LOW TEMPERATURE PROCESSING
OF SULFIDE AND OXIDE LITHIUM SOLID ELECTROLYTES
TO BRIDGE IONICALLY RESISTIVE BOUNDARIES

A Dissertation in
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by
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ABSTRACT

Solid electrolytes are enabling materials for solid-state batteries. The theme of the contributions in this thesis centers around low temperature processing of solid electrolytes and their resulting microstructures and ionic conductivities. Solid electrolytes are of interest for safer and more reliable replacements to liquid electrolytes at a wide range of operating temperatures.

Using pressure-temperature-assisted densification (200 °C and 190 MPa), ionically resistive pores were minimized and ionic conductivity was maximized in \( x \text{Li}_2\text{S} + (1-x)\text{P}_2\text{S}_5 \) (\( x = 0.70, 0.75, 0.80 \)) solid electrolytes. For \( 0.70 \text{Li}_2\text{S} + 0.30 \text{P}_2\text{S}_5 \), the powder-in-a-tube method was demonstrated as a method to fabricate 120 μm thin electrolytes with \( 10^{-3} \text{ S/cm} \) ionic conductivities at 25 °C for large area format batteries.

Using cold sintering, the solid electrolyte \( \text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3 \) (\( x = 0.50 \)) was densified to around 80% theoretical density in minutes at 120 °C and 400 MPa. In order to bridge ionically resistive grain boundaries, a 5 minute post-processing at 650 °C was required. High volume fractions of ceramic electrolyte could be co-sintered with polymer. Up to 95 vol. % \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 + 5 \text{ vol. % Poly(vinylidene fluoride hexafluoropropylene) composite electrolytes were cold sintered at 120 °C to densities exceeding 85%}. \) After soaking in 1 M \( \text{LiPF}_6 \) ethylene carbonate-dimethyl carbonate (50:50 vol. %), composite electrolyte ionic conductivities at 25 °C reached \( 10^{-4} \text{ S/cm} \). Using cold sintering, processing and integration of solid electrolytes and other important technical ceramics may now be possible at polymer processing temperatures.
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Chapter 1

Introduction

Motivation

Lithium solid electrolytes are of major interest for solid-state batteries and electrochemical capacitors. Currently, the material selection space is dominated by liquid electrolytes that consist of lithium salts paired with organic solvents. Improved safety, as well as the need for higher temperature and high voltage operation, open up opportunities for glass and ceramic alternatives in these important solid-state energy storage technologies.

State-of-the-art energy storage systems can be compared with a Ragone Diagram \(^1\). Usually, the Ragone Diagram is a 2D plot of power density vs. energy density. Power density and energy density metrics may either be normalized by volume or mass. Electrolyte ionic conductivity is an enabling property for high power density and high energy density systems. At temperatures where liquid electrolytes either freeze or volatilize, solid electrolyte-based cells outperform liquid electrolyte-based cells in terms of power density and energy density \(^2\) (Fig. 1-1). It is important to understand the fundamentals of what controls ionic conductivity to engineer high power and high energy density systems.
Figure 1—1. A Ragone plot comparing supercapacitors, Li-ion batteries, an Al-ion battery, Na-ion batteries, all-solid-state batteries, Li-S batteries, a Mg battery, and Li-O₂ batteries. At 100 ºC, Kato et al.² demonstrates that all-solid-state batteries have competitive gravimetric energy and power densities when compared to other state-of-the-art technologies.

Ionic Conductivity Fundamentals

Electrical conductivity is a material property that is dispersed over thirty orders of magnitude, from $10^{-18}$ to $10^{12} \ (\Omega \cdot cm)^{-1}$. Electrical conductivity is a broad term that includes both ionic conductivity and electronic conductivity. The unit for the engineering property of resistance, Ohm ($\Omega$), is named after the physicist Georg Ohm. Ohm’s Law, also named in his honor, relates the vector of current density, the vector of electric field, and the second rank tensor of electrical conductivity (Eq. 1-1).
$J_i = \sigma_{ij} E_j$ \hspace{1cm} (Eq. 1-1)

where

$J = \text{Current density (A/cm}^2\text{)}$

$\sigma = \text{Conductivity ((}\Omega\text{-cm})^{-1} \text{ or S/cm)}$

$E = \text{Electric field (V/cm)}$

Electrical conductivity can be expressed as the sum of all mobile species in a system (Eq. 1-2). In the case of a lithium-ion solid electrolyte, the only mobile species should be lithium ions.

$$\sigma = \sum_i n_i |Ze|_i \mu_i$$ \hspace{1cm} (Eq. 1-2)

where

$n = \text{Mobile ion concentration (m}^3\text{)}$

$Z = \text{Valence (dimensionless)}$

$e = \text{Fundamental charge (1.602 x 10}^{-19}\text{ C)}$

$\mu = \text{Mobility (m}^2/\text{V-s)}$

Mobility of species $i$ is related to the diffusion coefficient through the Nernst-Einstein Equation (Eq. 1-3).

$$\mu_i(T)k_B T = |Ze|_i D_i$$ \hspace{1cm} (Eq. 1-3)

where

$D = \text{Diffusion coefficient (m}^2/\text{s)}$

For ionic conductors with Arrhenius temperature dependence, the dependence of conductivity on temperature can be expressed as an exponential function (Eq. 1-4). The lower the activation energy, the smaller the conductivity difference between conductivity values at different temperatures.
\[
\sigma = \sigma_o \exp\left(\frac{-\Delta E_{\text{Act}}}{k_B T}\right) \quad (\text{Eq. 1-4})
\]

where

\[\sigma_o = \text{Pre-exponential factor ((}\Omega\text{-cm})^{-1} \text{ or } \text{S/cm})\]

\[\Delta E_{\text{Act}} = \text{Activation energy (eV)}\]

\[k_B = \text{Boltzmann’s constant (8.617 x 10^{-5} eV/K)}\]

\[T = \text{Absolute temperature (K)}\]

Conductivity measurements at different temperatures allow the calculation of activation energy (Eq. 1-4). Typically, \(\log_{10}(\sigma)\) vs. \(1000/T\) is plotted in an Arrhenius plot. Taking the logarithm of both sides of Eq. 1-4, yields Eq. 1-5, the slope (Eq. 1-6), and the activation energy (Eq. 1-7).

\[
\log_{10}(\sigma) = \log_{10}(\sigma_o) - \frac{\Delta E_{\text{Act}}}{1000 \cdot \ln(10) \cdot k_B T} \quad (\text{Eq. 1-5})
\]

\[
[slope \ of \ \log_{10}(\sigma) \ vs. \ 1000/T] = -\frac{\Delta E_{\text{Act}}}{1000 \cdot \ln(10) \cdot k_B} \quad (\text{Eq. 1-6})
\]

\[
\Delta E_{\text{Act}} = -[slope \ of \ \log_{10}(\sigma) \ vs. \ 1000/T] \cdot 1000 \cdot \ln(10) \cdot k_B \quad (\text{Eq. 1-7})
\]

The pre-exponential term for hopping conduction can be written as in Eq. 1-8. The activation energy of hopping conduction is intimately linked to structure. Beyond the simple 1D landscape is shown in (Fig. 1-2), structural considerations are treated in detail in the next section.

\[
\sigma_o = \frac{n|Z\epsilon|^2 \gamma \lambda^2 \nu_{\text{Debye}} \exp\left(\frac{\Delta S_m}{k_B}\right)}{k_B} \quad (\text{Eq. 1-8})
\]
where

\[ n = \text{Mobile ion concentration} \left( m^{-3} \right) \]

\[ Z = \text{Valence} \text{ (dimensionless)} \]

\[ e = \text{Fundamental charge} \left( 1.602 \times 10^{-19} \text{ C} \right) \]

\[ \gamma = \text{Geometric factor} \text{ (dimensionless)} \]

\[ \lambda = \text{Jump distance between potential wells} \left( m \right) \]

\[ \nu_{\text{Debye}} = \text{Debye frequency} \left( \text{Hz} \right) \]

\[ \Delta S_m = \text{Entropy of motion (hopping attempts)} \left( \text{eV/K} \right) \]

Figure 1—2. Ionic hopping potential energy landscape in 1D under an applied electric field (E) with a jump distance, \( \lambda \). Note that a negatively charged carrier would hop the other direction and that the periodic potential would tilt up going from left to right.
Lithium Solid Electrolyte Families of Interest

Many crystal structure families are known to transport lithium with conductivities in the range of $10^{-4} \, (\Omega \cdot \text{cm})^{-1}$ at 25 °C. Examples include argyrodite, lithium-stuffed $\text{Li}_5\text{La}_2\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) garnets reported by Thangadurai et al. in 2003, perovskites based on $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$ reported by Inaguma et al. in 1993, and LISICON (lithium-ion superionic conductor) reported by Hong in 1978. A summary plot by Kamaya et al. compares the temperature dependence of ionic conductivity for some of the highest performing lithium-ion electrolytes (Fig. 1-3). The NASICON (sodium-ion superionic conductor) and Thio-LISICON electrolyte families will be treated in detail.

![Arrhenius plot of lithium electrolytes](image)

**Figure 1—3.** Arrhenius plot of lithium electrolytes composed of (1) a polymer matrix and lithium salt, (2) a glass, (3) a crystalline material, (4) an organic, (5) an ionic liquid, and (6) a gel (lithium salt, polymer matrix, and organic) after Kamaya et al. 23.


NASICON

Hagman and Kierkegaard first reported NaM$_2$(PO$_4$)$_3$, where M = Ge, Ti, Zr in 1968 $^{45}$. Since the NASICON structure is open, it is prone to peculiar properties, such as negative thermal expansion $^{46,47}$. While NASICON is also of interest as a host for radioactive waste and catalyst supports $^{46}$, the property of interest for this thesis is ionic conductivity. In 1976, Goodenough, Hong, and Kafalas recognized that many M$^{3+}$ cation substitutions for Zr$^{4+}$ (Zr$^{4+}$ $\leftrightarrow$ Na$^+$ + M$^{3+}$) within the Na$_{1+x}$M$_x$Zr$_{2-x}$(PO$_4$)$_3$ (NZP) family could yield high Na$^+$ conductivity $^{32,33}$. There are two sites that conducting Na$^+$ cations can sit: A$_1$ and A$_2$ (Fig. 1-4). In fact, the structure is stable enough to accommodate large Cs$^+$ ions, as well as small Li$^+$ ions. Lithium-ion conductors that are isostructural with NZP include Li$_{1+x}$M$_x$N$_{2-x}$(PO$_4$)$_3$, M = Al, Cr, Ga, Fe, Sc & N = Ti, Ge.

In particular, Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ (LAGP), 0.3 $\leq$ x $\leq$ 0.8 is known to have high Li$^+$ conductivities in the range of 10$^{-4}$ (Ω-cm)$^{-1}$ at 25 °C $^{48-50}$. When x = 0, A$_1$ sites are fully occupied by Li$^+$ and A$_2$ sites are empty. When x > 0, substituting Al$^{3+}$ for Ge$^{4+}$ favors excess Li$^+$ on A$_2$ sites. One illustrative way to summarize the intrinsic structural considerations within a family of solid electrolytes is to plot the dependence of activation energy and ionic conductivity with different bottleneck sizes (distance between A$_1$ and A$_2$ sites in Fig. 1-4). In general, this summary plot (Fig. 1-5) shows that decreasing the bottleneck size correlates to increased conductivity and decreased activation energy. Workers have shown impedance complex plane plots in LAGP electrolytes fabricated by conventional sintering $^{25,26,51,52}$, spark plasma sintering $^{28,53}$, and crystallization of glasses $^{50,53-58}$ (Table 1-1). In order to compare these different studies, extrinsic processing effects and the lithium volatility control strategies of time and temperature reduction via spark plasma sintering, powder bed firing, and excess lithium addition
to control total grain size and ionic conductivity must be considered. Low temperature processing considerations of different electrolyte chemistries are a key component of this thesis.

Figure 1—4. NASICON structure showing A1 and A2 sites which sit between PO4 tetrahedra and GeO6 octahedra. The conduction channel is indicated by the red line.

Figure 1—5. Grain activation energies and grain ionic conductivities for different cation substitutions in Li1+xMxN2-x(PO4)3 result in different bottleneck sizes. Data are replotted based on references 14, 60-62.
Table 1.1. Polycrystalline solid electrolyte processing conditions and lithium volatility control strategies of time and temperature reduction & powder bed firing to control total grain size and ionic conductivity. Grain (G) and Grain boundary (GB) ionic conductivities and activation energies are reported in some studies 26, 28, 29, 37, 50-53, 56, 57, 63-65.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Electrolyte</th>
<th>Processing Method</th>
<th>Processing Conditions</th>
<th>Grain size (μm)</th>
<th>Ge + **</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anno et al. 51</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Conventional sintering</td>
<td>900 °C, 4 h + 1000 °C, 2 h</td>
<td>-</td>
<td>6.7 x 10^-2 G (Ω cm)</td>
<td>0.38 (G)</td>
</tr>
<tr>
<td>Mariappan et al. 26</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Conventional sintering</td>
<td>750 °C, 2 h</td>
<td>0.076</td>
<td>8.0 x 10^-3 G (Ω cm)</td>
<td>0.43 (G)</td>
</tr>
<tr>
<td>Chung and Kang 52</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Conventional sintering</td>
<td>900 °C, 2 h + 800 °C, 2 h</td>
<td>0.5</td>
<td>1 x 10^-1 G (Ω cm)</td>
<td>0.39 (G)</td>
</tr>
<tr>
<td>Delaize et al. 30</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Spark plasma sintering</td>
<td>700 °C, 2 min, 100 MPa</td>
<td>0.5</td>
<td>3.0 x 10^-3 G (Ω cm)</td>
<td>0.39 (Total)</td>
</tr>
<tr>
<td>Kubanska et al. 51</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Spark plasma sintering</td>
<td>650 °C, 2 min, 75 MPa</td>
<td>1</td>
<td>1.3 x 10^-2 G (Ω cm)</td>
<td>0.38 (G)</td>
</tr>
<tr>
<td>Kubanska et al. 51</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Crystallized glass</td>
<td>1200 °C, 30 min + 950 °C, 18 h</td>
<td>1</td>
<td>2.1 x 10^-3 G (Ω cm)</td>
<td>0.40 (Total)</td>
</tr>
<tr>
<td>Fu 50</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Crystallized glass</td>
<td>1350 °C to 1450 °C, 1.5 h + 7 °C, 12 h</td>
<td>0.5</td>
<td>3.0 x 10^-3 G (Ω cm)</td>
<td>0.37 (Total)</td>
</tr>
<tr>
<td>Cruz et al. 76</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Crystallized glass</td>
<td>1200 °C, 30 min + 618 °C, 30 min</td>
<td>8</td>
<td>7.6 x 10^-2 G (Ω cm)</td>
<td>0.46 (Total)</td>
</tr>
<tr>
<td>Xu et al. 51</td>
<td>Li1-xAlxGe3-xPO4-x NASICON</td>
<td>Crystallized glass</td>
<td>1350 °C, 2 h + 800 °C, 6 h</td>
<td>0.25</td>
<td>1.2 x 10^-2 G (Ω cm)</td>
<td>0.31 (Total)</td>
</tr>
<tr>
<td>Yi et al. 26</td>
<td>Li1-xAlxTi3-xSi3-xP3-xO12 NASICON</td>
<td>Conventional sintering</td>
<td>665 °C, 2 h + 1000 °C, 1 h</td>
<td>0.6 ± 0.2</td>
<td>2.5 x 10^-3 G (Ω cm)</td>
<td>0.30 (Total)</td>
</tr>
<tr>
<td>Cheng et al. 83</td>
<td>Li1-xAlxLa3-xZrO12 NASICON</td>
<td>Conventional sintering</td>
<td>1100 °C, 6 h</td>
<td>20 to 40</td>
<td>2.5 x 10^-3 G (Ω cm)</td>
<td>0.34 (Total)</td>
</tr>
<tr>
<td>Inada et al. 94</td>
<td>Li1-xSr3-x3Gex-x2O12 NASICON</td>
<td>Conventional sintering</td>
<td>1100 °C, 12 h + 1300 °C, 15 h</td>
<td>5 to 10</td>
<td>3.5 x 10^-3 G (Ω cm)</td>
<td>0.36 (Total)</td>
</tr>
<tr>
<td>Mizuno et al. 77</td>
<td>Li2Sn2 + 30P2S7 LiP2S7</td>
<td>Cold pressing</td>
<td>240 °C, 2 h</td>
<td>-</td>
<td>3.2 x 10^-3 G (Ω cm)</td>
<td>0.19 (Total)</td>
</tr>
<tr>
<td>Berhanu et al. 87</td>
<td>70Li2S + 30P2S7 LiP2S7</td>
<td>Powder-in-a-tube</td>
<td>262 °C, 5 min</td>
<td>-</td>
<td>3 x 10^-3 G (Ω cm)</td>
<td>0.34 ± 0.02 eV (Total)</td>
</tr>
</tbody>
</table>

** Table footnote: for most reported Arrhenius activation energies in literature and for the activation energies in this thesis, activation energies are reported with an error bar of ± 0.02 eV or smaller. In this thesis, activation energy errors were determined as follows: (1) temperature dependence of impedance was measured on a sample or set of identically synthesized samples, (2) Microsoft Excel was used to produce a best fit line, and (3) the error was reported using a 95 % confidence interval using the LINEST function in Microsoft Excel.**
For the model system, Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$, the composition dependence of ionic conductivity has been established by Fu $^{50}$ (Fig. 1–6). The $x = 0.50$ composition was selected for study in Chapters 4 to 6 since conductivity is least sensitive to deviations in $x$. Across the compositional tie line, there is an optimum between too few Li in the A$_2$ sites and too many Li in the A$_2$ sites. As an analog to ion flux, if one would like to move the most number of cars on a highway, there should be enough cars (mobile ions) to efficiently have high flux of cars but not too many cars to crowd the highway (reduce mobility). Also, cars prefer to travel on more mobile highways rather than off-road paths.

![Graph of ionic conductivities and activation energies](image)

**Figure 1—6.** Ionic conductivities at 25 °C and activation energies for Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ from Fu $^{50}$. For this thesis, $x = 0.50$ was selected for all LAGP studies because of the composition lies in a region of stable ionic conductivity (between $x = 0.30$ and $x = 0.70$).

**Thio-LISICON**

The second crystal family of interest has sulfur anions instead of oxygen anions. Additionally, amorphous and crystalline conductivities in Thio-LISICON are closer than in NASICON. A third difference is that the ratio of total lithium per formula unit increases from 33
to 42 % in x Li_2S + (1-x) P_2S_5 going from x = 0.70 to 0.80. In Li_{1+x}Al_xGe_{2-x}(PO_4)_3, the total lithium per formula unit increases from 7.1 to 9.1 % going from x = 0.30 to x = 0.70. Oxide and sulfide electrolytes are further compared in Table 4-1.

The term Thio-LISICON was coined by Kanno et al. in 2000 who discovered solid solution ranges in the lithium thiogermanates Li_{4-2x}Zn_xGeS_4 and Li_{4+x+δ}(Ge_{1-δ}-xGa_x)S_4 had structural analogs to the LISICON γ-Li_3PO_4. The formula Li_{4-2x}Zn_xGeS_4 is based on lithium vacancies from the substitution Zn^{2+} ↔ 2Li^+, while Li_{4+x+δ}(Ge_{1-δ}-xGa_x)S_4 is based on lithium interstitials from the substitution Ge^{4+} ↔ Li^+ + Ga^{3+}. Later, solid solution ranges were also discovered with the general formula Li_xM_{1-y}N_yS_4, where M = Si, Ge & N = P, Al, Zn, Ga, Sb. The electrolytes studied in Chapter 2 and 3 are analogs to the lithium thiophosphate binary Li_{3+5x}P_{1-x}S_4. Thio-LISICONs are further classified by Mizuno et al. according to their indexed monoclinic superlattice as belonging to Thio-LISICON II (Li_{3.25}P_{0.95}S_4) with a x 3b x 3c or Thio-LISICON III (Li_{3.2}P_{0.96}S_4) with a x 3b x 2c, emphasis intentionally added for 2c and 3c. Both Thio-LISICON II and Thio-LISICON III are not thermodynamically stable since they do not form after a solid-state reaction, but have been obtained from a heat treatment after mechanical milling. A summary of the material design strategy across LISICON and Thio-LISICON is seen in Fig. 1-7.
In this thesis, three lithium thiophosphate compositions are studied: \( x \) \( \text{Li}_2\text{S} \) + \((1-x)\) \( \text{P}_2\text{S}_5 \), where \( x = 0.70 \), 0.75, and 0.80. Properties for the known phases \( \text{P}_2\text{S}_5 \) (\( x = 0 \)), \( \text{Li}_7\text{P}_3\text{S}_{11} \) (\( x = 0.70 \)), \( \gamma\text{-Li}_3\text{PS}_4 \) (\( x = 0.75 \)), \( \text{Li}_7\text{PS}_6 \) (\( x = 0.875 \)), and \( \text{Li}_2\text{S} \) (\( x = 1 \)) are summarized in Table 1-2.

Table 1-2. List of lithium thiophosphate properties at 1 atm, 25°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal System</th>
<th>Theoretical Density (g/cm(^3))</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_2\text{S} ) (( x = 1 ))</td>
<td>Cubic</td>
<td>1.66</td>
<td>938</td>
</tr>
<tr>
<td>( \text{P}_2\text{S}_5 ) (( x = 0 ))</td>
<td>Triclinic</td>
<td>2.09</td>
<td>288</td>
</tr>
<tr>
<td>( \text{Li}_7\text{P}<em>3\text{S}</em>{11} ) (( x = 0.70 ))</td>
<td>Triclinic</td>
<td>1.98</td>
<td>700</td>
</tr>
<tr>
<td>( \gamma\text{-Li}_3\text{PS}_4 ) (( x = 0.75 ))</td>
<td>Orthorhombic</td>
<td>1.93</td>
<td>Phase transition to ( \beta\text{-Li}_3\text{PS}_4 ) at 300 °C</td>
</tr>
<tr>
<td>( \text{Li}_7\text{PS}_6 ) (( x = 0.875 ))</td>
<td>Cubic*</td>
<td>1.87</td>
<td>- - -</td>
</tr>
</tbody>
</table>

Footnote: * Another PDF card exists for a report of orthorhombic \( \text{Li}_7\text{PS}_6 \) at room temperature with no quality mark (B, Blank).
\[ x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5, x = 0.70 \]

Minami et al. has developed the phase diagram of 0.70 Li$_2$S + 0.30 P$_2$S$_5$ for glass-derived heating and melt-derived cooling treatments \(^6^9\) (Fig. 1-8).

![Phase diagram](image)

**Figure 1—8.** Phase diagram for 0.70 Li$_2$S + 0.30 P$_2$S$_5$ for glass-derived heating and melt-derived cooling treatments from Minami et al \(^6^9\).

Starting from the left of **Fig. 1-8,** Raman spectroscopy shows that mechanically milled glass consists of P$_2$S$_7^{4-}$ pyro-thiophosphate peaks and PS$_4^{3-}$ ortho-thiophosphate peaks units. Ionic conductivity at 25 °C is 5.4 x 10$^{-5}$ S/cm and activation energy is 0.39 eV. Li$_7$P$_3$S$_{11}$ was Rietveld refined by Yamane et al. \(^7^0\). Ball and stick models are drawn along the a, b, and c axes (Fig. 1-9) with activation energies for lithium vacancy migration included. Ionic conductivity at 25 °C is reported to be 3.2 x 10$^{-3}$ S/cm and activation energy is 0.19 eV. Hood et al. \(^7^1\) synthesized Li$_4$P$_2$S$_6$ with an ionic conductivity at 25 °C of 2.4 x 10$^{-7}$ S/cm and activation energy of 0.29 eV. Simulations suggest that Li interstitial sites contribute to ionic conduction.
Figure 1—9. Ball and stick models of triclinic Li$_7$P$_3$S$_{11}$ along the (a) $a$-axis, (b) $b$-axis, and (c) $c$-axis using the crystal structure data from Holzwarth et al. $^{72}$. Li is shown in navy blue, P in brown, and S in yellow (color online). The respective lithium-ion vacancy migration energies from Lepley et al. $^{73}$ are indicated. Images generated using CrystalMaker®. CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com).

The phase of Li$_3$PS$_4$ in Fig. 1-8 depends on temperature $^{74}$. In the low temperature $\gamma$-phase, the orientation of tetrahedra apex is in the same direction for all tetrahedra. In the intermediate temperature $\beta$-phase and high temperature $\alpha$-phase, tetrahedra are oriented in a zig-zag arrangement (Fig. 1-10). Liu et al. was able to stabilize nanoporous $\beta$-Li$_3$PS$_4$ from -20 to 100 $^\circ$C and proposes that surface conduction is the dominant conduction mechanism $^{75}$.

Figure 1—10. Tetrahedra orientation in $\gamma$- Li$_3$PS$_4$, $\beta$-Li$_3$PS$_4$, and $\alpha$-Li$_3$PS$_4$ after Homma et al. $^{74}$. Sulfur atoms are shown in yellow.
Li$_{3.2}$P$_{0.96}$S$_4$, a Thio-LISICON III analog to 0.8 \( \leq x \leq 1.0 \) in Li$_{4-x}$Ge$_{1-x}$P$_x$S$_4$, has not had properties reported since it has not been synthesized as the only phase. It is known to have lower conductivity than Li$_7$P$_3$S$_{11}$\textsuperscript{69}.

\( x \; \text{Li}_2\text{S} + (1-x) \; \text{P}_2\text{S}_5, \; x = 0.75 \)

Crystalline polymorphs of \( x = 0.75 \) (Li$_3$PS$_4$) have been discussed in the previous section. Amorphous \( x = 0.75 \) is of interest because it generates the least amount of H$_2$S(g) in comparison to glass-ceramic \( x = 0.67, 0.70, 0.75, \) and 0.80 & crystalline \( x = 1 \) \textsuperscript{76}. Chemical stability was explained by Muramatsu et al. to be due to the presence of more stable PS$_4^{3-}$, rather than S$^{2-}$ and P$_2$S$_7^{4-}$ structural units \textsuperscript{76}. Mendez \textsuperscript{77} compared electrochemical stability of crystalline \( x = 0.75 \) vs. Li metal for samples that were cold pressed to those hot pressed at between 130 and 190 °C using post-cycling microscopy, impedance spectroscopy, x-ray diffraction, and differential scanning calorimetry. Crystallinity decreased after 25 °C DC cycling with symmetric Li electrodes and particle-particle contact improved electrochemical performance.

\( x \; \text{Li}_2\text{S} + (1-x) \; \text{P}_2\text{S}_5, \; x = 0.80 \)

Crystalline \( x = 0.80 \) was found to be a multiphase by Hayashi et al. \textsuperscript{68}. In particular, a heat treatment at 240 °C contained Li$_2$S and Thio-LISICON II, heat treatment at 300 °C included Thio-LISICON III and Li$_2$S, and heat treatment at 500 °C included Li$_3$PS$_4$ and Li$_7$PS$_6$.

Amorphous, as-milled \( x = 0.80 \) was found to contain excess Li$_2$S. Now that both NASICON and
thio-LISICON have been discussed, the important characterization technique of impedance spectroscopy is described in the next section.

**Impedance Spectroscopy: Characterizing the Enabling Property of Ionic Conductivity**

So far, the structural considerations discussed pertain mostly to the crystalline grains. Usually ionically resistive grain boundaries control the total ionic conductivity in polycrystalline materials and their development depends heavily on the extrinsic processing conditions (Table 1-1). Total ionic conductivity is described by **Eq. 1-9**. Grain boundary conduction is treated in detail in the next sub-section after impedance spectroscopy is described in detail.

\[ \sigma_{Total} = \frac{1}{\rho_{Grain} + \rho_{Grain Boundary}} \quad (\text{Eq. 1-9}) \]

where

- \( \sigma_{Total} \) = Total ionic conductivity \((\Omega \cdot \text{cm})^{-1}\)
- \( \rho_{Grain} \) = Grain resistivity \((\Omega \cdot \text{cm})\)
- \( \rho_{Grain Boundary} \) = Grain boundary resistivity \((\Omega \cdot \text{cm})\)

Direct current vs. voltage measurements with non-blocking electrodes can be used to obtain ionic conductivity. On the other hand, impedance spectroscopy is a more powerful method to study conduction and dielectric properties of grains, grain boundaries, and electrodes.

In high school physics, most students learn Ohm’s Law as \( V = IR \), where \( V \) = voltage \((\text{V})\), \( I \) = current \((\text{A})\), and \( R \) = resistance \((\Omega)\). This is true for DC cases. For small signal AC, Ohm’s Law now involves impedance as a complex function (**Eq. 1-10**).

\[ v(t) = i(t)Z \quad (\text{Eq. 1-10}) \]

where
\[ v(t) = \text{Voltage phasor (V)} \]
\[ i(t) = \text{Current phasor (A)} \]
\[ Z = \text{Complex impedance (Ω)} \]

The voltage phasor and current phasor are out of phase by an angle, \( \theta \) and impedance can be written as a function of \( \theta \) as in \textbf{Eqs. 1-11, 1-12, 1-13}.

\[
v(t) = v_o \sin(\omega t + \theta) \quad (\text{Eq. 1-11})
\]

\[
i(t) = i_o \sin(\omega t) \quad (\text{Eq. 1-12})
\]

\[
Z(\theta) = |Z| \exp(j \theta) \quad (\text{Eq. 1-13})
\]

where

\( \theta = \text{Phase angle (rad)} \)

\( j = \sqrt{-1} \) (dimensionless)

\( \omega = 2\pi f \) (rad/s)

A number of relations now follow from Euler’s formula (\textbf{Eqs. 1-14, 1-15, 1-16}), where the magnitude of impedance is given by \textbf{Eq. 1-17}.

\[
Z(\theta) = |Z| \cos(\theta) + j|Z| \sin(\theta) \quad (\text{Eq. 1-14})
\]

\[
Z'(\theta) = |Z| \cos(\theta) \quad (\text{Eq. 1-15})
\]

\[
Z''(\theta) = |Z| \sin(\theta) \quad (\text{Eq. 1-16})
\]

\[
|Z(\theta)| = \sqrt{[Z'(\theta)]^2 + [Z''(\theta)]^2} \quad (\text{Eq. 1-17})
\]

Graphically, the phasors can be plotted and resolved in the complex impedance plane (\textbf{Fig. 1-11}). For a resistor, the phase angle is zero and \( Z = R \). For a capacitor, the phase angle is -90° and \( Z_C = 1/j\omega C \). For an inductor, the phase angle is +90° and \( Z_L = j\omega L \).
Figure 1—11. Phasor diagram of the voltage and current phasors in the complex impedance plane (left) and diagram of resolving the components of impedance in the complex impedance plane (right).

