

2020

Interfacial Strategies for Improved Solid- State Lithium Batteries

Doctoral Dissertation

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DEPARTMENT OF MATERIALS

This thesis is dedicated to David Kelly, whose unparalleled mentorship and genuine love of chemistry inspired me to realise my dream of going to Oxford and doing a DPhil. I will be forever grateful for our chats about science. Teachers with your level of dedication are rare indeed. Furthermore, your advice about my home chemistry experiments over the years probably saved me from accidentally blowing up my parents' shed.

Acknowledgments

Professional

I would like to thank Prof. Peter Bruce for his mentorship, and the invaluable scientific discussions we have had over the past few years. The opportunity to work so closely with such a world leader during my DPhil has been a real privilege and I will be eternally grateful for having had this experience. I am extremely appreciative of Dyson and the EPSRC for funding my research activities, without this funding my DPhil would have been impossible. In the same spirit, I would like to thank The Faraday Institution and The Henry Royce Institute for providing much of the equipment used.

I would like to thank Dr. Paul Adamson, Dr. Robert House and Dr. Gregory Rees for their advice on writing this thesis and I would like to pay extra special tribute to Dominic Spencer Jolly and Ziyang Ning; our deliberations have been extremely fruitful and have really helped advance my understanding of solid-state batteries. Many of the ideas in this work were also greatly advanced by conversations with Dr. Mathew Roberts, Dr. Lee Johnson, Dr. Benjamin Bergner, Dr. Liyu Jin and Dr. Xiangwen Gao. For their assistance with experiments, thanks is also given to Dr. Jennifer Holt (SEM), Dr. Sarah Fearn (ToF-SIMS), Dr. Phil Holdway (XPS), Chen Gong (TEM), Dr. Jingyuan Liu (SEM), Dr. Xiangwen Gao (electrochemical), Dr. Gregory Reese (NMR), Dr. Liyu Jin (NMR), Dr. Subhradip Paul (DNP-NMR), the CCIAS service at University of Sheffield, and Konstantinos Dimogiannis (QCM).

I would also like to thank the following colleagues for their help, advice and friendship during this work: Dr. Nadia Abdul-Karim, Dr. Robert House, Dr. Conrad Holc, Sam Wheeler, Dominic Forstermann, Dr. Stefanie Zekoll, Alexander Pateman, John-Joseph Marie, Shengda Pu, Chen Gong, Dr. Rong Hao, Dr. Boyang Liu, Dr. Christian Kuss, Dr. Francis Kinyanjui, Dr. Andy Naylor, Dr. Urmimala Maitra, Dr. Zhaoxin Yu, Dr. Jitti Kasemchainan, Dr. Felix Richter, Dr. Adam Sobkowiak, Dr. James Summerville, Dr. Sunyihik Ahn, Dr. Miguel Angel Perez, Dr. Sixie Yang, Dr. Xiaoyu Xu, Dr. Jili Yue, Dr. Edouard Boivin, Dr. Juan Lozano, Dr. Niccolo Guerrini, Dr. Kun Luo, Dr. Da Wang, Dr. Ryan Bayliss, Dr. Yajun Cheng, Issac Capone, Ceren Zor, Max Jenkins, Dominic Melvin, Varnika Agarwal, Miki Bennett, Dr. Erez Cohen, Zsafia

Lazaar, Dr. Hyeon Jeong Lee, Zachary Brown, Albert Xiao, Jack Fawdon, Christopher Doerrler and Kevin Hurlbutt.

Personal

To my parents, Andrea and Glyn, thank you for everything. Words fail to express how lucky and proud I am to be your son. Without your unwavering love and support at every stage of my life, and all the sacrifices you made for me along the way, I know I would not have gotten to where I am.

To my Grandad Clifford, thank you for supporting my education and always taking an interest in what I was working on. Who would have thought that my tinkering with scraps of wood in the garage, trying to emulate you, would eventually lead to me working on cutting edge batteries? To my Grandmas, Mary and Denise, thank you for your love, support, and always being just a phone call away.

I love you all.

Abstract of thesis

This project aims to help facilitate the step change in battery energy density (per volume) needed for improved consumer electronics and greatly increased electric vehicle adoption. The work in this thesis is focussed on enabling a lithium metal electrode to be successfully employed in a rechargeable battery as a negative electrode by using a protecting solid electrolyte.

In **Chapter 4**, the viability of using a solid-electrolyte (Li_3N) to protect a lithium metal anode is explored and the phenomena that occur at this metal/ceramic interface during the passage of current are determined.

Chapter 5 explores a novel strategy of using a solid-electrolyte (Li_3N) as a separator in a solid-electrolyte/liquid-electrolyte hybrid battery. By using liquid electrolyte, the cathodic instability of Li_3N , as well as the volume expansion issues of cathodes with solid-electrolytes and the self-discharge problems associated with Li_3N should theoretically be eliminated. The universality of solid-electrolyte/liquid-electrolyte interfacial phenomena are also examined by investigating an alternative solid-electrolyte (LLZTO) with a state of the art liquid-electrolyte used in commercial Li^+ ion batteries (LP30).

Chapter 6 explores the chemistry of $\text{Li}_3\text{N}\cdot\text{P}_2\text{S}_5$ solid-electrolytes, as it is speculated that the electrochemical reduction of a nitrogenous electrolyte would form an SEI rich in Li_3N , and would therefore produce self-healing and low resistance SEIs in contact with Li.

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List of abbreviations

EV	Electric vehicle
ICE	Internal combustion engine
SHE	Standard hydrogen electrode
DC	Direct current
AC	Alternating current
NiCd	Nickel cadmium battery
NiMH	Nickel metal hydride battery
NiH	Nickel hydride battery
NiZn	Nickel zinc battery
NiFe	Nickel iron battery
LIB	Lithium ion battery
LE	Liquid electrolyte
SE	Solid electrolyte
SEI	Solid electrolyte interphase
CEI	Cathode electrolyte interphase
LCO	Lithium cobalt oxide
LTO	Lithium titanate
NCA	Lithium nickel cobalt aluminium oxide
NMC	Lithium nickel manganese cobalt oxide
LFP	Lithium iron phosphate
LMO	Lithium manganese oxide
ASSB	All solid state battery
CV	Cyclic voltammetry
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital
MIECs	Mixed ionic electronic conductors
LiPON	Lithium phosphorus oxynitride
LGPS	Lithium germanium thiophosphate
LAGP	Lithium aluminium phosphate
LATP	Lithium aluminium titanium phosphate
LPS	Lithium thiophosphate
LISICON	Lithium super ionic conductor
NASICON	Sodium super ionic conductor
Gc	Gas chromatography
NMR	Nuclear magnetic resonance
MAS	Magic angle spinning
DNP	Dynamic nuclear polarisation
RF	Radio frequency
XRD	X-ray diffraction
PXRD	Powder X-ray diffraction
EDX	Energy dispersive X-ray diffraction
SEM	Scanning electron diffraction
XPS	X-ray photoelectron spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
EIS	Electrochemical impedance spectroscopy
EI-MS	Electron ionisation-mass spectrometry

FTIR	Fourier transform infrared spectroscopy
TOF-SIMS	Time of flight-secondary ion mass spectroscopy
GIXD	Grazing incidence X-ray diffraction
TEM	Transmission electron microscopy
X-CT	Contrast X-ray tomography
CCP	Critical current on plating
CCS	Critical current on stripping
BASE	Beta alumina solid electrolyte
DEMS	Differential electrochemical mass spectroscopy
PTFE	Polytetrafluoroethylene
SLEI	Solid liquid electrolyte interphase
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
EC	Ethylene carbonate
DMC	Dimethyl carbonate
DMSO	Dimethylsulfoxide
TEGDME	Tetraethylene glycol dimethyl ether
UV-VIS	Ultraviolet-visible spectroscopy
QCM	Quartz crystal microbalance
HETCOR	Heteronuclear correlation spectroscopy
TCE	Trichloroethylene
LiDMSI	Lithium-cyclo-difluoromethane-1,1-bis(sulfonyl)imide
LPSN	Lithium nitridothiophosphate
RPM	Revolutions per minute

Chapter 1: Introduction to batteries

1.1 Background

If humankind is to minimise anthropogenic climate change by reducing its greenhouse gas emissions, then the automotive industry will inevitably have to move away from the combustion of gasoline. A hydrogen economy, utilising hydrogen fuel cell cars is frequently posited as a likely future;^{1,2} however, it has yet to show real mass market viability for personal vehicular applications due to hydrogen production and storage challenges. As such, a complementary technology is needed. Electric vehicles (EVs) are attractive replacements for internal combustion engine cars (ICEs) as they can be powered with renewably derived energy. EVs are not only currently commercially available but they are rapidly becoming cheaper and more attractive to consumers than traditional ICEs. Additionally, electric motors are more efficient and suffer from lag less than ICEs; this enables quicker acceleration. However, market penetration has been limited by range, battery lifetime, charging rates and prohibitively expensive purchase costs. The EV market is now the main force driving the development of new batteries. For EV applications, batteries with higher specific power and charge / discharge rates will enable faster charging and greater acceleration. Three-phase charging stations can be used to charge these batteries in as little as 20 min but on-board cooling systems are required to protect the battery packs and this adds to the overall weight of the vehicle and therefore decreases overall range.³ For large scale EV adoption, a more extensive and standardised charging station infrastructure will be required. Lithium ion batteries are currently ubiquitous in EVs. Batteries with higher specific energy are needed to increase the distance travelled before recharging is required.⁴ The specific energy of commercial lithium ion batteries is currently about 1% that of gasoline. Since EVs have considerably fewer moving parts than ICEs, more space in the vehicle can be occupied by batteries than would normally be dedicated to a fuel tank. However, even with large optimised battery packs, the range of current EVs is limited to 200-300 miles (322-483 km).⁵ The range of EVs is continually increasing as lithium ion technology is refined. Increasing the cycle stability of batteries is imperative. For EVs to compete in all countries against ICEs, batteries will be required to operate in deserts and winter tundra's, with minimal degradation. Several

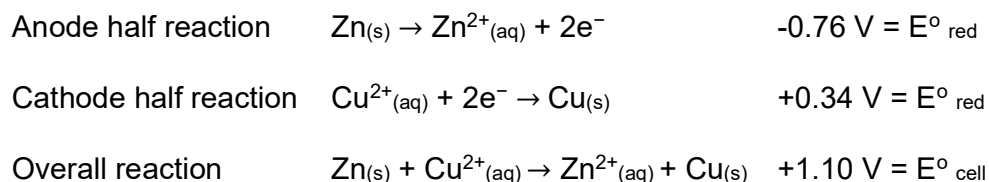
strategies exist to minimise the impact of battery degradation on the consumer. For example, some manufacturers have extended the overall lifetime of an EV battery pack to 10 years by adding an excess of batteries to a car as the extra capacity offsets long-term capacity fading. However, this adds weight, which reduces performance and adds to overall costs. Other companies have begun replacing batteries every 5 to 7 years. Replacing the battery packs is extremely expensive; therefore, batteries that can be cheaply recycled are desirable. Some manufacturers retain ownership of the battery and charge a monthly fee, e.g. Renault Zoe, this reduces consumer concern about degradation but also gives manufacturer a supply of Ni/Co in the future (when recycling will be possible).⁶ To summarise future batteries for EVs will require:

1. Improved safety.
2. Improved lifetime.
3. Higher specific energies.
4. Higher specific powers.
5. Greater Columbic efficiency.
6. Reduced manufacturing and recycling costs.
7. Widely available raw materials that can be extracted and modified by environmentally friendly methods.
8. Decreased raw material costs.

1.2 What is a battery?

Batteries are electrochemical energy storage devices that have been a common part of everyday life since the development of the first Daniell cells in the 1800s.⁷ Despite the vast array of battery designs that now exist, all batteries are in-series or in-parallel voltaic piles of electrochemical cells. The terms electrochemical cell and battery are now used interchangeably in the literature. Individual electrochemical cells have three indispensable components: a 'positive' electrode, an electrolyte and a 'negative' electrode.⁸ Electrolytes are electronic insulators, which electrically isolate half-cells and prevent self-discharging, whilst allowing ionic conduction. Isolated half-cells are thermodynamically stable. Dynamic equilibrium between the electrolyte and electrode occurs virtually instantaneously. For example; when a Zn electrode is suspended in a

$\text{ZnSO}_{4(\text{aq})}$ electrolyte solution, under equilibrium, both the oxidation half-reaction ($\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^-$) and the reduction half-reaction ($\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Zn}_{(\text{s})}$), take place at the same rate. Different electrode materials differ in reactivity and electrochemical potential. In reality, the potentials depend on a number of environmental conditions such as the ease of ion solvation.⁹ For convenience, the potentials of electrodes are defined relative to a standard half-reaction redox potential. Typically, the standard hydrogen electrode (SHE) is used. The standard cell potential between two half-cells can then be approximated from the standard cell potentials of the respective half reactions using $E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$. For example, the half reactions of the Daniel cell are:



Positive cell potentials are thermodynamically favourable and occur spontaneously under a closed circuit. These are termed Galvanic or Voltaic cells. On the other hand, reactions with negative potentials are termed electrolytic cells. Electrolytic reactions are thermodynamically unfavourable and require the application of electrical energy to occur.

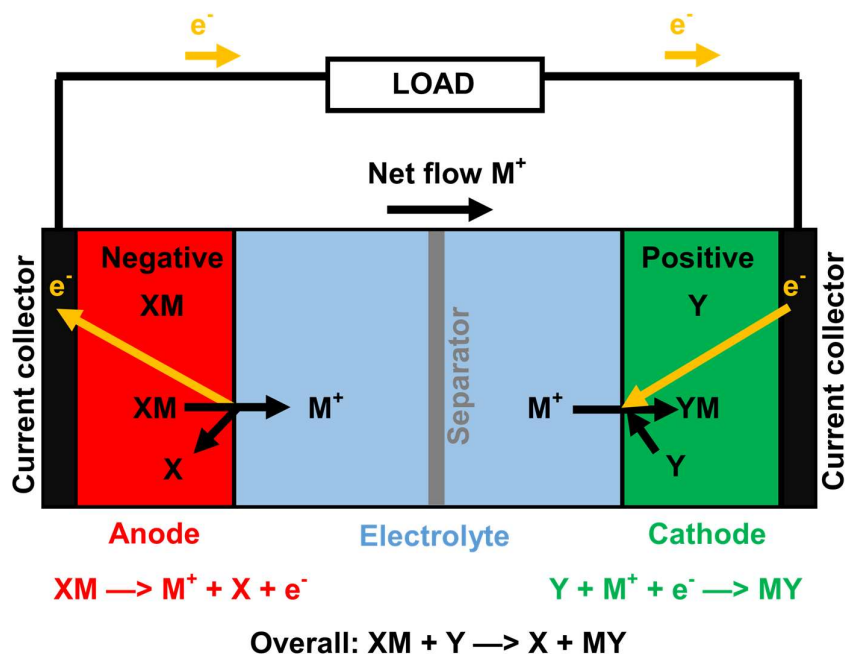
The reduction potential of an electrochemical cell also depends on environmental factors and can be evaluated using the Nernst equation:⁶

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{\alpha_{\text{red}}}{\alpha_{\text{ox}}} \right) \quad (1.1)$$

Where E is the cell potential (V) at the specified temperature, E° is the standard cell potential (V) at 298 K, R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature of operation (K), n is the stoichiometric number of moles of electrons

transferred in the reaction, F is Faraday's constant (96485 C mol^{-1}), α_{red} is the activity of the reduced species (dimensionless) and α_{ox} is the activity of the oxidised species.

By coupling these electrodes through an external electrical circuit, the redox reactions between the electrodes can be controlled and can be exploited to produce a direct electrical current (DC), which can be used to do work, [Figure 1.1](#). To retain charge neutrality, this process is necessarily accompanied by an equal ionic current through the electrolyte.



[Figure 1.1](#). A diagram of an electrochemical cell during discharge.

In practical cells, electrically insulating materials called separators, typically made of fibreglass or polymer which are permeable to electrolyte, are placed between the electrodes to enable the cell to be compacted without short-circuiting, [Figure 1.1](#).

The salts in the electrolytes of the respective half-cells can be the same or they can be different. However, where different electrolytes are used, a salt bridge must be employed to prevent charge accumulation, [Figure 1.2](#). Salt bridges contain salts that are compatible with both half-cells.

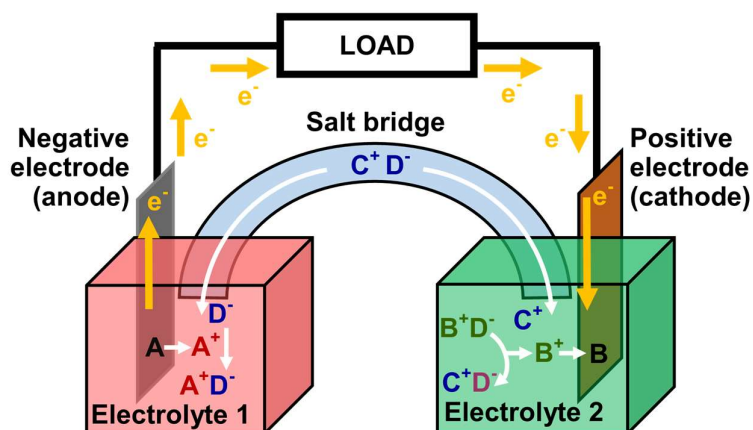
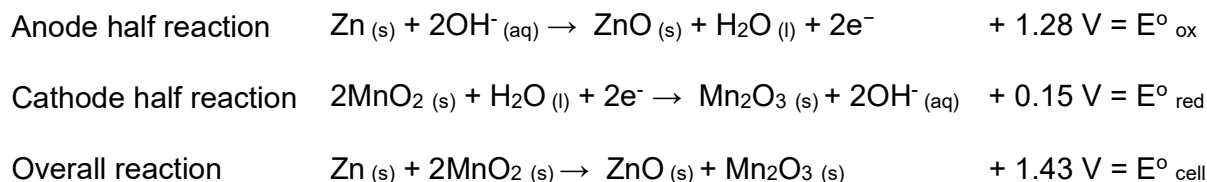


Figure 1.2. A diagram of a traditional discharging primary cell employing a salt bridge. A is the anode material, B is the cathode material, C^+D^- is the salt bridge electrolyte, e^- are electrons.

1.3 Primary cells / disposable batteries

Primary cells are disposable batteries; they can only be discharged once and are not rechargeable since the electrochemical reactions that occur are irreversible. The most widely used primary batteries are alkaline and zinc-carbon. In alkaline batteries, a zinc anode is typically discharged against a MnO_2 cathode in an aqueous alkaline electrolyte ($KOH_{(aq)}$) accordingly:¹⁰

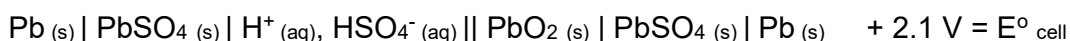


Primary cells have high energy densities; they are resistant to self-discharging and have long shelf lives. Primary batteries are able to produce low currents for extended periods. As such, these batteries commonly find applications in devices like smoke detectors, watches and hearing aids. Silver-oxide batteries have particularly high gravimetric energy densities. Analogous silver-zinc cells have exceptional specific energies.¹¹

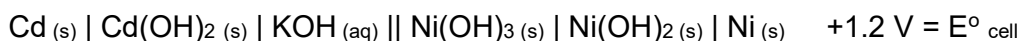
Primary cells often have low initial costs; as a result, they are common in single use devices. The rapid proliferation of consumer electronics over the past three decades has caused the global battery market to grow rapidly. However, disposables have begun losing their market share to rechargeable batteries because modern electronics are highly energy demanding. Frequently replacing primary batteries is less convenient, more expensive and less environmentally friendly than using rechargeables.

1.4 Secondary cells / rechargeable batteries

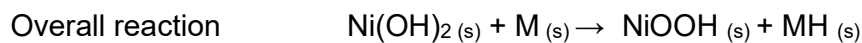
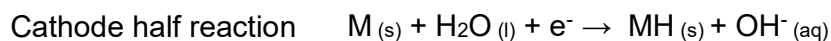
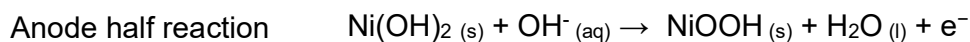
Unlike primary batteries, secondary cells can be recharged through the application of a potential bias. Applying a large reversed potential difference across a discharged cell, forces electrons to flow back from the positive electrode to the negative electrode and also stimulates an equivalent ion current flow through the electrolyte. In secondary batteries, the electrodes are renewed sufficiently for the cell to cycle many times with minimal capacity loss.¹² The lead-acid battery (Pb-acid), invented in 1860 by Gaston Planté, was the first conversion battery that could be cycled.¹³ Pb-acid batteries have been incredibly commercially successful. This success is owed to their high specific power, good cyclability and low cost. Lead acid batteries are still used as starting batteries for automobile combustion engines. Pb-acid batteries are typically in-series piles of cells with the discharge configuration:



A metallic lead anode and a lead dioxide cathode are suspended in an aqueous sulphuric acid electrolyte. During discharging, oxidation of $\text{Pb}_{(s)}$ to $\text{Pb}^{2+}\text{SO}_4^{2-}_{(aq)}$ occurs at the anode and reduction of PbO_2 to $\text{Pb}^{2+}\text{SO}_4^{2-}_{(aq)}$ takes place at the cathode. Consequently, protons are produced at the anode and are consumed at the cathode during the process. During charging, the reverse process happens. However, Pb-acid batteries are unavoidably bulky and have poor energy densities. The first rechargeable batteries small enough for use in hand held devices were nickel cadmium batteries (NiCd). These operated using the following discharge chemistry:⁶



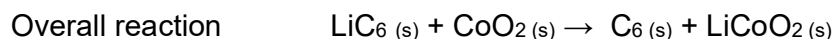
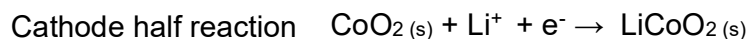
Although the cell voltage is low, NiCd batteries can be charged very quickly with minimal localized heating. Lessened heating effects, minimise volume changes and stresses. NiCd batteries suffer from the memory effect, in which the maximum capacity of the battery degrades over time. Despite considerable early commercial success, NiCd technology was eventually displaced by the nickel metal hydride battery (NiMH, where M is a given metal). The market transition occurred because of recyclability and capacity considerations and because the memory effect was slightly less of a concern. The following redox chemistry occurs in NiMH batteries during discharge:



Overcharging and short-circuiting are phenomena that affect all secondary batteries.¹⁴ These effects are dangerous and can lead to explosions. However, these effects in NiMH batteries tend to have relatively benign outcomes. NiMH cells have poor coulombic efficiencies, high self-discharge rates and low specific power. A large number of other secondary batteries are known, including: nickel-hydrogen (NiH), nickel-zinc (NiZn) and nickel-iron (NiFe) but most of these battery types have now been supplanted by lithium ion technology.

1.5 Lithium ion batteries

In the 1970s, Armand proposed a new type of cell called a rocking chair battery.¹⁵ If two electrodes, that can reversibly intercalate a particular type of mobile ion (at different potentials), are electrically isolated by an electrolyte, then they theoretically produce a secondary battery. The mobile ions are typically lithium or sodium but many different cations and anions are facile enough to be feasible. Organic carbonate or ether solvents are typically used as the liquid electrolyte (LE).¹⁶ During discharge, the anode is oxidized and mobile ions are deintercalated with the release of electrons. As with a primary battery, the mobile ions shuttle through the electrolyte and the electrons travel through an external circuit to the cathode. Reduction of the cathode is accompanied by intercalation. During charging, the reverse process ensues. Lazzari and Scrosati validated the feasibility of the rocking chair strategy by demonstrating the cyclability of lithium intercalation between tungsten dioxide and titanium disulfide electrodes.¹⁷ However, early rocking cells had limited voltage ranges. It was not until John Goodenough at Oxford did discover a class of high potential transition metal oxide intercalation cathodes in the early 1980s that rocking chair batteries showed viability for commercialization.¹⁸ Goodenough's team presented a class of intercalation compounds with the general formula LiMO_2 , (where $\text{M} = \text{Mn}, \text{Al}, \text{Fe}$ and most notably Co). Since these cathodes already contained mobile lithium, a lithium metal free battery was possible, which improved safety and made manufacturing significantly easier.¹⁹ This discovery, in conjunction with the development of solvent resistant specialty carbonaceous intercalation anodes by Yoshino,²⁰ Fong,²¹ Von Sacken, Dahn and countless others laid the foundations for the lithium ion battery,¹⁵ [Figure 1.2](#).



The storage capacity of lithium ion batteries is determined by the crystal structures of the active electrode materials, the reversibility of intercalation as well as the ability of

the host to change valence state.²² The operating voltage range for (LiC₆ | LiCoO₂) is typically between 3.0 and 4.2 V, limiting the voltage window prevents structural changes irreversibly effect cycle life.²³

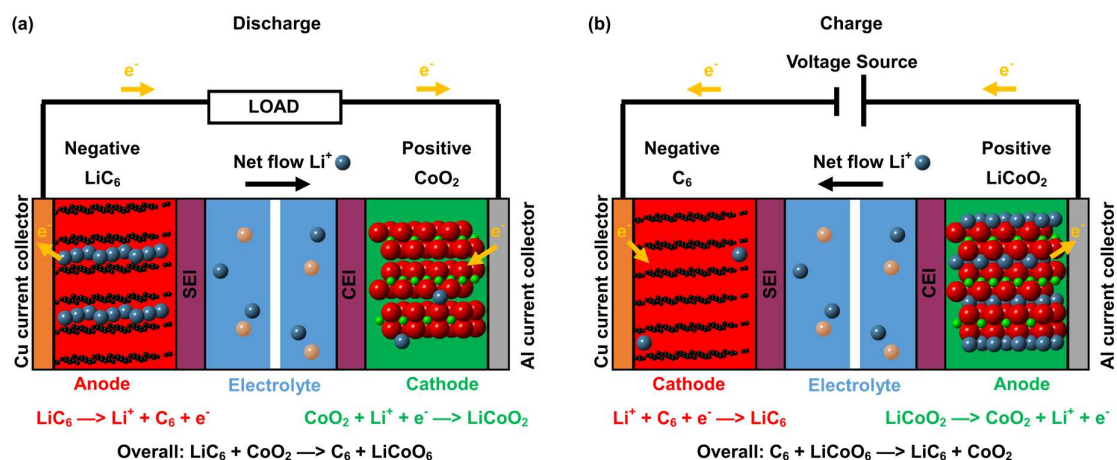


Figure 1.3. Schematics of a lithium ion battery composed of a graphite intercalation anode and a LCO intercalation cathode. (a) Shows discharging, (b) shows charging. Blue ions are lithium, brown ions are electrolyte counter ions, oxide ions are red, cobalt ions are green and carbon atoms are black. The white strip in the electrolyte represents a separator (designed to prevent short circuits). The purple regions represent interphases (SEIs and CEIs) that grow at the electrode/electrolyte interfaces with their thicknesses drawn greatly oversized).

Since their commercial launch by Sony in 1991, rechargeable lithium ion batteries have become commonplace in everything from portable electronics to medical devices. In fact, there is a very good chance you have several on your person at this very moment. However, despite already supplanting many other battery technologies and playing a huge part in our daily lives, Li ion batteries have yet to realise their full potential, in terms of both capabilities and applications. Over the past 25 years, the energy density of lithium ion batteries has been steadily increased and many electrode intercalation materials are now known.²⁴ It is important to note that different electrode materials are chosen for commercial batteries according to the specific uses of the product. For example, lithium titanate (LTO) is an effective intercalation anode for fast charging batteries. Crystalline silicon has also attracted interest as a potential high specific capacity anode material (theoretical value $\sim 4200 \text{ mAh g}^{-1}$). However, silicon anodes suffer from huge volume changes during cycling. Common cathodes include

lithium cobalt oxide (LCO), lithium-nickel-cobalt-aluminium (NCA), lithium-nickel-manganese-cobalt (NMC) and lithium-manganese spinel (LMO), corresponding advantages and disadvantages are shown in Figure 1.4. The most commonly used cathode material in lithium ion batteries for consumer electronics is lithium cobalt oxide (LCO) because LCO has excellent capacity retention. However, LCO contains high cobalt content and is expensive when ethical supply chains are used. NMC/NCA have a good balance of properties for electric vehicle applications. However, short-circuiting caused by battery destruction in a crash can trigger catastrophic electrolyte degradation, thermal runaway and battery fires for all organic LE based cells. Lithium ion batteries will ultimately reach a limit in terms of energy density.²⁵ As such, ‘beyond lithium ion’ battery technologies, lithium-rich cathodes,²⁶ lithium-air and lithium-sulfur will be required for large increases in energy density.²⁷

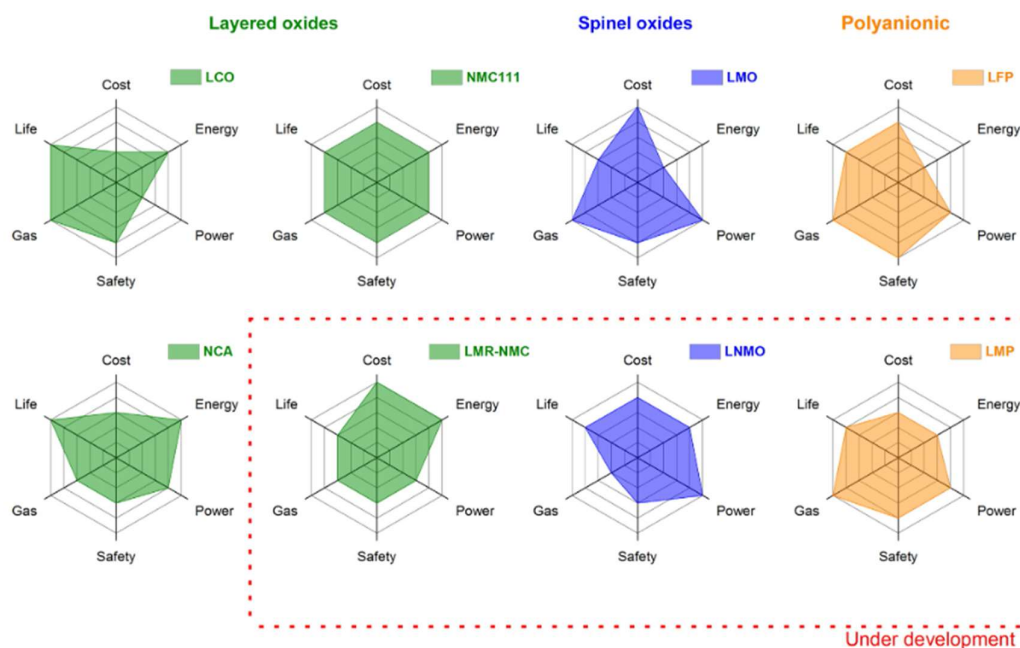


Figure 1.4. The present trade-offs of the different lithium-ion battery technologies. Figure reprinted from ref ²²². (<https://doi.org/10.1016/B978-0-08-102726-4.00010-7>)

1.6 Liquid electrolyte based lithium metal batteries

The maximum gravimetric capacity of graphite is only 372 mA h g^{-1} and the volumetric capacity is 330 mA h cm^{-3} .^{28–30} On the other hand, lithium metal possesses the highest

energy density possible, i.e., 3860 mA h g^{-1} / $2760 \text{ mA h cm}^{-3}$,³⁰ since lithium is the lightest metal and has an electropositivity of -3.04 vs. SHE.³¹ Furthermore, the use of a metallic anode eliminates “dead weight” because binders and conducting agents necessary for carbonaceous anodes are not required. Commercial primary lithium metal batteries have been around from the 1960s and are commonly used in many applications that require very long-battery life such as pacemakers. Secondary batteries, employing a lithium electrode including: Li-S, Li-O₂ and lithium ion cells employing high voltage lithium rich cathodes, should offer significantly higher energy density than lithium ion cells.²⁷ However, the replacement of carbonaceous intercalation anodes in secondary batteries with lithium metal has proven challenging and there are several key factors that have prevented large scale commercialisation, namely capacity fading and safety concerns due to a dendritic short-circuiting phenomenon, described hereafter in **Sections 1.7 & 1.8**.

1.7 Solid electrolyte interphases (SEIs) in lithium ion and lithium metal cells

Almost all LEs are electrochemically unstable at the low potential of charged anodes, therefore LEs commonly undergo reduction at the anode interface to form solid reaction products which remain adsorbed onto the electrode surface forming a solid electrolyte interphase (SEI),³² [Figure 1.5 \(a\)](#). SEIs have high electrical resistivity thus as the thickness of an SEI increases, electron transfer across the interface between the anode and the LE becomes increasingly hindered, which prevents the electrons from the anode from reducing the LE in a continuous manner; SEI growth consequently self-terminates.³³ SEIs passivate the surface of electrodes and protect the LE from degradation, which has proven to be highly beneficial for carbonaceous electrodes. Although it is worth noting that SEIs are relatively poor ionic conductors and act as a source of internal resistance, which reduces power density of the cell.³² Unlike carbonaceous anodes, the dynamics of lithium ion exchange across the lithium metal / LE interface result in SEI instability.³³ Metal electrodes undergo significant changes in volume during cycling, [Figure 1.5 \(b\)](#), because 100 % of the volume of the metal atoms is directly added to the surface electrode on charge and is removed on discharge; whereas the volume changes to the negative electrode are relatively small for intercalation compounds because intercalation / deintercalation only causes slight

perturbations to volume (~10 % during charge) of the graphitic lattice^{34,35} If lithium metal is used as the negative electrode, when the cell is charged, lithium is plated from the LE to the electrode from beneath the SEI.³¹ This strains the SEI and unless the SEI is extremely flexible, it will consequently fracture and exposes bare lithium to additional LE, [Figure 1.5 \(c\)](#).³⁶ Consequently, additional SEI can be formed. However, heterogeneity at the interface allows lithium to plate above the SEI, in direct contact with LE [Figure 1.5 \(d\)](#). The exposed surfaces of the freshly plated lithium cause further LE reduction. On stripping, these surface lithium filaments can become detached from the surface as 'dead SEI', therefore metal anode LE cells often suffer from significant capacity fading and poor columbic efficiency.³⁷ Excess lithium is required which reduces overall cell energy density³¹. As such, lithium metal batteries require LEs that react to form flexible, thin and relatively homogeneous SEIs for cycling stability. Although, ether based electrolytes have shown some promise, these systems have not been employed in commercial batteries,³³ in part because of safety concerns due to the extreme flammability of the LE and also due to the formation of dendrites as hereafter described.³⁸ A great deal of effort has been placed on the development of LE additives, with the purpose of aiding in the recovery of lithium from dead SEI in the LE but success in this endeavour has so far been limited.

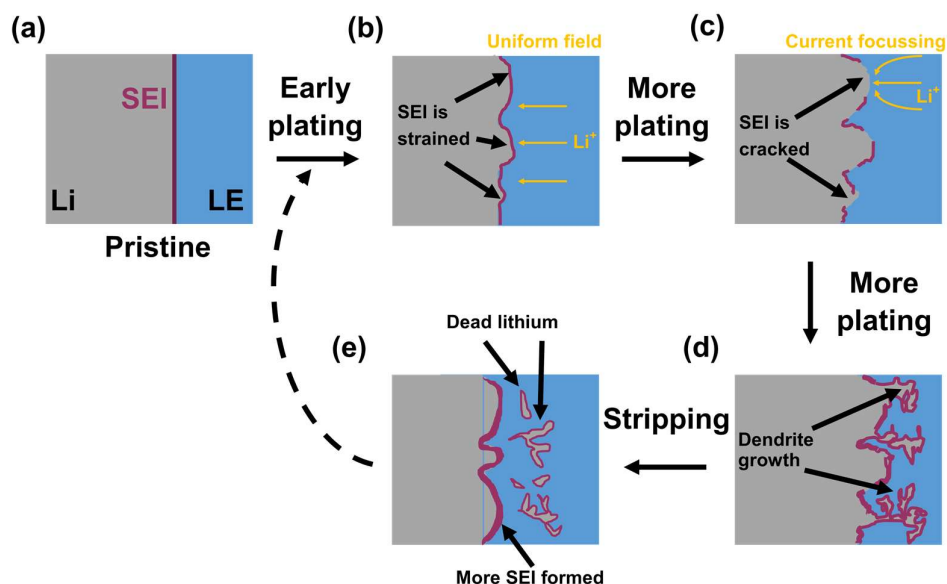
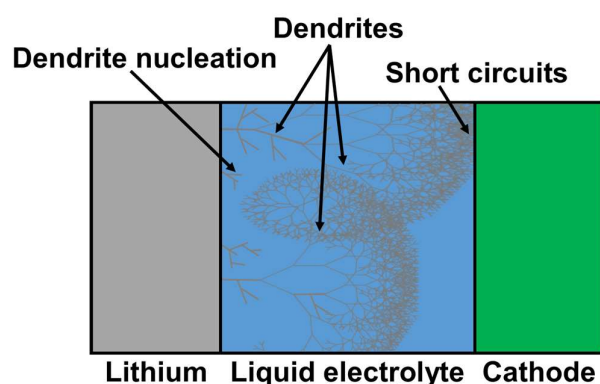


Figure 1.5. Schematic of SEI formation at a Li / LE interface and the SEI fracturing that occurs during cycling, outlining a mechanism of capacity fading. Grey indicates lithium metal, blue indicates LE and burgundy indicates SEI. (a) Pristine cell before cycling shows an SEI at the Li / LE interface. During charge, (b) lithium is plated beneath the SEI, the volume change puts considerable strain on the SEI and leads to (b) fracturing of the SEI which exposes bare Li to more LE. (c) This results in additional SEI formation and consumes lithium, causing capacity fading but also causes current focussing and plating of lithium above the SEI, leading to the formation of (d) dendrites as outlined in **Section 1.2.7**. (e) On stripping, lithium dendrites become detached from the electrode which leads to the capacity fading of the cell.

1.8 Dendritic short-circuit failure in LE cells

The greatest impediment to the development of commercial lithium metal batteries, is a catastrophic short-circuit type failure mechanism, in which fractal like lithium metal filaments, called dendrites, grow from the negative electrode towards the positive electrode during cell charging,³⁹ [Figure 1.5 \(d\)](#). Not only do dendrites cause capacity fading but they are able to perforate separators and cause electrical contact between the electrodes, which enables a rapid internal discharge to occur which can cause catastrophic thermal runaway and the ignition of the flammable LE, [Figure 1.6](#).⁴⁰



[Figure 1.6](#). Illustration of dendrite growth in the electrolyte leading to a short circuit. The branched lines in the electrolyte represent Li dendrites.

Before the passage of current, the cations and anions of the conduction salt are uniformly distributed through the LE. However, during charge, cations (Li^+) are consumed (plated as lithium metal) at the negative electrode surface and overall charge neutrality of the LE is maintained by a supply of cations from the positive electrode, which produces a cation concentration gradient across the LE. When the current density is low, and is greatly exceeded by the rate at which cations move in the LE, then cations are able to deposit uniformly across the electrode surface. However, above a critical current density, the cations cannot be supplied fast enough to the interface to compensate for the rate of deposition, this leads to localised depletions of cations in the LE at the electrode interface and a localized space charge.³³ As such, lithium becomes deposited at localized spots on the electrode surface, where the local concentration of cations remains high. The lithium electrode

surface changes from being flat to having small protuberances. This is the nucleation of the dendrite. The electric field is no longer uniform and the Li^+ flux becomes focused towards the tips of the dendrites, [Figure 1.5 \(c\)](#). As such, dendrites grow longer and current focusing increases in a positive feedback loop.³¹ The deposition occurs along the respective crystallographic lattice planes of the metal, such that dendrites grow out from the interface into the LE in fractal like patterns that adopt snowflake-like, tree-like, moss-like or brush-like morphologies, depending on the specific metal being plated.³¹ Electrochemical plating of many metals (Zn, Ni, Cu, Ag, Sn, Ca amongst others),^{33,41} at high current densities, has long been known to result in these inhomogeneous deposits at the electrode surface. This has not been overly problematic for the electrochemical plating industry because plating is typically only performed once therefore when optimized conditions are used, dendrite growth is fairly minimal. However, when metal anodes are employed in rechargeable batteries, the negative electrode is plated and stripped many times and under high relative current densities long dendrites can accumulate rapidly. The SEI fracturing mechanism examined in [Figure 1.5](#), acts to exacerbate the protrusion of lithium metal from the anode into the electrolyte, which leads to current focusing in the LE, therefore dendrites are common even at relatively low current densities. Additionally, during discharge, lithium stripping occurs which causes small shards of lithium dendrites to become electrically and physically isolated from the electrode in the LE. Over time this leads to a build-up of dead lithium in the electrolyte and capacity fading.³³ A number of strategies have been employed to lessen dendrite formation. For example, salt depletion and subsequent dendrite nucleation can be somewhat suppressed by high salt concentrations.³⁸ Additives such as LiNO_3 can make SEIs more uniform and therefore can blunt the tips of dendrite.³⁸ Furthermore, it is suggested that redox shuttles could enable the recovery of dead lithium.³⁸ Stable hosts (graphene oxide) can be used to reduce volume changes and minimize SEI fracturing. Coating the Li anode with artificial SEIs or polymer films can provide a mechanical barrier to dendrite nucleation.⁴² In reality, these strategies have proven inadequate for suppressing dendrites at high current densities and commercial lithium metal batteries so far remain elusive. However, as explained in **Chapter 2**, recent developments in the field of solid electrolytes, may enable the use of lithium metal as an anode.

Chapter 2: Inorganic solid electrolytes

2.1 Why solid electrolytes?

Like their liquid electrolyte (LE) counterparts, inorganic solid electrolytes (SEs) are materials with high ionic conductivity and high electrical resistivity that can be used to separate electrodes, [Figure 2.1](#). SEs are known for many mobile ions including F^- , O^{2-} , H^+ , K^+ , Na^+ , Cu^+ , Pb^+ , Ag^+ and Li^+ .⁴³ Although silver and copper SEs have notably high conductivities ($10^{-2} \text{ S cm}^{-1}$), Li^+ and Na^+ ion conductors are chiefly of interest for commercial battery applications. There are many purported advantages of SEs over LEs. It is frequently asserted that SEs have large electrochemical stability windows, high temperature stability and low flammability.⁴⁴ Such properties could enable safer more compact lithium metal batteries to be realised. Moreover, after long term cycling at high voltages, LE based Li^+ batteries often undergo catastrophic degradation because oxidation products that form at the LE / cathode interface, can diffuse across the cell and detrimentally coat the anode. On the other hand, the transport number for most SEs is virtually unity so cross-talk effects are eliminated.⁴⁵ Since the transport number in SEs is near unity, unlike LE based batteries, ASSBs do not suffer from concentration polarization effects and in principle could therefore be charged quickly.⁴⁶ Furthermore, a transport number of unity prohibits the possibility of cation depletion in the SE, on plating, at an interface with a metallic negative electrode, thus dendritic growth by the mechanism ascribed for LE batteries in **Section 1.8** should in principle be precluded.

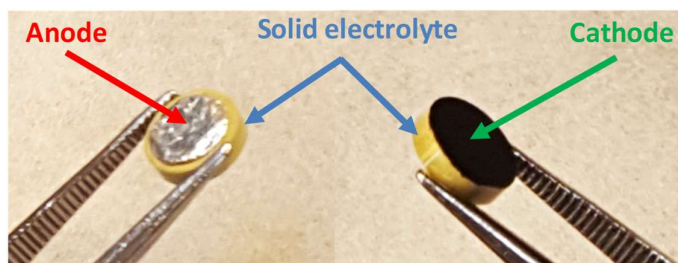


Figure 2.1. An example of an all solid-state cell using a glassy $80Li_2S \cdot 20P_2S_5$ SE, a binary lithium indium alloy anode and a composite cathode containing $LiCoO_2$, $80Li_2S \cdot 20P_2S_5$ and carbon conduction additive.

2.2 The theory of ionic conductivity

Ionic conductivity in solids results from the diffusion of ions between proximate and energetically equivalent sites in a crystal structure via connected channels. Ions can only move from occupied to vacant sites therefore crystal defects are ordinarily required for ionic diffusion. Since electroneutrality must be maintained in a crystal, only certain defects are permitted. Intrinsic defects include; Schottky defects (cation / anion pair vacancies) and Frenkel defects (interstitially displaced ions), as shown in Figure 2.2. In standard ionic solids, intrinsic defect proliferation is thermally induced at near melting point temperatures. Alternatively, extrinsic defects can be introduced through doping. For example, aliovalent doping with higher valent cations produces cation vacancies or anion interstitials whereas doping with lower valent cations produces cation interstitials or anion vacancies.⁴³

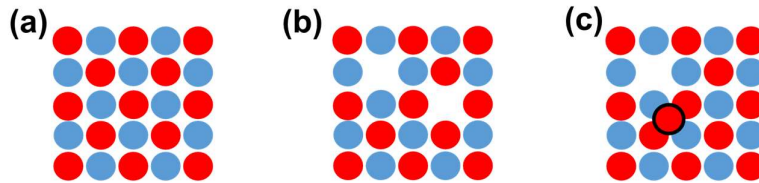


Figure 2.2. Illustrations of intrinsic defects (a) a perfect crystal, (b) a Schottky defect and (c) a Frenkel defect.

Ionic diffusion can occur through interstitial sites or via vacancies as shown in Figure 2.3. As ions diffuse between low energy normal positions in the lattice (or between interstitial positions), they pass through constricted high-energy 'bottle necks'. Ions must have sufficient kinetic energy to induce the local distortions required for the ions to pass through these bottle necks. Consequently, ionic diffusivity displays Arrhenius type behaviour and increases exponentially with temperature in accordance with:

$$D = D_0 e^{\left(\frac{-\Delta G_m}{K_B T}\right)} \quad (2.1)$$

where D is the diffusion constant, D_0 is the diffusion constant at absolute zero, ΔG_m is the motional Gibbs free energy of ion migration, k_B is the Boltzmann constant and T is the absolute temperature.⁴³

In reality, the diffusion mechanisms presented in Figure 2.3 are overly simplistic. Diffusion is frequently aided by a cooperative ion migration mechanism that arises from the long range electrostatic interactions between mobile ions.

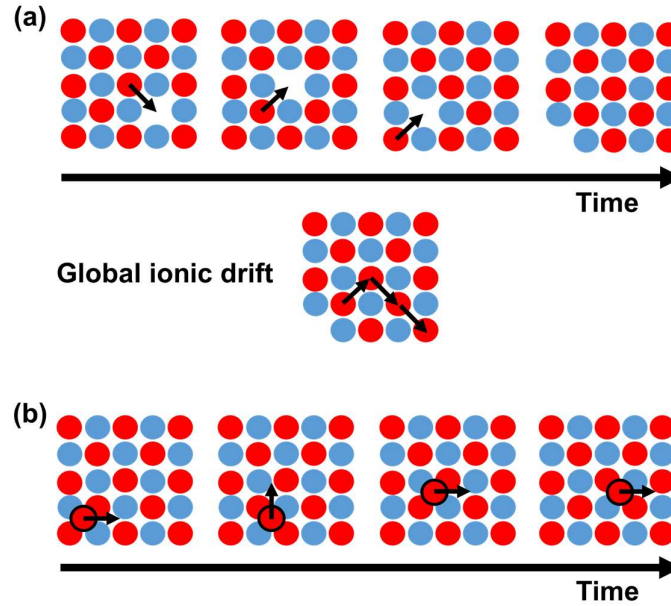


Figure 2.3. Illustrations of directional diffusion by (a) a simple vacancy mechanism, (b) a simple interstitial mechanism.

In ionic crystals the mobile species are charged ions, therefore their ionic mobility (u_i) should be considered rather than their diffusivity. The terms can be linked by the Einstein mobility equation:

$$u_i = \frac{Dq}{k_B T} \quad (2.2)$$

Diffusion is isotropic until an electric field is applied; in such a case, ionic diffusion becomes directionally favoured due to the charge on the mobile species. When a DC potential (E) is applied to an ionic conductor, an ionic current (i_0) flows from an ion

source to an ion sink. By measuring the induced current, the ionic conductivity (σ_i) can be determined:

$$i_0 = \sigma_i E \quad (2.3)$$

Ionic conductivity is dependent upon the mobility, charge (q) and concentration of the mobile ions / vacancies (c_i),

$$\sigma_i = c_i q u_i E \quad (2.4)$$

Although separation of c_i and u_i terms is experimentally difficult, the conductivity equation elucidates the underlying properties that can be tuned to produce good ionic conductors. However, $c_i q u_i$ are intimately linked terms. Using multivalent mobile ions rather than monovalent ions should theoretically increase conductivity but such increases are typically offset by decreased mobility. The design of new conductors is always a delicate balancing game. However, the ionic resistance of electrolytes is dependent on exchange dimensions as well as conductivity. For batteries, SEs should be made as thin as possible and the electrode / electrolyte contact area should be as large as possible to minimise the internal resistance (R_i).

$$R_i = \frac{L}{\sigma_i A} \quad (2.5)$$

L is the thickness and A is the area of the electrodes in contact with the electrolyte.

2.3 Ionic conductivity of SEs for battery applications

In order to compete with LE based lithium ion cells in terms of power density SEs will require high room temperature ionic conductivities (σ_{RT}) and will ideally also maintain high ionic conductivity over a wide temperature range (-20 °C to 60 °C) so that batteries can be used in EVs in all climates without the need for thermal management systems. The ionic conductivity of LEs used in commercial cells is typically σ_{RT} of $1 \times 10^{-2} \text{ S cm}^{-1}$. At present there are very few SEs with $\sigma_{RT} > 1 \times 10^{-2} \text{ S cm}^{-1}$, namely $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ (25 mS cm^{-1})⁴⁷, $\text{Li}_7\text{P}_3\text{S}_{11}$ (17 mS cm^{-1})⁴⁸ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, (12 mS cm^{-1})⁴⁹. As such, there is a strong desire for SEs with greater ionic conductivities. However, it is thought that SEs with σ_{RT} in the $10^{-3} - 10^{-4} \text{ S cm}^{-1}$ region, could be used in practical cells, provided they could be made sufficiently thin. To illustrate, a SE with an ionic conductivity of $\sim 5 \times 10^{-3} \text{ S cm}^{-1}$ would require a thickness of $< 100 \mu\text{m}$ to be comparable in resistance to a lithium ion battery employing a microfiber separator of typical thickness. There are several general classes of SEs with the ionic conductivity required for ASSB applications, including: Li_3N related nitrides; crystalline and amorphous sulphides; garnet, perovskites and NASICON structure type oxides, Figure 2.4.⁵⁰ High ionic conductivity alone is not a sufficient property for the selection of a SE for ASSBs, there are numerous properties such as electrochemical stability, mechanical properties and manufacturability that all require consideration.

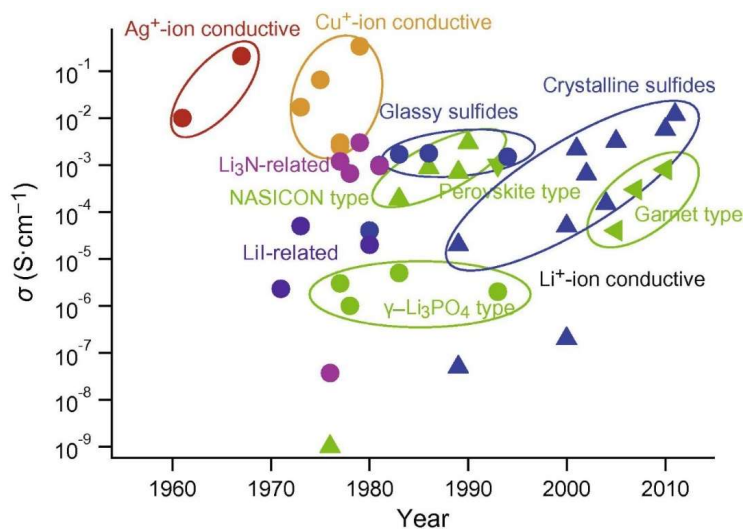


Figure 2.4. Comparison of the conductivities of well-known solid electrolytes. Figure reprinted from ref ⁵⁰. (<https://doi.org/10.1016/j.actamat.2012.10.034>)

2.4.1 Chemical and electrochemical stability between SEs and electrodes

As with LEs, SEs must have compatibility, though not necessarily electrochemical stability, with electrodes in order for a practical cell to be developed. In order to understand the SE / electrode interfacial electrochemical reactions, or lack thereof, the electrochemical stability window of the SE will be compared with the voltages of the respective electrodes during battery operation. Cyclic voltammetry (CV) is typically used to determine the stability window of a LE but CV is not an effective technique for SEs because slow reaction kinetics and low electronic conductivities typical for SEs limit degradation and often lead to overestimated electrochemical stability limits.⁵¹ Computational studies and experimental electrochemical techniques such as DC polarisation studies have therefore also been commonly used to determine the potentials at which SEs undergo oxidation and reduction. The electrochemical stability windows of the most intensely studied SEs were compared by Ceder et. al., as shown in Figure 2.5.⁵²

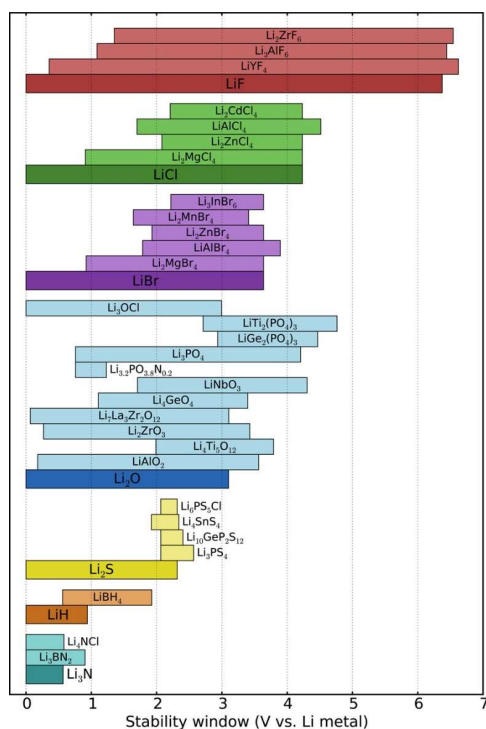


Figure 2.5. Electrochemical stability windows' for common SEs. The potentials are defined relative to lithium metal. Figure reprinted from.⁵² (<https://doi.org/10.1021/acs.chemmater.5b04082>)

2.4.2 Lithium / SE interface

Unlike LEs, there are SEs, such as Li_3N , which are electrochemically stable at 0 V vs Li, [Figure 2.5](#).⁵² However, most of the high ionic conductivity SEs have positive reduction potentials with respect to the potential of lithium; in these cases, electrons are able to transfer from the negative electrode to the lowest energy unoccupied molecular orbital (LUMO) of the SE. This results in the formation of an interphase at the Li / SE interface. The chemistry of these interphases is of great importance because the interface plays a key role in determining the overall cell performance. When SEs, which are based on non-metallic elements only (excluding lithium), are reduced by lithium metal, an SEI composed of inorganic binary lithium salts is formed. These lithium salts are poor electronic conductors but are able to somewhat conduct lithium ions, therefore the SEI passivates the lithium electrode. For example, $\text{Li}_7\text{P}_3\text{S}_{11}$ is reduced to form Li_3PS_4 , which is further reduced to Li_2S , Li_3P and P ;^{53,54,55} $\text{Li}_6\text{PS}_5\text{Cl}$ is reduced to form Li_2S , P and LiCl ;⁵⁶ and LiPON type SEs can be partially reduced to form Li_3N , LiPN_2 and Li_2O .⁵⁷ SEIs are typically low in ionic conductivity with respect to the SE and therefore contribute significantly to the resistance of the Li / SE interface. SEs which contain metallic elements (in addition to lithium) commonly react with lithium to form interphases which contain a metallic alloy phase. Metal alloys are electronic conductors and the other reaction products are ion conductors, therefore interphases of this type are called mixed ionic-electronic conductor (MIECs).⁵⁸ Electrons are able to move from the metal anode, through the MIECs to the SE interface and trigger additional reduction. Hence, MIECs are not self-terminating and continue to grow through the SE, until either the lithium electrode is totally consumed or a short circuit with the cathode has occurred. Many high ionic conductivity SEs are therefore considered incompatible with lithium. The LMPS family of electrolytes, with the general formula $\text{Li}_{11-x}\text{M}_{2-x}\text{P}_{1+x}\text{S}_{12}$ ($\text{M} = \text{Ge}, \text{Sn}, \text{etc.}$),⁵⁹ form MIECS; for example, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) is reduced to Li_2S , $\text{Li}_{15}\text{Ge}_4$ and Li_3P .^{60,58} NASICON type structures, with the general formula $\text{LiM}_2(\text{PO}_4)_3$ ($\text{M} = \text{Ti}, \text{Ge}, \text{Zr}, \text{Sn}, \text{Sr}, \text{etc.}$), such as $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ (LATP), are also reduced to form MIECS and cannot be used in lithium metal batteries without the use of a surface protecting layer.^{61–64}

2.4.3 Cathode / SE interface

Typical full cell ASSBs have composite cathodes, in which cathode active particles are embedded in a SE; carbon is typically added to increase electronic conductivity, [Figure 2.6](#). As such, cathode particles are in direct ionic and electrical contact with the SE, therefore interfacial redox reactions need to be considered. If the oxidation potential of SEs is greater than the operational voltage range of the cathode active particles, then electrochemical reactions do not occur. However, when the oxidation potential is lower than the potential of the electrode, electron transfer from the highest energy occupied molecular orbital (HOMO) to the cathode occurs. The oxidation of the SE results in the formation of a cathode electrolyte interphase (CEI). CEIs are typically poor electronic conductors and are self-terminating. Unlike SEIs, CEIs have depleted lithium content and are typically very poor ionic conductors. CEIs therefore contribute significant resistance to cells.⁶⁵ For example the oxidation of LGPS at 2.14 V yields GeS_2 , S and Li_3PS_4 , which can be further oxidised to S and P_2S_5 at 2.31 V.⁶⁰ As with the anode, cycling causes irreversible thickening of the CEI, which triggers charge and discharge end point capacity fading. Electrochemical stability of the SE with the cathode is therefore highly desirable. There are known SEs (LATP and LAGP) that have greater electrochemical stability than LEs at high potentials. However, few SEs are currently known which can be used in direct contact with high voltage cathodes ($> 5 \text{ V}$).

