

# Investigations of the Solid Electrolyte Interphase Using X-Ray Photoelectron Spectroscopy In situ Experiment on the Lithium-Based Solid Electrolyte LiPON

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Lithium phosphorus sulfuric oxide nitride (LiPON) is prepared by radio frequency (RF) sputtering using a sputter target with compositions of 50 wt%  $\text{Li}_3\text{PO}_4$  and 50 wt%  $\text{Li}_2\text{SO}_4$ . Knowledge about the present phases at the solid electrolyte–lithium anode interface, the so-called solid electrolyte interphase (SEI), is achieved by performing an in situ sputtering of metallic lithium on the electrolyte and subsequently measuring the chemical bonding by X-ray photoelectron spectroscopy (XPS). Information about the SEI is of essential interest to understand the process of lithium-ion conduction in the half cell. Therefore, the information about the formation of lithium phases in the SEI is crucial.


## 1. Introduction

Solid electrolytes are increasingly gaining importance for future battery cell concepts.<sup>[1]</sup> Worldwide exploration of such materials is driven by the hope for improved safety, higher energy density (through the potential use of lithium as an anode material), and a wider operating temperature range. Lithium-based solid electrolytes are currently used in thin-film microbatteries, with the solid electrolyte glassy lithium phosphorus oxide nitride (LiPON), introduced by Dudney and Neudecker,<sup>[2]</sup> being one of the popular choices for such applications. Due to the inherent safety and good thermal stability of LiPON and the resulting rapid charge transport, several systems based on LiPON are very promising.<sup>[3]</sup>

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Considering the multilayer structure of battery cells based on thin films, the reaction of the electrolyte with the anode is an important factor for solid-state battery performance. Nowadays, mostly used anode materials are carbon based or lithium alloys, which have been reported to form films with positive effects on the battery performance.<sup>[4]</sup> This surface film then is commonly identified as the so-called solid electrolyte interphase (SEI). Manifold surface species are formed in contact between the solid electrolyte and the anode material.

The SEI layer acts as a conductor for  $\text{Li}^+$  ions and an insulator for electron flow. Moreover, the SEI layer limits the electrolyte decomposition which in turn improves the cycle life performance, Coulombic efficiency, and safety of lithium-ion batteries. The SEI is known to grow in thickness or become nonprotective under certain battery operation conditions like prolonged electrochemical cycles, high temperature (above 60 °C), and high charge rates.<sup>[4]</sup> This leads to a degradation of the half-cell performance. With regard to a possible use in all solid-state batteries, the information gained concerning the SEI plays an important role. A lot of groups focused their work on SEI-related investigations by use of different solid electrolytes. Schwoebel et al. and Sicolo et al. are working on the system LiPON.<sup>[5,6]</sup> From their publications, it is known that various side reactions take place in contact between LiPON and metallic lithium.<sup>[5,6]</sup> However, formation of an SEI is not a phenomenon limited to LiPON. Wenzel et al. were dealing with solid electrolytes  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ ,<sup>[7]</sup>  $\text{Li}_7\text{P}_3\text{S}_{11}$ ,<sup>[8]</sup> and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .<sup>[9]</sup> The formation of an SEI was also obtained for these lithium-based solid electrolytes.

Here, we will focus on the SEI between the lithium-based sulfur-containing LiPON-like solid electrolyte lithium phosphorus sulfuric oxide nitride (LiPON) and metallic lithium. Its properties such as the composition and the high ionic conductivity ( $\sigma_{\text{ion}} \approx 10^{-5} \text{ S cm}^{-1}$ ) pretend to be more beneficial for lithium-based microbatteries than the properties of the well-known solid electrolyte LiPON (e.g.,  $\sigma_{\text{ion}} \approx 10^{-6} \text{ S cm}^{-1}$ ). The properties of the LiPON thin film and the dependency on its deposition parameters are already discussed in a previous publication.<sup>[10]</sup>

## 2. Experimental Section

A sputter target with composition of 50 wt%  $\text{Li}_3\text{PO}_4$  and 50 wt%  $\text{Li}_2\text{SO}_4$  was used for thin-film fabrication via radio frequency

