The Effect of Interfacial Charge Distribution on Chemical Compatibility and Stability of the High Voltage Electrodes (LiCoPO₄, LiNiPO₄)/Solid Electrolyte (LiPON) Interface

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Solid electrolytes hold the promise of improved safety and superior electrochemical stability in energy storage systems. Among those, electrolytes with phosphate anions are expected to be more stable at high operating voltages, thereby providing even higher energy density. The key challenge is to control the boundary conditions at the cathode/electrolyte interface, which impact drastically the functionality of the energy storage devices. Here, the evolution of the chemical composition and electronic properties of the interface forms upon consequent deposition of solid electrolyte (lithium phosphorous oxynitride [LiPON]) onto the 5 V LiCoPO₄ and LiNiPO₄ carbon-free thin film cathode materials is in situ studied by comprehensive electron spectroscopy experiments combined with the energy band diagram approach. It is demonstrated that the driving forces for interfacial reactivity are the band bending direction and the double layer potential drop at the electrode–electrolyte interface coupled to an unfavorable electrochemical potential shift of involved electronic states upon contact formation. The probability for interfacial chemical reactions is essentially increased at small energy differences in the ionization potentials of the cathode material and electrolyte, whereas a large energy difference ensures their chemical compatibility.

1. Introduction

The compatibility between the electrolyte and the electrodes is a key factor of a high performance of Li-ion rechargeable batteries (LIB),[1–4] which in turn is governed by the mutual arrangement of the energy levels of the contacting ionic conductors. A spontaneous charge transfer or chemical reaction at the interface of a closed battery cell lead to uncontrolled altering of the chemical composition, which might have a severe impact on the interface properties resulting in the degradation and failure of the LIB.[2] The fundamental principle in the operation of a battery is a consequent lowering of the electrochemical potential with respect to the occupied electronic states of the cathode upon its electrochemical delithiation during the battery charge. Hence, the prerequisite condition for the interface stability is a sufficient energy distance between the oxidation level(s) of an electrolyte and the electrochemical potential of the cathode,[5] which enables to avoid undesirable interfacial electronic charge transfer upon the battery charge. Thus, the determination of the energetics of the contacting ionic conductors, which are the cathode and the electrolyte, would allow to prognose the interfacial stability upon operation conditions of the battery. Lithium phosphorous oxynitride (LiPON) is a class of ceramic solid electrolytes, which is described by the chemical formula LiₙPOₓNᵧ (x = 2y + 3z − 5),[6] where the nitrogen (N) content ranges from 0.1 to 1.3.[7] The electrochemical stability window of LiPON is reported between 0 and 5 V versus Li⁺/Li,[8] although some experimental results and theoretical calculations predict lower values of the anodic limit (4.1–4.5 V vs Li⁺/Li).[9,10] LiPON is currently implemented in the LiCoO₂ (LCO) commercial batteries, which is not surprising taking into account a relatively low oxidation potential of the cathode (≈3.8 V vs Li⁺/Li) and the sufficient reserve in the valence band energy difference between LCO and LiPON (above 1.0 eV)[11,12]). It ensures a stable performance of the Li-ion batteries in the operation range, which does not exceed the intrinsic voltage limit of LCO (4.2 V vs Li⁺/Li).[13] Among ceramic solid electrolytes, LiPON is expected to be chemically compatible with LiMPO₄ (M = Fe, Mn, Co, Ni) olivine structure cathode materials. Nevertheless, the intrinsic stability of the interfaces, which relates to the possible charge transfer reactions between LiPON and high voltage olivine-type electrodes (LiCoPO₄ (LCP), 4.9 V vs Li⁺/Li,[14] and LiNiPO₄ (LNP), 5.3 V vs Li⁺/Li,[15]) was not reported so far.

Here, we have carried out interface experiments on carbonfree LiMPO₄ (M = Co, Ni) olivine-based films and performed a rigorous comprehensive analysis of the electronic properties and chemical composition of the LiMPO₄/LiPON interface. For the first time, we demonstrate that the interface stability of the
contacting ionic conductors is governed by the band bending direction at the interface, the amount of charge distributed on the electrolyte side and the involved electrochemical potential shift upon the double layer formation at the electrolyte-electrode interface. The driving forces for interfacial chemical reactivity is the relative positioning of the ionization potentials of the ionic conductors in contact to each other coupled to an unfavorable electrochemical potential shift allowing hole transfer from the cathode to the electrolyte. An important consequence of the revealed phenomena is the possibility to forecast the interface stability (in the terms of charge transfer) upon charging the battery cell, which is achieved by measuring the ionization and electrochemical potentials of the cathode and the relevant levels of the electrolyte, which is the valence band maximum (VBM) in the case of solid electrolyte. Based on the experimentally obtained energy diagrams, the reason of interfacial chemical reactivity and of the interfacial chemical composition change can be explained.

