Topical Review

All-solid-state thin-film batteries based on lithium phosphorus oxynitrides

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Received 18 May 2022, revised 27 June 2022
Accepted for publication 1 July 2022
Published 23 September 2022

Abstract

Lithium phosphorus oxygen nitrogen (LiPON) as solid electrolyte discovered by Bates et al in the 1990s is an important part of all-solid-state thin-film battery (ASSTFB) due to its wide electrochemical stability window and negligible low electronic conductivity. However, the ionic conductivity of LiPON about 2 × 10⁻⁶ S cm⁻¹ at room temperature is much lower than that of other types of solid electrolytes, which seriously limits the application of ASSTFBs. This review summarizes the research and progress in ASSTFBs based on LiPON, in the solid-state electrolyte of LiPON-derivatives with adjustable chemical compositions of the amorphous structure for the improvement of the ionic conductivity and electrochemical stability, in the critical interface issues between LiPON and electrodes, and in preparation methods for LiPON. This review is helpful for people to understand the interface characteristics and various preparation methods of LiPON in ASSTFBs. The key issues to be addressed concern how to develop solid-state electrolyte films with high conductivity and high-quality interface engineering as well as large-scale preparation technology, so as to realize the practical application of highly integrated ASSTFBs.

Keywords: LiPON, solid electrolyte, solid thin-film battery, interfacial property, preparation method

1. The development of LiPON in ASSTFB

An all-solid-state thin-film battery (ASSTFB) is a kind of solid-state battery in the form of a thin film whose total thickness is at the micron level, which has high capacity, long cycle life, excellent mechanical strength, and good thermostolerance. These advantages make it suitable for potential applications such as smart cards, microsensors, microelectronics, and micromechanical devices as micropower sources that could not be replaced by other chemical batteries [1–3]. It is composed of thin films of the cathode, solid electrolyte and anode constructed on a substrate in sequence, and the schematic of the representative fabrication process for ASSTFB based on lithium phosphorus oxygen nitrogen (LiPON) thin-film solid electrolyte is shown in figure 1. Since the 1980s, a lot of research on thin-film electrode materials and solid-state electrolytes in thin-film batteries has been conducted, and has obtained many satisfactory results (figure 2). There are two
kinds of thin-film lithium batteries that have attracted much attention for a long time. One is the thin-film battery assembled with the polymer solid electrolyte, and the other is the thin-film battery assembled with the inorganic solid electrolyte. However, the thin-film battery with polymer electrolyte has a narrow working temperature range, poor integration compatibility, and a lack of adaptability to various extreme environments, which is quite different from that with inorganic thin-film electrolyte. ASSTFB is constructed primarily by the physical vapor deposition technique, which can be coupled with modern semiconductor processes. Therefore, this kind of ASSTFB with a thickness of fewer than 10 µm is expected to be integrated into semiconductor devices to realize the miniaturization and integration of thin-film batteries.

Hitachi firstly reported on thin-film batteries in 1982 [4], but it could not drive the electronic devices at that time due to the low power of the thin-film batteries. In the past two decades, advances in semiconductor technology have led to many kinds of low-power devices such as complementary metal-oxide-semiconductor [5], ferroelectric random access memory [6] and liquid crystal displays [7], and it is feasible to make thin-film batteries work as power sources for these miniaturized low-power devices. With the rapid development of micro-electronic devices, the demand for the higher energy density of thin-film batteries is increasing in recent years. Fortunately, many commercial companies with ASSTFB are promoting the practical application of thin-film batteries. For example, Infinite Power Solutions has launched the active radio frequency identification devices (RFID) composed of an ASSTFB, an integrated chip, and a thin-film antenna. It can receive radio frequency (RF) through the antenna to charge ASSTFB, which provides the power source for active RFID tags. Cymbet provides ASSTFB for microelectronic devices as backup power. The thin-film battery integrates two parts of energy storage and power management and is packaged into a patch-type thin-film battery. The operation voltage of the battery is 3.9 V with the capacity of 100 µAh, and the attenuation of the capacity is less than 10% after 5000 cycles, with the operating temperature ranging from −20 to 70 °C.

In addition, ASSTFB with flexibility and no cytotoxicity is a key component of an integrated intra-oral light therapy device that is installed in the human’s dental arch in an adaptive manner (figure 3) [8].

The concept of ASSTFBs was first proposed in the 1980s [4]. TiS$_2$ prepared by chemical vapor deposition (CVD) method was used as cathode material in this battery, Li$_{3.6}$Si$_{0.6}$P$_{0.4}$O$_4$ solid electrolyte and metal Li anode were fabricated by RF sputtering method and vacuum thermal evaporation, respectively [9]. In addition, WO$_3$ and 0.63WO$_3$–0.37V$_2$O$_5$ cathodes that had been synthesized by reactive sputtering in the H$_2$–Ar atmosphere were also integrated into this kind of battery [10]. The first thin-film battery has a size of 4 mm × 4 mm, and an overall thickness of 6–8 µm, including 1–3.7 µm of TiS$_2$ cathode, 2–4 µm of electrolyte, and 4 µm of Li metal anode. The reaction platform of these batteries is at 2.5 V, the current density and the capacity of which are 3–16 µA cm$^{-2}$ and 45–150 µAh cm$^{-2}$.
separately. Nippon Telegraph & Telephone also developed a series of thin-film batteries fabricated by the RF sputtering method, in which the Li$_3$VO$_4$–Li$_4$SiO$_4$ solid solution system (Li$_x$Li$_{4-x}$VO$_4$Si$_4$O$_4$ and Li$_3$O–V$_2$O$_5$–SiO$_2$) were employed as the solid electrolyte, transition metal oxide (MnO$_2$, WO$_3$, and MoO$_3$) and evaporated Li metal was used as the cathode and anode, respectively [11–13]. These kinds of batteries are 1 cm$^2$ in size, with a cathode thickness of 1–5 $\mu$m, an electrolyte thickness of 1 $\mu$m, and a Li metal anode thickness of 4–8 $\mu$m. In the 1980s, Eveready Battery Company and Bellcore in the United States prepared thin-film batteries containing sulfide glass electrolytes such as Li$_4$P$_2$S$_7$ or Li$_3$PO$_4$–P$_2$S$_5$, using TiS$_2$ as cathode material and Li metal or LiI as anode [14–16], whose voltage range is 1.5–2.8 V, the current density is 10–135 $\mu$A cm$^{-2}$, and the cycle retention can reach more than 1000 times. Besides, Bellcore fabricated kinds of thin-film batteries with Li$_2$MnO$_4$ as the cathode material, lithium borophosphate glass as the solid electrolyte and Li metal as the anode, which can cycle more than 150 times between 3.5 and 4.3 V with 75% capacity retention after cycling [17].

