

Investigation of Structural and Electrochemically Active Frameworks for Li-S Cells

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Djuandhi, Lisa

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Investigation of Structural and Electrochemically Active Frameworks for Li-S Cells

by

Lisa Djuandhi



A thesis in fulfillment of the requirements for the degree of
Doctor of Philosophy

School of Chemistry

Faculty of Science

University of New South Wales, Australia

November 2021

1. THESIS TITLE AND ABSTRACT

Thesis Title and Abstract	Declarations	Inclusion of Publications Statement	Corrected Thesis and Responses
Thesis Title			
Investigation of Structural and Electrochemically Active Frameworks for Li-S Cells			
Thesis Abstract			
With a theoretical capacity of 1672 mA h g^{-1}, more than five times higher than any commercially available lithium-ion (Li-ion) cell systems, the lithium-sulfur (Li-S) cell is an attractive candidate for next generation energy storage. Despite this high theoretical capacity, Li-S cells generally suffer from poor capacity retention and working lifetimes that prevent them from mass commercialisation. This is mainly due to current limitations in managing the inherent Li-S redox reactions which involve diffusion and migration of electrochemically active polysulfides. One approach to prevent polysulfide migration is by rational design of the sulfur electrode framework. The aim of this research is to investigate the electrochemical implications of using different frameworks for entrapment of redox active species, mainly designed for the Li-S cell system. The two types of frameworks investigated are: (1) mixed-morphology carbon feeds derived from waste sources wherein the intention is for the carbon to purely act as a structural framework to trap lithium polysulfides, and (2) sulfur-rich copolymers wherein redox active sulfur is covalently bound within the framework. More specifically, the goals involve determining: (1) whether carbon acts purely as a structural framework to trap redox active species during electrochemistry, and (2) whether sulfur-rich copolymers act purely as a sulfur feed. Achieving these goals requires a thorough understanding of what properties in each framework are ideal for the Li-S cell. The main conclusion drawn from this work is that neither of the materials studied behaved as pure structural or covalent frameworks partaking in various side processes. Using specialised techniques such as X-ray powder diffraction, solid-state NMR, and X-ray absorption near-edge structure spectroscopy, the beneficial and parasitic side processes involved in each framework are able to be determined. Overall, a significantly enhanced understanding of the Li-S cell chemistry when using these materials is presented in this work.			

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Publication Details #1

Full Title:	Repurposing Waste Tires as Tunable Frameworks for Use in Sodium-Ion and Lithium–Sulfur Batteries.
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Status:	published
The Candidate's Contribution to the Work:	Primary author, preparation of samples, collection and analysis of results
Location of the work in the thesis and/or how the work is incorporated in the thesis:	Chapter 3 was written based on parts of this article.

Publication Details #2

Full Title:	Pyrolysed coffee grounds as a conductive host agent for sulfur composite electrodes in Li–S batteries.
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Location of the work in the thesis and/or how the work is incorporated in the thesis:	Contents of this article have been used in Chapter 1 and some results from this work are discussed in Chapters 6, 7, and 8 of the thesis

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Abstract

With a theoretical capacity of 1672 mA h g^{-1} , more than five times higher than any commercially available lithium-ion (Li-ion) cell systems, the lithium-sulfur (Li-S) cell is an attractive candidate for next generation energy storage. Despite this high theoretical capacity, Li-S cells generally suffer from poor capacity retention and working lifetimes that prevent them from mass commercialisation. This is mainly due to current limitations in managing the inherent Li-S redox reactions which involve diffusion and migration of electrochemically active polysulfides. One approach to prevent polysulfide migration is by rational design of the sulfur electrode framework.

The aim of this research is to investigate the electrochemical implications of using different frameworks for entrapment of redox active species, mainly designed for the Li-S cell system. The two types of frameworks investigated are: (1) mixed-morphology carbon feeds derived from waste sources wherein the intention is for the carbon to purely act as a structural framework to trap lithium polysulfides, and (2) sulfur-rich copolymers wherein redox active sulfur is covalently bound within the framework. More specifically, the goals involve determining: (1) whether carbon acts purely as a structural framework to trap redox active species during electrochemistry, and (2) whether sulfur-rich copolymers act purely as a sulfur feed.

Achieving these goals requires a thorough understanding of what properties in each framework are ideal for the Li-S cell. The main conclusion drawn from this work is that neither of the materials studied behaved as pure structural or covalent frameworks partaking in various side processes. Using specialised techniques such as X-ray powder diffraction, solid-state NMR, and X-ray absorption near-edge structure spectroscopy, the beneficial and parasitic side processes involved in each framework are able to be determined. Overall, a significantly enhanced understanding of the Li S cell chemistry when using these materials is presented in this work.

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Journal of Materials Chemistry A, **6**, 15132-15146 (2018)
2. ***Djuandhi, L.**; Sharma, N.; Cowie, B. C.; Nguyen, T. V.; Rawal, A., *Elucidation of Structures and Lithium Environments for an Organo-Sulfur Cathode.*
Physical Chemistry Chemical Physics, **21**, 18667-18679 (2019)
3. Barghamadi, M.; Djuandhi, L.; Sharma, N.; Best, A.S.; Hollenkamp, A.F.; Mahon, P.J.; Musameh, M.; Rüther, T., *In Situ Synchrotron XRD and sXAS Studies on Li-S Batteries with Ionic-Liquid and Organic Electrolytes.*
Journal of The Electrochemical Society, **167**, 100526 (2020)
4. ***Djuandhi, L.**; Gaikwad, V.; Cowie, B. C.; Sahajwalla, V.; Sharma, N., *Repurposing Waste Tires as Tunable Frameworks for Use in Sodium-Ion and Lithium–Sulfur Batteries.*
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5. ***Djuandhi, L.**; Gaikwad, V.; Wang, W.; Cowie, B. C.; Barghamadi, M.; Sahajwalla, V.; Sharma, N., *Pyrolysed coffee grounds as a conductive host agent for sulfur composite electrodes in Li–S batteries.*
Carbon Trends, **4**, 100053 (2021)
6. ***Djuandhi, L.**; Sharma, N.; Cowie, B. C.; Nguyen, T. V.; Rawal, A., *Mechanistic Implications of Li-S Cell Function Through Modification of Organo-Sulfur Cathode Architectures.*
Physical Chemistry Chemical Physics, **23**, 14075-14092 (2021)
7. Andersen, H. L.; **Djuandhi, L.**; Mittal, U.; Sharma, N., *Strategies for the Analysis of Graphite Electrode Function.*
In Press in Advanced Energy Materials. (2021) DOI: 10.1002/aenm.202102693

* Content from these published works have been included in the thesis.

Colloquia

1. *“Elucidation of structures and lithium environments for an organo-sulfur cathode”*
Conference proceeding at the International Union of Materials Research Societies – International Conference in Asia (IUMRS-ICA), Perth (22nd-26th Sep 2019)
and at the Australian and New Zealand Society for Magnetic Resonance (ANZMAG), Perth (25th-28th Nov 2019)
2. *“Shedding light on the subtle differences in Li-S cell operation when using safer ionic liquid-based electrolytes”*
Conference proceeding at the Australian Nuclear Science and Technology Organisation (ANSTO) User Meeting, Sydney (2nd-3rd Dec 2019)
3. *“Investigating the Role of Copolymeric Architectures in Electrode Materials for Efficient Li-S Battery Function”*
Poster presentation at the Australian Battery Society (ABS) Meeting, Online (28th-29th Oct 2021)

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Chapter 1: Introduction

1.1 The current state of energy storage systems

One of the challenges that impede widespread use of renewable sources such as wind and solar energy is the inability to store the harnessed energy efficiently. Lithium-ion (Li-ion) cells have been the primary electrical energy storage system in numerous everyday devices due to their light weight and reliable high energy-storage capacity compared to other types of cells.¹ While the energy density of commercialised Li-ion batteries has experienced almost a fourfold increase compared to the first model developed in 1991, according to Janek *et al.* it may soon reach its limit.² Moreover, the high energy density achieved by current commercialised Li-ion batteries (<300 mAh g⁻¹ for any well-known system, see **Table 1.1**³) relies on the use of transition metal oxides derived from finite resources.⁴ Thus, meeting the demands for sustainability and next generation battery energy storage systems relies on further developments in alternative materials and battery chemistries.

Table 1.1 – Comparison of cathode materials for lithium cells.³

Cathode material	Capacity / mAh g ⁻¹	
	Theoretical	Practical
LiCoO ₂	274	110-140
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	278	210
LiMn ₂ O ₄	148	110-120
LiFePO ₄	170	150
S	1672	-

1.2 The lithium-sulfur cell

Lithium-sulfur (Li-S) cells are alternative candidates for next-generation energy storage systems due to their high theoretical capacity relative to conventional Li-ion cells.⁵⁻⁶ This is largely due to the ability of elemental octasulfur (S₈) to accommodate 16 lithium ions (versus only 0.5/0.7 lithium ions per host such as LiCoO₂ in Li-ion cells),⁷ resulting in a theoretical energy storage capacity of 1672 mAh g⁻¹.⁸ Despite such promises to surpass state-of-the art Li-ion cell technologies, Li-S cells rely on

inherently different electrochemistry and thus different challenges still require further research to justify its commercial viability.⁹

1.3 Polysulfide shuttle and capacity fading

The principle of a Li-S cell relies on the reversible reaction simplified in **Eqn. 1.1**.



A typical Li-S cell involves a carbon/sulfur (C/S) composite cathode, a lithium anode, and an organic solution or gel-based electrolyte.¹⁰ In an ideal scenario, lithium from the anode surface is dissolved in the electrolyte to react with sulfur to form polysulfides during the discharging process. Upon charging, these polysulfides are converted back to sulfur on the cathode surface and reverse lithiation (lithium plating) occurs on the anode as depicted in **Figure 1.1**.¹¹

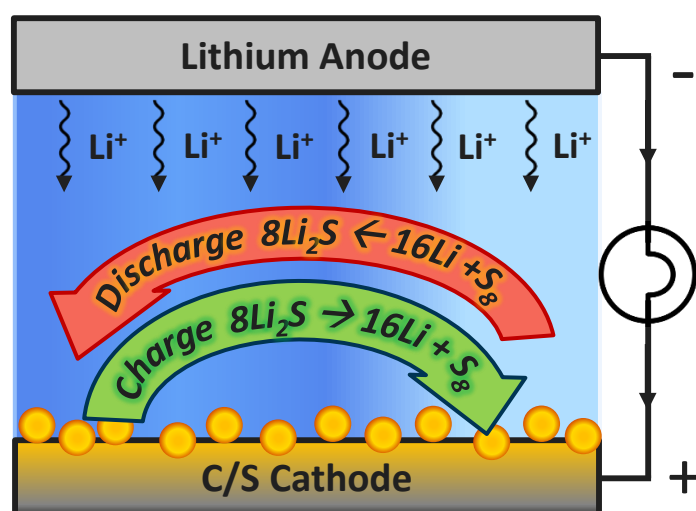


Figure 1.1 – Li-S cell schematic adapted from literature by Barghamadi *et al.*⁵

In practice the discharge reaction involves the formation of Li_2S_n polysulfides of a range of sulfur chain lengths from $n=8-2$ and variable solubilities in typical organic electrolyte solvents as proposed in **Figure 1.2**.⁵ The intermediate long-chain polysulfide species Li_2S_8 is soluble in organic solvent electrolytes and readily forms upon discharge whilst the most reduced state short chain polysulfide species, particularly Li_2S , is relatively insoluble.

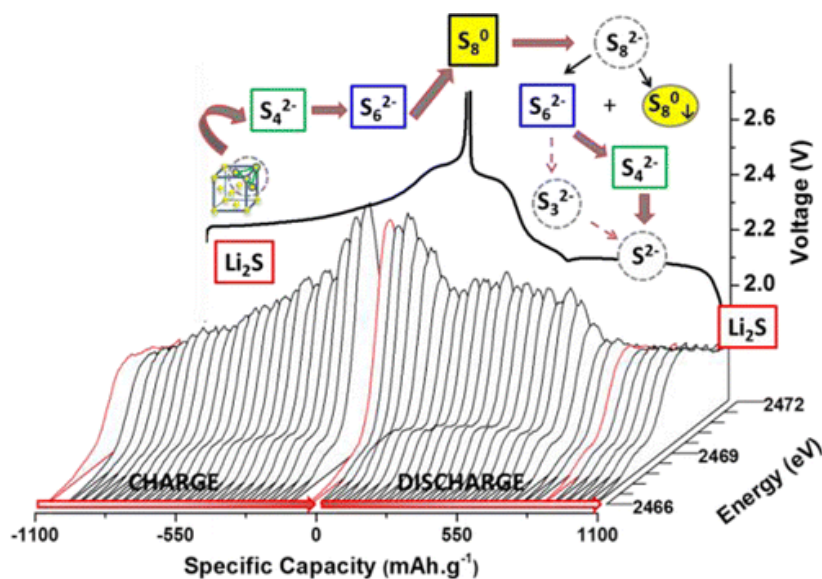


Figure 1.2 – Typical capacity vs. voltage profiles of a Li-S cell plotted against *in operando* UV-Vis spectroscopy data visualising the polysulfide species formed at signature voltage plateaus during the charge and discharge cycles of a Li-S cell.¹²

Since the intermediate long chain polysulfides are relatively soluble and hence mobile in the electrolyte, the deposition of the insoluble short chain polysulfide products can occur at both electrodes. Considering a larger concentration of Li^+ existing near the lithium anode, the insoluble polysulfides are more likely to form and deposit on the anode. This gives rise to the so-called “shuttle effect” where a passivating layer of insoluble species is formed on the anode surface, insulating the anode and thus halting the cell’s function completely.¹³ Moreover, the inherent conversion reactions to reduced polysulfide species from cyclic S_8 causes an overall volume expansion of $\sim 80\%$.⁵ Such a large expansion acts to pulverise the cathode material overtime and results in a rapidly fading capacity as contacts between particles and conductive media are destroyed.⁵

Combating this shuttling issue requires modification of components of the Li-S cell. The main components to modify are: (1) the lithium metal electrode, (2) the electrolyte, and (3) the sulfur-containing electrode. Modifications to the lithium metal electrode often involve protecting the surface layer from deposition of insoluble reaction products.¹⁴ Studies on improving the electrolyte system focuses largely on minimising the solubility of polysulfides without too much compromise on the conductivity of the Li-S cell.¹⁵ In terms of the sulfur-containing electrode, it has been of particular interest to design materials and frameworks for polysulfide confinement to improve Li-S cell capacity retention.⁹

1.4 Carbon frameworks from waste and biomass sources

The most common strategy in optimising the sulfur-containing electrode focuses on the use of carbon frameworks that can physically confine polysulfides to reduce diffusional capacity loss.¹⁶ Carbon is a popular choice of electrode additive in Li-S cells as it is conductive and highly porous in the micro and nano scale.¹⁷ According to Manthiram *et al.*,¹⁸ an ideal carbon-sulfur composite requires: (i) high electrical conductivity, (ii) electrochemical compatibility with sulfur, (iii) small pores to accommodate polysulfides, (iv) accessibility of the electrolyte to the active material, and (iv) a stable framework that can accommodate the volume changes of the active material (sulfur) during electrochemical cycling. Of particular interest is the use of carbon nanomaterials such as carbon nanotubes, carbon spheres, graphite, graphene oxide, and reduced graphene oxide as additives to the sulfur active electrode material.¹⁹⁻²³ These carbon nanomaterials generally can be probed easily with specialised analytical techniques, which facilitates structural and electrochemical characterisation.

Most of the studies conducted to improve the specific capacity of Li-S cells have involved maximising the surface area and porosity of the carbon-sulfur composite matrix. In principle, maximising the surface area would also effectively maximise the utilisation of active sulfur material.²⁴ High porosity could physically entrap lithium polysulfides from dissolving and diffusing into the electrolyte thus suppressing the aforementioned shuttle effect. Increasing the surface area and porosity generally involve heat treatment/pyrolysis and/or chemical treatment of carbons. In order to tune the pore structure of coal, Kang *et al.* used KOH to chemically treat the coal precursor, followed by heat treatment under N₂ at 750 °C.¹⁷ This treatment resulted in a specific surface area of up to 3461 m² g⁻¹, and a pore volume as high as 2.10 cm³ g⁻¹. When implemented in a Li-S cell, the physical entrapment of sulfur in this modified coal matrix contributed to a specific capacity of 1390 mAh g⁻¹, with 84% capacity retention after 100 cycles at a rate of 0.5C (836 mA g⁻¹). Other methods of increasing the porosity of carbons involve hard templating using nanoparticles. One example of hard templating is the use ZnO nanoparticles as employed by Strubel *et al.*, which resulted in a specific surface area of 3060 m² g⁻¹ and pore volume of up to 3.9 cm³ g⁻¹.²⁵ According to their results, the porosity and surface area is tuneable based on the

temperature of pyrolysis and the volatile contents initially present within the coal samples.

Indeed, while the use of numerous carbon/sulfur composites in the scope of Li-S cells have been widely reported, the ideal carbon morphology remains to be up for debate. Each type of pore morphology (i.e., micro <2 nm, meso 2-50 nm and macropores >50 nm) has their own limitations with regards to sulfur entrapment. Pertinently, work involving the use of carbon/sulfur nanocomposites in Li-S cells with markedly high specific capacities and long cycle life typically report that the carbon architecture is a mixture or hierarchy of various pore structures.²⁶⁻²⁹ Provided that a mixed pore morphology is favourable for effective sulfur entrapment in Li-S cells over pure pore morphologies, this begs the question of whether there is any benefit in rigorously processing carbon sources to yield pure pore morphologies.

Biomass is a large source of carbon or carbon-containing compounds hence there is an increasing demand for research dedicated to processing and utilising these carbons. Pure carbon nanomaterials such as carbon nanotubes^{19, 30-31} and carbon nanospheres³²⁻³⁴ are popular choices of materials for Li confinement at the electrode but can be costly and inviable for commercialisation. Reports of natural carbon sources as confining frameworks to immobilise polysulfides in Li-S cells are inarguably numerous³⁵⁻³⁷ – to name a few, these carbons can be derived from biomass such as rice husk,³⁸ or waste such as PET bottles,³⁹ and waste rubber products.⁴⁰ The research on waste carbon sources as electrode conductive additives demonstrates that biomass derived carbons harness sufficient porosity and surface area suitable for electrodes in Li-S cell function.

Whilst useful carbons can be obtained from a variety of sources, the composition and morphology of carbon can be inconsistent based on the processing treatment which ultimately dictates its functionality as an electrode material. This alludes to whether the carbon resembles a more graphitic or disordered hard carbon character, and the properties of these subcomponents themselves. In the case of Li-ion cells, the redox mechanism relies mostly on intercalation of Li⁺ ions into graphene-like layers (thus preference to more ordered graphitic materials), which means that the interlayer *d*-spacing and degree of graphitisation are properties to consider when designing a Li-ion carbon electrode.⁴¹ Switching to a Na-ion system, which relies on transfer of Na⁺ ions, a different functionality must be considered.⁴² Whilst energy storage via

intercalation to graphite-like layers in hard carbons (similar to Li-ion) is also possible in the Na-ion system, the reaction is thermodynamically unstable.⁴¹ Instead the redox mechanism generally benefits from the presence of defects in the carbon electrode, and thus alternative properties such as pore morphology or efforts to expand the interplanar distance of graphitic components are important considerations for Na-ion electrode design.⁴³⁻⁴⁴ Arguably, the rationale for designing most carbon-sulfur composite electrodes is based on a similar reliance on pore morphology and physical confinement of redox active species. Pertinently, many biomass-derived carbon matrices intended for Na-ion half cells have been similarly applied in Li-S electrodes as additive frameworks to confine sulfur, with generally favourable improvements compared to standard Li-S cell configurations (typically using commercial carbon black exclusively as the conductive additive of the sulfur-containing electrode).^{35-39, 45}

Although use of biomass-derived carbons for Li-S cells has been widely reported, limited research has been dedicated to investigating the role of the carbon framework in Li-S cell electrochemistry. Similar to in Na-ion cells, Li-S cells do not rely on intercalation redox behaviour and therefore are not expected to gain any additional benefit from utilising highly refined, highly ordered carbons in place of non-graphitisable hard carbon frameworks. Starting with natural or waste carbons inherently features impurities or imperfections and this needs to be considered. The remaining impurities may enhance or be detrimental to Li-S cell function or be beneficial from the recycling/process point of view – for example, impurities such as pre-existing crosslinked sulfur in vulcanised rubber sources⁴⁰ that would otherwise add cost and pose additional safety and environmental hazards to remove completely. There is an opportunity to investigate commercially viable carbon sources from directed sources for the development of carbon-sulfur composites.

1.5 Organosulfur frameworks

Recent studies have focused on using sulfur-rich copolymers, in place of C/S composites, as active cathode materials.⁴⁶⁻⁴⁹ Materials such as poly(sulfur-*random*-1,3-diisopropenylbenzene), abbreviated as (poly(S-*r*-DIB)), are believed to reduce mechanical stress on the cathode surface by chemically stabilising polymeric sulfur and preventing depolymerisation to occur under ambient conditions.⁵⁰ In these studies, copolymers such as poly(S-*r*-DIB) were synthesised *via* an inverse vulcanisation

method (visualised in **Figure 1.3**), where molten S_8 is used as a reaction medium as well as a sulfur-monomer to directly copolymerise with 1,3-diisopropenylbenzene (an olefinic crosslinker). The implementation of poly(S-*r*-DIB) exhibited one of the highest specific capacities reported for a polymer-based cathode in Li-S cells of 823 mA h g⁻¹ after 100 cycles.⁵⁰ Chung *et al.* suggested that the markedly improved performance was largely due to the structure's ability to suppress dissolution of soluble species and thus irreversible deposition of insoluble discharge products.⁵¹ They proposed that polysulfides are presumably entrapped on the copolymer surface, effectively reducing their mobility in the electrolyte.

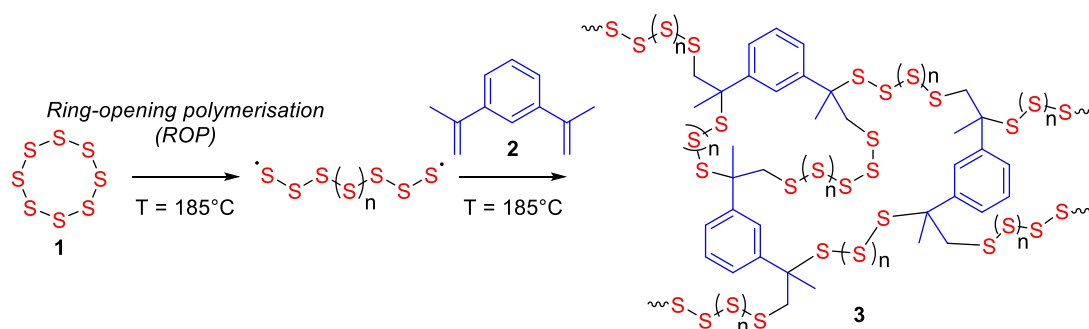


Figure 1.3 – Inverse vulcanisation of octasulfur (1) with 1,3-diisopropenylbenzene (2) to yield poly(sulfur-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) (3) based on work by Chung *et al.*⁵¹

In previous work conducted on poly(S-*r*-DIB), the marked improvement in capacity retention was rationalised to be due to entrapment of lithium polysulfides within the poly(S-*r*-DIB) copolymeric network.⁵² Solid-state ⁷Li NMR (⁷Li SSNMR) showed quasi-solid-state lithium environments within the cathode material extracted at different states of charge. Whilst a large portion of the capacity in the initial cycles are attributed to polycrystalline sulfur agglomerates, the presence of quasi-solid-state lithium environments suggests that the copolymeric units that exist in conjunction with these agglomerates effectively entrap sulfur within its architecture. Thus, based on this finding, it is the lithium accessibility of the copolymeric network that is essential for rational design.

1.6 Project aims and approach

This work explores the applications of two classes of materials as confining frameworks for polysulfide entrapment in Li-S cells, namely frameworks from waste and biomass sources (see **Chapter 3** and **Chapter 4**) and organosulfur polymer

frameworks prepared *via* inverse vulcanisation (see **Chapter 5**, **Chapter 6**, and **Chapter 7**).

Both these classes of materials mainly contain amorphous carbonaceous components *inter alia* that require characterisation using element selective techniques such as NMR and XANES spectroscopy. For organosulfur polymer frameworks, it is imperative that evaluation of structure and impact to Li-S cell redox and interfacial speciation considers comparison to other copolymeric architectures (i.e., comparison between materials discussed in **Chapter 5**, **Chapter 6**, and **Chapter 7**) including the exemplar material poly(S-*r*-DIB) explored in previous work.⁵² Combining this knowledge on the amorphous components with information about the bulk of the material and crystalline phases (obtained from methods such as XRD) can provide the necessary insight to make more informed decisions in design of future electrode frameworks.

In essence this project aims to achieve three key milestones, that are:

- (1) Develop selective strategies to characterise the crystalline and amorphous components of the confining frameworks using a combination of suitable analytical techniques
- (2) Provide mechanistic insight using these techniques to aid in the design of future confining electrode frameworks for Li-S cells
- (3) Contribute to a more informed understanding of the general limitations in Li-S cell electrochemistry to develop further improvements

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Chapter 2: Key analytical techniques

2.1 Introduction

In Li-S batteries, carbon-containing compounds play key roles in the device function, *i.e.*, as the host framework or part of the co-polymeric unit in the “S” cathode. It is therefore imperative to probe these carbon components to understand the interplay between structure, morphology, and physical properties, and understand their evolution during Li-S cell operation. The typical analytical approach involves a combination of materials characterisation and electrochemical evaluation (e.g., *via* cyclic voltammetry, galvanostatic charge-discharge tests) of Li-S cell performance and behaviour. Materials characterisation to investigate the role of the carbon-containing cathode material can either focus on (i) the properties of the pristine carbon cathode material (see **Table 2.1**), or (ii) their effects on the interfacial redox processes and speciation (see **Table 2.2**). Achieving a comprehensive understanding of the role of the carbon material in the Li-S battery requires insight from both these perspectives.

Table 2.1 – Overview of the analytical methods used to characterise the pristine carbon cathode material and their respective contributions to materials characterisation in this work.

Technique	Analyte	Application in this work	Reference
Combustion and XRF elemental analysis	Pyrolysed rubber tyre, pyrolysed waste coffee	Identification of phase impurities for Rietveld analysis to XRD data	Chapter 3, Chapter 4
X-ray powder diffraction (XRD)	Pyrolysed rubber tyre, pyrolysed waste coffee	Quantification of crystalline phase impurities, their <i>d</i> -spacings and crystallite sizes	Chapter 3, Chapter 4
	Poly(<i>S-r</i> -squalene), poly(<i>S-r</i> -limonene), poly(<i>S-r</i> -para-DIB) (90 wt. % sulfur)	Identification of crystalline sulfur phases	Chapter 5, Chapter 6, Chapter 7
Brunauer-Emmett Teller (BET analysis)	Pyrolysed rubber tyre, pyrolysed waste coffee	Pore morphology (<i>i.e.</i> , surface area, pore dimensions, mono/multilayer adsorption behaviour from adsorption isotherm)	Chapter 3, Chapter 4

Raman spectroscopy	Pyrolysed rubber tyre, pyrolysed waste coffee	Level of disorder of carbon component (I_D/I_G)	Chapter 3, Chapter 4
Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS)	Pyrolysed rubber tyre, pyrolysed waste coffee	Visualisation of carbon framework macro-meso-microstructure	Chapter 3, Chapter 4
	Pyrolysed waste coffee	Elemental mapping of distribution of active material and impurities	Chapter 4
Solution-state ^1H and ^{13}C NMR spectroscopy	Poly(<i>S-r</i> -limonene) (10-50 wt. % limonene)	Consumption of crosslinker and degree of polymerisation	Chapter 6
Solid-state ^1H - ^{13}C CP-TOSS NMR spectroscopy	Poly(<i>S-r</i> -squalene), poly(<i>S-r</i> -limonene), poly(<i>S-r</i> -para-DIB) (90 wt. % sulfur)	Spectral editing of copolymeric hydrocarbons	Chapter 5, Chapter 6, Chapter 7
Solid-state ^1H - ^{13}C HETCOR NMR spectroscopy	Poly(<i>S-r</i> -squalene), poly(<i>S-r</i> -limonene), poly(<i>S-r</i> -para-DIB) (90 wt. % sulfur)	Couplings and connectivities between carbon and proton environments within copolymeric hydrocarbons	Chapter 5, Chapter 6, Chapter 7
Size Exclusion Chromatography (SEC) analysis	Poly(<i>S-r</i> -limonene)	Polymer average molecular weight (M_n) and polydispersity (M_w/M_n)	Crockett <i>et al.</i> ¹ discussed in Chapter 6
Atmospheric pressure chemical ionization mass spectrometry (APCI-MS)	Poly(<i>S-r</i> -limonene)	Polymer average molecular weight	Crockett <i>et al.</i> ¹ discussed in Chapter 6
Thermogravimetric analysis (TGA)	Poly(<i>S-r</i> -squalene) (10-50 wt. % squalene)	Identification of thermal transitions and crystalline sulfur moieties	Chapter 5
X-ray spectroscopy techniques (i.e., X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES) spectroscopy)	Poly(<i>S-r</i> -squalene), poly(<i>S-r</i> -limonene), poly(<i>S-r</i> -para-DIB) (90 wt. % sulfur)	Characterisation of carbon and sulfur bonding environments (i.e., probing the C K-edge and S K-edge or S L-edge)	Chapter 5, Chapter 6, Chapter 7

Table 2.2 – Overview of the analytical methods used to evaluate the effects of the carbon material on redox processes and interfacial speciation, and their respective contributions to materials characterisation in this work.

Technique	Analyte	Applications	Reference
X-ray absorption near-edge structure (XANES) spectroscopy	Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes, poly(<i>S-r</i> -para-DIB) electrodes	Monitor evolution (or non-evolution) of components that are present in the cathode pre-electrochemical treatment (i.e., probing the C K-edge, S K-edge, F K-edge)	Chapter 5, Chapter 6, Chapter 7
	Pyrolysed rubber tyre carbon electrodes, pyrolysed waste coffee carbon electrodes, Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes, poly(<i>S-r</i> -para-DIB) electrodes	Identify interfacial components (predominantly related to oxidised sulfur sourced from electrolytic salts) and monitor their speciation over electrochemical cycling (i.e., probing the S K-edge)	Chapter 3, Chapter 4, Chapter 5, Chapter 6, Chapter 7
Solid-state ^7Li MAS NMR spectroscopy	Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes	Monitor evolution diamagnetic lithium populations (of different chemical shifts) over electrochemical cycling	Chapter 5, Chapter 6
Solid-state ^1H - ^7Li HETCOR NMR spectroscopy	Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes, poly(<i>S-r</i> -para-DIB) electrodes	Identify diamagnetic lithium chemical shifts associated with the copolymeric hydrocarbons	Chapter 5, Chapter 6, Chapter 7
Solid-state ^7Li saturation recovery NMR spectroscopy	Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes, poly(<i>S-r</i> -para-DIB) electrodes	Obtain T_1 relaxation times and quantification of lithium environments of different chemical shifts and molecular mobilities. Evaluate contributions to lithium immobilisation from direct adsorption to copolymeric/non-copolymeric electrode components (inferred from magnitude of T_1)	Chapter 5, Chapter 6, Chapter 7
Solid-state ^7Li - ^7Li EXSY NMR spectroscopy	Poly(<i>S-r</i> -squalene) electrodes, poly(<i>S-r</i> -limonene) electrodes, poly(<i>S-r</i> -para-DIB) electrodes	Evaluate contributions to lithium immobilisation from indirect absorption to copolymeric/non-copolymeric electrode components (inferred based on correlations between lithium environments of different chemical shifts)	Chapter 5, Chapter 6, Chapter 7

This chapter outlines the key techniques and analytical approach used in this work to characterise structure-property relationships. It should be noted that this chapter is designed to be concise as further specific details, including challenges and

approach are integrated in the following chapters with respect to each material and often correlated to a technique. Furthermore, fundamental approaches such as electrochemistry, Raman spectroscopy, Brunauer–Emmett–Teller (BET) analysis, Thermogravimetric analysis (TGA), and Scanning Electron Microscopy (SEM) are not detailed here but discussed with respect to results in the following chapters.

2.2 Importance of characterisation and analysis

2.2.1 Characterising the role of carbon frameworks

Considering the primary functionalities of carbon are simply as a conductive medium and as a structural framework, it would hence be reasonable to consider waste-derived carbon materials as an alternative to less accessible ultra-pure carbons. In using more crude carbon sources however, it is important to consider whether the impurities present would interfere with the cell electrochemistry, whether different carbon architectures would translate to a difference in cell performance, and whether additional more complicated processing steps are necessary to produce an adequate carbon source. Moreover, the carbon component would also be susceptible to alternative Li-ion reaction pathways related to decomposition of the electrolyte. Whilst this may initially serve as an additional source of capacity, it is important to monitor whether this effect is beneficial or detrimental in prolonging the Li-S cell lifetime.

2.2.2 Characterising the role of organosulfur frameworks

In addition to challenges involved in characterising the Li-S battery, understanding the role of inverse vulcanised copolymers also involves unique challenges in characterising the inherent copolymer properties. A lack of awareness on the relative variability in preparation of these copolymers versus carbon frameworks can also give rise to inconsistencies or contradictory interpretations of their role in electrochemistry. In preventing these inconsistencies, it is therefore critical for inverse vulcanisation conditions of the copolymer as well as other experimental conditions to be reported in sufficient detail (i.e., including atmosphere, temperatures, and durations of heating, as well as storage conditions).

Whilst this preparation is facile, inverse vulcanisation ultimately yields random copolymers with non-uniform assemblies. With similar qualities to vulcanised rubbers, this lack of precision in the crosslinking between the functional groups means that

complete characterisation of the material's properties and structure is not always attainable. Despite such challenges in characterisation, inverse vulcanised copolymers remain to be a topic of interest in their application as electrode materials due to their enhancement of the battery's overall performance and beneficial properties that are unique to other carbon-based electrode materials. Developing strategies to establish structure-property relationships of inverse vulcanised copolymers on battery electrochemistry can offer unique perspectives that can be applied to other disordered materials, as well as crystalline materials.

2.3 Characterising Li-S cell electrochemistry

It is important to address that the current understanding of Li-S redox in general is still relatively ambiguous such that the current perspectives offered on this matter can be contradictory.² More accurately, because of the shuttle effect the concentration of redox-active polysulfides within the Li-S cell is generally variable, often forming transient species that can be challenging to monitor.³ Some polysulfide species such as Li_2S_2 expected during Li-S redox are known to be difficult to capture experimentally and require the use of computational models to elucidate their formation.⁴ Resolving the inconsistencies surrounding the current understanding of Li-S redox requires extensive study of the mechanisms involved using a combination of diverse materials and a variety of analytical methods employing different strengths.

2.4 Solid-state Nuclear Magnetic Resonance (NMR) spectroscopy

The general principle behind nuclear magnetic resonance (NMR) relies on a relationship between the gyromagnetic ratios of nuclides (γ) and their resonant precession frequency (ω_0 , known as the Larmor frequency) about an external magnetic field (B_0). This phenomenon allows for spin magnetisation vectors to be measured at the intrinsic Larmor frequency of the selected nuclei.

In most spectroscopic techniques, the studied system is typically governed by the intrinsic properties of the sample itself that give rise to perceptible but relatively weak external perturbations. In NMR spectroscopy, this role is inverted such that information gained from measurements are generally dominated by nuclear interactions with the external apparatus more than with the sample itself.^{5, 6} This

dominance of interactions with the external apparatus on the studied system in NMR offers unprecedented selectivity to both microscopic and macroscopic properties, as well as to molecular dynamics over a broad range of timescales. By manipulating the experimental conditions, NMR can therefore offer insight on multiscale structure-property relationships such as expected in inverse vulcanised copolymers.

2.4.1 Motional averaging in solids

Spin interactions are largely dependent on molecular orientation. In solution state NMR, anisotropic effects arising from chemical shift anisotropy (CSA) and dipolar couplings are averaged out by the rapid isotropic tumbling of molecules, which results in sharp, highly-resolved peaks.⁷

In solid samples, CSA and dipole-dipole coupling terms which have an orientation dependence with respect to the static magnetic field ($\vec{B}_0$) become dominant due to restricted motion and preferred molecular orientations. This results in severe line shape broadening and loss of signal resolution.

To improve resolution in solid samples, these anisotropic effects can be averaged out by rapid mechanical spinning of the sample at an angle $\theta = 54.74^\circ$ with respect to $\vec{B}_0$ such that secular dipole-dipole coupling is averaged out to zero (i.e., $3\cos^2\theta - 1 = 0$).⁸ This is known as magic-angle spinning (MAS) with typical rotation speeds of ~ 6 - 14 kHz.

2.4.2 Total suppression of spinning sidebands (TOSS)

In the case that the sample rotation frequency (ω_r) is not sufficiently high, particularly in mixed environments, the presence of additional peaks called spinning sidebands, appearing at frequencies $\omega_j^{\text{iso}} + k\omega_r$ where k is an integer, can overlap and interfere with the identifying central resonances. These sidebands originate from the different molecular orientations and thus different directions of spin magnetisation vectors contained within solid samples.

These interfering sidebands can be removed using the total suppression of spinning sidebands (TOSS) scheme introduced by Dixon *et al.*^{9, 10} The scheme involves applying a series of properly timed π refocusing radiofrequency (RF) pulses following the initial $\pi/2$ RF pulse to generate sinusoidal spin echoes that add destructively to the spinning sidebands. Calculations to determine the pulse delays are

outlined in work by Dixon *et al.*¹⁰ The removal of spinning sidebands from the TOSS sequence reduces the overall amplitude of the NMR signal (specifically the free induction decay, FID), but this loss of sensitivity can be remedied by enhancing signal using other pulsed techniques such as cross polarisation.

2.4.3 Pulsed techniques based on cross polarisation

Since the anisotropic interactions are averaged out mechanically, they can be reintroduced using radiofrequency (RF) pulses to provide useful information on the structure and dynamic behaviour that determines the physical and mechanical properties of polymeric materials.¹¹ Using cross-polarisation (CP), the signal sensitivity of a dilute nucleus, in this case ^{13}C (abundance of 1.1%)¹² can be enhanced such that spectral assignments can be performed analogous to the solution-state.¹³ The principle behind CP is the transfer polarisation from more abundant nuclei (often ^1H or ^{19}F) to the dilute ^{13}C nuclei as a means to enhance the signal to noise ratio. This magnetisation transfer between spins of nuclei “j” and “k” (in this case ^1H and ^{13}C) is achieved by satisfying the Hartmann-Hahn condition described in Eqn. 2.1, wherein γ is the gyromagnetic ratio, and B_1 is the magnitude of the applied RF field.¹⁴

$$\gamma^j B_1^j = \gamma^k B_1^k \quad (2.1)$$

CP can also be applied in conjunction with gated decoupling where a delay in the ^1H decoupling field selectively reintroduces ^1H - ^{13}C heteronuclear dipolar couplings. This allows for a clear distinction between signals for carbons that are spatially close to protons (strong dipolar coupling) and non-protonated carbons (weak dipolar coupling). Note that the intensities of signals obtained in a gated decoupling experiment are also sensitive to molecular motion due to rotational modulation of the dipolar coupling.¹⁵ This technique is particularly useful as different overlapping carbon signals could be accurately distinguished from one another (i.e. CH_3 vs CH_2 , CH and quaternary C) providing unparalleled insight into the structure. Hence through solid-state NMR (SSNMR), copolymeric cathode materials could be characterised and a more detailed understanding of the copolymeric structure is achieved.

Furthermore, the signal enhancement of less abundant nuclei using the cross-polarisation technique can also be used in two-dimensional heteronuclear correlation (HETCOR) experiments such as ^1H - ^{13}C (and ^1H - ^7Li for electrochemically treated samples) HETCOR NMR which map strength of dipolar couplings between carbon (or

lithium) environments and surrounding protons. This is achieved by an initial $\pi/2$ RF to generate transverse magnetisation that is allowed to evolve within a set time t_1 . A second $\pi/2$ pulse is then applied to redirect the transverse magnetisation to the z-axis followed by a set delay or “mixing time” τ_m for spin exchange between nuclear environments, and a final $\pi/2$ pulse to convert the signal back to transverse magnetisation for detection in the t_2 dimension. In the context of copolymeric materials, these heteronuclear two-dimensional experiments can provide insight on the correlations between functional groups and degree of crosslinking within the copolymer (from ^1H - ^{13}C HETCOR NMR) and determine which lithium environments are associated with the copolymeric hydrocarbons (from ^1H - ^7Li HETCOR NMR).

^7Li NMR can also be used to evaluate lithium adsorption within the electrode matrix after subsequent electrochemical testing. ^7Li NMR provides information of the structure and dynamic behaviour of lithium species. The peak broadness or sharpness in the spectra can provide a clear distinction between dissolved- Li^+ species and Li^+ -containing solids in a sample.¹⁶ Chemical shifts in ^7Li NMR spectra relate to ion pairing, solvation and complexation of the lithium environment.¹⁷

Additional contrast in T_1 spin-lattice relaxation times or molecular mobility between lithium environments can also be achieved using saturation recovery ^7Li NMR measurements. These measurements initially involve applying a train of twenty $\pi/2$ pulses separated by short 1–5 ms delays to the sample to achieve total saturation of transverse magnetisation. The transverse magnetisation is then allowed to recover for a set duration τ in the z-axis. A second $\pi/2$ pulse is applied to convert this recovered signal for detection as a transverse component in the FID. The set duration for signal recovery τ is thus directly proportional to signal amplitude following the relationship: $\frac{M_z}{M_0} = 1 - e^{-\tau/T_1}$ for a spin environment with one T_1 component – wherein M_z is the amplitude of signal at τ , M_0 is the amplitude of signal at the limit τ for complete signal recovery/complete spin lattice relaxation, and T_1 is the spin-lattice relaxation time. This relationship allows for extrapolation of T_1 values by performing multiple measurements at various τ . Assessing the magnitude of T_1 can provide insight on immobility of lithium environments *via* direct adsorption to copolymeric and non-copolymeric electrode components.

Insight on immobilisation of lithium can also be obtained through two-dimensional homonuclear NMR experiments such as ^7Li - ^7Li exchange spectroscopy

(EXSY) of electrochemically treated electrodes. Correlations between lithium environments are achieved, similarly to the approach of a two-dimensional heteronuclear experiment, by allowing set mixing times for exchange of spin magnetisation between lithium environments of different chemical shifts. In an EXSY experiment, spin exchange can arise from dipolar couplings and dynamic processes. Assessing the correlations between lithium environments of different chemical shifts can provide insight on lithium immobilisation *via* indirect adsorption to copolymeric and non-copolymeric electrode components.

An analysis of the formation of solid and liquid lithium species over electrochemical processes should provide more detailed information on the electrochemistry of a Li-S cell.

2.5 Characterisation using soft X-ray spectroscopic techniques

One of the greatest challenges in developing a truly comprehensive understanding of Li-S cell operation is characterisation of the solid-electrolyte interface (SEI). The SEI is typically considered as a deposit of insoluble inorganic salts and organic products of partial electrolyte reduction.¹⁸ It is formed by reactions involving electrolyte components and polysulfides with the Li-anode in Li-S cells.¹⁹ Although formation of the SEI is inevitable and is even considered to be essential to permit practical cell lifetimes,²⁰ its effects can be detrimental considering its often low stability and disproportionate amounts of the SEI relative to other components in the cell in some cases.²¹

X-ray spectroscopy techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) allow distinction between different redox-active polysulfides based on its sensitivity to different oxidation states of a chosen elemental edge and to the different bonding environments. This sensitivity to different bonding environments can also offer insight on speciation of the solid-electrolyte interface (SEI) – a critical aspect of Li-S cell function

XPS involves X-ray irradiation of the sample at a fixed photon energy and measuring the intensity of directly emitted electrons as a function of their kinetic energy. The kinetic energy of the emitted electron is directly proportional to its binding energy to remain consistent with energy conservation rules. Since different electron

configurations correspond to characteristic binding energies, XPS is element specific and can offer useful information regarding SEI components in terms of their elemental composition, chemical states, as well as relative populations of unique chemical environments.

By comparison, X-ray Absorption Spectroscopy (XAS) is a measure of absorbed X-ray intensity over a scanned range of energies (typically *via* a monochromatic X-ray beam from a synchrotron radiation source). As both these techniques rely on photoelectric excitation, information regarding electron configuration obtained from XAS and XPS spectroscopy are essentially transferrable. Although the difference between these spectroscopic techniques may seem trivial, detection *via* secondary de-excitation pathways in XAS (as opposed to the primary photoelectron excitation event) means the incident photoelectron itself can remain in a bound state.²²

XAS involves the excitation of a core electron using X-ray radiation to a partially filled or empty state.²² In order to compensate for this excitation, energy is released either by ejection of an Auger electron or by filling of the empty state from a higher electron shell inducing radiative fluorescent photon emission. This process is visualised in **Figure 2.1**. Electron yield XAS measurements are typically conducted in total electron yield mode (TEY), partial electron yield mode (PEY) and total fluorescence yield mode (TFY). TEY mode involves the collection of electrons of all energies, and has a sampling depth of approximately 10 nm.²³ In PEY mode, only electrons of kinetic energy above the threshold energy are detected. PEY is used in a similar manner to TEY mode however often produces better spectra particularly for C and O K-edges as effects from undesirable and common carbon/oxygen contaminants are less significant.²³ Auger electron yield mode (AEY) is another surface sensitive mode where primary Auger electrons are directly collected. However, AEY mode is not typically used as it is known to encounter significant interference issues.²³ The emission of fluorescent photons, which arise from the top 200 nm (i.e., bulk sensitive) is collected as a total fluorescent yield (TFY) spectrum.²⁴ These signal contributions are visualised relative to the initial photon absorption event in **Figure 2.1**. In essence, a non-reliance on extended, free-body electrons to yield signal in XAS measurements means that the method is more sensitive to many-body effects and molecular geometries compared to XPS. The combined ability to perform measurements in transmission and electron yield modes also allows for information on the surface as

well as the bulk cathode material to be collected simultaneously. Such a technique should be beneficial in developing a more improved understanding of the adsorbed SEI components as well as evolution of the electrode material at various stages of Li-S cell operation.

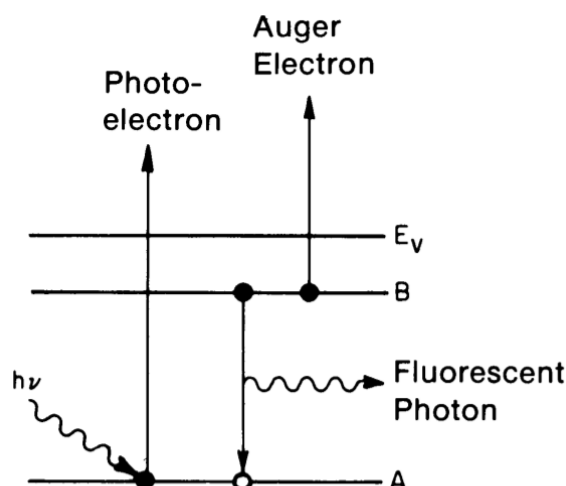


Figure 2.1 – Schematic diagram visualising a photon absorption event causing direct photoelectron emission from a core shell A. This event initially forms a vacancy, inducing secondary emission pathways either *via*: (1) filling of the vacancy from a higher electron shell B, resulting in radiative emission of fluorescent photons (TFY), or (2) non-radiatively through ejection of an Auger electron from the same atom (AEY). E_v denotes the vacuum level. Taken with permission from Stöhr.²⁵

XAS analysis can be performed to measure either the X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS) spectral regions, each with specific strengths and limitations. According to Aquilanti *et al.*, XANES measurements can offer sensitivity to oxidation states and site symmetry of the analyte, while quantitative insight on short-range order parameters (i.e., bond distances, coordination numbers and the chemical identity of nearest neighbours) can only be obtained through analysis of the EXAFS region.²⁶

XAS measurements at the S K-edge are notably dominated by contributions from electrolytic sulfates over reduced polysulfides, which makes it an ideal technique to monitor the effects of the electrode material to SEI speciation.²⁶ The XAS analysis conducted in this work only focuses on measurements of the XANES region conducted at the Soft X-ray beamline (SXR) at the Australian Synchrotron, with capabilities to generate low energy X-rays (100-3000 eV) thus offering compatible conditions to

measure C K- (i.e., C 1s, 280–340 eV) and S K-edges (i.e., S 1s, 2460–2540 eV) pertinent to the electrode materials explored in this work.²⁷

In essence, X-ray spectroscopy techniques such as XPS and XAS can provide valuable insight on the composition of the cathode matrix and its impact to interfacial speciation and Li-S redox. Furthermore, comprehensive mechanistic insight such as the quantification of redox-active sulfur components may require analysis using a combination of these techniques to overcome individual limitations.

2.6 X-ray powder diffraction (XRD)

One of the most commonly used techniques for structural characterisation of energy storage materials is X-ray powder diffraction (XRD). It provides long-range structural information of the active material and can be tailored to provide information on its evolution *via ex situ* measurements (i.e., analysing the material outside of the cell after electrochemical treatment) as well as *via in situ* (i.e., analysing the material within the cell after electrochemical treatment) or *in operando* measurements (i.e., analysing the material within the cell during electrochemical treatment).²⁸⁻³¹ XRD techniques are relatively insensitive to major components of interest in the Li-S cell that are either amorphous, nanocrystalline or formed in trace amounts. Focusing on using XRD techniques to structurally characterise the electrochemical processes also assumes that crystalline character and long-range order are essential and/or beneficial in the operation of a Li-S cell. For such reasons, alternative techniques should and are often considered to structurally characterise the electrochemical processes of a Li-S cell. Below a few examples of XRD studies on Li-S cells and materials are showcased.

XRD studies have been conducted to understand the Li-S cell operation in the past,³²⁻³⁴ and can indicate when the crystalline character of the active material disappears and reappears during cell operation. XRD has also been reported to reveal sulfur metastability within certain carbon³⁵ and copolymeric frameworks³⁶ – information that can reflect key details about the morphology of the confining framework. Thus, whilst XRD may not provide the capability to directly characterise the major amorphous/nanocrystalline structural components, indirect insight can still be obtained through characterisation of the crystalline components.

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Chapter 3: Waste tyre-derived carbon frameworks

3.1 Introduction

This chapter presents the published results of waste tyre-derived carbon frameworks and their application as electrode materials in Li-S cells.¹ Note this has been modified from the publication, specifically sections detailing work on Na-ion cells have been removed.

3.1.1 Repurposing waste rubber tyres

It is estimated that 1.5 billion rubber tyres are produced annually.² As waste products, they are not biodegradable and pose flammable risks when stored in landfill. Efforts to prolong the lifetime of these tyres as useful materials are therefore attractive from a cost perspective (due to the availability of the resource) as well as an environmental perspective.

Conductive carbon black (a major product in tyre recycling) can be reliably extracted through pyrolysis. From a structural perspective, most tyre formulations already incorporate ~10-100 nm spherical particles of carbon black to enhance mechanical properties.^{3, 4} It is important to note however that particularly at high pressures, pyrolysis results in the formation of carbonaceous deposits on the surface of carbon black particles that have a smoothing effect, ultimately mitigating surface activity.⁵ It is thus essential to tailor the pyrolysis conditions, (i.e., lower pressures and lower temperatures) such that these desirable mechanical properties are maintained as much as possible or to produce uniform and functional surface deposits depending on the application.

3.1.2 Applications in other energy storage systems

Previous works have explored the use of functionalised carbons derived from waste rubber tyres in various energy storage systems.^{4, 6, 7} It is clear from these works however that different preparatory conditions give rise to different properties. For instance, Naskar *et al.* reported that by digesting the rubber tyres in a hot oleum bath before pyrolysis at 1000 °C results in carbon residues that are suitable for Li-ion

batteries.^{4, 6} They further report that without this pre-sulfonation process, pyrolysis results in “low bulk density” carbon black, reminiscent of disordered hard carbons similarly observed by Li *et al.*⁷ Li *et al.* reports that pyrolysis of acid-treated rubber tyres at 1100 °C, 1400 °C and 1600 °C give rise to specific capacities of 179, 185 and 203 mAh g⁻¹ respectively when implemented in Na half-cells. Although no work has been undertaken on using waste tyre in Li-S systems, the presence of S and S-containing species in tyres could be beneficial for function.

This work explores the effects of pyrolysis at relatively low temperatures (700 and 900 °C) at short heating times, and a simple physical activation using CO₂ on four main aspects of the resulting tyre crumbs: (1) the morphology of the main carbon network through Brunauer-Emmett-Teller (BET) surface area analysis and Raman spectroscopy supported by X-ray powder diffraction (XRD); (2) the impurities present in the overall tyre crumb material afforded by XRD coupled with inductively coupled plasma optical emission spectrometry (ICP-OES), (3) how these differences may translate in terms of electrochemical performance inside a Li-S cell through assessment of the cell performance *via* galvanostatic testing and (4) how these differences may translate in a Na half-cell system which relies on inherently different redox reactions. *Ex situ* analysis of selected electrochemically treated electrodes is also conducted in order to assess the stability and solid electrolyte interface formation upon Li-S cell cycling using this class of materials.

3.2 Methodology

Waste rubber tyre shreds were prepared as outlined by the steps detailed in a previous publication.⁸ The chemical composition of the rubber tyre precursor was determined *via* X-ray fluorescence spectroscopy (XRF) and is outlined in **Table 3.1**.

The rubber shreds were pyrolysed at 700 °C under N₂ flow for 15 min in a horizontal tube furnace, resulting in black powder (RT700). The RT700 precursor subsequently underwent physical activation for 3h in a CO₂ atmosphere also at 700 °C to produce RTA700. Separately, RT900 was prepared by pyrolysis at 900 °C for 15 min without N₂ flow. This RT900 was used as a precursor for physical activation for 3h under CO₂ flow also at 900 °C yielding RTA900. In order to compare different thermal treatments of the tyre crumb samples under inert atmosphere, xRT900 was additionally prepared by pyrolysing the rubber shreds at 900 °C under N₂ flow. All

pyrolysis conditions resulted in a mean 36 wt.% yield of the tyre precursor. Details regarding these sample preparation conditions are outlined in Table 3.2.

Brunauer-Emmett-Teller (BET) surface area analysis (Micrometrics TriStar 3000 analyser) was used to obtain the specific surface area (S_{BET}), pore-size distribution, and total pore volume (V_{T}) of the samples via N_2 adsorption/desorption measurements. The mesopore surface area, pore volume and pore size were calculated using the Barrette-Joyner-Halenda (BJH) method. Raman spectra of the carbon samples were collected using a Renishaw inVia Raman Microscope equipped with an argon-ion laser set at 532 nm and were recorded over the range of 2000–700 cm^{-1} . XRD analysis was carried out using PANalytical X'pert Multipurpose X-ray diffraction system, in Bragg-Brentano geometry with $\text{Cu K}\alpha_1$ radiation (1.5418 Å). The XRD data of the raw materials were measured between $20^\circ < 2\theta < 120^\circ$. Inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 7300DV) was utilised to analyse the elemental composition to aid in selecting suitable phases to model with the XRD data for subsequent Rietveld analysis. Rietveld analysis of various phases deduced from the ICP-OES measurements to the collected XRD data was applied to identify and confirm the presence of these phases within the samples, and their relative phase fractions. Scanning electron microscopy (SEM) measurements were performed using a Hitachi TM4000Plus benchtop SEM (15 kV accelerating voltage).

For electrochemical tests, Li-S cell electrodes were constructed with a 37.5:37.5:20:5 ratio of elemental sulfur, tyre crumb active material, carbon black (Super C65, TimCal) and polyvinylidene difluoride (PVDF, MTI Corporation) binder which was stirred in N-methyl-2-pyrrolidone (NMP, MTI Corporation) solvent for 12 hours. It is important to note that carbon black (as well as elemental sulfur in the case of Li-S cells) are also expected to contribute to the cell's specific capacity. The ratios selected for this work aimed to maximise the loading of the tyre crumb, however it was also important that the resulting electrodes were still structurally sound to cast and functioned reliably upon electrochemical testing. This means that theoretically the scope of the tyre crumb used relates to 37.5% of the overall electrode mass.

The slurry was doctor-blade cast onto an aluminium foil current collector at 200 μm and dried at 373 K under vacuum for 1 hour. The electrode sheets were then pressed at 100 kN using a flat plate press (MTI Corporation) to ensure good contact

between the electrode and the Al foil substrate and dried for another 12 hours at 100 °C under vacuum to remove any remaining moisture before transferring into an Ar-filled glovebox for cell assembly. The resulting electrodes were assembled into CR2032 coin cells with a glass-fibre separator soaked in electrolyte and a Li metal counter electrode. The electrolyte used was a mixture of 0.38 M lithium bis(trifluoromethane)sulfonimide (LiTFSI), and 0.32 M lithium nitrate (LiNO₃) dissolved in a 1:1 v/v mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxy ethane (DME). For the electrochemical tests the fabricated coin cells were galvanostatically discharged and charged between 1.7-2.6 V at 167.2 mA g⁻¹ (C/10) using a cell cycler system (Neware BTS3000).

For *ex situ* characterisation of the electrochemically treated samples, the waste-rubber tyre electrodes were extracted after electrochemical Li insertion (i.e., after the first discharge step to 1.7 V) and after electrochemical Li extraction (i.e., after the first charge step to 2.6 V) inside an Ar-filled glovebox, washed with dimethyl carbonate (DMC, Sigma-Aldrich) and thoroughly dried for at least 12 h. For *ex situ* XRD analysis the dried electrodes were mounted on a P-type B-doped Si-crystal zero-background sample holder.

Ex situ X-ray Absorption Near-Edge Structure (XANES) spectroscopy measurements of electrochemically treated Li-S tyre crumb electrodes were conducted at the SXR beamline at the Australian Synchrotron as outlined in previous work.^{9, 10} Spectra were collected for the C K- (i.e. C 1s, 280–340 eV) and S K-edges (i.e. S 1s, 2460–2540 eV) using partial electron yield (PEY), total electron yield (TEY) and total fluorescence yield (TFY) modes. Particularly for the C K-edge, a clean Si photodiode was scanned as a reference to eliminate effects of carbon contamination from within the beamline and this reference was used to normalise the C K-edge spectra following the method outlined by Watts *et al.*¹¹ The C K-edge spectra were calibrated to the exciton resonance of an internal HOPG standard known to be positioned at 291.65(26) eV. S K-edge spectra were calibrated to the first resonance of a MoS₂ internal standard set at 2471.2 eV. Processing of the C K- and S K-edge XANES data was conducted using the Quick AS NEXAFS Tool (QANT) macro developed for Igor Pro.¹²

Table 3.1 – a) Ultimate and b) chemical analysis of the tyre crumb as determined by XRF analysis. Ashing was conducted at 650 °C.

a) Ultimate analysis of the tyre crumb								
	Ash	C	N	S				
wt%	5.79	82.68	0.34	1.56				
b) Chemical analysis of ash in tyre crumb								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	SO ₃	ZnO
wt%	28.7	2.31	2.62	1.18	3.08	8.08	6.99	11.89

Table 3.2 – The samples analysed in this work (RT700, RTA700, RT900, RTA900 and xRT900) and their respective treatment conditions

Sample	Pyrolysis temperature (°C)	Physical activation under CO₂ for 3h	Atmosphere
RT700	700	N	N ₂
RTA700	700	Y	N ₂ followed by CO ₂
RT900	900	N	Air
RTA900	900	Y	Air followed by CO ₂
xRT900	900	N	N ₂

3.3 Results and Discussion

3.3.1 Surface area, the porous network, structure and carbon disorder of the as prepared tyre crumbs

In order to identify differences in surface area and pore size/volume, BET measurements were conducted on the as-prepared tyre crumbs. Information on the porous network of each sample can provide an insight as to which treatment pathways lead to the most effective carbon materials for implementation inside Li-S cells. The adsorption isotherms and pore size distributions of the samples are shown in **Figure 3.1**, and the surface area, pore volume and pore size obtained from these measurements have been compiled in **Table 3.3**.

