Elucidating Interfacial Stability between Lithium Metal Anode and LiPON via In Situ Electron Microscopy

Zachary Hood
Massachusetts Institute of Technology

Xi Chen
University of Wisconsin-Milwaukee

Robert Sacci
Oak Ridge National Laboratory

Gabriel Veith
Oak Ridge National Laboratory

Xiaoming Liu
Oak Ridge National Laboratory

Yifei Mo
University of Maryland, College Park

Junjie Niu
University of Wisconsin-Milwaukee

Nancy Dudney (✉ dudneynj@ornl.gov)
Oak Ridge National Laboratory

Miaofang Chi (✉ chim@ornl.gov)
Oak Ridge National Laboratory

Article

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Abstract

Li phosphorus oxynitride (LiPON) is one of a very few solid electrolytes that have demonstrated stability against Li metal, and performed extended cycling with high coulombic efficiency. However, theoretical calculations show that LiPON does react with Li metal. Here, we utilize in situ electron microscopy to directly observe the dynamic evolutions at the LiPON-Li interface upon contacting and under biasing at the nanometer scale. We reveal that a thin interface layer (~60nm) develops at the LiPON-Li interface upon contact. This interface layer is conductive and robust, serving as an effective passivation layer keeping the interface stable over time and under biasing up to 5 V. Our results explicate the excellent cyclability of LiPON and reconciles the existing debates regarding the stability of LiPON-Li interface. This work demonstrates that glassy solid-state electrolytes with a sufficient ionic conductivity, though may not have a perfect initial electrochemical window with Li metal, may excel in future applications for ASSBs.

Main Text

A lithium metal anode represents one of the ultimate goals to improve portable and rechargeable electrochemical energy storage systems on the basis of volumetric energy density. In line with this goal, solid electrolytes (SEs) are widely considered to enable Li metal anodes, yet significant challenges have prevented the large-scale deployment of SEs in next-generation energy storage devices. SEs must have sufficient ion conductivity, be stiff enough to prevent Li filament growth from the interface, have low electronic conductivity, and maintain these properties over many charge-discharge cycles. Though most of the solid electrolytes have sufficient mechanical robustness, many of them still suffer the formation of Li filaments with critical current densities being lower than expected from a mere mechanical argument. Out of the plethora of SEs that have been applied to Li metal batteries, Li phosphorus oxynitride (LiPON), represents the only SE that has been able to cycle thousands of cycles with Li metal anode at a critical density as high as 10 mA cm$^{-2}$ without the development of dendrites. This excellent performance was attributed in part to the low electronic conductivity of LiPON compared to Li garnets and lithium thiophosphate.

Since being invented in the early 1990s at Oak Ridge National Laboratory, LiPON was demonstrated to have a wide electrochemical stability window with Li metal anode as well as with a variety of anode/cathode materials during cycling in all-solid-state batteries (ASSBs). LiPON was shown to be compatible with a Li metal anode from 0 to ~5 V with respect to Li/Li$^+$ by impedance spectroscopy. A number of full LiPON-based thin film batteries were successfully fabricated and cycled, such as the Li/LiPON/LiCoO$_2$, Li/LiPON/LiMn$_2$O$_4$, Li/LiPON/Li$_x$(Mn$_{1.5}$Ni$_{0.5-y}$Cr$_y$)O$_4$, and Li/LiPON/Li$_x$(Ni$_y$Mn$_{2-y}$)O$_4$ systems. More recently, LiPON was shown to cycle up to 10,000 times, together with a coulombic efficiency of 99.99%, using a Li metal anode and a spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode.

