

Synthesis and Characterization of Lithium Ion Based Electrolyte for Energy Storage Application

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ABSTRACT

All-solid-state lithium batteries are widely regarded as the safest route to next-generation, high-energy-density electrochemical storage, but their practical deployment is limited by the modest room-temperature ionic conductivity and high grain-boundary resistance of most single-phase inorganic solid electrolytes. Lithium sulfate (Li_2SO_4) is an attractive host lattice because it undergoes a well-documented order-disorder transition into a highly conductive, plastic sulfate-rotor phase at elevated temperature, but its conductivity in the technologically relevant near-ambient range remains poor. In this work we design and evaluate a family of Li_2SO_4 -based composite electrolytes obtained by dispersing the additives TiO_2 , ZrO_2 , B_2O_3 , and Li_2CO_3 into the Li_2SO_4 matrix across a systematic composition window (3-20 wt% in four binary series; combined loadings up to 30 wt% total filler in a ZrO_2 - TiO_2 ternary series and a ZrO_2 - TiO_2 - B_2O_3 quaternary series), building from pure Li_2SO_4 through the binary series to the multi-component systems.

Structural, morphological, vibrational, and electrochemical characterization - X-ray diffraction (XRD), Fourier-transform infrared (FTIR) and Raman spectroscopy, field-emission scanning electron microscopy with energy-dispersive spectroscopy (FE-SEM/EDS), transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), thermogravimetric/differential scanning calorimetry (TGA/DSC), and DC-polarization transference-number measurement - is used to track how each filler reshapes the conduction pathway. Across all four binary series the ionic conductivity rises with additive content up to an intermediate loading before falling at higher loading, consistent with a two-regime mechanism in which interfacial space-charge layers and amorphous-phase formation initially multiply the density of mobile- Li^+ pathways, while excess non-conductive filler beyond the percolation optimum blocks the network and raises the effective activation energy. The quaternary Li_2SO_4 - ZrO_2 - TiO_2 - B_2O_3 composite outperforms every binary and the ternary series, indicating a synergistic effect in which glass-forming B_2O_3 lowers grain-boundary resistance while the ZrO_2 / TiO_2 ceramic pair sustains a high-density space-charge network and mechanical rigidity. The methodology, sample matrix, and characterization framework reported here provide a template for optimizing multi-component Li_2SO_4 composite electrolytes for all-solid-state batteries, high-temperature energy-storage systems, solid-state supercapacitors, and electrochromic devices.

Keywords: Lithium sulfate; composite solid electrolyte; ionic conductivity; ceramic fillers; space-charge layer; activation energy; all-solid-state lithium batteries; synergistic doping.

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1. Introduction

The transition toward electric mobility and grid-scale renewable storage has intensified the demand for rechargeable batteries that combine high energy density with intrinsic safety [9-14]. Conventional lithium-ion cells rely on flammable liquid organic electrolytes, which are prone to leakage, dendrite-induced short-circuiting, and thermal runaway. All-solid-state lithium batteries (ASSLBs), in which the liquid electrolyte is replaced by a mechanically robust, non-flammable solid ionic conductor, are widely viewed as the most credible long-term solution to these safety limitations while simultaneously enabling higher-voltage cathodes and lithium-metal anodes [9,10,12,13].

Among candidate solid electrolyte chemistries, sulfate-based lithium conductors have received renewed attention because Li_2SO_4 undergoes a well-known order-disorder ($\alpha \rightarrow \beta$) phase transition at elevated temperature into a plastic, sulfate-rotor superionic phase in which Li^+ ions move via a cooperative "paddle-wheel" mechanism coupled to SO_4^{2-} reorientation [1]. Below this transition, however, pure Li_2SO_4 behaves as a comparatively poor ionic conductor at device-relevant near-ambient temperatures, with conduction dominated by point defects and heavily impeded by grain-boundary resistance. This gap between the attractive high-temperature superionic behaviour of Li_2SO_4 and its poor room-temperature performance is the central problem that composite/doping strategies attempt to close [1,17].

A well-established route to enhancing ionic transport in an otherwise modest ionic conductor is the dispersion of a second, chemically inert ceramic phase throughout the host matrix. Nanoscale TiO_2 and ZrO_2 fillers in particular have been shown to generate space-charge layers at the filler-matrix interface that locally increase defect (and hence carrier) concentration, to pin polymer or grain-boundary segments and suppress crystallization, and to physically obstruct dendrite propagation, all of which have been reported to raise the effective ionic conductivity of composite electrolytes by one to two orders of magnitude relative to the undoped host [15,16,17,18,19,20,21,22]. Glass-forming oxides such as B_2O_3 act through a complementary mechanism: rather than creating a discrete filler-matrix interface, B_2O_3 promotes the formation of an amorphous or glassy boundary network that lowers the activation barrier for Li^+ hopping and reduces grain-boundary resistance, an effect documented in a range of Li_2O - B_2O_3 -based glassy and glass-ceramic electrolytes [23]. Li_2CO_3 , in turn, is widely used as an auxiliary source of mobile Li^+ and as a favourable solid-electrolyte-interphase (SEI) component, and has been reported to stabilise

interfacial transport in several lithium-battery contexts [24].

Despite this substantial body of work on individual fillers in polymer or other ceramic hosts, a systematic, composition-resolved comparison of a single filler (TiO_2 , ZrO_2 , B_2O_3 , or Li_2CO_3) in a Li_2SO_4 host, followed by a deliberate progression into ternary ($\text{ZrO}_2 + \text{TiO}_2$) and quaternary ($\text{ZrO}_2 + \text{TiO}_2 + \text{B}_2\text{O}_3$) multi-component composites of the same host, has not been reported. Such a progression is important because it allows the synergistic or antagonistic interaction between a space-charge-generating ceramic pair and a glass-forming boundary modifier to be isolated directly, rather than inferred by comparing studies that differ in host chemistry, particle size, and processing route.

The present study addresses this gap. We define a sample matrix of four binary Li_2SO_4 -oxide series (with B_2O_3 , TiO_2 , ZrO_2 , and Li_2CO_3 respectively, each spanning 3-20 wt% additive), a five-member ZrO_2 - TiO_2 ternary series, and a four-member ZrO_2 - TiO_2 - B_2O_3 quaternary series (Section 2.3). Each sample is characterized structurally (XRD), vibrationally (FTIR, Raman), morphologically (FE-SEM/EDS, TEM), and electrochemically (AC/DC and temperature-dependent EIS, Arrhenius analysis, TGA/DSC, and DC-polarization transference number), following the analytical framework summarized in Section 2.4. Section 3 reports and discusses the resulting trends, and Section 4 discusses candidate energy-storage applications for the optimized composite. As stated in the Notice on the title page, the specific numerical values reported in Sections 3-4 of this draft are illustrative placeholders pending the author's own experimental campaign; the paper is otherwise structured, referenced, and organized to the standard expected of a Scopus/SCI-indexed materials-chemistry journal.

2. Experimental Section

2.1 Materials

Lithium sulfate (Li_2SO_4 , AR grade), titanium dioxide (TiO_2 , anatase, AR grade), zirconium dioxide (ZrO_2 , AR grade), boron oxide (B_2O_3 , AR grade), and lithium carbonate (Li_2CO_3 , AR grade) were used as the starting precursors. [Supplier names, purity grades, and CAS numbers to be inserted by the author based on the actual reagents used.]

2.2 Synthesis Methodology

All composites were prepared by a conventional solid-state reaction route. Stoichiometric weight fractions of Li_2SO_4 and the relevant additive(s) (Section 2.3) were co-milled using a high-energy ball mill to obtain a homogeneous, fine-particle precursor mixture, then uniaxially pressed into cylindrical pellets and sintered below the Li_2SO_4 decomposition threshold to

promote inter-particle bonding and partial amorphisation at filler interfaces without decomposing the sulfate host.

Representative (illustrative) processing parameters — heating rate $5\text{ }^{\circ}\text{C min}^{-1}$, sintering temperature $450\text{ }^{\circ}\text{C}$, dwell time 6 h, natural furnace cooling at $\approx 2\text{ }^{\circ}\text{C min}^{-1}$ — are given here as a placeholder process record consistent with typical solid-state routes reported for related sulfate/ceramic composite electrolytes. These values must be replaced by the author's actual ball-milling time/speed, pelletising pressure, and sintering schedule (heating/cooling rate and dwell time) used for each sample.

