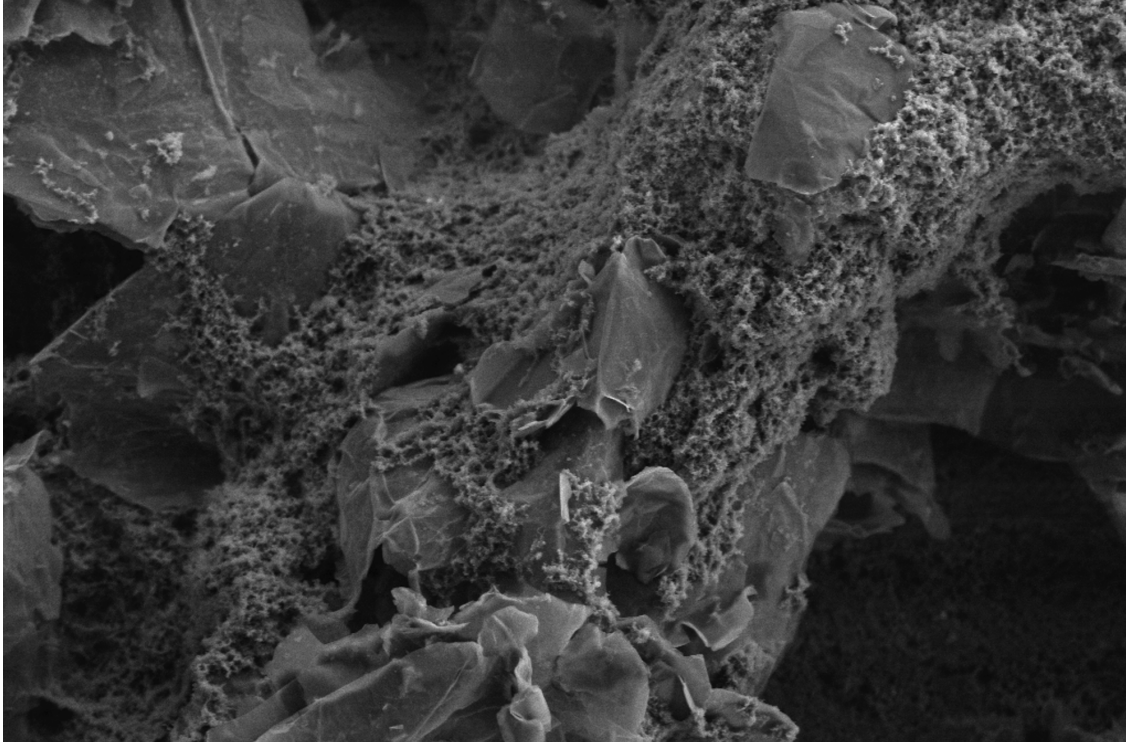




CHALMERS
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Synthesis of Water-soluble Binders for Sustainable Electrode Processing of Lithium-Sulfur Batteries

Master's thesis in Materials Chemistry

Malte Clark

DEPARTMENT OF INDUSTRIAL AND MATERIALS SCIENCE

CHALMERS UNIVERSITY OF TECHNOLOGY
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MASTER'S THESIS 2026

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Department of Industrial and Materials Science
Division of Materials and Manufacture
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Abstract

Lithium sulfur batteries (LSBs) have emerged as a promising alternative technology to lithium-ion batteries (LIBs) due to their much higher theoretical capacity. However, the intrinsic drawbacks, such as low conductivity, volume expansion, and polysulfide shuttling effect limit the cycling stability and energy density. A very crucial yet often overlooked component with great effect on the battery performance is the binder. However, conventional binders such as PVDF and PAA suffer from irreparable cracking during charge/discharge cycles and insufficient polysulfide adsorption ability. The former is especially problematic due to the undesirable toxicity of the solvent NMP, in addition to the increasingly stricter PFAS regulations limiting its future applicability. Hence, more advanced alternatives are necessary. Herein, a new water-soluble binder structure was synthesized through the free radical polymerization (FRP) of [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (DMAPS) and 2-hydroxyethyl acrylate (HEA), denoted as DMAPS-HEA. The successful synthesis was confirmed by nuclear magnetic resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopy. The zwitterionic (DMAPS) moiety features a cationic quaternary ammonium and anionic sulfonate, enabling strong polysulfide anchoring capabilities through synergistic interaction with both lithium and sulfur in the polysulfide structure, in addition to reversible bonding between charges, enabling self-healing properties. A superior capacity and cycling stability were demonstrated compared to the reference PAA-binder samples. At the rates 0.1 C, 0.5 C, and 1 C, the initial galvanostatic charge/discharge (GCD) capacities were 1219, 824, and 499 $mAhg^{-1}$ for the synthesized DMAPS-HEA binder, whereas PAA only achieved capacities of 858, 579 at the rates 0.1 and 0.2 C. The cell with DMAPS-HEA11 at 0.5 C also demonstrated superior capacity and cycling stability over the LSBs with PAA at 0.1 and 0.2 C within 10 cycles, whereas DMAPS-HEA11 at 1 C met the performance of PAA at 0.1 C after only 50 cycles and outperformed it within 70 cycles. CV and EIS measurements suggest improved electron transfer at the solid-electrolyte interphase (SEI) and polysulfide conversion kinetics. A closer inspection in SEM reveals evenly distributed discharge product deposition with higher aspect ratio, suggesting that the DMAPS-HEA11 binder also facilitates a beneficial Li_2S precipitate geometry, with the underlying mechanism a possible future research direction.

Keywords: Lithium sulfur batteries, LSBs, Binder, Zwitterion, DMAPS, HEA, Graphene, Gr/S.

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Malte Clark, Gothenburg, June 2026

Nomenclature

Abbreviation	Full Term
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
EV	Electric Vehicle
FRP	Free Radical Polymerization
FTIR	Fourier Transform Infrared Spectroscopy
GCD	Galvanostatic Charge/Discharge
Gr/s	Graphene/Sulfur
LIBs	Lithium-ion Batteries
LSBs	Lithium Sulfur Batteries
LiPSs	Lithium Polysulfides
NMR	Nuclear Magnetic Resonance
PAA	Polyacrylic Acid
PVDF	Polyvinylidene fluoride
SEI	Solid-Electrolyte interface
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis

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1

Introduction

1.1 Context

It is well established that rechargeable energy storage devices are becoming increasingly important as society electrifies, owing to the steadily growing demand for portable electronic products, particularly for electric vehicles (EVs), in addition to consumer products such as cell phones, computers, and smartwatches that are embedded in modern life [1],[2][3]. Additionally, the Paris treaty jointly decided by most countries requires a reduction in greenhouse gas emissions as soon as possible with the hope of achieving climate neutrality by the middle of the century. Due to the energy and transport sectors being among the most carbon emission intensive, rechargeable energy batteries have become a key technology to achieve this goal [4]. This is reflected in the rapidly growing diversity of consumer and industrial products utilizing batteries each year, particularly in the transport and power sectors [5]. Among the various options, lithium-ion batteries (LIBs) are particularly dominant due to their superior energy density, light weight, rate performance, and capacity retention during cycling compared to other rechargeable systems, all of which are essential for their success [1],[2][3]. Although some primary non-rechargeable LIBs have been commercially available since the late 1960s, with a large variety of different cathode materials under research, it wasn't until the 1980's that the modern, secondary lithium-ion batteries were developed [6], largely attributed to the work of John B. Goodenough, M. Stanley Whittingham and Akira Yoshino. In the year 1991, the first commercial rechargeable LIB was issued, and in 2019 the Nobel Prize in Chemistry was ultimately awarded for their contribution to the development of LIBs, a remarkable achievement that highlights its importance [3],[7].

With the improvement in lithium-ion battery technology and the reduction in cost of over 90% in the last 15 years, EVs are becoming increasingly common and competitive on the market, with high expectations for more advanced technologies with higher energy densities, unlocking previously unattained longer distance applications. Likewise, the implementation of next generation LIBs in grid energy storage allows for effective harvesting and long-term storage of clean energy sources, which has gradually developed to the point of competing with coal usage, a trend that is likely to be even more pronounced in the near future. Figure 1 below demonstrates the rapid implementation of LIBs in the global energy sector, with over a fourfold increase between 2020 and 2023, emphasizing the importance of advanced lithium batteries in future applications [1],[7],[5].

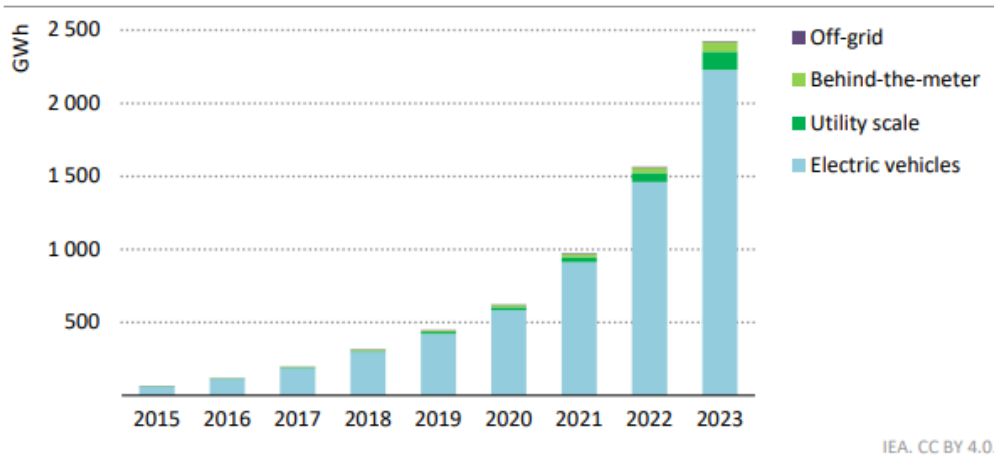


Figure 1.1: Volume of battery usage by application in the global energy sector. Reproduced from [5], under the terms of Creative Commons Attribution (CC BY 4.0) License.

While a variety of materials are required for the production of LIBs, the finite nature of such resources in combination with the increasing demand, environmental impact, and highly divided geographic allocation is a cause for concern. Among these materials, the extraction and refining of ore for typical active materials on the cathode such as Co, Fe, Mn, and Ni are considered among the most expensive cell components with more than half the material cost, which in addition to its low natural abundance and high weight contribution calls for alternative technologies. In particular, the cobalt mining industry is commonly criticized harshly for lack of social and ecological considerations. In recent years, a push towards a reduction in global dependence for battery resources has led to emerging technologies where the supply chain can be built and scaled to match the demand. In light of this, sulfur is a cheap, lightweight, environmentally friendly and naturally abundant material with very high energy density material that can react with Li, Mg, Na and other materials to form metal sulfides, serving as a promising replacement for the active material in the cathode [4].

1.2 Background

Depending on the application, different performance parameters become more important. These range from technical merits, such as energy density, cycle life, and rate performance, to broader considerations, including cost, safety, and environmental impact. For most portable electronics, energy density is generally considered the most critical parameter, allowing long operating times between charges, while a fast charge and discharge rate and high cycling stability are also highly desirable. Although capacity is especially important in EVs, with the range being very limited compared to conventional fossil-fuel-driven cars, factors such as cost, cycle life, and safety must also be considered [2]. The characteristics of battery component materials and cell engineering directly influence these critical parameters. While there is a strong motivation to push the gravimetric energy density much higher, from the current limit of about 250 Wh kg^{-1} towards 500 Wh kg^{-1} [1],[2],[8], achieving this goal is challenging due to inherent limitations in the materials developed for commercial LIBs. Most of the progress achieved in improving current battery technology is due to continuously optimizing existing systems, and it is inching closer towards the upper engineering limit of theoretical energy density, unable to meet the increasing demand for performance. As an example, graphite anodes alone have dominated commercial LIBs for more than 25 years. Reaching the next performance level will therefore require changing the underlying chemistry, and with it, a variety of new challenges have appeared. Current commercial LIBs rely on insertion-type electrodes such as graphite, which operate through reversible intercalation of Li^+ ions in the matrix of the electrode material, and organic liquid electrolytes, offering good stability and cycle life. In contrast, next-generation electrode materials relying on conversion chemistries are promising due to their much higher capacity of up to an order of magnitude higher compared to graphite anodes (372 mAh g^{-1}), such as silicon anodes (4200 mAh g^{-1}), sulfur cathodes (1675 mAh g^{-1}) and lithium-metal anodes (3860 mAh g^{-1}) [1],[2]. However, they suffer from major drawbacks in terms of stability. Si anodes may expand to as much as 400%, leading to rapid mechanical degradation and failure after relatively few cycles, while sulfur cathodes suffer from rapid capacity fading due to shuttling effects. Meanwhile, lithium-metal anodes suffer from excessive dendrite formation during the charge cycle, often causing sudden failure by piercing the separator and short circuiting [1].

Nonetheless, solving the challenges associated with conversion electrodes would set a new standard for LIBs, with a manifold increase in performance. This sets the stage for why lithium sulfur batteries (LSBs) have garnered so much interest in recent years as an alternative. Sulfur cathodes have exceptionally high theoretical capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) compared to commercial LIBs. Additionally, sulfur is a naturally abundant resource on Earth, of low atomic weight, inexpensive, and environmentally friendly, justifying its usage as a next-generation battery material for a more sustainable future. However, LSBs suffer from a set of new intrinsic challenges that must be addressed, hindering its practical application. These challenges range from the much larger volume change during the charge-discharge cycle of LSBs (80%), compared to that of LIBs (<10%),

to ionic and electronic conductivity issues, and shuttling effects. The expansion of the cathode material is harmful to the structural integrity, leading to deterioration, fragmentation of active materials, capacity loss, and lower lifespan of LSBs. Although problematic, the most critical and difficult challenge to address is the notorious shuttle effect of polysulfides formed in the charge-discharge process, leading to low coulombic efficiency (CE), conductivity, cyclic stability, active material utilization, self-discharge behaviour, and stagnant kinetics [8],[9].

In addition to the obstacles of conversion electrodes, the conventionally used organic liquid electrolytes are also problematic. In order to reduce the shuttle effect, ether solvents are utilized to reduce the solubility of polysulfides and facilitate interconversion reactions. However, the utilization of sulfur as an active material in the cathode, in addition to ether solvents, has raised concerns due to its combustible nature [9]. Frequent incidents involving fires and explosions in commercial LIBs have led to large-scale recalls and negatively impacted both the economy and public perception of these technologies. These failures typically stem from undesirable chemical reactions, gas formation, overcharging or deep discharging, thermal runaway in the presence of flammable components, and mechanical abuse from collisions or cell damage. Selecting inherently safer electrode materials and engineering for safety are therefore key steps in mitigating these risks [10].

When considering the design and implementation of next-generation battery materials, all of these challenges must first be addressed. Although many different strategies have been developed to mitigate the issues of second-generation LSBs, with a wide variety of battery designs utilizing different liquid and solid electrolytes, electrodes, conductive particles, carbon matrices, separators, and binders [9], and the optimization of said components, with the engineering of composition, interface, and architecture, there is currently no one-fit-all solution for all applications. Among these, an often overlooked part in battery performance is the crucial role of binders in the stability of the solid electrolyte interface (SEI), conductivity, kinetics, and adhesion between electrode and current collector, which are all essential for battery performance and lifetime [1].

1.3 Research gap

The current production of commercial LIBs commonly relies on polyvinylidene fluoride (PVDF) as a binder material, which has proven insufficient in tests of adhesion, mechanical properties, and conductivity for next-generation electrode systems [1]. Additionally, conventional LIB electrodes require the highly toxic and expensive N-methyl-2-pyrrolidone (NMP) to dissolve PVDF, since it is not water-soluble. This leads to negative environmental effects not only during manufacturing, but also during the separation of binder and active material from the current collector during recycling [11]. PVDF also falls under the category of per- and polyfluoroalkyl substances (PFAS), with increasingly strict regulations on its use due to issues with high activity and persistence in biological systems. As of the 14th of October 2025, a

proposal on the restriction of PFAS chemicals was issued by the European Chemical Agency (ECHA), which is expected to be implemented between 2026-2027 [12]. The growing global need for next-generation LIBs and the aforementioned issues necessitate the development of more advanced LSBs with enhanced stability, conductivity, and kinetic performance, whilst allowing for cheap and environmentally friendly manufacturing. An interesting strategy to achieve this goal is to develop multifunctional, water-processable binders [1]. Incorporating zwitterions into a copolymer is a useful way to achieve high water solubility and has shown to limit the inherent difficulties in lithium sulfur batteries with carbon black or CNTs as conductive material, achieving an increase in the electrochemical performance of the battery. However, further research is necessary to fully understand the performance and working mechanism in LSBs constructed from graphene-sulfur composites [13],[14].

