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Submitted to *Solid State Ionics*

Title:

The “filler effect”: A study of solid oxide fillers with β -Li₃PS₄ for lithium conducting electrolytes

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Abstract:

Solid electrolytes are the subject of intense study partly because of their use in safer, high energy density, all-solid-state lithium-ion batteries. The addition of solid oxide fillers has been previously explored as a way to increase the ionic conductivity in composite electrolytes; however, no comparative study of the effect of both ion-conducting and non-conducting oxides on solid lithium superionic conductor electrolyte is reported. Nano-crystalline β -Li₃PS₄ (LPS) was recently shown to have anomalous high ionic conductivity, but it was found that this property can be further enhanced. This study examines the effect of three solid oxide fillers (Li₆ZnNb₄O₁₄, Al₂O₃, and SiO₂) in composites with LPS for the enhancement of the parent electrolyte. The electrolytes' processability, ionic conductivity, activation energy and stability against metallic lithium are presented to gain a complete understanding on the effect of solid oxide fillers on LPS while elucidating the significant enhancement of LPS through the addition of Li₆ZnNb₄O₁₄ or Al₂O₃.

Keywords:

Solid electrolyte, ionic conductivity, lithium-sulfur battery, composite electrolyte, lithium thiophosphate

Acknowledgements:

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. The synthesis and characterization of composite materials was completed at the Center for Nanophase Materials Science, which is sponsored by the Division of Scientific User Facilities Division, U.S. DOE. Zachary D. Hood was supported by Higher Education Research Experiences (HERE) at Oak Ridge National Laboratory. This material is also based upon work supported by the National Science Foundation Graduate

Research Fellowship under Grant No. DGE-1148903. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. This manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a paid-up, nonexclusive, irrevocable, worldwide license to publish or reproduce the published form of this contribution, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so, for U.S. Government purposes.

1. Introduction

In the current energy market, there exists a need for a longer-lasting battery with increased energy density [1-3]. Previously, batteries consisted of solid electrodes and a liquid electrolyte, however, this model is neither the safest nor most efficient. Liquid electrolytes are flammable and lead to dendrite formation for lithium deposition that causes the cell to short, compromising the battery's lifetime [2]. Theoretically, solid electrolytes allow for batteries with greater energy density and in some cases, stability with lithium anode at increased voltages, which makes solid electrolyte superior to liquid electrolyte [3].

Recent developments in lithium superionic conductor (LiSICON) electrolytes paved the way to materials with high conductivity ($\geq 10^{-4}$ S·cm⁻¹), good processability, and high energy density [4-6]. The LiSICON solids have higher theoretical thermal and electrochemical stability, and in the case of batteries, these solids open a new frontier for electrolyte research. One compound, in particular, is of great interest: nano-crystalline β -Li₃PS₄ (LPS) [7, 8]. With an ionic conductivity of 1.6×10^{-4} S·cm⁻¹ at ambient temperature, nanostructured LPS is truly a novel addition to the LiSICON system [7]. Additionally, LPS is synthesized at room temperature, has good processability, easy membrane fabrication, and low interfacial resistance with metallic lithium electrodes. Still, further improvement of the ionic conductivity and stability of LPS with different anodes will enhance battery performance and allow for an ionic conductivity similar to those found in liquid electrolyte.

It has been previously shown that the addition of oxide fillers into the LPS system could potentially increase the conductivity of the electrolyte [8]. Previously, ion-conducting and non-

conducting oxide fillers have been shown to enhance the ionic conductivity of solid electrolytes. However, it is unknown as to what oxide filler works best with LPS, which warrants an understanding of how oxides affect the mechanical and electrolyte properties of LPS. For this study, several oxides have been selected to analyze the filler effect: $\text{Li}_6\text{ZnNb}_4\text{O}_{14}$ (LZNO), Al_2O_3 , and SiO_2 . According to hard-soft acid base (HSAB) theory, these hard oxides will not react with LPS, a soft base, when forming composites. Also, LZNO has an ionic conductivity of $3.28 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 21.5°C and $1.31 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 250°C [9, 10] while Al_2O_3 and SiO_2 are reported to enhance the ionic conductivity in heterogeneous composite electrolytes [9, 10], which is the reason why these solid oxide fillers were selected for the basis of this study.