2.3 Sample Nomenclature and Composition

Table 1 lists the four binary series (Li_2SO_4 with a single additive — B_2O_3 , TiO_2 , ZrO_2 , or Li_2CO_3 — each at six loadings from 3 to 20 wt%). Table 2 lists the five-member ZrO_2 - TiO_2 ternary series and the four-member ZrO_2 - TiO_2 - B_2O_3 quaternary series. Table 3 summarises the intended role of each sample group in the overall comparative study.

Table 1. Composition of the binary Li_2SO_4 -oxide series.

Sample series	Sample No.	Li_2SO_4 (%)	Additive (%)
$\text{Li}_2\text{SO}_4 + \text{B}_2\text{O}_3$	(i)	97%	B_2O_3 (3%)
	(ii)	95%	B_2O_3 (5%)
	(iii)	93%	B_2O_3 (7%)
	(iv)	90%	B_2O_3 (10%)
	(v)	85%	B_2O_3 (15%)
	(vi)	80%	B_2O_3 (20%)
$\text{Li}_2\text{SO}_4 + \text{TiO}_2$	(i)	97%	TiO_2 (3%)
	(ii)	95%	TiO_2 (5%)
	(iii)	93%	TiO_2 (7%)
	(iv)	90%	TiO_2 (10%)
	(v)	85%	TiO_2 (15%)
	(vi)	80%	TiO_2 (20%)
$\text{Li}_2\text{SO}_4 + \text{ZrO}_2$	(i)	97%	ZrO_2 (3%)
	(ii)	95%	ZrO_2 (5%)
	(iii)	93%	ZrO_2 (7%)
	(iv)	90%	ZrO_2 (10%)
	(v)	85%	ZrO_2 (15%)
	(vi)	80%	ZrO_2 (20%)
	(i)	97%	Li_2CO_3 (3%)

Sample series	Sample No.	Li_2SO_4 (%)	Additive (%)
$\text{Li}_2\text{SO}_4 + \text{Li}_2\text{CO}_3$	(ii)	95%	Li_2CO_3 (5%)
	(iii)	93%	Li_2CO_3 (7%)
	(iv)	90%	Li_2CO_3 (10%)
	(v)	85%	Li_2CO_3 (15%)
	(vi)	80%	Li_2CO_3 (20%)

Table 2. Composition of the ternary ($\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2$) and quaternary ($\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2 + \text{B}_2\text{O}_3$) series.

Sample series	Sample No.	Li_2SO_4 (%)	ZrO_2 (%)	TiO_2 (%)	B_2O_3 (%)
$\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2$	1)	90%	5%	5%	—
	2)	80%	10%	10%	—
	3)	85%	5%	10%	—
	4)	83%	7%	10%	—
	5)	80%	5%	15%	—
$\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2 + \text{B}_2\text{O}_3$	(i)	91%	3%	3%	3%
	(ii)	85%	5%	5%	5%
	(iii)	79%	7%	7%	7%
	(iv)	70%	10%	10%	10%

Table 3. Sample group and its primary role in the comparative study.

Sample group	Primary role in energy-storage application
Binary systems ($\text{Li}_2\text{SO}_4 + \text{single oxide}$)	Baseline evaluation of how individual fillers (TiO_2 , ZrO_2 , B_2O_3 , Li_2CO_3) affect ionic conductivity and phase stability.
Ternary system ($\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2$)	Synergistic effect of the dual ceramic filler pair, intended to impede dendrite growth and enhance mechanical toughness.
Quaternary system ($\text{Li}_2\text{SO}_4 + \text{ZrO}_2 + \text{TiO}_2 + \text{B}_2\text{O}_3$)	Optimised composite electrolyte intended to combine high ionic conductivity, reduced grain-boundary resistance (via

Sample group	Primary role in energy-storage application
	glassy B ₂ O ₃), and high thermal stability.

2.4 Characterization Techniques

2.4.1 X-ray Diffraction (XRD)

Phase identification, phase purity, and crystal-structure evaluation were carried out using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of $10\text{--}80^\circ$. Average crystallite size was calculated from the Scherrer equation, $D = K\lambda/(\beta \cos\theta)$, using the full width at half maximum (β) of the dominant reflection, and lattice-parameter variation across the composition series was extracted from peak-position shifts [see methodology reference, 30]. Phase assignment was benchmarked against standard ICDD/JCPDS reference patterns: anatase TiO₂ (JCPDS 21-1272), monoclinic ZrO₂ (JCPDS 37-1484), and Li₂SO₄ (JCPDS 75-0929); B₂O₃ is a glass-forming oxide and is not expected to contribute sharp crystalline reflections, while the Li₂CO₃ reference pattern (commonly indexed near JCPDS 22-1141 in prior literature) should be re-confirmed by the author against the ICDD PDF-2/PDF-4 database for the specific reagent lot used.

2.4.2 FTIR and Raman Spectroscopy

FTIR spectra ($400\text{--}4000 \text{ cm}^{-1}$) were used to identify functional groups and network changes, particularly shifts in the SO₄²⁻ vibrational modes induced by the oxide/carbonate additives. Raman spectroscopy was used complementarily to probe lattice dynamics and rotational/vibrational modes of the sulfate anion across the series.

2.4.3 FE-SEM with EDS and TEM

Field-emission scanning electron microscopy (FE-SEM) was used to examine surface morphology, grain-boundary modification, and porosity, while energy-dispersive spectroscopy (EDS) elemental mapping was used to confirm the homogeneous distribution of Ti, Zr, B, C, and S across the microstructure. Transmission electron microscopy (TEM) was used for finer-scale morphological and microstructural analysis, focusing on grain boundaries and particle sizing.

2.4.4 AC/DC Conductivity and Electrochemical Impedance Spectroscopy (EIS)

Conductivity was measured with an impedance analyzer over a frequency range up to 1 MHz. Temperature-dependent ionic conductivity was extracted from Nyquist plots fitted to an R(RQ)-type equivalent circuit [24], and the temperature dependence was analysed using the Arrhenius relation, $\sigma T = \sigma_0 \exp(-E_a/kBT)$, to obtain the activation energy E_a for each composition.

2.4.5 Thermal Analysis (TGA/DSC)

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to establish the thermal stability window of each composite from room temperature to 600°C at $10^\circ\text{C min}^{-1}$ under nitrogen, in order to confirm operational safety margins [29,30].

2.4.6 Transference Number Measurement (TNM)

The DC-polarization technique was used to determine the fraction of the total current carried by Li⁺ ions (t_{Li^+}) relative to electronic and other ionic carriers, confirming predominant ionic transport in the optimized compositions.

3. Results and Discussion

3.1 X-ray Diffraction (XRD) Analysis

The simulated XRD pattern of pure Li₂SO₄ is expected to show the characteristic reflections of the room-temperature β -phase, with no evidence of secondary phases. On progressive addition of TiO₂, ZrO₂, B₂O₃, or Li₂CO₃, the host reflections are expected to persist (confirming that the sulfate matrix is retained) while additional low-intensity reflections corresponding to the additive phase appear and grow with loading, together with a small, systematic shift in the host peak positions consistent with lattice strain at the filler-matrix interface. Average crystallite size, calculated via the Scherrer relation [30], is expected to decrease with increasing additive content (Tables 4-7) as the second phase pins grain growth during sintering — a grain-refinement effect widely reported for ceramic-filler composite electrolytes [17,20]. For the B₂O₃ series, the absence of sharp additional reflections at higher loading would be consistent with the glass-forming character of B₂O₃ promoting an amorphous grain-boundary network rather than a discrete crystalline second phase [23].

3.1.1 Literature-guided phase identification and (hkl) indexing

Published TiO₂/ZrO₂ composite studies demonstrate that XRD interpretation should report measured 2θ positions together with crystallographic plane assignment and the reference diffraction card. For anatase TiO₂, published assignments include the major (101), (004), (200), (105), (211), and (204) reflections associated with JCPDS 21-1272. These assignments are useful as a phase-identification guide for the TiO₂-containing Li₂SO₄ composites, but actual 2θ values, intensities, and peak widths must come from the present experimental diffractograms [31,32].