1.4 Problem statement

Lithium sulfur batteries suffer from poor cycling stability because of the shuttle effect, poor conversion kinetics, inherently insulating sulfur, and cathode expansion/-contraction cycles. Binders that are used commercially for lithium ion batteries perform poorly in lithium sulfur batteries, necessitating the development of more advanced binders for the latter.

1.5 Aim of the thesis

In this thesis, the performance and working mechanism of a previously unexplored zwitterionic copolymeric binder structure in graphene/sulfur (Gr/S) composite is investigated.

1.6 Research questions

1. Does the binder perform well in lithium sulfur batteries compared to the commercial water-soluble binder PAA?
2. Is the interaction between binder and graphene sulfur favourable?
3. What is the working mechanism behind the improvement in electrochemical performance of the battery?

1.7 Scope/limitations

Copolymeric binders with the following monomer ratios were investigated: 1:1, 4:1, 9:1, and 19:1. The conductive material was limited to graphene and carbon black, with a graphene/sulfur ratio of 70:30. A standard electrolyte ratio of 50 was used, with an average sulfur loading of 1 mg, with higher amounts not considered in this study. The Characterization techniques were limited to NMR, FTIR, TGA, SEM, CV, EIS, and GCD.

2

Theory

This section describes the working principle of lithium sulfur batteries (LSBs), with a deeper explanation of the aforementioned issues and principles behind conversion reactions. It also provides background for the importance and design principles of binders, including the structure, functionalities and reaction mechanism of the binder synthesized in this work.

2.1 Lithium Sulfur Battery Operating Principles, Polysulfide Shuttling, and Kinetic Limitations.

Lithium sulfur batteries consist of a sulfur cathode, which is the positive electrode, a lithium metal anode, the negative electrode, a separator in between, and an electrolyte solution encompassing all three. The separator is electrically insulating, forcing electrons to travel through the current collector, but is ionically conductive, allowing transfer of lithium ions between the electrodes [1],[9]. An illustration of a general lithium-sulfur battery setup is shown in Figure 2.1 below.

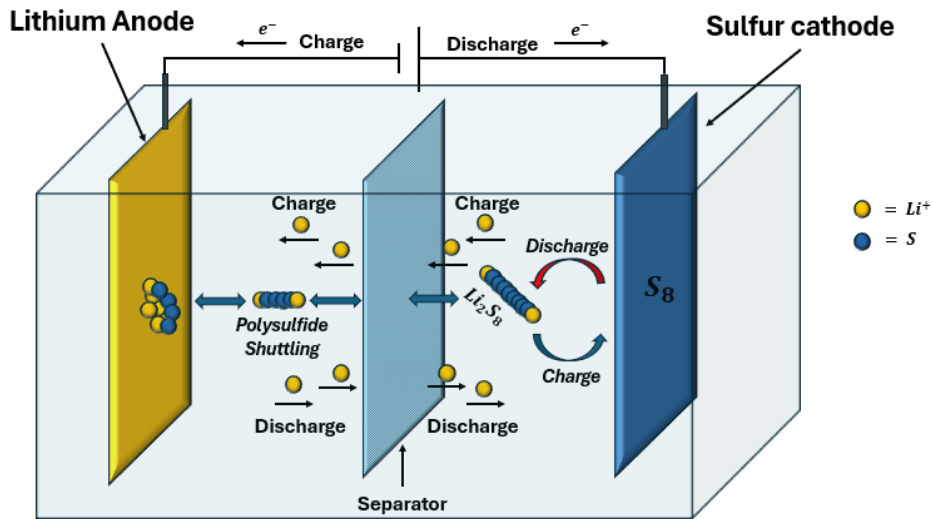


Figure 2.1: Illustration of a general lithium sulfur battery setup, showcasing the conversion reaction and polysulfide shuttling.

The discharge process starts with the oxidation of lithium at the surface of the anode, producing ions (Li^+) that dissolve in the electrolyte while transferring charges through the current collector. The local increase in dissolved ions near the anode leads to a concentration gradient, which, in addition to the electric field drives the diffusion towards the cathode, whereby solid S_8 accepts Li^+ , forming lithium polysulfides (LiPSs), as illustrated in Figure 2.1 [15]. Initially, soluble, long chained LiPSs classified as Li_2S_x , where $4 \leq x \leq 8$, are formed [16]. As the sulfur content is gradually removed through the subsequent reactions, energy is released, with the accompanying reactions shown in the second step of Figure 2.2a. If not successfully reduced further by the sulfur host material on the cathode, commonly composed of a conductive carbon matrix, such as graphene, [8],[9], they will proceed to diffuse through the electrolyte towards the anode, similarly driven by the concentration gradient [15]. As the reaction unfolds and more long-chain LiPSs are dissolved in the electrolyte, the viscosity increases, leading to a decrease in ionic conductivity of Li^+ ions, harming the cell efficiency [8],[17]. Additionally, upon arrival at the anode, the LiPSs will be further reduced due to the strongly reducing property of lithium metal, generating short polysulfides (Li_2S_2/Li_2S) that precipitate, forming a localized and solid, film-like insulating phase on the anode that cannot be re-oxidized (Figure 2.1). The accompanying reduction reactions can be seen in the third and fourth step in Figure 2.2a.

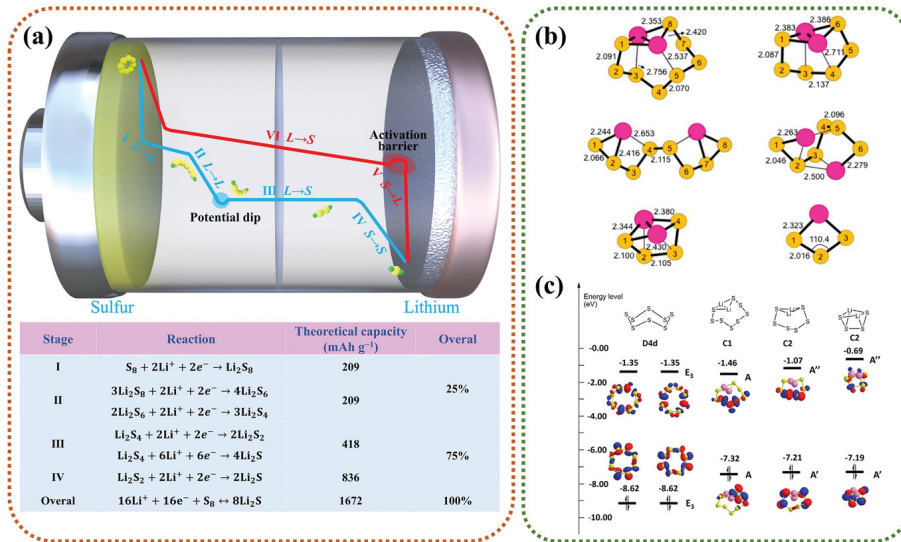


Figure 2.2: Illustration of the potential curves during charge and discharge, and associated reduction reactions. Reproduced from [15], under the terms of Creative Commons Attribution (CC BY 4.0) License.

Subsequently, lithium ions on the surface stuck under the deposition are inhibited, while the previously active sulfur material becomes inactive, with both contributing to severe capacity loss, low coulombic efficiency, and self-discharge behavior. Alternatively, once reduced on the anode, polysulfides commonly shuttle back to the cathode under the electric field, participating in unfavourable side reactions [18].

For instance, due to the much lower energy level of the LUMO of Li_2S_4 (-0.69 eV) compared to S_8 (-1.35 eV), spontaneous formation of Li_2S_6 (-1.07 eV) commonly occurs, as can be seen from the diagram in Figure 2.2c). In other words, because polysulfide species have different LUMO energy levels, electron transfers that yield parasitic side reactions such as disproportionation can occur during discharge, reducing the practical efficiency of the battery [15]. The migration back and forth between electrodes is termed polysulfide shuttling, and is one of the major issues limiting the practical application of LSBs, along with the challenges of the sluggish kinetics and insulating nature of polysulfides [19],[20],[21].

For lithium sulfur batteries, ether-based electrolytes such as DOM/DLE are utilized due to their high solubility of polysulfides and stable SEI interface, whereas dissolved LiTFSI salt is added to enhance the ionic conductivity [22]. There are two prominent discharge plateaus associated with sluggish reduction reactions between different phases, limiting efficiency. One between solid crown sulfur, S_8 , and liquid LiPSs (Figure 2.2 step 1), and the other during the formation of solid Li_2S_2/Li_2S (Figure 2.2 step 3), typically at 2.4 V and 2.1 V, respectively. Additionally, the first oxidative step between solid and liquid LiPSs when charging the battery faces an activation barrier, whereas the formation of S_8 is rapid, as can be seen in step 5 of Figure 2.2a. The theoretical energy density of the reduction reactions, bandgap energy levels, geometrical configurations, and associated potential changes during conversion are comprehensively illustrated in Figure 2.2 [15]:

The operating principle of lithium sulfur batteries is based on the energy derived during discharge, with the reduction of LiPSs species, and storage of energy during charging and oxidation of polysulfides. And yet, the greatest challenges associated with LSBs are similarly related to this mechanism. Hence, the optimization of battery design has primarily focused on preventing the shuttling of LiPSs between the anode and the cathode, which causes loss of active material, and hence lower capacity and lifespan of the batteries. Successful strategies addressing the shuttle effect can be largely divided into physical and chemical confinement of LiPSs at the cathode, tailoring of the liquid electrolytes or using solid-state electrolytes, and preventing the corrosion of the lithium anode by enhancing the solid-electrolyte interphase layer (SEI). $LiNO_3$ is a commonly used additive to improve the Li-anode stability, preventing degradation [15]. Typically, sulfur is loaded into a highly conductive and porous carbon matrix, impeding the diffusion and insulating effect of LiPSs, while mitigating volume change. Meanwhile, binders, interlayers, and separators utilize physical and chemical adsorption, electrostatic repulsion, or attraction to prevent polysulfide shuttling [8]. It is well reported in the literature that ion-ion bonding between functional groups made up of sulfur, nitrogen, or oxygen in polymer binders and the lithium ions of LiPSs ($Li^+ - X$, ($X = S, N, O$)), in addition to the bonding between imine or amine groups containing positive charges and the negatively charged sulfur in polysulfides, is highly beneficial in preventing the shuttle effect [1]. Other interesting approaches to alter the redox mechanism of S_8 from the traditional solid-liquid conversion reactions in ether electrolytes towards a single solid-phase reaction in carbonate electrolytes have been attempted. In these systems, microporous or polymeric structures containing sulfur atoms effectively avoid

the issue of soluble polysulfides dissolving and diffusing between cathodes, preventing active material loss and self-discharge behaviour. Although the cycling stability proved exceptional, the limitation of low sulfur content for these quasi-solid-state reactions hinders their practical application, and hence the development of binders that anchor polysulfides provides a more reliable approach [18].

Although previously mentioned methods increase the stability of the battery by preventing the shuttling effect of polysulfides, loss of active material utilization is still a large issue due to the accumulation of insulating Li_2S on the cathode surface, in addition to the slow kinetics associated with the transformation between soluble and insoluble LiPSs. The tunneling distance of electrons through the insulating Li_2S_2/Li_2S layer is generally less than 1-2 nm, meaning that only sulfur species at the surface layer of the deposited particles can react, with active material trapped within, resulting sluggish kinetics, low sulfur utilization and meager effective capacity [23]. Hence, homogeneous deposited of high aspect ratio Li_2S particles facilitate lower internal resistance to electron transfer, improving sulfur utilization and rate capacity, whereas a dense coating on the cathode surface should be avoided. [19],[24]-[26].

To prevent this, it is ideal to not only capture polysulfides on the cathode side, but also enhance the sulfur redox reactions to maximize the sulfur utilization and effective capacity [16],[19]-[22],[27]-[35]. As previously mentioned, the sluggish kinetics of polysulfide interconversion in LSBs are associated with the limited rate of reduction and oxidation reactions between the solid states Li_2S_2/Li_2S and S_8 , and the liquid state Li_2S_x , where $x \geq 4$). In general, the energy level of LUMOs increase with shorter LiPSs chain length, leading to overpotentials and gradually reduced kinetics during deeper discharge, especially during the second plateau. However, liquid polysulfides possess similar HOMO levels, suggesting that interconversion during oxidation has less overpotential, while it is large in the transition to solid species, elucidating the reason behind the sluggish transformation between phases [33]. In operational conditions, it is often reported that the actual reduction peaks of sulfur species lies in the range 2.2-2.4 V and 1.9-2.1 V vs. Li^+/Li depending on system design, instead of the typical values of 2.3 V and 2.1 V. The discrepancy can be attributed to internal electrolyte and electrode resistance, in addition to interfacial barriers, nucleation effects, and overpotentials. Hence, although there is a thermodynamic driving force for reduction at 2.4 and 2.1 V, kinetic limitations can lead to undesirable operating conditions [19],[21]-[24],[31]. A large hysteresis between discharge and charge plateaus causes a vast overpotential that must be overcome to oxidize and transform insulating and solid species into liquid phase [32]. Hence, a smaller polarization potential ΔE is indicative of faster redox kinetics [16].

2.2 Integrity and Adhesion of Cathode materials

Classical intercalation battery chemistries suffer from intrinsic capacity limitations due to the crystal structure’s inability to change on a larger scale, in addition to insufficient redox activity of the transition metal [36]. In comparison to the current commercial LIBs, batteries such as LSBs undergo large volume change, which is a consequence of the conversion reactions, and originates from the density difference between the final product Li_2S and the initial active material state, S_8 [9]. During the charge-discharge cycle, the sulfur cathode undergoes an expansion of up to 80%, which deteriorates structural integrity and fragments the active material [8],[9]. The leading cause of capacity loss and reduced lifespan of LIBs can be attributed to the degree of structural change in the electrode between cycles, highlighting the importance of a suitable polymer binder in mitigating degradation and maintaining performance by facilitating close proximity between conductive additives, current collector, and active and host materials, acting as a glue. In this regard, the molecular weight of the polymer plays an important role, with exceptionally high or low values resulting in weaker adhesion due to viscosity issues and uneven distribution of active material on the cathode surface [37]. Although larger molecular weight polymers are generally desired, the exact value depends on the strength of the interaction between the polymeric binder and active material, varying for each case. If the chain is excessively long and mobility is hindered, it can reduce the transport of Li^+ ions, and as such, an optimal weight range exists [38]. The structural integrity of the binder is kept in two distinct ways, with dependency on the mechanical properties and the adhesion between binder and substrate material, which is dependent on the molecular structure and surface characteristics of both the electrode components and binder. Hence, the failure mechanisms of binders can also be categorized into those of structural failure and delamination failure, with the latter more commonly occurring. Mechanical stress is transferred through the interfacial contacts to the polymer backbone, with no observed degradation when the structural strength is high enough. However, the large volume expansion necessitates flexible components, which is in direct contrast to the desired hardness, requiring a balance in the design of physical properties for binders [1],[9].

Among the interfacial forces, chemical bonding, intermolecular bonding, and mechanical interlocking have varying degrees of contribution to the structural integrity of the components in the electrode, with differences in their mechanisms of interaction. van der Waals forces are the weakest, with failure even at low stress levels, followed by hydrogen and electrostatic forces, whereas covalent bonding is the strongest [1],[9]. PVDF, one of the commercial binders, relies on the former, and its application in LSBs is hindered by its insufficient adhesion, ionic and electronic insulating properties, and brittleness due to high crystallinity. Although the fluoride moieties are polar, the symmetrical structure of the molecule nullifies this polarity [9]. Other types of bonding demonstrate unique characteristics and have their own advantages. For example, dynamic non-covalent bonds such as hydrogen, ion-ion, and ion-dipole bonding all exhibit self-healing effects, whereby previously lost intermolecular interactions between active materials, binder, and other compo-

nents caused by volume changes from former cycles can be recovered, which is of particular importance for high specific capacity materials with large expansion, and provides high stability through many cycles. A more advanced and commercially used binder than PVDF with these properties is polyacrylic acid (PAA), which has better performance in conversion electrodes due to the reversibility of the dense hydrogen bonding structure, and is commonly used as a reference for measuring the performance of advanced binder systems [1].

During the manufacturing process, active material, conductive carbon, and host material are ground together homogeneously. Graphene is a typical material used for the containment of sulfur in Li-S batteries due to its highly porous and conductive structure, serving as an interconnecting transport channel for electrons between active materials and current collector, in addition to the favourable interactions between the two. The non-polar nature of graphene and sulfur results in strong van der Waals interactions, which, together with the porous structure, greatly aid the containment of sulfur within the network, while simultaneously allowing the transport of lithium ions. However, polysulfides are polar molecules that cannot be immobilized solely relying on van der Waals forces, hence it is typically doped with heteroatoms. The introduction of defects in the alters the charge distribution, reducing the shuttle effect and allowing for improved stability and performance during cycling [39]. Although this method is viable, it is typically more expensive and complicated to produce a large amount of high-quality doped graphene compared to the relatively simple synthesis of multifunctional binders, with structures that are more easily altered for the desired purpose. Additionally, the flexible and strong nature of reasonably designed polymers can better accommodate the large volume changes during battery cycling compared to alternatives [9], [40].