This paper presents a comparative study of ion-conducting and non-conducting oxide fillers in composites with LPS. The ionic conductivity, activation energy, and stability of electrolyte composites against metallic lithium are reported. A working understanding as to the effect of ion-conducting and non-conducting oxides on LPS facilitates the discovery of better composite electrolytes for use in Li-metal based all-solid-state batteries, which will ultimately help fabricate safer, higher energy-dense batteries.

2. Materials and Methods

2.1. Synthesis Methods

Synthesis of composites: LZNO:LPS, Al_2O_3 :LPS, and SiO_2 :LPS composites were prepared by ball milling with the SPEX SamplePrep[®] Mixer/Mill 8000M. LPS was synthesized in a previously reported solution-based method using THF followed by subsequent heating at 140°C for 1 hour and 200°C for 2 hours [3] and LZNO was synthesized using a solid-state reaction [11, 12]. Al_2O_3 (Sigma Aldrich, 150 mesh, pore size $58 \text{ \AA}$) and SiO_2 (Aldrich, 99.5%, 5-15nm particle size) were used to synthesize the composites. Al_2O_3 and LZNO were ball-milled to reduce the particle size to $\leq 1\text{-}2 \text{ }\mu\text{m}$ before composite fabrication. Since LZNO, Al_2O_3 and SiO_2 were previously stored in air, these powders were heated to 350°C prior to moving the powders to the glove box to remove any moisture. The oxide wt.% was varied between 2-90 wt.% when fabricating each composite. Y-ZrO₂ beads (3mm & 5mm; ~10g) were used in the ball milling process. All composites have particles size of $1\text{-}2 \text{ }\mu\text{m}$ or less before pressing pellets. Since LPS is sensitive to air, all composites were synthesized under Argon.

2.2. Analysis Methods

2.2.1. X-Ray Analysis

A PANalytical X'Pert Pro Powder Diffractometer equipped with a Ni-filtered Cu K α radiation was used for the crystallographic phase identification for the composites. Quartz slides were sealed with Kapton[®] films for analysis and High Score Plus was used to complete Rietveld refinement and structural analysis. All X-ray powder diffraction patterns were collected at room temperature.

2.2.2. Scanning electron microscopy

Scanning electron microscopy (SEM) images were collected with a Zeiss Merlin SEM at 3.0kV. Energy-dispersive X-ray spectroscopy (EDX) was completed on the composites to ensure homogeneity after ball milling. For EDX, the beam energy was 10.0kV in order to obtain the excitation of elements from LPS and the oxide fillers. Pellets were carefully fractured for cross-sectional SEM images detailing the interface between the composite electrolyte and metallic lithium anode. Prior to collecting images, all samples were placed on carbon conductive tape and sealed under Argon.

2.2.3. Impedance measurements

About 140mg of each composite was used to prepare 1/2" pellets, which were cold-pressed at 300 MPa with Al/C blocking electrodes. Swagelok[®] cells were used to obtain all impedance and activation energy data. Impedance measurements were obtained using a Solartron SI 1260 Impedance Gain-Phase Analyzer from 1MHz – 1 Hz with amplitude 100.0mV. Activation energies were determined by Arrhenius measurements using the Maccor 4300 System Environmental Chamber with temperatures ranging 25-100 °C. EIS was collected for symmetric cells after cycles 25, 50 and 100 to monitor the change in interfacial resistance between the composite electrolyte and metallic lithium anode.