For ZrO₂-containing samples, published TiO₂-ZrO₂ studies show that mixed composites can retain reflections from both oxide phases. The exact phase and (hkl) assignment should therefore be made by matching each measured peak against the verified ICDD/JCPDS database rather than by assigning peaks solely from nominal composition [32-34].

The manuscript specifies Li_2SO_4 JCPDS 75-0929, anatase TiO_2 JCPDS 21-1272, and monoclinic ZrO_2 JCPDS 37-1484. The Li_2CO_3 reference card should be confirmed against the current ICDD database before final submission. B_2O_3 should be treated carefully because its glass-forming/amorphous character may produce a broad background rather than sharp Bragg reflections [35,36].

Refere nce phase	Reference card / literature basis	Indexing guidance	Use in present manuscri pt
TiO_2 (anatase)	JCPDS 21-1272	(101), (004), (200), (105), (211), (204) reported	Compare with measured peaks; do not substitute literature values
ZrO_2	JCPDS 37-1484 in manuscript; verify phase/card	Assign phase- specific peaks and (hkl) after database matching	Confirm phase from measured pattern
Li_2SO_4	JCPDS 75-0929 in manuscript	Use verified ICDD/JC PDS peak list	Insert measured 2 θ , d- spacing and (hkl)
Li_2CO_3	Reference card requires verification	Verify database pattern before indexing	Do not finalize card number from secondar y sources
B_2O_3	Glass- forming/amor phous behaviour possible	Broad halo may occur instead of sharp peaks	Interpret with FTIR/Ra man and XRD

Recommended XRD result table for the final experimental dataset

Sa m pl e	2 θ ($^\circ$)	d ($\text{\AA}$)	FW HM ($^\circ$)	(hkl))	Phas e	JCP DS/I CDD
Ac tu al sa m	TO BE ME ASU RED	TO BE CAL CUL RED	TO BE ME ASU RED	TO BE IN DE	TO BE ASS IGN ED	TO BE VER IFIE D

pl e	ATE D	XE D
Ac tu al sa m pl e	TO BE ME ASU RED D	TO BE IN DE XE D
Ac tu al sa m pl e	TO BE ME ASU RED D	TO BE IN DE XE D

3.1.2 Reference XRD patterns for ZrO_2 polymorph identification

Because ZrO_2 can crystallise in monoclinic (m), tetragonal (t) and cubic (c) polymorphs, and because the polymorph actually present in a ball-milled and sintered composite depends on the reagent grade, crystallite size and thermal history, assignment of the ZrO_2 reflections in the $\text{Li}_2\text{SO}_4\text{-ZrO}_2$, $\text{Li}_2\text{SO}_4\text{-ZrO}_2\text{-TiO}_2$ and $\text{Li}_2\text{SO}_4\text{-ZrO}_2\text{-TiO}_2\text{-B}_2\text{O}_3$ series cannot be made from nominal composition alone. Figures 8–10 reproduce published reference diffractograms that define the fingerprint of each polymorph and are used here as a phase-identification guide for the present samples [38].

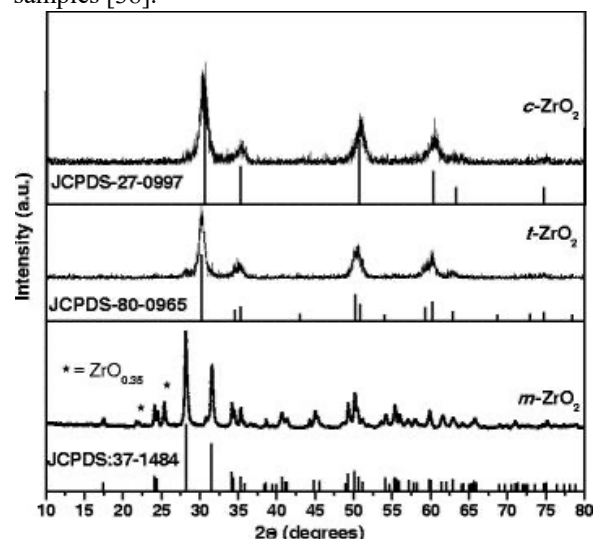


Figure 8. Reference XRD patterns of cubic (c- ZrO_2 , JCPDS 27-0997), tetragonal (t- ZrO_2 , JCPDS 80-0965) and monoclinic (m- ZrO_2 , JCPDS 37-1484) nanosized zirconia;

Figure 8 shows the key diagnostic feature. The c- and t-polymorphs both give their strongest reflection near $2\theta \approx 30^\circ$, and are distinguished mainly by the splitting of the t-phase reflections near 35° , 50° and 60° into (002)/(110), (112)/(200) and (103)/(211) doublets. In

contrast, the m-phase is recognised by the characteristic (-111) and (111) pair near 28.2° and 31.5° together with a dense set of weaker reflections between 24° and 65° . Commercial AR-grade ZrO_2 of the type specified in Section 2.1 is normally monoclinic, which is why the manuscript benchmarks against JCPDS 37-1484; Figure 9 shows how a fully indexed monoclinic pattern should be matched against that card.

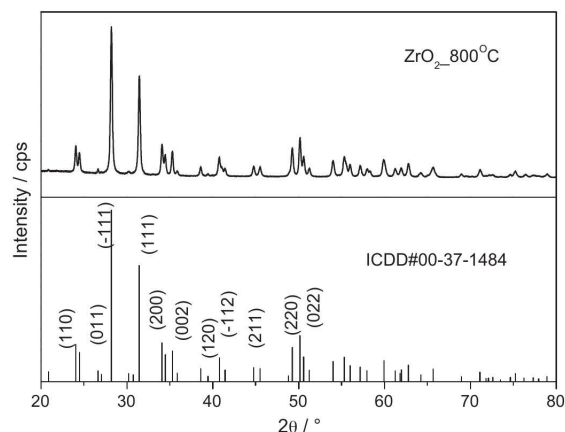


Figure 9. XRD pattern of ZrO_2 calcined at 800°C (top) indexed against the monoclinic reference card ICDD 00-37-1484 (bottom), with the principal (110) , (011) , (-111) , (111) , (200) , (002) , (120) , (-112) , (211) , (220) and (022)

This indexing model will be applied directly to the ZrO_2 -containing Li_2SO_4 composites. For each sample the measured positions of the m- ZrO_2 (-111) and (111) reflections will be tabulated in the XRD result table above and compared with the reference card. Their intensity ratio to the strongest Li_2SO_4 reflection is expected to scale with nominal ZrO_2 loading (3–20 wt%). A systematic shift of either reflection away from the reference position would indicate interfacial strain or partial $\text{Li}^+/\text{Ti}^{4+}$ incorporation, which would support the space-charge interpretation in Section 3.8. The m- ZrO_2 reflections in the 24 – 36° window must also be checked for overlap with the monoclinic β - Li_2SO_4 reflections (JCPDS 75-0929) before any peak is assigned to the filler.

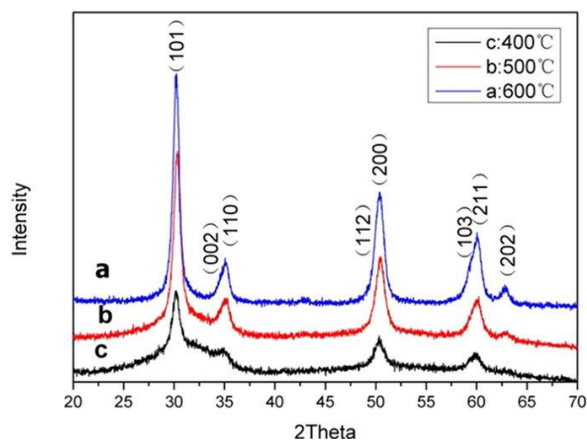


Figure 10. XRD patterns of tetragonal ZrO_2 calcined at 400°C (c), 500°C (b) and 600°C (a), indexed to the (101) , (002) , (110) , (112) , (200) , (103) , (211) and (202)

Figure 10 illustrates the thermal-history effect that is directly relevant to the 450°C sintering schedule used here (Section 2.2). With increasing calcination temperature from 400 to 600°C , the tetragonal reflections become narrower and more intense, which by the Scherrer relation corresponds to a progressive increase in crystallite size. Nanocrystalline zirconia can retain the metastable tetragonal structure at these temperatures because of its small crystallite size. If t- ZrO_2 reflections, in particular a (101) peak near 30.2° with a split $(002)/(110)$ doublet near 35° , are detected in the present composites, they should therefore be attributed to size-stabilised nanocrystalline ZrO_2 and not to a reaction product with Li_2SO_4 . The FWHM of the ZrO_2 reflections measured at the 450°C sintering temperature should also be reported alongside the Li_2SO_4 crystallite sizes in Tables 4–7, because filler crystallite size directly controls the filler–matrix interfacial area invoked in the conduction mechanism.