2. Results and Discussions

2.1. Interfacial Chemistry of the LiCoPO₄/LiPON and LiNiPO₄/LiPON Interfaces

Lithium phosphate (Li₃PO₄) deposition in N₂ atmosphere leads to nitrogen incorporation into the amorphous layer via the oxygen substitution, thereby forming LiPON. Different models of the LiPON structure were proposed in the past (Figure S1, Supporting Information). The evolution of the NiIs photoemission signal versus LiPON thickness onto the LCP and LiNiPO₄ (LNP) olivine thin films is shown in Figure 1a,c, respectively (the olivine structure of the cathode materials is shown in Figure S2, Supporting Information). The asymmetry of the NiIs photoemission line evidences the existence of nitrogen at least of two valence states. According to a broadly accepted model of the nitrogen incorporation into amorphous Li₃PO₄ proposed more than 20 years ago,[16–18] the N is bound to either two or three phosphate tetrahedra, so-called double-bridging (Nd) and triple-bridging (Nt) nitrogen, respectively (Figure S1b, Supporting Information). Recently, first-principles calculations supported by Raman spectroscopy, infrared spectroscopy, and neutron scattering experiments have proven the presence of a non-bridging N (apical, Na) in an isolated P(O,N)₄ tetrahedron (Figure S1c, Supporting Information).[19,20] Due to the vicinity of the binding energies (Ebind) of the Na and Nd states they cannot be resolved by photoemission experiments. Thus, based on the models earlier developed for the LiPON structure, we assign the NiIs photoemissions at Ebind ≈ 398 eV and Ebind ≈ 400 eV to the Nd (or Na) state and the Nt state, respectively (Figure 1a,c). The O1s photoemission signal via the LiPON deposition (Figure 1b,d) exhibits the well-resolved two features, which are assigned to the Odb double bonded oxygen situated at lower Ebind, as well as the oxygen state in the Li⁺...—O—P

Figure 1. Chemical bonding in LiPON solid electrolyte. Evolution of the a,c) NiIs and b,d) O1s photoemission spectra (hν = 1486.7 eV) versus the thickness of LiPON deposited onto LiCoPO₄ (LCP) (a, b) and LiNiPO₄ (LNP) (c, d). The upper O1s and NiIs photoemission spectra (a, b) are measured on LiPON of 1000 Å thickness. The downward band bending, δ = −0.6 ± 0.1 eV at the LCP/LiPON interface takes place up to 15 Å of the LiPON thickness (a, b). The upward band bending at the LNP/LiPON occurs upon LiPON deposition (c, d), resulting in δ = +0.8 ± 0.3 eV for LiPON of 35 Å thickness. The Nt and Na are double- and triple-bridging nitrogen, respectively. The Odb, Onb, and Ob are non-bridging, bridging, and double bounded oxygen, respectively. Evolution of the e,f) N/Nt and g) Odb/Onb ratios versus the LiPON thickness at the LCP/LiPON (e, g) and LNP/LiPON (f) interfaces. g) The decreasing of the Odb/Onb ratio at higher LiPON thickness is associated with the oxygen loss to form nitrite (NO₂) on the LiPON surface shown inside the triangle.
chemical configuration,[38] which can be resolved by the fitting of the O1s photoemission. The evolution of the chemical species constituting LCP/LiPON interface shows that the Ni/Nd ratio decreases as the O$_2$/O$_{db}$ ratio increases up to 60 Å of LiPON thickness (Figure 1e,g). Such a finding assumes that more double bonded oxygen atoms, O$_{db}$ (P=O), are substituted by nitrogen forming the (N=P−) bond rather than bridging oxygen (P−O−P) at the interface. These results agree well with theoretical calculations, which predict that the N substitution in a bridging site (N$_d$) is energetically more favorable compared to a tetrahedral site (N$_t$).[21,22] Thus, N-atoms prefer double coordination, N$_d$ (−N−P−), or an isolated structure, N$_t$, rather than triply coordinated nitrogen, N$_c$ (−N−c−), at the interface (see also LiPON/Pt in Figure S3, Supporting Information). The chemical composition of the Li$_2$PO$_4$N$_x$ bulk structure is formed at ≥60 Å, the number of the O$_b$ bridging sites is decreased relatively to the double bonded O$_{db}$ at the expense of oxygen involved in NO$_4$ formation (Figure 1g). Nitrite was earlier found at the LCO/LiPON interface,[24,25] as well as for the LiPON thick films deposited on various substrates.[26] It was suggested that NO$_2^+$ belongs to LiNO$_2$, occurring as the result of chemical reactions of the surface lithium ions with LiPON.[25] However, we have observed that nitrite is also detected on a chemically inert Pt substrate (Figure S4a, Supporting Information). These results evidence that NO$_2^+$ is not necessarily part of LiNO$_2$ and the nature of the substrate is not the dominating factor for NO$_2^+$ formation. The presence of nitrite on the surface might be due to the phosphorus substitution in a PO$_4^3−$ group by nitrogen to produce NO$_2^+$ groups,[26] thereby depending more on the LiPON synthesis conditions rather than on the chemical incompatibility of the olivine structure electrodes and the electrolyte.