A landmark move is that Oak Ridge National Laboratory (ORNL) used LiPON solid electrolyte for preparing thin-film batteries in the 1990s [18–20]. LiPON thin-film solid electrolyte was prepared by RF sputtering a Li$_3$PO$_4$ target in the N$_2$ atmosphere, which is very stable compared with other lithium oxide and sulfide glass electrolytes and possesses moderate ionic conductivity (about $2.3 \times 10^{-4}$ S cm$^{-1}$) and activated energy (0.55 eV) [20]. The I–V curve of LiPON showed that it has a wide electrochemical stability window whose range is 0–5.5 V (vs. Li/Li$^+$). They reported some thin-film batteries with LiPON solid electrolyte demonstrating excellent electrochemical performance, whose voltage range is from 2 V to 5 V, and the current density can reach 10 mA cm$^{-2}$ and the cycle can exceed 10 000 times. It is worth noting that Newdecker et al. reported a ‘lithium-free’ thin-film battery, that is, after the film battery with LiCoO$_2$ (LCO) as the cathode was charged for the first time, a layer of Li metal anode was in situ plated on the Cu current collector. This kind of method to prepare thin-film batteries avoids the presence of low melting lithium under the condition of welding reflo, which makes it possible to integrate the thin-film batteries into electronic circuits [21]. LiPON is now considered as one of the normative solid electrolytes for thin-film lithium batteries and is used by many research teams and several companies in the United States, such as Jet Propulsion Laboratory [22, 23], Korea Institute of Science and Technology [24, 25], Cymbet, Exellatron, etc. Baba and co-workers reported a new type of thin-film battery with LiPON as the solid electrolyte. Li, V$_2$O$_5$ or V$_2$O$_4$ was used as anode instead of metal lithium to construct V$_2$O$_5$/LiPON/Li, V$_2$O$_5$ and V$_2$O$_4$/LiPON/LiMn$_2$O$_4$ thin-film batteries. Since the metal Li is not used as the anode, this kind of rocking chair battery has obvious advantages in the preparation process and the safety, but it needs to be charged before the first use [26, 27]. This kind of battery experiences a dramatic increase in capacity to 10 $\mu$Ah cm$^{-2}$ at the first 20 times cycle, which can be attributed to the gradual reduction of interfacial resistance between the electrode and solid electrolyte [27]. Baba et al also prepared multiple cells on a single substrate to increase the voltage and current density of batteries, which can reach 3–6.5 V and 2 $\mu$A cm$^{-2}$, respectively [28]. West et al fabricated ASSTFB by using high-voltage cathode materials of Li$_4$Mn$_2$Ni$_{0.6}$O$_4$ and LiCoPO$_4$ as cathode, whose discharge plateau can reach more than 4.5 V [22, 23].

Thin-film batteries have also been studied by Ribes’s group in France since the 1980s, they focused on chalcogens compounds as cathode materials, such as In$_2$Se$_3$, TeO$_2$, GeSe$_{5.5}$, TiSe$_2$, etc [29–33]. Balkanski et al investigated the electrochemical properties of the thin-film batteries consisting of In$_2$Se$_3$ or InSe cathode, Li metal anode and lithium borate glass electrolyte, in which the cathode and electrolyte materials were prepared by flash evaporation and molecular beam deposition techniques, respectively [31]. Creus et al prepared Li/Li$_5$S-SiS$_2$/GeSe$_{5.5}$ and Li/0.7(0.4Li$_2$O-0.2B$_2$O$_3$-0.4P$_2$O$_5$)-0.3LiCl/0.7V$_2$O$_5$-0.3TeO$_2$ thin film batteries by RF sputtering and flash evaporation. Menetrier et al developed a thin-film battery using TiS$_2$ as cathode material and B$_2$S$_3$/Li$_2$S-Li as the vitreous electrolyte, whose open-circuit voltage is about 2.0 V and the capacity is 50–300 $\mu$Ah cm$^{-2}$ [30]. Kuwata et al prepared a thin-film battery with LCO as the cathode, Li$_{4-x}$V$_{0.5}$Si$_{29}O$_{53.6} glass as the solid electrolyte, and SnO as the anode material [34]. Each thin-film component in this kind of battery was in situ fabricated by only using the pulsed laser deposition (PLD) technique. The size of the battery is about 0.23 cm$^2$ and the thickness is about 2 $\mu$m. However, after the first charge, the SnO anode reacts with the lithium-ion to generate Sn-Li alloy and amorphous Li$_2$O, resulting in a large capacity loss. Such a thin-film cell was prepared by using micromachining technology, and its cross-section image was primarily observed by scanning electron microscope (SEM). The recent literatures on micromachined thin-film batteries were reviewed and they will not be introduced here [2, 35].

Although rechargeable lithium-ion batteries are strong candidates for high-performance flexible power sources, the compatible electrode material for bendable lithium-ion batteries is limited, and the electrochemical performance of the flexible battery is insufficient for application in flexible consumer electronic devices such as the flexible display. In 2012, Koo et al proposed the universal transfer approach to develop a bendable thin-film battery regardless of the chemical properties of the electrodes (figure 4(a)) [36]. This approach could transfer high-temperature annealed electrodes to the polymer substrates for the high-performance thin-film battery. Such a bendable lithium-ion battery can be integrated with a flexible light-emitting diode (LED) to construct an all-in-one flexible electronic device (figure 4(b)). Hallot et al prepared a thicker LiMn$_{1.5}$Ni$_{0.5}$O$_{4}$ (LNMO) layer for lithium-ion batteries by using the stacking layers of Cr and Pt metal as the current collector on aluminum oxide@Si wafer due to the adhesion improvement between aluminum oxide and platinum layers. When the thickness of LNMO film increases from
150 nm to 7400 nm, the areal capacity of which is significantly enhanced from 3 to 375 \text{ \( \mu \)Ah cm\(^{-2} \)}, and new opportunities seem to be opened for preparing thin-film batteries with high energy density and ultra-high rate capability (figure 5) [37]. Trask et al. illustrated the electrochemical properties of LCO textures [38]. The (003) plane (an unfavorable texture) is a strong texture of LCO due to its lowest surface energy, and the crystallization during anneal leads to the formation of more favorable LCO textures such as (101), (104), and (110) orientation (figure 6). The thin-film battery with texture-controlled cathode exhibited a discharge capacity of 600 mAh cm\(^{-2} \) at C/10 rate, and larger than 95% capacity retention after 100 times cycle at C/5 rate. The thin-film battery with the uncontrolled cathode (predominantly (003)) has a similar capacity, but the cycling performance and rate capability of which are severely diminished.

Up to now, ASSTFBs based on the LiPON thin-film solid electrolyte have been fabricated by various preparation methods. Yamamoto et al. prepared one layer of LCO cathode on LiPON film by using the aerosol deposition method without heating to construct an inverted-stack Li-free thin-film battery, which can stably cycle for over 100 times [39]. Tunnel structure Li\(_2\)MnO\(_3\) nanosheet arrays cathode material was prepared by an essential interfacial reaction between MnO\(_{2-x}\) with LiPON for infusing Li\(^+\) ion into MnO\(_{2-x}\) at a low temperature of 180 °C, and the ASSTFB Li\(_x\)MnO\(_2\)/LiPON/Li shows better rate and cycling properties than 2D MnO\(_{2-x}\) or traditional LiMn\(_2\)O\(_4\) (LMO) thin-film batteries [40]. Vertically aligned oxygen-deficient \( \alpha \)-MoO\(_{3-x}\) nanoflake arrays were reported as cathode material for thin-film batteries with LiPON as the electrolyte, which shows better performance than the 2D cathode owing to the larger electrode/electrolyte interface area and shorter Li\(^+\) ion diffusion pathway [41]. Chen et al. investigated the photonic methods for fast crystallization of LMO cathode in LiPON-based thin-film batteries, among which the xenon flash-lamp annealing is a promising technique for preparing high electrochemical performance electrode [42]. They also used the same method to prepare LCO cathode on Al foil to fabricate flexible thin-film batteries [43]. The \textit{in situ} annealing LCO cathode on a 500 °C substrate during the deposition process exhibits better crystal structure and electrochemical performance than the post-annealing one in thin-film batteries reported by Wang et al., which illustrated the value of \textit{in situ} annealing [44]. Zhang et al. used the RF magnetron sputtering method to prepare thin-film batteries with lithium trivanadate (LVO) cathode and LiPON electrolyte [45]. They found that the partially crystalline LVO...
performed better than the amorphous or the totally crystalline one, and the rate-limited steps such as phase-transformation reactions and ionic diffusion process during cycling of batteries are associated with the level of crystallization and operated temperature. Yim et al prepared thin-film LNMO cathode material on polyimide substrate by excimer laser annealing process, which is a promising technique with minute damage for polymer substrate, and the full cells are bendable and have stable cycling performance [46]. The thin-film batteries with Li4Ti5O12 (LTO) cathode prepared by using flame spray pyrolysis technique on polymer substrate also demonstrated great rate capability and stable cycling with negligible damage of substrate [47].