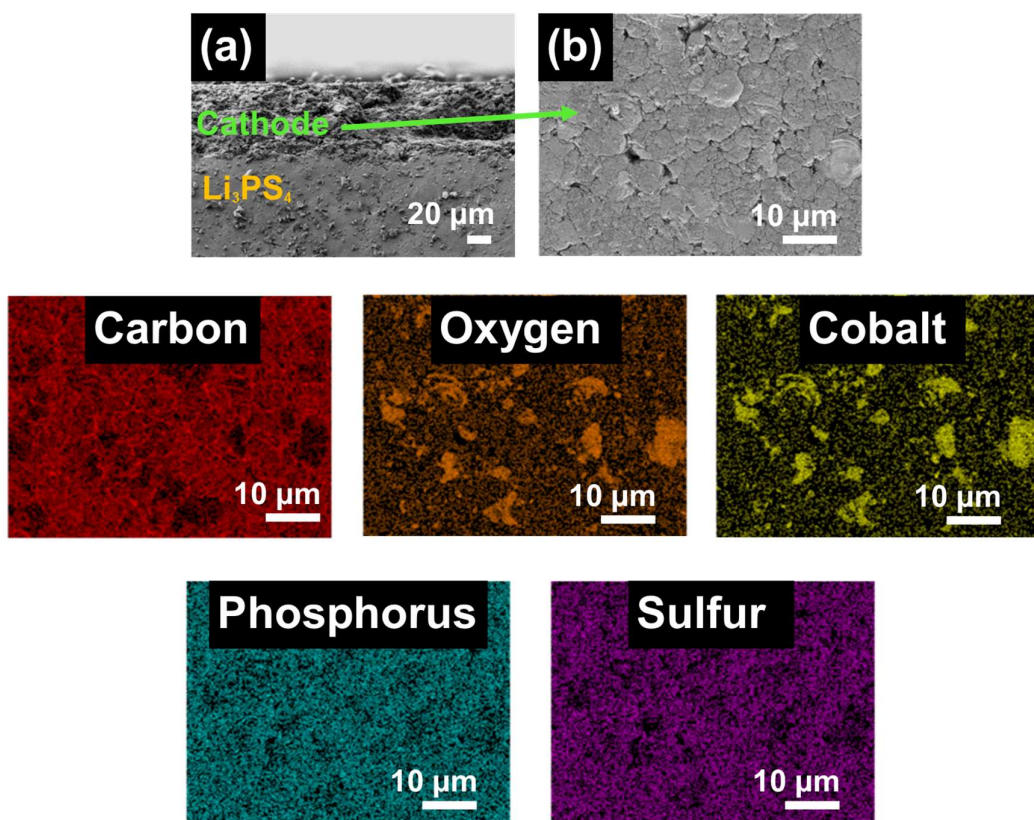


Figure 2.6. (a) Cross sectional SEM image of the interface between a Li_3PS_4 SE and a composite cathode comprised of LCO, C black and Li_3PS_4 . (b) Magnified SEM image of the composite cathode layer, with corresponding EDX elemental maps shown below, illustrating particle distributions.

It has been shown that the cycle efficiency and thermal stability of cathodes in liquid batteries can be improved by coating the cathode particles with thin films of: Al_2O_3 , ZrO_2 , SiO_2 , AlPO_4 or AlF_3 .^{66,67} Likewise, undesirable interphase growth can be suppressed significantly in SEs by coating the cathode particles (for example LiCoO_2) with electrochemically stable lithium salts such Li_2SiO_3 or LiNbO_3 .⁶⁸

2.5 Mechanical compatibility issues between SEs and electrodes

The intercalation / deintercalation of Li^+ ions, during battery cycling causes the lithium content and lattice parameters of intercalation electrode materials to change. These volume changes can occur for anodes and cathodes. In LE cells, volume changes during cycling are still somewhat problematic and particles can become isolated or

fractured, however the phenomenon is far less problematic than with SEs because LE is able to flow and maintain contact with the active particle during swelling and shrinking, such that stresses remain localised. SEIs and CEIs on the surfaces of the active particles are however stressed during the volume changes, which commonly results in their fracturing; repeated exposure of active particles to LE consumes the electrode active material and results in capacity fading.³⁴

In SEs cells, electrode volume changes are much more problematic. Consider a composite cathode in which active cathode particles are embedded in a SE matrix. Before any cycling is commenced, there is effective contact between the SE and the cathode particles. Unlike LEs however, a ceramic SE is not able to flow, so when the active cathode particles swell, a SE cannot accommodate the volume expansion therefore active cathode particles and the SE experience significant mechanical stresses. These stresses can cause the active cathode particles to crack, which can cause capacity fading and increased SE / cathode interfacial resistance. Furthermore, cracking of the SE can lead to short-circuit failure.²⁵ Likewise, when the active cathode particles contract, contact loss with the SE can occur because the SE is static and does not flow to maintain the interface. Therefore contact loss reduces the effective cathode active mass available for intercalation on subsequent cycles, producing capacity fading. In light of these problems, zero strain change cathodes would be preferred for ASSB applications. Mechanically soft SEs (low Young's modulus), such as lithium thiophosphates, are better able to accommodate electrode volume changes.²⁵ Unfortunately, many promising SEs (LLZO and LLZTO) have high Young's Moduli and lack the mechanical compliance required to minimise the effects.³⁴ Possible strategies for minimising such volume change effects include: applying considerable external spring pressure to the ASSB to maintain particle contact during cycling; coating the cathode particles with a thin layer of an elastic material, such as a polymer electrolyte, which is able to accommodate the volume changes; or directly adding polymer fillers to decrease the brittleness of the SE.⁶⁹ Unlike intercalation electrodes which have a 3D interface with the SE, in conventional cell architectures, metallic electrodes form a 2D interface with the SE. Since metal atoms are directly removed from the electrode during stripping, a pure metallic lithium electrode experiences volume changes of up to 100 % during cycling. As such, in order for contact between the lithium and the current collector to be maintained, spring pressure

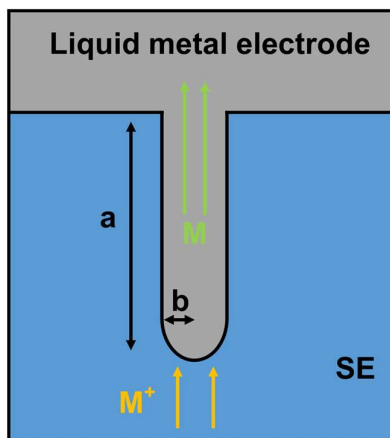
is needed. In **Chapter 4** of this thesis, the effect of pressure on the Li / SE is shown to play a considerable role in determining the performance of an ASSB.

2.6.1 Dendrites in SEs

Classical dendrite growth in LEs is the result of kinetic perturbations of the negative electrode interface. Given this mechanism is driven by salt depletion, it is often purported that replacing LE with a SE, with a transport number of unity, should prevent dendrite growth, however almost all ASSBs, employing a lithium metal negative electrode, suffer from a short-circuit type failure mechanism, at high C rates, on charge, due to the growth of thin lithium filaments which penetrate the SE thereby electrically contacting the positive and negative electrodes.⁷⁰ Although somewhat misleading, lithium filament growth in SEs is commonly referred to as dendrite growth despite the fact that lithium filaments do not appear to adopt branch like fractal structures in SEs as they do in LEs. Since SEs are mechanically strong compared with the traditional fibreglass or polymer separators (e.g. Celgard commercial separators) that are used in LE based lithium ion cells, researchers have posited that SEs should probably demonstrate some increased imperviousness to penetration by lithium dendrites.⁷¹ However, it has been experimentally reported that “Li dendrite formation in LLZO and Li₂S-P₂S₅ is actually much easier than that in liquid electrolytes of lithium batteries.”⁷² Clearly, understanding this failure mechanism is critical to enabling the lithium metal negative electrode. Short-circuiting of SEs was first observed in high temperature sodium/sulfur cells employing sodium β ''-alumina as a SE and molten metallic sodium as a negative electrode. Understanding this failure process provides a solid framework for understanding the current competing models of ‘dendrite growth’ in SEs at room temperature.

2.6.2 Dendritic failure of SEs with liquid metal anodes

Little change in the cycling behaviour of Na | β -alumina cells is observed over long periods, but then sudden cracking of the SE and short-circuiting ensues.⁷³ In 1974, Armstrong, Dickinson and Turner published an outstanding paper suggesting that the growth of sodium filaments through β -alumina type SEs occurs during plating, and that when these sodium filaments completely traverse the SE, a short-circuit occurs.⁷⁴ Their work showed that surface roughness has a marked effect on cell lifetime and concluded that, dendrites originate from pores in the SE surface. Their preliminary model suggested that extant pores were Griffith type surface flawsⁱ which are able to grow deep into the ceramic by ceramic fracture under the action of a Poiseuille pressureⁱⁱ produced by the flow of sodium into the crack during plating at the crack tip. Their model essentially marries two principles: that applied stress drives crack propagation above a critical value and that pressure develops due to fluid flow when sodium is plated into the crack. As a first approximation, this model assumes that a surface flaw is a cylindrical pore with a hemispherical tip perpendicular to the anode | SE interface, [Figure 2.7](#). It is also assumed that molten sodium fully wets the surface of the SE; given that the contact angle between sodium and sodium β "-alumina is $< 90^\circ$ at 300°C . Before cycling, the cylindrical pore is already completely filled with sodium.



[Figure 2.7](#). Schematic of dendrite nucleation via a hemispherically tipped cylindrical surface flaw as assumed in the Armstrong, Dickinson and Turner model.⁷⁴

It is known from basic mechanics that when a stress is applied to a hemispherically tipped cylindrical crack, the stress concentrates at the crack tip according to:

$$\sigma_{max} = \sigma \left(1 + 2\sqrt{\frac{a}{b}} \right) \quad (2.7)$$

Where σ is tensile stress, σ_{max} is the maximum tensile stress, a is the crack length and b is radius of curvature at the crack tip. The critical fracture stress for a ceramic can be determined using the standard Griffith equation:

$$\sigma_{critical} = \left(\frac{2E\gamma}{\pi(1-\nu^2)a} \right)^{1/2} \quad (2.8)$$

Where, E is the Young's Modulus of the SE, γ is the surface tension of sodium metal on the SE and ν is the Poisson's ratio of the SE. Therefore, the ceramic will fracture when $\sigma_{max} \geq \sigma_{critical}$. In this model, the stress is thought to be created by pressure generated when sodium plates into the crack. Before fracture, the total flux of sodium into the crack must equal the total sodium flux out of the crack which is analogous to the flow of a fluid through a pipe, where the pipe is a cylindrical crack, the fluid is sodium metal and the flow rate through the pipe is determined by the applied current density and the area of the crack. As such, the rate of flow of fluid through a pipe is related to the pressure difference across the pipe as described by the Hagen-Poiseuille equation:

$$\frac{\Delta V}{\Delta t} = \frac{\pi b^4(\Delta x)}{8\eta y} \quad (2.9)$$

Where $\frac{\Delta V}{\Delta t}$ is the rate at which a volume of fluid flows through the pipe, b is the radius of the pipe, Δx is the pressure difference across the ends of the pipe, η is the viscosity

ⁱ A **Griffith flaw** is a sharp preexisting crack in a brittle material, which is able to grow due to the release of elastic energy when two new surfaces of the crack are created during extension.

ⁱⁱ **Poiseuille pressure** is the pressure difference that occurs between the ends of a pipe along in which laminar flow of incompressible Newtonian fluid is occurring.

of fluid and y is the length of the pipe. The equation can be expressed in terms of moles of sodium flowing through the pipe:

$$V_m \frac{dN}{dt} = \frac{\pi b^4}{8\eta} \left(\frac{dP}{dx} \right) \quad (2.10)$$

Where V_m is the molar volume of sodium and $\frac{dN}{dt}$ is the rate at which moles of sodium flow through the crack and $\frac{dP}{dx}$ is the pressure dependence on crack length. It is worth noting that the Hagen-Poiseuille equation assumes the fluid is incompressible and that flow is laminar. The Poiseuille law implies that since there is always friction in a physical system, there must be a pressure difference across the pipe in order for a fluid to flow. Since, dendrites do not form in SEs without the application of current, the higher pressure must occur inside the crack and must necessarily be driven by sodium flux from the SE into the crack. As such, $\frac{dN}{dt}$ (the flux of sodium into the crack) is a constant and it can be used to determine the Poiseuille pressure for a given crack size.

$\frac{dN}{dt}$ can be expressed as:

$$\frac{dN}{dt} = \frac{2\pi ib(\Delta x)}{nF} \quad (2.11)$$

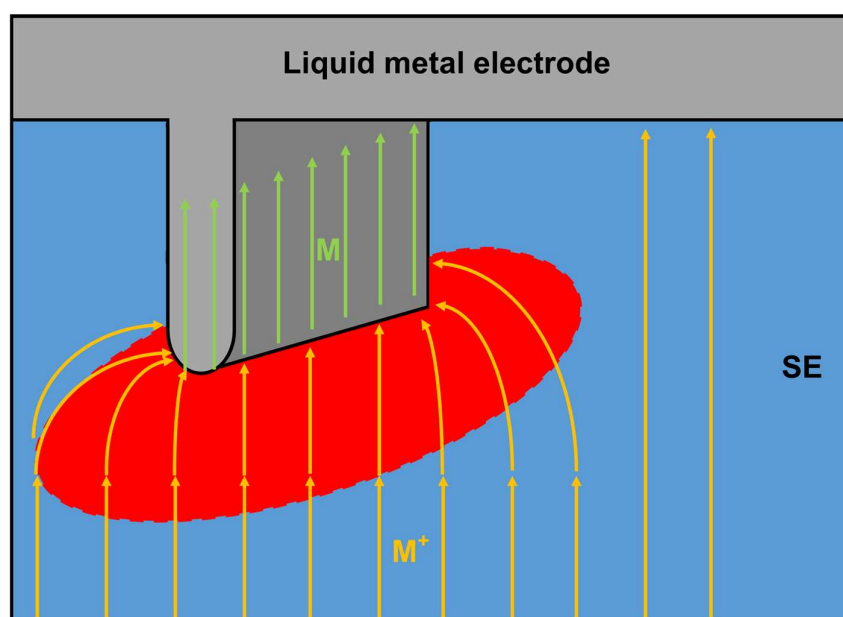
Combination and integration of 2.11 and 2.10 gives as an approximate formula for the Poiseuille pressure generated for a given applied current density and crack size.

$$\Delta P = \frac{8\eta i V_m a^2}{nF b^3} \quad (2.12)$$

As such, long cracks require less stress to propagate than short cracks. This implies that beyond a critical length, the flux of lithium into the crack induces a pressure greater than the fracture toughness of the sodium beta alumina, so crack propagation initiates and crack growth becomes exponential. However, as the crack expands, a short-lived drop in Poiseuille pressure is expected.⁷⁴ Therefore, according to this model, crack propagation occurs by stepwise repeated fracture with exponential ease. However,

the Armstrong, Dickinson and Turner model requires unrealistically long initial cracks for propagation. For example, under an applied current density of 100 mA cm^{-2} a crack with a diameter of 10^{-7} cm would need to be at least $5 \times 10^{-5} \text{ cm}$ in length. Cracks of this length were not present in the SE and the population of surface flaws had been carefully controlled by polishing.

In 1974, Richman and Tennenhouse produced a more realistic model by assuming surface flaws were parallel-sided rectangular cracks with semi-circular shaped tips, [Figure 2.8](#).⁷⁵ This crack geometry was suggested because lateral fracture of a pore is far more likely than tip fracture in a cylindrical pore since more strain energy can be relieved by the creation of new surfaces.



[Figure 2.8](#). Schematic of ionic current focussing in a SE towards a cylindrically tipped parallel-sided rectangular crack surface flaw during plating, leading to dendrite nucleation as assumed in the Richman and Tennenhouse model.⁶¹ The area shaded red represents the effective area through which all current is assumed to reach the crack tip.

Molten sodium is 10^6 times more electronically conductive than sodium β'' -alumina therefore the sodium filled crack has much lower resistance than the immediate surroundings.¹ As such, it is suggested that sodium ions will focus towards the crack from the area in the solid electrolyte near the crack, as shown in [Figure 2.8](#). Naturally,

the local current density of sodium ions across the interface inside the crack will be raised with respect to the average current density in the SE. A rigorous treatment of the current focussing using the Laplace equation was not performed, instead it was assumed that all flux within a distance L from the crack would focus into the crack tip. i_{eff} is the effective current density at the crack surface, A_{crack} is the area of the crack and A_{eff} is the effective area from which current is concentrated into the crack.

$$i_{eff} = \left(\frac{A_{eff}}{A_{crack}} \right) i \quad (2.13)$$

In this model the effective current density in the crack appears significantly increased with respect to the Armstrong, Dickinson and Turner model, therefore the critical crack length required for propagation becomes more realistic. Feldman and De Jonghe, developed a similar but more sophisticated model, in which ion current focussing was calculated by solving the electrical potential with suitable boundary conditions.⁷³ These early models incorrectly assumed an arbitrarily chosen crack width was maintained during crack propagation.⁷⁶ Furthermore, critical current densities calculated for crack propagation using these method are still far above experimentally determined values. This may be due to localised ion current enhancement, due to surface roughness, imperfect wetting of the SE and also the presence of contaminants at the interface, Figure 2.9.

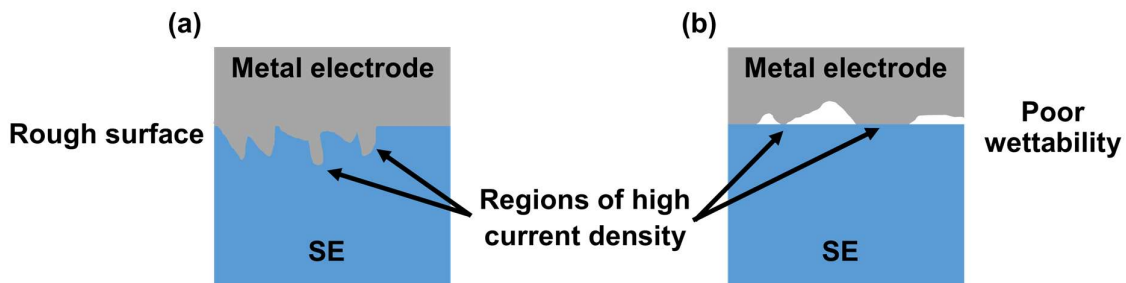


Figure 2.9. Schematics showing how imperfect interfaces can lead to localised ion current enhancement. (a) Non uniform SE surface with good wetting. (b) Uniform SE surface with poor lithium wettability.

These models provide excellent insight into how dendrite growth can occur in SEs. However, in ASSBs, the metallic electrode is solid and therefore cannot be understood purely in terms of a simple Poiseuille pressure driven mechanism.

2.6.3 Dendritic failure of SEs with solid metal anodes

At present the true nature of dendrite growth in ASSBs is poorly understood, with seemingly conflicting experimental observations having been reported and multiple models having been proposed. For example, it has been reported that high electronic conductivity may enable lithium to be directly deposited inside a SE, without direct connectivity of the dendrite to the electrode;⁷² yet, experimental studies have indicated that dendrite growth occurs along grain boundaries in polycrystalline garnet electrolytes, [Figure 2.10](#).^{77,78} Raj and Wolfenstine propose a model for dendrite nucleation into grain boundaries based on the electro-chemo-mechanical properties of Li at the SE interface with high shear moduli materials.⁷⁹

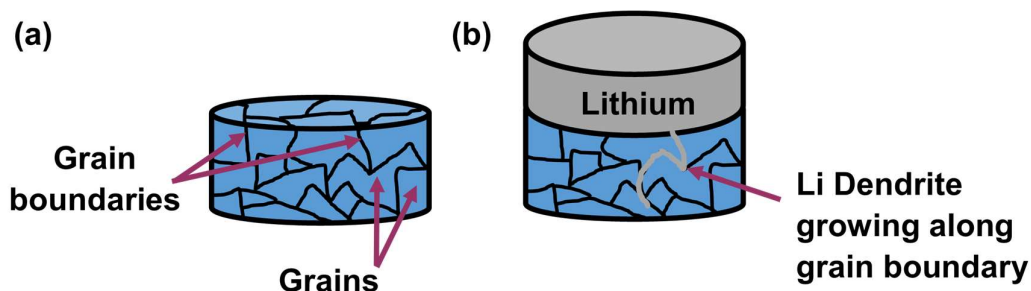


Figure 2.10. Schematics showing: (a) Granular structure of a crystalline SE and (b) the growth of a dendrite along the grain boundary as reported for garnet SEs.

Grains and grain boundaries at the surface of a polycrystalline SE are directly interfaced with a lithium electrode. As such, on plating, lithium can either be deposited directly from the grains of the SE into the electrode, or lithium can plate to the electrode via the grain boundary. By considering the energy contributions required for each of these plating paths, Raj and Wolfenstine were able to provide a rationale for grain boundary dendrite nucleation. When nucleation of a dendrite into a grain boundary occurs, an interface between the grain boundary and the growing dendrite is formed,

with a surface energy (γ). Some energy is released by the destruction of the original grain boundary (γ_{gb}). Therefore the γ and γ_{gb} energies determine the extent to which lithium can push apart the grain boundary.

$$\cos \theta = \frac{\gamma_{gb}}{2\gamma} \quad (2.14)$$

Where θ is the contact angle between the SE and the nucleated lithium dendrite, as shown in Figure 2.11.

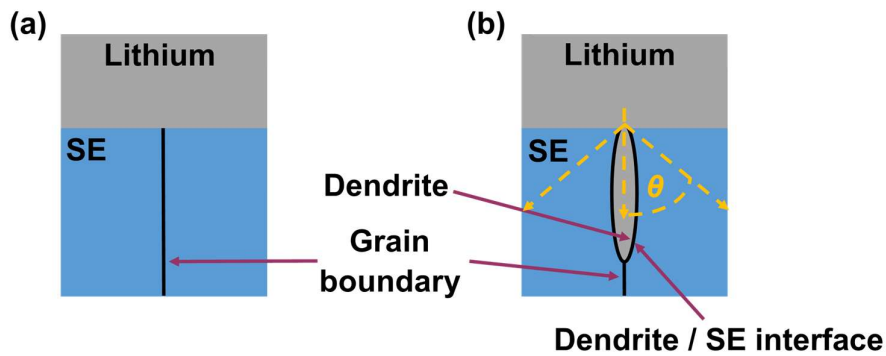


Figure 2.11. (a) Grain boundary interfacing with a lithium electrode before plating. (b) The nucleation dendrite along a grain boundary at the lithium electrode interface during plating.

The higher the grain boundary energy, the more favourable it is for lithium nucleation to occur and the wider the lithium dendrite can grow. Below a certain critical size, the surface to volume ratio of this is large. Once lithium has nucleated the grain boundary space, further plating is opposed by a back strain from the surrounding matrix, since in order to accommodate a greater volume of lithium, additional force is required to either force flow lithium down the grain boundary or to fracture the ceramic. As such, the plating becomes less favourable, with further dendrite growth only permitted when the local electrochemical potential of lithium at the anode interface is greater than the reference potential of bulk lithium metal. Since the electric field is the product of current density and resistivity, the local electrochemical potential experienced by lithium is increased at regions with higher current density or greater ionic resistance. It is known

that grain boundaries have higher ionic resistivity than grains.⁸⁰ Therefore the difference in ionic conductivity between the grains and grain boundaries leads to a local increase in the electrochemical potential of lithium. At high current densities this is sufficient to trigger nucleation. Once the dendrite has nucleated the grain boundary, current focussing is likely to drive dendrite propagation by the mechanism shown earlier in [Figure 2.8](#). Using this treatment, Raj and Wolfenstein were able to produce current limit diagrams showing the effect of fracture stress and ionic conductivity of a ceramic on the current density that can be practically used with minimised dendrite formation. Since this model requires the presence of grain boundaries, it would explain why amorphous LiPON has dendritic resistance, without needing to invoke electrochemical breakdown mechanisms.⁷² However, the model cannot explain why dendrite propagation is observed in amorphous grain boundary free LPS electrolytes and single crystal SEs,⁷⁰ therefore a more universal model is required.

In recent years, several models for dendrite propagation with a solid metal electrode have been developed,^{81,82} which build on the early models of liquid metal dendrite propagation in SEs from surface flaws, as described in **Section 2.6.2**. In these mechanisms, a crack type surface flaw is assumed in the ceramic SE electrolyte at the interface with the metal electrode. During charging of an ASSB with a lithium anode, lithium can either plate directly into the bulk of the lithium electrode via the existing lithium metal / SE interface, or if an empty crack is present at the SE surface, the lithium may plate from the lithium metal / SE junction at the crack opening and grow along the bare SE surface inside the surface crack to effectively form a new lithium metal / SE interface inside the crack. In order for lithium to directly plate along the surface of an empty crack, the sum of the surface energy of the bare SE in the crack, the energy of transferring lithium ions from the SE to lithium atoms in the anode under an applied pressure and the voltage supplied to the cell, must be greater than energy of forming a new interface between the SE and lithium metal along the surfaces of the crack. Assuming this criterion is satisfied, and provided sufficient capacity is being transferred during plating, the crack will become filled with lithium. Alternatively, if there is poor wettability between SE and lithium, the lithium will plate into the crack with convex meniscus type behaviour but when sufficient capacities are moved, filling

of the crack can still occur. Flux of lithium ions into the crack must be equal to the flux of lithium atoms out of the crack in order for the crack to remain filled. If the rate of flux into a filled crack exceeds the rate of flux out of the crack, the crack has to propagate due to the incompressibility of solids. Factors controlling flux into the crack are well known. Assuming the potential is uniform across the whole electrode, the rate at which lithium enters the crack is determined by the current density applied to the cell and the geometry of the crack. The higher the current density, the faster lithium can enter the crack. Flux into a crack is greater for long cracks since there is a greater area for plating. Furthermore, the ceramic fracture mechanics above a critical stress are well understood. In the solid state, lithium flow out of the crack cannot occur by a Poiseuille pressure driven mechanism. Instead, lithium is thought to undergo plastic flow by a creep mechanism.⁸³ However, it is unclear how the low yield strength of lithium (2.83 GPa)⁸⁴ could give rise to the internal pressures required for the SE to fracture;^{83,85} one would expect lithium to squirt out of the crack into the electrode, rather than cracking the ceramic, just like toothpaste exiting a squeezed tube. However, there are experimental reports that the yield strength of lithium is considerably increased at the micron length scale, typical for the surface flaw.⁸⁶ In a treatment by McMeeking, et.al., this increased yield strength value proved sufficient to induce crack stresses necessary for SE fracture.⁸¹

In light of these models, it is critical to determine whether the crack extension is driven by a filled crack, a partially filled crack, or by an electrochemical breakdown process at the tip of a lithium filament. Since in situ observation of dendrites deep in the SE by traditional microscopy techniques has proven challenging for practical purposes,⁸⁷ it is suggested tomographic experiments with high time resolution could be invaluable.

2.7.1 State of the art SEs employed in this thesis

There are many reported SEs that show promise for ASSB applications. However, none of these SEs currently fully meet the prerequisites for high power / high capacity commercially viable ASSBs.⁸⁸ In addition to manufacturing considerations (processing cost and difficulty of device integration), the SEs must have high ionic conductivity, electrochemical and mechanical compatibility with electrodes and show

imperviousness to the formation of dendrites at high current density.⁸⁸ Since the ultimate objective of this thesis is the realisation of a lithium metal anode, SEs must have ionic conductivity $> 10^{-4}$ S cm⁻¹ and must form a (kinetically or thermodynamically) stable interface with lithium. SEs that do not meet these minimum requirements are not investigated in this body of work. For example, lithium ion superionic conductors (LISICONs), lack the required ionic conductivity and lithium analogues of sodium superionic conductors (NASICONs) and perovskites (ABO₃ such as Li_{3x}La_{2/3-x}TiO), form fatal MEIs in contact with lithium. Brief introductions to the SEs employed in this body of work (Li₃N, LLZTO and Li₃PS₄) are provided.

2.7.2 Garnet-type oxides

In 2009, Weppner et. al., synthesised a lithium stuffed garnet (Li₇La₃Zr₂O₁₂, commonly referred to as LLZO).⁸⁹ The increased lithium content resulted in a bulk ionic conductivity ($10^{-3} - 10^{-4}$ S cm⁻¹), which was significantly higher than had previously been observed ($< 10^{-5}$ S cm⁻¹) for conventional Li₅La₃M₂O₁₂ (where *M* = Nb & Ta) type garnet structures.⁸⁹ LLZO adopts cubic (*Ia $\bar{3}$ d*) and tetragonal (*I4₁/acd*) phases, with the former displaying greater ionic conductivity, [Figure 2.12](#).⁹⁰ However, the cubic phase is thermodynamically unstable at room temperature.⁹¹ It has been shown that the cubic phase can be stabilised by doping with Ta⁵⁺,⁹² Nb⁵⁺,⁹³ Te⁶⁺,⁹⁴ W⁶⁺,⁹⁵ Ti⁴⁺,⁹⁵ Al³⁺,⁹³ and Ga³⁺,⁹⁶ or combinations thereof.⁹⁷ Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ (LLZTO), one of the SEs used for experiments in this body of work, is one of the most promising Garnets due to outstanding ionic conductivity and stability against lithium metal.⁹⁸ LLZO type Garnets have low grain boundary resistances. However, the interfacial resistance between LLZO and the lithium electrode, has frequently been reported to be much more significant than the interfacial resistance of lithium and other common SEs.⁹⁹ Multiple factors contribute to the interfacial resistance. For example, LLZO is unstable in air, therefore the preparation of LLZO in a lab atmosphere, as was typical in almost all early studies, allows a surface layer to form, comprised of LiOH, Li₂CO₃ and adventitious carbon species.⁹⁹ It is likely that when moisture adsorbs to the surface of LLZO, proton/Li⁺ exchange takes place and forms a surface layer of LiOH which is able to react with atmospheric CO₂ to produced Li₂CO₃.³⁰ As such, when lithium is subsequently applied to the LLZO pellet, the interposing surface layer provides an

artificially high resistance to ion exchange across the lithium / SE interface. Surface preparation is therefore key to developing an effective interface between lithium metal and LLZO. Sakamoto et al demonstrated that the interfacial resistance could be decreased to $2 \Omega \text{ cm}^2$ by removal of Li_2CO_3 from the surface by polishing using a diamond abrasive in a glycol-based extender followed by a heat treatment.¹⁰⁰ Several studies have shown that the interfacial resistance of lithium with LLZO is also high due to wettability considerations and it has been shown that surface coating LLZO with metals that alloy with lithium (Al, Ge and Au), can reduce the interfacial resistance with lithium considerably.^{101,102} Despite their many advantageous properties, garnet SEs also suffer from dendritic short-circuiting at high current density, even when near 100% dense,^{89,103} and densification can only be achieved at very high temperatures using energy intensive processes like spark plasma sintering and hot-pressing,¹⁰⁴ which is cost prohibitive for manufacturing. Although LLZO is stable at high potential ($> 3 \text{ V}$), long term cycling of ASSBs, employing LLZO as the SE, has proven elusive because of mechanical degradation effects due to volume expansion issues outlined in **Section 2.5**.¹⁰⁵

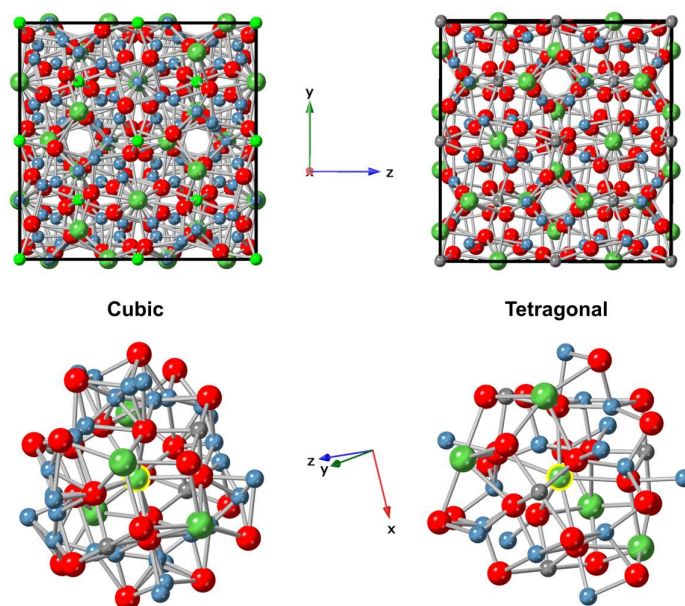


Figure 2.12. Crystal structures and local bonding for cubic and tetragonal phases of LLZO, produced using crystallographic data from ref ^{106,107}.

2.7.3 Li₃N type nitrides

Lithium nitride (Li₃N), exists as hexagonal Li₂N planes separated by interstitial Li ions, [Figure 2.13](#).¹⁰⁸ The lithium ions can diffuse easily along the interstitial planes, parallel to the Li₂N planes, but diffusion in the perpendicular direction, through the Li₂N planes is hindered. As such, single crystal Li₃N, produced by the Czochralski process, is a 2D lithium ion conductor.¹⁰⁹ At room temperature, the activation enthalpy for ionic conduction parallel to the Li₂N planes is 0.25 eV and ionic conductivity of a single crystal in this direction is $\sim 10^{-3} \text{ S cm}^{-1}$.¹¹⁰ Whereas the conductivity perpendicular to the Li₂N planes is markedly reduced ($\sim 10^{-5} \text{ S cm}^{-1}$) and has a 0.49 eV activation energy.¹¹¹ However, the ionic conductivity of polycrystalline Li₃N varies considerably depending on purity and crystallinity. High ionic conductivities for polycrystalline lithium nitride ($1.7 \times 10^{-3} \text{ S cm}^{-1}$, Bittihn) are often attributed to almost unavoidable hydrogen impurities.¹¹² Such hydrogen impurities cause NH²⁻ complexes to develop at N³⁻ sites, which results in Li vacancies. As such, hydrogen doping has been employed to controllably increase the ionic conductivity of Li₃N.

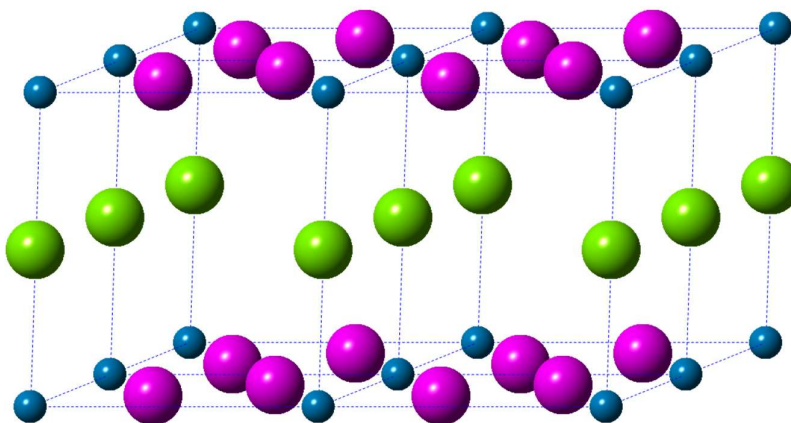


Figure 2.13. Crystal structure of Li₃N. Plane bound Li ions are purple, mobile inter-planar lithium ions are green, nitrogen ions are blue. Constructed using crystallographic data from ref ¹¹³.

Lithium nitride has a very low reduction potential and is thermodynamically stable against lithium metal. As such, Li₃N is ideal for investigations of the anode interface,

as explored in **Chapter 4**. Furthermore, α -Li₃N has a low density (1.27 g cm⁻³), comparable with LE, which is ideal for the production of a high gravimetrically energy dense cell. However, despite all these ideal properties, Li₃N has proven to be incompatible with cathodes. Li₃N has a low oxidation potential (0.44 V vs Li) and decomposes in contact with cathodes, [Figure 2.5](#).¹¹⁴ Additionally, Li₃N has a relatively high electronic conductivity which this leads to self-discharging in all solid-state cells. As such, Li₃N has become a somewhat forgotten SE in recent years. However, in **Chapter 5**, a hybrid strategy is explored for enabling Li₃N to be used with both a cathode and a lithium metal anode.

2.7.4 Lithium thiophosphate type sulfides

Sulfide SEs, namely compounds in the binary $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ (LPS) class of SEs, produced by the reactions of lithium sulfide (Li₂S) and phosphorus pentasulfide (P₂S₅),^{115,116} are particularly attractive for lithium battery applications due to exceptional ionic conductivity and acceptable interfacial compatibility with electrodes.¹¹⁷ At the local level, lithium thiophosphates can be thought of as anionic frameworks of polyhedral structural units comprised of phosphorus and sulphur; specifically: corner-sharing ortho-thiophosphate polyhedra (PS₄³⁻), P-S-P bridged pyro-thiophosphate (P₂S₇⁴⁻), edge-sharing hypo-thiodiphosphate polyhedra (P₂S₆⁴⁻), meta-thiodiphosphate polyhedra (P₂S₆²⁻) and meta-thiophosphate infinite chains (PS₃⁻), [Figure 2.14](#).¹¹⁸ The different polyhedra give rise to many possible long range orderings, therefore the LPS structure space is very complicated and many crystalline, amorphous phases and glass-ceramic composites are known, each has different ionic conductivity and requires different preparative conditions.

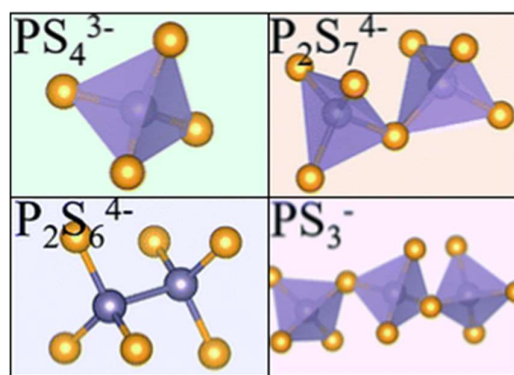


Figure 2.14. P-S polyhedra found in LPS compounds. Figure adapted from ref ¹¹⁵.
<https://doi.org/10.1039/C7TA06067J>

In early studies, Li_2S was annealed with P_2S_5 in various ratios. After reacting, the mixtures were cooled to room temperature to form crystalline materials with the general formula $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ (where x is the mol % of Li_2S in the reaction mixture). $\gamma\text{-Li}_3\text{PS}_4$, has the highest room temperature conductivity ($3 \times 10^{-7} \text{ S cm}^{-1}$) of the phases produced by simple annealing.¹¹⁹ $\gamma\text{-Li}_3\text{PS}_4$ is comprised of PS_4^{3-} units only and is isostructural to $\beta\text{-Li}_3\text{PO}_4$, Figure 2.15 (a). Conductivity is considerably higher in materials comprised of more diffuse ions. This is because heightened lattice polarizability decreases the activation energy of the ion diffusion pathways. As such, sulphide based electrolytes have higher conductivities than their respective oxygen analogues ($\sim 1 \times 10^{-8} \text{ S cm}^{-1}$).¹²⁰ $\gamma\text{-Li}_3\text{PS}_4$ production is maximised with the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ composition. When $\text{Li}_2\text{S} < 75 \text{ mol \%}$ is used, other low ionic conductivity thiophosphate phases such as $\text{Li}_4\text{P}_2\text{S}_6$ are formed. When $\text{Li}_2\text{S} > 75 \text{ mol \%}$ is used, the excess Li_2S remains unreacted. Since Li_2S is a poor ionic conductor, it decreases the effective ionic conductivity of the SE. Clearly, the ionic conductivity of $\gamma\text{-Li}_3\text{PS}_4$ is insufficient for battery applications. However, metastable LPS phases are known that have much higher ionic conductivity than $\gamma\text{-Li}_3\text{PS}_4$. At temperatures above 810 K, $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ mixtures react to form crystalline $\alpha\text{-Li}_3\text{PS}_4$. If $\alpha\text{-Li}_3\text{PS}_4$ is slowly cooled, then a reversible phase transition to crystalline $\beta\text{-Li}_3\text{PS}_4$ transpires between 720 K and 810 K.¹²¹ $\beta\text{-Li}_3\text{PS}_4$ ($\sigma_{500 \text{ K}} = 3.0 \times 10^{-2} \text{ Scm}^{-1}$), Figure 2.15.(b), has a much higher ionic conductivity than $\gamma\text{-Li}_3\text{PS}_4$. However on cooling, between 640-545 K, a $\beta\text{-Li}_3\text{PS}_4$ to $\gamma\text{-Li}_3\text{PS}_4$ phase transition occurs. As such, simple annealing cannot produce $\beta\text{-Li}_3\text{PS}_4$ at room temperature because these simple solid-state reactions can only produce thermodynamically stable materials. Rapid melt quenching has proven

challenging for the production of high purity LPS phases because the volatility of sulphur leads to poorly controlled stoichiometry.¹²² However, prolonged low-energy ball milling has proven to be particularly effective for accessing metastable high ionic conductivity LPS phases at room temperature.¹¹⁹

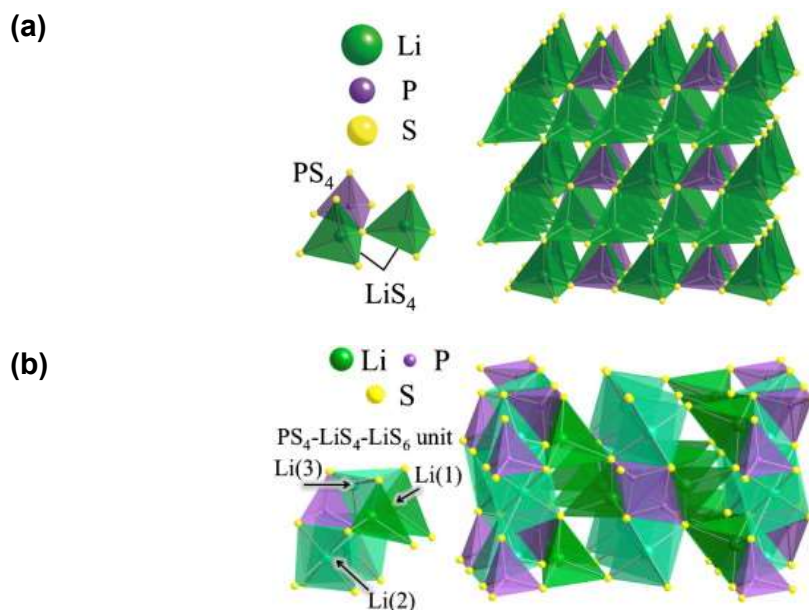


Figure 2.15. (a) γ - Li_3PS_4 , (b) β - Li_3PS_4 . Figures reproduced from ¹²¹.
<https://doi.org/10.1016/j.ssi.2010.10.001>

Amorphous chalcogenide SEs are produced by reactions between binary salts and glass formers.



Ball milling of Li_2S with P_2S_5 can form $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ amorphous glasses. These glasses are very soft and cold pressing is sufficient to eliminate grain boundary resistances. Like the crystalline LPS phases, these glasses contain locally organised P-S polyhedra (PS_4^{3-} , $\text{P}_2\text{S}_6^{4-}$ and $\text{P}_2\text{S}_7^{4-}$) but long range ordering of the polyhedra is not observed. Increased Li_2S starting content produces glasses with increased PS_4^{3-} content, **Figure 2.16**. However, the precise milling conditions used have a profound effect on the conductivity of these glasses. Hence, discrepancies exist within the literature, as to which ratio produces the highest ionic conductivity SE. For example,

Tatsumisago et al. first reported that the conductivities of the LPS glasses increased with y up to a maximum of $\sigma = 2.1 \times 10^{-4} \text{ S cm}^{-1}$ at $y = 80\%$. Their initial paper indicated that compositions with $\text{Li}_2\text{S} > 80 \text{ mol } \%$ displayed decreased conductivity.¹²³ However, Kawamoto observed that the $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ glass has the highest conductivity ($\sigma = 5.0 \times 10^{-4} \text{ S cm}^{-1}$) and that decreased conductivity occurs at $\text{Li}_2\text{S} > 75 \text{ mol } \%$ due to the presence of unreacted insulating Li_2S .¹²⁴ Subsequent work by Tatsumisago shows that the maximum conductivity for an optimised $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ glass system does indeed occur at $x = 75 \text{ mol } \%$ since this composition yields a glass almost exclusively composed of PS_4^{3-} polyhedra which can be regarded as amorphous Li_3PS_4 .¹²⁵ In reality, these vitreous materials are not truly amorphous, with crystallites of various crystalline phases being commonly observed. For example, crystallites of $\beta\text{-Li}_3\text{PS}_4$ can be observed in amorphous Li_3PS_4 . The activation energy for lithium ion conduction in the LPS glass compositions is between $34 - 50 \text{ kJ mol}^{-1}$. All-solid-state cells have already been produced with sulfide glasses; for example: $\text{In \{anode\} | } 80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5 \text{ (g) \{SE\} | LiCoO}_2 / 80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5 \text{ (g) \{composite cathode\}}$, can be cycled for 200 cycles with a near 100% charge-discharge efficiency using a discharge capacity of 100 mA h g^{-1} .¹²⁶

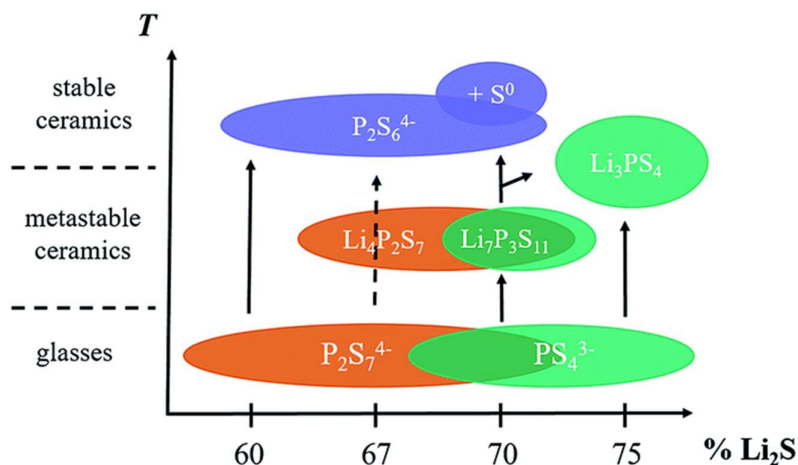


Figure 2.16. LPS phase diagram. Figure adapted from ref ¹¹⁵. (<https://doi.org/10.1039/C7TA06067J>)

Interestingly, heating the LPS glasses above their respective crystallization temperatures (typically $220\text{--}260 \text{ }^\circ\text{C}$), causes the crystallites present in the SE matrix to act as nucleation sites for the formation of highly conducting glass ceramics (gc)

that are inaccessible by simple precursor heating, [Figure 2.16](#). The initial glass composition determines the crystal structures that forms. For example, heating $67\text{Li}_2\text{S}\cdot 33\text{P}_2\text{S}_5$ (glass) forms a glass ceramic with crystals present adopting the thio-LISICON III type structure. The $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (gc) has a crystal structure mainly composed of pyrothiophosphate ions. The $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ (gc) has a thio-LISICON III type structure. $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (gc) has a thio-LISICON II structure and $87.5\text{Li}_2\text{S}\cdot 12.5\text{P}_2\text{S}_5$ (gc) has a thio-LISICON II type structure with unreacted Li_2S present. Most importantly, heating $70\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (g) forms $\text{Li}_7\text{P}_3\text{S}_{11}$ (gc). This composition has an activation energy of 17 kJ mol^{-1} ; this is the lowest of both the glass and gc compositions. Very high room temperature conductivities of up to $\sigma = 1.7 \times 10^{-2}\text{ S cm}^{-1}$ have been observed for $\text{Li}_7\text{P}_3\text{S}_{11}$ (gc).¹²⁷ Although $\text{Li}_7\text{P}_3\text{S}_{11}$ has an exceptional ionic conductivity, it is brittle and more difficult to handle than Li_3PS_4 .

It is worth noting that all LPS electrolytes readily undergo hydrolysis and degrade with atmospheric moisture to form H_2S .¹²⁸ Therefore, synthesis and handling of LPS SEs must always be performed under inert atmospheres or in dry rooms with lower dew points than previously required for the handling of cathode materials; this introduces an additional barrier to industrial cell fabrication. However, LPS SEs can be densified by cold pressing and low temperature sintering ($< 300\text{ }^\circ\text{C}$), which is much less energy intensive than the temperatures required for sintering of oxide ceramics.¹²² Furthermore, recent studies have shown that LPS SEs, most notably $\beta\text{-Li}_3\text{PS}_4$ ($\sigma_{RT} = 1.6 \times 10^{-4}\text{ S cm}^{-1}$), can be produced by wet-chemical methods, which are highly scalable.¹¹⁹

As discussed in **Section 2.4.2**, unlike many ternary and quaternary metal oxides, LPS SEs are not reduced to form MIECs, instead their reduction with the lithium electrode produces an SEI composed of electronic insulators with low ionic conductivity (Li_2S , LiP , and Li_3P). As such, the interfacial resistance between lithium and LPS SEs is significant. Furthermore, the heterogeneity of the SEI, may lead to inhomogeneous current distributions across the interface during cycling. In combination these factors, decrease the effective critical current density at which cell can be plated. The development of a sulfide type SE, with direct electrochemical stability at low potential, or the development of a sulfide type SE which produces a SEI against lithium, that has greater ionic conductivity but low electronic conductivity would be highly desirable. As

such, this supposition is explored in **Chapter 6**.

Chapter 3: Experimental Techniques

3.1.1 X-ray diffraction

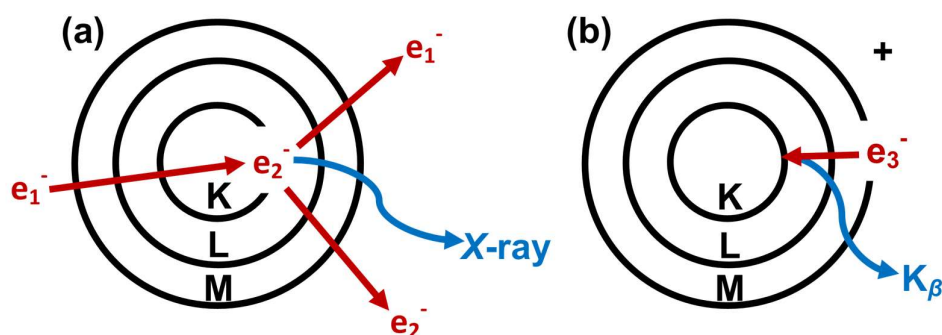
X-Ray diffraction is a powerful technique for determining the structure of crystalline solids. The technique uses x-rays to determine the atomic positions, bond lengths and bond angles in substances with long range order.¹²⁹

3.1.2 Laboratory X-ray generation

Typically, X-rays are generated in laboratory based diffractometers by Joule heating a metallic filament to liberate electrons which are subsequently accelerated via an electric field towards a cooled anode. When the electrons bombard the metal target, core shell electrons are ejected and Bremsstrahlung (white X-ray) radiation is emitted, [Figure 3.1 \(a\)](#).¹³⁰ The emission leaves the metal ion in a highly excited state, therefore electron relaxation from a higher energy shell occurs, which causes quantised X-ray radiation to be emitted with a discrete energy equivalent to the difference in energy between the shells, [Figure 3.1 \(b\)](#).¹²⁹ Using the Siegbahn notation:

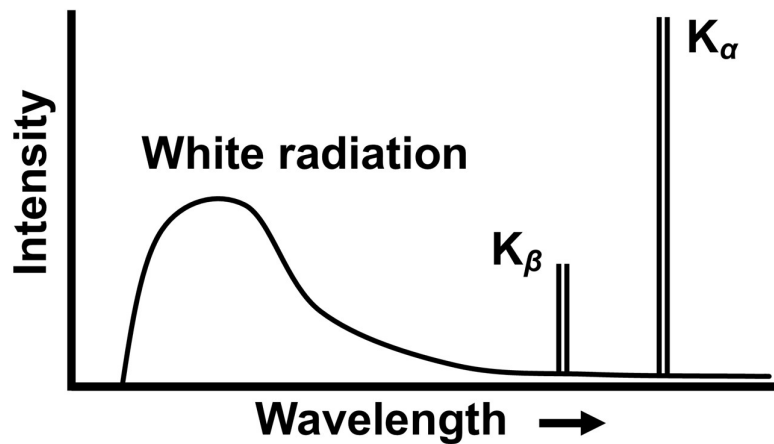
$K_{\alpha} = L \rightarrow K$ transition

$K_{\beta} = M \rightarrow K$ transition



[Figure 3.1](#). Models of: (a) Bremsstrahlung white X-ray radiation production and (b) characteristic X-ray production.

The typical X-ray emission spectrum therefore has white X-rays and has several discrete high intensity emission lines, [Figure 3.2](#). Closer inspection shows that the K_α lines can be resolved into doublets due to splitting of the p orbitals.



[Figure 3.2](#). Illustration of X-ray emission spectrum for a diffractometer anode.

In order to perform diffraction experiments the X-ray radiation is monochromated to a single wavelength by diffraction using a crystal (typically pyrolytic graphite or silicon).

3.1.3 Theory of X-ray diffraction (XRD)

The electromagnetic fields of X-rays are able to interact with the electric fields of electrons in atoms such that X-rays can be scattered off atoms in all directions. When waves are scattered via an ordered lattice, the scattered waves undergo interference. The interference is predominantly out of phase and destructive, however the scattered waves can be in-phase and thereby undergo constructive interference when the Bragg condition is satisfied. This simple model, shown in Figure 3.3, is used to derive Bragg's law as shown below.¹²⁹

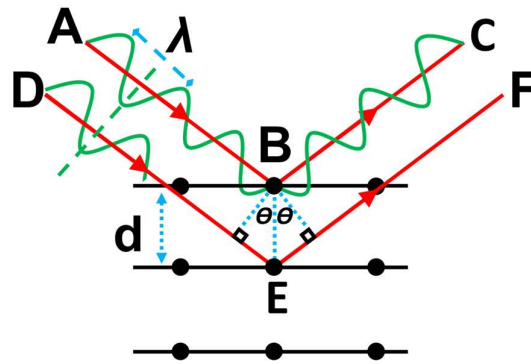


Figure 3.3. Schematic outlining Bragg's Law.

Consider the respective paths traversed by parallel X-ray beams undergoing specular reflection from neighbouring parallel crystallographic planes:

$$\begin{aligned}\overrightarrow{AB} + \overrightarrow{BC} &= \overrightarrow{AC} \\ \overrightarrow{DE} + \overrightarrow{EF} &= \overrightarrow{DF}\end{aligned}\tag{3.1}$$

In order for the reflected waves to be in phase, the Bragg condition asserts that the path difference between the beams, after being reflected by parallel crystallographic planes, must be integral multiples of the wavelength of the X-rays such that the:

$$\text{Path length difference} = n\lambda\tag{3.2}$$

where n is an integer multiple and λ is the wavelength of the incident X-rays.

Since $\overrightarrow{AB} = \overrightarrow{BC}$ and $\overrightarrow{DE} = \overrightarrow{EF}$, the path length difference is equivalent to:¹³⁰

$$\overrightarrow{DE} + \overrightarrow{AB} = \frac{1}{2} d \sin \theta$$
(3.3)

Therefore, Bragg's law can be written as:

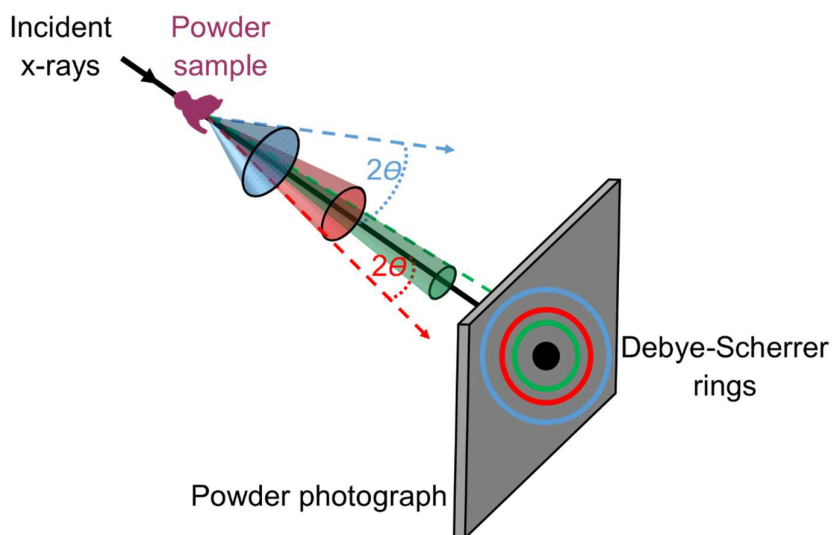
$$n\lambda = 2d \sin \theta$$
(3.4)

where d is the distance between the crystallographic planes.

Performing XRD on a single crystal produces a diffraction pattern comprised of discrete spots which is immensely effectual for determining the structural solution of the crystal. However, the fabrication of large high quality single crystals is non-trivial. For the purposes of phase identification, XRD can be performed on powder samples.

