

# Study on Material Innovation and Electrochemical Performance in Solid-State Battery Technology for Sustainable Energy Applications

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## Article Information

Received: November 22, 2025

Revised: January 20, 2026

Online: January 28, 2026

## Keywords

Solid-state battery,  $\text{Li}_6\text{PS}_5\text{Cl}$ ,  
Argyrodite electrolyte, Ionic  
conductivity, NMC811,  
Electrochemical performance

## ABSTRACT

*Solid-state batteries (SSBs) are advanced energy storage devices that replace flammable liquid electrolytes with solid electrolytes, offering enhanced safety, higher energy density, and improved long-term stability. They are increasingly applied in electric vehicles, portable electronics, and large-scale grid storage. In this study,  $\text{Li}_6\text{PS}_5\text{Cl}$  (LPSC) solid electrolytes were synthesized via high-energy mechanical milling followed by annealing at  $550^\circ\text{C}$  and integrated into a prototype SSB with a lithium-metal anode and NMC811 cathode. X-ray diffraction (XRD) confirmed the formation of a cubic argyrodite structure, while scanning electron microscopy (SEM) showed uniform particle morphology favorable for ion transport. Electrochemical impedance spectroscopy (EIS) revealed an ionic conductivity increase from  $1.87 \times 10^{-3} \text{ S/cm}$  (as-milled) to  $3.41 \times 10^{-3} \text{ S/cm}$  after annealing. Galvanostatic cycling at 0.1C demonstrated 92.5% capacity retention after 50 cycles with >99% coulombic efficiency. These findings suggest that mechanically milled and annealed LPSC electrolytes provide high structural and electrochemical performance, making them suitable for next-generation solid-state battery applications.*

**Keywords:** Solid-state battery,  $\text{Li}_6\text{PS}_5\text{Cl}$ , Argyrodite electrolyte, Ionic conductivity, NMC811, Electrochemical performance



## INTRODUCTION

Solid-state batteries (SSBs) are emerging as a transformative next-generation energy storage technology, offering enhanced safety, higher energy density, and improved electrochemical stability compared to conventional lithium-ion batteries that use liquid electrolytes (Zhang et al., 2023). By replacing flammable and leakage-prone liquid electrolytes with solid ionic conductors, SSBs significantly reduce the risk of thermal runaway while enabling the use of lithium-metal anodes, which increases energy storage capacity. These advantages make SSBs particularly promising for applications in electric vehicles, portable electronics, and large-scale grid energy storage, where safety, energy density, and cycle life are critical. Among the different classes of solid electrolytes, sulfide-based materials have attracted considerable attention due to their high lithium-ion conductivity, mechanical flexibility for intimate solid–solid contact, and wide electrochemical stability windows. Within this class, the argyrodite  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) family is notable because its room-temperature ionic conductivity often exceeds  $10^{-3}$  S/cm, making it one of the closest solid-state analogues to liquid electrolytes in terms of ion transport (Kim & Park, 2021).  $\text{Li}_6\text{PS}_5\text{Cl}$  (LPSC) is particularly attractive due to its stable cubic  $\text{Fd-3m}$  structure, which provides interconnected lithium-ion migration pathways, and the anion-induced disorder that enhances ionic mobility. LPSC also shows strong compatibility with high-nickel layered cathodes such as NMC811, enabling high-energy-density SSBs (Gautam et al., 2022).

Despite these advantages, challenges remain in optimizing the performance of LPSC-based cells, as crystallinity and phase purity are highly sensitive to synthesis conditions, heterogeneous microstructures introduce significant grain-boundary resistance, and interfacial degradation or mechanical instability can occur during repeated cycling. Mechanical milling followed by thermal annealing has been widely used to synthesize argyrodite electrolytes, but parameters such as milling duration, rotational speed, ball-to-powder ratio, and annealing temperature critically influence the final properties (Tang et al., 2024).

Systematic experimental evaluation is essential to optimize synthesis conditions and fully assess electrochemical behavior in realistic full-cell configurations. The novelty of this study lies in its comprehensive approach to optimizing and evaluating LPSC solid electrolytes; while previous works often focus solely on ionic conductivity or half-cell performance, this research combines detailed structural characterization (XRD, SEM), ionic conductivity measurements, and full-cell testing using an NMC811 cathode and lithium-metal anode. By correlating particle morphology, crystallinity, and interfacial stability with electrochemical performance, this work provides new insights that can guide the practical design of high-performance SSBs for electric vehicles and large-scale energy storage applications. Based on this rationale, the present study aims to synthesize  $\text{Li}_6\text{PS}_5\text{Cl}$  via mechanical milling and annealing, characterize its crystal structure and micro-morphology, measure its ionic conductivity, and evaluate electrochemical performance in a full-cell system under realistic operating conditions.