Except for LiPON solid thin-film electrolytes, other kinds of thin-film electrolytes used in ASSTFBs also have been reported in recent years. Nishio et al fabricated a bottom-current-collector-free thin-film battery with the high ordered and crystalline LiNi0.5Co0.2O2 epitaxial thin film as cathode material and Li2PO4 as the solid electrolyte, which shows stable battery operation due to anti-phase grain boundaries migration although the orientation of cathode thin film is unfavorable for ionic transport [48]. They also studied the structural and electrochemical properties of NMC(001) epitaxial thin film on the same electrolyte, which manifests low interfacial resistance and stable cycling [49].

Our research group has also carried out relevant research since 2000 and has made great progress. Many kinds of metallic oxide, nitride, and fluoride electrode film have been prepared effectively by PLD or RF magnetron sputtering such as LiMn2O4, LCO, Ta2O5, TiO2, ZnO, NiO, Ag80.3V2O5, MNx (M = Co, Fe, Ni, Mn), etc [50–57], all of which have good electrical or electrochemical properties. Great improvement has been made in the preparation of thin-film electrolytes, such as LiPON and Li–V–Si thin film was successfully prepared by PLD or electron beam evaporation [58–60]; Li/LiPON/V2O5, Li/LiPON/LCO thin-film batteries were satisfactorily prepared by combining PLD with vacuum thermal evaporation for the first time [59, 61]. The ‘lithium-free’ and ‘anode-free’ ASSTFB of stainless steel (SS)/LiPON/Ag was first reported, in which the solid electrolyte worked as the lithium source [62]. Lithium-ion was reduced at the anode (SS) surface to form a metallic lithium layer when the voltage of the battery was higher than 3.7 V, and a new phase Agx+1LiPO3N emerged at the cathode probably. At present, the ASSTFBs with a kind of Prussian blue compound (LiFeFe[CN]6, PB) as the cathode material were fabricated, in which the PB cathode was prepared by coating technology (figure 7) [63]. The LiFeFe[CN]6/LiPON/Li solid battery was made by the deposition of LiPON on PB cathode by RF magnetron sputtering and consequent thermal evaporation of Li metal, whose thickness and size were 16 µm and 10 cm², respectively. The electrochemical performance of the batteries at the temperature range of −30 ~ 80 °C was studied for the first time, which indicated that the discharge capacity of the third cycle at 60 °C is 82.5 mAh cm⁻² and the battery can stably cycle 200 times. These results provide the feasibility of assembling ASSTFBs by combining coating technology with vacuum technology.

2. LiPON based derivatives and analogs

After the fruitful preparation of LiPON by Bates et al at ORNL in the 1990s, this kind of thin-film glass electrolyte has been widely used to fabricate the thin-film batteries as mentioned above. It is generally accepted that the incorporation of N element in the amorphous Li2PO4 electrolyte could significantly improve the ionic conductivity of LiPON [20]. The structure of LiPON has been investigated by spectroscopic characterization techniques such as x-ray photoelectron spectroscopy (XPS), inferred spectrum, Raman spectrum, and nuclear magnetic resonance (NMR). However, it is not clear for the key issues to reveal the bonding mode of N atoms in LiPON. Previously, Bates et al hypothesized that there were two kinds of N species in LiPON, which were double- (N2) and triple- (N3) coordinated N, respectively [64]. One evidence to support this hypothesis is that the N 1 s XPS spectrum from LiPON shows two different kinds of N with the binding energy of 397.8 eV (N2) and 399.4 eV (N3), respectively. Recently, Lacivita et al put forward a different opinion according to the simulation of neutron pair distribution function (PDF) that N atoms in LiPON only form N4 and nonbridging apical N connecting to P atoms (N3) (figure 8) [65]. They also proposed that the binding energy of N3 is less than N2 and the signal at 399.4 eV corresponds to the N3 or the surface contamination of LiPON. With the increase of Li content, the amount of N3 is decreasing while the amount of N2 has an opposite trend, which is harmful to the ionic conductivity due to tighter bonding between Li⁺ ions with N3 than N2. To further improve the ionic conductivity and electrochemical stabilities of LiPON electrolyte, LiPON-based derivatives were studied and their chemical and electrochemical properties were investigated.

To date, many different silicon-doped derivative electrolytes of LiPON with outstanding electrochemical performance have been well-prepared. Lee et al fabricated a silicon-doped LiPON-based solid electrolyte LiSiPON by sputtering Li3PO4–Li2SiO3 mixed target, which shows a higher ionic conductivity (1.24 × 10⁻⁵ S cm⁻¹) in a certain Si:P ratio than most of the LiPON-type solid electrolyte (about 10⁻⁶ S cm⁻¹) due to the ‘mixed former effect’. It is found out that the activation energy of Li⁺ ion conduction decreases with the increase of Si content, leading to an increase in the conductivity of

Figure 7. (a) Typical photo and (b) cross-sectional SEM image of all-solid-state LiFeFe[CN]6/LiPON/Li battery; (c) film battery lighting a blue LED. Reprinted with permission from [63]. Copyright (2018) American Chemical Society.
LiBSO solid electrolyte, whose ionic conductivity can reach $2.5 \times 10^{-6}$ S cm$^{-1}$ and the electrochemical window is about 5.8 V [76]. The structure of LiSON was confirmed by experimental and calculational method, which illustrated that the N atoms introduced in the sputtering process replace the O atoms and prevent the recrystallization of LiSON [77]. Kurzman et al synthesized Li$_2$SO$_x$N which contains rare [SO$_3$N]$_{1-x}$ polyanion by Brønsted acid-base reactions, but the ionic conductivity of this compound is very poor [78]. Mascaraque et al synthesized a kind of glass electrolyte LiPSON by a melting process or mechanical milling, which shows a higher ionic conductivity than phosphate and oxynitride phosphate glass electrolytes with the same preparation method due to the introduction of this element [79, 80]. The 2D $^{31}$P NMR spectra of this LiPSON electrolyte indicated that the phosphate groups containing S element are integrated into the formation of the phosphate network rather than clusters. Michel et al first prepared LiPSON solid electrolyte by RF-sputtering Li$_2$SO$_x$–Li$_2$PO$_4$ mixed target, in which the ratio of double-coordinated nitrogen and triple-coordinated nitrogen (N$_2$/N$_3$) shows a great impact on ionic conductivity of LiPSON electrolyte, and the highest ionic conductivity of LiPSON is about $1.58 \times 10^{-5}$ S cm$^{-1}$, that is comparable with the conductivity of LiSON electrolyte [81]. They also investigated the interface between LiPSON electrolyte and metallic Li, indicating that the production from the interfacial reaction is less beneficial for ionic conductivity [82]. The LiPSON thin-film electrolyte was used for all-solid-state electrochromic devices by Lupo et al [83].