3.1.4 Powder X-ray diffraction (PXRD)

Powders of crystalline materials contain multitudinous randomly orientated crystallites. If monochromatic X-rays are shone on a powder, diffraction will occur because some crystallites will be orientated such that they contain crystallographic planes that satisfy the Bragg condition. The diffracted X-rays will leave the sample at a 2θ angles with respect to the primary beam axis such that the diffracted X-rays lie along the angle of a cone, called a Debye-Scherrer cone. The Debye-Scherrer cone has diffracted X-rays from equivalent d-spacing with different hkl values.¹³⁰ Diffraction is observed from all sets of lattice planes, therefore multiple concentric cones are observed, [Figure 3.4](#). Though it is worth noting there is significant overlap of cones with similar d-spacing. One method for visualising the diffraction pattern is to look at the Debye-Scherrer rings produced on a 2D plane by means of a powder photograph, but this is limited to shallow 2θ angles.¹³¹



[Figure 3.4](#). Schematic of X-ray cones produced by PXRD and the resulting powder photograph.

In a modern X-ray diffractometer, the detector is moved through an arc relative to the X-ray source such that the diffraction intensity can be measured from all angles along a single axis, [Figure 3.5](#). To obtain high quality diffraction patterns, the sample is commonly rotated as this maximises the number of crystallographic planes

contributing to the diffraction pattern. The peak heights depend on the degree of scattering from the respective crystallographic planes, with regions of high electron density producing more scattering. Hence intensities provide information about the atomic structure since heavier elements scatter more than light ones. The peak widths can be affected by number of factors including crystallite sizes and lattice defects.

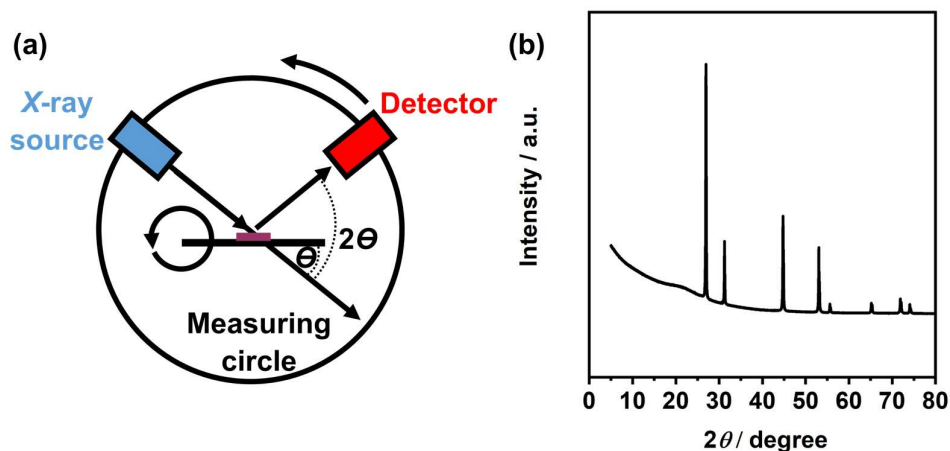


Figure 3.5. (a) Configuration of a X-ray diffractometer for PXRD. (b) Example PXRD pattern of lithium sulfide.

Direct indexing of the crystal structure from the diffraction pattern is challenging. PXRD is commonly used as a fingerprint technique. A diffraction pattern is obtained for a sample and it is then compared with reference patterns from a digital library. Rietveld refinement, a technique which applies a least squares approach to fit the PXRD line profile with Gaussian and Lorentzian contributions, can be used to refine crystal structures, as well as quantify mixtures of crystalline phases.

3.1.5 Grazing incidence X-ray diffraction (GIXD)

Thin films, interfaces and surface layers are often insufficiently thick to probe with conventional PXRD using laboratory spectrometers, especially when light elements with low attenuation coefficients are being investigated. The amount of sample exposed to the X-rays can be increased by irradiating the plane of the sample surface from a shallow angle of incidence (α_i), [Figure 3.6](#). High intensities of X-rays are

necessary for good quality spectra, therefore GIXD usually needs to be performed at a synchrotron.¹³⁰

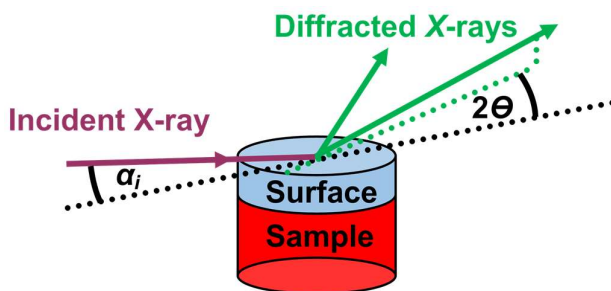


Figure 3.6: Schematic outlining GIXD.

3.2 X-ray photoelectron spectroscopy (XPS)

XPS is analytical technique which can be used to probe the bonding environments of surfaces. In a typical spectrometer, solid samples are placed under an ultra-high vacuum and are then irradiated with monochromatic X-rays of a known wavelength. Energy ($h\nu$) from an incident X-ray can be transferred to an electron in an atom present in the sample. In accordance with the photoelectric effect, if sufficient energy is supplied, the binding energy of the electron (E_b) can be overcome, such that a photoelectron will be ejected from the atom with a kinetic energy (E_k). The kinetic energy of the ejected photoelectron can be measured using a detector. As such, the energy level can be determined.

$$E_b = h\nu - (E_k - \phi) \quad (3.5)$$

Where ϕ is an instrument specific corrective term called the work function (ϕ) which accounts for the energy given up by the photoelectron during detection.¹³¹

The binding energy is unique for different bonding environments. Therefore XPS can be used to determine the elements present in a sample and therefore empirical formulae. XPS is a powerful technique as it can be used to determine the precise oxidation states of elements and the local bonding environments present in the sample. The mean free path of a photoelectron is short in solids therefore only photoelectrons produced close to the sample surface (~ 20 nm) are able to escape

and be detectable.¹³² As such, XPS is a surface sensitive technique, which is useful for interfacial investigations. However, care must be taken in interpreting XPS results, since surfaces are not always representative of the bulk, for example, due to surface contamination. Adventitious carbon is almost unavoidably detected by XPS. As such, it is common practice to employ an ion beam to remove the surface layer of material. The ion beam can be used in conjunction with XPS, for depth profile analysis, which has proven invaluable for the study of interfaces in batteries.

3.3 Raman spectroscopy

The oscillating electric field of a photon is able to interact with the electric field of electrically polarizable molecules such that scattering occurs. Almost all scattering events occur elastically, such that the photon has the same energy before and after scattering; this is termed Rayleigh scattering. Although significantly less frequent, inelastic scattering events also occur. Inelastic scattering produces a scattered photon with either more or less energy than the incident photon.¹³³ Given that the internal energy of a molecule is quantised, the energy difference between incident and scattered photons has a discrete value which is determined by the energy states of the molecule. The net transfer of energy from a photon to the molecule is called the Stokes Shift and this produces scattered light with an increased wavelength. On the other hand, a net transfer of energy from the molecule to the photon is termed the Anti-Stokes shift, [Figure 3.7 \(b\)](#). Raman spectroscopy is a technique that measures the Stokes and Anti-stokes shifts to probe the vibrational and rotational modes of a sample.¹³⁴ Since inelastic scattering is a rare event, Raman spectroscopy employs focused high intensity monochromatic laser light to illuminate the sample. Filters are

then used to remove the Rayleigh scattered light before the scattered light is measured using a photomultiplier and a spectrum is produced, Figure 3.7 (a).

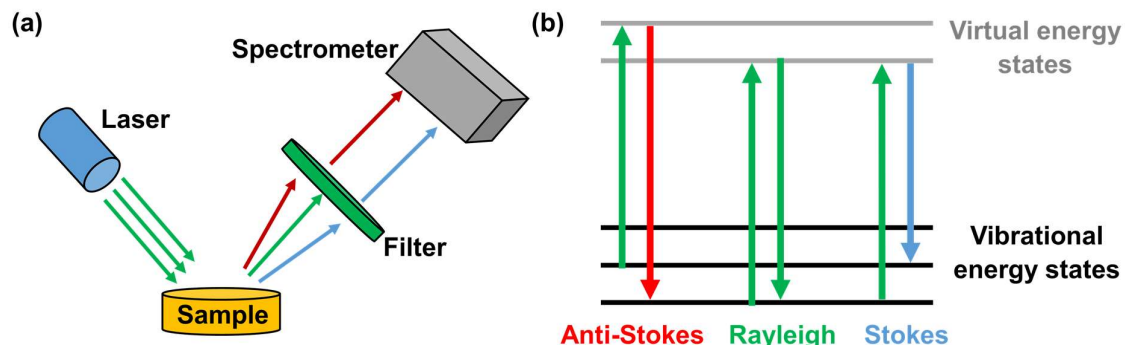


Figure 3.7. Schematic of a basic Raman Spectrometer. (b) Energy level diagram illustrating the types of Raman scattering.

3.4.1 Nuclear magnetic resonance spectroscopy (NMR)

Protons and neutrons are fermions and have $\pm \frac{1}{2}\hbar$ spin angular momentum. Since angular momentum is conserved, atomic nuclei have a nuclear spin value (I) equivalent to the combination of the nucleon spins. There are multiple possible spin states (m_i) for each nucleus as there are multiple allowable spin pairing combinations for every isotope, as shown for hydrogen and deuterium in Figure 3.8.¹³⁵

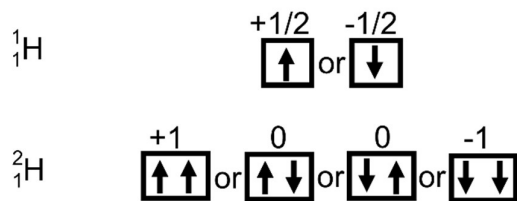


Figure 3.8. The m_i states for hydrogen and deuterium.

Nuclei with integer spin are bosons whereas nuclei with half integer spins are fermions, this can be determined using the simple rules in Table 3.1. Nuclei with spins greater than $\frac{1}{2}$ are said to be quadrupolar.¹³⁰

Proton number	Neutron number	Spin (<i>I</i>)
Even	Even	0
Even	Odd	½-integral
Odd	Even	½-integral
Odd	Odd	Integral

Table 3.1. Method for determining whether a nucleus is fermionic or bosonic according to number of nucleons.¹³⁶

Nuclei are electrically charged therefore nuclei with non-zero spin have an associated magnetic field. The nuclear magnetic moment (μ) is directly proportional to the nuclear spin (I)

$$\mu = \gamma I \quad (3.6)$$

Where γ is the gyromagnetic ratio of the specific isotope.

When an external magnetic field (B) is applied, the magnetic moments of the nuclei will orientate in the magnetic field and the degeneracy of the m_i spin states is lost. The resulting Zeeman splitting produces $2I + 1$ different energy levels with even energy spacing (ΔE), **Figure 3.9**.¹³¹

$$E = m_i \gamma B \hbar \quad (3.7)$$

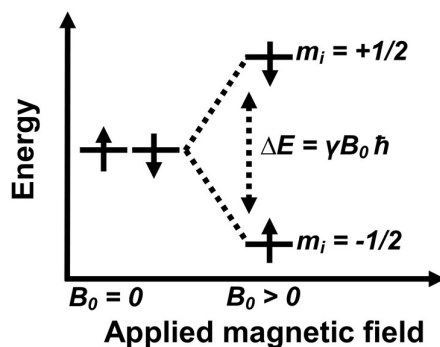


Figure 3.9. Energy diagram showing the Zeeman splitting of degenerate nuclear spin states in hydrogen due to an applied magnetic field.

In the lowest energy state the magnetic moment of the nucleus is aligned parallel with the direction of the magnetic field, whereas in the highest energy state the magnetic moment of the nucleus is aligned antiparallel to the magnetic field. Transitions can occur between the nuclear spin energy levels that obey the $\Delta m_i = \pm 1$ selection rule. For large numbers of nuclei, the ratio of the population of the energy states is given by the Boltzmann distribution, where T is temperature and k_B is the Boltzmann constant. Opposing angular momentums cancel out but there is always a slight nuclei spin excess because more nuclei are always present in the low energy state. Low temperatures and strong magnetic fields favour population of the low energy state therefore NMR spectrometers use cooled superconducting magnets to produce very strong magnetic fields to maximise the bulk magnetisation.

$$e^{-\frac{\gamma B_0 \hbar}{k_B T}} \quad (3.8)$$

The nuclei precess about the axis of the applied magnetic field at a frequency called the Larmor Frequency (ω).

$$\omega = \gamma B_0 \quad (3.9)$$

A radiofrequency (RF) pulse can be used to rotate the bulk magnetisation from the equilibrium position since the RF pulse generates a torque orthogonal to the magnetic field. Under this condition, the magnetic field of the nucleus is out of alignment with the external magnetic field and its precession can be indirectly determined by measuring the resulting induced voltage in a surrounding coil. As precession occurs, energy is lost by free induction decay until the low energy state is restored.

In reality a nucleus is surrounded by electrons. The changing electric field of the orbiting electrons generates a magnetic field which in turn partially shields the nucleus from the external magnetic field. As such, different chemical environments will produce diamagnetic shielding of varying strengths, with regions of greater electron density producing more shielding and decreased the Larmor frequencies. NMR spectroscopy is therefore used to probe the local chemical environments. When NMR measurements are made, a reference compound is usually added to the sample. The resonance frequency of the sample nuclei can then be measured relative to the

reference as a shift. For example, tetramethylsilane is commonly used as a reference for proton NMR. Since spectrometers differ, spectra are normalised to the spectrometer frequency to enable universal comparison.

$$\delta \text{ (ppm)} = \frac{\text{Shift (Hz)}}{\text{Spectrometer frequency (MHz)}} \quad (3.10)$$

NMR is incredibly powerful and is routinely used for structure determination, purity analysis and quantification of phase fractions. Moreover, NMR can be used to study many physical properties like diffusion or solubility.

3.4.2 Magic angle spinning nuclear magnetic resonance (MAS NMR)

When molecules are orientated at different angles with respect to the applied magnetic field they experience different nuclear dipole-dipole interactions and therefore different chemical shifts are observed. In solution, molecules are free to rotate therefore the orientations in the magnetic field are averaged out. Whereas, in the solid state the molecules are not free to rotate so the local fields are anisotropic and the NMR peaks are very broad. The spectral lines can be narrowed by spinning the sample very quickly at an angle of 54.74° with respect to the direction of the magnetic field as this mimics free rotational tumbling of the sample.

3.5 Electrochemical impedance spectroscopy (EIS)

In order to develop better batteries, an understanding of the dielectric properties of materials is needed. EIS is a technique which enables the resistance, capacitance, inductance and other behaviours of different dielectric environments to be resolved with frequency. When an electric field is applied to a system, charged species undergo dielectric polarisation and displace from their equilibrium positions. When the frequency of the applied ac electric field is comparable with the mobility of charge, there is a significant response to the electric field. The mobility of charge differs for different environments (i.e. charge transfer resistance at interfaces, ion conduction in bulk materials, grain boundaries, surface films etc.), consequently, the resistances and

capacitances of different regimes in a physicochemical device can be resolved with frequency. In practice, a small AC excitation voltage is applied to a medium, with angular frequency (ω), with a voltage at time = 0 of V_0 and where V_t is the voltage at a given time (t):

$$V_t = V_0 \sin(\omega t) \quad (3.11)$$

The pseudo-linear AC current response is measured and the resulting phase shift (φ) is determined:

$$I_t = I_0 \sin(\omega t + \varphi) \quad (3.12)$$

where, I_0 is the current at time 0 and I_t is the current at time t . The angular frequency is related to the linear frequency in Hertz (ν) by:

$$\omega = 2\pi\nu \quad (3.13)$$

By measuring the amplitude and phase shift of the response signal, the impedance of the system can be calculated using Ohms Law.¹³⁷

$$V = IR \quad (3.14)$$

$$z \frac{V_t}{I_t} = \frac{V_t \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = \frac{Z_0 \sin(\omega t)}{\sin(\omega t + \varphi)} \quad (3.15)$$

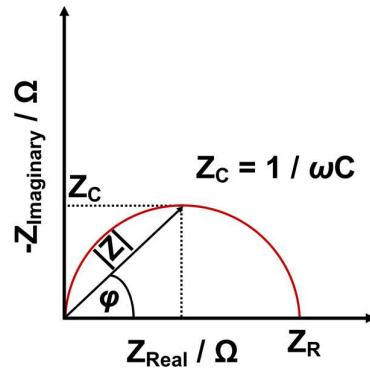
Using the Euler relationship,

$$e^{i\varphi} = \cos \varphi + i \sin \varphi \quad (3.16)$$

the impedance can be represented as a complex number:

$$z(\omega) = \frac{V}{I} = Z_0 e^{i\varphi} = Z_0 (\cos \varphi + i \sin \varphi) \quad (3.17)$$

There are several ways to plot impedance spectra, such as Bode plots (which allow resistance at specific frequencies to be determined) and Lissajous figures (typically displayed by early oscilloscopes); however, Nyquist plots are now the favoured choice among battery scientists for EIS studies due to their ease of interpretation. A Nyquist plot is produced by plotting the imaginary component ($i \sin \varphi$) on the Y axis and the real component ($\cos \varphi$) on the x axis, [Figure 3.10](#).



[Figure 3.10](#). Illustration of a Nyquist plot used in electrochemical impedance spectroscopy. Higher frequencies are on the left hand side of the graph.

Impedance is a vector and has a magnitude ($|Z|$) and a phase angle ($\arg Z$). Capacitance (C) and resistance (R) are related to impedance as follows:

$$|Z| = R \quad (3.18)$$

$$|Z| = \frac{1}{Ci\omega} \quad (3.19)$$

There are often multiple resistance and capacitance contributions to a physical system, therefore the individual impedance contributions of electrochemical cells can be understood by the production of a best fit model using combinations of equivalent circuits. For example, double layer capacitance, electron transfer resistance and electrolyte resistance can be modelled using a Randles cell, with a resistor and non-ideal capacitor in parallel, and with a second non-ideal resistor in series, [Figure 3.11 \(a\)](#). EIS can be performed with blocking electrodes, which prevent charge from moving across the interface, such that the interface acts as a

capacitor, [Figure 3.11 \(b\)](#). Alternatively, when EIS is performed with non-blocking electrodes, charge is able to pass across the electrode / SE interface, therefore the resistance contribution of the interfaces from each side of the cell are observed, [Figure 3.11 \(c\)](#).

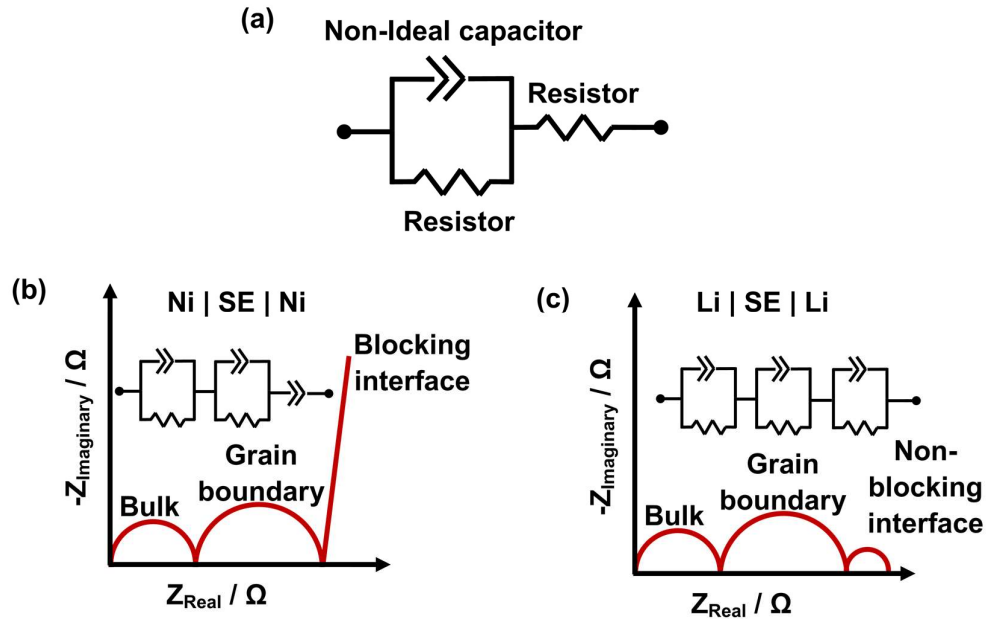


Figure 3.11. (a) Circuit diagram of a Randle cell. Nyquist impedance plots and idealised circuit element diagrams for the respective impedance contributions of a perfect polycrystalline SE with (b) Ni blocking electrodes and (c) Li non-blocking electrodes.

3.6 Galvanostatic cycling

Galvanostatic battery cycling, or chronopotentiometry as it was formerly known, is an electrochemical technique in which the potential (V) of a working electrode is measured with respect to a reference electrode by means a potentiostat, during the passage of a constant current (I), for a given time (t). The technique can be used to study the charge / discharge cycles of cells, within pre-defined voltage windows. As such, this technique can enable the practical capacity of activate materials to be determined and can be used to study the changes in cell performance during operation.

When current is moved at a constant rate, for a given time, a known capacity of lithium ions is moved across the cell, which when normalised to the active mass of the active material (m) in the electrode, can be expressed as a specific capacity (q):

$$q = \frac{I \cdot \Delta t}{m} \quad (3.20)$$

As such, the specific energy (W) of the cell can be determined:

$$W = \int V dq \quad (3.21)$$

The rate of cell cycling is commonly expressed in terms of a C-rate (C/t), where t is the time taken to either fully discharge or discharge the maximum theoretical capacity of the cell (q_{max}).

$$\frac{C}{t} = I = \frac{q_{max} \cdot m}{t} \quad (3.22)$$

In this thesis, galvanostatic cycling is primarily used to study SEs by means of symmetric Li electrodes. In this circumstance, there is no natural potential difference between the electrodes. Therefore a potential is applied to the cell by a potentiostat. Given Ohm's law (equation 3.14), the resistance of the cell can be determined at a specific time which provides great insights into the mechanisms at play during battery cycling, such as dendrite growth, SEI formation, and interfacial contact loss.

3.7.1 Mass spectrometry (MS)

Mass spectrometry is a class of incredibly powerful techniques for the identification and quantification of compounds by measuring the mass to charge ratio of ionised samples. In this work two types of MS were used.

3.7.2 Electron ionisation mass spectrometry (EI-MS)

Gaseous samples are directly flowed into a mass spectrometer with a carrier gas; liquid and solid samples first need to be volatilised. The sample gas is rarefied and a

small portion of sample is allowed to flow through a small pinhole into an ionisation chamber. Thermionic emission is used to generate electrons which are accelerated towards an anode. The high energy electrons bombard the gaseous molecules and induce ionisation. Molecular ions and multivalent molecular ions are consequently generated. Fragmentation of the molecular ions also occurs. The ions are accelerated by means of an electric field and are focussed with a slit to produce an ion beam. As the ions are accelerated through the electric field, they gain kinetic energy:

$$\frac{1}{2}mv^2 = zV \quad (3.23)$$

Where m is the mass of the ion, v is the velocity of the ion, z is the charge on the ion and V is the potential of the electric field.

In benchtop instruments the ion beam is then commonly deflected by a magnetic field (field strength $\mathbf{B}$) onto a detector. Magnetic deflection causes separation of the ions according to their charge to mass ratio. The deflected ions have radii of curvature (r).

$$r = \frac{mv}{z\mathbf{B}} \quad (3.24)$$

The mass to charge ratio can therefore be determined.

$$\frac{m}{z} = \frac{\mathbf{B}^2 r^2}{2V} \quad (3.25)$$

Mass spectrometers commonly employ detectors which produce an electric current when struck by ions, therefore the current detected is directly proportional to the concentration of the ions. In reality few ions reach the detector so electron multiplier circuits are employed to increase signal intensities. EI-MS is most effective for low molecular weight samples ($M_r < 600 \text{ g mol}^{-1}$).

3.7.3 Time of flight secondary ion mass spectrometer (TOF-SIMS)

SIMS is a variant of desorption mass spectrometry in which an ion beam (Cs^+ , Ar^+ , Bi^{3+} , etc.) is used to directly ionise and ablate molecules from the surface of a sample. The ejected ions are accelerated along a flight tube into a detector. The mass to charge ratio (m/z) is established by measuring the time taken (t) for the ions to traverse a flight tube of a fixed length (L).

$$\begin{aligned} \text{Given that } \frac{1}{2}mv^2 &= zV \text{ and } v = \frac{L}{t} \\ \frac{1}{2}m\left(\frac{L}{t}\right)^2 &= zV \therefore \frac{m}{z} = \frac{2Vt^2}{L^2} \end{aligned} \quad (3.26)$$

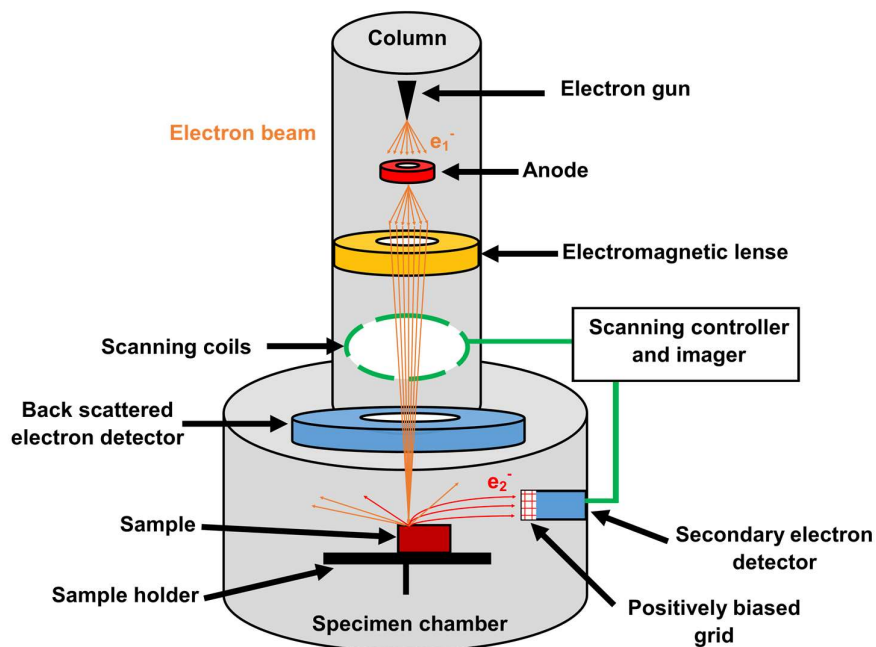
Ablation of the surface occurs layer by layer therefore ToF-SIMS can be used to depth profile samples.

3.8. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES is a type of atomic emission spectroscopy used to identify and quantify the concentrations of elements in a sample. In a typical instrument, a carrier gas such as Argon, is rarefied and is then flowed through the middle of a cooled helical induction coil. A high frequency oscillating electric current is applied to the coil, which induces a changing magnetic field inside the carrier gas. The gas is initially ignited by sparking with a Tesla coil, this produces a small number of ions and free electrons which experience electromagnetic induction and undergo rapid acceleration to produce high energy Eddy currents. When the accelerated ions and electrons collide with carrier gas atoms, further ionisation events are stimulated and an ionised plasma is produced. Solid samples are first dissolved and then peristaltically pumped at a controlled rate into the spectrometer. The solution is then atomised by means of a nebuliser and sprayed into the plasma. The plasma has a sufficiently high energy to break almost all chemical bonds and is able to thermally excite atoms of almost all elements. The atomic emission spectrum is collected. Standard solutions are used to produce concentration calibration curves for elements of interest which enables the concentration of elements in the sample to be quantified therefore ICP-OES is commonly used to determine the chemical formulae of compounds.

3.9 Scanning electron microscopy (SEM)

SEM is a microscopy technique used to image surface topography. In a typical instrument, [Figure 3.12](#), primary electrons are produced by a negatively charged cathode, typically a tungsten wire, by thermionic emission inside a column under ultra-high vacuum. The primary electrons are then accelerated towards the specimen chamber by a positively charged anode which has a central bore hole to allow the accelerated electrons to pass through. At this stage, the electron beam is broad and diverging. Therefore, the electron beam is subsequently focused using an electromagnetic lens. The beam is controlled by an electromagnetic deflector and is rastered over the sample. When primary electrons collide elastically with the sample, they are backscattered and can be detected by a backscattering detector. When primary electrons collide elastically with the sample they are able to knock out secondary electrons, which can then be somewhat directed by a positively biased grid to a secondary ion detector. By mapping the electron count at different sites during rastering, a computer can be used to produce a brightness contrast SEM image of the sample surface.



[Figure 3.12](#). Schematic of a SEM microscope.

3.10 Energy-dispersive X-ray spectroscopy (EDX)

EDX is a type of emission spectroscopy, typically used in conjunction with electron microscopy. When an electron beam is incident upon a sample during SEM, a primary electron (e_1^-) can scatter inelastically off a sample atom; during which, energy is transferred to a core shell electron (e_2^-). As a result, the energy of e_2^- exceeds the binding energy of the shell and as such the secondary electron is ejected from the atom, leaving an excited ion, as was previously illustrated in [Figure 3.1](#). Since the resulting ion now exists in an excited state, with a vacancy in the core shell, electrons in higher energy shells can cascade to the ground state. However energy is quantised, therefore this is accompanied by the emission of an X-ray with a discrete amount energy equivalent to the transition. Given there are multiple allowed transitions and since the energy of the shells is unique for different elements, the resulting X-ray emission spectrum is measured with a detector and can be used to determine the elemental composition of the sample. As such, SEM/EDX can be used to map the elements present at the surface of a sample.

3.11 Transmission electron microscopy (TEM) and electron diffraction

TEM is a powerful and widely used microscopy technique in which a beam of electrons is passed through a sample and an image is collected. As with SEM, electrons are generated by thermionic emission and are focussed into a beam using an electromagnetic lens. However, in TEM the detector is placed beneath the sample, so that the transmitted electrons are directly detected, rather than the scattered electrons. Transmission through the sample changes the amplitude and the phase of the electron wave, with transmission being decreased in regions of high electron density. TEM has outstanding spatial resolution but requires very thin samples.

Since, the wavelength of the electron is on the same order of magnitude as the length scale of typical crystallographic planes, in crystalline solids, when crystals are orientated with respect to the electron beam such that the Bragg criterion is satisfied, diffraction patterns will be produced, as discussed for X-rays in **Section 3.1.3**. As such, TEM can be used to perform electron diffraction and obtain a spot pattern which

can be used to identify the space group and crystal orientation of even very small crystallites.

3.12 X-ray computed tomography (X-CT)

X-CT is a non-destructive 3D imaging technique. When large numbers of X-rays are passed through materials, some X-rays are absorbed. The rate of absorption depends on the total electron density along the path traversed by the x-ray in accordance with the Beer-Lambert Law, where I_0 is the initial intensity of the X-ray beam, I is the intensity of the X-ray beam at a distance x into the sample, μ is the linear attenuation coefficient and ρ is the sample density.

$$I = I_0 e^{-\frac{\mu}{\rho}x} \quad (3.27)$$

When X-rays are passed through an object, they produce a 2D projection. By collecting the projections using a scintillator, from different angles through the sample, typically by rotating the sample along its central axis, a 3D picture can be reconstructed by a computer. Sophisticated algorithms are used to sum the grey levels of the respective projections. However this is non-trivial and is computationally very demanding due to the large number of image slices. Furthermore, machine learning is increasingly used to correct for image slice misalignments, for example due to sample movement during slice acquisition. The precise energy of the X-rays is chosen depending on the elements present in the material under investigation. Small low density objects require low energy X-rays for good absorption and good phase contrast. Whereas, large high energy density objects require high energy X-rays to ensure sufficient X-rays penetrate the sample to be detected. X-CT can be performed using laboratory instruments or at synchrotron beam lines. In this work, microstructural

changes in SEs and changes at buried interfaces in cells were investigated operando with X-CT.

3.13 Quartz crystal microbalance (QCM)

QCM is a technique for analysing small mass changes of surfaces with time. There are multiple variants of this technique, but in this work QCM is used to study the growth of surface films (solid electrolyte | liquid electrolyte interphases) on solid electrolytes during interfacial contact with liquid electrolytes. Solid electrolytes (Li_3N) are seeded atop a gold electrode, which is attached to a quartz crystal resonator. The resonator vibrates the quartz crystal and the frequency of the oscillation is measured by an acoustic wave sensor, which is then digitally recorded. If the mass of the solid materials adsorbed to the gold electrode changes, then the crystal oscillation frequency will vary accordingly and the mass change can be calculated. In these experiments, the solid electrolyte particles (adsorbed to the gold electrode) are suspended in liquid electrolyte and the mass change is examined with time (as possible interphases grow).

Chapter 4: Investigation of the dynamic changes at the metal anode | solid electrolyte interface during cycling

4.1 Abstract

Until recently, lithium metal solid state batteries had only been successfully operated at room temperature for long periods at low C-rates. Short-circuiting is almost always reported due to the growth of lithium dendrites through the ceramic electrolyte, when a critical current density on plating (CCP) is exceeded. This work however establishes the existence of a critical current density for stripping (CCS), ubiquitous to metal electrodes, which has severe implications for the development of solid state batteries. During discharge, the flux of lithium atoms from the metal anode to the solid electrolyte interface must exceed the rate at which lithium is being stripped, otherwise contact loss at the interface will ensue. Since flux of lithium to the interface can be increased through creep, the CCS is dependent of physical conditions, such as applied pressure. The loss of interfacial contact across the remaining interfacial contact points results in the local current density effectively increasing. The resulting voids are not fully refilled during subsequent plating therefore when the critical stripping current is exceeded, voids accumulate and the local current density at the interfacial contact points will continue to increase during cycling. In additional work, with $\text{Li} | \text{Li}_6\text{PS}_5\text{Cl} | \text{Li}$,¹³⁸ and $\text{Na} | \text{BASE} | \text{Na}$ cells,¹³⁹ it was shown that the contact loss due to stripping above the CCS inevitably leads to the current densities exceeding the CCP, therefore leading to cell failure on subsequent plating due to the formation of dendrites. In this Chapter, cells employing a lithium nitride SE were shown to behave somewhat atypically; above the CCS, the over-potential of the stripping electrode increased until the oxidation potential of Li_3N was exceeded, resulting in electrochemical breakdown of the solid electrolyte at the interface in close proximity with voids.

4.2 Introduction

LE based LIBs are a relatively mature technology, with state of the art commercial cells already offering gravimetric energy densities approaching $\sim 300 \text{ Wh kg}^{-1}$; the

theoretical energy density limit of these cells is 390 Wh kg^{-1} .^{25,140} A significantly increased energy density could be achieved by replacing graphitic anodes (372 mA h g^{-1}) with metallic lithium (maximum theoretical specific capacity of 3860 mA h g^{-1} , -3.04 V vs the SHE).¹⁴¹ Despite considerable academic and commercial efforts, a number of unsolved problems preclude the use of a metallic anode with LEs; for example, dendrite growth occurs on charge which leads to short-circuiting and catastrophic cell failure. LEs are highly flammable so thermal runaway presents a real safety risk. Accordingly the metallic lithium anode is widely considered to be incompatible with LEs for practical cells. Dendritic growth in LE arises due to localised depletion of anions therefore it has been posited that replacement of separator/liquid electrolyte by a mechanically rigid ceramic SE with a transference number of unity could mitigate dendrite growth. ASSBs also offer the advantage of improved safety due to the elimination of flammable solvents and highly toxic conduction salts. However, almost all known solid-electrolytes, including near 100 % dense ceramics like LLZTO, undergo short-circuiting when cycled at high current densities due to the growth of lithium filaments through the SE between the electrodes. Several mechanisms for dendrite growth in solids have been proposed but there has so far been insufficient experimental evidence to establish which, if any, is the superior phenomenological description. Experimental determination of the dynamics of the lithium metal | SE interface is critical for understanding dendrite growth and may be key to optimising battery performance. During battery cycling, there are two related kinetic processes that occur at the lithium metal / solid electrolyte interface as shown in [Figure 4.1](#). During discharge, 'stripping' of Li occurs. During stripping, dissolution of lithium atoms from the anode into lithium ions in the solid electrolyte occurs. Upon charge, the reverse process 'plating' occurs. The kinetics of plating and stripping processes are not the same, which may have significant implications for ASSBs.

Therefore, in this work, experiments were performed to resolve the dynamics of plating and stripping of the Li | SE interface.

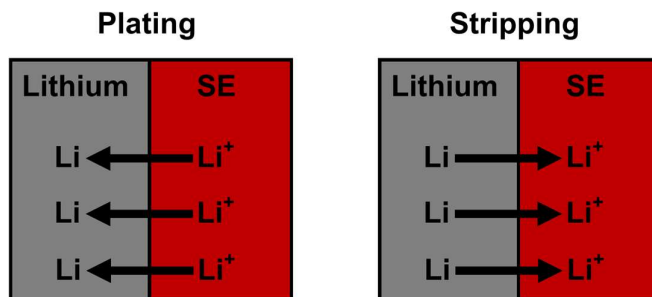


Figure 4.1 Illustration of ion current flow during lithium plating and lithium stripping of a lithium electrode; electron flow is not illustrated but occurs via an external circuit.

Li_3N has properties that are advantageous for fundamental investigations of the lithium | SE interface during cycling. Polycrystalline Li_3N has a reported room temperature ionic conductivity of $\sim 6.6 \times 10^{-4} \text{ S cm}^{-1}$ and an activation energy for intercrystalline ionic conduction of 68.5 kJ mol^{-1} , which is comparable with other state of the art SEs such as garnets, lithium thiophosphates and argyrodites.¹⁴² Unlike, the sulfide based SEs, Li_3N is electrochemically stable at 0 V versus lithium metal and therefore should not react to form an SEI, which would otherwise complicate analysis. Although garnet based SEs, especially LLZO and LLZTO, have garnered much attention, these materials are reported to have somewhat unique grain boundary chemistries that are not necessarily representative of all SEs. Furthermore, LLZO contains highly X-ray attenuating elements (lanthanum and zirconium) and is therefore impracticable for imaging of dendrite growth by X-CT, whereas Li_3N is an ideal material for operando X-CT investigations since nitrogen and lithium are relatively X-ray transparent.

In this chapter, a procedure for reproducibly producing dense, relatively clean pellets of Li_3N is established and their surface chemistry is examined. A series of galvanostatic cycling experiments are performed with Li | Li_3N | Li symmetric cells, using two and three electrode configurations, which allows the processes of plating and stripping to be resolved. A process of void formation (agglomerated vacancies) is found to occur in the metallic electrode during stripping at current densities exceeding

a critical limit. The phenomenon is explored and a model with potential ubiquity for metal anode | SE interfaces is proposed.

4.3.1 Sample preparation

In order to investigate the Li | Li₃N interface, a reliable method for producing highly dense pellets of single polymorph Li₃N, with outstanding ionic conductivity was needed. Single polymorph Li₃N could not be purchased commercially. The Li₃N precursor used in these studies contained α -Li₃N ($\sigma_{298\text{ K}} = 5.8 \times 10^{-4} \text{ S cm}^{-1}$) and β -Li₃N ($\sigma_{298\text{ K}} = 2.1 \times 10^{-4} \text{ S cm}^{-1}$). There are reports of a γ -Li₃N polymorph forming under extreme pressures (> 200 GPa),¹⁴³ but these pressures are not accessed in this study. Only α -Li₃N and β -Li₃N are fast ion conductors with relevance to battery applications, [Figure 4.2](#).¹⁴⁴ As discussed in **Section 2.7.3**, careful control of hydrogen doping, can also be used to maximise ionic conductivity.

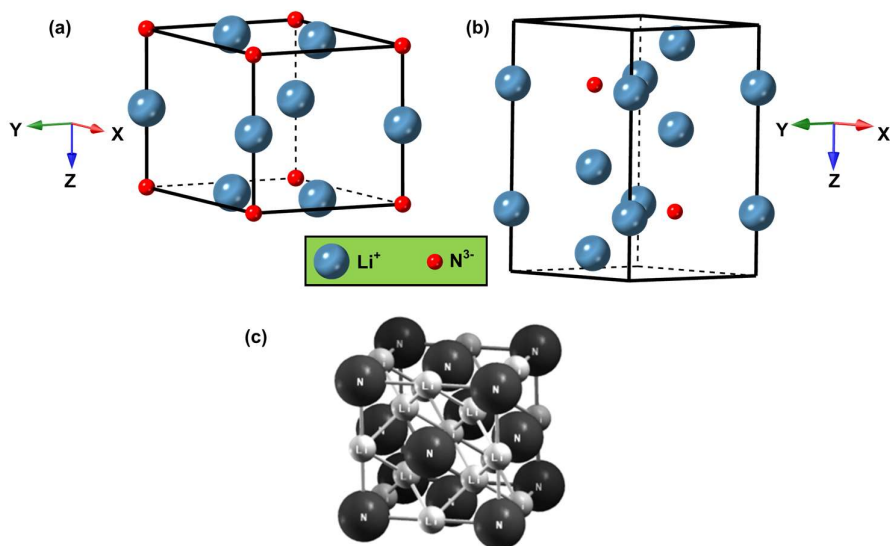
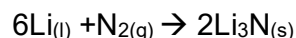


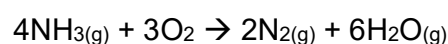
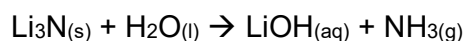
Figure 4.2. Crystal structures of Li₃N made using literature parameters from the ICSD crystallographic database: (a) α -Li₃N (P6/mmm), and (b) β -Li₃N (P63/mmc). Raw crystallographic data unavailable for γ -Li₃N, therefore structure from figure in ref 145 provided for (c) γ -Li₃N (Fm3m).^{146,147}

Li₃N was first synthesised by Ouvard in 1892 by heating Li in a stream of N₂ gas.⁷² This method was refined by Masdupuy and Gallais who showed that Li₃N could be produced by heating lithium at 400-450 °C under nitrogen in an iron pipe.¹⁴⁸ However,

this method produces relatively impure Li_3N (92.69 % evaluated purity).¹⁴⁹ In the modern context, lithium nitride is synthesised either by reacting lithium with a N_2 / Ar mix at 800°C, or by heating Li to 180 °C under N_2 gas at 6 atm pressure for several hours.¹⁴²



However, synthesis of large quantities of Li_3N is dangerous since Li_3N powder reacts violently with moisture to produce hot NH_3 , which ignites and results in an explosion.



This property was exploited during World War II, when a specialised incendiary bomb was designed which used a lithium nitride core.¹⁴⁹ In light of this, commercial Li_3N powder (99.6 %, Alfa Aesar) was used to produce pellets so that all stages of experiments could be performed inside an inert argon glovebox atmosphere as safely as possible. However, commercially available Li_3N contains both α - Li_3N and β - Li_3N polymorphs. Although α - Li_3N can be converted to β - Li_3N by ball milling,¹⁴⁴ it is more logical to convert β - Li_3N to α - Li_3N since α - Li_3N has higher ionic conductivity and is stable at the high temperatures required for sintering; cold pressing of Li_3N alone does not produce pellets with effective inter-grain Li^+ ion transport, as was demonstrated by measuring the ionic conductivity of a cold pressed Li_3N pellet with indium blocking electrodes, [Figure 4.3](#).

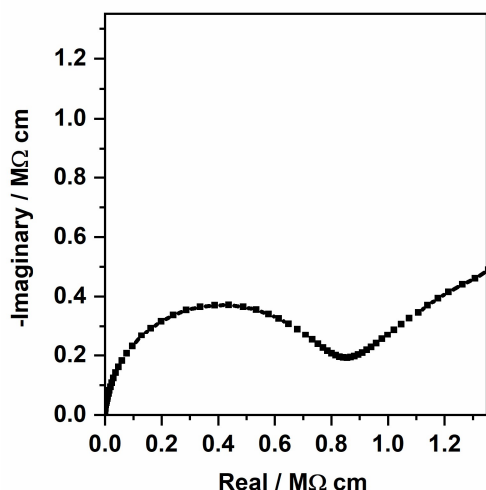


Figure 4.3. Nyquist plot of unsintered cold pressed Li_3N pellet with indium blocking electrodes (4.2 mm electrode diameter, 2.21 mm thick pellet).

Reported Li_3N sintering methods,¹⁴² outlined in the experimental, failed to produce high quality $\alpha\text{-Li}_3\text{N}$ pellets. In order to establish an effective sintering procedure, PXRD patterns were acquired during the heating and subsequent cooling of a cold-pressed Li_3N pellet under an inert argon atmosphere, **Figure 4.4(a)**. A PXRD pattern reveals that precursor Li_3N is a polymorphic mixture of $\alpha\text{-Li}_3\text{N}$ ($P6/mmm$) and $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$) with Li_2O ($Fm\bar{3}m$) contaminants also being observed. Given the low atomic masses of the elements in this system, it was important to ensure a low background, therefore the PXRD pattern was acquired using a single crystal silicon diffraction plate (no background noise from $2\theta = 20\text{-}120^\circ$ for Cu K_α). *In-situ* thermal X-ray diffraction of the Li_3N pellet was performed atop an inert carbon foil, whose prominent peak at $\sim 26.7^\circ$ was observed in the sample diffraction patterns at offset values due to the height difference between the carbon foil and the top of the pellet. Li_3N reacts with almost all materials at high temperature, including platinum, gold and ceramics, therefore the choice of crucible is very restricted; even iron boats which are used for Li_3N synthesis react with Li_3N above 500°C and therefore cannot be used for sintering.¹⁴⁹ Upon heating ($\geq 250^\circ\text{C}$), $\beta\text{-Li}_3\text{N}$ appeared to undergo a phase transition to $\alpha\text{-Li}_3\text{N}$.¹⁵⁰ The crystallinity of the sample was lost above 700°C as the sample melted, **Figure 4.4(a)**. The melting point of pure Li_3N is reported to be 814°C ; the presence of Li_2O impurities is likely responsible for the observed depressed melting point. Molten Li_3N appears to react with the carbon foil to produce Li_2CO_3 ($C1\ 2/c1$)

and Li_2C_2 (*Immm*). Consequently, Li_3N pellets were sintered at a limited temperature of 600 °C, [Figure 4.4\(b\)](#). Cooling at a rate of 10 °C min⁻¹ limits time available for the α - Li_3N to β - Li_3N transition at ~ 250 °C, therefore the sintered pellet becomes trapped in a predominantly α - Li_3N phase at room temperature. Rietveld refinements performed using the GSASII software indicate that the thermal treatment in [Figure 4.4\(b\)](#) changes the α - Li_3N : β - Li_3N ratio from 49.6 % : 50.4 % in the precursors to 95.8 % : 4.2 % in the cooled sintered pellet, [Appendix 1](#). To avoid thermal shock, rapid quenching of the pellets was not explored. After cooling, an XRD pattern was taken of the Li_3N pellet surface which had been in contact with the carbon foil during the sintering process; diffraction peaks corresponding to Li_2CO_3 and Li_2C_2 impurities were not observed, [Figure 4.4\(b\)](#), implying that solid Li_3N did not react with the foil to any significant extent during sintering. This was not the case when alternative crucible materials such as gold and zirconium oxide were used.

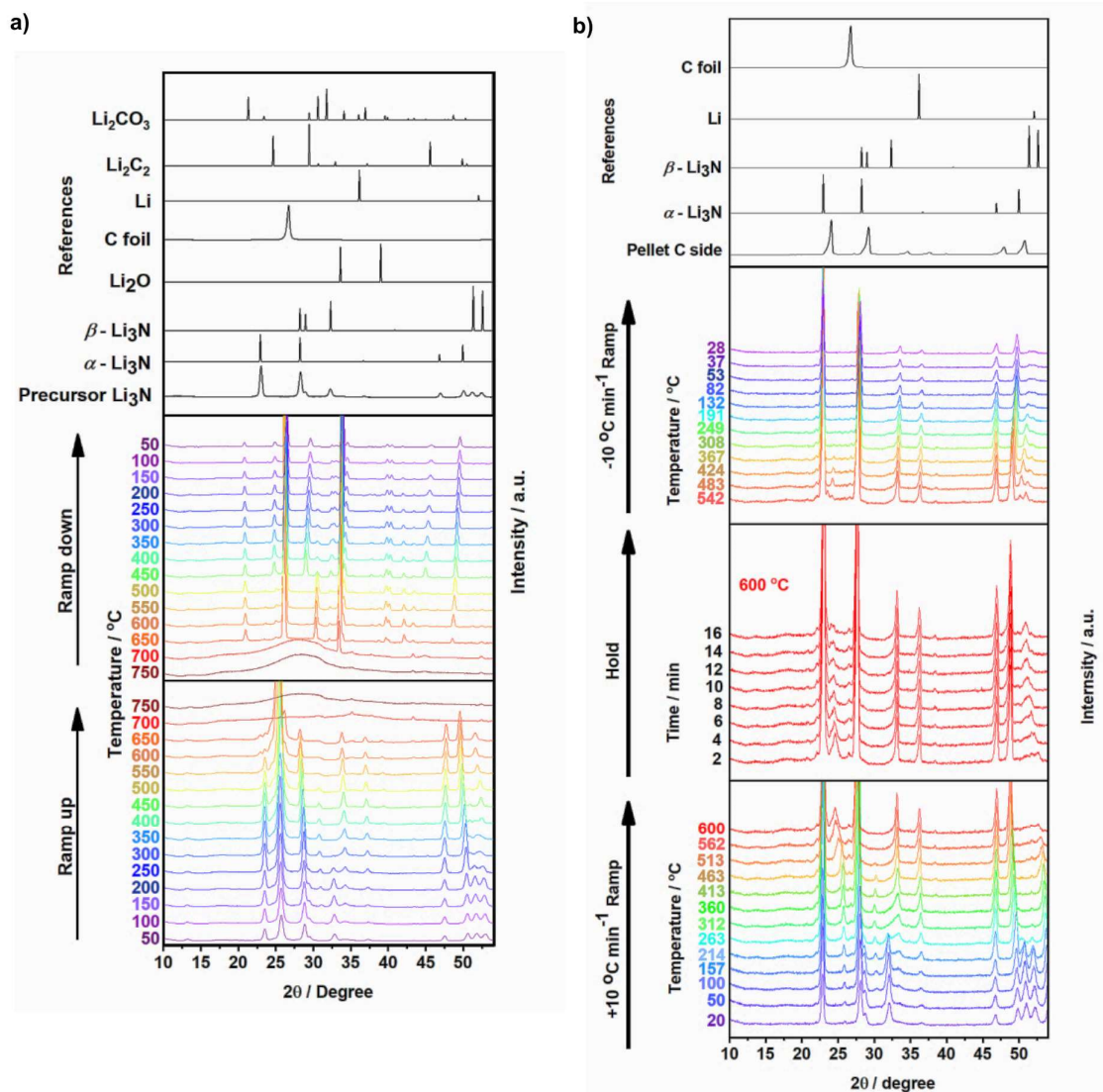


Figure 4.4. XRD diffraction patterns acquired *in-situ* during the sintering of Li₃N pellets. (a) Heating in 50 °C increments, with 15 min hold times, up to 750 °C. (b) Sintering procedure used for α-Li₃N pellet production; 10 °C min⁻¹ ramp to 600 °C, with 15 min hold time, followed by 10 °C min⁻¹ cooling to room temperature. Reference diffraction patterns are displayed for: Li₂CO₃ (*C1 2/c1*)¹⁵¹, α-Li₃N (*P6/mmm*)¹⁷², β-Li₃N (*P6₃/mmc*)¹⁴⁶, Li₂O (*Fm3̄m*)¹⁵², Li₂C₂ (*Immm*)¹⁵³ and lithium metal (*Im3̄m*)¹⁵⁴. I prepared the samples and performed the experiment with assistance from Dr. Robert House. The relative concentration of α-Li₃N and β-Li₃N phases present pellet (b) were compared before and after the thermal treatment by Rietveld Refinement, see Appendix 1.

Once this method of producing pellets (density ~ 88-90 % of theoretical density) with greater α-Li₃N content was established, it was imperative to study the cleanliness of pellet surfaces. The surfaces of the sintered Li₃N pellets were found to be rich in

oxygen after sintering, [Figure 4.5](#), indicating the presence of significant surface contaminants. Lithium hydroxide, lithium oxide and lithium carbonate are commonly found on the surfaces of ceramics such as SEs and electrodes, and in recent years significant effort has been dedicated to the development of polishing methods for their removal. However, a surface polishing method had hitherto not been reported for Li_3N .

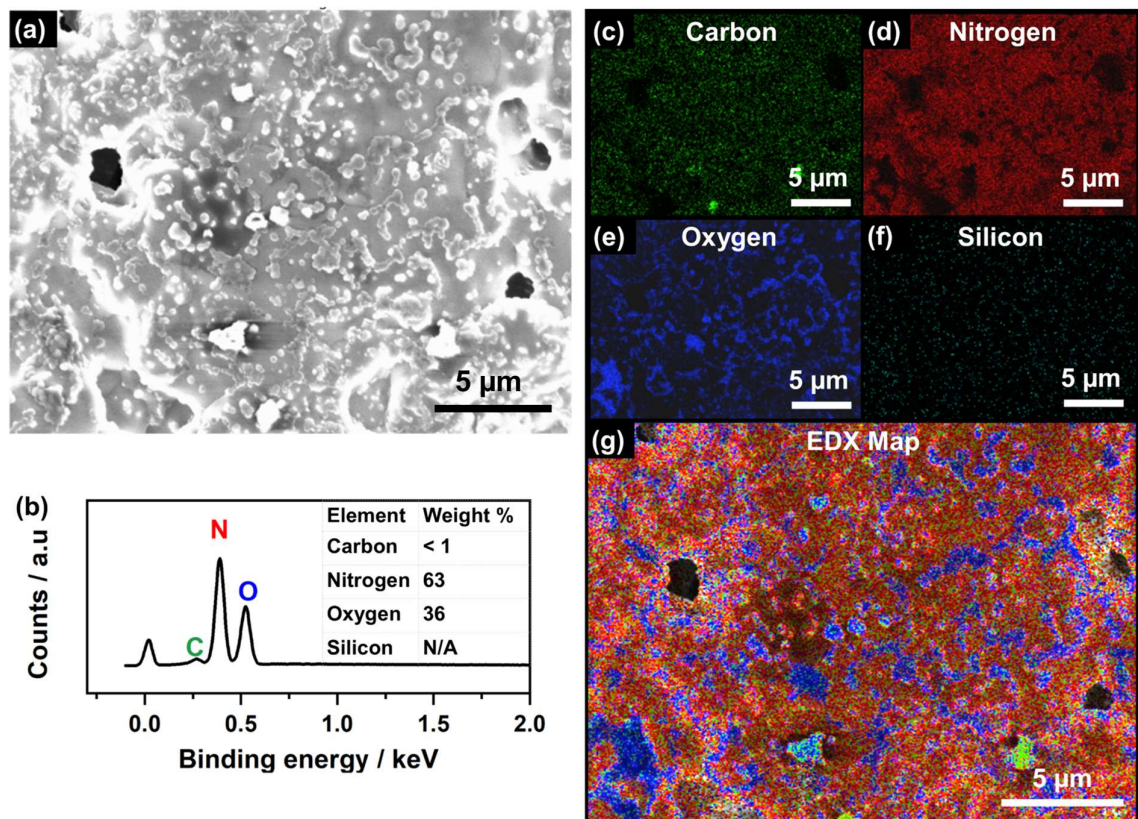


Figure 4.5. Unpolished surface of Li_3N pellet after sintering. (a) SEM image. (b) EDX spectrum of Li_3N Surface; the peak at 0 keV is the strobe peak. EDX surface mapping for: (c) carbon; (d) nitrogen; (e) oxygen (f) silicon (g) elements combined.

Unlike LLZTO, Li_3N cannot be polished with water due to the rapid, occasionally explosive, formation of NH_3 and stable LiOH . Unlike other SEs, Li_3N could also not be polished with ethanol or isopropyl alcohol as Li_3N reacts with alcohols to produce ethers.¹⁵⁵ Furthermore, Li_3N cannot be effectually polished with most non-protic organic solvents or ethylene glycol without the formation of a highly resistive surface layer as shown in [Figure 4.6](#).

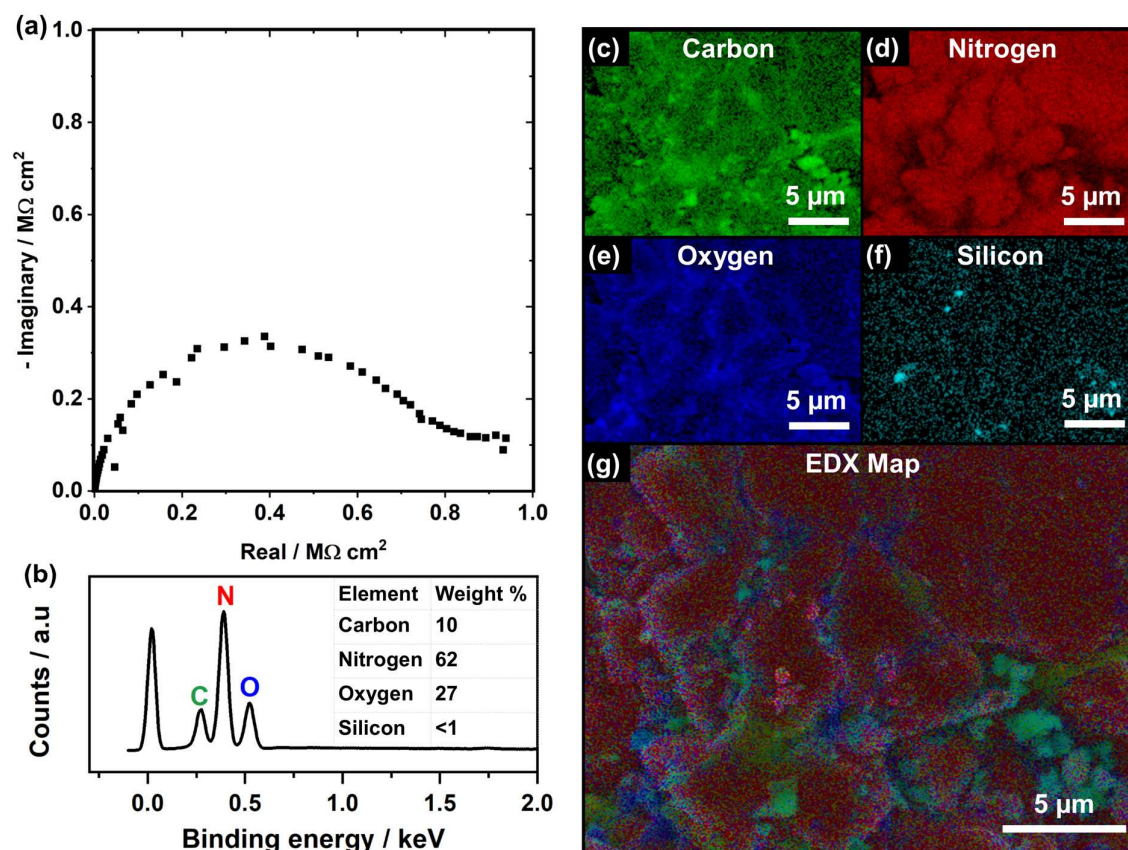


Figure 4.6. Sintered Li_3N pellet (1.5 mm thick) after polishing using tetrahydrofuran showing the formation of a highly resistive surface layer. (a) Nyquist impedance normalised to area of one electrode (4.8 mm) for the $\text{Li} | \text{Li}_3\text{N} | \text{Li}$ cell. (b) EDX spectrum of a Li_3N Surface; the peak at 0 keV is the strobe peak of the instrument. EDX surface mapping for: (c) carbon; (d) nitrogen; (e) oxygen (f) silicon (g) elements combined.