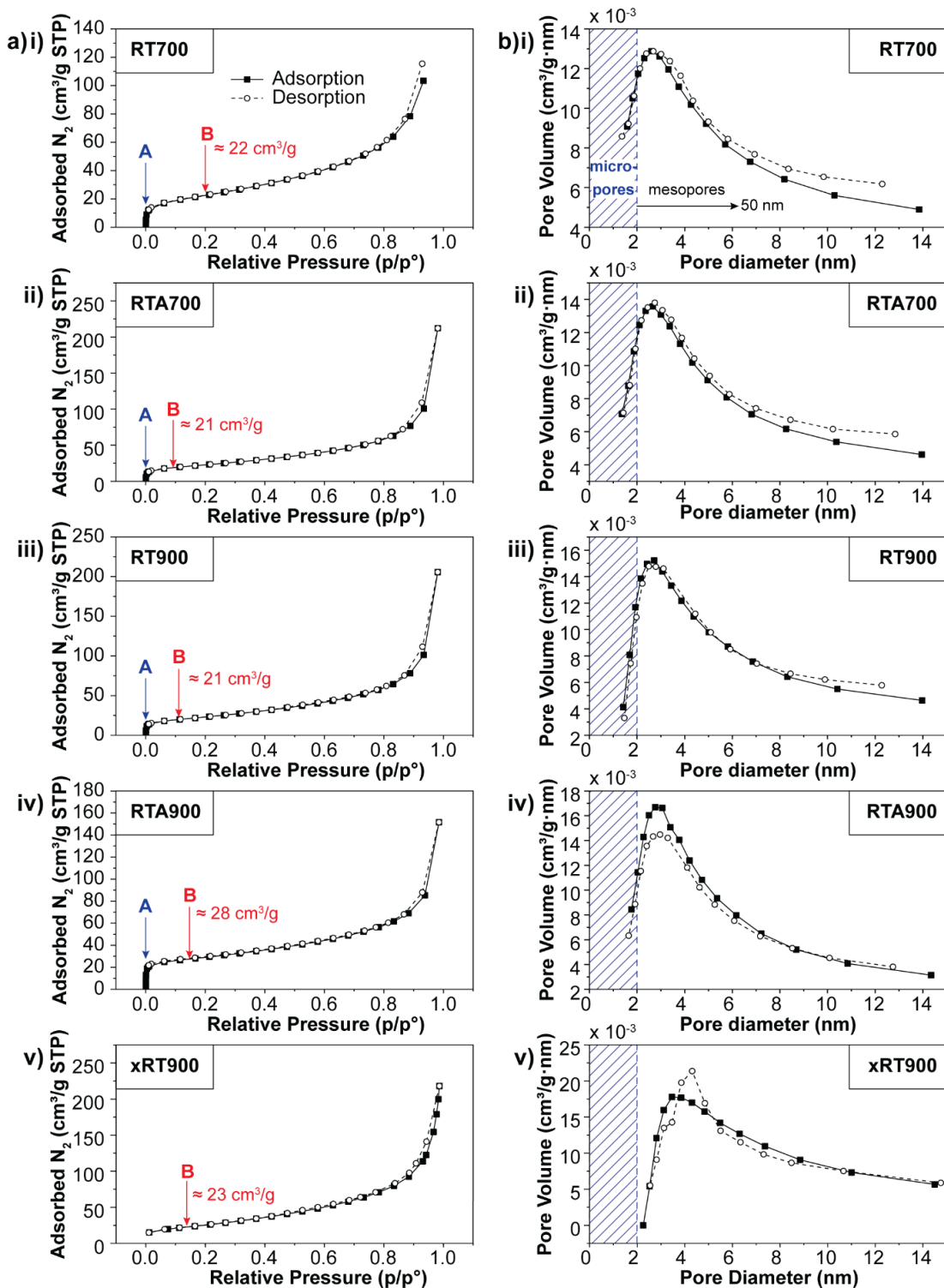


Figure 3.1 – The adsorption isotherms and pore size distributions of RT700, RTA700, RT900, RTA900, and xRT900 determined *via* BET analysis. Adsorption and desorption are denoted by filled and unfilled datapoints respectively. Features annotated by A and B are discussed in text – A points denoting sharp knees typically associated with micropore adsorption, and B points denoting points of inflection characteristic of Type II isotherms, specifically the end of monolayer coverage and beginning of multilayer adsorption.

Table 3.3 – Surface area, pore volume, pore size, calculated pore dimensions, pores per gram and I_D/I_G ratios of RT700, RTA700, RT900 (synthesised under air), and RTA900 determined *via* BET and Raman spectroscopy analysis. The adsorption isotherms and pore size distributions are shown in **Figure 3.1**. Calculated pore dimensions are based on a cylindrical anisotropic pore model.

Sample	S_{BET} (m^2/g)	Pore volume V_T (cm^3/g)	Pore size (nm)	Calculated pore depth (nm)	Calculated volume per pore (nm^3)	Calculated average no. of pores per gram ($\times 10^{17}$)	I_D/I_G
RT 700	81.86	0.118	4.95	7.43	143	7.7(6)	1.06(1)
RTA 700	82.17	0.116	4.99	7.49	146	7.5(5)	1.011(8)
RT 900 (air)	82.80	0.124	4.63	6.95	117	9(1)	1.026(8)
RTA 900 (air)	101.07	0.115	3.97	5.96	73.7	15(1)	1.14(2)
xRT900	94.75	0.361	12.56	18.8	2334	1.4(1)	0.59(1)

Based on the produced trendlines exhibited by the adsorption isotherms shown in **Figure 3.1**, all the prepared tyre crumbs (**Figure 3.1ai-v**) are Type II isotherms that are typically characterised by a point of inflection (point B in **Figure 3.1a**) generally associated with the end of monolayer coverage and beginning of multilayer adsorption.^{13, 14} In terms of pore size, as outlined in **Table 3.3**, all the pyrolysed tyre samples appear to be predominantly mesoporous (i.e., 2-50 nm). Whilst mostly mesoporous, the pore size distribution in **Figure 3.1bi-iv** indicates that a small portion of the measured pore volumes of RT700, RTA700, RT900 and RTA900 are associated with microporous adsorbents (i.e., <2 nm). This is also further suggested by the sharp knee or steep adsorption at low relative pressures observed in the isotherms measured for RT700, RTA700, RT900 and RTA900 (point A in **Figure 3.1ai-iv** respectively).¹⁴ All but the isotherm of xRT900 (shown in **Figure 3.1av**) exhibit this feature, implying that xRT900 does not contain an observable amount of micropores.

As outlined in **Table 3.3**, apart from xRT900, the differences in pore surface area, size and volume upon appear marginal at first glance. In order to better visualise the pore dimensions, modelling of the pore network is required. Upon visual inspection, all samples appear to demonstrate similar hysteresis loop shapes. Whilst the isotherms shown in **Figure 3.1a** most closely resemble type C or D De Boer hysteresis loops related to open-ended wedge shaped pores, modelling such shapes accurately would require more rigorous characterisation of the pore network.^{15, 16} This work models the pore dimensions using simpler cylindrical pore shapes as visualised in **Figure 3.3a**, wherein the upper limits are obtained from calculations based on the total pore volume and the lower limits based on the total pore surface area. Between RT700 and the activated derivative RTA700, as shown in **Figure 3.3a**, there are marginal differences in the number of pores ($7.7(6)$ and $7.5(5) \times 10^{17}$ pores g⁻¹ respectively) and pore dimensions (143 and 146 nm³ per pore respectively), implying physical activation of samples pyrolysed at 700 °C yields minimal difference to the pore network morphology. Upon heating to 900 °C to yield xRT900, indeed xRT900 contains the largest pore dimensions (2334 nm³ per pore) but also the least number of pores ($1.4(1) \times 10^{17}$ pores g⁻¹) compared to the other samples, at least $5.5\times$ less pores than RT700 and RTA700.

Pyrolysis in the presence of air and moisture however appears to suppress the formation of such large pores. As outlined in **Table 3.3** and visualised in **Figure 3.3a**,

RT900 appears to contain more pores per gram ($9(1) \times 10^{17}$ pores g^{-1}) with slightly smaller pore dimensions (117 nm^3 per pore) compared to both RT700 and RTA700. Upon activation, RTA900 follows a similar trend with even more pores per gram ($15(1) \times 10^{18}$ pores g^{-1}) and even smaller pore dimensions (73.7 nm^3 per pore). In contrast to xRT900, pyrolysis at the same high temperatures but in the presence of air and moisture appears to produce smaller and more abundant pores.

In order to determine whether the different treatments would affect the composition and extent of disorder of the carbons, Raman spectroscopy was conducted on the as-prepared tyre crumbs. The spectra are characterised by two prominent peaks at ~ 1340 and $\sim 1590 \text{ cm}^{-1}$ corresponding to the D or disorder-induced band and the G or graphitic band in the carbon. The I_D/I_G ratio calculated based on the ratio of peak intensities can thus be directly correlated to the extent of disorder of the carbon content present within the waste tyre crumbs. The peak intensity values were deconvoluted by fitting Gaussian line shapes to the D and G bands as shown in **Figure 3.2**. Unlike the BET measurements, differences in the extent of disorder of the carbon contents within the tyre crumbs are more apparent. As outlined in **Table 3.3** and visualised in **Figure 3.3b**, all tyre crumb samples apart from xRT900 exhibit $I_D/I_G > 1$ implying slightly more disordered carbon properties compared to graphitic. However, the ratios being close to 1 suggests that the carbon contents are not dominated by one type of environment, either graphitic or disordered but rather feature an even distribution of both.

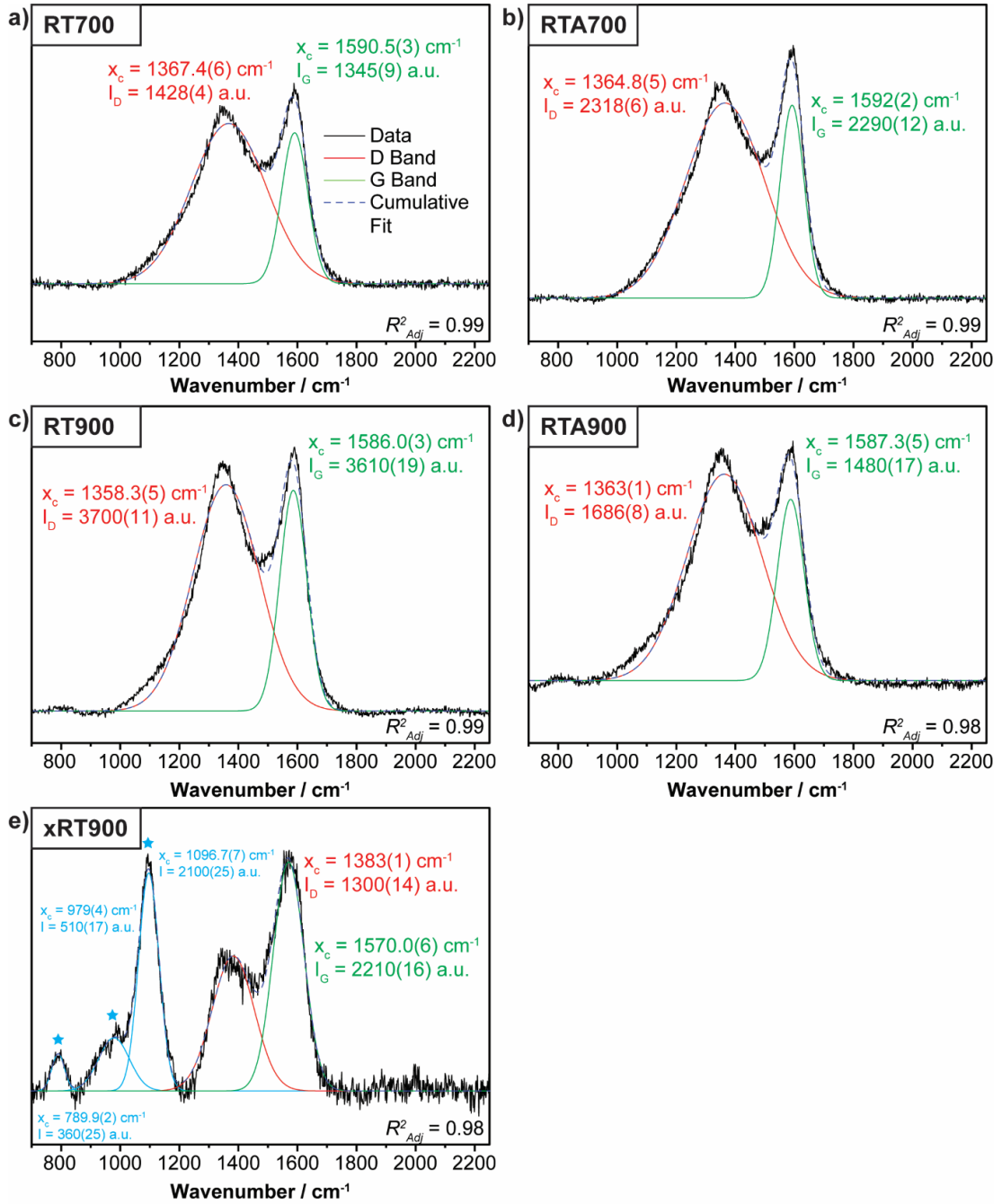


Figure 3.2 – Peak fitting of Gaussian lineshapes onto Raman data of **a)** RT700, **b)** RTA700, **c)** RT900, **d)** RTA900, and **e)** xRT900 for determination of I_D/I_G ratios.

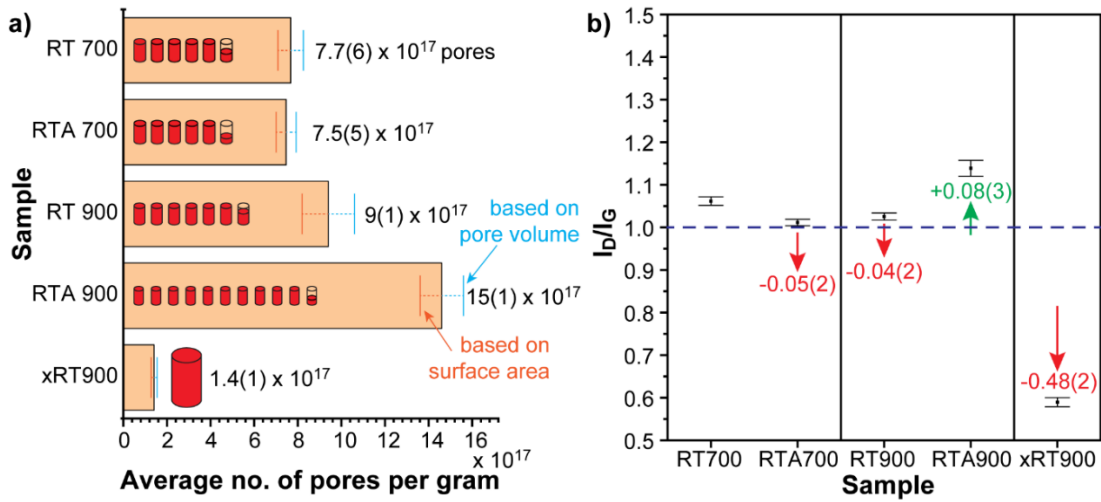


Figure 3.3 a) Average number of pores per gram of the measured samples based on BET results outlined in **Table 3.3** based on a cylindrical pore model. The red coloured cylinders represent the ratio of pores relative to each other in their respective pore dimensions. The blue upper limits are values obtained based on total pore volume and the orange lower limits are based on the total pore surface area. **b)** I_D/I_G values of tyre crumb samples calculated from intensity values that have been deconvoluted from Gaussian peak fits of the D and G bands from measured Raman spectra of the tyre crumbs. The dashed blue line marks $I_D/I_G=1$.

Considering N_2 environments, the tyre crumb heated at the lower temperature of 700 °C RT700 exhibits $I_D/I_G = 1.06(1)$. Comparatively, its physically activated analogue RTA700 exhibits $I_D/I_G = 1.011(8)$ ($\delta = -0.05(2)$ compared to RT700)), implying a small increase in graphitic character. This evolution towards a more graphitic carbon morphology could be due to prolonged heating at 700°C rather than from the effects of physical activation itself. The xRT900 shows the largest difference between the samples with $I_D/I_G = 0.59(1)$, or more graphitic in character, and is $\delta = -0.48(2)$ compared to RT700. Comparatively the observed I_D/I_G ratios for RT700, RTA700 and xRT900 seem to follow the general trend of increasing ordered graphitic character upon increased thermal treatment (i.e., prolonged heating or increased temperatures).

With exposure to air and moisture however as demonstrated by a comparison between RT700, RT900 and RTA900, the carbon morphology is observed to evolve in a less straightforward manner compared to under inert N_2 with thermal treatment. Thermal treatment to 900 °C in the presence of air and moisture (RT900) yields a slightly lower I_D/I_G ratio ($I_D/I_G = 1.026(8)$) compared to thermal treatment to 700 °C under N_2 ($\delta = -0.04(2)$ compared to RT700). Notably this ratio achieved by RT900 is much higher than for xRT900 ($I_D/I_G = 0.59(1)$) even though the tyre crumb is exposed

to the same high temperatures. Upon physical activation of RT900 to yield RTA900 also heated in the presence of air and moisture, I_D/I_G is observed to increase ($I_D/I_G = 1.14(2)$, $\delta = +0.08(3)$ compared to RT700). Note that these changes observed upon thermal treatment in the presence of air and moisture (compared to RT700) are both significantly smaller ($< 1/5^{\text{th}}$ in magnitude) compared to the I_D/I_G change observed for xRT900, and the ratios are still relatively close to $I_D/I_G = 1$.

Through XRD measurements, further insight on the tyre crumb crystalline composition can be determined. As seen in **Figure 3.4a**, the tyre crumbs contain numerous crystalline phases. Apart from these phases however, all the powder XRD patterns show relatively broad reflections at $2\theta \sim 24.7$ and 43° attributed to the (002) and (100) graphitic carbon reflections respectively, characteristic of disordered hard carbons.

The broad (002) graphitic carbon reflection was modelled using a Gaussian line shape as indicated by the red traces in the close-up **Figure 3.4a**. The (002) graphitic carbon reflection corresponds to the parallel stacking of graphite layers, whereas the (100) graphitic carbon reflection relates to the honeycomb structures of sp^2 hybridised carbon.^{17, 18} Whilst both the (002) and (100) graphitic carbon reflections can be qualitatively resolved from the diffraction patterns, due to the relatively low intensity of the (100) reflection, only the higher intensity (002) reflection is analysed by Gaussian peak-fitting. Gaussian peak-fitting of the (002) reflection provides information on both the interlayer d -spacing between the graphitic planes (d_{002}) correlated to the 2θ position of the reflection using Bragg's Law and the crystallite heights (L_c) or particle size distribution from the full width at half maximum (FWHM) using the Scherrer equation, with the results shown in **Table 3.4** and visualised in **Figure 3.4b** and **c** respectively. Across all the samples the differences appear to be marginal at first. However, in a similar fashion to the findings based on BET and Raman spectroscopy, subtle differences can be resolved.

The results of the Gaussian peak fits suggest that the variation in L_c is more significant than d_{002} across the samples. As visualised in **Figure 3.4b**, d_{002} of the tyre crumbs do not vary more than $0.130(9)$ Å from each other. The variation in L_c appears more significant (as shown in **Figure 3.4c**), the difference between the highest and lowest values being $2.0(1)$ Å. Further across all the samples, approximately two graphene layers can fit within the limits of the L_c parameter extracted from the

Gaussian fits, further confirming that the carbon associated with this feature are disordered hard carbons. Closer inspection of the d_{002} values show that the differences between the samples are real however, albeit small, and lie outside margins of error as visualised in the inset **Figure 3.4b**. This implies that even though the differences in L_c might appear larger and more significant, both L_c and d_{002} of the pyrolysed rubber tyres are observably impacted by different preparatory conditions.

As visualised in **Figure 3.4b** and **c**, between RT700 and RTA700, physical activation presents minimal, if any differences to the interlayer d -spacing ($d_{002} = 3.640(4), 3.633(4)$ Å respectively) or particle size distribution ($L_c = 8.71(8), 8.71(9)$ Å respectively) of the carbon environment. The direct effects of thermal treatment from 700-900 °C is evident through a comparison between RT700 and xRT900, wherein the tyre crumb is heated to 900 °C under N₂ flow (unlike the case of RT900). In xRT900, a larger particle size distribution (**Figure 3.4c** $L_c = 9.31(3)$, $\delta = +0.6(1)$ Å vs RT700) is observed compared to RT700. Additionally, the d_{002} is also slightly larger for xRT900 compared to that of RT700 and RTA700 ($\delta = +0.013(5)$ Å). Compared to air-treated samples however, this increase in d_{002} observed for xRT900 is only 21% and 11% the increase experienced by RT900 and RTA900 respectively (**Figure 3.4b** $d_{002} = 3.703(4)$, $\delta = +0.062(8)$ Å vs RT700 and $d_{002} = 3.763(5)$, $\delta = +0.12(1)$ Å vs RT700 respectively). This minimal change in d_{002} and large change in L_c achieved by xRT900 compared to air treated samples imply that increased heating alone from 700 to 900 °C (without evolution of impurities from air and moisture) can significantly impact particle size distribution without much effect on the interlayer d -spacing of graphene layers.

Whilst increased temperatures of pyrolysis appears to increase L_c as demonstrated by RT700 (and RTA700) vs xRT900, contrastingly an opposite decreasing trend in L_c is experienced by the air treated samples RT900 and RTA900. As visualised in **Figure 3.4c**, for RT900 $L_c = 7.99(8)$ Å which is 0.7(2) Å smaller than that observed for RT700. Upon activation to yield RTA900, this decrease appears to double in magnitude ($\delta = -1.4(2)$ Å vs RT700), with $L_c = 7.32(8)$ Å. Observing larger changes in the 002 peak profile between RT900 and RTA900 and not between RT700 and RTA700 suggests that these changes are mostly related to impurities that are introduced due to thermal treatment under air.

Characterisation of the crystalline phase impurities detected by XRD was performed *via* Rietveld refinement of major identifiable phases. In order to facilitate Rietveld fits of the crystalline impurity phases with the XRD data, contributions from the broad 002 graphitic reflection (as well as 100 for RT900) were modelled using a pseudo-Voigt function as part of the background that is mainly modelled using a Chebyshev polynomial (gold traces in **Figure 3.4a**). Note that the pseudo-Voigt functions were only used to minimise the large intensity contributions associated with the background such that the crystalline reflections can be modelled accurately. Namely for XRD patterns of RT700, RTA700 and xRT900 (shown in **Figure 3.4ai, ii, and v** respectively), refinement of a graphitic phase in the model is also necessary to limit the weighted residuals to <10% and may suggest the presence of large graphitic domains in the sample. In **Figure 3.4a**, these graphitic reflections are inferred to be at 2θ positions marked by teal stars. Of all the samples, a graphitic phase could be stably modelled *via* Rietveld refinement only for xRT900, RTA700 and RT700. The weight percentages of the graphite phase extracted from the refinements are 59.3(3), 17(1), and 10.4(5) % respectively, however due to the broadness of the 100 and 101 reflections ($40^\circ < 2\theta < 50^\circ$) and therefore inability to refine the lattice parameters for one graphite phase, these may not be representative of the true amount of graphitic carbon in the samples. This relative broadness of the 100 and 101 reflections could imply anisotropic character and smaller particle size distribution along these axes.

Graphitic features are not observed through XRD for RTA900 (shown in **Figure 3.4aiv**), however this could be due to the greater abundance and therefore relatively higher intensities of the other major identifiable impurity phases relative to the graphite present in the sample. Furthermore, for RT900 (shown in **Figure 3.4aiii**), due to the significant peak overlap with other identifiable phases, a graphitic phase could not be modelled against the data. The RT900 pattern appears to exhibit features similar to those seen in RT700, RTA700 and xRT900 that are associated with graphite however, and these positions are marked by empty stars annotated on **Figure 3.4aiii**.

3.3.2 Identification and quantification of impurities present in the as prepared tyre crumbs

In order to gain a full insight on how the properties of the tyre crumbs may affect the electrochemistry, an understanding of the impurities present apart from the main carbon content must be achieved. Through phase matching analysis based on ICP-OES

results of the pristine rubber tyre as well as the treated tyre crumbs, it can be deduced that the most prominent impurities (in addition to the previously mentioned graphitic phase) identifiable by XRD are: (1) CaCO_3 ($R\bar{3}c$), (2) ZnO ($P6_3mc$), (3) cubic ZnS ($F\bar{4}3m$), (4) hexagonal ZnS ($P6_3mc$), and (5) Ca(OH)_2 ($P\bar{3}m1$). ZnS exhibits either cubic or hexagonal symmetry. CaCO_3 is widely used in tyre manufacturing and the rubber/polymer industry as a particulate filler.^{19, 20} ZnO is used as an activator during sulfur vulcanization in tyres. A by-product from this are the ZnS phases due to the reaction between ZnO and sulfur.^{8, 19, 20} At higher temperatures and in the presence of moisture, CaCO_3 can also yield Ca(OH)_2 (via reaction of $\text{CaCO}_{3(s)} + \Delta H \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ followed by $\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Ca(OH)}_{2(s)} + \Delta H$). Several other components such as SiO_2 , Fe_2O_3 , Al_2O_3 , MgO , Na_2O , and SO_3 can be inferred in the pristine rubber tyre sample through ICP-OES analysis, however, are not resolved in the XRD patterns of the tyre crumbs. In addition to the previously discussed graphite phase, five major identifiable phases were modelled via Rietveld refinement of structural models with the data, and their weight percentages are compiled in **Table 3.5** and visualised in **Figure 3.4d**. Note these are semi-quantitative assessments (without the use of standards), however they do provide indicative assessments of the impurity phases present and their relative ratios.

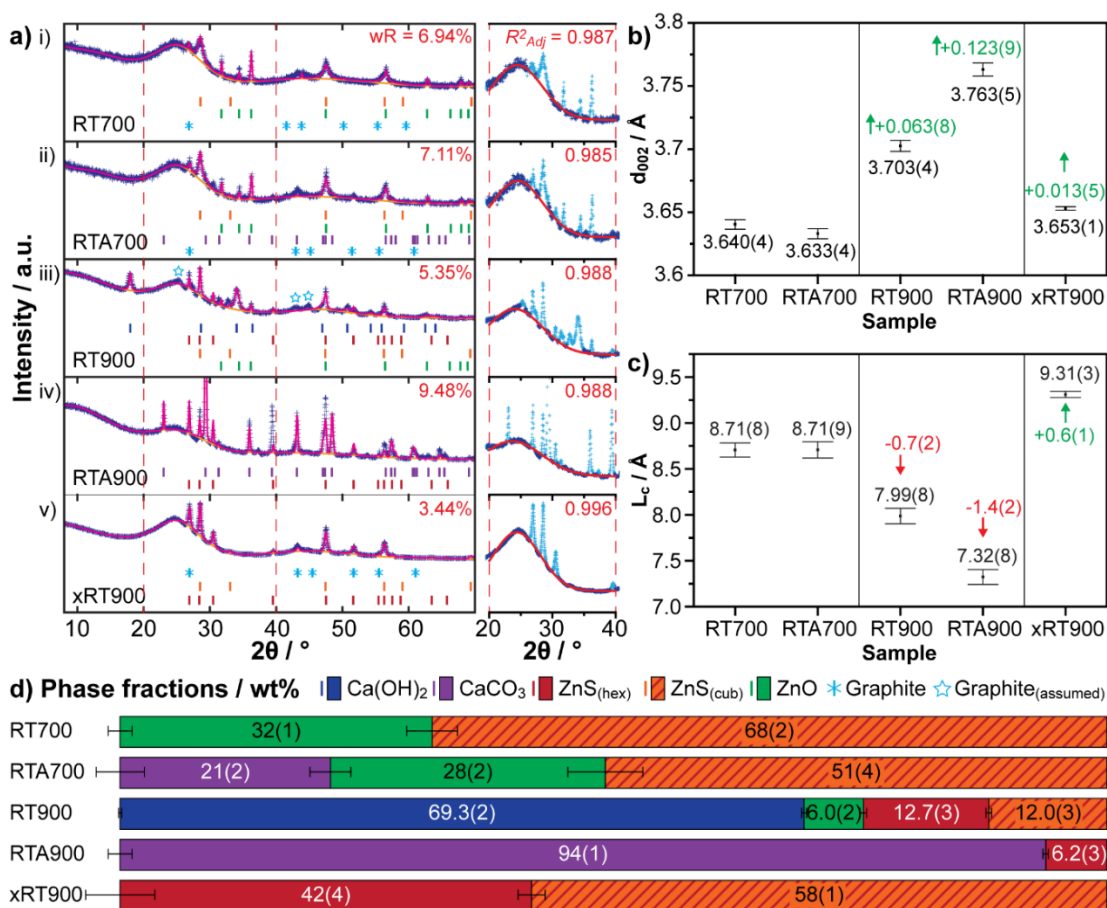


Figure 3.4 –a) X-ray powder diffraction data of **i)** RT700, **ii)** RTA700, **iii)** RT900, **iv)** RTA900 and **v)** xRT900 (blue crosses) plotted against models calculated from Rietveld refinement (model represented by a pink trace, and background by a gold trace). A close-up of the broad 002 graphitic reflection modelled separately by Gaussians (red trace) between the dashed lines (i.e. $20^\circ < 2\theta < 40^\circ$) is provided for each of the measured samples adjacent to the refinements. The light blue crosses are datapoints that had been omitted from the calculations for the Gaussian models. Note the teal stars in **iii)** indicate only assumed 2θ positions of graphitic reflections, not refined positions of a graphitic model. **b)** Interlayer d -spacing (d_{002}) and **c)** crystallite height (L_c) values extracted from the Gaussian models of the graphitic 002 reflection. Details regarding the Gaussian fit parameters and corresponding d_{002} and L_c values are also compiled in **Table 3.4**. **d)** Phase fractions (wt%) of the major identifiable impurity phases (excluding graphite) from Rietveld refinement, also compiled in **Table 3.5**.

Table 3.4 – 2θ positions, calculated d_{002} , FWHM, and calculated L_c of the (002) Bragg peak observed in background functions of RT700, RTA700, RT900, RTA900, and xRT900 extracted from Rietveld refinements. Standard errors are calculated based solely on the fit of the gaussian peak to the (002) reflection

Sample	$2\theta / ^\circ$	FWHM / $^\circ$	$d_{002} / \text{\AA}$	$L_c / \text{\AA}$
RT700	24.43(3)	9.44(7)	3.640(4)	8.71(8)
RTA700	24.48(3)	9.44(9)	3.633(4)	8.71(9)
RT900	24.02(3)	10.3(1)	3.703(4)	7.99(8)
RTA900	23.62(3)	11.2(1)	3.763(5)	7.32(8)
xRT900	24.346(9)	8.83(3)	3.653(1)	9.31(3)

Table 3.5 – Phase fractions extracted from Rietveld analysis shown in Figure 3.4 of the selected phases with XRD data of the treated tyre crumb samples.

Sample	Weight fractions / %				
	ZnO	ZnS _(cub)	ZnS _(hex)	CaCO ₃	Ca(OH) ₂
RT700	32(1)	68(2)	N/A	N/A	N/A
RTA700	28(2)	51(4)	N/A	21(2)	N/A
RT900	6.0(2)	12.0(3)	12.7(3)	N/A	69.3(2)
RTA900	N/A	N/A	6.2(3)	94(1)	N/A
xRT900	N/A	58(1)	42(4)	N/A	N/A

Table 3.6 – Crystallite sizes of the inorganic phase impurities present in the pyrolysed tyre samples determined by the Scherrer equation using FWHM values of reflections centred $20^\circ < 2\theta < 70^\circ$ estimated *via* the Rietveld method. The models used to determine the crystallite size values correspond to the same Rietveld models, visualised in **Figure 3.4**, used to determine the weight fractions of the impurities.

Crystallite size based on reflections centred $20^\circ < 2\theta < 70^\circ / \text{nm}$					
Sample	ZnO	ZnS _(cub)	ZnS _(hex)	CaCO ₃	Ca(OH) ₂
RT700	40(7)	8(2)			
RTA700	31(4)	14(2)		13(2)	
RT900	32(6)	27(6)	31(6)		12(4)

RTA900		32(9)	31(9)
xRT900	21(5)	19(4)	

Relating to the weight percentages (as shown in **Figure 3.4d**), for RT700 the dominant impurity phase appears to be cubic ZnS (wt% = 68(2)%) followed by ZnO (32(1)%). Upon physical activation of RT700 to yield RTA700, an additional CaCO₃ phase is detected (21(2)%), but the majority of the impurities detected still appear to be cubic ZnS (50(4)%) followed by ZnO (28(2)%). In the case of xRT900 (prepared under N₂ flow) ZnO is no longer observed. The remaining impurities are observed to be cubic ZnS (58(1)%), and a new hexagonal ZnS phase is also observed (42(4)%). Complete transformation of cubic to hexagonal ZnS typically requires heating at temperatures above 1020 °C.²¹ However there have been previous reports that show with optimal conditions, partial transformation is possible at lower temperatures.²¹⁻²³ The xRT900 simplifies the number of chemical components present in the sample, limiting it to ZnS and carbon as the major constituents.

The weight fractions observed for RT900 (tyre crumb pyrolysed at 900 °C under air) are completely different to that observed for xRT900 (pyrolysed under N₂). Most notably, the largest weight fraction observed for RT900 is associated with Ca(OH)₂ (69.3(2)%). From elemental analysis of the tyre crumb from previous work, CaO is known to be an available precursor which can form Ca(OH)₂ in the presence of moisture.⁸ Following this, hexagonal ZnS (12.7(3)%) and cubic ZnS (12.02(3)%) are also observed similar to xRT900. Unlike xRT900, some ZnO (6.0(2)%) is observed in RT900, however as a smaller fraction compared to RT700 and RTA700.

Upon physical activation of RT900 yielding RTA900 (pyrolysed under air) further changes are observed. ZnO is no longer observed, most of the impurities detected are attributed to CaCO₃ (94(1)%), and a minority to hexagonal ZnS (6.2(3)%). It is important to emphasise here that the precursor RT900 is prepared under air, rich in Ca(OH)₂. Upon additional heating and exposure to CO₂ gas used for physical activation, this excess Ca(OH)₂ readily converts to CaCO₃ *via* the following reaction pathway: $\text{Ca(OH)}_{2(s)} + \text{CO}_{2(g)} + \Delta H \rightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O}_{(l)}$. This evolution in the calcium-based components within the tyre crumb especially considering the relatively large portions of crystalline CaCO₃ observed for RTA900 could account for the significant

hysteresis of adsorption and desorption branches related to the pore size distribution previously discussed in the BET analysis (see **Figure 3.1**).

Based on assessment of the major identifiable phases determined from the Rietveld analysis, some general trends have been observed. One is that the presence of air and moisture as observed in RT900 appears to favourably produce $\text{Ca}(\text{OH})_2$. Another trend is that physical activation appears to generate $\text{Ca}(\text{CO}_3)_2$ based on its notable presence in both RTA700 and RTA900. It can also be said generally that an increase in pyrolysis temperature from 700-900 °C seems to eliminate ZnO and promote the formation of ZnS.

Notably in the case of xRT900, only ZnS is observed as an impurity through XRD (albeit as two different phases – cubic and hexagonal as visualised in **Figure 3.4d**). All the other samples contain at least two chemically different impurities. Based on the BET and Raman analysis (**Table 3.1**) indeed it is xRT900 that experiences the largest differences in carbon morphology compared to RT700 and between the other samples. Only observing one type of impurity (ZnS) in xRT900 and not the other samples generally suggests that the presence of impurities impacts the carbon morphology. Between the other samples RT700, RTA700 and air exposed RT900 and RTA900, more subtle differences in terms of the impurities are observed. The presence of four major identifiable phases in RT900 and high weight percentage of CaCO_3 (94(1)%) in the activated analogue RTA900 emphasises the impact of air and moisture on the evolution of the impurity (or additional) phases.

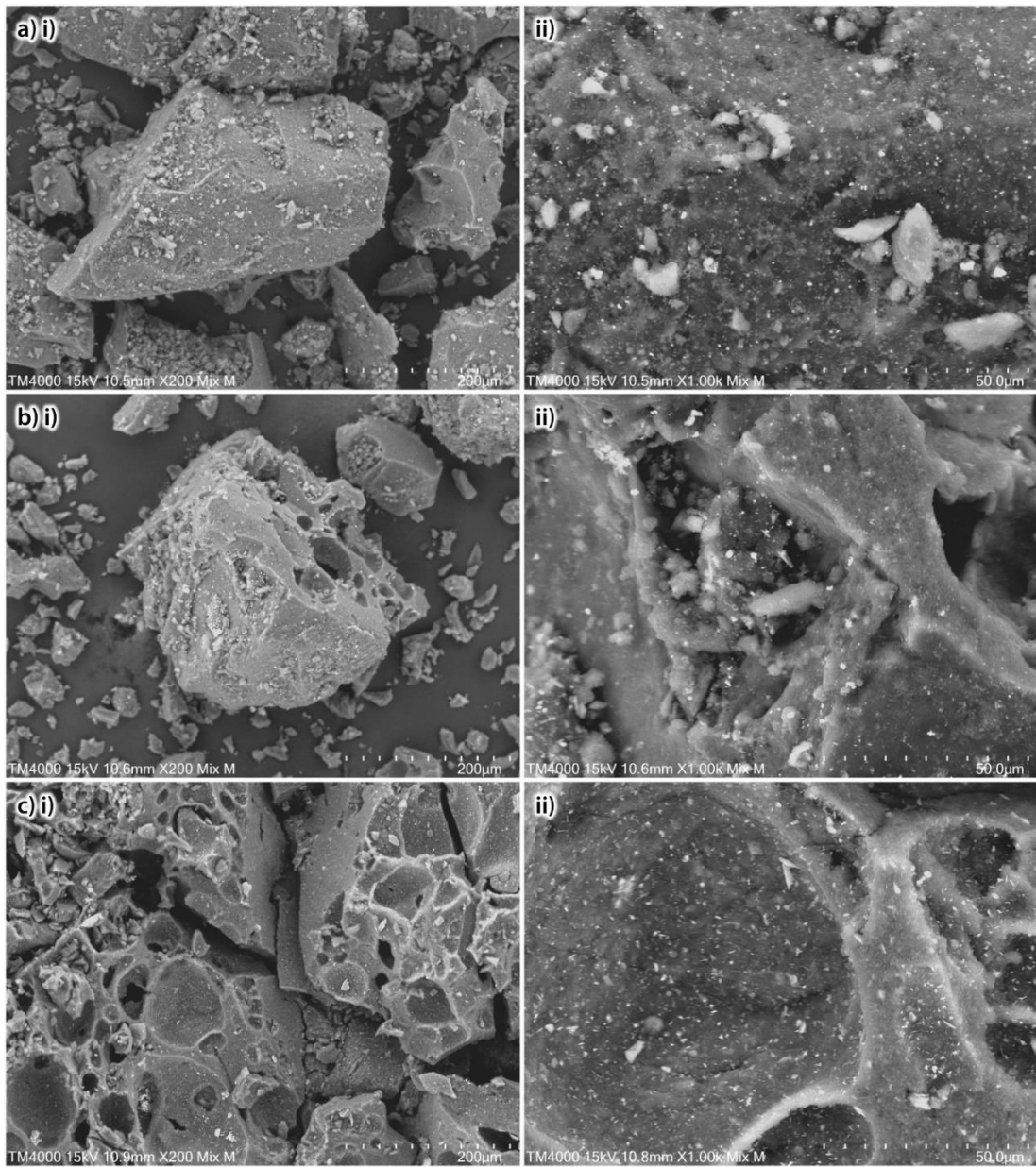
From the Gaussian peak analysis of the broad 002 graphitic reflection (shown in the close-up of **Figure 3.4a**), the difference in d_{002} and L_c parameters are also greater between RT900 and RTA900 compared to RT700 and RTA700. The largest difference in the evolution of phases identified by Rietveld analysis is observed for RT900 and RTA900 compared to the other processes e.g., comparing RT700 to RTA700 or RT900 to xRT900 *etc.* The speciation of crystalline impurity phases is likely to affect the evolution of the carbon environment during pyrolysis rather than the identity of the impurities themselves. This effect seems apparent in a nanoscale particularly with regards to the relatively large number of pores (9(1) and $15(1) \times 10^7$ pores g^{-1} respectively) and smaller pore dimensions (117 and 73.7 nm^3 per pore respectively) of RT900 and RTA900 compared to RT700 (7.7(6) pores g^{-1} , 143 nm^3 per pore) and RTA700 (7.5(5) pores g^{-1} , 146 nm^3 per pore).

A combination of the XRD, BET and Raman results provide evidence that growth, evolution, and speciation of major identifiable impurity phases affect the carbon morphology at both an Angstrom and nanometre scale. The expected outcome of pyrolysis at higher temperatures is demonstrated most accurately in this study through a comparison between RT700 and xRT900 (both prepared under N₂), wherein the xRT900 pore dimensions are larger ($\delta = +2191 \text{ nm}^3$ vs RT700) and in I_D/I_G observed to be significantly smaller ($\delta = -0.48(2)$ vs RT700) compared to values observed for RT700 determined by BET and Raman analysis (detailed in **Table 3.3** and visualised in **Figure 3.3**). In the case of xRT900, it appears that the only phases identifiable through XRD pertain to ZnS (as shown in **Figure 3.4d**). Whilst the air-exposed samples also pyrolysed 900 °C (RT900 and RTA900) also contain ZnS, but is accompanied with at least one other impurity – ZnO, Ca(OH)₂ or CaCO₃. In the air-exposed cases RT900 and RTA900, more subtle differences are experienced in the carbon morphology, with relatively smaller pore dimensions ($\delta = -26$ and -69.3 nm^3 vs RT700 respectively) and smaller differences in I_D/I_G ($\delta = -0.041(2)$ and $+0.08(3)$ vs RT700 respectively). Arguably, such subtle differences in the air-exposed case compared to RT700 suggests that the expected increase of pore dimensions and decrease in I_D/I_G when increasing the temperature of pyrolysis is suppressed by processes involving air and moisture. Pertinently, findings from XRD and Rietveld refinement show that the evolution of CaCO₃ and Ca(OH)₂ are dependent on the activation and presence of air and moisture, respectively during thermal treatment.

The crystallite size was estimated for all the phases present in the sample and are presented in **Table 3.5**. Most of the phases produced overlapping reflections which were modelled with the Rietveld method and therefore the calculated model was used for crystallite size determination. The average of the FWHM of all reflections from $20^\circ < 2\theta < 70^\circ$ belonging to each phase was used with the Scherrer equation to determine the values presented in **Table 3.5**. All phases were found to be of order of 10-50 nm suggesting small crystallites are present in the sample.

SEM images are provided in **Figure 3.5**. Comparison of SEM images of RT700 vs RT900 and xRT900 (shown in **Figure 3.5a, b, and c** respectively) reveal the presence of macropores (or large mesopores $\sim 50 \text{ }\mu\text{m}$ in diameter) at higher pyrolysis temperatures, however no observable differences in terms of smaller mesopores. As electrode materials for both for Na half-cells and Li-S cells (shown in

Figure 3.5d, e, and f, i and ii respectively), the macroporous (or large mesopores ~ 50 μm) network is not retained, and the samples show no observable differences.



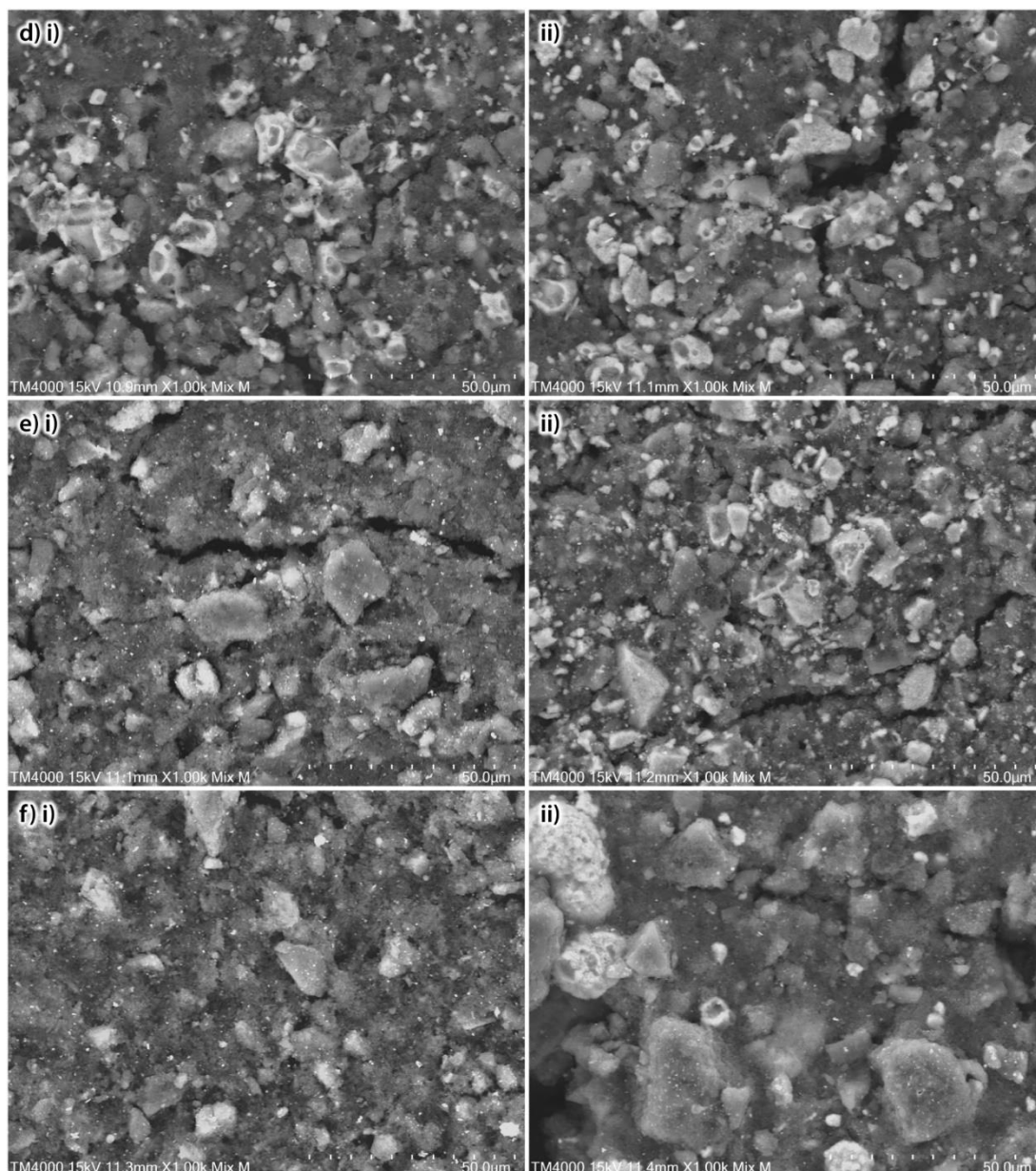


Figure 3.5 – SEM images of pristine **a)** RT700, **b)** RT900, and **c)** xRT900 at **i)** x200 and **ii)** x1000 magnification and electrodes using **d)** RT700, **e)** RT900, and **f)** xRT900 in **i)** Na half-cells and **ii)** Li-S cells at x1000 magnification.

3.3.3 Application of pyrolysed rubber tyres in Li-S cells

Although possessing inherently different redox chemistries, Li-S cells bear similarity to Na-ion half-cells in that they both operate effectively using non-graphitisable hard carbon frameworks. Careful consideration of the carbon content, morphology and impurities are undeniably a significant factor in governing the success of a Na half-cell.²⁴⁻³⁰ Utilising pyrolysed rubber tyres, the Na half-cell performance appears to be primarily governed by the carbon morphology that is also dependent on

the speciation of the impurities.³¹ With such strong emphasis on the impact of the carbon framework and impurities in efficient and successful Na half-cell function, it is hence unsurprising that the design of carbon materials for alternative systems such as lithium-sulfur (Li-S) would draw inspiration from these works, despite dealing with a completely different redox mechanism. Most research on the carbon component of the Li-S cell electrode have focused primarily on the carbon morphology,³²⁻³⁹ much like in the case of Na-ion and Li-ion cells. This is not unreasonable considering the primary role of carbon in a Li-S cell electrode is as a conductive framework. Whilst the role of carbon as a structural framework is undoubtedly a significant feature in determining the success of the Li-S cell electrode, it is important to also consider the impact of these carbons as competing sources of energy storage, and how this may impact the evolution of SEI surface speciation and overall cell performance. It is important to take into consideration that Li-S redox relies on conversion rather than insertion reactions. As a consequence, larger structural and compositional changes are expected to occur on the Li-S cell electrode compared to a Na-ion cell electrode, and thus the success and efficiency of a Li-S cell is often associated primarily to the formation of the SEI and surface speciation – a perspective more strongly emphasized in works focusing on Li-S electrolyte design.⁴⁰⁻⁴⁷ Moreover, with larger structural and compositional changes expected, it is reasonable to suspect that the presence of impurities in waste carbons to pose more significant and direct impact in the Li-S system compared to Li-ion and Na-ion systems, especially if those impurities are sulfur containing.

The performance of Li-S cells using RT900, xRT900 and RT700 as the primary carbon source of the negative electrode is visualized in Figure 3.6. Note, these were chosen as xRT900 produced the best performance in Na half-cells and RT700 is a lower temperature comparison.³¹ RT900 is tested to compare the effects of thermal activation under air and moisture as implemented in Na half-cells (see full results in published work).¹

In the Na half-cell case, xRT900 appears to improve cell performance compared to the other carbons.³¹ In the Li-S case, **Figure 3.6d** (black and red squares), whilst xRT900 initially produces a higher discharge capacity (1425 mAh g^{-1}) compared to RT900 (1327 mAh g^{-1}), a more dramatic capacity loss is experienced by cells using xRT900 compared to RT900. By the end of the 18th cycle, RT900 retains a higher discharge capacity (1003 mAh g^{-1} , ~76% of initial value) compared to xRT900 (865

mAh g⁻¹, ~61% of initial value) and RT700 (928 mAh g⁻¹, ~64% of initial value). The coulombic efficiencies of all the samples tested range between 99.9-100% by the end of the 18th cycle. Comparing the voltage capacity plots as shown in **Figure 3.6a** and **b**, there also appears to be a redox process occurring below 1.8 V annotated by the teal stars in **Figure 3.6b** and **c** observed in the initial discharge cycles when using xRT900 and RT700 respectively that is not observed in RT900.

The presence of the feature below 1.8 V could be interpreted as specific capacity earned *via* Li-ion insertion to the carbon content of the pyrolysed rubber tyres specifically graphitic carbon. All samples appear to have features reminiscent of graphitic carbon most likely at the nanoscale as observed by the broad (002) and (100) reflections in the XRD data (**Figure 3.4**). Between the three tyre crumb samples, xRT900 is notably the most graphitic in character ($I_D/I_G = 0.59(1)$), followed by RT900 (1.026(8)) and closely by RT700 (1.06(1)) based on Raman spectroscopy results shown in **Figure 3.3**. From Rietveld refinement of major identifiable phases to XRD patterns of the tyre crumbs, xRT900 contains the highest weight percentage of graphite (59.3(3)%) followed by RT700 (10.4(5)%), whereas a graphitic phase could not be resolved at all from the XRD pattern of RT900. A large SEI forms during the lithiation of graphite reducing capacity and as such the capacity is expected to drop for this process and could possibly explain why the feature below 1.8 V becomes virtually insignificant by the 10th cycle as seen in both **Figure 3.6b** and **c**. Moreover, an increase in the amount of irreversible lithiated carbon species on the electrode could be compromising to the overall structure and accessibility of sulfur, which is the main capacity source. This carbon could serve as an additional capacity boost in initial cycles; however such competing Li-ion and Li-S reaction pathways can be detrimental in prolonging the lifetime of the cell. The significant capacity loss over multiple cycles observed for xRT900 and RT700 could be due to a growing accumulation of irreversible lithiated carbon species on the electrode surface ultimately reducing accessibility for Li-S reaction pathways.

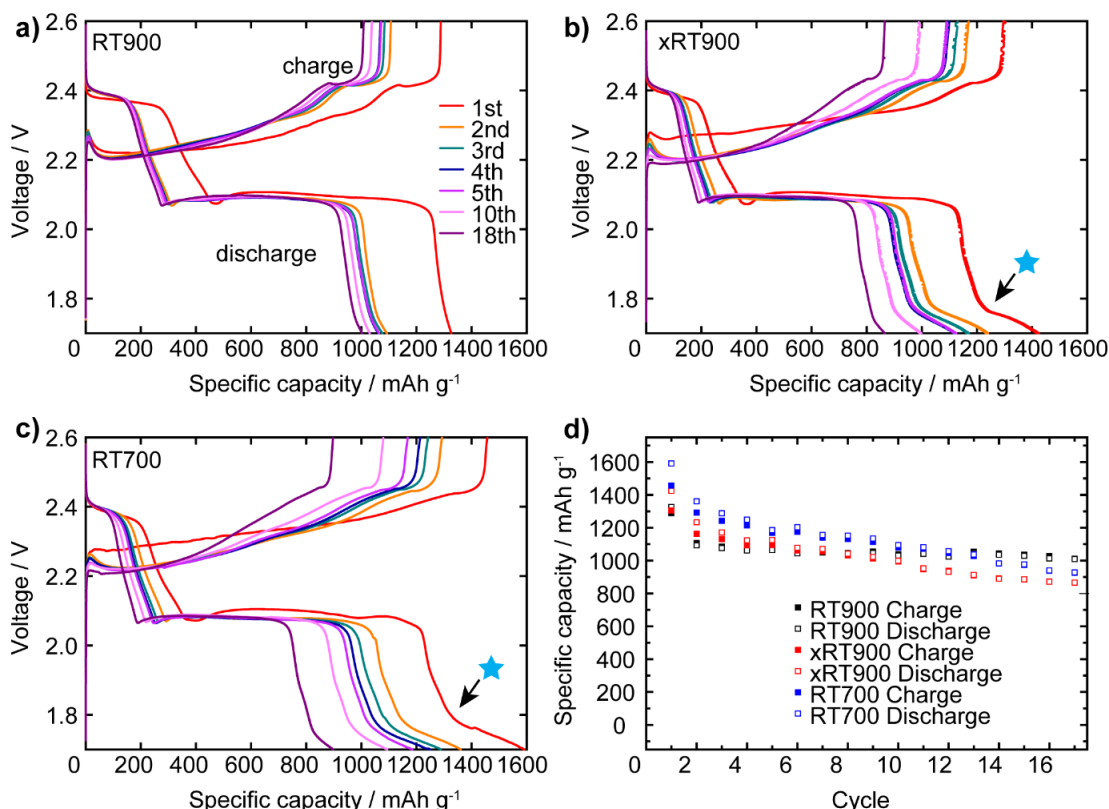


Figure 3.6 – Galvanostatic charge-discharge plots of Li-S cells using **a)** RT900, **b)** xRT900 and **c)** RT700 as the primary carbon source of the negative electrode. The specific capacity vs cycle number of the same cells are visualised in **d)**. The star and arrow annotations are referred to in text

It is also important to take into consideration which impurities in the pyrolysed rubber tyres would influence the performance of the Li-S cell. The species detected *via* XRD (see **Figure 3.4**) are CaCO_3 , ZnO , ZnS , and Ca(OH)_2 . CaCO_3 exists in equilibrium with Ca^{2+} and CO_3^{2-} when dissolved in water, both electrochemically active ions. The solubility of CaCO_3 is extremely poor in electrolytes used in Li-S cells however, and with minimal amounts of water inside the coin cell it is unlikely that dissolution of CaCO_3 occurs and would hence be relatively inert. Similar arguments can be made about Ca(OH)_2 . Likewise, ZnO is also most likely inert within the conditions of an operating Li-S cell. Whilst ZnO is a transition metal oxide and is widely used as an electrode material for Li cells,^{48, 49} its lithiation/delithiation potential window lies safely below the voltage window for Li-S cell operation (0.5-0.7 V),⁵⁰ and can thus be expected to be relatively inert in the Li-S cell system. Based on DFT calculations for crystalline ZnS , ZnS is reported to have a strong binding affinity to DOL and DME electrolyte solvents (-0.78 and -1.06 eV respectively), and its addition

can improve wettability of the Li-S cell electrode.⁵¹ Thus the impurity that is most likely to have significant impact on the Li-S cell system is ZnS.

Considering the role of the impurities, the feature below 1.8 V annotated by the blue star in **Figure 3.6b** and **c** could be related to ZnS components present in the sample. In such a case, typical ZnS vs Li/Li⁺ redox does occur within the potential window explored in this study. Two main redox reactions are expected: (1) related to the ZnS conversion to Zn metal and Li₂S and vice versa ($E_{p,c} = 0.7$ V and $E_{p,a} = 1.35$ V), and (2) the sequential lithiation/delithiation of Zn to form Li_xZn phases ($E_{p,c} = 0.01$ – 0.4 V and $E_{p,a} = \sim 0.3$ – 0.7 V).⁵² It is worth noting however that the amount of ZnS present in the sample is not expected to be large in comparison to carbon (S = 1.56 wt%, C = 82.68 wt% from **Table 3.1**).

Out of these three pyrolysed rubber tyre samples, xRT900 is observed to have the highest relative impurity weight percentage of ZnS (combined cubic and hexagonal phases = 100% excluding graphite), followed by RT700 (68(2)%) then RT900 (18.0(5)%) based on XRD analysis (see **Table 3.5** and **Figure 3.4**). Shin *et al.* reports an enhanced affinity of the electrode to the electrolyte solvents with the addition of ZnS (and thus requiring less DOL/DME solvent to operate), there appears to be no clear impact observed through electrochemical testing of these particular Li-S cells.⁵³ Rather the best performing active material between the three samples is observed to be RT900 with the least weight percentage of ZnS (18.0(5)%). Note, this also illustrates the challenges of such complex systems, although the impurity content of ZnS is highest in xRT900 this is a relative measure comparing internally for each sample. If the overall amount of impurities is lowest for xRT900, which appears to be the case from a visual inspection of the relative ratios of the carbon 002 reflection and the impurity reflection intensities, then this needs to be factored in. It is the combination of the concentration of impurities and type of impurities in addition to the carbon framework which determines the performance. Tailoring the waste with impurities becomes critical in performance.

Aside from ZnS vs Li/Li⁺, the feature below 1.8 V annotated by the blue star in **Figure 7b** and **c** could instead be related to the decomposition of the LiNO₃ salt which is expected to occur at potentials <1.8 V. Based on work exploring the effect of binders in LiNO₃ decomposition in Li-S cells, an enhanced decomposition of LiNO₃ at <1.8 V appears to be related to the salt's interaction with the oxygen-containing functional

groups present in the binder of the electrode.⁵⁴ This finding implies that the impurities, electrolyte (and additives) as well as architecture of the sulfur-electrode directly influences the redox involved, and thus the overall electrochemical performance of the Li-S cell.

In consideration of the carbon morphology based on BET analysis, RT900 has the highest number of pores and smallest pore dimensions compared to RT700 and xRT900. This particular morphology was previously discussed to be most likely due to the formation of $\text{Ca}(\text{OH})_2$ with exposure to air and moisture. Compared to the Na half-cell case wherein carbon is relied on as the main source of capacity, in the Li-S case the carbon is primarily intended to be a structural framework to trap lithium polysulfides. Contiguously, having smaller pores is consistent with more effective polysulfide entrapment, which could explain why RT900 exhibits the best capacity retention relative to RT700 and xRT900 with larger pore morphologies.

3.3.4 *Ex situ* characterisation of Li-S cell electrode surface species via XANES spectroscopy

Li-S cell function is based on a conversion type redox process that is more susceptible to variation of the electrode material architecture compared to Na half-cells. As reported in many previous works, the formation of the SEI and surface species that are often reliant on the initial cycles seem to be a crucial factor in determining the successful performance of a Li-S cell.⁵⁵⁻⁵⁷ Characterisation of the Li-S cell electrodes extracted at various electrochemical states *via* X-ray Absorption Near-Edge Structure (XANES) spectroscopy (see Figure 8), in particular measuring spectra at the S K-, C K-, and F K-edges, provides insight to how the surface environment can vary between utilisation of the different pyrolysed rubber tyre samples.

The S K-edge XANES spectra of RT900, xRT900 and RT700 electrodes are shown in **Figure 3.7ai, ii and iii** respectively. Initially in the fresh state as expected one S-S environment at ~2472 eV (as marked by the black dashed line) is observed. This S-S environment persists up to the 20th cycle with all the examined pyrolysed rubber tyres, indicating that redox active S-S remains accessible up to later cycles in all cases. In addition to S-S, after the 1st discharge (red trace) a feature at ~2478 eV (marked by the first navy vertical line) is formed, an observation shared again between RT900, xRT900 and RT700. S K-edge features at higher energies (i.e. >2475 eV) are

generally attributed to sulfate analogues arising from the LiTFSI electrolyte salt.⁵⁸⁻⁶⁰ This feature also appears to persist up to the 20th cycle in all cases.

There are some subtle variations in the 5th and 10th cycles between the three samples. As seen in **Figure 3.7ai**, in the case of RT900, higher energy features are observed at ~2478 and 2482 eV as indicated by the two navy lines. While varying in relative intensities over multiple charge and discharge points, these two features appear to be present up to the 20th cycle. In the case of xRT900 and RT700 however, as seen in **Figure 3.7a**ii and iii respectively, the highest edge feature is red shifted from ~2482 to ~2480 eV most noticeably in the 5th and 10th cycles, then returns back to profiles similar to those observed for RT900 in the 20th cycle. The overarching conclusion between these three pyrolysed rubber-tyre samples is that unsurprisingly LiTFSI analogues are present on the electrode surface – analogues that are intended as SEI protective species. The clear red shift from ~2482 to 2480 eV of the highest edge feature during the intermediate 5th and 10th cycles (**Figure 3.7a**ii and iii orange line) observed xRT900 and RT700 however, implies that the analogues formed from LiTFSI are different between RT900 and the other two examined samples. As seen in Figure 3.6d, the most significant capacity loss experienced by xRT900 and RT700 (red and blue squares) seems to begin at around the 6th cycle and is exacerbated by around the 9th-10th cycle, close to where significant differences in the sulfur surface environments are observed *via* S K-edge XANES.

Some insight as to what sulfur species give rise to the S K-edge features at higher edge energies (**Figure 3.7a** navy and orange lines) can be obtained by considering some of the possible analogues that could arise from LiTFSI electrolyte salt. LiTFSI has been previously reported to readily decompose to LiF, Li_xCF_y, Li₂NSO₂CF₃, and Li₂SO₂CF₃ analogues.⁶¹ This decomposition occurs initially by the breaking of the S-N bond upon the addition of an electron to liberate CF₃SO₂N⁻ and CF₃SO₂⁻. This is followed readily by the formation of CF₃SO₂ upon the addition of another electron, which decomposes further to CF₃ and SO₂ anions. CF₃SO₂N⁻ and CF₃SO₂⁻ can also further react with decomposed DOL solvent species such as LiOR (wherein R represents a functional group linked to O) to form Li_xSO₄²⁻.⁶² According to Aurbach *et al.*, it is the presence of LiNO₃ salt that allows for sufficient oxidation of CF₃SO₂N⁻ and CF₃SO₂ to form Li_xSO₄²⁻ in observable amounts.⁵⁶ Based on FTIR data of various electrolyte mixtures, they also suggest that the presence of Li₂S₆ could have an

attenuating effect on the lithium surface species reactivity, particularly this LiNO_3 salt oxidation to form $\text{Li}_x\text{SO}_4^{2-}$.