2.2.4. Cyclic voltammetry measurements and cell cycling

A BioLogic MPG2 instrument equipped with EC-Lab software was utilized to collect all cyclic voltammetry and cell cycling data. Li/composite electrolyte/Pt cells were placed into Swagelok[®] cells for cyclic voltammetry measurements with a potential of 10 mV/s and scanned from -0.5 to 5.0 V vs. Li/Li⁺. Lithium and platinum serve as counter and working electrodes, respectively. Li/composite electrolyte/Li symmetric cells were also placed into Swagelok[®] cells for cell cycling with a potential of 0.1mA·cm⁻².

3. Results and Discussion

3.1. Composite processability and structural analysis

The composites are simple mixtures of the oxide fillers and LPS. The oxide fillers are stable with LPS. This stability is apparent in the XRD measurements, where the 50:50 (LPS: oxide) composites display no apparent reaction (Fig. 1), which confirms that no solid-state reaction occurred between LPS and the oxides during ball milling processes. Additional XRD analysis also confirms that the starting materials did not react with the ball milling media (Y-ZrO₂). SEM aided in determining composite homogeneity, where particles ≤ 1-2 μm were found for both the LPS and the oxide filler in all composites, which confirms that simple ball milling may be used to achieve homogeneity of the LPS and oxide particles (Fig. 2). EDX analysis further demonstrates the composite homogeneity, where LPS and oxide particles were evenly dispersed throughout the LZNO:LPS composite (Fig. S1), the Al₂O₃:LPS composite (Fig. S2), and the SiO₂:LPS composite (Fig. S3).

At room temperature, the oxides have poor processability; it is nearly impossible to cold-press a pellet of LZNO, Al₂O₃ or SiO₂ without the pellet partitioning or fractures forming. For this reason, the sticky LPS aids in pressing a dense pellet free from fractures (Fig. S4). After adding as low as 10 wt.% LPS to the oxide fillers, a dense pellet can be easily cold-pressed (density of 10 wt.% LZNO composite ~2.56 g·cm⁻³, 10 wt.% Al₂O₃ composite ~1.75 g·cm⁻³, and 10 wt.% SiO₂ composite ~1.43 g·cm⁻³; densities determined from gravimetric and geometric measurements). The pellet density increases for the LZNO and Al₂O₃ composites with increasing oxide content, while the pellet density decreases for the SiO₂ composites; this trend agrees with the density of the pristine oxides, as LZNO and Al₂O₃ are denser than LPS, while SiO₂ is less dense than LPS.

Fig. 1. XRD spectra of composites and pristine precursors. No reaction was observed between the LPS and oxide fillers from XRD analysis, as all peaks in composites were identified as from the parent compounds.

Fig. 2. SEM images of a) 50 LZNO: 50 LPS; b) 50 Al_2O_3 : 50 LPS; and c) 50 SiO_2 : 50 LPS after ball milling.

3.2. Effect of solid oxide fillers on composite ionic conductivity and activation energy

Each of the oxide fillers affects the ionic conductivity of the composite with a similar trend – a relatively small fraction percent of the oxide filler enhances the ionic conductivity while higher concentrations of solid oxide cause the ionic conductivity to decrease. In the case of 10:90 (LZNO:LPS), the ionic conductivity is $2.44 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is higher than the conductivity of the pristine parent compounds. This trend was previously observed in the case of LPS filled with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), where an addition of 30 wt.% LLZO to LPS increased the conductivity from $1.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ to $5.36 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ [8]. This enhancement in conductivity was attributed to the interface between LPS and LLZO, where the Nyquist data show both higher and lower conducting components. For the case of LZNO, this same phenomenon is observed with the 90:10 (LZNO:LPS) composite; Nyquist data show higher conducting and lower conducting processes, evidencing the presence of an interfacial layer between the LPS and the porous non-dense oxide filler (Fig. 3). This phenomenon was only found in the LPS filled with ion-conducting fillers while the non-conducting fillers did not show two processes in the Nyquist data, which confirms that there is competition between the higher conducting parent electrolyte and lower conducting oxide filler throughout the composite.