As detailed in the experimental section significant surface contamination could be removed using a dry polishing method, [Figure 4.7](#). Which resulted in a $\text{Li} | \text{Li}_3\text{N}$ interface with significantly decreased resistance, [Figure 4.7 \(a\)](#). Although, substantial contamination was removed, oxygen containing contaminants were still observed on the Li_3N after dry polishing and small traces of silicon from the silicon carbide polishing grit were observed.

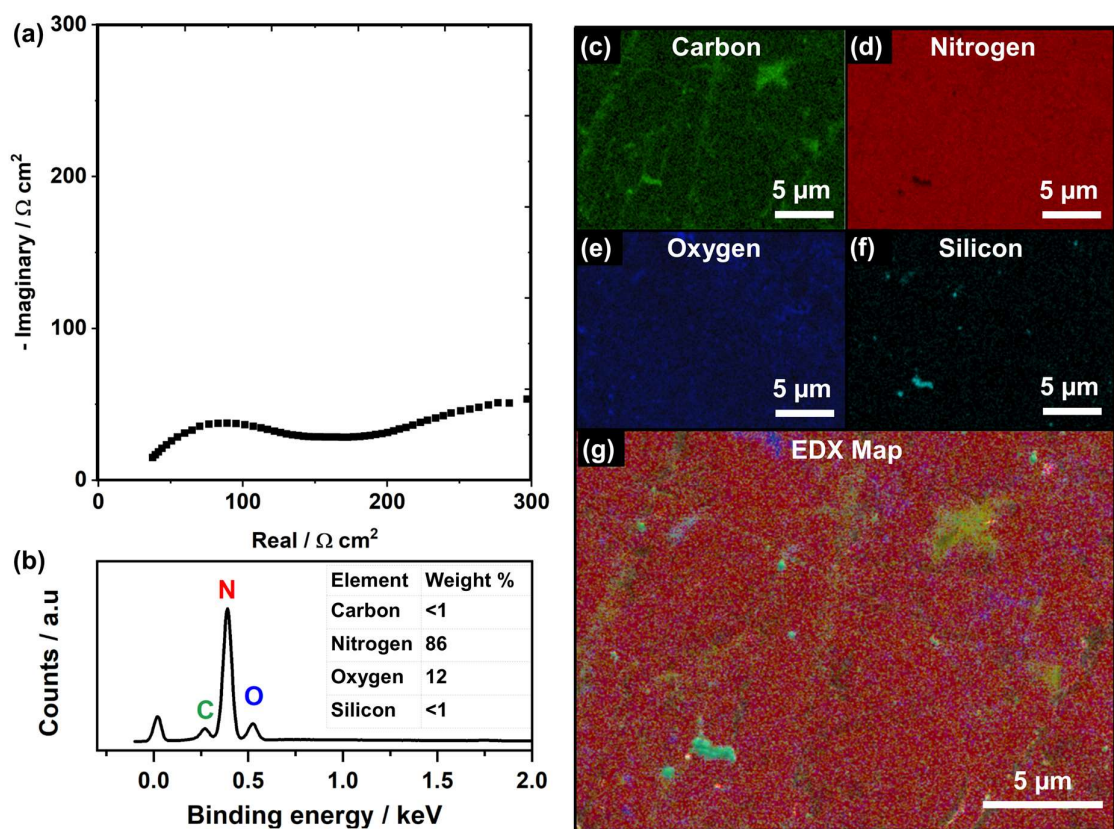


Figure 4.7: Surface analysis of sintered Li_3N pellet (1.1 mm thick) after dry polishing. (a) Nyquist impedance normalised to area of one electrode (2.2 mm) for the $\text{Li} | \text{Li}_3\text{N} | \text{Li}$ cell. (b) EDX spectrum of the Li_3N Surface; the peak at 0 keV is the strobe peak due to the instrument. EDX surface mapping for: (c) carbon; (d) nitrogen; (e) oxygen (f) silicon (g) elements combined.

In order to establish whether the pellet surface could be further cleaned, depth profiling XPS was used to compare the surface of the pristine polished sintered pellet with unsintered precursor Li_3N , which had also been cold pressed into a disk. C 1s XPS indicates that there is a significant concentration of adventitious aliphatic carbon at the surface of both pellets, [Appendix 2](#). Aliphatic carbon was detected at all penetration depths, therefore, spectra were charge corrected to 284.8 eV to allow binding energy comparisons.⁵⁴ Additional C 1s XPS overlapping peaks are present at 289.8 eV and 288.8 eV in pristine and cold pressed Li_3N pellets respectively, these binding energies are typical of carbonate species and indicate the presence of a surface layer containing Li_2CO_3 and organic carbonates.^{156,157} Peaks consistent with carbonate species were also observed at 531.3 eV by O 1s XPS, [Figures 4.8 \(a\)-\(c\)](#).¹⁵⁸ At all penetration depths, O 1s spectra contained a peak at 528.3 eV, indicating that Li_2O

contaminants are present in the precursor Li_3N powder.¹⁵⁸ The Li 1s XPS spectra, shown in [Appendix 3](#), appear to contain 'a relatively broad peak', which is thought to be comprised of multiple overlapping peaks due to the multiple lithium containing phases present on the pellet surface. The Li 1s peak shifts to higher binding energies with increased depth into the pellet surface, consistent with a chemically distinct surface layer. Accordingly, a large increase in N 1s XPS signal intensity was observed at increased sample depths, [Figure 4.8 \(d\)](#), the corresponding N 1s spectra are presented in [Appendix 4](#). The only conclusion that is drawn from the N 1s spectra, is that there is increased nitrogen at increased depths in the pellet. The nitrogenous species responsible N 1s XPS peaks are not assigned because after long sputter times, the N 1s spectra appear to contain an uncommonly low binding energy peak at ~393 eV; the species responsible for this peak is not understood and it is suggested that it could be an artefact of the sputtering ion ablation process. It is suggested that follow-up XPS investigations are required.

Examination of C/O ratios, [Appendix 5](#), indicates that the Li_2CO_3 rich surface layer was equally thick for the cold-pressed pellet and the polished sintered pellet, which suggests that the layer is either formed by a reaction with trace CO_2 in the glovebox atmosphere or in the transfer holder. Experiments were repeated with freshly regenerated gloveboxes and minimised exposure times to preclude the possibility of avoidably poor glovebox atmospheres having corrupted the results, however the surface layer was still observed with equivalent thickness for the cold-pressed Li_3N .

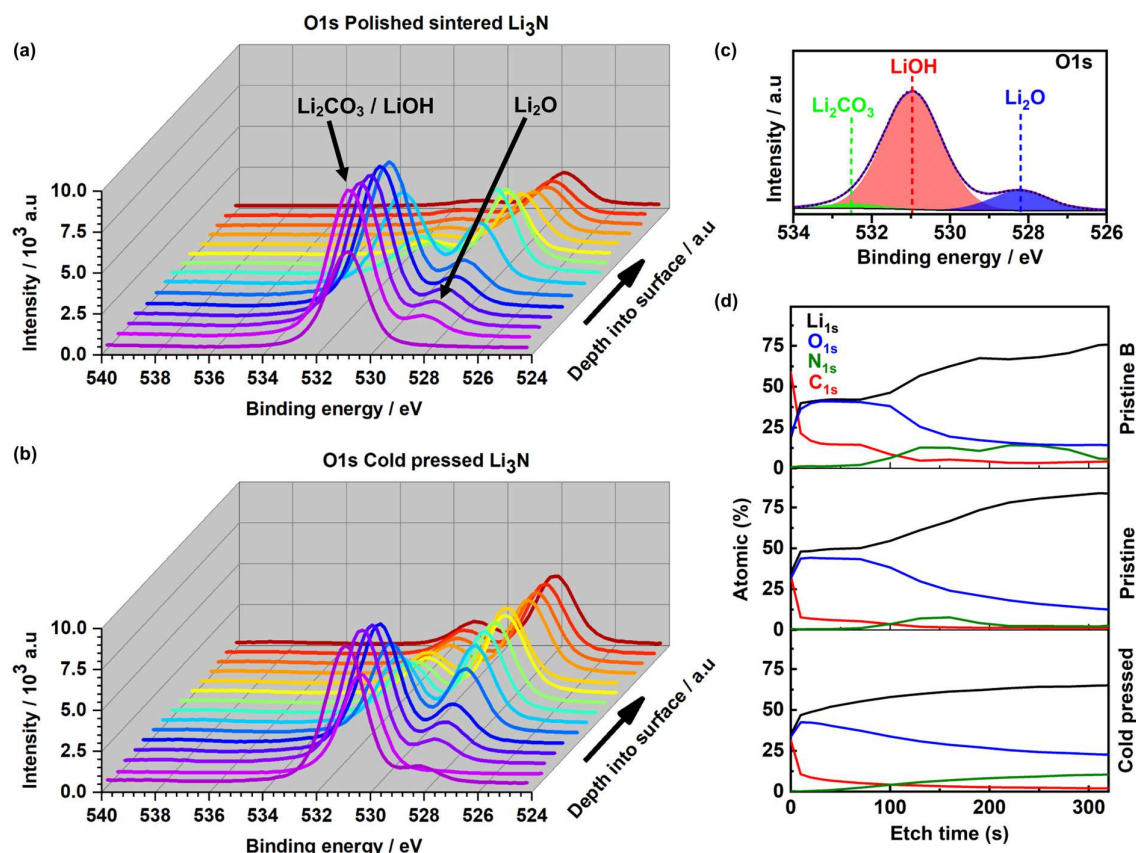


Figure 4.8. Depth profiled O1s XPS spectra of (a) Li₃N pellet after sintering and dry polishing, & (b) Cold pressed Li₃N pellet. (c) Deconvoluted O1s spectrum of polished Li₃N acquired after 10s of sputtering. (d) XPS derived relative elemental composition of the pellets with sputter depth. I prepared the samples and interpreted the data; the spectral acquisition was performed by Dr. Philip Holdway.

Using a pouch cell, [Figure 4.8 \(d\)](#), of custom internal design, [Figure 4.8 \(b\)](#), the ionic conductivity of this optimised polished sintered Li₃N pellet was examined using 2-electrode EIS. Using In blocking electrodes, the activation energy for ion conduction was determined to be ~ 0.18 eV, [Figure 4.8 \(a\)](#), and the ionic conductivity of the pellet was found to be $2.5 \times 10^{-3} \text{ S cm}^{-1}$ at 30 °C, [Figure 4.8 \(a\)](#). This outstanding ionic conductivity, is consistent with some of the fastest Li₃N SEs reported; indicating that beneficial hydrogen doping, from unavoidable impurities, as discussed in **Section 2.7.3**, is successfully achieved with the method herein developed.

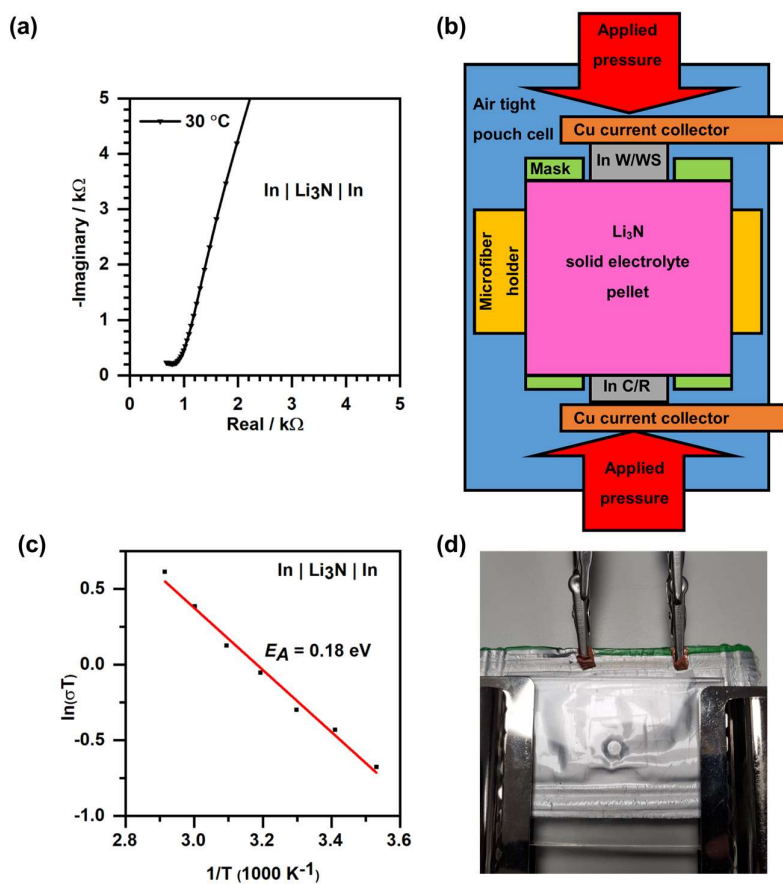


Figure 4.9. (a) Nyquist electrochemical impedance spectrum of Li_3N pellet (1.51 mm thick) with symmetric blocking indium electrodes (3 mm respectively). (b) Design schematic for a pouch cell. (c) Temperature dependence of ionic conductivities for Li_3N . (d) Photograph of clamped pouch cell during operation.

4.3.2 Cycling of Li | Li₃N | Li cells

In order to explore the Li₃N | Li interface, Li | Li₃N | Li symmetric cells were assembled as outlined in the experimental. Two-electrode galvanostatic cycling experiments were performed at current densities of 0.1, 0.2 and 0.5 mA cm⁻² respectively. In accordance with Ohm's law, higher potentials were required to achieve cycling at increased current densities. However, the application of pressure during cycling was found to have a profound effect. Under 3 MPa of applied pressure, the polarisation did not remain flat throughout the cycling process, instead the voltage increases after some capacity has been moved. Comparison of [Figure 4.10 \(a\), \(b\) & \(c\)](#) reveals that the increase in polarisation is most pronounced at high current density. [Figure 4.10 \(e\) & \(f\)](#) reveals that increased applied pressure (7 MPa) somewhat reduces the voltage required for cycling.

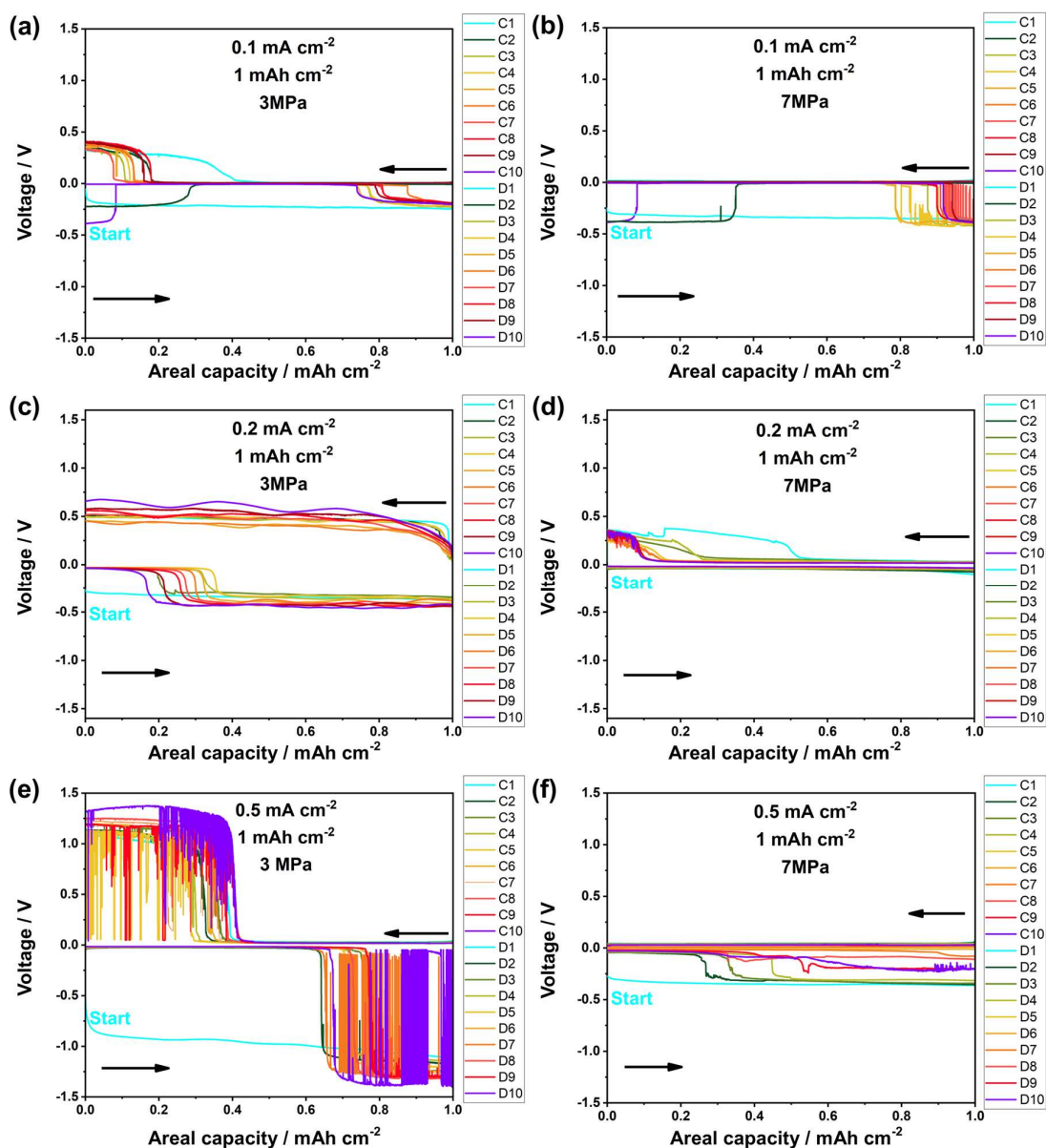


Figure 4.10. Voltage versus charge passed for two-electrode cells (1.5 mm electrode diameter) over $\times 10$ 1 mA h cm⁻² cycles. (a) 0.1 mA cm⁻², 3 MPa, 1.1 mm thick; (b) 0.1 mA cm⁻², 7 MPa, 1.3 mm thick; (c) 0.2 mA cm⁻², 3 MPa, 0.9 mm thick; (d) 0.2 mA cm⁻², 7 MPa, 1.4 mm thick; (e) 0.5 mA cm⁻², 3 MPa, 1.4 mm thick; and (f) 0.5 mA cm⁻², 7 MPa, 1.0 mm thick.

These preliminary cycling results are somewhat complicated by an unusual first cycle behaviour. When lithium electrodes were cold pressed onto the surface of Li₃N, large differences in the initial resistance of the cell was observed indicating variability between the Li | Li₃N interfaces. The voltages of the respective first half-cycles (D1) are significantly elevated with respect to the subsequent half-cycle (C1) for all

Li | Li₃N | Li symmetric cells shown in [Figure 4.11](#), indicating that electrochemical preconditioning occurs during D1. It is postulated that cold pressing the lithium electrodes onto the surface of the SE does not produce a good initial anode | SE interfacial contact. In a symmetric cell, if the voltage is determined by the interfacial resistance of the stripping side electrode (as subsequent results indicate), then poor starting interfacial contact will produce a high voltage on the first half cycle. Whilst lithium is stripped from the counter electrode, it is simultaneously electrochemically plated onto the working electrode thereby improving interfacial contact between the working electrode and the solid electrolyte, [Figure 4.11](#). Therefore, when the current direction is reversed, stripping will occur from an electrode with good SE interfacial contact. Poor starting interfacial contact therefore inevitably produces asymmetry between the electrodes and perturbs the results. Clearly, good initial contact between SE and Li is vital if proper conclusions are to be drawn from cycling data.

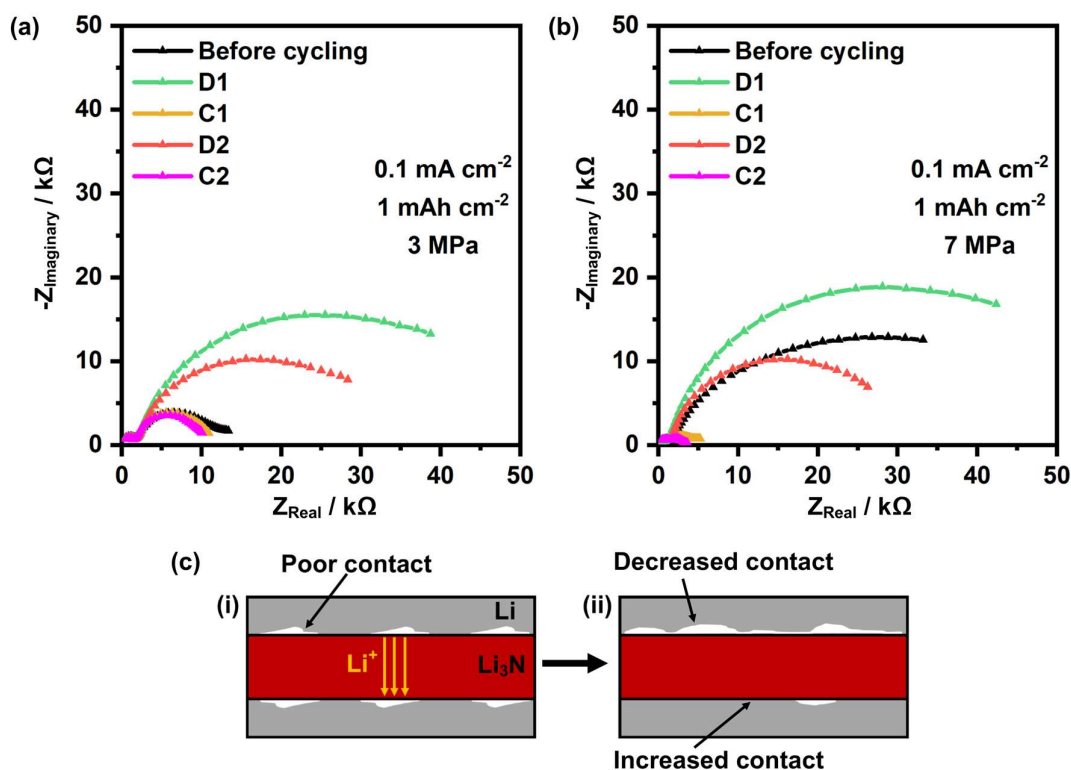


Figure 4.11. Nyquist plots showing the change in interfacial impedance for 2- electrode cells with cold pressed Li electrodes (1.5 mm diameter) under pressures of (a) 3 MPa (1.1 mm thick pellet) and (b) 7 MPa (1.3 mm thick pellet). (c) Illustration demonstrating how poor initial lithium electrode | SE contact leads to asymmetry between the electrodes during cycling.

A method for depositing lithium by thermal evaporation was developed and was used to produce $\text{Li} | \text{Li}_3\text{N} | \text{Li}$ cells with effectual $\text{Li} | \text{Li}_3\text{N}$ interfacial contact, see **4.5 Experimental**. Such cells did not display exaggerated voltage on the first half cycle, [Figure 4.12](#). However, pressure dependent polarisation behaviour was still observed during cycling. Under 3 MPa of applied pressure, the polarisation increased over the period of galvanostatic cycling at current densities of 0.1, 0.2 and 0.5 mA cm^{-2} respectively. Under 7 MPa of applied pressure, flat voltage profiles were observed at 0.1 mA cm^{-2} and 0.2 mA cm^{-2} . Under 7 MPa of external load, polarisation increased during cycling at 0.5 mA cm^{-2} .

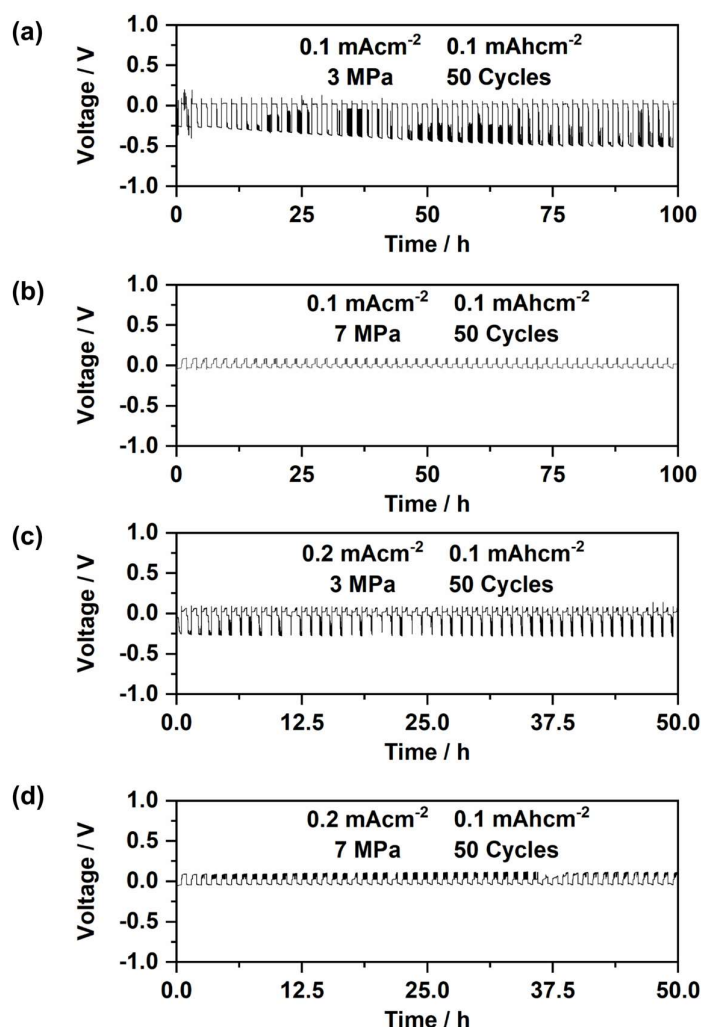


Figure 4.12. Galvanostatic cycling of Li | Li₃N | Li (with sputtered electrodes, 1.5 mm diameter, pellets all 1.3 mm thick), for x50 0.1 mAhcm⁻² cycles, using: (a) 0.1 mAcm⁻², 3 MPa; (b) 0.1 mAcm⁻², 7 MPa; (c) 0.2 mAcm⁻², 3 MPa; and (d) 0.2 mAcm⁻², 7 MPa.

In order to establish whether the polarisation was driven by a stripping side or a plating side process, three electrode cells were constructed which allowed the polarisation behaviour of the working and the counter electrode to be respectively measured against the potential of a reference electrode, [Figure 4.13](#).

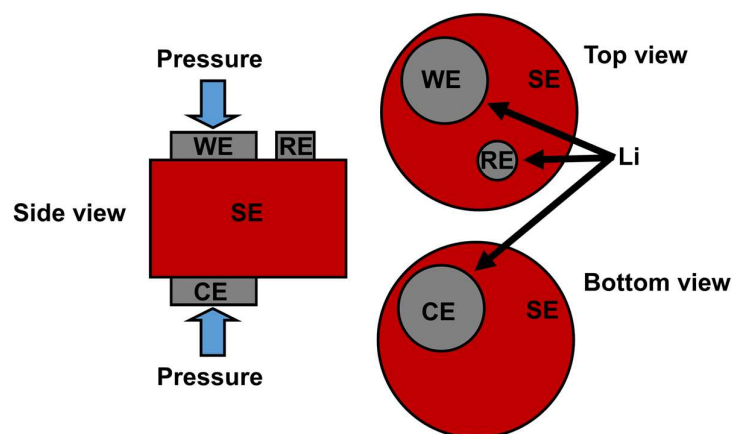


Figure 4.13. Schematic of three-electrode cell where RE is the reference electrode, WE is the working electrode and CE is the counter electrode.

Three-electrode cycling data reveals clear asymmetry between the processes of stripping and plating, Figure 4.14. The polarisation on plating remains low and flat throughout cycling at all current densities. As shown in Figure 4.14 (a), (c) & (e), under 3 MPa at 0.1 mA cm^{-2} , the plating voltage resides at $\sim 6\text{-}9 \text{ mV}$; at 0.2 mA cm^{-2} the plating voltage is $\sim 11.5\text{-}12 \text{ mV}$, and at 0.5 mA cm^{-2} the plating voltage is $15\text{-}30 \text{ mV}$. In the pressure range studied, plating behaviour does not exhibit a pressure dependence. On the other hand, stripping is more complicated, with non-flat voltage profiles and pressure dependent polarisation being observed during cycling. For example, at a current density of 0.1 mA cm^{-2} , under 3 MPa of applied pressure, the polarisation increases from 6.1 mV to 96.6 mV during the first half cycle. On subsequent cycles, stripping initiates at a low relatively flat voltage but then a relatively rapid rise in polarisation takes place. The voltage then slowly increases. When 7 MPa of pressure is applied, at low current densities (0.1 mA cm^{-2} and 0.2 mA cm^{-2}), the stripping voltage is flat and does not increase during cycling. Whereas the increased polarisation behaviour is observed for 0.5 mA cm^{-2} under 7 MPa of applied pressure, indicating that the increased polarisation observed for metal anodes when a pressure dependence critical stripping current is exceeded.

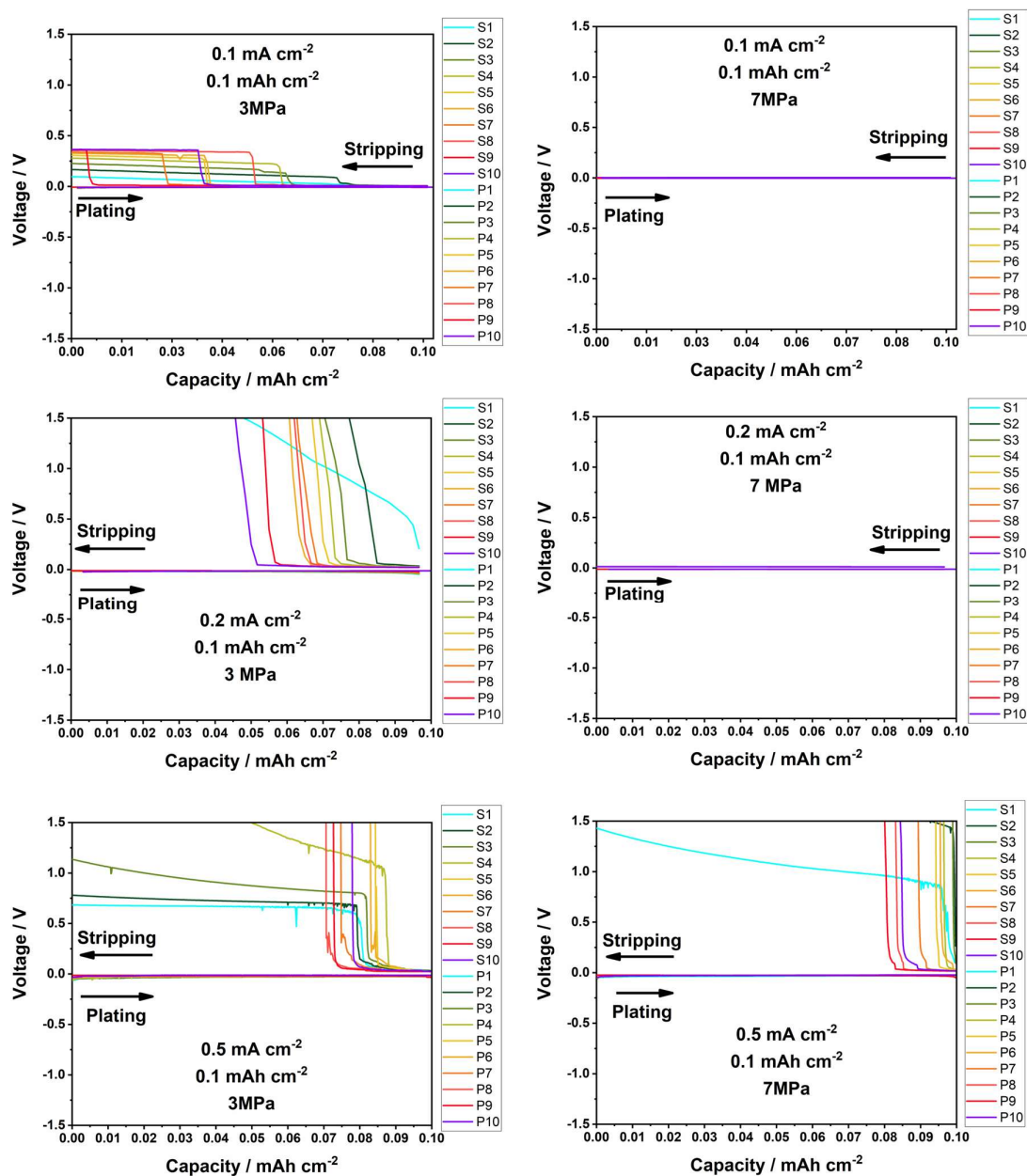


Figure 4.14. Voltage versus charge passed for three-electrode cells (1.5 mm diameter current carrying lithium electrodes, < 1 mm reference electrode and 1.3 mm thick pellets), showing plating and stripping of the working electrode over $\times 10^{-1}$ mA h cm⁻² cycles. (a) 0.1 mA cm⁻², 3 MPa; (b) 0.1 mA cm⁻², 7 MPa; (c) 0.2 mA cm⁻², 3 MPa; (d) 0.2 mA cm⁻², 7 MPa; (e) 0.5 mA cm⁻², 3 MPa; and (f) 0.5 mA cm⁻², 7 MPa. A voltage cut-off of 1.5 V was used.

The pressure dependence of the voltage behaviour on stripping implies a physical process rather than chemical change is affecting the Li | Li₃N interface during cycling,

therefore the interface was studied by SEM, [Figure 4.15](#). Cross sectional images reveal good initial contact between lithium metal and the SE before cycling, [Figure 4.15 \(a\)](#). After 10 cycles, contact loss between the electrode and SE was observed in cells which had exhibited increased polarisation on stripping, [Figure 4.15 \(b\), \(d\), \(e\)](#). Interfacial contact was maintained in cells which did not display the polarisation increase, [Figure 4.15 \(c\)](#). Direct imaging of the interface after stripping could not be performed for cells with high polarisation because the Li | Li₃N contact had been reduced so much that the electrodes repeatedly fell off during sectioning therefore cross-sectional images are only presented for the interfaces after plating. Close inspection of the SE surface reveals that a very thin layer of lithium is present on the SE surface inside some of the lithium voids. As such, some of the voids are effectively occluded from the SE interface.

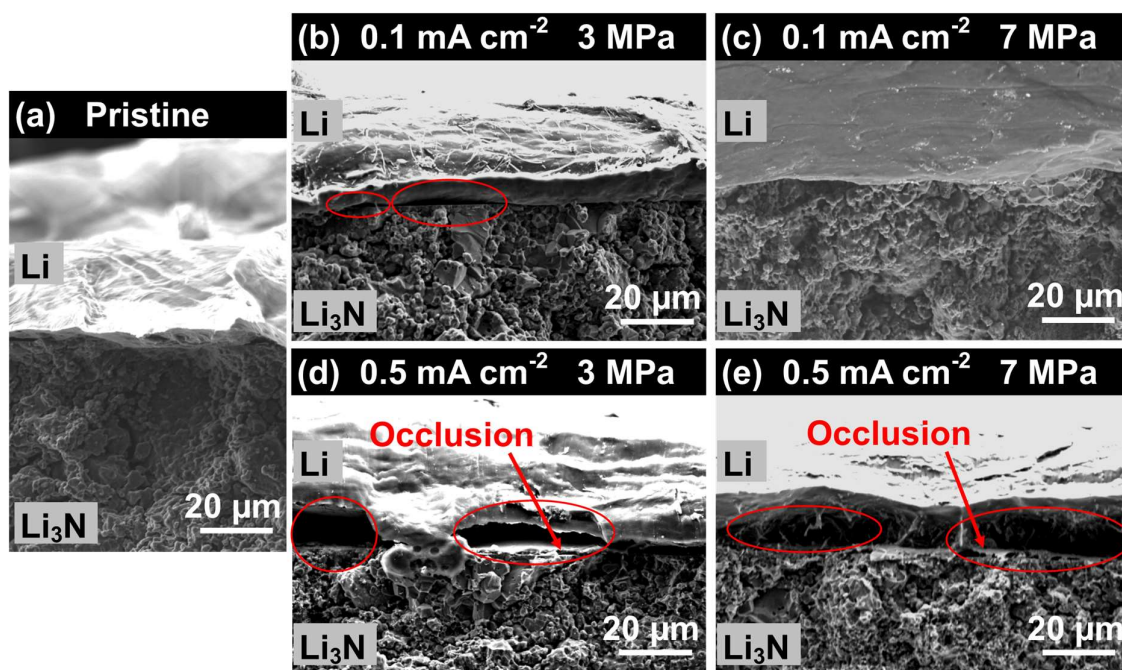


Figure 4.15. SEM cross-sections of Li | Li₃N interfaces. (a) Pristine interface after sputtering. (b) 0.1 mA cm⁻², 3 MPa; (c) 0.1 mA cm⁻², 7 MPa; (d) 0.5 mA cm⁻², 3 MPa; and (d) 0.5 mA cm⁻², 7 MPa, after 10 cycles.

In order to directly study the interfacial contact loss, X-ray computed tomography was used to visualise the plated interface and the stripped interface of a 2-electrode symmetric Li | Li₃N | Li cell before and after 1 half cycle, at low pressure (3 MPa) and

high current density (1.2 mA cm^{-2}). Before cycling, there is good interfacial contact between both electrodes and the SE, [Figure 4.16 \(c\)&\(e\)](#). Therefore the initial interfacial resistance of the cell was relatively low, [Figure 4.16 \(a\)](#). After half of a cycle, effective interfacial contact is maintained between the plated electrode and the SE, [Figure 4.16 \(d\)](#). However, considerable interfacial contact loss due to the formation of voids is observed on the stripped electrode, [Figure 4.16 \(f\)](#), and the overall interfacial resistance is considerably increased, [Figure 4.16 \(b\)](#). Voids with diameter $< 1 \text{ }\mu\text{m}$ are too small to be imaged, therefore it was not possible to estimate the area of interfacial contact loss. Due to the limited time available for beam time and the fact that prolonged exposure to the X-ray radiation was found to damage the sample holder, electrochemical experiments were performed at elevated current densities so that the voiding phenomena could be observed on the first half cycle.

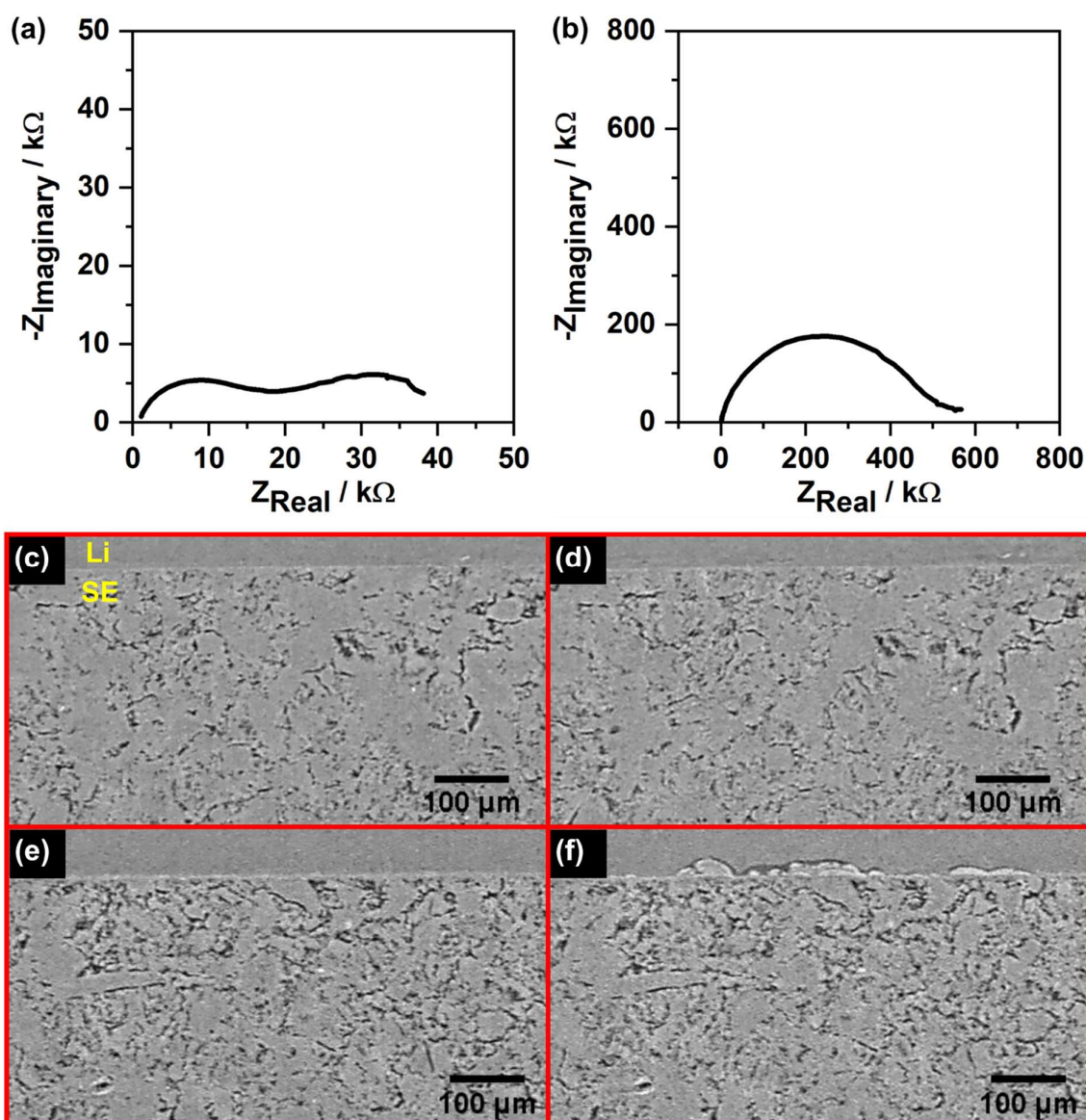


Figure 4.16. Nyquist EIS plot of Li | Li₃N | Li, (1.5 mm diameter lithium electrodes, 1.3 mm thick pellet), (a) before cycling, and (b) after galvanostatic passage of 1.5 mAh cm⁻² capacity at a rate of 1.2 mA cm⁻². Corresponding X-CT cross sectional image slices perpendicular to SE | Li interfaces. (c) Pristine plating side interface before plating. (d) Plating side interface after single plating. (e) Pristine stripping side interface before stripping. (f) Stripping side interface after single stripping. I prepared the samples, proposed the experiment, set-up the electrochemistry and interpreted the data. The tomography acquisition experiments and image reconstruction were performed by Ziyang Ning.

Given that void formation appears to a stripping phenomenon, the dynamic changes occurring at the electrode undergoing stripping side were imaged in real time; operando X-CT, reveals that small voids in the lithium electrode at the SE interface,

accumulate and grow with capacity passed, [Figure 4.17 \(b\)](#), which leads to an increase in cell over potential [Figure 4.17 \(b\)](#). Examination of the attenuation of the voids, indicates that the voids may not be entirely empty space, and may contain small amounts of an additional phase (with lower density than Li_3N) at the SE interface beneath the void. Possibly indicating local hot spots of electrochemical degradation. However, additional *in-situ* experiments, beyond the scope of this thesis will be required to investigate this. For example, differential electrochemical mass spectrometry (DEMS) analysis of the gases evolved during cycling and characterisation of the interface with GXRD, FTIR and Raman spectroscopy could be performed.

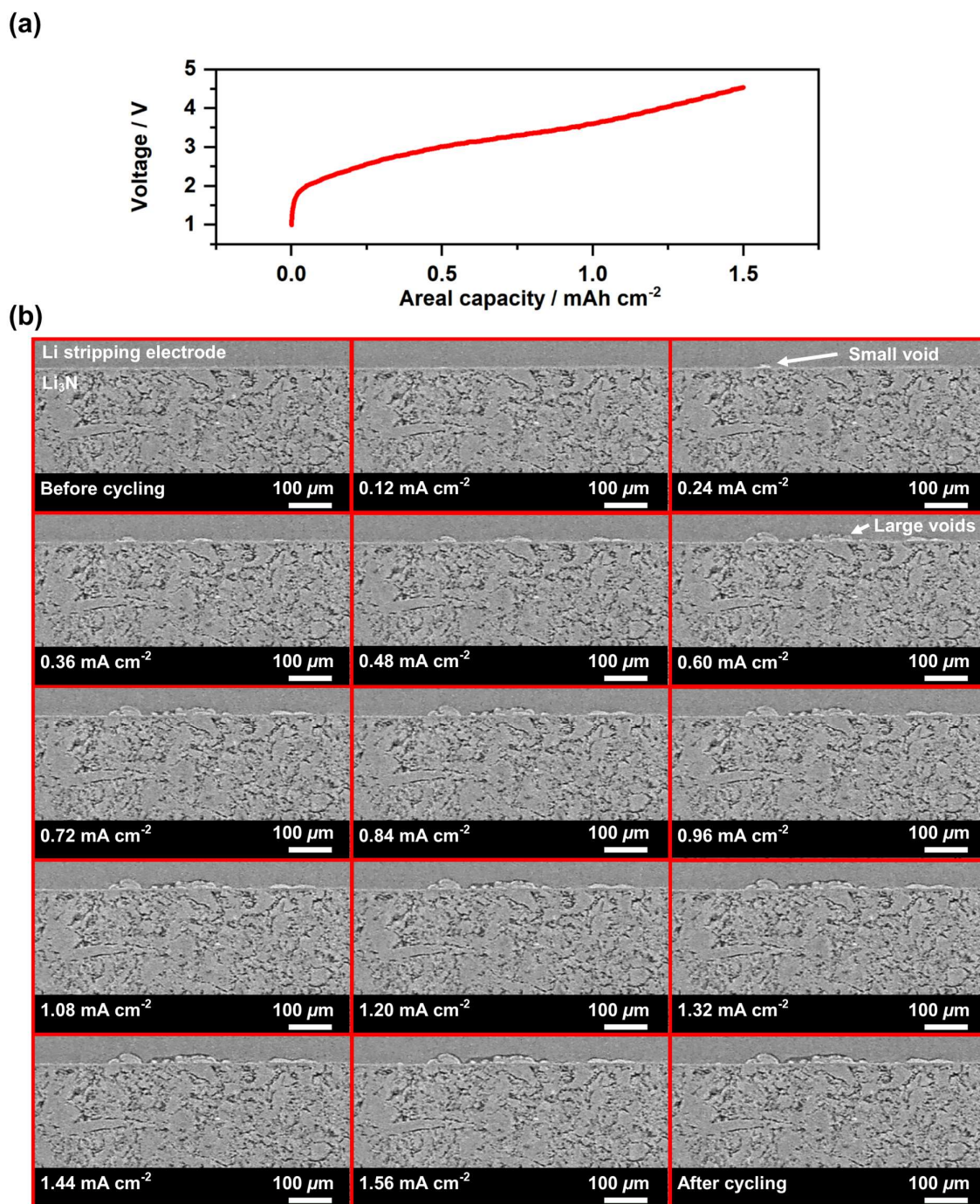


Figure 4.17. Operando phase contract X-CT of a Li | Li₃N | Li cell, (1.5 mm diameter lithium electrodes, 1.3 mm thick pellet), during galvanostatic passage of current in one direction at 1.2 mA cm⁻². (a) Profile of cell voltage versus charged passed. (b) Phase contract X-CT virtual cross sections of the Li | Li₃N stripping interface showing evolution with charge passed. The tomography acquisition experiments and image reconstruction were performed by Ziyang Ning.

The results outlined in this chapter indicate that there is a pressure dependent critical current density on stripping (CCS); when the CCS is exceeded voids form in lithium at the SE interface, leading to increased local interfacial current densities and increased overall cell potential. In order to establish, the approximate CCS value for the applied pressures used in this study, current was applied galvanostatically in 1 direction using 3-electrode cells, at different current densities (0.1, 0.2 & 0.5 mA cm⁻²) under the application of the chosen pressures (3 MPa and 7 MPa respectively), [Figure 4.18](#). As consistent with the results outlined earlier, the potential of the working electrode undergoing plating (electrode at negative potential) remained constant during the passage of current; this behaviour was independent of pressure and the potential varied with current density in accordance with Ohm's Law. On the other hand, stripping behaviour had clear current density and pressure dependence. A sustained increase in the potential of the counter electrode undergoing stripping (electrode at positive voltage) indicates the CCS has been exceeded. The potential of the counter electrode increased rapidly as charge was passed, when a current density of 0.5 mA cm⁻² and an applied pressure of 3 MPa were used. Under 7 MPa of applied pressure, the voltage increase occurred at a slower rate than at 3 MPa, but clearly 0.5 mA cm⁻² is above the CCS for both 3 MPa and 7 MPa of applied pressure. Under 3 MPa of applied pressure, the voltage of the counter electrode increases with capacity, using a current density of 0.2 mA cm⁻², therefore 0.2 mA cm⁻² is above the CCS for 3 MPa. However, under 7 MPa of applied pressure, the potential remains constant with charge passed at a current density of 0.2 mA cm⁻². As the CCS under 7 MPa of applied pressure is > 0.2 mA cm⁻², the voltage also remains constant during passage of charge at 0.1 mA cm⁻² at 7MPa. On the other hand, a steady increase in the counter electrode voltage is observed for 3 MPa at 0.2 mA cm⁻². At 3 MPa, the potential of the stripping electrode remained constant with 0.1 mA cm⁻² of applied current density. The Li₃N cells prepared in this study can be successfully operated at 0.1 mA cm⁻² under 3 MPa of pressure, and up to 0.2 mA cm⁻² under 7 MPa of pressure. The true CCS, will depend on the true starting interfacial contact area, therefore surface contaminants and methods of applying electrodes could lead to significant differences in the CCS values.

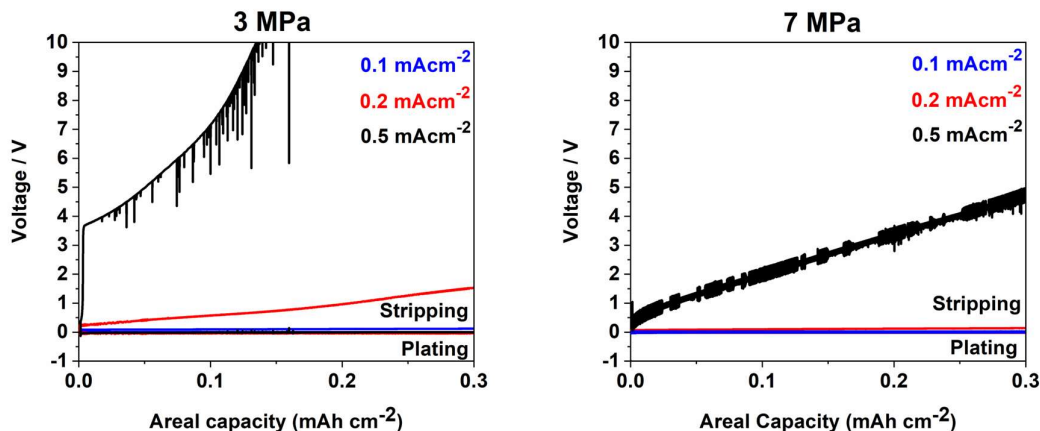


Figure 4.18. The voltages of a working electrode and corresponding counter electrode defined with respect to a reference electrode (1.5 mm diameter current carrying lithium electrodes, < 1 mm reference electrode and 1.3 mm thick pellets), showing simultaneous stripping and plating behaviour in Li | Li₃N | Li cells undergoing one half cycle at various current densities (0.1 mA cm⁻², 0.2 mA cm⁻², and 0.5 mA cm⁻²) under applied external pressures of 3 MPa and 7 MPa respectively.

4.4 Conclusion

During stripping, lithium atoms in the anode are oxidised and traverse the interface and become Li⁺ ions in the SE. However, above a critical current density, which shall be called the critical current for stripping (CCS), the flux of lithium across the cell, exceeds the flux at which lithium atoms can move to the interface, therefore vacancies necessarily develop in the Li at the interface with the SE.

The accumulation and agglomeration of vacancies produces voids in lithium at the SE interface, as directly shown by operando X-CT. These voids effectively decrease the area of interfacial contact between the SE and the lithium electrode. As such, the effective resistance of the cell increases. When cycling is performed galvanostatically, the overall current through the cell is constant, therefore the potential across the cell and the local current density at the interface increase when voids form. Increased current density, maximises voiding, therefore operation of cells above the CCS is catastrophic for cell performance. For example, the increased local potential of the

interface appeared to induce electrochemical breakdown of Li_3N at the interface with the stripping electrode.

Without the application of an applied pressure, the flux of lithium atoms to the interface during stripping is diffusion controlled. Consequently, when no pressure is applied, lithium voids develop rapidly, even at low current densities. However, lithium is able to undergo viscoplastic creep when stressed, therefore the application of an external pressure increases the flux of lithium atoms to the interface. As such, the CCS is pressure dependent. For example, under 3 MPa of applied pressure, voids will form in the lithium at the $\text{Li} | \text{Li}_3\text{N}$ interface when a current density of 0.2 mA cm^{-2} is applied. However, under 7 MPa of applied pressure, voids do not develop and the cell can be successfully cycled at 0.2 mA cm^{-2} for sustained periods.

In practical secondary cells, currents are reversed when the cell is charged, therefore it was important to establish whether voids are filled in during plating. It was shown that, lithium is able to plate along the surface of a SE, beneath a void, such that the void becomes occluded, [Figure 4.19 \(iii\)](#). However, the void was not fully filled in when the electrode was plated with the same capacity as was stripped from it, therefore occluded voids reopen on subsequent stripping.

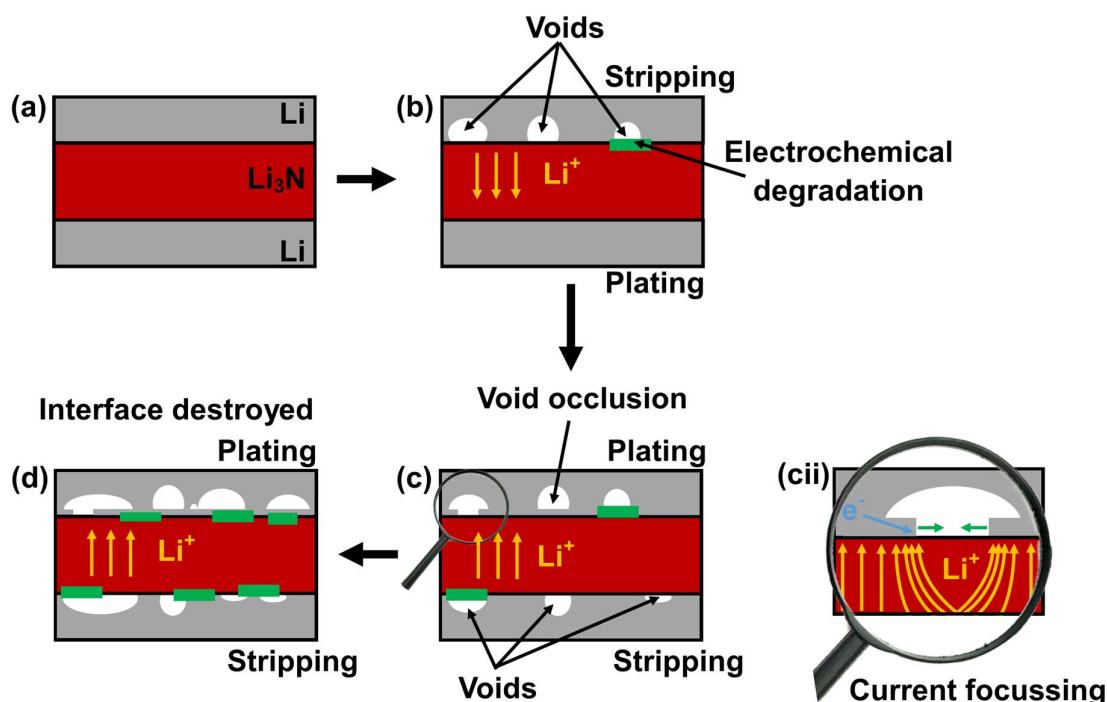


Figure 4.19. Proposed model for dynamic phenomena occurring at the Li | Li₃N interface during cycling. (a) Pristine cell before cycling, SE has good interfacial contact with both electrodes. (b) Cell after first half cycle; voids have developed in the electrode at the 1st stripped interface and some electrochemical degradation of the SE beneath the void is observed. The 1st plated interface remains unchanged. (c) Cell after first full cycle; voids are partially filled at the 1st stripped interface after subsequent plating and several of these voids are occluded by plated lithium. Non-occluded voids are now observed at the 1st plated electrode. (cii) Magnified void, showing occlusion developing on plating at the Li₃N / Li / void triple-point contact interface and current focussing due to poor interfacial contact. (d) Cell after multiple cycles; voids and interfacial electrochemical degradation products have accumulated on both electrodes, leading to high cell polarisation and potential dendrite formation.

