

Interfacial Engineering and Intercalation Electrochemistry in All-Solid-State Lithium-ion Batteries

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

The development of all-solid-state batteries (ASSBs) represents a breakthrough in energy storage technology by providing safer operation with superior energy density and better electrochemical stability than traditional liquid-electrolyte systems. Despite their advantages, all-solid-state batteries face persistent problems with high interfacial resistance between solid electrolyte (SE) and catholyte, lithium dendrite formation and ion transport barriers that demand basic knowledge of solid-state interactions. This thesis investigates two critical aspects of ASSB technology: This thesis addresses (i) the interfacial stability between tantalum-doped lithium lanthanum zirconium oxide (LLZTO) and lithium metal and the heteroionic lithium metal oxychloride (LMOC) type solid electrolyte for all-solid-state lithium-ion batteries (ASSLIBs) and investigates (ii) the intercalation electrochemistry of tantalum disulfide (TaS_2) layered material used in all-solid-state lithium-sulfur batteries (ASSLSBs).

In the first part of my thesis mainly focuses on optimizing the removal of passivation layer (i.e., Li_2CO_3 and LiOH) from the LLZTO surface by rapid acid treatment (RAT) and heat treatment (HT) followed by analyzing the $\text{Li}||\text{LLZTO}$ and $\text{LMOC}||\text{LLZTO}$ interface stability, lithium-ion transport kinetics, and mechanical behaviour during operation using electrochemical impedance spectroscopy, and microstructural analysis. The study systematically investigates symmetrical cell setups, which are affected by external pressure, interfacial contact, and lithium-ion diffusion mechanisms, to determine their influence on charge transfer resistance and morphological stability. Through this stability, we optimized that the interfacial impedance of $\text{Li}||\text{LLZTO}$ becomes small enough ($R_{\text{int}} < 10 \, \Omega \cdot \text{cm}^2$) and for heteroionic interfaces of $\text{LMOC}||\text{LLZTO}$, it is $80 \, \Omega \cdot \text{cm}^2$. However, we tried to show proof of concept that can be improved when designing the hybrid cell with multilayer SEs in ASSLIB for future research.

In the second part of this thesis, we reported the intercalation electrochemistry conversion of layered transition metal sulfide (TaS_2) and carbon (Ketjen black) as sulfur host when used as cathode materials in ASSLSBs which will serve as a neotype hybrid cathode with mixed electronic and ionic conduction (MEIC) contributes excess capacity. This layered structure, combined with its metallic conductivity, enables lithium-ion intercalation while simultaneously acting as a mediator for sulfur redox reactions to promote high gravimetric capacity. This approach resulted in high sulfur utilization of $\sim 99\%$ with $2.99 \, \text{mAh} \cdot \text{cm}^{-2}$ at a C/10 rate and retains 94% over 50 cycles. With a high active material loading of $9.96 \, \text{mg} \cdot \text{cm}^{-2}_{(\text{S}+\text{TaS}_2)}$ the $\text{S}/\text{TaS}_2/\text{C}$ electrode achieves a high areal capacity of $9.1 \, \text{mAh} \cdot \text{cm}^{-2}$.

This thesis improves our knowledge of the essential processes that control ASSB performance by studying interfacial dynamics in lithium-ion systems and intercalation mechanisms in lithium-sulfur systems. The findings lead to advanced solid-state electrolytes and electrode architectures, improving stability and efficiency while creating the foundation for next-generation energy storage systems.

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“To be trusted is a greater compliment than being loved.”

-George MacDonald

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Table of Contents

List of Figures	vii
List of Tables	ix
List of Abbreviations	x
Chapter 1 Introduction	1
1.1 Outline of All-Solid-State Lithium-Ion Batteries (ASSLIB)	1
1.1.1 Fundamentals of ASSLIB	2
1.1.2 Investigation of Solid Electrolytes	4
1.1.3 Investigation of high-performance cathode materials	6
1.2 Outline of All-Solid-State Lithium-Sulfur Batteries	8
1.2.1 Fundamentals and Working Principles of ASSLSBs	10
1.2.2 Challenges to overcome in ASSLSBs	11
1.2.3 Investigation of suitable sulfur host and cathode materials	12
1.3 Scope of this thesis	14
Chapter 2 Characterization and Analytical Techniques	15
2.1 Material Characterization	15
2.1.1 X-ray Diffraction	15
2.1.2 Scanning Electron Microscopy	16
2.1.3 Atomic Force Microscopy	18
2.1.4 Thermal Gravimetric Analysis	18
2.1.5 Brunauer-Emmett-Teller (BET) Analysis	19
2.2 Electrochemical techniques and measurements	19
2.2.1 Solid Cell Configuration	19
2.2.2 Galvanostatic cycling	20
2.2.3 Cyclic Voltammetry	21
2.2.4 Electrochemical Impedance Spectroscopy	21
2.2.5 DC Polarization	22

Chapter 3 Understanding the compatibility of lithium metal anode and lithium-metal-oxyhalide SEs versus surface-treated Ta-doped garnet solid electrolyte.....	23
3.1 Introduction.....	23
3.2 Experimental Section	24
3.3 Results and Discussion	27
Chapter 4 Highly crystalline layered 2H-TaS ₂ as an intercalation-conversion type cathode for All-Solid-State Lithium-Sulfur Batteries	41
4.1 Introduction.....	41
4.2 Experimental Section	42
4.3 Results and Discussion	43
Chapter 5 Summary and Future Perspectives	52
References.....	53

List of Figures

Figure 1.1 Schematic illustration of (a) Conventional liquid electrolyte battery and (b) Solid-state battery reproduced from reference ⁴	1
Figure 1.2 Illustration of (a) liquid Li-S battery and (b) Solid-state Li-S battery, reproduced from reference ¹³	9
Figure 2.1 Schematic illustration of Bragg's law, reproduced from reference ²⁶	15
Figure 2.2 Working principle of SEM, reproduced from reference ²⁷	17
Figure 2.3 Illustration of the cell setups (a-c) and the cell prototype (d-e) reproduced from the references ^{28,29}	20
Figure 3.1 Illustration of the cell A fabrication	26
Figure 3.2 (a) XRD pattern of annealed and sintered LLZTO, (b-c) SEM images of well-polished LLZTO pellet, (d-f) Optical images of the pellets (d) before sintering, (e) after sintering and well-polished and (f) Heat-Treated	28
Figure 3.3 (a) Raman spectrum of Heat-Treated (HT) pellet with glass cover, without glass cover (air-exposed) and LLZTO stored outside for 2 months, (b) Nyquist plot of Au LLZTO Au at 25°C.....	29
Figure 3.4 Illustration of KK test analyzis	30
Figure 3.5 (a,c) Nyquist plot of Li LLZTO with surface treatment and without surface treatment and (b,d) its corresponding DRT plot at 25°C	32
Figure 3.6 (a-b) Temperature-dependent Nyquist plots and (c) the Arrhenius plot calculating the activation energy for both bulk and grain boundary	33
Figure 3.7 The voltage profile and its impedance evolution profile show a contact loss after 10 h of restless stripping experiment at 1 mA.h.cm ⁻²	34
Figure 3.8 (a-d) Current density response with respect to time and its impedance data obtained from long-time plating and stripping experiment at 265 μ A.cm ⁻² at 60°C	35
Figure 3.9 (a) Nyquist plot of LMOC LLZTO and (b) its corresponding time-constant DRT plot at 25°C, (c) Arrhenius plot obtained within the temperature range of -50°C to 30°C.....	36
Figure 3.10 (a-b) Electrochemical profile and its cycling performance at 60°C	38
Figure 3.11 Custom setup for measuring the relative density using Archimedes' Principle	39
Figure 4.1 (a) XRD pattern of 2H-TaS ₂ , (b) TGA curve for the S/TaS ₂ /KB composite, and (c-d) SEM images of 2H-TaS ₂	44

Figure 4.2 (a) XRD pattern of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ and (b) its Nyquist plot.....	44
Figure 4.3 (a) Illustration of cross-sectional solid-state Li-S cell and (b) SEM image of the solid electrolyte and the whole cathode composite and their EDX elemental mapping.....	45
Figure 4.4 Examining the electrochemical conversion mechanism of solid-state Li-S battery. (a) CV profile with TaS_2 and without TaS_2 in the cathode composite, b) Charge and Discharge profile and (c) their corresponding ex-situ XRD profile	46
Figure 4.5 (a) Long cycle performance profile with active material of 2.47 mg.cm^{-2} and (b) Charge and Discharge profile for different carbon with the same optimized ratio	47
Figure 4.6 (a) Charge and Discharge profile of different weight ratios of the active material and (b) Long-term cycling profile of the active material with and without TaS_2	48
Figure 4.7 (a) Rate capability test with different current density, (b) Long-term cycling performance at the high current rate (1C), (c) Cycling performance at intermediate loading of $5.1 \text{ mg}_{(\text{S}+\text{TaS}_2)}.\text{cm}^{-2}$ and (d) Sulfur utilization associated with the low, intermediate and high active material loading	48
Figure 4.8 Electrochemical profile of high active material mass loading at C/10 rate	49

List of Tables

Table 1.1 Key terminologies and parameters related to the batteries	2
Table 1.2 Summary of oxide-based solid electrolytes	4
Table 1.3 Summary of sulfide-based solid electrolytes	5
Table 1.4 Summary of polymer-based solid electrolyte	5
Table 1.5 Summary of halide-based solid electrolytes	5
Table 1.6 Summary of layered oxide cathodes (NMC)	7
Table 1.7 Summary of polyanionic cathodes.....	8
Table 3.1 Comparison table of resistance, capacitance, time constants, frequency and the activation energy of individual solid electrolytes and the multilayer symmetric cell at room temperature	37
Table 4.1 Result summary compared with other reported literature.....	49
Table 4.2 The theoretical capacity of the active material with different weight ratios.....	51

List of Abbreviations

AC	Alternating Current
ACS	American Chemical Society
AFM	Atomic Force Microscopy
ASSB	All-Solid-State-Batteries
ASSLIB	All-Solid-State-Lithium-ion Batteries
ASSLSB	All-Solid-State-Lithium-Sulfur Batteries
BET	Brunauer-Emmett-Teller
CATL	Contemporary Amperex Technology Co., Limited
CCD	Critical Current Density
CE	Coulombic Efficiency
CNT	Carbon Nanotubes
CPE	Constant Phase Element
CV	Cyclic Voltammetry
DC	Direct Current
DOD	Depth of Discharge
DRT	Distribution of Relaxation Time
EBSD	Electron Backscatter Diffraction
EDX	Energy-Dispersive X-ray spectroscopy
EIS	Electrochemical Impedance Spectroscopy

EV	Electric Vehicles
FESEM	Field Emission Scanning Electron Microscopy
GEIS	Galvanostatic Electrochemical Spectroscopy
GO	Graphene Oxide
HF	High Frequency
HT	Heat Treatment
ICE	Initial Coulombic Efficiency
KB	Ketjen Black
KK	Kramers-Kronig Test
LATP	$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$
LF	Low Frequency
LFP	LiFePO_4
LGP	$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$
LGPS	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$
LIB	Lithium-ion Batteries
LLTO	LiLaTiO
LLZO	$\text{Li}_3\text{La}_7\text{O}_{12}\text{Zr}_2$
LLZTO	Ta-doped $\text{Li}_3\text{La}_7\text{O}_{12}\text{Zr}_2$
LLZTO _B	Ta-doped $\text{Li}_3\text{La}_7\text{O}_{12}\text{Zr}_2$ Bulk
LLZTO _{GB}	Ta-doped $\text{Li}_3\text{La}_7\text{O}_{12}\text{Zr}_2$ Grain Boundary
LMOC	Lithium-Metal-Oxyhalide

LMP	LiMnPO ₄
LPS	Li ₃ PS ₄
LPSC	Li ₆ PS ₄ Cl ₅
LTP	LiTi ₂ (PO ₄) ₃
LVP	Li ₃ V ₂ (PO ₄) ₃
LZP	LiZr ₂ (PO ₄) ₃
MEIC	Mixed electron/ionic conductor
MF	Mid-Frequency
NMC	LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂
OCV	Open Circuit Voltage
PDF	Powder Diffraction File
PEIS	Potentiostatic Electrochemical Spectroscopy
PEO	Poly-ethylene oxide
PSD	Pore Size Distribution
PVDF	Polyvinylidene fluoride
RAT	Rapid Acid Treatment
SE	Solid Electrolyte
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SOC	State of Charge
SPM	Scanning Probe Microscopy

SSB	Solid State Batteries
SSE	Solid State Electrolyte
TC	Theoretical Capacity
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMD	Transition Metal Dichalcogenides
TMS	Transition Metal Sulfides
TPB	Triple-Phase Boundaries
VGCF	Vapour-Grown-Carbon-Fiber
XRD	X-Ray Diffraction

Chapter 1 Introduction

1.1 Outline of All-Solid-State Lithium-Ion Batteries (ASSLIB)

The accelerated industrialization and digitalization of present-day society have resulted in a dramatic surge in energy requirements which demands the invention of effective and sustainable methods for storing energy. The worldwide adoption towards renewable energy sources and electrification technologies has created significant market demand for reliable high-performance energy storage solutions.¹ Traditional lithium-ion batteries (LIBs) have maintained dominance in the energy storage field for many years because they power numerous applications such as electric vehicles (EVs), portable electronics and grid energy storage solutions. Traditional LIBs have not been able to avoid multiple limitations which are especially evident in their safety, energy density, and longevity, even though they are widely adopted. The liquid electrolytes used in traditional lithium-ion batteries present safety concerns including fire risks and thermal runaway which prevents their use in high-power applications demanding high reliability. The performance of these systems over extended periods suffers from lithium dendrite formation together with electrolyte decomposition and gradual capacity loss.

All-solid-state lithium-ion batteries (ASSLIBs) represent an emerging promising solution to address the challenges faced by current battery technologies. ASSLIBs substitute liquid electrolytes with solid-state electrolytes (SSE) unlike traditional LIBs which creates improved safety and enables high-energy-density electrode materials like lithium metal anodes. The fundamental change in battery design presents multiple benefits such as better thermal stability, longer cycle life while enabling higher voltage operation and rapid charging abilities making them ideal candidates for next-generation EVs, laptops, smartphones and other portable electronic devices. The development of ASSLIBs progresses quickly as significant automotive and battery companies like Toyota, Nissan, Solid Power, Samsung SDI, CATL and QuantumScape make substantial investments in solid-state battery research². The modern world will see major gains from solid-state battery technology which will deliver extended driving distances and ultra-fast charging speeds along with the best safety features.³

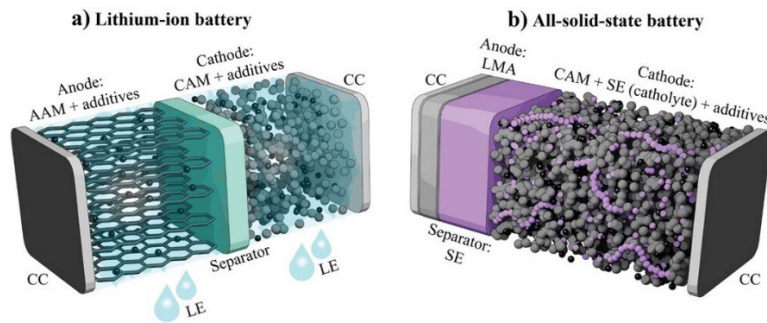


Figure 1.1 Schematic illustration of (a) Conventional liquid electrolyte battery and (b) Solid-state battery reproduced from reference ⁴

1.1.1 Fundamentals of ASSLIB

The fundamental structure of an all-solid-state lithium-ion battery consists of three key components: The three primary elements of an all-solid-state lithium-ion battery include the anode which stores lithium ions during charging; the solid electrolyte enabling lithium-ion movement and serving as a physical barrier to prevent electrical short circuits; and the cathode which enables lithium-ion intercalation and deintercalation during battery operation.⁴ The redox potential of the reaction at the electrode establishes the electrode potential in volts. The output power increases with the voltage difference between the cathode and anode because it depends directly on both current and voltage across these electrodes. The use of electrolytes with enough electrochemical stability becomes essential when a high potential difference is needed to maintain proper functionality and avoid decomposition in the electrochemical potential window of the battery cell.⁵ Traditional LIBs achieve quick lithium-ion movement through liquid electrolytes but ASSLIBs depend on solid-state diffusion which happens more slowly because solid electrolytes possess rigid lattice structures. The slow movement of ions creates increased interfacial resistance which presents a significant obstacle in creating high-performance ASSLIBs. The resistance arises because of inadequate physical contact between components, the formation of resistive interfacial layers through chemical reactions, and mechanical stresses that occur due to volume changes during cycling. During the galvanostatic cycling of a battery, the charge-discharge voltage profile shows how voltage and specific capacity relate to each other. Constant current conditions during recording produce a uniform electrochemical process for this profile. The evaluation of battery rate capability involves applying various current densities to measure its performance across different charge/discharge rates. The standard voltage-capacity curve makes key redox reactions together with their voltage plateaus easily identifiable. Two-phase transitions during lithium insertion/extraction create flat plateaus in profiles while continuous single-phase reactions present as gradual slopes during lithium intercalation. Electrochemical efficiency is measured by the voltage difference between the charging and discharging processes which is termed polarization. The reduction of this voltage gap is vital for energy efficiency because decreased polarization leads to fewer internal resistance losses and better reversibility in battery performance.⁶ There are some key terminologies in batteries to understand which are listed below:

Table 1.1 Key terminologies and parameters related to the batteries

Term	Definition	Formula (if applicable)	Explanation
Open-Circuit Voltage (OCV)	The voltage of a battery when no current flows.	$OCV = E_{\text{cathode}} - E_{\text{anode}}$	Determines battery charge state and depends on electrode redox potentials.

Capacity (C)	Total charge a battery can store and deliver.	$C = I \times t$	Higher capacity means longer operation; affected by ageing and temperature.
Energy Density (E)	Energy stored per unit mass or volume.	$E = V \times C$	Higher energy density allows more energy storage in a compact size.
Power Density (P)	Rate of energy delivery per unit mass or volume.	$P = V \times I$	Determines how quickly a battery can supply power.
Coulombic Efficiency (CE)	Efficiency of charge recovery.	$CE = (Q_{\text{discharge}} / Q_{\text{charge}}) \times 100\%$	Higher CE means minimal side reactions and better cycle life.
State of Charge (SOC)	Remaining charge relative to full capacity.	$SOC = (Q_{\text{remaining}} / Q_{\text{total}}) \times 100\%$	Used in battery management systems to prevent overcharging.
Depth of Discharge (DOD)	Percentage of capacity used.	$DOD = 100\% - SOC$	Deep discharge shortens battery lifespan.
Cycle Life	Number of charge/discharge cycles before capacity drops below 80%.	N/A	Longer cycle life means a more durable battery.
Internal Resistance (R)	Resistance inside a battery affects performance.	$V = E - IR$	Lower resistance improves efficiency and power output.
Charge Transfer Resistance (R_{ct})	Resistance at the electrode-electrolyte interface.	N/A	High R_{ct} slows charge transfer and reduces efficiency.
Interfacial Resistance (R_{int})	Resistance at the solid electrolyte-electrode interface.	N/A	High R_{int} leads to poor ion transport and increased overpotential; minimized via interface engineering.
Critical Current Density (CCD)	Maximum current before lithium dendrites form.	N/A	Higher CCD prevents short circuits in solid-state batteries.
C-Rate	Rate of charge/discharge relative to capacity.	$I = C \times C_{\text{rate}}$	1C means full charge in 1 hour; 2C in 30 minutes.

Activation Energy (E_a)	The energy required for lithium-ion movement.	$\sigma(T) = \sigma_o \exp(-E_a / kT)$	Lower E_a improves lithium-ion transport.
Voltage Hysteresis	Difference between charge and discharge voltage.	N/A	Lower hysteresis means higher efficiency.
Overpotential (η)	Extra voltage is needed to drive a reaction.	$\eta = V_{\text{applied}} - E_{\text{equilibrium}}$	Higher overpotential results in energy loss.

1.1.2 Investigation of Solid Electrolytes

Researchers have explored different solid electrolyte options to overcome various challenges and found that each type presents unique benefits and limitations.^{7,8}

a) Oxide-based solid electrolyte

Oxide electrolytes are known for their high electrochemical stability, good mechanical strength, and resistance to lithium metal. However, they generally have lower ionic conductivity compared to sulfides.

Table 1.2 Summary of oxide-based solid electrolytes

Solid Electrolyte	Electrochemical Stability Window (V vs. Li/Li⁺)	Ionic Conductivity (S/cm)	Physical Properties
LLZO	~6	$10^{-3} - 10^{-4}$	High chemical stability, rigid, brittle
LATP	~4.5	$10^{-3} - 10^{-4}$	Stable against oxidation, but unstable with lithium metal
LTP	~4.5	10^{-6}	Low ionic conductivity, thermally stable
LZP	~4.5	8×10^{-6} at 150°C	Phase transition from triclinic to rhombohedral, chemically stable
LGP	~4.5	10^{-6}	Rhombohedral structure, thermally stable

b) Sulfide-based solid electrolyte

Sulfide electrolytes offer the highest ionic conductivity (comparable to liquid electrolytes) and soft mechanical properties for better interface contact. However, they are sensitive to moisture, leading to H₂S gas formation.

Table 1.3 Summary of sulfide-based solid electrolytes

Solid Electrolyte	Electrochemical Stability Window (V vs. Li/Li ⁺)	Ionic Conductivity (S/cm)	Physical Properties
LGPS	5	10 ⁻²	Extremely high conductivity, moisture sensitive
Li ₇ P ₃ S ₁₁	4.5	10 ⁻²	Good mechanical flexibility, prone to degradation in air
Li ₆ PS ₅ Cl	4.8	10 ⁻³	Good deformability, sensitive to oxidation
Thio-LISICON	5	10 ⁻³	High conductivity, but air-sensitive

c) Polymer-based solid electrolyte

Polymers are lightweight and flexible, allowing easy processability. However, they suffer from low ionic conductivity at room temperature and require higher temperatures (>60°C) for effective ion transport.

Table 1.4 Summary of polymer-based solid electrolyte

Solid Electrolyte	Electrochemical Stability Window (V vs. Li/Li ⁺)	Ionic Conductivity (S/cm)	Physical Properties
PEO-Li salts	4	10 ⁻⁶ - 10 ⁻⁴	Soft, flexible, requires high temperature (>60°C)
PAN-based electrolytes	4.2	10 ⁻⁵	Flexible, moderate conductivity
PVDF-based electrolytes	4.5	10 ⁻⁶	Mechanically strong but lower conductivity

d) Halide-based solid electrolyte

Halide electrolytes exhibit high electrochemical stability and good ionic conductivity while being more stable in air than sulfides.

Table 1.5 Summary of halide-based solid electrolytes

Solid Electrolyte	Electrochemical Stability Window (V vs. Li/Li ⁺)	Ionic Conductivity (S/cm)	Physical Properties
Li ₃ InCl ₆	5	10 ⁻³	Air-stable, good lithium metal compatibility

Li_3YCl_6	5	10^{-3}	Good electrochemical and thermal stability
Li_3ErCl_6	4.8	10^{-3}	High-voltage stability, chemically stable
LiMOCl_4 (M=Nb, Ta)	5	$10.4 - 12.4 \times 10^{-3}$	High ionic conductivity, cold-pressed synthesis, excellent rate capability

1.1.3 Investigation of high-performance cathode materials

1.1.3.1 Layered Oxide Cathodes

All-solid-state lithium-ion batteries (ASSLIBs) typically use Nickel-Manganese-Cobalt (NMC) cathodes represented by $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x}\text{O}_2$ because they offer high energy density and rate capability while maintaining structural stability. The electrochemical performance is greatly affected by the proportion of nickel, manganese, and cobalt components. The most commonly used NMC cathode compositions are NMC111 ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$), NMC532 ($\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$), NMC622 ($\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$), and NMC811 ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$). Increased nickel content leads to enhanced capacity but results in decreased thermal stability while increased manganese content leads to improved structural integrity but reduced capacity.^{9,10}

Redox Reactions in NMC Cathodes

During battery charging and discharging NMC cathodes function by storing and releasing lithium ions through redox reactions of their transition metals.

a) Nickel ($\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+} \rightleftharpoons \text{Ni}^{4+}$)

Nickel provides the greatest capacity contribution because Ni^{3+} converts to Ni^{4+} during charging which enables more lithium to deintercalate. The reaction voltage ranges from 3.6 to 4.3 V versus Li/Li^+ based on the specific NMC composition. NMC811 cathodes with higher nickel content deliver greater capacity but experience reduced thermal and structural stability which leads to increased side reactions with solid electrolytes.

b) Cobalt ($\text{Co}^{3+} \rightleftharpoons \text{Co}^{4+}$)

The primary function of cobalt is to stabilize the layered structure while it serves a secondary purpose for charge compensation. Co^{3+} oxidizes to Co^{4+} at voltages between 4.2 to 4.3 V versus Li/Li^+ which adds more capacity to the system. By decreasing Co levels in NMC811 cathodes, manufacturers can cut expenses and environmental impact but need to adopt structural protection methods such as surface coatings with LiNbO_3 and Li_2ZrO_3 .

c) Manganese (Mn⁴⁺)

The role of manganese in materials is focused on enhancing structural stability instead of boosting storage capacity. Manganese in the form of Mn⁴⁺ does not participate in electrochemical reactions within layered NMC cathodes. Its presence improves cycle life and minimizes cation mixing.