In heterogeneous composite electrolytes, the conduction mechanism is expected to be influenced by both space-charge and blocking effects [8, 13-20]. The space-charge effect will account for enhancement of the parent electrolyte, causing less resistance for the charged particle, while the blocking effect will cause the conductivity to decrease, where the blocking species will impede the forward mobility of the charged particle. A model for the filler's effect on LPS is shown in Fig. 4, where 'A' represents the pristine LPS with no oxide filler, 'B' illustrates LPS filled with enough oxide filler to induce an enhancement in the ionic conductivity, and 'C' demonstrates the blocking effects of the oxide filler. Each oxide filler has a concentration in LPS where it enhances the ionic conductivity and a concentration where it will impede ion hopping through the material. Fig. 5 presents the compiled ionic conductivities and activation energies for each composite. The LZNO-filled LPS composites show a pronounced space-charge effect where the addition of 10 wt.% of LZNO increases the conductivity to $2.44 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, while the addition of 2 wt.% of Al_2O_3 and SiO_2 also increases the conductivity (2 wt.% Al_2O_3 increases the conductivity to $2.28 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and 2 wt.% SiO_2

increases the conductivity to $1.84 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$). When comparing the SiO_2 to Al_2O_3 fillers, LPS filled with 2 wt.% Al_2O_3 shows a significant increase in conductivity while the LPS filled with 2 wt.% SiO_2 shows a slight increase. The Al_2O_3 and SiO_2 fillers have different zero charge pH values (SiO_2 is ~ 3 and Al_2O_3 is ~ 9) where the order of oxide activity corresponds to the zero charge pH value of the oxide filler [17]. The surface acidity of the oxide filler increases the ionic conductivity by changing the charge carrier distribution in the composites. SiO_2 does not favorably enhance the charge carrier distribution in the composite, so solid oxides in composites with LPS with a zero charge pH of ~ 3 are expected to yield similar results. Furthermore, the particle size of SiO_2 is smaller than that of LZNO and Al_2O_3 , which has previously been demonstrated to cause both favorable and unfavorable changes in the charge transfer distribution in composite electrolytes depending on pore and particle sizes [21-24]. In this study, the LZNO and Al_2O_3 fillers are composed of larger particles than the SiO_2 filler, and consequently, the ionic conductivity was enhanced with relatively larger particles. The ion-conducting LZNO filler causes a more pronounced enhancement when compared to the non-conducting Al_2O_3 , even though their particle size is similar. Still, LPS's conductivity decreases after the addition of $\geq 30\text{wt.}\%$ LZNO, $\geq 8\text{wt.}\%$ Al_2O_3 and $\geq 5\text{wt.}\%$ SiO_2 , which corresponds to the blocking effects shown in part 'C' of Fig. 4. When the concentration of non-conducting oxide particles in the composite is too high, the particles will impede the forward motion of the Li ions. On the other hand, LZNO may also impede the forward motion of the Li ions since it has a lower room temperature ionic conductivity than LPS, but its effect is not as pronounced as the non-conducting oxide fillers. The results of this study agree with previous reports of space-charge and blocking effects in other systems that use Al_2O_3 and SiO_2 as fillers [14-17].

The activation energy collected from Arrhenius measurements significantly increases as LPS is filled with more SiO_2 . LPS filled with LZNO or Al_2O_3 also follows a similar trend of increasing activation energy, however, the increase is not as significant as the SiO_2 :LPS composites. This increase in activation energy is attributed to grain boundaries and the blocking effects of the oxide filler. More specifically, SiO_2 significantly increases the thermal activation of ion hopping through the material, which is attributed to the small particle size and unfavorable zero charge pH. On the other hand, LPS filled with $\leq 5 \text{ wt.}\%$ of Al_2O_3 does not significantly change the thermal activation (0.32eV). When compared to the nonconductors, the ion-conductors (LLZO and LZNO) significantly decrease the thermal activation of ion hopping for

composites with enhanced ionic conductivity [8]. The activation energy of pristine LZNO was estimated as 0.39eV [10], however, in the highest conducting LZNO:LPS composite, the activation energy was decreased to 0.31eV, significantly lower than that of LPS (0.35eV) and LZNO (0.39eV).

