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A detailed characterisation study of Argyrodite ionic conductors from several synthetic routes.

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Abstract

Studies of argyrodite Li$_6$PS$_5$Cl as solid electrolyte are increasing, motivated by its high ionic conductivity and its easy processability. However, development of All-Solid-State-Batteries lies on the ability to produce such compound with a good purity. This work presents the characterization results of different argyrodite grades: commercial and homemade one. In parallel, synthesis of Li$_6$PS$_5$Cl from Li$_4$P$_2$S$_7$ precursor is reported for the first time. The purity effect on these properties will be explored by using X-ray diffraction coupled with Raman spectroscopy and electrochemical impedance spectroscopy technics. Crystal properties investigations will be particularly conducted, given that smaller crystallite sizes would lead to an enhanced ionic percolation network by increasing the microstructure homogeneity in catholyte. Such SE could be obtained only by avoiding a post synthesis annealing treatment. Finally, electrochemical properties of the different reported grades will also be discussed in this study. We demonstrate here 1. the beneficial effect of Li$_4$P$_2$S$_7$ to obtain a pure sulfur-based solid electrolyte with nanometric crystallities without solid state synthesis and 2. the impact of impurities on its ionic and electrochemical properties.

Keywords: Solid State Battery; Solid Electrolyte; Argyrodite; Li$_6$PS$_5$Cl; Ionic conductivity; Mecanosynthesis
1. Introduction

Lithium secondary batteries have been widely used to provide power sources in electronic devices since its commercialization by Sony in 1991. Recently, higher energy density and longer cycle performance are required, mostly to target Electric Vehicles (EV) market to decrease our fossil energy dependence. However, there are safety concerns due to the flammability of liquid electrolytes 1,2. To adress the problem, scientific community tried to move on All-Solid-State-Batteries (ASSB), meaning the replacement of liquid electrolyte by solid electrolyte (SE), able to play both electronic insulating separator and ionic conductor. This trend is clearly observable in publications number concerning two classes of SE: polymer 3 and inorganic 4 families. The second category has attracted material scientists since the early 20th century and can also be divided in two parts: oxide and sulfide. Oxide SE can be handle at room atmosphere but have lower conductivity. They need high temperature for processing so as to get fully dense layers 5. Sulfide SE present higher ionic conductivity but are reacting with room atmosphere moisture, they are ductile so they can be compacted at room temperature with moderate external pressure 6. As an example of impressive conductivity, LGPS showed a value of 12 mS.cm⁻¹ at room temperature 7, creating a huge interest in sulfide SE since 2011. Since then, several phases based on the binary Li₅PS₃S₄ system were studied 8, so as to improve ionic conductivities. Moreover, several studies targeted to define the electrochemical stability of common SE. By DFT calculations 9,10, electrochemical windows seems to be extremely restrained, especially for sulfides SE.

In this work, a promising sulfide based solid electrolyte, Li₆PS₅Cl, will be studied. The high ionic conductivity 11 presented by this phase make it a competitive candidate for upsampling and industrial purpose 12. Many proofs of Li₆PS₅Cl efficiency in ASSB were showed, both in dry 13,14 and wet process 15,16 assembly. Nevertheless, one of the limitation of ASSB development is the ability to produce at larger scale Li₆PS₅Cl with decent purity. Despite the low quantity produced by most of the publications, most of them have reported Li₆PS₅Cl phase with several impurities 14,13,17 such as Li₅S, and LiCl precursors after ball milling process. To improve the resulting phase purity and crystallinity, an additional annealing treatment step at 550 °C is commonly added 18.

In this present study, by systematic X-ray diffraction coupled with Raman and electrochemical impedance spectroscopy, we will focus on 2 commercial argyrodite grades, in addition to our grade obtained by conventional mecanosynthesis. To increase the purity of the product, hepta-pyro-thiophosphate (Li₅P₂S₇) precursor will be synthetized for the first time and a new mecanosynthesis route will be proposed, leading to higher ionic conductivity of the resulting Li₆PS₅Cl. Finally, effect of SE’s purity on the electrochemical window will be investigated.