In additional published work,^{138,139} the CCS was explored for other metal electrode / SE interfaces (Li | Li₆PS₅Cl and Na | BASE). In these works, the pressure dependent CCS was shown to be a ubiquitous phenomenon. However, these SEs did not undergo electrochemical degradation beneath the voids at the stripping interface with lithium, as was uniquely observed with Li₃N, probably due to the low oxidation potential of lithium

nitride. Instead, the voiding was found to lead to locally high interfacial current densities on plating, which resulted in dendrite growth and short-circuit failure.

The work in this Chapter has several important implications for the field:

1. There is a critical current density for stripping, which is different to the critical current density on plating, therefore the maximum rate at which ASSBs can be charged can be equal to or higher than the maximum rate at which a cell can be discharged but when the CCS is exceeded, the CCP will inevitably be exceeded. Therefore, increasing the CCS is of paramount importance.
2. The CCS is dependent on the flow properties of the metal electrode. It is shown that pressure alone can increase the CCS but introducing high pressures ($> 1\text{ MPa}$) in commercial cells is thought to be challenging therefore the effects of temperature, electrode doping/alloying and combinations thereof should also be explored as strategies for increasing the CCS.
3. Reports of over potential increases during cycling which have previously been attributed to chemical degradation could in some cases be the result of voiding, in studies where care was not taken to control pressure at high C-rates. Likewise, until now, many studies have reported overall critical current densities but have not taken into account the effect of the CCS, therefore in some cases the CCP could be higher than originally reported.

4.5 Experimental

Pellet preparation conditions were systematically varied until the following optimised densification method was developed. In an argon filled glovebox, Li_3N (99.6 %, Alfa Aesar) was uniaxially cold pressed into cylindrical pellets (5 mm diameter), with a stainless steel die set, using 550 MPa of applied pressure. The pellets were subsequently heated under an argon atmosphere using an MTI muffle furnace, from room temperature to 600 °C, atop carbon foil, at a rate of 10 °C min⁻¹; the pellets were held at 600 °C for 1 h to maximise sintering, after which the pellets were cooled at 10 °C min⁻¹ to room temperature. In an argon filled glovebox, Li_3N pellets were sequentially polished with 250, 400, 600, 800, 1200, 2500 and 4000 grade SiC grit papers until pellets achieved a mirror like shine and all surface imperfections visible to

the naked eye were removed. Top down SEM images and EDX spectral maps of pellet surfaces were obtained using an FE-SEM (Zeiss-Merlin) instrument, with all transfers to the microscope being performed using an argon filled air-tight sample holder. Likewise, cross sectional SEM images were acquired by the same method, however cross sectioning was first performed using an ultrasonic knife, in an argon filled glovebox. XRD was performed using a Rigaku 9 kW Smart Lab diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54051 \text{ \AA}$), with *in-situ* temperature studies performed with a sample inside a Anton Parr XRK900 induction furnace, under the flow of a constant stream of argon gas. Analysis of diffraction patterns was performed using the CrystalDiffract software package. All the cell preparation methods used in this chapter were performed under an inert atmosphere inside an argon filled glovebox. A sheet of lithium metal was scratched with a PTFE scalpel to remove surface contaminants, then the sheet was extruded by uniaxial pressing in a PTFE pouch to produce a clean sheet of lithium approximately 50 μm thick; circular lithium disks (1.5 or 2.2 mm diameter) were cut from the sheet for use as non-blocking electrodes. Likewise, indium metal sheets were cut into disks (4 mm diameter) in the same manner for use as semi-blocking electrodes. Li_3N pellets were masked with polypropylene tape, with pre-cut templates for the electrode areas. Electrode disks were applied to the exposed Li_3N pellet surfaces by careful hand-pressing using a polypropylene plunger. Lithium electrodes, with improved interfacial contact were produced by the following method. Circular holes (1.5 mm diameter) were plunged into a Kapton-tape mask using an Amtech B1400 revolving leather punch plier. Li_3N pellets were then masked with the tape such that the holes were aligned on opposite faces of the pellet to provide a defined area for the lithium electrodes. The masked pellets were fixed to a sample stage inside a custom MBRAUN glovebox integrated thermal evaporation chamber. The chamber was pumped to ultra-high vacuum. Lithium granules in a molybdenum evaporation boat were heated by the passage of current. This triggered thermal evaporation, see [Appendix 6](#). A plate was used to cover the sample stage during the first 30 seconds of evaporation, preventing any deposition onto the samples until a stable power had been achieved. The plate was then remotely removed from the sputter cone path, exposing the samples to the lithium vapour. The thickness of the layer being deposited was measured in real-time by a calibrated QCM in the chamber. Once power instability was noticed, due to near complete lithium evaporation, the plate

was used to cover the samples and the power was turned off. Additional lithium was supplied to the boat and the process was repeated several times until a 1 μm thick layer of lithium had been deposited. The pellets were then turned around and were reattached to the sample stage. The PVD process was repeated for the other electrode. The masks were removed and polypropylene masks were reapplied. Lithium electrode disks (50 μm) thick were pressed atop the deposited electrodes; this provided the excess lithium reservoir required. After this attachment, assembled cells were vacuum sealed in custom (2- and 3-electrode) pouches, shown in [Figure 4.9 \(b\) & \(d\)](#). External pressure ($> 9 \text{ MPa}$) was then applied and the cells were heated for 12 h at 60°C to maximise electrode / SE contact. The cells were subsequently cooled to room temperature and spring pressures (3 MPa or 7 MPa) were applied for the electrochemical measurements. Galvanostatic cycling measurements were performed inside a custom MBRAUN glovebox-integrated temperature controlled chamber, using a Gamry Interface-1010E potentiostat. Potentiostatic EIS was performed at various temperatures, using the same instrumental setup, over a 1 MHz to 1 Hz frequency range, using a 10 mV applied perturbation voltage. EIS spectra were fitted with circuit element models using the ZView Software package. N 1s, C 1s, O 1s, and Li 1s XPS spectra were acquired using a Thermo Scientific XPS K_α instrument, with argon sputtering for depth profiling, using a microfocused monochromated Al X-ray source operated at 12 keV with a 400 μm spot size. XPS spectra were charge corrected to adventitious carbon (284.8 eV). Tomograms were recorded at the I13-2 beamline at the Diamond Light Source. Pink beam was used to improve the time resolution of imaging. For each tomogram, 1801 equiangular distributed projections were taken over 180° , with the resulting voxel size of 1.625 μm , and the field of view of $4.7 \times 4.4 \text{ mm}^2$. The projections were processed and reconstructed into tomograms using optimized routines from Diamond. The cell was assembled into a customized air-tight tube-cell, and electrochemically cycled with the Gamry Interface 1010 potentiostat.

Chapter 5: A SE/LE hybrid approach for stabilising the lithium anode and mitigating ASSB cathode side limitations

5.1 Abstract

Although it has been shown that Li_3N and garnet type solid electrolytes (LLZO, LLZTO, etc.) have somewhat promising compatibility with the lithium metal anode, these solid electrolytes have so far proven to be practically incompatible with cathodes, which has prevented the development of viable full cells. Garnet composite solid-state catholytes suffer from rapid capacity fading as a result of active cathode particle contact loss due to cathode particle volume changes during cycling. Li_3N SEs are chemically unstable at operational cathode voltages and are oxidised at 0.44 V vs Li^+ / Li . In this chapter, a strategy of using a liquid electrolyte to electrically separate the SE and cathode particles is investigated. Hybrid SE/LE batteries, which interpose a Li metal anode and a liquid catholyte should in principle enable existing cathodes that display outstanding performance in LE cells to be successfully employed in conjunction with a metal anode. However, the hybrid approach introduces a new hetero-ionic interface between LE and SE which can act as an additional source of internal resistance in the cell. In this chapter, the interface between Li_3N and 1 M LiTFSI in propylene carbonate is shown to significantly contribute to the internal cell resistance. The time-dependent evolution of the $\text{Li}_3\text{N} / 1\text{M LiTFSI}$ in PC interface is explored and the interfacial resistance is shown to increase with time and then stabilise due to the chemical formation of an interphase. Proposed reaction mechanisms for the interphase formation are then presented. Likewise the interface between the most widely explored SE (LLZTO) and state of the art commercial LP30 liquid electrolyte (LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v/v)) is explored as a possibility for the development of a hybrid cell. However, the LLZTO/LP30 interfacial resistance was shown to increase to impractically high values due to the chemical formation of an interphase predominantly composed of fragments of LiF , Li_2CO_3 , Li_2O and organic carbonates. These results highlight the importance of understanding the chemistry of

SE/LE interfaces in the development of lithium metal anode hybrid electrolyte cells for high voltage lithium ion, Li-S and Li-O₂ cells.

5.2 Introduction

Single electrolyte based ASSBs have so far demonstrated inferior performance to LE based batteries. In part, this is because the metallic anode requires a SE with several properties which are antithetical to the properties required for effectual cathode compatibility. For example, according to the models of dendrite growth in SEs presented in **Chapter 2**, it is thought that a mechanically rigid SE with high fracture toughness is needed to prevent SE cracking and subsequent lithium filament propagation between the electrodes during plating of the metallic negative electrode; whereas on the cathode side, it is suggested that a mechanically pliant SE is required which can accommodate the cathode particle volume changes during cycling without interfacial contact loss,²⁵ as this phenomenon produces rapid capacity fading and ceramic fracture.³⁴ Furthermore, most SEs have limited electrochemical stability windows and are often only stable in the operational voltage window of the anode or the cathode but rarely both, albeit with some exceptions such as oxide based Garnet SEs.^{52,159} In this chapter it is suggested that the compatibility challenges of metal anode with respect to the SE can be resolved from the cathode compatibility challenges by the use of dual electrolytes, [Figure 5.1 \(a\)](#). Hybrid cells employing a SE with either a polymer electrolyte or a LE have begun to gain attention in recent years,^{160,161} with SEs having already been successfully employed as separators in LE based cells as a strategy for preventing cross-talk between electrodes from: polysulfide shuttling in Li-S cells,^{162–164} and redox mediators in the case of Li-O₂ cells.^{165,166} As such, it is important to investigate whether a SE/LE strategy could enable lithium metal anode based full cells to be produced using SEs that are normally considered to be incompatible with conventionally employed cathodes.

In order to perform these investigations we must consider the expected processes required for Li⁺ ion transfer across the SE/LE interface in the hybrid cell presented in [Figure 5.1 \(a\)](#). On charge, Li⁺ ions from the conduction salt in the LE must adsorb onto the SE surface and become incorporated into the SE lattice; whereas on discharge,

Li⁺ ions must be able to solvate from the SE to the LE. The kinetic limitations of these processes at the hetero-ionic junction between a SE and LE, therefore act as a source of internal resistance in hybrid cells, which is not present in single electrolyte cells. Understanding and minimising charge transfer processes at the SE/LE interface is therefore key in the development of hybrid cells. In pioneering works by Ogumi and co-workers, the fundamental processes determining the interfacial resistance of a SE/LE interface were elucidated,^{167–169} and a number of SE/LE combinations were explored, including: NASICON / 0.05 M NaCF₃SO₃ in (PC or DMSO),¹⁷⁰ Na-β''-alumina / 0.05 M NaCF₃SO₃ in (PC or DMSO),¹⁷⁰ LLTO / 1 M LiCF₃SO₃ in PC,¹⁷¹ and NASICON-type structured OHARA glass (Li_{1+x+y}Al_x(Ge,Ti)_{2-x}P_{3-y}Si_yO₁₂) / 1 M LiCF₃SO₃ in (PC, DMSO and FEC).¹⁷² Li⁺ transport across a SE/LE interface depends on the solvation ability of the electrolyte solvent; in solvents which possess higher Gutmann donor numbers, such as DMSO (~29.8), the rate of desolvation is often slower than the rate of solvation.^{168,169} Whereas, the resistance of Li⁺ exchange across a SE/LE interface is mostly independent of current direction in solvents with lower donor numbers, such as PC (~15.1).¹⁶⁸ In such conditions, ion-ion interactions between Li⁺ and the corresponding LE anions, are reported to determine the rate for ion exchange across the SE/LE interface, therefore the choice of salt plays an important factor in determining R_{SE/LE}.¹⁶⁷ In early studies, the chemistry of the interface and the evolution of R_{SE/LE} with time were not investigated. However, recent studies by Janek et.al, have shown that many well-known SEs (LAGP, OHARA glass and LiPON) react with LEs to form an interphase at the SE/LE interface,^{173,174} referred to in the literature as a solid-/liquid electrolyte interphase (SLEI). SLEIs can contribute significantly to R_{SE/LE}. As such, before full hybrid cells can be developed and before their performance can be correctly evaluated, one must determine whether R_{SE/LE} changes with time. The chemistry of a SE/LE interface also needs to be investigated to see if the interface performance is being hindered by the formation of a SLEI. It is suggested that a thorough characterisation of SLEIs will provide a logical rationale for the development of possible SLEI mitigation strategies.

In this chapter, the SE/LE strategy is used to see if the voltage stability window of Li₃N can be effectively expanded, since a LE can electrically separate the SE from the cathode particles. It is also investigated whether a LE can be employed to avoid

cathode volume expansion problems that prohibit the use of LLZTO as a stabiliser for the metal.

5.3 Discussion of the interface between Li₃N and 1 M LiTFSI in PC

Full cell SE/LE hybrid batteries have multiple sources of internal resistance, including: the bulk ($R_{SE,bulk}$) and grain boundary resistances ($R_{SE,gb}$) of the SE, the resistance of the LE ($R_{LE,bulk}$), as well as the resistance contributions of interfaces in the cell between the anode and the SE ($R_{Li/SE}$), between the SE and the LE ($R_{SE/LE}$) and between the cathode and the LE ($R_{LE/cathode}$), as illustrated in [Figure 5.1\(a\)](#).

$$R_{Total} = R_{Li/SE} + R_{SE,bulk} + R_{SE,gb} + R_{SE/LE} + R_{LE,bulk} + R_{LE/cathode} \quad (5.1)$$

Conventional 2-electrode EIS spectroscopy is ineffective for decoupling the multiple sources of interfacial type resistance. However, by adopting a 4-electrode configuration, with symmetric electrodes, in which SE and LE are sandwiched between two reference electrodes, which are themselves positioned in-between the two current carrying electrodes, as shown in [Figure 5.1\(b\)](#), the $R_{LE/cathode}$ and $R_{Li/SE}$ contributions can be excluded.

$$R_{Observed} = R_{SE,bulk} + R_{SE,gb} + 2R_{SE/LE} + R_{LE,bulk} \quad (5.2)$$

A custom glass dual compartment 4-electrode H cell was designed which could be clamped around a SE pellet, in [Figure 5.1\(c\)](#). The setup was used to investigate the interface between Li₃N and LEs (1 M LiTFSI in PC, TEGDME, DMC and 1 M LiPF₆ in PC), [Figure 5.2 \(a\)-\(d\)](#).

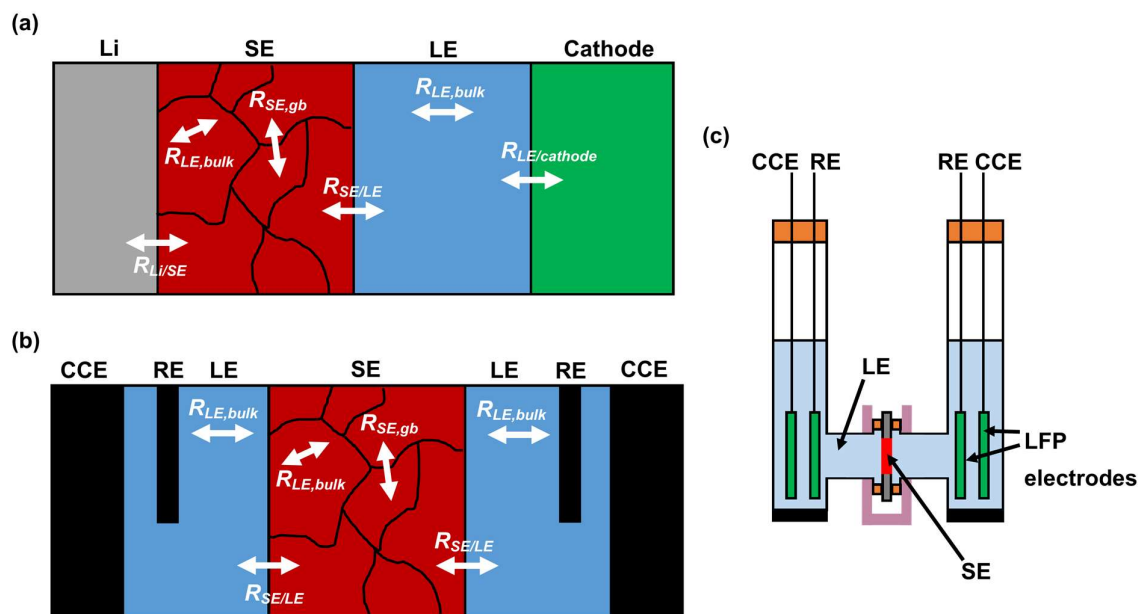


Figure 5.1. (a) Schematic showing the sources of resistance in a proposed full hybrid cell employing a lithium metal anode, a polycrystalline solid electrolyte, a liquid electrolyte and a cathode. (b) Schematic showing the resistances across a SE/LE interface which are isolated using a 4-electrode set up. (c) Diagram of the 4-electrode cell set-up used in the following experiments.

The Nyquist impedance plots obtained with the 4-electrode cell for the various Li_3N/LE combinations contain $R_{SE,bulk}$, $R_{SE,gb}$, $R_{LE,bulk}$ and $R_{SE/LE}$ resistance contributions. $R_{SE,bulk}$ and $R_{SE,gb}$ contributions are already known from investigations of Li_3N with blocking electrodes in **Chapter 4**, and $R_{LE,bulk}$ was determined to be negligible with respect to the other terms by measuring the resistance of the cell with LE but without the SE in place. As such, the large well resolved low frequency semi-circle can be confidently ascribed to the combined resistance of the two SE/LE interfaces. The resistance of the SE/LE interface is initially relatively small for $Li_3N / 1\text{ M LiTFSI}$ in PC, **Figure 5.2 (a)** but $R_{SE/LE}$ increases during the first 6 h of exposure, indicating the possible growth of a SLEI.¹⁷³ After 6 h of exposure, $R_{SE/LE}$ ceases to increase and remains relatively stable over a prolonged period of exposure (120 h), **Figure 5.2 (e)**. However, repeated fluctuations in the EIS spectra were observed over a prolonged period, which were attributed to temperature fluctuations because the change was periodic with the daily cycle; unfortunately this effect could not be mitigated with equipment available at the time of the experiment.

$R_{SE/LE}$ was found to increase with time for Li_3N with other LiTFSI based electrolytes, such as tetraethylene glycol dimethyl ether (TEGDME) and dimethylcarbonate (DMC), Figure 5.2 (b)&(c), which indicated that Li_3N may have been reacting with the LiTFSI salt. As such, $R_{SE/LE}$ was also studied using a 1 M $LiPF_6$ in PC electrolyte Figure 5.2 (d). However, $R_{SE/LE}$ also increased with time for Li_3N / 1 M $LiPF_6$ in PC. In order to establish whether the increases in $R_{SE/LE}$ were from the formation of SLEIs or were due to a different albeit somewhat ubiquitous phenomenon, the chemistry of the interface was studied using the Li_3N / 1 M LiTFSI in PC system as this combination exhibited the lowest value for $R_{SE/LE}$ after prolonged exposure. PC (< 10 ppm H_2O , determined by Karl Fisher titration) was distilled to ensure high purity.

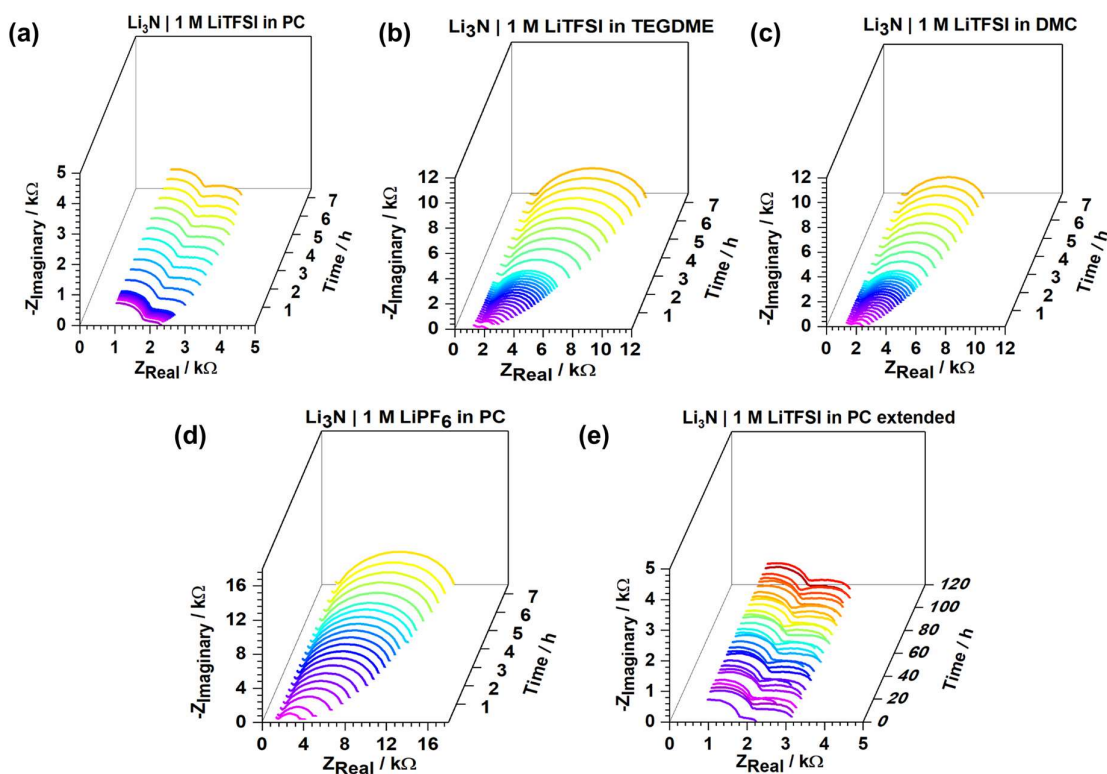


Figure 5.2. Nyquist impedance plots, with time, of SE/LE combinations, using a 4-electrode cell with LFP electrodes, Li_3N as the SE and the following LEs: (a) 1 M LiTFSI in PC, (b) 1 M LiTFSI in TEGDME, (c) 1 M LiTFSI in DMC, (d) 1 M $LiPF_6$ in PC and (e) 1 M LiTFSI in PC (prolonged exposure).

Li_3N pellets were placed in 1 M LiTFSI in PC for various periods of time (1 min, 15 min, 1 h, 7.5 h), then the pellets were removed and were immediately washed by gentle

dipping in PC, to minimise the precipitation of LiTFSI salt on the pellet surface during drying. The surfaces of the pellets were then studied using SEM, [Figure 5.3](#). The surface of a pristine Li_3N pellet, which had never been in contact with LE, appeared to be uniform, with only gentle surface striations from polishing just being visible, [Figure 5.3 \(a\)](#). However, even after short periods of exposure to LE, changes in the surface morphology could be seen, [Figure 5.3 \(b\)](#). Surface striations became exaggerated and the surface appeared to roughen. It is suggested that the surface of the Li_3N is reacting with the LE and the surface flaws from polishing may help accelerate nucleation. After exposure to LE (7.5 h), the surface of Li_3N appeared to be entirely covered with a morphologically distinct layer, indicating the possible formation of a SLEI, [Figure 5.3 \(e\)](#).

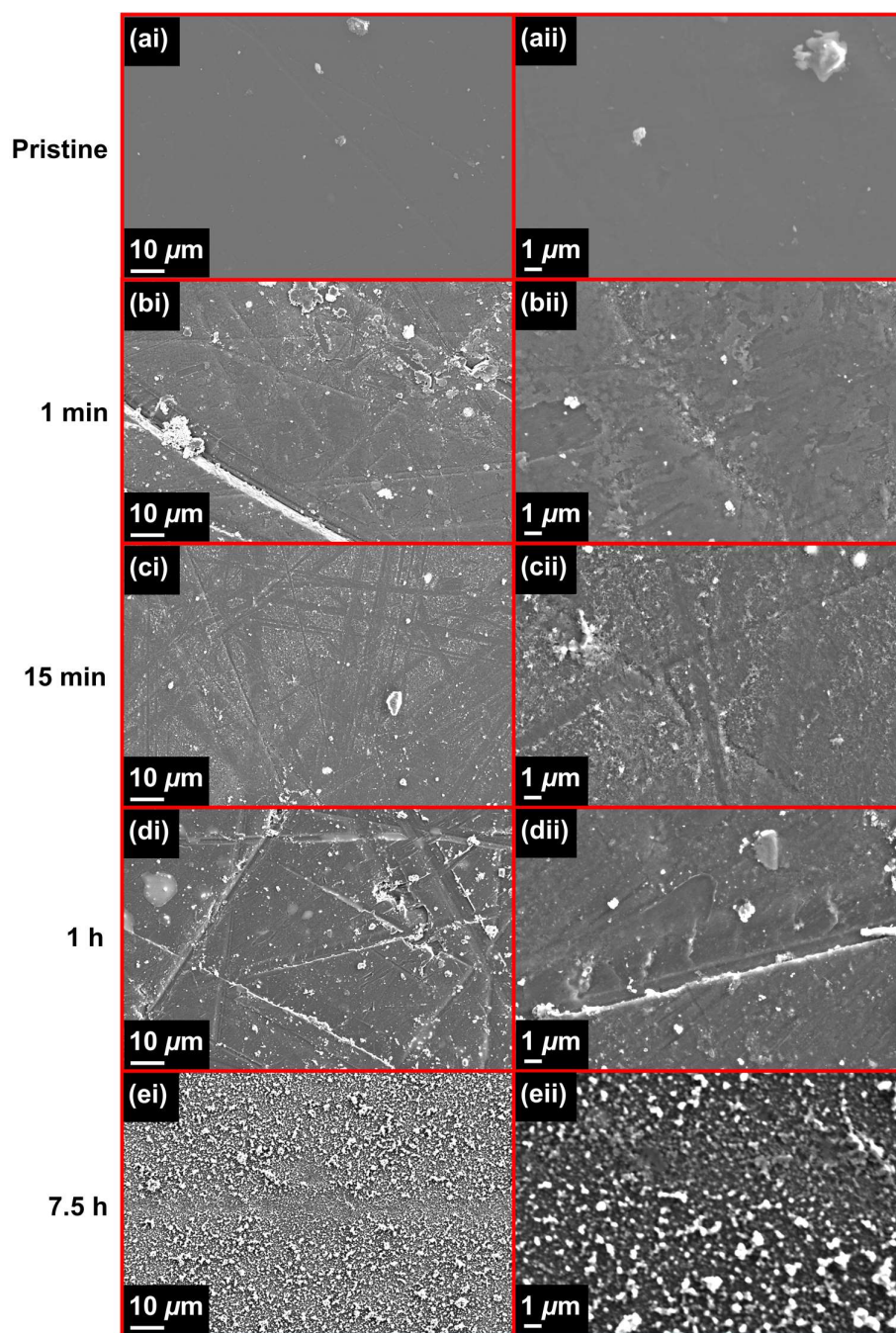


Figure 5.3. Top down SEM images of (ai & aii) a pristine Li_3N pellet, and Li_3N pellets after exposure to 1 M LiTFSI in PC for: (bi & bii) 1 min, (ci & cii) 15 min, (di & dii) 1 h, and (ei & eii) 7.5 h.

In order to establish whether the surface morphology changes to Li_3N observed by SEM were merely physical (roughening / etching) or chemical (reaction or precipitation), EDX was performed on the pellet surfaces, [Figure 5.4](#). Before exposure

to the LE, the Li_3N pellet had a predominantly nitrogenous surface, [Figure 5.4 \(a\) &\(b\)](#), with small amounts of oxygen present, likely due to practically unavoidable Li_2O and LiOH contaminants as discussed in **Chapter 4**. After short term exposure of Li_3N to 1 M LiTFSI in PC (1 min to 1 h), a decrease in the nitrogen content of the pellet surface was observed, which implied that the Li_3N surface may have become partially covered by a chemically distinct species. Concordantly, increased oxygen content was also observed on the pellet surface with increased exposure time. After 7.5 h of exposure, the nitrogen content of the surface had decreased considerably, indicating that the surface of the pellet was no longer predominantly Li_3N , [Figure 5.4 \(a\) & \(e\)](#); instead, the sulfur and fluorine content of the surface increased considerably. LiTFSI is the only source of fluorine and sulphur in the system, it is suggested that the surface changes observed in [Figure 3](#) are not merely physical; it is suggested that either LiTFSI salt is depositing on the pellet surface or LiTFSI and possibly PC are reacting with the Li_3N to form a SLEI.

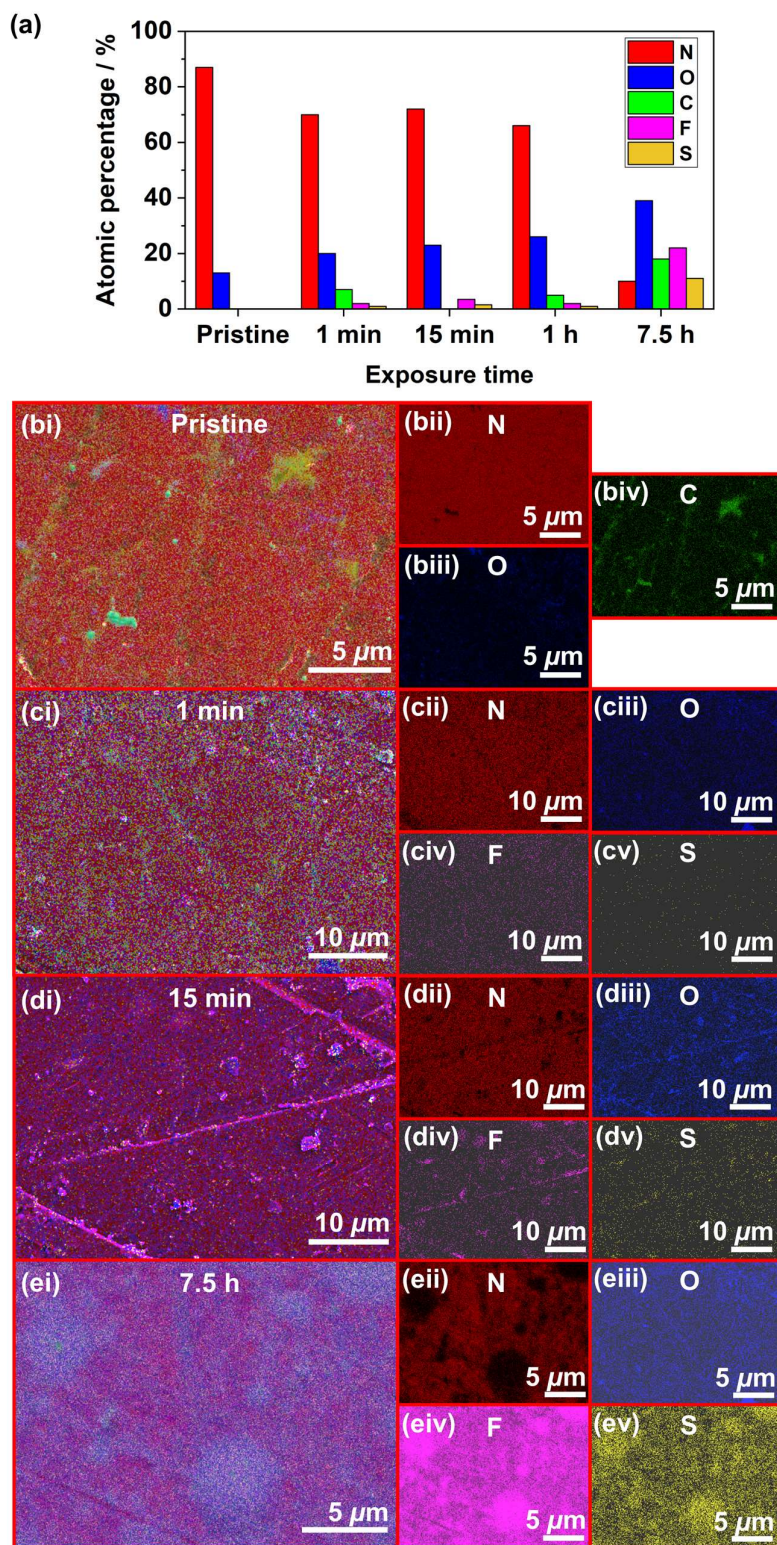
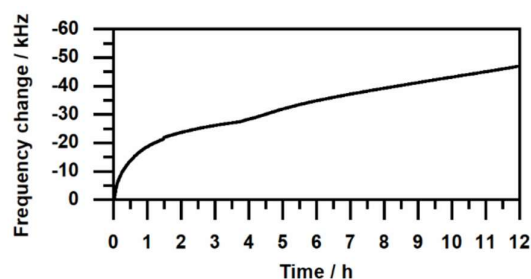


Figure 5.4. (a) Relative abundance of the elements on the surface of a Li_3N pellet after exposure to 1 M LiTFSI in PC as determined by EDX, (with lithium excluded). Combined and individual element EDX mappings for (b) a pristine Li_3N pellet, and Li_3N after exposure to 1 M LiTFSI in PC for: (c) 1 min, (d) 15 min, and (e) 7.5 h.

To confirm an interphase develops, quartz crystal microbalance (QCM) was used to qualitatively measure the change in mass of Li_3N powder after exposure to 1 M LiTFSI in PC. Under an argon atmosphere, Li_3N particles were drop cast onto a quartz crystal using hexane. Then after drying, 1 M LiTFSI in PC was added and QCM measurements were immediately commenced. After addition of LE, the mass of the Li_3N particles increased, resulting in a decrease in frequency with time, [Figure 5.5](#), confirming the development of a surface layer.



[Figure 5.5](#). QCM, showing the change in frequency with time for Li_3N particles in 1 M LiTFSI in PC. I proposed the experiment and prepared the samples; the experiment and interpretation of data was executed with Konstantinos Dimogiannis.

In order to establish whether LiTFSI and / or PC were indeed reacting with Li_3N , or whether LiTFSI was merely precipitating, TEM / electron diffraction measurements were performed on particles of Li_3N powder which had been exposed to the electrolyte solution for 12 h. After exposure to electrolyte, the particles were repeatedly washed with PC and were dispersed onto a copper TEM grid with PC, which was thereafter removed by evaporation under reduced pressure. Particles of Li_3N were observed by TEM, [Figure 5.6 \(a\)](#). LiTFSI crystallites were not observed by electron diffraction, indicating that LiTFSI was largely removed by washing. However, crystallites with lattice spacing's consistent with LiF, were observed by electron diffraction, [Figure 5.6 \(b\)](#). The 0.2 nm lattice fringe for the {200} LiF plane is shown in [Figure 5.6 \(a\)](#). The distribution of LiF on the Li_3N particles is shown by the phase colour mapped TEM image in [Figure 5.6 \(c\)](#). The LiTFSI salt used was of high purity, as such it is the only fluorine containing species present in the system, from which, LiF could be formed. This indicates that Li_3N is reacting with LiTFSI. However, this could be due to decomposition under the electron beam, as such additional analytical techniques were applied to ensure the presence of LiF and LiTFSI.

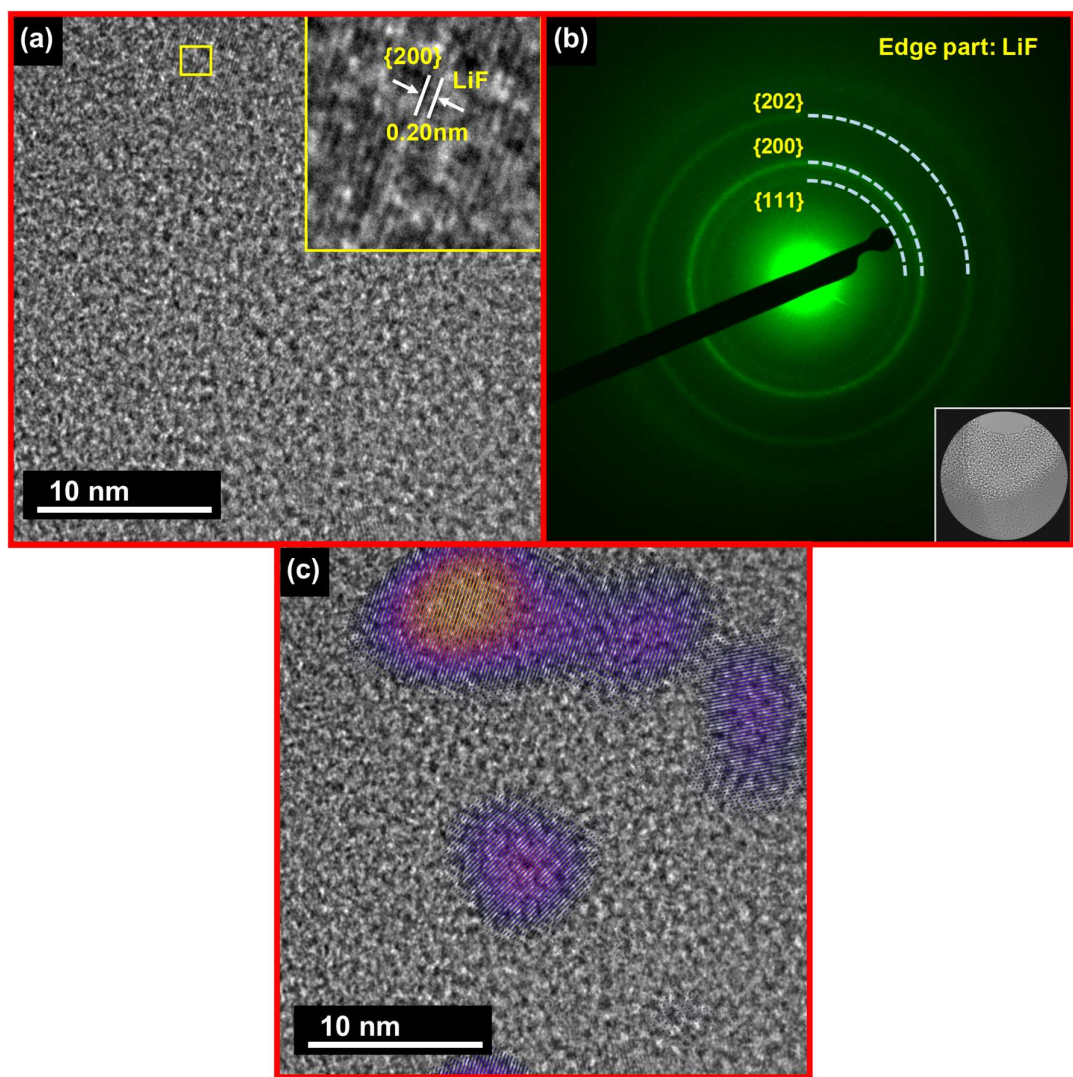


Figure 5.6. (a) TEM of Li_3N particle after 12 h of exposure to 1 M LiTFSI in PC, following washing with PC. (b) Electron diffraction spot pattern, indicating the presence of LiF, taken from the region indicated by the yellow box in (b). (c) LiF distribution on Li_3N particle as indicated by colour mapping, where no colouration indicates Li_3N , blue indicates LiF and red indicates high relative LiF concentrations. I proposed the experiments and prepared the samples; TEM / electron diffraction was performed by Chen Gong.

In order to establish whether Li_3N was also reacting with the PC solvent, Li_3N was directly exposed to PC for 12 h without any salt. After exposure and drying, particles were examined by TEM, [Figure 5.7 \(a\)](#). Electron diffraction, revealed that the centre of the particles is predominantly composed of Li_3N , [Figure 5.7 \(c\)](#). However, 2.48 nm lattice fringes, attributed to the $\{020\}$ lattice plane of Li_2CO_3 ,¹⁵¹ were clearly observed, with particular prevalence at the edges of the particle, [Figure 5.7 \(b\)](#), as confirmed by

the diffraction spot pattern shown in [Figure 5.7 \(d\)](#). Indicating some degradation of PC has occurred. In light of these results, the surface layer observed in [Figure 5.3](#) and [Figure 5.4](#), is likely due to a SLEI, rather than a mere salt deposition. However, the phases identified by electron diffraction are unlikely to be the only phases present since amorphous SLEI products could not be easily examined. Furthermore, the PC washing used in sample preparation is particularly aggressive for small particles and may have removed other solid but partially soluble SLEI products. However, to rule out that Li_2CO_3 is merely the result of decomposition of PC under the electron beam, additional analytical techniques were used to study the interphase.

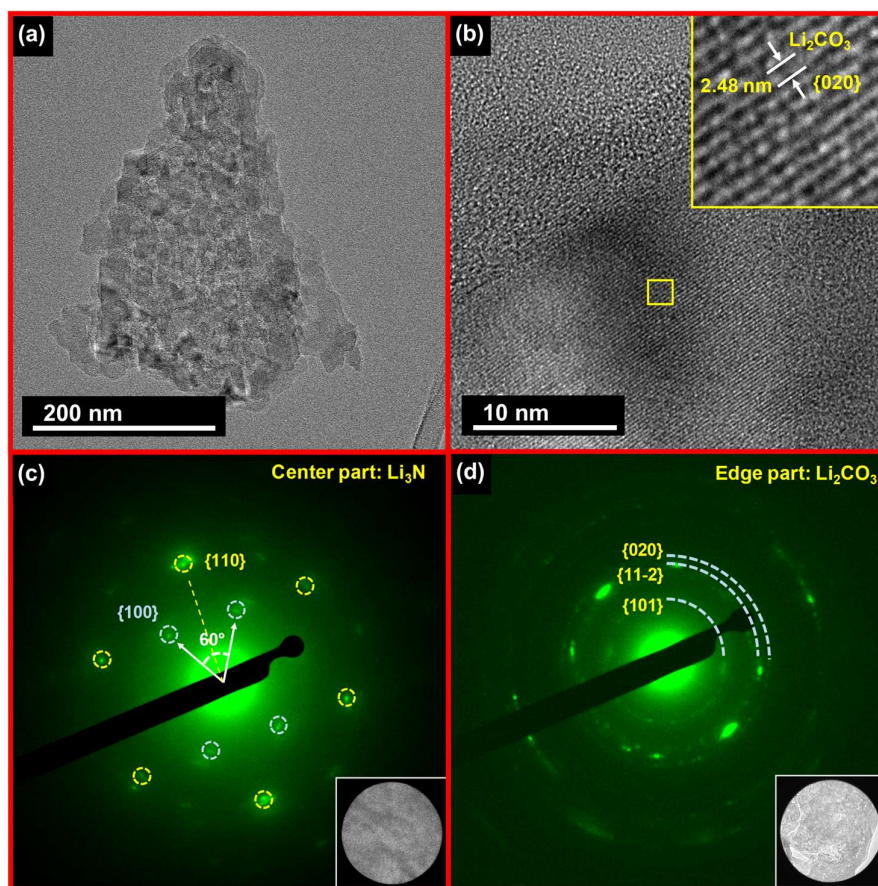


Figure 5.7. TEM of Li_3N particle after 12 h of exposure to PC acquired at (a) Low magnification and (b) high magnification. Electron diffraction spot patterns taken from the: (c) central part of flake, showing particle is predominantly Li_3N ; (d) edge part of the flake, indicated by the yellow box in (b), showing partial particle covering with Li_2CO_3 . I proposed the experiments and prepared the samples; TEM / electron diffraction was performed by Chen Gong.

In order to better understand the SLEI that forms, ToF-SIMS was used to depth profile the surface of a pristine polished reference Li_3N pellet and a Li_3N pellet after exposure to the electrolyte, following washing with PC. Unfortunately, although samples could be transferred to the instrument without exposure to air, due to the design of the transfer holder, the samples could not be removed from the instrument without air exposure, therefore, sputter times could not be related to true depth values by profilometry, as Li_3N reacts with air. However, the results presented are qualitatively very informative. High relative intensities of CO_3^- and O_2^- , were observed at the surface (sputter time < 35 s) of pristine Li_3N , [Figure 5.8](#), confirming the presence of surface contaminants, previously identified in **Chapter 4**; predominantly Li_2O and

LiOH, with smaller amounts of Li_2CO_3 . The presence of these impurities decreases the percentage of the surface that is Li_3N , therefore the intensity of $^7\text{Li}^-$ is somewhat depressed at the surface; this in part, is likely responsible for the Li | SE interfacial resistance observed in **Chapter 4**. However, at greater depths (sputter time > 35 s), such impurities are negligible and the $^7\text{Li}^-$ content increases substantially and plateaus. It is suggested that the gradual signal intensity decrease after longer sputter times is due to decreased signal reaching the detector, as a result of shadowing by the walls of the growing sputtering crater. Exposure to (1 M LiTFSI in PC) electrolyte changes the Li_3N pellet surface drastically. In this case, the $^7\text{Li}^-$ intensity increases more gradually with depth, reaching a maximum after 320 s of sputtering, implying a much thicker surface layer is present, consistent with the formation of a SLEI. As indicated by the shading of the figure, the SLEI appears to behave somewhat like a bilayer. Fragments, such as CF_3^- , which are indicative of LiTFSI salt or only partially degraded salt, are observed at shallow depths into the pellet (0 – 140 s of sputter time). However, at intermediate depths (140 – 320 s of sputter time) fragments such as Li_2S^- , which could not be attributed to unreacted LiTFSI, but which could be attributed to reacted LiTFSI were observed. As such S^{2-} fragments, present in salt and degraded salt, are observed at the outer and inner regions of the SLEI. High relative intensities of CO_3^- were found in the SLEI (0 - 320 s of sputter time), confirming PC degradation. These results indicate, that both LiFSI and PC react with Li_3N to form a SLEI at the SE | LE interface; some LiTFSI, or a species similar to LiTFSI remains adsorbed atop the SLEI, immediate to the LE contacting interface.

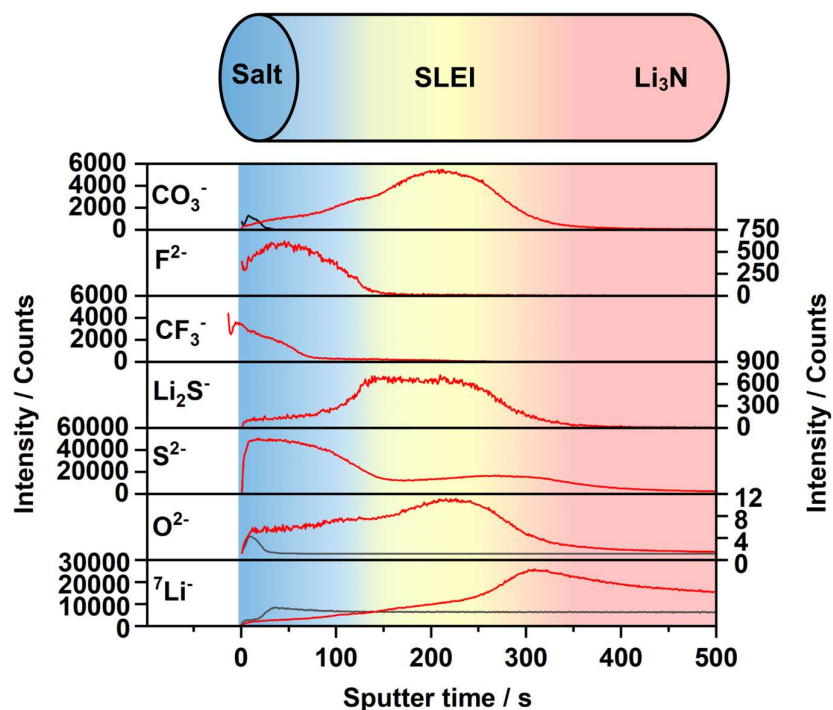


Figure 5.8. Depth profiling ToF-SIMS for various ions. Black curves are for a polished Li_3N pellet. Red curves are for Li_3N pellet after 12 h of exposure to 1 M LiTFSI in PC, following washing with PC and drying. I proposed the experiments and prepared the samples; ToF-SIMS was performed with Dr. Sarah Fearn.

The ToF-SIMS evidence that LiTFSI is reacting with Li_3N to form additional sulphurous products is supported by XPS. As expected, S 2p XPS spectra of pristine Li_3N indicate the absence of sulfur, [Figure 5.9 \(a\)](#). The S 2p XPS spectrum of LiTFSI is known to contain overlapping doublets due to S-O (169.6 eV), and SO_2 (170.8 eV) bonding 169.6 eV.¹⁷⁵ After 1 min of exposure to 1 M LiTFSI in PC, at the outer surface of the interphase (pink curve) on the Li_3N pellet, the spectrum observed is typical of LiTFSI. However, at greater depths into the interphase, additional peaks at lower binding energy were observed, [Figure 5.9 \(a\)](#). This suggests that an additional distinct sulphur phase has been formed. It is clear that the higher binding energy peaks, ascribed in part to LiTFSI, have decreased relative intensity, after greater exposure times (1 h and 7.5 h), [Figure 5.9 \(c\)&\(d\)](#), consistent with surface bound LiTFSI having undergone reaction.

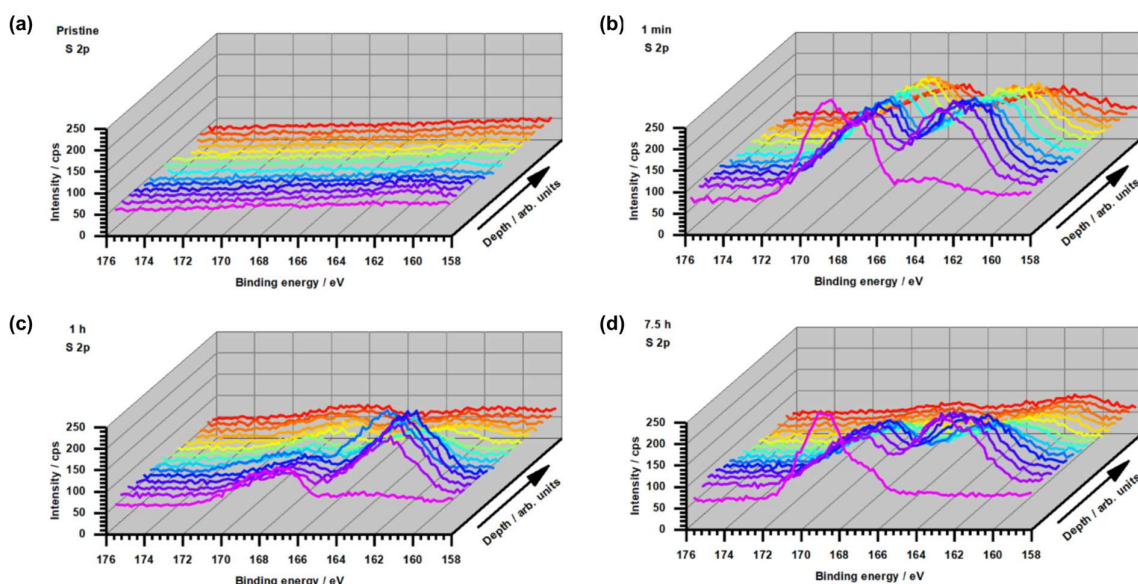


Figure 5.9. S 2p XPS spectral depth profiles of Li_3N pellets after exposure to 1 M LiTFSI for (a) 0 min/ pristine Li_3N , (b) 1 min, (c) 1 h, and (d) 7.5 h. I prepared the samples and interpreted the data; the spectral acquisition was performed with Dr. Philip Holdway.

In-situ MAS NMR was used to track reactions between Li_3N and 1 M LiTFSI in PC with time. Comparison with the overlaid Li_3N reference spectrum, confirms that the broad ^7Li MAS NMR resonance observed at 7.46 ppm, [Figure 5.10 \(a\)](#), is due to unreacted solid Li_3N . The sharp high intensity resonance observed ~ -0.80 ppm, has a comparable chemical shift to reference LiTFSI in PC,¹⁷⁶ therefore, the resonance is likely due to the presence of LiTFSI type species bound to the surfaces of Li_3N particles. After initial exposure of Li_3N to the LE, the resonance around -0.80 ppm is relatively narrow (~ 5 Hz), [Figure 5.10 \(bi\)](#). However, as exposure is prolonged, the resonance broadens, [Figure 5.10 \(bii\)](#), due to the development of a second overlapping resonance, indicating a chemical reaction in which surface bound lithium trifluorosulfonylimide is consumed and a different but chemically comparable species is formed. Ensuing results indicate the overlapped peak may be due to lithium bis[N-(trifluoromethylsulfonylimino)] trifluoromethanesulfonate ((LiOS(CF_3)(NSO $_2$ CF $_3$) $_2$), a common reduction product of LiTFSI,¹⁷⁷ whose structure is shown in [Figure 5.10 \(bi\)](#).

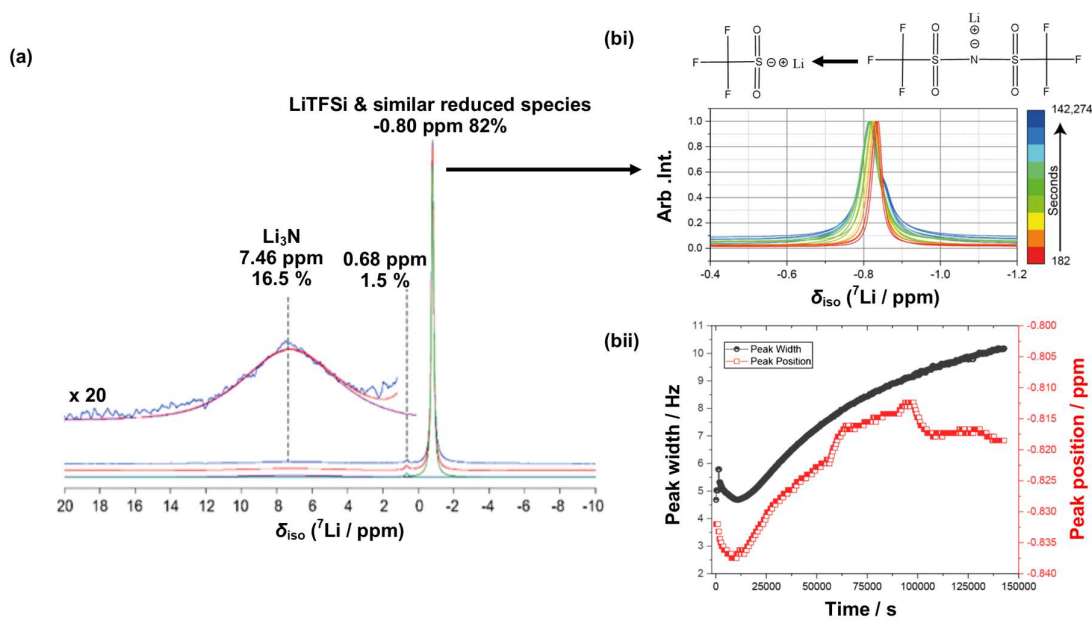


Figure 5.10. In-situ MAS NMR spectra of Li_3N in 1 M LiTFSI in PC: (a) ${}^7\text{Li}$ MAS (10 kHz) spectra acquired after exposures of 5 min (green), 125 min (blue) and 250 min (red). The 7.46 ppm peak of the green spectrum is shown at x20 magnification and is overlaid with the reference spectrum of Li_3N powder, shown in purple. (bi) In-situ ${}^7\text{Li}$ MAS (10 kHz) spectra, collected at 3 min intervals, showing the development of the resonance at ~ 0.8 ppm; (bii) the corresponding spectral peak width and height is plotted with time. I proposed the experiments, prepared the samples and interpreted the data; the experiment and spectra were produced by Dr. Gregory Rees.

An additional small resonance was observed at ~ 0.68 ppm. Since the species responsible for this resonance must be surface bound, the chemical shift of the resonance is likely to be offset from its true value as a bulk phase. However, there are many relevant species (Li_2CO_3 , LiF , LiOH and Li_2O) that have resonances at around this chemical shift, as shown in Figure 5.11, therefore a clear assignment of the peak at 0.68 ppm could not be provided.

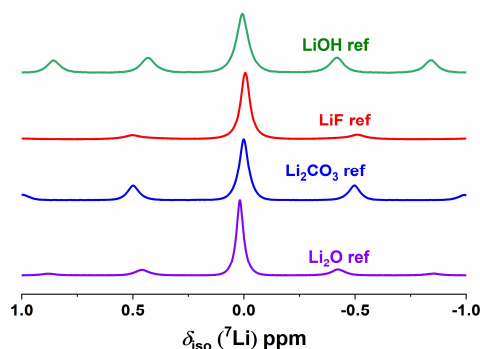


Figure 5.11. ^7Li MAS spectra of reference compounds: Li_2CO_3 , LiF , LiOH and Li_2O . was performed by Dr. Gregory Rees.