For solid electrolytes, the imaginary impedance axis, $Z''$, is negative because single crystal conduction is idealized as an equivalent circuit model of a resistor ($R$) and capacitor ($C$), in parallel (Fig. 1-12)\(^{78}\) and the capacitor phase angle is $-90^\circ$ with respect to the resistor.

Figure 1—12. Impedance complex plane plot for an equivalent circuit of a resistor ($R$) and capacitor ($C$) in parallel. The arrow points in the direction of increasing angular frequency ($\omega$).
The equivalent circuit for an ideal single crystal is said to exhibit Debye behavior and represents a leaky capacitor or lossy dielectric. A simple generalization to describe behavior which is intermediate between the fundamental circuit elements of $R$, $L$, and $C$ is to allow a single fitting parameter, $n$, to vary between -1 to 1. Experimentally, $n$ varies to account for sample roughness or inhomogeneity. From Eq. 1-18, if $n = 1$, the constant phase element (CPE) resembles a capacitor ($C$). At $n = -1$, the CPE resembles an inductor ($L$). At $n = 0$, the CPE resembles a resistor ($R$). Fig. 1-13 shows an impedance complex plane plot for a range of $n$ varying from 1 to 0.8. From this graphical representation, the CPE can be thought of as rotating the real and imaginary axes clockwise. The clockwise rotation of the axes makes the semicircle look as if it is being pushed down from the top and lowering of $n$ is said to depress the semicircle.

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad \text{(Eq. 1-18)}$$

where

$Q = (\Omega^{-1}s^{-n} \text{ or } F^{-1}s^{1-n})$

$n = \text{Fitting parameter (dimensionless)}$

![Figure 1—13. Simulated impedance complex plane plots for (R-CPE) in parallel for $R = 1 \ M\Omega$, $C = 0.1 \ nF$, and $n$ varying from 0.8 to 1 between 1 Hz and 0.1 MHz.](image)
Dielectric and conduction relaxation can be described with four interrelated data representations or formalisms: (1) complex electrical modulus ($M$), (2) complex impedance ($Z$), (3) complex admittance ($Y$), and (4) complex permittivity ($\varepsilon$)\textsuperscript{79}. Table 1-3 shows the four formalisms, which are analogous to the complex functions that describe mechanical moduli and relaxation. Each formalism emphasizes different data features (interfacial vs. bulk characteristics), which are especially important for separating electrically heterogeneous regions, such as those in composites or polycrystalline ceramics\textsuperscript{78}.

Table 1-3. Transformations between electrical modulus, impedance, admittance, and permittivity, where $C =$ vacuum capacitance ($\varepsilon_r = 1$) from Barsoukov and Macdonald\textsuperscript{79}

<table>
<thead>
<tr>
<th></th>
<th>$M^*$</th>
<th>$Z^*$</th>
<th>$Y^*$</th>
<th>$\varepsilon^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^*$</td>
<td>$M^*$</td>
<td>$j\omega C Z^*$</td>
<td>$j\omega C/Y^*$</td>
<td>$1/\varepsilon^*$</td>
</tr>
<tr>
<td>$Z^*$</td>
<td>$M^*/j\omega C$</td>
<td>$Z^*$</td>
<td>$1/Y^*$</td>
<td>$1/\varepsilon^* j\omega C$</td>
</tr>
<tr>
<td>$Y^*$</td>
<td>$j\omega C M^*$</td>
<td>$1/Z^*$</td>
<td>$Y^*$</td>
<td>$j\omega C \varepsilon^*$</td>
</tr>
<tr>
<td>$\varepsilon^*$</td>
<td>$1/M^*$</td>
<td>$1/j\omega C Z^*$</td>
<td>$Y^*/j\omega C$</td>
<td>$\varepsilon^*$</td>
</tr>
</tbody>
</table>

Characteristic circuit parameters, resistance ($R$) and capacitance ($C$), can be obtained by fitting different graphical representations such as complex plane plots and Bode plots (plotting a data formalism vs. logarithm of frequency) or Jonscher’s universal dielectric response\textsuperscript{80,81}. Using a Debye simplification, the DC conductivity ($\sigma_{DC}$) is determined from a plateau in the AC conductivity ($\sigma'_{AC}$), where $\omega \tau_{peak} << 1$, and takes the form $\sigma'_{AC}(\omega) = \omega \varepsilon''(\omega)$, where $\omega$ is the angular frequency and $\varepsilon''$ is the imaginary component of permittivity. Table 1-4 shows different representations used to display impedance data, type of spectra features observed, and parameters obtained for an ideal (Debye) RC circuit\textsuperscript{82,83} represented in Fig. 1-12.
### Table 1-4. Different data representations used to display impedance data, type of spectra features observed, and parameters obtained for an ideal RC circuit, adapted from Kidner

<table>
<thead>
<tr>
<th>Representation</th>
<th>Type of feature</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Complex plane plot</td>
<td>Semicircular arc</td>
<td>Diameter = ( R ) or ( \varepsilon / \omega C )</td>
</tr>
<tr>
<td>- ( Z'' ) vs. ( Z' ) or ( M'' ) vs. ( M' )</td>
<td></td>
<td>( \omega_{\text{top of arc}} = 2\pi f_{\text{top of arc}} = 1/RC )</td>
</tr>
<tr>
<td>(2) Imaginary impedance/modulus Bode plot</td>
<td>Peak</td>
<td>Peak location: ( \omega_{\text{peak}} = 2\pi f_{\text{peak}} = 1/RC )</td>
</tr>
<tr>
<td>- ( Z'' ) or ( M'' ) vs. ( \log_{10}(\omega) )</td>
<td></td>
<td>Peak height = ( R/2 ) or ( \varepsilon_{\omega}/2C )</td>
</tr>
<tr>
<td>(3) Real impedance/modulus Bode plot</td>
<td>Plateau</td>
<td>Plateau = ( R )</td>
</tr>
<tr>
<td>- ( Z' ) or ( M' ) vs. ( \log_{10}(\omega) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) Real capacitance Bode plot</td>
<td>Plateau</td>
<td>Plateau = ( C )</td>
</tr>
<tr>
<td>- ( C' ) vs. ( \log_{10}(\omega) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) Jonscher’s universal dielectric response</td>
<td>Plateau</td>
<td>Plateau = ( \sigma_{\text{DC}} )</td>
</tr>
<tr>
<td>- ( \sigma'<em>{\text{AC}} ) vs. ( \log</em>{10}(\omega) )</td>
<td></td>
<td>( \sigma'<em>{\text{AC}} = \omega \varepsilon''(\omega), \omega \omega</em>{\text{peak}} \ll 1 )</td>
</tr>
</tbody>
</table>

 Peaks in the imaginary modulus \((M'')\) vs. \(\log_{10}(\omega)\) Bode plot are proportional to the inverse of capacitance, \(1/C\). In the imaginary impedance \((Z'')\) vs. \(\log_{10}(\omega)\) Bode plot, \(Z''\) peaks are proportional to \(R\) \(^78\). In a heterogeneous material with equal \(C\) and differing \(R\), the Bode plot shows that \(M''\) peaks have the same height, while the more prominent \(Z''\) peak in the Bode plot is dominated by the higher resistance (often the interfacial) contribution (Fig. 1-14). Conversely, in a heterogeneous material with equal \(R\) and differing \(C\), the Bode plot shows that \(Z''\) peaks have the same height, while the more prominent \(M''\) peak in the Bode plot is dominated by the lower capacitance (often the bulk) contribution (Fig. 1-15).
Figure 1—14. When capacitances are equal but resistances are not equal, the imaginary modulus, $M''$, vs. log $\omega$ is a powerful plot to separate the two relaxations.

Figure 1—15. When resistances are equal but capacitances are not equal, the imaginary impedance, $Z''$, vs. log $\omega$ is a powerful plot to separate the two relaxations.
Grain Boundary Impedance

As mentioned earlier, total conductivity in polycrystalline materials depends on both grain resistivity and grain boundary resistivity (Eq. 1-9). In addition, grain boundary resistivity depends on heavily on processing for polycrystalline oxide ceramics. An important model for describing electrical properties of polycrystalline ceramics is the Brick Layer Model, which was first proposed by Bauerle. Grain conductivity is given in Eq. 1-19, grain boundary conductivity is given in Eq. 1-20, and the ratio of grain and grain boundary capacitances are given in Eq. 1-21.

\[
\sigma_{\text{Grain}} = R_{\text{Grain}} \left( \frac{t}{A} \right) \quad \text{(Eq. 1-19)}
\]

\[
\sigma_{\text{Grain Boundary}} = R_{\text{Grain Boundary}} \left( \frac{t}{A} \right) \left( \frac{d}{D} \right) \quad \text{(Eq. 1-20)}
\]

\[
\frac{C_{\text{grain}}}{C_{\text{grain boundary}}} = \frac{d}{D} \quad \text{(Eq. 1-21)}
\]

where

- \( A \) = Electrode limiting area \((m^2)\)
- \( t \) = Sample thickness \((m)\)
- \( d \) = Grain boundary width \((m)\)
- \( D \) = Grain size \((m)\)
- \( C \) = Capacitance \((F)\)

Two key limitations with the Brick Layer Model exist. First, without independent information, usually grain boundary widths obtained from transmission electron microscopy, it is not possible to calculate grain boundary properties. Second, experimentally, grains are not arranged as cubes, so the cube-like shape factor assumed by the Brick Layer Model
misrepresents the true microstructure. In the case of polycrystalline ceramics, grain and grain boundary relaxations are usually separated because of grain boundary capacitance is about three orders of magnitude higher than grain capacitance when grain sizes are in the tens of microns. In contrast to micron-sized ceramics, ceramics with grain sizes in the tens of nanometers, the capacitance ratio between grains and grain boundaries is much smaller.

The discussion will now shift to differences between what is known about grain boundary impedance for the two systems of interest: Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$($PO_4$)$_3$ and x Li$_2$S + (1-x) P$_2$S$_5$.

In the case of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$($PO_4$)$_3$, Mariappan et al. describes the origin of grain boundary resistance to be geometrical current constriction from limited grain boundary contact area. Activation energy of the grain and activation energy of the grain boundary are similar. Separate grain and grain boundary components can clearly be resolved across a wide range of impedance measurement temperatures.

Aside from Seino et al., the literature does not attempt to resolve grain boundary impedance for x Li$_2$S + (1-x) P$_2$S$_5$ as a separate component. From Eq. 1-21, if the d/D ratio is small and grain & grain boundary resistances are similar, grain and grain boundary conductivities will be very similar and hard to separate with impedance spectroscopy measurements.

Specific discussion on equivalent circuit modeling, as a way to resolve grain boundary impedance, is treated in the following chapters. Impedance Spectroscopy Genetic Programming is an alternative method that is given attention in the following chapters and in Appendix I. The last technical section in the introduction is focused on sintering fundamentals.
Sintering Fundamentals

Kinetic Limitations of Sintering

Sintering can broadly be divided into solid-state sintering and liquid phase sintering. The driving force for sintering is the reduction of the total Gibbs free energy of the system (Eq. 1-22).

\[ \Delta G_{Total} = \Delta G_{Volume} + \Delta G_{Grain\ Boundary} + \Delta G_{Surface} \]  
(Eq. 1-22)

where

\[ \Delta G_{Volume} = \text{Volume free energy (J/mol)} \]
\[ \Delta G_{Grain\ Boundary} = \text{Grain boundary free energy (m)} \]
\[ \Delta G_{Surface} = \text{Surface free energy (m)} \]

Suppose one has a 60% dense, 0.50 g pellet of Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3 with 1.0 \mu m particles and a density of 3.43 g/cm³ and surface energy of 0.50 J/m². The surface free energy difference is small (51 J/mol), as calculated using Eq. 1-23. Therefore, sintering is usually kinetically hindered and high temperatures of 2/3T_{melt}(K) are usually required for sintering.

\[ \Delta G_{Surface} = \frac{my}{\rho t} \]  
(Eq. 1-23)

where

\[ m = \text{Mass (g)} \]
\[ \gamma = \text{Surface energy (J/m²)} \]
\[ \rho = \text{Density (g/cm³)} \]
\[ t = \text{Particle size (m)} \]

\[ \Delta G_{Surface} = \frac{(0.50 \ g)(0.50 \ \frac{J}{m^2})(1 \ m^2)}{0.60(3.43 \frac{g}{cm^3})(1.0 \times 10^{-4} \ cm)} \times 417.7 \ g/mol = 51 \ J/mol \]
However, with 1 nm particles, a surface free energy difference in the tens of kJ/mol (51 kJ/mol) can be obtained using Eq. 1-23. This value is near the familiar standard heat of neutralization between a strong acid and strong base (-55.8 kJ/mol). Sintering driving forces in the tens of kJ/mol are not commonplace since reactive nanoparticles tend to agglomerate to reduce their surface energy in the first place. The weak bonding characteristic of agglomeration is very different than the strong bonding characteristic of a sintered body. To estimate the suppression of sintering temperature with particle size one needs to first find a link between particle size and sintering time. Then, one can find a link between sintering time and sintering temperature. Herring’s seminal work established scaling laws linking particle size and sintering time. The link between sintering time and sintering temperature is provided by an Arrhenius relationship. Mass transport (diffusion) is a thermally activated process.

An experimental study on TiO$_2$ by Yan and Rhoades shows the links between particle size, sintering time, and sintering temperature. To explain the suppression of sintering temperature from 1230 to 840 °C by decreasing particle size from 0.2 to 0.04 μm, Yan and Rhodes calculated expected sintering temperatures for various mass transport mechanisms and activation energies for TiO$_2$ sintering. Depending on the mechanism, the Herring scaling law exponent $n$ changes in Eq. 1-24. Mass transport mechanisms have been schematically represented in Fig. 1-16 and mechanistic scaling law exponents have been summarized in Table 1-5. Lowering sintering temperature is a focus of the “Specialized Sintering Approaches” section of this chapter and is an important theme in this thesis.

\[
\frac{t_2}{t_1} = \left( \frac{r_2}{r_1} \right)^n \quad (\text{Eq. 1-24})
\]

where
$t = $ Sintering time ($s$)

$r = $ Particle radius ($m$)

$n = $ Constant (Table 1-5) that depends on the mass transport mechanism (dimensionless)

Figure 1—16. Schematic of mass transport mechanisms from Rahaman 91.

Table 1-5. Mass transport mechanisms adapted from Herring 89, Rahaman 91, and Kang 92.
Note that some transport mechanisms contribute to densification, while others contribute
to coarsening. Often, multiple mechanisms operate simultaneously.

<table>
<thead>
<tr>
<th>Transport Mechanism</th>
<th>Source</th>
<th>Sink</th>
<th>Coarsening or Densification</th>
<th>Scaling Law Exponent ($n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
<td>4</td>
</tr>
<tr>
<td>Volume Diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
<td>3</td>
</tr>
<tr>
<td>Evaporation-Condensation</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
<td>2</td>
</tr>
<tr>
<td>Gas Diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
<td>3</td>
</tr>
<tr>
<td>Grain Boundary Diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Densification</td>
<td>4</td>
</tr>
<tr>
<td>Lattice Diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Densification</td>
<td>3</td>
</tr>
<tr>
<td>Plastic (Viscous) Flow</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Densification</td>
<td>1</td>
</tr>
</tbody>
</table>
Solid-State Sintering

The solid-state sintering process is divided into three stages: initial stage sintering, intermediate stage sintering, and final stage sintering. During initial stage sintering, tangential particle contacts form necks and grain boundaries form. Models developed by Kuczynski \(^9^3\) and Kingery \(^9^4\) describe fractional neck growth (neck growth normalized by the initial particle radius) for spheres in tangential contact. For example, Eq. 1-25 is derived for a mass source at the grain boundary to a mass sink at the neck. Similar to Eq. 1-25, various equations can be derived for the different source to sink conditions listed in Table 1-5.

\[
\frac{x}{r} = \left(\frac{20\gamma a^3 D^*}{k_B T}\right)^{1/5} r^{-3/5} t^{1/5} \tag{Eq. 1-25}
\]

where

- \(x\) = Neck growth \((m)\)
- \(r\) = Particle radius \((m)\)
- \(\gamma\) = Surface energy \((J/m^2)\)
- \(a^3\) = Atomic volume or vacancy volume \((m^3)\)
- \(D^*\) = Self-diffusion coefficient \((m^2/s)\)
- \(k_B\) = Boltzmann’s constant \((8.617 \times 10^{-5} \text{ eV/K})\)
- \(T\) = Absolute temperature \((K)\)
- \(t\) = Time \((s)\)

Intermediate stage sintering involves the majority of densification where continuous pore channels form at grain edges. What was once a spherical particle morphs into a tetrakaidecahedron, a 14-sided polygon. Final stage sintering is typified by isolated (or closed) pores and grain growth.
Liquid Phase Sintering

Liquid phase sintering occurs when 0.1 to 40 vol. % of a liquid phase is present during sintering. Viscous sintering is important when high percentages (> 40 vol. %) of liquid are present. When at Corning Glass, Scherer developed understanding of viscous sintering using low (15 %) density glass preforms which were sintered for subsequent drawing of optical fibers \(^95\).

When sintering in the presence of a liquid, viscosity becomes an important part of describing fractional neck growth (\(\text{Eq. 1-26}\)). According to Frenkel, energy dissipated in viscous flow is equal to the energy change from surface area reduction \(^96\). Unlike \(\text{Eq. 1-25}\), temperature does not appear explicitly in \(\text{Eq. 1-26}\). However, viscous flow is thermally activated, sometimes following the Vogel-Fulcher-Tammann Equation (\(\text{Eq. 1-27}\)). One focus area of this thesis, pressure-forming of sulfide electrolytes, can be classified as liquid phase sintering, especially for compacts densified near the glass transition temperature.

\[
\frac{x}{r} = \left(\frac{3\gamma}{2\eta \rho}\right)^{1/2} t^{1/2} \quad \text{(Eq. 1-26)}
\]

where

- \(x\) = Neck growth (\(m\))
- \(r\) = Particle radius (\(m\))
- \(\gamma\) = Surface energy (\(J/m^2\))
- \(\eta\) = Viscosity (\(Pa \cdot s\))
- \(\rho\) = Radius of curvature (\(m^{-1}\))
- \(t\) = Time (\(s\))

\[
\eta = \eta_0 e^{\frac{A}{T-T_0}} \quad \text{(Eq. 1-27)}
\]

where
\[ \eta = \text{Viscosity} \ (Pa - s) \]

\[ \eta_o = \text{Viscosity pre-exponential} \ (Pa - s) \]

\[ A = \text{Empirically-derived constant} \ (K) \]

\[ T = \text{Absolute temperature} \ (K) \]

\[ T_o = \text{Reference temperature} \ (K) \]

**Specialized Sintering Approaches**

Conventional sintering involves solely the application of external thermal energy to densify a compact. In contrast, specialized sintering approaches may increase the driving force for sintering by applying other combinations of variables, for example, external pressure and/or electric field, on top of external thermal energy to encourage sintering.

Specialized sintering approaches aim to minimize sintering time in order to maximize throughput and aim to minimize temperature in order to lower energy costs. Minimizing temperature may also contribute to maximizing throughput if the number of steps in a manufacturing line may be minimized. Further, minimizing temperature may give flexibility to the order of steps. Rearranging steps is important if certain materials in a component have a limited thermal budget. One focus area of this thesis, cold sintering of oxide electrolytes, represents a contribution that can be classified as specialized sintering. Both pressure-forming of sulfide electrolytes and cold sintering of oxide electrolytes fall within the target region of this thesis of low temperature and short time sintering (**Fig. 1-17**).
Figure 1—17. Master plot of sintering time vs. sintering temperature for two lithium solid electrolytes, Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ and Li$_7$La$_3$Zr$_2$O$_{12}$, and 0.03 Y$_2$O$_3$ + 0.97 ZrO$_2$ (mol frac) 98-101, a V$_0$ electrolyte. This thesis details progress in the low temperature densification of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ 102 and x Li$_2$S + (1-x) P$_2$S$_5$ 74, 103-105, which have been processed in the target time & temperature region in the red box. Note that the time denoted for flash sintering is the time that the electric field is applied and does not include the time needed to take the sample from room temperature to the sintering temperature.

In Fig. 1-17, a few specialized sintering approaches are categorized: hot pressing, microwave sintering, spark plasma sintering, field-assisted sintering, and flash sintering. Each technique will now be described briefly.

Hot pressing involves sintering under pressure using resistive or inductive heating elements. Sintering mechanisms in pressure-assisted sintering include plastic deformation, power-law creep, and diffusion & the driving force equations are accordingly modified to include a stress-intensity factor 92.

Microwave sintering, like microwave cooking, heats compacts placed within a susceptor. Microwave sintering can be applied to a broad range of materials including oxides, non-oxides, carbide semimetals, and powdered metals 106, 107.
In spark plasma sintering and field-assisted sintering, DC electric current is pulsed through a conducting die, such as graphite. Thermal energy is applied through Joule heating. Spark plasma sintering is somewhat of a misnomer since it is debated whether any “spark” or “plasma” is present during sintering\textsuperscript{108-112}.

Flash sintering is another sintering technique under a DC electric field. It usually occurs on dog bone shaped specimens without applied pressure. The “flash” refers to when the electrical conductivity spikes and grain boundary diffusion, a kinetically-limited phenomenon, quickly densifies the compact\textsuperscript{98, 100}. Since densification occurs very quickly, grain growth is minimized and dense, nanograin compact can be obtained. The temperature window allowed by flash sintering is controlled by the applied electric field (\textbf{Fig. 1-17}). Higher electric fields correspond to lower required temperatures for densification and vice versa. For example, a decrease in electric field from 120 to 60 V/cm results in a 200 °C sintering temperature suppression in yittria-stabilized zirconia\textsuperscript{98}. Raj argues that limited Joule heating since the local temperatures during the “flash” are much lower than the temperatures required to sinter a specimen in seconds\textsuperscript{113}.

From the discussion of specialized sintering techniques above, different combinations of applied pressure, temperature, and electric field are possible tunable variables to lower time and temperature for sintering.

\textbf{Thesis Organization}

This thesis is focused on low temperature processing routes to minimize ionically resistive pores or grain boundaries that limit conductivity in lithium solid electrolytes.
Battery technology requires materials with excellent ionic conductivities that can be processed inexpensively. Two model material systems have been identified for study: the sulfide electrolyte \( x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5 \) \((x = 0.70, 0.75, 0.80)\) and oxide lithium solid electrolyte \( \text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3 \) \((x = 0.50)\). Both families of electrolytes present unique processing challenges. Chapter-specific literature reviews and experimental details are contained in each chapter.

Chapter 2 introduces lithium thiophosphate electrolytes as materials which can be processed at low temperature \(< 200 \, ^\circ\text{C}\). The influence of \( x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5 \) \((x = 0.70, 0.75, 0.80)\) density and crystallinity on ionic conductivity is studied.

Chapter 3 presents powder-in-a-tube processing as a method to make sheet-like lithium thiophosphate electrolytes. Powder-in-a-tube electrolyte properties are compared to electrolyte pellets.

Chapter 4 focuses on impedance and equivalent circuit modeling studies of the lithium germanium aluminum phosphate electrolyte \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 \). In particular, the grain impedance and grain boundary impedance is studied for different heat treatments.

Chapter 5 focuses on cold sintering of \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 \) and minimizing grain boundary impedance. All post-processing is done at 650 \(^\circ\text{C}\) for 5 min.

Chapter 6 focuses on \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 + \text{Poly}(\text{vinylidene fluoride hexafluoropropylene}) \) polymer cold sintered composites that have been before and after soaking in 1 M \( \text{LiPF}_6 \) ethylene carbonate-dimethyl carbonate \((50:50 \, \text{vol. } \%)\) liquid electrolyte. All processing is limited to below 125 \(^\circ\text{C}\).

Chapter 7 addresses new avenues of work as a result of the contributions detailed in the thesis.
Content in this thesis was adapted with permission from four publications:


(3) S. S. Berbano, J. Guo, H. Guo, M. T. Lanagan, C. A. Randall, “Cold Sintering Process of Li1.5Al0.5Ge1.5(PO4)3 Solid Electrolyte,” Submitted 114.

Chapter 2

Pressure-Forming and Ionic Conductivity of Lithium Thiophosphates

Chapter Overview

Lithium thiophosphates in the family \( x \text{Li}_2\text{S}+(1-x)\text{P}_2\text{S}_5 \) (mol fraction) possess 25 °C ionic conductivities greater than \( 10^{-3} (\Omega\cdot\text{cm})^{-1} \) in crystallized \( x = 0.70 \), among the highest in inorganic solid-state electrolytes. In this chapter, the main consideration is the role of densification on the Li-ion conductivity. Densification behavior, as well as temperature-dependent measurements of ionic conductivity for three compositions, \( x = 0.70, 0.75, \) and \( 0.80 \), was studied. Results in this chapter demonstrate that dense, rather than porous, lithium thiophosphate solid electrolytes are important in the design of solid-state batteries and electrochemical capacitors.

Chapter Introduction

Better Understanding of Densification Enables Battery Development

Solid electrolytes are of interest for safe energy storage at all length scales in applications ranging from physiological microsensors to electric vehicles to load-leveling batteries. Solid electrolytes are safer alternatives to flammable, non-aqueous liquid electrolytes, such as LiPF\(_6\) dissolved in the organic co-solvent system of ethylene carbonate and dimethyl carbonate\(^{115}\). For
solid electrolytes to become ubiquitous in energy storage, a number of crucial improvements must be made: (1) lower interfacial impedance electrode-electrolyte architectures, (2) better cycleability at higher C-rates, (3) higher voltage stability, (4) broader temperature stability, and (5) easier to scale manufacturing and inexpensive processing. Understanding densification behavior and its impact on ionic conductivity is key to lower interfacial impedance electrode-electrolyte architectures and better cycleability at higher C-rates.

Mechanistically, the rate-controlling ion conduction process is not fully understood in the lithium thiophosphate family. Either surface or bulk conduction processes are possible. This open-ended question is associated with the fact that many studies on this system are on powder compacts and not densified, monolithic solid electrolytes\textsuperscript{103, 104}.

Previous work from Sakuda et al.\textsuperscript{103} supports that bulk conduction dominates. On the other hand, 95\% dense pellets of nanoporous $\beta$-Li$_3$PS$_4$ have been reported to be dominated by surface conduction since there is a positive relationship between ionic conductivity and surface area. Further, a lower activation energy is observed in nanoporous $\beta$-Li$_3$PS$_4$ than in bulk $\beta$-Li$_3$PS$_4$\textsuperscript{75}. The high surface energy of nanocrystalline materials alters the local energy for free-carrier (defect) generation\textsuperscript{116}. Both carrier concentration and activation energy may differ between bulk and nanoporous materials. Given the open questions in this field regarding bulk and nanoporous materials, as well as differences in surface conduction and bulk conduction, fundamental understanding of the relationship between density and ionic conduction is key to battery development.
Compositional Dependence of Ionic Conductivity and Activation Energy in Glassy Electrolytes

Glasses have been extensively studied to improve ionic conductivity for application as lithium solid electrolytes. An elementary understanding is that openness of a glass structure, reflected in the free volume, and disconnectedness of the glass network, reflected in the fraction of non-bridging units, determine the intrinsic transport properties \(^{117,118}\).

Ionic conductivity can be further tailored by changing composition. Fixing the concentrations of glass intermediate (Ga\(_2\)S\(_3\)), glass former (GeS\(_2\)), and alkali modifier (M\(_2\)S), systematic studies were performed by Yao and Martin to understand the variation of the alkali element, M’s, radius on the conducting alkali ion’s conductivity and activation energy \(^{119}\). Glasses with smaller alkali radii had higher ionic conductivities and lower activation energies than glasses with larger alkali radii (Fig. 2-1).

![Arrhenius plot of conductivity for different alkali radii in a gallium germanium sulfide glass (left) and activation energy vs. alkali radius (right). Larger alkali radius increases activation energy and decreases ionic conductivity at a given temperature adapted from Yao and Martin \(^{119}\).](image)

**Figure 2—1.** Arrhenius plot of conductivity for different alkali radii in a gallium germanium sulfide glass (left) and activation energy vs. alkali radius (right). Larger alkali radius increases activation energy and decreases ionic conductivity at a given temperature adapted from Yao and Martin \(^{119}\).