Even with these experimental evidences, the stability of LiPON and metallic Li anode currently is still under debate. Theoretical calculations show that LiPON has a narrow electrochemical window with a
reduction potential at 0.69 V with Li/Li$^+$.\textsuperscript{24} The thermodynamic phase equilibria against Li metal include Li$_3$N, Li$_2$O, and Li$_3$P. XPS measurements of the LiPON surface during stepwise exposure to lithium vapor show that LiPON decomposes to products including Li$_3$N, Li$_3$P, Li$_3$PO$_4$ and Li$_2$O.\textsuperscript{25} These studies suggest LiPON reacts with Li upon contact, however, this cannot explain the excellent cyclability of LiPON when it is being used in ASSBs. Both studies hypothesized the formation of passivation layer,\textsuperscript{24,25} however, direct evidence is needed and it is not clear how thick this passivation layer is and how stable this layer is under electrochemical biasing. These questions request a characterization technique that can \textit{i)} provide morphological and chemical information at the nanometer scale, as well as \textit{ii)} directly observe the interface responses during the contact of these two materials and under an electrochemical bias.

Our previous experiments on Li$_{6.25}$Al$_{0.25}$La$_3$Zr$_2$O$_{12}$ (LLZO) have demonstrated the success of observing the stability of the solid electrolyte with Li metal.\textsuperscript{26} While LLZO is relatively stable in ambient environments with low humidity and the fabrication of a TEM specimen is achievable using low-current, low voltage focused ion-beam (FIB) milling, LiPON is a glassy material that is more sensitive to air and is challenging to use Ar$^+$ beam for specimen thinning. To overcome this limitation, we use a modified setup to observe the interfacial stability of LiPON against Li metal, both upon contact and under a bias. Our results reveal the formation of a thin passivation layer right upon contacting LiPON with Li metal within a very short period of time. This layer, both its chemistry and thickness, stays stable with extended time and under a bias of 5 V. These results explicate the excellent cyclability of LiPON and reconcile the existing debates regarding the stability of the LiPON-Li interface.

\textbf{Observing \textit{in situ} interfacial evolutions at the nanoscale.} The configuration for observing the interface formation upon contact in vacuum between LiPON and Li metal tip is shown schematically in Figure 1A. In contrast to invasive specimen preparation methods for interrogating interfaces in batteries, we intentionally separated LiPON and Li metal at the start of the experiment in order to observe what occurs \textit{i)} upon first touching the anode and SE and \textit{ii)} upon an external bias across the interface. This configuration is different from the LLZO-Li we published earlier\textsuperscript{26} considering the challenges of thinning amorphous LiPON with FIB-based processing. A copper half grid was mechanically polished to \textasciitilde 20nm before depositing a thin layer of LiPON (\textit{ca.} \textasciitilde 100nm) using radio frequency magnetron sputtering in a reactive N$_2$ atmosphere following previous reports.\textsuperscript{18,19,23,27} This configuration assures the sample to be electron beam transparent with a suitable thickness for EELS measurements. The anode was fabricated by coating a tungsten tip with Li metal. Since Li metal can quickly oxidize under ambient conditions, special precautions were taken to minimize the exposure of the materials to air and moisture during sample preparation and transfer to the microscope. Contamination, namely Li$_2$O, on the Li tip can be removed by converging the electron beam and scanning the Li metal surface with an extended time. Microscopy measurements were followed until the oxidation layer on the tip is completely removed, which was confirmed by EELS analysis, which is particularly sensitive to oxygen.
In order to evaluate the interfacial behavior between Li metal and LiPON, TEM-based movies were recorded upon first forming the interface as well as under an external bias (Supporting Information, Video 1). The acceleration voltage and beam current of the electron beam were carefully chosen for imaging and spectroscopy such that electron irradiation was minimized. As seen in the video, LiPON does not show any changes in both the morphology and contrast under the electron beam until it is contacted with Li metal, indicating that subsequent reactions occur between the two materials. Representative time-lapse TEM images of the interface formation from Supplementary Video 1 are shown in Figure 2, including the images before contacting LiPON with Li metal and at different points without an external bias. At the start of the experiments, LiPON exhibits a smooth surface in this configuration, i.e. conformally to the Cu for RF-sputtered LiPON films.\textsuperscript{16} After Li metal contacts LiPON with the specialized piezo-controlled holder, a volume expansion at the surface region of LiPON was immediately observed, along with the obvious wetting of Li on the LiPON surface. Note that here Li source is extremely rich, and the consumption of Li can only be seen from a slightly brighter (thinner) contrast change of the Li tip. The expansion of the LiPON surface region quickly grows within approximately 45 seconds. Such volume change at the interface suggests that a reaction occurred at the LiPON-Li interface. We determine the thickness of this layer to be \textasciitilde60 nm. Notably, the reaction zone grows outward towards Li metal, suggesting that LiPON consumes Li upon forming the interfacial layer. After approximately 45 seconds, the interfacial layer stopped growing. At this point, we further interrogated the interface by applying a positive external bias (e.g. + 0.01 - 5 V) to the Li metal in order to evaluate the electrochemical window of the LiPON-Li interface. Our results indicate that the interfacial layer is stable even under an external bias of 5 V. The volume of the interfacial layer did not change under this bias (Figure S1).