2. Experimental Section

2.1. Preparation of Materials. Homemade Li₆PS₅Cl (sample A) was prepared by mecanosynthesis route from Li₅S (Sigma Aldrich 99%), P₂S₅ (Sigma Aldrich 99%) and LiCl (Acros Organic 99%) precursors mixed in stoichiometric proportions. The mechanical milling treatment was carried out for 1 g overall mass of mixed powders with 15 zirconia balls (ø10 mm, overall mass = 30 g) in a zirconia jar (45 mL). The ball milling was done with a Pulverisette 7 instrument at 600 rpm for 10 h. Subsequently, the powder was annealed for 5 h at 550 °C in a hermetic stainless-steel reactor sealed with a copper ring (sample A). For the new mecanosynthesis reaction route, Li₅P₂S₇ was first obtained by mechanical milling of Li₅S (Sigma Aldrich 99%) and P₂S₅ (Sigma Aldrich 99%) in stoichiometric proportions for 1 g overall mass of mixed powders with 6 zirconia balls (ø10 mm, overall mass = 12 g) in a zirconia jar (45 mL) using a Pulverisette 7 instrument at 600 rpm for 10 h. The synthesis of Li₆PS₅Cl (sample C) was then prepared by mecanosynthesis method between Li₅P₂S₇, Li₅S (Sigma Aldrich 99%) and LiCl (Acros Organic 99%) in stoichiometric proportions for 1 g overall mass of mixed powders with 15 zirconia balls (ø10 mm, overall mass = 12 g) in a zirconia jar (45 mL) using a Pulverisette 7 instrument at 600 rpm for 10 h. The commercial grades of Li₆PS₅Cl were purchased from Ampcera (sample B_Ampcera) and NEI (sample B_NEI).

2.2. Material Characterization. Crystallographic phase identification was performed using a Brucker D8 Advanced diffractometer with Cu radiation (λ = 1.54056 Å, λ = 1.54439 Å). Diffraction patterns were refined by Le Bail method using Fullprof software. Stainless steel in-situ cell with beryllium window 19 was used to prevent sample to be exposed to air. Raman spectroscopy was performed using a DXR3 Raman Microscope from Thermo Fisher with a 532 nm excitation source and a laser power of 1 mW. Peak deconvolution was processed using the Omnics software with a Voigt function. Electrochemical impedance spectroscopy (EIS) was used to evaluate the SE ionic conductivity as function of temperature, in the range of 0.1 Hz to 30 MHz by using MTZ-35 impedance analyser from Biologic. Signal amplitude was fixed at 50 mV. The measurements were conducted with 10 mm diameter pellet pressed at 625 MPa (5 tons), by cold pressing in glove box under argon. Pellet compacity reached a value close to 85 %. Electrochemical window was evaluated by galvanostatic cycles at Room Temperature (RT) with a VMP3 equipment from Biologic.
Voltage limits were settled between 0 - 2 V vs Li/Li for reduction reaction and 2 - 5 V vs Li/Li for oxidation reaction with a current density intentionally fixed to a low value (15 µA.cm²). The pseudo-battery assembled in pellet of 10 mm diameter (cf. Supporting Information) was based on 80 mg of Li₂PS₃Cl pressed at 125 MPa, then 10 mg of catholyte composed of Li₂PS₃Cl:Cs₂ (7:3) pressed at 375 MPa and a counter electrode composed of Li₀.5In²⁺.

3. Results and discussion

3.1. Comparison between Li₂PS₃Cl grades. Figure 1 shows X-ray diffraction (XRD) patterns and profile matching refinement of the different grades of Li₂PS₃Cl. Although main reflections can be indexed for all patterns with the face-centred cubic structure (space group Fd3m), several samples present precursors remains such as Li₂S precursor observed in XRD pattern, at 2θ = 27 °, for A₀₉M, A and Bₐₐₚ₅c₢ₜra samples. For A₀₉M sample especially, both precursors Li₂S and LiCl are highly visible leading to the assumption that the chemical reaction involving Li₂S, LiCl and P₂S₅ is not complete as reported in previous publications. In A sample, no impurities phases are detected, confirming the beneficial effect of the heat treatment step.

Table 1 : Information obtained for sample A₀₉M (mecanosynthesis), A (annealing at 550 °C after mecanosynthesis), Bₐₐₚ₅c₢ₜra and Bₙₚ₅ₑᵢₙ from refinement by the Le Bail method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter (Å)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀₉M</td>
<td>9.8406 (5)</td>
<td>15</td>
</tr>
<tr>
<td>A</td>
<td>9.8444 (2)</td>
<td>161</td>
</tr>
<tr>
<td>Bₐₐₚ₅c₢ₜra</td>
<td>9.8433 (2)</td>
<td>118</td>
</tr>
<tr>
<td>Bₙₚ₅ₑᵢₙ</td>
<td>9.8530 (2)</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 2 reminds the majors units visible by Raman spectroscopy. Given the complexity to obtain pure thiophosphate-based SE, we also present here polyhedra obtained in the case of the Li₂S-P₂S₅ binary system.