Ionic conductivity can be tailored by changing composition for a given glass modifier. Addition of a single glass modifier to a single glass former with common anions often increases
the fraction of non-bridging anion units that are ionically bonded to the transporting cation and usually enhances ionic conductivity. One exception is in B$_2$O$_3$ glasses where modifier is absorbed by the formation of tetrahedral BO$_{4/2}$ groups, which strongly influence compositional dependence on ionic conductivity at tetrahedral boron fractions < 0.5. For tetrahedral boron fractions > 0.5, non-bridging units form. Borate glass short range and intermediate range order exceptions aside, there is an optimal composition, with maximum conductivity corresponding to the maximum beneficial ionicity. After the maximum, there is a decrease in conductivity when adding more of the glass modifier endmember. The glass modifier endmember needs to be combined with a network former to form non-bridging units and conduct ions. Otherwise, a glass modifier without network former behaves like an insulating lithium salt. Excess Li$_2$S has been identified in x-ray diffraction patterns for x-values above the conductivity maximum in high modifier fraction x Li$_2$S + (1-x) P$_2$S$_5$ (Fig. 2-2), x Li$_2$S + (1-x) SiS$_2$ (Fig. 2-3), and x Li$_2$S + (1-x) AlS$_{1.5}$ (Fig. 2-4).

The x Li$_2$S + (1-x) P$_2$S$_5$ binary was first studied by Ribes et al. in 1979. The glass forming range was found to be 0.33 ≤ x ≤ 0.67. Ionic conductivity at 25 °C for x = 0.67 was reported to be 1.1 x 10$^{-4}$ S/cm$^{120}$ and was obtained by melt-quenching of glass. As seen in Fig. 2-2, mechanical milling allows expansion of the glass formation range to x = 0.75. The unique processing method of mechanical milling, employed by Hayashi et al. in 2001$^{121}$ for x Li$_2$S + (1-x) P$_2$S$_5$, is the focus of the next section.
Figure 2—2. X-ray diffraction patterns for mechanically milled $x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5$ (left) and 25 °C ionic conductivity & activation energy changes with composition (right)\textsuperscript{121}.

Figure 2—3. X-ray diffraction patterns for mechanically milled $x \text{Li}_2\text{S} + (1-x) \text{SiS}_2$ (left) and 25 °C ionic conductivity & activation energy changes with composition (right)\textsuperscript{122}. Pradel and Ribes, using twin roller quenching, report a glass formation range $0.30 < x < 0.60$\textsuperscript{123}. Four peaks associated with $\text{Li}_2\text{S}$ are seen at $x = 0.65$ and 0.70.

Figure 2—4. X-ray diffraction patterns for mechanically milled $x \text{Li}_2\text{S} + (1-x) \text{AlS}_{1.5}$ (left) and 25 °C ionic conductivity & activation energy changes with composition (right)\textsuperscript{124}.
Mechanical Milling to Extend the Glass Forming Range and to Amorphize Volatile Melts

Melt-quenching of volatile materials presents a challenge with controlling stoichiometry and batch scaling since precise thermal control is required. Mechanical milling is an alternative kinetic procedure to melt-quenching. Mechanical alloying (also called mechanical milling or mechanochemical milling) was first developed in the 1960s for oxide-dispersion strengthened alloys for use in aerospace applications. Mechanical alloying is a route to the amorphous state. Further, metallic alloys and ceramics made by mechanical milling exhibit glass transition behavior\(^{104,125}\). Mechanical milling is a preparation technique that may allow amorphization further from equilibrium than traditional melt-quenching (Table 2-1)\(^{126}\). Emphasis is intentionally added to draw attention to Solid-state quench and Mechanical milling. Intense pulverization during mechanical milling can extend the glass forming range in systems with high vapor pressure melts, such as those based on the glass former P\(_2\)S\(_5\)\(^{121,127}\).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Effective quench rate (K/s)</th>
<th>Maximum departure from equilibrium (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical cold work</td>
<td>- - -</td>
<td>1</td>
</tr>
<tr>
<td>Solid-state quench</td>
<td>(10^3)</td>
<td>16</td>
</tr>
<tr>
<td>Rapid solidification</td>
<td>(10^3 - 10^8)</td>
<td>24</td>
</tr>
<tr>
<td>Mechanical milling</td>
<td>- - -</td>
<td>30</td>
</tr>
<tr>
<td>Irradiation ion implantation</td>
<td>(10^{12})</td>
<td>30</td>
</tr>
<tr>
<td>Condensation from vapor</td>
<td>(10^{12})</td>
<td>160</td>
</tr>
</tbody>
</table>

Table 2-1. Non-equilibrium processing techniques adapted from Suryanarayana\(^{126}\).

Mechanical milling’s longer processing times and intense pulverization at lower temperatures is particularly suited for volatile materials since there is better stoichiometry control and fine powders are readily acquired for fabrication of high density solid electrolytes.

In addition to processing glasses, mechanical milling has yielded a transformation from a mixture of 0.75 Na\(_2\)S + 0.25 P\(_2\)S\(_5\) to a semicrystalline \(\alpha\)-Na\(_3\)PS\(_4\) or \(\beta\)-Na\(_3\)PS\(_4\)\(^{128}\) without heating.
or slowly cooling from the melt. Furthermore, Trevey et al. showed pathways from the precursor powders directly to the semicrystalline state. In this approach, a high-energy ball (SPEX®) mill was used to process lithium thiophosphates with 25 °C ionic conductivities greater than $10^{-3}$ (Ω·cm)$^{-1}$. Figure 2-5 summarizes possible transformation routes for unfired, unpulverized components activated by mechanical milling. Unfired, unpulverized components may become x-ray amorphous or partially crystalline directly from mechanical milling. In this thesis, mechanical milling was employed, rather than melt-quenching, to make x-ray amorphous lithium thiophosphate electrolytes, some of which exhibited glass transition behavior.

![Figure 2-5](image.png)

**Figure 2—5.** Starting with unfired, unpulverized components, possible states after milling are (1) x-ray amorphous as in Hayashi et al., Mizuno et al., Morimoto et al., and Berbano et al., & (2) partially crystalline phases, that did not exist as unmilled components, in a single-step as in Trevey et al., Morimoto et al., and Berbano et al. Work by Hayashi et al., Mizuno et al., and Trevey et al. is on the Li$_2$S + P$_2$S$_5$ binary. Morimoto et al. studied the borophosphate ternary SnO - B$_2$O$_3$ - P$_2$O$_5$, which was x-ray amorphous after ~ 65 hours of milling. Morimoto et al. studied the Li$_2$S + AlS$_{1.5}$ binary. Berbano et al. studied the Na$_2$S + P$_2$S$_5$ binary.
Experimental Methods

Synthesis by Mechanical Milling

Mechanically milled products were prepared by weighing appropriate amounts of Li$_2$S (Alfa Aesar, 99.9% metals basis, ~ 74 μm) and P$_2$S$_5$ (Sigma Aldrich, 99%) inside an Ar-filled glovebox. The powders were ground for five minutes in an agate mortar and pestle and then loaded into an 80 mL ZrO$_2$ pot. Twenty YSZ balls, 10 mm in diameter, were used as the milling media. The sample to milling media weight ratio was ~ 1:13. The pot was sealed under vacuum with a rubber gasket and taped shut with electrical tape to avoid air influx and contamination while the sample was milled outside the glovebox. Samples were mechanically milled at 370 rpm for 14, 20, or 26 h using a high-energy planetary mono-mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany).

Pressure-Forming

Mechanically milled powder was loaded into a hardened steel die with a light polytetrafluoroethylene (PTFE) spray coating (Dry Film Release Agent, Sprayon) and a thermocouple that screwed into the die’s inner sleeve (EQ-Die12-HC, MTI, Richmond, CA). A 93 MPa pre-press was performed on Tygon supports at 25 °C, causing a friction fit between the upper and lower punch. Next, the heating jacket was attached to the double-action die. When pressurized to 186 MPa, the die was heated at ~ 12 °C/min from 25 °C to the desired temperature. Pressure intermittently decreased primarily from the softening of the glassy powder and minimally from the change in the die-to-punch fit from differential thermal expansion.
Pressure was increased back to 186 MPa during heating. After reaching the desired temperature, the heater was turned off and the die was allowed to cool to 25 °C. Pressure-formed pellets were observed to be non-uniform in color until they were polished ~ 200 μm below the surface. A color change was also observed for the die punch. Therefore, it is plausible to assume that there was a reaction between the die punch and sample. Last, geometric density was determined by massing 1.27 cm diameter pellets on a balance and measuring their thickness using calipers. All pressure-forming took place inside the Ar glovebox.

**X-ray Diffraction**

A quartz low-background support covered with Kapton (Chemplex Industries, Palm City, FL) was characterized without any sample. Inside the glovebox, powder samples were loaded in the cavity of a quartz low-background support and covered with Kapton. Room temperature X-ray diffraction (XRD) patterns were collected using a θ/θ goniometer with Cu-Kα radiation, fixed slit incidence (0.5 deg. Divergence, 1.0 deg. Anti-scatter, specimen length 10 mm) and diffracted (0.5 deg. Anti-scatter, 0.02 mm nickel filter optics), (X’Pert Pro MPD, PANalytical, Westborough, MA). Data was collected at 45 kV and 40 mA from 25-80 deg. 2θ using a PIXcel detector in scanning mode with a PSD length of 3.35 deg. 2θ and 255 active channels for a duration of ~ 15 min.

**Impedance Spectroscopy**

Pellet faces (1.27 cm diameter) were electroded with air-dry Ag paste (Premetek, State College, PA) and allowed to dry overnight in the glovebox antechamber. Pellets (1.5 to 2.5 mm
thick) were loaded in a custom-built sample cell assembly consisting of brass covers, brass spacers, a Teflon guard, a Teflon spacer, silicone o-rings, and a compression spring. The sample cell was transferred from the glovebox to a N₂-purged, temperature-controlled chamber (9023, Delta Design, Poway, CA). Thermal equilibrium of the sample was determined from overlapping impedance spectra. Complex impedance spectra were measured using an impedance analyzer (SI 1287 and SI 1255B FRA, Solatron Instruments, Oak Ridge, TN) with a sinusoidal voltage amplitude 100 mV vs. OCV for \(-120 \, ^\circ C \leq T \leq -10 \, ^\circ C\) and \(1 \, Hz \leq f \leq 1 \, MHz\). Data were corrected for sample geometry and analyzed using ZView® (Version 2.2, Scribner Associates Inc., Southern Pines, NC). In all fitting routines, all parameters were allowed to float so that errors could be given.

Results & Discussion

Pressure-Forming of Mechanically Milled Powders

One method to control the densification of these glasses is through pressure-temperature-assisted sintering (or pressure-forming)\(^{104, 131, 132}\). For the purposes of this thesis, externally applied temperature and pressure should be controlled so as not to induce crystallization during pressure-forming. The crystallite phase fraction detectable by X-ray diffraction (5 vol. %) is much lower than what is required for crystalline percolation through the volume given randomly dispersed crystallites (30 vol. %). The volume fraction for percolation depends on crystallite size. Therefore, X-ray diffraction will serve as the characterization tool to determine whether crystallization occurs during pressure-forming. Then, meaningful ionic conductivity comparisons can be made between compacts of different density.
Differential scanning calorimetry was performed to see whether the mechanically milled x-ray amorphous powder exhibited a glass transition. A thermogram for x = 0.70 is seen below (Fig. 2-6). For other compositions, similar to Hayashi et al., a glass transition could not be clearly discerned in x = 0.75 and 0.80.

![Differential scanning calorimetry thermogram of 0.70 Li_2S + 0.30 P_2S_5 glass powder hermetically sealed within an Al pan. The glass transition temperature (216 °C) was obtained by the tangent method.](image)

In the same way thermal history influences thermal behavior, more intense milling conditions freeze in higher fictive temperature states and change the observed thermal behavior. When scanning below T_g for as-mechanically milled 0.60 Na_2S + 0.40 P_2S_5, Martin showed a 0.05 W/g peak-to-baseline enthalpy relaxation associated with volume relaxation from the initially compression-based high fictive temperature state\(^{133}\). Figure 2-6 shows no relaxation below T_g in 0.70 Li_2S + 0.30 P_2S_5 in the range of 0.05 W/g. Perhaps a longer milling time could allow for the observation of exothermic relaxation below T_g in lithium thiophosphates. Hayashi et al. reported a T_g shift depending on milling conditions for 0.70 Li_2S + 0.30 P_2S_5\(^{134}\). When using 10 Al_2O_3 balls, 10 mm in diameter, T_g was 200 °C, while when using 500 ZrO_2 balls, 4
mm in diameter, T₉ was 218 °C. Glass transition temperature shifts are not unique to Li-conducting lithium thiophosphates. Coupled thermal and mechanical relaxation is seen in the binary 0.80 GeS₂ + 0.20 Ga₂Se₃, studied by Delaizir et al., which exhibited increases in glass transition temperature and crystallization peak sharpening with milling time. Therefore, longer milling times and more intense milling conditions freeze in a higher fictive temperature states.

With Differential Scanning Calorimetry, Mendez studied the thermal behavior of 0.75 Li₂S + 0.25 P₂S₅ powders that had first been pressed at 25 °C at 360 MPa and then pressed at 47 MPa at 130 and 140 °C. For both 130 and 140 °C, the crystallization peak after pressure-forming was broadened compared to the crystallization peak of samples heat treated at the same temperature without externally applied pressure. Additionally, the sharp crystallization peak could be recovered after DC cycling the 130 and 140 °C pressure-formed samples between symmetric Li electrodes at 25 °C. Unique coupling of thermal, mechanical, and electrochemical relaxation of mechanically milled powders and pressure-formed compacts certainly will be a focus area in the future for glassy electrolyte systems.

In this thesis, pressure-induced crystallization is not observed at 25 °C for x = 0.70, 0.75, or 0.80 for uniaxial die pressing at 186 MPa. In Chapter 3, pressures lower than 186 MPa are estimated for powder-in-a-tube processing of x = 0.70. There is no crystallite development observed from X-ray diffraction after 25 °C powder-in-a-tube processing. In the work of Minami et al., pressure-forming milled x = 0.70 powders at 20 MPa for 1 h causes voids in glass at 230 °C. For the same pressure and time conditions, a smooth, dense compact is formed at 240 °C. When pressure-formed at 20 MPa for 1 h, surface crystallization occurs at a temperature of 250 °C. Precipitation of the crystal is evident for pressure-forming at 20 MPa for
1 h at 260 °C. Sakuda et al. shows that x = 0.75 mechanically milled glass remains x-ray amorphous after pressing at 25 °C, even up to pressures of 460 MPa.

Fixed pressure, variable temperature densification data are shown in Figures 2-7, 2-8, 2-9 for x = 0.70, 0.75, and 0.80, respectively. Similarly to 0.80 GeS2 + 0.20 Ga2Se3, a positive relationship was observed for fixed pressure, variable temperature pressing in glass powders below their glass transition temperature. Empirical linear fits with \( R^2 > 0.97 \) are shown by dashed blue lines in Figures 2-7, 2-8, 2-9.

\[
\text{Figure 2—7. Percent theoretical density (\( \Delta \)) of Li}_7\text{P}_3\text{S}_{11} \text{ using the value from Yamane et al. } \text{70 (1.98 g/cm}^3 \text{)} \text{ vs. temperature. An empirical linear fit of data (dashed blue line) and } R^2 \text{ are shown. The error bar width is } \pm 1.5 \%. \]
Figure 2—8. Percent theoretical density (Δ) of $\gamma$-Li$_3$PS$_4$ using the value from Homma et al. 74 (1.93 g/cm$^3$) vs temperature. An empirical linear fit of data (dashed blue line) and $R^2$ are shown. The error bar width is ±1.5%.

$$% \text{Density} = 0.1017 \times T(\degree C) + 73.116$$

$R^2 = 0.993$

0.75Li$_2$S + 0.25P$_2$S$_5$, 186 MPa
Figure 2—9. Percent experimental density (Δ) of the x = 0.80 multiphase mixture (1.88 g/cm³) vs. temperature. Mixture of four phases (Li₂S, Thio-LISICON III analogue Li₃₂P₀.₉₆S₄, γ-Li₃PS₄ (x = 0.75), and Li₇PS₆ (x = 0.875)) at 350 °C were identified by x-ray diffraction patterns that were compared to Hayashi et al. ⁶⁸. The error bar width is ± 1.5%.

Since the fit lines have no phenomenological significance, an attempt was made to fit the data using a phenomenological model. The intermediate stage sintering of amorphous powder under load can be modeled by Eq. 2-1 ¹³⁶. Eq. 2-1 assumes “applied pressure is much larger than the surface energy compressive force and that the yield point for creep deformation is low” ¹³⁷. The viscosities of alkali-modified oxide glasses ¹³⁸ and unmodified sulfide glasses have been reported ¹³⁹, while the viscosity of high modifier sulfide electrolytes and their surface energies has not been reported. However, both assumptions are met for the lithium thiophosphate case.
\[
\ln \left(1 - \frac{\rho_m}{\rho_t}\right) = \frac{-3P}{4\eta} t + \ln \left(1 - \frac{\rho_i}{\rho_t}\right) \tag{Eq. 2-1}
\]

where

\(\rho_m\) = Measured density (g/cm\(^3\))

\(\rho_t\) = Theoretical density (g/cm\(^3\))

\(P\) = Pressure (Pa)

\(\eta\) = Viscosity (Pa-s)

\(t\) = Time (s)

\(\rho_i\) = Initial density (g/cm\(^3\))

Using densification data of fixed time (2 minutes), fixed pressure (186 MPa), and fixed temperature (200 °C) the viscosity calculated using Eq. 2-1 is \(10^{10}\) Pa-s to cause densification of a 72% percent compact to 94% density.

From Angell’s fragility master plot, the apparent temperature for a viscosity of \(10^{10}\) Pa-s of lies between \(1.15T/T_g\) (strong liquid bound) and \(1.04T/T_g\) (fragile liquid bound)\(^{40}\).

**Equation 1-27** cannot be used since the reference temperature, \(T_o\) must be < 473 K to calculate viscosity below 473 K. Therefore, a two-parameter viscosity model is used (Eq. 2-2).

**Equation 1-27** usually describes fragile (super Arrhenius) liquids better, while **Eq. 2-2** usually describes strong (Arrhenius) liquids better. The effective temperatures read from Angell’s master plot (**Table 2-2**) are then substituted into **Eq. 2-2**. Now, for both the strong and fragile liquid bounds, one has a system of two equations and two unknowns and the parameters \(\eta_o\) and \(\Delta E_{Act}\) can be obtained. Last, the viscosity function can be substituted into **Eq. 2-1**. **Figure 2-10** shows the calculated densification curve from **Eq. 2-1** in red overlaid on the experimental densification data points from \(x = 0.70\).
\[ \eta = \eta_o \exp \left( \frac{\Delta E_{\text{Act}}}{k_B T} \right) \]  
(Eq. 2-2)

where

\( \eta \) = Viscosity \((Pa - s)\)

\( \eta_o \) = Viscosity pre-exponential \((Pa - s)\)

\( \Delta E_{\text{Act}} \) = Activation energy for viscous flow \((eV)\)

\( T \) = Absolute temperature \((K)\)

Table 2-2. Effective temperatures for the strong and fragile liquid bounds read from Angell’s master plot\(^{140}\).

<table>
<thead>
<tr>
<th></th>
<th>( \eta(10^{10} \text{ Pa-s}) )</th>
<th>( \eta(10^8 \text{ Pa-s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature for Strong Liquid Bound</td>
<td>( 1.15T_g = 473 \text{ K} )</td>
<td>( 1.32T_g )</td>
</tr>
<tr>
<td>Temperature for Fragile Liquid Bound</td>
<td>( 1.04T_g = 473 \text{ K} )</td>
<td>( 1.06T_g )</td>
</tr>
</tbody>
</table>

Figure 2—10. (a) Percent theoretical density \((\Delta)\) of \( \text{Li}_7\text{P}_3\text{S}_{11} \) using the experimental value from Yamane et al.\(^70\) \((1.98 \text{ g/cm}^3)\) vs. temperature. The density error bar width is \( \pm 1.5 \% \). The strong liquid bound is shown for \( t_{\text{viscous}} = 120 \text{ s} \). Longer times shift the curve to lower temperatures. The fragile liquid bound is not shown. Its viscosity behavior predicts all densification takes place between 195 and 205 \(^\circ\text{C}\).

From Fig. 2-10, one can conclude that viscous flow strongly influences densification above 160 \(^\circ\text{C}\). Although an attempt was made to phenomenologically describe the sintering behavior, the empirical linear fits are the most accurate way to represent the data. In the future, to design a sintering study, an integrated system to monitor die punch displacement and die temperature as a function of time is needed.
X-ray Diffraction of Milled Powders and Pressure-Formed Compacts

X-ray powder diffraction was recorded for the lithium sulfide and phosphorus sulfide starting materials and starting materials after mechanical milling (Fig. 2-11). Peak broadening, associated with particle size reduction is observed in lithium sulfide after 14 hours of milling. Phosphorus sulfide remains partially crystalline after 20 hours of milling.

\[ x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5, x = 0.70 \]

Figure 2-12 shows x-ray diffraction patterns for as-milled \(x = 0.70\), milled \(x = 0.70\) after pressure-forming at 225 °C and 186 MPa, and milled \(x = 0.70\) after crystallization at 300 °C, 10 min. Peaks of the crystalline composition corresponds to a single phase with a composition \(\text{Li}_7\text{P}_3\text{S}_{11}\) having a triclinic crystal structure\(^{70,72}\) and density of 1.98 g/cm\(^3\).\(^{70}\) The \(\text{Li}_7\text{P}_3\text{S}_{11}\) phase is associated with PDF # 04-014-8383.
Figure 2—11. X-ray diffraction powder patterns of Li$_2$S and P$_2$S$_5$ reagents, Li$_2$S mechanically milled 14 h, and P$_2$S$_5$ mechanically milled 20 h.

Figure 2—12. X-ray diffraction powder patterns of x = 0.70 mechanically milled 14 h, x = 0.70 mechanically milled 14 h after pressure-forming at 225 °C, 186 MPa, and x = 0.70 mechanically milled 14 h after crystallization at 300 °C for 10 min. PDF # 04-014-8383 is associated with Li$_7$P$_3$S$_{11}$. 
$x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5, \, x = 0.75$

X-ray diffraction patterns for as-milled $x = 0.75$ and $x = 0.75$ after pressure-forming at 213 °C and 186 MPa are shown in Fig. 2-13. Peaks of the crystalline Li$_3$PS$_4$ are indexed to $\gamma$-Li$_3$PS$_4$.

![X-ray diffraction patterns](image)

Figure 2—13. X-ray diffraction powder patterns of as-milled $x = 0.75$ and ground $x = 0.75$ powder from an $x = 0.75$ pellet pressure-formed at 186 MPa at 213 °C.

$x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5, \, x = 0.80$

Figure 2-14 shows x-ray diffraction patterns for as-milled $x = 0.80$ and a multiphase mixture of Li$_2$S, Thio-LISICON III analogue Li$_{1.2}$P$_{0.96}$S$_4$, $\gamma$-Li$_3$PS$_4$ ($x = 0.75$), and Li$_7$PS$_6$ ($x = 0.875$) obtained after pressure-forming at 350 °C, 186 MPa. Unreacted Li$_2$S is evident in as-
milled $x = 0.80$ even after 26 h of milling. No PDF card exists for the Thio-LISICON III analogue$^{35,36}$. Without including this phase, phase fractions can be obtained by whole pattern fitting for crystallization at 350 °C and 410 °C (Fig. 2-15). Higher temperature crystallization favors more Li$_7$PS$_6$ and less Li$_2$S, $\gamma$-Li$_3$PS$_4$, and amorphous phase.

Figure 2—14. X-ray diffraction powder patterns of as-milled $x = 0.80$ and ground $x = 0.80$ powder from an $x = 0.80$ pellet pressure-formed at 186 MPa at 350 °C.

Figure 2—15. Phase amounts for as-milled $x = 0.80$ pressure-formed at 186 MPa at 350 and 410 °C.
**Ionic Conductivity of Pressure-Formed Compacts**

Impedance complex plane plots have been the preferred method to present impedance spectroscopy data for $x = 0.70$ and $x = 0.80$. At the measurement high frequency limit ($f \sim 1 \text{ MHz}$), spectra of the high conductivity materials are dominated by the thermally activated electrode polarization capacitance, which is formed by the double layer of Li-ions at the electrode-electrolyte interface. The temperature dependence of conductivity was compared below 25 °C to prevent spurious crystallization during measurement. Below 25 °C, conduction relaxations can be observed at $f < 1 \text{ MHz}$. Above 1 MHz, inductance from the measurement cables can mask the sample response.

$x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5, x = 0.70$

**Figure 2-16** shows an impedance complex plane plot for 72 % and 94 % dense x-ray amorphous $x = 0.70$ electrolytes. An equivalent circuit fit of a single resistor and constant phase element (Eq. 1-18) in parallel is overlaid over the experimental data (Fig. 2-16). Fit parameters are listed in Table 2-3. Fit resistivity values change about one order of magnitude between the two densities, while the $Q$ and $n$ parameters of the constant phase element change much less than an order of magnitude. No useful information can be extracted from the low frequency electrode component, so it was not fit. Throughout this thesis, impedance spectra were collected to sufficiently low frequencies (sometimes 1 mHz) to rule out interfacial reaction between the electrode and electrolyte beyond slight bending of the phase angle away from the vertical (-90°).
Figure 2—16. Overlay of impedance complex plane plots for x-ray amorphous x = 0.70 for 72% (◊) and 94% (∆) dense pellets vs. Li7P3S11 value from Yamane et al.70 measured at –50°C. The frequencies corresponding to tan δ_max (lower frequency) and M''_max (higher frequency) are indicated. An equivalent circuit is shown in the inset.

Table 2-3. Fit parameters for a resistor and constant phase element in parallel for the impedance data measured at -50 °C in Fig. 2-16.

<table>
<thead>
<tr>
<th>Sample Density (± 1.5 %)</th>
<th>R_Bulk (Ω·cm)</th>
<th>R_Bulk (Error %)</th>
<th>CPE_Bulk Q (Ω^2·cm^1·s^n)</th>
<th>CPE_Bulk Q (Error %)</th>
<th>CPE_Bulk n (Dimensionless)</th>
<th>CPE_Bulk n (Error %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>3.65 x 10^6</td>
<td>2.14</td>
<td>3.01 x 10^11</td>
<td>11.4</td>
<td>0.898</td>
<td>1.01</td>
</tr>
<tr>
<td>94</td>
<td>7.86 x 10^5</td>
<td>0.778</td>
<td>1.66 x 10^11</td>
<td>6.69</td>
<td>0.901</td>
<td>0.556</td>
</tr>
</tbody>
</table>

Bulk (rather than surface) conduction was found to be the dominant mechanism in 72 % and 94 % dense x-ray amorphous x = 0.70 since Bode plots of Z'' and M'' vs. log₁₀ f had both Z'' and M'' peaks (Fig. 2-17).
Figure 2—17. Geometry-normalized imaginary impedance and electrical modulus vs. logarithm of frequency showing thermal activation of $Z''$ (○) and $M''$ (Δ) relaxation peak values for $x = 0.70$, 72% (left) and 94% dense (right) pellets using the 1.98 g/cm³ Li₇P₃S₁₁ density value from Yamane et al. ⁷⁰. The $Z''$ scale changes an order of magnitude between each temperature frame, while the $M''$ scale remains unchanged. Instrument ranging offsets at ~ 30 kHz, which do not affect the frequencies of $M''$ peaks, have been smoothed. Pressure forming the 94% dense pellet at 213 °C did not induce crystallization. Recall that $M^* = j\omega C Z^*$. See Table 1-3 for more relationships between data representation formalisms.

Figure 2-18 shows another data representation method to demonstrate that high density is important for high conductivity. Jonscher’s universal dielectric response between the 72 % and 94 % dense $x = 0.70$ compacts is shown by plotting the real part of conductivity, which is the product of the angular frequency and the imaginary permittivity (Table 1-4).
Figure 2—18. Real conductivity vs. frequency for $x = 0.70$, 72% (left) and 94% dense (right) pellets of Li$_7$P$_3$S$_{11}$ value from Yamane et al. $^{70}$. Two frequency regions are observed: low frequency electrode response and intermediate frequency conduction relaxation.

Before analyzing the temperature dependence and extracting activation energy for ionic conduction, mixing laws are presented as an additional layer of analysis. Series and parallel connection mixing laws usually bound the behavior of measured electrical properties. Since the resistivity of pores is infinite, neither of these equations is helpful since they simplify to describe the effective resistivity as the product of the matrix resistivity and volume fraction of matrix. Ionic conductivity increases more than what is expected from scaling conductivity with compact density ($94/72 \sim 1.3$) since resistivity changes over an order of magnitude. Similar behavior of conductivity increases greater than what is expected from scaling by density is observed in conductivity studies of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ electrolytes $^{28}$.

In 1957, Reynolds and Hough published resistivity mixing laws for a continuous phase with a randomly dispersed phase $^{142}$. When the resistivity of the dispersed phase is greater than ten times the resistivity of the continuous matrix phase, the relationship between the effective resistivity and the continuous matrix phase resistivity is given by Eq. 2-3. In the case of
compacts with varying levels of porosity, the randomly dispersed phase consists of infinitely resistive pores.

$$\rho_{Effective} = \rho_{Matrix} \frac{V_{Pore}}{1+\frac{V_{Pore}}{2}}$$

(Eq. 2-3)

where

$\rho_{Effective} = \text{Effective resistivity (}\Omega\text{-cm})$

$\rho_{Matrix} = \text{Resistivity of the continuous matrix phase (}\Omega\text{-cm})$

$V_{Pore} = \text{Pore volume fraction (dimensionless)}$

Using the fit resistivity values in Table 2-3 as effective resistivities, matrix resistivities were calculated using Eq. 2-3. Taking the inverse of effective resistivity, a plot was generated to describe the expected bounds of effective conductivities for conductivity at -50 °C (Fig. 2-19). Given the error in the measured density and fit resistivity values, the error bars for propagation error in Fig. 2-19 are about the width of the line.

