**Next Steps – SSEs**

Studies on polymer syntheses derived novel solid electrolytes open a new gate for research on SSEs for ASSBs. There are still much more to be done going forward. Below, a few possible near-future research objectives on the syntheses, applications and improvement for electrolytes derived from polymer syntheses are described.

**Polymer precursor coated SSE thin films**

Li metal dendrite formation resulting from nonuniform Li deposition is a well-established problem when cycling lithium-ion batteries (LIBs), which can lead to short circuiting wherein the dendrites penetrate the electrolyte layer and bridge to the cathode. Inorganic (ceramic) SSEs or ISEs were originally thought to offer a mechanical solution by blocking dendrite growth, but in fact they generally suffer from low fracture toughness and ductility, resulting in poor interfacial contact with electrodes. In fact, many ISEs are susceptible to dendrite penetration along grain boundaries, which also leads to short-circuiting [e.g., garnet-type LLZO (Li7La3Zr2O12)].

One solution to these problems is LiPON glasses. As introduced in the **LixPON and LixSiPON** page, they appear to resist dendrite penetration and wet with Li metal. However, LiPON glasses typically suffer from poor conductivities (10-8-10-6 S/cm) compared to, for example, LLZO (10-4-10-3 S/cm), and they must be introduced as interface materials at thicknesses of 50-200 nm to offer practical Li+ cycling. Consequently, LiPON thin films are typically fabricated through gas phase deposition methods.

Our **polymer syntheses derived LixPON-like precursors** offer a facile, low-cost alternative for the application of thin ceramic films. Furthermore, polymer precursors can be applied in a liquid format, which gives rise to the possibility of using scalable LiPON-like polymer precursors as coating materials that can act as binder/or adhesives for ceramic electrolytes, offering the potential to serve as an interface buffer layer between electrolyte and electrode.

Initial studies investigated a series of ceramic electrolyte substrates including **LiAlO2** (20-30 μm thick) and **Li1.7Al0.3Ti1.7Si0.4P2.6O12** (LATSP, ~25 μm thick) thin films derived from flame-synthesized nanopowders. These sintered substrates were dip-coated in the desired LiPON-like precursor solution (~0.1 g/mL in THF) using copper wire to suspend the sample. The coated films were dried (100 °C/12 h/vacuum), followed by heating to selected temperatures (400-600 °C/2 h) under N2.

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Coated LiAlO2 and LATSP films generally show dense and uniform coatings (~5 μm) with a well-defined interface between the coating and the substrate. Some coated films show the polymer precursor percolating into the LATSP substrate, resulting in a denser microstructure, and can be beneficial for ionic conduction.

All coated films generally show conductivities of 10-5-10-4 S/cm, similar to **LixPON-like polymer precursors**, suggesting their dominant contribution for Li+ conduction. It’s possible that the coating penetrates pores introducing Li+ conducting pathways not available before coating.

Although LiPON-like precursor coatings reduce the conductivity of LATSP by almost an order of magnitude, significant improvement in conductivity (up to four orders of magnitude) for LiAlO2 is exhibited. This is important as LiAlO2 substrates are much less costly substitutes.

The graph below shows representative SEM fracture surface microstructures and ambient ionic conductivities of coated SSE substrates heated to 400 °C/2 h/N2.

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The more important application of polymer precursor coatings is that they might offer improved interfacial properties that can lower interfacial resistance and stabilize the interfacial performance of ASSBs. As shown in the figure below for LTO/Li3SiPON/LiAlO2 heated to 400 °C/2 h/N2, clear bonding between the SSE LiAlO2 substrate and the anode LTO via Li3SiPON precursor coating is formed, and the resulting coating interface appears dense and uniform. Future studies should focus on the use of these polymer precursors for bonding between thin film ceramics and to assemble symmetrical and half-cells for electrochemical performance.

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**LixSiON precursor solid solutions with PEO**

Similar to the study on **LixPON-like polymer precursor** solid solutions with PEO, LixSiON-PEO solid solution polymer electrolyte (PE) films should also be investigated. Indeed, such PE films can be made by mixing LixSiON precursor with 60 wt.% PEO (*M*w = 900 kDa), and transparent and dense films form, especially for 60PEO/Li4SiON and Li6SiON PE films.

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Preliminary studies show that melting temperature (Tm) and crystallinity (*χ*c’%) decrease for 60PEO/LixSiON PE films compared to pristine PEO. The 60PEO/Li6SiON films show the highest conductivity of ~10-4 S/cm at ambient temperature, despite higher Tm and crystallinity compared to 60PEO/Li2SiON and Li4SiON films, which can be ascribed to its higher Li content.