Table 1.6 Summary of layered oxide cathodes (NMC)

NMC Type	Nickel Content (%)	Capacity (mAh/g)	Voltage Range (V vs. Li/Li ⁺)	Stability	Thermal Stability
NMC111	33	160	2.8–4.3 V	Excellent	High
NMC532	50	180	2.8–4.3 V	Good	Moderate
NMC622	60	200	2.8–4.3 V	Moderate	Lower
NMC811	80	220	2.8–4.3 V	Poor	Low

1.1.3.2 Polyanionic Cathodes

Polyanionic cathodes, particularly phosphate-, sulfate-, and fluorophosphate-based materials, have gained attention for their structural stability, safety, and tunable electrochemical properties in all-solid-state lithium-ion batteries (ASSLIBs). These materials benefit from the strong covalent bonding in the polyanion (PO₄, SO₄, etc.) groups, which stabilizes the framework and prevents oxygen release, improving thermal stability. However, they generally exhibit lower electronic conductivity and require modifications such as carbon coating and composite cathode designs to enhance performance.

a) LiFePO₄ (LFP) – Iron Phosphate Cathodes

LiFePO₄ (LFP) dominates lithium-ion and all-solid-state battery markets because of its superior cycle life along with exceptional thermal stability and structural strength. The material functions at a moderate voltage level of approximately 3.4V relative to Li/Li⁺ which ensures high stability across different operating conditions. During charging, Fe²⁺ is oxidized to Fe³⁺ and vice versa Fe³⁺ is reduced to Fe²⁺ when discharging.

Redox reaction: $\text{LiFePO}_4 \rightleftharpoons \text{FePO}_4 + \text{Li}^+ + \text{e}^-$

b) LiMnPO₄ (LMP) – Manganese Phosphate Cathodes

As a high-voltage (4.1V vs. Li/Li⁺) substitute for LFP LiMnPO₄ maintains a comparable polyanion structure while delivering increased specific energy. The material demonstrates limited rate capability because its ionic and electronic conductivity levels are insufficient. During charging, Mn²⁺ is oxidized to Mn³⁺ and vice versa Mn³⁺ is reduced to Mn²⁺ when discharging. Mn³⁺ is less stable when compared to Fe³⁺ which leads to capacity fading.

Redox reaction: $\text{LiMnPO}_4 \rightleftharpoons \text{MnPO}_4 + \text{Li}^+ + \text{e}^-$

c) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) – Vanadium Phosphate Cathodes

Multi-electron redox reactions enable $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ to serve as a high-capacity polyanionic cathode material operating at dual voltage plateaus (3.6V and 4.1V vs. Li/Li^+). $\text{V}^{3+} \rightleftharpoons \text{V}^{4+} \rightleftharpoons \text{V}^{5+}$ enables multi-electron transfer. The material allows the reversible removal of three lithium ions from each formula unit which generates a theoretical capacity of approximately 195 mAh/g.

Redox reaction: $\text{Li}_3\text{V}_2(\text{PO}_4)_3 \rightleftharpoons \text{Li}_x\text{V}_2(\text{PO}_4)_3 + (3-x)\text{Li}^+ + (3-x)\text{e}^-$

Table 1.7 Summary of polyanionic cathodes

Polyanionic Cathode Type	Capacity (mAh/g)	Voltage Range (V vs. Li/Li^+)	Stability	Thermal Stability	Key Redox Reactions
LiFePO_4 (LFP)	170	3.4 V	Excellent	High	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^-$
LiMnPO_4 (LMP)	150	4.1 V	Good	Moderate	$\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + \text{e}^-$
$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP)	195	3.8–4.1 V	Moderate	Lower	$\text{V}^{3+} \rightleftharpoons \text{V}^{4+} + \text{e}^-$

1.1.3.3 Sulfur cathodes

Sulfur cathodes in all-solid-state lithium-sulfur batteries operate between 1.5 V and 2.5 V vs. Li/Li^+ which is below the voltage range of traditional lithium-ion battery cathodes yet offers a much greater theoretical capacity of 1675 mAh/g. The sulfur cathode in ASSLSBs undergoes electrochemical reactions that convert elemental sulfur (S_8) into lithium sulfide (Li_2S) when discharging and back into elemental sulfur during charging.

Redox reaction: $\text{S}_8 + 16\text{Li}^+ + 16\text{e}^- \rightleftharpoons 8\text{Li}_2\text{S}$

1.2 Outline of All-Solid-State Lithium-Sulfur Batteries

A growing worldwide need for high-energy-density and safe sustainable energy storage has led researchers to investigate alternatives beyond traditional lithium-ion batteries (LIBs). Lithium-sulfur (Li-S) batteries represent next-generation battery technologies that achieve an ultra-high theoretical energy density of 2500 Wh/kg which makes them ideal for use in electric vehicles (EVs), aerospace applications and grid-scale energy storage systems. Liquid-electrolyte-based Li-S batteries show great energy storage capabilities but multiple critical problems prevent them from being commercially successful including safety issues and poor long-term performance.^{11,12}

The primary drawback of traditional Li-S batteries hinders from their dependence on organic liquid electrolytes because these materials pose serious fire hazards and can trigger thermal runaway

conditions. High-profile incidents including Samsung Galaxy Note 7 explosions and Boeing 787 battery fires along with Tesla EV battery malfunctions demonstrate the dangers of liquid-electrolyte-based lithium-ion batteries and highlight the urgency for developing safer alternatives. Elevated temperature conditions in standard Li-S battery systems trigger exothermic side reactions that raise the risk of combustion and explosion hazards thereby generating severe safety threats. Liquid electrolytes mixed with lithium metal anodes create lithium dendrites which can breach separators and generate internal short circuits resulting in battery failure. Organic liquid electrolytes decompose quickly which leads to capacity loss and reduced cycle life. The commercial use of Li-S batteries for high-energy-demand applications remains limited by these restrictions.

Traditional LIBs face a significant challenge because they have reached their energy density threshold (~ 300 Wh/kg) which prevents them from fulfilling the power needs of advanced EVs, aerospace missions, and high-performance electronics. Sulfur's abundance and sustainability make it cost-effective which positions lithium-sulfur batteries as a viable option against cobalt-based lithium-ion batteries. The cost of sulfur as raw material stands at \$0.10/kg which is substantially cheaper than cobalt-based LIBs costing around \$30/kg which making Li-S batteries an economically scalable and commercially viable energy storage option.

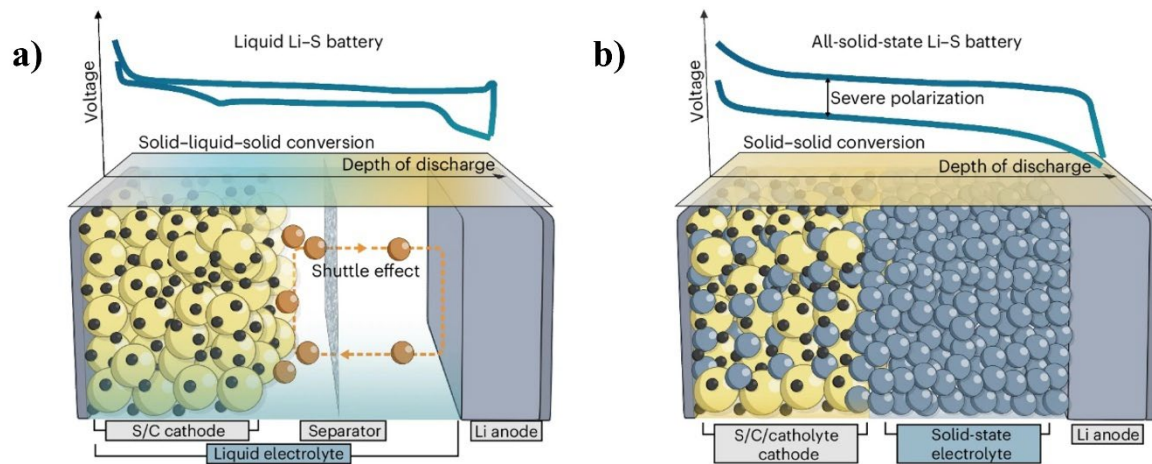


Figure 1.2 Illustration of (a) liquid Li-S battery and (b) Solid-state Li-S battery, reproduced from reference ¹³

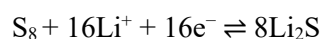
All-solid-state lithium-sulfur batteries (ASSLSBs) stand as revolutionary energy storage solutions to address the problems of liquid-electrolyte-based Li-S batteries. ASSLSBs enhance safety and durability through the use of solid-state electrolytes (SSEs) to replace flammable liquid electrolytes which eliminates risks like thermal runaway, leakage, and short circuits from dendrites.¹³ ASSLSBs deliver up to 500 Wh/kg of practical energy density which positions them as perfect solutions for high-performance applications in need of durable and efficient energy storage. Extreme operating environments like satellites and aerospace applications benefit from their superior electrochemical

stability and mechanical robustness due to their resistance to mechanical stress and temperature fluctuations.

Leading automotive and battery manufacturers such as Toyota, Volkswagen, QuantumScape and Samsung SDI continue to invest heavily in solid-state battery research and development as the international drive for advanced battery technologies moves forward.² Current research initiatives strive to push electric vehicle ranges beyond 600 miles per charge and enhance battery durability and effectiveness while speeding up the development of new energy storage technologies. The progress in solid electrolyte materials and sulfur cathode design paired with lithium metal anode stabilization makes all-solid-state lithium-sulfur batteries critical for the future of energy storage because they solve major safety, energy density and sustainability problems and support high-performance electric mobility with renewable energy systems.

1.2.1 Fundamentals and Working Principles of ASSLSBs

An ASSLSB contains three main elements: a solid electrolyte for ion transport and as a separator, a lithium metal anode for high-capacity storage and a sulfur-based cathode for redox reactions. The solid-state electrolyte functions as both an ionic conductor and a mechanical barrier which blocks lithium dendrite penetration while increasing battery system stability. The cathode for ASSLSBs is made predominantly from sulfur-based substances that participate in redox reactions throughout the charging and discharging processes. As sulfur functions as an electronic ($5 \times 10^{-30} \text{ S.cm}^{-1}$) and ionic insulator ($\sim 10^{-9} \text{ S.cm}^{-1}$) it requires the integration of conductive materials like carbon or transition metal sulfides to improve electron movement. The anode made of lithium metal achieves high theoretical capacity values yet demonstrates essential compatibility requirements with solid electrolytes to avoid interface degradation. While the functioning of ASSLSBs shares similarities with typical lithium-sulfur batteries the solid-state electrolyte introduces essential differences. As the typical sulfur cathode cell is in the charged state, it is initiated with the discharge process followed by charging and the electrochemical reaction in ASSLSBs operates based on a standard redox procedure as discussed before:



The discharge process initiates with lithium metal oxidation at the anode which releases lithium ions that migrate through the solid-state electrolyte until they reach the sulfur cathode. Electrons move through the external circuit to enable the reduction of sulfur at the cathode to create lithium polysulfides which transform into Li_2S . Solid electrolytes capture sulfur species inside the cathode and prevent capacity loss in contrast to liquid-based Li-S batteries which allow soluble polysulfide intermediates to move freely.

The charging process involves reversing the chemical reaction in which lithium ions migrate from the cathode to the anode where they undergo reduction and deposit as pure lithium metal. Through

oxidation of sulfur in the cathode elemental sulfur is regenerated which enables the battery to recharge. The voltage profile of ASSLSBs displays two distinct plateaus where the first plateau represents the formation of long-chain lithium polysulfides and the second plateau indicates their transformation into Li_2S . The performance of the battery depends heavily on the migration kinetics of ions within the solid-state electrolyte. SSEs enable single-ion conduction to support efficient lithium-ion transfer while reducing energy losses unlike traditional electrolytes which conduct multiple ions.¹⁴

1.2.2 Challenges to overcome in ASSLSBs

Their commercialization faces multiple fundamental challenges that require extensive research to achieve improved performance and scalability. The greatest obstacles to practical deployment include interface stability along with lithium dendrite formation, volume expansion, electrochemical instabilities and processing challenges. The main barrier to ASSLSB performance is interface stability which describes how well the solid-state electrolyte works together with electrode materials to facilitate proper ionic movement. Solid electrolytes face challenges because they lack a continuous phase between electrodes which results in poor interfacial contact that creates high interfacial resistance and impedes lithium-ion transport. Differences between the SSE thermal expansion coefficients and electrode electrochemical potentials create mechanical stress and chemical side reactions that damage the interface throughout cycling. Research has examined interface modification and composite electrolytes as solutions to these issues but requires ongoing optimization to maintain stable contact between interfaces across many cycles. The formation of lithium dendrites presents a significant challenge because it puts ASSLSB safety and longevity at risk. The growth of lithium dendrites in conventional lithium-metal batteries results in needle-like structures that penetrate the separator and create internal short circuits which lead to battery failure or thermal runaway.^{8,15} SSEs theoretically act as physical barriers to prevent dendrite penetration but some sulfide and oxide electrolytes permit dendrite growth as a result of uneven lithium deposition. Solid electrolyte engineering research together with interface coating development and pressure-induced densification targets the suppression of dendrite formation while promoting uniform lithium-ion transport.

Volume expansion in sulfur cathodes constitutes another significant challenge in battery technology. Sulfur experiences a massive 80% volume growth due to the density differences ($\rho_{\text{sulfur}} = 2.07 \text{ g.cm}^{-3}$ vs. $\rho_{\text{Li}_2\text{S}} = 1.66 \text{ g.cm}^{-3}$) during lithiation which generates mechanical stress and removes electronic connectivity while causing cathode delamination. The rigid nature of solid electrolytes prevents the accommodation of volume changes unlike liquid-based Li-S batteries where the electrolyte can absorb some expansion. The structural degradation occurs from repeated expansion and contraction which leads to poor cycling stability. Studies on flexible SSEs and nano-confined sulfur hosts together with composite cathodes present possible solutions to these challenges yet scalable answers remain elusive.

The commercialization of ASSLSBs faces barriers due to existing electrochemical instabilities. The use of solid electrolytes stops the polysulfide shuttle effect found in typical Li-S batteries yet creates fresh chemical compatibility challenges between lithium metal anodes and sulfur cathodes. Contact with lithium metal causes some SSEs to decompose into high-resistance interphases which restrict ion conduction. SSEs can interact with sulfur cathodes which leads to the creation of byproducts that cause battery performance to degrade over time. Research teams are investigating stable solid electrolyte compositions as well as protective coatings and interlayer engineering solutions to overcome these industry challenges. The manufacturing of electrodes in liquid-based batteries is simple but ASSLSBs need exact solid-state processing methods to maintain equal material distribution and close interface contact. The fabrication of conventional slurry-based electrodes cannot work with solid-state systems which require new advanced manufacturing techniques including wet and dry coating methods, infiltration processing, and high-temperature sintering. The mechanical integrity of batteries during assembly presents a significant challenge which necessitates external pressure to achieve adequate contact between interfaced components.

1.2.3 Investigation of suitable sulfur host and cathode materials

The electrochemical activity of sulfur in all-solid-state lithium-sulfur batteries (ASSLSBs) depends on the triple-phase boundary (TPB) that forms where the solid electrolyte (SSE), electronic conductive network, and sulfur cathode meet. The insulating properties of sulfur necessitate the formation of an efficient TPB to achieve proper lithium-ion movement, electronic conductivity, and redox reactions. The construction of a well-connected TPB introduces significant challenges because it leads to a higher proportion of inactive components within the cathode composite that reduces battery energy density. Recent research aims to address these limitations by refining the design of carbon materials and improving material compounding techniques to increase the effective TPB area while reducing inactive component content. Porous carbon materials represent a promising strategy because they enhance sulfur electronic conductivity while also promoting better reaction kinetics at the TPB. Solid-state battery systems experience performance issues with highly porous carbon structures used in liquid-electrolyte Li-S batteries because solid-state electrolytes cannot enter deep micropores effectively. Research efforts have focused on designing carbon structures that are optimized for solid-state systems because they enable solid-state electrolytes to access confined sulfur particles to achieve efficient electrochemical reactions.

Sun et al. designed N-doped carbon fibers with surface-restricted microporous layers which provided an outstanding surface area of 1519 m²/g.¹⁶ The main benefit of this design is the exclusive presence of the porous layer on the exterior surface which allows sulfur particles inside the pores to maintain direct contact with the solid-state electrolyte. The dense inner fiber structure boosts electronic conductivity which helps achieve faster charge transfer and better reaction kinetics. The assembled ASSLSB showed

impressive initial discharge performance with 1166 mAh/g at 0.05C and maintained 710 mAh/g specific capacity after 220 cycles at 0.1C which enhanced sulfur utilization and extended battery life. Furthermore Wang et al. proposed an innovative design for a mixed ionic/electronic conductive composite material consisting of integrated lanthanum lithium titanium oxide (LLTO) and carbon nanofibers which served as the host material for sulfur.¹⁷ The hybrid structure enlarged the active interface area which resulted in enhanced charge transfer efficiency and accelerated electrochemical reaction kinetics. The researchers increased battery energy density by constructing well-defined TPBs which eliminated inactive components. The breakthrough with mixed-conducting scaffolds shows that high ionic and electronic conductivity together produce superior results in ASSLSBs

Recent developments in composite cathode structures show that high-performance ASSLSBs are possible with sulfur and conductive carbon materials alone. In one such study, Sakuda et al. created a mesoporous carbon-based sulfur composite that featured a carbon matrix with interconnected mesopores (~5 nm) to ensure effective sulfur confinement and electron transport through the melt-diffusion method.¹⁸ The distinctive interconnected structure established an optimal conductive route for sulfur which improved sulfur utilization while preventing active material loss during multiple cycles. The ASSLSB demonstrated exceptional performance by sustaining a specific capacity of nearly 1100 mAh/g after 400 cycles at a current density of 1.3 mA/cm² thus proving its excellent cycling stability and rate performance.

TMS-based cathodes can be classified into three categories based on their electrochemical reaction mechanisms: intercalation-type, conversion-type, and anionic redox-driven-type materials. The intercalation-type TMS materials such as TiS₂, VS₂, and Mo₆S₈ allow reversible lithium-ion processes without significant structural alterations to maintain superior cycling performance. From Nazar group, Xu et al. engineered a hybrid intercalation-conversion cathode by combining VS₂ as a sulfur host which served as both an electronic and ionic conductor to achieve superior sulfur utilization. A hybrid cathode demonstrated high areal performance with 7.8 mAh/cm² capacity at 15.5 mg/cm² active material loading which establishes its potential for high-performance ASSLSBs.¹⁹ According to Oh et al. TiS₂ nanosheets demonstrated efficient lithium-ion transport because of their two-dimensional layered structure which achieved a discharge capacity of 291 mAh/g while maintaining 98.7% capacity retention after 50 cycles at 0.2C.²⁰

The conversion reaction mechanism enables conversion-type TMSs such as MoS₂, FeS, NiS, Co₃S₄, and CuS to transform lithium into metal nanoparticles and lithium sulfide (Li₂S) through reactions with the metal sulfide. Conversion-type TMSs deliver higher theoretical capacities compared to their intercalation-type counterparts but face challenges from substantial volume expansion and diminished initial Coulombic efficiency because of permanent side reactions. NiS-based cathodes achieved a specific capacity of 338 mAh/g at a discharge rate of 250 mA/g while maintaining stable cycling

performance for 100 cycles. The pairing of Co_9S_8 with $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte demonstrates robust cycling stability with 421 mAh/g capacity after 1000 cycles. CuS-S composite cathodes maintain high energy density with an exceptional capacity of 1580 mAh/g making them desirable for high-energy-density battery applications offer upto 15% compared to convention sulfur-carbon cathode electrode.^{21–}

23

ASSLSBs benefit from additional charge storage mechanisms and increased capacity due to the combined metal and anion redox reactions in anionic redox-driven TMSs. $\text{MoS}_3@\text{rGO}$ operates through anionic redox chemistry to maintain a stable capacity of 414.4 mAh/g for 500 cycles at 1 A/g while displaying excellent cycling stability and enhanced redox kinetics because of its reduced graphene oxide (rGO) support. The $\text{FeS}_2\text{-S}$ composite cathodes achieved high capacity values at 1200 mAh/g which suggests their suitability as components for future high-energy-density solid-state batteries.^{24,25}

1.3 Scope of this thesis

This thesis will explore the benefits of ideal interfacial studies and intercalated electrochemical conversion which enhance the battery performance. **Chapter 1** describes the detailed introduction on the global rise of future energy conversion storage devices and the consistent research approach towards ASSBs in the past. **Chapter 2** describes the characterization and analytical techniques used in this thesis. Followed by **Chapter 3**, which examines the interfacial stability between the $\text{Li}||\text{LLZTO}$ and $\text{LMOC}||\text{LLZTO}$ to accelerate the ionic migration. Finally, **Chapter 4** examines the layered 2H-TaS_2 that serves as an MEIC pathway utilized as cathode active material for ASSLSB.

Chapter 2 Characterization and Analytical Techniques

2.1 Material Characterization

2.1.1 X-ray Diffraction

The analytical method known as X-ray diffraction (XRD) emerged in the early 20th century after Wilhelm Rontgen discovered X-rays in 1895 and Max von Laue discovered X-ray diffraction in 1912. William Lawrence Bragg together with his father William Henry Bragg refined the technique by creating Bragg's Law which offered a theoretical framework for the interpretation of diffraction patterns. XRD has developed into an essential instrument for crystallography because scientists use it to examine the atomic and molecular structures of crystals.

X-ray diffractometers primarily consist of three essential components: an X-ray tube, a sample holder, and an X-ray detector. The production of X-rays inside a cathode ray tube requires heating a filament to create electrons. A high voltage makes electrons move quickly toward a target material leading to the bombardment of the target by these electrons. The absorption of sufficient energy by incoming electrons leads to the ejection of inner shell electrons from target atoms which produces characteristic X-ray spectra. The characteristic X-ray spectra usually present $K\alpha$ and $K\beta$ lines while having $K\alpha$ divided into $K\alpha_1$ and $K\alpha_2$ sub-lines. $K\alpha_1$ displays a marginally shorter wavelength while maintaining twice the intensity level of $K\alpha_2$. The target material determines the precise wavelengths of these lines which include elements like copper (Cu), iron (Fe), molybdenum (Mo), and chromium (Cr). The production of monochromatic X-rays required for diffraction studies involves the use of filters such as foil or crystal monochromators. The minimal wavelength difference between $K\alpha_1$ and $K\alpha_2$ lines results in the common use of their weighted average. Single-crystal diffraction primarily uses copper as the target material because $\text{Cu}K\alpha$ radiation emits at a wavelength of $1.5418 \text{ \AA}$.

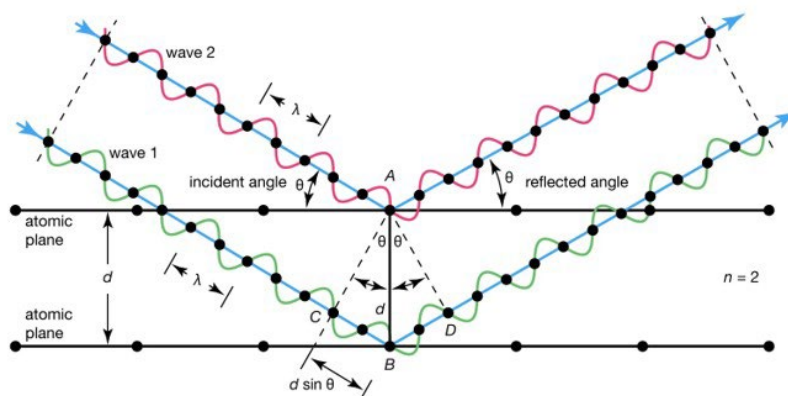


Figure 2.1 Schematic illustration of Bragg's law, reproduced from reference ²⁶

The operational system directs collimated X-rays toward the sample. During rotation both of the sample and the detector system the measurement of reflected X-ray intensity takes place. An intensity peak forms through constructive interference when both the incoming X-rays and the sample's structure adhere to Bragg's Law ($2d\sin\theta = n\lambda$).²⁶ The detector system processes the captured X-ray signal into count rate data which gets presented through a printer or computer monitor. The diffractometer configuration allows the sample to spin through the collimated X-ray beam at angle θ while positioning the X-ray detector to pivot at angle 2θ through its movable arm. A goniometer keeps precise angles and enables sample rotation. The 2θ range preset for X-ray scans typically covers an interval from 5° to approximately 70° during powder diffraction pattern data collection. The PANalytical Empyrean diffractometer used in this thesis included a PIXcel two-dimensional detector working under voltage range at 45 kV and current at 40mA with Cu-K α radiation ($\lambda = 1.5405\text{\AA}$). We used a zero-background silicon holder and a Kapton film sealed with vacuum grease to analyze air-sensitive samples.

