in the sputtering chamber during the deposition which creates much stronger bonds. At the beginning the oxygen signal consists of only one contribution attributed to CuO. During lithiation, a second contribution – Li_2O – arises. As the intensity of the oxygen signal of CuO does not seem to change over time, it is assumed that this component is not responsible for the formation of Li_2O . Instead, in accordance with **chapters 4.1** and **4.2** the lithium oxide formation originates from residual water in the XPS chamber

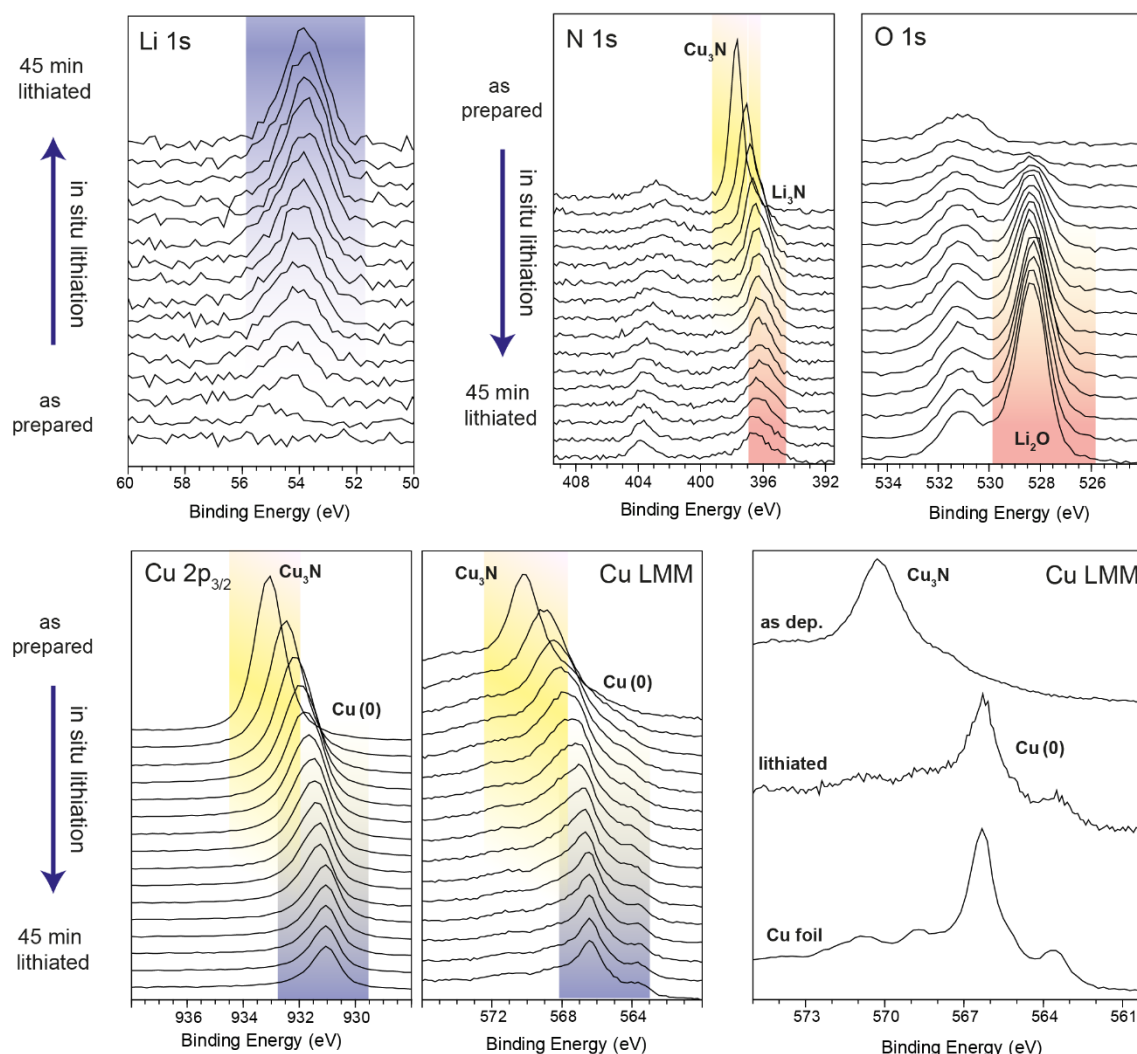


Figure A 18: *In situ* XPS measurements of Cu_3N . Upper left: Lithium signal. Center: nitrogen signal. Upper right: oxygen signal. Lower left: $\text{Cu } 2p_{3/2}$ signal. Center: Cu LMM signal. Lower right: Comparison of as deposited and lithiated Cu_3N with copper foil.

