Chalcogenide-based Lithium Solid Electrolytes Processed by the Powder-in-a-tube Method

Seth S. Berbano^{a,b,†}, Malick Y. Fofana^c, Clive A. Randall^{a,b}, Michael T. Lanagan^{a,b,c}

a. Center for Dielectrics & Piezoelectrics, Materials Research Institute

b. Department of Materials Science & Engineering

c. Department of Engineering Science & Mechanics

N-256 MSC, The Pennsylvania State University, University Park, PA 16802 USA

Phone: 814-863-1328, Fax: 814-865-8126

† Author to whom correspondence should be directed. E-mail: sethberb@psu.edu

Abstract

Solid electrolytes are candidate materials for solid-state batteries and electrochemical capacitors. **Viability** of a powder-in-a-tube (PIT) process, most commonly associated with processing of superconductor wires, is shown in sulfide-based lithium solid electrolytes. PIT processing is used to create thin (120 μm) electrolytes sheathed within an aluminum tube. Extrapolated room temperature ionic conductivities reach $10^{-3} (\Omega\text{-cm})^{-1}$ in both rolled PIT and pelletized $0.70 \text{ Li}_2\text{S} + 0.30 \text{ P}_2\text{S}_5$ (mol fraction) lithium thiophosphate solid electrolytes crystallized to form $\text{Li}_7\text{P}_3\text{S}_{11}$ **after heat** treatment.

Keywords: Electrical properties; Electroceramics; Electrolyte; Energy storage and conversion; Powder-in-a-tube

1. Introduction

In organic liquid electrolytes, interfacial resistance contributions between electrode/liquid electrolyte interfaces are much lower than the **resistance** contributions from electrode/solid electrolyte **interfaces. However**, there are often worries regarding flammability and safety in

liquid electrolytes. To maximize solid-state battery or electrochemical capacitor performance, the solid electrolyte's interfacial resistance contributions can be minimized by (1) *microstructural modification* – maximizing electrolyte ionic conductivity through densification and (2) *materials processing* – making the electrolyte as thin as possible. Solid electrolytes **must** have a minimum thickness because chemical continuity (**mobile ion concentration**) through the thickness, while densification creates a physically continuous conduction path. Therefore, maintaining chemical and physical continuity is important to minimize interfacial resistance contributions during charge-discharge cycles [1].

Powder-in-a-tube (PIT) processing allows electrolyte densification and naturally creates thin electrolytes that are hermetically encapsulated in a metal sheath. After encapsulation, the process can be carried out by conventional rolling in ambient atmosphere. PIT was pioneered by the superconducting community to create textured ceramic tapes and wires [2-5] and is a low-cost, solvent-free, non-vacuum technique. Further, PIT can be seen as a continuous process since long **tubes could** be filled with electrolyte powder and fed through rollers for yields in the tens of meters.

In PIT, rolling weakly-bonded glasses, such as chalcogenides with 215°C glass transition temperatures, is proposed to create higher density pre-formed electrolytes. The 0.70 Li₂S + 0.30 P₂S₅ glass electrolyte was selected because it could be added to a tube sheath as a milled powder, rolled, and crystallized to form a high 10⁻³ (Ω-cm)⁻¹ ionic conductivity electrolyte with a reported 5 V stability window vs. Li [6-8]. X-ray diffraction and impedance spectroscopy **results are used** to characterize the phases and electrical properties, respectively. Comparisons to other Li₂S + P₂S₅ processing routes are made to ensure there is no deleterious impact on ionic conductivity from PIT.

