Synthesizing Solid-State Electrolytes for Lithium-Ion Batteries

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Abstract:

This study focuses on the production of a lithium tin phosphorous sulfide (LSPS) based solid-state electrolyte that will replace the flammable liquid electrolytic solution normally used in lithium ion batteries and decrease the risk of dendrite production, theoretically improving the lifespan of the average battery. To achieve this objective, LSPS, an air-sensitive superionic material, is combined with polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene then polyethylene glycol via the solvent, Toluene. The ionic conductivity of each sample is then tested using Electrochemical Impedance Spectroscopy (EIS) and compared for the highest conductivity.

Introduction:

In lithium-ion based batteries, charge and discharge is traditionally accomplished via a liquid electrolytic solution transporting lithium ions back and forth between the positive and negative electrode. Despite their effectiveness in moving lithium ions and a notable ionic conductivity of 10^{-3} S/cm, liquid electrolytes have two main problems affecting their overall usability. The first disadvantage is that of a flammability risk which is a byproduct of alkyl carbonates included in the liquid electrolytic solution. This causes a safety concern as lithium batteries are used in cellular devices and overheating of these devices could lead to them igniting and harming users. The second disadvantage, dendrite production, occurs during recharging where lithium ions form deposits of metal inside the battery that can grow to form dendrites. If the dendrites grow large enough to reach the cathode in a battery, premature short circuiting of the battery can occur and negatively affect its lifetime. These main problems have led to the introduction of solid-state electrolytes (SSEs). SSEs are projected to replace the flammable liquid electrolytic solution as well as only allow lithium ions to exit the electrolyte at certain locations. This specificity will decrease the risk of metal deposits leading to dendrite production thus decreasing the risk of premature short circuiting.

Lithium tin phosphorous sulfide is a promising base for solid-state electrolytes due to its superionic nature. LSPS has the ability to produce lithium ions at room temperature as well as an ionic conductivity range of 10^{-4}S/cm-10^{-2} S/cm. It also allows the use of lithium metal as an anode material instead of graphite which increases the cell voltage and energy density of a battery. The main disadvantage of LSPS is its air-sensitivity where moisture in the air can cause it to become unstable and produce a flammable gas. Implementing pure LSPS into an electrolyte with the risk of air or moisture exposure would be futile in the efforts of producing a nonflammable electrolyte to utilize in common lithium-ion batteries.

In this study, effects of specific materials on the ionic conductivity and physical stability of LSPS are examined. These materials include polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene, polyethylene glycol, and toluene as a solvent selective for polystyrene. Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene proved to be a promising candidate due to its precedence when combined with anion exchange membranes to produce separators with high chloride ion conductivity. Due to it being an organic material, however, there was a risk of producing a highly viscous and thick film that wouldn't be usable in the sample batteries during testing. Polyethylene glycol proved to be a promising candidate due the precedence of polyethylene oxides, when combined with lithium-ion conducting materials, producing solid-state cells with impressive rate capability and cycling performance. The effects of combining these materials with LSPS were examined via Electrochemical Impedance Spectroscopy (EIS) where the internal resistance of the battery is measured. A high resistance translates to a low ionic conductivity. A Nyquist Plot was used to illustrate the accompanying EIS curve for each sample, representing the effective resistance of the electric current from the combined effects of ohmic resistance and reactance. Conductance of each sample was numerically calculated via the relationship, Ơ = t/RA, and compared to test the combination's effectiveness in achieving the objective.

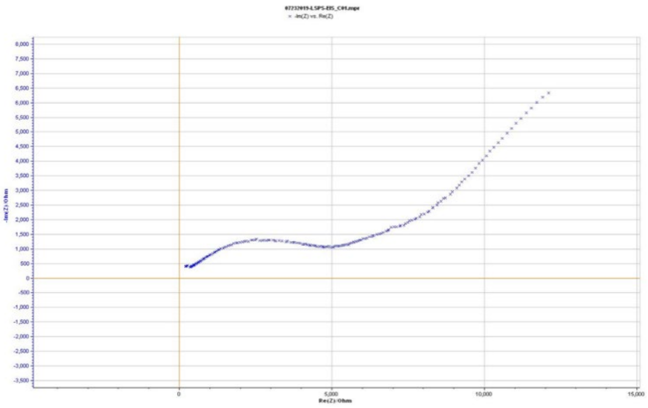

Figure 1. An EIS curve that's horizontal in nature of pure LSPS where its ionic conductivity (Ơ) is $6.264*10^{-4}$.

Procedure:

A literature study was conducted in order to find materials that would aid in accomplishing the objective of protecting LSPS without detrimentally affecting its ionic conductivity. The first material chosen was the organic polymer, polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene due to its precedence when combined with anion exchange membranes to produce separators with a high chloride ion conductivity. Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene also doesn't absorb water, so it was hypothesized that when combined with LSPS, this property would encompass the entire mixture.