Although LiPON manifests excellent electrochemical stability, ionic conductivity and mechanical strength in thin-film batteries, the change of oxidation state of P element during cycling can cause the variation in electronic conductivity [84]. Several research groups confirmed that the oxidation state of B is much more stable than that of P element [84]. Thus, Kim et al made a LiBON solid electrolyte as one of the LiPON analogs prepared by reacting sputtering under nitrogen plasma, which manifests the outstanding ionic conductivity of $2.3 \times 10^{-6}$ S cm$^{-1}$ [84]. The FTIR and XPS analysis of LiBON illustrated that the N atoms substituted the O atoms in the xLi$_2$O–B$_2$O$_3$ target and were incorporated into the Li–B–O matrix in the LiBON electrolyte. Additionally, the increase of Li$_2$O and the N-substitution in electrolyte caused the change of structure of borate from a ring-type one (B$_2$O$_3$) to an open structure one (B-O(N)-B), which creates more free space for higher mobility of Li$^+$. Dusszaue et al used FTIR analysis and DFT calculation to investigate the structural changes of LiBON after being prepared by the sputtering method as well as its mechanism of improving Li$^+$ conductivity [85]. It was found out that the nitrogen tends to form only B–N–B bridge bonds between two triangular boron units, which is opposite to the structure of LiPON with N$_2$ and N$_3$ nitrogen bonds. The increase of ionic conductivity in borate glass after introducing N atoms may be due to the charge delocalization within the B–N–B bridges and the reduction of electrostatic interaction with Li$^+$ ions. The LiBON thin-film electrolyte prepared by sputtering the LiBO$_2$ target in the N$_2$ atmosphere was also reported by Birke and Weppner [86].
LiBON electrolyte was likewise synthesized by the solid reaction from LiNO$_3$, Li$_2$CO$_3$, and B$_2$O$_3$ [87]. Song et al fabricated flexible thin-film batteries LCO/LiBON/Li on mica substrates with perfect mechanical properties on the bending condition, which showed outstanding capacity retention of 90% on the 1000th cycle [88]. Wu et al fabricated the LiBPON solid electrolyte by using the RF magnetron sputtering method in the N$_2$ atmosphere with the Li-B-P-O system as the target [89]. The LiBPON electrolyte deposited on a high-temperature substrate demonstrated higher ionic conductivity than that on a substrate with room temperature. The ‘mixed former effect’ and incorporation of N created more Li vacancy and more cross-link structure for improving the mobility of Li$^+$. Yoon et al also prepared LiBPON electrolyte by sputtering Li$_3$PO$_4$-Li$_3$BO$_4$ mixed target, and most of the B atoms introduced in LiBPON successfully replaced P sites [90]. Raman and XPS spectra indicated that the N$_i$ was dominant in the LiBPON electrolyte, indicating the difference different from the LiPON, in which the amount of N$_d$ atoms is more than N$_i$ atoms, and the ASSTFBs based on the LiBPON thin-film electrolyte manifested excellent cycling performance and initial capacity. Other nonmetallic elements doped into LiPON electrolytes were reported as well. LiPON electrolyte was prepared by doping fluorine into LiPON through a new melting process, and the results indicated that the substitution of O by N or F atoms increases the ionic conductivity due to the higher amount of Li in LiPFON through this synthesis route [91]. Lately, our research group also reported a new carbon-doped LiCPON solid electrolyte by RF magnetron sputtering method [92]. The LiCPON electrolyte showed higher ionic conductivity and air stability than the LiPON electrolyte. The data from XPS, XAS, and PDF analyses illustrated that C was successfully incorporated in the LiPON matrix film as the mixed glass former effect, and the C–N bridge bonding with the CO$_2$ (C$_2$O$^-$) group is one of the major structural features. Furthermore, we also fabricated ASSTFBs of LiFeFe(CN)$_6$/LiCPON/Li with two unit cells externally connected in parallel and series, respectively.

In addition to introducing non-metallic elements into the LiPON electrolyte, LiPON derivatives doped with some metal atoms are introduced. Jee et al prepared a kind of tungsten-incorporated solid electrolyte of LiPWON by sputtering Li$_3$PO$_4$ with WO$_3$, but it is not used in ASSTFBs due to the potential short circuiting [93]. Chen et al prepared LiAlTiPO solid electrolyte by sputtering Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_2$ target, and the higher temperature of the substrate during deposition is conducive to the formation of the denser and smoother LiAlTiPO electrolyte film, which could induce higher ionic conductivity [94]. Tan et al firstly reported that the LiAlTiPO solid electrolyte was prepared by the sputtering method in the N$_2$ atmosphere, and the thin-film electrolyte showed the highest ionic conductivity of 1.22 × 10$^{-3}$ S cm$^{-1}$ when the substrate temperature was 500 °C in the deposition process [95]. They thought that the substitution of N for O in electrolyte creates more crosslinking structure and decreases the electrostatic energy for Li$^+$ migration. In addition, the mixed structural effect of partial polycrystalline and amorphous glassy electrolyte may be another reason for high ionic conductivity. Luo et al introduced a small amount of La$_3$O$_5$ in LiAlPON solid electrolyte, in which the ionic conductivity of the electrolyte can be improved without obvious change in the network [96]. The N-doped LAGP thin-film electrolyte was prepared by magnetron sputtering method and an annealing process, whose ionic conductivity is 2.3 × 10$^{-4}$ S cm$^{-1}$. The addition of N element into LAGP makes the PO$_4^{3−}$ tetrahedral units facilitate the facial Li$^+$ diffusion [97].

Table 1 summarizes the structural diagram of these LiPON derivatives mentioned above, in which the incorporation of N, Si, B, S, C, F, and metal (M) elements into amorphous Li$_i$PO$_j$ changes the distribution of the phosphate anion chains. According to the substitution position of doped elements for O in the structure of amorphous phosphate glass, these derivatives can be divided into two categories. Similar to the substitution of oxygen position by nitrogen, one is the substitution of sulfur or fluorine anion for O. The other is the mixed glass structure with C, Si, B, or M and P as the mixed glass former effect. These doped elements are incorporated into LiPON glass as nitrogen incorporation of the mixed glass with CO$_2$ (C$_2$O$^-$), SiO$_2$ (Si$^-$), BO$_3$ (B$^3−$), PO$_4$ (P$^−$) (or Mo$^−$) structure in the cross-linked glass network of Li$_i$PO$_j$, respectively. Their chemical formula, ionic conductivity, and activation energy are listed in table 2. It is evident that most of these thin-film LiPON-based derivatives exhibit higher ion conductivities than those of LiPON. Undoubtedly, the investigation of these LiPON-based derivatives provides valuable information on the relationship between structure and properties. More works are still needed to develop LiPON-based derivatives for a suitable structure desirably and higher conductivity.

3. Interfaces of LiPON with electrodes

The interfaces of LiPON between anode and cathode play a critical role in the electrochemical performance of the batteries [98]. Therefore, it is necessary to investigate the interface property of LiPON before its large-scale application in energy storage devices. ASSTFB is an ideal research system to explore the electrolyte-electrode properties which have compactness, homogeneity, and smoothness for both electrode and electrolyte. This kind of battery system can simplify the research due to its clear structure and the distinctiveness of each component [99]. In all ASSTFBs, Li/LiPON/LCO is a classic one that has been commercialized. It consists of lithium cobalt oxide cathode, lithium metal anode, and LiPON solid electrolyte. This ASSTFB can be used as a research object to study the interface performance between the LiPON and the electrode. In addition to LCO cathode, the interface between other cathode materials and LiPON has been studied.

Interface impedance is one of the important interface properties between LiPON and the cathode. Iriyama et al explored the charge transfer reaction and charge transfer resistance of the LiPON/LCO interface in Li/LiPON/LCO batteries after thermal treatment [100]. The thermal treatment after the formation of the LiPON/LCO interface can improve the electrochemical reactivity of the ASSTFBs. According to the impedance spectra and Arrhenius equation, the activation energy of the charge transfer reaction remains unchanged before and
after heating treatment, but the charge transfer impedance decreases. Then the N1s XPS spectra of LiPON with and without thermal treatment show the ratio of N\textsubscript{t}/N\textsubscript{d} increased after thermal treatment. It implies that the crosslinking structure of the N atom in LiPON has changed after thermal treatment. The atomic rearrangement in this structural change increases the number of electrochemical active centers at the LiPON/LCO interface, resulting in the improvement of battery reactivity. Jeong et al. studied the modified interface between LiPON and LCO [98]. One thin layer of aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) as the interface layer was prepared by using RF magnetron sputtering technique. The composition characterization structure of the LiPON/Al\textsubscript{2}O\textsubscript{3}/LCO interface by Auger electron spectroscopy reveals that the thickness of aluminum at the interface after heat treatment is greater than that in the as-deposited alumina, indicating that aluminum atoms are mixed with LCO to form a kind of solid solution LiCo\textsubscript{1−y}Al\textsubscript{y}O\textsubscript{2}, which has very good ionic conductivity. Therefore, the introduction of the Al\textsubscript{2}O\textsubscript{3} layer and heat treatment can optimize the interface of LiPON/LCO for the improvement of the electrochemical performance battery. The effect of LiPON coating on the surface of LCO on the electrochemical performance and thermal stability of LCO cathode has been studied, which proves thermally stable LCO/LiPON [101].