The dynamic volume expansion of the LiPON-Li interface, as revealed by \textit{in situ} TEM, was further evaluated to better elucidate the potential reaction kinetics (Figure 3). The area expansion ratio, which is defined to be the volume change reference to a pre-defined area of pristine LiPON surface (marked in in the inset of Figure 3), was used to evaluate the volume evolution of the reaction layer that forms at the interface. The area expansion ratio of the interfacial layer was measured using ImageJ\textsuperscript{28} and plotted as a function of time as shown in Figure 2. The development of the volume changes shows three specific regions. The volume expansion happens right upon the contact and reveals a fast growth during the first 22 seconds (Region I) followed by a kinetically slower growth at the time of 22-40 seconds (Region II). After 40 seconds, with an interfacial layer of \textasciitilde60 nm thick, the volume expansion stops, suggesting the reaction reaches equilibrium around 45 seconds (Region III). In the second reaction zone (e.g. after 45 seconds), the interfacial reaction kinetics were particularly sluggish. It needs to be emphasized that no observable changes in the morphology of LiPON or its interface have been observed after an external bias of 5 V is applied to the interface inside the microscope, indicating that interphase layer here is self-limiting and is stable.

\textbf{Identifying the chemistry of the interfacial layer at the LiPON-Li interface.} At this point, our results clearly show that an interlayer forms between LiPON and Li metal anode upon contact, yet the identification of
decomposition products were previously elusive. Theoretical calculations predict the decomposition of LiPON to multiple other compounds depending on the potential. At 0 V (theoretical reduction potential of LiPON = 0.63 V), the predicted thermodynamic equilibrium decomposition products of LiPON are Li₃N, Li₃P, and Li₂O. At the oxidation potential (2.63 V), the thermodynamic phase equilibria suggest the possible decomposition of LiPON to P₅N₅, Li₄P₂O₇, O₂, and N₂. The formation of Li₄P₂O₇ involves the cleavage of P-O bonds and the formation of P-O-P chains, generating O₂ gas. As highlighted by the in situ TEM evolution of the LiPON-Li interface, the contrast between Li and the interphase is lower than that of pristine LiPON. This difference in the TEM contrast can be linked to the formation of compounds with decreased density, among other factors. The density of LiPON was experimentally determined to be 2.3 g/cc while Li metal has a density of 0.53 g/cc. The density is 1.27 g/cc for Li₃N, 1.44 g/cc for Li₃P, and 2.01 g/cc for Li₂O, all of which are lower than that of pristine LiPON. The decreased density of the binary phases can explicate the difference in the phase contrast of the interphase in the TEM images. The stoichiometry of LiPON is estimated to be Li₂.₉₉PO₃.₃₈N₀.₄₁. Table S1 displays the volume of Li₃P, Li₃N and Li₂O as reaction products. Assuming the mass of P, O and N remains the same, based on the density and molar mass of LiPON and the potential reaction products, there would be an overall 201.3% volume change at the LiPON-Li interface. If we simplify the LiPON-Li interface topography to a semi-cylindrical model, taking the half-arc surface in semi-cylindrical model as the main observation direction, the estimated area expansion ratio is 1.43, which coincides with the observed areal expansion ratio ~1.5.