With such a varied population, the intermediate analogues such as $\text{CF}_3\text{SO}_2\text{N}^-$ and CF_3SO_2^- can be oxidised further, and thus species interpreted as RSO_2^- , SO_3^{2-} , RSO_3^- and SO_4^{2-} (whereby R denotes a functional group linked to S) in XANES spectra are all possible decomposition products. Relating this knowledge to the S K-edge spectra shown in **Figure 3.7a**, the S K-edge feature at ~ 2478 eV (**Figure 3.7a** first navy line) is most likely related to RSO_2^- intermediate products such as $\text{CF}_3\text{SO}_2\text{N}^-$ and CF_3SO_2^- having the lowest oxidation state. These species are reported to occur readily and reliably in various forms *via* multiple reaction pathways, which would account for the maintained presence of the ~ 2478 eV feature across RT900, xRT900 and RT700. This assignment is also in accordance with previous S K-edge analyses and recorded references.⁶³⁻⁶⁵ In discerning between the higher energy features (orange and 2nd navy line), it is more likely that the feature observed at ~ 2480 eV (orange line unique to xRT900 and RT700) is related to SO_3^{2-} , RSO_3^- intermediate species – species not yet completely oxidised to SO_4^{2-} . The highest energy feature (2nd navy line) would thus be assigned to SO_4^{2-} . According to Hackett *et al.*, this relatively high energy feature could also arise from inorganic sulfates,⁵⁹ such as $\text{Li}_x\text{SO}_4^{2-}$.

These proposed S K-edge feature assignments form an interpretation of the surface evolution upon multiple charge and discharge of the RT900, xRT900 and RT700 Li-S cell electrodes. All electrodes (see **Figure 3.7ai**) appear to reliably form LiTFSI intermediates (RSO_2^- ~ 2478 eV, 1st navy line) as well as highly oxidised $\text{Li}_x\text{SO}_4^{2-}$ (SO_4^{2-} ~ 2482 eV, 2nd navy line) up to the 20th cycle. The reliable formation of $\text{Li}_x\text{SO}_4^{2-}$ is in accordance with what is expected of a model Li-S cell system with sufficient oxidation from the LiNO_3 salt, and abundant Li_2S_6 polysulfides from successful Li-S redox to attenuate this oxidation. In the case of xRT900 and RT700 (**Figure 3.7aii** and **iii**), while SO_4^{2-} is indeed observed upon the first cycle (2nd navy line), it is momentarily absent in the 5th and 10th cycles and is replaced by less oxidised intermediate products (orange line SO_3^{2-} , RSO_3^- , ~ 2480 eV) before it is observed to return in the 20th cycle. This brief absence of SO_4^{2-} observed in the 5th and 10th cycles suggest that sources to completely oxidise the intermediates to SO_4^{2-} are insufficient or inaccessible during this time. These conditions could relate to insufficient accessibility to LiNO_3 , to Li_2S_6 or both. This supports the argument that the surface

evolution of xRT900 and RT700 electrodes during multiple charge and discharge are different to that observed for RT900, such that LiNO_3 analogues are unable to sufficiently populate the electrode surface to facilitate complete oxidation of LiTFSI to $\text{Li}_x\text{SO}_4^{2-}$. Additionally, insufficient Li-S redox, perhaps due to competing reactions with Li-ion pathways, could also present as a decrease in Li_2S_6 in the Li-S cell system at the discharge state, which would also subsequently impede the complete oxidation of LiTFSI to $\text{Li}_x\text{SO}_4^{2-}$.

C K-edge XANES spectra of the same electrodes are shown in **Figure 3.7b**. In the fresh states (**Figure 3.7bi, ii, and iii** black trace) two edge features describe the sp^2 hybridised C-C, C-H environment present in the electrodes (marked by black dashed lines). The first edge feature at ~ 285 eV relates to the π^* resonance, followed by a C-H resonance at ~ 287 eV.⁶⁶ The resonance at 288 eV describes the population of the interlayer graphite structure, and the broad feature coloured in grey at ~ 292 eV is the corresponding σ^* resonance of the sp^2 hybridised carbons.⁶⁷ The σ^* resonance typically consists of two features – a sharp excitonic peak at ~ 290 eV (not observed in the fresh states) and the broad band-like feature at ~ 292 eV (observed – coloured in grey).⁶⁸ The absence of this excitonic peak in the fresh pyrolysed tyre electrodes imply a defect-rich graphene environment.⁶⁹ The profiles of these spectra of RT900, xRT900 and RT700 electrodes (see **Figure 3.7bi, iii and iii** respectively) in the fresh state appear almost identical, implying a similar local carbon environment.

In the 1st discharge state (**Figure 3.7bi, ii, and iii** red trace), in all RT900, xRT900 and RT700 cases, the excitonic peak expected at ~ 290 eV (navy line) is observed implying that the carbon environment becomes more ordered over cycling. An increase in sharpness of the C-H resonance at ~ 288 eV corresponding to the interlayer graphite structure is also observed over multiple cycling in all cases. Subsequently this could imply that in all cases, Li-ion reaction pathways with carbon occur to a certain degree. In the case of RT900 (**Figure 3.7bi**), in the first charged state following discharge (green trace) the sharp excitonic peak is no longer present, and the overall profile resembles the fresh state. In the following cycles, even though the sharp excitonic peak becomes observable again, the overall relative amount of signal of observed carbon on the electrode surface appears to decrease significantly. In contrast for the case of xRT900 (**Figure 3.7bii**) the signal intensity of carbon environments on the electrode surface is maintained. Similar to the case of RT700 (**Figure 3.7biii**), the

excitonic peak at ~ 290 eV also appears sharpest at the 5th and 10th cycles with xRT900. On the 20th cycle (**Figure 3.7bii**) this excitonic peak is no longer as prominent compared to the 5th and 10th cycles, which could imply an exhaustion of carbon sites accessible for Li-ion insertion.

The corresponding F K-edge spectra of these electrodes (provided in **Figure 3.8**) provide insight to the evolution of the fluorine environment mostly related to LiTFSI electrolyte salt analogues. Between the three pyrolysed rubber tyre samples, RT900 spectra (**Figure 3.8a**) appear to have the most varied profiles between charge and discharge states up to the 20th cycle. In contrast, profiles observed for xRT900 and RT700 (**Figure 3.8b** and **c** respectively) seem quite stable. The profiles of RT700 electrode spectra collected at the 5th, 10th and 20th cycles appear to be almost identical. This implies that the fluorine SEI environment becomes static at earlier cycles in the case of xRT900 and RT700 compared to RT900.

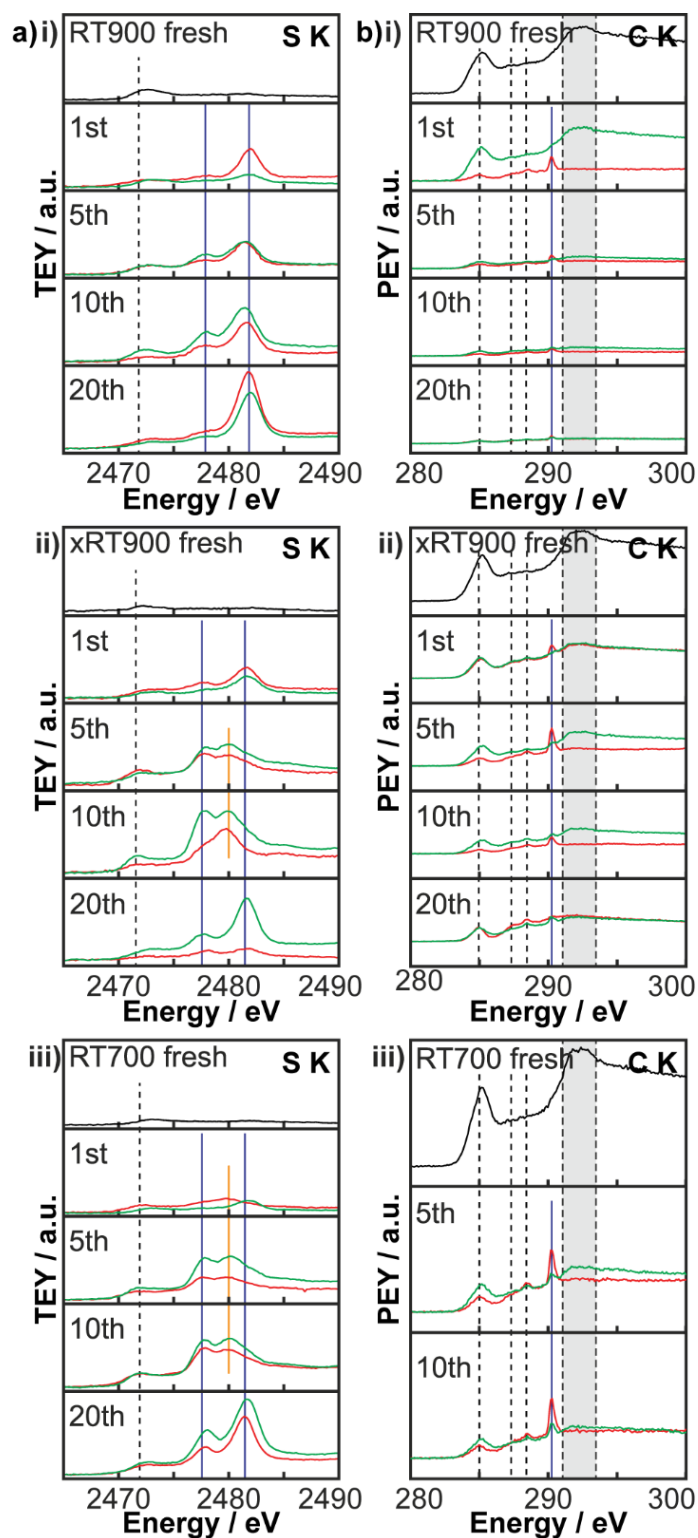


Figure 3.7 – XANES spectra at the **a)** S K-, and **b)** C K- edges of **i)** RT900, **ii)** xRT900 and **iii)** RT700 Li-S cell electrodes measured *ex situ* post-various electrochemical treatments. Black traces represent spectra of fresh untreated electrode samples. Red traces represent discharge states and green charge states. The vertical lines serve as a visual guide to compare edge feature positions and are referred to in-text. The light blue dashed lines in b) are C K-edge features related to the carbon-based adhesive of the carbon tape used to mount the sample for measurement.

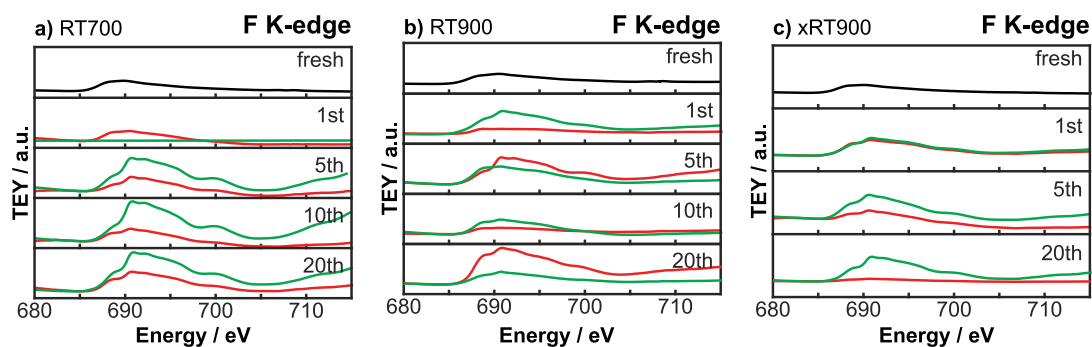


Figure 3.8 – F K-edge (F1s) XANES spectra of the **a)** RT700, **b)** RT900, and **c)** xRT900 tyre electrodes utilised in Li-S cells extracted at various electrochemical states

3.4 Conclusions

The performance of Li-S cells using a variety of pyrolysed waste rubber tyres as the active anode material were examined. Contiguously, the properties of the as prepared and electrochemically treated tyre crumb samples were also analysed. In terms of carbon morphology, whilst differences in surface area, pore size and volume (analysed by BET) are observed to be marginal for four of the five samples, increasing temperature and prolonged heating times appear to increase graphitic character as demonstrated by the relatively low I_D/I_G observed for xRT900. Notably, the presence of air and moisture shows significant impact in terms of the population and evolution of crystalline impurities as revealed through XRD, particularly the growing population of crystalline CaCO_3 and Ca(OH)_2 phases. The population growth of these phases appears to be related to the evolution of the carbon morphology, particularly with exposure to air and moisture during thermal treatment and activation appearing to suppress the carbon morphology from adopting a more graphitic character. The exposure to air and moisture upon thermal treatment appears to produce Ca(OH)_2 as demonstrated by RT900, which is also likely the precursor to form CaCO_3 upon physical activation using CO_2 as demonstrated by RTA900. In addition to CaCO_3 and Ca(OH)_2 , ZnO , $\text{ZnS}_{(\text{cub})}$ and $\text{ZnS}_{(\text{hex})}$ are also observed to be major identifiable phases within the pyrolysed rubber tyre samples, with $\text{ZnS}_{(\text{hex})}$ typically observed at with prolonged heating and at higher temperatures (i.e. samples heated to 900 °C) under N_2 .

In Li-S cells, using tyre crumbs sintered under N_2 at 900 °C (xRT900) and 700 °C (RT700) as an added carbon component produces higher initial capacities but decays more rapidly than tyre crumbs sintered in air at 900 °C (RT900) which shows stable capacities (1003 mAh g^{-1} , ~76% of initial value by the 18th cycle at 167.2 mAh

g⁻¹ or C/10). Based on the analytical methods employed in this work, this stable capacity could be a result of more effective sulfur entrapment in the mesopores found in RT900 (117 nm³ per pore) that are relatively smaller compared to those found in RT700 and xRT900 (143 and 2334 nm³ per pore respectively). As reflected in the galvanostatic charge-discharge tests and supported by *ex situ* characterisation via XANES, competing Li-ion reaction pathways utilising the hard carbon source can impede the intentional Li-S reaction pathways. XANES also reveals significant impact of these competing Li-ion reactions on the formation of the SEI on the electrode surface, a vital consideration in the Li-S cell system. The decaying capacities could be related to higher levels of the competing pathway slowly being used up (becoming irreversible).

Overall tyre crumb derived carbons prepared *via* facile pyrolysis are high quality carbons to produce excellent electrode components in Li-S cell systems, exhibiting specific capacities that are comparable to those achieved when using commercial carbon black frameworks.^{70, 71} Future work can be directed at exploring these systems at higher rate and for longer cycles. It would also be interesting to see how the crystallite size of the impurities direct carbon formation in future work or the combination of quantity and crystallite of the impurities can modulate the carbon network. This could be used as a lever to design an appropriate carbon. This work has tried to use a combination of detailed characterisation of the carbon frameworks produced and impurities persistent in combination with electrochemical examination and *ex situ* mechanistic studies to develop an in-depth understanding of function. The link between impurities in waste-streams and the subsequent products and their properties is critical for the application such streams to industry.

3.5 References

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Chapter 4: Waste coffee-derived carbon frameworks

This chapter presents the published results of waste coffee-derived carbon frameworks and their application as electrode materials in Li-S cells.¹

4.1 Introduction

With an estimated value of over six million tonnes of spent coffee grounds going to landfill per year,² porous carbon derived from spent coffee grounds have found applications in many areas such as gas separation³, methane storage⁴ and energy storage.⁵ Previous work has reported the formation of pores in the order of 100-300 Å in pyrolysed spent coffee grounds. Their specific surface area have been reported to be 94.35 m² g⁻¹ and can extend to values as high as 1121 m² g⁻¹ with chemical activation.^{3,5} Whilst being a green source of carbon, the high surface area and porosity of this carbon material are well suited for lithium polysulfide entrapment and can therefore be beneficial to prolonging the Li-S battery lifetime.

This work reports the performance of a Li-S cell using carbons derived from waste coffee grounds as the primary carbon source of the electrode. The Li-S cell maintains a specific capacity of 340 mAh g⁻¹ at 0.1 C after 100 cycles and coulombic efficiencies of >98% at 1 C even after 100 cycles. The preparation involves a facile one-step pyrolysis at 900 °C under N₂ flow for 15 mins, which results in a highly disordered hard carbon with smaller than 1 nm crystallite size domains as implied *via* X-ray powder diffraction (XRD) and Raman spectroscopy. XRD also provides some evidence for an expanded interplanar distance between graphene-like layers in the material. Analysis of the structural evolution of the material after various electrochemical treatment conditions is also afforded through X-ray Absorption Near-Edge Structure (XANES) spectroscopy.

4.2 Methodology

4.2.1 Preparation of pyrolysed coffee grinds and elemental analysis

Waste espresso pucks (Campos Superior Blend) previously subjected to 9 bars of pressure and heating at ~95 °C were used as the precursor for the carbon samples.

Weight % of ash, C, N, and S in the coffee grounds after drying, shown on **Table 4.1a**, were measured using an Elementar varioMACRO cube in the CNS mode. Chemical analysis of the ash present in the coffee grounds was determined by X-ray fluorescence spectroscopy (XRF) using a PANalytical PW2400 Sequential WDXRF Spectrometer and is detailed on **Table 4.1b**. The elements are expressed as wt. % of the oxides as these were used as the reference materials.

Table 4.1 – a) CNS combustion analysis of the coffee grounds and b) XRF chemical analysis of the ash component (ashing conducted at 815 °C) of the coffee grounds

a) CNS analysis of coffee grounds / wt. % of total coffee grounds													
Ash (815 °C)				C		N				S			
1.86				52.42		2.34				0.16			
b) Chemical analysis of ash in coffee grounds / wt. % of ash													
SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₃ O ₄	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	SrO	ZnO	CuO
0.19	0.03	0.04	0.25	0.25	12.98	8.39	1.54	42.69	14	5.59	0.05	0.07	0.16

These spent coffee grounds were then pyrolysed at 900 °C under N₂ flow (1L/min) for 15 min in a horizontal tube furnace to yield the black pyrolysed coffee carbon source.

4.2.2 Characterisation of pristine materials

XRD patterns of the pyrolysed coffee grounds were collected using a PANalytical Empyrean diffractometer (Co K α) at room temperature in the $10 < 2\theta^\circ < 90$ range, with a 0.026° step size and data collection of 750 s per step. Subsequent Rietveld refinement and quantitative analyses were conducted using the GSAS II⁶ software suite. Scherrer crystallite size analysis was conducted by peak fitting regimes using a Gaussian function to model each reflection using OriginPro 9. Raman spectra of the samples were collected using a Renishaw inVia microscope using a 532 nm laser source. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) measurements of the samples were performed using a Hitachi TM4000Plus benchtop SEM operating at 15kV, equipped with a Bruker SDD-EDS detector for elemental mapping. Wt. % of the elements for each sample were measured as an average of the SEM window. Brunauer-Emmett-Teller (BET) surface area analysis was conducted using a Micrometrics TriStar 3000 analyser *via* N₂ adsorption desorption measurements (77.35 K) for specific surface area and pore size determination of the pyrolysed coffee over a pore diameter range of 1-300 nm. Determination of mesopore surface area, pore volume and pore size were performed using the Barrett-Joynere-Halenda (BJH) method.

4.2.3 Characterisation of electrochemically treated samples

The C K, F K and S K-Edge XANES measurements were conducted on the soft X-ray beamline at the Australian Synchrotron⁷ following the same procedures outlined in previous work⁸. Data normalization of the C K-edge spectra was carried out following the procedure outlined by Watts *et al.*⁹ The C K, F K and S K-edge XANES data were calibrated and normalised using the Quick AS NEXAFS Tool (QANT) macro developed for Igor Pro.¹⁰

4.2.4 Coin cell fabrication and testing

The active material of the slurry was made up of a 1:1 wt% mixture of pyrolysed coffee and α -S₈ (meaning that only 50% of the powder can be considered as

electrochemically active). The electrode material was then prepared by mixing a 75:20:5 ratio of this pyrolysed coffee and α -S₈ mixture, TimCal Super P conductive carbon black and poly(vinylidene)difluoride (PVDF) binder in n-methyl pyrrolidone (NMP) solvent overnight. The resulting slurry was doctor-blade cast onto an Al-foil substrate at 200 μ m thickness, dried at 100 °C under vacuum and pressed at 1000 kN for 1 h to ensure good contact between the slurry and the conductive substrate before transferring into an Ar-filled glovebox. For comparison a S-only electrode was also made using the procedure with 75:20:5 ratio of α -S₈, carbon black, PVDF. The electrodes were assembled into CR2032 coin cells with a glass-fibre separator soaked in electrolyte and a Li foil anode. The electrolyte used was a mixture of 0.38 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) and 0.32 M lithium nitrate (LiNO₃) in a 1:1 v/v mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxy ethane (DME).¹¹ For the electrochemical tests the fabricated Li-S coin cells were galvanostatically discharged and charged (i.e., applying a constant current and measuring the changes in voltage of the cell) between 1.7-2.6 V at C/10 (167.2 mA g⁻¹ of α -S₈) and variable C rates using a cell cycler system (Neware BTS3000).

4.3 Results and Discussion

4.3.1 Composition and morphology of pyrolysed coffee grounds

Results obtained through Raman spectroscopy shown in **Figure 4.1** reveal that the pyrolysed coffee grounds are comprised mainly of hard carbons. A comparison of the intensities of the D band (centred at $\sim$ 1350 cm⁻¹) and the first-order G band (centred at $\sim$ 1580 cm⁻¹), i.e., the I_D/I_G ratio, can provide information on the level of disorder of the analysed carbon samples. The D band characterises the population of scattering processes associated to disordered sites in the carbon sample, whereas the G band characterises the population of scattering processes arising from C-C interactions within graphitic planes¹²⁻¹⁴. The black trace in **Figure 4.1** is a Raman spectrum of commercially available TimCal Super P carbon black, typically used as a source of disordered-hard carbons. The disordered nature of the carbon black is evident through the intensity of the D band relative to the G band. Relative to this profile, the pyrolysed coffee grounds show a broader D-band compared to that seen in carbon black. This broadening of the D-band and distorting overlap with the 1st order G-band is generally associated with an increased disorder within the carbon architecture.¹⁵ The presence

and intensity of the D band in both the pristine and electrode powder forms of pyrolysed coffee imply that the carbon source is mainly disordered.

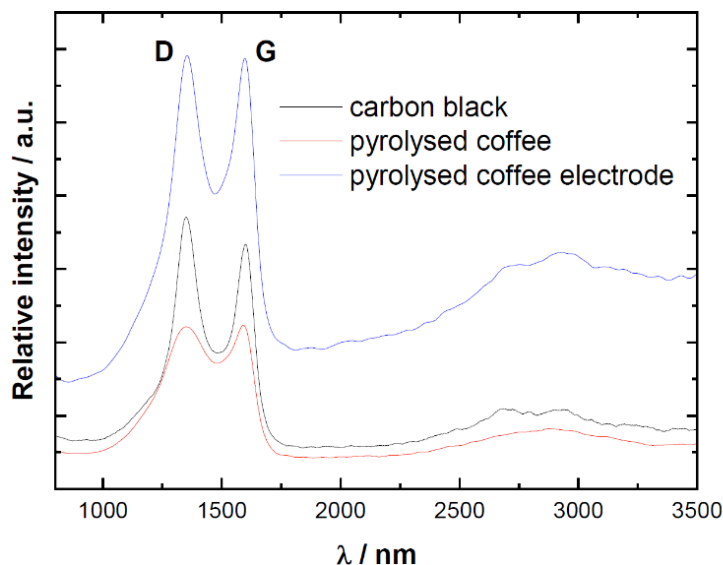


Figure 4.1 – Raman spectra of TimCal super P carbon black (black trace), pyrolysed coffee grounds in its pristine form (red trace) and as an electrode powder (green trace).

Determination of I_D/I_G values is afforded by comparing the intensities of the D and 1st order G bands deconvoluted using two models: (1) Lorentzian functions and (2) a combination of a Voigt function and a Breit-Wigner-Fano (BWF) function (to fit the D and G bands respectively) after background treatment, with the latter model achieving more accurate fit statistics. Details regarding these peak fits can be found in the appendix **Table A. 1** and **Figure A. 1**. As presented in the appendix **Table A. 1**, the pyrolysed coffee samples appear to exhibit similar I_D/I_G values comparable to that of commercially available carbon black (i.e., $I_D/I_G \approx 1$). Note that whilst ratios greater than 1 imply an observable significance of the D band, it is difficult to assign a concrete boundary to at which point hard carbons are considered to be highly disordered. An increasingly amorphous carbon character is known to cause line broadening effects, which can be disruptive in the deconvolution of D and G bands.¹⁶ Thus, interpretation of the I_D/I_G ratios extracted from Raman data (particularly in the case of hard carbons) should only be considered as an estimate. Nevertheless, the relative peak broadness of the D band observed in pyrolysed coffee grounds compared to that observed for commercial carbon black suggests that the material is characteristic of hard carbons. This level of disorder is also maintained after the electrode slurry preparation process, which indicates that the carbon source pre-electrochemical treatment is predominantly disordered hard carbons.

SEM imaging as shown in **Figure 4.2** visualises the morphology of the coffee grounds. Note that the resolution of the SEM instrument is preferentially sensitive to structures in the macro (>50 nm) and mesoporous scale (2-50 nm), and confirmation or detailed characterisation of microporous structures (<2 nm) is not explored as part of this work. Interpretation of the features revealed by SEM imaging provides insight to the macro and mesoporous architectures achieved in the pyrolysed coffee grounds. As shown in **Figure 4.2a**, before pyrolysis the untreated coffee grounds lack any features with an ordered structure, containing large macroporous voids sized ~ 19 μm in diameter. Upon pyrolysis, the macropores (indicated by the red lines in **Figure 4.2bii**) appear to be larger (~ 30 μm) compared to the untreated coffee grounds in **Figure 4.2a**. These macropores (red lines **Figure 4.2bii**) observed in pyrolysed coffee grounds are voids formed by a sheetlike framework that is ~ 0.5 -1 μm in thickness resembling the cell wall structures found in many lignocellulosic materials.¹⁷ In addition to these macroporous voids, the pyrolysed coffee grounds are also comprised of smaller macroporous regions less than ~ 2 μm in diameter within the larger macropores as indicated by the blue arrows in **Figure 4.2bii**. Such arrangement and disordered structure of the porous framework is only clearly evident in the pyrolysed coffee grounds and not the precursor. This sheetlike framework is not preserved during the electrode preparation process as shown in **Figure 4.2c**. The larger macroporous voids framed by cell wall structures indicated by red lines in **Figure 4.2bii** are no longer observed in the electrode morphology as shown in **Figure 4.2c**. It appears that the immersion in PVDF/NMP solvent mixture and milling process during electrode preparation compromises the fine ~ 0.5 -1 μm sheetlike structures previously achieved by the pyrolysed coffee grounds. The smaller macroporous structures less than ~ 2 μm in diameter appear to be preserved to an extent however as indicated by the blue arrows in **Figure 4.2cii**. Note that the electrode is composed only of 10 wt. % pyrolysed coffee (20 wt. % carbon = 10 wt. % carbon black + 10 wt. % pyrolysed coffee). EDS mapping of the electrode surface as shown in **Figure 4.2ciii** confirms that the regions marked by the blue arrows in **Figure 4.2cii** are related to carbon.

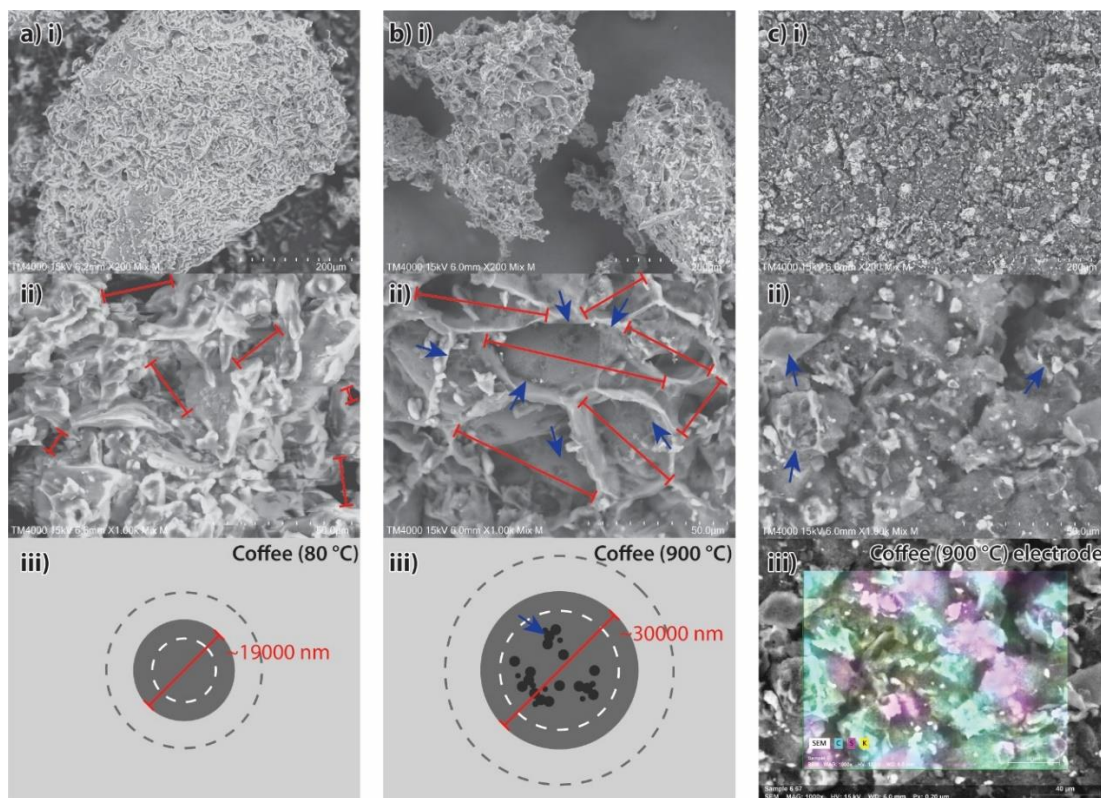


Figure 4.2 – SEM images of **a)** dried coffee grounds (80 °C), **b)** pyrolysed coffee grounds (900 °C) and **c)** Li-S cell electrode using pyrolysed coffee grounds as a carbon component. **i)** images are at 200x magnification and **ii)** at 1000x magnification. **a)** and **b)** **iii)** are visual depictions of the median value of the macroporous voids observed in the samples and provided to compare the sizes of the voids before and after pyrolysis. **c)** **iii)** is an EDS elemental map of the Li-S electrode using pyrolysed coffee grounds as a carbon component.

EDS maps of the pyrolysed coffee grounds provided in **Figure 4.3** reveal a homogenous distribution of elements that could be related to impurities in the sample. Particularly Mg (<1 wt%), K (18(14) wt%) and O (10(1) wt%) appear to be formations predominantly localised on the edges of the sheetlike carbon structures. Only Al (8(4) wt%) and P (<1 wt%) appear to be homogenous and have no affinity towards particular features of the carbon framework (62(26) wt%).

The inorganic elements detected in the EDS measurements correspond to those observed in the XRF chemical analysis of the coffee ash presented on **Figure 4.3b**. Based on the XRF analysis of the precursor, the largest contributors to the wt. % are K₂O (42.69 wt. % ash), P₂O₅ (14.00 wt. % ash), and MgO (12.98 wt. % ash). Pertinently these elements appear to have persisted in the pyrolysed coffee as observed in the EDS measurements. In addition to these elements, Al is also detected in the EDS measurement of the pyrolysed coffee despite its relatively low wt. % detected in the

precursor (see **Table 4.1b**, 0.04 wt. %). A combination of the EDS and XRF results suggest that K, P, Mg, and Al-containing impurities are present in observable amounts in the pyrolysed coffee samples. This observation is consistent with previous reports on the mineral composition of coffee.¹⁸

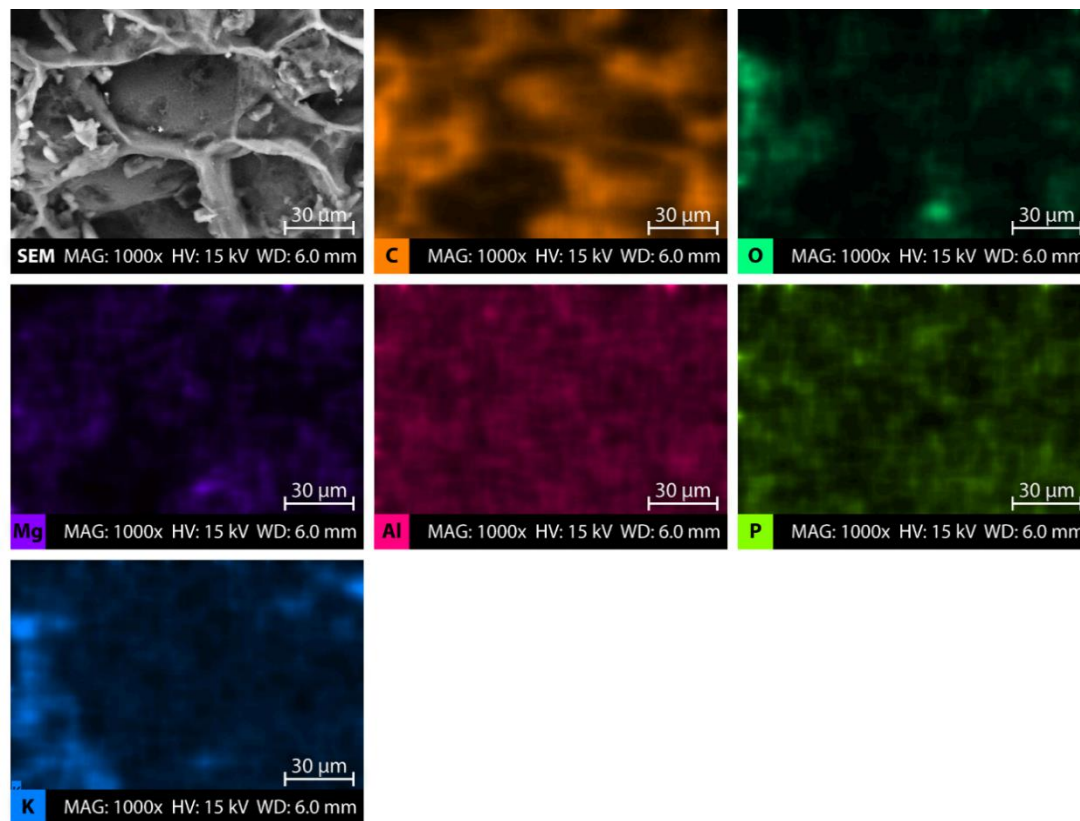


Figure 4.3 – EDS maps of pyrolysed coffee

Evidence for the presence of mesoporous structures alongside macropores is provided by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis of the coffee crumb (summarised in **Table 4.2**). BJH analysis of the pyrolysed coffee shows an average pore diameter of 9.7(1) nm at the lower end of the mesoporous range (~2-50 nm). The pore size distribution curves in **Figure 4.4a** (star datapoints) shows maxima at 4.8(1) and 4.3(1) nm pore diameter for adsorption and desorption respectively, even lower still in the mesoporous range.

Table 4.2 – Summary of BET and BJH results measured for pyrolysed coffee

Specific Surface Area / $\text{m}^2 \text{g}^{-1}$	Pore Volume / $\text{cm}^3 \text{g}^{-1}$	Average Pore Diameter / nm
1.06(1)	0.00634(6)	9.7(1)

Analysis of the pyrolysed coffee adsorption-desorption isotherm (as shown in **Figure 4.4b**) is also in support of a highly mesoporous architecture (i.e., 2-50 nm). Upon general inspection, the adsorption-desorption loops appear to exhibit profiles characteristic of Type III isotherms, absent of a knee at lower P/P_0 , typically indicative of monolayer adsorption.¹⁹⁻²¹ Closer inspection at lower relative pressures as shown in the inset **Figure 4.4b** however reveals a subtle point of inflection, typically associated with the end of monolayer adsorption and beginning of multilayer adsorption.²² Albeit discreet, the presence of this feature indicates that the pyrolysed coffee sample more accurately resembles the profile of a Type II isotherm rather than Type III.¹⁹⁻²¹ Confirmation of monolayer adsorption generally requires $C > 1$ at $P/P_0 \approx 0$ corresponding to the linear BET equation $\frac{(P/P_0)}{V(1-(P/P_0))} = \frac{1}{cV_m} + \frac{(C-1)(P/P_0)}{cV_m}$ wherein V denotes overall adsorbed volume and V_m adsorbed monolayer volume.^{22, 23} The point of inflection in the adsorption-desorption isotherms shown in **Figure 4.4b** is only perceived based on deviation of the first datapoints from an exponential Type III profile. Thus, the adsorption-desorption isotherms measured for pyrolysed coffee, particularly at lower P/P_0 , are insufficiently sensitive for accurate determination of C . The subtlety of this feature however implies that mesopores dominate over micropores (<2 nm) within the pyrolysed coffee architecture, since strong monolayer adsorption is most commonly observed in microporous solids with relatively smaller accessible volumes.²¹ Furthermore, it can be interpreted that the subtlety of the point of inflection in **Figure 4.4b** is due to concurrent monolayer and multilayer adsorption of N_2 into mesopores with relatively larger accessible volumes compared to micropores, accounting for an early occurrence of multilayer adsorption at lower P/P_0 . This dominance of mesopores over micropores is only implied however, considering the preferential sensitivity to mesopores in such N_2 adsorption-desorption measurements. Hence based on SEM and N_2 adsorption-desorption analysis, the pyrolysed coffee architecture appears to be comprised of mainly macropores and mesopores.

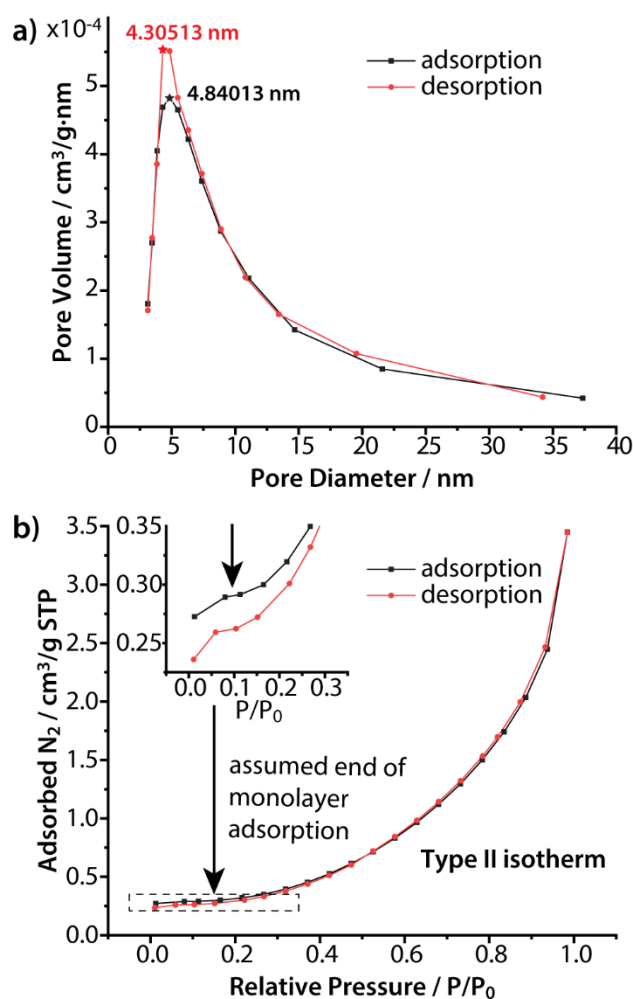


Figure 4.4 – a) Pore size distribution and b) N₂ adsorption-desorption isotherms for pyrolysed coffee

The X-ray powder diffraction (XRD) data of the resulting biochar in **Figure 4.5** shows that the sample is primarily comprised of hard carbon (non-graphitic carbon) in agreement with the analysis of the Raman spectrum. This is indirectly determined by the broad XRD features with minimal intense sharp reflections. The two broad characteristic peaks at $2\theta = 29$ and 51° , correspond to the (002) and (100) planes respectively of model graphite (*P6₃mc* COD ID 9008569²⁴), and the broad nature has been linked to graphite-like nanodomains in hard carbons,^{5, 25} as well as turbostratic character.²⁶ Hard carbon is known to be a good negative electrode material for Na-ion cells because it is considered to feature some expanded graphene sheet spacing²⁷ and nanodomains of graphite. In Na-ion cells, specific capacities are typically around ~ 350 mAh g⁻¹ and most of these reports fine tune the hard carbon pore morphology or in some instances modify the interplanar distance between graphene layers of the graphitic component.²⁸⁻³⁰ Despite substantial studies in the Na-ion cell system, to the

best of our knowledge, the effects of using hard carbons in Li-S cells has not yet been examined.

Scherrer crystallite size analysis by peak fit modelling as visualised in **Figure 4.5a** provides quantitative insight to the crystallite size of pyrolysed coffee hard carbons. The Scherrer analysis reveals the crystallite sizes to be $L_c = 12.03(7)$ and $9.2(1)$ nm for the (002) and (100) reflections respectively (see **Table 4.3**). Moreover, d_{002} of the (002) reflection at $2\theta = 28.77(1)^\circ$ ($d_{002} = 3.602(1)$ nm, **Table 4.3**), corresponding to the interlayer-spacing perpendicular to the graphene layer planes is relatively large compared to what is typically expected of graphite (d_{002} is typically 0.344 nm and graphite crystallite sizes are 100 nm or larger).³¹

Whilst XRD analysis of carbon derived from waste coffee grounds (or other carbonaceous wastes) have been reported in previous works, such interpretations predominantly focus on characterisation of the reflections related to the bulk carbon component.³²⁻³⁵ Supplementary to this, the presence of impurities in the waste precursor and how they might evolve under specific pyrolysation conditions should also be considered. Pertinently the simultaneously occurring evolution of the impurities could also impact the final bulk carbon morphology.

Indeed, as shown in **Figure 4.5b**, reflections in addition to those pertaining to bulk carbon (i.e., (002) and (100)) are also present in the XRD pattern which are likely related to impurities. The major identifiable impurity phase appears to be MgS ($Fm\bar{3}m$ ICSD Coll. Code 44930,³⁶ 65(9) wt%), followed by K_2CO_3 ($P6_3mmc$ ICSD Coll. Code 52535,³⁷ 23(7) wt%) and Al_2O_3 ($R\bar{3}c$ ICSD Coll. Code 68591,³⁸ 12(4) wt%). The presence of elements Mg, K, Al and O have been previously confirmed through EDS mapping of the pyrolysed coffee sample as shown in **Figure 4.3**. The chemical composition of the dried coffee grounds before pyrolysis, determined via XRF analysis (see **Table 4.1**), also includes Al_2O_3 (0.04 wt%), MgO (12.98 wt%), K_2O (42.69 wt%) and SO_3 (5.59 wt%), all of which are related to the impurity phases detected via XRD. CaO (8.39 wt%) and P_2O_5 (14 wt%) as well as other trace impurities are also observed in the dried coffee grounds through XRF analysis (see **Table 4.1**) however impurities related to these species could not be resolved through the XRD pattern of the pyrolysed sample (see **Figure 4.5b**).

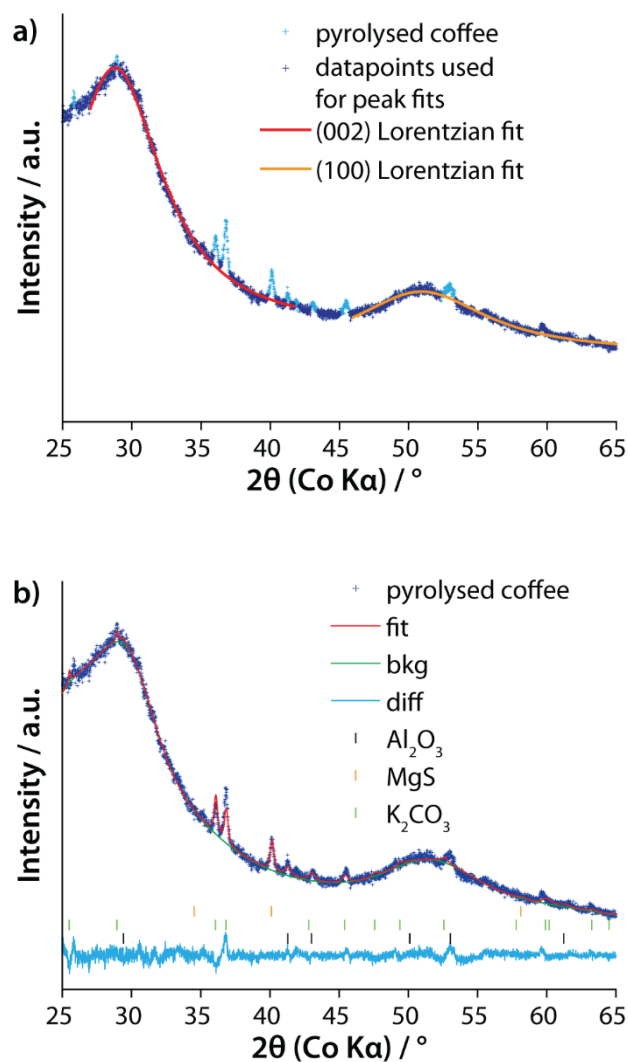


Figure 4.5 – a) Single Lorentzian peak fits of the (002) (red trace) and (100) (amber trace) reflections to powder XRD data of the pyrolysed coffee sample (blue crosses) for Scherrer crystallite size analysis. The calculated d -spacing and crystallite size can be found in **Table 4.3**. Details regarding the Lorentzian fits used to model the (002) and (100) reflections can be found in the appendix **Table A. 2**. **b)** Rietveld refinement of Al_2O_3 ($R\bar{3}c$ ICSD Coll. Code 68591), MgS ($Fm\bar{3}m$ ICSD Coll. Code 44930), and K_2CO_3 (P63mmc ICSD Coll. Code 52535) phases to the XRD data.

Table 4.3 – Single Lorentzian peak fit results modelling the (002) and (100) reflections observed in powder XRD data of the pyrolysed coffee grounds shown in **Figure 4.5a**

	(002)	(100)
<i>d</i>-spacing / nm	3.602(1)	2.082(1)
<i>L_c</i> / nm	1.203(7)	0.92(1)
<i>2θ</i> / °	28.77(1)	50.92(2)
FWHM / °	8.27(5)	11.6(1)
Adj. R²	0.996	0.973

4.3.2 Electrochemical Performance

In order to test its effectiveness in a Li-S cell system, the pyrolysed coffee was incorporated into the electrode slurry mixture as a conductive additive. The results of the electrochemical tests are shown in **Figure 4.6**, wherein the coffee-containing samples are compared against a standard α -S₈ electrode using carbon black. As shown by the black data points in **Figure 4.6a**, the coffee-containing electrode capacity shows a more stable capacity up to the 100th cycle in comparison to the variable capacity observed for the standard α -S₈-carbon black electrode composition marked in red. Whilst the standard α -S₈-carbon black electrode initially produced a higher discharge capacity of 771 mAh g⁻¹ compared to 489 mAh g⁻¹ (at 0.1 C) for the coffee-containing negative electrode, this is quickly lost within 20 cycles to 209 mAh g⁻¹. It should be noted that the intended active sulfur content (37.5 wt%) is 50% less than the standard >75 wt% amount traditionally used in Li-S electrodes. This capacity is observed to sporadically increase up to the 100th cycle, however this is likely to be linked to exfoliation of the electrode surface, thus increasing the surface area of active material over cycling or further utilisation of the S in the electrode. Conversely, when using the pyrolysed coffee electrode a smaller and more stable decrease is observed, slowly plateauing to ~340 mAh g⁻¹ by the 100th cycle (at 0.1 C). As emphasised in **Figure 4.6b**, although the specific capacity for the initial cycles is lower than the standard α -S₈, the coffee-containing samples proved to improve the stability of Li-S cells even at higher C rates.

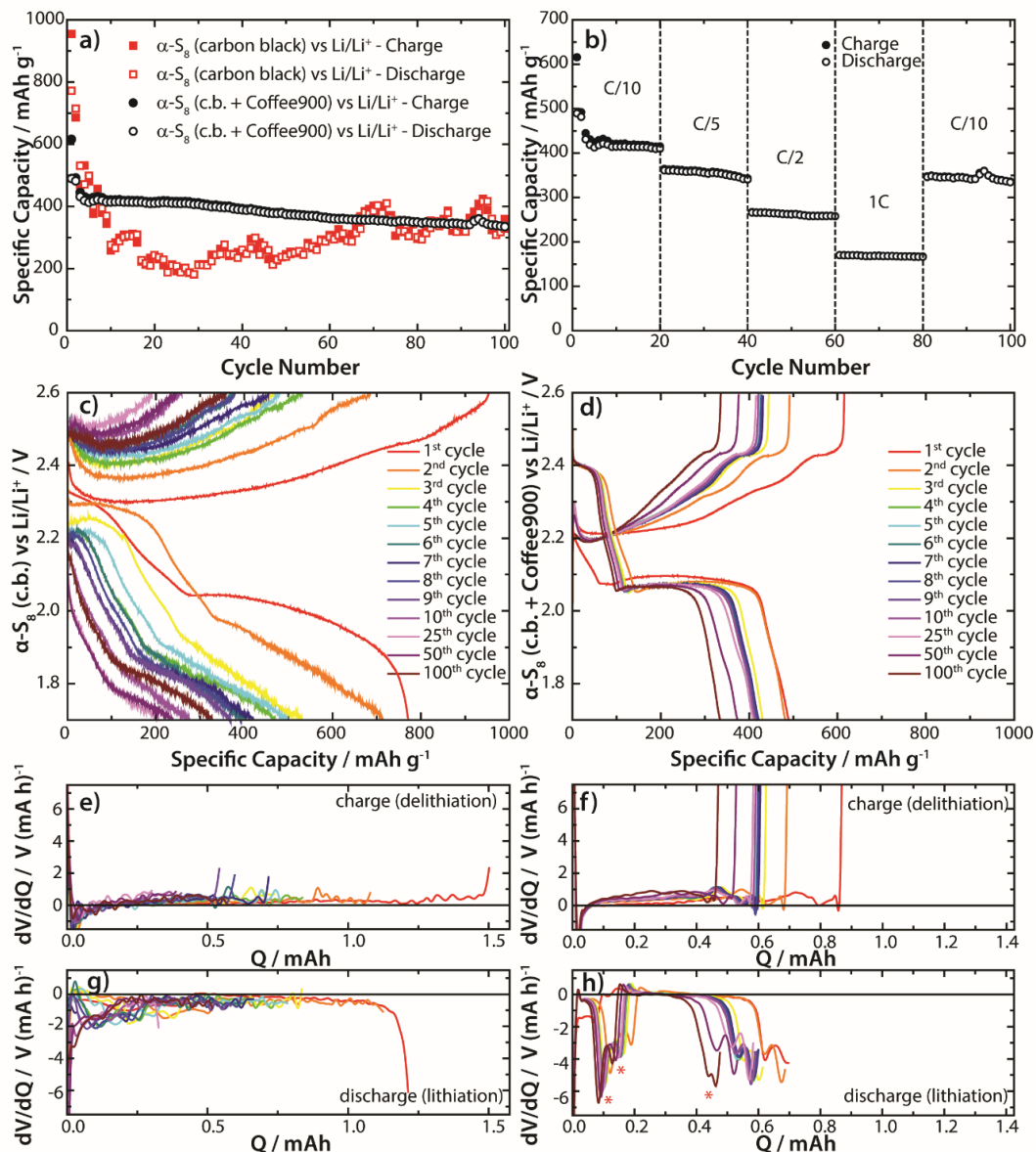


Figure 4.6 – **a)** Specific capacity versus cycle number of Li-S cells using only carbon black (red) and coffee-containing (black) electrodes, **b)** specific capacity versus cycle number of Li-S cells using coffee-containing electrodes cycled at various C rates wherein 1C = 1670 mA g⁻¹. Voltage capacity plots of Li-S cells using **c)** only carbon black and **d)** coffee-containing electrodes. Below are voltage capacitance plots based on c) and d) – **e)** and **g)** for α -S₈ and **f)** and **h)** for coffee-containing electrodes. * in h) emphasises the presence of dV/dQ peaks still present in the 100th cycle when pyrolysed coffee is incorporated in the electrode mixture, denoting that Li-S electrochemical conversion phenomena still occurs distinctly even at the 100th cycle.

Closer inspection of the reactions involved during cycling is afforded by the voltage versus capacity plots shown in **Figure 4.6c** and **d**. The points of inflection in these plots reflect the occurrence of a reaction, and thus the voltage capacitance plots

shown in **Figure 4.6 e, g** and **f, h** respectively are used to emphasise these occurrences. As shown by the lack of peak intensity in **Figure 4.6e** and **g** the redox processes involved during cycling a standard α -S₈-carbon black electrode are not well resolved. Towards later cycles, the initial plateau, reflective of the formation of Li₂S₄ from Li₂S₈^{39, 40} is not even present in the voltage versus capacity plot. This implies that the reduction step is no longer contributing to the overall specific capacity and is highly indicative of the polysulfide shuttle effect. Most of the reduction process involves the reduction of Li₂S₄ (solution) to Li₂S₂ and Li₂S (solids)³⁹, which means that most of the active material on the electrode surface is being used within the initial cycles. Comparing this to **Figure 4.6d, f, h**, the coffee-containing samples produced much more distinct peaks indicating more resolved redox processes. As shown in **Figure 4.6h**, the conversion from Li₂S₈→Li₂S (emphasised by the peaks marked by * in the dV/dQ plots) is still present and contributing to the overall specific capacity up to the 100th cycle. This indicates that the addition of pyrolysed coffee has beneficial effects to prolonging the reversible nature of the electrode. Additionally, there appears to be no unusual voltage capacitance features when using the coffee-containing samples (**Figure 4.6d**) which would suggest any observable contributions from competing reactions arising from MgS impurities.

It is important to note that whilst the specific capacity of the Li-S cell decreases with increasing C rate (as demonstrated in **Figure 4.6b**, from ~ 350 mAh g⁻¹ at 0.1 C vs ~150 mAh g⁻¹ at 1.0 C by the 100th cycle) minimal differences between these C rates are observed when considering the Coulombic efficiencies (CE) of the Li-S cells at each rate, i.e., output discharge capacity versus input charge capacity. As shown in the appendix **Figure A. 3**, all cells tested at the different C rates (0.1, 0.5 and 1.0 C) demonstrate high coulombic efficiencies of above 98% up to 100 cycles. Moreover, as demonstrated in the appendix **Figure A. 3** all Li-S cells cycled at different C rates, when using pyrolysed coffee in Li-S cells, begin to stabilize at ~98% CE by the 10th cycle. This is a significant contrast to CE values obtained for Li-S cells tested without the use of pyrolysed coffee as seen in the appendix **Figure A. 4**. Without the addition of pyrolysed coffee, the CE values appear to be unstable within the first 100 cycles even at a low 0.1 C rate. This contrast implies that the addition of pyrolysed coffee seems to result in a generally more stable Li-S cell system.

This enhanced stability afforded by addition of carbon structures has also been reported in previous studies. A previous investigation using carbon derived from the bark of plane trees by Xu *et al.* reports a high coulombic efficiency of 98% and specific capacity of 608 mAh g⁻¹ after 60 cycles at 0.2 A g⁻¹.³⁵ The authors concluded that the markedly improved performance is due to an increased stability and conductivity due to the three-dimensional, hierarchal porous carbon architecture afforded by the treated bark, i.e., the mixture of micro-, meso- and macro-pores. This claim is based on their observed marked improvement in electrochemical performance when compared to a mostly nanoporous structure such as multi-walled carbon nanotubes (MWCNTs). Similar conclusions were drawn from a study involving the use of carbons derived from waste cotton textiles.⁴¹ The authors report a reversible capacity of 434.5 mAh g⁻¹ after 300 cycles at 1C when using cotton-derived carbons. A study on carbon derived from almond shells by Benítez *et al.* also links an improved stability of Li-S cell performance to the microporous structure yielded from inedible biomass residues.⁴² These results clearly indicate that there is significant potential in using biomass derived carbons and our results are a valuable addition to the current literature with respect to the use of biomass-derived waste-streams.

4.3.3 Electrochemical characterisation through XANES

An understanding of the surface species formed over multiple cycling can be afforded by *ex situ* XANES measurements of extracted electrodes. This technique was used as a probe to characterise the S, C and F-K-edges. Monitoring of these specific edges can shed light on the effectiveness in sulfur entrapment, alterations in the carbon framework, as well as speciation of fluorinated salts on the electrode surface. In this work, the coffee-derived S electrode was probed and the XANES data is extremely sensitive to the surface chemistry and hence able to shed light on the electrode stability and the solid electrolyte interface (SEI) layer.

The S K-edge of electrode samples at different electrochemical states are shown in **Figure 4.7a**. In the fresh state (black trace, one edge peak at approximately 2472 eV is observed, which indicates the presence of elemental sulfur (σ^* S-S). Initially upon 1st discharge (red trace **Figure 4.7a**) the most prominent peak appears at approximately 2482 eV. Edge features at such high energies represent a higher

oxidation state of sulfur and have been previously attributed to sulfate species, whilst lower energy edge feature at ~2477 eV could pertain to lower oxidation state RSO_2^- intermediate species ($\text{CF}_3\text{SO}_2\text{N}^-$ and CF_3SO_2^-).⁴³⁻⁴⁶ Both these species are likely to be sourced from the electrolyte salts such as LiTFSI and analogues or solid polysulfide discharge species that may collect near the electrode after electrochemical treatment. In the following charged state (green trace **Figure 4.7a_{ii}**) this high energy feature is largely absent, suggesting electrochemical reversibility. Over multiple cycles, as represented in **Figure 4.7a_{iii}**, **iv**, and **v** of the 5th, 10th and 20th cycles respectively, the discharged (red trace) and charged (green trace) profiles appear to become increasingly similar, implying the formation of a stable SEI layer. Arguably there appears to be slight anomalies with regards to the profiles at 10th discharge (**Figure 4.7a_{iv}**), which are not present in the earlier 5th cycle (**Figure 4.7a_{iii}**) and later 20th cycle (**Figure 4.7a_v**) data. At most this anomaly may indicate that the SEI is slightly metastable and slight removal of the sulfate species at higher energies (or locally higher potentials/currents) can still occur at longer electrochemical cycles or intermittently. However, overall evaluation of the S K-edge at all the observed electrochemical states seems to suggest that the SEI is generally stable beyond the 5th cycle. Comparatively, this marked stability of the SEI, revealed *via* S K-edge XANES spectroscopy (reported in previous work), is not evident in Li-S cells utilising commercial carbon black, suggesting the effects relate to the use of pyrolysed coffee.⁴⁷

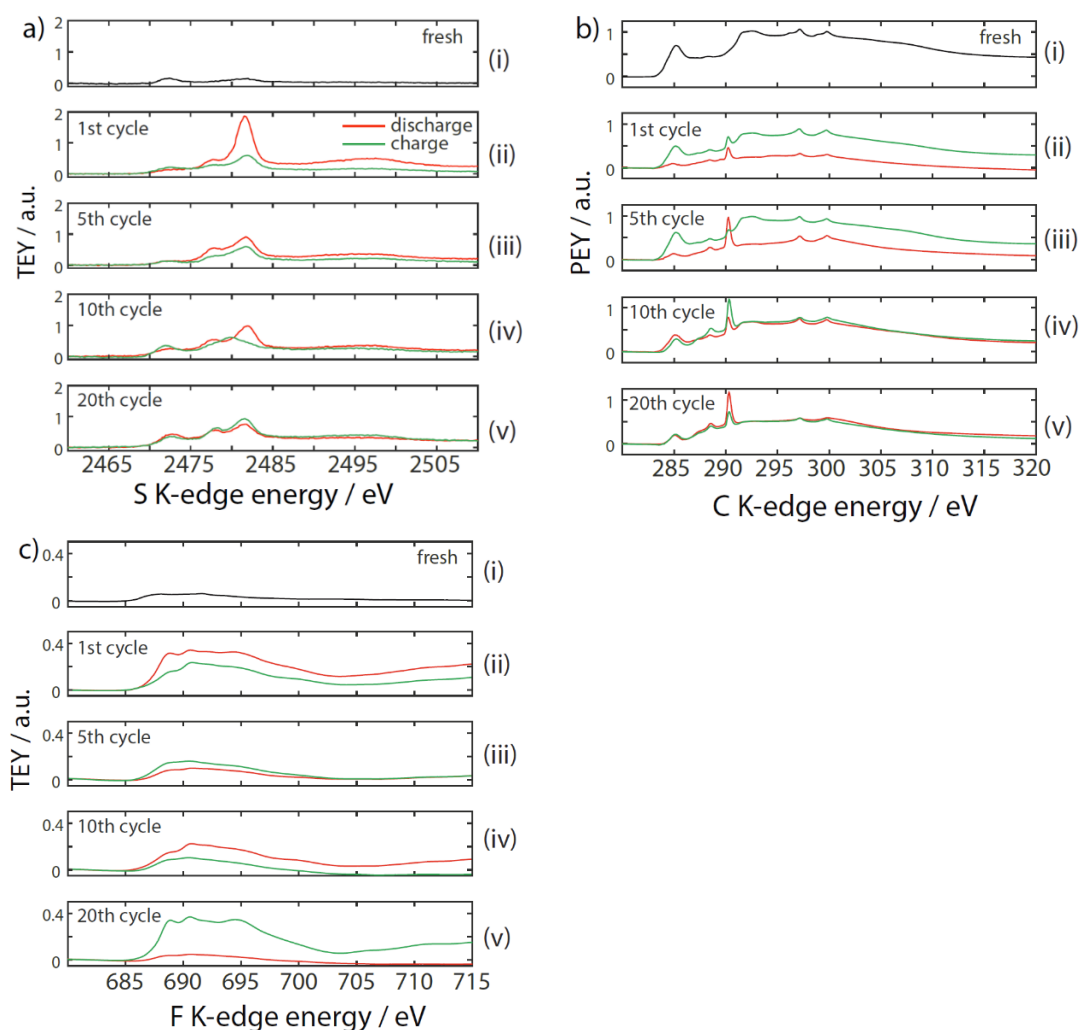


Figure 4.7 – a) S K-edge, b) C K-edge, and c) F K-edge XANES spectra at various electrochemical states. Black traces represent fresh electrode samples without any electrochemical treatment. The red traces represent the discharged states and the green traces represent the subsequent charged states.