The LiPON/LCO interfacial property in ASSTFB of Li/LiPON/LCO after a long cycle under high temperature was investigated by Wang et al [99]. An additional interface layer between LiPON and LCO was observed by the cross-sectional TEM image of the battery (figure 9(a)), whose structure and composition are different from bulk LCO. It is a highly disordered structure and is composed of lithium oxide and cobaltous oxide by electron energy loss spectroscopy (EELS) analysis. After thermal treatment, a thicker disordered interface layer was observed in the cross-sectional TEM image of the LCO/LiPON interface (figures 9(b) and (c)), implying that the main mechanism of battery failure is the thermal effect rather than electrochemical activation. Jacke et al investigated the growth mechanism of LiPON on LCO cathode and their interface reaction by in situ XPS [102]. They found that some new nitrogen-containing species of NO\textsubscript{2}− and NO\textsubscript{3}− were formed before the formation of stoichiometric LiPON during the deposition process of LiPON on the surface of LCO at different temperatures. The ratio of N\textsubscript{t}/N\textsubscript{d} at the LiPON/LCO interface is higher than that in bulk, which indicates that the interface between LiPON and LCO is not an ion-conductive layer.

It is known that the redistribution of carriers will happen on the interface when two kinds of materials contact each other due to the difference in their chemical potential. It can form a space charge layer and establish an electric field which can cause band bending on the interface and the change of conductivity [103]. The work completed by Schwöbel et al revealed the energy level alignment on the interface of LiPON/LCO, which is obtained by in situ XPS measurement (figure 10(a)) [104]. The binding energy of each element was got according to the XPS spectra during the deposition

**Table 1.** The structural characteristic of LiPON-derivatives.

| LiPON    | LiBPON   |
|----------|----------|
| LiSiPON  | LiPFON   |
| LiPSON   | LiPCON   |
| LiWPON (M = Al, Ti, W, etc) | |
process (figure 10(b)). The core level of LCO shifts 0.3 eV to higher binding energy with time, implying that the LCO/LiPON has a downward band bending of 0.3 eV. According to the binding energy of the valence band maximum (VBM) of LCO and LiPON and their core level before and after LiPON deposition, the difference in their VBM can be calculated and the value of ΔE_{VBM} is 1.26 eV. The change of work function ΔΦ is 0.25 eV and has a good agreement of the band bending, which indicates that no large interface dipole is at the LCO/LiPON interface.

Table 2. The chemical formula, ionic conductivity, and activation energy of LiPON-derivatives.

| Preparation method | Chemical formula | Ionic conductivity (S cm⁻¹ at room temperature) | Activation energy (eV) | Reference |
|--------------------|-----------------|-----------------------------------------------|------------------------|-----------|
| **Si-doped LiPON-derivatives** | | | | |
| Rf magnetron sputtering | L_{2.4}Si_{0.3}PO_{1.4}N_{1.1} | 5.65 × 10⁻⁶ | 0.500 | [66] |
| Rf magnetron sputtering | L_{1.9}Si_{0.28}PO_{1.1}N_{1.0} | 8.86 × 10⁻⁶ | 0.491 | [66] |
| Rf magnetron sputtering | L_{2.9}Si_{0.35}PO_{1.4}N_{1.26} | 1.00 × 10⁻⁵ | 0.487 | [66] |
| Rf magnetron sputtering | L_{2.9}Si_{0.45}PO_{1.6}N_{1.3} | 1.24 × 10⁻⁵ | 0.479 | [66] |
| Rf magnetron sputtering | L_{2.9}Si_{0.40}PO_{1.0}N_{1.32} | 5.4 × 10⁻⁶ | 0.47 | [68] |
| Rf magnetron sputtering | L_{2.9}Si_{0.39}PO_{2.75}N_{1.76} | 6.6 × 10⁻⁶ | 0.45 | [68] |
| Rf magnetron sputtering | L_{2.9}Si_{0.93}PO_{3.22}N_{1.14} | 9.7 × 10⁻⁶ | 0.41 | [68] |
| Rf magnetron sputtering | L_{1.0}Si_{0.36}P_{0.70}O_{2.17} | 1.49 × 10⁻⁶ | 0.57 | [69] |
| Rf magnetron sputtering | L_{1.0}Si_{0.36}P_{0.41}O_{2.19} | 2.00 × 10⁻⁷ | 0.56 | [69] |
| Rf magnetron sputtering | L_{2.0}Si_{0.81}P_{0.92}O_{1.28} | 4.09 × 10⁻⁷ | 0.51 | [69] |
| Rf magnetron sputtering | LiBO | 2.5 × 10⁻⁶ | 0.51 | [76] |
| Solid-state reaction | Li_{3}SO_{11}N | 1.03 | | [78] |
| Melting reaction | Li_{3}PO_{2.75}S_{0.01}N_{0.32} | 2.95 × 10⁻⁷ | 0.64 | [79] |
| Solid-state reaction | LiPON | 1.4 × 10⁻⁸–6.8 × 10⁻⁷ | N/A | [80] |
| Rf magnetron sputtering | LiPON | 1.58 × 10⁻⁵ | N/A | [81] |
| Rf magnetron sputtering | LiPON | 3.23–9.75 × 10⁻⁶ | 0.23–0.53 | [83] |
| **B-doped LiPON-derivatives** | | | | |
| Rf magnetron sputtering | L_{2.0}B_{0.36}N_{0.98} | 4.3 × 10⁻⁹ | N/A | [84] |
| Rf magnetron sputtering | L_{2.0}B_{0.31}N_{0.52} | 2.3 × 10⁻⁹ | N/A | [84] |
| Rf magnetron sputtering | LiBPON | 3.5 × 10⁻⁶ | 0.53 | [89] |
| Rf magnetron sputtering | L_{2.0}B_{0.31}P_{0.01}O_{3.01}N_{1.05} | 6.88 × 10⁻⁷ | 0.653 | [90] |
| **Melting reaction** | | | | |
| LiPFO | 1.26 × 10⁻⁷–6.61 × 10⁻⁸ | 0.69–0.71 | [91] |
| LiPFO | 1.95 × 10⁻⁷–5.74 × 10⁻⁸ | 0.66–0.68 | [91] |
| Rf magnetron sputtering | LiPFO | 3.06 × 10⁻⁵ | 0.43 | [92] |
| **Metallic element (M) doped LiPON-derivatives** | | | | |
| Rf magnetron sputtering | L_{2.0}M_{0.36}P_{0.008}O_{2.019}N_{0.364} | 1.5 × 10⁻⁷ | 0.51 | [93] |
| Rf magnetron sputtering | Li-Al-Ti-P-O | 0.34–2.46 × 10⁻⁵ | 0.32–0.33 | [94] |
| Rf magnetron sputtering | Li-Al-Ti-P-O-N | 1.22 × 10⁻⁶–1.22 × 10⁻⁵ | 0.44–0.63 | [95] |
| Melting reaction | Li-La-Al-P-O-N | 1.47 × 10⁻⁵ | 0.54 | [96] |
| Rf magnetron sputtering | Li-Al-Ga-P-O-N | 2.3 × 10⁻⁴ | 0.374 | [97] |

by way of XPS technique [105]. With the increase in annealing temperature, the interfacial reaction products (LiNOₓ, Li₂O, etc) between LCO and LiPON disappear. According to the species change at the interface during the annealing process, the chemical potential of elements can be derived with other additional data. The chemical potential of O element in LCO is higher than that in LiPON, as well as the Li element (figure 11(a)). The chemical potential of N element has maximum value around the LCO/LiPON interface because the N in LiNOₓ is bound to LiPON after annealing. The band bending in the LCO cathode is attributed to the formation of electrostatic potential gradient and the band bending
Figure 9. The cross-sectional TEM images of the (a) pristine LCO/LiPON interface, (b) the one was cycled at 25 °C, and (c) the one was cycled at 80 °C. Reprinted from [99]. Copyright (2016), with permission from Elsevier.