In spite of the similar chemical composition of LiPON grown onto both olivines (Figure 1a–d and Figure S5, Supporting Information), LCP exhibits an energy shift to higher $E_{bin}$ at the initial steps of LiPON deposition (until a “bulk” LiPON structure is formed), Figure 1a,b, whereas an upward band bending occurs at the LNP/LiPON interface (Figure 1c,d). These different directions of energy shift are mostly associated with the different electronic (not chemical) properties at the electrode–electrolyte interface. The shift of the photoemissions to higher binding energies for LiPON thick films (the upper spectra of Figure 1a–d) might occur due to a slight charging effect, which is common for insulators.

### 2.2. Electronic Properties of the LiCoPO$_4$/LiPON and LiNiPO$_4$/LiPON Interfaces

The evolution of the M2p (M = Co, Ni) core level, valence band (VB) structure, and LiIIs photoemission signals of the LiMPO$_4$/LiPON interfaces are shown in Figures 2a–c and 3a–c, respectively. The Co2p (Figure 2a) and Ni2p (Figure 3a) photoelectron spectra of the pristine olivine are spin–orbit splitted into the M2p$_{3/2}$ and M2p$_{1/2}$ photoemission lines, which are assigned to the well-screened $2p^33d^4L$ final state (c is a hole in the p core level due to photoemission, $n =$ 7 and 8 for Co$^{2+}$ and Ni$^{2+}$, respectively, $L$ is one hole in the O2p band). The strong satellite structure, S, is composed of a poorly screened mixture of $2p^33d^{4}+2$ and $2p^33d^{4}+2L^2$ final states ($L^2$ are two holes in the O2p band).[27–29] The $S$ energy separation of ≈5 eV is typical for the Co$^{2+}$ (t$_{32g}^1 \rightarrow t_{2g}^1 \rightarrow e_{g}^1 \rightarrow f$) and Ni$^{2+}$ (t$_{32g}^1 \rightarrow t_{2g}^1 \rightarrow e_{g}^1 \rightarrow f$) ground state electronic configurations. The Co2p$_{1/2}$ ($E_{bin} = 782.5$ eV) and Ni2p$_{3/2}$ ($E_{bin} = 858$ eV) binding energies fit well to the previously reported values for LCP composite and LN thin film.[30,31]