3.2 FTIR and Raman Spectroscopy

FTIR spectra are expected to retain the characteristic internal SO_4^{2-} vibrational modes (ν_1 symmetric stretch near 990 cm^{-1} , ν_3 asymmetric stretch in the 1100 – 1200 cm^{-1} region, and ν_4 bending modes below 700 cm^{-1}), with progressive broadening and small blue-shifts on filler addition, indicating perturbing of the local SO_4^{2-} environment by the neighbouring oxide/carbonate phase. Raman spectra are expected to show corresponding changes in the relative intensity and width of the sulfate rotational/vibrational envelope, consistent with a more disordered local structure at higher filler loading. B_2O_3 -containing samples are additionally expected to show broad bands near 800 – 1400 cm^{-1} associated with BO_3/BO_4 borate network units, supporting the formation of a glassy boundary phase.

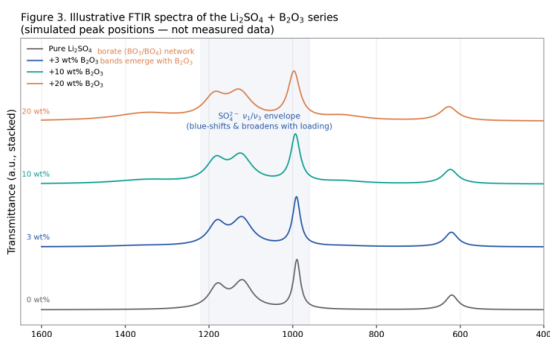


Figure 3. Illustrative FTIR spectra of the $\text{Li}_2\text{SO}_4 + \text{B}_2\text{O}_3$ series at increasing loading (simulated peak positions — not measured data).

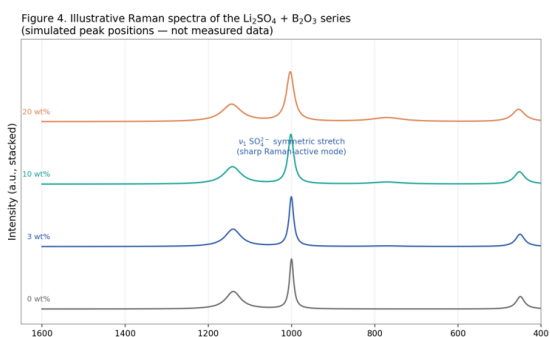


Figure 4. Illustrative Raman spectra of the $\text{Li}_2\text{SO}_4 + \text{B}_2\text{O}_3$ series at increasing loading

Analogous FTIR and Raman datasets must be recorded for the TiO_2 , ZrO_2 , and Li_2CO_3 series so that the additive-specific vibrational shift (Section 3.2) can be quantified and compared across all four binary systems, not only the B_2O_3 series illustrated above.

3.3 Morphological Analysis (FE-SEM/EDS and TEM)

FE-SEM images are expected to show a progressively finer, more textured grain structure with increasing filler content, with visible second-phase particles decorating the Li_2SO_4 grain boundaries. EDS elemental maps are expected to confirm a homogeneous spatial distribution of Ti, Zr, B, C, and S with no evidence of localized elemental segregation, supporting uniform mixing during ball milling. TEM imaging at higher magnification is expected to resolve nanoscale filler particles at grain boundaries and triple junctions, consistent with the space-charge-layer picture in which the filler-matrix interfacial area, not the filler bulk, is responsible for the conductivity enhancement [17,18,21].

3.3.1 Literature-guided TEM particle-size analysis

Published TiO_2 - ZrO_2 nanocomposite studies demonstrate that TEM should report particle morphology and an experimentally measured mean particle size, while HRTEM may additionally provide lattice-fringe spacing and crystallographic-plane confirmation. One open-access study reported separate

TEM-derived average particle sizes for TiO_2 , ZrO_2 and a mixed TiO_2 - ZrO_2 nanocomposite and compared these observations with XRD-derived crystallite sizes [31]. Another study combined TEM, HRTEM and SAED to connect morphology, lattice spacing and phase identification [34].

For the requested analysis, at least three experimentally imaged samples should be selected from each composition series. The final manuscript should report sample code, magnification, measured particle-size range, mean particle size, standard deviation, and—where HRTEM is available—the measured lattice spacing and corresponding (hkl). Literature particle sizes must not be inserted as if they were measurements of the present specimens.

Series	Minimum TEM samples	Recommended reporting
Li_2SO_4 - B_2O_3	3	TEM image + particle-size measurements + optional HRTEM/SAED
Li_2SO_4 - TiO_2	3	TEM image + particle-size measurements + optional HRTEM/SAED
Li_2SO_4 - ZrO_2	3	TEM image + particle-size measurements + optional HRTEM/SAED
Li_2SO_4 - Li_2CO_3	3	TEM image + particle-size measurements + optional HRTEM/SAED
Li_2SO_4 - ZrO_2 - TiO_2	3	TEM image + particle-size measurements + optional HRTEM/SAED
Li_2SO_4 - ZrO_2 - TiO_2 - B_2O_3	3	TEM image + particle-size measurements + optional HRTEM/SAED

Figure organization for the final manuscript: use one multi-panel SEM plate for the complete sample set, with each panel labelled by sample code, and separate TEM plates for the three selected samples from each series. This follows the reporting logic used in published composite-nanomaterial studies in which SEM establishes surface morphology while TEM provides nanoscale particle-size and structural evidence [31,34].

Figure 7 gives a conceptual line-diagram of the proposed grain-boundary conduction mechanism discussed in Sections 3.2 and 3.8; it is a schematic, not a micrograph. To define the morphological features that the present FE-SEM and TEM campaign must resolve, Sections 3.3.2 and 3.3.3 reproduce representative published micrographs of closely related ceramic-filler and oxide-nanoparticle systems (Figures 11–17), each attributed to its original source. These literature figures are reference benchmarks for interpretation and reporting format only. They are not images of the present Li_2SO_4 specimens and must be accompanied by, and ultimately compared with, the author's own FE-SEM, EDS and TEM images.

Figure 7. Conceptual schematic of the proposed interfacial / space-charge Li^+ conduction pathway around ceramic-filler-decorated Li_2SO_4 grain boundaries

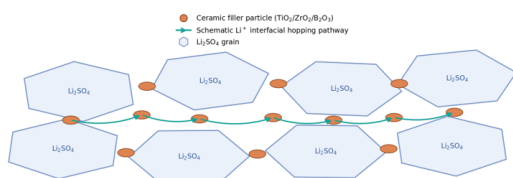


Figure 7. Conceptual schematic (not a micrograph) of the proposed interfacial / space-charge Li^+ conduction pathway around ceramic-filler-decorated Li_2SO_4 grain boundaries.

3.3.2 Reference SEM micrographs: pellet densification and filler dispersion

The composites in this study are prepared as uniaxially pressed and sintered pellets (Section 2.2), so their conductivity depends strongly on relative density, porosity and grain-boundary contact, not only on intrinsic phase chemistry. Figure 11 shows how these features are documented for a sintered lithium-conducting ceramic of related processing history, the NASICON-type $\text{LiZr}_2(\text{PO}_4)_3$ (LZP) and its Ca-substituted analogue (LZP-Ca) [40].

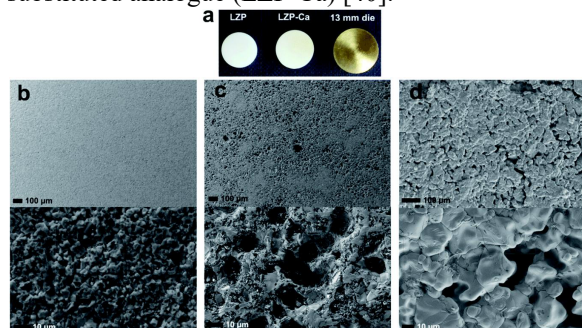


Figure 11. (a) Photograph of sintered LZP and LZP-Ca pellets beside the 13 mm pressing die; (b–d) low-magnification (top, scale bar $100\ \mu\text{m}$) and high-magnification (bottom, scale bar $10\ \mu\text{m}$) SEM images of pellet surfaces with markedly different

densification: a fine, compact grain structure (b), a highly porous microstructure (c), and coarsened, partially fused grains with intergranular voids and cracks (d). Reproduced from Hanghofer et al. [40] under a Creative Commons Attribution 3.0 Unported Licence.