2.1.2 Scanning Electron Microscopy

SEM provides outstanding resolution capabilities that allow scientists to examine structures and details at the nanometer level. The ability of SEM to examine structures at the nanometer scale creates significant impacts across various scientific fields including materials science, nanotechnology, biology, and geology. SEM provides multiple analytical tools including energy-dispersive X-ray spectroscopy (EDS) for elemental analysis and electron backscatter diffraction (EBSD) for crystallographic examination of materials. The operation of the Scanning Electron Microscope (SEM) depends on directing a fine electron beam at the surface of the specimen. The specimen undergoes scanning by an electron beam which moves in a raster pattern to interact with surface atoms. The specimen's surface interactions generate multiple phenomena such as elastic scattering, inelastic scattering and secondary electron emission. Secondary electron emission (SE) stands out as particularly vital for imaging because low-energy electrons released from the specimen's surface deliver essential data about its topographical and morphological characteristics. The SEM system uses detectors to capture and intensify signals which create high-resolution images showcasing the specimen's surface structure details.

The combination of accurate electron beam manipulation together with advanced signal processing enables SEM to deliver images that showcase outstanding clarity and detail. The images help researchers understand the specimen's surface morphology, texture and composition at the nanoscale. In addition to imaging, SEM offers elemental analysis through X-ray spectroscopy and crystallographic assessment by utilizing electron diffraction.

Scanning Electron Microscopy (SEM) imaging resolution depends on the scanning probe's diameter. The resolution capability for detecting fine surface features on specimens depends directly on the probe

size. To obtain high resolution in scanning electron microscopy, the probe diameter must be minimized. Multiple factors determine the Gaussian probe diameter, which is represented by d_p .

$$d_p = \left(\frac{4i_p}{\beta\pi^2\alpha_f^2} \right)^{\frac{1}{2}}$$

i_p – probe current

β – beam brightness

α_f^2 – convergence angle of the probe

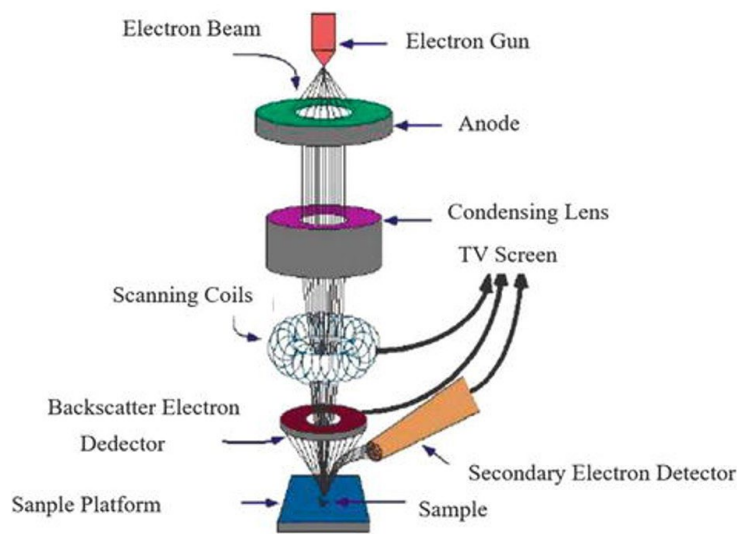


Figure 2.2 Working principle of SEM, reproduced from reference ²⁷

The electron beam's brightness depends on the electron gun type utilized.²⁷ Field emission guns provide high brightness which makes them a popular choice for advanced SEM systems. The brightness (β) of any electron gun type demonstrates a direct proportionality to its electron acceleration voltage (V_0) as shown by the relationship $\beta \propto eV_0$ with e representing the electron charge. Achieving the minimum probe diameter requires improving both electron beam brightness and convergence angle as indicated by the probe diameter equation. SEM uses electron beam acceleration voltages between 1 and 40 kV which are much lower than those used for Transmission Electron Microscopy (TEM). The SEM lenses demagnify the electron beam substantially by a factor of about 10,000 times with thermionic electron sources and between 10 to 100 times with field emission sources. SEM and EDX measurements in this thesis were performed on a Hitachi SU8700 FESEM instrument equipped with an Oxford EDX instrument.

2.1.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) operates as a scanning probe microscopy (SPM) system that achieves nanometer resolution and enables the imaging and manipulation of atomic-level matter. The development of AFM by Binnig, Quate, and Gerber during the mid-1980s marked a transformational moment in surface science and nanotechnology through its ability to produce detailed surface images along with the capacity to study nanoscale physical properties. AFM stands apart from conventional microscopy methods because it operates without the need for lenses or electron beams. The technique employs a mechanical probe that contacts the sample surface to gather information so it remains effective with various materials such as insulators, conductors, polymers, and biological specimens. This method achieves atomic-level resolution during surface imaging and characterization. The development of this technology represented a major breakthrough in microscopy which enabled researchers to study material properties at the nanoscale in a completely new way. AFM functions by moving a sharp tip attached to a cantilever across the sample surface. The interaction between the tip and sample surface causes cantilever deflections which are measured to obtain topographical data. AFM uses this method to produce detailed surface images and obtain accurate quantitative data about surface features including roughness and mechanical properties. Its capability to function in multiple environments including air, liquid, and vacuum increases its utility across diverse applications. AFM has secured its place as an essential instrument in scientific and industrial fields such as semiconductor manufacturing and biological research because it provides insights into the nanoscale world that were once impossible to achieve. The interaction between the AFM tip and sample surface during Atomic Force Microscopy is governed by several near-field forces that are critically important. Roughness measurements for this thesis were performed using the DI Nanoscope IV instrument.

2.1.4 Thermal Gravimetric Analysis

Under a controlled atmosphere, Thermogravimetric analysis (TGA) used to measure the material mass change with respect to temperature or time through thermal analysis. Researchers and industries use this technique to evaluate the thermal stability and composition of materials as well as their phase transitions and decomposition patterns across applications involving battery materials, polymers, pharmaceuticals, and inorganic compounds. A typical TGA experiment involves placing a sample in a thermobalance where it undergoes controlled heating at rates between 5–20°C/min while its weight loss is continuously recorded. These studies perform analysis in various environments like inert atmospheres (e.g., nitrogen or argon) or oxidizing conditions (e.g., air or oxygen) based on the research objectives. The TGA curve reveals important details about sample moisture content as well as thermal decomposition temperatures, oxidation resistance capabilities and the final residual mass including char or ash content. The thermal gravimetric analysis (TGA) executed in this study used a TA Instruments SDT Q600 analyzer with a continuous nitrogen atmosphere flow.

2.1.5 Brunauer-Emmett-Teller (BET) Analysis

The samples were subjected to a degassing process in a vacuum at 180°C before measurements to eliminate all adsorbed impurities. The degassing temperature for sulfur-containing samples was limited to 50°C to prevent sulfur from vaporizing. Nitrogen adsorption and desorption isotherms were recorded at 77 K with a liquid nitrogen bath to perform the analysis. The N₂ adsorption isotherm illustrates how the volume of nitrogen gas absorbed by the sample's surface varies with relative pressure in the sample chamber which reveals information about the sample's specific surface area and its pore structure. The sample placement inside the quartz tube underwent an initial evacuation step which removed all residual gases during the measurement process. The experimental procedure involved periodic releases of nitrogen gas which enabled it to adsorb onto the sample surface at designated pressures. The amount of nitrogen gas trapped by the material was calculated through comparison with the balance tube measurements. The Brunauer-Emmett-Teller (BET) method calculates sample surface area through a multi-point analysis approach. The total pore volume measurement was derived from the nitrogen adsorption data collected at a relative pressure of 0.99. The pore size distribution (PSD) emerged from the quenched solid-state functional theory (QSDFT) model which delivers an exhaustive evaluation of the material's porosity features. Micromeritics Gemini VII 2390a instrument was used in this thesis to examine the surface area and pore characteristics of the samples.

2.2 Electrochemical techniques and measurements

2.2.1 Solid Cell Configuration

In this thesis, there were two cell prototypes used to measure the electrochemical measurements. In order to determine the interfacial impedance a symmetrical sandwich cell setup as shown in **Figure 2.3 (a-b)** which consists of a lithium foil or 200 mg solid electrolyte powder on both sides of the LLZTO pellet pressed with the isostatic press or hydraulic press to make an intimate contact and applied a stack pressure in the aluminium frame. To examine the full-cell electrochemical performance, solid-state cells were assembled according to the configuration shown in **Figure 2.3 (c)**. In order to fabricate the cell, first 70 mg of solid electrolyte was pressed at 2 tons for 2 mins inside a PEEK cylinder between two titanium grade 5 piston rods. It was followed by the cathode composite and pressed at 3 tons for 3 mins. Then on the other side the Li/In alloy foil was pressed at 1 ton for 1 min. In order to avoid a short circuit, the cell was placed in between two side insulated cell holders and applied a torque of around 10.7 N.m (~54 MPa) during cycling. The illustration of all-solid-state battery cells is shown in **Figure 2.3 (d-e)**

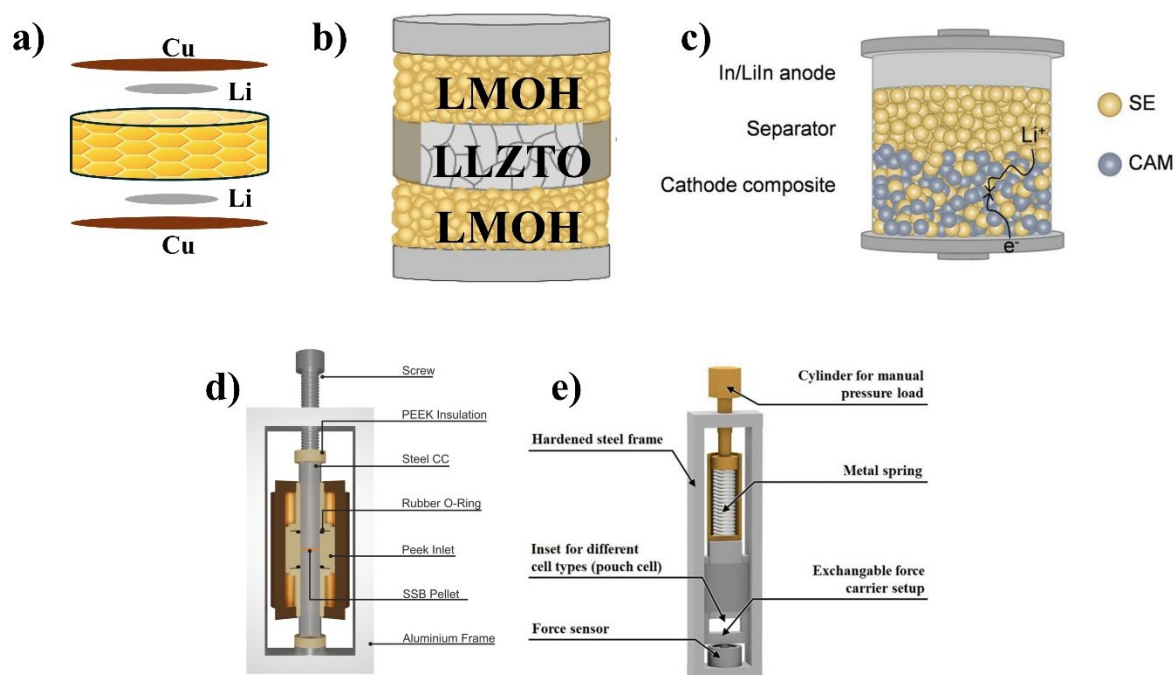


Figure 2.3 Illustration of the cell setups (a-c) and the cell prototype (d-e) reproduced from the references ^{28,29}

2.2.2 Galvanostatic cycling

Galvanostatic cycling operates as an electrochemical technique that evaluates rechargeable battery behaviour by maintaining a steady current to monitor voltage changes throughout the charge-discharge process. This technique plays an essential role in battery research and development by delivering important information about capacity, efficiency, and stability throughout numerous cycles. Galvanostatic cycling functions through the management of lithium-ion movement between a battery's anode and cathode. The charging process involves an external power source that delivers a constant current that drives lithium ions (Li^+) through the electrolyte from the cathode to the anode. At the same time electrons move through the external circuit to maintain electrical balance. Battery voltage continues to rise until it hits the cut-off voltage which stops the charging to protect against overcharging. The discharge process involves reversing the current direction which causes lithium ions to move from the anode back to the cathode while electrons pass through the external circuit to power the connected load. When the voltage reaches the lower cut-off voltage the discharge cycle concludes. Efficiency evaluation and assessment of degradation mechanisms and long-term stability of batteries are based on the measurements of charge and discharge capacities from each cycle. Different current densities were applied during a rate capability test to verify the reversing ability. A VMP3 potentiostat station from Bio-Logic instrument facilitated the galvanostatic cycling process in this work.

2.2.3 Cyclic Voltammetry

Cyclic voltammetry measures the current response resulting from the application of a linear potential variation to the working electrode. The method involves switching potential between forward and reverse sweeps repeatedly which generates the typical cyclic voltammogram (current versus voltage plot). The initial scan of cyclic voltammetry sees the applied potential rise from its starting voltage to a predetermined maximum to initiate oxidation reactions at the working electrode. The scan direction switches from forward to reverse when the set maximum voltage level is attained which brings the potential back to its initial value and prompts reduction reactions. The cycle repeats multiple times to monitor both the stability of electrodes and reaction kinetics. The peak oxidation and reduction potentials $E_{p,ox}$ and $E_{p,red}$ represent the specific voltage points where oxidation and reduction reactions take place whereas the peak current values $I_{p,ox}$ and $I_{p,red}$ reveal the reaction kinetics and charge transfer rates. A small peak separation (ΔE_p) around 59 mV proves that a one-electron process operates in an electrochemically reversible system. When ΔE_p values become large they show slower rates of electron transfer. The Randles-Sevcik equation provides the relationship between peak current and scan rate which helps to identify if a reaction proceeds by diffusion control or surface adsorption limits.

2.2.4 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) plays a major role for examining electrical properties along with reaction kinetics and charge transfer processes in battery systems alongside resistance contributions. Frequency-dependent analysis allows the separation of resistances from electrodes and electrolytes as well as the study of interfacial kinetics and diffusion processes. In EIS measurements, a small AC voltage perturbation between 5-10 mV is applied to electrochemical systems to determine current response patterns across various frequencies. The system impedance (Z) represents the ratio between the voltage applied (V) and the current measured (I).

$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$

where ω (omega) is the angular frequency. The impedance response includes both real (resistive) and imaginary (capacitive/inductive) components which can be expressed as:

$$Z(\omega) = Z'(\omega) + jZ''(\omega)$$

Z' stands for the real resistance while Z'' denotes the imaginary impedance due to capacitive or inductive properties. The representation of EIS data usually involves Nyquist plots together with Bode plots.

- a) **Nyquist Plot:** The Nyquist plot displays imaginary component Z'' versus real component Z' with a semicircle at high frequencies for charge transfer resistance and a low-frequency straight line for diffusion resistance.

b) Bode Plot: The Bode plot illustrates the impedance magnitude and phase angle variations across frequencies which help reveal time constants and electrochemical activities.

The Nyquist plot's semi-circle shows the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface while its low-frequency tail indicates lithium-ion diffusion resistance known as Warburg impedance (Z_w). The ohmic resistance (R_b) from bulk electrolyte and current collectors shows up as the high-frequency intercept in the plots. The ionic conductivity was measured using the values of bulk resistance, thickness and area of the electrode in the formula of

$$\sigma_i = \frac{t}{R_b A}$$

In order to determine activation energy (E_a) by performing the temperature dependence impedance measurements with a temperature range -50°C to 80°C and interpret the data in the Arrhenius equation and plot the slope of $\ln(\sigma)$ vs. $1/T$.

$$\sigma_i = \sigma_o \exp^{\frac{-E_a}{k_B T}}$$

2.2.5 DC Polarization

The DC polarization technique is a fundamental method for examining the electronic properties of electrode materials. This procedure involves applying a steady voltage to an electrochemical system followed by monitoring the current response over time. DC polarization experiments use either blocking or non-blocking electrode configurations based on the study's goals. Electronic conductivity (σ_e) can be calculated through Ohm's law from the steady-state current response.

$$\sigma_e = \frac{I_{steady} t}{VA}$$

where I_{steady} is the steady current, V is the applied voltage, t is the thickness and A is the area of the electrode.

Chapter 3 Understanding the compatibility of lithium metal anode and lithium-metal-oxyhalide SEs versus surface-treated Ta-doped garnet solid electrolyte

3.1 Introduction

As discussed in Chapter 1, researchers focus on all-solid-state lithium-ion batteries (ASSLIBs) as potential next-generation energy storage systems because they offer increased safety features and better energy density and cycle life than traditional liquid-electrolyte lithium-ion batteries. The garnet-type $\text{Li}_{17}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) electrolyte with Ta doping known as LLZTO emerges as one of the top choices among solid electrolytes because of its excellent ionic conductivity ($\sim 10^{-3}$ S/cm at room temperature), broad electrochemical stability window and strong chemical stability in contact with lithium metal. The practical use of LLZTO requires overcoming major obstacles that occur at the interfaces between lithium metal and LLZTO, as well as between the cathode material and LLZTO.^{30–33}

The performance of solid-state batteries (SSBs) depends heavily on the interface between the lithium metal anode and the solid electrolyte. Studies reveal that microvoids appear at the interface between the lithium metal anode and solid electrolyte during battery cycling when current density exceeds a critical value. The removal of lithium from the interface through stripping happens at a rate that exceeds the diffusion and creep replenishment processes which leads to void formation. The lack of balance between lithium stripping and replenishment results in void formation, which reduces the contact surface between lithium and the solid electrolyte. The reduction of the contact area between components increases local current density which promotes lithium dendrite formation, eventually threatening battery cell failure. To address this issue, it is critical to establish and sustain maximum contact between lithium metal and LLZTO during both initial cell assembly and subsequent cycling. Insufficient contact results in a concentrated current flow which accelerates lithium dendrite formation and induces internal short circuits. Solid electrolytes create more contact challenges with lithium than liquid electrolytes which maintain close lithium contact naturally. The common method for enhancing lithium-LLZTO contact utilizes pressure to reshape lithium metal due to its inherent ductility and malleability. The weak metallic bonding in lithium because of its single valence electron causes it to be extremely deformable at room temperature.³⁴ The property enables lithium metal to form closer contact with LLZTO surfaces when pressure is applied. The techniques of Cold Isostatic Pressing and Warm Isostatic Pressing serve as common approaches to achieve this purpose. A liquid medium enables these techniques to apply equal pressure across the lithium-LLZTO interface for optimal contact.

Alongside anode-side improvements, it remains crucial to tackle the fundamental interfacial limitations between the cathode and the LLZTO electrolyte. The emergence of chemically stable two-phase

boundaries at this interface represents a major obstacle because it disrupts lithium-ion transport efficiency and decomposes when employed to sintering both the garnet and the cathode.³⁵ To overcome these drawbacks a multilayer separator approach was developed by utilizing two different solid electrolytes to attain both electrochemical and thermodynamic stability. A configuration has been designed where one solid electrolyte (SE1) is chemically compatible with the cathode and another solid electrolyte (SE2) is selected because it interacts well with the lithium metal anode.^{29,36} The asymmetric design approach maximally utilizes both electrolytes' capabilities to reduce interfacial issues and maintain reliable ionic movement across solid-solid interfaces.^{37,38} Achieving efficient lithium-ion conduction requires selecting electrolyte combinations that form chemically stable interfaces. The use of superionic conductors that have ionic conductivities similar to conventional liquid electrolytes ($\geq 10 \text{ mS} \cdot \text{cm}^{-1}$) combined together with oxide-based solid electrolytes achieves robust lithium ion conduction pathways. Lithium metal oxychlorides (LMOC)³⁹ have been discovered recently as one of the remarkable ionic conductors because of their various advantageous properties which include superior ionic conductivity alongside enhanced chemical stability and excellent mechanical compliance which makes them ideal candidates for use with high-voltage cathodes in hybrid solid-state lithium-ion battery design. The natural flexibility and ductile characteristics of LMOC by enabling better electrode surface contact which reduces interfacial degradation within a multilayer separator structure providing a feasible solution to address cathode||LLZTO interface problems which results in improved performance and extended life of garnet solid-state battery systems.^{40,41}

Here we reported a nominal surface-treated LLZTO interfacial engineering strategy approach to suppress the interfacial ionic restriction both in the lithium metal anode and the lithium metal oxychlorides which were in direct contact with the surface modified LLZTO resulted in very low R_{int} ($< 10 \text{ } \Omega \cdot \text{cm}^2$ and $80 \pm 2 \text{ } \Omega \cdot \text{cm}^2$) through symmetrical cell-setup and further developed the hybrid multilayer solid-state lithium metal battery.

3.2 Experimental Section

Synthesis of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$

To prepare LLZTO, the required stoichiometric amounts of La_2O_3 (99.99%, Sigma-Aldrich), Ta_2O_5 (99.99%, Sigma-Aldrich), ZrO_2 (99.99%, Sigma-Aldrich) and excess⁴² of Li_2CO_3 (99.99%, Sigma-Aldrich) to avoid lithium loss were precisely weighed and placed into an 80 ml zirconia jar. To ensure homogeneous mixing and effective particle size reduction, a powder-to-ball-to-reagent alcohol mass ratio of 1:10:1 was maintained in each jar and initiated the milling process at 300 rpm for 24 hrs using a Fritsch Pulverisette 7 Premium ball mill. The slurry produced from milling was dried in a 90°C oven to remove any remaining alcohol. The dried powder was placed into an aluminium crucible before annealing at 900°C for 12 hours in air to begin phase formation. After annealing, the powder was

subjected to a second round of ball milling and dried as described above. The dried powder was pressed into a 12.7 mm diameter pellet and covered with the mother powder bed on the alumina boat. Finally, it was sintered in air at 1150°C for 16 hrs with a heating and cooling rate of 300°C/hr.

Synthesis of Oxyhalides (LMOC, M = Nb, Ta)

The preparation of LMOCs were carried out using a mechanochemical route followed by thermal annealing.^{39,43} The stoichiometric amounts of TaCl₅ or NbCl₅ (99.9%, Strem Chemicals) and LiOH (99.9%, Sigma Aldrich) were transferred into an 80 ml zirconia milling jar inside an argon-filled glovebox and sealed to prevent leakage. The powder-to-ball mass ratio was maintained at 1.5:70 for each jar, and the milling process was performed using a Fritsch Pulverisette 7 Premium ball mill at a rotation speed of 500 rpm for 8 hours, with alternating cycles of 30 minutes of milling and 15 minutes of rest to minimize excessive heating during homogeneous mixing. Following the milling procedure, the powders underwent thermal annealing in an inert atmosphere.

Surface Treatment of LLZTO

i) Rapid Acid Treatment (RAT)

The Li₂CO₃ layer on the LLZTO pellet surface was removed by immersing the pellets in 100 ml of 1 M HCl for 6 minutes and 30 seconds. The soaked pellets were removed with tweezers, and their surfaces were gently wiped with a tissue to eliminate any remaining solution. After drying the cleaned pellets with minimal heat from a heat gun, they were rapidly moved to an argon-filled glovebox to prevent Li₂CO₃ reformation which occurs in less than one minute of air exposure.

ii) Heat Treatment (HT)

The LLZO pellets were initially polished using sandpaper with grit sizes from P320 to P4000 on a polishing machine and treated with THF (99.9%, Sigma Aldrich) to get a smooth and shiny exterior surface. After polishing, the pellets were carefully transferred into the argon-filled glovebox. The pellets were further polished inside the glovebox using P1000 grit sandpaper and the surface was cleaned with a blower. The pellets were then sealed in a quartz tube under a high vacuum and annealed in a muffle furnace at 400°C for 3 hours.²⁹

Fabrication of symmetric cells

Cell A (Au||LLZTO||Au and Li||LLZTO||Li)

To measure ionic conductivity, the as-sintered and well-polished pellets were coated with gold (Au) of 8 mm diameter on both sides, which acted as a blocking electrode. Then, the gold-coated pellets were securely enclosed in a pouch cell configuration. A nickel tab was placed in direct contact with the gold layer on both sides of the pellet (Ni|Au|LLZTO|Au|Ni), acting as the current collector. The pouch cell was carefully sealed to prevent exposure to the atmosphere. An additional cell configuration was

designed to investigate the interfacial stability of the Li||LLZTO interface. To assemble that, the lithium foil (99.9%, Goodfellow) of 6 mm diameter and 100 μm thickness was cut and scratched the surface with a ceramic knife in order to remove the oxidised layer and then stucked at the centre of the 10 mm copper foil. Then, it was placed on both sides of the surface-treated pellet to form Cu|Li|LLZTO|Li|Cu and sealed under vacuum in a rubber bag and isostatically pressed at 450 MPa for 45 minutes to get intimate contact between lithium and the pellet.²⁸ Following compression, the cell was enclosed in a pouch cell to maintain a controlled testing environment. For both the ionic conductivity and interfacial stability impedance measurements, the assembled pouch cells were positioned on a pressure-controlled frame integrated with a force sensor and fitted with insulating plates to prevent short-circuiting.