After clarifying the conversion reaction, the next step is to examine the protective effect of Cu_3N on the lithium|electrolyte interface. For this an LPS pellet (150 mg) was made and Cu_3N was deposited on both sides before pressing a piece of lithium foil (*Rockwood Lithium GmbH*, diameter = 6 mm) on either side of the pellet. The foil was contacted with nickel current collector tabs and sealed in a pouch bag. Then time dependent impedance measurements for more than 400 h (2000 measurements) at room temperature were performed. A reference pellet from the same electrolyte powder using the same lithium foil but without Cu_3N layer in between was prepared, too.

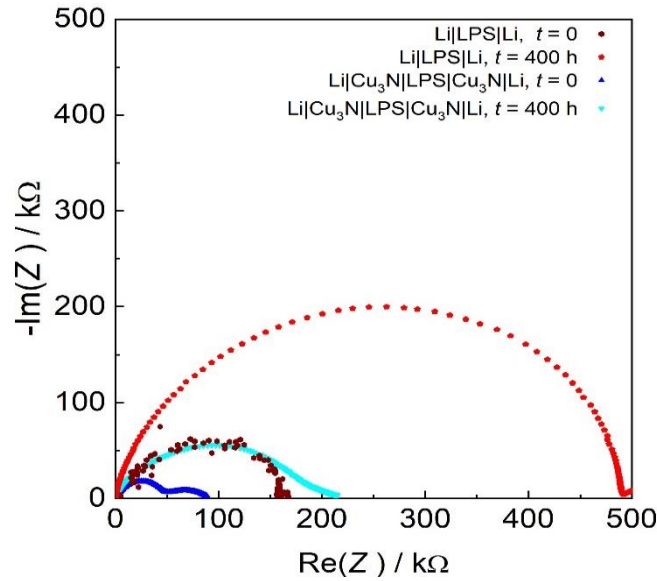


Figure A 19: Time-dependent Nyquist plot of an LPS pellet with and without Cu_3N protective layer in contact with lithium. Cu_3N decreases the cell resistance but does not prevent degradation.

The Nyquist plot of the first and last measurement of the samples with and without Cu_3N layer can be seen in **Figure A 19**. Two semicircles are visible, one in the high to mid-frequency range and a smaller one at low frequencies.

The resistance of the unmodified sample increases from $150 \text{ k}\Omega$ to $500 \text{ k}\Omega$, whereas the resistance of the sample with Cu_3N layer only increases from $50 \text{ k}\Omega$ to roughly $180 \text{ k}\Omega$. Although the absolute values of the protected and unprotected sample differ largely, the relative changes are in both cases between a factor of 3.3 and 3.6. Copper nitride does not prevent the electrolyte from reacting with lithium and does not even seem to slow down the decomposition reaction. As expected, the MIEC interphase does not have a protective effect. However, it seems to create a more intimate contact between the electrolyte and lithium and therefore reduce the interfacial resistance. Although Cu_3N is not suitable as a sacrificial interlayer to stop the electrolyte degradation, it may be a helpful addition to systems with high interfacial resistances and have a similar effect than the Ge layer applied by Liu et al. that was discussed in **chapter 2.3**.

Appendix K

List of conference contributions

Poster presentations

- Yurong Su, Jane Christine Falgenhauer, Angelika Polity, Bruno K. Meyer, **Matthias Geiß**, Thomas Leichtweiß, Jürgen Janek, *Lithium Phosphorous Sulfurous Oxynitride (LiPSON) as a New Solid Electrolyte Material for Application in Thin-Film Batteries and Electrochromic Devices*, 17th International Meeting on Lithium Batteries, June 10th - 14th 2014, Como, Italy
- Patrick Schichtel, **Matthias Geiß**, Thomas Leichtweiß, Joachim Sann, Dominik Weber, Jürgen Janek, *On the Impedance of solid state batteries in the Li|“LiPON“|Li₄Ti₅O₁₂ system*, 2nd Bunsen-Colloquium on Solid-State Batteries, November 23rd - 25th, 2016, House of Logistics and Mobility Frankfurt, Germany
- Sebastian Wenzel, **Matthias Geiß**, Thomas Leichtweiß, Joachim Sann, Jürgen Janek, *Interphase formation on Solid-state Electrolytes studied in-situ by Photoelectron spectroscopy*, 2nd Bunsen-Colloquium on Solid-State Batteries, November 23rd - 25th, 2016, House of Logistics and Mobility Frankfurt, Germany
- **Matthias Geiß**, Thomas Leichtweiß, Thomas Rempel, Jürgen Janek, *Properties of artificial interfaces in all-solid-state lithium-ion batteries*, 2nd Bunsen-Colloquium on Solid-State Batteries, November 23rd - 25th, 2016, House of Logistics and Mobility Frankfurt, Germany
- **Matthias Geiß**, Thomas Leichtweiß, Jürgen Janek, *Tailoring of interfaces and interphases in all-solid-state lithium-ion batteries*, 2nd German-Israeli Battery School, April 3rd - 6th, 2016, München, Germany
- **Matthias Geiß**, Joachim Sann, Jürgen Janek, *Thermodynamics of Lithium Metal Batteries*, Materialforschungstag Mittelhessen -June 28th, 2017
- **Matthias Geiß**, Joachim Sann, Jürgen Janek, *Thermodynamics of Lithium Metal Batteries*, 19th International Meeting on Lithium Batteries, June 17th - 22nd, 2018, Kyoto, Japan