Figure 2—19. Effective conductivity at -50 °C for x = 0.70 calculated using Eq. 2-4 vs. volume fraction of pores. Effective conductivity is bounded by the matrix conductivity calculated from experimental data.
Figure 2-20 shows an ionic conductivity Arrhenius plot summarizing the temperature dependence. Activation energies are different and do not overlap given the error (± 0.01 eV for 72 % dense and ± 0.03 eV for 94 % dense). Literature reports and additional data are summarized in Table 2-4. As a result of the different activation energies, conductivities are similar at 25 °C. Therefore, other lithium thiophosphate compositions were studied in order to better isolate the individual effects of density and crystallinity on ionic conductivity.

![Figure 2—20. Arrhenius plot of ionic conductivity vs. inverse temperature for x = 0.70, 72 % and 94 % dense. Note that activation energy is more significant than the error (± 0.01 eV for 72 % and ± 0.03 eV for 94 % dense).]
Table 2-4. Arrhenius ionic conductivity properties of 0.70 Li$_2$S + 0.30 P$_2$S$_5$ synthesized by various methods

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\sigma_{25^\circ C}$ (Ω-cm)$^4$</th>
<th>$\log \sigma_o$ (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{Act}$ (eV)$^*$</th>
<th>Comments$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mizuno et al. $^{37}$</td>
<td>5.4 x 10$^{-5}$</td>
<td>4.2$^*$</td>
<td>0.39</td>
<td>MM glass</td>
</tr>
<tr>
<td>Zhang and Kennedy $^{143}$</td>
<td>1.60 x 10$^{-4}$</td>
<td>5.34</td>
<td>0.37</td>
<td>MQ glass</td>
</tr>
<tr>
<td>Trevey et al. $^{129}$</td>
<td>2.5 x 10$^{-4}$</td>
<td>- -</td>
<td>- -</td>
<td>SSBM 55$^\circ C$ 20 h, partially crystalline</td>
</tr>
<tr>
<td>Minami et al. $^{69}$</td>
<td>4.1 x 10$^{-4}$</td>
<td>3.2$^\ddagger$</td>
<td>0.33</td>
<td>Crystallized from melt 700$^\circ C$ 48 hr. then quenched</td>
</tr>
<tr>
<td>Seino et al. $^{144}$</td>
<td>1.0 x 10$^{-3}$</td>
<td>2.1$^\dagger$</td>
<td>0.30$^\dagger$</td>
<td>MQ glass, crystallized 290$^\circ C$ 5 h</td>
</tr>
<tr>
<td>Mizio et al. $^{37}$</td>
<td>3.2 x 10$^{-3}$</td>
<td>0.66$^\ddagger$</td>
<td>0.19</td>
<td>MM glass, crystallized 240$^\circ C$ 2 h</td>
</tr>
<tr>
<td>Minami et al. $^{69}$</td>
<td>4.1 x 10$^{-3}$</td>
<td>0.067$^\ddagger$</td>
<td>0.15</td>
<td>MQ glass, crystallized 360$^\circ C$ 1 h</td>
</tr>
<tr>
<td>Minami et al. $^{131}$</td>
<td>5.2 x 10$^{-3}$</td>
<td>1$^\ddagger$</td>
<td>0.12$^\ddagger$</td>
<td>MM, 210$^\circ C$ 0.5 h then 280$^\circ C$ 1 hr. in a hot press</td>
</tr>
<tr>
<td>This work</td>
<td>4.5 x 10$^{-5}$</td>
<td>2.4</td>
<td>0.40 ± 0.01</td>
<td>MM, 72 ± 1.5 % dense</td>
</tr>
<tr>
<td>This work</td>
<td>6.5 x 10$^{-5}$</td>
<td>1.1</td>
<td>0.31 ± 0.03</td>
<td>MM, 94 ± 1.5 % dense</td>
</tr>
</tbody>
</table>

**Table footnotes:** Data are presented as $\sigma = \sigma_o \exp \left( \frac{-\Delta E_{Act}}{k_B T} \right)$ rather than $\sigma = \left[ \sigma_o T \right] \exp \left( \frac{-\Delta E_{Act}}{k_B T} \right)$ and ordered by $\sigma_{25^\circ C}$. In literature, only Yamane et al. $^{70}$ has reported an experimental relative density value of 96% of Li$_7$P$_3$S$_{11}$ in a crystallized sample. Their data are not included in the table since no direct conductivity measurements were reported in their paper $^{70}$.

$^\dagger$ MM = Mechanically milled, MQ = Melt-quenched, SSBM = Single-step ball milled

$^*$ Calculated from $\sigma_{25^\circ C}$ and $\Delta E_{Act}$, assuming Arrhenius temperature dependence.

$^\ddagger$ Please see the footnote in Table 1-1.

$^\ddagger$ Estimated from an Arrhenius plot.

x Li$_2$S + (1-x) P$_2$S$_5$, x = 0.75

An impedance complex plane plot for 75% and 94% dense electrolytes measured at -60 $^\circ C$ is shown in Fig. 2-21. Using a single (R-CPE) element, fits are overlaid on Fig. 2-21 and fit parameters are summarized in Table 2-5.
Figure 2—21. Overlay of impedance complex plane plots for $x = 0.75$, 75% ($\Diamond$) and 94% ($\Delta$) dense pellets vs. $\gamma$-Li$_3$PS$_4$ (Homma et al. 74) measured at -60 °C. The frequencies corresponding to $\tan \delta_{\text{max}}$ and $M''_{\text{max}}$ are indicated. An equivalent circuit is shown in the inset.

Table 2-5. Fit parameters for a resistor and constant phase element in parallel for the impedance data measured at -60 °C in Fig. 2-21.

<table>
<thead>
<tr>
<th>Sample Density (± 1.5 %)</th>
<th>R$_{\text{Bulk}}$ (Ω-cm)</th>
<th>R$_{\text{Bulk}}$ (Error%)</th>
<th>CPE$_{\text{Bulk}}$ Q (Ω$^{-1}$-cm$^{-1}$-s$^{-n}$)</th>
<th>CPE$_{\text{Bulk}}$ Q (Error%)</th>
<th>CPE$_{\text{Bulk}}$ n (Dimensionless)</th>
<th>CPE$_{\text{Bulk}}$ n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>2.03 x 10$^6$</td>
<td>1.39</td>
<td>1.55 x 10$^{-11}$</td>
<td>9.23</td>
<td>0.897</td>
<td>0.819</td>
</tr>
<tr>
<td>94</td>
<td>4.06 x 10$^5$</td>
<td>1.56</td>
<td>2.20 x 10$^{-11}$</td>
<td>14.9</td>
<td>0.870</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Density of the amorphous phase can be calculated from Eq. 2-4. For 10 vol. % $\gamma$-Li$_3$PS$_4$, in what is called the “94% dense $x = 0.75$” sample, the density of the amorphous phase is within ± 1.5 % error of the $\gamma$-Li$_3$PS$_4$ value. Tachez et al. has reported crystalline $\gamma$-Li$_3$PS$_4$ to have an ionic conductivity at 25 °C of 2.6 x 10$^{-7}$ (Ω-cm)$^{-1}$ and activation energy of 0.49 ± 0.02 eV 105.
Therefore, Eq. 2-3 is still valid since the dispersed $\gamma$-Li$_3$PS$_4$ phase is more than an order of magnitude more resistive than the continuous phase.

$$\rho_{\text{Measured}} = \sum_i V_i \rho_i \quad \text{(Eq. 2-4)}$$

where

$\rho_{\text{Measured}} =$ Measured density (g/cm$^3$)

$V_i =$ Volume fraction of phase $i$ (dimensionless)

$\rho_i =$ Density of phase $i$ (g/cm$^3$)

Fit resistivity values in Table 2-5 were taken as effective resistivities and matrix resistivities were calculated using Eq. 2-3. A plot was generated to describe the expected bounds of effective conductivities for conductivity at -60 °C (Fig. 2-22). Similar to $x = 0.70$, given the error in the measured density and fit resistivity values, the error bars for propagation error in Fig. 2-22 are about the width of the line.

Figure 2-23 shows an Arrhenius plot of samples of 75 % and 94 % density. Conduction properties, including literature data, are summarized in Table 2-6. In $x = 0.70$, the activation energy change is too large to make a conclusion about bulk conduction. In $x = 0.75$, no strong link can be drawn between ionic conductivity and density since the influence of crystallinity could not be clearly be separated from the influence of densification. Another composition ($x = 0.80$) was studied in an attempt to draw a strong link between ionic conductivity and density.
Figure 2—22. Effective conductivity at -60 °C for x = 0.75 calculated using Eq. 2-4 vs. volume fraction of pores. Effective conductivity is bounded by the matrix conductivity calculated from experimental data.

Figure 2—23. Arrhenius plot of ionic conductivity vs. inverse temperature for x = 0.75, 75 % and 94 % dense. Activation energies are reported ± 0.01 eV.
Table 2-6. Arrhenius ionic conductivity properties of 0.75 Li$_2$S + 0.25 P$_2$S$_5$

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\sigma_{25^\circ\mathrm{C}}$ (Ω-cm)$^{-1}$</th>
<th>$\log \sigma_\infty$ (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ $^*$ (eV)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayashi et al.</td>
<td>1.9 x $10^{-4}$</td>
<td>2.36</td>
<td>0.36</td>
<td>MM glass, 20 h</td>
</tr>
<tr>
<td>Hayashi et al.</td>
<td>2.6 x $10^{-4}$</td>
<td>1.35</td>
<td>0.29</td>
<td>MM glass and crystallized during impedance measurement</td>
</tr>
<tr>
<td>Trevey et al.</td>
<td>2.5 x $10^{-4}$</td>
<td>- - -</td>
<td>- - -</td>
<td>SSBM 55°C 20 h, included Thio-LISICON III and Li$_7$P$<em>3$S$</em>{11}$</td>
</tr>
<tr>
<td>Tachez et al.</td>
<td>2.6 x $10^{-7}$</td>
<td>1.63</td>
<td>0.49</td>
<td>Phase transition at 190 °C</td>
</tr>
<tr>
<td>Liu et al.</td>
<td>1.6 x $10^{-4}$</td>
<td>2.41</td>
<td>0.36</td>
<td>Nanoporous β-Li$_3$PS$_4$</td>
</tr>
<tr>
<td>This work</td>
<td>1.2 x $10^{-4}$</td>
<td>2.33</td>
<td>0.37 ± 0.01</td>
<td>MM, 71 ± 1.5 % dense</td>
</tr>
<tr>
<td>This work</td>
<td>6.5 x $10^{-5}$</td>
<td>2.53</td>
<td>0.36 ± 0.01</td>
<td>MM, 75 ± 1.5 % dense</td>
</tr>
<tr>
<td>This work</td>
<td>1.6 x $10^{-4}$</td>
<td>2.45</td>
<td>0.37 ± 0.01</td>
<td>MM, 75 ± 1.5 % dense</td>
</tr>
<tr>
<td>This work</td>
<td>5.8 x $10^{-4}$</td>
<td>2.58</td>
<td>0.34 ± 0.01</td>
<td>MM, 94 ± 1.5 % dense, 10 vol. % γ Li$_3$PS$_4$</td>
</tr>
</tbody>
</table>

$^*$ Please see the footnote in Table 1-1.

x Li$_2$S + (1-x) P$_2$S$_5$, x = 0.80

The composition x = 0.80 was selected for understanding densification without changes in the amount of background crystallinity. Further, the crystallization behavior was studied and micrographs are shown in Appendix A.

An impedance complex plane plot for 71% and 94% dense x = 0.80 is shown in Fig. 2-24. Using a single (R-CPE) circuit, three fitting parameters are sufficient to describe the observed bulk semicircle (Fig. 2-24). Fitting parameters and their error values are shown in Table 2-7. Since Li$_2$S is an insulator with a 25 °C ionic conductivity of $10^{-13}$ (Ω-cm)$^{-1}$ $^{145}$, the dispersed pores and Li$_2$S are highly insulating with respect to the matrix phase and Eq. 2-3 can be used to generate bounds for the effective resistivity as a function of volume fraction of pores. The effective conductivity is plotted in Fig. 2-25 using Eq. 2-3. Arrhenius behavior is observed (Fig. 2-26) and x = 0.80 results are compared to those in literature (Table 2-8).
Figure 2—24. Overlay of impedance complex plane plots for $x = 0.80$, 71% (◊) and 94% (∆) dense pellets vs. multiphase mixture measured at -70 °C. The frequencies corresponding to $\tan \delta_{\text{max}}$ and $M''_{\text{max}}$ are indicated. An equivalent circuit is shown in the inset.

Table 2-7. Fit parameters for a resistor and constant phase element in parallel for the impedance data measured at -70 °C in Fig. 2-24.

<table>
<thead>
<tr>
<th>Sample Density (± 1.5 %)</th>
<th>R_Bulk (Ω-cm)</th>
<th>R_Bulk (Error %)</th>
<th>CPE_Bulk Q (Ω^-1-cm^-1-s^n)</th>
<th>CPE_Bulk Q (Error %)</th>
<th>CPE_Bulk n (Dimensionless)</th>
<th>CPE_Bulk n (Error %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>1.63 x 10^7</td>
<td>0.754</td>
<td>1.81 x 10^-11</td>
<td>3.55</td>
<td>0.934</td>
<td>0.364</td>
</tr>
<tr>
<td>94</td>
<td>1.77 x 10^6</td>
<td>1.16</td>
<td>1.17 x 10^-11</td>
<td>7.82</td>
<td>0.920</td>
<td>0.646</td>
</tr>
</tbody>
</table>
Figure 2—25. Effective conductivity at -70 °C for \( x = 0.80 \) calculated using Eq. 2-4 vs. volume fraction of pores. Effective conductivity is bounded by the matrix conductivity calculated from experimental data.

Figure 2—26. Arrhenius plot of ionic conductivity vs. inverse temperature for \( x = 0.80, 71\%, 81\%, \text{ and } 94\% \text{ dense}. \) Activation energies are reported ± 0.01 eV.
Table 2-8. Arrhenius ionic conductivity properties of 0.80 Li$_2$S + 0.20 P$_2$S$_5$

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\sigma_{25^\circ}$ (Ω·cm)$^{-1}$</th>
<th>$\log \sigma_0$ (Ω·cm)$^{-1}$</th>
<th>$\Delta E_{act}$ (eV)*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayashi et al. $^{121}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>2.30</td>
<td>0.37</td>
<td>MM glass, 20 h</td>
</tr>
<tr>
<td>Hayashi et al. $^{68}$</td>
<td>$6.7 \times 10^{-4}$</td>
<td>2.65</td>
<td>0.34</td>
<td>MM glass and crystallized during impedance measurement</td>
</tr>
<tr>
<td>Trevey et al. $^{129}$</td>
<td>$1 \times 10^{-3}$</td>
<td>-</td>
<td>-</td>
<td>SSBM 55°C 20 h, included Thio-LISICON III, Li$_2$S, Li$_7$P$<em>3$S$</em>{11}$, and a new crystal</td>
</tr>
<tr>
<td>This work</td>
<td>$4.2 \times 10^{-5}$</td>
<td>1.71</td>
<td>0.36 ± 0.01</td>
<td>MM, 71 ± 1.5% dense, residual Li$_2$S</td>
</tr>
<tr>
<td>This work</td>
<td>$1.1 \times 10^{-4}$</td>
<td>2.62</td>
<td>0.39 ± 0.01</td>
<td>MM, 81 ± 1.5% dense, residual Li$_2$S</td>
</tr>
<tr>
<td>This work</td>
<td>$3.6 \times 10^{-4}$</td>
<td>2.65</td>
<td>0.36 ± 0.01</td>
<td>MM, 94 ± 1.5% dense, residual Li$_2$S</td>
</tr>
</tbody>
</table>

* Please see the footnote in Table 1-1.

Starting with 94% dense compacts of x = 0.80 pressure-formed at 190 °C, crystallization was performed at 300, 350, and 410 °C. Lithium volatility was controlled during crystallization by covering the pellet in a powder bed of the same composition. This experimental procedure is described in Fig. 3-4. After crystallization, density does not change relative to the as-pressed density beyond the error (± 1.5 %). An example impedance complex plane plot is shown in Fig. 2-27 for measurements performed at -60 °C. A single semicircle can be observed. Using a single (R-CPE) circuit, CPE $Q$ and $n$ can be fit and shown as a function of measurement temperature (Fig. 2-28).

![Figure 2-27. Overlay of impedance complex plane plots for x = 0.80, 90% dense pellets crystallized at 300, 350, and 410 °C & measured at -60 °C.](image-url)
Figure 2—28. Dependence of $Q$ on measurement temperature (a) and dependence of $n$ on measurement temperature (b) for crystallization temperatures of 300, 350, and 410 °C. Error bars are shown for fitting errors.

From Fig. 2-28, it is evident that fit parameters for 300 and 350 °C do not vary beyond what is expected from the error bars. For crystallization at 410 °C, the $Q$ and $n$ parameters deviate at higher temperature. It makes sense that $Q$ increases with temperature since, in the capacitance-like $Q$ term, there are more mobile Li-ions available to form a double layer at the blocking electrode-electrolyte interface. When $n$ deviates from 1, the semicircle becomes more depressed and the complex plane axes rotate clockwise (Fig. 1-13). The Arrhenius behavior of the 94% density pellet and 94% density pellets after crystallization at 300, 350, and 410 °C is shown in Fig. 2-29 and parameters. High temperature crystallization at 410 °C increases activation energy outside of the expected ± 0.01 eV error for the starting 94% dense pellets prior to heat treatment since the activation energy after 410 °C crystallization may be as low as 0.40 eV, while the starting activation energy can be as high as 0.38 eV.
Figure 2—29. Arrhenius plot of ionic conductivity vs. inverse temperature for $x = 0.80$, 94% dense pellets before crystallization and after crystallization temperatures of 300, 350, and 410 °C. Activation energies are reported ± 0.01 eV.

Table 2-9. Arrhenius ionic conductivity properties of 94% dense, crystallized 0.80 Li$_2$S + 0.20 P$_2$S$_5$

<table>
<thead>
<tr>
<th>Crystallization Temperature (°C)</th>
<th>$\sigma_{25^\circ\text{C}}$ ($\Omega\cdot\text{cm})^{-1}$</th>
<th>$\log \sigma_0$ ($\Omega\cdot\text{cm})^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$8.0 \times 10^{-4}$</td>
<td>3.20</td>
<td>$0.37 \pm 0.01$</td>
</tr>
<tr>
<td>350</td>
<td>$9.6 \times 10^{-4}$</td>
<td>3.80</td>
<td>$0.40 \pm 0.01$</td>
</tr>
<tr>
<td>410</td>
<td>$7.1 \times 10^{-4}$</td>
<td>3.92</td>
<td>$0.42 \pm 0.01$</td>
</tr>
</tbody>
</table>
Chapter Conclusions

Better understanding of densification in electrolytes enables battery development. Mechanical milling was the synthesis technique of choice for making x-ray amorphous lithium thiophosphate electrolyte powders with high loadings of Li$_2$S glass modifier. Densification curves were reported for $x = 0.70$, $0.75$, and $0.80$. Employing a phenomenological model developed by Murray et al. $^{136}$, viscous flow was predicted to strongly influence densification above $160$ °C. The densification curves were fit empirically with a slope-intercept equation with $R^2$ values greater than 0.97. Literature would benefit from additional fundamental studies of the thermal and mechanical behavior of lithium thiophosphate electrolytes since densification can occur at $25$ °C using uniaxial pressures $\sim 400$ MPa. Insight into coupled thermal, mechanical, and electrochemical relaxation is key to discovery of superionic structures available from non-equilibrium processing methods.

X-ray diffraction was used to probe the structures of mechanically milled electrolyte powders, milled powders after pressure-forming to 95% density, and pressure-formed pellets after crystallization. Mechanically milled electrolyte powders and milled powders densified by pressure-forming were not all x-ray amorphous. However, meaningful comparisons of ionic conductivity could be made within the same composition because no changes were observed between the x-ray diffraction patterns for samples of different density.

Impedance spectroscopy below $25$ °C showed thermally-activated conductivity relaxations that could be fit with a single (R-CPE) equivalent circuit. In terms of the bulk electrolyte properties, density is decisively important for the $0.80$ Li$_2$S + $0.20$ P$_2$S$_5$ composition.
In both batteries and electrochemical capacitors, a fundamental understanding of whether surface or bulk conduction dominates is important. The systematic improvement of ionic conductivity with increased density suggests that bulk conduction dominates surface conduction. For $x = 0.70$ at -70 °C, the 94% dense sample had ~ 5 times higher conductivity than the 72% dense sample. For $x = 0.75$ at -70 °C, the 94% dense sample had ~ 5 times higher conductivity than the 75% dense sample. For $x = 0.80$ at -70 °C, the 94% dense sample had ~ 10 times higher conductivity than the 71% dense sample.

However, only in the $x = 0.80$ composition could crystallinity effects be ruled out. The strongest evidence for bulk conduction is in $x = 0.80$ where the effects of densification and crystallization could be isolated by the fact that crystallization causes increases in the activation energies for conduction.

In addition to important fundamental studies regarding the mechanical and thermal behavior, there remain opportunities for novel device integration at lower temperature windows. With thermochemically compatible electrodes, employing multilayer ceramic capacitor manufacturing techniques at low temperatures has the potential to significantly advance the device integration of solid electrolytes in solid-state electrochemical devices. The next chapter addresses the engineering challenge of making thin, large area format electrolytes.
Chapter 3

Powder-in-a-Tube Processing of Lithium Thiophosphate Solid Electrolytes

Chapter Overview

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 tapes and 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 25 °C ionic conductivities reach $10^{-3} (\Omega\cdot\text{cm})^{-1}$ in both rolled PIT and pelletized 0.70 Li$_2$S + 0.30 P$_2$S$_5$ (mol fraction) lithium thiophosphate solid electrolytes crystallized to form Li$_7$P$_3$S$_{11}$ after heat treatment between 260 and 280 °C.

Chapter Introduction

In organic liquid electrolyte batteries, interfacial resistance contributions between electrode/liquid electrolyte interfaces are much lower than the resistance contributions from electrode/solid electrolyte interfaces in solid electrolyte batteries. 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. The common metric is ionic area specific resistance, the product of ionic resistivity and thickness (*Eq. F-1*). Solid electrolytes must have a minimum thickness to
maintain 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 146.

Powder-in-a-tube (PIT) processing allows electrolyte densification and naturally creates thin electrolytes that are hermetically encapsulated in a metal sheath. After encapsulation, PIT can be carried out by conventional rolling in ambient atmosphere. PIT was pioneered by the superconducting community to create textured ceramic tapes and wires 147-151 and is a low-cost, solvent-free, non-vacuum technique. A process flow schematic from Freyhardt and Hellstrom 148 is shown in (Fig. 3-1). PIT can be seen as a high throughput, semi-continuous process since long tubes could be filled with electrolyte powder and fed through rollers for electrolyte sheet yield lengths in the tens of meters.

![Process Flow schematic from Freyhardt and Hellstrom](image)

**Figure 3—1. Typical flowchart for making superconducting wires by PIT adapted from Freyhardt and Hellstrom** 148.

In PIT, rolling weakly-bonded glasses, such as chalcogenides with 215°C glass transition temperatures, are proposed to create high density, pre-formed electrolytes. The 0.70 Li₂S + 0.30
P$_2$S$_5$ 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$^{37,70,152}$. X-ray diffraction and impedance spectroscopy results are used to characterize the phases and ionic conductivities, respectively. Property comparisons to Li$_2$S + P$_2$S$_5$ processed by milling and pressure-temperature-assisted densification are made to ensure there is no deleterious impact on ionic conductivity from PIT. A comparison of a superconducting ceramic sandwich and idealized sulfide electrolyte sandwich is shown in (Fig. 3-2).

![Figure 3—2. Example of Ag - YBa$_2$Cu$_3$O$_x$ - Ag microstructure from Korzekwa et al. $^{151}$ (left) and idealized sulfide electrolyte sandwich sheathed between Al (right).](image)

**Experimental Methods**

**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 for 14 h, and taken into an Ar glovebox. One end of the tube was crimped and mechanically milled, glassy 0.70 Li$_2$S + 0.30 P$_2$S$_5$ electrolyte powder (milled for 14 hours at 370 rpm) was loaded into the tube. Milling
procedures are detailed in Chapter 2. 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. A detailed experimental schematic is shown in Fig. 3-3.

Figure 3—3. Detailed experimental schematic for PIT. The roller image was annotated by Rangarajan 153.
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 volatility near the electrolyte surface (Fig. 3-4). The brass mold was centered on a hot plate (IKA Works, Ceramag Midi) and was heated at 40 °C/min from 25 °C to the desired temperature. After reaching the desired temperature, the hot plate was turned off and allowed to cool to 25 °C.

Figure 3—4. Lithium volatility was controlled by covering the rolled PIT electrolyte with lithium thiophosphate powder of the same composition during firing.

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 following methods established in Chapter 2.
**Scanning Electron Microscopy**

Scanning electron micrographs were obtained on uncoated fracture surfaces (NanoSEM 630, FEI, Hillsboro, OR). To prevent air exposure, a transfer cell designed by Gordin was employed.

**Impedance Spectroscopy**

PIT electrolytes were electroded with silver paste, 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 as in Chapter 2.

**Results & Discussion**

**Powder-in-a-Tube Rolling and Densification**

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 total electrolyte thickness. In a thick wall Al tube, the sheathed electrolyte thickness reached 120 μm after five passes (Fig. 3-5). Dimensional changes of electrolyte and electrolyte density vs. pass number for a thin wall Al-electrolyte-Al sandwich structure are reported in Fig. 3-6. The 66 ± 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. With the weak dependence of
strain rate on maximum imparted pressure 155, warm (160 °C) rolling is important to achieve high density 104.

![Image](image_url)

**Figure 3—5.** Demonstration of thin, continuous electrolytes. *Left:* Polished cross-sections of thick wall Al-electrolyte-Al sandwich at 12x after pass 3, 4, and 5. Further rolling caused the tube wall to be breached and the sulfide electrolyte to be detrimentally exposed to air. *Right:* Top view of thick wall Al-electrolyte-Al sandwich with pass numbers, total thicknesses, and electrolyte thicknesses.

![Graph](graph_url)

**Figure 3—6.** Dimensional changes of electrolyte and electrolyte density vs. pass number for thin walled Al-electrolyte-Al sandwich structure.
Two sintering processes have been applied to densify lithium thiophosphates: uniaxial pressing at 25 °C and uniaxial pressing during heating. Densification at lower temperatures is important when species are volatile. In 0.75 Li₂S + 0.25 P₂S₅, greater than 90% relative density can be achieved at 25 °C when pressing glassy powder to 400 MPa rather than requiring external thermal energy to densify. 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 rolling density (ρ) is a function of pressure (P), temperature (T), time (t), and metal tube material (M). An iso-density function ρ(P, T, t, M) is important for tuning warm roll-on-roll processes, for potential continuous production of thin PIT solid electrolytes.

**X-ray Diffraction of Milled Powder; Milled & Rolled Powder; Milled, Rolled, & Crystallized Powder**

As-milled powders are x-ray amorphous (Fig. 3-7). Room temperature rolling does not cause crystallization. Differential scanning calorimetry results show the onset of the crystallization exotherm is 257 °C (Fig. 2-6). When crystallized above 257 °C, a superionic Li₇P₃S₁₁ phase forms consistent with Yamane et al.
Figure 3—7. X-ray diffraction patterns of milled 0.70 Li$_2$S + 0.30 P$_2$S$_5$ (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 Li$_7$P$_3$S$_{11}$ after $^{70}$ (JCPDS 04-014-8383) and density values are relative to 1.98 g/cm$^3$.

Scanning Electron Microscopy of Crystallized Sheet Electrolytes

X-ray amorphous electrolyte (66% dense) after PIT was compared to the same electrolyte after crystallization at 262 °C (Fig. 3-8). Some densification is observed but could not be quantified through a geometric density measurement. Archimedes density in mineral oil may show densification outside of the measurement error range. Comparing to literature, similar sized
1 μm pores are seen in the work of for 0.75 Li$_2$S + 0.25 P$_2$S$_5$ hot pressed between 130 °C to 170 °C at pressures over 350 MPa. Although the composition in **Fig. 3-8** differs from Mendez, Sakuda et al. shows that the mechanical properties, and hence the densification characteristics, between 0.70 Li$_2$S + 0.30 P$_2$S$_5$ and 0.75 Li$_2$S + 0.25 P$_2$S$_5$ are very similar.

**Figure 3—8.** Micrographs of fracture surfaces of 120 μm thick rolled 0.70 Li$_2$S + 0.30 P$_2$S$_5$ (left) and rolled 0.70 Li$_2$S + 0.30 P$_2$S$_5$ after crystallization at 262 °C (right).

**Impedance Spectroscopy of Crystallized Pellet and Sheet Electrolytes**

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. 3-9**). 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.
Figure 3—9. 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. \(^{37}\) and Berbano et al. \(^{104}\) from a crystallized pellet are shown. Activation energies are reported ± 0.02 eV.