A ^{13}C NMR spectrum, which shows both solution and solid species, was acquired after Li_3N had been suspended in LE for 250 min {with spinning}. Resonances consistent with literature spectra for PC were observed,¹⁷⁸ as shown highlighted in green in [Figure 5.12 \(aii\)](#). Additional resonances were observed at 114.9 ppm and 104.5 ppm; $^{19}\text{F} > ^{13}\text{C}$ CPMAS reveals that these peaks are due to solid species containing F-C coupling. It is suggested that the ^{13}C MAS NMR resonance at 104.5 ppm is due to LiTFSI ; a simulated spectrum (with no solvent) {generated at *cheminfo.org*} has a calculated resonance at 119.5 ppm, and the resonance at 114.9 ppm could be due to $((\text{LiOS}(\text{CF}_3)(\text{NSO}_2\text{CF}_3)_2)$; the corresponding simulated spectrum (with no solvent) has a calculated resonance at 121.2 ppm. These techniques are relatively insensitive for surface bound species with long relaxation times, therefore there are likely to be other undetected surface bound carbonaceous species present, such as Li_2CO_3 .

The MAS (8 kHz) ^{19}F NMR shows a mixture of solid state chemical shift anisotropy (CSA) broadened resonances and significantly narrower solution state resonances. The sideband manifold is representative of a non-axially symmetric environment, since the species are interfacially bound. A significant ^{19}F MAS NMR resonance was observed at -79.86 ppm, [Figure 5.12 \(b\)](#), which is close to literature values for solution LiTFSI .^{177,179} A solid phase resonance, with sidebands (designated by *), was observed at -123.46 ppm; $^{19}\text{F} > ^{13}\text{C}$ HETCOR indicates that this is actually two independent overlapping resonances. The differences in the 2D peak shapes and widths suggests that the resonances are from different molecules. The ^{13}C values suggest the peaks are due to surface bound LiTFSI and $((\text{LiOS}(\text{CF}_3)(\text{NSO}_2\text{CF}_3)_2)$.

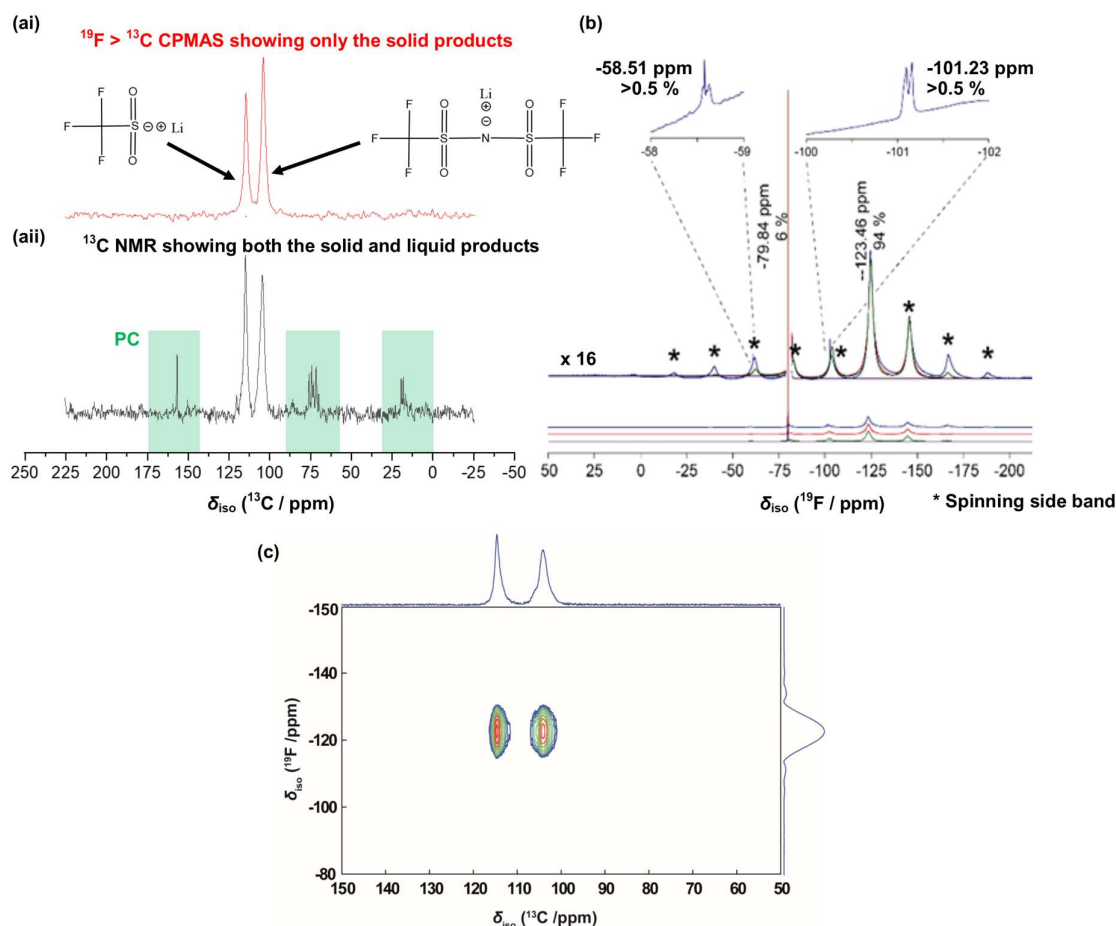


Figure 5.12. (ai) $^{19}\text{F} > ^{13}\text{C}$ CPMAS (red) spectrum, and (aii) ^{13}C MAS (12 kHz) NMR (^1H decoupling) spectrum (black) acquired using direct observation, cross polarization magic angle spinning and a frequency swept homonuclear Lee-Goldberg acquired after 250 min of exposure. (b) ^{19}F MAS NMR spectra of Li_3N taken in-situ after exposure to LE for 5 min (green), 125 min (blue) and 250 min (red). (c) $^{19}\text{F} > ^{13}\text{C}$ HETCOR 2D spectrum. I proposed the experiments, made the figure, prepared the samples and interpreted the data; the experiments were performed with and the raw spectra were produced by Dr. Gregory Rees.

Given the surface insensitivity of ^{13}C MAS NMR, the aforementioned results are only able to effectively probe the LiTFSI reaction products; however, Figures 5.7 & 5.8, indicate that PC solvent also reacts with Li_3N , therefore a method of enhancing surface signals was needed. As such, dynamic nuclear polarisation enhanced NMR (DNP), a technique in which radicals are added to the sample, to significantly amplify the signal intensity of the surface,¹⁸⁰ was performed, Figure 5.13. A bi-radical: TEKPol (structure shown in Figure 5.13 (e)), dissolved in 1,1,2,2-tetrachloroethane (TCE), was used to

sensitise samples for DNP measurements. The radical was added to pristine Li_3N powder and also to a Li_3N PC suspension after 1 week; upon radical addition the samples were immediately frozen to prevent reactions. ^1H MAS DNP produced an 80 fold signal enhancement. The spectrum of Li_3N + TEKPol/TCE was consistent with TCE, indicating minimal reaction with the biradical, [Figure 5.13 \(a\)](#). Additional peaks were observed for Li_3N in PC + TEKPol/TCE, probably due to surface-bound PC and possible reaction products. The presence of a surface layer was confirmed by comparing the bulk ^6Li MAS (12 kHz) NMR (^1H decoupling) spectrum with the surface indicative ^1H - ^1H homonuclear decoupled heteronuclear correlation experiment between ^6Li and ^1H , [Figure 5.13 \(b\)](#), because the change in chemical shift indicates the surface chemistry differs from the bulk. ^{13}C DNP of reference Li_3N produced a single resonance at 74 ppm due to TCE, this was used to reference the TCE resonance in the ^{13}C DNP spectrum of Li_3N in PC, coloured purple in [Figure 5.13 \(c\)](#). In this sample, resonances ascribed to C=O (140 ppm), CH_3 (3 ppm), CH (55 ppm) and (CH_2) (59 ppm) were observed. These resonances are consistent with surface-bound PC. However, these resonances may also have contributions from organic reaction products. A resonance was observed (highlighted green) which cannot be due to PC. The chemical shift of this resonance is indicative of C=C bonding, indicating that an alkene reaction product is formed from a reaction between the PC and Li_3N . ^{15}N MAS NMR (^1H decoupling) using direct observation did not detect nitrogen in bulk Li_3N over the timescale of the experiment, [Figure 5.13 \(d\)](#). However, cross polarization ^{15}N MAS DNP, revealed the surface of the Li_3N in PC, contained peaks typical of Li_3N only (reference spectrum shown in [Figure 6.4](#)). These results indicate that the reaction between Li_3N and PC does not produce a nitrogenous liquid or solid products. The logical inference is that nitrogen atoms are lost as dinitrogen gas, indicating that Li_3N is acting as a reducing agent. To test this assertion, mass spectrometry measurements were performed on gases produced.

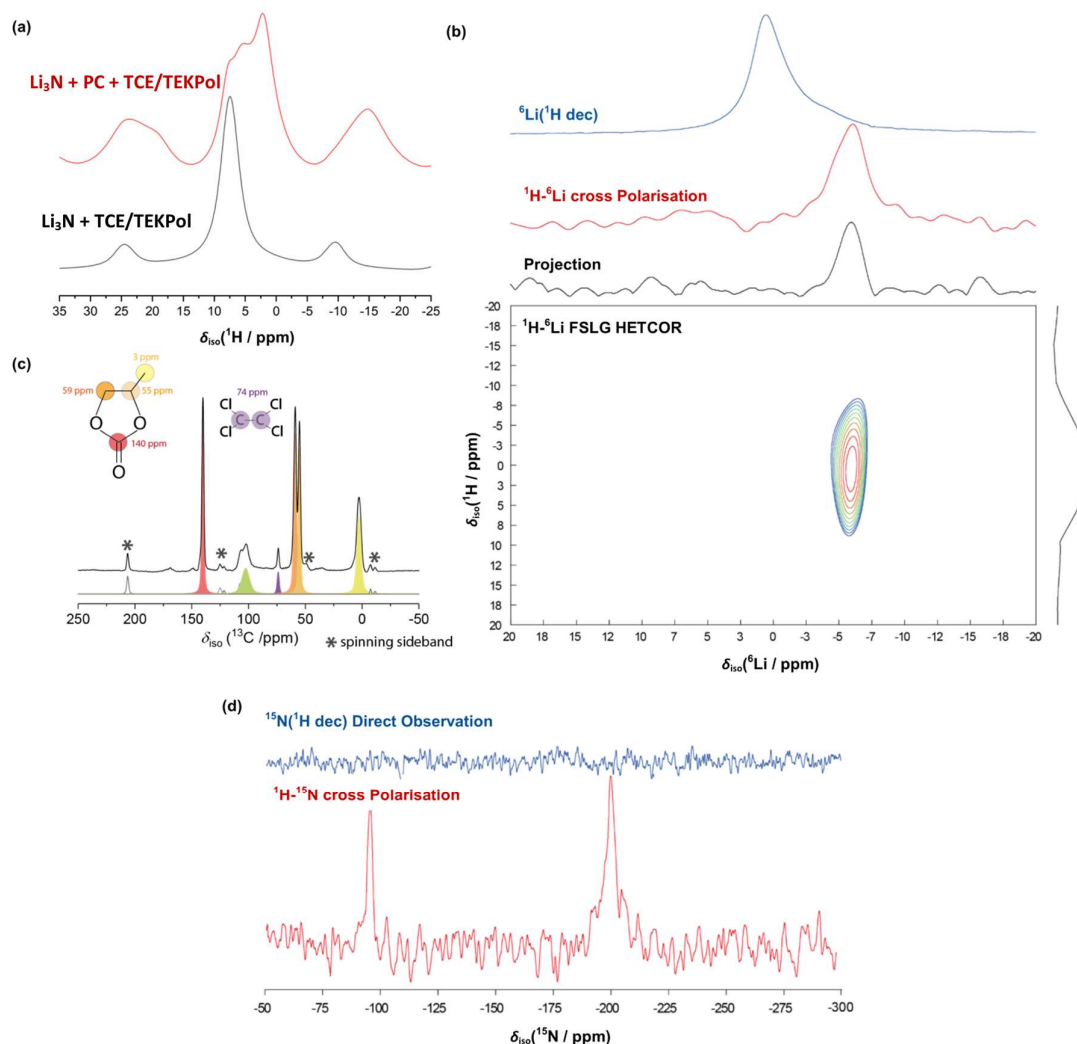
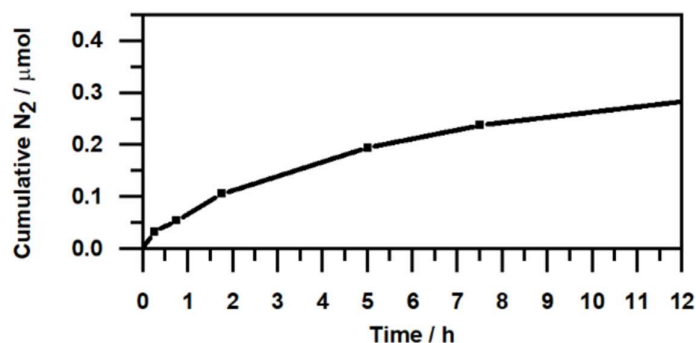
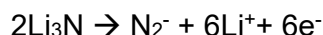


Figure 5.13. (a) ^1H MAS DNP spectra for Li_3N powder (black) and Li_3N in PC after 1 week. (b) ^6Li MAS (12 kHz) NMR (^1H decoupling) spectra acquired using direct observation, cross polarization magic angle spinning ($^1\text{H}>^6\text{Li}$), and a frequency swept homonuclear Lee-Goldberg $^1\text{H}-^1\text{H}$ decoupling heteronuclear correlation experiment between ^6Li and ^1H . (c) ^{13}C MAS DNP spectrum of Li_3N in PC after 1 week with assignments indicated by colouring (d) ^{15}N MAS (12 kHz) NMR (^1H decoupling) spectra acquired using direct observation and cross polarization magic angle spinning. (e) Chemical structure of TEKPol radical. I proposed the experiments, prepared the samples, made the figure and interpreted the data; the experiments were performed and the raw spectra were produced by Dr. Gregory Rees and Dr. Subhradip Paul.

Mass spectrometry was used to study the gasses produced by the reactions of PC and Li_3N . LiTFSI was not included because the salt is an additional nitrogenous source, and could potentially contribute to gaseous nitrogenous products; therefore, without prohibitively expensive ^{15}N isotopic labeling experiments, Li_3N oxidation could

not have been definitively concluded. Li_3N was placed inside an argon filled airtight ampule, connected to the mass spectrometer, with an open/shut valve and an argon carrier gas by-pass. Before PC was injected, N_2/O_2 contents in the ampule were measured and were used as a baseline. PC was added to the Li_3N powder and the N_2 content of the headspace was sampled by opening the valve after different periods of exposure. Increased N_2 gas was clearly observed, with respect to N_2/O_2 baselines after exposure, [Figure 5.14](#), indicating N_2 was being produced. The total N_2 evolved increased with time over 12 h of exposure but the rate of production decreased with time, showing that the reaction slows with time, probably as the Li_3N particles became encapsulated in SLEI which blocked further redox. Nitrogen supplied in the form of Li_3N greatly exceeded the N_2 evolved, confirming that the reaction did not slow merely due to consumption of precursors.



[Figure 5.14](#). Nitrogen evolution with time for Li_3N powder in PC, measured with mass spectrometry.

The results outlined, indicate that Li_3N reacts with 1 M LiTFSI in PC to form a heterogeneous SLEI. Li_3N appears to reduce PC to lithium carbonate and an alkene, and it also appears that Li_3N reacts with LiTFSi to form $((\text{LiOS}(\text{CF}_3)(\text{NSO}_2\text{CF}_3)_2)$, LiF and possible Li_2S . The resistance of the interface with the SLEI is considerable therefore cycling, even at low current densities (0.1 mA cm^{-2}) requires an impractically high over potential, [Figure 5.15](#).

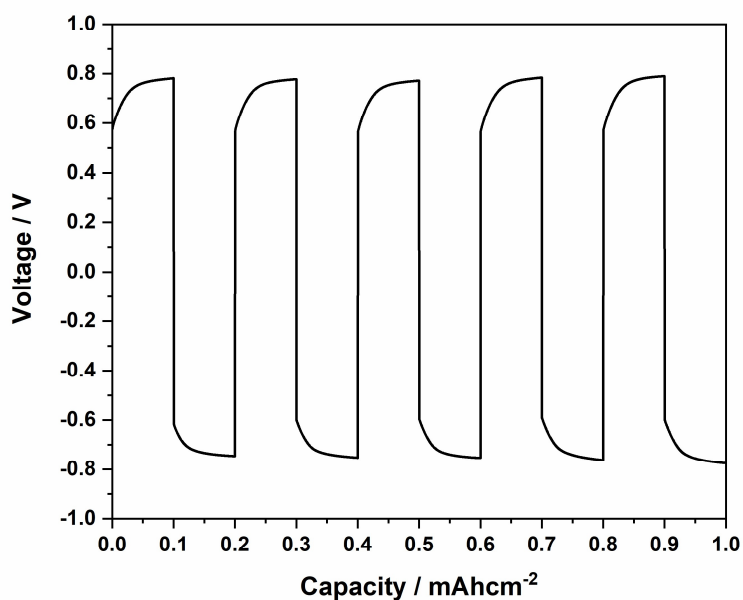


Figure 5.15. Galvanostatic cycling of 0.1 mAhcm^{-2} at a current density of 0.1 mA cm^{-2} of capacity using a LFP | LE | Li_3N | LE | LFP cell, in a 4-electrode configuration, where LE = 1 M LiTFSI in PC. After assembly the cell was left for 1 month before cycling was performed to ensure the SLEI to reach its maximal thickness, representative of the system that would be present in a real world full hybrid cell.

Electrode reactions [3.45 V]: $\text{Li}^+ + \text{e}^- + \text{Fe}(\text{PO}_4) \longleftrightarrow \text{LiFe}(\text{PO}_4)$

5.4 Discussion of the interface between LP30 and LLZTO

LLZTO is one of the most widely studied SEs and it has great promise for use in ASSBs employing a lithium metal electrode. However, as discussed in **Chapter 2**, LLZTO has so far demonstrated incompatibility with cathodes due to active material volume change and cathode | SE contact loss issues during cycling. As suggested in **Section 5.2**, this problem could in principle be avoided with a hybrid cell, using a LE to contact the cathode particles and a SE to stabilise the metal anode. As shown in **Section 5.3**, the introduced SE | LE interface can often be the most significant source of internal resistance in the cell and therefore the interface between LLZTO and LE should be investigated in detail before full hybrid cells are constructed. In this section, the interface between LLZTO and LP30 is investigated. LP30 (LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v/v), BASF battery-grade; $\text{H}_2\text{O} < 15$ ppm, $\text{HF} < 50$ ppm) is the state of the art electrolyte currently employed in many commercial lithium ion cells.

LLZTO (tap density = 5.345 g cm^{-3}), with $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ stoichiometry, as confirmed by ICP-OES, was successfully synthesised, as confirmed by PXRD, [Figure 5.16 \(a\)](#), using a modified Pechini sol-gel method. LLZTO disks (thickness: 2-2.5 mm, diameter: 1.4 cm, 98 % (± 1.1 %) of theoretical density) were then produced by spark plasma sintering and the polishing method outlined in the experimental, was subsequently applied to remove surface contaminants. This method resulted in decreased surface roughness as could clearly be seen by comparing pellets before and after the treatment, [Figure 5.16 \(b\)&\(c\)](#).

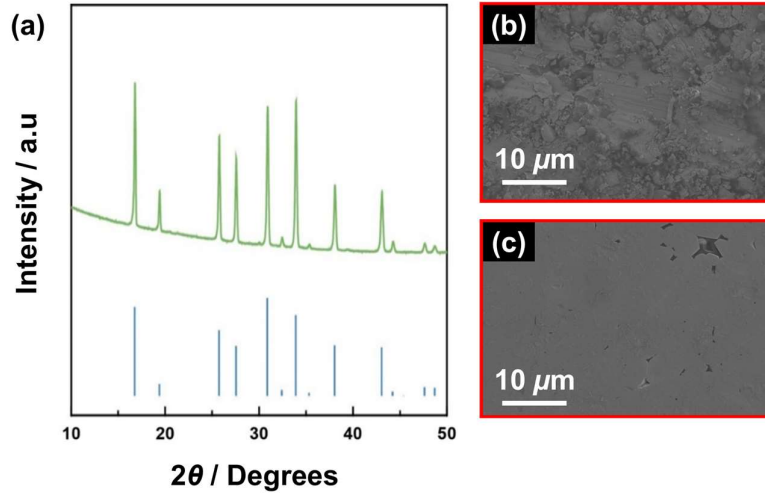


Figure 5.16. (a) The PXRD pattern of synthesised LLZTO powder (green),¹⁸¹ and the reference pattern for LLZTO ($La\bar{3}d$).¹⁸² SEM images of LLZTO pellet after sintering: (b) before surface treatment, and (c) after surface treatment.

The stability of the interface between an LLZTO pellet and LP30 was investigated with time, by 4-electrode EIS, using the H-cell set-up described in **Section 5.3**. The resistance ($R_{SE/LE}$) and capacitance ($C_{SE/LE}$) values of the interfacial impedance contribution were normalised to the area of contact between the SE and LE (i.e. the interfaces on both sides of the LLZTO pellet were taken into account) and the development was tracked with time, **Figure 5.17 (a) & (b)**. To aid understanding, exposure times have been divided into regimes (Regions I, II, III and IV), **Figure 5.17 (a) & (b)**. Within the first minute of LLZTO exposure to LP30, $R_{SE/LE}$ exceeds $220 \Omega \text{ cm}^2$. During the first 20 min of exposure (Region I, shown magnified in the figure inset), $R_{SE/LE}$ increased rapidly ($\sim 10 \%$). $R_{SE/LE}$ increased by a further $\sim 90 \%$ between 20 min and 20 h of exposure (Region II), however the rate of increase slowed substantially with time. The decreased rate is clearly observed between 30 h and 100 h (Region II), where $R_{SE/LE}$ only increases by $\sim 22 \%$. The outlined development of $R_{SE/LE}$ is consistent with the formation of a SLEI. If a SLEI of uniform thickness (r) has a greater resistivity (ρ) than the SE and the LE, then as the SLEI thickens the interfacial resistance should increase proportionally.¹⁸¹

$$R_{SE/LE} \propto \frac{\rho r}{A} \quad (5.3)$$

Where A is the area of the interface. Provided that SLEI growth is the only phenomenon at play, then the capacitance of the SE/LE interface should vary in an inversely proportional manner with respect to the interphase thickness (r).¹⁸¹

$$C_{SE/LE} \propto \frac{\varepsilon A}{r} \quad (5.4)$$

Where ε is electric constant. Between 30 h and 100 h of SE/LE contact (Region II) $C_{SE/LE}$ decreased rapidly, consistent with rapid SLEI growth, [Figure 5.17 \(b\)](#). Likewise, as the rate of resistance increase slowed (Region 3), [Figure 5.17 \(a\)](#), the rate of capacitance decrease also slowed, [Figure 5.17 \(b\)](#). However, consideration of $C_{SE/LE}$ during the first 20 min of exposure (Region I), reveals the process is not as simple as one might at first expect. Over Region I, $C_{SE/LE}$ actually increased by ~2 %. It is suggested that during early exposure times, LP30 reacts quickly in contact with LLZTO to form a SLEI; however, LP30 likely ingresses into pores and grain boundaries close to the SE/LE interface thereby acting to effectively increase the surface area of contact between the SE and LE. This hypothesis is supported by the evolution of the RC time constant, [Appendix 7](#).

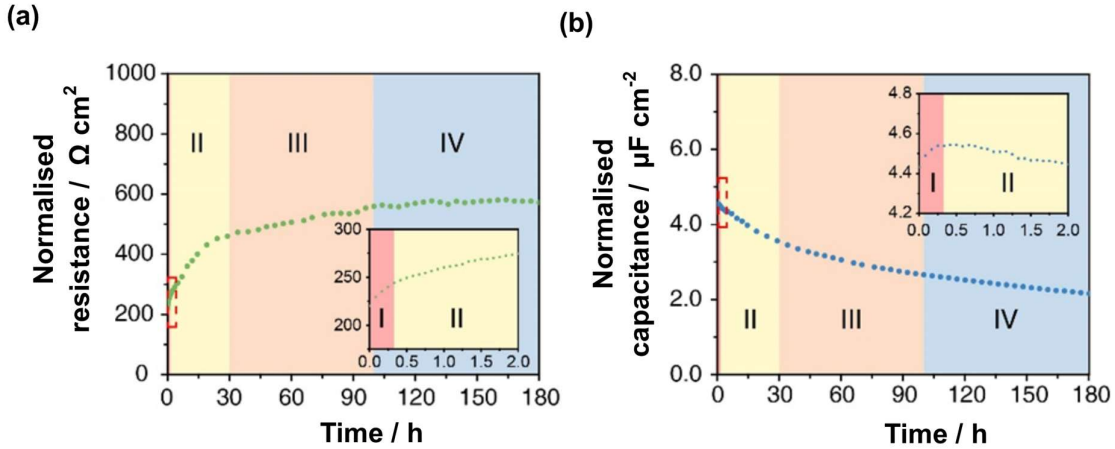
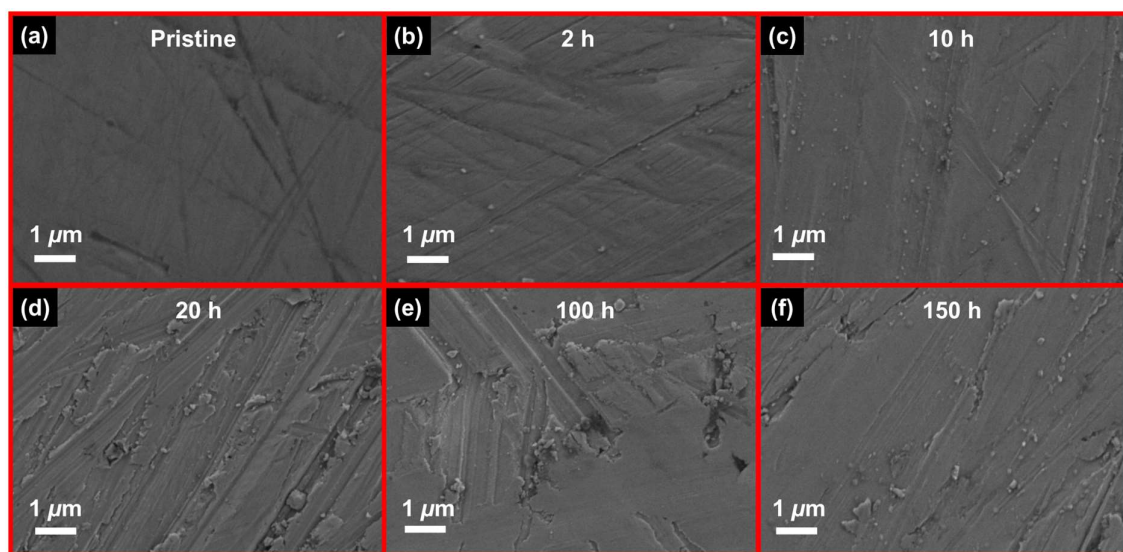


Figure 5.17. Investigation of the LLZTO | LP30 interface with time using EIS: (a) plot of $R_{SE/LE}$ and (b) plot of corresponding $C_{SE/LE}$.¹⁸¹ The experiment was performed by Dr. Jingyuan Liu and the figure was produced collectively by myself, Dr. Xiangwen Gao and Dr. Jingyuan Liu. See [Appendix 7](#) for plot of RC time constant evolution.

SEM images, acquired ex-situ, were used to evaluate the evolution of the LLZTO | LP30 interface; LLZTO pellets were submerged in LP30 for different periods

of time (2 h, 10 h, 20 h, 100 h and 150 h), then they were washed by gently dipping in DMC to prevent the precipitation of LiPF_6 and were dried by evaporation. Top-down SEM images of the LLZTO surface after exposure to LP30, [Figure 5.18](#), reveal the gradual growth of a SLEI. During the first 2 h of exposure, SLEI growth is minimal, with striations from polishing still being clearly visible at the pellet surface from a top-down view, [Figure 5.18 \(a\) & \(b\)](#). After 10 h, a large number of small deposits are visible atop the pellet surface, [Figure 5.18 \(c\)](#). Given that, significantly fewer deposits were observed after 2 h, it is suggested that these spots are not due to deposited salt but are SLEI nucleation hot-spots. From 10 h to 150 h the surface topography becomes less uniform and the pellet appears to become covered with a surface layer, consistent with a SLEI, [Figure 5.18 \(d\)-\(f\)](#)



[Figure 5.18](#). Top-down SEM images of (a) Pristine LLZTO pellet; and following washing with DMC after exposure to LP30 for (b) 2 h, (c) 10 h, (d) 20 h, (e) 100 h, and (f) 150 h.¹⁸¹ Images were acquired with Dr. Jingyuan Liu.

An ultrasonic knife was used to cross-section the LLZTO pellets after exposure to LP30. Cross-sectional SEM reveals that Pristine LLZTO does not contain a thick surface layer, [Figure 5.19 \(ai\)](#). However, exposure to LP30 causes a surface layer to form and thicken with time, [Figure 5.19 \(bi\)-\(gii\)](#).

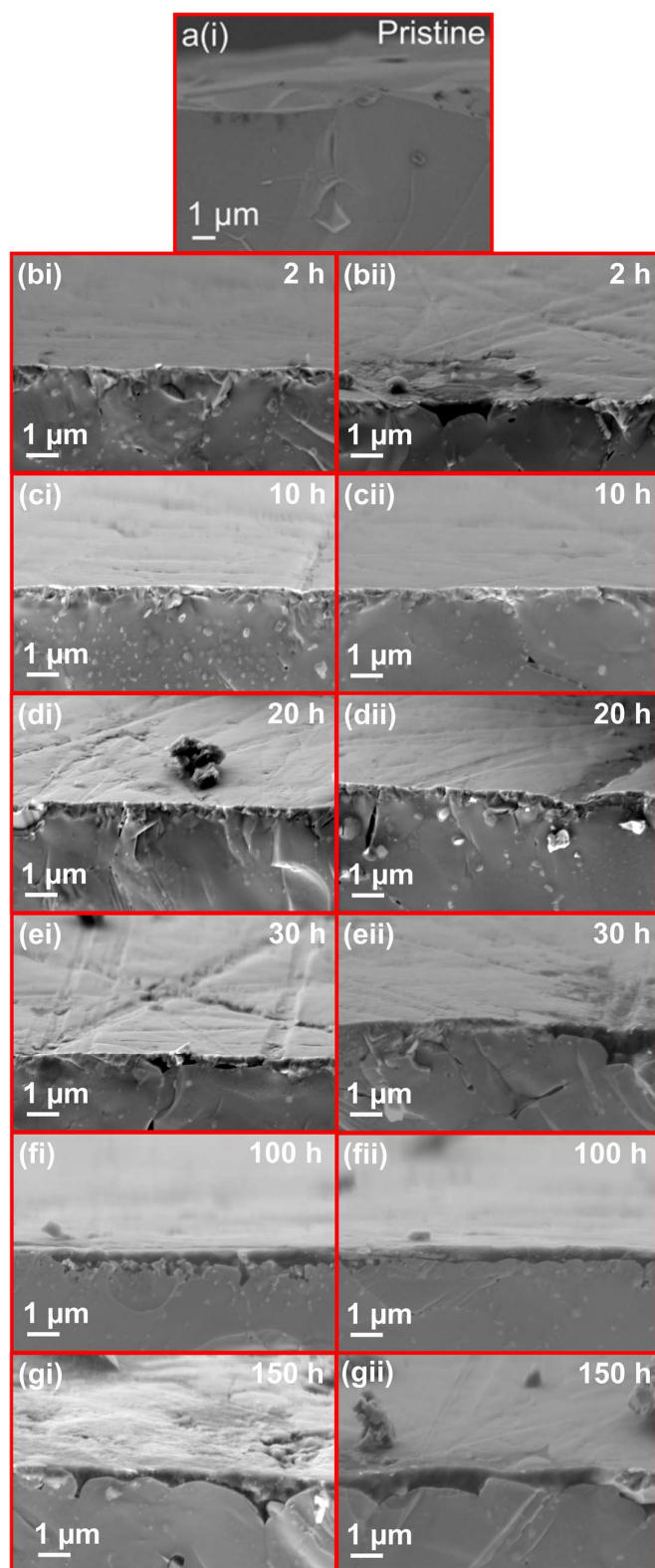
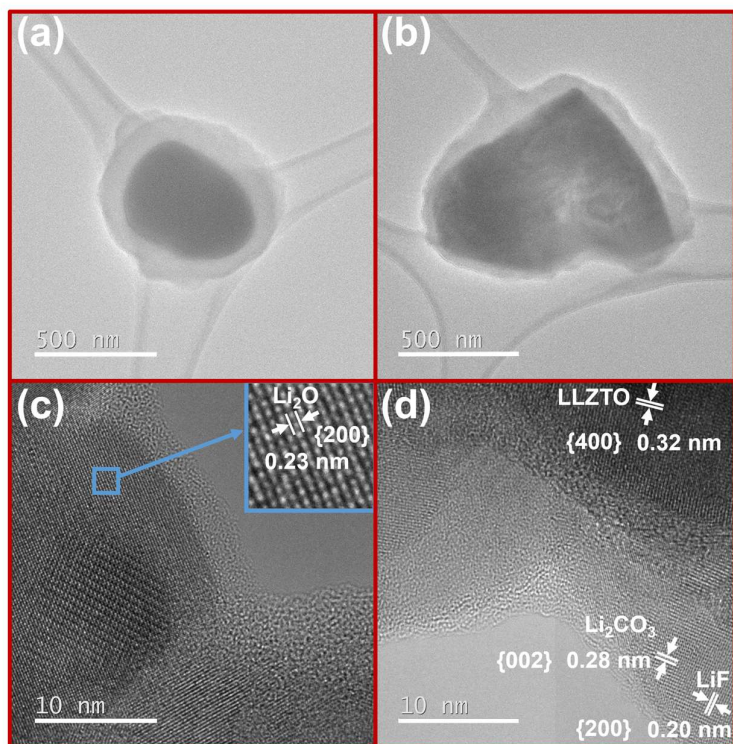


Figure 5.19. Cross-sectional SEM images of a (ai) Pristine LLZTO pellet. Images were taken from different cross-sections following exposure to LP30 for (b) 2 h, (c) 10 h, (d) 20 h, (e) 30 h, (f) 100 h, and (g) 150 h.¹⁸¹

In order to confirm the development of a SLEI atop the surface of LLZTO, after short periods of time, particles of LLZTO powder were examined by TEM after exposure to LP30 for 10 h, (following washing with DMC), [Figure 5.20](#). Particles of LLZTO, became encapsulated in a largely amorphous surface layer, [Figure 5.20 \(a\) & \(b\)](#), consistent with the formation of a SLEI. At high magnification, crystallites were observed, with fringe spacing's consistent with LLZTO, Li_2O , Li_2CO_3 and LiF [Figure 5.20 \(c\) & \(d\)](#).



[Figure 5.20](#). (a) & (b) TEM images of LLZTO particles after 10 h exposure to LP30 following washing with DMC. Increased magnification, reveals the presence of (c) Li_2O {200} with an interlayer spacing of 0.23 nm; (d) Li_2CO_3 {002} with an interlayer spacing of 0.23 nm, LiF {200} with an interlayer spacing of 0.20 nm, and LLZTO {400} with an interlayer spacing of 0.32 nm.¹⁸¹ I proposed the experiments and prepared the samples; TEM / electron diffraction was performed by Chen Gong.

Depth profiling ToF-SIMS of a LLZTO pellet after exposure to LP30, substantiated the formation of a SLEI, [Figure 5.21](#). LiF^- fragments, indicating LiF , and LiCO_3^- fragments indicating Li_2CO_3 , are concentrated at the surface of the pellet; their intensities decrease with depth into the pellet, whereas the ZrO^- content (indicative of LLZTO)

correspondingly increases. $\text{C}_2\text{H}_5\text{O}^-$ fragments were also observed in the surface layer, [Figure 5.21 \(d\)](#), indicating that the amorphous regions of the SLEI observed by TEM may be due to organic species.

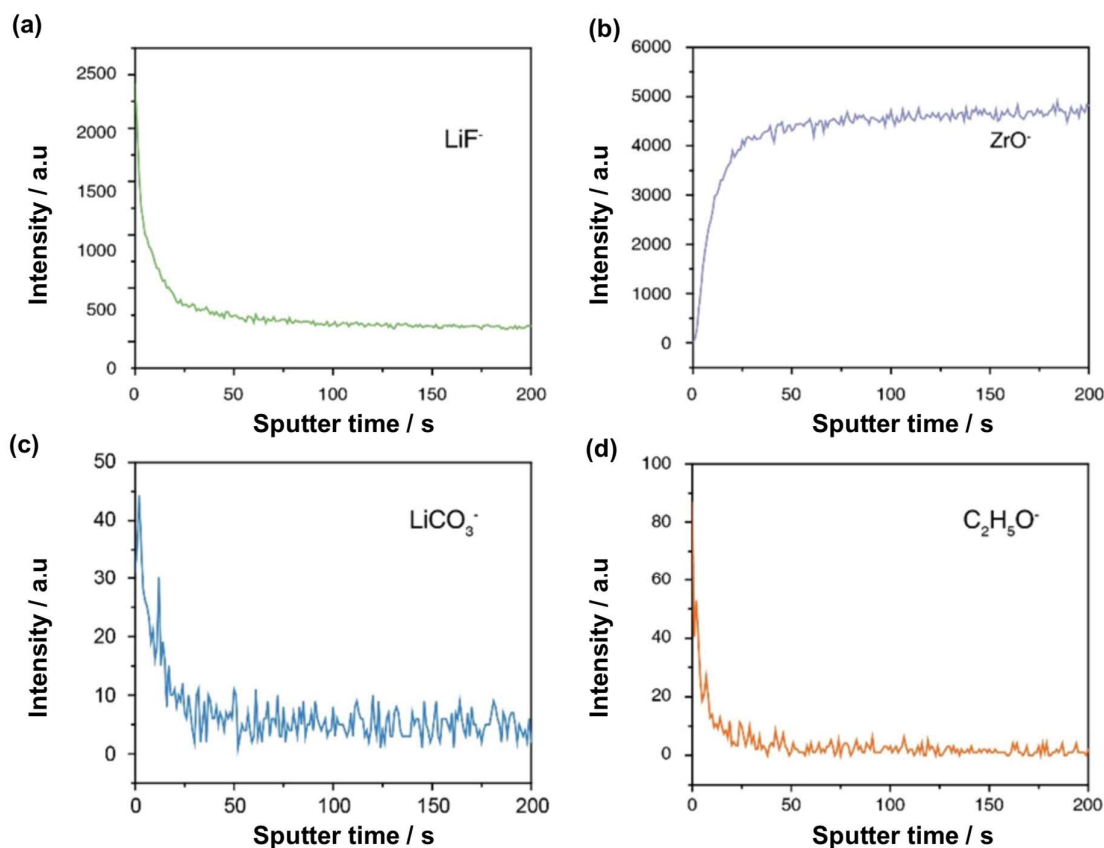


Figure 5.21. ToF-SIMS depth profiling of LLZTO pellet after exposure to LP30.¹⁸¹ Profiles for (a) LiF^- , (b) ZrO^- , (c) LiCO_3^- and (d) $\text{C}_2\text{H}_5\text{O}^-$ fragments. I proposed the experiments, Dr Xiangwen Gao prepared the samples and ToF-SIMS measurements were performed by Dr. Sarah Fearn.

In order to check whether the surface LiF^- signal is from LiF , ^{19}F MAS NMR was performed on LLZTO after exposure to LP30 for 10 h, [Figure 5.22 \(a\)](#). Comparison with a LiF reference confirms the presence of significant LiF . The spectrum contained a minor resonance at -77 ppm, which is attributed to species similar to LiPF_6 , due to the lack of sideband manifold due to the high point symmetry of the fluorine environments. LiF must originate from LiPF_6 . *In-situ* ^{19}F MAS NMR revealed that solid LiF forms with time, [Figure 5.22 \(b\)](#). In this experiment LLZTO is a powder in suspension and magic angle spinning was performed, therefore, the kinetics of

reaction cannot be quantitatively correlated to the rate of SLEI growth; however, the result is qualitatively informative as it confirms that a LiF containing SLEI does indeed develop with time.

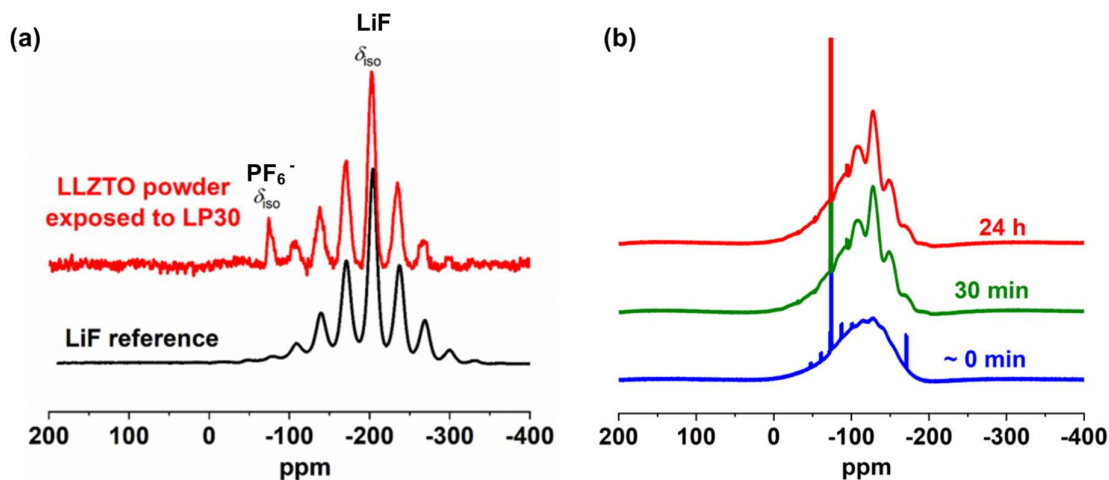


Figure 5.22. ^{19}F MAS NMR spectra of reference LiF (black) and LLZTO after exposure to LP30 (red).¹⁸¹ (b) In-situ ^{19}F MAS NMR spectra of LLZTO in LP30. I proposed the experiments, prepared the samples, made the figure and interpreted the data; the experiments were performed with and the raw spectra was produced by Dr. Gregory Rees.

XPS was used to investigate the chemistry of the SLEI atop LLZTO pellets which had been exposed to LP30 for different periods of time, [Figure 5.23](#). Peaks were not detected in the F 1s XPS spectrum of pristine LLZTO. However, after exposure to LP30, peaks with binding energies consistent with literature values for LiF, LiPF_6 and PF_y were detected.¹⁸³ In accordance with the results of NMR, TEM and ToF-SIMS, this indicates that a SLEI is formed containing unreacted LiPF_6 and LiF. O 1s and C 1s XPS, confirm that the SLEI contains Li_2O , CO_3^{2-} , and Li-O-C. Importantly, the relative intensity of the O 1s LLZTO peak decreases with exposure time with respect to the Li_2O and Li_2CO_3 peaks, confirming a surface covering with a SLEI. Interestingly, the O 1s peak corresponding to Li_2O increases in relative intensity with respect to the Li_2CO_3 peak, with time. It is suggested that Li_2CO_3 and Li_2O are formed in independent reactions at different rates, or it is possible that Li_2CO_3 may be formed from an initial reaction between LLZTO and LP30 but then Li_2CO_3 is then consumed in a subsequent reaction, for example with LiPF_6 to form LiF. Given that Li_2CO_3 and Li_2O cannot be resolved by ^7Li NMR, and given that Li_2CO_3 cannot be studied quantitatively with time

easily by ^{13}C NMR, the *in-situ* investigations needed to determine the true underlying SLEI formation reaction mechanism are beyond the scope of this work.

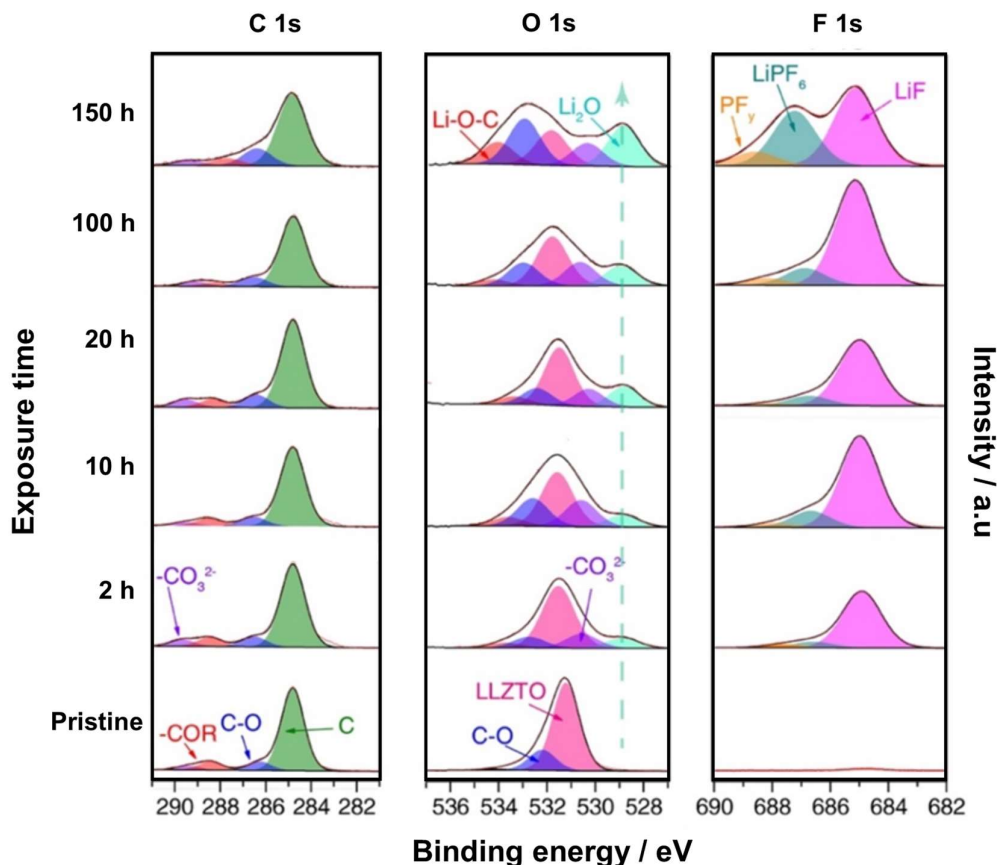


Figure 5.23. C 1s, O 1s and F 1s XPS spectra collected from the surfaces of LLZTO pellets which had been exposed to L30 for 0, 2, 10, 20, 100 and 150 h respectively.¹⁸¹ I prepared the samples and interpreted the data; the spectral acquisition was performed with Dr. Philip Holdway.

The results here presented, strongly imply that LLZTO reacts with LP30 to form a heterogeneous SLEI containing LiF, Li_2O , Li_2CO_3 , organic and LiPF_6 fragments. The resistance of the interface between LP30 and LLZTO is considerable due to the SLEI, therefore cycling, even at low current densities (0.1 mA cm^{-2}), requires high over potential, which is impracticable for commercial devices, [Figure 5.24](#).

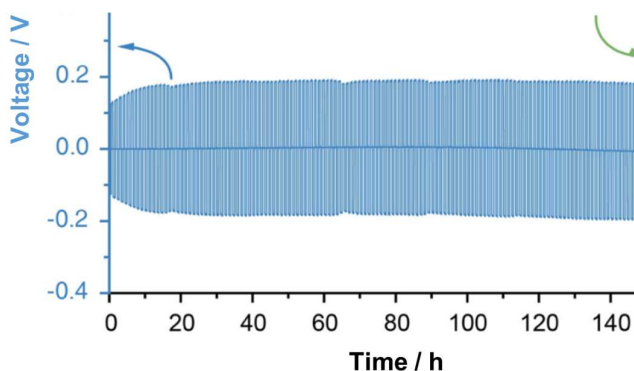


Figure 5.24. Galvanostatic cycling of 0.1 mAh cm^{-2} of capacity, performed at a current density of 0.1 mA cm^{-2} with a LFP | LP30 | LLZTO | LP30 | LFP cell, in a 4-electrode configuration.¹⁸¹ The experiments was performed by Dr. Jingyuan Liu.

5.5 Conclusions

It is proposed that a hybrid cell architecture, in which a SE interposes a metal anode and a LE catholyte, could enable a lithium metal battery to be successfully operated with an energy density greater than current lithium ion cells, by allowing the prohibitive cathode / SE incompatibility issues currently thwarting ASSBs to be circumvented. However, the SE | LE interface acts as an additional source of resistance in such cells, reducing power density and leading to impractical charging times. In this Chapter, 4-electrode electrochemical techniques were used to investigate the SE | LE interface for several different electrolyte combinations. Li_3N and 1 M LiTFSI in PC, and LLZTO and LP30 were investigated in detail, since of the LEs examined, 1 M LiTFSI in PC was found to be the LE which produced the lowest interfacial resistance with Li_3N , and because LLZTO | LP30 is the combination thought to have the most obvious prospective commercial relevance. In both systems $R_{\text{SE/LE}}$, was found to lead to high over potential; even for low current density (0.1 mA cm^{-2}) applications, this would be fatally prohibiting for commercial full cells. In order to understand why $R_{\text{SE/LE}}$ values were so high, the chemistry of the interfaces were examined in detail; it was established that the formation of a SLEI is in large part responsible for the high $R_{\text{SE/LE}}$ values of both systems. It was important to elucidate the chemistry of the SLEIs so that future mitigation strategies may be rationally developed.

LP30 was found to react with LLZTO to produce a SLEI which contributes significantly (> 50 %) to $R_{SE/LE}$. The SLEI is primarily composed of LiF, Li_2O , Li_2CO_3 with small amounts organics, $LiPF_y$ and unreacted $LiPF_6$ salt. The high LiF content of the SLEI, signposts that $LiPF_6$ is a poor choice of salt for hybrid cells. $LiPF_6$ is the most widely used salt in commercial lithium ion batteries because it passivates the aluminium current collector and reacts with carbonaceous electrodes to form a stable SEI.¹⁸⁴ However, these advantages are irrelevant for hybrid cells since there is no LE contact with the negative electrode, and because aluminium is unsuitable for a lithium metal cell due to alloying.¹⁸⁵ In light of the results herein presented, it is suggested that the interface between LLZTO and LEs based on alternative salts ($LiTFSI$, $LiFSI$, $LiDMSI$, $LiBOB$, *etc.*) and solvents with high voltage stability (nitriles, sulphones, *etc.*) should be explored.

In the Li_3N | 1 M $LiTFSI$ in PC system, it was shown that Li_3N reduces both the PC solvent and the $LiTFSI$ salt to form a heterogeneous SLEI. Li_3N is one of the strongest known bases and is capable of reacting with protons in organic compounds.¹⁴⁸ Li_3N reacted with PC to yield Li_2CO_3 and an alkene, which is thought to be propylene, in agreement with the known analogous reduction of PC with lithium metal. A proposed reaction mechanism for the reduction of PC is presented in [Figure 5.25](#).

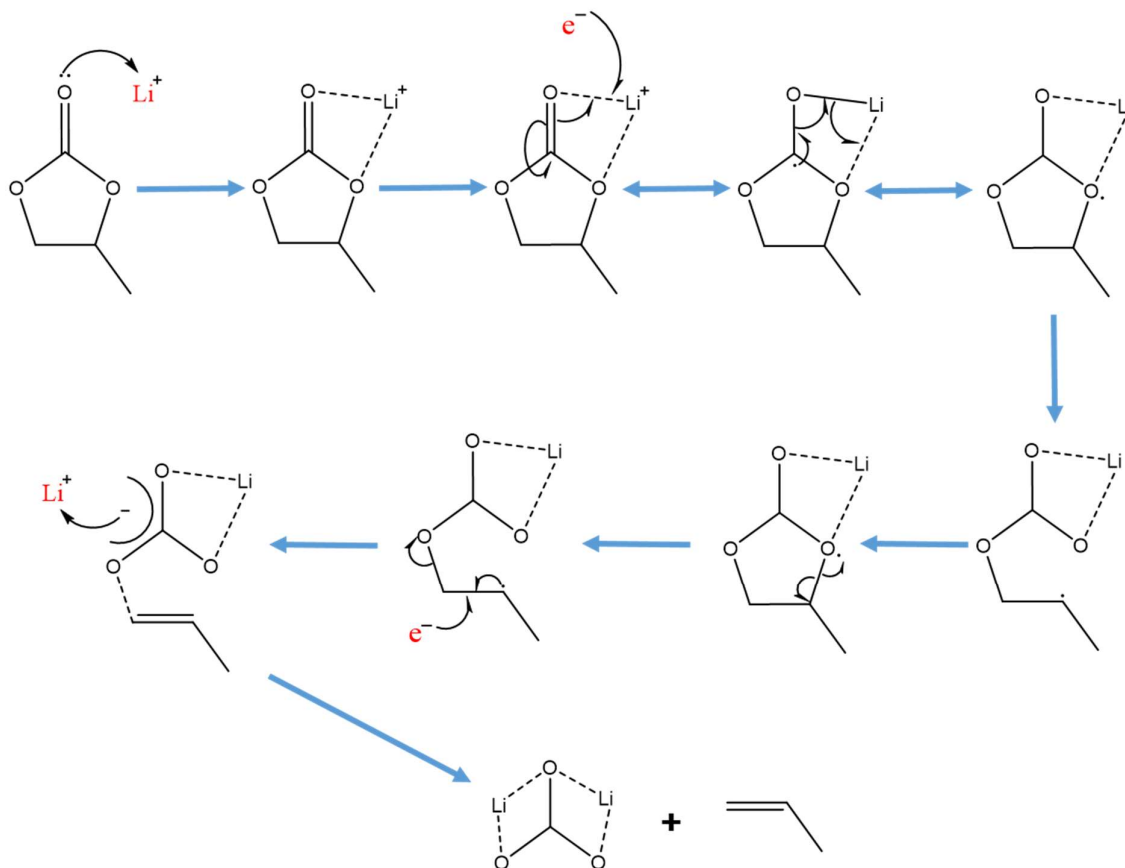


Figure 5.25. Proposed mechanism for PC reduction by Li_3N to form Li_2CO_3 and alkene components in the SLEI.

Consistent with reports of LiTFSi reduction with lithium metal, Li_3N was also found to react with LiTFSi , to produce LiF , possible Li_2S and a fluorinated species which is thought to be $(\text{LiOS}(\text{CF}_3)(\text{NSO}_2\text{CF}_3)_2$.¹⁸⁶

Although, LE can electrically separate Li_3N from active cathode particles, and therefore prevent catastrophic Li_3N oxidation, Li_3N is highly reducing and reacts with LEs to produce a highly ionically resistive SLEI. In light of these results, Li_3N / LE hybrid cells do not appear to offer a real advantage over lithium metal LE cells. Using a salt with greater electrochemical stability at low voltages, such as LiClO_4 , could be beneficial. However, LiClO_4 is considered unsuitable for commercial applications due to safety concerns.¹⁸⁴ Furthermore, a solvent would also be required with electrochemical stability at low voltage to eliminate the SLEI entirely and decrease $R_{\text{SE/LE}}$ to a practically acceptable value. In principle, the hybrid approach could be used

to enable high voltage cathodes because LEs with stability at high voltages such as nitriles and sulphones could be used. However, Li_3N is known to trimerise aromatic nitriles to triazines; likewise, Li_3N reacts with aliphatic nitriles to give the Thorpe reaction.¹⁴⁸ Therefore it is suggested that Li_3N is not a particularly suitable SE for the development of high voltage hybrid cells.

These results show that SLEIs can have a profound influence on the behavior of the interface between SEs and LEs. Clearly Li_3N is a non-ideal SE for hybrid applications. However, alternative SEs and LEs (which are not LiPF_6) based, warrant serious exploration.

5.6 Experimental

$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) powder was synthesised as followed using a modified Pechini sol-gel method. A metal alkoxide solution was prepared at 60 °C by combining 100 ml solutions containing 2.80g of $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma), 2.96 g of LiNO_3 (99.99%, Sigma), and 7.14 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Sigma), with 0.99 g of TaCl_5 (99.99%, Sigma) dissolved in 10 cm^3 of ethanol. The metal alkoxide solution was vigorously stirred and was then combined with a chelating agent solution (1.84 g of citric acid and 3.2 g of ethylene glycol dissolved in 100 cm^3 of distilled H_2O) to form a sol, which was subsequently heated at 90 °C to remove water and form a gel. The gel was ground to a fine powder and was heated for 10 h at 400 °C in air to burn off the organic compounds. After cooling to room temperature, additional grinding was performed and the resultant powder was uniaxially cold pressed (400 MPa) into pellets. Heating at 900 °C for 12 h under an argon atmosphere produced $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$, which was then powdered by grinding. The tap density of the LLZTO powder was determined to be 5.345 g cm^{-3} using a micromeritics AccuPyc II 1340 gas pycnometer. LLZTO pellets were then prepared using an FCT HP D 10-GB spark plasma sintering system; under an argon atmosphere, the LLZTO powder was loaded into a graphite die set. This LLZTO powder was pressed (50 MPa) Ab initio, then heated at a ramp rate of 100 °C min^{-1} until a temperature of 1150 °C was achieved, after which the temperature was held constant for 15 min. The pressure was then slowly released as the sample was cooled to room temperature at a rate of

30 °C min⁻¹. This procedure produced LLZTO pellets (thickness: 2-2.5 mm, diameter: 1.4 cm, 98 % ($\pm$ 1.1 %) of theoretical density); the envelop density of the cylindrical disks after polishing was calculated using a mass value determined by weighing and a volume calculated from the diameter and thickness of the disk. The surface of the LLZTO pellets were polished consecutively with P400, P1200 and P4000 grit silicon carbide papers. Following polishing, the pellets were heated under argon to 800 °C at a rate of at 2 °C min⁻¹ to remove surface contaminants. Li₃N pellets (5 mm diameter) were prepared in accordance with the sintering and polishing method developed in **Chapter 4**.