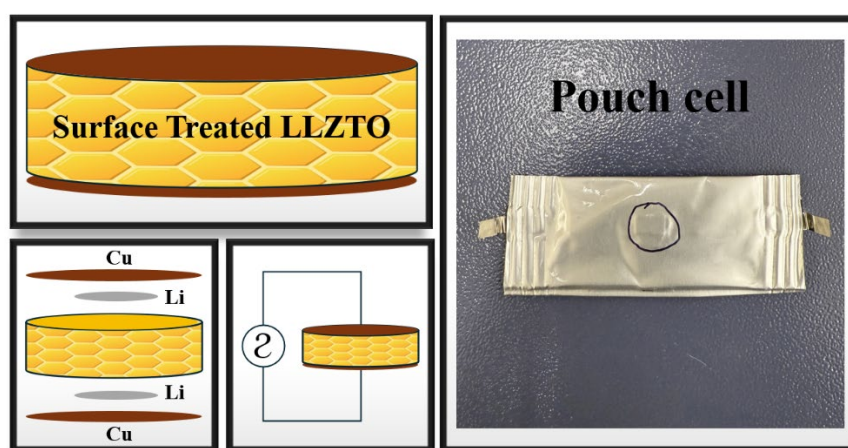


Figure 3.1 Illustration of the cell A fabrication

Cell B (LMOC||LLZTO||LMOC)

For this typical procedure, 200 mg of solid electrolyte powder was loaded on both sides of the surface-treated pellet in the PEEK mould, which was sandwiched in between the two piston rods (**Figure 2.3 d**) and pressed at 1.5 tons to densify the pellet. Then, the assembled cell was placed in the aluminium frame in order to apply a torque of 10 N.m (~ 54 MPa).

Fabrication of full cell:

To prepare the cathode composite, the active material (NMC 811), solid electrolyte (LMOC) and VGCF (Vapour Grown Carbon Fiber) were mixed in an agate mortar for 30 mins with the weight ratio of 60:35:5. To assemble full cell, the appropriate amount of solid electrolyte was hand pressed with piston rods in 10 mm diameter PEEK mould and the pre-pressed lithium pellet after surface treatment was placed on the top of solid electrolyte interlayer. Next, 200 mg of Cu powder was uniformly spread on the top of the lithium pellet to act as a current collector. On the other side, the cathode composite was

spread uniformly and applied a fabrication pressure of 5.7 N.m for 5 mins. Then, the cell was placed in the aluminium frame and the stack pressure of 2 N.m (~10 MPa) was applied.

Electrochemical Characterization

All Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) studies were carried out using the Biologic-SP200 potentiostat with a frequency range of 3 MHz to 100 mHz and 10 mV of voltage amplitude. Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) studies were carried out in the frequency range of 3 MHz to 1 Hz using different current densities. Arrhenius measurements were performed in the GWS benchtop mini humidity chamber at -50°C to 80°C. Further, the data was examined using the RelaxIS 3 software, and DRT plots were calculated using the Gaussian base function with a value of 0.001. Galvanostatic cycling was carried out in the VMP3 potentiostat with the voltage range of 2.8-4.3 V vs Li/Li⁺ at the elevated temperature of 60°C.

Physical Characterization

XRD data were collected using the zero background silicon holder on a PANalytical Empyrean instrument using Cu-K α radiation ($\lambda = 1.5405\text{\AA}$) with a PIXcel 2D detector operating under the voltage at 45 kV and current at 40 mA. SEM studies were conducted in a Hitachi SU8700 FESEM instrument to obtain the morphology and to visualize the density of the pellet. Raman spectroscopy was examined using a Senterra Raman spectrometer (Bruker), and to prevent the formation of a Li₂CO₃ passivation layer, the pellet was covered with a glass cover in the homemade sample holder with a rubber ring during the analysis. The relative density of the sintered pellets was determined using Archimedes' principle with a custom-built density measurement setup, employing a Sartorius ED124 analytical balance for precise mass measurements in both air and solvent (ethanol) to ensure accurate density calculations.

3.3 Results and Discussion

In order to determine the phase and structure purity, the as-synthesized LLZTO annealed powder and the sintered pellet were characterized with X-ray diffraction (XRD). Both samples revealed strong crystalline peaks without any impurity that correspond to the cubic phase and were in good agreement with the PDF: 01-090-2954. To calculate the relative density, the well-polished sintered pellet was weighed both in air and solvent (ethanol) based on the Archimedes principle which was shown in the calculation part below. The geometrical relative density was calculated as 93 $\pm$ 1% which was also confirmed by Scanning Electron Microscopy (SEM) imaging revealing the closed porosity in the micron scale. To effectively eliminate the passivation layer formed on the LLZTO surface^{41,44-46}, two distinct methods were employed: The LLZTO surface passivation layer removal was approached using Rapid Acid Treatment (RAT) and Heat Treatment (HT). The objective of both methods was to eliminate the insulating passivation layer from the surface yet Heat Treatment emerged as the superior

method. Microstructural defects emerged from the RAT process which led to increased porosity in the LLZTO pellet and it proved ineffective for total passivation layer removal. The HT method demonstrated a superior ability to remove and vaporize the passivation layer without damaging the pellet's compact microstructure.

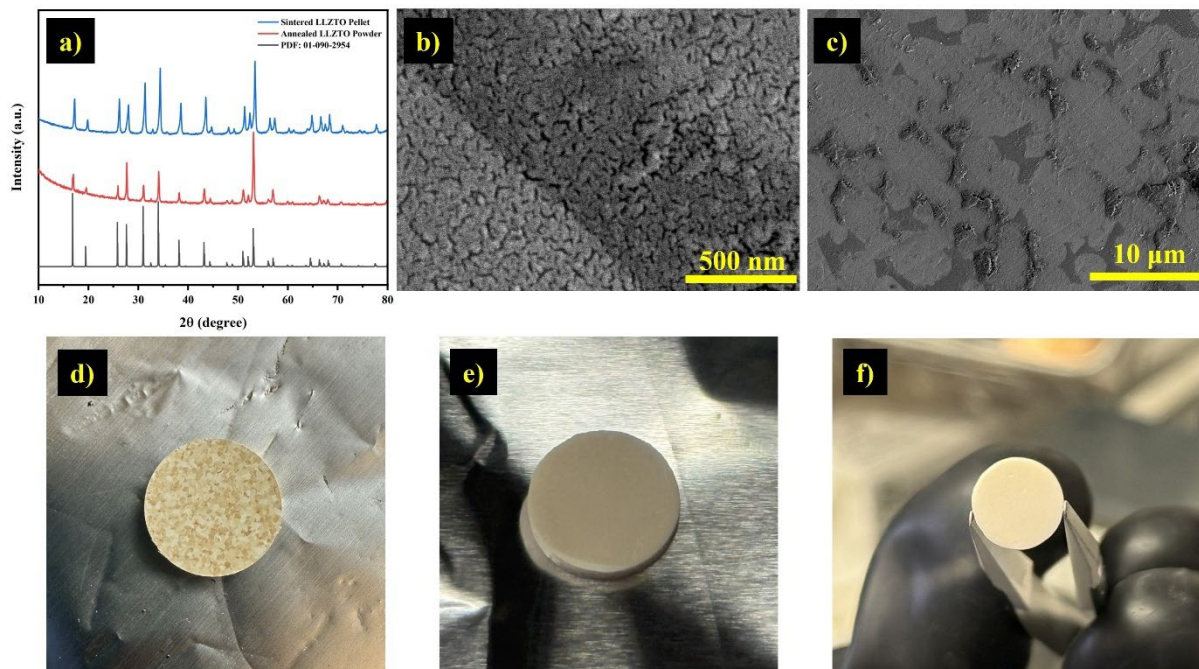


Figure 3.2 (a) XRD pattern of annealed and sintered LLZTO, (b-c) SEM images of well-polished LLZTO pellet, (d-f) Optical images of the pellets (d) before sintering, (e) after sintering and well-polished and (f) Heat-Treated

Raman spectroscopy was one of the well-known methods in garnet characterization in order to characterize the passivation layer formation.⁴⁷ To determine that, we took three different labelled samples with different ambient conditions which were described as follows: i) LLZTO which was kept outside in the ambient atmosphere for two months, ii) LLZTO which was surface treated scanned without glass cover and iii) LLZTO which was surface treated and covered with glass cover inside the glove box. According to previous research, the vibrational bands based on their frequency ranges can be categorized in Raman spectra. Typically Li-O bond vibrations in LiO_6 octahedral units were observed in the low frequency region which was below 300 cm^{-1} . While the mid-frequency region ($300\text{-}550 \text{ cm}^{-1}$) was contributing from LiO_4 tetrahedra and the high frequency above 550 cm^{-1} the stretching vibration band was attributed to Zr-O bonds in ZrO_6 octahedra (650 cm^{-1}) and Ta-O bonds in TaO_6 octahedra units (750 cm^{-1}). The prominent peak observed at 1090 cm^{-1} was due to the vibrational mode of the lithium carbonate (Li_2CO_3) layer formed on the surface of the LLZTO pellet when it was exposed to the ambient condition for period of time. Notably, we observed two peaks in the LLZTO exposed in the

ambient atmosphere for 2 months. The strong peak at 328 cm^{-1} was attributed to the vibrational mode of LiOH involving the movement of lithium cations relative to the hydroxide anions.⁴⁸ And as expected, the other peak at 1090 cm^{-1} corresponded to the Li_2CO_3 which we also observed with the surface-treated pellet where the Li_2CO_3 signal appeared less than a minute when the glass cover was removed from the sample holder. Exceptionally, the surface-treated pellet with a glass-covered sample holder prepared inside the glovebox showed no peaks from either LiOH or Li_2CO_3 . This confirmed that there was no passivation layer on the surface of the pellet to continue the symmetric cell measurements.

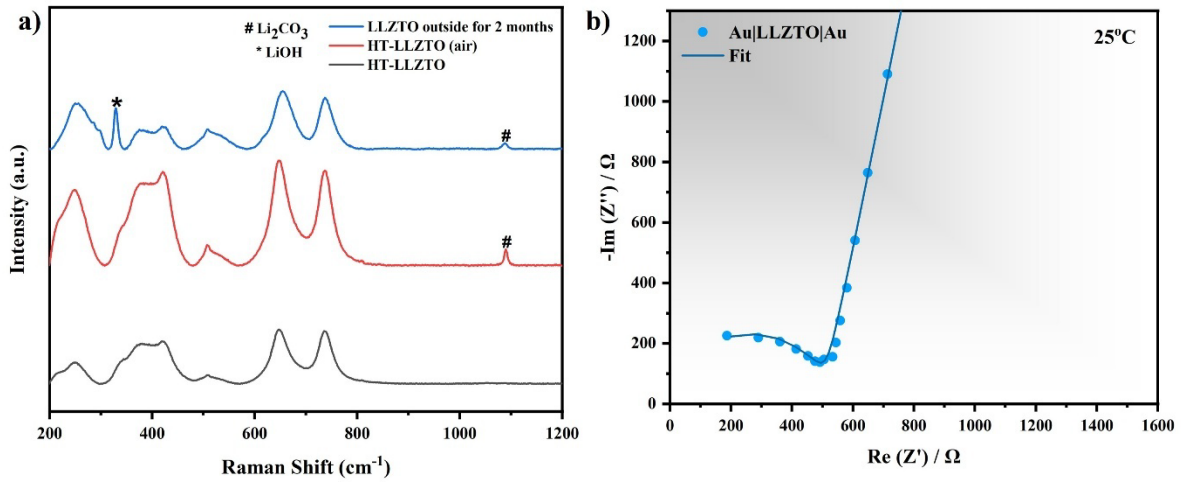


Figure 3.3 (a) Raman spectrum of Heat-Treated (HT) pellet with glass cover, without glass cover (air-exposed) and LLZTO stored outside for 2 months, (b) Nyquist plot of Au||LLZTO||Au at 25°C

To gain a better understanding of the constriction resistance theory different electrode symmetrical cell models were assembled to examine their impedance response.^{49,50} The ionic conductivity was determined with Cell A, where we used gold electrodes on both sides which act as blocking behaviour. At room temperature, distinguishing between the grain boundary and the bulk contributions using two CPE/resistor combination fittings was challenging. To account for this, a simplified circuit model using one CPE/resistor along with the CPE⁵¹ which corresponds to the blocking tail as shown in **Figure 3.3 b**. The impedance plot was fitted with RelaxIS software to determine the total resistance from which the total ionic conductivity was calculated to be 0.47 mS.cm^{-2} . In order to visualize the grain boundary and the bulk contribution of LLZTO it was evident at the low-temperature impedance measurements which can be identified with their respective frequency ranges.⁵² To know the basics of impedance fitting in the RelaxIS software which were explained below.

Kramers-Kronig (KK test) and Distribution of Relaxation Time (DRT) analysis

The Kramers-Kronig (KK) test functioned as the initial step to enhance data quality for effective impedance plot analysis. It is believed that the artefact in the low frequency affects the KK test. So the

test measures impedance data reliability by comparing real and imaginary components throughout the frequency range using a residual plot. According to Macdonald's 1984 study on electrochemical systems, the KK test remains essential for verifying impedance data validity by assessing system properties of causality, linearity, and stability. The KK test transforms real impedance data into imaginary data (or performs the reverse transformation) to compare the resulting data against the original impedance spectrum. Data reliability requires that relative residual errors between measured and transformed data stay under 5% (**Figure 3.4**) for accurate impedance model consistency. The KK test approach is commonly accepted as an effective method to confirm the suitability of equivalent circuit models used in impedance spectroscopy research according to Orazem & Tribollet (2008).⁵³

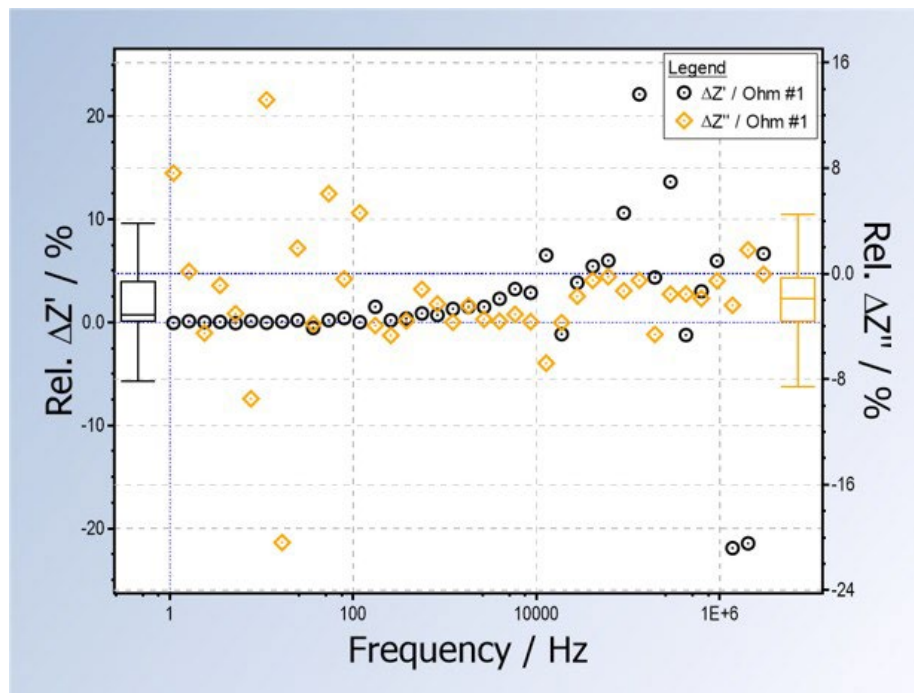


Figure 3.4 Illustration of KK test analyzis

The DRT technique uses mathematical deconvolution to process the impedance spectrum which converts frequency-dependent impedance data into relaxation time distributions.⁵⁴ This transformation determines the relaxation times that are associated with various electrochemical mechanisms. DRT analysis makes it possible to identify and distinguish overlapping signals in the Nyquist plot by showing peaks at time constants that are physically present in the spectrum that traditional circuit fitting methods find difficult to separate. The use of Gaussian discretization and polarization component subtraction provides an effective solution for reducing noise peaks caused by polarization effects at high time constants.⁵⁵ The Distribution of Relaxation Time (DRT) analysis becomes more accurate because this method improves the clarity of the signal. A low lambda (λ) value should be selected as the regularization parameter to ensure narrow and well-defined peaks appear in the DRT spectrum.

Decreasing the λ value reduces the degree of smoothing and enables easier identification and interpretation of distinct relaxation processes.

Li||LLZTO Interface

To examine the interfacial study and the constriction current resistance effect, the assembled pouch cell with the cell setup A configuration was subjected to Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) measurements with the constant stack pressure ~ 3 MPa monitored using the force sensor to ensure the mechanical contact. At room temperature, we observed low interfacial resistance close to $0 \pm 7 \Omega \cdot \text{cm}^2$ in the low apex frequency of around 25 Hz. In addition to the interfacial contribution the high (1.4 MHz) and mid (60 kHz) apex frequencies were attributed to the bulk and grain boundaries of the surface-treated LLZTO which was further corroborated with DRT analysis that can be identified by time-constant peaks within the frequency limit which was in good accordance with the fitted Nyquist plot using three resistors and three CPE elements as shown in **Figure 3.5 (a-d)**. The interfacial resistance value achieved here exhibits a significant reduction compared to typical LLZO systems, where ranging between $1000\text{--}30000 \Omega \cdot \text{cm}^2$ resistance values when untreated garnet pellets are exposed to the ambient conditions. The considerable reduction in interfacial resistance achieved in this study can be attributed to two critical factors: The reduction in interfacial resistance resulted from enhanced interface engineering, together with successful suppression of lithium carbonate (Li_2CO_3) formation. According to prior research ambient conditions encountered during sample preparation led to the formation of Li_2CO_3 on the surface as an insulating layer that blocks lithium-ion transport.^{44,56} This study achieved minimized carbonate formation through meticulous surface preparation methods which included keeping the LLZTO sample in a controlled environment with minimal air exposure to enhance ionic contact at the interface.

The low interfacial resistance achieved with a stack pressure of only 3 MPa is particularly notable, as earlier research studies had established that applying pressures >100 MPa was necessary to decrease interfacial resistance in garnet-based solid-state batteries. The restriction of ionic current flow due to limited contact points between the lithium metal anode and the LLZTO surface results in greater constriction resistance when operating at lower pressures. The contact geometry between the solid electrolyte and lithium metal determines constriction resistance because incomplete contact forces ionic current to move through isolated regions.^{49,57–60} The limited contact area between the lithium metal anode and LLZTO surface leads to increased local current densities which raise the effective interfacial resistance. However, in this study, the optimized interface geometry achieved through controlled surface preparation effectively minimized the constriction resistance effect, enabling stable ionic conduction despite the low applied pressure. This observation aligns with previous findings by Krauskopf et al. (2019),²⁸ where our strategic interfacial modifications successfully mitigated constriction resistance under reduced mechanical pressure.

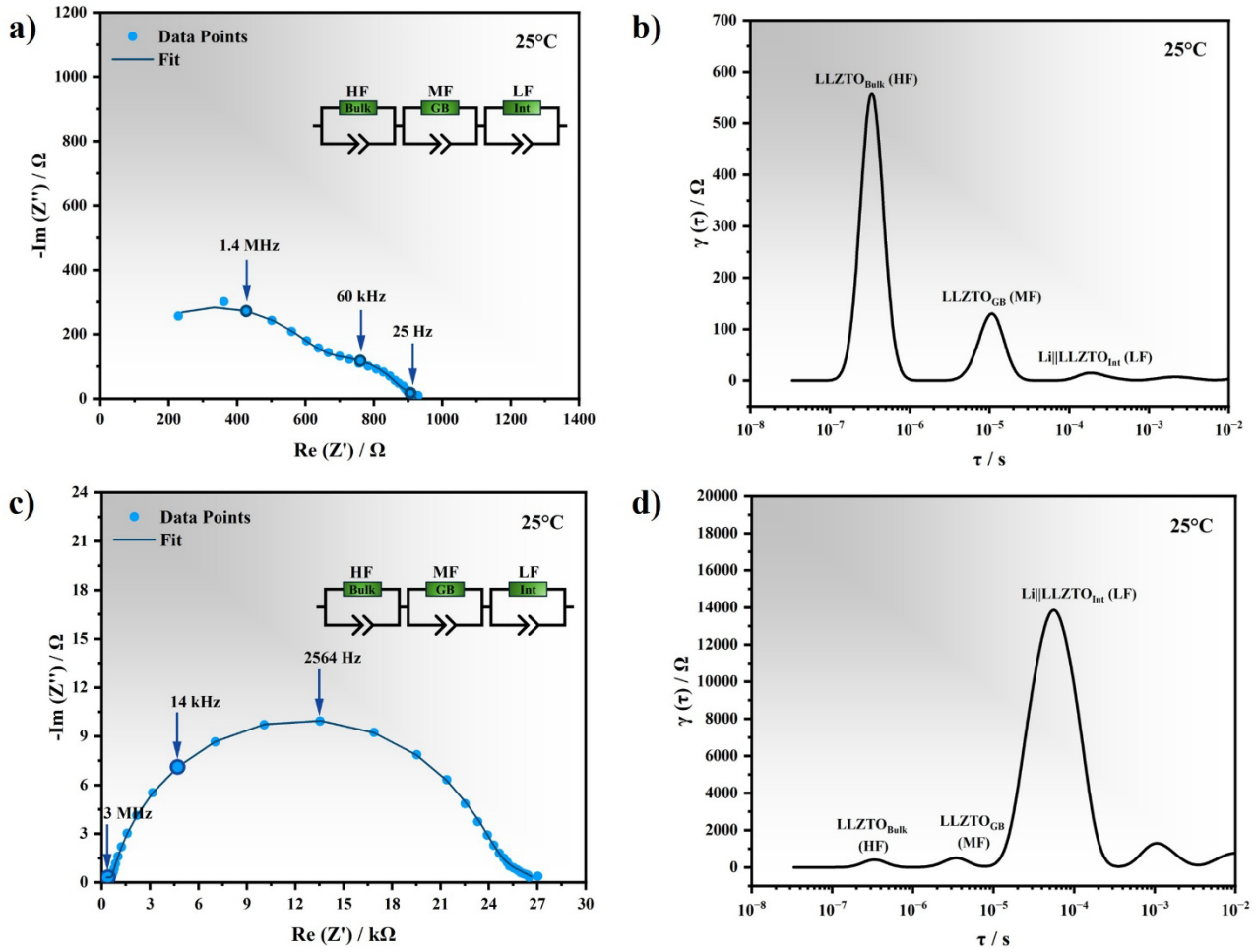


Figure 3.5 (a,c) Nyquist plot of Li||LLZTO with surface treatment and without surface treatment and (b,d) its corresponding DRT plot at 25°C

Temperature-dependent impedance analysis further supported the stability of the LLZTO electrolyte's conduction pathways.⁵² **Figure 3.6 (a-c)** shows the temperature-dependent Nyquist plot and its Arrhenius plot. From the Arrhenius plot, the activation energy was calculated as 0.43 eV for the bulk and 0.46 eV for grain boundaries. Conversely, grain boundary and interfacial resistances decreased significantly with increasing temperature, reflecting improved lithium-ion mobility in these regions. This behaviour is consistent with previous reports on garnet-type electrolytes, where interfacial and grain boundary resistances are known to decrease at elevated temperatures due to enhanced ionic transport.⁶¹ The temperature dependence of interfacial resistance further highlights the role of improved ionic diffusion in reducing the constriction resistance effect at higher temperatures. The observed reduction in interfacial polarization effects, achieved by employing Gaussian discretization and polarization subtraction during data analysis, further ensured accurate data interpretation.