Notably, also beyond the 5th cycle, the strength of the S K-edge feature at 2477 eV (RSO_2^-) appears to increase relative to the feature at 2482 eV (SO_4^{2-}), suggesting a decreased ability for sulfur to completely oxidise to SO_4^{2-} . According to Aurbach *et al.*, complete oxidation of sulfur to SO_4^{2-} is largely dependent on the accessibility of LiNO_3 salt.⁴⁸ Furthermore, the authors also claim that a high concentration of Li_2S_6 has an attenuating effect on the lithium surface reactivity, particularly LiNO_3 salt oxidation to form $\text{Li}_x\text{SO}_4^{2-}$. Whilst the SEI appears to be stable beyond the 5th cycle, as seen in **Figure 4.6a** (black datapoints), the specific capacity also appears to begin decreasing linearly at this point. This gradual decrease in capacity could be due to the stable SEI preventing complete oxidation of sulfur to SO_4^{2-} , producing a relatively larger population of intermediate species compared to in the initial cycles. Whilst not

clearly evident in voltage capacity plot shown in **Figure 4.6d**, the presence of MgS confirmed by XRD (**Figure 4.5b**) could result in competing Mg/S reactions which are known to have poor reversibility.⁴⁹ Such competing reactions would result in irreversible plating as well as an overall decrease in Li_2S_6 concentration ultimately suppressing complete oxidation of sulfur to SO_4^{2-} species. Thus, whilst a stable SEI appears to be formed after the first five cycles, it could contain species that suppress Li-S redox and compromise the specific capacity of the cell over cycling.

Considering the carbon environment, the C K-edge XANES spectra of the electrochemically treated samples are shown in **Figure 4.7b**. In the fresh state (black trace **Figure 4.7bi**) three main features are observed. The first signal at approximately 285 eV is typically associated with π^* C=C, 288 eV to σ^* C-S or C-H, and 292 eV to σ^* C-C^{46, 50, 51}. The π^* C=C and σ^* C-C signals are expected to arise from the hard carbon component. The σ^* C-H environment could arise from the PVDF binder in the electrode. Whilst the signal at ~288 eV has previously been attributed to σ^* C-S environments and it is not possible to resolve a difference between σ^* C-S and σ^* C-H from the obtained data unless the C-S environment is expected to be a large contribution. Although crosslinked sulfur environments (interpreted as σ^* C-S) are an impurity of pyrolysed coffee grounds, these are expected to be in relatively low quantities relative to PVDF and is hence unlikely to be a large contributor of this signal at 288 eV. Note, it is not expected that the added S is forming C-S during the electrode preparation process.

Comparing the C K-edge of the fresh state to later electrochemical cycles (**Figure 4.7b ii, iii, iv and v**), the profile of the fresh state (black trace **Figure 4.7bi**) seem to be maintained throughout, with the addition of a sharp peak at ~291 eV. This sharp feature appears to be the only dynamic feature and has been previously assigned to graphitic sp^2 hybridised carbon. The sp^2 hybridised graphitic carbon is reported to present as two characteristic signals at 285.2 eV and 290.2 eV in C K-edge XANES spectra.⁵² The sharp excitonic peak at ~291 eV is also typically accompanied by σ^* resonance contributions at higher energies, likely to be the peaks at ~297 and 300 eV observed from the fresh state to the 20th cycle.⁵³ The first expected signal overlaps with π^* C=C previously observed in the fresh state. The increase of the signal at ~291 eV from the fresh state (black trace **Figure 4.7bi**) to the 1st discharged state (red trace **Figure 4.7bii**) seems to indicate an increase in ordered graphitic properties over

cycling. Similar to observations in the S K-edge, the carbon environment appears to stabilise over multiple cycling, particularly from the 10th cycle (**Figure 4.7b iv**) onwards. This stable profile at later cycles support the hypothesis that the SEI becomes stable after or with multiple cycling.

With regards to the fluorine environment, the F K-edge spectra are shown in **Figure 4.7c**. Whilst the resolution of the spectra does not allow for detailed characterisation of individual fluorine environments, there are significant profile variations between each measurement condition. The most notable and expected sources of fluorine in the sample are from the electrolyte salt LiTFSI and PVDF binder in the electrode. LiTFSI, which is used here, is a salt used typically as a protective additive in the electrolyte for Li-S cells and is evidenced to play a significant role in stable SEI formation^{39, 54, 55}. In contrast, to the S K-edge and C K-edge, the F K-edge profiles vary from the fresh state up to the 20th cycle between charge and discharge. This variation implies that the fluorine based SEI environment remains dynamic even up to the 20th cycle.

4.3.4 Disordered carbons

The type of carbon and its role is good to discuss in terms of the electrode. Carbon structures in S-based electrodes serve functions of improving electrode stability and performance, typically by a combination of entrapment of S, enhancement of conductivity and the physical structure of the electrode in addition to other facets. A variety of factors influence reported performance results in carbon-sulfur electrodes, ranging from controllable parameters such as electrode loading, applied electrochemistry, electrode thickness, electrolyte concentrations to more challenging to establish and control parameters such as utilisation, disorder in the carbon and uniformity of electrode and composition. Therefore, the underlying carbon structure, its interaction with S during electrode preparation and during operation are critical to begin to understand.

It has been generally accepted that polysulfide species can be immobilised *via* physical entrapment. This relies on the knowledge that polysulfide molecules readily form aggregates in solution.⁵⁶ Biochars are inherently disordered and are likely to assist in entrapment however it is difficult to evidence such entrapment from highly disordered structures and whether it is the entrapment that prolongs cycle life.

Intuitively, smaller pore apertures are linked to more effective polysulfide entrapment. However, correlation between pore size and polysulfide entrapment to cell performance is not straightforward.

Whilst effective in mitigating polysulfide dissolution, entrapment in porous structures that are too small and compact can also completely inhibit access of the electrolyte to the active sulfur material – an essential interaction to allow Li-S redox to occur. This directly influences S utilisation. According to density functional theory (DFT) calculations, DME and DOL solvent interaction with long chain polysulfides in nanoporous (< 100 nm diameter) graphene structures is observed to play a crucial role in the dissociation of Li_2S_8 and Li_2S_6 to S_8^{2-} and S_6^{2-} dianions respectively and solvated Li ions. On the other hand, microporous carbon structures (< 2 nm diameter⁵⁷), inhibited access of electrolyte to the active material and presented a loss of capacity in a Li-S cell over multiple cycling.^{58, 59} Conversely when using microporous carbon structures (> 50 nm diameter⁵⁷) issues related to electrolyte access to the active material are less significant however the structure's ability to trap polysulfides is also lowered.

Other work suggests that improving the overall Li-S cell performance requires carbon structures with integrated benefits from multiple porous systems or various levels of porosity.⁶⁰ This work features the use of hierarchically ordered meso (between 2 nm and 50 nm diameter) and macroporous carbon in improving specific capacity and stability in Li-S cells. The authors propose that while the mesoporous component serves as “containers” for redox active sulfur species, the macroporous component allows for electrolyte solvent to access the active material. This perspective is also shared amongst other works observing high Li-S cell capacity and long cycle lifetimes.^{35, 42, 61}

Further work illustrated that very narrow micropores (i.e. ~1 nm) can result in a so called “quasi-solid-state reaction” (QSS) wherein Li reactions occur under solvent deficient conditions.⁶² This phenomenon is a similar observation to redox behaviour in solid-state Li-S cells wherein only one voltage plateau is observed in cyclic voltammetry during both reduction and oxidation. The authors argue that while discussion with regards to QSS phenomena typically points toward creating small sulfur molecules (~1 nm), this is not a necessary condition for QSS. Rather they emphasise how small porous structures play a key role in forming SEI type surface

films on the carbon-sulfur electrode. This SEI formation thus prevents direct contact between encapsulated sulfur and the electrolyte solvent, facilitating desolvation of Li ions. Hence nanoporous structures also play a key role in SEI formation which in turn can have an effect on sulfur entrapment during cycling – an explanation that is often missed/overlooked in favour of physical sulfur entrapment perceived in the original carbon structure.

Correlating pore structure and polysulfide dissolution in a disordered system is generally difficult particularly when it is an attempt to precisely determine factors that are responsible for observed improvements in Li-S cell performance. This is because finding the ratio of micro-, meso- and macropores that are ideal in a disordered carbon structure is in itself complex let alone relating the ratio to the best performing Li-S cell. Furthermore, the evolution of the pore structure and generation of the SEI are critical performance parameter and these are generated in-cell and in some cases evolve with cycling. Therefore, the original pore structure in a disordered system is modified in cell and this needs to be taken into account. Findings in this work through XANES analysis suggests that the coffee-derived nanoporous carbon structures in combination with the S may have a stabilising effect on the SEI thus impeding the polysulfide shuttle effect. However, the effect of direct physical sulfur confinement in the porous structures cannot be ignored in such arguments and are not directly evidenced here.

4.4 Conclusion

The simple addition of pyrolysed coffee grounds (yielded *via* facile one-step pyrolysis at 900 °C) to the negative electrode of a Li-S cell results in a markedly improved cell stability. This is most evident through the stable electrochemical performance – achieving specific capacities of $\sim 340 \text{ mAh g}^{-1}$ at 0.1 C after 100 cycles and coulombic efficiencies of $>98\%$ at 1 C even after 100 cycles. This marked improvement in stability is likely to be related to an enhanced stability of the SEI formed within the first 10 cycles, perhaps linked to the complexity of the macro-mesoporous carbon architecture and disordered hard carbon-based materials afforded by biomass waste coffee grounds.

Such enhanced stability afforded by the pyrolysed coffee is a promising achievement in the treatment of waste-derived carbons for applications in energy

storage, considering the facile pyrolysis protocol and no attempts to remove trace inorganic impurities. Whilst the electrochemical results did not reveal any unique redox behaviour to suggest any direct impact from the trace inorganic impurities, their indirect effects on SEI speciation and thus overall cell performance remains to be unexplored. Future work can be directed to investigate the use of pyrolysed coffee void of these trace inorganic impurities, and whether removal of the impurities improves the overall Li-S cell performance.

Ex situ electrochemical characterisation of the electrodes through XANES reveals observable accumulation of fluorine-containing species, most likely linked to the deposition of LiTFSI protective salt commonly associated with stable SEI formation. XANES analysis also reflects a stable sulfur environment after the 5th cycle, and a stable carbon environment beyond the 10th cycle. This evidence revealed through XANES spectroscopy supports the hypothesis that the carbon architecture resulting from biomass sources improve the stability of interphases involved in Li-S electrochemistry.

4.5 References

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Chapter 5: Poly(S-*r*-squalene)

This chapter presents the published results of poly(S-*r*-squalene) copolymeric frameworks and their application as electrode materials in Li-S cells.¹

5.1 Introduction

In the scope of sulfur-rich copolymers for use in Li-S cells, the goal is to synthesise a stable sulfur-rich copolymer with optimal sulfur chain lengths.² To copolymerise a monomer with S₈, the sulfur must first be heated up to at least its floor temperature (159 °C)³ to initiate a ring-opening polymerisation (ROP) reaction.⁴ This allows for the homolytic cleavage of S-S bonds and the formation of free thiyl radicals to attack other S₈ rings and grow longer polysulfide chains. However, this reaction is reversible, meaning that the thiyl radicals can depolymerise to expel S₈ and other oligomeric sulfur species⁴. Therefore, without a hydrocarbon-based cross-linker, the polysulfides are unstable and will revert to the more thermodynamically favoured S₈ ring conformation at ambient temperature.⁵

Therefore, in selecting a suitable monomer to copolymerise with elemental sulfur, the following should be considered: (1) The monomer should be an unfunctionalized polyene cross-linker, *i.e.*, contains two or more reactive C=C ends that can chemically attach to the thiyl radicals without interfering with the sulfur electrochemical activity and (2) the monomer's physical properties are compatible with the conditions for inverse vulcanisation copolymerisation, *i.e.*, the boiling point is higher than 159 °C. The polyterpene monomer squalene is shown in **Figure 5.1**. Squalene was chosen due to its low cost and abundance, but also because it was anticipated that the long alkene chains would structurally facilitate sulfur crosslinking during inverse vulcanisation. Further interest in the synthesis of poly(S-*r*-squalene) is based on the proposition that, due to similarities in functional groups involved, the polyterpene squalene units could give rise properties that are similar in terms of its malleability to vulcanised rubbers.⁶ In contrast to the bulkier structure of 1,3-diisopropenylbenzene containing an inactive aromatic ring, the long squalene chains were hypothesised^{7, 8} to provide a more branched network with incorporated S units. Provided there are differences between these architectures in terms of selective polysulfide entrapment, tuneability of the

copolymeric properties can thus be conducted based on choice of crosslinking monomer and predicted structures.

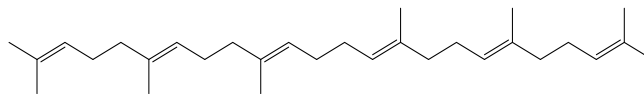


Figure 5.1 – The polyterpene cross-linking monomer squalene ($C_{30}H_{50}$).

This work reports a detailed structural characterisation of poly(S-*r*-squalene) copolymeric cathode material, (first developed by Sahu *et al.*)⁸ and how the difference in its chemical structure lends itself to different electrochemical-structural properties when implemented in Li-S cells in comparison to poly(S-*r*-DIB). The rationale and synthesis of poly(S-*r*-squalene) is discussed, and the material is thoroughly characterized using SSNMR, X-ray absorption near edge spectroscopy (XANES) and X-ray photoemission spectroscopy (XPS) techniques.

5.2 Methodology

5.2.1 Synthesis of Poly(S-*r*-squalene)

Synthesis of poly(S-*r*-squalene) was performed following the procedure outlined by Chung *et al.*² Sulfur (S_8 , 4.50 g, 17.6 mmol) was added to a round bottom flask fitted with a magnetic stir bar and heated 160 °C under N_2 flow in an oil bath until an orange molten phase was achieved. The monomer (squalene, 0.50 g, 3.16 mmol) was added to the molten sulfur directly *via* syringe. The reaction mixture was stirred and kept at 160 °C for another 15 minutes then cooled to room temperature affording an olive-grey solid (yield: 4.76 g, 95%).

5.2.2 Coin-Cell Fabrication and Electrochemical Testing

A cathode slurry was prepared by mixing a 75:20:5 wt% ratio of poly(S-*r*-squalene) (90 wt% sulfur), Timcal Super P® conductive carbon black and polyvinylidene difluoride (PVDF) binder in N-methyl-2-pyrrolidone solvent (NMP, 4.0 mL/g of total slurry powder). The slurry mixture was homogenized in a mortar and pestle prior to mechanical stirring at room temperature for 16 h. The resulting slurry was cast onto an Al-foil current collector at 200 μm thickness using a doctor blade and dried at 80 °C inside a vacuum oven for 24 h to remove the residual solvent, resulting in a copolymeric cathode with an average sulfur loading of 1.9 mg cm^{-2} . The cathodes

were transferred into an Ar-filled glovebox for assembly into CR2032 coin cells with a glassfibre-separator soaked in excess electrolyte and a Li-foil anode. The electrolyte used was 0.38 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.31 M lithium nitrate (LiNO₃) salts in a 1:1 v/v mixture of 1,3-dioxolane and 1,2-dimethoxyethane, following the composition used in previous work related to poly(S-*r*-DIB)⁹. Galvanostatic testing of the Li-S half cells were conducted using a Neware BTS3000 cell-cycler system between 1.7-2.6 V at C/10 (167.5 mAh g⁻¹) with an initial 6 h rest step after cell fabrication.

For *ex situ* experiments, the electrodes were extracted at the desired state of charge and dried for at least 24h under inert atmosphere in an Ar-filled glovebox without washing. The typical regime of washing the extracted electrodes with DME or DMC solvent was refrained in order to accurately capture the species formed on the surface of the electrodes after electrochemical treatment. The adsorption of electrolytic species was also an integral part in the analysis of this work and required the samples to be measured without any prior washing with solvent.

5.2.3 Solid-State NMR Measurements

The ¹³C NMR experiments were carried out on a Bruker Biospin Avance III 300 MHz spectrometer with a wide bore 7 T superconducting magnet operating at 75 MHz and 300 MHz for the ¹³C and ¹H nuclei respectively. The ⁷Li SSNMR experiments were conducted on a Bruker Biospin Avance III 700 MHz spectrometer with a standard bore 16.4 T superconducting magnet operating at 272 MHz and 700 MHz for the ⁷Li and ¹H nuclei respectively. Detailed procedures regarding packing of the samples, the ¹H-¹³C CP-TOSS and ¹H-¹³C HETCOR experiments (with respect to the as-synthesised copolymer), and the ⁷Li MAS, ¹H-⁷Li CP-MAS and ⁷Li-⁷Li EXSY experiments (with respect to the electrochemically treated samples) have been outlined in a previous work using poly(S-*r*-DIB) in place of poly(S-*r*-squalene).⁹

The experiments conducted to obtain spin-lattice (*T*₁) relaxation times followed the saturation-recovery pulse sequence. This consists of an initial 90 ° pulse comb, that is a train of twenty 90 ° pulses separated by 1-5 ms delays in order achieve maximum desaturation of signal magnetization, followed by another 90 ° pulse after a set delay τ where magnetisation is allowed to recover. These saturation recovery experiments were conducted at several τ = 10 ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms,

200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 650 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7.5 s, 10 s, 30 s and 60 s in order to obtain the T_1 relaxation times.

Analysis of the magnetisation signal recovery in the saturation recovery experiments for T_1 measurements was conducted using the Bruker Topspin® software 4.0.7 – from each spectrum the median values were taken as the signal recovered when the maximum signal intensity M_0 at the peak centre minus the signal intensity at time τ , M_z equals zero. The upper and lower bounds were taken when the maximum signal intensity M_0 at the peak centre minus the signal intensity at time τ , M_z is above or below twice the signal to noise of the spectrum at time τ . Subsequent fitting of the M_z/M_0 vs time τ plots to exponential functions was conducted using scripts developed in the group for MATLAB® in order to yield the T_1 values.

Note that the ^7Li NMR spectra obtained in this work is referenced to solid LiCl, set to 0.0 ppm, as opposed to the more typically used 1 M LiCl. Based on work by Meyer *et al.*, the chemical shift between 1 M LiCl and solid LiCl is upfield (i.e. lower chemical shift) by 1.1 ppm.¹⁰ According to Alam *et al.*, hydration available in 1 M LiCl can have a deshielding effect on Li^+ (i.e. higher chemical shift)¹¹ and thus it is expected that the chemical shifts obtained in the ^7Li NMR work is 1.1 ppm higher than shifts reported in literature. The ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) (0.0 ppm) and the CH_2 peak of solid adamantane at 38.48 ppm as a secondary reference.¹² All peak deconvolution of NMR spectra were conducted using DMfit software.¹³

5.2.4 TGA/DTG Measurements

Thermogravimetric and Derivative Thermogravimetry analyses of the samples were conducted using a METTLER TOLEDO Thermogravimetric Analyzer STAR^e system under nitrogen gas at a heating rate of 10 °C/min.

5.2.5 XANES and XPS Measurements

The C K and S K-Edge XANES measurements were conducted on the soft X-ray beamline at the Australian Synchrotron¹⁴ following the same procedures outlined in previous work.⁹ All samples were measured simultaneously with TEY of an Au mesh situated in front of the sample, the incident beam (I_0), for normalisation of the beam

energy between scans (i.e., PEY signal divided by the I_0 TEY signal). S K-edge spectra of the samples were also simultaneously measured with a MoS₂ reference foil maintained in the beamline with a known absorption edge centred at 2471.2 eV. For C K-edge spectra of the samples, contributions from internal carbon contamination of the beamline were accounted for by scanning a clean Si photodiode as reference that is then used for normalisation following the procedure outlined by Watts *et al.*¹⁵ The C K-edge spectra of the samples were also measured simultaneously with TEY of a pyrolytic graphite (HOPG) reference foil maintained in the beamline with a known absorption edge centred at 291.65(26) eV. Calibration and normalisation of the C and S K-edge XANES data were conducted using the Quick AS NEXAFS Tool (QANT) macro developed for Igor Pro¹⁶ and followed by analysis using the Athena software package.¹⁷

High resolution soft XPS measurements at the S L and C K-edge of the electrode samples were also conducted on the soft X-ray beamline at the Australian Synchrotron¹⁴ under the same sample conditions (i.e. under ultra-high vacuum (UHV) maintained at better than 1.5×10^{-9} mbar) using a SPECS Phoibos 150 Hemispherical Analyser. These measurements were conducted using synchrotron radiation energy set at 730 eV for both edges. Subsequent peak analyses were conducted using SPECSlab Prodigy and the Origin software package for peak deconvolution.

5.2.6 X-Ray Powder Diffraction Measurements

XRD patterns of the copolymer and cathode materials were collected using a Philips X'Pert MPD diffractometer working with Cu K α radiation at room temperature in the $10 < 2\theta^\circ < 90$ range, with a 0.026° step size and data collection of 750 s per step. Rietveld analyses were carried out using the GSAS II¹⁸ software suite. The parameters refined from the α - and β -sulfur phases were the lattice parameters, atomic displacement parameters of the atoms, combined with refinement of the Gaussian (U, V, W) and Lorentzian (X, Y, Z) profile parameters to account for effects of instrument and sample broadening.

5.3 Results and Discussion

5.3.1 Formation and characterisation of the crosslinks

The successful formation of sulfur crosslinks is suggested by the resonances observed in the solid state ^1H - ^{13}C CP-TOSS NMR spectra of the poly(S-*r*-squalene) copolymer shown in **Figure 5.2a**. Models were developed *via* peak deconvolution of the spectra, see the appendix **Figure A. 5** and **Table A. 3**. **Figure 1a** shows that whilst the copolymer retains some resonances shared with the squalene precursor (see **Figure 5.2b**), there are also new resonances observed, of particular note are the resonances centred at $\delta_{13\text{C}} > 40\text{-}60$ ppm in the aliphatic region (ppm range shaded in red with dashed lines marking the peak centres in **Figure 5.2a**). Resonances in this range have been observed in C-S crosslinks found in vulcanised rubbers, structures which are similar to what is expected to form in poly(S-*r*-squalene).¹⁸⁻¹⁹ However, assignment of each resonance to specific C-S-containing structures is not straightforward due to the complexity and significant overlap between the broad line shapes.

Provided that the goal is to maximise sulfur crosslinking, the ideal case would involve formation of sulfur crosslinks saturating both ends of all the double bonds of squalene. In such a case, the resulting copolymer would be expected to be completely aliphatic, with each squalene double bond exchanged for two sulfur crosslinks. Retention of the vinylic resonances centred at 136.8 and 126.3 ppm as shown in the ^1H - ^{13}C CPMAS NMR spectrum in **Figure 5.2a** indicates incomplete saturation of the double bonds of squalene during inverse vulcanisation. This incomplete saturation can either mean that:

- (1) some unreacted squalene precursor remains in the poly(S-*r*-squalene) copolymeric product although a S excess is used in the synthesis,
- (2) some but not all the double bonds in squalene react to form sulfur crosslinks.

Upon consideration of the reaction pathways for uncatalysed inverse vulcanisation, whilst not yet precisely understood, there are two pathways that have been widely agreed upon, of which are *via*: (1) direct sulfur addition to the double bond, and (2) hydrogen abstraction at the C- α position (i.e. adjacent) relative to the double bond (shown in **Figure 5.2c** and **d** respectively). A debate remains as to whether only one or both pathways occur under experimental conditions. Between these two pathways, direct sulfur addition to the double bond (see **Figure 5.2c**) involves a more stable

carbon free radical and is thus considered to be the more favourable pathway during inverse vulcanisation. Conversely some works on conventional vulcanisation of rubbers claim the formation of sulfur crosslinks *via* hydrogen abstraction at the C- α position (as shown in **Figure 5.2d**) to be the main reaction pathway.¹⁹⁻²³ The possibility of both pathways has also been reported to occur in several inverse vulcanised copolymers.²⁴⁻²⁶

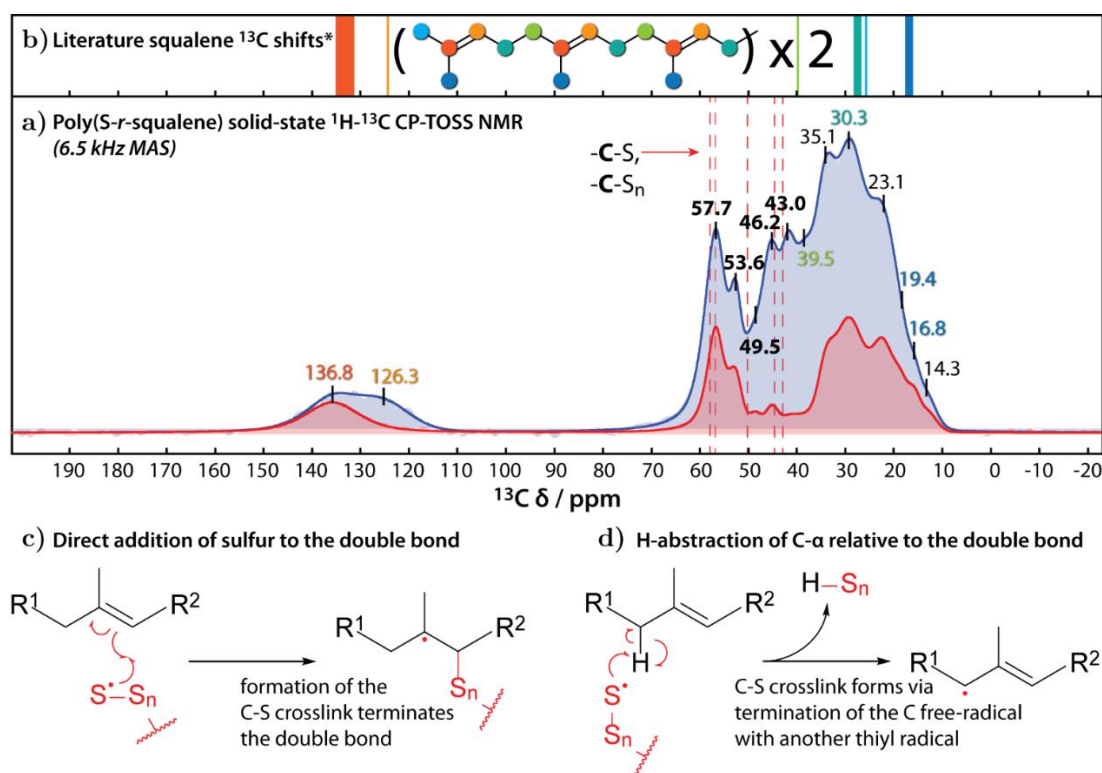


Figure 5.2 – a) ^1H - ^{13}C CP-TOSS solid-state NMR spectra of poly(S-*r*-squalene). The blue region is the proton-enhanced ^{13}C signal, and the red region is the signal acquired with a 40 μs gated decoupling filter. The bold blue and red traces are fitted models of the spectra which are convolutions of pseudo-Voigt line-shapes representing various ^{13}C resonances. Details regarding the peak fits and deconvolution of line-shapes from the NMR spectra to develop these models can be found in the appendix **Figure A. 5** and **Table A. 3**. The red dashed lines mark resonances related to carbon-sulfur crosslinks reported in literature. **B)** shows ^{13}C chemical shift positions related to the squalene precursor reported in literature, the colours of the shaded regions corresponding to the same colour carbon positions mapped in the inset squalene molecular diagram. The proposed mechanisms for C-S crosslinking are visualised in **c)** *via* direct addition of sulfur to the double bond and **d)** *via* H-atom abstraction of C- α relative to the double bond.

Despite the seemingly different structures formed upon the first crosslinking event (**Figure 5.2c** and **d**), either of the reaction pathways can result in preserved

double bonds in the copolymeric product. Considering direct sulfur addition to the double bond (see **Figure 5.2c**), provided the tertiary carbon free radical is terminated by liberating a H-atom at C- α adjacent to the double bond (instead of by forming a second crosslink with another thiyl radical), this would preserve the double bond similarly to as proposed *via* the alternate pathway (see **Figure 5.2d**). Thus, similar structures can be justified *via* either pathway. Based on our observations and the literature, the inverse vulcanisation of S₈ and squalene can undergo a combination of the two pathways.

It was hypothesised that, assuming all double bonds of squalene undergo direct sulfur addition to the double bond during inverse vulcanisation, the resulting copolymer would be completely aliphatic and thus have greater molecular mobility (that is mainly referring to rotation of polymeric segments around covalent bonds) compared to poly(S-*r*-DIB). With evidence showing the preservation of double bonds and possibility of multiple crosslinking pathways, the assumption that poly(S-*r*-squalene) would have greater mobility than poly(S-*r*-DIB) no longer necessarily holds true.

5.3.2 Structural analysis

Solid state 2D ¹H-¹³C HETCOR NMR (shown in **Figure 5.3**) provides insight to the molecular mobility of poly(S-*r*-squalene) as well as the spatial proximities between different copolymeric fragments. As a basis for comparison, the vinylic carbon-proton resonance at $\delta_{13C} = 130$ ppm and $\delta_{1H} = 5.5$ ppm (case 1, orange $\leftrightarrow$ orange ¹³C and ¹H coloured region in **Figure 5.3**) reflects the signal strength of a C=CH protonated environment, assumed to be a copolymeric fragment with restricted molecular mobility (i.e. signal arises mainly from direct C-H bonding). Whilst restricted molecular mobility generally translates to strong ¹H-¹³C dipolar interactions (thus stronger signal),²⁷ this vinylic carbon-proton resonance is relatively weaker than all the other cross-peaks observed. This weak signal could be due to the relatively low degree of protonation (i.e. C=CH), which results in weak ¹H-¹³C dipolar interactions (thus weaker signal).²⁷ It could also be due to the overall low abundance of vinylic fragments relative to the aliphatics as previously observed in the ¹H-¹³C CP-TOSS of the copolymer in **Figure 5.2b**.

Nonetheless, the strongest resonance is observed between aliphatic carbons and aliphatic protons at $\delta_{13\text{C}} = 10\text{-}70$ ppm and $\delta_{1\text{H}} = 1.6$ ppm (case 2, yellow $\leftrightarrow$ yellow ^{13}C and ^1H coloured region shown in **Figure 5.3**). Similar to the vinylic resonances, the main contributing factor to signal strength could be the degree of protonation (as opposed to molecular mobility), that is generally higher in aliphatics compared to vinylics. The larger population of protons directly bonded to aliphatic carbons (vs vinylic) could account for the significantly greater signal strength compared to the vinylic carbon-proton resonance.

Apart from the above two resonances, some degree of correlation is also observed between the vinylic carbons and aliphatic protons and vice versa. Arguably, because this cross-peak relates to different copolymeric fragments, effects of molecular mobility can be assumed to be a greater contributing factor to ^1H - ^{13}C dipolar coupling and thus signal strength of this resonance compared to the above two cases (that only describe correlations within the same copolymeric fragments). Greater resolution achieved in the ^{13}C dimension (compared to ^1H) reveals three peak centres ($\delta_{13\text{C}} = 54.8, 44.6, \sim 32$ ppm as shown in **Figure 5.3**, case 3, yellow $\leftrightarrow$ orange ^{13}C and ^1H coloured regions) that show correlation with the broad vinylic proton resonance ($\delta_{1\text{H}} = \sim 5.5$ ppm). The signal strength of this cross-peak is slightly stronger than experienced by vinylic carbons-protons ($\sim 1.7\times$ the strength) but significantly weaker than aliphatic carbons-protons ($< \sim 0.1\times$ the strength). Assuming that the aliphatic fragments are highly mobile as hypothesised, a stronger correlation with the vinylic fragments is expected, the limiting factor being the strength of the signal acquired for aliphatic carbons-protons. With this considered, the signal strength related to correlations between the vinylic and aliphatic fragments is relatively weak, reflecting that the copolymer has low molecular mobility overall. One possible explanation for this low molecular mobility could be due to the preservation of the double bonds in the copolymer.

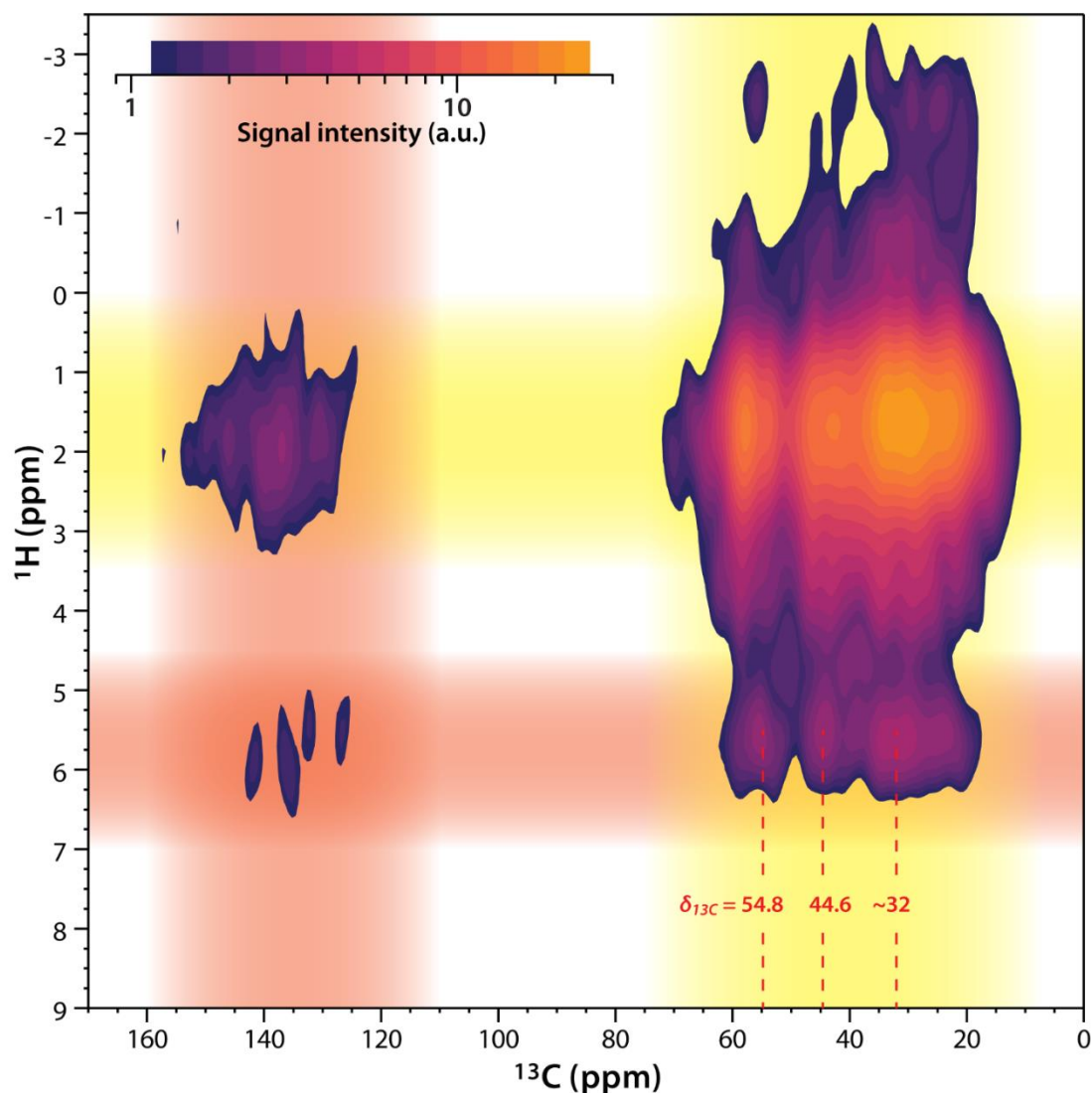


Figure 5.3 – ^1H - ^{13}C HETCOR NMR spectrum of poly(*S-r*-squalene), also shown later in **Figure 5.12c**. Yellow and orange regions highlight aliphatic and vinylic cross-peaks respectively and discussed in text.

5.3.3 The crystalline sulfur phases

X-ray powder diffraction on poly(*S-r*-squalene) allows for determination of the sulfur phases present in the copolymer and the prepared electrode. Previous work determined that this class of organo-sulfur compounds typically involve crystalline elemental-sulfur agglomerates as well as copolymeric sulfur.⁹ Poly(*S-r*-DIB) was found to be comprised of various permutations of sulfur-DIB copolymers, as well as a combination of α - S_8 (orthorhombic S_8 *Fddd*, ICDD, No. 01-078-1888) and β - S_8 (monoclinic S_8 *P2₁/c*, ICDD No. 01-071-0137) phases with a β - S_8 majority in the as-synthesised state. This finding implies that the poly(*S-r*-DIB) compound can stabilise the β - S_8 phase at room temperature. The powder X-ray diffraction data of poly(*S-r*-

squalene) in the as-synthesised state, **Figure 5.4a**, also shows a mixture of α -S₈ and β -S₈ phases. Unlike poly(S-*r*-DIB) however, poly(S-*r*-squalene) is mostly comprised of the more stable α -S₈ phase (black peak markers) as opposed to the β -S₈ phase (red peak markers) (phase fractions = 0.98(6):0.024(6)). When used as an active material in the cathode, the dominant sulfur phase remains as α -S₈, **Figure 5.4b**. Thus, unlike poly(S-*r*-DIB), poly(S-*r*-squalene) favours the α -S₈ phase in its composition.

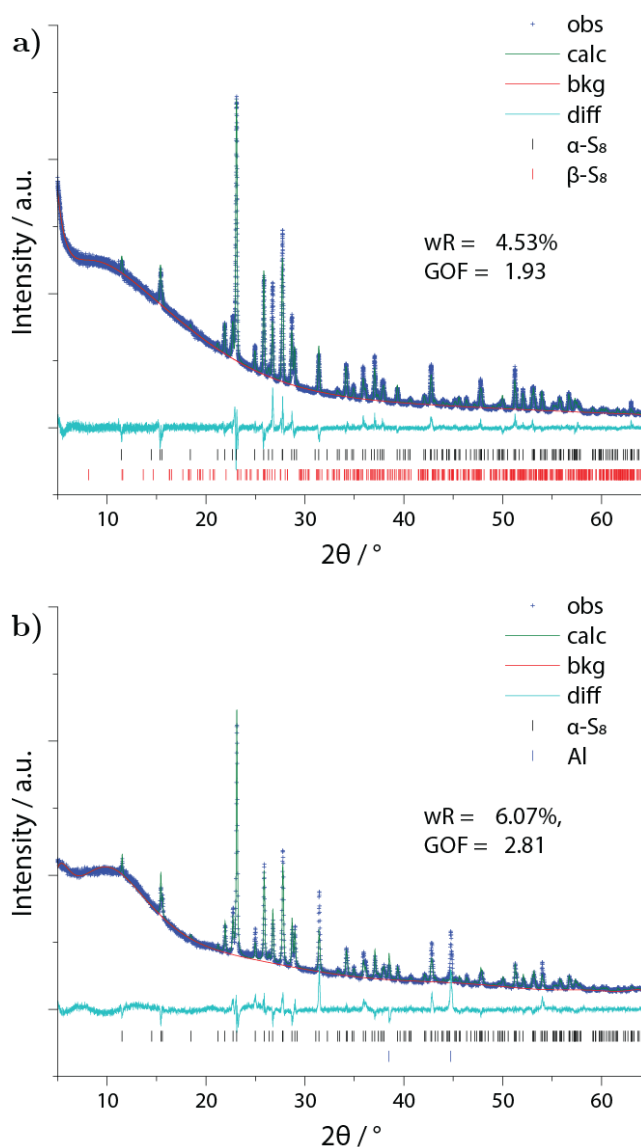


Figure 5.4 – Rietveld refinement of various sulfur phases with X-ray powder diffraction patterns of **a)** the as-synthesised poly(S-*r*-squalene) copolymeric compound and **b)** a cathode using the copolymer as the active cathode material (75:20:5 copolymer:carbon black:PVdF) casted onto an Al-foil substrate. The blue crosses represent the observed data points, green trace the calculated fit, red trace the calculated background, and teal trace the difference between the calculated and observed data. Black peak markers represent the α -S₈ phase, red the β -S₈ phase, and blue Al arising from the Al-foil substrate used in the cathode.

5.3.4 Characterisation of the local structure via XANES spectroscopy

To provide further insight into the structure of the polymeric component(s), the C K-edge XANES data were collected, and this revealed at least three carbon-bonding environments (see **Figure 5.5a**). The first edge-peak at 285.45 eV (indicated by the red dashed line) corresponds to a π^* C=C excitation,²⁸ which can be assigned to the vinylic functionalities, followed by σ^* C-S, C-H signals at 287.55 eV,²⁹ and σ^* C-C aliphatic carbons at 291.55 eV.²⁹ The relative intensity of the σ^* C-C aliphatic carbon signals at 287.55 and 291.55 eV compared to the π^* C=C excitation at 285.25 eV is also consistent with data from SSNMR measurements, suggesting that aliphatic carbons populate the copolymer more than vinylic carbons.

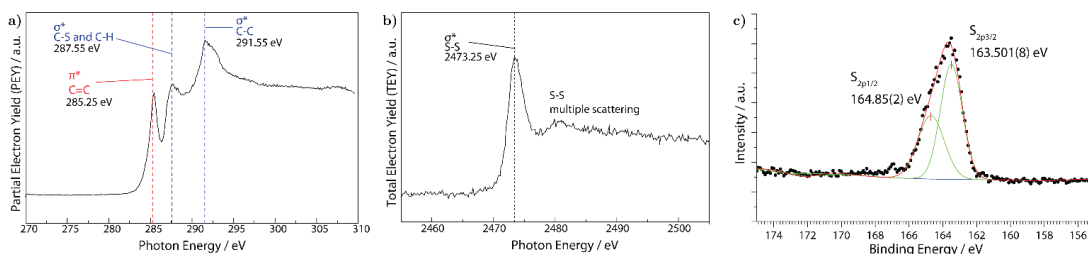


Figure 5.5 – **a)** shows XANES data for the C K-edge and **b)** the S K-edge of the untreated poly(S-*r*-squalene) cathode. The dashed lines mark different carbon and sulfur bonding environments. **c)** Soft XPS high resolution spectrum of the poly(S-*r*-squalene) cathode on the S L-edge conducted using synchrotron radiation at $h\nu = 730$ eV. The black dots indicate collected data points, blue trace calculated baseline, green traces are the gaussian peak fits, and the red trace is the cumulative fit of the peaks. Red peak markers denote the peak centres.

An assessment of the sulfur environment shows minimal differences in the bonding environment between poly(S-*r*-squalene) and poly(S-*r*-DIB) cathodes. S K-edge XANES profile of the poly(S-*r*-squalene) cathode shown in **Figure 5.5b** is identical to that of poly(S-*r*-DIB) (reported to be 2473.2 eV).⁹ A resonance at 2473.2 eV is observed for the poly(S-*r*-squalene) cathode indicating the presence of a σ^* S-S environment.³⁰ This indicates that the cathode contains sulfur chains, more specifically S-S environments, in agreement with previously discussed XRD data providing supportive evidence for the presence of elemental α -S₈ and β -S₈ phases. It is important to note that this XANES data alone does not have the sensitivity to differentiate between σ^* S-S environments arising from elemental or copolymeric sulfur.

Supplementary to the XANES study, soft-XPS measurements using synchrotron radiation were performed on the freshly untreated poly(S-*r*-squalene)

cathode, with a particular focus on the S L-edge. The S L-edge of bond-environments typically present as doublets $S_{2p3/2}$ and $S_{2p1/2}$ at a peak-area ratio of 2:1 split 1.2 eV apart,^{31, 32} and by analysis of the $S_{2p3/2}$ binding energy evidence for the formation of polysulfide chains can be obtained. The S L-edge spectrum of the poly(*S-r*-squalene) electrode (see **Figure 5.5c**) was fit at a fixed peak-area ratio of 2:1 $S_{2p3/2}:S_{2p1/2}$, which revealed binding energies of 163.501(8) and 164.85(2) eV for $S_{2p3/2}$ and $S_{2p1/2}$ signals respectively, slightly higher than 1.2 eV apart. The $S_{2p3/2}$ signal at 163.501(8) eV closely resembles the binding energy of central polysulfide sulfur³³, which confirms that poly(*S-r*-squalene) polysulfide chains are maintained in the fresh electrode.

A $S_{2p3/2}$ binding energy of 163.9 eV for terminal polysulfide sulfur is also expected based on previous work on commercial Li_2S .³³ Interestingly, this signal is not obvious in the poly(*S-r*-squalene) spectrum (see **Figure 5.5c**) which implies that there is no terminal polysulfide sulfur, which in turn likely indicates the presence of an S-C terminus to the polysulfide chain. The dominating $S_{2p3/2}$ signal at 163.501(8) eV corresponding to central polysulfide sulfur serves as strong evidence for the presence of copolymeric poly(*S-r*-squalene) in the cathode as initially proposed. C K-edge XPS of the cathode was also collected, shown in the appendix **Figure A.6**. The spectrum revealed a dominant peak at 284.384(4) eV corresponding to the carbon black environment present in the cathode.³⁴ The 10 wt% conductive carbon black component is an essential additive to guarantee the function of the Li-S cell. Whilst carbon environments from the copolymer are also expected as observed in NMR data, signals arising from this component is likely overwhelmed by signal arising from the carbon black component.

5.3.5 Thermal stability and decomposition of the copolymer

The thermal stability of poly(*S-r*-squalene) was analysed using thermogravimetric analysis (TGA). Through TGA, the stability of the copolymer at various temperatures can be monitored and is essential for insight in characterising the structural changes involved in the following experiments. The TGA curves produced by poly(*S-r*-squalene) using various squalene feeds are different to that of elemental sulfur (see **Figure 5.6**) further indicating that inverse vulcanisation occurs. Only poly(*S-r*-squalene) synthesised using 10 wt% squalene clearly shows a multi-step decomposition, as expressed by the two sharp peaks at approximately 250 and 350 °C

in the derivative of the curve (derivative thermogravimetry, DTG curve, dashed red trace, see **Figure 5.6**). The other samples synthesised using 20 and 30 wt% squalene (green and blue dashed traces respectively) only show one distinguishable first derivative peak at approximately 240 °C. In contrast, TGA of poly(S-*r*-DIB) presented in the appendix **Figure A.7** shows a multi-step decomposition for all feeds of DIB, with at least three distinct first derivative peak temperatures shown in the DTG. These three peaks suggest that poly(S-*r*-DIB) decomposes in at least three stages, and similarly poly(S-*r*-squalene) in at least one. One possible interpretation of this finding is that the different conformations in poly(S-*r*-DIB) decompose at different temperatures, whereas the conformations in poly(S-*r*-squalene) do not show any significant differences in terms of their thermal stability. Alternatively poly(S-*r*-DIB) is composed of multiple permutations of DIB monomeric units with S₈ as well as a mixture of α - and β -S₈.⁹

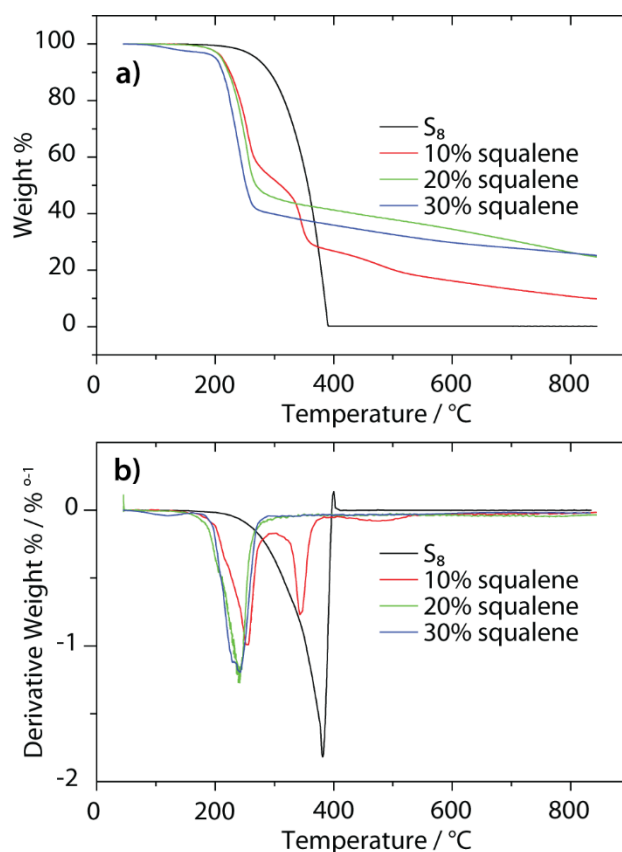


Figure 5.6 – a) Thermogravimetric analysis of elemental sulfur (black), and poly(S-*r*-squalene) synthesised using 10% (red), 20% (green), and 30% (blue) weight squalene feeds. Panel **b)** shows the derivative weight % based on panel a).

5.3.6 Electrochemical Performance and Behaviour

The electrochemical processes involved when using poly(*S-r*-squalene) electrodes in Li-S half cells were tested in triplicate at C/10 (equivalent to 167.5 mAh g⁻¹). The cells were tested within the nominal voltage range for this system (considered to be 1.7-2.6 V using poly(*S-r*-DIB) electrodes by Chung *et al.*)² with a lower limit of 1.7 V to prevent irreversible decomposition of LiNO₃ known to occur below 1.6 V.³⁵ Galvanostatic testing of the cells, **Figure 5.7a**, reveals a specific discharge capacity of 401 ± 25 mAh g⁻¹ at the second cycle and a specific discharge capacity of 339 ± 37 mAh g⁻¹ at 400 cycles (black data points). The specific charge capacity (green data points) is 419 ± 33 mAh g⁻¹ at the second cycle and 341 ± 37 mAh g⁻¹ at 400 cycles. It is important to note that the charge capacity of these Li-S half cells is generally higher than the discharge capacity due to an excess supply of Li from the electrolyte and the foil counter electrode, offsetting losses of Li in SEI formation and degradation of the electrolyte. A coulombic efficiency of 99.5 ± 1.0% is achieved at 400 cycles, demonstrating excellent cyclability indicative of stable SEI formation and minimal capacity fade over long-term cycling of the Li-S half cells. A lower coulombic efficiency and greater disparity between charge and discharge is experienced within the first 5 cycles, which can be interpreted as the formative stages of the SEI wherein the largest changes on the surface of either electrode are expected and concerns the main interest of this investigation. In terms of general trends in the electrochemical performance, a gradual decrease in the specific capacity is observed, which stabilises in the last 100 cycles. Further analysis of the voltage-capacity plots of one Li-S cell shows subtle differences in the electrochemical processes between cycles (voltage versus capacity and capacity with cycle number shown in **Figure 5.7c**). The voltage versus capacity plots generally follow typical sulfur redox behaviour with the expected plateau regions.³⁶ Upon further inspection by differential voltage (dV/dQ), **Figure 5.7c ii**, feature (1) is clearly observed in some cycles (in this case at cycle 20) but not others. Feature (1), appearing at lower voltages, is most likely attributed to the reduction of long chain polysulfides to short chain polysulfides. The absence of this feature in some cycles implies that this process is not guaranteed to occur under the conditions used. The presence of features (2) and (3) on the other hand, most likely attributed to the reduction of sulfur to long-chain polysulfides, unsurprisingly persists between all cycles.

The dV/dQ plots of up to 20 discharge cycles are calculated, and the charge (Q) of each feature (1-3) defined above determined in order to ascertain a trend in these electrochemical processes between cycles. This is wholly represented in **Figure 5.7e** wherein the Q values of each feature is plotted as a function of the discharge cycles. As expected, features (2) and (3) (red and orange data points) seem to persist between all the cycles and their Q values align with the trend in total charge, implying that the reduction of sulfur to long-chain polysulfides in this system is not challenging. Formation of the end products indicated by the presence of feature (1), does not occur until later cycles. As indicated by the amber data points, a clear feature (1) does not appear until the 8th cycle. This feature appears to be increasingly prominent until the 15th cycle, where feature (1) disappears, and reappears in the 16th cycle. The formation of end products occurs and reoccurs in later cycles, which could possibly be related to incomplete utilisation of the active material or a results of a dynamic solid electrolyte interface (SEI). Based on the collected XRD patterns in **Figure 5.4b**, elemental α -S₈ is observed in the bulk of the electrode and is used in excess during synthesis, if trapped within a polymeric framework or dynamic SEI, it may be accessible only at certain stages and would account for this unutilised sulfur.

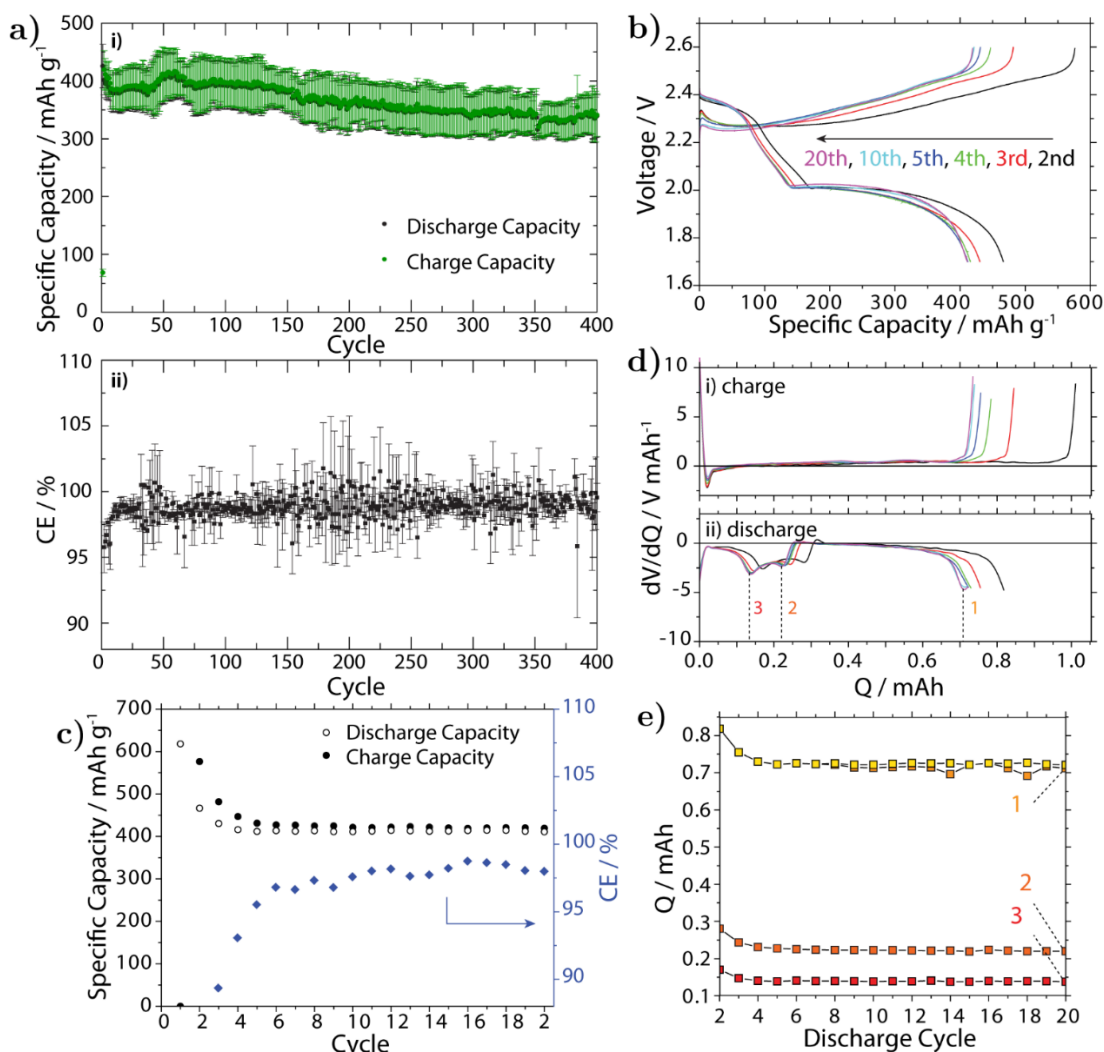


Figure 5.7 – Electrochemical performance of Li-S cells using poly(S-*r*-squalene) as the active cathode material. **a)** Specific capacity as a function of charge-discharge cycles tested in triplicate cycled at C/10 (167.5 mAh g⁻¹). The black and green dots displayed with error bars represent the mean specific discharge and charge capacities respectively. **b)** shows the mean coulombic efficiency also presented with appropriate error bars. **b)** Charge and discharge voltage-capacity plot of one Li-S cell showing the 2nd, 3rd, 4th, 5th, 10th and 20th cycles corresponding to black, red, green, blue, teal and magenta traces respectively. **c)** Specific charge and discharge plots and coulombic efficiency of the same cell up to 20 cycles, with filled black circles points representing charge capacity, open black circles for the discharge capacity and filled blue diamonds for the coulombic efficiency. **d)** The corresponding differential voltage (dV/dQ) plot vs. charge (Q) of data from a), with **i)** corresponding to the charge plots and **ii)** corresponding to discharge and **e)** describes features in d)ii) over the initial 20 cycles wherein the yellow squares represent the total Q when 1.7 V is reached upon discharge, while amber, orange and red squares represent the value of Q at features 1, 2 and 3 respectively in d)ii).

5.3.7 Mechanistic characterisation of electrode function

The predominantly surface-based structural evolution of the poly(S-*r*-squalene) cathode over electrochemical cycling was monitored through *ex situ* XANES presented on **Figure 5.8**. The electrochemical and dV/dQ profiles for each of the *ex situ* sample is shown in the appendix **Figure A.8**. For the sulfur environments (S K-edge), in the fresh state (black trace **Figure 5.8ai**), one main peak at 2472.3 eV, corresponding to the σ^* S-S environment is observed. At the end of 2nd discharge (red trace **Figure 5.8aii**), at least two new features are formed at 2477.6 and 2479.7 eV, which is most likely attributed to the sulfates present in the TFSI anion of the Li salt dissolved in the electrolyte.^{37, 38} These features corresponding to TFSI are also present in all the other following states – 2nd charge (green trace **Figure 5.8aii**), 8th discharge and charge (red and green traces respectively in **Figure 5.8aiii**). Another feature at 2475.1 eV is also present in all the electrochemically-treated samples – appearing subtly in the 2nd cycle and becoming more apparent in the 8th cycle. This feature most likely corresponds to the formation of solid Li_2S .^{37, 39}

Whilst the features corresponding to electrochemical treatment seem to be present in all the samples examined, the relative amounts vary based on different electrochemical treatments. This variation between profiles as a function of electrochemical states provides evidence reflecting a more dynamic SEI. In terms of the carbon environments (C K-edge, **Figure 5.8b**), in the fresh state three features at 285.10, 287.55 and 291.55 eV corresponding to π^* C=C, σ^* C-S, C-H and σ^* C-C aliphatic signals respectively are present. There is no significant variation in overall relative intensity between different electrochemical states of these features with electrochemical cycling which implies that the copolymeric environment remains relatively robust. However, after electrochemical treatment, in the 2nd and 8th discharge and charge states (**Figure 5.8bii** and **iii**) two new features at 288.46 and 290.25 eV are observed. These relatively high energy features most likely correspond to the fluoromethane environment from the TFSI anion of the Li salts present in the electrolyte.⁴⁰ The relative intensities of the features related to the TFSI anion seem to vary between the electrochemical states, similar to the variation observed in the corresponding features in the S K-edge.

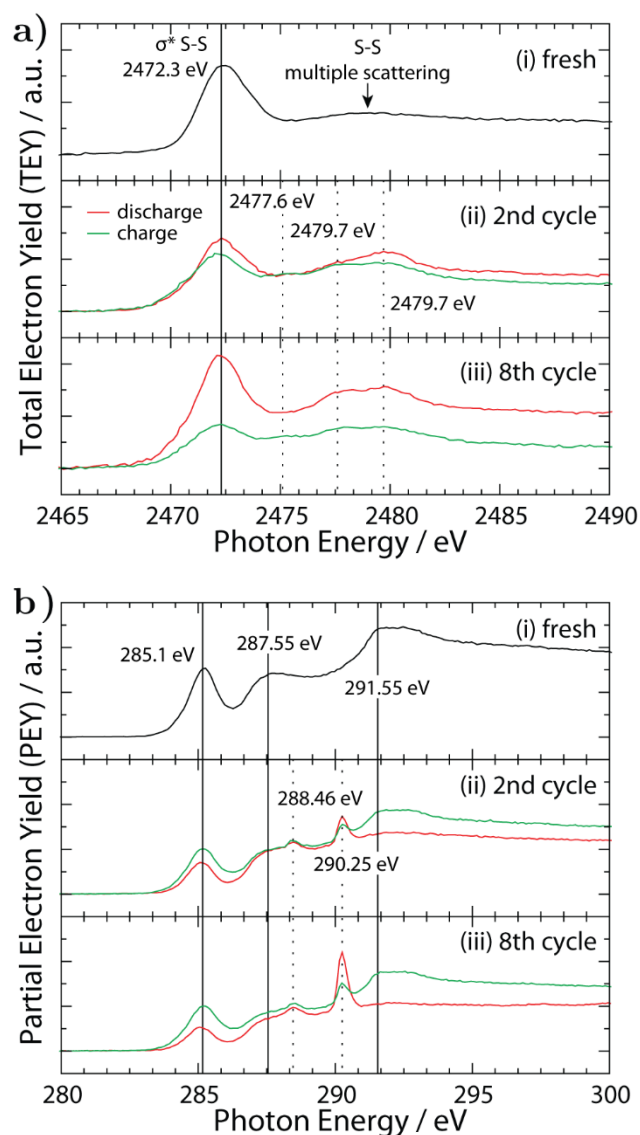


Figure 5.8 – XANES spectra at the **a)** sulfur K-edge and **b)** carbon K-edge of cathodes from Li-S cells using poly(S-*r*-squalene) as the active cathode material extracted at various electrochemical states. The red traces represent samples extracted at the end of discharge and green at the end of charge. The black vertical peak markers are a guide to the eye.