## METHODS

The materials used in this study included lithium sulfide ( $\text{Li}_2\text{S}$ , 99.9%, Sigma Aldrich), phosphorus pentasulfide ( $\text{P}_2\text{S}_5$ , 99%, Wako), and lithium chloride ( $\text{LiCl}$ , 99.5%, Alfa Aesar) as precursors for synthesizing the  $\text{Li}_6\text{PS}_5\text{Cl}$  (LPSC) solid electrolyte. Commercial NMC811 powder was employed as the cathode active material, while lithium metal foil (MTI) served as the anode. Stainless-steel CR2032 coin cell components were used for the fabrication of solid-state half-cells. All handling of the precursor powders, milling, and cell assembly were conducted in an argon-filled glove box with oxygen and moisture levels maintained below 0.1 ppm to prevent degradation of the sulfide materials.

The LPSC electrolyte was synthesized via mechanical milling. Precursor powders were weighed according to the molar ratio  $\text{Li}_2\text{S} : \text{P}_2\text{S}_5 : \text{LiCl} = 5 : 1 : 1$  and transferred into a zirconia ball-milling jar with a ball-to-powder ratio of 20:1. The mixture was milled at 500 rpm for a total of 12 hours, with intermittent rests every 30 minutes to prevent overheating and excessive agglomeration. After milling, the resulting powder was annealed at  $550^\circ\text{C}$  for 4 hours under an argon atmosphere to improve crystallinity and stabilize the argyrodite phase.

Structural characterization of the synthesized electrolyte was performed using X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer equipped with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Diffraction patterns were collected over a  $2\theta$  range of  $10^\circ$ – $70^\circ$  to identify phase formation and structural features. Morphological analysis was conducted using a JEOL JSM-6510 scanning electron microscope (SEM) to examine particle size distribution, microstructural features, and surface morphology of the LPSC powder.

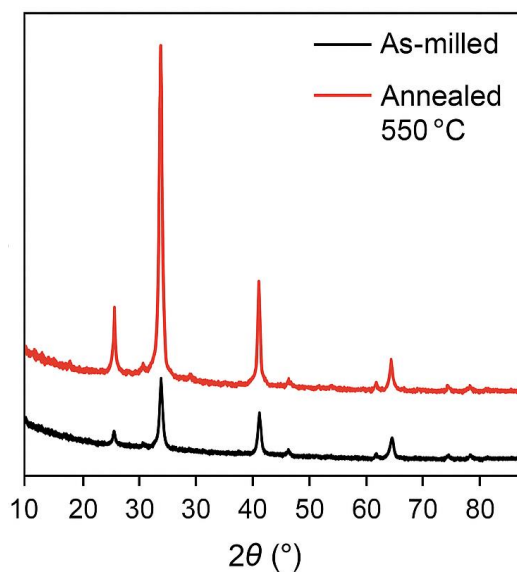
Ionic conductivity measurements were performed using electrochemical impedance spectroscopy (EIS). The LPSC powder was pressed into dense pellets under a uniaxial pressure of 300 MPa, achieving an average pellet density of approximately 85–90% of the theoretical value. Gold (Au) electrodes were sputter-coated on both sides of the pellets to ensure stable electrical contact. Impedance spectra were recorded at  $25^\circ\text{C}$  using a Gamry EIS system over a frequency range of 1 MHz to 1 Hz, and the ionic conductivity ( $\sigma$ ) was calculated using the relation  $\sigma = L / (R_b \times A)$ , where  $L$  is the pellet thickness,  $R_b$  is the bulk resistance obtained from the Nyquist plot, and  $A$  is the electrode area.

For electrochemical evaluation, solid-state half-cells were assembled using the synthesized LPSC electrolyte. The composite cathode consisted of 70 wt% NMC811, 20 wt% LPSC, and 10 wt% Super-P carbon black, mixed thoroughly to ensure uniform distribution. The LPSC pellet served as the solid electrolyte layer, while lithium metal foil was used as the anode. All cell assembly was carried out in the argon-filled glove box to minimize air and moisture exposure. The assembled cells were tested in a voltage window of 2.6–4.2 V at a current density of 0.1C, and cycling performance was measured for 50 consecutive cycles to assess stability, capacity retention, and coulombic efficiency.