Figure 10. (a) XPS spectra of Co 2p, O 1s, P 2p, and the valence band at the LCO/LiPON interface with increasing LiPON coverage; (b) Change of the core levels of the LCO and the P 2p level of the LiPON layer with time. Reprinted from [104]. Copyright (2016), with permission from Elsevier.

has no change after annealing (figure 11(b)). The difference in electrochemical potential of Li-ion between LiPON and LCO causes the Li-ion to divorce from LCO and insert into LiPON, which results in the formation of Li-vacancies in LCO and Li-interstitials in LiPON. Both of them accumulate at the interface in their own phase, forming the space charge layer. The space charge layer influences the formation of other element defects, such as the O-vacancies. The defect formation energy is essential to understand the ionic properties and ionic structure, which can be identified by the difference of chemical potential to the relative energy level. The energy level gap reveals the difference in defect formation energy. The Li-ion energy level diagram can be drawn by calculating the defect formation energies and the diagram illustrates the presence of the space charge layer at the interface.

The interface between LiPON and other kinds of cathode materials was investigated. LiPON was coated on the surface of cathode material as an artificial interface layer to modify its surface. Lv et al investigated the cycling performance and rate capability of high-voltage LNMO cathode with and without LiPON coating layer [106]. The LiPON coated LNMO shows better capacity and rate capability and less interfacial resistance than the pristine LNMO electrode. It was found that the ratio of content of Mn$^{4+}$/Mn$^{3+}$ in LiPON coated LNMO is higher than that in pristine LiPON, indicating the formation of space charge layer between LiPON and LNMO and the oxygen vacancy moving from LiPON to LNMO. Yada et al studied the modification by dielectric material BaTiO$_3$ (BTO) of the interface between LiPON and 5 V-class cathode Li$_{1-x}$Co$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_{4−x}$ (LNM) [107]. Previous studies have shown that Li/LiPON/LNM cannot be charged and discharged at 3.0–5.3 V, which is attributed to the huge charge transfer resistance at the LiPON/LNM interface. It may be related to a huge electric potential difference between two materials. BTO nanoparticles can change the interfacial electric potential distribution and induce the Li-ion distribution at the interface,
which leads to the formation of the ‘Li-ion pathway’ for charge transfer reaction and reduction of interfacial resistance by four orders of magnitude.

The interface characteristics between LiPON and cathode were found related to the preparation method and experimental conditions. West et al delved into the electrical properties of thin-film LiPON prepared by the PLD method (LiPON-PLD) from a crystalline Li$_2$PO$_3$N target and by RF magnetron sputtering [108]. The LiPON-PLD layer displays lower charge transfer resistance with a higher amount of triply coordinated nitrogen and a relatively lower amount of doubly coordinated nitrogen. Cherkashinin et al made an investigation of the interfacial chemical composition and electronic properties when LiPON was deposited on the 5 V LiCoPO$_4$ (LCP) and LiNiPO$_4$ (LNP) cathodes [109]. The preparation method of cathode material has a great influence on the electronic properties of the interface between LiPON and cathodes, and a suitable preparation method is one of the possible ways to improve the interfacial stability.

Lithium metal is one of the most ideal anodes in solid-state batteries because of its extremely high theoretical capacity (3680 mAh g$^{-1}$) and low reduction electrode potential ($-3.040$ V vs. Standard Hydrogen Electrode) [110]. Therefore, it is of great significance to study the interfacial reaction and interfacial chemical composition between LiPON and metal lithium. Schwöbel et al investigated the interface formation and related reaction between LiPON and metal Li by in situ XPS [111]. After the evaporation of Li metal, some products on the surface of LiPON can be detected, such as Li$_3$O, Li$_3$N, Li$_3$P, and Li$_3$PO$_4$, indicating a chemical reaction between LiPON and Li metal to form new chemical species. The ratio of bridging oxygen and non-bridging oxygen (O$_b$/O$_{nb}$) decreases after Li deposition, as well as the tendency of the ratio of N$_3$/N$_4$. This evidence indicates the LiPON network structure at the interface is destroyed after Li deposition due to the interface reaction between LiPON and Li metal.

However, they believe that the product of the interface reaction forms a passivation layer, which is thin enough to support the transfer of lithium ions. Hood et al utilized in situ electron microscopy to study the electrochemical stability and composition of the LiPON/Li interface [112]. They found that the interface reaction between Li metal and LiPON leads to the volume expansion of LiPON and the wetting of metal Li on the surface of LiPON. EELS elemental mapping shows two sublayers in the distribution of interface reaction products at the LiPON/Li interface. One is the O-rich and P-Free interfacial layer directly connected with LiPON, and the other is the P-rich interface layer directly connected with LiPON. Among the binary products of Li$_3$O, Li$_3$N, and Li$_3$P, Li$_3$P is the only one with ionic and electronic conductivity. Its separation from Li metal inhibits the side reaction and improves the stability of the LiPON/Li interface. These binary products can theoretically enhance the electrochemical window and stabilize the interface. Xiao et al investigated the LiPON/Li interface properties in the ASSTFB, in which amorphous V$_2$O$_5$ with many oxygen-vacancy sites was used as the cathode [113]. They utilized the facing target sputtering method which can prevent the film from plasma damage, to fabricate a uniform ultrathin Al$_2$O$_3$ (UT-AO) film with low roughness between LiPON and Li anode. The interfacial evolution of LiPON/Li with and without UT-AO (1 nm) additional layer before and after two cycles was investigated by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The TOF-SIMS depth profile shows the interfacial reaction between LiPON and Li, resulting in the consumption of Li metal and the formation of Li$_3$O and Li$_3$P by-products. However, there is no signal change at the interface with the presence of the UT-AO (1 nm) layer, which demonstrates the UT-AO layer suppresses the interface reaction and improves the stability of LiPON. The ab initio molecular dynamics (MD) simulations were used to study the interfacial interaction between LiPON and Li. The simulation results illustrate that the by-products from the
interfacial reaction, except Li$_2$O, have a strong chemical connection with Li metal, which is supported by the SEM spectra of the battery’s cross-section. On the contrary to the interface without UT-AO, the lithiated Al$_2$O$_3$ layer is thermodynamic and increases the stability of the Li/LiPON interface.

After using in situ XPS technique to investigate the properties of the LCO/LiPON interface, Schwöbel et al use the same method to reveal the energy alignment at the interface of Li/LiPON [104]. The initial XPS spectra of each element in LiPON illustrate that all the peaks shift about 1.5 eV to higher binding energy, which is related to the charge effect. The binding energy of Li 1 s XPS at 53.4 eV is observed on the surface of metallic lithium, which is lower than the reference value (54.9 eV), indicating the presence of a space charge layer and band bending at the Li/LCO interface. The binding energy of VBM shifts 0.5 eV to lower binding energy, which influences band bending and is 0.5 eV to upwards direction. The difference in the binding energy of VBM ($\Delta E_{\text{VBM}}$) between Li metal and LiPON is calculated to be 4.1 eV. Combining the data of both the LCO/LiPON and Li/LiPON interface can draw a total energy band profile of ASSTFB of Li/LiPON/LCO (figure 12). The difference in Fermi level between LCO cathode and Li anode is the cell voltage, which is calculated to be 2.76 eV and is close to the experimental value (2.8 eV). Moreover, the electron chemical potential makes a major contribution to the cell voltage and only 11% of voltage attributes to the Li-ion chemical potential.