Arrhenius ionic conductivity behavior can be described by \(\sigma = \sigma_o \exp\left(-\frac{\Delta E_{Act}}{k_BT}\right)\), where \(\sigma_o\) is the pre-exponential factor describing the ionic conductivity at the maximum temperature. Arrhenius behavior is observed (\(\Omega\)-cm\(^{-1}\)), \(\Delta E_{Act}\) 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. \(^{37}\). Density was not reported in \(^{37}\), but a pressure of 363 MPa was used and is estimated to yield 77 ± 2% density \(^{77}\). High density is important for high ionic conductivity when bulk conduction dominates surface conduction \(^{87, 104}\).
Chapter Conclusions

Powder-in-a-tube (PIT) processing was used to create 120 μm electrolytes. Thin electrolytes with high ionic conductivity are important for low area 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). In particular, the tube’s mechanical properties may be key to high density at 25 °C and preventing the tube from being breached after five passes. If warm rolling is done at 160 °C and 150 MPa, it is estimated that 90% dense 0.70 Li$_2$S + 0.30 P$_2$S$_5$ electrolytes can be made in Al 3003 tubes. 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. Focus in the next chapter will shift to novel processing of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$, which was synthesized through melt-quenching of glass and crystallization. The results of crystallized Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ are later compared with Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ densified at unprecedentedly low temperatures using cold sintering.
Chapter 4

Grain Conductivity Stability in Lithium Aluminum Germanium Phosphate Solid Electrolytes Synthesized by Crystallization of Bulk Glasses

Chapter Overview

The focus of this chapter shifts from lithium thiophosphate solid electrolytes to lithium aluminum germanium phosphate (LAGP) solid electrolytes. The goal of this chapter is to establish that the grain conductivity for many sets of crystallization conditions is stable.

Chapter Introduction

Oxide and Sulfide Electrolytes: A Story of Tradeoffs

From the start of the solid ionics field, non-oxides like Ag$_2$S and PbF$_2$ have been of interest. To quote Faraday directly in 1833 $^{157}$ “There is no other body with which I am acquainted, that, like sulphuret of silver, can compare with metals in conducting power for electricity…” Later in 1838 Faraday writes $^{158}$ “I formerly described a substance, sulphuret of silver, whose conducting power was increased by heat; and I have since then met with another as strongly affected in the same way: this is fluoride of lead.”

In the 180 years that have passed, numerous electrolytes have been discovered. A plot of all the systems studied would include single crystals, ceramics, glasses, polymer-in-salt electrolytes, gel (salt-in-organic solvent and polymer) electrolytes, ionic liquids, organic
electrolytes, and aqueous electrolytes with mobile ion species including Li⁺, Na⁺, K⁺, Cs⁺, Ag⁺, O²⁻, F⁻. Kato et al. highlights a few systems from the last 45 years of progress for Li⁺ and Na⁺ conductors (Fig. 4-1).

![Figure 4—1. Lithium and sodium-ion electrolyte ionic conductivity vs. year discovered from Kato et al.](image-url)

Focus will now be given to the merits and demerits present in oxide and sulfide electrolytes. Their processing and properties tell a story of tradeoffs (Table 4-1). Pronounced demerits are shown in red text, while important opportunities are shown in green text. As a result of the perceived merits and demerits, some reports combine oxide and sulfide electrolytes to take advantage of an oxide electrolyte’s electrochemical stability and a sulfide electrolyte’s ability to be densified at 25 °C in a bi-layer structure. Alternatively, oxide electrolyte core/sulfide electrolyte shell has been fabricated to take advantage of 25 °C densification of sulfide
electrolytes. This approach of combining different types of electrolytes is analogous to ceramic-in-polymer composite electrolytes where tradeoffs exist in terms of mechanical flexibility (polymer advantage), lithium dendrite penetration (polymer disadvantage), and transference number (polymer disadvantage). Table 4-1 conveys that stable, high ionic conductivity oxide electrolytes need not necessitate densification at high temperature as long as their grain boundary impedance is minimized. Higher temperature, as explained in Chapter 1, usually is accompanied by higher processing costs. However, total processing costs not only include the thermal energy input, but should also include raw material costs, as well as capital investment for equipment and other factors (Appendix C).

<table>
<thead>
<tr>
<th>Considerations</th>
<th>Oxides</th>
<th>Sulfides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Somewhat H₂O and CO₂ sensitive (will form Li₂CO₃)</td>
<td>More air-sensitive (generates toxic H₂S)</td>
<td></td>
</tr>
<tr>
<td>Higher temperature processing (melt-quenching glass and crystallization, conventional sintering, solution processing, spark plasma sintering)</td>
<td>Lower temperature processing (mechanical milling)</td>
<td></td>
</tr>
<tr>
<td>650 °C densification with spark plasma sintering 120 °C densification with cold sintering</td>
<td>25 °C densification with ~ 400 MPa</td>
<td></td>
</tr>
<tr>
<td><strong>Property</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower ionic conductivity than sulfide electrolytes unless superionic structure. Conductivity difference amorphous and superionic structure can be 5+ orders of magnitude in the case of Li₁ₓAlₓGe₂-x(PO₄)₃, 0.30 &lt; x &lt; 0.70 and residual amorphous phase is detrimental.</td>
<td>Ionic conductivity difference between amorphous and crystalline x Li₂S + (1-x) P₂S₅, 0.70 &lt; x &lt; 0.80 is small (can be less than an order of magnitude in x = 0.80 for crystallization &lt; 350 °C).</td>
<td></td>
</tr>
<tr>
<td>Grain boundary impedance can be very large</td>
<td>Grain boundary impedance often very low</td>
<td></td>
</tr>
<tr>
<td>7 to 9% Li/formula unit in Li₁ₓAlₓGe₂-x(PO₄)₃, 0.30 &lt; x &lt; 0.70</td>
<td>33 to 42% Li/formula unit in x Li₂S + (1-x) P₂S₅, 0.70 &lt; x &lt; 0.80</td>
<td></td>
</tr>
<tr>
<td>Higher mechanical moduli to stop Li dendrites</td>
<td>Lower mechanical moduli may stop Li dendrites and allow for better strain accommodation during galvanostatic cycling</td>
<td></td>
</tr>
<tr>
<td>Some garnet electrolytes stable vs. Li metal</td>
<td>Li₀.₈P₀.₈S₁₂ stable vs. Li metal</td>
<td></td>
</tr>
</tbody>
</table>
Oxide Electrolytes: Grain Boundary Impedance Variation with Processing

In Table 4-1, tradeoffs between oxide and sulfide electrolytes were acknowledged. In order to pave a way forward to lower grain boundary impedance of oxide electrolytes, it must first be established that grain boundary impedance is a strong function of extrinsic processing conditions, while grain impedance is a weak function of extrinsic processing conditions. To this end, various crystallization times and temperatures were employed on “uncovered” samples. Then, a fixed crystallization time and temperature was employed to study “covered” samples.

Experimental Methods

Glass-Ceramic Electrolyte Preparation

Glass melting and crystallization procedures were followed as detailed elsewhere \(^{102}\). Stoichiometric amounts of Li\(_2\)CO\(_3\) (Alfa Aesar, 99%), Al\(_2\)O\(_3\) (Tape Casting Warehouse, Inc.), GeO\(_2\) (Alfa Aesar, 99.98%), and NH\(_4\)H\(_2\)PO\(_4\) (Alfa Aesar, 98%) were ball milled for 24 h, calcined in air at 750 °C for 30 min, and again ball milled for 24 h. Milled powder was placed in a covered alumina crucible and melted in air at 1380 °C for 1 h before being splat-quenched. Splat-quenched glass was annealed at 450 °C for 3.75 h and crystallized in air with a ramp rate of 3 °C/min. To show extrinsic processing effects, some samples denoted as “covered” were fired. “Covered” samples were fired on an alumina plate and covered with an alumina crucible that was re-used from glass melting.
**Differential Scanning Calorimetry**

About 40 mg of ground, annealed glass powder was loaded into an alumina pan. Thermograms were collected in air at a heating rate of 10 °C/min (2960 SDT, TA Instruments, New Castle, DE).

**X-ray Diffraction**

XRD patterns were collected using methods established in Chapters 2 and 3. Unlike Chapters 2 and 3, powder holders were not covered with Kapton tape.

**Scanning Electron Microscopy**

Scanning electron micrographs were obtained on fracture surfaces or fractured, polished, & thermally etched surfaces sputter coated with Au (NanoSEM 630, FEI, Hillsboro, OR). Thermal etching took place in air on samples polished to 4000 grit that were fired for 30 minutes below the temperature that the bulk glass was crystallized.

**Impedance Spectroscopy**

Impedance spectroscopy samples were prepared by polishing glass-ceramics to 4000 grit SiC and sputtering symmetric 100 nm thick Au or Pt blocking electrodes (Q150R, Quorum Technologies, Laughton, UK). Temperature-dependent measurements were collected using a N2-purged, temperature-controlled chamber (9023, Delta Design, Poway, CA). Thermal equilibrium of the sample was determined from overlapping impedance spectra. Complex impedance spectra
were measured using an impedance analyzer with a sinusoidal voltage amplitude 50 mV vs. OCV for 0.01 Hz $\leq f \leq$ 1 MHz (Solartron Analytical AMETEK, ModuLab, Oak Ridge, TN). Data were corrected for sample geometry and analyzed using ZView® (Version 3.4f, Scribner Associates Inc., Southern Pines, NC) 73.

**Results & Discussion**

**Differential Scanning Calorimetry of Glass Powders**

Differential scanning calorimetry was performed on $x = 0.50$ LAGP glass to locate the glass transition and crystallization onset temperatures, 535 °C and 629 °C, respectively (Fig. 4-2). Glass transition and crystallization onset temperatures were used to design electrolytes with very different microstructures. In literature, studies have been performed on the crystallization kinetics of LAGP. Three reports claim bulk (volume) crystallization from the Avrami exponents or the coincidence of DSC crystallization peaks for monolithic and powder samples, which indicates that the glass nucleated internally 56, 164.
Figure 4—2. Differential scanning calorimetry thermogram of \( x = 0.50 \) LAGP glass shows a \( T_g \) at 535°C determined by the tangent method and crystallization onset at 629°C.

**X-ray Diffraction of Glasses Crystallized Uncovered and Covered**

Room temperature X-ray diffraction (XRD) patterns of LAGP glass after six different heat treatments are shown in [Fig. 4-3](#). Single-step heat treatments and two-step heat treatments, which included a nucleation step slightly above \( T_g \) as done by Cruz et al. 56, were studied. X-ray diffraction patterns and crystallite sizes were determined from peak full with at half maximum (FWHM) changes ([Fig. 4-4](#)).

As in [Table 1-1](#) and the sintering discussion of Chapter 1, many methods exist for densification. Starting powders can be made by a series of calcination and mixing steps 51, crystallizing bulk glass 50,52,53,55-57, or the flame creation method (FCM) 26.

In literature, GeO\(_2\) impurities were assigned for the x-ray diffraction peak at 25.8 degrees 2\( \theta \) for heat treatment at 850 °C, 2 h and 950 °C, 2 h 26. In the case of the 850 °C, 2 h heat
treatment, there was no AlPO$_4$ impurity paired with the GeO$_2$ impurity. In the case of the 950 °C, 2 h heat treatment, AlPO$_4$ was paired with the GeO$_2$ impurity. When 20 % excess lithium carbonate was added to a batch and after sintering for 800 °C, 2 h, GeO$_2$ was identified as a lone impurity phase $^{52}$. Last, AlPO$_4$ was identified as a lone impurity phase for an 825 °C, 8 h $^{55}$. From a charge and mass balance perspective, it makes more sense that purity phases would be paired together.

As a result of the conflicting conclusions in literature, it is important to clarify the presence or absence of GeO$_2$ in the LAGP synthesized in this thesis. As a first check, x-ray diffraction is used. The implications of the presence of GeO$_2$ would impact the processing methods in Chapters 5 and 6. The cold sintering processing method makes use of water and GeO$_2$ is known to be water soluble (4.5 g/L for hexagonal GeO$_2$ at 25 °C and 5.2 g/L for amorphous GeO$_2$ at 30 °C), but is insoluble for tetragonal GeO$_2$ at 25 °C $^{165}$.

In the PDF card of LiGe$_2$(PO$_4$)$_3$, a peak appears at a similar position as GeO$_2$. To better confirm or deny the presence of GeO$_2$ in LAGP synthesized in this thesis, lattice parameters were fit for experimental XRD patterns without considering GeO$_2$. Then, fixing the lattice parameters, the same patterns were re-fit allowing for the presence of GeO$_2$. If the angle difference for the peak thought to be either GeO$_2$ or LAGP was < 0.03 degrees 2θ, the presence of GeO$_2$ was ruled out. Similar to $^{26}$, at 950 °C, 2 h, 2 ± 1 vol. % GeO$_2$ and 5 ± 1 vol. % AlPO$_4$ is observed. In this case, the rejection criteria of 0.04 degrees 2θ was met. This result shows that high temperature heat treatments compromise phase purity and it would be useful to study the structures of LAGP subjected to even higher heat treatments to see if fractions of impurity phases increase or if they decrease to volatilization.
Archimedes densities in mineral oil were determined to be near $90 \pm 1.5\%$ theoretical density for phase pure $x = 0.50$ LAGP ($0.90*3.43$ g/cm$^3$). However, the LAGP glass crystallized at 950 °C, 2 h, has an indeterminate amount of phase pure LAGP, amorphous phase, GeO$_2$, and AlPO$_4$. The propagation error results in a much higher error bar for the reported density ($\pm 5\%$) for LAGP crystallized at 950 °C, 2 h.

**Figure 4-4** includes a comparison of crystallite sizes determined from XRD peak broadening for heat treatment at 825 °C, 2 h that was crystallized covered and uncovered. Diffraction patterns in **Fig. 4-5** show that no additional second phases are present between covered and uncovered crystallization at 825 °C, 2 h.
Figure 4—3. Room temperature X-ray diffraction patterns of LAGP glass after six different heat treatments (all uncovered). Unindexed peaks correspond to NASICON LiGe$_2$(PO$_4$)$_3$ (PDF-01 080 1922). At 950 °C, 2 h, 2 ± 1 vol. % GeO$_2$ and 5 ± 1 vol. % AlPO$_4$ is present. Note that ionic radii of Ge$^{4+}$ (0.53 Å) and Al$^{3+}$ (0.54 Å) are very similar.
Figure 4—4. Crystallite sizes for different heat treatment temperatures. Given the error bar of ± 100 nm, the (540 °C, 6 h + 600 °C, 30 min) and 825 °C, 8 h crystallite size differences are statistically significant.

Figure 4—5. Room temperature X-ray diffraction patterns of LAGP glass after 825 °C, 2 h crystallized covered and uncovered.
Scanning Electron Microscopy of Glasses Crystallized Uncovered and Covered

Scanning electron microscopy was employed to observe microstructures of thermally etched glass-ceramics (Fig. 4-6). It is of note that grain size does not change greatly across the three heat treatments. Whiskers of an electron beam-sensitive material are observed if wet polishing is performed. The origin of the needles is not known, but it is speculated that they may be lithium carbonate. Currently, there is a valid chemical explanation, but not a valid crystal morphology explanation. From the chemical perspective, lithium hydroxide can form via reaction of lithium-ions with water (Eq. 4-1 and Eq. 4-2). Then, lithium carbonate can form by a reaction of lithium hydroxide and carbon dioxide (Eq. 4-3). From a crystal morphology perspective, lithium carbonate at room temperature is monoclinic, a low symmetry crystal system. However, high symmetry crystal systems are known form needle-like morphologies, as in the case of rutile, which is tetragonal.

\[
\begin{align*}
Li^+ (s) & \overset{H_2O (l)}{\leftrightarrow} Li^+ (aq) \quad \text{(Eq. 4-1)} \\
2Li^+ (aq) + 2e^- + 2H_2O (l) & \leftrightarrow 2LiOH (aq) + H_2 (g) \quad \text{(Eq. 4-2)} \\
3LiOH (aq) + CO_2 (g) & \leftrightarrow Li_2CO_3 (s) + H_2O (g) \quad \text{(Eq. 4-3)}
\end{align*}
\]

Microstructures are shown for the highest conductivity crystallized glass Fig. 4-7(a) and the lowest conductivity crystallized glass Fig. 4-7(b). Samples were fractured and no additional heat treatment or polishing was performed after fracturing. There is a transition from intergranular fracture at the higher heat treatment temperature (Fig. 4-7(a)) to transgranular fracture at the lower temperature (Fig. 4-7(b)). Figure 4-8 compares micrographs of thermally etched glass-ceramics that were crystallized covered and uncovered. From the similarities between XRD and SEM results in covered and uncovered samples, meaningful comparisons can
be made between covered and uncovered samples. It should be noted that EDS mapping did not show Al-rich or Ge-rich regions. Therefore, EDS does not support the formation of AlPO₄ or GeO₂.

Figure 4—6. Micrographs of thermally etched, uncovered x = 0.50 LAGP with mean grain sizes indicated for 825 °C, 8 h (left); 825 °C, 8 + 8 h (middle); and 950 °C, 2 h (right). Lithium carbonate whiskers may form after polishing with water. Similar whiskers are seen in micrographs of thermally etched bulk glass crystallized at 850 °C for 12 h (Thokchom et al. 167) and 825 C, 8 h (Thokchom et al. 55). Mariappan et al. observes highly crystalline LAGP whiskers after sintering LAGP powder synthesized by the flash creation method for 540 °C, 2 h; 560 °C, 2h; and 650 °C, 2 h 26.

Figure 4—7. Micrographs of fracture surfaces, uncovered x = 0.50 LAGP (a) 825 °C, 8 h and (b) (540 °C, 6 h + 600 °C, 30 min). White flecks are observed in (b).
Figure 4—8. Micrographs of polished but not thermally etched of x = 0.50 LAGP (a) 825 °C, 2 h, *covered* and (b) 825 °C, 2 h, *uncovered*.

**Impedance Spectroscopy of Glasses Crystallized Uncovered and Covered**

**Uncovered**

Detailed analysis of the effect of heat treatment on grain boundary impedance has been reported by Mariappan et al. 26. **Figure 4-9** shows the impedance data and fits for the two most dissimilar total ionic conductivities, 825 °C, 8 h and (540 °C, 6 h + 600 °C, 30 min). These are the performance endmembers of the heat treatment conditions studied. Grain impedance is not greatly affected by time-temperature parameters when crystalline NASICON is above the percolation limit since channels exist for fast Li-ion conduction 26. However, grain boundary impedance can be tuned.

The equivalent circuit used is a 2 (R-CPE) (Resistor - Constant Phase Element) for a high frequency grain response and an intermediate frequency grain boundary response. As in Chapter 2, the low frequency electrode-electrolyte interface response is not fit since no meaningful data can be extracted from fitting the low frequency feature. For example, most attempts to fit the low
frequency feature with another R-CPE resulted in fits of $R$ on the order of $10^{20} \Omega$.

Similar to equivalent circuit models employed by Mariappan et al. \cite{26} for LAGP, the resistor is related to long-range ion transport. In addition to a CPE in parallel with the resistor, one difference is that grain component in the model of Mariappan et al. \cite{26} includes an additional capacitor to account for “fast electronic and vibrational polarization in the grains.”

An alternative to fitting data with equivalent circuits is Impedance Spectroscopy Genetic Programming (ISGP) \cite{16,170}. In ISGP, the distribution function of relaxation times is extracted directly from impedance data. In an optimization program, the distribution function of relaxation times is represented as an analytical function or combination of analytical functions. From the analytical function(s), physical meaning is assigned to each of the parameters. Background of ISGP is given in Appendix I.

Table 4-2 shows fit parameters for a 2(R-CPE) model employed in Fig. 4-9. Figure 4-10 shows an Arrhenius plot and Table 4-3 shows fit parameters from the Arrhenius plot.
Figure 4—9. Impedance complex plane plot of LAGP glass after a two-step heat treatment (540 °C, 6 h + 600 °C, 30 min) (blue). The re-scaled high frequency inset shows LAGP glass after crystallization at 825 °C, 8 h (red). Grain (G), grain boundary (GB), and electrode-electrolyte interface (E) regimes are labeled. Measurements were done at -60 °C. A 2(R-CPE) model is used. Symmetric Pt electrodes were used. Activation energy errors are ± 0.01 eV.
Table 4-2. Fit parameters for a 2(R-CPE) for impedance data measured at -60 °C with symmetric Pt electrodes in Fig. 4-9.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>$R_B$ (Ω-cm)</th>
<th>$R_B$ (Error%)</th>
<th>CPE_B-Q (Ω-cm-s$^{0.5}$)</th>
<th>CPE_B-Q (Error%)</th>
<th>CPE_B-n (Dimensionless)</th>
<th>CPE_B-n (Error%)</th>
<th>$R_{GB}$ (Ω-cm)</th>
<th>$R_{GB}$ (Error%)</th>
<th>CPE_GB-Q (Ω-cm-s$^{0.5}$)</th>
<th>CPE_GB-Q (Error%)</th>
<th>CPE_GB-n (Dimensionless)</th>
<th>CPE_GB-n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C, 8 h</td>
<td>4.02 x 10^6</td>
<td>2.89</td>
<td>2.06 x 10^{11}</td>
<td>11.8</td>
<td>0.868</td>
<td>1.07</td>
<td>1.86 x 10^7</td>
<td>8.92</td>
<td>2.04 x 10^{3}</td>
<td>32.8</td>
<td>0.615</td>
<td>8.05</td>
</tr>
<tr>
<td>540 °C, 6 h + 600 °C, 30 min</td>
<td>7.58 x 10^3</td>
<td>3.54</td>
<td>1.85 x 10^{11}</td>
<td>20.8</td>
<td>0.876</td>
<td>1.68</td>
<td>5.96 x 10^7</td>
<td>2.61</td>
<td>1.14 x 10^{-9}</td>
<td>5.50</td>
<td>0.738</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as $\sigma_{\text{Grain Boundary}} = \frac{\sigma_{\text{Grain Boundary}}(d)}{R_{\text{Grain Boundary}}} = \frac{\Delta}{t}$ rather than $\sigma_{\text{Grain Boundary}} = \frac{1}{R_{\text{Grain Boundary}}} = \frac{1}{\sigma_{\text{Grain Boundary}}(\Delta/t)}$. Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. $B$ or $G$ denotes the grain interior while $GB$ denotes the grain boundary.

Table 4-3. Arrhenius ionic conductivity properties of the grain conductivity and total conductivity components of bulk glasses crystallized at 825 °C, 8 h and (540 °C, 6 h + 600 °C, 30 min) with symmetric Pt electrodes.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>$\sigma^{25^\circ}$C (Ω-cm)$^{-1}$</th>
<th>$\log \sigma_0$ (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ (eV)</th>
<th>$\sigma^{25^\circ}$C (Ω-cm)$^{-1}$</th>
<th>$\log \sigma_0$ (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C, 8 h</td>
<td>7.0 x 10^{-3}</td>
<td>3.35</td>
<td>0.38 ± 0.01</td>
<td>1.1 x 10^{-3}</td>
<td>3.71</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>540 °C, 6 h + 600 °C, 30 min</td>
<td>2.6 x 10^{-5}</td>
<td>3.20</td>
<td>0.46 ± 0.01</td>
<td>5.3 x 10^{-4}</td>
<td>3.16</td>
<td>0.38 ± 0.01</td>
</tr>
</tbody>
</table>

* Please see the footnote in Table 1-1.
Figure 4—10. Arrhenius ionic conductivity plot of LAGP glass after a two-step heat treatment (540 °C, 6 h + 600 °C, 30 min) (blue) and LAGP glass after crystallization at 825 °C, 8 h (red). Symmetric Pt electrodes were used. Activation energy errors are ± 0.01 eV.
In Table 4-2, the fit parameter for $\rho_{\text{Grain}} \left( \frac{d}{D} \right)$ is about $2 \times 10^5$ (Ω-cm) for the (540 °C, 6 h + 600 °C, 30 min) heat treatment, while it is $6 \times 10^7$ (Ω-cm) for the 825 °C, 8 h heat treatment for a measurement temperature of -60 °C. In Fig. 4-10, the grain conductivity and total conductivity for the (540 °C, 6 h + 600 °C, 30 min) heat treatment differs about two orders of magnitude for a given measurement temperature because of the large grain boundary impedance contribution. In contrast, for the 825 °C, 8 h heat treatment has a small grain boundary impedance contribution. Therefore, grain conductivity and total conductivity are less than an order of magnitude different at a given temperature.

The grain conductivities at fixed temperature can be fit for a series of crystallization conditions (Fig. 4-11). It is observed that grain conductivity differs up to a factor of two across the different crystallization conditions.

![Figure 4-11. Grain conductivity at -60 °C for different heat treatment conditions. Grain conductivity is much more insensitive to the crystallization time and temperature than total conductivity. Symmetric Pt electrodes were used.](image-url)
Uncovered vs. Covered

Up until this point, all impedance spectroscopy spectra has been of uncovered crystallization conditions. Impedance complex plane plots and fits are presented for the uncovered and covered crystallization conditions (Fig. 4-12 and Fig. 4-13). In particular, a decrease in total conductivity was seen after covered crystallization. This observation was independent of heat treatment duration (2 vs. 8 h) and electrode selection (Pt vs. Au).

Figure 4—12. Impedance complex plane plot of LAGP glass after crystallization at 825 °C, 8 h covered (red) and uncovered (black). Measurements were done at -60 °C. A 2(R-CPE) model is used. Symmetric Au electrodes were used.
Figure 4—13. Impedance complex plane plot of LAGP glass after crystallization at 825 °C, 2 h covered (red) and uncovered (black). Measurements were done at -60 °C. A 2(R-CPE) model is used. Symmetric Pt electrodes were used.

Fit data of Fig. 4-12 and Fig. 4-13 are presented in Table 4-4. Note that up to 40% error is seen in the fit parameter for CPE_GB-Q in the case of 825 °C, 8 h, covered. Therefore, one may think to add an additional (R-CPE) (three fit parameters). Careful consideration must be given when adding additional fit parameters since adding more fit parameters reduces the describing power of the model. More details about another impedance modelling method, Impedance Spectroscopy Genetic Programming (ISGP), is given in Appendix I of this thesis.

Since grain conductivity stability is the focus of this chapter, precise fitting of the grain boundary component is not presently a concern.

Arrhenius behavior is observed in both uncovered and covered samples (Fig. 4-14). Activation energies remain within error (± 0.02 eV). Table 4-5 summarizes the Arrhenius ionic conductivity fit parameters in Fig. 4-14.
Figure 4—14. Arrhenius ionic conductivity plot of LAGP glass after crystallization at 825 °C, 2 h covered (red) and uncovered (black). Symmetric Pt electrodes were used. Activation energies are reported ± 0.01 eV.
Table 4-4. Fit parameters for a 2(R-CPE) for impedance data measured at -60 °C in Fig. 4-13 and Fig. 4-14.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>R_B (Ω-cm)</th>
<th>R_B (Error%)</th>
<th>CPE_B-Q (Ω-cm-s^n)</th>
<th>CPE_B-Q (Error%)</th>
<th>CPE_B-n (Dimensionless)</th>
<th>CPE_B-n (Error%)</th>
<th>R_GB (Ω-cm)</th>
<th>R_GB (Error%)</th>
<th>CPE_GB-Q (Ω-cm-s^n)</th>
<th>CPE_GB-Q (Error%)</th>
<th>CPE_GB-n (Dimensionless)</th>
<th>CPE_GB-n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C, 8 h (Uncovered)</td>
<td>3.64 x 10^9</td>
<td>4.57</td>
<td>1.45 x 10^{11}</td>
<td>22.1</td>
<td>0.900</td>
<td>1.87</td>
<td>4.08 x 10^6</td>
<td>9.02</td>
<td>2.53 x 10^8</td>
<td>39.6</td>
<td>0.585</td>
<td>9.70</td>
</tr>
<tr>
<td>825 °C, 8 h (Covered)</td>
<td>3.23 x 10^9</td>
<td>2.88</td>
<td>4.32 x 10^{12}</td>
<td>19.7</td>
<td>0.941</td>
<td>1.51</td>
<td>1.60 x 10^6</td>
<td>3.94</td>
<td>2.88 x 10^8</td>
<td>12.5</td>
<td>0.537</td>
<td>3.36</td>
</tr>
<tr>
<td>825 °C, 2 h (Uncovered)</td>
<td>4.28 x 10^9</td>
<td>1.91</td>
<td>1.58 x 10^{11}</td>
<td>12.8</td>
<td>0.877</td>
<td>1.05</td>
<td>1.10 x 10^6</td>
<td>2.70</td>
<td>1.31 x 10^8</td>
<td>11.8</td>
<td>0.614</td>
<td>2.71</td>
</tr>
<tr>
<td>825 °C, 2 h (Covered)</td>
<td>5.06 x 10^9</td>
<td>1.20</td>
<td>1.27 x 10^{11}</td>
<td>9.24</td>
<td>0.882</td>
<td>0.754</td>
<td>3.39 x 10^6</td>
<td>1.57</td>
<td>1.34 x 10^8</td>
<td>4.70</td>
<td>0.582</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as \( \rho_{\text{Grain Boundary}} \left( \frac{d}{D} \right) = R_{\text{Grain Boundary}} \left( \frac{A}{L} \right) \) rather than \( \rho_{\text{Grain Boundary}} = \frac{1}{\sigma_{\text{Grain Boundary}}} = \frac{1}{\frac{1}{R_{\text{Grain Boundary}}} \left( \frac{1}{A} \frac{d}{L} \right)} \). Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. B or G denotes the grain interior while GB denotes the grain boundary.