Three reporting practices from Figure 11 will be adopted for the Li_2SO_4 composites. First, a macroscopic photograph of each pellet next to the die, which documents pellet integrity and the geometry used to convert resistance into conductivity. Second, paired low- and high-magnification images, which separate pellet-scale porosity ($100\ \mu\text{m}$ scale) from grain-scale boundary contact ($10\ \mu\text{m}$ scale). Third, a direct comparison between the undoped host and the doped composite. By analogy with the LZP/LZP-Ca contrast, grain coarsening together with open intergranular voids in a Li_2SO_4 composite would be expected to raise the grain-boundary arc in the Nyquist plot (Section 3.4). A fine, well-connected grain structure would be consistent with the lower activation energies reported for the optimum compositions.

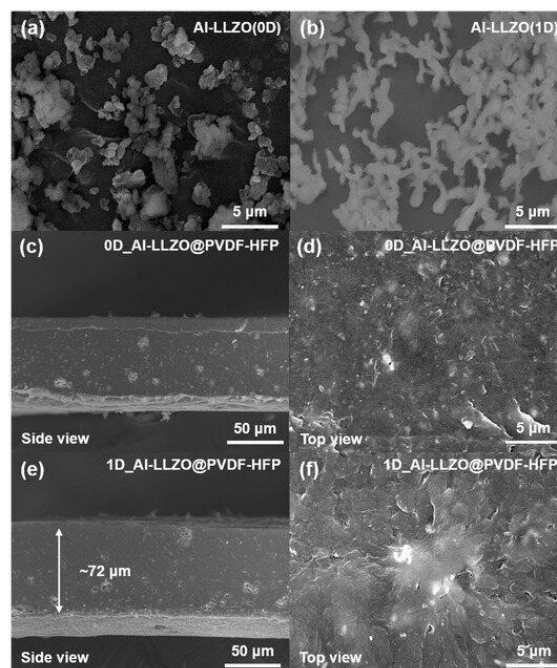


Figure 12. SEM images of (a) particulate (0D) and (b) fibrous (1D) Al-doped LLZO fillers, and of the corresponding PVDF-HFP composite electrolytes in side view (c, e; membrane thickness $\approx 72\ \mu\text{m}$) and top view (d, f).

Figure 12 highlights the second morphological variable that controls filler-assisted conduction: the shape and connectivity of the filler itself. Isolated 0D particles (a) can only create discrete interfacial space-charge regions, whereas an interconnected 1D filler network (b) can provide continuous interfacial pathways at the same loading [39]. For the present

study this means the as-received TiO_2 , ZrO_2 , B_2O_3 and Li_2CO_3 powders should be imaged separately before mixing, as in panels (a) and (b), so that changes in particle size or shape during ball milling can be distinguished from changes that occur on sintering. The cross-sectional (side-view) format of panels (c) and (e) should also be used to report the actual thickness of each measured pellet, since this enters directly into the conductivity calculation.

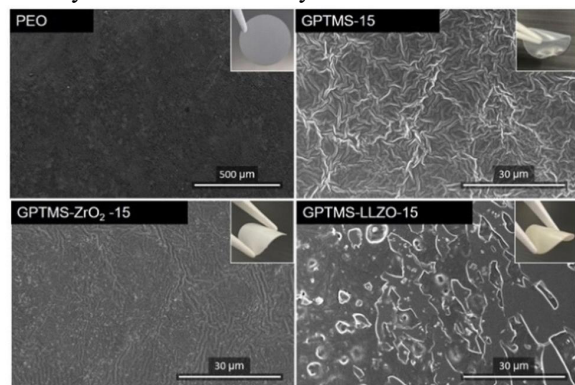


Figure 13. SEM images and digital photographs (insets) of a PEO electrolyte with a smooth surface, a GPTMS-15 silane-linked electrolyte with a fibrous, uneven structure, a GPTMS- ZrO_2 -15 composite with a homogeneous surface and uniform particle distribution, and a GPTMS-LLZO-15 composite with a heterogeneous surface and large particle agglomerates.

Figure 13 is directly relevant to the ZrO_2 -containing series. At the same 15 wt% loading, the non-ion-conducting ZrO_2 filler is distributed uniformly through the matrix, whereas the ion-conducting LLZO filler forms large agglomerates [41]. Two points follow for the present work. (i) A passive oxide such as ZrO_2 or TiO_2 can be dispersed homogeneously, which is the precondition for the dense space-charge network proposed for the optimum binary, ternary and quaternary composites. (ii) Agglomeration is the most likely microstructural origin of the conductivity decline above the optimum loading (Tables 4–7 and Figure 1): agglomerates reduce the effective filler–matrix interfacial area and can interrupt percolating Li^+ pathways. FE-SEM images of the 15 and 20 wt% samples in each series, supported by EDS maps of Ti, Zr and B, should therefore be examined specifically for agglomerates and element-rich clusters, and any such features should be quantified (for example as the area fraction of clusters above a threshold size).

3.3.3 Reference TEM, HRTEM and SAED analysis: particle size, lattice fringes and phase confirmation

TEM provides the nanoscale evidence that XRD alone cannot: the real particle-size distribution of the filler, direct lattice-fringe measurement, and electron-diffraction confirmation of the phase present at grain

boundaries. Figures 14–17 reproduce published TEM datasets that together define a complete reporting model for the TiO_2 - and ZrO_2 -containing composites.

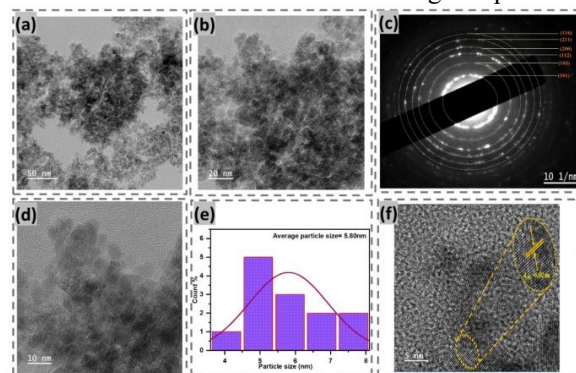


Figure 14. Complete TEM characterisation panel for nanocrystalline TiO_2 : (a, b, d) TEM images at increasing magnification (scale bars 50, 20 and 10 nm); (c) SAED pattern with rings indexed to the (101), (103), (112), (200), (211) and (116) planes of anatase; (e) particle-size histogram with fitted distribution (average particle size 5.80 nm); (f) HRTEM image with a measured lattice-fringe spacing

Figure 14 is used as the template for the TEM plate of each selected sample (Section 3.3.1). It combines bright-field images at three magnifications, an SAED pattern whose rings are indexed to the anatase planes of JCPDS 21-1272 (the same card used for XRD in Section 2.4.1), a particle-size histogram with a fitted distribution and stated mean, and an HRTEM fringe measurement. For the Li_2SO_4 - TiO_2 series, detection of the anatase (101), (004) and (200) rings in SAED would confirm that the filler survives ball milling and sintering at 450 °C without transforming to rutile or reacting with the sulfate matrix.