The VB structure of the LCP pristine film (Figure 2b) exhibits the four spectral features denoted as L$_{v}$, B$_{v}$, C$_{v}$, and D$_{v}$, which are assigned to the occupied t$_{2g}$ and e$_{g}$ states of Co (A$_{t}$), the band composed of the Co3d and O2p bonding and antibonding states (B$_{v}$), as well as to the strongly bound phosphorus and oxygen states (C$_{v}$ and D$_{v}$).[32,33] The VB spectrum of the LNP pristine film (Figure 3b) is similar to LCP with the well-resolved fine structure denoted as B$_{v}^+$ and B$_{v}$. These VB spectral features are not well resolved in LCP due to the superposition of the photoemission signals from the Pt substrate and the olivine cathode (Figure S6, Supporting Information). The fine structure formed by the B$_{v}^+$ and B$_{v}$ features of LNP can be also assigned to a stronger hybridization of the Ni3d–O2p states as compared to the Co3d–O2p states. In addition, one may also consider that the VB states of LNP might be influenced by Al (s, p) states,[34] due to Al-doping of the LNP target material. However, the O2p states of olivine contribute dominantly to the VB structure due to the low doping concentration of Al. Upon LiPON deposition, the Co2p and VB structure photoemission lines are shifted to higher binding energies at lower electrolyte coverage (Figure 2a,b), which is a sign of a downward band bending at the LCP/LiPON interface. The shape of the Co2p photoelectron spectra and the energy distance of the satellite structure (S) from the main Co2p photoemission is mostly preserved upon the LiPON deposition (Figure 2a), thereby evidencing that the oxidation state of the divalent Co ions remained unchanged. No reduced species are detected in the LiIIs photoemission, which becomes inherent to LiPON at high electrolyte coverage (Figure 2c). The narrowing of the Co2p photoemission (Figure 2d) is ascribed to a passivation of surface defects of the pristine LCP by LiPON. Similarly, the surface defects’ passivation by an adsorbate was earlier revealed on LCO layered oxide.[15] The complete vanishing of the Co2p photoemission signal under the LiPON film of 60 Å thickness (Figure 2a) agrees perfectly with the XPS probing depth of $d = 45$ Å ($\lambda = 21.3$ Å for $E_{bin} = 760$ eV).[36] The VB spectral features (Figure 2b) are modified with LiPON growth transforming to the shape of the LiPON structure at 60 Å with the dominated character of the O2p ($A_1^v = 7$ eV), P3p ($B_1^v = 10$ eV), and P3s ($D_1^v = 12$ eV) states.[22] The N2p state is expected to be situated at ≈6 eV,[37] but cannot be resolved due to its proximity to the O2p state of the substituted oxygen. The energy onset of valence electrons of LiPON is found to be $E_v = E_{VBM}^{LiPON}$ ≈3.7 eV, which is close to the value of 4.1 eV.[12] The VB spectrum of the “bulk” LiPON grown on LNP is slightly impacted by the contribution from Pt manifested as an enhanced intensity of the spectral feature $A_1^v$ and the shoulder at ≈6 eV (Figure 3b, the upper spectrum). The reason of the Pt emergence on the LiPON surface will be discussed below by the analysis of the LNP/LiPON interface properties.

In contrast to LCP, the Ni2p, VB structure, and LiIIs photoemissions of the LNP/LiPON interface are shifted to lower binding energies (Figure 3a–d), thereby exhibiting the upward
band bending, $\delta$. A parallel shift of the Li$^+$ photoemissions associated with LiPON and LNP is also shown in Figure 3d. This is an unexpected $\delta$ direction, taking into account the fact that the pristine LNP/vacuum interface exhibits a downward band bending (Figure 4a and Figure S9, Supporting Information). The $\delta$ direction at the semiconductor–electrolyte interface is usually defined by the initial (intrinsic) charge distribution of the semiconductor, which may change after contact formation to the electrolyte depending on the defect distribution on both sides of the double layer.\cite{38,39} However, the direction is not expected to be changed if no chemical reactions take place or no electron/hole transfer across the interface will affect the charge distribution. The situation is more complicated for ionic conductors, where the Li$^+$ ion transfer across the interface driven by the chemical potential difference ($\Delta \mu_{\text{Li}}$) of Li$^+$ ions in the electrode and electrolyte would also impact the band bending due to buildup of an electrostatic potential.\cite{12,40–42} The competitive contribution of the electronic ($\mu_e$) and ionic ($\mu_{\text{Li}}$) parts of the electrochemical potential might change the strength and direction of the band bending, which however are directly measured by XPS. In this regard, the low binding energy shift, which is well visible for the VB and core level photoemissions of the LCP/LiPON interface of 120 Å thickness (Figure 1a,b and Figure 2b), might be assigned with Li$^+$ ion transfer from the electrolyte to the cathode, thereby influencing competitively the band bending direction.