Table 4-5. Arrhenius ionic conductivity properties of the grain conductivity and total conductivity components of 825 °C, 2 h crystallized uncovered and covered.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>( \sigma_{25^\circ\text{C}} ) Total (Ω-cm)^{-1}</th>
<th>( \log_{10} \sigma_{25^\circ\text{C}} ) Total (Ω-cm)^{-1}</th>
<th>( \Delta E_{\text{Act}} ) Total (eV)</th>
<th>( \sigma_{25^\circ\text{C}} ) Grain (Ω-cm)^{-1}</th>
<th>( \log_{10} \sigma_{25^\circ\text{C}} ) Grain (Ω-cm)^{-1}</th>
<th>( \Delta E_{\text{Act}} ) Grain (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C, 2 h (Uncovered)</td>
<td>3.5 x 10^{-4}</td>
<td>3.38</td>
<td>0.40 ± 0.01</td>
<td>8.3 x 10^{-4}</td>
<td>3.51</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>825 °C, 2 h (Covered)</td>
<td>1.7 x 10^{-4}</td>
<td>3.37</td>
<td>0.42 ± 0.01</td>
<td>5.3 x 10^{-4}</td>
<td>3.55</td>
<td>0.40 ± 0.01</td>
</tr>
</tbody>
</table>

* Please see the footnote in Table 1-1.
Chapter Conclusions

Until Chapter 4, all experimental results focused on sulfide electrolytes. In order to justify that research in both sulfide and oxide electrolytes is important, general merits and demerits of sulfide and oxide electrolytes were presented. The main differences between these two classes of electrolytes is their grain boundary contribution to total conductivity and their processing costs. In particular, the grain boundary contribution to total conductivity in oxide electrolytes strongly depends on the extrinsic processing conditions. From varying the processing conditions and controlling microstructure & phase development, grain conductivity was shown to be much more stable than grain boundary conductivity in crystallized bulk glasses of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$. Across the heat treatment conditions studied, grain conductivity is much less sensitive to processing conditions when heat treated above the crystallization temperature. Grain conductivity does not change by more than a factor of two for the heat treatment conditions studied. With strong evidence that grain conductivity does not change, Chapters 5 and 6 proceed with ways to tune the grain boundary contribution and increase total ionic conductivity using novel, low temperature processing.
Chapter 5

Cold Sintering Process of Lithium Aluminum Germanium Phosphates

Chapter Overview

This chapter has two parts. First, the Cold Sintering Process (CSP) is introduced. Second, experimental data of density, microstructure, and impedance spectroscopy of cold sintered LAGP is presented. In the course of this thesis, grain/grain boundary contributions in $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) were compared for electrolytes processed in three ways: (1) Crystallization of bulk glasses (Chapter 4), (2) CSP of ceramics (Chapter 5), and (3) CSP of ceramic-polymer composites (Chapter 6).

In this chapter, using CSP, 80 % dense $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ electrolytes were obtained at 120 °C in 20 min. After a 5 min belt furnace treatment at 650 °C, 50 °C above the crystallization onset, Li-ion conductivity was $5.4 \times 10^{-5}$ S/cm at 25 °C.

Through fundamental understanding of densification, microstructural development, and impedance contributions within solid electrolytes processed by CSP, significant headway can be made towards new battery manufacturing methods.
Chapter Introduction

Low Temperature Processing of Electrochemically Functional Materials

In Chapter 1, specialized sintering approaches were introduced. Cold Sintering Process (CSP) is a class of techniques that has begun to be formalized in the past year \textsuperscript{102, 114, 171-179}. In short, CSP employs a transient solvent to enable liquid phase-assisted densification between 25 °C and \(\sim\)200 °C through mediating the dissolution-precipitation process. Before this technique is described, a brief overview of low temperature processing of electrochemically functional battery materials is given.

Lithium-ion batteries consist of a positive electrode (cathode), a negative electrode (anode), and an electrolyte. In batteries with liquid electrolytes, a polymer separator often soaks up liquid electrolyte and provides electrical and physical separation between the cathode and anode. For solid-state batteries, the function of the separator and liquid electrolyte is condensed into a solid electrolyte.

Low temperature processing of cathode and anode materials seems to be the focus of literature. In contrast, electrolyte research is less focused on low temperature processing and more on improving properties. Liquid electrolyte battery research is focused on improving safety and temperature/voltage performance by formulating flame retardant additives, understanding solid electrolyte interface (interphase) or SEI development \textsuperscript{154}, and loading polymer separators with ceramic filler \textsuperscript{180}. There is little space for discovery for low temperature processing of liquid electrolytes since lithium salts can dissolve in the organic co-solvent systems at room temperature.
In 2010, Tarascon et al. \textsuperscript{181} reviewed low temperature hydrothermal and solvothermal synthesis of LiFePO\textsubscript{4}, a common Li-ion battery cathode, to show how the battery community is trending towards “energy and material thrift.” Low processing temperature offers more than simply eco-efficient, green chemistry. Larcher and Tarascon \textsuperscript{182} emphasize the benefits of low temperature processing: (1) economy of atoms; (2) size, shape & texture control; (3) economy of energy (Fig. 5-1).

![Figure 5-1. Processing pyramid diagram showing the three main advantages of low temperature synthesis from Larcher and Tarascon \textsuperscript{182}.](image)

**Cold Sintering Introduction**

A number of variables are known to impact CSP. Important variables include (1) crystal structure, (2) particle size (active surface area), (3) solvent pH, (4) the stoichiometry of dissolution products (congruent or incongruent dissolution), (5) temperature, (6) time, and (7)
pressure. As a result of the many processing variables, understanding of CSP is in its infancy. Understanding CSP draws on a variety of fields relevant to ceramic sintering: aqueous thermodynamics (Pourbaix Diagrams), chemical weathering, sedimentary rock compaction, mechano-chemo-dissolution, and hydrothermal crystal growth.

CSP can be schematically compared to conventional (thermal, pressureless) sintering in terms of Gibbs Free Energy diagrams (Fig. 5-2). In particular, the sum of the individual stages proposed for CSP are smaller than in conventional sintering.

![Figure 5-2. Schematic of cold sintering process (left) compared to conventional sintering (right) from Guo et al.](image)

The basic process involves ceramic powders uniformly wetted with 1 to 40 wt. % of aqueous solution. Solid surfaces decompose and partially dissolve in the water, so that a controlled amount of liquid phase is intentionally introduced at the particle-particle interfaces. This sintering step can be accomplished by simply mixing in a few drops of water or acid solutions, or exposing the powders to a controlled, humid atmosphere. Alternatively, dissolved solutes in stoichiometric ratios can also be added. Under certain temperature and pressure conditions, the liquid phase redistributes itself. By the flowing of the liquid phase, the ceramic undergoes initial densification by the rearrangement of solid particles. Then, in the solution-precipitation process, ionic species and/or atomic clusters transport to the contacts to reduce the
local surface curvature of the particles, minimize the excess surface free energy, and reduce the porosity causing material to form a dense solid. Transient evaporation in and around the particle’s porous network may also aid the precipitation through the Gibbs-Marangoni Effect, adding local capillarity forces (surface tension gradient) and transport$^{186,187}$. **Figure 5-3** and summarizes the stages of cold sintering qualitatively, while **Figure 5-4** highlights the variables of pressure ($P$), surface tension ($\gamma$), and ion concentration ($c$).

![Figure 5-3. Schematic of cold sintering process from Guo et al. $^{173}$](image-url)
Two major pathways within the framework of cold sintering have been identified. The first relies on the addition of an aqueous solution that can be modified with either acid or base to control the dissolution process in terms of kinetics and predominant form of the dissolved species, yielding a congruent process that preserves the stoichiometry. Thus, the transient solution undergoes supersaturation and the stoichiometric solute grows epitaxially on the particle surfaces. If the process proceeds too quickly, a residual glassy–gel phase is quenched into the grain boundaries. If the process is incongruent, a passivated layer on the surfaces of particles can form and no densification takes place. The second method relies on adding pre-saturated solutions (about 1 to 40 wt. %) at the required stoichiometric ratios to enable particle rearrangement, growth, and therefore densification. Thus, this approach is universally applicable to both congruently and incongruently dissolving materials, and will be less reliant on aqueous solutions. A summary of these two cold sintering pathways is shown in Fig. 5-5.
Experimental Methods

Cold Sintering Process

Glass melting and crystallization procedures were followed as detailed in Chapter 4 and elsewhere. Starting powder for all CSP samples was LAGP bulk glass that was crystallized at 825 °C for 8 h in air, crushed, and sieved through a 74 μm mesh.

Thirty to 39 vol. % of deionized water or 50 to 56 vol. % ethanol was added to LAGP sieved glass-ceramic powder and homogenized in a mortar and pestle. This powder was pressed under 400 MPa uniaxial pressure at 25, 40, 60, 80, 100, 120, 140, and 160 °C for 20 min. All

Figure 5—5. Proposed cold sintering process densification routes from Guo et al. 179.
samples were annealed at 120 °C for 6 h to remove residual water and confirm density increases are not simply mass gain from undried water. For select samples, a 5 min treatment at 650 °C was performed (LA-306 IR Belt Furnace, Radiant Technology Corporation, Anaheim, CA).

X-ray Diffraction

XRD patterns were collected using methods established in Chapter 4.

Scanning Electron Microscopy

SEM micrographs were obtained on fracture surfaces using methods established in Chapter 4.

Impedance Spectroscopy

Impedance spectra were obtained using methods established in Chapter 4. Sputtered, 100 nm thick Au electrodes were used.

Results & Discussion

X-ray Diffraction of LAGP after CSP

Room temperature X-ray diffraction (XRD) patterns of LAGP CSP processed at 120 °C for 1 h is seen in (Fig. 5-6). In this and other patterns, no second phases are observed after CSP with water.
Figure 5—6. Room temperature X-ray diffraction patterns of LAGP glass after 825 °C, 8 h crystallized uncovered and 120 °C, 1 h, water CSP as compared to NASICON LiGe\(_2\)(PO\(_4\))\(_3\) (PDF-01 080 1922). Unindexed peaks correspond to LAGP. Note that ionic radii of Ge\(^{4+}\) (0.53 Å) and Al\(^{3+}\) (0.54 Å) are very similar.

CSP Densification of LAGP

For LAGP, the CSP stages include (1) congruent dissolution, (2) particle rearrangement, (3) evaporation of the transient solvent, and (4) quenching in of amorphous phase at the grain boundaries. In Stage (1), congruent dissolution occurs up to a temperature of 160 °C. Above 160 °C, incongruent dissolution is thought to occur since an intermediate is favored rather than an amorphous phase at the grain boundaries. Congruent dissolution causes partial etching of the particle surfaces. In Stage (2), particle rearrangement is assisted by pressure-assisted flow from the partially etched liquid-liquid interfaces. In Stage (3), the transient solvent evaporates since pressure and temperature are applied in an open system. In Stage (4), fast evaporation quenches in an amorphous grain boundary phase. While densification does occur by CSP, the quenched amorphous grain boundary phase is detrimental to high total ionic conductivity.
Fixing pressure (400 MPa), holding time (20 min), and water content (30 to 39 vol. %), a positive trend is seen between temperature and density between 25 and 160 °C (Fig. 5-7). The 25 °C pressed control had no water added. Between 40 and 160 °C, density increases from 75 to 79 ± 1.5 %. Fixing pressure (400 MPa), holding time (20 min), and ethanol content (50 to 56 vol. %), density at 120 and 140 °C was 75 ± 1.5 %. Controlling pressure, holding time, solvent addition, and temperature is important for the densification process. Clearly, the densities are higher than what could be obtained by dry pressing, but lower in density than what currently possible using CSP (> 98 % density). Systematic densification trends for CSP ceramics and composites are reported elsewhere for BaTiO$_3$, KH$_2$PO$_4$, K$_2$Mo$_2$O$_7$, and ZnO$^{173,178,179}$.

Figure 5—7. Relationship between the relative density (± 1.5 %) and pressing temperature for fixed pressure (400 MPa), time (20 min), and 30 – 39 vol. % water.

Scanning Electron Microscopy of CSP Ceramics

Fracture surfaces were analyzed by SEM (Fig. 5-8). Typical SEM sample preparation
involves fracturing, polishing, thermal etching about 50 °C below the sintering temperature for 30 min, or chemical etching. In the case of CSP ceramics and composites, no additional heat treatment was performed after fracturing. To isolate the effects of temperature and water addition on the densification, microstructures were compared for dry (25 and 120 °C) and wet pressing (25 and 120 °C). The most different obtained densities for the microstructures shown are from dry 25 °C pressing (63 ± 1.5 % density) and CSP at 120 °C (79 ± 1.5 % density). Neck growth is clearly seen in the CSP sample pressed at 120 °C. While the obtained density values do not suggest good sintering (> 95 % density), Fig. 5-8(d) suggests a ceramic that is about 90 % dense.

Polished fracture surfaces were analyzed by SEM (Fig. 5-9). After the analysis of three separate 300 x 300 μm regions of polished, fractured CSP ceramics, no macropores were observed. It is thought that macropores, although not observed, are still responsible for the average density of 79 % since non-uniform pressure distribution or non-uniform water distribution would result in hard-to-eliminate macropores. Although no macropores were observed, their presence is more plausible than easier-to-eliminate nanopores. Future work should include fractured, polished, and chemically etched micrographs.
Figure 5—8. Micrographs of LAGP pressed at 400 MPa for 20 min (a) dry, 25 °C; (b) with water, 25 °C; (c) dry, 120 °C; (d) with water, 120 °C. Pressure, temperature, holding time, and water addition are important to achieve neck growth observed in (d). Densities are reported ± 1.5 %. Note that (d) appears to be higher in density than the pellet density of 79 %.
Impedance Spectroscopy of CSP Ceramics

**Figure 5-10** contrasts the impedance behavior for 120 °C CSP with ethanol (measured at 50 °C) and 120 °C CSP with ethanol after a 650 °C, 5 min heat treatment (measured at -50 °C). The modest heat treatment temperature of 650 °C was selected as a result of DSC and TGA-MS analyses. From DSC (**Fig. 4-2**), the onset crystallization temperature of LAGP is 612 °C. TGA-MS analysis was performed with a Helium purge on CSP powders and CSP starting powders (LAGP glass crystallized for 825 °C, 8 h). A 0.35 wt. % change was observed in CSP powders, while CSP starting powders showed no measurable weight loss. All species (OH−, H2O, and CO2) in the powders after CSP burned off before 650 °C.

Prior to heat treatment, the grain component cannot be observed and a single (R-CPE) is used to fit the data. After heat treatment, both grain and grain boundary components are observed and a 2(R-CPE) model is used to fit the data. It was observed that microwave heating, in addition to using an IR belt furnace, is effective in crystallizing grain boundaries.
Using Transmission Electron Microscopy (TEM), core-shell-like microstructural models have been proposed by Ma et al. for \((\text{Li}_{3x}\text{La}_{2/3-x})\text{TiO}_3\) perovskites with lithium-poor grain boundaries\(^1\). Alternatively, grain boundaries can be analyzed through high field measurements in order to understand serial barriers\(^2\). As discussed in Chapter 1, by the Brick Layer Model, grain boundary thicknesses, observed using TEM, are needed in order to correctly report grain boundary conductivities.

Fit parameters for Fig. 5-10 are reported in Table 5-1. Figure 5-11 shows an Arrhenius plot of LAGP glasses from Leo et al.\(^{58}\); 120 °C CSP LAGP using ethanol; 120 °C CSP LAGP using water; LAGP glass heat treated 540 °C, 6 h + 600 °C, 30 min; 120 °C CSP LAGP using ethanol after a 650 °C, 5 min belt furnace heat treatment; and LAGP glass heat treated 825 °C, 8 h. Densification through CSP and grain boundary development during CSP may be further optimized. Specific suggestions for optimizing density and ionic conductivity are given in the thesis conclusions chapter. Table 5-2 summarizes total conductivities for the Arrhenius plot.

The 650 °C, 5 min belt furnace heat treatment is sufficient to increase conductivity and decrease activation energy, while not changing density, the observable phases (by XRD), or the microstructure (by SEM). This observation is in contrast to the work of Guo et al.\(^{17,5,17,6,17,9}\) where TEM observation shows the crystallization of a glassy carbonate grain boundary phase in \(\text{BaTiO}_3\) after a 900 °C, 3 h heat treatment. With a longer and higher temperature heat treatment in \(\text{BaTiO}_3\) as compared to LAGP, a significant change in density after heat treatment (88 to 97 %), an increase in dielectric permittivity (77 to 3100 at 120 °C and 1 kHz), and a decrease in loss tangent (0.5 to 0.05 at 120 °C and 1 kHz), are also observed. Therefore, across CSP, a heat treatment step may improve a dielectric’s properties, as in the case of \(\text{BaTiO}_3\), or improve a solid electrolyte’s properties, as in the case of LAGP.
Figure 5—10. Impedance complex plane plot of LAGP measured at 50 °C after 120 °C CSP using ethanol (blue) and at -50 °C after 120 °C CSP using ethanol & heat treatment in a belt furnace at 650 °C, 5 min (red). Activation energies, equivalent circuit fits, and schematic microstructures are shown in their respective colors. The grain boundary (GB) feature dominates the spectra in the CSP pellet prior to heat treatment. After heat treatment, the grain (G) and GB features are resolved.
Figure 5—11. Arrhenius plot of LAGP glass (red) Leo et al. 58; 120 °C CSP LAGP using ethanol (blue); 120 °C CSP LAGP using water (pink); LAGP glass heat treated 540 °C, 6 h + 600 °C, 30 min (gray); 120 °C CSP LAGP using ethanol after a 650 °C, 5 min belt furnace heat treatment (black); and LAGP glass heat treated 825 °C, 8 h (green). Please see Table 5-2 for activation energy error details.
Table 5-1. Fit parameters for a (R-CPE) or 2(R-CPE) for impedance data in Fig. 5-10. CSP 120 °C prior to 650 °C, 5 min was measured at 50 °C, while CSP 120 °C after 650 °C, 5 min was measured at -50 °C

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>$R_B$ (Ω·cm)</th>
<th>$R_B$ (Error%)</th>
<th>$CPE_B$-Q (Ω·cm·s$^{-1}$)</th>
<th>$CPE_B$-Q (Error%)</th>
<th>$CPE_B$-n (Dimensionless)</th>
<th>$CPE_B$-n (Error%)</th>
<th>$R_GB$ (Ω·cm)</th>
<th>$R_GB$ (Error%)</th>
<th>$CPE_GB$-Q (Ω·cm·s$^{-1}$)</th>
<th>$CPE_GB$-Q (Error%)</th>
<th>$CPE_GB$-n (Dimensionless)</th>
<th>$CPE_GB$-n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSP 120 °C, 20 min with Ethanol</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
<td>1.53 x 10$^3$</td>
<td>0.804</td>
<td>3.62 x 10$^{-11}$</td>
<td>4.44</td>
<td>0.876</td>
<td>0.454</td>
<td></td>
</tr>
<tr>
<td>CSP 120 °C, 20 min with Ethanol and 650 °C, 5 min</td>
<td>1.08 x 10$^6$</td>
<td>2.19</td>
<td>9.23 x 10$^{-12}$</td>
<td>11.2</td>
<td>0.845</td>
<td>0.920</td>
<td>6.21 x 10$^6$</td>
<td>0.884</td>
<td>1.09 x 10$^{-10}$</td>
<td>7.35</td>
<td>0.830</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as $\rho_{\text{Grain Boundary}} \left( \frac{d}{t} \right) = R_{\text{Grain Boundary}} \left( \frac{A}{t} \right)$ rather than $\rho_{\text{Grain Boundary}} = \frac{1}{\sigma_{\text{Grain Boundary}}} = \frac{1}{R_{\text{Grain Boundary}} \left( \frac{l}{A} \right) \left( \frac{A}{t} \right)}$. Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. $B$ or $G$ denotes the grain interior while $GB$ denotes the grain boundary.
Table 5-2. Arrhenius ionic conductivity of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP). Ionic conductivities at 25 °C, activation energies, pre-exponentials, and densities for glass, glass after crystallization, and cold sintering of crystallized glass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{25}$ Total (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ Total (eV)*</th>
<th>log $\sigma_0$ Total (Ω-cm)$^{-1}$</th>
<th>Absolute Density (g/cm$^3$)</th>
<th>Density (± 1.5 %)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>3.5 x $10^{-9}$</td>
<td>0.52</td>
<td>0.34</td>
<td>2.92</td>
<td>- - -</td>
<td>Electrical data from Leo et al. $^{58}$ Density data after annealing.</td>
</tr>
<tr>
<td>Glass after crystallization 540 °C, 6 h + 600 °C, 30 min</td>
<td>2.6 x $10^{-5}$</td>
<td>0.46 ± 0.01</td>
<td>3.2</td>
<td>3.06</td>
<td>89.2</td>
<td>At -60 °C, 1.8 x $10^{-5}$ $\sigma_{\text{Total}}$ and 1.1 x $10^{-6}$ $\sigma_{\text{Grain}}$</td>
</tr>
<tr>
<td>Glass after crystallization 825 °C, 8 h</td>
<td>7.0 x $10^{-4}$</td>
<td>0.38 ± 0.01</td>
<td>3.3</td>
<td>3.14</td>
<td>91.5</td>
<td>At -60 °C, 1.8 x $10^{-5}$ $\sigma_{\text{Total}}$ and 2.4 x $10^{-6}$ $\sigma_{\text{Grain}}$</td>
</tr>
<tr>
<td>CSP 120 °C, 20 min with Ethanol</td>
<td>3.6 x $10^{-6}$</td>
<td>0.61 ± 0.02</td>
<td>2.1</td>
<td>2.71</td>
<td>75.0</td>
<td></td>
</tr>
<tr>
<td>CSP 120 °C, 20 min with Water</td>
<td>7.9 x $10^{-6}$</td>
<td>0.51 ± 0.05</td>
<td>3.5</td>
<td>2.71</td>
<td>79.0</td>
<td>Low $R^2$ of 0.98 in Arrhenius fit and high activation energy error</td>
</tr>
<tr>
<td>CSP 120 °C, 20 min with Ethanol and 650 °C, 5 min</td>
<td>5.4 x $10^{-5}$</td>
<td>0.40 ± 0.01</td>
<td>2.3</td>
<td>2.71</td>
<td>75.0</td>
<td>At -50 °C, 1.4 x $10^{-7}$ $\sigma_{\text{Total}}$ and 8.3 x $10^{-7}$ $\sigma_{\text{Grain}}$</td>
</tr>
</tbody>
</table>

Table footnotes: For comparisons with LAGP literature, please see **Table 1-1**.

* For more information about activation energy error, please see the footnote in **Table 1-1**.
Chapter Conclusions

Low temperature processing of electrochemically functional materials is favorable for more than simply lower energy costs. In bio-assisted methods, like biomineralization, low temperature processing allows for economy of atoms, as well as size, shape, and texture control. This chapter painted CSP with a broad brushstroke and demonstrated that drawing from a number of disciplines is important to fully understand the mechanisms of densification. It is speculated that the main transport mechanism responsible for densification in LAGP is liquid-enhanced creep. To better support this speculation, creep studies as a function of pressure and temperature should be performed on this system.

Experimental details were given for cold sintering of LAGP by drop-to-drop addition of deionized water or ethanol. XRD, SEM, and Impedance results compared CSP ceramic electrolytes (wet, 120 °C press) to dry, 25 °C press ceramics pressed at 400 MPa. It was found that solvent addition is crucial for densification. Further, a heat treatment above the crystallization temperature is required to crystallize the quenched amorphous gel at grain boundaries and decrease activation energy. The next chapter seeks to reduce grain boundary impedance observed in CSP samples by ionically bridging grain boundaries using a (PVDF-HFP) polymer soaked with small amounts of liquid electrolyte.
Chapter 6

Cold Sintering Process of Solid Electrolyte Composites: Bridging Resistive Lithium Aluminum Germanium Phosphate Grain Boundaries with 5 vol. % Poly(vinylidene fluoride hexafluoropropylene) Polymer and ≤ 12 μL Liquid Electrolyte

Chapter Overview

Ceramic-polymer composites hold multiple design opportunities to improve material properties and achieve multifunctional devices. However, vastly dissimilar processing windows between polymers and ceramics limit the full range of desired properties \cite{188-191}. In Chapter 5, a belt furnace heat treatment (650 °C, 5 min) was necessary to bridge resistive grain boundaries after CSP. In this chapter, processing and properties of new CSP (100-x) LAGP – x (PVDF-HFP) composites soaked in a liquid electrolyte are reported. After soaking 95, 90, 80, 70, 60 vol. % Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3 in a 1 M LiPF_6 EC-DMC (50:50 vol. %) at 25 °C, Li-ion conductivities of 1.0 x 10^{-4} S/cm at 25 °C were obtained.

Chapter Introduction

Cold Sintering Enables Ceramic-Polymer Composites with > 90 vol. % Ceramic

Co-sintering ceramic and thermoplastic polymer composites in a single step with very high volume fractions of ceramics seems unlikely, given the vast differences in the typical sintering temperatures of ceramics versus polymers. These processing limitations are overcome with the introduction of CSP. In this chapter, improved electrical functionality is demonstrated
by the ability to co-process dense ceramics with polymers as the minor filler phase into previously unrealized CSP composites.

CSP, as described in Chapter 5, utilizes a transient solvent, such as water or water with dissolved solutes in stoichiometric ratios consistent with the ceramic composition, to control the dissolution and precipitation of ceramics and effect densification between 25 °C and ~ 200 °C. Under these conditions, thermoplastic polymers and ceramic materials can be jointly formed into dense composites. \( \text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 - \text{(PVDF-HFP)} \) is taken as an example to show the opportunities for composite material design using CSP. CSP should have a major impact on the processing of composite materials for targeted mechanical, thermal and electrical properties. In the journal article based on this chapter, \( \text{(Li}_2\text{MoO}_4 - \text{PTFE)} \) and \( \text{(V}_2\text{O}_5 - \text{PEDOT}:\text{PSS)} \) ceramic-polymer composites were studied to demonstrate microwave properties and electronic conductivity as additional functionalities that can be tuned using cold sintering.

The conventional thermal sintering process of ceramics is generally performed at high temperatures, typically ranging from several hundred to thousands of degrees Celsius, to enable the mass transport processes that allow the atoms, cations, or molecular groups to diffuse across the boundaries of adjoining particulates. To lower the sintering temperatures and/or reduce the sintering time, many sintering innovations have been developed. As discussed in Chapter 1, these specialized sintering approaches include liquid phase sintering, pressure-assisted sintering, microwave sintering, field-assisted sintering (FAST) and flash sintering. However, due to the slow solid-state diffusional processes or high temperature needed to form a liquid phase, these sintering processes are still restricted to high temperatures, which are not compatible with co-sintering thermoplastic polymers.
Most ceramic-polymer composites involve ceramic filler materials dispersed in a polymer matrix at a volume fraction that corresponds to a limit in and around the percolation limits.\(^{196,197}\) Percolation occurs when randomly dispersed ceramic particles create an interconnected pathway across a composite at a critical volume fraction. In Chapter 2, comparisons were made for ionic conductivities of \(x\) Li\(_2\)S + \((1-x)\) P\(_2\)S\(_5\) and mixing laws were applied below the percolation limit of conducting crystallites in an amorphous matrix \((\text{Eq. 2-3})\). For polymer-ceramic composites where the volume fraction of ceramic filler exceeds the percolation limits, there are often multiple integration processes required. First, the ceramic is sintered at a high temperature. Next, the ceramic is machined. Then, a polymer is infiltrated into the ceramic gaps to form the composite, with melting of a thermoplastic polymer or in-situ polymerization and cross-linking of a thermoset polymer. These processing restrictions severely limit how one fabricates high ceramic volume fraction composites and designs material functionality. The ceramic particle filling and dispersion process has limited particle–particle contact, which strongly compromises the desired physical properties of the composite. While CSP can allow composite engineers to take maximum advantage of a wide variety of ceramic properties (mechanical, dielectric, electromechanical, thermal), this chapter is dedicated to high ionic conductivity composites.

**Cold Sintering of Electrochemically Functional Ceramic-Polymer Composites**

Polymer electrolyte composites usually incorporate small amounts (< 30 vol. %) of insulating or ionically conducting ceramic fillers into a polymer/Li salt or polymer/liquid electrolyte matrix to improve temperature stability.\(^{198}\) Mechanically flexible electrolyte
composites have been made by solvent casting \(^{187, 199-202}\), electrospinning \(^{203-205}\), or other methods \(^{204, 205}\).

In addition to developing flexible electrolytes, there is a need for high volume fraction ceramic, high shear moduli composite electrolytes that can be paired with Li metal anodes. A 90 wt. \% \(\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3\) ceramic and 10 wt. \% PVDF polymer yields only 70 vol. \% \(\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3\) ceramic composite electrolytes \(^{198}\). CSP stands alone as a route to ceramic-polymer composites with high (95 vol. \%) fractions of oxide ceramic at compatible co-processing temperatures for both ceramics and polymers. To date, the lowest reported sintering temperature for LAGP is 650 °C, 2 min, 75 MPa for spark plasma sintered LAGP resulting in 87 \% dense compacts \(^{53}\) (Table 1-1). These high temperatures are not compatible with polymer processing. CSP composites allow a unique route to bridge this processing temperature gap and also bridge resistive grain boundaries to achieve high ionic conductivities \(\approx 10^{-4}\) S/cm at 25 °C. In general, CSP aids the understanding of processing-microstructure-property relations needed to minimize grain boundary resistance and maximize total ionic conductivity of composite solid electrolytes.

**Experimental Methods**

**Composite Cold Sintering**

Dense composites were prepared by CSP, as described in previous work \(^{102, 114, 171-179}\) and Chapter 5. Thirty to 39 vol. \% of deionized water was added to LAGP and homogenized in a mortar and pestle. LAGP and (PVDF-HFP) (Arkema, Kynar Powerflex LBG) was mixed by
swirling in liquid nitrogen and pressed under 400 MPa uniaxial pressure at 120 °C for 1 h. A 6 h anneal at 120 °C was performed to drive off excess water.

**X-ray Diffraction**

XRD patterns were collected using methods established in Chapter 4.

**Scanning Electron Microscopy**

SEM micrographs were obtained on fracture surfaces using methods established in Chapter 4.