The solvent toluene was selected because it’s a solvent selective for polystyrene due to its inability to be dissolved in water.

With these materials, the second phase of the investigation was conducted, focusing on polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene and dissolving it in toluene. Solutions with varying amounts of polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene were produced where the determining factors of each solution was its viscosity and the projected thickness of the pellet. The solution with the lowest viscosity and the solution that would produce the thinnest pellet was the most desirable.

The third phase included the amount of LSPS to implement into the solution then testing the effects of the addition via Electrochemical Impedance Spectroscopy (EIS) for a desirable conductivity. The solid pellets were produced by contact with a hotplate then cut into one-centimeter discs to be placed into a coin cell battery for testing. Two solutions were made with varying amounts of LSPS then tested and the results were illustrated on a Nyquist Plot. The samples were simultaneously observed when exposed to air for any physical changes. Polyethylene glycol was then added to the mixture while increasing the amount of solvent and LSPS. This solution was then tested and compared to the previous two trials regarding the varying conductivities.

Results and Conclusions:

Testing produced varying EIS curves where both trials only containing polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene, polyethylene glycol, LSPS and toluene had accompanying vertical curves proving their low ionic conductance [Fig.2,3].

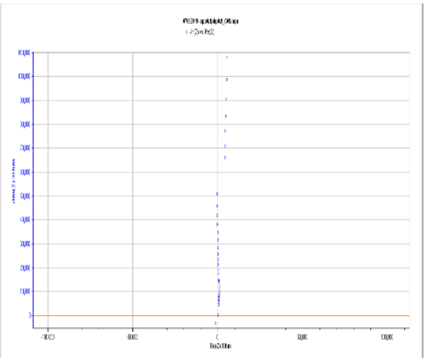

Figure 2. An EIS curve that's vertical in nature from the first trial containing LSPS, polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene, and toluene.

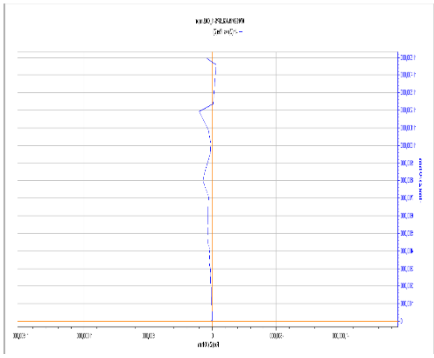

Figure 3. An EIS curve that's vertical in nature from the second trial containing LSPS, polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene, and toluene.

These samples were also tested to investigate their capabilities when exposed to air. After more than twenty hours of air exposure, the sample containing the higher concentration of LSPS retained the same physical properties suggesting it achieved the objective of protecting LSPS from moisture in the air. The third trial conducted where polyethylene glycol was included in the solution produced an EIS curve with a measurable ionic conductivity [Fig.4]. The relationship, Ơ = t/RA, produced an ionic conductivity of (Ơ). Since the EIS curve of the third trial was horizontal in nature, it was already suggested that it would contain an ionic conductivity higher than trials preceding it.

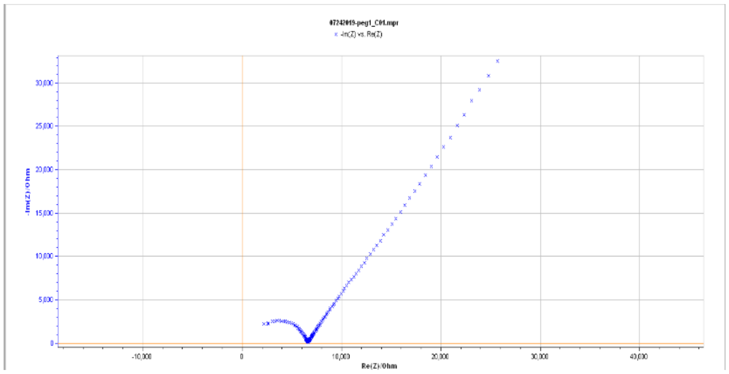

*Figure 4. An EIS curve that's horizontal in nature of a sample containing LSPS, polyethylene glycol, polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene, and toluene with an accompanying ionic conductivity of 1.11*10*$^{-3}$.

Despite PBP being able to effectively protect LSPS from oxidation, it was proven that it couldn't produce a usable conductivity when combined with LSPS. In comparison to trials where only PBP, LSPS, and Toluene were utilized, the trial where PEG was also included proved to be the most effective in retaining a desirable ionic conductivity. This discovery is imperative to the development of fully stable and functioning LSPS-based solid-state electrolytes that can withstand the effects of air sensitivity while simultaneously retaining a usable conductivity.

Future Work:

The Liu lab will continue testing this combination of materials in adverse conditions such as, direct contact with water and extreme temperatures, in order to investigate its full capabilities.

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