2. Experimental Methods

2.1 Powder-in-a-tube rolling

Thick wall (6.35 mm O.D. and 3.86 mm I.D.) and thin wall (7.14 mm O.D. and 6.43 mm I.D.) aluminum 3003 tubing was cleaned with ethanol, dried at 120°C overnight, and taken into an Ar glovebox. One end of the tube was crimped and mechanically milled, glassy 0.70 Li₂S + 0.30 P₂S₅ electrolyte powder (milled for 14 hours at 370 rpm) was loaded into the tube [9]. The other end of the tube was crimped to form a hermetic seal and taken outside of the glovebox for rolling. The electrolyte-filled Al tube was repeatedly passed through a rolling mill (Otto Frei, Oakland, CA). The distance between the rollers was dialed to be closer by about a half turn between each pass. The total rolling time is about 5 seconds per pass for tubes that are initially 100 mm long. To release a rectangular electrolyte sheet from the tube, the flattened tube was taken back into the glovebox and tin snips were used to make cuts around the sheath perimeter.

2.2 Electrolyte crystallization

Rectangular electrolyte pieces were embedded in a lithium thiophosphate powder bed and crystallized inside a brass mold, which was covered with a zirconia brick pre-charged with lithium thiophosphate powder to control lithium activity near the electrolyte surface. The brass mold was centered on a hot plate (IKA Works, Ceramag Midi) and was heated at 40°C/min from room temperature to the desired temperature. After reaching the desired temperature, the hot plate was turned off and allowed to cool to room temperature.

2.3 X-ray diffraction

Powder samples were loaded in a quartz low-background support and covered with Kapton inside the glovebox. Room temperature X-ray diffraction patterns were collected as in [9].

2.4 Impedance spectroscopy

PIT electrolytes were electroded, loaded into a sample cell, and transferred from the glovebox to an N₂-purged, temperature-controlled chamber. Complex impedance spectra were measured using an impedance analyzer [9].

3. Results and Discussion

3.1 Powder-in-a-tube rolling

Rolling of electrolyte inside thick and thin wall Al tubing was performed. Subsequent passes reduced total Al sheath-electrolyte-Al sheath thickness as well as reduced electrolyte thickness. In a thick wall Al tube, the sheathed electrolyte thickness reached 120 μm after five passes (**Fig. 1**). Dimensional changes of electrolyte and electrolyte density vs. pass number for a thin wall Al-electrolyte-Al sandwich structure are reported in **Fig. S1**. The $66 \pm 2.5\%$ relative density is consistent with the expected 150 MPa pressures from the Al 3003 tube walls constraining the electrolyte in the plastic regime [9, 10]. With the weak dependence of strain rate on maximum imparted pressure [10], warm (160°C) rolling is important to achieve high density [9, 11].

Two sintering processes have been applied to densify lithium thiophosphates: uniaxial pressing at room temperature [11] and uniaxial pressing during heating [9, 12, 13]. Densification at lower temperatures is important when species are volatile. In $0.75 \text{ Li}_2\text{S} + 0.25 \text{ P}_2\text{S}_5$, greater than 90% relative density can be achieved at room temperature when pressing glassy powder to 400 MPa [11] rather than requiring external thermal energy to densify [9]. The ability for a glass to densify is linked to average bond strength through composition (average matrix polarizability, fraction of non-bridging units, etc.) and is related to kinetic properties (ratio of absolute pressing

temperature to absolute glass transition temperature). Every glass has an iso-density plane where the resulting density (ρ) is a function of pressure (P), temperature (T) and time (t). An iso-density function $\rho(P, T, t)$ is important for tuning warm roll-on-roll processes, for potential continuous production of thin PIT solid electrolytes.

3.2 X-ray diffraction

As-milled powders are x-ray amorphous (**Fig. 2**). Room temperature rolling does not cause crystallization. Differential scanning calorimetry results show the onset of the crystallization exotherm is 257°C [9]. When crystallized above 257°C, a superionic $\text{Li}_7\text{P}_3\text{S}_{11}$ phase forms consistent with [8].