Future work should focus on electrochemical characterization of 60PEO/LixSiON PE films assembled in symmetrical and half cell forms towards ASSBs.

Table

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**LixSiO system - silica dissolution with ethylene glycol**

**LixSiON precursors** were synthesized by reacting spirosiloxane (SP) distilled from rice hull ash (RHA) with LiNH2. The reaction between SiO2 in RHA with a sterically hindered diol, hexylene glycol, in the presence of catalytic amount of an alkali base forms distillable SP with a spirocyclic structure.

Previously, our group reported similar reactions of fumed silica with ethylene glycol (EGH2) and an alkali base:

Shape

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**References**1,2

(1) Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. Synthesis of Pentacoordinate Silicon Complexes from SiO2. *Nature* **1991**, *353* (6345), 642–644. https://doi.org/10.1038/353642a0.

(2) Laine, R. M.; Furgal, J. C.; Doan, P.; Pan, D.; Popova, V.; Zhang, X. Avoiding Carbothermal Reduction: Distillation of Alkoxysilanes from Biogenic, Green, and Sustainable Sources. *Angew. Chem. - Int. Ed.* **2016**, *55* (3), 1065–1069. https://doi.org/10.1002/anie.201506838.

One can envision that if an intermediate amount of alkali base is used, e.g., 40 mol. % of SiO2, a mixture of metal glycolate silicate salt with Si(EG)2 polymer will form, which is analogous to a solid polymer electrolyte (SPE) system (lithium salt in polymer matrix). Therefore, as an initial study, a set of reactions were explored using selected amounts of LiOH (20, 40 and 60 mol.% to SiO2), and they are denoted as LixSiO (Li/Si = x = 0.2, 0.4 and 0.6). Here, fumed SiO2 is used.

As shown in the figure below, ambient ionic conductivity (σRT) improves when the Li content (Li/Si ratio) increases from 0.2 to 0.4, but decreases slightly when it further increases to 0.6. It’s noteworthy that when the LiOH amount increases to 60 mol.%, the reaction mixture no longer forms transparent solution, unlike the Li0.2SiO and Li0.4SiO syntheses, but rather a suspension. The slight decrease in conductivity for Li0.6SiO suggests that insoluble solids in the SPE impede Li+ mobility, as the polymer matrix facilitates Li+ conduction.

Diagram

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Overall, the LixSiO system shows limited ionic conductivities (≤10-6 S/cm), and generally lower than the **LixSiON system**. Improving the conductivity and fabricating processable solid electrolyte membranes for ASSBs assembly remain as future work. It is also important to optimize the synthesis procedure so that RHA can be used as the starting material, achieving a green synthetic method similar to the LixSiON SSE system.

**Sodium-Based Systems**

LIBs have been the electricity storage system of choice since the successful commercialization in 1991, owing to their high energy density, compact and lightweight designs, and excellent cycle life compared to other rechargeable battery technologies. Unfortunately, the high demand for lithium has outpaced the capability of raw material supplies as a result of the increased growth of lithium-based systems. LIBs are becoming too expensive for stationary, large-scale electrical energy storage. Therefore, it is necessary to develop new energy storage technologies, and sodium-ion batteries (SIBs) have been recognized as promising alternatives due to the natural abundance of sodium and its similar intercalation chemistry to lithium.

Initial efforts on Na-based systems investigated syntheses of NaxSiPON and NaxSiON precursors, similar to previous studies on **LixSiPON** and **LixSiON precursors**. Here, we simply replace LiNH2 used for the lithiation step to NaNH2 for sodiation, see below.

Shape

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For NaxSiPON precursors, the Na3SiPON precursor solutions were coated on **Na1.67Al10.33Mg0.67O17** (NAMO, SSE for SIBs) films following the same procedure discussed above. The coated films were treated at 400 °C/2 h/N2, SEMs show the average coating thickness is 7.5 μm, and the coating surface appears to be overall uniform with some agglomerates. The maximum ambient ionic conductivity was found to be ~6 × 10-7 S/cm.

For NaxSiON (x = 2, 4) precursors, they were impregnated onto Celgard separators showing ambient conductivity of ~10-6 S/cm.

Graphical user interface

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Overall, promising results are obtained. Future work should continue the investigation of different precursor compositions of Na-based systems, optimization of precursor syntheses as well as their electrochemical performance, and fabrication of symmetrical cells, half cells, and eventually full cells for practical applications.