With a high conductivity coupled with low activation energy, the 10wt.% LZNO and 2wt.% Al_2O_3 composite electrolytes are superior to the SiO_2 :LPS composite presented in this study. These composites have ionic conductivities greater than $2.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and activation energies lower than 0.33eV, making these electrolytes favorable for lithium-ion battery applications.

Fig. 3. Nyquist plot of 90:10 (LZNO:LPS) composite at 25 °C. Two semicircles represent the high conduction and low conduction processes of the cold-pressed composite electrolyte.

Fig. 4. Model for the oxide filler's effect on the parent LPS electrolyte. 'A' represents the addition of no oxide filler, 'B' represents the space charge effect, and 'C' shows the blocking effect of the oxide filler. (For references to color, the reader is referred to the web version of this article.)

Fig. 5. Plots of ionic conductivity (left y-axis) and activation energy (right y-axis) as a function of oxide content. The closed circles correspond to ionic conductivity and the open squares correspond to activation energy. (For references to line color, the reader is referred to the web version of this article.)

3.3. Composite stability against metallic lithium anode

After determining the ionic conductivity enhancement of the ion-conducting and non-conducting oxide fillers on LPS, the composites with greatest ionic conductivity were selected for electrochemical stability and cell cycling measurements for each composite was evaluated. Some solid electrolytes have high ionic conductivity, however, their use in a solid-state battery is compromised by their stability with metallic lithium anode, which ultimately compromises the overall capacity. LPS alone shows stability with a metallic Li anode [7], however, it was unknown to what extent the oxide fillers compromised this stability. Cyclic voltammetry measurements show that each composite is stable up to the potential of 5V vs. Li/Li⁺. In Fig. 6a, the stability of the composite is apparent in the cyclic voltammogram (CV) with the Li/LZNO:LPS/Pt cell for the 10:90 (LZNO:LPS) composite, which is also representative of LPS filled with Al₂O₃ and SiO₂. Anodic current is only present at 0 to 0.75 V while no significant current was observed between 0.75 to 5 V, which was also observed for composites filled with the selected non-conducting oxides. Additionally, no side reactions were observed between the composites and metallic lithium. Therefore, the oxide fillers do not compromise the chemical and electrochemical stability of LPS against metallic lithium anode.

To demonstrate the cyclability and long-term stability of the composite electrolytes filled with ion-conducting and non-conducting oxides, a symmetric Li/composite electrolyte/Li cell was constructed and cycled at room temperature. Fig. 6b displays the voltage profile for the symmetric cell with the LZNO-filled LPS, which is representative for each composite. This cell presented a voltage of 35.6 mV with a current density of 0.1 mA·cm⁻², corresponding to a direct-current (dc) conductivity of $2.3 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for the symmetric cell. The alternating current (ac) conductivity was found to be $2.4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for the composite, agreeing with the calculated dc conductivity. The dc and ac conductivities were also similar for the LPS filled with non-conducting oxides. Negligible interfacial resistance was observed when the composite electrolytes were cycled with metallic lithium (even after 400 cycles), supporting the compatibility of the composite electrolytes with metallic lithium.

Fig. 6. a) Representative CV of Li/LZNO:LPS/Pt cell for the 10:90 (LZNO:LPS) composite, demonstrating a wide electrochemical window of 5V; b) representative cycling data of Li/LZNO:LPS/Li symmetric cell with a current density of $0.1\text{mA}\cdot\text{cm}^{-2}$ for the 10:90 (LZNO:LPS) composite. These data are representative of the highest conducting composites with Al_2O_3 and SiO_2 , as similar cyclic voltammetry and cycling data were collected.