**Impedance Spectroscopy**

Impedance spectra were obtained using methods established in Chapters 4 and 5. For $(100-x)\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) – $x(-\text{CH}_2\text{CF}_2)_n[-\text{CF}_2\text{CF}(\text{CF}_3)_2]_m$ (PVDF-HFP) composites, Au electrodes, 100 nm thick, were sputtered on the pellet faces. Pellets were soaked in 1 M LiPF$_6$ EC-DMC (50:50 vol. %) (BASF Selectilyte LP 30) at 25 °C inside an Ar-filled glovebox with < 1 ppm O$_2$ and < 1 ppm H$_2$O (UNIlab Plus, MBraun, Stratham, NH) and wiped of excess liquid. Uptake of liquid was 5 to 10 wt. % (10 to 12 μL) relative to a polymer-free control of 80 % dense CSP LAGP. Soaked composites were loaded into a custom-built sample cell assembly consisting of brass covers, brass spacers, a Teflon guard, a Teflon spacer, silicone o-rings, and a compression spring.
Results & Discussion

Density of CSP Ceramic-Polymer Composites

Reagent grade (PVDF-HFP) (Kynar PowerFlex LBG) has a $T_g$ around -40 °C using Dynamic Mechanical Analysis at 1 Hz. Since pressing takes place well above the glass transition temperature region, it was first confirmed that temperature and pressure alone are not causing densification. From Table 6-1, it is clear that water addition is necessary to achieve improved densities. The density improvement with CSP is outside of the range of error (± 1.5 %). The absolute densities of (100-x) LAGP – x (PVDF-HFP) composite samples were calculated using a mixing law (Eq. 2-4). Percent relative densities range between 80 to 86 (± 1.5 %), indicating that the ceramic-polymer composites can be sintered by CSP, but the composites still contain open porosity.

Table 6-1. Densities LAGP – (PVDF-HFP) composites with high volume fractions of ceramic prepared by Cold Sintering Process (CSP) and pressing at 120 °C, 1 h with no water addition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>CSP 120 °C, 1 h Press With water (30 to 39 vol. %) 400 MPa</th>
<th>120 °C, 1 h Press No water (dry) 400 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (g cm$^{-3}$)</td>
<td>Relative Density (± 1.5 %)</td>
</tr>
<tr>
<td>LAGP</td>
<td>2.78</td>
<td>81</td>
</tr>
<tr>
<td>95 LAGP – 5 (PVDF-HFP)</td>
<td>2.91</td>
<td>86</td>
</tr>
<tr>
<td>90 LAGP – 10 (PVDF-HFP)</td>
<td>2.60</td>
<td>80</td>
</tr>
</tbody>
</table>

Reagent (PVDF-HFP) is lower density (1.78 g/cm$^3$) than LAGP (3.43 g/cm$^3$). Please see the x-ray diffraction discussion in Chapter 4 for details about LAGP phase purity and density. Given these density values, the absolute densities of the ceramic-polymer composites decrease
with increasing amount of polymer (Fig. 6-1). In Fig. 6-1, percent relative density generally increases with increasing polymer volume fraction since higher volume fractions of formable polymer are available. At the extreme of 100 (PVDF-HFP), 93% dense samples can be obtained without water addition for a 400 MPa pressure and 1 h holding time at 120 °C.

Visual evidence of densification in 95 LAGP – 5 (PVDF-HFP) for CSP is seen in Fig. 6-2. In Fig. 6-2, both samples were pressed at 120 °C for 1 h at 400 MPa. The dry sample is too low in density to have a mirror-like polish after polishing down to 4000 grit, while the CSP sample has a mirror-like polish.

![Figure 6-1](image_url)

**Figure 6—1.** Experimentally measured density (± 1.5 %) of cold co-sintered (100-x) LAGP – x (PVDF-HFP) composites.
Figure 6—2. Images of 95 LAGP – 5 (PVDF-HFP) pellets (a) pressed at 120 °C with no water (dry) and (b) pressed at 120 °C with water (wet, CSP). With 5 vol. % of polymer pressed well above its glass transition temperature, densification cannot happen without water addition when the ceramic volume fraction is 95 vol. %. The inset shows pellets before sputtering 100 nm thick Au electrodes. With CSP, pellets could be polished to a mirror-like finish. Densities are reported ± 1.5 %.

X-ray Diffraction of CSP Ceramic-Polymer Composites

There are no obvious impurity phases after the CSP (Fig. 6-3), revealing that the ceramics and polymers can be co-sintered into two-phase composites.
Scanning Electron Microscopy of CSP Ceramic-Polymer Composites

Energy Dispersive Spectroscopy (EDS) maps of CSP ceramic-polymer composites were superimposed on backscattered electron images shown in Fig. 6-4. (PVDF-HFP) was specifically selected since it is known as a battery separator. In addition, as a fluoropolymer, EDS analysis with (PVDF-HFP) was easier than with non-fluoropolymers, such as polyethylene oxide (PEO).

The (PVDF-HFP) fluoropolymer regions are represented by color maps highlighting elemental F (green), while the LAGP regions are indicated from color maps highlighting...
elemental Ge (purple). Regions of elemental O, P, and Al coincide with where elemental Ge is seen. All micrographs were from CSP samples pressed at 120 °C and 400 MPa for 1 h before soaking in 1 M LiPF$_6$ EC-DMC (50:50 vol. %). Using CSP, it is possible to prepare dense samples with small and large amounts of polymer. It is also observed that distinct regions of ceramic and polymer can be obtained after CSP at 120 °C. Dispersion could be quantified using an area fraction estimation.

![Figure 6—4. EDS maps of CSP ceramic-polymer composites before soaking in 1 M LiPF$_6$ EC-DMC (50:50 vol. %) for 20 LAGP – 80 (PVDF-HFP), 70 LAGP – 30 (PVDF-HFP), 80 LAGP – 20 (PVDF-HFP), and 90 LAGP – 10 (PVDF-HFP). Elemental Ge is shown in purple and elemental F is shown in green.](image-url)
Figure 6-5 shows a comparison of fracture surfaces of 95 LAGP – 5 (PVDF-HFP) pellets shown in Fig. 6-2. As in Fig. 5-8, partial neck growth occurs as a result of CSP.

Figure 6—5. Micrographs of 95 LAGP – 5 (PVDF-HFP) pellets (unsoaked) (a) pressed at 120 °C with no water (dry) and (b) pressed at 120 °C with 30 to 39 vol. % water (wet, CSP). Densities are reported ± 1.5 %. A transition is observed from intergranular fracture (no water addition) to intragranular fracture (with water addition).

Impedance Spectroscopy of CSP Ceramic-Polymer Composites

Low and High Density Ceramic-Polymer Composites Before Soaking in Liquid Electrolyte

For the same samples in Fig. 6-2 and Fig. 6-5, impedance spectra were compared at a measurement temperature of 120 °C (Fig. 6-6). Ionic conductivity on the no water added (dry) sample was $1.8 \times 10^{-7} (\Omega\text{-cm})^{-1}$, while ionic conductivity on the CSP sample was $3.6 \times 10^{-4} (\Omega\text{-cm})^{-1}$ at 120 °C.
Figure 6—6. Impedance complex plane plots for unsoaked 95 LAGP – 5 (PVDF-HFP) pellets pressed at 120 °C with no water (dry) shown on the left in black and pressed at 120 °C with water (wet, CSP) shown on the right in red. A re-scaled inset is shown in order to observe the semicircle. The observed semicircle features are grain boundary features. Both samples were measured at 120 °C.

In Chapter 4, it was established that grain conductivity and grain activation energy is less sensitive to extrinsic processing effects than total conductivity and total activation energy. In Chapter 5, it was shown that the total activation energy of Cold Sintered LAGP without polymer (0.60 eV) is consistent with a partially amorphous grain boundary (0.52 eV) and a heat treatment was required to crystallize amorphous grain boundaries and obtain a total activation energy of 0.40 eV. Grain boundaries dominate the total conduction and total activation energy of Cold Sintered LAGP without polymer and without a heat treatment. In contrast, the grain and grain boundary regions of well-crystallized, conventionally sintered LAGP have similar activation energies (0.40 ± 0.01 eV). Mariappan et al. describes the origin of grain boundary resistance to be geometrical current constriction from limited grain boundary contact area.

In CSP ceramic-polymer composites, increasing conductivity and bridging partially
amorphous grain boundaries through a 650 °C heat treatment is not possible. In general, the performance of ceramic-polymer composites depends on the properties of the component materials, their volume fractions, phase connectivity, particle sizes, porosity, etc. (PVDF-HFP) was selected as a bridging polymer since it is an excellent host for Li-salts in polymer gel electrolytes. Amorphous regions of the (PVDF-HFP) copolymer absorb liquid electrolyte when soaked and increase grain boundary contact area.

First, it must be shown that unsoaked (PVDF-HFP) is well-dispersed across grain boundaries. Since (PVDF-HFP) is itself an insulator, Reynolds and Hough mixing behavior (Eq. 2-3) can be applied to calculate mixing behavior for unsoaked (100-x) LAGP – x (PVDF-HFP) composites. However, Reynolds and Hough mixing behavior predicts conductivity to decrease an order of magnitude across the range of (PVDF-HFP) addition and does not capture the data trend observed in Fig. 6-7. With (PVDF-HFP) addition, ionic conductivity drops orders of magnitude in the unsoaked composites. Using conductivity vs. porosity data from Delaizir et al., a calibration curve was generated to describe the mixing behavior of a biphasic mixture of pores and LAGP. Treating (PVDF-HFP) as a well-dispersed pore, a calibration curve is overlaid in Fig. 6-7 and is seen to only represent a fraction of the conductivity decrease in the triphasic mixture of pores, LAGP, and (PVDF-HFP). Therefore, (PVDF-HFP) addition may be disrupting grain-to-grain contact area in LAGP beyond what is allowed by a biphasic mixture of pores and LAGP. Once the composite is soaked in liquid electrolyte, polymer sitting at boundaries can swell into a Li-ion conducting polymer gel to bridge ionically resistive boundaries.
Figure 6—7. Ionic conductivities of LAGP – (PVDF-HFP) composites. Conductivities at 25 °C were obtained from impedance measurements of LAGP – (PVDF-HFP) composites before soaking in 1 M LiPF₆ EC-DMC (50:50 vol. %). A calibration curve for the relationship between conductivity and porosity from Delaizir et al. 28 (blue) does not capture the observed data trend since PVDF-HFP disrupts grain-to-grain contacts.

High Density Ceramic-Polymer Composites After Soaking in Liquid Electrolyte

Resistive LAGP grain boundaries can be ionically bridged with conducting (PVDF-HFP) + 1 M LiPF₆ EC-DMC (50:50 vol. %). Figure 6-8 shows impedance complex plane plots for soaked composites for (100-x) LAGP – x (PVDF-HFP), x = 5, 10, 20, 30, and 40 measured at 0 °C. Conductivities at 25 °C of (100-x) LAGP – x (PVDF-HFP) composites soaked in 1 M LiPF₆ EC-DMC (50:50 vol. %) ranged from 3.3 × 10⁻⁵ to 1.4 × 10⁻⁴ (Ω·cm)⁻¹, while activation energies ranged from 0.28 to 0.43 eV (Fig. 6-9).

Table 6-2 summarizes fit parameters for an (R-CPE) equivalent circuit model, while Table 6-3 summarizes fit parameters for a 2(R-CPE) equivalent circuit model. Fitting errors are
as high in Table 6-3 as fitting errors in Table 6-2. It is likely that overfitting occurs if one employs a 2(R-CPE) model. Impedance Spectroscopy Genetic Programming (ISGP) may be a useful technique to understand the number of fit parameters above which impedance data are being overfit (Appendix I).

Figure 6—8. Impedance complex plane plot of (100-x) LAGP – x (PVDF-HFP) CSP composites measured at 0 °C for x = 5 (pink), 10 (red), 20 (blue), 30 (black), and 40 (green) after soaking in 1 M LiPF₆ EC-DMC (50:50 vol. %). Measurements were performed at 0 °C rather than 25 °C to observe the semicircle (GB) feature and electrode-electrolyte polarization (E). While fits for a 2(R-CPE) model are overlaid, Table 6-3 shows that this model may constitute overfitting. Fit parameters for the more favorable (R-CPE) model are shown in Table 6-2.
Figure 6—9. Electrical properties of ionic conductor-polymer LAGP – (PVDF-HFP) composites. Conductivities at 25 °C obtained from impedance measurements (left) and activation energies of LAGP – (PVDF-HFP) composites (right). Both conductivity and activation energy are plotted as a function of PVDF-HFP volume fraction before and after soaking in 1 M LiPF$_6$ EC-DMC (50:50 vol. %).

While co-sintering ceramic with polymer may physically bridge resistive grain boundaries, soaking the composite in liquid electrolyte is required to ionically bridge these resistive grain boundaries. Polymer swelling through liquid electrolyte uptake also increases grain boundary contact area. Compositions with polymer loadings $\geq 30$ vol. %, where polymer swelling changes the composite dimensions, have been reported in flexible, solvent cast composites$^{199-202}$. After sixty days of soaking in liquid electrolyte at 25 °C, dimensions did not change in (100-x) LAGP – x (PVDF-HFP) composite electrolytes for x $\leq 30$. The lack of dimensional change in composite electrolytes is related to the Cold Sintered ceramic constraining the polymer’s swelling.

At temperatures $< 0$ °C, the liquid electrolyte freezes out, while $> 50$ °C, the liquid electrolyte dries out. Therefore, outside of the modest temperature range of 0 °C to 50 °C, conductivity is not stable with holding time and does not reach steady-state after 1 hour of holding at the measurement temperature. The tradeoff for $10^{-4}$ (Ω-cm)$^{-1}$ conductivity at 25 °C is a
limited temperature window with added liquid electrolyte. Table 6-4 summarizes Arrhenius data for ceramic-polymer composites.

An Arrhenius plot (Fig. 6-10) summarizes the behavior of three state-of-the-art electrolytes: Li$_{10}$GeP$_2$S$_{12}$ ceramic, 1 M LiBF$_4$/EMIBF$_4$ ionic liquid, and 1 M LiPF$_6$/50 EC-50 PC (vol. %) organic; and three high performance electrolytes from this thesis: Li$_7$P$_3$S$_{11}$ synthesized by the powder-in-a-tube method, LAGP bulk glass crystallized 825 °C for 8 h, and cold sintered 80 LAGP – 20 (PVDF-HFP) after soaking in liquid electrolyte. Although the electrolytes made in this thesis do not have the highest conductivities in literature, the electrolytes in this thesis have been processed at lower temperatures than in literature.

![Arrhenius plot](image)

**Figure 6—10.** Arrhenius plot of three state-of-the-art electrolytes and three high performance electrolytes from this thesis. Li$_{10}$GeP$_2$S$_{12}$ ceramic, 1 M LiBF$_4$/EMIBF$_4$ ionic liquid, and 1 M LiPF$_6$/50 EC-50 PC (vol. %) organic; Li$_7$P$_3$S$_{11}$ synthesized by the powder-in-a-tube method from Chapter 3 (green), LAGP glass heat treated 825 °C, 8 h from Chapter 4 (black), 120 °C CSP 80 LAGP - 20 (PVDF-HFP) after soaking in liquid electrolyte from Chapter 5 (royal blue). Note that for 80 LAGP - 20 (PVDF-HFP), the -10 and -30 °C are not stable data points past the typical 20 min temperature equilibration holds.
Table 6-2. Fit parameters for an (R-CPE) for impedance data in Fig. 6-8 measured at 0 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>R_GB (Ω-cm)</th>
<th>R_GB (Error%)</th>
<th>CPE_GB-Q (Ω-cm*s⁻¹)</th>
<th>CPE_GB-Q (Error%)</th>
<th>CPE_GB-n (Dimensionless)</th>
<th>CPE_GB-n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 LAGP – 5 (PVDF-HFP) Soaked</td>
<td>3.49 x 10⁴</td>
<td>2.40</td>
<td>1.22 x 10⁻⁷</td>
<td>8.96</td>
<td>0.589</td>
<td>1.20</td>
</tr>
<tr>
<td>90 LAGP – 10 (PVDF-HFP) Soaked</td>
<td>4.01 x 10⁴</td>
<td>3.38</td>
<td>2.99 x 10⁻⁷</td>
<td>18.6</td>
<td>0.392</td>
<td>3.41</td>
</tr>
<tr>
<td>80 LAGP – 20 (PVDF-HFP) Soaked</td>
<td>2.31 x 10⁴</td>
<td>0.656</td>
<td>2.25 x 10⁻⁴</td>
<td>14.4</td>
<td>0.515</td>
<td>1.97</td>
</tr>
<tr>
<td>70 LAGP – 30 (PVDF-HFP) Soaked</td>
<td>2.50 x 10⁴</td>
<td>2.41</td>
<td>3.29 x 10⁻⁷</td>
<td>17.9</td>
<td>0.385</td>
<td>3.27</td>
</tr>
<tr>
<td>60 LAGP – 40 (PVDF-HFP) Soaked</td>
<td>4.03 x 10⁴</td>
<td>1.21</td>
<td>1.38 x 10⁻⁷</td>
<td>7.91</td>
<td>0.456</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as $\rho_{\text{Grain Boundary}} \left(\frac{d}{D}\right) = R_{\text{Grain Boundary}} \left(\frac{d}{t}\right)$ rather than $\rho_{\text{Grain Boundary}} = \frac{1}{\sigma_{\text{Grain Boundary}}} = \frac{1}{R_{\text{Grain Boundary}} \left(\frac{1}{\lambda}\right) \left(\frac{d}{t}\right)}$. Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. $B$ or $G$ denotes the grain interior while $GB$ denotes the grain boundary.
Table 6-3. Fit parameters for 2(R-CPE) for impedance data in Fig. 6-8 measured at 0 °C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>R_B (Ω-cm) (Error%)</th>
<th>R_B (Ω-cm-s^α) (Error%)</th>
<th>CPE_B-Q (Dimensionless) (Error%)</th>
<th>CPE_B-n (Dimensionless) (Error%)</th>
<th>R_GB (Ω-cm) (Error%)</th>
<th>R_GB (Ω-cm-s^α) (Error%)</th>
<th>CPE_GB-Q (Dimensionless) (Error%)</th>
<th>CPE_GB-n (Dimensionless) (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 LAGP – 5 (PVDF-HFP) Soaked</td>
<td>1.79 x 10^4</td>
<td>7.74</td>
<td>3.13 x 10^5</td>
<td>8.36</td>
<td>0.217</td>
<td>2.40</td>
<td>2.50 x 10^3</td>
<td>0.66</td>
</tr>
<tr>
<td>90 LAGP – 10 (PVDF-HFP) Soaked</td>
<td>1.58 x 10^4</td>
<td>7.63</td>
<td>5.09 x 10^7</td>
<td>25.6</td>
<td>0.325</td>
<td>4.27</td>
<td>1.84 x 10^3</td>
<td>5.08</td>
</tr>
<tr>
<td>80 LAGP – 20 (PVDF-HFP) Soaked</td>
<td>1.73 x 10^4</td>
<td>3.79</td>
<td>1.61 x 10^8</td>
<td>14.5</td>
<td>0.519</td>
<td>1.62</td>
<td>5.11 x 10^2</td>
<td>12.1</td>
</tr>
<tr>
<td>70 LAGP – 30 (PVDF-HFP) Soaked</td>
<td>1.29 x 10^4</td>
<td>4.91</td>
<td>3.68 x 10^7</td>
<td>16.6</td>
<td>0.349</td>
<td>2.58</td>
<td>9.22 x 10^2</td>
<td>5.65</td>
</tr>
<tr>
<td>60 LAGP – 40 (PVDF-HFP) Soaked</td>
<td>2.51 x 10^4</td>
<td>10.6</td>
<td>1.81 x 10^7</td>
<td>8.21</td>
<td>0.432</td>
<td>1.24</td>
<td>1.23 x 10^3</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as $\rho_{\text{Grain Boundary}} \left(\frac{\Omega}{\text{cm}}\right) = R_{\text{Grain Boundary}} \left(\frac{\Omega}{\text{cm-s^α}}\right)$ rather than $\rho_{\text{Grain Boundary}} = \frac{1}{\sigma_{\text{Grain Boundary}} \left(\frac{\Omega}{\text{cm-s^α}}\right)} = \frac{1}{R_{\text{Grain Boundary}} \left(\frac{\Omega}{\text{cm}}\right) \left(\frac{\Omega}{\text{cm-s^α}}\right)}$. Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. B or G denotes the grain interior while GB denotes the grain boundary.
Table 6-4. Summary of ionic conductivities at 25 °C, activation energies, pre-exponentials, and densities for LAGP – (PVDF-HFP) polymer composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{25 \degree C}$ Total (Ω-cm)$^{-1}$</th>
<th>$\Delta E_{\text{Act}}$ Total (eV)$^*$</th>
<th>$\log \sigma_{25 \degree C}$ (Ω-cm)$^{-1}$</th>
<th>Absolute Density $\rho$ (g/cm$^3$)</th>
<th>Density (± 1.5 %)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 LAGP – 5 (PVDF-HFP)</td>
<td>$6.1 \times 10^{-7}$</td>
<td>0.65 ± 0.01</td>
<td>5.1</td>
<td>2.91</td>
<td>85.9</td>
<td></td>
</tr>
<tr>
<td>Unsoaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95 LAGP – 5 (PVDF-HFP)</td>
<td>$2.2 \times 10^{-4}$</td>
<td>0.54 ± 0.01</td>
<td>5.5</td>
<td>3.12</td>
<td>92.2</td>
<td>Normalized by the unsoaked volume.</td>
</tr>
<tr>
<td>Soaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 LAGP – 10 (PVDF-HFP)</td>
<td>$1.5 \times 10^{-4}$</td>
<td>0.63 ± 0.01</td>
<td>2.9</td>
<td>2.67</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td>Unsoaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 LAGP – 10 (PVDF-HFP)</td>
<td>$1.4 \times 10^{-4}$</td>
<td>0.42 ± 0.01</td>
<td>3.2</td>
<td>2.87</td>
<td>86.0</td>
<td>Normalized by the unsoaked volume.</td>
</tr>
<tr>
<td>Soaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 LAGP – 20 (PVDF-HFP)</td>
<td>$2.0 \times 10^{-9}$</td>
<td>0.63 ± 0.03</td>
<td>2.0</td>
<td>2.65</td>
<td>82.0</td>
<td></td>
</tr>
<tr>
<td>Unsoaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 LAGP – 20 (PVDF-HFP)</td>
<td>$1.4 \times 10^{-4}$</td>
<td>0.28 ± 0.02</td>
<td>1.6</td>
<td>2.85</td>
<td>88.0</td>
<td>Normalized by the unsoaked volume.</td>
</tr>
<tr>
<td>Soaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 LAGP – 30 (PVDF-HFP)</td>
<td>$1.1 \times 10^{-4}$</td>
<td>0.51 ± 0.03</td>
<td>0.70</td>
<td>2.66</td>
<td>84.8</td>
<td></td>
</tr>
<tr>
<td>Unsoaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 LAGP – 30 (PVDF-HFP)</td>
<td>$1.5 \times 10^{-4}$</td>
<td>0.33 ± 0.02</td>
<td>1.7</td>
<td>2.92</td>
<td>93.4</td>
<td>Normalized by the unsoaked volume.</td>
</tr>
<tr>
<td>Soaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 LAGP – 40 (PVDF-HFP)</td>
<td>$4.6 \times 10^{-10}$</td>
<td>0.42 ± 0.01</td>
<td>-2.2</td>
<td>2.64</td>
<td>87.7</td>
<td>Pre-exponential was negative but conductivity not stable outside of 0 to 50 °C</td>
</tr>
<tr>
<td>Unsoaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 LAGP – 40 (PVDF-HFP)</td>
<td>$3.5 \times 10^{-4}$</td>
<td>0.43 ± 0.01</td>
<td>2.8</td>
<td>2.82</td>
<td>93.7</td>
<td>Normalized by the unsoaked volume. However, after soaking for 60 days, the compact expanded.</td>
</tr>
<tr>
<td>Soaked</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 (PVDF-HFP)</td>
<td>$3.7 \times 10^{-9}$</td>
<td>0.81 ± 0.04</td>
<td>5.3</td>
<td>1.65</td>
<td>92.9</td>
<td>Tarascon et al. 39 shows conductivity of 2.5 x 10$^{-4}$ S/cm for porous PVDF – 12 % HFP soaked in 1 M LiPF$_6$ EC/PC.</td>
</tr>
<tr>
<td>Soaked after 120 °C, 400 MPa, No water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Please see the footnote in Table 1-1.

Chapter Conclusions

As in Chapter 5, it was demonstrated that pressure, temperature, holding time, and solvent addition are important variables for CSP of ceramic-polymer composites even. This is the case when pressing is done above the glass transition temperature of the polymer and if the polymer is the minor phase. Water addition is crucial for sintering to occur even when pressure, temperature and holding time are fixed. After CSP, unsoaked LAGP – (PVDF-HFP) composites are fairly insulating. Reasons for improved ionic conductivity with liquid electrolyte soaking were discussed. The liquid electrolyte uptakes (5 – 10 wt. %) are lower than the > 55 wt. %
liquid electrolyte uptake in polymer membranes in literature\textsuperscript{180}. Therefore, less flammable liquid electrolyte would be available in a battery would be subject to thermal runaway. With low liquid electrolyte volume in ceramic-polymer composites, electrolytes will self-extinguish faster than high liquid electrolyte volume separators\textsuperscript{202}.

Impedance spectroscopy equivalent circuit modeling fitting errors were shown to favor a single (R-CPE) rather than a 2(R-CPE) model. As a result of additional circuit elements not adding understanding to the behavior of a ceramic-polymer composite soaked in liquid electrolyte, Impedance Spectroscopy Genetic Programming (ISGP) may be a useful technique to employ in the future (Appendix I).

The sintering conditions of CSP make it possible to co-sinter thermoplastic polymers and ceramic materials in a single-step sintering process. The data shown here would suggest that polymer manufacturing approaches could be modified for the sintering of both ceramics and ceramic-polymer composites, resulting in saving energy in production (Appendix C), increasing throughput, and also allowing novel composite designs.

CSP can bridge the processing gap of ceramics and polymers, & open up a simple and effective way for integration of material systems and devices using ceramics and polymers that are traditionally incompatible. Typically, hundreds of degrees separate the ability to co-process these materials in one step with high volume fractions of ceramic materials. It is anticipated that these approaches will have multiple impacts, including design of new material composites, new low temperature manufacturing processes, simplified integration of dissimilar materials, and sustainable manufacturing processes with lower costs.

With ceramics potentially using polymer manufacturing techniques, such as injection molding and lamination, it is expected larger area devices may be made with higher yields than
those typically made with conventional ceramic sintering processes. CSP electrolytes in this thesis were made with ~ 400 MPa uniaxial pressure. These pressures are higher than those realized by injection molding setups. For example, the injection molding conditions for glycol-modified poly (ethylene terephthalate), a common plastic beverage bottle material, prescribes pressures of ~ 83 MPa and a nozzle temperature of ~ 240 °C. For lamination, even lower pressures than injection molding are typical. High-pressure laminates are commonly under pressures between 8 to 14 MPa. Therefore, future work should focus on understanding how to lower the required pressure for cold sintering.

Beyond electrolytes, through bridging this processing temperature gap, there are now multiple applications that can be manufactured ranging from architectural materials, structural materials, thermal insulation, biomedical implants, as well as many electronic applications. Along with the composite electrolyte shown in this study, electrical applications include packaging substrates, microwave filters, electrochemical cells, and thermistors. Having bridged this processing gap to a common fabrication route, polymer, ceramic and nanomaterials now can more readily be integrated without compromising their individual properties at interfaces through poor physical contact, decomposition or chemical interdiffusion.

To realize the final manufacturing benefits of increased throughput and cost savings from CSP, fundamental scientific questions must be addressed. These future work directions are outlined in Chapter 7.
Chapter 7 Conclusions and Future Work

Conclusions

This thesis is focused on low temperature means to bridge ionically resistive boundaries in sulfide and oxide solid electrolytes (Fig. 7-1). The first bridge crosses resistive pores through densification, the second bridge focuses on grain boundary engineering to minimize resistive grain boundaries between conducting grains, and the third bridge uses cold sintering to allow simultaneous densification of ceramics and polymers.

Figure 7—1. Three main categories of ionically resistive bridges addressed in this thesis. Bridge I was discussed in Chapters 2 and 3 for x Li_2S + (1-x) P_2S_5 (x = 0.70, 0.75, 0.80). Bridge II was discussed in Chapters 4 and 5 for Li_{1+x}Al_xGe_{2-x}(PO_4)_3 (x = 0.50) & Bridge III was discussed in Chapter 6 for and Li_{1+x}Al_xGe_{2-x}(PO_4)_3 (x = 0.50) with (PVDF-HFP) and small amounts of liquid electrolyte.

Using Cold Sintering Process (CSP), processing and integration of technical ceramics may be done at food processing temperatures. New opportunities exist in designing target electrical and mechanical properties of co-sintered ceramic-polymer composites by tailoring polymer addition. While literature has been focused on flexible ceramic-polymer electrolytes with $\geq 30$ vol. % polymer loading, ceramic loadings of 95 vol. % have been demonstrated. Small
amounts of added liquid electrolyte were required to boost ionic conductivity. Nevertheless, the amount of required liquid electrolyte was small and may self-extinguish a flame rather than to act as fuel to feed a large fire in batteries subject to thermal runaway.  

Suggestions for future systematic study are focused on cold sintering. More generally, synergy with other fields is key to advancing understanding of CSP and may rely on controlled biomineralization. To quote Larcher and Tarascon in regards to lowering processing temperatures, “bio-assisted strategies are based on very efficient enzymatic and active biological processes intrinsically not wasting atoms.”