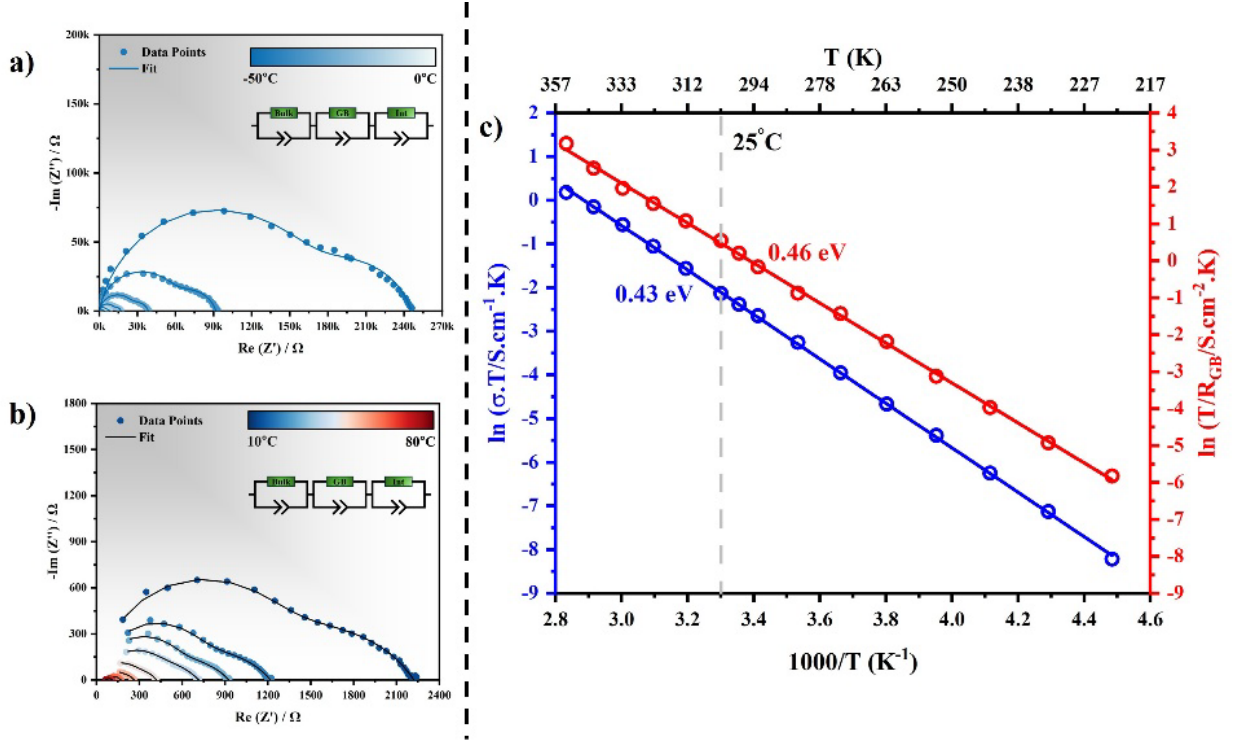


Figure 3.6 (a-b) Temperature-dependent Nyquist plots and (c) the Arrhenius plot calculating the activation energy for both bulk and grain boundary

In order to study the lithium kinetics under the low stack pressure, in situ cycling and impedance measurements were conducted using the Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) technique. Through this technique, we can able to understand the impedance evolution over time during cycling.²⁸ To employ this technique in the current system by applying a constant density of $100 \mu\text{A.cm}^{-2}$ we conducted a long-term stripping experiment at 25°C which resulted in not much increase in interfacial resistance up to 4 hrs after that there was a gradual increase in the resistance where we observed complete contact loss of lithium metal anode around 10 h (1 mA.h.cm^{-2}). This behaviour is characteristic of lithium metal void formation and contact loss at the $\text{Li}||\text{LLZTO}$ interface, which aligns with the vacancy diffusion model proposed.^{59,62–64} Under a sustained galvanostatic current, lithium stripping leads to the injection of vacancies into the lithium metal electrode. As these vacancies accumulate near the interface, voids begin to form, reducing effective contact and increasing the interfacial resistance. The sharp increase in potential following this resistance rise indicates a breakdown in the interfacial stability, where the localized void formation ultimately limits lithium-ion transport across the interface. The stable bulk and grain boundary resistances indicate that the primary failure mechanism is not linked to the intrinsic ionic conductivity of the Ta-doped LLZTO electrolyte but rather to the dynamic instability at the lithium interface. This nature of the interfacial resistance behaviour further suggests that the constriction resistance effect played a role in delaying catastrophic

failure.⁴⁹ With limited applied pressure, the physical contact between the lithium metal anode and the LLZTO surface was likely confined to discrete points. As lithium stripping progressed, these discrete contact points expanded gradually, resulting in localized resistance growth before reaching a critical threshold that triggered the voltage spike. This behaviour contrasts with systems utilizing higher mechanical pressures, where uniform contact minimizes constriction resistance and enhances long-term interfacial stability in the previously reported studies.^{28,31,32,36,42,44,57,65–67}

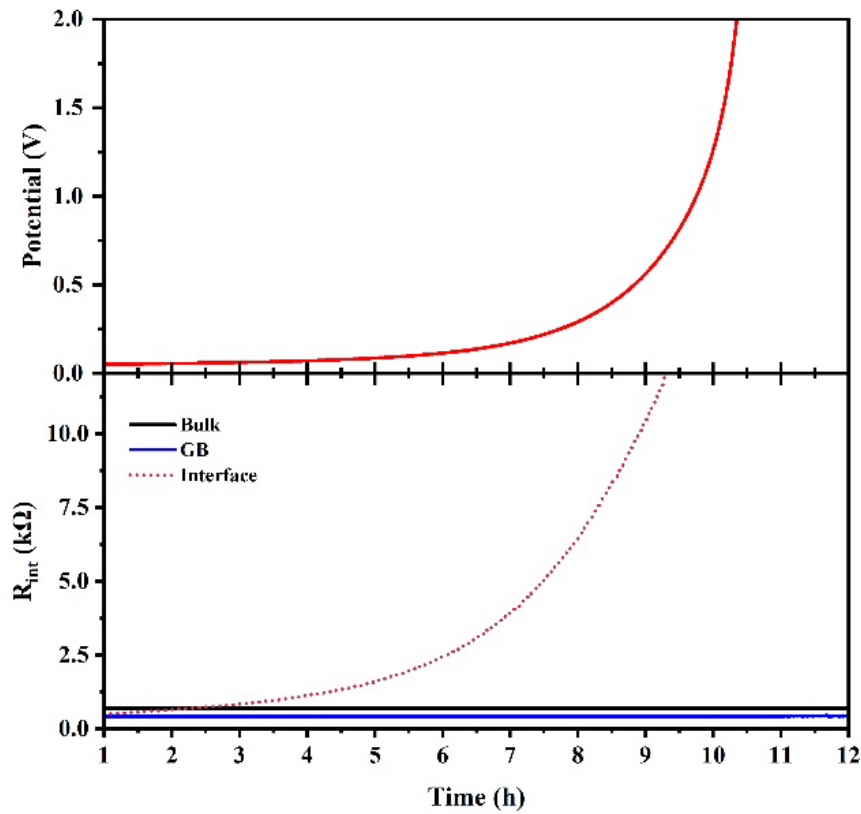


Figure 3.7 The voltage profile and its impedance evolution profile show a contact loss after 10 h of restless stripping experiment at 1 mA.h.cm^{-2}

To further understand these diffusion models, we conducted the plating and stripping experiments at 60°C with a current density of $265 \mu\text{A.cm}^{-2}$ with an interval of 1 min. The impedance data remained stable over prolonged cycling, with minimal increase in resistance observed after 9000 cycles and there was no significant rise or fall in current density which therefore confirmed no hard short circuit. This behaviour stands in contrast to several prior studies in which rapid growth of interfacial resistance was reported under similar cycling conditions. The stable resistance profile observed in this study indicates that despite the low pressure applied, effective suppression of void formation and contact loss was achieved. The absence of significant resistance growth is consistent with improved contact uniformity at the interface, which effectively minimized localized current hotspots that can otherwise induce pore

formation. However, a gradual increase in interfacial resistance during prolonged stripping cycles was observed, consistent with the vacancy diffusion model. According to this model, lithium vacancies generated during stripping accumulate near the interface, resulting in pore formation that disrupts contact integrity. The observed partial recovery in interfacial resistance during subsequent plating cycles further supports this interpretation, as lithium deposition effectively refilled the voids and restored intimate contact.^{34,46,49,50,59,62,68}

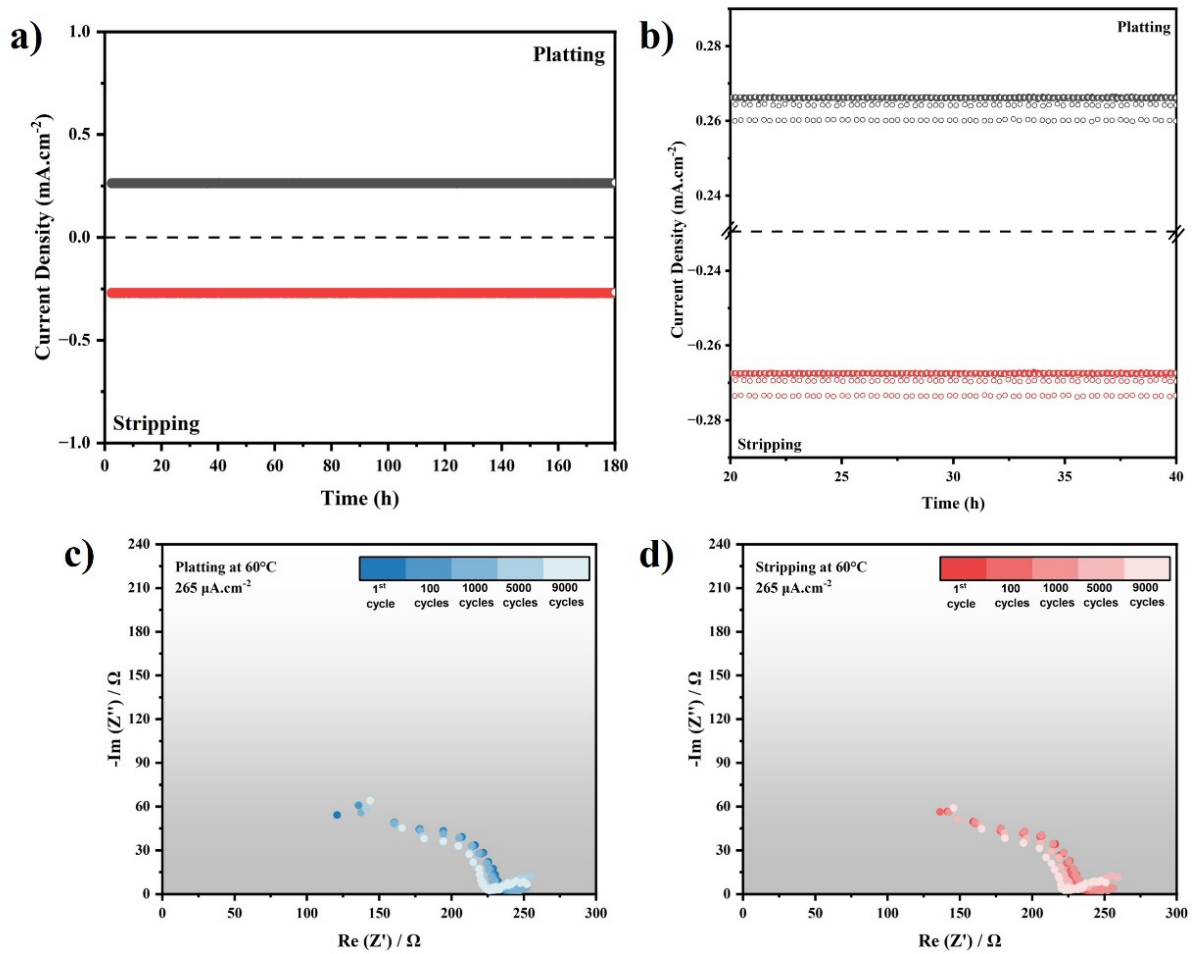


Figure 3.8 (a-d) Current density response with respect to time and its impedance data obtained from long-time plating and stripping experiment at 265 $\mu\text{A.cm}^{-2}$ at 60°C

LMOC||LLZTO Heteroionic Interface

To further move on to the heteroionic interface using the surface-treated LLZTO pellet (SE1) and lithium metal oxychloride (SE2) solid electrolytes, a multilayer symmetric cell configuration of LMOC|LLZTO|LMOC was employed for the impedance measurements in order to determine the interfacial compatibility of Oxyhalide||Oxide based solid electrolytes. These oxyhalide-based solid

electrolytes were very soft and deformable as it can be the right choice to use as an interlayer between the oxide-based solid electrolyte and the catholyte in order to compensate for the interfacial limitation between the LLZTO and the cathode.

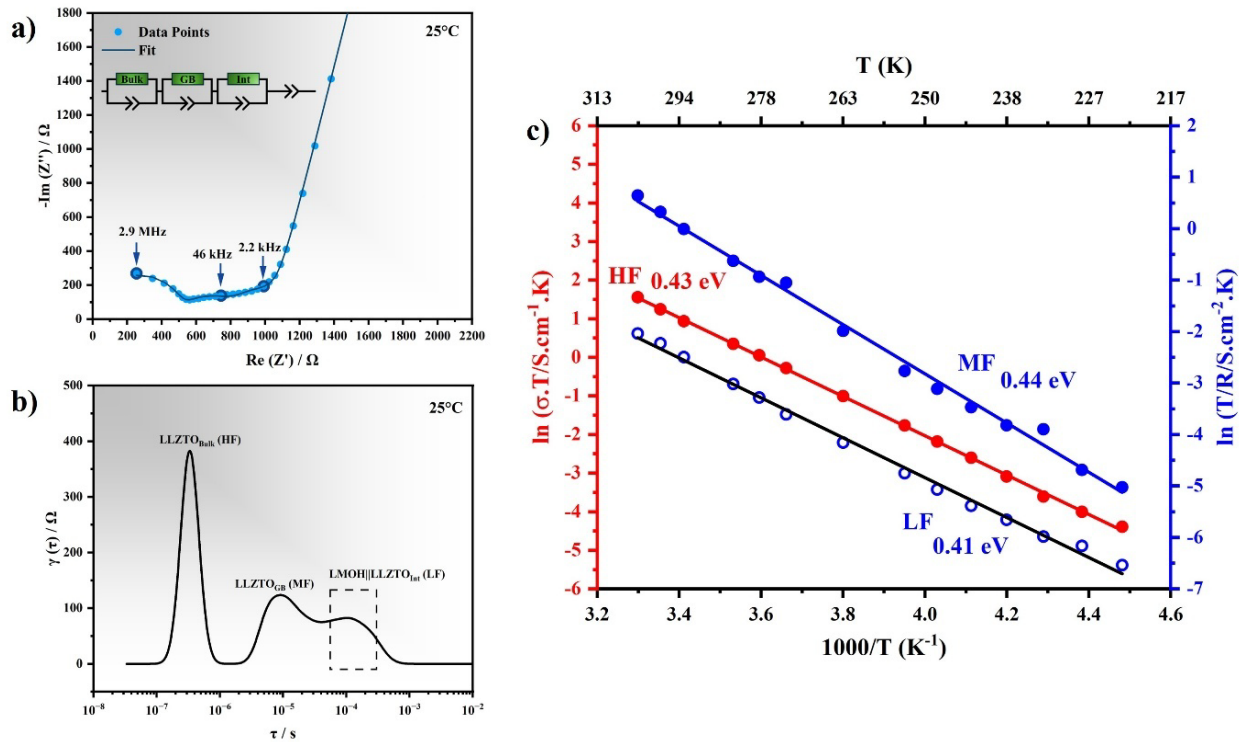


Figure 3.9 (a) Nyquist plot of LMO||LLZTO and (b) its corresponding time-constant DRT plot at 25°C, (c) Arrhenius plot obtained within the temperature range of -50°C to 30°C

Figure 3.9 a shows the Nyquist plot obtained at 25°C with 60 MPa stack pressure and fitted with three resistors and three CPE in series along with a CPE blocking element. There are three contributions associated with the frequency range as discussed earlier: i) the high-frequency region of about 3 MHz belongs to the LLZTO bulk, ii) the mid-frequency at 46 kHz corresponds to the LLZTO grain boundaries, and iii) the low-frequency region below 2.2 kHz corresponds to the heterionic interface of SE1||SE2. With the support of DRT analysis displayed in **Figure 3.9 b** qualitatively confirms the three main contributions with respect to the time constants. The shoulder peak near the mid-frequency was contributed by the heterionic interface since it cannot correspond to any other charge transfer process. Temperature-dependent studies were also conducted to determine the activation energies belonging to each frequency contribution and were summarized in the comparison table between each individual solid electrolyte and the multilayer symmetric cell at 25°C, which was in good agreement with the previously reported studies.^{29,36,44}

Table 3.1 Comparison table of resistance, capacitance, time constants, frequency and the activation energy of individual solid electrolytes and the multilayer symmetric cell at room temperature

SE1 and SE2	R (Ω)	C (F)	τ (s)	f (Hz)	E _a (eV)
LMOC	19±0.8	-	-	-	-
LLZTO _{Bulk}	428	1.633E ⁻¹⁰	0.070 x 10 ⁻⁶	2.27 x 10 ⁶	0.43
LLZTO _{GB}	498	1.703E ⁻⁹	0.848 x 10 ⁻⁶	0.19 x 10 ⁶	0.46
HF	506	1.07E ⁻¹⁰	0.0541 x 10 ⁻⁶	2.94 x 10 ⁶	0.43
MF	326	1.058E ⁻⁸	3.45 x 10 ⁻⁶	46 x 10 ³	0.44
LF	208	3.514E ⁻⁷	73.1 x 10 ⁻⁶	2.2 x 10 ³	0.41

The capacitance (C) value is determined by the Brug equation and the frequency is connected to the relaxation time constant (τ). So C, τ and f can be determined by the following equations which were described below

$$C = \left[\frac{Q}{R^{1-\alpha}} \right]^{1/\alpha}$$

$$\tau = R.C = R \cdot \frac{(Q.R)^{1/\alpha}}{R} = (Q.R)^{1/\alpha}$$

$$f = \frac{1}{2\pi\tau}$$

To calculate the R_{int} , the interfacial resistance was halved because two interfaces were measured simultaneously. The area of the pellet was calculated as 0.785 cm². The obtained R_{int} was multiplied by the area in order to get $R_{int} \Omega.cm^2$. From the obtained above values in the table, we observed 80±2 $\Omega.cm^2$ interfacial impedance which was very low when compared to the previous heterionic interface studies reported.^{29,36} (We also investigated pressure-dependent studies which are not included in this thesis and are still in progress to discuss in more detail and to be published in future)

Electrochemical analyzis of hybrid-cell architecture

To validate the proof of concept derived from the observed experimental results, a full-cell configuration was constructed, incorporating lithium metal as the anode, Ta-doped LLZTO and lithium metal oxychloride (LMOC) as a multilayer separator, and NMC811/LMOC as the catholyte. The cell

assembly was subjected to a stack pressure of approximately 10 MPa, achieved by applying a torque of 2 N·m. Galvanostatic cycling was conducted using the VMP3 potentiostat within the potential range of 2.8-4.3 V vs Li/Li⁺ at the elevated temperature of 60°C. Initially, the cell was activated with a C/20 rate which achieved 205 mAh.g⁻¹ charge capacity with 92% initial coulombic efficiency (ICE) and continued with a C/10 rate where it maintained 153 mAh.g⁻¹ with 99% CE over 15 cycles which as shown in **Figure 3.10**. The theoretical capacity was calculated assuming 1C = 200 mAh.g⁻¹.

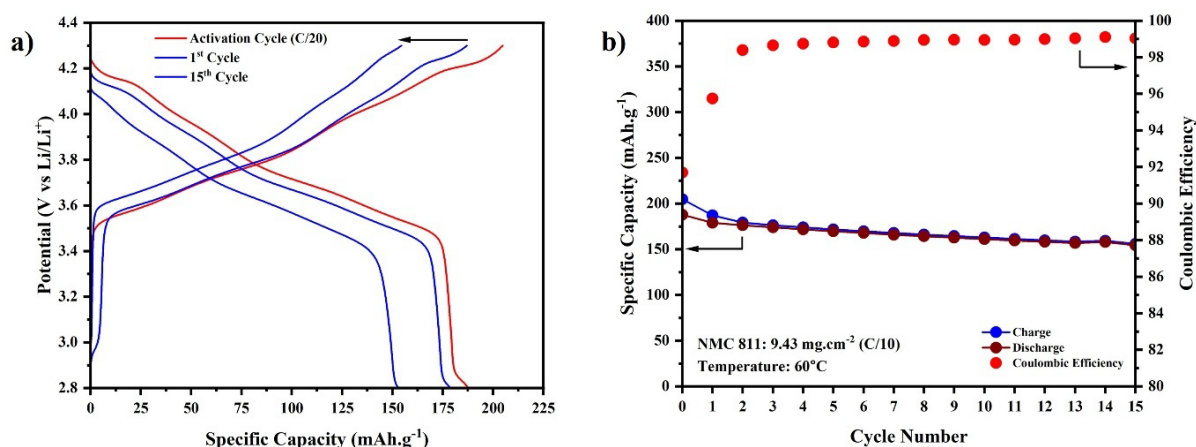


Figure 3.10 (a-b) Electrochemical profile and its cycling performance at 60°C

Calculation of relative density percentage using Archimedes' principle

Typically, the pellet was weighed in the air (as-measured: 0.6014 g) and then weighed in the solvent (as-measured: 0.5086 g) where the custom setup for the measurement is shown in **Figure 3.11**. Here we used ethanol as a solvent with a theoretical density of 0.789 g.cm⁻³ while the theoretical density of Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) was 5.5 g.cm⁻³. According to Archimedes' principle⁴², the density of as-sintered LLZTO and its relative density percentage was calculated using the formula below

$$\text{Density of as-sintered LLZTO} = \frac{\text{Mass in air}}{\text{Mass in air} - \text{Mass in ethanol}} \times \text{density of ethanol}$$

$$\text{Relative density percentage} = \frac{\text{Density of as-sintered LLZTO}}{\text{Theoretical density of LLZTO}} \times 100\%$$

From the above values, it was calculated that the relative density of the as-sintered LLZTO pellet was 93%. We also calculated the relative density of the as-sintered LLZTO pellet as 90% using its physical dimensions and mass of the pellet.



Figure 3.11 Custom setup for measuring the relative density using Archimedes' Principle

Conclusion

In this study, we successfully demonstrated the compatibility of surface-treated Ta-doped LLZO with both lithium metal and lithium metal oxychloride (LMOC) solid electrolytes through comprehensive impedance analysis, coupled with activation energy and interfacial resistance measurements. These findings provide valuable insights into the lithium-ion transport mechanisms across the solid-solid interfaces in these systems. Notably, our results revealed exceptionally low interfacial resistance values of $<10 \Omega \cdot \text{cm}^2$ for the $\text{Li}||\text{LLZTO}$ interface and $80 \pm 2 \Omega \cdot \text{cm}^2$ for the $\text{LMOC}||\text{LLZTO}$ interface, marking a momentous progression in mitigating interfacial resistance challenges in garnet-based solid electrolytes.

The remarkably low interfacial resistance values achieved in this study highlight the efficiency of our surface treatment strategy in enhancing ionic contact and minimizing interfacial polarization effects. These promising results present a substantial leap forward in the development of solid-state battery architectures. Building upon these insights, we successfully constructed a hybrid all-solid-state cell configuration that employed a lithium metal anode directly in contact with LLZTO, LMOC as an interfacial mediator layer and an LMOC/NMC 811 catholyte combination.

To the best of our knowledge, this work represents the first reported demonstration and factual fully operational garnet-based lithium-ion hybrid solid-state battery architecture. While this research is ongoing, and further investigations are underway to optimize cell performance and assess long-term cycling stability, these initial findings present a compelling step forward in the advancement of garnet-based solid-state batteries. These results are presented with permission from V. K. Singh, L. Merola,

M. Palmer, **K. N. Pugazhendhi**, P. Barai, I. You, Y. Wang, E. Carlson, V. Srinivasan, J. Sakamoto, J. Janek, and L. F. Nazar. [Ion Transport across the heteroionic interface of lithium-ion oxyhalide catholytes with Ta-LLZO to enable Li metal Solid-State Batteries].

Chapter 4 Highly crystalline layered 2H-TaS₂ as an intercalation-conversion type cathode for All-Solid-State Lithium-Sulfur Batteries

4.1 Introduction

As discussed in Chapter 1, advancing sustainable battery technologies with high energy density is essential for meeting expanding global energy needs across electric vehicles (EVs), portable electronics, and large-scale energy storage systems. All-solid-state lithium-sulfur batteries (ASSLSBs) have become a focal point in emerging battery research because they offer solutions to the limitations present in traditional lithium-ion batteries (LIBs). As lithium-sulfur (Li-S) systems achieve theoretical energy densities around 2500 Wh/kg, which greatly exceeds those of traditional LIBs, they stand out as strong prospects for future energy storage technologies. The practical use of Li-S batteries remains limited because of serious obstacles, including the polysulfide shuttle effect and poor sulfur utilization, along with low cycle stability, especially when using liquid electrolyte systems.^{69–72} The use of solid-state electrolytes (SSEs) allows for the resolution of these challenges while creating safer batteries by removing flammable organic liquid electrolytes. Sulfide-based electrolytes stand out among all-solid-state electrolytes because they exhibit excellent room-temperature ionic conductivity alongside beneficial mechanical flexibility and compatibility with lithium metal anodes.^{8,33,73,74} Li_{15.5}PS_{4.5}Cl_{1.5} (LPSC_{1.5}) delivers exceptional ionic conductivity at ≥ 10 mS.cm⁻¹ combined with outstanding deformability, which helps establish close contact with cathode materials and improves lithium-ion movement across interfaces.^{75,76}

The electrochemical performance of ASSLSBs can be significantly improved by using transition metal disulfides (TMDs) as hosts for sulfur and cathode materials. The structure of intercalation-type transition metal sulfides (TMDs) allows for reversible lithium-ion exchange while maintaining structural stability during battery cycling. The intercalation process produces strong rate capabilities and cycling stability, which makes TMDs excellent cathode materials. Their theoretical capacity remains below that of sulfide-based TMDs and other comparable materials despite their beneficial properties. Research has uncovered a restricted quantity of TMDs that operate solely through the intercalation mechanism. TMD materials like MoS₂, VS₂, TiS₂, CuS₂ and FeS₂ show improved electronic conductivity and structural stability while also facilitating sulfur redox reactions which makes them excellent candidates to advance sulfur utilization and battery lifespan.^{19,20,23,25,77}

On exploring similar properties of TMDs such as 2H-MoS₂, 1T-VS₂, 1T-CoS₂, 2H-WS₂, our group found that the hexagonal crystal structure of 2H-TaS₂ belongs to the P6₃/mmc space group and features each tantalum atom surrounded by six sulfur atoms arranged in a trigonal prismatic manner.^{78–84} The

TaS₂ units create layered structures where tantalum atoms sit between dual sulfur atom layers. Van der Waals forces weakly bond the layers together, enabling easy exfoliation while allowing lithium-ion insertion. The unique metallic conductivity, lithiophilic and electron delocalization properties of 2H-TaS₂ are due to the partially filled d-orbitals in Ta atoms. Within the TaS₂ framework, tantalum atoms supply 5d electrons, which fill conduction bands to support swift electron movement through the TaS₂ layers. The two-dimensional TaS₂ sheets support high electrical conductivity ($\sim 3.3 \times 10^4$ S/cm)⁸⁵ and low lithium-ion diffusion barrier (0.188 eV)⁸² because delocalized electrons can move freely across them. The inherent metallic-like feature of 2H-TaS₂ enables it to conduct electricity effectively by allowing quick charge transfer in electrochemical reactions.