After the grinding process, the binder is dissolved in a suitable solvent and then added, forming a slurry. If the slurry attains the correct viscosity, it is distributed evenly on the current collector. Subsequently, the solvent is evaporated [37]. Mechanical interlocking of the binder is mainly achieved through the penetration, adsorption, and intertwining of the polymeric solution with the porous structure of active material, conductive additives, and current collector, followed by solidification of the binder during the drying step, and cannot be repaired once it has ruptured. On top of the loss of structural integrity with each expansion and contraction, the affinity between the polymer binder and electrolyte poses its own challenges. If polar, swelling behavior is commonly observed, weakening the integrity of the cathode, although lithium ion diffusion is enhanced. Soluble binders can even dissolve and migrate, unable to provide the intended effect while increasing internal resistance. The affinity and swelling in electrolytes can be reduced by in-situ crosslinking of the binder, thereby increasing the cohesive forces. Another good way of avoiding this is by developing water-based binders, which are typically insoluble in ether electrolytes [1],[41].

2.3 Ionic Conductivity

The inherently low ionic conductivity of sulfur and LiPSs species limits the transport of Li^+ and electrons, leading to high polarization, slow kinetics, and hence buildup of deposits, causing gradual and irreversible capacity fading. The diffusion of lithium ions and the conversion of lithium polysulfides are the rate-limiting steps to achieve the desired high sulfur loading and capacity. For these reasons, in addition to the electronic conductivity of the carbon additive, it has been well established that improving the ionic conductivity of binders is important to take into consideration in order to achieve an improved electrochemical performance, particularly the rate performance, which is dependent on the lithium ion transfer between the electrodes. Implementing electronegative atoms such as ether, carboxyl, hydroxyl, nitrile, amino, fluorine, or ionic moieties not only improves cathode structural integrity but also facilitates the transfer of Li^+ through temporary interactions between the lone electron pairs and the positive charge of lithium ions, allowing them to hop between the functional groups, a mechanism known as reversible complexation [1],[9]. Among ionic binders, although cationic functional groups provide enhanced polysulfide retention, the ionic conductivity of lithium ions can suffer due to electrostatic repulsion effects. In contrast, anionic binders not only assist in preventing LiPSs shuttling but also enhance the conductivity of Li^+ ions through the aforementioned reversible complexation mechanism [42]. Another prerequisite for high conductivity is the homogeneous dispersion of crown sulfur, S_8 , on the cathode surface, which is facilitated by hydrophilic species and optimized viscosity of the binder, providing further benefit for the development of water soluble binders [1],[9].

"The internal dipole structure of zwitterions facilitates the alignment and interaction of Li^+ with the anion moieties of the zwitterionic groups, promoting the dissociation of lithium salts and improving ion mobility [26]. Zwitterionic materials form a unique ion-conductive network that can optimize the Li^+ coordination environment and enhance the availability of free Li^+ , thereby reducing ion-pairing effects that can hinder Li^+ transport"

2.4 Water solubility

Polymeric binders achieve water solubility through the introduction of hydrophilic moieties in the structure. Generally, natural polymers and their derivatives are water soluble since they contain abundant carboxyl and hydroxyl groups, facilitating favourable interaction with water through hydrogen bonding. Aqueous binders are therefore commonly made by chemically modifying naturally occurring polysaccharides like sodium carboxymethyl cellulose (Na-CMC), sodium alginate (Alg), xanthan gum (XG), and cyclodextrins, etc. In a similar fashion, synthetically made polymers such as polyacrylic acid (PAA) are easily hydrated due to dense hydrophilic functional groups [1]. In comparison, zwitterionic polymers are even more water soluble due to the strong ion-dipole interaction between positive and negative ions and hydrogen bonds in H_2O , creating an ionic solvation effect where the solvent molecules surround and stabilize the charged particles [43].

2.5 Binder Design

Throughout the journey from its classical applications in commercial batteries towards newer battery chemistries with increasingly harsher environments and demands on performance, the binder has evolved from being an adhesive glue-like compound only meant to enhance the integrity of electrodes towards achieving more functionalized goals. In this progression, the design has broadened from the mechanical viewpoint of adhesion, flexibility, and hardness to gradually including other important parameters for cell performance, such as ionic and electronic conductivity and self-healing effects. In lithium-sulfur batteries, especially, the sluggish kinetics of lithium sulfur polysulfides, their intrinsic insulating properties, and the detrimental effects associated with polysulfide shuttling necessitate the design of binders to truly be multifunctional, with all aspects taken into consideration. Herein, a series of novel binder structures utilizing zwitterionic and redox-active moieties is presented for application in LSBs, as can be seen in Figure 2.3 below.

The DMAPS-HEA binder features a zwitterionic part with the intended effect of enhancing adhesion between the cathode sulfur crown structure and quarternary cationic nitrogen atom through ion-ion bonding, while simultaneously allowing for three-dimensional electrostatic cohesion and self-healing behavior between chains through ionic interactions and hydrogen bonding, as seen in figure 2.5. Additionally, the structure provides the possibility of increasing the conductivity of Li^+ ions via the lone electrons on the sulfonate and oxygen groups. Moreover, zwitterionic structures are supremely effective in hindering the polysulfide shuttling effect through the simultaneous bonding of Li^+ end atoms with the sulfonate, and negatively charged sulfur atoms with the quarternary nitrogen cation, effectively capturing all the different LiPSs species. This prevents the aforementioned issues with loss of active material due to shuttling to the anode, and is illustrated in Figure 2.4 below [1],[44].

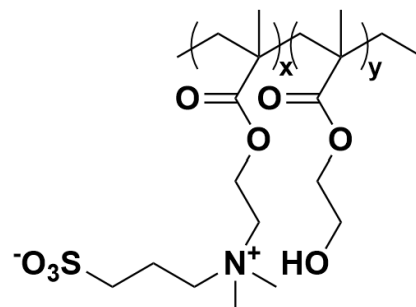


Figure 2.3: Molecular structure of DMAPS-HEA binder.

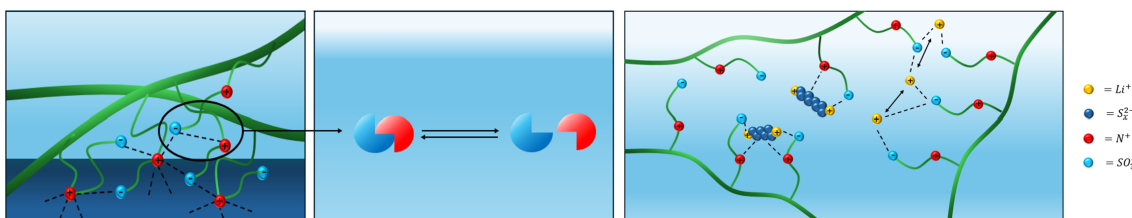


Figure 2.4: Advantageous self-healing effect and cathode adhesion (left), and dual ion-conducting/polysulfide anchoring ability (right) of DMAPS-HEA11 binder.

2.6 Reaction mechanism

This section provides a general overview of the reaction mechanism used in the binder synthesis. Additionally, the reasoning behind the control of radical formation, monomer ratios and molecular weight is provided.

2.6.1 Free radical polymerization

Free radical polymerization (FRP) is a polymerization method utilizing free radicals, usually created through bond cleavage in selected initiator molecules. The first step is denoted as initiation and requires external stimuli, such as heat, photolysis, or ionizing radiation. More specifically, peroxides and azo compounds are commonly used due to the instability of the O-O and N=N bonds, usually creating two active radicals per bond broken, signifying the start of the polymerization process. Furthermore, the reaction temperature must be carefully selected such that the degradation provides a steady but not overflowing source of free radicals, sustaining the reaction. A typical value lies in the range of $50 - 150^{\circ}\text{C}$. Once generated, the free radical is transferred from the initiating molecule to a monomer, which further propagates through continuous addition of monomer units to a growing chain, consistently generating new radical building blocks in the process. This second step is appropriately denoted propagation and is most efficient on the double bonds in vinyl monomers, due to its greater susceptibility for rearrangement once activated by an initiator. The electron pairs can be divided into those participating in a σ bond, held tightly, and those in weaker bonds, forming the π bond. The latter is especially reactive, easily forming a new bond with the attacking radical by transfer of one of the π -bonded electrons, whereas the other electron is transferred back to the second carbon atom, forming a new radical species that can further react with unsaturated monomers, leading to polymers of varying length and mass [45],[46]. The final step, termination, can occur by several differing mechanisms. Once two growing polymeric chains or radical species interact, they can either combine and form a longer chain or participate in a process called radical disproportionation, whereby a hydrogen atom is abstracted from one chain to the other, forming two terminal groups, one unsaturated and the other saturated. The former contributes to an initial increase in polymer length but puts an upper limit, whereas the latter only reduces it. Bearing in mind the termination step, it can be logically deduced that if longer chains are desired, the initiator concentration should be reduced, minimizing the probability of interactions between radical species and facilitating more propagation steps. The initiation, propagation, and termination steps are summarized in table 2.1 below, where the subscript index refers to the number of monomers in the chain [45].

Table 2.1: Initiation, propagation, and termination steps in free radical polymerization

Step	Reaction
Initiation	$I \xrightarrow{\Delta} 2 I\cdot$
	$I\cdot + M \rightarrow IM\cdot$
Propagation	$IM_n\cdot + M_1 \rightarrow IM_{n+1}\cdot$
Combination	$IM_n\cdot + IM_m\cdot \rightarrow I_2M_{m+n}$
Disproportionation	$IM_n\cdot + IM_m\cdot \rightarrow IM_n + IM_m$

Another mode of termination is intra- and intermolecular chain transfer, typically resulting in the creation of a new radical on a secondary carbon through the abstraction of a hydrogen atom, often unable to further propagate. This occurs at the expense of another radical and can similarly occur through several mechanisms, depending on whether it targets solvent molecules, monomers, initiators, or other polymers. A higher concentration of the targeted molecule during chain transfer, a weaker bond connecting the hydrogen to be abstracted, and a more stable resulting radical all increase the efficiency of chain transfer. Each case has a different result, and depending on the system, the sensitivity can vary, with peroxides commonly undergoing chain transfer [45]. Due to the effects of dissolved oxygen molecules, which scavenge free radicals and slow or inhibit FRP synthesis, it is usually conducted under an inert atmosphere, such as N_2 or argon, thoroughly flushing out unwanted reactive species in the system [47]. Radicals formed on the solvent and monomers through chain transfer are typically unreactive due to resonance stabilization effects, whereas polymers typically branch, and initiators react further. Overall, excessive termination, especially through disproportionation or chain transfer reactions, decreases the chain length [45].

2.6.2 Copolymerization

Copolymerization can be defined as a polymerization reaction in which the final polymer chain contains two or more different monomer species, and is classified according to its structural arrangement. They are typically divided into the three categories of alternating, statistical, and block copolymers, although many more exist. The former describes polymers with a consistently repeating alternating sequence of monomers A and B, whereas the composition and arrangement of monomers in a statistical copolymer is dependent on the mole fraction of each monomer. The latter is defined by the presence of different homopolymer segments of varying lengths linked through covalent bonds, often including junction blocks consisting of non-repeating units between sections. The type of copolymer formed can be predicted based on the terminal model for two monomers, assuming that the propagation rate depends only on the monomer at the growing end of the chain. In this way, one needs only compare the relative reaction rates of monomers in the system, derived based on the rate of disappearance of each monomer in equations 4-6 below. When $r_1 > 1$, monomer M_1 preferentially forms homopolymers, whereas the opposite result is obtained when $r_1 < 1$. Likewise, the same applies to all the other monomers in the system. In the case that both reaction rates exceed 1, block copolymers tend to form, and when $r_1 = r_2 = 0$, alternating copolymers are observed, since each monomer can only react with the other species. An ideal system can be defined where $r_1 = r_2 = 1$, with both monomers having equal reactivity towards each other, in which the copolymer composition fully depends on the molar ratios of the monomers [45].

$$-\frac{dM_1}{dt} = k_{11}M_1M_1 + k_{21}M_2M_1 \approx 0 \quad (4)$$

$$-\frac{dM_2}{dt} = k_{22}M_2M_2 + k_{12}M_1M_2 \approx 0 \quad (5)$$

$$\Rightarrow r_1 = \frac{k_{11}}{k_{12}}, \quad r_2 = \frac{k_{22}}{k_{21}} \quad (6)$$

2.7 Methodological background

2.7.1 Purification

Following a successful polymerization reaction, dialysis, which follows the pore-flow model, is commonly applied to separate the produced polymers from unreacted monomers or oligomers. Molecules in an isotropic fluid have no preferential direction of motion and move randomly. However, when a concentration gradient exists between two regions, such as the high concentration inside the polymer-filled membrane relative to the outside fluid, although such random motion will continue, statistically, the net transport will occur in the direction of lower concentration. Through this method, the microporous dialysis membrane filters permeants based on the size of the pores, with the lower molecular weight species diffusing through, whereas polymers above the molecular weight threshold remain inside, effectively separating the two [48]. Following the polymerization and dialysis steps, freeze-drying is typically employed to extract any remaining solvent. Initially, the liquid suspension of solvent and polymer is rapidly cooled using liquid nitrogen ($-196\text{ }^{\circ}\text{C}$), forming ice crystals. The sample is subsequently loaded in a sealed container connected to a vacuum, removing frozen solvent by sublimation under a vacuum, retaining an intact polymer structure [49],[50].

2.7.2 Cathode Manufacturing and Cell Assembly

Electrode manufacturing requires preceding steps to achieve high homogeneity of active material, conductive additive, host matrix, and binder. A preselected active to host material ratio precursor mixture is commonly prepared by ball-milling, crushing, and homogenizing particles, followed by melt diffusion. Without the latter, the resulting electrodes frequently suffer from active material loss, which is especially prevalent for sulfur cathodes. Typically, sulfur/graphene mixture in a ratio of 70:30 is sealed in a quartz tube container under an inert atmosphere at elevated temperatures above $155\text{ }^{\circ}\text{C}$ [51]. This process reduces the viscosity of sulfur particles, improving diffusion and further deepening the intrusion of sulfur in the porous carbon structure of graphene through capillary forces, trapping it and reducing delamination losses while simultaneously increasing actual loading. In recent years, melt diffusion has become the much preferred method over alternatives such as solution-based methods employing organic solvents or sulfur vapor deposition. Typically, carbon disulfide, or other options such as toluene or dimethyl sulfoxide, is used to dissolve sulfur, followed by a drying process to obtain the desired composite. However, this method is dependent on toxic chemicals, constituting a safety hazard. Similarly, sulfur vapor deposition vaporizes sulfur at high temperatures, with its own safety concerns, high energy intensity, and specialized equipment needed [52].

Once sulfur has successfully been introduced deeper into the graphene structure, the slurry is typically finalized by combining and mixing the resulting sulfur/graphene (Gr/S), carbon black, and binder in a ratio of 8:1:1 in a centrifuge at close to 2000 rpm for at least 15 minutes [38]. Although melt diffusion increases sulfur parti-

cle settling in the graphene mixture, increasing the sulfur loading above 2 mg/cm^2 can contribute to fractures and delamination, leading to aggravated shuttling and slower reaction kinetics. Improving the electrode morphology and properties is heavily dependent on optimizing the slurry suspension composition and casting/drying procedures [52].

Doctor blade coating is a widely applied low-cost technique to process precursor solutions into a thin film coated on a substrate material, useful for electrode manufacturing. It relies on the continuous movement of a blade positioned behind the slurry, with a small gap relative to the substrate current collector, resulting in an even coating thickness. Mass loading of sulfur is dependent on the slurry composition and selected gap size, affecting the film thickness. The process is finalized through the evaporation of solvent in a drying process in a vacuum oven. Circular electrodes of desired diameter are then cut out for the cell assembly in coin cells [53], [38]. The coin cell is a lab-scale version used for characterizing the cell performance quickly and cheaply. The sulfur cathode and lithium anode are separated by a separator that is wetted with a liquid electrolyte, forming a battery. The structure is completed by the addition of a spacer and spring on top of the anode, with a bottom and top casing closing the cell [18]. Although often overlooked, the non-electrode material components, such as the spacer, spring, and case, improve the stability and performance of batteries and are crucial for correct assembly with minimal damage to electrode components during the final crimping step, commonly performed in a hydraulic press [54].