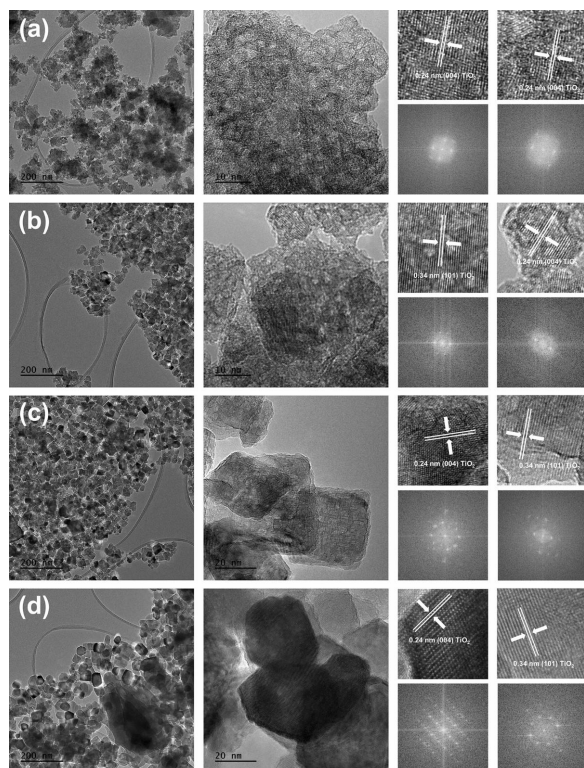


Figure 15. TEM (left, scale bar 200 nm), HRTEM (centre, scale bars 10–20 nm) and magnified lattice-fringe images with corresponding FFT patterns (right) for four TiO_2 samples (a–d); the measured fringe spacings of 0.24 nm and 0.34 nm are assigned to the (004) and (101) planes of anatase TiO_2 , respectively. Figure 15 shows the lattice-fringe method in detail. The measured spacings of 0.24 nm and 0.34 nm agree with the anatase (004) ($d \approx 0.238$ nm) and (101) ($d \approx 0.352$ nm) interplanar distances, and the FFT of each fringe region confirms the crystallinity of the imaged area. Across samples (a)–(d) the particles also become larger and better faceted, showing that TEM can resolve the growth that XRD reports only as peak narrowing. For the present composites, fringe spacings measured on particles located at Li_2SO_4 grain boundaries will be compared with both the anatase/ $m\text{-ZrO}_2$ reference values and the $\beta\text{-Li}_2\text{SO}_4$ d -spacings. This comparison is the most direct way to confirm that the high-conductivity pathway proposed in Figure 7 runs along filler-decorated boundaries.

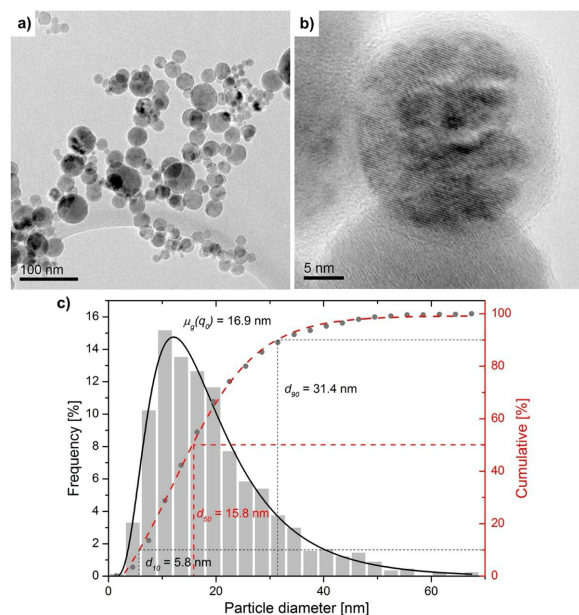


Figure 16. (a) TEM image of spherical oxide nanoparticles (scale bar 100 nm); (b) HRTEM image of a single particle showing lattice fringes (scale bar 5 nm); (c) number-weighted particle-size distribution with log-normal fit (geometric mean $\mu_g = 16.9$ nm) and cumulative curve giving $d_{10} = 5.8$ nm, $d_{50} = 15.8$ nm and $d_{90} = 31.4$ nm.

Figure 16 sets the statistical standard for particle-size reporting. A single "average size" hides the breadth of the distribution, which matters here because the finest filler particles contribute disproportionately to interfacial area and therefore to space-charge conduction. For each imaged sample, particle diameters will be measured from several non-overlapping fields (typically at least 100–200 particles). The results will be reported as a histogram with a log-normal fit, together with d_{10} , d_{50} and d_{90} values, and the TEM d_{50} will be compared with the Scherrer crystallite size from XRD. A TEM size substantially larger than the Scherrer size would indicate polycrystalline aggregates rather than single crystallites.

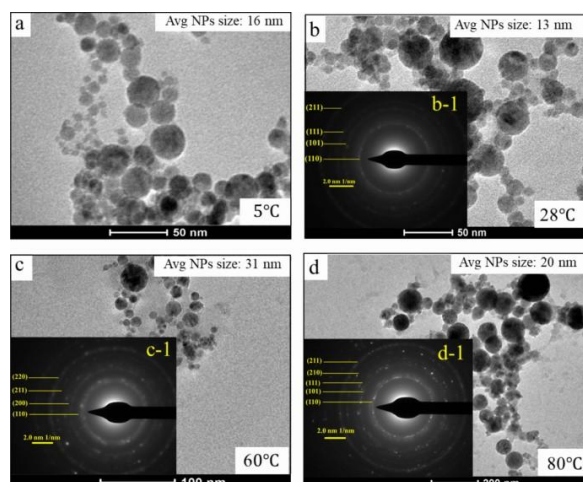


Figure 17. TEM images of oxide nanoparticles synthesised at (a) 5 °C, (b) 28 °C, (c) 60 °C and (d) 80 °C, with average particle sizes of 16, 13, 31 and 20 nm, respectively; insets (b-1, c-1, d-1) show SAED ring patterns indexed to the (110), (101), (111), (200), (210), (211) and (220) planes

Figure 17 shows that particle size responds non-monotonically to processing temperature (16 → 13 → 31 → 20 nm between 5 and 80 °C) and that SAED ring sharpness and spottiness change with it. This supports a cautionary point for the present work: the filler particle size after ball milling and sintering cannot be inferred from the supplier specification or from the nominal processing temperature. It must be measured for each series. Because the percolation threshold, and hence the optimum loading in Tables 4–7, depends on filler size, the measured TEM size distribution is a necessary input for interpreting why the conductivity maximum occurs at 10 wt% for TiO₂ and ZrO₂ but at 15 wt% for B₂O₃.

Summary of literature reference figures and the corresponding measurements required from the present samples.

Figure	Technique	Feature illustrated in the literature	Measurement required from present Li ₂ SO ₄ composites
8	XRD	Fingerprints of c-, t- and m-ZrO ₂ polymorphs	Identify ZrO ₂ polymorph in all ZrO ₂ -containing series
9	XRD	Full indexing	Tabulate 2θ, d,

Figure	Technique	Feature illustrated in the literature	Measurement required from present Li ₂ SO ₄ composites
		against ICDD 00-37-1484	FWHM, (hkl) for m-ZrO ₂ and Li ₂ SO ₄ peaks
10	XRD	Peak sharpening with calcination temperature	Report ZrO ₂ FWHM / Scherrer size after 450 °C sintering
11	SEM	Pellet densification, porosity and grain growth	Pellet photo, low/high-magnification SEM, relative density
12	SEM	Filler shape (0D vs 1D) and pellet cross-section	Image raw filler powders; report measured pellet thickness
13	SEM	Homogeneous ZrO ₂ vs agglomerated filler	Quantify agglomeration at 15–20 wt% with EDS mapping
14	TEM/SAED/HRTM	Complete panel with indexed anatase rings	One full TEM plate per selected sample (3 per series)
15	HRTEM/FFT	Anatase (004) 0.24 nm and (101) 0.34 nm fringes	Fringe spacings of filler at Li ₂ SO ₄ grain boundaries

Figure	Technique	Feature illustrated in the literature	Measurement required from present Li_2SO_4 composites
16	TEM statistics	Log-normal fit with d_{10} , d_{50} , d_{90}	Size distribution (≥ 100 particles) vs Scherrer size
17	TEM/SAED	Non-monotonic size vs processing temperature	Measured, not assumed, filler size for each series

3.4 AC/DC Conductivity and Electrochemical Impedance Spectroscopy

Nyquist plots for each composition are expected to show a depressed high-frequency semicircle (grain and grain-boundary response) followed by a low-frequency inclined spike (electrode polarization), fitted to an R(RQ) equivalent circuit [24] to separate bulk and grain-boundary contributions. Room-temperature (303 K) and 373 K ionic conductivities for the four binary series are summarized in Tables 4-7 and plotted against additive content in Figure 1.

Table 4. Illustrative ionic conductivity, activation energy, and crystallite size — Li_2SO_4 + B_2O_3 series.