Here, I reported the intercalation electrochemistry conversion of layered transition metal sulfide (TaS₂) and carbon (Ketjen black) as sulfur host when used as cathode materials in ASSLSBs resulted in high sulfur utilization of $\sim 99\%$ with 2.99 mAh.cm⁻² at a C/10 rate and retains 94% over 50 cycles. With a high active material loading of 9.96 mg_(S+TaS₂).cm⁻², the S/TaS₂/C electrode achieves a high areal capacity of 9.1 mAh.cm⁻² and maintains 100% coulombic efficiency.

4.2 Experimental Section

Synthesis of bulk 2H-TaS₂: In order to prepare 5g of tantalum disulfide, the required amount of tantalum (99.9%, Sigma-aldrich) and sulfur (99.9%, Sigma-aldrich) was mixed well in the argon atmosphere. Then, place it as a pellet in a carbon glassy crucible and seal it in a quartz tube under a high vacuum. The sheet growth mainly depends on the annealing procedure. So, it was annealed at 600°C for 48h with a ramp-up rate of 60°C/hr and then increased to 800°C for 48h and then gradually increased to 900°C for 48h and slowly cooled down to room temperature for a period of 2 weeks. The slow cooling rate led to obtaining a high purity 2H phase, whereas the fast cooling rate led to the formation of the 3R phase.

Synthesis of Li_{5.5}PS_{4.5}Cl_{1.5}: According to previously reported literature, the solid electrolyte was prepared under an argon atmosphere inside the glovebox (maintaining O₂<0.5 ppm and H₂O<0.5 ppm). All precursors such as Li₂S (99.9%, Sigma-Aldrich), P₂S₅ (99%, Sigma-Aldrich), and LiCl (99.9%, Sigma-Aldrich) were taken and well mixed using the mortar for 45 mins and then place it as 10 mm pellet in a carbon glassy crucible and seal it under the high vacuum. Then, it was placed vertically inside the muffle furnace and annealed with the heating and cooling rate of 30°C/hr at 550°C for 7 hrs.

Preparation of Cathode Composite: Both bulk sulfur and bulk 2H TaS₂ mixed well in a mortar, and then Ketjen black was added as an additive as well as sulfur host with the optimized ratio of 60:25:15. It was mixed homogeneously and melt-diffused at 155°C for 14 hrs. To prepare the cathode composite, the active material and the as-synthesized solid electrolyte at a weight ratio of 1:1 were transferred in an 80 ml zirconia jar consisting of zirconia balls and sealed inside the glovebox. Then, the one-step

milling process was performed in a Fritsch Pulverisette 7 Premium machine at a rotation speed of 400 rpm for 2 hrs. For comparison, different carbon (Carbon nanotubes and Vulcan carbon), without carbon and without TaS₂, were also prepared using the same method by maintaining the sulfur percentage same.

Physical Characterization: XRD data were collected on a PANalytical Empyrean instrument using Cu-K α radiation ($\lambda = 1.5405\text{\AA}$) with a PIXcel 2D detector operating under the voltage at 45 kV and current at 40 mA. SEM and EDS studies were conducted in a Hitachi SU8700 FESEM instrument. To analyze the sulfur content, TGA was carried out on a TA Instruments SDT Q600 analyzer under N₂ flow with a ramp up rate at 5°C.min⁻¹. In order to determine the specific surface area, BET analyses were collected from the Micromeritics Gemini VII 2390a instrument.

Electrochemical studies: In a typical procedure, 70 mg of solid electrolyte powder was put in a cylindrical peek and pressed in between two titanium piston rods of 10 mm diameter at 2 tons for 2 mins. The cathode composite (S/TaS₂/C/SE) was then uniformly spread and pressed at 3 tons for 3 mins. Then, the Li/In alloy (molar ratio maintained at <1) was pressed on the opposite side at 1 ton for 1 min. Finally, the cell was placed in between the cell holder and maintained a constant pressure applied by a torque of 10.7 N.m (~57 MPa). Galvanostatic cycling was carried out in the potential range of 1.4-3.1 V vs Li/Li⁺ and 0.8-2.5 V with respect to Li/In alloy. Cyclic voltammetry and Impedance studies were done at a scan rate of 0.1 mV.s⁻¹ and an amplitude of 10 mV in the frequency range of 200 mHz to 1MHz. All electrochemical measurements were conducted on a Bio-logic VMP3 potentiostat.

4.3 Results and Discussion

The bulk 2H-TaS₂ was prepared via a solid-state reaction with the elemental precursors. This was further analyzed with X-ray diffraction in order to confirm its phase purity, which was verified with PDF no: 01-080-0685. It revealed the characteristic sharp diffraction peaks, which correspond to the hexagonal P63/mmc space group with trigonal prismatic coordination, confirming its high crystallinity nature. To further visualize the morphological structure, scanning electron microscopy (SEM) reveals its well-developed micron-sized 2H-TaS₂ layered flakes that look like book sheets with sharp corner edges. Despite the poor surface area (0.74 m²/g) and pore volume (0.0012 cm³.g⁻¹) of TaS₂ limiting its sulfur hosting ability^{86,87}, we used Ketjen black due to its enormous high specific area (~1400 m²/g) and large pore volume 3.25 cm³.g⁻¹. The elemental sulfur was melt-diffused with the mixture of carbon and TaS₂, where it embedded through the pores and was uniformly distributed and coated over the layered metallic TaS₂. After 60 wt% of sulfur impregnation, the surface area and pore volume dropped to 98.16 m²/g and 0.23 cm³.g⁻¹. This was attributed to the bulk sulfur loading, and the weight percentage of sulfur was determined by TGA as shown in **Figure 4.1 b**. The complete evaporation of sulfur at around 250-300°C where the curve drops, indicates the weight loss of sulfur and is confirmed to be 60 wt%, respectively.

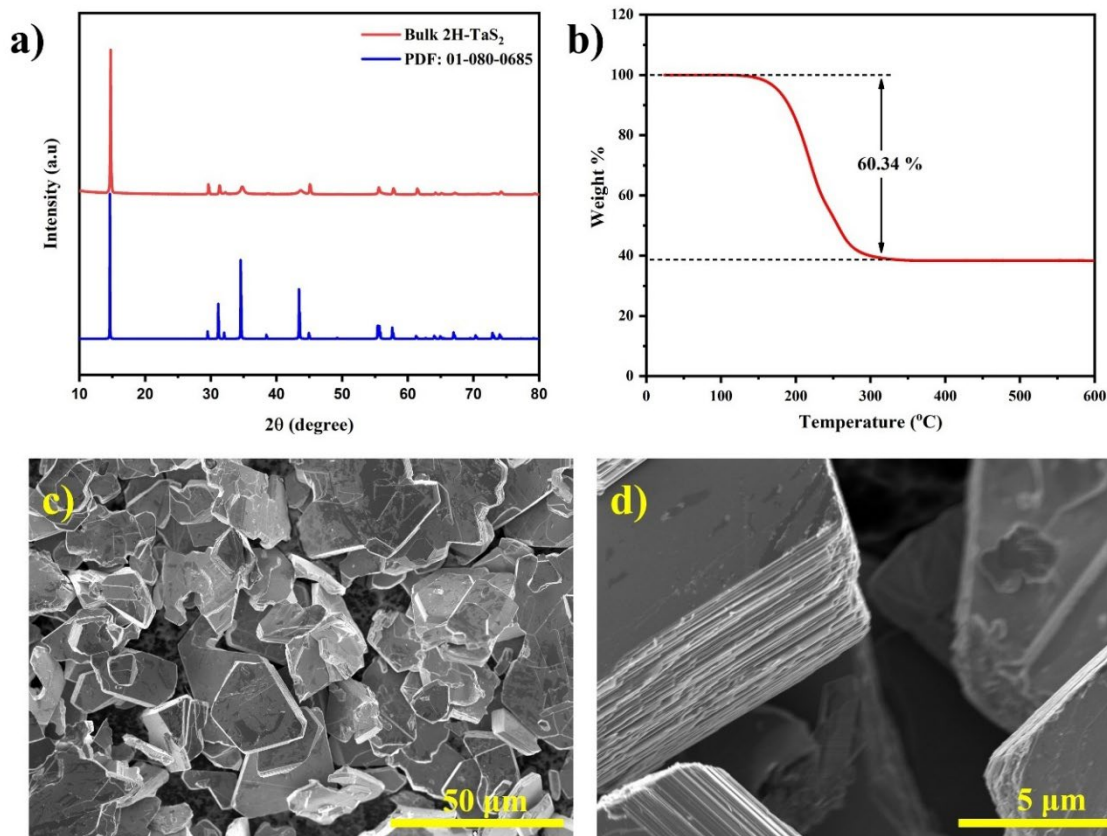


Figure 4.1 (a) XRD pattern of 2H-TaS₂, (b) TGA curve for the S/TaS₂/KB composite, and (c-d) SEM images of 2H-TaS₂

To promote ionic migration throughout the cycling, Li_{5.5}PS_{4.5}Cl_{1.5} was preferred as a solid electrolyte due to its superionic conduction (10 mS.cm⁻¹) and its high deformability by nature. Because of its mechanical properties, it was able to form triple-phase boundaries and good intimate contact within the sulfur cathode composite and accelerate the ionic/electronic transport when it was mixed via a one-step milling process with a respective weight ratio (Active material: Li_{5.5}PS_{4.5}Cl_{1.5} at 1:1).

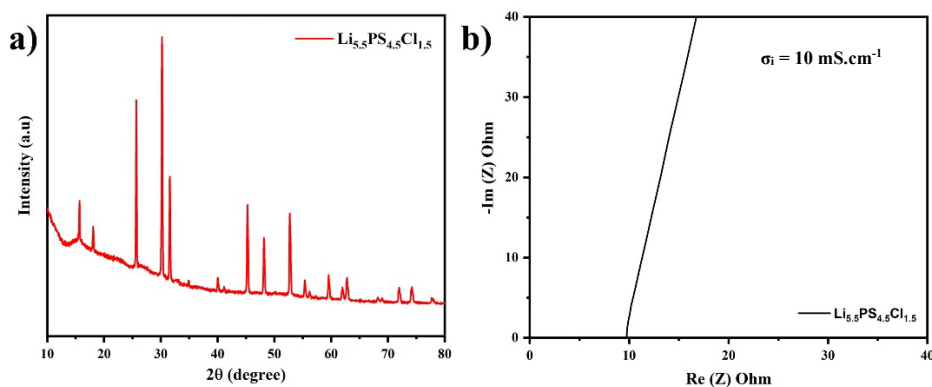


Figure 4.2 (a) XRD pattern of Li_{5.5}PS_{4.5}Cl_{1.5} and (b) its Nyquist plot

During milling, the cathode composite became amorphous with two vague broad peak of TaS_2 , which was due to the mechanical exfoliation that induced an impact on the stacking sheets and reduced its particle size, which was evident in XRD. It was believed that the amorphous cathode was highly beneficial in the conversion of sulfur to Li_2S because of low activation energy and to elevate the electrochemical performance. To further analyze the cathode active material distribution, EDX visualized the elemental mapping that sulfide SE coated over the active material very homogeneously.

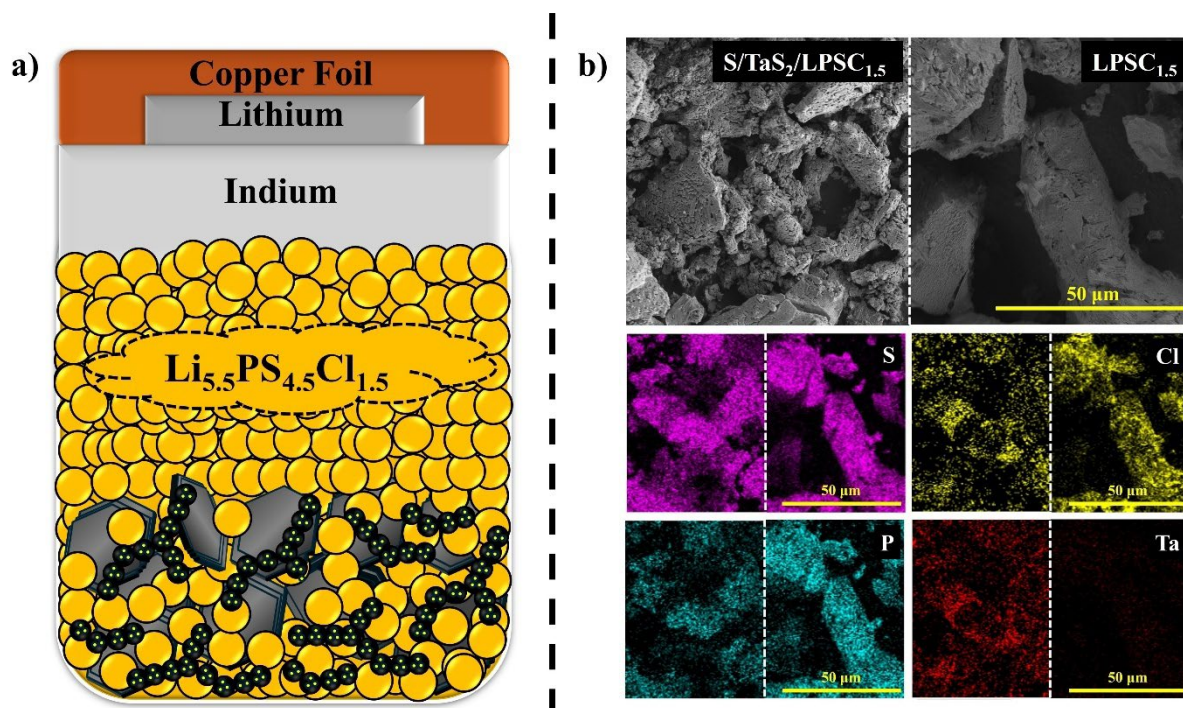


Figure 4.3 (a) Illustration of cross-sectional solid-state Li-S cell and (b) SEM image of the solid electrolyte and the whole cathode composite and their EDX elemental mapping

To understand the electrochemistry of the active material cathode, the assembled cell (**Figure 4.2 a**) with Li/In as anode, $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ as a separator and the cathode active material was subjected to galvanostatic discharge/charge cycling. The XRD data (**Figure 4.3 c**) revealed the intercalation and deintercalation electrochemical conversion reaction at 1.4 V vs 3.1 V with respect to Li/Li^+ . Due to the dominant peaks of solid electrolyte, it was very hard to differentiate the peaks, and some peaks overlapped each other. But still, the peak is located at 34° (012) and 42° (014) belongs to the formation of LiTaS_2 due to the Li^+ intercalated in TaS_2 and confirmed with the PDF No: 01-089-4218. Also, there were two small peaks that correspond to the conversion of S to Li_2S when the cell was discharged to 1.4 V vs Li/Li^+ . After charging to 3.1 V vs Li/Li^+ , the original phases of active material formed back, which is an indication of a reversible electrochemical reaction. To understand the potential redox activity, the cells with TaS_2 and without TaS_2 as a cathode active material were examined for CV

measurements. With TaS₂, we observed two redox peaks, which correspond to both the TaS₂ and S involved in the redox activity. On the other hand, without TaS₂, it exhibits low current response and above 2.5 V, we can see (Figure 4.4 a) the redox behaviour of SE apart from S, which will degrade the battery performance, which indicates that with TaS₂, it reduces the oxidation of SE within the triple phase boundary. Overall, this mechanism proved that LiTaS₂ act as a mixed electronic and ionic conductor (MEIC)^{17,88} as typical TMDs nature for better lithium-ion migrating pathway, and the metallic TaS₂ sheets⁸⁹ act as an electronic conductor in order to facilitate electrons and the solid electrolyte acts as a foremost ionic conductor to accelerate the lithium ions to move throughout cycling. To account capacity for the intercalated and converted cathode, the theoretical gravimetric capacity of (S+TaS₂) is calculated as $1C = 1214 \text{ mAh.g}^{-1}$.

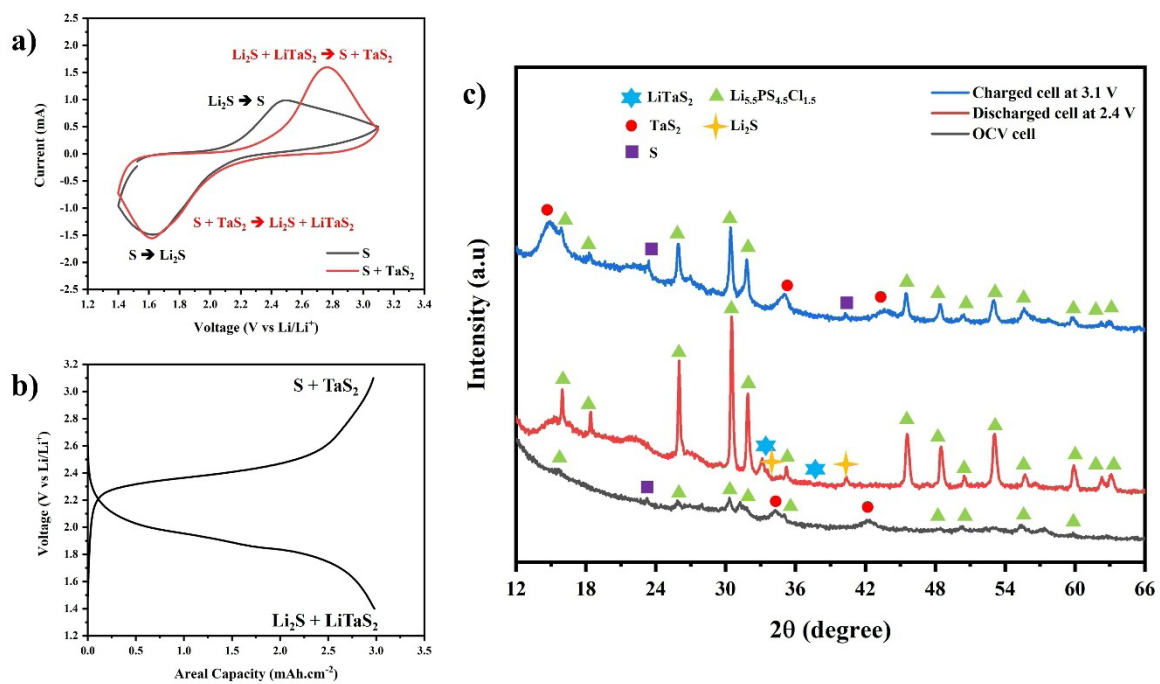


Figure 4.4 Examining the electrochemical conversion mechanism of solid-state Li-S battery. (a) CV profile with TaS₂ and without TaS₂ in the cathode composite, b) Charge and Discharge profile and (c) their corresponding ex-situ XRD profile

Electrochemical Performance

To evaluate the long cycling performance, the assembled battery was initiated to discharge with the low active material areal loading of $2.47 \text{ mg}_{(\text{S}+\text{TaS}_2)}.\text{cm}^{-2}$ at a current density of 0.3 mA.cm^{-2} that corresponds to a C/10 rate. The initial discharge capacity of 2.45 mAh.cm^{-2} was achieved, and after two cycles, it reached a high capacity of 2.99 mAh.cm^{-2} due to the redox of the solid electrolyte^{90–93}, which is activated above 2.5 V vs Li/Li⁺, where the initial coulombic efficiency of 82% was in good agreement as such as

the typical TMDs conversion type cathode in all solid-state Li-S batteries reported previously.^{23,25,77} According to the theoretical capacity of active material (S+TaS₂), the cathode reached very close to the theoretical capacity of 1209 mAh.g⁻¹ and maintained the Coulombic efficiency of 100%, which is stable thereafter. With the calculation of sulfur utilization, the normalized specific capacity of sulfur was calculated as 1666 mAh.g⁻¹ (~99% utilization) with the high sulfur loading of 30% in the cathode composite achieved where in contrast others loaded below 20% in the whole cathode composite which was still a challenge towards to improve high energy density batteries. The results were compared with different carbon sources, such as CNT (specific surface area = 500 m²/g) vs Vulcan carbon (specific surface area = 250 m²/g), and without carbon. In all three cases, it exhibited low capacity and high overpotential, which was attributed to the insulative sulfur layer covering the electronic pathway.

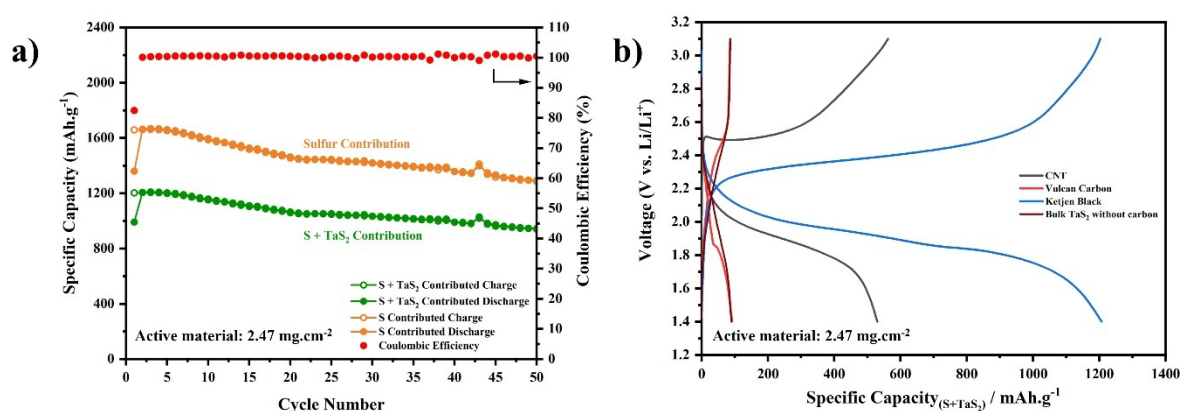


Figure 4.5 (a) Long cycle performance profile with active material of 2.47 mg.cm⁻² and (b) Charge and Discharge profile for different carbon with the same optimized ratio

With the good candidate of ketjenblack carbon as a sulfur host, we also investigated the different weight ratios of the active material, as well as those without TaS₂, to acquire an optimized ratio for high capacity and good retention ability. Nevertheless, the weight ratio of the TaS₂:S:KB (25:60:15) performed well as discussed before with high capacity and 94% capacity retention over 50 cycles. In contrast of without TaS₂ in the active material of 60%S-40%KB also showed the same capacity of 2.9 mAh.cm⁻² at 0.3 mA.cm⁻² in the first formation cycle obviously again because of the redox behaviour of SE but the capacity decayed very fast⁹⁴ with growing overpotential which retains only ~26% over 50 cycles due to the solid electrolyte decomposition which revealed that the electronic conductive carbon had a direct contact with the SE which hindered the ionic transport and resulted in high tortuosity. With account to the areal capacity, **Figure 4.6 b** shows the long cycling performance of the active material with and without TaS₂. This showed that TaS₂ supports as both a lithium-ion carrier and as an electronic conductor and provides excess capacity during cycling in order to maintain the retention which did not show up with the high porous carbon here.