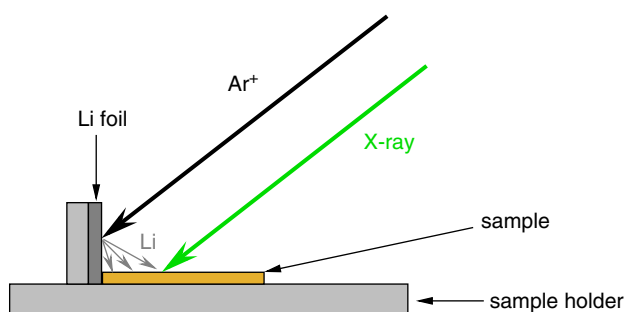
(RF) magnetron sputtering. The thin film was produced using argon and nitrogen as sputter gases. Soda-lime glass was mounted as the substrate in 5.3 cm distance of the sputtering target. The base pressure of the deposition chamber was in the range of  $10^{-7}$  mbar. The composition of the thin film and information about the chemical bonds were determined by X-ray photoelectron spectroscopy (XPS) using a PHI VersaProbe. X-rays were produced using an Al anode (Al  $K\alpha = 1486.6$  eV). Measurements were performed with a source angle of  $45^\circ$ . The experiment was realized with charge neutralization on the sample surface, and all spectra were referenced to the carbon signal (C 1s) at 284.8 eV binding energy. The core peaks were analyzed using a nonlinear Shirley-type background, and peak positions and areas were obtained by a weighted least-square fitting of model curves (60% Gaussian and 40% Lorentzian) to the experimental data. For the in situ XPS measurement, the sample was mounted on a sample holder in front of a lithium foil, as shown in **Figure 1**. With this setup, we were able to deposit lithium on our sample using the argon ion gun of the XPS setup and additionally perform an in situ measurement of the modified sample surface without any contact to atmosphere. A more detailed description of this setup can be found in a previous study.<sup>[7]</sup>

The photoelectron spectra were measured with 50 ms time per step, an energy step size of 0.2 eV, and a pass energy of 23.5 eV. To improve the signal-to-noise ratio, around 30 sweeps were performed for each signal. After the measurement of each signal, lithium was sputtered on top of the film. In situ argon-ion sputtering for lithium deposition was performed with an acceleration voltage of 4 kV of the argon ions. Lithium deposition was performed using different sputter time steps. The first three cycles were performed with a sputter time of 1 min. After that, five cycles with 2 min argon-ion sputtering were performed. For the last seven cycles, a sputter time of 5 min was chosen.

It should be noted that there was no voltage or any heating temperature applied to the sample. The reactions described later are therefore not triggered by any external force.

### 3. Results and Discussion

LiPON is a well-known type of glassy solid electrolyte.<sup>[2,5,6,11–24]</sup> For the use in all solid-state batteries the behavior in contact with



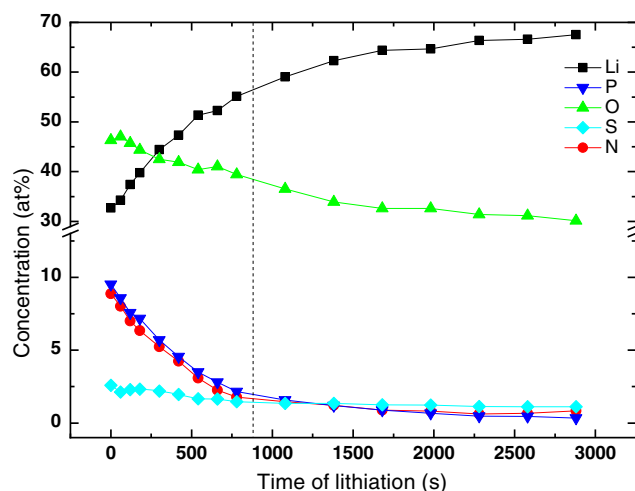
**Figure 1.** Scheme of the XPS setup for the in situ measurements. The sample is mounted in front of a lithium foil. Using the argon-ion gun, it is possible to deposit lithium on top of our thin film and investigate the modified surface using XPS.

the electrodes is crucial. Schwoebel et al. focused their work on the contact between LiPON and metallic lithium determining the changes using XPS.<sup>[5]</sup> However, in contrast to Schwoebel et al., we additionally have sulfur in our glassy system. To clarify the amount of the different elements in our RF-sputtered thin film, their concentration was determined using XPS. The overall amount of the different elements as a function of the time of lithiation is shown in **Figure 2**. Evidently, the lithium content is increasing with lithiation time up to about 67 at% after 2880 s of lithiation. The amount of nitrogen and phosphorus is decreasing antiproportional to the increasing lithium. Oxygen is decreasing to around 30 at%. After about 800 s of lithiation, the amount of nitrogen and phosphorus is decreased to nearly 1 at%. However, the amount of sulfur is nearly constant at around 1 at% during the lithiation time.