Sample No.	Additive (wt%)	$\sigma_{303\text{K}}$ (S/cm)	$\sigma_{373\text{K}}$ (S/cm)	E_a (eV)	Crystallite size (nm)
(i)	3%	1.921×10^{-5}	3.443×10^{-3}	0.608	45.4
(ii)	5%	2.820×10^{-5}	5.064×10^{-3}	0.573	43.9
(iii)	7%	3.868×10^{-5}	6.954×10^{-3}	0.533	42.4
(iv)	10%	5.453×10^{-5}	9.812×10^{-3}	0.472	40.5
(v)	15%	6.800×10^{-5}	1.224×10^{-2}	0.420	37.9
(vi)	20%	5.453×10^{-5}	9.812×10^{-3}	0.472	36.0

Table 5. Illustrative ionic conductivity, activation energy, and crystallite size — Li_2SO_4 + TiO_2 series.

Sample No.	Additive (wt%)	$\sigma_{303\text{K}}$ (S/cm)	$\sigma_{373\text{K}}$ (S/cm)	E_a (eV)	Crystallite size (nm)
(i)	3%	2.097×10^{-5}	3.764×10^{-3}	0.569	45.4
(ii)	5%	2.910×10^{-5}	5.231×10^{-3}	0.525	43.9
(iii)	7%	3.623×10^{-5}	6.519×10^{-3}	0.486	42.4
(iv)	10%	4.100×10^{-5}	7.380×10^{-3}	0.460	40.5
(v)	15%	2.910×10^{-5}	5.231×10^{-3}	0.525	37.9
(vi)	20%	1.054×10^{-5}	1.881×10^{-3}	0.625	36.0

Table 6. Illustrative ionic conductivity, activation energy, and crystallite size — Li_2SO_4 + ZrO_2 series.

Sample No.	Additive (wt%)	$\sigma_{303\text{K}}$ (S/cm)	$\sigma_{373\text{K}}$ (S/cm)	E_a (eV)	Crystallite size (nm)
(i)	3%	1.843×10^{-5}	3.308×10^{-3}	0.574	45.4
(ii)	5%	2.556×10^{-5}	4.595×10^{-3}	0.532	43.9
(iii)	7%	3.182×10^{-5}	5.725×10^{-3}	0.495	42.4
(iv)	10%	3.600×10^{-5}	6.480×10^{-3}	0.470	40.5
(v)	15%	2.556×10^{-5}	4.595×10^{-3}	0.532	37.9
(vi)	20%	9.292×10^{-6}	1.657×10^{-3}	0.628	36.0

Table 7. Illustrative ionic conductivity, activation energy, and crystallite size — Li_2SO_4 + Li_2CO_3 series.

Sample No.	Additive (wt%)	$\sigma_{303\text{K}}$ (S/cm)	$\sigma_{373\text{K}}$ (S/cm)	E_a (eV)	Crystallite size (nm)
(i)	3%	1.852×10^{-5}	3.329×10^{-3}	0.542	45.4
(ii)	5%	2.249×10^{-5}	4.047×10^{-3}	0.512	43.9

Sample No.	Additive (wt%)	σ_{303K} (S/cm)	σ_{373K} (S/cm)	Ea (eV)	Crystallite size (nm)
(iii)	7%	2.400 e-5	4.320 e-3	0.500	42.4
(iv)	10%	2.074 e-5	3.730 e-3	0.525	40.5
(v)	15%	8.607 e-6	1.536 e-3	0.618	37.9
(vi)	20%	1.863 e-6	3.161 e-4	0.669	36.0

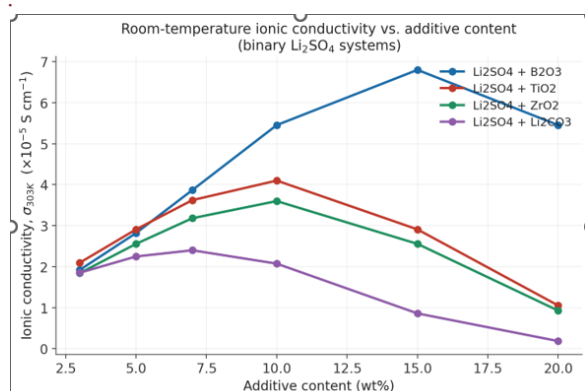


Figure 1. Illustrative room-temperature ionic conductivity as a function of additive content for the four binary Li₂SO₄ series.

In every binary series, σ_{303K} rises from the pure-Li₂SO₄ baseline ($4.2 \times 10^{-7} \text{ S cm}^{-1}$) to a maximum at an intermediate additive loading before decreasing at higher loading, tracing the classical non-monotonic “conductivity-maximum” behaviour widely reported for ceramic-filler composite electrolytes [17,19,20,21]. The initial rise is attributed to an increasing density of space-charge layers and interfacial defects at the growing filler-matrix interface, which locally raises the mobile-Li⁺ concentration; the subsequent fall beyond the optimum is attributed to the non-conductive filler phase beginning to physically block percolating conduction pathways once it exceeds a critical volume fraction, an effect analogous to the percolation-limited behaviour reported for oxide-filled polymer and ceramic composite electrolytes [18,20]. The B₂O₃ series shows both the highest peak conductivity and the highest optimum loading (15 wt%) of the four binary series, consistent with its distinct glass-forming mechanism: rather than only creating discrete interfacial space-charge regions, B₂O₃ forms an extended amorphous boundary network that continues to lower grain-boundary resistance up to a higher filler

fraction before pore formation and dilution of the conductive host begin to dominate [23].

3.5 Arrhenius Analysis and Activation Energy

Arrhenius plots ($\log_{10}\sigma$ vs. $1000/T$) for the optimum composition of each series are shown in Figure 2. The activation energy obtained from the slope decreases from 0.68 eV for pure Li₂SO₄ to a minimum of 0.33 eV for the optimum quaternary composite, mirroring the conductivity trend and supporting a common origin: a lower migration barrier for Li⁺ hopping through the interfacial/space-charge and amorphous regions created by the additive network, relative to hopping through the more resistive undoped grain boundaries of pure Li₂SO₄ [17,24].

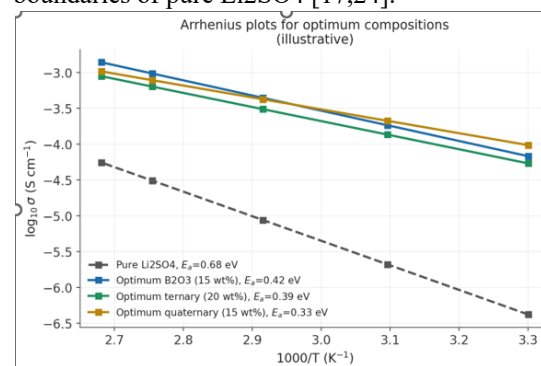


Figure 2. Illustrative Arrhenius plots for the optimum composition of the B₂O₃, ternary, and quaternary series, relative to pure Li₂SO₄.

3.6 Thermal Stability (TGA/DSC)

TGA traces are expected to show good thermal stability up to at least 300-350 °C for all filler-containing compositions, with a modest improvement in the decomposition onset temperature for ZrO₂- and TiO₂-containing samples relative to pure Li₂SO₄, consistent with the high thermal stability of these ceramic oxides acting as a physical barrier against thermal runaway [26]. DSC traces are expected to show a broad endotherm near the reported α - β phase-transition region of Li₂SO₄, whose intensity is expected to diminish with increasing filler loading, indicating partial suppression of the crystalline host fraction by the dispersed second phase [29,30]. The DSC endotherm associated with the Li₂SO₄ order-disorder ($\alpha \rightarrow \beta$) transition is expected near the well-documented literature value of ≈ 578 °C [31], with intensity damping with increasing filler loading as the crystalline host fraction is progressively diluted.