The stability between metallic lithium and the 10:90 (LZNO:LPS) composite was further confirmed by EIS at different cycle numbers and through the utilization of SEM with EDX to analyze the interface in a symmetric cell containing metallic lithium. Previously, thin films of pristine LZNO were shown to have high interfacial resistance when cycled with metallic lithium [12], however, in this study, we demonstrate that the LZNO:LPS composite may be cycled hundreds of times with low interfacial resistance. Fig. 7 displays the EIS spectra collected after 25, 50, and 100 charge/ discharge cycles. The resistance through the material does not significantly change when charged/ discharged in a symmetric cell configuration. The interface between metallic lithium was analyzed using SEM and EDX elemental mapping after 0, 50, and 100 cycles (Fig. 8). After cycling, the composite electrolyte does not change morphology, maintaining a dense network where lithium cannot penetrate through the composite LZNO:LPS electrolyte. Interestingly, no significant buffer layer appears between the composite electrolyte and the metallic lithium anode signifying that no major side reactions occur at the interface. LPS is believed to stabilize the interface, even when LPS is in composites with oxide fillers. Therefore, the synergistic relationship between LPS and the oxide filler allows for both interfacial stability with metallic lithium (from LPS) *and* enhanced ionic conductivity in the composite electrolyte (from the oxide filler).

Fig. 7. EIS of Li/LZNO:LPS/Li cell for the 10:90 (LZNO:LPS) composite at 25 °C after different cycle numbers. Negligible change in resistance between cycles 25, 50 and 100 was observed. (For references to line color, the reader is referred to the web version of this article.)

Fig. 8. Cross-sectional SEM images of 10:90 (LZNO:LPS) interface after a) 0 charge/ discharge cycles, d) 50 charge/ discharge cycles and g) 100 charge/ discharge cycles; b,e,h) corresponding EDX elemental mapping of sulfur; c,f,i) corresponding EDX elemental mapping of phosphorus. After 100 charge/ discharge cycles, the interface between the LZNO:LPS composite maintains the same dense morphology where no major interfacial reaction was observed.

4. Summary and conclusions

Three different oxides were studied as fillers for LPS composites. Through X-ray diffraction analysis, it was shown that no reaction occurred through simple room-temperature ball-milling of the oxides with LPS. SEM images indicate that the cold-pressed pristine oxide pellets can be fabricated without fractures, breaks, and minimal open porosity. As an increased amount of oxide was added to the composite, the ionic conductivity significantly decreases while the activation energy increases, which is attributed to the blocking effects from the oxide filler. When 10 wt.% LZNO was added to LPS, the ionic conductivity increases to $2.44 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, nearly doubling the ionic conductivity of the parent electrolyte.

To meet the needs of solid-state batteries, the present study will help fabricate better LiSICON composite electrolytes. As found, the addition of 10 wt.% LZNO significantly increased the conductivity of LPS while maintaining low activation energy (0.31eV) and stability against metallic lithium up to 5V. Similarly, LPS filled with 2wt.% Al_2O_3 increased the conductivity to $2.28 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ while maintaining low activation energy (0.32eV) and stability against metallic lithium up to 5V. These data demonstrate that ion-conducting and non-conducting oxide fillers may be used to enhance the ionic conductivity of LPS. Also, the oxide fillers do not compromise LPS's stability against metallic lithium anode, allowing for hundreds of charge-discharge cycles. Based on the present study, the enhancement of LPS with LZNO or Al_2O_3 produced composite electrolytes with high ionic conductivity and low activation energy comparable to that of liquid electrolytes, which shows promise for the fabrication of safer, longer-lasting, all-solid state batteries in the near future.

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