3.3 Impedance spectroscopy

Using a self-consistent method, electrolyte ionic conductivity was taken as the inverse of the low frequency electrode polarization feature extrapolated to the geometry-normalized real axis (Z') of the impedance complex plane plot (**Fig. 3**). Sub-optimal electrolyte density and surface roughness caused a diffuse transition between the electrolyte's RC semicircle corresponding to lithium charge transfer resistance through the bulk and the low frequency electrode polarization feature. Measurement at sub-ambient temperatures was required to see part of the RC semicircle, which is shifted past the high frequency limit of the instrument at ambient temperature.

Arrhenius ionic conductivity behavior can be described by $\sigma = \sigma_o \exp\left(\frac{-\Delta E_{Act}}{k_B T}\right)$, where σ_o is the pre-exponential factor describing the ionic conductivity at the maximum temperature Arrhenius behavior is observed $(\Omega\text{-cm})^{-1}$, ΔE_{Act} is the activation energy for ions to hop from a filled site to an empty site (eV), $k_B = 8.617 \times 10^{-5}$ eV/K, and T is the absolute temperature (K). In the temperature range measured, Arrhenius ionic conductivity behavior was observed with

activation energies between 0.31 and 0.36 eV.

With extrapolation of pre-exponential factors, high ionic conductivity values in literature were replicated by the PIT electrolyte, although activation energies are higher than the 0.19 eV reported by Mizuno et al. Density was not reported in [7], but a pressure of 363 MPa was used and is estimated to yield $77 \pm 2\%$ density. High density is important for high ionic conductivity when bulk conduction dominates surface conduction [9, 13].

4. Conclusions

For the first time, Powder-in-a-tube (PIT) processing is used to create 120 μm electrolytes. Thin electrolytes with high ionic conductivity are important for low equivalent series resistance, high efficiency energy storage devices. Ionic conductivities in sheet-like PIT processed electrolytes were favorably comparable with previous research of pelletized electrolytes.

Recommended future work is directed at understanding the dependence of electrolyte densification on processing variables such as rolling temperature, roller radii, elastic and shear moduli of rollers and tubing, and roller speed (strain rate) [10]. Based on the behavior of similar lithium thiophosphate compositions [9, 11], warm rolling at 160°C and 150 MPa are estimated to yield 90% dense 0.70 Li_2S + 0.30 P_2S_5 electrolytes. A comprehensive understanding of PIT rolling mechanics and material compatibility may allow one-step electrode/electrolyte/electrode integration in solid-state batteries and electrochemical capacitors utilizing low T_g solid electrolytes.

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Figures

Figure 1.

Demonstration of thin, continuous electrolytes. *Left:* Polished cross-sections of thick wall Al-electrolyte-Al sandwich at 12x after pass 3, 4, and 5. *Right:* Top view of thick wall Al-electrolyte-Al sandwich with pass numbers, total thicknesses, and electrolyte thicknesses.

Figure 2.

X-ray diffraction patterns of milled 0.70 Li_2S + 0.30 P_2S_5 (0.70 LiPS) powder (black), milled 0.70 LiPS powder after thin wall PIT rolling to 66% density (green), milled 0.70 LiPS powder after thin wall PIT rolling to 66% density and 262°C crystallization mixed with a 10 wt.% Ni standard (navy blue), milled 0.70 LiPS powder after densification to 92% density and crystallization at 300°C (red). The x-ray patterns in navy blue and red have been indexed to be $\text{Li}_7\text{P}_3\text{S}_{11}$ after [8] (JCPDS 04-014-8383) and density values are relative to 1.98 g/cm^3 .

Figure 3.

Impedance of electrolyte between Ag blocking electrodes. *Left*: Geometry-normalized impedance complex plane plot of milled 0.70 LiPS powder after thin wall PIT rolling to 66% density and 262°C crystallization. *Right*: Arrhenius plot of the $\log_{10}$ ionic conductivity vs. inverse temperature. Along with thin wall PIT electrolyte data, the 25°C data point from Mizuno et al. [7] and Berbano et al. [9] from a crystallized pellet are shown.