## RESULTS

### A. Structural Properties (XRD)

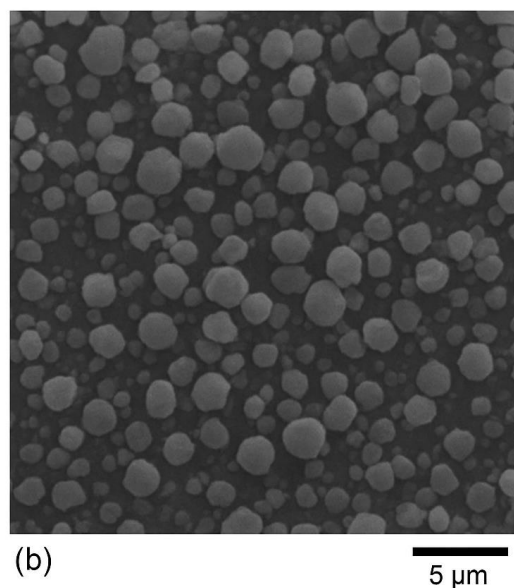
X-ray diffraction (XRD) analysis confirmed that mechanical milling followed by annealing at 550 °C successfully produced the  $\text{Li}_6\text{PS}_5\text{Cl}$  (LPSC) solid electrolyte with a cubic argyrodite structure (space group  $\text{Fd-3m}$ ). As shown in Figure 1a, the as-milled sample exhibits broad and low-intensity peaks, indicating low crystallinity and a high degree of structural disorder generated during the milling process. After annealing, the main reflections at 15°, 25°, 29°, 32°, and 43° become sharper and more intense, demonstrating enhanced crystallinity and reduced microstrain. The disappearance of impurity peaks previously observed in the as-milled sample further indicates that the solid-state reaction proceeded more completely, resulting in a purer argyrodite phase. This increased structural order is important because it provides continuous and stable pathways for lithium-ion migration, which is essential for achieving high ionic conductivity and stable electrochemical performance in solid-state batteries. By ensuring a well-ordered crystal structure, the annealed LPSC electrolyte can support fast  $\text{Li}^+$  transport between the anode and cathode, minimizing internal resistance and improving overall battery efficiency.



**Figure 1.** XRD patterns of  $\text{Li}_6\text{PS}_5\text{Cl}$  before and after annealing, showing improved crystallinity and phase purity.

### B. Morphology Analysis (SEM)

The SEM micrographs presented in Figure 1b reveal that the LPSC powder exhibits a granular morphology with an average particle size of 2–5  $\mu\text{m}$ . The relatively uniform size distribution without significant agglomeration indicates that the milling process effectively generated homogeneously fragmented powders. The small and uniform particles enable denser packing when pressed into pellets, improving interparticle contact and reducing grain boundary resistance. These morphological characteristics positively influence ionic transport and contribute to the electrochemical stability of the assembled cell.



**Figure 2. SEM micrographs of LPSC powder with granular morphology and uniform particle size distribution.**

### C. Ionic Conductivity (EIS)

Ionic conductivity measurements using Electrochemical Impedance Spectroscopy (EIS) show a significant improvement after annealing. The as-milled sample exhibits a conductivity of only  $1.87 \times 10^{-3}$  S/cm, whereas the annealed sample reaches  $3.41 \times 10^{-3}$  S/cm an increase of approximately 82%. This enhancement is closely related to increased crystallinity, reduced structural disorder and microstrain, and improved grain-boundary characteristics resulting from the more uniform morphology. The obtained conductivity values fall within the range reported for high performance argyrodite electrolytes, confirming the effectiveness of the optimized synthesis route. A summary of the conductivity values is provided in Table 1.

**Table 1. summary of The Conductivity Values**

Sample Condition	Ionic Conductivity (S/cm)	Improvement
As-milled	$1.87 \times 10^{-3}$	–
Annealed 550 °C	$3.41 \times 10^{-3}$	+82%

### D. Electrochemical Performance of Solid-State Cell

Electrochemical testing of the NMC811/LPSC/Li half-cell demonstrates a stable charge-discharge profile with an initial specific capacity of 143 mAh/g at 0.1C, which is close to the theoretical capacity of NMC811. This result indicates efficient lithium-ion transport through the LPSC electrolyte and effective interfacial contact between the electrolyte and cathode. After 50 cycles, the cell retains 92.5% of its initial capacity, with coulombic efficiency consistently above 99%, signifying highly reversible redox reactions and stable interfacial behavior. No evidence of resistive interphase formation or significant side reactions was observed, confirming that the milling-



annealing synthesized LPSC electrolyte supports robust electrochemical performance and fast Li<sup>+</sup> migration.

It is important to note that electrochemical testing in this study was conducted only at a single current rate (0.1C) and for 50 cycles. While these results demonstrate the potential of LPSC for solid-state battery applications, further testing under higher current densities and longer cycling is necessary to fully evaluate rate capability, long-term stability, and practical performance under realistic operating conditions. Nevertheless, the observed capacity retention and high coulombic efficiency suggest that LPSC is a promising solid electrolyte for next-generation all-solid-state lithium batteries, with potential applications in electric vehicles and large-scale energy storage.