Whilst XANES provides understanding of the predominantly surface-based features when using poly(S-*r*-squalene) electrodes in Li-S cells, it is important to consider the bulk components, in particular the amorphous copolymeric component. Apart from structural insight, ^7Li solid-state NMR can also provide information about the distinct chemical Li environments, their proximities and motional dynamics within the copolymer electrode. Detailed statistics regarding the peak fits are provided in the appendix **Table A.4** and **Table A.5**.

Upon 1st discharge, **Figure 5.9a**, the major discharge products assigned at 3.5 (yellow), 1.1 (orange) and 0.0 ppm (red) appear and are attributed to lithium near elemental sulfur, near the polymer and electrolytic lithium respectively or Li_2S , Li_2S_x ⁴¹ or Li_2CO_3 ,^{10, 42} and LiF or LiTFSI respectively.^{9-11, 42-45} According to Aurbach *et al.*, the formation of Li_2CO_3 is expected from interactions between the 1,3-dioxolane (DOL) solvent and LiNO_3 in the electrolyte.⁴⁶ Interestingly in addition to these three species, two additional peaks at 0.42 and -0.56 ppm (light blue and dark blue respectively) are required to obtain a reasonable model that accurately represents the data.

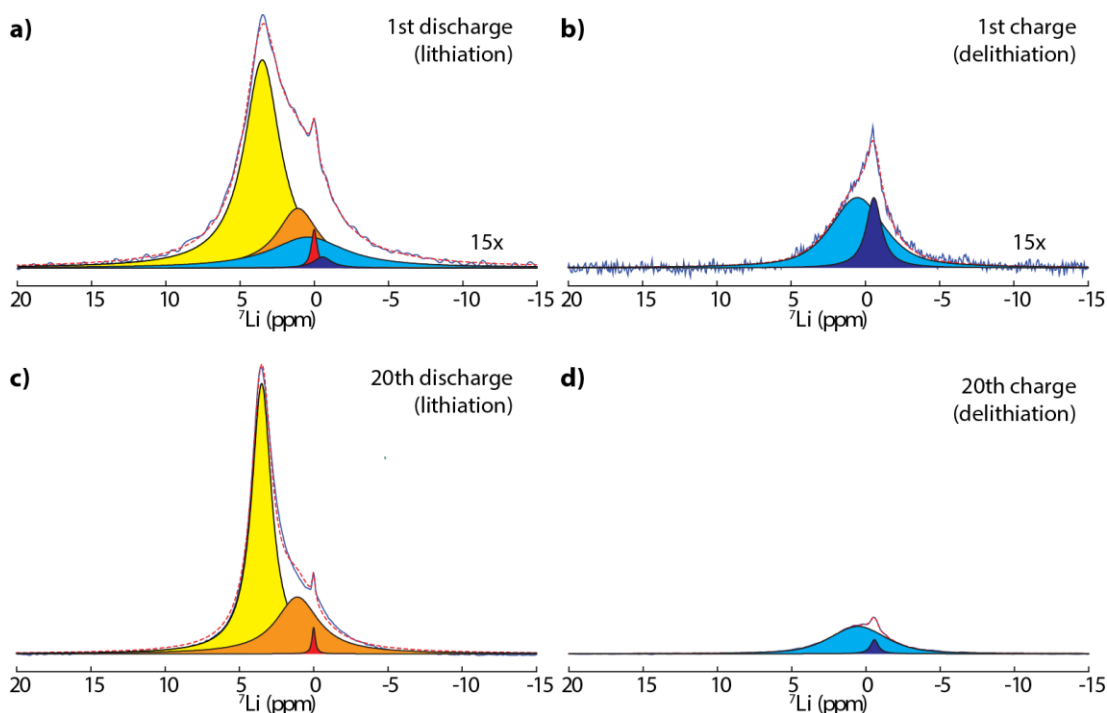


Figure 5.9 – 1D ^7Li MAS NMR spectra of poly(S-*r*-squalene) electrode powders extracted after **a)** 1st discharge, **b)** 1st charge, **c)** 20th discharge and **d)** 20th charge. The intensities of spectra a) and b) are multiplied by 15x relative to the scale used for spectra c) and d) to emphasise the features. The blue trace represents the measured data, and the red dotted trace a sum of Gaussian/Lorentzian peak shapes that form a model of the data. The colours of the peak shapes used to generate the models correspond to those used later in **Figure 5.10a**, with yellow, orange, light blue, red, and dark blue representing peaks centred at $\delta = 3.5$, 1.1, 0.45, 0.0, and -0.43 ppm respectively. The spectra were collected at 272 MHz at a MAS rate of 20 kHz.

Upon 20th discharge these two features do not appear to present any appreciable contributions in the 1D ^7Li MAS of the cycled electrode (**Figure 5.9c**) however are essential to adequately model projections at cross peaks of ^7Li - ^7Li EXSY of the same sample albeit as small contributions (light blue and dark blue peak shapes in **Figure**

5.10a). The chemical shifts of these two peaks lie within range that has previously been associated with LiNO_3 salt decomposition products such as Li_3N and LiNH_2 . Comparing 1st discharge to 20th discharge (as represented in **Figure 5.9c**), this implies that whilst the main discharge products at 3.5, 1.1, and 0.0 ppm (yellow, orange, red), and the LiNO_3 analogues at 0.42 and -0.56 ppm (light blue, dark blue) may all coexist on the copolymeric electrode at the discharge state, the ratio of LiNO_3 analogues to the main discharge products decrease over multiple cycling, to a point where they cannot be clearly distinguished by 20th discharge.

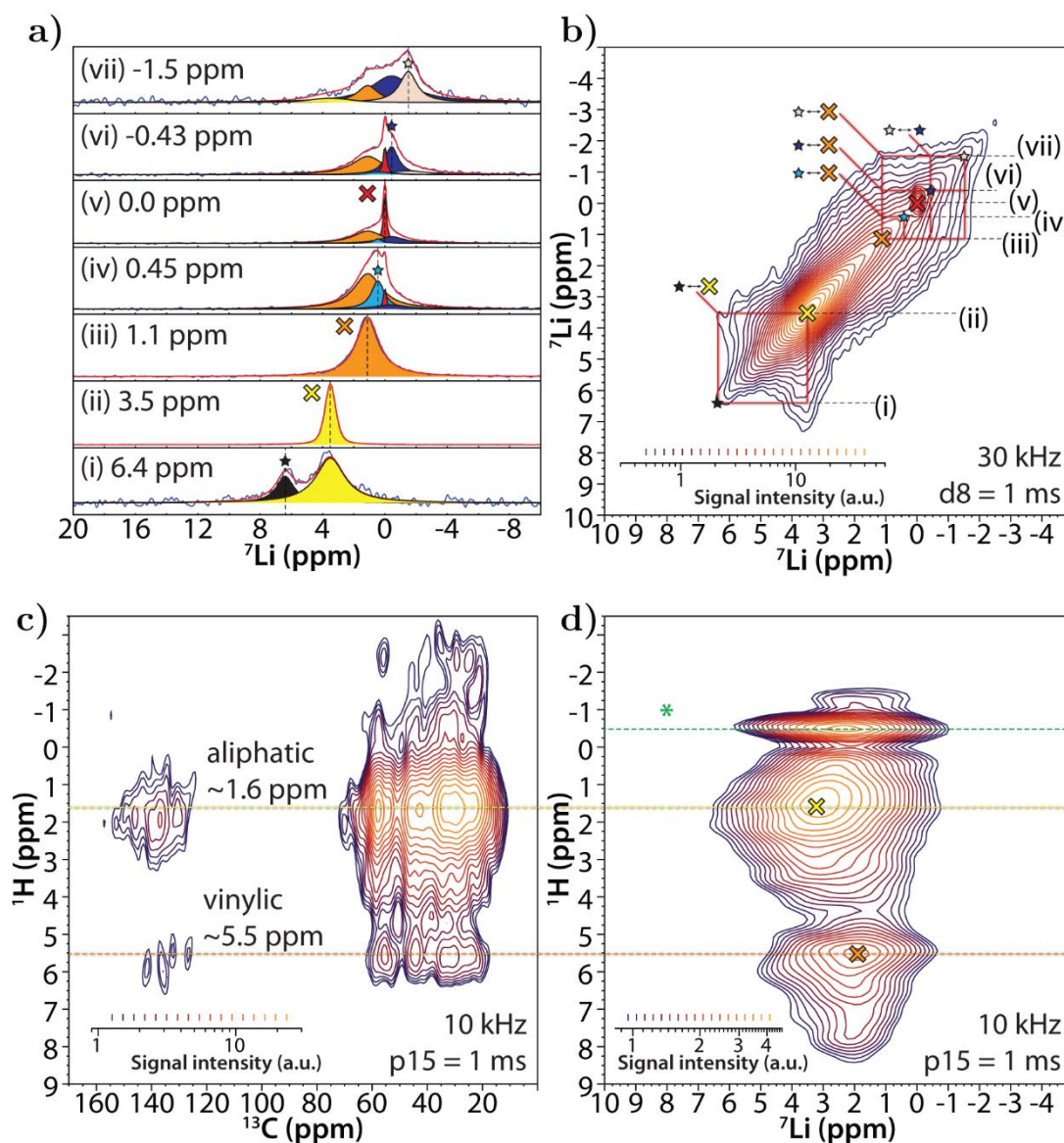


Figure 5.10 – a) Horizontal slices extracted at cross peaks emphasised by dotted red lines in the ^7Li - ^7Li EXSY NMR spectrum of the poly(S-r-squalene) electrode extracted after 20th discharge (shown in **b**, d8 = 1 ms) between signals detected at δ = 6.4, 3.5, 1.1, 0.45, 0.0, -0.43, and -1.5 ppm shown in **i**), **ii**), **iii**), **iv**), **v**), **vi**), and **vii**) respectively (dark blue traces). Peak deconvolution based on these slices are

conducted using a series of Lorentzian, Voigt, or Gaussian functions (where in $xG/(1-x)L$, $x = 0, 0.5$, and 1 respectively) correspondingly marked in black, yellow, orange, light blue, red, dark blue, and tan. The sums of these functions are represented by red traces. The spectra are normalized to their maximum intensity and the red stars indicate the chemical shift of interest. **c)** ^1H - ^{13}C HETCOR spectrum of the pristine poly(*S-r*-squalene) copolymer provided as a guide (enlarged in **Figure 5.3**) **d)** ^1H - ^7Li HETCOR spectrum of the poly(*S-r*-squalene) electrode powder extracted after 20th discharge. The dotted green line and * mark the zero-frequency artefact, and the dotted yellow and orange lines extending from c) to d) are discussed in-text.

Upon charging (i.e. delithiation), lithium is removed from the sulfur electrode and on 1st charge the major discharge products at 3.5 (yellow) and 1.1 ppm (orange) are no longer present, **Figure 5.9b**. Interestingly whilst the lithium environment at 0.0 ppm (red) associated with LiF or LiTFSI is also no longer present, LiNO₃ analogues at 0.42 and -0.56 ppm (light blue and dark blue) are the only remaining species detected within the sample. This confirms the dynamic behaviour of LiF or LiTFSI species in agreement with the lack of correlation detected with other lithium environments based on the ^7Li - ^7Li EXSY measurement of 20th discharge, **Figure 5.10b**. This result is also in agreement with the assumption (also based on the ^7Li - ^7Li EXSY experiments) that LiNO₃ analogues show strong correlation to the copolymer. The 20th charge state, **Figure 5.9d**, also reflects the presence of only lithium environments at 0.42 and -0.56 ppm (light blue and dark blue) associated with LiNO₃ analogues. It appears that Li₃N and LiNH₂ are stubborn deposits that are present in all electrochemical stages involved in this study, and thus in this case must be the most integral component of the static SEI, whereas LiF and LiTFSI are more dynamic protective species that are only detected in the discharged states.

Comparing the results of these cycled electrodes to the previously studied poly(*S-r*-DIB), based on measured NMR spectra, it appears that the lithium environments formed during charge and discharge exhibit more dynamic behaviour when poly(*S-r*-squalene) is used in place of poly(*S-r*-DIB). In poly(*S-r*-DIB), the species at 3.5 ppm is still detected even after charging/delithiating the sample at 1st charge. Moreover, the electrolytic species detected when using poly(*S-r*-DIB) seems to lie closer to -0.5 ppm, similar to the LiNO₃ analogues discussed in this work rather than LiF or LiTFSI assigned at 0.0 ppm. It appears that the architecture of poly(*S-r*-DIB) effectively traps the discharge products as well as protective LiNO₃ salt analogues within the sulfur electrode. On the other hand, poly(*S-r*-squalene) shows a

more dynamic SEI. The major discharge products apart from LiNO_3 analogues are completely absent in the charge states. In addition to this, LiF and LiTFSI species at 0.0 ppm (red) are strongly present in the 1st and 20th discharge states, whereas reasonable amounts of these species are not detected in the case of poly(*S-r*-DIB).

Focusing on the 20th discharged state (lithium inserted, **Figure 5.11a** and **Figure 5.11b**) the $\delta = 3.5$, 1.1 and 0.0 ppm are present. In the cross polarisation (CP) experiment, all of the signals are suppressed, and the shift at $\delta = 1.1$ ppm is observed to dominate (orange peak in **Figure 5.11b**). The only proton-containing environments expected in the system are either associated with the copolymer or residual electrolyte solvent (i.e., DOL/DME). The suppression of the signal at 0.0 ppm in **Figure 5.11b** further supports a peak assignment to LiF and/or LiTFSI environments, absent of ^1H in their structures. Arguably a $\delta = 3.5$ ppm shift can also be fitted as a contribution to the overall profile of the spectrum as indicated by the yellow peak in **Figure 5.11b** but it is in smaller quantities relative to the 1.1 ppm peak as significant signal retention would be expected based on the 1D ^7Li data of the 3.5 ppm peak. Moreover, 68% of the overall CP signal arises from the lithium environment at 1.1 ppm (orange) which suggests this lithium environment is associated most to the copolymer. This 1.1 ppm chemical shift also lies within the range of ^7Li shifts reported for other polymeric organosulfur-lithium compounds.⁴⁷⁻⁴⁹ For the CP data, peaks at 3.5 and 1.1 ppm required modelling using Gaussian and Voigt functions (see **Figure 5.11b**) to yield adequate fit statistics, whereas the 1D MAS data were adequately modelled by Lorentzian peak shapes (see **Figure 5.11a**). Signals that exhibit more Gaussian line shapes are generally more rigid and solid-like whereas signals with narrower more Lorentzian characteristics (similar to peaks observed in solutions) are generally more mobile structures.⁵⁰ Thus, the CP experiment reflects that the retained signals at 3.5 and 1.1 ppm (yellow and orange) – lithium environments associated with the copolymer – contain more rigid solid-like structures, possibly resulting from the squalene monomers functioning as an architectural backbone.

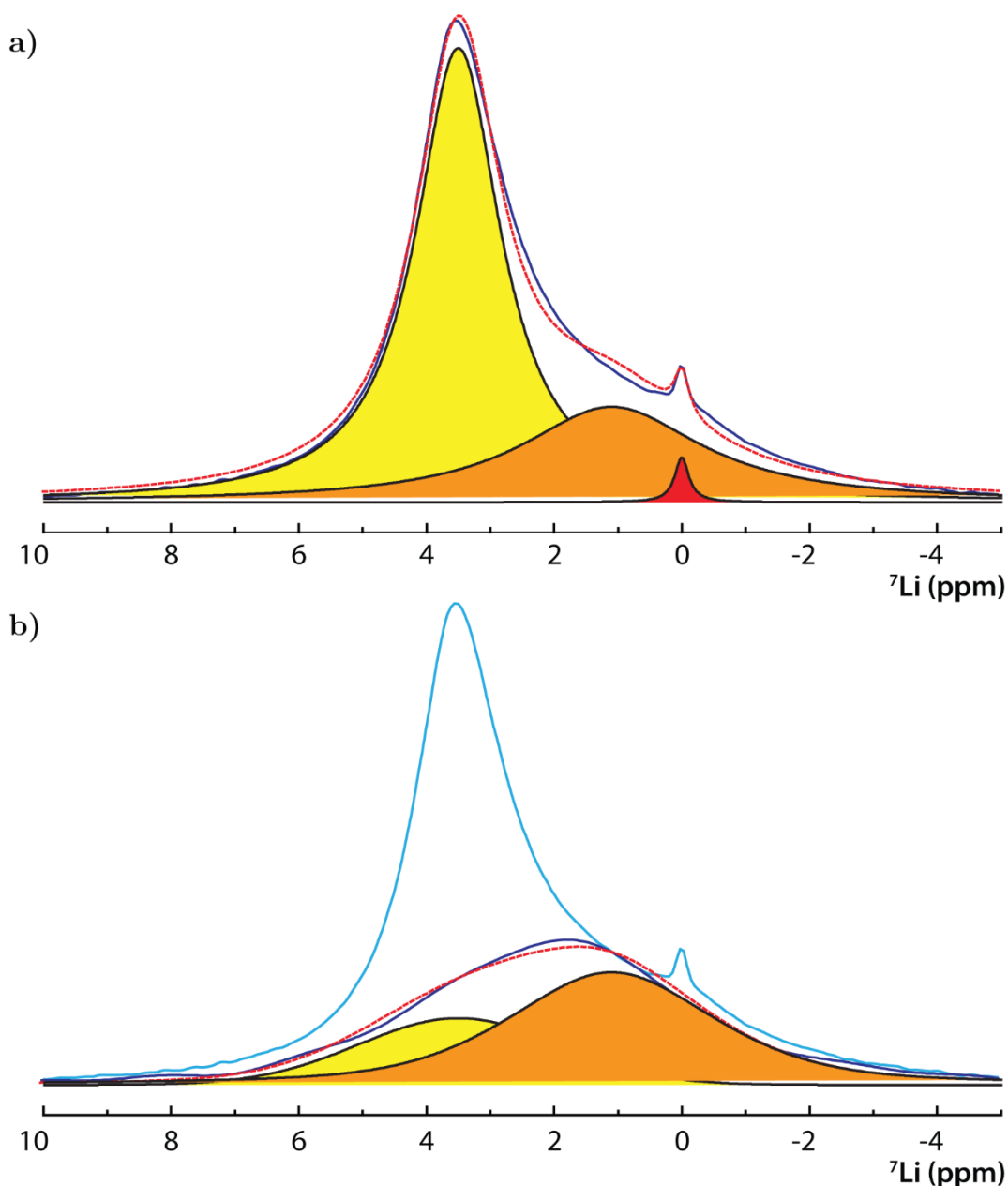


Figure 5.11 – a) 1D ^7Li MAS NMR spectrum of the poly(S-r-squalene) electrode after 20th discharge (dark blue traces). The dotted red trace is a sum of 3 line shapes, fixed at 3.5, 1.1 and 0.0 ppm, that are fitted to the data. **b)** ^1H - ^7Li CP-MAS spectrum of the same sample (blue trace) magnified to 50 $\times$ the obtained signal intensity with 1 ms contact time. The light blue trace is the original 1D ^7Li MAS NMR spectrum provided as a guide. The colours of the peak shapes used to generate the models correspond to those used in **Figure 5.10a**, with yellow, orange, and red representing peaks centred at $\delta = 3.5$, 1.1, and 0.0 respectively.

Further evidence of the structural dynamics is afforded by extraction of the T_1 relaxation time of the 20th discharged electrode *via* saturation recovery. Plots of the maximum intensities at variable τ per lithium environment are provided in the appendix **Figure A. 9a** and **b**. Considering the experimental setup, the fitting function

for the saturation recovery experiment should involve a single exponential factor relating to one T_1 value per lithium environment:

$$\frac{M_z}{M_0} = 1 - e^{\frac{-\tau}{T_1}} \quad (5.1)$$

Wherein M_z is the signal absolute value, M_0 signal anticipated at equilibrium taken as the signal measured at the longest delay $\tau = 60$ s, τ the applied T_1 relaxation delay before the final $\pi/2$ pulse is applied.

Based on the CP experiment, 3.5, 1.1 and 0.0 ppm are chosen as the major lithium environments to monitor. Apart from lithium environment at 0.0 ppm, appendix **Figure A. 9a**, the single exponential function **Eqn. 5.1** does not accurately represent the data particularly at the sharpest part (see arrows in **Figure A. 9a**) with fit values shown in the appendix **Table A. 6**. In order to improve the fit statistics, a different fit function is used to model the data. A second exponential term is introduced per lithium environment:

$$\frac{M_z}{M_0} = 1 - (Ae^{\frac{-\tau}{T_{1a}}} + Be^{\frac{-\tau}{T_{1b}}}) \quad (5.2)$$

wherein $A + B = 1$. Incorporating two exponential terms in the function means that each lithium environment involves multiple components sharing the same chemical shift with different T_1 relaxation times – T_{1a} corresponding to component A and T_{1b} corresponding to component B (coefficient constrained as 1-A in the fitting regime) of a particular lithium environment. This difference in T_1 is common in systems where the spin-lattice relaxation dynamics are different between the surface and the bulk. Thus, using this model, an assumption about the lithium environments is made – that each environment contains two components with unique T_1 relaxation times. The appendix **Figure A. 9b** shows the improved fits, and the values are presented in **Table 5.1**. Putting this together, there are multiple lithium environments each with two relaxation times, with one associated with the bulk and another associated with the surface.

The individual components related to the surface and bulk of each lithium environment revealed *via* the multi-exponential model appear to be vastly different from each other. The fast, more dynamic components T_{1a} are most likely related to the surface, 4900, 3300 and 800 ms for environments at 3.5, 1.1 and 0.0 ppm respectively.

Meanwhile the slow, more dynamically rigid components are most likely related to the bulk, 1700, 380 and 11 ms respectively. Note that the population of more dynamic and solution-like environments take longer to reach thermal equilibrium and thus this results in longer T_1 relaxation times compared to more rigid environments.⁵¹

Out of the three environments, 0.0 ppm shows significantly shorter T_1 relaxation times overall. This agrees with the assignment of 0.0 ppm to electrolytic LiF and LiTFSI species, with reliable reports showing T_1 relaxation times below 1 s for solid LiTFSI species.⁵² These relatively short T_1 relaxation times also explain why the environment at 0.0 ppm minimally correlates with other lithium environments. Moreover, based on this multi-exponential model, ~76% of the T_1 relaxation contributions related to the environment at 0.0 ppm arise from the fast component T_{1a} . Thus, whilst a relatively short T_{1b} relaxation time (11 ms) is detected of the bulk component, the impact of this component is not expected to be significant.

Environments at 3.5 and 1.1 ppm on the other hand appear to be comprised of approximately half surface and half bulk components. The fast, surface components T_{1a} related to environments at 3.5 and 1.1 ppm have relatively long relaxation times of greater than 3 s, which can be interpreted as a mobile solution-like surface component. Interestingly, whilst the bulk and slower T_{1b} component of 3.5 ppm (1681 ms) still has a relatively long T_1 relaxation time (>1 s), the T_{1b} component of 1.1 ppm has a relatively short relaxation time of 384 ms. The overall long relaxation times of 3.5 ppm components imply that both the surface and the bulk of this lithium environment are generally mobile and solution-like. In contrast, 1.1 ppm has relatively diverse surface and bulk properties (large T_{1a} and small T_{1b}) but the weight of these components are essentially equal. The multi-exponential model reveals that the surface component of 1.1 ppm is mobile, dynamic and solution-like, whereas the bulk component is more rigid and solid-like. This makes 1.1 ppm unique to 3.5 ppm and 0.0 ppm, both of which do not exhibit as significant relative differences based on different T_1 relaxation times between the surface and the bulk.

Table 5.1 – T_1 relaxation times of three main lithium environments observed in electrochemically lithiated poly(S-*r*-squalene) and their relative contributions, A , extrapolated from a multi exponential fitting regime (see Eqn. 5.2). More details regarding this fitting regime are provided in-text and in the appendix Figure S 6b.

^7Li (ppm)	A	T_{1a} (ms)	T_{1b} (ms)	R_{sq}	$T_{1\text{mean}}$ (ms)
3.5	0.4(1)	4900(800)	1700(200)	0.9998	3000(1000)
1.1	0.57(4)	3300(400)	380(50)	0.9976	2000(400)
0.0	0.76(3)	800(60)	11(6)	0.9907	630(80)

To further understand the spatial proximities of the lithium environments to ^1H nuclei, ^1H - ^7Li HETCOR measurements of the 20th discharge electrode was conducted, **Figure 5.10d**. The ^1H - ^{13}C HETCOR spectrum of the pristine poly(S-*r*-squalene) copolymer is provided in **Figure 5.10c** as a guide. Like the CP experiment, which relies on transfer of spin from more naturally abundant ^1H nuclei to ^7Li , the ^1H - ^7Li HETCOR spectrum only reflects protonated lithium signals and thus can only arise from either the copolymer or residual electrolyte solvent. As expected from the ^1H - ^7Li HETCOR, only lithium environments at $\delta = 3.5$ and 1.1 ppm show correlation to ^1H nuclei. Interestingly these ^1H correlations observed with the lithium environments all correspond to the ^1H shifts observed in the ^1H - ^{13}C HETCOR of the pristine poly(S-*r*-squalene) copolymer (see **Figure 5.10c**) as indicated by the dotted orange and yellow lines at $\delta = 5.5$ and 1.6 ppm respectively wherein these cross peaks appear the most intense. In the ^1H - ^{13}C HETCOR shown in **Figure 5.10c**, the ^1H shifts at 5.5 and 1.6 ppm are attributed to broadened vinylic and aliphatic copolymeric regions respectively. The observed cross-peaks reveal correlations between $\delta_{^7\text{Li}} = 3.5$ ppm $\leftrightarrow$ $\delta_{^1\text{H}} = 1.6$ ppm (aliphatics, yellow cross), and between $\delta_{^7\text{Li}} = 1.1$ ppm $\leftrightarrow$ $\delta_{^1\text{H}} = 5.5$ ppm (vinylics, orange cross). Apart from copolymeric ^1H nuclei, ^1H signals can also arise from residual electrolyte solvent which comprises of 1,3-dioxolane and 1,2-dimethoxyethane. However, ^1H shifts arising from these solvents are expected to be at $\delta = \sim 4.9, 3.9, 3.4$ and 3.3 ppm and are not obvious in the ^1H domain of the ^1H - ^7Li HETCOR shown in **Figure 5.10d**.

These correlations contrast to the case of poly(S-*r*-DIB), wherein only one strong correlation between one ^7Li environment and one ^1H environment is observed.⁹ Moreover, both aliphatic and vinylic groups and thus all protonated components of the

copolymer seem to show spatial correlation with lithium when using poly(S-*r*-squalene). In poly(S-*r*-DIB) only the aliphatic groups are observed to correlate with lithium, whereas the aromatic groups do not.⁹ This result implies that whilst both squalene and 1,3-diisopropenylbenzene primarily function as architectural backbones within the copolymer, using squalene as a precursor in place of 1,3-diisopropenylbenzene yields a copolymer that is more structurally participating in lithiation. The squalene precursor was initially chosen to determine whether the longer polyterpene units would affect the molecular mobility of the resulting copolymer and their affinity to lithium upon electrochemical cycling, as opposed to a bulkier and more compact structure such as 1,3-diisopropenylbenzene. A stronger correlation of lithium environments to the electrochemically treated poly(S-*r*-squalene) copolymer versus poly(S-*r*-DIB) supports this hypothesis.

In order to further investigate the lithium environments in electrochemically treated poly(S-*r*-squalene), ⁷Li-⁷Li EXSY measurements are conducted as shown in **Figure 5.10b**. In addition to the correlations identified above (3.5 ppm correlated to the aliphatic distal portions of the copolymer and the 1.1 ppm correlated to the vinylic backbone), there appears to be at least four additional subtle environments detected at $\delta = 6.4, 0.45, -0.43,$ and -1.5 ppm. In order to ascertain the presence of these environments and identify correlations, slices are taken at $\delta = 6.4, 3.5, 1.1, 0.45, 0.0, -0.43,$ and -1.5 ppm where cross peaks are observed or anticipated, **Figure 5.10a**. The three most abundant lithium environments at $\delta = 3.5, 1.1$ and 0.0 ppm show little to no correlation with each other. Spectra collected at different mixing times extending from $d8 = 30 \mu\text{s}, 100 \mu\text{s}, 300 \mu\text{s}, 1 \text{ ms}, 3 \text{ ms}, 10 \text{ ms}, 30 \text{ ms}, 100 \text{ ms}, 300 \text{ ms}, 1 \text{ s}$ are also collected (shown in the appendix **Figure A. 10**), further confirming that correlations between these signals are not resolvable until $d8 = 10 \text{ s}$. Only a weak correlation can be noted between 0.0 ppm and 3.5 ppm at large mixing times (**Figure 5.12e**).

Whilst their correlations with each other are minimal, these lithium environments appear to exhibit stronger correlations with the more subtle less abundant environments observed at $\delta = 6.4, 0.45, -0.43,$ and -1.5 ppm. As shown in **Figure 5.10ai**, it is apparent that the more subtle environment at 6.4 ppm (black) exhibits strong correlation with 3.5 ppm (yellow) previously attributed to Li₂S. Due to the relatively low signal detected and unusually high chemical shift, this resonance at 6.4 ppm is particularly challenging to assign with confidence.

Considering this contribution to arise from lithium insertion into carbon black, this chemical shift is within the range of lithiated carbons explored in other work.⁵³⁻⁵⁶ Lithiation and de-lithiation of carbon black however typically occurs below 1.0 V,⁵⁷ which lies well below the cut-off voltage employed in this work (1.7 V).

Alternatively, there has been some evidence in previous work that suggests organic π systems to cause a shielding effect on lithium.^{47, 58} Paratropic systems in particular have been observed to result in a downfield shift of the ^7Li signal, which could account for the relatively high ppm (6.4 ppm). Whilst it remains unclear what paratropic environments could give rise to this phenomenon, there are several cyclic structures inside the Li-S cell that can interact with lithium such as: (1) DOL (and DME) from the electrolyte, and (2) cyclic carbon structures or overlapping alkene chains within the copolymeric network. It is important to note however that most studies conducted on these cyclic organolithium compounds have involved the use of solvents which can also affect ^7Li chemical shift. Despite these challenges in assigning the lithium environment at 6.4 ppm, it is clear from the ^7Li - ^7Li EXSY experiment that it is the only signal that shows correlation with the major Li_2S contribution ascribed to the resonance at 3.5 ppm. Identifying this lithium environment prompts further characterisation of model organolithium structures in the absence of solvent.

Focusing on the signals at 0.45 and -0.43 ppm (horizontal slices from **Figure 5.10b** deconvoluted in **Figure 5.10a iv** and **vi**, light blue and dark blue peaks respectively), it is clear that these signals are correlated to the lithium environment only at 1.1 ppm (orange peak) previously attributed in this work to either Li_2S_x species,⁴¹ or Li_2CO_3 ^{10, 42} (see **Figure 5.10c**). Solely based on signal peak intensity, the lithium environment at -0.43 ppm (dark blue peak) appears to be more abundant than 0.45 ppm (light blue peak). Note that the correlation between -0.43 and 0.45 ppm (dark blue and light blue peaks) themselves appear to be minimal as there is no observable cross peak correlating the two environments. These signals at 0.45 and -0.43 ppm (light blue and dark blue peaks) could be attributed to LiNO_3 salt decomposition products such as Li_3N and LiNH_2 .^{46, 59-61} Correlation with the signal at 1.1 ppm (one possible component assigned to be Li_2CO_3) seems to suggest the expected reaction of salt with Li_2CO_3 where Li_3N would be expected to be spatially nearby.

There are also correlations between the subtle signal at -1.5 ppm (tan peak) and other lithium environments as seen in **Figure 5.10a vii**. The strongest correlations are observed to be with the signal at -0.43 ppm attributed to Li_3N (dark blue peak), followed by 1.1 ppm attributed to Li_2S_x or Li_2CO_3 (orange peak), then a slight correlation with 3.5 ppm attributed to Li_2S (yellow peak). Though it is unclear what species this peak could be assigned to, Xiao *et al.* has previously reported similar chemical shift values for Li_2S_x at 1.5 V.⁴¹ If this signal matches an assignment to Li_2S_x species (similar assignment to peak at 1.1 ppm), it would make sense for the correlations to -1.5 ppm (**Figure 5.10a vii**) to mirror that experienced by the signal at 1.1 ppm (**Figure 5.10a iii-vii**) as observed. The only uniquely observed correlation to -1.5 ppm is with 3.5 ppm (yellow peak), which could imply that the signal at -1.5 ppm results from a similar Li_2S_x type environment to 1.1 ppm but is at closer proximity to 3.5 ppm (assigned to Li_2S).

2D ^7Li EXchange SpectroscopY (EXSY) experiment provides an overall image of the spatial proximities between different lithium environments found in the electrode. In order to summarise the correlations discussed, **Figure 5.12** is provided as a visual guide. As illustrated, three main environments appear to be the most abundant – detected at: 3.5 ppm (yellow, assigned as Li_2S correlated to the distal aliphatic branches of the copolymer), 1.1 ppm (orange, assigned as Li_2S_x or Li_2CO_3 correlated to the vinylic copolymer backbone), and 0.0 ppm (red, assigned as LiF and LiTFSI electrolytic environments with no observable correlation to the copolymer). Homonuclear correlation between these abundant environments are relatively weak (not observed at 1 ms mixing time), however independently some these environments correlate with other more subtle lithium environments (confirmed through the presence of cross peaks). The environment at 0.0 ppm (red, assigned to LiF and LiTFSI) shows no obvious correlations to any other environments at short mixing times. Only one signal at 6.4 ppm (black, which could relate to lithiated paratropic compounds) shows correlation with 3.5 ppm (yellow, assigned as Li_2S), implying that despite its abundance Li_2S weakly correlates with other lithium environments in the cell. This suggests that significant correlations between lithiated salts and the electrode material are a feature that is unique to these copolymeric sulfur networks. The signal at 1.1 ppm (orange, assigned as Li_2S_x or Li_2CO_3) shows correlations with 0.45, -0.43 ppm (light blue and dark blue, assigned as Li_3N) as well as with -1.5 ppm (tan, assigned

to Li_2S_x formed at lower voltages). Since -1.5 ppm (tan) shows a notable correlation with 3.5 ppm (yellow) even at 1 ms mixing time, this environment is most likely between 3.5 ppm (yellow) and 1.1 ppm (orange). Both 3.5 ppm and 1.1 ppm signals demonstrate spatial correlations to the copolymer: 3.5 ppm correlated mostly to the aliphatic distal portions, whereas 1.1 ppm is correlated mostly to the more rigid vinylic backbones of the copolymer. Whilst observing spatial correlations with the more flexible aliphatic portions of the copolymer is not surprising, spatial correlations with the more rigid vinylic portions of the copolymer is not an expected result. The correlations of subtle lithium environments to the signal at 1.1 ppm suggest that the monomeric backbone of the copolymer also plays a role in the adsorption of protective LiNO_3 salt analogues. This could perhaps be attributed to the solid-like bulk and solution-like surface properties that are unique to 1.1 ppm as previously determined *via* saturation recovery (see the appendix **Figure A. 9**), which could be linked to its effectiveness in adsorption. Whilst these subtle environments are observable through ^7Li - ^7Li EXSY through correlations, elucidating these environments in 1D NMR spectra may be achievable by ^6Li enrichment of the copolymeric samples and subsequent investigation using ^6Li NMR with a lower quadrupolar moment.

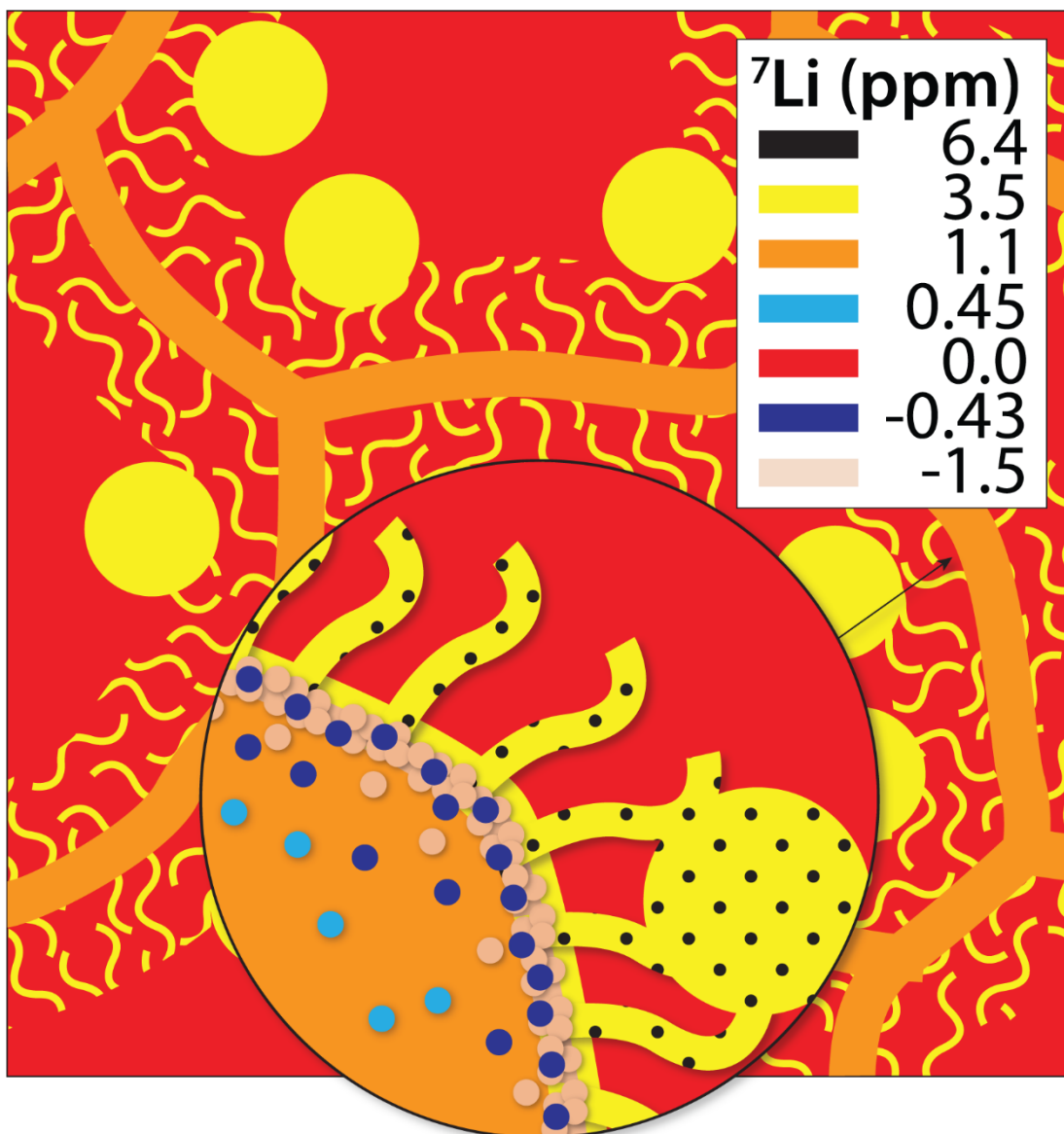


Figure 5.12 –A visualization of the spatial proximities between the different lithium environments based on findings from the ^7Li - ^7Li EXSY measurements with colours used corresponding to the presentation in **Figure 5.10a** and **b**. Specifically, lithium environments at $\delta = 6.4, 3.5, 1.1, 0.45, 0.0, -0.43$, and -1.5 ppm are marked by black, yellow, orange, light blue, red, dark blue, and tan respectively.

5.4 Conclusions

This work illustrates structural properties and function of the poly(*S-r*-squalene) copolymer in a Li-S cell. From ^1H - ^{13}C HETCOR SS-NMR, the structure of the poly(*S-r*-squalene) copolymer is generally flexible with a rigid structural backbone based on the squalene monomer. TGA/DTG, XANES and XPS studies confirmed the presence of C-S bonds. Based on XRD, poly(*S-r*-squalene) has α and β - S_8 phases present but

the dominant phase in the as-synthesised form is α -S₈ (more stable in ambient conditions). *Ex situ* XANES reveals that poly(S-*r*-squalene) exhibits a dynamic SEI when used as an active cathode material, yet the copolymeric environment is observed to be persistent over multiple cycling. The most integral part is perhaps the investigation of species present in the electrode and particularly SEI during cycling through SSNMR. There are correlations of multiple lithium environments with the copolymer, adsorption of LiNO₃ analogues to the copolymeric environment is revealed through ¹H-⁷Li HETCOR, and the poly(S-*r*-squalene) copolymeric environment increases reversible adsorption/desorption of LiF/LiTFSI species during discharge/charge. The architecture of the copolymer allows the LiF/LiTFSI species to pass through reversibly during cycling.

Differences in properties and correlations to Li environments between poly(S-*r*-squalene) and poly(S-*r*-DIB)⁹ demonstrate that the choice of crosslinking monomer indeed dictates the overall molecular structure and mobility of the copolymeric network, and pertinent behaviour in trapping lithiated species. It was observed that whilst the preservation of some vinylic portions in the squalene monomer gives rise to an overall structurally rigid copolymeric network, this rigid vinylic backbone also irrefutably shows correlation with Li₂S_x or Li₂CO₃ lithium environments. In contrast to poly(S-*r*-DIB) which by comparison exhibits greater molecular mobility, however, contains aromatic components that show no observable correlation with lithium. This comparison reveals that the vinylic components in poly(S-*r*-squalene) are more active in lithiation compared to aromatics in poly(S-*r*-DIB). Therefore, this comprehensive study on poly(S-*r*-squalene) reveals that changes in the vinylic monomer prior to vulcanisation can dramatically affect the lithium transport and SEI formation for the produced polymeric cathode.

There is yet to be any plausible evidence for beneficial/detrimental effects on Li-S cell function solely based on having covalent C-S bonds in the copolymeric structure. The longevity of the SEI using these copolymeric electrodes also prompts further investigation involving controlled amounts of lithium from the counter electrode and the electrolyte. Much of the evidence presented in this work points towards an overall change in the physical properties of the copolymer as having a stronger impact on what species are involved in SEI formation as well as lithium transport. With such

information synthetic monomeric targets can be iteratively optimised to ensure ideal SEI formation, in addition to ideal electrochemical performance.

5.5 References

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Chapter 6: Poly(S-*r*-limonene)

6.1 Introduction

Regioselectivity is generally considered unpredictable in free-radical polymerisation reactions (thus forming otherwise unexpected or thermodynamically less favourable byproducts). Despite unpredictable regioselectivity, inverse vulcanisation yields different copolymeric products based on the choice of monomer and reaction conditions. Moreover, considering the currently reliable manufacture of commercial analogous vulcanised polymers,¹⁻⁴ such as those involving the use of accelerating agents for vulcanised styrene-butadiene rubber,⁵ it would be reasonable to assume that the same level of knowledge and control over the reaction conditions can also be achieved in inverse vulcanisation reactions.

Limonene (structure (2) shown in **Figure 6.1**) contains two alkenes of unequal reactivity (exo and endocyclic). Whilst both sides can be totally consumed upon inverse vulcanisation, preferential reactivity to the less sterically hindered exocyclic alkene may influence the morphology of the copolymeric network. Moreover, like squalene (**Chapter 5**),⁶ limonene is a 1,5-diene with a greater susceptibility to dehydrogenation reactions compared to conjugated dienes with aromatic functionalities such as 1,3-diisopropenylbenzene (DIB), and therefore a larger number of copolymer fragment permutations would be intuitively expected.²

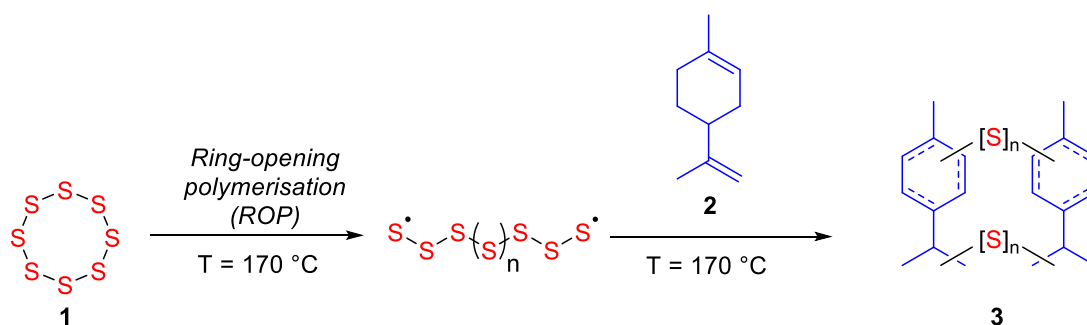


Figure 6.1 – Proposed mechanism for the inverse vulcanisation of limonene (2) with elemental sulfur (1) to yield poly(S-*r*-limonene) (3) by Crockett *et al.*⁷

In the 1,5-diene squalene, the large number of fragment permutations resulted in high molecular weight copolymers with low chain mobility as suggested by limited solubility in non-polar aprotic solvents⁸ and the solid-state NMR of the copolymer (in **Chapter 5**).⁶ This low chain mobility in poly(S-*r*-squalene) proved to be less effective in improving Li-S cell capacity retention (~67% initial capacity at 20th discharge, cycled at C/10 or 167.5 mA g⁻¹)⁶ compared to poly(S-*r*-DIB) (~74% initial capacity at 20th discharge, cycled at C/10 or 167.5 mA g⁻¹).^{9, 10} Despite this result for poly(S-*r*-squalene), the polymer from 1,5 diene limonene, poly(S-*r*-limonene) exhibits high capacity retention values (97% of initial capacity at 300th discharge, cycled at 0.5C, 1C undefined)¹¹ surpassing that of poly(S-*r*-DIB). Such promising results using poly(S-*r*-limonene) prompts further investigation on inverse vulcanised copolymers using 1,5-diene crosslinkers and how they can be effectively used or tuned to show optimal performance as electrode materials for Li-S cells.

While there are several reliable methods to characterize the bulk polymerization of limonene with sulfur (e.g., solution-state NMR,^{7, 8, 12} size-exclusion chromatography (SEC),^{7, 12} FT-Raman spectroscopy¹²), limited work has been dedicated to characterising the behaviour of these crosslinked networks (often insoluble with high sulfur feeds) for applications in energy storage devices. Previous work investigating the effect of the crosslinked networks to electrochemistry by Wu *et al.* used *ex situ* X-ray powder diffraction (XRD) and scanning transmission electron microscopy (STEM) to provide structural insight on poly(S-*r*-limonene) electrodes upon electrochemical treatment.¹¹ Whilst the combined results of this investigation suggested nanostructure evolution of the overall electrode material upon cycling, these analytical techniques were unable to discriminate whether the effects on the electrochemistry originated directly from the poly(S-*r*-limonene) copolymer or whether they were effects arising from other surrounding components within the electrode.

Moreover, whilst parameters that describe overall stability of the copolymeric framework (such as average molecular mass, polydispersity index, glass transition temperature) are indeed relevant and important to report, independently they are not reliable predictors on the efficacy of the copolymer as a Li-S cell electrode material. This is in part because the measured parameters cannot clearly distinguish between the molecular interactions responsible for crosslinking (e.g., crosslinks based on

hydrocarbons versus crosslinks based on sulfur) which can have a significant impact on the Li-S interaction.

Techniques employed in this work such as solid-state NMR and XANES offer selectivity in probing the hydrocarbon portions of the framework. Investigating the local structure evolution of poly(S-*r*-limonene) upon electrochemical treatment and how they compare to other inverse vulcanised copolymeric materials would provide useful insight on which types of copolymeric architectures are compatible for applications in Li-S cells. This informed understanding aids in the rational design of new inverse vulcanised copolymers that can effectively suppress polysulfide dissolution when used in Li-S cells.

6.2 Methodology

6.2.1 Synthesis of poly(S-*r*-limonene)

Synthesis of poly(S-*r*-limonene) using various wt. % ratios of S₈ and d-limonene was conducted within an enclosed environment under N₂ maintained at ~0.2 mmHg pressure to produce 5 g of the final copolymeric product.

Solid elemental sulfur powder (amounts are outlined on **Table 6.1**) was melted and maintained at 170 °C for 30 min using a pre-heated oil bath until a viscous orange liquid was formed. To the red molten sulfur medium, d-limonene (97%, Sigma-Aldrich®, amounts outlined on **Table 6.1**) was introduced *via* syringe. The reaction mixture was allowed to stir until a red-brown molten phase formed then maintained at 170 °C with stirring for an additional 1h to ensure complete crosslinking. All formulations transformed from orange to a red-brown molten phase within the first 10 mins after the addition of limonene except for 50:50 wt. % limonene:S₈ which required ~30 mins.

The reaction mixture was then cooled to 135 °C (i.e., lower temperature but still at a molten state) and subjected to 7 mbar of pressure for 5h, followed by an additional 2h maintained at 75 °C (i.e., solid phase) to distill p-cymene and other volatile by-products before cooling to room temperature to yield the copolymeric product.

Table 6.1 – Reagent amounts to prepare compositions of poly(*S-r*-limonene) and appearance of products.

	Limonene amounts			Sulfur amounts			Appearance of product
	Wt. %	Mass / g	n / mmol	Wt. %	Mass / g	ns / mmol	
(i)	50	2.5	18	50	2.5	78	Dark red-brown waxy solid
(ii)	40	2.0	15	60	3.0	94	Dark orange-brown solid
(iii)	30	1.5	11	70	3.5	109	Orange solid
(iv)	20	1.0	7.3	80	4.0	125	Orange solid
(v)	10	0.5	3.7	90	4.5	140	Orange solid

6.2.2 Coin cell fabrication and electrochemical testing

All electrode mixtures were formulated using poly(*S-r*-limonene) prepared with the highest 90 wt. % sulfur (i.e., 10 wt. % limonene, **Table 6.1(v)**) to maximise the sulfur loading. The electrode slurry was comprised of a 75:20:5 wt% ratio of poly(*S-r*-limonene) (10 wt. % limonene), Timcal Super P® carbon black and polyvinylidene difluoride (PVDF) binder. The powders were homogenised using an agate mortar and pestle, followed by mechanical stirring in *n*-methyl-2-pyrrolidone (NMP, 4.0 mL g⁻¹ of total slurry powder) solvent for 16 h. The resulting black slurry was doctor blade cast to an Al-foil current collector at 300 µm thickness (mean sulfur loading of 2.6(3) mg_s cm⁻²) and dried inside a vacuum oven at 80 °C for 24 h to remove residual solvent and moisture, followed by pressing at 100 kN using a flat plate press (MTI Corporation) to ensure good contact between the electrode paste and the Al-foil substrate. The electrode sheets were then cut to 12 mm diameter disks before transferring into the glovebox for assembly.

Li-S cells (CR2032 coin cells) were assembled. inside an Ar-filled glovebox maintained at <0.5 ppm O₂ and H₂O, using a Li foil anode (i.e., excess Li source) and a glassfibre separator soaked with electrolyte (0.38 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.31 M lithium nitrate (LiNO₃) salts in a 1 : 1 v/v mixture of 1,3-dioxolane and 1,2-dimethoxyethane following compositions used in previous work related to poly(*S-r*-DIB). i.e., excess electrolyte. Galvanostatic testing of the Li–S cells were conducted using a Landt CT3002 battery

test system (Landt instruments) between 1.7–2.6 V at C/10 (167.5 mA g⁻¹) with an initial 6 h rest step after cell fabrication.

For *ex situ* experiments, the electrodes were washed using DME solvent and dried for at least 24 h in an Ar-filled glovebox after extraction at the desired state of discharge or charge.

6.2.3 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) patterns were acquired using a Bragg-Brentano Bragg-Brentano geometry X-ray diffractometer (PANalytical, Cu K α = 1.54 Å) between 5° < 2 θ < 90° with a 0.0261 step size and data collection of 750 s per step. Solid copolymer samples were hand-milled using an agate mortar and pestle for the XRD measurements. Rietveld refinement of elemental sulfur crystallographic models (orthorhombic α -S₈ *Fddd*, ICDD, No. 01-078-1888, monoclinic β -S₈ *P2₁/c*, ICDD No. 01-071-0137) were performed using the GSAS-II software suite.¹³⁻¹⁵ The lattice parameters, atomic displacement parameters of the atoms, Gaussian (U, V, W) and Lorentzian (X, Y, Z) profile parameters of the α - and β -S₈ phases were refined to account for effects of instrument and sample broadening.

6.2.4 X-ray absorption near edge structure (XANES) spectroscopy

C K and S K-Edge XANES measurements were conducted on the soft X-ray beamline at the Australian Synchrotron¹⁶ following the same procedures outlined in previous work.^{6, 9, 17, 18} For normalisation of the beam energy between scans all samples were measured simultaneously with TEY of an Au mesh situated in front of the sample (*I*₀ signal), i.e., sample signal divided by the *I*₀ TEY signal. For edge energy calibrations, S K-edge spectra of the samples were also simultaneously measured with a MoS₂ reference foil maintained in the beamline with a known absorption edge centred at 2471.2 eV, and a pyrolytic graphite (HOPG) reference foil centred at 291.65(26) eV for C K-edge spectra. For C K-edge spectra, normalisation to account for contributions from internal carbon contamination of the beamline was achieved by scanning a clean Si photodiode reference following the procedure outlined by Watts *et al.*¹⁹ Calibration and normalisation of the C and S K-edge XANES data were performed using the Quick AS NEXAFS Tool (QANT) macro developed for Igor Pro.²⁰

6.2.5 NMR Measurements

^{13}C NMR experiments were performed on a Bruker Biospin Avance III 300 MHz spectrometer equipped with a wide bore 7 T superconducting magnet (75 MHz for ^{13}C and 300 MHz for ^1H). After drying inside an Ar-filled glovebox, approximately 80 mg of as-synthesised copolymer was packed into 4 mm outer diameter zirconia rotors with Kel-F® caps and spun to 6.5 kHz at the magic angle for measurement. Tetramethylsilane (TMS, 0.0 ppm) and solid adamantane (CH_2 peak at 38.48 ppm as a secondary reference) were used as references for the ^{13}C chemical shifts.

^{13}C NMR spectra were acquired using a ^1H – ^{13}C Hartman–Hahn cross-polarisation with a 1 ms contact pulse ramped from 70–100% for polarisation transfer. A 40 μs gated decoupling time was used to suppress the signals of the protonated carbon species. For ^{13}C and ^1H nuclei, 4 μs and 3.5 μs 90° pulse lengths were applied respectively. To suppress overlap of the spinning sideband signals with the isotropic peaks, a Total Suppression of Spinning Sidebands (TOSS) scheme, and Spinal-64 ^1H decoupling scheme with a 75 kHz decoupling field strength were used during acquisition. For the CP experiments optimised recycle delays of 2 s were used as they were determined to be sufficient for full equilibration of the ^1H magnetization, and up to 10k transients were signal averaged for sufficient signal-to-noise.

For 2D ^{13}C – ^1H Heteronuclear-Correlation (HETCOR) measurements, the ^1H magnetisation was allowed to evolve during an evolution time t_1 (64 increments of 43 μs each, 384 transients, and using a recycle delay of 3 s that resulted in an experimental time of 21 h for each 2D experiment) followed by transfer to ^{13}C via CP (variable contact times 0.1 ms and 1 ms) and detection of the ^{13}C signal. The resulting 2D spectrum, which correlates the ^1H and ^{13}C chemical shifts aids in separating signal overlap, and resolving ambiguities related to protonation states of the different carbon species. The ^1H t_1 evolution was measured with Frequency-Switch Lee-Goldberg (FSLG) scheme with a field strength of 86 kHz to suppress the ^1H – ^1H homonuclear dipolar couplings to ensure sufficient resolution in the ^1H dimension.

^7Li NMR experiments were performed using a Bruker Biospin Avance III 700 MHz spectrometer with a standard bore 16.4 T superconducting magnet (272 MHz for ^7Li and 700 MHz for ^1H). Dry electrochemically treated electrode powders (approximately 3 mg) were collected from three Li-S cells per condition and were packed into 2.5 mm outer diameter zirconia rotors with Vespel® caps in an Ar-filled

glovebox and spun to 20 kHz MAS under N₂ gas to avoid moisture absorption or oxidation of the samples during measurements. Solid LiCl (single ⁷Li signal set to 0 ppm) was used to reference the ⁷Li chemical shifts.

The 1D ⁷Li NMR spectra were acquired with a 0.75 μs pulse, recycle delays optimised to 3 s (duration sufficient for full equilibration of the ⁷Li magnetization) and 64 signal transients. For 2D ⁷Li–¹H HETCOR measurements, the sample was spun at 10 kHz MAS. Spectra were acquired in a similar manner to the ¹³C–¹H HETCOR, with a CP contact time of 1 ms. 2 s recycle delays and 768 signal transients co-added for each *t*₁ step resulting in a total experimental time of 27 h per experiment. The 2D ⁷Li–⁷Li exchange spectroscopy (EXSY) experiments were acquired at 20 kHz MAS using various mixing times of 0.03, 0.1, 0.3, 1, 3, 10, 30, 100, and 300 ms. 48 *t*₁ increments of 200 μs, a recycle delay of 3 s, and 64 signal transients were used resulting in a total experimental time of 3 h for each experiment.

The experiments conducted to obtain spin–lattice (*T*₁) relaxation times followed the saturation-recovery pulse sequence. This consists of an initial 90° pulse comb, that is a train of twenty 90° pulses separated by 1–5 ms delays in order to achieve complete saturation of signal magnetization, followed by another 90° pulse after a set delay *τ* where magnetisation is allowed to recover. These saturation recovery experiments were conducted at varying recovery times *τ* = 10 ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms, 200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7 s, 10 s, and 30 s in order to obtain the *T*₁ relaxation times.

Processing of the spectra was conducted using the Bruker Topspin® software (ver. 4.0.7). Deconvolution of the spectra was carried out using the DMfit software package,²¹ which yielded the relative intensities *M_z* of the different spectral components as a function of the recovery time. The intensities were normalized to the longest recovery time at 30 s, and plotted as the ratio *M_z*/*M*₀ vs. the recovery time *τ*. Subsequent fitting of the *M_z*/*M*₀ vs time *τ* plots to exponential functions was conducted using scripts developed for MATLAB® in order to yield the *T*₁ values.

6.3 Results and Discussion

6.3.1 Structural considerations of the polymeric structure based on NMR

As previously observed in other inverse vulcanised copolymers,^{6, 9} the ^{13}C NMR spectrum of poly(*S-r*-limonene) in the appendix **Figure A. 11** indicates that poly(*S-r*-limonene) is also a complex polymeric structure comprised of distinct molecular components. Of note is the presence of aromatic signals ~ 7 ppm in the poly(*S-r*-limonene) spectrum, implying the preservation of dehydrogenation products, that accompanies the broad and overlapping aliphatic signals.

In order to further understand the copolymeric structure and properties as a solid, poly(*S-r*-limonene) was investigated using solid-state NMR as shown in **Figure 6.2**. Combined peak deconvolution of the full ^{13}C NMR spectrum (blue trace) and associated spectrum of non-protonated/mobile carbons (red region) as shown in **Figure 6.2** reveals 2 $\times$ aromatic and 7 $\times$ aliphatic ^{13}C sites represented by orange and yellow peaks respectively. The acquired ^{13}C spectrum (shown in **Figure 6.2**) shows that the aromatic and aliphatic chemical shifts are within the ranges previously observed in solution state NMR spectra (shown in **Figure A. 11**) and by Crockett *et al.*⁷ Peak deconvolution, particularly the presence of relatively deshielded aliphatic ^{13}C signals at ~ 64 - 46 ppm also provides justification for the presence of oxidised components such as sulfoxides and sulfonates, as well as cyclic hydrocarbons as commonly observed in industrial vulcanisation. Characterisation through solid-state NMR reveals that similar chemical shifts and therefore similar hydrocarbon functional groups, including aromatic dehydrogenation products, are present in the copolymer in both the solution and solid states.

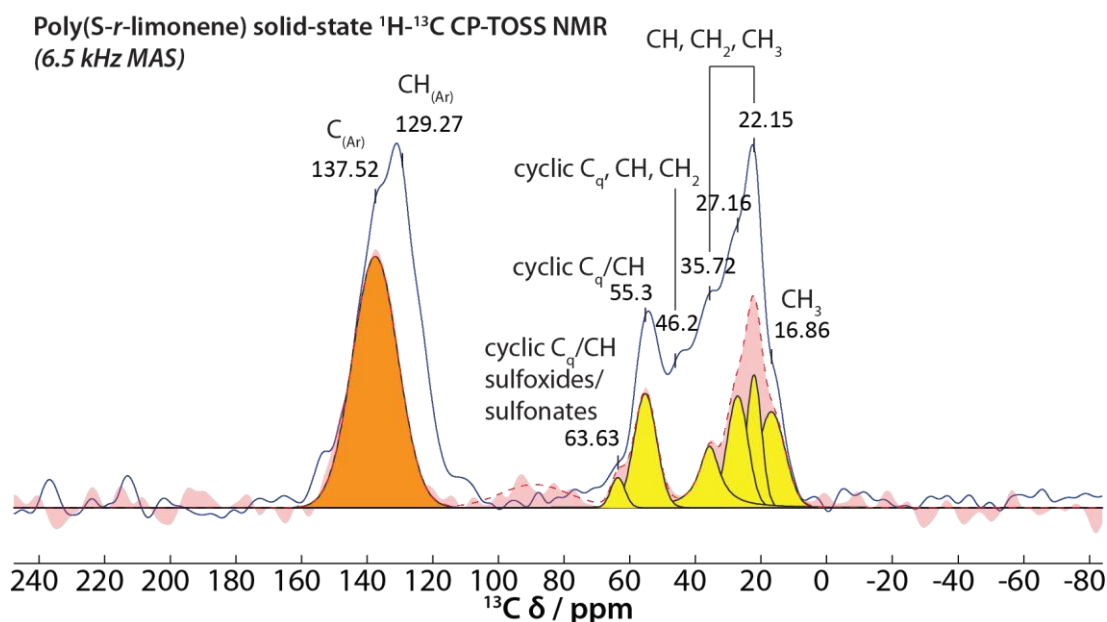


Figure 6.2 – ^1H - ^{13}C CP-TOSS solid-state NMR spectra of poly(*S-r*-limonene). The blue trace is the proton-enhanced ^{13}C signal, and the coloured red region is the signal acquired with a 40 μs gated decoupling filter. The dashed red line is a model of the gated decoupling signal based on a convolution of pseudo-Voigt line shapes (orange = aromatic carbons, yellow = aliphatic carbons). The red pseudo-Voigt contribution was included to suppress distortions from the background unrelated to the sample and stabilise the model fits.