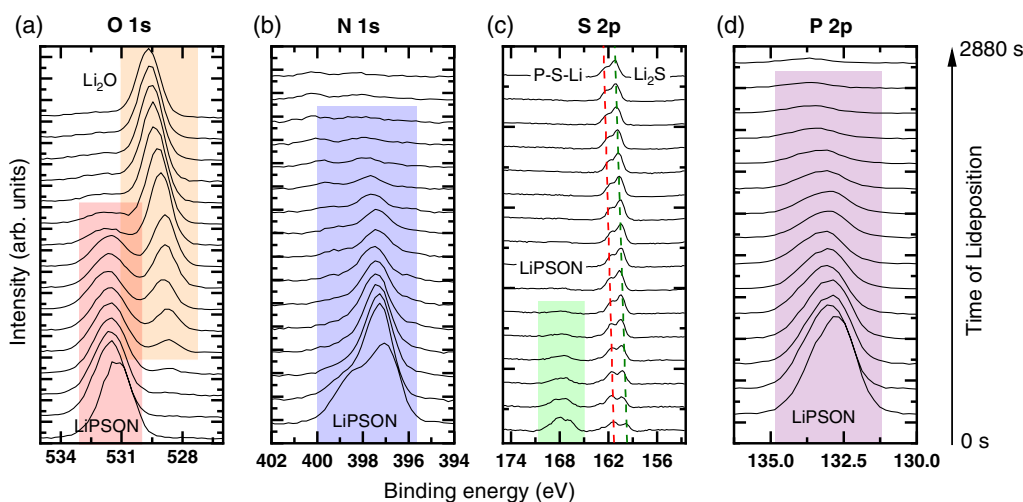
An effect which is observable in all spectra is the slight shift of the signals toward higher binding energies, as shown in **Figure 3**. This shift can be related to charging effects.

In the following paragraphs, we want to take a closer look at the different photoelectron signals of the constituent elements and their evolution while proceeding the lithiation process. From previous works on LiPON, it is known that the photoelectron signals O 1s, N 1s, and P 2p are expected to change.<sup>[5]</sup> Related to the addition of lithium on top new phases were detected.

Namely, a rising signal related to  $\text{Li}_3\text{N}$  was observed. Furthermore, a lithium oxide signal was detected in the oxygen signal of the glassy LiPON, and the phosphorus photoelectron signal showed a modification in its structure. With increasing lithium on top a phosphide phase was detected.<sup>[5,6]</sup> Accordingly, we observe changes in all photoelectron signals evaluated in this work, O 1s, N 1s, S 2p, and P 2p, respectively, as shown in **Figure 3a–d**. In the following paragraphs, we will discuss these changes in more detail.



**Figure 2.** Bulk atomic fractions of the five elements in the LiPON thin film during the in situ experiment evaluated from XPS measurements. The lithium content is increasing rapidly with time of lithiation. Nitrogen and phosphorus concentrations decrease strongly, nearly proportional to the lithium increase. Oxygen and sulfur contents are also declining into a plateau, which can be related to the uprising phases of the SEI.



**Figure 3.** Evolution of the measured photoelectron signals during the lithiation process. As shown, there are no changes observable in the b) N 1s and d) P 2p signals, whereas the structure of the a) O 1s and c) S 2p photoelectron signals is changing and new species, e.g.,  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{O}$ , are occurring. The step size of lithiation time in the diagram follows strictly the argon-ion sputter time mentioned in Experimental Section.

At first, we will focus on the nitrogen signal (N 1s) of our glassy film. As shown in Figure 3b, the nitrogen signal related to the LiPSON structure vanishes with time of lithiation. After a few steps of lithium deposition, no more nitrogen-related signals are observable. Therefore, the nitrogen in the LiPSON structure in contact with lithium does not react like the nitrogen in the LiPON structure, where an additional signal (assigned to a nitrogen bond in lithium nitride  $\text{Li}_3\text{N}$ ) is rising at about 394 eV binding energy.<sup>[5]</sup> However, the network containing double- and triple-coordinated nitrogen is decomposed.

The more or less same behavior is observed for the phosphorus signal, as shown in Figure 3d. The LiPSON-related signal structure vanishes after a few steps of lithiation, and there is no signal left in the P 2p region. Schwobel et al.<sup>[5]</sup> detected a new signal structure at  $\approx 127$  eV binding energy. This new signal was attributed to phosphides, i.e.,  $\text{Li}_3\text{P}$ . In the system LiPSON, this additional signal is not detected after the exposure to lithium metal, so we tentatively exclude side products containing phosphorus to be formed during the lithiation process.

The phosphorus signal is detected for a few more lithiation steps than nitrogen. This seems reasonable, because nitrogen is placed below the surface and the phosphorus is placed directly at the surface of the LiPSON thin film. The information depth of the XPS method is about 10 nm, and due to the in situ lithiation process, only about  $0.25 \text{ nm min}^{-1}$  lithium is deposited on top of the investigated thin film. This deposition rate was calculated from XPS measurements of such in situ lithium deposition on MgO single-crystal substrates. One has to assume that the deposition rate of  $0.25 \text{ nm min}^{-1}$  is just an estimation for a purely metallic overlayer. This procedure of thickness calculation is already reported in studies by Wenzel et al.<sup>[7]</sup> Due to the use of different substrates during this in situ experiment, the final deposition rate can be slightly different.