**Cold Sintering Future Work**

**Characterization of Densification and Grain Boundary Development**

In Chapter 5, ceramics after CSP were able to achieve densities that are significantly higher than cold pressing (65 vs. 80 % density). However, the densification of LAGP and its properties are not optimized. A clear direction for future work is to understand densification, grain boundary development, and the influence on processing on the pertinent property of ionic conductivity. It is well established that grain boundaries limit the total ionic conductivity in ceramics with micron-sized grains. One important area is to clarify the role of the transient solvent’s amount, dissolution rate, and evaporation rate on densification and grain boundary development. Minimizing the amorphous grain boundary thickness will prevent the need for a second crystallization heat treatment after CSP that is currently needed to improve ionic conductivity.
Thermogravimetric Analysis-Mass Spectroscopy (TGA-MS) coupled with Thermomechanical Analysis (TMA) will be an important technique to monitor shrinkage changes in compacts under uniaxial pressure as OH⁻, H₂O, and CO₂ species volatilize. TGA-MS experiments done in this thesis were on powders rather than on compacts under uniaxial pressure. If volatile species have to leave a compact for densification to occur, pressure application cannot be isostatic or else the species will not be able to leave. Entrapped, insoluble gas in pores controls densification during final stage sintering and there are instances when applied external pressure from hot isostatic pressing (HIP) cannot further densify microstructures with closed porosity. For example, in alumina, densified by “sinter plus HIP,” sintering at 1400 °C prior to HIP results in a higher relative density than sintering at 1500 °C prior to HIP. Microstructural control is important in systems other than alumina. Additional layers of understanding are required for how cold sintering can be translated into a viable technique for other ceramics like superconducting ceramics, which sinter using transient, yet volatile, liquid phase and whose properties require highly equiaxed grains.

Considering densification in electrolytes, a few percent of porosity may be tolerable in electrochemical applications. A handful of entries in Table 1-1 report LAGP densities between 78 and 88 %. Porosity is less tolerable in other electroceramics. For example, dielectric breakdown strength changes greatly with porosity. In large area format samples, this is detrimental. For example, in 8 cm in diameter, 90 % porous, and 1.6 mm thick samples, a void diameter of 150 μm may reduce breakdown strength to 30 % of the dense ceramic’s breakdown strength. Although void diameters are not expected to be in the microns rather than hundreds of microns, the important property of breakdown strength is still compromised with porosity.
One solution is to add high dielectric breakdown polymer and co-sinter it with ceramic using cold sintering.

Focusing again on electrolytes, preparation of electrolytes could be done in a controlled, CO$_2$-free atmosphere to prevent a scale of Li$_2$CO$_3$ from developing. An example of a controlled environment is an Ar glovebox with sodium hydroxide-based circulation purifier as a CO$_2$ sink. LAGP glass could be crystallized in air and milled to a fine powder, using procedures in previous chapters. A post treatment in a tube furnace attached to a glovebox could decompose the carbonate scale $\sim 650 \, ^\circ$C. Then, this powder could be cold sintered in a glovebox. Since aqueous solvents are an unfavorable choice for glovebox processing, new solvent systems may need to be developed. It is not yet understood if a non-aqueous solvent (dehydrated ethanol) is strong enough to cause the desired dissolution in LAGP or similar electrolytes.

While much less reactive than sulfide electrolytes, oxide electrolytes still interact with CO$_2$ and H$_2$O in the atmosphere $^{218-221}$. The surface chemistry changes and stability that influences long-term electrochemical stability needs to be understood. For example, Dudney and Kalnaus increased conductivity of oxide ceramic-polymer composites simply by handling in a glovebox where DMC solvent was used $^{207}$.

Cold sintered grain boundary properties could be characterized in depth using high-field impedance using protocols established by Gellert et al. $^{24}$. Ma et al. $^{18}$ studied the perovskite (Li$_{3x}$La$_{2/3-x}$)TiO$_3$. Based on HAADF-STEM and EELS analysis, it was concluded that the grain interior is La-poor (Li-rich) and the grain boundary core is La-rich (Li-poor). Similar microscopy techniques, coupled with electrical properties, will be valuable in furthering understanding of cold sintered electrolytes processed under different conditions. It is important to know how
residual transient solvent influences the electrochemical properties of cold sintered electrolytes, especially the rate at which these properties change with time and temperature.

**Electrochemical Cell Development**

For a solid-state electrochemical cell, cathode and anode materials that can be cold sintered must be identified. Here, it seems possible to construct a thin, multilayer cell in a single-step since the usual problems of thermomechanical mismatch (delamination) and unfavorable chemical inter-diffusion between the electrodes and the electrolyte upon firing can be avoided if low temperatures are used.

Cold sintering may be combined with other processing techniques such as microwave or powder-in-a-tube processing. There are innovative approaches to processing thin solid electrolytes using non-vacuum techniques, such as spray deposition\textsuperscript{222,223} that may be amenable to cold sintering. Cold spray deposition pressures are on the order of $10^5$ MPa\textsuperscript{224}, much higher than the 400 MPa pressures employed for cold sintering, and may result in far from equilibrium (low crystallinity) structures.

Cold sintering other important lithium electrolyte solid electrolyte families is another focus area since sourcing GeO\textsubscript{2} is costly (Appendix C). Substitution of Ti for Ge in the well-known Li\textsubscript{1.5}Al\textsubscript{0.5}Ti\textsubscript{1.5}(PO\textsubscript{4})\textsubscript{3} composition may be a viable option. However, this electrolyte, like lithium lanthanum titanate, suffers from a Ti reduction reaction vs. Li metal and would require a buffer layer between Li metal\textsuperscript{17,225}. The garnets\textsuperscript{4-15} are an attractive electrolyte candidate family since some varieties are electrochemically stable vs. Li metal.
Last, other cation conductors like sodium-ion or silver-ion based conductors could also be explored to open the application space of electrochemical capacitors or proton conductors could be explored to open up new opportunities in fuel cells.

The broader impact of this work will further the development of multilayer co-fired ceramic technologies, in particular solid-state multilayer battery fabrication. It is anticipated that, with full understanding of the sintering process, high quality electrolytes can be co-sintered into all-solid state Li-battery structures. With an electrolyte that can be sintered at < 200 °C through CSP, it is envisioned to improve the ease of integration of ceramic electrolytes into electrochemical cells for safer, higher performance batteries.
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Appendix A
Pellets and micrographs of \(0.80 \text{Li}_2\text{S} + 0.20 \text{P}_2\text{S}_5\) from literature and from this thesis.

![Figure A-1](image)

Figure A-1. Images of \(0.80 \text{Li}_2\text{S} + 0.20 \text{P}_2\text{S}_5\) electrolytes from Kitaura et al.\(^{132}\), where pellets were pressed at 360 MPa at (a) room temperature, 2 h; (b) 180 °C, 2 h; (c) 210 °C, 2 h; (d) 240 °C, 2 h; and (e) 210 °C, 4 h.
Figure A-2. Micrographs of 0.80 Li2S + 0.20 P2S5 electrolytes from Kitaura et al.\textsuperscript{132}, where pellets were pressed at 360 MPa at (a) room temperature, 2 h; (b) 210 °C, 2 h.
Figure A-3. Micrographs of 0.80 Li$_2$S + 0.20 P$_2$S$_5$ electrolytes. Processing conditions include pressed 228 °C, 186 MPa and pressed 210 °C, 186 MPa and crystallized at 351 °C. Micrographs were obtained on uncoated fracture surfaces. To prevent air exposure, a transfer cell designed by Gordin was employed $^{154}$. 
Figure A-4. Micrographs of 0.80 Li$_2$S + 0.20 P$_2$S$_5$ fracture surface, pressed 210 °C, 186 MPa and crystallized in a powder bed 294 °C. Unoptimized working distances (36 mm) were a result of the special sample holder. Micrographs were obtained on uncoated fracture surfaces. To prevent air exposure, a transfer cell designed by Gordin was employed 154.
Appendix B

Inductively coupled plasma emission spectrometry analysis of nominal composition of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ glass melted in alumina crucibles. A lithium metaborate dissolution was used. Data were collected by Henry Gong (PSU College of Earth & Mineral Sciences).

<table>
<thead>
<tr>
<th>Oxide Component (wt. %)</th>
<th>Melted 1380 °C, 1 h</th>
<th>Melted 1400 °C, 1.5 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$ Upper Limit</td>
<td>6.18</td>
<td>6.75</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$ Lower Limit</td>
<td>5.59</td>
<td>6.11</td>
</tr>
<tr>
<td>Ideal $\text{Al}_2\text{O}_3$</td>
<td>6.101</td>
<td>6.101</td>
</tr>
<tr>
<td>$\text{GeO}_2$ Upper Limit</td>
<td>37.13</td>
<td>35.63</td>
</tr>
<tr>
<td>$\text{GeO}_2$ Lower Limit</td>
<td>34.97</td>
<td>33.56</td>
</tr>
<tr>
<td>Ideal $\text{GeO}_2$</td>
<td>37.571</td>
<td>37.571</td>
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<tr>
<td>$\text{P}_2\text{O}_5$ Upper Limit</td>
<td>53.39</td>
<td>52.03</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$ Lower Limit</td>
<td>50.28</td>
<td>49</td>
</tr>
<tr>
<td>Ideal $\text{P}_2\text{O}_5$</td>
<td>50.963</td>
<td>50.963</td>
</tr>
<tr>
<td>$\text{Li}_2\text{O}$ Upper Limit*</td>
<td>5.98</td>
<td>5.46</td>
</tr>
<tr>
<td>$\text{Li}_2\text{O}$ Lower Limit*</td>
<td>5.41</td>
<td>4.94</td>
</tr>
<tr>
<td>Ideal $\text{Li}_2\text{O}$</td>
<td>5.365</td>
<td>5.365</td>
</tr>
</tbody>
</table>

* $\text{Li}_2\text{O}$ not measured directly
Appendix C

Cost estimate comparison for $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ made by conventional sintering and cold sintering.

$$TPC = RMC + PC \quad (\text{Eq. C-1})$$

where

$TPC =$ Total Processing Cost ($/m^2$)

$RMC =$ Raw Material Cost ($/m^2$)

$PC =$ Processing Cost ($/m^2$)

Note that $PC$ includes energy costs for mixing, energy costs for heating, and miscellaneous expenses (labor, capital investment for equipment insurance/maintenance, manufacturing/environmental permits, and engineering controls for safety). In the discussion in Chapter 4, it is thought that sulfide electrolytes will have higher miscellaneous expenses than oxide electrolytes.
Cost savings estimates for cold sintering considering both raw material and processing costs for 15 μm thick electrolytes of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ and Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ assuming a bulk electricity price of $0.05$/kWh.

**Table C-1. Raw material cost estimates.**

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>$/\text{ton}$</th>
<th>Amount (tons) for 1 ton batch</th>
<th>$/\text{ton}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$CO$_3$</td>
<td>6.00 x 10$^3$</td>
<td>0.146</td>
<td>8.74 x 10$^2$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.70 x 10$^2$</td>
<td>0.0670</td>
<td>24.8</td>
</tr>
<tr>
<td>(NH$_4$)$_2$HPO$_4$</td>
<td>4.80 x 10$^2$</td>
<td>1.04</td>
<td>4.99 x 10$^2$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.50 x 10$^2$</td>
<td>0.315</td>
<td>78.7</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>1.90 x 10$^6$</td>
<td>0.376</td>
<td>7.14 x 10$^5$</td>
</tr>
</tbody>
</table>

Sources for price estimates, accessed 28 June 2016:

Table C-2. Processing cost estimates.

<table>
<thead>
<tr>
<th>Processing Step</th>
<th>Energy Expenditure</th>
<th>$/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill</td>
<td>10 kWh/ton</td>
<td>0.50</td>
</tr>
<tr>
<td>Calcine</td>
<td>9 kWh/60 g</td>
<td>7500.00</td>
</tr>
<tr>
<td>Mill</td>
<td>10 kWh/ton</td>
<td>0.50</td>
</tr>
<tr>
<td>Melt</td>
<td>24 kWh/60 g</td>
<td>20000.00</td>
</tr>
<tr>
<td>Crystallize</td>
<td>13 kWh/60 g</td>
<td>10833.33</td>
</tr>
<tr>
<td>Mill</td>
<td>10 kWh/ton</td>
<td>0.50</td>
</tr>
<tr>
<td><strong>Conventional sintering</strong></td>
<td>13 kWh/60 g</td>
<td>10833.33</td>
</tr>
<tr>
<td><strong>Cold sintering</strong></td>
<td>100 kJ/g</td>
<td>1388.89</td>
</tr>
</tbody>
</table>

Table C-3. Estimated dollars per square meter for 15 μm Li₁₁.₅Al₀₅Ge₁₁.₅(PO₄)₃ and Li₁₁.₅Al₀₅Ti₁₁.₅(PO₄)₃ including both raw material and processing costs.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Area/ton (m²)</th>
<th>$/m² Conventional sintering</th>
<th>$/m² Cold sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₁₁.₅Al₀₅Ti₁₁.₅(PO₄)₃</td>
<td>2.15 x 10⁴</td>
<td>2.35</td>
<td>1.91</td>
</tr>
<tr>
<td>Li₁₁.₅Al₀₅Ge₁₁.₅(PO₄)₃</td>
<td>1.94 x 10⁴</td>
<td>39.33</td>
<td>38.84</td>
</tr>
</tbody>
</table>
Appendix D

Discharge time at rated power vs. system power ratings for energy storage devices going from 1 kW to 1 GW\textsuperscript{226,227}. While this figure emphasizes grid-scale energy storage, < 1 kW energy storage is important for “Internet of Things” applications and health sensors.

Abbreviations:
Uninterrupted Power Supply (UPS)
Transmission and Distribution (T&D)
Appendix E

Comparison of liquid and solid-state electrolyte cell advantages (shaded green), disadvantages (shaded red), and neutral conditions (unshaded) adapted from Jones et al. 228.

<table>
<thead>
<tr>
<th>Liquid electrolyte cell</th>
<th>Solid-state cell</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing</strong></td>
<td></td>
</tr>
<tr>
<td>Inexpensive processing</td>
<td>Expensive processing (need vacuum systems)</td>
</tr>
<tr>
<td>Large format in production</td>
<td>Only small format in production</td>
</tr>
<tr>
<td>Air-sensitive electrolytes</td>
<td>Electrolyte may be air-sensitive (sulfide) or air-stable (oxide)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties Affecting Safety and Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower mechanical modulus polymer separators accommodate some stress, but lithium dendrite penetration possible</td>
</tr>
<tr>
<td>Solid Electrolyte Interface (SEI) layer formation</td>
</tr>
<tr>
<td>Higher ionic conductivity near 25 °C, but poor thermal stability</td>
</tr>
<tr>
<td>Lower interfacial impedance since solvated lithium ions are easily able to wet the pores of the separator</td>
</tr>
<tr>
<td>More inactive materials, reduces energy density</td>
</tr>
<tr>
<td>Flammable electrolyte poses combustion hazard, more sensitive to overcharge</td>
</tr>
<tr>
<td>Electrolyte reactions limit cathode materials</td>
</tr>
<tr>
<td>Higher self-discharge limits shelf life</td>
</tr>
</tbody>
</table>
Appendix F

Technical metrics from the Department of Energy ARPA-E Integration and Optimization of Novel Ion Conducting Solids (IONICS) \(^{229}\).

Figure F-1. Radar diagram comparing technical metrics for three electrolytes.

* ASR (Area specific resistance)
Table F-1. Performance metrics proposed by the IONICS FOA.

<table>
<thead>
<tr>
<th>Performance Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enable cycling of Li metal at 25 °C</td>
<td>Modulus, surface, and microstructural properties that prevent Li metal shorting</td>
</tr>
<tr>
<td>Thermal operating range</td>
<td>-20 to 70 °C</td>
</tr>
<tr>
<td>Area with property values with ≥ 90% uniformity</td>
<td>≥ 30 cm²</td>
</tr>
<tr>
<td>Cost</td>
<td>≤ $10/m²</td>
</tr>
<tr>
<td>Ionic ASR at 25 °C</td>
<td>≤ 5 Ω·cm²</td>
</tr>
<tr>
<td>Capacity of Li metal moved per cycle</td>
<td>≥ 3 mAh/cm²</td>
</tr>
<tr>
<td>Current density</td>
<td>≥ 3 mA/cm²</td>
</tr>
<tr>
<td>Number of cycles without ≥ 20% degradation of other performance metrics</td>
<td>≥ 500</td>
</tr>
<tr>
<td>Electrochemical stability</td>
<td>0 - 4.5 V vs Li/Li⁺</td>
</tr>
<tr>
<td>Thickness</td>
<td>≤ 20 μm</td>
</tr>
<tr>
<td>Depth of discharge of Li electrode</td>
<td>≥ 80%</td>
</tr>
<tr>
<td>Electronic ASR at 25 °C</td>
<td>≥ 1x10⁵ Ω·cm²</td>
</tr>
<tr>
<td>Mechanical properties for handling and operation</td>
<td>Suitable for handling components with an area ≥ 30 cm²</td>
</tr>
<tr>
<td>Device integration</td>
<td>Suitable for integration in a cell that achieves ≥1000 Wh/L and ≥400 Wh/kg for the cell repeat unit of current collectors, electrodes, and separator</td>
</tr>
</tbody>
</table>

\[
\text{Ionic ASR} = \rho_{\text{Ionic}} * t \quad \text{(Eq. F-1)}
\]

where

- \( \text{Ionic ASR} \) = Ionic area specific resistance (Ω·cm²)

- \( \rho_{\text{Ionic}} \) = Ionic resistivity (Ω·cm)

- \( t \) = Thickness (cm)
Energy storage research and technology development roadmap from the National Science Foundation’s International Materials Institute for New Functionality in Glass workshop “Functional glasses: properties and applications for energy and information”.

**Roadmap IV: Energy Storage Technology**

*All Solid State Batteries (ASSB)*

**Part A**

**Overall challenges**
- higher energy and power density
- high ionic conductivity (faster rate)
- chemically durable glasses (safety aspects)
- Improved of the interfacial bonding (cycle life stability)

**Part B**

**Ion transport**
- ion migration process (Li⁺, Na⁺); grain boundary resistance & interface modifications
- quantitative structure-properties relationships

**Part C**

**Electrodes**
- chalcogenide glass anodes
  - LiFePO₄, Na₀.₉FeP₂O₇
- chemically stable non-silicate compositions
- crystallization around the liquidus temperature
- high temperature compatibility with metal
**Appendix H**

Boiling point, flash point, and ignition point for organic liquid electrolyte solvents adapted from $^{231}$ shown to emphasize the importance of solid electrolytes for safer energy storage technologies.

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>Boiling Point (°C)</th>
<th>Flash Point (°C)</th>
<th>Ignition Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-THF</td>
<td>80</td>
<td>-11</td>
<td>270</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>34</td>
<td>-40</td>
<td>160</td>
</tr>
<tr>
<td>Di-isoamyl ether</td>
<td>173</td>
<td>41</td>
<td>-</td>
</tr>
<tr>
<td>Di-isopropyl ether</td>
<td>68</td>
<td>-12</td>
<td>443</td>
</tr>
<tr>
<td>Dibutyl ether</td>
<td>142</td>
<td>25</td>
<td>194</td>
</tr>
<tr>
<td>Ethylimethyl ether</td>
<td>11</td>
<td>-37</td>
<td>190</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>-24</td>
<td>-41</td>
<td>-</td>
</tr>
<tr>
<td>Propylene carbonate(PC)</td>
<td>243</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene carbonate(EC)</td>
<td>240</td>
<td>132</td>
<td>-</td>
</tr>
<tr>
<td>Diethyl carbonate(DEC)</td>
<td>127</td>
<td>31</td>
<td>-</td>
</tr>
<tr>
<td>Ethylmethyl carbonate(EMC)</td>
<td>107</td>
<td>24</td>
<td>-</td>
</tr>
<tr>
<td>Dimethyl carbonate(DMC)</td>
<td>90</td>
<td>18</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix I

Overview of impedance spectroscopy analysis and fitting methods: a comparison of Impedance Spectroscopy Genetic Programming and equivalent circuit modelling.

In the solid ionics community, total ionic resistivity is often determined by a visual method. The low frequency polarization feature is extrapolated to the real impedance axis in an impedance complex plane plot. The single parameter of total ionic resistivity can be obtained using this visual method in the case of only observing a low frequency polarization feature and in the case of observing a low frequency polarization feature in addition to observing a higher frequency semicircular feature.

An added level of analysis is to use equivalent circuit modelling. The best practice is to observe minimal sum of squared error differences, as well as minimal visual differences between the experimental data and fit data in different data representation formalisms ($Z$, $M$, $\varepsilon$, $Y$). Of course, all fit parameters must be physical. For example, capacitance must be positive. Last, parameters should not be correlated. In Fig. I-1 and Table I-1, the fit clearly improves from adding parameters and moving from a (R-CPE) equivalent circuit to a 2(R-CPE).

There are many methods to prevent overparameterization of data. In the spectroscopic ellipsometry community, cross-correlation matrices are commonly used to see if adding additional parameters help the describing power of a model. Similarly, in the impedance spectroscopy community, the common software program used for impedance fitting, ZView®, has a built-in error message to warn users of a singular matrix. For example, a singular matrix error is returned when the user attempts to use a 3(R-CPE) model when a 2(R-CPE) is more appropriate (Fig. I-2). The rejection criteria for returning a singular matrix error occurs qualitatively when the iterative process creates a situation where changing a parameter’s value
has no effect on the fit. This can occur when a model already reflects all the physical sources of impedance, but some parameters do not contribute to fitting the measured data. In this case, two or more parameters may have identical effects on the fit and an infinite number of solutions are possible that fit the experimental data equally well. Quantitatively, the criteria for when ZView® detects that the model is diverging is not well defined without release of the code \(^{233}\).

Figure I-1. Impedance complex plane plot of LAGP bulk glass crystallized at 825 °C, 8 h. Experimental data points are shown by the black squares. The 2(R-CPE) fit (red) is clearly better than the R-CPE fit (blue).
Figure I-2. Screenshot from ZView® of a bad correlation matrix, singular matrix error when a 3(R-CPE) is attempted to be fit. The error is highlighted by a yellow oval.
Table I-1. Fit parameters for (R-CPE) and a 2(R-CPE) for impedance data measured at -60 °C with symmetric Pt electrodes in Fig. I-1.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>R_B (Ω-cm)</th>
<th>R_B (Error%)</th>
<th>CPE_B-Q (Ω-cm-s(^{-1}))</th>
<th>CPE_B-Q (Error%)</th>
<th>CPE_B-n (Dimensionless)</th>
<th>CPE_B-n (Error%)</th>
<th>R_GB (Ω-cm)</th>
<th>R_GB (Error%)</th>
<th>CPE_GB-Q (Ω-cm-s(^{-1}))</th>
<th>CPE_GB-Q (Error%)</th>
<th>CPE_GB-n (Dimensionless)</th>
<th>CPE_GB-n (Error%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825 °C, 8 h</td>
<td>5.11 x 10(^{5})</td>
<td>1.38</td>
<td>1.15 x 10(^{15})</td>
<td>21.9</td>
<td>0.745</td>
<td>2.15</td>
<td>---</td>
<td>---</td>
<td>8.92</td>
<td>2.04 x 10(^{8})</td>
<td>32.8</td>
<td>0.615</td>
</tr>
<tr>
<td>825 °C, 8 h</td>
<td>4.02 x 10(^{3})</td>
<td>2.89</td>
<td>2.06 x 10(^{11})</td>
<td>11.8</td>
<td>0.868</td>
<td>1.07</td>
<td>1.86 x 10(^{6})</td>
<td>---</td>
<td>8.05</td>
<td>8.92</td>
<td>0.615</td>
<td>8.05</td>
</tr>
</tbody>
</table>

Table footnotes: Grain boundary fit parameters are given as \( \rho_{\text{Grain Boundary}} \cdot \frac{d}{D} = R_{\text{Grain Boundary}} \cdot \frac{d}{\tau} \) rather than \( \rho_{\text{Grain Boundary}} = \sigma_{\text{Grain Boundary}} = \frac{1}{R_{\text{Grain Boundary}}} = \frac{1}{\sigma_{\text{Grain Boundary}}} \). Please see Eq. 1-9 and Eq. 1-20 for more discussion about the distinctions between grain conductivity, grain boundary conductivity, and total conductivity. \( B \) or \( G \) denotes the grain interior while \( GB \) denotes the grain boundary.
Another method used to prevent overparameterization in this thesis was Impedance Spectroscopy Genetic Programming (ISGP). Many combinations of equivalent circuits can be used to fit the same data and may mislead workers to assign the wrong equivalent circuit. Instead of cross-correlation matrices, a discrepancy-complexity plot is generated in the case of ISGP.

By fitting an equivalent circuit, one assumes the physical phenomena that are occurring and finds values to fit the model. However, the more fitting parameters are used, the lower the observed error (Fig. I-3). An alternative to equivalent circuit modelling is to model the distribution functional of relaxation times (DFRT). Genetic Programming refers to the model’s ability to implement evolutionary mutations between each generation (fitting iteration) to better represent the DFRT analytically. Evolutionary mutations include adding a peak, swapping a peak, or removing a peak.

![Figure I-3](image.png)

**Figure I-3.** Reduction in sum of squares error with increased number of fitting parameters is natural. Overfitting occurs in models that have numbers of fitting parameters past the plateau in sum of squares error. Statisticians have methods to determine whether increasing the number of fitting parameters is “significant” and adds significant describing power to the model. Therefore, Impedance Spectroscopy Genetic Programming (ISGP) is a more rigorous alternative to fitting impedance spectra than equivalent circuit models.
Suppose one has a Lorentzian distribution given by (Eq. I-1). Three fitting parameters are required to describe peak amplitude, peak width, and peak position. The distribution function is then substituted into (Eq. I-2) and compared to the experimental impedance values.

\[
\Gamma'(\log(\tau)) = \frac{A}{1 + \left(\frac{\log(\tau) - \log(\tau_0)}{\sigma}\right)^2} \tag{Eq. I-1}
\]

where
\[
\tau = \text{Time or frequency} \\
A = \text{Peak amplitude} \\
\sigma = \text{Peak width} \\
\tau_0 = \text{Peak position}
\]

\[
Z(\log(\omega)) = R_{\text{max}}(T) \int_{-\infty}^{\infty} \frac{\Gamma'(\log(\tau))}{1 + j\omega \tau} d(\log(\tau)) \tag{Eq. I-2}
\]

where
\[
j = \sqrt{-1} \\
\omega = \text{Angular frequency (rad/s)} \\
\tau = \text{Time constant (s)} \\
Z = \text{Complex impedance (}\Omega) \\
R_{\text{max}} = \text{Maximum resistance (}\Omega) \\
\Delta E_{\text{Act}} = \text{Activation energy (eV)} \\
T = \text{Absolute temperature (K)}
\]

For Debye behavior, described in Chapter 1, the DFRT would be a delta function. Two DFRT peaks are expected for a grain response and a grain boundary response. Therefore, for a 3-parameter Lorenztian model, six parameters are required to describe two DFRT peaks. Figure I-
4 shows DFRT fits for four different crystallization conditions measured at -60 °C. In the future, such fitting approaches may provide more insight into the electrical properties of heterogeneous materials such as polycrystalline solid electrolytes, mixed conductors (battery electrodes), and ceramic-polymer composite systems.

Figure I-4. Distribution function of relaxation times for LAGP glass crystallized at different temperatures. Only the distribution shown in green was covered during crystallization, while the others were crystallized uncovered. As concluded in Chapter 4, grain contributions are stable and are grouped in a tighter frequency band than frequency band for grain boundary (G.B.) contributions (highlighted in yellow).
Appendix J

Shear modulus vs. ionic conductivity for various classes of electrolytes showing that glass, ceramic, glass-ceramic, and superionic conductors lie above the dotted gray Li dendrite penetration threshold (left) and potential windows and ionic conductivities of various classes of electrolytes (right) from Dudney et al. 234.
Seth Sevidal Berbano was born in Iowa and has many fond memories of picnicking and biking on Iowa State’s Central Campus, shooting baskets at State Gym, making silly putty at VEISHEA, and listening to concerts in Music Hall. He graduated with his B.S. in Materials Engineering and minor in Economics, summa cum laude, from Iowa State University in 2011. At Iowa State, he worked in Prof. Steve W. Martin’s research group. He was a George Washington Carver Scholar and was actively involved with Supplemental Instruction, Material Advantage, Keramos, Golden Key, Tau Beta Pi, student government, church jazz band, and medical volunteering. Sponsored by the NSF International Materials Institute for New Functionality in Glass, Berbano completed summer REUs working with Prof. Masahiro Tatsumisago at Osaka Prefecture University, Japan (2009) and Prof. Hyo-Jun Ahn at Gyeongsang National University, South Korea (2010). He is the 2011 recipient of the Alfred R. Cooper Scholars Award, an undergraduate award recognizing excellence in glass science research, given by the Glass and Optical Materials Division of the American Ceramic Society.

After graduating from Iowa State, Berbano began Ph.D. studies in Materials Science & Engineering at Penn State, co-advised by Prof. Michael T. Lanagan & Prof. Clive A. Randall. Berbano was a Department of Energy Graduate Automotive Technology Education Fellow, a 3M Fellow, and National Science Foundation Graduate Research Fellow. Berbano served as a TA for MatSE 417 (Electrical & Magnetic Properties), communications committee member on the American Ceramic Society’s President’s Council of Student Advisors, served as an ASSIST student leadership council representative, volunteered for science outreach events like the 21st Century Automotive Challenge and Nanodays, and worked with Penn State CSATS to help design a hands-on solid-state battery workshop for 6th-12th grade teachers. During summer 2015, he interned at Taiyo Yuden’s R&D Center in Takasaki, Japan. Berbano will work with Murata Electronics North America and is excited to engage with academic, entrepreneurial, industrial, & government laboratory communities for new materials science and technology opportunities for the betterment of society.