To extract the crystallite size from previous refinement, NIST standard (LaB₁₀-Si powder) was used to access to the diffractometer resolution (cf. Supporting Information). The Table 1 below presents both cubic lattice parameter a and crystallite size for each sample. Interestingly, A₀₉M sample presents nano-crystallites, but the solid-state synthesis through the annealing treatment leads to an important growth of the crystals as shown by the value for A sample. This could be problematic in catholyte electrode formulated by dry process, as we require small SE’s particles to improve the microstructure homogeneity and so the ionic percolation network. An appropriate balance must be struck, by considering the phase purity and the ionic conductivity on one side and by trying to limit employment of a post synthesis annealing treatment to keep small crystallite sizes on the other side. Concerning commercial grades, we observe high crystallite sizes especially for Bₐₐₚ₅c₢ₜra sample, suggesting that a temperature step is performed during or after the synthesis.

Figure 3a shows Raman spectrum of each sample in the area of interest of ortho-thiophosphate units P₅S₃⁺⁺, which are isolated units in Li₂PS₃Cl face-centred cubic structure. Their expected principal Raman bands (stretching vibration mode v₃) are at 425 cm⁻¹ with two bands of lower intensities at 199 cm⁻¹ and 573 cm⁻¹, and another band associated to a bending vibration mode δ at 272 cm⁻¹. Nevertheless, sample Bₙₚ₅ₑᵢₙ presents an impurity around 480 cm⁻¹ previously reported as S-S vibration in S₈. Moreover, it is possible to extract accurate information about the presence of other P₅S₃⁺⁺ units.
between 370 cm\(^{-1}\) and 450 cm\(^{-1}\) \(^{25}\) and Figure 3b presents peak deconvolution of each sample in this range. Interestingly, A\(_{BM}\) sample shows an impurity centred at 405 cm\(^{-1}\) known as pyro-thiophosphate units (P\(_2\)S\(_{74}^{-}\)) \(^{26}\) which is the base for the amorphous network of Li\(_4\)P\(_2\)S\(_7\) \(^{5}\). Thus, this confirms the idea of an incomplete reaction as suggested previously, leading to the presence of Li\(_4\)P\(_2\)S\(_7\), LiCl and Li\(_2\)S in the powder obtained by ball milling only. Concerning the annealed sample and both commercial grades, only PS\(_{43}^{3-}\) are visible after the band deconvolution.

Figure 3b presents peak deconvolution of each sample in this range. Interestingly, A\(_{BM}\) sample shows an impurity centred at 405 cm\(^{-1}\) known as pyro-thiophosphate units (P\(_2\)S\(_{74}^{-}\)) \(^{26}\) which is the base for the amorphous network of Li\(_4\)P\(_2\)S\(_7\) \(^{5}\). Thus, this confirms the idea of an incomplete reaction as suggested previously, leading to the presence of Li\(_4\)P\(_2\)S\(_7\), LiCl and Li\(_2\)S in the powder obtained by ball milling only. Concerning the annealed sample and both commercial grades, only PS\(_{43}^{3-}\) are visible after the band deconvolution.

### Table 2: Ionic conductivities (\(\sigma_i\)) at 20 °C and activation energies (\(E_a\)) of A\(_{BM}\), A, B\(_{Ampcera}\) and B\(_{NEI}\) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compacity (%)</th>
<th>(\sigma_i) at 20 °C (S.cm(^{-1}))</th>
<th>(E_a) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(_{BM})</td>
<td>81</td>
<td>3.5 \times 10^{-4}</td>
<td>0.19</td>
</tr>
<tr>
<td>A</td>
<td>80</td>
<td>6.0 \times 10^{-4}</td>
<td>0.19</td>
</tr>
<tr>
<td>B(_{Ampcera})</td>
<td>88</td>
<td>1.1 \times 10^{-3}</td>
<td>0.18</td>
</tr>
<tr>
<td>B(_{NEI})</td>
<td>81</td>
<td>9.6 \times 10^{-4}</td>
<td>0.33</td>
</tr>
</tbody>
</table>