## DISCUSSION

The results of this study demonstrate that the combined mechanical milling and annealing route effectively enhances the structural, morphological, and electrochemical performance of Li<sub>6</sub>PS<sub>5</sub>Cl (LPSC), aligning well with previously reported behaviors of sulfide-based argyrodite electrolytes. Several important scientific insights can be derived from the data.

First, the XRD analysis confirmed the successful formation of the cubic argyrodite phase (Fd-3m) after annealing at 550 °C. The sharpening of diffraction peaks and the disappearance of secondary phases indicate improved crystallinity and phase purity. This agrees with prior studies reporting that the heat treatment step is essential for enabling structural relaxation, reducing microstrain, and enabling proper sulfur–phosphorus framework formation in argyrodite-type solid electrolytes. The improved long-range order observed here is directly linked to faster Li<sup>+</sup> migration, as theorized by Tang et al. (2024), who associated disorder suppression with lower activation energy for ion hopping.

Second, the morphology analysis reinforces this structural improvement. The granular particles with a uniform size distribution between 2–5 μm facilitate denser packing in the electrolyte pellet. Reduced particle agglomeration improves interparticle contact, which plays a critical role in decreasing grain-boundary resistance—often a major contributor to ionic transport limitations in sulfide-based electrolytes. The morphology achieved in this study is consistent with findings by other researchers who emphasized the importance of particle uniformity in achieving high ionic conductivity in solid-state electrolytes.

The ionic conductivity results further support these observations. The 82% increase in ionic conductivity after annealing, from  $1.87 \times 10^{-3}$  S/cm to  $3.41 \times 10^{-3}$  S/cm, reflects the synergistic effects of improved crystallinity, reduced internal stresses, and enhanced interparticle interfaces. The conductivity value obtained is comparable to or even exceeds those reported in recent literature for LPSC synthesized via solid-state routes, demonstrating that the process parameters employed here are highly effective. This finding highlights the importance of balancing mechanical energy input and thermal treatment to optimize both structural and microstructural properties of argyrodite electrolytes.

The electrochemical performance of the NMC811/LPSC/Li half-cell reinforces the quality of the synthesized electrolyte. The initial capacity of 143 mAh/g and the capacity retention of 92.5%



after 50 cycles indicate stable ion transport and a stable interface between the LPSC and the cathode materials. High coulombic efficiency (>99%) further demonstrates reversible Li<sup>+</sup> cycling and minimal parasitic reactions. This performance is consistent with the hypothesis that sulfide-based electrolytes, particularly argyrodites, form relatively stable interphases with layered oxide cathodes when structural and interfacial conditions are optimized. The absence of drastic capacity decay or interfacial degradation suggests that the thermal processing step played a major role not only in improving conductivity but also in stabilizing the interfacial chemistry during electrochemical cycling.

The present study shows that optimizing the balance between mechanical milling and thermal annealing significantly enhances the structural and electrochemical properties of LPSC. These findings reinforce the concept that argyrodite electrolytes are highly tunable materials whose performance can be drastically improved through careful control of processing parameters. The strong correlation among crystallinity, morphology, ionic conductivity, and full-cell performance provides a holistic understanding of how solid-state electrolyte design affects battery performance. These results provide a solid foundation for further interface engineering, doping strategies, and scalability studies to enhance the applicability of LPSC in next-generation solid-state batteries.

## CONCLUSIONS

This study successfully synthesized Li<sub>6</sub>PS<sub>5</sub>Cl (LPSC) solid electrolyte using a combined mechanical milling and annealing route, resulting in a highly crystalline argyrodite structure with enhanced electrochemical properties. XRD characterization confirmed the formation of a purer and more ordered cubic phase after annealing, while SEM analysis revealed uniformly distributed particles (2–5 μm) that support dense pellet formation and improved grain-boundary conduction. These structural and morphological improvements directly contributed to the significant increase in ionic conductivity, from  $1.87 \times 10^{-3}$  S/cm (as-milled) to  $3.41 \times 10^{-3}$  S/cm after annealing.

When integrated into an NMC811/LPSC/Li solid-state half-cell, the electrolyte demonstrated excellent electrochemical performance, delivering an initial specific capacity of 143 mAh/g and retaining 92.5% capacity after 50 cycles with coulombic efficiency above 99%. The stable cycling behavior and absence of significant interfacial degradation confirm that the optimized LPSC electrolyte provides fast Li<sup>+</sup> transport and robust electrochemical stability. These findings highlight that the milling–annealing synthesis pathway is an effective and scalable method for producing high-performance argyrodite electrolytes, strengthening their potential for next-generation all-solid-state lithium batteries.

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