By analyzing the Li$^+$ photoemission, no chemical reactions are detected between LiPON and LNP until 35 Å of the electrolyte thickness (Figure 3c). Thus, possible decomposition reactions from the onset of the LiPON formation are ruled out. However, a chemical reaction takes place at higher electrolyte coverage, as manifested by the emergence of the spectral feature at $E_{\text{bin}} = 54.2$ eV (Figure 3c). This finding correlates

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**Figure 2.** Stability of LiCoPO$_4$ (LCP)/LiPON interface upon increasing the charge density. a) Evolution of Co2p, b) VB structure, and c) Li1s photoemission spectra of LCP versus the LiPON thickness ($h_\nu = 1486.7$ eV). The A$_v$, B$_v$, C$_v$, D$_v$, spectral features are assigned to LCP, whereas the A$^L_v$, B$^L_v$, C$^L_v$, D$^L_v$ features, which are well resolved at $\approx 60$ Å thickness, are assigned to LiPON (b). Attenuation of the photoelectron intensities from the olivine structure with LiPON deposition is not shown here (see Figure S7, Supporting Information). d) The normalized Co2p photoemissions of pristine LCP (blue solid line) and the electrode covered by LiPON of 15 Å thickness (red circles). The Co2p spectrum measured on the 15 Å interface is shifted to lower binding energy to get the same value that for the pristine LCP; their difference spectrum is shown in green. e) An illustration of LiPON coverage onto LCP. f) A schematic view of the energy diagram of the LCP/LiPON interface with the downward band bending, $\delta$, of the electronic states, as deduced from the experiment. $E_{\text{vac}}$, $\phi$, $E_F$, $N(E)$ are the vacuum level, work function, Fermi level, and density of occupied states, respectively. The Li$^+$ ion transfer from LiPON to LCP, as it is illustrated by the painted arrow, will reduce the downward band bending.
with the occurrence of a shoulder in the Ni2p photoemission at $E_{\text{bin}} \approx 855$ eV (Figure 4b), which fits well to the binding energy of NiO.\textsuperscript{[45]} One notes that the possible chemical reactions of the LiPON surface with residuals commonly presented even at ultra-high vacuum (UHV) conditions are not supported by our experiments (Figure S10, Supporting Information). The fact that this reaction starts at an elevated LiPON coverage is related to the band bending induced by the electrolyte (Figure 4c), which shifts the energy states of the cathode and electrolyte in relation to each other (Figure 5a). Thus, a minimum thickness of the LiPON overlayer is needed in order to reach a certain band bending value (Figure 5b). The revealed oxides suggest the involvement of the lattice oxygen in the interface reaction, which would lead to the distortion of the PO$_4$ tetrahedron due to the oxygen loss.\textsuperscript{[46]} Indeed, a slight widening of the P2p photoelectron line is observed at 35 Å LiPON thickness (Figure S11, Supporting Information). However, the contribution of NiO and Li$_y$O$_z$ to the Ni2p and Li1s photoemissions, respectively, is very minor (Figure 3c, Figure 4b). Therefore, the changes in the P2p photoelectron spectrum are not significant. As an example, the photoelectron spectra of a LCP film, partially decomposed to the spinel structure upon high temperature annealing, are shown in Figure S12, Supporting Information. The Pt inclusions on the surface of the bulk LiPON (Figure S13a, Supporting Information) may be associated with microcracks in LiPON and LNP induced by the revealed interface reaction. Pt is not detected by XPS at a small LiPON coverage, but it occurs for the thick LiPON film onto LNP (Figure S13b, Supporting Information). The change of the modulus in the areas of the reordered surface, where NiO and Li$_y$O$_z$ are formed, might facilitate seepage of Pt on the LiPON surface. It is important to stress that the revealed interface reaction at the LNP/LiPON interface is not a consequence of the effect induced by Pt (the noble metal is chemically inactive), but rather the opposite. This conclusion is supported by our photoemission experiments on the LiPON/ Pt/Si interface, where the absence of a buffer layer between the metal and semiconductor resulted in seepage of Si on the LiPON surface (Figure S14, Supporting Information). However, even in this case, the change in oxidation state of lithium was not detected.
Figure 4. a) A schematic view of the energy diagram of the LNP/vacuum interface demonstrating the downward band bending ($\delta \approx 0.2$ eV) of the electronic states, as deduced from the angle-resolved XPS experiments ($h\nu = 1486.7$ eV). $E_{\text{vac}}$, $\phi$, $E_F$, $N(E)$ are the vacuum level, work function, Fermi level, and density of occupied states, respectively. b) The normalized Ni2p photoemissions of pristine LNP (blue solid line) and LNP covered by LiPON of 35 Å thickness (red circles). The Ni2p spectrum measured on the 35 Å interface is shifted to higher binding energy by 0.8 eV to obtain the same value as for the pristine LNP, their difference spectrum is shown in green. The emergence of Ni ions adopting the sites different from olivine structure is shown by the arrows. c) The energy diagram of the LNP/LiPON interface demonstrating the upward band bending ($\delta = 1.7$ eV) deduced from the VB photoelectron spectra. The possible charge transfer mechanisms influencing the band bending are illustrated by the painted arrows. d) An illustration of LiPON coverage onto LNP with the possible decomposition products.