PC (99.7 %, Sigma-Aldrich) and TEGDME (99 %, Sigma-Aldrich) solvents were respectively purified by distillation. PC, TEGDME and DMC solvents were then dried over molecular sieves; with the final water content being $\leq$ 10 ppm, as determined by Karl Fischer titrations. LiPF₆ (99.99 %, Sigma-Aldrich) and LiTFSI (99.95 %, Sigma-Aldrich) salts were dried at 100 °C under vacuum for 12 h. 1 M solutions of LiTFSI in PC, LiTFSI in TEGDME, LiTFSI in DMC and LiPF₆ in PC were then prepared for investigations with Li₃N. Commercial LP30 (LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v/v), BASF battery-grade; H₂O < 15 ppm, HF < 50 ppm), was used for investigations with LLZTO.

Inside a fan cooled argon filled glovebox, Li₃N and LLZTO pellets were sealed inside polypropylene rings (by a melting method); this produced a well-defined SE surface area, enabling electrochemical measurements using the H-cell shown in [Figure 5.1 \(c\)](#). Nitrile based O-rings, were sandwiched between the glass components of the cell and the propylene ring, this enabled the two halves of the H-cell to be fixed together using a C-clamp. The H-cell design prevented LE from moving between the two sides of the cell, such that all ion exchange across the respective halves of the cell had to occur via the SE by means of the SE | LE interface. The leak tightness of the H-cell was appraised following electrochemical measurements by adding ferrocene to one half of the cell, waiting 24 h, and then analysing the other compartment with UV-VIS spectroscopy, using a PerkinElmer Lambda 35 spectrometer. Partially oxidised two-phase Li_xFePO₄ (LFP), (3.45 V versus Li⁺/Li) electrodes were prepared and used for electrochemical measurements, to minimise electrochemical degradation of the LE and prevent contamination of the

SE | LE interface. After mixing with super p carbon (10 wt %) and PTFE (10 wt %), the electrodes were cast with on to a stainless steel mesh current collectors, which had been spot welded to stainless steel wire. These wires were fed thread through airtight subbaseal septum caps so that the H-cell was an enclosed system. In practice, the H-cell was fully assembled in an Argon filled glovebox and was placed in a grounded Faraday cage, then a chosen LE was injected via a syringe into the respective halves of the cell, and electrochemical measurements were commenced using a Gamry Interface 1010 potentiostat. 4-electrode EIS was performed over a 1 MHz to 1 Hz frequency range using a 10 mV applied perturbation voltage. $R_{SE/LE}$ and $C_{SE/LE}$ values were determined by fitting the ascribed SE | LE interface Nyquist impedance contribution with circuit elements using ZView programme. Using a Gamry Interface 1010 potentiostat, galvanostatic cycling (0.1 mAh cm^{-2} at 0.1 mA cm^{-2}) of a LFP | LP30 | LLZTO | LP30 | LFP cell, was performed in a 4-electrode configuration, immediately after LE was added. Whereas 4-electrode galvanostatic cycling (0.1 mAh cm^{-2} at 0.1 mA cm^{-2}) of LFP | 1M LiTFSI in PC | Li_3N | 1M LiTFSI in PC | LFP was only performed after the SE had been exposed to the LE for one month.

SEM images, EDX spectra and element maps of SE pellets after exposure to LE, were taken from a top-down views, and cross sectional-views following sectioning with an ultrasonic knife, using a FE-SEM (Zeiss-Merlin) instrument; with samples being transferred to the instrument by means of an air-sensitive sample holder. TEM images and electron diffraction spot patterns were acquired using a Jeol-3000F microscope at an acceleration voltage of 300 kV.

TOF-SIMS depth profiling experiments were conducted with a TOF-SIMS5-Qtac100 LEIS spectrometer with a Bismuth primary-ion source and a Caesium sputter gun. XPS depth profiling experiments were performed using a Thermo Scientific XPS K- α instrument, with argon sputtering for depth profiling, using a microfocused monochromated Al X-ray source operated at 12 keV with a $400 \text{ }\mu\text{m}$ spot size. Samples were transferred to the spectrometer using an airtight transfer holder. Spectra were charge corrected (284.8 eV for adventitious carbon) and Shirley backgrounds were used but no spectral smoothing was performed.

The solid state ^1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements were undertaken at 9.4 T using a Bruker Avance-III HD 400 spectrometer operating at a ^1H Larmor frequency of 399.89 MHz. The data was acquired using a Bruker 4 mm triple resonance (HXY) probe spinning at 12.0 kHz. A single pulse experiment was implemented using a $2.50\ \mu\text{s}$ pulse duration (flip angle of $\pi/2$) and a recycle delay of 2 s. This ^1H MAS NMR data were referenced to the primary standard of tetramethylsilane (TMS, $\delta_{\text{iso}} = 0\ \text{ppm}$). ^{13}C MAS NMR data was acquired with a 9.4 T Bruker Avance-III HD 400 spectrometer operating at a ^{13}C Larmor frequency of 100.64 MHz. A ^1H - ^{13}C cross-polarisation MAS (CPMAS) experiment was implemented using a Bruker 4 mm double resonance probe which enabled a rotation frequency of 12 kHz. A variable amplitude (70 - 100 %) CPMAS experiment employed an initial ^1H $\pi/2$ pulse of $2.5\ \mu\text{s}$, a contact period of 4 ms, a recycle delay of 5 s and a ^1H decoupling field of $\sim 100\ \text{kHz}$ during acquisition. The ^{13}C CPMAS NMR data was referenced to the primary standard of tetramethylsilane (TMS, $\delta_{\text{iso}} = 0\ \text{ppm}$) via a secondary solid alanine reference ($\delta_{\text{iso}}(\text{CH}_3) = 20.5\ \text{ppm}$, $\delta_{\text{iso}}(\text{CH}) = 50.5\ \text{ppm}$ and $\delta_{\text{iso}}(\text{COOH}) = 177.8\ \text{ppm}$). The direct observation ^{13}C (HPDEC) was completed with the high-power decoupling outlined above, a $3.0\ \mu\text{s}$ $\pi/2$ acquisition pulse and a 20 s recycle delay were implemented. The 2D ^1H - ^{13}C Lee-Goldberg heteronuclear correlation experiment used the same cross polarisation preparation as described above and implemented homonuclear Lee-Goldberg ^1H - ^1H decoupling during acquisition. No additional resolution enhancement in the ^1H spectrum was observed with the implementation of homonuclear decoupling. For the integer spin quadrupolar ^6Li ($I = 1$) nucleus MAS NMR studies were performed at 9.4 T using a Bruker Avance-III HD 400 instrument operating at a Larmor frequency of 58.84 MHz, respectively. A Bruker 4mm HXY probe yielded a spinning frequency of 12 kHz for all experiments. The spectra were referenced to 1M $\text{LiCl}_{(\text{aq})}$ ($\delta_{\text{iso}} = 0\ \text{ppm}$) and a $1\ \mu\text{s}$ excitation $\pi/4$ pulse was used for the direct observations. The CPMAS and FSLG-HETCOR experiments utilised the same decoupling schemes and relaxation times as in the ^{13}C experiments; an 8 ms contact time with a 90 - 100 % ramp was found to give the best signal to noise. The ^{15}N HPDEC and CPMAS spectra were acquired using the same spinning frequencies and decoupling schemes above, the recycle delay for the CPMAS and HPDEC were 5 s and 6 s, respectively. An 8.5 ms contact time with a 0-100 % ramp was used for the CPMAS and a $2.5\ \mu\text{s}$ excitation $\pi/4$ pulse for the HPDEC.

The spectra were referenced to the secondary reference of glycine_(s) ($\delta_{\text{iso}} = -347$ ppm). All ^7Li and ^{19}F experiments were completed on a Bruker Avance III 9.45 T spectrometer operating at Larmor frequencies of ($\nu_0 =$) 155.4 and 376.5 MHz, respectively. A Bruker HFX 4 mm double air bearing probe was utilized to achieve an ($\nu_r =$) 8 kHz MAS frequency (sidebands determined by varying the spinning frequency between 5 and 8 kHz). The temperature was stabilized to 298.1 K throughout all experiments. The MAS ^7Li experiment was referenced to 1 M $\text{LiCl}_{(\text{aq})}$ at 0 ppm and the ^{19}F experiment was referenced to Teflon® at -123.2 ppm. A $1.25\ \mu\text{s}$ (200 kHz) non-selective $\pi/4$ pulse and single pulse experiment was used to excite the ^7Li spin system, this was compared to a Hahn echo ($\pi/2$ - τ - π) experiment to ensure no broad components were missing. The ^{19}F experiments employed a $2.50\ \mu\text{s}$ 100 kHz $\pi/2$ pulse to excite the system and once again a single pulse experiment was corroborated with a Hahn echo to ensure no resonances were missing. Excessively long repetition times (> 30 min) were used in all experiments to ensure no slow relaxing species were neglected. The solid-state DNP CPMAS were recorded on a Bruker NMR spectrometer operating at 14.1 T (600 MHz for the ^1H Larmor frequency) controlled by an AVANCE-III console and equipped with a 3.2mm low-temperature DNP 1 H/X/Y magic-angle spinning (MAS) probe manufactured by Bruker. This spectrometer was equipped with a gyrotron that provided microwave (μw) irradiation of the sample. Specifically, the field sweep coil of the NMR magnet was set so that μw irradiation occurred at the maximum DNP enhancement of TEKPol. The estimated power of the μw beam at the output of the probe waveguide is ~ 5 W. The sample temperature (with μw switched on) was ~ 100 K with a MAS speeds ranging from 10 - 12 kHz. During the CPMAS experiments, the μw irradiation field was turned on. Moreover, the amplitude of the 1 H contact pulse (2 ms duration) in CPMAS experiments was linearly ramped to improve CP efficiency. All spectra were fitted using DMFit.

The gases produced by the reaction of Li_3N and PC were quantitatively analysed using a mass-flow-regulated Thermo Fisher Scientific Prima BT gas analyzer mass spectrometer (MS), with background N_2 content from air due to unavoidable micro leaks being accounted for by consideration of the air $\text{O}_2 : \text{N}_2$ expectation ratio.

PXRD measurements were performed, under a nitrogen atmosphere inside a glovebox, using a Rigaku miniflex X-ray diffractometer employing $\text{Cu K}\alpha$ radiation.

Chapter 6: Exploration of previously uncharacterised nitrogenous SEs

6.1 Abstract

In a study by Tatsumisago et al., the mechanochemical milling of Li_3N and P_2S_5 was reported to form a novel amorphous solid-electrolyte containing lithium sulfide.¹⁸⁷ However, the results presented in this chapter demonstrate that a new SE is not formed; instead, the ball-milling of Li_3N and P_2S_5 is shown to form a mixture of known lithium thiophosphates (Li_3PS_4 , $\text{Li}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_7$); lithium sulphide, with possible red phosphorus. For the first time, the phase responsible for the ionic conductivities of $\text{Li}_3\text{N} \cdot \text{P}_2\text{S}_5$ SEs is revealed to be amorphous Li_3PS_4 . Furthermore, the mechanisms for the milling induced reactions are elucidated.

6.2 Introduction

In order to achieve high C-rate charge/discharge cycles, internal cell resistances should be minimised as much as possible. Li^+ ion exchange across the SE/Li interface in an ASSB typically has an associated resistance,^{188–190} even when constriction resistances (identified in Chapter 4) are minimised.^{138,139} SE/Li interfacial resistance is often exaggerated by the presence of high resistance SEIs.^{53,191} Lithium stable SEs, which don't form SEIs, are therefore highly attractive candidates for use in practical ASSBs. However, there are few lithium stable solid-electrolytes with ionic conductivity $> 1 \times 10^{-4} \text{ S cm}^{-1}$; lithium nitride and Garnet SEs are amongst the few materials that meet these requirements but these SEs suffer from severe chemical and physical incompatibility with cathodes as discussed in **Chapter 5**.^{111,192} Although a hybrid approach was explored to mitigate the incompatibility of Li_3N and Garnet SEs with cathodes,¹⁸¹ this challenge remains unsolved for practical purposes. On the other hand, sulfide electrolytes, namely the lithium argyrodites (LPSX , where X is a halide) and the lithium thiophosphates (LPS), have ionic conductivities greater than $1 \times 10^{-4} \text{ S cm}^{-1}$ and also possess beneficial mechanical properties for cathode applications.¹⁹³ However, the sulfides are unstable in contact with lithium metal and are reduced at the interface with the anode to form stable SEIs containing binary

lithium salts (Li_2S , LiP , Li_3P and also LiX in the case of the argyrodites).¹⁹¹ Such SEIs are poor ionic conductors and contribute significantly to the interfacial resistance, decreasing the C-rate of the battery.¹⁹⁴ It has been shown that thin buffer layers, such as gold, can be deposited on the surface of the SE to improve the interfacial contact with lithium during cycling;¹⁹⁵ it has also been shown that the Li/SE interface can be stabilised by the deposition of a thin inorganic layer, such as Li_2S layer.¹⁹⁶ However, damage to the deposited surface layer incurred during cycling is unable to self-heal thus inhomogeneity at the interphase would accumulate with time, possibly leading to regions of increased Li^+ flux across the interface and leading to subsequent dendrite nucleation. As such, the development of a high ionic conductivity SE with ionically conducting and electrically insulating reduction products would be highly desirable, as the SEI would only produce a small interfacial resistance and the interface would be self-healing. Given that Li_3N would be an ideal SEI component due to its stability with lithium and its high ionic conductivity, nitrogen containing electrolytes warrant serious investigation. Furthermore, theoretical studies have indicated that the presence of nitride anions (N^{3-}) in SEs should provide unique stability at low potential.^{64,197} Experimental studies have already revealed that nitrogen doping of oxides can improve the performance of SEs against a lithium metal electrode.¹⁹⁸ For example, LiPON, a nitrogen doped lithium phosphate, has demonstrated outstanding cycling performance in ASSBs.¹⁰ Due to the low polarisability of the oxide ions, LiPON has low ionic conductivity ($\sim 10^{-6} \text{ S cm}^{-1}$), therefore LiPON ASSBs are limited to low power and low capacity applications, and are likely to remain unsuitable for automotive power trains.¹⁹⁹ New nitrogeneous solid electrolytes are of great interest.

Lithium nitridophosphates are a class of nitrogeneous solid electrolytes based on P centred polyhedra, which are analogous to lithium thiophosphates and lithium phosphates (Figure 6.1).^{200–202} The lithium nitridophosphates do not exhibit the high ionic conductivity of the lithium thiophosphates; the sulphide anion is less polarising than the nitride anion so Li^+ transport through the bottlenecks is less hindered in the lithium thiophosphates. Given that, PO_4^{3-} , PS_4^{3-} and PN_4^{7-} polyhedra are thermodynamically stable at room temperature, and given that nitrogen doping of lithium phosphates can produce stable PON_3^{6-} polyhedra, it is suggested that nitrogen doping of lithium thiophosphates may be able to form $\text{PS}_{(4-x)}\text{N}_x^{-(3+x)}$ type polyhedra, Figure 6.1 (e), (f) & (g). Lithium nitridothiophosphates (LPSN), containing polarisable

sulfide anions, may facilitate fast ion conduction and be capable of forming Li_3N rich SEIs in contact with lithium metal.²⁰²

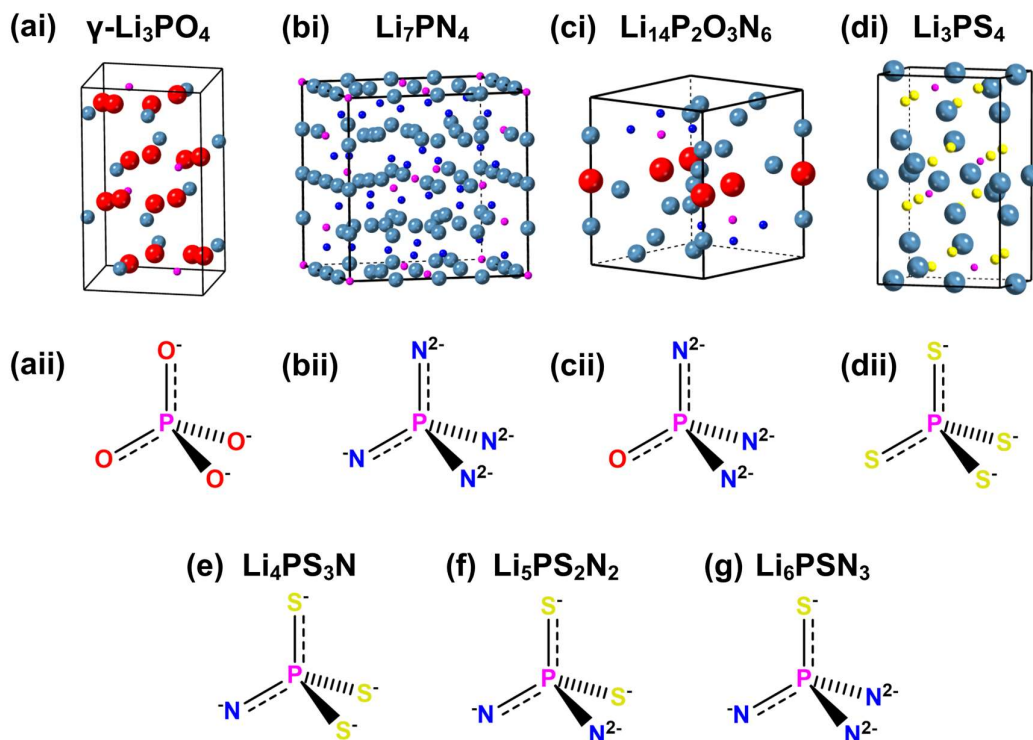


Figure 6.1. Crystal structures of (ai), $\gamma\text{-Li}_3\text{PO}_4$, (bi) Li_7PN_4 (ci) $\text{Li}_{14}\text{P}_2\text{O}_3\text{N}_6$ and (di) $\beta\text{-Li}_3\text{PS}_4$. Known polyhedra present in SEs: (aii) PO_4^{3-} , (bii) PN_4^{7-} , (cii) PON_3^{6-} , (dii) PS_4^{3-} . Proposed nitridothiophosphate polyhedral: (e) PS_3N^{4-} , (f) $\text{PS}_2\text{N}_2^{5-}$, (g) PSN_3^{6-} .

Studies on lithium nitridothiophosphates have so far been limited. However, Tatsumisago et. al., showed that the mechanochemical milling of Li_3N with P_2S_5 produced an amorphous SE with an ionic conductivity of $1.0 \times 10^{-5} \text{ S cm}^{-1}$.¹⁸⁷ The species responsible for the ionic conductivity was not identified. As significant nitrogen is present in the precursors, the production of an amorphous nitrogenous solid electrolyte is implied. This chapter explores the chemistry of SEs produced by the mechanochemical milling of Li_3N and P_2S_5 in depth and attempts to establish whether a lithium nitridothiophosphate is indeed synthesised, and whether these SEs are suitable for lithium metal anode ASSBs.

6.3 Discussion of various $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions

In the aforementioned report by Tatsumisago et al,¹⁸⁷ ball milling of Li_3N with P_2S_5 was used to produce materials with lithium ion conductivities $\sim 10^{-7} - 10^{-5} \text{ S cm}^{-1}$, with the $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ nominal composition giving the greatest ionic conductivity ($1 \times 10^{-5} \text{ S cm}^{-1}$). In their paper optimisation of the milling conditions was not reported. In this study, Li_3N and P_2S_5 were ball milled together for 20 h in a $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ ratio using several rotation speeds in order to find optimal conditions for maximising ionic conductivity [Figure 6.2 \(a\)](#). A rotation speed of 550 RPM was found to maximise the apparent ionic conductivity of $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ ($9.8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature), [Figure 6.2 \(a\)](#). Since the pellets in this study are produced by cold-pressing, it was important to establish the effect of pellet compaction on conductivity so that the results of this study could be compared to other work, where different pellet densities may have been used [Figure 6.2 \(b\) & \(c\)](#). The pellets discussed throughout the rest of this chapter were prepared by cold pressing at 510 MPa because this produced a relatively high density and relatively high ionic conductivity but it also minimised pellet crumbling

which was commonly observed when the pellets were removed from the die-set after higher pressures had been employed.

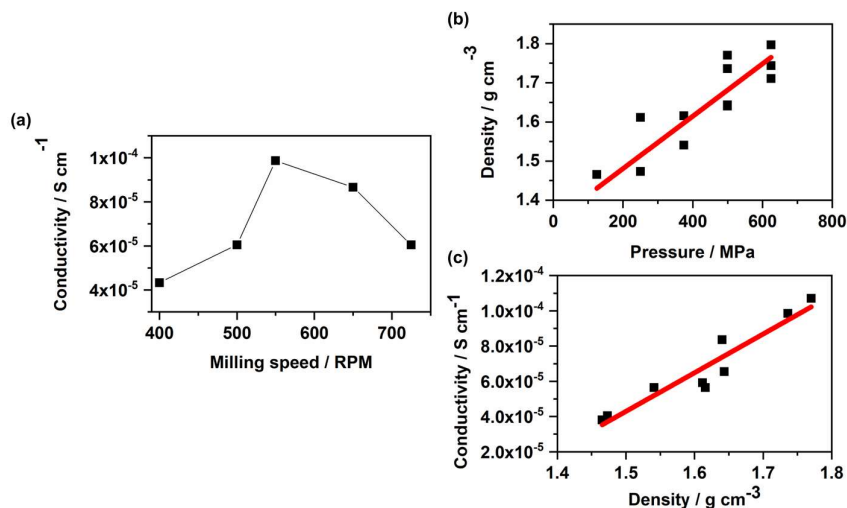


Figure 6.2. (a) The ionic conductivity of 60Li₃N·40P₂S₅ determined by impedance spectroscopy with indium blocking electrodes after ball milling at various rotation speeds for 20 h using magnesia stabilised zirconium oxide milling media; the pellets were cold pressed at 550 MPa. (b) The relationship between the compaction pressure used to cold press the pellets and the resulting pellet envelop density; established with 60Li₃N·40P₂S₅ (milled for 20 h at 550 RPM). (c) The envelop density of cold pressed pellets and their corresponding ionic conductivities.²²³

Li₃N and P₂S₅ were milled at 550 RPM in various ratios: xLi₃N·(100-x)P₂S₅, where x = 50, 55, 60, 65, 70, 75 and 80 mol %; the resulting materials were investigated by electrochemical impedance spectroscopy. 60Li₃N·40P₂S₅ had the greatest ionic conductivity of the ratios explored, confirming the results of Tatsumisago;¹⁸⁷ however, it should be noted that the conditions optimised for the 60Li₃N·40P₂S₅ composition also produced a marked improvement in ionic conductivity for all compositions. The impedance spectrum of 60Li₃N·40P₂S₅, and all other nominal compositions studied, were well fitted with a single semicircle using the equivalent circuit element diagram in Figure 6.3 (a). The corresponding capacitance values are in the 10⁻¹¹ F cm⁻¹ range; this is typical for a minor bulk phase which indicates that xLi₃N·(100-x)P₂S₅ materials contain a lithium ion conducting phase and at least one insulating phase.²⁰³ Furthermore, the lack of grain boundary resistance indicates that the ionically conducting phase must be largely amorphous.

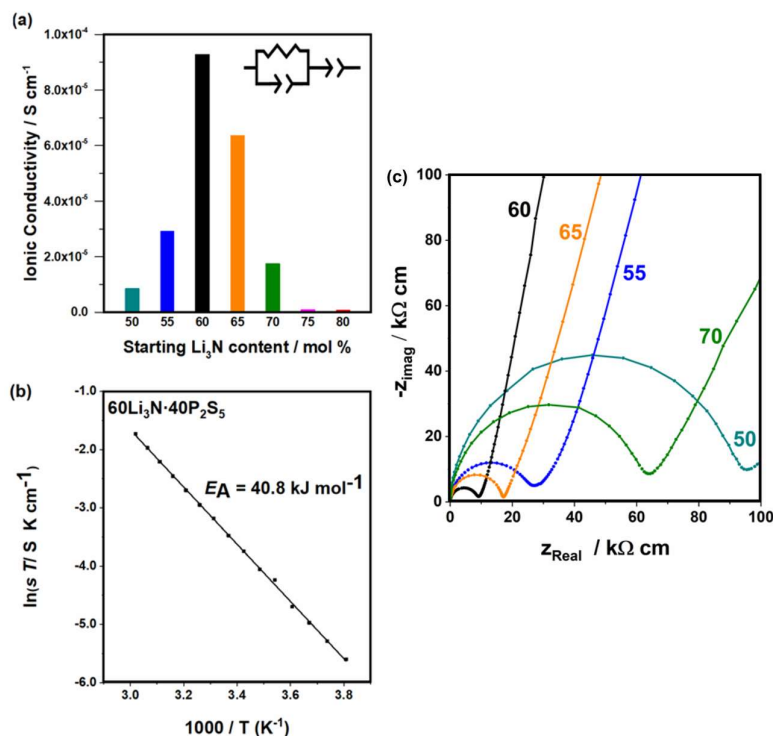


Figure 6.3. (a) Ionic conductivities of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h of ball milling at 550 RPM, with the corresponding circuit element diagram shown. (b) Measured impedance plotted with temperature for $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ used to determine the activation energy of ionic conduction. (c) Nyquist plots corresponding to the electrochemical impedance of $\text{In} | x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5 | \text{In}^{223}$

In order to assess whether $\text{Li}_3\text{N} \cdot \text{P}_2\text{S}_5$ SEs were indeed nitrogenous materials, the nitrogen content of the solids was investigated by several analytical techniques. The ^{15}N MAS-NMR spectrum of $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ did not show the presence of nitrogen atoms after milling, [Figure 6.4](#).

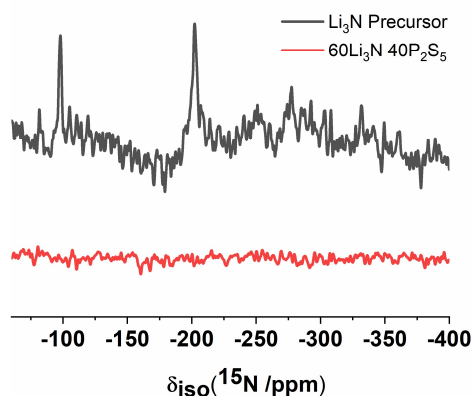


Figure 6.4. ^{15}N MAS-NMR spectra of reference Li_3N and $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ after ball milling.²⁰² I proposed the experiments, made the figure, prepared the samples and interpreted the data; the experiments were performed with and the raw spectra was produced by Dr. Gregory Rees.²²³

The nitrogen content of the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions was quantified using CHN elemental analysis. Significantly less nitrogen was detected in all compositions after milling than was supplied by the Li_3N precursor, [Figure 6.5 \(b\)](#). In order to preclude the possibility of systematic instrumental underestimation of the nitrogen content, a reference sample: 25 mass % of NH_4Cl and 75 mass % of P_2S_5 was also tested and expected nitrogen was quantified. Decreased nitrogen content was also observed by XPS, [Figure 6.5 \(b\)](#). However, XPS is only surface sensitive so this result should not be regarded as quantitatively representative of the bulk. These results clearly show that nitrogen loss must occur during milling; the logical implication being that a gas must have been evolved.

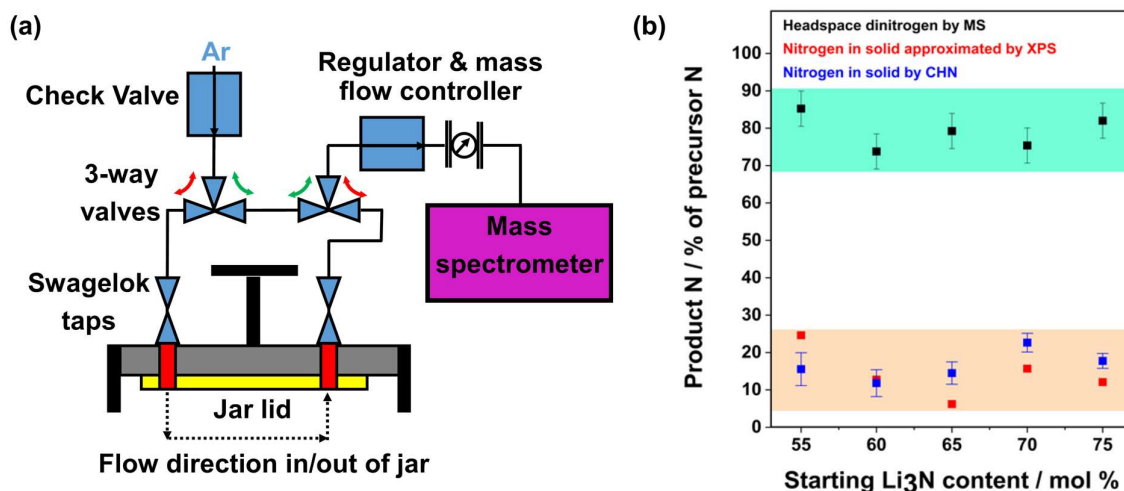
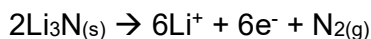


Figure 6.5. (a). Custom system to allow analysis of headspace gas in a ball milling jar. Green arrows show 3-way valves positions for bypass and red arrows show valves in 3-way valves in position for analysis. (b) Quantification of nitrogen in $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h ball milling by CHN elemental analysis and XPS, and in headspace as N_2 gas.²²³

Custom ball milling jar lids were fitted with Swagelok taps so that the headspace gas in the jar could be extracted and analysed. A custom gas line setup was developed to enable the headspace to be quantitatively analysed by mass spectrometry, Figure 6.4 (a). Milling jars were sealed in an argon filled glovebox and mass spectrometry was used to confirm their airtightness after milling without precursor powders; only negligible quantities of O_2 and N_2 were observed. Milling jars were loaded with nominal starting $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions under an argon atmosphere. Analysis of the headspace gas after 20 h of milling revealed significant concentrations of dinitrogen but no other gases (except for argon carrier gas) were observed. This indicates that Li_3N is oxidised to N_2 during ball milling with P_2S_5 :



As such, P_2S_5 is expected to undergo reduction during milling.

N 1s XPS spectra were acquired for all $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h of milling. Inspection of the spectra revealed the presence of two peaks in all of the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions; the peaks were low in intensity with respect to the background noise, Figure 6.6 (c). The N 1s spectrum of precursor lithium nitride, Figure 6.6 (b), also only contains peaks at 398.4 eV and 396.9 eV. This suggests that

the low concentrations of nitrogen detected by N 1s XPS are from residual amounts of unreacted precursor Li_3N . N 1s XPS did not provide strong evidence for the formation of a new nitrogeneous phase. In the literature, there are some reported N 1s XPS spectra for Li_3N that appear to contain two peaks, as shown in [Figure 6.6 \(b\)](#).²⁰⁴ However, in these reports, background noise is significant so the peaks are not assigned. Precursor Li_3N contains a mixture of $\alpha\text{-Li}_3\text{N}$ ($P6/mmm$) and $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$) polymorphs, as shown by PXRD patterns in [Figure 6.6 \(a\)](#). The two N 1s XPS peaks that were detected may therefore be from the respective Li_3N polymorphs. It is known from literature that ball milling can be used to induce the $\alpha\text{-Li}_3\text{N}$ to $\beta\text{-Li}_3\text{N}$ transition,¹⁴⁴ therefore milling was used to prepare isolated $\beta\text{-Li}_3\text{N}$, which was used as an XPS reference that enabled the peaks to be resolved, [Figure 6.6 \(b\)](#).

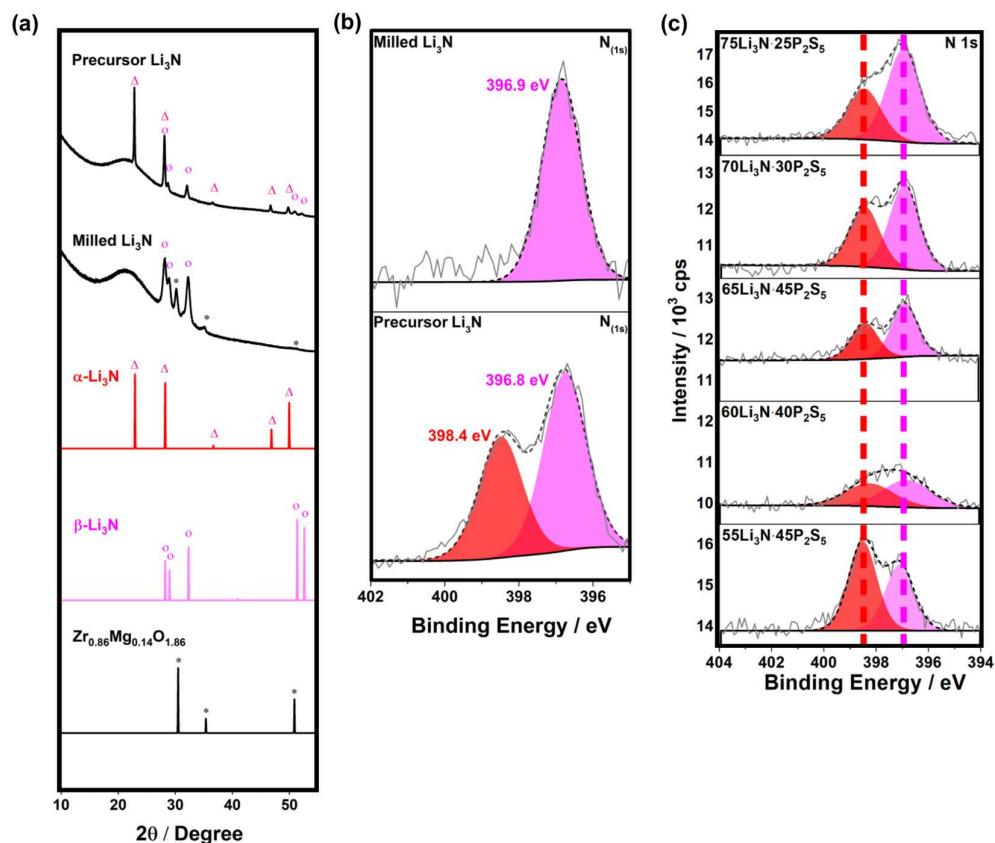


Figure 6.6. (a) PXRD patterns of precursor Li_3N , ball milled Li_3N which was used as a reference for $\beta\text{-Li}_3\text{N}$ in XPS experiments and literature PXRD reference patterns for $\alpha\text{-Li}_3\text{N}$ ($P6/mmm$),¹¹³ $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$),¹¹³ and $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ ($Fm\bar{3}m$) from milling media.²⁰⁵ $\text{N } 1s$ XPS spectra for: (b) ball milled Li_3N and precursor Li_3N , and (c) $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions.²⁰² I prepared the samples and interpreted the data; the spectral acquisition was performed with Dr. Philip Holdway.²²³

PXRD was used to study the samples after 20 h of milling. The diffraction patterns had non-flat backgrounds with several peaks (Figure 6.7), which indicates that the samples likely contain amorphous and crystalline phases. Precursor P_2S_5 ($P\bar{1}$) and $\alpha\text{-Li}_3\text{N}$ ($P6/mmm$) were not observed after milling in any of the investigated $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions,^{113,206} indicating the precursors had largely reacted. However, very low relative intensity peaks consistent with the diffraction pattern of $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$) were observed in $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ and $65\text{Li}_3\text{N} \cdot 35\text{P}_2\text{S}_5$.¹¹³ Amorphisation of Li_3N may also have occurred. Distinct crystal phases were observed in the diffraction patterns of the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions. In compositions with low nominal Li_3N content, i.e. $55\text{Li}_3\text{N} \cdot 45\text{P}_2\text{S}_5$, a dominant phase consistent with $\text{Li}_4\text{P}_2\text{S}_6$ ($P6_3/mcm$) was observed in the diffraction pattern.²⁰⁷ $\text{Li}_4\text{P}_2\text{S}_6$ is a well-known but low ionic conductivity lithium

thiophosphate.²⁰⁸ On the other hand, in compositions with high nominal Li_3N content, i.e. $75\text{Li}_3\text{N}\cdot 25\text{P}_2\text{S}_5$ and $70\text{Li}_3\text{N}\cdot 30\text{P}_2\text{S}_5$, the major crystalline phase observed was consistent with the diffraction pattern for Li_2S ($Fm\bar{3}m$).²⁰⁹ In compositions with intermediate Li_3N content, i.e. $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ and $65\text{Li}_3\text{N}\cdot 35\text{P}_2\text{S}_5$, $\text{Li}_4\text{P}_2\text{S}_6$ ($P6_3/mcm$) and Li_2S ($Fm\bar{3}m$) were both observed. $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ ($Fm\bar{3}m$) impurities from the milling media are present in all patterns.²⁰⁵ It is suggested that the liberation of N_2 gas occurs violently because damage to the milling balls is observed. Although, the relative intensity of the $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ peaks seem somewhat high relative to the other crystalline phases, due to the strong relative X-ray scattering of Zr and Mg, and because there is a significant amorphous component to the samples and ICP-OES reveals that $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ impurities account for $< 1\%$ of the mass of the SEs.

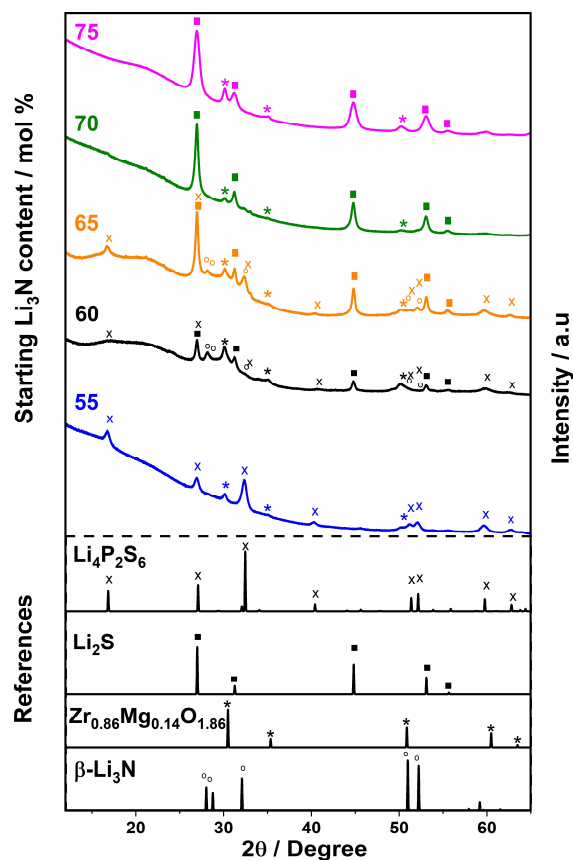


Figure 6.7. PXRD of $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions after ball milling and literature patterns for $\text{Li}_4\text{P}_2\text{S}_6$ ($P6_3/mcm$),²⁰⁷ Li_2S ($Fm\bar{3}m$),²⁰⁹ $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ ($Fm\bar{3}m$),²⁰⁵ and $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$).²²³

$\text{Li}_4\text{P}_2\text{S}_6$ ($P6_3/mcm$), Li_2S ($Fm\bar{3}m$) and $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ ($Fm\bar{3}m$) crystalline phases clearly cannot be responsible for the ionic conductivity exhibited by the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions. Although, $\beta\text{-Li}_3\text{N}$ ($P6_3/mmc$) has a bulk ionic conductivity that appears to be on a similar order of magnitude to the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions, it is known from the results presented in Figure 4.3 that sintering of Li_3N is required for effective inter-granular ion transport; the grain boundary resistance of cold-pressed Li_3N is far greater than the observed total resistance of the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions. Furthermore, the activation energy of $60\text{Li}_3\text{N}\cdot40\text{P}_2\text{S}_5$ (Figure 6.3 (c)) is not consistent with the observed ionic conductivity of Li_3N (Figure 4.9 (c)). The logical implication of these results is that an amorphous phase is responsible for the observed ionic conductivity of the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions.

Raman spectroscopy was used to probe the bonding environments of the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions, Figure 6.8 (ai). $\text{Li}_4\text{P}_2\text{S}_6$, which was detected by PXRD, is known to contain metathiodiphosphate polyhedra ($\text{P}_2\text{S}_6^{4-}$) which produce characteristic P-S stretching at a reported Raman shift of $382\text{-}385\text{ cm}^{-1}$.^{210,211} A peak could clearly be seen in all $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions at $379\text{-}386\text{ cm}^{-1}$ (highlighted in grey), confirming the presence of $\text{Li}_4\text{P}_2\text{S}_6$ in all samples. An additional peak was observed at $420\text{-}422\text{ cm}^{-1}$ (highlighted in yellow) in $55\text{Li}_3\text{N}\cdot45\text{P}_2\text{S}_5$, $60\text{Li}_3\text{N}\cdot40\text{P}_2\text{S}_5$ and $65\text{Li}_3\text{N}\cdot35\text{P}_2\text{S}_5$; this peak, is not attributable to the detected crystalline phases. As such, this peak may be indicative of an amorphous phase. The greater the relative intensity of the peak at $420\text{-}422\text{ cm}^{-1}$, the greater the ionic conductivity of the sample, Figure 6.3 (aii). In addition to meta-thiodiphosphate polyhedra ($\text{P}_2\text{S}_6^{4-}$), ortho-thiophosphate polyhedra (PS_4^{3-}) are commonly observed in lithium thiophosphates.²¹¹ PS_4^{3-} polyhedra in amorphous Li_3PS_4 have reported P-S stretching at a Raman shift of $418\text{-}422\text{ cm}^{-1}$.²¹¹ Therefore, it is suggested that the peak at $420\text{-}422\text{ cm}^{-1}$ is due to PS_4^{3-} , possibly from amorphous Li_3PS_4 . Reference amorphous Li_3PS_4 was synthesised by prolonged ball-milling of $75\text{Li}_2\text{S}\cdot25\text{P}_2\text{S}_5$. The Raman peak of the reference amorphous Li_3PS_4 matched well with the peak highlighted in yellow, Figure 6.3 (aii). The room temperature ionic conductivity of synthesised reference amorphous Li_3PS_4 , determined using a cold pressed pellet prepared under analogous conditions to $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions, was $5.3 \times 10^{-4}\text{ S cm}^{-1}$, Figure 6.9 (ai); an amorphous Li_3PS_4 phase is therefore capable of producing the observed ionic conductivities of the $x\text{Li}_3\text{N}\cdot(100-x)\text{P}_2\text{S}_5$ compositions, even if only present as a minor

phase as suggested by capacitances obtained from fitting of the impedance data in [Figure 6.3 \(c\)](#). When nominal $\text{Li}_3\text{N} \geq 70$ mol %, multiple additional Raman peaks (highlighted blue) are observed which overlap with the peaks ascribed to PS_4^{3-} and $\text{P}_2\text{S}_6^{4-}$ polyhedra. These additional peaks cannot be assigned to any of the crystalline phases detected by PXRD. Deconvolution was not performed because the peaks are significantly broadened and are highly overlapping. However, the peaks closely resemble the spectrum observed with an amorphous red phosphorus reference, [Figure 6.8 \(ai\)](#).

ATR-FTIR measurements support the Raman data. A peak is seen at $550 - 600 \text{ cm}^{-1}$ in the ATR-FTIR spectrum of reference amorphous Li_3PS_4 , [Figure 6.8 \(bii\)](#), which is ascribed to $\text{P}=\text{S}$ stretching. Likewise, a peak is observed in all $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions at $550 - 600 \text{ cm}^{-1}$. This indicates that thiophosphate polyhedra are observed in all compositions, [Figure 6.8 \(bi\)](#). It is suggested that the peak present at $550 - 600 \text{ cm}^{-1}$ is actually composed of multiple overlapping peaks due to several thiophosphate phases. This supposition is based upon the observed peak width for the respective $x\text{Li}_3\text{N} (100-x)\text{P}_2\text{S}_5$ compositions. In compositions, which were shown to contain high PS_4^{3-} content by Raman spectroscopy, i.e. $\text{Li}_3\text{N} \geq 55$ mol %, the ATR-FTIR peak appears to be broadened. Whereas, in compositions with nominal $\text{Li}_3\text{N} \leq 55$ mol %, in which $\text{P}_2\text{S}_4^{2-}$ is the predominant thiophosphate, the peak appears relatively narrow. A broad ATR-FTIR peak at $900 - 1100 \text{ cm}^{-1}$ grows in intensity with increased Li_3N content. The ATR-FTIR spectrum acquired for red P, [Figure 6.8 \(bii\)](#), also contains a peak at $900 - 1100 \text{ cm}^{-1}$. As such, Raman and ATR-FTIR both show evidence for the presence of a red P phase.

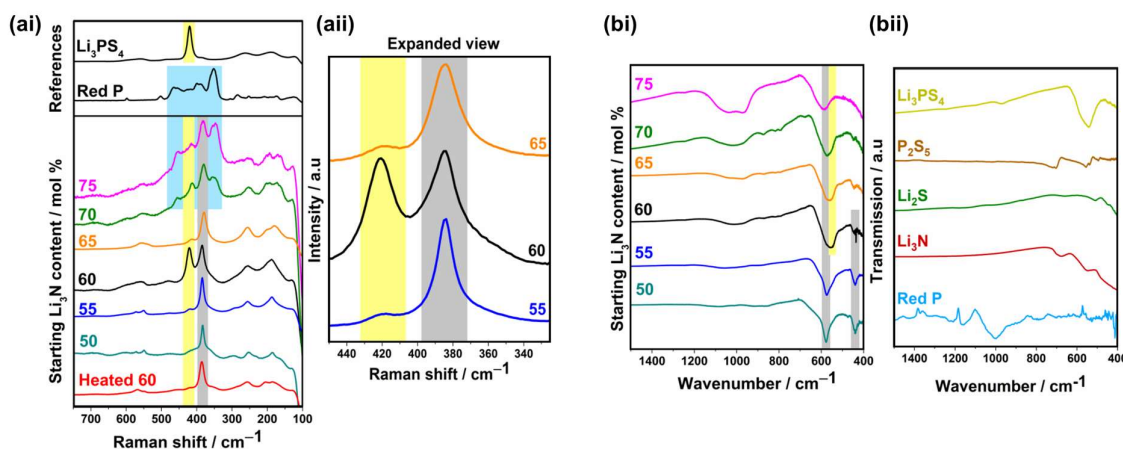


Figure 6.8. (ai) Raman spectra, (aii) Zoomed in region of Raman spectra, and (bi) ATR-FTIR spectra of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h of ball milling. (bii) ATR-FTIR spectra of reference substances.²²³

The supposition that the PS_4^{3-} containing phase, ascribed to amorphous Li_3PS_4 , is responsible for the conductivity of the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions was strengthened by the following experiment. When $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ is heated above 290–300 °C, under an Ar atmosphere, an exothermic process takes place, as shown by DSC in [Figure 6.9 \(c\)](#), which produces a significant decrease in the relative concentration of PS_4^{3-} as shown by the Raman spectrum in [Figure 6.7 \(a\)](#) (called Heated 60); the Heated 60 spectrum was acquired from a milled $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ powder which had been heated at 290 °C for 1 h. The decrease in PS_4^{3-} concentration coincided with a decrease in ionic conductivity from $9.8 \times 10^{-5} \text{ S cm}^{-1}$ to $1.2 \times 10^{-5} \text{ S cm}^{-1}$. Furthermore, measurements of impedance with temperature, revealed that the activation energy determined for $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ (40.8 kJ mol^{-1}), [Figure 6.9 \(b\)](#), matched well with the activation energy determined for reference Li_3PS_4 (38.1 kJ mol^{-1}); reported literature value of E_A for Li_3PS_4 is 41.9 kJ mol^{-1} .²¹²

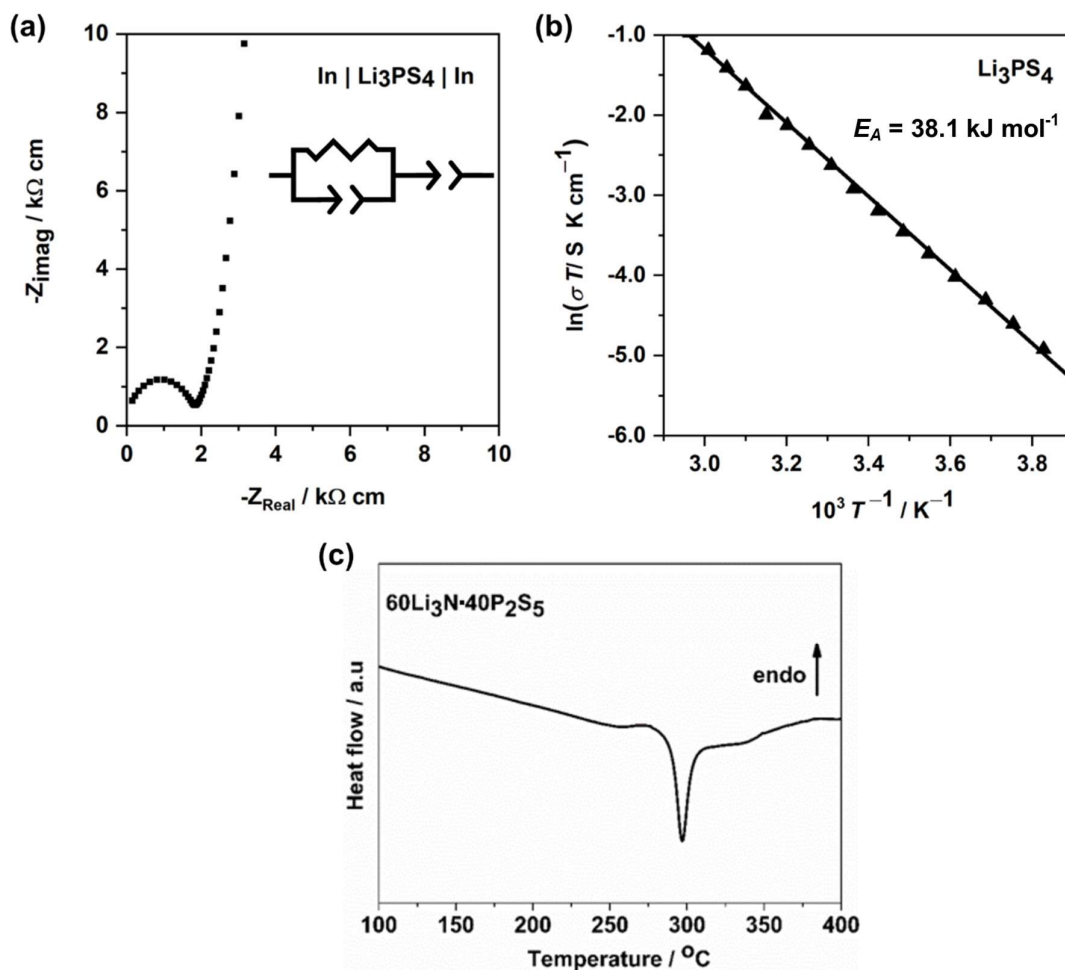


Figure 6.9. (a) Nyquist plot of amorphous Li_3PS_4 . (c) DSC curve of $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$.²²³

The results of PXRD and Raman spectroscopy suggest that $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions contain the following phosphorus based phases: amorphous Li_3PS_4 , amorphous red P, crystalline $\text{Li}_4\text{P}_2\text{S}_6$ and possible amorphous $\text{Li}_4\text{P}_2\text{S}_6$. To test these assignments, ^{31}P MAS NMR was performed on $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$. The spectrum was internally referenced by the addition of a Li_3PO_4 standard. Several resonances were observed, Figure 6.10 (a). Deconvolution revealed the presence of a peak (highlighted yellow) at a chemical shift 82 ppm; this is typical for reported values of PS_4^{3-} polyhedra,²¹³ confirming the presence of amorphous Li_3PS_4 . The resonances at 115 - 117 ppm (highlighted grey) are consistent with $\text{P}_2\text{S}_6^{4-}$ polyhedra, confirming the presence of $\text{Li}_4\text{P}_2\text{S}_6$.²¹³ Deconvolution also reveals a small peak at 92.7 ppm (highlighted orange); in studies of lithium thiophosphates, this peak is commonly observed and is ascribed to $\text{P}_2\text{S}_7^{4-}$. $\text{Li}_4\text{P}_2\text{S}_7$ based on $\text{P}_2\text{S}_7^{4-}$, is amorphous and was

therefore undetectable by PXRD.²¹³ Furthermore, $P_2S_7^{4-}$ polyhedra have reported Raman shifts of $402 - 406\text{ cm}^{-1}$, which means the Raman peak is likely to be hidden in the overlapping region between the dominant PS_4^{3-} and $P_2S_6^{4-}$ peaks.²¹¹ A very broad resonance is observed, with a maximum around 65 ppm. The width of this peak is indicative of a highly amorphous phase. Red phosphorus may be responsible for this resonance.²¹⁴

^6Li MAS NMR was also performed on the $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ sample, with the Li_3PO_4 internal reference. A peak was observed at 3.36 ppm, Figure 6.10 (b); this matched very well with a Li_2S reference, confirming the presence of Li_2S observed by PXRD. A resonance was observed at 1-2 ppm, Figure 6.10 (b), which suggests overlapping resonances from the respective lithium thiophosphates present in $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$, because reference Li_3PS_4 also contains a peak in this region.

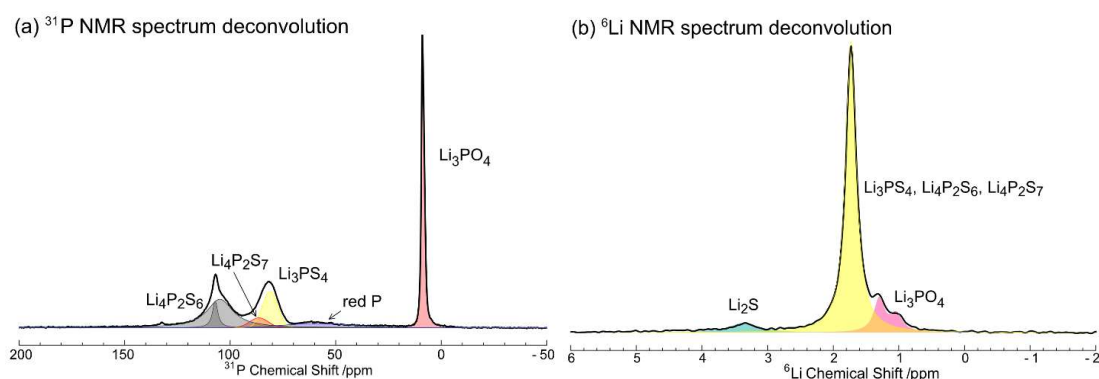


Figure 6.10. (a) ^{31}P and (b) ^6Li MAS NMR spectra of $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ sample after 20 h ball milling. I proposed the experiments, made the figure, prepared the samples and interpreted the data; the experiments were performed with and the raw spectra was produced by Dr. Liyu Jin.²²³

S 2p and P 2p XPS were used to probe the phosphorus and sulphur bonding environments present in all the $x\text{Li}_3\text{N}\cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h of ball milling, Figure 6.11. The spectra were deconvolved and were fitted with doublets, in accordance with the fittings previously used by Dietrich et al. for lithium thiophosphates.²¹⁵ Peaks consistent with S^{2-} , ostensibly from Li_2S are observed in the S 2p spectrum, Figure 6.11 (a).^{216,217} It is revealed that the relative intensity of S^{2-} is greater in samples with higher nominal Li_3N starting content, confirming the results of PXRD that higher Li_3N starting contents lead to greater Li_2S content. $\text{P}^{\delta+}\text{-S}^{\delta-}\text{-x}^-$ bonding

typifies Li_3PS_4 ($\text{P}^{\delta+}\text{-S}^{\delta- 3/4-}$), $\text{Li}_4\text{P}_2\text{S}_6$ ($\text{P}^{\delta+}\text{-S}^{\delta- 2/3-}$) and $\text{Li}_4\text{P}_2\text{S}_7$ ($\text{P}^{\delta+}\text{-S}^{\delta- 2/3-}$). In reported S 2p and P 2p XPS spectra, $\text{P}^{\delta+}\text{-S}^{\delta- x-}$ bonding is not resolved for the respective thiophosphate polyhedra,²¹⁵ instead one doublet is fitted for the average $\text{P}^{\delta+}\text{-S}^{\delta- x-}$ bonding environment, with a S 2p_(3/2) binding energy that varies between 161.2 - 163.2 eV and a P 2p_(3/2) binding energy that varies between 132.4 - 133.5 eV, in accordance with the specific ratio of $\text{P}^{\delta+}\text{-S}^{\delta- 3/4-}$ to $\text{P}^{\delta+}\text{-S}^{\delta- 2/3-}$ present in the sample.^{215,216} As such, the binding energy of the $\text{P}^{\delta+}\text{-S}^{\delta- x-}$ S 2p_(3/2) peak in this study was not constrained because different samples contained different ratios of $\text{P}^{\delta+}\text{-S}^{\delta- 3/4-}$ to $\text{P}^{\delta+}\text{-S}^{\delta- 2/3-}$. PS_4^{3-} and $\text{P}_2\text{S}_6^{4-}$, the predominant thiophosphate polyhedra in this study, do not directly contain $\text{P}^{\delta+}\text{-S}^{\delta-}$ or P-S-P type bonding. $\text{P}^{\delta+}\text{-S}^{\delta-}$ type bonding was not observed by XPS, NMR or Raman spectroscopy confirming that P_2S_5 had fully reacted. The P 2p XPS spectrum revealed the presence of P-P bonding, [Figure 6.11 \(b\)](#). Increased P-P bonding was observed in samples with greater starting nominal Li_3N content, [Figure 6.11 \(b\)](#), which is consistent with the formation of red phosphorus observed by Raman Spectroscopy as outlined in [Figure 6.8 \(a\)](#).^{218,219} Concordantly, a decrease in the relative concentration of $\text{P}^{\delta+}\text{-S}^{\delta- x-}$ was observed, [Figure 6.8 \(c\)](#).