Whilst analogous dehydrogenation products are also known to reliably form in other 1,5-dienes (such as squalene),² limonene contains the necessary cyclic backbone to form aromatic hydrocarbons upon vulcanisation. The primary phenylic by-product p-cymene is a volatile organic compound (**Figure 6.3**, structure 1, b.p.= 177 °C).^{2, 7} In previous work by Crockett *et al.*, this phenylic component is observed to persist (in ^1H and ^{13}C NMR spectra) even after vacuum distillation of the copolymeric material at 180 °C to remove the volatile components.⁷ This observation is consistent with the characterisation presented in this work, with similar ^1H NMR spectra produced across copolymers prepared using 10-50 wt. % limonene as shown in the appendix **Figure A. 11**.

Previous studies on the vulcanisation of limonene show compelling evidence for the formation of volatile by-products especially at high temperatures >140 °C,^{7, 22} namely cyclic monosulfides (**Figure 6.3** (4)-(7)) and hydrocarbons (e.g., p-cymene and p-isopropenyltoluene, **Figure 6.3** (2) and (3) respectively). These by-products can only be formed through anti-Markovnikov addition pathways (i.e., direct addition to the double bond on the less substituted carbon). Of these by-products, at least two

structures (**Figure 6.3** (3) and (7)) contain unsaturated alkenes (reported to form in trace quantities) which can participate in further crosslinking. It is therefore likely that the copolymeric product is comprised of aromatic and aliphatic cyclic hydrocarbons.

Furthermore, as determined *via* size exclusion chromatography (SEC) and atmospheric pressure chemical ionization (APCI) mass spectrometry by Crockett *et al.*, poly(*S-r*-limonene) prepared with 50:50 wt. % limonene:sulfur has a relatively low weight-average molar mass ($M_w = 242 \text{ g mol}^{-1}$ *via* SEC, $386\text{--}777 \text{ g mol}^{-1}$ *via* mass spectrometry), and relatively low polydispersity ($M_w/M_n = 1.16$).⁷ This low M_w of the copolymer can only accommodate 1-3 limonene units ($M_{\text{limonene}} = 136.24 \text{ g mol}^{-1}$) with up to 19 sulfur units per copolymeric fragment.⁷ Whilst the low polydispersity index (close to unity) implies size homogeneity, the expected mechanisms and evidence from NMR appears to point towards chemical heterogeneity between the copolymeric fragments. In other words, homogeneous in size but disperse in composition.

It is important to note that whilst inverse vulcanisation mechanisms to form poly(*S-r*-limonene) may be inherently complex, they seem to produce signatures and generally similar chemical shifts in solution-state ^1H NMR spectra using different sulfur feeds (10-50 %). This is even evident between separate studies using the same precursors.^{8, 10, 23, 24} The relative reproducibility of solution-state NMR spectra suggests that although difficult to predict, inverse vulcanisation can still be regioselective and influenced by the crosslinking monomer.

Despite this reproducibility however, detailed NMR characterisation of inverse vulcanised copolymers is not commonly performed due to significant broadening and overlap of signals. Therefore, even with potentially high regioselectivity, precise characterisation of the copolymeric structure remains difficult. The appearance of aromatic peaks in NMR spectra of copolymeric limonene however justifies the complex mechanisms and large number of permutations expected in inverse vulcanisation between S_8 and 1,5-dienes such as limonene.

Due to similarities between Arrhenius activation and bond dissociation energies of the processes involved, free-radical polymerisations such as inverse vulcanisation are known for complex kinetics and unpredictable regioselectivity.^{1, 2}

Previous work by Crockett *et al.* on solubilized poly(*S-r*-limonene) proposes that some aromatic component is retained within the copolymeric backbone, based on

the presence of distorted ^1H multiplets in the aromatic range ($\sim 6.5\text{--}8$ ppm) in acquired NMR spectra.⁷ The generic structure of poly(*S-r*-limonene) as proposed by Crockett *et al.* is shown in structure 1 **Figure 6.3**.

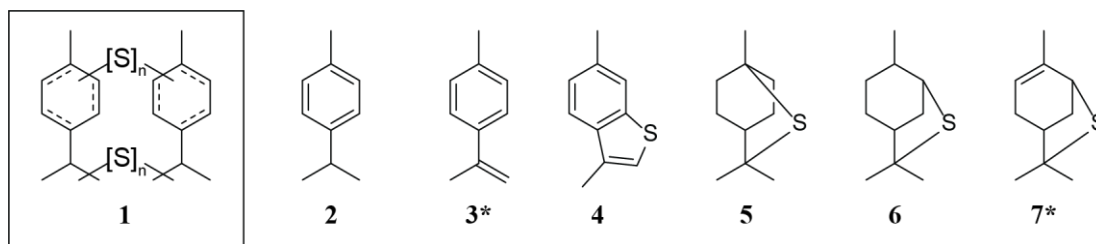


Figure 6.3 – Some products from sulfurisation of limonene proposed in the literature. (1) is the generic copolymeric structure proposed by Crockett *et al.*,⁷ (2)–(7) are dehydrogenation products reported by Porter.² Structures (3) and (7) marked with asterisks contain unsaturated alkenes and can participate in further crosslinking.

Further investigation of the solid copolymeric structure was performed using 2D ^1H - ^{13}C HETCOR NMR as shown in **Figure 6.4**. Investigation using 2D correlation NMR was anticipated to unambiguously resolve the nature of the sp^2 carbons ($\delta_{^{13}\text{C}} = 110\text{--}150$ ppm in **Figure 6.2**) and their significance to the copolymeric architecture. Indeed, through 2D ^1H - ^{13}C HETCOR NMR as shown in **Figure 6.4a** the ^1H signals acquired can be categorized into at least two major environments:

- (1) aliphatic protons ~ 2 ppm
- (2) aromatic protons ~ 7 ppm

In addition to these two proton environments, signal is also observed (albeit more subtly) at ~ 6 ppm overlapping with the broad aromatic site (see **Figure 6.4a**), corresponding to unreacted alkenes. This off-diagonal cross peak between aliphatic carbons and alkene protons is more clearly resolved when the spectrum is acquired with 5 ms spin diffusion as shown in **Figure 6.4b**. The relative strength of the cross-peak between sp^2 carbons (**Figure 6.4a**, $\delta_{^{13}\text{C}} = 110\text{--}150$ ppm) and aromatic protons (**Figure 6.4a**, $\delta_{^1\text{H}} = 7$ ppm) compared to alkenes alludes to the significance of aromatic functionalities to the overall poly(*S-r*-limonene) structure. Whilst the plausibility of aromatisation pathways during inverse vulcanisation between limonene and sulfur is generally agreed upon, this was based on the production of volatile and fugitive by-products such as *p*-cymene^{2, 7} that are considered irrelevant to the main copolymeric structure. The strength of this aromatic signal, especially compared to ^{13}C signal

correlations with alkene protons, confirms the proposed dehydrogenation pathways, the formation and preservation of aromatics in poly(*S-r*-limonene).

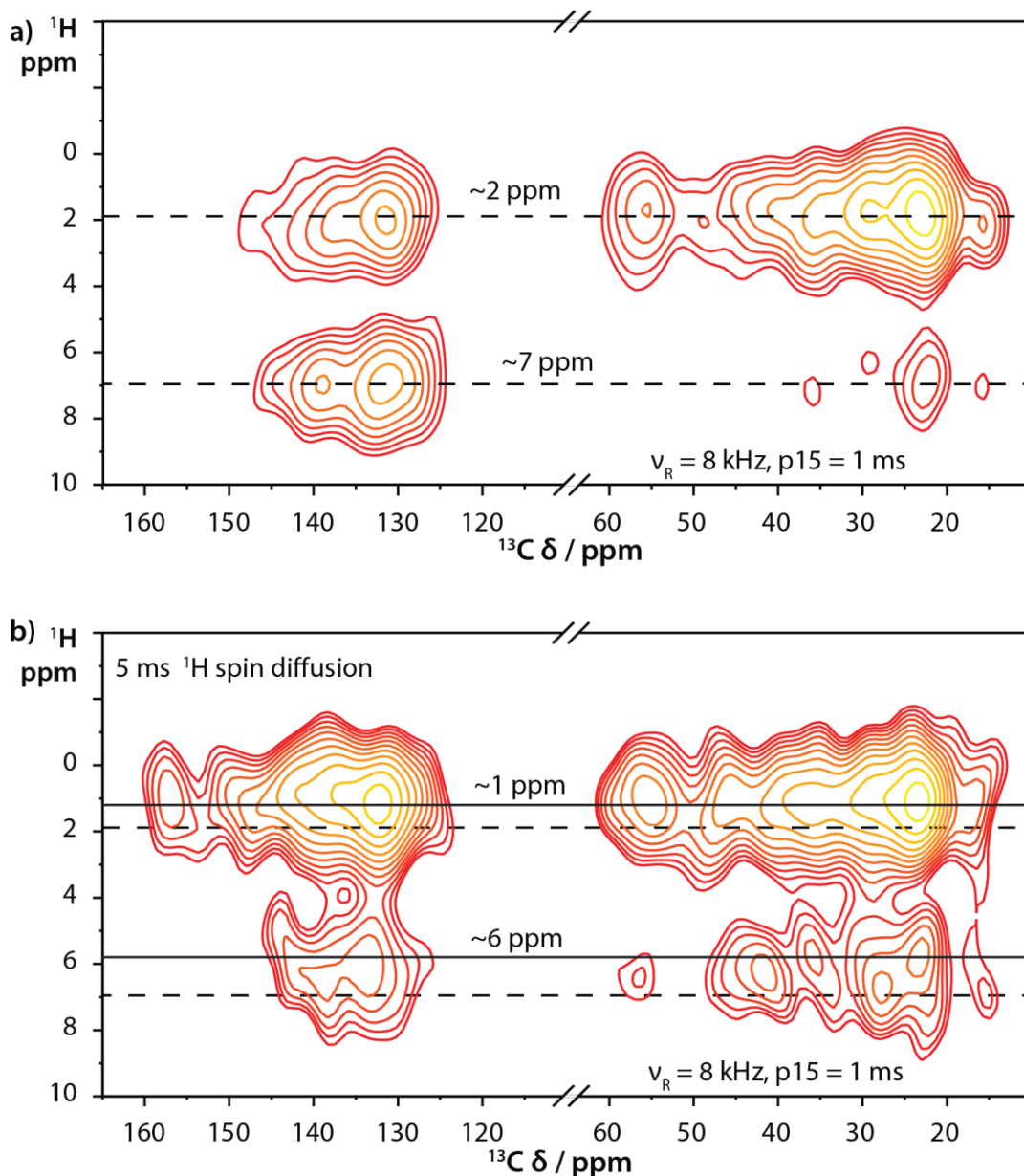


Figure 6.4 – ^1H - ^{13}C HETCOR spectrum of the pristine poly(*S-r*-limonene) copolymer **a)** without ^1H spin diffusion and **b)** with 5 ms of ^1H spin diffusion .

In addition to confirming the formation of aromatics, the 2D HETCOR of poly(*S-r*-limonene) displays significant correlations between the aliphatic and aromatic moieties, implying that the aromatic groups are major contributors (alongside aliphatics) to the overall polymeric structure. Note that the ^{13}C signal at ~ 55 -60 ppm only weakly correlates with the aromatic ^1H signal suggesting that this might be a small, oxidised component.

6.3.2 Determination of the crystalline sulfur phase composition via X-ray powder diffraction

Powder XRD measurements and Rietveld analysis revealed the presence of a dominant α -S₈ phase (orthorhombic α -S₈ *Fddd*, ICDD, No. 01-078-1888) within the poly(*S-r*-limonene) copolymer (10 wt. % limonene) as shown in the appendix **Figure A. 13**. This observation of crystalline α -S₈ in poly(*S-r*-limonene) is inconsistent with poly(*S-r*-limonene) prepared with a 50:50 wt. % ratio of limonene:S₈ which is observed to be completely amorphous producing no crystalline peaks.¹¹ Crystalline sulfur phases have been observed by other works investigating inverse vulcanised copolymers at high sulfur wt. % (~ 90 wt. %),^{6,9} which can be interpreted as an excess of un-crosslinked sulfur.

The presence and population of crystalline sulfur phases can shed light on the confining behaviour of the copolymeric framework. In previous investigations, some inverse vulcanised copolymers, namely poly(*S-r*-DIB) (using 1,3-diisopropenylbenzene, DIB), have been observed to contain the typically metastable β -S₈ phase under standard temperature and pressure conditions.⁹ Poly(*S-r*-DIB) is proposed to have a hyperbranched and highly crosslinked architecture which could be responsible for sustaining the β -S₈ phase metastability under standard temperature and pressure conditions. According to comparative works by Heinz *et al.* on strain recovery of glassy polymers networks using para- vs meta-substituted aromatics, the meta isomer generally produces a more compact copolymeric network than the para isomer.²⁵ This closer proximity to neighbouring chain segments is due to a dependence on α -type segmental rotations of the aromatic substituents to dissipate energy brought on by stress. The confinement and stabilisation of β -S₈ in poly(*S-r*-DIB) can therefore be rationalised by the relatively compact and strained configuration of its hydrocarbon framework.

Contrastingly, the preference to the α -S₈ phase in poly(*S-r*-limonene) is perhaps due to less restricted mobility of aliphatic monomer groups at elevated temperatures, similar to observed in poly(*S-r*-squalene).⁶ Unrestricted mobility of aliphatics at elevated temperatures would allow the β -S₈ phase to return to the α -phase upon cooling after inverse vulcanisation.

It is important to note however that considering similar efficacy to poly(*S-r*-DIB) in terms of electrochemical performance (discussed *vide infra*), the cyclability

of Li-S cells when using these copolymers as electrode materials is not directly related to stabilisation or presence of the β -S₈ phase.

6.3.3 Electrochemical testing

The performance of Li-S cells cycled at C/10 (or 167.5 mA g⁻¹ sulfur) using poly(S-*r*-limonene) as the sulfur electrode active material is shown in **Figure 6.5**. As shown in **Figure 6.5a**, a decrease in specific capacity (from 691 mAh g⁻¹ in the first cycle) is observed within the initial four cycles. The cell then experiences a slight increase in specific capacity in the 5th cycle (as indicated by the dashed line in **Figure 6.5a**) before plateauing to a stabilised value by the 16th cycle (595 mAh g⁻¹ in the 20th cycle, ~86% initial). This marked increase in specific capacity after the initial 5 cycles as well as good capacity retention is consistent with results obtained in similar poly(S-*r*-limonene) electrode architectures previously explored by Wu *et al.* (~97% initial capacity at 300th cycle at C/2).¹¹

Inspection of the individual voltage capacity plots for each charge/discharge step, as shown in **Figure 6.5b**, provides further insight on Li-S redox behaviour when using poly(S-*r*-limonene) electrodes. Whilst upon first glance, similar redox features are observed to when using previously studied poly(S-*r*-DIB) and poly(S-*r*-squalene) electrodes,^{6, 9} using poly(S-*r*-limonene) electrodes appears to produce subtle differences. Notably, as emphasized in **Figure 6.5b**, a prominent ohmic dip between the higher and lower voltage plateau regions is experienced during the first discharge process. This transition occurs more smoothly with further cycling as demonstrated in voltage capacity plots and corresponding derivatives at the 4th, 9th, and 19th discharge states shown in **Figure 6.5b** – a similar phenomenon was observed using poly(S-*r*-DIB) but not poly(S-*r*-squalene) electrodes. According to Zhang *et al.*, a smoother transition between the first higher voltage plateau to the second lower voltage plateau suggests a decrease in ohmic resistance over cycling either from electrolyte resistance (i.e., disproportionation of polysulfides) or precipitation.²⁶ The comparison between the three copolymeric materials above suggests a dependence of ohmic resistance on the disproportionation of electrolytic polysulfides that is based on the copolymeric network and properties.

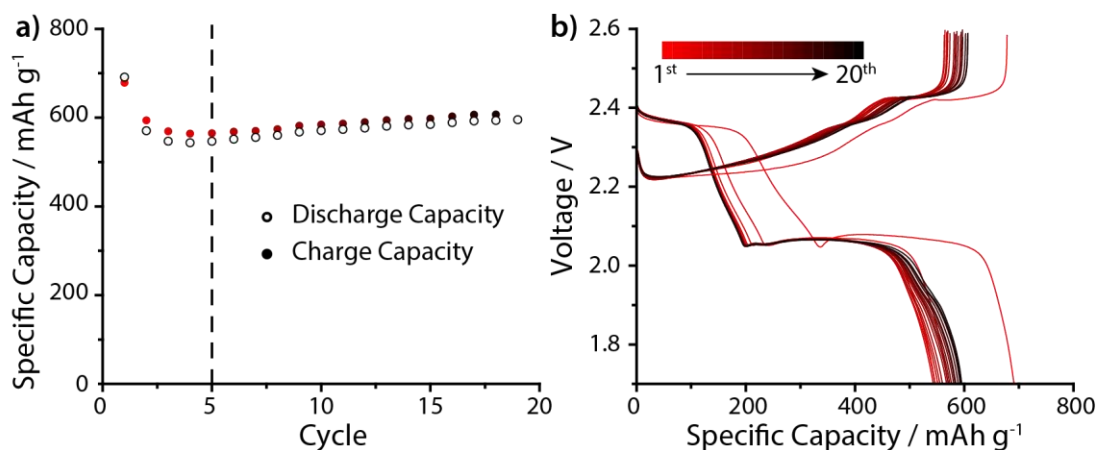


Figure 6.5 – **a)** Specific capacity vs cycle number and **b)** voltage vs capacity plots of Li-S cells up to 20 cycles at C/10 (167.5 mA g^{s-1}) using poly(S-*r*-limonene) (10 wt. % limonene) as the sulfur electrode active material. The dashed line in **a)** marks the cycle in which an increase in specific capacity is first observed.

6.3.4 Lithium-copolymer correlations

¹H-⁷Li HETCOR NMR was performed on an electrode extracted after 20th discharge to understand the lithium interactions with the copolymeric hydrocarbons upon cycling inside a Li-S cell. This correlation assumes that ¹H chemical shifts commonly observed between the ¹H-¹³C HETCOR of the copolymer (shown in **Figure 6.4**) and ¹H-⁷Li HETCOR NMR of an electrode extracted after 20th discharge (shown in **Figure 6.6a**) relate to the copolymeric component. As shown in **Figure 6.6a**, lithium is observed to correlate to aliphatic (~2 ppm) and alkene protons at (~6 ppm).

Strong correlation between lithium and diene protons implies that lithium is significantly adsorbed by the diene functionalities of the copolymer. Interestingly, instead of direct correlation with aromatic functionalities, previously identified as a major component of the copolymeric structure (annotated by the dashed black line ~7 ppm in **Figure 6.6a**), direct lithium coupling is observed more strongly with diene proton sites (~6 ppm). This lithium coupling effect generally with π -systems such as dienes and aromatics agrees with previously investigated poly(S-*r*-DIB) and poly(S-*r*-squalene).⁶ In poly(S-*r*-squalene) with no observable aromatic environments, there is a larger chemical shift difference between ⁷Li signals coupled with aliphatics vs dienes – correlation to the aliphatics deshielded to $\delta_{7\text{Li}} \sim 3.5$ ppm and to the dienes consequently shielded to $\delta_{7\text{Li}} \sim 1.1$ ppm. In poly(S-*r*-limonene), the ⁷Li signals correlated to aliphatic and diene protons are both centred about $\delta_{7\text{Li}} = 2.58$ ppm. These less polarised ⁷Li signals observed in poly(S-*r*-limonene) could imply some restriction

of Li-ion – π coordination, and therefore less polarised lithium environments with more aromatic functionalities and less dienes.

Although direct coupling between lithium and aromatics is not clearly observed (see **Figure 6.6a**), this correlation increases with ^1H spin diffusion as shown by the broadening of the lithium signal mainly correlated to diene protons towards $\delta_{1\text{H}} \sim 7$ ppm in **Figure 6.6b**. This increasing correlation between lithium and aromatic protons with ^1H spin diffusion implies indirect correlations perhaps through the diene functionalities. The decreased signal intensity between lithium and aliphatic protons with ^1H spin diffusion in **Figure 6.6b** implies smaller contributions of aliphatics to indirect correlations with lithium.

The increased significance of diene protons vs aromatics upon electrochemical treatment of poly(*S-r*-limonene) could imply evolution of the copolymeric structure over cycling. A comparison with two other copolymers poly(*S-r*-DIB) and poly(*S-r*-squalene) with diverse π systems reveals a preference of lithium correlation with dienes versus aromatics, irrespective of which π environment is initially dominant. One rationalisation for the presence of diene-lithium correlations (and lack of aromatics) in these copolymers could be due to Birch reduction of aromatic functionalities to form dienes over electrochemical cycling.²⁷ Favourable conditions for Birch reduction would also suggest the potential rearrangement of the copolymeric network and further ring substitution reactions over cycling.

Such mechanisms are also similarly encountered in selective polymerisation of dienes and styrenes using lithium catalysts.²⁸ According to Spirin *et al.*, in these polymerisation reactions, complexation of lithium with dienes is typically more stable than with styrene,²⁸ which agrees with the stronger correlation between dienes and lithium observed in this work. Moreover, in such polymerisation reactions, lithium or alkyl lithium is used in ethereal solvents such as THF to direct selectivity towards the formation of cis-isomer polymer chains.²⁸ Considering the stereoselectivity of these reaction pathways, the rearrangement of the copolymeric structure would therefore evolve towards a higher degree of order and cis-isomeric configuration dependent on its inherent Li-ion- π interactions.

Considering that the intuition in inverse vulcanisation is for total saturation of alkenes to form crosslinks, it is interesting to observe that dienes exhibit the strongest

coupling with lithium out of all the hydrocarbon functionalities. Additionally, supplementary coupling with lithium was intended to arise from the involvement of aromatic functionalities rather than dienes, such as commonly intended for poly(S-*r*-DIB).^{9, 10} A stronger lithium coupling with diene protons than aromatics is unsurprising however, considering strong Li-ion- π interactions have also been observed with dienes compared to aromatics in other systems.²⁹ This strong Li-ion- π interaction between lithium and diene functionalities can also be compared to the affinity and high solubility of lithium polysulfides in ether-based electrolytes.³⁰ In fact, the requirement for aromaticity to induce favourable π interactions has been widely contested,^{29, 31, 32} with no perceivable difference compared to interactions involving non-aromatic π systems. Rather, Mahadevi *et al.* notes that the strongest factors modulating favourable ion- π interactions are cooperativity, size and curvature within the material.³³ In such random copolymers anticipated to have highly disordered structures, modulating a cooperative diene-based π system is perhaps more feasible than a cooperative aromatic π system. Rational design of new inverse vulcanised copolymers should therefore be redirected to forming stable conjugated and/or cyclic alkene π systems if the goal is to ultimately enhance lithium coupling with the copolymeric component.

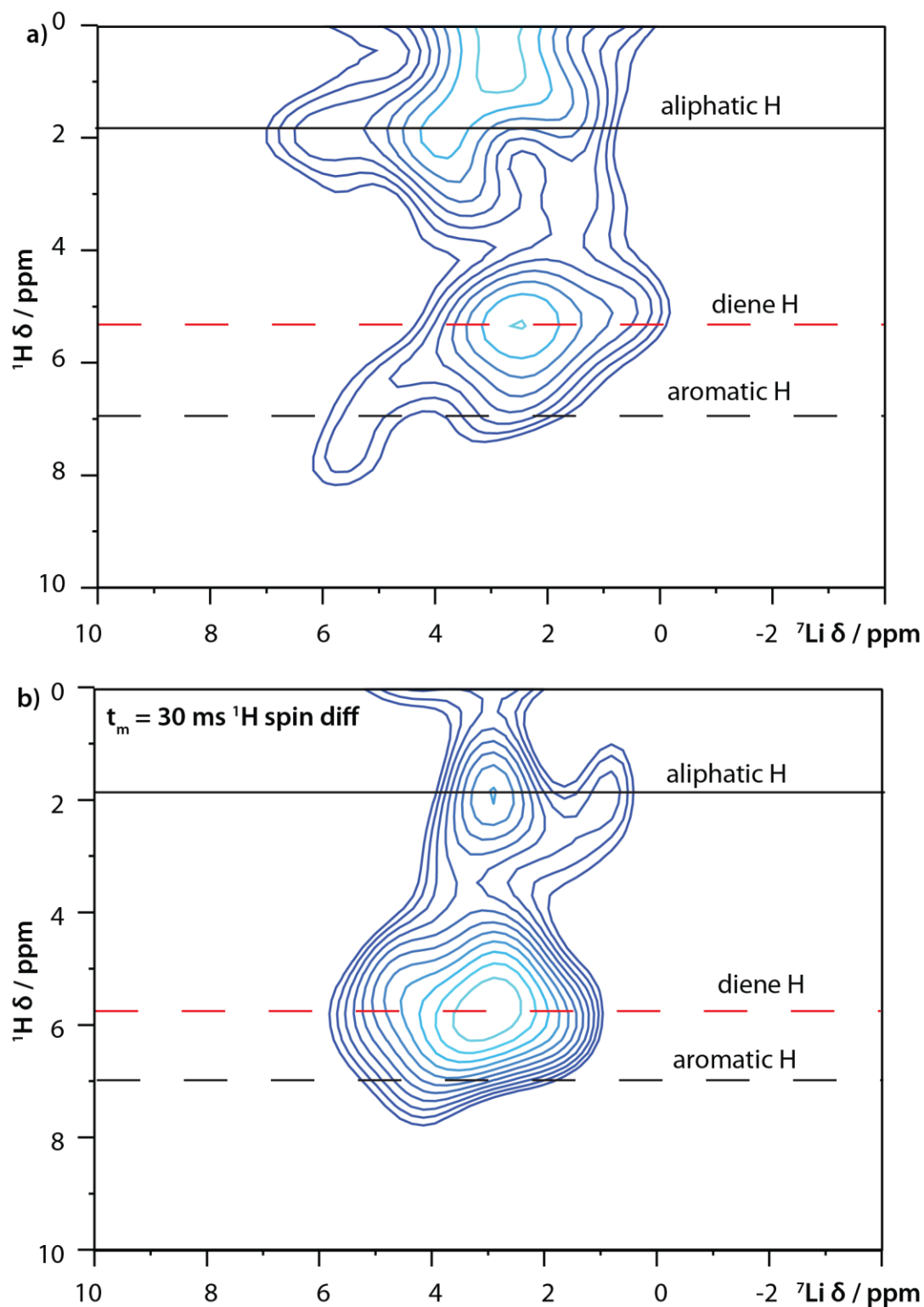


Figure 6.6 – ^1H - ^7Li HETCOR spectrum acquired **a)** without and **b)** with 30 ms ^1H spin diffusion of the poly(S-r-limonene) electrode powder extracted after 20th discharge.

6.3.5 Probing sulfur and carbon via XANES spectroscopy

The evolution of the sulfur and carbon environments at various states of discharge and charge was monitored using S K and C K-edge XANES spectroscopy

as shown in **Figure 6.7a** and **b**. XANES measurements, a surface probe, is sensitive to factors such as electronegativity, local symmetry, and molecular geometry of the absorbing atom, and thus provides structure-property insight on the SEI components formed on the surface of the electrode. Assignments of observed white lines from S K-edge (based on works by Pickering *et al.*^{34, 35} and Hackett *et al.*^{36, 37}) and C K-edge spectra are outlined on **Table 6.2a** and **b**.

As shown in **Figure 6.7a**, the surface of the poly(*S-r*-limonene) electrode is populated with at least five dynamic sulfur-containing SEI components that evolve over cycling, four of which are oxidised sulfur species. Whilst these oxidised sulfur species are indeed generally described as passivating interfacial components, the detrimental effects of passivation arise the formation of thick interfacial films that ultimately increase ohmic resistance. Fundamentally, the formation of an SEI containing passivating species such as Li_2S , ROSO_2Li , Li_2SO_3 , and Li_2SO_4 is essential for the stability of the electrode.³⁸ The dynamic evolution of all the sulfur environments observed on the poly(*S-r*-limonene) electrode over electrochemical cycling implies that they remain redox-active and do not parasitically accumulate at least within the first 20 cycles.

The first S K-edge feature, observed at 2472.3 eV shown in **Figure 6.7a I**, relates to the main S-S bonding environments within the copolymer and of elemental sulfur. This S-S environment is observed to broaden upon electrochemical treatment, suggesting increasingly disordered configurations (hence broader distribution) of the S-S environment over multiple cycles.³⁹ This increase of S-S disorder over cycling is plausible considering a rearrangement and scission of highly ordered crystalline sulfur components in the initial fresh state to disordered polysulfide species. Additionally, the relative population of this S-S environment also appears to evolve over cycling, suggesting that this modified S-S environment remains redox-active at least up to the 20 cycles investigated in this work.

Apart from the S-S environment (**I**), oxidised sulfur species are observed on the poly(*S-r*-limonene) electrode upon electrochemical treatment. Between the 1st-5th cycles, the highest energy/oxidation state S K-edge environment is mainly centred at 2479.7 eV (shown in **Figure 6.7a IV**) accompanied by relatively trace signals at 2475.1 eV (shown in **Figure 6.7a II**) – these environments are assigned as: (**IV**) - SO_3^{2-} , RSO_3^- , and (**II**) Li_2S . From the 5th-20th cycle, sulfur environments (**IV**) and (**II**)

become less dominant and the spectra gradually becomes more populated with signals arising from sulfur environments **(III)** and **(V)** – spectrum acquired of the 10th charge electrode is represented by a combination of sulfur environments **(I)**, **(II)**, **(III)**, and **(IV)**. The highest energy S K-edge signal (2481.0 eV assigned as SO₄²⁻ with the highest sulfur oxidation state, sulfur environment **V**), is not observed until the 20th cycle, implying that the formation of Li_xSO₄²⁻ occurs only after multiple cycling. Using a pyrolysed tyre carbon framework,¹⁷ the opposite phenomenon is observed where this higher oxidation state is initially observed in the 1st cycle but no longer observed beyond the 5th cycle, and the corresponding Li-S cells experienced a gradual loss of capacity over cycling. Using poly(*S-r*-limonene) electrodes, this access to higher oxidation states at later cycles could also rationalise the slight increase in capacity experienced after the 4th cycle as observed in the electrochemical cycling tests shown in **Figure 6.5a**.

Probing the carbon environment *via* C K-edge XANES as shown in **Figure 6.7b**, it is clear that the copolymeric hydrocarbon also evolves over multiple cycling, providing further evidence for copolymer participation in redox. Of note, electrochemical treatment results in the appearance of a sharp signal at 290.6 eV (**IV** assigned to σ^* CO₃²⁻/RO⁻ most likely from TFSI electrolytic salts⁴⁰) the relative intensities of carbon environments centralised at 287.6 and 288.7 (**II** and **III** assigned to σ^* CH/CS and σ^* CH₂ respectively⁴¹⁻⁴⁴) appear narrowed and more abundant after the 1st cycle compared to the fresh state. Dominance of carbon environments **II**, **III**, and **IV** particularly in discharged samples (red traces in **Figure 6.7b**) implies that this is an effect of lithiation and most likely a passivation of lithiated salts. Upon charging (green traces in **Figure 6.7b**), spectra of the poly(*S-r*-limonene) electrode is mainly populated with carbon environments **I** (π^* C=C⁴⁴) and **V** (σ^* C-C⁴⁴) resembling the fresh state, with most of the passivating carbon signals **II**, **III**, and **IV** removed. This active removal and replacement of the passivating carbon signals **II**, **III**, and **IV** implies that the poly(*S-r*-limonene) copolymeric framework gives rise to a reversible and redox-active SEI environment.

6.3.6 Impact of electrochemistry on ⁷Li NMR chemical shift

In order to understand the evolution of lithium environments during the initial formative 20 cycles, solid state 1D ⁷Li spectra were acquired for electrodes extracted from Li-S cells after 1st discharge, 1st charge, 20th discharge, and 20th charge (see

Figure 6.7c). Peak deconvolution based on the acquired spectra was performed to develop models representative of the lithium environments present in the samples.

An assessment of ^7Li spectra acquired of the 1st and 20th discharged electrodes suggests the presence of at least two distinct lithium contributions centered at ~ 3.5 (environment I, yellow peaks in **Figure 6.7c**) and ~ 2.8 ppm (environment II, orange peaks in **Figure 6.7c**). The broad ^7Li signal at ~ 2.8 ppm was previously attributed to the lithium directly correlated to the copolymer by ^1H - ^7Li HETCOR (see **Figure 6.6**) The main ^7Li signal at 3.5 ppm is absent from the ^1H - ^7Li HETCOR spectrum as it does not cross-polarize from the ^1H , confirming that this signal is Li inserted into the sulphur environment, with ≥ 1 nm distance from the organic species.

In previous works dedicated to investigating poly(S-*r*-DIB),⁹ as well as NMR characterisation by Huff *et al.* on the use of a baseline carbon black/sulfur electrode in Li-S cells,⁴⁵ lithium signal at ~ 3.5 ppm is generally associated with Li_2S . This resonance at 3.57 ppm (yellow peaks in **Figure 6.7c**) was therefore fixed in performing peak deconvolution of the electrode sample extracted after 1st discharge as shown on **Figure 6.7c**. With this applied constraint, the resonance assigned as lithium environment II is centralised about 2.83 ppm at a slightly higher resonance than after 20th discharge ($\Delta\delta_{^7\text{Li}} = -0.25$ ppm). Irrespective of the absolute peak centres, it is clear that the two observed ^7Li chemical shifts become more polarised and broadened after 20 cycles. The broadening particularly of the more deshielded environment I implies association with the copolymeric structure and a decreased structural mobility over cycling. This evolution of the ^7Li chemical shifts over cycling provides further evidence for the evolution of the copolymeric structure and its association with lithium over cycling.

Spectra of charged samples as modelled in blue in **Figure 6.7c** contain lithium signals that can be represented by one line shape centralised at lower chemical shifts < 1 ppm assigned as lithium environment II*. In previous works on poly(S-*r*-DIB) and poly(S-*r*-squalene),⁶ this charged species is associated with a static SEI buildup that increases over cycling. Based on the relative broadness of the line shape, this resonance is associated with copolymeric lithium. Using peak deconvolution, this II* (blue peaks in **Figure 6.7c**) resonance shifts only slightly from 0.7 ppm after 1st charge to 0.86 ppm after 20th charge ($\Delta\delta_{^7\text{Li}} = +0.16$ ppm) and is adequately polarised from the discharged state copolymeric lithium environment II. The difference in chemical shifts

between discharged II lithium and charged II* lithium environments implies an electrochemically active SEI build-up, however future work investigating the electrodes at longer cycles is necessary to ascertain the limit in which this component remains electrochemically active.

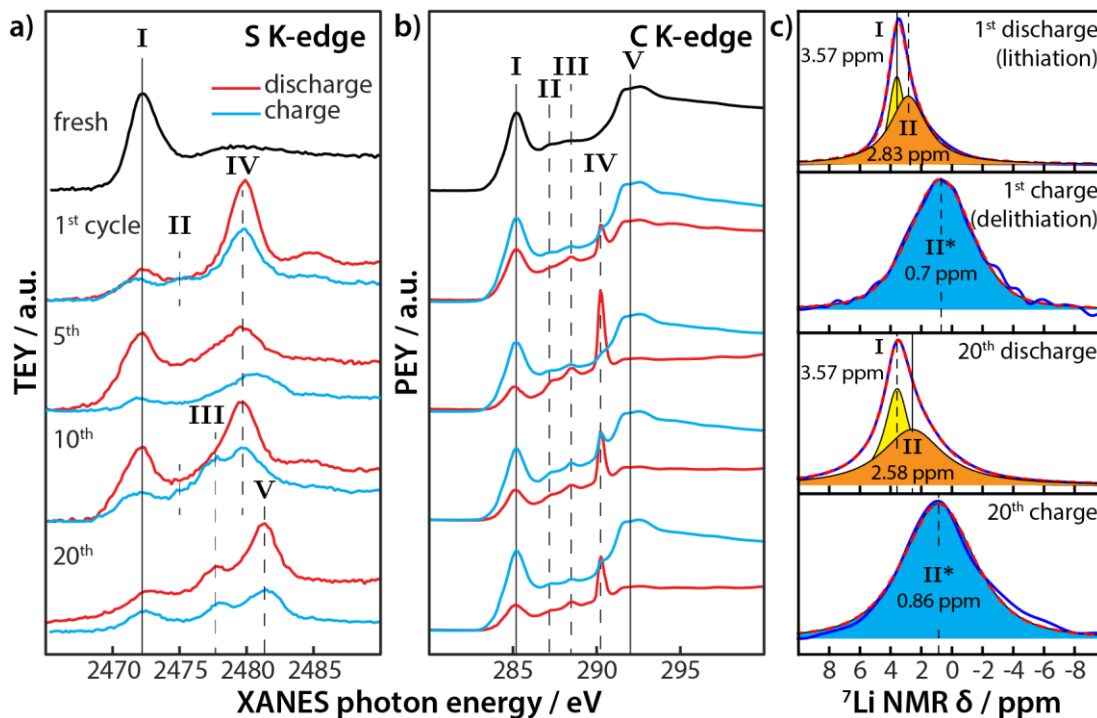


Figure 6.7 – a) S K-edge and **b)** C K-edge XANES spectra of poly(S-r-limonene) electrodes in the fresh state (black traces) and extracted at various states of discharge (red traces) and charge (blue traces), with lines indicating peak centres outlined and assigned in **Table 6.2**. **c)** 1D ⁷Li MAS NMR spectra (blue trace) of poly(S-r-limonene) electrode powders extracted after 1st discharge, 1st charge, 20th discharge and 20th charge. Dashed red lines are models of the data based on a sum of pseudo-Voigt line shapes (yellow I, orange II, blue II*) representing individual ⁷Li environments discussed in-text.

Table 6.2 – a) S K-edge and b) C K-edge white line assignments of spectra presented in Figure 6.7a and b respectively.

a) S K-edge white line assignments ³⁴⁻³⁷				
Index	Energy (eV)	Assignment	Appearance	Comments
I	2472.3	S-S	Fresh, 1 st -20 th cycle	Broadened over cycling
II	2475.1	Li ₂ S	1 st , 10 th charge	Lowest signal; only resolvable in 1 st and 10 th charge spectra
III	2477.6	RSO ₂ ⁻	10 th , 20 th cycle	
IV	2479.7	SO ₃ ²⁻ , RSO ₃ ⁻	1 st -10 th cycle	Highest energy phase up to the 10 th cycle
V	2481.0	SO ₄ ²⁻	20 th cycle	Highest energy phase only observed in the later 20 th cycle
b) C K-edge white line assignments				
Index	Energy (eV)	Assignment	Appearance	Comments
I	285.5	π^* C=C ⁴⁴	Fresh, 1 st -20 th cycle	Dominant in fresh and charged states
II	287.6	σ^* CH/CS ^{43, 44}	Fresh, 1 st -20 th cycle	Dominant in discharged states
III	288.7	σ^* CH ₂ ^{41, 42}	Fresh, 1 st -20 th cycle	Dominant in discharged states
IV	290.6	σ^* CO ₃ ²⁻ /RO ⁻ ^{41, 42}	1 st -20 th cycle	Dominant in discharged states
V	~292	σ^* C-C ⁴⁴	Fresh, 1 st -20 th cycle	Dominant in fresh and charged states

6.3.7 Investigation of lithium mobility *via* saturation recovery T_1 measurements

The molecular dynamics of the copolymeric lithium components after 20th discharge were investigated by saturation recovery experiments to determine T_1 spin-lattice relaxation times of identifiable lithium environments, which are outlined which are outlined on **Table 6.3**. Insight on lithium dynamics within the copolymeric electrode is pertinent to understanding its effects on polysulfide suppression during Li-S redox. Sequential peak deconvolution to model spectra measured at recovery times $\tau = 10$ ms – 30 s (spectra shown in **Figure 6.8**) revealed chemical shift contrast between three lithium environments I, II, and III centred at 3.53, 2.96, and 1.41 ppm respectively. Peak deconvolution performed for spectra measured at selected $\tau = 10$ ms and 30 s is provided in the appendix **Figure A. 14a** and **b** respectively.

Table 6.3 – Calculated T_1 relaxation times of deconvoluted ^7Li signals present in the poly(*S-r*-limonene) electrode extracted after 20th discharge obtained by modelling the datapoints to either a single-phase exponential decay function (i.e., one T_1 parameter, used for lithium environments I and II) or a two-phase exponential decay function (i.e., two T_1 parameters, used for lithium environment III). Further fit details and results are provided in the appendix **Figure A. 15**, **Figure A. 16** and **Table A. 7**)

	^7Li (ppm)		T_1 (ms)		R_{sq}	
I	3.53		2070(90)		0.992563	
II	2.96		5200(300)		0.98219	
	^7Li (ppm)	A	T_{1a} (ms)	T_{1b} (ms)	R_{sq}	$T_{1\text{mean}}$ (ms)
III	1.41	0.48(4)	15000(3000)	700(100)	0.985362	8000(2000)

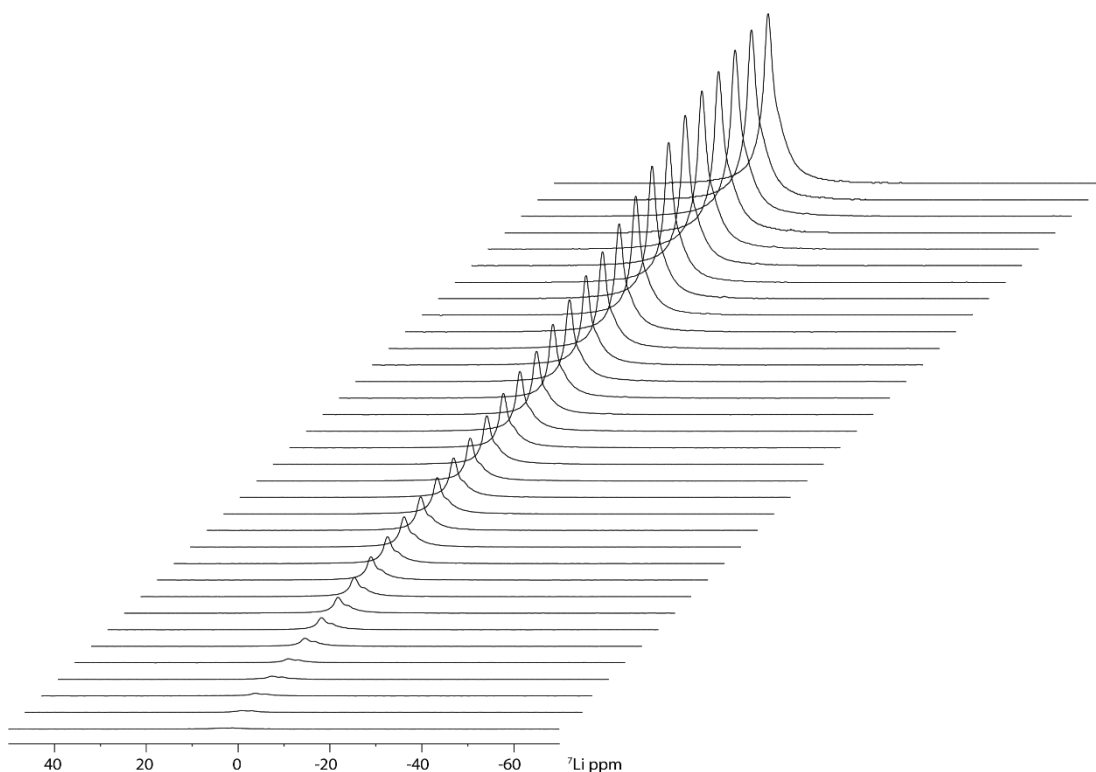


Figure 6.8 – Saturation recovery ^7Li NMR spectra acquired at $\tau = 10$ ms, 20 ms, 30 ms, 40 ms, 50 ms, 100 ms, 150 ms, 200 ms, 250 ms, 300 ms, 350 ms, 400 ms, 450 ms, 500 ms, 550 ms, 600 ms, 700 ms, 800 ms, 900 ms, 1 s, 1.25 s, 1.5 s, 1.75 s, 2 s, 2.5 s, 3 s, 4 s, 5 s, 7 s, 10 s, and 30 s.

The saturation recovery measurements of lithium environment I has a single exponential behavior yielding a T_1 of 2 s. **Table 6.3.** Modelling I with two T_1 components (see the appendix **Figure A. 16** and **Table A. 7b**) reveals the minor, but relatively immobile T_1 component ($A = 18(4)\%$) with significantly longer $T_{1a} = 8000(1000)$ ms. Lithium environment II also appears to have one major T_1 component, calculated to be 5200(300) ms as outlined in **Table 6.3.** The longer T_1 of this copolymeric lithium II compared to the major lithium I component implies an immobilising effect of the copolymeric framework on lithiated species. The electrolytic lithium environment III is most accurately modelled by two T_1 parameters as outlined in **Table 6.3**: a longer and thus immobile $\sim 48\%$ $T_{1a} = 15000(3000)$ ms, and a relatively mobile short $T_{1b} = 700(100)$ ms.

Comparing these values to other copolymeric electrode materials, the T_1 values of the copolymeric components II, and III (with notably long T_1 components 5200(300) and 15000(3000) ms respectively) are overall higher than previously observed in poly(*S-r*-squalene) (57(4)% $T_{1a} = 3300(400)$ ms and $T_{1b} = 380(50)$ ms); observed to be less effective in Li-S cell capacity retention (only $\sim 70\%$ initial capacity

retained at the 20th-100th cycle).^{6, 46} It is also important to highlight that a larger % contribution overall of the longer and immobile T_1 components in poly(*S-r*-limonene) electrodes (compared to ~40% short T_{1b} = 380(50) ms observed for poly(*S-r*-squalene), implying more effective lithium adsorption using poly(*S-r*-limonene) compared to poly(*S-r*-squalene). The relatively immobile copolymeric lithium also rationalises the higher capacity retention of Li-S cells when using poly(*S-r*-limonene) electrodes (~86 % initial capacity at 20th discharge).

In comparing the main lithium environment I however, poly(*S-r*-limonene) exhibits lower T_1 values (T_1 = 2070(90) ms from **Table 6.3a**) relative to poly(*S-r*-squalene) (40(10) % T_{1a} = 4900(800) ms and T_{1b} = 1700(200) ms). This overall lower T_1 of the main lithium environment when using poly(*S-r*-limonene) implies that its effects to Li-S cell capacity retention are less dependent on the adsorption of lithium environment I (components indirectly correlated to the copolymer), rather more dependent on immobilisation of lithium environments II and III directly correlated to the copolymer itself.

6.3.8 Monitoring lithium diffusivity using ^7Li - ^7Li EXSY NMR

^7Li - ^7Li EXSY NMR was performed on the 20th discharge electrode in order to elucidate the correlations between lithium environments and evolution in dynamics at various mixing times (t_m = 30 μs to 300 ms). As shown in **Figure 6.9**, the most prominent lithium environment at ~3.5 ppm is generally broad along the diagonal, implying spatial heterogeneity as previously observed in 1D ^7Li spectra shown in **Figure 6.7c**.

The lithium environment at ~3.5 ppm only weakly correlates with the broad copolymeric component centralised at 2.58 ppm, displaying a rounded-shape (Gaussian) distribution from t_m = 30 μs that begins to shift towards a more Lorentzian broadening behaviour (resembling a tilted six-pointed star shape) with t_m > 30 ms. Comparatively, a stronger correlation between lithium environments at 3.5 and ~2.58 would produce similarly broad signals, as experienced along the diagonals, along the off-diagonals, yielding a cross/star-like peak observed more clearly in electrochemically treated poly(*S-r*-squalene)⁶ and poly(*S-r*-DIB) electrodes.⁹ This relatively weak correlation implies that the main lithium environment at 3.5 ppm is only weakly adsorbed by the copolymeric 2.58 ppm component, in agreement with the

relatively short and mobile T_1 of the 3.5 ppm component as determined by saturation recovery.

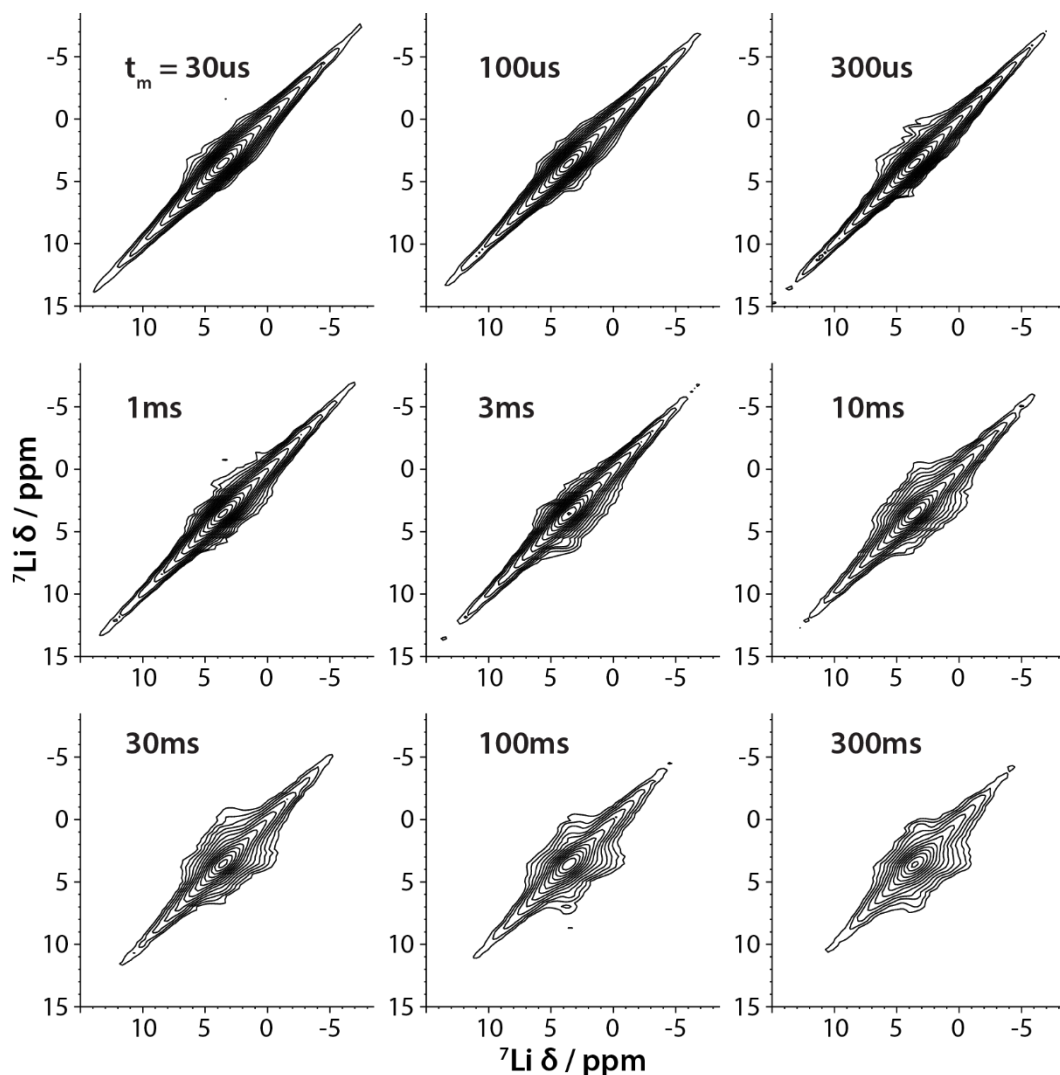


Figure 6.9 – ^7Li - ^7Li EXSY of the poly(S-r-squalene) electrode extracted after 20th discharge, showing correlations occurring at $t_m = 30\mu\text{s}$ to 300 ms

6.4 Conclusions

The findings of this work demonstrate that despite being a 1,5-diene crosslinker, inverse vulcanisation using limonene produces a relatively mobile copolymer framework that interacts with Li during redox. Based on the low M_w of poly(S-r-limonene) ($M_w = 242 \text{ g mol}^{-1}$ *via* SEC, $386\text{--}777 \text{ g mol}^{-1}$ *via* atmospheric pressure chemical ionization (APCI) mass spectrometry) and almost unity polydispersity index ($M_w/M_n = 1.16$ as determined *via* SEC and *via* by Crockett *et al.*), poly(S-r-limonene) is comprised of low molecular weight copolymeric fragments (1–3 limonene backbone units per fragment) that are dimensionally homogenous.⁷ Despite

this, in agreement with proposed by Crockett *et al.*,⁷ NMR spectra of poly(S-*r*-limonene) suggests that these copolymeric fragments are chemically inhomogeneous, most apparently through the presence of aromatic groups as products of dehydrogenation.

Whilst the molecular diversity of 1,5-diene inverse vulcanisation reaction products appears to be detrimental to chain mobility of poly(S-*r*-squalene), chemical inhomogeneity does not appear to compromise chain mobility of poly(S-*r*-limonene) as observed through solid-state ¹H-¹³C HETCOR. This retained chain mobility is perhaps due to the inability for limonene to form high molecular weight crosslinked structures upon inverse vulcanisation with sulfur. As dimensionally homogenous low molecular weight fragments, poly(S-*r*-limonene) would have adequately large free volume and accessible surface area to passively accommodate for Li-S redox. By comparison, high molecular weight, and therefore structurally rigid poly(S-*r*-squalene) would need to deform its chemical covalent crosslinks to liberate more active material during redox. Based on this interpretation, effective capacity retention should therefore depend on structural preservation of the crosslinked framework during Li-S redox.

XANES spectroscopy of electrochemically treated poly(S-*r*-limonene) electrodes reveal more significant evolution of the sulfur environment compared to carbon. The relatively unmodified carbon environment over cycling suggests no observable deformations to the polymeric hydrocarbon components of poly(S-*r*-limonene). Pertinently, the evolution of sulfur SEI species over electrochemical treatment suggests that, like poly(S-*r*-squalene), the poly(S-*r*-limonene) copolymeric framework impacts Li-S electrochemistry largely through its non-covalent interactions and ability to adsorb polarisable redox active polysulfides.

It should be emphasised that these findings do not generally imply that low copolymeric molecular weight directly enhances Li-S cell capacity retention. Indeed, previous investigations on poly(S-*r*-squalene) (**Chapter 5**) suggest that the long aliphatic chains of squalene (the most polarisable component) promote adsorption of lithiated species. Rather, the poorer capacity retention when using poly(S-*r*-squalene) electrodes is perhaps due to its low chain mobility and therefore poor self-healing capabilities of the framework during Li-S redox.

By contrast poly(S-*r*-limonene) appears to exhibit stronger correlation to lithium from its alkene and aromatic sites more than its aliphatics. Consequently, this results in long T_1 and relatively immobilised lithium environments directly correlated to the framework, however short T_1 and high mobility of the main lithium environment indirectly correlated to the framework. Despite high mobility of the main lithium environment, poly(S-*r*-limonene) produces excellent capacity retention in Li-S cells when used as an electrode material, implying that its efficacy is more dependent on the immobilisation of directly adsorbed lithium.

A combination of these effects, work in conjunction enhancing the impact of dispersion forces from the copolymeric hydrocarbons, rationalizes the marked improvement of Li-S capacity retention when using poly(S-*r*-limonene) electrodes. Ultimately the enhanced Li-S cell capacity retention when using poly(S-*r*-limonene) can be linked to its low copolymeric molecular weight, large free volume of the framework, and pertinently large dispersion forces with neighbouring copolymeric fragments and polarisable sulfur species. In addition to low molecular weight, poly(S-*r*-limonene) electrodes were also observed to preserve its copolymeric hydrocarbon structure over Li-S redox as implied by similar C K-edge XANES spectra of electrodes extracted at different states of discharge and charge. It is important to note that for another low molecular weight copolymer with a framework that would deteriorate with electrochemical cycling, this enhanced Li-S cell capacity retention cannot be guaranteed. Provided a designed copolymeric framework has adequate chain mobility, higher molecular weight (with greater impact of dispersion forces) could enhance lithium adsorption and improve capacity retention.

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Chapter 7: Poly(S-*r*-para-DIB)

7.1 Introduction

The efficacy of inverse vulcanised copolymers as electrode materials in Li-S cells have been commonly rationalised by “self-healing” capabilities.¹⁻² More specifically, the self-healing capability of polymeric materials often refers to their thermomechanical properties such as hardness (determined *via* methods such as indentation and tensile testing) or response to stress/strain.³ Whilst these parameters can be adequate descriptors of the bulk of the material, the expected evolution of sulfur crosslinks during Li-S redox calls for alternative strategies to selectively characterise this self-healing capability only on the hydrocarbon components of the framework.

In previous work exploring poly(S-*r*-limonene) (see **Chapter 6**), the copolymer’s favourable effects on specific capacity and capacity retention of the Li-S cell were attributed to the copolymeric electrodes self-healing capability that is controlled mainly by:

- (1) its relatively low molecular weight and almost unity polydispersity index, translating to high active material accessibility and thus rationalizing the relatively high specific capacity values produced when applied in Li-S cells
- (2) its strong correlations between functional groups based primarily on solid-state ¹H-¹³C HETCOR NMR, implying strong non-covalent interactions between the low molecular weight copolymeric fragments which ultimately contribute to the structural stability of the overall framework

In essence, one strategy to dissipate stress during Li-S redox in inverse vulcanised copolymers can perhaps involve minimising the average molecular weight of the copolymeric fragments whilst incorporating functional groups that exhibit strong non-covalent interactions with one another.

Whilst low connectivity between the copolymeric fragments may indeed be one way to minimise structural degradation from stress, alternative strategies involving the use of crosslinking monomers with more freely rotating functional groups may produce equally favourable results and should be considered.

In work by Heinz *et al.* on strain recovery of glassy polymers networks, polymeric networks based on para- versus meta-substituted aromatic monomers display remarkably different anelastic responses to compressive stress.⁴ Their different responses to stress is proposed to be mainly due to the larger segmental rearrangements (and thus larger network deformations) involved with meta-aromatic ring motions to dissipate stress compared to para-aromatic ring motions. Applying this concept to the extensively studied meta-aromatic network poly(S-*r*-DIB), inverse vulcanisation involving its para-isomer 1,4-diisopropenylbenzene (para-DIB, shown in **Figure 7.1**) could in principle result in a copolymer that experiences smaller structural deformations upon Li-S redox, thus allowing higher active material accessibility and perhaps more effective self-healing capabilities.

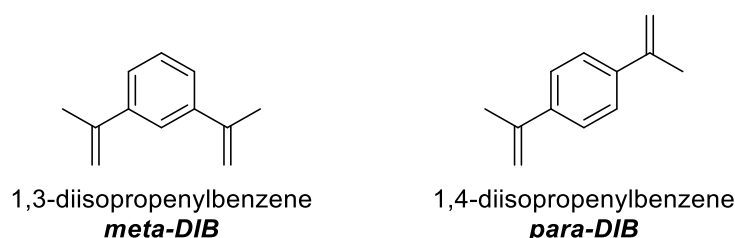


Figure 7.1 – Structural diagrams of isomers 1,3-diisopropenylbenzene (*meta*-DIB) and 1,4-diisopropenylbenzene (*para*-DIB)

This brief chapter details insight from solid-state NMR, X-ray powder diffraction, and XANES spectroscopy exploring the inverse vulcanised copolymer poly(S-*r*-para-DIB), and how it compares to its meta-isomer poly(S-*r*-DIB) when applied Li-S cells. Note, this chapter was proposed to be future work, however with COVID-19 impacting global mobility, this work was undertaken and brief results included in the thesis.

7.2 Methodology

7.2.1 Preparation of poly(S-*r*-para-DIB)

Solid elemental sulfur (4.5 g, 140 mmols) and solid 1,4-diisopropenylbenzene (para-DIB, 0.5 g, 3.0 mmol stored in an Ar-filled glovebox, 98.0+%, TCI America™) were homogenised using an agate mortar and pestle. The powder mixture was then transferred to a glass sample vial for annealing inside a muffle furnace, set to heat up to 200 °C under air (10 °/min from room temperature) and maintained at this temperature for 3 h before cooling to room temperature. This process yielded a glassy

red solid after the annealing process, which gradually transformed to the final opaque orange solid copolymeric product upon cooling over >12 h.

7.2.2 Coin cell fabrication and electrochemical testing

Li-S coin cell fabrication and electrochemical testing was conducted following the same procedure as outlined for poly(S-*r*-limonene) (see **Chapter 6**). Electrodes prepared using poly(S-*r*-para-DIB) were measured to have a sulfur loading of 2.6(3) mg cm⁻².

Galvanostatic testing of the Li-S cells was conducted using a Landt CT3002 battery test system (Landt instruments) between 1.7–2.6 V at C/10 (167.5 mA g⁻¹) with an initial 6 h rest step after cell fabrication.

Extracted electrodes for *ex situ* measurements were washed using DME solvent and dried and stored for >24 h in an Ar-filled glovebox.

7.2.3 Characterisation

Characterisation using solid-state NMR and XANES spectroscopy techniques was performed following the previous methodology for poly(S-*r*-limonene) described in **Chapter 6**. XRD measurements were also performed following the procedure outlined in **Chapter 6** however using a Co K α X-ray source.