Sicolo et al conducted an investigation into the interfacial instability and side reactions at the interface of LiPON and Li by using surface science techniques and quantum computation methods [114]. The interface model of LiPON/Li was established by quantum simulation and the Li atom can diffuse from bulk metal Li to the LiPON without barriers, leading to the breaking of the network structure of LiPON and atomic rearrangement at the LiPON/Li interface. The thermal stability of the LiPON/Li interface is calculated and the results illustrate that the LiPON can be spontaneously reduced by Li metal in thermodynamics and the products include Li$_2$O, Li$_3$N, Li$_2$P, and lithium phosphate. These byproducts form a passivation layer on the Li/LiPON interface and prevent from further reaction of LiPON with Li metal. UPS and XPS spectra also prove the formation of these chemical species. You et al used ab initio MD simulations to study the local structure of the interface of amorphous-LiPON/Li(100) and crystalline-Li$_2$PO$_3$N(100)/Li(100) and the diffusion property of Li-ion at the LiPON/Li interface [115]. The atom at the original LiPON/Li interface diffuse to each other to form a new interfacial layer. The calculation results indicate that the diffusion of Li-ion at the LiPON/Li interface is faster than that in the bulk LiPON, which is related to the structural change at the interface. According to the simulation results, there is about 20% of Li-ion forming the tetrahedral structure like Li[O$_2$N$_2$], Li[O$_2$N], and Li[O$_3$] in bulk LiPON. In the tetrahedral structure, Li is located at the center of the structure thus the diffusion of Li-ion is difficult and the ionic conductivity of Li-ion is very low. However, at the interface layer, the amount of these kinds of tetrahedral structures are less than those in bulk LiPON, as well as the decrease in the average coordination number of Li–O, Li–N, P–O, and P–N bond. Li-ion is less affected by the ionic bond of O and N due to the change in interfacial structure and coordination number, which results in the diffusion of Li-ion being less hindered. The conductivity of Li-ion at the interfacial layer is higher (2–3 orders of magnitude) than that of the bulk LiPON, which indicates that the interfacial layer has some positive effect on the performance of batteries.

The interface properties of LiPON with electrodes are essential to the performance of batteries. In ASSTFB, LiPON is considered to be one of the best solid electrolytes to build better interfaces with representative LCO and metal lithium, respectively. Many spectroscopic characterization methods such as in situ SEM, TEM, XRD, and EELS were used for studying the composition and structure of the interface layer due to their reaction between LiPON with electrodes. Besides, some special equipment is also utilized for investigation, such as DAISY-BAT (Darmstadt’s Integrated System for battery Research) [102, 105, 111, 114]. Some strategies were taken to improve the properties of the interface layer, such as thermal treatment and the addition of other layers between LiPON and electrode. The gap in the energy level between LiPON and electrode derives from the difference in electrochemical potential of Li-ion in different materials. The equilibrium of

![Figure 12](image-url) Complete energy band diagram of the LCO/LiPON/Li battery. Reprinted from [104]. Copyright (2016), with permission from Elsevier.
the electrochemical potential of Li-ion leads to the rearrangement of ions at the interface, which causes the formation of a space charge layer at the interface and the establishment of the internal electric field. This kind of electric field changes the conductive properties at the LiPON-electrode interface. Therefore, besides interesting aspects of the complex interface chemistry of the LiPON/electrode system, it is a great challenge to realize a perfect interface engineering for high performance of thin-film batteries. It needs to optimize electrode materials and preparation methods, preparation conditions, ultra-thin interface layer construction, and post-treatment.

4. Preparation methods for LiPON

The preparation and growth of LiPON are generally considered as the insertion of N atoms or replacing O atoms with N atoms into the amorphous or polycrystalline structure of Li$_3$PO$_4$. However, the chemical activity of N$_2$ is not enough to insert into the structure composed of the P–O bond. N plasma is induced by physical preparation methods such as magnetron sputtering, PLD technology, or nitrogen plasma-assisted deposition of electron beam evaporation as shown in figure 13, in which the plasma emission plume in the deposition process of LiPON thin films is produced by these methods. The bridging N$_4$ and non-bridging apical N$_4$ connect to P atoms are proposed for the possible pathway for the nitridation of Li$_3$PO$_4$. The electrochemical and physical properties of LiPON are reported to be strongly dependent on their preparation methods. They are briefly introduced as follows.

RF magnetron sputtering is the most commonly used preparation technique. In a typical magnetron sputtering equipment, Li$_3$PO$_4$ is used as the target, and N$_2$ is used as the reactive gas [116]. A mixed target of Li$_3$PO$_4$ and Li$_2$O has also been attempted to increase the ionic conductivity of the deposition film [116]. In addition to pure nitrogen, mixtures with other gases such as argon and helium are also used [58]. Its deposition parameters such as substrate temperature, substrate-to-target distance, reactive gas pressure, sputtering power, and sputtering time determine the deposition rate as well as the properties of the LiPON film, including but not limited to the microstructure of the film and LiPON’s electric properties [117]. For example, studies have shown that the islet microstructure may emerge accompanied by the elevated support temperature [117]. Compared with other preparation methods, the LiPON film obtained by RF magnetron sputtering has relatively higher ionic conductivity. However, the deposition rate of this method is relatively slow and the deposition area is usually limited. The former is determined by the mechanism of magnetron sputtering, and the latter is bound by the substrate-to-target distance and the size of the target [60]. As a physical deposition technique, it is difficult to obtain a highly-conformal step-coverage film onto the patterned surface with a high aspect ratio [118].

In contrast, PLD has a higher deposition rate. This technique contains a rotating holder to load the Li$_3$PO$_4$ target. As for the substrate, it is mounted opposite the target, just a few centimeters apart. The most critical part is the ultraviolet laser beam focused on the rotating target at a certain angle of incidence. According to the previous research, the fluence of the ultraviolet laser beam and N$_2$ pressure can significantly affect the ionic conductivity of LiPON film. First, increasing the laser fluence can improve the quality of N atoms incorporated into Li$_3$PO$_4$ within limited, which is beneficial for higher ionic conductivity of LiPON electrolyte. However, the laser fluence has a certain threshold beyond which the ionic conductivity is probably saturated. Besides, higher N$_2$ pressure within limited is favorable for increasing the ionic conductivity of LiPON, but excessive pressure can also be negative to the preparation of LiPON due to the contraction of the plume region. Similar to RF magnetron sputtering, substrate-to-target distance in the PLD technique is also influential to the surface roughness of LiPON electrolyte [58]. In addition to higher deposition rates, the PLD technique has other advantages, for example, the film can be deposited in ambient gases and the thickness of deposition film is relatively easy to control. However, the coagulated droplets would be present during the deposition process, which is unfavorable for the preparation of homogeneous LiPON electrolyte without roughness on the surface. At the same time, the deposition area of PLD is limited, and the nitridation efficiency is unsatisfactory.