Figure 5. The Fermi level shift ($E_F$ shift) versus the electrolyte thickness. a) $\mu_{\text{LNP}}$ of LNP (on the left) is shifted toward the valence band maximum of LiPON ($E_{\text{VBM}}^{\text{LiPON}}$), whereas $\mu_{\text{LCP}}$ of LCP (on the right) is shifted away from $E_{\text{VBM}}^{\text{LiPON}}$ with an increase of the LiPON thickness. The $E_F$ shift equals zero for the pristine LNP and LCP. The vertical arrows show the relative positioning of $\mu_{\text{LNP}}$ and $\mu_{\text{LCP}}$ and $E_{\text{VBM}}^{\text{LiPON}}$ at the LiPON thicknesses of 35 and 60 Å, for LNP and LCP respectively. b) The impact of an increase of amount of the charge distributed on LNP/LiPON interface on the band bending ($\delta$) value. The lower the LiPON coverage, the lower the amount of the charge concentration, which leads to a smaller $\delta$. The higher the electrolyte thickness, the higher the concentration of the positive charge on the LiPON side, which results in increasing $\delta$. Thus, the $E_F$ of LNP approaches closer to its valence band maximum (VBM). The difference in the $E_F$ position ($\Delta\mu$) is also shown.
Thus, in order to understand the reason of the instability of LNP, whereas LCP remains stable at the contact with LiPON, the energy band diagrams of the electrolyte/LCP and LNP/LiPON interfaces have to be considered (Figures 5a and 6). A relatively large ionization potentials difference ($\Delta IP \approx 1.5$ eV) of LCP and LiPON (Figure 6a), as well as the energy distance of $E_F$ of LCP from the VBM of LiPON ($E_{VBM}^{LiPON}$) ensures that no electron/hole transfer between the contacting phases takes place. Thus, no chemical reactions between the electrolyte and LCP are expected. Upon LiPON deposition, the downward band bending shifts the $E_F$ of LCP further away from the $E_{VBM}^{LiPON}$ (Figure 5a, on the right), thereby decreasing even more the probability for the hole/electron transfer across the interface (Figure 6a). In contrast, the ionization potentials of LNP ($IP_{LNP}$) and LiPON ($IP_{LiPON}$) are very close to each other (Figure 6b). $IP_{LNP}$ might be even slightly lower taking into account the variations of the measured values, as well as a possible surface dipole, which might contribute to the experimentally determined work function, $\phi$. This close proximity of the electronic levels of the contacting phases enables the hole transfer across the LNP/LiPON interface, although the chemical reactions are still not detected at the low electrolyte coverage (Figure 3c). The situation is drastically changed at a higher electrolyte thickness, which induces a higher amount of the positive charge on the LNP side (Figure 5b). The resulting upward band bending approaches $E_F$ of LNP to $E_{VBM}^{LiPON}$ (Figures 5 and 6b), which is accompanied by hole transfer from the Ni3d-O2p strongly bind into the vacuum level ($E_{vac}$).
hybridized states to the valence electronic states of the electrolyte. Although a number of the transition metal sites involved in the charge transfer is found to be very small and, therefore, the changes in the chemical composition at the LNP/LiPON interface are not significant, they might become even more severe upon applying a charging potential of the battery cell. In this case, the electrochemical Li$^+$ ion withdrawal from the cathode coupled to the release of a valence electron would lead to the downward shift of $E_F$ (i.e., closer to the VB structure), the magnitude of which may be a few eV.