2.8 Characterization techniques

2.8.1 Structural determination

Successful synthesis of polymeric structures is typically confirmed by measurement of the spin flip of nuclei in a magnetic field with nuclear magnetic resonance (NMR), resulting in resonance frequencies. The local electronic environment around a nucleus differs depending on neighbouring atoms, and consequently, a measurable difference in energy required to incite a spin-flip among nuclei of the same kind exists, termed nuclear shielding. Since the chemical environment is dependent on the local structure of the molecule, structural determination is possible by assigning unique peaks to each environment [55],[56]. Successful polymerization can be confirmed by whether any remaining monomer olefinic signals at 6.23-6.27 ppm exist. Additionally, the ratio between segments in the structure can be confirmed from the signal intensity and their integrated areas [57].

Similarly, fourier transform infrared (FTIR) spectroscopy can be utilized to identify the presence of characteristic bonds in the molecular structure and successful copolymer synthesis through the disappearance of the C=C double bond peak, indicating full conversion [58]. Depending on the atomic and molecular energy levels, different wavelengths of infrared radiation can induce molecular vibrations, rotations, and stretching/bending, with the latter typically employed in analysis of polymeric structures (mid-infrared region, 400-4000 cm^{-1}) [59].

Thermal gravimetric analysis (TGA) is a quantitative analytical technique used to confirm material thermal stability, composition, and moisture content. The analyzer consists of a sample pan inside a furnace where the material of interest is loaded, connected to a balance that can monitor changes in mass with time and temperature [60]. Sulfur decomposes in a single step between 190-300 °C, which is the source of weight loss in this interval, whereas the structure of graphene remains intact until temperatures above 550 °C. Hence, the sulfur content in the Gr/s composite after melt diffusion can be estimated based on the weight lost after the initial decomposition at 300 °C [61].

Scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) is an analytical techniques typically used to observe the morphology and elements of a sample. The focused electron beam excites atoms at the surface, generating a variety of detectable radiations that can be translated into an image and mapping the elemental composition [62]. The morphology and components of the manufactured cathode surface can similarly be distinguished through SEM-imaging. Typically, sulfur particles have a size ranging from nanometer to micrometer scale, typically in a rectangular shape with rounded edges [63], whereas super P is generally about 40 nm in size with a round and smooth surface. Scattered clustering of super P occurs in-between graphene sheets, forming larger spiky crystals that are observable on the micrometer scale [64]. For unused sulfur cathodes, a porous and rough morphology is commonly observed. When subjected to deeper discharge, a decrease in pore vol-

ume is observable due to the gradual formation of insulating Li_2S growth blocking the pores, which is reversible upon charging due to oxidation of Li_2S [65], [66]. The formation of continuous and solid insulating film-like layers on the conductive substrates impairs the cell performance since it blocks access to electrochemical reactions, causing electrode passivation. In comparison, dense deposition of particles with larger exposed surface area provide more active sites for conversion, increasing the sulfur utilization [67]. It also indicates a larger number of nucleation sites and polysulfide absorption capability of the binder, facilitating more efficient conversion and reduced LiPSs shuttling. Additionally, larger precipitates indicate worse cycling performance due to lower nucleation site density [68]. Although EDS is useful for mapping the elemental composition, lithium cannot be detected due to the low energy of the characteristic X-rays [69].

2.8.2 Electrochemical measurements

Cyclic voltammetry (CV) is an electrochemical technique used to test current-potential relationships for redox-active materials, based on the Nernst equation (7) below, with O representing the oxidized species reversibly accepting n electrons e , thereby reducing to species R .



The applied potential is linearly swept at a constant scan rate v until the set potential has been reached, whereupon it is reversed, forming one complete cycle, commonly repeated a number of times. It is initiated from the open circuit voltage (OCV), above that of the reduction potential. Once it approaches the reduction potential of the cell chemistry, the reaction described in the Nernst equation takes place at the electrode surface. For lithium sulfur batteries, this means that lithium ions have been reduced at the cathode side, forming polysulfides. Hence, as described in section 2.3, a concentration gradient forms between the lithium-rich electrolyte phase and the Li^+ deficient cathode surface. The resulting diffusion flux causes a measurable cathodic current that is proportional to the concentration gradient. Hence, the largest reduction activity can be found at the cathodic peak current and potential, $i_{p,c}$ and $E_{p,c}$, respectively. Thereafter, a reduction in current is observed due to depletion of accessible material. A peak anodic current and potential can similarly be observed during the inverse sweep, representing the oxidative reactions. For LSBs, the first reduction reaction can be found between 2.2-2.4 V, whereas the second lies between 1.9-2.1 V, depending on the system characteristics, resulting in two distinct peaks. Additionally, the oxidative reactions are commonly observed in the range 2.2-2.6 V, with the two peaks commonly jumbled together into one inseparable larger peak [71].

CV is useful not only for determining proper cell function, but also for mechanistic studies. For example, if the current increases linearly with the square of the scan rate, the cell does not impede Li^+ diffusion, whereas the effectiveness of polysulfide retention on the cathode side can be extrapolated from the cycling stability. Additionally, the catalytic effect towards polysulfide conversion can be observed by

comparing shifts in peak potential positions [71]. When the curve features broad peaks and low current, it suggests that the reaction kinetics are slow and that the redox activity is insufficient for effective conversion [35]. In comparison, for peaks starting at a higher voltage, the LiPSs conversion reactions are more efficient due to less overpotential. Furthermore, two oxidation peaks during the anodic scan suggest great electrocatalytic ability, whereas a single, broadened peak represents poor polysulfide conversion and sulfur utilization [16]. Additionally, a smaller peak separation between the second reduction, corresponding to the conversion between Li_2S_x and Li_2S_2/Li_2S , and the major oxidation peak is indicative of better sulfur utilization and polysulfide redox kinetics [72].

Electrochemical Impedance Spectroscopy (EIS) Nyquist plots are used to understand lithium-ion kinetics and the conversion of lithium polysulfides. The diameter of the semicircle in the low-mid frequency region, representing the charge transfer resistance (R_{ct}), should be minimized for efficient electron transfer and lithium-ion diffusion at the solid-electrolyte interphase (SEI) between electrolyte and electrode surface. The semicircle in the high-mid frequency region represents resistance from remaining polysulfides forming a thick, insulating layer on the electrode surface, hindering chemical reactions. A lower (R_o) is desirable for a more efficient battery and can be improved through better polysulfide immobilization with the binder and more thorough conversion between polysulfides [16].

Galvanostatic charge-discharge (GCD) tests are performed to estimate the capacity during cycling at different rates. It features two voltage plateaus at the same reduction potentials as in CV [71]. Higher capacity retention during cycling can be attributed to greater polysulfide immobilization and electrode stability by the binder, preventing dead lithium and sulfur deposits on the anode side. The conversion rate is higher for a lower polarization potential (ΔE), whereas a higher capacity ratio for low plateau (Q_L) and high plateau (Q_H), ($\frac{Q_L}{Q_H}$), indicates faster redox kinetics [16].

3

Methods

3.1 Synthesis of Binder

DMAPS-HEA copolymers were synthesized by a free radical reaction of the two monomers, [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide and 2-hydroxyethyl acrylate in ratios of 19:1, 4:1, 9:1, and 1:1, corresponding to 5, 10, 20, and 50 mole% HEA in the polymer structure and denoted as DMAPS-HEA191, DMAPS-HEA42, DMAPS-HEA91, and DMAPS-HEA11, respectively. Typically, a batch was prepared through the dissolution of 1g DMAPS monomer in 10 ml water, followed by addition and stirring of HEA monomer in solution, with the amount depending on the mole ratio. Subsequently, the round-bottom flask top was covered and degassed for 45 minutes with argon using a needle inserted through the rubber septum, with an additional small needle inserted to alleviate pressure buildup and allow for oxygen removal. While kept under an inert atmosphere, 1 mol % of the initiator potassium persulfate $K_2S_2O_8$ was added, followed by an additional half hour of degassing. Finally, the round flask was then lowered into silicone oil (polydimethylsiloxane) with a temperature of 70 °C and kept under an inert atmosphere for 24 hours. The rubber septum outlet was covered using an argon-filled balloon to prevent unwanted oxygen intrusion. The reaction procedure is shown below in figure 3.1a, with the chemical structure and reaction conditions for the synthesis of DMAPS-HEA copolymer in figure 3.1b.

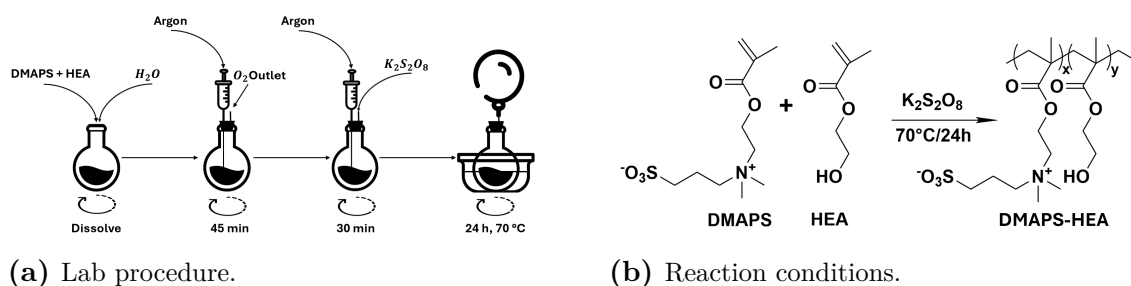


Figure 3.1: Procedure for the synthesis of DMAPS-HEA binder utilizing free radical polymerization (FRT) with potassium persulfate as initiator at 70 °C for 24 hours in water.

Dialysis of the copolymer was performed using a 3.5k molecular weight cut-off SnakeskinTM dialysis tubing kept in a beaker of deionized water with a magnetic stirrer for 72 hours. Water was exchanged twice a day during this period. Following the purification step, the sample was extracted and frozen in a liquid nitrogen bath, followed by freeze-drying using the ANTECH LyOrganic 8LU freeze dryer for 48 hours. The process steps are demonstrated in figure 3.2

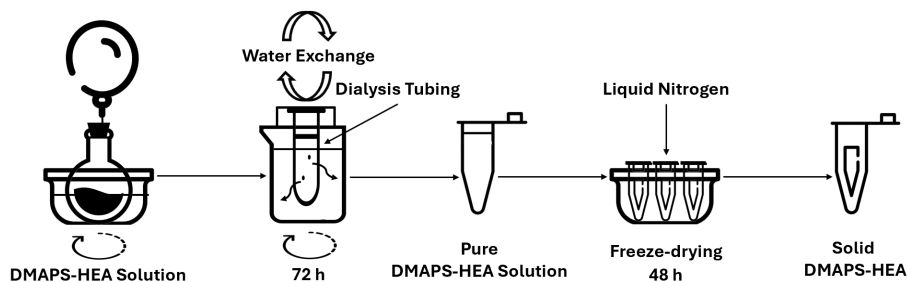


Figure 3.2: Dialysis and freeze-drying procedure.

3.2 Cathode Fabrication and Cell Assembly

Originally, attempts were made with the different DMAPS-HEA binders, coating thicknesses and slurry viscosities until the electrochemical performance was achieved. This also includes subjecting graphene/sulfur mixtures to different ball-milling and melt-diffusion settings until a homogeneous and high-performing mixture was obtained. Eventually, DMAPS-HEA11 was deemed best performing and further battery testing was performed on this binder. The optimized procedure after trial and error with different preparation methods is described below, with the resulting cathodes denoted as DMAPS-HEA11 (dissolved), whereas the gradual procedural improvement is described in the appendix, with the accompanying results.

Sulfur and reduced graphene oxide (Gr/S) mixtures were obtained by mixing the powder in a ratio of 70:30, followed by ball milling with the rpm was set to 200 rpm with 10 minutes of activity and 5 minutes of rest in each repetition, for a total of 3 repetitions, resulting in a homogeneous light grey mixture denoted as sample S1. Half of the sample was transferred to a glass vial with the top covered in aluminum foil (S2). Melt diffusion was performed at 160 °C for 6 hours to promote deeper sulfur intrusion and interaction with the graphene matrix. Polyacrylic acid (PAA) was dissolved in water in a ratio of 100 mg/ml, with a total of 0.2 ml transferred to a mortar and pestle with a micropipette. The solution was spread out evenly, followed by the addition of 160 mg of S2 and 20 mg of carbon black in a standard ratio of 8:1:1. Additional water was gradually added while mixing until the desired viscosity was achieved. Similarly, 20 mg of DMAPS-HEA11 binder was first dissolved and spread evenly, followed by the addition of the other slurry precursors according to the previous procedure. The slurries were cast onto carbon-coated aluminum foil and coated using the doctor-blade coating method, with the thickness set to 15 μm . The samples were air dried for 30 minutes followed by more thorough solvent evaporation in a vacuum oven set to 80 degrees for 12 h. The procedure for the slurry preparation and cathode coating is shown in Figure 3.3.

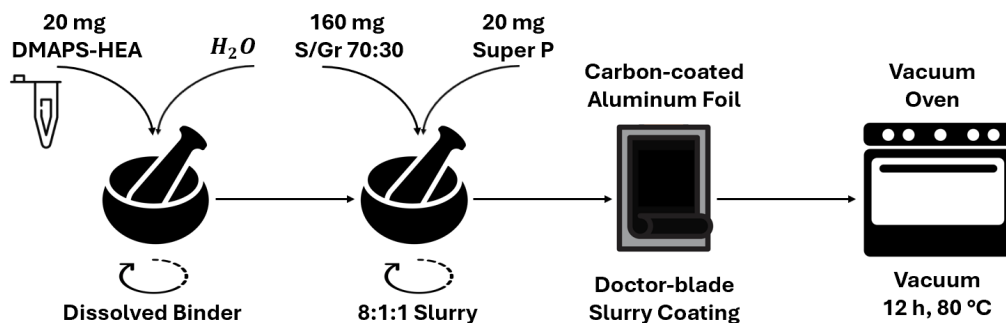


Figure 3.3: Procedure for slurry preparation and cathode coating

12 mm PAA and DMAPS-HEA11 cathodes were cut out of the dried coated aluminum sheets and weighed. Additionally, the weight of the current collector without any slurry coating was also measured to calculate the coating weight and sulfur loading. The typical value was close to 1 mg sulfur but varied depending on coat-

ing. Polypropylene membranes were selected as separators (Celgard 2500) and cut into circular sheets with a diameter of 19 mm. Assembly of CR2023 coin cells took place in an argon-filled glove box, with both oxygen and moisture levels confirmed below 0.1 ppm, following the illustration in Figure 3.4. Firstly, the sulfur cathode was inserted in the bottom casing and wet with a few drops of the electrolyte solution, which consisted of commercial 1,3-dioxolane (DOL)/1,2-dimethoxymethane (DME) solution with lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) salt dissolved. The polypropylene separator was added on top, followed by another round of wetting. 80 microliters and 50 microliters of the DME/-DOL solvent was added in total for the PAA and ZIP-HEA coin cells, respectively. The cell assembly was completed through the addition of a lithium metal anode on top of the separator, followed by spacer, spring, and finally the top casing, all of which was pressed together under high pressure (1100 psi) on a tablet press. Multiple cells were tested with 0.1, 0.2, 0.5 and 1 c rate, in addition to to rate performance measurements on single cells.

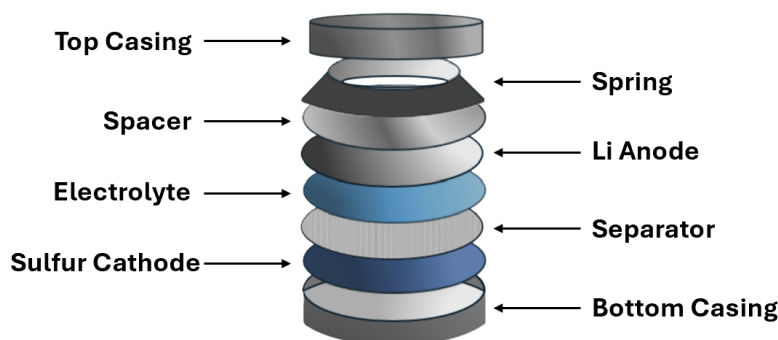


Figure 3.4: Illustration of a half-coin cell setup using lithium as anode and sulfur as cathode

3.3 Characterization Procedure

^1H and ^{13}C NMR test samples were prepared by dissolving 20 mg of each DMAPS-HEA binder in 0.7 ml of deuterium oxide (D_2O) as solvent. Similarly, Fourier Transform Infrared Spectroscopy (FTIR) was used to analyse the dry DMAPS-HEA11 binder structure. Thermogravimetric Analysis (TGA) samples were prepared by transferring 3-4 mg of Gr/S samples S1 and S2. The measurement was performed between 0 and 900 $^{\circ}\text{C}$. Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) measurements of all the LSBs were conducted using the Bio-Logic BCS-900 battery cycler and performed for the potential window between 1.7 V and 2.8 V at a scan rate of 0.1 mVs $^{-1}$. Galvanostatic charge/discharge measurements were initially performed with the Landt LBI-300 CH battery cycler for all the DMAPS-HEA binders at a rate of 0.1 C, similarly between 1.7 V and 2.8 V. Newly assembled cells were given 6 hours of rest before testing and the theoretical capacity was set to 1674 mAh g^{-1} . Due to the advantageous performance of DMAPS-HEA11, continuous testing with different cells at the rates 0.1, 0.2, 0.5 and 1 C for both PAA and ZIP-HEA11 was conducted. Additionally, rate performance was tested on LSBs with both binders, scaling between 0.1 C and 3 C. Post-mortem analysis of cycled cells at 0.1 - 1 C was performed with SEM-EDS imaging and compared with blank cathodes at magnifications of 500x, 10000x, and 20000x.

4

Results and Discussion

4.1 Structural determination

The ^1H nuclear magnetic resonance (^1H -NMR) spectra for the binders DMAPS-HEA11, DMAPS-HEA41, DMAPS-HEA91, and DMAPS-HEA191 were recorded with D_2O (4.79 ppm) as solvent and chemical shifts represented as values in ppm in Figures 4.1-4.5 below. Figure 4.1 shows the full ^1H -NMR spectra for the typical binder, DMAPS-HEA11, with the spectra shown between 6.0 and 0 ppm in Figure 4.2. The recorded proton resonance signals at 3.02 ppm, 2.32 ppm, 3.27 ppm, 3.63 ppm, 4.54 ppm, denoted as a, b, d, c-e, and f respectively, are assigned to the DMAPS moiety, whereas the signals at 4.20 and 3.82, denoted as i and j, belong to the HEA segment. A broader peak is also visible at 1.05-1.30 ppm, in addition to smaller peaks at 1.8 and 2.02 ppm, which have been assigned to the alkyl backbone segment of the copolymer. The observed ^1H -NMR peaks are overall consistent with reported values for zwitterions and HEA. No peaks were observed above 4.79 ppm, as shown in full NMR spectra (figure A.1) in appendix A, confirming the copolymer structure and that no monomer olefinic signals at 6.23-6.27 ppm exist. Hence, all the remaining reactant and byproducts after synthesis were successfully removed from the sample during dialysis and freeze-drying, respectively.

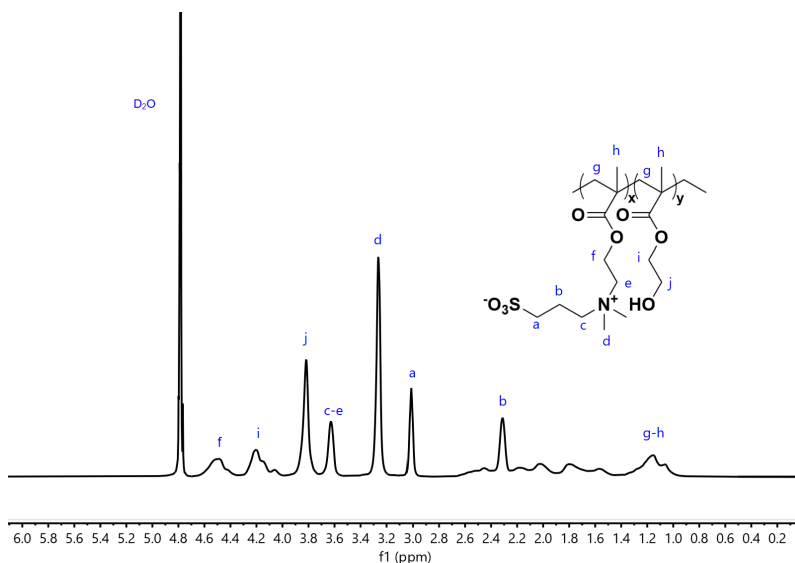


Figure 4.1: ^1H -NMR spectra of DMAPS-HEA11 binder in the region 6.0 - 0.0 ppm with corresponding peak annotation

As shown in figures A.2-A.4 in appendix A, the ^1H -NMR spectra for the remaining DMAPS-HEA binders differ only in the signals intensity at 4.20 and 3.82, corresponding to the i and j atoms in the HEA segment. Hence, the content of HEA in the copolymer was reduced for lower feed ratio of HEA in DMAPS-HEA41, DMAPS-HEA91, and DMAPS-HEA191, confirming a higher DMAPS:HEA ratio in the copolymer structures.

The ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectra was also recorded for the four binders DMAPS-HEA11 – DMAPS-HEA191 with D_2O as solvent. Figure 4.6 Shows the ^{13}C NMR spectra for ZIP-HEA11. The recorded ^{13}C resonance signal at 176-177 ppm corresponds to the carbonyl carbons that exist in both the DMAPS and HEA structure. The peaks at 47.38, 44.83, 41.51, 51.32, 62.41, and 63.43 ppm, denoted as a-c, d, and e-f were assigned to the DMAPS moiety, whereas the signals at 59.40 and 66.59 correspond to the k and l carbon atoms in the HEA segment. The peak at 18.31 ppm was assigned to the alkyl backbone of the copolymer structure. Similarly to the ^1H -NMR, no residual peaks were observed, confirming the structure and purity of the binder. Additionally, the signals at 59.40 and 66.59 were also reduced for lower monomer feed ratios of HEA as shown in figures A.5-A.7 in appendix A, providing further confirmation that these binders had lower HEA ratio in the final copolymer structure. It should also be noted that the carbonyl carbon signal at 176-177 ppm were not observed in the ^{13}C spectra for DMAPS-HEA91 and DMAPS-HEA191.

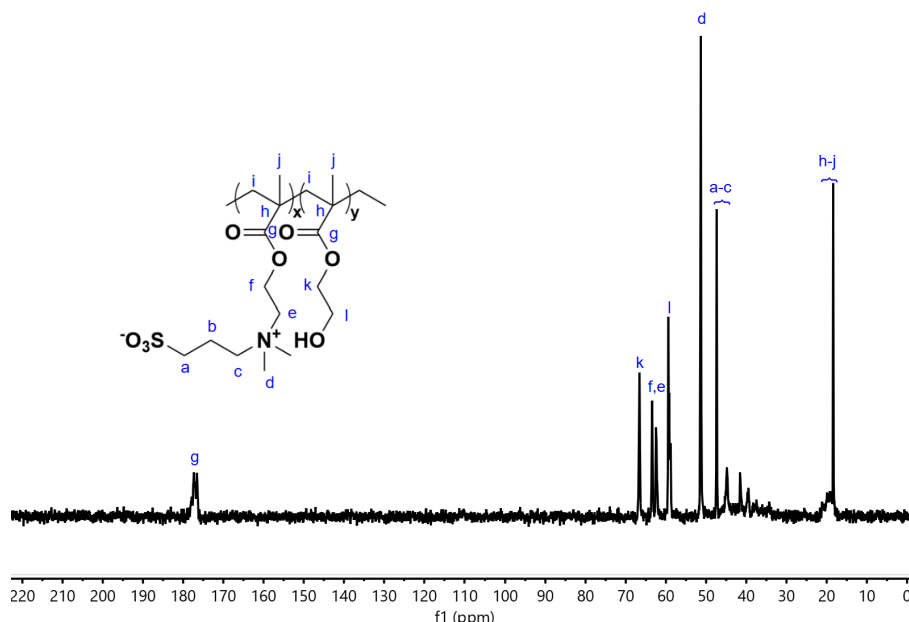


Figure 4.2: ^{13}C -NMR spectra of DMAPS-HEA11 binder with corresponding peak annotation

Fourier Transform Infrared (FTIR) spectroscopy was also performed to confirm the successful synthesis of DMAPS-HEA11 binder, as shown below in Figure 4.3, showcasing the spectra between 300-4000 cm^{-1} . The absence of a carbon double-bond peak indicates complete copolymerization. The broad peak at 3400 cm^{-1} indicates successful introduction of the HEA segment into the copolymer structure, whereas the characteristic peaks for quaternary ammonium cation (1465 cm^{-1}) and sulfonate group (1165 cm^{-1}) verifies the presence of DMAPS in the polymer framework. Finally, the peaks at 2950 cm^{-1} , 1720 cm^{-1} , and 1033 cm^{-1} , can be attributed to the vibrational stretching of C-H, C=O, and C-O bonds respectively, confirming the presence of ester and alkyl chains. Peaks at 1640-1680 cm^{-1} corresponding to alkene double bonds are negligible, suggesting low residual monomer and oligomer content.

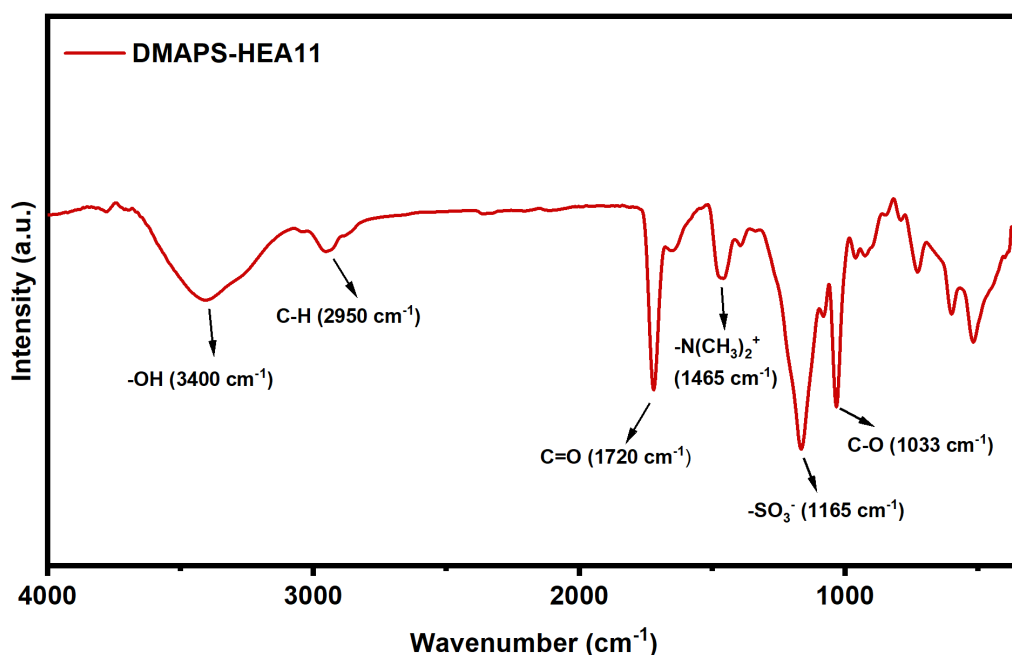


Figure 4.3: FTIR spectra of DMAPS-HEA11 binder in the range 300-4000 cm^{-1} .

The Thermogravimetric Analysis (TGA) of Gr/S samples S1. and S2. indicate an initial few percentages of mass loss, likely due to moisture content in the sample. A steep weight loss is also observed from approximately 200 $^{\circ}\text{C}$ until 330 $^{\circ}\text{C}$, corresponding to the decomposition temperature of sulfur as shown in figure 4.4. In the highlight, the calculated weight after the initial decomposition is marked. The sulfur content was determined to be 76.45, and 81.52 percent for samples S2 and S1, respectively. In addition to a difference in sulfur content, the initial temperature at which mass loss is observed was higher for the melt-diffused sample S2, indicating better sulfur loading into the graphene matrix. The discrepancy between the determined sulfur loading can be explained by the overestimation of sulfur due to the method not incorporating residual moisture or oxygen groups from rGO in the calculation of mass loss. However, due to the mixture only constituting of 30% graphene, this is estimated to have minimal impact on the final sulfur loading calculation. It can more reasonably be explained by loss of graphene during transfer

between sample vials, ball milling, and melt diffusion steps.

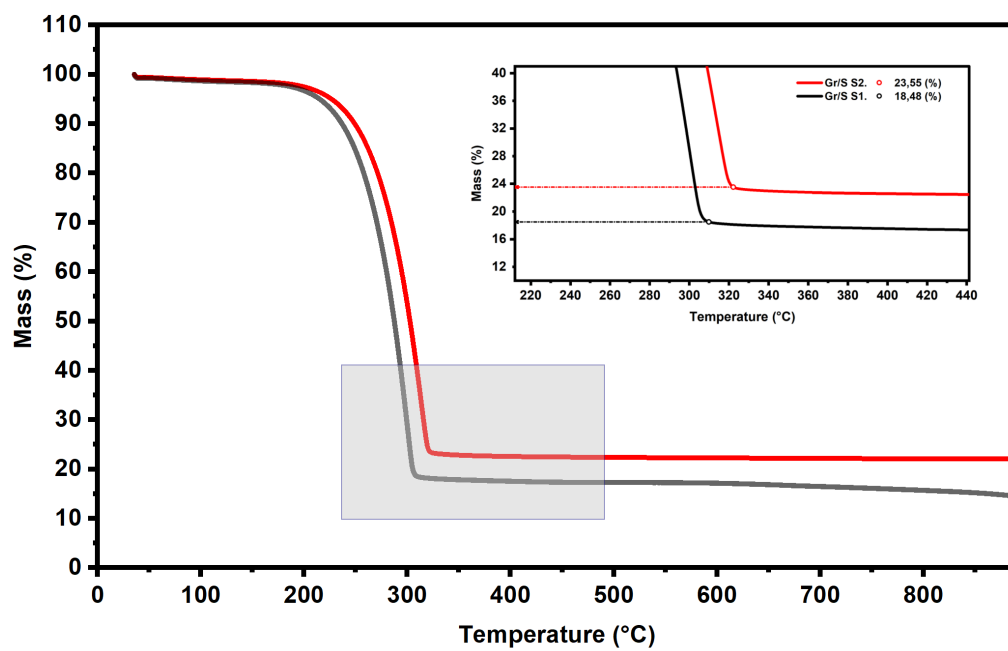


Figure 4.4: TGA analysis of samples S1 and S2

4.2 Cell performance

After initial investigation into the binder performances in coin cells, the DMAPS-HEA11 was deemed the best performing and further battery testing was performed on this binder. As seen in Figure 4.5a, electrochemical impedance spectroscopy (EIS) was recorded both for pristine binder and after 10 cycles. In the initial cycle, nyquist plot displayed a single semicircle for both the PAA binder and DMAPS-HEA11 binder. The former demonstrated an R_{ct} of 95, whereas the latter had 109. However, after 10 cycles, the semicircle of DMAPS-HEA11 displayed a significantly lower diameter of 47 compared to PAA with a value of 75. This is indicative of the improved electron transfer and Li^+ diffusion at the interface for DMAPS-HEA11 during actual cycling conditions. A comparison between pristine DMAPS-HEA11 and after 10 cycles is shown in Figure 4.5b.

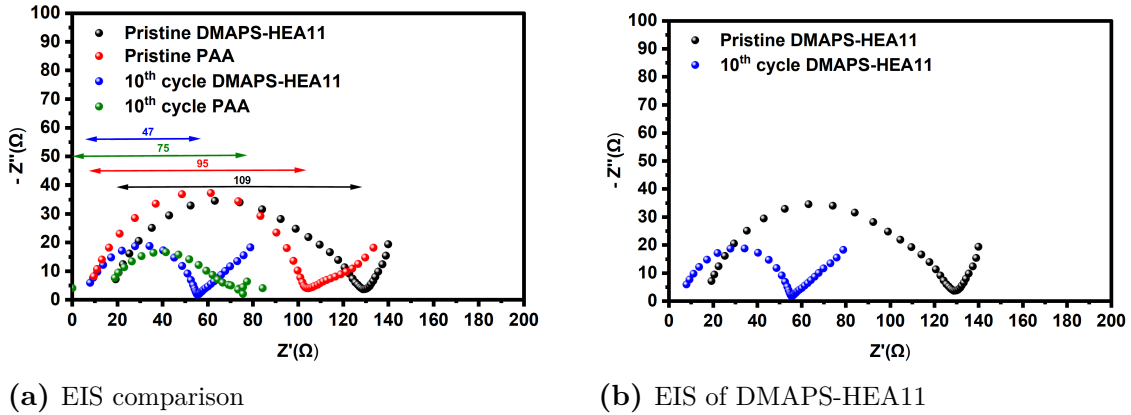


Figure 4.5: Electrochemical Impedance Spectroscopy of pristine and cycled reference binder PAA and synthesized DMAPS-HEA11.

The cyclic voltammograms (CV's) of both DMAPS-HEA11 binder and PAA displayed a typical two-step sulfur reduction process during the cathodic scan, with the former featuring sharp peaks at 2.30 and 2.01 V, corresponding to the conversion of S_8 to Li_2S_x , where ($4 \leq x \leq 8$), and subsequently to Li_2S_2/Li_2S . Similarly, during oxidation two peaks are visible at 2.34 and 2.4 V, indicating a clear two-step conversion process from Li_2S to polysulfides and S_8 . Meanwhile, the cell constructed with PAA as binder displayed reduction peaks at 2.29 and 1.96 and oxidation peaks at 2.32 and 2.4 V. Furthermore, the CV of cells constructed from DMAPS-HEA11 displayed a more stable cycling profile. Notably, the onset voltage during the cathodic scan was higher for DMAPS-HEA11, indicating faster kinetics for reduction of polysulfide species. Additionally, the sharper peaks, more visible two-step oxidation peaks during the anodic scan, and smaller peak separation between the second reduction and inverse reaction for DMAPS-HEA11 (324 mv), compared to PAA (363 mv), all indicates faster redox reactions.

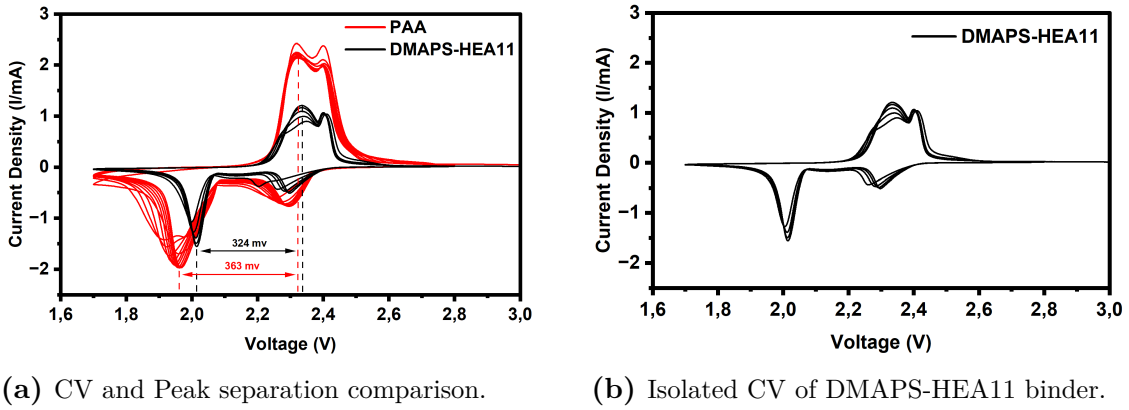
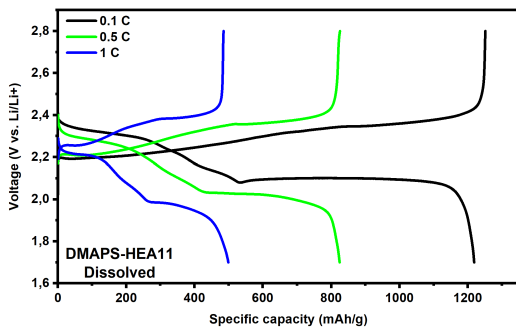


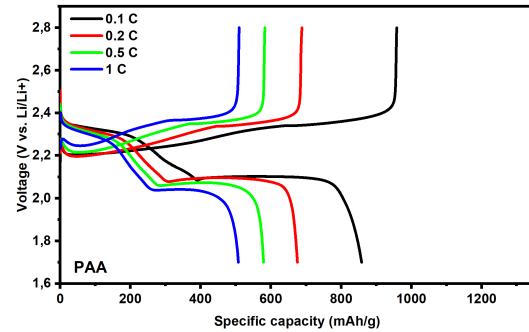
Figure 4.6: Cyclic voltammograms of DMAPS-HEA11 and PAA as binder

The initial specific capacities obtained from the galvanostatic charge-discharge (GCD) profiles of LSBs with DMAPS-HEA11 and PAA as binder are shown in Figure 4.7a and 4.7b, respectively, featuring a typical two-step reduction process with plateaus at 2.35 V and 2.1 V. Whereas former demonstrated superior capacities of 1219, 824, and 499 mAh/g for the rates 0.1, 0.5, and 1 C, respectively, the latter only displayed capacities of 858, 675, 579, and 508 mAh/g, indicating significantly worse sulfur utilization in PAA. In Figure 4.7c, the GCD curves of DMAPS-HEA11 and PAA are compared, illustrating the lower polarization potential ΔE , providing supporting evidence that the polysulfide conversion kinetics are enhanced. Additionally, the ratio between the capacity in the low plateau region (Q_L) and high plateau (Q_H) was similar for both binders, with neither drastically outperforming the other. Long-term cycling test were conducted to understand the ability of the binders to stabilize the LSBs (Figure 4.7d and 4.7f). The cells were initially cycled at 0.1 C for three initiation cycles, followed by the designated rate. The LSBs with DMAPS-HEA11 at 0.5 C and 1 C demonstrated initial capacities of 824 and 499 mAh/g, while retaining a capacity of 580 and 426 after 190 and 110 cycles, respectively. This corresponds to a capacity loss of 0.37 % and 0.77 % per cycle, although it should be noted that the loss is generally higher when fewer cycles have been measured due to the drastic initial loss in capacity. Hence, if testing was conducted for 500⁺ cycles, a lower capacity loss per cycle would have been foreseeable. These results are comparable and even exceed that of the LSBs with PAA as binder at rates of 0.1 and 0.2 C, which had initial capacities of 840 and 450. The cell with DMAPS-HEA11 at 0.5 C demonstrated superior cycling stability within 10 cycles whereas DMAPS-HEA11 at 1c met the performance of PAA at 0.1 C after only 50 cycles and outperformed it within 70 cycles. This can be attributed to the superior anchoring ability of the quaternary nitrogen cation and sulfonate towards the polysulfides, retaining them on the cathode sides and greatly limiting the effects of shuttling. Hence, the capacity loss is significantly reduced compared to LSBs with PAA as binder, even at a reduced rate. The full GCD profile at 0.5 C is shown in figure 4.7e. Due to the time constraint of the LSBs with DMAPS-HEA11 binder only being optimized towards the end of this Master's thesis, only 190 and 110 cycles were conducted at 0.5 C and 1 C, respectively. Longer cycling tests were also performed at the rates 0.1, 0.2, 0.5, and 0.5, in addition to rate tests, before the DMAPS-HEA11 cathodes were

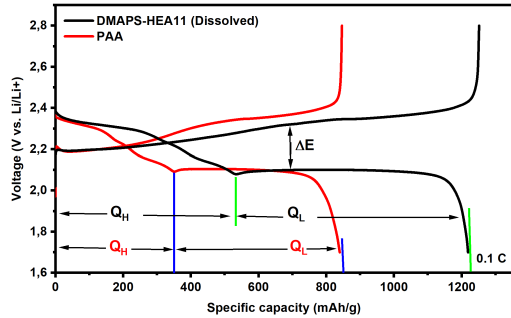
fully optimized, and are displayed in Appendix A. Figures A.8-A.11 demonstrate the initial rate performance of PAA and DMAPS-HEA11. After the procedure had been optimized by dissolving the binder before mixing, the improved result in Figure A.12 was achieved. Similarly, the initial cycling performance before optimization is seen in Figures A.13-A.16. As can be seen, although the LSBs outperformed PAA at 0.1 and 0.2 C, the capacity was still relatively low and unstable. This is even more exaggerated at 1 C where the initial capacity is below the highest capacity achieved, at around 80 cycles. This is indicative of the importance of optimizing the slurry and coating process, in addition to the use of initiation cycles, for a stable and high capacity sulfur cathode.



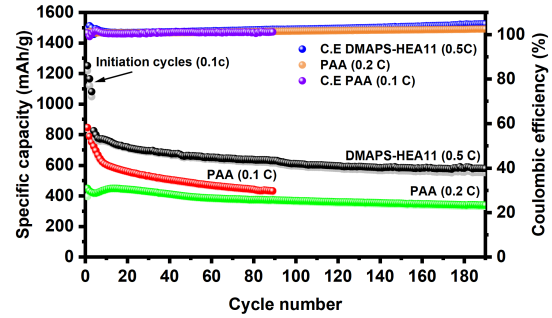
(a) GCD curves of DMAPS-HEA11 at the rates 0.1, 0.5, and 1 C.



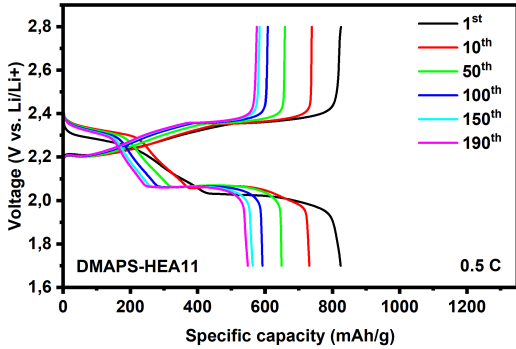
(b) GCD curves of PAA at the rates 0.1, 0.2, 0.5, and 1 C.



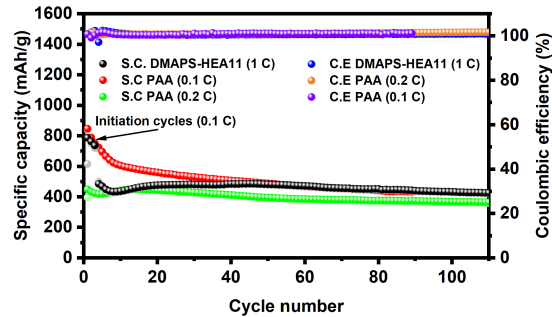
(c) GCD curves of DMAPS-HEA11 and PAA at 0.1 C



(d) Cycling performance of DMAPS-HEA11 (0.5 C) vs PAA (0.1 and 0.2 C).



(e) GCD profile of DMAPS-HEA11 at 0.5 C



(f) Cycling performance of DMAPS-HEA11 (1C) vs PAA (0.1 and 0.2 C)

Figure 4.7: Performance of LSBs with DMAPS-HEA11 and PAA as binder.

4.3 Post mortem analysis

Due to time constraints, SEM-imaging was only conducted on the DMAPS-HEA11 cathodes cycled at 0.2 C, as shown in Figures A.10 and A.14 in Appendix A, before the optimized LSBs with superior rate performance had been constructed. Initial observation of the fresh DMAPS-HEA11 and PAA (Figure 4.8a, 4.8c) cathodes magnified 500 times in SEM reveals that both surfaces exhibit a similar open-pore morphology with large, flaky graphene particles, smaller clusters of Super P aggregates spanning in-between, and sulfur particles mixed together. When compared with the post-mortem analysis of the retrieved cathode surfaces after cycling for 250+ cycles at 0.2 C, ending on a discharge, the PAA sample (Figure 4.8b) is highly perforated and fragmented, whereas the DMAPS-HEA11 cathode (Figure 4.8c) features a more homogeneous and smooth surface, which can be attributed to the superior cathode integrity and self-healing effect of DMAPS-HEA11 binder, allowing for continuous expansion/contraction cycles without excessive cracks or fissures. The less perforated structure is also indicative of the decreased pore volume in DMAPS-HEA11 due to gradual formation of insulating Li_2S_2/Li_2S growth blocking the pores, suggesting that the binder aids in reducing the polysulfide shuttling, achieving deeper discharge and preferential deposition buildup on the cathode compared to anode during cycling.

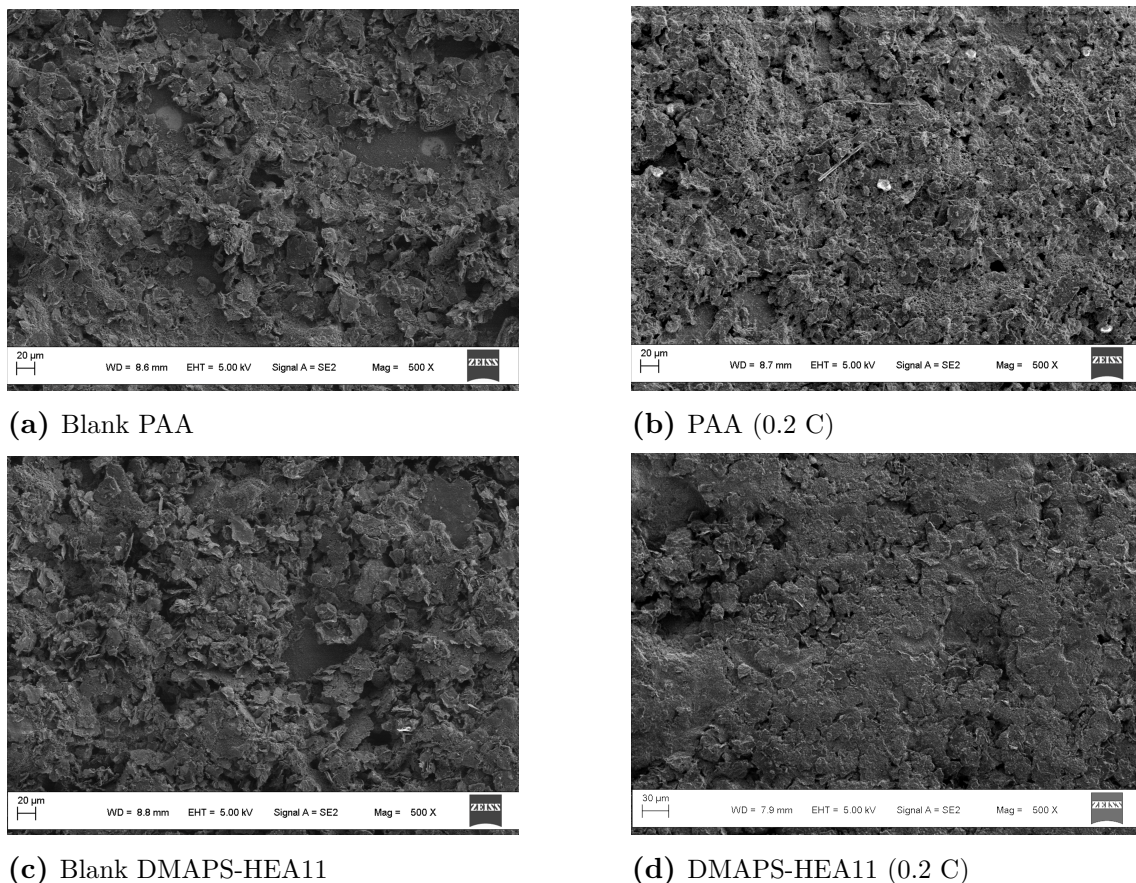


Figure 4.8: 5.0 kV SEM images of both blank and discharged cathodes after 250+ cycles at 0.2 C magnified 500x.

A closer inspection at a higher magnification of 10000x in the blank samples (Figure 4.9a and 4.9d) reveals the morphology of carbon black, coated in clusters on the graphene sheets, which is similar for both blank samples. After cycling for 250+ cycles at 0.2 C, both samples demonstrate a significantly different structure, with visible spherical and large Li_2S_2/Li_2S particle aggregates in the case of PAA (Figure 4.9b), whereas the typical area in DMAPS-HEA11 cathodes displayed an unusual microstructure with homogeneous deposition of smaller, flake-like aggregates (Figure 4.9e). This dense deposition of particles with higher aspect ratio and consequently larger exposed surface area provides more active sites for conversion, likely contributing to higher sulfur utilization observed in the LSBs with DMAPS-HEA11 as binder. This discovery suggest that the zwitterionic binder provides a more stable SEI interface, facilitating more efficient conversion reactions between polysulfide species, on top of the previously known anchoring effect. In comparison, the large spherical precipitates of PAA indicate worse cycling performance due to lower nucleation site density and more inactive sulfur inside the large volume of the deposits. A more clearly visible comparison is demonstrated in Figures 4.9c and 4.9f, magnified 20000x. This is consistent with the results obtained during EIS and CV measurements, which demonstrated a smaller charge transfer resistance R_{ct} , smaller peak separation and sharper peaks for DMAPS-HEA11 cathodes, suggesting superior kinetics, electron transfer, and Li^+ diffusion at the interface. It also explains

4. Results and Discussion

the higher initial capacity and superior cycle retention, achieving a more efficient conversion of Li_2S_2/Li_2 deposits and higher sulfur utilization.

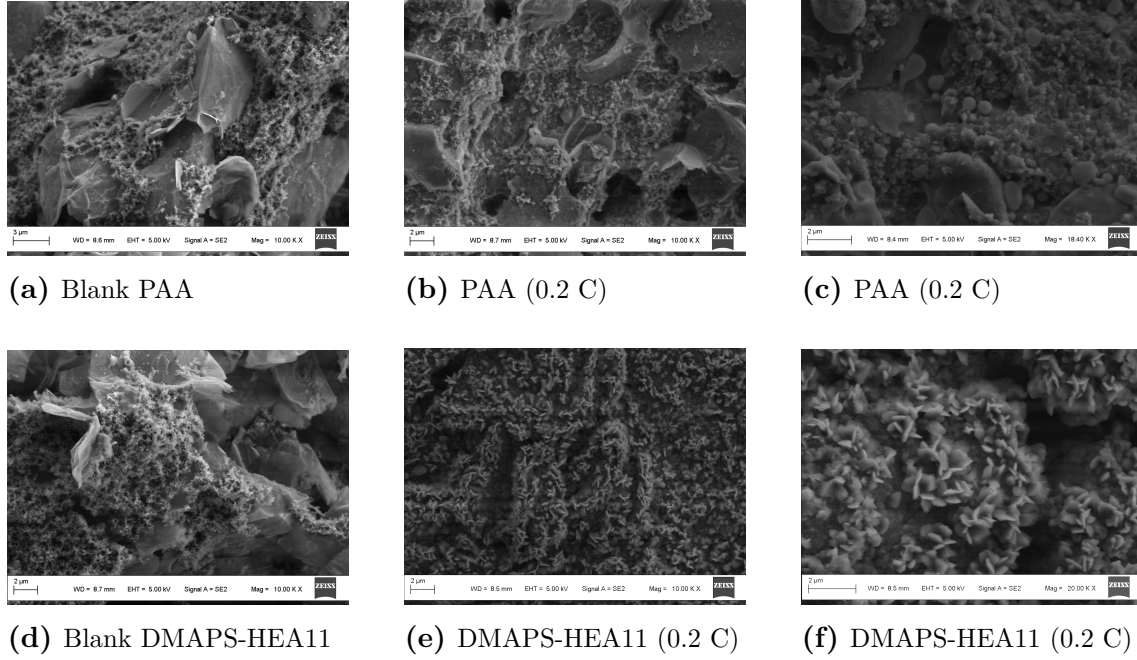


Figure 4.9: 5.0 kV SEM images of PAA (a-c) and DMAPS-HEA11 (d-f) for both blank samples (a,d) and post-mortem analysis of LSBs after cycling at 0.2 C for 250+ cycles, at the magnifications 10000x (b,e) and 20000x (c,f).

EDS imaging was also taken of the DMAPS-HEA11 samples cycled at 0.2 C, further demonstrating the homogeneous composition of the cathode, with carbon, oxygen, sulfur, nitrogen, fluorine, and sodium present (Figure 4.10). The most likely sources of fluorine and nitrogen is the decomposition product of LiTFSI, in addition to the binder for the latter. Similarly, LiTFSI and the binder can contribute to the oxygen and sulfur composition, although the largest contributor of the latter should be the active material. The presence of a small amount of sodium could possibly originate from the counterion in the sulfonate group of the binder. Since quantification of lithium is not possible due to the low energy of its characteristic x-rays, confirmation of the Li_2S_2/Li_2S deposits relies on the SEM-imaging alone.

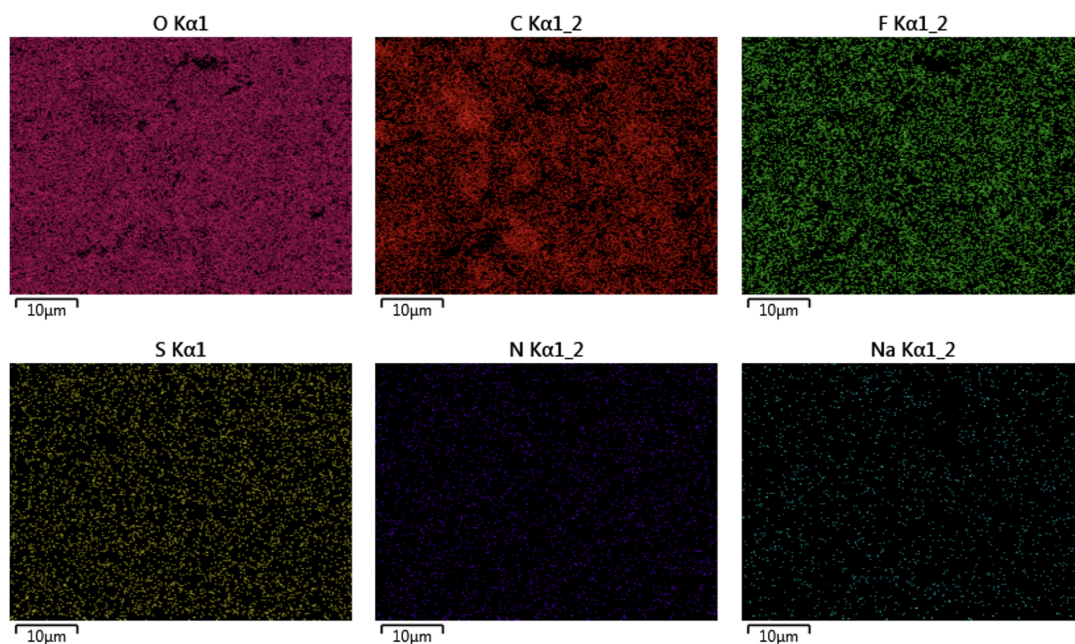


Figure 4.10: EDS imaging of DMAPS-HEA11 cathode cycled at 0.2 C for 250+ cycles.

5

Conclusion

In conclusion, the synthesized zwitterionic DMAPS-HEA11 binder effectively raised the sulfur utilization and cycling stability of LSBs due to its polysulfide anchoring ability, whilst providing a water-soluble alternative to the commercial binders PVDF and PAA. It made the processing more environmentally friendly, safe, and easy. An unexpected finding was the binder's apparent enhancement of both polysulfide conversion kinetics and SEI formation. This conclusion is supported by the lower charge-transfer resistance observed in EIS measurements, the sharper peaks and higher onset voltage in the CV curves, the high aspect ratio Li_2S_2/Li_2S deposits observed in the SEM images, and the high specific capacity of 1219 mAh g^{-1} achieved during the initiation cycles at 0.1 C. However, more research is necessary to ascertain the reason behind the favourable Li_2S precipitate structure.

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Appendix 1

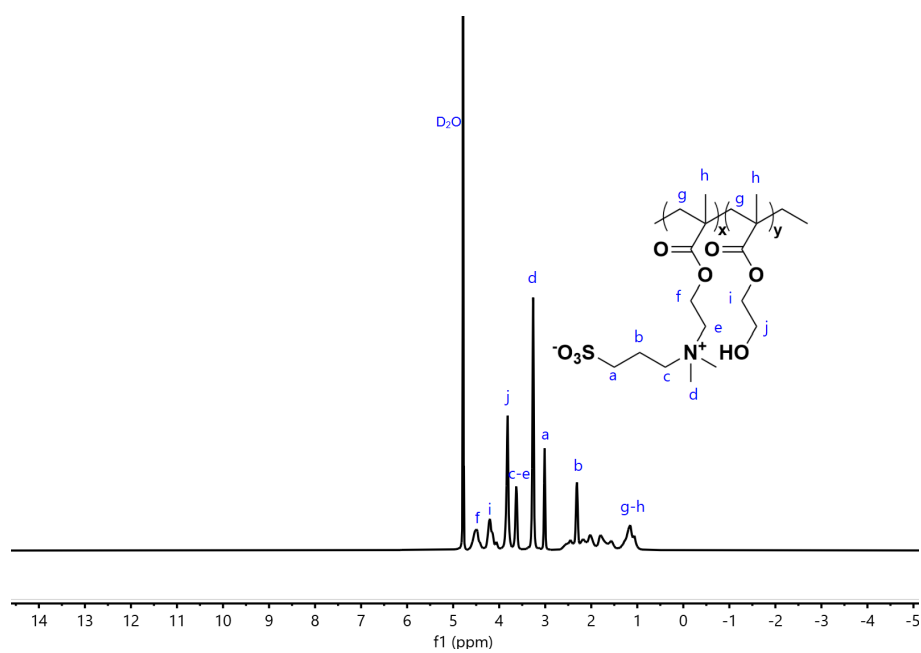


Figure A.1: Full ^1H -NMR spectra of DMAPS-HEA11

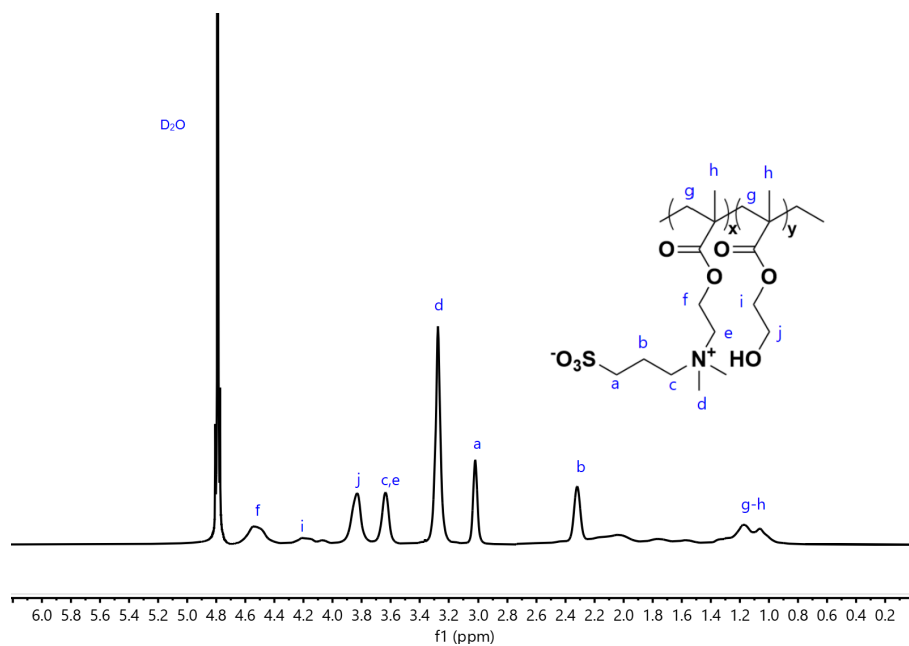


Figure A.2: ^1H -NMR spectra of DMAPS-HEA41 binder with corresponding peak annotation

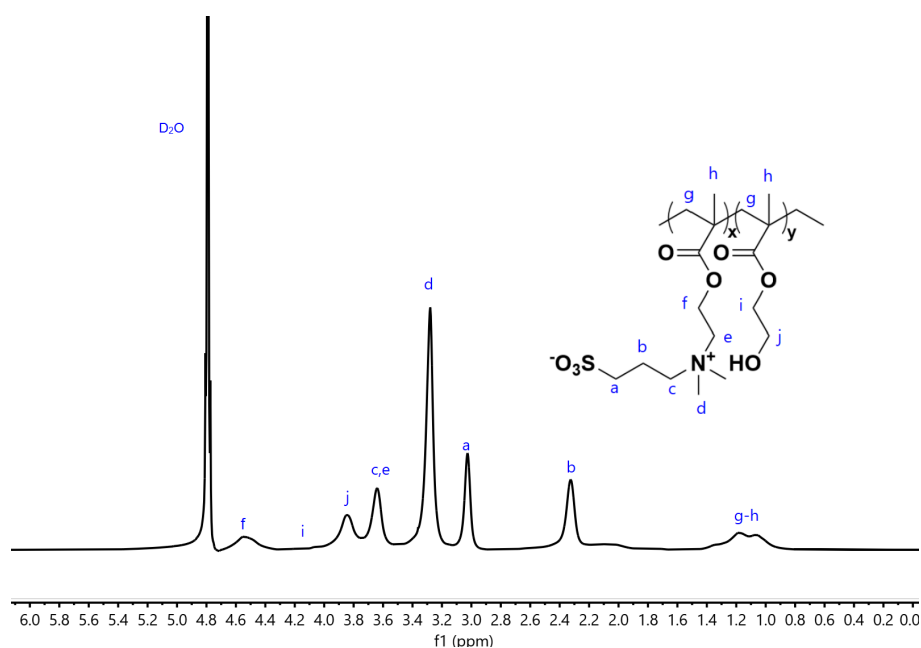


Figure A.3: ^1H -NMR spectra of DMAPS-HEA91 binder with corresponding peak annotation

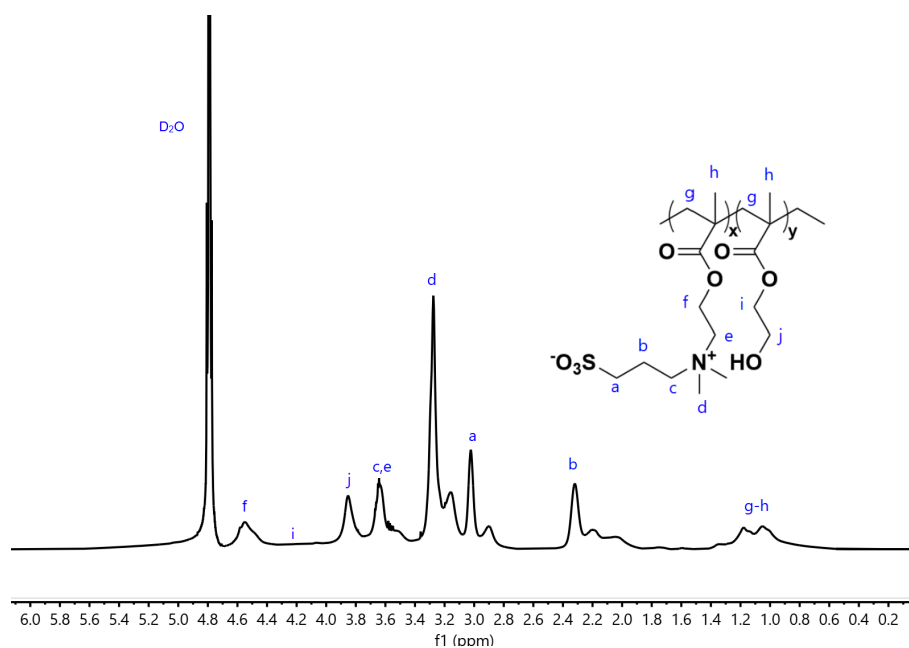


Figure A.4: ^1H -NMR spectra of DMAPS-HEA191 binder with corresponding peak annotation

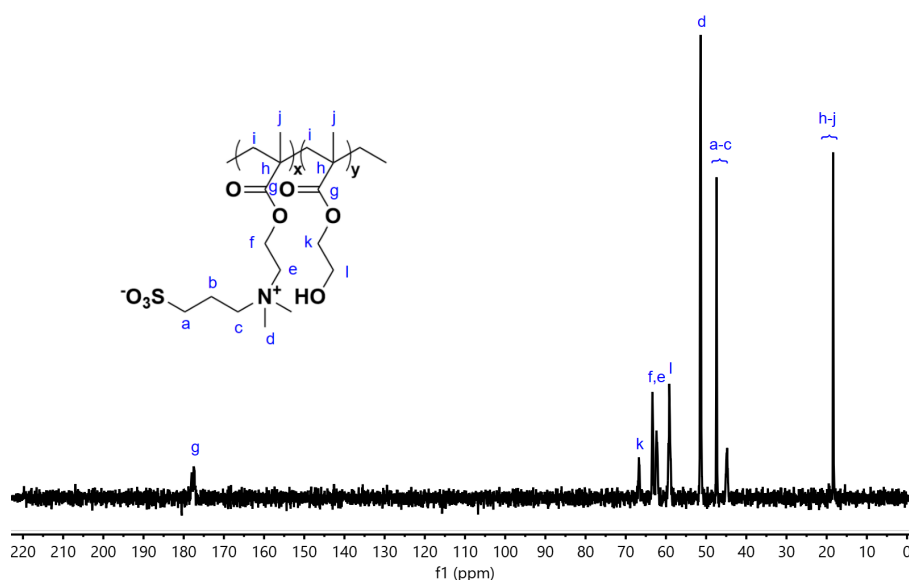


Figure A.5: ^{13}C -NMR spectra of DMAPS-HEA41 binder with corresponding peak annotation

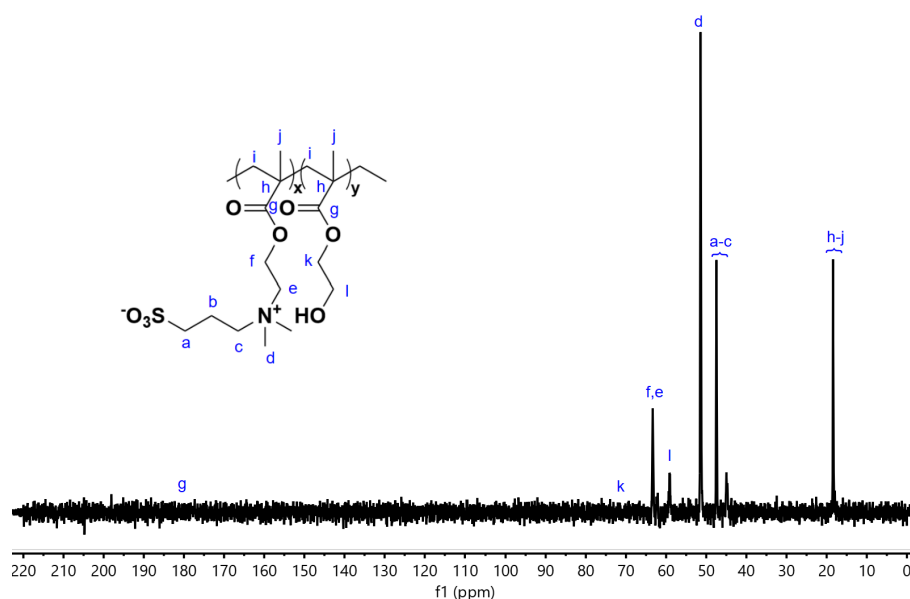


Figure A.6: ^{13}C -NMR spectra of DMAPS-HEA91 binder with corresponding peak annotation

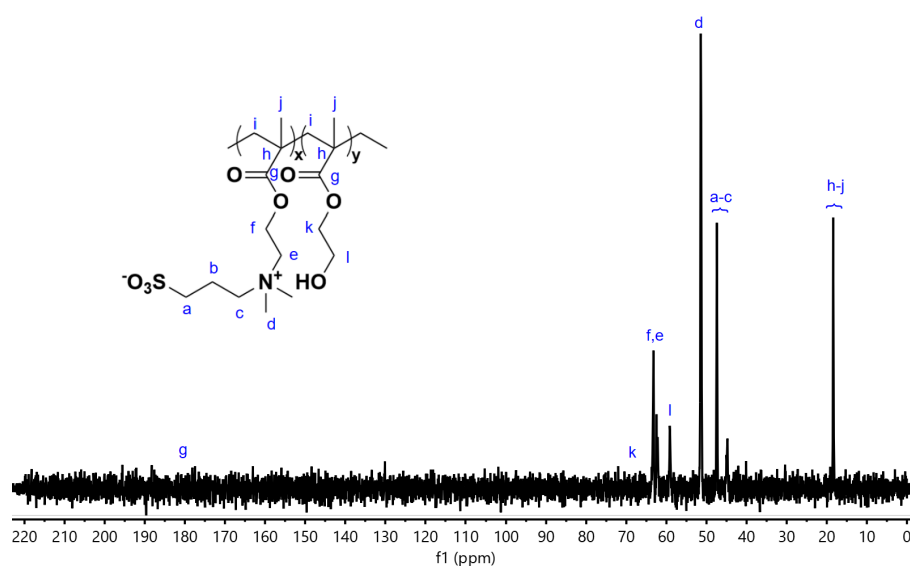


Figure A.7: ^{13}C -NMR spectra of DMAPS-HEA191 binder with corresponding peak annotation

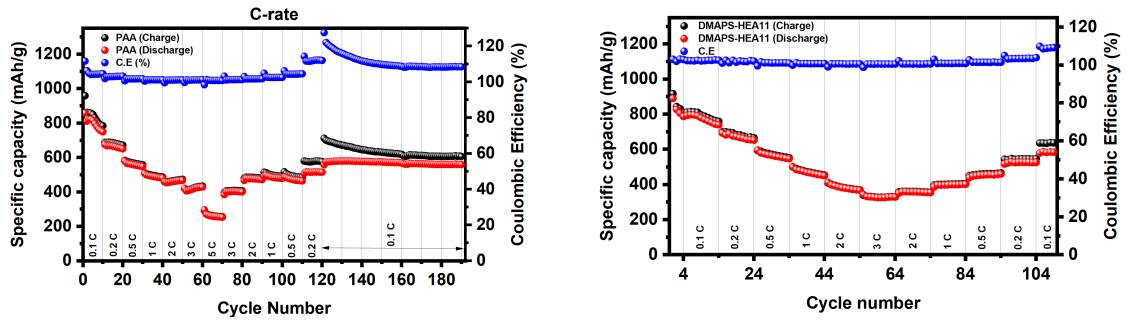


Figure A.8: Comparison of initial rate performances of LSBs with DMAPS-HEA11 and PAA.

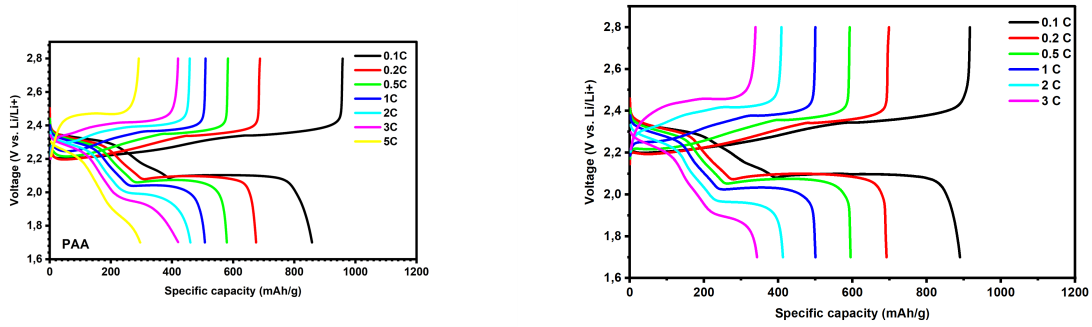


Figure A.9: Initial specific capacities during discharge for both LSBs constructed with DMAPS-HEA11 and PAA as binder, at each rate.

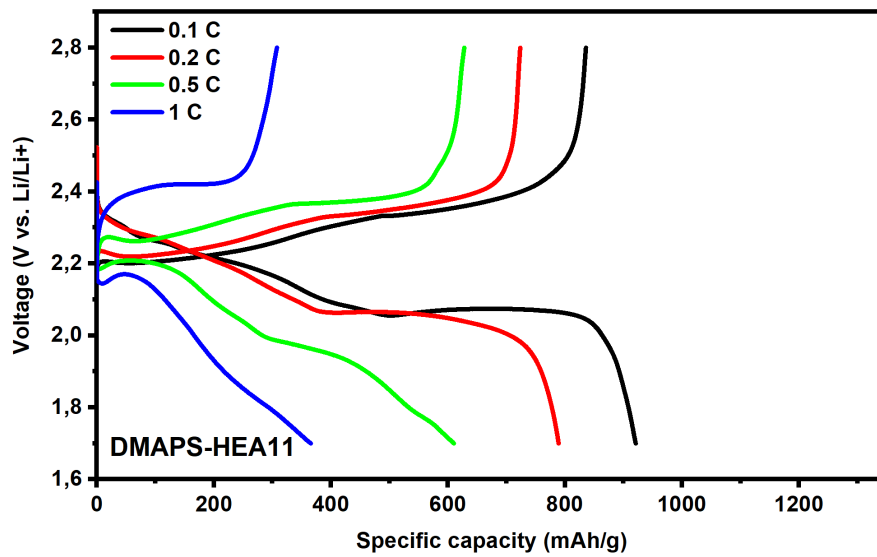


Figure A.10: Initial specific capacity of DMAPS-HEA11 LSBs before optimization

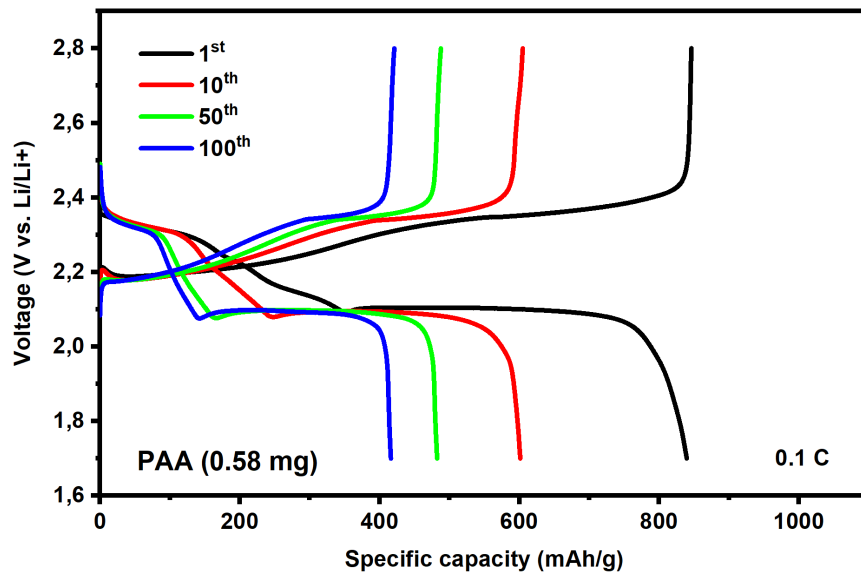


Figure A.11: Initial specific capacity of PAA at a low sulfur loading of 0.58 mg

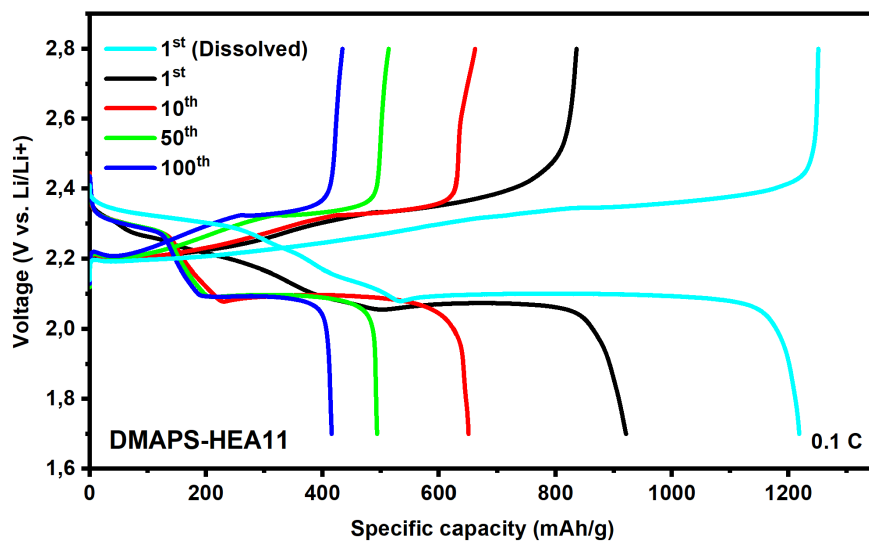


Figure A.12: Improvement in capacity of optimized DMAPS-HEA11 binder (Dissolved), compared to initial results.

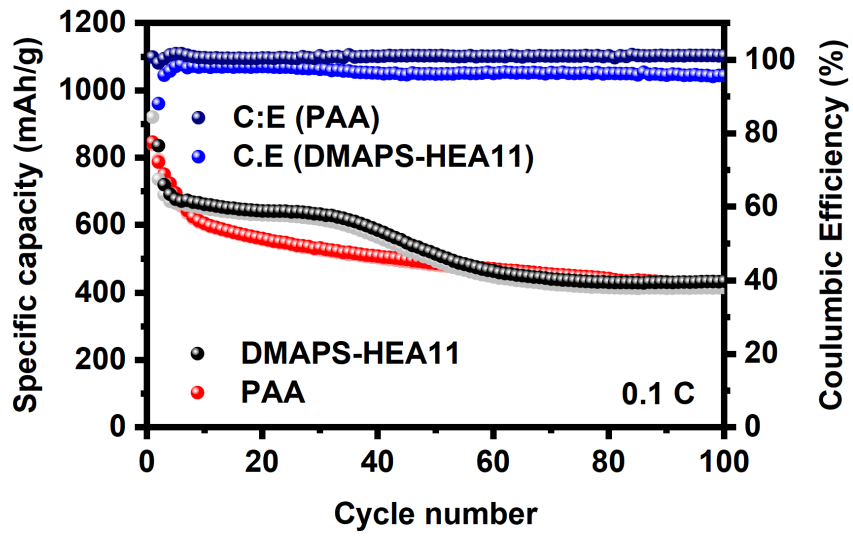


Figure A.13: Initial result for DMAPS-HEA11 vs PAA at 0.1 C

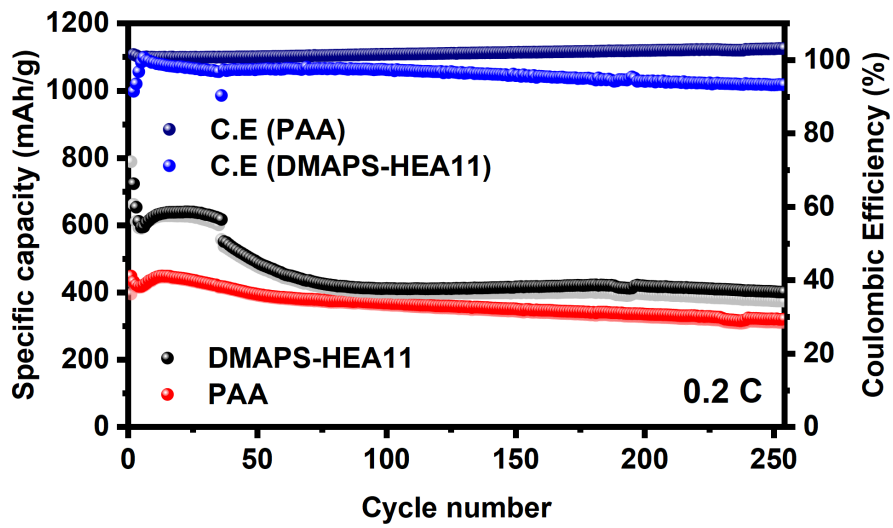


Figure A.14: Initial result for DMAPS-HEA11 vs PAA at 0.2 C

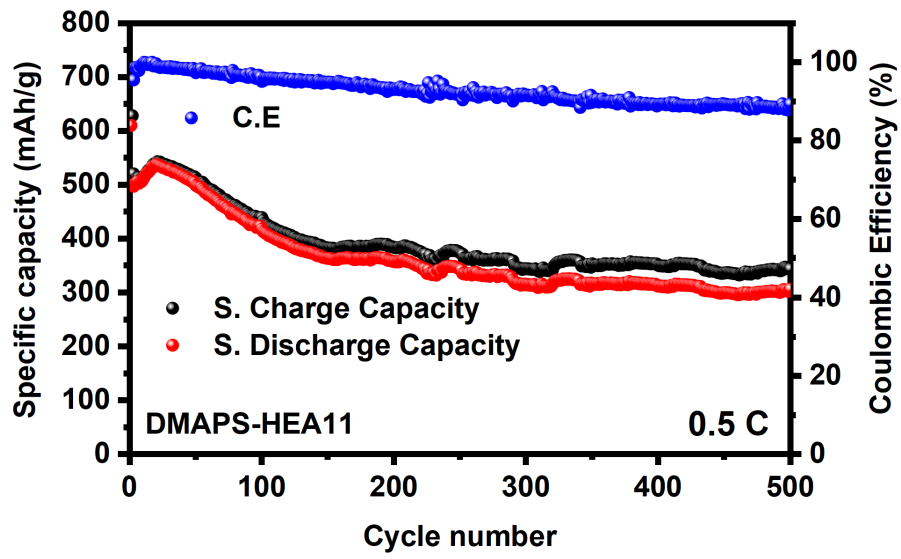


Figure A.15: Initial result for DMAPS-HEA11 at 0.5 C

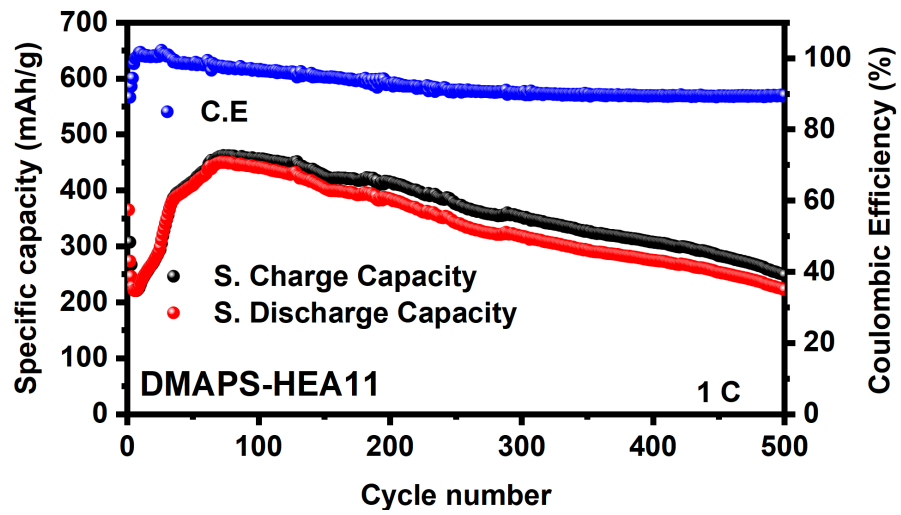


Figure A.16: Initial result for DMAPS-HEA11 at 1 C

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