### Figure 4a
The Nyquist plot of each sample at 20 °C. The semi-circles attest the presence of only one ionic contribution. Figure 4b presents the resulting Arrhenius plot based on the linear regression of experimental data between 20 °C and -20 °C. Impact of annealing treatment is clearly noticeable from A\(_{BM}\) to A samples, meaning controlling the purity of Li\(_6\)PS\(_5\)Cl is a vital step that influence drastically the resulting ionic conductivity. A surprising result here is the conductivity of B\(_{NEI}\) and particularly its activation energy (\(E_a\)). The behaviour is completely different from other Li\(_6\)PS\(_5\)Cl grades, with higher ionic conductivity at high temperature. The presence of S\(_8\) could be at the origin of this particular behaviour and will be investigated in part 3.2.

### Figure 5a
Study of B\(_{NEI}\) before (green) and after treatment at 130 °C (brown) with a. Raman spectrum with PS\(_{43}^{3-}\) units (\(\triangle\)) and S\(_8\) at 480 cm\(^{-1}\) and b. Arrhenius plot from the linear regression of experimental data.

This result shows the relationship existing between the phase purity and its ionic conductivity. For the development of large-scale synthesis, it is mandatory to carefully control the synthesis stages, with or without a post annealing treatment.

### 3.3. New synthesis route using Li\(_4\)P\(_2\)S\(_7\).
According to the incomplete reaction showed for A\(_{BM}\) sample along with impurities, a new synthesis of Li\(_6\)PS\(_5\)Cl is proposed through Li\(_4\)P\(_2\)S\(_7\) precursor. First, the synthesis of Li\(_4\)P\(_2\)S\(_7\) was...
conducted by ball milling of Li$_2$S and P$_2$S$_5$ according to the following reaction:

$$P_2S_5 + 2Li_2S \rightarrow Li_4P_2S_7$$

Figure 6 presents the Raman spectrum of the resulting powder with a peak deconvolution between 360 and 450 cm$^{-1}$ showing the presence of PS$_{3}^{3-}$, P$_2$S$_7^{4-}$ and P$_2$S$_6^{4-}$ units. The presence P$_2$S$_7^{4-}$ units confirmed that some Li$_4$P$_2$S$_7$ was successfully synthesized. XRD and EIS at RT are presented in Supporting Information and attest the presence of an amorphous phase which is expected for Li$_4$P$_2$S$_7$ obtained by ball-milling, and a conductivity of $4.4 \times 10^{-5}$ S.cm$^{-1}$ consistent with the one assumed by Dietrich et al. 25.

Figure 6: Raman spectrum of Li$_4$P$_2$S$_7$ obtained by the new mecanosynthesis method. Peak deconvolution between 370 cm$^{-1}$ and 450 cm$^{-1}$ with PS$_{3}^{3-}$ units (purple), P$_2$S$_7^{4-}$ units (orange) and P$_2$S$_6^{4-}$ units (cyan).

Secondly, the synthesis of Li$_6$PS$_5$Cl was performed by the following reaction:

$$Li_4P_2S_7 + 3Li_2S + 2LiCl \rightarrow 2Li_6PS_5Cl$$

Figure 7 presents XRD patterns and profil matching refinements of the resulting powder after ball-milling (C sample). This sample shows Li$_6$PS$_5$Cl structure with small crystallite size as suggested by peaks broadening. This size was evaluated to be around 12 nm, comparable to the one obtained for A$_{BM}$ sample. Thus, the synthesis through Li$_4$P$_2$S$_7$ leads to higher purity argyrodite compound with a similar crystallite size compared to the classical reaction between Li$_2$S, P$_2$S$_5$ and LiCl.

Figure 7: Profile matching of Li$_6$PS$_5$Cl grades. Remind of conventional mecanosynthesis (sample A$_{BM}$) and synthesis from Li$_4$P$_2$S$_7$ precursor (sample C$_{BM}$). Bragg positions for Li$_6$S (▲), LiCl (▽), Fe (◼) and Be (⊙).

Figure 8a presents Raman spectrum of sample C. Compared to A$_{BM}$ sample, we can conclude that the powder purity was improved because only PS$_{3}^{3-}$ vibrations are observed. Figure 8b shows the Arrhenius plot of both A$_{BM}$ and C$_{BM}$ samples with an interesting enhancement of the ionic conductivity by a factor 5. This highlight the relationship between the impact of synthesis and the phase purity, correlated with the resulting ionic conductivity, which is higher for the new mecanosynthesis.

