**LixPON and LixSiPON**

Most solid-state electrolytes (SSEs) suffer from low ionic conductivities, a limited stability window, or form irreversible reduction (e.g. NASICON-type SSEs) on cycling or lithium dendrite growth along grain boundaries (e.g. garnet-type SSEs) leading to short circuiting. Fortunately, amorphous lithium phosphorus oxynitride (LiPON) glasses have been found to offer protection against both processes.

LiPON is one of the most commonly employed solid-state electrolytes owing to its broad electrochemical stability window (0-5 V *vs*. Li+/Li), high critical current density (>10 mA/cm2), and negligible electronic conductivity (10-13 S/cm). It is also resistant against dendrite penetration and wets well with Li metal. However, due to its limited ionic conductivity (typically up to ~10-6 S/cm), its application is restricted to thin-film batteries with limited energy densities and capacities.

Silicon-containing LiPON (or LiSiPON) has also attracted attention due to its increased ionic conductivity induced by Si doping, as suggested by the figure below.1 Generally, with Si doping, ionic conductivities of LiSiPON are up to ~10−5 S/cm vs. 10-6 S/cm for LiPON. Note that the effect of nitridation is discussed in the **Intro** page.

Chart, diagram

Description automatically generated

(1) Famprikis, T.; Galipaud, J.; Clemens, O.; Pecquenard, B.; Le Cras, F. Composition Dependence of Ionic Conductivity in LiSiPO(N) Thin-Film Electrolytes for Solid-State Batteries. *ACS Appl. Energy Mater.* **2019**, *2* (7), 4782–4791. https://doi.org/10.1021/acsaem.9b00415.

Unfortunately, to date LiPON glasses are fabricated through gas phase deposition methods, which generally have low deposition rates (typically <100 nm/min) and require specialized apparatus. As a result, fabrication of large and homogeneous composition targets is costly at commodity scales. Thus, there are considerable economic and performance mandates driving the search for easier processing routes to the same materials especially for the practical processing of ASSBs. The use of chemical precursor routes to the same materials seems to offer considerable potential to solve these issues.

Our designed approach uses easily available starting materials, either OPCl3 or [Cl2P=N]3. The resulting precursors are typically oligomers or low molecular weight (MW) polymers derived from lithiation of OP(NH2)3-x(NH)x [from OP(NH)3],OP(NH2)3-x(NHSiMe3)x and [P=N]3(NHSiMe3)6-x(NH)x, respectively (see the schematic below). Selected amounts of LiNH2 provide varying degrees of lithiation and Li+ conducting properties commensurate with Li+ content. Overall, the LixPON and LixSiPON precursors mimic LiPON and LiSiPON glasses respectively, while LixSiPHN precursors explore new possibilities of fully replacing O with N.

A picture containing text

Description automatically generated

In-depth characterization of these precursors provides detailed analyses of various structural components, and Li+ environments. A diverse set of analytical methods were used including GPC, TGA, MALDI, NMR and XPS. Furthermore, FTIR, XRD, SEM-EDX and EIS characterization was conducted on all precursors following heating to 100-600 °C, as phase and compositional changes are anticipated to influence materials’ processing methods and conductivities.

By using MALDI-ToF combined with the program *MALDI-Calculation*, we conclude that all precursors show MWs of 1-2 kDa. Their representative predicted structures and MW summaries are given below.

Graphical user interface, application

Description automatically generated

TGA-DTA studies show the precursors are thermally stable to 150-200 °C. FTIR spectra fit well with traditional LiPON glasses synthesized by gas phase methods. 7Li NMR suggests that Li+ ions in these precursors are well solvated and dissociated, which is beneficial for their electrochemical performances. The structures of Si (C) containing precursors were further investigated by 1H, 13C and 29Si NMR studies, which suggest that Si doping was achieved by bonding NH-SiMe3 with P=O or P-N=P onto the polymer backbone.

XRD, XPS and EDX studies show all precursors exhibit higher N/P ratios (1-3) compared to traditional gas phase methods (<1), and there seems to be a correlation between the N/P ratio and 7Li NMR chemical shift (δLi). N/P ratio is an indicator of the degree of nitridation. As discussed in the **Intro** page, ionic conductivity generally increases with the degree of nitridation (or N/P ratio).

In general, the room temperature (RT) ionic conductivities (σRT) of polymer precursor pellets seem to follow the trend of Li2SiPHN > Li6SiPON > Li3PON > Li6PON > Li3SiPON, which relates largely to the N/P ratio. A maximum conductivity of 2.7 × 10-4 S/cm at RT is achieved for Li2SiPHN after heating at 400 °C/2 h/N2. Representative data are given below.

A screenshot of a video game

Description automatically generated with medium confidence

To further study electrochemical properties, these LiPON emulating polymer precursors were coated with Celgard separators fabricating polymer electrolytes and used as stable interface between Li metals for symmetrical cells, and Li and a sulfur-based cathode (SPAN) for half cells. Polymer electrolytes impregnated in/on Celgard exhibit Li+ conductivities up to ∼1 × 10-5 S/cm at RT, correlating with the Li content and N/P ratio. High Li transference number (tLi+) of >0.7 are exhibited for all precursors, comparable to inorganic solid electrolytes. The SPAN/Celgard + Li6SiPON/Li half-cell exhibits an initial capacity of 2000 mAh/gsulfur and excellent cycle performance at 0.25 and 0.5 C rate over 120 cycles at RT with stable capacity of ~750 mAh/gsulfur and columbic efficiency (CE) of ~92 %.

Graphical user interface

Description automatically generated

The possibility of using the polymer precursors (60 wt.%) as active fillers in PEO matrix forming solid polymer electrolyte films (SPE) was also explored. PEO solid-solution films exhibit enhanced ionic conductivities of ∼0.1-2 × 10-3 S/cm at ambient, a maximum ionic conductivity of 2.8 × 10-3 S/cm is achieved for the 60PEO/Li3SiPON, and all films show *t*Li+ ≥ 0.5 (typically PEs show *t*Li+ < 0.5). The enhancement in conductivity the PE films can be ascribed to the suppression of the PEO crystallinity and increased N/P ratio. Improved *t*Li+ indicates that anion mobility is limited due to the polymer precursor bulky backbone, especially for Li2SiPHN (*t*Li+ ≈ 0.8). In addition to the enhanced ionic conductivities *vs*. traditional PEO electrolytes, these active polymer precursor fillers offer improved stability against Li metal at higher current densities. Galvanostatic cycling of the SPAN/PEs/Li cell shows discharge capacities of 1000 mAh/gsulfur at 0.25 C and 800 mAh/gsulfur at 1 C. The cell also shows high-capacity retention over 100 cycles with ~100 % coulombic efficiency.

Graphical user interface

Description automatically generated

In summary, compared to traditional gas phase deposition methods, although our polymer precursor synthesis route provides less precise compositional control while also uses hazardous chemicals, it does offer a fast, scalable, low-cost and low-temperature fabrication, beneficial for commodity scale production while showing improved conductivities. The graph below compares the two approaches: advantages in **green** and disadvantages in **orange**.

Graphical user interface, text, application, chat or text message

Description automatically generated

Detailed description, analyses and discussions are reported in the following papers: