Mechanistic Study and Processing of Lithium Composite Garnet Electrolytes for All Solid State Batteries



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Abstract

Batteries offer the ability to store and release energy from renewable sources, whether on or off-grid, enabling the decarbonisation of the global transport and energy sectors. However, safety concerns regarding conventional lithium-ion batteries have placed heavy restrictions around safety, affecting their deployment and energy density. All solid-state batteries present themselves as a promising alternative to address these concerns. However, persistent challenges, such as the growth and propagation of lithium metal dendrites, hinder the widespread implementation of this technology.

High electronic conductivity in solid electrolytes has been identified as a source of formation and propagation of these dendrites. Yet, the role of electronic conductivity, the subsequent electrodynamics and its resultant impact on solid electrolyte properties is currently an underexplored research area.

This thesis looks to further elucidate the fundamental role of electrical conductivity and its effect on electrodynamics within lithium garnet solid electrolytes. Developing a better understanding around these mechanisms of degradation may lead to future solutions that further suppress failure mechanisms arising from the lithium metal anode.

In this thesis, Chapter 1 introduces a general background on batteries, their components, and the theory behind the fundamental mechanisms that govern the electrochemical system. The all-solid-state battery is introduced, as well as lithium garnet solid electrolytes and the current literature on dendritic growth and degradation mechanisms which can manifest from lithium metal anodes. Furthermore, the literature surrounding electrolyte processing by tape casting and current advances in film architectures are explored. A background to the experimental methods employed during this thesis including structural, electrochemical, spectroscopic, processing, and computational modelling techniques are provided in Chapter 2.

The first results chapter, Chapter 3, focuses on the introduction of differing quantities of manganese into a lithium stuffed garnet system of general formula $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4-x}\text{Mn}_x\text{O}_{12}$ (x = 0.035, 0.05, 0.07, 0.105). The subsequent synthesis yielded composite solid electrolytes with an embedded secondary phase that held a higher electrical conductivity. By employing complementary electrochemical and spectroscopic methods, it was found that at low levels the secondary phase did not affect the electrical conductivity of the composite solid electrolyte. Galvanostatic

cycling with lithium metal however revealed a change in electrochemical response, arising from oxidation of the embedded secondary phase. Furthermore, at low levels the secondary phase enhanced the properties of the solid electrolyte reducing interfacial resistance and increasing the critical current density from 0.1 to 0.3 mA $\rm cm^{-2}$. However, once a percolation threshold was reached, detrimental effects on the characteristics of the system were observed with a highly resistive interface, revealing that embedded secondary phases affect overall properties of a solid electrolyte.

Chapter 4 utilised X-ray diffraction computed tomography (XRD-CT) and finite element method (FEM) to further uncover the local interplay between structure and electrodynamics arising from the embedded secondary phase. XRD-CT revealed a systematic decrease in weight fraction of the incorporated secondary phase following galvanostatic cycling, indicating electrochemical activity. Whilst the use of FEM revealed that under an applied potential of 1 V, the current density at the secondary phase was raised $6 \times 10^{-8} \mu A \mu m^{-2}$ more than the surrounding composite. Furthermore, the chapter draws together the results from the previous chapter by discussing the consequences of the incorporated secondary phase with differing electrical properties.

The development of composite solid electrolytes was further investigated in Chapter 5, where a composite free-standing bilayer film was fabricated using tape casting. The solid electrolyte film integrated both a mixed ionic electronic conducting (MIEC) and a non-MIEC lithium garnet phase. To address initial challenges in producing a dense free-standing film, Li_2O , LiCl, Li_3PO_4 and commercially available Asahi glass (AVX) were examined as potential sintering aids. The most effective sintering aid was found to be Li_2O , increasing the density from *ca.* 43 % to 88 %.

A summary of the results and future work is presented in Chapter 6, where a perspective is given on directions for further research into solid electrolyte composites and how they may be used to enhance desirable solid electrolyte properties.

Acknowledgments

As I sit down to write this last part of my thesis, I realise that it represents the culmination of a long and yet very short journey over a four year period of my life. Like many theses preceding mine, it embodies the hard work, collection, and collation of data by a student in the pursuit of academic recognition. The result, never adequately explaining the trials and tribulations faced, often presenting a seemingly effortless foray into the chosen subject matter, with only few people understanding the adversity a candidate may have faced. However, what it truly fails to convey is the importance of the people that have been a part of this journey - whether they've helped face adversity, shared joy, celebrated achievements, provided friendship, love or through any other form of support on a journey that that has been both challenging and rewarding.

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Thank you everyone.

Declaration

I, the author, confirm that the Thesis is my own work. I am aware of the University's Guidance on the Use of Unfair Means. This work has not been previously been presented for an award at this, or any other, university.

Signed: Sebastian John Altus

Contents

A	bstra	ict					i
A	cknov	wledgr	nents				iv
D	eclar	ation					v
\mathbf{Li}	st of	Figur	es				xi
\mathbf{Li}	st of	Table	S			XX	cvii
Li	st of	Abbr	eviations			x	xix
Li	st of	Publi	cations and Presentations			X	xxi
1	Intr	roduct	ion				1
		1.0.1	The Lithium-ion Battery				3
		1.0.2	The All Solid-State Battery				10
		1.0.3	The Solid Electrolyte				16
		1.0.4	Processing of Solid Electrolyte Thin Films for All Solid St	at	te		
			Batteries				32
		1.0.5	Summary of Thesis Aims				38
2	Exp	oerime	ntal Methods				41
	2.1	Synth	esis and Processing	•			41
		2.1.1	Solid State Reaction				41
		2.1.2	Particle Size Reduction and Mixing				43
		2.1.3	Tape casting \ldots	•			45
		2.1.4	Sintering				50
	2.2	Chara	acterisation Techniques				53
		2.2.1	Powder X-Ray Diffraction				53
		2.2.2	Rietveld Refinement				55
		2.2.3	X-ray Diffraction Computed Tomography				57
		2.2.4	Scanning Electron Microscopy				61
		2.2.5	Energy Dispersive X-ray Spectroscopy				62

		2.2.6	X-ray Photoelectron Spectroscopy
		2.2.7	X-ray Absorption Spectroscopy
		2.2.8	Particle Size Analysis
		2.2.9	Thermogravimetric Analysis
		2.2.10	Archimedes Density
	2.3	Electro	ochemical Analysis
		2.3.1	Electrochemical Impedance Spectroscopy
		2.3.2	DC Polarisation
		2.3.3	Galvanostatic Cycling
		2.3.4	Cyclic Voltammetry
	2.4	Comp	utational Modelling
		2.4.1	Finite Element Analysis
3	Ele	ctroche	emical and Structural Dynamics of Garnet Composite
	Ele	ctrolyt	es 85
	3.1	Introd	uction
	3.2	Experi	imental \ldots \ldots \ldots 87
	3.3	Result	s and Discussion
		3.3.1	Structure and Morphological Characterisation
		3.3.2	Electrochemical Characterisation
		3.3.3	X-ray Photoelectron Spectroscopic Characterisation 105
	3.4	Conclu	usion
	3.5	Ackno	wledgments
4	Mic	rostru	ctural Characterisation of Garnet Composite Electrolytes111
	4.1	Introd	uction
	4.2	Experi	imental
	4.3	Result	s and Discussion
		4.3.1	X-ray Diffraction Computed Tomography
		4.3.2	Finite Element Method Analysis
	4.4	Conclu	1sion
	4.5	Ackno	wledgments
5	Mix	ed Ion	ic-Electronic Conducting Garnet Electrolyte Bilayer Films
	for	Lithiu	m Metal Batteries 133
	5.1	Introd	uction
	5.2	Experi	imental
	5.3	Result	s and Discussion
		5.3.1	Particle Size Analysis
		5.3.2	Single Film Processing of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$
		5.3.3	Density Improvement using Sintering Aids

		5.3.4	Synthesis of $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$	155
		5.3.5	Composite Bilayer Film Processing $\ldots \ldots \ldots \ldots \ldots$	157
	5.4	Conclu	usion	163
6	Con	clusior	ns and Future Work	165
	6.1	Conclu	usion	165
	6.2	Future	e Work	168
Al	PPE	NDICE	ES	172
A	Cha	pter -	3	173
в	Cha	pter -	5	177
Re	efere	nces		181

List of Figures

1.1 Schematic representation of a conventional lithium-ion battery. The negative anode material is graphitic carbon formed by layers of carbon atoms (black). Whilst the positive, cathode is layered-oxide LiCoO_2 , the two electrodes are separated by a porous polymeric membrane to prevent short circuiting of the cell. During charge and discharging of the battery, Li^+ ions (green) are deintercalated from between the layers of the respective electrode and subsequently transported through the liquid electrolyte - a solution of LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate - before intercalating into the opposing electrode, simultaneously electrons move around the external circuit.

5

- 1.2 (a) Layered oxide LiCoO₂; monovalent Li⁺ (green) and trivalent Co³⁺ (blue, CoO₆ octahedra) ions are located at octahedral sites in a cubic close-packed array of oxide ions (red) in alternating planes of rock salt structure. (b) Spinel LiMn₂O₄; Mn^{3+/4+} ions (purple, MnO₆-) are octahedrally located with Li⁺ (green) in tetrahedral sites in a cubic close-packed array of oxide ions (red). (c) Olivine structured LiFePO₄; divalent Fe²⁺ (brown, FeO₆) and monovalent Li⁺ (green) octahedrally located, whilst PO₄ tetrahedron (grey) are located between.
- 1.3 Schematic representation of an all-solid state battery. The anode is composed of metallic lithium with the solid electrolyte acting as the separator with the cathode. The cathode is mixed with the solid electrolyte to form a composite, facilitating lithium diffusion to all cathode particles. Reproduced (adapted) with permission from Springer Nature.[47] Copyright 2023, Springer Nature Limited . . . 10

1.4	(a) The mechanism of void and dendrite formation at the solid elec-	
	trolyte interface, lithium metal stripping at a rate exceeding the	
	replenishment rate results in void formation. The small remaining	
	areas of contact increase the local current density facilitating the	
	growth and propagation of metal dendrites. Reproduced (adapted)	
	with permission from Springer Nature, Copyright 2019.[72] (b) The	
	preferential plating of lithium metal at grain boundaries in a solid	
	electrolyte. Reprinted from ref. [73] Copyright 2016, with permission	
	from Elsevier.	14
1.5	Schematic representing the proposed mechanisms of lithium metal	
	dendrite formation in garnet electrolytes. Reprinted (adapted) with	
	permission from ref.[82] Copyright 2017 American Chemical Society.	15
1.6	Ionic conductivity and radar plot of various solid electrolytes. (a) Total	
	ionic conductivities of lithium conducting solid electrolytes at room	
	temperature. The ionic conductivity of liquid electrolyte of EC/DMC	
	1 M LiPF ₆ is represented by a dashed grey line. Reprinted (adapted)	
	with permission. Copyright 2016 American Chemical Society.[99] (b)	
	Radar chart demonstrating the varying capabilities of differing lithium	
	conducting solid electrolytes. Adapted and reprinted.[100] Copyright	
	2019, with permission from Elsevier.	17
1.7	Frenkel and Schottky point defects in a NaCl crystal, green spheres	
	are Cl^- ions and blue Na^+ . The Frenkel defect is characterised by	
	an ion missing its position in the lattice, creating a vacancy, and	
	occupying an interstitial site nearby. The Schottky defect is formed	
	when oppositely charged ions are absent from their lattice sites and	
	become incorporated at the surface, due to the opposite nature of the	
	vacancies, overall electrical neutrality is maintained	20
1.8	(a) The three general charge carrier diffusion mechanisms in crystalline	
	solids: vacancy, direct interstitial, and correlated (interstitialcy). (b)	
	The energy profile for direct vacancy or interstitial site jumping of ions	
	and (c) the energy profile for correlated jumping. E_m and v_0 represent	
	the activation energy for ionic vacancy migration and the "jump"	
	frequency, respectively. Reproduced and adapted with permission	
	from Springer Nature Limited, Copyright 2019.[80]	22
1.9	Schematic representing high and low angle interface grain boundaries.	
	Reused with permission.[108]	24
1.10	Schottky barrier formation at a metal-semiconductor interface (a)	
	Equilibrium condition at the interface. (b) Reverse bias decreases	
	the barrier, prohibiting current flow. (c) Forward bias, decreases the	
	barrier promoting current flow. Adapted and redrawn.[109]	25

1.11 Schematic representing differing chemical compositions of silicate garnet and lithium containing garnets, Li₃, Li₅, Li₆, and Li₇. The polymorphic nature of Li₇ is shown with the possible cubic and tetragonal phases. Reprinted and adapted with permission from the American Chemical Society.[103] Copyright 2020 American Chemical Society.

- 1.12 Lithium occupies the Li(1) tetrahedral (24d) and Li(2) octahedral (48g)/distorted octahedral (96h) sites in cubic lithium stuffed garnets(≥ Li₅). (a) A high activation energy is required to move one Li⁺ ion from the Li(1) site to the neighbouring Li(2) in Li₃La₃Te₂O₁₂, demonstrating the low ion mobility observed in Li₃ garnets. The differing conduction mechanisms and their subsequent activation energies, (b) Route A and (c) Route B of Li₅La₃Nb₂O₁₂, Li₇La₃Zr₂O₁₂ respectively as displayed alongside inserts indicating the path by arrows. Route A displays the Li⁺ ion migration favoured in Li₅ garnets, between octahedral sites (48g/96h), omitting the tetrahedral site. Route B, indicates the ion migration path observed in cubic Li₇ garnets, with Li⁺ ion migrate via shared tetrahedra faces around Li(1) and Li(2) sites. Reprinted and adapted with permission from: M. Xu, M. S. Park, J. M. Lee, T. Y. Kim, Y. S. Park, E. Ma, Physical Review B, 2012, 85, 052301.[124] Copyright 2012 by the American Physical Society. 30
- 1.13 Preferred site, oxidation state of a range of elemental hypothetical dopants for Li₇La₃Zr₂O₁₂, calculated by DFT. The colour indicates the most stable cation site. The shade of the colour represents the defect energy with darker colours indicating the lowest defect energy in eV. Reprinted (adapted) with permission from the American Chemical Society. Copyright 2015 American Chemical Society.[129] 32
- 1.14 Logarithmic total ionic conductivity as a function of density for solid electrolyte Li_{6.19}Al_{0.27}La₃Zr₂O₁₂. Reproduce with permission from John Wiley & Sons, Inc.[146] Copyright 2016 The American Ceramic Society.
 33

1.16	Lithium garnet solid electrolyte trilayer architecture in a porous-dense- porous configuration. Reprinted from Hitz <i>et al.</i> .[156] Copyright 2018	
	with permission from Elsevier	36
1.17	SEM images of 3D-printed LLZO conformal (a)-(c) and self-supporting (d)-(f) architectures. Reproduced with permission from ref.[158] Copy-	
	right 2018 Wiley-VCH	37
1.18	Fracture surface of sintered freeze-tape-cast LLZO architectures. (a) Sintered porous-dense (140 μ m/36 μ m) bilayer. (b) Porous-dense- porous trilayer (130 μ m/37 μ m/130 μ m). SEM micrograph of the dense (c) 14 μ m layer and (d) porous scaffold. Reprinted (adapted) with permission from ref.[160] Copyright 2020 American Chemical Society.	38
2.1	A process schematic of a typical solid state reaction route. Stoichio- metrically weighed out reagents are ground in an agate pestle and mortar or mechanical mill to mix and reduce particle size. The pro- cessed particles are then placed in a box furnace for heat treatment	
2.2	to facilitate a reaction to form the required polycrystalline powder Images of commonly used ball mills with rotational schematics. (a) Planetary ball milling is employed by the Fritsch Pulverisetter 7 plane- tary ball mill. (b) Tumbler ball mill by Retsch (formerly Glen Creston).	42
	(c) Attrition mill Model 01-Lab Attritor from Union Process.(d) Mixer mill MM500 nano by Retsch that utilises vibration ball milling	44
2.3	To overcome agglomeration and flocculation ceramic particles are covered with a polymeric layer. This layer unfurls and keeps them in a stable suspension via steric repulsion	47
2.4	Simple schematic representation of the tape casting process. The prepared slurry is deposited on a supportive non-stick film (Mylar) that is held in place by a dynamic vacuum on the casting bed. A doctor blade set to the desired film height traverses over the slurry casting it on the Mylar.	49
2.5	Schematic representation of particle sintering process. Unsintered particles display large interstitial pores and high surface area. During sintering neck formation occurs by diffusion resulting in decreased pore and surface area. Pores and surface area continue to decrease resulting in a large fused structure	50
2.6	Schematic representation of liquid phase sintering process. An additive is added to the mixed particle state which under sintering conditions transforms into a liquid phase. Capillary forces lead to particles being	00
	drawn into rearrangement followed by grain growth and densification.	51

2.7	Schematic of the SPS technique for the sintering of powdered particu-	
	lates. Under uniaxial pressure, samples placed within the graphite die	
	under vacuum are subjected to high-frequency pulsed DC currents.	
	This process rapidly heats and densifies the powder via Joule heating.	52
2.8	(a) Schematic representation of Cu $1s$ electron ionisation followed by	
	a $2p$ electron dropping into the $1s$ electron level, the excess energy	
	released generates $K\alpha$ X-rays. (b) Bremsstrahlung, $K\beta$ and $K\alpha$ shown	
	on a characteristic Cu X-ray emission spectra. Illustration adapted	
	and reused.[180]	53
2.9	Bragg's law of reflection from a set of crystal planes of atoms (yellow	
	spheres). The X-rays are incident at an angle θ on lattice planes	
	separated by interplanar spacing distance d_{hkl} . Beams of identical	
	wavelength and phase are scattered of two differing atoms, the require-	
	ments for constructive interference are met when the path travelled	
	by the second beam $(2d_{hkl}\sin\theta)$ is equal to an integer multiple of the	
	wavelength of the radiation.	55
2.10	Illustration of a synchrotron with its individual sections, adapted	
	and reused with permission.[185] The sections are designated as: 1)	
	linear accelerator (linac), 2) booster synchrotron, 3) storage ring 4)	
	individual beam line, 5) front end, 6) optics hutch, 7) experimental	
	hutch, 8) control hutch, and 9) radio frequency cavity	58
2.11	Illustrative representation of XRD-CT data collection. The incident	
	X-ray I_0 hits the sample of interest which is predominantly phase	
	1 but includes a secondary phase (labelled 2). As the samples is	
	translated across the beam, diffraction patterns along the whole path	
	are collected by an area detector.	60
2.12	Schematic representation (a) of an SEM and the constituent parts.	
	Diagram (b) of electron volume within the sample and the various	
	resulting sample-electron interactions which may be utilised to provide	
	a range of different information pertaining to the sample	61
2.13	Diagram of X-ray photoelectron spectroscopy (XPS) illustrating the	
	basic mechanism of X-rays hitting the surface of a sample. The X-rays	
	subsequently interact with core level electrons which are emitted due	
	to energy absorption from incident photoelectrons	64
2.14	Experimental setup of an XAS experiment, incident radiation I_0 from a	
	synchrotron source is passed through a monochromator before hitting	
	the sample. Detectors are subsequently able to measure resultant	
	X-ray fluorescence $I_{\rm f}$ and transmitted X-ray intensity $I_{\rm t}$	66
2.15	Schematic example of a XAS spectrum highlighting the three regions	-
-	of interest: Pre-edge, XANES and EXAFS	67

2.16	Illustrative representation of Faunhofer (left) and Mie diffraction theory (right). Fraunhofer (left) does not account for phenomena such as absorption, refraction or reflection and works on the principle of diffraction. The theory is best suited to larger particle sizes. Mie theory (right) takes particle scattering phenomena into account, particle size analysis is possible to 10 nm, the materials refractive index is however required	68
2.17	Gaussian distribution with the three axis values for quantification of particle size	69
2.18	Schematic representation of Archimedes' principle used with a spe- cialised balance to measure the density of a sample	71
2.19	Image of a full assembled (left) Swagelok cell with exploded view (right). Individual parts of the Swagelok cell are labelled in the diagram.	72
2.20	Schematic representation of the relationship between applied voltage $E(t)$ and output current I(t) in a steady state condition. The subsequent ratio of both sinusoidal responses results in the impedance of the system.	74
2.21	Schematic representation of a Nyquist plot of the real impedance vs imaginary impedance showing the response of an electron resistant material with partially blocking electrodes	75
2.22	Typical [RC] equivalent circuit composed of resistors and capacitors for fitting impedance spectroscopy measurements	76
2.23	Schematic representation of GCPL where (a) the applied current is constant until a voltage limit is reached and a subsequent reverse bias is applied until the minimum voltage limit is reached thereby completing a full cycle. (b) GC with removed voltage limits to evaluate the performance of a solid electrolyte at forward and reverse currents of ever increasing magnitude until failure occurs	79
2.24	Characteristic voltammogram (a) displaying a current vs voltage plot. The E_{pc} and E_{pa} show peak potentials for cathodic and anodic reductions respectively. I_{pc} and I_{pa} show the peak cathodic and anodic currents of the redox reactions. The potential wave form (b) during cyclic voltammatry shows the voltage being swept forward before reaching a defined maximum limit, where it is subsequently reversed to a defined minimum.	81

- 3.2 Lattice parameter results for calcined samples obtained from Rietveld refinement analysis (blue star). Garnet lattice parameters do not follow linear substitution as expected by Vegard's law, thereby indicating that an inclusion of manganese is unlikely. Further supportive evidence is seen in the linear increase of the fraction of secondary phase La₃LiMnO₇ (green diamond). The error bars of the measured lattice parameters are masked by the symbol due to them being too small.

- 3.5 Figure displaying (a) Rietveld refinement of powder X-ray diffraction of 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.105) after SPS. Bragg reflections of cubic LLZTO and RP1, La₄LiMnO₈ phases are shown below. The fit is in good agreement with the collected data having an R_{wp} = 11.61 % and $\chi^2 = 3.68$. A dashed box displays an enlarged region from 30° to 35° (b), showing significant Bragg peaks from RP1 La₄LiMnO₈. . . 94

3.6	SEM images and EDX spot analysis of 'Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ ' (a) $x = 0.035$ (b) $x = 0.07$ (c) $x = 0.105$. Pellets were broken in half for a representative cross section; the subsequent fracture surface appears to be transgranular in nature with minimal visible grain boundaries present. EDX spot analysis on visible grain boundaries as well as non-grain boundary regions are highlighted by red circles. Results revealed elevated levels of manganese at the grain boundaries with little to none on particles surfaces, suggesting negligible incorporation of manganese into the grains. EDX results related to locations 1-12 are tabulated in Table 3.1
3.7	Nyquist impedance plot 'Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ ' ($x = 0, 0.035, 0.05, 0.07, 0.105$) with Au, Li ⁺ blocking electrodes performed at 20 °C, the inset shows the high frequency response. Equivalent circuit fits may be seen as a solid lines, with the equivalent circuit displayed in the graph. This equivalent circuit was used for all samples apart from $x = 0.105$ which required an extra RQ element in series 97
3.8	Activation energy of garnet $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ and garnet composite ' $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4-x}\text{Mn}_x\text{O}_{12}$ ' ($x = 0, 0.035, 0.05, 0.07, 0.105$) samples. The results show a largely invariant activation energy
3.9	(a) Electrochemical impedance spectroscopy results of symmetric Li Li cell for 'Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ ' ($x = 0, 0.035, 0.05, 0.07, 0.105$) performed at 25 °C. (b) Magnification of the high frequency response with (c) displaying the final magnification in order to capture clear resolution. Equivalent circuit fits may be seen as solid lines, fitting required the use of two equivalent circuits: [RQ][RQ] for $x = 0$ and 0.035 whilst all other samples required the addition of an extra [RQ]. Equivalent circuits are summarised in Figure A.2
3.10	Galvanostatic cycling of LLZTO and LLZTO composites in a Li Li symmetrical cell at 25 °C under no external pressure. The current was increased every hour by 10 μ A cm ⁻² until a short circuit occurred. Failure of LLZTO occurs at a CCD of 0.1 mA cm ⁻² . As the secondary phase is increased to $x = 0.035$, $x = 0.05$ and $x = 0.07$ an increase in CCD is observed to 0.15 mA cm ⁻² , 0.22 mA cm ⁻² and 0.3 mA cm ⁻² respectively. A limit is however observed at $x = 0.07$ where after the
0.11	performance is decreased to 0.12 mA cm for $x = 0.105$ 102

3.11 Manganese containing pellets displayed a darkening following Li-metal stripping and plating. The darkening appears to be spread significantly across the pellet indicating redox behaviour of the secondary RP1 phase.103

3.12	Cyclic voltammetry of $x = 0.05$ was conducted at 25 °C between 0
	V and 5 V. Initial cycles displays stable behaviour of the composite
	solid electrolyte with the characteristic lithium deposition peak at 0.5
	V. However, cycle 5 sees the appearance of an oxidative peak at 4.2
	V, indicated by *. CV was conducted with a sweep rate of 100 $\mu \mathrm{V}$
	$\rm s^{-1}$ at 20 °C, Au and Li-metal were attached to the pellet as working
	and counter electrode respectively
3.13	XPS measurements of as sintered, 'pristine' and 'dark' LLZTO and
	Mn-LLZTO pellets ($x = 0.07$) (a) Spectra of Mn 2p, red displays the
	results from the sintered non-cycled 'pristine' sample, whilst black
	displays the results from the 'dark' regions following Li-metal attach-

- 3.14 X-ray absorption spectroscopy (XAS) measurements (a) of the Mn K edge for the light and dark regions of composite LLZTO as well as Mn³⁺ standard Mn₂O₃ and the Mn⁴⁺ standard MnO₂. All samples are observed to lie between both standards revealing a mixed oxidation state of Mn³⁺ and Mn⁴⁺. The dashed box highlights the pre-edge region displayed in (b), pre-edge spectra appear to hold a slight bowing upwards, similar to that of MnO₂, indicative of propensity to a Mn⁴⁺ configuration.
- 4.1 (a) Full 9×9 array of cubes, the FEM geometry represents the model for LLZTO garnet composite. (b) Location of the disc in the geometry representing the secondary phase La₄LiMnO₈, it may be seen as residing on the grain boundary indicated by a red arrow. (c) Application of the current conservation around the geometry to apply continuity equations. (d) Electrical insulation boundary conditions assigned to the external surfaces. The top (e) and bottom (f) surfaces were assigned electrical terminals, and a potential of 1 V was applied. 115

- 4.3 Summed diffraction patterns (900 pixels, 30 μ m x 30 μ m area) extracted from the XRD-CT measurements for composite samples 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂': x = 0.035 and 0.07 (pristine, light, and dark) the data has been normalised to the main garnet phase. The dashed box indicates the region of interested magnified in Figure 4.4. 120

- 5.1 Thermal heating regime for sintering LLZO based solid electrolyte tapes.137
- 5.2 Calculated Rietveld refinement fit and PXRD of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ after 950 °C calcination. Bragg reflections of the cubic target phase are shown below. The fit is in good agreement with the collected data having an $R_{wp} = 8.15$ % and $\chi^2 = 7.18...$ 138
- 5.4 Particle distribution graphs for $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$. (a) The particle distribution of 'as synthesised' LLZTO displayed a Gaussian distribution with a calculated D₅₀ of 13.5 μ m. Particle reduction using the Retsch MM500 at 7 Hz yielded a bimodal distribution with a particle D₅₀ of 5.5 μ m. (c) Particle size following ball milling at 25 Hz displayed a bimodal distribution with a D₅₀ of 1.2 μ m. 140

5.5	PXRD patterns of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO). The 'as synthe-
	sised' (black) pattern displays phase pure cubic LLZTO prior to
	further processing. The addition of the dispersant, Hypermer KD1
	(red) displayed a small degree peak broadening of the cubic LLZTO
	pattern which is attributed to the addition of the polymeric coating
	on LLZTO particles. Sintering of the LLZTO green tape with 1.2 $\mu {\rm m}$
	particles without mother powder (blue) resulted in decomposition of
	the phase. The addition of mother powder during sintering (green)
	however resulted in the retention of the cubic LLZTO phase with
	small quantities of ZrO_2 and $La_2Zr_2O_7$ impurities indicated by \circ and
	* respectively

5.7	Cross sectional SEM micrographs of green tape $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ at
	varying magnifications. The cross sectional fracture surface displays a
	well dispersed polymer network, indicating complete and homogeneous
	covering of LLZO particles. The thickness of the green tape is seen to
	be a uniform <i>ca.</i> 100 μ m
5.8	Dried $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ green tape punched into a disc of 18 mm
	diameter. The surface shows a good dispersion with a homogeneous,
	streak free surface

- 5.12 Cross sectional SEM micrograph of sintered $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape displaying an intergranular fracture mode. Mother powder was used to prevent the loss of lithium and retain the desired phase during the sintering process. The fracture surface of the tape however reveals a high porosity, the relative density was estimated at *ca.* 45 %. 148
- 5.13 SEM micrographs (a)-(b) and EDX maps of (c) La, (d) Si, (e) Zr and (f) Ta of sintered Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ tape with Li-Si based (AVX) sintering aid. (a) The Cross sectional SEM of the sintered tape displays an intergranular fracture mechanism with visible porosity in the structure, the relative density was estimated as 65 %. (b) Arrows indicate the visible presence of agglomerated Li-Si sintering aid within the tape microstructure and was further confirmed by EDX (d) displaying the Si signal where a relative 5.7 at. % Si was measured.150

5.16	SEM micrographs display the fracture surface of the sintered garnet
	$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape using Li_2O as a sintering aid. The fracture
	surface is of an intergranular nature. LLZTO particles are seen to
	have fused together increasing the relative density of the tape, which
	was estimated at 88 %. A uniform thickness of $ca.$ 90 $\mu {\rm m}$ has been
	maintained during sintering

- 5.19 Calculated Rietveld refinement for powder X-ray diffraction of garnet $\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$. Bragg reflections of cubic Fe-LLZO and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, $\text{Li}_8\text{La}_{18}\text{Fe}_5\text{O}_{39}$, $\text{La}_2\text{Zr}_2\text{O}_7$, Li_2ZrO_3 impurity phases are shown below. The fit is in good agreement with the collected data having an $R_{wp} = 7.13$ % and $\chi^2 = 6.15...$ 157

- 5.21 (a)-(b) SEM micrographs and EDX maps of (c) La, (d) Ta, (e) Fe and (f) Zr for Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂/Li_{6.4}Fe_{0.2}La₃Zr₂O₁₂ (LLZTO/Fe-LLZO) bilayer green tape. (a) Bilayer tape cross section, a division between the two doped LLZO phases is marked by a dotted yellow line. The microstructure displays well dispersed particles within a polymer matrix with some textural difference between LLZTO and Fe-LLZO. (b) Green tape region subjected to EDX analysis. (d) Ta shows the division of the two LLZO analogues where the signal is only detected on the LLZTO side. (e) Low Fe levels resulted in predominantly background signal. An impurity of Fe is however seen and is attributed to cross contamination during sample preparation. (f) Due to the difference in moles of Zr a difference in intensity was observed between the two doped LLZO phases. 160

A.2 Equivalent circuit models for AC impedance with Li blocking electrodes. 174

A.3 Equivalent circuit models for AC impedance with Li-metal electrodes. 175

A.4	Collated results from CCD measurements for ' $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ '
	(x = 0.05, 0.07, 0.105). Initial CCD appears to increase before decreas-
	ing at $x = 0.105$
B.1	Powder X-ray diffraction pattern highlighting the contained impurities
	of final synthesised $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$. Following 52 hours heating,
	cubic stabilised Fe-LLZO held several impurities following synthesis,
	these included: $Li_8La_{18}Fe_5O_{39}$ (\blacklozenge), Li_2ZrO_3 (\clubsuit), pyrochlore $La_2Zr_2O_7$
	(*), and tetragonal $Li_7La_3Zr_2O_7$ (\blacktriangle)
B.2	Early iteration of LLZTO tape casting failure. The green tape is seen
	to have cracked during and displays no flexibility or malleability. In
	addition to this a rough surface texture may be seen. This indicates
	poor particle dispersion during slurry formation
B.3	Early iteration of LLZTO tape casting failure. The green tape displays
	an inhomogeneous consistency and thickness. Uncoated regions of
	mylar may be seen displaying air pockets within the formed slurry 178
B.4	18 mm dia. LLZTO green tape failure. The green tape displays
	an inhomogenous consistency. Furthermore, pitting from bubble
	formation during slurry formation and casting may be seen 179
B.5	Sintering failure of LLZTO tape. The tape displayed complete loss of
	structural strength following sintering. Pitting from bubble formation
	during sintering are observed on the surface. Furthermore, a rough
	surface displays inhomogeneous particle distribution during slurry
	formation

List of Tables

2.1	Concise collection of material information extractable from peak posi-	55
		00
2.2	XAS edges with responding orbital notation	65
2.3	Capacitance values with their corresponding ceramic sample regions.	
	Adapted and reused with permission from John Wiley and Sons.[192]	77
3.1	List of elemental composition in atomic percentage taken from EDX	
	spot analysis of garnet composites, numbers listed relate to numbers	
	displayed in Figure 3.6. Bold red numbers indicate elevated levels of	
	Mn. Due to EDX being unable to detect lithium elemental weight	
	percentage ratios are only relative to detected elements	96
3.2	AC impedance fit results and ionic conductivity estimates from fitting	
	equivalent circuit components for LLZTO and Mn-LLZTO samples	
	('Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ ') with secondary phase La ₄ LiMnO ₈ . Li ⁺	
	blocking Au electrodes were used and all measurements were under-	
	taken at 20 °C	97
3.3	Estimated electronic conductivity, ionic and electronic transference	
	numbers of LLZTO and Mn-LLZTO samples (' $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$	$_{2}')$
	with secondary phase La_4LiMnO_8	99
3.4	Estimated AC impedance equivalent circuit fit results for individual	
	components for $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ and $'Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ '	
	composites with secondary phase La_4LiMnO_8 . AC impedance was	
	conducted with Li-metal electrodes at 25 °C. Subscripts $b,\ In,$ and Sp	
	represent bulk, interface, and secondary-phase respectively 1 $$	100
4.1	Rietveld refinement results from summed diffraction patterns for	
	manganese bearing 'Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ ' composite samples x	
	= 0.035 and 0.07. The phase fraction decreases systematically from	
	the 'pristine' to 'dark' states whilst lattice parameters remain invariant.	119
4.2	Tabulated FWHM and peak integral results. for samples $x = 0.035$	
	and 0.07 ('Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _{x} O ₁₂ '), 'pristine', 'light' and 'dark'	122

5.1	Summary of LLZTO and Fe-LLZO slurry formulation constituents 136
5.2	Summary of particle size analysis for the 'as synthesised', 7 Hz and
	25 Hz samples. D_{10} , D_{50} , D_{90} and the Span are displayed. The
	results indicate that the high energy milling reduces the particle size
	of LLZTO particles
5.3	Tabulated Rietveld refinement details of $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$. The
	space group, lattice parameters and weight fraction of each present
	phase is indicated. The largest impurity phase detected was tetragonal
	LLZO at 11.1 %
Δ 1	Collated results from Biotyold refinement of pro SPS garnet samples
Π.1	Conated results from filetveid remement of pre-51.5 garnet samples
	$Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$
A.2	Collated results from Rietveld refinement post-SPS garnet samples
	'Li _{6.4} La ₃ Ta _{0.6} Zr _{1.4-x} Mn _x O ₁₂ '. Garnet lattice parameters do not follow
	linear substitution as expected by Vegard's law, thereby strongly
	indicating no manganese cation substitution within the lattice. Further
	supportive evidence is seen in the linear increase of the secondary
	phase La_4LiMnO_8

List of Abbreviations

- AC Alternating Current
- \mathbf{ASR} Area specific resistance
- **ASSB** All solid state battery
- ${\bf BBP}$ Benzyl butyl phthalate
- **BLM** Brick Layer Model
- **CCD** Critical Current Density
- \mathbf{CPE} Constant Phase Element
- \mathbf{DC} Direct Current
- ${\bf DESY}$ Deutsches Elektronen-Synchrotron
- EDX Energy Dispersive X-ray Spectroscopy
- **EIS** Electrochemical Impedance Spectroscopy
- **FAST** Field Assisted Sintering Technique
- **FEA** Finite Element Analysis
- ${\bf FEM}$ Finite Element Method
- \mathbf{HZB} Helmholtz-Zentrum Berlin
- LDA Laser Diffraction Analysis
- LLZO $Li_7La_3Zr_2O_{12}$
- **LLZTO** $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$
- MEK Methyl ethyl ketone
- $\ensuremath{\mathbf{MIEC}}$ Mixed Ionic Electronic Conductor
- **PVB** Polyvinyl butyral

- **PXRD** Powder X-ray Diffraction
- ${\bf RP}$ Ruddlesden-Popper
- ${\bf SEM}$ Scanning Electron Microscopy
- ${\bf SOFC}$ Solid Oxide Fuel Cell
- ${\bf SPS}$ Spark Plasma Sintering
- **TGA** Thermogravimetric Analysis
- ${\bf XAS}$ X-ray Absorption Spectroscopy
- \mathbf{XPS} X-ray Photoelectron Spectroscopy
- **XRD-CT** X-ray Diffraction Computed Tomography
- \mathbf{YSZ} Yttria-stabilized Zirconia

List of Publications and Presentations

Contribution to Peer Reviewed Journals

 I. McClelland, H. El-Shinawi, S. G. Booth, A. Regoutz, J. Clough, S. Altus,
 E. J. Cussen, P. J. Baker, S. A. Cussen. The Role of the Reducible Dopant in Solid Electrolyte-Lithium Metal Interfaces. Chemistry of Materials, 2022.

Conference Presentation

Oral Presentations

- Material Science and Engineering Post Graduate Researcher Conference, University of Sheffield, April 2021 & 2022
- Faraday Institution Early Career Researcher Conference, University of Warwick, November 2022
- Materials Research Society, Boston, Massachusetts, November 2022

Poster Presentations

- 5th Royal Society of Chemistry Energy Sector Early Career Chemistry Symposium, Burlington House, London, November 2021
- Electrochem 2022, The University of Edinburgh, September 2022
- Royal Society of Chemistry Solid State Chemistry Group Christmas Meeting, University of Cambridge, December 2022
- LLZO4WC 4th World Conference on Solid Electrolytes for Advanced Applications: Garnets and Competitors, Tromsø, Norway, September 2023

Chapter 1

Introduction

As the world grapples with a growing need for energy and confronts the existential threat of climate change, the necessity to reduce our dependence on hydrocarbonbased energy has never been more critical. Confronted with the unprecedented increase in CO_2 and other greenhouse gases in the atmosphere, the pursuit of clean, renewable, and sustainable energy solutions for power generation and transportation has emerged as a crucial challenge of the 21st century. In response, governments worldwide have undertaken significant actions to resolve the rise in global greenhouse emissions, including expansions in solar and wind energy generation, alongside policy initiatives aimed at phasing out internal combustion engines. Whilst positive, the adoption of clean technology still presents several challenges. For instance, the intermittent nature of solar and wind technologies can result in shortfalls during peak demand periods and overproduction during off-peak times. To address this issue, the deployment of efficient energy storage becomes crucial. Storing surplus energy generated during low demand periods and bolstering based loads during high demand phases the technology provides stability regardless of the intermittent nature of solar and wind energy generation. Importantly, the use of energy storage not only supports renewable energy generation but also has significant implications for the transportation sector. It offers the opportunity to replace highly polluting internal combustion engine cars with no-emissions, low pollution electric vehicles.

Batteries are the technology that is best placed to meet the demands of energy storage for both these sectors. Scalability is a key factor that enables the successful deployment in various applications, including large scale grid storage devices, batteries for electric vehicles, and even microbatteries for small electrical devices. Some of the most significant progress has been made in the transportation sector, where the transition from internal combustion engine to highly efficient electric motors has been facilitated by advancements in battery technology. The advantages are so profound that numerous governments worldwide have committed to banning the sale of internal combustion cars by 2040[1] alongside ambitious targets for the widespread adoption of batteries in maritime and aviation industries. With such a rapid and significant shift in technologies, the need for a global research effort towards high performing, cheap and sustainable batteries has never been more important.

In 1780, Italian physician, physicist, and biologist, Luigi Galvani, discovered that the muscles of dead frogs legs contracted when hung from an iron railing with brass hooks connected through the spinal cord.[2] Believing it to be a form of electricity arising from the cells of the frog he coined the phenomenon "animal electricity". Building on Galvani's findings, fellow Italian physicist and chemist Alessandro Volta initiated a series of experiments believing the observed phenomenon to be a result of dissimilar metals joined by a wet conductive medium. By 1800 the first recorded demonstration of an electrochemical battery was presented by Volta. Coined the 'Voltaic Pile' the configuration involved the simple stacked configuration of individual copper and zinc discs separated by brine soaked paper.[3] The stacked configuration of individual galvanic or voltaic cell was able to generate a electric current by a simple redox reaction.

By the early 1800s an iteration of the Volta's pile was produced by Scottish chemist William Cruickshank.[4] The 'Trough battery' devised a solution to problems faced by the voltaic pile, namely electrolyte leakages, by placing copper and zinc plates horizontally in a box. However, providing only a modest current and large fluctuations in voltages, these early batteries did not provide an effective source of electricity past a laboratory setting.[5]

A more reliable source of current and voltage was provided in 1832 by English chemist John Frederic Daniell. With a theoretical open circuit voltage of *ca.* 1.1 V and a more stable current the 'Daniell cell' became the first practical source of electricity.[6] However, it was not until 1860 that the most commonly recognisable battery was invented by French physicist Gaston Planté.[7] For the first time, the lead acid battery provided a rechargeable electrochemical energy source with high currents. The efficacy of the battery was such that after several iterations of improvement the lead acid battery is still used to this day as primary energy source for starter motors in internal combustion engine cars. Forty years later, as a direct competitor, Swedish engineer and inventor Waldemar Junger created the NiCd battery achieving higher current loads, energy density and longevity than the lead acid battery.[8] More recently, the development of the nickel metal hydride battery (NiMH),[9] has led to the global rise of the portable electronics industry.

M. Stanley Whittingham established the first use of a lithium energy storage device in 1974. Conceiving intercalating electrodes, he demonstrated Li^+ ion intercalation between a TiS_2 anode and lithium-aluminium cathode.[10] Intercalation electrodes refer to a material capable of accommodating ions between its layers or within its structure during the process of charging and discharging in a battery. Allowing for the reversible insertion and extraction of ions, making a battery rechargeable.
Complementing his work in 1980, American chemist John B. Goodenough replaced the cathode with a $LiCoO_2.[11]$ However, real success was not realised until 1985, when Japanese chemist Akira Yoshino replaced the lithium metal anode with carbonaceous material fabricating the first lithium-ion battery for which he received a patent.[12] The subsequent configuration was commercialised and mass-produced in 1991 by Sony.[13] The impact of the invention of the lithium-ion battery on today's society has been so profound that in 2019, M. Stanley Whittingham, John B. Goodenough, and Akira Yoshino were awarded the Nobel Prize in Chemistry.[14, 15]

In 2023, lithium-ion batteries permeate every aspect of modern life. From portable electronics such as laptops, mobile phones, or headphones to power tools. More recently, they have been leading the way in facilitating the transition from internal combustion engine cars to electric vehicles. Initially pioneered by disruptive companies like Tesla, this shift is now being adopted by the more established vehicle manufacturers. To alleviate power grid fluctuations, large scale stationary energy storage sites such as the 150 MW Hornsdale Power Reserve located in Australia are being commissioned.[16] Set up to harness the energy created by the co-located wind farm, the installation is aiding Australia's transition to renewable wind and solar energy. Not only are batteries aiding the energy transition for electric vehicles and grid storage, they're revolutionising the face of aviation, where in 2021 Rolls Royce's 'Spirit of Innovation' become the world's fastest all-electric aircraft, reaching a top speed of 555.9 km h⁻¹.[17] Innovations have continued as, in 2022, the world's first all-electric ferry, the MS Medstraum, embarked on its zero-emission maiden voyage from the port city of Stavanger, Norway.[18]

The high energy and power densities of the lithium-ion batteries has positioned them as the leading electrochemical storage device of choice. Consequently, with the continuous rise in demand for battery performance, ambitious targets for have been set to meet the needs of modern life. These targets aim to achieve volumetric and gravimetric energy densities ranging between 750 - 950 Wh 1^{-1} and 320 - 360 Wh kg⁻¹, respectively, by 2030.[19, 20] Meeting these ambitious objectives will require further advancements in lithium batteries technology with current best performing commercially available cells attaining practical gravimetric energy densities of *ca.* 270 Wh kg⁻¹.[21, 22]

1.0.1 The Lithium-ion Battery

The conventional lithium-ion battery is a galvanic electrochemical cell that relies on the transport of Li⁺ ions between two opposing electrodes as displayed in Figure 1.1. Separated by a porous polymeric membrane, the two opposing electrodes. In a electrochemical cell the electrodes are known as an anode and a cathode and are immersed in an electrolytic solution. At the anode an oxidation reactions occur whereas at the cathode a reduction reaction. However, as in the case of a battery, such as the Li-ion battery, both reactions may occur when the battery is charging or discharging. As such it is better to refer to the electrodes as positive and negative; where, the electrode with the higher potential than the negative is named as the positive. The danger of using anode and cathode to identify the positive and negative electrodes is that during discharge the positive electrode is a cathode and the negative the anode. Conversely, on charge this is reversed and the positive electrode becomes the anode whilst the negative electrode is the cathode. Within the battery community however, the terms anode and cathode have become synonymous with identifying the negative electrode as the anode, often graphite, whilst the cathode the positive electrode often a layered transition metal oxide. For simplicity, from here on the terms anode (negative electrode) and cathode (positive electrode) are used to identify the electrodes in a Li-ion battery.

Operation of the electrochemical cell proceeds such that during discharge lithium atoms at the anode are ionized into an organic lithium salt electrolyte and move towards the cathode. Simultaneously, electrons move from the anode through an external circuit to the cathode thus providing an electric circuit. Under an externally applied current the process is reversed and Li⁺ ions flow from the cathode back to the anode in a process known as charging. This (de)intercaltion of ions results in the insertion (intercalation) and extraction (dintercalation) of lithium ions from the electrode structure. This movement of lithium ions between the positive and negative electrodes induces a change in the oxidation state of the electrode materials. In the case commercially available lithium-ion battery as seen in Figure 1.1 the electrochemical half reactions may be defined as:

At the negative (anode) electrode

$$LiC_6 \rightleftharpoons Li^+ + e^- + C_6$$

At the positive (cathode) electrode

$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$

Full reaction

$$\underbrace{LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2}_{\text{left to right, displayed right to left, shares}$$

left to right: discharge, right to left: charge

To enable this reversible flow requires the electrolyte to demonstrate high ionic conductivity while maintaining low electronic conductivity, allowing for ionic transfer without enabling electron transfer, which would lead to short circuit in the cell. Additionally, the polymer separator plays a crucial role in preventing short circuits, by keeping the electrodes separated while also allowing the uninhibited transport of Li^+ ions. The mechanism of charging and discharging the electrochemical cell is known as 'cycling' and a simplified operational diagram of a common graphite- LiCoO_2 lithium-ion battery is presented in Figure 1.1. Each component plays a crucial role in the performance or amount of energy stored in the electrochemical cell and much work has been conducted on the discovery and optimisation of new materials to improve lithium-ion battery performances.



Figure 1.1: Schematic representation of a conventional lithium-ion battery. The negative anode material is graphitic carbon formed by layers of carbon atoms (black). Whilst the positive, cathode is layered-oxide LiCoO₂, the two electrodes are separated by a porous polymeric membrane to prevent short circuiting of the cell. During charge and discharging of the battery, Li⁺ ions (green) are deintercalated from between the layers of the respective electrode and subsequently transported through the liquid electrolyte - a solution of LiPF₆ dissolved in ethylene carbonate and dimethyl carbonate - before intercalating into the opposing electrode, simultaneously electrons move around the external circuit.

As mentioned, the operation of the battery is governed by the movement and storage of Li⁺ ions between the two opposing electrodes. This intercalation and deintercalation redox mechanism between the two electrodes are driven by the electrochemical potential, or voltage E_{cell}^0 of the galvanic cell and may be defined by the relationship

$$E_{cell}^0 = -\frac{\Delta G}{nF} \tag{1.1}$$

where the ΔG is the change in Gibbs free energy, n the number of electrons transferred in the balanced half reaction, and F is Faraday's constant. If the Gibbs free energy is negative ($\Delta G < 0$) then the reaction becomes spontaneous driving a current through the externally applied circuit. In a lithium-ion battery, the event is associated with the discharge of the battery resulting in a redox reaction between the two electrodes whereby Li⁺ ions flow from the negative anode to the positive cathode. Once $\Delta G = 0$ the cell has reached equilibrium, and no further reactions takes place and the cell is said to have been discharged. During charging, an external power source is applied to the battery and the current is reversed, ΔG once again becomes negative and facilitates the transfer of Li⁺ ions from the cathode to the anode. Important to note is that in a battery, the electrode that releases atoms during discharge is always known as the anode and is always negative, the electrode that absorbs electrons is known as the cathode and is always positive. This is against conventional nomenclature but is used to simplify electrode assignments in a rechargeable cell such as lithium-ion battery. Characterising the electrochemical potentials across the cell is crucial to battery operation. Known as the open circuit potential (E_{cell}^0) , or open circuit voltage (OCV) the potential is measured under the absence of current flow and may be calculated from the electrochemical potentials of the individual electrodes:

$$E_{cell}^0 = E_{anode}^0 - E_{cathode}^0 \tag{1.2}$$

The electrochemical potential relates to the driving force of the chemical reactions. However, the storage and subsequent release of Li^+ ions led to a further key metric of lithium-ion batteries, the quantification of the amount of energy contained in the cell as a result of the stored electrons and Li^+ ions. Two key energy density metrics describe this: gravimetric or specific capacity, indicating the energy stored per unit weight of a battery, and the volumetric capacity signifying the energy stored per unit volume of a battery. The specific battery capacity may be calculated with Equation 1.3 and generally holds units of mAh g⁻¹.

$$Q_g = \frac{nF}{M_w} \tag{1.3}$$

Where n is the number of charge carriers, F is Faraday's constant and M_w the molecular weight of the electrode material. The volumetric energy density is characterised by

$$Q_V = Q_g \cdot \rho \tag{1.4}$$

where Q_g is the specific capacity, and ρ the density of the electrode. The volumetric energy density is often expressed in units of mAh cm⁻³. The overall theoretical and accessible specific capacity of the lithium-ion battery is however limited to the electrode with the lowest capacity. In commercial lithium-ion batteries the anode is often composed of a graphite with a theoretical specific capacity of 372 mAh g⁻¹, currently no commercially available cathode exceeds this benchmark. As a consequence, the overall capacity is often limited by the cathode with the early adopted LiCoO₂ cathode holding a theoretical capacity of 274 mAh g⁻¹. Moreover, commercially attainable specific capacities are lower than theoretical values, with LiCoO₂ commonly attaining 145 mAh g⁻¹, far below that of the graphite anode.[23] Research efforts over the years have therefore been focused on improving and discovering new transition metal oxide cathodes to increase the attainable specific capacity. The bulk of the new discovered materials may be generally paced into three classes: layered oxides, spinel oxides and polyanion oxide/olivines.[23]

Layered oxides include LiCoO₂ (LCO) LiNiO₂ (LNO), and hold a rhombohedral, α -NaFeO₂ structure ($R\overline{3}m$) with alternating planes of the rock salt structure with cubic close-packed planes of oxygen ions. Lithium cations reside between layers of transition metal and oxygen in a ABCABC sequence. Within the lithium plane, the conduction of Li⁺ ions is facilitated by a conduction network formed by adjacent tetrahedral voids that share faces with three octahedra. Upon the removal of lithium, the oxygen layers however rearrange into a hexagonal close-packed plane.[24] Whilst holding a high theoretical capacity, practical attainable capacities for LiCoO₂ are significantly lower, achieving only roughly 180 mAh g⁻¹.[25] Coupled with questions around ethical mining[26, 27] and the toxicity[28] has led to several co-doping strategies to reduce the reliance on cobalt, resulting in the discovery of the notable material known as NMC (LiNi_xMn_yCo_{1-x-y}O₁₂) in 2001.[29]

First proposed in 1983 by Thackery *et al.*, the most prominent cathode of the spinel class oxides is LiMn_2O_4 (*Fd3m*). Closely related to a α -NaFeO₂ layer structure the spinel differs in cation distribution among available octahedral and tetrahedral sites.[30] Empty, low energy barrier octahedral sites facilitate the conduction of Li⁺ ions from one free tetrahedral site to another. Whilst this class of cathode benefits from the abundance and low cost of manganese, it is plagued by performance issues, e.g. manganese dissolution which leads to transition metal build-up at the anode and large capacity fade.[23, 31]

In recent years, LiFePO₄ (LFP), has seen a renaissance and is set to be a prime candidate for large scale grid storage. LFP was initially identified in 1996 as part of the polyanion cathode class with an olivine related structure. It comprises relatively inexpensive, abundant earth elements that have a comparatively low environmental impact for minerals and metal use and exhibits excellent safety.[32, 33] Coupled with high cycle life and capacity retention, it has become a leading cathode of choice for large scale battery energy storage systems. LFP exhibits an orthorhombic structure (*Pnma*) with PO₄ tetrahedra located between the LiO₆ and FeO₆ octahedra. A disadvantage of LFP however is the a low average potential and low electrical conductivity often restricting its use in high performance applications.[24, 34–36]



Figure 1.2: (a) Layered oxide $LiCoO_2$; monovalent Li^+ (green) and trivalent Co^{3+} (blue, CoO_6 octahedra) ions are located at octahedral sites in a cubic close-packed array of oxide ions (red) in alternating planes of rock salt structure. (b) Spinel $LiMn_2O_4$; $Mn^{3+/4+}$ ions (purple, MnO_6 -) are octahedrally located with Li^+ (green) in tetrahedral sites in a cubic close-packed array of oxide ions (red). (c) Olivine structured $LiFePO_4$; divalent Fe^{2+} (brown, FeO_6) and monovalent Li^+ (green) octahedrally located, whilst PO_4 tetrahedron (grey) are located between.

Whilst the specific capacity is governed by the inherent properties of the electrode material to store Li^+ ions, a further important metric of lithium-ion batteries is energy density. This metric is often used to compare cells of different chemical compositions as a function of their nominal voltage. Expressed as gravimetric (Wh kg⁻¹) and volumetric (Wh L⁻¹) energy densities, the battery standard may be calculated by multiplying the nominal battery voltage by the respective capacity, highlighting the importance of capacity and voltage in the determination of battery performance. Increasing the voltage attainable is therefore desirable in order to achieve higher energy densities cells which has led to several high voltage cathodes being developed.

Operating at higher voltages however results in several challenges faced by the lithium-ion battery. High voltage cathodes experience degradation mechanisms including but not limited to particle cracking, transition metal dissolution, dendrite formation and irreversible structural degradation. [37, 38] Elevating the voltage levels of lithium-ion batteries presents a further challenge from unwanted side reactions arising from the use of liquid electrolytes. Typically, commercial liquid electrolytes rely on lithium salts such as $LiPF_6$, dissolved in a carbonate solution. If operated outside of the electrochemical stability range, these electrolytes may undergo a reduction at the anode or oxidation at the cathode surface, generating various gaseous species. This electrolyte degradation can lead to significant pressure build-up within the cell, causing swelling and potential thermal runaway. Ultimately, this could result in the catastrophic failure of the cell, leading to potential explosions, fires, and the release of harmful gases, including HF.[39] One beneficial side reaction however is the formation of passivation layer known as the solid electrolyte interface (SEI). The SEI forms on the electrode surface as a result of decomposition products of the electrolyte. This process occurs when the redox potential of the electrodes falls beyond the electrochemical window of the electrolyte. [40] The formation of this interface occurs during the first initial cycle of a lithium-ion battery and blocks electron transfer between electrodes and the liquid electrolyte whilst permitting the transfer of Li⁺ ions.

As previously noted, extensive research efforts have been conducted into the discovery of new cathode materials to increase their specific capacity, as the energy density in lithium-ion batteries is not solely reliant on voltage but is significantly impacted by the specific capacity. An alternative method to increase the energy density is by increasing the specific capacity of the anode. The utilisation of lithium metal anodes has long been regarded as the holy grail for lithium-ion batteries. The lithium metal anode exhibits a low density of 0.53 g cm⁻³ and a remarkable theoretical capacity of *ca*. 3861 mAh g⁻¹. These values are promising, as they offer the potential to substantially reduce the overall mass and volume of the battery cell, leading to increased energy densities. Furthermore, the low reduction potential of the lithium metal would significantly increase the operating voltage window of the cell.

The adoption of lithium metal anodes has however been impeded due to the growth of branch like lithium metal dendrites between the anode and the cathode during battery cycling.[41] The growth of these dendrites leads to short circuits, resulting in thermal runaway and subsequent catastrophic failure.[42] The employment of liquid electrolytes in lithium-ion batteries not only significantly raises the risk of catastrophic failure and toxic gas emission, but it also hinders the use of high energy density lithium metal anodes. As a result, focused research efforts have been undertaken to substitute the liquid electrolyte with an alternative that leads to safer, high energy density batteries.

1.0.2 The All Solid-State Battery

All solid-state batteries (ASSBs) have been widely regarded as the answer to overcome safety concerns arising from the use of liquid electrolytes. Similar to conventional lithium-ion batteries, the ASSB is based on an electrochemical redox reaction between the anode and a cathode composite. However, the flammable liquid electrolyte is replaced with a solid electrolyte that acts as the separator and electrolyte simultaneously. The replacement of the flammable liquid electrolyte with a solid electrolyte mitigates concerns over surrounding toxic gas emissions and the risk of explosion upon catastrophic failure. The greatest potential, however, lies in the realisation of lithium metal anodes, enabling high theoretical capacity (*ca.* 3861 mAh g^{-1}) and a large electrochemical stability window (0 - 6 V).[43] Enabling high energy densities and the use of high-voltage cathodes without inducing detrimental cathode or electrolyte degradation, allowing high stability cycling. Furthermore, eliminating the liquid electrolyte's safety hazards enables a reduction in safety packaging requirements. This not only reduces overall costs but also trims down weight and raw material usage, consequently allowing for further increases in energy density. Moreover, it brings additional benefits such as heightened thermal stability and the feasibility of the bipolar stacking of cells for high voltage systems. [44, 45] The potential efficiency of a solid state battery has been demonstrated by a high stability, high voltage (5 V) solid-state microbattery, achieving a long device lifetime of 10,000 cycles with >99.8 % coulombic efficiency. [46]



Figure 1.3: Schematic representation of an all-solid state battery. The anode is composed of metallic lithium with the solid electrolyte acting as the separator with the cathode. The cathode is mixed with the solid electrolyte to form a composite, facilitating lithium diffusion to all cathode particles. Reproduced (adapted) with permission from Springer Nature.[47] Copyright 2023, Springer Nature Limited

To ensure the effective functioning of an ASSB, it is crucial to maintain the system's stability, i.e. the ability of battery components to endure repeated cycles while retaining their original configuration, ensuring no compromise in performance or structural integrity. The stability challenges encountered by materials and interfaces in ASSBs commonly fall into four key categories: thermal, electrochemical, chemical, and mechanical stability.[48]

The thermal stability of ASSBs has historically been less studied due to the initial assumption that their solid electrolyte configuration inherently ensured non-flammability. In contrast to lithium-ion batteries, where safety predominantly relies on the thermal stability of the liquid electrolyte, ASSBs, utilising solid electrolytes, generally demonstrate superior thermal resistance; with garnets based conductors in particular, being non-flammable.[48] Differential scanning calorimetry studies however revealed that exothermic reactions still occurred within an ASSB, although only producing a third of the total heat generated by that of a lithium-ion battery.[49] A more focused study on the solid electrolyte highlighted a thermal runaway event when lithium metal contacted the solid electrolyte at temperatures exceeding 200 °C.[50] Despite reducing fire and thermal risks significantly, further clarification on the intrinsic thermal properties of the ASSB is required.

It is widely considered that due to the wide electrochemical window (0 - 6 V vs Li/Li^+) solid electrolytes exhibit superior electrochemical stability. However, recent studies have highlighted challenges on the cathode side, where, under electrochemical cycling decomposition at the electrode was observed, resulting in diffusion of transition metals into the electrolyte.[51] Furthermore, high voltage cycling may induce significant polarisation at the solid electrolyte/electrode interface, alongside the formation of resistive interphase layers due to electrochemical decomposition. This coupled with low electrical conductivity of the solid electrolyte prevents the charge-transport percolation, i.e. the ability to supply electrons and ions to all regions in the cathode, further contributing to a variety of challenges at the cathode interface.[48, 52, 53]

The overall chemical stability of the solid electrolyte dictates fabrication, storage conditions and material selection. An ideal solid electrolyte should remain inert when exposed to ambient conditions and exhibit no reactivity at the electrode/electrolyte interface. However, several solid electrolytes experience degradation when exposed to ambient conditions.[48] Notably, in lithium garnet oxides a H^+/Li^+ exchange has been observed.[54] This exchange leads to the formation of surface interlayers such as Li₂CO₃ and LiOH, resulting in poor 'wettability' of lithium metal and increased interfacial resistance between the electrode and electrolyte.[55, 56] This can present a significant problem despite their stability when in direct contact with Li-metal, exhibiting low 'wettability' towards the metal as a result of these passivation layers. This low 'wettability' creates inadequate contact between interfaces, resulting in increased gaps and voids. Consequently, the poor physical contact elevates interfacial impedance. As such, kinetic limitations are imposed on how fast ions can be transported between the interface regions. This significantly impacts the rate capability of the battery, i.e. the speed at which ions are (de)intercalated between electrodes, which in turn dictates the charge and discharge rate of the battery. To quantify these resistances at the electrode/electrolyte interfaces, a crucial metric known as the area specific resistance (ASR, Ω cm²) is employed.

It is clear that the electrode/electrolyte interface region plays a crucial role in dictating the performance of the ASSB. In a lithium-ion battery, the ubiquitous interfacial contact between electrolyte and electrodes facilitated by the liquid electrolyte results in a low ASR. However, to mitigate the reduced point-to-point contact surface area due to poor 'wettability' or contact issues in ASSB, several techniques have been employed. Addressing lithium metal contact, these approaches aim to reduce ASR, enhance intimate physical contact, and mitigating chemical and electrochemical instabilities to facilitated facile Li⁺ transport at the interface. These techniques include high stack pressures,[57] the deposition of graphite, nitrides (Li₃N), lithiummetal alloys (Li-In), metal layers (Ge, Al, Mg), and oxides (Al₂O₃).[58–64] Of note is the atomic layer deposition of oxide Al₂O₃, the use of this technique has shown to reduce interfacial impedance to a negligible number from 1,710 Ω cm² to 1 Ω cm².[64] The results demonstrated by ALD of Al₂O₃ appear extremely promising, however the scalability cost of this technique have retained serious questions surrounding implementation and scalability in ASSB production.

Initially, one of the most anticipated benefits of utilising a solid electrolyte was the perceived suppression of lithium metal dendrites originating from the lithium metal anode during electrochemical cycling. This suppression was attributed to the inherent hardness, notably observed in oxide-based solid electrolytes. Investigations have however shown they are not invulnerable to dendritic penetration, in either the polycrystalline or single crystalline form.[65]

This form of mechanical failure originates from the inhomogeneous electrodeposition process resulting in the formation of dendrites during charging or discharging, ultimately resulting in a short circuit. Dendrite formation and propagation arise from plating instability induced by the rate of electrodeposition during the charge and discharge cycles, culminating in short-circuit failure. The current density at which this mechanism occurs is known as the critical current density (CCD), defining the threshold at which a short circuit will occur. The CCD of most inorganic solid electrolytes never surpasses 0.3 mA cm⁻², with recent studies suggesting that the natural CCD of garnets is 0.28 mA cm⁻², [66] far below the requirement of ≥ 5 mA cm⁻².[67, 68] Several factors have been identified as affecting the formation of lithium metal dendrites including temperature, electronic conductivity, surface flaws and ASR.[65, 66, 69, 70]

The precise failure mechanism concerning the nucleation and propagation of lithium dendrites remains incompletely understood. Consequently, concerted research efforts are being led to comprehensively reveal the fundamentals behind the observed non-uniform electrodeposition of lithium. The current prevailing theory suggest that dendrites nucleate and propagate from the lithium metal anode. The initial formation of dendrites is attributed to the inhomogeneity and void formation at the interface between the anode and electrolyte. Voids emerge when the diffusion and creep of lithium metal toward the electrolyte interface fall below the necessary rate of replenishment of dissolved and transported lithium metal at the solid electrolyte interface. The edge of these voids generate localised regions of high current densities, leading to initial dendrite nucleation. Continual stripping and plating facilitates the sustained growth and propagating of dendrites from these areas of high current density (Figure 1.4).[71, 72]

As such, it is key to maintain physical contact between electrodes and electrolyte to avoid increases in localised current density and facilitate the effective diffusion of ions across the interface. In addition to the as mentioned surface modifications, it has been suggested that the use of stack pressure aids in prevention of void formation as well as lowering the required overpotential to cycle ASSBs.[57]

The formed dendrites subsequently plate and propagate preferentially along grain boundaries and/or within voids, leading to short circuit, this was demonstrated by SEM analysis following lithium metal cycling. Figure 1.4 illustrates lithium metal dendrites plating between grain boundaries while leaving the grains themselves intact.[73] As a result it has been suggested that manufacture of high density garnets with minimal grain boundaries would prevent dendritic growth.[74, 75] However, several studies on single crystal SSEs have demonstrated that dendrites still nucleate and propagate through the solid electrolyte revealing a more nuanced problem.[65, 76]

The formation and propagation of dendrites within specific regions of the solid electrolyte render these areas vulnerable to volumetric changes during cycling. This induces stress points,[77] leading to interface delamination and crack propagation at both the anode and the cathode.[52, 78–80] This mechanical cracking process represents an alternative failure mode observed in ceramic separators. During cell operation, stress and electrochemical pressures cause crack formation, allowing lithium deposition within the cracks. This deposition further applies pressure, exacerbating crack propagation until subsequent short circuit.[81]

A theory proposes that the inherent electronic conductivity within the solid electrolyte could be the root cause of dendrite formation. It suggests that electrons penetrating the bulk might directly initiate the nucleation of lithium metal dendrites within the bulk, rather than originating solely from the anode interface.[69] Additionally, investigations focusing on the electronic conductivity reveal that when an applied external electric field exceeds a threshold voltage, the solid electrolyte will exhibit a surge in electronic conductivity. This surge leads to widespread recombination of electrons and Li-ions at the grain boundaries.[83] This was further supported by



Figure 1.4: (a) The mechanism of void and dendrite formation at the solid electrolyte interface, lithium metal stripping at a rate exceeding the replenishment rate results in void formation. The small remaining areas of contact increase the local current density facilitating the growth and propagation of metal dendrites. Reproduced (adapted) with permission from Springer Nature, Copyright 2019.[72] (b) The preferential plating of lithium metal at grain boundaries in a solid electrolyte. Reprinted from ref.[73] Copyright 2016, with permission from Elsevier.

Aguesse *et al.* who proposed that lithium metal may crystallise by gaining electrons from oxygen present in the garnet or via residual electronic conductivity.[82] Furthermore, computational studies suggest that excess electrons may accumulate along grain boundaries, pores and crack surfaces, consequently contributing to formation lithium metal formation.[84]

Studies investigating the relationship between grain boundary electronic conduc-



- (b) Li dendrite growth and Li⁰ deposition
- (c) Li⁰ formation (e⁻ transfer from oxygen framework)
- (d) Li⁰ formation (e⁻ transfer from residual conductivity)

Figure 1.5: Schematic representing the proposed mechanisms of lithium metal dendrite formation in garnet electrolytes. Reprinted (adapted) with permission from ref.[82] Copyright 2017 American Chemical Society.

tivity and dendrite propagation have revealed a connection to the bandgap dynamics of the system. The results indicate that an increase grain boundary electronic conductivity originated from a narrowing in the LLZO band gap at the grain boundary.[85] A subsequent study focused on the examination of the energy band structures and defect states of crystalline Ta-doped LLZO. Using direct electronic structure analysis, the results revealed that propensity for intergranular lithium metal propagation was a result of a lowered Schottky barrier height due to high defect density at the grain boundaries. To mitigate this, the authors successfully increase the band gap of the grain boundary, effectively impeding the lithium dendrite formation by blocking the electron injection.[86] These studies collectively emphasise the pivotal, interwoven relationship between electronic conductivity and grain boundaries. Furthermore, the introduction of defects and impurities during synthesis, particularly in the presence of transition metals, tends to aggregate at grain boundaries, potentially increasing the electronic conductivity and/or providing nucleation points for metallic lithium.

To be a viable candidate for use in an ASSB, the solid electrolyte must exhibit a range of properties, including high ionic conductivity, good electrode compatibility, good mechanical properties, excellent chemical, and electrochemical stability. It is evident that despite these challenges, [47, 48, 87–90] extensive research efforts are

underway to alleviate the issues faced by solid electrolyte in ASSB, paving the way for safer and higher-density battery systems.

1.0.3 The Solid Electrolyte

Michael Faraday's groundbreaking work in 1839 marked the first recorded instance of ionic conduction within a solid. Through research on heated As_2S and PbF_2 , he unveiled the phenomenon of ionic conduction in solid electrolytes.[91] This pivotal discovery laid the foundation for the field of solid state ionics, sparking a new realm of scientific inquiry and technological advancement. His work was continued by fundamental contributions from German physicist Walther Nernst, famous for his derivation of the Nernst equation. He detected ionic conduction in heterovalently doped zirconia, later commercialising the discovery in the form of his Nernst lamp. [92, 93] Since the late 20th and into the early 21st century, substantial efforts have been devoted to synthesising and characterising novel solid electrolytes for their application in various technologies, such as fuel cells, sensors, and solid-state batteries. A significant breakthrough emerged in the 1970s with the rise of polymer science. During this period, researchers discovered that polyethylene oxide (PEO) readily formed conductive complexes by dissolving alkali metal salts (e.g., Li⁺/Na⁺). This discovery led to the development of a PEO-Li salt solid polymer electrolyte, exhibiting an ionic conductivity of ca. 10^{-4} S cm,⁻¹ at 40 - 60°C.[94–96] The discovery and subsequent commercialisation of lithium polymer batteries (LiPo batteries) resulted in a breakthrough for solid electrolytes. Due to their high energy density and discharge rates, LiPo batteries saw wide scale adoption and extensive use in personal electronics and radio controlled equipment such as drones. However, due to its low electrochemical window, PEO begins to decompose at ca. 3.8 V, potentially leading thermal runaway when overcharged. [97] Coupled with a propensity towards dendrite formation when used with lithium metal anodes, [98] safety concerns of these batteries have been raised, restricting their application to smaller-scale uses. The emergence of solid polymer electrolytes allows for two general classifications for solid electrolytes, solid polymer electrolytes and inorganic solid electrolytes.

Inorganic solid electrolytes in particular are emerging as serious candidates to replace conventional liquid electrolytes due to their enhanced safety, stability and high energy density. These solid electrolytes fall into distinct categories based on the anion present in their crystal lattice, such as sulphides, phosphates, nitrides, halides, hydrides, and oxides. Further classification of these solid electrolytes may be based on their crystal structures. For instance electrolytes may adopt structures like garnets, perovskites, anti-perovskites, Argyrodites, LISICON-like (Lithium Super Ionic Conductor), and NASICON-like structures (sodium superionic conductor).[99, 101] The variety of crystal structures inevitably leads to a range of properties for



Figure 1.6: Ionic conductivity and radar plot of various solid electrolytes. (a) Total ionic conductivities of lithium conducting solid electrolytes at room temperature. The ionic conductivity of liquid electrolyte of EC/DMC 1 M LiPF₆ is represented by a dashed grey line. Reprinted (adapted) with permission. Copyright 2016 American Chemical Society.[99] (b) Radar chart demonstrating the varying capabilities of differing lithium conducting solid electrolytes. Adapted and reprinted.[100] Copyright 2019, with permission from Elsevier.

these solid electrolytes. This variability is demonstrated in Figure 1.6a, summarising the differing ionic conductivities of different classes of solid electrolytes.

Oxide based electrolytes, notably lithium based garnets, exhibit adequate ionic conductivity and high stability with lithium metal anodes at high voltages.[102–104] Despite these advantages, challenges involving high interfacial resistance with electrodes (*c.f.* ASR, Figure 1.6b), susceptibility to dendritic growth, stability concerns with air, and difficulties related to mass production and device integration, have hindered their commercialisation.[88]

LISICON-like and Argyrodite structured sulphides solid electrolytes approach ionic conductivities comparable to current liquid electrolytes (EC:DMC 1 M LiPF₆) used in commercial batteries. However, inherent challenges such as their limited stability against lithium metal, their susceptibility to decomposition at high voltages and narrow electrochemical stability window, restrict their effectiveness, especially in conjunction with high-voltage cathodes for lithium metal batteries.[105] In addition to this, the production of sulphide solid electrolytes face significant challenges; due to their significant decomposition issues in the presence of air and moisture.[99, 101, 105] As such, the electrolytes would have to be produced in an inert environment with low oxygen and moisture levels.

In contrast, oxide solid electrolytes such as lithium stuffed garnets, demonstrate remarkable stability against lithium metal and broad electrochemical window making them a credible choice. Current, drawbacks however concern mass production and process optimisation and reduction of electrode interfacial resistances. With extensive ongoing research aimed at mitigating these limitations' impact and favourable stability with lithium metal, it appears that lithium stuffed garnets are set to be implemented as the electrolyte of choice as opposed to sulphide based electrolytes. The radar plot presented in Figure 1.6b allows for a simplistic visualisation of capabilities presented for solid electrolytes.

Ionic Transport in the Solid

Similar to liquid electrolytes, solid electrolytes require high ionic conductivity ($\geq 10^{-3} \text{ S cm}^{-1}$) to facilitate rapid charge and discharge rates. As mentioned, extensive research has been conducted to discover and optimise fast ionic conductors meeting this criterion, yielding a range of results. In all these materials, performance variability may be explained by the fundamentals of ionic conductivity that subsequently underpin these mechanisms. The phenomenon of conduction in a solid - regardless of ionic or electronic conduction - is generally described by the total conductivity, σ , which may be given by

$$\sigma = \eta \ q \ \mu \tag{1.5}$$

where η is the number of charge carriers, q their charge and μ their mobility. In the case of ionic conduction in solid electrolytes, the charge carriers are cations or anions whilst electronic conduction is governed by holes or electrons. In the case of mixed ionic-electronic conduction, conductivity σ is the sum of both ionic and electronic conductivities σ_{ion} and $\sigma_{electron}$. However, in a perfect defect-free crystal, ions are arranged in a periodic fashion often stacked in a close-packed form, prohibiting the diffusion of ions with the remaining available space only permitting ion vibration about its equilibrium position.[106] As a result, ions lack the necessary thermal energy to deviate from their lattice sites. However, increasing the thermal energy in the system results in an increase in ionic conduction. This increase is due to ions vibrating more vigorously and results in higher defect concentration. The primary mechanism of ionic conduction in crystalline solids involves the movement of ions through the crystal lattice via the diffusion pathways along open tunnels or layers composed of stable and/or metastable sites commonly consisting of tetrahedral and octahedral coordination in an anion framework (e.g. O^{-2}).

A such, ionic conductivity arises from the migration of ions facilitated by the availability and interconnectivity of differing sites within the crystal lattice. In a crystalline structure, these pathways are often created by cationic vacancies or interstitials, which serve as pathways for ion transport. These vacancies or interstitials are typically generated through one of two primary mechanisms. Firstly, through the application of heat, which exponentially increases the number of vacancies in thermodynamic equilibrium, these vacancies are an *intrinsic* number to the system. The second method involves the addition of aliovalent impurities that generate vacancies to maintain charge balance. Such vacancies are *extrinsic*, having not been present in the pure crystal system. Typically, at room temperature the number of thermally generated *intrinsic* to *intrinsic*. Intrinsic defects play a crucial role in ionic conduction of crystalline solids and may further be sorted into two categories, 'Schottky' and 'Frenkel', these, belonging to the class *point defects*.

Schottky defects are a stoichiometric defect, in which a pair of vacancies is generated by the absence of a cation and anion, since both cation and anion are absent from the lattice the overall electrical neutrality of the crystal is maintained. This type of defect readily occurs in an ionic crystal where the anion size is almost the same as the cation. Frenkel defects on the other hand are characterised by a solitary ion missing from its customary place in the lattice and occupies an interstitial site within the same crystal. This mechanism often occurs when the anion radii is substantially larger than the cation. Schottky and Frenkel defects both create vacant sites that enable an ion in the immediate vicinity to "jump" or "hop" to that location, subsequently leaving the previous site vacant in a mechanism known as *vacancy diffusion*. This continuous process facilitates the transport or conductivity



Figure 1.7: Frenkel and Schottky point defects in a NaCl crystal, green spheres are Cl⁻ ions and blue Na⁺. The Frenkel defect is characterised by an ion missing its position in the lattice, creating a vacancy, and occupying an interstitial site nearby. The Schottky defect is formed when oppositely charged ions are absent from their lattice sites and become incorporated at the surface, due to the opposite nature of the vacancies, overall electrical neutrality is maintained.

of ions in the solid, commonly referred to as ionic conduction. However, for an ion to "jump" from vacant to vacant site it must undergo a transition between stable ground-states and/or intermediate metastable sites. To achieve this, it must overcome an energy barrier known as the activation energy E_m . In the case of crystalline solids, ionic conduction of the charged species may typically be classified into three general cases of diffusion mechanism: vacancy diffusion, direct interstitial, and correlated interstitialcy. In direct interstitial migration, the ion moves from an interstitial site, subsequently jumping to a neighbouring vacant interstitial site, which facilitates the long term migration of ions. The final mechanism, *correlated interstitialcy*, is when a joint transfer of two more ions occurs via a 'knock-on' effect. Where an ion "jumping" to an adjacent interstitial or occupant site results in the displacement of a neighbouring atom. The highest activation energy (E_m) requirements for hopping are that of *vacancy diffusion* as ions must overcome transition from a stable site to an adjacent stable site. Conversely ion diffusion via *direct interstitial* requires a lower activation energy as ions inhabit metastable interstitial sites between stable lattice sites. The different types of mechanisms and activation energy requirements are displayed in Figure 1.8. As mentioned, ionic conduction is a temperature dependent phenomenon that relies on the number of available vacant sites and the ion mobility. As such the ion, or charge carrier mobility, μ may be defined by an Arrhenius relationship

$$\mu = \mu_0 \, exp\left(-\frac{E_m}{k_B T}\right) \tag{1.6}$$

where μ_0 is a mobility prefactor, E_m the activation energy for ionic vacancy migration, k_b the Boltzmann's constant and T the temperature. Similarly, the concentration or number of intrinsic vacancies available for conduction may be characterised by

$$N_v = N \, exp\left(-\frac{E_f}{k_b T}\right) \tag{1.7}$$

where N_v is the number of vacancies/defects, N the total number of atomic sites, E_f the activation energy required to form a vacancy. It is clear to see that both the equilibrium constant of vacancies and the charge carrier mobility increase with temperature. These relationships are directly associated with the number of charge carries, n, and charge carrier mobility, μ as described in Equation 1.5. Upon analysis of Equation 1.5 it is evident that (with a with a fixed charge q), the total ionic conductivity σ is contingent upon the concentration of charger carriers and their mobility, or in simple terms, the availability of vacant sites, which is controlled by the density of defects in the crystal and the ease with which an ion can jump to another site. As both terms are temperature dependent, the total ionic conductivity may be expressed by the modified Arrhenius equation

$$\sigma = \sigma_0 T^{-1} exp\left(-\frac{E_a}{k_B T}\right) \tag{1.8}$$

where σ_0 is the pre-exponential factor that contains terms for vibrational frequency of the potentially mobile ions. E_a is the activation energy required for ionic conduction which includes the energy needed to form vacancies E_f , and E_m , the activation energy for ion vacancy migration.

Equation 1.8 relates to the atomistic diffusion of ions. However, diffusion extends across an entire sample at the macro scale, consequently occurring throughout a system that involves the bulk, grain boundaries and interfacial regions. The transfer of ions is consequently linked with mass transfer in the solid electrolyte volume. As such the macroscopic diffusivity and ionic conductivity may be linked to the Nernst–Einstein equation

$$\sigma = \frac{nq^2D}{k_BT} \tag{1.9}$$

where n is the number of ions per unit volume, q is its charge and D the self-diffusion coefficient that is expressed by

$$D = \frac{zNc(1-c)a_0^2v_0}{k_BT}$$
(1.10)

where N is the density of the number z nearest neighbour sites, c the concentration of ions, a_0 the distance between sites and v_0 the "jump" frequency.[106]

The diffusion mechanisms described are all related to the conduction of ions in a solid considering their mobility and temperature. Specifically, these mechanisms address behaviour influenced by temperature and charge. Further factors that may



Figure 1.8: (a) The three general charge carrier diffusion mechanisms in crystalline solids: vacancy, direct interstitial, and correlated (interstitialcy). (b) The energy profile for direct vacancy or interstitial site jumping of ions and (c) the energy profile for correlated jumping. E_m and v_0 represent the activation energy for ionic vacancy migration and the "jump" frequency, respectively. Reproduced and adapted with permission from Springer Nature Limited, Copyright 2019.[80]

affect diffusion are concentration gradients. However, the diffusion of ions in a battery may also be influenced by the presence of an electric field. As such, a suitable equation is required to describe the movement of ions under the influence of both concentration gradients and electrical potentials. This behaviour can be effectively characterised by the Nernst-Planck equation

$$J = -D\nabla c + \frac{qF}{k_B T} Dc\nabla\phi \qquad (1.11)$$

where J is the flux of the ions, D is the diffusion coefficient, c the concentration gradient, ∇ the gradient operator, q the charge of the ion, F is Faraday's constant, and ϕ the electric potential. Within the equation, the first term $(-D\nabla c)$ corresponds to Fick's first law, encompassing the gradient of concentration. This term represents the flux caused by the concentration gradient, i.e., ions moving from areas of high concentration to low concentration. Whilst the second term $(\frac{qF}{k_BT}Dc\nabla\phi)$ includes the influence of the electric field on ion movement.[107] However this equation is typically employed in modeling electrochemical systems rather than for the fundamental characterization of ionic movement within a crystalline solid.

The diffusion of ions in a solid electrolyte occurs at the atomic length scale, however as mentioned, the overall conductivity is governed by many factors, including at the macroscopic scale which incorporates, bulk, grain boundary and interfacial properties. As such, measurements of ionic conduction need to be considered at varying length scales that incorporate the effects arising from a crystal lattice to a complete ASSB. Several techniques exist and may be utilised, from impedance spectroscopy to continuum modelling. A combination of techniques will however be required to fully elucidate the conduction mechanisms at all length scales to enable the understanding of ASSBs.

The Grain Boundary

It is evident that defects play a crucial role within the conduction mechanism of the solid electrolyte. In addition to point defects several other defects present themselves in solids. These extended defects may be classified as linear or planar defects. The most common type of linear defect is a dislocation, which is a localised misalignment, or fault in the linear arrangement of atoms in a crystal lattice. Generally, there are two basic types of dislocation – an edge and screw dislocations. In an edge dislocation an additional plane of atoms is placed within the regular arrangement of atoms within the lattice. This results in localised lattice distortion where the atoms above the dislocation line are squeezed together and the atoms below, pulled apart. The screw dislocation may be visualised as forming by shear stress, where along the dislocation line the front region of the crystal is shifted one atomic position relative to the bottom portion of the crystal, similarly, this defect is linear along the dislocation line. Generally, dislocations govern a crystalline materials response to plastic deformation and its subsequent mechanical properties.

There are several planar, or interfacial defects however two of the most common are the crystal surface and the grain boundary. The crystal surface, or more simply, the external surface is where the crystal structure terminates. The interface however does not result in the termination of a perfect crystal boundary and real surfaces result in a rough surface, their own point defects, and hold a higher energy state than the atoms located in the interior. An additional planar defect is the grain boundary. This planar defect is the boundary separating two adjoining grains with different crystallographic orientations in polycrystalline materials. The boundary is typically only several angstroms wide displaying various degrees of misalignment. When this degree of misalignment is low ($\theta < 15^{\circ}$) the grain boundary is termed low angle grain boundary, conversely, a high degree ($\theta \ge 15^{\circ}$) of misalignment is termed high angle grain boundary and display a larger degree of disorder.



Figure 1.9: Schematic representing high and low angle interface grain boundaries. Reused with permission.[108]

Similar to the interface, the atoms along the grain boundary are bonded less regularly resulting in an elevated interfacial or grain boundary energy compared to those atoms located within the interior. The magnitude of this grain boundary energy is a function of the severity of misalignment displayed by the atoms. Due to this energy, grain boundaries often hold an elevated level of chemical reactivity compared to the grains themselves. In addition to misalignment, the interfacial energy is a function of the grain size. Large or coarse grains hold a lower interfacial energy compared to small or fine grains due to their lower total boundary area. As such, impurities preferentially segregate or precipitate onto these boundary regions due to their higher energy states ultimately strongly affecting several of the macroscopic properties of the material including the electrical properties.

Schottky barriers

The periodicity of an ideal crystal is broken by all defects and may affect the electrical properties of crystal system as was discussed with point defects. The same may be said for planar defects, where many electronic properties of materials involved in electrochemical reactions depend on surface effects. As such the interface between two mediums, such as Li-metal and the solid electrolyte or a grain boundary-grain boundary interface require careful attention.

In solid state physics the Fermi level is defined as the highest filled energy level that an electron may occupy at zero Kelvin and is located between the valence and conduction bands for a non metal. Within the bulk the Fermi level is usually controlled by the energy levels and may be controlled by doping. At the interface however it is surface energies associated with subsequent surface defects or adsorbates that play a crucial role. It is such that the Fermi level relative to the band edges may differ at the interface compared to the bulk. As the Fermi level however is the same throughout the solid at equilibrium the band energies at the surface themselves must be altered.



Figure 1.10: Schottky barrier formation at a metal-semiconductor interface (a) Equilibrium condition at the interface. (b) Reverse bias decreases the barrier, prohibiting current flow. (c) Forward bias, decreases the barrier promoting current flow. Adapted and redrawn.[109]

When initially placed in intimate contact the electrochemical potential around the interface are dissimilar, this results in charge carriers being transferred between the two materials across the interface until equalisation of the Fermi levels is achieved and the potential difference is removed. This leads to the altering of the band energies at the interface and is termed band-bending referring to electronic band structure at the interface of two mediums either curving up, for n-type (electron mobility) or down, for p-type (hole mobility) semiconductors. The bending of bands at the interface leads to the potential barrier for electrons known as a Schottky barrier. The Schottky barrier, in its simplest form is a potential energy barrier

for electrons and is denoted by its barrier height, ϕ_B which is dependent on the interfacial contact between a metal and a semiconductor. In some cases the Fermi level may not equilibrate and the may become pinned to the center of the band gap and may cause the Schottky barrier height to be higher or lower than at equilibrium (Figure 1.10 b&c). In a rectifying Schottky barrier current may only pass in one direction and is governed by the barrier height. In a reverse bias band bending is increased providing a larger barrier height prohibiting electron movement. Under a forward bias the energy barrier for electron movement from the semiconductor to the metal is reduced. Important to note is that in the case of an electrochemical interface, between a semiconducting electrode and electrolyte solution, the band edges are fixed but the surface Fermi level positioning may be altered by varying the potential of the semiconducting electrode with respect to a reference electrode. The formation of Schottky barriers play a crucial role in regions of interfacial contact between two mediums and as such have been considered in studies involving lithium ion batteries and solid state electrolytes. Often leading to high interfacial resistance, deteriorating battery performance, as such several efforts have been conducted to tuning the band alignment by interfacial engineering. [110, 111] A deep understanding of Schottky barriers in relation to mixed conductor interfaces is however still largely lacking.

Percolation Theory

The as previous mentioned formation of secondary phases on grain boundaries may impact the electrical properties of the material sample, at low volume concentration however these phases may not have an adverse affect on the material system. Not until they reach a critical level, or a threshold whereby they interact with each other do they become disruptive to the overall properties of the system, percolation theory best describes this mechanism.

The percolation threshold is the critical threshold at which large clusters with a long-range connectivity first appear. This results in a continuous pathway from one boundary to another along these cluster sites. The critical volume fraction at which this occurs for secondary phases in a composite system concerned with resistivity is typically *ca.* 16 %.[112] At this level, the secondary phase within the composite may interconnect forming a conduction path that results in the critical alteration of the overall electrical conductivity of the sample. This theory has been successfully used in the study of electrical conductivity and conduction mechanisms of two phase sodium bismuth titanate materials.[113]

Whilst the use of percolation theory has not been applied for a similar study of secondary phase resistivity in lithium conducting electrolytes such as LLZO based solid electrolytes, it has been utilised for several other aspects of solid-state electrolytes. One such study investigated optimum binder distribution and subsequent polymer interaction clusters for hybrid solid electrolytes composed of organic (polymer) and inorganic (Al doped LLZO) ion conducting materials.[114]

Another use of percolation theory in the investigation of solid electrolytes was presented by Park *et al.*.[115] Simulating a range of graphite/Ta doped LLZO composite electrodes, the authors presented a systematic investigation of the effect of dimensional controlled solid electrolyte particle on the electrochemical performance of the composite electrode. Varying the particles dimensions between a 0D (Spherical), 1D (Fiber-like), and 2D (Plate-like) the authors mapped the percolation pathways (ionic pathways) of these different dimensions revealing 0D particles as the most effective morphology for the shortest percolation pathway.[115] It is notable that this paper was focused on the performance and shortest percolation pathway as a result of different solid electrolyte dimensions within a graphite electrode and not the percolation threshold. None the less, the work provides an intriguing insight into the use of percolation theory in the research of solid electrolytes for all solid state batteries.

Percolation theory is a well established area of statistical physics and mathematics that has seen application in a wide range of fields including materials science and may provide further comprehension to the field of solid state electrolytes; providing an effective tool for the visualisation and study of critical networks within the complex system.

Garnet Type Solid Electrolytes

Much expectation has been placed on garnet-type solid electrolytes, due to their high ionic conductivity, relative lithium metal stability and wide electrochemical window (≤ 6 V vs Li/Li⁺), making them a credible prospect for use in ASSBs.[102, 104, 116, 117] The garnet fast-ion conductors that are known today are based on the silicate mineral with a general structure of $A_3B_2(SiO_4)_3$. Where the A site is usually a divalent cation such as Ca, Mg, Fe, or Mn, whilst the B site is usually a trivalent cation such as Al, Fe, or Cr. The A site cations are in a eight oxygen coordinated cation environment, with B cations consisting of BO_6 octahedrons and C cations in a tetrahedral coordination environment. The cations fully occupy their coordinates, with the compound crystallising in a cubic structure of space group Ia3d. This garnet structural prototype may be modified/synthesised so that they incorporate lithium atoms into the lattice, leading to the first reported lithium containing garnets in 1968, with a composition of $\text{Li}_3 Ln_3 M_2 O_{12}$ (M=Te, W; Ln =Y, Pr, La, Nd).[118] However the first significant report for their potential use as solid electrolyte did not occur until 2003 when Thangadurai et al. reported the lithium stuffed garnet, $Li_5La_3M_2O_{12}$ (M = Ta, Nb), which attained high ionic conductivities of 10^{-5} S cm⁻¹

at 25°C.[119]

Typically, lithium containing garnets may be classified into four different subtypes: Li_3 , Li_5 , Li_6 , and Li_7 , which are categorised by the amount of lithium per formula in the garnet. Generally, as the content of lithium is increased the ionic conductivity increases. To understand the role between lithium site occupancy and the observed ionic conductivities, $Li_3Ln_3Te_2O_{12}$ (Ln = Y, Pr, Nd, Sm-Lu) was studied by X-ray and neutron powder diffraction. Lithium ions were found to exclusively reside in the tetrahedral sites independent of temperature, revealing the reason behind experimentally observed, low ion mobility and high activation energy. [120] Subsequent studies, where the lithium content in $Li_{3+x}Nd_{3}Te_{2-x}Sb_{x}O_{12}$ was incrementally increased by the substitution of Sb^{5+} for Te^{6+} resulted in the adjustment of lithium cation distribution across the tetrahedral and octahedral interstices. It was found that vacancies are created onto the tetrahedral site as lithium is incorporated into the octahedral sites, leading to an increase in activation energy and Li⁺ conduction that is observed in the \geq Li₅ compositions. Using NMR it was however noted that the tetrahedral located lithium in $Li_{4.5}Nd_3Te_{0.5}Sb_{1.5}O_{12}$ remained immobile and bound to the coordinate. [121]

Previous studies of the lithium-rich garnet $\text{Li}_5\text{La}_3M_2\text{O}_{12}$ (M = Ta, Nb) failed to conclusively determine the exact crystal structure and subsequent site occupation of Li ions. However, using neutron powder diffraction, Cussen confirmed the space group as $Ia\overline{3}d$ with a structure composed of La^{3+} , M⁵⁺ and O²⁻ ions framework where lithium-ions are distribution across three different interstitial sites: Li(1) tetrahedral (24d) and Li(2) octahedral (48g)/distorted octahedral (96h).[122] Whilst in Li₃, Li-ions are immobile and solely located on the tetrahedral (24d) site, in lithium-stuffed garnets ($\geq \text{Li}_5$), excess lithium are incorporated into the octahedral sites resulting in tetrahedral vacancy formation. Furthermore, due to the increased occupancy of Li-ions at the octahedral 48g site, lithium is further displaced into the distorted octahedral 96h site.[122] Consequently, this high amount of lithium ion disorder leads to facile ion transport within the lattice, making a high lithium content garnet desirable for fast-ion transport.

To further increase the lithium content, partial substitution of trivalent La³⁺ with divalent ions in Li₅La₃M₂O₁₂ (M = Ta, Nb) lead to the Li₆ phase. With a general formula of Li₆ALa₂M₂O₁₂ (A = Mg, Ca, Sr, Ba, and M = Nb, Ta), these stuffed garnets reported an ionic conductivity of 4×10^{-5} S cm⁻¹.[102] However, the highest lithium stuffed garnet Li₇La₃Zr₂O₁₂ (LLZO) was first synthesised by Murugan *et al.* in 2007. LLZO demonstrated a low activation energy and a high total ionic conductivity of 3×10^{-4} S cm⁻¹ and exhibiting a cubic crystal (*Ia*3*d*) structure.[117] Successive, dedicated optimisation efforts have led to the highest reported ionic conductivity rising from 10^{-7} S cm⁻¹ to 10^{-3} S cm⁻¹, achieved by a lithium content of *ca.* 6.4.[123]



Figure 1.11: Schematic representing differing chemical compositions of silicate garnet and lithium containing garnets, Li_3 , Li_5 , Li_6 , and Li_7 . The polymorphic nature of Li_7 is shown with the possible cubic and tetragonal phases. Reprinted and adapted with permission from the American Chemical Society.[103] Copyright 2020 American Chemical Society.

The mechanisms and required activation energies for ionic conduction for Li_3 , Li₅, and Li₇ garnet type structures in the cubic phase were evaluated by *ab initio* calculations.[124] Calculations based on Li₃La₃Te₂O₁₂ confirmed that due to low lithium occupancy of the Li(2) octahedral site a high activation energy of 1.5 eV was required to allow lithium migration from the tetrahedral site to the octahedral site. This was found to be in close agreement with experimental observations by O'Callaghan *et al.* of 1.22(15) eV,[120] further confirming the extremely low ionic conductivity at room temperature due to the constraint on Li⁺ mobility.

Further calculations for high ionic conductivity in Li_5 and Li_7 lithium stuffed garnets were based on $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ respectively. Figure 1.12 shows that two proposed routes of ionic migration. Route A, which is favoured when lithium concentration is low, occurs via ion migration between octahedral sites (48g/96h), skipping the tetrahedral site. This mechanism requires relatively high activation energy of 0.8 eV to transition over the interstice "bottlenecks", the results are however acknowledged by the author as being higher than experimental observations. Conversely, Route B, which is favoured for lithium stuffed garnets, allows ion migration via the shared triangular faces that separate the polyhedra around Li(1) and Li(2) to move from one octahedral (48g/96h) site trough the tetrahedral (24d)



Migration Path

Figure 1.12: Lithium occupies the Li(1) tetrahedral (24d) and Li(2) octahedral (48g)/distorted octahedral (96h) sites in cubic lithium stuffed garnets (\geq Li₅). (a) A high activation energy is required to move one Li⁺ ion from the Li(1) site to the neighbouring Li(2) in Li₃La₃Te₂O₁₂, demonstrating the low ion mobility observed in Li₃ garnets. The differing conduction mechanisms and their subsequent activation energies, (b) Route A and (c) Route B of Li₅La₃Nb₂O₁₂, Li₇La₃Zr₂O₁₂ respectively as displayed alongside inserts indicating the path by arrows. Route A displays the Li⁺ ion migration favoured in Li₅ garnets, between octahedral sites (48g/96h), omitting the tetrahedral site. Route B, indicates the ion migration path observed in cubic Li₇ garnets, with Li⁺ ion migrate via shared tetrahedra faces around Li(1) and Li(2) sites. Reprinted and adapted with permission from: M. Xu, M. S. Park, J. M. Lee, T. Y. Kim, Y. S. Park, E. Ma, Physical Review B, 2012, 85, 052301.[124] Copyright 2012 by the American Physical Society.

site to the other octahedral (48g/96h) (Figure 1.12). The "bottleneck" occurs at the shared tetrahedra interface of Li(1) and Li(2), the subsequent activation energy requirements to overcome this barrier were calculated as 0.26 eV, seemingly in good agreement with experimentally observed results of *ca.* 0.27 eV.[124, 125] This 24d tetrahedron and 48g/96h octahedra face sharing arrangement (Figure 1.12) forms a 3D framework of conduction that facilitates the observed high lithium-ion conduction in the lithium stuffed garnet system.

However, LLZO may exist in two different phases: cubic $(Ia\overline{3}d)$ and tetragonal $(I4_1/acd)$. The tetragonal phase exhibits total ionic conductivity of $ca. 5.59 \times 10^{-7}$ S cm⁻¹, 2-3 orders of magnitude lower than that of the cubic garnet phase.[126] In the tetragonal polymorph the tetrahedral lithium sites are completely filled, and similar to the cubic phase, occupying three distinct symmetry independent sites within the unit cell. Tetrahedrally coordinated Li(1) atoms occupy the 8a site, Li(2) the distorted octahedral (16f) sites, with the Li(2') atoms occupy the distorted octahedral (32g) sites.

To therefore ensure high conductivity of the lithium stuffed garnet solid electrolyte it is imperative to retain the cubic phase of the polymorph. The effects of temperature on stabilising the crystal structure in either the cubic or tetragonal phase was initially investigated by Awaka *et al.* where results indicated that the tetragonal phase formed at comparatively lower temperatures of 980 °C compared to the required 1230 °C to attain the cubic phase.[126] To gain further clarity on the stability of cubic and tetragonal phases, LLZO was sintered using crucibles of platinum and aluminium, subsequent results showed the incorporation of small amounts of aluminium on lithium sites, stabilising the highly conductive cubic phase.[127] These observations were further substantiated with studies utilising Al₂O₃ as a sintering aid, which lowered the sintering temperature by 230 °C to 1000 °C, suppressing the formation of La₂Zr₂O₇ and attaining high total ionic conductivity of 1.4×10^{-4} S cm⁻¹, whilst no crystal structural characterisation was conducted it is likely that the presence of Al₂O₃ during sintering stabilised the cubic phase as observed by Geiger *et al.* during sintering in platinum and aluminium crucibles.[128]

The incorporation of Al in the crystal lattice of LLZO has led to elemental doping strategies being developed to disrupt the ordering of the tetragonal phase and facilitated the highly conductive, isotropic 3D conduction of the cubic phase. Doping induces structural changes by generating Li⁺ vacancies to maintain charge neutrality and increasing the entropy within the framework, facilitating the stabilisation of the highly conductive cubic phase. Computational work carried out using density functional theory (DFT) was able to calculate the defect energy and site preferences of all hypothetical dopants for Li₇La₃Zr₂O₁₂.

A summary of the results may be seen in Figure 1.13,[129] confirming the wellknown incorporation of Al^{3+} on the Li⁺ site. Experimentally validated dopants have

														8	18 VIIIA			
1	1+ H	2 114	5	tabili	ity of	Dop	bants	$\sin I$	$\Lambda_7 La$	$_{3}Zr_{2}$	O_{12}	Garno		14 11/4	15 VA	16 VIA	17 VIIA	He
2	2.660 Li	$\begin{array}{c c} & & & \\ \hline & & \\ i & & \\ Be \end{array} \begin{array}{c} Li-Site (1+) \\ La-site (3+) \\ Symbol \end{array} \begin{array}{c} Oxi \\ Symbol \\ \end{array}$											0	F	Ne			
3	Lithium 1+ Na	1.020 2+ Mg		Zr-site (4+) E_{defect} 2210 2.710 3.950 $Origen Plauti3+ 4+ 3+ 4+ 3+ 4+ 4+ 4+ 4+ 4+ 4+ 4+ 4$										Flourine 5+ CI	Ar			
	2.340 1+	1.220 2+	3 IIIA 3+	4 IVB	5 VB 5+	6 VIB 3+	7 VIIB 4+	8 VIIIB 3+	9 VIIIB 4+	10 VIIIB	11 IB 2+	12 IIB	1.360 3+	2.350 4+	3.550 5+	2.640 4+	2.750 3+	Argon
4	K 2.360	Ca 1.030	Sc 0.760	Ti 0.430	V 2.000	Cr 1.050	Mn 0.530	Fe 1.324	Co 0.900	Ni 1.270	Cu 1.740	Zn 1.320	G a 1.160	Ge 1.110	As 2.160	Se 1.240	Br 3.080	Kr Krypton
5	1+ Rb	2+ Sr	3+ Y	Zr	5+ Nb	4+ Mo	4+ Tc	4+ Ru	3+ Rh	4+ Pd	1+ Ag	2+ Cd	3+ In	4+ Sn	5+ Sb	4+ Te	5+ I	Xe
6	1.290 1+ Cs	0.700 2+ Ba	La-Lu	4+ Hf	0.920 5.+ Ta	0.130 4+ W	-0.610 Re	0.310 Os	0.990 4+ Ir	0.220 4+ Pt	2.750 3+ Au	1.090 2+ Hg	0.790 3+ TI	0.310 4+ Pb	0.980 3+ Bi	1.440 Po	0.980 At	Rn
	3.100	1.260	Lanthanide	0.110 Rf	0.940	1.270	Rhenium	Osmium	0.390	0.270 Ds	2.390	1.940	1.110	0.360 Uua	0.700 Uup	Polonium	Astatine	Radon
'	Francium	Radium	Actinide.	Ruther- fordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Darm- stadtium	Roentge- nium	Ununbium	Ununtrium	Ununqua- dium	tium	Ununhexium	Ununsep- tium	Ununoctium
			\mathbb{N}	La	4+ Ce	3+ Pr		3+ Pm	3+ Sm	2+ Eu	3+ Gd	3+ Tb		3+ Ho	3+ Er	3+ T m	Yb	3+ Lu
				Lanthanum	0.230 4+	0.220 5+	0.140	0.260	0.220	1.530	0.350	0.440	0.500	0.560	0.660	0.740	'Ytterbium	0.930
				Ac 0.010	Th 1.050	Pa 0.860	U Uranium	Np 17.30	Pu 13.38	Am Americium	Cm Curium	Bk Berkelium	Cf Californium	Es Einsteinium	Fermium	Md Mendele- vium	No Nobelium	Lr Lawrencium

Figure 1.13: Preferred site, oxidation state of a range of elemental hypothetical dopants for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, calculated by DFT. The colour indicates the most stable cation site. The shade of the colour represents the defect energy with darker colours indicating the lowest defect energy in eV. Reprinted (adapted) with permission from the American Chemical Society. Copyright 2015 American Chemical Society.[129]

included a large range of those that have been computationally predicted and include but are not limited to: Al, Ta, Nb, Ga, Ca, Te, Fe, W, Sr, and Ba.[102, 130–141] Furthermore, the possibility of incorporating multiple elements via co-doping has been demonstrate by the addition of Ga and Al.[142] The versatility of the lithium garnet is such that it may accommodate a large range of dopants at differing sites.[104] A recent study demonstrates a high entropy lithium garnet that incorporated Ga, Nd, Nb, Ta, Ce, Hf, and Ti into the crystal lattice.[143] Whilst stabilising the cubic phase, not all dopants have a positive effect on the electrical properties and lithium metal stability of cubic LLZO. The addition of W and Fe for instance, facilitates a reduction reaction that results in resistive interfaces at electrode/electrolyte as well as between solid electrolyte electrolyte grains.[144, 145] Careful selection of the dopant is therefore required when stabilising the cubic phase of LLZO.

1.0.4 Processing of Solid Electrolyte Thin Films for All Solid State Batteries

Optimising the electrochemical properties of lithium garnet electrolyte materials is a crucial aspect in the realisation of ASSBs. However, careful cell level design and engineering will be required to attain a practical ASSB configuration. This involves aspect of solid electrolyte design and thickness, cathode and anode structure, current collectors, and packaging. This section will however focus on the design and engineering of the solid electrolyte, enabling optimised electrode integration.

To reach maximum energy and power densities of ASSBs, thin, dense structures of solid electrolytes will have to be fabricated in a consistent, uniform, and high throughput process. A thin dense layer is desirable as the conductivity and power density are linked to final film thickness and density. Figure 1.14 demonstrates the link between density and ionic conductivity, whilst film thickness may affect power density and rate capabilities.



Figure 1.14: Logarithmic total ionic conductivity as a function of density for solid electrolyte $Li_{6.19}Al_{0.27}La_3Zr_2O_{12}$. Reproduce with permission from John Wiley & Sons, Inc.[146] Copyright 2016 The American Ceramic Society.

Laboratory scale research utilises electrolyte pellets in thickness usually ≥ 5 mm. Whilst convenient for small scale research, to be considered an alternative to lithiumion batteries, thickness should be as thin as possible. The required solid electrolyte thickness may be calculated using a design consideration drawn from the fabrication of solid oxide fuel cells (SOFC). Now heavily employed in the ASSB community, the area specific resistance (ASR) (Equation 1.12) may be used to provide the specific internal resistance of a targeted section in a layered system.

$$ASR = \frac{L}{\sigma} \tag{1.12}$$

Where L is the thickness of the electrolyte and σ is the ionic conductivity. Using the equation, it is possible to calculate the maximum electrolyte thickness permissible for ASSBs to be competitive with lithium-ion batteries. Schnell *et al.* stipulated a Li-ion benchmark ASR,[147] where a theoretical liquid system with a 25 µm thick film of liquid electrolyte and conductivity of 20×10^{-3} S cm⁻¹ would yield an ASR of 0.125 Ω cm². Considering the tortuosity of a porous separator, this value was increased to 3.75 Ω cm². Using the benchmark of 3.75 Ω cm², it is easy to calculate the required conductivity of a range of thicknesses. In Figure 1.15, a depiction of solid electrolyte conductivities is presented alongside their corresponding maximum permissible thicknesses for ASSB application. The perovskite and LISICON candidates consistently fall below 10 μ m, often failing to exceed a thickness in excess of 1 μ m. In contrast, NASICON and garnet candidates display broader ranges spanning from 11.25 μ m to 67.5 μ m, underscoring the intrinsic link between conductivity and effective solid electrolyte thickness. As mentioned, lithium garnet electrolytes display a high ionic conductivity and a wide electrochemical window against lithium metal. Coupled with a benchmark minimum of 37.5 μ m maximum permissible thickness, cubic garnet compositions present an excellent candidate for film processing and the electrolyte of choice for processing studies presented in this thesis. Furthermore, any subsequent reductions achieved below the maximum permissible thickness would reduce the ASR, thus increasing performance.



Figure 1.15: Conductivities of different electrolytes at or close to room temperature. Text colour in legend indicates structure, Blue = NASICON, Green = Garnet, Red = Perovskite, and Purple = LISICON. The 1 μ m, 10 μ m, and 50 μ m lines are the minimum conductivity required at stated thickness for a competitive resistivity of 3.75 Ω cm², equal to that of a Li-ion cell. Electrolytes need to fall above the line of thickness to meet requirement. The Second Y axis in the graph indicates the maximum permissible thickness that an electrolyte may possess whilst still meeting the 3.75 Ω cm² resistivity for a viable solid-state battery electrolyte. Data extracted from ref.[101]

Various fabrication techniques have been utilised to create thin, high density solid electrolytes. Among these methods are vapour deposition techniques such as pulsed laser deposition, sputtering, atomic layer deposition.[87, 147] While these approaches enable the production of films with thicknesses $\leq 1 \ \mu$ m, their practical application has presented significant challenges. Their high cost, low Technological Readiness Level (TRL), and scalability issues have constrained their potential for widespread use in ASSBs. However, these techniques have found recognition in the realm of micro batteries, particularly for powering Internet of Things (IoT) devices.[148, 149]

However, techniques with a higher TRL poised for implementation are once again

drawn from the SOFC community. Notably, screen printing and tape casting stand out among these methods. The techniques utilise a suspension system that deposits a film of electrolyte which, when further processed, results in the formation of dense freestanding oxide film. The success of the techniques has meant that they are in current commercial use for SOFC and are predicted as primary fabrication technology for oxide solid electrolytes.[147, 150] Whilst few examples of screen printing exist,[151] tape casting appears to have been the preferred technology of choice for processing and development.

Early studies demonstrated the potential of tape casting as an fabrication route for lithium garnet solid electrolytes.[152] However, initial attempts yielded low density films around *ca.* 500 μ m, indicating the requirement for optimisation. Subsequent efforts by Gao *et al.* achieved highly dense films (99 %) at *ca.* 200 μ m thickness with high ionic conductivity of 0.52 mS cm⁻¹. Based on Equation 1.12, the maximum thickness of the solid electrolyte should not exceed *ca.* 20 μ m. Nonetheless, the authors demonstrated the feasibility of producing dense LLZO based oxide films without structural loss or pore formation, often linked to deleterious lithium volatilisation.[153]

Further advancements demonstrated the creation of a free standing perovskite type $Li_{0.34}La_{0.56}TiO_3$ with a final thickness of 25 μ m.[154] Results however noted that the thickness significantly impacted the film strength. The breaking force dramatically decreased from 1959 to 109 mN for thicknesses of 115 to 25 μ m respectively. An optimal film thickness sturdy enough for use in an ASSB assembly was determined as 41 μ m and above. Producing films below 100 μ m poses challenges, as thinner electrolyte films become increasingly brittle with higher density, reducing fracture toughness.[146]

Fabrication of films can be extremely challenging due to the need for mechanical support, and thin film electrolytes may be extremely brittle as increasing density decreased the electrolytes fracture toughness.[146] Moreover, the limited interfacial contact area between flat planar interfaces exacerbates this issue. Volumetric changes arising from electrochemical cycling results in cracking and failure and decrease the anode contact area, impeding Li-ion diffusion, elevating interfacial impedance, and promoting dendrite formation. While thin, high-density films optimise ionic conductivity and bulk resistivity, they simultaneously exhibit lower fracture toughness.

Architecture Engineering

One approach to address these challenges involves providing a mechanical support. In recent years, studies have focused on 3D architectures that provide a porous structural network either side of a thin solid electrolyte film. The aim is to mitigate challenges related to low fracture toughness and contact issues arising from electrode volumetric changes. Initial investigations resulted in a bi-layer configuration designed to increase the film strength by incorporating a porous electrolyte onto a planar surface.[155] Subsequent optimisation efforts lead to a more promising tri-layer configuration (Figure 1.16), composed of two porous host sections encasing a thin dense central layer. These architectures have been successfully demonstrated on multiple occasions.[156, 157]



Figure 1.16: Lithium garnet solid electrolyte trilayer architecture in a porous-denseporous configuration. Reprinted from Hitz *et al.*.[156] Copyright 2018 with permission from Elsevier.

The lithium garnet electrolyte was deposited using a tape casting method. To incorporate pores into the structure, PMMA microspheres were added during the casting process. The subsequent sintered film resulted in scaffold with a central electrolyte thickness as low as 14 μ m, surrounded by a porous network, achieving an overall solid electrolyte thickness of *ca.* 150 μ m.[156] The authors demonstrated the structure's ability to withstand dendrite formation over hundreds of cycles, even under high current densities of up to 10 mA cm⁻². Furthermore, the mechanical strength was evaluated through a direct comparison between a 20 μ m dense layer and a 20 μ m dense layer surrounded by two 50 μ m porous layers. This comparison revealed a notable increase in strength, from 36.7 mN to 321 mN, increasing the mechanical strength by a factor of nine. The 3D porous-dense-porous architecture increases fracture toughness, enabling successful handling and tape manufacture of thin dense solid electrolyte configurations.

Additionally, the porous scaffold facilitates electrode infiltration, effectively mitigating electrode volume expansion and deleterious effects stemming from contact loss. This not only improves adhesion in comparison to planar surfaces but also reduces ionic diffusion distance between electrodes. This innovative 3D architecture not only demonstrates the potential for fabricating thin, dense layer films but also addresses challenges related to the low mechanical strength and resolves issues associated with Li-metal contact on planar surfaces.

The incorporation of a porous framework introduces a complexity in providing a tortuous path for ionic transport, thus complicating the diffusion of Li⁺ ions. For optimal efficiency, the transport pathway should be as direct as possible, approaching unity, facilitating infiltration, and minimizing the length of the Li⁺ diffusion route.

Enhanced control over the porous structures can be attained through various methods, such as 3D printing and freeze tape casting (FTC). Employing 3D printing for LLZO scaffolds enables the creation of uniform, regulated arrays, and grids atop a thin, dense layer of LLZO electrolyte. Within their study, the authors showcased two types of 3D printing: a conformal ink that adhered to the substrate's surface and a self-supporting ink allowing for stacked structures.[158]



Figure 1.17: SEM images of 3D-printed LLZO conformal (a)-(c) and self-supporting (d)-(f) architectures. Reproduced with permission from ref.[158] Copyright 2018 Wiley-VCH

The versatility of this technique enabled the production of a wide array of architectures (Figure 1.17). However, challenges persist regarding the scalability and cost of the technique, as well as resulting larger gaps between features, which could potentially lead to reduced ionic transport.

The preparation of FTC closely resembles the conventional tape casting process. A ceramic slurry undergoes vigorous mixing and is subsequently cast onto a cooling bed. Exposed to a temperature gradient, solidification of the solvent occurs from top to bottom, leading to phase separation and vertical growth of the frozen solvent. Subsequent sintering resulted in a ceramic scaffold characterised by vertically oriented channels with minimal tortuosity, aligning roughly parallel to the current's direction. This stark contrast in pore alignment and structure between the use of polymeric pore formers and FTC becomes evident when comparing Figure 1.16 and 1.18.[159–161]

Both mentioned 3D geometries mitigate critical issues, including high interfacial impedance between the electrolyte and the electrode, as well as mechanical issues like delamination and electrolyte fracture arising from electrode volumetric changes. The development of novel 3D architectures is a crucial development in achieving ASSBs. Moreover, further design and engineering of these architectures by integrating electrolytes of similar chemistry but differing electrical properties shows promise for



Figure 1.18: Fracture surface of sintered freeze-tape-cast LLZO architectures. (a) Sintered porous-dense (140 μ m/36 μ m) bilayer. (b) Porous-dense-porous trilayer (130 μ m/37 μ m/130 μ m). SEM micrograph of the dense (c) 14 μ m layer and (d) porous scaffold. Reprinted (adapted) with permission from ref.[160] Copyright 2020 American Chemical Society.

enhancing electrode integration. This concept, albeit in its early stages of exploration, holds potential for optimised performance, as highlighted in recent research.[162]

FTC and traditional tape casting hold a high TRL and offer cost-effective, scalable methods for mass-producing solid electrolytes. However, they tend to lack precise control over porous architecture, leading to highly tortuous networks. Conversely, 3D printing shows promise in creating bespoke and highly customisable architectures. Yet, due to its lower TRL, 3D printed electrolytes remain an emerging technology. Consequently, tape casting stands out as the preferred fabrication technique for the mass production of solid electrolytes, given its established reliability and maturity from years of advances in the SOFC community.

1.0.5 Summary of Thesis Aims

All solid-state batteries are poised to provide fast-conducting, high energy density and stable batteries for the world's future energy needs. Extensive research efforts have provided the rapid development of future materials to meet the challenging requirements of an all solid state battery system. Although results have been promising, the inherent nature of solid state brings challenges such as poor interfacial contact, high area specific resistivity, lower power densities and challenging processability. Compounding the problem is the formation and propagation of lithium metal dendrites limiting high current densities, ultimately culminating in short circuit and
subsequent battery failure.

Recent studies have indicated that dendrite growth is a result of high electronic conductivity. To therefore better understand how electronic conductivity influences the mechanism behind dendrite growth and solid electrolyte degradation, the known garnet-structured compound $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ was aimed to be modified using Mn^{4+} . Modification of the solid electrolyte was conducted in a controlled degree to carefully modulate the electronic conductivity of the system. A comprehensive collection of analytical techniques is applied, including the use of conventional and synchrotron diffraction, electrochemical, spectroscopic, and computational techniques facilitated extensive characterisation of the synthesised solid electrolyte's properties and structure.

Overcoming interfacial resistance and processability issues pose additional challenges. Present solid electrolyte configurations rely on planar lab-based pellets. Recent studies, however, suggest engineered porous architectures, realised through tape casting, could enable thinner configurations, maximizing electrode contact area consequently minimizing interfacial resistance.[156] These structures however often present a homogeneous ionic conductivity with low electronic conductivity, impeding ion and electron flow at crucial electrode interfaces. One of the aims of this thesis is to produce a thin, tape-cast garnet solid electrolyte bi-layer, demonstrating the possibility for engineered solid electrolyte structures with differing properties. One side will possess potential mixed-ionic electronic conductivity $\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$, facilitating efficient electron and ion percolation at the electrode. Meanwhile, the other side will feature lithium garnet $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ which holds a low electronic conductivity.

To summarise, this thesis aims to investigate the correlation between electrical conductivity and the formation of dendrites, as well as the subsequent degradation in solid electrolytes. Additionally, it aims to evaluate the processability and compatibility of tailored layered solid electrolyte films containing solid electrolytes with differing properties, aiming to facilitate seamless integration with electrodes.

Chapter 2

Experimental Methods

This chapter provides details on all techniques, protocols and methods employed for the synthesis, processing and characterisation of materials used in this thesis. An overview of basic principles are provided to aid in the understanding of these methods. Specific details on processing, characterisation parameters and materials used for synthesis are provided in the experimental section at the beginning of each chapter.

2.1 Synthesis and Processing

2.1.1 Solid State Reaction

Synthesis of novel and known inorganic solids are often achieved via solid-state reaction. The method is one of the oldest and simplest ways of preparing inorganic solid compounds and is used extensively in industry and academia. In order to achieve the desired target phase, starting reagents are precisely weighed in stoichiometric ratio and mixed or ground together using an agate pestle and mortar. However, for larger quantities over *ca.* 5 g, mechanical mixer mills, as discussed in Chapter 2.1.2, are commonly employed. Furthermore, mechanical mills allow for greater use of volatile organic solvents such as acetone, ethanol, or isopropanol to facilitate greater dispersion and mixing during operation.

The mixing and subsequent grinding reduces individual particles in size and achieves a distributed, mixed state on a particle level. The homogenous mixing of particles is required as by definition a solid-state reaction takes place at temperatures below the melting point of solids, typically *ca.* 2/3 of the melting point (T_m) . This is known as the Tammann rule which was developed in the early 20th century and states that at temperatures higher than about two thirds of the melting point, charge carrier concentration in solids becomes substantial and reactions may occur between solid-state materials.[163] As a consequence of decreased temperatures, primary reactions only occurring at the interface of two solids and are propagated via diffusion from the bulk to the interface. As such, a highly homogeneous mixture of small particles is desirable to increase the available surface area and minimise the solid-state diffusion lengths. Interfacial reactions often may not occur at room temperature or over an acceptable timescale and therefore require a sufficient amount of thermal energy to overcome the barrier for reaction. Box furnaces such as seen in Figure 2.1 use resistance heating to achieve temperatures up to 1500 °C, thereby facilitating a reaction environment for diffusing particles to overcome thermodynamic restrictions of interfacial reactions.

Furthermore, furnace atmospheres may also be tailored with the use of oxygen, argon, hydrogen/nitrogen mix or a bespoke mix to enable the desired reaction. Nevertheless, overall reaction times may often still exceed many hours to achieve complete reaction such to form the desired polycrystalline material.

In order to contain the solids during the reaction, and restrict undesirable side reactions with the furnace lining, vessels are used throughout heating regimes. The reaction vessel, or crucible, needs to be suitably inert towards the reagents, so as not to react with the compounds as well be able to withstand the high temperature environment of the furnace. Crucibles often used for this are made of SiO_2 , Al_2O_3 , ZrO_2 , MgO or even Pt; in some cases, a reaction may not be able to be conducted in an open atmosphere and a sealed glass ampule may be used instead.

In this work, solid electrolyte material for processing and investigation was synthesised via the solid-state reaction route using a Carbolite Gero Laboratory Chamber Furnace. Stoichiometric powders were mixed/milled in a Retsch Mixer mill MM500 Nano, seen in Figure 2.2d to synthesise target material batches in excess of 10 g.



Figure 2.1: A process schematic of a typical solid state reaction route. Stoichiometrically weighed out reagents are ground in an agate pestle and mortar or mechanical mill to mix and reduce particle size. The processed particles are then placed in a box furnace for heat treatment to facilitate a reaction to form the required polycrystalline powder.

2.1.2 Particle Size Reduction and Mixing

In powder processing it is often necessary to reduce the particle size of the desired material for further processing, the most common, and simplest way to reduce the particle size is through mechanical milling. Auspiciously, mechanical milling also offers additional advantages to particle size reduction, providing blending for heterogeneous mixtures or homogeneous distribution of particulates. This may be achieved by either the mixing of reagents, or the incorporation of polymers and dispersants. Mechanical milling involves loading the desired sample into a vessel along with objects known as grinding media. Grinding media may come in a variety of shapes and sizes dependent on the desired outcome of operation. During this work, spherical balls and cylinders of yttria-stabilized zirconia (YSZ) were used. The grinding media should possess a hardness rating greater than that of the sample and match the chemical composition of the vessel lining. However, alternative materials used for the media and lining often include ZrO₂, WC, stainless and hardened steel. In order to achieve the desired outcome of particulates, several types of milling may be employed, the most common being: planetary, tumbler, attrition and vibration ball milling.

In planetary ball milling the jars revolve around the centre on what is commonly known as the sun wheel, while the jars themselves undergo a counter rotation, resulting in strong centrifugal forces in combination with Coriolis acceleration. Maximum rotational speeds of up to 2200 rpm are achievable, whilst rotational ratios during operation may be tailored: for example, a ratio 1:-2 corresponds to one sunwheel rotation to two jar rotations in the opposite direction. During rotation, the grinding media and particles become dislodged from the wall, and reconnect with the opposing wall delivering a large amount of kinetic energy from the milling media upon impact with the sample which allows for effective particle size reduction and mixing. The large amount of kinetic energy is also known to achieve chemical synthesis for several materials including battery cathodes, a process which is known as mechanochemistry.[164, 165] This type of high energy milling is well suited to smaller quantities of powder (<60 ml).

Attrition milling as seen in Figure 2.2c places the material within the container alongside a large number of grinding particles, providing a considerably high degree of surface contact. An inserted impeller rotates within the stationary container housing producing a differential movement between the grinding media and material. Rotational actions subsequently result in a large degree of irregular movement for the grinding media, translating into constant impact forces. Additional shear forces occur due to the random movement of grinding media that with high surface contact exact shear forces on the surrounding particles. In comparison to other milling types less grinding occurs at the container walls, which act primarily acts as containment.



Figure 2.2: Images of commonly used ball mills with rotational schematics. (a) Planetary ball milling is employed by the Fritsch Pulverisetter 7 planetary ball mill. (b) Tumbler ball mill by Retsch (formerly Glen Creston). (c) Attrition mill Model 01-Lab Attritor from Union Process.(d) Mixer mill MM500 nano by Retsch that utilises vibration ball milling.

Attrition milling often operates at speeds from about 60 rpm to 300 rpm and can be implemented in either batch or continuous processes.

Tumbler milling utilises gravitational forces to achieve milling. Grinding media and powder particles are loaded into a cylindrical vessel, which is rotated horizontally about its axis. Rotational speeds may be tailored to achieve different types of milling actions. At lower rpm, media cascade down one another, thereby inducing friction and shear forces. Whilst higher speeds induce the media to fall from the top of the vessel thereby impacting and transferring kinetic energy into the powder particles. The speed of the mill should be carefully selected to ensure the desired effect of the grinding media on the particles. Subjecting the grinding media to centrifugal forces by exceeding the recommended speeds will cause them to impinge on the wall. Conversely, low speeds will prevent the grinding media from achieving grinding by causing them to remain at the bottom of the vessel. Several other variables should similarly be considered, including, the loading rate of grinding media and powdered particles. This is to ensure the desired milling action of the tumbler. The scalability of the tumbler mill is such that it may be employed in a laboratory setting with quantities as low as 5 g up to industrial applications into several hundred kg. Furthermore, the process may be batch or, with an applied tilt to the axis, a continuous process.

In this work tumbler milling was used for the mixing of synthesised powders with solvents and commercially available organics to form tape casting slurries. However, all initial mixing of powdered reagents, as well as synthesised powder particle reduction was conducted via vibrational ball milling. Where, in contrast to the other forms of milling, particle agitation is achieved by a horizontal movement of the vessel in radial oscillations; as a result milling frequencies are measured in Hz rather than rpm. The operational movement leads rounded grinding media to impact with high energy onto the sample and vessel walls, thereby reducing the particle size. As with planetary mills, high frequency vibrational mills are capable of mechanochemistry, due to the high kinetic energy and subsequent release of thermal energy. Use of lower frequency oscillations and smaller media allows for mixing of samples rather than particle size reduction.

2.1.3 Tape casting

Tape casting, is a technique established in the 1940s for the high throughput production of ceramic films with thicknesses ranging between 5 to 500 µm.[166] In the most basic explanation, a ceramic powder is combined with a range of solvents, polymers, and dispersants to form a slurry/slip. The resultant slurry is deposited on a non-stick surface where a doctor blade, set to a gap to produce the desired ceramic film thickness, is traversed over the slurry. After casting on the supportive non-stick substrate, the slurry is dried. Following drying and volatilisation of the solvents, the slurry is known as a green body or green tape. The desired green tape properties, such as malleability, ease of handling and structural cohesion allow for further processing; including lamination, which is often utilised to increase the powder packing, or combine tapes of different properties prior to sintering. The compositional make up of a slurry may vary, however some core components of the system always include: ceramic powder, solvent, dispersant, binder, and plasticiser.

The ceramic powder is the material of interest in tape casting and should be the remaining constituent following sintering of the green body. It is therefore of importance that the ceramic powder is of the desired phase and chemical purity post sintering. In order to obtain the desired tape consistency and shape, the powder particles need to be of the correct size for processing. A small particle size is generally desired for effective particle packing and increased surface contact area which aid in green body malleability and sinterability. Excessively small particle size may however lead to drawbacks of tape shrinkages and slurry gelling as a result from large surface area.[167] The particle size and morphology therefore has a great effect on the viscosity, castability, and sinterability of the slurry, and consequently on the properties of the tape; particles must therefore be carefully characterised and optimised.[167]

In order to form a ceramic slurry, a solvent is required. The solvent has several roles, including facilitating the dissolution of organic materials and allowing for the homogenous distribution of all constituent components throughout the slurry. It must however not react with the ceramic powder and only act as an organic solvent, as well as carrier for the ceramic particles. Volatility and polarity of the solvent need to be carefully considered, as solvent properties contribute to the control of the slurry viscosity, organic particle dissolution and evaporation speed. Undissolved organic materials will lead to streaking and surface inhomogeneities such as uneven thickness, whilst volatility dictates drying times of the green tape, which in turn greatly controls processing times. Care is required in order not to shorten drying times excessively, as this may lead to cracking, warping or the formation of a skin during the casting process. Solvents for tape casting are often toxic, inflammable and expensive, thereby requiring safety measures such as fume hoods during processing. As a result, several concerted efforts are being made to mitigate the associated hazards as well as reduce the high costs by replacing these solvents with aqueous solutions.[167, 168]

Mixing stages, such as tumbler milling or shear mixing of all components during slurry preparation often result in a homogenous distribution of the ceramic powders within the solvent carrier. However, due to electrostatic or Van der Waals forces, the ceramics powder can agglomerate and settle within the solvent following these processes. This leads to poor viscosity of the slurry during casting as well as inhomogeneous particle dispersion within the tape. In order to prevent this, a dispersant or deflocculant is used to create electrostatic/steric repulsion forces, keeping ceramic particles in a stable suspension. [169] In the case of steric repulsion, which has been used in this thesis; repulsion is achieved via the addition of polymeric additive known as a deflocculant. The deflocculant is dissolved in the solvent and coats on the outside of the ceramic powders, polymeric chains then unfold and stretch into the space between particles. Polymer chains of neighbouring particles interact with each other forming steric repulsions, resulting in particle repulsion as seen in Figure 2.3. The required amount of dispersant needs to be sufficient to prevent agglomeration but must be kept to a minimum to ensure the lowest level of polymer chains between particles, which, with excessive use, results in agglomeration.

In order for the ceramic powder to retain its shape following solvent evaporation, a binder is required. The binder provides strength and malleability to the green tape, imparting formability and handleability between processes, as well as permitting lamination of green tapes. Commonly used families of binders are vinyl, acrylic and cellulosic binders. The choice of binder is important as they strongly govern



Figure 2.3: To overcome agglomeration and flocculation ceramic particles are covered with a polymeric layer. This layer unfurls and keeps them in a stable suspension via steric repulsion.

the rheology of the slurry, with low molecular weight polymers resulting in lower viscosities. Quantities of binder similarly play an important role, too much binder results in voiding of the sintered tape, leading to lower densities, and too little resulting in cracking of the green tape. The type of binder must further be considered during sintering, as it must display rapid and clean burnout leaving no residue within the tape, but also not sudden combustion in order to avoid rapid gas volume expansion which leads to anisotropic shrinkage, delamination, cracking and bubbles within the tape.[170]

To retain the malleability and flexibility following solvent evaporation, the binder needs to be softened via the use of a plasticiser. The function of the plasticiser is to break the close alignment and bonding of binder molecules, thereby reducing the strength of the green film and subsequently improving flexibility. The choice of plasticiser may fall into two categories: Type 1 – Glass transition temperature modifier and Type 2 – Internal lubricant of polymeric chains. Type 1 plasticisers soften the chains allowing for more stretch within the tape. Large quantities however cause excessive elasticity and tape tackiness. Optimised quantities must therefore be found experimentally. Examples of type 1 plasticisers include phthalates such as Dioctyl phthalate, Dibutyl phthalate, Butyl benzyl phthalate. [171] Type 2 plasticiser provide internal lubrication of polymeric chains increasing their mobility and reducing cracking of tapes as well as providing increased plasticity, ideal for lamination and deformation around topography in multilayer systems. Examples of type 2 plasticisers often include glycols in polymeric form such as Poly(ethylene glycol) or Poly(propylene glycol).[171] The ceramic slurry is a complex multicomponent system; selection of the type and amount of dispersant, binder and plasticiser is often an extensive trial and error process that has seen tape casting dubbed as a "dark art". Minor changes to the system may yield vastly different results to the properties of the slurry, and as such much optimisation may be dedicated to slurry systems in order to yield satisfactory results for processing. In general, the constituents of the slurry are adjusted to find a formulation that delivers: defect-free drying, cohesive, malleable green sheets with homogeneous microstructure that can be effectively laminated; with good binder burnout characteristics and results in high mechanical strength after sintering.[171]

Preparation of the slurry is performed in a multistage process; the exact process and steps vary greatly between material system and experimental set up and only a general guidance on preparation may be provided. The initial stage is the intimate mixing of dispersant with ceramic powder in solvent, which can be achieved via low level mechanical ball milling, often in a tumbler ball mill using milling media. This is to ensure agglomerates are broken up and a homogeneous coating of dispersant is achieved on the ceramic powder particles.

Simultaneously, in a separate process the polymer binder is dissolved in the slurry solvent via agitation. Following separate mixing and homogenising steps, the two components may be combined and further processed via ball milling or shear mixing to form the desired slurry. The ratio of each constituent element and mixing times must be determined experimentally, as each component interact with each other differently. High ceramic particle content and a low binder content are desired however, subsequent casting properties may be negatively affected with incorrect ratios. A compromise must therefore be found in order to balance workability and high solid loading. The amount of ceramic powder included must therefore be experimentally determined to find the optimum ratio for processing. The ceramic powder ratio must therefore be accurately quantified and is expressed as the solid loading $S_{\rm L}$ in Equation 2.1, where solid loading equals the ratio of the powder volume to the total volume of the suspension.

$$S_{\rm L} = \frac{V_{\rm powder}}{V_{\rm powder} + V_{\rm liquid}} \cdot 100 \tag{2.1}$$

Correct ratios of constituent elements for processing need to be determined experimentally; however, in general, a set of conventional rules for processing may be followed to allow for the successful tape casting slurry preparation. These rules include achieving the lowest possible organic component to ceramic powder ratio, fixing the solvent level at a minimum to maintain a homogeneous slurry, using the minimum necessary amount of dispersant to ensure slurry stability, and adjust the binder/plasticiser ratio to create a flexible resistant and easy to use tape.[171]

The casting of the slurry is conducted using a doctor blade on a supportive, nonstick substrate where either the blade or the supportive substrate moves. Small scale laboratory settings often employ the discontinuous technique where the doctor blade is traversed along the supportive substrate, this is mostly performed on small tape casters. A schematic of the process is displayed in Figure 2.4. Conversely large scale applications for mass production use continues casting where a reservoir of slurry is held fixed, and the substrate is continuously moved. This thesis utilised the discontinuous method.



Figure 2.4: Simple schematic representation of the tape casting process. The prepared slurry is deposited on a supportive non-stick film (Mylar) that is held in place by a dynamic vacuum on the casting bed. A doctor blade set to the desired film height traverses over the slurry casting it on the Mylar.

During casting, the doctor blade is set at a desired gap height h, for the green film thickness and then traversed at a set velocity v, casting the film along the supportive substrate. Using these parameters, the shear rate, $\dot{\gamma}$, of the tape may be determined:

$$\dot{\gamma} = \frac{v}{h} \tag{2.2}$$

The shear rate $\dot{\gamma}$, is measured in reciprocal seconds, the velocity v, is measured in meters per second and the gap height h, in meters.

Height adjustments of the doctor blade results in thicker or thinner tapes, and these changes, will affect the shear rate of the slurry and subsequently the viscosity, impacting overall mechanical properties and castability. Following casting, the tape is dried of all solvents to produce a green tape, drying times may vary and may be decreased with the assistance of heaters. Drying times however need to be closely monitored as elevated times may result in warping or cracking of the green film, excessively slow drying times however result in long processing times. Dried green films may be removed from the substrate and further processed via lamination, cutting or punching. The final step in the process for green films is the sintering, where it is important that sintering parameters allow for slow binder burnout in order to ensure minimisation of porosity formation from gas volatilisation. The subsequent sintered tape may then be further processed as desired.

2.1.4 Sintering

Sintering is the process of consolidating loose powder particles into a continuous, dense structure through the application of high heat and/or pressure, without melting the powders. The densification of powders decreases the number of pores, increases density, and offers increases in mechanical strength. These attributes are extremely pertinent to that of ceramic solid-state electrolytes, as high strength and density are often required for processability and optimum conductivity values.

As powders are heated, atomic diffusion occurs at particle necks, propagating and eliminating pores. The mechanistic driving force is due to a change in the free/chemical potential energy resulting from the decrease in surface area, the solidgas interface is decreased and replaced by a new lower energy solid-solid interface resulting in an overall decrease in total energy of the system (Figure 2.5). As such, control of thermal parameters is important due to their direct effect on kinetic diffusion rates; however, other factors similarly contribute to the sintering process such as: particle size, particle distribution, chemical composition, and furnace atmospheres.



Figure 2.5: Schematic representation of particle sintering process. Unsintered particles display large interstitial pores and high surface area. During sintering neck formation occurs by diffusion resulting in decreased pore and surface area. Pores and surface area continue to decrease resulting in a large, fused structure.

In scenarios where the sintering duration may need to be decreased or particulate fusing is particularly difficult, liquid phase sintering may be employed (Figure 2.6). The technique utilises a liquid phase to accelerate and facilitate improved interparticulate bonding. Powerful capillary forces lead to particles being drawn into rearrangement during sintering and, additionally, mass transport is enhanced due to diffusional mechanisms being orders of magnitude higher than in solids. Liquid phase sintering is an excellent technique for materials which are otherwise difficult to densify.[172]

Conventional sintering in a laboratory setting often occurs in a chamber furnace as seen in Figure 2.1. The compacted powders are placed inside of the furnace and heated to the desired temperature. The furnace affords precise control of heating



Figure 2.6: Schematic representation of liquid phase sintering process. An additive is added to the mixed particle state which under sintering conditions transforms into a liquid phase. Capillary forces lead to particles being drawn into rearrangement followed by grain growth and densification.

rates, dwell times and temperature set points. For the work discussed in Chapter 5, conventional sintering and liquid phase sintering were used where components were placed in Al_2O_3 crucibles and densification was conducted in a chamber furnace.

A more advanced technique for powder consolidation is *spark plasma sintering* (SPS), involving the application of high pressure and temperature in the presence of an electric field to achieve densification via Joule heating. The name SPS is often disputed due to the lack of consensus over the presence of plasma during operation. For this reason, the technique is often also known as *field assisted sintering* (FAST).[173–175]

In SPS, powdered samples are placed in a graphite foil-lined graphite die housing, with graphite discs encasing the top and bottom of the sample (Figure 2.7). The purpose of the liner and discs is to prevent the sample from adhering to the graphite die walls and ram rods. Uniaxial pressure between 50 and 250 kN is applied via inserted graphite ram rods, delivered by hydraulic rams. The process takes place under vacuum, and high pulsed electric currents of 1 to 10 kA with low voltages (<10 V) are applied. Temperature is recorded using a thermocouple placed inside the die housing. The pulsed current induces rapid heating through Joule heating, $Q = I^2 R$ (Q: heat generated in joules, I: electric current in amperes, R: electrical resistance in ohms).

Current flow and subsequent heating mechanism are dictated by the electrical conductivity of the powder as well as the die, and are therefore governed in three possible ways: conductive powder and insulating die, non-conductive powder and conductive die, conductive powder and conductive die.[175] With a conductive powder and an insulating die, the current is forced to flow through the sample resulting in the highest possible current densities which directly heat the sample. In the second case, with a non-conductive powder and a conductive die, the current flows through the die housing and the sample is heated through thermal conduction. A



Figure 2.7: Schematic of the SPS technique for the sintering of powdered particulates. Under uniaxial pressure, samples placed within the graphite die under vacuum are subjected to high-frequency pulsed DC currents. This process rapidly heats and densifies the powder via Joule heating.

conductive powder and die will allow for the same effect as the first scenario albeit with a lower current density through the sample. The applied pressure promotes the compaction and facilitates the consolidation of the individual powder particles. The process is highly efficient and can achieve high densities for samples in a short time compared to traditional furnace sintering techniques. The success of this technique has led to its utilization in the research of metals and ceramics. More recently, it has found applications in battery materials, such as garnet solid electrolytes, where a high relative density is required.[173, 176] Whilst effective, the process still requires advanced machinery and instrumentation, and coupled with a requirement for large amount of operational space, the process becomes cumbersome and expensive and therefore remains unlikely to be adopted for high output production purposes.

SPS was utilised for the work discussed in Chapter 3 and a schematic of the overall SPS set up is provided in Figure 2.7. However, the major disadvantages of SPS is the requirement of either high thermal energy, resultant low processing output or long sintering times; other sintering techniques are therefore currently under development which include sintering at lower temperatures,[177] microwave sintering,[178] and flash sintering.[179]

2.2 Characterisation Techniques

2.2.1 Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) has become one of the most consistently used analytical techniques to assess the purity and structural parameters of crystalline powders. The generation and use of X-rays is not just central to PXRD in general, but also plays a crucial role in many analytical techniques used extensively throughout this thesis.

In 1895 German physicist Wilhelm Röntgen discovered X-rays, for which he would later win the 1901 Nobel Prize in Physics. X-rays occur at wavelengths between $10^{-12} \leq \lambda \leq 10^{-9}$ m and reside between γ -rays and the ultraviolet region on the electromagnetic spectrum, corresponding to an energy range between 0.1 – 100 keV.



Figure 2.8: (a) Schematic representation of Cu 1s electron ionisation followed by a 2p electron dropping into the 1s electron level, the excess energy released generates K α X-rays. (b) Bremsstrahlung, K β and K α shown on a characteristic Cu X-ray emission spectra. Illustration adapted and reused.[180]

A common method of X-ray generation in a laboratory setting occurs with the use of an X-ray tube, where an electrically heated tungsten filament emits electrons into a vacuum. The emitted electrons are accelerated via a high potential difference towards a metal target of Cu, Fe, Cr, Mo, or Ag. When the high energy charged electrons interact with metal target X-rays produced result in two different X-ray emissions: polychromatic Bremsstrahlung radiation and characteristic X-ray radiation, which is composed of unique monochromatic wavelengths related to the target material (Figure 2.8b). Bremsstrahlung occurs when the incident electrons are slowed or stopped by collision and subsequent lost energy is converted into electromagnetic radiation. The monochromatic X-rays are produced when an accelerated electron ionises an inner shell electron of the target material. An outer orbital electron subsequently drops down to fill the vacancy thereby emitting the characteristic energies as sharp intense X-ray peaks known as $K\alpha$ and $K\beta$ as shown in Figure 2.8b. The frequency of the resultant $K\alpha$ and $K\beta$ photons is defined by the difference in energy of the electron orbits in target material. These unique emission lines occur following the ionisation of the inner most electron from the K shell (n = 1). The subsequent vacancy is filled by a descending electron from the L shell (n = 2) giving the $K\alpha$ line whilst electrons from the M shell (n = 3) give rise to the $K\beta$ lines.

A common example is the use of Cu as a target where following the 1s electron ionisation (Figure 2.8a), the two characteristic radiation wavelengths may be produced whereby the orbital is either filled from by an electron from the 2p or 3p orbitals; the subsequent K α and K β radiation lines are produced at *ca*. 1.54 Å and 1.39 Å respectively. The energy of K α transition is split into two by spin-orbit coupling to give two discrete wavelengths K α_1 and K α_2 . These can be separated by use of an appropriate monochromator, although the work in this thesis uses unmonochromated K α .

The characteristic wavelength of the target metal differs due to the atomic number Z, where an increasing number shifts the lines to shorter wavelengths. In X-ray diffraction, traditionally the K α radiation is selected for characterisation due to its greater intensity. To filter out the K β and Bremsstrahlung, filters are generally used. In the case of Cu, a thin metal foil of Ni is used which is effective at absorbing the Cu K β radiation and most of the Bremsstrahlung. Generally, the atomic number of the filter element is one or two less than the target material.

Traditionally, when crystals diffract X-rays, two approaches may be used in the analysis. The Laue equations which provide mathematically robust vector equations and the much simpler and more widely used Bragg's law. Bragg's law considers crystals as layers of atomic planes with an interplanar spacing d_{hkl} , where ordered atoms may diffract incident radiation with a defined wavelength λ . However, diffraction of elastically scattered X-ray beams may only be observed when conditions for constructive interference are fulfilled, resulting in scattered X-ray beams being observed at specific angles 2θ . Bragg's law may thus be defined as:

$$n\lambda = 2d_{hkl}\sin\theta \tag{2.3}$$

Where *n* is the integer of order of reflection, λ is the wavelength of incoming radiation, d_{hkl} is the spacing between crystal planes and θ the angle of incidence, which is also known as the Bragg angle.

As the incident wavelength is fixed and the intensity of radiation collected is a function of known angles, it is possible to calculate lattice plane spacing and crystal structures using Bragg's law. Bragg-Brentano geometry uses reflection from a flat sample to re-focus the diffracted beam into a detector located on the same radius as



Figure 2.9: Bragg's law of reflection from a set of crystal planes of atoms (yellow spheres). The X-rays are incident at an angle θ on lattice planes separated by interplanar spacing distance d_{hkl} . Beams of identical wavelength and phase are scattered of two differing atoms, the requirements for constructive interference are met when the path travelled by the second beam $(2d_{hkl} \sin \theta)$ is equal to an integer multiple of the wavelength of the radiation.

the X-ray source with the sample stage and detector rotating by θ and 2θ respectively. In this work, a Rigaku MiniFlex benchtop PXRD instrument was used using Cu $K\alpha_{1/2}$ ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å) utilising the Bragg-Brentano geometry.

2.2.2 Rietveld Refinement

Powder diffraction are typically presented as a plot of peak intensity as a function of angle and the peak position, width and intensity all hold information on the sample's crystalline structure parameters as summarised in Table 2.1.

Peak Position	Peak Intensity	Peak Width
	Atomic positions	
	Atomic site fractions	
Lattice parameters	Form factors	Crystallite size
Crystal Symmetry	Thermal parameters	Microstrain
	Phase fractions	
	Absorption	
	Texture	

Table 2.1: Concise collection of material information extractable from peak position, intensity and width.

To extract the encoded information of the diffraction pattern, a numerical model is constructed where mathematical parameters related to crystal structure may be refined to provide an accurate representation of the observed diffraction pattern. This technique is known as Rietveld refinement, first proposed by Hugo Rietveld for the refinement of crystal structure parameters from neutron powder diffraction data containing overlapping Bragg peaks.[181] The method uses the non-linear least squares regression analysis approach to refine a theoretical model to match the experimentally collected data. For successful refinements, reasonable initial parameters need to be estimated including unit cell parameters, peak shape, and atomic positions. Where the structure is related to a known phase, published crystallographic information may be used as an initial starting point. The efficacy of the technique is such that it may be used to garner information of unit cell dimensions, phase quantities, crystallite size and shape, atomic coordinates, micro strains, texture, and atomic vacancy fractions.

As mentioned, the method achieves this via the least squares approach. Several iterative steps result in the refinement of a theoretical crystallographic model until the calculated diffraction pattern matches the experimentally collected pattern as closely as possible. The difference between collected data and the theoretically modelled fit may be described by the difference function M, which is defined as by the equation:

$$M = \sum_{i}^{n} w_i \left[y_i^{obs} - \frac{1}{c} y_i^{calc} \right]^2 \tag{2.4}$$

Where w_i is the statistical weight factor, C is an overall scale factor, y_i^{obs} is the observed data, y_i^{calc} is the calculated data. Due to the numerical method of the refinement, it is important to quantify the accuracy of the model and subsequent fit through a statistical representation of the accuracy. Several such figures of merit to characterize the quality of the refinement include:

Weighted profile residual (R_{wp}) :

$$R_{wp} = \left(\frac{M}{\sum_{i}^{n} w_{i}(y_{i}^{obs})^{2}}\right)^{\frac{1}{2}} \cdot 100 \%$$
(2.5)

Expected profile residual (R_{exp}) :

$$R_{exp} = \left(\frac{n-p}{\sum_{i}^{n} w_{i}(y_{i}^{obs})^{2}}\right)^{\frac{1}{2}} \cdot 100 \%$$
(2.6)

Goodness of fit (χ^2) :

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}}\right)^2 \tag{2.7}$$

The weighted R-factor, R_{wp} (Equation 2.5) follows from the square root of the quantity minimised - in effect, this represents the difference between the experimental data and the computed model. From a mathematical perspective, R_{exp} (Equation

2.6) is a theoretical minimum error as the numerator is the residual minimised, a "best possible" R_{wp} , where n defines the number of data points and p is the number of parameters. The number of data points should be significantly larger than the number of parameters. As such, the subtraction of the number of parameters is often ignored. The last statistical concept is χ^2 (Equation 2.7), and is a measure of how well the fitted model accounts for the data.[182] Initially starting out large, the value decreases towards unity during iterative steps as the model produces better agreement with the collected diffraction data. Rietveld refinements for this thesis were performed using the *Generalised Structure Analysis System II* (GSAS II).[183]

2.2.3 X-ray Diffraction Computed Tomography

X-ray diffraction computed tomography (XRD-CT) provides diffraction information with high spatial resolution. Initially developed in the 1980s on a laboratory diffractometer[184], the technique is mostly applied at synchrotron facilities where state of the art detectors and production of brilliant X-rays leads to fast and high quality data collection and increased X-ray penetration into samples.

The application and use of X-rays at a synchrotron particle accelerator differs from laboratory generated X-rays. However, in the first instance charged particles (typically electrons) are similarly generated via the heating of a high voltage cathode known as an electron gun; under vacuum the electrons are then accelerated using an electric field in a linear accelerator up to energies of several GeV. These high energy electrons are typically injected into a booster synchrotron, further accelerating the electros to the required GeV energy of the main synchrotron storage ring. Dipole electrostatic or dipole magnetic fields are utilised along the booster ring in order to constrain electron movement in an approximately circular path during acceleration.

Operation of the storage ring is conducted under constant vacuum in order to minimise electron-molecule interaction during operation. A series of electromagnets known as bending magnets placed at curved intersections deflect the electron beam to maintain its circular path around the storage ring. As the electron beam passes a bending magnet, it is subjected to further acceleration, and energy in the form of electromagnetic radiation is emitted, which is also known as synchrotron radiation. Beamlines are connected at each of these intersections of the storage ring and utilise the synchrotron radiation as a source of X-rays for various experiments.

The structure of the storage ring appears to be circular in nature, although it is actually a series of bends connected to straight sections to make up the orbital nature of the ring. Along these straight sections, magnetic insertion devices known as wigglers and undulators are located. Far more advantageous to the production of X-rays, these devices force electrons into a sinusoidal or helical path, thereby collimating and increasing the brilliance of the X-rays. The term "brilliance" is synonymous with intensity and is the primary figure of quantification to compare different sources of synchrotron radiation. In simple terms, it is the measure of the total flux of photons and is characterised by the equation:

$$brilliance = \frac{photons}{second \cdot mrad^2 \cdot mm^2 \cdot 0.1BW \%}$$
(2.8)

Where $mrad^2$ is the divergence, mm^2 the beam area and 0.1BW % the wavelength spread. In short, the brilliance describes the number of photons of a given wavelength and direction present on a spot per unit of time. Electrons that have lost energy from produced X-ray radiation continue to circulate around the storage ring, while lost electron energy is replenished via the use of a radiofrequency (RF) cavities, where oscillating electromagnetic fields provide an increase in energy.



Figure 2.10: Illustration of a synchrotron with its individual sections, adapted and reused with permission.[185] The sections are designated as: 1) linear accelerator (linac), 2) booster synchrotron, 3) storage ring 4) individual beam line, 5) front end, 6) optics hutch, 7) experimental hutch, 8) control hutch, and 9) radio frequency cavity.

The number of beamlines per synchrotron differs between facilities, and the capabilities of each beamline differs vastly. Broadly speaking however, each beamline may be classified into 4 sections: front end, optics hutch, experimental hutch, and control cabin. A schematic representation of a synchrotron and its constituent sections is presented in Figure 2.10.

XRD-CT is predominantly conducted at synchrotrons, the working principle is based on X-ray diffraction where the diffraction signal of crystalline samples is utilised in the identification and imaging of samples. Following reconstruction of the images, each pixel corresponds to an equivalent location yielding a single diffraction pattern. Highly detailed spatial maps may therefore be created of individual phases or chemical species. This powerful technique allows for the visualisation, identification, and separation of chemical species within complex multicomponent systems such as batteries.[186] XRD-CT effectively provides a powder XRD measurement with high spatial resolution. In its simplest form, data acquisition of XRD-CT is achieved via a stepped scan approach. Samples are mounted perpendicular to a monochromatic pencil X-ray beam and translated in step sizes similar to the diameter of the incoming X-ray beam. As the sample is translated, scattered X-rays for every translation step subsequently result in a diffraction pattern which is collected using an area detector. The total length of the translational steps may be the same as the width of the sample but are often extended slightly longer to compensate for sample movements or misalignment. The number of steps may be defined as:

$$N = \frac{L}{S} \tag{2.9}$$

Where S is a translational step and L translational length. Following translation, the sample is rotated angularly, and the translation scan is repeated. The typical range of rotation for the sample ranges from 0 to 2π , effectively completing a full order of rotation. A schematic of the setup is displayed in Figure 2.11. Whilst being the simplest method, the stepped scan approach is slow and time consuming. Optimisation of the sample movement in order decrease overall acquisition time of the XRD-CT scan is therefore required. One such optimised movement is the use of a zigzag scan: here an optimisation in data acquisition time is achieved by reducing dead time resulting from resetting the starting position of the traverse scan for the new angle. Compared to the step scan, the zigzag scan's starting position will alternate 0 and 2π for every step, as supposed to returning to 0 following every scan. Whilst significantly improving the data acquisition time, the zigzag scan requires additional post processing of the collected data prior to tomographic reconstruction.

The raw collected data from a tomographic scan results in a 4D matrix where the collected diffraction data is the size of the 2D diffraction image $(X \cdot Y)$ multiplied by the amount of translation steps N, and the number of rotational steps R. Azimuthal integration reduces the 2D diffraction image into a 1D diffraction pattern representing the number of observations points P in the 1D pattern thereby effectively reducing the initial 4D matrix into a 3D matrix $(N \cdot R \cdot P)$. This initial projection of the object following the tomographic scan is known as a sinogram and represents a volume where there third dimension is in the form of extracted PXRD patterns (often referred to as the spectral dimension).

Following data acquisition, tomographic image reconstruction is conducted using a reconstruction algorithm. Several different algebraic iterative process approaches



Figure 2.11: Illustrative representation of XRD-CT data collection. The incident X-ray I_0 hits the sample of interest which is predominantly phase 1 but includes a secondary phase (labelled 2). As the samples is translated across the beam, diffraction patterns along the whole path are collected by an area detector.

exist for this task, however, one of the simplest used techniques is the back-projection algorithm. As the name suggests, each projection is back-projected onto the object plane, which is then rotated through the angles of collection, the subsequent results are a sum of back-projected, initially collected projection spectra. However, this often yields blurred images and is consequently adapted into the most used technique known as the filtered back projection. The filtered back projection overcomes blurring by applying a convolution filter with the help of the inverse Radon transform; named after Johann Radon the transform computes the line integrals from multiple sources. In this thesis a filtered back projection was used for the reconstruction of tomographic images. Further in-depth details behind the reconstruction of tomographic images using algorithms have been omitted from this thesis. Reconstructions of the collected data were performed by Dr Stephen W.T Price from Finden Ltd.

The reconstruction of tomographic images is far from straightforward and may often result in artefacts within the images, one such artefact that occurs with prevalence in crystallite systems is known as "streaking". Streaking is related to the over saturation of pixels during the tomographic scan. Visibly seen as streaks across an image, they occur when the crystallite size is similar to the size of the X-ray beam. This is in due to the crystallites diffracting in a similar fashion to single crystals, resulting in spots rather than smooth Debye-Scherrer rings, which consequently lead do streaking artefacts during tomographic reconstruction.

The reconstructed data results in a 3D matrix with two spatial dimensions and a third spectral dimension in the form of PXRD pattern. Utilising this information, it is possible to create phase distribution maps of multiple present crystalline phases. In addition to this, traditional PXRD analysis such as Rietveld refinement, phase identification, unit cell parameters, crystallite size, and strain characterisation may be conducted. Maps of the sample may then be created corresponding to any of these criteria yielding spatially coupled quantitative information. Data for XRD-CT in this thesis was collected at beamline P07 (EH2) at the PETRA III synchrotron at DESY. The collected data was analysed using the Data Analysis WorkbeNch (DAWN) software[187], as well as scripts written in python and visualised using Spyder IDE.[188]

2.2.4 Scanning Electron Microscopy

The ability to accelerate electrons to high energies means that electron microscopes are able to move beyond the optical limit imposed by the wavelengths of visible light and readily observe into the nm domain.

In order to image a specimen using an SEM an electron gun produces a stream of electrons from a tungsten filament cathode. An anode places the electrons under a positive charge accelerating the beam with a characteristic energy ranging from 0.2 to 40 KeV. A series of objective lenses, magnets, and apertures condense the beam to a spot size of about 0.4 to 6 nm; magnetic deflectors direct the beam onto the sample along the x - y axes, continuously scanning the sample surface in horizontal lines. A schematic representation of an SEM and its elements are displayed in Figure 2.12a.



Figure 2.12: Schematic representation (a) of an SEM and the constituent parts. Diagram (b) of electron volume within the sample and the various resulting sampleelectron interactions which may be utilised to provide a range of different information pertaining to the sample.

In contrast to optical microscopes, SEM spatial resolution is not limited to the diffraction limit of light but is instead governed by the electron spot size, which in turn is governed by the selected wavelength energy as well as the interaction volume of the beam. As the beam interacts with the sample, electrons are ejected and collected via a range of detectors. Dependent on the type of ejected electron, the detectors digitally transform the signal for optical output. The type of electron ejected is dependent on the beam's interaction with the sample at a range of depths, where various types of electrons are ejected (Figure 2.12b). Inelastic and elastic scattering of electrons produces low energy secondary electrons (SE) and high energy backscattered (BSE) electrons respectively. Low energy SE are produced a few nm below the surface of the sample and provide detailed topographic and morphological images. SE are traditionally used to provide high resolution images. Conversely, due to the higher energy nature of BSE, the electrons originate from deeper within the sample resulting in lower resolution images. An advantage of BSE however is their scattering length being strongly correlated with the atomic number of an atom; images produced from BSE may therefore provide information of elemental distribution within the sample. BSE often produce a characteristic black and white colour contrasting images, highlighting regions of elemental variation. It may however not provide the identity of these elements. With increased volume penetration depth of the sample, electrons remove core electrons from atoms, and as electrons drop down to fill the vacant hole, characteristic X-rays are produces. These characteristics wavelengths may be assigned to individual elements, and their respective quantities measured and mapped, in a technique known as energy dispersive X-ray spectroscopy (EDX). Details of this technique are discussed in Chapter 2.2.5. In addition to these modes, bespoke detectors may collect information from cathodoluminescence. Whereby light is emitted by atoms from high energy electrons, information is collected in the form of sample emitted light, and displayed in real colour, and/or have the wavelengths analysed and displayed as a spectrum. In this thesis, SEM was conducted on a FEI Inspect F50 with SE and BSE.

2.2.5 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDX or EDS) allows for the analysis of the elemental composition of solid materials. This non-destructive technique is often employed in conjunction with SEM (discussed in Chapter 2.2.4). The principle of EDX is based on the interaction between a generated electron beam and core electron of an element present in the analysed sample. This interaction results in the excitation and ejection of the electron, creating an electron hole. Subsequently, an electron from a higher energy orbital drops down to fill the hole, releasing the excess energy as an X-ray. The released X-rays are detected by energy sensitive

detectors. As each element holds a unique atomic structure, the emitted X-rays have specific frequencies related to their atomic number. The governing principle is that the atomic number and subsequent peak positions may be predicted by Moseley's law (Equation 2.10), which states that the square root of the frequency of the emitted X-ray is approximately proportional to the atomic number:

$$\sqrt{v} = A(Z - b) \tag{2.10}$$

Where v is the frequency of the observed X-ray emission line, A and b are constants dependent on experimental set up and Z is the atomic number of the element. The collated data allows for the elemental composition of a specimen to be measured via elemental mapping, which is useful in highlighting segregated or elementally mixed areas of samples. Furthermore, spot imaging allows for information to be gathered from a localised area within the field of view, providing precise and targeted data acquisition on regions or features of interest. Analysis conducted from resultant EDX spectrums may provide elemental quantities in either atomic or weight percentages. Drawbacks however exist, a lack of sensitivity means that if elemental concentrations are too low (<0.1 wt%), the released X-ray energy of the element may be insufficient to accurately measure the elemental proportion. Furthermore, limitations in detection for lighter elements (Z < 4) makes the detection of elements such as hydrogen and helium unfeasible. In particular, lithium results in a very low photon energy level making detection complex, a major drawback for the characterisation of lithium ion battery materials. Within this work, elemental mapping and spot EDX were both performed using an Oxford Instruments X-Max 80mm² SDD detector equipped to an FEI Inspect F50 and analysed using Oxford Instruments AZtec program.

2.2.6 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique based on the photoelectric effect. It allows for the identification of surface elemental composition of the measured sample as well as the electronic state and chemical structure. The technique is a surface sensitive technique meaning effective depth of analysis is limited to <10 nm, sampling depths however may be increased with the use of ion beam milling, this removes small layers of sample to increase the depth of measurements or remove surface contaminants. The photoelectric effect is the name attached to photoemission of electrons in response to illumination with radiation where the photon energy exceeds the work function of the material. The emitted electrons are formally known as photoelectrons. In XPS, an incident light beam with a characteristic photon energy irradiates a material which emits electrons at a measurable kinetic energy. The photon energy may be characterised by the equation:

$$E_p = hf \tag{2.11}$$

Where h is Planck's constant, f is the wave frequency. The measured kinetic energy of the emitted electron may be characterised by the equation:

$$E_k = \frac{1}{2}mv^2 \tag{2.12}$$

Where m is the mass and v the velocity. With both the photoelectron energy and the electrons kinetic energy known, the electron binding energy may be calculated using the photoelectric effect equation:

$$E_{binding} = E_p - (E_k + \phi) \tag{2.13}$$

The work function ϕ in the equation is a constant related to instrumental correction of the spectrometer. Spectroscopic measurements are conventionally taken on solids due to ultra-high vacuums (< 10⁻⁶ Pa) required for accurate data collection. Of primary interest is the binding energy, as it may help determine important factors such as chemical composition and oxidation state. The XPS detector subsequently measures the number of electrons detected at a specific binding energy, which is processed and displayed in an XPS spectrum plot. The displayed characteristic peaks directly correspond the electron configuration of the electrons within the atoms. The amount of element within the XPS sampling volume is directly related to the detected number of electrons in each peak and may determine quantitative compositions of an element within the sample. Additionally, XPS may provide information on the local bonding environment of an atomic species which is affected by the oxidation state, thereby providing valuable information on atomic oxidation states within the analysed sample.



Figure 2.13: Diagram of X-ray photoelectron spectroscopy (XPS) illustrating the basic mechanism of X-rays hitting the surface of a sample. The X-rays subsequently interact with core level electrons which are emitted due to energy absorption from incident photoelectrons.

2.2.7 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a potent non-destructive technique that can provide information on the electronic structure and local coordination environment of atoms. The working principle relies on the interaction between core electrons and incident X-rays. When the incoming radiation is equal or above the binding energy (0.1 - 100 keV) of a core electron, the electron is ejected to an unoccupied higher energy orbital or the continuum. As the incident X-ray energy is scanned across the binding energy of a core electron, a sudden increase in absorption is evident, marking the point known as the absorption edge. The relationship between incident X-ray and the absorption coefficient may be characterised by the Beer-Lambert law:

$$I_{\rm t} = I_0 e^{-\mu(E)x} \tag{2.14}$$

Which if rearranged allows for the X-ray absorption coefficient to be found:

$$\mu(E) = \frac{ln\left(\frac{I_0}{I_t}\right)}{x} \tag{2.15}$$

Where I_t is the intensity transmitted through the material, I_0 the initial X-ray intensity, $\mu(E)$ the X-ray absorption coefficient and x the sample thickness. The absorption edge is a reference to the characteristic increase in X-ray absorption observed at specific energy of the measured element. Due to each electron shell holding a unique binding energy, each edge occurs at different energies, which increase with increasing atomic number. The uniqueness of each edge consequently allows for the identification and characterisation of individual elements within the sample of interest. The nomenclature for characterising the absorption edges refers to the principal quantum number of the excited electron and are listed in Table 2.2:

Table 2.2: XAS edges with responding orbital notation.

Edge	Orbital
K	1s
L	2s, 2p
Μ	3s, 3p, 3d
Ν	4s, 4p, 4d, 4f

Furthermore, splitting of edges may occur as a result of differing electrons at similar core levels. In order to distinguish between these different edges a system of roman numerals is employed in order of decreasing energy.(i.e. $L_I (2s)$, $L_{II} (2p_{1/2})$, $L_{III} (2p_{2/3})$. The incident X-ray energy is increased from below the edge energy of the element of interest to above it, thereby resulting in the characteristic XAS spectra displayed in Figure 2.15. As target electrons are typically excited from the 1s or 2p orbitals, the use of high energy X-rays is required. As a result, measurements are often conducted at synchrotrons radiation facilities. The access to hard X-rays from synchrotron radiation sources allows for deeper penetration depths, thereby providing quantification of elements within a sample devoid of any compositional change that may occur at the surface. During XAS measurements, elemental information may be obtained in two different ways: Transmission and Fluorescence (Figure 2.14).



Figure 2.14: Experimental setup of an XAS experiment, incident radiation I_0 from a synchrotron source is passed through a monochromator before hitting the sample. Detectors are subsequently able to measure resultant X-ray fluorescence I_f and transmitted X-ray intensity I_t

Transmission is the most commonly used configuration and is most suited to homogenous samples with a high concentration of the element of interest. In scenarios where the sample is either too thick or the measured elemental levels too low, fluorescence may be employed. In the case of fluorescence, information is gained from emitted photons following excited electrons returning to a lower energy state. In such a case the X-ray absorption coefficient may be characterised by:

$$\mu(E) \propto \frac{I_{\rm f}}{I_0} \tag{2.16}$$

The plotted XAS spectra may be broken into three distinct regimes, X-ray absorption near edge structure (XANES), Extended X-ray Absorption Fine Structures (EXAFS) and the Pre-Edge. An example of a Mn edge is displayed in Figure 2.15. All regions of the spectra may provide value material information.

EXAFS is representative of the oscillation of the absorption coefficient from ca. 100 - 1000 eV after the absorption edge. An oscillating signal is detected as a result from interactions of backscattered photoelectrons emitted from the target atom. The region provides information about an atom's local environment and can provide details such as coordination number, disorder to neighbouring atoms and distance of neighbouring atoms; the technique is highly sensitive and effective in the analysis of non-crystalline materials.



Figure 2.15: Schematic example of a XAS spectrum highlighting the three regions of interest: Pre-edge, XANES and EXAFS.

XANES, which has been used in this thesis, is generally described as the region 50 eV either side of the absorption edge. The location of the absorption edge is directly related to the element of interests' electron configuration and may therefore provide valuable information on the oxidation state and electronic structure. This is due to the electron binding energy; higher oxidation states require more energetic X-rays for core electron excitation. This arises due to the nucleus being less shielded and carrying a higher effective charge, consequently the absorption edge is shifted to higher energies. With the use of "standards" of known elemental oxidation states it is possible to qualitatively compare the edge positions of the standards vs the specimen in question. Although only providing an estimation of the oxidation state, this technique allows for quick analysis and is extremely useful for samples with mixed valence, as the absorption edge will be located somewhere between the measured "standards". A more elucidating analysis may be conducted using linear combination fitting, where the quantity of each differing valency is characterised via a modelled fit. A further aspect of the XANES region is the pre-edge feature. Occurring prior to the absorption

edge, the pre-edge is characteristic of the excitations of less energetic orbitals, such as 1s to 3d, and are observed for every first row transition metal if the 3d orbital is not fully occupied. Although forbidden by dipole selection rules, the transition may become evident due to 3d to 4p orbital mixing or in non-centrosymmetric geometries. XAS data for this thesis was collected at the Helmholtz-Zentrum (HZB) light source BESSY II on the KMC-3 beamline. XANES data from collected measurements was analysed using the Demeter software package.[189]

2.2.8 Particle Size Analysis

To acquire the particle sizes distribution of powder samples prior to further processing, laser diffraction analysis (LDA) was employed. LDA is a convenient and fast measurement technique that allows for rapid quantification of particle sizes for selected powder samples. Powders are either pumped via air stream towards detectors or dispersed in a liquid, liquid dispersion however requires samples to be insoluble and to withstand agglomeration.

The theory underlining modern LDA equipment is the Fraunhofer diffraction or Mie scattering theory which correlate the measurement of angular variation as well as intensity of light scattered as a laser beam passes through a particulate dispersion. Particle sizes are consequently reported by measurements of laser intensity and incident radiation scattering angles as light passes through the sample dispersion. Scattering is highly dependent on particle size, large particles relative to the laser beam scatter light at high intensity with a small angle, whereas smaller particles result in lower intensity with a larger angle.



Figure 2.16: Illustrative representation of Faunhofer (left) and Mie diffraction theory (right). Fraunhofer (left) does not account for phenomena such as absorption, refraction or reflection and works on the principle of diffraction. The theory is best suited to larger particle sizes. Mie theory (right) takes particle scattering phenomena into account, particle size analysis is possible to 10 nm, the materials refractive index is however required.

Whilst modern equipment utilises both theories, both the Fraunhofer and Mie theory hold advantages and disadvantages in the detection of particle sizes. The Fraunhofer theory only considers the particle outline, providing the advantage of no required knowledge of the sample refractive index, limitations in the theory however render the technique only valid for incident angles less than 30° as well as a particle size requirement of greater than 10 times the incident wavelength.[190] The theory results in large errors for particles smaller than 20 μ m.

In contrast, the Mie theory measures the scattering of electromagnetic waves not only considering the diffraction at particles contours but also the refraction, reflection, and absorption of light. The theory is more capable of providing accurate measurements for finer particles, the limitation of the technique however is that it requires knowledge of the refractive index of the material. The theory however allows for the detection limits of around 10 nm. As the light energy being measured is proportional to the volume of the particles, the results from the analysis are inherently volume-weighted, meaning that the particle size distribution represents the volume of particulates in different size classes. Due to the proportionality an assumption is made that particles are of an equivalent spherical diameter; particle shape is therefore not possible to be determined using this technique.



Figure 2.17: Gaussian distribution with the three axis values for quantification of particle size.

Common graphical representation of LDA is the volume-weighted particle size distribution shown as density distribution. Results are quantified and presented numerically using standardised notations:

- \mathbf{D}_{50} Median Volume-weighted diameter, separating the upper 50 % from the lower 50 % of the data.
- \mathbf{D}_{10} Volume-weighted diameter of the size below 10 %
- \mathbf{D}_{90} Volume-weighted diameter of the size below 90 %
- $([\mathbf{D}_{90} \mathbf{D}_{10}]/\mathbf{D}_{50})$ The Span, measure of the width of the volume-based size distribution.

Particle size distribution of materials for this thesis were analysed using a Mastersizer 3000 from Malvern Panalytical via wet dispersion in isopropanol.

2.2.9 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) involves measuring the mass of a substance as a function of temperature over time. The technique may provide information about phase transitions, absorption, adsorption and desorption behaviour of analysed materials. Analysis is predominantly conducted in N_2 and Ar, but may also utilise a range of other atmospheres including, vacuum, air or CO_2 . For operation the sample is placed into a heating pan and heated at a constant temperature rate while the mass and temperature are continuously measured; as such a dynamic record of change in mass vs temperature is recorded. Under variably heating gaseous decomposition of materials may occur at different times and such are recorded accurately via TGA; for thermal analysis such as solid to solid decomposition techniques such as *differential scanning calorimetry* (DSC) are required. In this thesis a TGA was conducted on a Perkin Elmer Pyris 1.

2.2.10 Archimedes Density

The density of solid electrolytes, in particular ceramics and have been shown to impact ionic conduction mechanism.[191] It is therefore important to quantify the ceramic sintered density in order to ensure comparable densities during experimental setups. Subsequently, density may be excluded as a variable during electrochemical analysis of solid electrolytes. The simplest way to determine an object's density is by the equation:

$$\rho = \frac{m}{V} \tag{2.17}$$

Where ρ is the density of the sample, *m* the mass and *V* the volume. Volume calculations of a sample with an irregular shape, however, are often difficult and may be challenging. Archimedes' principle provides a more accurate technique to determine the density of an irregularly shaped object. The principle works on the basis that the upward buoyant force exerted on a body immersed in liquid is equal to the weight of the liquid that has been displaced.

$$F_b = \rho_f V g \tag{2.18}$$

Where F_b is the buoyancy force, ρ_f is the density of the fluid, V is the volume of the sample and g is the gravitational constant. To determine the density, the principle is then used by weighing the sample in air W_a followed by weighing the sample fully immersed in the liquid W_i , the difference is equal to the buoyancy force F_b :

$$F_b = W_a - W_i \tag{2.19}$$

The volume of the object may be found by rearranging 2.18 to make V the subject and combining 2.19:

$$V = \frac{W_a - W_i}{\rho_f g} \tag{2.20}$$

As the weight of the object in air W_a is the product of m and g we may rearrange 2.20 to find the density of the object:

$$\rho = \frac{W_a \rho_f}{W_a - W_i} \tag{2.21}$$

The derived sample density is subsequently divided by the theoretical crystallographic density, to obtain the relative density of the pellet. In this work samples were measured in isopropanol using the Archimedes principle with a Mettler Toledo MS-43 balance.



Figure 2.18: Schematic representation of Archimedes' principle used with a specialised balance to measure the density of a sample.

2.3 Electrochemical Analysis

Electrochemical analysis is the collection of techniques that use electrical stimulation to analyse the chemical reactivity of a system. Vital information related to kinetics, concentration, diffusion, mechanism of reaction may be gathered by the controlled measurements of oxidation and reduction (redox) mechanisms, using an analytical instrument known as a potentiostat. The primary function of a potentiostat is to control and measure the potential difference between two electrodes. Measurements are generally conducted on a three electrode cells which consists of: the working electrode (WE), which is oxidised and the material under interest, the counter electrode (CE), which is often inert (e.g. Au or Pt) that allows for complementary reaction to provide charge balance, and a reference electrode (RE) which is used to control the potential close to the WE surface. In the case of solid electrolyte measurements, the nomenclature of electrodes may be further expanded. Applied electrodes to the surface of the material of interest may generally fall into three types: ion-blocking, electron-blocking and reversible (non-blocking). Ion-blocking electrodes do not provide or accept ions of the material tested, which in the case of this thesis is lithium but may be any number of ions. They do however allow for the passage of electrons, examples of ion-blocking electrodes include gold, stainless steel (SS), and platinum. Electron-blocking as the name suggests, prevent the passage of electrons, and may sometimes be used to isolate the ionic component of charge transport in mixed ionic-electronic conductors (MIECs) such as in cathode or anode materials. In the case of the final electrode, the reversible electrode, both ionic and electronic transport are facilitated. In the case of this thesis lithium metal is used as a reversible electrode, however, other materials such as lithium alloys or intercalating electrodes may be used. The reversible electrode should be carefully selected depending on the requirements of the study. Blocking or non-blocking electrodes may be assigned to either CE or WE electrode roles depending on the electrochemical analysis in question.



Figure 2.19: Image of a full assembled (left) Swagelok cell with exploded view (right). Individual parts of the Swagelok cell are labelled in the diagram.

Electrochemical measurements on solid electrolytes are generally conducted with the use of a specialised cell known as a Swagelok. Pictured in Figure 2.19, the SS cell is made up of central chamber insulated by Mylar which houses the pellet and SS current collectors. Plungers, ringed with sealing Teflon ferrules are inserted into the chamber on either side along with a spring, which maintains a constant pressure. Caps are placed on either side and tightened completing the cell assembly. Holes within the plunger allow cell to be connected to the potentiostat. In this thesis, analysis was carried out on a range of potentiostats. Specific models and parameters are defined in the experimental section of each chapter. Lithium attached electrochemical testing as well as DC polarisation was conducted with the use of a Swagelok Cell, seen in Figure 2.19.

2.3.1 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) allows for the characterisation and quantification of important electrochemical properties that are inherently related to bulk, grain boundaries or the sample surface of solid state materials, these may include total ionic conductivities or resistances at these domains. The versatile technique allows for the study of various electrochemical reactions over an assortment of materials and their applications including, but not exclusively, fuel cells, batteries, supercapacitors, and ferroelectrics.

The technique is based on the perturbation of an electrical system in equilibrium or steady state via the application of a sinusoidal voltage signal E(t) over a range of frequencies whilst monitoring the sinusoidal response. Important to note, is that the measured oscillating current response I(t) holds the same frequency response as the input voltage but may differ in phase and amplitude (Figure 2.20).

Measurements are conducted across a scanned frequency of typically between 10^{-2} to 10^7 Hz. The wide frequency range allows for the characterisation assignment of different regions within ceramic specimens, which is especially useful in characterising electrical contributions from secondary phases or reactions and mechanisms at sample/electrode interfaces.[192]

The impedance Z(t), which is the quotient of the voltage E(t) and current response I(t) directly relates to Ohms' law and may therefore be defined by Equation 2.22.

$$Z(t) = \frac{E(t)}{I(t)} \tag{2.22}$$

However, due to the sinusoidal nature of the applied voltage E(t), angular frequency must be considered, therefore redefining voltage as:

$$E(t) = |\Delta E| \sin(\omega t) \tag{2.23}$$



Figure 2.20: Schematic representation of the relationship between applied voltage E(t) and output current I(t) in a steady state condition. The subsequent ratio of both sinusoidal responses results in the impedance of the system.

Where $|\Delta E|$ is the amplitude to the applied voltage, t the time and ω the angular frequency. The corresponding measured current similarly follows a sinusoidal form and is therefore defined as:

$$I(t) = |\Delta I| \sin(\omega t + \phi) \tag{2.24}$$

Where $|\Delta I|$ is the amplitude of the measured current and ϕ the phase shift from the applied voltage. The angular frequency may be defined as $\omega = 2\pi f$, where f is the frequency in Hz; alternating the frequency at different time scales allows for a range electrochemical processes to be observed. At high frequencies, fast system responses such as short range ion migration become evident, whereas at low frequencies, responses are indicative of slower processes such as macroscopic scale diffusion. As both voltage (Equation 2.23) and current (Equation 2.24) contain important phase and magnitude information the newly defined terms may be substituted into Equation 2.22 and expressed as:

$$Z = \frac{|\Delta E|sin(\omega t)}{|\Delta I|sin(\omega t + \phi)}$$
(2.25)

With the use of Euler's relationship $(e^{jx} = cos(x) + jsin(x))$, where $j = \sqrt{-1}$ it is possible to express the impedance as a complex function:

$$Z = \frac{|\Delta E|e^{j\omega t}}{|\Delta I|e^{j(\omega t+\phi)}} = |Z|e^{-j\phi} = |Z|(\cos\phi - j\sin\phi)$$
(2.26)
This in turn is conventionally expressed as:

$$Z = Z' - jZ'' \tag{2.27}$$

Where Z' and Z" represent the in-phase and out-of-phase parts of impedance known as the real and imaginary components respectively. Following data collection, EIS spectra are commonly presented in two complementary data formats, the Nyquist plot (Figure 2.21) and the Bode plot. In the Nyquist plot the -Z" is plotted against Z'. Plotting negative Z" allows for the display of the plot to fall in the first quadrant rather than the fourth, thereby improving readability. The Nyquist plot however yields no frequency information and as such a Bode plot may be presented, where $\log(|\mathbf{Z}|)$ and phase angle ϕ are plotted against $\log(f)$.



Figure 2.21: Schematic representation of a Nyquist plot of the real impedance vs imaginary impedance showing the response of an electron resistant material with partially blocking electrodes.

A typical Nyquist plot of a lithium solid state electrolyte is seen in Figure 2.21, showing a characteristic semi-circle with a lower frequency tail at 45 degrees. The end of the semi-circle is characteristic of the electrolyte resistance R, which is equal to the magnitude of Z' when the ϕ is zero. Whilst the lower frequency tail is indicative of electrode behaviour and can often be adjusted by changing the electrode material. Impedance spectroscopy can successfully characterise several regions within a solid electrolyte material in this manner, by resolving different responses from interfaces, bulk, grain boundaries and secondary phases. This is due to unique impedance responses from each region when subjected to variable frequencies. The differing domain responses are characterised by a resistance and a capacitance, which will define magnitude and origin of the response and may simply be represented by:

$$Z = Z' + Z'' = R + \frac{1}{j\omega C}$$
(2.28)

Where R, the resistance, is assigned to the real part of the impedance and C, the capacitance to the imaginary part. However, in order to extricate this information accurately and assign quantitative information to the respective domains, equivalent circuit fitting is required, a typical circuit is seen in Figure 2.22.



Figure 2.22: Typical [RC] equivalent circuit composed of resistors and capacitors for fitting impedance spectroscopy measurements.

The objective of equivalent circuit fitting is to model the system and provide numerical estimates of the different components to the overall impedance of the sample. Due to the relationship between impedance, resistance and capacitance, an equivalent circuit is composed of a combination of resistors and capacitors in parallel. The characteristic time constant τ of each RC element, or region is defined by:

$$\tau = RC \tag{2.29}$$

$$\omega_{max}RC = 1 \tag{2.30}$$

The domain response from each RC element may therefore be separated by the relationship of Equation 2.30 where the apex of the semicircle in the Nyquist plot is equal to 1. As each RC element will hold a different time constant, variable responses can subsequently be assigned to appropriate regions of the solid electrolyte.

Experimental variability however results in non-ideal scenarios and as such measured systems do not reflect ideal equivalent electrical components. This is often the case with the capacitive part of the equivalent circuit. In order to overcome these limitations, it is often preferential to use a circuit element known as a constant phase element (CPE). The role of the CPE is to model imperfect capacitance resulting from imperfect conditions such as rough interfaces or variability in reaction rates. The mathematical definition of a CPE is closely related to that of a capacitor and may be described as:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \tag{2.31}$$

Where Q is value for a CPE and n is the constant phase $(-90 \times n)^{\circ}$, which is a number between 0 and 1, where 0 is perfect resistive behaviour and 1 is ideal capacitive

behaviour. Subsequently, capacitance from the CPE may then be calculated by:

$$C = \frac{(RQ)^{\frac{1}{n}}}{R} \tag{2.32}$$

The measured capacitance values for the RC elements may then be assigned to differential domains of the ceramic specimen; Table 2.3 outlines the different domains that may arise from measured capacitance responses.

Table 2.3: Capacitance values with their corresponding ceramic sample regions. Adapted and reused with permission from John Wiley and Sons.[192]

Capacitance (F)	Phenomenon
10^{-12}	Bulk
10^{-11}	Minor, second phase
10^{-11} - 10^{-8}	Grain boundary
10^{-9} - 10^{-7}	Surface layer
10^{-7} - 10^{-5}	Sample - electrode interface
10^{-4}	Electrochemical reactions

In addition to being able to assign a domain to a resultant impedance response, collected resistive values allow for the calculation of inherent electrochemical properties such as ionic conductivity. The reciprocal of resistivity, it may be characterised by:

$$\sigma = \frac{1}{\rho} = \frac{L}{RA} \tag{2.33}$$

Where σ is the conductivity, ρ the resistivity, R the resistance, L and A the sample thickness and area respectively. The conductivity may therefore be calculated for the entire system from the total resistance measured or for specific individual domains where the resistance is measured from individual RC components. Furthermore, when coupled with variable temperature measurements, it is possible to calculate the activation energy for ionic motion in solid electrolytes. This is achieved with the use of the Arrhenius equation:

$$\sigma T = \sigma_0 exp\left(-\frac{E_a}{k_B T}\right) \tag{2.34}$$

Where σ_0 is a pre-exponential factor, k_B is the Boltzmann's constant, T the temperature and E_a the activation energy. The data may be plotted between $\ln(\sigma T)$ vs 1000/T, where the logarithmic relationship yields a straight line. EIS allows for the characterisation and quantification of important electrochemical properties of a material system, from classification of total ionic conductivities to resistances at interface or grain boundaries. EIS measurements for this thesis were conducted using Swagelok cells as seen in Figure 2.19 on a Biologic VMP-300, variable temperature EIS was conducted on a Biologic MTZ-35 using an ITS-e (enhanced intermediate

temperature system). Further experimental details pertaining EIS are listed in the experimental section of the corresponding chapter.

2.3.2 DC Polarisation

Direct current (DC) polarisation has been extensively used in the field of solid electrolyte materials and has become an important measurement technique to determine ion transport mechanisms. Several DC techniques for the extrication of ionic transport mechanisms exist,[193] among these, one of the most readily used technique for the extrication of ionic and electronic contributions in mixed systems is Wagner's DC polarisation method.[194]

The Wagner method is extremely useful at separating small electronic contributions in a system that is otherwise dominated by ionic transport mechanisms. For the experimental set up, a sample is sandwiched between a blocking and non-blocking electrode, although two blocking electrodes may similarly be used. A constant DC potential is then applied across the sample, where the current is subsequently recorded as a function of time and displayed in a typical current versus time plot. As an electric potential is applied the current spikes before tending towards zero, this is due to the ionic charge carries becoming fully polarised, in mixed ionic electronic systems the current however tends towards a non-zero value.

In this case the final residual current is due to the moving electrons/holes in the system and subsequently quantitative information of the extent of ionic and electronic contributions to the total conductivity $\sigma_{\rm T}$, may be determined through transference numbers of the ionic and electronic charger carries. Since $\sigma_{\rm T} = \sigma_{\rm ion} + \sigma_{\rm e}$, the transference numbers may be calculated by:

$$t_{\rm ion} = \frac{\sigma_{\rm ion}}{\sigma_{\rm T}} = \frac{I_{\rm ion}}{I_{\rm T}} = \frac{(I_{\rm i} - I_{\rm f})}{I_{\rm i}}$$
(2.35)

$$t_{\rm e} = \frac{\sigma_{\rm e}}{\sigma_{\rm T}} = \frac{I_{\rm e}}{I_{\rm T}} = \frac{I_{\rm f}}{I_{\rm i}}$$
(2.36)

Where $\sigma_{\rm ion}$, $\sigma_{\rm e}$ and $t_{\rm ion}$, $t_{\rm e}$ are the conductivity and current distributions due to ion and electron respectively. Transference numbers may subsequently be calculated from the polarisation current versus time plot with the Equations 2.35 and 2.36, where $I_{\rm i}$ is the initial current and $I_{\rm f}$ is the final current.

The electrical resistance is determined via Ohm's law using the final steady state current. The estimated electronic conductivity may then be calculated utilising Equation 2.37, where L is the thickness of the sample, A is the area of the effective contact with electrodes and R is the resistance.

$$\sigma_e = \frac{L}{RA} \tag{2.37}$$

Whilst the Wagner method is one of the most extensively used techniques to determine electronic contributions, other DC methods exist for the evaluation of electronic transport within a solid electrolyte.[195] In this thesis, DC polarisation was conducted in a Swagelock cell (Figure 2.19) on a Biologic VMP-300 at 0.6 V, 0.9 V and 1.2 V between 12 and 24 hours.

2.3.3 Galvanostatic Cycling

Galvanostatic cycling with potential limitation (GCPL) is an electrochemical technique that is used to assess of battery performance. The technique measures the voltage of an electrochemical cell under a constant applied current until a specified voltage limit is reached. Voltage limits are often set to prevent unwanted redox mechanisms within the system and maintain electrode stability. These limits are often referred to as the voltage window of the electrochemical cell and may be determined by cyclic voltammetry (CV). During GCPL the constant current is set either to positive or negative to simulate either the charge or the discharge of the system. Reaching the voltage limits, the current will switch thereby simulating a full cycle of an electrochemical cell, a schematic behaviour of this may be seen in Figure 2.23a. The set current may be modified to observe battery dynamics under a variety of charge/discharge rates, illuminating mechanistic behaviour of batteries under cycling conditions. The rate of current is known as the 'C-rate'. The rate is expressed as C/n where n indicates the number of hours taken to complete the charge.





(b) GC to measure CCD in electrolytes

Figure 2.23: Schematic representation of GCPL where (a) the applied current is constant until a voltage limit is reached and a subsequent reverse bias is applied until the minimum voltage limit is reached thereby completing a full cycle. (b) GC with removed voltage limits to evaluate the performance of a solid electrolyte at forward and reverse currents of ever increasing magnitude until failure occurs.

GCPL may be used in the investigation of solid electrolytes, to study mechanism of dendritic growth. In a measure of 'Critical Current Density' (CCD), GCPL is conducted without potential limits in a cell with symmetric metallic electrodes composed of the relevant species e.g., lithium or sodium metal. The cell is subjected to constant current to initiate ionic diffusion across the solid electrolyte. The cell is placed under a forward bias and held for a defined amount of time before a reverse bias is applied thereby initiating stripping and plating of metal electrodes at the interfaces of the electrolyte. The current is periodically increased following a full cycle until a short circuit results in cell failure. The current reached at failure is known as the CCD, a schematic representation of the current behaviour is seen in Figure 2.23b. Galvanostatic cycling was used in this thesis to study the CCD of synthesised samples.

2.3.4 Cyclic Voltammetry

A powerful electrochemical technique employed to investigate electron transfer reactions in battery materials is known as cyclic voltammetry (CV). In CV a linear potential is applied to the sample and swept back and forth at a defined scan rate between a defined upper and lower limit, the wave form of such an experiment is displayed in Figure 2.24b. The subsequent current response is recorded as function of the potential measured between the working electrode and the counter electrode, whilst the potential is measured between the working electrode and reference electrode. These measurements provide the characteristic cyclic voltammogram seen in Figure 2.24a.

Peak positions on the voltammogram define the peak potentials for cathodic E_{pc} and anodic E_{pa} processes. Similarly, figures for the current at these peaks are provided by I_{pc} and I_{pa} . The measurement technique displays reductive and oxidative processes within the sample occurring at specific potentials and thereby the cyclic and reversible nature of the electrochemical system. In addition to the elucidation of redox mechanisms the technique allows the stable voltage window of a material to be classified where no decomposition is observed.[196] CV in this thesis was used to observe redox activity within solid electrolytes. Measurements were conducted in a Swagelok cell (Figure 2.19) with lithium metal as reference electrode and sputtered Au electrodes as a counted electrode with a scan rate of 0.05 mVs^{-1} .



(a) Schematic display of a voltammogram.

(b) Voltage wave form in a cyclic voltammogram

Figure 2.24: Characteristic voltammogram (a) displaying a current vs voltage plot. The E_{pc} and E_{pa} show peak potentials for cathodic and anodic reductions respectively. I_{pc} and I_{pa} show the peak cathodic and anodic currents of the redox reactions. The potential wave form (b) during cyclic voltammatry shows the voltage being swept forward before reaching a defined maximum limit, where it is subsequently reversed to a defined minimum.

2.4 Computational Modelling

2.4.1 Finite Element Analysis

Finite element method (FEM) has wide-ranging applications in diverse fields such as structural mechanics, fluid dynamics, heat transfer, electromagnetics, and more. It enables engineers and scientists to simulate and analyses complex systems that are otherwise difficult or impractical to solve analytically. Valuable insights may be provided into the behaviour of materials, structures, and physical phenomena, aiding in the design optimisation, failure prediction and understanding of real-world mechanisms.

FEM is a numerical method allowing for the conversion of a continuous problem, such as differential equations that represent an underlying physical behaviour, into a simplified system of algebraic equations that can be solved computationally. The procedure utilises discretisation, assembly and solving to provide solutions which can be post-processed to provide a deeper understanding into the problem. An initial geometrical representation of the problem is constructed using a combination of points, lines, surfaces, and volumes. The material properties and governing equations, such as Maxwell's laws may then be assigned to subsequent regions. To ensure the correct response, carefully considered boundary conditions are required, these may simply be an applied voltage or applied current conservation as well as symmetry to the surfaces. Having established a geometry, discretisation is conducted, a process whereby the geometry is divided into smaller finite elements in a process known as meshing. The elements may take the form of a variety of shapes including polyhedral such as cuboids and prisms, more commonly however, the creation of tetrahedra. Typically, a geometry maybe discretised into millions of tetrahedral elements. The assembly of the system is then achieved whereby a global matrix of equations are formed by the combination of equations assigned to each element, their properties or boundary conditions. These equations result in a full description of the entire system and the size and computational time to solve them scales significantly with number of elements. A balance must therefore be found between using smaller elements, which improve the solution's accuracy (referred to as convergence), and the computational time and power needed to solve the model. FEM analysis in this thesis was performed using COMSOL Multiphysics.[197]

FEM was utilised in Chapter 4 to investigate changes in electronic current flow and density within the synthesised composite system which is presented in Chapter 3. The modelled geometry depicts an ideal microstructure consisting of a 9 × 9 array of cubes (sides = 11 μ m). Within each individual cube an additional cube was created (sides = 10 μ m) to represented a Li_{6.4}La₃Ta_{0.6}Zr_{1.4}O₁₂ (LLZTO) 10 μ m grain bulk with a 1 μ m grain boundary border. Both domains were assigned an electronic conductivity of 10⁻⁹ S cm⁻¹ and 10⁻⁸ S cm⁻¹ for the bulk (central block) and the grain boundary domain, respectively. The secondary phase, La₄LiMnO₈ was modelled as a small disc (r = 1 μ m, h = 0.1 μ m) with an electrical conductivity of 7.5 × 10⁻⁴ S cm⁻¹, a value which was extrapolated from Battle *et al.*[198]

As mentioned, to ensure the functionality of the model several boundary conditions are required. These included electrical insulation boundary conditions which were assigned to the outside four walls of the geometric 9×9 array with the two remaining parallel surfaces being assigned as terminals. The electrical insulation boundary condition may be characterised by

$$n \cdot J = 0 \tag{2.38}$$

where n, is the surface normal, J the current density. The boundary condition effectively sets the current to zero at the boundary, meaning that no electric current flows into the boundary, thereby constraining electrodynamics within the geometry. The geometry was then assigned a 'current conservation' which adds continuity equations based on Maxwell's equations for the electrical potential. The equations used are defined below.

An initial potential of 1 V was applied to the terminals, which using Equation 2.39 allowed for the electric field to be calculated. The equation describing the electric field

$$E = -\nabla V \tag{2.39}$$

where E is the electric field and V is the voltage. The current for the system

may then be obtained by using

$$J = \sigma E + J_e \tag{2.40}$$

where J is the current density, σ is the electrical conductivity, E the electric field and J_e the external applied current density. The final equation used in the current conservation node is

$$\nabla \cdot J = Q_{j,v} \tag{2.41}$$

where $Q_{j,v}$ is the volumetric source of current from boundaries inside the selected layers (i.e between bulk and grain boundary). A Physics-controlled mesh of normal size was applied to the whole geometry before two stationary studies were conducted to solve for steady-state conditions where all loads and constraints were kept constant. The data of the two studies were combined, in order to extricate any increase in current density. A filter of $> 0.32 \times 10^{-2}$ A m⁻² above the global current density was applied to the data and the subsequent results subtracted from each other. This resulted in any current above the filter being visualised in the model. A subsequent volume integration of the filtered results revealed the sphere of influence arising from increased current density. Further details are provided in the experimental section of Chapter 4.

Chapter 3

Electrochemical and Structural Dynamics of Garnet Composite Electrolytes

3.1 Introduction

The solid electrolyte cubic garnet phases based on doped Li₇La₃Zr₂O₁₂ (LLZO) have been the focus of intense research as a ceramic electrolyte for all solid-state batteries (ASSBs). Undoped, LLZO holds a tetragonal (space group $I4_1/acd$) phase with low room temperature ionic conductivity of 10^{-7} and 10^{-6} S cm⁻¹.[126, 199] However, when appropriately doped, LLZO stabilises in a cubic (space group $Ia\overline{3}d$) phase that exhibits excellent electrochemical properties with a high conductivity up to 1 mS cm^{-1} and a wide electrochemical stability window (0 - 6 V vs Li/Li⁺).[103, 117, 200] Furthermore, acceptable stability to atmosphere and Li-metal, coupled with non-flammability, have made it an excellent candidate for ASSBs. [201, 202] Cubic LLZO solid electrolytes however still face major challenges preventing wide scale use in lithium-ion batteries. [89, 203] Amongst the leading issues are the formation of metallic lithium dendrites, formed by the heterogeneous deposition of lithium. Dendrites resemble tree like structures and their formation is initiated at critical current density (CCD) values far below the current commercialisation benchmark level of 5 mA cm⁻².[66–68, 72] The growth and propagation of the dendrites culminate with a connection between electrodes resulting in a cell short circuit. Despite substantial research efforts into the mechanisms of this phenomenon, there are differing hypotheses regarding the importance of various contributing factors.

Efforts from initial studies of the Li|LLZO interface observed void formation during stripping in the Li-metal interface when the current density exceeded the rate at which Li is replenished at the surface.[204] During subsequent plating the formed voids resulted in inhomogeneous Li-metal contact leading to non-uniform, elevated,

local current densities that initiated dendrite formation.[205, 206] This was further corroborated by Liu *et al.* who demonstrated that smaller pits merged to form larger pits which further elevated local current densities leading to dendrite formation within interfacial pits.[207] As a result, the increased local current density at the interface has been sought to be mitigated by increasing Li contact and minimising void formation through a variety of interfacial engineering solutions.[208–212] An alternative proposition however has been made that the direct electronic conductivity of the solid electrolyte correlates with dendrite formation, reporting that lithium dendrites nucleate and propagate directly inside of a Ta-doped LLZO as a result of the inherent electronic conductivity of the solid electrolyte.[69] The authors stipulate that higher electronic conductivities allow for Li⁺ to combine with electrons within the solid electrolyte when the potential reaches the Li plating potential. Furthermore, the electronic conductivity of cubic LLZO may inherently be susceptible to increases during plating and stripping due to a direct reduction of the LLZO.[213]

Any source of enhanced electronic conductivity in the electrolyte ensemble may therefore induce dendrite formation. Optical observations of dendrite formation within the solid electrolyte found preferential nucleation along grain boundaries before resulting in a short circuit, revealing an intriguing role of the grain boundary in solid electrolytes.[73, 214] The role of grain boundaries is further elucidated with a recent investigation reporting that the electronic structure of the LLZO grain boundary underwent a narrowing of the band gap.[85] The resultant increase in electronic conductivity in the interface regions readily allows the flow of electrons along grain boundaries, thereby facilitating Li⁺ ion reduction at the grain boundary during cycling. This directly leads to formation of lithium filaments, which under cycling conditions eventually connect, resulting in a short circuit. These studies provide an intriguing insight into the importance of electronic properties at solid electrolyte grain boundaries.

Grain boundaries may not be the only foundation of enhanced electronic conductivity that enables dendrite formation. A recent study showed that incorporating a reducible dopant (W⁶⁺) into the garnet structure resulted in a change in grain boundary resistance with no observed change in ionic or electronic conductivity.[144] Whilst further studies report critical current densities to have been altered by the incorporation of Ti^{4+}/Ti^{3+} into garnets.[209] Additionally, unwanted diffusion of Co from a LiCoO₂ cathode into Al/Ta-doped LLZO has recently been reported.[51] Where the deposition of a Co containing secondary phase on grain boundaries was observed to readily alter the CCD of the host garnet. These recent investigations highlight the fact that electronic variability in solid electrolytes affects the nucleation and propagation of lithium dendrites. Further exploration into the electrochemical dynamics of grain boundaries, electrochemical reactions, impurities and the interplay between electrical conductivity, microstructure and dendrite formation is therefore required.

The aim of this investigation was to introduce a small, controllable amount of electronic variation to the Ta-doped LLZO garnet system, $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ (LLZTO). A systematic approach would allow for a controlled investigation into the affects and contribution of electronic conductivity on dendrite growth and degradation mechanisms. This was to be achieved by the partial substitution of Zr with Mn; whilst unsuccessful, the unexpected formation of a secondary phase (La_4LiMnO_8) along the grain boundaries was observed. The electronic conductivity of the secondary phase was estimated at *ca.* 7.5×10^{-4} S cm⁻¹, a value extrapolated from Battle *et al.*.[198] Consequently, this secondary phase provides an increase of electronic conductivity within the macroscopic solid electrolyte. This chapter therefore presents how small inclusions of a secondary phase (La_4LiMnO_8) along the grain boundaries can affect the Li-plating and stripping behaviour, and subsequently the CCD of the parent compound. It is hypothesised that the secondary phase affects the electrodynamics of the host LLZTO system and plays an active electrochemical role during stripping and plating with a likely overall deleterious outcome.

3.2 Experimental

The partial substitution of Zr with Mn was targeted using the general formula of ${}^{'}\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4-x}\text{Mn}_x\text{O}_{12}{}^{'}$ (x = 0.035, 0.05, 0.07, 0.105) and by solid state reaction. Li₂CO₃ (Aldrich, 99 % min), La₂O₃ (Aldrich, 99 % min), Ta₂O₅ (Aldrich, 99 % min), ZrO₂ (Aldrich, 99 % min) and MnO₂ (Aldrich, 99.9 %) were used as the reagents. Stoichiometric amounts were calculated and weighed out; a 10 wt% excess of Li₂CO₃ was added to compensate for lithium depletion at high temperatures. Powders were milled in a Retsch Mixer Mill MM500 Nano at 7 Hz for 20 hours in 4 segments with 5 min rest in between. Mixed powders were calculated at 900 °C and 950 °C for 12 hours with a ramp rate of 5 °C min⁻¹, hand grinding followed each calcination step.

Calcined samples were sintered using Spark Plasma Sintering (SPS). Three grams of the powdered samples were placed into the graphite crucible as seen in Figure 2.7. The assembled graphite die was then heated to 1090 °C under vacuum with a ramp rate of 50 °C min⁻¹ and held for 10 min. Following the dwell time of 10 min, the pressure was reduced to 5 kN for 1 min and then fully released and allowed to cool to room temperature. The density of the samples were determined using an Archimedes density balance in isopropanol, the relative density was then calculated using the theoretical crystallographic density of the composites.

All powder X-ray diffraction (PXRD) was performed using a benchtop Miniflex Rigaku diffractometer using Cu K $\alpha_{1/2}$ ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å) source over a $10 \le 2\theta/^{\circ} \le 80$ range at a step speed of 5 ° min⁻¹ and step size of 0.02°. Rietveld refinements were conducted using GSAS II.[183] Rietveld refinement fits were

calculated using CIF files from the Inorganic Crystal Structure Database (ICSD) for LLZTO (ICSD 894) garnet phase, La₃LiMnO₇ (ICSD 99405) and La₄LiMnO₈ (ICSD 94927). A 9th order shifted-Chebyschev function was used to fit the background and a pseudo-Voigt function to fit the diffraction peaks. VESTA 3 was used for structure visualisation.[215] SEM and EDX data were collected on a FEI Inspect F50 high resolution microscope equipped with an Oxford Instruments X-Max 80 mm² SDD detector at 10 kV with a working distance of *ca.* 10 mm and spot size of 3-4 nm. Samples were coated in a layer of Au using an Agar Automatic Sputter Coater.

Electrochemical properties were investigated via EIS, DC polarisation, galvanostatic cycling and cyclic voltammetry. All measurements were performed on cells assembled under an argon atmosphere. For EIS and DC polarisation Li⁺ blocking, gold electrodes were applied using an Agar automatic sputter coater. To ascertain ionic conductivities and activation energies of the pellets, EIS measurements were performed on a Biologic MTZ-35 with an Intermediate Temperature System (ITS) that provided a controlled temperature environment. These measurements were conducted at frequencies between 1 Hz and 1 MHz with a 100 mV perturbation in stepped 20 °C temperature intervals for 0 °C to 120 °C. DC polarisation, Li attached EIS and galvanostatic cycling were performed in Swagelok cells on a Biologic VMP-300 at 25 °C.

Prior to Li attached galvanostatic and EIS cycling, pellets were polished using 1500 grit SiC sandpaper, Li-metal was attached to pellets with a stamp pressure of 100 kg and assembled in a Li|Li symmetric cell, measurements were performed under no stack pressure with an initial 30 min rest period. Cyclic voltammetry was performed using a Biologic VMP-300 with a potential sweep from 0 to 5 V (vs. Li/Li⁺) with a sweep rate of 100 μ V s⁻¹. Au electrode and Li-metal were attached to the pellet as working and counter electrode respectively.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Supra instrument with a monochromated aluminium source with an area of analysis 700 μ m by 300 μ m, with one area per sample analysed. High-resolution Mn 2p and C 1s XPS scans were collected at 20 eV pass energy and 0.1 eV intervals over an appropriate energy range with a 300 sec sweep collection time. Mn 2p was collected as multiples of two sweeps of 300 sec which were later summed to increase the signal to noise ratio. Sputtering of the surface was carried out using an argon cluster source, an Ar₁₀₀₀⁺ cluster at 10 keV was used over an area 3 mm by 3 mm. The data were calibrated using a transmission function characteristic of the instrument to make the values instrument independent. The data can then be quantified using theoretical Schofield relative sensitivity factors.[216]

X-ray absorption spectroscopy (XAS) measurements were conducted on the KMC-3 beamline at the Helmholtz-Zentrum Berlin (HZB) light source BESSY II. Mn K-edge data were collected under fluorescence mode with a spot size of 350 $\mu m \times 350 \ \mu m$, samples were sealed within Kapton tape in order to prevent exposure to atmosphere during measurements. Four consecutive scans of *ca.* 8 min were conducted over a photon energy range of 6423 eV to 7088 eV. Standards of Mn₂O₃ and MnO₂ were measured for the use in XANES analysis. Measurements were normalised by control of the value of the pre-edge range and normalisation range parameters. The two regions represent data before before and after the edge respectively. The pre-edge region is linearly regressed whilst the normalisation range is regressed to the data by use of a quadratic polynomial. The subsequent normalised data was analysed using the Demeter software package.[189]

3.3 Results and Discussion

3.3.1 Structure and Morphological Characterisation

The initial synthesis of garnet samples were conducted under the assumption that manganese would be readily incorporated into the garnet unit cell as predicted by simulation,[129] thereby altering the electronic conductivity of Ta-doped LLZO ($\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ from here on referred to as LLZTO). Isovalent substitution of Zr^{4+} with Mn^{4+} was targeted due to the identical charge of the cation as well as the unpaired 3*d* electrons of Mn^{4+} ([Ar] 3*d*³), which due to octahedral ligand field splitting occupy the t_{2g}^{3} orbitals giving a spherical ion and avoiding the Jahn-Teller activity associated with Mn^{3+} . A consequence of ligand field splitting is the possibility for electronic transitions between the *d* orbitals; the partially filled *d* shell allowing for long range electron transport via a hopping mechanism between the Mn centres. The subsequent substitution would therefore in theory enable mixed ionic-electronic conduction in the compound. The resultant substitution may be represented by 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.035, 0.05, 0.07, 0.105) and from here on referred to as Mn-LLZTO.¹

Following multiple synthetic approaches, the manganese containing samples did not deliver a manganese containing single-phase garnet. As shown in Figure 3.1 the diffraction patterns provided an initially good match to the garnet, but patterns collected from manganese containing samples indicated a subset of peaks that could not be indexed using the garnet structure. The majority of the peaks could however be satisfactorily indexed with the familiar body centred cubic cell ($Ia\bar{3}d$, a = 12.9372(3) Å) of LLZO related garnets, all of the peaks from the x = 0 (Li_{6.4}La₃Ta_{0.6}Zr_{1.4}O₁₂) sample, which was synthesised for reference, were successfully indexed.

Searching against the Cambridge Structural Database and the ICSD revealed that the additional, weak diffraction peaks provided an excellent match to Ruddlesden-

¹The synthesised composite series is represented by this formula, it is however important to note that this structure was not achieved and the formula is used for ease of comprehension.

CHAPTER 3. ELECTROCHEMICAL AND STRUCTURAL DYNAMICS OF GARNET COMPOSITE ELECTROLYTES



Figure 3.1: Figure of (a) Powder X-ray diffraction patterns of solid state synthesised $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ (black) and ' $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ ' (x = 0.035, 0.05, 0.07, 0.105) after 950 °C calcination. The identified Ruddlesden Popper secondary phase La_3LiMnO_7 is labelled *. (b) Unit cell diagram of Ruddlesden Popper n = 2, La_3LiMnO_7 . Lithium is blue, manganese white, and both are octahedrally coordinated, lanthanum is yellow and oxygen red.

Popper phase La₃LiMnO₇. The n = 2 Ruddlesden-Popper (RP2) phase were first synthesised in 1958 by S. N. Ruddlesden and P. Popper.[217] The RP structures are described with the general formula $A_{n+1}B_nO_{3n+1}$ (n = 1, 2, 3) and consist of double layers of the perovskite slabs separated by rock salt layers of LaO. The observed secondary phase La₃LiMnO₇ holds an RP n = 2 configuration with the unusual aspect of two-dimensionally ordered distribution of Li and Mn in the octahedra sites as shown in Figure 3.1b.

Rietveld analysis of the diffraction data used a multiphase refinement of the cubic garnet and the tetragonal RP phases. The atomic coordinates of both the garnet and the La₃LiMnO₇ phase were fixed at literature values whilst the lattice parameters were refined freely. The plotted lattice parameter of the garnet phase, seen in Figure 3.2, displayed a slight increase following an initial decrease. This is contrary to the predicted lattice parameters, which according to Vegard's law should display a linear decrease, due to differing ionic radii of substituted elements (Mn⁴⁺ = 0.54 Å, Zr⁴⁺ = 0.72 Å) .[218, 219] Furthermore, refinement subsequently enabled the quantification of the amount of secondary phase which increased linearly with manganese inclusion, holding a R^2 value of 0.98 strongly indicating correlation. The negligible increase in lattice parameters coupled with increasing amount of secondary phase therefore strongly indicate no cation substitution within the LLZTO lattice. Figure 3.3a displays the diffraction pattern and Rietveld refinement of sample x = 0.105; this sample displays the highest amount (3.8 wt fr.% (0.117(2) mol)) of RP2

secondary phase (La₃LiMnO₇) within this substitution series as shown in Figure 3.1. Full refinement results for all samples are presented the appendix in Tables A.1. SPS was used to form pellets for further electrochemical testing. The density of these pellets was consistently in excess of 98 % as determined using an Archimedes balance.



Figure 3.2: Lattice parameter results for calcined samples obtained from Rietveld refinement analysis (blue star). Garnet lattice parameters do not follow linear substitution as expected by Vegard's law, thereby indicating that an inclusion of manganese is unlikely. Further supportive evidence is seen in the linear increase of the fraction of secondary phase La_3LiMnO_7 (green diamond). The error bars of the measured lattice parameters are masked by the symbol due to them being too small.

SPS treatment could cause reaction or decomposition of the sample, and this was investigated by collecting diffraction data from the sintered samples. Figure 3.4 shows these data displaying the characteristic peaks of the garnet phase and weak diffraction peaks of the secondary phase. Upon further analysis however, it was revealed that the RP2 phase underwent a phase transition to RP1 with a general structure of La₄LiMnO₈, thereby undergoing a reduction from Mn⁴⁺ to Mn³⁺. A potential reaction step during SPS is proposed as:

$$\frac{4}{3}La_3LiMnO_7 \longrightarrow La_4LiMnO_8 + \frac{1}{3}LiMnO_2 + \frac{2}{3}O_2 \tag{3.1}$$

Here, the existing La_3LiMnO_7 undergoes a phase transition to La_4LiMnO_8 along with the formation of LiMnO₂. Negligible concentration levels of LiMnO₂ would



Figure 3.3: Figure displaying (a) Rietveld refinement of powder X-ray diffraction of 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.105) after 950 °C calcination prior to SPS. Bragg reflections of cubic LLZTO and RP2 La₃LiMnO₇ phases are shown below. The fit is in good agreement with the collected data having an R_{wp} = 7.1 % and $\chi^2 = 11.56$. A dashed box displays an enlarged region from 30° to 35° (b), showing significant Bragg peaks from RP2 La₃LiMnO₇.

CHAPTER 3. ELECTROCHEMICAL AND STRUCTURAL DYNAMICS OF GARNET COMPOSITE ELECTROLYTES



Figure 3.4: (a) Powder X-ray diffraction pattern of reference and composite samples following Spark Plasma Sintering (SPS). $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ (black) and ' $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ ' (x = 0.035, 0.05, 0.07, 0.105) after SPS, the identified RP1 secondary phase La_4LiMnO_8 is labelled *. (b) Unit cell diagram of Ruddlesden Popper n = (1) La_4LiMnO_8 . Lithium is blue, manganese white, and both are octahedrally coordinated, lanthanum is yellow and oxygen red.

however make detection via PXRD improbable. The formation of La₄LiMnO₈ has however been previously reported where similar studies attempting LLZO doping with Ni and Co metal cations led to the formation of the RP1 secondary phase in the structure of La₄Li MO_8 (M = Ni, Co).[220, 221] Whilst a more recent investigation highlights the formation of La₄LiCoO₈ within a doped LLZO solid electrolyte garnet as a result of Co diffusion from a LiCoO₂ (LCO) cathode. In the study the authors highlight the potential of further phase formation of LCO within the garnet electrolyte.[51] The formation of LiMnO₂ (LMO) during the SPS step as highlighted in Equation 3.1 may therefore be possible; it is however extremely difficult to collect supporting data on the formation of LMO. Any XRD signal from LMO would be masked by heavier scattering elements from the LLZTO garnet and RP secondary phase. This couple with only a third of LMO for every RP secondary phase would result in the complete suppression of any XRD signals arising from any LMO inclusions.

La₄LiMnO₈ with a single perovskite layer containing a statistical distribution of lithium and manganese. This structure with I4/mmm space group symmetry, was observed in all manganese containing samples and is represented in Figure 3.4. In order to quantify the weight fraction of this secondary phase, Rietveld analyses were performed using the structural model by Burley *et al.*.[222] Analysis of the collected data is seen in Table A.2, which similarly displays a linear increase in weight fraction percentage of 0.7 %, 1.2 %, 1.8 % and 2.8 % for x = 0.035, 0.05, 0.07 and 0.105



Figure 3.5: Figure displaying (a) Rietveld refinement of powder X-ray diffraction of 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.105) after SPS. Bragg reflections of cubic LLZTO and RP1, La₄LiMnO₈ phases are shown below. The fit is in good agreement with the collected data having an R_{wp} = 11.61 % and $\chi^2 = 3.68$. A dashed box displays an enlarged region from 30° to 35° (b), showing significant Bragg peaks from RP1 La₄LiMnO₈.



respectively; indicating that manganese remained unincorporated following sintering.

Figure 3.6: SEM images and EDX spot analysis of $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ (a) x = 0.035 (b) x = 0.07 (c) x = 0.105. Pellets were broken in half for a representative cross section; the subsequent fracture surface appears to be transgranular in nature with minimal visible grain boundaries present. EDX spot analysis on visible grain boundaries as well as non-grain boundary regions are highlighted by red circles. Results revealed elevated levels of manganese at the grain boundaries with little to none on particles surfaces, suggesting negligible incorporation of manganese into the grains. EDX results related to locations 1-12 are tabulated in Table 3.1.

The location of the RP1 secondary phase was ascertained via SEM and EDX spot analysis. The sintered pellets were fractured in half in order to image a representative cross section. Figure 3.6 shows that all samples fractured in a transgranular nature with a highly dense microstructure and few visible grain boundaries. This highly dense microstructure is a likely consequence from the nature of SPS where an elevated pressure allows for high particle compaction, whilst the relatively short sintering times minimise grain growth only allowing for particle fusion. This appearance of high density is in good agreement with the > 98 % measured density of the samples.

Further analyses reveal variations in the contrast from the backscatter detector indicative of the presence of the secondary phase at the grain boundaries. Here the darker regions relate to areas of lower electron density and whereas lighter

regions reflect high electron density arising from elements with higher atomic number. Results from EDX spot analysis are listed in Table 3.1 and reveal the analysed grain boundary regions holding a large atomic percentage of manganese corresponding to the secondary RP1 phase La_4LiMnO_8 , whereas grain surface regions displayed little to no manganese. Coupled with PXRD in Figure 3.4 the EDX analysis confirms a composite of the predominant LLZTO garnet with the grain boundary located RP1 phase, La_4LiMnO_8 .

Table 3.1: List of elemental composition in atomic percentage taken from EDX spot analysis of garnet composites, numbers listed relate to numbers displayed in Figure 3.6. Bold red numbers indicate elevated levels of Mn. Due to EDX being unable to detect lithium elemental weight percentage ratios are only relative to detected elements.

Spot no.	La %	Zr %	Ta %	Mn %	0 %
1	19.8	8.6	4.8	0.1	66.7
2	17.9	8.6	4.0	0.1	69.3
3	46	6.0	1.8	1.6	44.6
4	5.3	2.4	-	24.8	67.5
5	72	-	-	8.4	19.6
6	0.8	0.3	1.1	51.2	46.5
7	17.4	2.2	1.0	31.6	47.7
8	18.8	8.1	4.8	0.3	67.7
9	15.4	6.4	4.2	12.8	61.2
10	11.8	4.8	3.5	23.1	56.8
11	17.9	7.5	4.9	0.4	69.4
12	16.7	7.3	4.4	0.6	71.1

3.3.2 Electrochemical Characterisation

The room temperature electrical conductivity of the RP1 phase La₄LiMnO₈, is estimated to be *ca.* 7.5×10^{-4} S cm⁻¹, based on extrapolation from Battle *et al.*.[198] To therefore ascertain any effect on the electrochemical properties of the sintered composite material, AC impedance, DC polarisation, cyclic voltammetry and galvanostatic cycling on a Li|Li symmetric cell was performed.

Impedance analysis was used to evaluate the Li⁺ charge mobility within the sample. The data are presented in the form of Nyquist plots in Figure 3.7 that compare the single phase Li_{6.4}La₃Ta_{0.6}Zr_{1.4}O₁₂ with the composite structures. Due to high ionic conductivities most high frequency arcs, which correspond to intra-grain ionic motion, lie outside of the experimentally accessible frequency range 20 °C. One strategy to capture the high frequency arcs would be to reduce the temperature of measurement. This would decrease ionic motion and allow for the visualisation of the high frequency arcs. It is noteworthy that all samples apart from x = 0.105 show similar impedance spectra.

To understand the individual contributions to impedance spectra, equivalent circuit models were fitted to the gathered impedance spectra. The impedance spectra contain portions of semi-circular arcs that could be modelled using a resistor (R) and a constant phase element (Q) connected in parallel. The spectra were fitted using equivalent circuits composed of two such components in series with interfacial polarisation at the electrode being modelled by an additional constant phase element as shown in Figure 3.7. Interestingly, sample x = 0.105 displayed an additional suppressed arc and subsequently required the addition of an extra parallel [RQ].



Figure 3.7: Nyquist impedance plot 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0, 0.035, 0.05, 0.07, 0.105) with Au, Li⁺ blocking electrodes performed at 20 °C, the inset shows the high frequency response. Equivalent circuit fits may be seen as a solid lines, with the equivalent circuit displayed in the graph. This equivalent circuit was used for all samples apart from x = 0.105 which required an extra RQ element in series.

Table 3.2: AC impedance fit results and ionic conductivity estimates from fitting equivalent circuit components for LLZTO and Mn-LLZTO samples ('Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂') with secondary phase La₄LiMnO₈. Li⁺ blocking Au electrodes were used and all measurements were undertaken at 20 °C.

Composition	\mathbf{R}_b (k Ω cm)	$C_b \ (pF \ cm^{-1})$	$\mathbf{R}_{el} \; (\mathbf{k} \Omega \; \mathbf{cm}^2)$	$C_{el} \ (\mu F \ cm^{-1})$	$\mathbf{R}_{\mathbf{Gb}} (\Omega \mathbf{cm})$	C_{Gb} (nF cm ⁻¹)	$\sigma_{\rm Total}~({\rm S~cm^{-1}})$
x = 0	2.87	7.5	536.5	0.5	-	-	$3.49(1) \times 10^{-4}$
x = 0.035	4.5	6.1	187.6	0.2	-	-	$2.21(3) \times 10^{-4}$
x = 0.05	3.8	64.0	1.7	0.5	-	-	$2.656(6) \times 10^{-4}$
x = 0.07	3.9	7.5	202.7	0.2	-	-	$2.54(2) \times 10^{-4}$
x = 0.105	9.2	6.9	8.0	0.5	2457.7	0.7	$9.94(2) \times 10^{-5}$

The fit to the high frequency semi-circle resulted in an estimate of the capacitance of *ca.* 10^{-12} F, indicating that this portion of the impedance arose from

the intra-grain/bulk response. The calculated capacitance values of parallel circuit element $[R_{el}Q_{el}]$ lie within the 10^{-6} F range, indicating a likely contribution from the sample/electrode interface.[192] Generally, a distinct frequency response can be assigned to the grain boundary contribution of the impedance. However, high relative densities and observed minimal grain boundaries of the pellets are likely to render the resistance at the grain boundaries negligible, leading to masking by the larger interfacial effects arising from the Li⁺ blocking electrodes.



Figure 3.8: Activation energy of garnet $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ and garnet composite 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0, 0.035, 0.05, 0.07, 0.105) samples. The results show a largely invariant activation energy.

The sample containing the highest concentration of manganese showed a qualitatively different impedance response. Displaying a clearly pronounced second arc, subsequently requiring an additional circuit element. The capacitance value of the new [RQ] element lies within the 10^{-9} F range, revealing the arc to be a grain boundary contribution as commonly observed in LLZO based garnet samples. The measured contribution likely arising from the secondary phase reaching a detectable limit during impedance measurements, thereby contributing to a grain boundary impedance response. Notably, the total ionic conductivity of all samples appeared to be unaffected by the inclusion of the secondary phase. The first semi-circle is indicative of a bulk response and as such the first inflection point is the resistance of the intra-grain/bulk response, the subsequent calculated ionic conductivity ranged from $2.21(3) \times 10^{-4}$ to $3.49(1) \times 10^{-4}$ S cm⁻¹. However, a fall in total ionic conductivity was observed with the detection of grain boundary contribution for the sample with the highest secondary phase concentration. Recent work by Scheld *et al.*, similarly, found a decrease in ionic conductivity of the composite LLZO based garnet that held a detectable level of the secondary phase La₄LiCoO₈.[51] Without a significant change in lattice parameters relative to the other manganese containing garnets, it is likely that the overall ionic conductivity is hindered by the secondary phase as opposed to a change in ionic conduction pathways of the host LLZTO garnet. This is further corroborated by the temperature dependent ionic conductivity of the compounds, which was measured between 0 - 120 °C. The results of Arrhenius analyses are displayed in Figure 3.8 and show a largely invariant activation energy of *ca.* 0.42 eV for all compositions. Full tabulated results of equivalent circuit fitting are displayed in table 3.2.

Table 3.3: Estimated electronic conductivity, ionic and electronic transference numbers of LLZTO and Mn-LLZTO samples (' $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$ ') with secondary phase La_4LiMnO_8 .

Composition	Electronic Conductivity (S cm^{-1})	Ionic transference	Electronic transference
x = 0	$2.6(1) \times 10^{-9}$	99.83%	0.16%
x = 0.035	$2.6(5) \times 10^{-9}$	99.39%	0.61%
x = 0.05	$2.6(6) \times 10^{-9}$	99.31%	0.69%
x = 0.105	$5(2) \times 10^{-9}$	98.56%	1.44%

DC polarisation measurements showed that every sample had a similar value for the electronic conductivity of $ca. 3 \times 10^{-9}$ S cm⁻¹. It is notable that this is in good agreement with literature values for single phase LLZO based garnets,[223] and shows that incorporating the relatively highly electronically conducting ($ca. 7.5 \times 10^{-4}$ S cm⁻¹) secondary phase at low levels had no impact on the DC transport. This may be due to the minimal amount of secondary phase dispersed in an unconnected network within the composite electrolyte thereby lying below the percolation threshold. The electronic transference percentage is however observed to increase linearly with inclusion of the secondary phase.

To ascertain the effect of the secondary phase on electrochemical properties in contact with Li-metal, as well as reversible lithium stripping and plating performance of the composite, AC impedance and galvanostatic cycling were performed with Li-metal electrodes. Each pellet was prepared identically to ensure consistency between measurement results. The sample surface preparation, Li stamp pressure, and cell rest times were consistent between measurements and are described in the experimental section.

AC impedance was conducted on Li|Li symmetrical cells prior to galvanostatic cycling and are displayed in Figure 3.9. The high frequency arcs which are assigned to bulk conductivities are extremely similar for all compositions and hold an average resistance of 1.07 k Ω cm⁻¹. This indicates that the intra-grain impedance behaviour



Figure 3.9: (a) Electrochemical impedance spectroscopy results of symmetric Li|Li cell for 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0, 0.035, 0.05, 0.07, 0.105) performed at 25 °C. (b) Magnification of the high frequency response with (c) displaying the final magnification in order to capture clear resolution. Equivalent circuit fits may be seen as solid lines, fitting required the use of two equivalent circuits: [RQ][RQ] for x = 0 and 0.035 whilst all other samples required the addition of an extra [RQ]. Equivalent circuits are summarised in Figure A.2.

Table 3.4: Estimated AC impedance equivalent circuit fit results for individual components for $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ and ' $\text{Li}_{6.4}\text{La}_3\text{Ta}_{0.6}\text{Zr}_{1.4-x}\text{Mn}_x\text{O}_{12}$ ' composites with secondary phase $\text{La}_4\text{LiMnO}_8$. AC impedance was conducted with Li-metal electrodes at 25 °C. Subscripts *b*, *In*, and *Sp* represent bulk, interface, and secondary-phase respectively.

Composition	\mathbf{R}_b (k Ω cm)	$\mathbf{C}_b \ (\mathbf{pF} \ \mathbf{cm}^{-1})$	$\mathbf{R}_{\mathbf{In}}$ (k Ω cm ²)	$C_{In} (nF cm^{-1})$	$\mathbf{R}_{\mathbf{Sp}}$ (k Ω cm)	C_{Sp} (nF cm $^{-1}$)
x = 0	1.0	81.1	75.3	29.4	-	-
x = 0.035	0.87	82.3	18.5	85.6	-	-
x = 0.05	1.0	48.8	3.8	35.0	8.7	19.7
x = 0.07	1.0	147.9	0.4	12.5	7.1	90.9
x = 0.105	1.5	220.5	217.4	79.3	1.5	11.5

of samples was unperturbed by the presence of the secondary phase as well as formation and assembly of the cell with Li electrodes, a feature similarly seen with Au, Li⁺ blocking electrodes in Figure 3.7.

The impedance of the symmetric cell does show significant changes in interfacial dynamics as the quantity of the secondary phase is adjusted. Introduction of the secondary phase leads to a decrease in the interfacial resistance from 75.3 k Ω cm² from single phase garnet to 0.4 k Ω cm² for the x = 0.07 sample. Increasing the Mn content to x = 0.105 however increases the resistance at the interface significantly. The low frequency arcs are indicative of the high interfacial resistance and may result from low Li-metal wettability, which has been reported to arise from the presence of small quantities of lithium carbonate forming at the surface due to reaction with moist air. [201] The secondary phase appears to improve Li-metal contact, decreasing the resistance up to x = 0.07 before reaching a limit. Whilst further increases in the secondary phase, La₄LiMnO₈, may provide an ionically resistive interface thereby increasing the resistance. A third [RQ] component was fitted for x > 0.05 onwards, with a capacitance in the range of 10^{-9} indicating the grain boundary and subsequently the secondary phase. Notably, the resistance of the grain boundary decreases significantly with the increase of the secondary phase whilst the electrode-electrolyte interfacial resistance increases. It is likely that as the quantity of the secondary phase increases on the grain boundaries, the resistance decreases due to electronic contributions from the electronically conducting secondary phase.

Galvanostatic cycling of the samples used increasing current in steps of 10 μ A cm⁻² every hour up to the CCD. The first electrolyte to fail was the single phase material LLZTO at 0.1 mA cm⁻². This is in good agreement with Krauskopf *et al.*, as the maximum current density achievable for a mophological stable interface in a polycrystalline Li|LLZO|Li cell without external pressure.[205] An investigation by Flatscher *et al.* however demonstrated that in single crystal Ga-doped LLZO the natural current density achievable, without external pressure was 0.28 mA cm⁻².[66] The variation in reported results from polycrystalline to single crystal LLZO based solid electrolytes highlights the contributing impact in variation of microstructure and grain boundaries.

Figure 3.10 shows that the CCD increases with the quantity of secondary phase, reaching a maxima of 0.3 mA cm⁻² for x = 0.07. Further increasing the Mn content to x = 0.105 resulted in a decrease to 0.12 mA cm⁻². The results of the CCD may be linked to the observed change in the interfacial impedance (*cf.* Figure 3.9), whereby a decrease of interfacial resistance has allowed for an increase in CCD. A simple summation of the results is displayed in Figure A.4.

Two mechanisms are proposed as possible origins for a reduction of interfacial resistance up to x = 0.07. The first, as a resultant change in surface present Li₂CO₃



Figure 3.10: Galvanostatic cycling of LLZTO and LLZTO composites in a Li|Li symmetrical cell at 25 °C under no external pressure. The current was increased every hour by 10 μ A cm⁻² until a short circuit occurred. Failure of LLZTO occurs at a CCD of 0.1 mA cm⁻². As the secondary phase is increased to x = 0.035, x = 0.05 and x = 0.07 an increase in CCD is observed to 0.15 mA cm⁻², 0.22 mA cm⁻² and 0.3 mA cm⁻² respectively. A limit is however observed at x = 0.07 where after the performance is decreased to 0.12 mA cm⁻² for x = 0.105.

and the second, which could be attributed to an interfacial layer of La₄LiMnO₈. The RP1 phase holds a significant electronic conductivity (*ca.* 7.5×10^{-4} S cm⁻¹), which would provide a more homogeneous Li⁺ flux and electric field at the interface and grain boundary. An inhomogeneous strong electric field has been shown to spur the formation and propagation of dendrites.[224] It therefore stands to reason that the homogenisation of the electric field reduces the interfacial resistance and as such the propensity for dendrite growth. This has been corroborated by similar work where the inclusion of a conductive interface at the Li/electrolyte boundary increased Li contact and homogenised the Li flux and electric field, thereby increasing the CCD.[208, 225, 226]

A reduction in CCD and increase in interfacial resistance is however seen at x = 0.105. The weight factor of the secondary phase may be at a critical level whereby an ionically insulating interface is created as well as a conductive network within the sample. This ultimately expedites the growth of Li filaments, deteriorating electrochemical properties and resulting in a short circuit at lower CCD.

After cycling, cells were transferred into a glove box and disassembled for postcycling analysis. Lithium electrodes were removed and the surface was optically examined. Figure 3.11 displays post cycling 'darkening' or 'dark' discoloration on the pellet surface which was seen on both sides and across all manganese bearing samples.



Figure 3.11: Manganese containing pellets displayed a darkening following Li-metal stripping and plating. The darkening appears to be spread significantly across the pellet indicating redox behaviour of the secondary RP1 phase.

This 'darkening' is contradictory to previous reports that demonstrated that Li dendrites are observed as macroscopic dark spots following cell short circuiting.[73] These macroscopic dark spots are often localised spots, conversely, the 'darkening' on manganese bearing pellets appears to be widespread rather than isolated Li filament growth. Similar widespread darkening mechanisms within LLZO have previously

been reported, the incorporation of reducible tungsten dopant, resulted in darkening of the pellet and was determined to be a result of a partial reduction of W^{6+} to W^{4+} was observed.[144] Darkening was further observed with Fe³⁺ stabilised LLZO, the pellet was seen to darken upon contact with Li-metal, forming a resistive tetragonal LLZO interface, indicating Li-metal instability. The authors hypothesise that the darkening as a result of partial reduction of Fe³⁺ to Fe²⁺.[145] More recently, this darkening effect has been further reported by Scheld *et al.*, which observed the mechanism with the inclusion of a Co bearing RP1 phase.[51] It therefore suggests that the darkening of the pellet is a consequence of manganese redox activity under cycling conditions, indicating that the RP1 phase is electrochemically active.

To further gain insight into the redox behaviour of the manganese containing sample with Li electrodes, cyclic voltammetry was conducted on x = 0.05. The cyclic voltammogram in Figure 3.12 displays cycles 1 - 10. Initial cycles display the characteristic Li deposition peak at 0.5 V and subsequent stable behaviour from 0 V to 5 V against Li-metal as expected. Cycle 5 onwards however shows the appearance of an oxidative peak at 4.2 V indicating secondary electrochemical activity. The peak location is comparable to the Mn^{3.5+} to Mn⁴⁺ transition of LiMnO₂ which result from Li-rich to Li-poor phases.[110]



Figure 3.12: Cyclic voltammetry of x = 0.05 was conducted at 25 °C between 0 V and 5 V. Initial cycles displays stable behaviour of the composite solid electrolyte with the characteristic lithium deposition peak at 0.5 V. However, cycle 5 sees the appearance of an oxidative peak at 4.2 V, indicated by *. CV was conducted with a sweep rate of 100 μ V s⁻¹ at 20 °C, Au and Li-metal were attached to the pellet as working and counter electrode respectively.

The insert shows the subsequent peak current increase with successive sweeps,

which in the case of LMO indicates a structure transformation of layered LiMnO₂ into a spinel like phase.[227, 228] Whilst the presence of LMO is predicted via reaction during the SPS step (*cf.* Equation 3.1), presence of the structure within the composite cannot be confirmed and as such the quantity is unlikely to be sufficient to elicit an oxidative response as seen at 4.2 V. A more likely mechanism is that the RP1 phase displays manganese oxidative behaviour as result of electrochemical activity, which would support the discolouration observed in the pellets. Such an oxidative behaviour would display a current peak in a similar vicinity to 4.2 V. Subsequent cycles however show an increase in the current peak which may indicate a continuous oxidation of Mn^{3+} to Mn^{4+} . Similar to LMO, continuous oxidation of manganese in the RP1 phase would have to be facilitated by a extraction of lithium from the lattice and as such a change in the crystal structure, a potential reaction may therefore be proposed as:

$$La_4 Li MnO_8 \longrightarrow La_4 Li_{0.5} MnO_8 + Li_{0.5}$$

$$(3.2)$$

Interestingly, the reverse sweeps do not present a corresponding reduction peak, demonstrating an irreversible nature. A consequence for the irreversible nature may be that during cycling, Li ions are easily extracted out of the manganese bearing RP1 secondary phase whilst reinsertion is energetically less favourable. Extracted Li ions would therefore preferentially conduct within the LLZTO electrolyte towards the electrodes or, begin plating within the solid electrolyte. The extraction of Li from the RP1 lattice would therefore result in a structure change for the RP1 phase, potentially to La₄MnO₈, which has been computationally predicted as a tetragonal $I4_1/amd$ or orthorhombic Cmmm.[229] This concept is further explored in Chapter 4. Such a structural change would induce manganese oxidation which would result in the darkening on the pellets (*cf.* Figure 3.11) and observed current peak increase at 4.2 V (*cf.* Figure 3.12).

3.3.3 X-ray Photoelectron Spectroscopic Characterisation

To further examine the oxidative behaviour and the nature of the darkening in these pellets, X-ray photoelectron spectroscopy (XPS) was utilised. Samples were subsequently assigned one of three identifiers: 'Pristine', representing a sintered pellet; 'dark' signifying the visible dark regions (Figure 3.11) on a pellet following Limetal cycling; and 'light', denoting sections that retained the pellets' original colour between the darkened regions. Initial scans of two manganese bearing samples (x = 0.07) 'dark' and 'pristine' revealed noisy spectra due to the very low concentration of Mn, which at 0.3 at% was just above the level of detection of about 0.1 at%. The noise in the spectra was mitigated by increasing the analysis time, but the resulting spectra were found still to be too noisy to resolve the multiplet splitting expected for

manganese. The spectra may be compared to reference spectra in Figure 3.13c.[230] As expected, the peak bonding energies at approximately 642 eV for Mn $2p_{3/2}$ is too high to be metallic manganese (*ca.* 639 eV) and too low for Mn⁷⁺ (*ca.* 647 eV). The shape of the Mn $2p_{3/2}$ peak however appears to be most similar to the Mn⁴⁺. The results therefore appear to suggest that the surface manganese is present as Mn⁴⁺, this is contrary to the PXRD results presented in Figure 3.4 which display the presence of RP1 La₄LiMnO₈ which hold manganese in a Mn³⁺ configuration. Interestingly the 'pristine' XPS data appears to be identical to the 'dark' sample alluding to the potential presence of Mn⁴⁺ in the as-made pellet. As XPS is a surface measurement technique with a penetration depth of *ca.* 5 nm and is therefore highly sensitive surface reactions. Coupled with concentration of manganese this meant that the data were unable to reveal if the configuration was exclusively Mn⁴⁺ or a mixed oxidation state.

Scans of the C 1s peaks reveal a change in the formation Li_2CO_3 . Sample x =0.07, prior to Li-metal attachment (pristine) reveals a predominant contribution of Li_2CO_3 which has been shown to cause a resistive interface with Li-metal. [201] The XPS spectra of the 'dark' sample shows a decrease in the lithium carbonate peak; an observation that has been similarly noted by Scheld *et al.* during XPS measurements of cobalt containing RP1 secondary phases in an aluminium-tantalum doped LLZO.[51] This apparent decrease in the quantity of lithium carbonate may indicate a reaction between Mn ions forming an analogue of lithium manganate at the surface. Once again, a more likely scenario would be that the reduced quantity of Li_2CO_3 is a result of a reaction with the RP1 secondary phase. This change in surface chemistry would result in the formation of and release of gaseous CO_2 during cycling, however, detection of CO_2 is not possible in the current Swagelok cell set up. Importantly, the observed decrease in Li_2CO_3 further corroborates one of the proposed mechanisms explaining the resultant decrease in interfacial resistance (cf. Figure 3.9 and Table 3.4) and subsequent increase in CCD (cf. Figure 3.10). However, once detrimental levels (x = 0.105) of RP1 secondary phase are reached an increase in interfacial resistance, decrease in CCD, and drop in grain boundary ionic conductivity are observed which as mentioned may be due to the build-up of an ionically blocking layer of La₄LiMnO₈.

Due to uncertainty from collected XPS data, X-ray absorption spectroscopy (XAS) experiments were carried out to further quantify the oxidation state of manganese. Measurements were conducted on the KMC-3 beamline at the Helmholtz-Zentrum Berlin (HZB) light source BESSY II. Figure 3.14a shows the XANES region of the XAS data with Mn K-edge for the 'dark' and 'light' sections of composite samples (x = 0.035, 0.07, 0.105) as well as reference standards for Mn³⁺ and Mn⁴⁺.

The normalised data reveals that all composite samples fell between the reference samples thereby revealing a mixed oxidation state of the Mn^{3+} and Mn^{4+} . Closer



Figure 3.13: XPS measurements of as sintered, 'pristine' and 'dark' LLZTO and Mn-LLZTO pellets (x = 0.07) (a) Spectra of Mn 2p, red displays the results from the sintered non-cycled 'pristine' sample, whilst black displays the results from the 'dark' regions following Li-metal attachment and cycling. The low levels of manganese caused high levels of noise in the spectra and it was not possible to discern between Mn³⁺ and Mn⁴⁺. (b) Spectra of C 1s for 'pristine' and 'dark' (blue and black) the pristine sample shows the presence of Li₂CO₃ along with a carbonaceous contamination. On the contrary results from the 'dark' regions following Li-metal attachment and cycling show a large reduction of Li₂CO₃. (c) Reference spectra of Mn 2p for Mn²⁺, Mn³⁺ and Mn⁴⁺. [230]

examination of the pre-edge region (Figure 3.14b), marked by a dotted box in Figure 3.14a, reveals a minor shoulder within the measured samples. The XAS pre-edge is sensitive to d orbital occupancy displaying 1s to 3d transitions and as such is an indicative response arising from a change in d orbital occupancy. The observed shoulder in the pre-edge region is inherent in the MnO₂ reference standard and the measured samples are seen to be exhibiting the beginnings of this shoulder indicating a propensity towards a Mn⁴⁺ state. For further quantification, the energy positions of all samples were taken at the normalised absorption coefficient $\mu(E)_{0.5}$ displayed in Figure 3.15. The 'dark' and 'light' sections appeared to hold no significant difference from one another and display a mixed oxidation state of the manganese. The depth of analysis must be considered, XAS was conducted under fluorescence mode and holds a penetration depth of *ca.* 50-100 nm. Whilst, a more significant depth is



Figure 3.14: X-ray absorption spectroscopy (XAS) measurements (a) of the Mn K edge for the light and dark regions of composite LLZTO as well as Mn^{3+} standard Mn_2O_3 and the Mn^{4+} standard MnO_2 . All samples are observed to lie between both standards revealing a mixed oxidation state of Mn^{3+} and Mn^{4+} . The dashed box highlights the pre-edge region displayed in (b), pre-edge spectra appear to hold a slight bowing upwards, similar to that of MnO_2 , indicative of propensity to a Mn^{4+} configuration.



Figure 3.15: XANES energy shift at $\mu(e)_{0.5}$ for 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.05, 0.07, 0.105). Measurements were taken on the 'Light' areas, which displayed no darkening and on the 'Dark' regions which are representative of the darkening.

probed in comparison to XPS, length scale and depth of penetration the dark sections must be considered. XAS and XPS analysis show that the sample holds a mixed oxidation state of Mn^{3+} and Mn^{4+} at the interface and the immediate region within the bulk (*ca.* 50-100 nm). With an initial PXRD pattern indicating a RP1 phase (La₄LiMnO₈), the manganese is expected to hold a 3+ oxidation state, XAS and XPS however reveal a change towards Mn^{4+} . It is likely that phase change occurs at a long length scale during cycling, initially beginning at the interface and subsequently moving through the sample. Diffraction is sensitive to long-range, crystalline order and would be largely insensitive to changes in local oxidation state changes driven by surface reactivity.

3.4 Conclusion

In this chapter the composite polycrystalline solid electrolyte of the general formula, 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.035, 0.05, 0.07, 0.105) has been presented. Powder X-ray diffraction (PXRD) analysis performed on the synthesised garnet, observed the formation of a composite structure, where the target cubic phase $Ia\bar{3}d$ was synthesised along with the presence of perovskite-related Ruddlesden Popper n = 2 secondary phase La₃LiMnO₇. PXRD analysis following pelleting via spark plasma sintering found the predominant garnet phase to have been retained whilst the secondary phase was observed to undergo a phase transformation to n = 1, La₄LiMnO₈. SEM/EDX images obtained located the secondary phase along the grain boundaries of the garnet composite.

The RP1 secondary phase was estimated to hold a vastly increased electrical conductivity (ca. $7.5 \times 10^{-4} \text{ S cm}^{-1}$) in comparison to the LLZTO garnet, which retains an electronic conductivity of 10^{-9} to 10^{-10} S cm⁻¹. AC impedance and DC polarisation were used to understand the effect of different electronic properties on the composite structure. Only minor changes in ionic conductivity were observed up to x = 0.07, with a decrease in the ionic conductivity of an order of magnitude for x =0.105. Electrical conductivity measurements however revealed no significant change in overall electronic conductivity of the composite structure. To further understand the role of the secondary phase on the composite in contact with Li-metal, and during cycling, AC impedance, galvanostatic cycling and cyclic voltammetry were performed. Results revealed increasing amounts of secondary phase reduced resistance in contact with Li, subsequently leading to an increase in CCD from 0.1 to 0.3 mA cm⁻². A maxima however appears to be reached at x = 0.07, whereupon the secondary phase counteracts the interfacial resistance, thereby reducing the CCD. Post-cycling analysis revealed the formation of a dark discolouration across all manganese bearing pellets that alluded to a redox behaviour. Cyclic voltammetry was conducted to further investigate the nature of the discolouration, results displayed an initial stability in

contact with Li from 0 to 5 V, later cycles however revealed the appearance of an oxidation peak at 4.2 V, analogous with Mn oxidation.

To quantify any potential oxidative behaviour of the secondary phase XPS and XAS were performed. XPS measurements further revealed likely oxidative behaviour of the secondary phase at the Li-electrolyte interface, from Mn^{3+} to Mn^{4+} . Additionally, information could be gained from the XPS spectra of the C 1*s*, where a reduction in Li₂CO₃ with the attachment of Li-metal was revealed. The reduction of the lithium carbonate may be an explanation for the observed increase in CCD. It was however not possible to fully quantify the oxidation state of manganese from XPS due to the low concentration of Mn ions. For further clarification XAS data was collected; the XANES region of the data revealed a mixed oxidation state of $Mn^{3/4+}$. The mixed oxidation state may be a result of a slow transition during dynamic conditions, which is supported by CV measurements where Mn oxidation peaks are only observed in latter cycles; thereby hinting at the oxidation of the secondary phase under Li stripping and plating measurements.

In chapter 4 post cycling XRD-CT analysis will explore and gain an insight into the change in crystal structure of the secondary phase, whilst finite element analysis will attempt to illuminate the role of the secondary phase on current distributions within the sample.

This chapter provides an intriguing insight into the role of secondary phases within solid electrolytes. In this instance the different electrical and electrochemical properties mean that even at low levels they can affect the electrochemical attributes of the whole system. It therefore stands to reason that further efforts need to be placed into understanding the role and electrodynamics of grain boundary located secondary phases in LLZO based electrolytes. With the use of an appropriate secondary phase, it may even be possible to alter the electrodynamics of a system in order to control the cyclability and degradation mechanisms of LLZO solid electrolytes.

3.5 Acknowledgments

XPS was conducted and analysed at the Sheffield Surface Analysis Centre of The University of Sheffield by Dr Debbie Hammond. XAS data was collected on the KMC-3 beamline at the Helmholtz-Zentrum Berlin (HZB) light source BESSY II with the assistance from instrument scientist Dr Götz Schuck.
Chapter 4

Microstructural Characterisation of Garnet Composite Electrolytes

4.1 Introduction

The formation of the n = 1 Ruddlesden-Popper (RP1) secondary phase La₄LiMnO₈ on the grain boundaries of garnet Li_{6.4}La₃Ta_{0.6}Zr_{1.4}O₁₂ (LLZTO) was discussed in Chapter 3. Subsequent electrochemical and spectroscopic characterisation showed that the secondary phase became electrochemically active during galvanostatic cycling with Li-metal, affecting the electrodynamics of the whole composite system. XANES and XPS measurements revealed that the manganese of the RP1 phase changes oxidation state resulting in a mixed oxidation of Mn³⁺ and Mn⁴⁺. The change in oxidation state and its subsequent effect on electrochemical properties were accompanied by a darkening of the pellets (*cf.* Figure 3.11).

The techniques utilised in Chapter 3 provided a good understanding of the effect of the RP1 phase on the composite, solid electrolyte (SE). To gain a more detailed understanding, the composite's performance was analysed using X-ray diffraction computed tomography (XRD-CT) and Finite Element Method (FEM). XRD-CT allows the construction of images of spatially resolved information as images from inside a sample. These images are a three-dimensional (3D) array, where each voxel/pixel corresponds to a unique diffracted intensity from which a diffraction pattern may be extracted, delivering information on crystalline phases located within that volumetric portion of the object. In simple terms, the technique allows for the location and identification of phases within the bulk, readily enabling the identification, isolation, and quantification of any changes to the RP1 phase arising from galvanostatic cycling with Li-metal.

Early application of the technique for battery analysis saw the characterisation of a Li-ion coin cell and a commercial Ni/MH AAA battery.[186] The authors demonstrated a reliable non-destructive method of obtaining *in situ*, structural and textural

detail directly from constituent elements of these batteries. The examination encompassed cell components as well as the composition of the cathode film demonstrating the method's comprehensive proficiency in characterising detailed structural features. As the technique continues to develop, its characterisation capabilities have improved, facilitating more detailed spatial and temporal descriptions of batteries.

Recent research has extended the scope with full cell characterisation of a commercial Li-ion cylindrical cell. This work successfully demonstrated the *ex-situ* characterisation of active battery materials following charge and discharge. The authors were able to distinguish between different $\text{Li}_x \text{C}$ species, providing lattice parameters and revealing chemical heterogeneities within the commercial cell. These findings provide intriguing observations into chemical dynamics of electrode evolution as a function of cell cycling.[231, 232]

Virtually deconstructing the cell through XRD-CT and focusing on dynamics of battery electrodes has resulted in highly detailed spatial and temporal characterisation, as well as the quantification of crystallographic heterogeneities. The capabilities of the technique have provided comprehensive insights into structural alterations, stoichiometric differences between particles, compositional gradients, and phase heterogeneities within particles of common battery electrode materials such as NMC, LFP, LMO and Si-graphite.[233–236] As such, XRD-CT is a potent technique in the characterisation of battery materials, providing compelling quantitative and visual data that allow for the in depth examination of materials behaviour within a battery.

XRD-CT has been used in this thesis for the investigation into the RP1 (La₄LiMnO₈) bearing garnet LLZTO. Post-cycling analysis following CCD measurements revealed that dark regions on the composite pellets (*cf.* Figure 3.11) contained manganese in states from Mn^{3+} to Mn^{4+} . A potential mechanism was proposed (*cf.* Equation 3.2), whereby Li extraction under dynamic cycling drives the oxidation state change within the RP1 phase.

Standard diffraction techniques could have been utilised to characterise a change of crystal structure, phase, lattice parameter, or the emergence of additional peaks associated with the 'dark' regions. However, traditional diffraction provides an average global analysis of long range order. Actively selecting the 'dark' regions of the pellet for analysis would therefore be extremely challenging, with collected results prohibiting accurate and detailed characterisation, likely leading to inaccurate or misleading interpretation.

Furthermore, inaccuracy would occur from mounting pellets of different heights within a laboratory based diffractometer, resulting in false positive peak shifting. Coupled with unpredictable post-cycling surface finish, the reliability of the collected data would further come into question. Conversely, the grinding of pellets would lead to the dispersal and dilution of the 'dark' regions of interest, arguably masking

any new peak or positional changes in the RP1 phase.

XRD-CT therefore provides a unique and non-destructive analysis technique to precisely target specific regions of interest. This method not only delivers high quality, two-dimensional spatial maps of individual phases and their heterogeneity but also a third dimension in the form of extracted PXRD patterns (often referred to as the spectral dimension). Furthermore, to the authors knowledge, as of this thesis publication, it would be the first such measurement on a garnet solid electrolyte.

Computationally assisted XRD measurements are extremely powerful in segregating and visualising crystallographic, structural and phase heterogeneities and allow for detailed investigation into specific regions of interest; they however do not reveal electrodynamic mechanisms within the solid electrolyte composite. Due to the variations in electrical conductivity of the two constituent phases within the composite, these dynamics can be usefully interrogated simulating the composite using FEM; producing a representative model to determine the impact of the second phase on local current densities.

FEM studies have previously been used in the two-dimensional modelling of a full cell with Li-metal as anode, $LiCoO_2$ as cathode and Li_3PO_4 as solid electrolyte.[237] The authors studied the variation of Li⁺ concentration under different charge/discharge rates. However, a more relevant recent investigation investigated the current density at the solid electrolyte interface with Li-metal, which provided a simple model and was able to show the current density distribution throughout the sample.[71] The model varied the current density to illustrate the electrodynamics under dynamic current conditions while taking Li⁺ diffusion into account. Although simplistic, the model provides a valuable visual and quantitative insight into the electrodynamics and current distribution at the interface of LLZO and the Li-metal electrode. It emphasises the advantage of an FEM model to describe and visualise the natural phenomenic process occurring within the solid electrolyte. In this chapter a similar approach will be adopted by developing a model of garnet LLZTO with simplified grain boundaries incorporating the presence of RP1 La_4LiMnO_8 . The aim is to provide an insight into the electrodynamics of the system and the impact of the RP1 phase on the current density.

4.2 Experimental

XRD-CT diffraction data were collected for the synthesised garnet composite of general formula 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.035 and x = 0.07). Three regions of interest were measured from the two stated composites and are each assigned the following identifier: 'Pristine', 'Light' and 'Dark'. 'Pristine' refers to a sintered sample without Li-metal attachment. 'Dark' represents the dark regions following Li-metal attachment and cycling (*cf.* Figure 3.11); on the contrary, 'light' refers to

regions from the same pellet as those from 'dark', which however did not display any of the discolouration.

XRD-CT measurements were performed at beamline P07 (EH2) at the PETRA III synchrotron at DESY using a 73.75 keV ($\lambda = 0.1681$ Å) monochromatic X-ray beam focused to have a spot size of $10 \times 1 \ \mu m$. Two-dimensional powder diffraction patterns were collected using a Pilatus3 X CdTe 2M hybrid photon counting area detector. Post cycling, the pellets were fractured to generate shards, this resulted in shards of an asymmetrical nature that narrowed into a point and held varying dimensions ranging from ca. 50 - 150 mm in length by ca. 50 - 70 mm in width. That included portions of material that had contacted metallic lithium as well as regions from the internal portion of pellet. These were mounted onto a goniometer which was placed on a rotation stage [231] - the narrow cross section was required to allow sufficient beam transmission and to give constant intensity throughout the sample. Given the hardness of the samples, the fracturing to create the shards resulted in uneven cross-sections. The goniometer was mounted on a translation stage that permitted movement of the different portions of the sample into the beam. The XRD-CT scans were measured by performing a series of zigzag line scans in the z (vertical) direction.

An exposure time of 5 ms and an angular range of 0° – 360° with 500 projections in total were used for each XRD-CT dataset. The translation step size was 1 μ m in continuous translation (fast axis), and stepped rotation (slow axis).[238] The detector calibration was performed by Dr Stephen W.T Price from Finden Ltd, using a CeO₂ standard. An instrument parameter file was created from information derived from the full profile analysis of a CeO₂ diffraction data collected during the beamtime experiment. An 8th order Chebyshev polynomial was used to fit the background and a pseudo-Voigt profile function to fit the diffraction peaks. Every 2D diffraction image was calibrated and azimuthally integrated to a 1D powder diffraction pattern both without and with a 5 % trimmed mean filter using the pyFAI software package and Finden Ltd, in-house developed scripts.[239–241] The integrated diffraction patterns were reshaped into sinograms, centred, and the air scatter signal was subtracted from the data. The data were reconstructed using the filtered back projection algorithm, with the voxel size in the reconstructed images being 10 × 10 × 1 μ m³.

Rietveld refinements were conducted on summed diffraction patterns using GSAS II software.[183] Rietveld refinements fits used established structures from the ICSD for LLZTO (ICSD 894) garnet phase and La₄LiMnO₈ (ICSD 94927). Shifted-Chebyschev and pseudo-Voigt functions were used to fit the background and peak shapes respectively.

Finite element analysis was conducted using the COMSOL Multiphysics software package.[197] Following solving, post-processing is used to visualise and analyse the solution. An initial 9×9 array of cubes of 11 µm sides was created (Figure 4.1).



Figure 4.1: (a) Full 9×9 array of cubes, the FEM geometry represents the model for LLZTO garnet composite. (b) Location of the disc in the geometry representing the secondary phase La₄LiMnO₈, it may be seen as residing on the grain boundary indicated by a red arrow. (c) Application of the current conservation around the geometry to apply continuity equations. (d) Electrical insulation boundary conditions assigned to the external surfaces. The top (e) and bottom (f) surfaces were assigned electrical terminals, and a potential of 1 V was applied.

Centred within each of these a smaller cube of 10 µm sides. The assembly was used to represent a LLZTO 10 µm grain bulk (the smaller inner cube) enclosed within a 1 µm grain boundary border. The domains were assigned an electronic conductivity of 10^{-9} and 10^{-8} S cm⁻¹ for the bulk (central cube) and the grain boundary domain respectively. The secondary phase La₄LiMnO₈ is included in the geometry as a smaller disc (r = 1 µm, h = 0.1 µm) with an electrical conductivity of 7.5 × 10^{-4} S cm⁻¹, a value which was based on extrapolation from Battle *et al.*[198] The disc was located on the grain boundary to emulate the location of the secondary phase.

Electrical insulation boundary conditions were assigned to the external side surfaces, setting the current to zero at the boundary, prohibiting the electrical current from flowing into the boundary and constraining the electrodynamics within the geometry. The geometry was then assigned a 'current conservation' which adds continuity equations based on Maxwell's equations for the electrical potential. The top and bottom surfaces were designated as electric terminals, and an initial potential of 1 V was applied.

A mesh size of 0.594 µm to 3.3 µm was applied to the entire geometry before two stationary studies were conducted to solve for steady-state conditions, one with the secondary phase present and one where it was absent. The impact of the secondary phase on current flow was determined by subtraction of the 'secondary phase absent' simulation, from the results obtained when the secondary phase was present. A data set was subsequently produced that highlighted the influence of the secondary phase on current flow, while eliminating other factors such as grain size or electrode configuration. In order to emphasise the significant changes in current density, a filter was applied so that only values above 0.0032 Am^{-2} are shown. A subsequent volume integration of the filtered results revealed the magnitude of the current densities' sphere of influence (region of enhanced current density) within the structure. The simulation represents the stationary electrodynamics of an RP phase inclusion within a LLZTO ceramic.

4.3 Results and Discussion

4.3.1 X-ray Diffraction Computed Tomography

Data Analysis

Initial analysis of the collected data showed that the non-filtered back-projection data suffered from streak artefacts. Streaking will occur when the crystallite size matches or is larger than the dimensions of the incident beam (i.e., 1 μ m). This occurrence leads to single crystal diffraction that appear as spots rather than concentric rings in the initial Laue projection stage. The subsequent back projection reconstruction will

exhibit streaking, which appears as lines in the generated tomograms. An example of streaking is shown in Figure 4.2c where distinct blue lines are interlaced over the image.

One approach to mitigate streak artefacts is the application of a convolution filter specifically a mean-trimmed filter. However, the filtered data even at low levels of intensity almost entirely removed the contribution of the secondary phase, prohibiting spatial mapping. The filter's characteristics involve the removal of extreme pixel values from the raw 2D data. [239] Due to low intensity levels, this process resulted in the removal of signals originating from the RP1 phase. The decision was therefore made to proceed with the unfiltered data, regardless of the streak artefacts. Using initial XRD data from Chapter 3, unique (321) and (101) reflections were identified and selected for the garnet phase and RP1 phase respectively. Using a pseudo-Voigt function for fitting, the intensities of these peaks were used to map their respective spatial distributions within the composite samples. To remove any background signal surrounding the samples a 30% filter was added to the max intensity of the selected peaks. Intensity values below this threshold were subtracted from the image in a mask assigned to the colour black, subsequently resulting in the black regions of the image. Intensity values of the respective phase reflections were assigned red for the garnet phase and blue for the RP1 phase. The processed phase distribution of each individual reflection was subsequently combined with the mask into the spatial map in Figure 4.2. Due to processing issues arising from the mean trimmed data, a colour intensity scale linked to phase fraction or each other was not possible. As such the spatial mapping from the unfiltered data scale is a binary 0 or 1, present or not present for the phases, leaving qualitative data.

To obtain quantitative data, a region of 30 x 30 µm was selected from the dataset for each sample. Each voxel/pixel corresponds to a unique diffracted intensity from which a diffraction pattern may be extracted. The resulting, summed diffraction patterns, obtained by combining *ca.* 900 pixels for each sample, are depicted in Figure 4.3. These were subsequently normalised to the intensity of the main garnet phase and overlaid. Figure 4.4 displays the region of interest focusing on the primary RP1 reflections, presenting the overlaid diffraction patterns. The specific area is highlighted by the dashed box in the former figure. Each summed diffraction pattern was evaluated for phase distribution using Rietveld refinement. During refinement, lattice parameters were permitted to refine freely whilst atomic positions were fixed.

Results Analysis

Spatial mapping in Figure 4.2 reveals a subtle change in the dispersion patterns of the garnet and RP1 phases. For both composites (x = 0.035, 0.07), the RP1 phase is evenly distributed throughout the garnet in all three regions of interest (pristine,

light, dark). All pixels in the maps containing either only the main phase, or a combination of the main and RP1 phases. Noticeably, the representative red and blue phase colours in the 'dark' sample appear to become smaller, more dispersed, and less agglomerated, in contrast to the 'pristine' and 'light' samples. This may indicate a morphological change, such as a change in crystallite size under cycling conditions. The observed black regions present within the garnet sample are attributed to variation in the crystallinity, local changes in density/morphology at the micron scale, as given by the variations in peak height, a probable inducement may be localised micro-voids or grain boundaries, as observed in the SEM images in Figure 3.6 of the sample resulting in low intensity and subsequently being coloured black from the application of the mask. Spatial mapping of the sample displays a heterogeneous nature of the two phases, with apparent crystallite changes under cycling conditions.

To understand any potential change in the RP1 phase under cycling conditions summed diffraction patterns for each sample were analysed. The region of interest relating to the summed and overlaid diffraction patterns are displayed in Figure 4.4. Initial analysis of the RP1 impurity peaks, hkl 101, 103 and 110 reveal a systematic decrease in the peak height from 'pristine' to 'light' through to 'dark'. The conducted two phase Rietveld refinement further quantify the observed changes. Analysis of the data (Table 4.1) shows that the phase fraction of RP1 decreases, verifying that the a decrease in visible peak height is linked to a decrease in phase fraction.

One plausible explanation would have been a change in lattice parameters of the RP1 phase, however, as the results show, these remain invariant. Without change in lattice parameters the observed change in intensity arising from the RP1 reflections may stem from a phase transition proposed in Equation 4.1 as well as in Chapter 3. Under cycling conditions, extraction of lithium from the RP1 phase would result in a size decrease of the B site. Any decrease in the A or B site of the RP1 phase $(A_{n+1}B_nO_{3n+1})$ is known to cause a lowering of symmetry as a result of octahedral tilting, the structure subsequently undergoes a transition from tetragonal (I4/mmm) to orthorhombic (Pnma).[242, 243] Whilst lattice parameters of a tetragonal structure are equal to $a=b\neq c$, a change to orthorhombic would result in parameters of $a\neq b\neq c$, even minor alterations would modify the crystal lattice angles and inevitably the positioning of the hkl 103 and 110 reflection.

$$\begin{aligned} La_4 Li MnO_8 &\longrightarrow La_4 Li_{0.5} MnO_8 + Li^0 \\ Tetragonal &\longrightarrow Orthorhombic \end{aligned}$$
(4.1)

Inevitably, due to the emergence of new reflections, Rietveld refinements centred around the La_4LiMnO_8 phase would see variations in peak intensity and peak width. At low concentrations, new reflections may however be masked by the present



Figure 4.2: XRD-CT 2D spatial mapping with a field-of view of 100 μ m × 100 μ m from composite samples 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂': x = 0.035 (a) pristine, (b) light, (c) dark; x = 0.07 (d) pristine, (e) light, (f) dark. The garnet phase is in red and RP1 in blue. Normalised intensity is shown for both phases where black = 0, and red and blue = 1 for garnet and RP1 respectively. The RP1 phase is evenly distributed throughout the solid electrolyte in all three states. The heterogeneity of the sample appears to result in finer variations from 'pristine' to 'dark'.

Table 4.1: Rietveld refinement results from summed diffraction patterns for manganese bearing 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' composite samples x = 0.035 and 0.07. The phase fraction decreases systematically from the 'pristine' to 'dark' states whilst lattice parameters remain invariant.

	Fit Statistics		ics	La_4LiMnO_8			LLZTO
Sample	R_{wp}	χ^2	GOF	Wt Phase fraction	a = b (Å)	c (Å)	a = b = c (Å)
0.035 'pristine'	13.795	43.9	0.23	2.6(1) %	3.783(1)	12.937(7)	12.9164(7)
'light'	14.768	55.5	0.26	2.3(1) %	3.783(1)	12.92(1)	12.9145(8)
'dark'	15.579	52.8	0.25	2.0(2) %	3.783(1)	12.930(4)	12.9137(7)
0.07 'pristine'	21.499	17.1	0.14	6.8(3)~%	3.784(1)	12.930(4)	12.916(1)
'light'	17.523	12.6	0.12	5.5(2) %	3.786(1)	12.939(5)	12.9175(9)
'dark'	14.825	44.4	0.23	4.5(1) %	3.784(1)	12.934(5)	12.9163(8)





Figure 4.4: Summed diffraction patterns extracted from XRD-CT measurements; overlaid and magnified for region between 1.7 and 2.7 Q (Å⁻¹). The data is normalised to the peak maximum of main garnet phase to show the relative changes in the 101, 103 and 110 reflections arising from the RP1 phase *****. The LLZTO 103 reflection is indicated at *ca.* 1.82 Q (Å⁻¹).

 La_4LiMnO_8 peaks and may only appear with sufficient quantities as peak splitting, or asymmetry of existing La_4LiMnO_8 peaks. The refinement model would consequently only focus on La_4LiMnO_8 reflections whilst mathematically compensating for a decrease in intensity/change in broadening by decreasing the phase fraction. Moreover, such a phase change may explain the observed morphological alteration in the RP1 crystallites.

Observations are compatible with this claim, and analysis of the diffraction profile was conducted. Results of peak width (Q (Å⁻¹)) and peak intensity are displayed in Figure 4.5. Indicative of crystallite size and strain; an increasing peak width is associated with a decrease in crystallite size and increase in strain. Whilst the peak integral is a function of the intensity of scattering from the given plane, or in simple terms how much of the plane is intersected by the incident beam. Analysis of peak intensity shows a systematic decrease for both compositions from 'pristine' to 'light' to 'dark', indicating a decrease in the detection of 103 and 110 hkl planes. This is concurrent with the results from Rietveld refinement. Once again alluding to the proposed phase change to orthorhombic and indicating a change in distribution of atoms within the unit cell.



Figure 4.5: Analysis of the peak width reveals a notable change. Sample (a) x = 0.035 displays an overall reduction in peak width for reflections hkl 101, 103, and 110 across all regions of interest ('pristine', 'light', and 'dark'). Conversely, sample (b) x = 0.07 exhibits a general increase, alluding to a change in crystallite size of the La₄LiMnO₈ secondary phase. The subsequent peak integral for the same reflections in (c) x = 0.035 and (d) x = 0.07 display a consistent decrease from 'pristine' to 'light' to 'dark', indicating a reduction in scattering intensity associated with these reflections. This trend aligns well with the systematic decrease observed in the weight fraction of La₄LiMnO₈.

Table 4.2: Tabulated FWHM and peak integral results. for samples x = 0.035 and 0.07 ('Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂'), 'pristine', 'light' and 'dark'.

		FWHM		Peak Integral			
Sample	hkl 101	hkl 103	hkl 110	hkl 101	hkl 103	hkl 110	
0.035 'pristine'	1.67×10^{-2}	2.26×10^{-2}	3.11×10^{-2}	6.14×10^{-4}	1.16×10^{-3}	9.80×10^{-4}	
'light'	1.86×10^{-2}	2.31×10^{-2}	2.79×10^{-2}	9.85×10^{-4}	2.79×10^{-2}	7.48×10^{-4}	
'dark'	1.83×10^{-2}	2.15×10^{-2}	2.49×10^{-2}	8.43×10^{-4}	2.49×10^{-2}	7.00×10^{-4}	
0.07 'pristine'	1.56×10^{-2}	1.77×10^{-2}	1.57×10^{-2}	2.04×10^{-3}	1.57×10^{-2}	2.48×10^{-3}	
'light'	1.74×10^{-2}	1.48×10^{-2}	1.76×10^{-2}	1.88×10^{-3}	1.48×10^{-2}	2.38×10^{-3}	
'dark'	1.84×10^{-2}	2.16×10^{-2}	2.31×10^{-2}	1.46×10^{-3}	2.16×10^{-2}	1.72×10^{-3}	

The peak width appears to increase from the' pristine' to the 'dark' for sample x = 0.07, which supports the observations from spatial mapping, where it appears that the RP1 phase crystallites become smaller. Furthermore, the extraction of lithium would result in the build-up of inhomogeneous strain and may be considered

a contributing factor to the measured peak broadening.

In comparison, the peak width of sample x = 0.035, appears to decrease from 'pristine' to 'dark'. The contradiction of these two results may be the factor of strain. Both samples appear to hold a finer RP1 crystallite size from 'pristine' to 'dark', and both samples display a decrease in the peak intensity. As such the strain on the crystallites may be less for sample x = 0.035, which may be a consequence of lower inclusion level of the RP1 phase for x = 0.035 resulting in a smaller number of crystallites under inhomogeneous strain following the transition to the orthorhombic configuration. However, a greater quantity of orthorhombic crystallites would be detectable as is the case with x = 0.07.

As a phase transition would alter the axis parameters $(a=b \rightarrow a\neq b)$, a subsequent alteration in peak position, asymmetry or splitting as well as intensity would be detected. In order to observe any alterations, the magnified region for the hkl 103 and 110 peaks of 'pristine' and 'dark' samples for x = 0.035 where overlaid, red vertical lines mark the central apex of the 'pristine' hkl 103 and 110 (Figure 4.6). The peaks appear to show a degree of asymmetry from the 'pristine' to the 'dark' sample, which indicate the transition to orthorhombic from tetragonal.



Figure 4.6: Summed XRD-CT diffraction pattern normalised to the main garnet phase and magnified between 2.1 and 2.5 Q (Å⁻¹) region for samples x = 0.035 'pristine' and 'dark'. Red vertical lines show the apex and centre of hkl 103 and 110 for 'pristine' samples. The hkl peaks of the 'dark' sample exhibit a degree of asymmetry and peak splitting of the 103 reflection.

XRD-CT provides an intriguing insight into structural changes of the RP1 (La_4LiMnO_8) secondary phase resulting from galvanostatic cycling with Li-metal.

Notably, a systematic decrease in the weight fraction was observed between all three regions of interest from the sintered 'pristine' pellet to the 'dark' regions. Moreover, a decrease in crystallite size and change in strain further indicated activity of the RP1 phase under electrochemical cycling conditions. A hypothesis of Li extraction from La_4LiMnO_8 under dynamic current conditions was proposed. However, confirming the validity of this theory requires further investigation. Specifically, synthesising La_4LiMnO_8 and analysing it with *Ex Situ* or *In Situ*/Operando techniques would allow for a controlled and comprehensive understanding of Li extraction and subsequent phase change of the RP1 phase.

4.3.2 Finite Element Method Analysis

Finite element method analysis was applied to gain a better understanding of the electrodynamics within the composite solid electrolyte. The conductivity value of the RP1 secondary phase was estimated as *ca.* 7.5×10^{-4} S cm⁻¹, by extrapolation from data in range $100 \leq T$ (K) ≤ 300 by Battle *et al.*[198] In contrast the garnet (LLZTO) matrix displays a significantly lower conductivity of 10^{-9} S cm⁻¹; comparatively, resulting in a highly resistive medium. Using the software analysis package COMSOL Multiphysics,[197] FEM was employed to gain a mechanistic understanding of how electrical currents within the composite differ from those in a single phase garnet electrolyte.

The geometry displayed in Figure 4.7 shows an initial 9×9 array of cubes with equal sides of 11 μ m, situated within each cube is an individual smaller cube with equal sides of 10 μ m. The subsequent configuration displays a simplified ceramic model of bulk and grain boundaries known as a brick layer model (BLM); this is often used to aid in the interpretation of EIS results from polycrystalline electroceramics. The model was first developed over 50 years ago to aid in the description of experimental findings arising from their electrical properties.[244] Similar to EIS measurements the BLM has been used in this instance to simplify the complex solid electrolyte system in order to model the electrodynamics of the composite.

Experimentally validated bulk electronic conductivity $(10^{-9} \text{ S cm}^{-1})$ from Chapter 3 were assigned to bulk components of the model. Grain boundaries were assigned a conductivity of $10^{-8} \text{ S cm}^{-1}$ following recent reports on dynamics of grain boundary conductivity where a narrowing in the LLZO band gap and consequently a reduction in electronic resistance was observed.[85] Two stationary solvers were applied to simulate dynamics of the BLM. The first, without the RP1 phase present and the second, including the RP1 phase. The subsequent data of the two stationary solvers was combined into one data set for further processing.

Using a current threshold filter it was possible to extricate any elevated change in



Figure 4.7: A 9 × 9 geometric FEM model representing a brick layer model of solid electrolyte composite LLZTO with a RP1 inclusion on one of the grain boundaries nearest the centre of array. Application of a 1 V potential between the top (z = 1) and bottom (z = 0) faces of the array lead to the current densities indicated by the colour scale. The RP1 phase is represented as a small disc on the grain boundary which under the 1 V potential increases the current density by *ca*. $6 \times 10^{-8} \mu A$ μm^{-2} . The sphere however may be seen to hold a region of influence exceeding the immediate physical space occupied, which is represented by the blue volume expanding from the disc.

current density above the results from the RP1 free LLZTO based solid electrolyte system. Results show that the RP1 phase elevates the current density within the system, with the core of the RP1 phase resulting in an increase of up to $6 \times 10^{-8} \mu A \ \mu m^{-2}$ more than the surrounding composite. This increase in current density affects the charge flow within the whole composite solid electrolyte system. From the model (Figure 4.7) it is possible to see that the RP1 phase has a zone of influence that extends beyond the dimensions of the RP1 inclusion. The simulated disc was calculated to occupy a volume of 0.314 μm^3 , on a total grain boundary. Under a potential of 1 V the sphere of influence, originating from the RP1 phase is visually seen to extend along the grain boundary. Using volume integration, the area of influence was calculated as 21.71 μm^3 , an area of influence that affected 8.97 % of the grain boundary. Thus, the RP1 phase influenced the electrodynamics of a volume of garnet that was nearly seventy times larger than the physical volume occupied by the inclusion.

The model provides an intriguing insight into the electrodynamics of the solid electrolyte composite. The RP1 phase may be seen to exact an increased area of influence past its initial physical area of occupation. With a difference in electrical conductivity the result was expected, however, the simulation provided a numerical quantification of the extent of influence, highlighting the magnitude of influence.

Furthermore, closer inspection of Figure 4.7a displays the directionality of the sphere of influence, propagating along the grain boundary, the increase in current appears to leave the LLZTO grain core unaffected, affirming unperturbed intra-grain conductivity of RP-LLZTO (*cf.* Figure 3.9c). The direction of influence likely follows the grain boundary due to the higher electrical conductivity compared to the grain core and as such the increase of current density is seen along the grain boundary. A consequence of this mechanism is the increase of grain boundary susceptibility to electron-Li⁺ recombination and subsequent crystallisation of Li-metal.

The addition of current density lines (Figure 4.8) further substantiate that the current path is altered by the RP1 phase; without the presence of the RP1 phase the current is likely to flow down the least electrical resistive channels (i.e., grain boundaries) substantially increasing the current density at intersecting grain boundary triple points.

The extent of the sphere of influence from the RP1 phase, as well as the flow of current points to a critical level of percolation. Below the percolation level the secondary phase would provide little effect on the solid electrolyte composite. However, once the critical level is reached, an extended network of interconnected spheres of influence would be created. This network would facilitate the conduction of electrons proliferating the nucleation and propagation of lithium dendrites whilst reducing the electrochemical performance of the garnet. This is especially seen in



Figure 4.8: Geometric FEM model of solid electrolyte composite LLZTO with the RP1 (La₄LiMnO₈) inclusion. The 9×9 brick layer displays red lines that represent current flow within the system, whilst the volume is indicative of the increased current density and area of influence of the RP1 (La₄LiMnO₈) phase.

Chapter 3 where the percolation threshold of sample x = 0.105 appears to have been reached and electrochemical performance decreases. The RP1 secondary phase increases the regional current density and provides a nucleation point for Li-metal dendrites.

It therefore seems likely that the redirected current facilitates extraction of lithium from the B-site octahedra of La_4LiMnO_8 , as shown by Equation 4.1. Lithium extraction from the lattice would consequently lead to a transition from a tetragonal to an orthorhombic phase. To compensate for the removal of Li⁺, manganese would need to undergo oxidation from Mn^{3+} to Mn^{4+} which is visibly displayed by the 'dark' patches on the sample (*cf.* Figure 3.11) and indicated by the measured mixed oxidation state from XPS and XAS in Chapter 3.

The use of FEM further highlights the significant role of the incorporated La_4LiMnO_8 phase in influencing the electrodynamics of the solid electrolyte composite. Notably, the presence of the secondary phase inadvertently leads to an increase in current density beyond its physical vicinity, thereby resulting in a region of enhanced electronic conduction. Once a level of percolation is reached the secondary phase detrimentally affects the RP-LLZTO composite.

The combination XRD-CT and FEM modelling has significantly improved the comprehension of the influence of secondary phases embedded in a LLZTO solid electrolyte. XRD-CT has effectively revealed crystallographic changes, whilst computational modelling elucidated the modifications in current density and flow within the system. The presented work not only enhances the broader scientific understanding of the role of electrical conducting secondary phases and the impact on dendrite resistance in polycrystalline LLZTO, but also opens opportunities for characterising other oxide based solid electrolyte systems.

4.4 Conclusion

Localised characterisation of structural and electrodynamic alterations arising from the n = 1 Ruddlesden-Popper (RP1) secondary phase La₄LiMnO₈ embedded in a LLZTO solid electrolyte were conducted via XRD-CT and FEM analysis. Spatial phase mapping revealed a heterogeneous dispersion of the secondary phase in all the samples with a proliferating smaller crystallite size from 'pristine' to 'dark'. Analysed peak width indicated a reduction in crystallite size, a trend that was consistent with the spatial mapping. Two phase Rietveld refinements of the summed diffraction patterns revealed a decrease in weight fraction for the RP1 secondary phase from the 'pristine' to 'light', further decreasing for the 'dark' samples. Whilst a decrease in weight fraction was observed the lattice parameters of both the RP1 and LLZTO phases remained largely invariant. The systematic decrease in peak intensity suggests a reduction in scattering from the specific atomic planes, which in turn, implies a phase change. Closer visual examination of the hkl 103 and 110 reflections of sample x = 0.035 were carried out. A slight change in asymmetry and splitting between the 'pristine' and 'dark' regions were revealed, indicating a change in peak location, and alluding to the tetragonal to orthorhombic phase transition.

With an indication that the secondary phase was electrochemically active FEM modelling was used to gain further insight into localised electrodynamics mechanisms of the grain boundary located La_4LiMnO_8 . The modelled geometry showed that the RP1 phase increased current density in an extended sphere of influence significantly, extending past its initial physical presence along grain boundaries. Notably, the grain bulks appeared unperturbed indicating the effect to be predominantly a grain boundary phenomenon. Calculations showed that under a potential of 1 V the region of influence increased from 0.13 % to 8.97 %, an increase of *ca.* 69 times. Whilst the current density observed an increase of up to 6 $\times 10^{-8} \ \mu A \ \mu m^{-2}$ more than the surrounding composite. At exceptionally low levels, the presence of the secondary phase is unlikely to significantly disturb overall electrodynamics within the solid electrolyte composite. However, once a percolation threshold is reached the spheres of influence are likely to overlap creating an interconnected network of regions with increased current density. Once this threshold has been reached the secondary phase becomes detrimental to the electrical performance of the solid electrolyte, leading to decreased ionic conductivity, electrochemical performance and result in the nucleation and propagation of Li-metal dendrites.

This model provides a fundamental insight into the influence of the secondary phase on current distribution within the composite under an applied potential. Notably, it underscores the substantial impact of the secondary phase on the overall behavior of the composite material, providing an impactful initial assessment of the electrodynamics within the system. However, enhancements could be made to improve the efficacy and accuracy of the model. One pivotal area lies in reassessing the assumptions governing grain boundary conductivity and the extrapolated conductivity attributed to the secondary phase. Improving the accuracy of these regions with experimental data would significantly improve the models capabilities and further align it towards a more representative system. Additionally, incorporating a more representative grain structure is pivotal to accurately represent the electrodynamic response, of a complex network of grain boundaries and grain sizes that are observed in real ceramic samples. Further improvements may be made by incorporating other variables such as an applied current or investigating mechanisms of Li⁺ ion diffusion across the composite; thereby offering a more comprehensive insight into the composite's behavior. Nonetheless, these results provide an intriguing insight into the electrodynamics of a two phased solid electrolyte composite.

The exploration of multiphase solid electrolyte composites remains an under explored area, with limited research conducted so far. Initial efforts in composite

fabrication involve layering differing LLZO based electrolytes.[209] However, the fabrication of multiphase composite has not been explored particularly in conjunction with the use of FEM to investigate changes in electrodynamics. While certain FEM studies have shed light on current dynamics at the solid electrolyte interface, these investigations have primarly focused on revealing crucial mechanisms at the electrolyte/electrode interface, lacking emphasis on microstructure or the inclusion of a secondary phase.[71] Consequently, there appears to be a gap in research regarding the understanding of the potential of multicomponent systems especially concerning lithium conducting solid electrolytes.

In contrast, in the field of dielectric materials has investigated similar concepts, focusing on ceramic-ceramic dual phase composites to enhance desired properties. Notably, FEM has been employed to model the grain structure of these dual-phase composites and analyse the resulting changes in conductivity and permittivity.[245] Furthermore, there are other instances where FEM was utilised to characterise the alteration of the electric field across a polymer-ceramic capacitor composite comprising two phases.[246] These studies in dielectric materials demonstrate the effective application of FEM in comprehending the electrodynamic behaviors within diverse composite systems. The use of FEM in modeling the grain structure and analysing electrodynamic changes offers valuable insights into the complex interactions within these multiphase materials,

With the use of XRD-CT and FEM modelling, this chapter demonstrates that the incorporation of a secondary phase readily alters the electrodynamics of a solid electrolyte, highlighting its potential for electrochemical activity. There may therefore be a possibility for incorporating various other secondary phases potentially offering a mechanism for adjusting the performance of solid state electrolyte assemblies. This would contrast with the common approach of solely adjusting the behavior of a single-phase electrolyte providing an intriguing alternative.

Exploring the addition of secondary phases could offer diverse possibilities for modifying the solid electrolyte behaviour. For instance, a secondary phase may form a passivation layer at the electrode/electrolyte interface, enhancing wettability or mitigating high localised current densities. Similarly, a secondary phase with high electrical resistance could potentially mitigate electron recombination at grain boundaries or homogenise electric fields, reducing high current densities at lithium filament tips or potential sites of lithium metal nucleation.

Presently, minimal research has been conducted to explore the potential benefits derived from a composite system, presenting an opportunity for further research. While this work provides an initial investigation into the impact of an electrochemically active secondary phase on the electrodynamics of a composite system. It highlights the necessity for a deeper understanding regarding the incorporation and the potential benefits of secondary phases.

4.5 Acknowledgments

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Chapter 5

Mixed Ionic-Electronic Conducting Garnet Electrolyte Bilayer Films for Lithium Metal Batteries

5.1 Introduction

Targets for volumetric and gravimetric energy densities for lithium-ion batteries in 2030 currently range between 750 - 950 Wh l^{-1} and 320 - 360 Wh kg⁻¹ respectively.[19, 20] All solid state batteries (ASSBs) based on the solid electrolyte, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) are believed to be able to meet this demand with predicted volumetric and gravimetric energy densities of ca. 1000 Wh l⁻¹ and 320 Wh kg⁻¹ respectively.[20] However, to facilitate their use in ASSBs as a replacement for conventional lithium-ion batteries, significant challenges in both production and cell integration need to be resolved. One key aspect is thickness of the solid electrolyte separator; commercial cells require thickness ranging from 20 to 50 μ m to achieve these targets and be competitive with conventional lithium-ion batteries.[247] However, current established fabrication techniques rely on pelletisation, which offers an ideal, convenient, and simplified form for assembling electrochemical cells and evaluating cell chemistry. Although well suited for laboratory based experiments, these pellets result in thickness greater than 1 mm and are produced as single batch items that often require extensive post-sintering modification. The commercialisation of ASSBs with a LLZO solid electrolyte necessitates a scalable, high volume industrial production process capable of meeting future demands, a capability currently unattainable through batched pelletisation. In addition, the intimate integration of electrode interfaces is imperative to mitigate elevated area specific resistances (ASR) and allow for fast ion transport to realised fully integrated cells. This challenge is exacerbated by planar interfaces which lead to elevated current densities, lithium dendrite formation, electrode delamination, and high ASR.

To therefore be competitive with conventional lithium-ion batteries, the highvolume fabrication process must consistently yield high density, thin ($<50 \ \mu$ m), LLZO based solid electrolyte with tailored interfaces that require minimal post sintering modification. This is not only to reduce cost and timescales of manufacture but also streamline the fabrication of engineered films with bespoke interfaces. Such improvements will inevitably lead to increased current densities, enabling the highest achievable energy densities sought after in ASSBs.[248]

One such technique to meet the stated requirements is ceramic tape casting, adapted in recent years from the well-established fuel cell community, to enable LLZO based solid electrolyte films. Successful demonstration of the technique was presented by Gao *et al.* with the fabrication of a Ta-doped LLZO film holding a high relative density (99 %). The requirements for a tailored architecture to allow for electrode integration was however demonstrated by a trilayer configuration. Featuring a porous-dense-porous architecture that accommodates a thin, *ca.* 15 μ m dense LLZO based solid electrolyte is supported on either side by a porous LLZO based solid electrolyte configuration. This engineered architecture provides the advantage of porous infiltration by Li-metal mitigating low critical current densities (*ca.* <0.3 mA cm⁻²) observed in planar LLZO pellets overcoming limitations to achieve stable Li-metal cycling at 10 mA cm⁻².[156] It is currently believed that the increase in CCD is observed as a result of a *ca.* 40 times higher contact area compared to the planar configuration of pellets, effectively reducing localised interfacial current densities by factor of 40.

These results indicated that for any future commercial success, an architecture that maximises electrode contact area and reduces the interfacial resistance is required. Tape casting successfully affords the high throughput manufacturing volumes as well as the bespoke porous electrolyte architecture required. Moreover, the trilayer configuration presents a distinctive advantage. Through thermocompression the solid electrolyte film's porous architecture may be customisable, opening the possibility for tailored tape architectures.

One such opportunity may be the further optimisation of electrodes at the porous interface of LLZO based solid electrolyte. Incorporating a LLZO solid electrolyte, with an enhanced electronic conductivity, such as a mixed-ionic electronic conductor (MIEC) may improve cathode integration. Thereby potentially reducing the necessity for mixed LLZO cathode composites in full cell configurations.[249] Alternatively, the application of an MIEC on the anode side may facilitate a continuous electronic pathway from the current collector to the dense separator layer, decreasing the occurrence of localised regions of high current (hot spots) that result in dendrite formation. The potential of such a configuration has been demonstrated by examples using cubic LLZO with a 3D-MIEC framework, incorporating a coating of carbon nanotubes and achieving a low interfacial resistance and increased CCD.[250] Further studies utilising single phase LLZO based MIECs in the porous-denseporous(MIEC-LLZO|LLZO|MIEC-LLZO) architecture achieved a current density of 60 mA cm⁻².[162] To therefore advance the capabilities of LLZO based solid electrolyte in ASSBs, custom architectures will need to be designed and engineered.

The objective of this chapter is to demonstrate the fabrication of a porous-dense solid electrolyte bilayer. Porous and dense regions are based on cubic LLZO with the porous side exhibiting MIEC properties. Cubic garnet $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) was chosen as the anode side due to its compatibility and stability with Li-metal. Whilst the opposing side, $\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (Fe-LLZO) was identified as a potential candidate for MIEC. Unfortunately, initial investigations revealed significant interfacial resistance with Li-metal, the instability indicates Fe-LLZO as unsuitable for use on the anode side.[145] However, upon further examination the authors report a darkening mechanism upon contact with Li-metal. This mechanism appeared to be similar to what was observed in the manganese bearing LLZTO discussed in previous chapters. The authors hypothesised a partial reduction of Fe³⁺ to Fe²⁺ resulting in a MIEC garnet. As such, Fe-LLZO was selected to be integrated into a bilayer (Fe-LLZO/Ta-LLZO) garnet architecture which would allow for a Li-metal anode on the Ta-LLZO side and the integration of a cathode on the Fe-LLZO side.

5.2 Experimental

Synthesis of target compound $\text{Li}_{6.4}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$ (x = 0.6) (LLZTO) was conducted using reagents, Li_2CO_3 (Aldrich, 99 % min), La_2O_3 (Aldrich, 99 % min), Ta_2O_5 (Aldrich, 99 % min) and ZrO_2 (Aldrich, 99 % min). A 10 wt% excess of Li_2CO_3 was added to compensate for lithium volatilisation at high temperatures. Powders were milled in a Retsch Mixer Mill MM500 Nano at 7 Hz for 20 hours in 4 segments with 5 min rest in between. Mixed powders were calcined at 900 °C and 950 °C for 12 hours with a ramp rate of 5 °C min⁻¹, hand grinding followed each calcination step. Further particle reduction steps were carried out at 7 Hz and 25 Hz for 20 hours in 4 segments with 5 min rest in between. Particle size characterisation was carried out using a Panalytical Mastersizer 3000 in a wet dispersion; a refractive index of 1.4 was assigned to LLZTO powder.[251]

The second target compound $\text{Li}_{7-3x}\text{Fe}_x\text{La}_3\text{Zr}_2O_{12}$ (x = 0.2) (Fe-LLZO) was synthesised using the reagents Li_2CO_3 (Aldrich, 99 % min), La_2O_3 (Aldrich, 99 % min), Fe₂O₃ (Alfa Aesar, 99.995 % min) and ZrO₂ (Aldrich, 99 % min). A 15 wt% excess of Li_2CO_3 was added to compensate for lithium volatilisation at high temperatures. Powders were milled in a Retsch Mixer Mill MM500 Nano at 7 Hz for 20 hours in 4 segments with 5 min rest in between. Mixed powders were calcined at 950 °C for 24 hours followed by 1000 °C for 20 hours with a ramp rate of 5 °C min⁻¹, hand grinding followed each calcination step. Further particle reduction steps were carried out at 25 Hz for 20 hours in 4 segments with 5 min rest in between.

Powder X-ray diffraction (PXRD) was conducted using a benchtop Miniflex Rigaku diffractometer, as described in in Chapter 3. Initial Rietveld refinement models were calculated using CIF files from the Inorganic Crystal Structure Database (ICSD) for LLZTO (ICSD 894) garnet phase, Fe-LLZO (ICSD 431393), $Li_7La_3Zr_2O_{12}$ (ICSD 246817), $Li_8La_{18}Fe_5O_{39}$ (ICSD 247328), $La_2Zr_2O_7$ (ICSD 26853), and Li_2ZrO_3 (ICSD 94893). A 9th order shifted-Chebyschev function was used to fit the background and a pseudo-Voigt function to fit the diffraction peaks.

The synthesised powders were rotationally milled on a Glen Creston Tumbler ball mill with an addition of 2.5 wt% of dispersant 'Hypermer KD1' (CRODA Smart Materials). The milling time was 20 hours in 45 ml of isopropanol, with 20 individual \emptyset 10 mm × 10 mm milling cylinders of yttria stabilized zirconia (Y-TZP) in a 125 ml HDPE (High-density polyethylene) bottle. Following milling, the mixtures were centrifuged using a Centrifuge Rotina 380 from Hettich at 8000 rpm for 2 min. The subsequent supernatant was discarded, and the powders were dried at 60 °C for 2 hours in air.

For the slurry formation, LLZTO+KD1 (42.1 wt%), polyvinyl butyral (PVB 9.7 wt%) benzyl butyl phthalate (BBP 5.3 wt%) and a 50/50 mixture (41.8 wt%) of ethanol and methyl ethyl ketone (MEK) were added and sheer mixed in a THINKY ARE-250 (Intertronics) for 5 min at 2000 rpm followed by a degas step of 2200 rpm for 45 sec. Individual sintering aids (relative to the weight of LLZTO+KD1), Li₂O (Sigma Aldrich, 97 % (6 wt%)), LiCl (Alfa Aesar, 98 % (6 wt%)), Li₃PO₄ (Alfa Aesar, 99.98 % (1 wt.%)) and commercially available Asahi glass (AVX, 1 wt%) were added to the previous step. Subsequent slurries were cast at 200 μ m onto a commercially available polyethylene terephthalate (PET) release film (Mylar) at 10 mm sec⁻¹ and dried in air for 24 hours at room temperature. Tapes were laminated for 15 min at 60 °C with a pressure of 500 kg. The laminated tapes were punched into 18 mm discs, covered in mother powder, and sintered between two Al₂O₃ substrates. A two stage heating regime was employed; discs were initially heated to 600°C for 2 hours at 1 °C min⁻¹ followed by 1050 °C for 1 hour at 3 °C min⁻¹.

SEM and EDX data were collected on a FEI Inspect F50 high resolution micro-

Ingredient	Details	Supplier	Weight percentage
Solid Electrolyte	LLZTO	Laboratory Synthesised	42.08 %
Solvent	MEK/Ethanol 50 % (v/v)	SLS / Sigma-Aldrich	41.80 %
Dispersant	Hypermer KD1	Croda	1.08~%
Plasticiser	Benzyl butyl phthalate	Sigma-Aldrich	5.34~%
Binder	Polyvinyl butyral	Sigma-Aldrich	9.70~%

Table 5.1: Summary of LLZTO and Fe-LLZO slurry formulation constituents.



Figure 5.1: Thermal heating regime for sintering LLZO based solid electrolyte tapes.

scope equipped with an Oxford Instruments X-Max 80 mm^2 SDD detector at 10 kV with a working distance of *ca.* 10 mm and spot size of 3-4 nm. Samples were coated in a layer of Au using an Agar Automatic Sputter Coater.

5.3 Results and Discussion

15 g of the target compound LLZTO was synthesised by solid state reaction. The resultant PXRD data was analysed using the Rietveld refinement method with the computational fit and Bragg reflections displayed in Figure 5.2. The analysis confirmed the synthesis of phase pure cubic garnet $Ia\overline{3}d$. The refined lattice parameters of 12.9372(3) Å are in good agreement with previous studies for the target composition.[123]

The ability to batch synthesise 15 g of LLZTO via ball milling whilst attaining a high phase purity facilitated the subsequent tape casting trials which required large amounts of solid electrolyte powder. Moreover, the phase purity of the synthesised LLZTO allowed for the powder utilisation as reference material in investigations presented in Chapter 3 and 4.

However, attaining a fully phase pure sample is challenging and becomes increasingly difficult as quantity is increased. To therefore produce large scale synthesis options numbering in the kg or even tonnage will require the use of specialist industrial equipment as well as moving away from the batch process to a continuous process to achieve high throughput yields.



Figure 5.2: Calculated Rietveld refinement fit and PXRD of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ after 950 °C calcination. Bragg reflections of the cubic target phase are shown below. The fit is in good agreement with the collected data having an $R_{wp} = 8.15$ % and $\chi^2 = 7.18$.

5.3.1 Particle Size Analysis

To facilitate formation into a high density ceramic substrate, the average particle size should be reduced to *ca.* 1 μ m.[252] However, exceedingly small particle sizes may lead to production defects such as gelling.[167] As such careful characterisation of the particle size needs to be conducted. The initial size of, LLZTO particles was determined by SEM. Micrographs (*cf.* Figure 5.3) displayed agglomerated and non-uniform particle sizes between *ca.* 10 to 50 μ m and so additional particle reduction was conducted prior to further processing.

These powders were ground using a Retsch Mixer Mill MM 500 Nano at frequencies of 7 Hz and 25 Hz. The frequencies were selected to examine the role of grinding energy in the particle size reduction process. The visual analysis of particle size using SEM only provides for a qualitative assessment, increased accuracy and quantitative analysis of particle sizes following the different reduction regimes was therefore provided by laser diffraction analysis (LDA). LDA of the hand-ground, 'as synthesised' garnet corroborate the estimated particle size from collected SEM micrographs.

Results in Figure 5.4a display a Gaussian response with particle distributions, D_{10} , D_{50} and D_{90} measured as 9.4 μ m, 13.5 μ m and 37.6 μ m respectively. Results from 7 Hz milling frequency (Figure 5.4b) however displayed a bimodal distribution,



Figure 5.3: SEM micrographs of 'as synthesised' $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ particles following 950°C synthesis. The particle size appears to lie in the range of 10-50 μ m.

indicating a mixture of larger and smaller particles. The D₅₀ is noted to decrease to 5.5 μ m indicating a reduction of 62.92 % in the average particle size. Furthermore, the calculated span of 3.18 indicates a larger level of variation in the granulation compared to the 'as synthesised' particles which held a span of 2.09. Particle distribution results from 7 Hz milling thereby confirm the requirement for higher milling energy in the reduction of particles. However, with a measured D₅₀ of 5.5 μ m, the particle size was still too large for successful tape casting trials, the frequency was therefore increased to 25 Hz. Subsequent LDA results at 25 Hz are shown in Figure 5.4c, similar to 7 Hz they exhibit a bimodal distribution. The uniformity of granulation is however increased with a recorded span of 2.34, whilst the D₅₀ was decreased by 78.18 % to 1.2 μ m, resulting in ideal average particle size for high-density substrates. Of further advantage is the bimodal distribution; indicative of a split between submicron particles and larger 1.2 to 3.3 μ m particles. The distribution may further aid sintering due to smaller particles filling into voids generated by larger particles. A summary of the particle size analysis is displayed in Table 5.2.



(c) 25 Hz particle reduction.

Figure 5.4: Particle distribution graphs for $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$. (a) The particle distribution of 'as synthesised' LLZTO displayed a Gaussian distribution with a calculated D_{50} of 13.5 μ m. Particle reduction using the Retsch MM500 at 7 Hz yielded a bimodal distribution with a particle D_{50} of 5.5 μ m. (c) Particle size following ball milling at 25 Hz displayed a bimodal distribution with a D_{50} of 1.2 μ m.

Table 5.2: Summary of particle size analysis for the 'as synthesised', 7 Hz and 25 Hz samples. D_{10} , D_{50} , D_{90} and the Span are displayed. The results indicate that the high energy milling reduces the particle size of LLZTO particles.

Composition	D ₁₀	D ₅₀	D ₉₀	Span
As synthesised	$9.4~\mu{ m m}$	$13.5 \ \mu \mathrm{m}$	$37.6 \ \mu \mathrm{m}$	2.09
7 Hz	$2.3~\mu{ m m}$	$5.5~\mu{ m m}$	$19.8 \ \mu \mathrm{m}$	3.18
25 Hz	$0.49~\mu{ m m}$	$1.2~\mu{ m m}$	$3.3~\mu{ m m}$	2.34

5.3.2 Single Film Processing of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$

Preparation of the ceramic slurry system followed milling. A critical aspect of the slurry system is ensuring uniformity in particle dispersion. A deflocculant may be used to mitigate aggregation and ensure particle dispersion, this was achieved by rotational mixing the prepared solid electrolyte powder with cationic polymeric dispersant 'Hypermer KD1', this ensured a homogeneous coating of the polymeric additive across all ceramic particles. The efficacy of Hypermer KD1 is such that it has been used in the processing of solid oxide fuel cell electrolytes and was therefore chosen for use in this thesis.[253] However, a range of alternatives are available, including, popular oil based dispersants such as the commonly used menhaden fish oil.[254]



Figure 5.5: PXRD patterns of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO). The 'as synthesised' (black) pattern displays phase pure cubic LLZTO prior to further processing. The addition of the dispersant, Hypermer KD1 (red) displayed a small degree peak broadening of the cubic LLZTO pattern which is attributed to the addition of the polymeric coating on LLZTO particles. Sintering of the LLZTO green tape with 1.2 μ m particles without mother powder (blue) resulted in decomposition of the phase. The addition of mother powder during sintering (green) however resulted in the retention of the cubic LLZTO phase with small quantities of ZrO_2 and $La_2Zr_2O_7$ impurities indicated by \circ and * respectively.

The conductivity of the doped LLZO is linked to cubic phase purity, as such, if reactive sintering of the tapes is not being utilised it is imperative to retain the required phase throughout all of the processing steps. The solid electrolyte was therefore characterised via PXRD following the mixing with Hypermer KD1, Figure 5.5 (red trace) shows that the desired cubic ($Ia\bar{3}d$) structure with no side phases. Peak broadening is however observed and is attributed to the amorphous nature of the polymer coating on the garnet crystallites.

Simultaneously, whilst the solid electrolyte powder was milled with the deflocculant, a 50/50 mixture of MEK and ethanol was prepared and the required amount of PVB was added during agitation to allow for full dispersion. Addition of PVB to the 50/50, MEK and ethanol mix allowed for complete homogeneous dispersion of

the PVB binder, inclusion of the binder in dry form would not allow for complete dispersal within the solid electrolyte powder, leading to a raised, rough texture that resulted in streaking and a brittle nature of the green tape, indicating poor dispersion of the polymeric binder (see Appendix B and Figure B.2 for unsuccessful tape casting runs).

The prepared LLZTO+KD1 solid electrolyte powder was weighed out and added to the solvent/PVB mix along with Benzyl butyl phthalate (BBP). BBP acts as a plasticiser to reduce the gel formation temperature to room temperature or lower. Cast tapes with gelled liquids dry at a slower rate, this is due to the restriction of solvent flowing to the surface during drying, as such embedded solvents may only leave the green tape via diffusion, the advantage of this mechanisms is that the binder (PVB) does not migrate to the surfaces thereby retaining a homogeneous matrix of polymer binder. Additionally, the plasticiser enables the flexibility of the tape, increasing handleability. Optimum binder/plasticiser concentration must however be found, because while an increase in plasticiser concentration leads to flexibility, the interparticle distances and green tape density decreases. As a result, void formation occurs during sintered of tapes resulting in highly porous structures.[171]

The processed slurry held a solid loading content of 42.08 wt% and a total organic content of 16.12 wt% and was tape cast to a thickness of 200 μ m with a shear rate of 50 s⁻¹. Figure 5.6 shows the dried green film following casting with a thickness of ca. 100 μ m and a dry solid loading of 72.30 %. The surface of the tape is observed to hold a smooth, streak free surface, indicating full and homogeneous dispersion of all particulates, demonstrating successful mixing during the applied processing steps. Cross-sectional SEM (Figure 5.7) of a cut green tape reveals a dense microstructure with tightly bonded particles, the formed coherent structure displaying desired microstructural homogeneity, further indicating successful dispersal of all constituent elements. The results demonstrate that the binder/plasticiser ratios and solid loading appear to be of appropriate concentrations. Post drying, the green tape (Figure 5.6) exhibited excellent flexibility whilst still bound to the Mylar substrate, demonstrating the required flexibility provided by the polymer binder. This was further corroborated with the removal of the green tape from the Mylar release film, the mechanical strength, flexibility, and malleability enabled ready manipulation of the film for further processing.

Thermocompression, also known as lamination, is a technique that is employed to increase the density and or thickness of a green tape. Furthermore, it enables the binding of different green tapes for multilayer structures such as the targeted LLZTO/Fe-LLZO bilayer configuration. To ensure the process as viable, the initial LLZTO solid electrolyte green tape was laminated and subsequently cut into a desired shape of 18 mm diameter discs with a thickness of *ca.* 150 μ m. Cut discs (Figure 5.8) were observed to have retained the desired shape and consistency, indicating



Figure 5.6: (a) Green tape $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ following casting at 200 μ m dried to 100 μ m in thickness, the surface is a homogeneous, smooth consistency with no processing defects visible. (b) Demonstration of high flexibility and malleability of the green tape following casting which is required for further processing and indicated a correct polymer - plasticiser ratio. (c) Flexibility of punched 18 mm diameter green tape discs, the tape is still attached to the Mylar supportive substrate. (d) Peeling and release of green tape from Mylar release film qualitatively shows a degree of mechanical strength and flexibility.



Figure 5.7: Cross sectional SEM micrographs of green tape $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ at varying magnifications. The cross sectional fracture surface displays a well dispersed polymer network, indicating complete and homogeneous covering of LLZO particles. The thickness of the green tape is seen to be a uniform *ca.* 100 μ m.

good thermocompression and mechanical properties of the green tape, evidencing the feasibility for multilayer structures.

Successful sintering of green tapes requires the control of thermal parameters to ensure regulated binder and organics burnout. Failure to do so would result in rapid gas volatilisation and volume expansion leading to excessive porosity, anisotropic shrinkage, delamination, cracking, or bubbles within the tape.[170]

To identify the organics burnout region and establish an appropriate sintering regime TGA analysis was conducted on the green tape (Figure 5.9). Results show a 36 % weight loss of the green tape, with the PVB and remaining organics completing combustion at 650 °C, which are in good agreement with the literature.[255] The remaining change in weight above 700 °C is attributed to lithium oxide volatilisation from the garnet. It is however noted that a 5 % weight loss resulting solely from lithium oxide is excessive and as such the observed loss may be a result from a contribution of Li₂CO₃. A heating regime (Figure 5.1) of 600 °C for 2 hours with a ramp rate of 1 °C min⁻¹ was selected to ensure gradual but complete combustion of the constituent organics. The gradual ramp rate ensures the suppression of rapid vapour build up to minimise tape defects, whilst an extended hold at 600 °C



Figure 5.8: Dried $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ green tape punched into a disc of 18 mm diameter. The surface shows a good dispersion with a homogeneous, streak free surface.



Figure 5.9: TGA analysis of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ green tape. Initial heating to 650 °C saw a weight loss of 36 % following PVB and organics burnout. Subsequent heating revealed a 5 % weight loss which is attributed to the volatilisation of lithium oxide.

ensures no organic residue that may hinder electrochemical performance of the solid electrolyte. The temperature was subsequently raised to 1050 °C at 3 °C min⁻¹ and held for 1 hour to complete ceramic densification, whilst cooling was conducted at 5 °C min⁻¹ to room temperature to minimise warping.

Initial sintering trials of the LLZTO electrolyte were conducted on a single Al_2O_3 plate. This however, led to warping (Figure 5.10) which is a likely consequence of anisotropic shrinkage arising from uneven organic burnout. An additional Al_2O_3 plate was therefore placed on the top in subsequent sintering treatments. Furthermore, visual inspection revealed rough bumps on the surface of the disc, indicating displacement of LLZTO particles and widespread pore formation as a result of rapid lithium vaporisation during the sintering stage.



Figure 5.10: Sintering on top of Al_2O_3 plate without mother powder resulted in warping and a rough surface finish.

PXRD data collected from the resultant material (Figure 5.5, blue trace) indicate complete decomposition of the cubic garnet phase. The excessive lithium volatilisation at high temperature results in catastrophic lithium loss from the LLZTO lattice leading to decomposition. The mechanisms of lithium volatilisation following binder burnout are alluded to in the TGA analysis (Figure 5.9), where a weight loss of 5 wt% in the LLZTO solid electrolyte was observed.

To counteract this deleterious effect, the discs were embedded in loose LLZTO powder (Figure 5.11a); referred from here on as mother powder (MP). The MP acted as a lithium source during sintering as well as providing a localised lithium rich atmosphere which prevented decomposition of the cubic garnet phase, the subsequent PXRD plot (Figure 5.5, green) shows the retention of the main cubic garnet phase albeit with a small amount of $La_2Zr_2O_7$ pyrochlore and ZrO_2 impurities. The use of MP during sintering was therefore required in the retention of single phase cubic LLZTO. Additionally, the MP acts as a barrier between the LLZTO discs and the Al₂O₃ substrates, this effectively reduced any undesirable aluminium reactions with Ta-doped LLZO that occur at high temperature.[127, 256] Post-sintering visual inspection of the discs revealed little to no warping, indicating the requirement for a


Figure 5.11: (a) To prevent lithium volatilisation and phase loss, the sintering LLZTO discs with Li_2O as sintering aid were enveloped in a covering of mother powder before being placed between two large Al_2O_3 plates. (b) The sintered LLZTO disc displayed only a small degree of warping on the edges and good mechanical strength for handling was displayed. (c) A slight rough, powdery surface on the discs was due to residue from the LLZTO mother powder.

top and bottom Al_2O_3 plate.

5.3.3 Density Improvement using Sintering Aids

Having established the need for MP in the retention of the main garnet phase, the next crucial aspect of tape fabrication was attaining a high relative tape density (≥ 98 %). Characterisation of the relative density was conducted with the use of SEM and geometrical calculations. The SEM micrographs (Figure 5.12) revealed a highly porous structure, the particles appear not to have fused, and the subsequent relative density was estimated at 43 %. The challenge of sintering LLZO based



Figure 5.12: Cross sectional SEM micrograph of sintered $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape displaying an intergranular fracture mode. Mother powder was used to prevent the loss of lithium and retain the desired phase during the sintering process. The fracture surface of the tape however reveals a high porosity, the relative density was estimated at *ca.* 45 %.

solid electrolytes is well recognised and is often experimentally overcome using spark plasma sintering, hot-press sintering [130] or similar high pressure, high temperature, rapid sintering technologies. These technologies are however unsuited for large scale adoption due to substantial equipment space requirements, high cost and low batch output. Furthermore, the techniques are incompatible with tape casting and are often only able to produce single, thick (> 3 mm) pellets. Traditionally, in ceramic sintering, temperatures and sintering times may be raised to increase the density. However, as shown, high rates of lithium volatilisation occur at elevated temperature and time, leading to decomposition of the cubic phase, making simple temperature and time increases challenging. As such, several studies have been solely dedicated to the investigation of cubic LLZO densification. Within these, several mechanisms have been explored to increase the density during pressureless sintering, including the strategies of co-doping, [257] changing the sintering atmosphere, [258] or decreasing the particle size. [252] These strategies are however unsuitable for the densification of LLZO based solid electrolyte tapes, co-doping would affect the electrochemical properties of the full system and require thorough investigation prior to processing to

ascertain how co-doping affected the electrochemical properties. A further decrease in particle size to the nanometre scale would result in slurry processing problems such as gelling, hindering successful casting of the solid electrolyte tapes. A change in sintering atmosphere would deviate from the simplest, in air sintering approach of the process, requiring extensive and expensive optimisation of atmospheric conditions within the furnace. It is however noted that the use of a covering MP is likely resulting in a localised, lithium rich atmosphere and has been previously shown to increase the density of LLZTO pellets.[259]

A further approach is the use of sintering aids; the addition of sintering aid during the processing would allow for minimal change in processing conditions whilst improving the density of the ceramic tape. Four lithium bearing sintering aids were selected to investigate improvements in the tape relative density. LiCl, Li₃PO₄, Li₂O, and the use of lithiated silica Asahi glass were chosen. All compounds have previously been shown to increase the density of LLZO based solid electrolytes.[153, 260–264] Moreover, the compounds provide a further lithium source to suppress lithium volatilisation and therefore the decomposition of the main cubic phase.

Due to the success of lithium containing glass systems such as Li₂-B₂O₃-SiO₂ [264] and Li₂-SiO₂, [263] as sintering additives commercially available Asahi glass from AVX (Li₂-BaO-CaO-SrO-SiO₂) was selected. SEM micrographs in Figure 5.13 display a denser microstructure compared to sintering with just a covering of MP (cf. Figure 5.12) however, a degree of porosity is still observed. EDX analysis revealed the expected presence of Si at 5.7 at. % within the scan region. The regions associated with the Si signal hold a smooth, glassy appearance and appear to have agglomerated within the structure rather than forming a distributed connected network along the grain boundaries, strongly indicating inhomogeneous distribution of the sintering aid in the green tape. PXRD analysis of the sintered tape (Figure 5.17, blue trace) revealed the presence of several impurities related to the sintering additive, these included: La₂CaO, BaLa₂O₄, Sr₆Ta₂O₁₁, tetragonal Li₇La₃Zr₂O₇ and the pyrochlore $La_2Zr_2O_7$. Whilst previous success has been found with the use of glasses in improving the density of LLZO based solid electrolytes, the results here, appear to have only marginally improved the densification of the LLZTO tapes. The relative density was estimated at 65 %, far from the required target of > 98 % relative density and is as such not adequate.

The utilisation of LiCl as a sintering aid has previously been shown to increase the density of LLZTO pellets due to a liquid phase sintering mechanism.[260] Post sintering SEM micrographs in Figure 5.14 however show a negligible improvement in density in comparison to no sintering aid. A high degree of porosity is still observed with only few particles displaying a degree of fusing. It is however not possible to accredit the fusing as a function of the liquid phase sintering additive LiCl, or to the natural diffusion mechanism of sintering at 1050 °C. The subsequent relative density



Figure 5.13: SEM micrographs (a)-(b) and EDX maps of (c) La, (d) Si, (e) Zr and (f) Ta of sintered $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ tape with Li-Si based (AVX) sintering aid. (a) The Cross sectional SEM of the sintered tape displays an intergranular fracture mechanism with visible porosity in the structure, the relative density was estimated as 65 %. (b) Arrows indicate the visible presence of agglomerated Li-Si sintering aid within the tape microstructure and was further confirmed by EDX (d) displaying the Si signal where a relative 5.7 at. % Si was measured.





Figure 5.14: SEM micrographs (a)-(b) and EDX maps of (c) Cl, (d) La, (e) Ta and (f) Zr of sintered $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape with LiCl sintering aid. (a) The Cross sectional SEM displays an intergranular fracture mechanism of the sintered tape with a maintained uniform thickness. High porosity is visible in the structure resulting in an estimated relative density of 58 %. (b) The magnified region shows a low amount of particle fusing, red circles however highlight regions where partial fusing was observed. EDX mapping of the Cl signal (c) revealed background noise indicating no measurable Cl residue within the structure.



Figure 5.15: SEM micrographs (a) and EDX maps (b)-(e) of sintered garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape with Li_3PO_4 sintering aid. (a) The Cross sectional SEM displays an intergranular fracture mechanism of the sintered tape with a large amount of visible porosity. The relative density was estimated at 53 %. (b)-(e) EDX maps of (b) La, (c) Zr, (d) Ta and (e) P, the P signal displays a low level concentration level synonymous with background noise.

was estimated as 58 %. EDX mapping of the tape exhibited no measurable trace of Cl remaining within the sample, which was further corroborated by collected atomic percentage indicating 0 % Cl remaining. The melting temperature of LiCl is *ca.* 600 °C,[265] full sintering at 1050 °C would therefore result in complete combustion of the sintering aid. Post sintering PXRD (Figure 5.17, red trace) revealed very minor inclusions of secondary phases, $La_2Zr_2O_7$, Ta_2O_5 and La_3TaO_7 . There is a notable decrease in the number of impurity phases formed in comparison to the use of lithiated silica.

 Li_3PO_4 melts at the grain boundary in a similar manner to LiCl and thus may improve Li ion conductivity and the relative density. [261] With a melting point of ca. 837 °C, [266] the liquid phase sintering would enhance densification of the microstructure. EDX characterisation following sintering (Figure 5.15) displayed a small amount of phosphorus inclusion, quantification from the mapping was however unsuccessful at presenting an accurate atomic percentage. This is due to the EDX energy of phosphorus (2.037 KeV) being similar to gold (2.120 KeV); having coated the samples in gold for SEM/EDX imagining, collection of the atomic percentage was not possible. One possible way to overcome this issue is to use an alternative conductive coating such as carbon (0.277 KeV). Visual inspection of the SEM micrographs reveals a low sample density with large voids and unfused particles. The estimated relative density of the sample was 53 %, far below the density requirement for LLZO based solid electrolyte films. PXRD characterisation (Figure 5.17, green) indicated the presence of minor side phases, ZrO_2 and Ta_2O_5 . Comparatively to LiCl and AVX glass sintering aids, Li₃PO₄ displayed a reduced quantity of secondary phases present. Furthermore, the overall cubic LLZTO phase is successfully maintained.

The final sintering aid investigated was Li_2O , previous studies found that the inclusion of 6 wt% increased the density by 5.8 % and has previously been used in the fabrication of 99 % dense LLZTO tapes. [153, 262] SEM micrographs in Figure 5.16 appear to show an increased density in the microstructure comparatively to the other samples. Whilst the magnified images reveal porosity the particles appear to be more fused to a greater extent than the previous samples, thereby resulting in a lower level of observed porosity. The relative density measurement of the sample was estimated ca. 88 %, a notable improvement upon the other samples. The density is still below the target level for a functional solid electrolyte membrane in an ASSB. The structure was however more mechanically robust and able to be handled with tweezers and supported its own weight (Figure 5.11). The discs exhibited minimal warping, furthermore, the observed powdery texture on the surface was a result of the covering MP and was able to be brushed off. EDX imaging of the sample was not undertaken as no detectable secondary phases from the sintering aid were predicted. PXRD characterisation (Figure 5.17, purple) revealed the successful retention of the main cubic garnet phase with a negligible amount of secondary ZrO_2 impurity



Figure 5.16: SEM micrographs display the fracture surface of the sintered garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ tape using Li_2O as a sintering aid. The fracture surface is of an intergranular nature. LLZTO particles are seen to have fused together increasing the relative density of the tape, which was estimated at 88 %. A uniform thickness of *ca.* 90 μ m has been maintained during sintering.

present. It is probable that similar to the use of MP, that Li_2O amplifies the localised lithium rich atmosphere, thereby aiding in the retention of lithium within the crystal lattice of the cubic garnet phase, simultaneously providing a liquid phase sintering effect to the tape. The use of Li_2O sintering aid appears to be the best choice for the tape casting process.

Overall results indicated that the use of sintering aids may improve the density of LLZTO tapes. Whilst the final relative densities of the sintered tapes were insufficient to reach the target of > 98 %, they do indicate promising results that with a systematic variation in weight percentage an optimum level for high density may be found. It is however noted that only varying the inclusion level of sintering aid is unlikely to yield the required density alone and an increase in temperature and time should similarly need to be investigated. This will however require further extensive phase and microstructure characterisation. The use of Li₂O resulted in a relative density of *ca.* 88 % following sintering, consequently, the solid electrolyte held insufficient mechanical strength to electrochemically test or integrate into a device. However, the decision was taken to proceed with the fabrication of the



Figure 5.17: Post sintering powder X-ray diffraction patterns of LLZTO and LLZTO with sintering aids, LiCl, Li₃PO₄, Li-Si glass (AVX) and Li₂O. The LiCl bearing LLZTO pattern (red) displayed the impurities: Ta₂O₅ (\bigstar), La₃TaO₇ (\blacktriangledown), and pyrochlore La₂Zr₂O₇ (\bigstar). The Li-Si (AVX) bearing LLZTO pattern (blue) held impurities which included: La₂CaO (∇), pyrochlore La₂Zr₂O₇ (\bigstar), BaLa₂O₄ (\blacktriangleleft), Sr₆Ta₂O₁₁ (\triangleright), and Li₇La₃Zr₂O₇ (\bigstar). LLZTO phase with Li₃PO₄ (green) held the impurities: pyrochlore La₂Zr₂O₇ (\bigstar) and ZrO₂ (\circ). The use of Li₂O displayed the lowest number of impurities in LLZTO with a negligible amount of ZrO₂ (\circ) present.

Fe-LLZO/LLZTO garnet bilayer to demonstrate the feasibility of combining two differing LLZO based solid electrolyte garnets in a bilayer tape.

5.3.4 Synthesis of $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$

The iron doped LLZO phase, $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$ (Fe-LLZO) was synthesised via solid state reaction. Fe-LLZO was selected due to its potential MIEC behaviour as a result of suspected Fe³⁺ to Fe²⁺ reduction.[145] Initial synthesis attempts following the same route as LLZTO however proved unsuccessful and required increased temperature and time to reach the target phase.

Figure 5.18 shows the diffraction results of subsequent syntheses attempts. Each pattern (excluding LLZTO) follows the previous temperature and times, from 900 °C to 1000 °C. As such, the same Fe-LLZO sample was submitted to a total calcination time of 52 hours to achieve incorporation of Fe³⁺ to stabilise LLZO in the conductive cubic phase. Figure 5.19 shows the diffraction pattern of the final synthesised Fe-LLZO garnet. Several extra Bragg reflections were visible, clearly indicating that a phase pure sample of Fe-LLZO was not attained. A search of crystallographic databases revealed that the impurity phases included: Li₈La₁₈Fe₅O₃₉, Li₇La₃Zr₂O₁₂, La₂Zr₂O₇, and Li₂ZrO₃. Tetragonal Li₇La₃Zr₂O₁₂, La₂Zr₂O₇ pyrochlore, and Li₂ZrO₃



Figure 5.18: Powder X-ray diffraction patterns of $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$ following consecutive thermal heat treatments for synthesis. LLZTO (black) is included as a reference cubic phase. Fe-LLZO required extensive thermal energy and time to incorporate Fe into the LLZO lattice to stabilise the cubic phase and minimise impurities.

are all well known impurities in the synthesis of LLZO, whilst cubic $Li_8La_{18}Fe_5O_{39}$ is a previously unreported impurity phase observed in the formation of Fe-LLZO. The constituent weight fractions of the impurities are tabulated in Table 5.3. For ease of comprehension a diffraction plot of Fe-LLZO with the contained impurities alongside LLZTO as a reference standard are presented in Figure B.1. The effect that a secondary phase can have on a solid electrolyte composite has been discussed in the previous two chapters, as such it is without a doubt that these secondary phases may alter the electrochemical properties of the solid electrolyte. Several techniques including EIS, DC polarisation CV and galvanostatic cycling would therefore be required to characterise the electrochemical dynamics of the system. Rietveld refinement fits were calculated for the collected diffraction data employing a multiphase refinement using the cubic garnet and the impurity phases. Atomic coordinates were fixed whilst the lattice parameters were free to refine. The subsequent pattern is displayed in Figure 5.19 with the refined lattice parameters and weight fraction percentages in Table 5.3. The refinement indicates that the desired, acentric cubic phase $I\overline{4}3d$ was attained; the lattice parameters of 12.9703(1) Å are within range for Fe^{3+} stabilised LLZO, as reported in literature.[267]



Figure 5.19: Calculated Rietveld refinement for powder X-ray diffraction of garnet Li_{6.4}Fe_{0.2}La₃Zr₂O₁₂. Bragg reflections of cubic Fe-LLZO and Li₇La₃Zr₂O₁₂, Li₈La₁₈Fe₅O₃₉, La₂Zr₂O₇, Li₂ZrO₃ impurity phases are shown below. The fit is in good agreement with the collected data having an $R_{wp} = 7.13$ % and $\chi^2 = 6.15$.

Table 5.3: Tabulated Rietveld refinement details of $Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$. The space group, lattice parameters and weight fraction of each present phase is indicated. The largest impurity phase detected was tetragonal LLZO at 11.1 %.

Compound	Compound Space Group		b (Å)	c (Å)	Weight fraction	
$Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$	$I\overline{4}3d$	12.9703(1)	-	-	83.8~%	
$\rm Li_7La_3Zr_2O_{12}$	$I4_1/acd$	13.108(2)	13.108(2)	12.750(2)	11.1~%	
$Li_8La_{18}Fe_5O_{39}$	$Pm\overline{3}n$	12.175(1)	-	-	2.3~%	
$La_2Zr_2O_7$	$Fd\overline{3}m$	10.8041(7)	-	-	1.4~%	
Li_2ZrO_3	C2/c	5.43(1)	9.024(3)	5.41(1)	1.4~%	

5.3.5 Composite Bilayer Film Processing

Preparation of Fe-LLZO based slurry was conducted in the identical manner as the LLZTO slurry, including the addition of 6 wt% Li_2O to ensure enhanced densification. All casting parameters of the slurry were kept the same as that of initial LLZTO trials to ensure consistency between green films. The subsequent cast green film (Figure 5.20a) held a smooth surface indicating homogeneous dispersion of ceramic and organic components. Dried LLZTO and Fe-LLZO green films were laminated together via thermocompression to form a homogeneous structure, mechanical properties of

the laminated tape possessed similar characteristics as that of the single LLZTO tape; flexibility and green film strength were sufficient for further handling and processing. Discs of 18 mm in diameter were cut, with the Fe-LLZO side displayed in Figure 5.20b and the reverse LLZTO in Figure 5.20c. The distinctive brown colour differentiates the Fe-LLZO from the LLZTO side, both sides appear to be predominantly the respective doped LLZO phase, however, some cross contamination on the opposing side was observed. Thermocompression may have resulted in sufficient mechanical force to result in regions of penetration into the opposing film side. As such careful optimisation of applied force during lamination is required. Originally cast at 200 μ m for both LLZTO and Fe-LLZO, the overall green tape thickness measured ca. 80 μ m, with 45 μ m for the LLZTO segment and 35 μ m for the Fe-LLZO region, demonstrating the significant reduction in thickness resulting from drying and thermocompression. SEM and EDX analysis of the green bilayer tape are displayed in Figure 5.21. The LLZTO side, layered on top, is seen to show a well bonded interface with the Fe-LLZO side. EDX mapping indicates the Ta signal to originate from the topmost layer only, displaying successful, full lamination of the bilayer. The EDX signals from Fe however appear extremely weak and show no clear boundary between the two tapes, this may however be a result of low concentration level of Fe within the Fe-LLZO analogue making detection challenging. A small inclusion of Fe may be observed within the LLZTO layer and is considered a result of cross contamination during sample preparation. Visual analysis of the micrographs indicated a morphological difference between the respective sides; a slightly lower degree of polymer component is observed in the LLZTO component of the film compared to the Fe-LLZO region. The contrast in appearance may be a result of dissimilar particle properties resulting in a variation in PVB binder-particle interaction and dispersion; mitigation of differences may be achieved by adjustment of solid loading for the Fe-LLZO system.

Following sintering the discs were analysed via SEM and EDX (Figure 5.22). Results indicate the maintained separation of the two doped LLZO phases with a clear division of the Ta signal on the left side compared to the right side of the structure. The observation is further supported by the Zr signal, where the LLZTO side shows a lower relative detected intensity compared to the Fe-LLZO side, this is due to LLZTO holding lower amount of moles $(Zr_{1.4})$ compared to Fe-LLZO (Zr_2) . As with the green tape the Fe signal appears too low to indicate any more than background signal. From EDX it appears that no Ta diffusion has occurred across the interface of the two doped LLZO solid electrolytes, Ta/Fe diffusion at the immediate interface following sintering may however not be ruled out from EDX alone. The interface between differing doped LLZO layers presents an intriguing region of interest. Not only would diffusion following sintering have to be considered but also following electrochemical cycling as diffusion of transition metal cations at



Figure 5.20: (a) Image of slurry cast $\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ green film, the cast surface is of a smooth and homogeneous appearance with streaking or processing defects indicating good mixing of the system components. (b) The Fe-LLZO side of a laminated bilayer, some white from the LLZTO side may be seen indicating excessive lamination pressure resulting in visually observable defects. This is similarly seen on the LLZTO side of the disc (c), where spots of the distinctive brown colour of Fe-LLZO can be seen.







Figure 5.21: (a)-(b) SEM micrographs and EDX maps of (c) La, (d) Ta, (e) Fe and (f) Zr for $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}/\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZTO/Fe-LLZO) bilayer green tape. (a) Bilayer tape cross section, a division between the two doped LLZO phases is marked by a dotted yellow line. The microstructure displays well dispersed particles within a polymer matrix with some textural difference between LLZTO and Fe-LLZO. (b) Green tape region subjected to EDX analysis. (d) Ta shows the division of the two LLZO analogues where the signal is only detected on the LLZTO side. (e) Low Fe levels resulted in predominantly background signal. An impurity of Fe is however seen and is attributed to cross contamination during sample preparation. (f) Due to the difference in moles of Zr a difference in intensity was observed between the two doped LLZO phases.



Figure 5.22: (a)-(b) SEM micrographs and EDX maps for (c) La, (d) Ta, (e) Fe and (f) Zr of sintered Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂/Li_{6.4}Fe_{0.2}La₃Zr₂O₁₂ (LLZTO/Fe-LLZO) bilayer tape. (a) Sintered bilayer tape cross section with an overall thickness of 70 μ m, a yellow line indicates the interface between the LLZTO and Fe-LLZO sides which are 40 μ m and 30 μ m respectively; a red oval indicates a region of delamination. The fracture surface is of an intergranular nature. The particles appear to be partially fused resulting in an estimated relative density of 88 %. Particles of the Fe-LLZO side are larger than those on the LLZTO side. (b) region of EDX mapping. (d) The varying intensity of Ta indicates the division between the two layers, this is further supported by the variation observed by (f) Zr, which arose due to a difference in mole concentration. (e) Fe signal was not detected and only displayed background signal.

solid electrolyte interfaces are not well understood. The interface of any bi/trilayer with differing solid electrolytes would therefore be subjected to unique degradation mechanisms that would have to be fully analysed and characterised.

The microstructure following sintering (Figure 5.22) exhibits a density below 98 %, with partial particle fusing observed, resulting in a porous structure. Due to the bilayer configuration relative density measurements utilising theoretical crystal density proved difficult, additionally the use of Archimedes density measurements was unsuccessful due to a high degree of buoyancy exhibited by the discs. The density was therefore estimated as *ca.* 88 % using colour thresholding (Figure 5.23). Whilst the addition of Li₂O increased the density it is possible to see that further densification is required, this may be achieved with the careful optimisation of increased sintering time and temperature. Systematic increases would however have to be made to retain the desired cubic phases.



Figure 5.23: Colour thresholding of sintered $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}/Li_{6.4}Fe_{0.2}La_3Zr_2O_{12}$ (LLZTO/Fe-LLZO) bilayer tape determined the relative density as *ca.* 88 %.

At the interface between the doped LLZO solid electrolytes, a degree of fusing and bonding is observed with a clear interface boundary displayed (Figure 5.22). The required outcome is the intimate fusing of particles at the interface resulting in an imperceptible boundary. This is in order to maintain structural integrity, retain highly conductive ionic pathways, and reduce any potential interfacial resistance. However, variations in sintering dynamics of the two differing doped LLZO powders may result in irregular densification, anisotropic shrinkage, as such delamination may occur. Evidence of delamination at the interface is observed in Figure 5.22a highlighted by a red oval - displaying a large porous region. A further mechanism

that may result in the delamination of individual layers is the as mentioned shrinkage behaviour. A disproportionate degree of shrinkage originating from an individual layer during sintering would result in uneven stresses upon the bilayer, leading to delamination and structural failure of the bilayer. As such different strategies, such as the inclusion of further organics to aid in the mitigation of differential shrinkage should therefore be investigated.

The work presented in this chapter lays out the steps towards a MIEC bilayer structure of a LLZTO and Fe-LLZO solid electrolyte membrane. However, several challenges including the densification and shrinkage mechanisms of differential ceramic powders and tapes remain. The production of bilayer structures therefore requires optimisation prior to electrochemical testing. Nonetheless, the recent reports of high performing, trilayer solid electrolyte films based on doped LLZO with MIEC properties demonstrate the potential for fast charging, high energy density ASSBs.[162] Further research into bespoke LLZO based solid electrolyte structures should therefore be considered.

5.4 Conclusion

Initial fabrication results on LLZTO films revealed the pivotal influence of particle size, requiring the reduction of synthesised powders to ca. 1 μ m in size. Similarly, the densification of LLZTO films proved challenging and required an extended investigation into the minimisation of Li volatilisation during sintering to retain the desired cubic phase. A range of techniques were employed including the use of a covering mother powder and the use of a range of sintering aids. Li₂O, LiCl, Li₃PO₄ and commercially available Asahi glass from AVX (Li₂-BaO-CaO-SrO-SiO₂) were trialled to increase the density. Li_2O yielded the highest relative density at *ca.* 88 %, increased from an initial 43 % without sintering aid. To fabricate the MIEC incorporated bilayer, target garnet Li_{6.4}Fe_{0.2}La₃Zr₂O₁₂ was synthesised. The attainment of the cubic phase required an extended heating regime in comparison to LLZTO stabilising with ca. 11 % tetragonal LLZO impurity. Synthesised Fe-LLZO was processed into a green film alongside LLZTO and laminated by thermocompression to form a green bilayer tape. Sintering yielded a bilayer with an estimated relative density of 88 %. Whilst extensive further work is required to increase the relative density of the bilayer tapes, an initial proof of concept for the fabrication combining cubic LLZTO and Fe-LLZO via a tape casting process has been demonstrated. Additional work should therefore be focused on the optimisation of sintering temperature and time, as well as the optimum level of Li₂O sintering aid. The increase in density would permit electrochemical testing and quantification of the bilayer for use in ASSBs and subsequently confirm the hypothesis of enhanced cathode integration.

Chapter 6

Conclusions and Future Work

6.1 Conclusion

Solid electrolytes based on doped $\text{Li}_7\text{La}_3\text{Zr}_2O_{12}$ (LLZO) have long held the promise to realise high energy density all-solid-state-batteries (ASSBs). However, the formation of lithium dendrites still hinders their practical utilisation in ASSBs. Much work has been conducted on understanding the mechanisms behind the formation and propagation of these metallic dendrites. However, little is understood about the role of electronic conductivity within these doped LLZO systems and its effect on subsequent solid electrolyte performance and degradation mechanisms.

Chapter 3 and 4 utilised a dual-focused experimental and computational approach to fundamentally understand the electronic properties of the solid electrolyte composite, $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ (LLZTO) with a grain boundary incorporated secondary phase La_4LiMnO_8 . The former took a mechanistic standpoint, using diffraction, spectroscopy and electrochemical techniques to uncover the formation structural changes of an electrochemical active secondary phase that impacted the electrodynamics of the solid electrolyte. Concurrently, the computational workstream employed COMSOL to investigate how local changes in electronic environment can holistically influence the material properties of the solid electrolyte.

In Chapter 5 a systematic approach was taken to investigate the processability of doped LLZO solid electrolyte using the tape casting process. The overarching aim was to investigate the feasibility of fabricating a composite bilayer structure aimed at optimised electrode integration. Laminating LLZTO with a suitably doped LLZObased mixed ionic electronic conductor (MIEC) presents an opportunity to enhance electrode integration, thereby decreasing resistive interfaces. Building upon prior studies, a prospective cubic MIEC-LLZO material (Fe-doped LLZO) was identified, and a bilayer structure comprising two distinct cubic polymorphs of LLZO was successfully manufactured. A systematic enhancement in electronic conductivity of single phase

 $Li_{6.4}La_3Ta_{0.6}Zr_{1.4}O_{12}$ was targeted by the isovalent substitution of Zr^{4+} with Mn^{4+} in the general formula $Li_{6.4}La_3Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$. With an initial focus on characterising the impact of mixed conduction on the growth of lithium dendrites and system degradation. A resulting two phase composite solid electrolyte was synthesised, composed predominantly of LLZTO with a (n = 1) Ruddlesden-Popper phase (RP1) La₄LiMnO₈ located on grain boundaries. Previous research has shown promising results that the modification of LLZO grain boundaries may lead to an improvement in dendrite resistance and air stability. [86, 268, 269] However the change in electrodynamics or electronic conductivity as result of these modifications was only considered in one study.[86] The estimated electrical conductivity of the RP1 phase (ca. $7.5 \times 10^{-4} \text{ S cm}^{-1}$) was ca. five orders of magnitude higher than that of LLZTO providing an inclusion with enhanced electrical conductivity. Despite these properties, at low concentration levels the secondary phase had a negligible impact on ionic and electronic conductivities of the solid electrolyte composite. Increased concentrations, however, were found to elevate the maximum attainable critical current density. The notable change was attributed to an observed reduction of lithium carbonate present at the lithium-electrolyte interface. Measured using XPS the reduction of lithium carbonate may be a result of an active passivation layer or a reaction arising from the secondary phase potentially improve air stability. However, once a threshold was reached at x > 0.07 a negative impact on interfacial resistance and ionic conductivity of the composite was observed. Despite this, the estimated electronic conductivity of the solid electrolyte appeared to be unaffected. However, interfacial post-mortem analysis of the galvanostatically cycled cells revealed observable dark regions, previous studies have correlated surface darkening to the reduction of dopant transition metal. [144] Cyclic voltammetry was therefore used to provide further comprehension, revealing a non-reversible oxidative behaviour at 4.2 V. This was attributed to the RP1 secondary phase, highlighting that the secondary phase exhibited redox-type activity in the composite solid electrolyte. Spectroscopic methods of the solid electrolyte interface confirmed this observation with a mixed $Mn^{3+/4+}$ oxidation state. Chapter 3 emphasises that the inclusion of a secondary phase, even at low levels, with differing electrochemical properties can affect the overall electrical properties and electrochemical dynamics of the system. Much of the electrodynamics within the LLZO solid electrolyte are still not well understood and the incorporation of a secondary phase to beneficially control the material properties of the solid electrolyte may be a viable approach.

To build on the experimental evidence of the influence of the secondary phase the focus was directed towards the impact of the secondary phase on the electrodynamics at the grain boundary level. The aim of Chapter 4 was to answer these questions with the help of advanced computational approaches. X-ray diffraction computed tomography (XRD-CT) allowed for the characterisation of the dark regions observed in the solid electrolyte composite to understand potential crystallographic changes of the RP1 phase. Identification and targeted analysis of the RP1 La₄LiMnO₈ secondary phase allowed for the extraction of X-ray diffraction patterns of pre and post cycled samples. Spatial mapping indicated a heterogeneous dispersion of the RP1 phase throughout the solid electrolyte composite. Bragg reflections from extracted diffraction patterns revealed a reduction in intensity and calculated weight fraction of the RP1 inclusion in the dark regions following galvanostatic cycling. To explain the results observed under dynamic current conditions a hypothesis was posed theorising that lithium deintercalated from the shared occupancy site with manganese leading to a phase change from tetragonal to orthorhombic; this is supported by the mixed oxidation state of manganese within the RP1 phase found by XAS and XPS. To fundamentally understand current distributions and electrodynamics at a micro/meso scale, finite element method (FEM) was utilised to simulate a simplified composite system. Under a 1 V potential the model revealed significant changes to the electrodynamics of the solid electrolyte. The secondary phase was shown to affect the current density of the local grain boundary region from an initial 0.13~%to 8.97 %, an increase of ca. 69 times and increasing the density by up to 6 $\times 10^{-8}$ $\mu A \ \mu m^{-2}$ more than the surrounding composite.

Further post processing highlighted the preferential flow of current along grain boundaries towards the secondary phase, emphasising the role of high current density locations and potentially nucleation points for lithium dendrites. The model indicates that at low levels the presence of the secondary phase is unlikely to affect the overall system, however, once a percolation threshold is reached the inclusion becomes detrimental to the whole solid electrolyte system. The overall results from chapter 3 and 4 indicate that caution is required when synthesising LLZO based solid electrolytes, a small inclusion of high electrical conducting secondary phase may affect the entire system.

The observed significant changes in the electrodynamics of the solid electrolyte prompted the hypothesis that integrating a cubic MIEC-LLZO phase into a LLZObased architecture to form a composite bilayer, could enhance electrode compatibility. An MIEC layer would introduce improved electronic conductivity allowing for an optimised integration of electrodes, reducing interfacial resistance, and enhancing charge transfer kinetics. Fabrication efforts of the LLZO based bilayer were presented in Chapter 5. Significant challenges arise in the processing of solid electrolyte films including, densification and loss of desired phase. Therefore, to retain the desired phase and attain the high density required for further processing, a range of process optimisation and sintering aids were similarly investigated.

Trials utilised LiCl, Li_3PO_4 , Li_2O , and commercially available lithiated silica (AVX glass). Results revealed the greatest increase in density arose from the use of

Li₂O, which increased the relative density of the ceramic film to *ca.* 88% from an initial *ca.* 43%. Iron doped LLZO was selected due to its suspected MIEC properties from an observed mixed $Fe^{3+/2+}$ oxidation state.[145] Initial efforts revealed good thermocompression of the green films between the two differing doped LLZO phases. Subsequent sintering of the LLZTO/Fe-LLZO bilayer resulted in a relative density of 88%, a clear interface boundary showcased the separation of the two distinct regions. This work presents an initial proof of concept for a doped LLZO based bilayer with two differing electrical properties. Nevertheless, substantial efforts are needed to further optimise the density and mechanical properties of the solid electrolyte film to allow for electrochemical characterisation.

This thesis describes a collection of research using an interdisciplinary approach designed to study the complex chemistry of LLZO based solid electrolytes, encompassing mechanistic understanding, processability assessment, and the integration of both traditional and cutting-edge computational methods. It highlights the complex and dynamic nature of these garnet type solid electrolytes and the requirement for extensive research to realise an LLZO based solid electrolyte in an ASSB.

6.2 Future Work

Chapter 3 demonstrated the impact of the grain boundary located n = 1 Ruddlesden-Popper (RP1) phase La₄LiMnO₈ on a Ta-doped LLZO solid electrolyte. Under an applied current the secondary phase exhibited electrochemical activity that resulted in a mixed 3+/4+ oxidation state of manganese. By correlating results from electrochemical and spectroscopic methods a hypothesis was proposed that Li is extracted from the La₄LiMnO₈ lattice during electrochemical operation, resulting in the observed change in manganese oxidation state.

This theory could be confirmed with the synthesis of phase pure La_4LiMnO_8 and subsequent electrochemical characterisation. Utilisation of a graphite $|La_4LiMnO_8$ cell with liquid electrolyte would confirm any reversible delithiation as well as any resulting phase changes. Whilst a Li-metal symmetrical cell (Li $|La_4LiMnO_8|Li$) may be used to study the CCD of the RP1 phase. Moreover, DC polarisation would enable a more accurate estimation of electronic conductivity in comparison to extrapolated results from previous studies.

An alternative approach may be taken with the use of conductive Atomic Force Microscopy (C-AFM). A conductive tip would be scanned in contact with the sample surface crossing grain boundaries as well as the location of the La₄LiMnO₈ phase. An applied voltage between the tip and the sample would generate a current and topographic image, identifying features on the surface that are conducting more or less current. A detailed spatial distribution could therefore be built of the composite solid electrolyte, identifying regions susceptible to higher current conduction. The observed 'dark' regions which alluded to an increase in electronic conductivity proved difficult to target with XAS. Due to the size as well as lack of visual guidance on beam positioning, a more comprehensive measurement could be provided by micro beam XAS. This would allow for an improved analysis of the oxidation state of the dark regions measured.

An additional theory proposed was that, as a consequence of increased current density, the secondary phase provided a nucleation site for Li-metal. This theory may be explored via cross sectional scanning transmission electron microscope (STEM) on a composite solid electrolyte prior to short circuiting. The use of STEM would negate the difficulty in detecting lithium from SEM or EDX and indicate whether a nucleation point was provided, or lithium dendrites formed exclusively from the interface. Furthermore, this study has the potential to further advance comprehension related to dendrite formation in phase pure cubic LLZO. If Li-metal nucleates at the secondary phase as a result of high current density, it may also nucleate at grain boundary triple points exhibiting elevated current density.

The RP1 phase appears to readily form in the presence of Mn, Co or Ni.[51, 220, 221] This presents a compelling concern for electrode compatibility with the LLZObased solid electrolyte separators, as most commercial cathodes are based around these elements. The likely diffusion of transition metals from cathode electrodes will result in the formation of La₄Li MO_8 (M = Mn, Co, Ni) leading to a loss in electrochemical performance and potentially negating the predicted high operational voltage window of ASSBs. Building on previous research that observed the diffusion of Co and the formation of La₄LiCoO₈ from a doped LLZO solid electrolyte separator with a LCO cathode, [51] further studies involving a Mn or Ni bearing cathodes could be conducted.

FEM analysis in Chapter 4 provides a simplified model of the solid electrolyte composite system. The presented geometry, a 9 \times 9 brick layer model, offered an intriguing insight into the electrodynamics of the LLZTO polycrystalline system with La₄LiMnO₈ located on the grain boundary. Further optimisation could however be conducted with an applied current. A modification of the applied current would further highlight the electrodynamics within the solid electrolyte composite and more accurately reflect experimental parameters during galvanostatic cycling. Additionally, to better represent a real system a more representative microstructural polycrystalline LLZTO system could be constructed. This may be achieved with open source software such as Dream.3D,[270] or an in-house (University of Sheffield) coded Voronoi tessellation. Furthermore, the scope could be expanded to include Limetal electrodes and integrate them into the overall model using Fick's law and the Butler-Volmer equations. The equations describe diffusion of Li⁺ ions and subsequent electrode reactions at the electrode-electrolyte interface further revealing electrodynamics of the system. All these options exist to expand and optimise the current model presented in this thesis, to further model a comprehensive FEM representation of a doped LLZO solid electrolyte with incorporated secondary phase.

The furthest commercial potential may be gained in the optimisation of the solid electrolyte tape casting process in Chapter 5. Initial efforts should focus on increasing the relative density by optimising the duration and temperature with the utilisation of Li₂O sintering aid. Densities exceeding ≥ 98 % have been achieved at 1100 °C for 6 hours as well as 1115 °C for 3 hours and would provide good initial parameters.[153, 271] However, careful characterisation would be required to confirm the retention of the desired cubic phase due to the long sintering time.

Furthermore, a more comprehensive study of sintering aids ranging from 1 % to 6 % would enable a controlled understanding of their optimal quantity in LLZTObased tapes. Moreover, investigating a wider array of sintering aids is recommended. Past studies showed the efficacy of MgO during the tape casting process, achieving a relative density of 91.1 % .[271] Li₃BO₃ (LBO) also increased the density and maintained the cubic phase without requiring covering mother powder.[272] However, removing the mother powder exposes the green tape to Al₂O₃ during high-temperature sintering, leading to aluminium impurities arising from a reaction between the doped LLZO and the Al₂O₃ setter plates.[127, 256] These unwanted reactions may be mitigated by the use of a pyrolytic graphite sheets, however an inert Ar atmosphere would be required to prevent oxidation of the graphite sheets.[271] It is clear that a large scope of future work exists to standardise the sintering of high density LLZO based ceramic films.

Additionally, addressing anisotropic shrinkage in the sintered solid electrolyte bilayer architecture requires attention. Establishing an intimately fused interface with robust mechanical strength to prevent delamination becomes crucial. A range of differing organic constituents such as polyethylene glycol may therefore be investigated to facilitate lubrication between the different layers during sintering. With sufficient mechanical strength and an intimately bonded interface, further electrochemical testing becomes viable. Successful fabrication of an MIEC bilayer architecture presents substantial opportunities for further exploration.

Fe-LLZO was selected for its potential MIEC properties as such measurements should therefore be conducted to elucidate any electronic conductivity arising reported Fe mixed oxidation state. In the case that MIEC is not proven in Fe-LLZO, a different doped LLZO solid electrolytes would have to be considered. Recent studies have presented a series of doped MIEC LLZO based solid electrolytes for trilayer film architectures. A substantial increase in electronic conductivity was demonstrated from $ca. 10^{-9}$ S cm⁻¹ for LLZTO to $ca. 10^{-4}$ to 10^{-5} S cm⁻¹ and attained current densities of 60 mA cm⁻² with cumulative lithium plating capacity of 18.5 Ah cm⁻².[162] The study demonstrates the requirement for an MIEC layer and presents the opportunity to investigate the change in electrodynamics for a phase pure sample compared to a

170

composite, as well as any subsequent changes at interfaces or grain boundaries. The ideas presented here are not an exhaustive list of possible further research. They however lay the groundwork for further exploration of composite solid electrolytes based on doped LLZO.

As the performance of single phase LLZO based solid electrolytes appears to plateau, incorporating secondary phases to tailor the electrodynamics of a system can offer the opportunity to further enhance the desired properties. The combination of different structures or phases into composites is likely to lead to a large unexplored range of material properties which are hard to predict. As such, changes may readily occur in the electrochemical, electrodynamical or mechanical response of the system; effecting change in extended cycle life, enhanced interfacial and rate compatibility, mechanical properties or improving dendrite resistance. Composites are already widely used in other areas of materials science and engineering and may provide a new direction of research for solid electrolyte materials; ultimately enabling effective ASSBs.

Appendix A

Chapter - 3

Table A.1: Collated results from Rietveld refinement of pre-SPS garnet samples $L_{1.4-x}Mn_xO_{12}$.

	Fit Statistics			La ₃	LLZTO		
Sample	R_{wp}	Chi ² (χ^2)	GOF	Wt Phase fraction	a = b (Å)	c (Å)	a = b = c (Å)
x = 0	8.15 %	7.21	2.68	-	-	-	12.9372 (3)
x = 0.035	8.86 %	14.75	3.84	1.99(7) %	5.404(1)	20.291(7)	12.9200 (1)
x = 0.05	9.33~%	9.68	3.11	2.57(8) %	5.4073(8)	20.294(4)	12.9222 (3)
x = 0.07	7.72 %	11.92	3.45	2.81(6) %	5.4043(5)	20.281(3)	12.9235(2)
x = 0.105	7.11 %	11.56	3.40	3.79(6)~%	5.4052(4)	20.274(2)	12.92886 (8)

Table A.2: Collated results from Rietveld refinement post-SPS garnet samples ${}^{Li_{6.4}La_3}Ta_{0.6}Zr_{1.4-x}Mn_xO_{12}$. Garnet lattice parameters do not follow linear substitution as expected by Vegard's law, thereby strongly indicating no manganese cation substitution within the lattice. Further supportive evidence is seen in the linear increase of the secondary phase La₄LiMnO₈.

	Fit Statistics		La ₄ LiMnO ₈			LLZTO	Pellet	
Sample	R_{wp}	Chi ² (χ^2)	GOF	Wt Phase fraction	a = b (Å)	c (Å)	a = b (Å)	density %
x = 0	5.77~%	2.27	1.51	-	-	-	12.9198(3)	99
x = 0.035	7.19~%	4.06	2.02	0.86(9) %	3.786(2)	12.95(1)	12.9226(1)	99
x = 0.05	10.93~%	17.75	4.21	1.175(4) %	3.785(1)	12.958(7)	12.9267(6)	98
x = 0.07	12.66~%	17.96	4.24	1.7(1) %	3.786(1)	12.947(6)	12.9252(4)	99
x = 0.105	11.62~%	3.69	1.92	2.7(2) %	3.7877(7)	12.95(3)	12.9293(1)	99



Figure A.1: DC polarisation experiment using (a) LLZTO and Mn-LLZTO (b) x = 0.035, (c) x = 0.07, (d) x = 0.105 with Au, Li⁺ blocking electrodes. Three potentials, 0.6, 0.9 and 1.2 V were applied across the cell for 24 hours for all but x = 0.105 which ran for 12 hours. Results from DC polarisation are displayed in Table 3.3.



Figure A.2: Equivalent circuit models for AC impedance with Li blocking electrodes.



Figure A.3: Equivalent circuit models for AC impedance with Li-metal electrodes.



Figure A.4: Collated results from CCD measurements for 'Li_{6.4}La₃Ta_{0.6}Zr_{1.4-x}Mn_xO₁₂' (x = 0.05, 0.07 0.105). Initial CCD appears to increase before decreasing at x = 0.105.

Appendix B

Chapter - 5



Figure B.1: Powder X-ray diffraction pattern highlighting the contained impurities of final synthesised $\text{Li}_{6.4}\text{Fe}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$. Following 52 hours heating, cubic stabilised Fe-LLZO held several impurities following synthesis, these included: $\text{Li}_8\text{La}_{18}\text{Fe}_5\text{O}_{39}$ (\blacklozenge), Li_2ZrO_3 (\clubsuit), pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ (\bigstar), and tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_7$ (\bigstar).



Figure B.2: Early iteration of LLZTO tape casting failure. The green tape is seen to have cracked during and displays no flexibility or malleability. In addition to this a rough surface texture may be seen. This indicates poor particle dispersion during slurry formation.



Figure B.3: Early iteration of LLZTO tape casting failure. The green tape displays an inhomogeneous consistency and thickness. Uncoated regions of mylar may be seen displaying air pockets within the formed slurry.



Figure B.4: 18 mm dia. LLZTO green tape failure. The green tape displays an inhomogenous consistency. Furthermore, pitting from bubble formation during slurry formation and casting may be seen.



Figure B.5: Sintering failure of LLZTO tape. The tape displayed complete loss of structural strength following sintering. Pitting from bubble formation during sintering are observed on the surface. Furthermore, a rough surface displays inhomogeneous particle distribution during slurry formation.

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