Figure 8: Raman spectrum and Arrhenius plot of C$_{BM}$ (dark blue) and A$_{BM}$ (black) with a. the peak deconvolution between 370 cm$^{-1}$ and 450 cm$^{-1}$ with PS$_{3}^{3-}$ (purple) and P$_2$S$_7^{4-}$ units (orange) and b. Arrhenius plot from the linear regression of experimental data.

3.4. Electrochemical stability. All samples were evaluated in pseudo-battery system in order to study the impact of powder purity on their electrochemical window stability. SE powders were used as active material and mixed with C45 in a ratio of 7:3. The reduction and oxidation reactions of Li$_6$PS$_5$Cl, involving respectively 798 mAh.g$^{-1}$ and 499 mAh.g$^{-1}$ are shown below:

$$(\text{Red}) \ Li_6PS_5Cl + 8Li^+ + 8e^- \rightarrow LiCl + Li_3P + 5Li_2S$$

$$(\text{Ox}) \ Li_6PS_5Cl \rightarrow LiCl + \frac{1}{2}P_2S_5 + \frac{5}{2}S + 5Li^+ + 5e^-$$

Figure 9a and Figure 9b present the reduction and oxidation studies of the different samples. First, we can clearly observe
the difference of capacities between reduction and oxidation reactions, respectively more than 200 mAh.g⁻¹ and around 3 mAh.g⁻¹. Secondly, all samples allowed the oxidation or reduction on the first step (charge or discharge) of the galvanostatic cycles. We think that these samples are not stables and they decompose. Indeed, we assist to the reduction of phosphorous around 1 V vs Li⁺/Li during the first discharge, as showed in literature 30. Concerning reduction capacity values, $A_{BM}$ shows the higher one (469 mAh.g⁻¹) followed by $B_{Ampcera}$ (425 mAh.g⁻¹), $B_{NEI}$ (312 mAh.g⁻¹) and $A$ (180 mAh.g⁻¹). According to these results, it seems that the capacity is not linked to Li$_2$PS$_4$Cl degradation but rather to the presence of LiS-PS$_7$ impurities, as A sample does not contain amorphous phase after annealing treatment at 550 °C.

To identify accurately the electrochemical window, the derivative curves of every 1st cycle were plotted (cf. Supporting Information). It appears that voltage limits are contained within the range of 1 V to 2,7 V vs Li⁺/Li, +/- 100 mV according to the sample. This is in good agreement with the literature even if the oxidation potential was reported a little bit lower (2,4 V vs Li⁺/Li) 28 but this may be linked to the different morphologies and percentages of carbon additive in the catholyte.

4. Conclusions

The combination of XRD, Raman and EIS have allowed us to attest that the conventional mecanosynthesis based on Li$_2$S, P$_2$S$_5$ and LiCl mixture is not complete and the resulting powder still contains the precursors along with an amorphous phase identify as Li$_2$PS$_4$. It was also shown the importance of the heat treatment at 550°C in order to complete the reaction by solid state synthesis, along with the drawback to increase crystallite sizes. To enhance the product purity right after ball milling in order to keep the nanometric size of the electrolyte, the synthesis of Li$_2$PS$_4$Cl was modified with the proposition of a new synthetic route using Li$_2$P$_2$S$_7$ precursor. The synthesis of Li$_2$P$_2$S$_7$ was conducted and the resulting powder showed amorphous phase by XRD, with the presence of P$_2$S$_7$²⁻ units by Raman. The subsequent ball milling step of Li$_2$P$_2$S$_7$ with Li$_2$S and LiCl leads to pure Li$_2$PS$_4$Cl as confirmed by XRD and Raman spectroscopy. The effect of phase purity was thus correlated to the ionic conductivity with the conclusion that synthesis optimization still need to be studied, to decrease side product presence which have a negative effect on the ionic conductivity. Indeed, compounds such as Li$_2$S and LiCl are insulators and it is mandatory to avoid them in SE, especially if fast-charge applications are targeted. Finally, the correlation between phase purity and electrochemical window did not seem to exist but we still observed that degradation capacities were higher for grades with lower purity. With those informations, we are insisting here on the viability of ASSB technology based on sulfide SE, which could be only unlocked by a consequent work on positive active materials and lithium metal protection.

Supporting Information

Supporting Information is available.

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