To obtain better nitridation efficiency, ion beam assisted deposition (IBAD) is used to prepare LiPON thin film. In a typical IBAD system, in addition to the regular Li$_3$PO$_4$ target and substrate, it additionally contains two ion sources, one of which provides a kind of ion beam to control the sputter atoms from the target, and the other one provides another ion beam to bombard the target. With the adjustment of the flow ratio of the reactive gas and the process gas, the nitrogen content of LiPON can be effectively adjusted [119]. Correspondingly, the hardness, elastic modulus, and the residual stress of LiPON film also change over the flow ratio. Research has shown that as the flow ratio of reactive gas and process gas increases within a certain range, the residual stress will decrease while the hardness will increase [119]. It is worth mentioning that in the IBAD system, the substrate is spatially separated from the sputter plasma, which is believed to help reduce the formation of an interfacial reactive layer [116]. The biggest disadvantage of IBAD is that the process is complicated and the deposition area is small. To obtain a larger deposition area, LiPON film can be also prepared using e-beam evaporation. The core component of the equipment employed in this technique is the e-beam evaporator, which is attached to an inductively coupled plasma reactor and other regular parts [60]. The larger deposition area, as well as the higher uniformity of the film, originate from the long substrate-to-target distance up to 40 cm. While having a faster deposition rate, this method is less efficient in nitriding. Likewise, same as RF magnetron sputtering and PLD, e-beam evaporation is limited to planar substrates because of shadow effects and film rupture may occur because of thermal tensile stress coming from the temperature difference between the substrate and the deposited film [120].

The target-based format dictates that all kinds of LiPON film obtained by the methods above are planar. However, in the application process, researchers prefer to conformally
coat high aspect ratio nanostructures with thin, uniform layers, atomic layer deposition (ALD) and metal-organic CVD (MOCVD) can meet this requirement. On the one hand, these two methods can deposit a kind of homogeneous and highly-conformal film on highly structured substrates. On the other hand, they also get rid of the shackles of lithium phosphate and even nitrogen. That is to say, as long as there are precursors that can provide P element and N element, they may be used to prepare LiPON thin films.

In a typical quaternary ALD process (figure 14), four precursors including lithium tert-butoxide (LiO\textsubscript{t}Bu), deionized H\textsubscript{2}O, trimethylphosphate (TMP), and plasma N\textsubscript{2}, are used to deposit the LiPON film [121]. First, the argon carrier gas is used to transport LiO\textsubscript{t}Bu into the ALD chamber. Then H\textsubscript{2}O is introduced to participate in the reaction, thereby obtaining smaller LiOH units on the substrate. The third step is to add TMP to get surface-bound methyl phosphate species. However, the phosphate species obtained at this time are separated from each other, to cross-link them with each other, it is necessary to add the core precursor, i.e. plasma N\textsubscript{2} [121]. That is, in this step, the N content in the final LiPON film can be regulated by changing the duration of the N pulse. Atomic-scale thickness controllable thin film deposition can be achieved by setting the number of cycles or reaction time. As for the precursors that do not participate in the reaction and reaction by-products, they can be blown out of the reaction chamber with the inert gas. Unfortunately, the deposition rate in the ALD method is relatively slow [120], and the ionic conductivity of the LiPON film is slightly lower than the film based on lithium phosphate and nitrogen. To improve the ionic conductivity, ALD processes using different precursors are being developed [122]. At the same time, in order to control deposition rates and film properties, ALD requires a specialized apparatus [71], which is not conducive to the popularization of this method.

In a classic MOCVD case (figure 15(a)), lithium dipivaloylmethane (Li(DPM)), triethyl phosphate (TEP), and NH\textsubscript{3} are used as precursor materials to prepare LiPON thin film [123]. During the process flow, the vaporized Li(DPM) and TEP are brought into the reaction chamber by nitrogen [123]. Vapor deposition is achieved by regulating the flow rates of the three precursor gases. With the increasing temperature of the

Figure 13. Plasma plume photos of (a) radio frequency magnetron sputtering; (b) pulsed laser deposition; (c) ion beam assisted deposition.

Figure 14. The flow chart of atomic layer deposition for LiPON. Reprinted with permission from [121]. Copyright (2015) American Chemical Society.
substrate, while the deposition rate increases, the ratio of N to N also increases, which helps to improve the ionic conductivity of LiPON film. The main purpose of using metal organics as precursors is to maintain a low growth temperature, thereby effectively reducing the defect density in the film. The constituent elements of the film enter the reaction chamber in the form of gas, and the composition of the film can be controlled by the mass flow meter and the switch. At the same time, various properties of the epitaxial layer can be controlled by precisely controlling the flow of various gases. This method can obtain better thin-film samples on many amorphous substrates, which is mainly due to the lower reaction barrier, which reduces the orientation requirements of the substrate. Most importantly, MOCVD is an industrial-oriented method suitable for large-area thin film growth and mass production. Adducts are formed within a certain temperature range and it is a big problem because the deposition rate can be restricted by the presence of adducts, and the gas line may be blocked. What makes matters worse is that carbon-containing polymeric by-products can severely reduce the conductivity of the prepared film.

All the methods described above require specific and complex instruments to complete gas phase deposition. In fact, satisfactory LiPON film can also be prepared by simple chemical reactions. For example, one of the simplest structures of the LiPON has been prepared by the following reaction equation through a high-temperature solid-state reaction method:

\[
\text{Li}_2\text{O} (s) + \frac{1}{5}\text{P}_2\text{O}_5 (s) + \frac{1}{5}\text{P}_3\text{N}_5 (s) \rightarrow \text{Li}_2\text{PO}_2\text{N} (s)
\]

In the product, the planar P-N-P-N backbone is stabilized by the N 2p π states, which contributes to its stability at high temperatures as well as in the ambient environment. In another example, the polymer precursor method is also used to produce LiPON film. First, phosphoramide OP(NH₂)₃ is obtained by ammonolysis of OPCl₃. Stepwise condensation reactions are then completed before the Li source is added for lithiation to obtain LiPON. This synthesis route permits the control of Li contents by varying the degree of lithiation, which is difficult to achieve using other methods, especially for gas-phase-based techniques. Meanwhile, the ratio of N content and P content is higher and the electrochemical stability window is wider. The above advantages enhance the ionic conductivity of the obtained LiPON film.

5. Conclusion and outlook

ASSTFBs have become one of the most efficient, reliable, clean, and sustainable energy storage devices. LiPON is one of the key components for perfecting the overall properties of ASSTFBs. In this review, we summarily introduced the recent development of ASSTFB based on LiPON and its applications. Due to the low conductivity of LiPON (far lower than that of liquid electrolyte), it is difficult to achieve high
energy densities of ASSTFBs, which limits its practical application. To improve the ionic conductivity and electrochemical stability of LiPON, the electrical properties and physical characteristics of various derivatives doped with B, C, F, Si, and other elements in amorphous structure are highlighted in this review. In addition, the morphology, composition, and electronic structure of the interface layer between LiPON and cathode materials as well as lithium metal anode are summarized, respectively. The thermodynamic stability and the decomposition kinetics of the LiPON/electrode interface layer were revealed. These investigations on the interface between LiPON/electrodes provide very important information for exploring high-quality interfaces. Further exploration of LiPON derivatives with higher ionic conductivity has the potential to improve their chemical stability and thus the electrochemical performance of ASSTFBs. Over the past ten years, advanced technologies were employed for the preparation of LiPON, such as ALD, CVD, and polymer precursor methods. Their own characteristics are described in this review. Among these methods, magnetron sputtering technology has been widely accepted as the most suitable preparation for LiPON thin film in fabricating these ASSTFBs. The low efficiency and high cost of these technologies is the main obstacle in these technologies for the large-scale preparation of LiPON thin film presently. Thin-film lithium batteries can generally be constructed into micron-sized thin-film batteries through a micromachining process to realize the so-called micro-battery. Thin-film batteries should be the best choice to realize energy miniaturization and integration such as three dimensions high-density integration of micro-batteries and an energy integrated system with micro-fuel cells, micro-battery. Thin-film batteries should be the best choice to realize energy miniaturization and integration such as three dimensions high-density integration of micro-batteries and an energy integrated system with micro-fuel cells, micro-piezoelectric energy collectors for the self-generating and energy storage. The application of ASSTFBs within these devices is hopeful to revolutionize thin-film batteries.

Acknowledgments

This work was financially supported by the NSAF (Grant No. U20A20336), and Tianmu Lake Institute of Advanced Energy Storage Technologies Scientist Studio Program [No. TIES-SS0002].

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