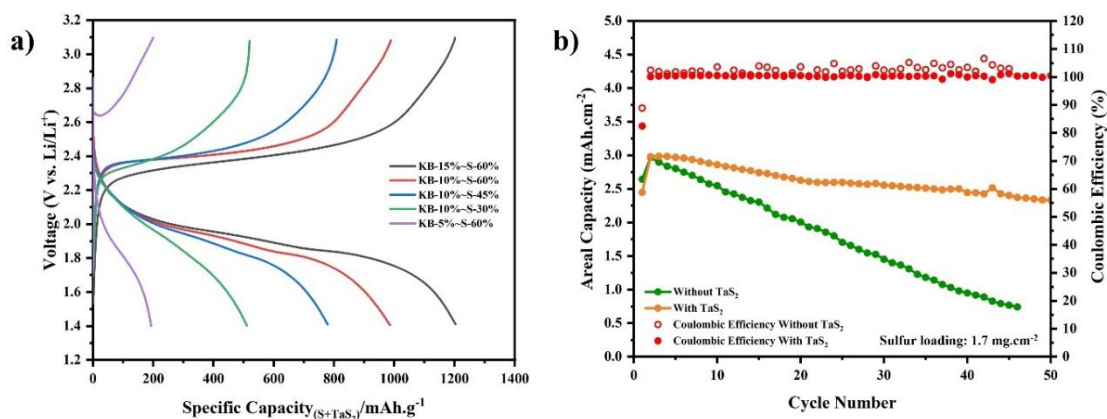


Figure 4.6 (a) Charge and Discharge profile of different weight ratios of the active material and (b) Long-term cycling profile of the active material with and without TaS₂

To demonstrate the rate capability, the assembled cell with the above-optimized weight ratio of active material showed an areal capacity of 2.8 mAh.cm⁻² with a low current density of 0.3 mA.cm⁻² (C/10) and gradually increased to different current densities and reached to 1.0 mAh.cm⁻² at 6 mA.cm⁻² (2C) which then relapsed back to the same 0.3 mA.cm⁻² and regained its capacity up to 2.7 mAh.cm⁻² with good reversible capacity, To gain up high areal capacity with high current density we also demonstrated the cell cycled at 1C for over 50 cycles which shows up ~68% sulfur utilization with good reversibility.

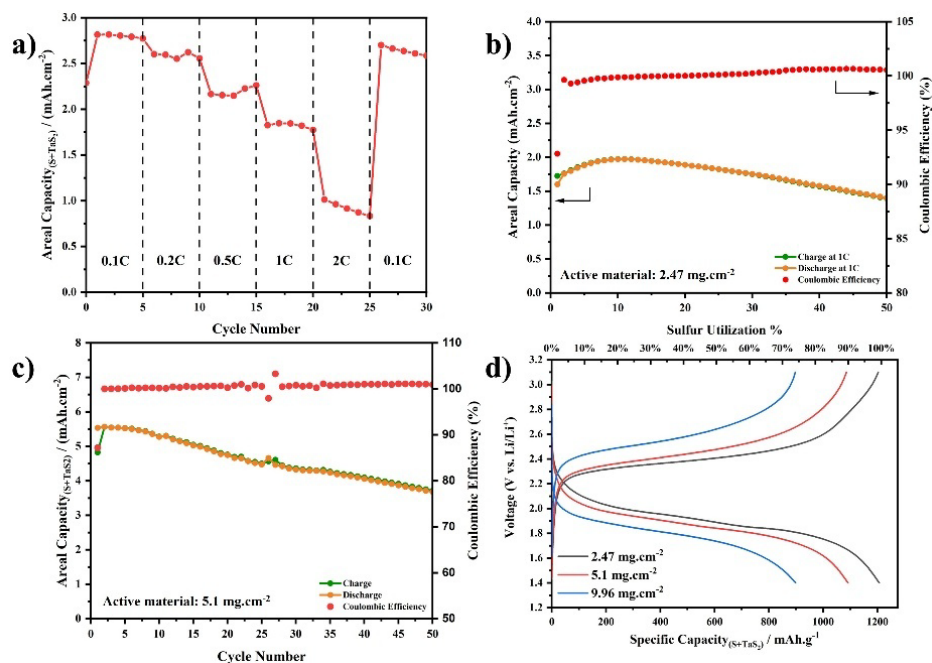


Figure 4.7 (a) Rate capability test with different current density, (b) Long-term cycling performance at the high current rate (1C), (c) Cycling performance at intermediate loading of 5.1 mg(S+TaS₂).cm⁻² and (d) Sulfur utilization associated with the low, intermediate and high active material loading

To further test the high cathode loading, we started with an intermediate loading of $5.1 \text{ mg}_{(\text{S}+\text{TaS}_2)}.\text{cm}^{-2}$ at $0.6 \text{ mA}.\text{cm}^{-2}$ ($\text{C}/10$) which reached up to $5.6 \text{ mAh}.\text{cm}^{-2}$ agreed to $\sim 90\%$ active material utilization. To further load about $9.96 \text{ mg}_{(\text{S}+\text{TaS}_2)}.\text{cm}^{-2}$ boosted the capacity to $9.1 \text{ mAh}.\text{cm}^{-2}$ with an initial CE of 100% and retention of about 85% over 25 cycles. Although it was a basic study, the higher fraction of sulfur was loaded in whole cathode composite when compared with the previously reported literature, and it can be improved by impregnating nano-sulfur in the exfoliated TMD nanosheet materials in our future studies in order to accommodate the volume changes of sulfur within the metallic nanosheet further reduce carbon content for better sustainability and high energy density batteries. Note that all our electrochemical studies were done at room temperature.

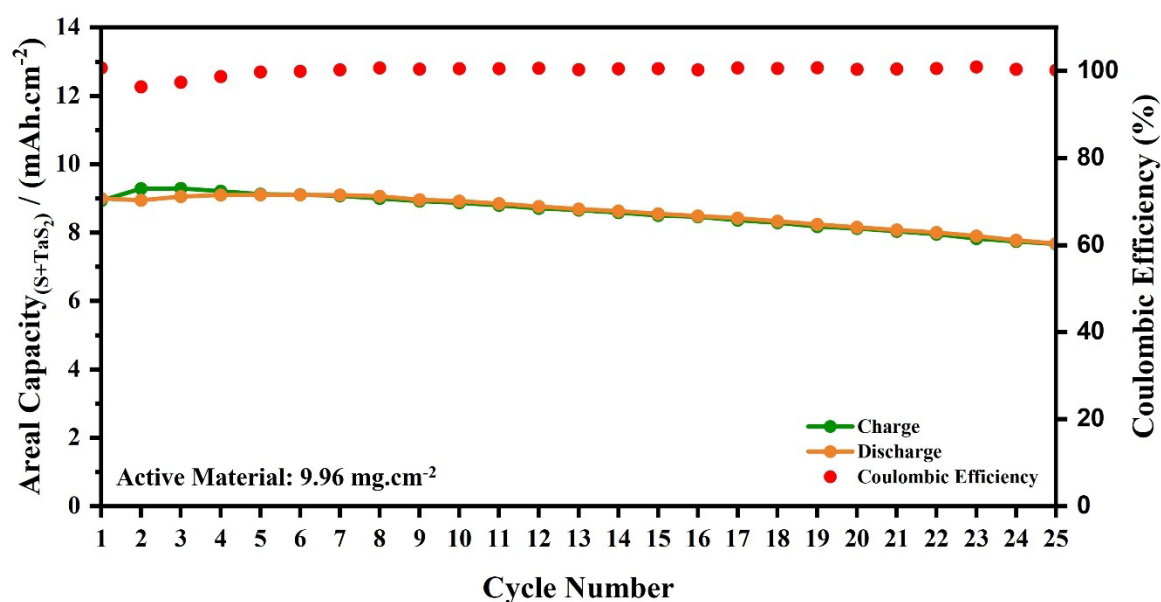


Figure 4.8 Electrochemical profile of high active material mass loading at $\text{C}/10$ rate

To compare the results with other recently reported conversion and intercalation type cathode materials for ASSLSBs with the active material were summarized below:

Table 4.1 Result summary compared with other reported literature

Type of Cathode	Cathode composite ratio	Solid electrolyte	Active material ($\text{mg}.\text{cm}^{-2}$)	Areal Capacity ($\text{mAh}.\text{cm}^{-2}$) and Current Density ($\text{mA}.\text{cm}^{-2}$)	References
Anionic redox type	$\text{FeS}_2+\text{S}+\text{C}$ (30:30:40)	$\text{LiI}-\text{Li}_3\text{PS}_4$	$5 \text{ mg}.\text{cm}^{-2}$	$3.55 \text{ mAh}_{(\text{FeS}_2+\text{S})}.\text{cm}^{-2}$ at $0.15 \text{ mA}.\text{cm}^{-2}$ ($\text{C}/42$)	25

Anionic redox type	FeS ₂ +S+C (56:24:20)	Li ₁₀ Ge ₂ PS ₁₂	0.8 mg.cm ⁻²	0.1 mAh _(FeS₂+S) .cm ⁻² at 0.24 mA.cm ⁻² (1C)	95
Conversion type	CuS+S+C (40:20:40)	LiI-Li ₃ PS ₄	5 mg.cm ⁻²	7 mAh _(CuS+S) .cm ⁻² at 0.1 mA.cm ⁻² (C/80)	23
Conversion type	Mo ₆ S ₈ +S (80:20)	Li ₃ PS ₄	12.7 mg.cm ⁻²	4.87 mAh _(Mo₆S₈+S) .cm ⁻² at 3.51 mA.cm ⁻² (C/2), 80°C	96
Conversion type	S+(KB+C) (56:44)	LGPS	6.5 mg.cm ⁻²	8.87 mAh.cm ⁻² at 0.2 mA.cm ⁻² (C/56)	93
Conversion type	S+CNT (52:48)	LGPS	3 mg.cm ⁻²	3.46 mAh.cm ⁻² at 0.25 mA.cm ⁻² (C/20)	97
Conversion type	S+KB (71:29)	Li ₃ PS ₄	4.5 mg.cm ⁻²	4.3 mAh.cm ⁻² at 0.72 mA.cm ⁻² (C/10), 60°C	92
Intercalation and conversion type	Mo ₆ S ₈ +S (67.5:32.5)	Li ₃ PS ₄ /LGPS	1 mg.cm ⁻²	0.8 mAh.cm ⁻² at 0.08 mA.cm ⁻² (C/10)	98
Intercalation and conversion type	VS ₂ +S (67:33)	Li ₃ PS ₄	15.5 mg.cm ⁻²	7.8 mAh.cm ⁻² at 0.12 mA.cm ⁻² (C/72)	19
Intercalation and conversion type	MoS ₂ +S+C (60:33:7)	Li ₆ PS ₅ Cl	12.8 mg.cm ⁻²	10.4 mAh.cm ⁻² at 1.27 mA.cm ⁻² (C/8), 60°C	77
Intercalation and conversion type	TaS ₂ +S+KB (25:60:15)	Li _{5.5} PS _{4.5} Cl _{1.5}	9.96 mg.cm ⁻²	9.1 mAh.cm ⁻² at 1.21 mA.cm ⁻² (C/10)	This Work*

Calculation for sulfur contributed capacity:

To account for the sulfur contribution¹⁹, the highest practical capacity was measured as 2.34 mAh_(S+TaS₂), which corresponds to the active material loading of 1.938 mg_(S+TaS₂). To eliminate the contribution of TaS₂ capacity from the whole cathode measured capacity by considering the theoretical capacity of TaS₂ is 109 mAh.g⁻¹ based on one Li⁺/e⁻ intercalated in the sheet to form LiTaS₂. Based on that, the capacity can be calculated as follows: 109 mAh.g⁻¹ x 0.57 mg_(TaS₂) = 0.062 mAh. The capacity of sulfur alone can be calculated as (2.34 mAh_(S+TaS₂) - 0.062 mAh_(TaS₂)) / 1.368 mg_(S) = 1666 mAh.g⁻¹. The

percentage of sulfur utilized can be calculated from the theoretical capacity as follows: Sulfur utilized % = $1666 \text{ mAh.g}^{-1} / 1675 \text{ mAh.g}^{-1} \times 100$. This is attributed to ~99% sulfur utilization.

Calculation of theoretical capacity of active material:

In order to calculate the active material theoretical capacity, $TC_{(S+TaS_2)} = 60\%TC_{(S)} + 25\%TC_{(TaS_2)} / \text{Total percentage}_{(S+TaS_2)}$. The theoretical capacity of the active material with different weight ratios is described below:

Table 4.2 The theoretical capacity of the active material with different weight ratios

TaS₂:S	35:60 (KB~5%)	60:30 (KB~10%)	45:45 (KB~10%)	30:60 (KB~10%)	25:60 (KB~15%)
Theoretical Capacity	1098 mAh.g ⁻¹	631 mAh.g ⁻¹	892 mAh.g ⁻¹	1153 mAh.g ⁻¹	1214 mAh.g ⁻¹

Conclusion

In summary, we reported that the utilization of layered transition metal sulfide with a combination of high porous carbon material as a sulfur host via a single-step milling process exhibited significant enhancement in the electrochemical performance of ASSLSBs. This superior hybrid neotype cathode design, leveraging the mixed electronic and ionic conduction (MEIC) properties of 2H-TaS₂, effectively improves both lithium-ion mobility and sulfur redox kinetics. The layered structure of 2H-TaS₂, paired with its metallic nature, facilitates efficient lithium-ion intercalation while concurrently acting as a mediator for the sulfur conversion processes. This dual function resulted in remarkably high sulfur utilization of approximately 99%, achieving a discharge capacity of 2.99 mAh.cm⁻² at a C/10 rate with 94% capacity retention after 50 cycles. Moreover, with a high active material loading of 9.96 mg_(S + TaS₂).cm⁻², the S/TaS₂/KB cathode delivered a notable areal capacity of 9.1 mAh.cm⁻², revealing its potential for high-energy-density battery applications. These findings highlight the efficiency of integrating 2H-TaS₂ as a hybrid conversion-intercalation cathode material, offering a promising path towards the emerging high-capacity, stable, and scalable ASSLSBs for future energy storage devices.

Chapter 5 Summary and Future Perspectives

The research presented in this thesis provides new insights into the fundamental processes that determine all-solid-state battery performance through a systematic analysis of lithium-ion interfacial dynamics and lithium-sulfur intercalation-conversion mechanisms. These studies provide essential insights that direct the development of sophisticated solid-state electrolytes and electrode structures to improve the durability, performance, and mass production potential of future energy storage devices.

The first segment of this study examined how surface-treated LLZTO interacts with lithium metal and lithium metal oxychloride (LMOC) solid electrolytes. The behavior of lithium-ion movement along with constriction resistance effects at the solid-solid interface were studied using quantitative electrochemical approaches like Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) and Galvanostatic Electrochemical Impedance Spectroscopy (GEIS). The study presents new perspectives on how interfacial resistance develops and reveals fundamental processes that regulate ionic transport within garnet-based solid-state systems. The investigation demonstrated promising interfacial performance yet future work must explore post-mortem characterization to understand interphase degradation and morphological changes. Operating hybrid multilayer-stacked full cells under low stack pressure at room temperature fails to deliver consistent performance which remains a significant hurdle to reach commercial viability. Further research needs to optimize high-voltage cathode materials together with scalable binder systems to create durable solid-state battery architectures suitable for manufacturing.³

The second part of the thesis investigated 2H-TaS₂ as a transition metal dichalcogenide with layered structure for its capability as a hybrid intercalation-conversion cathode in all-solid-state lithium-sulfur batteries. The combination of metallic conductivity and layered crystal structure facilitated efficient lithium-ion intercalation while serving as an electronic mediator for sulfur redox reactions which resulted in a notably higher gravimetric capacity. This initial study revealed that the cathode composite had considerably more sulfur loading than previous research indicated. Advancements in future research should focus on embedding nano-sized sulfur particles into expanded TaS₂ nanosheets because this method will improve sulfur volume management while decreasing carbon content and enhancing both electrochemical reversibility and energy density. These advancements will help to establish ASSLSBs as sustainable and scalable solutions for electric vehicle applications and energy storage systems at the grid level.

This study provides a strong foundation that supports ongoing advances in interface-stabilized solid electrolytes and multifunctional cathode materials. Progress in the field of all-solid-state lithium-based batteries depends on future efforts to tackle existing issues with interface engineering, cathode optimization, and material scalability.

References

- (1) Goodenough, J. B.; Park, K.-S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, *135* (4), 1167–1176. <https://doi.org/10.1021/ja3091438>.
- (2) Top 10: Solid-State Battery Developers. *EV Magazine*. 2025. <https://evmagazine.com/top10/top-10-solid-state-battery-developers>.
- (3) Ahmad, N.; Fan, C.; Faheem, M.; Liang, X.; Xiao, Y.; Cao, X.; Zeng, C.; Dong, Q.; Yang, W. Key Challenges and Advancements toward Fast-Charging All-Solid-State Lithium Batteries. *Green Chem.* **2024**, *26* (18), 9529–9553. <https://doi.org/10.1039/D4GC01068J>.
- (4) Schmaltz, T.; Hartmann, F.; Wicke, T.; Weymann, L.; Neef, C.; Janek, J. A Roadmap for Solid-State Batteries. *Advanced Energy Materials* **2023**, *13* (43), 2301886. <https://doi.org/10.1002/aenm.202301886>.
- (5) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22* (3), 587–603. <https://doi.org/10.1021/cm901452z>.
- (6) Tarascon, J.-M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414* (6861), 359–367. <https://doi.org/10.1038/35104644>.
- (7) Chen, R.; Li, Q.; Yu, X.; Chen, L.; Li, H. Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces. *Chem. Rev.* **2020**, *120* (14), 6820–6877. <https://doi.org/10.1021/acs.chemrev.9b00268>.
- (8) Du, L.; Wu, R.; Wu, Z.; Huang, H.; Xia, Y.; Gan, Y.; Zhang, W.; Xia, X.; He, X.; Zhang, J. Research Progress of All-Solid-State Lithium–Sulfur Batteries with Sulfide Solid Electrolytes: Materials, Interfaces, Challenges, and Prospects. *Mater. Chem. Front.* **2023**, *7* (22), 5760–5785. <https://doi.org/10.1039/D3QM00607G>.
- (9) Huang, Q.; Liu, J.; Chen, X.; Zhang, P.; Lu, L.; Ren, D.; Ouyang, M.; Liu, X. Recent Progress and Challenges of Li-Rich Mn-Based Cathode Materials for Solid-State Lithium-Ion Batteries. *Advanced Materials* **2025**, *37* (5), 2410006. <https://doi.org/10.1002/adma.202410006>.
- (10) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. Li_xCoO_2 ($0 < x < 1$): A New Cathode Material for Batteries of High Energy Density. *Materials Research Bulletin* **1980**, *15* (6), 783–789. [https://doi.org/10.1016/0025-5408\(80\)90012-4](https://doi.org/10.1016/0025-5408(80)90012-4).
- (11) Manthiram, A.; Fu, Y.; Chung, S.-H.; Zu, C.; Su, Y.-S. Rechargeable Lithium–Sulfur Batteries. *Chem. Rev.* **2014**, *114* (23), 11751–11787. <https://doi.org/10.1021/cr500062v>.

- (12) Yao, W.; Liao, K.; Lai, T.; Sul, H.; Manthiram, A. Rechargeable Metal-Sulfur Batteries: Key Materials to Mechanisms. *Chem. Rev.* **2024**, *124* (8), 4935–5118. <https://doi.org/10.1021/acs.chemrev.3c00919>.
- (13) Kim, J. T.; Su, H.; Zhong, Y.; Wang, C.; Wu, H.; Zhao, D.; Wang, C.; Sun, X.; Li, Y. All-Solid-State Lithium–Sulfur Batteries through a Reaction Engineering Lens. *Nat Chem Eng* **2024**, *1* (6), 400–410. <https://doi.org/10.1038/s44286-024-00079-5>.
- (14) Nagata, H.; Chikusa, Y. Activation of Sulfur Active Material in an All-Solid-State Lithium–Sulfur Battery. *Journal of Power Sources* **2014**, *263*, 141–144. <https://doi.org/10.1016/j.jpowsour.2014.04.032>.
- (15) Ding, B.; Wang, J.; Fan, Z.; Chen, S.; Lin, Q.; Lu, X.; Dou, H.; Kumar Nanjundan, A.; Yushin, G.; Zhang, X.; Yamauchi, Y. Solid-State Lithium–Sulfur Batteries: Advances, Challenges and Perspectives. *Materials Today* **2020**, *40*, 114–131. <https://doi.org/10.1016/j.mattod.2020.05.020>.
- (16) Sun, X.; Li, Q.; Cao, D.; Wang, Y.; Anderson, A.; Zhu, H. High Surface Area N-Doped Carbon Fibers with Accessible Reaction Sites for All-Solid-State Lithium-Sulfur Batteries. *Small* **2022**, *18* (6), 2105678. <https://doi.org/10.1002/smll.202105678>.
- (17) Wang, L.; Yin, X.; Li, B.; Zheng, G. W. Mixed Ionically/Electronically Conductive Double-Phase Interface Enhanced Solid-State Charge Transfer for a High-Performance All-Solid-State Li–S Battery. *Nano Lett.* **2022**, *22* (1), 433–440. <https://doi.org/10.1021/acs.nanolett.1c04228>.
- (18) Sakuda, A.; Sato, Y.; Hayashi, A.; Tatsumisago, M. Sulfur-Based Composite Electrode with Interconnected Mesoporous Carbon for All-Solid-State Lithium–Sulfur Batteries. *Energy Tech* **2019**, *7* (12), 1980393. <https://doi.org/10.1002/ente.201980393>.
- (19) Xu, S.; Kwok, C. Y.; Zhou, L.; Zhang, Z.; Kochetkov, I.; Nazar, L. F. A High Capacity All Solid-State Li-Sulfur Battery Enabled by Conversion-Intercalation Hybrid Cathode Architecture. *Adv Funct Materials* **2021**, *31* (2), 2004239. <https://doi.org/10.1002/adfm.202004239>.
- (20) Oh, D. Y.; Choi, Y. E.; Kim, D. H.; Lee, Y.-G.; Kim, B.-S.; Park, J.; Sohn, H.; Jung, Y. S. All-Solid-State Lithium-Ion Batteries with TiS₂ Nanosheets and Sulphide Solid Electrolytes. *J. Mater. Chem. A* **2016**, *4* (26), 10329–10335. <https://doi.org/10.1039/C6TA01628F>.
- (21) Long, P.; Xu, Q.; Peng, G.; Yao, X.; Xu, X. NiS Nanorods as Cathode Materials for All-Solid-State Lithium Batteries with Excellent Rate Capability and Cycling Stability. *ChemElectroChem* **2016**, *3* (5), 764–769. <https://doi.org/10.1002/celec.201500570>.
- (22) Yao, X.; Liu, D.; Wang, C.; Long, P.; Peng, G.; Hu, Y.-S.; Li, H.; Chen, L.; Xu, X. High-Energy All-Solid-State Lithium Batteries with Ultralong Cycle Life. *Nano Lett.* **2016**, *16* (11), 7148–7154. <https://doi.org/10.1021/acs.nanolett.6b03448>.

- (23) Hosseini, S. M.; Varzi, A.; Ito, S.; Aihara, Y.; Passerini, S. High Loading CuS-Based Cathodes for All-Solid-State Lithium Sulfur Batteries with Enhanced Volumetric Capacity. *Energy Storage Materials* **2020**, *27*, 61–68. <https://doi.org/10.1016/j.ensm.2020.01.022>.
- (24) Zhang, Q.; Ding, Z.; Liu, G.; Wan, H.; Mwizerwa, J. P.; Wu, J.; Yao, X. Molybdenum Trisulfide Based Anionic Redox Driven Chemistry Enabling High-Performance All-Solid-State Lithium Metal Batteries. *Energy Storage Materials* **2019**, *23*, 168–180. <https://doi.org/10.1016/j.ensm.2019.05.015>.
- (25) Ulissi, U.; Ito, S.; Hosseini, S. M.; Varzi, A.; Aihara, Y.; Passerini, S. High Capacity All-Solid-State Lithium Batteries Enabled by Pyrite-Sulfur Composites. *Advanced Energy Materials* **2018**, *8* (26), 1801462. <https://doi.org/10.1002/aenm.201801462>.
- (26) X-Ray Diffraction. *The Editors of Encyclopaedia Britannica*. <https://www.britannica.com/science/X-ray-diffraction>.
- (27) Temiz, C. Scanning Electron Microscopy. In *Electron Microscopy*; Mhadhbi, M., Ed.; IntechOpen, 2022. <https://doi.org/10.5772/intechopen.103956>.
- (28) Krauskopf, T.; Hartmann, H.; Zeier, W. G.; Janek, J. Toward a Fundamental Understanding of the Lithium Metal Anode in Solid-State Batteries—An Electrochemo-Mechanical Study on the Garnet-Type Solid Electrolyte $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$. *ACS Appl. Mater. Interfaces* **2019**, *11* (15), 14463–14477. <https://doi.org/10.1021/acsami.9b02537>.
- (29) Merola, L.; Singh, V. K.; Palmer, M.; Eckhardt, J. K.; Benz, S. L.; Fuchs, T.; Nazar, L. F.; Sakamoto, J.; Richter, F. H.; Janek, J. Evaluation of Oxide|Sulfide Heteroionic Interface Stability for Developing Solid-State Batteries with a Lithium–Metal Electrode: The Case of LLZO| $\text{Li}_6\text{PS}_5\text{Cl}$ and LLZO| $\text{Li}_7\text{P}_3\text{S}_{11}$. *ACS Appl. Mater. Interfaces* **2024**, *16* (40), 54847–54863. <https://doi.org/10.1021/acsami.4c11597>.
- (30) Cheng, L.; Crumlin, E. J.; Chen, W.; Qiao, R.; Hou, H.; Franz Lux, S.; Zorba, V.; Russo, R.; Kostecki, R.; Liu, Z.; Persson, K.; Yang, W.; Cabana, J.; Richardson, T.; Chen, G.; Doeff, M. The Origin of High Electrolyte–Electrode Interfacial Resistances in Lithium Cells Containing Garnet Type Solid Electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16* (34), 18294–18300. <https://doi.org/10.1039/C4CP02921F>.
- (31) Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C. High Electronic Conductivity as the Origin of Lithium Dendrite Formation within Solid Electrolytes. *Nat Energy* **2019**, *4* (3), 187–196. <https://doi.org/10.1038/s41560-018-0312-z>.