On the contrary, we observe a new signal structure rising in the oxygen region, as shown in Figure 3a. The LiPSON-related signal at around 531.5 eV decreases with time of lithiation, and

after a few seconds, a side product structure at 529.7 eV can be identified. This structure is related to  $\text{Li}_2\text{O}$ . The formation of this side product is known from previous theoretical and experimental publications.<sup>[5,6,24]</sup> The small amount of sulfur seems not to have a significant effect on the side reaction of the additional lithium offered due to lithiation and the surface oxygen contained in the LiPSON thin film. Thus, the oxygen in our LiPSON thin film shows similar reactions known from LiPON thin films.<sup>[5,6]</sup>

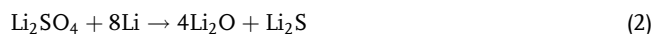
The most evident changes are detected in the photoelectron signal of sulfur. In Figure 3c, it is shown that the LiPSON-related sulfur signal decreases immediately upon surface lithiation, and a new structure at lower binding energies is formed. The signal at around 160 eV thereby is related to a sulfide, e.g.,  $\text{Li}_2\text{S}$ . The signal at 161.5 eV is attributed to a  $\text{P}-\text{S}^--\text{Li}^+$  bond.<sup>[25]</sup>

Altogether, the findings of the individual signals upon lithiation underline that the LiPSON network at the surface is decomposed, and an SEI containing  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{O}$  is formed.  $\text{Li}_2\text{O}$  is known for its poor electronic conductivity. Considering the fact that a weak electronic conductivity is aimed at for applications  $\text{Li}_2\text{O}$  may not be a bad candidate. However, because of its also poor ionic conductivity in the range of  $10^{-9} \text{ cm}^{-2}$   $\text{Li}_2\text{O}$  is not the species of choice upon SEI formation.<sup>[26]</sup> The same holds true for the  $\text{Li}_2\text{S}$  phase. Therefore, the ionic conductivity of the formed SEI does not satisfy the essential properties of a thin film, which has a positive effect on the battery properties.

One possible reason for the formation of  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{O}$  might be the fact that at the surface of the LiPSON thin films nearly the same structures as for LiPON are present, e.g., a  $\text{PO}_4$  tetrahedral structure.<sup>[6]</sup> From former works, it is known that phosphorus is replaced by sulfur in our LiPSON thin films.<sup>[10]</sup> Due to this, we state that at the surface, only phosphorus, oxygen, and sulfur exist. Consequently, the reaction between the lithium offered by the lithiation process proceeds primarily with the oxygen and sulfur species from the structures at the surface. If one considers the Gibbs energies from similar structures, the reaction products  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{S}$  may be the preferred ones. A negative

Gibbs energy indicates a reaction which is expiring spontaneously. The Gibbs energies of the similar structures  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  are way more negative than the Gibbs energies of  $\text{H}_3\text{N}$  and  $\text{H}_3\text{P}$ .<sup>[27]</sup> Because of this, one cannot observe a signal related to  $\text{Li}_3\text{N}$  or  $\text{Li}_3\text{P}$  in the spectra.

We propose the following reactions between lithium and the LiPSON thin film at the surface



However, no  $\text{Li}_3\text{P}$ -related signal is monitored in the P 2p photoelectron signal, so the second reaction might be the more prominent one at the interface between LiPSON and metallic lithium which also makes sense if the Gibbs energies of similar structures were considered.

In summary, one must consider that the known LiPON-like SEI formation does not apply for the contact of LiPSON and lithium. Here, one has to respect the fact that ion-isolating species, e.g.,  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{S}$ , form at the interface prominently. Related to this behavior LiPON as a glassy electrolyte seems to be the superior choice for thin-film solid-state batteries compared with LiPSON.

## 4. Conclusions

After exposing a LiPSON thin film to metallic lithium, we found evidence for different chemical reactions at the surface. Similar to LiPON, a clear decrease in the amount of network-forming structure units was visible. The reactions between LiPSON and metallic lithium lead to a decomposition into smaller units like  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{S}$ . However, LiPON-typical reaction educts like  $\text{Li}_3\text{P}$  and  $\text{Li}_3\text{N}$  were not detected. The small amount of sulfur is responsible for the formation of a different SEI, containing only  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{O}$  phases. Considering the SEI formation at the glassy electrolyte LiPON in contact with metallic lithium, the formation of the SEI for LiPSON in contact with metallic lithium is not as beneficial. However, the SEI formation of LiPSON and metallic lithium so far is not a well-studied process and further investigations have to be conducted. A possible solution for the negative influence of the SEI could be a protection layer in between the solid electrolyte and metallic lithium. Investigations to tackle this problem are ongoing.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

inorganic solid electrolytes, lithium phosphorus sulfuric oxide nitride, solid electrolyte interphases, X-ray photoelectron spectroscopy

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