Detailed chemical and electronic structures would further confirm a change at the LiPON-Li interface upon contact. EELS was performed to probe the electronic structure and chemistry of the interphase formed in situ between LiPON and Li metal, comparing the spectra with the those acquired before contact. Figure 4A-C shows the Li-K edge, P-L edge, N-K edge, and O-K edge from the pristine LiPON and the interphase regions. Dramatic changes were observed in the Li K-edge for the interfacial layer. Instead of multiple peaks observed in the Li K-edge for pristine LiPON, there were two main peaks in the Li K-edge for the interfacial layer, implying that the Li bonding configuration is significantly altered within the interphase, e.g. indicating a significant change of the chemical phases. Less resolvable fine structures also suggest that the interphase compounds have overlapping Li peaks if multiple compounds are confined to this space. It is interestingly noted that the nearest neighbors of Li in LiPON are primary O and N, based on previously reported theoretical calculations and Neutron scattering. Peaks “a” and “c” in Figure 4A primarily arise from the coordination of Li with O, while peak “b” can be attributed to the coordination with N, based on previously reported EELS fine structure of Li oxides and nitrides. Similar fine structure changes also occurred to P L-edges (Figure 4B), where four distinctive peaks are clearly visible in the pristine spectra, the one from the interphase appear as a delayed edge. The nearest neighbors of the P atoms in LiPON include O and N, the P-L fine structures, such as peaks “a” and “b” may largely corresponds to its bonding with O and N. In contrast, the interphase P-L contain less feature with a relatively earlier starting edge “e”, similar to P₃⁻: EELS characters (EELS atlas, 1987), which could be a result from valence change from a phosphate to phosphide. As the beam current and the acquisition time used in this experiment are low, the signal-to-noise ratio of EELS at the higher energy loss, e.g. in...
Figure 4C for the N K-edge and the O K-edge, is relatively low compared to those of the Li K-edge and the P L-edge. However, the fine structural changes in O K-edge, are clearly visible. While the pristine O-K contains distinct three peaks that correspond to its multiple neighboring species, the interface spectrum is shown to have one apparent peak followed with extended structure, potentially due to a simpler bonding environment. Further, it is noticed that the spectra from interface region overall have weaker signal compared to pristine LiPON, possibility from a reduced density of each elements or the enhanced electron beam sensitivity. These fine structure changes in Li-K, O-K and in P-L show that they most likely form binary compounds instead of compound containing multiple elements. However, confirmation using reference spectra of pristine Li$_3$N, Li$_3$P and Li$_2$O that are acquired under the same experimental conditions are desired to confirm the interfacial phases. Future studies are needed to provide an absolute determination of the end phases and to reveal their distribution. A characterization technique that is capable of spatially resolving chemical analysis of light elements with limited specimen damage is especially preferred.

Our microscopy results, including both in situ imaging and EELS analysis provide two important points regarding the stability of LiPON with Li metal, which is schematically shown in Figure 4D. First, when LiPON is contacted with Li metal, an interphase forms as a result of LiPON decomposition at the very surface of LiPON; second, the thickness of this interphase layer is limited to ~60 nm and does not grow with time or upon a bias of 5V, which means that this interphase layer effectively stabilizes the interface of LiPON with Li metal and may contribute to the long-cycling life of LiPON being used in ASSBs. Information provided in this work fills the knowledge gap regarding the electrochemical window of LiPON and its high stability and cyclability in ASSBs. Since the interphase layer is most likely composed of Li$_3$N, Li$_3$P, and Li$_2$O, these compounds could theoretically fill in the electrochemical window gap, e.g. 0.69 eV between LiPON and Li/Li$^+$, thus stabilizing the interface (Figure S2). Further, this interphase containing a high concentration of phases with high Li ionic conductivity, such as Li$_3$N and Li$_3$P, which may explain the good interfacial conductance of the LiPON-Li interfaces.$^{16,24}$