- (32) Do-yoon, P. Synthesis of High-Density $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ Membrane and Lithiophilic Interlayer for Solid-State Batteries. <https://hdl.handle.net/10371/210312>, Seoul National University Graduate School, 2024. <https://dcollection.snu.ac.kr/common/orgView/000000182615>.
- (33) Banerjee, A.; Wang, X.; Fang, C.; Wu, E. A.; Meng, Y. S. Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes. *Chem. Rev.* **2020**, *120* (14), 6878–6933. <https://doi.org/10.1021/acs.chemrev.0c00101>.
- (34) Narayan, S.; Anand, L. A Large Deformation Elastic–Viscoplastic Model for Lithium. *Extreme Mechanics Letters* **2018**, *24*, 21–29. <https://doi.org/10.1016/j.eml.2018.08.006>.
- (35) Hayashi, N.; Watanabe, K.; Shimanoe, K. Co-Sintering a Cathode Material and Garnet Electrolyte to Develop a Bulk-Type Solid-State Li Metal Battery with Wide Electrochemical Windows. *J. Mater. Chem. A* **2024**, *12* (9), 5269–5281. <https://doi.org/10.1039/D3TA06747E>.
- (36) Hüttel, J.; Seidl, C.; Auer, H.; Nikolowski, K.; Görne, A. L.; Arnold, M.; Heubner, C.; Wolter, M.; Michaelis, A. Ultra-Low LPS/LLZO Interfacial Resistance – towards Stable Hybrid Solid-State Batteries with Li-Metal Anodes. *Energy Storage Materials* **2021**, *40*, 259–267. <https://doi.org/10.1016/j.ensm.2021.05.020>.
- (37) Huo, H.; Janek, J. Solid-State Batteries: From ‘All-Solid’ to ‘Almost-Solid.’ *National Science Review* **2023**, *10* (6), nwad098. <https://doi.org/10.1093/nsr/nwad098>.
- (38) Daems, K.; Yadav, P.; Dermenci, K. B.; Van Mierlo, J.; Berecibar, M. Advances in Inorganic, Polymer and Composite Electrolytes: Mechanisms of Lithium-Ion Transport and Pathways to Enhanced Performance. *Renewable and Sustainable Energy Reviews* **2024**, *191*, 114136. <https://doi.org/10.1016/j.rser.2023.114136>.
- (39) Tanaka, Y.; Ueno, K.; Mizuno, K.; Takeuchi, K.; Asano, T.; Sakai, A. New Oxyhalide Solid Electrolytes with High Lithium Ionic Conductivity $>10 \text{ mS cm}^{-1}$ for All-Solid-State Batteries. *Angew Chem Int Ed* **2023**, *62* (13), e202217581. <https://doi.org/10.1002/anie.202217581>.
- (40) Hitz, G. T.; McOwen, D. W.; Zhang, L.; Ma, Z.; Fu, Z.; Wen, Y.; Gong, Y.; Dai, J.; Hamann, T. R.; Hu, L.; Wachsman, E. D. High-Rate Lithium Cycling in a Scalable Trilayer Li-Garnet-Electrolyte Architecture. *Materials Today* **2019**, *22*, 50–57. <https://doi.org/10.1016/j.mattod.2018.04.004>.
- (41) Sharafi, A.; Kazyak, E.; Davis, A. L.; Yu, S.; Thompson, T.; Siegel, D. J.; Dasgupta, N. P.; Sakamoto, J. Surface Chemistry Mechanism of Ultra-Low Interfacial Resistance in the Solid-State Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. *Chem. Mater.* **2017**, *29* (18), 7961–7968. <https://doi.org/10.1021/acs.chemmater.7b03002>.

- (42) Raj, V.; Naik, K. G.; Vishnugopi, B. S.; Rana, A. K.; Manning, A. S.; Mahapatra, S. R.; Varun, K.; Singh, V.; Nigam, A.; McBrayer, J. D.; Mukherjee, P. P.; Aetukuri, N. P. B.; Mitlin, D. Dendrite Growth—Microstructure—Stress—Interrelations in Garnet Solid-State Electrolyte. *Advanced Energy Materials* **2024**, *14* (15), 2303062. <https://doi.org/10.1002/aenm.202303062>.
- (43) Singh, B.; Wang, Y.; Liu, J.; Bazak, J. D.; Shyamsunder, A.; Nazar, L. F. Critical Role of Framework Flexibility and Disorder in Driving High Ionic Conductivity in LiNbOCl₄. *J. Am. Chem. Soc.* **2024**, *146* (25), 17158–17169. <https://doi.org/10.1021/jacs.4c03142>.
- (44) Sharafi, A.; Yu, S.; Naguib, M.; Lee, M.; Ma, C.; Meyer, H. M.; Nanda, J.; Chi, M.; Siegel, D. J.; Sakamoto, J. Impact of Air Exposure and Surface Chemistry on Li–Li₇ La₃ Zr₂ O₁₂ Interfacial Resistance. *J. Mater. Chem. A* **2017**, *5* (26), 13475–13487. <https://doi.org/10.1039/C7TA03162A>.
- (45) Kim, D.; Nguyen, M. H.; Chun, S. H.; Jeon, J.; Kim, B.-K.; Park, S. Stabilization of Li₇ La₃ Zr₂ O₁₂ Solid Electrolyte through Ga-Based Precipitates and the Ga–Au Surface Layer. *International Journal of Energy Research* **2024**, *2024* (1), 9050890. <https://doi.org/10.1155/2024/9050890>.
- (46) Wang, M.; Sakamoto, J. Correlating the Interface Resistance and Surface Adhesion of the Li Metal-Solid Electrolyte Interface. *Journal of Power Sources* **2018**, *377*, 7–11. <https://doi.org/10.1016/j.jpowsour.2017.11.078>.
- (47) Brooker, M. H.; Bates, J. B. Raman and Infrared Spectral Studies of Anhydrous Li₂CO₃ and Na₂CO₃. *The Journal of Chemical Physics* **1971**, *54* (11), 4788–4796. <https://doi.org/10.1063/1.1674754>.
- (48) Gorelik, V. S.; Bi, D.; Voinov, Y. P.; Vodchits, A. I.; Gorshunov, B. P.; Yurasov, N. I.; Yurasova, I. I. Raman Spectra of Lithium Compounds. *J. Phys.: Conf. Ser.* **2017**, *918*, 012035. <https://doi.org/10.1088/1742-6596/918/1/012035>.
- (49) Boyer, L.; Noel, S.; Houze, F. Constriction Resistance of a Multispot Contact: An Improved Analytical Expression. *IEEE Trans. Comp., Hybrids, Manufact. Technol.* **1991**, *14* (1), 134–136. <https://doi.org/10.1109/33.76522>.
- (50) Eckhardt, J. K.; Fuchs, T.; Burkhardt, S.; Klar, P. J.; Janek, J.; Heiliger, C. Guidelines for Impedance Analysis of Parent Metal Anodes in Solid-State Batteries and the Role of Current Constriction at Interface Voids, Heterogeneities, and SEI. *Adv Materials Inter* **2023**, *10* (8), 2202354. <https://doi.org/10.1002/admi.202202354>.
- (51) Brug, G. J.; Van Den Eeden, A. L. G.; Sluyters-Rehbach, M.; Sluyters, J. H. The Analysis of Electrode Impedances Complicated by the Presence of a Constant Phase Element. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *176* (1–2), 275–295. [https://doi.org/10.1016/S0022-0728\(84\)80324-1](https://doi.org/10.1016/S0022-0728(84)80324-1).

- (52) Yonemoto, F.; Nishimura, A.; Motoyama, M.; Tsuchimine, N.; Kobayashi, S.; Iriyama, Y. Temperature Effects on Cycling Stability of Li Plating/Stripping on Ta-Doped Li₇La₃Zr₂O₁₂. *Journal of Power Sources* **2017**, *343*, 207–215. <https://doi.org/10.1016/j.jpowsour.2017.01.009>.
- (53) Esteban, J. M.; Orazem, M. E. On the Application of the Kramers-Kronig Relations to Evaluate the Consistency of Electrochemical Impedance Data. *J. Electrochem. Soc.* **1991**, *138* (1), 67–76. <https://doi.org/10.1149/1.2085580>.
- (54) Fitzek, K.; De Haart, U.; Fang, Q.; Lehnert, W. High-Frequency Features in the Distribution of Relaxation Times Related to Frequency Dispersion Effects in SOFCs. *J. Electrochem. Soc.* **2022**, *169* (1), 014501. <https://doi.org/10.1149/1945-7111/ac4372>.
- (55) Wan, T. H.; Saccoccio, M.; Chen, C.; Ciucci, F. Influence of the Discretization Methods on the Distribution of Relaxation Times Deconvolution: Implementing Radial Basis Functions with DRTtools. *Electrochimica Acta* **2015**, *184*, 483–499. <https://doi.org/10.1016/j.electacta.2015.09.097>.
- (56) Huo, H.; Luo, J.; Thangadurai, V.; Guo, X.; Nan, C.-W.; Sun, X. Li₂CO₃: A Critical Issue for Developing Solid Garnet Batteries. *ACS Energy Lett.* **2020**, *5* (1), 252–262. <https://doi.org/10.1021/acsenenergylett.9b02401>.
- (57) Singh, D. K.; Fuchs, T.; Krempaszky, C.; Mogwitz, B.; Burkhardt, S.; Richter, F. H.; Janek, J. Overcoming Anode Instability in Solid-State Batteries through Control of the Lithium Metal Microstructure. *Adv Funct Materials* **2023**, *33* (1), 2211067. <https://doi.org/10.1002/adfm.202211067>.
- (58) He, M.; Cui, Z.; Chen, C.; Li, Y.; Guo, X. Formation of Self-Limited, Stable and Conductive Interfaces between Garnet Electrolytes and Lithium Anodes for Reversible Lithium Cycling in Solid-State Batteries. *J. Mater. Chem. A* **2018**, *6* (24), 11463–11470. <https://doi.org/10.1039/C8TA02276C>.
- (59) Lodding, A.; Mundy, J. N.; Ott, A. Isotope Inter-Diffusion and Self-Diffusion in Solid Lithium Metal. *Physica Status Solidi (b)* **1970**, *38* (2), 559–569. <https://doi.org/10.1002/pssb.19700380206>.
- (60) Jia, L.; Zhu, J.; Zhang, X.; Guo, B.; Du, Y.; Zhuang, X. Li–Solid Electrolyte Interfaces/Interphases in All-Solid-State Li Batteries. *Electrochem. Energy Rev.* **2024**, *7* (1), 12. <https://doi.org/10.1007/s41918-024-00212-1>.
- (61) Thompson, T.; Sharafi, A.; Johannes, M. D.; Huq, A.; Allen, J. L.; Wolfenstine, J.; Sakamoto, J. A Tale of Two Sites: On Defining the Carrier Concentration in Garnet-Based Ionic Conductors for Advanced Li Batteries. *Advanced Energy Materials* **2015**, *5* (11), 1500096. <https://doi.org/10.1002/aenm.201500096>.
- (62) Dologlou, E. Self-Diffusion in Solid Lithium. *Glass Phys Chem* **2010**, *36* (5), 570–574. <https://doi.org/10.1134/S1087659610050056>.

- (63) Koshikawa, H.; Matsuda, S.; Kamiya, K.; Miyayama, M.; Kubo, Y.; Uosaki, K.; Hashimoto, K.; Nakanishi, S. Dynamic Changes in Charge-Transfer Resistance at Li Metal/Li₇La₃Zr₂O₁₂ Interfaces during Electrochemical Li Dissolution/Deposition Cycles. *Journal of Power Sources* **2018**, *376*, 147–151. <https://doi.org/10.1016/j.jpowsour.2017.11.082>.
- (64) Gireaud, L.; Grugeon, S.; Laruelle, S.; Yrieix, B.; Tarascon, J.-M. Lithium Metal Stripping/Plating Mechanisms Studies: A Metallurgical Approach. *Electrochemistry Communications* **2006**, *8* (10), 1639–1649. <https://doi.org/10.1016/j.elecom.2006.07.037>.
- (65) Zhang, L.; Guo, H.; Zhang, Q.; Wang, A.; Su, Y.; Chen, Y.; Li, Y.; Shen, F.; Han, X. In Situ Formed Surface Layer to Improve the Air Stability of LLZTO and Its Contact with the Li Metal. *Energy Fuels* **2023**, *37* (18), 14341–14349. <https://doi.org/10.1021/acs.energyfuels.3c02237>.
- (66) Eckhardt, J. K.; Kremer, S.; Fuchs, T.; Minnmann, P.; Schubert, J.; Burkhardt, S.; Elm, M. T.; Klar, P. J.; Heiliger, C.; Janek, J. Influence of Microstructure on the Material Properties of LLZO Ceramics Derived by Impedance Spectroscopy and Brick Layer Model Analysis. *ACS Appl. Mater. Interfaces* **2023**, *15* (40), 47260–47277. <https://doi.org/10.1021/acsami.3c10060>.
- (67) Zhu, C.; Fuchs, T.; Weber, S. A. L.; Richter, Felix. H.; Glasser, G.; Weber, F.; Butt, H.-J.; Janek, J.; Berger, R. Understanding the Evolution of Lithium Dendrites at Li₆.₂₅Al_{0.25}La₃Zr₂O₁₂ Grain Boundaries via Operando Microscopy Techniques. *Nat Commun* **2023**, *14* (1), 1300. <https://doi.org/10.1038/s41467-023-36792-7>.
- (68) Schmalzried, H.; Janek, J. Chemical Kinetics of Phase Boundaries in Solids. *Ber Bunsenges Phys Chem* **1998**, *102* (2), 127–143. <https://doi.org/10.1002/bbpc.19981020202>.
- (69) Mikhaylik, Y. V.; Akridge, J. R. Polysulfide Shuttle Study in the Li/S Battery System. *J. Electrochem. Soc.* **2004**, *151* (11), A1969. <https://doi.org/10.1149/1.1806394>.
- (70) Pan, H.; Cheng, Z.; He, P.; Zhou, H. A Review of Solid-State Lithium–Sulfur Battery: Ion Transport and Polysulfide Chemistry. *Energy Fuels* **2020**, *34* (10), 11942–11961. <https://doi.org/10.1021/acs.energyfuels.0c02647>.
- (71) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J.-M. Li–O₂ and Li–S Batteries with High Energy Storage. *Nature Mater* **2012**, *11* (1), 19–29. <https://doi.org/10.1038/nmat3191>.
- (72) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104* (10), 4303–4418. <https://doi.org/10.1021/cr030203g>.
- (73) Umeshbabu, E.; Zheng, B.; Yang, Y. Recent Progress in All-Solid-State Lithium–Sulfur Batteries Using High Li-Ion Conductive Solid Electrolytes. *Electrochem. Energ. Rev.* **2019**, *2* (2), 199–230. <https://doi.org/10.1007/s41918-019-00029-3>.

- (74) Wu, Z.; Li, X.; Zheng, C.; Fan, Z.; Zhang, W.; Huang, H.; Gan, Y.; Xia, Y.; He, X.; Tao, X.; Zhang, J. Interfaces in Sulfide Solid Electrolyte-Based All-Solid-State Lithium Batteries: Characterization, Mechanism and Strategy. *Electrochem. Energy Rev.* **2023**, *6* (1), 10. <https://doi.org/10.1007/s41918-022-00176-0>.
- (75) Adeli, P.; Bazak, J. D.; Park, K. H.; Kochetkov, I.; Huq, A.; Goward, G. R.; Nazar, L. F. Boosting Solid-State Diffusivity and Conductivity in Lithium Superionic Argyrodites by Halide Substitution. *Angew Chem Int Ed* **2019**, *58* (26), 8681–8686. <https://doi.org/10.1002/anie.201814222>.
- (76) Bandyopadhyay, S.; Nandan, B. A Review on Design of Cathode, Anode and Solid Electrolyte for True All-Solid-State Lithium Sulfur Batteries. *Materials Today Energy* **2023**, *31*, 101201. <https://doi.org/10.1016/j.mtener.2022.101201>.
- (77) Li, H.; Wang, R.; Song, J.; Liu, D.; Gao, H.; Chao, Y.; Tang, H. In Situ-Constructed Li_xMoS_2 with Highly Exposed Interface Boosting High-Loading and Long-Life Cathode for All-Solid-State Li–S Batteries. *Energy & Environ Materials* **2023**, e12687. <https://doi.org/10.1002/eem2.12687>.
- (78) Gamo, H.; Hikima, K.; Matsuda, A. Transition-Metal Sulfides for High-Performance Lithium Sulfide Cathodes in All-Solid-State Lithium–Sulfur Batteries. *ACS Omega* **2023**, *8* (48), 45557–45565. <https://doi.org/10.1021/acsomega.3c05635>.
- (79) Martincová, J.; Otyepka, M.; Lazar, P. Oxidation of Metallic Two-Dimensional Transition Metal Dichalcogenides: 1T-MoS₂ and 1T-TaS₂. *2D Mater.* **2020**, *7* (4), 045005. <https://doi.org/10.1088/2053-1583/ab9dd4>.
- (80) Mühlberger, R.; Butz, T.; Lerf, A. Kinetics of the Lithium Intercalation of 2H-TaS₂. *Physica B+C* **1981**, *105* (1–3), 218–222. [https://doi.org/10.1016/0378-4363\(81\)90248-5](https://doi.org/10.1016/0378-4363(81)90248-5).
- (81) Reshak, A. H. Full-Potential Calculations of the Electronic and Optical Properties of 1T and 2H Phases of TaS₂ Intercalated with Lithium. *Physica B: Condensed Matter* **2006**, *373* (1), 1–7. <https://doi.org/10.1016/j.physb.2005.10.103>.
- (82) Wong, H.; Hossain, M. D.; Xu, M.; Cai, Y.; Tamtaji, M.; Zhang, K.; Luo, Z. High Lithiophilicity and Li Diffusion Rate on 1T Phase Transition Metal Dichalcogenides as Effective Li Regulating Materials for Dendrite-Free Metal Anodes. *J. Mater. Chem. A* **2024**, *12* (35), 23810–23818. <https://doi.org/10.1039/D4TA03686G>.
- (83) Sun, X.; Wang, Z. Ab Initio Study of Adsorption and Diffusion of Lithium on Transition Metal Dichalcogenide Monolayers. *Beilstein J. Nanotechnol.* **2017**, *8*, 2711–2718. <https://doi.org/10.3762/bjnano.8.270>.

- (84) Jayasubramaniyan, S.; Kim, S.; Sung, J. Redox Mediators for Lithium Sulfide Cathodes in All-Solid-State Li-S Batteries: Recent Advantages and Future Perspective. *Journal of Energy Chemistry* **2025**, *103*, 535–542. <https://doi.org/10.1016/j.jechem.2024.12.007>.
- (85) Liu, Y.; Wu, J.; Hackenberg, K. P.; Zhang, J.; Wang, Y. M.; Yang, Y.; Keyshar, K.; Gu, J.; Ogitsu, T.; Vajtai, R.; Lou, J.; Ajayan, P. M.; Wood, B. C.; Yakobson, B. I. Self-Optimizing, Highly Surface-Active Layered Metal Dichalcogenide Catalysts for Hydrogen Evolution. *Nat Energy* **2017**, *2* (9), 17127. <https://doi.org/10.1038/nenergy.2017.127>.
- (86) Jin, T.; Liang, K.; Yu, J.-H.; Wang, T.; Li, Y.; Li, T.-D.; Ong, S. P.; Yu, J.-S.; Yang, Y. Enhanced Cycling Stability of All-Solid-State Lithium–Sulfur Battery through Nonconductive Polar Hosts. *Nano Lett.* **2024**, *24* (22), 6625–6633. <https://doi.org/10.1021/acs.nanolett.4c01210>.
- (87) Kim, H.; Choi, H.; Kim, M.; Kansara, S.; Kim, J. T.; Shin, M.; Hwang, J.; Jung, H.; Ming, J.; Sun, Y. Hierarchical Nanowire Host Material for High-Areal-Capacity All-Solid-State S/SeS₂ Batteries. *Adv Funct Materials* **2025**, *35* (7), 2415299. <https://doi.org/10.1002/adfm.202415299>.
- (88) Kızılaslan, A.; Kızılaslan, R.; Miura, A.; Tadanaga, K. Mixed Ion-Electron Conductive Materials: A Path to Higher Energy Density All-Solid-State Lithium-Ion Batteries. *Nano Today* **2025**, *60*, 102556. <https://doi.org/10.1016/j.nantod.2024.102556>.
- (89) Peng, J.; Yu, Z.; Wu, J.; Zhou, Y.; Guo, Y.; Li, Z.; Zhao, J.; Wu, C.; Xie, Y. Disorder Enhanced Superconductivity toward TaS₂ Monolayer. *ACS Nano* **2018**, *12* (9), 9461–9466. <https://doi.org/10.1021/acsnano.8b04718>.
- (90) Cronk, A.; Wang, X.; Oh, J. A. S.; Ham, S.-Y.; Bai, S.; Ridley, P.; Chouchane, M.; Huang, C.-J.; Cheng, D.; Deysher, G.; Yang, H.; Sayahpour, B.; Vicencio, M.; Lee, C.; Lee, D.; Song, M.-S.; Jang, J.; Lee, J. B.; Meng, Y. S. A Highly Utilized and Practical Lithium-Sulfur Cathode Enabled in All-Solid-State Batteries. August 12, 2024. <https://doi.org/10.26434/chemrxiv-2024-hj829>.
- (91) Nagao, M.; Hayashi, A.; Tatsumisago, M. Sulfur–Carbon Composite Electrode for All-Solid-State Li/S Battery with Li₂S–P₂S₅ Solid Electrolyte. *Electrochimica Acta* **2011**, *56* (17), 6055–6059. <https://doi.org/10.1016/j.electacta.2011.04.084>.
- (92) Alzahrani, A. S.; Otaki, M.; Wang, D.; Gao, Y.; Arthur, T. S.; Liu, S.; Wang, D. Confining Sulfur in Porous Carbon by Vapor Deposition to Achieve High-Performance Cathode for All-Solid-State Lithium–Sulfur Batteries. *ACS Energy Lett.* **2021**, *6* (2), 413–418. <https://doi.org/10.1021/acsenerylett.0c01956>.
- (93) Duan, C.; Cheng, Z.; Li, W.; Li, F.; Liu, H.; Yang, J.; Hou, G.; He, P.; Zhou, H. Realizing the Compatibility of a Li Metal Anode in an All-Solid-State Li–S Battery by Chemical Iodine–Vapor Deposition. *Energy Environ. Sci.* **2022**, *15* (8), 3236–3245. <https://doi.org/10.1039/D2EE01358D>.

- (94) Song, H.; Münch, K.; Liu, X.; Shen, K.; Zhang, R.; Weintraut, T.; Yusim, Y.; Jiang, D.; Hong, X.; Meng, J.; Liu, Y.; He, M.; Li, Y.; Henkel, P.; Brezesinski, T.; Janek, J.; Pang, Q. All-Solid-State Li–S Batteries with Fast Solid–Solid Sulfur Reaction. *Nature* **2025**, *637* (8047), 846–853. <https://doi.org/10.1038/s41586-024-08298-9>.
- (95) Mwizerwa, J. P.; Zhang, Q.; Han, F.; Wan, H.; Cai, L.; Wang, C.; Yao, X. Sulfur-Embedded FeS₂ as a High-Performance Cathode for Room Temperature All-Solid-State Lithium–Sulfur Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12* (16), 18519–18525. <https://doi.org/10.1021/acsami.0c01607>.
- (96) Li, M.; Pan, H.; Liu, T.; Xiong, X.; Yu, X.; Hu, Y.-S.; Li, H.; Huang, X.; Suo, L.; Chen, L. All-in-One Ionic–Electronic Dual-Carrier Conducting Framework Thickening All-Solid-State Electrode. *ACS Energy Lett.* **2022**, *7* (2), 766–772. <https://doi.org/10.1021/acsenergylett.1c02666>.
- (97) Pan, H.; Zhang, M.; Cheng, Z.; Jiang, H.; Yang, J.; Wang, P.; He, P.; Zhou, H. Carbon-Free and Binder-Free Li–Al Alloy Anode Enabling an All-Solid-State Li–S Battery with High Energy and Stability. *Sci. Adv.* **2022**, *8* (15), eabn4372. <https://doi.org/10.1126/sciadv.abn4372>.
- (98) Li, M.; Liu, T.; Shi, Z.; Xue, W.; Hu, Y.; Li, H.; Huang, X.; Li, J.; Suo, L.; Chen, L. Dense All-Electrochem-Active Electrodes for All-Solid-State Lithium Batteries. *Advanced Materials* **2021**, *33* (26), 2008723. <https://doi.org/10.1002/adma.202008723>.