List of publications

- Yurong Su, Jane Falgenhauer, Thomas Leichtweiß, **Matthias Geiß**, Christian Lupó, Angelika Polity, Shengqiang Zhou, Jaroslava Obel, Derck Schlettwein, Jürgen Janek, Bruno K. Meyer, *Electrochemical properties and optical transmission of high Li^+ conducting LiSiPON electrolyte films*, *Physica status solidi b*, Volume 254, issue 2 (2017)
DOI: 10.1002/pssb.201600088
- Patrick Schichtel, **Matthias Geiß**, Thomas Leichtweiß, Joachim Sann, Dominik Weber, Jürgen Janek, *On the impedance and phase transition of thin film all-solid state batteries based on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ system*, *Journal of Power Sources*, Volume 360, 31 August 2017, Pages 593–604
DOI: 10.1016/j.jpowsour.2017.06.044
- Peter Adler, Peter Jeglič, Manfred Reehuis, **Matthias Geiß**, Patrick Merz, Tilén Knaflič, Matej Komelj, Andreas Hoser, Annette Sans, Jürgen Janek, Denis Arčon, Martin Jansen, Claudia Felser, *Verwey-type charge ordering transition in an open-shell p-electron compound*, *Science Advances* 19 Jan 2018, Vol. 4, no. 1, eaap7581
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- Manuel Weiss, Beatrix–Kamelia Seidlhofer, **Matthias Geiß**, Clemens Geis, Martin R. Busche, Maximilian Becker, Nella M. Vargas–Barbosa, Luca Silvi, Wolfgang G. Zeier, Daniel Schröder, Jürgen Janek, *Unraveling the Formation Mechanism of Solid–Liquid Electrolyte Interphases on „LiPON“ Thin Films*, *ACS Appl. Mater. Interfaces*, 2019, 11 (9), pp 9539–9547
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- Tilén Knaflič, Peter Jeglič, Matej Komelj, Andrej Zorko, P.K. Biswas, Alexey N. Ponomaryov, Sergei A. Zvyagin, Martin Reehuis, Andreas Hoser, **Matthias Geiß**, Jürgen Janek, Peter Adler, Claudia Felser, Martin Jansen, Dennis Arčon, *Spin-dimer ground state driven by consecutive charge and orbital ordering transitions in the anionic mixed-valence compound Rb_4O_6* , *Physical Review B* 101, 024419 (2020)
DOI: 10.1103/PhysRevB.101.024419
- Martin R. Busche, Thomas Leichtweiß, Carsten Fiedler, Thomas Drossel, **Matthias Geiß**, Manuel Weiß, Achim Kronenberger, Dominik A. Weber, Jürgen Janek, *A comprehensive study on the formation of the solid-/liquid electrolyte interphase „SLEI“*, *ChemRxiv*, 2020
doi.org/10.26434/chemrxiv.11734740.v1
- **Matthias Geiß**, Joachim Sann, Jürgen Janek, *SEI Formation in Solid State Batteries and Concepts for Lithium Anode Protection*, to be submitted

- **Matthias Geiß**, Thomas Leichtweiß, Joachim Sann, Jürgen Janek, *The SEI of „LiPON“-growth, composition, and properties*, to be submitted
- **Matthias Geiß**, Felix Walther, Thomas Leichtweiß, Joachim Sann, Jürgen Janek, *P₃N₅ as a sacrificial anode|electrolyte interface in all-solid-state lithium batteries*, to be submitted