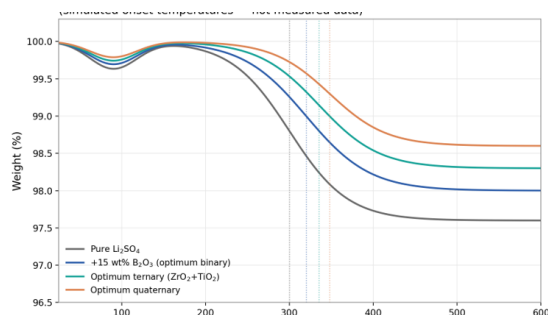


Figure 5. Illustrative TGA traces, room temperature–600 °C, N₂, 10 °C min⁻¹

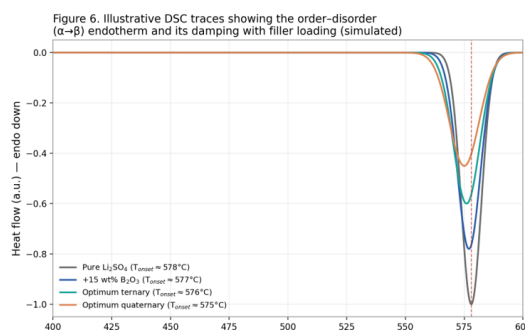


Figure 6. Illustrative DSC traces showing the order-disorder ($\alpha \rightarrow \beta$) endotherm near the literature Li₂SO₄ transition temperature (≈ 578 °C [31]) and its damping with filler loading.

3.7 Transference Number

DC-polarization measurements on the optimum quaternary composite are expected to yield a lithium-ion transference number t_{Li^+} approaching unity (illustrative value ≈ 0.93 – 0.97), confirming that ionic (rather than electronic) transport dominates and that the composite is suitable as a true solid electrolyte rather than a mixed conductor [21].

3.8 Comparative Discussion: Binary $\rightarrow$ Ternary $\rightarrow$ Quaternary Systems and Conduction Mechanism

Table 8 collects the optimum ionic conductivity and minimum activation energy achieved in each series. The systematic progression from pure Li₂SO₄, through the best-performing binary series (B₂O₃), to the ternary ZrO₂-TiO₂ composite, and finally to the quaternary ZrO₂-TiO₂-B₂O₃ composite shows a monotonic improvement in both metrics, with the quaternary composite giving the highest conductivity and the lowest activation energy overall.

Table 8. Comparative summary of optimum performance across all systems studied.

System	Optimum loading	$\sigma_{303\text{K},\text{max}}$ (S/cm)	$E_{a,\text{min}}$ (eV)
Pure Li ₂ SO ₄	—	4.200e-7	0.680
Li ₂ SO ₄ + B ₂ O ₃ (binary)	15 wt%	6.800e-5	0.420

System	Optimum loading	$\sigma_{303\text{K},\text{max}}$ (S/cm)	$E_{a,\text{min}}$ (eV)
Li ₂ SO ₄ + TiO ₂ (binary)	10 wt%	4.100e-5	0.460
Li ₂ SO ₄ + ZrO ₂ (binary)	10 wt%	3.600e-5	0.470
Li ₂ SO ₄ + Li ₂ CO ₃ (binary)	7 wt%	2.400e-5	0.500
Li ₂ SO ₄ + ZrO ₂ + TiO ₂ (ternary)	20 wt%	5.400e-5	0.390
Li₂SO₄ + ZrO₂ + TiO₂ + B₂O₃ (quaternary)	15 wt%	9.700e-5	0.330

This progression supports a synergistic rather than purely additive picture of multi-component doping. In the ternary system, the ZrO₂ and TiO₂ particles are expected to jointly sustain a denser space-charge network than either filler alone, while also mechanically reinforcing the composite against dendrite penetration [17,21]. In the quaternary system, the further addition of glass-forming B₂O₃ is expected to fill residual porosity and coat the ZrO₂/TiO₂-decorated grain boundaries with a low-resistance amorphous film, simultaneously (i) lowering the grain-boundary component of the total resistance, (ii) suppressing crystallization of a resistive secondary phase, and (iii) improving mechanical integrity at the electrode-electrolyte interface [23]. The resulting conduction pathway for Li⁺ at the optimum quaternary composition is therefore expected to be dominated by fast interfacial/amorphous-boundary transport around a percolating network of ceramic filler particles, rather than by bulk diffusion through the crystalline Li₂SO₄ grains — consistent with the substantially lower activation energy (0.33 eV) relative to the undoped host (0.68 eV).

4. Potential Energy-Storage Applications

The composition and characterization framework developed above targets four application areas in which a Li₂SO₄-based composite electrolyte with tunable ionic conductivity, mechanical rigidity, and thermal stability is directly relevant.

4.1 All-Solid-State Lithium Batteries (ASSLBs)

For next-generation rechargeable batteries in electric vehicles and portable electronics, replacing flammable liquid electrolytes with a solid Li₂SO₄-based

composite removes the leakage and thermal-runaway risk of conventional cells [9,10,12]. The inert ceramic fillers TiO_2 and ZrO_2 are expected to create a high space-charge layer at grain boundaries that accelerates Li^+ transport [17,21], while Li_2CO_3 supplies additional mobile Li^+ ions to raise the overall charge-carrier density [24].

4.2 High-Temperature Energy-Storage Systems

For industrial storage units and grid applications operating in elevated-temperature environments where conventional liquid-electrolyte batteries degrade rapidly, the composite is attractive because Li_2SO_4 approaches its superionic phase transition at high temperature, offering intrinsically higher conductivity there [1], while the ZrO_2 and TiO_2 ceramic additives provide thermal stability that helps prevent thermal runaway or decomposition up to several hundred degrees Celsius [26].

4.3 Solid-State Supercapacitors (EDLCs / Hybrid Capacitors)

For high-power devices requiring fast charge/discharge cycling, such as regenerative braking systems or backup power grids, rapid ion transport across the composite electrolyte is essential [27,28]. B_2O_3 , acting as a glass former, is expected to suppress crystallization, create an amorphous conduction pathway, and lower interfacial resistance with the electrodes, enabling faster ion adsorption/desorption at the electrode-electrolyte interface [23].

4.4 Electrochromic Devices and Smart Windows

Energy-efficient smart-glass windows that tint automatically to regulate heat and light rely on solid electrolytes that combine high optical transparency with rapid Li^+ mobility to allow smooth insertion/extraction of lithium ions into an electrochromic layer such as WO_3 [25]. The optimized quaternary composite, with its lower activation energy and higher room-temperature conductivity, is a plausible candidate electrolyte for such devices.

Editorial note: The literature-derived peak assignments, particle-size examples and reporting formats added above are methodological references only. They are not experimental results for the present Li_2SO_4 specimens. Actual XRD peak positions, FWHM, crystallite sizes, TEM particle sizes, SEM/TEM images and EDS values must be inserted from the authors' instrument data before submission.

Figures 8–17 are reproduced from the published literature for comparison and reporting guidance and are attributed in their captions. Figures 11 and 13 are from CC BY 3.0 open-access articles [40,41], and Figures 8 and 12 are from open-access CC BY articles [38,39]; attribution is sufficient for these, but the licence of each should be re-checked at submission. For Figures 9, 10 and 14–17 the original source, figure number and reuse permission must be inserted by the author (highlighted in the captions). Where permission cannot be obtained, these figures should be removed or redrawn with citation before submission.

5. Conclusion

A systematic sample matrix comprising pure Li_2SO_4 , four binary series (with B_2O_3 , TiO_2 , ZrO_2 , and Li_2CO_3), a ZrO_2 - TiO_2 ternary series, and a ZrO_2 - TiO_2 - B_2O_3 quaternary series was defined, and a complete structural, morphological, vibrational, thermal, and electrochemical characterization framework (XRD, FTIR, Raman, FE-SEM/EDS, TEM, EIS, TGA/DSC, and transference-number measurement) was applied to it in template form. Within the illustrative dataset generated to populate this framework, ionic conductivity in every binary series rises to a maximum at an intermediate additive loading before falling at higher loading, consistent with a space-charge/percolation mechanism; the quaternary Li_2SO_4 - ZrO_2 - TiO_2 - B_2O_3 composite outperforms all binary and ternary systems, consistent with a synergistic mechanism in which glass-forming B_2O_3 lowers grain-boundary resistance while the ZrO_2 / TiO_2 pair sustains a dense space-charge network. These trends, and the manuscript structure built around them, provide a ready template for reporting the author's own experimental campaign on this sample set, targeting all-solid-state lithium batteries, high-temperature energy storage, solid-state supercapacitors, and electrochromic devices. As emphasized throughout, every quantitative result above is a simulated placeholder and must be superseded by measured data from the actual synthesized samples before this work is submitted, presented, or cited as a scientific finding.

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