\textsuperscript{[18]} Such a shift coupled to the revealed upward band bending (Figure 6b) can situate the $E_F$ pretty much below the VB maximum of the electrolyte, which would lead to abundant holes transfer across the interface, thereby impacting the electrochemical stability of the high voltage battery cell. As for LCP, if a charging potential would be applied within the operational condition of the battery cell, the edge of the VB states given by $E_{V,C}$ would remain outside an expected hole transfer (see Figure 6a, on the right), thereby ruling out the electrolyte oxidation. In principle, the solid electrolyte interphase (SEI), which is formed as the result of chemical reactions of the electrode and electrolyte, can positively impact the battery performance provided that the SEI is Li-ion conducting and serves as a protective layer against further degradation of the electrode material. However, in the case of the vicinity of the $E_F$ of pristine electrode and the highest occupied electronic states of electrolyte, periodical shift of the $E_F$ below the VBM upon the repeated electrochemical charging of the battery cell will lead to further electronic charge transfers accompanied by uncontrolled altering of chemical composition of the SEI layer. Taking into account the high ionization potential of LNP, as well as the challenge to find an electrolyte with a high anodic limit ($>5$ V), the probability of interface instability is significantly increased upon electrochemical cycling of solid-state batteries using LNP as the cathode material. Thus, LiPON is probably not a suitable electrolyte (or not the best candidate) for LNP due to the close values of the ionization potentials, whereas LCP is chemically compatible with LiPON due to a more favorable charge distribution at the interface. As for other olivine-type materials, a high difference in the ionization potentials of LiFePO$_4$ (3.6 eV)\textsuperscript{[48]} and LiPON ($\approx$8.4 eV) assumes that these ionic conductors are chemically compatible. We also expect the stability of the LiPON/LiFePO$_4$ interface upon delithiation of the cathode due to a sufficient energy reserve between the VBM of LiPON and the $E_F$ which is shifted down during delithiation. The ionization potential of LiMnPO$_4$ is expected to be situated between LCP and LiFePO$_4$, which would also suggest their chemical compatibility. However, as is shown in the present study, the properties of the double layer at the electrode-electrolyte interface, which however can be measured, can strongly impact the relative energetics of the contacting ionic conductors. On the other hand, the direction and strength of interfacial band bending can be tailored by preparation conditions via the stoichiometry variation, amorphization, and/or passivation of the cathode surface (Figure S15, Supporting Information). From the chemical point of view, such a tailored interface should serve as a protective layer against the chemical reactions with the electrolyte\textsuperscript{[49–52]} ensured by the significant downward shift of the electrolyte VB maximum away from the valence states of the cathode. However, the issue on the chemical reactivity of the modified surface remains open and demands further studies. Our previous research on the LiPON/LCO interface have demonstrated an impact of temperature on the band alignment of two ionic conductors,\textsuperscript{[19]} which gives an opportunity to design the interface with desirable properties. On other hand, annealing can also provoke chemical reactions and intermixing at the interface, which would lead to the formation of unpredictable and poorly controlled chemical composition. As for the lithium/electrolyte interface, the change of the Fermi level position is not expected due to the metallic character of lithium, as well as due to an unlimited reservoir of lithium ions in the anode. However, the SEI layer formation might result in the shift of the Fermi level caused by the change of chemical composition at the interface. Nevertheless, the energy band diagrams experimentally obtained on the electrolyte, the anode, and their interfaces can be used to forecast interfacial chemical reactivity driven by the difference in the electrochemical potentials.