While our results also indicate the presence of a critical thickness of the interphase layer that forms and effectively stabilized the LiPON-Li interface, it should be noted that the thickness of the interfacial layer may vary depending on the composition of LiPON and the method used in forming the interface. In the case of directly contacting LiPON with Li metal in vacuum as in our experiments, the critical thickness of the interphase likely is defined by the chemical concentration of LiPON and the distribution of Li$_3$P at the interface. This result could be possibly due to the high ionic conductivity and undesirable electronic conductivity of Li$_3$P when compared to that of Li$_3$N and Li$_2$O. Forming a composite network of Li$_3$N and Li$_2$O in which embedded Li$_3$P are effectively isolated from Li metal may define the thickness of the interphase layer. Thus, the critical thickness of the interphase may vary with the exact compositions.

It is believed that different methods used to form the interfaces between LiPON and Li metal could largely change the thickness of the interphase. The thickness revealed in this experiment, e.g. ~60 nm, is limited to the particular batch of LiPON used in the experiment and the setup used in this microscopy experiment,
e.g. direct contact of Li and LiPON in a high vacuum system (<10^{-7} Torr). For example, Li anodes are generally evaporated onto LiPON for LiPON-based microbatteries, a Li-rich LiPON interlayer may firstly form and modify the interfacial chemistry. Further, the TEM specimen is exposed to air for ~3 mins during the sample transfer from a glove bag to the microscope chamber; though there was no detectable carbon on the LiPON, we imagine a slight contamination of carbon or hydrogen from the ambient environment may result in an increased interphase thickness. It is also worth to mention that our results may not directly correlate with studies observing the Li plating behavior at the electrolyte-current collector interface, where Li metal may form at an preexisting interface and chemical changes may happen at the LiPON interface prior to plating Li metal anode. Such studies provide insights into ASSBs that utilize Li plating to create the anode; alternatively work here represents the case of an ASSB assembled via direct pressing of solid electrolyte with Li metal.

In summary, we report a real-time, high spatial-resolution observation of the formation of an interphase at the LiPON-Li metal interface upon direct contact. By combining the in situ observation of the morphological evolution of LiPON interfaces and the chemical comparison of the LiPON surface prior to and after contact, we reveal the instantaneous formation of a thin interphase layer with a thickness of a tens of nanometers within 45 seconds upon contact. More importantly, this layer stays intact and under a bias of 5V, demonstrating a stable LiPON-Li interface consistent with its exceptional electrochemical performance in ASSBs previously published previously. Given the excellent cyclability and being currently the only solid electrolyte that does not suffer from dendrite growth, LiPON can serve as a base material for the design of future high-performance solid electrolytes. The information gained in this work regarding the interface of LiPON and Li-metal provides guidance in tuning the stability and the thickness of the interphase layer in similar SE systems.

Declarations

Author Information

Corresponding Authors:

* chim@ornl.gov (M.C.)

* dudneynj@ornl.gov (N.J.D.)

Author Contributions

+ Z.D.H. and X.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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**Supplementary Videos**
Supplemental videos were not provided with this version.

**Figures**

A) Experimental setup for observing the interface between metallic Li and LiPON using in situ S/TEM. B) TEM image of LiPON deposited on a polished and milled Cu half grid.

**Figure 1**

A) Experimental setup for observing the interface between metallic Li and LiPON using in situ S/TEM. B) TEM image of LiPON deposited on a polished and milled Cu half grid.
Figure 2

Initial interphase formation upon contacting Li metal with LiPON, probed by in situ TEM. The sequential TEM images show the volume expansion and wetting of Li metal across the LiPON-Li interface. The initial contact point is marked with an arrow; after contacting (0s), the tip did not mechanically move further. The lithium metal wetting on LiPON surface is clearly revealed.
Figure 3

Area expansion ratio of the interfacial layer as a function of time. Area used as the reference to estimate the area expansion is outlined with a dashed boarder line.
Figure 4

EELS analysis of the A) Li K-edge, B) P L-edge, C) N K-edge and O K-edge for pristine LiPON and the interphase between LiPON and Li metal after contacting. Li metal. D) Schematic representation of the interphase formation between Li metal and LiPON.

Supplementary Files

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