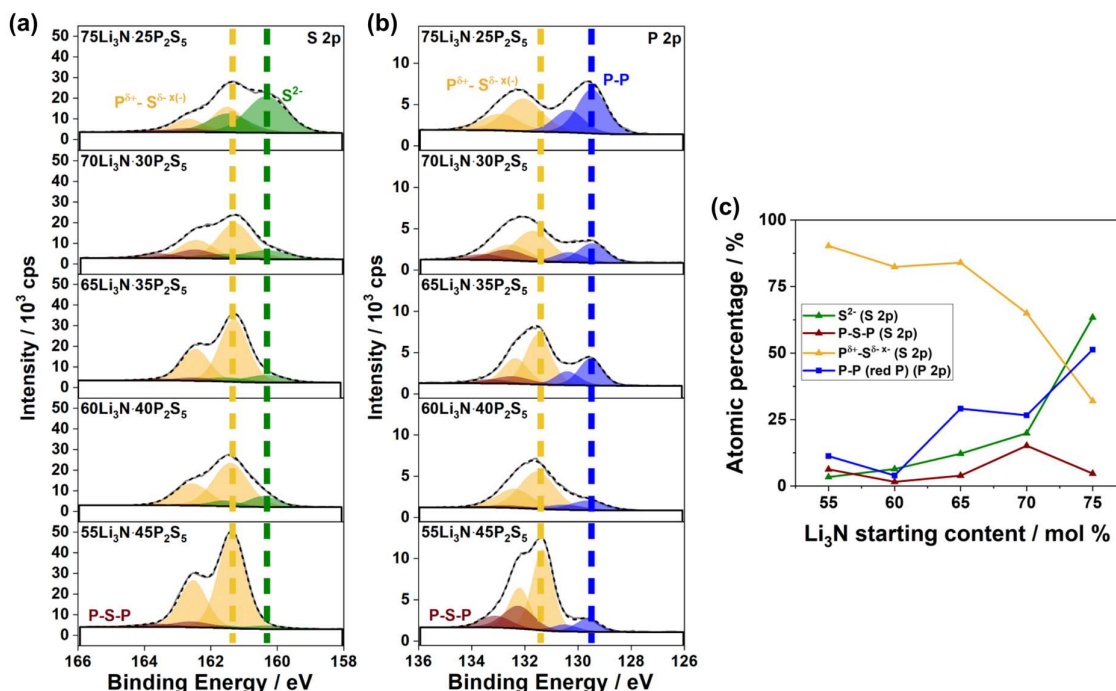


Figure 6.11. (a) S 2p and (b) P 2p XPS spectra for $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions after 20 h of ball milling. (c) Relative concentration changes for corresponding ascribed bonding environments.²⁰² I prepared the samples and interpreted the data; the spectral acquisition was performed with Dr. Philip Holdway.²²³

$x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ powders were cold pressed into pellets and their respective surface morphologies were investigated by SEM. A comparison of the extent of frittage

ⁱⁱⁱ shown in Figure 6.12, reveals that samples with higher observed Li₃PS₄ content have a higher degree of densification, Figure 6.12 (fi),(fii), (gi) and (gii), with 60Li₃N·40P₂S₅ and 65Li₃N·35P₂S₅ having the greatest densification. This is because the Li₃PS₄ phase is more easily cold pressed into a relatively dense pellet than the other phases, as implied in Figure 6.12 (ai) & (aii).²²⁰ The increased particle interconnectivity also matches the trend of the ionic conductivity observed in Figure 6.3.

ⁱⁱⁱ **Frittage** is the extent of compaction of the solid material after the application of pressure (or heat below the point of liquefaction).

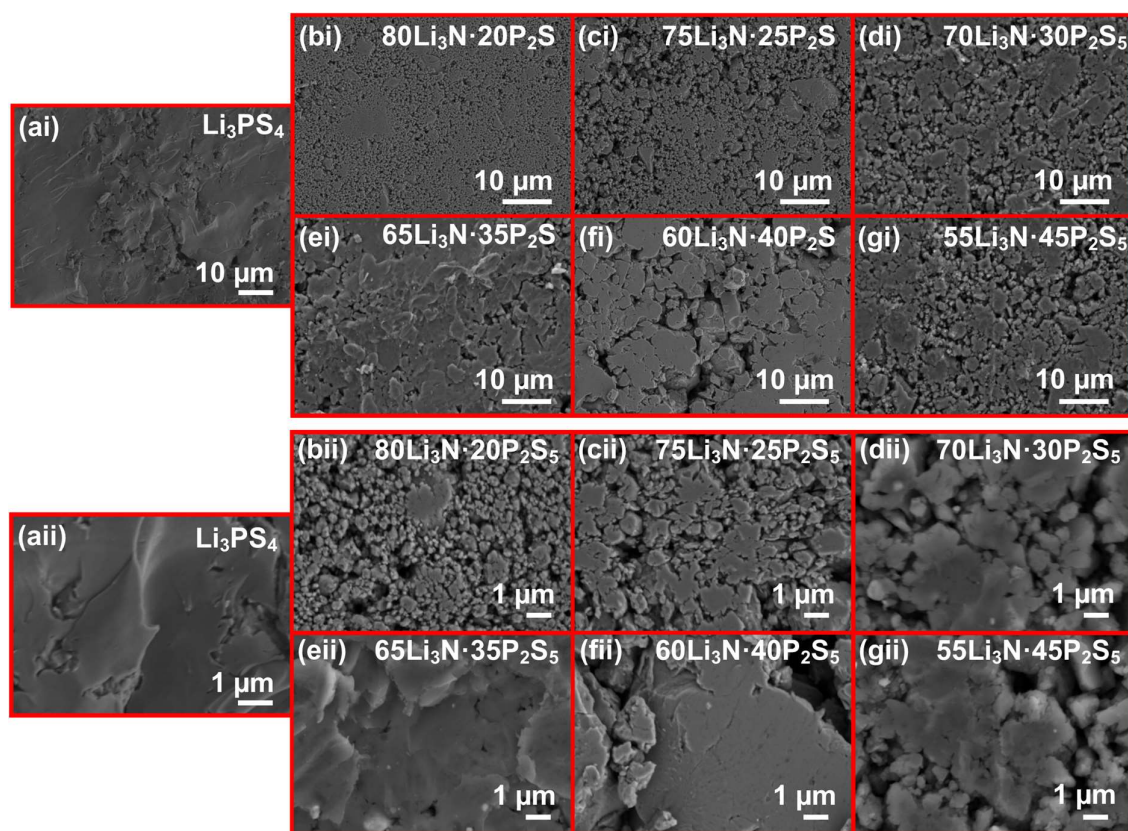


Figure 6.12. Top-down SEM images of cold pressed $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ pellets.²²³

6.4 Investigations of the reactions occurring during the milling of $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$

In **section 6.3**, it was shown that after 20 h of milling, $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ reacted to form Li_2S , amorphous Li_3PS_4 , crystalline and amorphous $\text{Li}_4\text{P}_2\text{S}_6$, amorphous $\text{Li}_4\text{P}_2\text{S}_7$, and amorphous red P. The large number of products indicates several reaction processes may be occurring during milling. In order to deconvolute the reaction processes and gain mechanistic insights, $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ was investigated after different periods of milling. The N_2 content of the headspace gas in the milling jar was quantified after 1, 2, 5, 10 and 20 h of ball milling, **Figure 6.13**. The evolved gas was measured relative to the N_2 content of the jar before milling. A considerable concentration of N_2 gas is evolved during the first 1 h of milling. Very little additional N_2 is detected after more milling. This indicates that oxidation of Li_3N predominantly occurs during the first 1 h of milling.

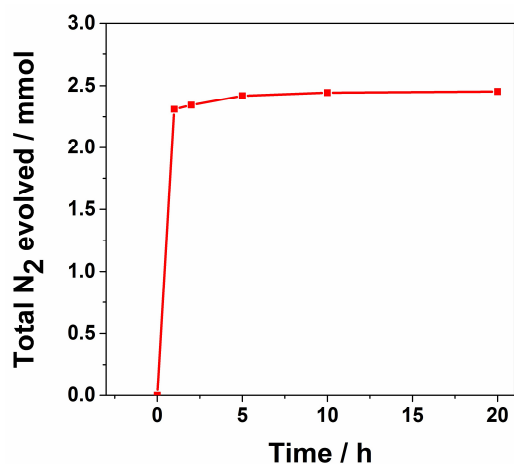


Figure 6.13. Quantification of N₂ gas produced during milling.²²³

PXRD was used to analyse the evolution of the crystalline phases with time, Figure 6.14. After only 30 min of milling, precursor P_2S_5 ($P\bar{1}$), α -Li₃N ($P6/mmm$) and β -Li₃N ($P6_3/mmc$) appeared to have reacted to near completion with Li₄P₂S₆ ($P6_3/mcm$) and Li₂S ($Fm\bar{3}m$) phases having been formed. Zr_{0.86}Mg_{0.14}O_{1.86} impurities from the milling media were also observed. Between 5 h and 20 h, the relative intensity of the Li₄P₂S₆ phase appeared to decrease. A broad halo peak, between 13 – 20 °, increased in relative intensity with respect the crystalline peaks with increased milling time, indicating that an amorphous phase is gradually formed during prolonged milling.

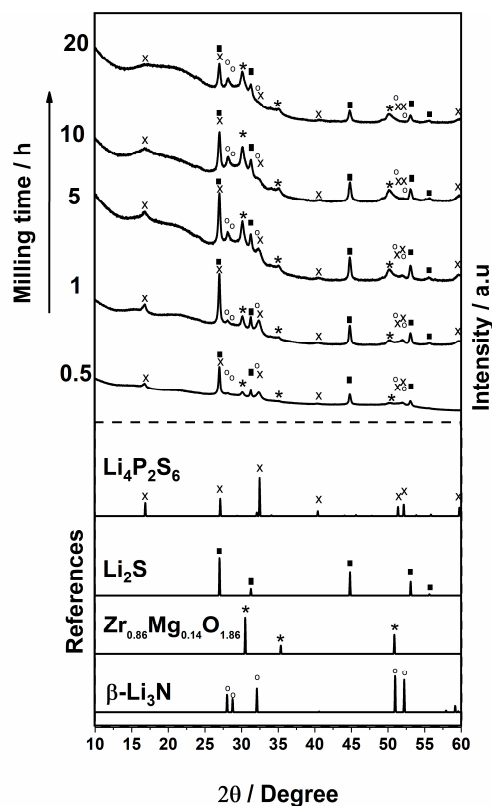


Figure 6.14. PXRD patterns of 60Li₃N·40P₂S₅ after 0.5, 1, 5, 10, 20 h of ball milling and literature patterns for Li₄P₂S₆ (*P6₃/mcm*),²⁰⁷ Li₂S (*Fm $\bar{3}$ m*),²⁰⁹ Zr_{0.86}Mg_{0.14}O_{1.86} (*Fm $\bar{3}$ m*),²⁰⁵ and β -Li₃N (*P6₃/mmc*).²²³

Raman spectroscopy was used to study 60Li₃N·40P₂S₅ after 0.5, 1, 2, 5, 10, 20 h of ball milling, [Figure 6.15 \(a\)](#). A peak was observed in the respective spectra at 379-386 cm⁻¹; as discussed in **section 6.3**, this peak is ascribed to P₂S₄⁴⁻. An additional peak, ascribed earlier to PS₄³⁻, was observed at 420-422 cm⁻¹; with increased milling time, the PS₄³⁻ peak increased in relative intensity with respect to the P₂S₆⁴⁻ peak. This indicates that Li₄P₂S₆ is predominantly formed during the first 1 h of milling and that Li₃PS₄ is either formed slowly during prolonged milling, or Li₄P₂S₆ is consumed during prolonged milling leading to an apparent relative increase in PS₄³⁻ peak intensity, or both processes are occurring simultaneously.

ATR-FTIR spectra were also acquired after 0.5, 1, 2, 5, 10, 20 h of ball milling, [Figure 6.15 \(b\)](#). In the spectrum acquired after 30 min of ball milling, peaks (highlighted red) were observed which matched well with the reference spectrum of Li₃N shown in [Figure 6.8 \(aii\)](#); this indicated that precursors had not entirely reacted after 30 min of

ball milling. However, after 1 h of milling, the precursors appeared to have been fully consumed. As explained earlier, a peak was observed at 550 - 600 cm^{-1} due to P=S stretching. It was shown in **section 6.3** that the P=S stretching peak appears wider in compositions with more Li_3PS_4 and appears narrower in compositions with more $\text{Li}_4\text{P}_2\text{S}_6$. The peak appears to widen with increased milling time, **Figure 6.15 (b)**, which verifies that Li_3PS_4 is slowly formed during prolonged milling. Close inspection of the spectra reveals that the weak broad peak observed at 900 – 1100 cm^{-1} , previously ascribed to red phosphorus, increases in relative intensity with milling time, suggesting that the formation of Li_3PS_4 is accompanied by the formation of red P.

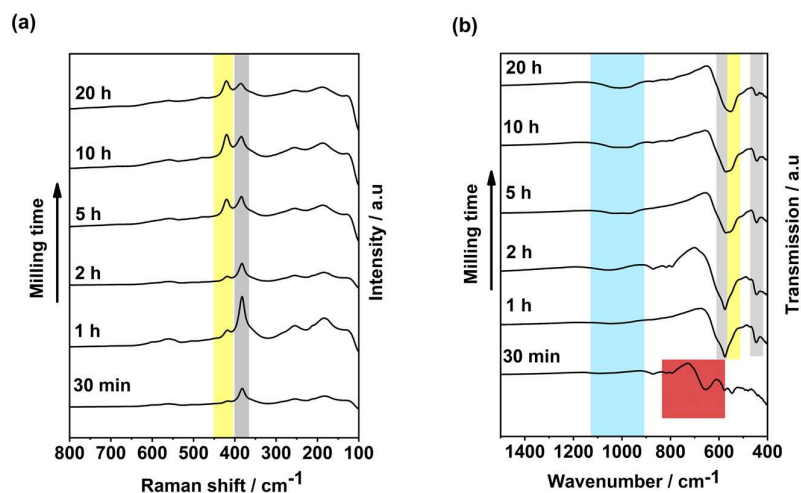


Figure 6.15. (a) Raman spectra and (b) ATR-FTIR spectra of $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ after 0.5, 1, 2, 5, 10, 20 h of ball milling. Yellow highlighting indicates PS_4^{3-} polyhedral, grey highlighting indicates $\text{P}_2\text{S}_4^{4-}$, blue highlighting indicates P-P bonding, and red highlighting indicates Li_3N .²²³

^{31}P MAS NMR spectra were acquired for $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ samples which had been ball milled for 1, 2, 5, 10 and 20 h periods respectively, **Figure 6.16 (a)**. In order to protect the spectrometer, MAS NMR was not performed on the $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ sample after 30 min of milling because ATR-FTIR had shown that some Li_3N was still present in this sample and it would therefore likely undergo violent oxidation to N_2 during sample spinning. Known amounts of an internal standard (Li_3PO_4) were added to the respective samples after milling to enable quantification of the P based phases with time as shown in **Figure 6.16 (c)**. Deconvolution of the spectra, confirmed the presence

Li_3PS_4 (82 ppm), $\text{Li}_4\text{P}_2\text{S}_6$ (115 and 107 ppm), $\text{Li}_4\text{P}_2\text{S}_7$ (92.7 ppm), and amorphous red phosphorus (65 ppm). The crystalline $\text{Li}_4\text{P}_2\text{S}_6$ phase (115 ppm) and the amorphous $\text{Li}_4\text{P}_2\text{S}_6$ phase (107 ppm) were treated as a single resonance for the purposes of quantification. After 1 h of milling, a high concentration of $\text{Li}_4\text{P}_2\text{S}_6$ was detected in the samples. The concentration of $\text{Li}_4\text{P}_2\text{S}_6$ decreased with milling time beyond 1 h, confirming that $\text{Li}_4\text{P}_2\text{S}_6$ is predominantly formed within the first 1 h of ball milling and is subsequently consumed during prolonged milling. The peak at 82 ppm, ascribed earlier to Li_3PS_4 , has low intensity after 1 h of milling but the peak gradually increases in intensity with longer milling, suggesting that $\text{Li}_4\text{P}_2\text{S}_4$ reacts to form Li_3PS_4 during prolonged milling. Furthermore, the underlying broad peak at 65 ppm ascribed to red phosphorus also increased with milling time, [Figure 6.16 \(c\)](#).

^6Li MAS NMR was used to probe the changes in the chemistry of $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$ with milling time, [Figure 6.16 \(b\)](#). As discussed in **section 6.3**, deconvolution of the spectra reveals the presence of Li_2S at 3.36 ppm and lithium thiophosphates which contribute to a peak between 1 and 2 ppm. Absolute quantification of the lithium containing phases using ^6Li MAS NMR could not be performed because ^6Li has a very long recycle delay time in Li_2S ($T_1 > 150$ s). As such, only the relative intensity changes of Li_2S in the sample was measured with respect to the added Li_3PO_4 reference. After 1 h of milling, a high relative concentration of Li_2S was present in $60\text{Li}_3\text{N}\cdot 40\text{P}_2\text{S}_5$, [Figure 6.16 \(b\)](#). Milling for longer than 1 h caused the relative intensity of Li_2S to decrease with respect to the added Li_3PO_4 reference, which suggests that Li_2S is consumed in a reaction during sustained milling. Furthermore, the peak between 1 and 2 ppm, moves to higher chemical shifts with increased milling time; consistent with a relative increase in the PS_4^{3-} concentration with respect to $\text{P}_2\text{S}_6^{4-}$.

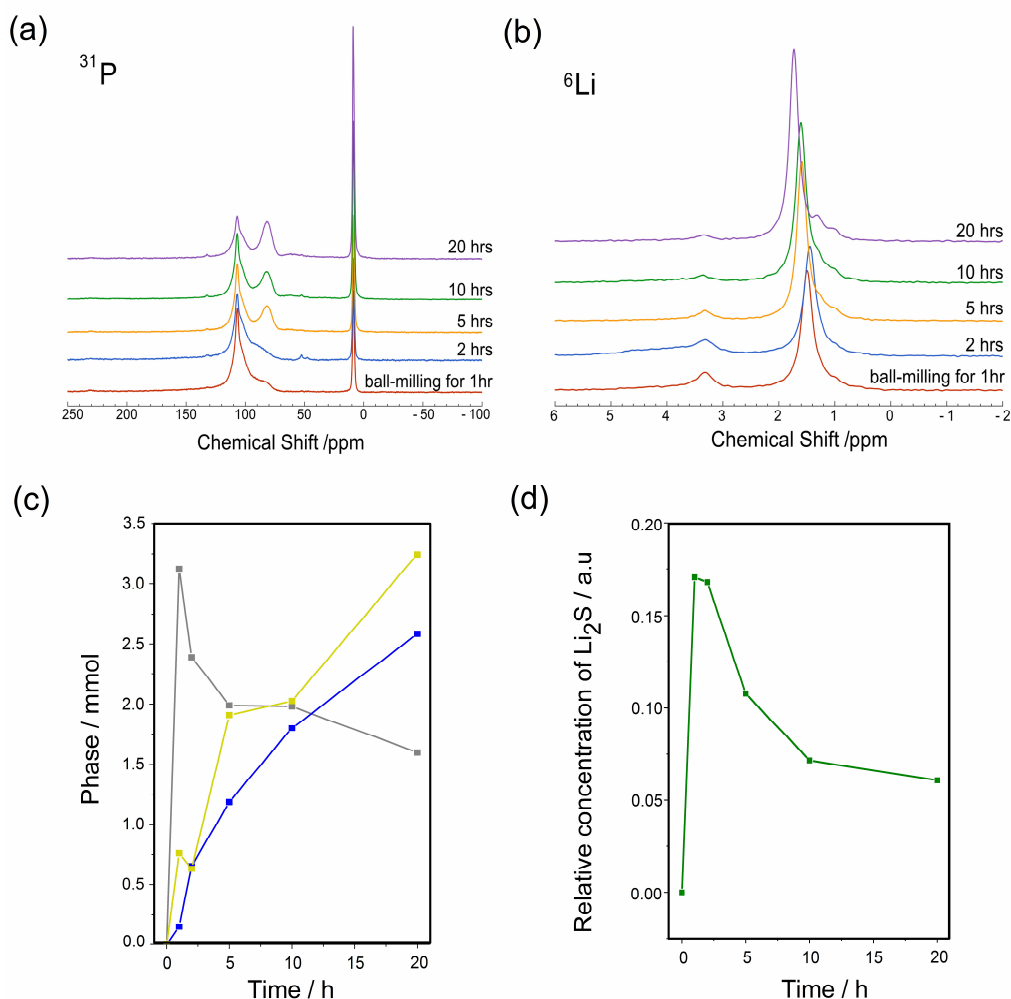


Figure 6.16. (a) ^{31}P and (b) ^6Li MAS NMR spectra of 60Li₃N·40P₂S₅ after 1, 2, 5, 10, 20 h of ball milling. (c) Corresponding quantification of phosphorus phases with time: Li₄P₂S₆ (grey), Li₃PS₄ (yellow) and red phosphorus (blue). (d) Corresponding relative concentrations of Li₂S with respect to Li₃PO₄ reference. I proposed the experiments, made the figure, prepared the samples and interpreted the data; the experiments were performed with and the raw spectra was produced by Dr. Liyu Jin.²²³

Raman spectroscopy, ^{31}P and ^6Li MAS NMR, ATR-FTIR spectroscopy and PXRD all indicate that Li₃N oxidises P₂S₅ to Li₄P₂S₆, Li₂S and red P within the first hour of milling and that milling for longer than 1 h causes the Li₂S to react with Li₄P₂S₆ to form amorphous Li₃PS₄ and additional red phosphorus. Given that the results in **section 6.3** indicate that amorphous Li₃PS₄ is responsible for the ionic conductivity of the xLi₃N·(100-x)P₂S₅ compositions, it is expected that increased milling should result in a higher observed ionic conductivity. As such, the ionic conductivity of 60Li₃N·40P₂S₅ was measured after 1, 2, 5, 10 and 20 h of ball milling respectively,

Figure 6.17. Concordantly, the ionic conductivity of the sample increased with increased milling time.

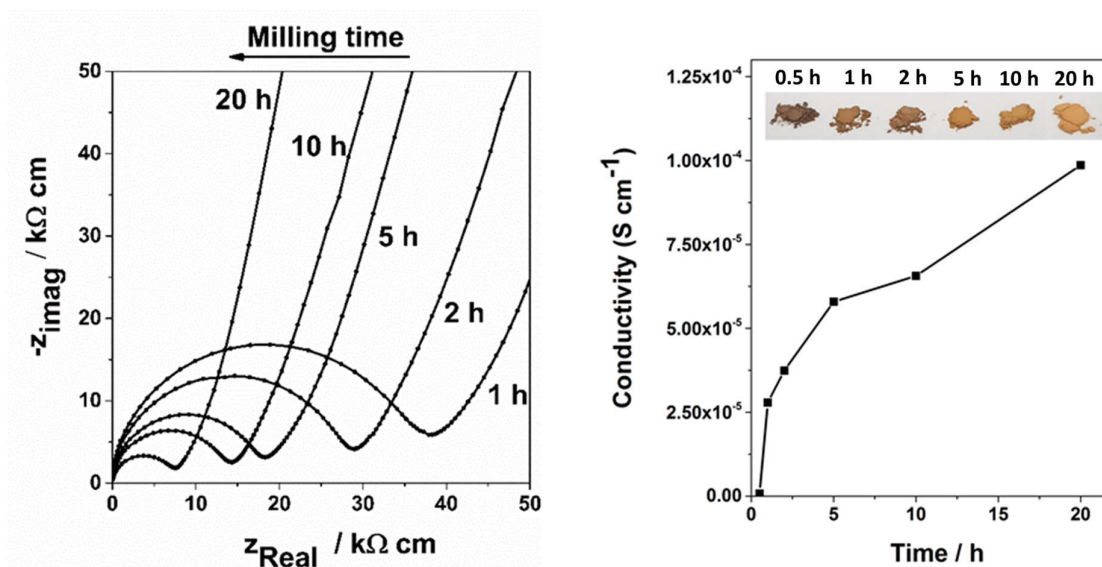


Figure 6.17. (a) Normalised impedance nyquist plots and (b) corresponding ionic conductivities of In | 60Li₃N·40P₂S₅ | In, with SE produced with 1, 2, 5, 10, 20 h of ball milling; with photos of the powder after the various stages of milling.²²³

In order to assess whether 60Li₃N·40P₂S₅ was a suitable SE for ASSB applications, galvanostatic cycling was performed using symmetric lithium 2-electrode cells, Figure 6.18. The cold pressed solid electrolyte pellet was not sintered, to avoid the reactions at high temperature which in **section 6.3** were shown to eliminate Li₃PS₄ and substantially decrease ionic conductivity to unacceptably low values. At high current density (1.0 mA cm⁻²), cells experienced rapid short-circuit failure, within the first half cycle, attributed to dendritic growth, Figure 6.18 (d). Although, cells could be cycled for longer at lower current densities, Figure 6.18 (b) & (c), short-circuiting was always observed, even at 0.1 mA cm⁻², Figure 6.18 (a). These current densities are low, with respect to the critical current densities of known phase pure Li₃PS₄, which indicates that the additional phases present in 60Li₃N·40P₂S₅ do not improve Li₃PS₄ as a SEs for lithium metal anode type applications.²²¹

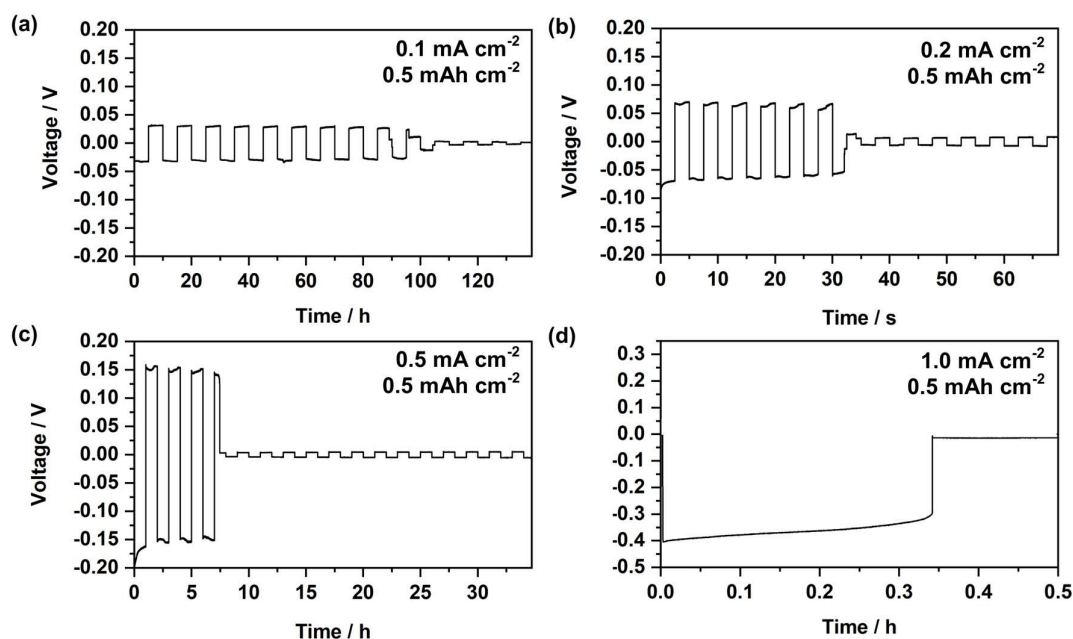
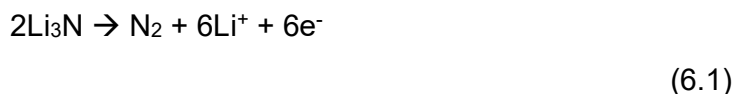


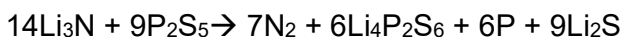
Figure 6.18. Galvanostatic cycling (0.5 mAh cm^{-2} of capacity) for $\text{Li} \mid 60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5 \mid \text{Li}$ cells, at 25°C , at a current densities of: (a) 0.1 mA cm^{-2} , (b) 0.2 mA cm^{-2} , (c) 0.5 mA cm^{-2} and (d) 1.0 mA cm^{-2} .²²³

6.5 Conclusion

In this chapter it was shown that the mechanochemical milling of Li_3N with P_2S_5 does not form lithium nitridothiophosphates as was inferred from the report by Tatsumisago,¹⁸⁷ in which milling of Li_3N with P_2S_5 was concluded to produce an amorphous SE. Instead we show that the milling of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ produces Li_2S , amorphous Li_3PS_4 , crystalline $\text{Li}_4\text{P}_2\text{S}_6$, amorphous $\text{Li}_4\text{P}_2\text{S}_6$, amorphous $\text{Li}_4\text{P}_2\text{S}_7$ and amorphous red phosphorus.²⁰² The compositions of the various $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions can be understood through the following proposed reaction schema. During early stages of milling ($< 1 \text{ h}$), Li_3N is rapidly oxidised to N_2 .

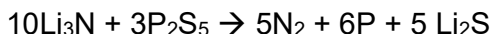


This causes P_2S_5 to be reduced. The extent of P_2S_5 reduction depends upon the relative ratio of Li_3N to P_2S_5 . For example, when the P_2S_5 concentration is high relative to Li_3N , the following reaction is favoured:



(6.2)

Whereas, when the Li_3N concentration is high, the P_2S_5 can be reduced further:



(6.3)

It is worth noting these reactions are stochastic and occur to some extent for all of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions. However, examination of various $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions (where $x = 50, 55, 60, 65, 70, 75$ and 80 mol %), clearly shows that a gradual change of reaction predominance from *Reaction 6.2* to *Reaction 6.3* occurs at increased Li_3N starting contents, with Li_2S being the predominant phase at nominal $\text{Li}_3\text{N} \geq 70$ mol % and $\text{Li}_4\text{P}_2\text{S}_6$ being the predominant phase at nominal $\text{Li}_3\text{N} \leq 55$ mol %. The products of these early stage reactions ($\text{Li}_4\text{P}_2\text{S}_6$, P and Li_2S) are not sufficiently ionically conducting to be responsible for the observed ionic conductivity of the samples after 20 h of milling. It was shown that the ionic conductivity of the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ SEs is due to the formation of an amorphous Li_3PS_4 phase. By tracking milling with time, it was shown that Li_3PS_4 is formed in a slow second step from Li_2S and $\text{Li}_4\text{P}_2\text{S}_6$ which were produced in the early stages of milling:



(6.4)

Reaction 6.4 is promoted in samples, which contain high concentrations of both $\text{Li}_4\text{P}_2\text{S}_6$ and Li_2S . Amorphous Li_3PS_4 is therefore maximally produced in the $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ composition because this starting ratio enables *Reactions 6.2* and *6.3* to both occur to a significant extent during early milling. As such, $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ had the highest ionic conductivity of all the compositions investigated. However, due to the corresponding production of red phosphorus, milling of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ cannot produce phase pure amorphous Li_3PS_4 . Therefore, the measured ionic conductivity of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ samples were depressed with respect to phase pure Li_3PS_4 . Furthermore, $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$, the best performing composition, had inferior cycling to phase pure Li_3PS_4 , indicating that the additional phases produced no added benefit.

In light of the properties examined, I suggest that ball milled $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ SEs do not warrant further investigation for battery applications. However, the synthesis of genuine lithium nitridothiophosphates, based on PSN polyhedra, remains of great

interest due to the postulated similarity to sulfide electrolytes with high ionic conductivity and the entailed unique anode compatibility of the nitride anion.

6.6 Experimental

All sample preparation was performed without exposure to air, in an inert argon atmosphere glovebox. Nominal $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions ($x = 50, 55, 60, 65, 70, 75$ and 80 mol %), were prepared with a combined pre-milling mass of 1.2 g of Li_3N (99.6 %, Alfa Aesar) and P_2S_5 (98 %, Sigma-Aldrich). The respective $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions were then ball milled in 45 ml zirconium oxide milling jars, respectively filled with 170×5 mm $\text{Zr}_{0.86}\text{Mg}_{0.14}\text{O}_{1.86}$ balls, under argon atmospheres; such milling media are typical for the production of lithium thiophosphate SEs.¹²⁵ Milling was performed at 550 RPM to maximise the ionic conductivity of the samples. 550 RPM was determined to be the optimal milling speed for the production of high ionic conductivity samples by examination of the ionic conductivity of $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ at different rotation speeds, Figure 6 (b). In order to determine the ionic conductivity of the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions, pellets were cold pressed from the milled powders under 510 MPa of pressure (the suitability of this pressure was established in Figure 6 (b) & (c)); blocking indium electrodes were applied, then the half-cell was sealed in a vacuum sealed pouch cell and electrochemical impedance spectroscopy was performed at 25 °C with a BioLogic SP-300 potentiostat over a 3 MHz to 1 Hz frequency range using a 10 mV applied perturbation voltage. By acquiring impedance spectra at various temperatures, by means of an oil bath, activation energies were determined. The aforementioned ball milling jars were fitted with in/out Swagelok taps, which allowed head space gas to be sampled before and after milling; by means of the flow system shown in Figure 6.4 (a). Using above atmospheric pressure argon carrier gas, the headspace gas was quantitatively analysed with a mass-flow-regulated Thermo Fisher Scientific Prima BT gas analyzer mass spectrometer (MS). A Vario MICRO cube CHN analyser (0.3% mass detection limit and a $\pm 0.3\%$ mass tolerance) was used to perform triplicate CHN elemental analysis on the $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions. $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ compositions were transferred to a Thermo Scientific XPS K- α instrument and N 1s, P 2p and S 2P XPS spectra were acquired with a microfocused monochromated Al X-ray source operated at 12 keV with a

400 μm spot size; spectra were charge corrected (284.8 eV for adventitious carbon) and Shirley backgrounds were used but no spectral smoothing was performed. XPS analysis was performed using Casa XPS software; spectra were fitted using Gaussian (70 %)-Lorentzian (30 %) curves. MAS NMR experiments were performed using a 3.2 mm probe head on a 400 MHz Bruker Avance III HD spectrometer at Larmor frequencies (ν_0) of 40.5 MHz for ^{15}N , 58.9 MHz for ^6Li , and 162.0 MHz for ^{31}P . A MAS frequency of 20 kHz was utilized for ^6Li and ^{31}P , while 12 kHz was used for ^{15}N . To ensure valid quantification analyses, for ^{31}P spectra, a $\pi/6$ pulse (250 kHz) with a recycle delay of 120 s was applied, while for ^6Li , a $\pi/2$ pulse (72 kHz) with a recycle delay of 60 s was found to be sufficient. ^6Li and ^{31}P spectra were externally referenced to 1 M $\text{LiCl}_{(\text{aq})}$ and 85 wt % $\text{H}_3\text{PO}_{4(\text{aq})}$, respectively, both at $\delta_{\text{iso}} = 0$ ppm. The spectral deconvolution was completed using Dmfit. The ^{15}N measurements were performed with an 83 kHz excitation pulse and a Hahn-echo ($\pi/2$ - τ - π -acq) sequence utilizing 100 kHz of proton decoupling. All ^{15}N CPMAS NMR data were calibrated against the primary ^{15}N reference of CH_3NO_2 in CHCl_3 via a secondary solid reference of histidine (three ^{15}N shifts of δ_{iso} -333.1, -204.3, and -191.0 ppm). In order to perform PXRD, samples were loaded into borosilicate capillaries inside an argon filled glovebox and were sealed. PXRD patterns were collected with a Rigaku 9 kW Smart Lab diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54051$ Å). Samples were hermetically sealed under an argon atmosphere and DSC was performed using a Mettler Toledo DSC1 STAR^e system. Attenuated total reflectance infrared spectroscopy (ATR-FTIR) was performed with a Thermo scientific Nicolet 6700 FT-IR spectrometer using a smart orbit probe inside a nitrogen filled a glovebox. Raman spectra were measured with samples under Ar atmospheres using a Renishaw inVia spectrometer equipped with a diode laser (1.5 mW laser power and $\lambda = 785$ nm). Scanning electron microscopy (SEM) images of $x\text{Li}_3\text{N} \cdot (100-x)\text{P}_2\text{S}_5$ pellets were taken from a top-down view using a FE-SEM (Zeiss-Merlin) instrument; with samples being transferred to the instrument by means of an air-sensitive sample holder. Two-electrode galvanostatic cycling of $\text{Li} \mid 60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5 \mid \text{Li}$ was performed in pouch cells at 25 °C using a Biologic VMP3 potentiostat.

Chapter 7: Conclusions of thesis

7.1 Conclusions of Chapters

There are immense commercial, governmental and societal pressures to develop electrochemical storage devices with ever increasing volumetric and gravimetric energy density. Traditionally, the impetus for research and development in this area was provided by the portable consumer electronics market. However, in recent years the demand for improved batteries has been driven by the electric car market. Mass adoption of EVs has become a key objective of many nations due to societal concerns over anthropogenic climate change and harmful smog in congested cities. Although consumer interest in EVs has skyrocketed in recent years, prohibitively high costs, range anxiety, slow charging rates, lack of charging infrastructure, poor battery lifetimes, safety concerns, non-renewable sources of electricity generation, difficulties of switching from existing manufacturing processes to new methods and underdeveloped supply chains, have all acted to limit the rate of EV adoption. Lithium ion batteries are currently predominant in EV applications due to their balance of energy density and power. However, as the theoretical energy density limits of lithium ion technology loom ever closer, it is becoming increasingly clear that beyond lithium ion technologies, such as: Li metal anode cells with high voltage lithium rich cathodes, Li-S, or Li-O₂ type cells, will be needed to achieve the desired step change in energy density. Replacing the carbonaceous negative electrode with lithium metal, is therefore a key milestone for the field, as it could facilitate a substantial increase in energy density. However, 30 years of intense research in this area has revealed lithium metal to be incompatible with LEs for practical cells, since LEs are electrochemically unstable at low potential and the resulting SEIs are physically unstable during cycling, which leads to capacity fading; furthermore, dendritic growth on charge leads to catastrophic short-circuiting. ASSBs, in which LE is replaced with a SE, have consequently begun garnering significant attention. ASSBs have so far only been successfully operated at low C-rates; plating above a critical current density, causes short-circuiting to occur due to the formation of dendrites through the SE. ASSB development has also been severely hindered by cathode side issues. For example, volume changes in active materials can lead to cracking of the SE and

particle contact losses, which lead to rapid capacity fading. Understanding the dynamic processes at the anode interface during cycling and mitigating SE/cathode interfacial problems is therefore critical to developing beyond lithium ion technologies. The work presented in this thesis, advances the understanding of the dynamic processes occurring during cycling at the lithium | SE interface. A SE | LE hybrid strategy for circumventing the cathode / SE incompatibility issues is investigated, and the chemistry of a previously uncharacterised SE is elucidated.

The results presented in **Chapter 4**, advance the understanding of the dynamics at play at the SE | Li interface and reveal that in addition to a critical current density on plating (CCP), there is also a critical current density on stripping (CCS). When the critical current on stripping is exceeded, lithium is stripped faster than it can be resupplied to the interface, therefore voids develop in the lithium. This leads to interfacial contact loss. As a result, during galvanostatic cycling, the local current density / local potential increases at the interface. Importantly, it was shown that plating does not fully refill these voids. Instead the voids are only partially refilled and often become occluded from the interface such that voids accumulate during cycling. Above the CCS, cell failure by either electrochemical degradation or by the formation of dendrites on plating, becomes inevitable. The transport of lithium in the metal electrode, to the interface with the SE, is not merely diffusion controlled but is driven by creep. Therefore, the CCS can be increased by the application of pressure, which increases the lithium metal creep rate. This phenomenon is ubiquitous for SEs with metal anodes. The work in **Chapter 4** also demonstrates that below the CCS, the Li | SE interface is dynamically stable during cycling, therefore strategies for increasing the CCS will be key for realising high power density ASSBs.

Although the work presented in **Chapter 4** takes us a step closer to the realisation of lithium metal batteries, ASSBs are still plagued by unsolved cathode side issues, including: capacity fading due to interfacial contact losses, active cathode particle / SE fracturing and electrochemical degradation. It is important to approach battery development holistically. In **Chapter 5**, a hybrid electrolyte approach was outlined, in which a metal anode and a LE based catholyte were interposed with a SE. In such a cell, the problematic SE | cathode and Li | LE interfaces are avoided entirely. Instead, Li | SE and LE | cathode interfaces are present, and a new SE | LE interface is

introduced. Since it was shown in **Chapter 4**, that Li | SE is dynamically stable at low current densities, and since the LE | cathode interface is already effective in commercial LE cells, it was important to explore the nature of the SE | LE interface for a number of electrolyte combinations. The resistance of the SE | LE interface between LLZTO and LP30 increased to an impracticably high value due to the growth of an interphase (SLEI) at the interface, composed predominantly of LiF, Li₂O and Li₂CO₃. Likewise, SLEI growth was observed for a number of Li₃N | LE combinations. By examining the Li₃N | 1 M LiTFSI in PC interface in detail, it was shown that Li₃N reduces both the solvent and salt to form a SLEI containing LiF, possible Li₂S, a fluorinated species which is thought to be (LiOS(CF₃)(NSO₂CF₃)₂ and Li₂CO₃. As such, **Chapter 5** demonstrates that for high power applications, stable SE | LE interfaces will be required that do not form highly ionically resistive SLEIs.

Since the advent of high ionic conductivity SEs, (such as lithium thiophosphates), it has becoming increasingly clear that interfacial phenomena are now what limit the operating power of ASSBs. For example, high interfacial resistances lead to a significant IR drop during cycling. Therefore, decreasing interfacial resistances is a priority for battery development. Lithium thiophosphates have excellent ionic conductivities but are electrochemically unstable in contact with lithium metal and react to form a SEI. Many nitrogenous electrolytes have remarkable electrochemical stability at low voltages but they also can have low ionic conductivity (LiPON) or instability at the operational voltages of cathodes (Li₃N). As such, in **Chapter 5**, it was suggested that nitrogen containing sulfide based electrolytes (lithium nitridothiophosphates), may have high ionic conductivity as well as electrochemical stability at low potential. Investigations on nitrogen doped sulfide electrolytes have so far been limited. An amorphous SE, had been reportedly synthesised by ball milling Li₃N with P₂S₅,¹⁸⁷ but the structure and chemistry of this material were largely uncharacterised, therefore this SE was explored in detail. It was found that Li₃N reacts with P₂S₅ to form known lithium thiophosphates and red phosphorous, with nitrogen being lost as N₂ gas. By studying the reactions of different Li₃N : P₂S₅ starting ratios and by tracking the chemistry of the reactions with time, detailed mechanistic understanding of the reactions occurring during milling was outlined. It was shown that Li₃PS₄ is responsible for the ionic conductivity of the SEs. Therefore, there is a need to explore the production of lithium nitridothiophosphates by alternative synthesis methods.

7.2 Future work

The results presented in **Chapter 4** reveal that the critical current on stripping is limited by the rate at which lithium can creep to the interface. Although, it was shown that pressure can be used to increase the CCS. It is likely to be exceedingly difficult to engineer commercially viable cells that are able to maintain the pressures required for cell cycling, at rates comparable with LE cells (5.0 mA cm^{-2}). It is therefore important to explore additional methods of increasing the flux of lithium to the interface. It is suggested that lithium creep could be increased by operating cells under pressure at higher temperatures. Likewise, work is now underway to explore the rate of creep of metal electrodes that are softer than Li (Na, K). Doped lithium and Li alloys may enable higher diffusion rates to the interface and should be explored. On a more fundamental level, the CCS values are not identical for different SEs. It is suggested that the surface roughness and wettability of the SE may have a profound effect on the true area of interfacial contact and the shape and ease of void formation. Likewise the effects of SEIs and surface contaminants on the CCS should be investigated.

The SE / LE hybrid approach results presented in **Chapter 5**, clearly demonstrates that Li_3N is a poor choice of SE, as it easily reduces LEs. Likewise LiPF_6 type salts are also non ideal as they readily form SLEIs, even with LLZTO. However, the hybrid approach remains of interest and should be explored with alternative SEs and LE combinations. In addition to LE / SE combinations, work is being undertaken to examine the viability of SE / polymer electrolyte hybrid cells, with the same purported advantages. Further work in this area should focus on the development of full cells and it is important to investigate the respective rates of Li^+ ion exchange across the interface in the forward and reverse directions.

The work in **Chapter 6**, revealed that lithium nitridothiophosphates are not produced by the mechanochemical milling of Li_3N with P_2S_5 . However, nitrogen doped lithium thiophosphate SEs still remain of great interest. Given that Li_3PO_4 can be doped with N_2 by PVD to form LiPON, it is suggested that structurally analogous Li_3PS_4 and other lithium thiophosphates could also be nitrogen doped by sputtering or PVD with a nitrogen or nitrogeneous carrier gas. Lithium nitridothiophosphates may have high

conductivity and may form a favourable interface with lithium metal. Regardless, of whether nitrogen doping can be induced, the production of thin films of sulfide SEs would be highly advantageous in its own right, as a thin and dense highly ionically conductive SE would enable cells with very low internal resistance to be manufactured. As such, it is suggested that substantial research effort should be placed on developing thin films of sulfide based SEs.

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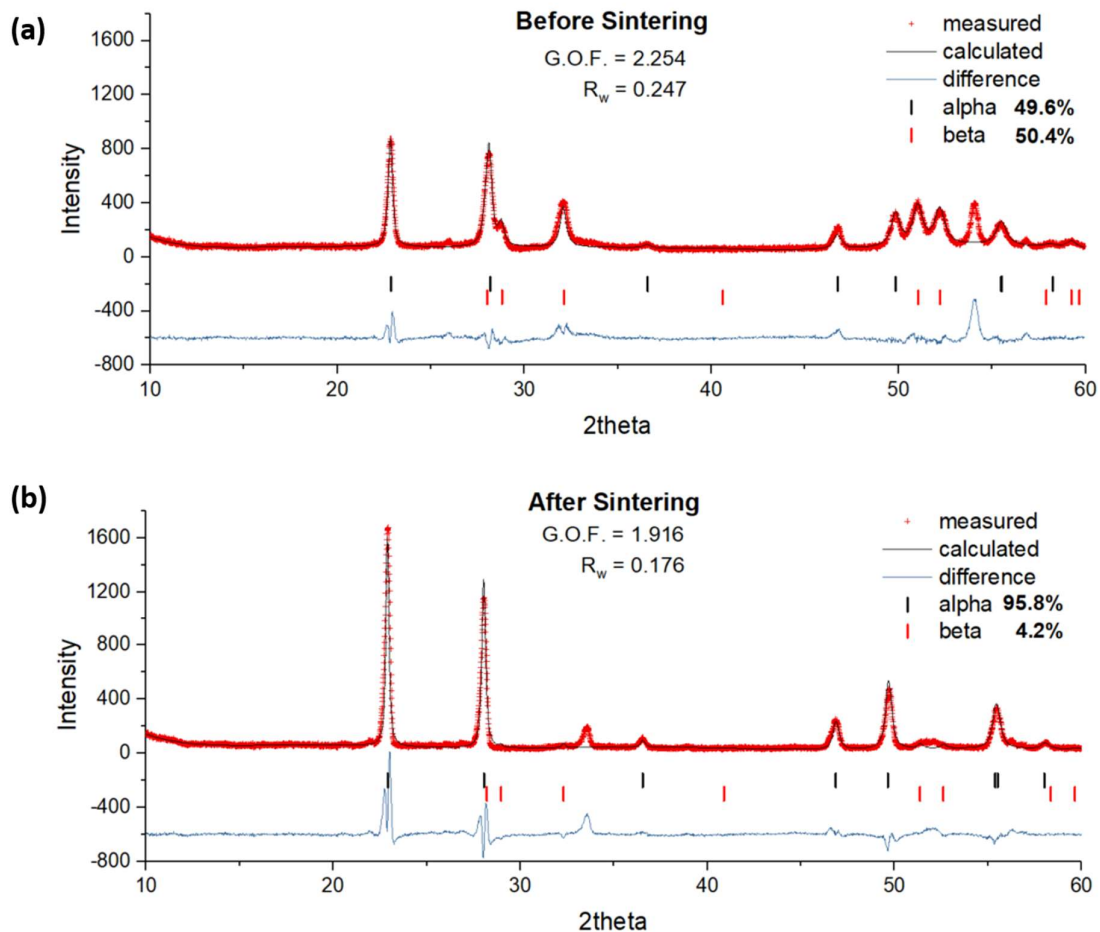
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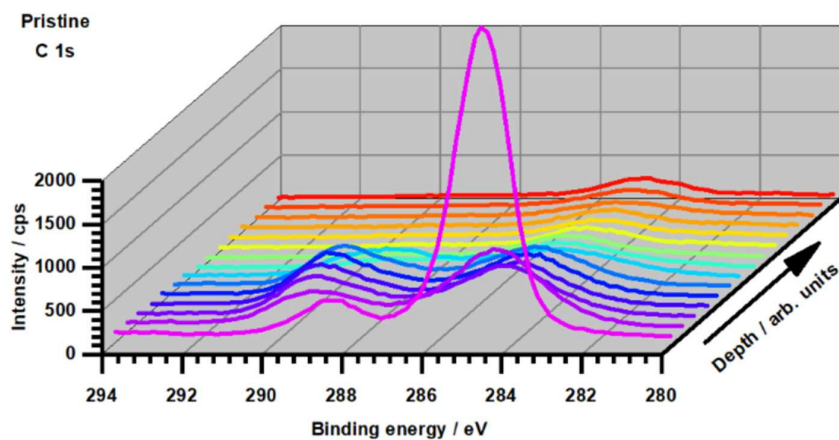
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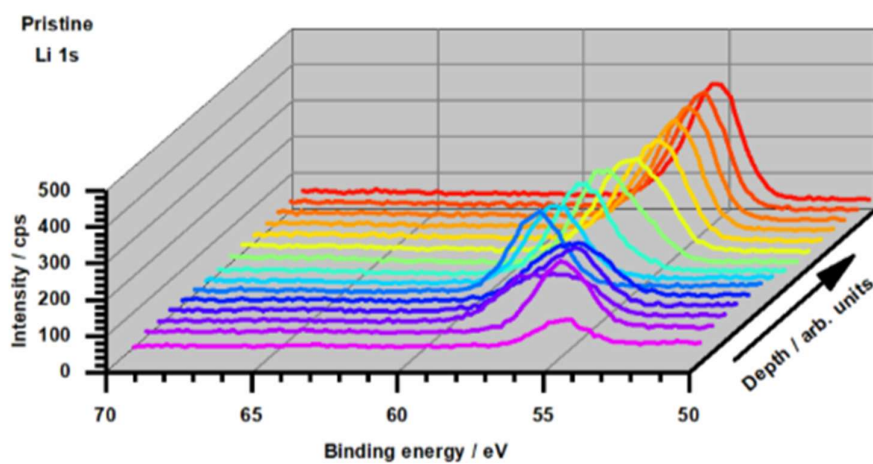
Appendices



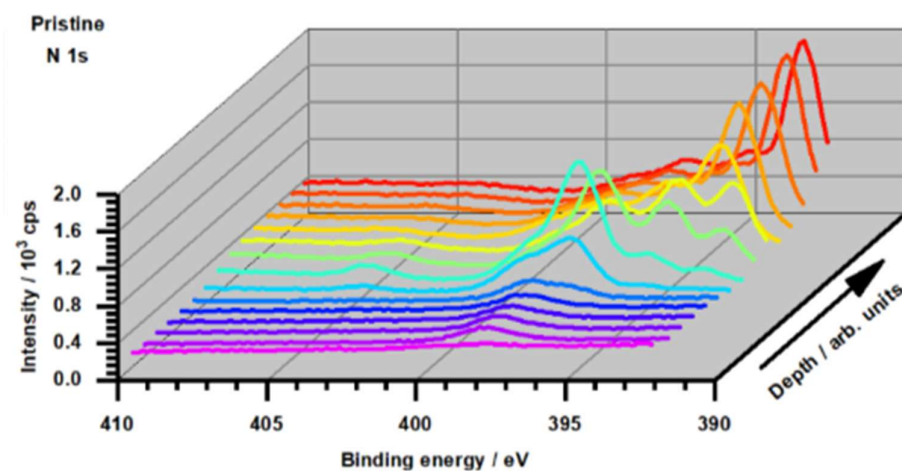
Appendix 1: Rietveld refinements of the Li₃N pellet (a) before and (b) after sintering in the experiment in [Figure 4.4 \(b\)](#). Reference diffraction patterns used for the refinements: α -Li₃N ($P6/mmm$)¹⁷², β -Li₃N ($P6_3/mmc$)¹⁴⁶ and Li₂O ($Fm\bar{3}m$)¹⁵². The refinements were performed by Dr. Robert House.



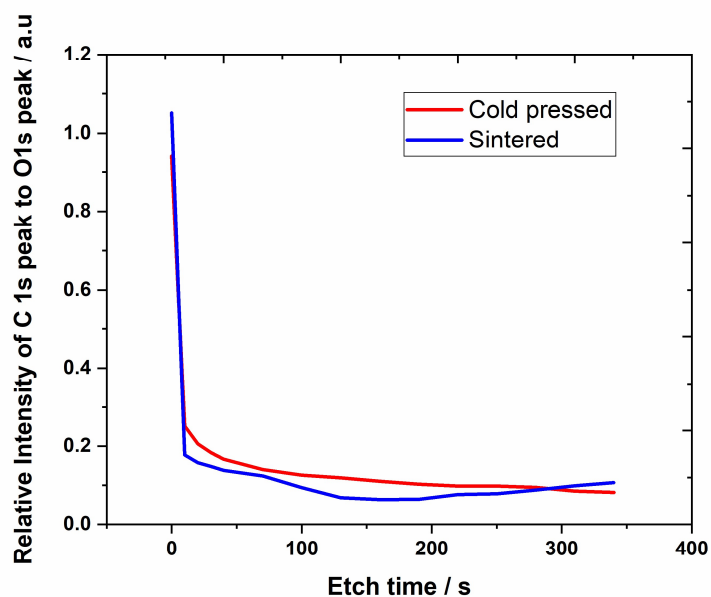
Appendix 2: Depth profiled C 1s XPS spectra of (a) Li_3N pellet after sintering and dry polishing.



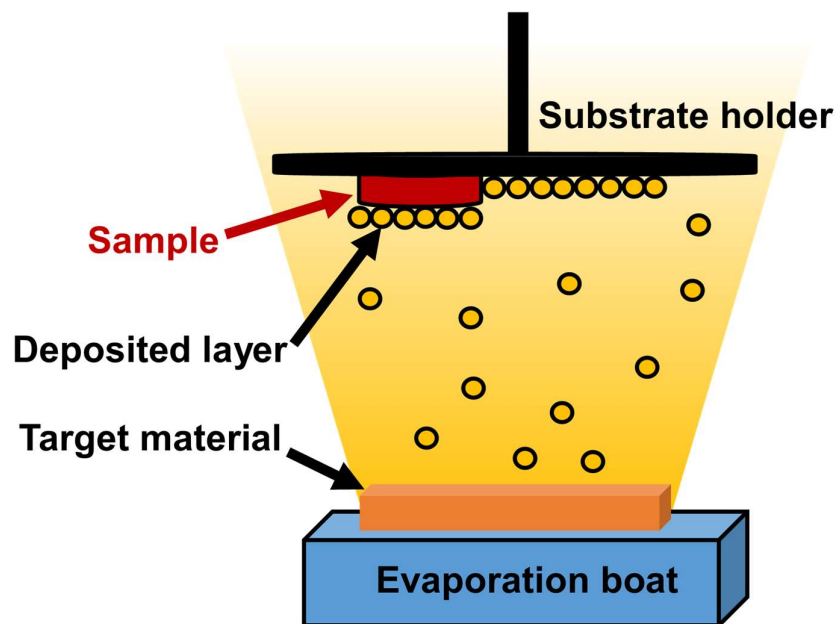
Appendix 3: Depth profiled Li 1s XPS spectra of (a) Li_3N pellet after sintering and dry polishing.



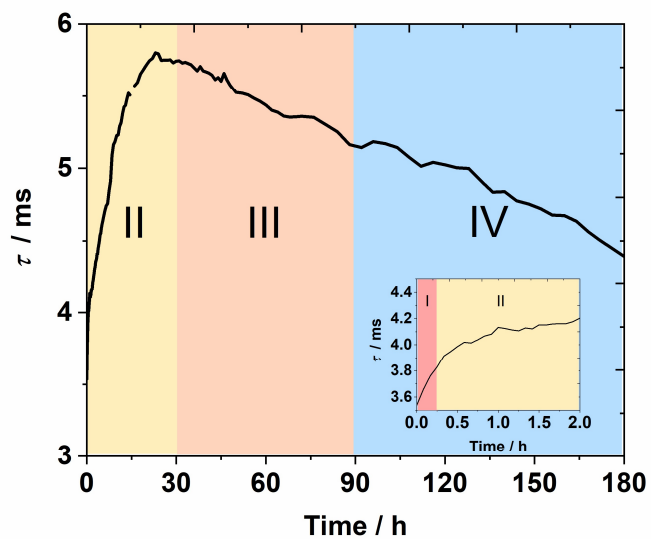
Appendix 4: Depth profiled N 1s XPS spectra of (a) Li₃N pellet after sintering and dry polishing.



Appendix 5: C/O atomic ratios, with sputter depth, derived from C 1s and O 1s XPS spectra for cold-pressed (red) and Li₃N pellet after sintering and dry polishing (blue).



Appendix 6: Illustration of thermal evaporation set-up.



Appendix 7: RC time constant (τ) evolution with time for the LLZTO | LP30 interface determined using EIS.