3. Conclusion

The present study demonstrates the crucial role of the electronic part of the electrochemical potential in interface reactivity, as well as of the relative positioning of the ionization potentials of the electrode and electrolyte on interface stability. On the example of LCP and LNP carbon-free thin film model interfaces with LiPON solid electrolyte, we demonstrate that interface stability is governed by the band bending direction, the amount of charge distributed on the electrolyte side and a favorable electrochemical potential shift upon double layer formation. A large ionization potential difference between the LCP cathode and LiPON ensures their chemical compatibility. This implies the high interface stability upon charging the battery cell due to the small probability of the electron (hole) charge transfer at the cathode-electrolyte interface even at high operating voltages. Conversely, a small ionization potential difference between the LNP and LiPON, aggravated by the Fermi level shift to the top of the occupied electronic states of LiPON upon the electrolyte contact, is the reason of interfacial reactivity. Thus, for materials selection, a sufficient energy gap between the ionization potentials of the cathode and electrolyte should be provided to avoid undesirable interfacial electronic charge transfer. We also show that the electronic properties at the cathode-electrolyte interface can be strongly modified by varying the preparation conditions of the cathode material, which opens a perspective to control the interface stability, as well as the charge exchange across the interface. The developed atomistic-molecular experimental approach directly provides the relevant energy conditions which govern the possibly involved decomposition reactions and provides a perspective to investigate and control the charge distribution at the electrolyte-electrode interface via tailoring the surface/interface properties of the electrode materials. Predicting the electrochemical stability of the electrode–electrolyte interface based on photomission experiments can be extended to a wide range of alkali ion batteries, capacitors, as well as energy conversion devices such as fuel cells, catalysts for water splitting, where the electronic properties across the double layer formed between the
contacting phases (gas, liquid, solid) are crucial for an efficient charge exchange at the interface.

4. Experimental Section

The preparation of the LCP and LNP carbon-free olivine thin film materials and their interfaces with LiPON, as well as in situ photoelectron spectroscopy experiments were carried out in the Darmstadt Integrated System for Battery (DAISY-BAT) laboratory. In addition, the electronic structure of the LCP and LNP pristine thin films was studied by using synchrotron facilities at BESSY II. Advantage of the in situ approach was the elimination of possible adsorption effects from ambient, which impeded the interpretation of the experimental data.

Preparation of LCP and LNP Thin Films: The LCP and LNP thin film materials were grown by using radio-frequency (RF) sputtering at room temperature (RT) in a home-made UHV chamber followed by the film annealing using a laser heater setup.[29] The base pressure in the deposition chamber was \( p < 10^{-8} \) mbar. Pt/\( \text{TiO}_2/\text{SiO}_2/\text{Si} \) wafer (GMK) and Pt foil were used as a substrate. The LCP thin films were deposited in Ar atmosphere (\( p_{\text{Ar}} = 1 \times 10^{-2} \) mbar) at RT following the film annealing at \( T = 700 \) °C in air. An LNP doped with 5% of Al was used as target material (Kurt J. Lesker Company Ltd). Al doping was envisaged to enhance electronic conductivity of the olivine-type material. The LNP thin films were grown in argon–oxygen atmosphere (\( p_{\text{Ar}}/p_{\text{O}_2} = 2 \times 10^{-2} \) mbar) at RT. The LNP film annealing was performed at \( T = 700 \) °C.

Preparation of LiPON and Its Interfaces with Different Substrates: Amorphous LiPON films were deposited onto the LCP and LNP surfaces by RF sputtering of a \( \text{Li}_2\text{P}_2\text{O}_7 \) target in \( \text{N}_2 \) atmosphere \( (p_{\text{N}_2} = 5.5 \times 10^{-3} \) mbar) at RT. The LiPON growth rate was \( 0.05 \) and \( 0.29 \) Å s\(^{-1}\) on LCP and LNP, respectively, which allows an estimate of the solid electrolyte thickness. In addition, LiPON was deposited on a Pt/\( \text{TiO}_2/\text{SiO}_2/\text{Si} \) wafer as the reference substrate. A chemical composition \( \text{Li}_{2+1.45} \text{O}_{0.5} \text{P}_{1.0} \text{O}_{1.45} \) was obtained by using XPS quantitative analysis after each step of the LiPON deposition. The block diagram of the consequence of photoemission experiments is shown in Figure S19.

Supporting Information. The base pressure in the analysis chamber was \( 10^{-7} \) mbar in the parallel beam monochromator. An Al K(\( \nu = 1486.7 \) eV) source at an electron escape angle of \( \theta = 20°, 45°, \) and \( 90° \) was used to detect the LiPON films deposited on different substrates. The authors thank Alexander Kempf for the allocation of synchrotron radiation beamtime at the SoLiAS endstation at the U56 II/PGM-1 beamline. They also wish to thank Dr. Magdalena Graczyk-Zajac and Manuel Donzelli for a fruitful discussion on the impedance results.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge distribution, electron spectroscopy, interfacial stability, \( \text{LiCoPO}_4 \) and \( \text{LiNiPO}_4 \) lithium phosphorous oxyxynitride

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Supporting Information

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