7.3 Results and Discussion

7.3.1 Characterisation of the poly(S-*r*-para-DIB) hydrocarbon

The local structure of the poly(S-*r*-para-DIB) hydrocarbon framework was characterised using solid state ¹H-¹³C-CP TOSS and ¹H-¹³C HETCOR NMR shown in **Figure 7.2** and **Figure 7.3** respectively. Solution-state spectra could not be acquired due to insolubility of poly(S-*r*-para-DIB) in non-polar aprotic solvents. This insolubility of the copolymer in non-polar aprotic solvents implies significant contributions from polymer chain entanglements to the network crosslinks.

As shown in the solid-state ¹H-¹³C-CP TOSS in **Figure 7.2** and emphasised in the 2D ¹H-¹³C HETCOR in **Figure 7.2**, the poly(S-*r*-para-DIB) copolymer exhibits no pendant alkenes (which would produce a ¹H signal at ~6 ppm), suggesting complete crosslinking of 10 wt. % para-DIB with 90 wt. % elemental sulfur. In previous investigations on the meta-isomer poly(S-*r*-DIB) also at 90 wt. % sulfur feeds with 10

wt. % meta-DIB pendant alkenes as revealed by solid-state NMR were still present. Considering similar heating times were implemented compared to para-DIB (note despite maintaining the temperature of the reaction mixture at 185 °C for only ~15-30 mins, vulcanisation with meta-DIB, liquid at room temperature, requires a pre-melt of sulfur requiring ~2h to induce ROP), the total consumption of alkenes observed for poly(S-*r*-para-DIB) implies faster reaction kinetics when using para-DIB in place of meta-DIB. This observation agrees with observations by Heinz *et al.*, which notes higher pre-yield anelastic strain (i.e., larger deformations during inverse vulcanisation) of the para-polymer network compared to meta.⁴

Aside from the total consumption of alkenes, as shown in **Figure 7.2** the poly(S-*r*-para-DIB) hydrocarbon framework appears to retain its aromatic functionalities ($\delta_{^{13}\text{C}} = 110\text{-}150$ ppm), with a population of aliphatic groups relatively similar to those previously observed in its meta-isomer poly(S-*r*-DIB). The relative strength of cross correlation peaks between aromatic protons and aliphatic carbons (and vice versa) in the ^1H - ^{13}C HETCOR shown in **Figure 7.3** also suggests strong interactions between aliphatic and aromatic functionalities within the poly(S-*r*-para-DIB) copolymer.

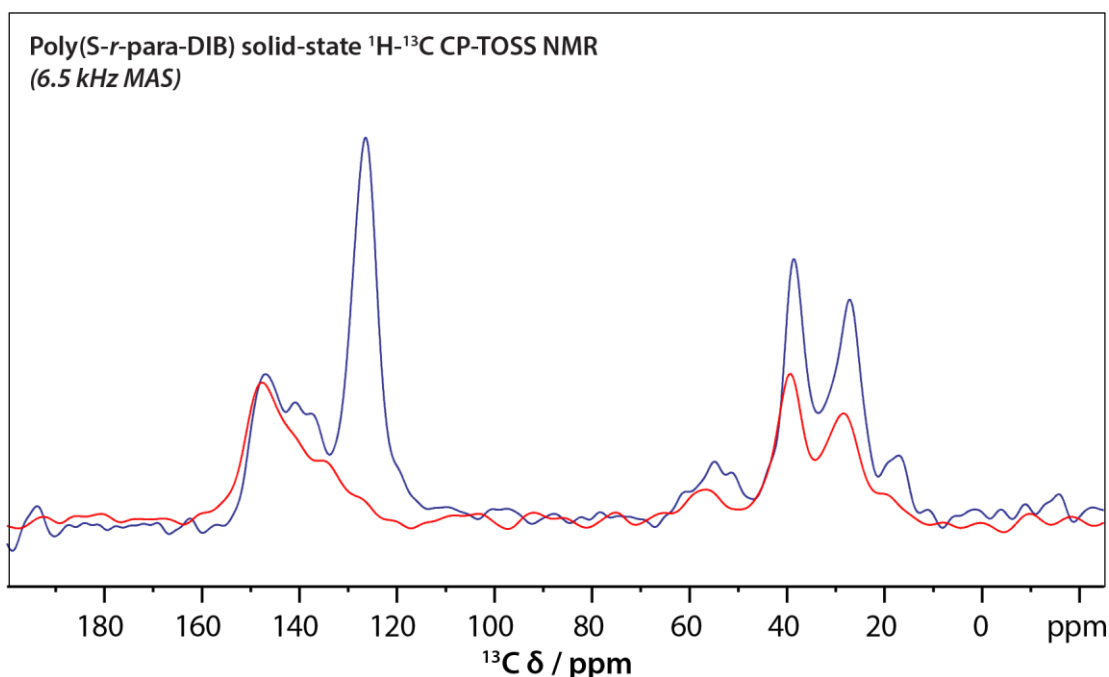


Figure 7.2 – ^1H - ^{13}C CP-TOSS solid-state NMR spectra of poly(S-*r*-para-DIB) prepared using 10 wt. % para-DIB. The blue trace is the proton-enhanced ^{13}C signal, and the red trace is the signal acquired with a 40 μs gated decoupling filter.

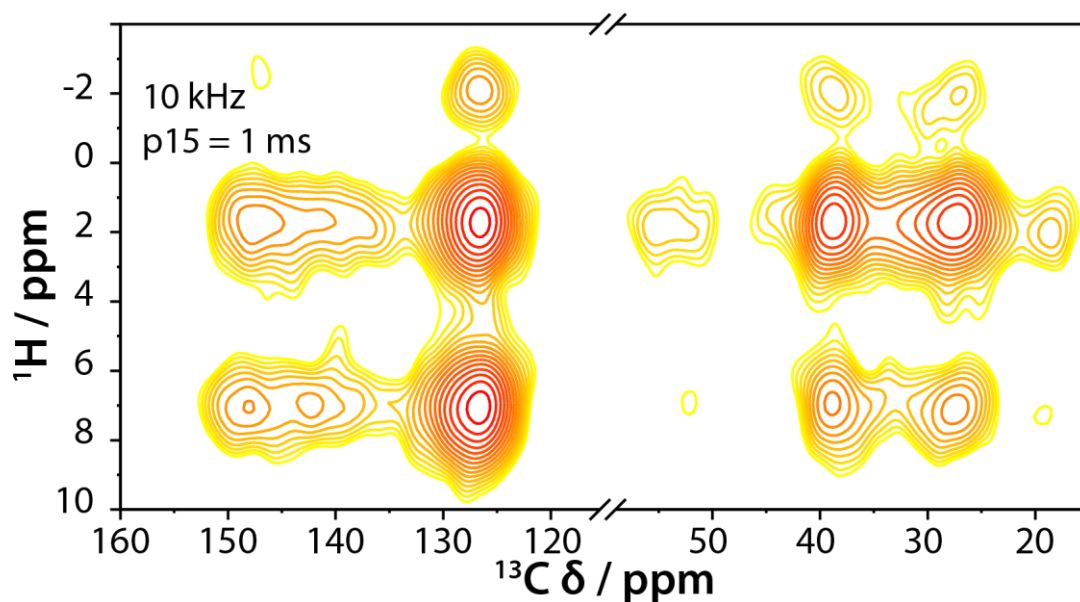


Figure 7.3 – ^1H - ^{13}C HETCOR NMR spectrum of poly(S-*r*-para-DIB) prepared using 10 wt. % para-DIB.

7.3.2 Determination of the crystalline sulfur phase composition via X-ray powder diffraction

The X-ray powder diffraction (XRD) pattern of poly(S-*r*-para-DIB) is provided in **Figure 7.4**. Rietveld refinement of α -S₈ (orthorhombic α -S₈ *Fddd*, ICDD, No. 01-078-1888) and β -S₈ (monoclinic β -S₈ *P2₁/c*) reveals a dominance of α -S₈ over the β -S₈ phase in poly(S-*r*-para-DIB) (α -S₈ = 92(1) wt. %, β -S₈ = 8.1(4)%). This contrasts to that previously observed for poly(S-*r*-DIB), which exhibits a dominance of β -S₈ (typically stable at $T > 95\text{ }^\circ\text{C}$) over the α -S₈ phase (α -S₈ = 0.13(1), β -S₈ = 0.87(1)) in the pristine copolymer.⁵ This preference towards α -S₈ in poly(S-*r*-para-DIB) further suggests a less constrained hydrocarbon framework compared to its meta-isomer, which would allow metastable β -S₈ to return to the more stable α -S₈ phase upon cooling after inverse vulcanisation.

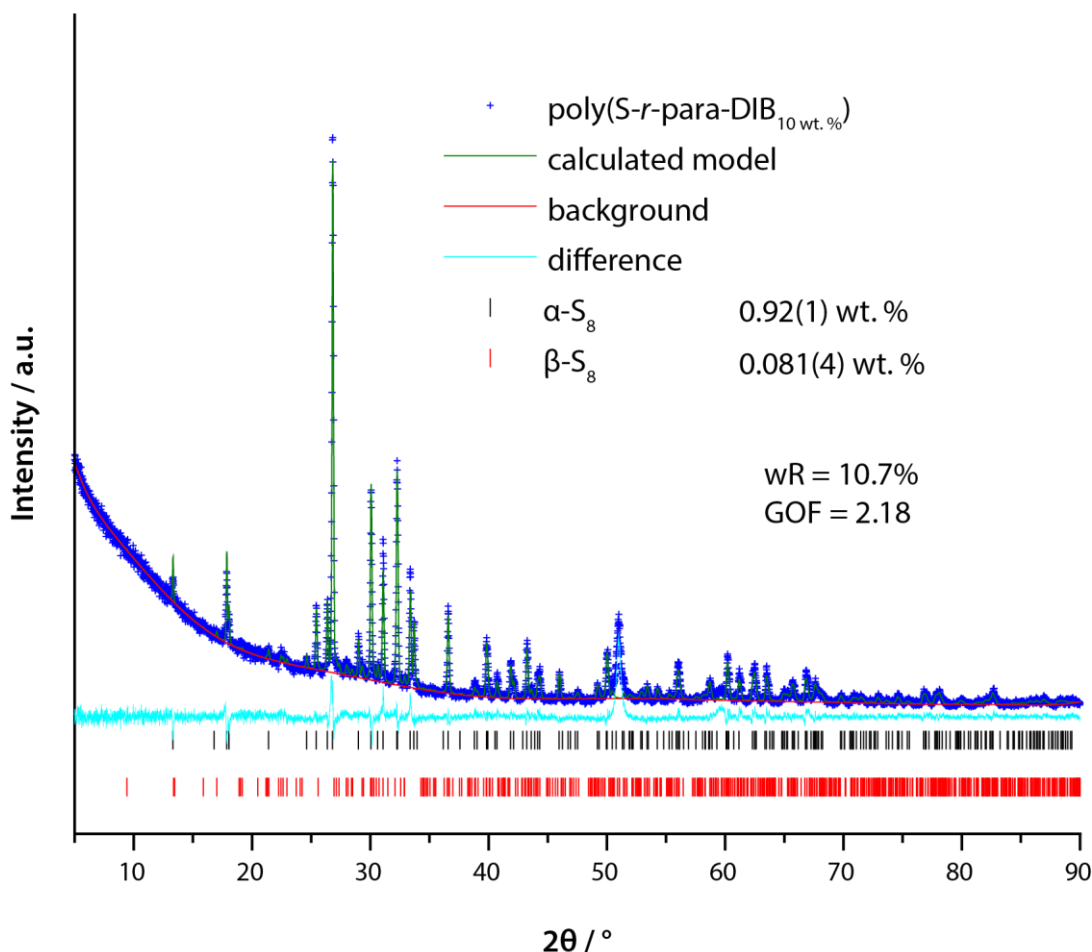


Figure 7.4 – XRD pattern of poly(S-*r*-para-DIB) prepared with 10 wt. % para-DIB and 90 wt. % elemental sulfur (blue crosses), and a calculated model (green trace) based on Rietveld refinement of α -S₈ (orthorhombic α -S₈ *Fddd*, ICDD, No. 01-078-1888, black peak markers) and β -S₈ (monoclinic β -S₈ *P2₁/c*, ICDD No. 01-071-0137, red peak markers)

7.3.3 Electrochemical performance

The electrochemical performance of a Li-S cell using poly(S-*r*-para-DIB) as an electrode material was determined *via* galvanostatic testing as shown in **Figure 7.5**. As shown in **Figure 7.5a**, the use of poly(S-*r*-para-DIB) electrodes in Li-S cells produces an initial gravimetric discharge capacity of 689 mAh g⁻¹, which decreases and stabilises to ~520 mAh g⁻¹ by the 20th cycle (~75% initial) when cycled at 0.1 C (167.5 mAh g⁻¹ of sulfur). In terms of areal capacity, these values equate to 1.8 and 1.34 mAh cm⁻² respectively (considering a sulfur loading of ~2.6 mg cm⁻²), remarkably higher than observed for poly(S-*r*-DIB) (initial areal capacity ~0.8 mAh cm⁻² cycled at 0.1C, calculated based on the reported gravimetric value 1100 mAh g⁻¹ and a sulfur loading of 0.8 mg cm⁻² in work by Chung *et al.*).¹ These relatively high areal capacity

values demonstrate higher active material accessibility in the poly(S-*r*-para-DIB) framework compared to its meta-isomer.

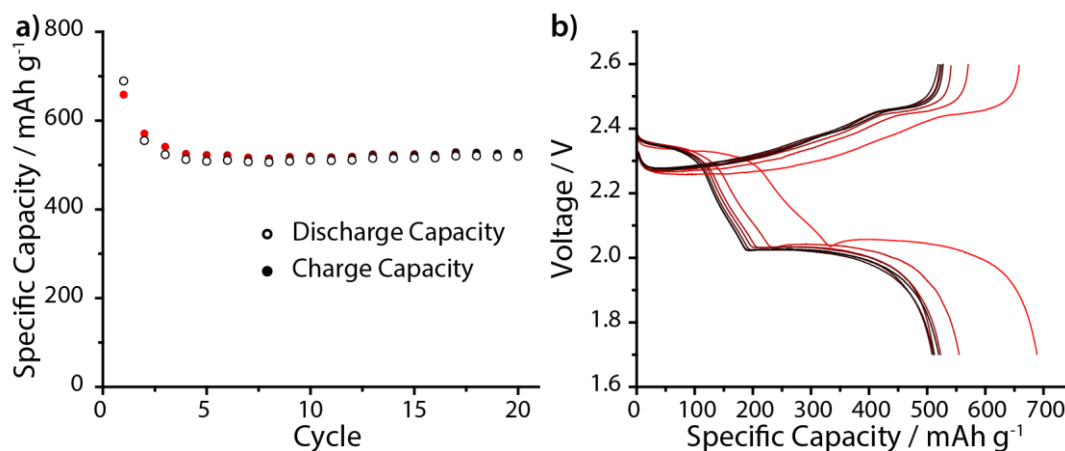


Figure 7.5 – (a-b) Electrochemical performance of a Li-S cell using a poly(S-*r*-para-DIB) electrode (10 wt. % para-DIB) cycled at C/10 or 167.5 mA g⁻¹ of sulfur, **a)** Specific charge and discharge capacities over cycling, and **b)** corresponding voltage vs capacity plots with red→black traces representing the 1st-20th cycles

7.3.4 Probing sulfur and carbon via XANES spectroscopy

XANES spectra was performed to identify the SEI surface species of poly(S-*r*-para-DIB) electrodes at various states of discharge and charge. S K-edge and C K-edge XANES spectra are shown in **Figure 7.6a** and **b** respectively, with detailed white line assignments outlined in **Table 7.1**. Notably in the S K-edge XANES spectrum of the fresh poly(S-*r*-para-DIB) electrode, two sulfur environments are observed at ~2472.3 eV (labelled as S K-edge feature I in **Figure 7.6a**) attributed to S⁰ or S-S bonding environment and ~2479.7 eV (labelled as S K-edge feature III in **Figure 7.6a**) attributed to S⁴⁺ most likely SO₃²⁻, RSO₃⁻.⁶⁻⁹ The presence of sulfite peaks implies that the fresh poly(S-*r*-para-DIB) electrode already contains oxidized sulfur bonding environments prior to electrochemical treatment. This S K-edge feature III appears to persist from the fresh state up to 20th discharge (bottom red trace in **Figure 7.6a**).

The other S K-edge feature is centred about ~2477.6 eV (labelled as S K-edge feature II in **Figure 7.6a**) attributed to S²⁺ most likely RSO₂⁻, which only becomes apparent in the 1st charged state (2nd blue trace in **Figure 7.6a**). Upon cycling, the S K-edge environment of the poly(S-*r*-para-DIB) electrode surface appears to evolve between varying populations of these three sulfur bonding environments, generally dominated by contributions from S-S (I) and S⁴⁺ (III) in **Figure 7.6a**. Contrastingly,

poly(*S-r*-DIB) electrodes were previously observed to exhibit dominating S K-edge contributions from a signal at 2477.8 eV (corresponding to an assignment to S^{2+} in this work) particularly on the surface of discharged electrode samples.⁵ The different S K-edge morphologies between electrochemically treated poly(*S-r*-para-DIB) and poly(*S-r*-DIB) electrodes demonstrate the impact to SEI speciation from different isomeric configurations and/or levels of oxidation.

Corresponding C K-edge XANES spectra of the poly(*S-r*-para-DIB) electrodes (shown in **Figure 7.6b**) exhibit 5 unique bonding environments (assigned in detail in **Table 7.1**) similar to previously observed in other inverse vulcanised copolymer electrodes^{5, 10} (see **Chapter 6** on poly(*S-r*-limonene)). The C K-edge profile of the fresh state (black trace in **Figure 7.6b**) appears to be recovered in the charged states (blue traces), implying minimal distortions to the carbon morphology upon electrochemical cycling.

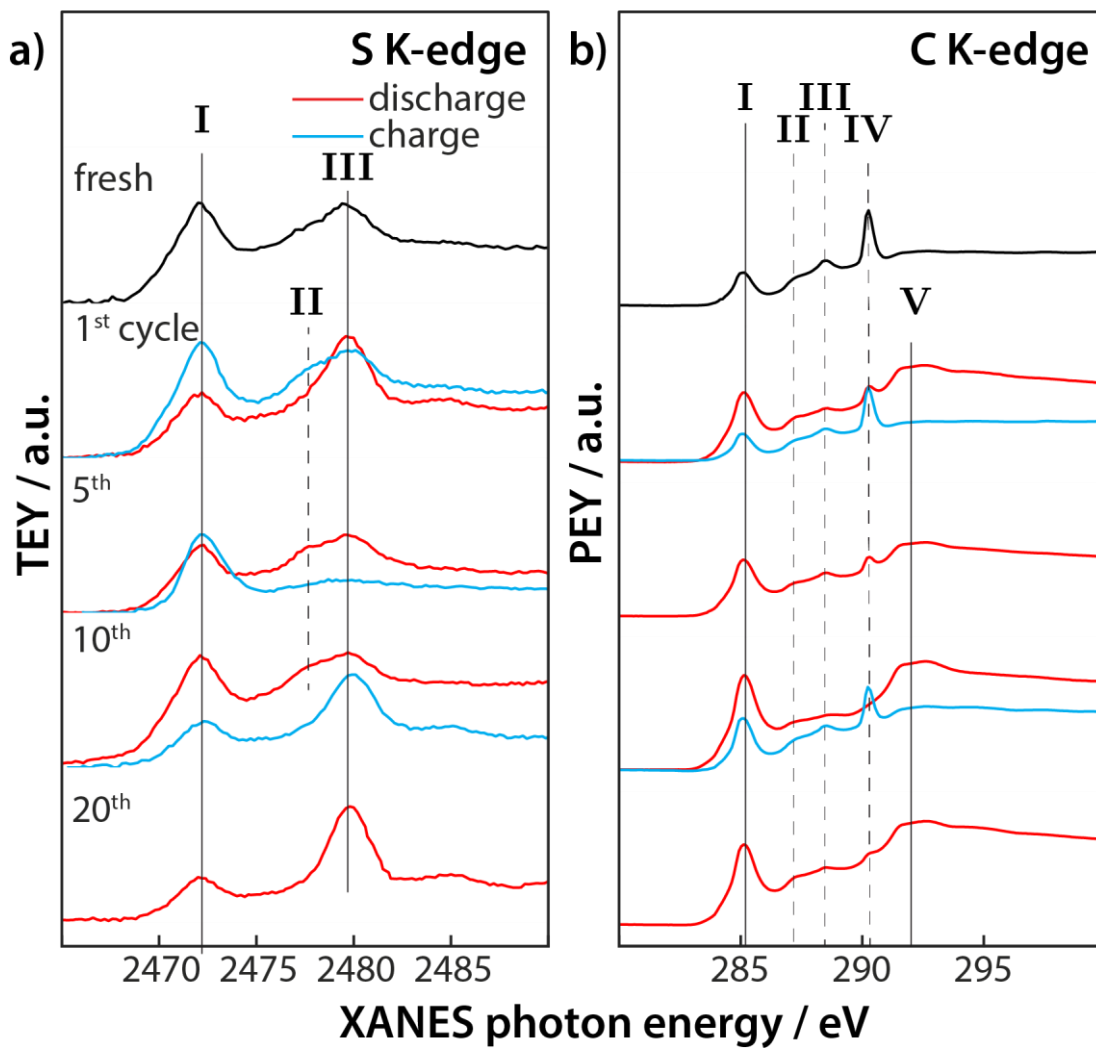


Figure 7.6 – (a-b) XANES spectra of electrochemically treated poly(S-*r*-para-DIB) electrodes (cycled at C/10, 167.5 mA g⁻¹ of sulfur) extracted at various states of charge and discharge – **a)** S K-edge and **b)** C K-edge spectra. White line assignments are outlined on **Table 7.1**.

Table 7.1 – a) S K-edge and b) C K-edge white line assignments of spectra presented in Figure 7.6 a and b respectively.

a) S K-edge white line assignments ⁶⁻⁹				
Index	Energy (eV)	Assignment	Appearance	Comments
I	2472.3	S-S	Fresh, 1 st -20 th cycle	Competing dominance with S K-edge environment III
II	2477.6	RSO ₂ ⁻	1 st -10 th cycle	Formed after cycling
III	2479.7	SO ₃ ²⁻ , RSO ₃ ⁻	Fresh, 1 st -20 th cycle	Competing dominance with S K-edge environment I
b) C K-edge white line assignments				
Index	Energy (eV)	Assignment	Appearance	Comments
I	285.5	π^* C=C ¹¹	Fresh, 1 st -20 th cycle	All identified C K-edge signals initially present in the fresh state. Charged state signals resemble the fresh state more closely than discharged states
II	287.6	σ^* CH/CS ¹¹⁻¹²	Fresh, 1 st -20 th cycle	
III	288.7	σ^* CH ₂ ¹³⁻¹⁴	Fresh, 1 st -20 th cycle	
IV	290.6	σ^* CO ₃ ²⁻ /RO ⁻ ¹³⁻¹⁴	Fresh, 1 st -20 th cycle	
V	~292	σ^* C-C ¹¹	Fresh, 1 st -20 th cycle	

7.3.5 Lithium-copolymer correlations and molecular dynamics

Identification of lithium-copolymer correlations was performed using solid-state ^1H - ^7Li HETCOR NMR of poly(S-*r*-para-DIB) electrode powder extracted after 20th discharge. As shown in **Figure 7.7a**, lithium appears to correlate exclusively to lower shift aliphatic proton signals in the poly(S-*r*-para-DIB) electrode. Unlike what was previously observed for poly(S-*r*-DIB) no significant correlations are observed between lithium and aromatic protons. Even when acquired with 10 ms ^1H spin diffusion as shown in **Figure 7.7b**, this cross correlation between lithium and the aromatic protons are still observed to be relatively weak compared to with aliphatic protons, implying only weak and indirect lithium correlation with aromatic protons. This limited correlation between lithium and the aromatic functionalities in the poly(S-*r*-para-DIB) copolymer matrix could also be rationalised by its presumably less compact structural arrangement compared to poly(S-*r*-DIB) and therefore greater distance between lithium and the copolymeric hydrocarbons.

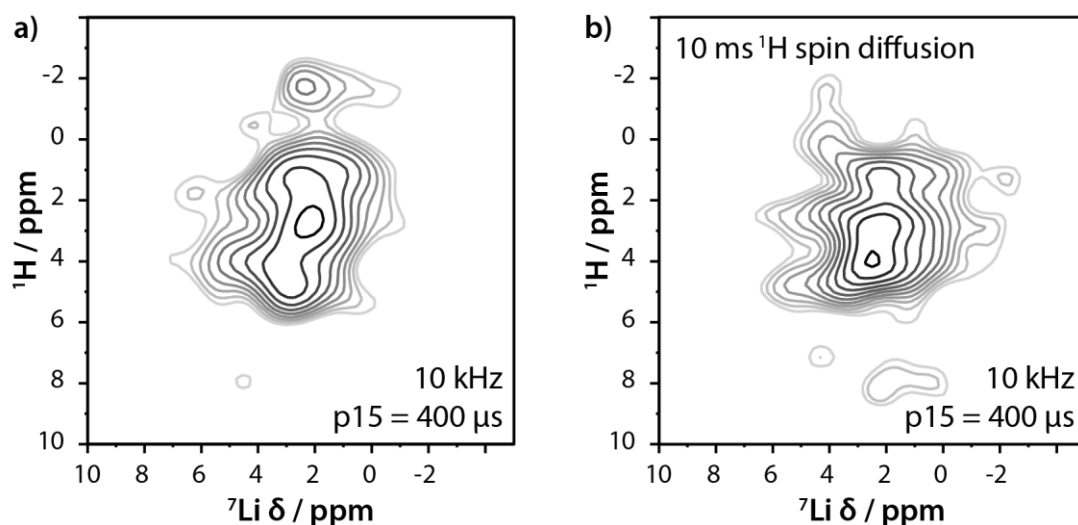


Figure 7.7 – Solid-state NMR spectra of a lithiated poly(S-*r*-para-DIB) electrode extracted after 20th discharge (cycled at C/10, 167.5 mA g⁻¹ of sulfur) and rinsed with DME solvent – **a)** ^1H - ^7Li HETCOR NMR of the poly(S-*r*-para-DIB) electrode, with **b)** showing solid-state ^1H - ^{13}C HETCOR NMR of the pristine poly(S-*r*-para-DIB) electrode (10 wt. % para-DIB) previously shown in **Figure 7.3** as a guide.

Comparing the lithium shifts correlated to the copolymer matrix based on ^1H - ^7Li HETCOR to ^7Li - ^7Li EXSY of the same sample (shown in **Figure 7.8a**) measured with $\tau_m = 1$ ms), the copolymeric ^7Li shift of ~ 2 ppm is a minor broadened component that shows some homonuclear ^7Li correlation with the major component at ~ 3.5 ppm. This ^7Li - ^7Li correlation between copolymeric lithium and the major lithium

component (not directly correlated to any protons) is also observed in other inverse vulcanised copolymer electrodes^{5, 10} and can be linked to Li adsorption within the copolymeric framework.

Assessment of ^7Li - ^7Li EXSY spectra with various mixing times $\tau_m = 1, 10, 100$ ms (shown in **Figure 7.8a, b and c** respectively) shows a broad main lithium environment at $\delta_{^7\text{Li}} \sim 3.5$ ppm along the diagonal observed at a similar scale compared to poly(S-*r*-DIB) (as well as poly(S-*r*-squalene)). This narrow ridge along the diagonal is an effect of spatial heterogeneity of the ^7Li signal, with different parts of the analyte experiencing different effective magnetic fields.¹⁵ This main lithium component at ~ 3.5 appears to narrow with higher mixing times $\tau_m = 100$ ms as shown in **Figure 7.8c**. This implies that the lithium ions display motional dynamics on 10-100 ms timescales.

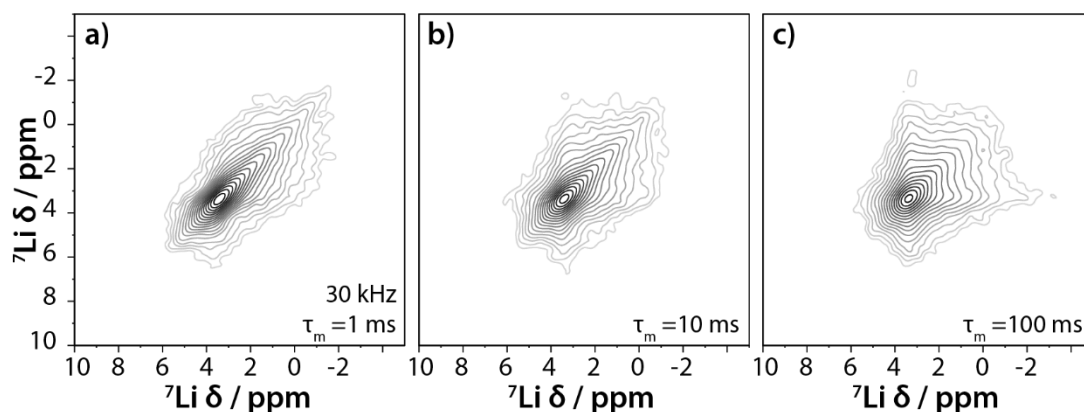


Figure 7.8 – ^7Li - ^7Li EXSY spectra of the poly(S-*r*-para-DIB) electrode acquired with different mixing times $\tau_m =$ **a)** 1 ms, **b)** 10 ms, and **c)** 100 ms.

7.4 Conclusions

The use of meta- vs para-aromatic crosslinkers in inverse vulcanised copolymers appears to produce different effects to Li-S cell electrochemical performance. This effect is most clearly observed when comparing areal capacity values, with the poly(S-*r*-para-DIB) electrodes exhibiting higher values than its meta isomer.

This higher areal capacity can be linked to greater active material accessibility based on characterisation of the copolymeric electrode matrix after electrochemical treatment using solid-state ^1H - ^7Li HETCOR NMR. Investigations using solid-state NMR show a strong correlation between lithium and only the aliphatic protons in the electrode matrix. This could be due to the hypothesised poly(S-*r*-para-DIB)

architecture with higher rotational freedom of functional groups compared to the meta isomer, which would allow for greater lithium accessibility.

^7Li - ^7Li EXSY NMR of the copolymer electrodes show similar lithium dynamics in poly(S-*r*-para-DIB) and poly(S-*r*-DIB) electrodes, i.e., relatively fast mobility of the Li-ions in the elemental sulfur and the copolymeric domains. This coincides with the lithiation capabilities and thus rationalises the similar capacity retention values produced when applied in Li-S cells. Moreover, differences between poly(S-*r*-para-DIB) and poly(S-*r*-DIB) particularly in S K-edge XANES spectra of electrochemically treated electrodes demonstrate their impact to speciation and the relative populations of electrolytic SEI components.

Although a brief snapshot, this chapter reinforces how tuning the monomer can have a dramatic impact on the electrode copolymer and its subsequent electrochemical performance. Furthermore, the electrochemical properties can be rationalised with reference to the copolymeric properties and their evolution.

7.5 References

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Chapter 8: Conclusions and outlook

8.1 Carbon frameworks

8.1.1 Summary of the findings

The findings based on the use of pyrolysed tyre and coffee carbons in Li-S cells explored in this work, as well as similar successes reported for other waste carbons suggest a promising outlook for the reliable use of crudely processed carbon frameworks in next generation energy storage devices. This work also incorporates multiple characterisation techniques such as powder XRD, BET analysis, Raman, XPS, and XANES spectroscopy, all of which were pertinent in rationalising the role of the waste carbon frameworks on Li-S cell performance.

Analysis using each of these techniques offered multiple perspectives on which factors should be considered in the processing of waste/biomass-derived carbon sources for practical applications in Li-S cells. Below is a summary on the key insights offered by techniques used to characterise pyrolysed carbons:

- (1) XRD (and elemental combustion and XRF analysis) – Specifically in its application to evaluate the impact of pyrolysis conditions to on crystalline growth of impurities in pyrolysed tyre carbons, and pertinently their impact to Li-S cell performance. XRD analysis on phase impurities identified by elemental analysis suggested that minimising Li-S cell capacity loss may not require complete removal of impurities from crude carbon sources. Rather, a more effective approach could be through controlling the crystalline growth of certain impurities (in this case cubic and hexagonal ZnS) that may influence the pore morphology of the pyrolysed carbon matrix.
- (2) Raman spectroscopy – This technique enabled crude quantification of carbon disorder/graphitic character of the pyrolysed carbons through I_D/I_G calculations. Based on the analysis conducted in this work, although the level of disorder of the pyrolysed carbons appeared to depend on the preparation conditions, it had no observable impact to Li-S cell performance.
- (3) BET analysis (and SEM/EDS) – Insight on surface area and pore morphology of pyrolysed carbons was provided by a combination of these techniques. Since

an ideal pore morphology is yet to be reported, the information gained from these techniques alone was insufficient to rationalise the material's impact to Li-S cell performance in this work (i.e., it is unclear whether the differences are large enough to be considered significant). The impact of pore morphology (characterised by BET and SEM/EDS analysis) is evaluated through other techniques.

- (4) XPS and XANES spectroscopy – X-ray spectroscopy techniques revealed influence of the pyrolysis conditions on the speciation of sulfur and fluorine related interfacial compounds when pyrolysed carbons are used in Li-S cells. They also helped in the rationalisation of unusual redox behaviour observed in Li-S cells when using pyrolysed tyre carbons (e.g., correlating the presence of additional plateau regions at earlier cycles to the onset appearance of certain interfacial species such as sulfones)

The key findings from these techniques can be used to inform future cost-effective strategies in production of carbon Li-S cell electrode materials from crude waste/biomass sources.

8.1.2 Remaining challenges and outlook

Understanding the role of carbons in Li-S batteries is mainly limited by current approaches in their direct characterisation as well limitations in monitoring the surrounding Li-S redox components. Whilst changes to the carbon framework is challenging to monitor during electrochemistry, current methods (such as UV-vis spectroscopy, XANES, and ^7Li NMR) that are sensitive to variability of the surrounding redox-active species are generally not universal to all Li-S cell configurations. Considering the potential application of carbons crudely sourced from renewable waste-streams and biomass, it is critical to develop further strategies to monitor the Li-S cell that are not exclusive to specific or pure morphologies. These considerations in analysis can limit investigations of Li-S redox to the use of highly ordered carbon frameworks that may not necessarily ideal and can be costly to process. Each analytical technique involves different strengths and limitations and investigating the role of carbons in Li-S batteries requires assessment from a combination of these techniques.

8.2 Copolymeric frameworks

The amenable conditions for inverse vulcanisation can mislead to assumptions that the behaviour of sulfur and crosslinking mechanisms involved are consequently simple and thus equivalent across all inverse vulcanised copolymers. It is important to consider that the formation and transformation of sulfur allotropes are sensitive to minor variations in temperature, impurities, and time.¹ Moreover, polydispersity based on Trommsdorf-Norrish autoacceleration effects can also result in heterogenous products and further inconsistencies between different investigations. This means that results can be difficult to replicate, and reproducibility depends on well-defined conditions.

This inherent complexity of sulfur-copolymers can give rise to inconsistencies between reported observations discussing similar materials. **Table 8.1** shows conditions for the preparation of sulfur-squalene copolymer reported by Sahu *et al.*² and Parker *et al.*³ in two separate investigations. Whilst both investigations shared the aim to prepare sulfur-squalene copolymer with 90 wt. % sulfur, Sahu *et al.* and Parker *et al.* employed preparation regimes that varied in terms of scale (2 vs. 15 g batch respectively), temperature (180 vs 175 °C respectively), time (15 vs 25 min respectively), as well as treatment post-synthesis (110 °C, 24 h vs 140 °C, 18 h).^{2, 3} The resulting copolymers varied in terms of their dominant sulfur phases (revealed *via* XRD) implying differences in other properties related to the overall material.

Table 8.1 – Conditions for the preparation of sulfur-squalene copolymer (90 wt. % sulfur) outlined by Sahu *et al.*² and Parker *et al.*³ in separate investigations.

Inverse vulcanisation conditions						Post-synthesis conditions				
Squalene	S ₈	Calc. wt. % S ₈	T / °C	Time	Atm.	T / °C	Time	Atm.	Dominant sulfur phase at STP	Ref
233 µL, 0.2 g, 0.49 mmol	1.8 g, 7.02 mmol	90	180	15 min	air	110	24 h	vacuum	α-S ₈	[2]
1748 µL, 1.50 g, 3.65 mmol	13.5 g, 52.63 mmol	90	175	25 min	N/S	140	18 h	N/S	γ-S ₈	[3]

It is thus important to consider the implications of preparation conditions such as scale, time, temperature, and crosslinker feed to the properties of the resulting copolymer. Ensuring well-defined conditions and thorough characterisation of the material's properties in consideration of these conditions can prevent inconsistencies or contradictory results between separate investigations.

Whilst the presence of covalent C-chalcogen bonds in the copolymer is generally accepted (and can be diagnosed using a wide selection of techniques such as XPS, Raman, and FTIR spectroscopy),²⁻⁶ their direct influence on the specific capacity of the battery as an electrode material is challenging to assess. One perspective supposes that this crystalline sulfur moiety is covalently bound to the copolymeric matrix.⁷ In defence of this perspective, stabilisation of the copolymer relies on the formation of this C-chalcogen covalent bond. One *ex situ* XRD investigation conducted on sulfur-limonene polysulfide-based electrodes suggests that the copolymer is an active participant in electrochemistry.⁸ In this work, investigations were primarily carried out on copolymers prepared using a 1:1 wt.% sulfur to d-limonene ratio (a relatively high monomer feed) such that no crystalline sulfur moieties could be resolved from the measured XRD pattern. Upon first discharge and charge, XRD measurements of the cycled electrodes revealed new reflections that correspond to redox-active sulfur species. The speciation of crystalline sulfur moieties upon cycling suggests that the copolymer actively participates in electrochemistry and acts as a sulfur source at least within the first cycle. It also suggests however that the original copolymeric structure is not preserved during cycling, and thus the long-term role of these covalently bound chalcogen moieties remains to be a topic of debate.

Alternatively, this crystalline moiety could instead be physically bound as a separate component from the copolymeric matrix within the material. In the investigation of STI copolymer, Li *et al.* elaborates on the relationship between the copolymeric and chalcogen moieties based on findings from HRTEM.⁵ The observations on STI copolymer based on HRTEM reveals a heterogenous morphology with localised crystalline and amorphous regions. Based on this finding, the authors suppose that the STI copolymer demonstrates a “watermelon-like structure”, with β sulfur nanocrystals embedded like seeds within the amorphous copolymeric moiety. Indeed, whilst this study demonstrates that the material contains heterogenous crystalline and amorphous environments, the role and participation of the amorphous

moiety in electrochemistry remains unknown. This challenge in differentiating between covalent and physically bound chalcogen moieties subsequently presents as an issue in further characterisation of the copolymer and their role in battery electrochemistry.

There is yet to be a straightforward diagnostic tool that can be used to determine whether crystalline sulfur moieties observed in the as-synthesised material are physically or covalently bound to the copolymeric matrix, and which of these conformations are more beneficial for battery applications. Phase-metastability in carbon-sulfur composites typically rely on physical confinement within nanostructure morphologies,⁹⁻¹⁷ and thus it would seem reasonable to apply the same rationalisation to inverse vulcanised copolymers. However, such as in the case of layered structures, chemical bonding and structural distortions have also been known to provide pathways for local energy minima and phase metastability.¹⁸⁻²¹ Previous works that have observed stabilisation of β or γ sulfur phases in inverse vulcanised copolymers relate this phenomenon cautiously to the structure or functionalities within the organosulfur matrix.^{3, 5, 22} Whether this structural attribute refers to crosslinking and covalent C-S bonds cannot yet be substantiated nor denied.

8.2.1 Insight on framework confinement from analysis of the pristine copolymer

Assessment of the crosslinks involved within the copolymer requires gross characterisation of the entire framework as well as selectively of the sulfur and hydrocarbon components. Comparative studies involving a diverse set of copolymers (as opposed to analysis conducted exclusively on one copolymer) can also aid in the analysis. The analysis of four selected copolymers listed (two of which are explored in detail on **Chapter 5** and **Chapter 6**) are summarised in this work:

- i. **Poly(S-r-DIB)** – Developed by Chung *et al.* using 1,3-diisopropenylbenzene (DIB) crosslinking monomer ($M_w = 158.24 \text{ g mol}^{-1}$) as an exemplar material introducing the concept and application of inverse vulcanized copolymers in Li-S cells.²³ DIB is an aromatic compound with two equally reactive alkene substituents arranged in a meta- 1,3- configuration about the ring.
- ii. **Poly(S-r-squalene) (Chapter 5)** – prepared using squalene crosslinking monomer ($M_w = 410.73 \text{ g mol}^{-1}$); a relatively high molecular weight 1,5-diene with six potentially reactive double bonds

- iii. **Poly(S-*r*-limonene) (Chapter 6)** – prepared using limonene crosslinking monomer ($M_w = 136.24 \text{ g mol}^{-1}$); a 1,5-diene with similar molecular weight to DIB with two alkenes of unequal reactivity.
- iv. **Poly(S-*r*-para-DIB)** – prepared using 1,4-diisopropenylbenzene (para-DIB) crosslinking monomer ($M_w = 158.24 \text{ g mol}^{-1}$); the para-isomer of DIB expected to allow greater rotational freedom of copolymeric fragments about the aromatic ring.

Gross characterisation of all the crosslinks involved in the framework as outlined in **Table 8.2** have been conducted using methods such as:

- Size exclusion chromatography (SEC) and/or atmospheric pressure chemical ionization (APCI) mass spectrometry to determine weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (M_w/M_n)
- Solubility/insolubility tests in non-polar aprotic solvents to crudely measure polymer chain entanglements (which can be followed by rheological measurements to quantify polymer viscosity or modulus)

Selective characterisation of the sulfur and hydrocarbon components within the copolymer as outlined in **Table 8.3** can be conducted using methods such as:

- X-ray powder diffraction (XRD) and Rietveld analysis to identify crystalline sulfur phases confined within the framework
- NMR for spectral editing and to assess spatial proximity between hydrocarbon functional groups

As outlined in **Table 8.4**, there are notable differences in electrochemical performance between Li-S cells using different copolymer electrodes. Comparing the 1st areal specific discharge capacities at 0.1C (167.5 mA g⁻¹), poly(S-*r*-para-DIB) (1.8(2) mAh cm⁻²) produces the highest value, closely followed by poly(S-*r*-limonene) (1.55(1) mAh cm⁻²) then poly(S-*r*-squalene) (1.21(1) mAh cm⁻²). Trailing furthest behind is surprisingly the exemplar material poly(S-*r*-DIB) (0.576(5) mAh cm⁻²). Considering retained and working capacities measured at 20th discharge, poly(S-*r*-para-DIB) and poly(S-*r*-limonene) equally produces the highest areal capacities (1.34(1), and 1.34(1) mAh cm⁻² respectively), followed by poly(S-*r*-squalene) (0.8(1) mAh cm⁻²), then poly(S-*r*-DIB) (0.426(1) mAh cm⁻²). This equates to 86%, 75% 74%,

67% of the initial capacity retained at 20th cycle for poly(S-*r*-limonene), poly(S-*r*-para-DIB), poly(S-*r*-DIB), and poly(S-*r*-squalene) respectively.

In essence, out of the four selected copolymers, poly(S-*r*-limonene) electrodes produce overall the greatest improvements to the Li-S cell performance (specific capacity and capacity retention). Isomers poly(S-*r*-DIB) and poly(S-*r*-para-DIB) exhibit similar capacity retention values, however higher areal capacity values are produced by poly(S-*r*-para-DIB). Whilst poly(S-*r*-DIB) produces the lowest specific areal capacity, Li-S cells using poly(S-*r*-squalene) electrodes suffer the greatest capacity loss over long term cycling.

Loosely we can rationalise the effects to Li-S cell electrochemical performance as follows:

- Better areal capacity → Higher accessibility to active material
- Better capacity retention → Greater structural durability of framework

The overall greater specific areal capacity and capacity retention produced by poly(S-*r*-para-DIB) and poly(S-*r*-limonene) would translate to relatively high active material accessibility and structural durability of these frameworks. Contrastingly, the relatively poor areal capacity produced by poly(S-*r*-DIB) suggests that the framework morphology is inherently obstructive to Li-S redox. Whilst poly(S-*r*-squalene) initially produces relatively high specific capacity, reflecting high active material accessibility during redox, the significant capacity loss suggests it suffers most from structural deterioration over cycling.

Correlating this interpretation to insight on the framework morphologies explored in this work, rationalisation for copolymer effects to Li-S cell electrochemistry have been provided as follows:

- Poly(S-*r*-DIB)** – Exhibiting the lowest overall specific capacity values (0.576(5)-0.426(1) mAh cm⁻² from 1st to 20th discharge at 0.1C, 167.5 mA g⁻¹ of sulfur), the low active material accessibility of poly(S-*r*-DIB) suggests a relatively compact hydrocarbon arrangement compared to the other selected copolymers. This constrained arrangement is also inferred by the presence of β -S₈ (typically metastable under standard temperature and pressure conditions) as revealed by XRD and Rietveld analysis, as well as the presence of strong

off-diagonal cross peaks between aliphatic and aromatic hydrocarbons as revealed through solid-state ^1H - ^{13}C HETCOR NMR.⁴

Considering its relatively low capacity retention compared to poly(S-*r*-limonene) (~74% initial capacity at 20th discharge at 0.1C), structural deterioration of the hydrocarbon framework can be related, at least in part to the relatively high average molecular weight of copolymeric fragments which could be more susceptible to structural deterioration compared to smaller fragments.

- ii. **Poly(S-*r*-squalene)** – The relatively high initial specific capacity produced by poly(S-*r*-squalene) (1.21(1) mAh cm⁻², see **Chapter 5**²⁴) suggests the hydrocarbon chains are more loosely arranged than poly(S-*r*-DIB) allowing for greater active material accessibility. Considering poly(S-*r*-squalene) is a relatively high molecular weight copolymer with significant polymer chain entanglement contributions (suggested by low solubility in non-polar aprotic solvents), this high accessibility to the sulfur active material suggests that the stability of the copolymeric architecture is reliant on weak polymer chain entanglements, perhaps between redox active sulfur chains.

Pertinently, the facile destruction of the copolymeric architecture to access sulfur active material would result in capacity loss over cycling (~67% initial capacity at 20th discharge at 0.1C). Moreover, being comprised mostly of aliphatic groups with bulky substituents, the hydrocarbon framework would be structurally constrained and susceptible to structural deterioration over cycling.

- iii. **Poly(S-*r*-limonene)** – Whilst solid-state NMR analysis suggests strong interactions between the hydrocarbon components, being comprised of low molecular weight fragments, poly(S-*r*-squalene) would grant high active material accessibility, thus producing relatively high specific capacity values (1.55(1)-1.34(1) mAh cm⁻² from 1st to 20th discharge at 0.1C, see **Chapter 6**). The relatively high capacity retention when using poly(S-*r*-limonene) electrodes could be based on the long T_1 and thus relative immobility of lithium directly correlated to the copolymer as suggested by saturation recovery measurements of poly(S-*r*-limonene) electrodes (see **Chapter 6**).
- iv. **Poly(S-*r*-para-DIB)** – Strong correlations between the aliphatic and aromatic groups is suggested by solid-state NMR analysis, as well as overall large

contributions of polymer chain entanglements (based on insolubility in non-polar aprotic solvents). Despite these implications that poly(S-*r*-para-DIB) is a highly crosslinked network, it produces relatively high specific capacities (1.49(1)-1.34(1) mAh cm⁻² from 1st to 20th discharge at 0.1C) and therefore high active material accessibility. This high active material accessibility could perhaps be rationalised by the para configuration of substituents about the aromatic rings within the copolymer, which could allow greater rotational freedom compared to its meta-isomer poly(S-*r*-DIB).

This greater rotational freedom based on the para-aromatic configuration of the crosslinking monomer could also rationalise the similar capacity retention values to poly(S-*r*-DIB) despite a presumably higher weight average molecular weight (due to insolubility in non-polar aprotic solvents), reflecting relative resistance of the framework to deterioration from stress upon electrochemical cycling.

Table 8.2 – Weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (M_w/M_n) of four selected inverse vulcanised copolymers **i)** poly(S-*r*-DIB), **ii)** poly(S-*r*-squalene), **iii)** poly(S-*r*-limonene), and **iv)** poly(S-*r*-para-DIB) prepared using 50 wt. % crosslinking monomer with 50 wt. % elemental sulfur from size exclusion chromatography or mass spectroscopy reported in literature.

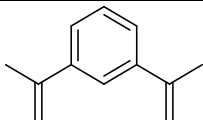
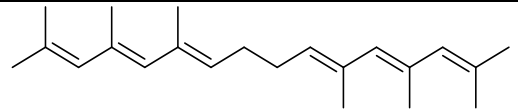
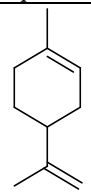
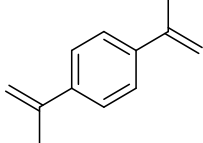
	Monomer (50 wt. %)	M_w / g mol ⁻¹	M_n / g mol ⁻¹	M_w/M_n	Method/remarks
(i)	 1,3-diisopropenylbenzene	1260	467	2.7	Size exclusion chromatography ²³
(ii)	 Squalene	N/A	N/A	N/A-	Low/no solubility in non-polar aprotic solvents ^{2, 3, 24} – significant polymer chain entanglements
(iii)	 Limonene	242	210	1.16	Size exclusion chromatography ⁶
(iii)	 Limonene	386-777	-	-	Atmospheric pressure chemical ionization (APCI) mass spectrometry ⁶
(iv)	 1,4-diisopropenylbenzene (10 wt.%)	N/A	N/A	N/A-	Insoluble in non-polar aprotic solvents – significant polymer chain entanglements

Table 8.3 – Summary of solid-state NMR and XRD analysis on four selected inverse vulcanised copolymers **i)** poly(S-*r*-DIB), **ii)** poly(S-*r*-squalene), **iii)** poly(S-*r*-limonene), and **iv)** poly(S-*r*-para-DIB) prepared using 10 wt. % crosslinking monomer with 90 wt. % elemental sulfur.

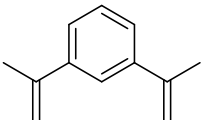
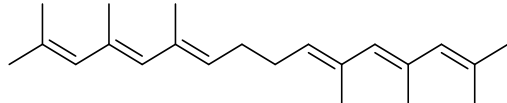
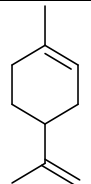
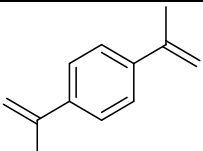
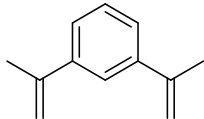
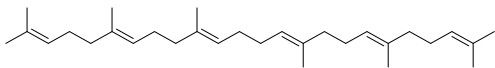
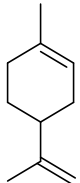
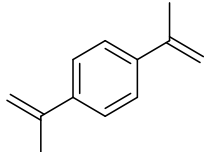
	Monomer (10 wt. %)	Structure of hydrocarbon framework from solid-state ^1H - ^{13}C CP TOSS and ^1H - ^{13}C HETCOR NMR	Crystalline sulfur phase from XRD	Remarks about covalent crosslinks
(i)	 1,3-diisopropenylbenzene	Aromatic groups retained, no pendant alkenes; strong off-diagonal cross peaks between aliphatics and aromatics ⁴	β -S ₈ ⁴	High M_w fragments with low rotational freedom due to steric hindrance Crosslinked hydrocarbon framework can stabilise β -S ₈
(ii)	 Squalene	Some pendant alkenes; strong correlations between aliphatic groups (see Chapter 5) ²⁴	α -S ₈ ²⁴	High M_w fragments with low rotational freedom due to steric hindrance
(iii)	 Limonene	Presence of aromatic groups, no pendant alkenes; strong off-diagonal cross peaks between aliphatics and aromatics (see Chapter 6)	α -S ₈	Low M_w fragments (1-3 limonene backbone units) with low rotational freedom due to steric hindrance
(iv)	 1,4-diisopropenylbenzene	Aromatic groups retained, no pendant alkenes; strong off-diagonal cross peaks between aliphatics and aromatics	α -S ₈	High M_w fragments with relatively greater rotational freedom due to para- (1,4) arrangement of aromatic substituents

Table 8.4 – Electrochemical performance of Li-S cells (with similar electrode/electrolyte compositions and cycling conditions) using inverse-vulcanised copolymer electrodes prepared using four selected inverse vulcanised copolymers **i**) poly(S-*r*-DIB), **ii**) poly(S-*r*-squalene), **iii**) poly(S-*r*-limonene), and **iv**) poly(S-*r*-para-DIB) with 10 wt. % crosslinking monomer and 90 wt. % elemental sulfur from literature^{2, 4, 8, 23, 24} and from this work

Monomer (10 wt. %)	Reference	Areal S mass / mg cm ⁻²	1 st specific discharge capacity at 0.1C (167.5 mA g ⁻¹)		20 th discharge capacity at 0.1C (167.5 mA g ⁻¹)		
			mAh g ⁻¹	mAh cm ⁻²	mAh g ⁻¹	mAh cm ⁻²	% of initial
	[23]	0.8	1100	0.9	(100 th) 823	0.7	75%
1,3-diisopropenylbenzene (meta-DIB)	[4]	0.7(2)	809 ± 276	0.576(5)	598 ± 204	0.426(1)	74%
	[2] (at 0.2C; 1C = 1672 mA g ⁻¹)	1.2-1.5	(2 nd) 1023	1.4	(100 th) 713	1.0	~70%
Squalene	[24] Chapter 5	2.0(4)	618 ± 114	1.21(1)	411 ± 76	0.80(1)	67%
	[8] (at 0.5C; 1C not defined)	~3.0	956	2.9	(300 th) 932	2.8	97%
Limonene	Chapter 6	2.2(3)	691 ± 78	1.55(1)	595 ± 67	1.34(1)	86%
	This work	2.6(3)	689 ± 80	1.8(2)	520 ± 57	1.34(1)	75%
1,4-diisopropenylbenzene (para-DIB)							

8.2.2 Insight on framework confinement from analysis of electrochemically treated copolymer electrodes

Further insight on the copolymeric architecture and its impact to Li-S cell electrochemistry is provided using solid-state NMR techniques, probing ^1H and ^7Li nuclei. ^1H - ^7Li HETCOR NMR measurements of electrochemically treated samples elucidate correlations between lithium and specific functionalities of the copolymeric hydrocarbon components. ^7Li - ^7Li EXSY NMR of electrochemically treated copolymer electrodes (mixing time $\tau_m = 100$ ms) as presented in **Figure 8.1**, reveal that different copolymer architectures give rise to lithium environments with varying mobilities.

Most evidently in electrochemically treated poly(S-*r*-limonene) as shown in **Figure 8.1iii**, the main lithium environment at ~ 3.5 ppm is observed with minimal correlation to the copolymeric component. This weak correlation between the main lithium environment to copolymeric lithium justifies the short T_1 and thus high mobility of the main lithium relative to the highly immobilised copolymeric component. The immobilisation of lithium observed in the poly(S-*r*-limonene) electrode matrix, unique to the other selected copolymers, directly reflects its efficacy in retaining specific capacity of Li-S cells.

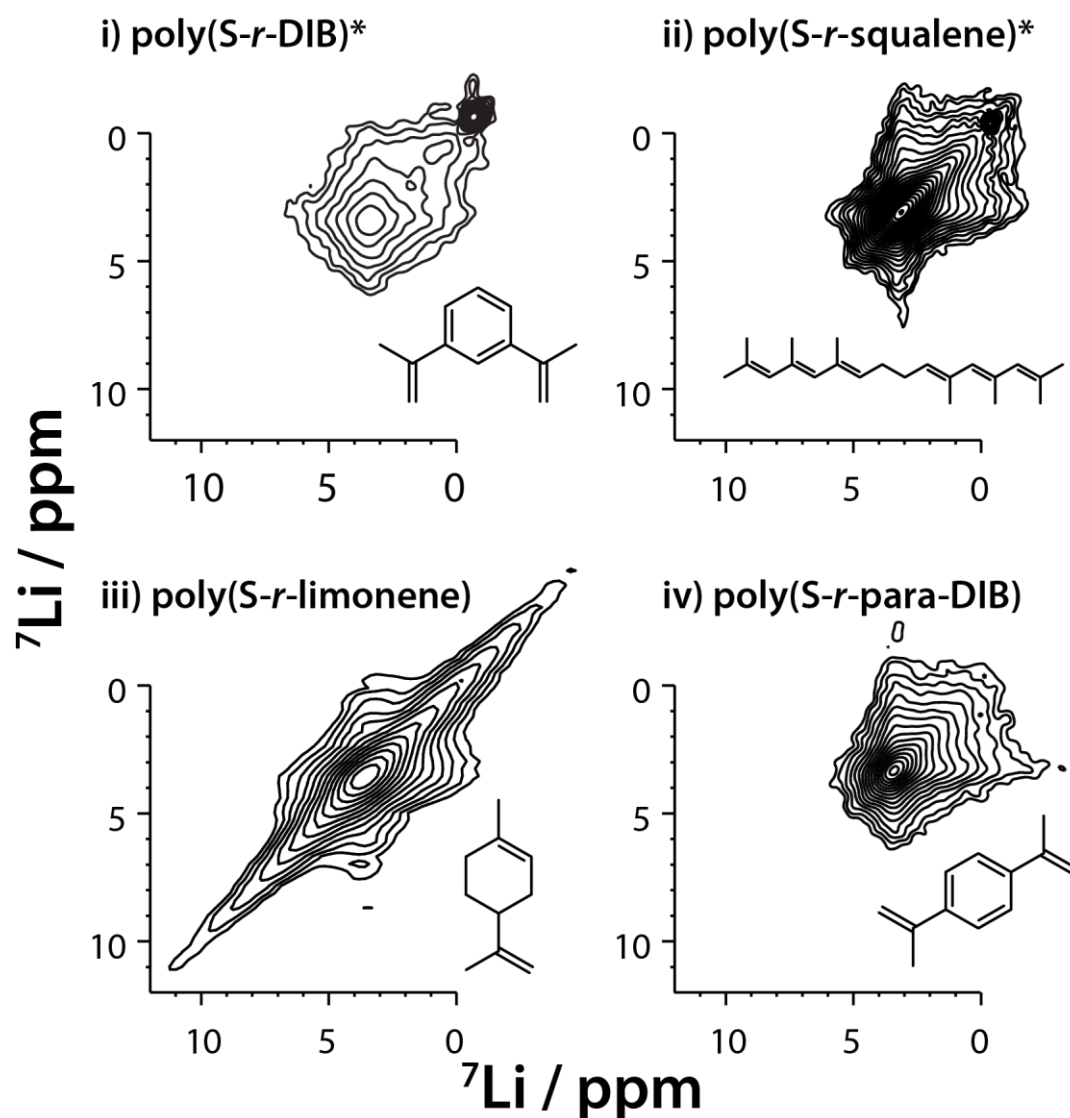


Figure 8.1 – Solid-state ^7Li - ^7Li EXSY NMR spectra of electrochemically lithiated inverse-vulcanised copolymer electrodes prepared using four selected inverse vulcanised copolymers **i**) poly(S-r-DIB) (after 1st discharge, unrinsed), **ii**) poly(S-r-squalene) (after 20th discharge, unrinsed), **iii**) poly(S-r-limonene) (after 20th discharge, rinsed with DME solvent prior to acquisition), and **iv**) poly(S-r-para-DIB) (after 20th discharge, rinsed with DME solvent prior to acquisition) with 10 wt. % crosslinking monomer and 90 wt. % elemental sulfur.

XANES analysis of electrochemically treated copolymer electrodes also allows for selective characterisation of individual elemental edges (particularly S K-edge and C K-edge). A particular limitation in this XANES analysis compared to NMR is the obscuring overlap of signals arising from similar bonding environments and inability to deconvolute individual contributions. Despite such limitations, the ability to probe the sulfur environment through XANES analysis of the electrodes can be especially useful in elucidating the framework effects on SEI speciation of lithiated

sulfur compounds, which can also be supplementary to further analysis of corresponding ^7Li - ^7Li EXSY NMR spectra as demonstrated for poly(*S-r*-squalene) electrodes (see **Chapter 5**).

8.2.3 Outlook on the rational design of future inverse vulcanised copolymers for applications in Li-S cells

In essence, a comprehensive understanding of the electrode material is required before interpreting its participation during electrochemistry. The combined findings from the strategies discussed suggest two key implications for the rational design of future inverse vulcanised copolymers for applications in Li-S cells:

1. Structurally constrained frameworks are generally unfavourable in improving Li-S cell capacity retention
2. Most profoundly, “degree of crosslinking” is less important than the framework’s resistance to stress over cycling to improve capacity retention whilst allowing sufficient active material accessibility.

In dissipating framework stress from long term cycling, the remarkable Li-S cell performance of two chemically diverse copolymeric frameworks (poly(*S-r*-limonene) and poly(*S-r*-para-DIB)) suggest that “self-healing” capabilities can be incorporated to the framework through different conceptual approaches (e.g., low M_w but strongly interacting copolymeric fragments in poly(*S-r*-limonene) versus high M_w entangled copolymer network but relatively high rotational freedom about aromatic functionalities in poly(*S-r*-para-DIB)).

8.2.4 Scope and impact of inverse vulcanised copolymers in rational design of energy storage materials

Whilst the specific areal capacities produced by the most effective copolymers (poly(*S-r*-limonene) and poly(*S-r*-para-DIB)) have been referred to as high values relative to the other selected materials, they are overall much lower than can be achieved in competing Li-S cell electrode materials. A generally greater disparity in literature reports of gravimetric capacity compared to areal capacity values (as outlined in **Table 8.4**) also highlights the importance of balancing framework permeability/active material accessibility with confinement capabilities in rational design of inverse vulcanised copolymers. Although the rational design of inverse

vulcanised copolymers for applications in Li-S cells is still arguably new and amid development, the low areal capacity values achieved thus far may imply some inherent limitations. With significant mass contributions, a reliance on electrochemically inert architectures for ideal confinement capabilities may compromise the gravimetric capacity of the overall Li-S cell.

Nonetheless, even less effective inverse vulcanised copolymers (such as poly(*S-r*-squalene) and poly(*S-r*-DIB)) appear to still reliably improve Li-S cell capacity retention. Comparative analysis of inverse vulcanised copolymers such as explored in this work demonstrates effective confinement of redox active species in hydrocarbon matrices, which can be conceptually relevant in the rational design of other energy storage materials. The concepts and methods explored are broadly transferrable to the design of other confining hydrocarbon matrices beyond inverse vulcanised copolymers such polymeric electrode binders, electrolyte separators, and electrolyte formulations.

8.2.5 Outlook on future strategies

In essence, a comprehensive understanding of the electrode material is required before interpreting its participation during electrochemistry. At a molecular scale, methods such as SEC, XRD, EPR, and NMR spectroscopy can be used to characterise the copolymeric electrode material and optimise inverse vulcanisation conditions. Separate strategies based on NMR, XRD and microscopy can provide information on impact to the copolymeric material and surrounding components over electrochemical cycling. Relating these two approaches and interpreting results from electrochemically treated samples require a well-rounded fundamental understanding of the copolymeric material.

In addition to challenges involved in characterising the Li-S battery, understanding the role of inverse vulcanised copolymers also involves unique challenges in characterising the inherent copolymer properties. A lack of awareness on the relative variability in preparation of these copolymers versus carbon frameworks can also give rise to inconsistencies or contradictory interpretations of their role in electrochemistry. In preventing these inconsistencies, it is therefore critical for inverse vulcanisation conditions of the copolymer as well as other experimental conditions to be reported in sufficient detail (i.e., including atmosphere, temperatures,

and durations of heating, as well as storage conditions). Generally, the reliable and reproduceable reporting of battery-based data is gaining significant momentum with numerous articles being reported recently to provide researchers with a check-list which would enable better comparisons to be drawn.^{25, 26} Nonetheless, Li-S batteries with carbon or polymeric frameworks are very interesting to probe and characterise.

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Appendix A: Waste coffee-derived carbon frameworks

Table A. 1 – I_D/I_G values extracted from modelled fits applied to Raman data of the samples by comparison of peak intensity of fitted Lorentzian functions (detailed in the appendix Figure A. 1) and using multiple functions (detailed in the appendix Figure A. 2).

Model	Lorentzian		Multiple function (Voigt and BWF)	
Sample	I_D/I_G (from peak intensity)	I_D/I_G (from peak area)	I_D/I_G (from peak intensity)	I_D/I_G (from peak area)
TimCal Super P (carbon black)	1.12(1)	1.78(3)	1.077(6)	1.2(1)
Pyrolysed coffee powder	1.11(2)	2.41(6)	0.836(5)	1.1(1)
Pyrolysed coffee electrode	1.06(2)	1.93(3)	0.939(6)	1.01(8)

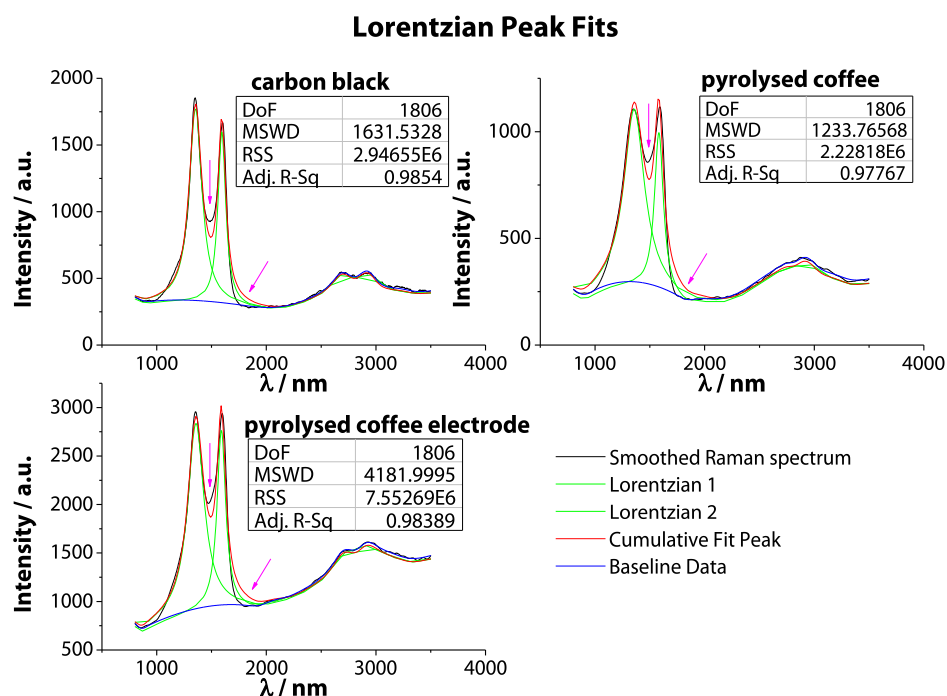


Figure A. 1 – Smoothed Raman data and peak fitting analysis using a series of Lorentzian functions to model the D and G bands. Smoothing of the data was conducted with a Savintzky-Golay filter using 50

data points in order to proceed with the peak fitting regime. The peak intensities obtained from the deconvoluted Lorentzian functions are used to determine the I_D/I_G values of the samples. The magenta arrows are used to direct attention to the asymmetry of the first order G band and are referred to in-text.

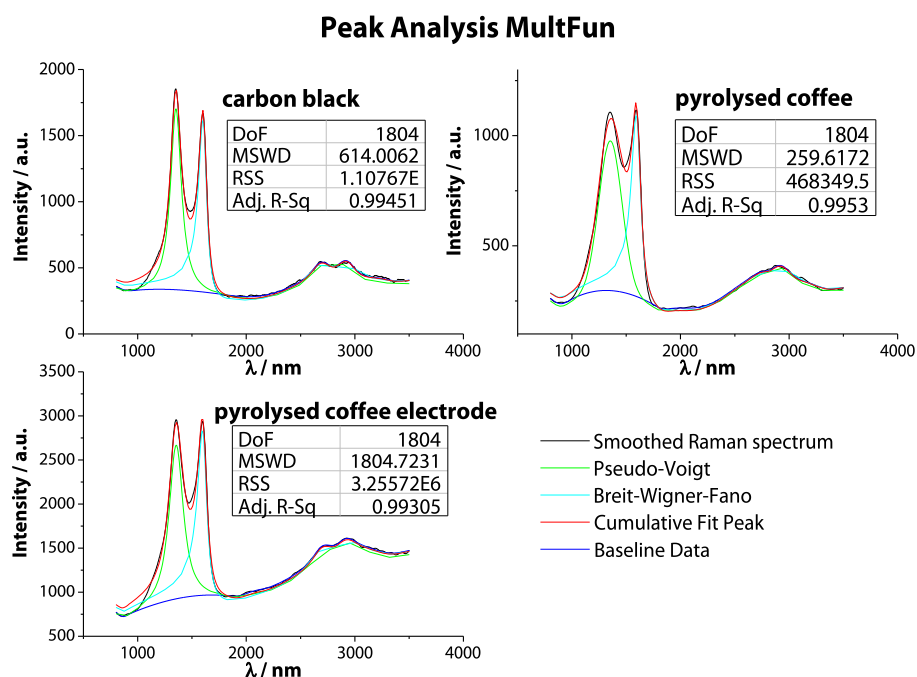


Figure A. 2 – Smoothed Raman data with an alternative peak fitting model using a Voigt function to model the D band and an asymmetric Breit-Wigner-Fano function to model the G band. Smoothing of the data was conducted with a Savintzky-Golay filter using 50 data points in order to proceed with the peak fitting regime. The background functions used in this fitting regime are identical to that used in the Lorentzian model.

Table A. 2 – Lorentzian peak fits used to model the (002) and (100) reflections observed in the measured powder XRD pattern of the pyrolysed coffee shown in the main article **Figure 4.5a**. The 2θ and FWHM parameters derived from the fits were used to determine the d -spacing based on Bragg’s law, and crystallite size based on the Scherrer equation which are provided in the main article **Table 4.3**.

<i>a) Parameters</i>	(002)	(100)
Intensity offset / a.u.	839(8)	515(5)
2θ / °	28.77(1)	50.92(2)
FWHM	8.27(5)	11.6(1)
Area / a.u.	50366(352)	16472(233)
Height at 2θ / a.u.	3875(8)	902(5)
<i>b) Statistics</i>	(002)	(100)
Number of Points	975	1368
Degrees of Freedom	971	1364
Reduced Chi-Sqr	5603	1917
Residual Sum of Squares	5440981	2614556
Adj. R-Square	0.996	0.973

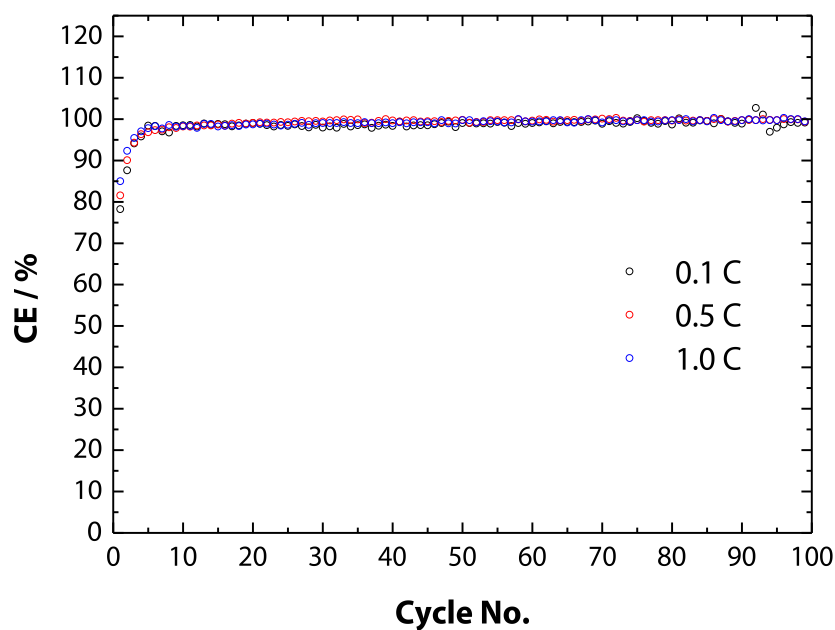


Figure A. 3 – Rate capability of Li-S cells using pyrolysed coffee in the sulfur electrode demonstrated by comparison of coulombic efficiencies (i.e. output discharge capacity over input charge capacity) obtained when cycling at 0.1 (black), 0.5 (red) and 1.0 C (blue) wherein 1.0 C = 160 mA g⁻¹. All of the tested half cells require an initial discharge step to initiate the Li-S electrochemical tests (i.e. initiate lithiation of sulfur), however the values obtained from this initial step are omitted from the CE calculations as they are not truly related to the subsequent charge step. The discharge capacity taken as the “first” discharge in these calculations are therefore the second discharge capacity values obtained in the measurement.

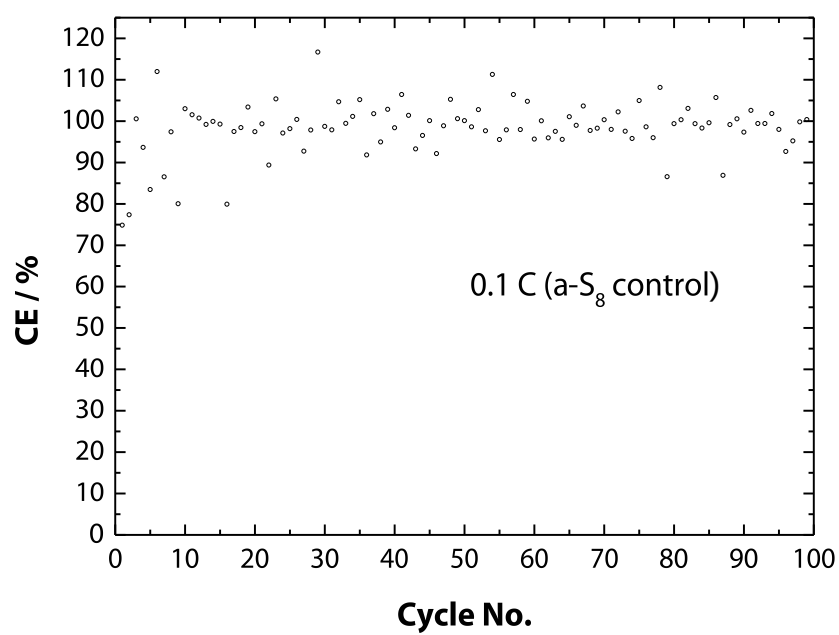


Figure A. 4 – Rate capability of Li-S cells using α -S₈ electrodes without addition of pyrolysed coffee demonstrated by coulombic efficiencies obtained when cycling at 0.1 C.

Appendix B: Poly(S-r-squalene)

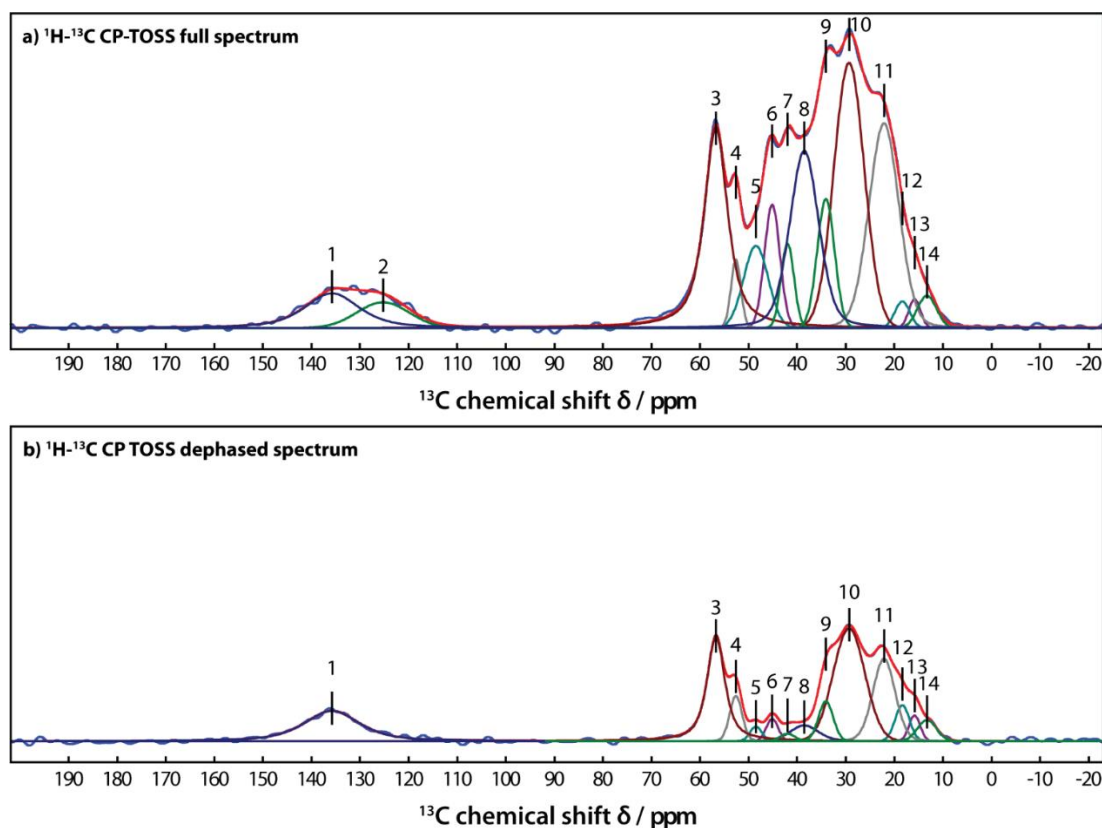


Figure A. 5 – Deconvolution and elucidation of the peak centres of **a)** the full and **b)** dephased ^1H - ^{13}C CP-TOSS spectra of the as-synthesised poly(S-r-squalene) copolymer also explored in the main article in Figure 5.2a (blue and red peak areas respectively). Details regarding the profiles and fit results of each peak annotated 1-14 are provided below in the appendix **Table A. 3**

Table A. 3 – Peak deconvolution fit results based on ^1H - ^{13}C CP-TOSS of poly(S-r-squalene) visualised in the appendix **Figure A. 5**.

no.	$\delta_{13\text{C}}$ / ppm	a) full spectrum					b) dephased spectrum				
		amp / a.u.	wid / ppm	xG/(1-x)L	Intensity / a.u.	% area	amp / a.u.	wid / ppm	xG/(1-x)L	Intensity / a.u.	% area
1	133.83	99.37	13.28	0.41	131607.4	6.01	86.69	13.43	0.41	116038	15.5
2	123.32	73.45	12.64	1	74502.78	3.4	0	0	1	0	0
3	54.77	573.83	5.67	0.27	346836.3	15.84	299.52	4.32	0.27	138281.4	18.47
4	50.66	195.46	2.37	0.91	38696.28	1.77	129.07	3	0.91	32355.1	4.32
5	46.54	234.44	5.97	1	112332.8	5.13	41.34	2.88	1	9565.02	1.28
6	43.2	351.92	3.74	1	105463.5	4.82	63.13	2.91	1	14762.64	1.97
7	40.03	240.86	3.12	1	60259.95	2.75	21.18	3.5	1	5940.49	0.79
8	36.59	506.55	7	0.73	318384.4	14.54	44.87	6.86	0.73	27630.63	3.69
9	32.14	368.31	4.21	1	124267.2	5.68	113.48	3.56	1	32421.67	4.33
10	27.36	757.05	7.33	1	445192.4	20.34	321.8	7.68	1	198338.9	26.5
11	20.18	584.2	7.27	0.89	356657.4	16.29	235.39	5.38	0.89	106508.9	14.23
12	16.4	75.62	3.64	1	22060.79	1.01	102.13	3.5	1	28686.62	3.83
13	13.87	82.36	2.86	1	18919.01	0.86	73.02	2.73	1	15972.62	2.13
14	11.33	92.14	4.57	1	33807.94	1.54	59.78	4.59	1	22033.4	2.94

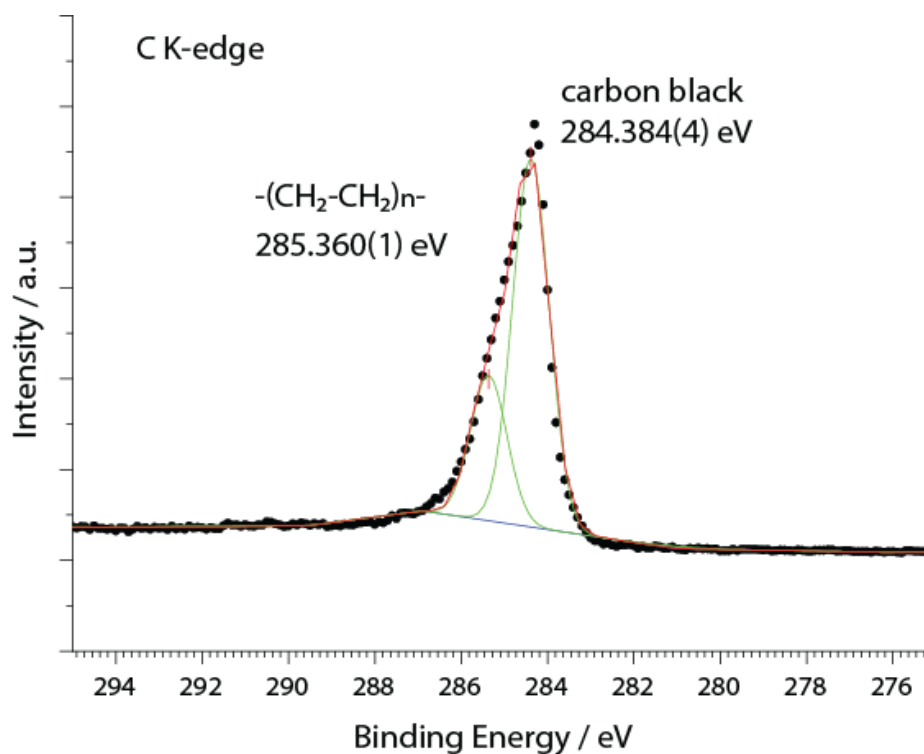


Figure A.6 – High resolution carbon K-edge soft-XPS spectrum collected using synchrotron radiation energy set at 730 eV of a poly(*S-r*-squalene) cathode. The black dots indicate collected data points, blue trace calculated baseline, green traces are the gaussian peak fits, and the red trace is the cumulative fit of the peaks. Red peak markers denote the peak centres.

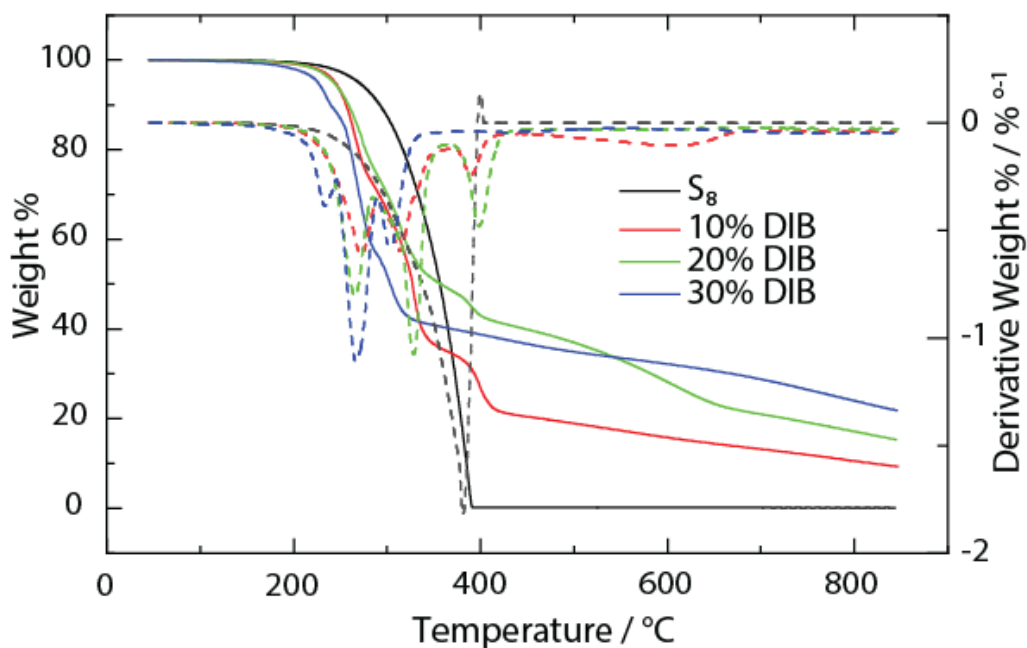


Figure A.7 – Thermogravimetric analysis data (bold lines) and the first derivative (DTG, dashed lines) of elemental sulfur (black), and poly(*S-r*-DIB) synthesised using 10% (red), 20% (green), and 30% (blue) weight DIB feeds.

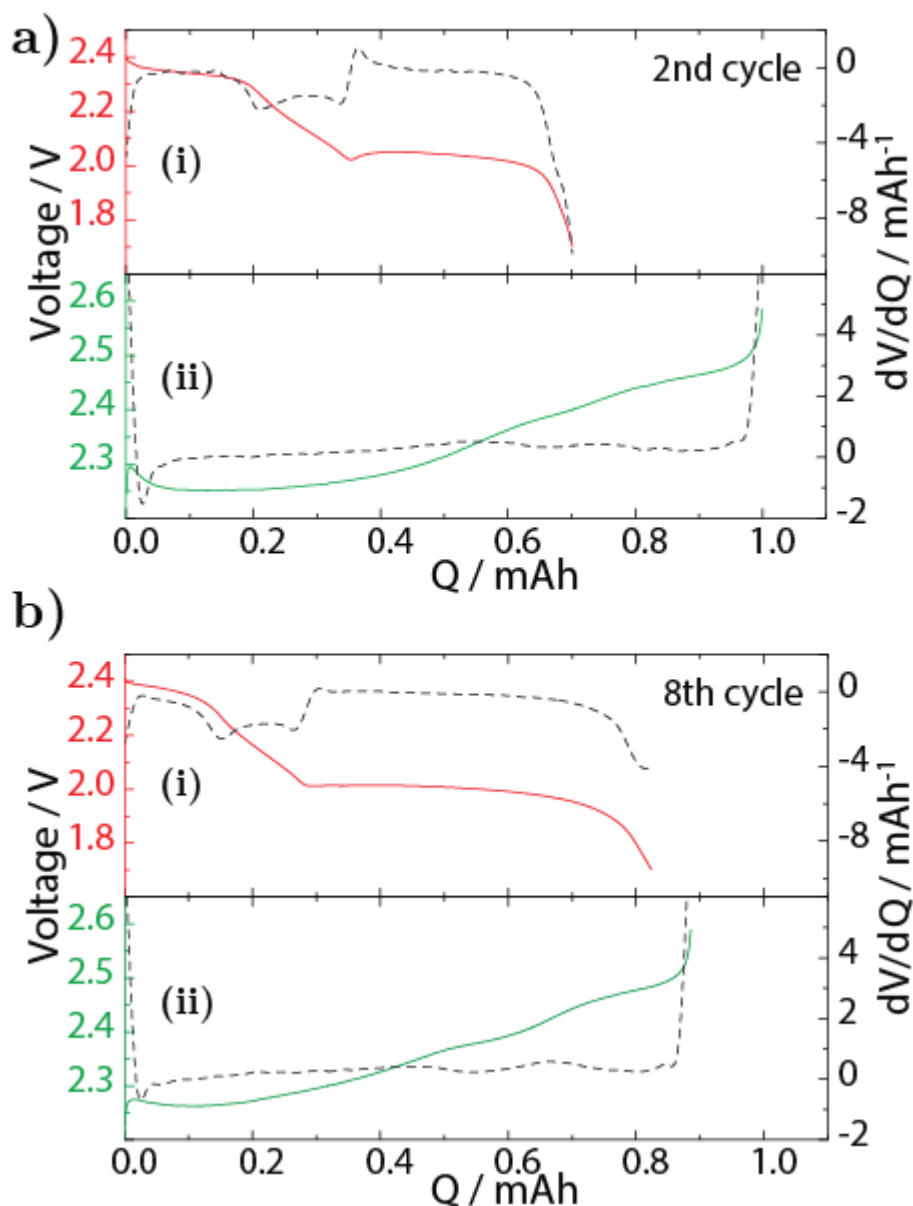


Figure A.8 – Voltage capacitance plots (discharge and charge plots correspond to red and green traces respectively) and the derivative (dV/dQ , dashed black traces) of Li-S cells using poly(S-r-squalene) as the active cathode material extracted at **a)** the 2nd cycle **i)** discharge and **ii)** charge and **b)** the 8th cycle. **i)** discharge and **ii)** charge. This data corresponds to samples used for *ex situ* XANES characterisation featured in **Figure 5.8** of the main article, with **a)i)** corresponding to the red traces in **Figure 5.8ai** and **bi**, **a)ii)** to the green traces in **Figure 5.8ai** and **bi**, **b)i)** to the red traces in **Figure 5.8aii** and **bii**, and **b)ii)** the green traces in **Figure 5.8aii** and **bii**.

Table A.4 – Fit results of peak deconvolution *via* least-squares method using Gaussian/Lorentzian line shapes to the 1D ^7Li MAS spectrum measured for 20th discharge (spectrum in **Figure 5.12ai**). The Gaussian/Lorentzian ratio is included in the fitting protocol by the $xG/(1-x)L$ parameter wherein G = Gaussian, L = Lorentzian, meaning that when $x = 1$ the line shape is purely Gaussian and when $x = 0$ the line shape is purely Lorentzian.

^7Li (ppm)	% Peak	$xG/(1-x)L$
3.5	68.9(6)	0
1.1	30.1(7)	0
0.0	1.0(1)	0

Table A.5 – Fit results of peak deconvolution *via* least-squares method using Gaussian/Lorentzian line shapes to the 1D ^1H - ^7Li CP-MAS spectrum measured for 20th discharge (spectrum in **Figure 5.12a**ii). The Gaussian/Lorentzian ratio is included in the fitting protocol by the $xG/(1-x)L$ parameter wherein G = Gaussian, L = Lorentzian, meaning that when $x = 1$ the line shape is purely Gaussian and when $x = 0$ the line shape is purely Lorentzian.

^7Li (ppm)	% Peak	$xG/(1-x)L$
3.5	34.3(6)	1
1.1	65.7(6)	0.5

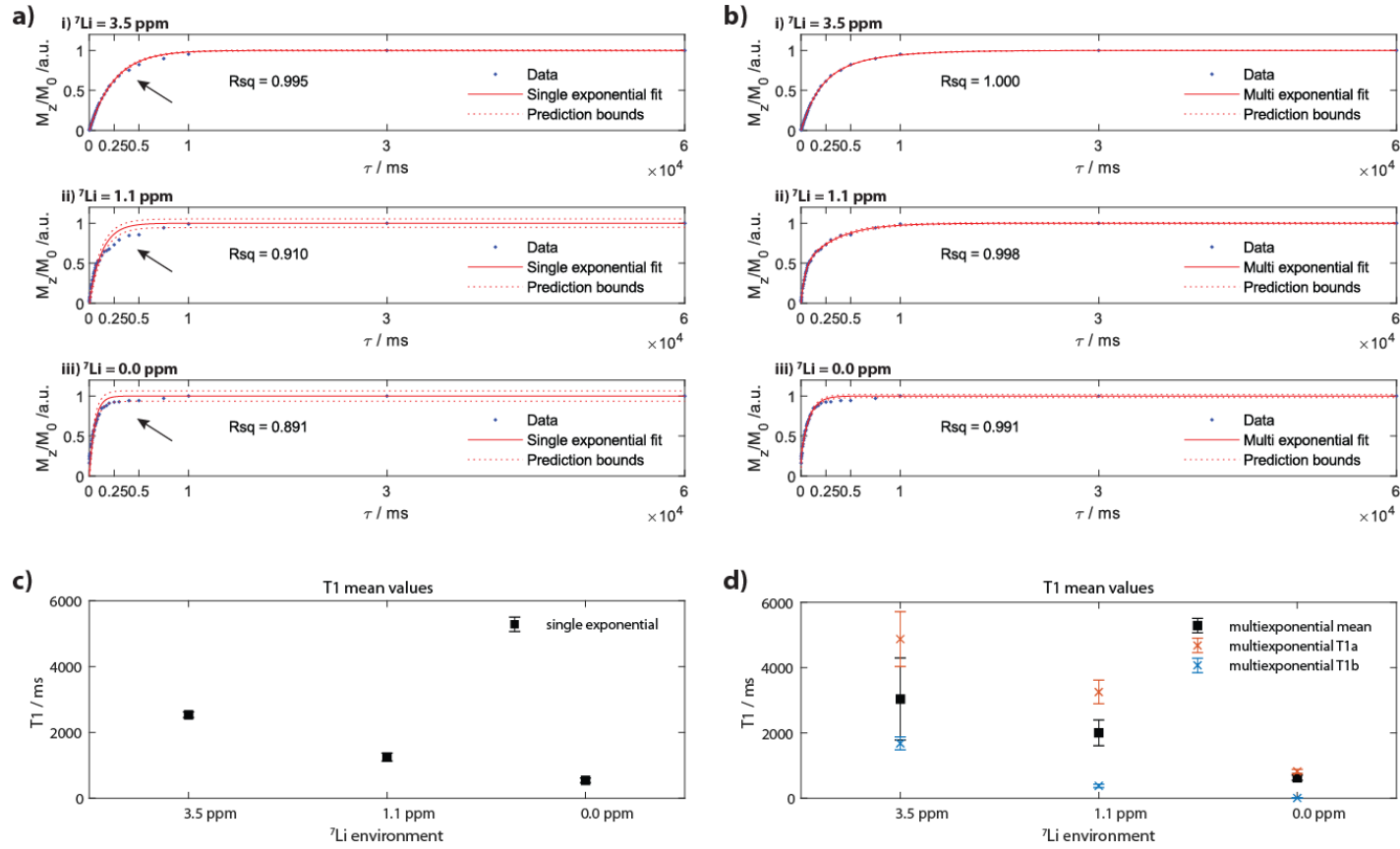


Figure A. 9 – Spin-lattice (T_1) relaxation times of lithium environments measured for the poly(S-r-squalene) electrode extracted after 20th discharge via a series of saturation recovery experiments conducted with various delays $\tau = 10 \text{ ms}$ to 60 s . **a)** Single-exponential function fitting regime and **b)** multi-exponential function fitting regime used to model the data of each lithium environment. **c)** T_1 values extracted from the fits based on the **i)** single-exponential fit function model and **ii)** multi-exponential fit function model

Table A. 6 – T_1 relaxation times of three main lithium environments observed in electrochemically lithiated poly(S-*r*-squalene) extrapolated from a single exponential fitting regime, $\frac{M_z}{M_0} = 1 - e^{-\frac{\tau}{T_1}}$, wherein M_z is the signal absolute value, M_0 signal anticipated at equilibrium taken as the signal measured at the longest delay $\tau = 60$ s, τ the applied T_1 relaxation delay before the final $\pi/2$ pulse is applied. This tabulated data relates to the fitting regime visualised in the appendix **Figure A. 9a**.

^7Li (ppm)	T_1 / ms	Rsq
3.5	2500(90)	0.995
1.1	1300(100)	0.910
0.0	550(70)	0.891

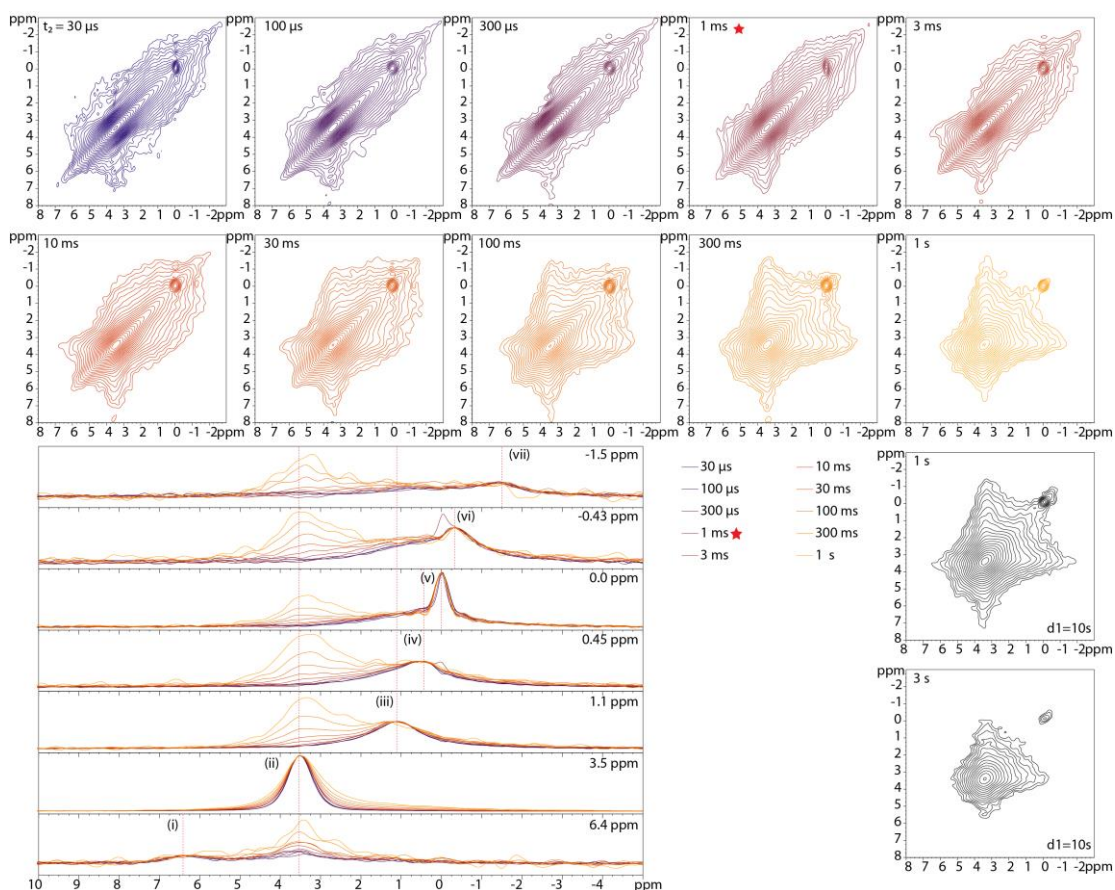


Figure A. 10 – a) ^7Li - ^7Li EXSY spectra of electrochemically treated poly(S-*r*-squalene) electrode powder extracted after 20th discharge collected at mixing times $d_8 = 30 \mu\text{s}$, $100 \mu\text{s}$, $300 \mu\text{s}$, 1 ms , 3 ms , 10 ms , 30 ms , 100 ms , 300 ms and 1 s (30 kHz spin rate, $d_1 = 3 \text{ s}$). **b)** are slices of each spectrum in a) taken at (i) 6.4, (ii) 3.5, (iii) 1.1, (iv) 0.45, (v) 0.0, (vi) -0.43, and (vii) -1.5 ppm. **c)** Spectra of the same sample measured with a longer recycle delay $d_1 = 10 \text{ s}$ at mixing times (i) $d_8 = 1 \text{ s}$ and (ii) $d_8 = 3 \text{ s}$.

Appendix C: Poly(*S-r*-limonene)

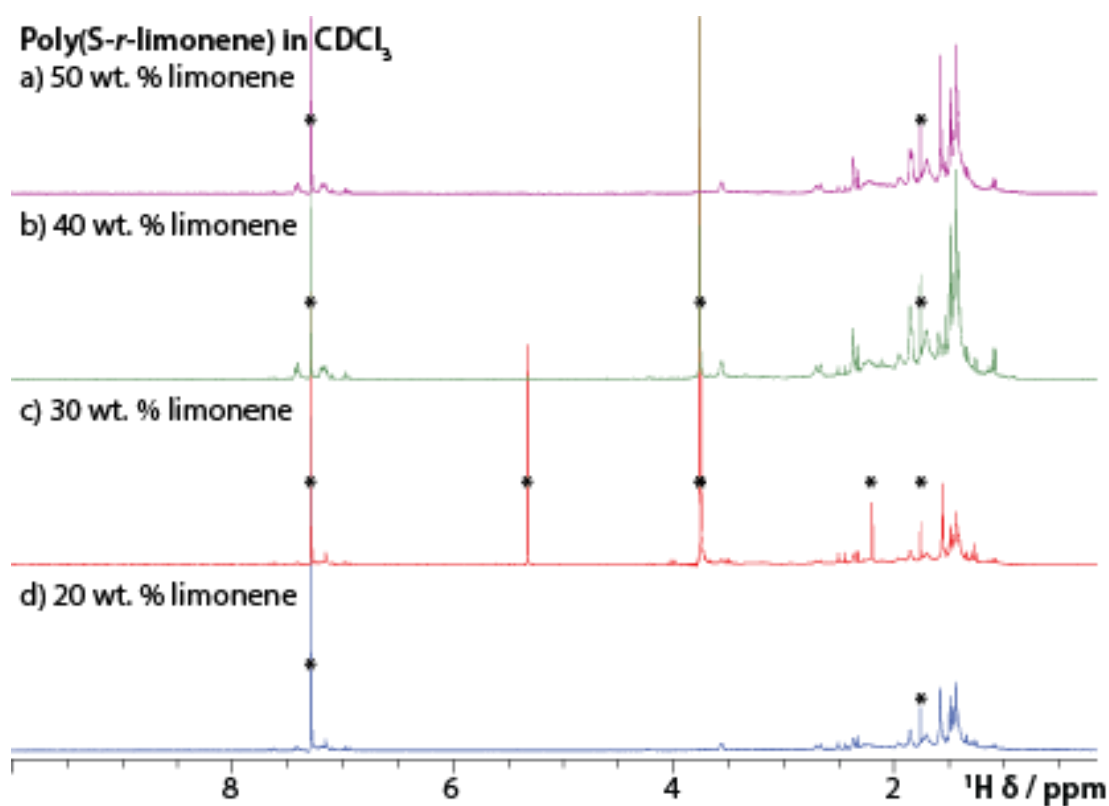


Figure A. 11 – Solution state ¹H NMR spectra of poly(*S-r*-limonene) in CDCl₃ prepared with **a)** 50, **b)** 40, **c)** 30, **d)** and 20 wt. % limonene crosslinking monomer and corresponding elemental sulfur amounts. Asterisks denote residual solvent peaks unrelated to the copolymer analytes.

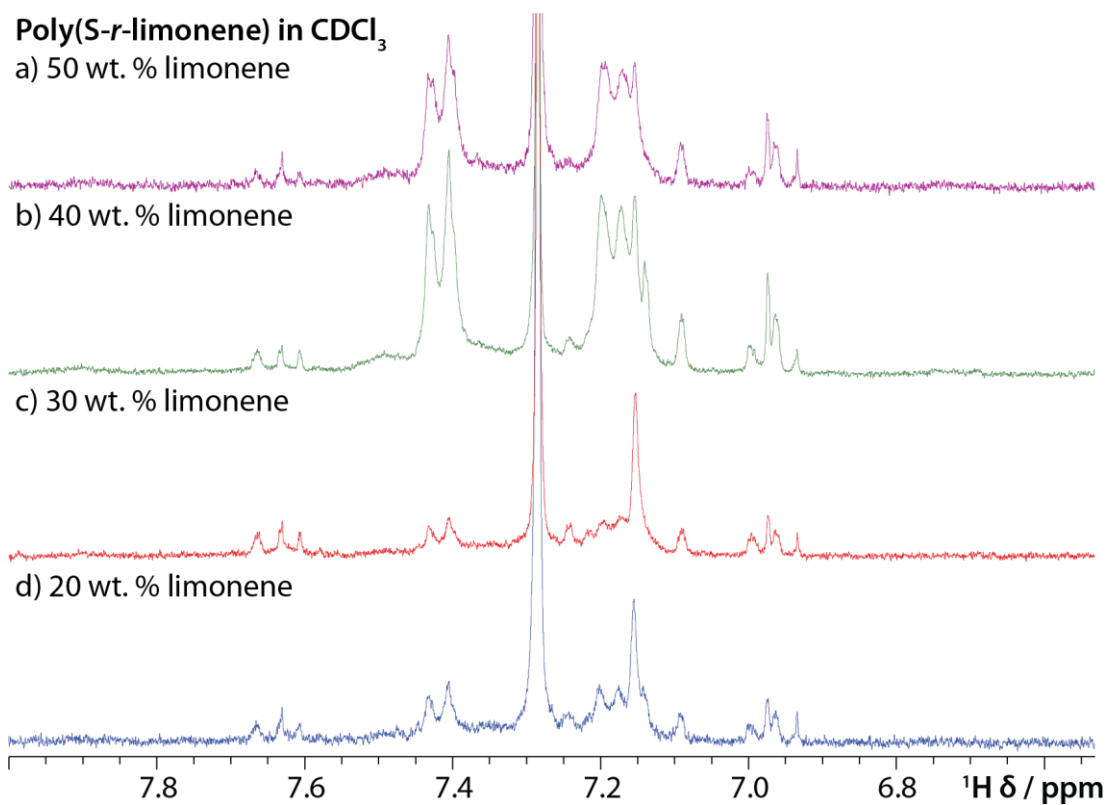


Figure A. 12 – Close up on the aromatic region of poly(*S-r*-limonene) spectra shown in **Figure A. 11**.

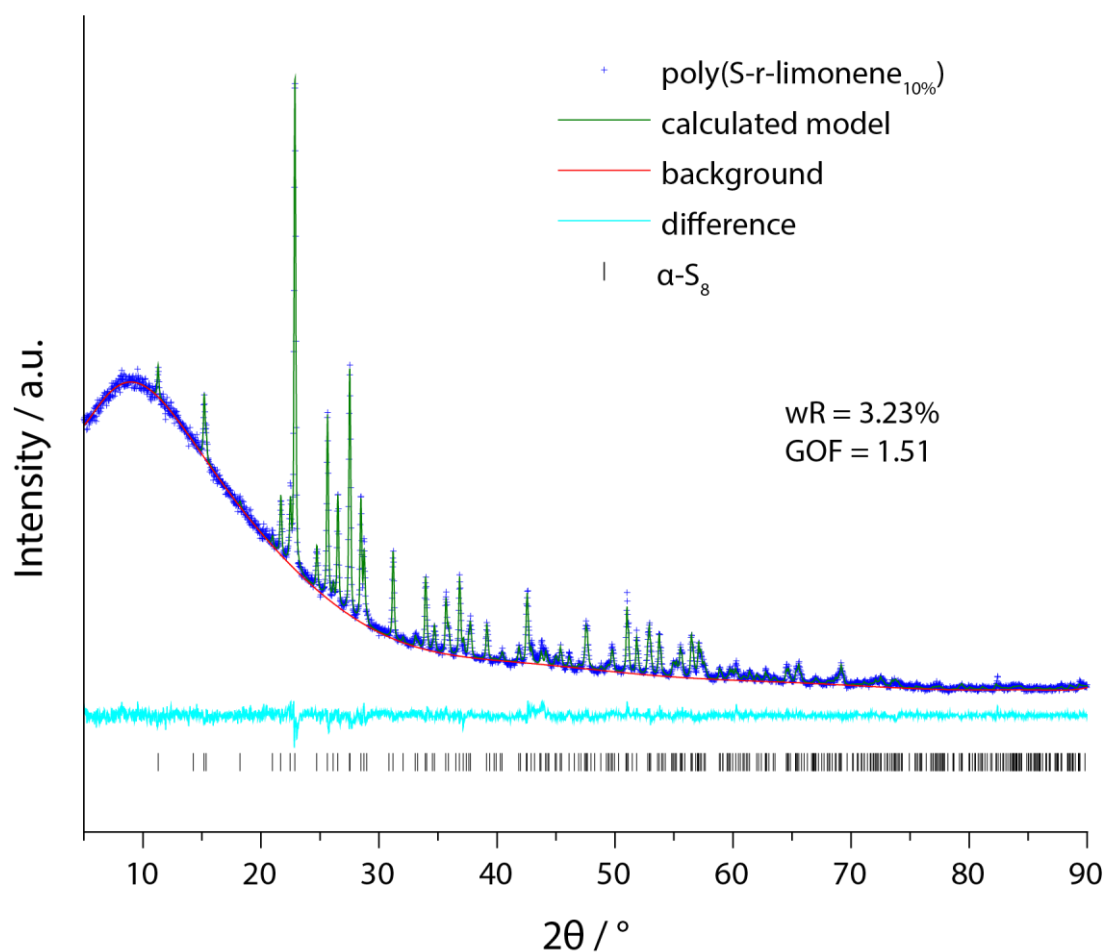


Figure A. 13 – X-ray powder diffraction pattern of poly(S-r-limonene) prepared using 10 wt. % limonene (blue crosses) and a model of the data (green trace) calculated *via* Rietveld refinement of α -S₈ (orthorhombic α -S₈ *Fddd*, ICDD, No. 01-078-1888) and β -S₈ (monoclinic β -S₈ *P2₁/c*, ICDD No. 01-071-0137). A fit of only the α -S₈ (black peaks markers) with no contributions from β -S₈ adequately represents the data.

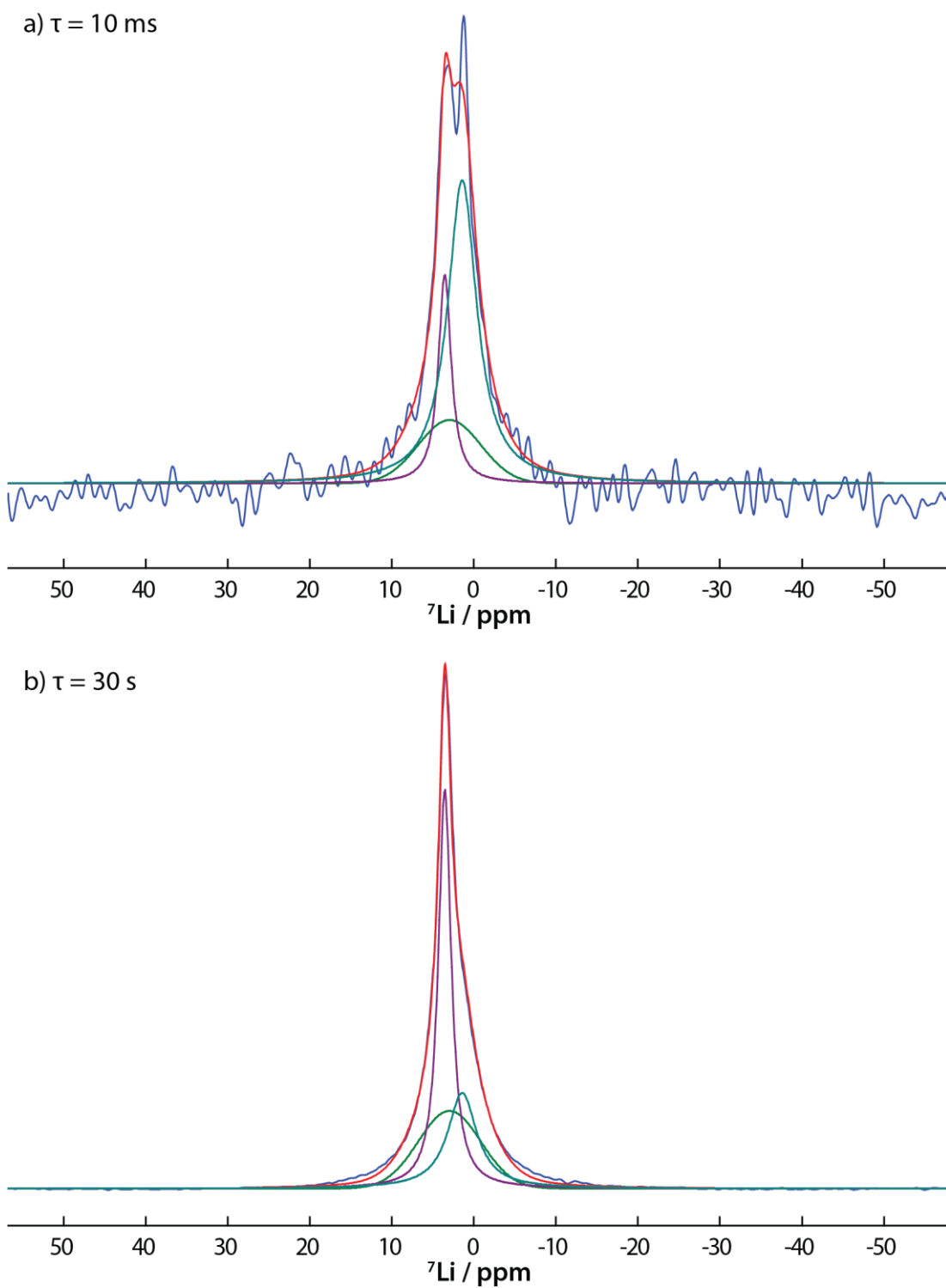


Figure A. 14 – Peak deconvolution of ^7Li spectra acquired with **a)** $\tau = 10$ ms signal recovery and **b)** $\tau = 30$ s signal recovery for T_1 saturation recovery measurements.

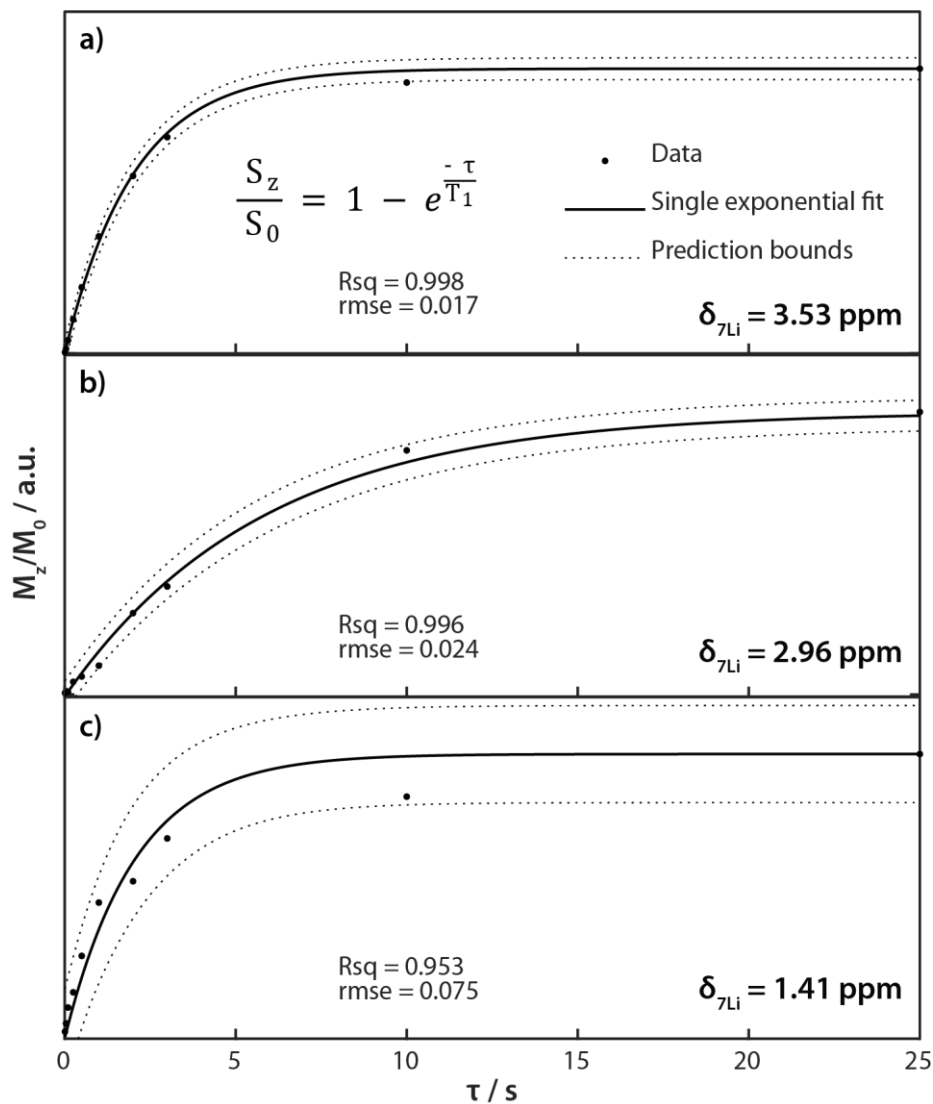


Figure A. 15 – Single- phase exponential decay fits to normalised solid-state ^7Li saturation recovery NMR signal intensity values (M_z/M_0 , black crosses) at peak centres $\delta_{7\text{Li}} = 3.51, 2.86, 2.39$, and 1.23 ppm plotted vs $\tau = 10 \text{ ms}, 20 \text{ ms}, 30 \text{ ms}, 40 \text{ ms}, 50 \text{ ms}, 100 \text{ ms}, 150 \text{ ms}, 200 \text{ ms}, 250 \text{ ms}, 300 \text{ ms}, 350 \text{ ms}, 400 \text{ ms}, 450 \text{ ms}, 500 \text{ ms}, 550 \text{ ms}, 600 \text{ ms}, 700 \text{ ms}, 800 \text{ ms}, 900 \text{ ms}, 1 \text{ s}, 1.25 \text{ s}, 1.5 \text{ s}, 1.75 \text{ s}, 2 \text{ s}, 2.5 \text{ s}, 3 \text{ s}, 4 \text{ s}, 5 \text{ s}, 7 \text{ s}, 10 \text{ s},$ and 30 s . The black traces represent fits to the function $\frac{M_z}{M_0} = 1 - e^{-\frac{\tau}{T_1}}$ to determine T_1 relaxation times. The dotted lines represent 95% confidence intervals.

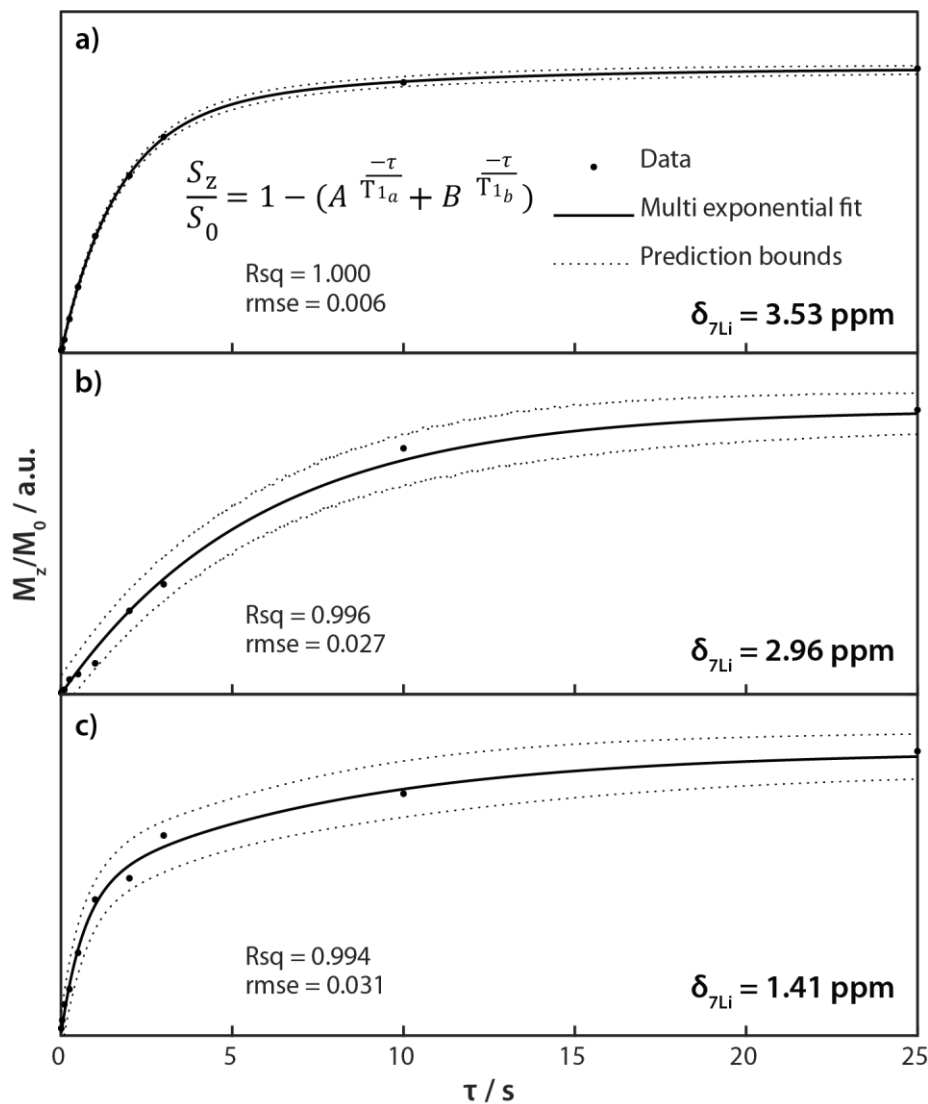


Figure A. 16 – Two-phase exponential decay fits to normalised solid-state ^7Li saturation recovery NMR signal intensity values (M_z/M_0 , black crosses) at peak centres $\delta_{7\text{Li}} = 3.51, 2.86, 2.39$, and 1.23 ppm plotted vs $\tau = 10 \text{ ms}, 20 \text{ ms}, 30 \text{ ms}, 40 \text{ ms}, 50 \text{ ms}, 100 \text{ ms}, 150 \text{ ms}, 200 \text{ ms}, 250 \text{ ms}, 300 \text{ ms}, 350 \text{ ms}, 400 \text{ ms}, 450 \text{ ms}, 500 \text{ ms}, 550 \text{ ms}, 600 \text{ ms}, 700 \text{ ms}, 800 \text{ ms}, 900 \text{ ms}, 1 \text{ s}, 1.25 \text{ s}, 1.5 \text{ s}, 1.75 \text{ s}, 2 \text{ s}, 2.5 \text{ s}, 3 \text{ s}, 4 \text{ s}, 5 \text{ s}, 7 \text{ s}, 10 \text{ s},$ and 30 s . The black traces represent fits to the function $\frac{M_z}{M_0} = 1 - (A e^{\frac{-\tau}{T_{1a}}} + (1 - A) e^{\frac{-\tau}{T_{1b}}})$ to determine T_1 relaxation times. The dotted lines represent 95% confidence intervals.

Table A. 7 – T_1 values calculated from **a)** single-phase and **b)** two-phase exponential decay fits to the saturation recovery measurements for lithium environments I, II, and III shown in the appendix **Figure A. 15** and **Figure A. 16** respectively. A fit to lithium environment II using the two-phase exponential decay function did not yield conclusive parameter values which have been omitted.

a) Single-phase exponential decay $\frac{M_z}{M_0} = 1 - e^{\frac{-\tau}{T_1}}$							
	^7Li (ppm)		T_1 (ms)		R_{sq}		
I	3.53		2070(90)		0.993		
II	2.96		5200(300)		0.9823		
III	1.41		2800(700)		0.6303		
b) Two-phase exponential decay $\frac{M_z}{M_0} = 1 - (Ae^{\frac{-\tau}{T_{1a}}} + (1 - A)e^{\frac{-\tau}{T_{1b}}})$							
	^7Li (ppm)		A	T_{1a} (ms)	T_{1b} (ms)	R_{sq}	$T_{1\text{mean}}$ (ms)
I	3.53	0.18(4)		8000(1000)	1590(60)	1.000	2600(600)
II	2.96	-		-	-	-	-
III	1.41	0.48(4)		15000(3000)	700(100)	0.985	8000(2000)